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**DESIGN AND MOLECULAR ENGINEERING OF
NANOSTRUCTURED ZEOLITES AND
MESOMORPHOUS MATERIALS
- ADVANCING THROUGH THE PORES**

by
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INTRODUCTION

An exciting new scientific trend emerged in the 80's for exploring zeolites and mesomorphous materials as advanced solid-state materials. Zeolites and mesomorphous materials or commonly referred to as molecular sieves are porous materials with nanometer dimension (0.3 – 10 nm) windows, channels and cavity architectures. They represent a '*new frontier*' of solid-state chemistry with great opportunities for innovative research and development. The most recent efforts is to find several novel applications which include molecular electronics, '*quantum*' dots/chains, zeolite electrodes, batteries, nonlinear optical materials, enzyme mimics, chemical sensors, molecular wires and nanodevices [1].

The growing interest in these novel systems is due to the bulk behaviour of these nanostructured materials which can be designed and tailored by controlling their cluster nanostructures which lead to greatly improved performance. In addition, the characteristics of these nanomaterials could be purposely engineered by the variation of the chemical composition, structure and size distribution [1-4].

My involvement with zeolite science began in 1985 when I started pursuing my PhD research in Cambridge. Four years of intimate relation with these remarkable materials have kept my

devotion to zeolite activities ever since. Fifteen years on, the Zeolite and Porous Material Research Group (ZPMG), of UTM, the first in the country, comprising of ten zeolite scientists (excluding student researchers) has been established. With mere ideas and fundamental knowledge to begin with, the group has flourished modestly in terms of reputation, size, and financial support. The ability of our scientists to independently engineer novel structures at the molecular levels in our own laboratory has resulted in the creation of novel nanoporous and nanocrystalline systems with a wealth of potential applications. Our research fields include synthesis, characterization and molecular level understanding of the structure and energetics of zeolites and mesomorphous materials as well as their surfaces and applications.

In tandem with numerous research findings which are continuously being reported by about 20,000 zeolite scientists globally, we have made some important discoveries that contribute to the development in the science and nanotechnology of zeolites and mesomorphous materials. This paper presents a general review of our contributions and recent advances in the design and investigation of these fascinating family of nanostructured materials.

ZEOLITES AND MESOMORPHOUS MATERIALS

Zeolites are crystalline, hydrated aluminosilicates with open three-dimensional framework structures [2-3] built of $(\text{SiO}_4)^{4-}$ and $(\text{AlO}_4)^{5-}$ tetrahedra linked by sharing of an oxygen atom, to form regular intracrystalline cavities and channels of molecular dimensions. The first natural zeolite molecular sieve, stilbite, was discovered by Cronstedt in 1756. He named it '*zeolitos*' which means boiling stone, because the mineral appeared to boil when heated. Since then, about 45 natural zeolites have been identified.

Natural zeolites are formed as a result of chemical reaction of the volcanic ash and alkaline water a few thousand millennia ago. It is therefore not surprising that natural zeolites are found in abundant in volcanic areas. Almost the entire state of Nevada and most of the islands in Indonesia are covered with mordenite and clinoptilolite. Zeolites have been used in various parts of the world for centuries. Many of the pyramids in Mexico and

buildings in Rome were built from zeolite blocks. Zeolites are used as talcum powder and other health products in Hungary. Animals are fed with zeolites in Japan for weight gain and health benefits. Due to limitations in its availability, large variations in mineral composition, crystal size, porosity and pore diameter, natural zeolites have not been commercially important.

In 1862, St. Claire Deville attempted, unsuccessfully, to prepare a synthetic zeolite. Barrer's pioneering work in 1940's demonstrated that a wide range of zeolites could be synthesized from aluminosilicate gels [1,2]. In 1956, Linde A, the first commercial zeolite was synthesized by Breck [4]. In 1962, Mobil Oil introduced the use of synthetic zeolite X as a cracking catalyst, followed by the synthesis of the high silica zeolites beta and ZSM-5. Today, at least 150 synthetic zeolites are known.

The major discoveries and advances in synthetic zeolites are summarised in Table 1.

Table 1 Evolution of Synthetic Zeolites

Late 40's to Early 50's	Low Si/Al Ratio Zeolites
Mid to Late 60's	High Si/Al ratio zeolites
Early 70's	SiO ₂ Molecular sieves
Late 70's	AlPO ₄ Molecular sieves
Early 80's	SAPO and MeAPO Molecular Sieves
Late 70's	Metallo-silicates, aluminosilicates
Mid 80's	AlPO ₄ based Molecular Sieves
Late 80's	Large pore zeolites
Early 90's	Mesoporous molecular sieves

Some of the earlier synthetic zeolites include zeolites A, X, Y, L, ZSM-5, and omega [5]. More recently, zeolites with low aluminium content have been produced: Silicalite, the pure silica analogue of ZSM-5, ferrierite, mordenite and zeolite beta. Other molecular sieves such as the porous aluminophosphates (AlPOs), VPI-5 molecular sieves and their derivatives have been discovered [6]. The most recently synthesized molecular sieves are the nanostructured MCM-41 and silica aerogel. Mesoporous MCM-41 and aerogels are nanostructured materials with great potential as catalyst and nanocomposites [7-8].

The interest in new zeolite-like materials or mesomorphous materials reflects the importance of improving the performance of zeolites as molecular sieves or catalysts. The major problem in the zeolite area is an apparent restriction of pore size to less than 0.8 nm. There have been numerous attempts to incorporate the selectivity and resilience of zeolite into a structure which has significantly larger pore size which is capable of processing large hydrocarbon molecules. With mesoporous solids, for instance, shape selectivity whose effects on reactants, products and transition states are well known in microporous systems may be extended to larger molecules.

ZEOLITE INDUSTRY

In spite of a large global consumption of nearly 4 million metric tons per annum, natural zeolites are used in areas of low-tech applications of limited market value. Research has been done to use zeolites for natural gas storage for vehicles and to cut air conditioning costs in homes and buildings by up to 90 percent using zeolite construction brick and tile. Currently, zeolites are used in cat litter, shoe deodorizers, odour and moisture removers in animal stalls and refrigerators, soil enhancers, and harmful gas removers in aquarium and pond filters. The global consumption of natural zeolites is projected to grow to 4.58 million metric tons per annum by 2005.

The commercially significant zeolites are synthetic and manufactured hydrothermally. With great demand for commercial applications, zeolites are produced in large quantities as detergent builders, petroleum refining and petrochemical processing catalysts and a variety of adsorbents or molecular sieves in treatment of nuclear waste and extraction of ammonium ions from municipal waste water. The consumption of synthetic zeolites is estimated to be 1.36 million metric tons per annum and is expected to reach to 1.61 million metric tons per annum by the year 2005. The overall consumption of zeolites is expected to rise from the current 5.34 million tons per annum to 6.19 million tons per annum by 2005. The value of the market is estimated to be USD2.15 billion at present, rising to USD2.52 billion by 2005. The global consumption of zeolites in the year 2000 is given in Table 2.

Table 2 Global consumption of zeolites (2000)

Zeolite type	Consumption in thousands of metric tons per annum				
	United States	Western Europe	Japan	Other Global Regions	Total
<i>Natural zeolites</i>	32	30	120	3800	3982
<i>Synthetic zeolites</i>	470	606	110	176	1362
<i>Detergents</i>	365	555	95	145	1160(85%)
<i>Catalysts</i>	70	26	10	11	117(8)
<i>Adsorbents</i>	35	25	5	20	85(7%)
Total	502	636	230	3976	5344

In the Asia-Pacific region excluding Japan, the total demand for synthetic zeolites is estimated to be around 160,000 metric tons per annum. Major countries are Korea (85,000 metric tons per annum), Thailand (40,000 metric tons per annum), China (13,000 metric tons per annum) and India (12,000 metric tons per annum). The present Malaysian market size is about 9000 metric tons per annum. About five detergent manufacturers and three oil and gas companies are believed to be users of zeolite A [11]. However, a large number of companies and petrochemical industries in Malaysia are potential users or currently using imported zeolites.

STRUCTURAL CHARACTERISTICS

(i) Zeolites

The various types of zeolites are characterized by the distinct topology of their three-dimensional framework, the relative content of silicon and aluminium, the ordering of the silicon and aluminium atoms in the tetrahedral sites of the framework, and the type and distribution of cations. The framework, topology and morphology of zeolites contribute to the remarkable physical and chemical properties of these microcrystals.

The aluminosilicate zeolites are described by the formula:



where $M_{x/n}$ is the non-framework exchangeable cation of valence n ; $[]$ is the aluminosilicate framework; zH_2O is the non-framework zeolitic water and $y > x$. The Si/Al ratio (y/x) of the framework affects the structure and properties of the zeolite.

Non-framework cations, Mn^+ , are required to balance the charge of the framework. Typically these are mono- or divalent cations such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} , and their total charge is equal to the number of framework T' atoms. For example, when Al^{3+} is tetrahedrally substituted for Si^{4+} , the resulting framework has the composition $[(Al_xSi_{1-x})O_2]^{x-}$. Each electrostatic charge has to be balanced by a positive ion, such as sodium.

The topology of zeolite framework types is described in terms of finite component units called 'secondary building units' (SBU) as shown in Figure 1.

