

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE SURVEY

2.1 Introduction to Metal Alkoxide

Metal alkoxides exhibit great differences in physical properties, depending primarily on the position of the metal in the periodic table, and secondarily on the alkyl group. Many alkoxides are strongly associated by intermolecular forces (Bradley *et al.* 1960; Wardlaw, 1956), depending on size and shape of the alkyl groups. Many metal methoxides are non-distillable solids because the small methyl group has little screening effect on the metal atom. With a larger number of methyl groups and smaller atomic radius of the metal, methoxides become sublimable and even distillable.

Metal alkoxides are used for a great variety of purpose (Harwood, 1963), especially, adding a metal into an organic solution for a homogeneously catalyzed reaction. They are mainly used in catalysis with partial or complete hydrolysis, alcoholysis, transesterification and sol-gel application. The most outstanding property of metal alkoxides is the ease of hydrolysis. This is specially used for sol-gel application (Klein, 1981; Dislich, 1971; Heistand, 1986; Lacourse, 1986).

2.2 Sol-Gel Process

Traditional ceramic and glass processes use high temperatures to transform inorganic powders into dense objects by melting or sintering. However, the agglomeration of powders resulting from high temperatures is often limit control of obtaining microstructure, properties, shape and surface features.

Sol-gel technology is a low temperature chemical process used to prepare ceramic, glass, or composite materials by preparation via gelation process. This process has ability to produce net-shape, net-surface objects, or composites that can be used commercially after a minimum of additional processing step. The technology is Potential advantages of the sol-gel process include:

- (1) Ability to maintain high purity

- (2) Ability to vary compositional homogeneity at a molecular level
- (3) Lower temperatures of processing that lead to saving in energy
- (4) Preparation of new crystalline phases and new noncrystalline solids
- (5) Ability to produce samples in different physical forms
- (6) Ultrastructure control of materials by manipulating network formation from early stages of sol formation
- (7) Preparation of materials having improved physical properties

In general, the sol-gel process is the synthesis of an organic network at low temperature by a chemical reaction in solution. This technique involves the transition characterized by a relatively rapid change from a liquid (solution or colloidal solution) into a solid (gel-like state). The process can be divided into two types, colloidal and polymeric methods. The first method involves the suspension of solid particles in a liquid to form a sol while the other involves the polymerization of organometallic compounds, such as, alkoxides providing a convenient source for “inorganic” monomers to form a gel with three-dimensional network structure. The metal alkoxides, $M(OR)_n$, generally consist of metal atom, M, bonded through oxygen to one or more alkyl groups, where n is the valence of the metal.

Generally, a precursor is dissolved in a suitable organic solvent to obtain a solution. The solvent must be carefully selected, so that a solution with high concentration of the required component is obtained.

The sol-gel process involves 4 different steps, viz. hydrolysis of precursor, polycondensation, gel formation and organic pyrolysis by heat treatment. At the first step, starting material (metal alkoxide) is mixed in the selected solvent system to form a solution. In the gelation process, the transition from a solution into solid, involves simultaneous hydrolysis and polycondensation of metal alkoxide precursor. Many factors influence the rate of hydrolysis and condensation because both processes often occur simultaneously. The most important variables are temperatures, nature and concentration of electrolyte, nature of solvents and types of alkoxide precursor. To convert gel into a useful form, pyrolysis is necessary.

At the present time, metal alkoxides are used as the precursors for polymeric gel in sol-gel processing. The organic solvents, which are usually alcohols,

are used as solvent to hydrolyze precursor into solution. The hydrolytic reaction transforms metal alkoxide to metal hydroxides or hydrated oxide. Normally, there are many factors that need to be considered for the selection of alkoxide which include metal content, reactivity, availability, cost, moisture sensitivity and decomposition temperature. For alkoxides with different alkyl groups, the reactivity usually increases in the order of methyl > ethyl > propyl > butyl > higher order alkyl groups (Kwok *et al*, 1993).

