

## CHAPTER II

### BACKGROUND

#### 2.1 Molecular Sieves MCM-41

Two classes of materials that are used extensively as supports of heterogenous catalysts and adsorption media are microporous (pore diameters  $< 20\text{\AA}$ ) and mesoporous ( $\sim 20\text{-}500\text{\AA}$ ) inorganic solids. A major subclass of the microporous materials is molecular sieves. These materials are exemplified by the large family of aluminosilicates known as zeolites in which the micropores are regular arrays of uniformly-sized channels (Szostak, 1989; and Meier, 1986).

Mesoporous materials are typically amorphous or paracrystalline such as silica (Iler, 1979) or transitional aluminas (Wefers and Misra, 1987) or modified layered materials such as pillared clays and silicates (Pinnavaia, 1983; Vaughan, 1988; Landis *et al.*, 1991; and Tindwa *et al.*, 1985). The pores in these materials are generally irregularly spaced and broadly distributed in size (Vaughan and Lussier, 1980; and Meier, 1986).

The new mesoporous material, named MCM-41 (Mobile Composition of Matter), which is silicoaluminate referred to as  $\text{SiAl}_x\text{C}_n$ , where  $x$  is the mole ratio Si/Al and  $n$  the surfactant chain length) has been synthesized from alkyltrimethylammonium bromides with different chain lengths as surfactant templates ( $x = 32$  and  $n = 8, 12, 14, 16, 18$ ) and of aluminum isopropoxide as a source of aluminum with different framework Si/Al ratios ( $n = 14$ ,  $x = 8, 32$  and purely siliceous SiC14) (Dobias, 1984). This mesoporous material, MCM-41, can be controlled to have pore size distributions nearly as sharp as that of the conventional molecular sieves. The synthesis procedure of MCM-41 is a considerably easy controllable technique for induction of mesoporosity,

based on self-organized surfactant liquid-crystalline phases. Some characteristics of this family of materials include ordered amorphous structure, discrete pore size(20-100 Å<sup>0</sup>), unconnected pore channels with diameters that can be tailored in the range 1.6-10 nm, large specific surface area (600-1300 m<sup>2</sup>/g), large internal pore volume (1.0 cm<sup>3</sup>/g), and hydrocarbon sorption capacity of greater than 0.7 cm<sup>3</sup>/g. Experimental evidence is consistent with the postulate that the pore walls in MCM-41 materials are amorphous. The pores are roughly cylindrical in shape, and the surface resembles that in amorphous silica or alumina-doped silica (Beck *et al.*, 1992; Kresge *et al.*, 1992; Tanev and Pinnavaia, 1995; and Meziani *et al.*, 1997).

The concept of using organic-guest species of nanoscale porosity in molecular sieve synthesis has been initially developed for framework stabilizing purposes. The role of molecular water as a universal stabilizer in the early syntheses has been gradually shared or taken over by organic molecules which provide structural specificity in the composition (Barrer, 1989). It is believed that the organic guest species can act as (1) void filters, (2) structure – directing agents, or (3) templates.(Davis and Lobo, 1992). Classical examples of organic guests are the quaternary ammonium ions and amines which have been successfully used for formation of different zeolitic structures (Szostak, 1989). By resemblance to the naturally occurring zeolites, which are predominantly aluminosiliceous minerals, aluminum and silica have been chosen as framework building components in the early syntheses( Flanigen, 1980).

The structure- directing role has been evidenced in the synthesis of pure siliceous compositions. These systems contain only silica, water, organic species, and low concentrations of alkali metal hydroxides. The pure siliceous product is hydrophobic and uncharged. The predominant interaction between the organic molecules and the silicate species is van der Waals force. The H-SiNMR result has shown that a close contact between the

tetraalkylammonium ions and the silicate species is established prior to the development of long-range crystalline order. A recent study concluded the aluminum-rich zeolites are less amenable to structure direction by organic species than high-silica zeolites (Burkett and Davis, 1995). Since alkali metal ions are necessary to balance their negatively charged framework, the zeolite cannot accommodate a sufficient number of organic cations in the void space. Thus, the structure-directing role of the organic guests is suppressed, perhaps in part due to the nature of the primary electrostatic interactions between the organic molecules and the inorganic species. A schematic of the structure directing role in zeolite synthesis is shown in Figure 2-1.

