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# MESOPOROUS ZEOLITES AS CATALYSTS FOR THE PRODUCTION OF SPECIALTY AND FINE CHEMICALS

## (ZEOLIT MESOLIANG SEBAGAI MANGKIN BAGI PENGHASILAN BAHAN KIMIA KHUSUS DAN HALUS)

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# ABSTRACT

*(Keywords: mesoporous silica, rice husk, catalyst, nanomaterial, fine chemicals)*

The mesoporous molecular sieves MCM-41 and MCM-48 have been hydrothermally synthesized from rice husk ash as an active source of silica in the presence of organic surfactant as structure-directing agent. The surfactant-templated approach has created periodic porosity as well as catalytic functions (acid-base, redox and host for catalytically active sites) in the molecular sieve catalysts. A deliberate design of pores is possible in the pore size range of 2 to 10 nm with controlled chemical compositions and structures. Mesoporous oxides in which metals (Ti, Zr, V, Nb, Mo, W, Mn, Fe, Co, Sn, Li, Cs, La) partially substitute for silicon in the porous network of MCM-41 and MCM-48 were prepared via two routes: (i) the post synthesis thermal treatment of silica mesophases by the "molecularly designed dispersion" technique and, (ii) the *in situ* synthesis of framework incorporated metal ions. The resulting materials were characterized with various techniques: XRD, FTIR, DRUV-Vis, ESR, $^{14}$Li, $^{13}$C, $^{27}$Al and $^{29}$Si MAS NMR spectroscopy, FESEM, TEM, AAS, TG-DTA, TPDRO, surface acidity using probe molecules, BET and $N_2$ adsorption isotherms. Highly-ordered mesoporous materials with all of the appropriate catalytic requirements including large surface areas (>1000 $m^2g^{-1}$) and pore volumes (0.9-2.0 $cm^3g^{-1}$) readily accessible to large molecules have therefore been produced. The mesostructured silica materials could form spherical or fibrous rodlike morphologies depending on reaction conditions. The catalysts have been optimized for stability, activity, and selectivity in batch processes. The mesoporous materials possessed high thermal and hydrothermal stability similar to that of microporous zeolite-based catalysts and the atomic ordering in the pore walls remained intact during various stages of the preparation. The metal oxide modified mesoporous catalysts displayed extraordinarily high activity and selectivity in liquid phase oxidation of aromatic alcohol using $H_2O_2$ as oxidant under mild conditions with or without the presence of solvent. Furthermore, the metal leaching by solvent was observed to be negligible suggesting that the catalyst could be recycled. Mesoporous materials MCM-41 and MCM-48 with aluminium in the framework were selective acid catalysts in the Friedel-Crafts acylation of aromatic compounds while metal organic complexes encapsulated in the mesopores effectively catalyzed the one step oxidation of benzene to phenol. Also bifunctional catalysts with highly dispersed acidic and redox active sites were achieved when acidic mesoporous catalysts were incorporated with metal oxide particles such as NbO*x*, TiO*x* and LnO*x* with different loading through ion exchange and impregnation method. The synergistic effects of the two functions have enabled highly selective aldol, nitroaldol and Claisen-Schmidt condensation of aldehyde and epoxidation of alkene, that have never been possible using traditional catalysts employing either Lewis or Brönsted acidity alone. On the other hand, silylated mesoporous silica materials were hydrophobic, and performed well as matrices for immobilization of conducting polymer and polymer electrolyte. Polymer modifications on MCM-41 and MCM-48 by *in situ* synthesis, miniemulsion polymerization, melt and solution intercalation methods yielded polymeric nanocomposites with enhanced thermal stability as well as catalytic, optical, conducting or dielectric properties. In addition, zeolite/mesoporous molecular sieve composites were also synthesized as an alternative approach to increasing the acidity of MCM-41 and MCM-48 catalysts for high temperature acid catalysis of reactions such as cracking and hydrocracking.

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# ABSTRAK

*(Kata Kunci: silika mesoliang, sekam padi, mangkin, bahan nano, bahan kimia halus)*

Penapis molekul mesoliang MCM-41 dan MCM-48 telah disintesis secara hidroterma daripada abu sekam padi sebagai sumber silika yang aktif dengan mengggunakan surfaktan organik sebagai agen pengarah struktur. Kaedah penemplatan surfaktan telah menghasilkan keliangan bertertib dan juga fungsi-fungsi pemangkinan (asid-bes, redoks dan perumah bagi tapak aktif pemangkinan) pada mangkin penapis molekul. Reka bentuk liang boleh direncanakan sehingga dapat menghasilkan saiz liang dalam julat 2 hingga 10 nm dengan komposisi kimia dan struktur yang terkawal. Oksida mesoliang yang logam di dalamnya (Ti, Zr, V, Nb, Mo, W, Mn, Fe, Co, Sn, Li, Cs, La) menjadi pengganti sebahagian silikon dalam rangkaian mesoliang MCM-41 dan MCM-48 telah disediakan melalui dua laluan: (i) pengolahan haba pasca-sintesis terhadap silika fasa meso melalui teknik "penyebaran molekul terancang" dan, (ii) sintesis *in situ* dengan penggabungan ion logam bingkaian. Bahan-bahan yang terhasil telah dicirikan melalui pelbagai teknik: XRD, FTIR, DRUV-Vis, ESR, spektroskopi $^{14}$Li, $^{13}$C, $^{27}$Al dan $^{29}$Si MAS NMR, FESEM, TEM, AAS, TG-DTA, TPDRO, keasidan permukaan menggunakan molekul prob, BET dan isoterma penjerapan $N_2$. Bahan mesoliang bertertib julat jauh dengan keperluan pemangkinan yang sesuai termasuk luas permukaan (>1000 $m^2g^{-1}$) dan isipadu liang (0.9-2.0 $cm^3g^{-1}$) yang tinggi selain mudah didatangi molekul-molekul besar telah dihasilkan. Bahan silika berstruktur meso boleh membentuk morfologi sfera atau rod berserabut bergantung pada keadaan tindak balas. Kestabilan, aktiviti dan sifat memilih mangkin tersebut telah dioptimumkan dalam proses berkelompok. Bahan mesoliang tersebut mempunyai kestabilan terma dan hidroterma yang tinggi serupa dengan mangkin mikroliang berasaskan zeolit dan susunan atom pada dinding liangnya tidak terjejas semasa menjalani berbagai-bagai langkah penyediaan. Ubahsuaian mangkin mesoliang dengan oksida logam menghasilkan keaktifan dan kepilihan yang luar biasa baik bagi pengoksidaan alkohol aromatik dalam fasa cecair dengan adanya $H_2O_2$ sebagai pengoksid pada keadaan sederhana dengan berpelarut atau tanpa pelarut. Lagi pula, keterlarutresapan logam dalam pelarut adalah sangat kecil mencadangkan mangkin tersebut boleh digunakan semula. Bahan mesoliang MCM-41 and MCM-48 mengandungi aluminium bingkaian merupakan mangkin asid yang selektif terhadap pengasilan Friedel-Crafts sebatian aromatik sedangkan kompleks logam-organik dipegun dalam mesoliang memangkinkan secara efektif pengoksidaan benzena kepada fenol dalam satu langkah. Mangkin dwifungsi dengan tapak asid dan tapak aktif redoks yang tersebar luas turut dihasilkan apabila mangkin mesoliang berasid tersebut ditambahkan dengan zarah logam oksida seperti NbO*x*, TiO*x* and LnO*x* dengan muatan berbeza-beza secara kaedah penukaran ion dan pengisitepuan. Kesan sinergi kedua-dua fungsi tersebut menghasilkan mangkin berkepilihan tinggi terhadap tindak balas kondensasi aldol, nitroaldol dan Claisen-Schmidt serta pengepoksidaan alkena, yang belum pernah tercapai menggunakan mangkin tradisional yang semata-mata asid Lewis atau Brönsted sahaja. Sebaliknya, silika mesoliang tersililkan bersifat hidrofobik dan menunjukkan prestasi yang baik sebagai matriks bagi pemegunan polimer pengalir dan polimer elektrolit. Modifikasi MCM-41 and MCM-48 dengan polimer melalui kaedah sintesis *in situ*, pempolimeran miniemulsi, dan interkalasi leburan dan larutan telah menghasilkan nanokomposit polimer dengan pertambahan kestabilan terma, ciri-ciri pemangkinan, optik, pengalir atau penebat elektrik. Sebagai tambahan, komposit zeolit/penapis molekul mesoliang juga disintesis sebagai kaedah alternatif bagi meningkatkan keasidan mangkin MCM-41 dan MCM-48 dalam tindak balas pemangkinan berasid yang lazimnya beroperasi pada suhu tinggi seperti peretakan dan hidro-peretakan.

# PENYELIDIK UTAMA

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# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background and Problem Statement

Malaysia has been found as one of the major rice production country, whereby 425,080 hectares (3.21% of the total land in peninsular Malaysia) of the land have been used for paddy plantation [1]. Therefore, it generates abundance of waste namely rice husk, a thin but abrasive skin in nature covering the edible rice kernel. It has been reported that Malaysia produces a *ca.* 18 million tons of paddy in which about one fifth of it is the husk [2]. This means that the annual production of rice leaves behind about 3.6 million tons of husk as waste product, usually disposed by combustion (Figure 1.1). Unfortunately, the 20% of the rice husk ash (RHA) residues left after the combustion constitutes environmental problems due to severe air and water pollution problems. However, RHA can be considered as a potential feature of the rice husk, which the RHA residues can be employed as raw materials in a variety of applications (Figure 1.2). Previous research had shown that the rice husk ash containing 96-99% $SiO_2$ can exist either in amorphous phase or in crystalline phases such as, $\alpha$-cristobalite and tridymite [3-4]. In fact, the amorphous silica is the most active silica precursor in the synthesis of zeolites. Hence, the large amount of silica freely obtained from this source provides abundant and cheap alternatives of silica for many industrial uses.

Figure 1.1: Disposal of rice husk, an agriculture waste by uncontrolled burning in Malaysia poses a significant environmental problem.

Figure 1.2: White rice husk ash obtained from combustion of rice husk can be utilized as an active silica source for production of mesoporous catalysts

From the previous report, MCM-41 has been successfully synthesized by using the silica extracted from RHA [5]. However, no report has been found on the synthesis of MCM-48 directly from RHA, since the synthesis of MCM-48 mesoporous materials seems to be more challenging than the synthesis of MCM-41. By using rice husk ash as the silica source in the synthesis of MCM-48, the production costs can be reduced subsequently besides helping to overcome environmental pollution. Indeed, it should be noticed that RHA is considered slightly impure silica. The content of silica and all impurities in RHA vary depending on the variety, climate and geographic location [6]. Therefore, in order to transform the RHA to valuable mesoporous materials, modification and optimization of the synthesis condition were carried out.

The use of the currently available microporous and mesoporous oxides is limited by their attainable pore sizes, pore architectures, the uniformity of the structures and the extent to which catalytically active heteroatoms can be introduced [7-9]. In the case of zeolites, the small size of the pores is the main limitation to their use in fine chemical or pharmaceutical synthetic application as most substrate and product molecules are too large to enter or leave the pore system. Mesoporous materials on the other hand, have as a main disadvantage their noncrystallinity, resulting in lower thermal and mechanical stability and in broader pore size distributions, and, hence, lower substrate/product selectivities compared with those found for zeolites. Moreover, the lack of crystallinity means a high concentration of structural defects, i.e. the presence of high degree of surface silanol groups. For mesoporous aluminosilicates, an incomplete incorporation of aluminium into the framework and a less rigid lattice environment means that their acidity is considerably lower than for zeolites, which limits their use as acid catalyst in reactions with large substrate species.

Nanometer-sized catalytic species may be dispersed into the pores of a mesoporous host material in order to maximize the available surface area of that catalytic species and to prevent sintering at elevated temperatures. In this respect, zeolite crystallites, metal oxide species and even nanometer-sized metal particles may be introduced into a mesoporous host. Whilst mesoporous materials in themselves can be catalytically active materials, great potential lies in the possibility of their functionalization. One area of advancement for this field is the heterogenization of homogeneous catalysts. Mesoporous materials can provide the perfect supports for known homogeneous catalysts to facilitate this.

One of the major driving forces behind the development of mesoporous molecular sieves as catalysts is the necessity to develop better, cleaner manufacturing processes for the multitude of fine chemicals for daily life. The substitution of homogeneous Lewis acids with a solid acid is one of many challenges. Many of the catalysts traditionally used by industry are "dirty" as well as expensive. Aluminium chloride, $AlCl_3$, used in the production of aromatic ketones is a good example; the catalyst is not reusable, and creates environmentally harmful waste. More than three decades ago, zeolites were identified as possible alternatives [10]. Zeolites are solid acids rather than liquid, so they are more stable and they do not leach into the environment. They are also reusable, so the reactor needs charging far less often, reducing down-time on the production line.

The aluminium-containing mesoporous materials MCM-41 and MCM-48 have bulk compositions similar to those of the zeolites, that is silica framework containing aluminium in tetrahedral environments. This led to the hope that these materials would be equivalent in acidity to the zeolites, and would represent large pore strongly acidic catalysts. Previous attempts in this area were disappointing, as the materials only displayed acidity of moderate strength [10, 11].

Solid base catalysts are now able to replace homogeneous bases in many reactions that can be performed at higher temperatures or in the vapour phase. Characterization of base strength relies mainly on probe molecules combined with spectroscopies and catalytic test reactions. Recently, modification of MCM-41 with covalently bonded organic species, especially functional organosilanes, has attracted much attention in order to design hybrid materials with engineered properties for applications in catalysis and selective adsorption of organics. At the same time, the grafting of alkylsilane on MCM-

41 surface has provided an opportunity to obtain hydrophobic materials with tailored pore size and high surface area.

Among the goals of our research is to develop a general synthetic methodology by which well-defined metal oxide catalyst can be incorporated into the surface structures of support materials. Traditional approaches to supported metal catalysts to on metal oxide supports usually yield a variety of supported species with different activities, but more importantly with different selectivities with respect to oxidation chemistry. A general synthetic approach to the creation of well-defined supported metal catalysts in which all the sites were, by design, the same would represent a significant advance in the science of supported catalysts and would represent an important new approach to the efficient use and management of many valuable natural resources.

In heterogeneous catalysis the surface structure of the catalyst determines the catalytic properties. To satisfy the demands of activity and selectivity, a catalyst system needs to be prepared that catalyzes the desired reactions and eliminates all side reactions. This “designing” of a catalyst system requires a thorough control of the surface morphology. Molecular Designed Dispersion (MDD) of metal complexes on a highly porous support is a novel method to obtain high quality heterogeneous catalysts. The design of the catalyst system is aimed at decorating the surfaces of mesoporous silica support with a monolayer of metal oxides having the desired structures. An important feature is that the strategy allows metal nanoparticles to be well dispersed on a variety of oxides with few restrictions on their physical and chemical properties. Following this synthetic procedure, efficient nanostrucured catalysts for green chemistry processes, such as the production of aldehydes and ketones from the selective oxidation of primary, aliphatic and aromatic alcohols were developed.

In this research, nanostructured catalysts have been developed via modification of silica mesophases prepared from local rice husk ash with metal precursors by the molecular designed dispersion (MDD) method. The ability to create a uniform dispersion of nanoparticles is one advantage of the MDD method. The homogeneous dispersion of nanoparticles is achieved by first adsorbing or ion exchanging metal oxide precursors onto preformed silica mesophases. In a consecutive step, the adsorbed species is then locked in place, without aggregation, through careful calcination. at elevated temperatures. These nanomaterials showed thermal stability up to 700-800 $^{o}$C and possessed large specific surface areas and controllable, ordered pore structure of molecular dimensions (2 to 50 nm).

Applications using ordered mesoporous materials are undergoing intensive development and commercialization because of their applicability as catalysts in a broad range of industrial processes that are environmentally sensitive. High activity combined with shape selectivity under mild reaction conditions make these materials very promising in fine chemical processes allowing waste minimization, higher efficiency, and cheaper feedstocks. The great variety of frameworks combined with the presence in the mesopores of highly dispersed catalytic species, opens new frontiers in the set up of innovative applications of ordered mesoporous materials for eco-compatible organic syntheses. In particular, an emerging line is the use of mesoporous-microporous composite materials for hydrotreating or mild hydrocracking processes. The main obstacle towards viable application is the presence on the market of much cheaper amorphous alternatives, mainly based on silica gels.

To date there have been numerous approaches to the design of heterogeneous asymmetric catalysts, since Schwab and coworkers first demonstrated that Cu and Ni could be supported on chiral silica surfaces [12, 13] and that the resulting catalysts could give low enantioselection in the dehydration of butan-2-ol. Figure 1.3 shows three models of heterogeneous asymmetric catalysis, i.e. chirally modified solid surfaces, attaching chiral auxiliaries to reactant and intrinsically chiral solid or surface.

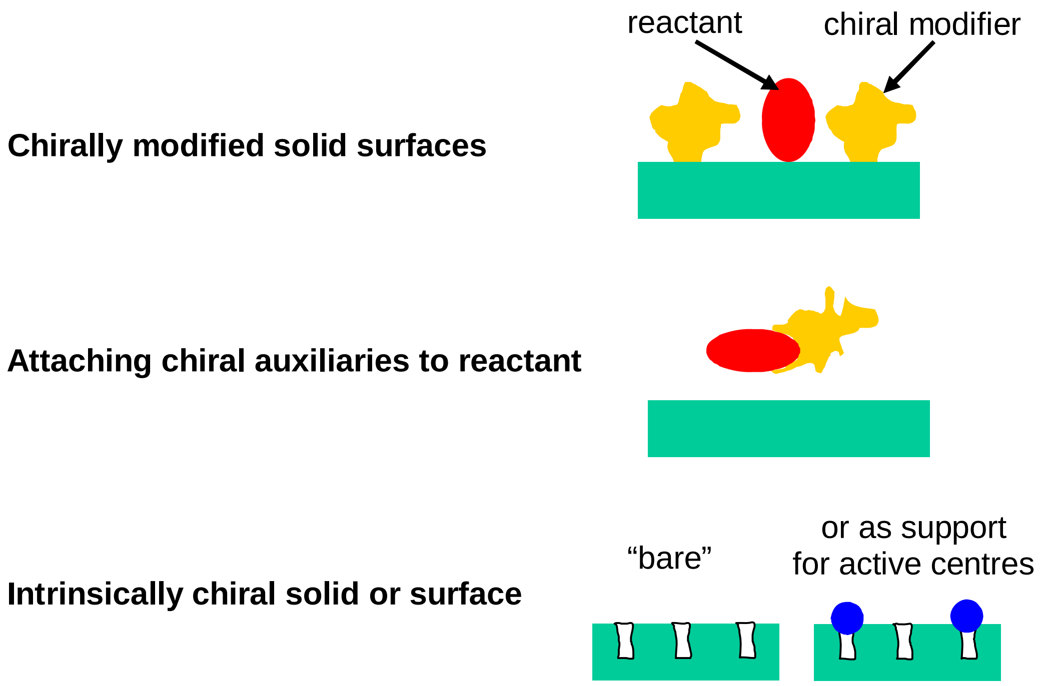

Figure 1.3: Models of heterogeneous asymmetric catalysis.

At present, attaching chiral auxiliaries to reactant is one of the most popular approaches to the design of highly efficient heterogeneous asymmetric catalysts. The strategy employed tends to depend on the reaction being catalyzed, but overall this method has the potential for designing generic heterogeneous asymmetric catalysts applicable to many reaction types.

The research strategy is based on the ideas that the chiral reactions could be induced by chiral amino acids and the use of heterogeneous micellar catalysis for synthetic purposes will overcome practical separation problems. In order to realize these ideas, chiral amino acid needs to be attached to the hydrophilic part of hydrolyzed octadecyltrichlorosilane (OTS). Amino acids such as L-glutamic acid, L-leucine and L-phenylalanine have been chosen because of their water-soluble properties; hence they can be easily removed by treatment with water. It is expected that the attachment of amino acid would result in a chiral solid catalyst with bimodal hydrophobic-hydrophilic character (see Figure 1.4). In addition, due to OTS has three chloro functional groups, one expects that the OTS has high tendency to polymerized.

One considers that a catalyst which possesses both hydrophobic and hydrophilic components exhibits amphiphilic character. The flexibility of the hydrophobic octadecyl groups therefore allows the formation of micellar aggregates in the system containing immiscible organic and aqueous phases. Schematic representation of heterogeneous micellar catalysis is depicted in Figure 1.5 in which the hydrophilic microdomains in micellar aggregates are expected to act as "chiral pool" for acid chiral reaction.

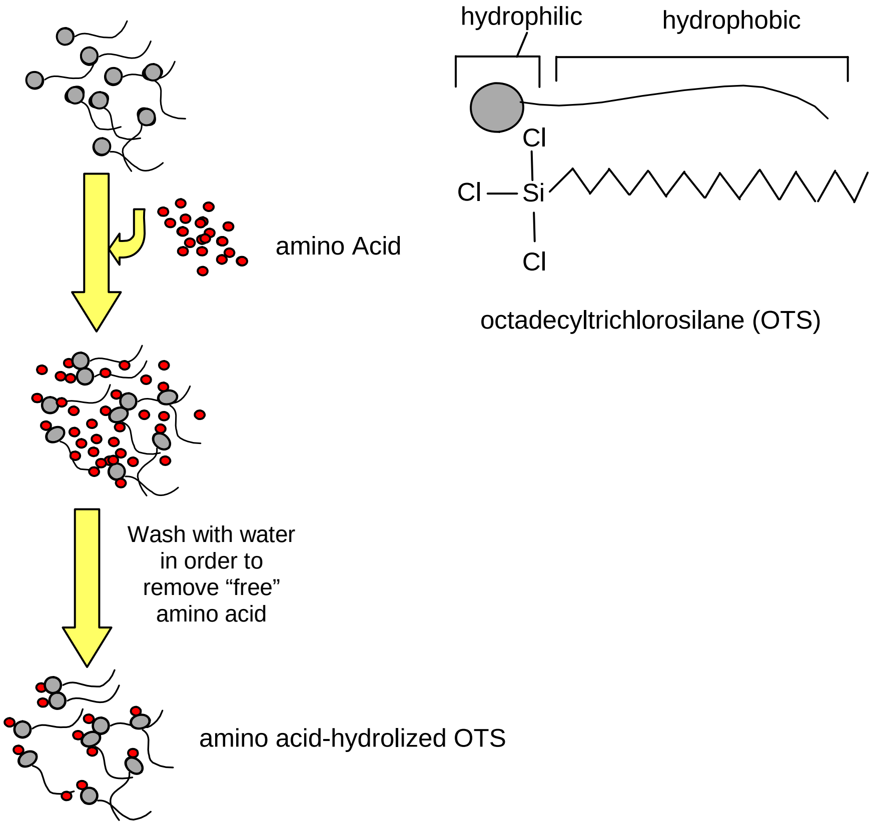

Figure 1.4: Attachment of chiral amino acid onto the hydrophilic part of hydrolyzed OTS.

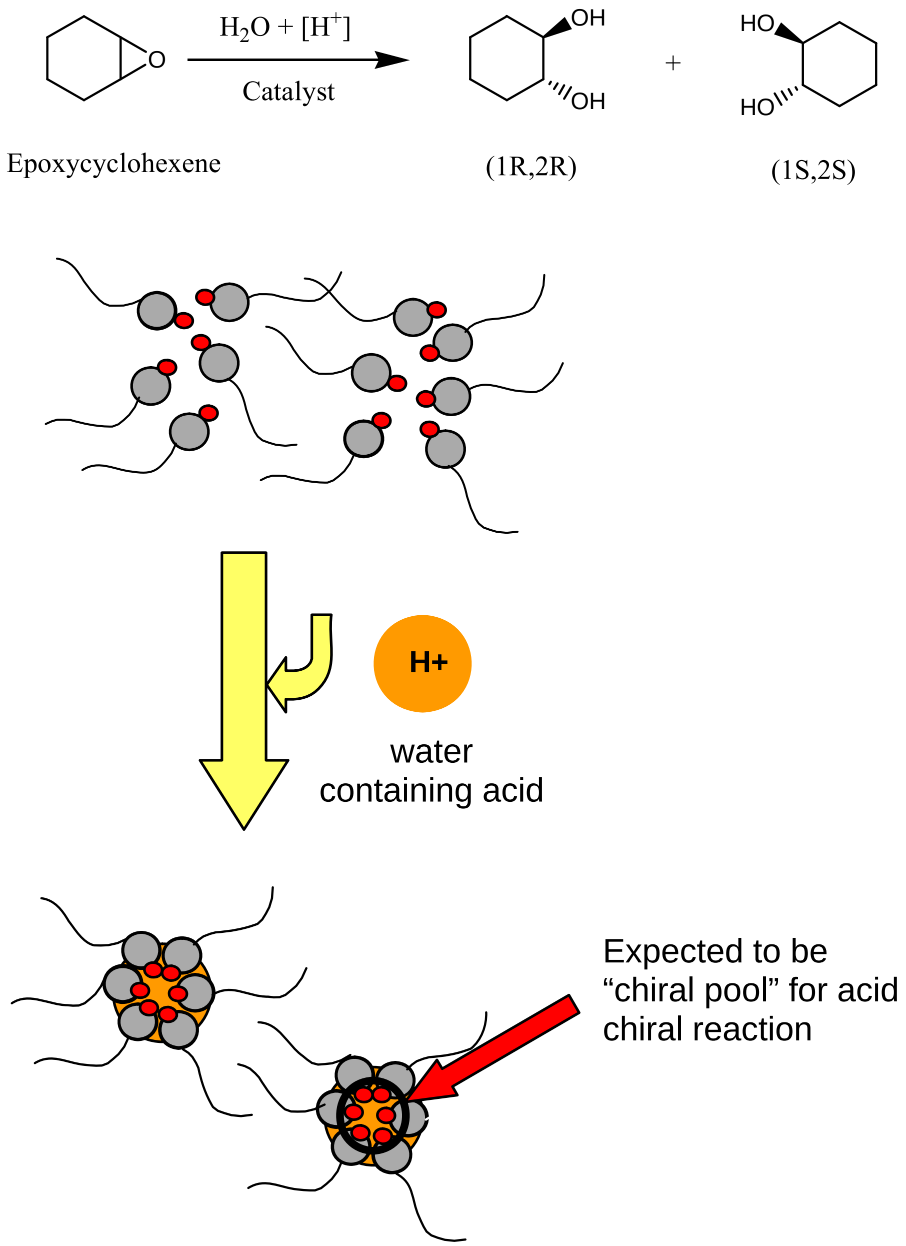

Figure 1.5: Amphiphilic chiral solid catalyst as heterogeneous micellar catalyst in enantioselective hydration of epoxycyclohexene.

Among the activities of this research is to develop a novel heterogeneous asymmetric catalyst by attachment of chiral amino acid onto the hydrophilic part of hydrolyzed octadecyltrichlorosilane (OTS). Namely, this research will lead to the synthesis of heterogeneous asymmetric catalyst. The new catalysts are expected to possess tunable activity and selectivity for enantioselective hydration of epoxyclohexene. Structural and mechanistic aspects as well as key to the catalytic performance were determined by physical and chemical characterization methods.

Other potential applications of ordered mesoporous materials are in chromatographic applications, separation of biological molecules, and drug delivery system, for which their uniform large pores can allow the development of new ways to products of high added value [14-17]. The field of sensors is also promising [18].

## 1.2 Research Objectives

According to the original research proposal the work has been organized around three tasks.

i. To promote the alternative applications of rice husk silica as value added primary products in the fine chemical industries.
ii. To establish a viable, low-cost route to conversion of rice husk ash into precursors for silica-based mesoporous materials.
iii. To synthesize mesoporous materials with chirality environment and chiral modifiers as the catalysts for asymmetric reactions.

## 1.3 Scope of Research

In this research, studies on the synthesis of all-silica, aluminosilicates, and metal containing mesoporous materials were conducted to identify ways of producing high surface area, thermally stable materials, with well defined mesopores and suitable distribution of catalytically active sites. These materials are mostly zeolites and ordered mesoporous materials, but also amorphous materials such as silica and polymer-silica nanocomposites are target materials. The driving force for such development is typically catalytic processes for which an advantageous use of such high surface area materials is envisaged. The research scope is to synthesize and test inorganic mesoporous catalysts to address the growing demand for improved catalysts for the processing of large and bulky substrates.

The main phases of this research program are as follows: Phase one involves the optimization of synthesis of mesoporous silica and zeolites from rice husk ash (RHA) by the surfactant templating method. Rice hush ash obtained from an open burning site was utilized as a silica source for preparing mesoporous molecular sieves MCM-41 and MCM-48 using combination of neutral and cationic surfactants as the structure directing agent. The work involves the elucidation of the synthetic principles by which mesoporous acid or oxidation catalysts may be constructed in which self-assembly of surfactant micelles play a role in structuring the silica matrix. This work has resulted in the inclusion of metal ions of various chemical compositions (Al, Ti, Sn, Mn, Co, Mo, V, Li, Cs, La, Fe, W, Zr) into the walls of MCM-41 and MCM-48 materials during hydrothermal synthesis and via post-synthesis isomorphous substitution of the framework silicon in aqueous media. Alternatively, reactive components such as organosilanes can be used to incorporate organo-species within the wall structure of MCM-41 and MCM-48 by wet impregnation, ion exchange, grafting and solid-state mixing.

The catalytic activities of the mesoporous materials were studied within the context of solid acid or solid base and oxidation reactions. Additionally, we have been working to identify system features that would enable selective catalysis of aromatic compounds (e.g. benzene) to more useful reactive intermediates for chemical synthesis (e.g. phenol, benzaldehyde). For the examples the Friedel-Crafts alkylation and acylation, epoxidation, cracking and hydrocracking reaction of palm oil to gasoline, Knoevenagel condensation, aldol condensation and Claisen-Schmidt condensation were readily achieved at mild conditions..

Mesoporous MCM-41 and MCM-48 were synthesized from rice husk ash followed by incorporation of polymers to produce nanocomposites. The various compositions of mesoporous materials with polymers were achieved by three methods, namely intercalation, *in situ* synthesis methods and melt inclusion method. Lastly, mesoporous materials were synthesized from rice husk ash followed by organic functionalization as adsorbent for pesticides and dyes.

Phase two involves detailed characterization of the both the porous matrix and catalyst active sites. Characterization of the surface nature, adsorption and catalytic properties is aimed at understanding the unique properties of mesoporous materials and composites in order to discover their applicability in various advanced materials such as storage devices, sensors, new catalysts for synthesis of fine chemicals, and adsorbency of pollutants. Characterization techniques employed are powder X-ray diffraction, FTIR, ESR, Diffuse Reflectance UV spectroscopy, Solid-State MAS NMR and nitrogen adsorption.

The final phase of the project involves establishing structure-property relationship between a designed catalyst and its properties (activity, selectivity, regenerability, life-time). Subsequently, catalytic testing was conducted to evaluate the materials in Friedel-Crafts reactions and in the field of selective oxidation reactions reported in Chapter 4.

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# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Zeolites and Porous Materials

Porous materials have been intensively studied with regard to technical applications as catalysts and catalyst supports. According to the IUPAC definition, porous materials are divided into three classes; microporous (pore size < 2nm), mesoporous (2–50nm), and macroporous (>50nm) materials [1]. Materials from the former two classes have found great utility as catalyst and separations media for industrial applications. The openness of their nanostructures allows molecules access to the relatively large internal surfaces and cavities enhance their catalytic and adsorptive activity.

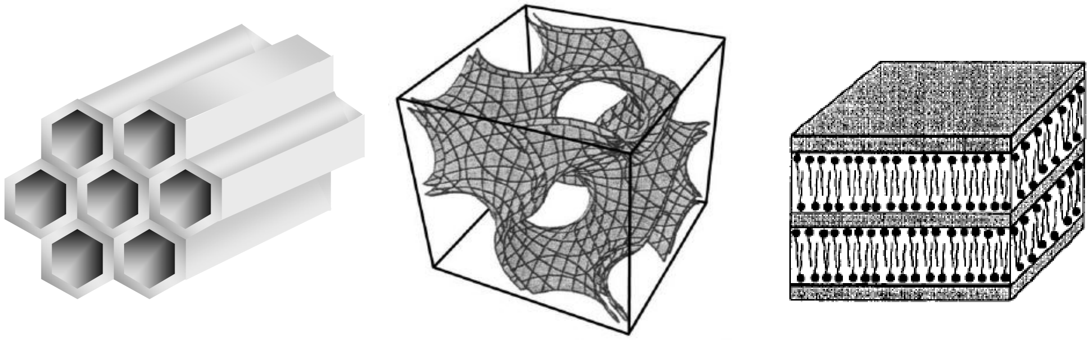
Zeolites are well-known members of the microporous class materials since they occupy uniqueness of adsorption ability, high ion exchange capacity and shape selectivity in catalysis. Zeolites are materials composed of porous crystalline aluminosilicates in which their micropores are ordered and regular arrays of uniformly-sized channels [2]. Since the dimensions of these pores are such as to accept for adsorption molecules of certain dimensions while rejecting those of larger dimensions, these materials are known as ‘molecular sieves’ and are utilized in a variety of ways to take advantage of these properties. Syntheses and modifications of zeolites as acids, base and redox catalysts have attracted strong attention in the development of environmentally benign processes for instance by substitution of liquid acid, base or redox reagent by solid catalysts.

