UNIVERSITI SAINS MALAYSIA

Laporan Akhir Projek Penyelidikan Jangka Pendek

A Fundamental Studies Zeolite Membrane Structure – Activity Relationship And Its Role In Gas Separation And Pervaporation Process

by
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FINAL REPORT

RESEARCH UNIVERSITY GRANT

TITLE OF RESEARCH

A FUNDEMENTAL STUDIES ZEOLITE MEMBRANE STRUCTURE – ACTIVITY RELATIONSHIP AND ITS ROLE IN GAS SEPARATION AND PERVAPORATION PROCESS

PROJECT LEADER

PROFESSOR ABDUL LATIF BIN AHMAD

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Geran Penyelidikan Universiti Laporan Akhir

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(i)	**Title of Research: A Fundemental Studies of Zeolite Membrane Structure – Activity Relationship and Its Role in gas Separation and Pervaporation Process** *Tajuk Penyelidikan:*
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B.	**PERSONAL PARTICULARS OF RESEARCHER** / *MAKLUMAT PENYELIDIK:*
(i)	**Name of Research Leader: Prof. Abdul Latif Ahmad** *Nama Ketua Penyelidik:*
	Name of Co-Researcher: Dr. Tye Chin Thian *Nama Penyelidik Bersama:*
(ii)	**School/Institute/Centre/Unit : School of Chemical Engineering** *Pusat Pengajian /Institut/Pusat/Unit :*
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*

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E. **ABSTRACT OF RESEARCH**

(An abstract of between 100 and 200 words must be prepared in **Bahasa Malaysia and in English**. This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

Two types of eolite membranes, SAPO-34 and zeolite A, have been synthesized using direct in-situ crystallization and microwave heating. The zeolite membranes synthesized were characterized using different analytical techniques. This includes Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray diffraction (XRD), Thermal Gravimetric Analysis (TGA), Energy Dispersive Spectroscopy (EDS) and Nitrogen Adsorption, Fourier Transformed Infra-Red. The effect of microwave heating time and temperature toward the formation of SAPO-34 zeolite membranes with different zeolite crystal sizes and thickness was studied. The selected zeolite membrane was subjected to gas separation studies of CH_4/CO_2 and H_2/CO_2 binary gas mixtures over wide ranges of temperature (30-180 ^{o}C) and pressure difference across the zeolite membrane (100-500 kPa). Zeolite A membrane was synthesized on unseeded and seeded supports using microwave heating. The zeolite A membranes were subjected to studies of recovery of organic liquids from aqueous solution by pervaporation over temperature of 69-70 ^{o}C, isopropanol feed concentration of 0.81-0.96 % and permeate pressure of 1 kPa. The zeolite membrane structures were correlated with the separation process parameters.

Abstrak Penyelidikan

(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris**.
Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

Membran zeolit telah disintesis menggunakan penghabluran langsung in-situ dan pemanasan gelombang mikro. Membran zeolit yang disintesis telah dicirikan dnegan menggunakan teknik analisis yang berbeza. Ini termasuklah Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray diffraction (XRD), Thermal Gravimetric Analysis (TGA), Energy Dispersive Spectroscopy (EDS) and Nitrogen Adsorption, Fourier Transformed Infra-Red. Kesan masa pemanasan gelombang mikro dan suhu ke atas pembentukan membran zeolit dengan saiz kristal zeolit yang berbeza dan ketebalan telah dikaji. Membran zeolit yang dipilih dikaji untuk pemisahan campuran-campuran gas penduaan CH_4/CO_2 dan H_2/CO_2 untuk julat suhu (30-180 oC) dan perbezaan tekanan merentasi membran zeolit (100-500 kPa) yang luas. Satu lagi jenis membran zeolit yang disintesis dan dikaji untuk pemisahan cecair organik dari larutan akueus dengan menggunakan pervaporation. Struktur membran zeolit yang berkait rapat dengan parameter proses pemisahan telah dikaji.

F. RESEARCH BACKGROUND

Latar Belakang Penyelidikan

Increasingly stringent market and environmental demands mandate large improvements in processes and catalysts as well as novel manufacturing technologies (McLeary et al., 2006). In the new millennium, membrane technology has gained importance in view of several emerging separation and reaction application. The separation of CO_2 from natural gas (CH_4) is a classical example of one such application (Li et al., 2005b). CO_2 separation from CH_4 is important in enhancing the energy content of the natural gas. In addition, the acidic and corrosive behavior of CO_2 in the presence of water within the transportation and storage system have led to the importance of CO_2 removal before it is passed to the pipeline (Li et al, 2005a). There are several methods of separation CO_2 from CH_4 such as conventional adsorption process using amine and cryogenic distillation. However, these hydrocarbon separations performed in the petrochemical industry are generally costly and involve high operating costs (Engelien, 2004).

The increasing prices of crude petroleum in the international market have led to the need for an alternative fuel. Hydrogen is one of the potential fuel especially to power our vehicles due to its environmental friendly nature. Combustion of hydrogen only produces energy and water but no any pollutants. Steam reforming of natural gas is one of the methods for producing synthesis gas, which is mixture of hydrogen and carbon monoxide (CO). The hydrogen produced can be separated from carbon monoxide (Koh et al., 2007). Anyway, traces of CO left in the H_2 after separation need to be removed to obtain pure H_2, since even trace of CO present in H2 gas could easily spoil the operation of hydrogen fuel cells used in automotives.

Organic solvents are widely used in various industrial applications. These solvents form azeotropes (constant boiling mixture) at certain concentrations with water and thus difficult to separated using convectional distillation technology. It is necessary to recover the organic solvent from its aqueous solution from environmental and economic point of view. Recovery of organic compounds from aqueous solutions in the industry is frequently sought but difficult especially when an azeotrope is involved. The difficulty of separating an azeotropic mixture was encountered in the production of bio-ethanol. Fuel-grade bio-ethanol production has gained attention recently because it is being used to replace methyl *t*-butyl ether as a fuel oxygenate, and it has potential to reduce pollution as well as dependence on non-domestic sources of petroleum (Bowen et al., 2007). The dehydration of the azeotropic mixture formed (ethanol/water) is normally carried out using azeotropic distillation. Recently, Cardona Alzate and Sanchez Toro (2006) reported that if pervaporation is used as dehydration method instead of azeotropic distillation, further energy savings can be obtained in the bio-ethanol production plant.

Membrane separation and pervaporation have drawn attention of researchers in recent years due to its low energy cost and environmental benignity (Sridhar et al., 2007). Membrane separation process is easier to operate and more energy efficient than the other separation processes. Polymeric membrane (organic membrane) such as hollow fibre module is one the main categories used for industrial application. However, the thermal instability of polymer membranes has limited its application (Engelien, 2004). In addition, swelling tends to alter the polymeric membrane properties and generally leads to higher permeability and lower selectivity during pervaporation. In particular, inorganic membranes such as zeolite and silica are suitable for gas separation of carbon dioxide from natural gas or gaseous mixtures at high temperature and high pressure, due to their superior thermal, mechanical and chemical stability, good erosion resistance, and high pressure stability compared to conventional polymeric membranes (Li et al., 2005b). Inorganic membranes are also posssed with high solvent-resistant properties and free of swelling (Li et al., 2007).

Zeolites are microporous silicate or alumino-silicate crystalline materials, suitable for steady state separation of gaseous mixtures due to their well-defined pores of molecular dimensions as well as their adsorption properties. (Bernal et al., 2003). Zeolite membrane is formed when zeolites grows as films. It has uniform microporous structure, good thermal stability, high mechanical strength and resistance to relatively extreme chemical environment (Shan et al., 2004).

There are two main ways of membrane synthesis: (a) in situ crystallization from concentrated gels and (b) two-step crystallization using externally synthesized seeds fixed on the support (Noack et al., 2002). Although many different strategies have been employed, the issue of preparing high quality supported zeolite membranes has not been successfully achieved (Berenguer-Murcia et al., 2005). Membrane synthesis still imposes challenges such as control of thickness, grain size, crystal orientation, minimization of the effect of grain boundary defects (such as channel blockages). Hence, a more facile and controllable approach to synthesize zeolite membrane or films are still needed (Shan et al., 2004). A zeolite membrane should be high selective with high flux (Pinar Zeynep Culfaz et al., 2006). A cost-effective synthesis method for zeolite membrane is worth to be explored for this study.

The fundamental understanding of the mechanism of crystal growth and zeolite membrane structure – activity relationship, as well as the orientation of zeolite crystal is very essential in facilitating the task of engineering zeolite film microstructure. The correlation between membrane structure, synthesis procedure and composition need to be investigated (McLeary et al., 2006). The two critical stages: (a) nucleation and (b) crystal growth, during the formation of supported zeolite membrane are important to be considered. These two stages are highly sensitive to the experimental conditions such as synthesis solution composition and can be manipulated to control the crystal growth. Besides the influence of the synthesis parameters, the shape and orientation of the zeolite seeds and membranes are strongly dependent on the use of structure directing agent (SDA). Tetrapropylammonium hydroxide (TPAOH) and tetrapropylammonium bromide (TPABr) are the most currently used SDA for synthesis of MFI membranes (Lai et al., 2004). The secondary growth of supported zeolite seed layers, is now recognized as one of the most attractive methods for orienting the formation of consolidated thin membrane. This method provides improved flexibility for crystal growth and greater control of film microstructure separately and results in short crystallization time. One of the limitations for zeolite membrane synthesis is the long synthesis time using classical heating method. Microwave (MW) heating is a fast, simple and energy efficient method, which reduces significantly the synthesis time of zeolite while improving the properties of zeolite membrane. The synthesis of zeolite membranes with preferred orientation and controlled thickness has been reported within a few hours using MW assisted hydrothermal synthesis of a seeded support (Motuzas et al., 2007).

Intensive membrane studies on gas separation has been focused on different kinds of zeolite membranes and these include silicate-1 and ZSM-5, due to its importance in membrane separation since the pore structure of MFI zeolite is near to the sizes of many industrially important organic molecules (Bernal et al., 2003). However, MFI-types zeolite membranes have pore diameters of ~0.58nm, which are still too big to selectively separate small gaseous molecules such as CO_2 (0.33nm kinetic diameter) and CH_4 (0.38nm kinetic diameter). The small-pore molecular sieves such as zeolite T (0.41 nm pore diameter), DDR (0.36 X 0.44 nm), and SAPO-34 (0.38 nm) with sufficiently small pores to allow separation on the basis of size exclusion need to be developed. These membranes are reported to have high CO_2/CH_4 selectivities, due to a combination of differences in diffusivity and competitive adsorption (Li et al., 2005b). A thorough understanding of the mechanism of gaseous molecules movement through the zeolite membrane pore as well as the absorbate - non absorbate interaction need to be studied for right type of zeolite membrane structure needed for selective separation of gaseous molecule from the gaseous mixture.

For separation of organic compounds from aqueous solutions, the strong hydrophilic nature of NaA type zeolite membrane enables the achievement of excellent water separation from aqueous organic mixtures. NaA zeolite membrane has been the target of many investigations due to its high Al/Si ratio and small pore size (4.1 Å) (Pera-Titus et al., 2007). Van Hoof et al. (2006) compared the dehydration performance of a commercial inorganic NaA type zeolite membrane with the polymeric membranes for dehydration of the binary mixtures iso-propanol/water, acetonitrile/water and methylethylketone/water. For all the solvents that were tested, the zeolite membrane shows the best separation properties at low water concentrations.

Seed size is one of the main factors influencing the formation of seed layers that determines the qualit supported zeolite membranes. In addition, the seed sizes used in previous membranes synthesis are usua small (<200nm). Smaller seed size requires more difficulty in seed preparation and hence makes the proc for large scale applications. Thus, it is necessary to elucidate the effects of seed sizes on the growth of ze membranes in order to develop a feasible method for the large-scale synthesis of zeolite seeds and memb (Zhang et al., 2006).

There is need of membranes with larger surface area in order to fulfill the processing demands in industrial production (Pinar Zeynep Culfaz et al., 2006). There have been a number of studies on producing membranes with enlarged surface area by changing the support shape from a flat disc to a tube geometry (Noack et al., 2002; Bernal et al., 2003; Pinar Zeynep Culfaz et al., 2006). There is need for a fundamental understanding of zeolite membrane structure which could result into large-area and high quality membranes.