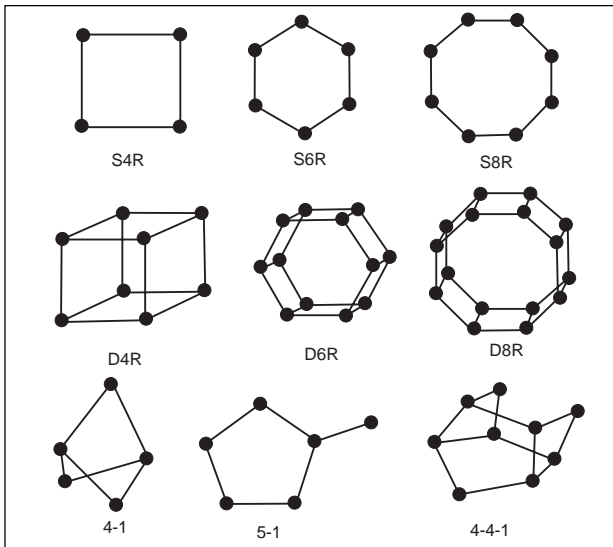


Figure 1 Secondary building units in zeolites. The oxygen atoms between silicons and aluminiums are omitted for simplicity

In these SBUs the Si or Al is present at each corner as represented by the circles. The oxygen atoms which are located near the mid-points of the lines are not shown.

There are a wide variety of possible zeolite structures due to the large number of ways in which the SBU can be linked to form various polyhedra which when combined create networks of regular channels and cavities [3,21]. One such polyhedron is the truncated octahedron; better known as the sodalite cage (Figure 2) and some other polyhedra are shown in Figure 3. Each sodalite cage consists of 24 linked tetrahedral which are further linked to form different zeolites with distinct framework topologies as depicted in Figure 4.

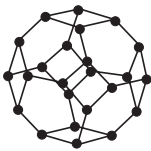


Figure 2 The truncated octahedron

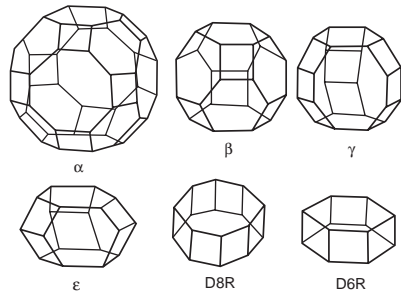


Figure 3 Some polyhedra found in zeolitic structures

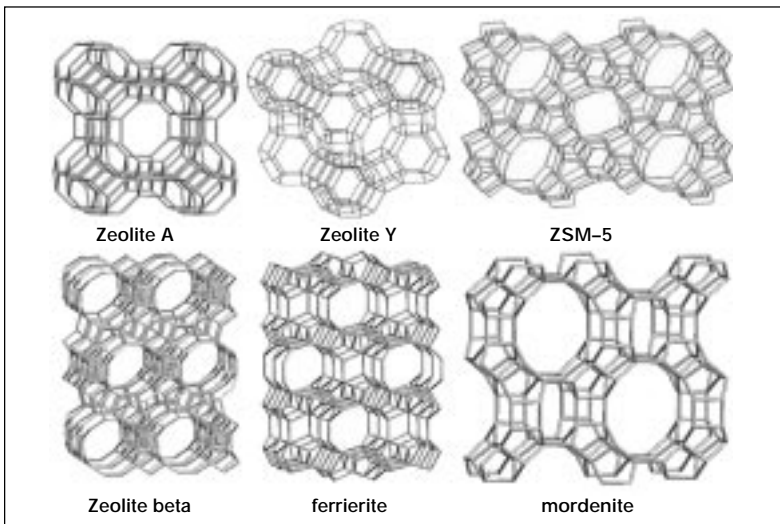


Figure 4 Framework topologies of various zeolites

(ii) Aluminophosphate Molecular Sieves

In 1982, a major discovery of a new class of aluminophosphate molecular sieves was reported [6]. By 1986, some elements were reported to be incorporated into the aluminophosphate frameworks, which include Li, Be, B, Mg, Si, Ti, Mn, Fe, Co, Zn, Ge, and As. These new generations of molecular sieve materials which are designated as AlPO_4 -based molecular sieves, comprise more than two dozen structures and two hundred compositions. Framework topology of the AlPO_4 -5 and its tubular unit are depicted in Figure 5. It is an aluminophosphate molecular sieve consisting of alternating Al and P tetrahedra and in one-dimensional structure with a 12-membered ring along the c-axis with a pore size of 0.7–0.8 nm.

A new family of aluminophosphate materials is VPI-5, a material with very large pores reported by Davis [6]. The VPI-5 structure is hexagonal outlined by a unidimensional channel of an 18-membered ring with a free pore diameter of 1.25 nm (Figure 6). The total volume of VPI-5 is very large and the framework is stable without any phase transition even after being heated above 800°C.

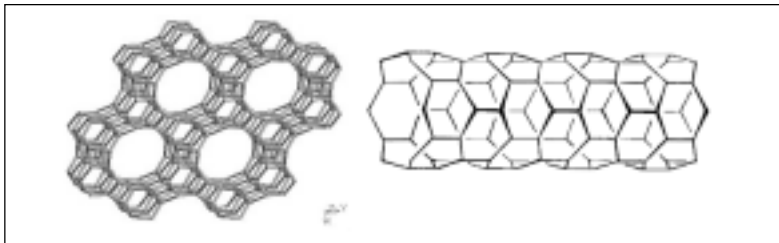


Figure 5 Framework topology of the AlPO_4 -5 and its tubular unit

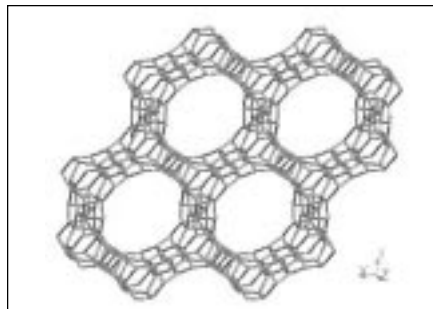


Figure 6 Framework structure of VPI-5

The silicon analogue family of the aluminophosphate molecular sieves is the silicoaluminophosphates (SAPO). In the metal aluminophosphate (MeAPO) family, the framework composition contains metal, aluminium, and phosphorus. The metal (Me) species include the divalent forms of Co, Fe, Mg, Mn and Zn, and trivalent Fe. The MeAPSO family further extends the structural and compositional diversity found in the SAPO and MeAPO molecular sieves. These quaternary frameworks contain metal, Al, P, and Si species. Additional elements such as Li, Be, B, Ga, Ge, As, and Ti have been incorporated into the AlPO_4 and SAPO frameworks to form EIAPO and EIAPSO families respectively.

(iii) Mesomorphous MCM-41

In 1992, a new family of silicate mesoporous materials, designated as M41S, with exceptionally large uniform pore structures has been synthesized. Among these materials, the so-called MCM-41 family which shows a hexagonal array of uniform mesopores in the range between 1.6 nm and 10 nm as shown in Figure 7. The MCM-41 structures were found to be constructed mainly from amorphous inorganic silica walls of 0.9 to 1.2 nm in thickness around surfactant molecules. The calcined material have specific surface areas of about 700 m^2 per gram. A so-called liquid crystal templating mechanism in which surfactant liquid crystal structures serve as organic templates has been proposed to explain the formation of such large pore sizes in the mesoporous materials. Burning off of the organic material then leaves back the cylindrical pores.

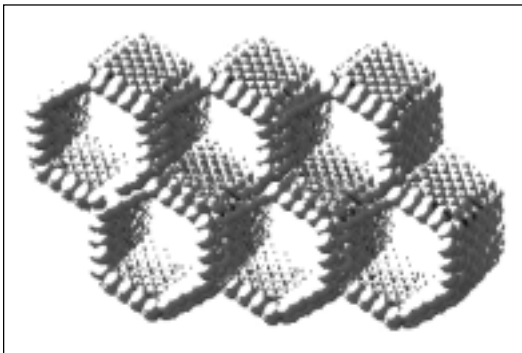


Figure 7 Schematic representation of the structure of a MCM-41 phase with an inter pore distance of 3.5 nm, amorphous wall structure and hexagonal pores.

(iv) Silica Aerogel

In a recent issue of *Science*, aerogel was rated among the top ten scientific and technological developments [7]. Aerogels are advanced materials yet are literally next to nothing. They consist of more than 96 percent air and the remaining four percent is a matrix of silica (Figure 8). Aerogels are unique materials with pores and properties which are smaller than the wavelength of light. Aerogel is the lightest solid material known; it has only three times the density of air and has tremendous insulating capability.

Aerogel is a good insulator because of its large internal surface area. It disperses heat throughout its complex structure and aerogel makes possible development of extremely interesting applications in vacuum and heat insulation of hot water tanks and boiler, refrigerators, and industrial ovens. A double pane window filled with a one inch layer of aerogel provides the same insulating value as 15 standard thermopanes. It is just a question of time as to when the technology and markets will offer the benefits of 'translucent' building components that feature full control of heat performance. A promising material for translucent roofing is silica aerogel.

