UNIVERSITI SAINS MALAYSIA

UNIVERSITY RESEARCH GRANT
FINAL REPORT
Geran Penyelidikan Universiti
Laporan Akhir

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A.	**PARTICULARS OF RESEARCH** / *MAKLUMAT PENYELIDIKAN:*
(i)	**Title of Research: Advanced Functionalized Materials For Chemical Process** *Tajuk Penyelidikan:*
(ii)	**Account Number: 1001/PJKIMIA/814003** *Nombor Akaun:*
B.	**PERSONAL PARTICULARS OF RESEARCHER** / *MAKLUMAT PENYELIDIK:*
(i)	**Name of Research Leader: Profesor Abdul Latif Ahmad** *Nama Ketua Penyelidik:*
	Name of Co-Researcher *Nama Penyelidik Bersama:* **Prof. Abdul Rahman Bin Mohamed** **Prof. Bassim H. Hameed** **Prof. Subhash Bhatia** **Prof. Madya Ahmad Zuhairi Abdullah** **Prof. Madya Lee Keat Teong** **Prof. Madya Sharif Hussein Sharif Zein** **Dr. Mohd Azmier Ahmad**
(ii)	**School/Institute/Centre/Unit :** *Pusat Pengajian /Institut/Pusat/Unit :* **Pusat Pengajian Kejuruteraan Kimia**
C.	**Research Platform (Please tick (/) the appropriate box):** *Pelantar Penyelidikan (Sila tanda (/) kotak berkenaan):* ☐ **A. Life Sciences** *Sains Hayat* ☐ **B. Fundamental** *Fundamental* ☑ **C. Engineering & Technology** *Kejuruteraan & Teknologi*

	☐ **D. Social Transformation** *Transformasi Sosial* ☐ **E. Information & Communications Technology (ICT)** *Teknologi Maklumat & Komunikasi* ☐ **F. Clinical Sciences** *Sains Klinikal* ☐ **G. Biomedical & Health Sciences** *Bioperubatan Sains Kesihatan*
D.	**Duration of this research :** *Tempoh masa penyelidikan ini :* ***Duration : 4 Tahun** *Tempoh :* **From : Oktober 2007** **To : September 2011** *Dari:* *Ke :*
E.	**ABSTRACT OF RESEARCH** **-Sila rujuk Laporan Lengkap Penutupan Geran seperti yang dilampirkan-**
F.	**SUMMARY OF RESEARCH FINDINGS** *Ringkasan dapatan Projek Penyelidikan* **-Sila rujuk Laporan Lengkap Penutupan Geran seperti yang dilampirkan-**
G.	**COMPREHENSIVE TECHNICAL REPORT** **-Sila rujuk Laporan Lengkap Penutupan Geran seperti yang dilampirkan-** **List the key words that reflectour research:** *Senaraikan kata kunci yang mencerminkan penyelidikan anda:*

English	Bahasa Malaysia
-	-

H. **a) Results/Benefits of this research**
Hasil Penyelidikan

No. *Bil:*	Category/Number: *Kategori/ Bilangan:*	Promised	Achieved
1.	**Research Publications (Specify target journals)** *Penerbitan Penyelidikan (Nyatakan sasaran jurnal)*	-	**107**
2.	**Human Capital Development**		
	a. Ph. D Students	-	**6**
	b. Masters Students	-	**19**
	c. Undergraduates (Final Year Project)	-	**2**
	d. Research Officers	-	-
	e. Research Assisstants	-	-
	f. Other: Proceedings	-	**47**
3.	**Patents** *Paten*	-	**2**
4.	**Specific / Potential Applications** *Spesifik/Potensi aplikasin*	-	-
5.	**Networking & Linkages** *Jaringan & Jalinan*	-	**2**
6.	**Possible External Research Grants to be Acquired** *Jangkaan Geran Penyelidikan Luar Diperoleh*	-	-

- Kindly provide copies/evidence for Category 1 to 6.

-Sila rujuk Laporan Lengkap Penutupan Geran seperti yang dilampirkan-

b) Equipment used for this research.
Peralatan yang telah digunakan dalam penyelidikan ini.

Items *Perkara*	Approved Equipment	Approved Requested Equipment	Location
Specialized Equipment Peralatan khusus	-	**Sun Run 10 ton Hydraulic Press** **Shaking Water Bath** **Peristaltic pump** **Ashing & Burn Off Furnace** **Surface Analyzer**	**School of Chemical Engineering, USM**
Facility Kemudahan	**Desktop computer (PC)**	**Desktop computer (PC)**	**School of Chemical Engineering, USM**
Infrastructure Infrastruktur	-	-	-

- Please attach appendix if necessary.

-Sila rujuk Laporan Lengkap Penutupan Geran seperti yang dilampirkan-

I. **BUDGET** / *BAJET*

Total Approved Budget	: RM 874,100.00
Total Additional Budget	: RM -
Grand Total of Approved Budget	: RM 874,100.00

Yearly Budget Distributed

Year 1	: RM 527,700.00
Year 2	: RM 203,700.00
Year 3	: RM 142,700.00

Additional Budget Approved

Year 1	: RM -
Year 2	: RM -
Year 3	: RM -

Total Expenditure	: RM 869,539.82
Balance	: RM 4,560.18

- **Please attach final account statement from Treasury**

-Sila rujuk lampiran yang disertakan-

4 Nov. 2011

Signature of Researcher
Tandatangan Penyelidik

Date
Tarikh

PROFESOR ABDUL LATIF AHMAD CEng FIChemE
Dekan Penyelidikan
Pelantar Sains Fundamental
Pejabat Pelantar Penyelidikan
Bahagian Penyelidikan & Inovasi
Universiti Sains Malaysia
11800 Pulau Pinang

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H. **COMMENTS OF PTJ'S RESEARCH COMMITTEE**
KOMEN JAWATANKUASA PENYELIDIKAN PERINGKAT PTJ

General Comments:
Ulasan Umum:

Two projects have been successfully completed with excellent output in terms of publication and human capital development

PROFESOR AZLINA HARUN @ KAMARUDDIN
Dekan
Pusat Pengajian Kejuruteraan Kimia
Kampus Kejuruteraan
Universiti Sains Malaysia, Seri Ampangan
14300 Nibong Tebal, Seberang Perai Selatan
Pulau Pinang.

.....
Signature and Stamp of Chairperson of PTJ's Evaluation Committee
Tandatangan dan Cop Pengerusi Jawatankuasa Penilaian PTJ

Date : .....
Tarikh :.....

Signature and Stamp of Dean/ Director of PTJ 9/11/11
Tandatangan dan Cop Dekan/ Pengarah PTJ

Date : .....
Tarikh :.....

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Purchase Requisition ▸ Purchase Order ▸ Suppliers ▸ Maintenance ▸ Financials ▸ Code Info ▸ Report ▸ Admin ▸

UserCode: NORMIE / USMKCTLIVE / PJKIMIA **Program Code: Votebook9100** **Current Program : Votebook (Header)**

Current Date : 24/11/2011 10:20:15 AM **Version: 15.01, Last Updated at 30/05/2011** **DB: 13.00, 9/18/2010 VB: 13.01, 3/14/2011** **Switch Language : English /Malay**

Wildcard : eg. Like 100%, Like 10%1, Like %1

Element 1: 1001 Element 2: % Element 4: PJKIMIA

Element 5: 814003 Year: 2011

Detail	Excel	Budget Rule	Budget Control	Account Description	Budget Account Code	Roll over	Budget	Cash Received	Advanced	Commit	Actual	Available	Percentage
Detail	Excel	46	T	Projek Kumpulan Wang Uni Penyelidikan	1001.111.0.PJKIMIA.814003	201,400.56	0.00	0.00	0.00	0.00	6,900.00	194,500.56	0.00%
		46	T	SubTotal		201,400.56	0.00	0.00	0.00	0.00	6,900.00	194,500.56	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.221.0.PJKIMIA.814003	-20,667.95	0.00	0.00	0.00	0.00	0.00	-20,667.95	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.223.0.PJKIMIA.814003	4,500.00	0.00	0.00	0.00	0.00	0.00	4,500.00	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.224.0.PJKIMIA.814003	9,000.00	0.00	0.00	0.00	0.00	0.00	9,000.00	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.226.0.PJKIMIA.814003	-3,530.00	0.00	0.00	0.00	0.00	0.00	-3,530.00	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.227.0.PJKIMIA.814003	-27,458.27	0.00	0.00	0.00	16,463.00	6,504.83	-50,426.10	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.228.0.PJKIMIA.814003	50,805.75	0.00	0.00	0.00	0.00	2,440.00	48,365.75	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.229.0.PJKIMIA.814003	8,131.92	0.00	0.00	0.00	0.00	13,748.00	-5,616.08	0.00%
		47	T	SubTotal		20,781.45	0.00	0.00	0.00	16,463.00	22,692.83	-18,374.38	0.00%
Detail	Excel	48	T	Projek Kumpulan Wang Uni Penyelidikan	1001.335.0.PJKIMIA.814003	208,784.00	0.00	0.00	0.00	185,000.00	195,350.00	-171,566.00	0.00%
		48	T	SubTotal		208,784.00	0.00	0.00	0.00	185,000.00	195,350.00	-171,566.00	0.00%
		9999		GrandTotal		430,966.01	0.00	0.00	0.00	201,463.00	224,942.83	4,560.18	0.00%

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FINAL REPORT

RESEARCH UNIVERSITY GRANT

"SCHOOL NICHE AREA"

TITLE OF RESEARCH

ADVANCED FUNCTIONALIZED MATERIALS FOR CHEMICAL PROCESS

1001/PJKIMIA/814003

PROJECT LEADER

PROFESSOR ABDUL LATIF BIN AHMAD

School of Chemical Engineering

DURATION OF RESEARCH :
Start Date : OCTOBER 2007
End Date : MARCH 2011
Revised Date (if any) : SEPTEMBER 2011

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UNIVERSITI SAINS MALAYSIA

RESEARCH UNIVERSITY GRANT FINAL REPORT

Advanced Functionalized Materials For Chemical Process
1001/PJKIMIA/814003

A.	TITLE OF RESEARCH :	ADVANCED FUNCTIONALIZED MATERIALS FOR CHEMICAL PROCESS
B.	NAME OF RESEARCHER :	PROF. ABDUL LATIF AHMAD (PROJECT LEADER) PROF. DR. ABDUL RAHMAN BIN MOHAMED PROF. BASSIM H. HAMEED ASSOC. PROF. DR. LEE KEAT TEONG ASSOC. PROF. AHMAD ZUHAIRI ABDULLAH DR. MOHD AZMIER AHMAD ASSOC. PROF. DR. SHARIF HUSSEIN SHARIF ZEIN PROF. SUBHASH BHATIA
C.	DURATION OF RESEARCH :	Start Date : OCTOBER 2007 End Date : MARCH 2011 Revised Date (if any) : SEPTEMBER 2011

D. **PROJECT 1:**

BIMODAL POROUS CERAMIC MEMBRANE VIA NANOSIZED POLYSTYRENE AND V_2O_5 NANOTUBE TEMPLATING

ABSTRACT

Ceramic membrane was optimized by introducing bimodal porous ceramic membrane templated using vanadium oxide nanotube. Styrene oxidation can be improved using vanadium oxide-based composite catalysts (Al_2O_3/V_xO_y, CNT-V_xO_y, and CNT-V_xO_y/Al_2O_3) with anhydrous H_2O_2 as an oxidant. The catalyst type, structure and reaction conditions have a strong effect on the styrene oxidation reaction. Vanadium oxide nanotube, synthesized through a hydrothermal method has relatively poor performance due to the oxidative degradation. However, by using CNTs as a template, this shortcoming can be overcome. The main products of the styrene oxidation are benzaldehyde and styrene oxide, but for all of types of catalysts, the selectivity for benzaldehyde is very high. By employing CNT-V_xO_y/Al_2O_3 as catalytic membrane, conversion of styrene decrease but selectivity of benzaldehyde increase compare to nanocomposite particle because prevent side reaction. This is because the membrane could prevent side reaction by isolating the product for further reaction with H_2O_2.

ABSTRAK

Membran seramik dioptimumkan dalam kajian ini dengan memperkenalkan membran seramik berliang dwimod yang dipercontohkan dengan menggunakan tiub nano vanadium oksida. Pengoksidaan stirena dapat diperbaiki dengan menggunakan pemangkin komposit berasaskan vanadium oksida (Al_2O_3/V_xO_y, CNT-V_xO_y, dan CNT-V_xO_y/Al_2O_3) dengan H_2O_2 anhidrous sebagai pengoksida. Jenis pemangkin, struktur dan keadaan tindakbalas mempunyai pengaruh besar dalam tindakbalas pengoksidaan stirena. Tiub nano vanadium oksida, yang disintesis melalui kaedah hidroterma menunjukkan prestasi yang lemah secara relative disebabkan degradasi oksidaan. Namun demikian, dengan menggunakan tiub karbon nano (CNT) sebagai templat, kelemahan tersebut dapat diatasi. Produk utama dari pengoksidaan stirena ialah benzaldehid dan stirena oksida, tetapi semua jenis pemangkin, selektiviti bagi benzalaldehid adalah sangat tinggi. Dengan menggunakan CNT-V_xO_y/Al_2O_3 sebagai membrane pemangkin, penukaran stirena berkurangan tetapi selektiviti benzaldehid bertambah, berbanding partikel nano komposit; disebabkan tindakbalas sampingan tertindas. Ini adalah disebabkan keupayaan membrane untuk mengasingkan produk dari bertindakbalas selanjutnya dengan H_2O_2.

PROJECT 2:

DEVELOPMENT OF CARBON NANOTUBES USING FLOATING IRON-BASED CATALYSTS

ABSTRACT

The unique combination of light weight, small dimensions, structural diversity, excellent mechanical strength and remarkable electronic properties make carbon nanotubes (CNTs) an attractive field of discovery for a wide range of characteristics and potential applications, from reinforcing materials to molecular sensing. Various methods have been proposed of which the chemical vapor deposition (CVD) appears to be the most promising method for high yield synthesis of CNTs due to the lower temperature requirement, higher yield and excellent self-assembly. Floating catalyst (FC)-CVD method is introduced recently in view of its ability to produce continuously high purity CNTs, industrial-scale up production of CNTs and it is involved with simple equipment set-up. In addition, compared with other CVD techniques, FC avoids special time consumed for catalyst preparation and catalyst activation. In this study, catalytic decomposition of methane as highly abundant, less toxic and low cost gas was employed for producing CNTs. Two types of iron precursors, namely (i) iron (III) chloride ($FeCl_3$) as inorganic catalyst and (ii) ferrocene (Fe(C5H5)2) as organometallic catalyst were used. Ferrocene as organometallic catalyst has easy accessibility, stability in air and volatility. $FeCl_3$ catalyst has also some advantages such as easy available, nontoxic, low price and ease of volatilisation reagent. The effects of several synthesis parameters – including temperature, time, and gases flow rate have been invetigated on the growth of CNTs. The amount of catalyst was kept constant at 200 mg. The role of the purification process including oxidation and acid treatment on the purity of as-grown CNTs has also been considered. It was found that an increase in the reaction temperature, reation time and the gases flow rates to an optimum level increased the yield of CNTs. In addition, the reaction temperature and methane flow rate affected the growth, morphology and alignment of CNTs, especially while using ferrocene. The optimum process conditions predicted by Design of Experiment (DoE) for methane decomposition using $FeCl_3$ were found to be a reaction temperature of 1055 °C, reaction time of 65 min, methane flow rate of 380 sccm and

nitrogen flow rate 200 sccm, which gave the CNTs yields of 87.08%. The optimum process conditions for CNT synthesis using ferrocene were a reaction temperature of 947 °C, reaction time of 58 min, methane flow rate of 357 sccm and nitrogen flow rate 195 sccm, which gave the CNTs yields of 90.75%. Various characterisation tests, including thermogravimetric analysis (TGA), scanning electron microscopic (SEM), energy-dispersive X-Ray analyser (EDX), transmission electron microscopy (TEM), high-resolution of transmission electron microscopy (HRTEM) and Raman spectroscopy, were carried out in order to comprehend the properties of the produced CNTs and criteria required to grow higher quality CNTs in high yield. In all instances, multi-walled carbon nanotubes (MWCNTs) were the only products observed.

ABSTRAK

Kombinasi yang unik antara berat yang sangat ringan, berdimensi kecil, kepelbagaian struktur, kekuatan mekanik yang sangat baik dan sifat elektronik yang luar biasa menjadikan nanotiub karbon (CNTs) bidang yang telah menarik minat para saintis dalam penemuan baru melalui ciri-cirinya dan berpotensi dalam pelbagai bidang aplikasi termasuklah bahan-bahan yang diperkuat sehinggalah penderiaan molekul.Pelbagai kaedah telah dicadangkan untuk mensintesis CNTs. Pemendapan/penguraian wap kimia (CVD) merupakan kaedah sintesis yang paling efektif kerana memerlukan suhu yang lebih rendah, di samping berupaya menghasilkan CNTs dengan kualiti dan kuantiti yang tinggi. Kaedah mangkin terapung (FC)-CVD baru-baru ini telah diperkenalkan memandangkan kemampuannya untuk menghasilkan CNTs yang berketulenan tinggi, penghasilan secara skala industri dan melibatkan penyediaan peralatan yang mudah. Selain itu, jika dibandingkan dengan kaedah CVD yang lain, FC dapat mengelakkan waktu khusus untuk penyediaan dan pengaktifan mangkin. Dalam kajian ini penguraian metana sebagai gas yang sangat melimpah, kurang toksik, mempunyai kos yang rendah bermangkin diaplikasikan untuk menghasilkan CNTs. Dua jenis prekursor ferum digunakan, iaitu (i) ferum (III) klorida ($FeCl_3$) sebagai mangkin inorganik dan (ii) ferrocene ($Fe(C5H5)2$) sebagai mangkin organologam. Ferrocene yang bertindak sebagai mangkin organologam ada aksesibiliti, kestabilan di udara dan kemeruapan. Mangkin $FeCl_3$ juga mempunyai beberapa kelebihan seperti mudah disediakan, tidak toksik, harga yang rendah dan boleh bertindak sebagai reagen untuk pemeruapan. Kesan terhadap beberapa sintesis parameter - termasuklah suhu, masa, dan halaju aliran gas telah dikaji terhadap pertumbuhan CNTs. Jumlah mangkin dijaga konstan pada 200 mg. Kesan terhadap proses penulenan yang melibatkan proses pengoksidaan dan rawatan asid pada ketulenan CNTs juga telah dikaji. Oleh itu, didapati bahawa peningkatan suhu tindak balas, masa tindak balas dan aliran gas ke tahap optimum akan meningkatkan kuantiti CNTs yang dihasilkan. Selain itu, suhu tindak balas dan halaju aliran gas metana akan mempengaruhi pertumbuhan, morfologi dan penyelarasan CNTs, terutamanya ketika menggunakan ferrocene. Keadaan proses optimum dianggarkan dengan Design of Experiment (DoE) untuk penguraian metana menggunakan $FeCl_3$ melibatkan suhu tindak balas pada 1055 °C, masa tindak balas selama 65 minit, halaju aliran metana sebanyak 380 sccm dan halaju aliran nitrogen sebanyak 200 sccm. Keadaan tindak balas ini telah memberikan hasil CNTs sebanyak 87.08%. Keadaan optimum untuk mensintesis CNTs dengan menggunakan ferrocene adalah pada suhu tindak balas sebanyak 947 °C, masa tindak balas selama 58 minit, halaju aliran metana sebanyak 357 sccm dan halaju aliran nitrogen sebanyak 195 sccm, yang memberikan hasil CNTs sebanyak 90.75%. Pelbagai ujian pencirian, termasuk analisis termogravimetri (TGA), pengimbasan mikroskopik elektron (SEM), tenaga-dispersive X-Ray penganalisis (EDX), mikroskop transmisi elektron (TEM), mikroskop

elektron transmisi resolusi tinggi (HRTEM) dan spektroskopi Raman, dilakukan untuk memahami sifat dan morfologi CNTs yang dihasilkan dan kriteria yang diperlukan untuk pertumbuhan CNTs yang berkualiti dan berkuantiti tinggi . Dalam semua kes, didapati bahawa CNTs dinding berlapis (MWCNTs) merupakan produk yang terhasil.

PROJECT 3:

DEVELOPMENT OF FUNCTIONALIZED ADSORBENTS FOR REMOVAL OF POLLUTANTS FROM WASTEWATER

ABSTRACT

Functionalized adsorbents were developed for the removal of dyes from wastewaters. The activated carbons were derived from agricultural waste by-products (oil palm agricultural waste such as oil palm empty fruit bunch and oil palm fibre), while the low cost adsorbents were developed from the rejected tea. The oil palm empty fruit bunch activated carbon (EFBAC) and oil palm fibre activated carbon (PFAC) were prepared by H_3PO_4 assisted chemical activation, and the optimum operating conditions such as activation temperature, activation time and chemical impregnation ratio were evaluated. The prepared activated carbons were functionalized with ammonia solution while the rejected tea was treated using chemical modifying agents. Both the treated and untreated adsorbents were characterized by N_2–physisorption for the BET surface area and pore size distribution, SEM, FTIR, TGA and elemental analysis. The adsorptive property was quantified using methylene blue as dye model compound. Batch method was adopted for the adsorption of dye solution in the case of activated carbons, while both batch and fixed bed column were used for the removal of dye from wastewater in the case of rejected tea. The results indicated that the functionalized adsorbents are suitable for the treatment of wastewaters.

ABSTRAK

Bahan penjerap berfungsi telah dicipta untuk menyingkirkan pewarna daripada air sisa. Karbon teraktif yang berasal daripada produk sampingan sisa pertanian (sisa pertanian kelapa sawit seperti tandan buah kelapa sawit dan serabut kelapa sawit), manakala bahan penjerap kos rendah telah dicipta daripada teh yang ditolak. Karbon teraktif tandan buah kosong kelapa sawit (EFBAC) dan karbon teraktif serabut kelapa sawit (PFAC) disediakan melalui aktivasi kimia berpandukan H_3PO_4, dan keadaan operasi optimum seperti suhu aktivasi, masa aktivasi dan nisbah impregnasi kimia telah dinilai. Karbon teraktif yang disediakan difungsikan dengan larutan ammonia manakala teh yang ditolak dirawat dengan menggunakan agen modifikasi kimia. Kedua-dua bahan penjerap yang terawat dan tanpa dirawat dicirikan dengan N_2-jerapan fizikal bagi luas permukaan BET dan distribusi saiz lubang. , SEM, FTIR, TGA dan analisis elemen. Ciri-ciri jerapan dikuantitikan dengan menggunakan metilena biru sebagai kompaun model pewarna. Kaedah kelompok digunakan untuk penjerapan larutan pewarna bagi karbon teraktif, manakala kedua-dua turus kelompok dan berkatil tetap digunakan untuk menyingkirkan pewarna daripada air sisa bagi teh yang ditolak. Keputusan mengindikasikan bahawa penjerap fungsian adalah sesuai untuk rawatan air sisa.

PROJECT 4:

REMOVAL OF SO_2 AND NO USING SORBENTS DERIVED FROM AGRICULTURAL WASTE

ABSTRACT

In the present work, the effect of various reactor operating parameters affecting sorption capacity of rice husk ash (RHA)/CaO/CeO_2 sorbent and the kinetic behavior between RHA/CaO/CeO_2 sorbent and SO_2/NO at low temperature based on the breakthrough curves were investigated. It was found that the presence of NO and SO_2 accelerated the SO_2 and NO sorptions, respectively. However, at high level of SO_2/NO concentration, the competition in sorption of NO and SO_2 on the sorbent active sites might occur. A lower space velocity resulted in a higher SO_2 and NO sorptions. Relative humidity was shown to enhance the SO_2 sorption of the reference sorbent, but not for NO sorption. Higher operating temperatures were favored for SO_2 and NO sorptions. Nevertheless, beyond 150°C the SO_2 sorption was found to decrease. The kinetic parameters such as deactivation rate constant, initial sorption rate constant, activation energy and frequency (pre-exponential) factor of the SO_2 an NO sorptions were estimated using deactivation kinetic model from the breakthrough data through nonlinear regression analysis. The activation energy and frequency factor for the SO_2 sorption were found to be 18.0 kJ/mole and 7.37×10^5 cm^3/g.min, respectively. Whereas the activation energy and frequency factor for the NO sorption, were estimated to be 5.64 kJ/mole and 2.19×10^4 cm^3/g.min, respectively. The deactivation kinetic model was found to give a very good agreement with the experimental data of the SO_2/NO sorptions with error less than 10%.

ABSTRAK

Dalam kajian ini, kesan perubahan pelbagai parameter kendalian reaktor yang mempengaruhi kemampuan bahan serap abu sekam padi (RHA)/CaO/CeO_2 dan kelakuan kinetik antara bahan serap RHA/CaO/CeO_2 dan SO_2/NO pada suhu rendah berdasarkan data pemunculan eksperimen telah dikaji. Dalam kajian ini didapati bahawa kehadiran NO dan SO_2 masing-masing mempercepatkan kemampuan bahan serap untuk menyerap SO_2 dan NO. Namun, pada kepekatan SO_2/NO yang tinggi, persaingan dalam menyerap NO dan SO_2 pada tapak aktif bahan serap mungkin berlaku. Halaju ruang yang rendah menyebabkan kemampuan bahan serap terhadap SO_2 dan NO menjadi tinggi. Kelembapan relatif didapati meningkatkan kemampuan bahan serap rujukan terhadap SO_2, tetapi tidak terhadap NO. Suhu operasi yang tinggi adalah sangat sesuai untuk menyerap SO_2 dan NO. Walau bagaimanapun, suhu yang melebihi 150 °C menyebabkan serapan SO_2 menurun. Parameter-parameter kinetik seperti pemalar kadar pendeaktifan, pemalar kadar serapan permulaan, tenaga pengaktifan dan faktor frekuensi bagi serapan SO_2 dan NO diperolehi daripada analisis regresi tak-linear data pemunculan eksperimen dengan menggunakan model kinetik pendeaktifan. Tenaga pengaktifan dan faktor frekuensi bagi serapan SO_2 didapati masing-masing sebanyak 18.0 kJ/mol dan 7.37×10^5 sm^3/g.min. Manakala untuk tenaga pengaktifan dan faktor frekuensi bagi serapan NO adalah masing-masing sebanyak 5.64 kJ/mol dan 2.19×10^4 sm^3/g.min. Model kinetik pendeaktifan didapati menepati data eksperimen serapan SO_2/NO dengan ralat kurang daripada 10%.

PROJECT 5:

DEVELOPMENT OF NOVEL FUNCTIONALIZED MESOPOROUS SOLID BASE MATERIALS FOR OLEOCHEMICAL CONVERSION

ABSTRACT

Various advanced porous materials were also developed and subsequently functionalized with metal oxides and acid functional groups. Those materials were then characterized and subsequently used in suitable chemical reactions including transesterification, esterification and advanced oxidation process assisted by ultrasonic energy. Due to high surface area, high stability, and even distribution of active components, the catalysts showed high catalytic activity.

ABSTRAK

Pelbagai bahan berliang termaju juga telah dibangunkan dan kemudiannya difungsikan dengan oksida logan serta kumpulan berfungsi asid. Bahan-bahan tersebut kemudiannya dicirikan dan digunakan dalam beberapa tindakbalas kimia yang sesuai teramasuk transesterifikasi, esterifikasi dan proses pengoksidan termaju berbantukan tenaga ultrasonic. Mangkin-mangkin ini menunjukkan activiti yang tinggi yang dikaitkan dengan luas permukaan dan kestabilanyang tinggi serta penyeberan komponen aktif yang baik.

PROJECT 6:

PRODUCTION OF FUNCTIONALIZIED ACTIVATED CARBON AND CARBON MOLECULAR SIEVES FROM AGRICULTURAL WASTES

ABSTRACT

In this project, agricultural wastes such as banana stalk, periwinkle shell, rambutan peel, mangosteen peel, cocoa pod husk, coffee husk and palm shell have been successfully converted into activated carbon. In addition some of them (cocoa pod husk and palm shell) were further treated into carbon molecular sieve (CMS). For activated carbon production; physical and physiochemical activation method were used. The activated carbon preparation conditions were optimized using response surface methodology. The preparation variables consist of activation temperature, activation time and chemical impregnation ratio whereas the responses were activated carbon yield and dyes removal. Dyes used in this work consist of basic (methylene blue and malachite green) and reactive (Remazol Brilliant Violet 5R, Remazol Brilliant Blue R, Remazol Black R and Remazol Brilliant Orange 3R) dyes. The activated carbons prepared demonstrated high surface area and well-developed porosity suitable for dyes removal from aqueous solution. On the other hand, CMS prepared by further treated activated carbon by carbon vapour deposition step shows promising adsorbent for gas separation (CO_2, CH_4, O_2 and N_2).

ABSTRAK

Di dalam projek ini, sisa pertanian seperti tangkai buah pisang, kulit siput laut, kulit buah rambutan, kulit buah manggis, tempurung buah koko, hampas buah kopi dan tempurung buah sawit telah berjaya ditukarkan kepada karbon teraktif. Sebahagian daripadanya (tempurung buah koko dan tempurung buah sawit) telah mengalami

proses lanjutan bagi menghasilkan tapisan molekular karbon (TMK). Untuk penghasilan karbon teraktif, pengaktifan fizikal dan fizi-kimia telah digunakan. Keadaan penyediaan karbon teraktif dioptimumkan dengan menggunakan kaedah permukaan sambutan. Parameter penyediaan yang terlibat terdiri daripada suhu pengaktifan, masa pengaktifan dan nisbah enap jerap kimia manakala sambutan terdiri daripada hasilan karbon teraktif dan penyingkiran bahan pencelup. Bahan pencelup yang digunakan didalam kajian ini terdiri daripada pencelup asas (metilina biru dan malacit hijau) dan pencelup reaktif (Remazol Brilliant Ungu 5R, Remazol Brilliant Biru R, Remazol Hitam R dan Remazol Brilliant Jingga 3R). Karbon teraktif yang disediakan menunjukkan luas permukaan yang tinggi dan pembentukan liang yang sempurna dimana sesuai digunakan untuk penyingkitran bahan pencelup didalam larutan akuas. Di sebelah pihak lagi, TMK yang terhasil daripada proses lanjutan karbon teraktif secara pemendapan wap karbon menunjukkan TMK sebagai bahan penjerap yang baik untuk pemisahan gas (CO_2, CH_4, O_2 dan N_2).

PROJECT 7:

DEVELOPING CARBON NANOTUBES BASED NANOCOMPOSITES BY CREATING GOOD INTERFACE BETWEEN CARBON NANOTUBES AND DESIRED MOLECULES

ABSTRACT

Carbon nanotubes (CNT) have generated a great and sustained interest in carbon-based materials and nanotechnologies. CNT have been shown to possess exceptional electrical, mechanical and thermal properties, which are attractive for diverse potential applications ranging from nano-electronics to biomedical devices. However, using CNT in practical applications has been largely limited by their poor processability, since they are practically insoluble and infusible. Many efforts have been made to combine CNT and metal oxides to produce functional composite materials with superior properties.

ABSTRAK

Karbon tiubnano (CNT) telah menjana minat yang besar dan berterusan dalam bahan berdasarkan karbon dan nanoteknologi. CNT telah ditunjukkan untuk memiliki sifat-sifat elektrik, mekanikal dan haba yang luar biasa, yang menarik bagi pelbagai aplikasi yang berpotensi terdiri dari nano elektronik kepada alat-alat bioperubatan. Walau bagaimanapun, menggunakan CNT dalam aplikasi praktikal telah sebahagian besarnya terhad oleh keupayaan proses mereka yang lemah, kerana mereka boleh dikatakan tidak larut dan *infusible*. Banyak usaha telah dibuat untuk menggabungkan CNT dan oksida logam untuk menghasilkan bahan-bahan komposit yang berfungsi dengan sifat-sifat unggul.

PROJECT 8:

DEVELOPMENT OF FUNCTIONALIZED ZEOLITE MEMBRANE AS CATALYST FOR XYLENE ISOMERIZATION

ABSTRACT

Reactive separation of para-xylene from xylene isomers in a catalytic membrane reactor depends on the right choice of catalytic membrane. This membrane should not only catalyze xylene isomerization reaction but also

separate para-xylene (*p*-xylene) from its isomers (ortho-xylene (*o*-xylene) and meta-xylene (*m*-xylene)). In the present study, silicalite-1 and two types of acid-functionalized silicalite-1 membranes: (1) propylsulfonic acid-functionalized silicalite-1 membrane and (2) arenesulfonic acid-functionalized silicalite-1 membrane were synthesized on disc type α-alumina support, pre-coated with mesoporous silica layer. The physical and chemical properties of the membranes were characterized using different techniques such as XRD, SEM, TEM, ^{29}Si MAS NMR, ^{13}C CP-MAS NMR, FTIR, TGA, EA, NH_3-TPD, acid-base titration and nitrogen adsorption–desorption. The nitrogen permeation and permporosimetry tests were conducted to evaluate the quality and the presence of non-zeolite pores in the membranes. Design of experiments (DoE) was applied in the optimization process of *p*-xylene separation from *p*-/*o*-xylene binary mixture and *p*-/*o*-/*m*-xylene ternary xylene mixture using silicalite-1 membrane. The optimum *p*-xylene flux of 3.83 x 10^{-6} mol/m^2.s and *p*-/*o*-xylene separation factor of 46 were obtained at a temperature of 198 °C, *p*-xylene feed partial pressure of 0.15 kPa and *p*-xylene feed composition of 0.80. The optimum *p*-xylene flux of 5.94 x 10^{-6} mol/m^2.s, *p*-/*o*-xylene separation factor of 19 and *p*-/*m*-xylene separation factor of 20 were achieve at temperature of 198 °C and *p*-xylene feed partial pressure of 0.22 kPa in ternary xylene mixture separation. The Maxwell-Stefan diffusion model, in combination with the Ideal Adsorbed Solution (IAS) theory and single-component adsorption parameter were used to predict the permeation flux of *p*-xylene and *o*-xylene for binary xylene mixture through a silicalite-1 membrane in the temperature range of 150 °C – 250 °C. Acid-functionalized silicalite-1 membranes were tested for their catalytic activity in *m*-xylene isomerization reaction in the temperature range of 355 °C to 450 °C. At 450 °C. *m*-xylene conversion was 57% with 33% *p*-xylene yield over arenesulfonic acid-functionalized silicalite-1 membrane, synthesized using 15 mol% of phenelthytrimethoxysilane as an organosilane source. The enhancement in *p*-xylene yield was due to the continuous separation of the reaction products through the catalytic membrane, which exhibited good structural stability for 120 hours of operation.

ABSTRAK

Pemisahan reaktif para-xilena dari isomer-isomer xilena dalam reactor membran bermangkin adalah bergantung kepada pilihan membran bermangkin yang sesuai. Membran ini seharusnya memangkinkan tindak balas pengisomeran xilena, dan juga memisahkan para-xilena (*p*-xylene) dari isomer-isomernya (*ortho*-xilena (*o*-xilena) dan *meta*-xilena (*m*-xilena)). Dalam kajian ini, membran silicalit-1 dan dua jenis membran silikalit-1 berfungsikan asid: (1) membran silicalit-1 berfungsikan asid propilsulfonik dan (2) membran silicalit-1 berfungsikan asid arenasulfonik telah disintesiskan di atas α-alumina yang berbentuk cakera, yang dipra-salut dengan lapisan silika berliang meso. Sifat-sifat fizik dan kimia membran-membran telah dikaji dengan menggunakan teknik-teknik yang berbeza seperti XRD, SEM, TEM, ^{29}Si MAS NMR, ^{13} CCP-MAS NMR, FTIR, TGA, EA, NH_3-TPD, pentitratan asid-bes, penjerapan-penyahjerapan nitrogen. Penerapan nitrogen and ujian permporosimetri dijalankan untuk menilai kualiti dan kewujudan liang-liang bukan-zeolit dalam membran. Reka bentuk eksperimen diaplikasikan dalam proses pengoptimuman pemisahan *p*-xilena daripada campuran dedua *p*-/*o*-xilena dan campuran tetiga *p*-/*o*-/*m*-xilena dengan menggunakan membran silikalit-1. Fluks *p*-xilena yang optimum sebanyak 3.83 x 10^{-6} mol/m^2.s dan faktor pemisahan *p*-/*o*-xilena sebanyak 46 telah diperolehi pada suhu 198 °C, tekanan separa *p*-xilena dalam suapan sebanyak 0.15 kPa dan komposisi suapan *p*-xilena sebanyak 0.80. Fluks *p*-xilena yang optimum sebanyak 5.94 x 10^{-6} mol/m^{2}s, faktor pemisahan *p*-/*o*-xilena sebanyak 19 and pemisahan faktor *p*-/*m*-xilena sebanyak 20 telah dicapai pada suhu 198 °C, tekanan separa *p*-

xilena sebanyak 0.22 kPa dalam pemisahan campuran tetiga isomer xilena. Model resapan *Maxwell-Stefan*, dengan kombinasi teori larutan jerap unggul dan parameter penjerapan satu-komponen telah digunakan untuk meramalkan fluks penerapan *p*-xilena dan *o*-xilena dalam campuran *p*-/*o*-xilena melalui membran silicalit-1 pada julat suhu 150 °C- 250 °C. Aktiviti bermangkin dalam tindak balas pengisomeran *m*-xilena bagi membran silicalit-1 berfungsikan asid telah diuji dalam julat suhu dari 355 °C ke 450 °C. Pada suhu 450 °C, penukaran *m*-xilena adalah sebanyak 57 % dengan hasi *p*-xilena sebanyak 33% bagi membran silicalit-1 berfungsikan asid arenasulfonik yang disintesis dengan menggunakan 15 mol% pheniltiltrimetoksisilana sebagai sumber organosilana. Peningkatan dalam hasil xilena adalah disebabkan oleh pemisahan produk tindak balas melalui membran bermangkin, yang menunjukkan kestabilan struktur selepas beroperasi selama 120 jam.

E. INTRODUCTION

PROJECT 1:

Research Problems

γ-Al_2O_3 has been widely studied for the preparation and modification of catalytic membranes using the sol–gel method because these types of membranes can be used for oxidation reaction purposes. when AlOOH is applied, the surface onto which γ-Al_2O_3 is catalytically embedded must be free of cracks following calcination. Therefore, choosing a suitable binder that can be burned off in the calcination step without negative side effects on the catalyst or membrane is important. to our best knowledge no studies on the use of vanadium oxide (V_xO_y) supported on multi-walled carbon nanotubes (CNTs) or vanadium oxide NTs for styrene oxidation in catalytic membranes were investigated this one may be because of problem with this catalyst for this purpose.Due to their large surface area and outstanding thermal, chemical and mechanical stabilities, carbon nanotubes (CNTs) are promising for the development of advanced composite materials that undergo catalytic oxidation reactions. Embedding carbon nanotubes and vanadium oxides into γ-Al_2O_3 poses several critical challenges that must be overcome to capture the full potential of CNT composites. The uniform dispersion of CNTs in the host matrix material is essential. As a result of van der Waals forces, CNTs are likely to form agglomerates or bundles instead of individual tubes, and this can produce defects in composite membranes. The second main challenge is associated with strengthening the interaction between CNTs and the host matrix to produce stable composite materials.

Research Objectives

1- To synthesize vanadium oxide nano structure composite catalyst
2- To investigate the performance of nano structure composite catalyst for styrene oxidation
3- To develop mixed matrix vanadium oxide catalytic nanocomposite membrane
4- To study optimal operating conditions for the vanadium oxide based catalytic membrane in styrene oxidation
5- Comparison of styrene oxidation using catalyst in both powder and membrane form.
6- Knetic study of styrene oxidation

PROJECT 2:

Literature Survey

Carbon Nanotubes

CNTs are members of the fullerene structural family. The cylindrical nanotube usually has at least one end capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotube is in the order of a few nanometers, while they can be up to several millimeters in length (Yu, Li et al. 2004). The nature of the bonding of a nanotube is described by applied quantum chemistry, specifically, orbital hybridization. The chemical bonding of nanotubes is composed entirely of sp^2 bonds, similar to those of graphite. This bonding structure, which is stronger than the sp^3 bonds found in diamond, provides the molecules with their unique strength. Their small size, large aspect ratio, large current carrying density, ballistic transport properties, and exceptional mechanical properties make CNTs a choice material for nanoelectronics and nanomechanics, as well as for composites, field emission displays, ultrastrong yarns, interconnects and batteries. So far a lot of different nanoscale devices based on CNTs as active elements such as single molecule transistors, nanobalances, and nanosensors have been successfully produced. Many applications such as reinforced polymer composites, field emission displays, ultrastrong yarns, interconnects and batteries need very pure, well defined and cheap CNTs on a bulk scale. Various types of nanotubes were described, e.g. SWCNTs, DWCNTs, MWCNTs, helically coiled CNTs, weather they can be synthesized as closed and open ones.

Most SWCNTs have a diameter of close to 1 nm, with a tube length that can be many thousands of times longer. The structure of a SWCNT can be considered as long wrapped graphene sheets. The SWCNTs are a very important variety of CNT because they exhibit important electric properties that are not shared by the MWCNTs variants. One useful application of SWCNTs is in the development of the first intramolecular field effect transistors. SWCNTs are still very expensive to produce, and the development of more affordable synthesis techniques is vital to the future of carbon nanotechnology. MWCNT can be considered as a collection of concentric SWCNTs with different diameters. The length and diameter of these structures differ a lot from those of SWCNTs and, of course, their properties are also very different. In the past decade, the synthesis of MWCNTs has attracted intense interest because of the potential applications of MWCNTs for electronic devices, nanomechanical systems, electrochemical energy storage and production, scanning probes and sensors, field emission sources, and composite materials (Hou, Schaper et al. 2003).

Synthesis of Carbon Nanotubes (CNTs)

Since the studies of CNTs by Iijima (Iijima 1991), several techniques have been developed to produce CNTs. The synthesis of CNTs has attracted much attention because of their unique characteristics and potential applications in many fields. Various techniques to grow CNTs have been developed including arc discharge (Journet, Maser et al. 1997), laser ablation (Rinzler, Liu et al. 1998) and chemical vapor deposition (CVD) (Nikolaev, Bronikowski et al. 1999) methods. CVD process is the most promising method for industrial scale production due to the lower temperature requirement, higher yield and excellent self-assembly (Wei, Zhang et al. 2008). Unlike the other methods that are mentioned above, CVD is capable of growing CNTs directly on a desired substrate, whereas the CNTs must be collected in the other growth techniques. The growth sites are controllable by careful deposition of the catalyst. Furthermore, no other growth methods have been developed to

produce vertically aligned nanotubes.

There are two main approaches to the CVD synthesis of CNTs: one method entails passage of a gas phase carbon source over a supported catalyst (catalytic chemical vapor deposition (CCVD) technique) whilst in the other method both the catalyst and carbon source are in the gas phase (unsupported/ FC-CVD method).

CCVD process is an efficient technique which can be used to scale up the production of CNTs and is the most widely used method for nanotube synthesis. The formation of carbon filaments and fibers from CCVD of carbon bearing reactants over different substrates has been known for a long time. Different carbon structures can be formed by the reaction of gaseous carbon containing precursors over metal surfaces, particularly Fe (Perez-Cabero, Rodriguez-Ramos et al. 2003), Co (Ago, Ohshima et al. 2005) and Ni (Zhang, Wen et al. 2002). These reactions, a distinction should be made between the carbon that is formed by interaction with the metal and that which is co-produced. However, continuous synthesizing CNTs over supported catalyst in a CVD process is hardly achieved and the synthesized CNTs typically contain impurities such as amorphous carbon, nanoparticles, C60 and other fullerenes.

FC-CVD method is one of the most promising methods for generating a high yield of CNTs, which is discussed in more detail later in this section. FC-CVD method is introduced recently in view of its ability to produce continuously high purity CNTs, and simple equipment set-up (Fan, Kaufmann et al. 2006; Ren, Li et al. 2006). CVD coupled with FC-CVD method has been recognized as the suitable process for industrial-scale production of CNTs. In addition, compared with other CVD techniques, FC avoids special time consumed for catalyst preparation and catalyst activation.

Floating Catalyst CVD Method

Many studies have been performed on the CVD formation of CNTs by using FC-CVD method. The main advantage of this method is that removal of CNTs from the substrate (as a support) and the preparation of the substrate are not required. Furthermore, it is a continuous process and therefore could be used in industry to produce CNTs once reaction conditions have been optimized. The amount of catalytic metal particles exposed to the gas is much higher than that found using a substrate method. One dimensional carbon materials, such as SWCNTs (Satishkumar, Govindaraj et al. 1998; Chaisitsak, Nukeaw et al. 2007), DWCNTs (Ci, Zhou et al. 2003; Wei, Jiang et al. 2004), MWCNTs (Rao and Govindaraj 2002; Mohlala, Liu et al. 2007), CNFs (Cheng, Zhang et al. 2004; Yang, Liu et al. 2006), as well as aligned CNTs (Zhang, Cao et al. 2002; Deck and Vecchio 2006) have been synthesized by the FC-CVD method. Two main approaches can be employed to synthesize CNTs via FC-CVD: The first method is involved with pumping or spraying (injection method) a catalyst precursor into a furnace and the precursor is typically metallocene hydrocarbon solution. The second method is to paralyze carbon-containing molecules such as (hydrocarbons) methane (Kuo, Bai et al. 2005; Lu, Rider et al. 2006), acetylene (Ci, Xie et al. 2001; Vivekchand, Cele et al. 2004), ethylene (Zhang, Yu et al. 2008) on metal particles in the gas phase.

The FC-CVD method typically requires volatile organometallic complexes to make CNTs. Extensive work on the use of simple organometallic complexes such as ferrocene (Fe(C5H5)2) (Ci, Xie et al. 2001; Nyamori

and Coville 2007) and iron carbonyl (Fe(CO)5) (Kuo, Bai et al. 2005) as the FC precursors are reported. Few studies have also been conducted using inorganic catalyst such as $FeCl_3$ (Hou, Schaper et al. 2003) and iron(III) nitrate (Mauron, Emmenegger et al. 2002).

The FC-CVD method is a very popular and effective approach for the controllable synthesis of CNTs in an expected large-scale (Ren, Li et al. 2006). Further advancement of this approach to the controllable synthesis of CNTs requires a clear understanding of their growth mechanism. In particular, the CVD using FC technique has been proven very effective in the synthesis of well-aligned and high-yield CNTs (Liu, Lee et al. 2003). Compared with other methods, this technique avoids drawbacks such as noncontinuous operation, special time-consuming preparation, or the activation of a catalyst-impregnated material. Thus, many literatures on CNTs growth mechanism have been reviewed and some syntheses of CNTs based on FC-CVD method will be compared in this study.

Catalysts Used for CNTs Growth

From the literature review of growth of CNTs by using FC-CVD method, it is apparent that the catalysts used have mainly been transition metals and their forms such as iron, cobalt, nickel and also organometallic catalysts.

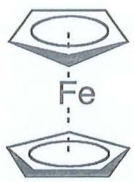
Inorganic Catalyst

Nanosized transition metal particles, in metallic forms particularly iron, cobalt and nickel have been used to catalyze CNT formation. The most important property of the metals with regard to the CNT growth is their ability to catalytically decompose gaseous carbon-containing molecules. Few papers in the literature, have reported the growth of CNTs using iron (Cassell, Raymakers et al. 1999; Lacerda, Teh et al. 2004; Song, Ci et al. 2006), nickel (Nasibulin, Moisala et al. 2006; Moon, Lee et al. 2009) and cobalt (Herrera, Balzano et al. 2001) as floating catalysts.

A wide variety of transition metals in the form of chlorides dissolved in either benzene or methanol, were used as potential growth catalysts (Deck and Vecchio 2006). MWCNTs formation was catalyzed by cobalt or iron nanocrystals; toluene served as both the solvent and the carbon source for nanotube growth (Smith, Lee et al. 2006). The floating catalyst method has been shown to yield Y-junction MWCNTs using a vertical electric furnace with iron as a catalyst, hexane as a carbon source and a small amount of thiophene as promoter (Zhu, Ci et al. 2002). The study on the synthesis of CNTs using $FeCl_3$ as a catalyst precursor had been reported by Hou et al. (2003). A mixture of toluene with N,N-dimethylaminoacetate (DMAc) was introduced as carbon source and hydrogen served as the essential carrier gas in the synthesis of CNTs. In addition, Zhang and co-workers (Zhang, Yu et al. 2008) synthesized CNFs from ethylene using $FeCl_3$ as a floating catalyst. Oriented nanotube films were synthesised on flat silicon substrates by CVD of a gas mixture of acetylene and nitrogen (Mauron, Emmenegger et al. 2002). For this purpose, Mauron et al., (2002) used metal oxide clusters formed by spin coating an iron (III) nitrate ethanol solution onto a silicon substrate and subsequent heating. Hence, among all inorganic catalyst, Iron (III) chloride with the formula $FeCl_3$ is preferred to use due to be an efficient catalyst for producing CNTs, easy availability and handling, non-toxicity, low price, and ease of volatilization.

Organometallic Catalyst

The metal source can be an organometallic complex, and a wide range of metals have been deposited by this procedure (Mohlala, Liu et al. 2005). Organometallic complexes have often been used in the synthesis of CNTs, carbon fibers, and carbon microspheres (Nyamori and Coville 2007). The advantages of using organometallic compounds are that they do not need to have a counterion and they act both as a catalyst and as a carbon source to form the CNTs. Numerous approaches have been used to study the effect of organometallic complexes on the formation of CNTs. Up to now, Ferrocene (Bai, Li et al. 2003; Barreiro, Hampel et al. 2006; Chaisitsak, Nukeaw et al. 2007), Fe(CO)5 (Vivekchand, Cele et al. 2004; Kuo, Bai et al. 2005) and iron-(II)-phethalocyanine (PcFe) (Hou, Schaper et al. 2003) have been the compounds commonly used as organometallic complexes FC precursors. Ferrocene is shown schematically in Scheme 1.



Scheme 1. Schematic structure of ferrocene molecule.

However, the subsequent filamentous carbon and carbon tube growth is monitored by metallic iron (α-Fe), or triggered by an intermediate iron carbide phase (FeC, Fe2C, Fe3C, Fe7C3) as the active catalyst (Hou, Schaper et al. 2003) is still a matter of debate. Remarkably, ferrocene has been implicated as the most promising catalyst in the synthesis of SWCNTs (Chaisitsak, Nukeaw et al. 2007), DWCNTs (Wei, Lijie Ci et al. 2003), MWCNTs (Satishkumar, Govindaraj et al. 1999), amorphous CNTs (Urones-Garrote, Ávila-Brande et al. 2005), spheres (Nyamori and Coville 2007) ,etc. This arises from the easy accessibility, price, stability in air and volatility of Ferrocene. Part of the reason for the limited investigations into the use of alternative organometallic complexes as gas phase catalysts in CNTs synthesis relates to the poor solubility and low vapor pressure of many potential organometallic catalysts. Hence, among all organometallic complex catalyst, ferrocene is used as the most promising chemical reagent in this research due to be an efficient and versatile additive which can be used as a FC.

Carbon Source Used for CNTs Growth

The synthesis of CNTs requires some source of carbon to create the carbon structures and this can be supplied by a catalyst and/or by an external source. When supplied by a catalyst such as Ferrocene and Fe(CO)5, C is derived from the Cp ligands. In some cases, to make CNTs, additional carbon sources must be included because of the low carbon/iron ratio within the pure precursor compound. In most studies the carbon used to make the CNTs is derived from an external source and this can be any carbon containing material. Different carbon sources have been reported in the literature and play a crucial role in CNTs synthesis using unsupported/floating CVD method. Typically, hydrocarbons are used such as methane (Kuo, Bai et al. 2005; Lu, Rider et al. 2006), ethylene (Awasthi, Singh et al. 2003; Zhang, Yu et al. 2008), acetylene (Lee, Kim et al. 2003; Vivekchand, Cele et al. 2004), benzene (Mayne, Grobert et al. 2001; Bai, Li et al. 2003), toluene (Hou, Schaper et al. 2003; Li, Li et al. 2007), xylene (Horvath, Kertesz et al. 2006; Gong, Li et al. 2007), pentane (Liu,

Huang et al. 2002), hexane (Zhu, Jiang et al. 2002), anthracene (Hou, Schaper et al. 2002; Nyamori and Coville 2007), etc.

The morphology of the CNTs should be influenced by the carbon source. It appears that almost any hydrocarbon that contains C-H, C-C, and C-O bonds will produce CNTs by bond cleavage reactions. In case of the injection method, metal-hydrocarbon solutions have been shown to yield a high quality of CNTs as well as aligned CNTs. The hydrocarbons which have been reported include: xylene, benzene, toluene, hexane, pentane and heptane. Among these hydrocarbons toluene, xylene and benzene are the most effective for the preparation of high quality CNTs. On the other hand, in paralyze method, hydrocarbons in the gaseous phase have shown to be more economic. The hydrocarbon in the gaseous phase can be used directly in the reactor without prior preheating, whereas liquid carbon sources need to be firstly preheated to transfer to reactor. The hydrocarbons that have been reported include: methane, ethylene and acetylene. Among previously-mentioned carbon sources, methane gas is more economic and safe in comparison with acetylene and benzene (Kuo, Bai et al. 2005).

Physical Parameters

The synthesis CNTs based on CVD method is strongly influenced by the temperature and pressure conditions. The decomposition temperatures of the catalyst and the carbon source influenced the reaction (Chaisitsak, Nukeaw et al. 2007). Most reactions have been carried out at atmospheric pressures but in few studies reactions at high pressures have been reported (Yang, Mercier et al. 2005; Barreiro, Hampel et al. 2006). The gas flow rates for introduction of the catalyst/carbon source in the CVD process also influence the type, quality and quantity of CNTs produced. Barreiro and co-workers (Barreiro, Kramberger et al. 2007) and Tapaszt et al. (2005) have made a similar observation. They suggested that the strong effect of flow rate on the average CNTs diameter. On the other hand, the nanotube yield strongly depends on the reaction time (Nyamori, Mhlanga et al. 2008). Monthioux. M et al., (2006) have reported that while the inner diameter may remain the same as a function of time the outer diameter can grow with time.

Reactor Design

All previous researchers to date have focused on developing a suitable reactor to synthesize the CNTs. All designers have tried to ensure that catalyst can be transferred into a reactor. In most methods the vapor of organometallic catalyst was passed through a furnace held between 700 and 1200° C. In high temperature range, use of a quartz reactor tube preferences use of a metal reactor. Because the metal reactor wall possibility plays a part in the reaction in this high range. In general there are two kinds of reactors that can be used for the FC-CVD method: the first one is the vertical reactor (Kuo, Bai et al. 2005; Yang, Hou et al. 2005), in which the liquid carbon source and catalyst precursor are injected into the chamber from the top (or bottom) of the reactor in the presence of a carrier gas such as Ar. The carbonaceous products are collected at the bottom (or top) of the reactor. The second one is the horizontal reactor (Andrews, Jacques et al. 1999), in which liquid or gaseous reactants and the vapor of the catalyst are carried into the reaction chamber by carrier gases such as H2 and/or Ar. The synthesis of aligned CNT arrays are mostly produced in horizontal reactors while all the reported carbonaceous products produced in vertical reactors are randomly arranged (MWCNTs, CNFs including SWCNTs bundles). This method is commonly known to be used for the bulk production of CNTs/CNFs. A

double stage furnace is required because of the different temperatures needed for catalyst sublimation and CNT growth. However in some reviews the organometallic catalyst is a solid at room temperature like ferrocene in this work, a frequent method have been used to introduce the catalyst into a horizontal reactor included two furnace system in which the catalyst is placed in a low temperature furnace under a flow of an inert gas (and/or carbon source) and transfers catalyst to a second to a second higher temperature furnace.

In other reviews used dissolved catalyst like ferrocene in xylene transfers directly to the horizontal and vertical reactor designs hot zone. More recently the most successful method has been an upsurge of interest in the synthesis of CNTs by pyrolysis of organometallic complexes in a confined space such as a stainless steel autoclave or sealed glass vessels, at autogenous pressure, especially using Fe and Co metal catalysts.

Designing the Experiments by the Software of Design of Expert (DOE)

Design of experiments (DOE) which is an efficient procedure for planning experiments had been served to discover the possible interaction taken place between the parameters. The effective parameters will be found out after doing some preliminary experiments and will be used in the final experiments. By using DOE, the data obtained can be analyzed to generate valid and objective conclusions. The role of experimental design is considered when estimating the effects of several variables separately, simultaneously and combinations if there are any (Sanchez, Martinez et al. 1997).

CCD is the most commonly used design for fitting a second order model. This might be used because of its ability to run sequentially. It estimates linear, interaction as well as curvature effects. As the design can provide much information on experiment variable effects and overall experimental error in a minimum number of required runs, it can be considered as a very efficient design. It also has the ability to be used under different experimental regions of interest and operability because of accessibility of several varieties of CCD (Montgomery 2001). A second order polynomial equation (Equation(1)) was fitted to the experimental data obtained, based on the above design, in order to generate the response surface model (Jo, Rene et al. 2008).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} X_i X_j + \varepsilon \qquad (1)$$

where:

Y = response calculated by model (dependent variables)

β0 = constant coefficient

βi = coefficients for the linear effect

βii = coefficients for the quadratic effect

βij = coefficients for the cross-product effect

Xi, Xj = variables corresponding to factors (independent variables)

ε = error

i and j = Number of factors

Problem Statement

Even though CNTs have been successfully synthesised via various approaches, there are still technical challenges that must be investigated and overcomed. Currently, researches on CNTs production include variety

of problems which are now considered in this study such as: (I) Conventional synthesis of CNTs involves the use of complicated and sophisticated equipment (such as LA, EAD, microwave oven, and etc). (II) CNTs grown by conventional supported catalyst also need to have very complicated purification process to remove the catalyst impurities. (III) Batch production limits the large-scale production of CNTs. Thus continuous production of CNTs using FC-CVD techniques will be more desired. (IV) Other hydrocarbon sources for producing CNTs, such as benzene, acetylene, CO, are harmful and it is not economical to be used in synthesizing CNTs. (V) In addition, the FC-CVD method favours very high reaction temperatures (900-1200 °C) for producing CNTs.

Research Objectives

The main goal of this research is to investigate the growth of CNTs using floating catalyst (FC)-CVD method of methane, with a focus on the preferential CNTs yield and formation of CNTs. This research project is planned and carried out to address the following objectives:

- To produce CNTs via the FC-CVD method using two types of iron FCs (i) iron (III) chloride ($FeCl_3$) as inorganic metal catalyst and (ii) ferrocene (Fe(C5H5)2) as organometallic catalyst.
- To evaluate and optimise the effects of different process parameters including reaction temperature, reaction time, methane flow rate and nitrogen flow rate on the CNTs yield.
- To purify the as-grown CNTs using acid treatment and to remove other probably produced carbonaceous materials by oxidation.
- To characterise the structure and morphology of as produced and purified CNTs.
- To analyse, model and optimise the functional relationship between the operation variables on the desired response (CNTs yield) based on the reliability of response surface methodology (RSM) in conjunction with central composite design (CCD).

Significance of Research

Benefits resulting from CNTs technology as scientific research and its applications should be shared with society as whole and within the international community, in particular with developing countries. Since Malaysia is the largest producer of natural gas in South East Asia and third in the world, natural gas is easily available here at low cost. In this work, synthesizing CNTs is done by utilizing natural gas (methane) as carbon source. If Malaysia as a developing country is threatened by declining demands of its natural resources, it could initiate CNTs projects that are tailored to increase these demands by new useful products. CNTs are one of the most innovative materials of the 21st century. In terms of mechanical properties, nanotubes are among the strongest and most resilient materials known to exist in nature. The extreme sensitivity of electronic property on structural parameters is unique for CNTs.

Expected Output and Applications

1. A simple method to produce CNTs continuously using FC-CVD.
2. Optimize the process for producing CNTs through FC-CVD method.
3. A potential approach to utilize natural gas to produce valuable CNT products.

PROJECT 3:

Research Problems

Concern about environmental protection has increased over the years from a global viewpoint. Textile dyes represented the main source for aquatic pollution with colored compounds. Inefficiencies in the dyeing of textiles result in large amounts of the non-biodegradable, toxic and inhibitory nature of spent dye baths being lost directly into wastewater and consequently having a considerable detrimental effect on flora, fauna, and environmental matrix [1]. The real hazard setting aside aesthetic considerations is caused when colored agents interfere with the transmission of light through water, retard photosynthetic activities in aquatic life, inhibit the growth of biota, damage the quality of the receiving streams and toxic to food chain organisms, thus upsetting biological processes within streams, resulting in ecological imbalance [2].

Adsorption using activated carbon has been found to be more superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of dyes even from dilute solutions [3]. Commercially available activated carbons are usually derived from natural materials such as wood or coal, and therefore, are still considered expensive. This has led to the search for cheaper substitutes. Hence, low-cost adsorbents based on agricultural solid wastes are most desirable. The aim behind using waste materials as adsorbents is that it will provide a twofold advantage with respect to environmental pollution. First, the volume of waste materials could be partly reduced, and second, the low-cost adsorbent, if developed, can reduce the pollution of wastewaters at a reasonable cost [4].

Literature Review

Today, rapidly changing technologies, industrial products and practices generate waste that if improperly managed, could threaten public health and the environment [5]. Various industries such as textiles, paint and varnishes, ink, plastics, pulp and paper and cosmetics use different types of organic dyes and dye intermediates. Among the different pollutants of an aquatic ecosystem, dyes are a large and important group of industrial chemicals with over 700,000 tons of waste produced annually [6]. Considering the inherent toxic nature of industrial effluents and the unavailability of clean technologies, the necessity of developing new methodologies for efficient treatment of effluents is evident. For this purpose, activated carbon has been proven to be an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media, or from gaseous environment [7]. Despite its prolific use in water and wastewater treatment, its use is restricted sometimes due to the higher cost of activated carbon [8]. Therefore, in recent years, many researchers have tried to produce activated carbons for removal of various pollutants using renewable and cheaper precursors which were mainly industrial and agricultural by-products.

In this regards, we are proposing this research to overcome the high cost of commercially available activated carbons. The objectives of this research are to prepare powerful adsorbents from cheapest agriculture solid wastes such as oil-palm solid waste, tea waste etc and also to enhance the adsorptive capability by introduction of new functional groups for the adsorption of textile dye.

Research Objectives

The main objectives of this proposed research are to:

1. Prepare a series of functionalized adsorbents from cheapest agriculture solid wastes.
2. Characterize the functionalized adsorbents for their physical and chemicals properties.
3. Evaluate the performance of functionalized adsorbents for removal of dyes.
4. To develop the isotherms, kinetic and thermodynamics of the adsorption process.
5. To construct the breakthrough curves for the textile wastewater and adsorption system

PROJECT 4:

Research Problems

Air pollution control has gained importance due to increase environmental regulation, pressure from environmental groups and public awareness. The air pollutants generated from burning fossil fuels, such as coal, oil, and natural gas, in industrial and commercial facilities, and in electric power plants, have been the most influential factors in the deterioration of air quality [1]. Among these pollutants, sulfur dioxides (SO_2) and nitrogen oxides (NO_x) are well-known as a precursor of acid rain. Various SO_2/NO emission control technology have been developed and applied in coal-fired plants to remove them from the flue gases before emitting into the atmosphere. The dry sorption method is now considered as the most attractive way to treat waste gases containing SO_2 and NO. Unfortunately, only limited study have been reported to remove NO and SO_2 simultaneously using the dry method [2,3], especially using siliceous materials such as rice husk ash (RHA). RHA is an agricultural waste material that is available abundantly in rice-producing countries such as Malaysia.

Recently, we have reported the sorption characteristic of SO_2/NO over the RHA/CaO-supported metal oxides [4,5]. The results showed that RHA/CaO sorbents supported with CeO_2 displayed the highest sorption capacity among other supported metal oxides for the simultaneous desulfurization and denitrification processes. However, concerning the gas-solid reaction analysis, especially kinetic behaviour of this sorbent, have not been thoroughly studied yet. Even in the literatures, only a few studies concerning the kinetic of the reaction between Ca-based sorbent (e.g. $CaCO_3$, $Ca(OH)_2$ or CaO alone without any addition of siliceous materials) and SO_2 at low temperature were reported. The range of temperature studied is basically categorized to low (< 150 °C) [6-8], medium (300-600°C) [9,10] and high temperatures (>700 °C) [11-13]. As the sorbent for dry desulfurization process is mostly Ca-based, therefore, the primary reaction of this process would produce $CaSO_3$/$CaSO_4$.

Apart from that, the kinetic study of simultaneous desulfurization and denitrification processes at low temperature using sorbent prepared from siliceous materials are also very limited. Only a few studies has been carried out on the kinetic behaviour of desulfurization process using sorbent prepared from Ca-based/coal fly ash. Garea et al. [14] reported the desulfurization of $Ca(OH)_2$/coal fly ash sorbent at low temperature (52-67 °C) in a fixed bed reactor, whereby the reaction rate was based on the SO_2 sorption on a non-ideal surface as the controlling step. It was also concluded that relative humidity (RH) was the most important variable that effect the kinetic of the sorbent. Whereas Liu et al. [15] described the reaction kinetics of $Ca(OH)_2$/coal fly ash sorbent by the surface coverage model which assumes that the reaction rate was controlled by chemical reaction on

sorbent grain surface and takes into account the surface coverage of by products. They also reported that the kinetic behaviour of this sorbent was similar to the reaction of pure $Ca(OH)_2$ with SO_2. Christopher-Chia et al. [16] has proposed a relatively simple global rate equation to describe the kinetic of the desulfurization reaction between SO_2 and sorbent prepared from coal fly ash/CaO/$CaSO_4$ which was carried out under isothermal conditions at various operating parameters.

Until now, the kinetics studies developed to represent the reaction of siliceous/Ca-based sorbents were only based on the desulfurization process (concentration of SO_2), reaction temperature, properties of the sorbent structure (surface area and quantity) and relative humidity. However, if SO_2 and NO is to be removed simultaneously, the kinetic of denitrification process need to be incorporated/developed as well. Therefore, the main objective of this work is to study the kinetic behaviour between RHA/CaO sorbents supported with CeO_2 and SO_2/NO at low temperature based on the breakthrough curves obtained in a packed bed reactor. This will be useful for proposing reaction mechanism, model for prediction of reactor performance under different conditions and as well as a tool for design and optimization of the simultaneous flue gas desulfurization and denitrification processes.

Research Objectives

The undertaken research project aims to achieve the following objectives:

1. To evaluate the effect of temperature, relative humidity (RH), space velocity and feed concentrations on SO_2/NO breakthrough curves for sorbent synthesized from rice husk Ash (RHA)/CaO-Supported CeO_2.
2. To study the kinetics of the desulfurization and denitrification processes at low temperature
3. To propose reaction mechanism for the desulfurization and denitrification processes at low temperature

PROJECT 5:

Research Problems

Glycerol is a key co-product of biodiesel industry. Presently, rapid increase in biodiesel production is followed by an excess of glycerol generated. The oversupply of glycerol reduces its price. The low cost and the increase in glycerol availability make it attractive to exploit glycerol for synthesis of valuable products. For example, glycerol has been converted into high yield of 1,2-propanediol in the presence of Pt impregnated NaY zeolite as a catalyst and acrolein has been synthesized via dehydration of glycerol performed on a WO_3/ZrO_2 catalyst in a continuous flow fixed bed reactor (D'Hondt et al., 2009; Ulgen et al., 2009). Glycerol is also used for commercial production of monoglyceride through transesterification of glycerol with fat (triglyceride) or with fatty acid methyl ester (FAME) using homogeneous basic catalyst. Besides of that, monoglyceride is also produced industrially via esterification of glycerol with fatty acid.

Currently, direct esterification of glycerols with fatty acids for monoglyceride production relies on homogeneous catalysts typically strong mineral acid (Bosaert *et al.*, 1999; Corma and Kumar, 1998; Formo, 1958). However, this technology creates large amounts of by- products and waste, and utilizes high energy (Nakamura *et al.*, 2008). Solid acid catalysts can offer advantages in the process design and may improve yield

and selectivity to the desired product (Corma *et al.*, 2005).

Acidic resins and zeolites have been used as solid acid catalyst for this application (Aracil *et al.,* 1992 ; Heykants *et al.*, 1996 ; Pouilloux *et al.*, 1999). However, they were unfavorable for monoglyceride production due to small pore diameter less than 8 Å, which makes them unsuitable for reactions involving synthesis of the bulky molecule like fatty acid (Perez-Pariente *et al.,* 2003). In addition, Wilson and Clark (2000) suggested that the effective solid acids having pore sizes between 20-100 Å were required for liquid phase reactions. On the other hand, MFI zeolite loaded with Pt was useful for fatty acid chemistry i.e. hydrogenating methyl elaidate (trans isomer) from an equimolar mixture with methyl oleate (cis isomer) as recently reported in the literature (Philippaerts et al., 2010).

Mesoporous silica SBA-15 having surface area (500-1500 m^2/g), large pore size (50-100 Å) with narrow pore size distribution and thermal stability has been incorporated with sulfated zirconia on their surface to generate solid acid catalyst via direct synthesis or post synthesis route. It exhibited high activity for esterification reactions such as reaction of fatty acid with methanol for biodiesel (Chen *et al.,* 2007), cyclohexanol with acetic acid (Garg *et al.,* 2009), and acetic acid with n-butanol, as well as for transesterification of triacetin with methanol (Du *et al.*, 2009). However, sulfated zirconia functionalized SBA-15 catalyst for the direct esterification of glycerols with fatty acids to monoglyceride has not been reported so far.

The earliest, mesoporous silicas of MCM-41 and HMS functionalized with organosulfonic acid were found to be excellent catalysts for formation of bisfurylalkanes and polyol esters (van Rhijn et al., 1998). Meanwhile, SBA-15 functionalized with organosulfonic acid via direct synthesis route, followed by an oxidation step to create HSO_3SBA-15 catalyst has also been studied. The HSO_3SBA-15 catalyst was applied for esterification of fatty acid with glycerol (Diaz *et al.,* 2001). It was found that the catalyst gave 50 % conversion and 57 % selectivity to monoglyceride in the esterification at 120 °C for 24 h reaction. Furthermore, in the esterification at 150 °C for 6 h, the HSO_3SBA-15 catalyst gave 93 % fatty acid conversion but lower selectivity to monoglyceride (around 20 %). The poor performance of the SBA-15 catalysts was caused by the existence of organosulfonic acids in the high presence of structural micropores, so that the esterification would be slowed down. This finding is consistent with that reported by the other researchers (Hou *et al.*, 1995; Zou *et al.,* 1998).

PROJECT 6:

Research Problems

Almost 45% of textile dyes produced worldwide belongs to the reactive class. Reactive dyes are common dyes used for dyeing cellulosic fibres due to their favorable characteristics of bright color, water-fastness, simple application techniques and low energy consumption. They are usually characterized by nitrogen to nitrogen double bonds (N=N azo bonds) where the color of azo dyes is due to this azo bond and the associated chromophores. The formation of a covalent bond between the dye molecule and the fibre is much stronger than the physio-chemical bond between other classes of dyes and cellulose. However, reactive dyes pose the greatest problem in textiles wastewater since they are not easily biodegradable, and thus colour may still remain in the effluent. In fact, the expanded uses of azo dyes and their reaction products such as aromatic amines are highly carcinogenic. The discharge of these wastewaters into receiving streams causes damage not only to aquatic life

but also to human beings.

In recent years, many processes have been applied for the treatment of reactive dyes from wastewater including biological, physical and chemical process. Among them, adsorption process with activated carbon has been proved to be superior compared to other techniques in terms of its simplicity of design, high efficiency and ease of operation. However, the manufacturing costs of commercial activated carbons are in fact rather high. As such, there is a need to produce activated carbon with high adsorption performance from alternative material that is cheaper and readily available. In this work, an attempt was made in preparing activated carbon from agricultural wastes; durian peel, banana stalk, periwinkle shell, rambutan peel, mangosteen peel, cocoa pod husk, coffee husk and palm shell. Due to the high consumption of edible part, massive amounts of the peels/husks/shells are disposed, causing a severe problem in the community as they gradually ferment and release off odours. Therefore, by utilizing those wastes into activated carbon will decrease the cost of wastes disposal and also converted this waste into value-added product.

Research Objectives

i) To prepare activated carbons from agricultural wastes; durian peel, banana stalk, periwinkle shell, rambutan peel, mangosteen peel, cocoa pod husk, coffee husk and palm shell.

ii) To study the optimum activated carbon preparation conditions including activation temperature, activation time and chemical impregnation ratio using response surface methodology.

iii) To characterize the activated carbons prepared in terms of surface area, pore volume, pore size distribution, surface morphology, proximate content, elemental composition and surface chemistry.

iv) To study the effects of adsorbate initial concentration, contact time, solution temperature, solution pH, isotherms, kinetics and thermodynamics for adsorption of basic (methylene blue and malachite green) and reactive (Remazol Brilliant Violet 5R, Remazol Brilliant Blue R, Remazol Black R and Remazol Brilliant Orange 3R) dyes on the activated carbons prepared using batch adsorption tests.

Significance of Research

From the literature, there has been no information yet for using those wastes as precursors for activated carbon production particularly by physiochemical activation method. Thus, this study investigated the feasibility of preparing activated carbon for application in removing basic (methylene blue and malachite green) and reactive (Remazol Brilliant Violet 5R, Remazol Brilliant Blue R, Remazol Black R and Remazol Brilliant Orange 3R) dyes from aqueous solution. In addition, CMS were successfully prepared by further treated activated carbon using carbon vapour deposition method. The CMS prepared were suitable for gas separation application.

PROJECT 7:

Research Problems:

Using CNT in practical applications has been largely limited by their poor processability, since they are practically insoluble and infusible.

Research Objective :

To synthesis CNT/metal oxides nanocomposites by creating good interface between CNT and desired molecules

Significance of Research :

This research has great significance on seeking a better way to utilize the CNT and metal oxides such as manganese oxide (MnO_2). This research is useful because reinforcement of CNT into the metal oxides will able to produce nanocomposites with better properties. They possess distinctive electrical, mechanical, biological and physical properties. Thus, this process will contribute to the development of CNT based nanocomposites as material with advanced properties.

PROJECT 8:

Research Problems

The current technologies for *p*-xylene production and recovery consume high energy and incur high operating cost. Due to the increasing demand and rising price of *p*-xylene over the global market, researchers have devoted considerable effort over the past 10 years in finding economic process route for the production and recovery of *p*-xylene. MFI-type zeolite membrane emerged as a potential effective alternative to be used in a membrane reactor.

The synthesis of a well-intergrown and high quality (thin, compact and low defects) silicalite-1 (MFI type zeolite) membrane still poses many challenges for various researchers. During the synthesis and template removal steps, defects such as intercrystalline boundary and cracks can easily form. A high quality membrane is needed for the separation of xylene isomers because a minor defect in the membrane structure will affect the separation performance. Although the methods to produce minimum defects zeolite membrane have been reported in the literature (Hedlund *et al.*, 2002, Bernal *et al.*, 2004), the results are not reproducible which are mainly due to the complex mechanism of zeolite crystal growth that has not been fully understood. Hence, reproducibility of the synthesis method is another challenging task for the synthesis of zeolite membrane.

