

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Catalyst for *n*-Octane Aromatization

Ever since the discovery of Pt/KL in 1980 by Bernard, controversy has arisen as to why Pt/KL is unique for the aromatization of *n*-hexane reaction. Davis, 1993 found that there are roughly five different possible explanations attesting to the uniqueness of Pt/KL for aromatization, and these explanations offer either geometric or electronic interpretations:

(a) *Molecular Die (Geometric) Effects*: The *n*-hexane would preferentially adsorb onto the Pt cluster at a terminal carbon, which would favor ring closure to form benzene (Bernard *et al.*, 1980).

(b) *Preorganization of *n*-hexane for ring closure*: The space inside the L-zeolite was similar to that of a cyclic, six carbon species. Therefore, the adsorbed hexane curls around on itself in the zeolite cage in order to maximize its van der Waals interactions. Therefore, the resulting transition state would put the free terminal carbon in close proximity with the active Pt cluster. This preorganization of the *n*-hexane molecule favored ring closure, and was responsible for the high activity and selectivity of Pt/KL for aromatization (Bernard, 1980 and Derouane and Vanderveken, 1988).

(c) *Electronic Effects*: The high activity and selectivity of Pt/KL catalysts for aromatization derived from a unique electronic structure. Larger, softer, cations like Ba^{+2} , with diffuse charge, would allow greater donation of electron density from zeolite oxygen anions to the Pt metal, whereas smaller, harder, cations like Mg^{+2} , would interfere with this transfer. As a test, the competitive hydrogenation of benzene and toluene was used. Since toluene is a better electron donor than benzene, hydrogenation of toluene was expected to be hindered with increased electron donation from the support. $K_{toluene}/K_{benzene}$ increased with Lewis acidity ($Mg > Ca > Ba$) (Bernard, 1980 and Ko and Ahn, 1999).

(d) *Inhibition of Bimolecular Pathways*: The uniqueness of Pt/KL catalysts with the ability of KL's microporous structure to inhibit bimolecular

reactions leading to the formation of coke on the surface of the Pt clusters (Jacobs *et al.*, 1999).

(e) *Stabilization of Small Pt Clusters*: The exceptional reactivity for Pt/KL resulted from the ability of the ellipsoid cages making up the channels of the KL zeolite, to stabilize small clusters (Jacobs *et al.*, 2001).

For the high activity and selectivity, most authors agree that an effective catalyst should have as much Pt as possible inside the channels of the zeolites.

Jacobs *et al.* (1999) prepared catalysts for n-hexane and n-octane aromatization by impregnation method. In the report, they synthesized catalysts via two different methods, vapor phase impregnation method (VPI) and incipient wetness impregnation method (IWI). The result showed the same trend as other work, VPI catalyst had a high dispersion with a majority of small Pt clusters inside the L-zeolite channels. This morphology resulted in high catalyst stability and selectivity to aromatic formation, even in the presence of sulfur, in contrast with IWI, which showed lower selectivity and more rapid deactivation.

Jacobs *et al.* (2001) also found that Pt/KL catalysts were synthesized by different methods including ion-exchange (IE), IWI and VPI and investigated the effect of metal loading. The catalysts were pretreated at two different reduction temperatures at 400 and 500°C to investigate the sensitivity of each catalyst to thermal treatment. All catalysts showed high dispersion and H/Pt ratio greater than unity. And from FTIR of adsorbed CO showed the characteristic dispersion and location of Pt cluster by each method. IE catalysts were found to have a high fraction of Pt cluster located at external surface of L-zeolite and were the most sensitivity to thermal treatment. These catalysts deactivated easily by coke formation. IWI and VPI catalysts showed a majority of Pt cluster located inside channel of L-zeolite. After thermal treatment, IWI catalysts were damaged by half of their activity, while the performance of VPI catalyst maintained. Furthermore difference VPI method was studied, including moderate vacuum and a helium flow. Both of them showed similar result as including high vacuum. Therefore, the possible scaling up process is deal with VPI technique including moderate vacuum or operate in helium atmosphere.