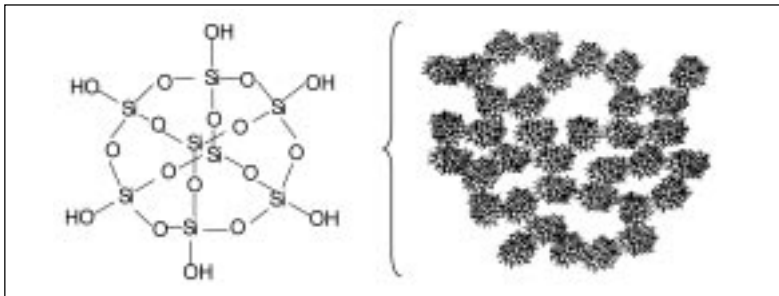


Figure 8 Silica matrix in aerogel

Aerogels are inert, non-toxic, environmentally friendly insulation materials and its superior performance over other foam materials is finally being recognized by designers, engineers and architects. Silica aerogel is a potential substitute for silicon dioxide, the reigning dielectric. Silica aerogel offers a better way to keep the interconnecting wires from shorting across the

narrow dividing space between transistors which avoid propagation delays and excessive crosstalk and subsequently may double computer speeds.

Ultralow density (ULD) silica aerogels have been taken on NASA space shuttle missions to capture high velocity cosmic dust particles. Aerogels have been used by NASA to insulate the rover vehicle for the Mars Pathfinder project in 1997.

DESIGN AND SYNTHESIS OF ZEOLITES AND MESOMORPHOUS MATERIALS FROM RICE HUSK

Zeolites are formed under mild hydrothermal conditions. A typical zeolite synthesis takes place in a highly alkaline aqueous solution at temperatures up to 200°C. The reaction mixtures contain silicon (as soluble silicate or colloidal silica), aluminium (as aluminate) and various kinds of cations. The nature of the product in the typical $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system depends on the gel composition, the physical and chemical nature of the reactants used in preparing the reaction mixture, the overall chemical composition of the latter, the types of cations present and the crystallization conditions.

The type of zeolite or porous material grown depends not only on the chemical composition, temperature and pressure, but most important, on the nature of the chemical sources needed as listed in Table 3.

Table 3 Chemical sources and their function in zeolite synthesis

Sources	Functions
SiO_2	Primary building units(s) of the framework
AlO^{2-}	Origin of framework charge
OH^-	Mineralizer, guest molecule
Alkali cation, template	Counterion of framework charge, guest molecule
Water	Solvent, guest molecule

The principle reactants needed for the synthesis of zeolites are alumina and silica. The usual sources of aluminium are aluminium hydroxide, aluminium isopropoxide, sodium aluminate or alumina sols of different concentrations. Amorphous silica, sodium silicate, sodium metasilicate, silica glass, silicic acids and various concentrations of silica sols are common silicon source used. Numerous research on the synthesis of zeolites and zeolite-like materials revealed that particular Si-source might favour specific crystallization as the rate of dissolution can influence the rate of nucleation and crystallization of the desired product. Therefore, the choice of reactants or primary sources needed for synthesis of zeolites still remain the main area of research and discussion.

The main problem in zeolite research is the availability and cost of raw material specifically the silica source. Commercial silica (made of sand) which is available in either gel, sol, fumed or amorphous solid is found to be variable in reactivity and selectivity. In the last 10 years, we have established that rice husk can provide a good alternative source of highly active silica source for the synthesis of zeolites [8-10]. In the laboratory, we have proven that the amorphous silica from rice husk (25 percent w/w) is an excellent source to produce a variety of important zeolites. The market study results indicate that Malaysia has an abundant supply of rice husk (a consistent generation of 9000 M/T per month, not counting the amount accumulated over the years) [11].

With accumulated amount of 2.2 million metric ton of rice husk per year, disposal is a problem. Present disposal by rotting and open burning is hazardous to the environment. Incineration provides the best option due to the capability of volume reduction, energy recovery and to obtain silica, which is above 97 percent in the rice husk ash, as raw material for various industries.

We have used rice husk ash as the silica source for the synthesis of zeolites. Amorphous silica is a highly reactive silicon source, but not all silica which is amorphous to XRD is equally suitable. The local structure of amorphous silica was investigated

by ^{29}Si MAS NMR and FESEM in order to optimize the process. The results show that amorphous silica extracted by physical combustion with controlled temperature contains only $^*\text{Si}(\text{OSi})_4$ tetrahedral units and is the most reactive. The presence of crystalline cristobalite and tridymite phases and SiOH groups render the silica less active (Figure 9)[8-12].

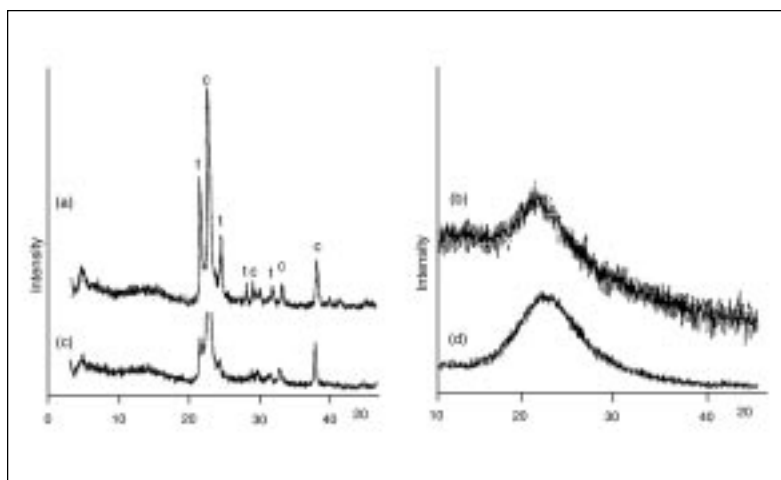


Figure 9 XRD pattern of crystalline (a and c) and amorphous (b and d) silica from rice husk

In order to obtain amorphous silica and prevent ash agglomeration, the applied combustion temperature was 600-700°C. Crystalline silica would be formed at combustion temperature above 800°C. Ash agglomeration would only occur at temperature above 1500°C. We have carried out structural characterization of rice husk silica prepared by various methods using ^{29}Si MAS and $^1\text{H} - ^{29}\text{Si}$ CP/MAS NMR in tandem with field emission scanning electron microscopy (FESEM) and XRD. ^{29}Si MAS NMR is powerful in determining the structure of the various silica species present and the degree of amorphicity of the samples, properties which cannot be measured by XRD. Silica samples which are completely amorphous to XRD

contains different phases which are identifiable by ^{29}Si MAS NMR. (Figure 10)

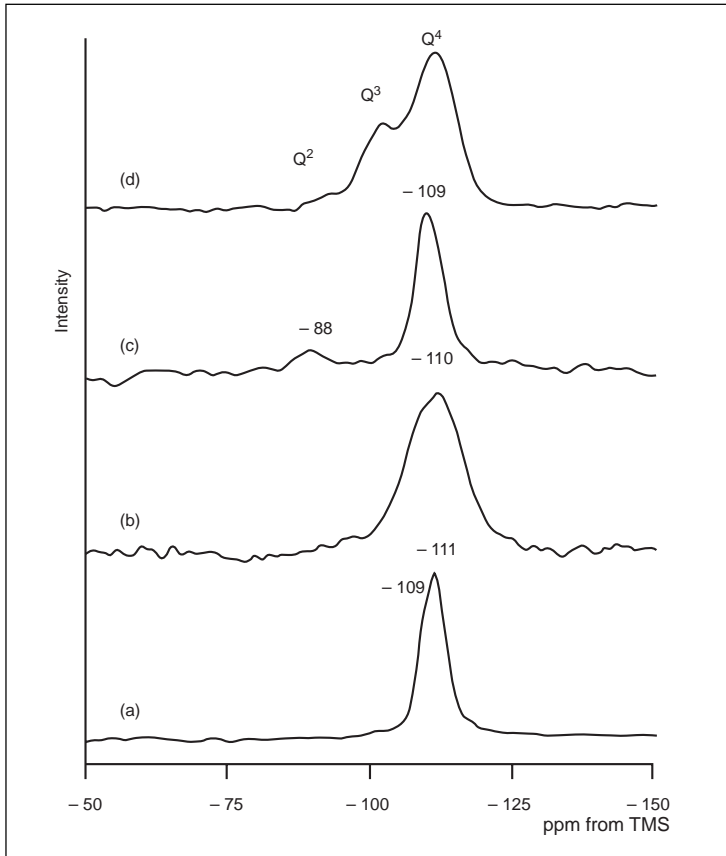


Figure 10 ^{29}Si MAS NMR of crystalline (a and c) and amorphous (b and d) silica

Combustion at 700°C produces the most reactive silica source which predominantly contains pure amorphous SiO_4 tetrahedra and no SiOH groups as found in large amount in the amorphous sample. The SiOH groups must have been created during the chemical treatment of the ash. The presence of SiOH groups and crystalline phases in the silica sources reduces the reactivity of the silica in the synthesis of zeolites. Since silica

from rice husk can be prepared under controlled temperature without any chemical treatment, it is a potential source of highly active amorphous silica.

FESEM micrograph of amorphous silica sample composed of regular spherical platelets of almost equal sizes (40-50 μm) appearing in parallel rows, appears like aggregates of clearly defined layers of loose flakes. The flaky morphology of the amorphous silica sample aggregates as seen in the SEM micrograph (Figure 11) suggests that the surface is more loosely bound, which makes it highly reactive. Samples containing crystalline cristobalite and tridymite phases are not active silica sources in the synthesis of zeolites.