Most of the xylene separation studies using MFI type zeolite membrane reported in the literature have focused on the effect of membrane quality such as orientation, thickness, microstructure and defects. The effect of separation process variables such as temperature, xylene feed composition and feed partial pressure, as well as their interactions are not systematically investigated. To the best of our knowledge, optimization of the operating process variables in xylene separation has not been reported. Therefore, there is a need to use the statistical approach to study the separation performance of the membrane. This approach with minimum number of experiments will provide information about i) interactions between the process variables, ii) important variables in the separation process and iii) identification of the optimum operating condition. The conventional approach reported in the literature for the study needs large number of experiments using one process variable studied at a time and keeping other variables constant. This one-factor-at-a-time method generally fails to consider the possible interactions between the factors (Montgomery, 2005). Therefore, a statistical Design of Experiment (DoE) approach to fully evaluate the effect of operating variables and interactions between the factors to the membrane separation performance is much needed.

Although the reported results show the potential of H-ZSM-5 in membrane reactors for xylene isomerization; the membrane shows moderate to low selectivity of *p*-xylene (Kim *et al.*, 1998; Zheng *et al.*, 2006). There is a need to synthesize a catalytic membrane with improved conversion, *p*-xylene yield and *p*-xylene separation rate. Silicalite-1 membrane has shown good performance in *p*-xylene separation, due to its higher diffusion rate compared to its isomers, *m*-xylene and *o*-xylene (Stephane Haag *et al.*, 2006). However, silicalite-1 is an aluminum-free analogue of ZSM-5 (Si/Al = ∞) which is catalytically inactive in its pure form. The selective and continuous removal of *p*-xylene from the reaction system could enhance the xylene isomerization toward higher selectivity and yield. Therefore, it has drawn an interest in the synthesis of silicalite-1 membrane with catalytic acid sites.

In order to introduce the acid sites in silicalite-1 membrane, organic-functional groups could be added into the synthesis mixture. Jones *et al.* (1999) reported that the introduction of organic group into the zeolite micropore is difficult due to the large size of organic species, which resulted in a disruption of the crystal structure and multiphase, and thus, crystalline/amorphous mixture is produced. The transformation of organic-functional group present in the amorphous phase to organosulfonic acid group resulted in the formation of acid-functionalized zeolite. The main advantage of this material is the absence of pore blockage in the zeolite crystalline phase and most of the acid sites are located in the amorphous phases of the structure.

However, the synthesis of acid-functionalized silicalite-1 catalytic membrane using organo-functional group is a new task and therefore imposes many challenges. The problems encounters for the synthesis of this new-type membrane are:

- Method for synthesis of membrane and the choice of organo-functional group
- For obtaining well-intergrowth membrane, optimum concentration of the organo-functional group present in the synthesis mixture need to be studied
- Stability of the membrane after functionalization
- The presence of acid sites on the membrane which depends on the amount and type of amorphous species.

After having an appropriate design of acid functionalized silicalite-1 catalytic membrane reactor, the challenge is to test the performance of the membrane in xylene isomerization. By far, the development of acid-functionalized silicalite-1 catalytic membrane reactor for the application of combined xylene isomerization reaction and separation will be an arduous task due to the acid-functionalized silicalite-1 membrane is first synthesized in the present work. The membrane should possess the ability of xylene isomerization as well as separation of *p*-xylene from the reaction products. In order to optimize *p*-xylene yield and to avoid side reactions other than isomerization, a suitable operating condition such as weight hourly space velocity for isomerization of xylene need to be studied. Another challenge is the selective separation of *p*-xylene after isomerization reaction. High separation factor of *p*-xylene to its isomers should be achieved. By reactive separation of *p*-xylene from the reaction products, it is believed that the conversion of xylene and selectivity of *p*-xylene will be improved.

Research Objectives

The objectives of the present research are:

1) To synthesize and characterize silicalite-1 and acid-functionalized silicalite-1 membranes.
2) To test the performance of silicalite-1 and acid-functionalized silicalite-1 membranes for the separation of binary and ternary xylene mixture.
3) To study the performance of acid-functionalized silicalite-1 membranes as catalyst in xylene isomerization reaction and to determine the reaction rate parameters.

Significance of Research

In present research, silicalite-1 and acid-functionalized silicalite-1 membranes were synthesized and characterized. The transformation of organic-functional group present in the amorphous phase to organosulfonic acid group resulted in the formation of acid-functionalized zeolite. The main advantage of this material is the absence of pore blockage in the zeolite crystalline phase and most of the acid sites are located in the amorphous phases of the structure. Present study explored the conditions for synthesis of acid-fucntionalized silicalite-1 membranes, such as the optimum concentration of the organo-functional group required in the synthesis mixture and the stability of the membrane after functionalization. One of the significances of present research was the optimization studies for the of the process variables, which has not been reported, to our best knowledge. silicalite-1 is an aluminum-free analogue of ZSM-5 (Si/Al = ∞) which is catalytically inactive in its pure form. Catalytic silicalite-1 membrane with improved conversion towards xylene isomerization and separation had been synthesized in present study. The membranes possed the ability of xylene isomerization as well as separation of *p*-xylene from the reaction products. The p-xylene yield was optimized by running a suitable operating condition such as weight hourly space velocity for isomerization of xylene.

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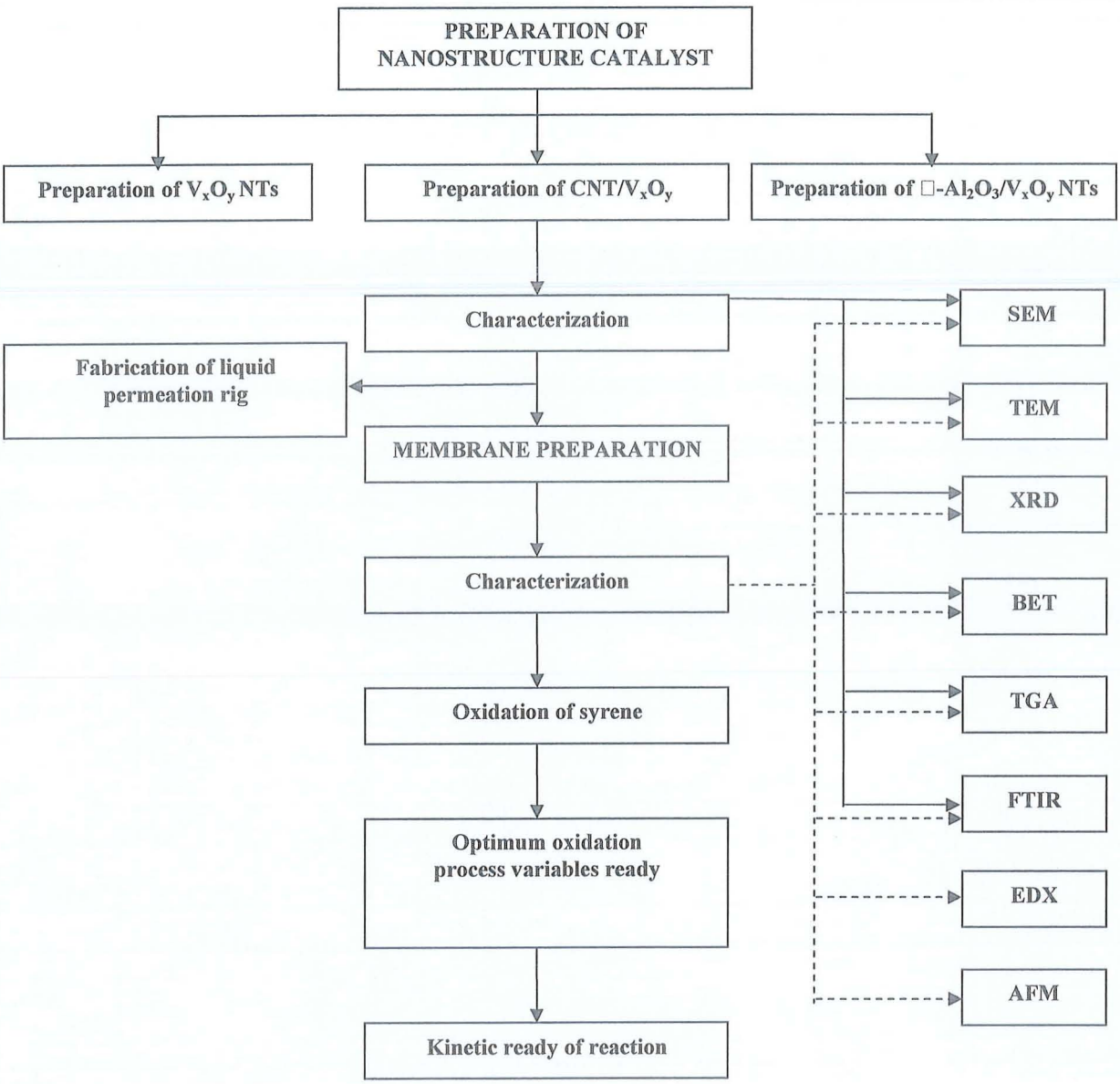
F. RESEARCH METHODOLOGY

PROJECT 1:

Milestones achievement

No	Milestone Name	Status (Yes/No)	Deliverable
1	Complete study on material interaction and selection of casting dope	Yes	Dec. 2007
2	Complete in boehmite sol preparation	Yes	May 2008
3	Complete synthesized and assembled templating unit	Yes	June 2009
4	Complete of impregnation catalyst	Yes	January 2010
5	Complete of styrene oxidation study	Yes	August 2010

Flowchart


PREPARATION OF NANOSTRUCTURE CATALYST
Preparation of V_xO_y NTs
Preparation of CNT/V_xO_y
Preparation of □-Al_2O_3/V_xO_y NTs
Characterization
Fabrication of liquid permeation rig
MEMBRANE PREPARATION
Characterization
Oxidation of syrene
Optimum oxidation process variables ready
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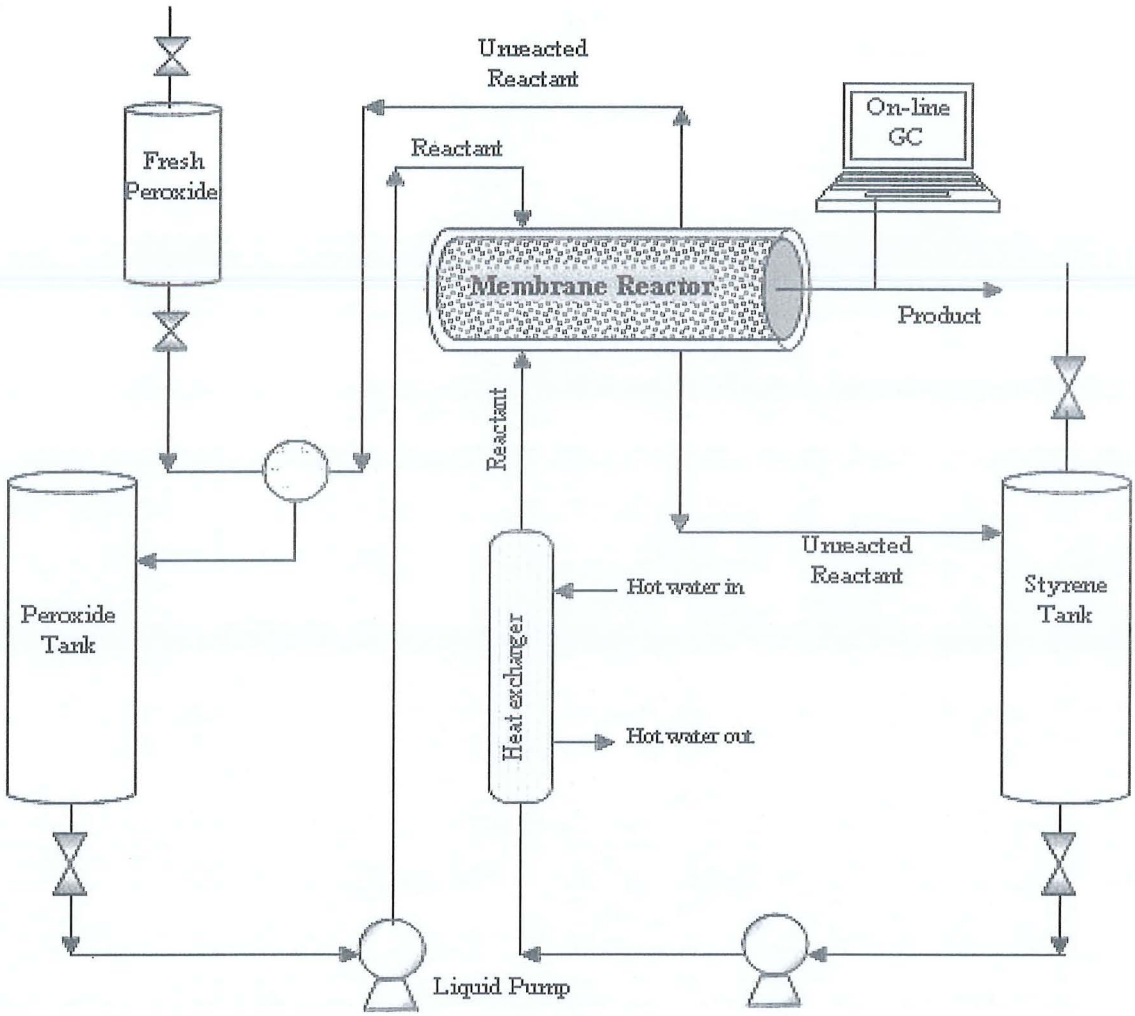
Schematic Diagram for the Experimental Set-Up



PROJECT 2:

Experiment and Requirement

Experimental method

Among the various methods identified for synthesis CNTs, the FC-CVD method will be utilized using ferrocene as organometallic catalyst and $FeCl_3$ as metal salt inorganic catalyst. Synthesis of CNTs by serving FC is included some vital reason and some aims which have been noticed in literature survey. FC attracts attention because of its ability for continuous production of high purity CNTs, simple equipment, low reaction temperature and low cost. Thus it has potential as an industrial process for high yield production of pure CNTs.

Chemical Requirements

Among all organometallic complex catalyst ferrocene is used as most promising chemical reagent in this research due to be an efficient and versatile additive which can be used as a FC. This arises from the easy accessibility, price, poisonous less, stability in air and volatility of Ferrocene. Iron(III) chloride, with the formula $FeCl_3$ as inorganic catalyst is also used in this research due to be an efficient catalyst for producing CNTs, easy availability and handling, non-toxicity, low price, and ease of volatilization.

In this study, methane is used as a carbon source. This is due to the fact that methane, a major component of natural gas, is highly abundant at low cost. Methane gas is more economic and safe (least toxicity) in comparison with other hydrocarbon. Furthermore, it is stable at elevated temperatures, thus preventing thermal pyrolysis. For this reason, catalytic decomposition of methane is a very attractive method for producing CNTs. Synthesis of CNTs by ferrocene requires the presence of reducing agent to ensure ferrocene remains in a low oxidation state. This can be achieved by hydrogen that was decomposed from methane as carbon source. Nitrogen is also used as a carrier gas.

Experimental Equipment

Component	Specification	Function
Mass flow controllers (MKS, model 246°C)	Max. flow range: 0.00-500.00 sccm	To regulate and control the flow rate of methane gas.
Mixing chamber	OD=½"	To create turbulent flow for better mixing of both methane and nitrogen gases
Pressure gauge(Ashcroft, USA)	Set at 1 atm	To measure the pressure in the reactor
Tubular furnace (Carbolite, Model)	Max. temperature=1200.00 °C, Heated length=600 mm, ID=110 mm	To obtain the desired reaction temperature in the reactor
Quartz tube	OD=30 mm, ID=28 mm, L=900 mm	To provide a chamber for the reaction to occur.
Thermocouple probe (Type K)	D=3 mm, L=600 mm	To measure the actual reaction temperature in the reactor
Quartz boat	L=50 mm	To put catalyst in the reactor
Heating plate	-	To heat the mixture of CNTs and acid solution for purification purposes
Flat bottom flask	With 3 necks, 1000 cc	To contain the mixture of CNTs and acid solution for purification purposes
Magnetic stirrer	L=30mm	To stir the mixture of CNTs and acid solution for purification purposes
Condenser	Normal condenser	To condense the acid vapour in purification process.

Designing of the Experimental Rig and Set the Conditions

The schematic representation of CNT synthesis apparatus has been shown in Scheme 2. The horizontal reactor consists of a quartz tube and a furnace fitted with independent temperature controllers. The horizontal quartz tube of 28 mm inner diameter and 900 mm length also the length of the hot zone of furnace is 550 mm. A quartz boat about 5 cm in length, for putting ferrocene in a quartz tube.

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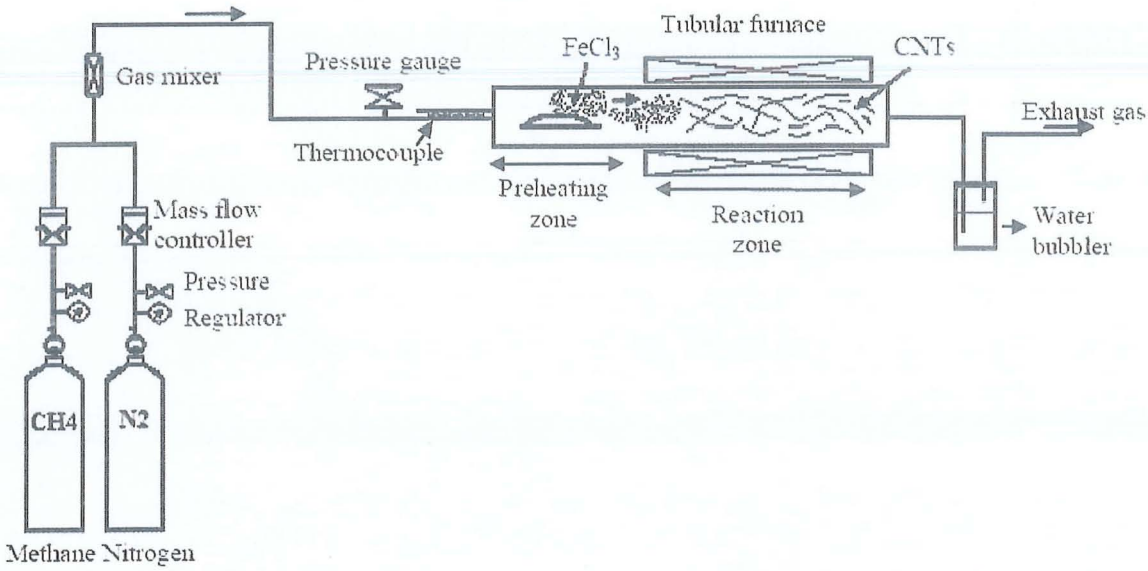


Scheme 2. Schematic diagram of the apparatus used for the synthesis of CNTs.

The rig involves two mass flow meters to control the gas flow rates and temperature controllers to control the rate of heating in the various reaction times. The acetone bubbler served to prevent crystallization of the ferrocene in the outlet tube and to decrease environmental pollutions. First the quartz boat, full of ferrocene is put 10 cm away from the left end of furnace where temperature is almost 300°C. Furnace is heated at 500 to 1100°C. The vaporization of ferrocene is performed under nitrogen as a carrier gas and methane as a carbon source without using substrate in the reactor. The major impurity of synthesis of CNT is the substrate which is eliminated in the experiments by free substrate FC-CVD method. Then the reactor was cooled down until room temperature. In this work, it is expected that CNTs grown on the inner wall of the reactor which will be easily separated from wall by scratching. One point to synthesize CNTs it is to use methane and ferrocene as nontoxic carbon source and catalyst, respectively. The other point it is to vaporize of the ferrocene as catalyst without solute in liquid hydrocarbon without using hydrogen as carrier gas.

Characterizing the As-synthesized CNTs

The deposited carbon products will be collected either as powder or as layers from the reactor wall and their weight are determined for calculating the yield. Morphologies of the deposited layers and powders are determined the quantity, quality, and properties of the nanotubes by analytical investigations equipment.

Morphological Analysis

The morphology and structure of the as-synthesized CNTs will be characterized by TEM and SEM

techniques, respectively. The percentage of exist elements of CNTs samples will be analyzed using EDX. TGA technique will be served to determine the product purity and the yield of CNTs quantitively. Raman Spectroscopy is also used to detect the presence of nanotubes and also to identify SWCNTs or MWCNTs. A high and uniform crystallinity of the produced CNTs is an important measurement of the quality.

Purification of the As-synthesis CNTs

Purification of FC-CNTs generally refers to the separation of CNTs from other entities, that it can be amorphous carbon and trapped catalyst material. If there is any impurity, the samples will be heated at 400 °C for 4 hrs in air to remove the amorphous carbon, which also will expose the catalyst metal surface. Then, they were put into a concentrated hydrochloric acid in an acid bath for 12 hrs. Finally, the samples will wash carefully with water several times to remove the acid and dried in the oven.

Characterization of the As-purified CNTs

The quality of the purification process will be determined by characterizing the as-purified CNTs using SEM analysis equipped with EDX analysis, TEM, TGA and Raman spectroscopy.The Optimization of the Experimental Effective Parameters based on Design of Experiment (DOE)

In order to optimize the CNTs production process, variety of experimental conditions will be investigated by design of experiment (DOE) software, such as flow rate ratio of methane and carrier gas, reaction time, growth temperature. The effective parameters will be found out after doing some preliminary experiments and will be used in the final experiments. By using DOE, the data obtained can be analyzed to generate valid and objective conclusions. Finally, the experimental results will be analyzed and optimized by analysis of variance (ANOVA).

Milestones achievement

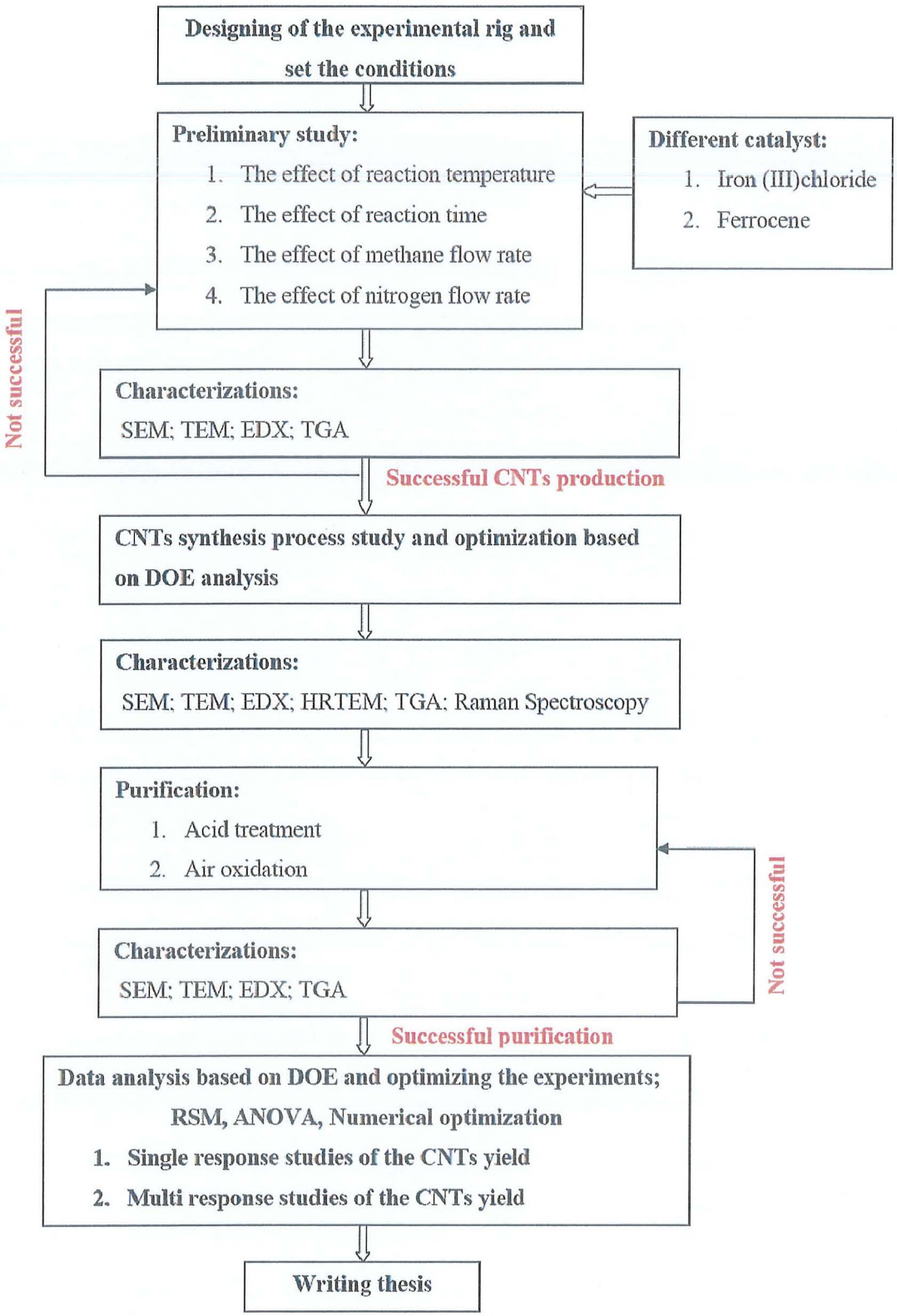
No.	Milestone Name	Date
1	Modification of the experimental rig and set the conditions	September 2008
2	Synthesize and characterization of the as- synthesis CNTs	Feburary 2009
3	Process study and Optimization	November 2009
4	Purification of the as- synthesis CNTs	April 2010

Flowchart

The experiments have been done in four different parts;

1) Preliminary study on synthesizing CNTs in order to determine the effective parameters.
2) Optimisation of synthesizing CNTs based on the effective parameters.
3) Purification of as- grown CNTs
4) Characterisation of as- grown CNTs

Scheme 3 presents the overall flowchart of the present experimental work. This is to give an overview of the research activities that have been performed throughout this study.



Scheme 3. Overall experimental flowchart.

PROJECT 3:

Experiment and Requirement

There are five steps for the proposed research methodology for the wastewater treatment via functionalized adsorbent assisted adsorption process:

Design and fabrication of the current experimental set-up for preparation of functionalized adsorbents.

Currently, the experimental set-up for preparation of activated carbons is available (See Fig. 1-3); and the programmable temperature tubular furnace was replaced.

Fig. 1:
Experimental set-up for preparation of activated carbon

Fig. 2:
New reactor and tubular furnace

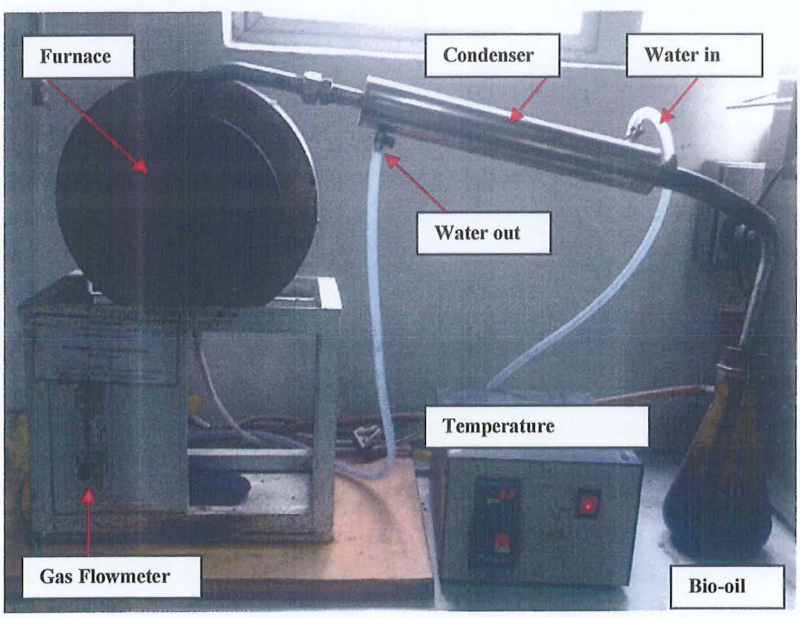


Fig. 3: Experimental setup for preparation of activated carbons

Preparation of functionalized adsorbents from agricultural solid waste

Oil palm fibre, oil palm empty fruit bunches and rejected tea, the abundantly available agricultural solid wastes in Malaysia were used as the raw precursors for the preparation of adsorbents.

Characterization of the prepared adsorbents

The prepared adsorbents were be characterized using:

- Scanning electron microscopy (SEM)
- Surface area and pore size distributions
- Fourier Transform Infrared (FTIR) Spectrometry
- Thermogravimetric analyzer (TGA)
- CHNS-O –Elemental analyzer

Evaluation of the adsorption performance of the prepared adsorbents

Adsorption performance of the prepared adsorbents was investigated in both batch and column studies based on the parameters as shown below:

- Contact Time
- Solution pH
- Temperature
- Concentration

The following analytical instruments (Fig. 4) were used to analyze the concentrations of dyes and also intermediate products:

- **UV-Visible spectrophotometer.**

Fig. 4a: Uv-Vis spectrophotometer

Fig. 4b: Uv-Vis spectrophotometer

The adsorption and desorption studies were carried out using water-bath shakers and fixed-bed continuous adsorption system (Fig. 5).

(a) (b)

Fig. 5: Water-bath shaker (a) and fixed-bed adsorption continuous system (b)

Isotherm, kinetic and thermodynamic studies

Isotherm, kinetic and thermodynamic studies were conducted for describing the relationship between adsorbate molecules and adsorbent surface, and determination of the adsorption rate constant and thermodynamic parameters (Gibbs free energy change, enthalpy change and entropy change) of the system.

Project Milestones

No	Milestone name	Date	Deliverables	Achieved (Yes/No)
1	Completion of preparation of raw materials and testing experimental setup.	06/2008	06/2008	Yes
2	Completion of synthesis and Characterization of functionalized adsorbents	03/2009	03/2009	Yes
3	Completion of functionalization/characterization of functionalized adsorbents.	12/2009	12/2009	Yes
4	Completion of modification and evaluation the performance of functionalized adsorbents.	09/2010	09/2010	Yes

PROJECT 4:

Experiment and Requirement

Sorbent Preparation

The sorbents will be prepared from rice husk ash (RHA), lime (CaO) and cerium nitrate/acetate solution. Prior to use, the RHA will be sieved to produce less than 200 μm particle size. Two steps of sorbent preparation will be used. Water hydration method (Lin et al., 2003) will be used to prepared RHA/CaO sorbent based on the optimum hydration conditions reported in our previous studies (Dahlan et al., 2006). Then, pore volume impregnation method (Tseng et al., 2003) will be separately employed to obtain RHA/CaO-supported CeO_2, which will be prepared by thermal decomposition of the $Ce(NO_3)_3$. $6H_2O$. The sorbent obtained in the powder form will then be pelletized, crushed and sieved in order to achieve the required particle size (250 – 300 μm) for the sorption capacity/activity test toward SO_2/NO by subjecting it to simulated flue gas.

Sorbent Characterization

Selected sorbents, before and after the desulfurization/denitrification reaction, will be characterized based on its physical and chemical properties using various analytical instruments. For instance, the chemical composition of RHA will be determined using X-ray Fluorescence (XRF) spectrometer. The specific surface area of the sorbents and raw materials will be determined using BET (Brunner-Emmett-Teller) methods on an Autosorb-1 Quantachrome analyzer. Scanning electron microscope (SEM) will be used to examine the sorbent surface morphologies and X-ray diffraction (XRD) spectrum will be recorded using X-ray diffractometer to investigate the various phases present in the sorbent. Thermogravimetric analyzer (TGA) will be used to characterize product of reaction between the sorbent and SO_2/NO. The acidity of sorbent will be measured using Temperature-programmed desorption (TPD) analyzer.

Gathering of Kinetic Data

A synthetic flue gas containing sulfur dioxide (SO_2), nitrogen oxide (NO), oxygen (O_2), water (H_2O), and nitrogen (N_2) will be used in this experiment. The desulfurization/denitrification activity will be carried out by packing 0.5 g of sorbent in the center of the heated reactor supported by 0.05 g of glass wool (Figure 1). The concentration of SO_2 and NO in the flue gas will be measured before and after the sorption process. A synthetic flue gas stream will be passed through the sorbent, and the concentration of SO_2 and NO will be recorded continuously for every minute until 1 – 2 hours. The sorption capacity of the sorbent will then be recorded by measuring the composition of the flue gas before and after going through the reactor. The effects of various operating variables will be studied, such as:

1. Feed concentration of SO_2 (500 – 2000 ppm)
2. Feed concentration of NO (0 – 1000 ppm)
3. Reaction temperature (50 – 300 °C)
4. Relative humidity (0 – 80 %)
5. Space velocity (5,000 – 15,000 hr^{-1})

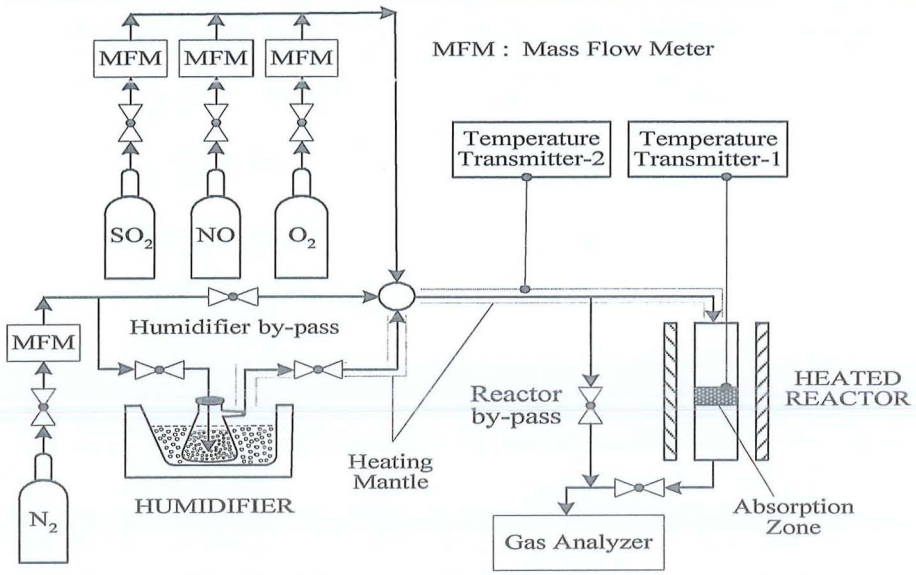


Figure 1. Schematic diagram of the experimental rig for fixed bed desulfurization/denitrification process

PROJECT 5:

Experiment and Requirement

Post synthesis modification (grafting) that involves synthesizing SBA-15 silica materials before surface functionalization allows the synthesis of modified SBA-15 with highly ordered silica geometries even at moderately high organic loadings after the functionalization (Hoffmann *et al.*, 2006 ; Garcia *et al.*, 2007). Herein, we compared the pore structural properties between SBA-15 functionalized with organo sulfonic acid via post synthesis-grafting and SBA-15 incorporated with sulfated zirconia and we also studied their catalytic activity in esterification of glycerol with fatty acid at 160 °C for 6 h reaction.

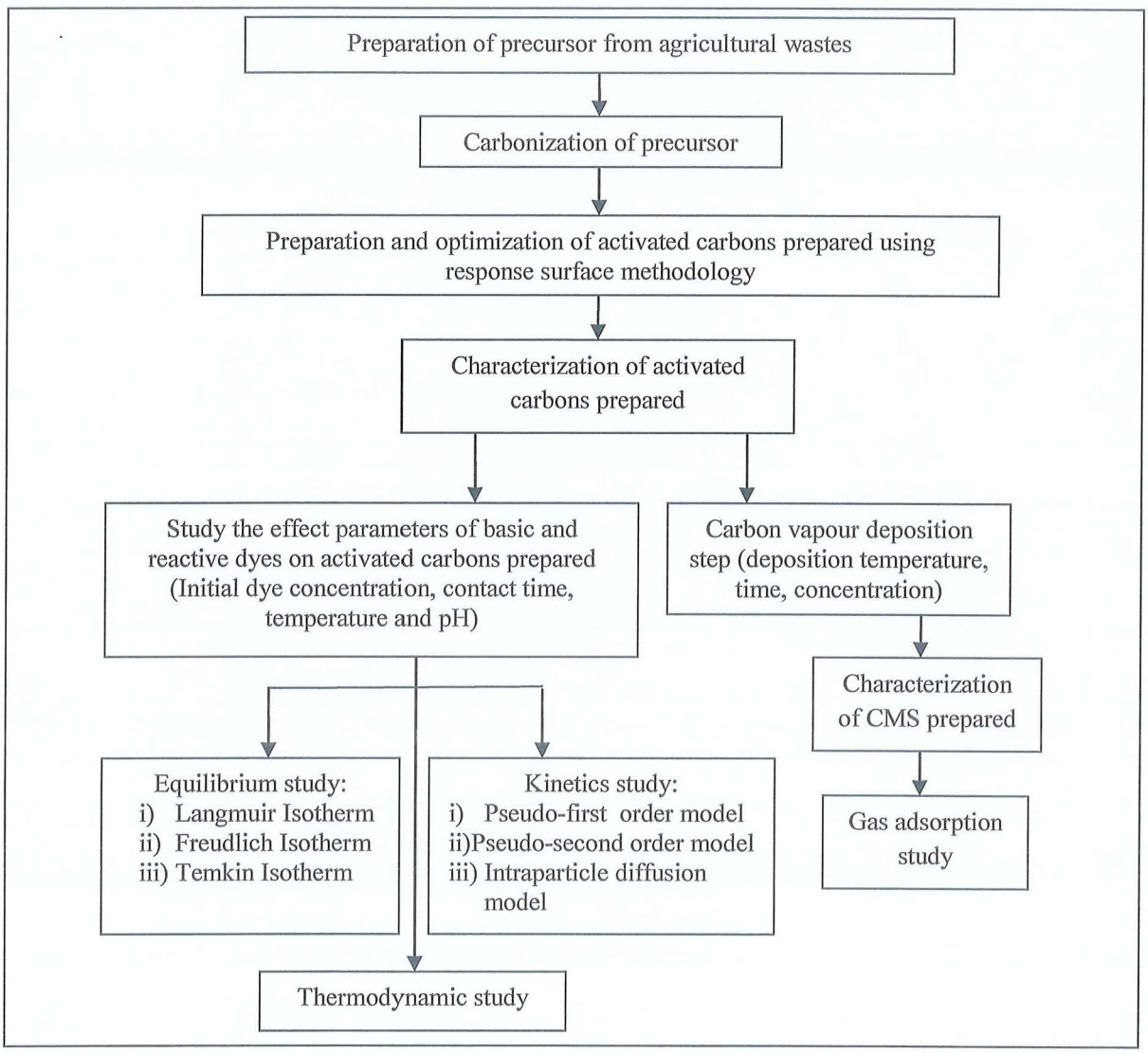
The SBA-15 incorporated with 3-(mercaptopropyl)trimethoxysilane (MPTMS) was prepared by post synthesis-grafting. Mild oxidation was carried out to obtain acid catalyst (HSO_3SBA-15). SBA-15 immobilized with sulfated zirconia was prepared by reacting SBA-15 with a solution of zirconiumoxychloride and urea at 90 °C to give ZrO_2-SBA-15. SZSBA-15 as acid catalyst was obtained by sulfation of the ZrO_2-SBA-15 with H_2SO4 solution at room temperature. *Monoglyceride synthesis through glycerol esterification with lauric acid over a propyl sulfonic acid functionalized SBA-15 mesoporous catalyst (HSO_3SBA-15) was studied under reduced pressure to continuously remove water formed. Effects of various reaction parameters such as reaction temperature (413-433 K), catalyst loading (1-5 %) and glycerol/lauric acid molar ratio (2:1 and 4:1) on lauric acid conversion and products selectivity were successfully elucidated and correlated with reaction scheme and kinetic model.*

PROJECT 6:

Milestones achievement

No.	Milestone Name	Status (Yes/No)	Deliverables
M1	Sample / test rig preparation completed	Yes	December 2007
M2	Carbonization precursor completed	Yes	March 2008
M3	Physiochemical activation / deposition studies completed	Yes	November 2008
M4	Characterization of samples completed	Yes	April 2009
M5	Optimization studies completed	Yes	December 2009
M6	Kinetic mechanism and adsorption equilibrium studies completed	Yes	September 2010

Flowchart

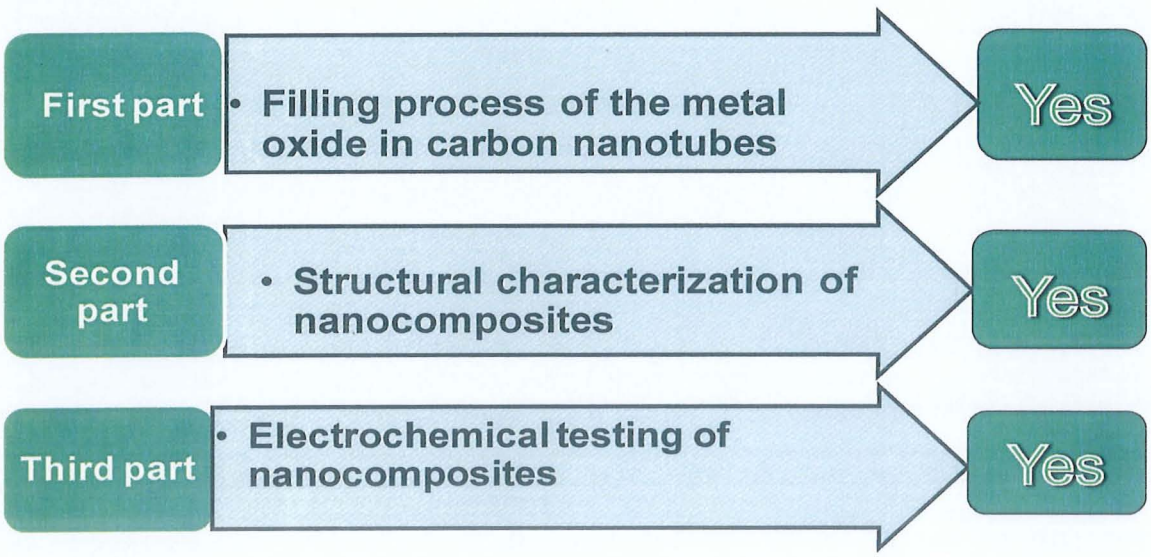


PROJECT 7:

Milestones achievement

No.	Milestone Name	Status (Yes/No)	Deliverables
M1	Synthesizing nanocomposites based on carbon nanotube and the transition metal oxides.	Yes/Expected nanocomposites have been already synthesized.	March 2008
M2	Morphological and structural testing of the nanocomposites	Yes/TEM, SEM and XRD have been done on the prepared nanocomposites.	October 2008
M3	Electrochemical testing of the as-synthesized nanocomposites	Yes/Electrochemical Testings has shown good results	March 2009

Flowchart

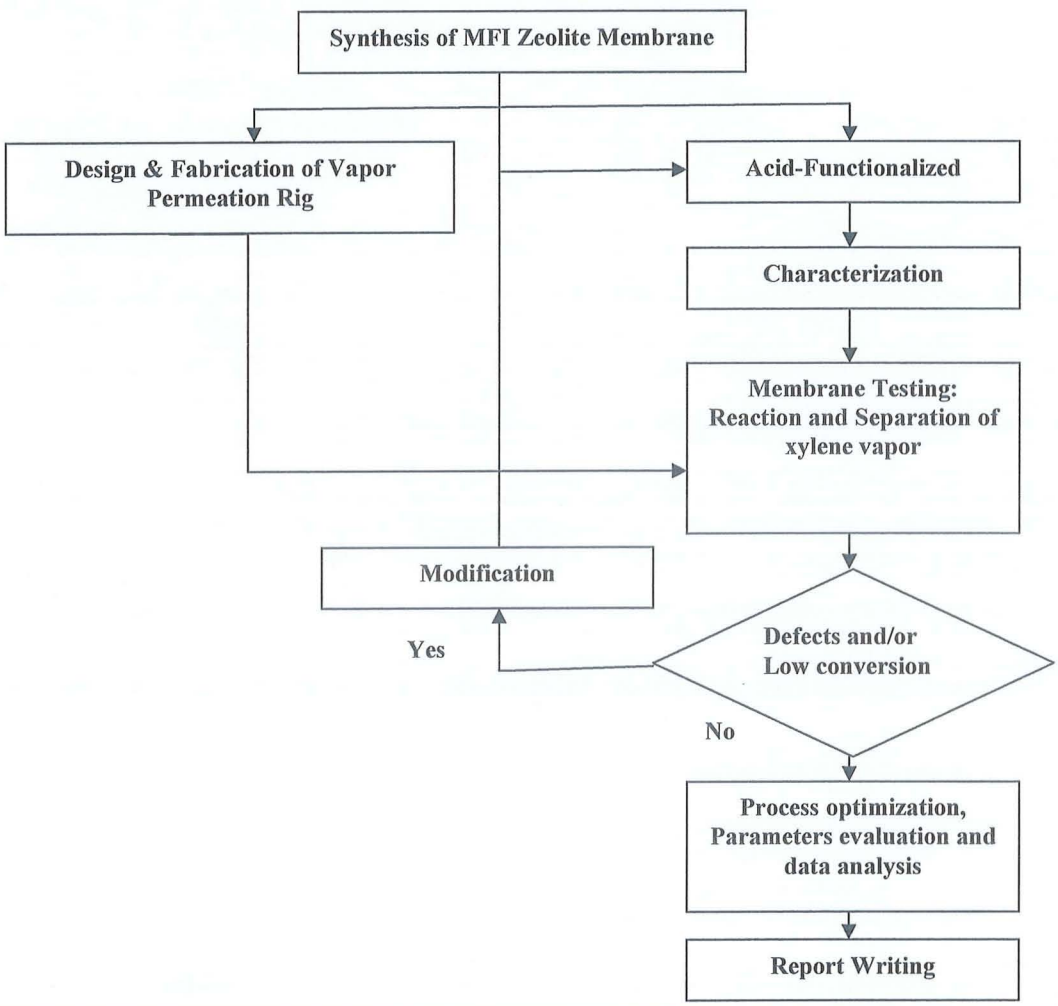


PROJECT 8:

Milestones achievement

No.	Milestone Name	Status (Yes/No)	Deliverables
M1	Completion of Experimental rig	Yes	February 2008
M2	Synthesis of Functionalized MFI Zeolite Membrane	Yes	October 2008
M3	Characterization of Functionalized Zeolite Membrane	Yes	March 2009
M4	Combined Separation and Reaction Studies	Yes	January 2010
M5	Process parameters optimization studies	Yes	September 2010
M6	Project Completion	Yes	December 2010

Flowchart



G. **COMPREHENSIVE TECHNICAL REPORT (maximum of 2 pages)**

PROJECT 1:

The research is focused on membrane fabrication technologies which involve the application of functional ceramic membrane in oxidation reactor. Works done included the preparation, characterization and catalytic evaluation of vanadium oxide nanotubes (V_xO_y-NTs), vanadium oxide impregnated gamma alumina (γ-Al_2O_3/V_xO_y), vanadium oxide impregnated carbon nanotube(CNTs-V_xO_y) and vanadium oxide carbon nanotube coated with γ-Al_2O_3 particle (CNTs-V_xO_y/γ-Al_2O_3) nanocomposite catalysts. Mixed matrix Vanadium Oxide Catalytic Nanocomposite (V_xO_y-CNTs,V_xO_y-NTs and V_xO_y/Al_2O_3 nano particle) Membrane, were prepared and its oxidation of styrene to benzaldehyde in presence of anhydrous hydrogen peroxide (H_2O_2) were studied. All of catalysts were found to be active for oxidation reaction with anhydrous H_2O_2 while aqueous H_2O_2 (30%) catalysts didn't show considerable activity for oxidation reaction.

This study describes an easy and cost-efficient hydrothermal method for the synthesis of VO_x-NTs using vanadium oxide as precursor. The use of an ultrasonic frequency of 37 kHz with an RMS power of 150 W and maximum peak power of 600 W helped to better distribute the hexadecylamine throughout the homogeneous slurry mixture. Ultrasonication did not reduce the particle size in fact, enhanced the suspension homogeneity of vanadium oxide with hexadecylamine for better and faster formation of NTs. The ultrasonic treatment for the duration of 15 minutes produced well developed nanotubes with only small amount amorphous or lamellar by-products but for the duration of 30 minutes it also produced VOx-NTS with longer length and similar diameter.

A remarkable increase of 70–85% in different batches on the preparation conditions such as precursor, time of suspension homogenization by ultrasonic, method of distribution, and hydrothermal time was evident. The obtained product had a well-ordered layer-like structure and tube-like morphology. By applying ultrasonics and using acetone as the solvent for hexadecylamine, the reaction time was substantially decreased in terms of the following: (1) mixing time from 48 h (normal mixing time) to 24 h, and (2) hydrothermal conditioning from 7 days (hydrothermal treatment time normally reported) to 5 days. This method proves to be a desirable approach toward preparing VOx-NTs. However, in spite of the good structural characterization of the V_xO_y-NTs and a homogeneous catalyst distribution, the stability of V_xO_y- NTs is poor during the reaction with H_2O_2 as the oxidant agent.

Particles of γ-alumina-supported V_2O_5 with an average particle size of 5 to 10 nm and a surface area of 174.8 m^2/g were prepared through a wet impregnation method. These materials were found to be effective in the selective oxidation of styrene to benzaldehyde using anhydrous H_2O_2. A significant increase in the conversion and selectivity of the desired product, benzaldehyde, was achieved when anhydrous H_2O_2 was used as the oxidant in the oxidation of styrene. The main products of the styrene oxidation reaction were benzaldehyde and styrene oxide as main by-product. In all solvents tested, the selectivity of benzaldehyde is high. The following optimal conditions was suggested through DOE for styrene oxidation: a temperature of 62.7°C, a time of 5.1 h, a molar ratio of H_2O_2/styrene of 2.7:1 and a catalyst loading of 0.34 g. These

conditions yielded a better styrene conversion (68.23%) and maximal selectivity (57.32%) of benzaldehyde. The experimental data confirm the theoretical predictions, with accuracies of 95% for styrene conversion and 97% for styrene selectivity.

The oxidation of styrene by anhydrous hydrogen peroxide as an environmental friendly oxidant on γ-alumina-supported V_2O_5 nanoparticles catalysts was performed with the continuous adsorption of water by anhydrous $MgSO_4$. This catalyst, with a surface area of 174 m^2/g, showed good selectivity for benzaldehyde. A considerable decrease was observed in the conversion of styrene due to porous filling of the catalyst with $MgSO_4$ powder, therefore decreasing the effective sites of the catalyst but benzaldehyde selectivity was improved. The optimal conditions for styrene oxidation were predicted using the optimization function of Design Expert Software. A temperature of 63.1°C, a time of 4.9 h, and a H_2O_2/styrene/anhydrous $MgSO_4$ molar ratio of 2.7:1:1.08 and a catalyst loading rate of 0.34 g were found to be the most favorable conditions for achieving maximal styrene conversion (61.76%) and selectivity (84.23%) of benzaldehyde. The experimental data confirm the theoretical predictions, with an accuracy of 96% for styrene conversion and 95% for styrene selectivity.

It is apparent that styrene oxidation can be improved using vanadium oxide-based composite catalysts (CNT-V_xO_y, and CNT-V_xO_y/Al_2O_3) with anhydrous H_2O_2 as an oxidant. The catalyst type and structure have a strong effect on the styrene oxidation reaction. The nature of the solvent also influences the catalytic activity and the selectivity for benzaldehyde. With the aim of producing benzaldehyde with the highest selectivity and maximal styrene conversion acetone is preferred for both the CNTs-V_xO_y catalyst and CNTs-V_xO_y/Al_2O_3 which resulted in high selectivity of benzaldehyde at 95.59% and 91.05% respectively.

The structure and morphology of the catalytic membranes synthesized on the alumina support were extremely sensitive to the pretreatment method. Methods such as ultrasonic cleaning, modifying surface functional groups and adding a binder could be employed to prepare uniform membranes. The coated membranes had a smooth, homogeneous surface layer, and no cracking or delaminating phenomena were observed between the underlying membrane and the coating layer. The catalytic contactor membrane with CNT-V_xO_y catalyst oxidized styrene to benzaldehyde at a styrene conversion rate of 25% and a benzaldehyde selectivity of 85% under optimum conditions, which included a temperature of 45 °C, an H_2O_2:styrene molar ratio of 1.5:1, a differential pressure of 1.5 bar and a catalyst loading of 30%.On the other hand styrene conversion for membrane prepared from V_xO_y-NTs and V_xO_y/Al_2O_3 nano particles is less than conversion for membrane prepared with CNT-V_xO_y, because of the surface area of membranes is less than membrane with CNT-V_xO_y,.

PROJECT 2:

The unique combination of light weight, small dimensions, structural diversity, excellent mechanical strength and remarkable electronic properties make carbon nanotubes (CNTs) an attractive field of discovery for a wide range of characteristics and potential applications, from reinforcing materials to molecular sensing. Various methods have been proposed of which the chemical vapor deposition (CVD) appears to be the most promising method for high yield synthesis of CNTs due to the lower temperature requirement, higher yield and excellent self-assembly. Floating catalyst (FC)-CVD method is introduced recently in view of its ability to produce continuously high purity CNTs, industrial-scale up production of CNTs and it is involved with simple equipment set-up. In addition, compared with other CVD techniques, FC avoids special time consumed for catalyst preparation and catalyst activation. In this study, catalytic decomposition of methane as highly abundant, less toxic and low cost gas was employed for producing CNTs. Two types of iron precursors, namely (i) iron (III) chloride ($FeCl_3$) as inorganic catalyst and (ii) ferrocene (Fe(C5H5)2) as organometallic catalyst were used. Ferrocene as organometallic catalyst has easy accessibility, stability in air and volatility. $FeCl_3$ catalyst has also some advantages such as easy available, nontoxic, low price and ease of volatilisation reagent. The effects of several synthesis parameters – including temperature, time, and gases flow rate have been invetigated on the growth of CNTs.

The amount of catalyst was kept constant at 200 mg. The role of the purification process including oxidation and acid treatment on the purity of as-grown CNTs has also been considered. It was found that an increase in the reaction temperature, reation time and the gases flow rates to an optimum level increased the yield of CNTs. In addition, the reaction temperature and methane flow rate affected the growth, morphology and alignment of CNTs, especially while using ferrocene. The optimum process conditions predicted by Design of Experiment (DoE) for methane decomposition using $FeCl_3$ were found to be a reaction temperature of 1055 °C, reaction time of 65 min, methane flow rate of 380 sccm and nitrogen flow rate 200 sccm, which gave the CNTs yields of 87.08%. The optimum process conditions for CNT synthesis using ferrocene were a reaction temperature of 947 °C, reaction time of 58 min, methane flow rate of 357 sccm and nitrogen flow rate 195 sccm, which gave the CNTs yields of 90.75%. Various characterisation tests, including thermogravimetric analysis (TGA), scanning electron microscopic (SEM), energy-dispersive X-Ray analyser (EDX), transmission electron microscopy (TEM), high-resolution of transmission electron microscopy (HRTEM) and Raman spectroscopy, were carried out in order to comprehend the properties of the produced CNTs and criteria required to grow higher quality CNTs in high yield. In all instances, multi-walled carbon nanotubes (MWCNTs) were the only products observed.

PROJECT 3:

The performance of modified and unmodified rejected tea (RT), oil palm fibre (PF) and oil palm empty fruit bunch (EFB) as low-cost adsorbents were studied in continuous system to establish the breakthrough curves for the adsorbents-methylene blue dye system. The effects of different parameters such as adsorbent high, flow rate and dye concentration were studied for unmodified and modified adsorbent. Phosphoric acid was used as an activating agent for the activation process. The potential feasibility of prepared ACs was tested

for the removal of methylene blue (MB). The prepared activated carbons were characterized for their physical and chemical properties. The adsorption capacities of unfunctionalized oil palm fibre activated carbon (EFBAC) and oil palm fibre activated carbon (PFAC) were 243.90 and 370.37 mg/g, respectively at 30°C. The adsorption capacities of the functionalized EFBAC and PFAC were 357.143 and 476.190 mg/g, respectively at 30°C.

PROJECT 4:

In this study, simultaneous removal of SO_2 and NO using sorbents derived from RHA has been successfully carried out. However, the performance of sorbent varies depending on type of RHA (RHA_{raw}, RHA_{inc}) used for sorbent preparation, parameters during sorbent preparation (CuO loading, RHA/CaO ratio, hydration period and NaOH concentration) and operating conditions for activity study (operating temperature, initial concentrations of SO_2 and NO). Apparently, RHA_{raw} sorbent was found to have potential of applicability in industry. CuO loading and NaOH concentration were found to be significant towards desulfurization and denitrification activity of RHA_{raw} sorbent. RHA_{raw}/CaO ratio was found to be significant only in denitrification activity. By using Design Expert software, optimum sorbent preparation parameters were determined to be 3.06% CuO loading, RHA_{raw}/CaO ratio of 1.41, 8.05 hours of hydration period and NaOH concentration of 0.80M. SO_2 and NO sorption for sorbent derived with optimum preparation parameters were 12.60mg/g and 3.08mg/g, respectively.

For RHA_{inc} sorbent, NaOH concentration was found to be significant towards sorbent desulfurization and denitrification activity. RHA_{inc}/CaO ratio was only significant towards the denitrification activity. Subsequently, optimum sorbent preparation parameters for RHA_{inc} sorbent were determined as 3.04% CuO loading, RHA_{inc}/CaO ratio of 1.41, 19.95 hours of hydration period and NaOH concentration of 0.20M. SO_2 and NO sorption with the optimum preparation parameters were 7.50mg/g and 2.47mg/g respectively. The analysis of operating conditions towards desulfurization and denitrification for RHA_{raw} and RHA_{inc} sorbent were found to show no clear trend. Two types of performances investigated were sorption at which 100% pollutants removal was sustained and equilibrium removal efficiency. Effect of operating conditions towards sorbent activity was different, depending on which type of RHA used for sorbent preparation. Moreover, optimum operating conditions for RHA_{raw} sorbent was 100°C, 2000ppm SO_2 and 500ppm NO. Optimum activity of RHA_{inc} sorbent, on the other hand, occurs at 200°C, 1000ppm SO_2 and 1000ppm NO.

PROJECT 5:

Focus was given to the synthesis of titania and mesoporous SBA-15 material by varying the synthesis conditions including gel composition, temperature, ageing time and the use of swelling agent. The materials were then functionalized using alkali metals, alkali earth metals and transition metals. The properties of those materials were elucidated by characterizing them using XRD, SEM/EDX, TEM, surface analysis, FTIR, NH_3-TPR, XRF etc. The performance of the catalysts was evaluated based on their behaviors in the transesterification of vegetable oil with methanol, esterification of glycerol with fatty acid, and sonocatalytic degradation of organic pollutants in water. Behaviors of the catalysts were elucidated and correlated with their properties. The performance was based on reactant conversion, product yield and selectivity to the desired

product.

PROJECT 6:

For mangosteen peel based activated carbon (MPAC) for the removal of Remazol Brilliant Blue R (RBBR) dye from aqueous solution, results showed that the RBBR dye was favourable at acidic pH whereas the adsorption uptake was found to increase with increase in initial concentration, contact time and solution temperature. Langmuir isotherm model fitted well the adsorption equilibrium data. The adsorption kinetic was found to follow the pseudo-second-order kinetic model. Boyd plot indicated that the adsorption of RBBR on MPAC was controlled by film diffusion. The adsorption process was found to be endothermic with the reaction mechanism follows a physisorption process. For MPAC for malachite green (MG) removal, the MG adsorption uptake was found to increase with increase in initial concentration and contact time. The MG adsorption was unfavourable at pH<4. The equilibrium data were best represented by Freundlich isotherm model, showing maximum monolayer adsorption capacity of 411.43 mg/g. The adsorption rates were found to obey the rules of pseudo-second order model with good correlations. MPAC prepared were mesoporous in nature with relatively high mesopore surface area with average pore diameters larger than 2.2 nm. MPAC demonstrated homogeneous type pore structures. FTIR analyses indicated the presence of functional groups such as hydroxyl, carbonyl and alkyl on the surfaces of the MPAC prepared.

For rambutan peel-based activated carbon (RPAC), the RBBR and MG dyes adsorption were found to increase with increase in initial concentration, contact time and solution temperature. The adsorption equilibrium data were best represented by the Freundlich model. Adsorption kinetic was found to follow the pseudo-second-order kinetic model. The mechanism of the adsorption process was determined from the intraparticle diffusion model. Boyd plot indicated that the dyes adsorption on the RPAC was controlled by film diffusion. All the adsorption processes were mainly governed by the film-diffusion-controlled mechanism. RPAC demonstrated heterogeneous type pore structures.

For coffee husk based activated carbon (CHAC) the adsorption of Remazol Brilliant Orange 3R (RBO3R) dye was found to increase with increase incontact time, initial dye concentration and solution temperature. The adsorption of RBO3R on CHAC was favored at acidic medium. The Langmuir isotherm model was well described by the equilibrium data with maximum adsorption capacity of 66.76 mg/g at 303K. The pseudo-second-order kinetic model fits well with the kinetic data. From Boyd plot, the adsorption of RBO3R on CHAC took place by film diffusion mechanism. The positive values of ΔH^0 indicated that the adsorption process was endothermic in nature. E_a value of 2.77kJ/mol shows that the rate-limiting step in RBO3R adsorption process is physically controlled.

For cocoa pod husk based activated carbon (CPHAC), at the lowest initial Remazol Black B reactive (RBBR) concentration (20 mg/L), the highest percentage RBBR dye removal by CPHAC was achieved (76.3%). Equilibrium was reached within 350 min. The equilibrium data follows Langmuir model with maximum adsorption monolayer coverage of 22.12 mg/g. The pseudo second-order model provided the best correlation for the adsorption of RBBR dye on CPHAC. The adsorption process was found to be feasible,

endothermic and spontaneous. Both the mean free energy of adsorption and the activation energy values obtained shows that the adsorption process follows a physiosorption mechanism.

For carbon molecular sieve (CMS) prepared from palm shell, the performance of CMS was examined by assessing the adsorption kinetics of O_2, N_2, CO_2 and CH_4 gases. All CMS samples showed a small N_2 and CH_4 uptake compared to the O_2 and CO_2. The suitable conditions for carbon vapour deposition (CVD) were found at 800°C, 30 min and 30 vol% benzene of deposition temperature, time and benzene concentration, respectively. At this point the O_2/N_2 and CO2/CH4 uptake ratios arrived 7.1 and 16.0, respectively. For CMS prepared from cocoa pod husk, the molecular sieving behaviour in CMS is found to depend greatly on the deposition temperature. Deposition temperature of 600°C was too low and 800°C was the most suitable temperature to yield good CMS, which attained CO_2/CH_4 and O_2/N_2 selectivities of 5.98 and 3.16, respectively.

PROJECT 7:

A comprehensive technical report of the research activities obtained in the framework of this project entitled, "Developing carbon nanotubes based nanocomposites by creating good interface between carbon nanotubes and desired molecules" is presented and attached separately.

PROJECT 8:

Silicalite-1 and two types of acid-functionalized silicalite-1 membranes: (1) propylsulfonic acid-functionalized silicalite-1 membrane (coded as MAFS-P) and (2) arenesulfonic acid-functionalized silicalite-1 membrane (coded as MAFS-A) were synthesized on disc type α-alumina support in the present study. The hydrothermal crystallization was used for the synthesis of silicalite-1 membrane. Propylsulfonic acid-functionalized silicalite-1 membrane was synthesized via one step co-condensation hydrothermal crystallization by varying the molar ratio of organosilane source, 3-mercaptopropyltrimethoxysilane (3MP) to tetraethylorthosilicate (TEOS) in the range of 0.05 to 0.20, and subsequent oxidation of thiol group to propylsulfonic acid using hydrogen peroxide (H_2O_2). Arenesulfonic acid-functionalized silicalite-1 membrane was synthesized using phenethyltrimethoxysilane (PE) as an organosilane source followed by sulfonation of phenethyl group to arenesulfonic acid group under strong sulphuric acid treatment. The molar ratio of PE to TEOS was varied from 0.05 to 0.20. The physical and chemical properties of all the synthesized membranes were characterized using HR-XRD, SEM, TEM, SAED, ^{29}Si MAS NMR, ^{13}C CP-MAS NMR, FTIR, EA, acid-base titration, NH_3-TPD, TGA and nitrogen adsorption–desorption. The differences in the properties of both acid-functionalized silicalite-1 membranes were compared and explained based on molecular weight of PE and 3MP.

The performance and process optimization of *p*-xylene separation from *p*-/*o*-xylene binary mixture and ternary xylene mixture through silicalite-1 membrane using statistical design of experiments (DoE) were demonstrated in the present study. Acid-functionalized silicalite-1 membranes were tested for their catalytic activity in *m*-xylene isomerization reaction in the temperature range of 355 °C to 450 °C.

H. SUMMARY OF FINDINGS / RESULTS (maximum of 2 pages)

PROJECT 1:

A novel gamma-alumina membrane which is templated using vanadium oxide nanotube has been successfully developed in this research project. The functionality membrane is an energy saving equipment which combines the separator and reactor in a single operational unit. Some technical knowledge was developed on the preparation of membrane which highly contributes to energy conservation especially in chemical plants.

From the studies done in this research, it shows porous membranes are attractive supports for catalytic nanoparticles. The membrane operated as flow-through contactors facilitate contact between liquid phase reactants and the solid catalyst and eliminate diffusion limitation.Catalytic membrane help to produce benzaldehyde, at lower temperatures and lower concentration of anhydrous H_2O_2 in mixed matrix membrane compared to the conventional particle catalyst. The selective oxidation of styrene is particularly difficult, because it is a kinetically rapid reaction, so it is of great importance to control the reaction to avoid side reactions. These membrane achieved 25% conversion of styrene with 85% selectivity for benzaldehyde at flux as high as 197.45 $l/m^2.h$. Catalytic membrane assist protect product from future reaction with catalyst trough short contact time with catalyst.

In kinetic studies, the reaction followed a second-order reaction and the rate constant values were reasonable but there is not any reference for comparison. The Arrhenius equation model was applied to the experimental data obtained from the oxidation studies with different reaction time to determine the kinetic parameters. The activation energy to produce benzaldehyde (E_1) is more than activation energy for styrene oxide (E_2) in both Al_2O_3/V_xO_y and CNT/V_xO_y catalysts but for $CNT/V_xO_y/\gamma\text{-}Al_2O_3$ catalyst E_2, is higher than E_1. On the other hand, activation energy to produce benzaldehyde (E_1) is less than activation energy for styrene oxide (E_2) in Mixed Matrix Vanadium Oxide Catalytic Nanocomposite (V_xO_y-CNTs) membrane.

PROJECT 2:

This study showed that $FeCl_3$ is an effective precursor for methane floating catalyst (FC) CVD for producing high purity MWCNTs. And also, aligned CNTs were successfully prepared by the FC method with ferrocene and methane at different reaction parameters. This study included three main parts which conclusion is given separation as follow:

In the preliminary experiments of the synthesis of CNTs, the effects of the reaction temperature, reaction time, methane flow rate and nitrogen flow rate on CNTs yield were investigated. The effect of each parameter was studied by changing one parameter and fixing other parameters. The most effective ranges of parameters using $FeCl_3$ catalyst are: reaction temperature (1000 to 1100 °C), reaction time (60 to 90 min), methane flow rate (350 to 450 sccm) and nitrogen flow rate (175 to 225 sccm).The most effective ranges of parameters using ferrocene catalyst are: reaction temperature (900 to 1000 °C), reaction time (30 to 60 min), methane flow rate

(350 to 450 sccm) and nitrogen flow rate (150 to 200 sccm). Based on the findings from preliminary experiments, the best ranges of each parameter need to be added and analysed in DoE.

Process study of methane decomposition was performed using $FeCl_3$ and ferrocene after considering the said catalyst possessed a good control in producing high yield CNTs. The reliability of the surface methodology (RSM) on the formation of CNTs in conjunction with CCD, were used to determine the functional relationship between four operating parameters i.e.reaction temperature, reaction time, methane flow rate and nitrogen flow rate with the aim of optimising one response (CNTs yield). For single response optimisation of CNTs yield using $FeCl_3$, the highest CNTs yield of 85.57%achived at 1050 °C, 67.5 min, 400 sccm and 200 sccm. Numerical optimisation was also performed to find the optimal process parameters such that the CNTs yield was maximised. The predicted solution from DoE to achieve the maximum desirability for the CNTs yieldwas 87.08%.However, the new experiment with almost similar condition of reaction temperature of 1055 °C, reaction time of 65min, methane flow rate of 380 sccm and nitrogen flow rate 200 sccm, gave the CNTs yield of 82.53%. For single response optimisation of CNTs yield using ferrocene, the highest value of CNTs yield of 87.10% achived at 950 °C, 45 min, 425 sccm and 175 sccm.The maximum desire ability for the CNTs yield as predicted solution of DoE was90.75%. However, the new experiments with almost similar condition of reaction temperature of 947°C, reaction time of 58 min, methane flow rate of 357 sccm and nitrogen flow rate 195 sccm, gave the highest CNTs yield of 86.92%.

The experimental results also showed that simple purification method was effective for purifying the FC products without causing severe damage on the MWCNTs. The success of this synthesis and purification method provided an option for producing high purity MWCNTs from methane at a large scale in near future. Purity of higher than 92.8% was obtained after purification as-grown CNTs using $FeCl_3$ with air oxidation and acid treatment. The TEM showed that the produced CNTs possessed the average diameter of 40 nm and Raman scattering revealed the high IG/ ID ratio of 1.72, indicating a high degree graphitised structure. Purity of higher than 97%was obtained after purification as-grown CNTs using ferrocene. The average diameter of produced CNTs was 50 nm and Raman scattering showed the IG/ID ratio of 1.81, indicating a high degree graphitised structure. Both of products from using $FeCl_3$ and ferrocene had the expected peaks for the D and G bands at about 1342 cm-1 and 1571 cm-1, respectively indicating that MWCNTs were the major products. The ratio of *IG/ID* calculated for the product from ferrocene (1.81) was higher and better than from $FeCl_3$ (1.72). However, these values were approximately similar, but this suggests a higher degree of graphitisation in the ferrocene-based CNTs due to contain fewer amorphous carbon deposits and less defects within the tubes.

The CNTs produced using ferrocene had the capability in controlling their growth to the desired structures, morphologies and uniformity at a lower temperature. The SEM images showed that the entangled CNTs were formed when $FeCl_3$ used but using ferrocene lead to form aligned CNTs. However, the morphology and shape of the CNTs produced from these two catalysts were different (curly CNT from $FeCl_3$ and aligned CNTs from ferrocene), but Raman spectroscopy revealed that they were similar in the type of CNTs (MWCNTs). In general, EDX results showed that the amount of metal impurity on the surface of CNTs using $FeCl_3$ less than ones using ferrocene.

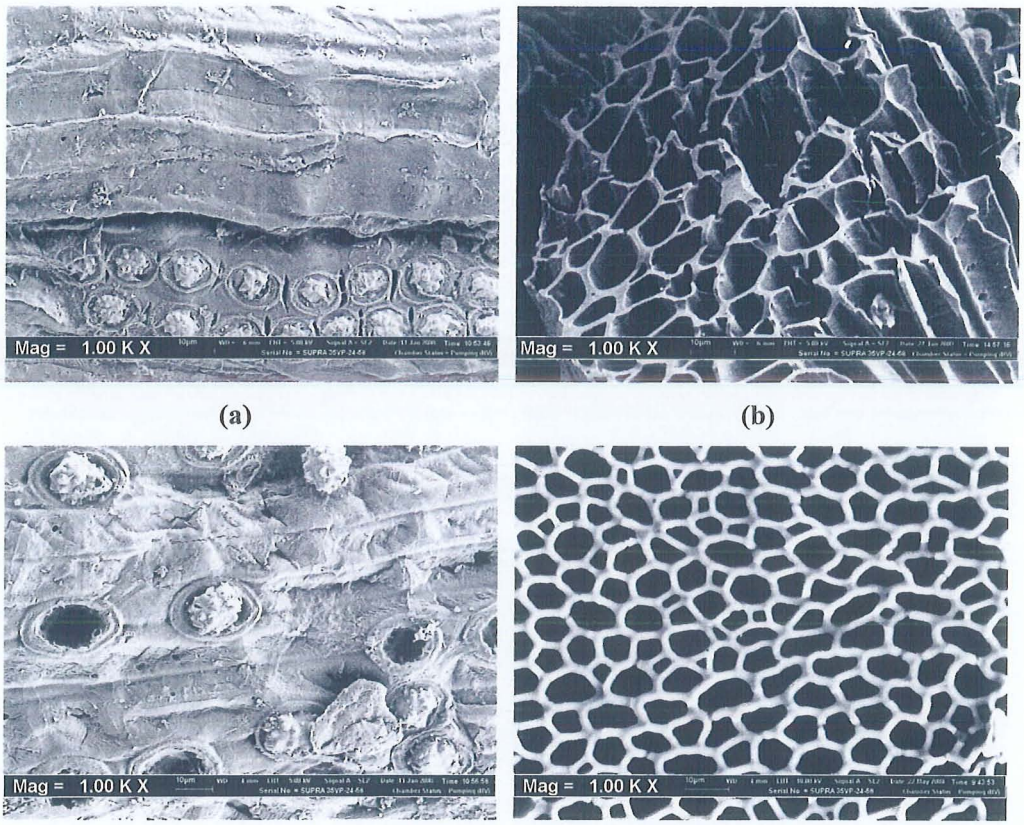
The TGA data also showed that the CNTs prepared from ferrocene attributed to its higher thermal stability and better graphitised than that of from $FeCl_3$. Furthermore, the TGA data revealed that the CNTs synthesised from ferrocene were of higher purity than CNTs synthesised from $FeCl_3$. Ferrocene was a covalent complex and at high temperatures can produce Fe, H and C. when ionic iron was used e.g $FeCl_3$ then Fe and Cl were found in the gas. The Cl ions were the counter ions for Fe. They could affect the activity of the Fe. Ferrocene does not suffer from this problem.

PROJECT 3:

The operational parameters in relations to the development of the activated carbon and the removal of textile dyes from wastewater was investigated. Parameters such as activation temperature, activation time, and chemical impregnation ratio were studied, while the response factors were carbon yield and adsorption capacity. The ranges of operating conditions applied to prepare the activated carbons from EFB and PF were found as: 550 °C activation temperature, 20 impregnation ratio and 2 h time, respectively. The adsorption performance of the prepared activated carbon for methylene blue was highly satisfactory, with the adsorption capacity of 243.90 and 370.37 mg/g, respectively at 30°C. This shows that the activated carbon prepared in this work was suitable to be used to remove color and from aqueous solutions.