2.2.1 Gelation Process

There are 2 main reactions in sol-gel process, which are partially hydrolysis and polycondensation reactions. Hydrolysis and condensation reactions are illustrated as follows;

Reaction (1)



Reaction (2)



Reaction (3)



2.2.2 Aging of Gel

Aging represents the time between the formation of a gel and the removal of solvent. As long as the pore liquid remains in the matrix, a gel can undergo many transformations. For alkoxide derived gels, condensation between surface functional groups continuously occurs after the gel point. This process can actually be desirable because it leads to a more cross-linked network that is mechanically stronger and easier to handle.

2.2.3 Drying

Drying is the removal of solvent from a gel network. Similar to aging, a gel is not static during drying and, for that reason, drying can be viewed as part of the overall aging process. The properties of product are thus dependent on the drying method and drying condition.

2.2.4 Calcination/Sintering

Heat treatment is often done in the presence of a reactive gas (e.g. flowing air, oxygen, or hydrogen) to burn off any residue organics or to oxidize (or reduce) the sample. Exposure of a sample to a high temperature over an extended period of time leads to sintering, and consequently a decrease in surface area. The process can also cause the material to crystallize into different structure forms. Thus, the physical characteristics of the product depend on several parameters, such as temperature, heating rate, time and gaseous environment.

Normally, sol-gel chemistry is also considered to play an important role in zeolite synthesis (Feijen *et al.*, 1994). However, small pore size caused a limit of some applications, especially, when large molecules were involved. In 1992, scientists from Mobil Oil Research and Development announced a direct synthesis of the first broad family of mesoporous molecular sieves (denoted as M41S) using cationic surfactant to assemble silicate anions from solution. These mesoporous aluminosilicate materials with well defined pore size of 15-100 Å and extremely high surface area of $>1000 \text{ m}^2/\text{g}$ introduced many interesting and desirable properties.

2.3 Chemistry of Mesoporous Molecular Sieve

Mesoporous molecular sieves are of interest for many scientists in past few years due to their uniformed pore structure and adjustable process. Controlling different synthesis condition, variety of meso-structure mimicking surfactant template can be obtained. Mesoporous silica can be successfully synthesized in both alkaline and acid routes, using amphiphile as template. In the acid route, the hydrolysis is predominant as compared to condensation, leading to the formation of linear silicate ion due to most condensation at the ends of silica polymers. In contrast, the alkaline catalysis favors both hydrolysis and condensation, resulting in formation of highly condensed and compact structure. To study their rich morphologies, the acid route is more appropriate while the alkaline route usually provides more stable and ordered materials because silica is highly condensed.

Normally, it has been demonstrated that the preparation of mesoporous molecular sieve can be achieved by using a broad spectrum of surfactant and a wide range of synthesis condition (i.e. temperature, pH, reaction time) (Hou *et al.*, 1994). Thus, the second important is how the interaction between surfactant and silicates are organized. The isoelectric point of silicate is around pH=2, below this value the silicate contains a positively charge whereas the negative charge is concerned in the alkaline route (Mou and Lin, 1996).

The formation of mesoporous materials has been proposed in several models to explain and to provide a rational basis for various synthesis routes. The model predicated upon the presence of surfactants in the solubilized inorganic precursors to guide the formation of inorganic mesostructure is one of the most widely used. In a simple binary system of water-surfactant, surfactant molecules manifest themselves as very active components with variable structure in accordance with increasing concentration, as shown in Figure 2.1.

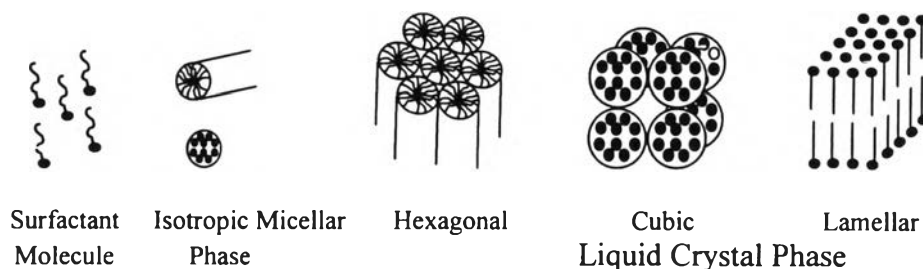


Figure 2.1 Phase transition of a surfactant-water binary system.

