

## CHAPTER II

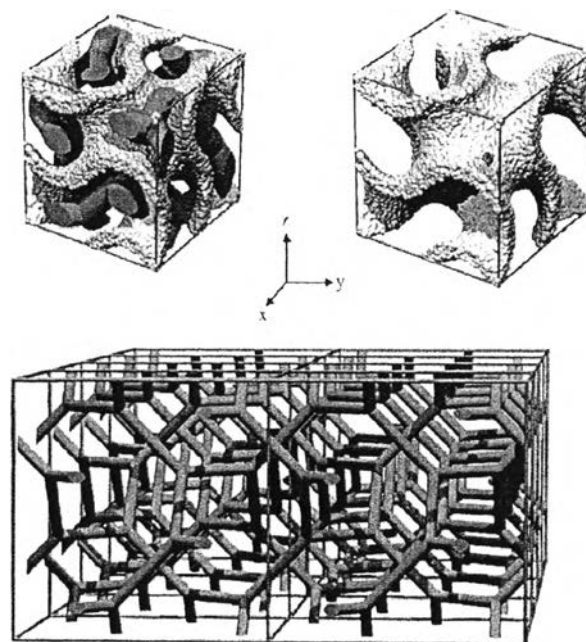
### THEORETICAL BACKGROUND AND LITERATURE SURVEY

#### 2.1 Introduction to MCM-48 Materials

The researchers at Mobil Research and Development Corporation published the synthesis of a molecular sieve which possessed larger pores, as compared to the microporous ones, since 1992, known as Mobil Composition of Matter and abbreviated as MCM-41, MCM-48 and MCM-50 [Kresge C.T. *et al.*, 1992; Beck J.S. *et al.*, 1992]. They used alkyltrimethyl ammonium halides as the structure-directing agent surfactants and combination of sodium silicate, tetraethoxy silicate (TEOS), fumed silica, or Ludox as the silica source. The basic catalysts introduced in the aqueous synthesis solutions were sodium hydroxide or tetraethyl ammonium hydroxide. The synthesis solutions were kept at temperature ranging from 100° to 150°C for 24–144h. After that the solid products were filtered, washed and dried. Finally, the calcination of materials was operated at 540°C under a gas flow of alternate nitrogen and air, resulting in porous structures.

The structure of MCM-48 has a gyroid minimal surface shape with *Ia3d* symmetry and provides a three-dimensional bicontinuous pore system, as confirmed by Monnier *et al.* (1993). In contrast to the MCM-41, it has a unidirectional pore structure which provides only one-dimension for the reactants and product to go through. However, the synthesis of MCM-48 is required a longer period of time and has an irreproducible problem in comparison to the synthesis of MCM-41 [Kruk M. and Jaroniec M., 1999; Xu J. *et al.*, 1999; Mathieu M. *et al.*, 2001].

The gyroid minimal surface or G-surface divides the cube into two identical but separates compartments, creating two independent units, but intertwining enantiomeric 3D pore system. Corresponding to Meynen *et al.* (2009) report, the schematic in figure 2.1 represents the unit cell with two micelle systems (red and blue rods), followed by the pore system. The two independent pore systems are interconnected and never cross or join each other.



**Figure 2.1** Cubic unit cell of MCM-48 with two independent micelle systems (red and blue rods) separated by the pore wall (upper). The bottom represents the 2x4 cubic unit cells without the pore walls and two independent rod micelle systems (red and blue) moving towards the [100] direction [Meynen V. *et al.*, 2009].

## 2.2 How to Synthesize Mesoporous Silica Materials

Generally, combination of sol-gel process, consisting of hydrolysis and condensation reactions, and supramolecular self-assembly with hydrothermal conditions has been widely used as the synthesis process. Silica precursors are first dissolved into aqueous solution containing surfactant before the hydrolysis and the condensation processes taken place to obtain “sol”. This step composes of oligomeric and polymeric silicate species. Then, the gel is formed after polymerization of the oligomeric and the polymeric silicate species proceeds. Finally, the self-assembled surfactant-silicate precipitates out of solution. The solid materials are filtered and washed. Mesoporous silica materials are obtained after the removal of surfactant by calcinations or solvent-extraction [Asefa T. and Tao Z., 2012].

### 2.3 Mechanisms

Kresge *et al.* and Beck *et al.* (1992) proposed a liquid crystal templating (LCT) mechanism to explain how highly ordered structures of mesoporous materials in the M41S family were formed. The mechanism composes of four steps: (1) surfactant micelles are formed in the aqueous solution and assembled into cylindrical micelles; (2) the cylindrical micelles are stacked into a regular array of liquid crystalline structures; (3) anionic silicates in the solution are adsorbed onto the crystalline structures to create positively charged surfaces and (4) the mesoporous silicas are obtained after the removal of surfactant templates. Moreover, they also described that the step 3 occurred at the same time as steps 1 and 2.