Chemical activation method was used to prepare activated carbon from oil palm waste using phosphoric acid (H_3PO_4) as chemical agent. The Brunauer Emmett-Teller (BET) surface area, total pore volume and average pore diameter for EFBAC and PFAC were 1140.271 m^2/g, 0.655 cm^3 /g and 1.55 nm, and 1317.915 m^2/g, 0.812 cm^3 /g and 2.47 nm, respectively, indicating that the prepared activated carbons were in the mesopores region. The result revealed that the prepared activated contained relatively large surface area and total pore volume compared to commercially available activated carbons such as BDH from Merck, F100 and BPL from Calgon Corporation with BET surface area of 1118, 957 and 972 m^2/g as well as total pore volume of 0.618, 0.526 and 0.525cm^3/g, respectively. The prepared activated carbons were further modified via ammonia treatment to enhance the effectiveness of the activated carbons. The adsorption capacities of the functionalized EFBAC and PFAC were 357.143 and 476.190 mg/g, respectively.

Fig. 6 (a)–(d) shows the SEM images of the oil palm fibre precursor, PFAC, empty fruit bunch precursor and EFBAC, respectively. Large and well-developed pores were clearly found on the surface of the PFAC and EFBAC, compared to the original precursor. The H_3PO_4 and activation process were effective in creating well developed pores on the surfaces of the PFAC and EFBAC, hence leading to large surface area activated carbon with good porous structure (mesopores).



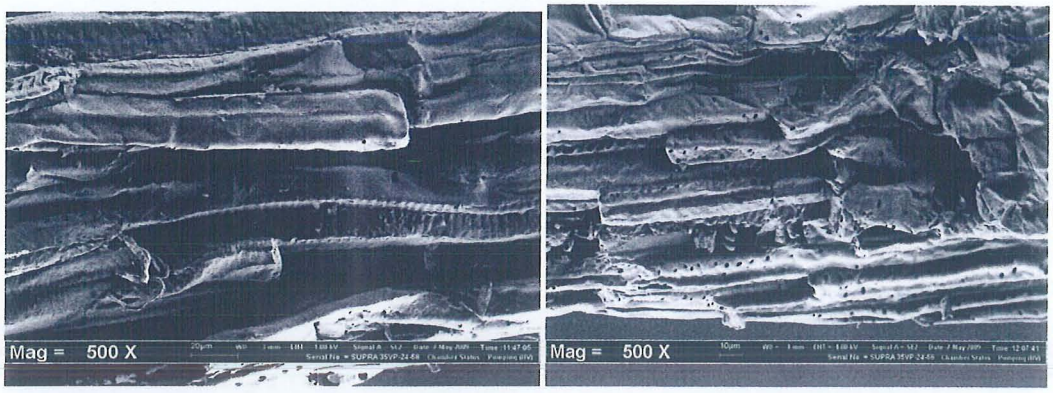
(a) (b)

(c) (d)

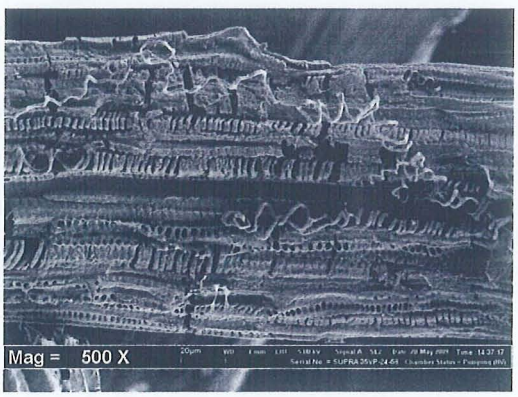
Fig. 6: SEM micrographs (x1000) of the (a) PF precursor (b) PFAC (c) EFB precursor and EFBAC (d)

In another work, the performance of modified and unmodified rejected tea (RT) were utilized as low-cost adsorbents were studied in continuous system to establish the breakthrough curves for the adsorbents-methylene blue dye system. After acid modifications with HCl, HNO_3, H_2SO_4 and Acetic Acid, MB adsorption capacity of respected adsorbents are lower than raw tea waste (water washed). This observation indicates that acid solution will change the cellulose structure of the rejected tea, contributing to loss MB molecule binding activity and structure breakdown. All the modified adsorbent by base solution exhibited somewhat higher adsorption capacity towards MB. This showed that hydroxyl group was important functional group in the adsorption of cationic dyes, MB. Numerous hydroxyl groups in the molecules of these compounds represent main active sites for binding of ionic compounds usually by an ion-exchange mechanism. The adsorption capacities of the unfunctionalized and NaOH functionalized rejected tea were 147.00 and 250.00 mg/g, respectively at 30°C.

The surface morphological structure of rejected tea (RT), NaOH treated-RT and KOH treated-RT was depicted in Fig. 7. The SEM photograph of RT exhibits cave-like gaps and smooth surface morphology. After modification with KOH solution, rough surface with its pores are scattered, and the uneven sizes seem to appear on the KOH treated-RT. However, it is clear that there are good enhancements in pores of the NaOH treated- surface which exhibits pores like honeycomb shape gaps.



(a) (b)



(c)

Fig. 7: SEM micrographs (x500) of the (a) RT precursor (b) KOH treated RT (c) NaOH treated RT

PROJECT 4:

The main objective of this research is to synthesize a sorbent from rice husk for simultaneous removal of SO_2 and NO from flue gas. In this study, two types of rice husk ash (RHA), i.e. RHA_{raw} and RHA_{inc} were used. RHA was hydrated with CaO in NaOH solution and subsequently impregnated with CuO. The research was carried out by a statistical investigation on sorbent preparation parameters using Design Expert software. Investigated sorbent preparation parameters were CuO loading, RHA/CaO ratio, hydration period and NaOH concentration. The results showed that CuO loading and NaOH concentration are the major parameters that affect the sorbent's desulfurization and denitrification activity. The optimum sorbent preparation for RHA_{raw} and RHA_{inc} sorbents were 3.06% CuO loading, RHA_{raw}/CaO ratio of 1.41, 8.05 hours of hydration period, NaOH concentration of 0.80M and 3.04% CuO loading, RHA_{inc}/CaO ratio of 1.41, 19.95 hours of hydration period, NaOH concentration of 0.20M, respectively. In addition, the effect of operating parameters such as temperature, initial SO_2 and NO concentration towards RHA_{raw} and RHA_{inc} sorbents' desulfurization and denitrification activity were also studied. Two types of performances investigated were sorption at which 100% pollutants removal was sustained and equilibrium removal efficiency. The breakthrough curves showed that the reactions between sorbents and pollutants were affected differently, depending on which type of RHA used for sorbent preparation. In general, RHA_{raw} sorbent has higher performance than RHA_{inc} sorbent. In this study, highest sorption capacity at 100% pollutants removal for RHA_{raw} and RHA_{inc} sorbents were 53.40mg SO_2/g sorbent and 6.90mg NO/g sorbent; and 14.40mg SO_2/g sorbent and 4.95mg NO/g sorbent, respectively.

PROJECT 5:

A series of mesoporous silicas (MS-1–MS-9) were successfully synthesized at different gel compositions using a triblock copolymer (TCP), poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), as the surfactant. The interactive effects of acidity, the contents of tetraethyl orthosilicate (TEOS) and the surfactant, and the gelling temperature on the characteristics of the final material were simultaneously characterized. Increasing acidity favored mesopore formation. A material with a surface area of 760m2/g, mostly in the mesoporous range, was obtained at 1.0(TEOS):0.017(TCP):7.3HCl:115.7H2O. Mesopore formation was predominantly determined by the TEOS:TCP ratio and was promoted with its increase from 1.56:1 to 2.09:1. A further increase to 2.61:1 was detrimental. Whereas increasing the TCP content to 3.5% w/w improved micellization, a further increase to 4.6% should be avoided. Mesoporous silicas showed low crystallinity but a high degree of hexagonal mesoscopic organization. The weak surface acidity was attributed to surface silanols, the number of which was proportional to mesoporosity.

Titanium dioxide nanotubes (TiO_2 NTs) were also synthesized via combined sol-gel and hydrothermal method and annealed at various temperatures. The morphology and crystalline structures of the prepared TiO_2 NTs were characterized using scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS), transmission electron microscope (TEM), X-ray diffraction (XRD) and surface area analyzer. The sonocatalytic activity of the prepared TiO_2 NTs was evaluated based on sonocatalytic degradation of Rhodamine B in aqueous solution. Effects of annealing temperature were successfully elucidated and TiO_2 NTs annealed at 300 °C had the highest surface area and pore volume. Its sonocatalytic activity could increase by a factor of 3.7 times as compared to the conventional TiO_2 powder. Sonocatalytic activity of the annealed TiO_2 NTs decreased with increasing annealing temperature above 300 °C due to the destruction of tubular structure, a decrease in the surface area and pore volume and phase transformation from anatase to rutile. Reusability study did not reveal any significant drop in the efficiency for 4 successive cycles under investigation. The morphology, catalyst composition, specific surface area, pore size and pore volume were also investigated after each catalytic cycle.

Montmorillonite K10 was intercalated with lithium hydroxide (LiK10) and used as catalyst for transesterification methyl laurate with glycerol. Effects of calcination temperature (250 - 650 °C) and tetramethyl ammonium hydroxide (TMAOH) addition (0.5-2.2 wt. %) on catalytic activity were particularly elucidated. Successful intercalation of Li leading to improved water hydration was demonstrated. Calcination temperatures above 450 °C could reduce the basic strength and activity of LiK10 catalyst. Significant losses of porosity and basicity were attributed to excessive loss of hydrated water. Higher basicity of the catalyst led to better reactant's conversion but poorer selectivity to glycerol monolaurate (GML). TMAOH addition improved the activity of the catalyst and selectivity to GML. At a glycerol/methyl laurate ratio of 6.5:1 and 130 °C, 40 % GML yield was achieved in 5 h. The addition of 2 % TMAOH increased the yield to 89.9 %. An increase in reaction temperature beyond 130 °C would reduce the catalytic activity due to a decrease in the surface tension of surfactant and its partial degradation. Thus, TMAOH could significantly improve activity of LiOH-MMT catalyst with corresponding improvement in selectivity to GML.

Acid-functionalized silicalite-1 membranes were tested for their catalytic activity in *m*-xylene isomerization reaction in the temperature range of 355 °C to 450 °C. *m*-xylene conversion and *p*-xylene yield were comparable with the values reported with HZSM-5 catalyst showing that acid-functionalized silicalite-1 membrane acted as catalyst for the reaction. Among acid-functionalized silicalite-1 membranes studied, the best results were achieved using MAFS-A15, with *m*-xylene conversion of 57 %, *p*-xylene selectivity of 65 % and *p*-xylene yield of 33 % at 450 °C. The higher acid density played its role as catalytic sites but the enhancement in *m*-xylene isomerization was also due to the contribution of effective separation of reaction products through membrane, with *p*-xylene flux of 5.66 x 10^{-6} mol/m^2 at 450 °C over MAFS-A15 membrane. Both catalytic membranes exhibited good structural and thermal stability after subjected to isomerization reaction study for 120 hours operation. The reaction kinetics was modelled by triangular reaction mechanism based on time on stream (TOS) studies. The kinetic parameters as determined from triangular reaction scheme model indicated that *m*-xylene isomerization reaction rates in both membranes were affected by the diffusional mass transfer rates. The enhancement in *m*-xylene conversion and *p*-xylene yield using arenesulfonic acid-functionalized silicalite-1 membrane as compared to propylsulfonic acid-functionalized silicalite-1 membrane was due to its lower activation energies and presence of higher acidity. The simulated results were in good agreement with the experimental data within an error of ± 5%.

I. PERFORMANCE AGAINST OBJECTIVE / CHALLENGES / CONSTRAINTS / ISSUES

PROJECT 1, 2, 3, 4, 5, 6, 7 & 8

Progress of this project progress as schedule. All deliverable and objectives are achieved.

J. PROJECT ACHIEVEMENTS

i-HUMAN CAPITAL DEVELOPMENT :

- **MSc/PhD**

	Ongoing		Graduated	
	Local	International	Local	International
MSc/PhD	4	1	14	6
Total	**5**		**20**	

**the following below are the details:*

No.	Full Name	Matric Number	Thesis Title	Ongoing/ Graduated	Local/ International
1.	Leo Choe Peng	PJD 0028	Bimodal porous ceramic membrane via nanosized polystyrene templating : Synthesis, characterization and	Graduated (Year 2008)	Local

			performance evaluation		
2.	Behnam Koohestani Mostafa	PJD 0060	Membran Pemangkin Komposit Nano Vanadium Oksida Secara Matriks Bercampur untuk Pengoksidaan Stirena	On-going	International
3.	Mehrnoush Khavarian	PJM 0163	Development of carbon nanotubes using floating iron-based catalysts	Graduated	International
4.	Farra Wahida Binti Shaarani	PJM 0142	Adsorption of methylene blue and 2-4-Dichlorophenol onto modified activated carbons prepared from agricultural waste	Graduated	Local
5.	Norhaslinda Binti Nasuha	PJM 0169	Adsorption of methylene blue onto modified factory tea waste: Batch and Fixed bed column	Graduated	Local
6.	Irvan Dahlan	PJD 0027	Removal of SO2 and NO from Simulated Flue Gas Using Rice Husk Ash/CaO/CeO2 Sorbent	Graduated	International
7.	Sumathi Sethupathi	PJD 0032	Removal of SO2 and NO from Simulated Flue Gas Using Cerium-Modified Palm Shell Activated Carbon	Graduated	Local
8.	Lau Lee Chung	PJM 0183	Removal of SO2 and NO from Flue Gas Using Sorbent Derived from Rice Husk Ash	Graduated	Local
9.	Henry Foo Chee Yew	PJM0182	Mathematical Modeling for Simultaneous Removal of SO2 and NO Using Sorbent Synthesized from Ash	Graduated	Local
10.	Babak Salamatinia	PJD 0044	Intensified Biodiesel Production Using Ultrasonic-Assisted Heterogeneous Catalytic Process And Product Quality Evaluation	Graduated in 2011	International
11.	Hamidah Abdullah	PJM 0113	Bimetallic Monolithic Catalyst For Selective Catalytic Reduction Of Nox In Diesel Engine Exhaust	Graduated in 2008	Local
12.	Noraini Razali	PJM 0137	Synthesis And Characterization Of Mesoporous Base Catalyst For Transesterification Of Palm Oil	Graduated in 2009	Local
13.	Hamed Mootabadi	PJM 0136	Development Of Ultrasonic-Assisted Methyl Ester Process From Palm Oil Using Alkaline Earth Metal Oxide Catalysts	Graduated in 2010	International

14.	Lilis Hermida	PJM 0162	Acid Functionalization Of Sba-15 Mesoporous Catalyst For Glycerol Esterification To Monoglyceride.	Graduated in 2010	International
15.	Siti Aminah Md Ali	PJM 0013	Behaviors Of Sonocatalytic Degradation Of Methyl Orange In Aqueous Effleunts.	Graduated in 2009	Local
16.	Nur Azimah Jamalluddin	PJM 0006	Evaluation Of Catalytic Activity Of Fe(Iii0/Tio2 In The Removal Of Reactive Dye In Aqueous Solution Under Ultrasonic Irradiation.	Graduated in 2010	Local
17.	Wan Nurul Huda Wan Zainal	PJM 0012/08	Adsorption of basic dyes on cocoa pod husk based activated carbon (CPHAC): Equilibrium, kinetics and mechanism studies	Graduated (2009)	Local
18.	Rasyidah Alrozi	PJM 0007/09	Preparation of activated carbon from tropical fruit wastes for the removal of basic and reactive dyes.	Graduated (2010)	Local
19.	Nur Izzatul Akmal Binti Mohd Zaki	PJM 0266	Preparation of activated carbon from fruit waste for wastewater treatment.	Ongoing	Local
20.	Norhidayah Ahmad	PJM 0265	Synthesis of agrowaste based activated carbons by physicochemical activation for dyes removal.	Ongoing	Local
21.	Ayshah Rosli	PJM 0268	Functionalized adsorbent for wastewater treatment.	Ongoing	Local
22.	Mohamad Firdaus Mohamad Yusop	PJM 0267	Heat treatment of agrowastes using automated control kiln for production of char.	Ongoing	Local
23.	Meisam Valizadeh Kiamahalleh	PJM 0145	Synthesis and electrochemical performance evaluation of manganese-nickel oxides/multiwalled carbon nanotube/Poly (3,4-ethylenedioxythiophene) nanocomposite for supercapacitor materials	Graduated	International
24.	Saiful Izwan bin Abd Razak	PJM 0161	Polymerization, preparation and characterization 'in-situ' conducting nanocomposite of polyaniline/multiwalled carbon nanotubes/manganese dioxide	Graduated	Local

25.	Yeong Yin Fong	P-JD 0031	Silicalite-1 membrane: Synthesis, modification, characterization and its performance for the reactive separation of para-xylene from xylene isomers,	Graduated	Local

- **RO/RA**

N/A

- **FYP**

No.	Full Name	Research Title
1	Mohd Hizami Bin Mohd Yusoff,	Adsorption of 4-nitrophenol and methylene blue on modified activated carbon
2	Nadiah Binti Sahimi	Preparation and characterization of hydrochars from oil palm by-products

ii-PUBLICATIONS (JOURNAL) :

The output of this research grant that have been publish = 107 journals

**the following are the details of publications:*

No. Authors, Year, Title of Paper, Name of Journal, Volume, Page Number

1 Ahmad, A. L., Leo, C. P. & Abd. Shukor, S. R. 2008. Tailoring of a γ-alumina membrane with a bimodal pore size distribution for improved permeability. Journal of the American Ceramic Society, 91, 246-251.

2 Ahmad, A. L., Leo, C. P. & Abd. Shukor, S. R. 2009. Statistical design of experiments for dye-salt-water separation study using bimodal porous silica/(-alumina membrane. Desalination and Water Treatment, 5, 80-90.

3 Ahmad, A. L., Leo, C. P. & Shukor, S. R. A. 2008. Preparation of silica/γ-alumina membrane with bimodal porous layer for improved permeation in ions separation. Journal of the American Ceramic Society, 91, 2009-2014.

4 Ahmad, A. L., Leo, C. P. & Shukor, S. R. A. 2008. Preparation of γ-alumina thin layer with bimodal pore size distribution for diminution of transport resistance in bi-layered membrane. Thin Solid Films, 516, 4319-4324.

5 Ahmad, A. L., Leo, C. P. & Shukor, S. R. A. 2009. Vanadium oxide supported γ-alumina with bimodal porous structure for intra-particle diffusion enhancement in styrene oxidation reaction. Journal of Porous Materials, 16, 33-40.

6 Ahmad, A. L., Koohestani, B., Bhatia, S. & Ooi, B. S. 2010. Synthesis of vanadium oxide nanotubes via an ultrasonic method. Journal of Sol-Gel Science and Technology, 56, 327-332.

7 Ahmad, A. L., Koohestani, B., Bahtia, S. & Ooi, B. S. Oxidation of styrene to benzaldehyde by anhydrous hydrogen peroxide on γ-alumina-supported V_2O_5 nanoparticle catalysts: optimization studies using RSM. International Journal of Applied Ceramic Technology Accepted.

8 Mehrnoush Khavarian, Chai Siang-Piao, Soon Huat Tan, Abdul Rahman Mohamed, "Floating catalyst CVD synthesis of carbon nanotubes using iron (III) chloride: Influences of the growth parameters" Nano, Vol. 4, No. 6 (2009) 359–366.

9 Mehrnoush Khavarian, Chai Siang-Piao, Soon Huat Tan, Abdul Rahman Mohamed, "Iron (III) chloride as floating catalyst precursor to produce multi-walled carbon nanotubes from methane" Nano, Vol. 5, No. 3 (2010) 167–173.

10 Mehrnoush Khavarian, Chai Siang-Piao, Soon Huat Tan, Abdul Rahman Mohamed, "Effects of temperature for the synthesis of carbon nanotubes by $FeCl_3$ as a floating catalyst precursor" Fullerenes, Nanotubes and Carbon Nanostructures, Vol. 19 (2011) 575–583.

11 N. Nasuha, B.H. Hameed, 2011. Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea, Chemical Engineering Journal 166, 783-786.

12 N. Nasuha, B.H. Hameed, Azam T. Mohd Din, 2010, Removal of methylene blue from aqueous solution by NaOH-modified rejected tea, Journal of Hazardous Materials 175, 126–132.

13 F.W. Shaarani, B.H. Hameed, 2011. Ammonia-modified activated carbon for the adsorption of 2,4-dichlorophenol, Chemical Engineering Journal 169, 180-185.

14 B.H. Hameed, I.A.W. Tan, Nitric acid-treated bamboo waste as low-cost adsorbent for removal of cationic dye from aqueous solution, Desalination and Water Treatment, 21 (2010) 357–363.

15 Irvan Dahlan, Keat Teong Lee, Azlina Harun Kamaruddin, Abdul Rahman Mohamed, 2008, "Analysis of SO_2 Sorption Capacity of Rice Husk Ash (RHA)/CaO/NaOH Sorbents Using Response Surface Methodology (RSM): Untreated and Pretreated RHA", Environmental Science and Technology, American Chemical Society, Vol 42 (5), pp 1499-1504.

16 Keat-Teong Lee, Kok-Chong Tan, Irvan Dahlan, Abdul Rahman Mohamed, 2008 "Development of Kinetic Model for the Reaction between SO_2/NO and Coal Fly Ash/CaO/$CaSO_4$ Sorbent", Fuel, Elsevier, Vol. 87 (10-11), pp 2223-2228.

17 Irvan Dahlan, Gui Meei Mei, Azlina Harun Kamaruddin, Abdul Rahman Mohamed, Keat Teong Lee, 2008 "Removal of SO2 and NO Over Rice Husk Ash (RHA)/CaO-Supported Metal Oxides", Journal of Engineering Science and Technology, Taylor's University College, Vol. 3 (2), pp 109-116.

18 Irvan Dahlan, Keat Teong Lee, Azlina Harun Kamaruddin, Abdul Rahman Mohamed, 2009 "Evaluation of Various Additives on the Preparation of Rice Husk Ash (RHA)/CaO-Based Sorbent For Flue Gas Desulfurization (FGD) at Low Temperature", Journal of Hazardous Materials, Elsevier, Vol. 161 (1), pp 570-574.

19 S. Sumathi, S. Bhatia, K.T. Lee, A.R. Mohamed, 2009 "Optimization of Microporous Palm Shell Activated Carbon Production for Flue Gas Desulfurization: Experimental and Statistical Studies", Bioresource Technology, Elsevier, Vol. 100 (4), pp 1614-1621.

20 Keat Teong Lee and Ooi Wan Koon, 2009 "Modified Shrinking Unreacted-Core Model for the Reaction between Sulfur Dioxide and Coal Fly Ash/CaO/$CaSO_4$ Sorbent", Chemical Engineering Journal, Elsevier, Vol. 146 (1), pp 57-62.

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26 Irvan Dahlan, Zainal Ahmad, Muhammad Fadly, Keat Teong Lee, Azlina Harun Kamaruddin, Abdul Rahman Mohamed, 2010 "Parameters Optimization of Rice Husk Ash (RHA)/CaO/CeO_2 Sorbent for Predicting SO_2/NO Sorption Capacity Using Response Surface and Neural Network Models", Journal of Hazardous Materials, Elsevier, Vol. 178 (1-3), pp 249-257.

27 S. Sumathi, S. Bhatia, K.T. Lee and A.R. Mohamed, 2010 "Cerium Impregnated Palm Shell Activated Carbon (Ce/PSAC) Sorbent for Simultaneous Removal of SO_2 and NO - Process Study", Chemical Engineering Journal, Elsevier, Vol. 162 (1), pp 51-57.

28 S. Sumathi, S. Bhatia, K.T. Lee and A.R. Mohamed, 2010 "Adsorption Isotherm Models and Properties of SO_2 and NO removal by Palm Shell Activated Carbon Supported with Cerium (Ce/PSAC)", Chemical Engineering Journal, Elsevier, Vol. 162 (1), pp 194-200.

29 Lee Chung Lau, Keat Teong Lee, Abdul Rahman Mohamed, 2010 "Rice husk ash sorbent doped with copper for simultaneous removal of SO_2 and NO: Optimization study", Journal of Hazardous Materials, Elsevier, Vol. 183 (1-3), pp 738-745.

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41 Subhash Bhatia, Cheng Teng Wong and Ahmad Zuhairi Abdullah (2009). Optimization of air-borne butyl acetate adsorption on dual function Ag-Y adsorbent-catalyst using response surface methodology, Journal of Hazardous Materials, 164, 1110-1117. (Publisher: Elsevier).

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50 Tri Yogo Wibowo, Ahmad Zuhairi Abdullah and Ridzuan Zakaria (2009). Cationic surfactant-modified clay catalysts for selective synthesis of glycerol monolaurate through glycerol esterification with lauric acid, Applied Clay Science, 50, 280-281. (Publisher: Elsevier).

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iii-PUBLICATIONS (PROCEEDINGS) :

The finding from this research grant have also been presented in many local and international conferences = 47 proceedings

**the following are the details:*

No.	Authors,Venue, Name of Conference
1	A.L. Ahmad, C.P. Leo, S.R. Abd Shukor. Statistical design of experiments for dye-salt water separation study using bimodal porous silica/ γ-alumina membrane. Desalination for Clean Water and Energy (Euromed 2008) , 9-13 November 2008, King Hussein Bin Talal Convention Center, Dead Sea, Jordan.
2	B. Koohestani, A. L. Ahmad, S. Bhatia, and B. S. Ooi. Vanadium oxide carbon nanotube composite embedded γ-Al_2O_3 catalytic membranes for oxidation reaction. Symposium and workshop Membrane Science and Technology 23-26 Agust 2011 Singapore.
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40 Abd Razak S.I., Ahmad A.L., Adeli H. and Sharif Hussein Sharif Zein (2008). Ternary nanocomposites film of polyaniline/ multi-walled carbon nanotubes/manganese dioxide. International Conference on Science & Technology: Application in Industry & Education (ICSTIE 2008).

41 Yeong, Y.F., Abdullah, A.Z., Ahmad, A.L., Bhatia, S. (2006). Zeolite membrane based selective gas sensors for monitoring and control of gas emissions: development and their performance. In International Conference on Environment (ICENV), 13-15 November, Universiti Sains Malaysia, Pulau Pinang, Malaysia.

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44 Yeong, Y.F., Abdullah, A.Z., Ahmad, A.L., Bhatia, S. (2008). Synthesis, characterization of phenethyltrimethoxysilane (PE) functionalized Silicalite-1 molecular sieves and its transformation into solid acid materials. In International Conference on Multifunctional Materials and Structures (MFMS 2008), 28-31 July, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong.

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46 Yeong, Y.F., Abdullah, A.Z., Ahmad, A.L., Bhatia, S. (2009). Optimization of p-xylene separation from ternary xylene mixture over Silicalite-1 membrane using response surface methodology. In 7th International Conference on Membrane Science and Technology (MST 2009), 12 – 15 May, Kuala Lumpur.

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iv-AWARDS

1. Gold Medal

   International Trade Fair: Ideas-Inventions- New Products (IENA 2009), 5-8 November 2009, Nuremberg Exhibition Center, Nuremberg, Germany

   Product title : γ-Alumina with bimodal pore size distribution: transport resistance diminution in bi-layered membrane

2. PECIPTA 2007 (International Exposition of Research and Inventions of Institutions of Higher Learning 2007) – Gold Medal for the invention "*Rice Husk Ash-Based Sorbent/Catalyst As A Novel Industrial Gas Cleaning Technology*"

   Ministry of Higher Education Malaysia & Universiti Sains Malaysia

3. PECIPTA 2007 (International Exposition of Research and Inventions of Institutions of Higher Learning 2007) – Malaysian Higher Education Ministers' Award for the invention "*Rice Husk Ash-Based Sorbent/Catalyst As A Novel Industrial Gas Cleaning Technology*"

   Ministry of Higher Education Malaysia & Universiti Sains Malaysia

4. International Trade Fair of Ideas-Inventions-New Products 2009 (iENA), Nuremberg, Germany 2009 – Gold Medal for the invention "*Rice Husk Ash-Based Sorbent/Catalyst As A Novel Industrial Gas Cleaning Technology*"

5. Lee Keat Teong, Abdul Rahman Mohamed, Subhash Bhatia, Sumathi Sethupati, 2011, Gold Medal for the invention "Oil palm shell-based sorbent/catalyst as a novel industrial gas cleaning technology (CePAC)", Malaysian Technology Expo 2011, Malaysia

6. Silver Award, Malaysian Technology Expo 2008, Kuala Lumpur, 21-23 February 2008.

7. Silver Award, Malaysian Technology Expo 2009, Kuala Lumpur, 19-21 February 2009.

8. Bronze Award, BioInno Award 2009, Kuala Lumpur, 17-19 November 2009.

9. Gold Medal 2011: Final Year Project of my student Lidya Amira Bt Zukimi

   Functionalized Multiwalled Carbon Nanotubes / Poly Lactic Acid Nanocomposite Scaffolds For Tissue Engineering. 22-25th June 2011, Universiti Sains Malaysia, Penang – Malaysia.

10. Gold Medal and Overall Best Project 2008: Final Year Project of my student Fan Mun Sing

    The Development Of Carbon Nanotubes Based Nanocomposites For Supercapacitor Materials. 20-22nd May 2009, Universiti Sains Malaysia, Penang – Malaysia.

v-INTELLECTUAL PROPERTY

i) Method of development activated carbon by chemical activation

Search report = ISD 426/13/1 (PS2009-060050)

Certificate of Filling = PI 2010003015

Date = 24 June 2010

ii) Green drainage system

Search report = ISD 426/13/1 (PS2009-100107)

Certificate of Filling = PI 20095660

Date = 30 December 2009

vi-NETWORKING & LINKAGES / COLLABORATORS (Please explain)

International collaborators:

- *Dr. David S. McPhail (Imperial College London, UK)*
- *Prof. Dr. Aldo R. Boccaccini (University of Erlangen-Nuremberg, Germany)*

K. LIST OF EQUIPMENT(S)

Item	List of Equipment Approved by USM (as in offer letter)	List of Equipment Bought	Location
Specialized Equipment	-	Sun Run 10 ton Hydraulic Press Shaking Water Bath Peristaltic pump Ashing & Burn Off Furnace Surface Analyzer	School of Chemical Engineering, USM
Facility	Desktop computer (PC)	Desktop computer (PC)	School of Chemical Engineering, USM
Infrastructure	-	-	-

L. POTENTIAL FOR COMMERCIALIZATION

N/A

M. SUCCESS STORY

PROJECT 1:

Optimization of ceramic membrane was achieved by introducing bimodal porous ceramic membrane templated using vanadium oxide nanotube. A novel gamma-alumina membrane, template using vanadium oxide was developed through studies of various membrane fabrication technologies, which involved application of functional cerami membrane in styrene oxidation reactor. Styrene oxidation can be improved using vanadium oxide-based composite catalysts (Al_2O_3/V_xO_y, CNT-V_xO_y, and CNT-V_xO_y/Al_2O_3) using anhydrous H_2O_2 as an oxidant. The catalyst type, structure and reaction conditions have significant influence on the styrene oxidation reaction. Vanadium oxide nanotube, synthesized through a hydrothermal method has relatively poor performance due to the oxidative degradation. However, by using CNTs as a template, this shortcoming was overcome. Two main products of the styrene oxidation are benzaldehyde and styrene oxide, but for all of types of catalysts, the selectivity for benzaldehyde is very high. By employing CNT-V_xO_y/Al_2O_3 as catalytic membrane, conversion of styrene decrease but selectivity of benzaldehyde increase compare to nanocomposite particle. This is because the membrane could prevent side reaction by isolating the product for further reaction with H_2O_2.

PROJECT 2:

- The photos of the major components of the experimental rig setup are shown in Figure 1.

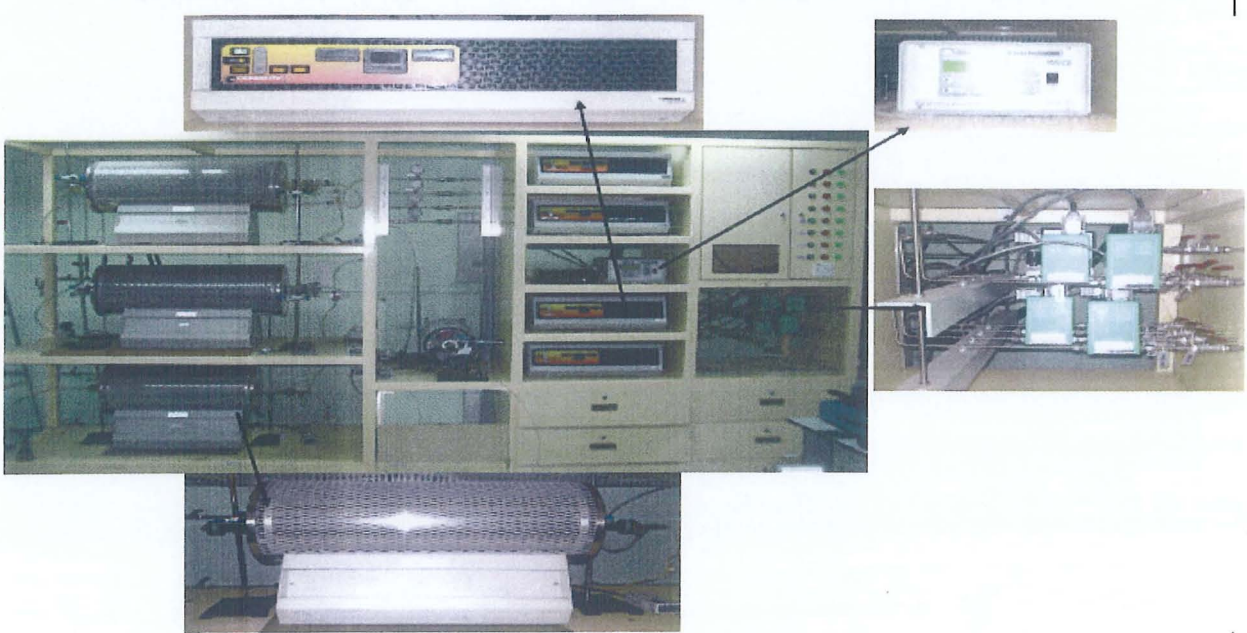
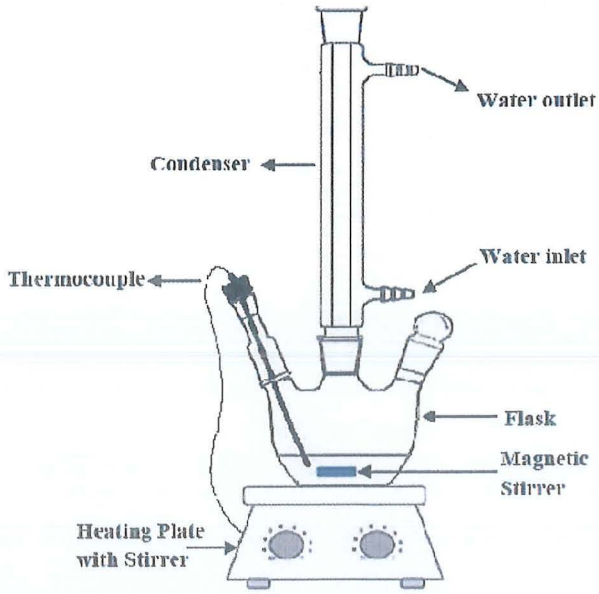


Figure 1. Experimental rig setup and the major components of the rig.

- A schematic of the apparatus used for acid treatment of as-grown CNTs is shown in Scheme 4. The main equipment consists of a flat bottom flask with three necks, condenser, digital heating plate with controllable temperature indicator and a magnetic stirrer capsule. A furnace was also used for air oxidation as one step of purification of as-grown CNTs.



Scheme 4. Experimental setup for purification of as-grown CNTs by acid treatment.

- The CNTs were grown on the inner surface of the quartz tube as a uniform black film as shown in Figure 2.

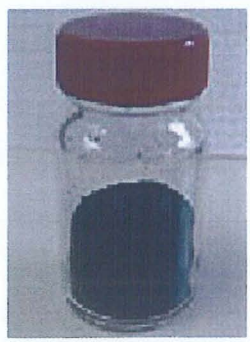


Figure 2. Produced Carbon Nanotube

PROJECT 3, 4, 5 & 6

N/A

PROJECT 7:

Manganese oxide (MnO_2) is one of the most promising pseudocapacitors electrode materials with respect to both its SC value and cost effectiveness. Manganese can be present in various valence states, and its oxides are promising candidates for supercapacitors because of their low cost and being environmentally friendly.

In the present work, the hybrid nanocomposite of MnO_2 filled in multiwalled carbon nanotubes (MWCNTs) was obtained by reduction of manganese nitrates solution in the narrow cavity of MWCNTs using wet chemical method, which is simple, convenient, and cheap compared with other methods.

Three stages maybe exist during the filling of MnO_2 into MWCNTs, as illustrated in Fig. 1. The first stage shows the closed MWCNTs were opened and cut off after being treated with nitric acid (Fig. 1a and 1b). When the acid-treated MWCNTs were stirred with manganese nitrate solution in the second stage, the solution was impregnated into the inner core of the MWCNTs by capillary force (Fig.1c). In the third stage, the MnO_2 nanoparticles in the inner cavity further grew up and yield a dense and discontinuous filling formed nanoparticles while annealing at 300°C in stream of argon (Fig. 1d).

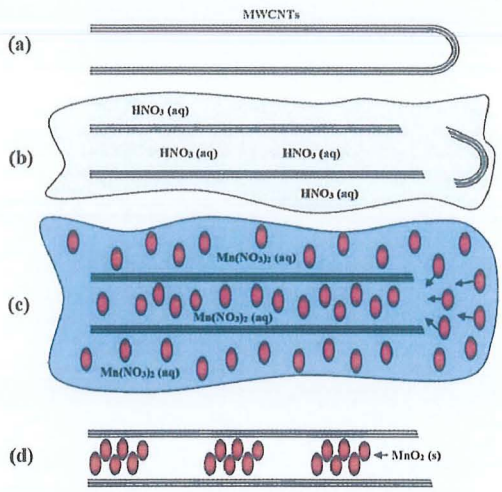


Figure 1.Schematic diagram of the MnO_2 filling process into MWNTs: (a) as closed MWCNTs; (b) as opened and cut by nitric acid treatment; (c) as filled with manganese nitrate particles; (d) prepared MnO_2/MWCNTs nanocomposite.

PROJECT 8:

The acid-functionalized silicalite-1 membranes have been synthesized successfully with the exploration of the effects of process variables. The membranes exhibited good performance in the combined separation and reaction studies.

N. OTHER COMMENTS

N/A

APPENDIX I

HUMAN CAPITAL DEVELOPMENT

(MSc/PhD)

BIMODAL POROUS CERAMIC MEMBRANE VIA NANOSIZED POLYSTYRENE TEMPLATING: SYNTHESIS, CHARACTERIZATION AND PERFORMANCE EVALUATION

by

LEO CHOE PENG

Thesis submitted in fulfillment of the requirements
for the degree of
Doctor of Philosophy

February 2008

ADSORPTION OF METHYLENE BLUE AND 2,4-DICHLOROPHENOL ONTO MODIFIED ACTIVATED CARBONS PREPARED FROM AGRICULTURAL WASTE

FARRA WAHIDA BINTI SEAARANI

UNIVERSITI SAINS MALAYSIA
2010

ADSORPTION OF METHYLENE BLUE ONTO MODIFIED FACTORY TEA WASTE: BATCH AND FIXED BED COLUMN

NORHASLINDA BINTI NASUHA

UNIVERSITI SAINS MALAYSIA
2011

REMOVAL OF SO_2 AND NO FROM SIMULATED FLUE GAS USING RICE HUSK ASH/CaO/CeO_2 SORBENT

by

IRVAN

Thesis submitted in fulfillment of the requirements
for the degree of
Doctor of Philosophy

March 2009

REMOVAL OF SO_2 AND NO FROM SIMULATED FLUE GAS USING CERIUM-MODIFIED PALM SHELL ACTIVATED CARBON

by

SUMATHI SETHUPATHI

Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

April 2010

REMOVAL OF SO_2 AND NO FROM FLUE GAS USING SORBENT DERIVED FROM RICE HUSK ASH

by

LAU LEE CHUNG

Thesis submitted in fulfillment of the requirements
for the Degree of
Master of Science

March 2010

MATHEMATICAL MODELING OF SIMULTANEOUS REMOVAL OF SO_2 AND NO USING SORBENT SYNTHESIZED FROM ASH

by

HENRY FOO CHEE YEW

Thesis submitted in fulfillment of the

requirements for the degree of

Master of Science

June 2010

BIODIESEL PRODUCTION USING ULTRASONIC-ASSISTED HETEROGENEOUS CATALYTIC PROCESS

BABAK SALAMATINIA

UNIVERSITI SAINS MALAYSIA
2011

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BIMETALLIC MONOLITHIC CATALYST FOR SELECTIVE CATALYTIC REDUCTION OF NO_x IN DIESEL ENGINE EXHAUST

HAMIDAH BINTI ABDULLAH

UNIVERSITI SAINS MALAYSIA
2008

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Hamidah Abdullah, Julai 2008

SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS BASE CATALYST FOR TRANSESTERIFICATION OF PALM OIL

NORAINI BINTI RAZALI

UNIVERSITI SAINS MALAYSIA
2009

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I would also like to express my deepest and most heart-felt gratitude especially to my beloved husband, Mohd Azrolsham bin Abdullah for his prayers, endless love, support, encouragement and care to me throughout this study. Not forget also to my adored parents, Mr. Razali bin Abdullah and Mrs. Siti Aminah binti Ngah and my siblings for their prayers and blessing to me in completing my study.

A million thanks to the biodiesel research group for their knowledge sharing and guidance, Babak, Hamed, Jibrail, Lip han and Siti, thanks a lot. Last but not

DEVELOPMENT OF ULTRASONIC-ASSISTED METHYL ESTER PROCESS FROM PALM OIL USING ALKALINE EARTH METAL OXIDE CATALYSTS

HAMED MOOTABADI

UNIVERSITI SAINS MALAYSIA

2010

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I would also like to express my appreciation to the Dean, Prof. Dr. Azlina Bt. Harun @ Kamaruddin and Deputy Deans, Assoc. Prof. Dr. Lee Keat Teong and Assoc. Prof. Dr. Mohamad Zailani Bin Abu Bakar for their continuous support and help rendered throughout my studies. My sincere thanks to all the respective lecturers, staff and technicians, School of Chemical Engineering for their cooperation and support. Thousand thanks to Mr. Shamsul Hidayat Shaharan and Mr. Mohd. Faiza Ismail for their valuable and kind help in laboratory works. I highly appreciate all the help and supports from Mrs. Aniza Abd. Ghani for her assistance in the official work during my studies. I am also indebted to School of Chemical Sciences and School of Material and Mineral Engineering in USM for AAS and SEM analysis. Very special thanks goes to Mr. Babak Salamatinia for his kind helps and support in forwarding this thesis.

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PENYELIA UTAMA

ACID FUNCTIONALIZED MESOPOROUS CATALYST FOR GLYCEROL ESTERIFICATION TO MONOGLYCERIDE

LILIS HERMIDA

UNIVERSITI SAINS MALAYSIA

2010

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First of all, I would like to thank Allah the Almighty for endowing me with life and blessing me to pursue MSc study. It is with great pleasure I express my deepest appreciation to my main supervisor, Associate Professor Dr.Ahmad Zuhairi Abdullah for unfailing guidance, invaluable advices, fruitful discussions, and encouragement all through this research work. I would also like to thank my co-supervisor Professor Dr. Abdul Rahman Mohamed for his support and advices throughout the research.

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BEHAVIOURS OF SONOCATALYTIC DEGRADATION OF METHYL ORANGE DYE IN AQUEOUS EFFLUENTS

SITI AMINAH BINTI MD ALI

UNIVERSITI SAINS MALAYSIA

2009

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PM Ahmad Zuhairi Abdullah

SYNTHESIS, CHARACTERIZATION, AND EVALUATION OF CATALYTIC ACTIVITY OF FE (III)/TiO_2 IN THE REMOVAL OF REACTIVE DYE IN AQUEOUS UNDER ULTRASONIC IRRADIATION

NUR AZIMAH BINTI JAMALLUDDIN

UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
Diterima pada
18 MAY 2010
Pusat Pengajian Kejuruteraan Kimia

UNIVERSITI SAINS MALAYSIA

2010

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ADSORPTION OF BASIC DYES ON COCOA POD HUSKS BASED ACTIVATED CARBON (CPHAC): EQUILIBRIUM, KINETICS AND MECHANISM STUDIES

WAN NURUL HUDA BINTI WAN ZAINAL

UNIVERSITI SAINS MALAYSIA

2009

ADSORPTION OF BASIC DYES ON COCOA POD HUSKS BASED ACTIVATED CARBON (CPHAC): EQUILIBRIUM, KINETICS AND MECHANISM STUDIES

ABSTRACT

Activated carbon (AC) adsorption has been found to be an effective and widely employed means of wastewater treatment. However, commercial available ACs are very expensive due to the use of non-renewable starting material. Thus, the purpose of this work is to produce AC from cocoa pod husk waste for removal of malachite green (MG) and methylene blue (MB) dyes from aqueous solution. Physical activation by carbon dioxide was used to prepare the AC at various activation conditions. The experimental design results showed that the activation temperature and activation time were important variables affecting the mesopore volume, surface area and adsorption performance of MG and MB dyes. AC prepared at temperature 700°C and 2 h activation time gave the highest mesopore volume, surface area as well as the adsorption capacity of both MG and MB dyes. The effects of initial dye concentration, contact time and solution temperature on AC were evaluated through batch adsorption studies. Both adsorption of MG and MB dyes best described by Freundlich isotherm and pseudo-second-order model for adsorption equilibrium and kinetic, respectively. Meanwhile for mechanism study, the Boyd film diffusion model was more favourable compared to intraparticle diffusion model of MG and MB dyes adsorption.

PREPARATION OF ACTIVATED CARBON FROM TROPICAL FRUIT WASTES FOR THE REMOVAL OF BASIC AND REACTIVE DYES

RASYIDAH BT ALROZI

UNIVERSITI SAINS MALAYSIA

2010

PREPARATION OF ACTIVATED CARBON FROM TROPICAL FRUIT WASTES FOR THE REMOVAL OF BASIC AND REACTIVE DYES

ABSTRACT

Commercially available activated carbons are still considered expensive due to the use of non-renewable and relatively expensive starting material such as bituminous coal. Therefore, this study investigates the potential use of tropical fruit wastes such as mangosteen peel (MP) and rambutan peel (RP) that available in Malaysia, as the precursor for the preparation of activated carbon which can be applied for the removal of two types of dyes, which are basic Malachite Green (MG) and reactive Remazol Brilliant Blue R (RBBR) from aqueous solution. Physiochemical activation consisting of potassium hydroxide (KOH) impregnation plus carbon dioxide (CO_2) gasification was used to prepare the activated carbons. The experimental design results revealed that CO_2 activation temperature, CO_2 activation time and KOH impregnation ratio (IR) were important factors influencing the activated carbons yields and adsorption performance for MG and RBBR. The optimum conditions obtained for preparing the activated carbons from the selected precursors for CO_2 activation temperature, CO_2 activation time and IR were 778-834 ^{o}C, 1-1.8 h and 2.7-3.5, respectively. All the activated carbons prepared were mesoporous with high mesopores surface area, mesopore volumes and average pore diameter larger than 2.2 nm. Scanning electron microscopy (SEM) analyses proved the activated carbons prepared from MP and RP demonstrated homogeneous and heterogeneous type pore structures, respectively. Fourier Transform Infrared (FTIR) analyses revealed the presence of various functional groups on the activated carbon surfaces. The effects of adsorbate initial concentration (25-500 mg/L for MG and 25-250 mg/L for RBBR), contact time, solution temperature (30-60 ^{o}C), solution pH (2-

SYNTHESIS, CHARACTERISATION AND ELECTROCHEMICAL TESTING OF MULTIWALLED CARBON NANOTUBES BASED NANOCOMPOSITES FOR SUPERCAPACITOR MATERIALS

by

MEISAM VALIZADEH KIAMAHALLEH

Thesis Submitted in Fulfilment of the Requirements
for the Degree
of Master of Science

April 2010

SYNTHESIS AND CHARACTERIZATION OF POLYANILINE/MULTIWALLED CARBON NANOTUBES BASED NANOCOMPOSITES

by

SAIFUL IZWAN ABD RAZAK

Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science

October 2010

SILICALITE-1 MEMBRANE: SYNTHESIS, MODIFICATION, CHARACTERIZATION AND ITS PERFORMANCE FOR THE REACTIVE SEPARATION OF PARA-XYLENE FROM XYLENE ISOMERS

YEONG YIN FONG

UNIVERSITI SAINS MALAYSIA

2009

APPENDIX II

PUBLICATIONS

(JOURNAL & PROCEEDINGS)

journal

J. Am. Ceram. Soc., 91 [1] 246–251 (2008)
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Tailoring of a γ-Alumina Membrane with a Bimodal Pore Size Distribution for Improved Permeability

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School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Penang, Malaysia

Porous γ-alumina with a bimodal pore size distribution has been developed by adding nanosized polystyrene beads to boehmite sol as templating units. The primary pore diameter is in the range of 4–6 nm and the secondary pore diameter is ca. 50 nm with minor pore shrinkage. The unsupported γ-alumina with different porous structures are characterized using thermogravimetric analysis, Fourier transform infrared spectra, X-ray diffraction, N_2 adsorption/desorption, and transmission electron microscopy. γ-alumina with a bimodal porous structure shows reduced transport resistance compared with γ-alumina with a unimodal porous structure in the dye adsorption test. Although the thickness of γ-alumina thin layer increases when more secondary pores are generated, a γ-alumina membrane with a bimodal pore size distribution shows diminution of transport resistance in the water permeability study also.

Nomenclature

C_e	equilibrium concentration (mg/L)
C_t	dye concentration in solution at time t (mg/L)
C_0	initial dye concentration in solution (mg/L)
D_0	diffusion coefficient (m/s)
ΔP	applied pressure difference across the membrane (bar)
Δq	standard deviation
F	fractional uptake of solute
η	liquid viscosity (bar · s)
J	volumetric flux (m/s)
k_1	rate constant of pseudo-first-order model (L/min)
k_m	permeability coefficients of overall membrane (m)
k_α	permeability coefficients of the α-alumina support (m)
k_γ	permeability coefficients of the γ-alumina thin layer (m)
L_m	membrane thickness (m)
m	mass of unsupported γ-alumina (g)
Q	maximum adsorption capacity (mg/g)
q_e	adsorption capacity in equilibrium (mg/g)
q_t	amount of adsorption at time t, (mg/g)
r	particle radius (mm)
r_m	specific resistance (m^2)
t	time (min)
V	volume of solution (L)

I. Introduction

Porous materials with a highly defined pore distribution are imperative in chemical engineering, especially catalysis. Among the porous materials, nanoporous ceramics are crucial because of their large surface area and great resistance against severe operating conditions.[1] Consequently, nanoporous ceramics have been engineered into thin layers that have broad applications such as gas-separating membranes and catalytic membrane reactors.[2–4] Nanoporous ceramic membranes are usually prepared by the sol–gel method using colloidal sols of nanometer-sized metal oxide particles, formed by hydrolysis and condensation of metal-organic precursors in aqueous media. Sol is then deposited on an adequate macroporous support and calcined to form a thin layer of membrane with a narrow pore distribution and a high surface area.[5]

Nanoporous ceramics with a narrow pore size distribution is not always a definite option. The formation of bimodal porosity in nanoporous material is more practical as the presence of secondary pores considerably enhances the diffusion of molecules. In this regard, several researchers have reported that bimodal porous materials exhibit reduced diffusion resistance and enhanced catalytic function in heterogeneous reactions.[6–9] Until now, incorporation of different types of templates into the sol–gel method has been prevalent in the preparation of bimodal porous ceramics. The templates include emulsion droplets,[10] foam,[11] and solid templates.[12,13] For creating symmetrical secondary macropores, however, scientists often select polymer beads such as polystyrene and polymethyl methacrylate.[14–17] This is the reason why orderly arranged and uniform secondary pores can be generated after assembling of polymer beads using a centrifuge or a filter.[18] Besides this, the control of the primary pore size distribution is independent of additional templating units in the sol. Li–La–Ti–O, ZrO_2, TiO_2, and SiO_2 with well-ordered secondary macropores have been successfully produced using this method.[16,19–21]

Although the preparation of ceramics with a bimodal porous structure is greatly reported, not much work was published on the synthesis of ceramic membranes with a bimodal pore size distribution. Alonso *et al.*[22] only described the preparation of a porous silicon–titanium oxycarbide membrane with a bimodal pore size distribution. Meanwhile, Tsuru *et al.*[23] synthesized a bimodal porous α-alumina membrane for steam reforming of methane. Owing to the lack of related work, it is important to synthesize thin layers of ceramics with a bimodal pore size distribution and to understand their characteristics for further applications in catalysis. In this work, secondary mesopores are tailored in γ-alumina, which plays important roles in industrial chemical processes such as hydrodesulfurization, metathesis, and cracking. From a chemical viewpoint, γ-alumina constitutes a metastable transition alumina phase, resulting in the dehydration of boehmite. Alumina in the γ-phase possesses a large surface area, high pore volume, and great catalytic properties.[24] The catalytic properties of γ-alumina strongly depend on its crystalline structures and textural characteristics.[25] Hence, bimodal porous γ-alumina is synthesized with intermediate crystallization of boehmite. Nanosized polystyrene beads (diameter ca. 50 nm) are selected in this research for tailoring secondary mesopores in γ-alumina with the aim of achieving minor pore shrinkage. This is because severe pore shrinkage usually occurs when macrosized polymer beads are utilized as a template.[26]

Furthermore, a simple dye adsorption test is used to compare the diffusion kinetics of unsupported γ-alumina with a unimodal pore size distribution and unsupported γ-alumina with a

A. Krell—contributing editor

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PROOF
DWT JO163

Statistical design of experiments for dye-salt-water separation study using bimodal porous silica/γ-alumina membrane

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ABSTRACT

Treatment of textile wastewater using conventional methods is either inefficient or costly. This is because it usually involves reactive dye, great amounts of salt and high temperature. In this study, a bimodal porous silica/γ-alumina membrane with improved permeability was tested in dye–salt water separation. The effects of temperature, feed concentration of dye, feed concentration of salt, pH and the pressure on permeate were examined using a response surface method. In general, the newly developed membrane showed satisfactory dye rejection (>90%) at common operating conditions. From the statistical analysis, it was found that the variation of salt rejection depends on the feed concentration of salt, feed concentration of dye and the pressure. Meanwhile, only the permeate flux is unaffected by the feed concentration of the dye.

Keywords: Dye; Salt; Membrane; Ceramic

1. Introduction

Textile wastewater is the most significant source of pollution in the industry due to its quantity and composition [1]. In the common dyeing process, an average of 70–150 L water, 0.6–0.8 kg NaCl and 30–60 g reactive dyes are used for 1 kg cotton [2]. The treatment bath containing more than 80% of the feed salt and 90% of the initial color is then discharged as wastewater. Treating such a great amount of effluent is a difficult task since conventional methods such as biological treatments, coagulation-flocculation, adsorption using activated carbon, electrochemical processes and ozone treatment have been found to be either costly or inefficient [2,3]. Consequently, textile wastewater treatment using membrane technology has been widely studied. Compared to other treatments, membrane separation not only shows high efficiency in color removal but also allows recycling of water and dyes for sustainable development in textile industry [3].

In general, membranes with different ranges of molecular weight cut-off (MWCO) can be utilized to achieve different treatment purposes in the textile industry. Microfiltration membranes and ultrafiltration membranes are useful for eliminating colloidal dyes, particles and marcomolecules; while nanofiltration (NF) membranes are applicable for removing reactive dyes [4]. Since reactive dyes are the major coloring agent in the textile industry [3], studies on reactive dye removal from textile effluent with high concentrations of salts using NF membranes

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Preparation of Silica/γ-Alumina Membrane with Bimodal Porous Layer for Improved Permeation in Ions Separation

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Creating secondary pores in the intermediate layer of hierarchical ceramic membranes successfully increases the permeability of bi-layered membranes by reducing the density of the separating layer. With the optimum secondary pore volume, the permeability of the silica/γ-alumina membrane with low secondary volume is enhanced with a satisfactory retention of organic ions and inorganic ions. However, the silica layer is not well formed when excessive secondary pores were generated in the intermediate layer. This is likely because the bimodal porous structure of γ-alumina with high secondary pore volume is inadequate to prevent the penetration of silica sol into the α-alumina support during dip coating. Thus, the bi-layered membrane with high secondary pore volume shows insufficient retention of Reactive Orange 16 dye and NaCl at low pH.

I. Introduction

MEMBRANE technology is energy efficient and cost effective. It represents promising alternative to conventional separation methods such as energy-intensive distillation, cryogenic separation and pressure swing adsorption.[1,2] Ceramic membranes have the advantages of thermal stability, solvents and chemicals resistance, sterilization ability and biocompatibility compared with polymeric membranes.[3] They are not only widely applied in separation and purification,[4] but also in fuel cells[5] and catalytic membrane reactors.[6]

Among the ceramic membranes, porous silica membranes have drawn the greatest attention from researchers and technologists. Silica membranes show promising molecular sieving characteristics in gas separation.[7,8] Besides that, silica membranes have been successfully utilized in pervaporation[9] and electrolyte separation.[10] Porous silica membranes with tunable pore sizes can be processed by a simple sol–gel method or chemical vapor deposition. More importantly, silica membrane can even be templated with orderly arranged mesopores, uniform pores, enormous surface area, and high pore volume using surfactant.[11]

In general, macroporous supports are coated with an intermediate layer (such as γ-alumina or titania) before the deposition of silica membrane. It is difficult to coat silica membrane directly on macroporous supports with pore sizes substantially larger than 50 nm due to occurrence of defects.[12] Besides facilitating the deposition of a defect-free overlying silica thin layer, intermediate layer also improves the electrolyte retention at pH values close to iso-electric points of separating layer.[10] However, the permeate flux is largely reduced when a bi-layered membrane is utilized. Chowdhury *et al.*[13] demonstrated that intermediate layer contributes significant transport resistance in silica/γ-alumina membrane that reduces the applicability of silica membranes.

To further improve permeability of silica/γ-alumina membrane, Tsai *et al.*[12] have introduced additional coating of surfactant templated silica between γ-alumina and microporous silica layer. Meanwhile, Yoshino *et al.*[14] have introduced fourth layer of α-alumina, which located between the silica/γ-alumina membrane and membrane support. The thickness of the γ-alumina membrane was reduced in the four layers configuration. Apart from creating more hierarchical structure, some researchers such as Lee *et al.*[15] and So *et al.*[16] used soaking and vapor-deposition method to create thin and uniform membrane as intermediate layer in the porous support.

In our previous study,[17] γ-alumina thin layer with bimodal pore size distribution has been successfully coated on the α-alumina support. The bimodal porous γ-alumina thin layer shows lower specific resistance compared with conventional γ-alumina thin layer. Thus, the bimodal porous γ-alumina layer is facilitated as intermediate layer in this work to improve the permeability of silica/γ-alumina membrane. For detailed study of the silica membrane formed on bimodal porous intermediate layer, separation test of organic and inorganic ions using silica/γ-alumina membranes with different intermediate layers are conducted in this study.

II. Experimental Procedure

In the preparation of γ-alumina, boehmite sol was first synthesized using sol–gel method as described by Lambert *et al.*[18] Polyethylene glycol (PEG) (Merck Company, Malaysia) was added into the deionized water as binder and the amount of PEG is 2 wt% of final solution. Aluminum sec-butoxide (Fluka, Malaysia) was the sol precursor which was allowed to stir openly to evaporate butanol at 85°C for 15 min. Dilute HCl (Merck Company, Malaysia) was then added as a peptization agent with the final molar ratios of $Al:H_2O:HCl = 1:100:0.07$. The resulting solution was stirred 16 h at 80°C in a closed container to form a clear, stable boehmite sol.

For preparation of γ-alumina with bimodal pore size distribution, nanosized polystyrene beads (diameter is *ca.* 50 nm) were added into boehmite sol to tailor secondary pore size. The nanosized polystyrene beads (*ca.* 50 nm in diameter) were synthesized through emulsion polymerization.[19] The latex was washed with distilled water using ultrafiltration membrane and then freeze dried. 0.5 g nanosized polystyrene beads was added into 20 mL of boehmite sol and stirred overnight. This sample was labeled as A050. Using the same method, sample A025 was prepared by adding 0.25 g nanosized polystyrene beads. Then, alumina supports were dip coated with boehmite sol (labeled as A000), A025 and A050. The porous membrane supports used in this work are α-alumina discs with diameter of 28.0 mm and average thickness of 1 mm. The mean porosity of the membrane support is 32% and average pore size is 0.1 μm. The preparation of the membrane supports has been reported in the earlier work.[20] After dip coating, the nanosized polystyrene beads in A025 and A050 were assembled using vacuum filtration force.

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Preparation of γ-alumina thin layer with bimodal pore size distribution for diminution of transport resistance in bi-layered membrane

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Abstract

Porous γ-alumina with bimodal pore size distribution (average pore size of primary mesopores is 4–5 nm and diameter of secondary mesopores is ca. 50 nm) was introduced into bi-layered membranes as an intermediate layer for diminution of transport resistance. The secondary mesopores were tailored in γ-alumina using nanosized polystyrene beads (ca. 50 nm) as templating units. Surfactant templated silica was stacked on top of the γ-alumina with different pore structures to form bi-layered membranes. Besides characterizing using X-ray diffraction, transmission electron microscope, scanning electron microscope and X-ray microanalysis, bi-layered membranes with different types of intermediate layers were also studied using a dead-end stirred cell. The water permeabilities of the bi-layered membranes with secondary mesopores in intermediate layers are much higher than the permeability of the conventional bi-layered membrane. The molecular weight cut-off of the improved membrane was estimated at 400 Da, same as the molecular weight cut-off of the conventional membrane.
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Keywords: γ-alumina; Bimodal; Bi-layer membrane; Scanning electron microscopy; Transport through membranes

1. Introduction

Generally, inorganic nanofiltration membranes are susceptible to low retention of electrolytes at pH values which are near to their iso-electric points (IEP), as this corresponds to a high membrane potential [1]. Without addition of acid or base, most of the ceramic membranes perform unsatisfactorily as the pH of most aqueous electrolyte solutions are usually close to the IEPs of common ceramics membranes (IEP of titania ≈6, zirconia ≈7 and γ-alumina ≈8) [2]. Apparently, the application of ceramic membranes to selectively remove differently charged species at a wide pH range is less practical.

A probable solution of this hitch is to create a stack of layers of materials with different IEPs [3,4]; for example, bi-layered membranes with silica layer supported on the γ-alumina layer. Recently, De Lint et al. [2] showed that the retention of NaCl was maintained higher than 90% in the range of pH 4 to pH 10 by using silica/γ-alumina membrane in the electrolyte separation. The sustainability of NaCl retention in a wide pH range using the bi-layered membrane is considerably better than systems with only a γ-alumina layer [5] or TiO_2 layer [6]. However, the permeate flux is largely reduced when a bi-layered membrane is utilized. Chowdhury et al. [7] demonstrated that pure water permeability of a silica/γ-alumina membrane is far lower than a silica membrane or a γ-alumina membrane. It is evident that the intermediate layer contributes significant transport resistance which reduces the applicability of bi-layered membranes. Fuelled by these reasons, porous γ-alumina with bimodal pore size distribution is introduced in this work as an intermediate layer in silica/γ-alumina membranes for diminution of the transport resistance. Using porous ceramic with a bimodal pore size distribution, it has been shown that secondary macropores enhanced the intraparticle diffusion rate drastically in heterogeneous catalytic reactions [8,9]. However, not much work was reported on the application of porous materials with secondary pores in membrane separation. Alonso et al. [10] described the preparation of porous silicon–titanium oxycarbide membrane with bimodal pore size distribution. Meanwhile, Tsuru et al. [11] reported the preparation and

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Vanadium oxide supported γ-alumina with bimodal porous structure for intra-particle diffusion enhancement in styrene oxidation reaction

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Abstract Porous γ-alumina with well arranged secondary mesopores has been contrived using nanosized templating units. The pore size of templated mesopores is precisely controlled as the pore shrinkage is insignificant. The primary pore diameter is ca. 4 nm and the secondary pore diameter is ca. 50 nm. The porous material was characterized using N_2 adsorption/desorption, TEM, XRD and FT-IR. γ-alumina with bimodal pore size distribution shows improved intra-particle diffusion compared to γ-alumina with unimodal pore size distribution in a simple dye adsorption test. γ-alumina with different porous structures were then impregnated with vanadium oxide for catalytic effect comparison. It was perceived that secondary pores improve the styrene oxidation rate after the conversion of styrene reaches 30%.

Keywords γ-Alumina · Vanadium oxide · Template · Bimodal · Oxidation

Abbreviation

C_t	Dye concentration in solution at time t (mg l^{-1})
C_e	Equilibrium concentration (mg l^{-1})
q_e	Adsorption capacity in equilibrium (mg g^{-1})
C_0	Initial dye concentration in solution (mg l^{-1})
D_0	Diffusion coefficient (m s^{-1})
F	Fractional uptake of solute
k_i	Rate parameter of intraparticle diffusion model (mg dye g^{-1} particle $min^{-0.5}$)
m	Mass of unsupported γ-alumina (g)
q_t	Amount of adsorption at time t (mg g^{-1})
r	Particle radius (mm)
t	Time (min)
Q	Maximum adsorption capacity (mg g^{-1})
V	Volume of solution (l)
Δq	Standard deviation

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1 Introduction

Porous materials with highly defined pore distribution are imperative in chemical engineering, chiefly catalysis, adsorption and separation. Among the porous materials, nanoporous ceramics are crucial because of their large surface area and great resistance of severe operating conditions [1]. Consequently, nanoporous ceramics such as alumina and silica have found great utility as catalysts support [2, 3] and membrane reactor in chemical industry [4, 5]. Nanoporous ceramics can be prepared by sol–gel method using colloidal sols of nanometer-sized metal oxide particles, formed by hydrolysis and condensation of metal–organic precursors in aqueous media. After drying and calcinations, nanoporous ceramics with narrow pore distribution and high surface are formed [6].

Nanoporous ceramics with narrow pore size distribution is not always a definite option. In catalysis, the formation of bimodal porosity in nanoporous material is more practical as the presence of secondary pores greatly enhances the diffusion of molecules to active sites. Considerable numbers of researchers have reported that bimodal porous materials exhibit reduced diffusion resistance and enhanced catalytic function in heterogeneous reactions [7–10]. Until now, incorporating different types of templates in sol–gel method is prevalent in the

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ORIGINAL PAPER

Synthesis of vanadium oxide nanotubes via an ultrasonic method

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Abstract Vanadium oxide nanotubes were synthesized using V_2O_5 powder as the precursor and hexadecylamine as the structure-directing template using a sol-gel reaction method followed by a one-step hydrothermal treatment. The effect of ultrasonics on the formation of nanotubes is reported. The structure and morphology of the nanotubes were investigated by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The inner and outer diameters of the nanotubes varied from 20 to 40 nm and 80 to 100 nm, respectively. The nanotubes measured several micrometers in length.

Keywords Vanadium oxide · Nanotubes · Ultrasonic · Hydrothermal synthesis

1 Introduction

The discovery of carbon nanotubes (CNT) [1] led to determining a unique structure for novel products, in addition to their physical properties and interesting shapes. A comprehensive development in synthetic routes to nanostructured materials was reported in 1991 [2, 3]. The synthesis of different types of inorganic nanomaterials became the motivation for chemists, physicists, and material scientists to focus their attention on the design of a variety structures containing nanoparticles, such as nanocomposites [4–8], whether tubular or otherwise. Vanadium oxide nanotubes (VOx-NTs) are useful materials, due to their high potential applicability in electrochemical devices and catalytic processes, especially widely used for dehydrogenations or partial oxidations of alkanes to olefins [9–14]. Among several Magneli phases of vanadium oxide, VO_2 has received most attention because of its reversible magnetic, electric and optical properties at temperatures around 70 °C [15].

The first successful approach to producing tubular vanadium oxide used CNT as a template [16]. Different types of vanadium oxide precursor may consist of vanadium penta oxide (V_2O_5), vanadium dioxide (VO_2), vanadium oxytrichloride ($VOCl_3$), and vanadic acid (HVO_3) as vanadium source, in addition to alkyl amines ($C_nH_{2n+1}NH_2$) ($4 \leq n \leq 22$) with alkyl chain lengths of a large size range or other types of amines (H_2N [CH_2]n NH_2) ($12 \leq n \leq 20$). Aromatic amines, as direct structural agents, can be used for the successful synthesis of VOx-NTs [17]. Unfortunately, it remains unclear how organic molecules serve as structure-directing templates and cause the deep structural evolution of bulk crystalline V_2O_5 into nanoscrolls [18]. With the proper choice of structure-directing templates involved in the hydrothermal process, VOx-NTs can be prepared with high yields and the unique structures of multilayer scrolls, the interlayer distances of which can easily be controlled. In a hydrothermal synthesis, the reaction path is sensitive to experimental conditions such as temperature, pH, and hydrothermal treatment time [19]. Beginning with a vanadium penta oxide precursor and amine, the sol-gel reaction, combined with a subsequent hydrothermal treatment, could lead to the formation of VOx-NTs. This highly ordering procedure is repeatable and leads to excellent tube yields. The organic template molecules are fixed among vanadium oxide layers in the interior the tube walls. The synthesis of VOx-NTs can be approached via three methods: (1) Adding a

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Oxidation of styrene to benzaldehyde by anhydrous hydrogen peroxide on γ-alumina-supported V2O5 nanoparticle catalysts: Optimization studies using RSM

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FLOATING CATALYST CVD SYNTHESIS OF CARBON NANOTUBES USING IRON (III) CHLORIDE: INFLUENCES OF THE GROWTH PARAMETERS

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Carbon nanotubes (CNTs) were synthesized by a low-cost floating catalyst (FC) chemical vapor deposition (CVD) method in a horizontal reactor. It was found that iron (III) chloride ($FeCl_3$) is a high efficient FC precursor for methane CVD to grow CNTs. In this study, the effects of reaction temperature and flow ratio of methane to nitrogen (CH_4:N_2) on the morphology of the CNTs were investigated. The morphological analysis by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed that increasing the reaction temperature and flow ratio of CH_4:N_2 grew CNTs of larger diameters. Energy dispersive X-ray (EDX) and thermogravimetric analysis (TGA) were employed to study the purity of the produced CNTs. As shown by the TGA, the highest yield of 74.19% was recorded for the CNTs grown at 1000°C and flow ratio CH_4:N_2 of 300:200.

Keywords: Floating catalyst; chemical vapor deposition; carbon nanotubes; methane; nitrogen; iron (III) chloride.

1. Introduction

The synthesis of carbon nanotubes (CNTs) has attracted much attention due to their unique characteristics and potential applications in many fields. Numerous potential applications such as electronic devices, nanomechanical systems,[1] electrochemical energy storage,[2,3] scanning probes and sensors,[4] field emission sources[5] and composite materials[6,7] are proposed. Various methods of producing CNTs have been reported, including electric arc-discharge,[8,9] laser ablation[10] and chemical vapor deposition (CVD).[11–15] In order for CNTs to be commercially utilized, the production of CNTs has to be achieved at high yield, low cost, high purity and with much greater control over the key characteristics such as length and diameter. So far, the CVD process is the most promising method for industrial scale production due to the lower

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IRON (III) CHLORIDE AS FLOATING CATALYST PRECURSOR TO PRODUCE MULTI-WALLED CARBON NANOTUBES FROM METHANE

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Multi-walled carbon nanotubes (MWCNTs) were prepared by floating catalyst (FC) method, using methane as a carbon source and iron (III) chloride ($FeCl_3$) as a catalyst precursor, followed by purification with air oxidation and acid treatment. The as-grown and purified MWCNTs were characterized by transmission electron microscopy, scanning electron microscopy, energy dispersive spectroscopy, thermogravimetry analysis and Raman spectroscopy. The average inner and outer diameters of the MWCNTs were 25 and 39 nm, respectively. The purity and yield of the purified MWCNTs were more than 92% and 71% weight fraction, respectively.

Keywords: Methane; iron (III) chloride; floating catalyst; multi-walled carbon nanotube; purification.

1. Introduction

The most important techniques developed to produce carbon nanotubes (CNTs) include electric arc discharge,[1] laser ablation[2] and a variety of chemical vapor deposition (CVD) methods.[3] More research efforts have been put to reach the economical ways of synthesis with high yield, low cost, high purity and much greater control over the key characteristics such as length and diameter. Among these methods, CVD holds certain advantages over other methods in the ease of large-scale production, low reaction temperature and controllable fabrication. CVD coupled with FC method has been recognized as one of the most promising methods for producing CNTs for commercial quantities. However, continuous synthesizing CNTs over supported catalyst in a CVD process is hardly achieved and the synthesized CNTs typically contain impurities such as amorphous carbon, nanoparticles, C_{60} and other fullerenes.[4] Floating catalyst (FC) CVD method is introduced recently in view of its ability to produce continuously high purity CNTs involving

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Effects of Temperature on the Synthesis of Carbon Nanotubes by $FeCl_3$ as a Floating Catalyst Precursor

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The influence of temperature on the growth of carbon nanotubes (CNTs) by chemical vapor deposition (CVD) using $FeCl_3$ as a floating catalyst (FC) precursor and methane as a carbon source was studied. $FeCl_3$ was found to be an efficient FC precursor for methane CVD into CNTs without the need of introducing hydrogen in feed. The optimum temperature for growing CNTs was 1050°C, giving off 80% yield of CNTs. The electron microscopy analysis shows that the produced CNTs possessed the average diameter of 30 nm and Raman scattering reveals the low I_D/I_G ratio of 0.62, indicating the presence of high graphitized structure.