At low concentration, the surfactant will exist as monomolecules. With increasing concentration to decrease the system entropy, surfactant molecules will aggregate to form micelle. The initial concentration threshold at which mono-atomic molecules aggregates to form isotropic micelles, called “CMC” (critical micellization concentration). As the concentration process continues, hexagonal close packed arrays appear, producing hexagonal and lamella phases, respectively. (Client, 1992)

2.3.1 Liquid Crystal Templating Mechanism (LCT)

This mechanism was proposed by Mobil researchers, based on the similarity between liquid crystalline surfactant assemblies. This technique depends

on the hydrocarbon chain length of the surfactant tail group (Beck *et al.*, 1994), the effect of variation of the surfactant concentration (Client, 1992) and the influence of organic swelling agent (Feng *et al.*, 2000 ; Sayari *et al.*, 2001). For MCM-41 having hexagonally packed cylindrical mesopores, two mechanistic pathways were assumed.

1. The preexisting hexagonal liquid crystal was formed, followed by the deposition of silicate precursor on the micelle rods.
2. The silicate ion may influence the order of surfactants into the hexagonal arrangement.

In both mechanisms, the silicate anion and the positive charge of surfactant head group will interact and condense into hexagonal array. The resulting organic-inorganic mesostructure could be alternatively viewed as a hexagonal array of surfactant micelle rods embedded in a silica matrix. The removal of the surfactant produced the open, mesoporous MCM-41 framework. Nowadays, the actual detail of MCM-41 formation has not yet been fully agreed. For the second mechanistic pathway of LCT, several mechanistic models have been advanced for the formation below the CMC.

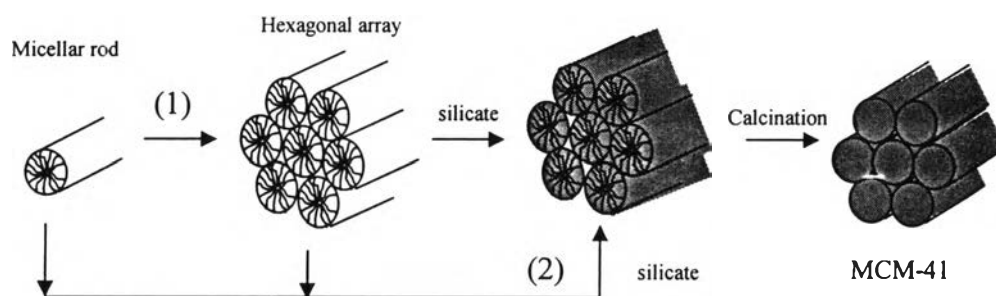


Figure 2.2 Two possible pathways for the LCT mechanism.

2.3.2 Generalized LCT Mechanism: Electrostatic Interaction

The supra-molecular assembly of mesoporous molecular sieves can be achieved through various types of interactions at the micelle-solution interface. One of them is called ‘**electrostatic charge-matching pathway**’. It involves the interaction between cationic or anionic surfactant micelles and charged inorganic precursors. Among these, so called S^+I^- and S^-I^+ pathways represent the most commonly encountered electrostatic assembly pathways. Other processes of

electrostatic charge-matching pathways were called counterion-mediated and neutral pathways.

2.3.3 Application of Mesoporous Molecular Sieve

Because of their unique physical properties of mesoporous molecular sieve, it makes these materials highly desirable for many applications. For examples, catalysis, mesoporous zeolitic materials, thin films and membranes, hollow tubules and other bulk morphologies, ship in the bottle and adsorbents.