However, the applications of zeolites in catalysis are limited due to the mass transfer problem when reactants with size above the dimensions of the pores have to be processed, especially in the case of synthesis of fine chemicals [3]. This problem was the starting point for developing molecular sieves with pore size within the mesoporous range. Despite these efforts, mesoporous molecular sieves with regular, well-defined and ordered pore channel systems have remained elusive until the early 1990s. It was finally in 1992, researchers from Mobil (now known as ExxonMobil) gave the first full description on synthesis and characterization of molecular sieves with mesoporous channels ordered in a particular way and having a unique pore size [4, 5]

## 2.2 Mesoporous Molecular Sieves

M41S, the new family of mesoporous molecular sieves discovered by the Mobil researchers consisted of several unique members having different mesophases. They are (i) MCM-41 which has a hexagonal arrangement of unidimensional pore channels; (ii) MCM-48 which has a three dimensional cubic pore structure; and (iii) MCM-50 which is lamellar structure in the non-calcined form [6]. Figure 2.1 illustrates the M41S member's different mesophases. These materials were first synthesized hydrothermally in the presence of alkyltrimethylammonium surfactant cations having an alkyl side chain greater than six carbon atom.

Among these mesoporous molecular sieves, MCM-41 and MCM-48 are the most important for potential application in catalysis since the mesoporous structure of the lamellar phase MCM-50 collapses upon calcination. The most striking fact about the MCM-41 and MCM-48 is that, although composed of amorphous silica wall, they possess long range ordered framework with uniform mesopores. These materials also possess large surface area, which can be up to more than 1000 $m^2g^{-1}$. Moreover, the pore diameter of these materials can be well controlled within mesoporous range between 1.5 to 20 nm by adjusting the synthesis conditions and/or by employing surfactants with different chain lengths in their preparation [7-11].



**(a)** **(b)** **(c)**

Figure 2.1 Members of M41S family with different mesophases: (a) MCM-41, hexagonal; (b) MCM-48, cubic; and (c) uncalcined MCM-50, lamellar.

Nowadays, members of the M41S can be synthesized following a wide variety of preparation procedures. However, the syntheses of these mesoporous molecular sieves always involve the presence of a precursor of silica and a surfactant as a template in a (mainly) aqueous medium [12]. Most commonly used surfactant for the syntheses is cetyltrimethylammonium halide. The syntheses are mostly prepared hydrothermally in alkaline condition under autogeneous pressure.

Surfactant or surface active agent consisted of two parts within the same molecule, namely hydrophilic head group and long hydrophobic tail group. The surfactant functions as structure directing agent during the polymerization of the silica. When silica precursor is introduced in the reaction medium, mesostructures are formed by a cooperative self assembly of surfactant/ silicate ion pairs that arrange themselves in various ordered arrays [13].

The surfactant to silica (Sur/Si) molar ratio is the key factor in obtaining the different mesophases found in the M41S family [16], although other parameters such as pH, synthesis temperature and crystallization time may have an effect as well [8, 14]. As the Sur/Si molar ratio was varied, the product formed could be grouped into three main categories as shown in Table 2.1.

Table 2.1: Effect of Sur/Si molar ratio on the mesophases obtained.

| **Category** | **Mesophase** | **Parameter (Sur/Si molar ratio)** |
|---|---|---|
| MCM-41 | Hexagonal | <1 |
| MCM-48 | Cubic | 1-1.5 |
| MCM-50 | Lamellar | 1.2-2 |

The synthesis mechanism was first described by Beck et al. along with their first report on the synthesis of M41S family [5]. In the synthesis, they found that the resultant mesostructures occur in different morphologies closely analogues to the lyotropic liquid crystal phases seen in the pure amphophilic lipid or surfactant/water systems. Therefore, they proposed a liquid crystal templating (LCT) mechanism that suggested two main pathways; in which either (i) the liquid crystal phase is intact before the silicate species are added, or (ii) the addition of the silicate results in the ordering of the subsequent silicate-encased surfactant micelles.

The LCT mechanism was further generalized by Stucky and co-workers based on the specific type of electrostatic interaction between a given inorganic precursor, I and surfactant head group, S [15]. Based on the nomenclature of the original LCT mechanism, which involved the cationic quaternary ammonium surfactant and the anionic silicate species, they could be categorized as the $S^+I^-$ pathway. By extension, other charge-interaction pathways are $S^-I^+$, $S^+X^-I^+$ ($X^-$ is counter anion), and $S^-M^+I^-$ ($M^+$ is a metal cation).

Usually, MCM-48 mesoporous materials can be synthesized by using various types of commercial available silica sources such as fume silica Cab-O-Sil [54], TEOS [16], colloidal silica (Ludox) [17], and many more. In this study, rice husk ash (RHA) obtained from open burning site will be employed directly as a cheaper alternative silica source for preparing the Si-MCM-48 mesophase since there are no reports on it until this moment. Si-MCM-48 will be synthesized using mixed cationic-neutral templating route which was proposed by Ryoo R. *et al.* [17]. Modification of the gel compositions proposed by Ryoo *et al.* should be carried out since the nature of the RHA is totally different from the common commercial available silica sources. Moreover, untreated RHA consists of a variety of impurities [18], which will greatly affect formation of mesophase. Therefore, optimization experiments should be carried out intensively in order to obtain pure phase and high quality of MCM-48 materials in optimizes condition. The optimization experiments will focus on the pH value, Na2O/SiO2, Sur/SiO 2 and H2O/SiO2 of the initial gel compositions. The resulting mesoporous materials will be structurally characterized by using powder X-ray diffraction technique.

## 2.3 Introduction to Catalyst

Catalyst is defined as a substance that increases the rate of approach to equilibrium of a chemical reaction without being substantially consumed [19]. Normally, a catalyst offers an alternative path for a reaction, which is energetically more favourable. The activation energy of the catalyst added reaction is significantly smaller than that of the similar reaction but without catalyst; hence, the rate of the former is much higher. The action of a catalyst in acceleration of such chemical reaction is called catalysis.

Catalysts accelerate reactions and thus enable industrially important reactions to be carried out efficiently under practically attainable conditions. Much of the food we eat and the medicines we take, many of the fabrics and building materials that keep us warm and almost all the fuels that transport us by road, sea or air are produced with the aid of catalysts [200]. Nowadays, the chemical industry is largely based upon catalysis. In 2001, global top 50 chemical sales exceeded USD 404.4 billion. Roughly 85-90% of these chemicals were produced throughout the world in chemical manufacturing processes that involved catalysis [21]. In the same year, the world merchant market for catalysts (i.e., excluding catalysts manufactured and consumed internally by industrial companies) was worth about USD 10 billion [22].

Catalysts are generally divided into two basic types, heterogeneous and homogeneous, depending on their state relative to the reaction medium [23]. Heterogeneous catalysts are present in different phase to the reaction medium. In most cases the catalyst is a solid with the reactants being either in the gas or liquid phase. On the other hand, homogeneous catalysts are present in the same phase (the gas phase or most often the liquid phase) as the reactants. The most widely used homogeneous catalysts are acids (e.g. sulfuric acid), bases (e.g. sodium hydroxide) and (organo)metallic complexes. Overview comparisons between these two types of catalysts are summarized in Table 1.1.

Table 2.2: Comparison of heterogeneous and homogeneous catalysts [23].

| Heterogeneous | Homogeneous |
|---|---|
| Usually distinct solid phase | Same phase as reaction medium |
| Readily separated | Often difficult to separate |
| Readily regenerated and recycled | Expensive/difficult to recycle |
| Rates not usually as fast as homogeneous | Often very high rates |
| May be diffusion limited | Not diffusion controlled |
| Quite sensitive to poisons | Usually robust to poisons |
| Long service life | Short service life |
| Poor mechanistic understanding | Often mechanism well understood |

Majority of the fine, speciality, and pharmaceutical chemicals manufacturing processes rely on homogeneous catalysts, with solid heterogeneous catalysts used in little beyond hydrogenation processes [24]. Many of these homogeneous catalysis processes generate huge amount of inorganic waste and toxic by-products. Since the early 1990s, the issues concerning the environmental impact of the hazardous waste and by-products from chemicals manufacturing processes have alarmed the public and environmentalists. Public concern is a potent influence; industry sectors are now looking towards innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products. In this respect, there is no doubt that heterogeneous catalysts with their advantages such as ready separability, recyclable, reduction of waste can play a key role in replacing the conventional homogeneous catalysis route towards environmentally benign processes. Consequently, developing heterogeneous catalysts for various kinds of chemical reactions that are involved in the industrial processes become a new challenge to scientists and researchers.

The replacement of conventional stoichiometric oxidation and alkylation/acylation processes by environmental friendly catalytic processes is a widely accepted strategy in fine chemicals industry. However, a technological shift in this direction is hindered by the limited availability of efficient, heterogeneous catalysts which can utilize the clean oxidants molecular oxygen, $H_2O_2$ and alkyl peroxides and the too narrow application range of available heterogeneous catalysts. The use mesoporous molecular sieves as catalysts for the synthesis of intermediates and fine chemicals are a growing area of research in heterogeneous catalysis. Mesoporous materials such as MCM-41 are similar to zeolites in that they are both made of silica and both become catalytically active when metal is incorporated into the silica framework. In MCM-41, the dimension of the pores vary from 20 Å to 100 Å in regular fashion, as opposed to the 2-13 Å pores of zeolites [5].

Mesoporous MCM-41 may become an industrial useful materials in the future because they are, when suitably modified with metals such as aluminium, nickel, molybdenum, vanadium, titanium, rhenium and zirconium, ideal as shape selective catalysts for reactions requiring electrophilic catalysis (alkylation, acylation, isomerization, dehydration), and they also promote oxidation [25]. The materials have not been utilized in any commercial processes.

The diversity of MCM-41 properties and wide range of metals which can be incorporated into the framework should enable one to to design catalysts with the desired pore and acid strength properties. It has been established that MCM-41 zeolites possess large number of Lewis acid sites and the acid strength of these materials is weaker than in zeolites [26]. It appears that the best possibilities for these materials in catalysis will be in processes needing moderate acidity and involving bulky size molecules.

Hence, processes that can take advantage of the properties of the MCM-41 is the catalytic transformations of oxygen-containing compounds and hydrocarbons with emphasis on dehydration and derivatization reactions of monohydroxy compounds, rearrangements of aliphatic and diaryl diols, ring opening and isomerization of epoxides and Friedel-Crafts alkylation reactions of hydrocarbons. These reactions are interesting and important from an industrial point of view since many different products (alkenes, dienes, ethers and carbonyl compouds) may be formed depending on the reaction conditions and the structure of the starting materials. In some cases the isolated products may be useful in pharmaceauticals and as fragrances in perfumes and detergents [27]. For example, some of the highly desired bulky aromatic compounds in pharmaceuticals which may be prepared by acylation of methoxynaphthalene via mesoporous zeolite catalysis are listed in Table 1. The intermediates could be used to prepare naproxen, a non-steroidal anti inflammation drug [28]

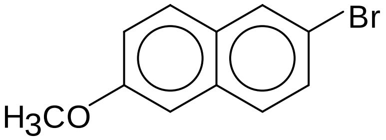
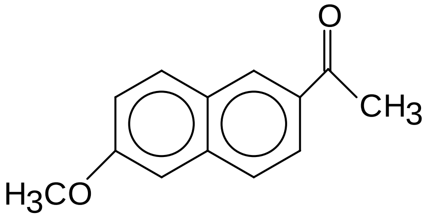
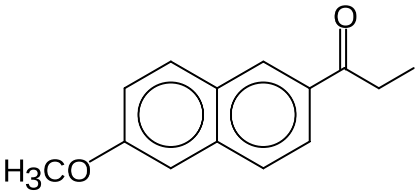
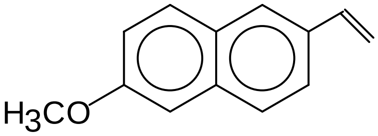
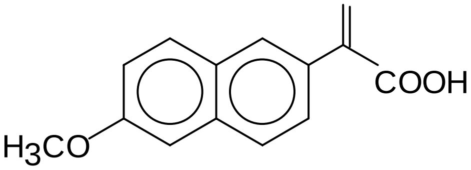
| Structure | Compound |
|---|---|
|  | 2-bromo-6-methoxynaphthalene |
|  | 2-acetyl-6-methoxynaphtahlene |
|  | 2-methoxy-6-propionylnaphthalene |
|  | 2-methoxy-6-vinylnaphthalene |
|  | A possible intermediate for the synthesis of naproxen, still not available |

Figure 2.2: Potential intermediates for the production of anti-inflammatory agents

## 2.4 Polymeric-Silicate Nanocomposite

Organic-inorganic hybrid composites are one of the most important classes of synthetic engineering materials. Organic and inorganic materials are absolutely different from each other in their properties. Glass and ceramics which are inorganic materials are hard and stony but they usually have low impact resistant, brittle and fragile, whereas organic material such as polymer or oligomer is resilient, flexible and elastic. Nevertheless, organic polymer normally has low heat resistant and tendency of natural degradation upon aging. In general, inorganic materials usually have higher thermal stability, better mechanical and optical properties whereas organic materials would give flexibility, elasticity and hydrophobicity properties [29, 30]. Organic- inorganic hybrid materials could then give desired combinations of the features of both organic and inorganic components. The preparation, characterization and application of organic-inorganic hybrid materials have grown into a rapid expanding area of research in material science.

Recently, there are numerous researches being done to find a simpler synthesis routes and the improvement in properties of nanocomposites. Generally, there are three methods of synthesis leading to the formation of nanocomposite 2 materials. These are solution intercalation method; melt inclusion method and *in-situ* polymerization [31].

Solution intercalation method is based on a solvent system in which the polymer is soluble and the mesoporous silicate materials are swellable [32]. The mesoporous silicate materials are first swollen in a solvent such as chloroform or toluene. When the polymer and mesoporous materials solutions are mixed, the polymer chains intercalate and displace the solvent within the channels system of mesoporous materials. Upon solvent removal, the intercalated structures remain, giving the polymeric nanocomposites. While on the contrary, by *in situ* polymerization method, the mesoporous silicate materials are swollen within the liquid monomer or a monomer solution so that the polymer formation can occur inside the channel system of mesoporous silicate materials [32, 33]. Polymerization can be initiated either by heat, radiation or by the diffusion of a suitable initiator. Among the three methods, *in situ* polymerization could be an effective way to solve the problem of non-homogeneity dispersion of inorganic particles. This problem is due to the aggregation of inorganic particles which favored on energy considerations.

The hydrophilic property possessed by silanol groups of mesoporous materials makes it unfavorable to interact with hydrophobic organic polymer. Organic modification of silicates allows precise control over the properties and pore sizes of mesoporous materials, while at the same time stabilizing the materials towards hydrolysis for a particular application. Vansant *et al.* [34] has studied the silylation effects on the porosity, adsorption characteristic and thermodynamic background of micro-, meso- and non-porous oxides by employing different type of silylation agents. Their works on hydrophobic MCM-48/VO*x* catalysts using alkylchlorosilanes as coupling agents for the molecular designed dispersion of $VO(acac)_2$ showed the products were stable up to 500 $^{o}C$ and exhibited significant improvement in structural stability. Moreover, the crystallinity of silylated materials does not decrease significantly after hydrothermal treatment in autoclave at 160 $^{o}C$.

Surface modifications on mesoporous materials can be done in which the organic groups are "terminally bonded" or grafted to the silica wall, so that the organic groups can protrude into the mesopores. There are two ways in which these 9 processes can be carried out either by post-synthesized grafting or one-step co-condensation. Post-synthesis grafting has been widely used to attach alkyl silanes onto mesoporous material surface. This process is done after calcination of mesoporous materials. Silanol groups of mesoporous material are essential for functionalization of the organic compounds thus it is important not to remove all of the silanol groups present in mesoporous materials. Silylation and esterification are the most common reaction used in surface modifications. Examples of these reactions are shown in Equation 1.1, 1.2 and 1.3, respectively. Normally, organochlorosilanes or organoalkoxysilanes can be used as precursors in silylation [29, 30, 33].

$$\equiv Si\text{-}OH + Cl\text{-}SiR_3 \xrightarrow[\text{base}]{25\,^{0}C} \equiv Si\text{-}OSiR_3 + HCl \qquad \text{(Eq. 1.1)}$$

$$\equiv Si\text{-}OH + R'O\text{-}SiR_3 \xrightarrow{100\,^{0}C} \equiv Si\text{-}OSiR_3 + HOR' \qquad \text{(Eq. 1.2)}$$

$$\equiv Si\text{-}OH + HN(SiR_3)_2 \xrightarrow{25\,^{0}C} \equiv Si\text{-}OSiR_3 + NH_3 \qquad \text{(Eq. 1.3)}$$

The mesoporous material and silylation reagent must be dried to remove moisture prior to silylation process to prevent self-condensation or hydrolysis of the precursor. Usually the structure of mesoporous is maintained after the silylation process [33]. The grafting rates are dependant on the reactivity of precursors, diffusion limitation, and steric factors. The pore size of the mesoporous materials can be adjusted by varying the quantity or chain length of silylating agents. Normally, 85% of mesoporous materials surface can be reacted with silylating agents especially by using trimethychlorosilane as precursors [29, 30].

The one-step co-condensation is based on the co-condensation of precursors of siloxane which act as building block to construct the framework. This process can be carried out using one or more organosiloxanes which contribute to the formation of silicate frameworks and the organic surface functional groups in templating environment. The advantages of using this method are high loading of organic functional groups, homogeneous surface coverage, shorter preparation time and wider range of reaction conditions.

The silylated product is expected to increase the compatibility of hydrophobic polymer and hydrophilic silica wall of mesoporous materials. Besides the effect of silylation, reaction condition of polymer incorporation also relies on the reaction temperature. Higher reaction temperature will promote the mobility of polymer chain and thus higher introduction of polymer chain into the mesopore channel [29]. Loosely attached polymer on the exterior surface can be washed away by using solvent. It is therefore important to choose an appropriate solvent with certain amount to minimize the salvation of intercalated chain from drawn out from the pores [30, 33].

## 2.5 Adsorption Properties of the Mesoporous Zeolites

In heterogeneous catalysis, the reacting species are held on the surface of the catalyst by a physical attraction called adsorption while the reaction takes place. Adsorption may be relatively weak (physical adsorption) or may have a strength comparable to the strengths of chemical bonds (chemisorption). In either case adsorption is generally not uniform across a solid surface. Adsorption, and therefore catalysis, occurs primarily at certain favorable locations called active sites. An active site is a part of the surface which is particularly good at adsorbing things and helping them to react.

For the design and preparation of catalysts for specific chemical reactions, it is very important to understand the adsorption processes and the interactions between the adsorbates and the adsorbents. Textual and surface properties are the two important aspects that determine the adsorption properties of the adsorbents. Mesoporous zeolites with high surface area are beneficial for adsorption because of the large number of adsorption sites on the adsorbent surfaces. Increasing pore size enables the adsorption of larger molecules and ions [35, 36, 37]. Narrow pore size distribution can provide good selectivity by sieve effects.

Adsorption effects in heterogeneous liquid phase reactions are seldom considered or recognized as important. Liquid phase adsorption is also poorly understood for typical reaction mixtures and hardly any models are available for its description. Catalyst deactivation or coking by the reactant (adsorbate) is a major problem in liquid phase catalysis reaction. The deactivation of catalyst maybe attributed to sintering of catalysts leading to collapse of the pore structures. Hence, study on adsorption properties of mesoporous zeolites should be carried out to understand further the interaction between adsorbate and the catalyst surface (adsorbent).

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# CHAPTER 3

# METHODOLOGY

## 3.1 Research Methodology

In this research, mesoporous zeolites were synthesized from rice husk ash. The rice husk ash was obtained from open burning of rice husk, local agriculture waste (Figure 3.1). The chemical composition of the rice husk ash is shown in Table 3.1.

The mesoporous zeolites were modified and applied into three major studies, namely catalysis, nanocomposite and adsorption (Figure 3.2). First, synthesis of mesoporous materials (MCM-41 and MCM-48) from rice husk ash followed by modifications for catalysis applications (Figure 3.3). Second, synthesis of mesoporous materials (MCM-41 and MCM-48) from rice husk ash followed by incorporation of polymer via intercalation or in situ synthesis methods to produce nanocomposite (Figure 3.4). Third, synthesis of mesoporous materials (MCM-41 and MCM-48) from rice husk ash followed by modification and tested as adsorbent for pesticides and dyes (Figure 3.5).

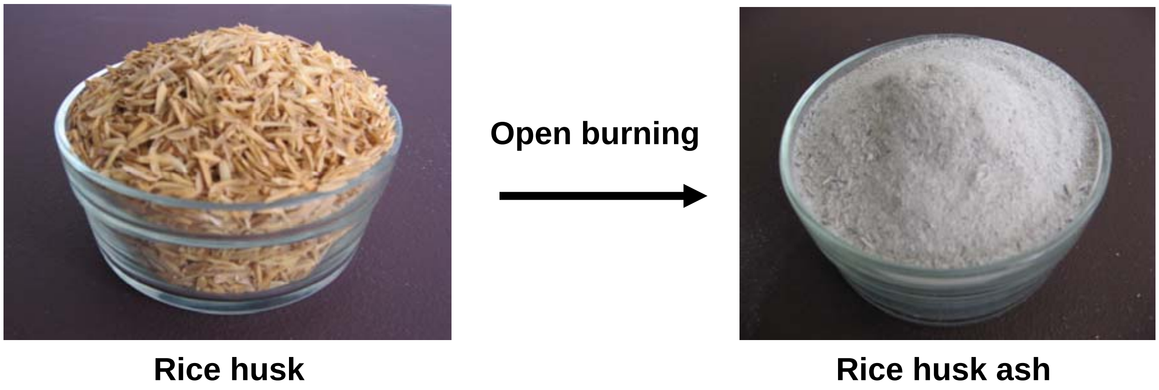

Figure 3.1: Rice husk ash was obtained from open burning.

Table 3.1 Chemical composition of rice husk ash.

| Compound | Percentage / % |
|---|---|
| $SiO_2$ | 98.12 |
| $Al_2O_3$ | 0.19 |
| $Fe_2O_3$ | 0.07 |
| CaO | 0.32 |
| MgO | 0.51 |
| $Na_2O$ | 0.01 |
| $K_2O$ | 1.64 |
| LOI | 2.14 |

*LOI = Loss of Ignition

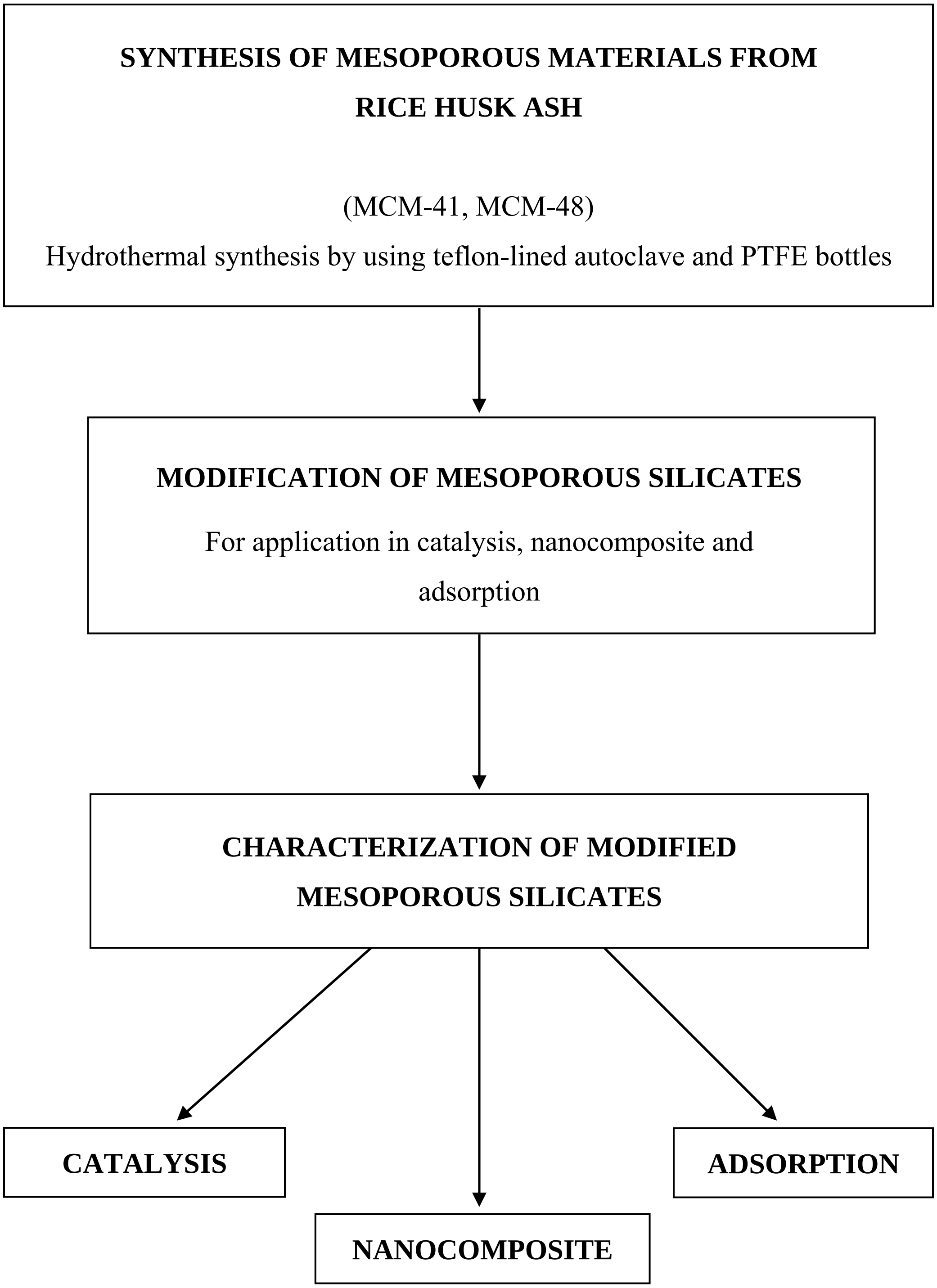

Figure 3.2: Overall research design of synthesis of mesoporous zeolites as catalysts for the production of specialty and fine chemicals.

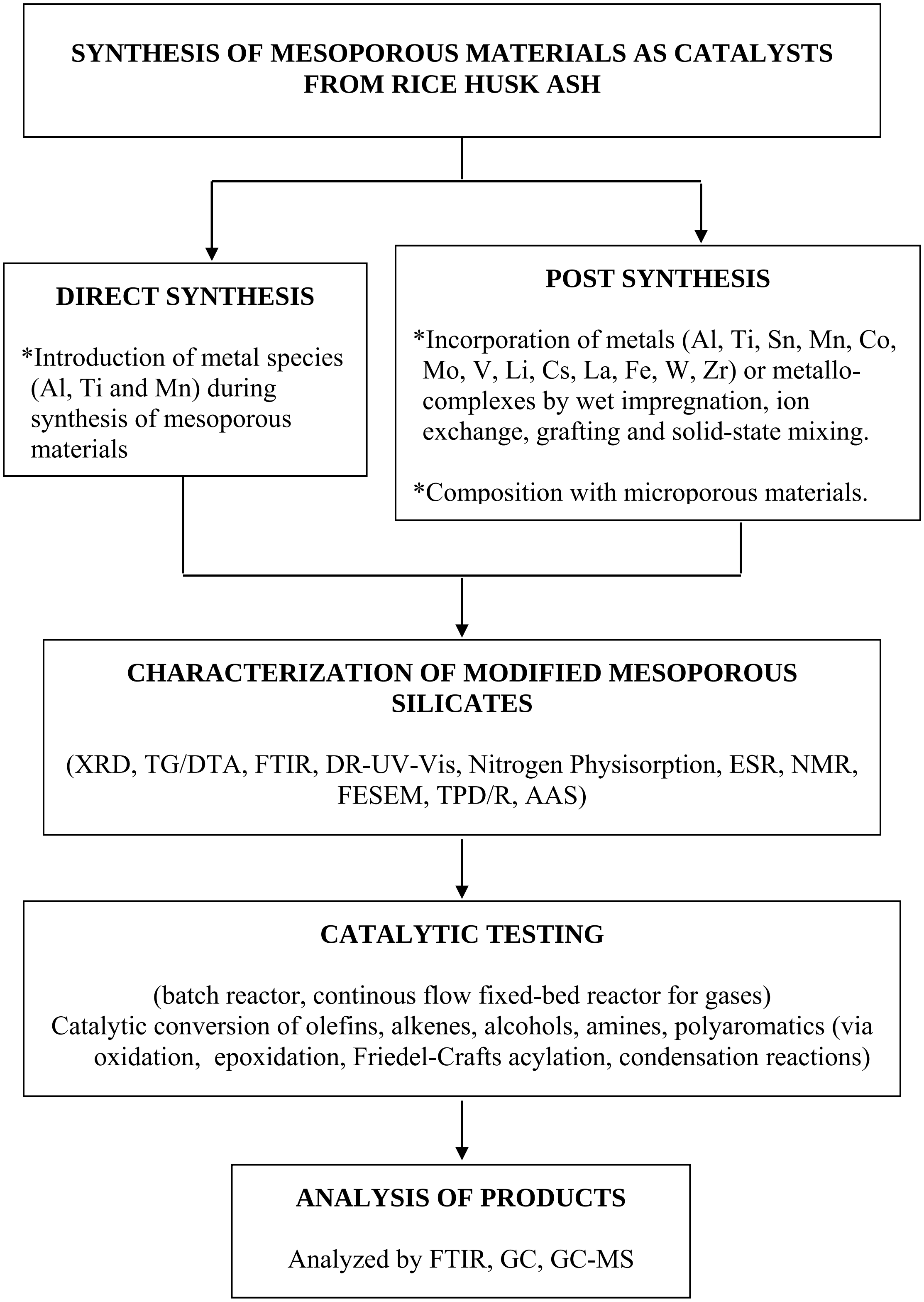

Figure 3.3: Research methodology for mesoporous materials as catalysts.

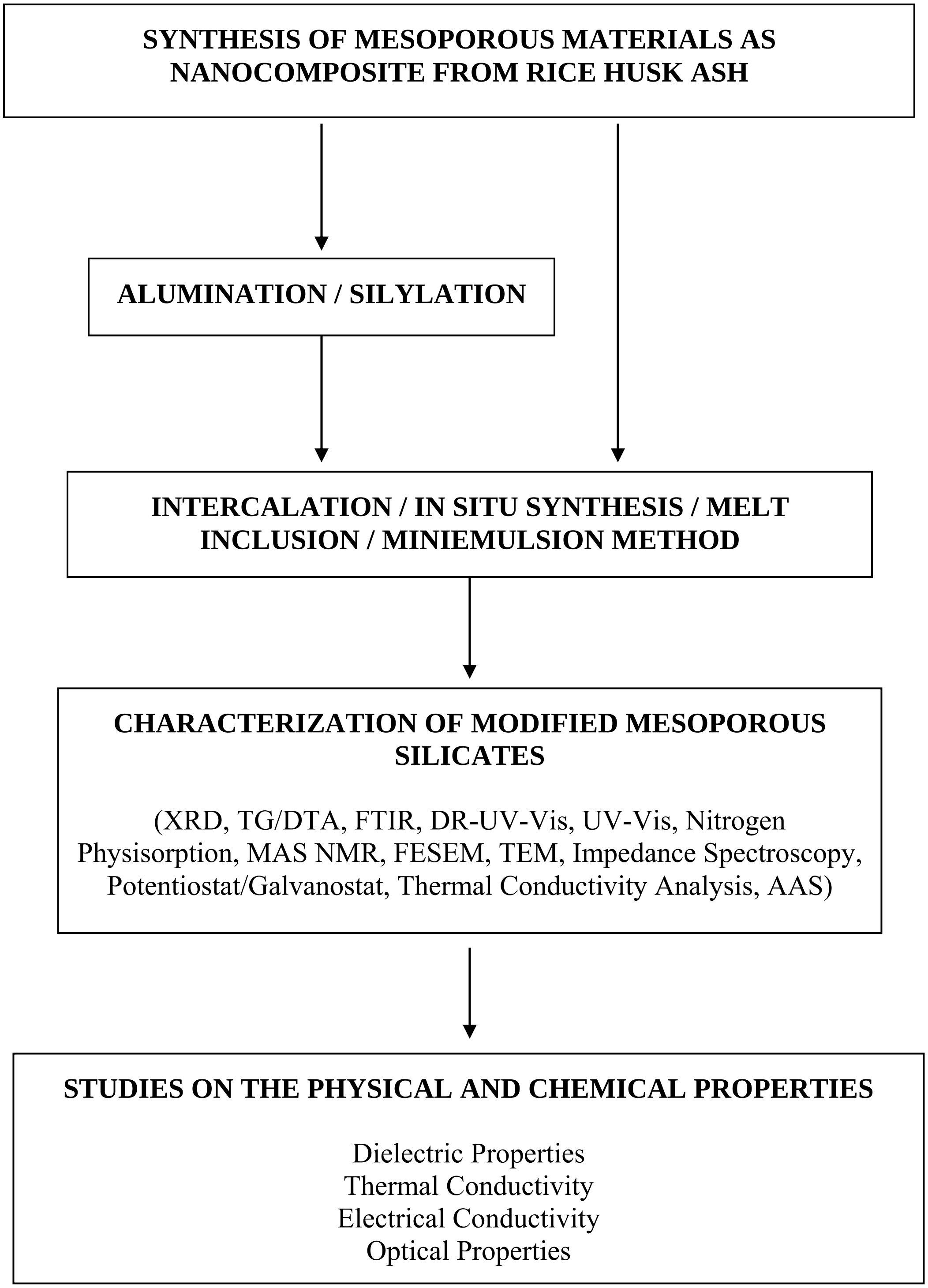

Figure 3.4: Research methodology for mesoporous materials as nanocomposites.