2.2 M41S Family

Two classes of molecular sieve materials that are widely used extensively as heterogeneous catalysts, catalyst supports and adsorption media are microporous and mesoporous molecular sieves. The utility of these materials is manifested in their microstructures which allow molecules access to large internal surfaces and cavities that enhance catalytic activity and adsorptive capacity (Beck *et al.*, 1992).

According to the International Union of Pure and Applied Chemistry (IUPAC) definition, porous materials are divided into three classes, as following in Table 2.1.

Table 2.1 Pore size definition of zeolite and molecular sieves (Zhao *et al.*, 1996)

Pore size (Å)	Definition	Typical material	Ring size of T-atom	Pore diameter (Å)
>500	macroporous			
20-500	mesoporous	MCM-41		15-100
<20	microporous ultralarge pore	cloverite	20	6.0x13.2
		JDF-20	20	6.2x14.5
		VPI-5	18	12.1
		AlPO4-8	14	7.9x8.7
	large pore	faujasite	12	7.4
		AlPO4-5	12	7.3
		ZSM-12	12	5.5x5.9
	medium pore	ZSM-48	10	5.3x5.6
		ZSM-5	10	5.3x5.6 5.1x5.5
	small pore	CaA	8	4.2
SAPO-34		8	4.3	

The first synthesis of an ordered mesoporous material was described in a patent registered in 1969. However, due to a lack of analysis, these materials were not recognized (Takuchi and Schüth 2005). In the early 90'S, scientists from Mobil Oil Corporation synthesized the allied materials via liquid crystal templates, which contain resemble silica-based that designated as M41S family, including MCM-41 (hexagonal phase), MCM-48 (cubic phase) and MCM-50 (lamellar phase).

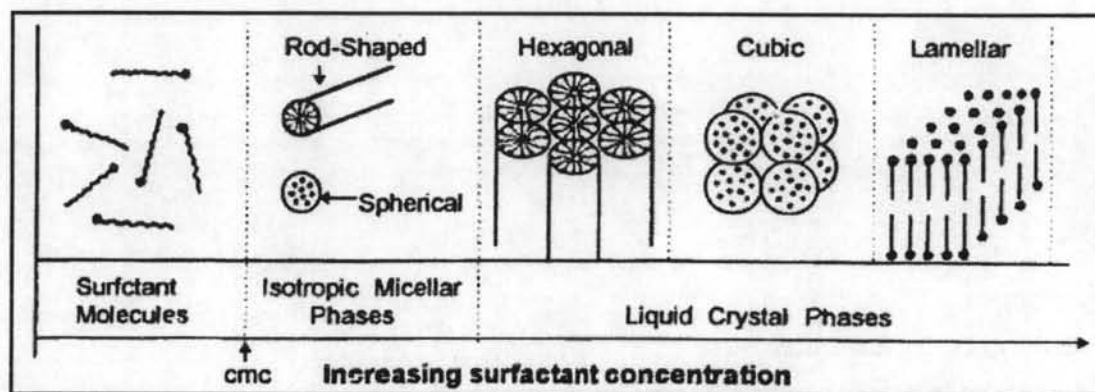


Figure 2.1 Phase sequence of surfactant-water binary system (Zhao *et al.*, 1996).

The successful synthesis of this new family of mesoporous silicate and aluminosilicate molecular sieves with high surface area, uniform pore size distribution and large pore volume has greatly expanded the capacities of heterogeneous catalysts. Accordingly, MCM-41 has been investigated extensively because the other members in this family are either thermally unstable or difficult to obtain (Vartuli *et al.*, 1994).

2.3 MCM-41

MCM-41, Mobil Composition of Matter number 41 (Takuchi and Schüth, 2005), is a silicate obtained by a templating mechanism. It is ordered to some degree, so that there are arrays of non-intersecting hexagonal channels and the wall of the channels are amorphous SiO_2 . These materials typically have uniform pore openings in the range of 15 to 100 Å and high surface areas above $700 \text{ m}^2/\text{g}$ (Beck *et al.*, 1992).