In 1993, Stucky and coworkers synthesized MCM-41 at different temperatures for different reaction times, and studied the structures and compositions of the mesoporous materials. They explained the formation of the ordered mesoporous silicas and proposed the model as follows: The oligomeric silica polyanions (denoted as  $I^-$ ) bound with cationic head groups of surfactants (denoted as  $S^+$ ), then the surfactant-silicate complexes ( $S^+I^-$ ) were formed due to the charge density matching at the interface between silicate anions and surfactant cations. In the early stage, the lamellar structures were formed due to the thermodynamics favored. After the polymerization of silicate species proceeded, the charge density matching of anion silicates decreased. In order to match the reduced charge density and kept the constant of silicate-to-surfactant ratio, the expansion of the head group area of the surfactant assembly occurred, resulting in the formation of hexagonal mesophases.

Huo *et al.* (1994) extended the model from Stucky and coworkers and this model could be explained the formation of various mesostructured nanomaterials. The model could be applied to  $S^+I^-$  by varying  $[H^+]$  in solutions. Beside the  $S^+I^-$  system, both negatively charge of surfactant and inorganic moieties ( $S^-$ ,  $I^-$ ) and positively charge ( $S^+$ ,  $I^+$ ) could be explained by this model. The formation of mesophases and their structures in this case was assisted by the counterions (i.e.  $X^+$  =

alkaline metal ions and  $X^-$  = halide ions) to form a sandwich-like triple-layer ( $S^-X^+I^-$  or  $S^+X^-I^+$ ).

## 2.4 Literature Review

Israelachvili *et al.* (1976) developed a microscopic model according to a dimensionless packing parameter ( $g$ ) which plays a key role in a prediction of the structure of surfactant aggregates and the corresponding mesophase structures in surfactant–water systems. The number  $g$  is defined as  $g=V/a_0l_c$ , where  $V$  is the effective volume of the hydrophobic chain of the surfactant,  $a_0$  is the effective aggregate surface area of the hydrophilic head group, and  $l_c$  is the effective hydrophobic chain length. In addition, Stucky *et al.* (1994) expanded the model to the ternary system which composed of sodium hydroxide or NaOH/cetyltrimethyl ammoniumbromide or CTAB/tetraethoxysilane or TEOS. They also created a synthesis-space diagram of mesophase structures.

Vartuliet *al.* (1994) found that the surfactant/silica ratios affected the formation of mesostructures. They varied the surfactant/silica ratio from 0.5 to 2.0 and obtained the products with hexagonal, cubic (Ia3d), lamellar and uncondensed cubic octamer composite structures. After that Gallis and Landry (1997) reported the phase transformation from MCM-41 to MCM-48 using temperature modification. They also proposed that ethanol played important role in the transformation process through increasing the surfactant packing parameter ( $g$ ) and incompletely polymerized silicate framework induced the transformation.

Alfredsson *et al.* (1997) studied the MCM-48 samples using electron microscopy (SEM and TEM) and found that the particles had a crystal or cubosome shape associated with them. They noticed that an existing shape was the truncated octahedron even though all the particles were not perfect polyhedral. In 1998, Kim and coworkers (1998) synthesized micrometer-sized of MCM-48 single crystals (truncated rhombic dodecahedra), using alcohol (methanol, ethanol) as additive for controlling mesophase in the sodium silicate/CTAB solution. The mixture was

heated to 100°–130°C in a sealed autoclave to prevent the alcohol evaporation. They found that the loss of alcohol during the synthesis provided a disordered phase, indicating that the alcohol affected the structure of the surfactant-inorganic composite during condensation.

Díaz *et al.* (2004) studied the structural phase changes in mesoporous family and found that the transformations depended on the synthesis conditions by using X-ray diffraction (XRD), high resolution transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE-SEM). The initial mesophase of the synthesis gel was the hexagonal MCM-41. When the gel was treated with thermal for 20h, the structure changed to cubic MCM-48 and the lamellar structure obtained after 48h.

Lysenko *et al.* (2008) investigated the effects of synthesis conditions (the ratio of the template, the skeleton-forming elements, and the temperature factor) on the structure transformation in the CTAB-TEOS-NaOH-H<sub>2</sub>O system. They determined the boundary concentrations of the reagents for the synthesis of MCM-48. Similar to the Roth (2009) report, he studied the phase transformations of MCM-48 and found that the cubic phase was developed from the initially hexagonal phase of MCM-41 and further slowly changed to the lamellar MCM-50.