Keywords Floating catalyst, carbon nanotubes, $FeCl_3$, temperature, degree of graphitization

Introduction

Since the discovery by Ijima in 1991 (1), carbon nanotubes (CNTs) have been receiving much more attentions for their unique structural, mechanical and electronic properties. Extensive research work on the synthesis of CNTs, including laser-ablation (2), electric arc discharge (3) and chemical vapor deposition (CVD) (4,5), has been carried out. The scale-up synthesis of CNTs with high yield and quality is of great significance for both theoretical research and practical use. Among the distinguished variant techniques of CVD, floating catalyst (FC) CVD is considered to be one of the most promising methods for commercial production of high purity CNTs. This is attributed to its continuous process characteristics, and it involves only a simple equipment set-up (6–8). A systematic study of the process parameters for FC-CVD needs to be developed. The yield, length and purity of CNTs produced by this method have been found to depend on the catalyst precursors, carbon sources, reaction temperatures, gas flow rate and so on (9–11). Among these parameters, the catalyst precursors and the reaction temperatures have been identified as important factors in producing CNTs of high yield (9). Ferrocene (12,13) and $Fe(CO)_5$ (14,15) are the most commonly used FC precursors. On the other hand, $FeCl_3$ has also been explored to synthesize CNTs (16) and nanofibers (17), and the average diameters of the CNTs produced by

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Short communication

Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea

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ABSTRACT

In this work, the removal of a basic dye, methylene blue (MB) from aqueous solution using NaOH-modified rejected tea (N-RT) was investigated. Equilibrium adsorption and kinetics were studied. The results confirmed that the adsorption isotherm data fitted well to Langmuir isotherm with monolayer adsorption capacity of 242.11 mg/g. The kinetics of MB adsorption process was found to follow pseudo-second-order rate expression. The results suggested that the N-RT would be an excellent alternative for the removal of MB by adsorption process.

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1. Introduction

Many studies have been conducted to evaluate levels of aquatic toxicity, phototoxicity, and metal bioavailability for specific class of dyes from different water sources. Findings of these studies have led to the emergent of stringent environmental regulation laws [1]. This issue puts many in the textile dyeing industry and dyestuff manufacturing industry in somewhat awkward situation and now taking substantial measures to treat the dye containing wastewater. Besides, dyes are considered an objectionable type of pollutant because of they are toxic and cause allergy, dermatitis, skin irritation, cancer, and mutations in humans [2,3]. Not only this, they also interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic communities present in ecosystem [4].

Adsorption by activated carbon is the most common process for dye removal from wastewater. Although, the process is highly effective, the running costs are high with the need for regeneration after each sorption cycle [5]. This has led to the search for other potentially suitable alternative, that is more economical and equally an effective materials for dye removal by adsorption [6]. A number of investigations have shown that agricultural by-products such as clay [7], durian shell [8], *Hevea brasiliensis* [9], banana stalk waste [10] and mango seed kernel powder [11] have the potential of being used as low cost adsorbent for the removal of dyes in textile wastewater. Some of the advantages of using agricultural waste for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective of adsorption effluent, low cost, free availability and easy regeneration [12]. Beside, the exhausted adsorbents can be disposed off by burning and the heat used for steam generation [13].

However, the application of untreated agricultural or plant waste as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant wastes [14].

Therefore, the agricultural wastes need to be treated or modified before being used as adsorbent. In our previous work, we examined the use of rejected tea for methylene blue (MB) removal [15]. The objective of this work was to study the adsorption of MB onto sodium hydroxide modified rejected tea (N-RT).

2. Materials and methods

2.1. Adsorbate–methylene blue

Methylene blue (MB), $C_{16}H_{18}ClN_3S{\cdot}3H_2O$ supplied by Sigma Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate. Stock solution was prepared by dissolving 1.0 g of methylene blue (MB) in 1 L distilled water.

2.2. Adsorbent preparation and characterization

Raw rejected tea (R-RT) was prepared as described previously [15]. The dried rejected tea was treated in 0.05 M sodium hydroxide

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Rejected tea as a potential low-cost adsorbent for the removal of methylene blue

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ABSTRACT

The adsorption of methylene blue (MB) from aqueous solution using a low-cost adsorbent, rejected tea (RT), has been studied by batch adsorption technique. The adsorption experiments were carried out under different conditions of initial concentration (50–500 mg/L), solution pH 3–12, RT dose (0.05–1 g) and temperature (30–50 °C). The equilibrium data were fitted to Langmuir and Freundlich isotherms and the equilibrium adsorption was best described by the Langmuir isotherm model with maximum monolayer adsorption capacities found to be 147, 154 and 156 mg/g at 30, 40 and 50 °C, respectively. Three kinetic models, pseudo-first-order, pseudo-second-order and intraparticle diffusion were employed to describe the adsorption mechanism. The experimental results showed that the pseudo-second-order equation is the best model that describes the adsorption behavior with the coefficient of correlation $R^2 \geq 0.99$. The results suggested that RT has high potential to be used as effective adsorbent for MB removal.

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1. Introduction

Methylene blue (MB) or tetramethylthionine chloride is one of the basic dyes with the structure of heterocyclic aromatic chemical compound. The cationic dyes were commonly used initially for dyeing of silk, leather, plastics, paper, cotton mordanted with tannin, and also in manufacturing of paints and printing inks [1]. Though MB is not hazardous compared to other dyes, acute exposure to MB will cause increased heart rate, vomiting, and shock [2,3]. Hence, the necessity for the dye containing water to undergo treatment before disposal to the environment. Various conventional methods of color removal from wastewater have been used. These include biological and physical–chemical process. However, these processes are difficult to handle and are not always effective and economical. The adsorption technique appears to offer the best prospects over others and proved itself as one of an effective and attractive process for the treatment of dye containing wastewater [4]. Moreover, this method will become economically attractive, if the sorbent material used is cheap and at affordable production cost.

In fact, activated carbon (AC) is known to be a very effective adsorbent material due to its highly developed porosity, large surface area (that can reach 3000 m^2/g), variable characteristic surface chemistry, and high degree of surface reactivity [5,6]. These unique characteristics make activated carbon very versatile material, which can remove a wide range of pollutants from various matrices. In addition, it has high adsorption capacity and fast adsorption kinetics [7]. However, its uses is limited because it is expensive, the higher the quality of AC, the greater the cost [5].

In recent years, attention has been shifted towards the materials which are byproducts of wastes from large scale industrial operations and agricultural waste materials. The major advantages of these materials include: low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, and regeneration of adsorbent and possibility of effluent recovery [8]. Studies reveal that various agricultural waste materials such as grass waste [9], rice hull [10], garlic peel [11], cotton plant waste [12] and broad bean peels [13] have been investigated.

Rejected tea (RT) which is a waste material obtained from tea plantation is proposed as adsorbent for the removal of MB from the aqueous solution. Tea refers to the agricultural products of the leaves, leaf buds and internodes of Camelia Sinensis, which has been prepared and cured by various methods. In Malaysia, tea plants are commonly grown in the highland area located at Cameron Highland, Pahang. In the plantation, the harvested tea is only selected from the top leaves of the fresh grown shoots. The harvesting of the tea leaves are done every 15 days, to allow for growth of new leaves. The yield consists of mixed tea harvest and some overgrown woody shoots. This woody overgrown shoots were not treated by tea factory and thus constitute rejected tea. Moreover, during the tea planting procedure, tea producers usually trimmed the tea trees to a height of 1.5–2 m after every 3 years to allow for fresh growth of shoots. These also form part of undesired tea during production

Abbreviations: RT, rejected tea; AC, activated carbon; MB, methylene blue; FTIR, Fourier transform infrared; SEM, scanning electron microscope; BET, Brunauer, Emmett, and Teller.

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Ammonia-modified activated carbon for the adsorption of 2,4-dichlorophenol

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ABSTRACT

In this study, an oil palm empty fruit bunch-based activated carbon was modified using ammonia aqueous solution. The effect of the chemical modification on the adsorption capacity of modified activated carbon (MAC) for 2,4-dichlorophenol (2,4-DCP) adsorption was investigated. The monolayer adsorption capacity of MAC was 285.71 mg/g at 30 °C. Adsorption isotherm fitting revealed that Langmuir model was applicable for the MAC. The adsorption kinetics of 2,4-DCP onto MAC was described by the pseudo-second-order kinetic model. The surface modification of the activated carbon using ammonia was shown to be able to increase its adsorption capacity for 2,4-DCP.

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1. Introduction

In recent years, increasing concern over pollution of water courses arising from different anthropogenic activities has resulted in growing demand of activated carbons [1]. They have proved to be effective for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media, or from gaseous environments [2]. However, activated carbon is expensive which limits its large scale application [3]. A potential method to reduce its cost is to produce activated carbon from low-cost materials such as agricultural by-products, which has attracted an increasing research interest in recent years [4].

The excellent performances of activated carbons is well known to be closely related to the well developed porous structures, large surface area and a wide spectrum of surface functional groups. It is an established fact that the activated carbon surface can display acidic, basic and/or neutral characteristics depending on the presence of surface functional groups [5]. Thus, these days more studies have focused on how to modify as well as to characterize the surface functional groups of carbon materials in order to improve or enhance their affinities towards certain contaminants [3,6,7].

The heteroatoms on the surface of activated carbon took significant role on its application. The heteroatoms of porous carbon surface mainly contained oxygen, nitrogen, hydrogen, halogen, etc., which bonded to the edges of the carbon layers and governed the surface chemistry of activated carbon [8]. Among these heteroatoms, the oxygen-containing functional groups as well as nitrogen-containing functional groups were the widely recognized and the most common species formed on the surface of carbons.

The presence of nitrogen-containing functional groups was claimed to increase the basicity of activated carbon surface and thus increased the adsorption of acidic agents such as phenolic derivatives. Practically, nitrogen is introduced into structure of activated carbon according to several procedures including treatment with ammonia or urea [9,10].

Adsorption of phenolic derivatives on activated carbons has been intensively investigated [11], but relatively less work is reported related to modified carbons [12]. In this work, oil palm empty fruit bunch-based activated carbon was treated with ammonia solution to modify its surface functional groups. The adsorption performance of the modified activated carbon on 2,4-DCP was then evaluated.

2. Materials and methods

2.1. 2,4-Dichlorophenol

2,4-Dichlorophenol (2,4-DCP) of analytical reagent grade (Merck) was used as an adsorbate in this study. 2,4-DCP has a chemical formula of $C_6H_3Cl_2OH$, with a molecular weight of 163.0 g/mol.

2.2. Preparation of activated carbon

Oil palm empty fruit bunch (EFB) used for preparation of activated carbon was obtained from United Oil Palm Industries Sdn Bhd, Malaysia. The procedure used to prepare the activated car-

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Nitric acid-treated bamboo waste as low-cost adsorbent for removal of cationic dye from aqueous solution

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ABSTRACT

The feasibility of nitric acid-treated bamboo waste (NBW) for the removal of methylene blue (MB) from aqueous solutions was investigated. Batch adsorption studies were conducted to study the effects of contact time (0–180 min), initial concentration (45–375 mg/L) and solution pH (2–10) on the removal of dye at 30°C. The experimental data were analyzed by using four different types of linearized Langmuir and the Freundlich isotherms. Equilibrium data fitted well with the type 1 Langmuir model, yielding maximum monolayer MB adsorption capacity of 87.719 mg/g. The kinetic data were found to conform to pseudo-second-order kinetic model with good correlation. Intraparticle diffusion model was further tested to identify the diffusion mechanism. The scanning electron micrographs showed that MB was adsorbed on the rough surface of NBW. The NBW prepared in this study was shown to be a promising low-cost material for adsorption of MB from aqueous solutions.

Keywords: Adsorption; Bamboo waste; Isotherm; Kinetics; Methylene blue

1. Introduction

Textile industry is growing in Malaysia and consequently produces large amounts of color effluent that is unacceptable under Malaysian environmental regulation and should be treated before discharge. The treatment of textile effluents is of interest due to their toxic and esthetic impacts on receiving waters. There are many treatment processes applied for the removal of dyes from wastewater. A critical review on current treatment technologies with a proposed alternative was reported by Robinson et al. [1].

Adsorption process using commercial activated carbons is very effective for removal of dyes from wastewater, but its high cost has motivated the search for alternative materials. Most of the adsorption studies have been focused on untreated plant/agricultural wastes such as orange peel [2], rice husk [3], oil palm trunk fiber [4], Aspergillus fumigatus [5], wheat straw [6], durian (Durio zibethinus Murray) peel [7], Eucalyptus bark powder [8], almond shells [9], clay materials [10], pomelo (Citrus grandis) peel [11], Luffa cylindrica fibers [12], Parthenium biomass [13], castor seed shell [14] and granular kohlrabi peel [15]. Recently, an extensive list of adsorbent literature for dye removal has been compiled by Allen and Koumanova [16].

Although the application of untreated agricultural waste attracted much research recently, two problems are associated with it: low adsorption capacity and release of soluble organic compounds contained in the

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Analysis of SO_2 Sorption Capacity of Rice Husk Ash (RHA)/CaO/NaOH Sorbents Using Response Surface Methodology (RSM): Untreated and Pretreated RHA

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The SO_2 sorption capacity (SSC) of sorbents prepared from rice husk ash (RHA) with NaOH as additive was studied in a fixed-bed reactor. The sorbents were prepared using a water hydration method by slurrying RHA, CaO, and NaOH. Response surface methodology (RSM) based on four-variable central composite face centered design (CCFCD) was employed in the synthesis of the sorbents. The correlation between the sorbent SSC (as response) with four independent sorbent preparation variables, i.e. hydration period, RHA/CaO ratio, NaOH amount, and drying temperature, were presented as empirical mathematical models. Among all the variables studied, the amount of NaOH used was found to be the most significant variable affecting the SSC of the sorbents prepared. The SSC for sorbent prepared with the addition of NaOH was found to be significantly higher than sorbents prepared without NaOH. This is probably because NaOH is a deliquescent material, and its existence increases the amount of water collected on the surface of the sorbent, a condition required for sorbent–SO_2 reaction to occur at low temperature. The effect of further treatment of RHA at 600 °C was also investigated. Although pretreated RHA sorbents demonstrated higher SSC as compared to untreated RHA sorbents, nevertheless, at optimum conditions, sorbents prepared from untreated RHA was found to be more favorable due to practical and economic concerns.

Introduction

Sulfur dioxide (SO_2) and its derivative pollutants are ubiquitous threats and it has negative effect on aquatic ecosystems, crops, manmade materials, and poses risks to forests and even to human health (*1*). Most of SO_2 emissions are attributed to fossil fuel-burning (i.e., oil, gas, and coal) mainly in thermal power station. Currently, world primary energy consumption is still based on these fossil fuels (*2*). For example, Malaysia, as one of the fastest developing countries in the southeast Asian region, is still strongly dependent on fossil fuels, i.e., fossil fules account for about 94% of Malaysia's energy requirements in 2003 (*3*).

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As energy consumption increases, especially resulting from the burning of coal (which has the highest content of sulfur among fossil fuels), total SO_2 emission will also increase particularly in the Asian region whereby an increase from 56.4 million tons in 1995 to 61 million tons in 2000 was reported (*4*). Further increase in SO_2 emission is estimated to occur in this region with China being the highest SO_2 emitter (25.5 million tons) compared to any country in the world in 2005 (*5*). Therefore, there is an urgent need and importance to reduce SO_2 emission using efficient yet economical desulfurization technology, typically by means of wet or dry methods. Although wet methods are currently the most widely adopted in industry, dry technologies, however, have fewer problems of corrosion, scaling-up, easier byproduct handling, and they require no wastewater treatment (*6, 7*). Nevertheless, acid–gas sorption capacities of dry technologies are generally low. Consequently, enhancing the sorption capacities of dry sorbent toward SO_2 has been a challenging issue.

Previously, we have reported that sorbents prepared from coal fly ash, CaO, and $CaSO_4$ (*8, 9*) using hydration process have higher SO_2 sorption capacity (SSC) due to higher surface areas. Coal fly ash (mainly consist of SiO_2/Al_2O_3) which is a pozzolanic material, can react with Ca-based compounds to form calcium silicate hydrates in the presence of water. These pozzolanic products usually are poorly crystallized and have relatively high surface areas which can enhance SSC (*10, 11*). In our more recent study using other siliceous materials, i.e. oil palm ash (*12–14*) and rice husk ash (*15, 16*), we have shown that these ashes can also be utilized to prepare sorbents that are highly reactive toward SO_2 sorption.

The successful utilization of sorbents prepared from various waste-derived siliceous materials can not only further cut down the operating cost of the desulfurization process but also help to utilize these waste-derived siliceous materials, which otherwise have no commercial value, from industries. Therefore, more studies are required to further increase the SSC of these kind of sorbents. Ruiz-Alsop and Rochelle (*17*) studied the use of various salt additives during the preparation of sorbent using $Ca(OH)_2$. Most of the additives tested were found to increase the sorption capacity of the sorbent toward SO_2, especially sodium salts and chlorides. Kind et al. (*18*) synthesized fly ash and CaO sorbents with $CaCl_2$ as an additive, which exhibited higher reactivity than those sorbent without $CaCl_2$. The addition of $CaCl_2$ was also reported by Brodnax and Rochelle (*19*) with similar results. On the other hand, Peterson and Rochelle (*20*) examined the SSC of fly ash/$Ca(OH)_2$ sorbents with the addition of NaOH. The SSC of the sorbent was greatly enhanced, possibility due to the increasing dissolution of silica from fly ash. These results were also supported by other researchers (*21, 22*).

Much research has been carried out and reported the various effects of sorbent preparation variables on the sorbent SSC. However, the general practice in determining the optimal conditions of these variables is by varying one parameter at one time while keeping the others constant. Such work is extremely laboratorious and time-consuming. In this study, response surface methodology (RSM) coupled with central composite face centered design (CCFCD) was utilized with an attempt to further enhance the SSC of sorbents prepared from rice husk ash (RHA). RHA, which is produced from the burning of rice husk at about 300 °C, has been chosen as the source of siliceous material in this study and is available abundantly in Malaysia, i.e., ±81 thousand metric tons of RHA is generated annually (*23*). Apart from that, it was reported that the silica in RHA undergoes

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Development of kinetic model for the reaction between SO_2/NO and coal fly ash/CaO/$CaSO_4$ sorbent

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Abstract

Sorbents for semidry-type flue gas desulfurization (FGD) process can be synthesized by mixing coal fly ash, calcium oxide, and calcium sulfate in a hydration process. As sorbent reactivity is directly correlated with the specific surface area of the sorbent, reacting temperature, concentration of the reacting gas species and relative humidity, two major aim in the development of a kinetic model for the FGD process are to obtain an accurate model and at the same time, incorporating all the parameters above. Thus, the objective of this work is to achieve these two aims. The kinetic model proposed is based on the material balance for the gaseous and solid phase using partial differential equations incorporating a modified surface coverage model which assumes that the reaction is controlled by chemical reaction on sorbent grain surface. The kinetic parameters of the mathematical model were obtained from a series of experimental desulfurization reactions carried out under isothermal conditions at various operating parameters; inlet concentration of SO_2 (500 ppm $\leqslant C_{0,SO_2} \leqslant$ 2000 ppm), inlet concentration of NO (250 ppm $\leqslant C_{O,NO} \leqslant$ 750 ppm), reaction temperature (60 °C $\leqslant T \leqslant$ 80 °C) and relative humidity (50% $\leqslant$ RH $\leqslant$ 70%). For a variety of initial operating conditions, the mathematical model is shown to give comparable predictive capability when used for interpolation and extrapolation with error less than 7%. The model was found useful to predict the daily operation of flue gas desulfurization processes by using CaO/$CaSO_4$/coal fly ash sorbent to remove SO_2 from flue gas.
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Keywords: Coal fly ash; Flue gas desulfurization; Finite difference; Kinetic model; Sorbent

1. Introduction

The increasing world population has pushed the global demand of energy to a higher limit. Although there are many sources of energy, both renewable and non-renewable, however, coal still plays an important role as a source of energy in countries with large population like China, India and USA. Nevertheless, increasing environmental awareness has instigated the need to have an effective flue gas desulfurization technology to remove sulfur dioxide (SO_2) from coal-fired power plants. At the same time, the technology should be cheap so that it could be affordable by power plants in developing countries like China and India. Currently, the control of SO_2 emissions is focused on the post-combustion desulfurization process. Lately, the removal of SO_2 through sorption process using sorbents prepared from $Ca(OH)_2$/CaO/$CaSO_4$ and coal fly ash has received considerable attention [1–10]. It was reported that when $Ca(OH)_2$/CaO/$CaSO_4$ and coal fly ash were mixed at proper proportion in a hydration process, sorbents with high SO_2 sorption activity could be attained. These sorbents with high surface area are a product of the pozzolanic reaction between silica eluted from the coal fly ash and $Ca(OH)_2$/CaO/$CaSO_4$. Upon absorbing SO_2, the sorbents are converted to SO_3^{2-} (sulfite) and/or SO_4^{2-} (sulfate) salts. The use of coal fly ash as the base material in sorbent synthesis is attractive both economically and environmentally, as it is the most voluminous by-product of coal-fired power plants.

The reactivity of sorbent derived from coal fly ash/CaO/$Ca(OH)_2$/$CaSO_4$ varies significantly under different

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REMOVAL OF SO_2 AND NO OVER RICE HUSK ASH (RHA)/CaO-SUPPORTED METAL OXIDES

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Abstract

The activity of rice husk ash (RHA)/CaO-based sorbent supported with various metal oxides for the removal of SO_2 and NO from simulated flue gas of combustion process has been studied. In this study, RHA/CaO-based sorbents were impregnated with an appropriate metal nitrates solution followed by drying and calcinations, which resulted in the sorbent having the following active phases; MgO, MnO, CoO, ZnO, Al_2O_3, Fe_2O_3, and CeO_2. The sorbent-catalysts were tested in a fixed bed reactor by passing mixture gas consisting of SO_2 (2000 ppm), NO (500 ppm), O_2 (10 %), water vapor (50%) and N_2 as a balance at a total flow rate of 150 mL/min and reaction temperature of 87°C. The results showed that RHA/CaO sorbents impregnated with CeO_2 displayed the highest sorption capacity among other impregnated metal oxides for the simultaneous removal of SO_2 and NO. Infrared spectroscopic results indicate the formation of both sulfate (SO_4^{2-}) and nitrate (NO_3^-) species due to a catalytic role played by CeO_2.

Keywords: Rice husk ash (RHA), Metal oxides, Sorbent-catalysts, SO_2, NO.

1. Introduction

It is well known that acid rain is one of the most serious environmental issues related to large-scale fossil fuel combustion, especially in urban areas. Sulfur oxides (SO_x) and nitric oxides (NO_x) are the main anthropogenic acid gases that not only lead to formation of acid precipitation, but also impose adverse effects on human health, aquatic ecosystems, crops and manmade materials. Typically, SO_x and NO_x in flue gases consist of more than 98% of sulfur dioxide (SO_2) [1]

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Short communication

Evaluation of various additives on the preparation of rice husk ash (RHA)/CaO-based sorbent for flue gas desulfurization (FGD) at low temperature

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ABSTRACT

This paper examines the effectiveness of 10 additives toward improving SO_2 sorption capacities (SSC) of rice husk ash (RHA)/lime (CaO) sorbent. The additives examined are NaOH, $CaCl_2$, LiCl, $NaHCO_3$, NaBr, $BaCl_2$, KOH, K_2HPO_4, $FeCl_3$ and $MgCl_2$. Most of the additives tested increased the SSC of RHA/CaO sorbent, whereby NaOH gave highest SSC (30 mg SO_2/g sorbent) at optimum concentration (0.25 mol/l) compared to other additives examined. The SSC of RHA/CaO sorbent prepared with NaOH addition was also increases from 17.2 to 39.5 mg SO_2/g sorbent as the water vapor increases from 0% RH to 80% RH. This is probably due to the fact that most of additives tested act as deliquescent material, and its existence increases the amount of water collected on the surface of the sorbent, which played an important role in the reaction between the dry-type sorbent and SO_2. Although most of the additives were shown to have positive effect on the SSC of the RHA/CaO sorbent, some were found to have negative or insignificant effect. Thus, this study demonstrates that proper selection of additives can improve the SSC of RHA/CaO sorbent significantly.

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1. Introduction

Acid rain and the acidification of the environment has emerged as a serious global problem during recent decades. Sulfur dioxide (SO_2), represents 98% of the sulfur oxide pollutants generated mainly from large-scale fossil fuel combustion, is commonly accepted as the most important precursor to acid rain [1,2]. The removal of SO_2-containing gasses has received considerable attention in recent decades due to a variety of effects caused by this pollutant. Dry sorbent injection control technologies is among the general method which has been widely accepted by reason of being simple with less equipment, lower capital and operating costs, limited secondary waste generation, and fewer problems of corrosion and scaling-up [3–5]. Nevertheless, acid gas sorption capacities are generally lower than those achieved with wet control technologies. Therefore, enhancing the sorption capacities of dry sorbent toward SO_2 has been an important issue for dry-type methods application.

There are a number of dry-type sorbents that have been considered in the literature for usage in desulfurization process. Previously, we have reported the preparation of siliceous/calcium dry-type sorbents prepared from coal fly ash [6,7], oil palm ash [8,9] and rice husk ash [10]. It was found that, those prepared sorbent have higher SO_2 sorption capacity (SSC) relating to higher surface areas due to the fact that coal fly ash, oil palm ash and rice husk ash are a pozzolanic material (mainly consist of SiO_2/Al_2O_3). These pozzolanic materials can react with Ca-based in the presence of water to form calcium silicate hydrates (near-amorphous/poorly crystallized compounds) which have a very high surface area. Apart from that, the structural properties and sorption capacities of these types of sorbents are also affected by siliceous material/Ca-based ratio and the hydration conditions. Among those sorbents prepared, rice husk ash (RHA)/CaO sorbent shows highest SSC. However, our recent study on RHA/CaO sorbent [11] revealed that higher SSC did not show any correlation with specific surface area. On the other hand, many studies indicate that relative humidity has the greatest impact on the SSC of dry Ca-based sorbents at low temperature [12–17]. The relative humidity is consecutively connected to moisture content of the solids. In addition, some additives have been employed to alter the moisture content on the prepared sorbent surface in equilibrium with a gas phase of a given relative humidity [18–23]. Thus, the use of additive would then be expected to improve the sorbent SSC in desulfurization processes in the way of altering the sorbent particle's physical/chemical properties. Therefore, the scope of this work is to evaluate the effectiveness of various additives in the preparation of RHA-based sorbent for desulfurization process at low temperature.

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Optimization of microporous palm shell activated carbon production for flue gas desulphurization: Experimental and statistical studies

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ABSTRACT

Optimizing the production of microporous activated carbon from waste palm shell was done by applying experimental design methodology. The product, palm shell activated carbon was tested for removal of SO_2 gas from flue gas. The activated carbon production was mathematically described as a function of parameters such as flow rate, activation time and activation temperature of carbonization. These parameters were modeled using response surface methodology. The experiments were carried out as a central composite design consisting of 32 experiments. Quadratic models were developed for surface area, total pore volume, and microporosity in term of micropore fraction. The models were used to obtain the optimum process condition for the production of microporous palm shell activated carbon useful for SO_2 removal. The optimized palm shell activated carbon with surface area of 973 m^2/g, total pore volume of 0.78 cc/g and micropore fraction of 70.5% showed an excellent agreement with the amount predicted by the statistical analysis. Palm shell activated carbon with higher surface area and microporosity fraction showed good adsorption affinity for SO_2 removal.

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1. Introduction

Activated carbon is one of the most effective adsorbents, because of its well-developed porous structures, large active surface area and good mechanical properties. Activated carbons have been used in many adsorption processes ranging from liquid to gas (Burchell, 1999). Commercial activated carbons can be manufactured from a variety of carbonaceous precursors such as lignite, coal, wood, and various agricultural and forest by-products, by either a physical or steam-pyrolysis or chemical method. In physical processes gases such N_2 and CO_2 will be used whereas for chemical processes the starting materials are impregnated with a dehydrating agent (example $ZnCl_2$, H_3PO_4 and KOH). Steam-pyrolysis is done using high-temperature steam (Zhang et al., 2004; Ioannidou and Zabaniotou, 2007).

Currently interests are growing in the use of low-cost and abundantly available lignocellulosic material as the precursor for the preparation of activated carbon. One of these is oil palm fruit waste that is palm shell which is abundantly available from the palm oil processing mills in Malaysia. Despite its wide use already for bioproducts production, there is still much to be done to optimize the utilization of biomass for cogeneration in Malaysia (Sumathi et al., 2008).

Palm shell (also known as endocarp) has been used as starting material for preparing activated carbon for various applications (Sumathi et al., 2008; Lua and Guo, 1998; Lua et al., 2006). Guo and Lua (2002, 2003) have studied the adsorption of SO_2 with and without impregnation. However, there is no report in the literature referring to an optimum production of microporous palm shell activated carbon (PSAC) to remove SO_2, particularly from flue gas by using response surface methodology (RSM) approach.

Removal of SO_2 from flue gas has gained the interest of many researchers. This is because SO_2 is one of the main precursors of acid rain and human fatalities (De Nevers, 2000). Most of the global productions of SO_2 come from combustion of fossil fuels such as coal and oil. To minimize the adverse impacts, many efforts have been taken to eliminate the SO_2 emission. One of the most promising existing flue gas desulphurization technologies is dry removal of SO_2 using activated carbon. This method has been reported by many researchers as a capable approach to remove SO_2 from flue gas (Qiang et al., 2005; Tseng et al., 2003).

Hence, in this study, RSM optimization has been applied to prepare PSAC. RSM is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. RSM was originally developed by Box and Wilson (1951). Researches related to RSM applications performed for optimization of activated carbon production are very rare. In the present work, the preparation of microporous activated carbon from palm shell and its potential for flue gas desulphurization were focused. This preparation procedure involves many factors. Thus, in assessing

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Modified shrinking unreacted-core model for the reaction between sulfur dioxide and coal fly ash/CaO/$CaSO_4$ sorbent

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ABSTRACT

The kinetics for non-catalytic solid gas reaction between SO_2 and sorbent prepared from coal fly ash, CaO and $CaSO_4$ in a fixed-bed reactor at low temperature were modeled and simulated. A modified shrinking unreacted-core model (SCM) with chemical reaction coupled with diffusion as the rate limiting step were developed to predict the breakthrough curves of the desulfurization reaction. The kinetic parameters of the mathematical model were obtained from a series of experimental desulfurization reactions conducted under isothermal conditions at various operating parameters; SO_2 initial concentration (500 ppm $\leq C_{SO} \leq$ 2000 ppm), NO initial concentration (250 ppm $\leq C_{NO} \leq$ 750 ppm), reaction temperature (60 °C $\leq T \leq$ 90 °C) and relative humidity (50% $\leq$ RH $\leq$ 80%). MATLAB software was used to solve the partial differential equations using finite difference method. The SCM model was found to give a good description of the experimental data with error less than 5%. The validated model was then used to simulate the desulfurization reaction under a wide range of operating conditions. It was found that higher initial concentration of SO_2 reduces the desulfurization activity. In contrast, the presence of higher concentration of NO, reaction temperature and relative humidity in the system enhanced the desulfurization activity of the sorbent.

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1. Introduction

Lately, the negative impact of sulfur dioxide (SO_2) released from power plants to the environment has led to national and international legislation to limit the emissions of SO_2. Since the requirement to limit sulfur emissions are being implemented in more and more countries throughout the world, many coal-fired plants are currently under pressure to install flue gas desulfurization (FGD) unit. The commercial technology currently available for FGD is using the wet-process method with lime stone derivatives as the absorbent. However, this technology requires high investment cost that might not be economically viable for small scale power plants. Recently, it was reported that sorbent prepared from various siliceous material such as coal fly ash, rice husk ash and oil palm ash can be used to remove SO_2 from flue gases using the dry-process. This dry-process is significantly cheaper and simpler than the current wet-process, making it a viable option for small scale power plants. The preparation, characterization and activity study of sorbent made from various siliceous material had been thoroughly reported in the literature [1–4], however, reports on kinetic modeling of the sulfation reaction between the sorbent and SO_2 has not been conclusive.

In a study by Liu and Shih [5], modified surface coverage model was proposed for the desulfurization reaction between $Ca(OH)_2$/fly ash sorbent and SO_2. The reaction between the dry sorbents with SO_2 was studied under the conditions similar to those in the bag filters in the spray-drying flue gas desulfurization system. The hypothesis of this model was that the sorbent was made up of plate grains and that the reaction rate was controlled by chemical reaction on the surface of the grain. The reacting surface area of the grain decreases as the reaction progresses further. Based on the proposed model, the reaction reached an ultimate conversion when the entire reacting surface was covered by the product. Besides that, it was assumed that the change of sorbent surface coverage with reaction time depends on the reaction rate, the dispersion of Ca and the way by which the product deposits on the surface. In another study, Bausach et al. [6] investigated the kinetics of the non-catalytic solid gas desulfurization reaction between $Ca(OH)_2$ and SO_2 at low temperature. In their study, they reported a modified deactivation model (DM) to improve the fitting of the desulfurization experimental data. The deactivation model assumed that the reaction between the gas molecules and the solid sorbent depends mainly on the concentration of the gas on the solid surface, which was referred to as active surface and the ratio of active surface of

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Performance of an activated carbon made from waste palm shell in simultaneous adsorption of SOx and NOx of flue gas at low temperature

S. Sumathi, S. Bhatia, K. T. Lee and A. R. Mohamed

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Short communication

Selection of metal oxides in the preparation of rice husk ash (RHA)/CaO sorbent for simultaneous SO_2 and NO removal

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ABSTRACT

In this work, the removal of SO_2 and NO from simulated flue gas from combustion process was investigated in a fixed-bed reactor using rice husk ash (RHA)/CaO-based sorbent. Various metal precursors were used in order to select the best metal impregnated over RHA/CaO sorbents. The results showed that RHA/CaO sorbents impregnated with CeO_2 had the highest sorption capacity among other impregnated metal oxides for the simultaneous removal of SO_2 and NO. Infrared spectroscopic results indicated the formation of both sulfate (SO_4^{2-}) and nitrate (NO_3^-) species due to the catalytic role played by CeO_2. Apart from that, the catalytic activity of the RHA/CaO/CeO_2 sorbent was found to be closely related to its physical properties (specific surface area, total pore volume and average pore diameter).

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1. Introduction

Acid rain has been identified as one of the most serious threats to the global environment ever faced in human history. Undoubtedly, the most dominant air pollutants contributing to acid rain are sulfur oxides (SO_x) and nitric oxides (NO_x). The major sources of SO_x and NO_x emission by human activities are from the combustion of fossil fuels, mainly in electric power plant. The SO_x and NO_x formed are then released into the environmental together with the boiler flue gas. Typically, SO_x and NO_x in flue gases consists of more than 98% of sulfur dioxide (SO_2) [1] and over 90–95% of nitric oxide (NO) [2]. Consequently, considerable attention has been given to removal of SO_2 and NO from flue gas combustion system. Nevertheless, the most common technology used to date still uses two separate systems to remove these pollutants. For example, the SNOX process of Haldor Topsoe which combine the wet-gas sulfuric acid process for SO_2 removal and the selective catalytic reduction (SCR) process for the removal of NO [3].

Attempts have been made to find a suitable method for the removal of SO_2 and NO simultaneously. Dry sorption method is now considered to be the most attractive way to treat waste gases containing SO_2 and NO. These methods have the advantages of being simple with less equipment, lower capital and operating costs, and limited secondary waste generation [4,5]. At the moment, there are only a few reports on removal SO_2 and NO simultaneously by the dry method. Some of these reports include: Ca-based sorbent [6,7], Ca-based with fly ash [8], natural manganese ore [9], activated carbon [10–12], activated carbon-impregnated catalyst [13–15] and metal catalyst [16–19]. Apart from these, the simultaneous removal of SO_2 and NO at low temperature using sorbent prepared from siliceous materials are also very limited, especially using rice husk ash (RHA). RHA is an agricultural waste material that available abundantly in rice-producing countries such as Malaysia. It was estimated that more than 22.8 million metric tons of RHA is produced annually worldwide, of which Malaysia alone produces more than 77,000 metric tons of RHA annually [20].

Previously, we had reported the sorption characteristics of SO_2 by RHA/CaO sorbent [21–25]. However, this sorbent was unable to remove NO gases. Currently, a wide range of metals/metal oxides have been reported to have good activities for NO removal from waste gases. In this work, RHA/CaO sorbent has been prepared by employing impregnation method with various metal oxides. This was done with a view to improve its ability to capture SO_2 and NO from simulated flue gas. The experiments were performed in a fixed-bed reactor at low temperature.

2. Experimental

2.1. Preparation of sorbent

The raw rice hush ash (RHA) used in this work was collected directly without any pretreatment from Kilang Beras & Minyak Sin Guan Hup Sdn. Bhd., Nibong Tebal, Malaysia and the CaO was obtained from BDH Laboratories, England. Prior to use, the RHA

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Rice Husk Ash/Calcium Oxide/Ceria Sorbent for Simultaneous Removal of Sulfur Dioxide and Nitric Oxide from Flue Gas at Low Temperature

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Abstract

The reduction of sulfur dioxide (SO_2) and nitric oxide (NO) emissions has become an isssue of great importance to government regulatory agencies and general public due to their negative effect towards the environment and human health. In this work, the simultaneous removal of sulfur dioxide (SO_2) and nitric oxide (NO) from simulated flue gas was investigated in a fixed-bed reactor using rice husk ash (RHA)/CaO/CeO_2 sorbent. Attention was focused on the major reactor operation parameters affecting sorption capacity of RHA/CaO/CeO_2 sorbent, which include feed concentration of SO_2 and NO, relative humidity (RH), operating temperature and space velocity (GHSV). This is because such information is unavailable for RHA-based sorbent and the effects of these parameters reported in the literature are also not reliable. Enhancement effect of NO on removal of SO_2 was observed and the presence of SO_2 was essential to the removal of NO. However, at a high level of SO_2/NO concentration, competition in the sorption of NO and SO_2 on the sorbent active sites might have occurred. RH was found to significantly enhance the SO_2 sorption of the RHA/CaO/CeO_2 sorbent. By contrast, NO sorption capacity decreases when RH was further introduced, as it was not easy to sorb NO in the presence of water. Apart from that, the results also shows that there was a threshold value for the RH to ensure higher SO_2 and NO removal and this value was observed at 50% RH. Higher operating temperatures were favored for SO_2 and NO removal. Nevertheless, beyond 150°C the SO_2 removal was found to decrease. On the other hand, a lower space velocity resulted in a higher SO_2 and NO removal.

Key words: rice husk ash; sorbent; SO_2/NO sorption; breakthrough curves; flue gas

Introduction

RECENTLY, THE COMBUSTION OF SOLID FUEL to generate electricity has caused the emission of sulfur oxides (SO_x) and nitric oxides (NO_x) to the environment. Normally SO_x and NO_x consists of more than 98% sulfur dioxide (SO_2) (Probstein and Hicks, 2006) and more than 90% of nitric oxide (NO) (Zhu *et al.*, 2005). Thus, the control of SO_2 and NO emissions has become an issue of great importance to governmental regulatory agencies and the general public due to their negative effect toward the environment and human health. This has led, and in a way, forced countries around the world (including Malaysia) to impose a more stringent regulation on the release of these air pollutants into the atmosphere. The need to lower the emissions of these pollutants creates a high demand for a technical solution that can meet the environmental regulations but yet are economically attractive. Presently, SO_2 and NO are being removed using various types of control technology. Nevertheless, the most common technology used today is still by a two-separated system to remove these acidic gas pollutants, although both gases are from the same source. Some examples included the SNOX process of Haldor Topsoe (Kohl and Nielsen, 1997), the DESONOX/REDOX process (Blumrich and Engler, 1993), and activated coke process (Tsuji and Shiraishi, 1997; Olson *et al.*, 2000).

Due to the drawbacks of wet-type methods (Ishizuka *et al.*, 2000; Lin *et al.*, 2003), researchers have shifted their attention to dry methods for the simultaneous removal of SO_2 and NO. Unfortunately, there have been only a limited number of studies on the simultaneous removal of SO_2 and NO at low temperatures using dry agricultural waste sorbents, particularly using waste materials resulted from rice mill activities. Rice husk ash (RHA) is a major waste product in the modern rice milling industry resulting from rice husk burning. RHA is available abundantly in rice-producing countries like Malaysia. It was estimated that more than 22.8 million metric tons of RHA is produced annually worldwide, of which Malaysia alone produces more than 77 thousand metric

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SO_2 and NO Simultaneous Removal from Simulated Flue Gas over Cerium-Supported Palm Shell Activated at Lower Temperatures—Role of Cerium on NO Removal

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Cerium (Ce) supported on palm-shell-activated carbon (PSAC) has been found to significantly increase its activity in simultaneous removal SO_2 and NO from simulated flue gas. In the present study, the role of Ce on SO_2 and NO removal was studied through reaction adsorption. The catalyst was characterized using BET, EDAX, and SEM. It was found that PSAC could remove SO_2 only without the addition of Ce, and NO could be removed in the presence of Ce loaded over PSAC. The experimental results showed Ce10/PSAC catalyst at 100 °C yield the best breakthrough time for simultaneous removal of NO and SO_2. NO removal lasted for 115 min, whereas SO_2 for 165 min. As the Ce content was increased from 5 to 12%, NO conversion increased significantly, but dropped with further increase in Ce content. Higher temperatures do not encourage the simultaneous adsorption of SO_2 and NO. It was found that SO_2 and NO create competitive phenomenon toward the active sites of PSAC and Ce/PSAC. SO_2 removal was not affected by the addition of Ce because PSAC played an important role of SO_2 adsorption and Ce presences promoted the adsorption rate.

Introduction

Currently in Malaysia, it is estimated that the power stations flue gas emission load is about 16% from the total air pollutant.[1] SO_2 and NO are the 2 major contributors of power stations flue gas. Hence serious efforts have to be taken in order to curb this problem before it diversifies. Among various emission control technologies available today, calcium based flue gas desulphurization and selective catalytic reduction (SCR) by NH_3 are the most effective technologies for SO_2 and NO removal, respectively.[2−5] However, in order to lower the capital cost of equipment and operating cost, it is desirable to remove SO_2 and NO simultaneously in a single unit.

Currently, catalysts supported over activated carbon (AC) based sorbents are well-known for their potential of removing SO_2 and NO simultaneously. There are mainly two types of catalyst-sorbents, activated carbon/coke (all termed AC) at temperatures of 140−150 °C[6,7] and CuO/Al_2O_3 to be used at temperatures of 350−400 °C[8,9] are reported. The AC-based technology is profitable because of its readiness of being retrofitted into current boiler systems, which reduces the equipment costs and warrants higher boiler efficiencies. Normally in this technology, SO_2 is removed first at the lower part of the reactor then NO is removed by SCR. Recently metal oxides supported over AC have drawn interest because it could do the job simultaneously in a single-step process. Many types of metal oxides have been studied, including Fe, Mn, Ca, V, Cu, and Cr oxides in comparison to AC alone[10−13] but so far none have reported the usage of Cerium (Ce). In Malaysia, palm shell biomass generated during the palm oil refining process can be utilized in the production of activated carbon. Hence in this research, palm-shell-activated carbon (PSAC) has been successfully supported with Ce metal oxide to remove SO_2 and NO gases. The reaction mechanism presented the role of Ce supported over PSAC in simultaneous removal of SO_2 and NO.

2. Experimental Section

2.1. Catalyst Preparation. The AC used is a palm-shell-derived product made from physical activation with N_2 and CO_2 gas. The details and quality of the PSAC has been reported elsewhere.[14] The Ce/PSAC catalyst was prepared through a conventional pore volume impregnation procedure using an appropriate aqueous solution of cerium nitrate ($Ce(NO_3)3 \cdot 6H_2O$). After the impregnation, the sample was dried in air at 110 °C for 12 h and calcined in Argon gas at 500 °C for 4 h. The Ce/PSAC samples prepared are termed

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Short communication

Selection of best impregnated palm shell activated carbon (PSAC) for simultaneous removal of SO_2 and NOx

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ABSTRACT

This work examines the impregnated carbon-based sorbents for simultaneous removal of SO_2 and NOx from simulated flue gas. The carbon-based sorbents were prepared using palm shell activated carbon (PSAC) impregnated with several metal oxides (Ni, V, Fe and Ce). The removal of SO_2 and NOx from the simulated flue gas was investigated in a fixed-bed reactor. The results showed that PSAC impregnated with CeO_2 (PSAC-Ce) reported the highest sorption capacity among other impregnated metal oxides for the simultaneous removal of SO_2 and NOx. PSAC-Ce showed the longest breakthrough time of 165 and 115 min for SO_2 and NOx, respectively. The properties of the pure and impregnated PSAC were analyzed by BET, FTIR and XRF. The physical–chemical features of the PSAC-Ce sorbent indicated a catalytic activity in both the sorption of SO_2 and NOx. The formation of both sulfate (SO_4^{2-}) and nitrate (NO^{3-}) species on spent PSAC-Ce further prove the catalytic role played by CeO_2.

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1. Introduction

Worldwide, air pollution is a growing threat to human health and the natural environment. One of the major effects of air pollution is acid rain and it is caused by sulfur dioxides (SOx) and nitrogen oxides (NOx) gases. Fuel combustion processes and power plants are the largest contributor of these gases in the form of flue gas. A typical composition of coal-fired power plant flue gas contains about 500–2000 ppm of SO_2 and over 125 ppm of NOx [1]. Due to its high toxicity and negative impact on the global environment, major effect has been taken to reduce both these emissions simultaneously.

Among the widely used reducing methods are flue gas desulfurization (FGD) and selective catalytic reduction (SCR). The literatures show that CuO/Al_2O_3-based catalysts and activated carbon-based catalyst are active for simultaneous removal of both the toxic gases [2–5]. Apart from these, the simultaneous removal of SO_2 and NOx at lower temperatures are preferred comparatively because flue gas temperatures at stack burners range at lower temperature, i.e. from 120 to 250 °C. Earlier studies revealed that activated carbon (AC) showed a promising future to remove SO_x and NOx gas simultaneously [6,7] however these studies are done at elevated temperatures (300 °C and above).

One of the latest types of AC in the current market is biomass based AC [8]. Currently in Malaysia palm shell based AC is gradually finding its way out for a useful utilization [9]. Hence it can be very handful as well as economical to use palm shell activated carbon (PSAC) as an alternative to the existing commercially available AC for this study.

Previous studies discovered that the locally made PSAC can be used to remove SO_2 and H_2S gas [10–12] but none have been reported to remove NOx or the simultaneous removal of both NOx and SO_2. Presently there are a number of studies that report the usage of metal oxides for simultaneous removal of SO_2 and NOx [13–15]. Prior to this study we had also reported the sorption characteristics of PSAC to remove SO_2 and NOx [16]. However PSAC was unable to remove NOx gas. Thus in this work the usage of PSAC as a modified (impregnated with various metal oxides) sorbent were tested for its possibility in capturing both SO_2 and NOx simultaneously from a simulated coal-fired power plant flue gas at low temperature.

2. Experimental

2.1. Preparation of sorbent

The PSAC used in this work was prepared by physical activation using CO_2 gas. The details of the preparation method can be seen elsewhere [16]. Prior to the impregnation process the PSAC was sieved to a size of 1 mm. The PSAC was subjected to pore volume impregnation by metal oxides. First the PSAC was impregnated with metal nitrate of an appropriate con-

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Parameters optimization of rice husk ash (RHA)/CaO/CeO_2 sorbent for predicting SO_2/NO sorption capacity using response surface and neural network models

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ABSTRACT

In this work, the application of response surface and neural network models in predicting and optimizing the preparation variables of RHA/CaO/CeO_2 sorbent towards SO_2/NO sorption capacity was investigated. The sorbents were prepared according to central composite design (CCD) with four independent variables (*i.e.* hydration period, RHA/CaO ratio, CeO_2 loading and the use of RHA_{raw} or pretreated $RHA_{600^\circ C}$ as the starting material). Among all the variables studied, the amount of CeO_2 loading had the largest effect. The response surface models developed from CCD was effective in providing a highly accurate prediction for SO_2 and NO sorption capacities within the range of the sorbent preparation variables studied. The prediction of CCD experiment was verified by neural network models which gave almost similar results to those determined by response surface models. The response surface models together with neural network models were then successfully used to locate and validate the optimum hydration process variables for maximizing the SO_2/NO sorption capacities. Through this optimization process, it was found that maximum SO_2 and NO sorption capacities of 44.34 and 3.51 mg/g, respectively could be obtained by using RHA/CaO/CeO_2 sorbents prepared from RHA_{raw} with hydration period of 12 h, RHA/CaO ratio of 2.33 and CeO_2 loading of 8.95%.

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1. Introduction

Among the several air pollutants that contaminate our planet, SO_x and NO_x have received special attention due to the fact that these two pollutants have toxic and acidic characteristics. SO_x and NO_x, which are mainly resulted from the combustion of fossil/solid fuels, have been linked to the formation of acid rain and many other undesirable environmental hazards [1]. In general, SO_x and NO_x in flue gases consists of more than 98% of sulfur dioxide (SO_2) [2] and more than 90% of nitric oxide (NO) [3]. Most of the researchers are still focused on the removal of SO_2 and NO separately. Only in the last two decades, many processes have been developed for combined removal SO_2/NO technology in a complete single process which has the potential to reduce the cost of environmental pollution control technology.

Unfortunately, only limited study on the simultaneous removal of SO_2 and NO using dry method were reported at low temperature. In particular, the use of sorbent prepared from agricultural waste-derived siliceous materials, such as rice husk ash (RHA) is also scarcely reported. RHA is produced from the burning of rice husk, which is abundantly available through the rice milling process in rice-producing countries like China, India and Malaysia. In Malaysia alone, it is estimated that more than 80 thousand tones of RHA is produced annually [4,5]. Previously, we have reported the sorption characteristics of SO_2 over RHA/CaO sorbents [6–9]. It was found that the RHA/CaO ratio, type of RHA, amount of additive and hydration period used in the preparation step significantly influenced the SO_2 sorption capacity of the RHA/CaO sorbent. It was also found that this RHA/CaO sorbent was unable to remove NO gases. The simultaneous removal of SO_2 and NO can only be obtained by impregnating RHA/CaO sorbent with various metal oxides and the RHA/CaO sorbent incorporated with cerium dioxide (CeO_2) displayed the highest SO_2/NO sorption capacities [10].

Despite several reports on the simultaneous SO_2 and NO removal using dry method and the effect of sorbent preparation variables on the sorbent sorption capacity, there are no studies reported in the literature on the parameters optimization of this kind of processes. Higher sorption capacity of the sorbent can only be obtained, if all parameters are optimized. Recently, a number of statistical experimental designs with response surface methodol-

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Cerium impregnated palm shell activated carbon (Ce/PSAC) sorbent for simultaneous removal of SO_2 and NO—Process study

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ABSTRACT

The simultaneous removal of SO_2 and NO from simulated flue gas by cerium oxide supported over palm shell activated carbon (Ce/PSAC) was studied in a fixed bed adsorber. The effects of adsorber temperature, presence of humidity, feed gas concentration and space velocity were studied as the process parameter. The results were illustrated as sorption breakthrough curves. From the experimental results, it was found that at higher space velocity, the SO_2 and NO sorption capacity was reduced. Humidity enhanced the SO_2 sorption capacity but deterred the NO sorption at percentage more than 15%. Temperature played an important role in the simultaneous removal of SO_2 and NO by cerium supported over PSAC. The maximum simultaneous sorption capacity of SO_2 and NO was achieved at temperature 150 °C with 121.7 and 3.5 mg/g, respectively. This study shows that cheap biomass based activated carbon can be a potential sorbent for simultaneous removal of SO_2 and NO from flue gas.

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1. Introduction

The acidification of land and water through air pollution has received extra attention in recent years due to its growing threat to human health and nature. One of the prominent contributors of air pollution is fuel combustion process with stationary and mobile sources. The most widespread and dangerous outputs of this process are oxides of nitrogen (NOx) and oxides of sulfur (SOx) [1]. There are a number of technologies available to remove these gaseous pollutants. The literatures show that calcium based flue gas desulfurization, selective catalytic reduction (SCR) by NH_3 and CuO/Al_2O_3-based catalysts are the most effective technologies for SO_2 or NO removal [2–5]. However in order to lower the capital cost of equipment and operating cost, it is desirable to remove SO_2 and NO simultaneously in a single unit with a cheap sorbent. One of the good choices is via activated carbon (AC).

There are many types of AC prepared from various carbonaceous materials and impregnated with a variety of additives. Some of these AC have been used to remove NOx and SOx simultaneously. Researchers reported that metal oxides supported over AC have drawn interest because it could do the job simultaneously in a single step process. Many types of metal oxides have been studied, including Fe, Mn, Ca, V, Cu and Cr oxides in comparison to AC alone but so far none have reported on cerium (Ce) [6–13].

Currently interests are growing in the use of low-cost and abundantly available lignocellulosic material as the precursor for the preparation of AC. One alike is palm shell activated carbon (PSAC) made from oil palm fruit waste, *i.e.* palm shell which is abundantly available from the palm oil processing mills in Malaysia [14]. Palm shell based AC with and without impregnation have been used to remove SO_2 [15–18], however none have reported on NO removal or simultaneous removal of NO and SO_2.

In the present work, the potential of PSAC as a modified (impregnated with cerium oxide) sorbent was tested for its possibility in sorbing both SO_2 and NO gas simultaneously from a simulated flue gas at different process operating conditions.

2. Experimental

2.1. Preparation of sorbent

The PSAC was first prepared by thermal charring of the palm shell. Then it is followed by a physical activation using CO_2 gas at temperature 1100 °C. Details of the preparation method are reported elsewhere [17]. Prior to the impregnation process, PSAC was sieved to a size of 1 mm. The PSAC was subjected to pore volume impregnation by cerium nitrate. First, the PSAC was impregnated with cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) of an appropriate concentration to obtain around 10 wt% of metal content per gram of PSAC (10 ml of 10 wt% metal solution/gram of PSAC). In this study cerium nitrate from Fluka was used as the metal precursor. During the impregnation, the solution of metal nitrate was continuously mixed with PSAC for 5 h. Then the samples were heated

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Adsorption isotherm models and properties of SO_2 and NO removal by palm shell activated carbon supported with cerium (Ce/PSAC)

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ABSTRACT

The adsorption of SO_2 and NO onto palm shell activated carbon supported with cerium oxide (Ce/PSAC) was studied in a fixed bed adsorber. This paper reports the adsorption equilibrium of SO_2 and NO in a simulated flue gas on Ce/PSAC. The experimental results show that within the experimental conditions at different inlet concentration of SO_2/NO, the adsorption capacities of Ce/PSAC can be well fitted by Langmuir compared to Freundlich adsorption isotherms. The binary mixtures of SO_2 and NO at different initial concentration can be well-correlated by the extended Jain and Snoeyink (JS) Langmuir model compared to extended Langmuir model. The physical properties of Ce/PSAC were calculated and it was consistent with the isotherm parameters obtained from the adsorption results. The adsorption was controlled by physisorption.

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1. Introduction

Combustion processes and its emission *i.e.* flue gas has been a long time setback to nature as well as human kind. It has been reported that SO_2 and NO contained in flue gas are the primary agents responsible for the acid rain and ground-layer ozone formation. Due to these factors, interest in reducing these emissions simultaneously has been increasing lately to save the global health. Among the famous reducing methods are dry-type methods such as selective catalytic reduction, adsorption and flue gas desulphurization [1–5].

Activated carbon as an agent for adsorption has been used for many years in many field. Gas-phase adsorption by activated carbon is a separation process in which adsorbate molecules are transferred to the pore surface of solid activated carbon [6]. Activated carbon is predominantly amorphous material that has large surface area and pore volume. Activated carbons are made from variety of starting material [7]. For gaseous removal, activated carbon made from bituminous coal and coconut are the prominent ones [8]. Currently palm shell-based activated carbon is introduced for gas phase applications because it has similar property as coconut shell [9].

Few discussions were made in the literature about adsorption behavior of SO_2, O_2, CO_2, N_2, CH_4 and H_2S on palm shell activated carbon (PSAC) [10–14]. However none have been reported on NO removal or simultaneous removal of SO_2 and NO. Moreover these researchers did not study the adsorption kinetics using model isotherms. Bae and Lee [15], examined the adsorption kinetics of 8 different gases (O_2, H_2, N_2, Ar, CO, CO_2, SO_2 and CH_4) on a carbon molecular sieve using three different isotherms, *i.e.* Dubunin–Radushkevich (DR), Langmuir and Freundlich–Langmuir (LF). Juray et al. [16] developed a transient kinetic model using Langmuir ideal surface and Elovich real surface model for simultaneous adsorption of NO and SO over Na/γ-AlO sorbent.

In this study, the most commonly used adsorption isotherm equations *i.e.* Langmuir and Freundlich were used to describe single gas adsorption of SO_2 and NO over Ce/PSAC. A modified extended Langmuir (MEL) was used to predict the binary mixture. Different inlet concentrations (*i.e.* 1000–2500 mg/l of SO_2 and 100–700 mg/l of NO) and equilibrium temperatures (*i.e.* 100–300 °C) were used to describe the adsorption isotherm and heat of adsorption.

2. Materials and methods

2.1. Preparation of sorbent

The PSAC was prepared by physical activation using CO_2 gas. The details of the preparation method are reported elsewhere [17]. Prior to the impregnation process, PSAC was sieved to a size of 1 mm. The PSAC was subjected to pore volume impregnation by cerium metal nitrate. First the PSAC was impregnated with cerium metal nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) of an appropriate concentration to obtain around 10 wt% of metal content per gram of PSAC (10 ml of 10 wt% metal solution/g of PSAC). In this study cerium nitrate from Fluka was used as the metal precursors. During the impreg-

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Rice husk ash sorbent doped with copper for simultaneous removal of SO_2 and NO: Optimization study

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ABSTRACT

In order to reduce the negative impact of coal utilization for energy generation, the pollutants present in the flue gas of coal combustion such as sulfur dioxide (SO_2) and nitrogen oxide (NO) must be effectively removed before releasing to the atmosphere. Thus in this study, sorbent prepared from rice husk ash that is impregnated with copper is tested for simultaneous removal of SO_2 and NO from simulated flue gas. The effect of various sorbent preparation parameters; copper loading, RHA/CaO ratio, hydration period and NaOH concentration on the sorbent desulfurization/denitrification capacity was studied using Design-Expert Version 6.0.6 software. Specifically, Central Composite Design (CCD) coupled with Response Surface Method (RSM) was used. Significant individual parameters that affect the sorbent capacity are copper loading and NaOH concentration. Apart from that, interaction between the following parameters was also found to have significant effect; copper loading, RHA/CaO ratio and NaOH concentration. The optimum sorbent preparation condition for this study was found to be 3.06% CuO loading, RHA/CaO ratio of 1.41, 8.05 h of hydration period and NaOH concentration of 0.80 M. Sorbent characterization using SEM, XRD and surface area analysis were used to describe the effect of sorbent preparation parameters on the desulfurization/denitrification activity.

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1. Introduction

Increasing world population and rapid economic development has caused the worlds' energy consumption to increase annually. In tandem with this, the quantity of power plants worldwide has also been increasing rapidly especially in developing countries like China and India to ensure adequate supply of energy. The thought of renewable energy such as biomass, solar, hydroelectric, geothermal and wind energy being an alternative is not forthcoming considering their uncertainty and instability in ensuring long term energy security. Therefore, renewable energies could not be treated as significant sources of energies yet, at least for the time being. The main sources of fuel used for energy production in power plants are fossil fuels like petroleum, natural gas and coal. Coal, which is relatively cheaper and in abundance as compared to other fossil fuels is widely used over the world and its consumption rate has been increasing due to the volatility of oil and natural gas prices. Nevertheless, the combustion of coal in power plants emit pollutants to the atmosphere, causing severe air pollution which affects the ecosystems including human beings; namely global warming and acid rain.

Two of the main air pollutants produced are sulfur oxides (SO_x) and nitrogen oxides (NO_x). SO_x is produced when sulfur compound in coal reacts with oxygen in the air during combustion and 98% is released as sulfur dioxide (SO_2) [1]. SO_2 with the existence of oxygen in the atmosphere would form sulfur trioxide (SO_3) which would subsequently be hydrated by water in the air to produce sulfuric acid and finally drop to earth as acid rain. On the other hand, NO_x is formed due to the oxidation of molecular nitrogen in the combustion air at high temperature, with 90–95% consisting of nitrogen oxide (NO) [2]. NO could form photochemical smog after reacting with ozone which can damage human respiratory system [3]. In addition, nitrogen oxide is also recognized as an acid rain precursor and one of the greenhouse gases with high global warming potential. Therefore, there are necessities to develop technologies to abate the release of these air pollutants to the atmosphere.

For SO_2 emission control, wet type flue gas desulfurization (FGD) technology using calcium based sorbents such as calcium oxide and calcium hydroxide are commonly adopted in large scale coal-fired power plants and industrial boilers [4]. However, this wet type method requires extensive investment cost due to high equipment cost and requirement to handle corrosive liquid. As an alternative, dry type FGD which is cheaper and simpler with lower capital cost would be a better option for developing countries like China and India which has high energy consumption growth rate but lower investment ability when it comes to environmental abatement system. In addition, dry type FGD generates solid waste that avoids

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Documents

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Performance of palm shell activated carbon impregnated with CeO2 and V2O5 catalyst in simultaneous removal of So2 and NO

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Abstract
This study examined the SO2 and NO sorption capacity of modified Palm Shell Activated Carbon (PSAC). The PSAC was modified using vanadium and cerium metal oxides and the effects were studied for simultaneous removal of SO2 and NO at temperatures of 100-300°C. The weight percentage of metal added and their calcination temperature were also analyzed. It was found that cerium based PSAC showed a higher sorption capacity compared to vanadium. Calcination procedure plays an important role in provoking the oxide formation from the impregnated metal nitrates. A 10% loading of Ce onto PSAC resulted in 121.7 mg g-1 of SO2 and 3.5 mg g-1 of NO sorption capacity g-1 of Ce/PSAC at temperature 150°C compared to vanadium which shows a much lower sorption capacity. Lower temperatures are favorable for the SO2 removal and higher temperature are favorable for NO reduction. © 2010 Asian Network for Scientific Information.

Author Keywords
Cerium; No; Palm shell; Simultaneous; So2; Vanadium

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Simultaneous SO_2 and NO removal using sorbents derived from rice husks: An optimisation study

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ABSTRACT

In this study, rice husk-derived ash (RHA) was hydrated with CaO and then impregnated with copper to synthesize a sorbent that was subsequently tested for its capacity in simultaneous removal of SO_2 and NO from a simulated flue gas. The effect of various sorbent preparation parameters, including copper loading, RHA/CaO ratio, hydration period and NaOH concentration, on the desulphurisation/denitrification capacity of the sorbents was studied using Design-Expert Version 6.0.6 software. Specifically, central composite design (CCD) coupled with response surface method (RSM) was used. The individual parameters that were found to significantly affect the sorbent capacity were RHA/CaO ratio and NaOH concentration. In addition, the interactive effect between RHA/CaO ratio, hydration period and NaOH concentration was also found to have a significant effect on the sorbent activity. The preparation condition for optimal sorbent activity was found to be CuO loading of 3.0%, RHA/CaO ratio of 1.4, hydration period of 20.0 h and NaOH concentration of 0.2 M. Characterisation of the sorbent was performed using scanning electron microscopy (SEM), X-ray diffraction (XRD) and nitrogen adsorption–desorption method to describe the effect of the sorbent preparation parameters on its desulphurisation/denitrification activity.

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1. Introduction

Developing economies rely heavily on coal combustion, which causes the emission of SO_2 and NO to rise continuously. These pollutants emitted to the atmosphere can form acid droplets with water molecules in the air and subsequently drop to the ground in the form of acid rain with a pH in the range of 3–5 that destroys plant and aquatic life as well as corrodes buildings and causes huge monetary losses. Furthermore, NO is one of the precursors that undergoes photochemical reactions with volatile organic compounds (VOCs) and sunlight to form tropospheric ozone (O_3), which is a reactive oxidant gas that causes atmospheric smog. Exposure to tropospheric ozone can cause health problems, especially in the respiratory system [1]. Currently, SO_2 and NO control technologies are carried out in a multi-stage operation. Desulphurisation is mainly carried out through flue gas desulphurisation (FGD) technology by spraying slurry calcium compounds (sorbents), such as calcium hydroxide ($Ca(OH)_2$) and calcium oxide (CaO), in the flue gas stream. On the other hand, the currently preferred technique for reducing NO emissions is the post-combustion process, named as selective catalytic reduction (SCR). Metal oxides such as vanadium oxide (V_2O_5) [2,3], platinum (Pt) [4], zirconia (ZrO_2) [4], copper (Cu) [5], manganese (Mn) [6] and cerium oxide (CeO) [6] have been utilised as the active components in catalytic reactions with NO. This multi-stage removal of pollutants from flue gas is very expensive due to high capital and operating cost. To make matter worse, stringent pollutants emission limit has been imposed on flue gas worldwide by policy makers to protect the environment. In order to overcome this problem, simultaneous removal of SO_2 and NO from flue gas can be a potential and crucial solution to reduce the capital and operating cost of air pollutants control technology, making it more economically feasible.

Dahlan et al. demonstrated the application of metal oxides supported on RHA/CaO sorbents for simultaneous SO_2 and NO removal [7]. The use of rice husk ash (RHA) is very promising because many countries in the world including Malaysia have an extensive rice industry. The ash, also known as siliceous material, is fast becoming a threat to the local environment because of the massive amount of waste produced during rice husk combustion. As shown in Table 1, an analysis conducted by FAO Statistic Division, world paddy production has increased from 2005 through 2007, from approximately 632 million tonnes to 660 million tonnes [8]. This is in accordance with the increase in world population since paddy is the staple food in many countries, particularly those in Asia. After the paddy is processed in a rice milling factory, a large amount of rice husk, comprising about 20% of the paddy production is left over [9]. The rice husk is usually combusted to generate heat because it contains a caloric value of 16,720 kJ/kg [10]. Currently, a large amount of rice husk ash is discarded, resulting not

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Elucidation of interactive effects of synthesis conditions on the characteristics of mesoporous silicas templated using polyoxide surfactant

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Abstract

A series of mesoporous silicas (MS-1–MS-9) were synthesized at different gel compositions using a triblock copolymer (TCP), poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), as the surfactant. The interactive effects of acidity, the contents of tetraethyl orthosilicate (TEOS) and the surfactant, and the gelling temperature on the characteristics of the final material were simultaneously characterized. Increasing acidity favored mesopore formation. A material with a surface area of 760 m^2/g, mostly in the mesoporous range, was obtained at 1.0(TEOS):0.017(TCP):7.3HCl:115.7H_2O. Mesopore formation was predominantly determined by the TEOS:TCP ratio and was promoted with its increase from 1.56:1 to 2.09:1. A further increase to 2.61:1 was detrimental. Whereas increasing the TCP content to 3.5% w/w improved micellization, a further increase to 4.6% should be avoided. Mesoporous silicas showed low crystallinity but a high degree of hexagonal mesoscopic organization. The weak surface acidity was attributed to surface silanols, the number of which was proportional to mesoporosity.
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Keywords: Mesoporous; Silica; Synthesis; Gel composition

1. Introduction

Despite their successful application in many industrial processes, microporous materials such as zeolites become inadequate when processing reactants with sizes above the dimensions of the micropores (> 1 nm) [1]. Thus, mesoporous silica materials have introduced a new degree of freedom in the conception of catalysts. Recently, mesoporous silica materials with larger pore size and better stability were synthesized in an acidic medium using nonionic triblock copolymers (TCPs) as the surfactant [2]. These materials, exemplified by hexagonal (*p6mm*) SBA-15, have long-range order, large monodispersed mesopores (up to 50 nm) [3] and thicker walls (typically between 3 and 9 nm) [4].

The most commonly used surfactant for mesoporous silica synthesis is poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), or EO_n–PO_m–EO_n, with various m and n values [5]. The successful synthesis of SBA-15 has been reported using EO_{20}–PO_{70}–EO_{20}, whereas the use of EO_{106}–PO_{70}–EO_{106} results in cubic SBA-16 [6]. The materials display a relatively narrow pore size distribution, larger pores (6–9 nm) and a thicker pore wall (6 nm). All these characteristics are desirable if superior-quality mesoporous catalyst supports or molecular sieves are to be obtained. Furthermore, the correct proportion of acid and silica sources, such as tetraethyl orthosilicate (TEOS), could also significantly improve the quality of the final material [7,8].

A basic understanding of the synthesis conditions is indispensable, because mesoporous materials with desirable characteristics can only be obtained by suitably controlled synthesis procedures and conditions [3]. Therefore, specific behaviors of the synthesis system must be investigated, particularly those concern the relationship between the synthesis conditions and the characteristics of the material [4]. The widening of the range of suitable

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Synthesis, characterization and material evaluation of mesoporous silicas templated by a polyglycols triblock copolymer for catalytic applications

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Abstract

Mesoporous silicas (MS-1 to MS-9) were synthesized using a polyglycols triblock copolymer (TCP) as the surfactant. The effects of acidity, tetraethyl orthosilicate (TEOS) and TCP contents, gelling temperature and stabilities of the materials were investigated. Increasing acidity favored mesopores formation. A material with a total surface area of 760 $m^2 g^{-1}$, mostly in mesoporous size range was obtained at a gel composition of 1.0(TEOS):0.017(TCP):7.3HCl:115.7H_2O. The controlling mechanisms for mesopores formation were mainly influenced by the TEOS:TCP ratio. Increasing the ratio from 1.56:1 to 2.09:1 promoted the mesoporosity while further increase to 2.61:1 was detrimental. An increase in TCP content to 3.5% (w/w) improved micellization. Silanols caused weak acidity of mesoporous silica, especially in highly mesoporous silicas. Thermal and hydrothermal treatments reduced mesoporosity by 19.2 and 32.6%, respectively, with the formation of secondary nanopores. At 75 MPa, MS-3 retained more than 80% of its surface area.
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Keywords: Silica; Mesoporous; Catalyst; Synthesis; Characteristics; Stabilization

1. Introduction

Despite successful application in many industrial processes, microporous materials such as zeolites become inadequate when processing reactants with sizes above the dimensions of the micropores (>1 nm) [1,2]. Thus, mesoporous materials have introduced a new degree of freedom in the conception of catalysts. Mesoporous materials are very high surface area materials (up to 1600 $m^2 g^{-1}$) having monodispersed pore diameters in the range 2–50 nm and a stereoregular arrangement of these channels [3]. They are produced by using surfactant assemblies as the templates, which ensures the formation of an ordered mesopores. Because of the pore size, these materials allow the processing of large molecules and the eventual accommodation of bulky intermediate transition states [4]. This capability enables them to form catalysts or acting as catalyst support materials in a wider range of industrial reactions.

Among the earliest mesoporous materials developed are the M41S family that includes hexagonal MCM-41, cubic MCM-48 and lamellar MCM-50. Their preparation involves ionic structure directing agents and occurs via liquid–crystal templating (LCT) mechanism. These materials have uniform pores which pore sizes can be tailored in the range of 1.6–10 nm by changing the length of the alkyl chain of the surfactant, auxiliary chemicals and reaction conditions used in their synthesis [2]. However, the main drawback for successful application of M41S in industrial processes is its low thermal and hydrothermal stability [1,5]. This weakness results from its thin wall that tends to collapse under extreme conditions.

Recently, mesoporous silica (MS) materials with larger pore size and better stability were synthesized in an acidic medium with the template of nonionic triblock copolymers (TCP). These materials, exemplified by hexagonal (*p6mm*) SBA-15, have long-range order, large monodispersed mesopores (up to 50 nm) and thicker walls (typically between 3 and 9 nm) that make them more thermally and hydrothermally stable than previous materials [5,6]. The cubic phase mesoporous material SBA-16 (*1m3m*) possesses three-dimensional channel system and uniform-sized pore of super large cage-like structure with a cubic symmetry [7,8]. These materials are also characterized by the presence of micropores and small mesopores within the silica walls, attributed to the partial occlusion of TCP hydrophilic end into

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Effect of the addition of potassium and lithium in Pt–Sn/Al_2O_3 catalysts for the dehydrogenation of isobutane

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Abstract

Dehydrogenation of isobutane (iC_4) to isobutene has recently received considerable attention because of the increasing demand for methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE), as additives for gasoline to increase the octane number and to substitute lead. Among several catalysts, Pt–Sn/γ-Al_2O_3 catalyst is one of the most suitable ones. In this study, Pt–Sn, Pt–Sn–K and Pt–Sn–Li catalysts supported on γ-Al_2O_3 have been investigated. The catalysts were prepared by co-impregnation using

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Catalytic oxidation of butyl acetate over silver-loaded zeolites

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Abstract

The performance of silver-loaded zeolite (HY and HZSM-5) catalysts in the oxidation of butyl acetate as a model volatile organic compound (VOC) was studied. The objective was to find a catalyst with superior activity, selectivity towards deep oxidation product and stability. The catalyst activity was measured under excess oxygen condition in a packed bed reactor operated at gas hourly space velocity (GHSV) = 15,000–32,000 h^{-1}, reaction temperature between 150 and 500 °C and butyl acetate inlet concentration of 1000–4000 ppm. Both AgY and AgZSM-5 catalysts exhibited high activity in the oxidation of butyl acetate. Despite lower silver content, AgY showed better activity, attributed to better metal dispersion, surface characteristics and acidity, and its pore system. Total conversion of butyl acetate was achieved at above 400 °C. The oxidation of butyl acetate followed a simple power law model. The reaction orders, *n* and *m* were evaluated under differential mode by varying the VOC partial pressure between 0.004 and 0.018 atm and partial pressure of oxygen between 0.05 and 0.20 atm. The reaction rate was independent of oxygen concentration and single order with respect to VOC concentration. The activation energies were 19.78 kJ/mol for AgY and 32.26 kJ/mol for AgZSM-5, respectively.

Keywords: Butyl acetate; Silver; Zeolites; Catalyst; Characterization; Activity; Kinetic

Article Outline

1. Introduction
2. Experimental
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   2.2. Experimental setup
3. Results and discussion
   3.1. Catalyst characterization
   3.2. Role of the silver in VOC oxidation
   3.3. Catalyst activity of AgY and AgZSM-5
   3.4. Kinetic study
4. Conclusions

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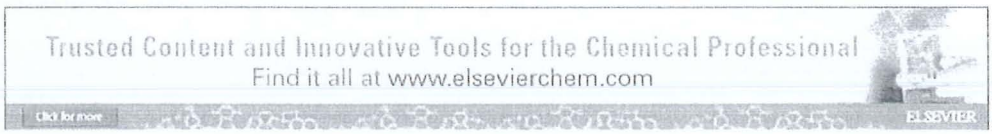

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Adsorption of butyl acetate in air over silver-loaded Y and ZSM-5 zeolites: Experimental and modelling studies

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Abstract

Adsorption behaviours of butyl acetate in air have been studied over silver-loaded Y (Si/Al = 40) and ZSM-5 (Si/Al = 140) zeolites. The silver metal was loaded into the zeolites by ion exchange (IE) and impregnation (IM) methods. The adsorption study was mainly conducted at a gas hourly space velocity (GHSV) of 13,000 h^{-1} with the organic concentration of 1000 ppm while the desorption step was carried out at a GHSV of 5000 h^{-1}. The impregnated silver-loaded adsorbents showed lower uptake capacity and shorter breakthrough time by about 10 min, attributed to changes in the pore characteristics and available surface for adsorption. Silver exchanged Y (AgY(IE)) with lower hydrophobicity showed higher uptake capacity of up to 35%, longer adsorbent service time and easier desorption compared to AgZSM-5(IE). The presence of water vapour in the feed suppressed the butyl acetate adsorption of AgY(IE) by 42% due to the competitive adsorption of water on the surface and the effect was more pronounced at lower GHSV. Conversely, the adsorption capacity of AgZSM-5(IE) was minimally affected, attributed to the higher hydrophobicity of the material. A mathematical model is proposed to simulate the adsorption behaviour of butyl acetate over AgY(IE) and AgZSM-5(IE). The model parameters were successfully evaluated and used to accurately predict the breakthrough curves under various process conditions with root square mean errors of between 0.05 and 0.07.