The concept of supramolecular templating (the guest species are no longer single molecules, but spatially organized arrays of surfactant micelles or surfactant liquid-crystalline phases), which results in the formation of larger openings ( $15\text{-}100 \text{ \AA}^0$ ) upon removal of the template (Beck *et al.*, 1992) as shown in the Figure 2-2. In this work, it was to combine both approaches by utilizing molecular and supramolecular guest species simultaneously to control porosity in the micro-and the mesopore range.

MCM-41 is of particular interest because it fills two important roles,

- Its narrow pore size distribution and straight, unconnected channels make it an ideal model adsorbent for fundamental theoretical studies of fluid behavior in confined regions.
- Its large and controllable pore size enables it to host much larger molecules than alternative catalytic materials, bringing it into the size range required for hosting biological materials (Maddox *et al.*, 1997).

MCM-41 is also an ideal adsorbent for several potential applications,

- 1) Purification applications (which generally depend on surface selectivity for polar or polarizable molecules such as water, CO<sub>2</sub>,

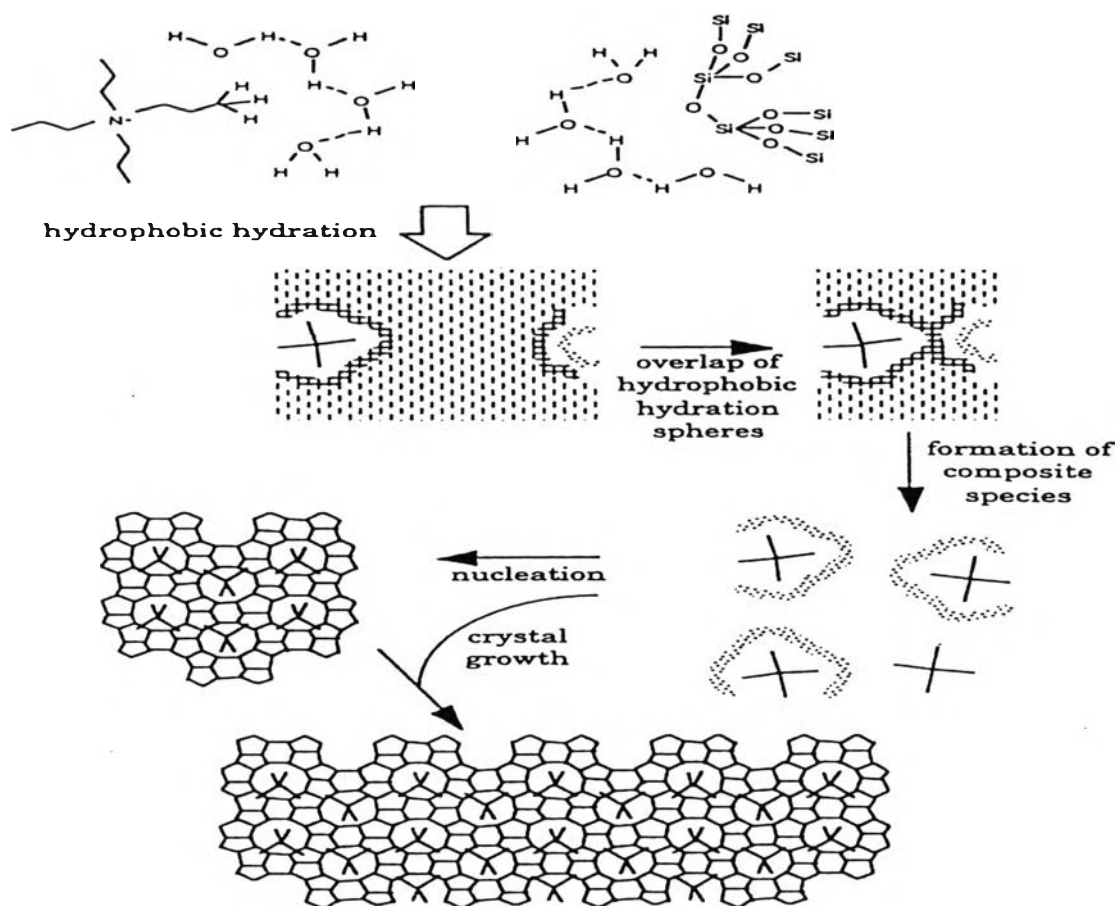


Figure 2-1 Proposed mechanism of structure direction in the TPA- mediated synthesis of Si-ZSM5 (Burkett., 1995)

or sulfur compounds), and include natural gas drying and sweetening; cryogenic air separation; removal of  $\text{NO}_x$  and  $\text{SO}_x$  pollutants.