And also, these materials contain high thermal and hydrothermal stability, possibility of controlling its pore size and its hydrophobicity and acidity. These characteristics have made MCM-41 a promising material as catalyst support and used as hosts for the inclusion of compounds and nanosize clusters, and molecular sieves for large molecules, namely; OX and EB.

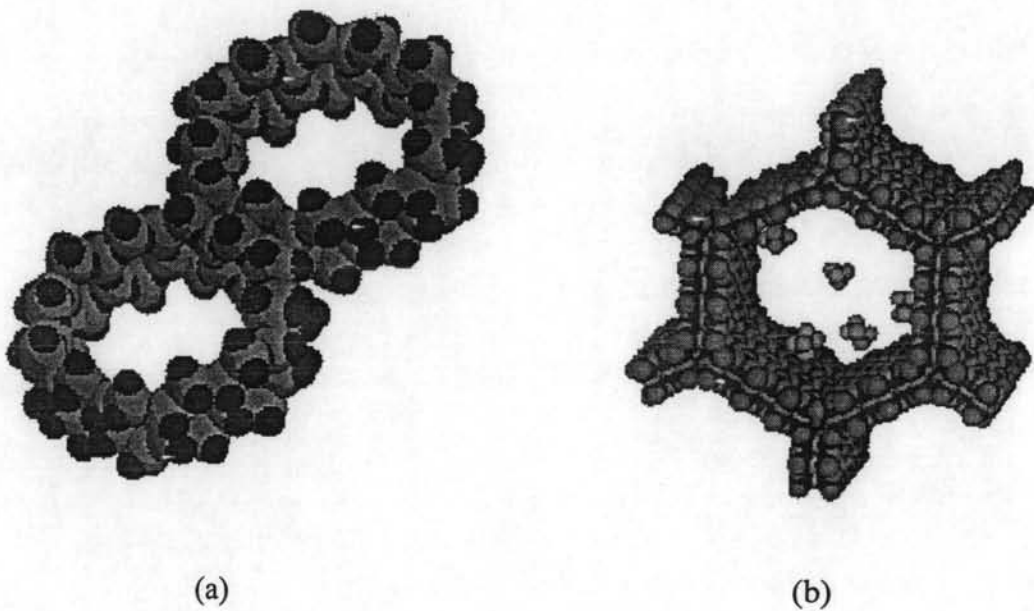


Figure 2.2 Structure of MCM-41; a) link of two hexagonal channels of MCM-41, b) methane and ethane inside hexagonal pores of MCM-41 (Gusev *et al.*, 1996).