The quality of zeolite membrane is determined by intercrystalline porosity (defects), the crystal orientation relative to the membrane layer, size of the crystal and the thickness and uniformity of the zeolite layer. Present research efforts have therefore been directed to finding solutions to the above problem. The present research is mainly focusing on the systematic studies for development of small and homogenous zeolite seeds, and able to control their size, shape and homogeneity by applying MW-assisted rapid synthesis method. The influence of chemical composition of the starting sol and the hydrothermal synthesis conditions such as duration and temperature on the characteristics of the derived seeds will be studied. This will help to design a zeolite membrane structure needed for a particular application in the gaseous separation or water removal from organic liquids. A tubular membrane separator will be designed and fabricated in order to study the performance of zeolite membrane synthesized over separation of gaseous CO_2 from the gaseous mixtures of CO_2/CH_4 and H_2 recovery from the gaseous mixture of H_2/CO at different temperature. Pervaporation study will also be done to separate water from the isopropanol and ethanol aqueous solutions through the zeolite membrane. The membrane selectivity, separation factor and flux data will be correlated with the parameters related with zeolite membrane structure.

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b) Objective(s) of the Research
Objektif Penyelidikan

1. To synthesize and characterize high quality zeolite membranes with controlled thickness and crystal orientation.
2. To study the effect of seed sizes and process parameters on the formation and microstructure of zeolite membranes.
3. To study the separation mechanism of CH_4/CO_2 and H_2/CO_2 gaseous mixture using zeolite membrane separator.
4. To study the performance of the synthesized zeolite membrane for the recovery of organic liquids from aqueous solution of organic liquids by pervaporation.
5. To correlate the separation process parameters with the zeolite membrane structure.

G. RESEARCH METHODOLOGY
Kaedah Penyelidikan

The project will be conducted in the integrated phases as shown in the flow chart (Figure 1) for both studies on gaseous mixtures separation and water-organic compound pervaporation.

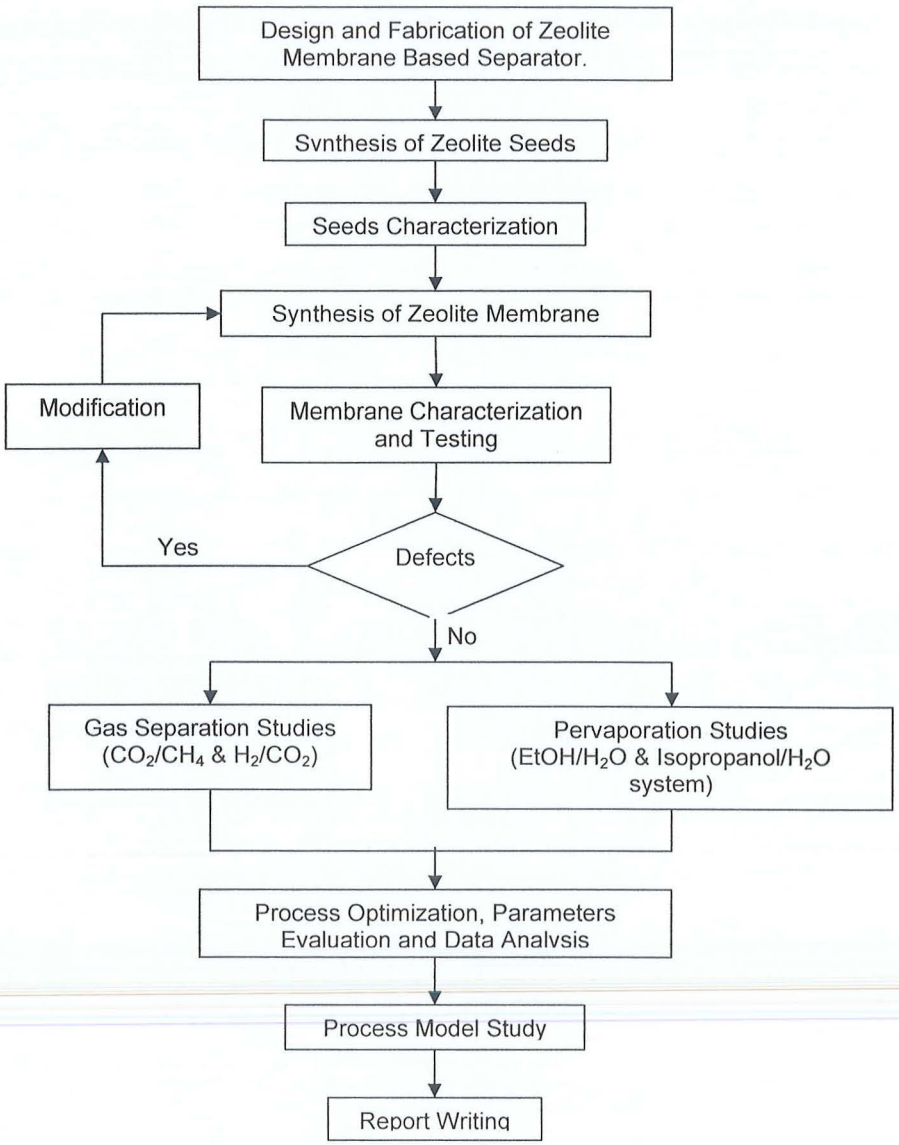

Figure 1: Proposal Research Flow Chart

1.1 Synthesis and Study of Zeolite Seed Sizes Effect on Zeolite Membrane Formation

Microwave (MW) assisted hydrothermal synthesis method will be used to synthesize zeolite seeds. MW-assisted synthesis is a promising method for a very rapid synthesis of small and homogenous zeolite seeds. The chemical composition of the starting sol, the sol stirring time and the hydrothermal synthesis conditions will be varied to synthesize zeolite seeds with different sizes. The hydrothermal synthesis parameters such as microwave power, temperature, duration, number of synthesis step will be studied and optimized in order to control the morphological characteristic of zeolite seeds. The effect of the structure directing agent (SDA) on the shape or orientation of the zeolite seeds will also be studied in the present research. The effect of seed sizes on the formation and microstructure of zeolite membrane will be studied. Figure 2 shows the synthesis process for zeolite membrane.

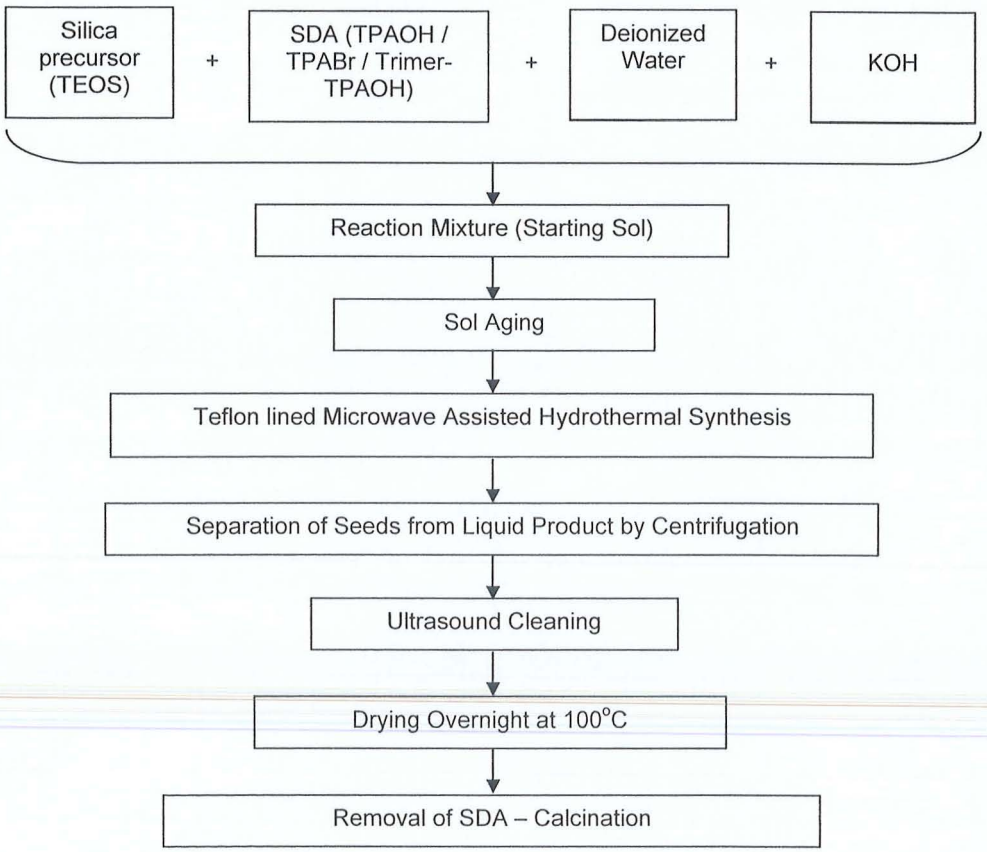

Figure 2: Preparation of Zeolite Seeds by Microwave Assisted Hydrothermal Synthesis

1.2 Study of the Process Parameters Responsible for Obtaining High Quality Zeolite Membranes with Controlled Thickness and Crystal Orientation.

Zeolite membrane will be synthesized in this research. α -alumina support will be used due to its better mechanical strength and thermal stability which makes the handling and sealing easier. In the present research, the seeds prepared at the first part will be used for preparation of supported zeolite membrane by secondary growth synthesis method. Secondary growth methods offers advantages such as flexibility improvement for the crystal growth, elimination of the nucleation step, better control of the membrane microstructure and enhanced reproducibility. Zeolite membrane synthesis conditions will be studied for production of high quality zeolite membrane. Thus, the zeolite membrane delivered using different conditions will be compared in terms of membrane morphology, thickness, orientation and defects. Figure 3 shows the synthesis process for zeolite membrane.

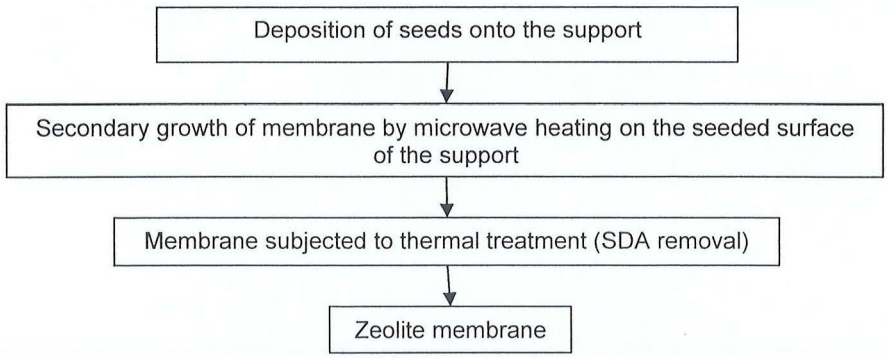

Figure 3: Synthesis of Zeolite Membrane by MW Heating

1.3 Zeolite Membrane Characterization

Characterization of the zeolite membranes will be conducted as given in Table 1. These characterization studies will help in better understanding of the properties of zeolite seeds and membranes.

Table 1: Characterization of Zeolite Membrane

Method	Properties
N_2 adsorption	BET Surface area, pore size distribution, micropore and mesopore volume and isotherm.
X-ray diffraction (XRD)	Crystallinity, structure and orientation
Scanning Electron Microscope (SEM)	Microstructure, crystal size and thickness
Thermogravimetric Analysis (TGA)	Water content, SDA content and thermal stability

1.4 Design and Fabrication of Zeolite Membrane Separator for Gaseous Mixtures Separation

(a) Gaseous Separation Studies

Vapor Permeation Membrane Test Rig will be used to test the performance of the zeolite membrane in separation of gaseous mixture H_2 (0.289nm) and SF_6 (0.55nm). The zeolite membrane's role in permeation of single gas and gaseous mixtures of CO_2/CH_4 and H_2/CO will also be studied.

The schematic diagram of the set up is shown in Figure 4. It consists of vacuum pump, furnace, tubular type membrane, back pressure regulator, flow meter, mass flow controller and vacuum pump.