Keywords: Butyl acetate adsorption; Y and ZSM-5 zeolites; Breakthrough curve; Humidity; Adsorption model

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   2.2. Measurement of adsorption capacity
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   3.3. Products analysis
4. Results and discussion

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Selective Catalytic Reduction of Nitric Oxide in Diesel Engine Exhaust over Monolithic Catalysts Washcoated with Bimetallic Cu-Zn/ZSM-5

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Abstract

Selective catalytic reduction (SCR) of nitric oxide (NO) in diesel engine exhaust over Cu-Zn/ZSM-5 washcoated ceramic monolithic catalysts is reported. The washcoat component was prepared by ion-exchanging ZSM-5 (Si/Al=40) with zinc while copper was incorporated through impregnation. The dispersed washcoat component was then incorporated into 400 cpsi ceramic monolith through a dipping process with the final loadings between 19.6 wt. % and 31.4 wt. %. The SCR process was studied with a feed comprising of 900 ppm NO, 2,000 ppm iso butane and 3 % oxygen at gas hourly space velocities (GHSV) between 5,000 and 13,000 h^{-1}. NO conversion increased until a loading of 23.6 wt. % to give a conversion of 88 % at 400 °C. The activity dropped at higher loadings due to the partial blockage of cell openings and diffusion limitations while unstable washcoating adherence was also demonstrated. After an initial deactivation of about 10 % in the first 48 h, this catalyst showed stable residual activity. Between 325 and 375 °C, minimal effect on the activity was detected when the space time was reduced from 0.94 s to 0.24 s, suggesting the absence of external mass transfer limitations for up to a GHSV of 16,000 h^{-1}.

Keywords: NO; selective catalytic reduction; ZSM-5; ceramic monolith; performance.

1. Introduction

Diesel engine owes its popularity to its high fuel efficiency, reliability, durability and relatively low fuel price. This engine is run under oxygen excess condition in a so called lean-burn operation. However, the operation increases the production of toxic gas e.g. nitric oxides (NO) which cause severe environmental and health problems. Catalytic processes have been widely investigated for NOx removal and selective catalytic reduction (SCR) being the most popular one (Solis *et al.*, 2001; Pisarello *et al.*, 2002 and Bennici *et al.*, 2005). The SCR technology is still immature and several drawbacks are yet to be satisfactorily addressed.

For a deNOx unit, pressure drop is a key issue (Odenbrand *et al.*, 1999 and Makkee *et al.*, 2002). In a car exhaust or a power plant flue gas system, the pressure drop should ideally be below 10-20 mbar (Seijger *et al.*, 2001). Additional demands comprise low sensitivity to dust and resistance to thermal shock. Structured packings, like monolithic are gaining interest for application in NOx reduction (Zamaro *et al.*, 2005 and Bueno-Lopez *et al.*, 2005) as the pressure drop in these catalysts is significantly lower than that of randomly packed bed catalysts (Cybulski *et al.*, 1999). Among various types of monolith, ceramic monoliths being the most widely used substrate material, mainly because of its relatively low manufacturing costs and high thermal stability (Heck *et al.*, 2001). However, the specific surface of most structured supports is below 1 m^2/g, which is way too low for catalytic purposes. The specific surface area can be enhanced up to about 40 m^2/g by washcoating with suitable microporous or mesoporous materials. As zeolites have a specific surface area of 300-700 m^2/g, a monolayer of zeolite may serve the need for surface area and porosity (Seijger *et al.*, 2001). The ZSM-5 washcoated ceramic monolith catalysts provide interesting advantage in the SCR of NOx starts receiving attention among researchers (Zamaro *et al.*, 2005 and Li *et al.*, 2008). ZSM-5 possesses high surface area of about 370 m^2/g and has been demonstrated to have high hydrothermal stability and suitability in many environmental catalysis applications in our earlier works (Deeng *et al.*, 2004; Abdullah *et al.*, 2003 and Abdullah *et al.*, 2006).

Among metals studied as the active component of the catalyst are Cu (Deeng *et al.*, 2004), Pt (Ismail *et al.*, 2002) and Co (Ren *et al.*, 2002). By reviewing the results, Cu should provide superiority on the basis of high activity, high stability, low toxicity and low cost. Therefore, it was used in this study. Recently, the bimetallic catalysts have created particular interest due to the promoting effect between metal species (Ismail *et al.*, 2002). The second metal should be able to

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Optimization of air-borne butyl acetate adsorption on dual-function Ag–Y adsorbent-catalyst using response surface methodology

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Abstract

The low concentration and high flow rate of air-borne butyl acetate (BA) could be effectively removed using combined adsorption-catalytic oxidation system. Ag–Y (Si/Al = 80) dual-function adsorbent was investigated for the adsorption step of 1000 ppm of butyl acetate at gas hourly space velocity of 13,000 h^{-1} at ambient temperature under dry and humid feeds. A central composite design (CCD) coupled with response surface methodology (RSM) was employed to obtain the optimum process conditions and the interactions between process variables were demonstrated and elucidated. Humidity and increasing organic concentration shortened the adsorption service time. The effect of moisture was more pronounced at low BA concentration. The interactions between the BA concentration and humidity were statistically significant at 95% confidence level. The optimum conditions were found to be at 4500 ppm of BA with 37 min saturation time to give 58 mg BA/g as adsorption capacity. The simulated data fitted the experimental data satisfactorily. The simulated data also correctly demonstrated the overall behaviors of the adsorption process.

Keywords: Butyl acetate; Adsorption; Silver–Y; Dual-function; Response surface methodology; Interactions

Article Outline

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   3.2. Adsorption study
   3.3. Analysis of variance (ANOVA)

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Biocatalytic esterification of citronellol with lauric acid by immobilized lipase on aminopropyl-grafted mesoporous SBA-15

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ABSTRACT

Mesoporous SBA-15 was synthesized under acidic condition at 40 °C with a non-ionic triblock copolymer (P123) as the template. The synthesis gel composition used was 1 SiO_2:0.017 P123:2.9 HCl:202.6 H_2O. Functionalization of SBA-15 with 3-aminopropyltriethoxysilane (APTES) by post-synthesis method was performed under reflux for 2 h. The mesoporous samples were characterized using Fourier transform infrared (FT-IR), nitrogen adsorption, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). They were then utilized as supports for the immobilization of lipase to be subsequently used for the esterification of citronellol and lauric acid. Leaching and reusability tests were also conducted on the immobilized enzymes. Functionalization resulted in about 10% improvement in enzyme loading, leading to higher activity. The immobilized enzyme was also more stable to low pH and high temperature while showing better retention (up to 95%) of enzyme molecules. Immobilized lipase maintained 90% of its esterification activity in non-aqueous system even after 4 cycles of use. The improvements were associated with enhanced surface hydrophobicity, changes in pore shapes and stronger enzyme–support interactions with minimal effects to the enzymatic activity.

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1. Introduction

Lipases are one of the enzymes of considerable physiological and industrial significance [1,2]. However, they are unstable and the recovery from the reaction mixture is usually difficult. The immobilization of these enzymes within mineral hosts is a popular, but challenging approach to design new biocatalysts with unlimited future applications [3,4]. The immobilized lipases have many advantages over soluble counterparts in terms of stability, reusability and applicability to continuous processing. They also show better stability to pH while having low substrate-inhibition effects [5]. The handling of immobilized lipases is relatively easy as they usually strongly bind to a solid phase and easy to be separated from the reaction mixture [6]. The stability of the immobilization often depends on the immobilization method and type of support. Therefore, it is important to choose the most suitable support to immobilize enzymes so that the enhancement of thermal and operational stabilities, the minimization operating cost and the reusability of the enzyme can be achieved [2].

Ordered mesoporous silicas, in particular SBA-15, have been found to be promising host matrixes for immobilization of enzymes and some research works on various conversions have been initiated by several research groups [3,7]. SBA-15 has a BET surface areas of between 690 and 1040 m^2/g, large pore sizes of between 50 and 100 Å and unusually large pore volumes of up to 2.5 cm^3/g. Its silica wall thickness ranges from 3.1 to 6.4 nm [3]. In addition, the pore size of SBA-15 can be easily tuned by employing different swelling agents and the functionalization of its surface could render it suitable for specific catalytic applications [8]. All these characteristics make the materials potential candidates to act as suitable support materials for large molecules like enzymes. In our earlier work, a highly porous SBA-15 material with well-organized array of straight channels and narrow pore size distribution has been developed [9]. The correlations between its surface characteristics and the synthesis conditions have also been successfully elucidated.

Though SBA-15 support has been demonstrated to protect the enzyme from aggregation [10], the insufficient strength of interaction between enzyme and the mesoporous support causes significant enzyme leaching from the support [3]. Thus, surface modification of mesoporous silicas with organofunctionalities was actively investigated to reduce the degree of enzyme leaching [2,3,8]. Through organic functionalization of the internal surface, certain functional groups can be attached to the surface of the mesoporous material to strengthen interactions with the enzyme. In addition, the surface functionalization also partially reduces the pore openings, especially at the external surface. This will 'trap' the enzyme molecules within the pores but still allowing reactant and product molecules to diffuse in and out of the pores [3].

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Optimization of mesoporous K/SBA-15 catalyzed transesterification of palm oil using response surface methodology

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ABSTRACT

K/SBA 15 was investigated for the transesterification of palm oil. The influence of temperature, reactants' ratio, catalyst loading and reaction time on the biodiesel yield was studied using a Central Composite Design (CCD). The process optimization using Response Surface Methodology (RSM) was performed and the interactions between the operational variables were elucidated. The optimum conditions were found to be 70 °C for the reaction temperature, 11.6 mol/mol for methanol to oil ratio, 3.91 wt.% for the catalyst loading and 5 h for the reaction time to achieve 93% of biodiesel yield. High catalytic activity was attributed to high surface area of the catalyst and the relatively easy diffusion of reactants in the mesopores. The effect of catalyst loading and reaction time was relatively more dominant in affecting the biodiesel yield. High potential of SBA-15 as catalyst for biodiesel production was demonstrated.

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1. Introduction

As traditional fossil energy resources are limited and greenhouse gas emissions are becoming a greater concern, research is now being directed towards the use of alternative renewable fuels that are capable of fulfilling an increasing energy demand. Biodiesel, an alternative diesel fuel, is a promising, non-toxic and eco-friendly fuel [1]. It is conventionally produced by transesterification process of oils and fats. The presence of catalysts in the process plays an important role in improving in the reaction rate and yield [2]. Due to environmental problem, easier catalyst separation, and economic concerns, current research trend in catalysis has been focusing on the transformation of homogeneous catalytic system into heterogeneous systems [3]. It should be noted that biodiesel needs to have full compliance with either ASTM D6751-07 or EN 14214:2003 standards to be used as a fuel. The compliance is basically influenced by many factors such as the purity of the fatty acid methyl esters content, the success of the purification process, the original constituents in the feedstock oil etc. [2].

There are numerous heterogeneous catalysts currently available that can catalyze the transesterification reactions. A great variety of catalysts such as alkaline-earth metals oxides and hydroxides [4], alkali metals (Na and K) hydroxides or salts supported on alumina [1,5,6], zeolites [7], hydrotalcites, as well as some solid acids [2] have been investigated under various reaction conditions and with a variable degrees of success. Calcinations turn the salts into more stable forms that can better resist leaching during the reaction. Zeolites are one of the catalyst supports that have attracted strong attention in the field of catalysis due to their unique pore system, high surface area and high stability. However, these materials present severe limitations when large reactant molecules are involved, especially in liquid-phase systems as is frequently the case in the synthesis of fine chemicals. It is due to the fact that mass transfer limitations are very severe for the microporous materials [8]. Similarly, catalysts with small pores are not suitable for biodiesel production because of the diffusion limitation of the large fatty acid molecules (triglyceride). Therefore, many researchers now turn into with mesoporous materials instead of zeolites to be applied as the catalyst support in order to overcome this limitation.

The advantage of using ordered mesoporous solids in catalysis are the relatively large pores which facilitate mass transfer and the very high surface area which allows high concentration of active sites per mass of material [8]. Mesoporous SBA-15 possesses a high surface area (600–1000 m^2/g) and is formed by a hexagonal array of uniform tubular channels with tunable pore diameters (5–30 nm) and thicker pore walls (3–6 nm) [9]. It has high thermal stability which promises great opportunity for the application as catalysts or catalytic supports [10]. However, the process of transesterification is affected by various factors, depending upon the reaction condition used. Some of the effects are free fatty acid and moisture of the source of oil, type of oil, catalyst type and loading, molar ratio of alcohol to oil, type of alcohol, reaction time and temperature, mixing intensity and effect of solvents [11]. Recent studies have also revealed that functionalized mesoporous silica, such as tin oxide-modified mesoporous SBA-15 [12], titanium-grafted mesoporous silica [13] and Mg–MCM-41 [14] appeared to be very promising in catalyzing various transesterification reactions. Despite highly promising catalyst reported for various

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Heat treatment effects on the characteristics and sonocatalytic performance of TiO_2 in the degradation of organic dyes in aqueous solution

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ABSTRACT

The ambient sonocatalytic degradation of congo red, methyl orange, and methylene blue by titanium dioxide (TiO_2) catalyst at initial concentrations between 10 and 50 mg/L, catalyst loadings between 1.0 and 3.0 mg/L and hydrogen peroxide (H_2O_2) concentrations up to 600 mg/L is reported. A 20 kHz ultrasonic processor at 50 W was used to accelerate the reaction. The catalysts were exposed to heat treatments between 400 and 1000 °C for up to 4 h to induce phase change. Sonocatalysts with small amount of rutile phase showed better sonocatalytic activity but excessive rutile phase should be avoided. TiO_2 heated to 800 °C for 2 h showed the highest sonocatalytic activity and the degradation of dyes was influenced by their chemical structures, chemical phases and characteristics of the catalysts. Congo red exhibited the highest degradation rate, attributed to multiple labile azo bonds to cause highest reactivity with the free radicals generated. An initial concentration of 10 mg/L, 1.5 g/L of catalyst loading and 450 ppm of H_2O_2 gave the best congo red removal efficiency of above 80% in 180 min. Rate coefficients for the sonocatalytic process was successfully established and the reused catalyst showed an activity drop by merely 10%.

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1. Introduction

Presently, it is estimated that about 10,000 different types of commercial dyes and pigments exist and over 700,000 tones are produced annually [1,2]. About 10–20% of the total world production of dyes is lost during the dyeing process and is released into the effluents [3]. Industrial dyestuffs constitute one of the largest groups of organic compounds that cause an increasing environmental concern [4]. Therefore, a lot of studies have been dedicated to treat this wastewater by using advanced oxidation process which involves hydroxyl (•OH) radicals to mineralize the organic compounds. Different degrees of success have been reported but the methods could subject to some common drawbacks like high capital and running costs, the needs for toxic chemicals and low removal efficiency, especially at low concentrations. Photocatalytic degradation is another plausible method but its practicality is generally limited with heavily colored effluent, high photocatalyst loading and high volume operation due to low penetration of the UV light [3,4].

The application of ultrasounds in water with a frequency range of between 18 and 100 MHz can result the phenomenon of acoustic cavitation. It involves the formation, growth and collapse of cavity bubbles that entrapped dissolved gases or vapors surrounding water [5,6,7]. Subsequently, many local hot spots with extremely high temperature (up to 5000 K) and high pressure (up to 1000 atm) are generated to consequently induce the dissociation of water (Eqs. (1)–(4)), oxygen molecules (Eqs. (5)–(8)) and hydrogen peroxide (H_2O_2) (Eq. (9)) in the case of its addition into the effluent [5,7,8].

$$H_2O \xrightarrow[TiO_2]{))))} \cdot OH + H\cdot \quad (1)$$

$$^{\bullet}OH + H^{\bullet} \rightarrow H_2O \quad (2)$$

$$2\,^{\bullet}OH \rightarrow H_2O_2 \quad (3)$$

$$2\,^{\bullet}OH \rightarrow H_2O^{\bullet} + O^{\bullet} \quad (4)$$

$$O_2 \xrightarrow[TiO_2]{))))} 2O\cdot \quad (5)$$

$$^{\bullet}O + H_2O \rightarrow 2\,^{\bullet}OH \quad (6)$$

$$O_2 + H^{\bullet} \rightarrow {}^{\bullet}O_2H \quad (7)$$

$$^{\bullet}O_2H + {}^{\bullet}O_2H \rightarrow H_2O_2 + O_2 \quad (8)$$

$$H_2O_2 \xrightarrow[TiO_2]{))))} 2 \cdot OH \quad (9)$$

As a semiconductor material, TiO_2 is characterized by a filled valence band and an empty conduction band [3,4]. In the presence of suitable energy source, the excitation of electron from the valence band to the conduction band could occur. With the presence of UV light or ultrasonic irradiation as the energy source,

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Optimization of Process Parameters for Alkaline-Catalysed Transesterification of Palm Oil Using Response Surface Methodology

(Pengoptimuman Parameter Proses untuk Transesterifikasi Minyak Sawit Bermangkin Alkali Menggunakan Kaedah Sambutan)

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ABTRACT

Biodiesel (fatty acid methyl esters) was synthesized from direct transesterification of vegetable oils, where the corresponding triglycerides react with methanol in the presence of a suitable catalyst. The alkali catalysts are the most common catalyst used in biodiesel industry, because the process proves faster and the reaction conditions are moderated compared to the acid catalyst. In the present study, biodiesel production using heterogeneous alkaline-catalysed transesterification process (KOH supported on SBA 15) was proposed. The influence of reaction temperature x_1 (50 - 90°C), ratio methanol to oil, x_2 (6:1 – 14:1 mol/mol), amount of catalyst, x_3 (1 – 5wt.%), and reaction time, x_4(2 - 6h) to the reaction was studied. These four conditions were studied using design of experiment (DOE), based on four-variable central composite design (CCD) with $\alpha = 2$. The process variables were optimised using the Response Surface Methodology (RSM) in obtaining the maximum yield of biodiesel. This method was also applied to determine the significance and interaction of the variables affecting the biodiesel production. The biodiesel produced in the experiment was analysed by gas chromatography, which considered five major fatty acid methyl esters. The optimal conditions of response were found to be 70°C for reaction temperature, 11.6 wt/wt of ratio methanol to oil, 3.91wt.% of weight of catalyst and 5 h for reaction time with 93% of biodiesel yield for predicted value and 87.3% from experimental.

Keywords: Base catalyst; biodiesel; response surface methodology

ABSTRAK

Biodiesel telah disintesis daripada transesterifikasi langsung minyak sayuran yang melibatkan trigliserida bertindak balas dengan metanol dengan kehadiran mangkin yang sesuai. Mangkin beralkali adalah mangkin yang biasanya digunakan di dalam industri biodiesel kerana proses terbukti lebih cepat dan keadaan tindakbalas sederhana berbanding dengan mangkin berasid. Dalam kajian ini, penghasilan biodiesel menggunakan proses transesterifikasi bermangkinkan heterogen beralkali (KOH disokong di atas SBA-15) telah dikaji. Kesan suhu tindakbalas, x_1 (50 - 90°C), nisbah metanol kepada minyak, x_2 (6:1 – 14:1 mol/mol), berat mangkin, x_3 (1 – 5wt.%), dan masa, x_4(2 – 6 h) terhadap tindakbalas dikaji. Empat keadaan ini telah dikaji menggunakan rekabentuk eksperimen (DOE) berdasarkan kepada empat pembolehubah rekabentuk gabungan berpusat (CCD) dengan $\alpha = 2$. Pembolehubah proses telah dioptimumkan menggunakan kaedah sambutan permukaan (RSM) dalam mendapatkan hasil biodiesel yang maksimum. Kaedah ini juga digunakan untuk menentukan kepentingan dan interaksi pembolehubah-pembolehubah yang mempengaruhi hasil biodiesel. Biodiesel yang dihasilkan telah dianalisis melalui kromatografi yang mengambilkira lima metil ester asid lemak utama. Keadaan optimum sambutan didapati pada suhu tindakbalas 70°C, nisbah metanol kepada minyak 11.6 mol/mol, berat mangkin 3.91 wt.% dan 5 h masa tindakbalas dengan 93% hasil biodiesel yield untuk nilai jangkaan dan 87.3% daripada eksperimen.

Kata kunci: Biodiesel; kaedah sambutan permukaan; mangkin beralkali

INTRODUCTION

Due to environmental, green chemistry and economic concerns, current research trend in catalysis has been focused on the transformation of homogeneous catalytic system into heterogeneous systems. The replacement of homogeneous catalysts by heterogeneous catalysts would have various advantages, most important being the application of easier working up procedures, the easy catalyst separation from the reaction mixture and the reduction of environment pollutants (Venkatesan et al. 2004). Besides that, the process of transesterification is affected by various factors depending upon the reaction condition used. Some of the effects are free fatty acid and moisture of the source of oil, type of oil, catalyst type and concentration, molar ratio of alcohol to oil, type of alcohol, reaction time and temperature, mixing intensity and effect of solvents (Meher et al. 2004; Lopez et al. 2005)). The economic and environmental interest in using oil and fats involved in the production of biodiesel.

The objective of this study was to optimize process variables of transesterification process. The process variables studied were reaction temperature, ratio methanol

Influence of the silica-to-surfactant ratio and the ph of synthesis on the characteristics of mesoporous SBA-15

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Abstract: *Mesoporous silica SBA-15 was synthesised with two different sets of synthesis conditions and was characterised using nitrogen adsorption, X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The effects of the ratio of tetraethylorthosilicate/triblockcopolymer (TEOS/TCP) (1.52–3.38) and pH (1.3-3.0) were particularly studied. Well-ordered hexagonal mesoporous silicas were formed at a TEOS/TCP ratio of 2.25 and a pH above 2. The highest surface area and an intense XRD pattern were shown by those synthesised at a ratio of 1.52 (669 m^2/g and 0.5 cc/g). A high TEOS amount disturbed the condensation of the silica network, causing failure in the formation of the Si-O-Si network.*

Keywords: Mesoporous, SBA-15, TEOS/TCP ratio, pH, characteristics.

1. INTRODUCTION

The presence of porous materials has been known for more than a century[1]. Since the discovery of M41S mesoporous materials in 1992, there has been an increasing interest in the design of novel porous materials tailored with various pore organisations and dimensions for potential applications in separation, catalysis, chemical sensing and optical coating[2-3]. The use of mesoporous materials of MCM-41 as carriers for basic guest species has been proposed by Weitkamp et al.[4]. This material is usually synthesised in a basic medium and in the presence of surfactant cations[5]. However, MCM-41 material is limited to a pore size of about 80 Å, and, because of this, it is not suitable for processing large biomolecules such as protein and enzymes[6]. Even though this material has a quite high thermal stability, it loses its structure when exposed to high-temperature steam or boiling water. The collapse of the structure limits the applications of MCM-41, especially in catalytic reactions involving aqueous solutions[7].

Recently, a new type of ordered mesoporous material has attracted great attention in the field of catalysis. SBA-15 materials possess high surface areas (600-1,000 m^2g^{-1}) and are made up of hexagonal arrays of uniform tubular channels with tunable pore diameters in the range of 5-30 nm. The pore walls are

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Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: A critical review

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ABSTRACT

Glycerol emerges as a significant worth chemical that can be converted into high value products. In the prospect of biorefinery industries and great demand towards renewable sources, glycerol has proved to have tremendous potential to be transformed, thus supersede conventional petroleum derived fuel additive. Various types of oxygenated biocomponents and rigorous studies of glycerol transformation into fuel additives are presented in this review paper. Particular focus is given to etherification, acetylation and acetalation processes with specific behaviors in the respective reaction system.

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1. Introduction

The development and commercial use of biodiesel has been encouragingly and rapidly expanding in Europe and US for over 10 years. The prominent superiority of biodiesel over petroleum diesel towards health and environment (free sulfur content, low content of harmful emission, e.g. particulate matter, HC, CO, etc., better lifecycle of CO_2 for global warming alleviation) as well as engine performance (enhance lubricity, high cetane number for complete combustion) [1,2] has enticed Asia to use biodiesel as alternative fuels and innovative solution to curb the polluted air emitted from growing vehicle population [3].

Despite the rapid pace of biodiesel development and commercialization, there are several key challenges emerging and these must be addressed efficiently. One key problem that is being ultimate focused is the inevitable low value production of glycerol as co-product of biodiesel from transesterification and esterification of vegetable oil [4]. Stoichiometrically, glycerol is produced by

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Optimization of ultrasonic-assisted heterogeneous biodiesel production from palm oil: A response surface methodology approach

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ABSTRACT

The use of ultrasonic processor in the heterogeneous transesterification of palm oil for biodiesel production has been investigated. Response surface methodology was employed to statistically evaluate and optimize the biodiesel production process catalyzed by two alkaline earth metal oxide catalysts i.e. BaO and SrO. SEM, surface analysis, AAS analysis and the Hammett indicator methods were used for characterization of the catalysts. Four different variables including reaction time (10–60 min), alcohol to oil molar ratio (3:1–15:1), catalyst loading (0.5–3.0 wt.%) and ultrasonic amplitude (25–100%) were optimized. Mathematical models were developed and used to predict the behavior of the process. The models were able to accurately predict the biodiesel yield with less than 5% error for both catalysts. The basic strength of the catalysts was the main reason of their high activities. This study confirmed that the ultrasonic significantly improved the process by reducing the reaction time to less than 50 min and the catalyst loading to 2.8 wt.% to achieve biodiesel yields of above 95%. The optimum alcohol to oil ratio was found to be at 9:1 while the best amplitudes were ~70 and ~80% for the BaO and SrO catalysts, respectively.

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1. Introduction

Recently, particular focus is been given on global warming and exhaustion of non-renewable resources. These problems are primarily attributed to the heavy consumption of fossil fuels. Much attention has been given to biomass resources as alternatives for energy sources. The typical biodiesel fuel is produced by the transesterification of vegetable oils with low alcohol in the presence of homogeneous base-catalyst such as KOH or NaOH [1]. Transesterification can occur in the absence of a catalyst, but it can be effectively intensified by the use of suitable catalyst [2]. However, for the satisfactory use of the product as diesel fuel, the catalyst must be removed from the product mixture and this requires cumbersome purification processes while huge amount of wastewater is generated at the same time [3].

Heterogeneous catalytic process is expected to be future biodiesel production process. This process lowers the cost and minimizes the environmental impacts due to the simpler production steps and purification processes which are normally carried out under very mild conditions. The heterogeneous catalysts capable to be used are such as, titanium-silicates [4], alkaline earth metal compounds and hydroxides [4–6], and alkali metal hydroxides or salts supported on γ-alumina [7–9] or zeolites [10]. The common problem associated with the heterogeneous biodiesel production process is its low reaction rate due to poor interaction between the oil and alcohol during the reaction due to their mutual immiscibility [4,5].

The demand for biodiesel in the world is sharply increasing. Thus, increasing the production rate for biodiesel in order to meet the demand seems to be essential. Therefore, new accelerating technologies are of great interest among researchers in this area. Ultrasonic radiations can accelerate the biodiesel production rate with homogenous catalyst [1,11]. Hanh et al. [2] found that the methanolysis of oil in aqueous catalyst solutions (e.g. NaOH, KOH) can be accelerated by low frequency ultrasound which led to the intensification of the overall process. Reports on the beneficial use of ultrasound for homogeneous catalytic process for biodiesel production are also published very recently [1,2,12]. Despite widely investigated for accelerating homogeneous reaction systems, heterogeneous biodiesel production process has never been intensified using ultrasonic energy. The benefit offered to the homogeneous process is theoretically possible in the case of heterogeneous process in a similar manner. However, report on the use of ultrasonic-assisted heterogeneous process for the production of this renewable fuel is still hardly found in the literature.

Fig. 1 shows the five step reaction mechanism generally proposed for the role of metal oxide catalyst in the transesterification reaction. Steps 1 and 2 describe the adsorption of alcohol and fatty acid on two neighboring free catalytic sites, respectively. In step 3, the two adsorbed groups react to form a surface intermediates. These surface intermediates will further decompose in step 4 and finally desorb (step 5). According to Hattori et al. [13], the rate-determining step of this mechanism with catalysts having a higher basicity, such as BaO and SrO, is the surface reaction step. Forward reaction promotes the formation of esters to result in high biodiesel yield. In this respect, higher alcohol

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Ultrasonic-assisted biodiesel production process from palm oil using alkaline earth metal oxides as the heterogeneous catalysts

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ABSTRACT

The ultrasonic-assisted transesterification of palm oil in the presence of alkaline earth metal oxide catalysts (CaO, SrO and BaO) was investigated. Batch process assisted by 20 kHz ultrasonic cavitation was carried out to study the effect of reaction time (10–60 min), alcohol to palm oil molar ratio (3:1–15:1), catalysts loading (0.5–3%) and varying of ultrasonic amplitudes (25–100%). The activities of the catalysts were mainly related to their basic strength. The catalytic activity was in the sequence of CaO < SrO < BaO. At optimum conditions, 60 min was required to achieve 95% yield compared to 2–4 h with conventional stirring. Also, the yields achieved in 60 min increased from 5.5% to 77.3% (CaO), 48.2% to 95.2% (SrO), and 67.3% to 95.2 (BaO). Fifty percentage amplitude of ultrasonic irradiation was deemed the most suitable value and physical changes on the catalysts after the ultrasonic-assisted reaction were successfully elucidated. BaO catalyst underwent relatively more severe activity drop in the catalyst reusability test. Catalysts dissolution was found to be mainly responsible for activity drop of the reused catalysts, especially with BaO catalyst.

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1. Introduction

Biodiesel is an eco-friendly and alternative energy source for diesel engines that can be synthesized by transesterification of vegetable oil or animal fat with alcohols [1]. The reaction can be catalyzed by alkalis, acids, or enzymes [2]. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially [1]. Nevertheless, the alkali catalyst compounds have some drawbacks, i.e. they must be neutralized after the reaction, thus, eliminating the possibility for the reusability of the catalyst [3,4]. The neutralization process also generates large amount of wastewater that deserves treatment, to the significant increase in the production costs [5].

Heterogeneous catalysis have many advantages: they are relatively non-corrosive, environmentally benign and present fewer removal problems. They are also much easier to be separated from liquid products and can be designed to give higher activity, selectivity and longer catalyst lifetimes [6]. Alkaline-earth metals oxides and hydroxides [7–9], alkali metals (Na and K) hydroxides or salts supported on γ-alumina [3,10–11], zeolites [12], hydrotalcites [5,13] have been investigated with a variable degree of success. Single component alkaline earth metal oxides (BaO, SrO, CaO, MgO) which have higher basicity, lower solubility in alcohol and capable of producing higher biodiesel yield have also been reported [9]. However, complete behavior of these catalysts in the transesterification process is yet to be fully understood [9,14].

As oil and methanol are not completely miscible, the mixing efficiency can affect the course of the transesterification reaction. The reaction can only occur in the interfacial region between the methanol, oil and catalyst and the alkaline earth oxide catalysts are essentially insoluble in the two phases. Continuous and vigorous mixing is then required to increase the area of contact between the three phases [15,16]. The mixing process generally increases energy input for biodiesel production process, yet the biodiesel yield is generally lower then that in the homogeneous process [9].

Low frequency ultrasound is theoretically seen as an efficient, time saving and economically functional method to accelerate biodiesel production process [17]. Ultrasonic mixing can produce smaller droplets of the reacting phases than conventional agitation, leading to a drastic increase in the interfacial area and improved mass transfer [18]. As a result, the mixing requirement during the process is also significantly lowered, translating in reduced energy consumption [15]. Ultrasonic can also 'grind' the catalyst into smaller particles to create new active sites for the subsequent reaction. Thus, the solid catalyst is expected to last longer in the ultrasonic-assisted process.

The main aim of this study was to characterize the effects of ultrasonic energy in presence of alkaline earth metal oxides as heterogeneous catalysts. As reported in literature, most of the transesterification processes for biodiesel production use some oils other than palm oil such as rapeseed oil [19] and soybean oil [4,8,10]. As

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Cationic Surfactant-Modified Clay Catalysts for the Synthesis of Monoglyceride through the Esterification of Glyceroland Lauric Acid

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Abstract

The preparation, characterization and activity study of clay catalysts prepared from sodium-montmorillonite (NaMMT) are reported. The clay was functionalized with cetyl trimethyl ammonium bromide (CTAB) and tetra-n-butylammonium bromide (TBAB) to produce CTMMT and TBMMT catalysts, respectively using an ion exchange method performed at 60 °C. The catalysts were characterized using XRD, FTIR, TGA and surface analysis methods. The catalytic activity was evaluated by reacting glycerol with lauric acid at 130 °C for up to 8 h. Intercalation of surfactants increased the basal spacing of the clay, reduced the adsorbed water and caused some chemical changes in the clay lattice. With TBAB catalyst, was a glycerol monolaurate selectivity of about 73 % was obtained at a lauric acid conversion of about 80 %. Symmetrical onium salts in TBAB was responsible for higher activity and selectivity than that of unsymmetrical onium salts in CTAB.

KEYWORDS: Montmorillonite ; cationic surfactant ; glycerol, lauric acid ; esterification.

1. Introduction

Glycerol is a renewably biomass and is a by-product from oleochemical and biodiesel industries. The increasing supply of glycerol would create a glut in the market and new applications for this substance need to be found. Thus, the development of an economical follow-up chemical technology for glycerol is of great economical interest. Glycerol transformation into glycerol monoesters has significant applications as the esters can act as emulsifiers especially in food, pharmaceutical and cosmetic products due to their physicochemical properties and the hydrophilic-hydrophobic balance [Sonntag, 1982]. These esters have been generally obtained either through the esterification of glycerol with fatty acids or by the transesterification of fatty acid triglyceride with glycerol. In both processes, a mixture of mono-, di- and triglycerides is obtained at variable proportions, depending on process conditions and chemical properties of the reactants used.

For the esterification route, the use of strong mineral or organic acid catalysts like para-toluene sulphonic acid (PTSA) or H_2SO_4 is usually involved. However, there are some drawbacks for these types of homogeneous catalyst, especially from the safety and environmental aspects such as excessive waste generation, corrosiveness, chemical hazards of waste catalysts etc. These are critical if the products were to be used for edible purposes. A number of solid acids have been used as catalysts for the fatty acid esterification of glycerol in order to avoid the problems associated to the use of homogeneous catalysts just described. Recently, some studies involving alternative heterogeneous catalytic routes have been reported. These include glycerol esterification with lauric and oleic acids using solid cationic resins [Abro et al., 1997], zeolitic molecular sieves [Heykants et al., 1996 ; Machado et al., 2000], sulfated iron oxide [Guner et al., 1996], functionalized mesoporous materials [Bossaert et al., 1999], multi valent metal salts [Nakamura et al., 2008] and heterogenized sulfonic acids over MCM-41 [Díaz et al., 2005] as catalysts. However, the problems associated with low catalytic activity and low selectivity towards the desired product still remains unsatisfactorily solved.

In the strategy to improve the monoglyceride selectivity, several attempts have already been made in order to tune the hydrophilicity of the catalyst. MCM-41 functionalised with amines have been used to perform glycidol esterification [Cauvel et al., 1997]. As that reagent had only one hydroxyl function, monoglyceride was reported to be obtained with relatively high yield. Barrault et al. [2004] synthesized less hydrophilic supports like pure silica MCM-41 which could be used to increase the

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Catalytic Technology for Carbon Dioxide Reforming of Methane to Synthesis Gas

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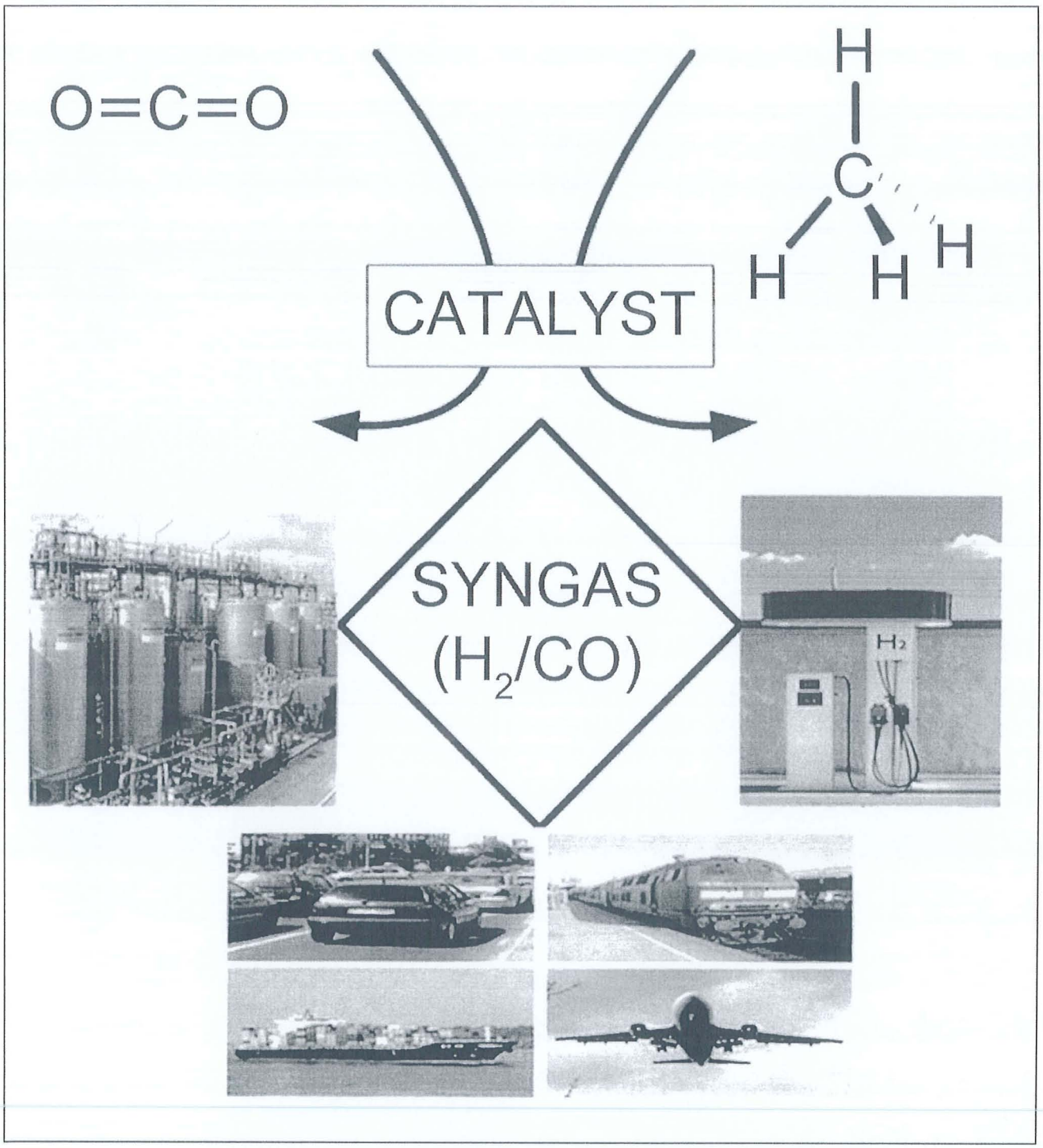

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OPTIMIZATION OF THE SELECTIVE CATALYTIC REDUCTION OF NO IN DIESEL EXHAUST OVER CU-ZN/ZSM-5 CATALYST USING CENTRAL COMPOSITE DESIGN

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ABSTRACT : The optimization of the operating conditions in nitric oxide (NO) selective catalytic reduction (SCR) process over Cu-Zn/ZSM-5 bimetallic catalyst using combined Response Surface Methodology (RSM) and Central Composite Design (CCD) is reported. A bimetallic catalyst containing 6 wt. % Cu and 8 wt. % Zn was prepared through a combined impregnation and ion-exchange process. The process conditions investigated were temperature (300 - 400 °C), NO concentration (900-2,000 ppm) and iso-butane (reductant) concentration (900 - 2,000 ppm). The weight hourly space velocity (WHSV) was fixed at 13,000 h^{-1}. Cu-Zn/ZSM-5 catalyst proved its potential for the SCR process. Statistical analyses showed that the NO reduction was affected by all the operating conditions with the temperature as the most dominant one. Based on the experimental design, a second order mathematical model was successfully developed and satisfactory fitting to the experimental data was demonstrated. Interactions between variables were also analyzed at 99.99 % confidence level. The optimum conditions obtained were 624 ppm for the NO concentration, 2,440 ppm for the iso-butane concentration and 389 °C for the reaction temperature to give a corresponding NO reduction of 96.13 %.

KEYWORDS: *SCR; gases; catalysis; zeolite; Central Composite Design; optimization.*

5. INTRODUCTION

Diesel-powered engines always offer better fuel economy than stoichiometric gasoline engines because of the lean-burn conditions at high pressure that yield higher combustion temperatures [1-3]. However, diesel engine exhaust has many adverse environmental effects, particularly due to the emission of nitrogen oxides (NOx). NOx directly involve in the formation of irritating ground level ozone. Their reactions with other chemicals present in the air also lead to the formation of other toxic chemicals such as nitrate particles and acid aerosols [4]. The lean-burn conditions also produce an exhaust containing high concentration of oxygen. Such an oxidative environment complicates conventional approaches to chemically reduce NOx to environmentally benign nitrogen gas [5].

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Selective Glycerol Esterification Over Organomontmorillonite Catalysts

(Pengesteran Gliserol yang Terpilih Menggunakan Pemangkin Organomontmorillonite)

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ABSTRACT

Organomontmorillonites were synthesized by grafting cationic surfactants i.e quaternary ammonium compounds into the interlayer space and were characterized using XRD, FTIR and N_2 adsorption/ desorption analysis. The organomontmorillonites were applied as catalyst for the esterification of glycerol (GL) with lauric acid (LA). The catalyst which had symmetrical onium salts (tetrabuthylammoniumbromide, TBAB) gave higher activity than that of unsymmetrical onium salts (cetyltrimethylammoniumbromide, CTAB). Over the TBAB-montmorillonite catalyst, glycerol monolaurate was obtained with a selectivity of about 80%, a lauric acid conversion of about 71% and a glycerol monolaurate yield of about 57%.

Keywords: Esterification; lauric acid; monoglyceride; montmorillonite; reaction

ABSTRAK

Organomontmorillonite telah disintesis melalui percantuman penuka-pemuka kation iaitu sebatian ammonia kuartener kepada ruang lapisan-antara dan dicirikan menggunakan analisis XRD, FTIR dan jerapan/penyahjerapan N_2. Organomontmorillonite ini telah digunakan sebagai mangkin bagi pengesteran gliserol (GL) dengan asid laurik (LA). Pemangkin yang mempunyai garam-garam onium simetri (tetrabuthylammoniumbromide, TBAB) memberikan aktiviti yang lebih tinggi berbanding pemangkin yang mempunyai garam-garam onium tak simetri (cetyltrimethylammoniumbromide, CTAB). Melalui pemangkin TBAB-montmorillonite, gliserol monolaurat telah diperolehi dengan kememilihan sebanyak 80%, penukaran asid laurik sekitar 71% dan hasilan gliserol monolaurate sekitar 57%.

Kata kunci: Asid laurik; monogliserida; montmorillonite; pengesteran; tindak balas

INTRODUCTION

In the last decade, renewable raw materials have become very important in the search for a sustainable chemistry. Vegetable oils and fats are the largest source of renewable raw materials used in the chemical industry. The most important benefits from oleochemicals are their biodegradability and nontoxic characters, which allow the preparation of environmentally friendly surfactants.

Malaysia is the world's leading producer of palm oil. This industry promotes several downstream industries among which are oleochemical and biodiesel industries. The main reactions used in oleochemistry are the hydrolysis or the methanolysis of triglycerides leading to glycerol and fatty acids or fatty methyl esters. However, as these reactions also lead to the formation of glycerol and there is an urgent need to find valuable applications for this low value side-product.

The glycerol transformation into glycerol monoesters (monoglycerides) has significant applications in food, pharmaceutical, cosmetics or in detergent chemistry (Lauridsen 1976). The monoglycerides are generally obtained from: (1) the glycerolysis of triglycerides, (2) the hydrolysis of triglycerides or (3) the direct esterification of glycerol with fatty acids (Figure 1). The current industrial processes for monoester production lead to blends of mono-, di- and even some tri-glycerides, and dissolved glycerol. These blends typically contain 40–60% monoglyceride, and 35–45% diglycerides. However, as the emulsifying properties of diesters are poor and the surface properties of the blends relies upon their monoester content. Therefore, for many applications, energy consuming vacuum molecular distillation has to be used to raise the monoglyceride content up to ~90 %. Another drawback of current processes is the generation of waste chemicals due to the need to neutralise and remove the catalysts used in the reaction, either basic or acid.

A number of solid acids have been used as catalysts for the fatty acid esterification of glycerol in order to avoid the problems associated with the use of homogeneous catalysts. The development of alternative catalysts for the esterification, which have high activity, high productivity, and easy recovery without severe environmental pollution, is the emerging topics concerning the aspect of the green-chemical processes. Recently, some studies involving alternative heterogeneous catalytic routes have been reported such as the glycerol esterification with lauric and

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Effect of annealing temperature on the characteristics, sonocatalytic activity and reusability of nanotubes TiO_2 in the degradation of Rhodamine B

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ABSTRACT

Titanium dioxide nanotubes (TiO_2 NTs) were synthesized via combined sol–gel and hydrothermal method and annealed at various temperatures. The morphology and crystalline structures of the prepared TiO_2 NTs were characterized using scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS), transmission electron microscope (TEM), X-ray diffraction (XRD) and surface area analyzer. The sonocatalytic activity of the prepared TiO_2 NTs was evaluated based on sonocatalytic degradation of Rhodamine B in aqueous solution. Effects of annealing temperature were successfully elucidated and TiO_2 NTs annealed at 300 °C had the highest surface area and pore volume. Its sonocatalytic activity could increase by a factor of 3.7 times as compared to the conventional TiO_2 powder. Sonocatalytic activity of the annealed TiO_2 NTs decreased with increasing annealing temperature above 300 °C due to the destruction of tubular structure, a decrease in the surface area and pore volume and phase transformation from anatase to rutile. Reusability study did not reveal any significant drop in the efficiency for 4 successive cycles under investigation. The morphology, catalyst composition, specific surface area, pore size and pore volume were also investigated after each catalytic cycle.

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1. Introduction

Chemical effect of ultrasound results from the phenomenon of acoustic cavitation which consists of the formation (nucleation), rapid growth (expansion) and violent collapse (implosion) of cavitation bubbles in a liquid [1]. Cavitation bubbles are generated during rarefaction cycles where negative acoustic pressure is sufficient to pull water molecules from each other to create tiny microbubbles [2]. The collapse of these cavitation bubbles could generate local high temperatures (up to 5000 K) and high pressures (above 1000 atm). Under such extreme conditions, the locally generated hot spots will be capable of sonolyzing water (H_2O) molecules to produce highly reactive species including hydroxyl (•OH), hydrogen (•H) and hydroperoxyl (•OOH) radicals [3,4]. These radicals are capable of initiating and promoting transformation reactions to mineralize organic pollutants.

The similarity between photocatalytic and sonocatalytic processes is the requirement to restrain the recombination of electron–hole pairs for enhancing the catalytic activity of semiconductor catalysts [5–7]. Sonocatalytic process occurs based on the sufficient energy obtained from acoustic cavitation which equals to or is greater than the semiconductor bandgap energy. This will lead to the excitation of electrons from the valence band and their subsequent transfer to the conduction band, leaving behind holes at the valence band [6]. The holes will then cause oxidation reactions of adsorbed organic compounds or of organic compounds that are in close proximity to the surface of the semiconductor. The major difference between photocatalytic and sonocatalytic processes is the type of energy source that leads to the formation of free radicals to initiate the oxidation reactions [4].

However, low penetrability of UV light in water medium (limited to several millimeters), high photocatalyst loading and the screening effect by the catalyst could limit the excitation of electrons and the success in actual wastewater treatment system [4,6]. The problem of spatial limitations can be eliminated when ultrasonic irradiation is used as the energy source. Moreover, the sonochemical degradation process can transform organic compounds through either oxidation with •OH radicals or high-temperature pyrolysis reactions inside cavitation bubbles. The sonochemical and pyrolytic degradation mechanisms are usually reported to be significant at high ultrasonic frequency and power. Meanwhile, non-volatile or hydrophilic organic compounds such as Rhodamine B are more difficult to be oxidized inside cavitation bubbles. Thus, it is mostly likely to be degraded by •OH radicals at the bubble surface or in the bulk solution [8–10].

Titanium dioxide (TiO_2) is the common catalyst used in photocatalytic and sonocatalytic oxidation processes to degrade organic pollutants due to its excellent physical and chemical properties

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Research note

Simple Kinetic Modeling of Selective Reduction of Nitric Oxide in Diesel Exhaust Over Cu-Zn/ZSM-5 Monolithic Catalyst

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Abstract

An integral reactor-based kinetic model for the selective reduction of nitric oxide over Cu-Zn/ZSM-5 washcoated monolithic catalysts is reported. The active component was washcoated onto a 400 cpsi ceramic monolithic substrate at a loading of 23.6 wt. % usage. 2,000 ppm iso-butane was used as the reductant. High activity without significant pressure drop was achieved at a GHSV of 16,000 h^{-1}. Third order polynomial satisfactorily fitted the activity versus space time data and a low activation energy of + 30.3 kJ/mol was obtained. The applicability of the model was demonstrated within 300-400 °C and space time of 0.12-0.94 s.

Keywords: *NO, Selective Catalytic Reduction, Monolith Cu-Zn/ZSM-5, Kinetics, Integral reactor*

Introduction

Despite its popularity to high fuel efficiency, reliability and cheaper fuel, diesel engines produce a significant amount of NOx which causes environmental and health problems. Selective catalytic reduction (SCR) is a plausible method for NOx removal [1], but high pressure drop that can affect the performance of the engines is always a key issue [2]. Thus, monolithic catalysts are recently gaining interest for application in NOx reduction [1, 2] as the pressure drop is much lower than that caused by particulate catalysts. For this reason, the monolithic reactor should be able to handle high throughput or, in other words, the handling of higher volumetric gas flow is possible without experiencing a significant pressure drop.

The main drawback of a monolithic catalyst is low available surface area to provide a fast reaction. However, the specific surface area of the monolithic catalyst can be enhanced up to about 40 m^2/g by washcoating with suitable porous materials such as zeolites. ZSM-5-washcoated monolithic catalysts are receiving attention in the SCR of NOx applications [2, 3]. Bimetallic Cu and Zn has been demonstrated to be beneficial towards achieving improved activity and stability of

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Comparison of sonocatalytic activities on the degradation of Rhodamine B in the presence of TiO_2 powder and nanotubes

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Abstract-**Titanium dioxide (TiO_2) powder and nanotubes (NTs) were used as the catalysts for sonocatalytic degradation of Rhodamine B in aqueous solution. The effect of parameters such as initial concentration of between 50-150 mg/l, catalyst loading of between 0.5-3.0 g/l, hydrogen peroxide (H_2O_2) concentration up to 16 mM and ultrasonic power 20-100 W at 35 kHz had been investigated and the optimum condition for sonocatalytic degradation Rhodamine B had been establish. Higher sonocatalytic degradation efficiency of Rhodamine B can be achieved through TiO_2 nanotubes as compared to TiO_2 powder. The highest degradation efficiency of Rhodamine B occurred at the initial concentration of 50 mg/l, 2.0 g/L of TiO_2 NTs, 8 mM of H_2O_2, ultrasonic power of 50 W with the presence of air flow which give the efficiency of above 85 % in 120 min.**

I. INTRODUCTION

Presently, there is over 7 x 10^5 tons annual worldwide production of dyes has been reported in the literature and it is estimated that 10–15 % of the dyestuff is lost in the effluent during the dyeing processes [1]. Methods such as coagulation, filtration and adsorption by activated carbon are only able to transfer the organic pollutants from one phase to another [2]. Therefore, a lot of studies have been dedicated to treat this wastewater by using advanced oxidation process which involves hydroxyl (•OH) radicals to mineralize the organic compounds.

The method of ultrasonic irradiation is usually used to treat some dyestuff wastewaters owing to its advantages such as cleanness, high efficiency and non-secondary pollution generated [3]. Application of ultrasounds in water will cause the chemical effect of acoustic cavitation which represented by the formation, growth and implosive collapse of cavities. The temperature and pressure could rise up to 5000 K and 100 MPa, respectively inside the cavitation bubbles [1, 4]. Under such extremely condition, H_2O molecules were sonolysed to form some reactive radicals such as •OH, •H and •OOH.

In the sonocatalytic degradation of organic dye, the TiO_2 was used as sonocatalyst because of its biological and chemical properties such as high catalytic activity, high chemical stability, inexpensive and low toxicity [3, 5]. Many researchers have shown that the presence of TiO_2 could increase the sonocatalytic degradation of organic pollutants [1, 3, 6]. Recently, there are a few studies using modification of TiO_2 such as mixing with other elements (rare metals, rare-earth metals) through doping or composite method in order to restrain the recombination of generated holes and electron pairs in addition to reduce the energy band gap of anatase TiO_2 powder [7-9]. This could enhance the sonocatalytic degradation efficiency of organic dyes.

To our knowledge, sonocatalytic degradation using titanium dioxide nanotubes (TiO_2 NTs) have not been reported yet. In this work, the TiO_2 NTs were prepared by the combination of sol–gel process with hydrothermal treatment before treating the organic dye in aqueous solution under ultrasonic irradiation. TiO_2 in the form of nanotubes have improved properties compared to TiO_2 powder such as high aspect ratio, high surface to volume ratio, high sedimentation rate and versatile chemistry with the conventional advantages and properties of TiO_2 [10, 11]. These special features provide more channels for enhanced electron transfer and interpenetration of holes transport materials, thereby helping to increase the degradation efficiency.

II. APPROACH AND METHODS

A. *Materials and apparatus*

Rhodamine B was obtained from Sigma-Aldrich as commercially available dye. Hydrochloric acid, HCl 37 %, sodium hydroxide, NaOH (99 % purity), tetra-n-butyl-orthotitanate, $C_{16}H_{36}O_4Ti$ or $Ti(OBu)_4$ for synthesis (≥98 % purity), ethanol, CH_3CH_2OH (96 % extra purity), hydrogen peroxide solution, H_2O_2 (30 % w/w) were obtained from Merck. Potassium hydroxide, KOH (≥98 % purity) was purchased from System Chemical Company. The ultrasonic irradiation source was obtained from an ultrasonic bath (Elma Transsonic series TI-H5), which was operated at frequency of 35 kHz and effective power output up to 100 W through manual adjusting. A general schematic diagram of experimental scheme is illustrated in Fig. 1. The experimental conditions adopted throughout the whole experiments were initial dyes concentration of 50 mg/L, 2 g/L of TiO_2 amount and neutral initial pH unless other conditions is noted. The concentrations of the samples were determined using Aquamate™ Plus UV–vis spectrophotometer (Thermo Scientific Company) to monitor the degradation of Rhodamine B.

B. *Procedures*

TiO_2 powder was prepared using the sol–gel and subjected to the heat-treatment. $Ti(OBu)_4$ was dissolved in ethanol solution with a volume ratio of 4:1 for 1 h under constant stirring [5]. Then, a known quantity of 0.1 M HCl was added to control the pH of solution to prevent the precipitation of TiO_2. The mixture was hydrolyzed at room

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Post Synthetically Functionalized SBA-15 with Organosulfonic Acid and Sulfated Zirconia for Esterification of Glycerol to Monoglyceride

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Abstract: The pore structural properties and catalytic activity of SBA-15 post synthetically functionalized with organo sulfonic acid and with sulfated zirconia are presented. The SBA-15 incorporated with 3-(mercaptopropyl) trimethoxysilane (MPTMS) was prepared by post synthesis-grafting. Mild oxidation was carried out to obtain an acid catalyst (HSO_3SBA-15). Whilst SBA-15 immobilized with sulfated zirconia was prepared by reacting SBA-15 with solution of zirconiumoxychloride and urea at 90°C to ZrO_2-SBA-15. SZSBA-15 acid catalyst was obtained by sulfation of the ZrO_2-SBA-15 with H_2SO_4 solution at room temperature. The catalysts were characterized by surface area analysis, EDX, SEM, Fourier transform infrared (FTIR) spectroscopy and pulse chemisorptions of NH_3, followed by TPD of NH_3. The organo sulfonic acid functionalized SBA-15 catalysts (HSO_3SBA-15) were found to be more efficient solid acid catalysts for the esterification of glycerol with lauric acid to monolaurin at 160°C for 6 h using molar ratio of fatty acid to glycerol of 1:4. Excellent lauric acid conversion (94%) with high selectivity to monolaurin (70%) can be achieved using organo sulfonic acid functionalized SBA-15 catalyst with preparation condition of 20 h reflux time and MPTMS amount of 1 mL g^{-1} SBA-15.

Key words: SBA-15, post synthesis functionalization, organosulfonic acid, sulfated zirconia, glycerol, monoglyceride production

INTRODUCTION

Glycerol is a key co-product of biodiesel industry. Presently, rapid increase in biodiesel production is followed by an excess of glycerol generated. The oversupply of glycerol reduces its price. The low cost and the increase in glycerol availability make it attractive to exploit glycerol for synthesis of valuable products. For example, glycerol has been converted into high yield of 1,2-propanediol in the presence of Pt impregnated NaY zeolite as a catalyst and acrolein has been synthesized via dehydration of glycerol performed on a WO_3/ZrO_2 catalyst in a continuous flow fixed bed reactor (Ulgen and Hoelderich, 2009). Glycerol is also used for commercial production of monoglyceride through transesterification of glycerol with fat (triglyceride) or with Fatty Acid Methyl Ester (FAME) using homogeneous basic catalyst. Besides of that, monoglyceride is also produced industrially via esterification of glycerol with fatty acid.

Currently, direct esterification of glycerols with fatty acids for monoglyceride production relies on homogeneous catalysts typically strong mineral acids (Corma and Kumar, 1998; Formo, 1958). However, this technology creates large amounts of by- products and waste and utilizes high energy (Nakamura *et al*., 2008). Solid acid catalysts can offer advantages in the process design and may improve yield and selectivity to the desired product (Corma *et al*., 2005).

Acidic resins and zeolites have been used as solid acid catalyst for this application (Pouilloux *et al*., 1999; Aracil *et al*., 1992; Heykants *et al*., 1997). However, they were unfavorable for the monoglyceride production due to small pore diameter less than 8 Å, which makes them unsuitable for reactions involving the bulky molecule like fatty acid for monoglyceride formation (Perez-Pariente *et al*., 2003). On the other hand, MFI zeolite loaded with Pt was useful for fatty acid chemistry i.e., hydrogenating methyl elaidate (trans isomer) from an equimolar mixture with methyl oleate (cis isomer) as recently reported in the literature (Philippaerts *et al*., 2010). According to Wilson and Clark (2000), the effective solid acids having pore sizes between 20-100 Å were required for liquid phase reactions

Mesoporous silica SBA-15 having surface area (500-1500 $m^2 g^{-1}$), large pore size (50-100 Å) with narrow pore size distribution and thermal stability has been incorporated with sulfated zirconia on their surface to generate solid acid catalyst via direct synthesis or post synthesis route. It exhibited high activity for esterification reactions such as reaction of fatty acid with methanol for

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Utilization of greenhouse gases through carbon dioxide reforming of methane over Ni–Co/MgO–ZrO_2: Preparation, characterization and activity studies

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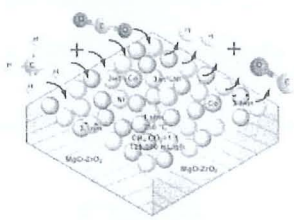
Abstract

MgO–ZrO_2 mesoporous support (Zr/Mg molar ratio = 9) impregnated with 6 wt% Ni, 6 wt% Co and 3 wt% of both Ni and Co were prepared using a novel surfactant assisted-impregnation method. Carbon dioxide reforming of methane using these catalysts was studied in a quartz tube microreactor at a CH_4/CO_2 feed ratio of 1, 750 °C, 1 atm with a gas hourly space velocity of 125,000 mL/g/h. Based on reactant's conversion and syngas production, the bimetallic catalyst was the most suitable catalyst for the reaction. The catalyst exhibited high and constant activity during 40 h reaction time with methane and carbon dioxide conversions of 80% and 84%, respectively with a syngas ratio close to unity without significant deactivation as compared to the respective monometallic catalysts. For longer time on stream, the catalyst showed constant activity up to 60 h after which it gradually decreased. The bimetallic catalyst also exhibited excellent regenerability by restoring its initial catalytic activity after 1 h of regeneration in air. The catalysts were also characterized by XRD, XPS, N_2-physisorption, H_2-chemisorption, TGA-DTA, HRTEM, H_2-TPR, TPH and SEM. The high performance of the bimetallic catalyst was due to the stabilization of t-phase in zirconia, better metal dispersion, small metal particle size and synergetic effect between Ni and Co particles. The XPS results showed that bimetallic catalyst had the ability to hinder metal oxidation and exhibited presence of higher surface basicity which were responsible to maintain the stability of the catalyst.

Graphical abstract



Research highlights

▸ Greenhouse gases utilization in the production of syngas (CO + H_2 mixture). ▸ Bimetallic catalyst (Ni–Co) supported on binary support (MgO–ZrO_2). ▸ High metal dispersion and nano-size metal particle on the surface. ▸ High conversion of reactants and syngas ratio of unity.

Keywords: Nickel–cobalt catalyst; MgO–ZrO_2 support; Carbon dioxide reforming; Methane; Syngas

Article Outline

1. Introduction

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Reactive dye degradation by combined Fe(III)/TiO_2 catalyst and ultrasonic irradiation: Effect of Fe(III) loading and calcination temperature

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ABSTRACT

The development of Fe(III)/TiO_2 catalysts for sonocatalytic degradation of Reactive Blue 4 (RB4) dye in water was carried out using sol–gel method. Their surface morphology, phase transformation and surface characteristics were studied using SEM, XRD and surface analyzer, respectively. Phase transformation from amorphous to anatase occurred at 500 °C and transformation of anatase to rutile phase occurred at 700 °C. Complete rutile phase was formed at 900 °C with corresponding increase in the particle size. Increasing in Fe(III) loading led to a reduction in the anatase phase and with the formation of weaker and broader of diffraction peaks. Surface morphology of the prepared catalyst was clearly observed with increasing calcination temperature. Surface area of the prepared catalyst decreased with increasing calcination temperature or increasing Fe(III) loading. The combination of 0.4 mol% of Fe(III)/TiO_2 with ultrasonic irradiation gave the highest sonocatalytic activity in the removal of RB4 from the aqueous solution. On the other hand, the presence of even small amount of rutile inhibited the catalytic activity of catalyst. 1.5 g/L was the optimum amount of catalyst that led to the highest sonocatalytic degradation of RB4 with an efficiency of 90%. Aeration significantly accelerated the reaction rate. Higher removal at 96% could be achieved with the combination of 0.4Fe(III)/TiO_2 and aeration under ultrasonic irradiation.

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1. Introduction

Water pollution by organic dyestuffs occurs when the effluents are directly released into the receiving bodies without proper treatment. Generally, many treatment processes have difficulty in meeting wastewater discharge limits, particularly with regard to dissolved solids, ionic salts, pH, COD, color, and sometimes, heavy metals [1]. A wide range of methods [2–5] have been developed for the elimination or mineralization of organic dyes from wastewater in order to minimize their impact towards environment. The most commonly used method is by adsorption on activated carbon. This method is claimed as a relatively cheap method and can reach high adsorption capacities of the organic dyes. Unfortunately, this method does not degrade the molecules and just decolorizes the substances by adsorbing it into the activated carbon. The accumulation of spent activated carbon creates secondary pollution and its regeneration is generally not so effective and causes high operational cost. Other methods such as biological treatment are time consuming whereby longer time is needed for the pollutants to be removed.

In order to overcome these weaknesses, advanced oxidation processes (AOPs) such as ozonation, peroxone, photocatalysis, Fenton and a combination of photo-Fenton, UV/O_3, UV/H_2O_2 have been widely developed [6]. Fenton process is consider as the simplest advanced oxidation process as it uses a combination of hydrogen peroxide (H_2O_2) and Fe(III) or Fe(II) ions. Compared with other AOPs reagents, this method is less expensive and the process is relatively easy to be operated and maintained. Therefore, it is always being chosen to degrade dyes in wastewater. However, due to some drawbacks of this process, a new technology in treating dyes wastewater is urgently needed. This is because ferrous ions are consumed very rapidly and they cannot be regenerated. As a result, more Fe(III) or Fe(II) ions dosage is needed to keep the production of hydroxyl radicals at the desired levels so that the degradation efficiency can be maintained. This results in a large amount of ferric hydroxide sludge during neutralization stage of the Fenton process which requires additional separation process and disposal.

Considerable research and development works have been carried out to resolve the long standing problem of dyeing. Ultrasonic irradiation is found to be the most attractive and suitable system in decolorization and mineralization of organic dyes [7–11]. This method not only decolorizes the color of organic dyes but active radicals generated from sonication could decompose dye molecule structures to achieve complete degradation. The generation of active radicals such as ·OH and ·H is caused by the dissociation of H_2O molecules that is associated with high temperature and

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High sensitivity and fast response SnO_2 and La-SnO_2 catalytic pellet sensors in detecting volatile organic compounds

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ABSTRACT

The characteristic and effectiveness of pure and modified tin dioxide catalytic pellets as volatile organic compound sensors are discussed. The pure and La-doped SnO_2 thick film sensor pellets exhibited highest sensitivity to ethanol, methanol and acetone vapour at sensing temperature 300 °C. The highest sensitivity towards 500 ppm of ethanol, acetone and methanol was achieved by 5 at.% of La-doped SnO_2 with values of ~57, ~55 and ~59, respectively. The enhancement of the sensitivity of La-doped SnO_2 can be explained by the increase of surface areas; decrease of crystallites sizes and the basicity of the lanthanum dopants. The response times for the developed sensors were about 13–15 s for both pure SnO_2 and La-doped SnO_2 illustrated a fast response sensor that could be used as VOC sensors.

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Keywords: Sol–gel; Tin dioxide; Lanthanum; VOCs sensor

1. Introduction

Semiconductor based materials have shown a great potential for wide range of applications (Capone et al., 2003). Metal oxides such as SnO_2, ZnO, WO_3 and TiO_2 have been reported to be applicable as gas sensors (Alessandri et al., 2007; Khadayate et al., 2007; Zhao et al., 2006; Zhu et al., 2004). Among these, tin dioxide SnO_2 has been proven to be the most attractive metal oxide for gas sensor application, owing to its chemical stability and gas sensitivity (Bakrania and Wooldridge, 2009; Yuasa et al., 2009). It is known that by modifying the metal element or by doping of noble metals such as Pt, Pd or rare earth metal, the sensitivity and selectivity toward certain gases can be enhanced (Bakar et al., 2008; Choi et al., 2008; Senguttuvan et al., 2007; Vaishanv et al., 2006). These dopants act as catalysts, and surface sites for adsorption of oxygen. They promote porosity improvement, thermal stability and gas sensing characteristics of gas sensing matrix (Korotcenkov et al., 2004).

Lanthanum oxide was chosen in this study as the catalytically active material because it has been reported to be a promising promoter for SnO_2-based C_2H_5OH sensors (Shi et al., 2009; Van Hieu et al., 2008). It is well known that the catalytic properties of semiconductor metal oxides gas sensor are strongly related to their acid/base characteristics (Weber et al., 2008). SnO_2 is a predominantly acidic oxide (isoelectronic point, i_{ep} = 4–7), while the rare earth oxide La_2O_3 is basic ($i_{ep}La_2O_3$ = 10–12) (Reed, 1995). The La-doped SnO_2 has become the preferred choice due to the electronegativity of the cation present in system (and thereby automatically related to the acid/base characteristics) (Weber et al., 2008). La^{3+} is grouped into low negativity cation which can enhance the sensitivity of the sensor. Results from previous studies show that ethanol, for example can undergo 2 different types of oxidation; dehydration and dehydrogenation, depending on the chemical characteristic of the catalyst. If the catalyst is an acidic oxide, dehydration predominates, and if it is a basic oxide, dehydrogenation is likely to occur (Seal and Shukla, 2002; Weber et al., 2008). Therefore, dehydrogenation route is highly favorable and the sensitivity of a sensor increases when SnO_2 is doped with basic oxide La_2O_3. Although it is understood that La-doped SnO_2 enhance ethanol vapour detection, the effect of La-doped SnO_2 in sensing of other VOCs, however, remained unclear.

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Optimization of sonocatalytic degradation of Rhodamine B in aqueous solution in the presence of TiO_2 nanotubes using response surface methodology

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ABSTRACT

Efficiency in the sonocatalytic degradation of Rhodamine B dye catalyzed by TiO_2 nanotubes as a function of initial concentration of dye, catalyst amount and power of ultrasonic irradiation at a frequency of 35 kHz was studied. A central composite design (CCD) was used for response surface modeling to evaluate the combined effects of these variables as well as to optimize the degradation efficiency of Rhodamine B. Satisfactory prediction based on a second-order model with high coefficient of determination (R^2) of 0.98 was achieved for the optimized sonocatalytic degradation process. Lastly, the significance and adequacy of the model were analyzed using analysis of variance (ANOVA). The optimal conditions for sonocatalytic degradation efficiency of Rhodamine B were found at 44.8 mg/L of Rhodamine B, 2.14 g/L of TiO_2 nanotubes and ultrasonic power of 68.9 W to achieve 94.6% dye removal under ultrasonic irradiation in 3 h. The significance of the findings at a confidence level of 95% was demonstrated. It was found that ultrasonic power, initial dye concentration and interaction between dye concentration and catalyst loading had important effects in the sonocatalytic degradation efficiency of the Rhodamine B by TiO_2 nanotubes.

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1. Introduction

The annual production of organic dyes in the world is currently reported to be more than 700,000 tons and a significant portion of this amount will go to textile industry [1]. Considering water consumption utilized per kilogram of textile product which is around 100–200 L coupled with the wastewater generated from dyeing and finishing operations, textile industry is rated as one of the most polluting industries [2]. It is estimated that about 10–30% of the total world production of dyes is lost during the dyeing process and released together with effluents [2,3]. Rhodamine B is a basic dye of the xanthene class. It is widely used in industrial purposes and capable to causes irritation to the skin, eyes, gastrointestinal tract and respiratory tract [4]. Therefore, treatment of dye-containing effluents, i.e. Rhodamine B is a topic of significant interest among researchers.

A lot of studies have been dedicated to treat and neutralize these wastewater by using advanced oxidation process (AOP) through the generation of highly reactive hydroxyl (•OH) radicals to mineralize the harmful organic compounds. Among the AOPs, sonocatalytic degradation of organic dyes has appeared as an emerging destructive technology. This oxidation process has strong penetration ability even in colored effluent [5]. Ultrasonic irradiation in the frequency range of 30–1000 kHz will result in the formation, growth and implosive collapse of cavities in a liquid. Subsequently, many local hot spots with extreme conditions (≈5,000 K and ≈1,000 atm) are generated [4,6]. Under such extremely high temperature and pressure, acoustic cavitation is able to provide sufficient energy to produce many holes and create many •OH radicals to attack and degrade the organic compounds.

Many researchers have shown that the presence of TiO_2 nanoparticles could increase the sonocatalytic degradation of organic pollutants [3,5]. The potential applications of TiO_2 nanotubes as photocatalysts have attracted much attention in recent years [7–9]. However, the performance of TiO_2 nanotubes on the ultrasonic-assisted degradation of organics dyes is hardly reported in previous publications. Sonocatalytic degradation using titanium dioxide (TiO_2) nanotubes has been recently investigated and it showed remarkable improvement in the degradation efficiency of Rhodamine B as compared to TiO_2 powder [10]. TiO_2 in the form of nanotubes have improved catalytic properties compared to TiO_2 powder such as high aspect ratio, high surface to volume ratio, high sedimentation rate and versatile chemistry [11,12]. The special features of TiO_2 nanotubes provide more channels for enhanced electron transfer and interpenetration of holes transport materials to help in increasing the degradation efficiency.

Recent studies on the optimization of the operational factors in a sonocatalytic reactor system to degrade organic pollutants are

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Effect of tetramethyl ammonium hydroxide on the activity of LiOH-intercalated montmorillonite catalyst in the transesterification of methyl laurate with glycerol

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ABSTRACT

Montmorillonite K10 was intercalated with lithium hydroxide (LiK10) and used as catalyst for transesterification of methyl laurate with glycerol. Effects of calcination temperature (250–650 °C) and tetramethyl ammonium hydroxide (TMAOH) addition (0.5–2.2 wt.%) on catalytic activity were particularly elucidated. Successful intercalation of Li leading to improved water hydration was demonstrated. Calcination temperatures above 450 °C could reduce the basic strength and activity of LiK10 catalyst. Significant losses of porosity and basicity were attributed to excessive loss of hydrated water. Higher basicity of the catalyst led to better reactant's conversion but poorer selectivity to glycerol monolaurate (GML). TMAOH addition improved the activity of the catalyst and selectivity to GML. At a glycerol/methyl laurate ratio of 6.5:1 and 130 °C, 40% GML yield was achieved in 5 h. The addition of 2% TMAOH increased the yield to 89.9%. An increase in reaction temperature beyond 130 °C would reduce the catalytic activity due to a decrease in the surface tension of surfactant and its partial degradation. Thus, TMAOH could significantly improve activity of LiOH–MMT catalyst with corresponding improvement in selectivity to GML.

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1. Introduction

Glycerol esters of fatty acid have important applications in food, cosmetics, pharmaceutical and textile and fiber industries due to their polyfunctional nature and emulsifying, complexing, and lubricants properties [1]. These esters are generally prepared either through hydrolysis of triglyceride, esterification of glycerol with fatty acids or by glycerolysis of triglycerides i.e. transesterification of glycerol with fatty methyl esters. Transesterification process is a base catalyzed reaction. Industrial esterification and transesterification processes generally involve the use of homogeneous acid catalyst (e.g. sulfuric, phosphoric, or organic sulfonic acid) or homogeneous basic catalysts (e.g. KOH, $NaCH_3O$ or $Ca(OH)_2$), which often leads to product mixtures containing 40–60% monoglycerides, 30–45% diglycerides, 5–15% triglycerides, 1–5%, 1–5% free fatty acids and/or their salts, and 2–10% glycerol [2]. Pure monoglycerides can generally be obtained by molecular distillation process which further raises the production cost [3]. The drawbacks associated with the use of homogeneous catalysts are the need for neutralization step, the formation of soaps, high salt content in the product and the generation of wastewater that deserves further treatment [4,5].