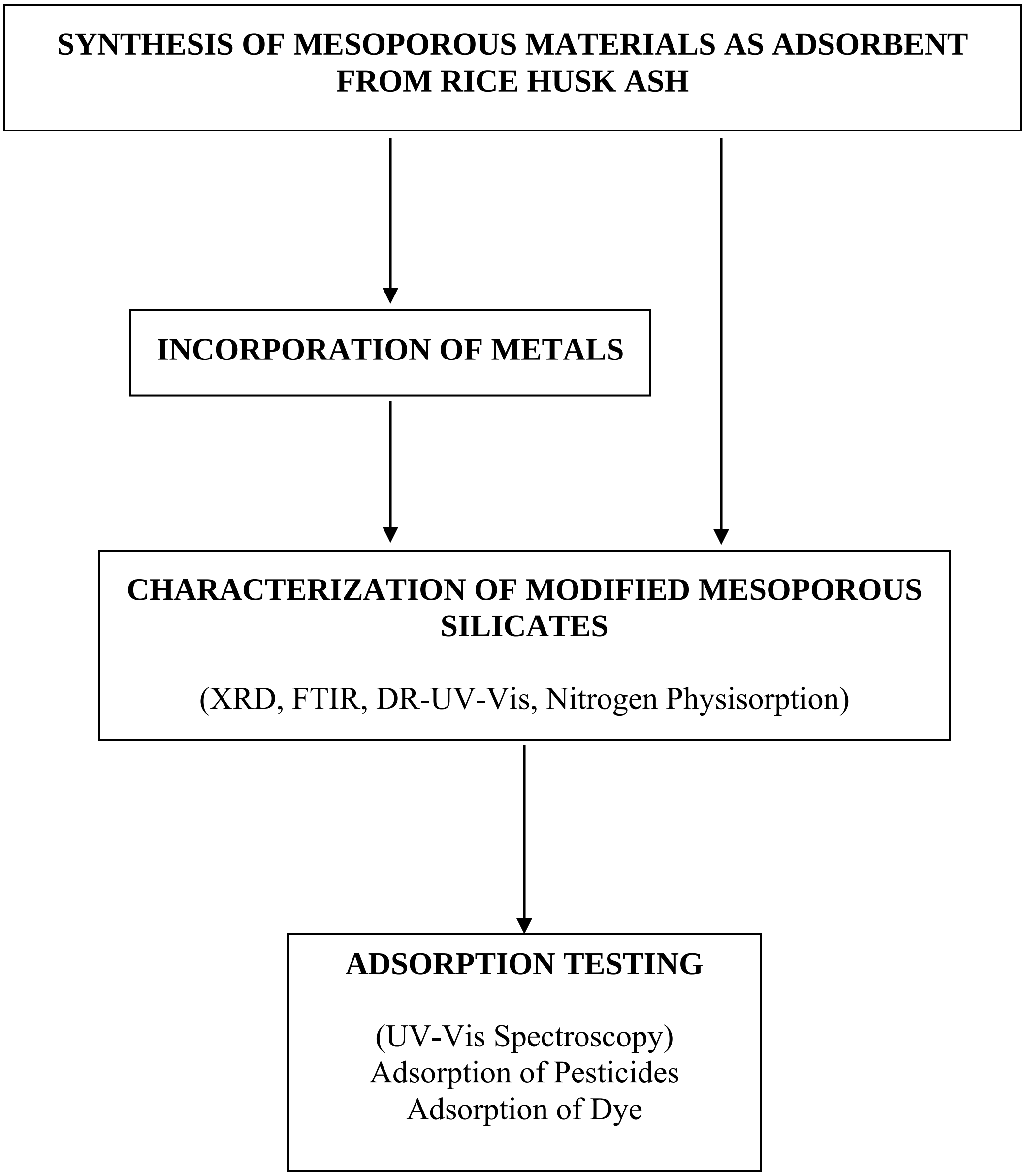

Figure 3.5: Research methodology for mesoporous materials as adsorbents.

# CHAPTER 4

# PROJECT AND SCIENTIFIC RESULTS

Overview of the different studies under this project was summarized in Table 4.1. Details descriptions of the studies are given in the following sections (Section 4.1 to Section 4.44).

Table 4.1: Title of research abstracts.

| Section | Title | Researchers |
|---|---|---|
| 4.1 | Optimized Synthesis of Si-MCM-48 and its modification to Al-MCM-48 by Secondary Synthesis | Lau Chin Guan, **Salasiah Endud** |
| 4.2 | Mesoporous MCM-48 Synthesized From Rice Husk Ash Silica: Physicochemical Properties and Its Catalytic Activity in Acylation Reaction | Lau Chin Guan, **Salasiah Endud** |
| 4.3 | Direct Synthesis of Mesoporous Zeolite from Rice Husk Ash | Kung Chui Ling, **Salasiah Endud** |
| 4.4 | Modification of Al-MCM-41 by Surface Silylation as Hydrophilic Catalyst in the Oxidation of Cyclohexanone | Lee Tzyh Sheng, **Salasiah Endud** |

| | | |
|---|---|---|
| 4.5 | Synthesis and Characterization of Modified Mesoporous Al-MCM-41 for the Dibenzoylation of Biphenyl | Rino Rakhmata Mukti, **Halimaton Hamdan**, **Mohd Nazlan Mohd Muhid**, **Salasiah Endud** |
| 4.6 | Friedel-Crafts Acylation Over Aluminosilicate MCM-41 Catalyst | Yusri Bin Md Yunus, **Salasiah Endud** |
| 4.7 | Synthesis and Characterization of Mesoporous Material Based in Niobium Oxide Supported MCM-41 | Mohd Rozaimi Zahari, **Salasiah Endud** |
| 4.8 | Friedel-Crafts Acylation of of 2-methoxynaphtalene with Acetyl Chloride using Zeolite H-Beta | Jayakumar a/l Kuppuchamy, **Salasiah Endud** |
| 4.9 | Catalytic Activity of Zeolite Beta/MCM-48 Composite in Acylation of 2-methoxynaphtalene with Acetyl Chloride | Abdullah Mukmin Mohd Radzi, **Salasiah Endud** |
| 4.10 | Synthesis and Characterization of Zeolite/Mesoporous Molecular Sieve Composite Materials | Syamsul Qamar Rosli, **Salasiah Endud** |
| 4.11 | Zeolite/Mesoporous Silica MCM-41 Composite: Morphology and Acidity Property | Mohd Zariff bin Zahari, **Salasiah Endud** |
| 4.12 | Effect of Hydrogen on Palm Oil Cracking Over MCM-41/ZSM-5 Composite Catalysts | Siti Kartina A. Karim, **Nor Aishah Saidina Amin**, **Salasiah Endud** |
| 4.13 | Bifunctional Oxidative and Acidic Titanium Silicalite (TS-1) Catalysts for One Pot Synthesis of 1,2-Octanediol from 1-Octene | Didik Prasetyako, **Zainab Ramli**, **Hadi Nur**, **Salasiah Endud** |
| 4.14 | Synthesis of Titanium Catalyst Supported on MCM-41 | Heng Chui Ping, **Salasiah Endud** |
| 4.15 | Mesoporous Material Ti-MCM-48 as Catalyst in Oxidation of Aromatic Compounds | Kamariah Abdullah Khairi, **Salasiah Endud** |

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|---|---|---|
| 4.16 | Catalytic Epoxidation of Cyclohexene Over Titanosilicate MCM-48 | Khairul Nizam Bin Nawi, **Salasiah Endud** |
| 4.17 | Synthesis and Characterization of Tin-modified Mesoporous Silica MCM-48 for Selective Oxidation of Alcohol to Aldehyde | Wong Ka Lun, **Salasiah Endud** |
| 4.18 | Lewis Acids Catalyzed Oxidation of Secondary Alcohol using Mesoporous Materials Tin-Containing MCM-48 | Siti Fairus Binti Mohd Yusoff, **Salasiah Endud** |
| 4.19 | Impregnation of Manganese Oxide in MCM-41 by Direct Synthesis | Lee Huey Shiuan, **Salasiah Endud** |
| 4.20 | Synthesis and Catalytic Activity of Mn (II) Supported in Si-MCM-41 | Mohd Taib bin Haji Ibrahim, **Salasiah Endud** |
| 4.21 | Secondary Synthesis of Cobalt-supported Si-MCM-41 in Aqueous Solution and Methanol: Characterization of Structure and Catalytic Activity | Norhafizah Hj. Jaafar, **Salasiah Endud** |
| 4.22 | Catalytic Activity of Mesoporous Zeolite Molybdenum Oxide Supported MCM-41 in Oxidation of Carbon Monoxide | Idzan Shafina Mohd Idris, **Salasiah Endud** |
| 4.23 | Application of Mesoporous Catalyst Based on MCM-41 Silica in Epoxidation of Monoterpene and Acetylation of Aldehyde | Rosita Yohana Md. Idrus, **Salasiah Endud** |
| 4.24 | Surface Acidity Study of Mesoporous Zeolite V/AlMCM-41 and V/Al-MCM-48 using FTIR Spectroscopy | Lim Kheng Wei, **Salasiah Endud** |
| 4.25 | Amine Functionalized MCM-41 As Bronsted Base Catalyst In Knoevenagel Condensation | Noor Ashikin Mohd Yusoff, **Salasiah Endud** |
| 4.26 | Amine Functionalized MCM-41 As Brönsted Base Catalyst in Aldol Condensation of Aldehyde and Ketone | Mohd Faisal Bin Ab. Latib, **Salasiah Endud** |

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|---|---|---|
| 4.27 | Synthesis and Characterization of Mesoporous Base Catalyst Cs-MCM-41 | Siti Marlia Abd Rahim, **Salasiah Endud** |
| 4.28 | Mesoporous Silica MCM-48 Containing Lanthanum as Active Catalyst for Claisen-Schmidt Condensation of Aromatic Compounds | Leong Siew Ming, **Salasiah Endud** |
| 4.29 | Fe (III) Supported Si-MCM-41 as Lewis Acid Catalyst in Friedel-Crafts Acylation | Noor Aisyah Ahmad Shah, **Salasiah Endud** |
| 4.30 | Iron (III)-Porphyrin Immobilized On Mesoporous Al-MCM-41 And Polymethacrylic Acid As Catalysts For The Single-Step Synthesis Of Phenol From Benzene | Helda Hamid, **Zainab Ramli**, **Hadi Nur**, **Salasiah Endud** |
| 4.31 | Synthesis, Characterization And Catalytic Activity of μ-Oxo Bridged Dinuclear Iron 1,10-Phenanthroline Incorporated In MCM-48 | Lau Su Chien, **Salasiah Endud** |
| 4.32 | Design and Application of Chiral Solid Catalysts Synthesized by Molecular Imprinting Method with Polyaminoacid as Chiral Promoter for Producing Pharmaceutical Products | Lim Kheng Wei, **Hadi Nur**, **Salasiah Endud** |
| 4.33 | Synthesis of Ordered Structure Polystyrene with Encapsulated Cadmium Sulfide Nanoparticles | Eriawan Rismana, **Hadi Nur**, **Salasiah Endud** |
| 4.34 | Synthesis of Poly(methylmethacrylate) -MCM-41 Nanocomposite via Mini-Emulsion Polymerization. | Siti Aisyah A. Bakar, Md. Nasir Katun, **Salasiah Endud** |
| 4.35 | Polyethylene Oxide-MCM-41 and Polyaniline-MCM-41 Nanocomposites Physicochemical and Conducting Properties | Norizah Bt. Abdul Rahman, **Hadi Nur**, **Salasiah Endud** |
| 4.36 | Synthesis and Characterization of Conducting Polymeric Nanocomposite Poly(Methyl Methacrylate)/Lithium-Exchanged Al-MCM-48 | Soh Wei Kian, Md. Nasir Katun, **Salasiah Endud** |

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|---|---|---|
| 4.37 | Synthesis and Characterization of Polymeric Nanocomposite Poly (methyl methacrylate)/Al-MCM-48 Prepared via Solution Intercalation Method | Koh Chee Heng, Md. Nasir Katun, **Salasiah Endud** |
| 4.38 | Synthesis of Poly(Vinyl Acetate)-Silylated Mesoporous Si-MCM-41 Nanocomposite and Its Characterization | Nurul Izza Taib, Md. Nasir Katun, **Salasiah Endud** |
| 4.39 | Polyurethane Modified With Mesoporous Sili<br>Polymeric Nanocomposites With<br>Improved Physicochemical Properties | Yah Weng On, Md. Nasir Katun, **Salasiah Endud** |
| 4.40 | Synthesis and Characterization Of Polyme<br>Nanocomposites Polystyrene/Silylated Mesoporo<br>Material MCM-41 | Ruzanna Bt. Abdul Manap, Md. Nasir Katun, **Salasiah Endud** |
| 4.41 | Adsorption of Pesticide using Synthetic Zeolite(Al-MCM-41-30 and Natural Zeolite (Clinoptilolite) | Yap Siew Yung, Asiah Hussain, **Salasiah Endud** |
| 4.42 | Adsorption of Paraquate using Synthetic Zeolite MCM-48 | Goh Mey San, Asiah Hussain, **Salasiah Endud** |
| 4.43 | Modified Zeolite(Zirconium- Al-MCM-41-30 as Adsorbent for Synthetic Dye | Masida bt Rasyed, Asiah Hussain, **Salasiah Endud** |
| 4.44 | Synthesis Characterization of Dye-loaded Mesoporous Material | Rabiatul Adawiyah Awang, **Salasiah Endud** |

## 4.1 Optimized Synthesis of Si-MCM-48 and its modification to Al-MCM-48 by Secondary Synthesis

Lau Chin Guan

Mesoporous molecular sieve Si-MCM-48 materials with cubic pore structure have been synthesized via two routes using cationic cetyltrimethyl ammonium bromide surfactant (CTABr) or a mixture of cationic CTABr and neutral Triton X-100 (TX-100) surfactants as templates, respectively. Both methods use colloidal silica, Ludox ($SiO_2$, 30 wt. %) as a silica source. Phase purity and the degree of crystallinity of each sample were characterized by various techniques which include XRD, FTIR, nitrogen adsorption measurements and $^{29}$Si MAS NMR spectroscopy. Using the mixed cationic-neutral templating route, highly crystalline Si-MCM-48 material was obtained in high yields in which 3.5 mole of silica was produced per mole of the template surfactant used. Si-MCM-48 was used as the parent zeolite in the secondary synthesis of Al-MCM-48 using sodium aluminate as the aluminating reagent in an aqueous environment. In this work, Si-MCM-48 was treated with sodium aluminate solutions (0.1 M, 0.25 M, 0.5 M and 1.0 M) at 60 $^{o}$C for 3 h or upon heating at 100 $^{o}$C for 12 h. A range of mesoporous molecular sieves Al-MCM-48 with the framework Si/Al ratio as low as 3.0 have been synthesized and characterized using XRD, FTIR and $^{29}$Si MAS NMR spectroscopy. The XRD patterns and the FTIR spectra of the Al-MCM-48 samples indicate that the degree of crystallinity decreases with increased concentration of the $NaAlO_2$ solutions at a constant temperature but increased concentration (1M) upon heating at 100 $^{o}$C resulted in the samples becoming completely amorphous. The nature and concentration of the acid sites have been monitored by temperature-programmed desorption of ammonia ($NH_3$-TPD). The Al-MCM-48 samples were found to exhibit two types of acid sites comprising of weak and moderate strength, respectively, with the maximum desorption temperature ($T_{max}$) ranging between 563 and 758 K. In contrast, the Si-MCM-48 samples have shown only one type of acid sites of weaker strength at a lower $T_{max}$ than that found for Al-MCM-48. In general, the concentration of acid sites decreased with increased concentration of sodium aluminate used.

## 4.2 Mesoporous MCM-48 Synthesized From Rice Husk Ash Silica: Physicochemical Properties and Its Catalytic Activity in Acylation Reaction

Lau Chin Guan

The cubic structural mesoporous molecular sieves Si-MCM-48 has been successfully controlled by optimizing the gel compositions via a mixed surfactant templating route using cationic cetyltrimethylammonium bromide (CTABr) and neutral Triton X-100 (TX-100) surfactants. Rice husk ash, an agricultural waste obtained from an open burning site with high silica content (93 % $SiO_2$) has been utilized as active silica reagent in the synthesis process. The Si-MCM-48 mesoporous materials were structurally characterized by X-Ray Powder Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR). The results show that the crystallinity and phases of the products depend on the compositions of $Na_2O$, surfactants, $H_2O$ and pH values. Moreover, $^{13}C$ CP/MAS NMR technique had been developed to quantify a mixture of cubic MCM-48 and hexagonal MCM-41 mesophases by means of interpretation of their surfactant organization, which cannot be determined by XRD technique. In order to generate active sites for catalytic applications, aluminomesoporous materials Al-MCM-48 were prepared by post-synthesis alumination of mesoporous Si-MCM-48 and post-synthesis alumination of Si-MCM-48 mesophase using sodium aluminate as the aluminium reagent. The aluminated MCM-48 materials were characterized using XRD, $^{27}Al$ MAS NMR, FTIR and nitrogen adsorption-desorption measurements. The results reveal that unimodal Al-MCM-48, which possesses narrow pore size distribution around 26 Å, had been synthesized from post-synthesis alumination of mesoporous Si-MCM-48. Whereas, bimodal Al- MCM-48, which possesses dual narrow pore size distributions around 26 Å and 38 Å had been generated by post-synthesis alumination of uncalcined Si-MCM-48 mesophase. $^{27}Al$ MAS NMR results depict that aluminium had been tetrahedrally incorporated into the framework structure of MCM-48. The nature and the concentration of acid sites of Al-MCM-48 materials have been monitored by IR spectroscopy using pyridine as the probe molecule and temperature-programmed desorption of ammonia (TPDA). Acidity studies on the samples demonstrated that the acidity strength of samples prepared via post-synthesis alumination of mesoporous Si-MCM-48 is greater than samples prepared via post-synthesis alumination of Si-MCM-48 mesophase. Aluminated MCM-48 materials have been employed in the acylation of bulky aromatic compound, 2-methoxynaphthalene with acetic chloride to produce 2-acetyl-6-methoxynaphthalene, which is intermediate for preparing naproxen, a non-steroidal anti inflammation drug. Catalytic activities have been investigated in solvents with different polarity and the results illustrate that the conversion and selectivities of products rely on the polarity of solvent. The conversion of the 2-methoxynaphthalene can be as high as 42 % with 86 % selectivities towards the desired 2-acetyl-6-methoxynaphthalene in polar solvent, nitrobenzene. Whereas, the conversion of the 2-methoxynaphthalene is 30 % with 56 % selectivity of 2-acetyl-6-methoxynaphthalene in non-polar solvent, cyclohexane.

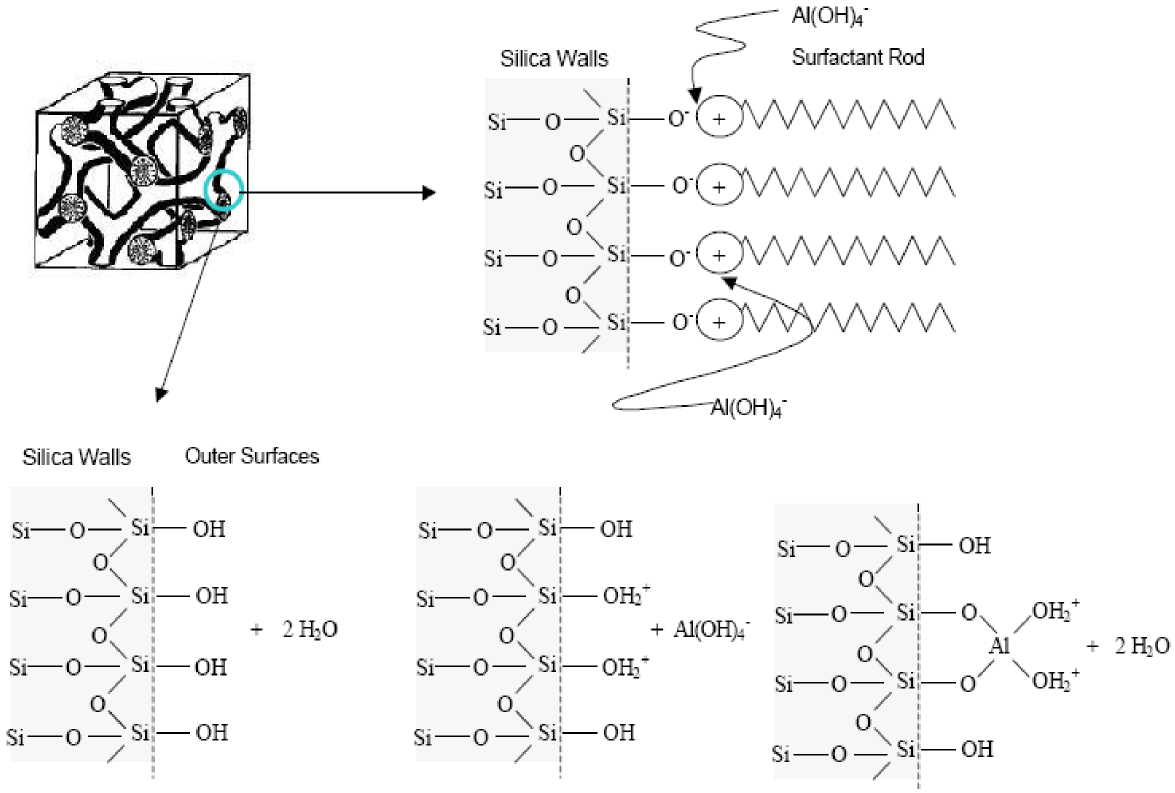
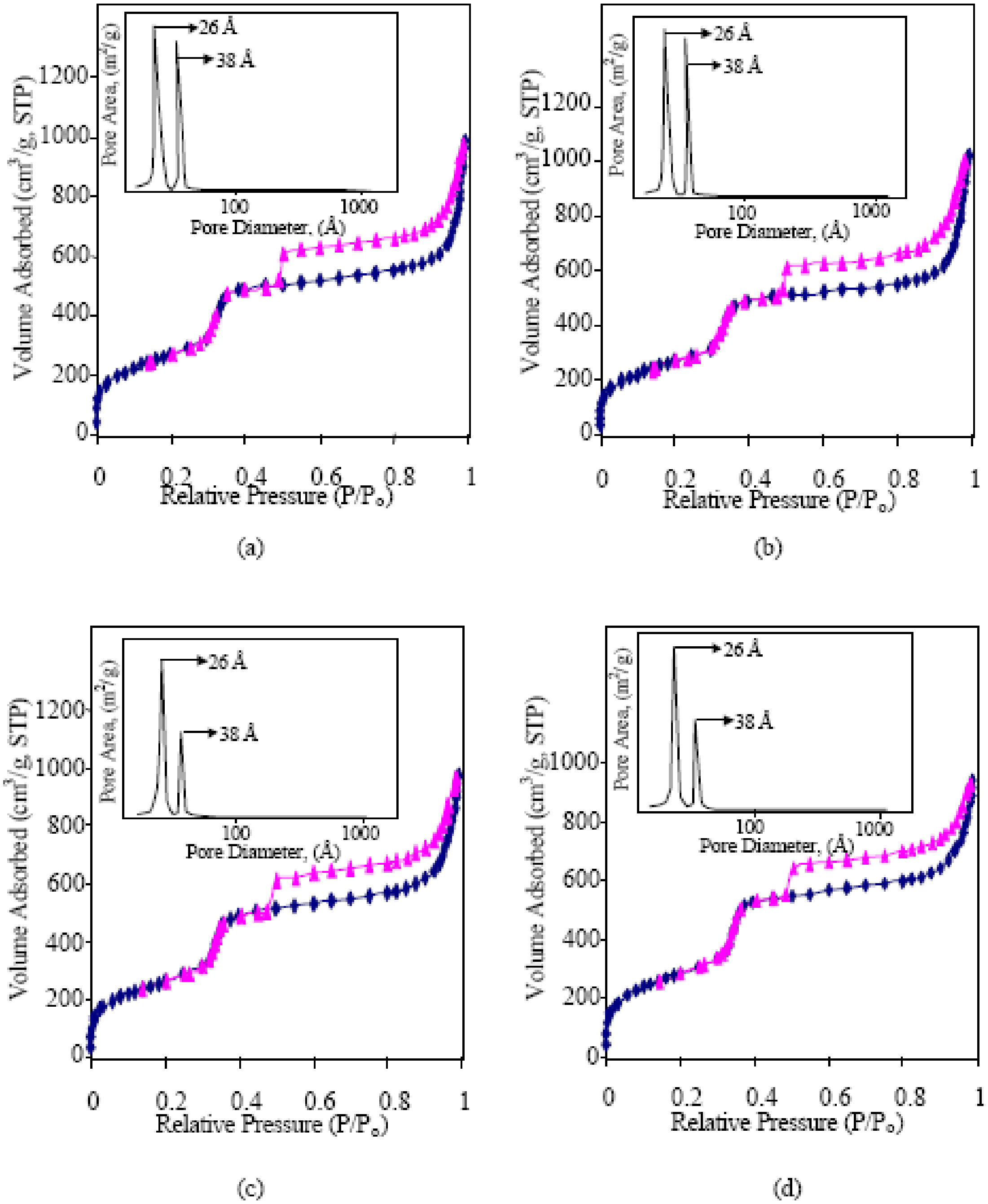


Figure 4.1: Proposed mechanism of post-synthesis alumination of Si-MCM-48 mesophase.



(a) (b) (c) (d)

Figure 4.2: $N_2$ adsorption-desorption isotherms and their corresponding poresize distributions curve (inset) of aluminosilicate Al- MCM-48 samples prepared by post-synthesis alumination with various Si/Al ratios; (a) 20, (b) 30, (c) 50, and (d) 100. The pore size distribution curves confirmed that bimodal Al- MCM-48, which possesses dual narrow pore size distributions around 26 Å and 38 Å had been generated by post-synthesis alumination of uncalcined Si-MCM-48 mesophase.

## 4.3 Direct Synthesis of Mesoporous Zeolite from Rice Husk Ash

Kung Chui Ling

Mesoporous zeolite MCM-41 was directly synthesized with an initial molar composition of 6 $SiO_2$ : 1 CTABr : $1.5Na_2O$ : $0.15(NH_4)_2O$ : $250H_2O$ : $xAl_2O_3$. The Si/Al ratio (x) was varied between 0.1 and 0.3. The samples were characterized by means of powder x-ray diffraction (XRD), infrared spectroscopy (FTIR) and nitrogen adsorption measurements. The results have shown that highly crystalline Al-MCM-41-20 (Si/Al = 20) with specific surface area of 800 $m^2/g$ was obtained from rice husk ash as the silica source and sodium aluminate as the aluminium source via direct synthesis. Synthesis optimization of Al-MCM-41-20 was carried out by varying the molar ratios of surfactant/$SiO_2$, $H_2O/SiO_2$, and $NaOH/SiO_2$ and the duration of aging at room temperature. Results of the analyses showed that the optimum Al-MCM-41-20 crystallization conditions were found to occur for the following molar composition: $6SiO_2$ : 1 CTABr : $1.5Na_2O$ : $350H_2O$ : $0.15(NH_4)_2O$ and without any aging at room temperature. Acidity studies were carried out for both Si-MCM-41 and Al-MCM-41 samples by adsorption and desorption of pyridine followed by FTIR spectroscopy. The result indicated that the optimized sample Al-MCM-41-20 exhibited higher concentration of Brönsted acid sites compared to that of the original sample which was prepared without optimization. The catalytic activity of this sample was tested in the acylation of anisole with acetic anhydride to give *p*-methoxyacetophenone. In this study, results of the chromatographic analysis showed the % conversion of anisole and % selectivity of *p*- methoxyacetophenone are 24.7% and 96.9% respectively.

## 4.4 Modification of Al-MCM-41 by Surface Silylation as Hydrophilic Catalyst in the Oxidation of Cyclohexanone

Lee Tzyh Sheng

Mesoporous molecular sieves Al-MCM-41 was directly synthesized from rice husk ash with an initial molar composition of 6 $SiO_2$ : 1 CTABr : 1.5 $Na_2O$ : 0.15 $(NH_4)_2O$ : 250 $H_2O$ : 0.3 $NaAlO_2$. The Al-MCM-41 samples were modified by silylation using trimethylchlorosilane (TMCS), hexamethyldisilazane (HMDS) and octadecyltrichlorosilane (OTS) to produce hydrophobic zeolites. The samples were characterized by means of X0ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), $^{13}C$ CP MAS Nuclear Magnetic Resonance (NMR) spectroscopy, specific surface area ($S_{BET}$) and water adsorption study. The XRD analysis showed that the framework structure of silylated Al-MCM-41 was still intact but the degree of crystallinity of the sample decreased after silylation. The $^{13}C$ CP MAS spectra confirmed that alkylsilane groups were present on the surface of silylated Al-MCM-41. The results of water adsorption experiments showed that the surface silylated Al-MCM-41 materials were more hydrophobic than before silylation. In this study, OTS modified Al-MCM-41 shows the least affinity for water molecules, suggesting that the silylation with OTS significantly increase the hydrophibicity of the Al-MCM-41 surface due to the higher numbers of carbons than TMCS or HMDS. Also, the results of the oxidation of cyclohexane using hydrogen peroxide as oxidant demonstrated that the OTS modified Al-MCM-41 was active and selective catalyst towards the formation cyclohexanone and cyclohexanol. The gas chromatographic (GC) analysis showed the % conversion of cyclohexane and % selectivity of cyclohexanone are 35.4% and 18.4%, respectively.

## 4.5 Synthesis and Characterization of Modified Mesoporous Al-MCM-41 for the Dibenzoylation of Biphenyl

Rino Rakhmata Mukti

Modified mesoporous Al-MCM-41 (H-Al-MCM-41) was used in the dibenzoylation of biphenyl reaction using benzoyl chloride as benzoylating agent. H-Al-MCM-41 was synthesized in direct alumination and followed by ammonium nitrate ion exchange modification in order to create Brönsted and Lewis acidity strength. H-Al-MCM-41 was chosen owing to enhanced properties such as large surface areas, pore size diameter, uniform pore volume in the range of 943-1186 $m^2 g^{-1}$, 2.74-3.06 nm and 0.84-0.9 $cm^3 g^{-1}$, respectively, therefore the goal of this research carrying out the distribution reaction producing 4,4'-dibenzoylbiphenyl can be achieved. Basically, 4,4'-dibenzoylbiphenyl is a very important material due to its utilization as a monomer to form poly(4,4'-diphenylene diphenyl ninylene) or PDPV. Analysis by gas chromatography-mass spectrometry (GC-MS) indicates that 4,4'-dibenzoylbiphenyl was the only product formed in the dibenzoylation of biphenyl over H-Al-MCM-41 with various Si/Al ratios (HCM-1, HCM-2, HCM-3 and HCM-4); implying the presence of Brönsted and Lewis acid sites corresponding to the tetrahedral Al and octahedral Al, respectively. $^{27}$Al MAS NMR shows that both acid sites are present in H-Al-MCM-41 as peak due to the tetrahedral Al at 53.0 ppm and octahedral Al at 0 ppm. The effect of extraframework Al (EFAL) and framework Al on the product formation has been studied by correlating the octahedral Al to tetrahedral Al ratios ($Al^{oct}/Al^{tet}$ ratio) with the initial rate of product yield. The results show that the dibenzoylation of biphenyl with benzoyl chloride over H-Al-MCM-41 catalyst can produce disubstituted 4,4'-dibenzoylbiphenyl whereby the highest yield of 0.45 μmol was obtained using the sample HCM-4 in a 3 h reaction time while the effective initial rate of 4,4'-dibenzoylbiphenyl formation correspondingly increased within the $Al^{oct}/Al^{tet}$ ratio of 0.6.