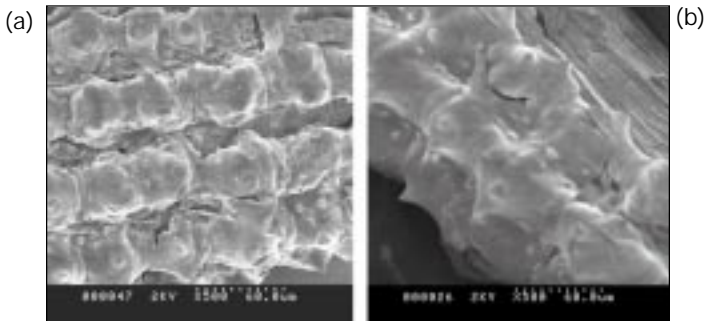


Figure 11 SEM micrographs of silica from rice husk (a) amorphous silica and (b) crystalline silica

In 1991, we introduced the application of rice husk as a source of silica in the production of highly crystalline zeolite A (Figure 12) [13]. Since then, the synthesis of many other types of zeolites has been achieved. Other zeolites which have been successfully designed from rice husk ash in our own laboratory are zeolites X, Y, ZSM-5, beta, ferrierite and P (Figure 13).

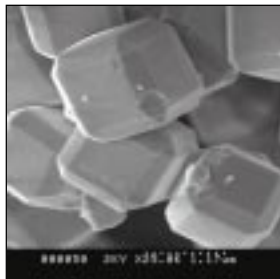


Figure 12 Zeolite A from rice husk

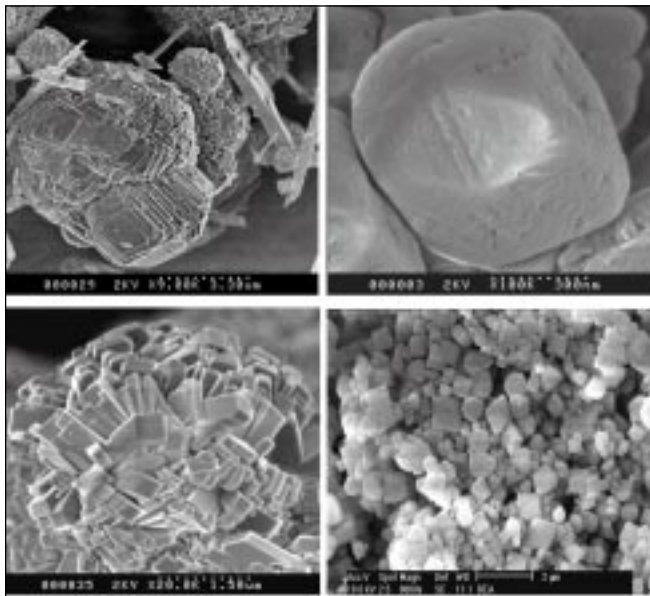


Figure 13 SEM of various crystalline zeolites synthesised from rice husk showing distinct morphologies

The most challenging achievement yet, for the first time, we managed to prepare mesoporous [Si,Al]-MCM-41 with Si/Al ratios as low as 2.5 from rice husk by direct synthesis (Figure 14). Our extensive work on the synthesis of zeolites have proven that silica from rice husk is an active source of silica never before demonstrated by other researchers.

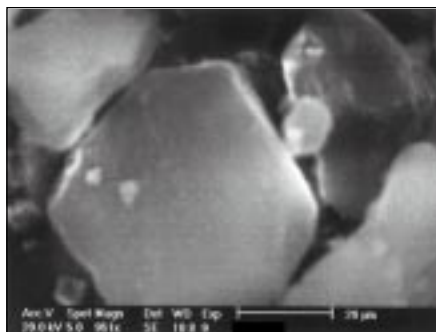


Figure 14 SEM of SiMCM-41 prepared from rice

A novel nanomaterial, Maerogel (Malaysian aerogel), is a silica aerogel which is directly prepared from rice husk (Figure 15). It is a nanomaterial of a highly divided state and exhibits unconventional properties which offers more cost effective methods of production and application. Maerogel is more superior in quality than the current commercial TEOS aerogel. Being an inert, non-toxic and environmentally friendly amorphous material, Maerogel possesses established physico-chemical properties al listed in Table 4 which can be modified for specific applications.

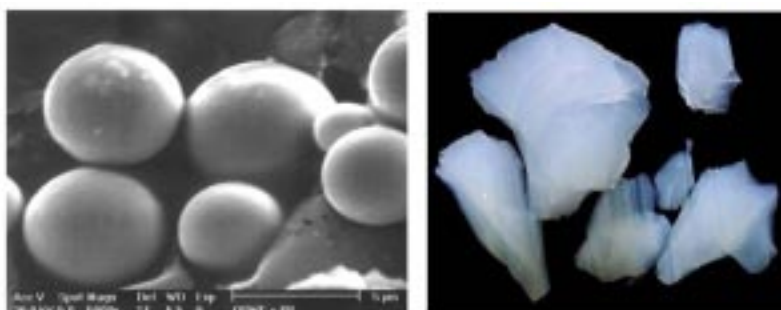


Figure 15 SEM micrograph and photograph of Maerogel

Table 4 Physical properties of Maerogel

Property	Maerogel
Apparent density	0.03 g/cm ³
Internal Surface Area	800-900 m ² /g
Mean Pore Diameter	20.8 nm
Thermal Tolerance	to 500°C, mp > 1200°C
Thermal Conductivity	0.099 Wm ⁻¹ K ⁻¹

SECONDARY SYNTHESIS

Properties of zeolites are intimately related to the type of occupancy of the tetrahedral sites. Modification of the composition of the framework by increasing the silicon content

increases the thermal stability of the samples. The catalytically active centres in zeolites are the acidic Brönsted hydroxyl groups associated with tetrahedrally coordinated framework aluminium atoms. Catalytic activity is thus strongly dependent on the concentration and location of aluminium in the framework.

It is clearly desirable to be able to alter the Si/Al ratio of the framework particularly important in the case of faujasitic zeolites X and Y, pentasil zeolites and mesoporous MCM-41. We have demonstrated how this can be conveniently achieved by 'secondary synthesis', i.e, by isomorphous substitution of Si or Al on the tetrahedral sites after the completion of the original zeolite crystallization [14-16].

The secondary synthesis route has been shown successful in substituting aluminium into the tetrahedral framework positions in a number of preformed crystalline zeolites. When treated under proper conditions, aluminium can be removed from zeolites or reinserted into the frameworks without loss of crystallinity. It has been demonstrated that for zeolite Y, the extra-lattice aluminium is incorporated into framework by the treatment with an aqueous solution of potassium hydroxide. We have also established that aluminium can also be incorporated into MCM-41 silicate frameworks after the completion of synthesis. This novel approach has the potential for allowing a wider range of compositions to be prepared which is efficient and very convenient for the preparation of acidic MCM-41 catalysts.

(i) Realumination of Zeolite

The ^{29}Si MAS NMR spectra of of zeolite Y samples treated with KOH (lower traces in Figure 16(a)) are dramatically different from those of the starting materials. The intensities of the Si(OAl) signals are greatly reduced, and the intensities of the Si(1Al), Si(2Al), Si(3Al) and Si(4Al) signals correspondingly increased, signifying that a considerable amount of aluminium has entered the zeolitic framework. This is consistent with the observed increase in the unit cell parameter.

^{27}Al MAS NMR spectra of the dealuminated and realuminated sample in Figure 16(b) show that the signal at ca. 60 ppm corresponding to tetrahedral framework aluminium decreases upon dealumination and increases again on reinsertion

of Al into the framework. Any loss of crystallinity of the treated sample (not observed in this case) is indicated by the formation of non-framework octahedral aluminium which resonates at about 0 ppm.

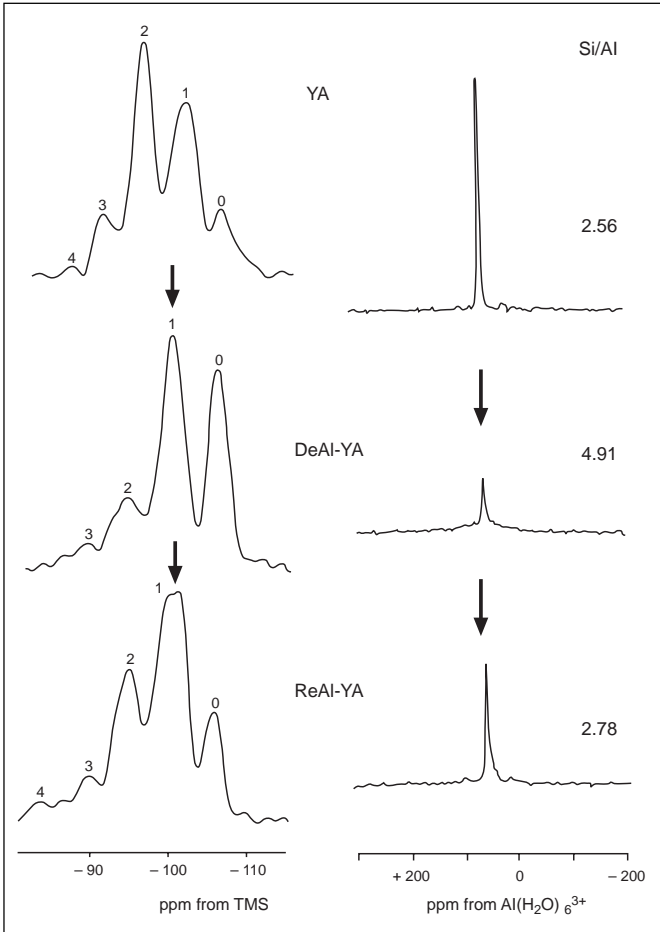


Figure 16(a) ^{29}Si and **(b)** ^{27}Al MAS NMR spectra of realuminated samples

^{27}Al quadrupole nutation NMR in Figure 17 for the first time reveals the presence of four kinds of aluminium in dealuminated zeolite Y: Framework Tetrahedral Al (F), Nonframework

Tetrahedral Al (NFT), Distorted Tetrahedral Al (DFT) and Extraframework Al (EFAL) which appears in amorphous phase. This confirms the reinsertion of aluminium into the framework by isomorphous substitution [17-19].