Several attempts have been made to minimize problems associated with the use of homogeneous catalytic process by developing heterogeneous catalyst systems. The use of solid base catalysts is a promising approach to replace alkaline homogeneous catalysts. It helps in minimizing soap formation, difficulty in product separation, corrosion and environmental problems. At laboratory scale, some studies involving solid base catalysts have been reported including MgO, CeO_2, La_2O_3, as well as alkali-doped MgO (Li/MgO and Na/MgO). These catalysts are generally found to be active catalysts for the transesterification of methyl stearate with glycerol [6–8]. The authors also reported that the nature of these oxides had small effects on monoester selectivity. Usually, active catalysts could promote the formation of di- and triglycerides to result in poor selectivity to monoglyceride. The distribution of the esters obtained was also reported to be similar to that obtained with homogeneous basic catalysts.

Corma et al. [9] reported that the glycerolysis of methyl oleate with glycerol could be carried out over solid basic catalyst such as hydrotalcites. However, Al–Li mixed oxide catalyst resulted in an active Lewis base catalyst with better performance than MgO and hydrotalcite catalysts. From this heterogeneous catalytic route, glycerol esters were obtained at a yield of 80% with 80% selectivity to monoglycerides. The main weakness with respect to this process is high reaction temperature (around 200 °C) needed to obtain reasonable activity.

Recently, there has been considerable interest to use clays to catalyze organic reactions [10]. Clays, either natural or modified,

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Process behavior of TiO_2 nanotube-enhanced sonocatalytic degradation of Rhodamine B in aqueous solution

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ABSTRACT

Sonocatalytic degradation of Rhodamine B was investigated using titanium dioxide (TiO_2) powder and titanium dioxide nanotubes (TiO_2 NTs) which were synthesized using sol–gel and hydrothermal method, respectively. Structural and crystalline information for both types of catalyst were characterized using transmission electron microscope (TEM), X-ray diffractometer (XRD) and surface analyzer. Remarkable improvement in the sonocatalytic activity of TiO_2 NTs was achieved due to their high specific surface area and unique pore system. Effects of reaction parameters such as pH (2–10), ultrasonic power (20–100 W), ultrasonic frequency (35 kHz and 130 kHz) and the presence of air flow (1 L/min) were also investigated. Under optimum conditions, i.e., with 8 millimolar (mM) of hydrogen peroxide (H_2O_2) and 1 L/min of air flow at neutral pH, 85% degradation of 50 mg/L Rhodamine B could be achieved in 120 min by the system with 2 g/L of TiO_2 NTs. The sonocatalytic process was observed to behave according to a pseudo-first-order kinetics under different experimental conditions. In conclusion, sonocatalytic degradation in the presence of TiO_2 NTs shows a great potential for the efficient treatment of organic dyes in wastewater.

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1. Introduction

The release of persistent and complex dyes with toxic, carcinogenic and mutagenic properties may cause negative impacts to human health and ecosystem. In 1974, Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) found that basic and diazo direct dyes have the highest toxicity among 4000 dyes tested [1]. Rhodamine B is a member of basic dyes. It is capable of causing irritation to the skin, eyes and respiratory tract if swallowed [2]. It is estimated that 10–15% of this dyes is lost in the effluent during dyeing process [3]. Therefore, there is a need to study the removal of Rhodamine B from polluted streams to avoid any hazardous and harmful effects towards environment and human health.

As the presence of dyes in industrial effluent is highly undesirable, many methods have been investigated for their removal. Methods such as coagulation, filtration and adsorption by activated carbon are only able to transfer the organic pollutants from one phase to another to consequently cause the release of secondary pollutants into the environment [3,4]. As such, degradation methods such as oxidation are preferred as no secondary pollutant is created. Many advanced oxidation processes (AOPs) that are able to generate highly reactive hydroxyl (•OH) radicals emerge as promising alternatives for the effective removal of recalcitrant organic pollutants from effluents. One plausible method is photocatalytic process using UV light. However, low penetrability of UV light in water medium (limited to several millimeters) leads to poor degradation efficiency and limits the success in actual wastewater treatment system [4,5]. In this respect, sonocatalytic degradation of organic pollutants appears to be a better destructive technology. Generally, it has a strong penetration ability which can usually reach 20–30 cm from the energy source [6]. Reactive radicals such as •OH, •H and •OOH generated during ultrasonic irradiation are used to oxidize and degrade the organic compounds [7].

The selection of TiO_2 is based on its biological and chemical properties such as high catalytic activity, high chemical stability, low cost and low toxicity [4,8]. Many researchers have shown that the presence of TiO_2 could increase the sonocatalytic degradation of organic pollutants [4,6,7]. However, report on sonocatalytic degradation using titanium dioxide nanotubes (TiO_2 NTs) is hardly found in the literature. In this work, TiO_2 NTs catalyst was prepared by the combination of sol–gel process with hydrothermal treatment to be used for the degradation of organic dye in aqueous solution under ultrasonic irradiation. TiO_2 in the form of nanotube has improved properties compared to TiO_2 powder such as high aspect ratio and high surface to volume ratio to result in higher specific surface area [9,10]. These special features provide more channels for enhanced electrons and holes transfer to increase the degradation efficiency. Furthermore, higher sedimentation rate of TiO_2 NTs makes the process more technically viable as the catalyst recovery and reusability will be relatively easy [8,11]. In the present study, sonocatalytic degradation of Rhodamine B (as the

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Hydrogen production from carbon dioxide reforming of methane over Ni–Co/MgO–ZrO_2 catalyst: Process optimization

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Abstract

Greenhouse gases, carbon dioxide and methane are utilized in the production of hydrogen through carbon dioxide reforming of methane catalyzed by Ni–Co/MgO–ZrO_2 catalyst. Design of Experiments (DOE) was used to study the effects of process variables such as, carbon dioxide to methane ratios (1–5), gas hourly space velocity (8400–200,000 mL/g/h), oxygen concentration in the feed (3–8 mol%) and reaction temperature (700–800 °C) over methane conversion and yield of hydrogen. The ANOVA analysis indicated that the effect of each process variable was significant to its respective responses in the proposed quadratic model. The response surface methodology (RSM) was used to find the optimum value of the process variables by maximizing the hydrogen yield in the process model. The optimum space velocity as 145,190 mL/g/h at reaction temperature 749 °C with carbon dioxide to methane ratio of 3 and 7 mol% of oxygen in the feed gave 88 mol% of CH_4 conversion and 86 mol% of hydrogen yield, respectively. The experiments were run at the optimum condition gave 87.7 mol% methane conversion and 85.5 mol% of hydrogen yield, which were in good agreement with the simulated values obtained from the model. The catalyst stability and its regeneration characteristics were studied at the optimum condition by monitoring methane conversion and hydrogen yield with time on stream.

Keywords: Response surface methodology; Carbon dioxide; Methane; Reforming; Bimetallic catalyst; Hydrogen production

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A Review: Mesoporous Santa Barbara Amorphous-15, Types, Synthesis and Its Applications towards Biorefinery Production

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Abstract: Problem statement: Santa Barbara Amorphous (SBA-15) is significant mesoporous silica with exclusive and important properties of highly ordered mesopores, hydrothermally stable and thick wall, profusely large surface area and huge pore volume which render it as promising catalyst for wide applications. However, the purely siliceous SBA-15 which lacks of acidity characteristic hinders its ideal capabilities as catalyst. Moreover, functionalization and modification of SBA-15 could enhance and optimize its catalytic activity. **Conclusion/Recommendations:** Thus, in this review, the various types and different synthesis of modifying SBA-15 are discussed in detail towards its application in biorefinery production. The catalytic activities in various operating conditions and reactions are also reviewed for future reference and scope of studies.

Key words: Mesoporous materials, biorefinery production, Santa Barbara amorphous, Tetramethyl Orthosilicate (TMOS), catalytic activity, mesoporous structure

INTRODUCTION

Mesoporous material, as defined by IUPAC nomenclature, is material with pore of free diameters in the range of 2-50 nm (McCusker *et al.*, 2003). Generally, mesoporous materials is defined with the term of host, pores and chemical composition of its host and guests (Liebau, 2003). Mesoporous materials is more preferred for its highly ordered mesostructure, apart from high surface area, which allows diffusion and adsorption of larger molecules for wide applications than that of microstructure which only limits to separation and fine chemical catalysis (Fedeyko *et al.*, 2006). Moreover, microporous material has selective thermal stability based on size and shape of cage or channel within lattice of selected organic moieties during synthesis, which restricts its potentiality to limited applications (Morey *et al.*, 1998). Mesoporous materials are widely applied in catalysis (Abdalla *et al.*, 2009), drug control delivery (Pasqua *et al.*, 2009), biosensors (Xu *et al.*, 2009b), biofuel (Ooi and Bhatia, 2007), sorption (Chang *et al.*, 2008) and membrane separation (Zornoza *et al.*, 2009). Typical compounds of mesoporous material include silica (Xia and Mokaya, 2003), alumina (Xu *et al.*, 2009a), carbon (Chen *et al.*, 2009)and transition metal oxides (Rao and Antonelli, 2009).

Silica is widely employed as main building block of mesoporous materials because it is inexpensive, thermally stable, chemically inert, harmless (Nandiyanto *et al.*, 2009) and abundantly available in the Earth's crust (Draggan, 2008). Unlike zeolitic materials which are silica self-assembles reliance upon heating, mesoporous silica is formed in the presence of self-associating molecules such as cationic surfactant for MCM-41 synthesis and block copolymers for synthesis of SBA-15 (Liebau, 2003). Figure 1 shows typical synthesis of mesoporous silica MCM-41.

Mesoporous silica was first discovered in 1990 by researchers in Japan (Yanagisawa *et al.*, 1990) and later was produced in Mobil Corporation Laboratories (Chen *et al.*, 2009) and named as M41S. MCM-41, MCM-48 and MCM-50 are among the widely known mesoporous silica in M41S family (Vartuli *et al.*, 2008) which have different methods of synthesis and applications based on instability and limitation of mesoporous structure (Tatsumi *et al.*, 1999, Zhang *et al.*, 2007).

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A Response Surface Methodology Based Modeling of Temperature Variation in an Ultrasonic-Assisted Biodiesel Production Process

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Abstract: Application of ultrasonic energy at 20 kHz transesterification of vegetable oil is reported. Effects of 5 important variables i.e. pulse on (s), pulse off (s), reaction time (min), power (%) and oil volume (ml) at a constant alcohol to palm oil molar ratio (9:1) and initial reaction temperature of 35°C were studied. A central composite design (CCD) based on response surface technology (RSM) was employed. The system reached its steady state temperature within the first few minutes. Longer pulse on and lower the pulse off at 70% of the maximum power of could bring the reaction to desired temperature for an oil volume of up to 60 ml. A model was proposed based on heat capacity of reactants for conversion of ultrasonic into heat and the steady state temperature of the system could be predicted. This model was tested with 5 types of vegetable oil including used palm oil, canola oil, sunflower oil and corn oil to study the effect of specific heat capacity of the oil. Three different types of catalyst i.e. BaO, SrO and CaO with varying heat capacities were also tested for verification and the model showed good predictions with less than 5% errors.

Key words: Ultrasonic-assisted • Transesterification process • Biodiesel • Heating effects • Response surface methodology • Process modeling

INTRODUCTION

Recently, the increasing demand on fossil fuels leading to the depletion of these resources has drawn the attention of researchers for exploring other alternative energy resources. With the current rate of crude oil consumption, the reserves could finish in less than 50 years [1]. The necessity of replacing conventional fossil fuels with an environmental friendly substitute to fulfill the increasing energy demand has been a great concern [2-4]. Recently, fatty acid methyl esters derived from renewable sources or also known as biodiesel, has been considered as an alternative fuel to be used in diesel engines [5-6]. Biodiesel fuel is produced by transesterification of vegetable oils and animal fats. This fuel is a biomass-based alternative to fossil fuels due to its specifications [7]. The properties of biodiesel depend very much on the nature of its raw material as well as the technology or process used for its production [8].

Typically, catalysts used for production of biodiesel are homogeneous based such as KOH and NaOH. This process can produce high methyl ester yield in just 1-4 h under atmospheric pressure with reaction temperatures between 50-65°C [7, 9-10]. Lately, due to environmental concerns, the interest in biodiesel production has been shifting towards the use of heterogeneous catalysts. This is due to easier catalyst removal without the need for solvents, reusability of the catalyst and less corrosive character of heterogeneous catalysts [11]. However, it usually subject to low reaction rate as compared to homogeneous ones. It is associated with their immiscibility so that the reaction between oil and alcohol in biodiesel production process can only occur at the interface of the two phases [6].

The use of ultrasonic energy to accelerate biodiesel production process has become an area of interest for many researchers [12-15]. Conventionally, mechanical stirring or agitation is used to homogenize the reactants to enhance interfacial area between the two phases [16-17]. In a conventional stirring reactor system to achieve high biodiesel yield (>90%), a temperature of 50-65°C in the presence of catalyst at 0.5-3.0 wt.% and a

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Review on sonochemical methods in the presence of catalysts and chemical additives for treatment of organic pollutants in wastewater

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ABSTRACT

Removal of toxic recalcitrant organic compounds in wastewater has become a matter of considerable interest. There has been a rapid development in a wide range of treatment methods to solve this problem. Many efforts have been devoted to improve the degradation efficiency and possible mineralization of the organic pollutants, especially in the case of hydrophilic compounds. Heterogeneous sonocatalytic degradation process involving different types of catalyst particularly titanium dioxide (TiO_2) appears to be the most promising technology. To further improve the degradation efficiency, some researchers focus on the enhancement of the catalyst by modifying it through metal ion doping or the use of composite semiconductor materials to prohibit rapid recombination of electron/hole pairs and backward reactions. Effects of the addition of chemical additives e.g. hydrogen peroxide, Fenton reagent, various types of salts and ozone have also been elucidated. Different methods for enhancing free hydroxyl radical (•OH) generation which lead to higher oxidation rates have been investigated. This paper critically reviews up-to-date technologies to be applied in conjunction with sonochemical degradation process for enhancing degradation of recalcitrant organic compounds. The addition of catalysts and chemical additives with ultrasonic irradiation are particularly reviewed as effective methods to increase the generation of free •OH.

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Effect of pH and Catalyst Dosage on the Leaching of Fe from Fe (III) Doped Zeolite Y used for Sonocatalytic Degradation of Acid Red B

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Abstract

Performance of iron loaded zeolites Y (Fe (III)/Y) catalyst, prepared by wet impregnation method with different iron loadings is addressed. Ultrasonic irradiation at low frequency (20 kHz) was used as a substitution to hydrogen peroxide sources in combination with Fe (III)/Y to degrade acid red B in aqueous solution. The prepared catalyst with 0.2 wt % of Fe (III)/Y exhibited the highest degradation efficiency (79.2 %) in 120 min of irradiation. Catalytic activity was influenced by high surface area of the catalyst and good dispersion of Fe (III) ions on the support. The degradation of acid red B was accelerated by the reaction between Fe (III) ions and hydrogen peroxide (H_2O_2) generated in-situ by the ultrasonic-mediated dissociation of water molecules. The performance was greatly affected by the initial pH of the solution.

The highest efficiency was achieved at an initial pH of 3 with 99.9% degradation in less than 60 min. By increasing the catalyst dosage from 1.5, 2.0, 2.5 to 3.0 g/L, at the condition of pH 6.8, the degradation efficiency within 120 min increased from 74.2 to 88.8 % and dramatically decreased from 78 to 77 % respectively. Leaching test was also conducted for the effect of the amount of Fe (III) loading, catalyst dosage and pH. All the prepared catalyst met the Malaysia discharge standard which requires iron content of less than 5 ppm. Lastly, the prepared catalyst also showed good structural stability which showed no significant changes in the particles size distribution before and after use.

Keywords: Sonocatalytic degradation, ultrasonic irradiation, Fe (III) doped zeolite catalyst, acid red B.

Introduction

Fenton-like reaction is an advanced oxidation process (AOPs) that emphasizes the production of highly reactive hydroxyl radicals (•OH) from a mixture of ferrous ions (Fe^{3+}) and hydrogen peroxide (H_2O_2). The reaction between the Fe (III) ions and H_2O_2 as shown in equation (1)-(4)[1] leads to the formation of complex $Fe–OOH^{2+}$. Hydroperoxyl radicals (HO_2•) formed from the $Fe–OOH^{2+}$ decomposition are much less active as compared to the •OH radicals. Thus, this is the concrete reason for the slower rate of the Fenton-like process at the beginning of the reaction. The formation of OH radicals by the decomposition of H_2O_2 by Fe^{2+} would increase the degradation performance as OH radicals are very active.

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe–OOH^{2+} + H^+ \quad (1)$$
$$Fe–OOH^{2+} \rightarrow HO_2\bullet + Fe^{2+} \quad (2)$$
$$Fe^{2+} + H_2O_2 \rightarrow \bullet OH + Fe^{3+} \quad (3)$$
$$Fe^{3+} + HO_2\bullet \leftrightarrow Fe^{2+} + O_2 + H^+ \quad (4)$$

There has been a growing interest in using this method for treating organic pollutants in the lab scale and some progress has been published in scientific journals. One of the advantages is the ability to accomplish a complete degradation and colour removal of the organic pollutant. Additionally, the Fenton's reagent used throughout the degradation reaction is considered as cheap and very simple to handle over the other AOPs such as ozonation and photocatalysis. Despite the advantages of this method, Fenton process suffers some drawbacks such as high-cost resulting from the high consumption of hydrogen peroxide, pH limitations and difficulty in separating the iron ions from the treated aqueous solution after the treatments[2]. These weaknesses hinder Fenton process from successful application in industry [3].

Since the beginning of the investigation on sonochemistry processes in 1927, a major focus has been dedicated to the ultrasonic irradiation as one of the alternative methods for the organic dyes abatement [4]. The production of oxidizing species such as hydroxyl radicals (•OH), hydrogen radicals (H•), hydroperoxyl radicals (HO_2•) and hydrogen peroxide (H_2O_2) is initiated by the collapsing bubble generated by ultrasound in water which occurs under localized high pressure and temperature. However, total mineralization of organic pollutants by means of ultrasound irradiation alone still remains a difficult task, especially for refractory organic compounds. Thus, application of ultrasound for an industrial plant is still impractical[5] since the concentration of OH radicals generated is quite low.

For these reasons, the combination of ultrasound with Fe (III) ions is considered as a convenient route in the degradation of organic dyes[5,6,7]. Thus, the addition of H_2O_2 into the dye solution can be eliminated as the presence of ultrasound itself can generate H_2O_2. Despite donating hydrogen peroxide during the reaction, ultrasound also

AIChE

A Study of NO Conversion into NO_2 and N_2O Over Co_3O_4 Catalyst

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The catalytic activity of Co_3O_4 catalyst was examined in a differential reactor for converting NO to NO_2 and N_2O. It was observed that mostly NO was oxidized to NO_2 rather than N_2O over the catalyst at temperatures above 250°C in the presence of 5% oxygen and 10% water. The maximum conversion was 71% at 300°C. However, the presence of H_2O slightly suppressed NO_2 generation due to the occupation of active sites by H_2O but no such effect was observed during N_2O generation. At calcination temperature of 300°C, the maximum activity of the catalyst for NO conversion was observed due to the sintering of the catalyst at higher temperatures. In the presence of hydrocarbon, inhibition of NO conversion was also observed. This was due to the hydrocarbon competition with NO for the active sites of the catalyst. Moreover, on comparing with other workers, the activity of NO conversion over Co_3O_4 catalyst was found to be more selective towards NO_2 generation at a wide range of temperatures resulting in less N_2O generation. The activation energy (E_a) and pre-exponential factor (A_o) values were found to be 37.7 kJ mol^{-1} and −7.26 ppm^{-2} s^{-1}. © 2011 American Institute of Chemical Engineers Environ Prog, 00: 000–000, 2011

Keywords: NO oxidation, Co_3O_4, N_2O generation, NO_2 formation, hydrocarbon

INTRODUCTION

NO_2 plays an important and decisive role in future exhaust gas treatment techniques and numerous other industrial applications. It is used as an oxidizing agent in many industrial processes especially in the production of sulfuric acid in lead chamber process. The production of nitric acid is another example in which the concentration of HNO_3 depends upon the dissolution of NO_2 in water. It also plays an important role in reducing the emission of NO_x, which are emitted from the mobile and stationary resources. Up to 50% conversion of nitric oxide in to NO_2 gives 10 times higher reaction rate compared with other reduction processes. It can also indirectly enable to reduce the SCR catalyst volume [1–3]. Another important role of NO_2 is the NO_x storage and reduction catalyst presented first by Toyota [4]. The strong oxidizing power of NO_2 is also used to continuously oxidize the soot collected on a particulate filter at comparatively low temperature in a continuously regenerating trap, as proposed by Johnson Matthey [5]. Like other nitrogen oxides, N_2O is also very important component and it is commonly used in surgery and dentistry for its anesthetic and analgesic effects. However, along with other nitrogen oxides, N_2O is also a green house gas [6, 7].

Several metal oxide catalysts such as MnO_x, CuO_x, etc. have been investigated for NO oxidation but the conversion has been found to be unsatisfactory. Misono *et al.* [8] and Qi and Yang, [9] studied a number of different oxidizing catalysts for determining their reaction activities for NO oxidation. Misono *et al.* [8] reported that Cr_2O_3 and Mn_2O_3 catalysts were more appropriate for NO conversion but they both gave nearly 53% conversion at 350°C. However, they failed to find CeO_2 and Ce (15%)-ZSM-5 appropriate ones for NO conversion. However, Qi and Yang, [9] used MnO_x, CeO_2, and mixed oxide of MnO_x (0.3)-CeO_2. They found that the mixed oxide of MnO_x (0.3)-CeO_2 was

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Effect of Calcination Temperature and Tmaoh on Catalytic Activity of Basic Clay

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Abstract: Montmorillonite K10 was intercalated with lithium hydroxide and used for the transesterification Methyl Laurate (ML) with glycerol. This modified clay was characterized to elucidate the influence of added Tetramethylammonium Hydroxide (TMAOH) on its catalytic activity. Effects of calcination temperature (350-650°C) on the catalytic properties of basic clay were investigated with the goal of determining the optimum pretreatment conditions. The basic clay calcined at 450°C exhibited the optimum activity when used together with TMAOH. The results showed that TMAOH played an important role in improving the efficiency of the basic clay. By using a glycerol/methyl laurate ratio of 8:1 without any addition of TMAOH at a temperature reaction of 130°C, 60.1% methyl laurate conversion and 56.5% selectivity to monolaurate were achieved over the LiK10 calcined at 450°C for 5 h. Meanwhile, the addition of TMAOH increased the ML conversion and selectivity to monolaurate to 82.5 and 88.2%, respectively.

Key words: Clay, LiOH-montmorillonite, transesterification, glycerol monolaurate, selective synthesis

INTRODUCTION

Monoglycerides are non ionic surfactants which have important applications as emulsifier in food, pharmaceutical and cosmetics production due to their physicochemical properties, basically the hydrophilic/hydrophobic balance (Lauridsen, 1976; Ahmed *et al.*, 2000). These esters are generally manufactured on industrial scale by continuous glycerolysis of fats and oils at high temperatures (220-250°C) using alkaline catalysts under a nitrogen gas atmosphere (Sonntag, 1982). Since the required product is the highly pure monoglyceride, the mixture is molecular distilled to obtain higher monoglycerides purity (~80%) (Fregolente, 2007).

A number of solid bases have been used as catalysts for the transesterification of glycerol in order to avoid drawbacks associated with the use of homogeneous catalysts such as low yield, dark color and burnt taste. Abro *et al.* (1997) and Barrault *et al.* (2004) showed that basic solid catalysts such as MgO, CeO_2 and La_2O_3, as well as alkali-doped MgO (Li/MgO and Na/MgO) were active catalysts for the transesterification of methyl stearate with glycerol. The authors also noted that the nature of the oxide had a small effect on monoester selectivity, and that the distribution of the esters obtained was similar to that obtained with homogeneous basic catalysts.

Corma *et al.* (2005) reported that the glycerolysis of triolein with glycerol could be carried out over solid basic catalyst such as hydrotalcites. Al-Li mixed oxide resulted in an active Lewis base catalyst with better performance than MgO and hydrotalcite. From these heterogeneous catalytic routes, glycerol esters were obtained at 90% yield with 75% selectivity to onoglycerides. However, high temperature and a glycerol/triolein molar ratio of 12 were necessary to reach such results.

In its origin or modified forms, montmorillonite K 10 is a type of acidic stratified silicate mineral with a three-layer structure with an ideal chemical formula of $(Al_{2-y}Mg_y)$ Si_4O_{10} $(OH)_2 \cdot nH_2O$ which widely used as adsorbent (Fan *et al.*, 2006) as acid catalyst, or as catalyst support (Iqbal *et al.*, 1988; Choudhary *et al.*, 2004; Bahulayan *et al.*, 2003; Bokade and Yadav, 2009; Fatimah *et al.*, 2009). In its natural form, montmorillonite K 10 clay is Brønsted acidic but it can be easily made basic by treating them with a basic cation-containing solutions e.g., K_2CO_3 (Dintzner *et al.*, 2006), NaOH, KOH

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Utilization of Greenhouse Gases through Dry Reforming: Screening of Nickel-Based Bimetallic Catalysts and Kinetic Studies

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A series of bimetallic catalysts containing nickel supported over $MgO–ZrO_2$ were tested for activity in the dry reforming of carbon dioxide. A nickel–cobalt bimetallic catalyst gave the best performance in terms of conversion and coke resistance from a range of Ni–X bimetallic catalysts, X=Ca, K, Ba, La, and Ce. The nitrogen-adsorption and hydrogen-chemisorption studies showed the Ni–Co bimetallic supported catalyst to have good surface area with high metal dispersion. This contributed to the high catalytic activity, in terms of conversion activity and stability of the catalyst, at an equimolar methane/carbon dioxide feed ratio. The kinetics of methane dry reforming are studied in a fixed-bed reactor over an Ni–Co bimetallic catalyst in the temperature range 700–800 °C by varying the partial pressures of CH_4 and CO_2. The experimental data were analyzed based on the proposed reaction mechanism using the Langmuir–Hinshelwood kinetic model. The activation energies for methane and carbon dioxide consumption were estimated at 52.9 and 48.1 $kJ\,mol^{-1}$, respectively. The lower value of CO_2 activation energy compared to the activation energy of CH_4 indicated a higher reaction rate of CO_2, which owes to the strong basicity of nanocrystalline support, $MgO–ZrO_2$.

Introduction

Carbon dioxide and methane are classified globally as the main contributors of global warming.[1] Consequently, the utilization of both greenhouse gases has become an important research topic in the last few years.[2] Dry reforming of methane using carbon dioxide utilizes both greenhouse gases whilst producing the valuable chemical precursor syngas.[3] Carbon dioxide reforming, or dry reforming, produces syngas in a H_2/CO ratio close to unity, which fulfills a requirement of the Fischer–Tropsch synthesis.[4] Nickel-based catalysts are known to be active in this reaction but have limited application due to severe catalyst deactivation.[5] Recently, several researchers have reported the use of bimetallic catalysts in dry reforming, finding them to accumulate significantly reduced amounts of coke.[6] Literature for other bimetallic catalysts is limited, however, with most studies focusing on the combination of nickel and cobalt.[6c,7] We have screened a wide combination of nickel-based bimetallic catalysts, including alkaline earth metals and transition group metals. There has been progressive research in the nickel-based catalysis of dry reforming and a kinetic study for nickel bimetallic catalysis has been reported.[8] Kinetic parameters are needed for the commercialization, optimization, and scale-up of the reactor system for the dry reforming process. Whereas many research papers cover kinetic studies of monometallic catalysts, kinetic models for bimetallic catalysts are lacking in the literature.[9] We present a kinetic study of the Ni–Co/$MgO–ZrO_2$ bimetallic catalyst, which has been screened for conversion activity against various combinations of bimetallic catalysts in a partial pressure range of 45–360 kPa at reaction temperatures between 700 and 800 °C. A kinetic model has been proposed and reaction parameters of the model were determined as a function of temperature.

Experimental

Preparation of support

The magnesium oxide-zirconium oxide ($MgO–ZrO_2$) catalyst support was prepared by means of surfactant assisted-incipient wetness impregnation. Firstly, MgO was prepared through a surfactant-assisted method by dissolving polyvinyl alcohol (PVA) (R&M Chemicals, PVA, MW: 70000 $g\,mol^{-1}$, 95–98%) in water at 90 °C and under continuous stirring to form a transparent solution. $Mg(NO_3)_2{\cdot}6H_2O$ (Merck, 99%) was dissolved in aqueous PVA solution. The metal ion to PVA monomer unit mole ratio (M/PVA) was 1:3. Aqueous ammonia (Merck, analytical reagent) was added drop wise at room temperature to the resulting viscous liquid mixture under continuous stirring until pH 10-11 was reached. Following precipitation, the slurry was stirred for another 30 min and then refluxed overnight at 80 °C under continuous stirring. The mixture was then cooled to room temperature, filtered and washed with hot (60 °C) deionised water for effective removal of the PVA. The final product was dried at 80 °C for 24 h and calcined at 800 °C in a muffle furnace. The resulting MgO powder was pressed into pellets, crushed, and sieved to 250–300 μm. The sieved powder was impregnated with $ZrO(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich, 98%) through the incipient wetness technique. Aqueous solution of $ZrO(NO_3)_2{\cdot}6H_2O$ with a ZrO_2/MgO mole ratio of 9:1 was mixed with MgO powder. After impregnation, the product was dried at 110 °C for 24 h and calcined at 800 °C for 3 h. The resultant

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A RESPONSE SURFACE METHODOLOGY BASED MODELING OF TEMPERATURE VARIATION IN ULTRASONIC-ASSISTED BIODIESEL PRODUCTION PROCESS

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ABSTRACT

The use of ultrasonic energy for mixing and the subsequent conversion to heat energy in the transesterification reaction of vegetable oil is reported. Effects of 5 important variables i.e. pulse on (s), pulse off (s), reaction time (min), power (%) and oil volume (ml) at constant alcohol to palm oil molar ratio (9:1) and initial reaction temperature of 35 °C were studied. A central composite design (CCD) using response surface technology (RSM) was employed. The results indicated that the reaction time did not play much role as the system reached steady state within the first few minutes. Longer the pulse on and the lower the pulse off at 70 % of the maximum power of could bring the reaction to desired temperature for volume of up to 60 ml. A model was proposed based on heat capacity of reactants for conversion of ultrasonic into heat and the final temperature of the system could be predicted. This model was tested with 5 types of vegetable oil including used palm oil, canola oil, sunflower oil and corn oil to study the effect of specific heat capacity of the oil. Three different types of catalysts with varying heat capacities were also tested for verification of the model. The model developed showed good predictions with less than 5 % error in different conditions.

Keywords: *Ultrasonic; transesterification; immiscible reactants; heating; response surface methodology.*

1. INTRODUCTION

Recently, the increasing demand on fossil fuels leading to the depletion of these resources has drawn the attention of researchers for exploring other alternative energy resources. With the current rate of crude oil consumption, the reserves could finish in less than 50 years[1]. The necessity of replacing conventional fossil fuels with an environmental friendly substitute to fulfill the increasing energy demand has been a great concern [2-4]. Recently, fatty acid methyl esters derived from vegetable oil known as biodiesel, has been considered as an alternative fuel to be used in diesel engines [5-6]. Biodiesel fuel is produced by transesterification of vegetable oils and animal fats. This fuel is a biomass based alternative to fossil fuels due to its specifications [7]. The properties of biodiesel depend very much on the nature of its raw material as well as the technology or process used for its production [8].

Typically, catalysts used for production of biodiesel are homogeneous base catalysts such as KOH and NaOH. This process can produce high methyl ester yield under atmospheric pressure and reaction temperatures between 50-65 °C and usually takes 1-4 hours [7, 9-10]. Lately, due to environmental concerns, the interest in biodiesel production has been shifting towards the use of heterogeneous catalysts. This is due to easier catalyst removal without the need for solvents, reusability of the catalyst and less corrosive character of heterogeneous catalysts[11].

The use of ultrasonic energy for biodiesel production has become an area of interest for many researchers [6, 10, 12-15]. Because of the immiscibility of a liquid-liquid heterogeneous system, the reaction between oil and alcohol occurs at the interface of the two phases[6]. Conventionally, mechanical stirring or agitation is used to homogenize the reactants to enhance interfacial area between the two phases[2, 16-17]. In conventional method of stirring to achieve high yields (>90 %), a temperature of 50-65 °C in the presence of catalyst 0.5-3 % and reaction duration of more than 2 h are required [4, 18]. According to Kalva *et al.* (2009), the reaction rate is very dependent on the interfacial contact between the two phases and also the generation of alcohol anions which initiate the biodiesel production reaction.

The use of ultrasonic energy as the source of mixing has became a great interest by two means. First, it can produce a homogeneous mixture in a very short time to subsequently increase the biodiesel production yield. Ultrasonic has been reported to show its effects on liquid-liquid immiscible reaction systems through a phenomenon called cavitation [10, 19-20]. The asymmetric collapse of the cavitation bubbles disrupts the phase boundary and impinging of the liquids creates micro jets, leading to intensive mixing of the system near the phase

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Comparative study on the process behavior and reaction kinetics in sonocatalytic degradation of organic dyes by powder and nanotubes TiO_2

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ABSTRACT

Sonocatalytic degradation of various organic dyes (Congo Red, Reactive Blue 4, Methyl Orange, Rhodamine B and Methylene Blue) catalyzed by powder and nanotubes TiO_2 was studied. Both catalysts were characterized using transmission electron microscope (TEM), surface analyzer, Raman spectroscope and thermal gravimetric analyzer (TGA). Sonocatalytic activity of powder and nanotubes TiO_2 was elucidated based on the degradation of various organic dyes. The former catalyst was favorable for treatment of anionic dyes, while the latter was more beneficial for cationic dyes. Sonocatalytic activity of TiO_2 nanotubes could be up to four times as compared to TiO_2 powder under an ultrasonic power of 100 W and a frequency of 42 kHz. This was associated with the higher surface area and the electrostatic attraction between dye molecules and TiO_2 nanotubes. Fourier transform-infrared spectrometer (FT-IR) was used to identify changes that occurred on the functional group in Rhodamine B molecules and TiO_2 nanotubes after the reaction. Sonocatalytic degradation of Rhodamine B by TiO_2 nanotubes apparently followed the Langmuir–Hinshelwood adsorption kinetic model with surface reaction rate of 1.75 mg/L min. TiO_2 nanotubes were proven for their high potential to be applied in sonocatalytic degradation of organic dyes.

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1. Introduction

Treatment of textile industry wastewater is often needed due to the incomplete fixation of synthetic dyes during the dyeing process. It was estimated that approximately 10–15% of the 700,000 tons of synthetic textile dyes used annually were lost to effluents [1]. Most of the organic dyes have serious implications to human health and aquatic life due to their toxic, mutagenic and carcinogenic potentials [2]. They are harmful if swallowed by human beings or animals and may cause irritation to the skin, eyes and systemic effects including cyanosis, blood changes, gastrointestinal tract and respiratory tract [3]. As the presence of dyes in industrial effluent is highly undesirable, many methods have been investigated for their removal. Methods such as coagulation, filtration and adsorption by activated carbon are only able to transfer the organic pollutants from one phase to another and consequently result in the release of secondary pollutants into the environment.

Degradation methods such as oxidation are preferred because they can degrade pollutants rather than accumulating them on a certain medium to create secondary pollutants. Advanced oxidation processes that generate hydroxyl radicals (·OH) to degrade organic compounds have been increasingly attractive in recent years [4–6]. Ultrasonic irradiation generates the phenomenon of acoustic cavitation, i.e. nucleation, growth and implosive collapse in liquid. Rapid collapse of microbubbles which entrap gas/vapors (lifetime in the order of microseconds) could produce small localized hot spots (transient temperatures up to 5000 K and pressures higher than 1000 atm) [7]. In these extreme situations, the oxidation pathway will depend on the compound volatility and reactivity under different conditions [8].

In this work, titanium dioxide (TiO_2) powder and nanotubes were employed as sonocatalyst in sonocatalytic degradation of various organic dyes. While titanium dioxide (TiO_2) powder has been well reported in the literature [1,3,6], the use of TiO_2 nanotubes for the same application is rather rare or its catalytic behaviors are poorly understood. Thus, the behaviors of these two types of material were comparatively studied. The use of TiO_2 nanotubes in this study was due to their high surface-to-volume ratio and specific surface area as compared to that of powder form. This could result in more surface available for the separation of electron–hole pairs to enhance the electron transfer and the interpenetration of holes transport materials [9,10]. However, there is insufficient information available concerning the adsorption and catalytic behavior of powder and nanotubes TiO_2, the effect of the chemical structure of the various types of dyes and the reaction kinetics during the sonocatalytic degradation process. Hence, the objective of this study was to investigate the sonocatalytic activity of both types of catalyst with respect to their process behavior to treat various organic dyes, and to establish the reaction kinetics from the experimental data.

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Synthesis of monoglyceride through glycerol esterification with lauric acid over propyl sulfonic acid post-synthesis functionalized SBA-15 mesoporous catalyst

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ABSTRACT

Monoglyceride synthesis through glycerol esterification with lauric acid over a propyl sulfonic acid functionalized SBA-15 mesoporous catalyst (HSO_3SBA-15) was studied under reduced pressure to continuously remove water formed. Effects of various reaction parameters such as reaction temperature (413–433 K), catalyst loading (1–5%) and glycerol/lauric acid molar ratio (2:1 and 4:1) on lauric acid conversion and products selectivity were successfully elucidated and correlated with reaction scheme and kinetic model. The parent and functionalized SBA-15 were characterized using FT-IR, ammonia chemisorptions, surface analysis, TEM and SEM. Reusability behavior of the catalyst was also demonstrated. Glycerol esterification could be modeled as irreversible parallel reactions and the kinetic data were successfully fitted to a second order kinetic model. The apparent activation energy for monoglyceride formation using a catalyst loading of 5% and glycerol/lauric acid molar ratio of 4:1 was found to be 42 kJ/mol. The HSO_3SBA-15 catalyst could be reused up to four times without significant loss of catalytic activity.

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1. Introduction

Monoglyceride has various applications in food products, cosmetics, pharmaceutical formulations, drug delivery systems, oil well drilling operations, etc. [1,2]. Synthesis of monoglyceride through glycerol transesterification with oleic acid methyl ester using solid basic catalysts in solvent free condition was found to be favourable at an elevated temperature (473 K) over rehydrated Al–Mg mixed oxides and Al–Li mixed oxides catalyst that had Bronsted basic sites and Lewis basic sites, respectively [3]. Meanwhile, glycerol transesterification with lauric acid methyl ester over montmorillonite intercalated with lithium hydroxide (LiK10) catalyst and in the presence of tetramethylammonium hydroxide (TMAOH) was recently reported to show excellent performance at a relatively lower temperature (403 K) [4]. However, the use of organic solvent will result in an extra step for its separation during product purification process. Residual solvent content in the product will also limit the application of the monoglyceride, especially when food products are considered [5–7]. Glycerol esterifications with fatty acids at low temperature in solvent free condition using solid acid catalysts such as acidic resins, conventional zeolites, and sulfated iron oxide were reported to be unfavourable for the reaction due to small pore diameters of less than 8 Å [8,9].

To accelerate the reaction involving bulky molecules such as fatty acids, effective solid acids having pore sizes between 20 and 100 Å are required [10,11]. HSO_3SBA-15 catalyst with a pore size of 67 Å synthesized via post synthesis route was found to be an active solid acid catalyst for monoglyceride formation through the glycerol esterification with lauric acid [12]. However, no sufficient information has been reported on the influence of important process variables, reaction pathway and kinetic model on the product formations in the esterification process. As such, a study on these aspects is deemed necessary for the purpose of advancement of knowledge in this research area.

Reaction pathway is essential to be used for constructing a kinetic model that can be applied to predict the changes in amount of specific product obtained during a reaction process. In order to obtain a better understanding of the reaction pathway, several researchers have undertaken various studies on glycerol esterification with different fatty acids and solid acid catalysts to produce monoglycerides [9,13–15]. Based on their observations, it can be concluded that the reaction pathways of glycerol esterification with fatty acid could be modeled either as consecutive reactions (Fig. 1) following the first order kinetic model with respect to glycerol or as irreversible parallel reactions (Fig. 2) following second order kinetic model with respect to fatty acid and glycerol. The reaction orders reported in the open literatures can be summarized in Table 1.

In the present work, glycerol esterification with lauric acid over the HSO_3SBA-15 is reported. The main focus is to investigate the effect of temperature, glycerol/lauric acid molar ratio and catalyst

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Cationic Surfactant-Modified Clay Catalysts for the Synthesis of Monoglyceride Through the Esterification of Glycerol and Lauric Acid

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Abstract

The preparation, characterization and activity study of clay catalysts prepared from sodium-montmorillonite (NaMMT) are reported. The clay was functionalized with cetyl trimethyl ammonium bromide (CTAB) and tetra-n-butylammonium bromide (TBAB) to produce CTMMT and TBMMT catalysts, respectively using an ion exchange method performed at 60 °C. The catalysts were characterized using XRD, FTIR, TGA and surface analysis methods. The catalytic activity was evaluated by reacting glycerol with lauric acid at 130 °C for up to 8 h. Intercalation of surfactants increased the basal spacing of the clay, reduced the adsorbed water and caused some chemical changes in the clay lattice. With TBAB catalyst, was a glycerol monolaurate selectivity of about 73 % was obtained at a lauric acid conversion of about 80 %. Symmetrical onium salts in TBAB was responsible for higher activity and selectivity than that of unsymmetrical onium salts in CTAB.

KEYWORDS: Montmorillonite ; cationic surfactant ; glycerol, lauric acid ; esterification.

1. Introduction

Glycerol is a renewably biomass and is a by-product from oleochemical and biodiesel industries. The increasing supply of glycerol would create a glut in the market and new applications for this substance need to be found. Thus, the development of an economical follow-up chemical technology for glycerol is of great economical interest. Glycerol transformation into glycerol monoesters has significant applications as the esters can act as emulsifiers especially in food, pharmaceutical and cosmetic products due to their physicochemical properties and the hydrophilic-hydrophobic balance [1]. These esters have been generally obtained either through the esterification of glycerol with fatty acids or by the transesterification of fatty acid triglyceride with glycerol. In both processes, a mixture of mono-, di- and triglycerides is obtained at variable proportions, depending on process conditions and chemical properties of the reactants used.

For the esterification route, the use of strong mineral or organic acid catalysts like para-toluene sulphonic acid (PTSA) or H_2SO_4 is usually involved. However, there are some drawbacks for these types of homogeneous catalyst, especially from the safety and environmental aspects such as excessive waste generation, corrosiveness, chemical hazards of waste catalysts etc. These are critical if the products were to be used for edible purposes. A number of solid acids have been used as catalysts for the fatty acid esterification of glycerol in order to avoid the problems associated to the use of homogeneous catalysts just described. Recently, some studies involving alternative heterogeneous catalytic routes have been reported. These include glycerol esterification with lauric and oleic acids using solid cationic resins [2], zeolitic molecular sieves [3, 4], sulfated iron oxide [5], functionalized mesoporous materials [6], multi valent metal salts [7] and heterogenized sulfonic acids over MCM-41 [8] as catalysts. However, the problems associated with low catalytic activity and low selectivity towards the desired product still remains unsatisfactorily solved.

In the strategy to improve the monoglyceride selectivity, several attempts have already been made in order to tune the hydrophilicity of the catalyst. Cauvel et.al. [9] used MCM-41 functionalised with amines to perform glycidol esterification. As that reagent had only one hydroxyl function, monoglyceride was reported to be obtained with relatively high yield. Barrault et al. [10] synthesized less hydrophilic supports like pure silica MCM-41 which could be used to increase the monoglyceride selectivity. Besides the pore size and the strength of the active acid sites, the relative affinity of the catalyst for the highly hydrophilic

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Note

Organo-montmorillonites as catalysts for selective synthesis of glycerol monolaurate

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ABSTRACT

Montmorillonite was modified with cetyl trimethylammonium bromide (CTAB) and tetra-n-butylammonium bromide (TBAB) to catalyze the production of glycerol monolaurate. The reaction was conducted at 130 °C for up to 8 h. With TBAB montmorillonite, a higher glycerol monolaurate selectivity of about 73% was obtained at a lauric acid conversion of about 80%.

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1. Introduction

Glycerol monoesters have significant applications as emulsifiers in food, pharmaceutical and cosmetic products (Diaz et al., 2005). Potential green catalytic routes have been reported using various solid catalysts but selectivity for monoglycerides remains a problem. In this study, the activity of montmorillonite intercalated with cetyl trimethyl- and tetra-n-butylammonium ions were evaluated for the esterification of lauric acid with glycerol. The alkylammonium ions can act as phase-transfer catalysts to accelerate the slow reaction that stems from poor interaction between the reactants (Ghiaci et al., 2005).

2. Experimental

2.1. Organo-montmorillonites

5.0 g of Na-MMT (Kunimine Industry Co., Japan) was dispersed in 500 ml of distilled water under stirring at 600 rpm for 20 h. Amounts of CTAB (Fisher Scientific) or TBAB (Sigma Aldrich) were slowly added to the montmorillonite dispersion at 60 °C and stirred for 1 h to exchange the sodium ions. The organo-montmorillonites were denoted CTMMT and TBMMT and were subsequently characterized using XRD (Bruker Advance) and surface analyzer (Micromeritics ASAP 2020).

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2.2. Catalytic activity

The esterification reaction was performed in a continuously stirred open flask reactor under atmospheric pressure. The molar ratio of glycerol:lauric acid was 6:1, and the reaction temperature was 130 °C. The amount of organo-montmorillonite used was 5 mass% related to limiting reactant (lauric acid). A gas chromatograph equipped with a Zebron ZB-5HT Inferno column was used for the product analysis.

3. Results and discussion

3.1. Characterization of catalysts

The basal spacings of the organo-montmorillonites are shown in Table 1. The montmorillonite had a specific surface area of 24 m^2/g. The pore diameters were within the meso-size range so that internal mass transfer was negligible, especially for a slow reaction like the esterification of fatty acids with glycerol. As expected, the cation exchange reduced the specific surface area and increased the pore diameter.

3.2. Catalytic activity

Montmorillonite is an acidic material due to the polarization of water molecules (Ghiaci et al., 2005) as indicated also in this study by the good catalytic activity of Na-MMT (Fig. 1). Lauric acid conversion as high as about 75% was achieved after 8 h. Such high activity is comparable to results reported for mesoporous sulfonic acid catalysts (Diaz et al., 2005) and for molecular sieve catalysts (Machado et al., 2000). Almost similar conversions were achieved with TBMMT while CTMMT showed slightly

SONOCATALYTIC DEGRADATION OF VARIOUS DYES IN WASTEWATER OVER HEAT-TREATED TiO_2 CATALYSTS AND ASSISTED BY HYDROGEN PEROXIDE*

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The ambient temperature sonocatalytic degradation of congo red, methyl orange, and methylene blue by heat-treated titanium dioxide (TiO_2) catalyst to high temperature at an initial concentration of between 10-50 mg/l, catalyst loading of between 1.0-3.0 mg/l and hydrogen peroxide (H_2O_2) concentration up to 600 mg/l at 20 kHz and 50 W has been investigated. Proper amount of rutile phase of TiO_2 form on anatase had better sonocatalytic effect that the pure anatase. The degradation of organic dye depends on the chemical structure and molecular weight. With the highest molecular weight and highest reactivity with hydroxyl (·OH), peroxyl (HO_2•) and superoxide (O_2•-) radicals, congo red exhibit higher degradation rate. The highest degradation efficiency of congo red occurred at the initial concentration of 10 mg/l, 1.5 g/L of catalyst loading and 450 mg/L of H2O2 to give the efficiency of above 45% in 75 min.

1. Introduction

Application of ultrasounds in water with frequency range 18 kHz-10 MHz can result in acoustic cavitation, namely, the formation, growth and collapse of cavity bubbles that entrapped dissolved gasses/vapors surrounding water [1, 2]. Subsequently, many hot spots with local extremely high temperature (up to 5,000 K) and high pressure (up to 1,000 atm) are generated and then induce the dissociation of water (Equation (1)), oxygen molecules (Equation (4)) hydrogen peroxide (Equation (8)) [3, 4].

$$H_2O \xrightarrow[TiO_2]{)))} \cdot OH^{\bullet} + {}^{\bullet}H \quad (1)$$

$${}^{\bullet}OH + \cdot H^{\bullet} \rightarrow H_2O \quad (2)$$

$$2\,{}^{\bullet}OH \rightarrow H_2O_2 \quad (3)$$

$$O_2 \xrightarrow[TiO_2]{)))} 2\,{}^{\bullet}O \quad (4)$$

$${}^{\bullet}O + H_2O \rightarrow \cdot 2\,{}^{\bullet}OH \quad (5)$$

$$O_2 + \cdot H^{\bullet} \rightarrow \cdot O_2H \quad (6)$$

$${}^{\bullet}O_2H + {}^{\bullet}O_2H \rightarrow H_2O_2 + O_2 \quad (7)$$

$$H_2O_2 \xrightarrow[TiO_2]{)))} 2\,{}^{\bullet}OH \quad (8)$$

In this study, the TiO_2 powder was adopted as sonocatalyst as its advantages such as inexpensive, nontoxic, biologically stable and reusable [5, 6]. With the presence of a heterogeneous catalyst, it can increase the rate of formation and growth of cavitation bubbles which will then increase the rate of formation ${}^{\bullet}OH$ radicals [7]. The aim this study is to investigate effects of sonocatalytic degradation on organic dyes and different heat-treated TiO_2 catalysts. Other factors such as initial dye concentration, TiO_2 catalyst loading and H_2O_2 concentration were examined as well.

2. Experimental

2.1. *Materials and Apparatus*

The TiO_2 powders (R & M Marketing, Essex, U.K.) were adopted as sonocatalysts with and without heat-treatments. H_2O_2 30% (Merk Bchuchardt OHG) was bought to be used as a promoter for the sonocatalytic degradation process. Congo red, methyl orange and methylene blue powders (R & M Marketing, Essex, U.K.) were used as model compounds for confirming the sonocatalytic activity of heat-treated TiO_2 powders.

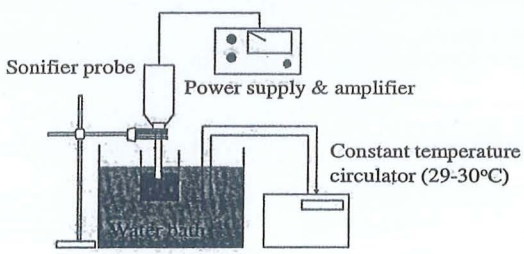

Figure 1. Schematic illustration of sonocatalytic degradation experiment apparatus.

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Removal of Remazol Brilliant Violet-5R dye using periwinkle shells

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The purpose of this research is to obtain optimal processing conditions for the adsorption of Remazol Brilliant Violet-5R (RBV-5R) dye onto activated carbon prepared from periwinkle shells (PSAC) by chemical activation with KOH using response surface methodology. Central composite design (CCD) was used to determine the effects of three preparation variables; CO_2 activation temperature, CO_2 activation time and KOH:char impregnation ratio (IR) on two responses; percentage RBV-5R dye removal and PSAC yield. Based on the CCD, two quadratic models were developed for percentage RBV-5R dye removal and PSAC yield, respectively. The most influential factor on each experimental design response was identified from the analysis of variance (ANOVA). The optimum conditions for the adsorption of RBV-5R dye onto PSAC were CO_2 activation temperature of 811 °C, CO_2 activation time of 1.70 h and IR of 3.0, resulting in 81.28% RBV-5R dye removal and 28.18% PSAC yield. PSAC prepared under optimum conditions was mesoporous with a Brunauer–Emmett–Teller surface area of 1894 $m^2 \cdot g^{-1}$, total pore volume of 1.107 $cm^3 \cdot g^{-1}$ and average pore diameter of 2.32 nm. The surface morphology and functional groups of the activated carbon were respectively determined from the scanning electron microscopy and Fourier transform infrared analysis.

Keywords: periwinkle shell activated carbon; adsorption; central composite design; dye; responses

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1. Introduction

Water pollution is one of the most undesirable environmental problems in the world that requires urgent solution. Textile industries produce a lot of wastewater, which contains different contaminants, including acidic or caustic dissolved solids, toxic compounds and different type of dyes. Many of the organic dyes are hazardous and may affect aquatic life causing various diseases and disorders [1]. Synthetic dyes are used extensively for textile dyeing and other industrial applications. Total world colourant production is estimated to be ~800,000 ton·year^{-1}. More than 10,000 dyes are commercially available and at least 10% of the dyestuff used enters the environment as wastes [2]. These industrial effluents are toxic and are characterised by high chemical oxygen demands (CODs)/biological oxygen demands (BODs), suspended solids and intense colour [3]. Furthermore, these coloured molecules are highly conjugated and can be extremely injurious to the life [4]. Synthetic dyes, classified by their chromophores, have different and stable chemical

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Response Surface Modeling and Optimization of Remazol Brilliant Blue Reactive Dye Removal Using Periwinkle Shell-Based Activated Carbon

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This work investigates both batch and optimization studies of adsorption of Remazol Brilliant Blue Reactive (RBBR) dye onto activated carbon prepared from periwinkle shells (PSAC). The effects of three preparation variables: CO_2 activation temperature, CO_2 activation time, and KOH: char impregnation ratio (IR) were studied using Response Surface Modeling (RSM). Based on the central composite design (CCD), a quadratic model and two-factor interaction models (2FI) were developed to correlate the three preparation variables to the two responses: RBBR dye removal and PSAC yield. The optimum conditions for preparing PSAC for adsorption of RBBR dye were found as follows: CO_2 activation temperature of 811°C, CO_2 activation time of 1.7 h and IR of 2.95, which resulted in 82.76% of RBBR dye removal and 35.83% of PSAC yield. Experimental results obtained agreed satisfactorily well with the model predictions. The activated carbon prepared under optimum conditions was mesoporous with BET surface area of 1894 m^2/g, total pore volume of 1.107 cm^3/g and average pore diameter of 2.32 nm. The surface morphology and functional groups of PSAC were respectively determined from the scanning electron microscopy (SEM) and Fourier transform infrared analysis (FTIR).

Keywords activated carbon; central composite design; mesoporous; periwinkle shells

INTRODUCTION

The extensive use of dyes brings about pollution problems in the form of colored wastewater and discharge into water bodies. Synthetic dyes are widely used in textile dyeing, paper printing, food, cosmetics, pharmaceutical, and color photography (1). Residual dyes are the major contributors to color in wastewaters generated from textile and dye manufacturing industries. These residual dyes are stable and fast, difficult to degrade, toxic, rendering the water unfit for its intended use. Color removal is also not adequate when conventional chemical and biological treatments are employed. These dyes, apart from making wastewater aesthetically displeasing, some of them undergo anaerobic degradation to potentially carcinogenic amines (2). These dyes contain chromophoric groups such as azo, anthraquinone, triarylmethane etc. and reactive groups, for example, vinyl sulphone, chlorotriazine, trichloropyrimidine, etc. Remazol Brilliant Blue R (RBBR) is one of the most important dyes in the textile industry. RBBR, an anthraquinone derivative, represents an important class of toxic and recalcitrant organopollutants (3,4). Marine snails in general are part of the family Gastropoda. They are found in oceans all over the world. The major species available in the lagoon and mudflats of Nigeria's Niger Delta, between Calabar in the east and Badagry in the west, are *Typanostonus spp.* and *Pachmellania spp.* Over the years, large quantities of periwinkle shells have accumulated in many parts of the country such as Bori, Western Ijaw, Burutu, Agoro, Ogalaga, and Lotugbene thereby constituting a menace to the environment. They are usually 1.3 to 2.5 cm in height, and their coloration varies from grey to black. The shell is fairly heavy and solid. They live in the intertidal zone (the area of the shore that has alternating periods of exposure to air and water).

The conventional approach for optimization of process variables requires determination of the dependent variable at each and every combination of independent variables by varying only one at a time and keeping others as constants in batch studies. Such approach would obviously require a very large number of experiments to be performed, which would be very expensive and time consuming. Moreover, it would not be able to reveal the influence of the interactions between the process variables on the dependent variable (5). Response surface methodology (RSM) is a useful method for studying the effect of several variables influencing the responses by varying them simultaneously and carrying out a limited number of experiments. Studies employing experimental design and optimization modeling

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Optimization of rambutan peel based activated carbon preparation conditions for Remazol Brilliant Blue R removal

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ABSTRACT

The optimal conditions for preparation of rambutan peel based activated carbon (RPAC) for removal of Remazol Brilliant Blue R (RBBR) reactive dye from aqueous solution were investigated. The RPAC was prepared using physiochemical activation method which consisted of potassium hydroxide (KOH) treatment and carbon dioxide (CO_2) gasification. The central composite design (CCD) was used to determine the effects of the preparation variable, activation temperature, activation time and KOH impregnation ratio on RBBR percentage removal and RPAC yield. Two quadratic models were developed to correlate the preparation variables for both responses. The significant factors on each experimental design response were identified from the analysis of variance (ANOVA). The optimum conditions for RPAC preparation were obtained by using activation temperature of 789 °C, activation time of 1.8 h and IR of 3.5, which resulted in 78.38% of RBBR removal and 18.02% of RPAC yield.

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1. Introduction

Reactive dyes are used extensively for dyeing cellulosic fibre. They consist of a chromophore and a functional group that binds the dyestuff to the fibre [1]. The functional group also bonds to water, creating hydrolysis and hence 10–50% of the dye is remains in the dye bath waste. In fact, the expanded uses of reactive dyes and their reaction products such as aromatic amines are highly carcinogenic [2]. Discharge of these wastewaters into receiving streams cause damage not only to aquatic life but also to human beings [3].

Adsorption is an effective treatment method that is widely used in the removal of contaminants from water and wastewater. Adsorption process with activated carbon (AC) as an adsorbent has been proved to be superior compared to other techniques in terms of its simplicity of design, high efficiency and ease of operation [4]. From the literature, adsorption of reactive dyes on coal-based commercial AC has been studied [5,6]. However, its usage has been limited due to the expensive starting material [7]. As such, there is a need to produce AC from alternative material that is cheaper, renewable and readily available. In recent years, focus has been given on the preparation of low cost AC from agricultural wastes such as coir pith [8], sugar beet pulp [9], sugarcane bagasse pith [10] and jute fibre [11] for the adsorption of reactive dyes.

In this work, an attempt was made in preparing AC from rambutan peel (RP) precursor. Native to South-Eastern Asia, rambutan (*Nephelium lappaceum* L.) is a popular tropical fruit which belongs to Sapindaceae family [12]. In Malaysia, an average rambutan tree may produce 5000–6000 or more fruits (60–70 kg per tree). Normally, after consuming the rambutan fruit, the peel is thrown away and disposal of the peel usually poses environmental problem in the community. Therefore, conversion of RP into AC reduces the cost of waste disposal and provides a potentially cheap alternative resource for AC production.

Response surface methodology (RSM) is a useful tool to study the interactions of two or more factors. A standard RSM design called a central composite design (CCD) is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters [13]. CCD has been used for the optimization of AC production from rattan sawdust [4], tamarind wood [14] and Turkish lignite [15] by chemical activation whereas coconut husk [13] and oil palm empty fruit bunch [16] by physiochemical activation method. The goal of this work was to optimize the RPAC preparation variables; activation temperature, activation time and impregnation ratio for the removal of Remazol Brilliant Blue R (RBBR) dye from aqueous solution.

2. Materials and methods

2.1. Adsorbate

Remazol Brilliant Blue R (RBBR) supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate. Deionized water was used to prepare all solutions. RBBR has a chemical formula

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Research Article

Adsorption of Remazol Brilliant Violet-5R reactive dye from aqueous solution by cocoa pod husk-based activated carbon: kinetic, equilibrium and thermodynamic studies

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ABSTRACT: The adsorption of Remazol Brilliant Violet-5R (RBV-5R) reactive dye on cocoa pod husk activated carbon (CPHAC) was investigated in batch process. The effects of initial dye concentration, contact time, solution temperature and pH were evaluated. The equilibrium data were fitted into Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. It was found that Freundlich model fitted the adsorption data most. The kinetic data were fitted into pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models. Adsorption of RBV-5R dye on CPHAC was best described by pseudo-second-order kinetic model. The adsorption of RBV-5R dye was favored at acidic pH. Thermodynamic parameters such as standard free energy ΔG^0, standard enthalpy ΔH^0 and standard entropy ΔS^0 were calculated. The adsorption interaction of RBV-5R reactive dye on the adsorbent was found to be feasible, spontaneous and endothermic. The adsorption process followed a physisorption mechanism. © 2011 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: activated carbon; cocoa pod husk activated carbon; Remazol Brilliant Violet-5R reactive dye; adsorption isotherm; thermodynamics

INTRODUCTION

Textile industries in Malaysia contribute to the country's economic development. It grows rapidly to meet up with the growing demands. These industries use dyes or pigments as their main raw material to color textile materials.[1] There are varieties of dyes used in textile industry, for example acid dyes, basic dyes, reactive dyes, direct dyes, solvent dyes, sulfur dyes and disperse dyes. The effluents produced from textile industry contain heavy metals, ammonia, alkali salts, toxic solids and large amounts of pigments. Dye consists of complex aromatic molecular structures which make them inert and difficult to biodegrade when discharged into waste streams.[2] Improper discharge of these compounds is not only aesthetically displeasing but also impedes light penetration and thus upsetting biological processes in streams.[3]

Cocoa (*Theobroma cacao*) is a plant specie from the family of *Sterculiaceae*. It is an ever-green tree growing crop 6.0 to 8.0 m high in the tropical rainforest. Cocoa pod husks (CPH) are produced after the removal of the cocoa bean from the fruit. Basically, each ton of dry cocoa bean is equivalent to about 10 tons of CPH. Most of the husks are disposed as waste which in turn resulted in landfill problem. In Nigeria, more than 1.5 million tons of CPH are wasted annually and some of the CPH are used as organic fertilizer, soap making and animal feed production, while in Malaysia, an estimated amount of CPH are available.[4] Thus in this work, CPH was utilized for the preparation of activated carbon. The advantage in the conversion of CPH to activated carbon is to turn the discarded agricultural waste to useful and valuable adsorbent. In addition, the dye effluent from textile industries can be treated by using CPH.[5]

The adsorption of Remazol Brilliant Violet-5R (RBV-5R) dye on cocoa pod husk activated carbon (CPHAC) was investigated. Factors studied include; initial dye concentration, contact time, solution temperature and

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Utilization of Cocoa Pod Husk for the Removal of Remazol Black B Reactive Dye from Aqueous Solutions: Kinetic, Equilibrium and Thermodynamic Studies

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ABSTRACT

This study aims at investigating the adsorption of Remazol Black B reactive (RBBR) dye on cocoa pod husk based activated carbon (CPHAC) in batch process. The effects of initial dye concentration, contact time, temperature and pH were evaluated. At the lowest initial dye concentration (20 mg L^{-1}), the highest percentage RBBR dye removal by CPHAC was achieved (76.3%). Equilibrium was reached at 300 and 350 min, respectively. The equilibrium data were fitted into Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. It was found that Langmuir model fitted the adsorption most with maximum adsorption monolayer coverage of 22.12 mg g^{-1}. Two kinetic models were used to fit the kinetic data; pseudo-first-order and pseudo-second-order models. The pseudo second-order model provided the best correlation for the adsorption of RBBR dye on CPHAC. Thermodynamic parameters such as change in Gibb's free energy $\Delta G°$, change in enthalpy $\Delta H°$ and change in entropy $\Delta S°$ were calculated. The adsorption process was found to be feasible, endothermic and spontaneous. Both the mean free energy of adsorption and the activation energy values obtained shows that the adsorption process follows a physiosorption mechanism.

Key words: Adsorption, feasible, endothermic, spontaneous, activation energy

INTRODUCTION

Waste waters containing different dyes are often discharged in aqueous effluents from dyestuff manufacturing, dyeing and textile industries. The physical process of dye removal from effluents may be divided into two main categories: adsorption and membrane separation (Slokar and Le Marechal, 1998; Vandevivere *et al*., 1998; Hao *et al*., 2000). Adsorption is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes in an effluent. In this regard, activated carbon has been extensively used for removal of color resulting from the different classes of dyes and is now the most widely used adsorbent for dyes. However, adsorption using activated carbon as adsorbent is very expensive, the cost of regenerating the spent

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Equilibrium, kinetics and thermodynamic of Remazol Brilliant Orange 3R dye adsorption on coffee husk-based activated carbon

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ABSTRACT

In this work, coffee husk based activated carbon (CHAC) was prepared by physicochemical activation for the removal of Remazol Brilliant Orange 3R (RBO3R) dye from aqueous solution. The effects of dye initial concentration, contact time, solution temperature and pH on RBO3R adsorption were investigated. Result showed that the adsorption of RBO3R was favorable at acidic pH. The adsorption uptake was found to increase with increase in initial RBO3R concentration, contact time and solution temperature. Langmuir isotherm model fitted well the adsorption equilibrium data with monolayer saturation capacity of 66.76 mg/g at 303 K. The adsorption kinetic was found to follow the pseudo-second-order kinetic model. Boyd plot indicated that the adsorption of RBO3R on CHAC was controlled by film diffusion. The adsorption process was found to be endothermic with the reaction mechanism follows a physisorption process.

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1. Introduction

About 10,000 different dyes weighing approximately 0.7 million tons are produced annually for various industrial processes. A considerable amount of these dyes are released into the effluent during the dyeing process. Most of the dyes have been identified as toxic or even carcinogenic to aquatic organism as well as to human life [1]. In addition, it can cause allergic dermatitis, skin irritation and cancer to human being [2]. Reactive dyes particularly are the most common dyes used due to their favorable characteristics of bright color, water-fastness, simple application techniques and low energy consumption. They exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups [3]. They are not easily biodegradable, thus, even after extensive treatment, the color may still remain in the effluent [4].

Many methods for dye effluent treatment such as activated carbon sorption, chemical coagulation, ion exchange, electrolysis, and biological treatments have been developed. Among these methods, activated carbon sorption has been used extensively due to high adsorption capacity and efficiency [1]. The activated carbon properties such as high internal surface area, well developed internal pore structure and the presence of a wide spectrum of surface functional group make it the most popular adsorbent [5]. However, the commercial activated carbons are quite expensive and have limited their application. The discovery of alternative activated carbon precursors especially from agricultural wastes is highly encouraged. In literature, Posidonia oceanica dead leaves [6], olive tree pruning waste [7], cashew nut shell [8] and mangosteen peel [9] have been used as raw materials for activated carbon preparation. In addition the conversion of these agricultural wastes into activated carbons will decrease the waste disposal and also convert these wastes into value-added products.

The purpose of this work is to prepare the activated carbon from coffee husk waste by using physicochemical activation for removal of Remazol Brilliant Orange 3R (RBO3R) reactive dye from aqueous solution. The effects of different parameters such as contact time, initial dye concentration, temperature and pH were studied. Adsorption isotherms and kinetics were investigated and different models were used to explain the possible adsorption mechanism. Thermodynamic studies were also carried out to estimate the standard free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°).

2. Materials and methods

2.1. Activated carbon preparation

Coffee husk was obtained from the local factory located in Serdang, Kedah, Malaysia. Coffee husk was washed and subsequently dried at 378 K for 12 h to remove the moisture content. The dried coffee husk was ground and sieved to the desired particle size of 1–2 mm. The sieved sample was loaded in a stainless steel vertical

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Removal of malachite green dye from aqueous solution using rambutan peel-based activated carbon: Equilibrium, kinetic and thermodynamic studies

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ABSTRACT

The adsorption of malachite green (MG) dye onto rambutan peel-based activated carbon (RPAC) was carried out in this work. The effects of different reaction parameters such as the initial MG concentration, contact time, solution temperature and initial pH on MG adsorption were investigated. MG adsorption uptake was found to increase with increase in initial concentration, contact time and solution temperature. The adsorption equilibrium data were best represented by the Freundlich model. Adsorption kinetic was found to follow the pseudo-second-order kinetic model. The mechanism of the adsorption process was determined from the intraparticle diffusion model. Boyd plot indicated that the MG adsorption on the RPAC was controlled by film diffusion. Thermodynamic parameters ΔG°, ΔH°, ΔS° and E_a were also determined.

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1. Introduction

Malachite green (MG), which is classified as a basic dye is widely used in the silk, wool, cotton, leather and paper industries for coloring purposes. It is also employed as therapeutic agent to treat parasites, fungal and bacterial infections [1]. Despite its extensive use, MG dye consists of toxic properties which are known to cause carcinogenesis, mutagenesis, teratogenesis and respiratory toxicity [2]. Therefore, the removal of MG from wastewater before discharging to the environment is necessary and very important. The techniques for removing dyes in wastewater can be divided into three main categories which are physical, chemical and biological methods. Chemical treatment used coagulating or flocculating agent to remove dyes but this process is not good for highly soluble dyes [3]. On the other hand, biological treatment is incapable of removing dyes from effluent on a continuous basis. In addition, longer time is required for decolourisation–fermentation processes [4]. Lastly, physical treatments such as precipitation, ion exchange, membrane filtration, electrochemical destruction, irradiation, ozonation and adsorption are widely used to treat the dyes wastewater. Most of these processes are costly and lead to generation of sludge or formation of by-products [5]. However adsorption is known to be the most efficient method especially if the adsorbent is inexpensive and exhibits high adsorption capacity suitable for removing the dyes from wastewater [6].

Activated carbons as adsorbent have relatively high surface area and total pore volume. The commercially available activated carbons from bituminous coal, lignite and petroleum coke are expensive, thus limited their applications [7]. Other precursors of activated carbon production were investigated especially from agricultural wastes which are inexpensive, abundantly available and renewable materials. From the literature, bamboo [5], oil palm empty fruit bunch [8], date stone [9], orange peel [10] and rubber seed coat [11] were used to prepare activated carbons.

Rambutan (*Nephelium lappaceum* L.) is a popular tropical fruit which belongs to *Sapindaceae* family [12]. In Malaysia, a rambutan tree may produce approximately 5000–6000 rambutan fruits with total weight of 60–70 kg. There are products related to rambutan such as jams, marmalade, spread, jelly and canned food have been produced. However, due to the high consumption of rambutan's edible part, massive amount of the peel is disposed, causing a severe problem in the community as they gradually ferment and release off odours. Therefore, conversion of rambutan peel into activated carbon would provide a potentially cheap alternative precursor and reduce the cost of waste disposal as well [13].

In the present investigation, rambutan peel-based activated carbon (RPAC) was prepared by physiochemical activation for its potential to remove MG dye from aqueous solution. The equilibrium and kinetic data of the adsorption process were then analyzed to study the adsorption isotherms, kinetics, thermodynamic and mechanism of MG on the RPAC.

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Optimization of preparation conditions for mangosteen peel-based activated carbons for the removal of Remazol Brilliant Blue R using response surface methodology

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ABSTRACT

This study investigates the optimal conditions for preparation of activated carbons from mangosteen peel (MP) for removal of Remazol Brilliant Blue R (RBBR) reactive dye from aqueous solution. The MP activated carbon was prepared using physiochemical activation method which consisted of potassium hydroxide (KOH) treatment and carbon dioxide (CO_2) gasification. Central composite design (CCD) was used to determine the effects of the three preparation variables; CO_2 activation temperature, CO_2 activation time and KOH impregnation ratio (IR) on RBBR percentage removal and activated carbon yield. Based on the CCD, a quadratic model and a two-factor interaction (2FI) model were respectively developed for RBBR percentage removal and carbon yield. The significant factors on each experimental design response were identified from the analysis of variance (ANOVA). The optimum conditions for MP activated carbon preparation were obtained by using activation temperature of 828 °C, activation time of 1 h and IR of 3.0, which resulted in 80.35% of RBBR removal and 20.76% of activated carbon yield.

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1. Introduction

Almost 45% of textile dyes produced worldwide belongs to the reactive class [1]. Reactive dyes are common dyes used for dyeing cellulosic fibres due to their favorable characteristics of bright color, water-fastness, simple application techniques and low energy consumption [2]. They are usually characterized by nitrogen to nitrogen double bonds (N=N azo bonds) where the color of azo dyes is due to this azo bond and the associated chromophores [3]. The formation of a covalent bond between the dye molecule and the fibre is much stronger than the physio-chemical bond between other classes of dyes and cellulose [4]. However, reactive dyes pose the greatest problem in textiles wastewater since they are not easily biodegradable, and thus color may still remain in the effluent [5]. In fact, the expanded uses of azo dyes and their reaction products such as aromatic amines are highly carcinogenic. The discharge of these wastewaters into receiving streams causes damage not only to aquatic life but also to human beings [6].

In recent years, many processes have been applied for the treatment of reactive dyes from wastewater including biological, physical and chemical process [7]. Among them, adsorption process with activated carbon has been proved to be superior compared to other techniques in terms of its simplicity of design, high efficiency and ease of operation [8]. However, the manufacturing costs of commercial activated carbons are in fact rather high. As such, there is a need to produce activated carbon with high adsorption performance from alternative material that is cheaper and readily available. From the literature, many studies have been carried out to prepare low cost activated carbons from agricultural wastes such as sugar beet pulp [2], bamboo [5], pomegranate peel [8], date stone [9], vetiver roots [10], corn grain [11], cotton stalk fibre [12], oil palm empty fruit bunch [13], coconut husk [14] and rice straw [15].

In this work, an attempt was made in preparing activated carbon from mangosteen peel (MP) precursor. Mangosteen (*Garcinia mangostana* L.), a tropical evergreen tree has been planted in Malaysia with the total acreage between 7000 and 8000 ha [16]. It is also being planted in other countries such as India, Thailand, Vietnam and Philippines. This fruit has become an economically important species since the demand in the domestic and export markets are tremendous. However, due to the high consumption of mangosteen's edible part, massive amounts of the peels are disposed, causing a severe problem in the community as they gradually ferment and release off odours [17]. Therefore, by utilizing MP into activated carbon will decrease the cost of wastes disposal and also converted this waste into value-added product [18].

Currently no study has been done on optimization of the production of activated carbon from MP using the response surface methodology (RSM) approach. RSM has been found to be a useful

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Preparation of carbon molecular sieves from palm shell: effect of benzene deposition conditions

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Abstract Application of carbon molecular sieve (CMS) for gas separation has been found much attention recently. In this work, CMS was prepared from locally available palm shell through carbonization, steam activation and carbon vapour deposition (CVD) technique. After carbonization step, the char produced was subjected to steam activation at various activation times. The activated carbon obtained at 53.2% burn-off, which contain the highest amount of micropore volume was further used in CVD step by using benzene vapour at various deposition conditions. The performance of CMSs produced was examined by assessing the adsorption kinetics of O_2, N_2, CO_2 and CH_4 gases. All CMS samples showed a small N_2 and CH_4 uptake compared to the O_2 and CO_2. The suitable conditions for CVD were found at 800°C, 30 min and 30 vol% benzene of deposition temperature, time and benzene concentration, respectively. At this point the O_2/N_2 and CO_2/CH_4 uptake ratios arrived 7.1 and 16.0, respectively.