## 4.6 Friedel-Crafts Acylation over Aluminosilicate MCM-41 Catalyst

Yusri Bin Md Yunus

Mesoporous molecular sieve is widely used as heterogeneous catalyst in the Friedel-Crafts reaction. Aluminosilicate MCM-41 has many advantages as catalyst such as pores of uniform size in the meso range and possessing Brönsted and Lewis acid as the active site. Al-MCM-41 has been prepared by secondary synthesis via reaction of Si-MCM-41 with sodium aluminate at 60 $^{o}$C for 3 hours. The resulting Al-MCM-41 materials have been characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), nitrogen adsorption and desorption and pyridine adsorption analysis. The results of FTIR spectra and pyridine adsorption show that the Al-MCM-41 catalyst possesses Brönsted and Lewis acidity of moderate strength. The catalytic activity of Al-MCM-41 has been tested in the Friedel Crafts acylation of toluene with acetic acid at 120$^{o}$C. The products were analyzed using Gas Chromatography and Mass Spectrometry-Gas Chromatography (GC-MS). Based on the catalytic study, it was shown that the percentage conversion of toluene was 83.56% while the percentage selectivity towards methylacetophenone was 86.72%.

## 4.7 Synthesis and Characterization of Mesoporous Material Based in Niobium Oxide Supported MCM-41

Mohd Rozaimi Zahari

Purely silicious and aluminosilicate MCM-41 molecular sieves have been reported to possess excellent properties as catalyst support such as high mechanical and thermal stabilities, uniform hexagonal mesopores which can be tailored in the size range between 1.6 - 10 nm as well as high surface area. In this research, Si-MCM-41 and Al-MCM-41 ($SiO_2/Al_2O_3$ = 10) have been prepared at 97 °C using sodium silicate as the silica source and sodium aluminate as the aluminium source. The $Nb_2O_5$/Si-MCM-41 and $Nb_2O_5$/Al-MCM-41 catalyst systems containing 1, 3 and 5 wt% loadings of niobium were prepared by using impregnation technique with niobium ethoxide as niobium source. Characterization techniques employed were X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR) and diffuse reflectance ultraviolet-visible spectroscopy (DRUV-Vis). The DRUV-Vis spectra, it showed that the niobium species were in tetrahedral and octahedral environments, respectively that act as the active sites in Nb-Si-MCM-41 and Nb-Al-MCM-41. The prepared catalyst $Nb_2O_5$/Al-MCM-41 was tested for its reactivity in the epoxidation of cyclohexene.

## 4.8 Friedel-Crafts Acylation of of 2-methoxynaphtalene with Acetyl Chloride using Zeolite H-Beta

Jayakumar a/l Kuppuchamy

Zeolite beta generally possesses high acidity and potentially active as heterogeneous catalysts in the Friedel-Crafts acylation of aromatic compounds. In this study, samples of zeolite beta with $SiO_2/Al_2O_3$ = 30 (H-Si-30) and $SiO_2/Al_2O_3$ = 60 (H-Si-60) have been synthesized using rice husk ash via hydrothermal method. The zeolite beta was then modified into the hydrogen form as zeolite H - beta, by ion-exchange with ammonium nitrate solution followed by calcination at 500 $^oC$. Characterization of structure and pore properties of the zeolites were carried out by weans of X-Ray Powder Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) and nitrogen gas adsorption-desorption methods. The XRD and FTIR results indicated the presence of zeolite beta and nitrogen gas adsorption-desorption showed isotherm of Type I which can be defined as microporous material with pore size around 2.38 nm. Besides, IR-pyridine adsorption indicated that the both Brönsted and Lewis acid sites were present in zeolite beta. The activity of zeolite H-beta as catalyst were investigated in Friedel-Crafts acylation of 2-methoxynaphtalene with acetyl chloride in nitrobenzene solvent. This Friedel-Crafts acylation produced 2-acytyl-6-methoxynaphtalene, which is intermediate for preparing *naproxen*, a non-steroidal anti inflammation drug. Results of the catalytic studies showed that the yield of 2-acytyl-6-methoxynaphtalene was increase significantly when the temperature increases from 30 $^oC$ to 120 $^oC$ and also increase significantly with the reaction time. In the optimum parameters, that is at 120 $^oC$ for 24 hours sample H-Si-60 gave the highest conversion of 2-methoxynaphtalene (52%) compared to the sample H-Si-30 (44%) even though both H-Si-60 and H-Si-30 with selectivity at 100%.

## 4.9 Catalytic Activity of Zeolite Beta/MCM-48 Composite in Acylation of 2-methoxynaphtalene with Acetyl Chloride

Abdullah Mukmin Mohd Radzi

Zeolite beta/MCM-48 composite was synthesized by addition of zeolite beta to mesophase of MCM-48 subsequently re-crystallization at 97$^{o}$C. The sample was characterized by means of FTIR spectroscopy, x-ray diffraction (XRD), nitrogen gas adsorption and Field Emission Scanning Electron Microscopy (FESEM). The XRD pattern of the calcined zeolite beta/MCM-48 composite sample showed peaks which correspond to those of the parent zeolite beta and MCM-48. Acidities study by pyridine adsorption –FTIR spectroscopy showed that no Brönsted acidity and Lewis acidity were observed in MCM-48. On the other hand, zeolite beta/MCM-48 composite has both Brönsted and Lewis acid sites. The activity of composite beta/MCM-48 as catalyst was investigated in Friedel-Crafts acylation of 2-methoxynaphtalene with acetyl chloride in nitrobenze at 120$^{o}$C. The product of the reaction was 2-acetyl-methoxynaphtalene with selectivity at 78.2% compared with 0.42 mmol produced with selectivity at 38.8% for the reaction catalyzed by commercial zeolite beta.

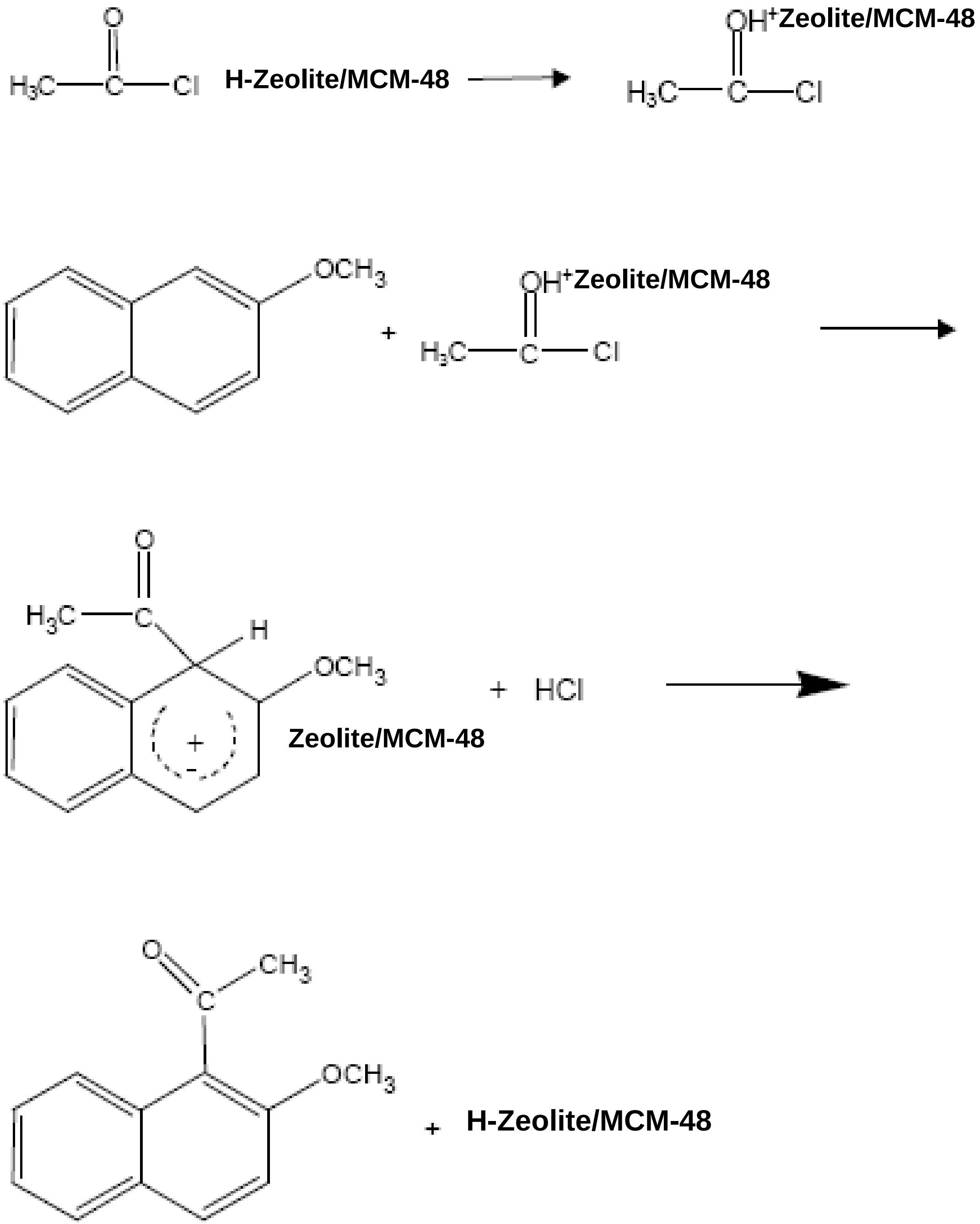


Figure 4.3: Proposed mechanism of the acylation of 2-methoxynaphthalene with acetyl chloride over Brönsted acid sites in protonated H-Zeolite/MCM-48 nanocomposites.

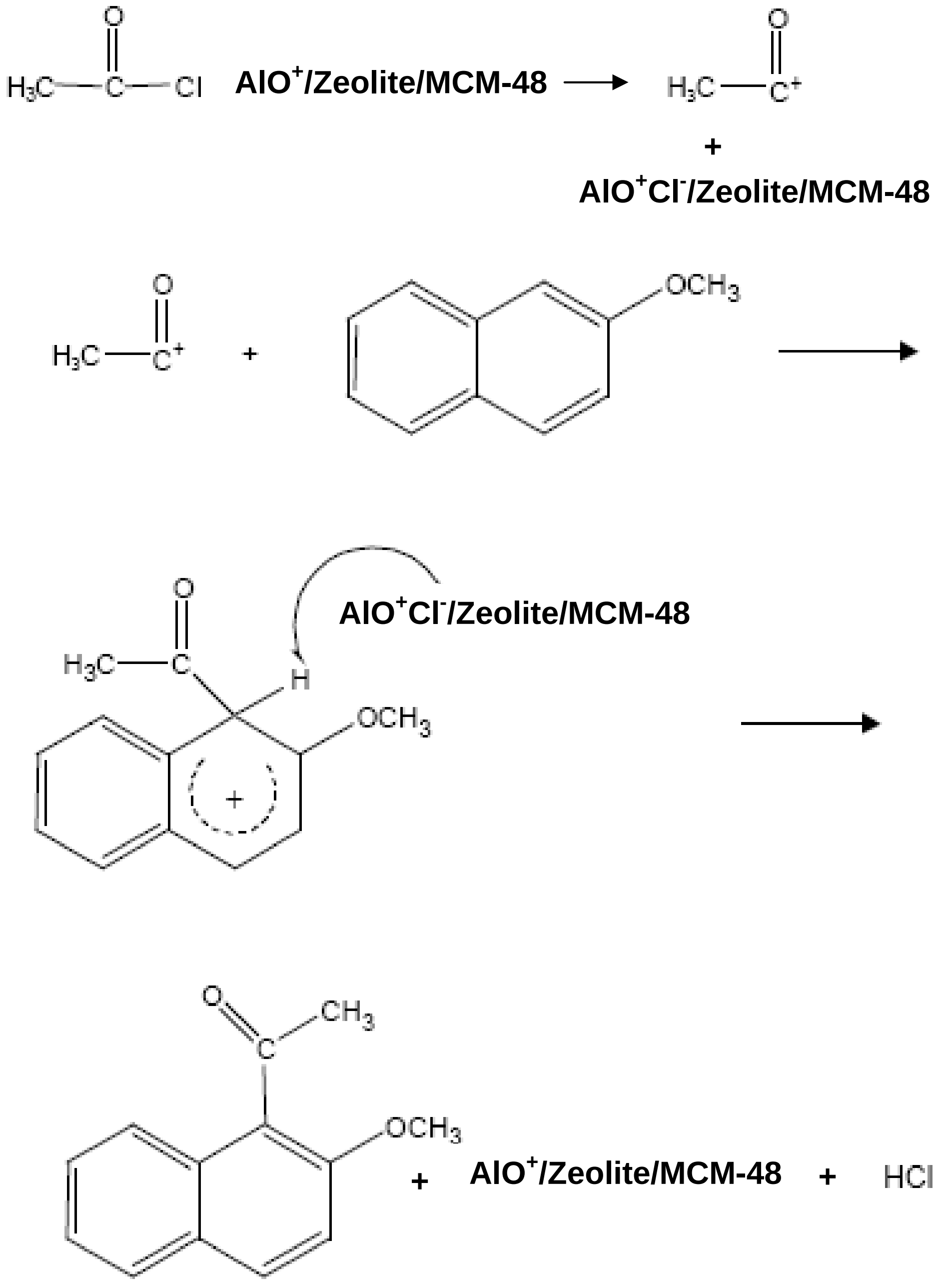


Figure 4.4: Proposed mechanism of the acylation of 2-methoxynaphthalene with acetyl chloride over Lewis acid sites in protonated H-Zeolite/MCM-48 nanocomposites.

## 4.10 Synthesis and Characterization of Zeolite/Mesoporous Molecular Sieve Composite Materials

Syamsul Qamar Rosli

It has been recognized that the amorphous nature of the walls of pure silica MCM-48 mesoporous molecular sieve (MMS) resulted in low acid strength and low hydrothermal stability compared to zeolites. This was thus a strong incentive to try to prepare new materials that would combine both the ordered mesopore structure of MCM-48 and the crystalline structure of microporous zeolites. In this work, purely siliceous mesoporous silica MCM-48 (Si-MCM48) with the composition of 5 $SiO_2$ : 1.25 $Na_2O$ : 0.85 CTABr : 0.15 Triton X-100 : 400 $H_2O$ has been synthesized using sodium silicate as the silica source and CTABr as the template surfactant. Meanwhile the zeolite/mesoporous molecular sieves were prepared as follows: the mesoporous MCM-48 mesophase was first prepared, followed by addition of zeolite ZSM-5 or zeolite beta crystals and subsequently re-crystallization of the mesoporous material MCM-48 at an appropriate temperature. Both zeolites and the composite samples were characterized by X-Ray Diffraction (XRD), nitrogen ($N_2$) adsorption measurements and Field Emission Scanning Electron Microscopy (FESEM). The XRD patterns of the calcined zeolite/MMS composite samples showed peaks which match those of the zeolite and MCM-48. The data indicate that the initially amorphous walls of the mesoporous material MCM-48 has transformed into crystalline nanoparticles. The BET isotherms for both ZSM-5/MCM-48 and Beta/MCM-48 showed that the pore shapes were different from the parent zeolites with narrow-mouthed non uniform shape of pores for ZSM-5/MCM-48 and non-uniform slit shape pores for Beta/MCM-48. Acidity studies by pyridine adsorption–FTIR spectroscopy showed that MCM-48 did not possess acidity while the composites, ZSM-5/MCM-48 and Beta/MCM-48 were shown to have both Brönsted and Lewis acidity.

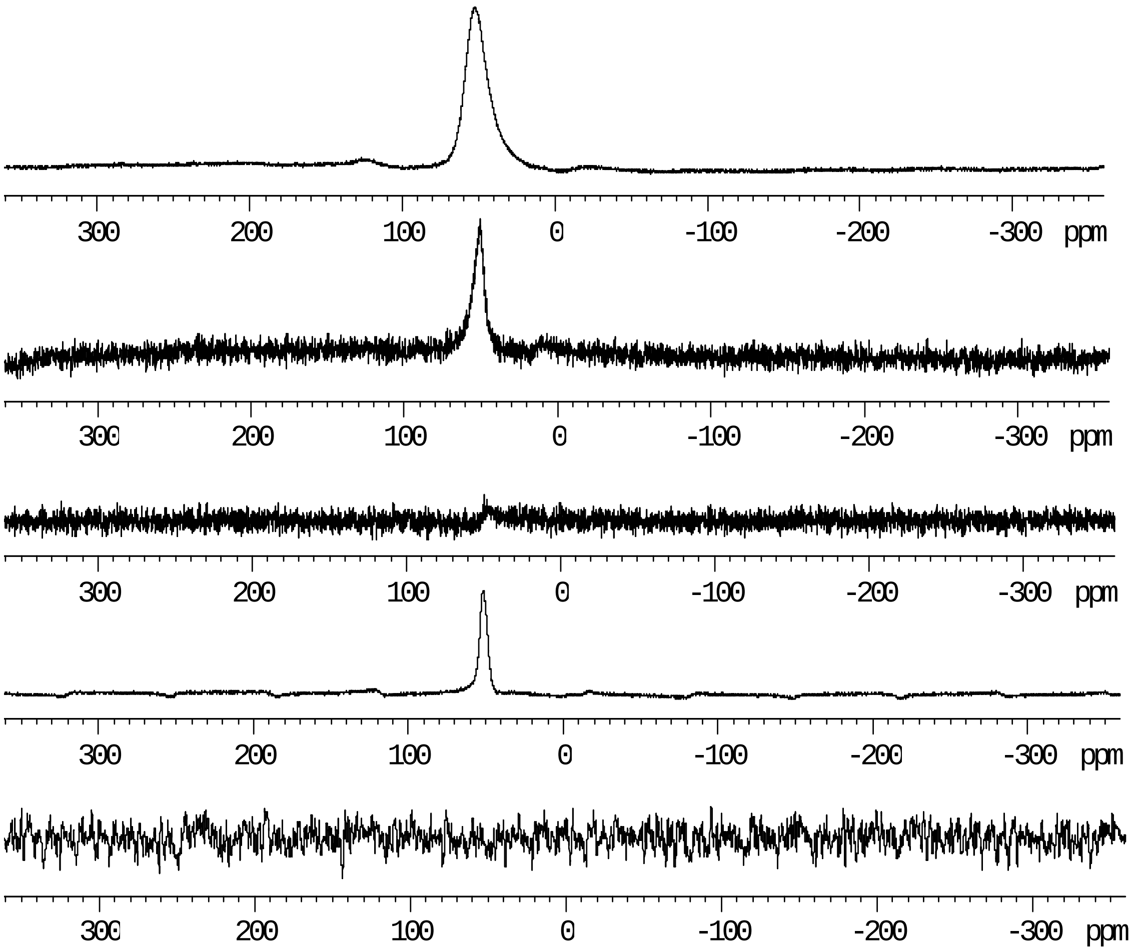


Figure 4.5: The $^{27}$Al MAS NMR spectrum for (a) MCM-48, (b) ZSM-5, (c) ZSM-5/MCM-48, (d) Beta/MCM-48 and (e) Zeolite-Beta

## 4.11 Zeolite/Mesoporous Silica MCM-41 Composite: Morphology and Acidity Property

Mohd Zariff bin Zahari

The amorphous property of silica mesoporous MCM-41 is known to be responsible for the low Brönsted dan Lewis acidity and the low thermal stability of the material. Hence the latest innovation is to produce a nano-structured catalysts which possess high acidity and surface area through the combination of high surface area mesoporous silica MCM-41 and microporous zeolite which possesses both the Brönsted dan Lewis acid site. In this research, zeolite X, zeolite Y and zeolite ZSM-5 each was combined with MCM-41 to produce the composite of zeolite X/MCM-41, zeolite Y/MCM-41 and zeolite ZSM-5/MCM-41, respectively. The products were synthesized through direct synthesis alumination of silica MCM-41 followed by addition of zeolite X, zeolite Y and zeolite ZSM-5 at temperature 80 $^{o}$C. All the samples were characterized using FTIR spectroscopy, X-Ray Diffraction (XRD) and Thermogravimetry Analysis (TG/DTA). The XRD results show that zeolite/MCM-41 composites possess the hexagonal structure of MCM-41 and microporous property of zeolite. The composite morphology studied by Field Emission Scanning Electron Microscopy (FESEM) showed the particles of MCM-41 and zeolites are in the nano meter range. The FTIR and pyridine adsorption study proved the presence of Brönsted dan Lewis acid sites in the composites. The acidity of the composites is higher than pure MCM-41 but lower than the corresponding parent zeolite. The acidity increased by the following sequence Al-MCM-41< zeolite X/Al-MCM-41< zeolite Y/Al-MCM-41< zeolite ZSM-5/Al-MCM-41. The composites produced through direct synthesis possess lower Brönsted dan Lewis acidity compared to the mechanical mixture of MCM-41 and zeolite. The above results suggest that rearrangement of MCM-41 atoms has occurred after addition of the zeolite and confirm that chemical interaction takes place during the synthesis process.

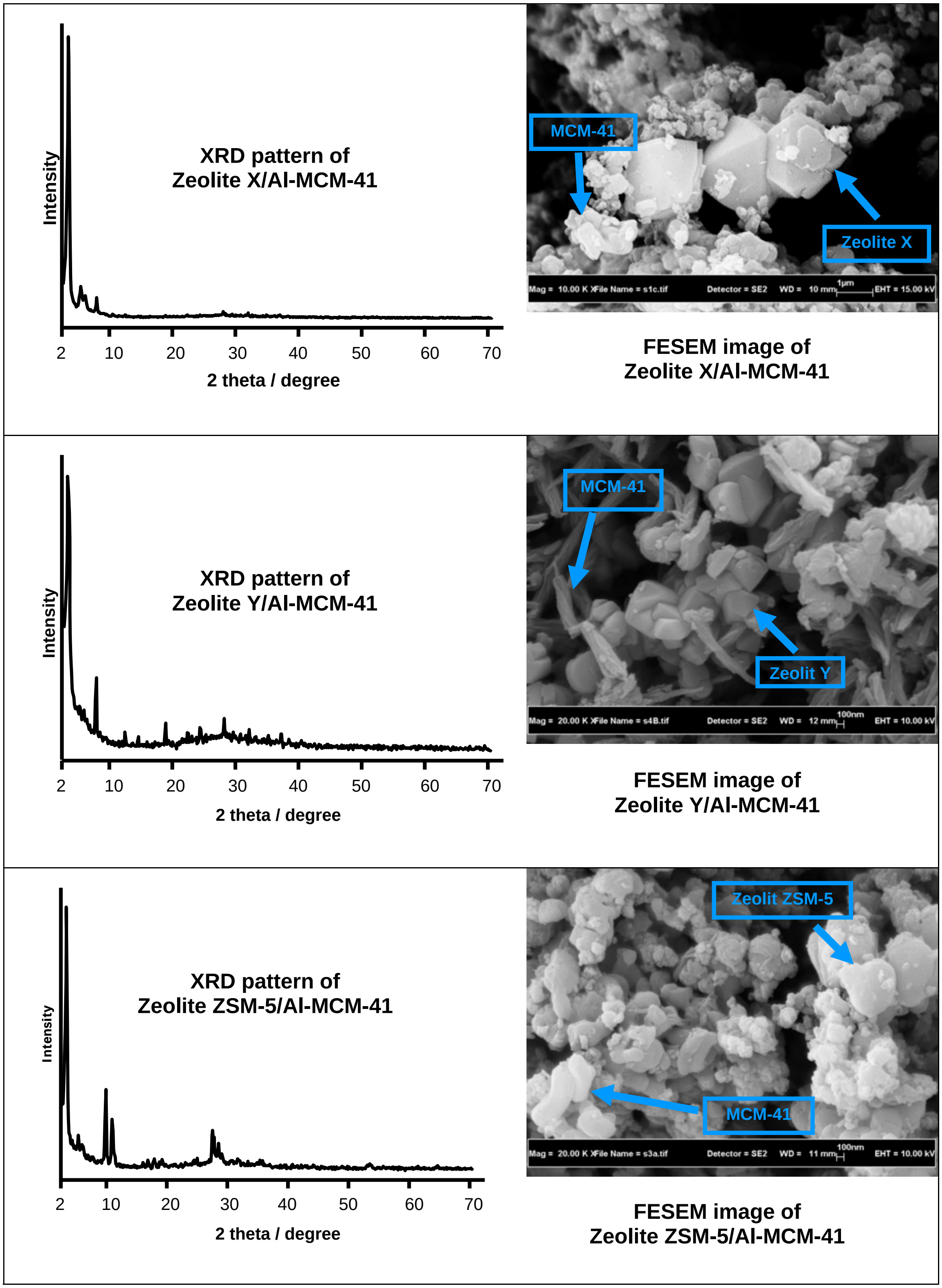


Figure 4.6: XRD pattern and FESEM image of zeolite/MCM-41 composites.

## 4.12 Effect of Hydrogen on Palm Oil Cracking Over MCM-41/ZSM-5 Composite Catalysts

Siti Kartina A. Karim

The diminishing source of non-renewable energy has spurred the interests of researchers to explore the possibility to use alternative sources. Catalytic cracking of vegetable oil to liquid fuels was studied by a number of individuals and the results were encouraging to continue with this study. Composite catalyst, MCM-41/ZSM-5 was used to catalytically convert palm oil to gasoline. The effects of temperature and hydrogen on palm oil cracking were investigated. Experiments were conducted in a fixed bed reactor at atmospheric pressure. Comparative performance of MCM-41/ZSM-5 catalysts synthesized using different methods was evaluated before further testing. The variables tested were temperature (525 to 575°C) for cracking and hydrocracking reaction, palm oil to hydrogen ratio of 1:2 to 1:3.5, hydrotreatment flow rate (0.5 to 1.5 L/h) and hydrotreatment duration (1 to 3h). Catalysts used were characterized using X-ray Diffraction (XRD), Nitrogen Adsorption (NA) and Pyridine Infrared Spectrophotometry (Py-IR) methods. The liquid and gaseous products were analyzed using Gas Chromatography. Conversion increased with temperature, whether in cracking or hydrocracking. Increase in hydrogen to palm oil molar ratio and longer catalyst hydrotreatment duration decreased palm oil conversion and gasoline selectivity. On the other hand, increasing the flow rate of catalyst hydrotreatment increased conversion, organic liquid products' yield and gasoline selectivity. Aromatics were absent or nearly absent with hydrocracking and longer hydrotreatment duration. Gaseous products consisted of mainly $C_3$ and $C_4$ compounds.

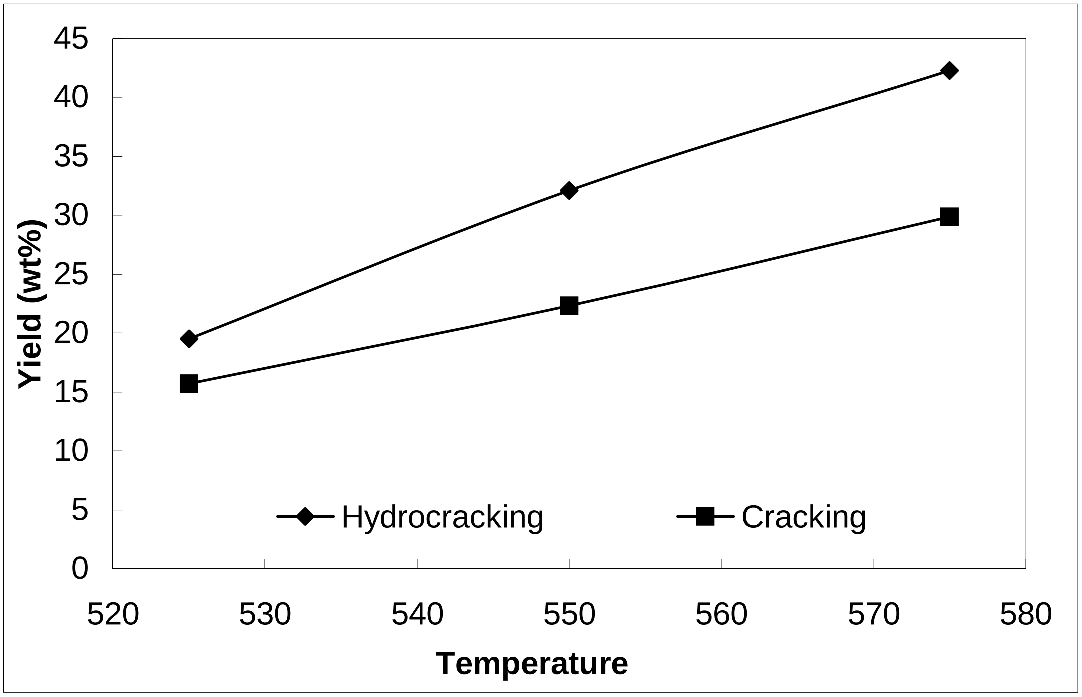


Figure 4.7: Effect of temperature on gas yield for palm oil hydrocracking and cracking over MCM-41/ZSM-5 composite catalyst synthesized *in situ*

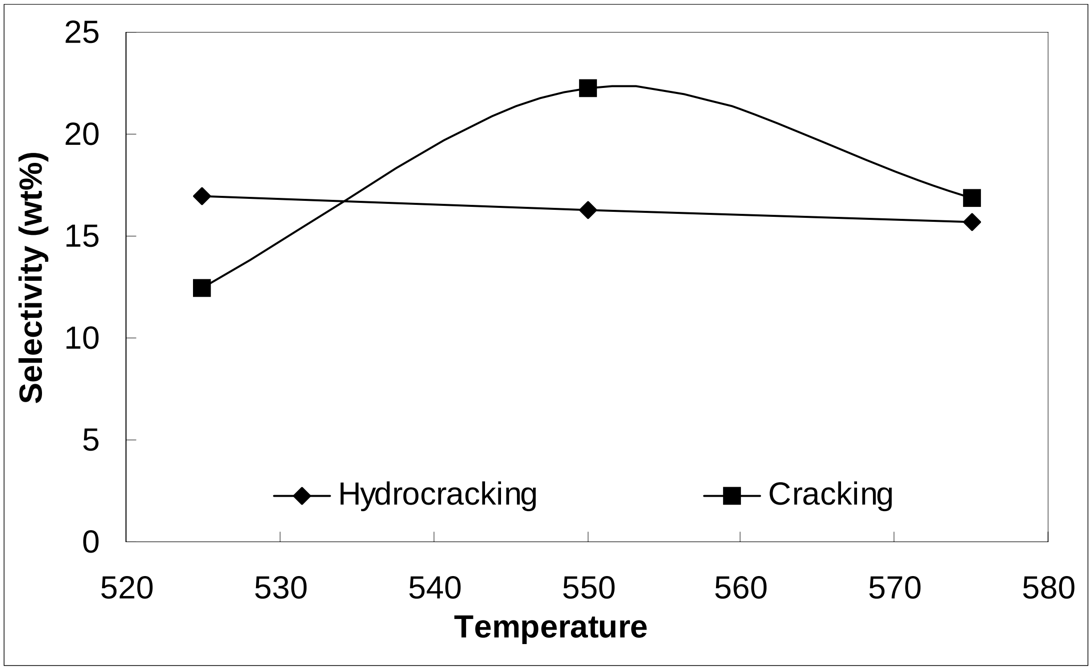


Figure 4.8: Effect of temperature on gasoline selectivity for palm oil hydrocracking and cracking over MCM-41/ZSM-5 composite catalyst synthesized *in situ*.