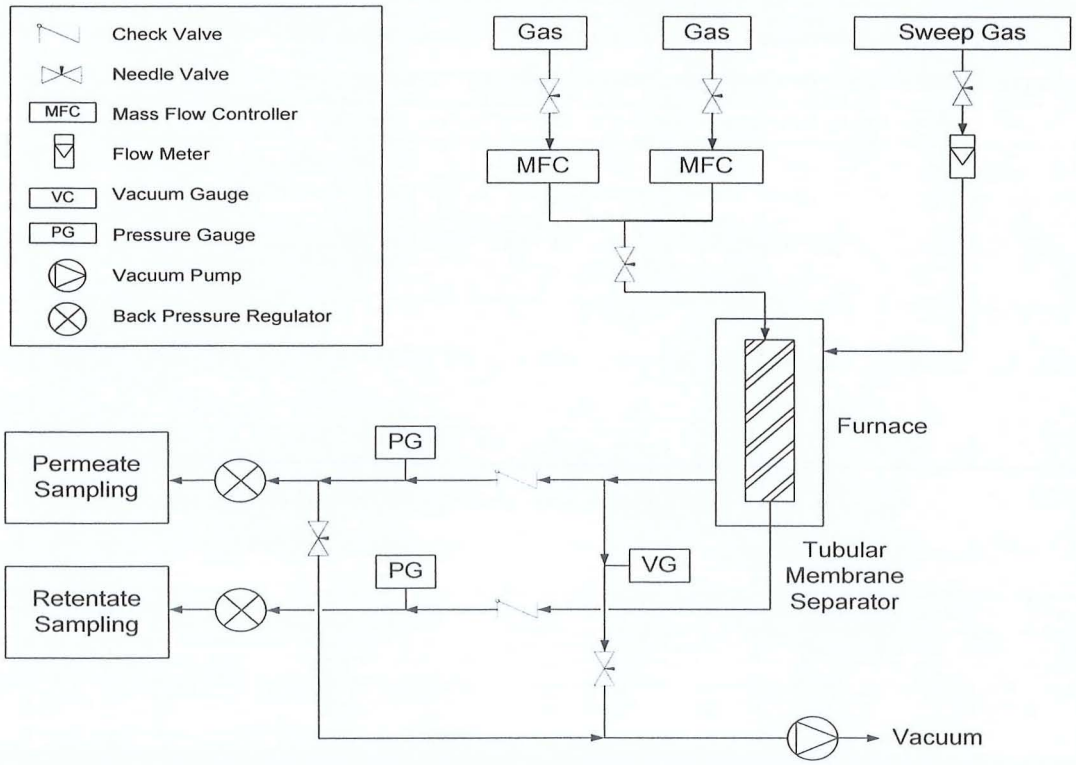

Figure 4: Schematic of Vapor Permeation Membrane Test Rig

(b) Pervaporation Studies

Pervaporation studies will be conducted using a pervaporation unit as shown in Figure 5. Isopropanol and ethanol aqueous solutions will be used for the pervaporation experiments. Water is continuously separated from isopropanol and ethanol aqueous solutions through the membrane. The synthesized zeolite membrane are operated using the same unit and exchangeable membrane cells. The effect of temperature, feed concentration and pressure difference across membrane will be studied in order to obtain the optimum operating conditions for the pervaporation studies.

The feed will be placed in the feed tank, heated and re-circulated. On the downstream side, a vacuum pressure is applied. The permeate pressure will be maintained at 5 – 10 mbar. Permeate will be condensed by the cold traps filled with liquid nitrogen and two traps will be set in parallel allowing the experiment to be carried out in a continuous mode. Retentate and permeate samples will be collected at a fixed interval.

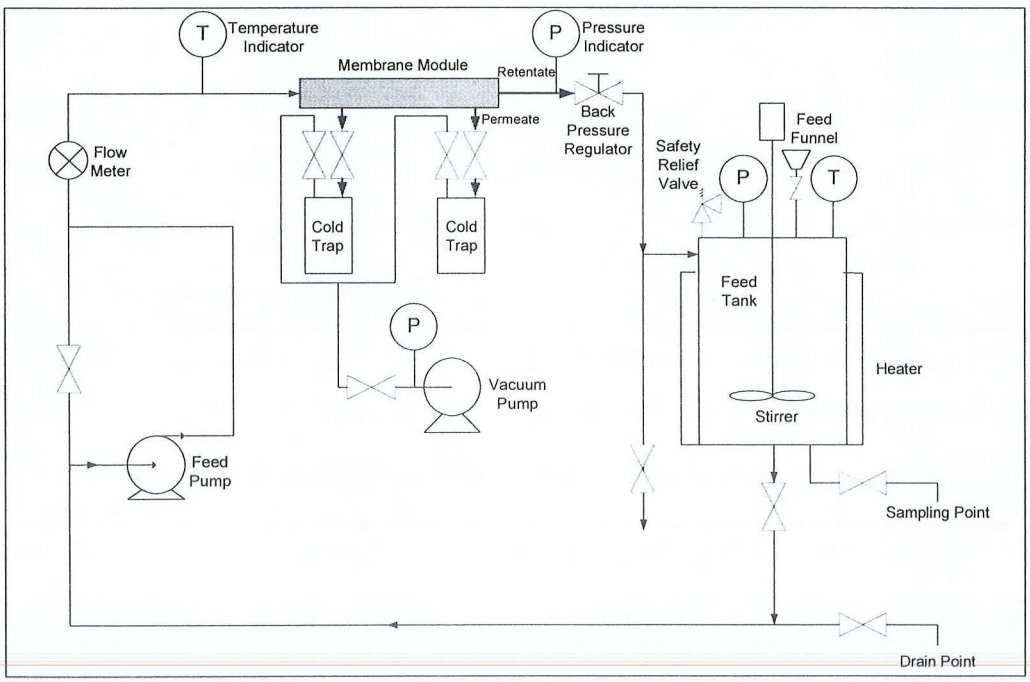

Figure 5: Schematic of Pervaporation Unit

1.5 Separation and Pervaporation Performance Studies of the Zeolite Membrane

Both the separation and pervaporation studies on zeolite membrane will be evaluate in term of flux and selectivity.

Flux is defined as

$$F_i = \frac{W_i}{A} \quad \text{.....(1)}$$

Where F_i = flux of the component i, mol/(mol^2.s)

W_i = moles of the component *i* transferred per unit time, mol/s

A = membrane area, m^2

i = H_2, CO_2, CH_4, water and organic compounds

Selectivity is defined as

$$\alpha_i = \left(\frac{y_i / y_j}{x_i / x_j} \right) \quad \text{.....(2)}$$

Where α_i = separation factor for component *i* with respect to component *j*

y_i = weight of component *i* in the permeate

y_j = weight of component *j* in the permeate

x_i = weight of component *i* in the retentate

x_j = weight of component *j* in the retantate

1.6 Correlation of Zeolite Membrane Structure with the Separation Process Parameters

Zeolite membrane structure will be studied using different analytical tools. Information about the pore size, pore size distribution, zeolite crystal orientation, crystallinity, defects in the membrane and types of pores will be correlated with the selectivity and flux data. The membrane structure will be tuned by adjusting synthesis parameters and conditions in order to enhance the separation selectivity and activity of the zeolite membrane. The mode and mechanism of separation, separation parameters will be studied and its relation with the membrane structure will be established for better understanding of the separation process using a mathematical model. The model will be simulated and results will be compared with the experimental data.

H. SUMMARY OF RESEARCH FINDINGS
Ringkasan dapatan Projek Penyelidikan

SAPO-34 zeolite membranes were synthesized before subjected to to gas separation studies of CH_4/CO_2 and H_2/CO_2 binary gas mixtures. The zeolite crystals size and membrane thickeness increased with the increase in microwave heating from 0.5 to 3 hours. The optimum condition for the formation of SAPO-34 zeolite membrane was microwave heating time of 2 hours at temperature of 200 °C. The SAPO-34 zeolite membrane displayed good separation performance for CH_4/CO_2 binary gas mixture. The SAPO-34 zeolite membrane was found to be CO_2-selective compared to CH_4.

Zeolite A membranes were studied for recovery of isopropanol from isopropanol-water mixture using pervaporation method. The performance for the membrane synthesized with seeding was much better than those sytnhesized without seeding.

I. COMPREHENSIVE TECHNICAL REPORT
Laporan Teknikal Lengkap

There are two parts for the present project: (a) Synthesis and characterization of SAPO-34 zeolite membranes for gas separation studies of CH_4/CO_2 and H_2/CO_2 binary gas mixtures and (b) Synthesis and characterization of zeolite A membrane for studies of recovery of isopropanol from isopropanol-water mixture.

1. *SAPO-34 Zeolite Membrane:*

SAPO-34 zeolite membranes have been successfully synthesized on 25 mm –diameter α -alumina supports through two methods: (1) direct in-situ crystallization and (2) microwave (MW) heating. The synthesis time for SAPO-34 zeolite membrane was significantly shortened to 2 hours at 200 °C using MW heating compared to 24 hours at 200 °C required by using conventional hydrothermal synthesis. The SAPO-34 zeolite membranes were characterized using SEM, EDS, XRD, TEM, SAED, TGA, FTIR and N_2 adsorption-desorption measurement. SEM and XRD analyses revealed that the zeolite crystal size of SAPO-34 zeolite membrane increased with increase in MW synthesis time from 0.5 to 3 hours at 200 °C. MW heating time of 2 hours was found to be the optimum for the formation of SAPO-34 membrane. The SAPO-34 sample formed with MW heating at 200 °C for 2 hours displayed comparable peak intensity with SAPO-34 sample formed with direct in-situ crystallization at 200 °C for 24 hours. Microwave heating time of more than 2 hours resulted in excessive zeolite crystal growth, as was observed from the intercrystalline voids in the SEM images. The SAPO-34 zeolite membrane formed using microwave heating at 200 °C for 2 hours was thinner than the membrane formed using direct in-situ crystallization at 200 °C for 24 hours. Microwave heating formed orthorhombic SAPO-34 zeolite crystals with higher uniformity in crystal sizes (< 1 μ m) compared to direct in-situ crystallization. TGA analysis showed that the SAPO-34 zeolite powder samples formed using conventional hydrothermal synthesis and MW heating were thermally stable up to 900 °C. From the N_2 adsorption-desorption measurement, it was shown that MW heating at 200 °C for 2 hours formed SAPO-34 zeolite powder sample with larger external surface area (31.71 m^2/g) compared to those formed by direct in-situ crystallization (11.44 m^2/g). This is because that the zeolite crystals formed by MW heating were of smaller size compared to those formed by direct in-situ crystallization.

In present study, the MW-synthesized SAPO-34 membrane gave better CO_2 separation perform 125.27 % increase in CO_2 permeance and 20.17-63.30 % increase in separation selectivity) in the permea equimolar CH_4/CO_2 and H_2/CO_2 gas mixtures at 30 °C and 100 kPa pressure difference, compared to SAP membrane which was formed using direct in-situ crystallization. The effects of temperature (30-180 °C) an difference (100-500 kPa) on the binary gas permeation through the MW-synthesized membrane were stud zeolite membrane was able to display high CO_2/CH_4 separation selectivities (23-103) with CO_2 permeance ^{8} mol/m^2.s.Pa, due to selective separation of CO_2 from the CH_4/CO_2 gas mixture. The CO_2/H_2 separation s (1.8-7.9) was lower than CH_4/CO_2 separation selectivity. Owing to much smaller size of H_2 (0.29 nm) comp (0.34 nm) and CH_4 (0.38 nm), it is harder to separate CO_2 from H_2/CO_2 gas mixture compared to removal CH_4/CO_2 gas mixture. However, the CO_2 permeance were of 19-39$\times 10^{-8}$ mol/m^2.s.Pa for the separation o mixture.

2. *Zeolite A Membrane:*

Zeolite A membranes were successfully synthesized on α -alumina tubular supports using microwave heating. The effect of seeding on the membrane synthesis was also investigated. All the membranes were characterized using XRD, SEM/EDS and TGA analysis. SEM revealed that the zeolite film thickness for membrane synthesized in unseeded and seeded supports was 70 and 21 μ m respectively. The XRD and SEM analysis showed that the membrane synthesized on seeded support was better than the one synthesized on unseeded support. The thermal stability of the membrane studied using TGA analysis showed that the membranes synthesized were stable up to temperature of 800 °C.

