FRGS: A study on behavior of organic compounds incorporated into sol-gel silica matrix

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Kertas kerja

1. Ismail Ab Rahman, Bahruddin Saad, Rohana Ariffin, Muhammad Idiris Saleh, Anis Tasnim Md Yusof dan Abkariah Azahari, " Pencirian nanotiub silika yang disediakan secara sol-gel', akan dibentang di Seminar Kimia Analisis ke 16, Kucing Sarawak, pada 9-11 Sept. 2003.

2. I. A. Rahman[1], A. T. M. Yussof, B. Saad, R. Adnan, M. S. Adzahar, M. S. Idiris Formation of silica nanotubes using citric acid as structure stabilizer via sol-gel process. Telah dihantar ke Asean Journal on Sci. & Tech. Pada 20 Mac. 2004.

3. I.A. Rahman[1], A. T. M. Yussof, B. Saad and R. Adnan. Formation of silica nanocubes using tartaric as structure modifier via sol-gel process. To be published.

4. Azrat Hkan Abd Rahim Siddiqe, Jamil Ismail, Ismail Ab Rahman, Mohamad Abu Bakar. Synthesis os silica nanosphere via sol-gel process, Postal RCYC 13 – 14 April 2004. USM

5. Chong Ching Ching, Bahruddin Saad, Abdussalam Salhin, Ismail Ab Rahman, Norita Mohamad, Idirid Saleh. Simultaneous solvent extraction of metal ions with thiacrown ethers using ICP-MS. RCYC. 13 – 14 April 2004. USM.

6. Anis Tasnim Md Yusof, Ismail Ab Rahman, Bahruddin Saad. A study of silica nanoparticles morphology by sol-gel method in the presence of carboxylic acid. RCYC 13 – 14 April 2004. USM

7. Bahruddin Saad, Chong Ching Ching, Abdussalam Salhin, Ismail Ab Rahman, Idiris Saleh, Selective removal of heavy metal ions by thiacrown ethers immobilized sol-gel and SPE column. To be published.

PENCIRIAN NANOTIUB SILIKA YANG DISEDIAKAN SECARA SOL-GEL

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ABSTRAK

Nanotiub silika telah dihasilkan secara sol-gel dengan menggunakan templat. Hasil dicirikan dengan menggunakan kaedah SEM, TEM, FTIR, TGA dan BET. Analisis SEM dan TEM menunjukkan nanotuib wujud dalam pelbagai saiz dengan diameter luar antara 200 – 300 nm, diameter dalam 100 – 70 nm dengan panjangnya > 250 nm. Keputusan kajian menunjukkan pembentukan nanotuib amat bergantung kepada kehadiran templat. Luas permukaan bertambah daripada 1.6 $m^2 g^{-1}$ kepada 121 $m^2 g^{-1}$ dengan pertambahan templat sehingga 11 %. Berdasarkan pencirian TGA dan FTIR yang dilakukan, peranan templat dalam pembetukan nanotiub dicadangkan.

Katakunci: Nanotiub silika, sol-gel.

PENDAHULUAN

Perkembangan terkini tentang penghasilan nanosaiz silika sama ada dalam bentuk morfologi sfera atau tiub telah menyumbang kepada pelbagai aplikasi baru dalam pelbagai teknologi. Pelbagai cara penyediaan yang strategik telah digunakan dengan menggunakan kaedah sol-gel yang pertama kali dipelopori oleh Stober et. al[1].

[1]Pembentang kertas

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the cultivated area of Kemajuan Tanah Jengka 15, in Chenor district, Pahang. Top soil samples were collected using auger at a 0-6 cm depth, cleaned from all roots, dried in an oven at 50°C, grinded to a powder form, sieved using 500 micron sieve and kept in a sealed plastic container about 400 g each. This sample was then allowed to stabilized for at least 3 weeks before counting. Using top soils collected fro the forest reserved area as a control, one can see the distribution of K-40 in the cultivated soils which has the effect of fertilization on it.

ORAL ABSTRACT VA5

SIMULTANEOUS SOLVENT EXTRACTION OF METAL IONS WITH THIACROWN ETHERS USING INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (ICP-MS)

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Ismail Ab. Rahman, Norita Mohamad and Muhammad Idiris Saleh
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Simultaneous liquid-liquid extraction of several metal ions (Mg^{2+}, V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}) using three cyclic thiacrown ethers namely, 1,4,7,10-tetrathiacyclododecane (12S4), 1,4,7,10,13-pentathiacyclopentadecane (15S5) and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) in 1,2-dichloroethane was studied. Picrate was used as counter ion and metal ion concentrations were determined using inductively coupled plasma-mass spectrometry (ICP-MS). The effect of key extraction variables such as contact time, pH, ligand and counter ion concentrations were studied. These ligand exhibit high selectivity towards Ag^{+} and Hg^{2+} over other metal ions studied. The ligands were successfully applied towards the extraction of Ag^{+} in river water samples. Research activities involving the immobilization of these ligands in sol-gel silica matrix and future application will also be discussed.