Keywords Adsorption · Palm shell · Carbon molecular sieves · Uptake ratio

1 Introduction

Gas separations are a major production cost in the chemical industry today. Production of industrial gases by pressure swing adsorption (PSA) is expected to grow much faster than by the cryogenic distillation. PSA utilizes CMS as adsorbent to separate various gases, especially nitrogen from air (Ruthven 1984). CMS is a microporous material having a pore size similar to that of the critical dimensions of the gas molecules to be separated (Reid and Thomas 2001). The pore surface area of CMS is usually less, and the pore size distribution narrower than that of commercial activated carbons.

Several methods have been developed for CMS production such as pyrolysis (Braymer et al. 1994), activation and carbon vapour deposition (CVD) (Vyas et al. 1994; Nguyen and Do 1995; Villar-Rodil et al. 2005; Freitas and Figueiredo 2001; Kawabuchi et al. 1996). Among them, the CVD approach has been found particularly suitable and has received considerable attention. By this approach, an active carbon of high adsorption capacity is conferred molecular selectivity through CVD at the micropore mouths, thus reduced the pore size. Properly prepared CMS required that the sizes of carbon species entering the micropores be limited so that the overall adsorptive capacity of the material is as high as possible (Hu and Vansant 1995). The carbon species should have adequate reactivity to be adsorbed and pyrolyzed on the pore mouth. It must also have an appropriate shape to produce a flat coating on the pore mouth. In addition, the hydrocarbon should have high chemical stability in the gas phase and not produce intermediate species, which make deposition easier to be controlled (Kawabuchi et al. 1996). Thus the pore mouth will narrow to the smallest dimension of the hydrocarbon molecule.

Accordingly, benzene, naphthalene and their aromatic homologs appear to be suitable for the above objective. These substances may control the width of the pore when they have access to the pore wall and can be selectively carbonized within the pore. Benzene with molecular thickness of 0.37 nm has been provided the necessary selectivity by preferential deposition and the most employed one (David

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CARBON MOLECULAR SIEVE FROM COCOA POD HUSK WASTE: INFLUENCE OF DEPOSITION TEMPERATURE ON GASES KINETIC SELECTIVITIES

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ABSTRACT - *Carbon molecular sieve (CMS) is a unique type of activated carbon (AC) with a relatively high adsorption capacity and high kinetic selectivity. In this work, CMS was prepared from locally available cocoa pod husk (CPH) by thermal treatment. The pyrolysis of CPH followed by activation at 700°C for 30-120 min produced ACs with various degrees of burn-off. AC with the highest micropore volume, which was obtained at 45.3% of burn-off was found suitable to be used as precursor for CMSs production. Subsequent benzene deposition onto AC at temperatures from 600-900°C resulted in a series of CMSs with different O_2/N_2 and CO_2/CH_4 kinetic selectivities.*

Key words: Cocoa pod husk, activation, benzene deposition, carbon molecular sieve

INTRODUCTION

CMS has become an interesting area of adsorption due to their favorable separation factor on size and shape selectivity basis for many gaseous systems. It has narrow pore size distribution (PSD) similar to the critical dimensions of the gas molecules. The surface area of CMS is usually less than ordinary AC (Freitas, 2001). CMS is suitable to be used as adsorbent for gas separation, like nitrogen and oxygen from air and carbon dioxide and methane from their mixtures. It also has high thermal resistance and high resistance in alkaline and acid medium (Kim *et al*, 2002).

There are two major approach to prepare CMS; one is based on controlled pyrolysis of carbon precursor and the other is the modification of existing porosity of an activated structure through carbon vapour deposition (CVD) by using hydrocarbon (Miura, 1999). In controlled pyrolysis process, the precursor is pyrolyzed under suitable temperature. The adsorption capacity must be carefully increases while avoiding excessive widening of porosity, which can be detrimental to selectivity. The CMS produces usually has low adsorption capacity and this may impose serious limitations on the performance of the CMS (Tan and Ani, 2004 and Villar-Rodil *et al.*, 2005). On the other hand, CMS prepares by CVD approach has high adsorption capacity and high selectivity. High adsorption capacity is related to high micropore volume in AC, whereas selectivity is provided by CVD technique (Villar-Rodil *et al.*, 2002). If CMS is produced directly from the raw material, the activation process must be carefully controlled in order to obtain AC with high micropore volume before CVD step could be done (Ahmadpour *et al.*, 2002). Therefore in this work, AC was prepared first from CPH by CO_2 activation before conferring the molecular selectivity through depositing benzene at the AC pore mouth.

MATERIALS AND METHODS

The raw material used in this study was CPH obtained from the Cocoa Research and Development Centre, Cocoa Board Malaysia, Hilir Perak. AC from the CPH was prepared by CO_2 activation in vertical tube reactor. The dried CPH was ground and sieved to the size between 1.0 to 2.0 mm. Then, 150 g of CPH was heated at 700°C under nitrogen flow for 30 min before being activated with CO_2 for 30-120 min at flowrate 150 ml/min in a stainless steel reactor. After the desired time lapse, the reactor was cooled to room temperature under nitrogen flow. The different ACs produced was indicated by the degree of carbon burn-off, θ (wt%) achieved, which was calculated as follows:

$$\theta = \frac{W_I - W_T}{W_I} \times 100 \qquad (1)$$

where W_I and W_T were the initial CPH mass and AC mass, respectively. The AC that produced the highest micropore volume will be used in CVD step. The main

ADSORPTION ISOTHERMS AND KINETICS STUDIES OF METHYLENE BLUE ON COCOA POD HUSK BASED ACTIVATED CARBON

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Malaysian Cocoa J. 5: 55 - 62

ABSTRACT - *The adsorption characteristic of methylene blue (MB) on activated carbon prepared from cocoa pod husk was evaluated. The effects of MB initial concentration, contact time and temperature on MB adsorption were studied. MB adsorption uptake was found to increase with increase in initial concentration and contact time. However the adsorption was decreased with increase in temperature, which indicated that the process was exothermic. The adsorption equilibrium data were best represented by the Freundlich isotherms. The adsorption kinetics was found to follow the pseudo-second-order kinetic model.*

Key words: Cocoa pod husk, activated carbon, methylene blue, isotherm, kinetics

INTRODUCTION

The removal of dyes from aquatic environment is extremely important from the healthiness point of view. Most of these dyes are toxic, causing allergy, skin irritation and mutagenic (Caritá and Marin-Morales, 2008). Therefore, industrial effluents containing dyes need to be treated before being delivered to environment (Pavan *et al.*, 2008). The most efficient procedure for removal of dyes from industrial effluents is the adsorption process. The dyes are transferred from the water effluent to a solid phase, diminishing the effluent volume to a minimum. Subsequently, the adsorbent can be regenerated or kept in a dry place without direct contact with the environment (Royer *et al.*, 2009).

Activated carbon (AC) is the most employed adsorbent for dye removal from aqueous solution because of its excellent adsorption properties. The high adsorption capacity of an AC is associated with the high surface area and porous structure (Tan *et al.*, 2008). The adsorption capacity of AC is dependent on the precursor as well as the experimental conditions employed in the activation processes (Royer *et al.*, 2009). In the present work, cocoa pod husk based activated carbon (CPHAC) will be used as adsorbent for removal of methylene blue (MB) dye from aqueous solutions. The equilibrium and kinetic data of the dye adsorption process onto the CPHAC is studied.

MATERIALS AND METHODS

The CPHAC used was obtained from previous work (Ahmad and Wan Zainal, 2009a, 2009b), which contained high surface area and total pore volume of 502.7m^2/g and 0.504 cm^3/g, respectively. This sample was produced at activation temperature of 700°C for 120 min. MB dye supplied by Sigma-Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate. The characteristics of the dye are listed in Table 1. Distilled water was used for preparing all solutions.

Batch equilibrium and kinetics studies

Batch equilibrium tests were carried out for MB adsorption on the CPHAC prepared. The effects of MB initial concentration, contact time, and temperature on the adsorption uptake were investigated. The MB solutions were withdrawn at equilibrium to determine the residual concentrations. The MB solutions were filtered using syringe filter prior to analysis in order to minimize interference of the carbon fines with the analysis. The MB concentrations in the supernatant solutions before and after adsorption were determined using a double beam UV-Vis spectrophotometer (Shimadzu UV-1601, Japan) at its maximum wavelength of 668 nm. The MB uptake at equilibrium, qe (mg/g), was calculated by Eq. 1.

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (2)$$

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Adsorptive removal of a synthetic textile dye using cocoa pod husks

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The adsorption of a synthetic textile dye (Remazol Brilliant Black Reactive) on cocoa pod husk-based activated carbon was investigated in batch process. The adsorbent prepared was characterized by gas adsorption surface analysis (Brunauer Emmett Teller, BET), scanning electron microscopy, and Fourier transform infrared spectroscopy. The effects of initial dye concentration, contact time, solution temperature, and solution pH were evaluated. Equilibrium data were fitted to Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models, the first being the best with maximum monolayer coverage of 111 mg g^{-1}. Kinetic data were fitted into pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models; the pseudo second-order model provided the best correlation. Maximum adsorption was observed at pH 7. Standard free energy, standard enthalpy, and standard entropy were also calculated. The adsorption interaction was found to be endothermic and spontaneous. Both the mean free energy of adsorption and the activation energy show that the mechanism is by physisorption.

Keywords: adsorption; cocoa pod husk activated carbon; Remazol Brilliant Black Reactive dye; isotherm; kinetics

Introduction

Synthetic dyes are commonly used in textile, leather, tanning, paper, rubber, plastics, cosmetics, pharmaceutical, and food industries. Synthetic dyes, classified by their chromophores, have different and stable chemical structures to meet various coloring requirements and are not often degraded and/or removed by conventional physical and chemical processes (Ahn, Chang, and Yoon 1999; Robinson et al. 2001). Remazol Brilliant Black Reactive (RBBR) dye is one of the most important dyes in the textile industry. RBBR dye, an anthraquinone derivative, represents an important class of toxic and recalcitrant organopollutant (Deveci, Unyayar, and Mazmanci 2004; Eichlerová et al. 2007). Conventionally, commercial activated carbon is used for adsorption process. However, it has several disadvantages. It is quite expensive, its regeneration is expensive, and also results in loss of adsorbent. For this reason, there is growing interest in utilizing biomass wastes/alternatives to activated carbon as low-cost adsorbents (Bailey, Olin, and Dean 1999; Gupta and Ali 2002; Babel and Kurniawan 2003; Gupta and Suhas 2009; Gupta and Mittal 2010).

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STRUCTURAL AND INTERACTION PROPERTIES OF ENCAPSULATED MnO_2 NANOWIRES FILLED MWCNTs

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Uniform encapsulated MnO_2 nanowires were achieved within the cavity of multiwalled carbon nanotubes (MWCNTs). The Raman spectra revealed a charge-transfer shifts between the MnO_2 particles and the inner tube of MWCNTs. Thin, uniform and continuous MnO_2 was observed with a diameter of 9 nm.

Keywords: Carbon nanotubes; nanowires; manganese dioxide.

1. Introduction

The purpose of chemical functionalization is to make carbon nanotubes (CNTs) soluble in different media,[1] compatible in composite systems,[2] react as sensors[3] and many other interesting applications. All functionalization methods of CNTs can be divided into two major groups: functionalization from outside (exohedral) and functionalization from inside (endohedral).[4] An example of exohedral functionalization includes wrapping of CNTs by polymers.[5,6] Functionalization from inside means that CNTs are functionalized by filling them with different nanoparticles; this can be achieved by exploiting the phenomenon of spontaneous penetration when nanotubes are filled with colloidal suspensions followed by evaporation of the carrier liquid.[4] A CNT provides capillary pressure inversely proportional to its inner tube diameter.[4] The first experiments on filling multiwalled CNTs (MWCNTs) with Cs, Se and S empirically found that materials with surface tension less than 200 mN/m could fill the nanotubes by capillary action.[7] Another endohedral method is the wet chemical method in which the CNTs are filled with some compounds, which react under particular thermal or chemical conditions and produce nanoparticles. The structure of the encapsulated materials significantly deviates from the structure of bulk materials.[8] Earlier work on MWCNT filling was done with Ag.[9] First, nanotubes were filled with molten $AgNO_3$ salt. Then, under an electron beam in the transmission electron microscope (TEM) chamber, the $AgNO_3$ was decomposed and Ag nanoparticles were formed inside the nanotubes. The filling efficiency was estimated to

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EFFECT OF PARA-HYDROXYBENZENE SULFONIC ACID ON THE PROPERTIES OF *EX SITU* PREPARED POLYANILINE/MULTIWALLED CARBON NANOTUBES–MnO_2

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New *ex situ* polyaniline (PANI)/MnO_2-filled multiwalled carbon nanotubes (MWCNTs) nanocomposites using para-hydroxybenzene sulfonic acid (PHBSA) as a dopant and linker exhibit enhanced electrical conductivity and interfacial interaction. Strong and enhanced interfacial interaction was observed on the surfaces of the filled carbon nanotubes and PANI. Transmission electron microscope (TEM) demonstrated clearly the improved bonding at the interface compared to the nanocomposite without PHBSA.

Keywords: Polyaniline; conducting polymer; multiwalled carbon nanotubes; nanocomposites.

1. Introduction

The concept of hybridizing the properties of organic and inorganic materials to form a unique material has been thought of for decades. The combination of nanosized materials with multifunctionality has remarkable impacts. Conducting polymers, in particular PANI, are the most interesting due to their low cost, good processability, environmental stability, unique active conduction mechanism,[1] and reversible control of conductivity both by charge-transfer doping and protonation.[2] Combination of PANI and MWCNTs to form nanocomposites has been reported having potential applications in optics, electronics, electrodes, etc.[3–5] MnO_2 is preferred compared to other transition metals due to its good combination of initiator, oxidation,[6] and conduction[7] properties. Mostly, the use of *in situ* technique has proven to be successful in achieving good compatibility between PANI and MWCNTs with high conductivity. Another method of preparation is the *ex situ* (solution process) method. While this method is valuable for both MWCNTs deaggregation and composite formation, its resulting conductivity is less.[3] The compatibility of this method remains a problem because the solvent removal process does not induce any wrapping of tubes usually obtained by *in situ* that promotes charge transfer process. In the hope to increase the compatibility of PANI with other polymer or solvent, some authors protonated PANI by functionalized protonic acids (camphorsulfonic acid, dodecylbenzenesulfonic acid, phosphoric acid

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Multiwalled Carbon Nanotubes Filled with Transition Metal Oxides as Supercapacitor Materials

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Abstract: Manganese oxide (MnO_2), nickel oxide (NiO), copper oxide (CuO) and iron oxide (Fe_2O_3)/multiwalled carbon nanotubes (MWCNTs) nanocomposites for supercapacitor electrodes were synthesized by wet chemical method using acid treated MWCNTs and respective salts. Structural and morphological characterizations of metal oxides encapsulated in MWCNTs were carried out using transmission electron microscopy (TEM) and energy dispersive x-ray (EDX). The electrochemical performances of MnO_2/MWCNTs, NiO/MWCNTs, Fe_2O_3/MWCNTs and CuO/MWCNTs on aqueous electrolytic supercapacitor were investigated using cyclic voltammetery (CV), galvanostatic charge-discharge. The MnO_2/MWCNTs and NiO/MWCNTs nanocomposite electrodes showed more significant capacitive behavior than other electrode materials of Fe_2O_3/MWCNTs, CuO/MWCNTs and pure MWCNTs. The average specific capacitance (SC) of the pure MWCNTs, NiO/MWCNTs and MnO_2/MWCNTs nanocomposites electrodes were found to be 68.56, 134.40 and 302.41 F/g, respectively.

Key words: Supercapacitor • Nanocomposites • Specific capacitance • Metal oxides

INTRODUCTION

The electrochemical capacitor (EC, also named as supercapacitor) is a novel type of energy storage device whose capacitance is 20–200 times higher than that of an electrolytic capacitor [1, 2]. The supercapacitor has several advantages of high power density, long cycle life, short charge time and safety over the battery and attracts great interests for energy storage devices [3].

Depending on charge-storage mechanism, they are basically classified into two types: electric double layer capacitors (EDLCs) based on carbon electrodes and pseudocapacitors with certain metal oxides (RuO_2, IrO_2, NiO, CoO_x, SnO_2 and MnO_2) [4, 5] or conducting polymers as electrode materials [6]. Carbon materials with high specific surface area, such as activated carbon, activated carbon fibers, carbon aerogels/foams and carbon nanotubes (CNTs) are the main electrode materials for supercapacitor application [7-9].

CNTs are attractive materials for electrodes of electrochemical energy storage devices due to their high conductivity, chemical stability, low mass density and large surface area. CNTs are mainly classified in to two groups; single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs) where both of them have been recognized as potential electrode materials for supercapacitors. The capacitance of CNT-based supercapacitor electrodes can be improved by various techniques such as activating CNTs with heat/acid treatment [10] modification of CNTs with conducting polymers [11] or with certain transition-metal oxides [12, 13].

Ruthenium oxides are widely used in electrochemical supercapacitors due to their high specific capacitance (SC) and prominent properties, [14, 15]. However, the high cost of ruthenium (Ru) has retarded its commercial acceptance as electrode materials in electrochemical capacitors. Recent researches have been focused on

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Remarkable Stability of Supercapacitor Material Synthesized by Manganese Oxide Filled in Multiwalled Carbon Nanotubes

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Abstract: Improving the electrochemical stability of manganese oxide/multiwalled carbon nanotubes (MnO_2/MWCNTs) nanocomposites is of great importance to many electrochemical supercapacitor applications. In this study, the electrochemical properties of MnO_2 filled inside the cavity of MWCNTs were investigated for the first time. The prepared nanocomposite was characterized by means of X-ray photoelectron spectroscopy (XPS), X-ray diffraction patterns (XRD), transmission electron microscopy (TEM) images, scanning electron microscopy (SEM) together with energy dispersive X-ray spectroscopy (EDX) and thermogravimetric analyses (TGA). Electrochemical characterization has been performed using cyclic voltammetry (CV), galvanostatic charging/discharging (CD) test. The TEM image, XRD analysis confirmed the high structural stability and CD test complied the high electrochemical stability of the prepared nanocomposite. Besides, MnO_2/MWCNTs nanocomposite supercapacitor showed superior cycling stability in the potential range of 0–1.0V due to the filling of the electroactive material inside the tubes and retained 96% of initial capacitance even over 200 cycles.

Keywords: Carbon nanotubes, wet chemical, filling, nanocomposite, specific capacitance, stability.

INTRODUCTION

In response to change the global landscape, supercapacitor has matured significantly over the last decade in energy storage. Energy storage devices are classified according to their energy and power densities [1]. Based on the charge storage mechanism, there are two major categories [2]: (1) electric double-layer capacitors (EDLC) and (2) redox capacitor (pseudocapacitors). To take full advantage of double-layer capacitance and pseudocapacitance, many metal oxide/carbon composite electrodes prepared by different methods have been investigated as hybrid electrode materials for supercapacitors [3, 4]. Regardless to their satisfaction results, searching for less energy loss and high stability of the supercapacitor materials have been the major subjects in supercapacitors research.

In terms of long cycle-life and high specific capacitance (SC) value, Carbon materials, such as acetylene black (AB) [5], activated carbon (AC) [6] and multiwalled carbon nanotubes (MWCNTs) [7] have been recognized as promising electrode materials for supercapacitors. Among all carbonaceous materials, MWCNTs are attractive materials for supercapacitors because of their superb properties, such as unique network of mesopores, high electrochemically accessible surface area of porous nanotubes arrays, excellent electronic conductivity and useful chemical stability [8,9]. Despite the high SC value of carbonaceous materials, they suffer from poor specific energy density [10]. Therefore recently, most of the researchers have focused on the hybrid supercapacitors because of their high working voltage and energy density.

Various metal oxides, such as RuO_2, Co_3O_4, NiO, Fe_2O_3, Ir_2O_3, SnO_2, MnO_2 etc., are being studied for the hybrid supercapacitors applications [11-17]. MnO_2 is one of the most promising pseudocapacitors electrode materials with respect to both its SC value and cost effectiveness [18,19]. Manganese can be present in various valence states, and its oxides are promising candidates for supercapacitors because of their low cost and being environmentally friendly [20].

It is noteworthy that most of the supercapacitors materials have highest decrease in capacitance in their first 200 cycles of galvanostatic charging/discharging (CD) test. Hence, the high initial fading of the capacitance decrease the overall stability of the supercapacitors. Wu *et al.*, [21] proposed that the capacitance fading mainly arises from mechanical failure of the electrode structure caused by the volume variation-induced stress, leading to loose contact between the oxide particles and carbon material and/or detachment of the oxide particles from the electrode matrix. Hence, in this work we decide to fill the metal oxides particle inside the narrow cavities of the MWCNTs in order to decrease the MnO_2 detachments. The encapsulation of MnO_2 inside MWCNTs not only complemented electrochemical window of the nanocomposite but also showed more stability and promising application in hybrid supercapacitors.

However, the main obstacle to overcome is the decrease in capacitance caused by the poor initial cycling stability of MnO_2/MWCNTs nanocomposites. So far, there is still no report on the hybrid supercapacitors fabricated with MnO_2 nanoparticles filled in MWCNTs to our best knowledge. In the present work, the hybrid nanocomposite of MnO_2 filled in MWCNTs was obtained by reduction of manganese nitrates solution in the narrow cavity of MWCNTs using wet chemical method, which is simple, convenient, and cheap compared with other methods [19, 22].

EXPERIMENTAL

Preparation of MnO_2/MWCNTs Nanocomposite and Morphological Characterization

The MWCNTs, in this work, were prepared by catalytic decomposition of methane using Ni/TiO_2 based catalyst [23-27]. Multi-step purification process consisting of oxidation in the air followed by acid reflux has been applied to purify the MWCNTs. MWCNTs with highest purity of ~99.9% was achieved and the complete description of the purification process was well defined and given our previous work [25]. In short, the MWCNTs were suspended in nitric acid (supplied by Sigma-Aldrich, 70%) and refluxed in the sonication bath for 3 h at 100°C in order to open the close end tips MWCNTs. The acid-treated MWCNTs were rinsed and filtered with distilled water at PH=7 and were subsequently dried at 70°C in the oven. 0.3 M of manganese nitrate (supplied by ACROS, 98%) solution has been prepared and as dried MWCNTs were suspended in the solution. The floating suspension of all manganese nitrate/MWCNTs sample was then stirred for 24 h at room temperature. The obtained suspensions were further washed with

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MnO_2-filled multiwalled carbon nanotube/polyaniline nanocomposites with enhanced interfacial interaction and electronic properties

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This paper reports the synthesis and characterization of new ternary nanocomposites combining polyaniline (PANI), multiwalled carbon nanotubes (MWCNTs) and manganese dioxide (MnO_2). MnO_2 was successfully incorporated within the MWCNTs. In situ polymerization of aniline in the presence of MWCNTs–MnO_2 was carried out to form PANI/MWCNT–MnO_2 nanocomposites, which were characterized by UV–visible and Fourier transform infrared spectroscopy, X-ray diffraction, field emission scanning electron microscopy with energy-dispersive X-ray analysis, and transmission electron microscopy, as well as electrical conductivity measurements. The PANI/MWCNT-MnO_2 nanocomposites showed enhanced electrical conductivity compared to neat PANI and PANI/MWCNTs without MnO_2 addition.
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Keywords: Polyaniline; Carbon nanotubes; Nanocomposites; Electrical properties; Transmission electron microscopy (TEM)

Polyaniline (PANI) is a conducting polymer that shows potential for future use due to its good processibility, environmental stability, unique active conduction mechanism [1] and reversible control of conductivity both by charge-transfer doping and protonation [2]. Potential applications of PANI include secondary batteries, electromagnetic interference shielding, molecular sensors, nonlinear optical devices, electrochromic displays and microelectronic devices [3–6]. Multiwalled carbon nanotubes (MWCNTs) can act as nanowires based on their much higher electric current-carrying capability in comparison to metallic wires of similar dimensions [7]. Filled MWCNTs with transition metals, particularly using MnO_2, has shown potential to improve the electrochemical [8] and conduction properties of MWCNTs [9,10]. Recently, the combination of PANI and MWCNTs to form nanocomposites has been reported [11–13]. However, to the best of our knowledge, the use of MnO_2-filled MWCNTs to generate a ternary PANI-based nanocomposite has not yet been investigated. This paper reports on the preparation of PANI/MWCNT–MnO_2 nanocomposites, investigating the effect of MnO_2 filling on the nanocomposite properties.

MWCNTs were produced by catalytic decomposition of methane using Ni/TiO_2-based catalyst as reported elsewhere [14]. The filling of MWCNTs was achieved by a wet chemical method. Complete descriptions of the synthesis of MWCNTs, their purification and filling with MnO_2 have been given in detail elsewhere [14–16]. The nanocomposites were synthesized by polymerization of aniline (ACS grade, Acros) with ammonium persulfate (Merck) as the oxidizing agent, with an oxidant to aniline molar ratio of 1.25:1 in the presence of the MnO_2-filled MWCNTs. A solution of HCl containing a predetermined amount of MWCNT–MnO_2 composites with respect to aniline volume was sonicated at room temperature. Aniline monomer was dissolved in HCl solution and added to the MWCNT–MnO_2 suspension and stirred for 30 min. Both the aniline solution and the suspended MWCNTs–MnO_2 were mixed and sonicated for 1 h. The oxidant was dissolved in HCl solution and then slowly added dropwise to the reaction

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MnO_2-FILLED MULTIWALLED CARBON NANOTUBE/POLYANILINE NANOCOMPOSITES: EFFECT OF LOADING ON THE CONDUCTION PROPERTIES AND ITS PERCOLATION THRESHOLD

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This paper reports the synthesis and characterization of ternary nanocomposites consisting of polyaniline (PANI), multiwalled carbon nanotubes (MWCNTs) and manganese dioxide (MnO_2) at different MWCNT–MnO_2 loadings. The composite electrical percolation threshold is investigated as well. The *in situ* nanocomposites were characterized by UV-visible, Fourier transform and Raman spectroscopy, thermogravimetric analysis, field emission scanning electron microscopy, and electrical conductivity measurements. The conductivity of the nanocomposite reached up to 78.79 Scm^{-1} with 50 wt.% addition of MWCNT–MnO_2 with good conduction stability and reversibility. The percolation threshold of this nanocomposite was achieved at 0.5 wt.%. Using the scaling law of the percolation theory, it was found that the theoretical conductivity of the nanocomposite exhibited an exponential factor, (t) of 1.38 instead of the universal t value of 2.

Keywords: Polyaniline; electrical conductivity; carbon; nanocomposite; percolation.

1. Introduction

Polyaniline (PANI) is one of the most interesting conducting polymers due to its low cost, good processability, environmental stability, unique active conduction mechanism[1] and reversible control of conductivity both by charge-transfer doping and protonation.[2] PANI can exist in a number of different oxidation states. It can exist as the fully oxidized pernigraniline via protoemaraldine to the fully reduced leucoemaraldine. The 50% oxidized polymer had been termed emaraldine.[3] PANI becomes conducting when the emaraldine base (EB) form is protonated and charge carriers are generated. The protonated emaraldine salt (ES) has conductivity many orders of magnitude higher than that of common polymers but lower than that of typical metals. Generally, ES and EB forms of PANI can be interchanged by doping and dedoping with acid and base[4] and the conductivity of PANI can be controlled, ranging from 10^{-11} to 10^{3} Scm^{-1}.[5] Potential applications of PANI include secondary batteries, electromagnetic interference shielding, molecular sensors, nonlinear optical devices, electrochromic displays and microelectronic devices.[6–9] Carbon nanotubes (CNTs) have received much interest for their use in fabricating new classes

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HIGHLY EFFICIENT HYBRID SUPERCAPACITOR MATERIAL FROM NICKEL-MANGANESE OXIDES/MWCNTs/PEDOT NANOCOMPOSITE

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A novel ternary nanocomposite of nickel-manganese oxides/multi-walled carbon nanotubes (NMO/MWCNTs) coated with poly (3,4-ethylenedioxythiophene)(PEDOT) was prepared by chemical oxidation method. The filling of NMO particles inside MWCNTs and the uniform coating of NMO/MWCNTs with PEDOT intensified the capacitive behavior of MWCNTs. The lowest IR drop (0.1 V) and highest specific capacitance (SC) values of 526.55 F/g of NMO/MWCNTs/PEDOT imply it as highly efficient hybrid supercapacitor materials in 6 M KOH electrolyte.

Keywords: Nickel-manganese oxides; PEDOT; nanocomposite; chemical oxidation; polymerization; specific capacitance.

1. Introduction

In recent years, supercapacitors are attracting great attention because of their high capacitance and potential applications in electronic devices.[1] The present trend in the research of supercapacitor is to develop economical electrode material of high performance. Recently, multi-walled carbon nanotubes (MWCNTs) have been recognized as potential electrode materials for supercapacitors[2] and their capacitance can be further increased by doping transition metal oxides[3] and modifying their surfaces with conducting polymers.[4]

Of the various transition metal oxides/MWCNTs, nanocomposite Ruthenium oxide (RuO_2)/MWCNTs presents the highest specific capacitance (SC) value,[5] but it has the inherent disadvantage of being both expensive and toxic.[6] In view of finding an inexpensive alternative to RuO_2, manganese oxide (MnO_2)[7] and nickel oxide (NiO)[8] have recently been found to possess capacitive characteristics with acceptable SC value.

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Review

Development of functionalized zeolite membrane and its potential role as reactor combined separator for *para*-xylene production from xylene isomers

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Abstract

Zeolite membranes are relatively new class of advanced materials where its characteristics have opened up the new opportunities of their application in separator, sensitive chemical sensors, and catalytic membrane reactor. The present review focuses on the development of functionalized zeolite membrane and subsequently its usage in the catalytic membrane reactor for combined separation and reaction of xylene isomers in a single unit. Synthesis of functionalized zeolite microporous crystal, development of functionalized zeolite membrane and xylene isomerization are presented and discussed. The models representing combined separation and reaction using functionalized zeolite membrane are also suggested.
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Keywords: Functionalized zeolite membrane; Synthesis; Xylene isomerization; Catalytic membrane reactor; Modeling

1. Introduction

The industrial production and recovery of *para*-xylene is an important step in a large petrochemical plant. Xylene has three isomers namely *para*-xylene (molecular size ~0.58 nm), *ortho*-xylene and *meta*-xylene (molecular size ~0.68 nm) and are used as industrial solvents or intermediates for many derivatives [1–5]. Of the three xylene isomers, *para*-xylene has the largest commercial market. As reported by Ministry of Economy, Trade and Industry (MITE), Japan, the worldwide demand for *para*-xylene will increase to 27.8 million tonnes in year 2008 from 18.7 million tonnes in year 2002. *Para*-xylene is the feed for the production of pure terephthalic acid (PTA), which in turn is used in the production of polyester resin and fibers.

In order to meet the *para*-xylene demand, *para*-xylene is currently produced in the petrochemical industry through two different routes: (1) separation of *para*-xylene from its isomers and (2) conversion of less used *ortho*- and *meta*-xylenes to *para*-xylene through xylene isomerization reaction. Separation of *para*-xylene from its isomers is an important operation in the petrochemical industry, but it is difficult to separate the isomers due to their close boiling points, *para*-xylene (boiling point = 138.4 °C), *meta*-xylene (boiling point = 139 °C) and *ortho*-xylene (boiling point = 144.4 °C). Thus, the xylene isomers are currently separated by cryogenic crystallization, or selective adsorption process Parex, which is highly energy intensive. The current technology for xylene isomerization process such as XyMax (ExxonMobil) also consumes high energy. Therefore, there is a need to develop an efficient and energy saving technology to recover and separate *para*-xylene from its isomers.

Zeolite membranes or films have been in focus in recent years because of their well-defined micropore structure, good thermal and structural stability, high mechanical strength, feasible for steady-state operation, low energy consumption, resistance to relatively extreme chemical environment and great potential for combined steps of reaction/separation [2,6–10]. Zeolites are crystalline, microporous aluminosilicates which find extensive industrial usage as catalysts, adsorbents, and ion exchangers with high capacities and selectivities [9,11,12]. When zeolites are grown as films, zeolite membrane is formed. The characteristics of zeolite membrane have found its new application in gas, vapor and liquid separation especially in petrochemical industry based on their properties adsorption, preferential diffusion,

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SYNTHESIS AND CHARACTERISATION OF SULPHONIC ACID 3-MERCAPTOPROPYLTRIMETHOXYSILANE FUNCTIONALISED SILICALITE-1 MEMBRANE

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Abstract

10% and 20% of 3-mercaptopropyltrimethoxysilane was introduced into the silicalite-1 pore-structure by utilising in situ deposition method and subsequently oxidized to sulphonic acid silicalite-1 membrane. The resulting organic-inorganic hybrid membrane was characterized for its crystallinity and orientation (XRD), surface morphology and thickness (SEM) and elements present in the membrane (EDAX). Sulphonic acid functionalised silicalite-1 membrane is a new type of catalytic shape selective membrane which may be useful for combined separation and reaction process.

Keywords: Synthesis, Characterisation, Functionalised Silicalite-1 Membrane.

1. Introduction

Zeolite membranes or films have been well known of their well-defined micropore structure, good thermal and structural stability, high mechanical strength, feasible for steady-state operation, low energy consumption, resistance to relatively extreme chemical environment and great potential for combined steps of reaction/separation [1-6]. Zeolites are crystalline, microporous aluminosilicates which find extensive industrial uses as catalysts, adsorbents, and ion exchangers with high capacities and selectivities [7-8]. When zeolites are grown as films, zeolite membrane is formed. The characteristics of zeolite membrane have found its new application in gas, vapour and liquid separation especially in petrochemical industry based on their properties adsorption,

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Synthesis, Characterization of Phenethyltrimethoxysilane (PE) Modified Organic-Inorganic Hybrid Silicalite-1 Molecular Sieves and Its Transformation into Solid Acid Materials

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Keywords: Organic-inorganic hybrid materials, Synthesis, Characterization, Solid Acid Materials

Abstract. Organic-inorganic hybrid nanoporous materials with silicalite-1 structure were synthesized in one step co-condensation technique and subsequent transformed into solid acid materials. The tetraethoxysilane (TEOS) was used as the primary inorganic silica source with the phenethyltrimethoxysilane (PE) as an organic modifier. The effect of the PE presence in the initial synthesis mixture was studied by varying the molar ratio of PE to TEOS in the range of 0.05 to 0.20. The resulting organic-inorganic hybrid materials were characterized for its crystallinity (X-ray diffraction, XRD), surface morphology (scanning electron microscopy, SEM) and elemental composition (elemental analysis). The degree of chemical interactions between the organic and inorganic phases was determined by Fourier transform infrared spectroscopy (FTIR). The acid strength of the organic-inorganic hybrid solid acid materials was also obtained by titration technique.

Introduction

In the recent year, the increasing demand of nanostructured materials with tailored chemical and physical characteristic has resulted in the development of new class of organic-inorganic hybrid nanoporous materials [1]. Various organic moieties, including thiol, amine, phenyl, or allyl groups, have been successfully incorporated into mesoporous structure and subsequently transformed into organosulfonic acid group (M41S and SBA-15),following different synthesis methods [2]. The combination of inorganic and organic fragments inside the structure of porous materials significantly modify the physical and chemical properties of inorganic materials; resulting into new desirable advanced properties [3].

The weak hydrothermal stability and inhomogeneous distribution of active sites in the mesoporous hybrid materials have limit their practical and potential applications [1]. Nevertheless, the modification of microporous zeolites with organic group can be of interest and achieved little success [4-5]. Combining inorganic and organic moieties to form well-defined hybrid materials is a challenging task for microporous zeolite. In the present study, synthesis of organic-inorganic hybrid microporous materials having silicalite-1 structure is reported. The effect of the organosilanes at various concentrations present in the initial synthesis mixtures on the formation of hybrid microporous materials was systematically studied. The organic moieties were subsequently transformed into organosulfonic acid solid via sulfonation. The resulting hybrid materials are characterized by a number of physical and chemical techniques to provide detailed information about the chemical nature of the incorporated organic moieties and their effect on the microstructure of the parent silicalite-1.

Experimental

Samples preparation. Organic-inorganic hybrid materials having silicalite-1 structure were synthesized by mixing tetrapropylammonium hydroxide (TPAOH, 1 M, Merck), deionized (DI)

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Process optimization studies of *p*-xylene separation from binary xylene mixture over silicalite-1 membrane using response surface methodology

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ABSTRACT

The process optimization of *p*-xylene separation from *p*-/*o*-xylene binary mixture through silicalite-1 membrane using statistical design of experiments (DoE) is reported in the present study. The silicalite-1 membrane was synthesized and characterized using different analytical techniques. The effect of three important process variables, temperature (150–250 °C), *p*-xylene feed partial pressure (0.04–0.50 kPa) and *p*-xylene feed composition (0.20–0.80) on the separation performance of the membrane was studied. The response surface methodology (RSM) coupled with central composite design (CCD) was used to develop three models to correlate the effect of process variables to three responses: (i) *p*-xylene flux, (ii) *o*-xylene flux and (iii) *p*-/*o*-xylene separation factor. The most influential factor on each of the response was identified using the analysis of variance (ANOVA). The interaction between the three variables was systematically investigated based on three-dimensional response surface plots. The optimum operating condition for the process was determined by setting the optimization criteria to maximize the *p*-xylene flux and *p*-/*o*-xylene separation factor, and to minimize the *o*-xylene flux. The optimum *p*-xylene flux of 3.83×10^{-6} mol/m^2 s and *p*-/*o*-xylene separation factor of 46 were obtained at a temperature of 198 °C, *p*-xylene feed partial pressure of 0.15 kPa and *p*-xylene feed composition of 0.80. The simulated values obtained from the statistical model were in agreement with the experimental results within an average error of ±2.70%. The mass transport of xylene isomers and its separation in the silicalite-1 membrane was related with the characteristics of the membrane.

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1. Introduction

The industrial production and recovery of *p*-xylene is an important operation in a large petrochemical plant. Xylene has three isomers namely *p*-xylene (molecular size ~0.58 nm), *o*-xylene and *m*-xylene (molecular size ~0.68 nm), and is used as industrial solvents or intermediates for many derivatives [1–5]. Of the three xylene isomers, *p*-xylene has the largest commercial market. The isomer *p*-xylene is the feed for the pure terephthalic acid (PTA) production, which in turn is used in the production of polyester resin and fibers.

Separation of *p*-xylene from its isomers is an important operation in petrochemical industry. However, the process is difficult because their boiling points (*p*-xylene: 138 °C, *m*-xylene: 139 °C and *o*-xylene: 144 °C) are close. Xylenes isomers are currently separated by cryogenic crystallization, or selective adsorption process Parex, which is highly energy intensive. Therefore, there is a need to develop an efficient and energy saving technology to recover and separate *p*-xylene from its isomers.

Zeolite membranes have been in focus in recent years due to their potential application in wide range of industrial processes especially in petrochemical industry [6–10]. Zeolite membrane with well-defined micropore structure, good thermal and structural stability have potential for its application in membrane reactor, catalytic membrane reactor, sensitive chemical sensor and gas sensor [6,8,11–15]. Currently, zeolite membrane is reported its application in corrosion protection and antimicrobial coatings [16,17].

MFI-type zeolite membranes (ZSM-5 and Silicalite-1) are the most common membranes reported by the researchers. MFI type membranes have the pore structure of straight (*b*-oriented), circular pores (0.54 × 0.56 nm) interconnected with sinusoidal (*a*-oriented), elliptical pores (0.51 × 0.54 nm) and a tortuous path along the *c*-direction [1], which are near to the sizes of many industrially important organic molecules. Therefore, these membranes can be used in the separation of organic compounds with kinetic diameters close to their pores. Moreover, zeolite membrane might offer significant advantage compared to existing technology for the separation

Abbreviations: ANOVA, analysis of variance; CCD, central composite design; DF, degrees of freedom; DoE, design of experiments; *F* value, measurement of distance between individual distributions (fit value); MFI, Mobil-Five (Zeolite Socony Mobil-Five, ZSM-5); Prob, probability; RSM, response surface methodology; SEM, scanning electron microscope; XRD, X-ray diffraction.

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Separation of *p*-xylene from binary xylene mixture over silicalite-1 membrane: Experimental and modeling studies

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ABSTRACT

The permeation of single component and binary mixture containing *p*-xylene and *o*-xylene through silicalite-1 membrane was studied experimentally in the temperature range of 150–250 °C at feed partial pressure of 0.26 kPa for *p*-xylene and 0.22 kPa for *o*-xylene. The model for single component flux based on the combination of dual-site Langmuir isotherm and Maxwell–Stefan formulation was derived. The adsorption parameters were estimated by minimizing the difference between the experimental flux and simulated flux. The heat of adsorption and entropy values obtained were in good agreement with the reported values. The effect of feed partial pressure in the range of 0.20–1.50 kPa on xylene flux was predicted using the adsorption parameters and compared with the experimental values. The Maxwell–Stefan diffusion model, in combination with the ideal adsorbed solution (IAS) theory and single-component adsorption parameters was used to predict the permeation flux of *p*-xylene and *o*-xylene for binary xylene mixture through the silicalite-1 membrane. The simulated results were in good agreement with the experimental data. The simulated adsorption isotherm in higher temperature range of 150–250 °C using the model and derived adsorption parameters could provide useful information for adsorption of xylene molecules on silicalite-1 membrane at a higher operating temperature.

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1. Introduction

Separation of *p*-xylene from its isomer, *m*-xylene and *o*-xylene using MFI-type zeolite membrane has attracted much attention in the recent years (Gu et al., 2006; Lai and Tsapatsis, 2004; Tarditi et al., 2006a, 2006b; Xomeritakis et al., 2001). MFI-type zeolite membranes, ZSM-5 and silicalite-1 with the uniform dimensions of circular ($0.54 \times 0.56\ nm^2$) and elliptical pores ($0.51 \times 0.54\ nm^2$) (Choudhary et al., 1997), are capable to separate close-boiling point xylene isomers, which are currently separated by energy intensive technology such as cryogenic crystallization or selective adsorption process Parex. Although highly selective separations of xylene isomers could be achieved based on molecular sieving effect, it is reported in the literature that *p*-xylene adsorbs selectively on MFI zeolite membrane compared to its isomers and its permeation behavior is controlled by an adsorption–diffusion mechanism (Gu et al., 2006; Lai and Tsapatsis, 2004; Tarditi et al., 2006a, 2006b, 2008; Xomeritakis et al., 2001). The two factors that influence the selectivity of the separation are: (i) differences in the adsorption characteristics of the individual species, and (ii) differences in the mobilities (diffusivities) of the components (Krishna, 2001a). Thus, the characteristics of the zeolite membrane dominate the transport of xylene molecules through the membrane (Tarditi et al., 2008).

Extensive studies of adsorption and diffusion of hydrocarbon on silicalite-1 membrane have been reported by Krishna and coworkers (Calero et al., 2001; Kapteijn et al., 2000; Krishna and Paschek, 2000a, 2001b; Krishna and van Baten, 2005; Vlugt et al., 1999). For the description of the equilibrium adsorption in silicalite-1 membrane, the molecular shape and size of the component significantly affect molecular locations in the channels and intersections of silicalite-1, resulting in different adsorption behaviors (Zhu et al., 2000). Therefore, various adsorption models, i.e. Langmuir isotherm, dual site Langmuir isotherm, extended Langmuir isotherm, Ideal Adsorbed Sorption Theory (IAST) and Real Adsorbed Sorption Theory (RAST) have been applied to describe the adsorption isotherms for single component, binary mixture and multicomponents mixture. Krishna et al. (1999) reported that single component adsorption isotherm of benzene, *p*-xylene, *n*-hexane, *n*-heptane and branched alkanes in silicalite-1 membrane is adequately modeled using a dual-site Langmuir model due to the preferential location of molecules at certain sites in the silicalite-1 structure. A distinction between two sites with different sorption characteristics was accounted in this model: site A, refers to the intersections between the straight channels and the zig-zag channels, and site B, refers to the channel interiors (straight or zig zag channels) (Krishna et al., 1999; Krishna and Paschek, 2000a). Narkiewicz-Michalek et al. (1997) confirmed and reported that the two types of adsorption sites were involved in the adsorption of benzene and *p*-xylene on ZSM-5 zeolites.

It is generally accepted that the Maxwell–Stefan formulation offers the most nearest quantitative prediction for diffusion of

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Xylene isomerization kinetic over acid-functionalized silicalite-1 catalytic membranes: Experimental and modeling studies

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ABSTRACT

m-Xylene isomerization kinetics has been studied using acid-functionalized silicalite-1 catalytic membrane in the temperature range of 355–450 °C. Two types of catalytic membranes: (1) propylsulfonic acid-functionalized silicalite-1 membrane and (2) arenesulfonic acid-functionalized silicalite-1 membrane were synthesized on α-alumina support via one-step *in situ* hydrothermal crystallization and subsequent post-synthesis modifications. The membranes were characterized by scanning electron microscopy (SEM), ammonia temperature-programmed desorption (NH_3-TPD) and Fourier transform infrared spectroscopy (FT-IR). Arenesulfonic acid-functionalized silicalite-1 membrane with its higher acidity gave better catalytic activity as compared to propylsulfonic acid-functionalized silicalite-1 membrane. The continuous removal of reaction products over the membrane contributed in the higher *p*-xylene yield. A triangular reaction scheme based on time on stream (TOS) model was used to analyze the experimental data. The simulated results were in good agreement with the experimental results, within an error less than ±5%. The estimated activation energies indicated that conversion of *m*-xylene to *p*-xylene in both acid-functionalized silicalite-1 membranes is affected by the mass transfer rate through the membrane, while conversion of *m*-xylene to *o*-xylene is controlled by the reaction rate.

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1. Introduction

Para-xylene (*p*-xylene) is the feed for pure terephthalic acid (PTA) production which has the largest commercial market as compared to its isomers, meta-xylene (*m*-xylene) and ortho-xylene (*o*-xylene). With increasing demand of *p*-xylene, selective production of *p*-xylene by *m*-xylene isomerization using zeolite catalyst has gained considerable interest over the years and much attention has been focused on ZSM-5 zeolite as catalyst due to its high activity and shape selectivity [1,2]. Recently, the application of zeolite membrane as catalytic membrane has been reported by number of researchers [3–8] to improve *p*-xylene yield by selective removal of the product from the reactor. The application of catalytic membrane reactor has proven flexibility of its operation and improvement in product selectivity in Knoevenagel condensation reaction between benzaldehyde and ethyl acetoacetate [9–11].

van Dyk et al. [6] reported that *p*-xylene yield of about 10% was enhanced in an extractor-type membrane reactor as compare to the conventional fixed bed reactor. An increment in *p*-xylene production of 28% was observed by Tarditi et al. [5] using 100% exchanged Ba-ZSM-5 in the membrane reactor. Haag et al. [7] also reported 15% higher *m*-xylene conversion and 10% more *p*-xylene selectivity in H-ZSM-5 catalytic membrane reactor as compared to the conventional packed-bed reactor. Recently, Zhang et al. [8] reported that an increment of 26% *p*-xylene yield could be achieved in a silicalite-1 membrane reactor packed with H-ZSM-5 catalyst. However, H-ZSM-5 in membrane reactors gave moderate to low selectivity of *p*-xylene [12,13].

There is a need to develop a catalytic membrane in order to improve *p*-xylene yield, selectivity and separation rate. Due to the higher diffusion rate of *p*-xylene compared to *m*-xylene and *o*-xylene, *p*-xylene could be separated though silicalite-1 membrane [14–16]. However, silicalite-1 is catalytically inactive in its pure form (an aluminum-free analogue of ZSM-5 (Si/Al = ∞)). It is reported in the literature that selective and continuous removal of *p*-xylene from the reaction system could enhance xylene isomerization and thus higher selectivity and yield. Therefore, it has drawn an interest in the synthesis of silicalite-1 membrane with catalytic acid sites.

To best of our knowledge, synthesis of acid-functionalized silicalite-1 membrane and its performance in *m*-xylene isomerization has not been reported. Earlier, we reported the introduction of acid sites in silicalite-1, by adding organic-functional groups into the synthesis mixture and subsequent transformation of organic-functional group into acid-functionalized silicalite-1 [17]. The catalytic activity of these membranes in xylene isomerization

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Propylsulfonic acid-functionalized partially crystalline silicalite-1 materials: synthesis and characterization

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Abstract Propylsulfonic acid-functionalized partially crystalline silicalite-1 materials were synthesized via one step co-condensation technique by varying the molar ratio of organosilane source, 3-mercaptopropyltrimethoxysilane (3MP) to tetraethylorthosilicate (TEOS) in the range of 0.05–0.30, and subsequent oxidation of thiol group to propylsulfonic acid using hydrogen peroxide (H_2O_2). These materials were characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and nitrogen adsorption–desorption method. The structure of these materials was determined by Fourier transform infrared spectroscopy (FT-IR) and ^{29}Si and ^{13}C solid state NMR. XRD results show that % crystallinity of the materials decreased with the increase in 3MP concentration in the synthesis mixture. Selected area electron diffraction (SAED) showed the presence of crystalline and amorphous phases in the samples. An amorphous phase was formed when 3MP concentration was 30 mol% of the total silica source. After elimination of the structure directing agent (SDA) by calcination at 420 °C, thermogravimetric analysis (TGA) shows that the structure was thermally stable up to 550 °C. Ammonia temperature-programmed desorption (NH_3-TPD) shows that the acid capacity of these materials was in the range of 1.19–1.83 mmol H^+/g, which shows that these materials could be used as potential heterogeneous acid catalyst.

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1 Introduction

Zeolites are crystalline microporous aluminosilicates materials with well-defined pore structure which generated considerable interest in their application in the field of catalysis, adsorption and separation [1]. The application of zeolites as catalysts for industrial processes has been widely reported in the literature [2, 3]. From a catalytic point of view, the efficiency of zeolites as catalyst is related to their crystalline structure, strength and nature of the acid sites present. These properties are important to the shape selectivity catalysis for reactions occurring within the micropore system [4, 5].

A variety of modification methods over ZSM-5 zeolite (MFI-type zeolite) such as by varying Si/Al ratio, crystallite size and morphology, or modifications of extra-framework by cation exchange, pore blockage, isomorphous substitution, metal substitution and functionalization with organic group [3, 6–9], have been reported in order to obtain high selectivity of desired products in the catalytic reactions such as toluene disproportionation, isomerization and alkylation reaction [10]. There are reports to synthesize zeolites with smaller crystal sizes [4, 5] which shorten the intracrystalline diffusion path for the reactants and products and at the same time increase in the surface area provides a large number of external active sites [11–14].

In the synthesis of ZSM-5 by varying Si/Al ratio, the increase in Al increases the acid capacity of the catalyst,

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Synthesis, structure and acid characteristics of partially crystalline silicalite-1 based materials

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ABSTRACT

A series of partially crystalline silicalite-1 based materials were synthesized by varying the molar ratio of organosilane source, phenethyltrimethoxysilane (PE) to tetraethylorthosilicate (TEOS) in the range of 0.05–0.50, using one step co-condensation hydrothermal synthesis method. The phenethyl group was subsequently sulfonated to arenesulfonic acid group following strong acid treatment. The resulting materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption and desorption and elemental analysis. The structure of these materials was determined by Fourier transform infrared spectroscopy (FTIR), ^{29}Si and ^{13}C solid state NMR. The % crystallinity of the partially crystalline silicalite-1 as determined from XRD was in the range of 33–73%. The average crystallite size decreased with the increase of PE concentration in the synthesis mixture. The thermogravimetric analysis shows that the structures were thermally stable up to 550 °C after elimination of the structure directing agents (SDAs) by calcination at 420 °C. The acid capacities of these materials ranged from 2.52 to 6.63 mmol H^+/g.

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1. Introduction

Zeolites are crystalline microporous aluminosilicates materials with well-defined micropore structure, good thermal and structural stability and resistance to relatively extreme chemical environment [1,2]. The use of zeolites as acid catalysts for industrial processes, particularly in petroleum refining and petrochemicals, has been widely reported in the literature [3,4]. The most important applications are found in the field of cracking, hydrocracking, isomerization, alkylation and reforming reactions [5,6]. In the utilization of zeolitic catalysts, the reaction activity and product selectivity depend strongly on the number, strength and nature of the acid sites present, crystal/particle size and morphology, as well as the shape and size of the micropores which can induce different shape-selectivity effects on the product distribution [7]. These particular properties are obtained by varying Si/Al ratio, crystallite size and morphology, or modifications of extra-framework by cation exchange, pore blockage and elimination of external sites, isomorphous substitution and functionalization with organic group [4,8–11].

Among all the zeolites, MFI-type (ZSM-5 and silicalite-1) has been extensively studied for industrial processes because of its medium pore-size dimension (0.54 × 0.56 nm). A significant research effort has been devoted to the synthesis of MFI zeolite with smaller crystal size due to its advantages [12]. In the early 1980s, Jacobs et al. [13] reported the synthesis of partial crystalline ZSM-5 zeolite which contained small crystallites of less than 8 nm in size within an amorphous matrix, using shorter hydrothermal synthesis times. Nicolaides et al. [3,4,14] reported the synthesis of partially crystalline ZSM-5 based materials (NAS materials) using lower synthesis temperatures, ranging from 25 to 140 °C. ZSM-5 based materials with XRD crystallinity level as low as 2% exhibited superior catalytic performance (higher selectivities and yields) in the skeletal isomerization of linear butenes to *iso*-butene, due to the decreased of zeolite pore lengths presented in these low crystalline materials [4]. These materials with XRD crystallinities lower than 30%, partially crystalline samples possessing 30–70% crystallinity and highly crystalline materials with >70% XRD crystallinity, were tested for their catalytic performance in *n*-hexane cracking activity. They reported that the number of strong Bronsted acid sites and *n*-hexane cracking activity were found to be disproportionately low for the samples with XRD relative crystallinities <30%, and both become significantly higher only at crystallinity levels higher than 30% [14].

In reviewing the reports on the improved catalytic performance by using smaller crystal size and partially crystalline ZSM-5, it has drawn interest to synthesize partially crystalline silicalite-1 based materials. These materials could produce smaller crystal size and extra-framework (amorphous species) with active acid sites. Silicalite-1 is an aluminum-free analogue of ZSM-5 (Si/Al = ∞) which is catalytically inactive in its pure form. In defining the acidity of the

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Synthesis, characterization and reactive separation activity of acid-functionalized silicalite-1 catalytic membrane in *m*-xylene isomerization

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ABSTRACT

Propylsulfonic acid-functionalized silicalite-1 membrane and arenesulfonic acid-functionalized silicalite-1 membrane were synthesized over α-alumina support via one-step *in situ* hydrothermal crystallization and subsequent post-synthesis modification. Propylsulfonic acid-functionalized silicalite-1 membrane was synthesized using 3-mercaptopropyltrimethoxysilane (3MP) as an organosilane source whereas for arenesulfonic acid silicalite-1 membrane, phenethyltrimethoxysilane (PE) was used as an organosilane source. The acid capacity of the membrane was varied by adjusting the concentration of organosilane from 5 mol% to 20 mol%. The membranes were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen gas permeation. Ammonia temperature-programmed desorption (NH_3-TPD) and Fourier transform infrared spectroscopy (FT-IR) showed the presence of strong Brönsted acid sites in both membranes. The total acid capacity increased with increase in organosilane concentration in the synthesis mixture. Both membranes were tested for their catalytic activity in *m*-xylene isomerization reaction in the temperature range of 355–450 °C. Due to higher acid density, arenesulfonic acid-functionalized silicalite-1 membrane gave higher catalytic activity compared to propylsulfonic acid-functionalized silicalite-1 membrane. At 450 °C, *m*-xylene conversion of 57% with 33% *p*-xylene yield was achieved using arenesulfonic acid-functionalized silicalite-1 membrane with 15 mol% of phenethyltrimethoxysilane, while *m*-xylene conversion of 46% with 28% *p*-xylene yield was achieved using propylsulfonic acid-functionalized silicalite-1 membrane with 15 mol% of 3-mercaptopropyltrimethoxysilane. The enhancement in *p*-xylene yield was due to the simultaneous isomerization reaction and separation of the reaction products through the catalytic membrane. Both catalytic membranes exhibited good structural stability after subjected to isomerization reaction study for 120 h.

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1. Introduction

Para-xylene (*p*-xylene), meta-xylene (*m*-xylene) and ortho-xylene (*o*-xylene) are the three isomers of xylene and used as industrial solvents or intermediates for many derivatives. Among the three isomers, *p*-xylene has the largest commercial market. *p*-Xylene is the feed for pure terephthalic acid (PTA) production, which is generally produced in the petrochemical industry following: (1) separation of *p*-xylene from its isomers (cryogenic crystallization or selective adsorption process Parex) and (2) conversion of *o*-xylene and *m*-xylene to *p*-xylene through xylene isomerization (XyMax, ExxonMobil) [1–3]. The current technologies for *p*-xylene production are highly energy intensive, and therefore, continuous efforts have been directed to reduce the production cost of *p*-xylene and to improve *p*-xylene yield and selectivity [4–6].

Zeolite membranes have been in focus in recent years because of their well-defined micropore structure, good thermal and structural stability. These membranes are suitable for their application in membrane reactors at high temperature [7–10]. Most of these studies reported MFI type (ZSM-5 and silicalite-1) membranes, due to their pore structure near to the sizes of many important organic molecules [7,8]. The application of zeolite membrane as catalytic membrane reactors has improved catalytic activity, i.e., conversion, selectivity and yield by selective removal of the product from the reactor [11,12]. The combined separation and reaction in a single unit has also provided better flexibility of operation and enhancement in the reaction process [13].

Xylene isomerization is an acid-catalyzed reaction and the use of H-ZSM-5 as catalyst in the membrane reactor as well as H-ZSM-5 catalytic membrane has been reported by a number of researchers. van Dyk et al. [4] reported that *p*-xylene yield of about 10% was enhanced in an extractor-type membrane reactor as compare to the conventional fixed bed reactor. Haag et al. [10] also reported 15% higher *m*-xylene conversion and 10% more *p*-xylene selectivity in H-ZSM-5 catalytic membrane reactor as compared to the conven-

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Separation of *p*-xylene from ternary xylene mixture using silicalite-1 membrane: process optimization studies

Yin Fong Yeong, Ahmad Zuhairi Abdullah, Abdul Latif Ahmad and Subhash Bhatia*

Abstract

BACKGROUND: The design of experiments (DoE) is applied to the process optimization of *p*-xylene (pX) separation from its isomers *m*-xylene (mX) and *o*-xylene (oX) mixture using silicalite-1 membrane supported on α-alumina. A central composite design (CCD) coupled with response surface methodology (RSM) was used to correlate the effect of two separation process variables, temperature (150–250 °C) and pX feed partial pressure (0.10–0.26 kPa) to three responses: (i) pX flux; (ii) pX/oX separation factor; and (iii) pX/mX separation factor. The significant factors affecting each response were elucidated from the analysis of variance (ANOVA). The interaction between two variables was investigated systematically based on three-dimensional response surface plots.

RESULTS: The optimization criteria were used to maximize the value of pX flux, pX/mX separation factor and pX/oX separation factor. The optimum pX flux of 5.94 × 10^{-6} mol m^{-2} s^{-1}, pX/oX separation factor of 19 and pX/mX separation factor of 20 were obtained at a temperature of 198 °C and pX feed partial pressure of 0.22 kPa.

CONCLUSIONS: The experimental results were in good agreement with the simulated values obtained from the proposed models, with an average error of ±2.90%. In comparison with the conventional approach, DoE provides better flexibility of the process studies and a useful guideline for the membrane process operation for pX separation.
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Keywords: separation; ternary xylene mixture; silicalite-1 membrane; design of experiments (DoE); optimization

INTRODUCTION

Zeolite membranes have been the focus of attention in recent years because of their characteristics (well defined micropore structure, good thermal and structural stability), and have found new applications in gas, vapor and liquid separation, especially in the petrochemical industry.[1–5] One particular process in which zeolite membranes offer significant advantages over existing technology is the separation of close-boiling point hydrocarbons, xylene isomers, which are difficult to separate by distillation or other complex and energy-intensive processes.[6–10]

Separation of para-xylene (pX) from its isomers, meta-xylene (mX) and ortho-xylene (oX) is an important operation in the petrochemical industry, but is difficult due to the close boiling points of xylene isomers (pX: 138 °C, mX: 139 °C and oX: 144 °C). MFI-type zeolite membranes (ZSM-5 or Silicalite-1) could be utilized for energy-efficient xylene separation because their pore openings are close to the kinetic diameters of the isomers (0.58 nm for pX and 0.68 nm for both mX and oX)

Various research groups have studied the separation of xylene isomers using zeolite membranes. Keizer *et al.*[4] obtained separation factors of pX/oX < 1.0 at 25 °C and > 200 at 102–142 °C, for 0.31 kPa pX and 0.26 kPa oX binary mixture. The results showed that the separation factors were significantly dependent on the operating temperature. Sakai *et al.*[11] reported on a self-supporting MFI-type zeolite membrane for the separation of ternary mixtures of xylene isomers. The separation studies were performed at temperatures between 30 °C and 400 °C, and feed partial pressures between 0.30 kPa and 5.1 kPa. The separation factors pX/mX and pX/oX showed the same maximum value of 250 at 200 °C.

Xomeritakis *et al.*[12] investigated the separation of xylene isomer vapors with oriented MFI membrane in the temperature range 22 °C to 275 °C and xylene feed partial pressures up to 0.7–0.9 kPa. They found that the separation performance of these membranes is directly related to the synthesis conditions and membrane microstructure. Hedlund *et al.*[13,14] synthesized ultra thin MFI-membrane on porous α-alumina support by a two-step masking technique. High pX permeance value of 3×10^{-7} mol m^{-2} s^{-1} Pa^{-1} was obtained together with pX/oX separation factors varying from 3 to 17 in the temperature range 100–390 °C. Tsapatsis and co-workers[3,6] reported the best results for vapor permeation separation of xylene isomers using MFI-type zeolite membranes.

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Modeling and simulation of an acid-functionalized silicalite-1 membrane reactor for xylene isomerization

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ABSTRACT

A mathematical model representing *m*-xylene isomerization reaction and subsequent separation of xylene isomers in a catalytic membrane reactor is proposed. Propylsulfonic acid-functionalized silicalite-1 and arenesulfonic acid-functionalized silicalite-1 membranes were used as the catalytic membranes. A triangular reaction scheme was used as the reaction model while *m*-xylene conversion, *p*-xylene selectivity, *p*-xylene yield, *p*-xylene flux and *p*-/*o*-xylene separation factor under isothermal condition were calculated from the model. The simulated results were analyzed and showed good agreement with the experimental data within an error of ±5%. The effects of *p*-xylene diffusivity on *m*-xylene conversion, *p*-xylene flux and *p*-/*o*-xylene separation factor were investigated. Simulated results showed that the increase in *p*-xylene flux enhanced *m*-xylene conversion. *p*-Xylene yield increased with an increase in *m*-xylene conversion. *m*-Xylene conversion by arenesulfonic acid functionalized silicalite-1 membrane was higher compared to that of propylsulfonic acid functionalized silicalite-1 membrane due to higher diffusion rate of *p*-xylene. The removal of *p*-xylene through the membrane contributed to higher *m*-xylene conversion in both of the membranes.

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1. Introduction

In recent years, attention has been focused on greater economy and energy efficiency in the chemical industry. This has promoted process intensification strategies such as combined separation and catalytic reaction in a single step of operation [1,2]. Catalytic membrane reactor (CMR) permits simultaneous reaction and separation. Thus, conversions higher than the thermodynamic equilibrium could be achieved by selective removal of reaction products from the reactor [3]. The subsequent separation offers energy savings as compared to conventional separation processes.

Production of *p*-xylene is one of the processes in which a great deal of energy is used in the reaction and separation stages. *p*-Xylene (para-xylene) has the largest commercial market compared to other isomers i.e. *m*-xylene (meta-xylene) and *o*-xylene (ortho-xylene). *p*-Xylene is the feed for pure terephthalic acid (PTA) production. It is generally produced in the petrochemical industry through separation of *p*-xylene from its isomers (cryogenic crystallization or selective adsorption process Parex) and conversion of *o*-xylene and *m*-xylene to *p*-xylene through xylene isomerization (XyMax, ExxonMobil) [4–6]. The current technologies used for *p*-xylene production are highly energy intensive. Therefore, efforts have been directed towards reduction in the production cost of *p*-xylene and to improve *p*-xylene yield and selectivity [7–9] so that better overall process economy can be achieved.

Zeolite membranes have been in focus in recent years because of their well-defined micropore structure, good thermal and structural stability. The use of H-ZSM-5 zeolite as a catalyst in a packed bed membrane reactor (PBMR) as well as H-ZSM-5 catalytic zeolite membrane in catalytic membrane reactor (CMR) for the xylene isomerization has been reported by a number of researchers [7,9–11]. Despite showing enhanced conversion, H-ZSM-5-based membrane reactor for xylene isomerization usually shows moderate to low selectivity to *p*-xylene [12,13]. In our previous paper [14], we reported the synthesis and characterization of acid-functionalized silicalite-1 membranes as well as their activities for *m*-xylene isomerization reaction. An increase in *m*-xylene conversion in the membrane reactor was observed and these values exceeded the equilibrium values due to the continuous removal of reaction product through the membrane. However, the contribution of permeation properties such as reactant diffusivity and products permeation flux needs to be investigated.

In order to develop a scale-up procedure for potential application of catalytic membrane reactor in industrial processes, modeling studies have been reported by a number of researchers. Sousa and coworkers [1,15,16] reported the mathematical modeling of polymeric catalytic membrane reactor by assuming different reactor configurations i.e. plug-flow and well-mixed flow patterns for different kinds of equilibrium reaction under isothermal condi-

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Bimodal porous silica/gamma-alumina membrane for nanofiltration of salt-dye-water

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In general, ceramic membranes for nanofiltration consist of separating layer and intermediate layer which are supported on porous support. Besides facilitating the deposition of a defect-free separating layer, intermediate layer also improves the electrolyte retention at values close to iso-electric points of separating layer. However, the permeate flux is largely reduced when a bi-layered membrane is utilized. In this work, bi-layered membrane was engineered with bimodal porous intermediate layer in order to improve the membrane perme-

ability. Surfactant templated (pore size ≈0.9 nm) was supported on bimodal porous gamma-alumina (primary pore size ≈5.3 nm and secondary pore size ≈50 nm) which was tailored using nanosized polystyrene spheres. The overall liquid permeability of bimodal porous silica/gamma-alumina membrane raised almost 64% compared to conventional silica/gamma-alumina membrane. Furthermore, the bi-layered membrane with improved permeability was applied in the separation of dye-salt-water mixture. Response surface method (RSM) with central composite design (CCD) was performed to study the effect of common operating conditions on the quality and quantity of permeate. The CCD was composed of five factors: temperature (25–50°C), feed concentration of dye (1–3 g/L), feed concentration of salt (20–80 g/L), pH (pH 5–9) and pressure (5–10 bar). The response which were of interest in this study are the percentage retention of dye, the percentage retention of salt and the permeate flux. Polynomial models were generated to represent the significant effect of these factors on the interested responses. The concluded model shows the dye rejection is synergistically affected by feed concentration of dye and pressure. Meanwhile, salt rejection is synergistically affected by pressure and antagonistically affected by feed concentration of salt and feed concentration of dye. The synergistic factors for permeate flux are temperature and pressure while the antagonistic factors for permeate flux are pH and feed concentration of salt.

Keywords: Bimodal; Ceramic membrane; Dye; Salt; Nanofiltration

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Statistical design of experiments for dye-salt-water separation study using bimodal porous silica/γ-alumina membrane

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Résumé / Abstract

Treatment of textile wastewater using conventional methods is either inefficient or costly. This is because it usually involves reactive dye, great amounts of salt and high temperature. In this study, a bimodal porous silica/γ-alumina membrane with improved permeability was tested in dye-salt water separation. The effects of temperature, feed concentration of dye, feed concentration of salt, pH and the pressure on permeate were examined using a response surface method. In general, the newly developed membrane showed satisfactory dye rejection (>90%) at common operating conditions. From the statistical analysis, it was found that the variation of salt rejection depends on the feed concentration of salt, feed concentration of dye and the pressure. Meanwhile, only the permeate flux is unaffected by the feed concentration of the dye.

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Vanadium oxide carbon nanotube composite embedded γ-Al_2O_3 catalytic membranes for oxidation reaction

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Mesoporous vanadium oxide-carbon nanotube composite embedded γ-Al_2O_3 catalytic membranes have successfully been synthesized on the surface of α-alumina disk by dip coating. The support's surface was cleaned and modified by aqueous solutions. The resulting film coating has been characterized for checking formation, morphology and Permeation properties by SEM, TEM, XRD, N_2 adsorption–desorption and(TGA). Gas permeation testing was carried out in a Wicke–Kallenbach cell to evaluate the separation properties of the synthesized membranes. The different permeance between H_2, N_2, CO_2 and O_2 through the membranes results most probably from the different diffusion constraints of the two molecules which is a physical effect. The capability of γ-Al_2O_3 membrane with different porous structures based on choosing different types of binders was examined and optimized for partial oxidation reaction of hydrocarbons

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Effect of Different Parameters on the Morphology of Carbon Nanotubes Structures Grown by Floating Catalyst Method

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Abstract: Carbon nanotubes (CNTs) were synthesized by a Floating Catalyst (FC) chemical vapor deposition (CVD) method in a horizontal reactor. This method led to achieve high yield synthesis of CNTs with controlled structure. Present study showed that iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) was an efficient FC precursor for CVD of methane into CNTs. The effects of different process parameters such as reaction temperature and reaction time on the morphology of CNTs had been investigated. The deposited layers containing CNTs and CNFs were analyzed by the Transmission Electron Microscopy (TEM) and the yield of the as-grown nanotubes was investigated by the thermogravimetric analysis (TGA).

Key words: Floating catalyst, carbon nanotubes, reaction temperature, methane, catalyst particle

INTRODUCTION

Since the discovery by Ijima (1991), carbon nanotubes (CNTs) have been receiving much more attentions for their unique structural, mechanical and electronic properties. Extensive research work on the synthesis of CNTs, including laser-ablation (Thess *et al.*, 1996), electric arc discharge (Journet *et al.*, 1997) and Chemical Vapor Deposition (CVD) (Endo *et al.*, 1995) has been carried out to produce high quality CNTs for the applications in electronic, mechanical and gas storage fields. More research efforts have been put to reach the economical ways of synthesis with much greater control over the key characteristics such as length and diameter. Among the distinguished variant techniques of CVD, Floating Catalyst (FC) is considered to be the most promising commercial method for producing high purity CNTs because of the attribute of possible continuous producing by a simple equipment set-up (Fan *et al.*, 2006). Therefore, FC-CVD is a suitable approach for industrial production of high purity CNTs at low cost. Besides CNTs, carbon nanofibers (CNFs) can also be synthesized by the FC-CVD process. CNFs are important materials that can substitute CNTs in some applications in view of CNFs are much easy to be commercially produced (Bai *et al.*, 2003). However, a systematic study of the process parameters for FC-CVD needs to be developed. The yield, length and purity of CNTs produced by this method have been found to depend on the reaction temperature, type of catalyst precursor, type of reactant, reaction time and reactant flow ratio. Up to now, Ferrocene (Yang *et al.*, 2008; Cheng *et al.*, 2008) and $Fe(CO)_5$ (Rao and Govindaraj, 2002; Andrews *et al.*, 1999) are the common FC precursors. On the other hand, $FeCl_3.6H_2O$ (the transition metal salts) has been explored to synthesize CNTs in the CVD method. It was reported by Hou *et al.* (2003) that a dilute solution of $FeCl_3$ in toluene and N,N-dimethylaminoacetate shows high-efficiency for CNTs synthesis.

In this study, we report a simple FC-CVD method to prepare CNTs in a horizontal reactor, i.e., using iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) as the FC precursor and methane as the carbon source. The main objective of this study was to investigate the influence of reaction temperature and synthesis time on the morphology of the CNTs grown. CNTs with different diameters can be prepared by carefully controlling the reaction temperature. The as-grown CNTs were characterized by Transmission Electron Microscopy (TEM), thermogravimetric analysis (TGA) and Differential Thermal Analysis (DTA).

MATERIALS AND METHODS

CNTs synthesis through FC-CVD: The synthesis of CNTs was carried out by the FC method in a horizontal tubular reactor made of quartz tube with a diameter of 25 and 900 mm in length. The reactor was inserted into a horizontal tubular furnace that can provide controllable

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Effects of gases flow rate for the synthesis of carbon nanotubes by $FeCl_3$ as a floating catalyst precursor

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The influence of gases flow rate on the growth of carbon nanotubes (CNTs) by chemical vapor deposition (CVD) using $FeCl_3$ as a floating catalyst (FC) precursor and methane as a carbon source was studied. This method led to achieve high yield synthesis of CNTs with controlled structure. $FeCl_3$ was found to be an efficient FC precursor for methane CVD into CNTs. The deposited layers containing CNTs and CNFs were analyzed by the scanning electron microscopy (SEM), the yield of the as-grown nanotubes was investigated by the thermogravimetric analysis (TGA) and Raman spectra indicate the graphitization of CNTs.

***Keyword**; Floating catalyst; Flow rate; Carbon nanotubes; Methane; Nitrogen; Iron (III) chloride.*

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Mesoporous Solid Base Catalyst for the Heterogeneous Transesterification of Palm Oil to Biodiesel

A. Z. Abdullah*, N. Razali, K. T. Lee, B. Salamatinia and H. Mootabadi

Abstract—**Mesoporous silica supports, SBA-15 was successfully synthesized with the template of nonionic triblock copolymers (TCP) and tetraethylorthosilicate (TEOS) as silica source using one pot synthesis method at a temperature of 40 °C and a reaction time of 3 h. Mesoporous catalyst of different sodium hydroxide (NaOH) loadings (5-10 %) supported on mesoporous silica were prepared by impregnation technique. The activity of the sodium impregnated mesoporous material in the transesterification process of palm oil for biodiesel production was investigated. The transesterification process was carried out in batch mode using two necked round bottom flask, 250 ml of reactant at various methanol to oil ratios at 70 °C, and reaction time of up to 4.5 h and 1 g of the catalyst amount. Results showed that the highest conversion of palm oil to biodiesel was achieved using 10 wt % of sodium loading on mesoporous silica. A conversion of aver 70 % was achieved. The catalyst also showed high stability in this reaction with minimal changes to its surface characteristics. Therefore, mesoporous silica catalyst was proven to be potential novel catalyst for heterogeneous biodiesel production.**

Keywords: Mesoporous, base catalyst, heterogeneous, SBA-15, transesterification, biodiesel

I. Introduction

There is increasing worldwide concern for environmental protection and for the conservation of non-renewable natural resources. Fatty acid methyl esters (FAME) show great potential as diesel substitutes and they are known to be sources of biodiesel [1]. Biodiesel is synthesized from direct transesterification of vegetable oils where the corresponding triglycerides react with a short-chain alcohol in the presence of a catalyst [2]-[5].