Both membranes synthesized on unseeded and seeded supports were evaluated for the separation of isopropanol from aqueous solution using pervaporation. Under the same operating conditions, the membrane performance for the seeded support (selectivities of 4-58 and permeation flux of 1.01-16.72 kg/m^2.h) was better compared to the one synthesized on unseeded support (selectivities of 2-34 and permeation flux of 2.66-21.48 kg/m^2.h). Although the permeation flux for the membrane synthesized on unseeded support was higher, the selectivity was lower which indicates that there was a higher content of alcohol in the permeate. This result shows that seeding resulted in a better membrane formation, thus gave a better performance.

List the key words that reflectour research:
Senaraikan kata kunci yang mencerminkan penyelidikan anda:

English	Bahasa Malaysia
Zeolite	Zeolit
Membrane	Membran
Microwave	Gelombang mikro
Gas separation	Pemisahan gas
Pervaporation	Pervaporation

J.

a) **Milestone Achievement**

No.	Milestone Name	Status (Yes/No)	Deliverables
M1	Synthesis and characterization of different kinds of zeolite membranes.	Yes	Development (synthesis and characterization) of zeolite membranes.
M2	Separation of CO_2 from CO_2-CH_4 gaseous mixture.	Yes	Separation studies.
M3	Separation of hydrogen (H_2) from H_2-CO_2 gaseous mixture.	Yes	Separation studies.
M4	Recovery of organic liquid (ethanol/isopropanol) in high purity from aqueous solution of organic liquid mixture using pervaporation process.	Yes	Pervaporation studies.
M5	Membrane structure correlation studies with separation process parameters.	Yes	Separation studies
M6	Process modeling and simulation studies	Yes	Process model studies
M7	Project completion	Yes	Project completion.

b) **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)*	8	13
2.	**Human Capital Development**		
	a. Ph. D Students	1	2
	b. Masters Students	2	1
	c. Undergraduates (Final Year Project)	-	1
	d. Research Officers	-	-
	e. Research Assisstants	-	-
	f. Other: Please specify	-	-
3.	**Patents** *Paten*	1	-
4.	**Specific / Potential Applications** *Spesifik/Potensi aplikasin*	-	-
5.	**Networking & Linkages** *Jaringan & Jalinan*	1	-
6.	**Possible External Research Grants to be Acquired** *Jangkaan Geran Penyelidikan Luar Diperoleh*	1	-

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

Items *Perkara*	Approved Equipment	Approved Requested Equipment	Location
Specialized Equipment Peralatan khusus	Online gas chromatograph; reaction vessel; Microwave vessel set; Homogeneizer	Mass flow controller; GC injector	Petroleum laboratory, School of Chemical Engineering, USM
Facility Kemudahan	Glove box	Magnetic hot plate stirrer	Petroleum laboratory, School of Chemical Engineering, USM
Infrastructure Infrastruktur			

K. BUDGET / *BAJET*

Total Approved Budget : RM 565,500.00
Total Additional Budget : RM -
Grand Total of Approved Budget : RM 565,500.00

Yearly Budget Distributed
Year 1 : RM 313,500.00
Year 2 : RM 123,500.00
Year 3 : RM 128,500.00

Additional Budget Approved
Year 1 : RM
Year 2 : RM
Year 3 : RM

Total Expenditure : RM 564,984.85
Balance : RM 515.15

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

Signature of Researcher
Tandatangan Penyelidik

10/1/11
Date
Tarikh

UserCode: SHARIDA / USMKCLIVE / PJKIMIA Program Code: Votebook9100 Current Program : Votebook (Header)

Current Date : 05/12/2011 11:59:10 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: 811043 Year: 2011

Detail	Excel	Budget Item	Budget Control	Account Description	Budget Account Code	Roll Over	Virement	Cash Received	Reserved	Commit	Actual	Available	% Usage
		46	T	Projek Kumpulan Wang Unt Penyelidikan	1001.111.0.PJKIMIA.811043	81,200.00	0.00	0.00	0.00	0.00	35,928.18	45,271.82	0.00%
		46	T	SubTotal		81,200.00	0.00	0.00	0.00	0.00	35,928.18	45,271.82	0.00%
		47	T	Projek Kumpulan Wang Unt Penyelidikan	1001.221.0.PJKIMIA.811043	-1,338.49	0.00	0.00	0.00	0.00	6,822.00	8,160.49	0.00%
		47	T	Projek Kumpulan Wang Unt Penyelidikan	1001.223.0.PJKIMIA.811043	800.00	0.00	0.00	0.00	0.00	100.00	700.00	0.00%
		47	T	Projek Kumpulan Wang Unt Penyelidikan	1001.224.0.PJKIMIA.811043	8,000.00	0.00	0.00	0.00	0.00	0.00	8,000.00	0.00%
		47	T	Projek Kumpulan Wang Unt Penyelidikan	1001.226.0.PJKIMIA.811043	16,000.00	0.00	0.00	0.00	0.00	0.00	16,000.00	0.00%
		47	T	Projek Kumpulan Wang Unt Penyelidikan	1001.227.0.PJKIMIA.811043	59,217.32	0.00	0.00	0.00	1,038.90	44,682.35	13,496.07	0.00%
		47	T	Projek Kumpulan Wang Unt Penyelidikan	1001.228.0.PJKIMIA.811043	7,125.00	0.00	0.00	0.00	0.00	18,355.00	-11,230.00	0.00%
		47	T	Projek Kumpulan Wang Unt Penyelidikan	1001.229.0.PJKIMIA.811043	13,526.82	0.00	0.00	0.00	400.00	14,022.40	1,095.58	0.00%
		47	T	SubTotal		103,330.65	0.00	0.00	0.00	1,438.90	84,181.75	15,710.00	0.00%
		48	T	Projek Kumpulan Wang Unt Penyelidikan	1001.335.0.PJKIMIA.811043	35,966.67	0.00	0.00	0.00	0.00	22,000.00	57,966.67	0.00%
		48	T	SubTotal		35,966.67	0.00	0.00	0.00	0.00	22,000.00	57,966.67	0.00%
		9999		Grand Total		148,563.98	0.00	0.00	0.00	1,438.90	142,109.93	3,015.15	0.00%

* After deduction of RM 2,500.00 for salary in December, left RM 515.15.

APPENDIX:

THESIS

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

by

YEONG YIN FONG

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

May 2010

SYNTHESIS, CHARACTERIZATION AND PERFORMANCE OF ZEOLITE A MEMBRANE FOR THE RECOVERY OF ALCOHOL FROM ALCOHOL-WATER MIXTURE USING PERVAPORATION PROCESS

by

WEE SHIN LING

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

June 2010

SYNTHESIS, CHARACTERIZATION AND MODIFICATION OF SAPO-34 ZEOLITE MEMBRANE FOR SEPARATION OF CO_2 FROM BINARY GAS MIXTURES

by

CHEW THIAM LENG

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

December 2011

JOURNAL PUBLICATION

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Synthesis, characterization and reactive separation activity of acid-functionalized silicalite-1 catalytic membrane in *m*-xylene isomerization

Yin Fong Yeong, Ahmad Zuhairi Abdullah, Abdul Latif Ahmad, Subhash Bhatia*

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Catalytic activity
p-Xylene yield
Reactive separation

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.

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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Xylene isomerization kinetic over acid-functionalized silicalite-1 catalytic membranes: Experimental and modeling studies

Yin Fong Yeong, Ahmad Zuhairi Abdullah, Abdul Latif Ahmad, Subhash Bhatia*

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Kinetic modeling
Activation energy

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.

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 ($Si/Al = \infty$)). 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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Research Article

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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.

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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Propylsulfonic acid-functionalized partially crystalline silicalite-1 materials: synthesis and characterization

Yin Fong Yeong · Ahmad Zuhairi Abdullah · Abdul Latif Ahmad · Subhash Bhatia

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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Keywords Synthesis · Characterization · Propylsulfonic acid-functionalized · Partially crystalline silicalite-1 · 3-mercaptopropyltrimethoxysilane · Oxidation · Characterization

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, 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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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,

Synthesis and Characterization of Acid Functionalized Silicalite-1 Materials by Utilizing Phenethyltrimethoxysilane (PE) as an Organosilane Source

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Abstract.

Organic-functionalized silicalite-1 materials were synthesized via one step co-condensation hydrothermal crystallization by utilizing tetraethylorthosilicate as an inorganic silica source and phenethyltrimethoxysilane as an organosilane source. The organic groups were subsequently sulfonated to arenesulfonic acid silicalite-1 materials under strong acid treatment. 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 acid functionalized silicalite-1 materials were characterized for its crystallinity, surface morphology, elemental composition, acid capacity, chemical interaction and thermal stability.

Keywords: Synthesis; Characterization; acid-functionalized silicalite-1; phenethyltrimethoxysilane.

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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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Silicalite-1 membrane
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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.

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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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.

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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Review

Membrane separation process—Pervaporation through zeolite membrane

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ABSTRACT

Membrane separation process has become one of the emerging technologies that undergo a rapid growth for the past few decades. Pervaporation is one of the membrane separation processes that have gained increasing interest in the chemical and allied industries. It is an effective and energy-efficient technology that carries out separations, which are difficult to achieve by conventional separation processes. Inorganic membrane such as zeolite membranes with uniform, molecular-sized pores offer unique type of pervaporation membrane for a number of separation processes. This review presents the role of zeolite membrane and its progress in the pervaporation process. The fundamental aspects of pervaporation over different types of membranes are reviewed and compared. The focus of this review is on zeolite membrane covering: (a) synthesis of zeolite membranes; (b) membrane characterization; (c) pervaporation studies; (d) its applications in alcohol dehydration, organic/organic separations and acid separations. The transport mechanism during pervaporation is discussed and the issues related with pervaporation are addressed. Innovation and future development of zeolite membrane in pervaporation are also presented.

Contents

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Process optimization studies for the dehydration of alcohol–water system by inorganic membrane based pervaporation separation using design of experiments (DOE)

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ABSTRACT

In the present study, commercial ceramic membrane from Pervatech BV was used to study the dehydration of isopropanol–water mixture by pervaporation. The effects of feed temperature, feed concentration, permeate pressure and feed flow rate on the membrane separation performance were studied by using design of experiments (DOE) coupled with response surface methodology (RSM). The center composite design (CCD) was used to obtain optimum process condition. The results showed that in order to obtain optimum permeation flux and selectivity, the temperature, feed concentration of alcohol, permeate pressure and feed flow rate were 75 °C, 94 wt%, 1 kPa and 84 dm^3/h, respectively. Under optimum operating condition, the permeation flux and selectivity was 2.41 kg/m^2 h and 1131, respectively. The optimum permeation flux of 9.16 kg/m^2 h was obtained at temperature of 90 °C with feed concentration 81 wt% alcohol, permeate pressure of 1 kPa and feed flow rate of 100 dm^3/h, respectively. However, the optimum selectivity of 1415 was observed at the temperature of 69 °C, feed concentration 96 wt% alcohol, 1 kPa permeate pressure and feed flow rate of 41.05 dm^3/h, respectively. The effect of operation time on the performance of the membrane was also investigated by running the pervaporation process for 8 h continuously. It was observed that the permeation flux changed with time but the selectivity remained nearly constant after 8 h of continuous pervaporation.

1. Introduction

During the past few decades, membrane separation processes has become one of the emerging technology which underwent a rapid growth. It has drawn the attention of researchers in the separation technology field with its better performance compared to the conventional separation technology. The main membrane separation technologies include microfiltration, ultrafiltration, reverse osmosis and nanofiltration, electrodialysis, gas-separation and pervaporation [1]. Most of the membrane separation technologies are well-developed and established. Among these technologies, pervaporation is still a rapidly developing membrane separation technology [1]. Pervaporation is a mild process and hence very effective for the separation of those mixtures which cannot survive the harsh conditions of distillation. Pervaporation has advantages in terms of low energy consumption. No entrainer is required in the pervaporation process, thus there is no contamination of the original mixtures [2]. It can used for breaking azeotropes, separation of close boiling, isomeric or heat sensitive liquid mixtures, dehydration of solvents and other volatile organics and organic/organic separations such as ethanol or methanol removal [3].