The metal supported mesoporous silicate has been found in variety of reactions. The support MCM-41 effects on the catalytic activity of hydrodesulfurization (HDS) (Wang *et al.*, 2002), hydrodenitrogenation (HDN) and mild hydrocracking (MHC) were also investigated (Corma *et al.*, 1995) due to increasingly higher content of sulfur and nitrogen. Furthermore, the universal environmental concerns are reflected into more and more stringent regulation, imposing lower level of sulfur and other heteroatoms in the refined products.

Mesoporous material, with their high surface area predominantly localized in uniformly distributed large diameter pores, present a clear new opportunity for the hydrothermal treatment catalyst. The large pore of MCM-41 allowed a fast diffusion of the products out from the pore lattice to avoid over-cracking. Very high activity was observed on Ni, Mo-MCM-41 catalyst which was attributed to a combination of high surface area and large pore size that favors a high dispersion of the active species couples with easy accessibility of the large feedstock molecule.

For catalytic oxidation, Ti (V, Cr)-MCM-41 was reported to be an excellent material in the presence of hydrogen peroxide or even the bulky oxidant THP (terbutylhydroperoxide) (Tanev *et al.*, 1994; Corma *et al.*, 1994). Although, both Ti-MCM-41 and TS-1 are effective catalysts, but the advantage of Ti-MCM-41 over TS-1 is to allow large substrate to go into internal surface where the active sites (isolated Ti) are located.

Recent studies have shown that the walls of mesostructured silica-alumina can be converted to a zeolitic product, but the microporous zeolite phase is separated from the mesostructure, giving rise to FAU/MCM-41 and ZSM-5/MCM-

41 composites containing inter-connected mesopore and micropore lattice (Kloetstra *et al.*, 1996; Karlsson *et al.*, 1999; Huang, 2000). These composites exhibited an improvement in stream stability for purely siliceous and enhanced acidity for hydrocarbon cracking in comparison to mechanical mixture of ZSM-5 and MCM-41. In addition, these materials containing partially crystalline bimodal pore system with combined micro- and mesopores, designated as ITQ, have been achieved by delaminating the layered zeolite MCM-22 and ferrierite (FER). The nanocrystals embedded in the continuous amorphous inorganic matrix to form semicrystalline wall structure while preserving the mesoporous structure to improve hydrothermal stability and acidity. These features open new possibilities for using this type of material as acid catalysts.

In membrane separation, adsorption and electronic/optical applications, the mesoporous M41S family also offers an excellent potential for those applications due to their high surface area and homogeneity of pore structure. The formation of defect-free oriented thin films is a very important parameter in membrane application of mesoporous structures. The orientation of the pore channel axis in vertically direction respect to the solid substrate or liquid surface would also be particularly useful for many potentials applications, such as, membranes for biomolecular separations and sensors for large molecules. The use of external forces to influence the ordering of pores in mesoporous films was examined (Hillhouse *et al.*, 1997; Tolbert *et al.*, 1997). Applying the external force will induce the preferred orientation of film.

Lin and Mou reported that several micron-sized hierarchical structure, i.e. tubular-within-tubular (TWT) (1996) and hollow pillared spheres (HPS) (1998) could be successfully synthesized through soft and bendable intermediates. It was reported that hollow tubules of 0.3-3 μm in diameter could be produced by carefully control of the surfactant-water content and the rate of silica condensation at high pH value. The wall of these tubules consisted of coaxial cylindrical MCM-41 mesopore. It was proposed that solvent-separated multilayer of periodic hexagonal MCM-41 silicate could be formed and further bent into hollow microtubules. Thus, the preparation of mesoporous aluminosilicate materials was elevated to an exciting new level by having at least two length scales, micrometers and nanometers. The ability

to control structure in both length scales will have crucial impacts on catalysis, separation technologies, optoelectronics and design of the nanomaterials

Due to their uniform pore structure and large pore size, this type of molecular sieve is thus widely used. Broad channels of MCM-41 are used in the concept of 'ship in the bottle' (Fisher, 1995), in which the mesopore can act as "bottle" to "ship" quantum-sized particles inside the pore. Nanosized catalyst have been introduced into the channel of MCM-41 and converted into nanometer bimetallic cluster in MCM-41 channel which displayed high catalytic activity after heat treatment.