## 4.13 Bifunctional Oxidative and Acidic Titanium Silicalite (TS-1) Catalysts for One Pot Synthesis of 1,2-Octanediol from 1-Octene

Didik Prasetyako

New bifunctional catalysts containing both oxidative and Brönsted acidic sites have been prepared and used for the consecutive transformation of alkenes to the corresponding diols via the formation of epoxides with aqueous hydrogen peroxide as oxidant. The catalytic system was designed in order such that two kinds of active sites would allow for the epoxidation of alkenes to take place within the pore channels of titanium-containing molecular sieve while acid catalysis of the epoxides to diols occurs on the external surface of the catalyst. Based on this design, titanium silicalite (TS-1), an excellent and commercial oxidation catalyst known so far, has been chosen. The TS-1 was then modified with different acidic oxide precursors. Synthesis of the series of bifunctional catalysts was achieved by deposition of various loadings of acidic oxide precursors up to 25 wt% onto TS-1 powder. The $Ti^{4+}$ and acidic oxides in the TS-1 molecular sieve served as oxidative and acidic sites, respectively. The thus obtained bifunctional catalysts were sulfated TS-1 ($SO_4^{2-}$/TS-1), sulfated titanium oxide supported on TS-1 ($SO_4^{2}$-Ti/TS-1), tungsten oxide supported on TS-1 ($WO_3$/TS-1), sulfated zirconia supported on TS-1 (SZ/TS-1), and niobium oxide supported on TS-1 (Nb/TS-1). The X-ray diffraction analysis revealed that TS-1 still retained the MFI structure after incorporation of the acidic oxides even when the crystallinity is lower. The infrared (IR) and ultra-violet diffuse reflectance (UV-Vis DR) spectra showed that the titanium in TS-1 was mainly in tetrahedral coordination after incorporation of acidic oxides. Results of pyridine adsorption followed by IR spectroscopy showed the presence of Brönsted acid sites in $WO_3$/TS-1, Nb/TS-1 and highly loaded SZ/TS-1 but not sulfated samples of TS-1 ($SO_4^{2-}$/TS-1 and $SO_4^{2}$-Ti/TS-1). In the consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane, all the catalysts showed a significant increase in the rate of formation of 1,2-epoxyoctane with respect to TS-1. The presence of acidic oxides in TS-1 was proposed to explain the increased hydrophilic character of the catalysts, which is responsible for the higher rate of formation of reactive oxo-titanium species. Moreover, the acid sites were shown to effectively catalyze the formation of 1,2-

octanediol with the 10 wt% niobium oxide supported on TS-1 giving the highest yield. Comparison of the catalytic performance of the prepared bifunctional catalysts with that of the mechanical mixture comprising of TS-1 and H-ZSM-5 (Brönsted acid), showed that the bifunctional catalysts were more active; suggesting that specific location of the two active sites plays an important role in the consecutive transformation of alkenes to epoxides and then diols. The higher activity of the bifunctional catalysts was supposedly due to the location of the acidic sites in the immediate vicinity of the oxidative sites which enabled the epoxidation products to undergo hydrolysis rapidly at the Brönsted acid sites that were located on the external surface of TS-1.

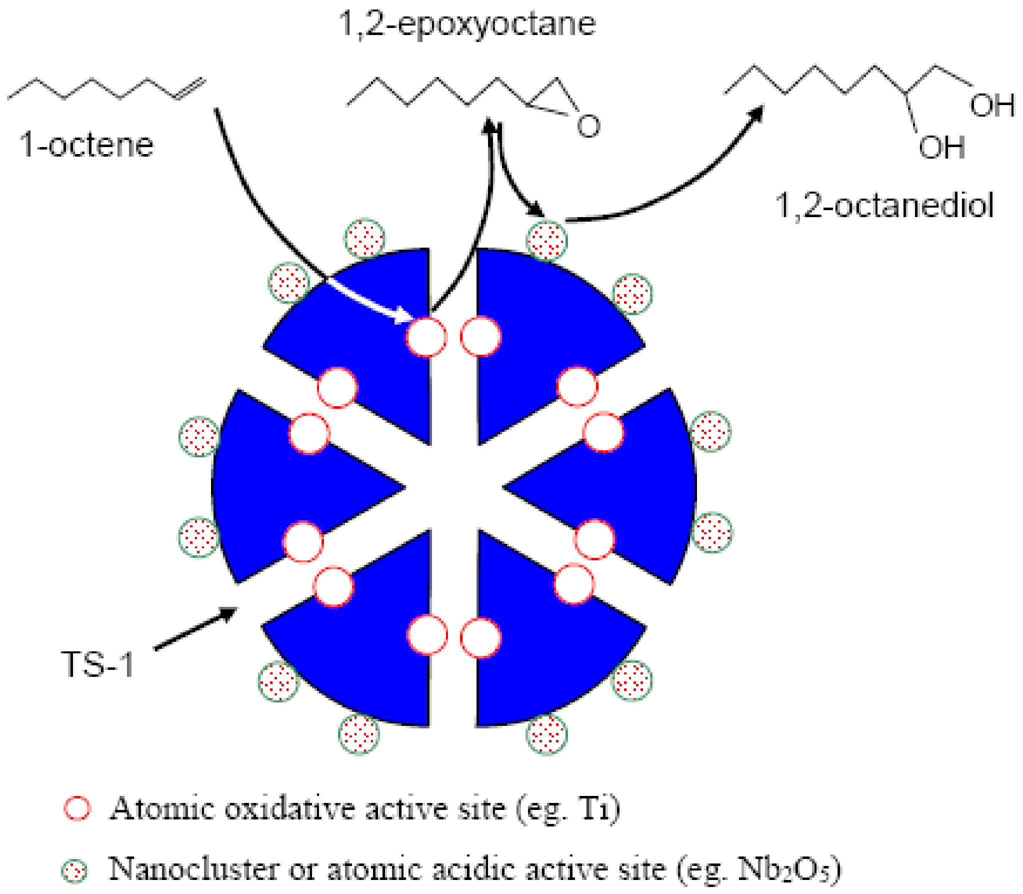


Figure 4.9: Oxidative and acidic catalyst for consecutive oxidation and acid catalytic reactions.

## 4.14 Synthesis of Titanium Catalyst Supported on MCM-41

Heng Chui Ping

Mesoporous molecular sieves Si-MCM-41 was directly synthesized from rice husk ash with an initial molar composition of 6 $SiO_2$ : 1 CTABr : 1.5 $Na_2O$ : 0.15 $(NH_4)_2O$ : 250 $H_2O$. Mesoporous catalyst Ti-MCM-41 wa prepared by grafting titanocene dichloride onto Si-MCM-41 in chloroform and triethylamine. A series of sample containing different loading of Ti in Si-MCM-41 were prepared such as 1%, 3%, 5% and 10wt% Ti. The samples were characterized by means of powder X-ray diffraction (XRD), infrared spectroscopy (FTIR), scanning electron microscopy (SEM), BET specific surface area measurement and diffuse reflectance ultraviolet-visible spectroscopy (DRUV-Vis). The XRD results show only a slight change in the unit cell parameters (($d_{100}$ and $a_o$) after titanium was grafted but the long range order and the hexagonal symmetry of Si-MCM-41 were still intact. The specific surface areas (BET) of Ti-MCM-41 are in the range of 800-950 $m^2/g$, even for the less crystalline Ti-MCM-41 samples indicating that titanium species were homogeneously dispersed on the support. Ti-MCM-41 samples exhibit absorptions at 220 nm to 280 nm in the DRUV-Vis spectrum. At higher Ti content, the DRUV-Vis absorption band becomes broader and the shoulder at > 240 nm are probably due to Ti(IV) sites undergoing a coordination change to octahedral. The catalytic activity of Ti-MCM-41 was tested in the epoxidation of 1-octene with hydrogen peroxide to give 2-methyl-3-hepthyloxirane. Results of the catalytic study showed that the supported catalyst was active in the epoxidation reaction but the conversion of 1-octene and the selectivity towards 2-methyl-3-hepthyloxirane were very poor.

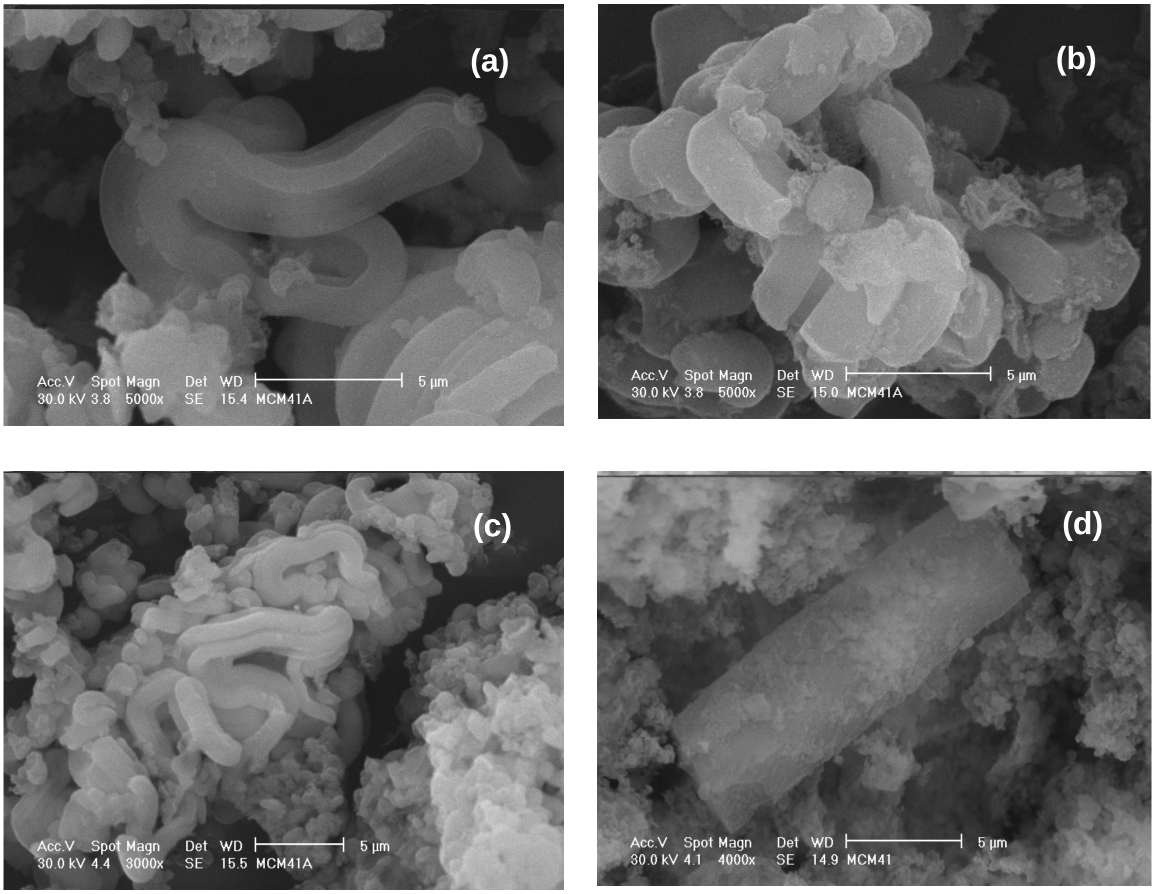


Figure 4.10: SEM image of Si-MCM-41 samples. Two kind of particle morphologies were obtained, i.e. 'worm' type with diameter ~5 μm and length 10 to 30 μm (Figure 4. (a), (b), (c)), hexagonal type (Figure 4. (d)).

## 4.15 Mesoporous Material Ti-MCM-48 as Catalyst in Oxidation of Aromatic Compounds

Kamariah Abdullah Khairi

A series of titano-silicate mesoporous molecular sieves MCM-48 with 3%, 5% and 10% wt% loading of Ti have been produced by post-synthesis modification method using titanocene dichloride ($TiCp_2Cl_2$) to functionalise Si-MCM-48 in the presence of chloroform and triethylamine. The mesoporous material were characterized suing X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), diffuse reflectance UV-Vis spectroscopy, and single point BET measurement. The XRD result show slight changes in the unit cell parameters ($d_{211}$ and $a_o$) after incorporation of titanium but long range order of the cubic structure of Si-MCM-48 was still retained. All the Ti-MCM-48 materials exhibit adsorption at ~220 nm in the DRUV-Vis spectra which indicates the presence of tetrahedral Ti(IV) species as active sites. The catalytic activity of Ti-MCM-48 was investigated in the oxidation of 1-napthol with hydrogen peroxide to produce 1,4-napthoquinone. The product was characterized using gas chromatography (GC) and gas-chromatography-mass spectrometry (GC-MS) techniques. Among the Ti-MCM-48 catalysts used in the oxidation reaction, the sample containing 10 wt% Ti loading gave the highest conversion of 1-napthol and showed 100% selectivity towards 1,4-napthoquinone after 22 hours of reaction both at $60^{o}$C and $90^{o}$C.

## 4.16 Catalytic Epoxidation of Cyclohexene over Titanosilicate MCM-48

Khairul Nizam Bin Nawi

Titanosilicate MCM-48 (Ti-MCM-48) with 1%, 3% and 5% weight percentages of titanium were synthesized by the grafting of titanocene dichloride ($TiCp_2Cl_2$) on the surface of Si-MCM-48 in the presence of chloroform and triethylamine. The titanosilicate MCM-48 was characterized using Fourier Transform Infrared (FTIR) spectroscopy, X-Ray Diffraction (XRD) and Diffuse Reflectance Ultraviolet-visible (DRUV-Vis) spectroscopy. The XRD results show contraction of the parameter unit cell ($d_{211}$ and $a_o$) after incorporation of titanium in Si-MCM-48 but the cubic structure of MCM-48 was still intact. All the Ti-MCM-48 samples exhibit an absorption band at around 220 nm in the DRUV-Vis spectra, indicating the presence of Ti(IV) species in tetrahedral coordination which function as active site. The catalyst was found to be active and selective in the epoxidation of cyclohexene using hydrogen peroxide oxidant and acetonitrile as the solvent. The reaction products were characterized using Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS). The results showed that the main product of the oxidation reaction was 1,2-epoxycyclohexane and the by-product was 1,2-cyclohexanediol.

## 4.17 Synthesis and Characterization of Tin-modified Mesoporous Silica MCM-48 for Selective Oxidation of Alcohol to Aldehyde

Wong Ka Lun

Tin-modified mesoporous silica MCM-48 with various Si/Sn ratios has been prepared by post synthesis modification in alkaline medium. Local rice husk ash (RHA) has been used as Si precursor in the synthesis of Si-MCM-48 samples while $SnCl_2$ was used as the tin source in the modification. The tin-modified MCM-48 samples were characterized by using powder X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy, ultraviolet-visible diffuse reflectance (UV-Vis DR) spectroscopy, nitrogen physisorption measurement, field emission scanning electron microscopy (FESEM) and temperature-programmed reduction (TPR) analysis. Surface acidity of the prepared samples was determined by using pyridine adsorption-desorption measurement followed by FTIR spectroscopy. In addition, thermal and hydrothermal stability testing for the tin-modified samples were carried out. The FTIR, UV-Vis DR and XRD results show that tetrahedral tin species can be introduced into the mesoporous material without destroying the framework structure of the molecular sieves. Surface acidity studies confirm that Lewis acid sites had been generated on the mesoporous silica MCM-48 by post-synthesis modification. The generation of Lewis acid sites could be due to the introduction of tin species and/or because of defect sites that had been created during post-synthesis modification. Tin-modified sample SnM60 (Si/Sn = 60) possessed highest amount of Lewis acidity. In oxidation of benzyl alcohol, all the tin-modified samples gave 100% selectivity to benzaldehyde in reaction time under 22 hours. The catalytic activity can be correlated with the Lewis acid sites generated by post-synthesis modification. Purely siliceous MCM-48 and physically mixed tin-containing MCM-48 samples that possesses no Lewis acidity gave poor performance in the catalytic reaction. With the increase in the amount of oxidant in the reaction mixtures, the conversion of benzyl alcohol increased significantly but the selectivity for benzaldehyde was reduced. For reusability test, the catalytic performance of the re-used samples was maintained within 5-10% after two cycles of reuse without significant loss of activity. Comparison of the catalytic performance of SnM60 in the oxidation of unsaturated primary alcohols and saturated aliphatic primary alcohol towards the corresponding aldehydes showed higher % conversion of the unsaturated primary alcohols than that of the saturated aliphatic primary alcohol.

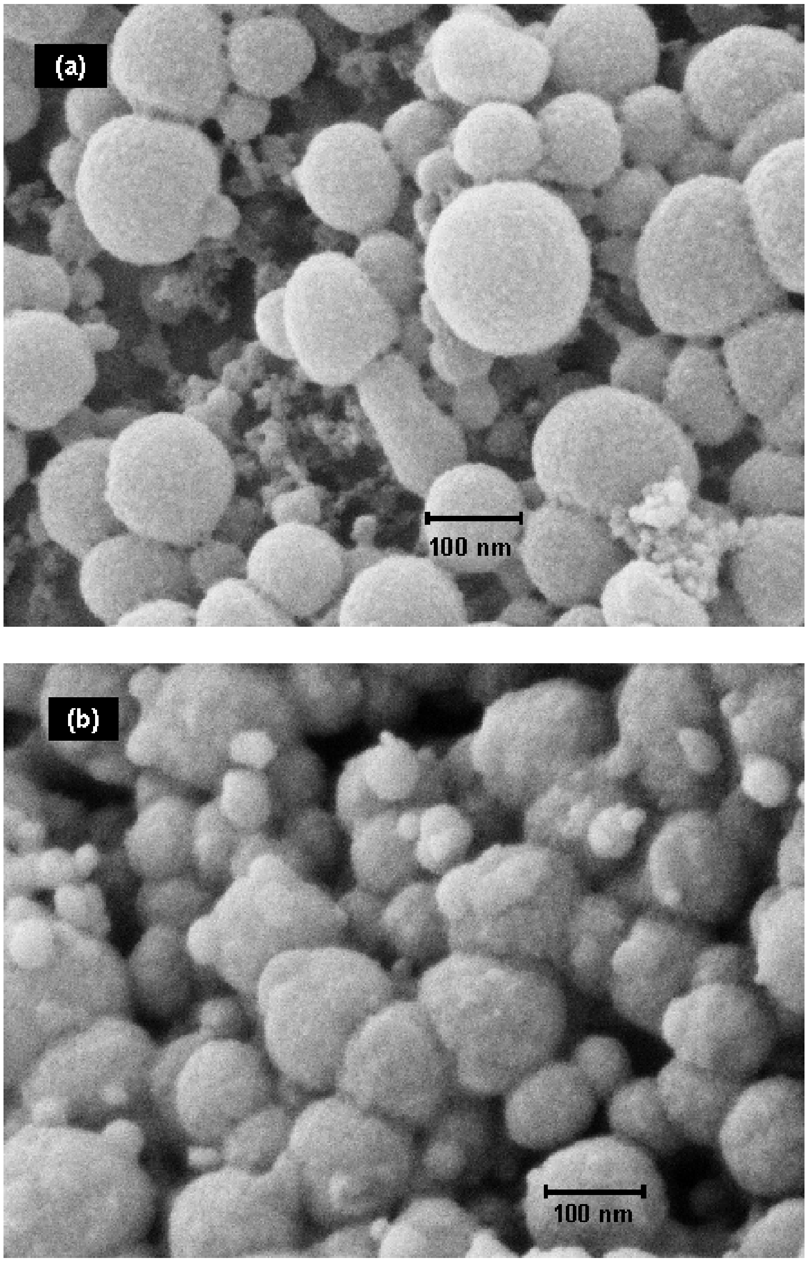


Figure 4.11: FESEM images of calcined (a) purely siliceous Si-MCM-48 and (b) SnM100.

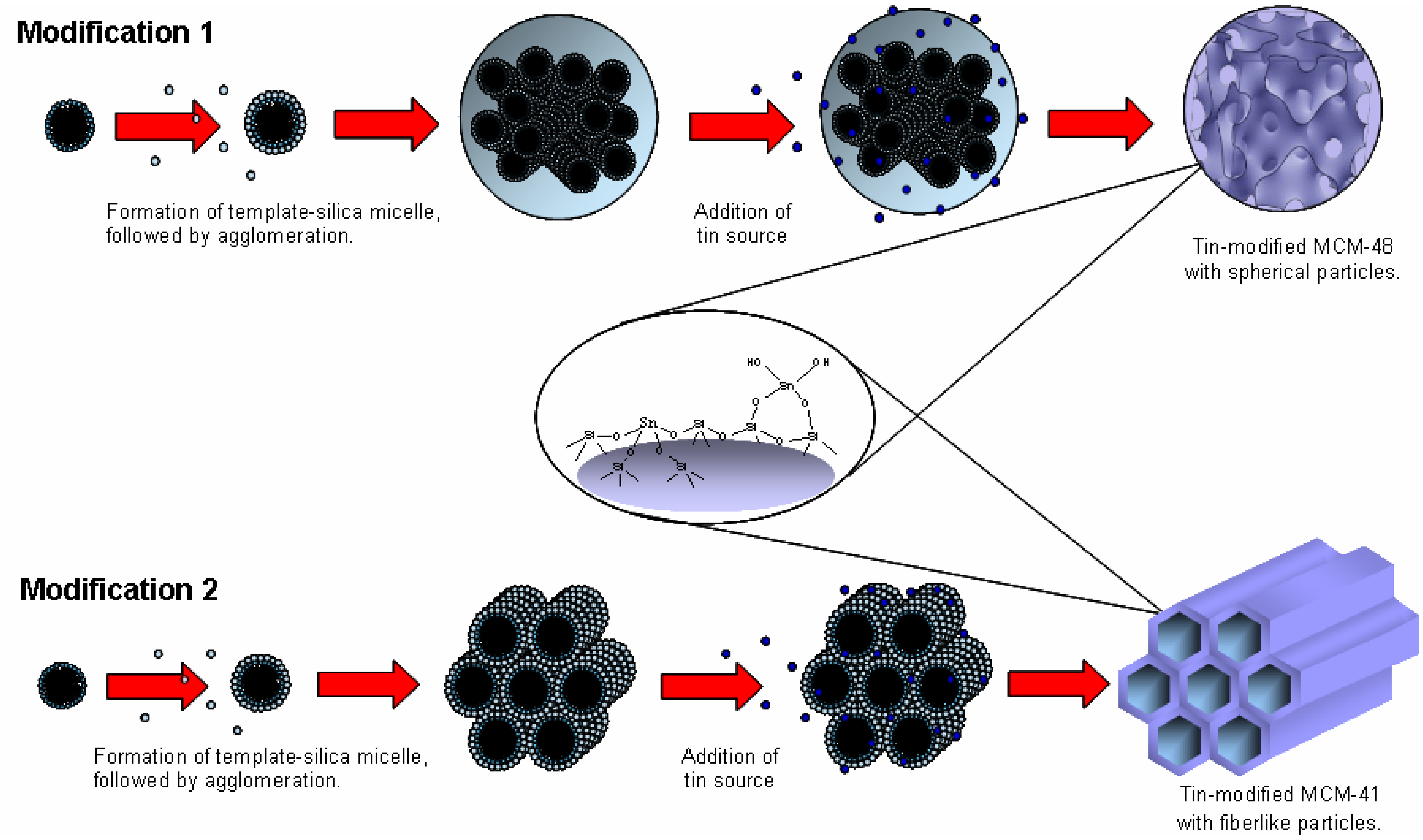


Figure 4.12: Molecularly designed dispersion (MDD) of tin species on mesoporous molecular sieves.

## 4.18 Lewis Acids Catalyzed Oxidation of Secondary Alcohol using Mesoporous Materials Tin-Containing MCM-48

Siti Fairus Binti Mohd Yusoff

Tin containing MCM-48 molecular sieves have been prepared via post synthesis modification at 80 ºC with $SnCl_2$ as a tin source and rice husk silica (93 % $SiO_2$) as the silica source. The tin containing MCM-48 materials were characterized using X-ray diffraction, UV-Vis DR, single-point BET analysis and FTIR. The nature and strength of acid sites of tin containing MCM-48 have been monitored by IR spectroscopy using pyridine as the probe molecule. The result shows that only weak Lewis acid sites are present in the tin containing MCM-48. The UV-Vis DR spectra show that tetrahedral tin species can be introduced into mesoporous material MCM-48 without destroying the framework structure. The surface area analysis shows that increasing the amount of tin resulted in the decrease of surface areas of tin containing MCM-48. The results suggest that the tin species are mainly located in the mesopores. The mesoporous tin catalyst has been tested in the conversion aromatic compound namely the oxidation of secondary of alcohol, Meerwein-Ponndorf-Verley reduction and Oppenauer's (MPVO) oxidation and Baeyer-Villiger (BV) oxidation at 80 ºC. However, the tin containing MCM-48 catalyst was active only in the oxidation of secondary alcohols giving the corresponding aldehydes. In the oxidation of benzyl alcohol in acetonitrile for 20 hours, benzaldehyde was formed with 100% selectivity. Results of the catalytic study confirm that tetrahedral tin species in MCM-48 are predominantly weak Lewis acids, and thus are inactive in promoting MPVO and BV reactions. This suggests that oxidation and reduction of carbonyl group of aromatic compounds in those reactions require active sites of higher acid strength.

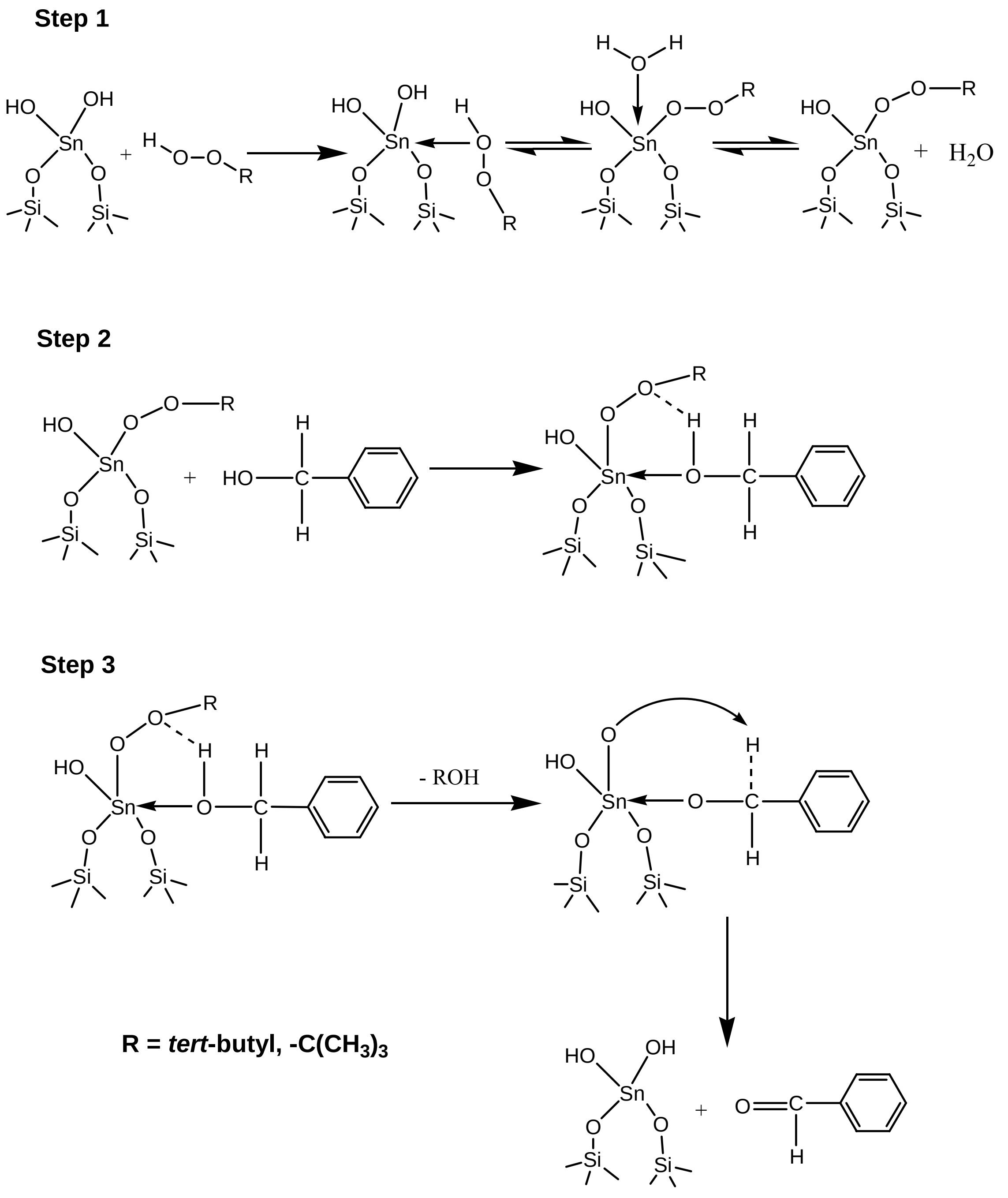


Figure 4.13: The proposed mechanism for oxidation of benzyl alcohol over tin-modified MCM-48 samples prepared by post synthesis modification.

## 4.19 Impregnation of Manganese Oxide in MCM-41 by Direct Synthesis

Lee Huey Shiuan

Manganese oxide supported MCM-41 mesoporous molecular sieves with Si/Mn composition between 5 and 50 were synthesized by direct synthesis using manganese chloride dihydrate as a source of manganese. The samples were characterized by means of X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), nitrogen adsorption measurement and diffuse reflectance ultraviolet-visible spectroscopy (UV-VIS-DRS). The XRD analysis showed that the framework structure of MCM-41 containing manganese oxide was still intact but the degree of crystallinity of the sample decreased with the decrease of Si/Mn ratio due to insertion of Mn into the framework of MCM-41. The UV-VIS-DRS spectra for the manganese oxide supported MCM-41 showed two broad peaks around 300 nm and 320 nm. The peak around 320 nm exhibited the charge transfer transition of $O^{2-}$ to $Mn^{3+}$ in $Mn_3O_4$ in which Mn was octahedrally coordinated with oxygen. The peak around 300 nm was due to $Mn_3O_4$ species in tetrahedral coordination. The activity of manganese oxide supported MCM-41 as redox catalyst was tested in the oxidation of cyclohexane with aqueous hydrogen peroxide solution as oxidant in a batch reactor. Gas chromatography (GC) was used to identify the two main products cyclohexanone and cyclohexanol. The presence of manganese oxide in MCM-41 resulted in the increase of the rate of decomposition of hydrogen peroxide to water and oxygen. Subsequently, the conversion of cyclohexane to cyclohexanone and cyclohexanol decreased when the concentration of manganese oxide in the sample increased.

## 4.20 Synthesis and Catalytic Activity of Mn (II) Supported in Si-MCM-41

Mohd Taib bin Haji Ibrahim

Mesoporous molecular sieves Si-MCM-41 containing manganese ions (Mn-MCM-41) were prepared by wet impregnation technique using manganese(II) acetylacetonate and manganeses(II) sulphate. The mesoporous materials Mn-MCM-41 have been characterized using ESR, FTIR, DRUV-Vis spectroscopy technique and XRD. X-ray diffraction (XRD) analysis show that hexagonal pore structure of Si-MCM-41 remain unchanged after impregnation with 3wt% and 5wt% Mn. Increase of the parameter value unit cell ($a_o$) values for Mn-MCM-41 indicated the incorporation of Mn into the framework of the Si-MCM-41 host. The present of Mn(II) species as active sites in Mn-MCM-41 was confirmed by electron spin resonance. (ESR) and diffuse reflectance ultraviolet-visible (DRUV-Vis) spectroscopy. It shown that Mn-MCM-41 was active heterogeneous catalyst in the oxidation reaction of phenol with hydrogen peroxide ($H_2O_2$) as a oxidizing agent at room temperature, giving the highest selectivity (100%) towards *p*-benzoquinone. Phenol conversion was found to increase with increasing of weight percent of Mn in the Mn-MCM-41 sample.