Recovery of organic compounds from aqueous solutions in the industry is frequently sought but face difficulties in the separation especially when an azeotrope is involved. The conventional methods such as azeotropic distillation, extractive distillation and liquid–liquid extraction exhibit some drawbacks [1]. Pervaporation and vapor permeation on the other hand offer a more promising and energy-efficient alternatives for azeotropic separation. Pervaporation is a process that has many similarities with vapor permeation, which uses gaseous components on the feed side of the membrane. In recent years, a large number of researches on the pervaporation and vapor permeation applications such as dehydration of alcohol [4–7] are reported. Vapor permeation is a simple process as compared to the pervaporation with no phase change occurs during the permeation. However, the strong dependence of the separation characteristics on the feed pressure, the sensitivity to friction losses in the feed stream and the possibility of condensation are some of the disadvantages of vapor permeation [8]. Recently pervaporation has gained increasing interest on the part of the chemical industry with a better separation capacity and energy efficiency which could lead

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Ordered mesoporous silica (OMS) as an adsorbent and membrane for separation of carbon dioxide (CO_2)

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Membrane

ABSTRACT

Separation of carbon dioxide (CO_2) from gaseous mixture is an important issue for the removal of CO_2 in natural gas processing and power plants. The ordered mesoporous silicas (OMS) with uniform pore structure and high density of silanol groups, have attracted the interest of researchers for separation of carbon dioxide (CO_2) using adsorption process. These mesoporous silicas after functionalization with amino groups have been studied for the removal of CO_2. The potential of functionalized ordered mesoporous silica membrane for separation of CO_2 is also recognized. The present paper reviews the synthesis of mesoporous silicas and important issues related to the development of mesoporous silicas. Recent studies on the CO_2 separation using ordered mesoporous silicas (OMS) as adsorbent and membrane are highlighted. The future prospectives of mesoporous silica membrane for CO_2 adsorption and separation are also presented and discussed.

Contents

1. Introduction

The emission of carbon dioxide (CO_2) is one of the serious environmental problems due to its significantly increased concentration in the past five decades and most notably in last 15 years [1]. CO_2 has been identified as greenhouse gas, which contributes to the global climate change and global warming. According to the report by Intergovernmental Panel on Climate Change (IPCC), there has been global increment of the atmospheric concentration of CO_2 by about 100 ppm (36%) over the last 250 years, from a range of 275–285 ppm in the pre-industrial era (1000–1750) to 379 ppm in 2005. The highest average growth rate of atmospheric CO_2 concentration was

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Rapid synthesis of thin SAPO-34 membranes using microwave heating

Thiam Leng Chew · Abdul Latif Ahmad · Subhash Bhatia

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Abstract SAPO-34 membranes were prepared by microwave (MW) heating method using a colloidal solution containing tetraethylammonium hydroxide as a template. SAPO-34 in the form of seed and membranes were investigated for their properties such as morphology, pore characteristic, crystallinity and thickness, using characterization method of scanning electron microscope (SEM), X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), FT-IR and nitrogen adsorption-desorption. SAPO-34 membrane was also prepared using conventional hydrothermal heating and studied for its comparison with those formed by MW heating. SAPO-34 membrane containing homogenous SAPO-34 crystals with average size of ~0.7 μm was formed during MW heating. Compare to the conventional hydrothermal heating, MW heating facilitates formation of SAPO-34 crystals with narrower size distribution due to the highly uniform volumetric heating provided by microwave heating. MW heating was able to produce thinner SAPO-34 membrane (1–2 μm) where as hydrothermal heating formed thicker SAPO-34 membrane (~3.6–5.5 μm). The synthesis time for membrane formation was significantly shortened from 24 h for conventional hydrothermal heating to 2 h for microwave heating at 200 °C.

Keywords Hydrothermal synthesis · Microwave heating · SAPO-34 · Membrane

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1 Introduction

Zeolites is microporous and crystalline zeolite with well defined pore structure which has exhibited excellent performance in the field of catalysis, adsorption and separation [1]. In recent years, there have been increasing interest on the study of SAPO-34 (a silicoaluminophosphate zeolite) in gas separation application due to its small pore size, medium acidic strength and high thermal stability [2, 3]. The chabazite framework with pore diameter of 0.38 nm of SAPO-34 [4], which is close to the sizes of gas molecules such as CH_4 and CO_2, has been a promising material for CO_2 separation [2, 4].

There are number of studies reported on the SAPO-34 membrane for gas permeation and separation [2–5]. Although high separation factors were obtained in these studies but the SAPO-34 membrane exhibited low gas permeance. An ideal membrane should perform with high gas permeance as well as separation factor, and thus require the membrane to be thin enough. Reduction in zeolite crystal size, is an important issue in recent years because the properties of the materials are greatly influenced by the change in zeolite crystal dimensions [6]. Zeolite crystal dimension plays impact on the thickness and morphology of the membrane formed.

Conventionally, SAPO-34 is synthesized by time-consuming hydrothermal heating method. There was also effort in synthesizing SAPO-34 film using vapor phase transport (VPT) method [7]. Microwave (MW) heating appears to be an attractive method for the membrane synthesis due to its number of advantages over conventional hydrothermal heating. These advantages are shorter synthesis time, production of small zeolite crystals with narrow size distribution and high purity, rapid and uniform heating [8–10]. Venna and Carreon [11] reported the

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Ba-SAPO-34 membrane synthesized from microwave heating and its performance for CO_2/CH_4 gas separation

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ABSTRACT

H-SAPO-34 membrane was successfully synthesized using microwave heating at 473 K within a period of 2 h. The H-SAPO-34 membrane was ion-exchanged with alkaline earth cations. A comparison study was conducted to obtain the separation performance of different cation-exchanged membranes. The CO_2 permeances reduced with cation-exchanged membranes in the order of $Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+}$. The highest increase in CO_2/CH_4 separation selectivity of about 240% was obtained by ion-exchanging the H-SAPO-34 membrane with Ba^{2+}. Separation of equimolar of CO_2 and CH_4 was conducted at different separation temperatures and pressure differences across the Ba-SAPO-34 membrane. The maximum CO_2/CH_4 separation selectivity of 103 with CO_2 permeance of 37.6×10^{-8} mol/m^2 s Pa was obtained for equimolar feed mixture of CO_2 and CH_4 at 303 K and 100 kPa pressure difference across Ba-SAPO-34 membrane.

1. Introduction

Removal of greenhouse gases, especially carbon dioxide (CO_2) from gaseous mixtures has drawn attention of many researchers due to rapid increasing concentration of CO_2 in the atmosphere in recent years. Separation of CO_2 from natural gas is one of the important processing steps before natural gas can be utilized in the production of chemicals or power generation plants. Conventional technologies used for CO_2 separation from gas mixtures include absorption using amine based solvents and pressure swing adsorption [1,2]. These methods posses number of drawbacks such as high energy consumption for solvent regeneration, equipment corrosion and flow problems caused by viscosity of solvent [3,4].

Membrane separation technology has therefore appeared to be more energy efficient in terms of relative low capital costs (due to absence of requirement to regenerate the absorbents) compared to conventional separation technologies [1,5,6]. The polymer membranes are instable at high temperatures and their separation performance could decrease in the presence of high CO_2 pressure due to plasticizing effect [7,8]. Zeolite membranes are the microporous inorganic membranes which are gaining increasing interest among the researcher as an alternative candidate for gas separations, in view of their higher thermal, mechanical and chemical stability compared to organic membranes [8]. Its uniform and molecular-sized pore structure with controlled host–sorbate interactions makes it attractive as shape-selective material for gas separation [9,10].

There are number of studies of various zeolite membranes reported for gas permeation or gas separation, such as MFI-type [11–16] and FAU-type [7,17,18]. There is increasing interest for the development of small-pore zeolite membranes for gas separation such as A-type [19–22], DDR [23,24], T-type [25,26] and SAPO-34 membranes [1,27]. These small-pore zeolite membranes are potential candidates for CO_2/CH_4 separation due to their pores size which are close to size of CH_4 molecules but are larger than CO_2 molecules.

Extensive studies have been reported using SAPO-34 membrane on gas permeation and separation [1,27–35]. These SAPO-34 membranes were synthesized by hydrothermal synthesis method. Hydrothermal heating has number of limitations such as long synthesis time and production of zeolite crystals with broad size distribution. Microwave (MW) heating is an emerging technology offering number of advantages against conventional hydrothermal heating such as shorter synthesis time, rapid heating rate and production of small zeolite crystals with narrow size distribution [36–38]. To our best knowledge, our group has been the first to report synthesis of SAPO-34 zeolite membrane using MW heating [39].

Ion exchange is one of the methods reported to affect the gas permeance and separation of zeolite membranes. Hasegawa et al. [40] reported the reduction of CO_2 permeance after ion-exchanging NaY-type membrane with solution of K^+, Rb^+ and Cs^+. The CO_2/N_2 selectivity for the equimolar mixtures was increased from 19 to 39, 40 and 34 after ion-exchange with K^+, Rb^+ and Cs^+, respectively [40]. Reduction in gas permeances (N_2 and CH_4)

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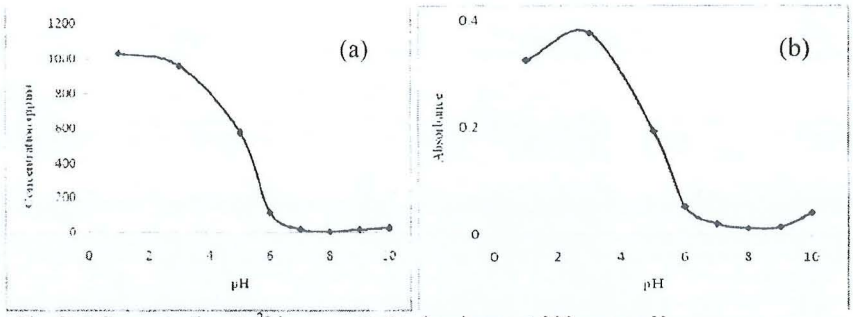

Fig. 2(a) Concentration Cu^{2+} ions vs pH, (b) absorbance at 800 nm vs pH

Conclusion

The stability of metal-tannins complexes is dependent on pH. In the present study, Zn^{2+} and Cu^{2+} ions began to form complexes at pH 3 - 5 and the maximum formation of Zn-tannins and Cu-tannins complexes are at pH 7 and pH 8, respectively.

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Keywords: Mangrove tannins, AAS, UV-Vis, FT-IR, SEM.

Formation of SAPO-34 Molecular Sieve using Microwave Irradiation Heating and Conventional Hydrothermal Heating

Thiam Leng Chew[1] and Subhash Bhatia[1]

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Abstract

Crystallization of SAPO-34 molecular sieve with microwave irradiation heating and conventional hydrothermal heating was investigated in the colloidal solution using tetraethylammonium hydroxide as a template. Different hydrothermal conditions (microwave power and synthesis time) were varied in this studies. Microwave irradiation heating has significantly shortened the synthesis time for SAPO-34 and reduced the size of SAPO-34 zeolite particles synthesized. SAPO-34 zeolite particles with average size of 600 nm were successfully synthesized with microwave irradiation heating at 180 °C, 560W microwave power for 10 hours. Meanwhile, synthesis time of 24 hours was required to synthesis SAPO-34 with conventional heating at 180 °C and the zeolite particles formed were in average size of 1000 nm. Figure 1 and 2 show respectively the XRD patterns and SEM images of SAPO-34 synthesized with microwave irradiation heating and conventional hydrothermal heating. The crystallization yield increased when the synthesis time increased. In addition, the crystallization rate of SAPO-34 increased with the rise of microwave power. However, increasing the microwave power beyond 560W increased no more the crystallization rate. Crystallization with microwave irradiation heating becomes a promising alternative for conventional hydrothermal heating, and yet synthesizing zeolite molecular sieve with better properties (i.e. crystal size).