In addition, mesoporous structure can be used as hosts for quantum semiconductor structure of low dimensionality. The synthesis of molecular wires and quantum wires can be achieved in the cylindrical channels of the mesoporous structure and the silicate based framework can provide electrical isolation of the conducting wires. Wu and Bein (1994) reported the adsorption of aniline filaments encapsulated in the 3 nm wide pore channels. The final nanosized carbon wired exhibited a high thermal stability (more than 800°C) and low-field conductivity, which indicated that they still supported mobile charge carrier.

Not only using in catalysis and membrane separation, but mesoporous materials also showed an excellent property for using as adsorbents. Because they contain huge pore volume and the adjustable composition, hexagonal mesoporous materials can be widely exploited for selective adsorption of gases, liquids and binding metal. The adsorption storage increases with increased surface area per unit volume of the adsorbent. The MCM-41 adsorbent has higher total storage capacities for argon, nitrogen and light hydrocarbon vapors than typical microporous adsorbents. However, in some application, pores smaller than 20 Å might be desirable for optimization of the gas affinity. The MCM-41 adsorbent was shown to be highly selective, for example, it adsorbed mercury, silver and lead ions while allowing sodium, barium and zinc to pass through in the producing drinking water process. This example represented a powerful application of functionalized mesoporous materials as a selective adsorbent with ultra-high surface activity.

2.4 Literature Review

Sodium ethoxide was the first metal alkoxide described in 1837. The alkoxides of many transition metals were developed after World War II. (Bradley, 1965; Bradley, 1960; Mahrotra, 1967). The synthesis method was explained in many different routes, such as, a route from metal and alcohol (Bradley, 1965), a route from metal oxides and hydroxides (Halbig, 1931), a route from metal halides (Jenning *et al.*, 1936; Bradley, 1950), a route from metal amines and a route of alcoholysis or transesterification. Simple metal alkoxide are thermodynamically unstable in aqueous solution. They are strongly caustic and decomposed by the humidity of the air or moisture of the skin, requiring of protective glasses and gloves. The hydrolytic inertness of alkoxide is necessary to control the reactivity toward nucleophilic attraction. The inertness can control by the size of the organic and the number of alcohol groups in the ligands (Brinker and Scherer, 1990). For example, the metal alkoxide in the series of 'metalatrane' are quite inertness toward hydrolysis. The structure of metalatrane is composed of intramolecular complex cyclic ester of aminotrialkoxy derivatives. Laine *et al.* (1991) investigated a straightforward and low-cost synthesis of metal alkoxide precursor. The synthetic method used inexpensive metal oxide precursor synthesized in one step called "Oxide One Pot Synthesis Process (OOPS)". This method was successfully synthesized a group I metal alkoxide with ethylene glycol (Laine, 1995; Blohowiak, 1992).

Wongkasemjit *et al* (2001) also synthesized alumatrane and silatrane using the OOPS process. This group was successfully synthesized not only atrane complex, but also the metal glycolate, especially, Ti, Zr, Ce, Sn and Mo (Ksapbutr *et al.*, 2001; Phontammaçhai *et al.*, 2003; Sadtayanon *et al.*, 2004). Those precursors obtained are highly pure for studying via the sol-gel process to give high surface porous metal oxide suitably used as a catalyst or a catalyst support, such as TiO₂ or TS-1 for being used as photocatalysts. These materials were widely used in oxidation and photocatalysis process.