ORAL ABSTRACT VB1

STRUCTURAL STUDIES OF ORGANO GROUP 15 DERIVATIVES OF $RuOs_3$ CLUSTERS

Pereira Leonard

A high yield route, via lightly stabilized $Ru(CO)_4(C_2H_4)$, to a stable tetranuclear dihydrido heteronuclear cluster, $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ 1, has been developed. The unique Ru vertex directs the reactivity of 1, causing preferential substitution to occur there. Only mild conditions are required to effect the synthesis of a series of monosubstituted and disubstituted ER_3 clusters (ER_3 = PPh_3, $AsPh_3$, $SbPh_3$, $P(C_6F_5)_3$, PMe_3, $P(n\text{-}Bu)_3$, $P(t\text{-}Bu)_3$, PCy_3, PCy_2Ph). The number and type of isomers detected depends on the nature of the ligand attached to 1. An attempt has been made to deduce the solution structures of the isomers, as well as the pathways for the intramolecular and intermolecular hydride exchange processes using COSY, HMBC, VT NMR and EXSY experiments for both ^1H and ^{31}P nuclei. Through the simulation of the ^1H and ^{31}P VT spectra, the kinetic and thermodynamic parameters for the two main exchange processes occurring in $RuOs_3(\mu\text{-}H)_2(CO)_{13}(ER_3)$ (E = P, As, Sb) have been extracted; of particular interest is migration of the ER_3 ligand between the Ru and Os vertices. The PCy_2Ph ligand has been found to display unusual broadening in the ^1H VT spectra of its derivatives as the temperature is lowered. For the ligands with smallest cone angles, PMe_3 and $P(n\text{-}Bu)_3$, structures disubstituted at the Ru vertex have been isolated or implied. The similarity of the Ru and Os atoms in the cluster results in disorder in many of the disubstituted crystal structures. The reaction of 1 with PPh_2H led to a series of phosphido-bridged clusters via P–H bond cleavage: $RuOs_3(\mu\text{–}H)_3(CO)_{11}(\mu\text{–}PPh_2)$ 20, $RuOs_3(\mu\text{–}H)_2(CO)_9(\mu\text{–}CO)(\mu\text{–}PPh_2)_2$, $RuOs_3(\mu\text{–}H)_4(CO)_9(\mu\text{–}PPh_2)_2$ and the "butterfly" structure $RuOs_3(\mu\text{–}H)_3(CO)_{11}(\mu\text{–}PPh_2)(PPh_2H)$. Cluster 20 was also reacted with PPh_3 to form $RuOs_3(\mu\text{–}H)_3(CO)_{10}(\mu\text{–}PPh_2)(PPh_3)$ and the "butterfly" structure $RuOs_3(\mu\text{–}H)_3(CO)_{11}(\mu\text{–}PPh_2)(PPh_3)$. Initial studies show that reacting 20 with $P(n\text{-}Bu)_3$ and $SbPh_3$ lead to similarly substituted clusters.

ORAL ABSTRACT VB2

SYNTHESIS AND CHARACTERISATION OF A NOVEL HETEROGENEOUS CATALYST FROM RICE HUSK ASH – THE FRIEDEL-CRAFT BENZYLATION OF TOLUENE WITH BENZYL CHLORIDE

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Silica supported iron catalyst was prepared from rice husk ash (RHA) via the sol-gel technique using an aqueous solution of iron(III) salt in 3.0 M HNO_3. The sample was dried at 110 °C and labeled as RHA-Fe. A sample of RHA-Fe was calcined at 700 °C for 5 hours and labeled as RHA-Fe700. X-Ray diffraction spectrogram showed that both RHA-Fe and RHA-Fe700 were amorphous. The SEM/EDX results showed that the metal was present as agglomerates and were not homogeneously distributed in the silica matrix. The FTIR spectra of the samples exhibit similar absorption bands to that of RHA silica. The specific surface area for RHA-Fe and RHA-Fe700 were determined by BET nitrogen adsorption studies and found to be 87.4 and 55.8 m^2g^{-1} respectively. Both catalysts showed high activity in the reaction between toluene and benzyl chloride. The mono substituted benzyltoluene was