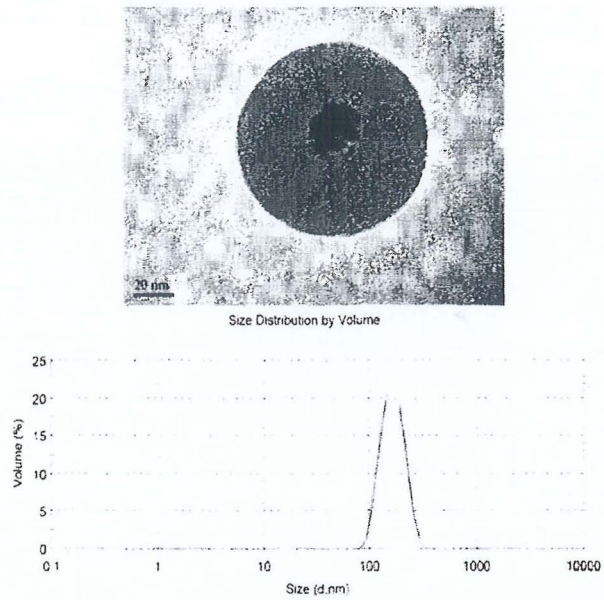

Fig. 1 (a) TEM image (b) DLS results of core-shell structured monodispersed magnetic nanoparticles

Keywords: Magnetic nanoparticles; core-shell structure; enzyme immobilization; biocatalysis; chloroperoxidase;

Synthesis and Characterization of Acid-Functionalized Silicalite-1 Membrane

Y. F. Yeong, A. Z. Abdullah, A. L. Ahmad and S. Bhatia

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Abstract

The synthesis of 3-mercaptopropyltrimethoxysilane (3MP) functionalized silicalite-1 membrane via one step *insitu* hydrothermal crystallization on α-alumina support is reported in the present study. The effect of the 3-mercaptopropyltrimethoxysilane concentration in the range of 5 to 20 mol% on the formation of the membrane was investigated. The membrane was subsequently oxidized to acid functionalized silicalite-1 membrane and characterized by X-ray diffraction (XRD) scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and nitrogen gas permeation. The XRD results (Figure 1) show that the acid functionalized silicalite-1 membrane was successfully formed and the crystallinity of the membranes gradually decreased with increasing 3MP concentration in the synthesis mixture. The relative crystallinity of the acid functionalized membranes compared to silicalite-1 membrane were 85% for 5 mol% 3MP to 75% for 10 mol% 3MP and 58% for 15 mol% 3MP, respectively. However, the typical XRD peaks corresponding for silicalite-1 structure were absent for 20 mol% 3MP acid functionalized membrane. This indicated that the membrane crystalline structure could not be retained once 3MP concentration increased to 20 mol% of the total silica source. The higher concentration of organosilane resulted in the disruption of the crystal structure due to the difficulties in incorporating of longer organic fragment into the silicalite-1 structure [1].

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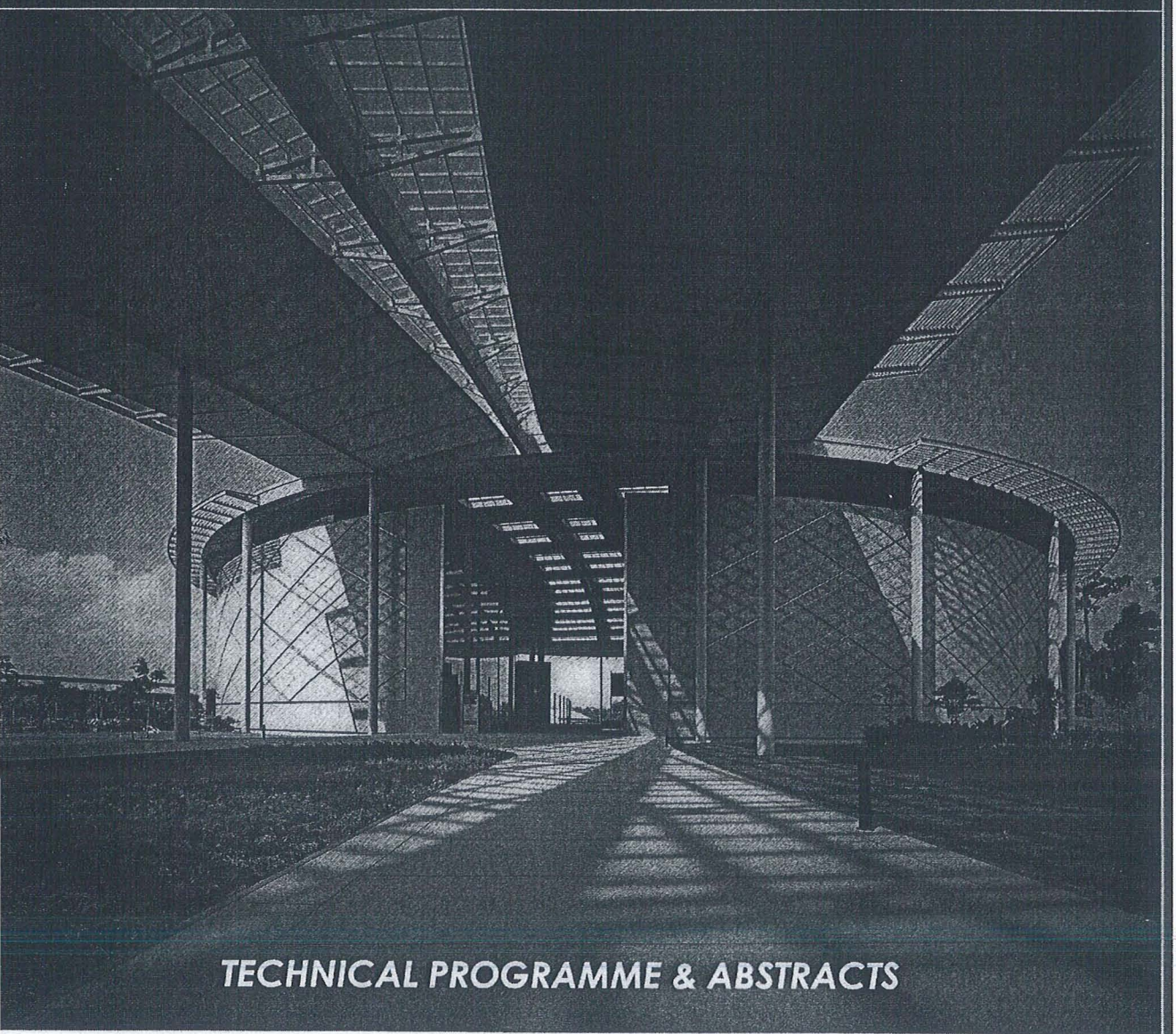

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ABSTRACTS
ORAL PRESENTATIONS

PEAO1_AMD_1

Asymmetric Composite Membranes From Chitosan and Tricalcium Phosphate Useful for Guided Tissue Regeneration

Hung-Yin Tai (Tamkung universuty, Taiwan); Hung-Te ... Tamkung University, Taiwan, Taiwan); Man-Chin ... (Tamkung University, Taiwan); Shiu-Huey Chou (Fu ... Catholic University, Taipei County, Taiwan); Trong-... ng Don (Tamkang University, Taiwan)

...mmetric guided tissue regeneration (GTR) barrier ...branes having a porous layer for permeability and ...esiveness to bone and a skin layer were prepared from ...san (CS) and tricalcium phosphate (TCP) by combining ...eating process and lyophilization. The preheating before ...hilization produced a skin layer that could increase the ...hanical strength of the membranes and also prevent the ...sion of other tissue such as connective tissue. The subsequent ...hilizatio resulted in a porous layer for permeability and ...esiveness to bone. In addition, the preheating time could ...controlled to moderate porosity, average pore size, water ...rption, and mechanical properties of the membranes. From ... preliminary in-vitro cell culture, the TCPCS membrane ...ined by preheating for 40 min before lyophilization seems ...e a good candidate as a barrier membrane for providing ...al migration of gingival epithelial cell and maintaining an ...ted space for promoting the regeneration of alveolar bone ...

PEAO1_AMD_2

Evaluation of Catalytic Cracking Reactivity of Zeolites Using 1-Dodecene as a Model Feedstock -Effect of Hydrogen Transfer Reactivity

...shio Tsutsui (Kasgohima University, Japan); Yasuhiro ...eda (Kagoshima University, Japan); Kazuya Ijichi (Kagoshima University, Japan); Kei Mizuta (Kagoshima ...niversity, Japan); Yoshimitsu Uemura (UTP, Malaysia)

...rder to find a suitable zeolite for improving FCC process, in ...ch octane number and gasoline yield are highly enhanced, ...ny types of zeolite were used in cracking reaction of ...odecene. From the product distribution, zeolites were ...ssified into three types in FCC reaction. With the type I ...olites, such as SAPO-11, the product pattern was mono-peak ...tribution by carbon number with high content of olefins and ...y small content of aromatics. On the other hand, the type ... zeolites such as ZSM-5 produced two-peak distribution with ...gh content of aromatics and iso-paraffin in gasoline range. ...ta and FCC equilibrium catalyst were classified as the type ... zeolites, which showed the intermediate nature between ...pe I and II. From these results, the three types of the zeolite ...activity for FCC could be shown schematically. Octane ...mber of gasoline fraction was estimated from the product ...mposition, and it was found that the octane enhancement ...as attained by use of the type I or type II zeolites, but the ...multaneous increase of gasoline yield was obtained by the ...pe II zeolites.

PEAO1_AMD_3

Microwave Heating for Rapid Synthesis of SAPO-34 Zeolites

Thiam Leng Chew (Universiti Sains Malaysia, Malaysia); Abdul Latif Ahmad (Universiti Sains Malaysia, Malaysia); Subhash Bhatia (Universiti Sains Malaysia, Malaysia)

Microwave (MW) heating was introduced for the crystallization of SAPO-34 zeolites using a colloidal solution containing tetraethylammonium hydroxide as a template. The effects of MW power and synthesis time on the formation of SAPO-34 zeolites were studied and optimized in view of the zeolite properties such as morphology and crystallinity. MW heating was compared with the conventional hydrothermal synthesis for the formation of SAPO-34 zeolites. MW heating formed SAPO-34 zeolites with narrower size distribution within significantly shortened time compared to hydrothermal synthesis. Full crystallization of SAPO-34 zeolites was achieved in only 10h by microwave heating instead of 24h required by conventional hydrothermal synthesis at 180 °C.

PEAO1_GTR_1

Reaction Conditions of Two-Step Batch Operation for Biodiesel Fuel Production From Used Rapeseed Oils

Takami Kai (Kagoshima University, Japan)

For the biodiesel-fuel production by methanolysis, the reaction mixture is composed of a methyl-ester phase and a glycerol phase. One of the reactants, triglyceride, is mainly contained in the ester phase. The other reactant, methanol, is easily dissolved in the glycerol phase. Therefore, the methanol in the system is not effectively used for the reaction due to interface mass transfer resistance. An excess amount of methanol is required to increase the conversion in single-step operation. Since the glycerol phase is removed during the operation, a two-step batch operation can effectively intensify the process. In the present study, the optimal operating conditions to increase the conversion are obtained for the methanolysis of used rapeseed oil using a KOH catalyst.

PEAO1_GTR_2

Gasification of Oil Palm Empty Fruit Bunch (EFB) Fibers in Hot Compressed Water for Synthesis Gas Production

Kelly Yong Tau Len (MICET, Universiti Kuala Lumpur, Malaysia); Lim (Universiti Sains Malaysia, Malaysia); Lee Teong (Universiti Sains Malaysia, Malaysia)

The study on the hot compressed water (HCW) gasification of oil palm empty fruit bunch (EFB) fibers was investigated in a batch system using high-pressure autoclave reactor. Reaction parameters subjected for investigation were solid loading and reaction temperature. Solid particle size, amount of water and reaction time were fixed at $250 < X < 500$ µm, 300.0g water and 30 min respectively. The optimum reaction conditions found were 5.0g solid loading and 380°C which produced gases mainly of CO_2, CO, H_2 and CH_4 with gasification efficiency of 32.15% and H_2 yield of 7.22%. The study also focused on the role of a homogenous catalyst, K_2CO_3 and its effects towards the reaction. The optimal amounts identified were 3.0 wt.%

interface. At low pH the PAA block collapses and the inherent, planar alignment tendency of 5CB at a water interface prevails. As pH increases, the polyelectrolyte block becomes increasingly charged and expands, producing a change to homeotropic anchoring. SGLCP blocks can translate conformational changes of a responsive hydrophilic block into rapid, reversible changes in the director field.