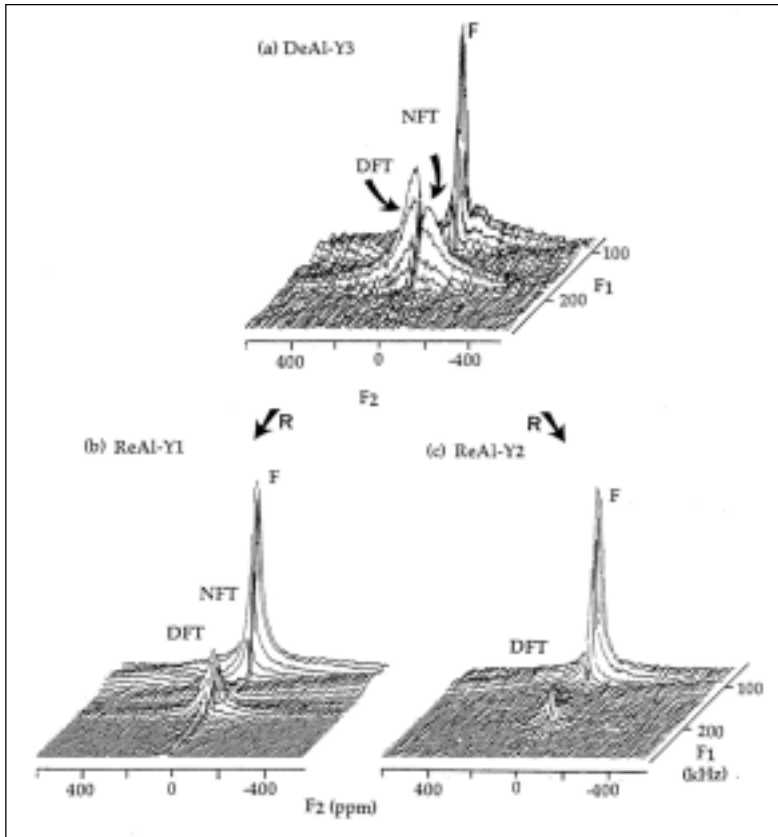


Figure 17 ^{27}Al quadrupole nutation NMR of dealuminated zeolite Y

(ii) Alumination of Silicalite

Silicalite is the siliceous counterpart of zeolite ZSM-5, a powerful Brønsted acid catalyst for a variety of chemical reactions. Silicalite is not a catalyst but it is hydrophobic and organophilic and can

remove a variety of dissolved organic compounds from water. We demonstrated that Al content can be altered *after* the completion of synthesis in *both* directions (starting from the siliceous or the aluminous end member) and that intermediate Si,Al compositions are also accessible [20-21].

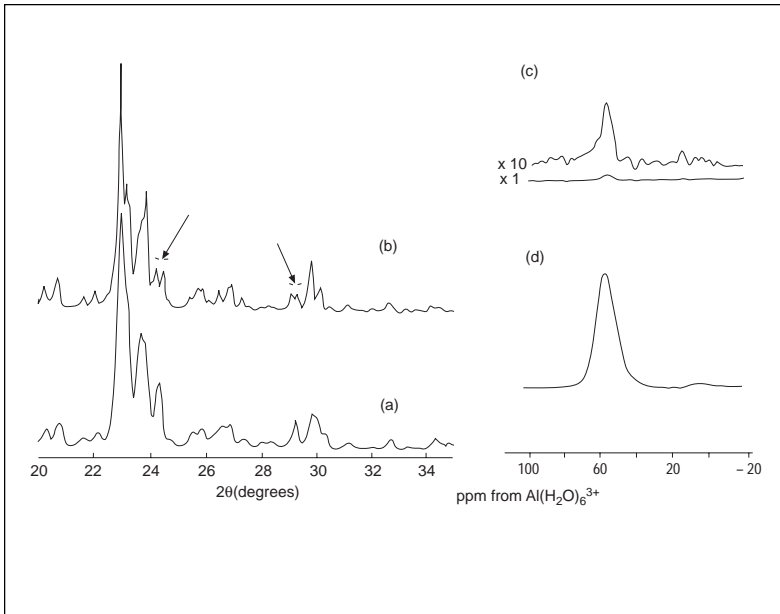


Figure 18 X-ray diffraction and ^{27}Al MAS NMR spectra of aluminated silicalite (a) and (d); siliceous silicalite (b) and (c)

^{27}Al MAS NMR spectra given in Figure 18 on the absolute intensity scale show that aluminated silicalite contains, substantial amounts of tetrahedrally coordinated aluminium, and silicalite contains only traces of tetrahedral Al introduced as an impurity in silica used for the synthesis. It is clear that aluminated silicalite sample is the aluminous end-member as proven by the ^{29}Si MAS NMR spectrum in Figure 19.

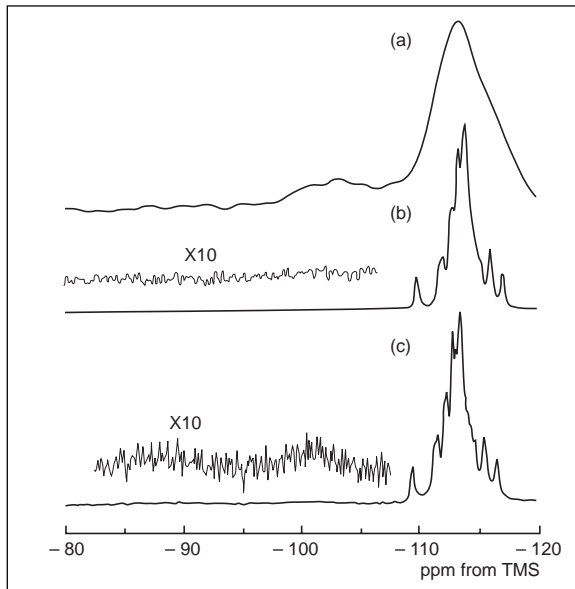


Figure 19 ^{29}Si MAS NMR spectra of (a) Silicalite and (b) Silicalite (calcined) and (c) Aluminated silicalite

(iii) Alumination of MCM-41

Purely siliceous mesoporous [Si]-MCM-41 has been aluminated using an aqueous solution of sodium aluminate, NaAlO_2 , to form [Si,Al]-MCM-41 with the framework Si/Al ratio as low as 1.9 has been produced by this process without affecting the long range order of the mesopores and structural stability of the framework.

^{27}Al MAS NMR in Figure 20 show that all aluminium is incorporated in the framework. The well-resolved XRD pattern of calcined [Si,Al]-MCM-41 indicates that the mesopore system is stable, and that the channel diameter decreases with the increased degree of incorporation of Al. The extent and efficiency of the reaction depend on the temperature, duration of treatment and especially on the kind and concentration of the basic solution. The degree of crystallinity and the thermal stability of the products are primarily controlled by the composition of the parent material [22-24].

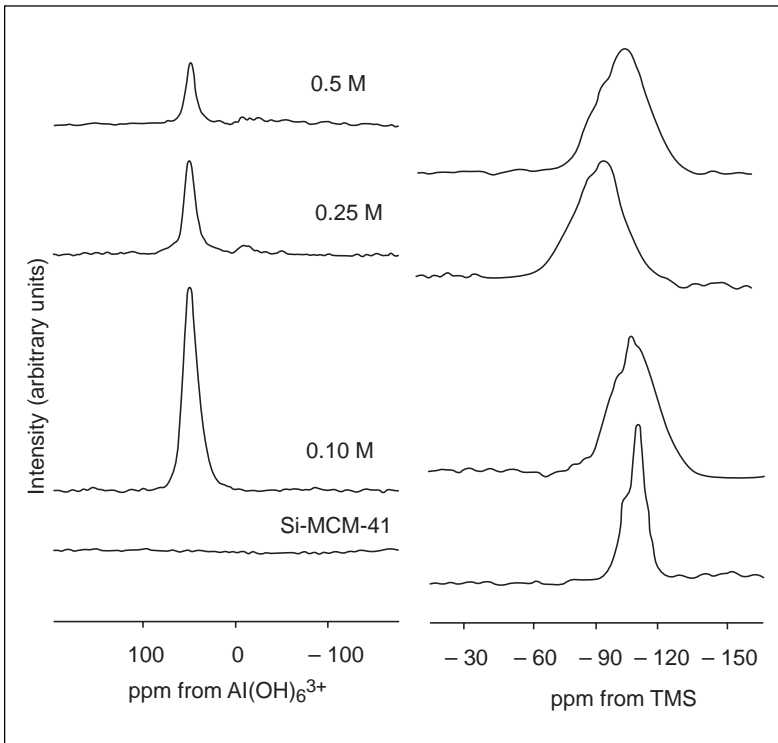


Figure 20 ^{27}Al and ^{29}Si MAS NMR spectra of MCM-41 aluminated with various concentrations of sodium aluminate solution

REMARKABLE CHARACTERISTICS

Zeolites and mesomorphous materials are of great interest because of their unique qualities. The combination of many properties which include nano, micro and mesoporous character with uniform pore dimensions, the ion exchange properties and the ability to develop internal acidity, the high thermal stability and internal surface area. Like other solids, they are safe to handle and are easy to use and have applications in food, drugs, cosmetic products, and detergents. Zeolite A, for example show essentially no toxicity via oral, dermal, ocular and respiratory routes of exposure.