To obtain Cr-MCM-48, Sakthivel *et al.* (2001) reported the synthesis and characterization of chromium-containing mesoporous MCM-41 and MCM-48 silicate molecular sieves. They prepared Cr-MCM-48 samples by hydrothermal synthesis with a molar gel composition of 1SiO<sub>2</sub>:0.30(CTA)<sub>2</sub>:0.25Na<sub>2</sub>O:62H<sub>2</sub>O:0.01Cr<sub>2</sub>O<sub>3</sub> at 110°C for 8 days, and further used them as catalysts for the liquid phase oxidation of ethylbenzene. The results showed that these materials behaved as truly heterogeneous catalysts and the active chromium ions were stabilized in the matrix.

Shao *et al.* (2008) synthesized the Cr-MCM-48 with the molar gel composition of 1.0TEOS:0.65CTAB:0.5NaOH:62H<sub>2</sub>O:xCr(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O where x = 0.005–0.04 and found that the incorporation of Cr into the framework of MCM-48 materials improved the hydrothermal stability in boiling water. At the 50 Si/Cr ratio

of the prepared sample was the optimum hydrothermal stability which the mesoporous structures could still maintain after refluxing in boiling water for 36h. The reason for this improvement was the formation of nonstructural Cr species on the surface and the Si-O-Cr bond which were more resistant to water attack.

Considering metals incorporated MCM-48, Shao *et al.* (2005) synthesized the hydrothermally stable and long-ranged ordered Ce-MCM-48 at 120°C for 24h by adding fluoride ions to the initial gel without post treatment and pH adjustment. The composition for the synthesis of Ce-MCM-48 was 1.0TEOS:0.65CTAB:0.5NaOH:62H<sub>2</sub>O:xCe(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O:0.1NaF where x = 0.005–0.04. Results showed that the Ce-MCM-48 with a Si/Ce of 200 and 100 could still maintain their structures after refluxing in boiling water for 3 days. Moreover, they found that the Ce<sup>4+</sup> ions in the Ce-MCM-48 existed partly in tetrahedral coordination in the framework and partly as CeO<sub>2</sub> particles on the surface of framework which both provided the protection against water attack.

Wang *et al.* (2006) first reported on the improvement of the hydrothermal stability of metal-doped MCM-48 with the aid of Na<sub>2</sub>SO<sub>4</sub> by one-step synthesis. They successfully synthesized hydrothermally stable Ce-MCM-48 with 100 Ce/Si ratio within a short time (120°C, 10h). The molar composition of the reactant mixture used was 1.0SiO<sub>2</sub>:0.25Na<sub>2</sub>O:0.65CTAB:62H<sub>2</sub>O:0.1Na<sub>2</sub>SO<sub>4</sub> with 0.097g of Ce(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O. According to the results, they also suggested that the addition of sulfate anion to the sol-gel synthesis of MCM-48 caused the dehydration of cationic CTAB and anionic silicates which accelerated the formation and growing of CTAB micelle, the condensation between anionic silicates, and the electronic interaction between CTAB and silicates.

Wangcheng *et al.* (2008) successfully synthesized cerium-doped MCM-48 molecular sieves with the molar composition of SiO<sub>2</sub>:xCe:0.5NaOH:0.5CTAB:55H<sub>2</sub>O where x=0.02-0.06). The results showed that all samples maintained the structure of MCM-48 and Ce could incorporate into the MCM-48 framework. Nevertheless, there was the presence of CeO<sub>2</sub> crystallites as secondary phase in the extraframework of MCM-48 at 0.04 or 0.059 Ce/Si molar ratio.

For Ti-substituted mesoporous materials, Thanabodeekij *et al.* (2005) successfully synthesized titanium incorporated MCM-41 at low temperature using silatrane and titanium glycolate precursors synthesized via oxide one-pot synthesis process. They investigated the percentage of titanium and found that Ti-MCM-41 in the range of 1-5%Ti loadings provided surface area as high as 2300 m<sup>2</sup>/g. Moreover, an increasing of titanium loading did not affect the MCM-41 structure. When titanium loading was less than 10%, the titanium incorporation is mainly in the form of isolated titanium species.

Yuan *et al.* (2008) reported the synthesis of Ti-containing MCM-48 by using TiF<sub>4</sub> and Ti(OEt)<sub>4</sub> as titanium sources. The results indicated that the types of titanium sources affected the formation of Ti-MCM-48. Furthermore, the using of TiF<sub>4</sub> as precursor provided the long-range ordered mesoporous structure with simple and fast synthesis. It could be suggested that the slow hydrolysis rate of TiF<sub>4</sub> and F<sup>-</sup> ions generated during hydrolysis led to the highly dispersed titanium species in the silica matrix. However, the Ti-MCM-48 could not be obtained when using Ti(OEt)<sub>4</sub> precursor.