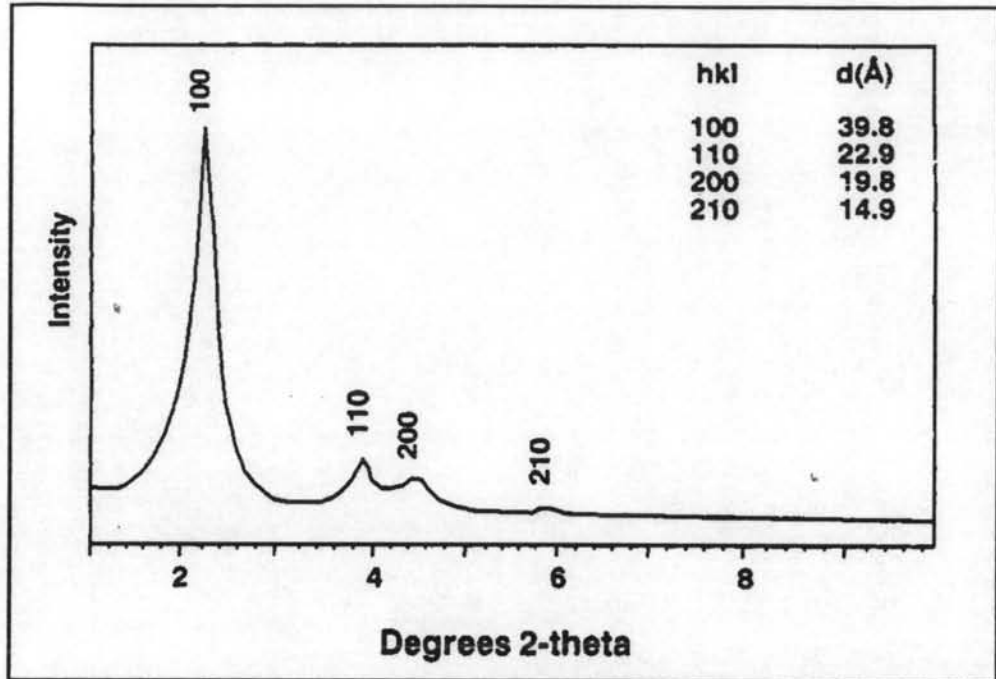


Figure 2.3 XRD-pattern of MCM-41 (Beck *et al.*, 1992).

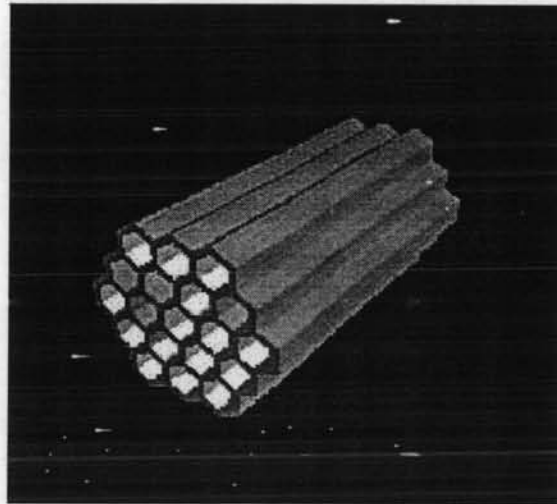


Figure 2.4 Possible structure of MCM-41 (Tanamura *et al.*, 2001).

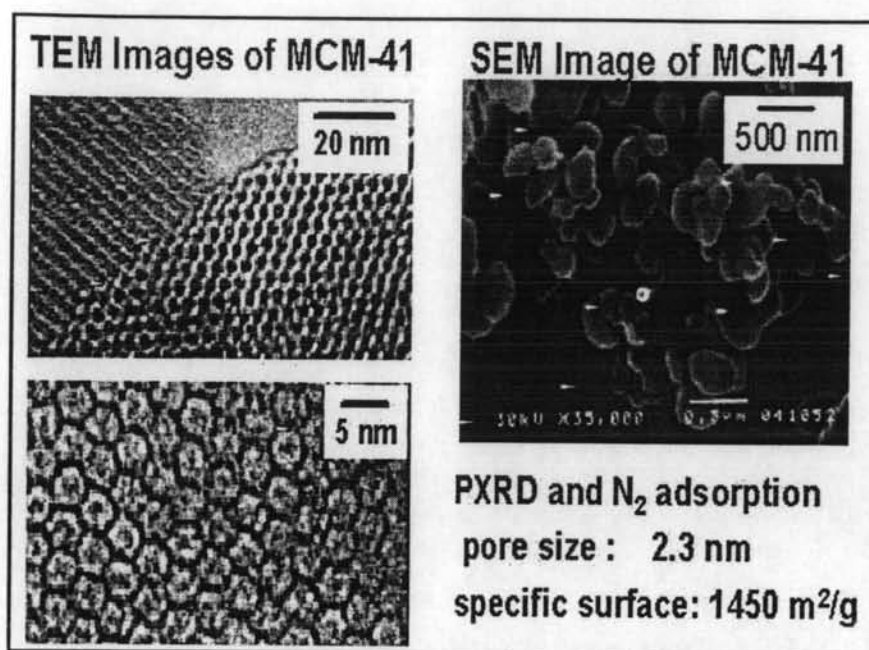


Figure 2.5 TEM and SEM images of MCM-41 (Tanamura *et al.*, 2001).