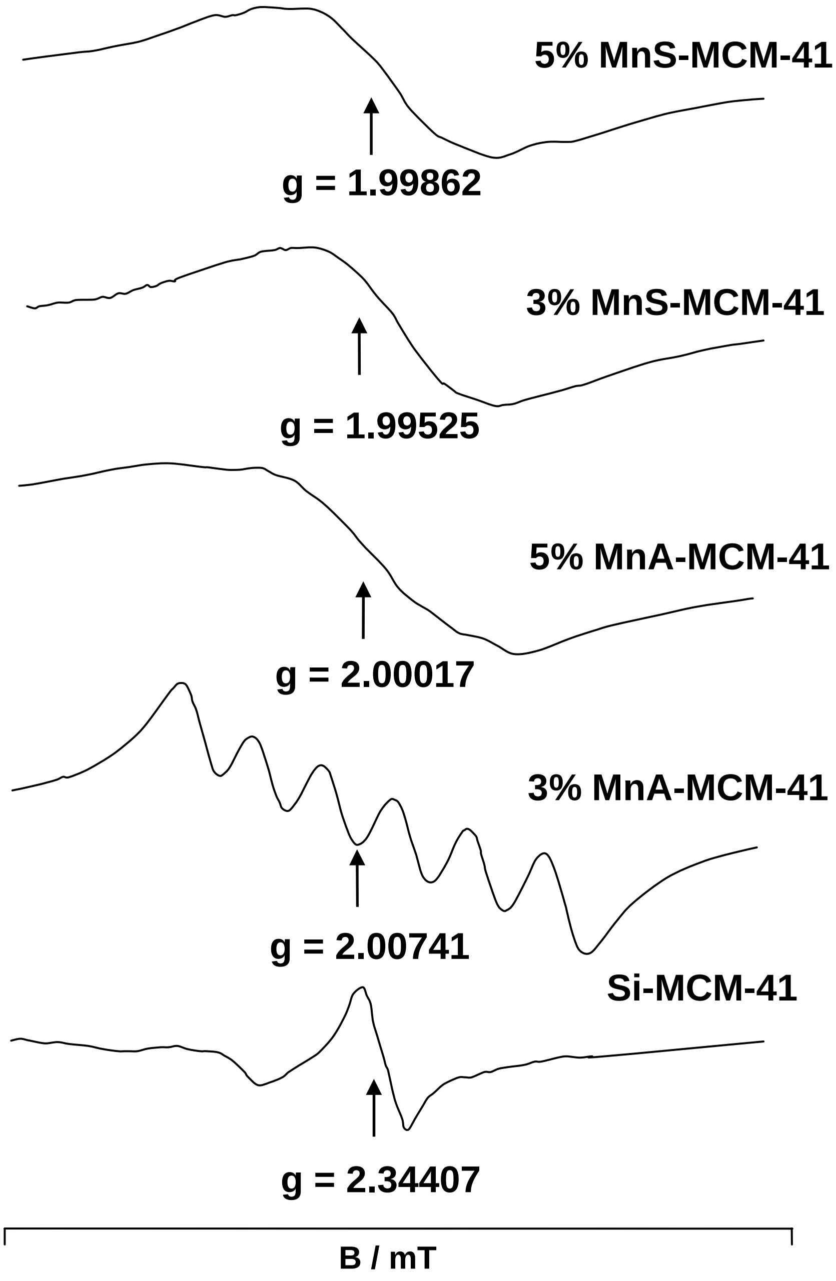


Figure 4.14: ESR spectra of Mn-MCM-41 samples prepared by wet impregnation technique using manganese(II) acetylacetonate (denoted as MnA-MCM-41) and manganeses(II) sulphate (denoted as MnS-MCM-41) with different loading of Mn species.

## 4.21 Secondary Synthesis of Cobalt-supported Si-MCM-41 in Aqueous Solution and Methanol: Characterization of Structure and Catalytic Activity

Norhafizah Hj. Jaafar

Mesoporous materials cobalt-supported Si-MCM-41 (Co/Si-MCM-41) with 1wt% and 3wt% loadings of cobalt were prepared via secondary synthesis by treatment of cobalt(II) acetate with Si-MCM-41 at 80°C in aqueous solution and in methanol. The products were characterized by means FTIR, XRD, DRUV-Vis and nitrogen adsorption measurement. The XRD results show that the structure of MCM-41 in methanol is still maintained after the impregnation of cobalt into Si-MCM-41 whereas it becomes partially amorphous after treatment in aqueous solution due to collapse of the silica framework. The result suggests that the collapse of the MCM-41 structure in aqueous solution could be attributed to the presence silanol groups in Si-MCM-41. Interaction of the hydroxyl groups with water molecules was found to facilitate the rate of hydrolysis of the MCM-41 silica framework at the reaction temperature used in this study. Nitrogen adsorption analysis on samples of Co/Si-MCM-41 containing 1wt% and 3wt% cobalt show the presence of mesopores with the average diameter of 2.8 nm and 3.5 nm respectively, and surface areas of higher than 600 $m^2/g$. Generally, the surface area of Si-MCM-41 (1061 $m^2/g$) was significantly reduced after modification with cobalt which indicates the filling of pores of the support by cobalt. Dispersion of the cobalt species on the surface Co/Si-MCM-41 was evidenced by DRUV-Vis spectra which show an absorption band at around 250-270 nm assigned for ionic species of Co(II) and Co(III) in tetrahedral coordination and a wide band at around 350-560 nm for the formation cobalt complexes in octahedral symmetry. However, the study on the catalytic activity of catalyst which was prepared in methanol shows that it was not active as catalyst in the oxidation of phenol to hydroquinone at 60 °C and 90 °C using hydrogen peroxide as oxidant.

## 4.22 Catalytic Activity of Mesoporous Zeolite Molybdenum Oxide Supported MCM-41 in Oxidation of Carbon Monoxide

Idzan Shafina Mohd Idris

Mesoporous zeolites $MoO_3$/Si-MCM-41, $MoO_3$/Al-MCM-41 and $MoO_3$/H-Al-MCM-41 containing 1%, 3%, 5% and 10% w/w Mo were synthesized as catalysts for the oxidation of carbon monoxide. Surface modification of the zeolites were achieved by wet impregnation of ammonium heptamolybdate onto MCM-41 as catalyst support, followed by calcination of the samples at 500 $^{o}$C. Structural characterization of MCM-41 was carried out by means of FTIR spectroscopy and X-ray diffraction (XRD) analysis. The surface properties and the BET surface area of MCM-41 were determined by nitrogen adsorption technique. Catalytic properties of $MoO_3$/Si-MCM-41, $MoO_3$/Al-MCM-41 and $MoO_3$/H-Al-MCM-41 in the oxidation of CO to $CO_2$ were studied using a microreactor and FTIR spectroscopy. The results showed that $MoO_3$ supported MCM-41 catalysts were active in the oxidation of CO with the percentage of conversion higher than 96% at temperature between 400 $^{o}$C and 450 $^{o}$C. XRD analysis showed that the degree of crystallinity of the MCM-41 decreased with increased loadings of $MoO_3$. The MCM-41 phase has become amorphous due to the presence of Mo in the sample. However, the percentage of conversion of CO to $CO_2$ was found to increase when the Mo loadings increased up to 10% w/w.

### 4.23 Application of Mesoporous Catalyst Based on MCM-41 Silica in Epoxidation of Monoterpene and Acetylation of Aldehyde

Rosita Yohana Md. Idrus

Mesoporous molecular sieves Si-MCM-41 and Al-MCM-41 of the molar gel composition $6SiO_2$ : $xAl_2O_3$ (x=0 and 0.6) : 1.5 $Na_2O$ : 1 CTABr : $0.15(NH_4)_2O$: 250 $H_2O$ have been synthesized and used for preparing the MCM-41 supported $MoO_3$ catalysts $MoO_3$/Si-MCM-41 and $MoO_3$/Al-MCM-41 with Mo loading of 1%, 5% and 10% respectively, via wet impregnation with sodium molybdate. All the MCM-41 catalysts were characterized by using FTIR spectroscopy, XRD, nitrogen adsorption measurements and $^{29}$Si MAS NMR spectroscopy. The catalytic activities of H-Si-MCM-41 and H-Al-MCM-41 were tested in acetalization of benzaldehyde with methanol to benzaldehyde dimethylacetal while the $MoO_3$/Si-MCM-41 and $MoO_3$/Al-MCM-41 catalysts were used in the epoxidation of *R*-(+)-limonene to limonene oxide (a mixture of *cis* and *trans*) in the presence of 70% *tert*-butyl hydroperoxide. The products of these reactions have been characterized by gas chromatography-mass spectroscopy (GC-MS). The results of the catalytic testing showed that H-Si-MCM-41 and H-Al-MCM-41 were active and selective in the conversion of benzaldehyde with the selectivity towards benzaldehyde dimethylacetal was greater than 90%. However, $MoO_3$/Si-MCM-41 and $MoO_3$/Al-MCM-41 showed high *R*-(+)-limonene conversion of 70% but lead to low limonene oxide selectivity (about 2.5%) due to formation of by-products.

## 4.24 Surface Acidity Study of Mesoporous Zeolite V/AlMCM-41 and V/Al-MCM-48 using FTIR Spectroscopy

Lim Kheng Wei

Mesoporous zeolite Al-MCM-41 (hexagonal) and Al-MCM-48 (cubic) with molar composition $6SiO_2 : 0.6Al_2O_3 : 1.5Na_2O : 0.55$ CTABr : 112 $H_2O$, were synthesized using sodium silicate as the silica source, sodium aluminate as the aluminium source and cetyltrimethyl ammonium bromide (CTABr) as the surfactant template. Modification of MCM-41 and MCM-48 were carried out by secondary synthesis with ammonium metavanadate to give samples containing 0.1 M, 0.25 M and 0.5 M vanadium. All MCM-41 and MCM-48 samples were characterized by means of FTIR spectroscopy, XRD and nitrogen adsorption measurements. The type of hydroxyl groups and surface acidity (Brönsted and Lewis) of all vanadium containing MCM-41 and MCM-48 were determined by IR spectroscopy using pyridine as the probe molecule. The infrared spectra of both series sample showed the presence of both Lewis and Brönsted acidity. In general, the number of Lewis acid sites was higher than Brönsted acid sites in both series of samples. Both acid sites in V/Al-MCM-48 were stronger than the acid sites in V/Al-MCM-41.

## 4.25 Amine Functionalized MCM-41 as Bronsted Base Catalyst in Knoevenagel Condensation

Noor Ashikin Mohd Yusoff

The recent discovery of the M41S family of molecular sieves opened up new possibilities for preparing catalysts with uniform pores in the mesoporous region. Despite extensive research, few solid Brönsted base catalysts with an analogous mesophase structure have been successfully obtained. In this research synthesis of Brönsted base catalysts had been successfully obtained by functionalization siliceous MCM-41 with primery amine and quaternary ammonium. This project describes the preparation, characterization and catalytic activities of Si-MCM-41 modified with primery amine (OFMS) and quaternary ammonium (SOCM). OFMS catalyst was prepared by grafting 3-aminopropyltrimethoxy silane on the surface of pure silica MCM-41 while SOCM catalyst was obtained through direct synthesis Si-MCM-41 using cetyltrimetylammonium bromide surfactant as template. Characterization of OFMS and SOCM was done using XRD, FTIR spectroscopy, nitrogen adsorption, TG/DTA and $^{13}$C CP/MAS NMR techniques. The possibility of OFMS and SOCM as Brönsted base was studied in the oxidation of benzene to phenol at 70 $^{o}$C. The catalysts were also found to be active for the Knoevenagel condensation between benzaldehyde and malonic acid to give cinnamic acid. The products of benzene oxidation and Knoevenagel condensation were characterized by GC and GC-MS techniques. The analysis of Knoevenagel condensation showed that, the percent conversion of benzaldehyde for both SOCM and OFMS catalysts were between 30% and 40% at 120$^{o}$C. The results also gave high selectivity of cinnamic acid for SOCM and OFMS with 79.28% and 100% respectively after 3 hours of reactions.

## 4.26 Amine Functionalized MCM-41 as Brönsted Base Catalyst in Aldol Condensation of Aldehyde and Ketone

Mohd Faisal Bin Ab. Latib

The preparation, characterization and catalytic activities of Si-MCM-41 modified with primary amine (OFMS) and quaternary ammonium (SOCM) were investigated. Mesoporous material Si-MCM-41 and SOCM of molar ratios $6SiO_2$: 1CTABr: $1.5Na_2O$: $0.15(NH_4^+)$: 0.25 $H_2O$ have been prepared. The properties of Si-MCM-41 were modified by functionalization of Si-MCM-41 with primary amine and quaternary ammonium surfactant to create Brönsted base catalysts. The organic functionalized molecular sieves MCM-41 (OFMS) were prepared by grafting of 3-aminopropyltrimethoxysilane on the surface of Si-MCM-41. The amine functionalized MCM-41 catalysts were characterized by FTIR spectroscopy, XRD, nitrogen adsorption, TGA/DTA and $^{13}C$ CP/MAS NMR spectroscopy and their catalytic were compared to those of Cs-MCM-41 and Al-MCM-41-amine. The activities of SOCM and OFMS as base catalysts were tested in aldol condensation of benzaldehyde with acetophenone to give chalcone, a biological compound for antibacterial, antifungal, antitumoral and anti-inflammatory properties. However, the catalytic study showed that chalcone was not produced in the reaction due to poisoning of the strong basic sites by benzoic acid, a side-product formed by the oxidation of benzaldehyde. In another test reaction, the base-catalyzed nitroaldol condensation of 2-chlorobenzaldehyde with nitroethane gave the aimed product, 1-(2-chlorophenyl)-2-nitropropene, confirming that OFMS is basic in character.

## 4.27 Synthesis and Characterization of Mesoporous Base Catalyst Cs-MCM-41

Siti Marlia Abd Rahim

Pure siliceous MCM-41 have been reported to possess properties of excellent properties of catalyst support as they have high surface area (more than 1000 $m^2g^{-1}$), uniform hexagonal mesopores that can be tailored in the range between 1.6 and 10 nm and high thermal and hydrothermal stability. In the present study, mesoporous material Si-MCM-41 is synthesized in molar ratio of 6 $SiO_2$ : 1 CTABr : 1.5 $Na_2O$ : 0.15 $(NH_4)_2O$ : 250 $H_2O$ at 97 ˚C as catalyst support for Cs-MCM-41. Wet impregnation method I used to prepare base catalyst by grafting cesium acetate onto the surface of Si-MCM-41 with percentage loading of 6, 9 and 12wt (w/w) followed by calcination at 550˚C. The samples were characterized by means of Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), diffuse reflectance UV-Vis (DRUV-Vis), and gas chromatography (GC). In the ion exchange method, an aqueous solution of cesium acetate (0.25 M) was mixed with Si-MCM-41, and the product was calcined at 550 ˚C. The activity of the catalyst is tested in aldol condensation of benzaldehyde and acetophenone to give chalcone at 75 ˚C.

## 4.28 Mesoporous Silica MCM-48 Containing Lanthanum as Active Catalyst for Claisen-Schmidt Condensation of Aromatic Compounds

Leong Siew Ming

In this study, mesoporous materials La-MCM-48 with cubic pore structure have been prepared via ion-exchange or wet impregnation methods. In the ion-exchange method, purely siliceous Si-MCM-48 was treated with various concentration of $La(NO_3)_3.6H_2O$ solutions (0.1 M, 0.25 M, 0.5 M and 1.0 M) at 60 ºC for 3 h. Wet impregnation of mesoporous Si-MCM-48 was carried out by loading 3, 5 and 10 wt% of lanthanum, respectively, in mesoporous Si-MCM-48 at room temperature for 16 h. Each sample was characterized by XRD, FTIR, nitrogen adsorption measurement; FESEM and UV-Vis diffuse reflectance spectroscopy. The results show that the ion-exchanged lanthanum samples have higher crystallinity and higher surface area (> 800 $m^2/g$) than those lanthanum containing samples prepared by wet impregnation technique. The samples also retained their structural integrity after the post-synthesis modification with lanthanum. The ion-exchanged lanthanum samples were tested as catalysts in Claisen-Schmidt condensation of acetophenone with benzaldehyde at 150 ºC for 3 h to produce chalcone, a biological compound with potential antibacterial, antifungal, anti-malarial and anti-inflammatory properties. The results of the catalytic study show that chalcone was formed due to the presence of both Lewis acid and basic sites in the catalyst. Among the samples, the ion-exchanged sample prepared using 0.25 M lanthanum nitrate solution was the most active catalyst towards Claisen-Schmidt condensation, giving around 33.3% conversion of acetophenone and 77.8% selectivity to chalcone.

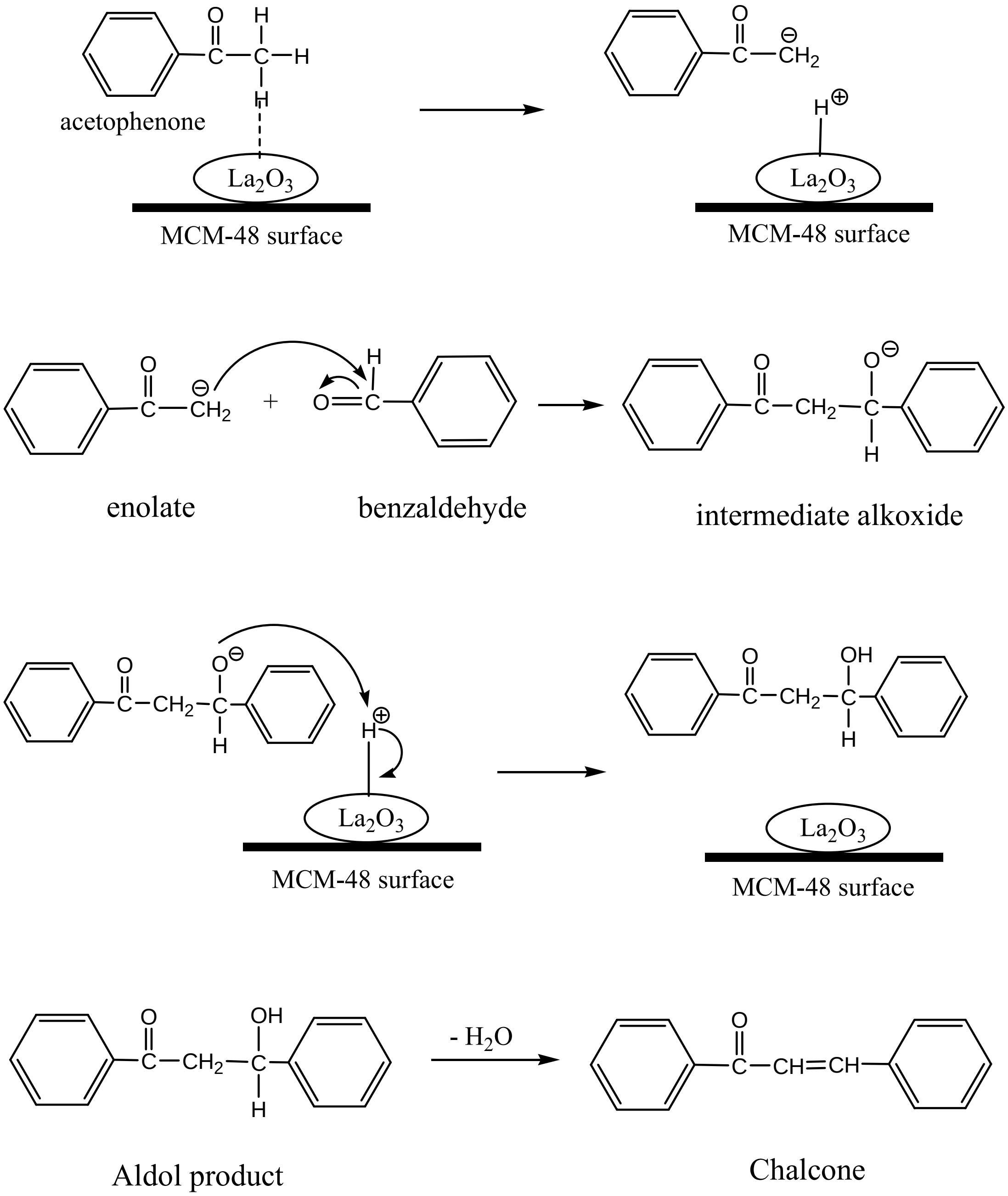


Figure 4.15: Mechanism proposed for Claisen–Schmidt condensation showing the role of La-MCM-48 as Lewis base catalyst.

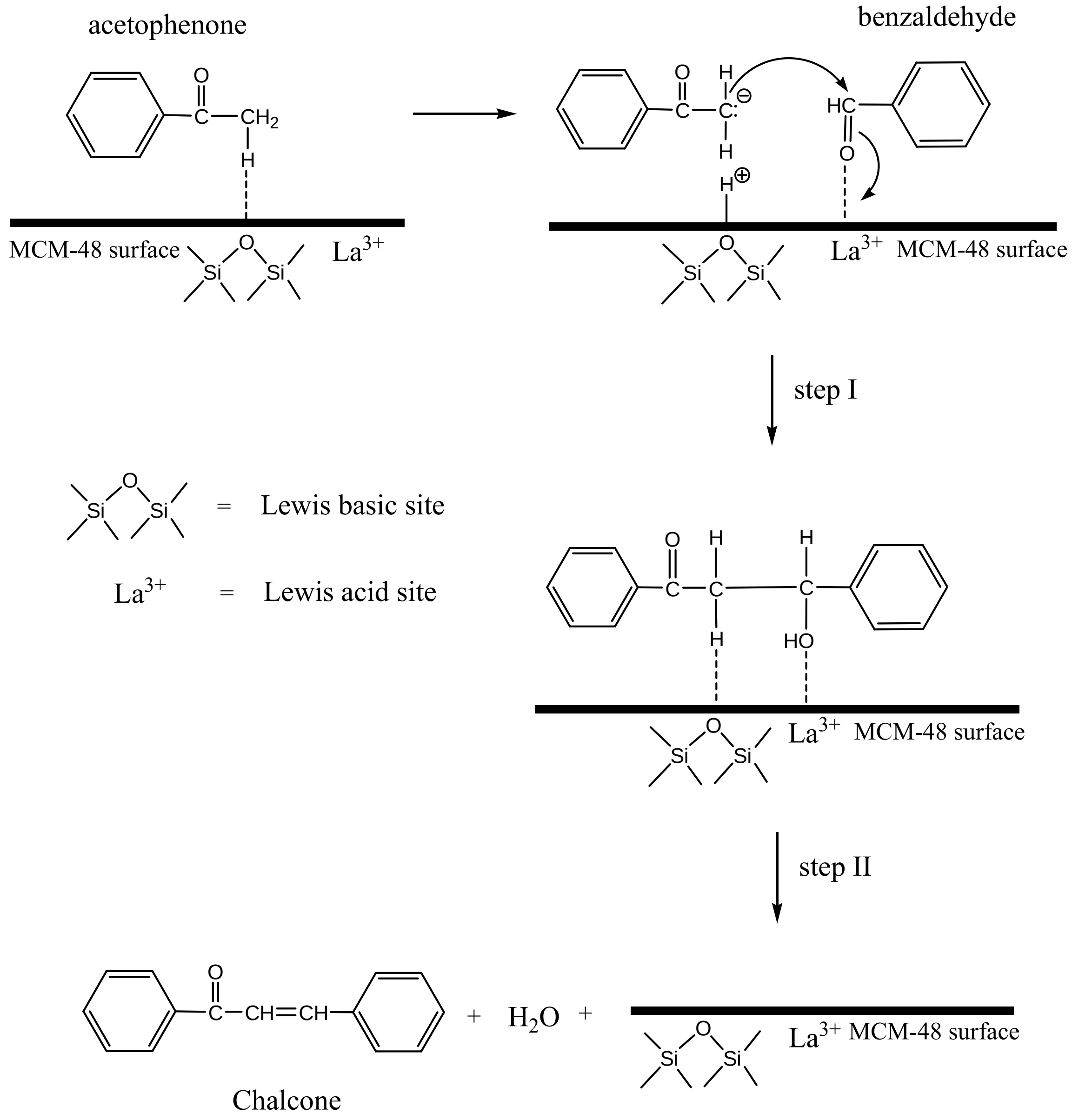


Figure 4.16: Mechanism proposed for Claisen–Schmidt condensation showing the role of La-MCM-48 as Lewis acid catalyst.

### 4.29 Fe (III) Supported Si-MCM-41 as Lewis Acid Catalyst in Friedel-Crafts Acylation

Noor Aisyah Ahmad Shah

A series of supported Lewis acid catalyst was prepared by incorporating anhydrous $FeCl_3$, $FeCl_3.6H_2O$ and $Fe(NO_3)_3.9H_2O$ into mesoporous molecular sieves Si-MCM-41 as support. Pyridine adsorption and FTIR spectroscopy were used to determine the nature, amount and strength of the acid sites in the Fe(III)/ Si-MCM-41 materials. Infrared spectra after pyridine adsorption of the samples showed that only Lewis asic sites were present. The catalyst synthesized from anhydrous $FeCl_3$ exhibited higher and stronger Lewis acid site compared to others. The catalytic activity of this catalyst as heterogeneous Lewis acid was evaluated in Friedel-Crafts acylation of 2-methoxynapthalene in nitrobenzene. Acylation of 2-methoxynapthalene was found to occur at C-1, C-6 and C-8 positions. Acylation of 2-methoxynapthalene at C-6 position is of particular interest because this derivative is useful in production of anti-flammatory agent, Naproxen. The use of Fe(III) supported on Si-MCM-41 catalyst for acylation of 2-methoxynapthalene gave high conversion and high selectivity towards 6-acetyl-2-methoxynapthalene at 100 $^oC$ by using acetyl chloride as acylation agent. The migration of the acyl group from the C-1 to the C-6 position and protiodecylation of acyl group at C-1 position could easily occur due to the present of stable Fe(III) species on Si-MCM-41 support. The use of mesoporous molecular sieves Si-MCM-41 has also increased the selectivity of the product towards 6-acetyl-2-methoxynapthalene.

## 4.30 Iron (III)-Porphyrin Immobilized On Mesoporous Al-MCM-41 and Polymethacrylic Acid as Catalysts For The Single-Step Synthesis Of Phenol From Benzene

Helda Hamid

Mesoporous molecular sieve Al-MCM-41 with Si/Al=20 and polymethacrylic acid (PMAA) were used as supports for the immobilization of bulky iron(III)-5,10,15,20-tetra-(4-pyridyl) porphyrin (Fe-TPyP). Metalloporphyrin of Fe(III) was encapsulated inside the mesopores of the ordered structure of Al-MCM-41 by sequential synthesis of Fe-TPyP via treatment of $FeCl_3$ with 5,10,15,20-tetra-(4-pyridyl) porphyrin (TPyP), followed by encapsulation of Fe-TPyP. Fe-TPyP complexes were also successfully encapsulated into PMAA by polymerizing methacrylic acid (MAA) with a cross-linker around the Fe-TPyP complexes. The materials obtained were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Ultraviolet Visible Diffuse Reflectance (UV-Vis DR), Electron Spin Resonance (ESR), Luminescence and $^{13}C$ CP/MAS NMR spectroscopies, Thermogravimetric Analysis (TGA) and elemental analysis. The powder XRD data confirmed that the ordered structure of mesoporous Al-MCM-41 remained intact after encapsulation process. Characterization of Fe-TPyP composite with Al-MCM-41 and PMAA using FTIR, UV-Vis DR and ESR confirmed that the structure of Fe-TPyP in inorganic and polymer supports is similar with bare Fe-TPyP. The specific interaction of Fe-TPyP in Al-MCM-41 and/or PMAA was studied by ESR, $^{13}C$ CP/MAS NMR and Luminescence spectroscopies. The ESR spectra of Fe-TPyP/Al-MCM-41 and Fe-TPyP/PMAA composites showed that there is a shift towards a higher g-value confirming the interaction between Fe-TPyP and supports is occurred. By quenching of the luminescence spectra of Fe-TPyP/PMAA with various concentration of Fe-TPyP, it is evidenced that there is the interaction between Fe-TPyP and PMAA. Further evidence of interaction was corroborated by $^{13}C$ CP/MAS NMR spectra with show that the peak of carboxyl of PMAA is shifted to higher magnetic field. Single-point BET surface area analysis was used to determine specific surface area of the composites.

It is revealed that the surface area of Fe-TPyP/Al-MCM-41 composites is decreased with an increase in Fe-TPyP, suggesting the encapsulation of the complex in the pores of Al-MCM-41 has been achieved. With mesoporous molecular sieve (Al-MCM-41) and the polymer (PMAA) as supports, the immobilized iron-porphyrin system has demonstrated excellent activity for the single-step synthesis of phenol from benzene under mild reaction conditions. The effect of reaction time, solvent, amount of Fe-TPyP loading, temperature and the performance of the recovered catalysts have been studied. The immobilized iron-porphyrin in PMAA (Fe-TPyP/PMAA) gives a higher activity compared to Fe-TPyP supported on Al-MCM-41 (Fe-TPyP/Al-MCM-41). However, the product selectivity of Fe-TPyP/PMAA is not as good as that of Fe-TPyP/Al-MCM-41. Thus, it is reasonable to assume that the hydrophobic nature of Fe-TPyP/PMAA would for the high activity, while the rigid, ordered structure of Fe-TPyP/Al-MCM-41 would contribute towards the high selectivity in the single-step synthesis of phenol from benzene in the present study.

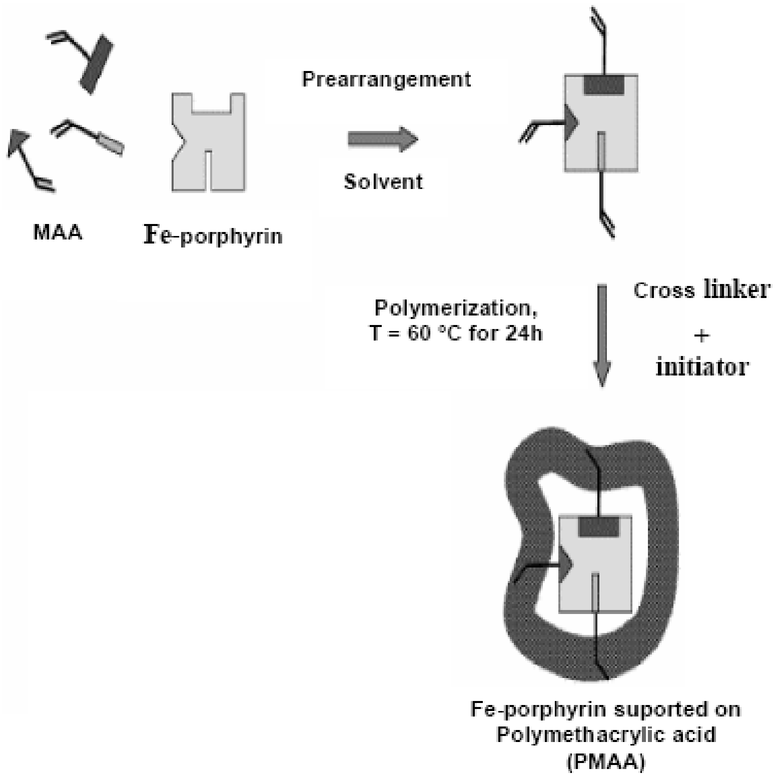


Figure 4.17: Schematic representation of the procedure of synthesis of composite Fe-porphyrin-polymethacrylic acid.

## 4.31 Synthesis, Characterization and Catalytic Activity of μ-Oxo Bridged Dinuclear Iron 1, 10-Phenanthroline Incorporated In MCM-48

Lau Su Chien

A series of μ-oxo bridged dinuclear iron 1,10-phenanthroline complex (Fe-phen) supported MCM-48 mesoporous molecular sieves with 0.1 mmol, 0.3 mmol, 0.5 mmol and 0.7 mmol loadings of the complex have been synthesized by post-synthesis modification method. The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption measurement, diffuse reflectance ultraviolet-visible spectroscopy (UV-VIS DRS), thermogravimetric analysis (TGA), atomic absorption spectroscopy (AAS) and electron spin resonance (ESR). The XRD results showed that the long range order of MCM-48 structure is maintained even after the incorporation of Fe-phen. The increase of unit cell parameter showed that encapsulation of Fe-phen in MCM-48 has caused the expansion of the unit cell. The UV-VIS-DRS spectra for Fe-phen-MCM-48 showed three peaks at 230 nm, 265 nm and 370 nm which correspond to the $\pi \rightarrow \pi^*$ transitions of phenanthroline ligands, charge transfer from μ-oxo to Fe orbital and d-d transitions of Fe, respectively. The catalytic activity of Fe-phen-MCM-48 was tested in the oxidation of 1-naphthol with aqueous hydrogen peroxide as oxidant. Gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) analyses showed that the only reaction product was 1,4-naphthoquinone after 20 hours of reaction at 80 $^{o}$C. The conversion of 1-naphthol for the first use of catalyst was in the range of 65 – 75%. Fe-phen-MCM-48 showed its reusability with 44 – 51% conversion of 1-naphthol. This may be due to the leaching of Fe-phen into the solution during reaction.