Heating a hydrated zeolite drives out the water (which explains the boiling stone phenomena), leaving empty holes (pores) for occupation by other molecules which are commonly referred to as the 'guest' species. The effective pore size of a zeolite depends mainly on the aluminosilicate structure and to a lesser extent, on the nature of the cations which may be introduced. Cavities or channels can run in one, two, or three dimensions and the restrictions between cavities are referred to as 'windows'. In some structures, cavities are absent and only channels exist. Industrially useful zeolites consists of windows with effective diameters more than 0.5 nm. Framework structures containing smaller apertures are not commercially important because they only admit small molecules such as water, whereas most of the molecules of interest in industries today are large.

ADSORPTION

Adsorption is a special characteristic of zeolites. Zeolite frameworks provide substrates that support the mobilities of the nonframework cations that make them good ion exchangers. Due to the presence of never ending intricate pore and channel systems of controlled dimensions and accessibilities, zeolites become excellent sorbents and molecular sieves. Zeolitic materials can offer extremely large specific surface areas. A spoonful of zeolite Y of about 1 gram in weight for example, has a surface area of 800 m², which is as large as the size of a football field. Zeolites are used to adsorb a variety of materials which include application in drying, purification, and separation.

Pores are classified on the basis of their diameters: d , the smallest are micropores ($d < 0.2$ nm), intermediate are mesopores (0.2 nm $< d < 50$ nm) and larger are macropores ($d > 50$ nm). These pore apertures are uniform throughout the entire structure of a particular zeolite. As a result, regular channels run through the pore apertures, linking between the larger void volume known as supercages. In X- and Y-type zeolites, the free pore apertures have diameters of 0.74 nm whilst the supercage diameter is 1.3 nm.

As a direct consequence of the extension of the channel system throughout zeolite crystals, up to half of the total volume defined by the external surfaces is in fact void and available for penetration by gas phase molecules. It is important to realize that there is selective adsorption on the internal surfaces governed by the size and shape of the molecule concerned. For example, it is evident from comparison of Figure 21 that benzene will be unable to penetrate through the pore aperture of an A-type zeolite and is thus excluded from adsorption on the internal surfaces. In fact, the largest molecules which are able to pass through the unobstructed A-type aperture are linear alkanes, whilst branched chain alkanes are excluded.

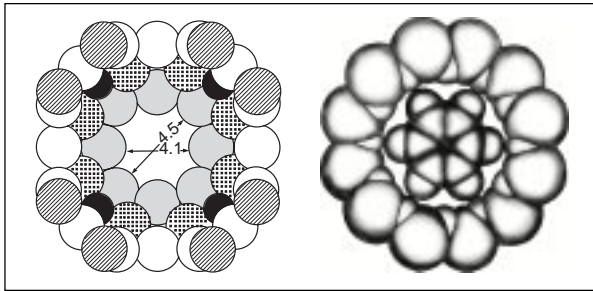


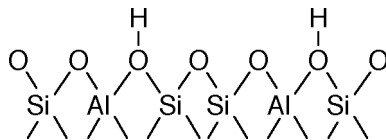
Figure 21 Space-filling models of pore apertures in zeolite A (left): On the right, similar model of the benzene molecule appears, aligned in the same plane as the pore aperture of zeolite Y

The sorptive properties of zeolites are modified by charge-balancing cations which can undergo ion exchange when the zeolite is treated with salt solutions. The other non-framework component is the zeolitic water, which fills the channels and cavities and may be removed by heating. In some zeolites, heating or dehydration irreversibly alter the framework structure and cation positions. On the other hand, removal of zeolitic water may leave the framework of some zeolites intact to sorb other water, organic and inorganic molecules. These unique properties of synthetic zeolites have been used in commercial applications as detergent builders, radioisotope separation, and removal of ammonium ions from wastewater streams and aquaculture ponds.

CATALYSIS

The third and most important application of zeolites is as heterogeneous catalysts. Zeolite catalysts are different from most other heterogeneous catalysts in that the catalytically active sites are distributed uniformly throughout their bulk. The voids and channels are accessible to certain reactant molecules. In order to be useful as catalysts, the zeolites must have channels which are at least 0.4 nm wide. Even at this early stage, it should be apparent that molecular sieve or size selective action by zeolites should be a very significant aspect of heterogeneous catalysis. Obviously, it is the crystalline nature of zeolites; which is vital in this respect. Amorphous porous materials, such as silica-alumina, will not usually have regular pore structures. Thus, whilst silica-aluminas do offer high specific surface areas, they will not show size selective action.

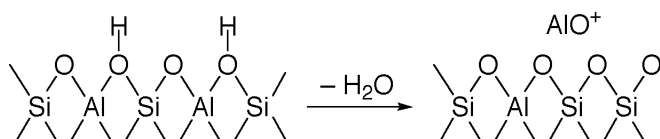
Much of the chemistry that takes place in catalysis derives from the acidity of sites within the zeolites. There are two kinds of acidic sites in zeolitic frameworks. Brønsted acid sites are the protons attached to framework oxygens bonded to silicon atoms which are present in the vicinity of aluminium atoms. The acid strengths of these sites depend on their environment. The protons can be introduced into the structure by ion exchange, thermal decomposition of the ammonium-exchanged forms, hydrolysis of water of hydration of cations or reduction of cations to a lower valency state.



Brønsted acidity in zeolites

Upon further heating, Lewis acid sites are produced. Lewis acid sites are believed to be more acidic than Brønsted sites, although relatively little is known about their nature. Understanding the chemistry of the acid sites are important in the tailoring of zeolites as efficient catalysts. Various aspects of acidity such as the particular natures of the acid site environments,

concentrations and the stabilizing effects have been studied [25-28].



Representations of a Lewis acid site in zeolite

A conventional organic chemist would regard that it is practically impossible to produce gasoline from synthesis gas or from a simple alcohol. Within less than 20 years the initial laboratory synthesis of gasoline from alcohol in a single stage process by the outstanding ZSM-5 catalyst has led to a commercial production process for gasoline which is able to satisfy about one-third of New Zealand's transportation fuel needs. The ability to control the flow of molecules by ZSM-5 zeolites involves separate diffusion of reactant and product molecules along the connected pore systems. In addition, the steric environment of the site restricts the geometry of the transition state in a reaction.

In addition, the zeolitic framework structure determines shape selectivity effects. A well-known example of such selectivity is the alkylation of toluene with methanol using the ZSM-5 catalyst. This is an important early step in the production of polyesters, produced via oxidation of para-xylene (Figure 22). Process economics are greatly improved if the concentration of p-xylene in the C8 aromatic feed stock is high. One way to accomplish this is by shape-selective catalysis using zeolites.

Other main application areas are in petroleum refining, synfuels production and, petrochemical production in reactions such as alkylation, cracking, hydrocracking, dewaxing, isomerization, hydrogenation, dehydrogenation, hydrodealkylation, methanation, shape selective reforming, dehydration, methanol-to-gasoline and methanol-to-olefin conversions, organic catalysis, inorganic reactions, H₂S

oxidation, reduction of NO to NH₃, decomposition of water and CO oxidation. No wonder there is a saying that *'every drop of oil goes through zeolite'*.

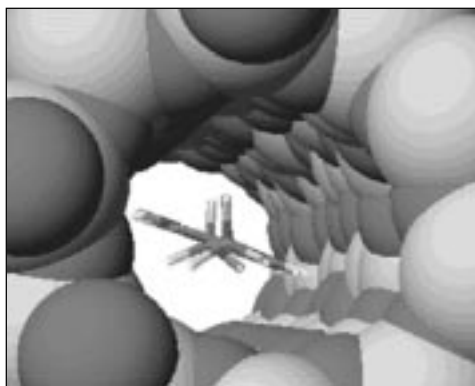
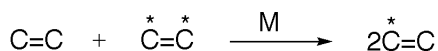


Figure 22 p-Xylene in the channels of ZSM-5

Zeolites also provide possible supports for metal atoms such as platinum, rhenium, iron, cobalt, nickel, magnesium, and molibdenum. Re₂O₇ supported on γ-alumina, among other transition metals, is proven the most active heterogeneous catalyst for metathesis of olefins. Metathesis of olefin is an organic reaction with many potential industrial applications, particularly in the polymer industry [29-30]. The term metathesis describes the interchanging of carbon atoms between a pair of double bonds as shown below:



Where M is the appropriate metal complex

In our study, for example, successful metathesis of 1-hexene will give 5-decene and ethene as the products. The reaction proceeds only in the presence of a suitable transition metal compound-based catalyst and most often, in conjunction with co-catalysts as promoters. However, its activity is significant only when the concentration of rhenium on the support is >18 wt percent, which is economically unfavourable.