ORAL ABSTRACT VIA4

INTERFACIAL PROPERTIES OF GLYCOLIPIDS AT OIL-WATER INTERFACE

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This work explores interfacial properties of Sucrose Monolaurate (SML) and Dodecyl β-D-Maltoside (DDM) at o/w interface using dynamic drop volume technique, and compares these with the interfacial properties of Brij 35p and Sodium Dodecyl Sulphate (SDS). Note that all surfactant studied in this work contain same number of $-CH_2-$ groups at their apolar hydrophobic tail, whereas they differ in their polar head group composition. This implies that the surfactants tested here differ in polarity and their affinity to polar solvent like water, whilst their affinity to apolar liquid like oil remain same. DDM and SML with least polar head group and HLB value of 16 showed highest degree of interfacial tension reduction among the surfactant tested, suggesting that head group polarity of the surfactants play important role in determining their properties at oil-water interface. As far as transport of surfactant from bulk solution to liquid-liquid interface is concerned, it seems that in addition to bulk surfactant concentration and interface age it is also affected by head group polarity. As far as transport kinetics is concerned, under the given sets of flow rates and surfactant concentration domains, it is found to be dominated by diffusion controlled kinetics, the driving force of which is being surfactant concentration gradient. Like wise the surfactant transport rate constant, which was estimated from the slope of the line of the interfacial tension time profile, depended on surfactant head group polarity and surfactant concentration. The diffusion coefficient of the surfactants at the given sets of experimental conditions depended on both the surfactant concentration and interface age.

ORAL ABSTRACT VIA5

A STUDY OF SILICA NANOPARTICLES MORPHOLOGY BY SOL-GEL METHOD IN PRESENCE OF CARBOXYLIC ACID

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This research was carried out in order to obtain nano particles silica using a sol gel process at room temperature. Nano particles silica have been prepared through the sol gel reaction of tetraethyl-orthosilicate (TEOS) in the presence of citric acid (CA), malic acid (MA) and tartaric acid (TA) as template or pore forming agent followed by washing with distilled water to remove organic molecules. The materials are characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA) and Tapping Density. Result showed that the silica nano particles were obtain by using the carboxylic acid.

ORAL ABSTRACT VIB1

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC ANALYSIS OF FLAVONES FROM THE ANTI-INFLAMMATORY FRACTION OF *ORTHOSIPHON STAMINEUS* CHLOROFORM EXTRACT

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Orthosiphon (O) stamineus also known as Misai Kucing (Cat's Whiskers) is a popular medicinal herb in Malaysia. It has been used traditionally as diuretic and for the treatment of rheumatism, diabetes, hypertension and inflammation. Fraction Cf2B from the crude chloroform extract of *O. stamineus* was found to be most active in inhibiting carrageenan-induced hind paw oedema in mice thus indicating the most active anti-inflammatory fraction of the extract to be fraction Cf2B [1]. Two compounds have been isolated and identified from this active fraction, namely 5,3'-dihydroxy-6,7,4'-trimethoxyflavone (**1**) and 5,6,7,3',4'-pentamethoxyflavone (**2**) . Compounds (**1**) and (**2**) are flavones commonly known as eupatorin (EU) and sinensetin (SI) respectively. Both compounds were identified and their structures elucidated through spectroscopic methods [2]. A simple, rapid and accurate high-performance liquid chromatographic (HPLC) method was developed for the analysis of these two flavones in the fraction Cf2B. The HPLC system consisted of Linear UVIS 204 model detector set at 340nm, Hitachi D-2500 model integrator, Gilson model 302 pump and RP-18, Purospher®STAR 250x4.6mm (5µm) column with ACN:H_2O (40:60) as the mobile phase. In the quantitative determination, the concentration of EU and SI was found to be 0.0505 mg/ml and 0.0286 mg/ml respectively in 1 mg/ml of Cf2B active fraction. The method used is precise with relative standard deviation for these two constituents ranging between 1.27-4.52% (intraday) and 2.17-4.52% (interday).

P51:

SYNTHESIS, CHARACTERIZATION, MOLECULAR MODELLING STUDIES OF A NOVEL LIQUID CRYSTAL FOR USE IN LASER- ADDRESSED DISPLAYS

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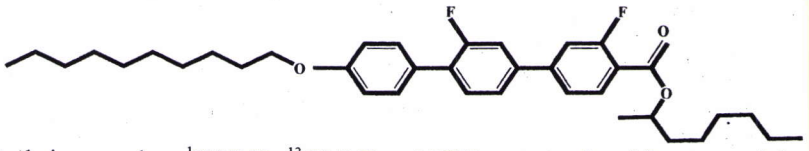
R-(+)- and S-(-)-2-octyl-[4"-decyloxy-3,3'-difluoro]-4-terphenylate (4-DDOT; see figure 1) were synthesized and characterized completely for possible use in laser- addressed displays. The pertinent structural features in this compound are the 3,3' positions of the lateral Fluorines in the ring and the respective donor- acceptor effect of the alkoxy terminal functionalities to extend aromatic conjugation. A not so large Fluorine separation favors the formation of a Smectic A phase, the phase, which is desirable for the aforementioned type of displays.