- 2) Bulk separation, such as normal/iso-paraffin separation and xylene separation. The traditional ion-exchange applications include radioactive waste storage, and removal of ionic pollutants from wastewater.

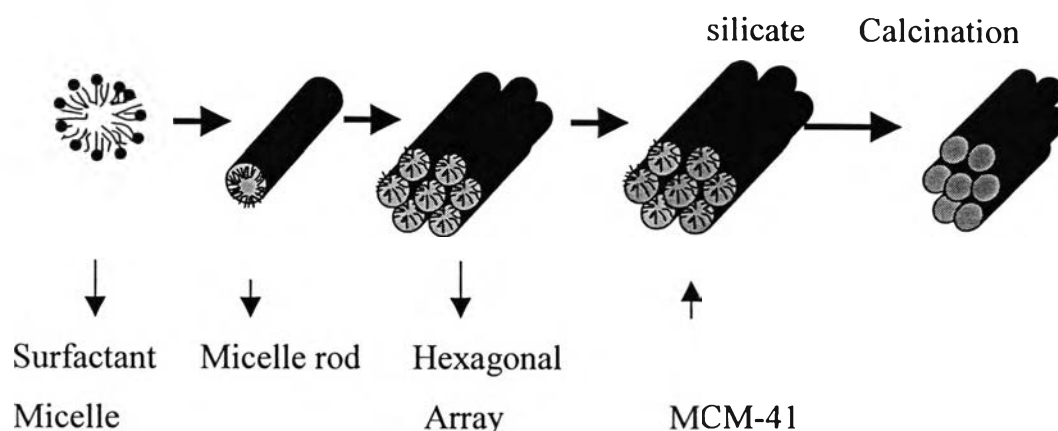


Figure 2-2 The formation steps of MCM-41 mechanistic pathways: (1) liquid crystal phase initiated and (2) silicate anion initiated (Kresge *et al.*, 1992)

## 2.2 Adsorption of Surfactant at Solid-Liquid Interface

A surfactant (Surface-active agent) has an amphipathic structure which consists of lyophilic (hydrophobic) and lyophobic (hydrophilic) parts as shown in Figure 2-3. When present at a low concentration in a system, it will have the property of adsorbing onto the surface or interfaces of the system. The molecule at a surface has higher potential energies than one in the interior of the surface. It will lead to reduction of the surface tension of the water and also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it as presented in Figure 2-4. The adsorption of surfactant ions from aqueous solutions onto oppositely charged surfaces is based on two fundamental interactions: electrostatic and hydrophobic. According to electrostatic interaction, surfactant ions are

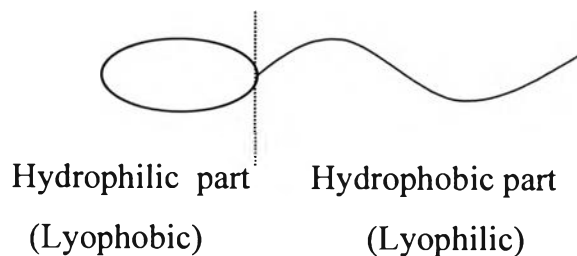


Figure 2-3 Structure of surfactant molecule consisting of hydrophilic head group and hydrophobic tail (Rosen, 1989)

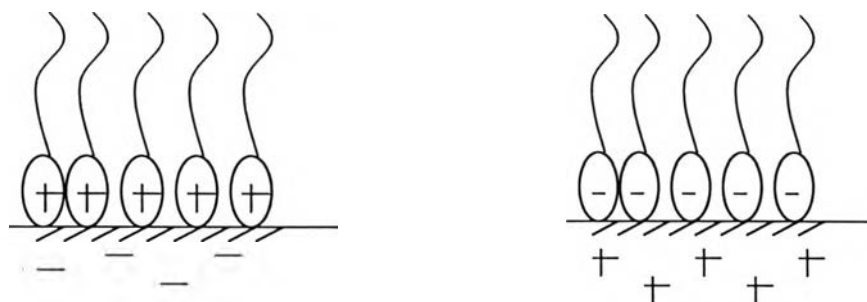


Figure 2-4 Adsorption of surfactant molecules on the solid substrate surface by a result of having opposite charge (Rupprecht and Gu, 1991)