Development of a heterogeneous catalyst using zeolite as the support for Re_2O_7 is a potential alternative that is expected to be more superior to conventional alumina and silica-alumina supports. Zeolite Y, used in the study was modified by dealumination to form an ultrastable zeolite support of various acidity. Catalytic study on metathesis of 1-hexene indicates that Re_2O_7 -zeolite Y system is an active catalyst with >90 percent selectivity, producing a maximum of 57.4 percent yield of 5-decene. Other factors such as reaction temperatures, types of solvent and wt percent of rhenium loadings influence the activity of the catalytic system.

Characterization of $\text{AlPO}_4\text{-5}$ and $\text{MeAlPO}_4\text{-5}$ [Me = Mg, Co, Mn and Zn] by x-ray diffraction (XRD), chemical analysis and temperature-programmed desorption (TPD) indicated that Mg, Mn, Co, and Zn were incorporated into the $\text{AlPO}_4\text{-5}$ framework by isomorphous substitution. The incorporation of metals into $\text{AlPO}_4\text{-5}$ occurred with preferred orientation of the crystal and distortion of the unit cells as shown in Figure 23. The structural distortion in $\text{AlPO}_4\text{-5}$ was correlated with the ionic radii of Me atoms and the strength of the Brönsted acid proposed by the Structure-Acidity Model (SAM) as in the following order: $\text{Mn} > \text{Zn} > \text{Co} > \text{Mg}$. Conversion of cyclohexanol as a test reaction indicated that the incorporation of Me atoms in $\text{AlPO}_4\text{-5}$ increases the Brönsted acidity and decreases the basicity at the localized structure. These reactions provide a diagnostic means of determining the acid-base character of solid surfaces [31-32].

We have also demonstrated that AlMCM-41 by secondary synthesis (sec) is a potential heterogeneous catalyst in the Friedel-Crafts alkylation of bulky aromatic compound. The data shows that at 120°C , 2,4-di-*t*-butylphenol conversion is the highest over conventional catalyst, AlCl_3 , followed by AlMCM-41(sec) and AlMCM-41(dir) . The higher conversion with AlCl_3 is due to its strong Lewis acidity as compared with the AlMCM-41 which only exhibits a mild acidity. The SiMCM-41 as expected did not show any conversion of 2,4-di-*t*-butylphenol due to the absence of acid sites. The highly acidic zeolites, HZSM-5 and H-USY, contrary to expectation, did not show any conversion

of the bulky aromatic compound which is much bigger than the pore size of the zeolite. These results prove that this problem is overcome when AIMCM-41 with mesoporous dimension is used as the catalyst [33].

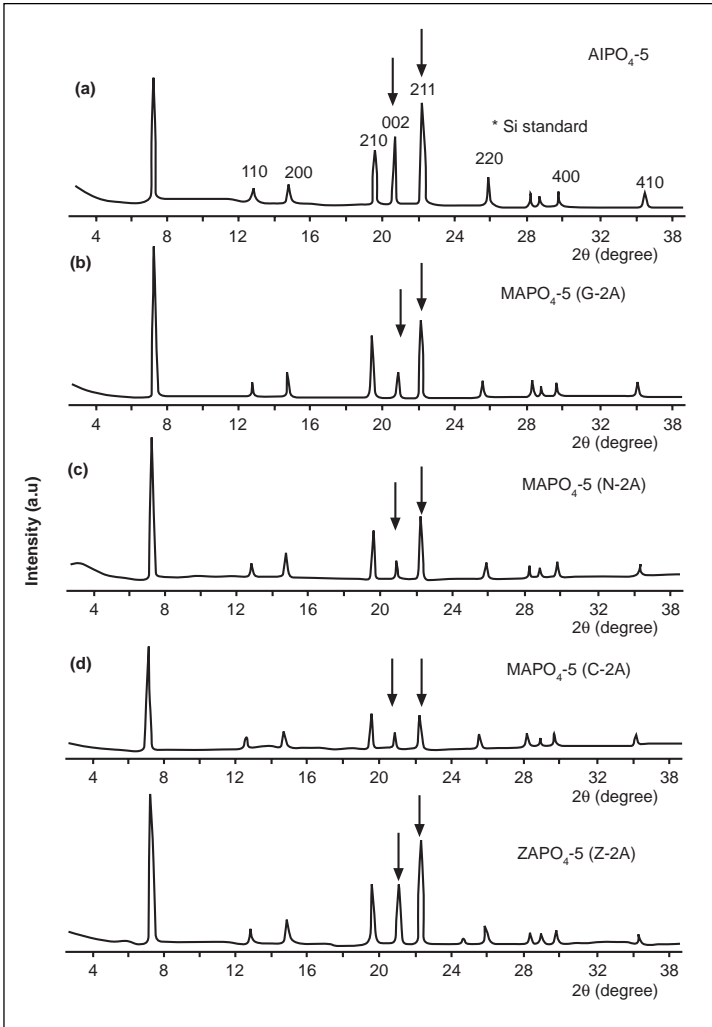


Figure 23 XRD patterns of ALPOs showing preferred orientation upon incorporation of metals

As for AIMCM-41, conversion of 2,4-di-*t*-butylphenol gives products 2, 3 and a new compound, 3-benzyl-1,2-dihydronaphthalene which has never been observed by other researchers. Catalytic reaction of 2,4-di-*t*-butylphenol at 120°C by AIMCM-41(sec) proves to be superior than AIMCM-41, synthesised directly, as it gives a higher conversion (38 percent).

Benzoylation, a significant Friedel Crafts acylation reaction is significantly used in the synthesis of intermediates such as benzophenone and its substituted analogues for the manufacture of dyes. The disubstituted product 4,4_-dibenzoylbiphenyl is a potential monomer in the synthesis of poly(4,4_-diphenylene diphenylvinylene) or PDPV, a material for applications in electroluminescence and light-emitting diode (LEDs). Currently, the monomer can only be obtained via the difficult homogeneously catalysed process over AlCl_3 . We have reported for the first time the synthesis of disubstituted 4,4_-dibenzoylbiphenyl in a heterogeneous system over H-Al-MCM-41 [34].

NEW DIRECTIONS

(i) Nanostructured Materials

Large pored zeolites, mesomorphous MCM-41 and silica aerogels are naturally nanomaterials due to the existence of pores and crystalline network of nano dimension. Changes in the molecular properties of materials at the nanoscale greatly enhance their physical and chemical properties. Due to its stable and flexible framework of variable sizes, the zeolite lattice may also be used as a host for encapsulated complexes or metallic clusters allowing the control of nuclearity of these active species and the steric constraints imposed on the reactants. MCM-41 and VPI-5, for example, have been used to host polymer, metal complexes and enzymatic species to form molecular wires and zeozymes.

The development of heterogeneous oxidation catalysts which contain metal complexed Schiff bases such as phthalocyanine, porphyrin and salen that mimic catalytic activity of metalloenzyme is of interest [35]. Encapsulated metal

complex, as the guest molecule, into molecular sieves with suitable pore sizes such as zeolite Y, VPI-5 and MCM-41 as the host, via covalent or ionic bonding is expected to be as active as those present in enzyme, structurally and thermally more stable, remain unchanged during reactions and give higher conversions (Figure 24).

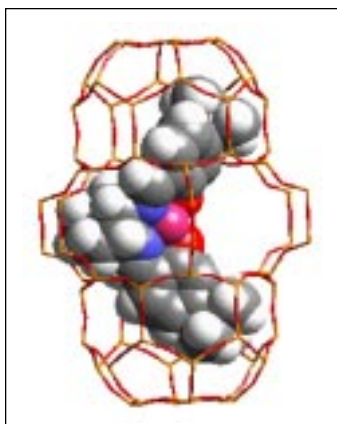


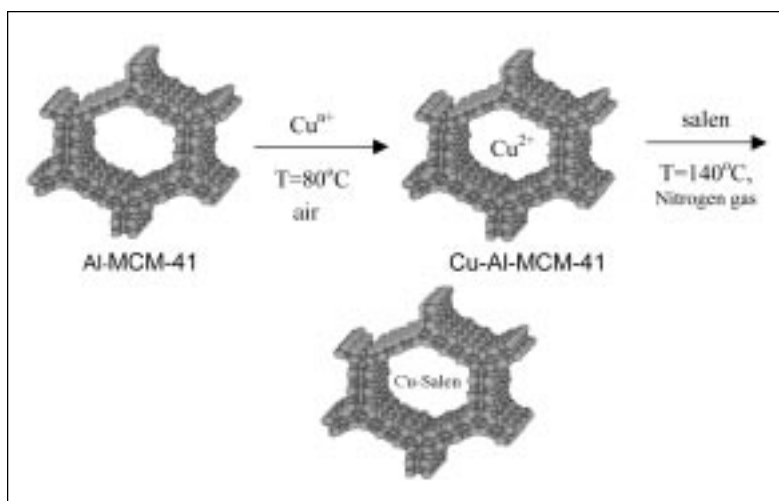
Figure 24 Metal complex encapsulated molecular sieves

In situ synthesis of Fe(III)-salen and Cu(II)-salen complexes, Mn(III) complexes based on diimine and aroylhydrazone ligands in the cavities of Al-MCM-41, by the flexible ligand method has been attempted with success in our laboratory. The catalytic activity of the Fe(III)-salen-Al-MCM-41 complex was studied in the oxidative polymerisation of bisphenol-A using aqueous 30 percent H_2O_2 at room temperature.