2.4 Formation Pathways of MCM-41

As mentioned earlier, the synthesis of MCM-41 is a considerably easy controllable technique for induction mesoporosity by using self-assembly surfactant liquid-crystalline phases. The concept of using structure-directing template (organic-guest species of nanoscale porosity) in molecular sieve synthesis has been 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 composition. It is believed that organic species can act as void filters and structure-directing agents used as template (Selvam and Bhatia, 2001). Generally, *n*-alkyl quaternary ammonium cationic surfactants are widely used as a template for formation of different pore size distributions. In these systems, the products contain only silica source, water, organic template and low concentration of alkali metal hydroxides. The predominant interaction between the organic species and silicate is *Van der Waals force*.

And also, the second formation for synthesis of MCM-41 is 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 (15-100 Å) upon removal of the template (Beck *et al.*, 1992) as shown in Figure 2.6. In this work, it was to use the second approach by utilizing supramolecular guest species simultaneously to control porosity in the mesopore range.

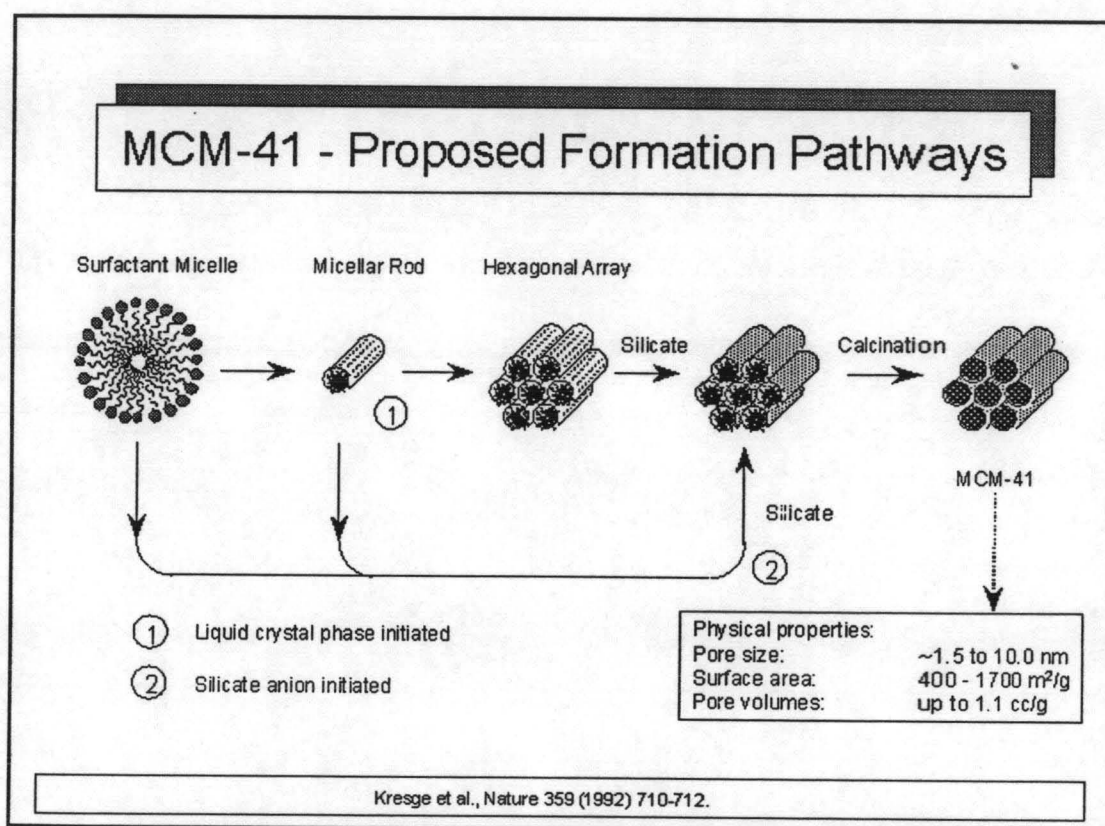


Figure 2.6 MCM-41 proposed formation pathways.