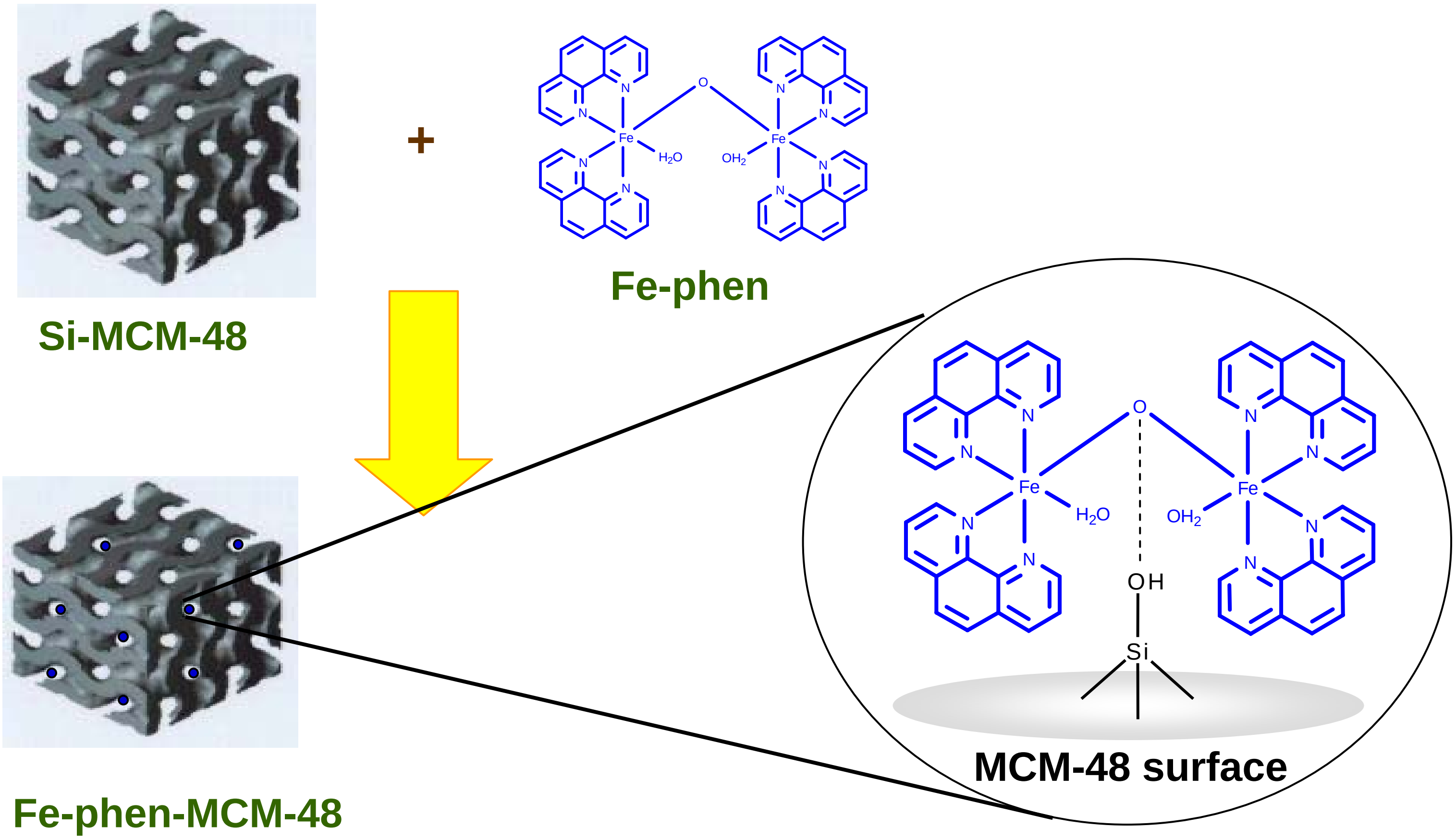


Figure 4.18: Immobilization of μ-oxo bridged dinuclear iron 1,10-phenanthroline complex (Fe-phen) in MCM-48 mesoporous molecular sieves by post-synthesis modification method.

## 4.32 Design and Application of Chiral Solid Catalysts Synthesized by Molecular Imprinting Method with Polyaminoacid as Chiral Promoter for Producing Pharmaceutical Products

Lim Kheng Wei

Heterogeneous asymmetric catalysis remains an exciting research field in chiral catalysis since the heterogeneous catalyst can be separated easily from the reaction mixture compared to conventional homogeneous catalyst. The aim of this research is to develop a novel heterogeneous asymmetric catalyst using amino acid as chiral promoter. The catalysts were synthesized by attachment of amino acids such as L-glutamic acid, L-leucine and L-phenylalanine onto the hydrophilic part of hydrolyzed octadecyltrichlorosilane (OTS). The short-range order structure of silicon and organic groups in the catalysts has been characterized by solid-state $^{29}$Si and $^{13}$C cross-polarization magic-angle-spinning (MAS) NMR spectroscopies, respectively. The solid state MAS NMR results showed that the amino acids interacted with hydrolyzed OTS. This phenomenon was supported by $^{13}$C NMR spectra which showed the peaks of L-glutamic acid, L-leucine and L-phenylalanine were shifted towards a higher magnetic field. It was confirmed by $^{29}$Si NMR spectra which showed the peaks of cross-linked –(OH)Si(R)-O-(OH)Si(R)- (R=octadecyl group) in amino acid-hydrolyzed OTS whereas those of R–Si≡(OSiR)$_3$ were not present. This result suggested that the amino acid was attached via cross-linked –(OH)Si(R)-O-(OH)Si(R)- of the hydrolyzed OTS. The amino acid-hydrolyzed OTS materials were used as catalysts for the asymmetric hydration of epoxycyclohexene to yield two diastereoisomers, namely (1R,2R)-trans-1,2-cyclohexenediol and (1S,2S)-trans-1,2-cyclohexenediol as well as cis-1,2-cyclohexenediol.

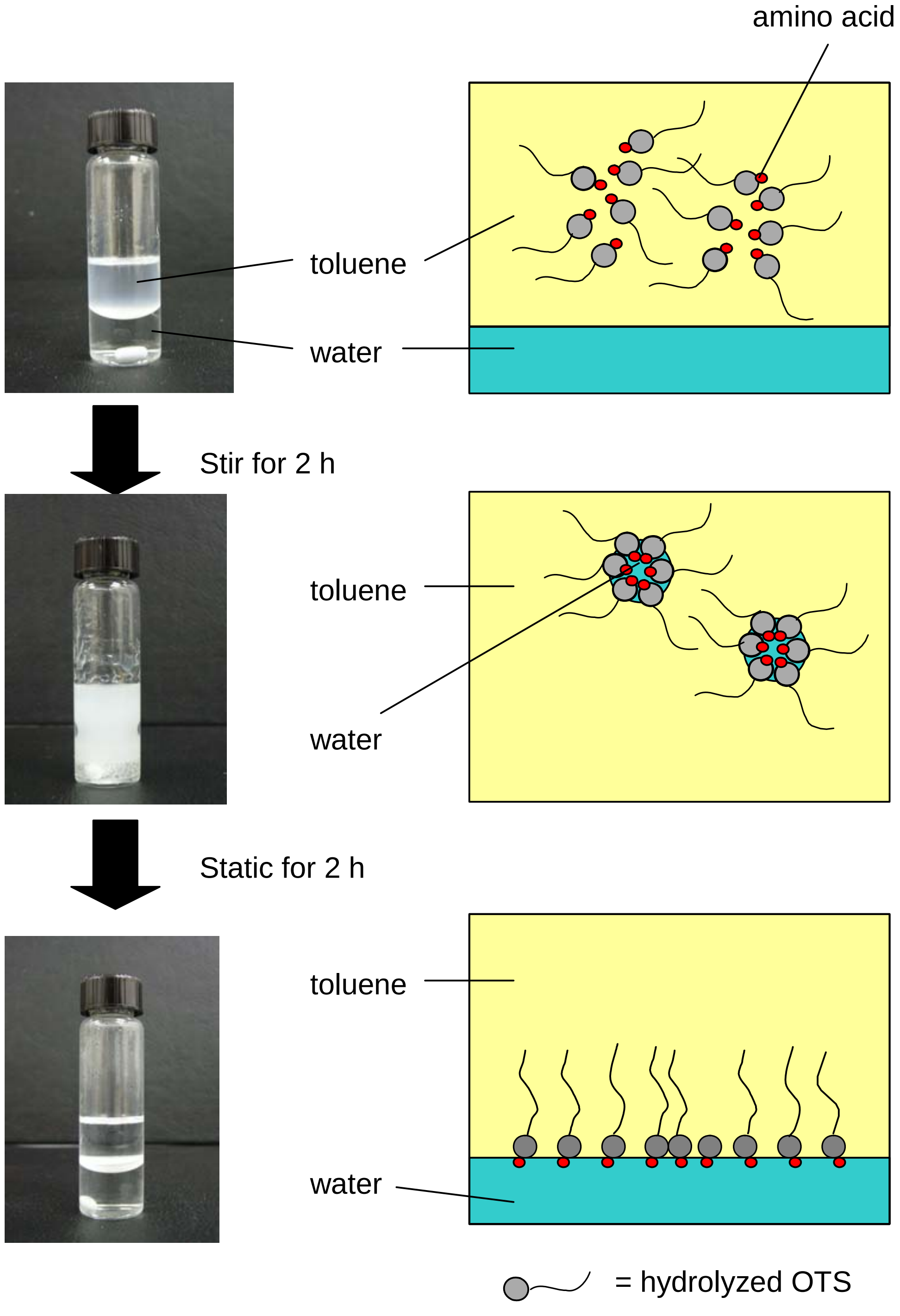


Figure 4.19**:** Dispersibility of hydrolyzed OTS-Glu in a mixture of toluene and water under stirring and static conditions.

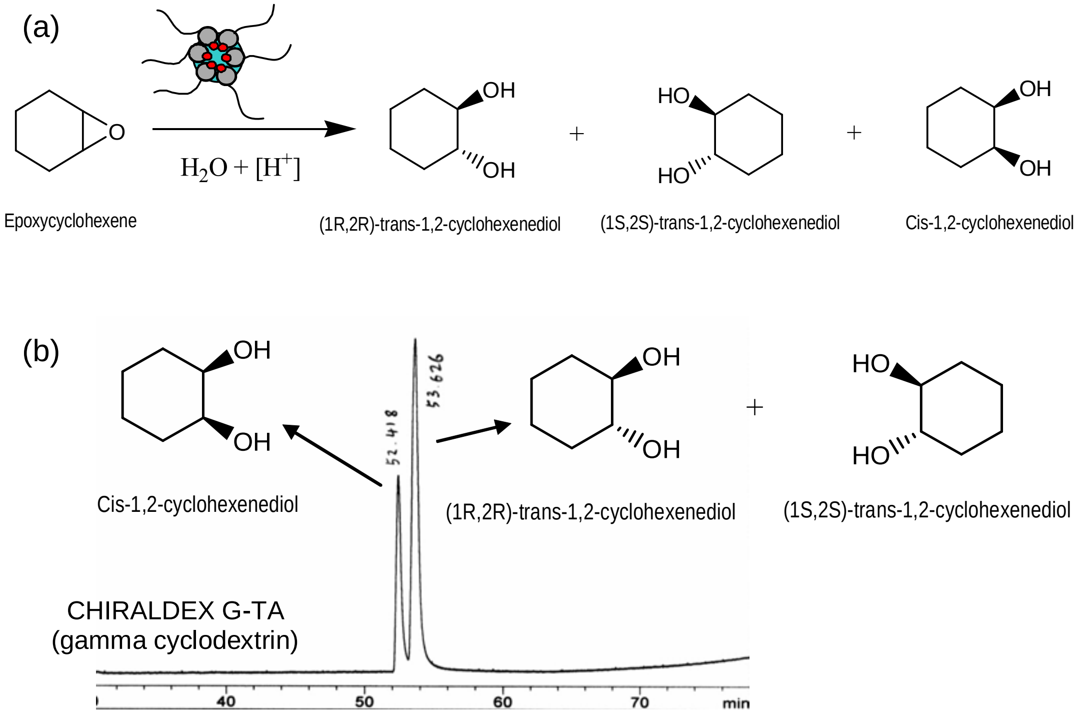


Figure 4.20: (a) Possible products of hydration of epoxycyclohexene and (b) example of GC chromatogram of products identified by using Chiraldex G-TA column.

## 4.33 Synthesis of Ordered Structure Polystyrene with Encapsulated Cadmium Sulfide Nanoparticles

Eriawan Rismana

Template synthesis is commonly used tool in preparation of ordered structure material. The aim of this research was to design and prepare a polymeric material containing semiconductor nanoparticles with novel ordered structure. Ordered structure polystyrene (PS) has been prepared by miniemulsion polymerization using cross-linker polyethyleneglycol dimethacrylate acid (PEDMA) with encapsulated semiconductor cadmium sulfide (CdS) nanoparticles as template and active site for photocatalysis and other applications. In this research, the semiconductor CdS nanoparticles were synthesized by reverse micelles in quaternary miniemulsion. The polymer resin has been characterized using FTIR spectroscopy in which the spectra of CdS-PS-PEDMA showed an excellent agreement with that of additional peaks due to PS and PEDMA. The onset of Absorption wavelength from the diffuse reflectance UV-Visible (DR UV) spectra of CdS nanoparticles encapsulated inside polystyrene was blue-shifted compared to those of CdS nanoparticles in miniemulsion and bulk CdS. Based on the onset wavelength, the particles size of CdS estimated using the Brus equation was approximately 4 nm. The amount of CdS inside polystyrene without acid-etching from the analysis of cadmium using Inductively Couple Plasma (ICP) is 1328.24 mg/kg. The X-ray diffraction analysis of CdS encapsulated polystyrene showed a strong peak at 2.3 degree 2-theta suggesting that the presence of CdS nanoparticles within the polystyrene matrix has resulted in ordered structure polymer. This phenomenon was supported from the data of CdS analysis after acid-etching process. The amount of CdS in polystyrene after acid-etching was found to be smaller than before acid-etching. The disappearance of peaks in the XRD pattern indicated that the acid-etching process has removed CdS nanoparticles from the polymer leading to collapse of the ordered structure of polystyrene.

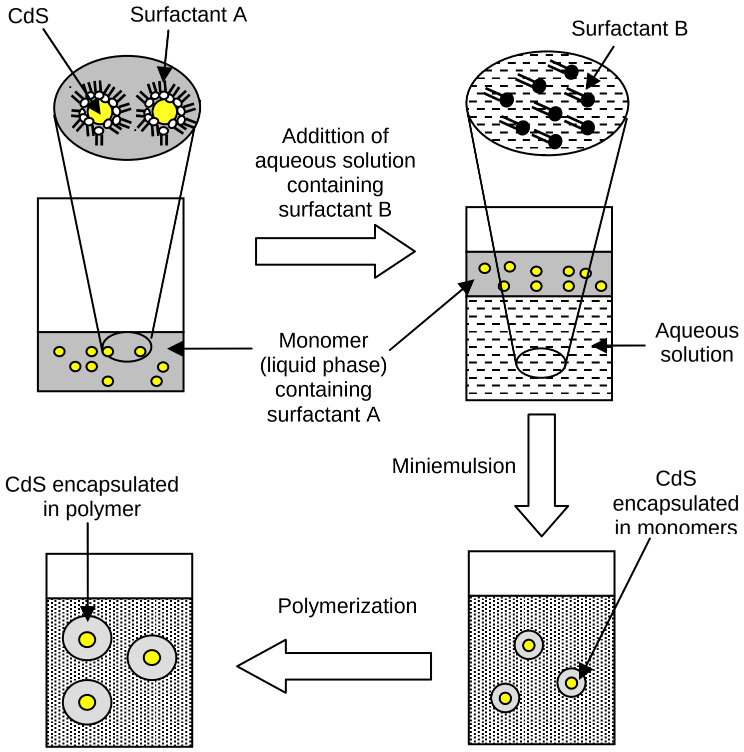


Figure 4.21: General route in preparation of ordered structure polymer with encapsulated CdS nanoparticles by minielmusion method.

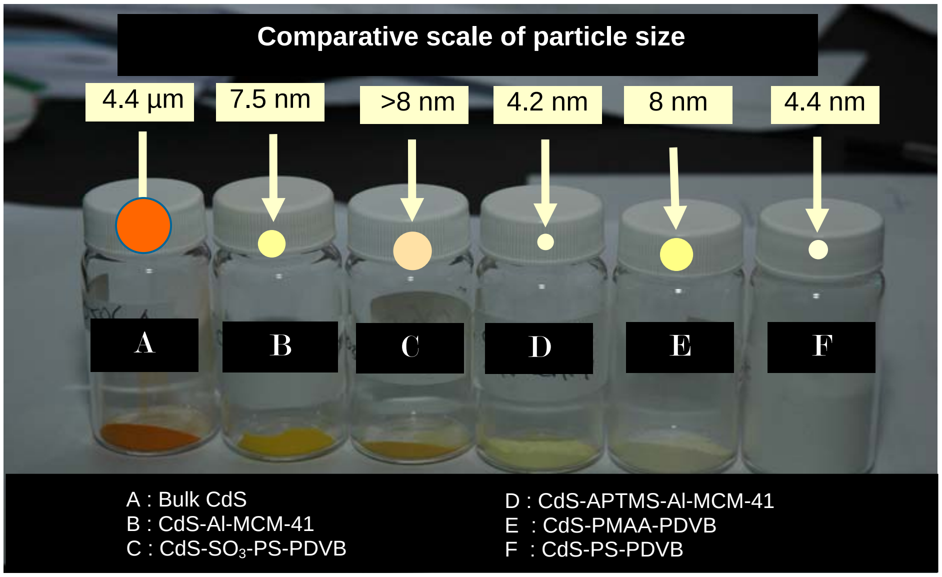


Figure 4.22: Photographs of materials containing different-sized CdS nanoparticles inside polymers and mesoporous Al-MCM-41 matrices.

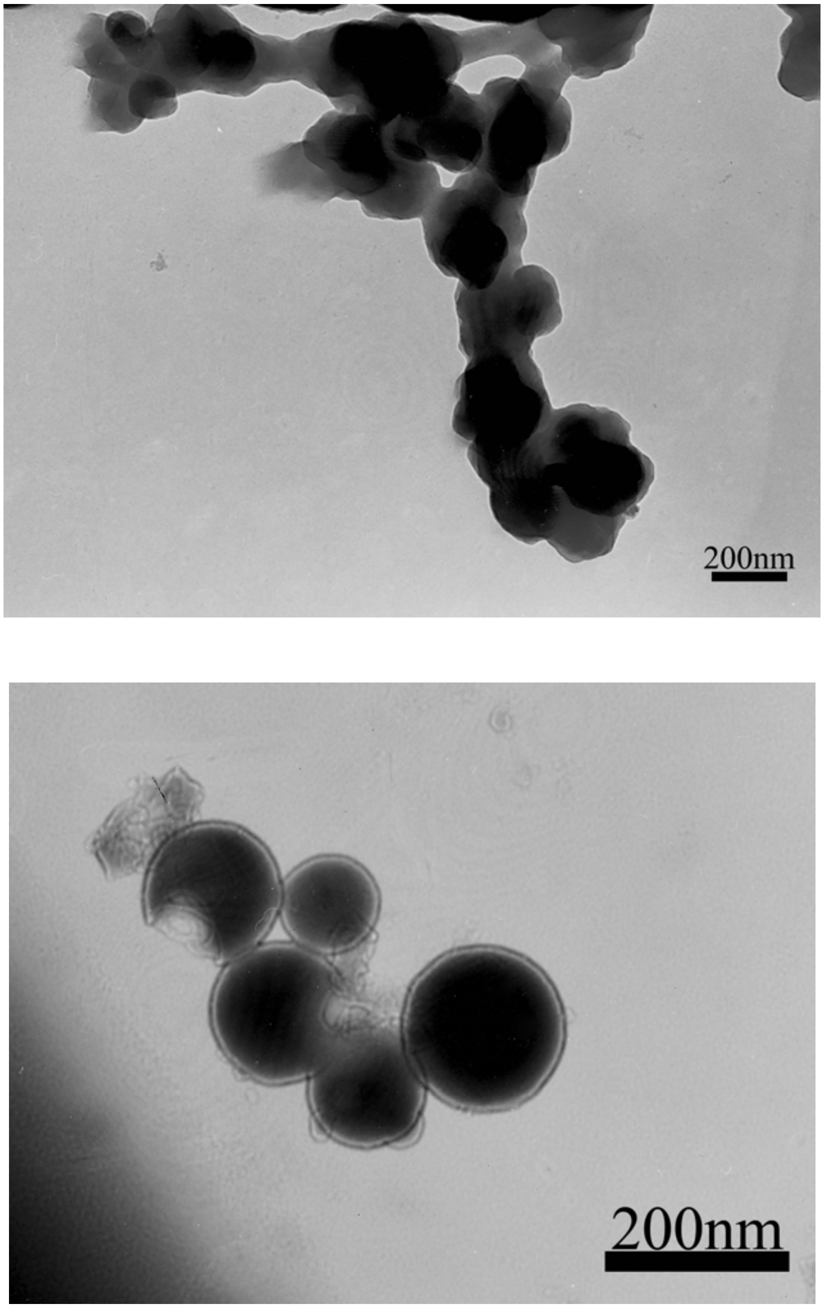
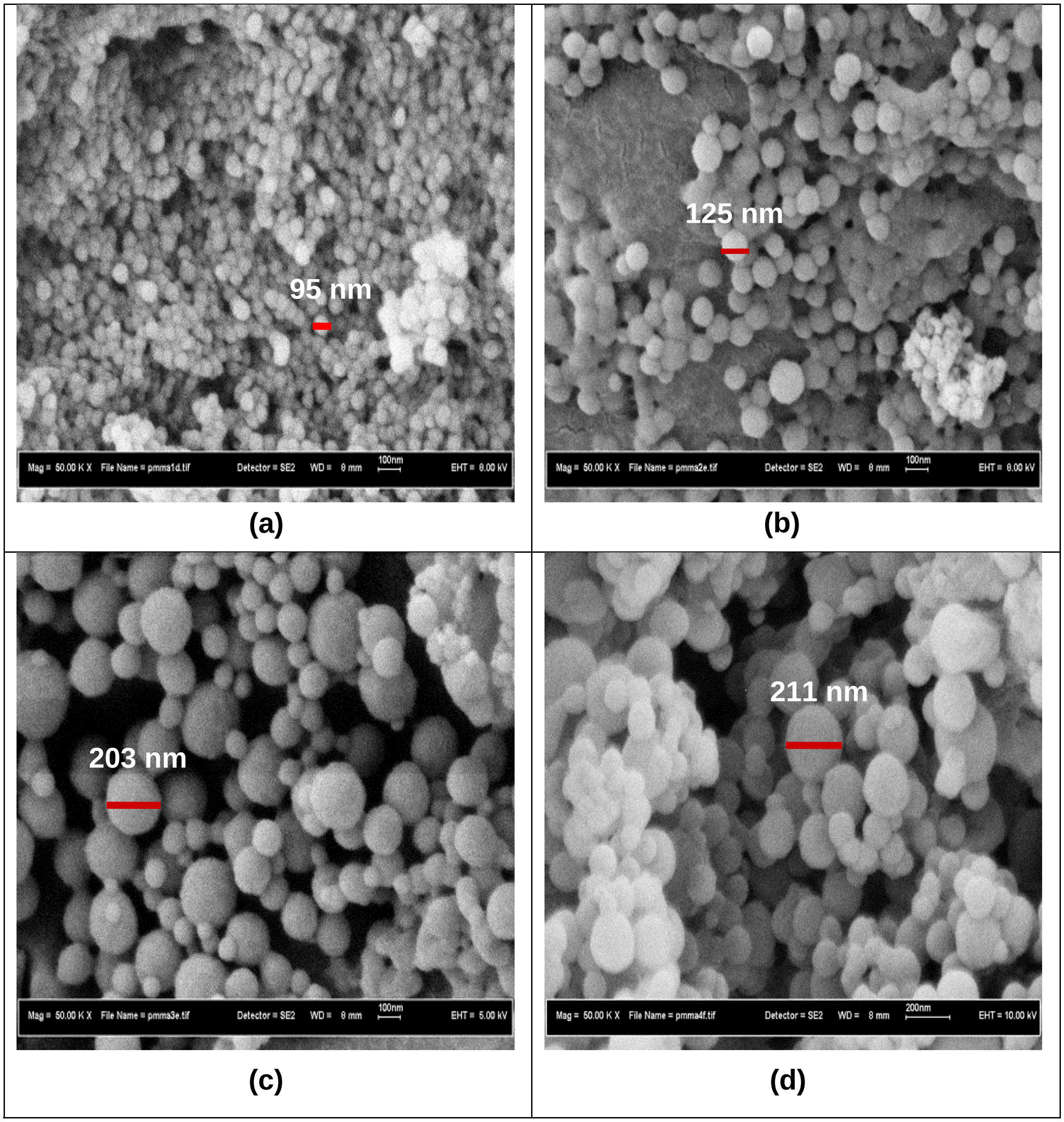


Figure 4.23: Transmission Electron Micrograph of ordered structure polystyrene encapsulated CdS nanoparticles.

## 4.34 Synthesis of Poly(methylmethacrylate)-MCM-41 Nanocomposite via Mini-Emulsion Polymerization

Siti Aisyah A. Bakar

Synthesis of polymer nanocomposites has been attracting a lot of attention because of its potential to improve physical features of materials such as stiffness, strength and heat resistance. Recently, the miniemulsion polymerization has been reported as the best method to obtain nanocomposite particles. The MCM-41/poly(methylmethacrylate) polymer nanocomposite particles were synthesized through miniemulsion polymerization by using sodium dedocyl sulphate surfactant (SDS), 2-propanol co-stabilizer, water and azobisisobutyronitrile (AIBN) as initiator. X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Thermogravimetry Analysis (TGA), Fourier Transform Infrared (FTIR), Dielectric Constant ($\xi r$) and Nitrogen Adsorption were used to characterize each sample of the polymer nanocomposites. In this study, the effect of co-stabilizer on the size of polymer nanocomposite shows that the size of polymer nanocomposite was influenced by the quantity of 2-propanol used in miniemulsion mixture. The result shows that the particle size of polymer nanocomposite increased with the increasing of 2-propanol. The increase in polymerization temperature from 65 °C to 80 °C was successful in increasing the yield of the polymer nanocomposite. The effect of particle size to the dielectric constant ($\xi r$) shows that the bigger the size of nanoparticle size, the dielectric constant becomes smaller.



(a) (b)

(c) (d)

Figure 4.24: FESEM images of Polymer/MCM-41 nanocomposites. (a) PMMA-MCM-41 (0 wt% 2-propanol), (b) PMMA-MCM-41 (1.8 wt% 2-propanol), (c) PMMA-MCM-41 (3.6 wt% 2-propanol) and (d) PMMA-MCM-41 (5.4 wt% 2-propanol)

## 4.35 Polyethylene Oxide-MCM-41 and Polyaniline-MCM-41 Nanocomposites Physicochemical and Conducting Properties

Norizah Bt. Abdul Rahman

Polymer nanocomposites (PNC) is one of the exciting developments in material science today possess enhanced and novel properties not exhibited by the individual organic and inorganic materials. The physicochemical and conducting properties of two types of polymer nanocomposites, *i.e.*, PEO/Li-MCM-41 and PANI/MCM-41 have been investigated in this thesis. The aim was to obtain a more detailed understanding of how the combination of polymers with the mesoporous MCM-41 is related to the conducting properties. Melt and solution intercalation methods have been used to synthesize PEO/Li-MCM-41. Before PEO is combined with MCM-41, several modifications of MCM-41 have been done such as ion exchange of MCM-41 with LiCl and silylation of MCM-41 with trimethylchlorosilane (TMCS) and functionalization of MCM-41 with sulfonic acid. The PNC obtained were characterized by X-ray diffraction (XRD), infrared (IR) spectroscopy, scanning electron microscopy (SEM), thermal analysis and chemical analysis followed by $^{27}$Al, $^{7}$Li and $^{13}$C/CP MAS NMR spectroscopy. It is confirmed that the structure of MCM-41 remains intact after composite with polymers. The results from the study have proven that the PNC possesses conducting properties. It is revealed that the conductivity of PANi/MCM-41 is very much higher than those of PEO/Li$^{+}$-MCM-41 since PEO is a polymer electrolyte and PANI is a conducting polymer. It is expected that the combination of PEO-MCM-41 cause an increased conductivity by intercalation of PEO inside the pore of MCM-41. However, it is demonstrated that unmodified Li-MCM-41 exhibit conductivity similar to the PNC. The NMR results suggested that occurring the interfacial interactions between the PEO and Li-Al-MCM-41 is insufficient to improve conductivity of the PEO/Li-MCM-41. In other hand, PANi/MCM-41 nanocomposite which was obtained by *in situ* polymerization method showed an interesting thermal stability of conductivity properties. It is revealed that although conductivity of PANI reduces after addition of MCM-41, its thermal stability of conductivity was improved.

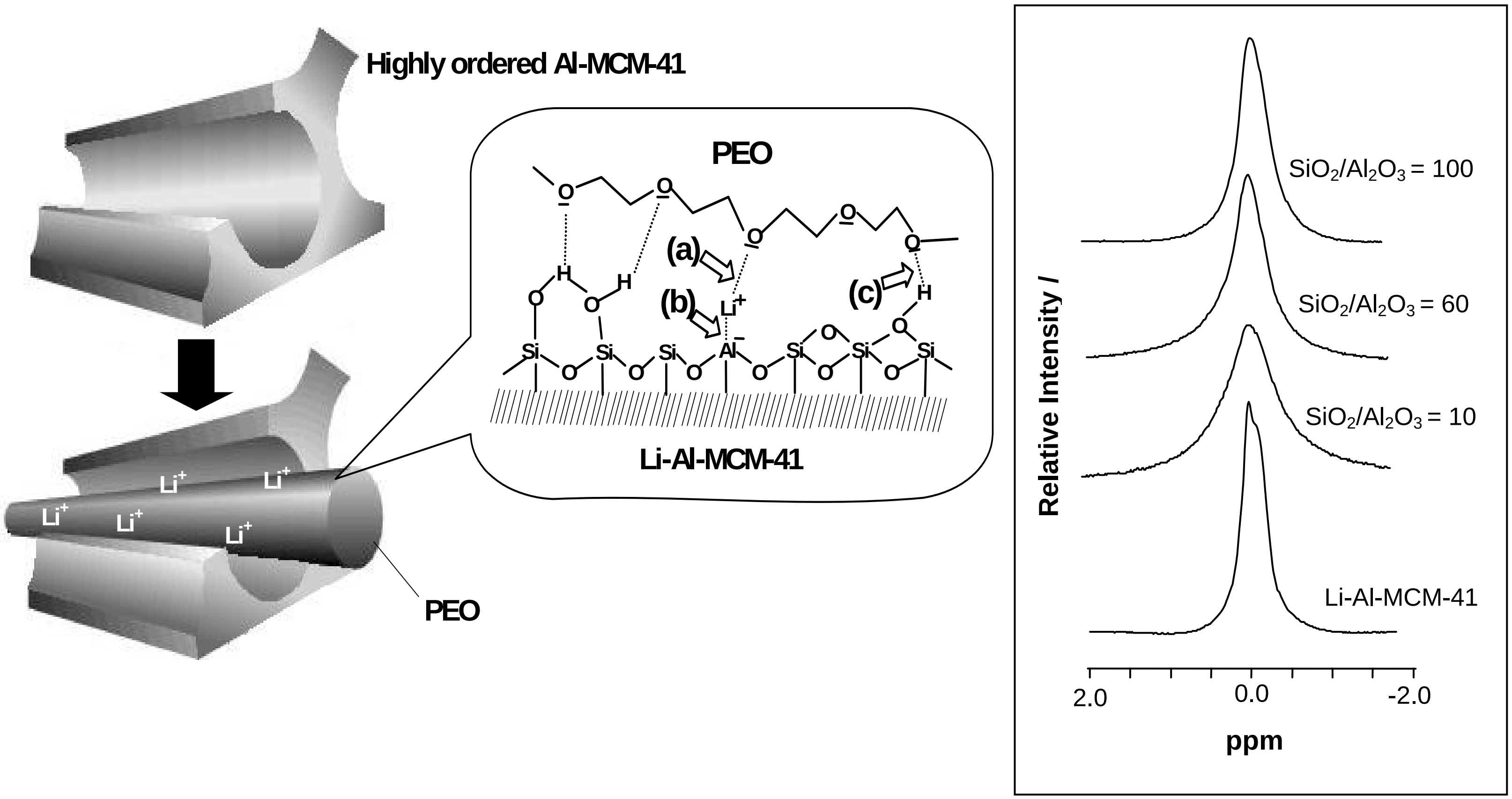


Figure 4.25: Proposed intermolecular interactions of polyethylene oxide (PEO) segments with Li-Al-MCM-41 surface groups. The *dashed lines* indicate possible hydrogen-bond donating (MCM-41)/hydrogen-bond accepting and Al-Li-O interaction sites. The degree of the electrostatic interaction of (c) and (b) is larger than (a). This was proved by the $^7$Li MAS NMR spectra of Li-Al-MCM-41 ($SiO_2/Al_2O_3 = 10$) and PEO/Li-Al-MCM-41 with various $SiO_2/Al_2O_3$ ratios.