PEAO6_AMD_2

Development Pure and La-Doped SnO_2 Catalytic Pellet by Sol-Gel Method for Ethanol Sensing

Xian-Ju Tan (Universiti Sains Malaysia, Malaysia); Guat Wei Lim (Universiti Sains Malaysia, Malaysia); Gaik Tin Ang (USM, Malaysia); Mohamad Zailani Abu Bakar (Universiti Sains Malaysia, Malaysia)

This articles describes the development of pure and lanthanum doped tin dioxide catalytic pellets in detecting ethanol vapour prepared by sol-gel method and pressed into pellet. Sintering treatment at 500 °C was carried out for 4 hours. Structural characterization was performed using X-ray Diffraction (XRD), Transmission Electronic Microscopy (TEM) and BET surface area analyzer. The results of structural analysis showed that lanthanum has been successfully incorporated into the SnO_2 crystal lattice. The catalytic pellets gas sensing performance revealed that the sensitivity of the sensor is improved by the addition of lanthanum. The linear dependence of the sensitivity on the ethanol vapour concentration is observed in the range of 800 – 3000 ppm. The maximum sensitivity is exhibited by 10 at.%La-SnO_2 catalytic pellet at operating temperature of 300 °C. The response and recovery time are increased by introduction of lanthanum into tin oxide. Pure SnO_2 catalytic pellet gives the fastest response and recovery time which are 22.8 seconds and 243.8 seconds respectively.

PEAO6_AMD_3

Acid-Functionalized Silicalite-1 Membranes: Synthesis, Characterization and Its Performance in M-Xylene Isomerization

Yin Fong Yeong (Universiti Sains Malaysia, Malaysia); Ahmad Zuhairi Abdullah (Universiti Sains Malaysia, Malaysia); Abdul Latif Ahmad (Universiti Sains Malaysia, Malaysia); Subhash Bhatia (Universiti Sains Malaysia, Malaysia)

Propylsulfonic acid functionalized silicalite-1 membranes were synthesized on α-alumina support via one-step insitu hydrothermal crystallization by utilizing 3-mercaptopropyltrimetoxysilane as an organosilane source. The thiol group was subsequently transformed to acid group and acid capacity of the membranes was adjusted by varying the concentration of 3-mercaptopropyltrimetoxysilane in the range of 5 mol% to 15 mol%. The membranes were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and ammonia temperature-programmed desorption (NH3-TPD). The membranes were tested for m-xylene isomerization in the temperature range of 355 °C to 450 °C. At 450 °C, m-xylene conversion of 46% with 28% p-xylene yield was achieved. The improvement in m-xylene conversion and the enhancement in p-xylene yield were due to continuous separation of the reaction products through the membrane.

PEAO6_AMD_4

Adsorbents Derived From Mg-Al Hydrotalcite-Like Compounds for High-Temperature Hydrogen Storage

Ruzanna Ibrahim (Universiti Teknologi Petronas, Malaysia); Ye Lwin (Universiti Teknologi PETRONAS, Malaysia)

The coprecipitation method was used to prepare Mg-Al Hydrotalcite-like compounds (HTlcs). The precipitated and calcined Mg-Al HTlcs were characterized using powder X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The XRD patterns for the materials indicated the presence of the hydrotalcite structure. The IR spectrum for calcined Mg-Al HTlcs with Mg/Al molar ratio of 2 showed reduction in water and CO2 characteristics due to their removal during calcination. Subsequent to the calcination, the materials were reduced using temperature programmed reduction (TPR) in order to determine the H_2 uptake. The H_2 gas consumption was found to be very small and further modifications of the material synthesis are required to yield better results.

PEAO6_AMD_5

Topography and Electrical Characteristics of Silicon Oxide Nanodot Grown by AFM Lithography on Silicon Substrate

Sabar D. Hutagalung (Universiti Sains Malaysia, Malaysia); Teguh Darsono (Universiti Sains Malaysia, Malaysia); Zainal Ariffin Ahmad (Universiti Sains Malaysia, Malaysia); Kuan Cheong (Universiti Sains Malaysia, Malaysia); Samsudi Sakrani (Universiti Teknologi Malaysia, Malaysia)

The atomic force microscopy (AFM) was used for patterning and characterization of nanoscale silicon oxide dot. The nanodot was grown on Si(100) substrate via local-anodic-oxidation, where a non-contact conductive AFM mode has been applied to oxidize silicon surface. Current-voltage (I-V) characterization of grown nanodot was performed by contact AFM mode using a gold-coated AFM tip. From I-V characteristics obtained the oscillation peak at about 3.5 V indicates Schottky barrier of SiO_x/Si interface. Moreover, breakdown voltage at the out of dot position is lower compared to the on dot.

PEAO6_AMD_6

How to Produce Activated Carbon with More Homogeniouse Pore Size Distribution?

Arash Arami-Niya (University of Malaya, Malaysia); Wan Mohd Ashri Wan Daud (University of Malaya, Malaysia); Farouq S. Mjalli (University of Malaya, Malaysia)

Oil palm shell was used as a raw material for the preparation of pore size controlled activated carbon adsorbents. The chemical treatment was followed by further physical activation with CO_2. Samples were treated with CO_2 flow at 850 °C by varying activation time to achieve different burn-off activated carbons. Chemically activated samples with H_3PO_4 showed

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T002

Microwave Irradiation Heating for Synthesis of Thin SAPO-34 Membrane

Thiam Leng Chew, Abdul Latif Ahmad, Subhash Bhatia

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia.
E-mail address: edvinchew_83@yahoo.com

Abstract

Microwave irradiation heating for synthesis of SAPO-34 membrane was investigated in the colloidal solution using tetraethylammonium hydroxide as a template. Different hydrothermal condition (synthesis time) were varied in this studies. Microwave irradiation heating has significantly shortened the crystallization time for SAPO-34 and reduced the size of SAPO-34 zeolite particles synthesized compared to conventional hydrothermal synthesis. Hence, thinner SAPO-34 membrane can be formed using microwave irradiation heating. Crystallization with microwave irradiation heating becomes a promising alternative for conventional hydrothermal heating, and yet synthesizing membrane with better properties (i.e. thickness).

Keywords: *Microwave; Membrane; SAPO-34; Hydrothermal Heating.*

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Abstract

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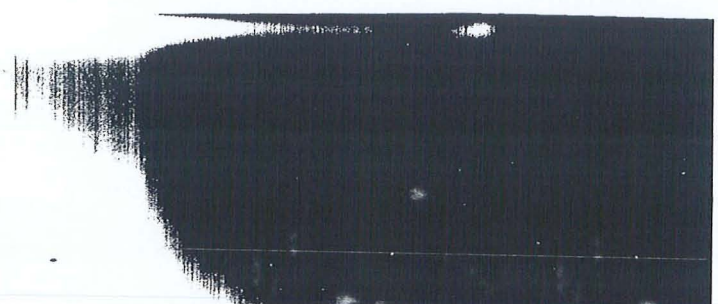

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Y001

Synthesis and Characterization Acid-Functionalized Silicalite-1 Membranes

Yin Fong Yeong, Ahmad Zuhairi Abdullah, Abdul Latif Ahmad and Subhash Bhatia*

School of Chemical Engineering , Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang. Malaysia

Abstract

Acid-functionalized silicalite-1 membranes were synthesized on α -alumina support via one-step *insitu* hydrothermal crystallization by utilizing an organosilane source. The organic-functional group was subsequently transformed to acid group and acid capacity of the membranes was adjusted by varying the concentration of organosilane source in the range of 5 mol% to 15 mol%. The membranes were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Ammonia temperature-programmed desorption (NH_3-TPD) and Fourier transform infrared spectroscopy (FT-IR) results show that different strength of acid sites were presented in the membranes and the total acid capacity increased with increase in organosilane concentration in the synthesis mixture. The membranes were tested for *m*-xylene isomerization in the temperature range of 355 °C to 450 °C. The improvement in *m*-xylene conversion and the enhancement in *p*-xylene yield were due to continuous separation of the reaction products through the membrane. The catalytic membranes exhibited good structural stability after subjected to isomerization reaction study.

Keywords: *Synthesis, Characterization, Acid-functionalized silicalite-1 membrane, m-xylene isomerization, p-xylene yield.*

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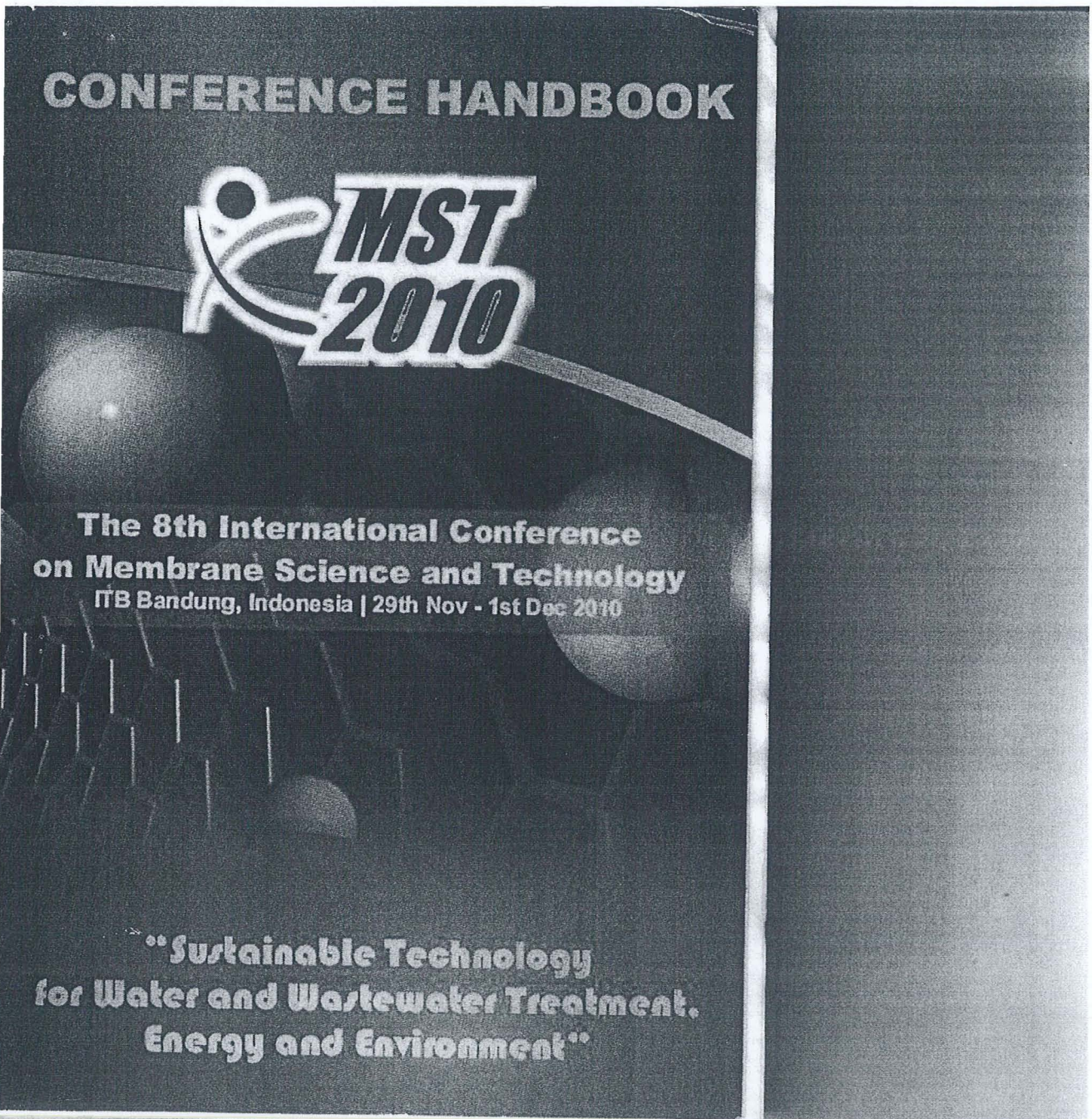