Spectroscopic techniques such as ^{1}H NMR, ^{13}C NMR and FTIR were employed for structural determination. DSC (for determination of transition temperatures), OPM and X-ray (for mesophase identification) measurements were also done. These compounds were also subjected for polarimetric measurements. Cambridge and ACD lab Software molecular modeling programs were employed for structural determination and theoretical comparison.

Figure 1. Chemical structure of 4-ddot.

P52:

PREPARATION AND CHARACTERIZATION OF POLYMER CLAY NANOCOMPOSITES

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Urea-formaldehyde clay composites were synthesized by in-situ polymerization of urea-formaldehyde containing dispersed bentonite under different conditions. Dispersion of the layered silicate within the urea-formaldehyde matrix was verified by using x-ray diffraction technique. Layer spacing was observed more than 28Å in some samples. Examination of these materials by TEM showed that formation of the intercalated and partial exfoliated composites at low clay contents.

P53:

HARD TISSUE PROSTHESIS FROM NATURAL ORIGIN: A REVIEW ON CORAL AND HYDROXYAPATITE

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Development in bone reconstruction has created new problem due to the high operations cost, limited supply of fresh graft and risk of disease transfer. These problems increase the interest to look for suitable materials that can serve as a synthetic bone graft. A synthetic bone substitute should be able to tolerate with human body without causing any adverse reaction and have appropriate mechanical properties. Natural sea coral and hydroxyapatite are well known material use to repair bone defect due to their excellent biological and physiochemical properties which is comparable to human bone. Hydroxyapatite derived from certain coral species through replamineform process has controlled porosity with interconnected pores. Porous structure gives better integration between the host tissue and the implant. This review paper focuses on the works that have been carried out on natural sea coral and hydroxyapatite as a bone substitute.

P54:

SYNTHESIS OF SILICA NANOSPHERE VIA SOL-GEL PROCESS

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Silica nanosphere powder were chemically synthesized by sol-gel technique using tetraalkoxysilanes (TEOS) as a precursor. The powder physical properties were studied by using scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), BET and packing density. In this study, we found that ammonium hydroxide (NH_4OH) volume, mixing mode and mixing time affect the morphology of silica nanosphere powder. The last finding in this work will be reported.

Formation of silica nanotubes using citric acid as structure stabilizer via sol-gel process

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Abstract

Silica nanotubes with pore diameters varying from 2.0 – 2.8 nm have been prepared by sol-gel process in the presence of citric acid in basic condition. Based on computer modeling and experimental work, it is suggested that the formation of nanotube is due to the stabilization effect of ammonium citrate inside the tube structure. The nanotubes were formed after washing with water and calcining at ~ 600 °C. The samples were characterized by TGA, SEM, TEM and porosimeter. The results of the analysis revealed the important role played by citric acid in the tube formation. The results indicated that the surface area of materials increases with increase in the amount of citric acid up to 11%. The nanotubes formed are of different range of sizes with outside diameter 200 – 300 nm, inside diameter 70 – 100 nm and > 300 nm in length.

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Formation of silica nanocubes using tartaric as structure modifier via sol-gel process

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Abstract

Silica nanocubes with pore diameters varying from 2.0 – 2.8 nm have been prepared by sol-gel process in the presence of tartaric basic condition. It is suggested that the formation of nanocubes is due to the structure modifier effect of ammonium tartarate. The nanocubes were formed after washing with water and calcining at ~ 600 °C. The samples were characterized by TGA, SEM, TEM and porosimeter. The results of the analysis revealed the important role played by tartaric acid in the cube formation. The nanocubes formed are in a wide range of sizes depending on the amount of tartaric acid added into the starting mixture after prehydrolysis process.

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Selective Removal of Heavy Metal Ions by Thiacrown Ethers Immobilized Sol-gel and SPE Column

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Abstract

The thiacrown ethers 1,4,7,10-tetrathiacyclododecane (12S4), 1,4,7,10,13-pentathiacyclopentadecane (15S5) and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) were immobilized into sol gel matrix and commercial available SPE column. The metal ions extraction was carried out with two approaches (i) batch method using sol-gel matrix and (ii) off-line preconcentraction using SPE column. Characterization of sol-gel immobilized thiacrown ether was conducted by FTIR, EDX and TGA analysis. The metal ions extraction profiles were investigated by optimizing the key parameters such as pH, contact time/flow rate and legand concentraction. In competitive experiment in with the aqueous solution contains mixture of 11 metal ions ((Mg^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}, V^{4+} and Hg^{2+}), all the immobilized thiacrown ether exhibited high selectivity toward Ag+ despite some interference from Hg^{+} and Cu^{+}. However, the extraction of other studied metal ions were negligible. In addition, the reusability of the solid supports is possible as the degree of extraction remains consistent after 3 repeated cycles. These optimized procedures were successfully applied to the separation and determination of Ag^{+} from the natural water samples.

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