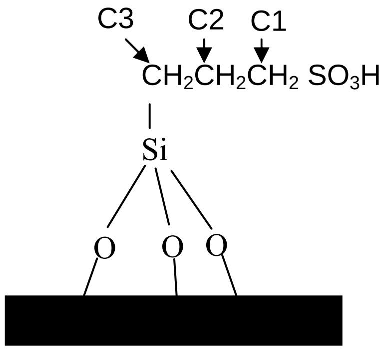


Figure 4.26: The proposed structure of Si-MCM-41 functionalized sulfonic acid, Si-MCM-41SO$_3$H

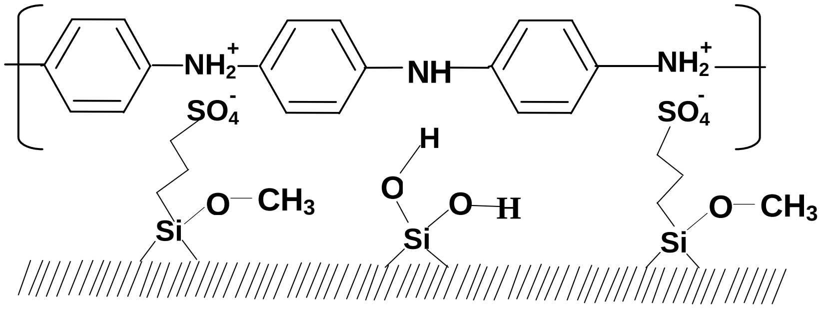


Figure 4.27: The propose interaction between polyaniline and Si-MCM-41SO$_3$H in PANI/Si-MCM-41SO$_3$H nanocomposite.

## 4.36 Synthesis and Characterization of Conducting Polymeric Nanocomposite Poly(Methyl Methacrylate)/Lithium-Exchanged Al-MCM-48

Soh Wei Kian

Polymeric nanocomposite is of great interest in research due to its potential in providing enhanced properties when compared to the pure polymer or silicate species itself. In the synthesis of this nanoscale material via the solution intercalation method, MCM-48, a member of the M41S family of mesoporous materials, with large and twisted channel, has been chosen as the inorganic host for polymer incorporation. Organic modification has been performed to increase the surface hydrophobicity of MCM-48 in order to allow the diffusion of polymer chains into the cavities to form the polymeric nanocomposite. A series of polymer nanocomposites with different PMMA content based on weight ratio were synthesized. The nanocomposites were characterized using XRD, FTIR spectroscopy, $^{13}C$ CP/MAS solid states NMR ad impedance spectroscopy. The electrical properties of poly(methyl methacrylate)/Li-exchanged Al-MCM-48 at ambient temperature has been studied as an indirect means to reveals the interactions between silica walls, lithium ion and PMMA chains. Incorporation of PMMA up to five weight percent into MCM-48 enhanced the ionic conductivity of the nanocomposites. It was proposed that $Li^+$---O=C interactions were present in the nanostructures with the lithium ion acting as intermediary in the interaction between silica wall and PMMA chains.

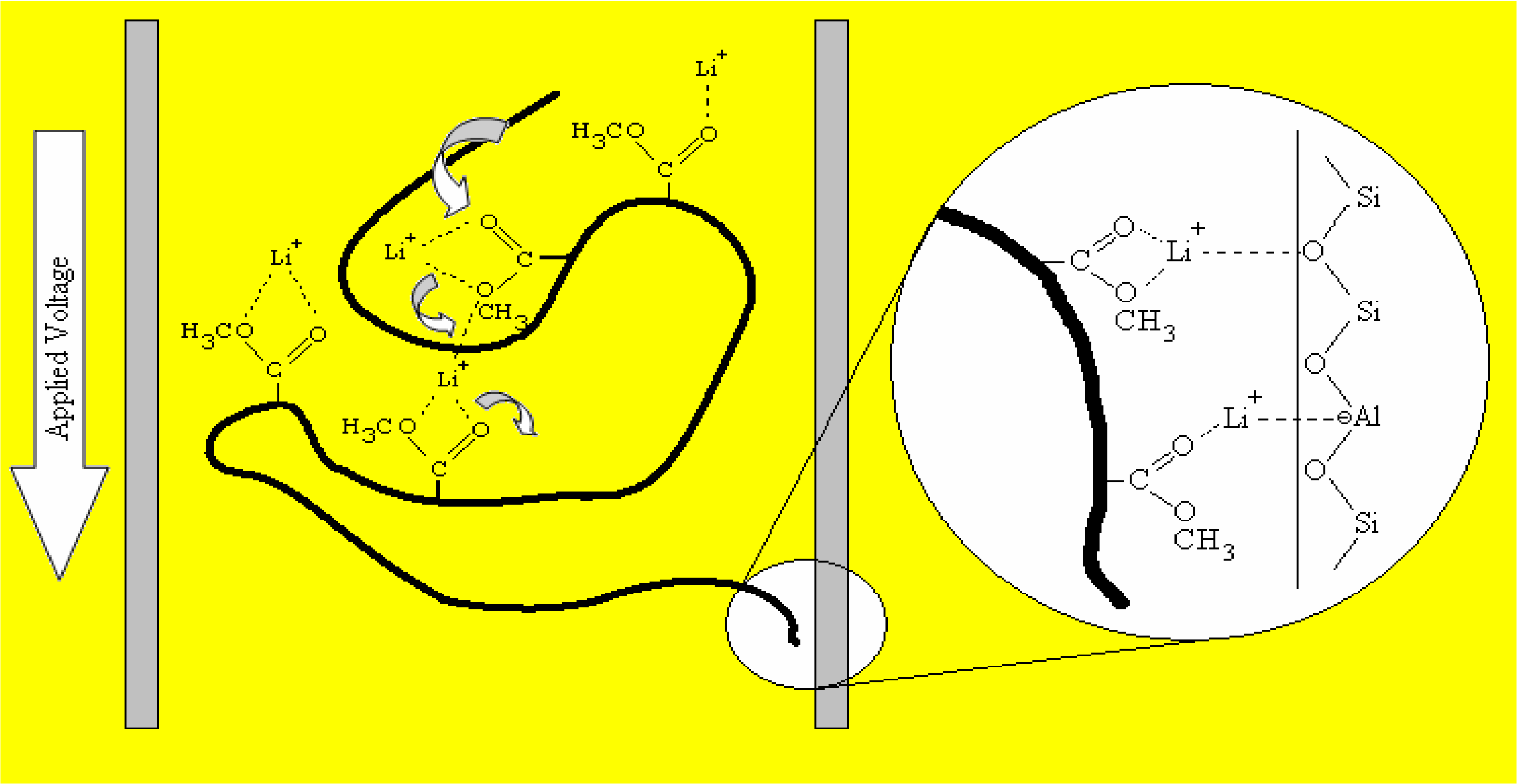


Figure 4.28: Proposed interactions and conduction mechanism

## 4.37 Synthesis and Characterization of Polymeric Nanocomposite Poly (methyl methacrylate)/Al-MCM-48 Prepared via Solution Intercalation Method

Koh Chee Heng

Polymeric nanocomposite constitutes a new class of material in which a silica matrix is incorporated with polymer in the nanometer scale. It has been reported that the polymeric nanocomposite often exhibits improved physicochemical properties when compared to the individual polymer and silica respectively. In this study, mesoporous material Al-MCM-48 was incorporated with 10, 20 and 30 w/w% poly (methyl methacrylate) (PMMA) by solution intercalation method. The silica matrix was also modified with silylating agents in order to increase the compatibility between hydrophobic PMMA and hydrophilic Al-MCM-48. Polymeric nanocomposites with different PMMA contents in silylated Al-MCM-48 were also synthesized. All samples were characterized by means of FTIR, X-Ray Diffraction (XRD), TG/DTA, nitrogen adsorption-desorption measurements, Field Emission Scanning Electron Microscopy (FESEM) and chemical stability test in organic solvent. The results of FESEM analysis indicate that the morphology of the nanocomposites of PMMA/Al-MCM-48 and PMMA/silylated Al-MCM-48 are similar, showing homogeneous spherical nanoparticles and that PMMA was successfully incorporated in the mesoporous silica matrix. The interaction between PMMA and Al-MCM-48 or silylated Al-MCM-48 has resulted in polymeric nanocomposites with improved thermal and chemical stability compared to pure PMMA.

## 4.38 Synthesis of Poly(Vinyl Acetate)-Silylated Mesoporous Si-MCM-41 Nanocomposite and Its Characterization

Nurul Izza Taib

Incorporation of polymers into mesoporous molecular sieves has been the subject of much recent research because the resulting new materials usually have significantly improved properties than those of the polymer or the pure mesoporous molecular sieve itself. In this research, formation of a nanocomposites structure based on silylated MCM-41 and Poly(vinyl acetate) (PVAc) was prepared via solution intercalation. Poly(vinyl acetate) is chosen as guest molecules that would be incorporated into uni-dimensional mesopores of MCM-41 which act as the silicate host. The hydrophilic surface of MCM-41 was modified to increase the hydrophobicity via silane treatment using trimethylchlorosilane (TMCS). A series of polymer nanocomposites with different PVAc content was synthesized. Characterizations were done using XRD, SEM, FTIR spectroscopy, TGA, single point BET surface area analysis. Besides, $^{13}$C CP/MAS NMR was used to determine the compatibility between PVAc and the silicate host. XRD study reveals that the framework of silylated Si-MCM-41 was not altered upon incorporation of PVAc. However, the long range order of Si-MCM-41 decreases with the increase in PVAc incorporated. FTIR study showed that characteristic peak assigned to carbonyl group in PVAc was observed around 1741.6 cm$^{-1}$ for all the nanocomposites indicating the presence of PVAc in the silylated Si-MCM-41. $^{13}$C CP/MAS NMR showed the increase of line width of the peak assigned to C=O carbonyl group indicating the increase in randomness of polymer chains in confined space. The shifting of the C=O carbonyl group is a sign of the change in chemical environment of the carbonyl owing to the interaction of PVAc with the silica matrix of silylated Si-MCM-41. Meanwhile, BET surface area for all the nanocomposites decrease with the increase of PVAc content. Thermogravimetric analysis (TGA) proved that the nanocomposites are stable towards heat up to 500 $^{o}$C. More importantly, thermal stability of PVAc was significantly enhanced after composite with silylated Si-MCM-41.

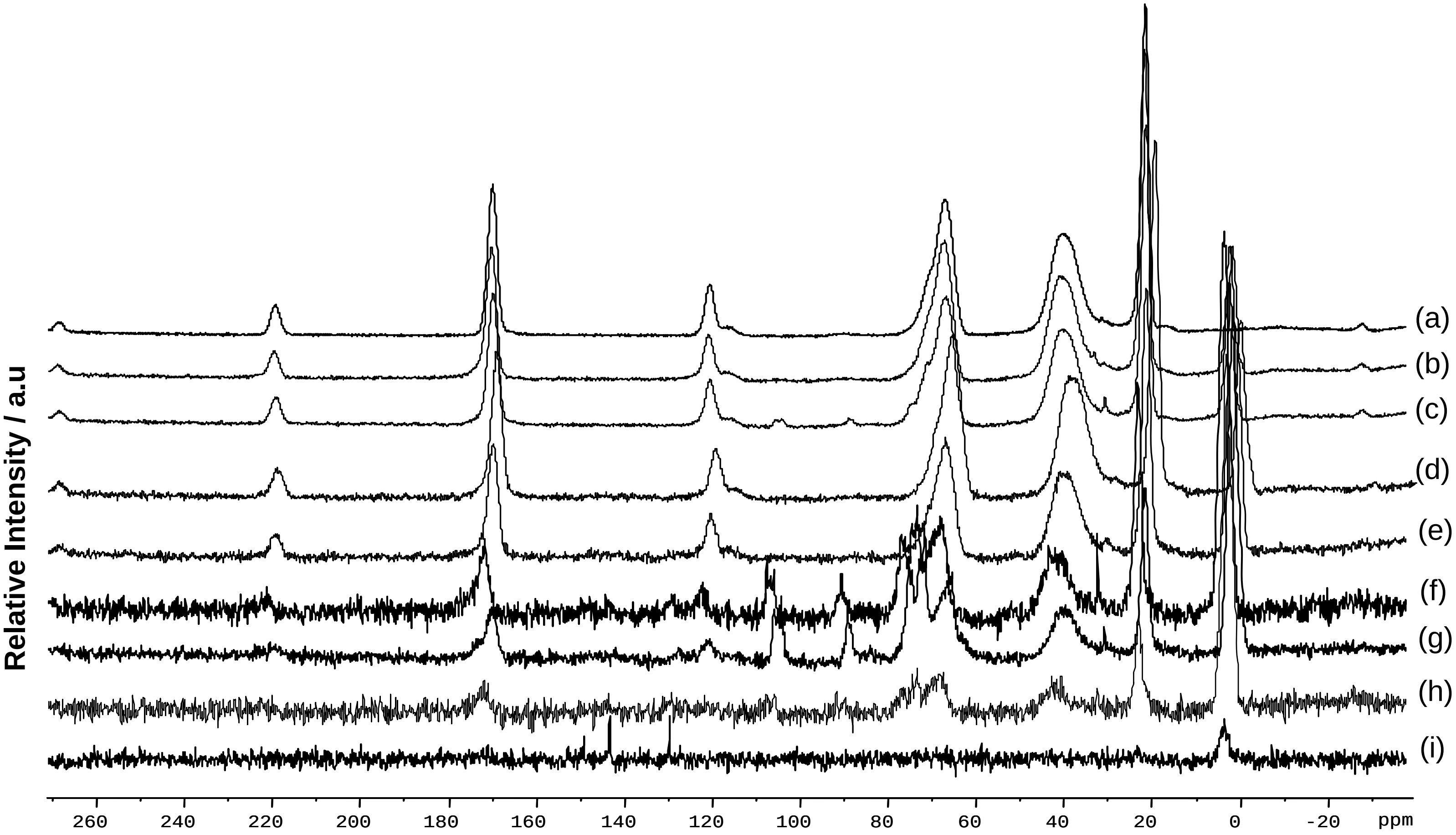


Figure 4.29: $^{13}$C CP/MAS NMR spectra (a) pure PVAc, (b) PVAc-50, (c) PVAc-40, (d) PVAc-30, (e) PVAc-20, (f) PVAc-10, (g) PVAc-8, (h) PVAc-5 and (i) PVAc-2

## 4.39 Polyurethane Modified With Mesoporous Silica: Polymeric Nanocomposites with Improved Physicochemical Properties

Yah Weng On

Polymer-mesoporous silica nanocomposites are one of the most important classes of synthetic engineering materials due to their enhanced properties when compared to the intrinsic properties of polymer and silica. These nanostructured composite materials have been prepared successfully via *in situ* polymerization method. MCM-48 has been selected as the inorganic host for the polymer incorporation. In order to increase the compatibility between the hydrophobic polymer and hydrophilic inorganic host, surface modification of MCM-48 has been carried out by silylation. The nanocomposites of PU/MCM-48, PU/silylated MCM-48 and PU/silica gel as well as pure PU are compared in terms of their morphology, thermal stability and solvent resistance. A series of polymeric nanocomposites with different PU content in MCM-48, silylated MCM-48 and silica gel were characterized by several techniques including X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), FTIR spectroscopy, TG/DTA, Nitrogen Adsorption-Desorption measurement and $^{13}C$ CP/MAS NMR spectroscopy. The FESEM of the MCM-48 based nanocomposite showed that nearly spherical particles of MCM-48 with size around 100 nm are dispersed well in PU matrix. The intercalation of PU in the channel system of MCM-48 results in higher thermal stability than in nanocomposites of PU/silylated MCM-48, PU/silica gel and pure PU. Furthermore, the remarkable improvement in solvent resistance of PU/MCM-48 nanocomposite relative to that of pure PU is ascribed to the excellent barrier properties of MCM-48 silicate frameworks.

## 4.40 Synthesis and Characterization of Polymeric Nanocomposites Polystyrene/Silylated Mesoporous Material MCM-41

Ruzanna Bt. Abdul Manap

Incorporation of polymers into mesoporous molecular sieves MCM-41 has attracted great interest in research due to its potential in providing enhanced properties when compared to the pure polymer or inorganic component. Polymeric nanocomposites based on purely siliceous MCM-41 and an aluminosilicate MCM-41 molecular sieve with polystyrene was prepared via solution intercalation method. Organic modification via silane treatment using trimethylchlorosilane (TMCS) has been performed to increase the surface hydrophobicity of MCM-41 in order to allow the diffusion of polymer chains into the MCM-41 channels to form the polymeric nanocomposites. A series of polymeric nanocomposites containing various weight percentage of polystyrene were prepared and characterized for purity and crystallinity using XRD, FTIR, $^{13}$C CP/MAS NMR, FESEM, TGA and Nitrogen adsorption-desorption. Incorporation of polystyrene up to 30 wt% into silylated mesoporous material MCM-41 were found to enhance the thermal stability of the nanocomposites. Thermogravimetric Analysis (TGA) proved that nanocomposites stable towards heat up to 500 °C. The XRD analysis revealed that the framework structure of MCM-41 was still intact but the surface areas of the samples decreased when the content of polystyrene was increased above 30 wt% due to filling of the pore channels of MCM-41. More importantly, the interaction between the hydrophobic surface of silylated MCM-41 and polystyrene was significantly strong as evidenced by the results of TGA after extraction with hot toluene for three days.

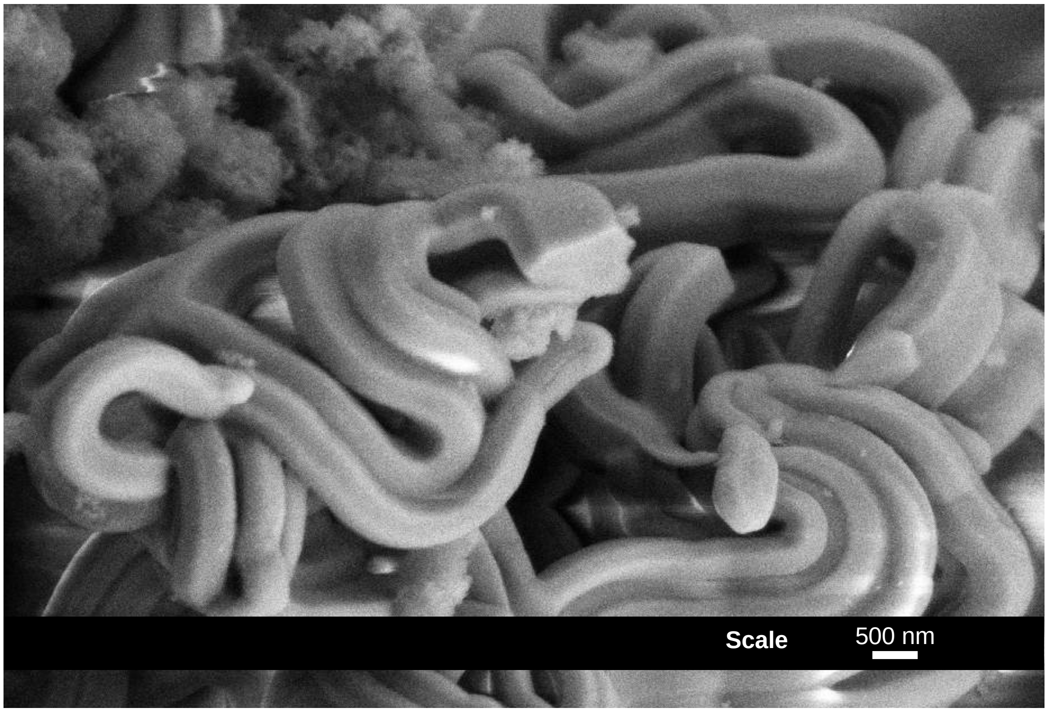


Figure 4.30: FESEM image of aluminosilicate Al-MCM-41 particles showing fiberlike morphology of nano-meter scale

## 4.41 Adsorption of Pesticide using Synthetic Zeolite(Al-MCM-41-30) and Natural Zeolite (Clinoptilolite)

Yap Siew Yung

The wide use of pesticides in agriculture nowadays has led to numerous negative effects on human beings and the environment. Mesoporous molecular sieve MCM-41 with a uniform hexagonal mesopores is a potential adsorbent for pesticide in wastewater treatment processes. In this study, Al-MCM-41-30 with Si/Al composition of 30 was synthesized and used to analyze the adsorption properties on pesticides. The synthesized Al-MCM-41-30 was characterized by Fourier transformed infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetry analysis (TGA) and nitrogen adsorption techniques. Nitrogen adsorption results indicate the presence of mesopores in Al-MCM-41-30 with an average pore diameter of 35 Å and surface area of 1113.78 $m^2/g$. In order to determine the adsorption capacity of Al-MCM-41-30, three types of pesticides of different molecular weights namely paraquat (186.14 g/mol), quinalphos (298.30 g/mol) and chlorpyrifos (348.93 g/mol) were used as the adsorbates. The adsorption capacity of Al-MCM-41-30 was compared with that of natural zeolite, clinoptilolite. The equilibrium isotherms for the adsorptions of the three pesticides on Al-MCM-41-30 and clinoptilolite were studied using the Freundlich adsorption equations. The results showed that Al-MCM-41-30 had the highest adsorption capacity towards paraquat. Studies of the effects of pH and temperature on the adsorption capacity were also carried out. It was found that the adsorption capacity increased with the increase of pH and temperature.

## 4.42 Adsorption of Paraquate using Synthetic Zeolite MCM-48

Goh Mey San

The rapid growing of contamination of pesticides has threatened the ecosystem of agriculture area. The treatment of these contamination usually consist of the usage of molecular sieve as adsorbent, example zeolite, activated carbon, soil, etc.In this study, zeolite mesoporous Si-MCM-48 and al-MCM-48 with Si/Al composition of 30 has been synthesized and used to analyze the adsorption properties on paraquat. The synthesized Al-MCM-48-30 and Si-MCM-48 was characterized by Fourier transformed infrared spectroscopy (FTIR), X-ray diffraction (XRD) and nitrogen adsorption techniques. Nitrogen adsorption results indicate that the presence of mesopores in Al-MCM-48-30 and Si-MCM-48 with an average pore diameter of 43.37 Å, 37.76 Å and surface area of 1011.95 $m^2/g$. 949.70 $m^2/g$. In order to determine the adsorption capacity of Al-MCM-48-30 and Si-MCM-48 were compared with Al-MCm-41-30 and clinoptilolite. The equilibrium isotherms for paraquat on Al-MCM-48-30, Si-MCM-48, Al-MCM-41-30 and clinoptilolite were studied using Freundlich and Langmuir adsorption equations. The results showed that Al-MCM-48-30 had the highest adsorption capacity was also carried out. It was found that the adsorption capacity decrease with the increase of temperature.

## 4.43 Modified Zeolite(Zirconium-Al-MCM-41-30) as Adsorbent for Synthetic Dye

Masida bt Rasyed

Zeolite has a good potential as an adsorbent in textile wastewater treatment processes. In this research, zeolite mesoporous Al-MCM-41-30 containing zirconium has been used as the adsorbent for synthetic basic dyes. Mesoporous material Zr-Al-MCM-41-30 was characterized by Fourier-transform infrared spectroscopy (FTIR), nitrogen adsorption measurement and X-ray diffraction technique (XRD). Based on the nitrogen adsorption results, it was shown that Zr-Al-MCM-41-30 sample has the type IV isotherm which indicates the presence of mesoporous. Four synthetic basic dyes with different molecular weights and sizes were used, namely Basic Blue-66, Brilliant Yellow-11, Basic Green-1 and Orange Acid-15. The different molecular weights and sizes of the dyes employed resulted in different adsorption capacities for the Zr-Al-MCM-41-30 samples. Other factors, which have influenced the adsorption capacity, were the pH and adsorption time. Generally, the results showed that Al-MCM-41-30 has a higher adsorption capacity than Zr-Al-MCM-41-30.

## 4.44 Synthesis Characterization of Dye-loaded Mesoporous Material

Rabiatul Adawiyah Awang

Recently, dye-loaded molecular sieves have attracted interest for different applications such as optoelectronic or photocatalytic materials and chemical sensors. However, such applications for zeolite molecular sieves are limited by their relatively small pore openings (< 2 nm). The guest–host materials based on dye loaded mesoporous materials exhibit particular advantages because the larger pore diameter of the porous host would allow incorporation of almost any dye molecule. In this research, dye-loaded mesoporous molecular sieves MCM-41 have been synthesized by post- modification method. The siliceous mesoporous molecular sieves were first synthesized by cationic surfactant templating method. This was followed by impregnation of Basic Blue 66 dye of various concentrations on surfactant-containing and surfactant-free MCM-41 samples. All of the materials were characterized by XRD, FTIR, UV-Vis and DR-UV-Vis spectroscopy.

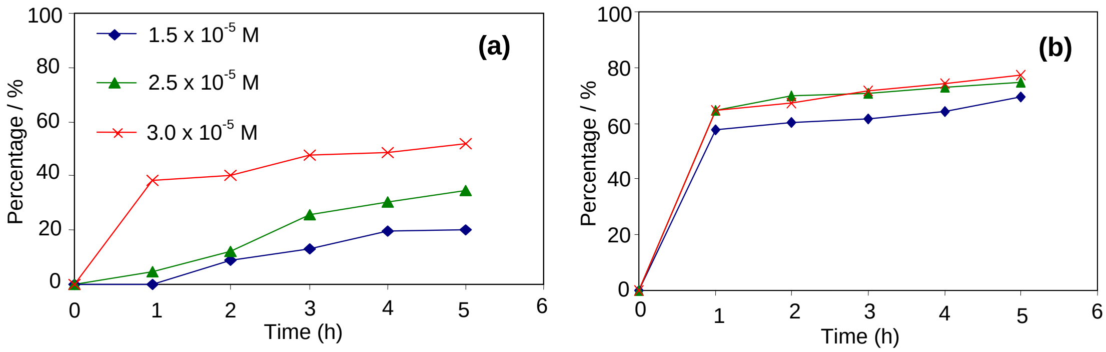


Figure 4.31: Dye adsorption percentage for MCM-41 (a) with surfactant and (b) without surfactant in different concentration.

# CHAPTER 5

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

The key to the present research project is to develop a low coast synthesis method for the mass production of structurally stable and highly ordered mesoporous silica materials from rice husk ash, to address the growing demand for improved catalysts for the processing of large and bulky substrates. Studies on the synthesis of all-silica and metal containing mesoporous materials have been conducted to identify ways of producing high surface area, thermally stable materials, with well defined mesopores and suitable distribution of catalytically active sites.

The project results broadly followed the original objectives, achieving successes in addressing all of these objectives. Important advances have been made in both the fundamental understanding and practical implementation of surfactant templating routes to mesoporous silica molecular sieves. Moreover, significant insights have been gained in the molecularly designed synthesis of nanostructured catalysts based on MCM-type materials. In addition, results acquired during these studies have helped to stimulate and greatly progress research in areas (e.g. polymer-silica nanocomposites and heterogeneous chiral catalysts) that were only tentatively envisaged in the original proposal. The project has already led to more than 30 publications and two recognitions at national and international levels. Research on the project was led by the various researchers and postgraduate students funded by the project, with further support from departmental undergraduate students.

The research has been concentrated on the hydrothermal synthesis of mesoporous materials from rice husk ash using cationic and neutral surfactants as a supramolecular templating agent. The silica materials have been obtained in the various structures including the one dimensional channels of MCM-41, the 3-dimensional structure of MCM-48 (cubic *Ia3d* structure), polymer-silica and microporous-mesoporous hybrid materials. The resulting materials were identified by powder X-ray diffraction, surface area and porosity measurements, and various spectroscopic techniques. In the case of MCM-41 and MCM-48, highly porous solids with pore diameters 1.5 - 10 nm and surface areas reaching > 1000 $m^2 g^{-1}$ have been prepared by varying synthesis conditions (e.g. silica source, pH, temperature, silica/surfactant ratio, synthesis time).

Different modification strategies were required to activate the mesoporous materials towards specific catalytic purposes. The activation has been done by incorporation of heteroelements or transition metals in the framework structure or by a hydrophilic/hydrophobic modification of the surface. The acid/base character of the mesoporous materials have been modified independently by varying the aluminium content of the framework or by incorporation of metal complex species in the porous silica walls. The most stable materials have been used as a basis for introducing inorganic species (metal oxide structures of Mn, V, Nb, Mo, Ti, Zr, Co, Fe, Sn, La ) in the structure to create the desired active sites for redox catalysis. Optimization of the general approach for creating atomically dispersed metal and acid sites within a mesoporous silicate building block network has been achieved by a *molecularly designed dispersion* technique. Subsequently, several acid-base and oxidations reactions in the gas and liquid phase have been used to compare the catalytic activity/selectivity of the novel materials with that of "standard" zeolites and conventional catalysts.

Further improvement in catalytic activity has been achieved through the post-synthesis modification by organic-functionalization with secondary amines (APTS, CTABr), silylation (TMCS, OTS and HMDS) and encapsulation of guest molecules (porphyrin, phenanthroline). Also, bifunctional acid oxidation catalysts have also been prepared in order to perform two different reaction steps over the same material. In addition, the preparation of microporous-mesoporous composite materials, has allowed the synthesis of thermally stable mesoporous catalysts preserving the highly acidic character of microporous zeolites. High activity combined with shape selectivity under mild reaction conditions make these composites very promising in fine chemical processes allowing waste minimization, higher efficiency, cheaper feedstocks. The great variety of frameworks combined with the presence in the mesopores of highly dispersed zeolite crystallines, opens new frontiers in the set up of innovative applications of mesoporous materials for eco-friendly organic syntheses. These findings were corroborated with the results of the catalytic studies involving the Friedel-Crafts acylation of aromatic compounds and cracking of palm oil over MCM-41/zeolite composite catalysts.

Synthesis of new silica materials has also been attempted in order to develop new polymer-silica nanocomposites as conducting, optical and dielectric materials. We have prepared successfully different types of polymers in the host channels of MCM-41 with conducting properties. Interestingly, the MCM-41/PMMA composite prepared by miniemulsion polymerization technique has been shown to possess dielectric property which is highly promising for a range of potential applications in separations, chemical sensing, heterogenous catalysis, microelectronics and photonics.

## 5.2 Recommendations

For future work, production of polymeric nanocomposite materials based on mesoporous silica for application in nanotechnology should be explored. Magnetic properties of the nanoparticles can also be exploited, for example the tendency of small magnetic nanoparticles to be super paramagnetic. One of the applications of this phenomenon is in magnetic resonance imaging (MRI).

# APPENDICES

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27. Asiah Hussain, Salasiah Endud, Pok Yit Ling. "Penjerapan Bahan Pencelup Bes Menggunakan Bahan Mesoliang (Al-MCM-41)." *Prosiding upaya membina kemandirian bangsa melalui sains dan teknologi kimia material: Seminar sehari 70 tahun Noer Mandsjoeriah Surdia*, 11 January 2003, Bandung, Indonesia. 6-13.

28. Asiah Hussain, Salasiah Endud and Yap Siew Yung, "Penjerapan Pestisid Menggunakan Zeolit Sintetik (Al-MCM-41-30) dan Zeolit Semulajadi (Klinoptilolit*)". Prosiding Seminar Kimia Bersama UKM-ITB Ke-5*, Universiti Kebangsaan Malaysia, Bangi Selangor, Malaysia, 16-17 Julai 2002, hlm. 75-82.

29. N. A. Rahman, S. Endud, H. Hamdan and H. Nur, "A simple method to synthesize intercalated nanocomposite of polyethylene oxide/Li-exchanged Al-MCM-41 as conducting material", *Book of abstracts of Simposium Kimia Analisis ke 15 (SKAM 15)*, 10-12 September 2002, Pulau Pinang, Malaysia. p. 62.

30. Lim Kheng Wei, Lau Chin Guan and Salasiah Endud, High Surface Area Catalysts for Alkylation and Oxidation Reactions". Poster presentation at the 15th Simposium Kimia Analisis Kebangsaan (SKAM-15), Universiti Sains Malaysia, Minden, Pulau Pinang, 10-12 September 2002.

# LIST OF AWARDS AND RECOGNITION

1. Best Poster Presentation Award Winner (First Place), Annual Fundalmental Science Seminar (AFSS) 2007, Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia.

2. Best Poster Presentation Award Winner (Second Place), Annual Fundalmental Science Seminar (AFSS) 2006, Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia.

3. Gold medal winner, Industrial Arts and Technology Exhibition (INATEX) 2006, Universiti Teknologi Malaysia.

4. Gold medal winner, 55th World Exhibition of Innovation, Research and New Technology, Brussels Eureka 2006, Brussels, Belgium.

5. Poster Competition Award (Didik Prasetyoko, Zainab Ramli, Hadi Nur and Salasiah Endud), International Conference on X-Ray and Related Techniques (ICXRI2004), 15-16 September 2004, Penang, Malaysia

6. The best undergraduate thesis of the year 2002 by Persatuan Sains Analisis Malaysia (ANALIS) on 12 September 2002 awarded to Norizah Abdul Rahman.

7. Invited to give lecture on "Synthesis and Characterization of Zeolites" to researchers of Mineral Research Center, Department of Minerals and Geoscience Malaysia, Ipoh, 3-6 May 2005.

8. Sijil Penghargaan Pencapaian Cemerlang (Bidang Penyelidikan) Fakulti Sains 2006, Universiti Teknologi Malaysia.

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UNIVERSITI TEKNOLOGI MALAYSIA

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# SELECTED PUBLICATIONS