The encapsulation of Fe(III)-salen was further confirmed by nitrogen adsorption measurement and infrared spectroscopy (Table 5). The loading of complexes in Al-MCM-41 was dependent on the quantity of framework aluminium incorporated in the MCM-41. This suggests that there is electrostatic interaction between the positively charged encapsulated complexes and negatively charged Al-MCM-41 framework. The catalytic test results (Table 5) indicate that the higher the loading of iron complexes, the higher the conversion of bisphenol-A, with a maximum of 67 percent, significantly higher than that produced by homogeneous Fe-salen catalyst.

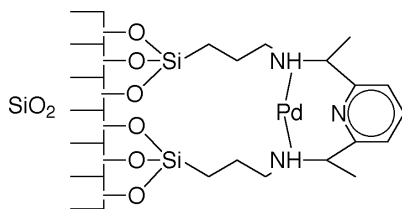
Table 5 Characterisation data of Fe-salen-Al-MCM-41 catalyst

Sample	SiO ₂ /Al ₂ O ₃	Fe/Al-MCM-41 (wt/wt percent)	CH ₂ -N peak area of complexes at 1602 cm ⁻¹ stretching (au) ^a	bisphenol-A conversion
1 ^b	120	0.62	600	33
2 ^b	60	0.91	900	62
3 ^b	40	1.23	1600	67
Fe- salen ^c	-	-	-	19

^aAnalysed by FTIR^bHomogeneous catalytic system^cHeterogeneous catalytic system**ZEOZIM CU - Salen - Al - MCM - 41**

Supported palladium catalysts are synthesized by anchoring the palladium complexes onto the functionalized Si-MCM-41 with chelating nitrogen ligands. The Schiff-bases compounds were prepared by condensation of 3-aminopropyltriethoxysilane and 2-acetylpyridine or 2,6-diacetylpyridine followed by reduction to secondary amines. Then, the Si-MCM-41 will be modified with the reduced

Schiff-bases followed by reaction with $[\text{PdCl}_2(\text{PhCN})_2]$. The anchored Pd-complexes are currently being tested as catalysts in the organic reactions such as the Heck reaction of iodobenzene with ethyl acrylate and styrene.



Supported palladium catalyst

Silica aeroglass is a glass formulated for the first time, from silica aerogel which has been directly prepared from rice husk (Figure 25). The high porosity, low density and dielectric properties of silica aerogel have been applied to produce silica aeroglass that is strong and light with excellent insulation properties. Silica aeroglass has a wide variety of applications, mainly as insulating glass and window panes, optical and audio parts, computer and space craft materials. Aerosilica glasses $(\text{SiO}_2)_x(\text{Na}_2\text{O})_{1-x}$ are obtained by the densification of silica aerogel by heat treatment at 1100°C , a temperature which is lower than that required by conventional glass melt process. The aeroglass exhibits thermal insulation property that is superior than conventional sodium silicate glass ($1.4 - 1.6 \text{ Wm}^{-1}\text{K}^{-1}$). It is also harder and stronger and contains less water than glass.



Figure 25 Silica aeroglass designed from silica aerogel from rice husk

(ii) Nanocomposites

Nanocomposites are a new class of composites based on nanoscale fillers, that are particle-filled polymers for which at least one dimension of the dispersed filler particle must be in the nanometre (10^{-9}m) range. Al-MCM-41 molecular sieve is a potential host material of polymers because it has excellent properties such as mesoporosity, ion exchange properties, thermal stabilities and high surface area. Polyethylene oxide (PEO)/Li-exchanged Al-MCM-41 nanocomposites were synthesized by incorporation of PEO into Li-exchanged Al-MCM-41 with melt intercalation technique under vacuum conditions. A series of these materials were synthesized based on weight percentage of PEO in the samples and characterization by XRD, FTIR, ^{29}Si MAS NMR and nitrogen adsorption measurements indicated that PEO was intercalated in the pores of Li-exchanged Al-MCM-41 (Figure 26). This has led to most dramatic changes in its physical properties, demonstrated by a remarkable increase in ionic conductivity of PEO/Li-exchanged Al-MCM-41 nanocomposite.

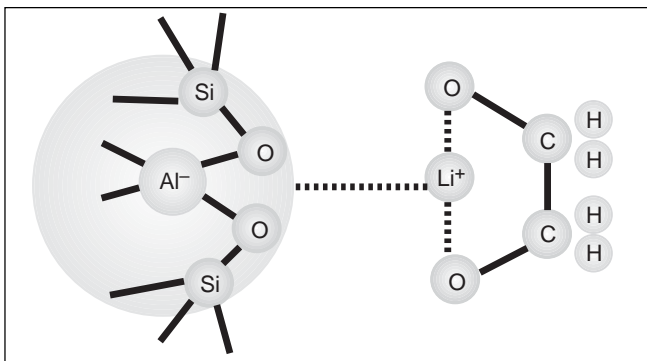


Figure 26 Schematic representation of PEO/Li-exchanged Al-MCM-41 nanocomposite

CONCLUDING REMARKS AND FUTURE OUTLOOK

Several features of the structural chemistry of zeolites are related to their importance as sorbents, molecular sieves, and catalysts.

Zeolites are potentially very active catalysts due to the topology of the framework, shape and size of the pores which can be modified to accommodate sorbates and impose shape selective constraints on the products of the reaction. More applications of these remarkable zeolite systems will be realised as our knowledge of the chemistry and structure of the framework continues to grow. Improvements in the technologies for the synthesis of zeolites and development of zeolites with larger pore sizes hold great promise in better use of the depleting petroleum resources.

Industrial application of aerogel-based catalyst or catalyst supports have so far been limited due to the rather expensive method of preparation and difficulties in reactors operation. Production of silica aerogel from rice husk does not only reduce the cost but at the same time minimises prolonged environmental problem. The future beneficial use of aerogels in catalysis mainly requires tailoring and design of the surface structure and overcoming the technical limitations.

The extraction of active amorphous silica from rice husk and its application in the synthesis and design of new materials is a novel approach. The novel applications have resulted in patents being file. The knowledge and expertise of the local zeolite researchers which is growing in number is a great asset specifically to UTM. After many years of studies and advancing through the pores, the projects are ready to be explored for commercialisation.

Since its discovery two centuries ago, there has been rapid growth in the science and technology of zeolites and mesomorphous materials, as testified by the exponential increase of papers and patent applications, the increasing number of industrial zeolite and mesomorphous-based processes and their expansion into organic chemicals manufacture, and the recent progress in matters of accessibility range, matrix behaviour, lattice components and framework structures. By virtue of their size, pore dimension, stability and regenerability, these materials are suited for incorporation into nanotechnology and new generation processes in which clean technology and environmental friendliness are major issues.

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BIODATA
Professor Dr. Halimaton Hamdan

Halimaton Hamdan was born in Malacca in 1956 and received her secondary education in Sekolah Tun Fatimah Johor Bahru. Halimaton earned her Bachelor of Science degree (1979) in Chemistry from Indiana University, Bloomington, Masters of Science degree (1979) from Marshall University, W. Virginia USA and her PhD (1989) in physical chemistry from University of Cambridge, UK. She has been an academic for 20 years and was appointed the first woman Professor at UTM in 1996. Her field of expertise is solid-state chemistry, specifically the chemistry of zeolites and she is a solid-state NMR spectroscopist. Halimaton has been the Director of Ibnu Sina Institute for Fundamental, Science Studies UTM, since August 2000.

Halimaton is the country's leading Zeolite and Porous Material scientist. Her current research activities focus on aerogel, nanocomposites, hybrid catalyst and encapsulation of enzyme in zeolites. She has received grants and sponsorships from which many post-graduates, commendable research findings, international publications, patents and awards have been produced. She was responsible in the establishment of the Zeolite and Porous Material Research Group, the only group in this field in the country. The research programme entitled 'Development of Zeolites and Derivatives as Catalysts in the Production of Fine Chemicals' was awarded a grant of RM11.3 million under the IRPA 8th Malaysian Plan. She received the Petronas Inventor's Award in 1993 for her innovative work on synthesis of zeolites from rice husk. She received a Research Fellowship from the British High

Commission for an attachment in Cambridge in 1993. Her innovation on silica aerogel from rice husk by one of her students has been selected the top 20 in the Young Inventor's Award, Far Eastern Economic Review 2000 and a Silver Medal at the Seoul International Invention Fair 2002, Korea.

Besides research, Halimatun has written, translated and produced a collection of academic books. She has written more than 50 journal publications and 15 scientific books. Her book entitled *Keselamatan Makmal* was the first book published by DBP, written and produced by the author. She co-authored *Kimia asas Sains dan Kejuruteraan* which has been published and sold about nine thousand copies through four reprints. In addition, Halimatun is an international translator and editor.

As a scientist, Halimatun continuously promotes the teaching and learning of science. She initiated the Excellent Scientists Programme at UTM designed specifically to nurture students of science to become prominent scientists. She is also the anchor person towards the establishment of the Space Science Research Center in UTM. She is a member of Peterhouse, Cambridge, Honorary Member of the Golden Key International Honour Society, Analysis and Science Expert Panel in the Ministry of Science, Technology and Environment Malaysia and the Malaysian Academy of Science.