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B-2

Thin SAPO-34 Zeolite Membrane for Separation of CO_2/CH_4 Mixture Gas

Thiam Leng Chew[a], Subhash Bhatia[a,*] and Abdul Latif Ahmad[a]

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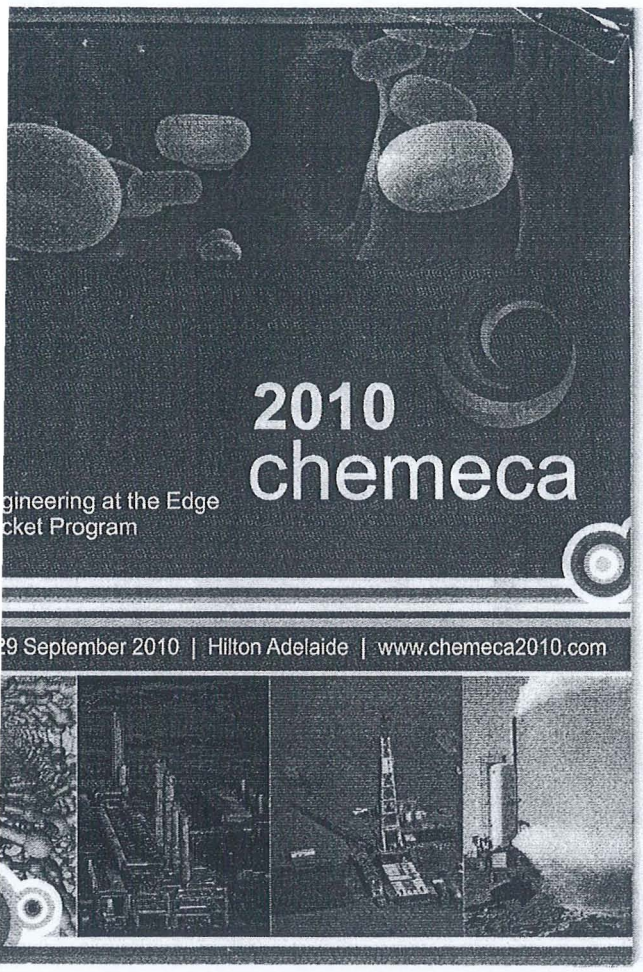
ABSTRACT

Thin SAPO-34 zeolite membrane was synthesized from a colloidal solution containing tetraethylammonium hydroxide, silica source, phosphorus source and aluminium source under microwave heating. The synthesis time for SAPO-34 membrane was significantly shortened to 2 hours under microwave heating at 200 °C compared to 24 hours required by conventional hydrothermal synthesis. The SAPO-34 phase, either in the form of powder or membrane, was characterized using methods such as scanning electron microscope (SEM) and X-ray diffraction (XRD). The thin SAPO-34 membrane formed was tested for its single gas permeance of carbon dioxide (CO_2) and methane (CH_4). Gas separation of CO_2/CH_4 mixture gas was performed on the SAPO-34 membrane over different temperature and feed pressure.

Keywords: Zeolite membrane; SAPO-34; microwave heating; gas separation.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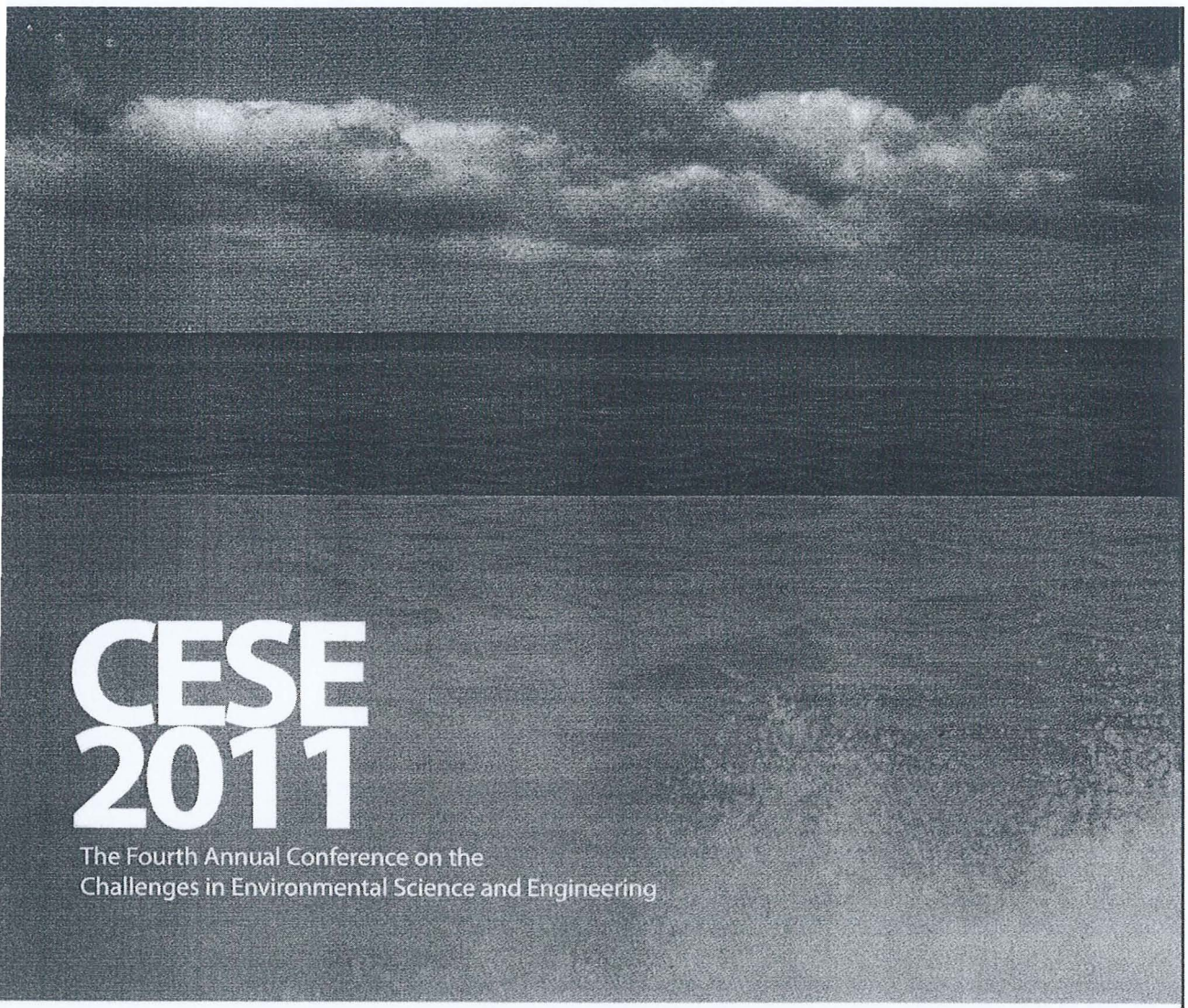

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attachment, perform analysis on microbial population and dominant population by constructing 16S rDNA cone library and PCR-DGGE and at the same time analyze components and composition with atomic absorption spectrometry and ICP. Results: it was found by 16S rDNA cone library study that microorganisms of the attachment mainly included Thiobacillus (4%), δ Proteobacteria (35%), γ Proteobacteria (40%) and Actinomycetes (16%), and microbial resources in the attachment were comparatively novel with great possibility of belonging to new species. According to PCR-DGGE analysis, the main dominant bacteria were Pseudomonas (45%), sulfate reducing bacteria (38%), Actinomycetes (14%) and potential new strains (3%). Components and composition analysis performed by atomic absorption spectrometry , X-ray Diffraction (XRD),XPS, and ICP indicated that the main components were Si>Fe>S>Mg. The cause of attachment formation had been preliminarily analyzed, Pseudomonas and Actinomycetes provided materials for growth of SRB strains on surface of metal conductive rod, resulted in local anaerobic environment, stimulated reproduction of SRB, aggravated corrosion and leaded to that dehydrator can not run.

Keywords: Attachment, 16S rDNA Cone Library;PCR-DGGE; Component Analysis

Applying commercial composts for deca-bromodiphenyl ether biopdegradation

Yi-Tang Chang [a], Lo Tsui [b], Yi-Fen Laio [a], Houng-Toung Chen [b], Shin-Ling Chou [a], Cheng-Chen Lin [a]*

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[b]Department of Safety Health and Environmental Engineering, Min-Chi University of Technology, Tai-Shan, New Taipei City, 24301, Taiwan (E-mail: tsui@mail.mcut.edu.tw; bd75511@yahoo.com.tw)

Abstract
Deca-bromodiphenyl ether (BDE-209), one of distinguished emerging contaminants, as easily is detected on surface water in Taiwan. Anaerobic compost provides anaerobic microorganism and electron donor to remove refractory chemicals. In this study, the reductive debromination at first time was applied for biotreatment of 20 mg/kg BDE-209 with three selected commercial composts, the mixture of sugarcane bagasse/pig manure under different maturity (2 or 6 months) and the kitchen compost. The results presented as an effective removal of BDE-209 in the range of 68-80% in 97 days. The maximum *pseudo* first order decreasing rate of BDE-209 was achieved to 0.0169 day^{-1} (r^2=0.8935). Some contributions might be ascribed to the sorption of BDE-209 onto the compost contained with high organic carbon matters (22.60 mg/kg-33.19 mg/kg). Debrominated byproducts in anaerobic composting process were measured by HSGC-HSMS. BDE-17, BDE-28, BDE-49, BDE-47, BDE-66, BDE-100, BDE-153, BDE-154 and BDE-156 in the 2-month-maturity mixed compost was increased at 42th days then decreased at 97th days. Accumulated byproducts such as BDE-47, BDE-66 and BDE-153 were detected in the mixed compost of 6-month-maturity and the kitchen sample. A biological pathway of BDE-209 debromination therefore was predicted in anaerobic composting processes. Moreover, bacterial community was illustrated by PCR-DGGE-CLONING. Domain *Bacteria* and *Archaea* was monitored in this study. DGGE bands were similar in the beginning then significantly changed in anaerobic composting process, which was calculated by cluster analysis and principal component analysis on the DGGE profiles.

Keywords: decabromodiphenyl ether; reductive debromination; sorption; HSGC-HSMS; PCR-DGGE-CLONING

Separation of CO_2 from CO_2/CH_4 binary gas mixture using Ba-SAPO-34 membrane synthesized from microwave heating: Process optimization studies

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Abstract
H-SAPO-34 membrane was synthesized using microwave heating at 473 K for 2 hours. Ba-SAPO-34 membrane was obtained by ion-exchanging the H-SAPO-34 membrane with Ba^{2+} cation. The separation of CO_2 from CO_2/CH_4 binary gas mixture was studied using design and analysis of experiments (DoE). The response surface methodology (RSM) coupled with central composite design (CCD) was used for modeling and analysis of the contribution of operating parameters (temperature, feed pressure, CO_2 concentration in the feed) on the responses (CO_2 permeance and CO_2/CH_4 separation selectivity) during Ba-SAPO-34 membrane separation process. The process parameters were varied in the range of 303-453 K of temperature, 200-600 kPa of feed pressure and 5-50 % of CO_2 concentration in the feed. The optimum condition for the process parameters was determined by setting the criteria so as to maximize the CO_2 permeance and CO_2/CH_4 separation selectivity. The optimum CO_2 permeance of 26.90 x 10^{-7} mol/m^2.s.Pa and CO_2/CH_4 separation selectivity of 276 were obtained at temperature of 303 K, feed pressure of 200 kPa and 5 % CO_2 concentration in feed.

Keywords: Ba-SAPO-34; Membrane; Microwave; Carbon dioxide; Gas separation

Treatment of landfill leachate by Fenton-like process and post-treatment evaluation through GAC-biofiltration

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Abstract
In recent year, the municipal solid wastes were eliminated in sanitary landfill. Landfill leachate may contain large amount of organic refractory constituents such ammonia and heavy

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

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Ulasan Umum:

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