attracted to the adsorbent by Coulombic forces between the charged-head groups and oppositely charged adsorption sites on the surface. Hydrophobic interaction is exhibited by the non-polar parts of the surfactant ions (hydrocarbon chains) and due to Van der Waal attraction (Rupprecht and Gu, 1991). Additionally, silica is a classical sorbent to study adsorption of cationic surfactants on negatively surfaces. The driving forces for adsorption of cationic surfactants on silica are the Coulombic attractions between surfactant ions and charged surface groups and the hydrophobic interactions between hydrocarbon moieties (Goloub and Sidorova, 1992). The adsorption of

surfactants at solid-liquid interface is strongly influenced by a number of factors:

- 1) The nature of the structural groups on the solid surface: negatively or positively charge and the surfactant is adsorbed by the opposite charge head group on the surface.
- 2) The molecular structure of the surfactant being adsorbed (the adsorbate) that effects to the ability of adsorption.
- 3) The environmental conditions of the aqueous phase: pH, electrolyte content, and temperature. The charge on the solid oxide surface can be handled to be either negative or positive by adjusting the pH of the contacting aqueous solution.

As the pH of the aqueous phase is lowered, a solid surface will usually become more positive, or less negative because of adsorption onto charged sites of the protons from the solution (Conner and Ottewill, 1971). The reverse is true when the pH of the aqueous phase is raised. The pH that makes the charge on the surface equal zero is called the Point of Zero Charge (PZC). When the pH of the contacting aqueous solution is below the PZC of the solid surface, the surface will be protonated and become more positive. Vice versa, the solid surface will be negatively charged at a pH over the PZC. For example, silica having  $2 < \text{PZC} < 3$  will be negatively charged if the pH of the aqueous phase exceeds 3 (Iler, 1979). As a result, cationic surfactants such as octyltrimethylammonium bromide or any quaternary ammonium surfactants adsorb readily on the surface of silica and MCM-41 which is a siliceous solid when the pH of the contacting aqueous phase is greater than 3.

Improvement screening of the surface charge by the surfactant ions:

- 1) A specific attraction between the surfactant head group and the charged group of the surface.

- 2) A specific interaction between the aliphatic tail and the hydrophobic parts of the surface.
- 3) Lateral attractions between surfactant ions adsorbed head-on lead to strong binding of surfactant molecules with the surface and promote the creation of new negatively charged sites at the surface.

The ability of the surface to adjust its charge density will depend on the experimental conditions: initial pH, surface to solution volume ratio, and amount of ionized silinol groups (Goloub and Sidorova, 1992).

The adsorption isotherm of ionic surfactants on oxide surfaces is typically an elongated 'S' -shaped curve when one plots the log of the equilibrium concentration of surfactant versus the amount of surfactant adsorbed (Somasundarun and Fuerstenau, 1966; Scamehorn *et al.*, 1982). Generally, this 'S' -shaped isotherm can be separated into four regions (Rosen, 1989), as shown in Figure 2-5. Region I corresponds to both very low concentration and low adsorption of surfactant. This region is commonly referred to as the Henry's law region because the adsorbed surfactant is considered to be in infinite dilution in the surface phase and, thus, the interaction between molecules of surfactants is negligible. Adsorbed surfactants in this region are viewed as being adsorbed alone and not forming aggregates. The Henry's law region is AB where the line of unit slope indicates proportionality between amount adsorbed and bulk surfactant concentration. Region II is distinguished by a sharply increased isotherm slope relative to the slope in the region I and is known to be an effect of the cooperative interaction between hydrocarbon tails of the adsorbed surfactant molecules, which results in the formation of surfactant aggregates on the most energetic patches (Scamehorn *et al.*, 1982). These adsorbed surfactants aggregated are called admicelles (Harwell *et al.*, 1985) or hemimicelles (Somasundarun and Fuerstenau, 1966), depending upon whether the aggregates are viewed as bilayers or monolayers. The admicelle is considered