Transesterification of vegetable oils to biodiesel with methanol can be carried out using both homogeneous (acid or base) and heterogeneous (acid or base) catalysts. Homogeneous base catalysts provide much faster reaction rates than heterogeneous catalysts in transesterification [3]. However, large amount of water is required to transfer the catalysts from the organic phase to a water phase. Therefore, it is considerable costly to separate homogeneous catalysts [4]. Heterogeneous is an economically and ecologically important field in catalysis research because these catalysts have many advantages: they are non-corrosive, environmentally benign and present fewer disposal problems. They are also much easier to separate from liquid products and they can be designed to give higher activity, selectivity and longer catalyst lifetimes [4]. Many types of heterogeneous catalysts such as alkaline earth metal oxides, various alkaline metal compounds supported on alumina, silica or zeolites can catalyze the transesterification reactions.

Conventional catalyst supports for the transesterification reaction usually have broad pore size distribution, low surface area and low thermal stability [6]. Micropores present in those materials usually limit the diffusion of large molecule reactants to cause lower reaction rate [2]. Recently developed ordered mesoporous silica namely MCM-41, SBA-15 and meso-cellular foam (MCF) have large surface area (500-1200 m^2/g), uniform sized pores and thermal stability up to 823 K and would be interesting solids to act as catalyst supports [6]. In this study, mesoporous SBA-15 was used to be impregnated with NaOH as the catalyst for transesterification of palm oil with methanol to produce FAME. The characteristics of the catalysts were elucidated and correlated to their observed behavior in the transesterification reaction.

II. Experimental

Pluronic p123 triblock copolymer was used as the surfactant. The molar composition of the synthesis gel was 1 SiO_2:0.017 P123:2.9 HCl:202.6 H_2O. After mixing, the gel was heated at 40 °C for 24 h. the white precipitate was then filtered, washed with distilled water and oven dried. Then, the dry precipitate was calcined at 500 °C for 6 h. NaOH/SBA-15 catalysts (5-15 wt. %) were prepared using an impregnation method and vacuum dried. The catalysts formed were characterized using SEM, TEM and surface analysis.

The transesterification of palm oil with methanol was conducted in a two-necked flask with a reflux condenser and a magnetic stirrer. 50 ml of palm oil was used and the methanol:oil ratio was 6:1. After the reaction, the catalyst was separated by centrifugation and two liquid phases appeared: FAME at the upper layer and glycerol in the bottom layer. After separating, the biodiesel was washed with distilled water to remove contaminate. The analysis of

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N-15

Synthesis and Characterization of Organic-Inorganic Mesoporous Silica Prepared Through Silanation and Graphted on Surface Silanols

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Abstract

The introduction of phenyltriethoxysilane $(EtO)_3Si$-Ph, 3-aminopropyltriethoxysilane $(EtO)_3Si$ $PrNH_2$ and 3-chloropropyltriethoxysilane $(EtO)_3Si$-PrCl through post-synthesis graphting method into a mesoporous silica is studied. Mesoporous silica was prepared as a ge composition of 1 SiO_2: 0.017 P123: 2.9 HCl: 202.6 H_2O using non-anionic triblock co-polyme as the structure directing agent. Silanation process was completed in toluene under reflux for 8 h. The finished material was then characterized using surface analysis, XRD, SEM/EDX, TEM and FTIR. A mesoporous material with a BET surface area of 455 m^2/g, average pore diamete of 4.9 nm with a narrow pore distribution was obtained. Silanation resulted in a significant drop the BET surface area and a reduction in average pore diameter, attributed to the introduction o silanating agents into the internal and external pores. FTIR and EDX analyses confirmed the graphting of those agents into the mesoporous silica. The straight mesoporous channels were also found to be slightly distorted due to the stress caused by the silanation. The effects on the framework structure were very minimal.

Keywords: Mesoporous silica, silanation, organic-inorganic, graphting, characteristics.

CM-O-2

Functionalized Mesoporous Silica (SBA-15) as A Support for Lipase Immobilization: Activity and Stability Studies

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Abstract

Functionalized of mesoporous silicas (SBA–15) with arrays of straight hexagonal pores were prepared using a non-ionic triblock co-polymer and were used as supports for lipase. Aminopropyl–, phenyl- and chloropropyl– functionalized SBA–15 with siloxypropane tether were synthesized using post-synthesis grafting method, characterized with TEM and used for the immobilization of lipase (from *Candida rugosa*). The esterification of citronellol with lauric acid to produce citronellyl laurate in batch mode at 37 °C was used to determine the performance of the immobilized enzymes. Characterization of the supports revealed the satisfactory development of mesoporosity with uniform internal channels distribution. Pure SBA–15 showed the typical hexagonal pore with straight channels while the functionalized SBA–15 with triethoxysilane has smaller pore size and distorted internal channels, hence improved the degree of immobilization. The best support among the four was the 3-aminotriethoxysilane functionalized SBA–15 which shows about 77% acid conversion after 24 h. The stability of lipase immobilized on this functionalized mesoporous SBA–15 was also investigated. It was found that the immobilized enzyme onto functionalized mesoporous SBA–15 is significantly stable with minimal leaching. Repetition reaction using the same immobilized enzyme also showed promising result with nearly 60% acid conversion after 3 cycles.

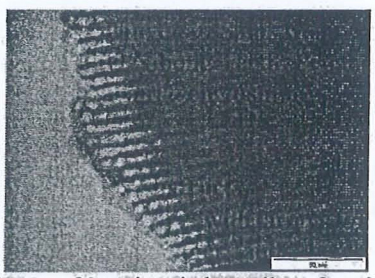

Figure 1. TEM image of 3-aminotriethoxysilane functionalized SBA-5

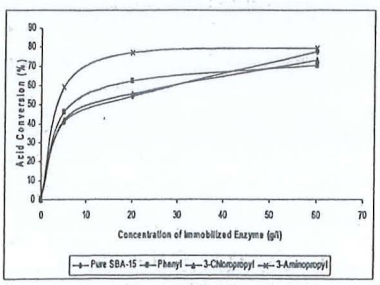

Figure 2. Acid conversion by lipase immobilized on different functionalized SBA-15.

Keywords: Mesoporous silica, functionalization, lipase, immobilization, activity, stability.

SELECTIVE CATALYTIC REDUCTION (SCR) OF NITRIC OXIDE IN DIESEL EXHAUST OVER ZSM-5 WASHCOATED CERAMIC MONOLITH CATALYST

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1. Introduction

The diesel engine owes its popularity to its high fuel efficiency, reliability, and relatively low fuel price but the operation increases the production of toxic gas e.g nitric oxides (NO) which cause severe environmental and health problems. Selective catalytic reduction (SCR) has been widely investigated for NOx removal (Pisarello *et al.*, 2002; Bennici *et al.*, 2005). For a deNOx unit, pressure drop is a key issue (Odenbrand *et al.*, 1999, Makkee *et al.*, 2002) and monolithic catalysts provide interesting solution to this problem.

2. Materials and Method

Cu/ZSM-5 was prepared by impregnation process Then, the Cu/ZSM-5 was subjected to ion-exchange of Zn followed by calcinations. Ceramic monolith catalysts were prepared by dip coating method. Ultrasound treatment was used for coating adherence test. The SCR experiments were carried out in a continuous flow system with a feed composition of 900 ppm NO, 2000 ppm iso-butane, 3 % oxygen and N_2 balance at a GHSV of 13,000 h^{-1} and a flow rate of 150 ml/min. The gas analysis was done with a GC.

3.Results and Discussion

The multiple dipping processes increased the catalyst loading in ceramic monolith until 2.4 g of the catalyst was loaded onto the monolith but it led to a decrease in the stability of the washcoat by due to the increases of % weight loss. This stable coating was due to the average particle size of the slurry used for coating which was significantly smaller than the macropore size of the monolith walls (Fig. 1).

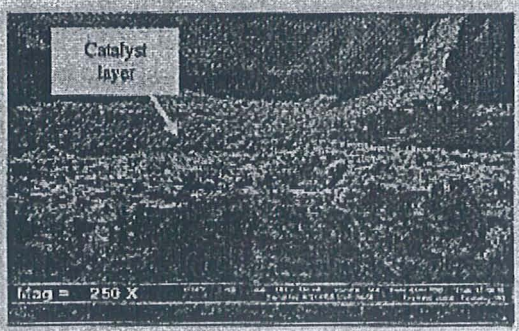

Fig. 1: Morphology of the wall of the ceramic monolith catalyst.

The % NO reduction was found to increase up to a loading of 1.8 g (Fig. 2). The monolith catalyst with 1.8 g of powder shows a higher % NO reduction than that with 1.5 g, which can be partly attributed to the difficulty in achieving an even distribution of washcoat at lower loading. On the other hand, when loading was increased to 2.2 g and 2.4 g, it showed a decrease in % NO reduction because some of the cell openings in the ceramic monolith were blocked, creating local accumulations of powder that was prone to loss due to attrition or shock. This agreed with the result of ultrasound test whereby the weight loss of sample 2 was not so severe indicating stable coating. Therefore, the optimal loading is expected to be close to 1.8 g.

SELECTIVE GLYCEROL ESTERIFICATION OVER ORGANOMONTMORILLONITE CATALYST

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ABSTRACT

Organomontmorillonites were synthesized by grafting cationic surfactants such as quaternary ammonium compounds into the interlayer space and were characterized using XRD, FTIR and N_2 adsorption/ desorption analysis . The Organomontmorillonites were applied as catalyst for the esterification of glycerol (GL) with lauric acid (LA). The catalyst which has symmetrical onium salts (tetrabuthylammoniumbromide, TBAB) gave higher activity than that of unsymmetrical onium salts (cetyltrimethylammoniumbromide, CTAB). Over an TBAB-Montmorillonite catalyst, glycerol monolaurate was obtained with selectivity of about 80% and conversion of lauric acid of about 71%.

Keywords : lauric acid, monoglyceride, esterification, reaction, catalyst

INTRODUCTION

In the last decade, renewable raw materials have become very important in the search for a sustainable chemistry. Vegetable oils and fats are the largest source of renewable raw materials used in the chemical industry. The most important benefits from oleochemicals are their biodegradability and nontoxic character, which allow the preparation of environmentally friendly surfactants.

Malaysia is the world's leading producer of palm oil. This industry promotes several downstream industries among which are oleochemical and biodiesel industries. The main reactions used first in oleochemistry were the hydrolysis or the methanolysis of triglycerides leading to glycerol and fatty acids or fatty methyl esters. However, as these reactions also lead to the formation of glycerol and there is an urgent need to find valuable applications for this side-product.

The glycerol transformation into glycerol monoesters (monoglycerides) has significant applications in food, pharmaceutical, cosmetics or in detergent chemistry (Lauridsen, 1976). The monoglycerides are generally obtained from: (*i*) the glycerolysis of triglycerides, (*ii*) the hydrolysis of triglycerides or (*iii*) the direct esterification of glycerol with fatty acids (fig. 1). The current industrial processes for monoester production lead to blends of mono-, di- and even some tri-glycerides, and dissolved glycerol. These blends typically contain 40–60% monoglyceride, and 35–45% diglycerides. However, as the emulsifying properties of diesters are poor, the surface properties of the blends relies upon their monoester content. Therefore, for many applications, energy consuming vacuum molecular distillation has to be used to raise the monoglyceride content up to ~90%. Another drawback of current processes is the generation of waste chemicals due to the need to neutralize and remove the catalysts used in the reaction, either basic or acid.

OPTIMIZATION OF PROCESS PARAMETERS FOR ALKALINE-CATALYZED TRANSESTERIFICATION OF PALM OIL USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT

Biodiesel (fatty acid methyl esters) are synthesized from direct transesterification of vegetable oils, where the corresponding triglycerides react with methanol in the presence of a suitable catalyst. The alkali catalysts are the most common catalyst used in biodiesel industry, because the process proves faster and the reaction conditions are moderated compared to the acid catalyst. In the present study, biodiesel production using heterogeneous alkaline-catalyzed transesterification process (KOH supported on SBA 15) was proposed. The influence of reaction temperature x_1 (50 - 90°C), ratio methanol to oil, x_2 (6:1 – 14:1 mol/mol), amount of catalyst, x_3 (1 – 5wt.%), and reaction time, x_4(2 - 6h) to the reaction was studied. These four conditions were studied using design of experiment (DOE), based on four-variable central composite design (CCD) with $\alpha = 2$. The process variables were optimized using the Response Surface Methodology (RSM) in obtaining the maximum yield of biodiesel. This method also applied in understanding the significance and interaction of the variables affecting the biodiesel production. The biodiesel produced in the present experiment was analyzed by gas chromatography, which considered five major of fatty acid methyl esters. The optimal conditions of response were found to be 70°C for reaction temperature, 11.6 wt/wt of ratio methanol to oil, 3.91wt.% of weight of catalyst and 5 h for reaction time with 93% of biodiesel yield for predicted value and 87.3% from experimental.

INTRODUCTION

Due to environmental, green chemistry and economic concerns, current research trend in catalysis has been focused on the transformation of homogeneous catalytic system into heterogeneous systems. The replacement of homogeneous catalysts by heterogeneous catalysts would have various advantages, most important being the application of easier working up procedures, the easy catalyst separation from the reaction mixture and the reduction of environment pollutants (Venkatesan *et al.*, 2004). Besides that, the process of transesterification is affected by various factors depending upon the reaction condition used. Some of the effects are free fatty acid and moisture of the source of oil, type of oil, catalyst type and concentration, molar ratio of alcohol to oil, type of alcohol, reaction time and temperature, mixing intensity and effect of solvents (Meher *et al.*, 2004, Lopez *et al.*, 2005)). The economic and environmental interest in using oil and fats involved in the production of biodiesel.

The objective of this study was to optimize process variables of transesterification process. The process variables studied were reaction temperature, ratio methanol to oil, weight of catalyst and reaction time. RSM was applied to relate these four process variables with the response (biodiesel yield) and to find the optimal combination of process variables that would maximize the biodiesel yield. Otherwise, the purpose of this research is to present the feasibility and reliability of the DOE method on the optimization of the process variables.

Comparative study of SBA-15 functionalized with different acid sites as solid acid catalysts for esterification of glycerol towards monolaurine production

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ABSTRACT

A comparison of the pore structural properties and catalytic activity of SBA-15 functionalized with different acid sites, i.e. sulphated zirconia and organo sulfonic acid is presented. The SBA-15 incorporated with propylsulfonic acid was prepared via post synthesis-grafting method by reacting the SBA-15 and 3-mercaptopropyl trimethoxysilane at 388K for 20 h to propylthiol groups. The Acid catalyst (SO_3HSBA-15) were obtained by mild oxidation of the thiol groups (-SH) to the sulfonic acid form (–SO_3H). Whilst SBA-15 immobilized with sulphated zirconia was prepared using urea hydrolysis method by reacting SBA-15 with solution of Zirconiumoxychloride and urea at 90°C for 5 h to ZrO_2-SBA-15. The SZ-SBA-15 as acid catalyst was obtained by sulfation of the ZrO_2-SBA-15 with H_2SO_4 solution at room temperature. The catalysts were characterized by BET analysis, EDX in combination with SEM analysis, and fourier transform infrared (FTIR) spectroscopy. The catalytic activities were tested for direct esterification of glycerol and lauric acid towards monolaurine production in the solvent free conditions at 160°C for 6 h using molar ratio fatty acid : glycerol =1 : 4

Key word : SBA-15, acid functionalization, organosulfonic acid, sulphated zirconia, esterification, monoglyceride production

1. Introduction

Glycerols are a key co product of the oleochemical and the biodiesel industries. Rapidly increasing the both industries make plenty of glycerol available to the world market. However, its application is limited to consequently result in the decline of prices of this chemical. With the aim of exploring one of the glycerol usages, the technology of monoglyceride production using glycerols as raw material has to be developed.

Currently, direct esterification of glycerols by fatty acids for monoglyceride production relies on homogeneous catalysts using strong mineral acid [1- 3]. However, this technology creates large amounts of by products and waste, and utilizes high energy [4]. Solid acid catalysts can offer advantages in process design and may improve yield and selectivity to the desired product [5].

Acidic resins [6] and zeolites [7-9] have been used as solid acid catalyst for this application. However, they were fault-finding for the monoglyceride production, because acidic resins were unfavourable for the esterification reaction at elevated reaction temperature (> 150°C) and zeolites gave a low monoglyceride yield due to the small pore diameter of around <8°A , which makes them unsuitable for reactions involving bulky molecules like monoglycerides [10]. This observation is consistent with that reported by Wilson et al., [11]. The discovery of the M41S family of

Degradation of reactive blue 4 dye by a combination of Fe (III)/TiO_2 catalyst and ultrasonic irradiation: Effect of Fe (III) loading and aeration

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Abstract—**Fe(III)/TiO_2 catalysts for sonocatalytic degradation of reactive blue 4 (RB4) dye was developed using sol-gel method. The Fe (III) loadings were varied from 0-1.0 mol % with a calcination temperature of 500 °C. The degradation performance was conducted using an ultrasonic bath with the power and frequency of 50 W and 35 kHz, respectively. The combination of 0.4 mol % of Fe (III)/TiO_2 under ultrasonic irradiation gave the highest sonocatalytic activity on the dye removal from the aqueous solution with 82 % efficiency. Meanwhile, an excess amount of Fe (III) loading higher than 0.4 mol % hindered the degradation efficiency. The use of aeration in dye solution gave a positive effect in enhancing the degradation of RB4. A combination of aeration, 0.4Fe (III)/TiO_2 and ultrasonic irradiation accelerated the reaction rate with the removal efficiency of 96 %.**

Keywords: Reactive blue 4; sonocatalytic; Fe (III)/TiO2 catalyst; aeration; combined process.

I. INTRODUCTION

Water pollution by organic dyestuffs can be defined as a contamination of water bodies such as lakes, rivers, oceans, and groundwater by dyes discharged from textile, cosmetic, plastic, rubber and pigments industries. It arises when the effluents are directly released into the receiving bodies without proper treatment [1].Considerable research and development has been carried out to resolve the long standing problem of dyeing operation. Ultrasonic irradiation found to be the most attractive and suitable system in decolorization and mineralization of organic dyes [2-6]. This method not only decolorizes organic dyes but the active radicals generated from sonication, subsequently decomposes dye molecule structures to achieve a complete degradation. The generation of active radicals such as OH and H is achieved through the dissociation of H_2O molecules that is associated by high temperature and pressure induced in the cavitation in collapsing gas bubbles available in aqueous solution.

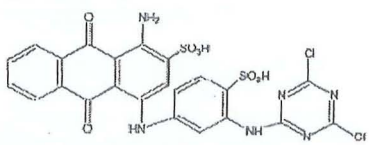
The main restrictions of this method is its high cost as longer reaction time is needed for the reaction to be completed. Thus, it is impossible for the ultrasonic system to operated at low frequency while, at the same time, degrades dyes within short time. As an alternative, a catalyst which is usually TiO_2 is introduced in conjunction with the ultrasound to achieve higher rate of sonocatalytic degradation. However, some modifications are needed for the sake of improving the sonocatalytic degradation of organic dyes. Moreover, it has been suggested by [7] that Fe (III) ions also can act as shallow charge traps in the TiO_2 lattice and result in high catalytic activity. Thus, particular efforts have been dedicated to modify TiO_2 with Fe (III) ions. In this study, the aim is to investigate the effect of Fe (III) loading and calcination temperatures in the catalyst preparation. Finally, the influence of aeration was also conducted for the rationale of further enhancing the sonocatalytic degradation of organic dyes.

II. EXPERIMENTAL

A. Materials

Reactive blue 4 (RB4) was purchased from Sigma Aldrich (M) and was used without further purification. The properties of the RB4 are tabulated in Table I. Tetrabutyl orthotitanate (>99% purity), absolute ethanol, iron nitrate nanohydrate, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were supplied from Merck. Distilled water was used throughout this study.

TABLE I. PROPERTIES OF REACTIVE BLUE 4

Properties	
Common name	Reactive blue 4
CAS number	13324-20-4
Class	Anthraquinone
Solubility	Soluble in water
Empirical formula	$C_{23}H_{14}Cl_2N_6O_8S_2$
Chemical structure	
Molecular weight (g/mol)	637.43
Maximum wavelength (nm)	596

B. Fe (III)/TiO_2 catalyst preparation

Fe (III)/TiO_2 catalyst were synthesized using sol-gel method [8]. The procedure began with the addition of tetrabutyl-ortotitanate (TBT) into an ethanol solution. Next, the mixture was stirred for 2 hours to ensure that both solutions were well-mixed. After that, metal solutions

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Ultrasonic-assisted Fast Transesterification of Palm Oil Using Strontium Oxide as Heterogeneous Catalyst

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Abstract **- The ultrasonic-assisted transesterification of palm oil in the presence of strontium oxide (SrO) was investigated. Batch transesterification process assisted by 20 kHz ultrasonic cavitation was carried out to study the effect of reaction time (10–60 min), alcohol to palm oil molar ratio (3:1–15:1), catalysts loading (0.5–3 %) and varying of ultrasonic amplitudes (25-100 %). At optimum conditions, 60 min was required to achieve 95 % yield compared to 2-4 h with conventional mechanical stirring. Also, the yields achieved in 60 min increased from 48.2 % to 95.2 %. The methanol to oil ratio and catalyst loading were also significantly reduced. 50 % amplitude of ultrasonic irradiation was deemed the optimum value.**

Keywords: Ultrasonic-assisted transesterification ; biodiesel ; heterogeneous catalyst ; intensification.

I. INTRODUCTION

Biodiesel is an eco-friendly and alternative energy source for diesel engines that can be synthesized by transesterification of vegetable oil or animal fat with alcohols. This fuel is considered to contribute much less to global warming than fossil fuels [1]. The reaction can be catalyzed by alkalis, acids, or enzymes [2]. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially [1].

The typical production method for biodiesel is a base-catalyzed process with homogeneous catalysts such sodium hydroxide or methoxide. Nevertheless, these alkali compounds have some drawbacks i.e. they must be neutralized after the reaction, thus, eliminating the possibility for the reusability of the catalyst. Homogeneous catalysts also dissolve fully in the glycerin layer and moderately in the fatty acid methyl ester (FAME) layer to make the product separation difficult [3, 4]. Therefore, conventional homogeneous catalysts are expected to be replaced in the near future by more environmentally friendly heterogeneous catalysts.

Heterogeneous catalysis is an economically and ecologically important field in catalysis research because these catalysts have many advantages: they are relatively non-corrosive, environmentally benign and present fewer removal problems. They are also much easier to be separated from liquid products and can be designed to give higher activity, selectivity and longer catalyst lifetimes [6]. A wide variety of solid bases have been examined for this purpose. Alkaline-earth metals oxides and hydroxides [7-9], alkali metals (Na and K) hydroxides or salts supported on γ-alumina [3, 10-11], zeolites [12], hydrotalcites [5, 13] have been investigated to date under various reaction conditions with a variable degree of success. One of the emerging catalyst groups to be used is single component alkaline earth metal oxides (BaO, SrO, CaO, MgO) which have higher basicity, lower solubility in alcohol and capable of producing higher biodiesel yield [9]. However, complete behavior of these catalysts in the transesterification process is yet to be fully understood despite some reports in recent years [9, 14].

As oil and methanol are not completely miscible, the mixing efficiency is identified as one of the most important factors affecting the course of the transesterification reaction. The reaction can only occur in the interfacial region between the methanol, oil and catalyst and the alkaline earth oxide catalysts are essentially insoluble in the two phases. Continuous and vigorous mixing is then required to increase the area of contact between the three phases [15, 16].

Low frequency ultrasound is theoretically seen as an efficient, time saving and economically functional method to accelerate biodiesel production process. It offers a lot of advantages over the conventional mechanical stirring method [17]. Ultrasonic mixing can produce smaller droplets of the reacting phases than conventional agitation, leading to a drastic increase in the interfacial area for the reaction to occur [18]. Because of improvement in mass transfer, the mixing requirement during the process is also significantly lowered, translating in reduced energy consumption [15].

Previous studies reported in the literature generally focus on the use of ultrasonic-assisted transesterification process in homogeneous catalytic process for biodiesel production. Thus, the main aim of this study was to characterize the effects of ultrasonic energy in presence of strontium oxide as heterogeneous catalysts. As reported in literature, most of the transesterification processes for biodiesel production use some oils other than palm oil such as rapeseed oil [19] and soybean oil [4, 8, 10]. Particular focus was given to the effects of reaction time, oil to alcohol molar ratio and catalyst loading. As the intensity of irradiation is expected to affect the level of interaction between the two reactants, the effects of varying of ultrasonic amplitude were also characterized. Until very recently, information on such topics of the process is hardly found in the literature.

DEPENDENCE OF MESOPOROUS SILICA (SBA 15) CHARACTERISTICS SYNTHESIZED USING NONIONIC TRIBLOCK COPOLYMERS ON SYNTHESIS GEL COMPOSITION

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Keywords: mesoporous material, SBA-15, triblock copolymer

ABSTRACT

Mesoporous silicas (SBA 15) was synthesized using a triblock copolymer (TCP), poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), as the surfactant was very attractive in the area of adsorption, catalysis and separation. Structure, particle morphology, and size distribution are all material properties that need to be monitored for application purposes. The study encompassed the effect of gelling temperature (30-50^{0}C), the ratio of TCP/TEOS (1.52 – 3.15), and the concentration of HCl (1-3M). The SBA-15 was subjected to the characterization using nitrogen adsorption (BET), x-ray diffraction (XRD) and transmission electron micrograph (TEM) to obtain detailed information on the structure of mesoporous formed. From the result, it could be observed that aging temperature at higher temperature presents higher porosity while well ordered mesostructure could satisfactorily be formed at lower than 3.00 wt/wt% of TCP/TEOS ratio.

INTRODUCTION

Recently, a new type of ordered mesoporous material has attracted great attention in the field of catalysis. SBA 15 material, possess high surface area (600-1000m^2g^{-1}) and is made up of hexagonal array of uniform tubular channels with tunable pore diameters in the range 5-30nm, thicker walls (3-6nm) and also have high thermal stability which promises great opportunity for application as

A short review: Degradation of organic dyes in wastewater by ultrasonic irradiation enhanced by Fenton's reagent

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Abstract **- Removal and degradation efficiency of organic dyes in wastewater have become a matter of considerable interest due to their potential toxicity. As a result, a wide range of methods have been rapidly developed to solve this problem. Many efforts have been devoted to improve the degradation efficiency and mineralization of organic dyes by ultrasonic irradiation. The coupling of ultrasound with chemical oxidation utilizing hydrogen peroxide (H_2O_2) or ferrous ion presents interesting and attractive approaches. The aim of this paper is to provide an overview of process fundamentals and the trend in the application of ultrasound combined with the use of homo- and heterogeneous Fenton reagents for environmental remediation to treat organic dyes in wastewater, with the emphasis on recent developments and its important achievements.**

Keywords: Ultrasonic irradiation, organic dyes, wastewater, H_2O_2, Fenton's reagent

I. INTRODUCTION

Recently, there is no available data on the exact amount of annual production of organic dyes in the world. However, more than 100,000 commercially available dyes exist and over 7 x 10^5 tonnes annual production worldwide have been often reported in the literature [1, 2]. In textile dyebaths, the degree of fixation of dyes to fabrics is never complete and definitely resulted in coloured substances in industrial effluents. In 1978, it was estimated that 2% (9000 tonnes) of the 450,000 tonnes of dye produced worldwide were discharged in effluent from manufacturing operations whereas textile industry occupied about 9% (40000 tonnes), giving a total coloured effluent almost about 50000 tonnes [3, 4]. Due to large-scale production and extensive application of organic dyes, it has the possibility to cause serious environmental pollution and health-risk issues.

Therefore, a variety of conventional treatment methods are presently available for the treatment of textile wastewater. However, it has been reported that majority of organic dyes only adsorbed on the sludge and cannot be degraded easily because these organic dye compounds in wastewater contain one or several benzene rings [5, 6]. Hence, a lot of studies have been dedicated to treat this wastewater by using advanced oxidation process which involves hydroxyl (•OH) radicals to mineralize the organic compounds. Ideally, the end products of oxidation processes are carbon dioxide, water and inorganic mineral salts.

Since 1990, there has been an increase of interest in the use of ultrasound (US) to destroy organic contaminants present in wastewater [7]. The advantages of high power ultrasonic irradiation are safety, cleanness, high degradation efficiency and energy conservation without generation of secondary pollutant [8]. Furthermore, the penetrability of ultrasound through the water medium is very strong which can attain 25-30 cm penetrability depth [9]. Therefore, ultrasonic irradiation is advisable to treat non- or low-transparent wastewater as compared to other advanced oxidation processes like UV irradiation.

II. SONOCHEMICAL PROCESSES

Ultrasound is defined as any wave frequency that greater than the upper limit of human hearing at frequencies above 16 kHz (16 000 cycles per second) [10, 11]. Three ranges of frequencies are reported for three distinct uses of ultrasound [11]: low frequency, applied for conventional power ultrasound (20–100 kHz), medium frequency, used for "sonochemical-effects" ultrasound (300–1000 kHz), high frequency, used for diagnostic ultrasound (2–10 MHz). The phenomenon of cavitation consists of the subsequent and distinct three steps: formation (nucleation), rapid growth (expansion) during the compression/rarefaction cycles until finally reach a critical size and then violent collapse (implosion) of the cavitation bubbles in a liquid [12]. This creates three regions for high energy chemical reaction to take place as shown in Figure 1: inside of the cavitation bubble, interfacial liquid region between cavitation bubbles and the liquid bulk solution and bulk solution region.

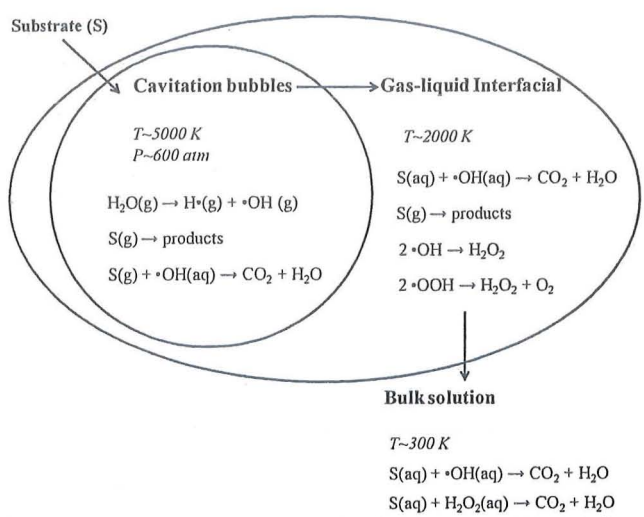

Figure 1. The reaction mechanism of cavitation bubbles (adapted from Adewuyi [10]).

UTILIZATION OF COCOA POD HUSK WASTE FOR PRODUCTION OF HIGH POROUS ADSORBENT ACTIVATED CARBONS AND CARBON MOLECULAR SIEVES

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ABSTRACT

A series of experiments were conducted to produce activated carbons (ACs) and carbon molecular sieves (CMSs) from a locally available cocoa pod husk (CPH). The process involves activation and carbon vapour deposition (CVD). Activation of the dried CPH using carbon dioxide atmosphere at 600°C-900°C for 1h was carried out to obtain ACs with different degree of burn-offs. In order to produce high quality CMSs, the AC with the highest micropore volume is subjected to CVD at 550-850°C for 30 min. The characterizations of the ACs and CMSs were assessed by physical adsorption of N_2 at 77 K. The ACs performance was tested in removing the pollutants from wastewater. Meanwhile, the CMSs performance was examined by measuring the kinetic adsorption of CO_2 and CH_4.

Keywords: Activated carbon; carbon molecular sieves; cocoa pod husk; activation; benzene cracking

1. INTRODUCTION

Malaysia was one of the major cocoa industries in South East Asia, beside Indonesia and Thailand with approximately 30,800 hectares of cocoa plantation, which producing 31,937 tons of cocoa beans annually. Despite of that, tonnes of cocoa pod husk (CPH) are produced as by-product (Redgwell et al., 2003). Approximately one ton of dry cocoa beans represent about ten tons of CPH. The use of CPH is very limited as livestock feed by some animal due to *Theobromine* content, which is significant source of disease inoculums (Serra and Ventura, 1999). Thus most of the CPH was directly disposed as waste. So, it is an advantage if the CPH can turn into useful and valuable products such as activated carbons (ACs) and carbon molecular sieves (CMSs). AC is a predominantly amorphous solid that has extraordinary internal surface area and pore volume. It is mainly used in wastewater treatment and can be produced by either physical or chemical activation. In physical activation, the precursor is carbonized under carbon dioxide or steam atmospheres at high temperatures. In chemical activation, the precursor is first impregnated with chemicals such sodium carbonate or potassium hydroxide before activated at temperatures in the range of 450-900°C (Guo and Lua, 2003).

CMS is a special group of AC having small pore sizes with a sharp distribution in micropore range suitable for gases separation and purification (Casa-Lillo et al., 1998). It allows gases molecules such as nitrogen and oxygen in air to discriminate on the basis of their size and shape. The ability to control the size of the pore openings in CMS is a major challenge in preparing CMS. The process must be carefully controlled start from activation steps in order to obtain AC with high-micropore volumes till in deposition step. Otherwise the pore samples will close, which will cause in reducing the CMSs adsorption capacity.

The objective of this work is to produce ACs from cocoa pod husk, which then will be used as precursor for CMSs production. The ACs and CMSs produced are to be used for wastewater treatment gases adsorption study, respectively.

2. MATERIALS AND METHODS

2.1 Materials

The raw material used in this study was cocoa pod husk (CPH) obtained from the Cocoa Research and Development Centre, Cocoa Board Malaysia, Hilir Perak. The wastewater sample was obtained from Kampung Rawa drainage which flow into Sungai Pinang, Penang. The water was highly polluted and contributed to the water pollution. The COD and iron concentration of this water were 358 mg/L and 0.94 mg/L, respectively. The gases used for gases kinetic study were supplied by MOX Sdn. Bhd. with the following purities: methane (99.995%) and carbon dioxide (99.995%). The hydrocarbon used as carbon source for deposition was benzene (Merck, analytical grade).

2.2 Procedures

ACs from the CPH was prepared by conventional CO_2 activation in vertical tube reactor. The activation apparatus and the preparation procedure are described elsewhere (Ahmad et al., 2008). The dried CPH was ground and sieved (1.0 to 2.0 mm). Then, 150g of CPH was heated at 600°C under nitrogen flow before

USEFULNESS OF RAW SUGARCANE BAGASSE FOR WASTEWATER TREATMENT

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ABSTRACT

In the present work raw sugarcane bagasse residues of sugar industries, was treated and converted into adsorbent for wastewater treatment. The wastewater sample, which contains high chemical oxygen demand (COD) and iron content, was taken from Kampung Rawa drainage, which flows into the Sungai Pinang, Penang. Sugarcane bagasse was impregnated with potassium hydroxide (KOH) before activated in the fixed bed reactor. The best activation conditions were obtained at activation temperature and impregnation ratio of 800°C and 1:1, respectively. At this point, the yield, specific surface area, COD removal and iron removal were 24.5%, 750m^2/g, 91.6% and 91.8%, respectively.

Keywords: Activated carbon; Wastewater; Sugarcane baggase; Chemical activation

1. INTRODUCTION

Commercially activated carbon (AC) is produced from bituminous or lignite coal. The long-term availability of coal, environmental impacts and potentially increasing cost has encouraged researchers to find other alternatives, which may be cost effective and equally potential. Recently, there has been an increasing trend towards more efficient utilization of renewable agro-industrial residues including sugarcane bagasse (SB). SB is a byproduct of sugarcane industries, which obtained after the extraction of sugarcane juice for production of sugar. About 54 million dry tones of bagasse are produced annually throughout the world (Ahmedna et al., 2000). It offers the advantage of being a cheap, plentiful and low polluting fuel. On the average, SB contains about 45–50% moisture, 43–52% fiber, and 2–6% soluble solids. The typical composition of SB fiber is about 26.6-54.3% cellulose, 22.3-29.7% hemicellulose, and 14.3-24.45% lignin (Walfrido et al., 2008).

SB is used primarily in the sugar mills to meet their own internal energy needs. However, the remaining SB is usually stockpiled and continues to be a menace to the environment. Several processes and products have been reported that utilize SB as a raw material. These include paper, pulp and board manufacture, compost, cattle feed, ethanol manufacture and as adsorbent (Ashok et al., 2000). Sugarcane bagasse based activated carbon (SBAC) was widely used especially as an adsorbing agent for the removal of reactive dye from aqueous solutions (Nevine, 2008). Dimitrios et al. (2008) prepared SBAC and found that SBAC had good adsorption capacities with respect to arsenic, humic acid and phenol. They removed 80% of phenol at the equilibrium time of 4h. For the landfill leachate treatment, the results showed that, with 30 g/L of SBAC, it was possible to remove 70% and 60% of COD and colour, respectively. Karnitz Júnior *et al.* (2007) have reported the use of SBAC for removal of Cu^{2+}, Cd^{2+} and Pb^{2+} from aqueous solutions. From the adsorption studies, the SBAC exhibited a maximum adsorption capacity of 114 mg/g for Cu^{2+}, 196 mg/g for Cd^{2+} and 189 mg/g for Pb^{2+}.

The present study utilized the raw sugarcane bagasse for production of SBAC to be used for wastewater treatment. The SBACs were prepared by KOH activation at different activation temperatures and impregnation ratios in the fixed bed reactor. Determination of SBACs characteristics could guide researches in identifying its suitability as an adsorbent for adsorption purpose.

2. MATERIALS AND METHODS

2.1 Preparation of material

The sugarcane bagasse (SB) was obtained from Kangar, Perlis. The bagasse was first cleaned and then dried under air atmosphere. The dried bagasse was then crushed into small pieces using crusher. The pieces were then ground to an average size of 2.0 mm using an electrically operated grinder. The wastewater sample was

RUBBER WOOD WASTE AS POTENTIAL ADSORBENT FOR WASTEWATER TREATMENT

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ABSTRACT

Rubber wood based activated carbons (RWACs) were successfully prepared by chemical activation with potassium hydroxide (KOH). A series of experiments have been conducted to access the effect of activation temperatures (500°C-800°C) and impregnation ratios (0.5-1.5) for short activation time of 15 min on the RWACs properties as well as the capacity to remove pollutant in wastewater. The adsorptive properties and liquid phase adsorption of the activated carbons were measured by using gas adsorption analyzer and spectrophotometer, respectively. The optimum activation conditions were found at activation temperature of 700°C with impregnation ratio of 1.0. At this point, the yield and surface area were 27.4% and 722m²/g, respectively. Meanwhile the percentage removal of manganese (Mn) and chemical oxygen demand (COD) achieved as high as 94.5% and 71.0%, respectively.

Keywords: Activated carbon; Wastewater; Rubber wood; Chemical activation

1. INTRODUCTION

In Malaysia, rubber wood (RW) is one of the main plantation crops with an estimated plantation area of 1.82 million hectares. Local latex production increased from 1.13 million tonnes in 2005 to 1.33 million tonnes in 2006 (Srinivasakannan and Bakar, 2004). The largest consumers of rubber were latex products, followed by tyres and tyre-related products, and industrial and general rubber products. Despite of that, the production of latex is uneconomical after 25 to 30 years of age and the trees are felt for replanting. According to Lim et al. (2000), the amount of available dry RW due to replanting activities was around 3.47 billion kg per year. Some portion of the trees is utilized as solid fuel and furniture and the residue is considered as waste. It is an advantage if the RW residue can be turned into useful and valuable product such as activated carbon (AC).

AC is a microcrystalline form of carbon with very high porosity and surface area. It can be produced from any carbonaceous material rich in elemental carbon such as wood, coconut shell, anthracite and bituminous coal by either physical or chemical activation (Prakash Kumar et al., 2005). Physical activation is generally carried out at elevated temperatures between 750 and 1100°C using oxidants such as steam (Satya Sai et al., 1997), carbon dioxide (Linares-Solano et al., 2000) or mixture of these gases (Daud and Ali, 2004). Chemical activation is usually carried out by impregnating the precursor with activating agents, such as phosphoric acid (Jagtoyen et al., 1998; Solum et al., 1995), zinc chloride (Ayg¨un et al., 2003) and alkaline metal compounds (Guo et al., 2000; Guo et al., 2003) and pyrolyzed between 400 and 800°C in the absence of oxygen. One can design AC for adsorption of specific adsorbate, using appropriate precursor and by optimizing the activation process conditions. In this work, an attempt was made to use RW residue for AC production.

2. MATERIALS AND METHODS

2.1 Preparation of material

The rubber wood (RW) residue was obtained from plantation ground at Batu Pahat, Johor. The RW was first cleaned from debris and dried before cutting them into small pieces. The pieces are further grind using a grinding machine and sieved for 30 minutes using stainless steel Retch Test Sieve. The samples with size 2.0 mm were used in the rest of the experimental work. The wastewater sample was obtained from Kampung Rawa drainage, which flows into Sungai Pinang, Penang. The COD and manganese concentration of water sample were 358 mg/l and 0.82 mg/l respectively. These values show that the Kampung Rawa drainage water was highly polluted and contributed to the water pollution of Sungai Pinang. Potassium hydroxide (KOH) of purity 99.9% (Hamburg Chemicals, Germany) was used as an activation agent.

2.2 Impregnation and Activation

Approximately 50.0 g of RW was weighted and put into the beakers. The KOH solutions were prepared by dissolving 3 different weights of KOH salts, which give an impregnation ratio (IR) of 0.5, 1.0 and 1.5. The IR is calculated based on equation shown below:

RESPONSE SURFACE METHODOLOGY APPROACH FOR OPTIMIZATION OF ACTIVATED CARBONS SYNTHESIS FROM COCOA POD HUSK

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ABSTRACT

Cocoa pod husks have been utilized for the synthesis of activated carbons (ACs) by physical activation. The effects of the synthesis variables which were activation temperature and activation time on the mesopore volume, surface area and adsorption capacity on methylene blue (MB) and malachite green (MG) dyes were studied by using central composite design (CCD). From the analysis of variance, the most influential factor on each experimental design response was identified. The optimal CPHAC was obtained using 700°C activation temperature and 2 h activation time, resulting in 0.273 cm^3/g of mesopore volume, 502.7 m^2/g of surface area, 326.76 mg/g of adsorption capacity on MG and 112.38 mg/g of adsorption capacity on MB.

Keywords: Cocoa pod husk; Activated carbon; Methylene blue; Malachite green, Central composite design.

1. INTRODUCTION

Malaysia is one of the major cocoa industries in South East Asia, beside Indonesia and Thailand with approximately 30,800 hectares of cocoa plantation, which producing 31,937 tons of cocoa beans annually. Despite of that, pod husks (CPHs) are produced as by-product (Redgwell et al., 2003). Approximately one ton of dry cocoa beans represent about ten tons of CPH. The use of CPH is very limited as livestock feed by some animal due to *Theobromine* content, which is significant source of disease inoculums (Serra and Ventura, 1999). Thus most of the CPH is directly disposed as waste. So, it is an advantage if the CPH can turn into useful and valuable product such as activated carbon (AC).

AC has extraordinary internal surface area and pore volume. It is mainly used in wastewater treatment and can be produced by either physical or chemical activation. In physical activation, the precursor is carbonized under carbon dioxide or steam atmospheres at high temperatures. In chemical activation, the precursor is first impregnated with chemicals such sodium carbonate or potassium hydroxide before activated at temperatures in the range of 450-900°C (Guo and Lua, 2003). Physical activation is preferred than chemical activation due to economic and environmental considerations involved with chemical treatments (Byrne and Marsh, 1995). In this work, CPH will undergo CO_2 activation process in order to produce cocoa pod husk based activated carbon (CPHAC) for dyes removal study.

The most important characteristic of an AC is its adsorption performance which is highly influenced by the preparation conditions. Experimental design technique is a very useful tool for this purpose as it provides statistical models which help in understanding the interactions among the variables that have been optimized (Alam et al., 2007). Response surface methodology

ADSORPTION OF MALACHITE GREEN ONTO COCOA POD HUSK-BASED ACTIVATED CARBON: KINETICS AND EQUILIBRIUM STUDIES

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Abstract
A series of experiments was carried out for the sorption of malachite green (MG) dye onto cocoa pod husk based activated carbon (CPHAC). CPHAC was prepared by CO_2 activation of cocoa pod husk (CPH). The adsorption was carried out in a batch system as a function of initial dye concentration, contact time and temperature. For adsorption equilibrium study, Freundlich isotherm shows better compare to Langmuir and Temkin isotherms for MG adsorption onto CPHAC. Results from kinetic study show that the MG adsorption proceeds according to the pseudo-second-order model. As the adsorption temperature increased, the MG adsorption decreased, which confirm that the process was exothermic.

Keywords: Cocoa pod husk, Activated carbon, Malachite green, Isotherm, Kinetics

1. INTRODUCTION

Dyes are important pollutants, causing environmental and health problems to human being and aquatic animals. Malachite green (MG), a basic dye, is most widely used for coloring purpose, amongst all other dyes of its category (Crini et al., 2007). MG is widely used in the aquaculture industry worldwide as a biocide as well as in the silk, wool, cotton, leather, paper, and acrylic industries as a dye. Furthermore, it is also employed as therapeutic agent to treat parasites, fungal and bacterial infections in fish and fish eggs and as antiseptic (Oualid et al., 2008). Despite its extensive use, MG is a highly controversial compound due to its reported toxic properties which are known to cause carcinogenesis, mutagenesis, teratogenesis and respiratory toxicity (Berberidou et al., 2007). However, despite the large amount of data on its toxic effects, MG is still used in aquaculture and other industries. Therefore, the removal of MG from wastewater before discharging is necessary and very important.

Various carbonaceous materials, such as coal and lignite are used in the production of activated carbon (AC) for dyes removal (Hayashi et al., 2000). However, the abundance and availability of agricultural by-products make them good precursor for AC production. Agricultural by-products are renewable sources and to reuse these waste materials are greatly desired. Disposal of agricultural by-products is currently a major economic and ecological issue, and the conversion of by-products to AC, represents a possible outlet (Malik et al., 2007). In the present investigation, cocoa pod husk (CPH), which is one of the agricultural by-product was used to prepare AC for MG dye removal from aques solution. The equilibrium and kinetic data of the adsorption process were then analyzed to study the adsorption isotherms and kinetics of MG on the CPHAC.

Synthesis of carbon molecular sieves (CMSs) from bituminous coal based activated carbon through carbon vapour deposition technique

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Abstract
Carbon molecular sieves (CMSs) have been prepared from bituminous coal based activated carbon (BCAC) by carbon vapour deposition (CVD) technique using benzene. Benzene deposition onto BCAC at temperature range from 500-800°C have resulted in a series of CMSs with different properties. The molecular sieving behavior of the CMSs was assessed by kinetic adsorption isotherms of O_2, N_2, CO_2 and CH_4 at room temperature. The best CMS obtained at deposition temperature 700°C has O_2/N_2 and CO_2/CH_4 kinetic selectivity of 4.15 and 8.68, respectively.
Keywords: Bituminous coal, Carbon molecular sieves, Carbon vapour deposition

1. Introduction

CMS is a special group of activated carbon that has small pore sizes in ultramicropore range [1]. CMS was produced from a variety of carbonaceous materials such as coconut shell [2], walnut shell [3], nutshells [4], lignite coal [5] and anthracite coal [6]. In general, there were two major approaches to prepare CMS; one was based on controlled pyrolysis of carbon precursors and the other is the modification of existing porosity of an activated structure through carbon vapour deposition (CVD) [7]. In controlled pyrolysis process, the precursor was pyrolyzed under suitable temperature and environment. The adsorption capacity must be carefully increased through creation of micropores while avoiding excessive widening of porosity, which can be detrimental to selectivity. The CMS produced usually has low adsorption capacities and this may impose serious limitations on the performance of the CMS [8]. Meanwhile the CVD technique tailored the pore apertures to match the size of the desired adsorbate. This technique has became an attractive area of adsorption for many gaseous systems [2]-[4],[9]-[10]. The CMS produced has high adsorption capacity and high selectivity. High adsorption capacity is related to high micropore volume, whereas selectivity is provided by CVD technique. Several carbon sources that can be used as CVD agents were acetylene [11], benzene [4], methane [9] and cyclohexane [12]. Benzene has been widely employed because it does not produce intermediate species in the cracking process, which makes deposition easier to be controlled. In this work, bituminous coal based activated carbon (BCAC) was subjected to CVD step by using benzene. The adsorption kinetics of CMS produced was study in order to determine molecular sieving behaviour of the product.

2. Experimental

2.1 Materials

The major material used in this study is bituminous coal based activated carbon (BCAC) from NORIT Ltd.. The gases used for adsorption study were supplied by Malaysian Oxygen Sdn. Bhd. (MOX) and has the following purity; nitrogen (99.999%), methane (99.995%), oxygen

PRODUCTION OF SUGARCANE BAGASSE BASED ACTIVATED CARBON FOR REDUCING WATER POLLUTION

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ABSTRACT

In the present work, an effort has been made to develop suitable process conditions for synthesis of sugarcane bagasse based activated carbons (SBACs) for wastewater treatment. The wastewater sample was taken from Kampung Rawa drainage, which flows into the Sungai Pinang, Penang. The water was highly polluted and contains high chemical oxygen demand (COD) and ferum content. The process of making SBACs involves chemical activation with potassium hydroxide (KOH) at various activation conditions. The best SBAC for pollutant removal were obtained at activation temperature of 800°C and impregnation ratio of 1:1. At this point, the yield, specific surface area, COD removal and ferum removal were 24.5%, 750m^2/g, 91.6% and 91.8%, respectively.

Keywords: Activated carbon; Wastewater; Sugarcane baggase; Chemical activation

INTRODUCTION

In recent years, there has been an increasing trend towards more efficient utilization of renewable agro-industrial residues including sugarcane bagasse (SB). SB is a residue produced in large quantities during the processing of sugarcane in sugar mills. It offers the advantage of being a cheap, plentiful and low polluting fuel. On the average, SB contains about 45–50% moisture, 43–52% fiber, and 2–6% soluble solids. The typical composition of SB fiber is about 26.6-54.3% cellulose, 22.3-29.7% hemicellulose, and 14.3-24.45% lignin [1]. Bagasse is used primarily in the sugar mills to meet their own internal energy needs. However, the remaining bagasse is usually stockpiled and continues to be a menace to the environment. Several processes and products have been reported that utilize SB as a raw material. These include paper, pulp and board manufacture, compost, cattle feed, ethanol manufacture and as adsorbent [2]. Sugarcane bagasse based activated carbon (SBAC) was widely used especially as an adsorbing agent for the removal of reactive dye from aqueous solutions [3]. Dimitrios *et al.* (2008) prepared SBAC and found that SBAC had good adsorption capacities with respect to arsenic, humic acid and phenol. They removed 80% of phenol at the equilibrium time of 4 h. For the landfill leachate treatment, the results showed that, with 30 g/L of SBAC, it was possible to remove 70% and 60% of COD and colour, respectively [4].

Karnitz Júnior *et al.* (2007) have reported the use of SBAC for removal of Cu^{2+}, Cd^{2+} and Pb^{2+} from aqueous solutions [5]. From the adsorption studies, the SBAC exhibited a maximum adsorption capacity of 114 mg/g for Cu^{2+}, 196 mg/g for Cd^{2+} and 189 mg/g for Pb^{2+}.

The present study describes the preparation of SBACs to be used for wastewater treatment. The SBACs were prepared by KOH activation at different activation temperatures

SYNTHESIS OF ACTIVATED CARBONS FROM COCOA POD HUSK IMPREGNATED WITH SODIUM CARBONATE FOR WATER TREATMENT

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ABSTRACT

Cocoa pod husk based activated carbons (CPHACs) were successfully prepared by chemical activation with sodium carbonate (Na_2CO_3). A series of experiments have been conducted to access the effect of activation temperatures (500°C-900°C) for short activation time of 15 min on the CPHACs properties. The CPHACs performance produced were tested in removing COD and ferum of the wastewater samples. The wastewater sample was taken from Kampung Rawa drainage, which flows into the Sungai Pinang, Penang. The activation temperature optimum was found at 700°C, which produced yield, specific surface area, ferum removal and chemical oxygen demand (COD) removal of 19.63%, 725m^2/g, 73.71% and 61.97%, respectively.

Keywords: Activated carbon; Wastewater; Cocoa pod husk; Chemical activation

INTRODUCTION

Malaysia was one of the major cocoa industries in South East Asia, beside Indonesia and Thailand with approximately 30,800 hectares of cocoa plantation, which producing 31,937 tons of cocoa beans annually. Despite of that, tonnes of cocoa pod husk (CPH) are produced as by-product [1]. Approximately one ton of dry cocoa beans represent about ten tons of CPH. The use of CPH is very limited as livestock feed by some animal due to *Theobromine* content, which is significant source of disease inoculums [2]. Thus most of the CPH was directly dumped or dispose as waste. So, it is an advantage if the CPH can turn into useful and valuable products such as activated carbon (AC).

AC is a predominantly amorphous solid that has extraordinary internal surface area and pore volume. AC can be produced by either physical or chemical activation. In physical activation, the precursor is carbonized under carbon dioxide, oxygen, or steam atmospheres at high temperatures. In chemical activation, the precursor is first impregnated with chemicals such sodium carbonate ($NaCO_3$) or potassium hydroxide (KOH) followed by activation at temperatures in the range of 450-900°C [3]. Compared to physical activation, chemical activation is preferred due to low temperature operation and short activation time. In this work, AC was prepared from CPH by Na_2CO_3 activation to be used for wastewater treatment.

MATERIALS AND METHODS

Preparation of material. The main material used in this study was CPH obtained from the Cocoa Research and Development Centre, Cocoa Board Malaysia, Hilir Perak. The CPH was

PREPARATION OF RUBBER WOOD BASED ACTIVATED CARBON VIA CHEMICAL ACTIVATION FOR MANGANESE AND COD REMOVAL

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ABSTRACT

A series of experiments were conducted to produce activated carbons (ACs) through chemical activation with potassium hydroxide (KOH) from a locally available rubber wood. The process involves two stages; impregnation and activation. The effects of activation temperatures and impregnation ratios onto ACs characteristics and manganese removal were investigated. The highest surface area of AC was obtained at activation temperature of 700°C with impregnation ratio of 1.0. At this point, the yield and surface area were 27.4% and 722m^2/g, respectively. Meanwhile the percentage removal of manganese (Mn) and chemical oxygen demand (COD) achieved as high as 94.5% and 71.0%, respectively.

Keywords: Activated carbon; Wastewater; Rubber wood; Chemical activation

INTRODUCTION

In Malaysia, rubber wood (RW) is one of the main plantation crops with an estimated plantation area of 1.82 million hectares. Local latex production increased from 1.13 million tonnes in 2005 to 1.33 million tonnes in 2006 [1]. The largest consumers of rubber were latex products, followed by tyres and tyre-related products, and industrial and general rubber products. Despite of that, the production of latex is uneconomical after 25 to 30 years of age and the trees are felt for replanting. According to Lim *et al.* (2000), the amount of available dry RW due to replanting activities was around 3.47 billion kg per year. Some portion of the trees is utilized as solid fuel and furniture and the residue is considered as waste [2]. It is an advantage if the RW residue can be turned into useful and valuable product such as activated carbon (AC).

AC is a microcrystalline form of carbon with very high porosity and surface area. It can be produced from any carbonaceous material rich in elemental carbon such as wood, coconut shell, anthracite and bituminous coal by either physical or chemical activation [3]. Physical activation is generally carried out at elevated temperatures between 750 and 1100°C using oxidants such as steam [4], carbon dioxide [5] or mixture of these gases [6]. Chemical activation is usually carried out by impregnating the precursor with activating agents, such as phosphoric acid [7,8], zinc chloride [9] and alkaline metal compounds [10,11] and pyrolyzed between 400 and 800°C in the absence of oxygen. One can design AC for adsorption of specific adsorbate, using appropriate precursor and by optimizing the activation process conditions. In this work, an attempt was made to use RW residue for AC production.

MTE-1

SYNTHESIS AND PERFORMANCE EVALUATION OF POLY (3,4-ETHYLENEDIOXYTHIOPHENE)/MULTIWALLED CARBON NANOTUBE/MANGANESE-NICKEL OXIDES COMPOSITE MATERIALS FOR SUPERCAPACITOR APPLICATION

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Doping conducting polymers with carbon nanotubes (CNTs) enhances both electronic and ionic conductivity in the polymers. Poly (3,4-ethylenedioxythiophene) (PEDOT) is an interesting material in view of its good thermal and chemical stability. However, the specific capacitance of PEDOT was smaller than that of Polypyrrole and Polyaniline due to monomer units (3,4 ethylenedioxythiophene, EDOT) with the greater molecular weight than pyrrole and aniline. In addition, their composites are often prepared with active carbon or carbon nanotubes (CNTs) doped with transition metal oxides to enhance their specific capacitance further. In the present study the electrochemical properties of composite prepared from an electrically conducting polymer (PEDOT) and multiwalled carbon nanotubes (MWCNTs) filled with manganese-nickel oxides (MNO) have been investigated for supercapacitor application. The morphological characterization of this nanocomposite is examined in terms of the X-ray diffraction patterns (XRD), Fourier-transform infrared spectrometer (FTIR), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images. Electrodes prepared from such composite material were used in supercapacitors operating in alkaline (6M KOH) electrolytic solution. The supercapacitance values were estimated by galvanostatic, cyclic voltammetry and impedance spectroscopy techniques with two electrode cell configuration. The results demonstrate that electrochemical properties of PEDOT/ MWCNTs/ MNO electrode are significantly greater than MWCNTs/ MNO and pristine MWCNTs electrode in the same medium.

Keywords: *Supercapacitor, PEDOT, Mwcnts, Manganese-Nickel Oxide and Electrochemical Properties*

MTE-2

APPLICATION OF LIGNIN FROM COCONUT FIBER IN SURFACTANT FLOODING

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The use of surfactant in enhanced oil recovery can help to increase oil production by lowering the interfacial tension at oil-water interfaces. However, due to high cost of surfactant derive from petroleum-based source, it have put a setback on the use of surfactant in EOR processes. To solve this problem, the non-petroleum-based (agriculture-based) surfactant can be use to replace the petroleum-based surfactant. In this study, lignin was extracted from black liquor obtained by pulping sample (coconut fiber) with NaOH. Then the properties of extracted lignin were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Ultraviolet (UV) and Nuclear Magnetic Resonance (^{13}C-NMR). Then the extracted lignin was used with amine and Sodium Dodecyl Sulfate (SDS) to formed surfactant formulation for application in enhanced oil recovery. The stability and IFT of the formulation formed were determined. Based on the ^{13}C-NMR and UV results there were no significant differences between extracted lignin and standard lignin. The FTIR results also showed that there were no significant differences in terms of functional groups that exist in both lignins. For the formulation, results show that this formulation is stable and it can produce lower IFT compare to SDS and amine itself. This result shows that lignin from EFB have a potential to be used in surfactant flooding.

Keywords: *Enhanced Oil Recovery, Surfactant, Lignin, Coconut Fiber and Black Liquor*

Electrochemical Properties of Multiwalled Carbon Nanotubes Filled with Manganese Oxide and Nickel Oxide Using Wet Chemical Method

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Abstract

Manganese oxide (MnO_x) and nickel oxide (NiO_x)/ multiwalled carbon nanotubes (MWCNTs) nanocomposites for supercapacitor electrodes have been synthesized by chemical reduction method using acid treated MWNTs and respective salts. MWCNTs used in this study were produced by catalytic decomposition of methane using Ni/TiO_2 based catalyst. Structural and morphological characterizations of metal oxide dispersed MWNTs have been carried out using powder X-ray diffraction (XRD), transmission electron microscopy (TEM). Electrochemical performance of these electrodes has been investigated on aqueous electrolytic supercapacitor using cyclic voltammetry, galvanostatic charge-discharge. Specific capacitance of MnO_x and NiO_x filled MWNT electrodes increases compared to that pure MWNTs electrode due to the pseudocapacitance of the metal oxides nanoparticles encapsulated in MWNTs. The cycle life of these electrodes was also very stable for thousand of cycles.

Keywords: supercapacitor, nanocomposites, specific capacitance: metal oxides

High performance asymmetric supercapacitor from manganese oxide–carbon nanotube based composite electrode

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Development of transition metal oxide-carbon composites have gained interest in recent years owing to their potential applications requiring both high energy and high power densities, which are much sought in present day portable electronics, specially supercapacitors. Supercapacitors (ultracapacitors) are attractive energy source because of high power density, fast energy delivery, short charge time, long shelf and cycle life and safety over than battery. Carbon nanotubes (CNTs) have been already proposed as electrode materials for supercapacitors. However, CNTs filled and doped with mixed metal oxides show more attractive electrodes than Pure CNTs. In this paper a nanocomposite consisting of carbon nanotubes and MnO_2 is synthesised by mixing carbon nanotubes and manganese nitrate together with different ratios using wet chemical method. Due to test supercapacitance properties of the electrode, an asymmetric type pseudo-capacitor electric double layer capacitor is considered and its electrochemical properties are investigated. By using the as-prepared cathode of a MnO_2-carbon nanotube composite electrode, the asymmetric supercapacitor exhibits high energy density, stable power and short charge-discharge time. The redox properties of the nanocomposite are exhibited ideal capacitive behaviour in a KOH solution. The morphological characterization of this nanocomposite is examined in terms of the X-ray diffraction patterns (XRD) and transmission electron microscopy (TEM) images. Cyclic voltammetry, galvanostatic charging discharging tests were applied to investigate the performance of the composite electrodes. The results demonstrate that electrochemical properties of MnO_2 CNT electrode are significantly greater than pristine CNTs electrode in the same medium.

Keywords: Carbon nanotube, MnO_2 composite, Supercapacitor, Electrochemical properties

profile occurs near the circumference of the chamber; furthermore unwanted backflow (negative velocity) observed in a wide region at the center. In addition, four other inlet designs have been considered: radial, a radial offset and axial offset. Radial offset entry turned to be the best choice as it offers the highest unifor while maintaining the lowest loss in pressure across the chamber. Furthermore, unlike the radial entry, ra offset could provide swirl flow at the upstream of the distributor. Therefore a design with radial offset entry the plenum chamber has finally been chosen.

THE EFFECT OF DENSITY INVERSION ON THE TRANSIENT NATURAL CONVECTION OF WATER IN A RECTANGULAR CAVITY.

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The effect of density inversion on the transient natural convection of water in a rectangular cell is numeric studied. A non-Boussinesq approach is employed and the results are compared to previous studies. The ca was not filled completely full of water, and a small gap is left at the top in order to have a free surf Simulations are carried out with water having initial temperatures of 8, 12, 16 and 20 °C, which is equa temperature of the opposing walls, while the entire cavity is insulated. The fluid is initially still and temperature of one vertical wall is suddenly lowered to 0 °C. Measurements of the temperature distribution the cavity were made at three different vertical positions: y1 = 0.01785 m, y2 = 0.07545 m and y3 = 0.1353 Comparison of both predicted flow patterns and calculated temperatures to the previous study are presen which confirms that good agreements are obtained.

TERNARY NANOCOMPOSITE FILM OF POLYANILINE/MULTI-WALLED CARBON NANOTUBES/MANGANESE DIOXIDE

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Since the discovery of carbon nanotubes (CNTs), great interest has been stimulated for their potential applicat in ultra-strong wires, nanoelectronic devices, field emission devices and supercapacitors. CNTs exhibit ex mechanical, electrical and thermal properties. They enable new applications of materials containing CN Conducting Polyaniline (PANI) may be an effective way to synthesize new type of nanometer materials. Tho several studies have been done on PANI/CNTs nanocomposites, electron conduction and stability of nanocomposites still remains an issue. The use of transition metals as filling materials for CNTs might be a to improve the interaction between CNTs and PANI that may lead to an enhancement in the properties. In study, we have successfully synthesized a new type of ternary nanocomposites film consisting polyaniline/multi-walled carbon nanotubes/manganese dioxide (PANI/MWCNT-MnO_2). Several characteriza techniques were done to evaluate properties of the ternary nanocomposites films namely thermogravime analysis (TGA), Fourier transform infrared spectroscopy (FTIR), UV-Vis spectrophotometer, resisti measurement, X-ray diffraction (XRD) and scanning electron microscope (SEM). Testing showed that M filling had desirable effects on the film; increased in thermal stability, increased in conductivity and be nanotubes-polymer interaction based on the shift in transition of UV-vis and presence of benzoid and quin rings of FTIR spectra. Thus, this new nanocomposites film has potentials to be used as a multifunctional mater Field: Science and technology

Keywords: Conducting polymer, polyaniline, multi-walled carbon nanotubes, manganese diox nanocomposites

COMPUTATIONAL FLUID DYNAMICS (CFD) STUDIES ON FIXED BED ADSORPTION OF CO FROM NATURAL GAS

[1]Salma Awad Nouh, [2]Lau Kok Keong, [3] Azmi Bin Mohd Shariff
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Generally, carbon dioxide (CO_2) is highly corrosive in the present of water. Higher content of CO_2 in the nat gas (NG) tends to decrease the heating value of it and subsequently lower the price of the NG per unit volu Due to these factors, CO_2 has become one of the important operating factors in NG processing industry.

APPENDIX III

(AWARDS & IP)

URKUNDE/CERTIFICATE

INTERNATIONALE FACHMESSE
»IDEEN-ERFINDUNGEN-NEUHEITEN«
NÜRNBERG
INTERNATIONAL TRADE FAIR
»IDEAS-INVENTIONS-NEW PRODUCTS«
NUREMBERG

Erfindung Universität / Hochschule

Prof. Abdul Latif Ahmad; Dr. Syamsul Rizal Abd Shukor;Dr. Leo Choe Peng
Universiti Sains Malaysia
11800 USM, PENANG

MALAYSIA

wurde für hervorragende Leistungen eine
Goldmedaille
verliehen.

Erfindung/ Neuheit
γ-Aluminiumoxid mit bimodaler Porengrößenverteilung: Transportwiderstand-Minderung in zweischichtigen Membranen
γ-Alumina with bimodal pore size distribution: transport resistance diminution in bi-layered membrane

International Jury of iENA 2009

Kom. Rat Volkwin Hoffelner
Vorsitzender der Jury/Chairman of the jury

7. November 2009

International Exposition of Research and Inventions of Institutions of Higher Learning 2007
10 - 12 August 2007 Kuala Lumpur Convention Centre (KLCC)

3.(9) 6

Certificate of Award

GOLD

EXHIBIT

RICE HUSK ASH-BASED SORBENT/ CATALYST AS A NOVEL INDUSTRIAL GAS CLEANING TECHNOLOGY

EXHIBITOR(S)

Dr. Lee Keat Teong, Prof. Dr. Abdul Rahman Mohamed, Assoc. Prof. Dr. Azlina Harun@Kamaruddin, Irvan Dahlan

DATO' MUSTAPA MOHAMED
MINISTER OF HIGHER EDUCATION
MALAYSIA

PROFESSOR DATO' DZULKIFLI ABDUL RAZAK
CHAIRMAN
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UNIVERSITI SAINS MALAYSIA

Pusat Konvensyen Kuala Lumpur (KLCC)

pecipta07

MALAYSIA

EKSPO PENYELIDIKAN DAN CIPTAAN INSTITUSI PENGAJIAN TINGGI ANTARABANGSA 2007

INTERNATIONAL EXPOSITION OF RESEARCH AND INVENTIONS OF INSTITUTIONS OF HIGHER LEARNING 2007

Anugerah

MENTERI PENGAJIAN TINGGI MALAYSIA

REKAAN / CIPTAAN

Rice Husk Ash-Based Sorbent/ Catalyst As A Novel Industrial Gas Cleaning Technology

PEREKA / PENCIPTA

Dr. Lee Keat Teong , Prof. Dr. Abdul Rahman Mohamed ,
Assoc. Prof. Dr. Azlina Harun@Kamaruddin , Irvan Dahlan

DATO' MUSTAPA MOHAMED
MENTERI PENGAJIAN TINGGI
MALAYSIA

Anjuran Bersama:

3.697

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»IDEAS-INVENTIONS-NEW PRODUCTS«
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Erfindung Universität / Hochschule

Dr. Lee Keat Teong; Prof. Abdul Rahman Mohamed; Prof. Azlina Harun; Dr. Irvan Dahlan
Universiti Sains Malaysia
11800 USM, PENANG

MALAYSIA

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Erfindung/ Neuheit
Sorbens / Katalysator auf der Basis von Reishülsenasche als neuartige Reinigungstechnologie für Industriegas
Rice husk ash-based sorbent / catalyst as a novel industrial gas cleaning technology

International Jury of iENA 2009

Kom. Rat Volkwin Hoffelner
Vorsitzender der Jury/Chairman of the jury

7. November 2009

MARS

MALAYSIAN ASSOCIATION OF RESEARCH SCIENTISTS

Gold Medal

This Certificate of Award is presented to

Prof. Dr. Abdul Rahman Mohamed

Assoc. Prof. Dr. Lee Keat Teong

Prof. Subhash Bhatia

Dr. Sumathi Sethupathi

For the invention/innovation of

Oil Palm Shell-Based Sorbent/Catalyst as a Novel Industrial Gas Cleaning Technology (CePAC)

Malaysia Technology Expo 2011
17 - 19 February 2011
Kuala Lumpur

(Y. Bhg. Dato' Ir. Haji Yahaya Ahmad)
President
Malaysian Association of Research Scientists

(Dr. Wan Manshol Bin W. Zin)
Chairman
Organizing Committee MTE 2011

MARS

MALAYSIAN ASSOCIATION OF RESEARCH SCIENTISTS

Silver Medal

MALAYSIA TECHNOLOGY EXPO 2008

This Certificate of Award is presented to

Dr Ahmad Zuhairi Abdullah

Hamidah Abdullah

Prof Subhash Bhatia

For the invention/innovation of

Novel Catalytic System for Cleaning of Diesel Engine Exhaust Gas

Malaysia Technology Expo 2008
21 - 23 February 2008
Kuala Lumpur

(DATUK DR. DAUD MOHAMAD)
President
Malaysian Association of Research Scientists

(DR. WAN MANSHOL B. W. ZIN)
Chairman
Organizing Committee MTE 2008

MARS

MALAYSIAN ASSOCIATION OF RESEARCH SCIENTISTS

This Certificate of Award is presented to

Dr Ahmad Zuhairi Abdullah

Professor Subhash Bhatia

Babak Salamatinia

Hamed Mootabadi

For the invention/innovation of

Innovative Ultrasonic-assisted Reactor System for Enhanced Biodiesel Production from Waste Oil

Malaysia Technology Expo 2009
19 - 21 February 2009
Kuala Lumpur

(DATUK DR. DAUD MOHAMAD)
President
Malaysian Association of Research Scientists

(DR. WAN MANSHOL B. W. ZIN)

MALAYSIA TECHNOLOGY EXPO 2009

BioInno Awards 2009

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BRONZE

This certificate is awarded to

ASSOC. PROF. DR. AHMAD ZUHAIRI ABDULLAH,
PROF. SUBHASH BHATIA, BABAK SALAMATINIA,
HAMED MOORABADI

INNOVTIVE HETEROGENEOUS SONOREACTOR SYSTEM FOR ENHANCED AND GREENER BIODIESEL PRODUCTION PROCESS

Y.Bhg. Datuk Dr. Daud Mohamad
President
Malaysian Association of Research Scientists, MARS

Y.Bhg. Dato' Iskandar Mizal Mahmood
Chief Executive Officer
Malaysian Biotechnology Corporation, BiotechCorp

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Universiti Sains Malaysia

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Vice-Chancellor

Universiti Sains Malaysia

NATIONAL RESEARCH AND INNOVATION COMPETITION

PATENT REGULATION 1986
[REGULATION 10(2)]

STATEMENT JUSTIFYING THE APPLICANT'S RIGHT TO THE PATENT/CERTIFICATE

I	Agent's file reference	:	
II	Title of Invention	:	METHOD FOR PRODUCTION OF ACTIVATED CARBON FROM RICE HUSK USING CHEMICAL ACTIVATION
III	Applicant	:	UNIVERSITI SAINS MALAYSIA
IV.	Application No. (If known)	:	

V. I/We believe that the inventor(s)/innovator(s) of the above-mentioned application is as follow:-

NAMES	ADDRESS
1. Ismail Bin Abustan (670109086817) 2. Zainal Arifin Bin Ahmad (590415085871) 3. Mohd Azmier Bin Ahmad (780617085703) 4.Nasehir Khan Bin E.M Yahaya(660510075699) 5. Muhamad Faizal Bin Pakir Mohamed Latiff (841017075145)	UNIVERSITI SAINS MALAYSIA, SCHOOL OF CIVIL ENGINEERING, 14300 NIBONG TEBAL, PENANG

VI. Statement justifying the applicants right to the patent/~~certificate~~ :

The applicant's right to the invention is by virtue of being the inventors' employer.

Signature :
Name : Prof. Madya Dr. Ismail Bin Abustan
Deputy Dean
Industrial and External Relations
School of Civil Engineering
Engineering Campus
Universiti Sains Malaysia

Date : 23/6/2010

PATENT REGULATION 1986
[REGULATION 10(2)]

STATEMENT JUSTIFYING THE APPLICANT'S RIGHT TO THE PATENT/CERTIFICATE

I Agent's file reference :

II Title of Invention : GREEN DRAINAGE SYSTEM

III Applicant : UNIVERSITI SAINS MALAYSIA

IV. Application No. (If known) :

V. I/We believe that the inventor(s)/innovator(s) of the above-mentioned application is as follow:-

NAMES	ADDRESS
1.Hamidi Bin Abdul Aziz (651126085679) 2. Ahmad Husaini Bin Sulaiman (550317085919) 3. Nordin Bin Hamdan (541204015397) 4. Mat Supri Bin Kasa (600526025237) 5. Ismail Bin Abustan (670109086817) 6. Hazizan Bin Md. Akil (710701065509) 7. Zainal Arifin Bin Ahmad (590415085871) 8. Mohd Azmier Bin Ahmad (780617085703) 9.Nasehir Khan Bin E.M Yahaya(660510075699) 10. Muhamad Faizal Bin Pakir Mohamed Latiff (841017075145)	UNIVERSITI SAINS MALAYSIA, SCHOOL OF CIVIL ENGINEERING, 14300 NIBONG TEBAL, PENANG

VI. Statement justifying the applicants right to the patent/~~certificate~~ :

The applicant's right to the invention is by virtue of being the inventors' employer.

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