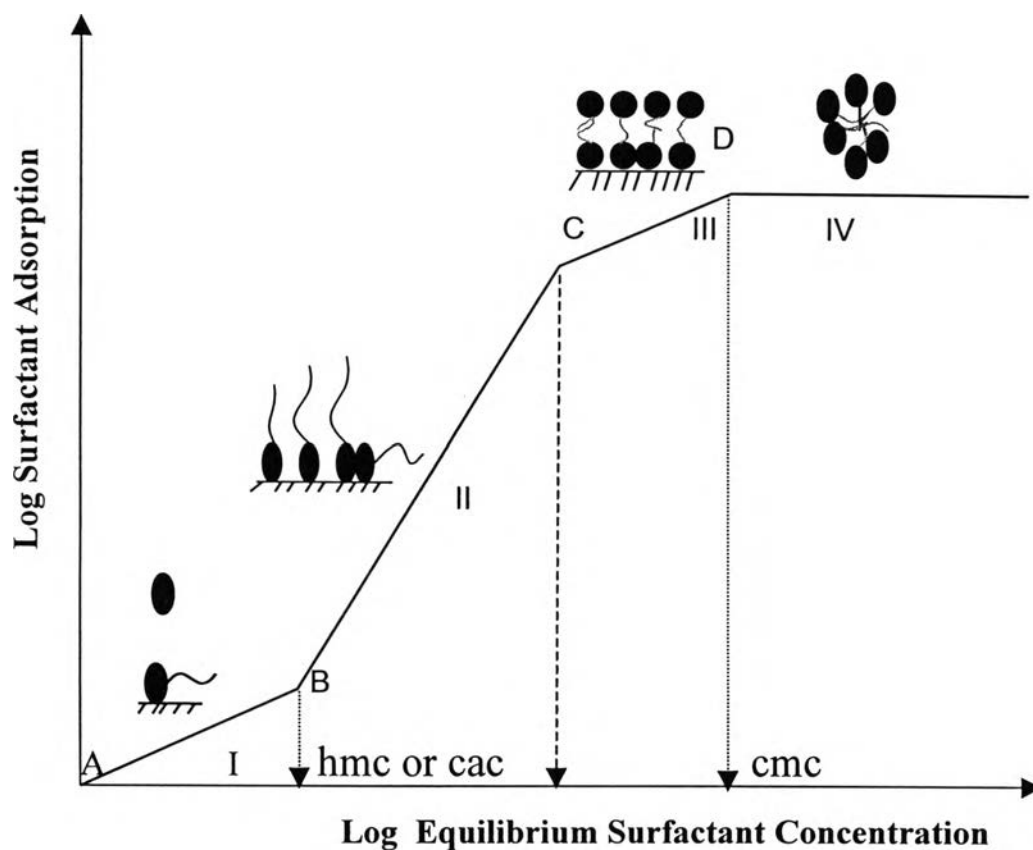


Figure 2-5 Typical adsorption isotherm of surfactant on oppositely - charged solid surface (Rosen, 1989)

as local bilayer structure with a lower layer of head groups adsorbed on the substrate surface and an upper layer of head groups in contact with solution. The hemimicelle is a monolayer structure having the polar group oriented towards the solid surface and presents a hydrophobic patch of closely packed alkyl groups to the aqueous phase. The transition point from region I to region II, representing the first formation of adsorbed surfactant aggregates, is called the critical admicelle concentration (cac) (Harwell *et al.*, 1985) or the hemimicelle concentration (hmc) (Somasundarun and Fuerstenau, 1966). In systems where hemimicelles form before admicelles, as surfactant concentration is increased, the concentration at which the transition from one

type of aggregate to the other takes place depending mainly on electrostatic effects (Yeskie and Harwell, 1988). Thus, high counterion binding, high surface charge densities and higher dielectric constants all favour the formation of admicelles before the formation of hemimicelles. Conversely, low counterion binding, low surface-charge densities and low dielectric constants all favour formation of a hemimicelle at a lower surfactant concentration than necessary for an admicelle to form.

In region III, the slope of the isotherm decreases because of competition between admicelle. This is thought to be caused by either repulsion between the like-charged head groups on the surface or the beginning of admicelle formation on lower energy surface patches. The adsorption now must overcome this electrostatic repulsion between the oncoming ions and the similarly charged solid. Region IV is the plateau region, the position of this plateau usually corresponds to a maximum adsorption of either one or two monomolecular layers on the solid surface, having almost constant surfactant adsorption with increasing surfactant concentration. Typically, the equilibrium surfactant concentration at the transition point from region III to region IV is approximately at the Critical Micelle Concentration (CMC).