In 1992, researchers at Mobil Research and Development Corporation reported the exciting discovery of the novel family of molecular sieves called M41S (MCM-41, MCM-48 and MCM-50) (Beck and Vartuli, 1994; Huo *et al.*, 1994; Stucky *et al.*, 1994). The original M41S family of mesoporous molecular sieves was

synthesized, in general, by the combination of appropriate amounts of a silica source (e.g. tetraethylorthosilicate (TEOS), Ludox, fumed silica, sodium silicate), an alkyltrimethylammonium halide surfactant (Cabrera *et al.*, 2000) (e.g. cetyltrimethylammonium bromide (CTAB)), a base (e.g. sodium hydroxide or Tetramethylammonium hydroxide (TMAOH)), and water. Aluminosilicate M41S was synthesized by the addition of an aluminum source to the synthesis mixture. The mixture was aged at elevated temperature ($\geq 100^{\circ}\text{C}$) for 24 to 144 hr, resulting in a solid precipitate. The organic-inorganic mesostructured product was filtered, washed with water and air-dried. The product was calcined at about 500°C under a flowing gas to burn off the surfactant, to yield the mesoporous material. Many research groups (Smarsly *et al.*, 2001) all over the world exploited this technique of supramolecular templating to produce not only mesoporous silicate and aluminosilicate materials, but also mesostructured metal oxides. The extension of this liquid-crystal templating (LCT) mechanism into the field of transition metal oxide synthesis represented a major step forward towards tailoring catalytic, electronic and magnetic properties of these redox-active materials (Smarsly *et al.*, 2001).

The influence of alkyl chain length and the addition of mesitylene on the pore size have been taken as a strong evidence for the LCT mechanism, since this phenomenon is consistent with the well-documented surfactant chemistry (Cabrera *et al.*, 2000). The auxiliary organic species added to the reaction gel can be solubilized inside the hydrophobic regions of micelles, causing an increase in micelle diameter so as to increase the pore size of MCM-41. The observed pore size increase of the aluminosilicates compared to the siliceous MCM-41 was due to the replacement of the shorter Si-O bonds (1.6 \AA) by the longer Al-O bonds (1.75 \AA) (Liu *et al.*, 2000; Schacht *et al.*, 1998). Not only adding the auxiliary organic species that can expand the pore size, Huo *et al.* (1994) and Firouzi *et al.* (1995) suggested that ion exchange between surfactant anions (OH^- , Br^- , Cl^-) and multiply charged anionic silica oligomer (D4R, D3R) may take place in a surfactant-silicate aqueous solution. This multidentate bonding can screen the intraaggregate electrostatic head group repulsions so as to reduce the average head group area of the surfactants. The

collective results can further decrease the local curvature of the aggregate, implying that the cooperative assembly of inorganic-organic species is formed with structures different from that of the precursor micelles.

Tranev *et al.* (1996) studied the preparation of MCM-41 and HMS silica molecular sieves and their physical properties. The electrostatic and neutral assembly pathways were used. Their results showed that the electrostatic pathways gave long-range hexagonal order when carried out under hydrothermal at 100°C whereas neutral pathway was best prepared at ambient temperature. Their results showed the thicker framework wall of HMS but lower long range hexagonal order. However, the thicker framework wall gave superior thermal stability upon calcinations and a small crystal size improved access to the framework confined mesopores.

In year 1996, Hou *et al.* examined how the molecular shapes of covalent organosilanes, quaternary ammonium surfactants and mixed surfactants in various conditions can be used to synthesize different phase of silica-based mesoporous solid. In this work, they reported that high quality of MCM-41 can be prepared using postsynthesis hydrothermal treatment at 100°C. After treatment, MCM-41 obtained has large pore size (up to 6 nm), big pore volume and large surface area ($>1,000 \text{ m}^2 \text{ g}^{-1}$). They also reported the role of adding co-solvent as structure directing agent by varying the polarity and hydrophilic/hydrophobic surfactant molecule. The phase transition of hexagonal (MCM-41) to cubic (MCM-48) and lamellar (MCM-50) by changing reaction temperature and time was shown.

In 1999, Mokaya *et al.* reported the preparation method for synthesis of high quality of large crystal MCM-41. Their work has been achieved by using calcined small crystallite MCM-41 as seeds in secondary stage preparation. The MCM-41 obtained has larger crystal size which may be used for fabrication in thin film application.

Normally, the precursors used in the synthesis method of MCM-41 are TEOS and fumed silica. Recently, Haskouri *et al.* (2000) reported the synthetic method of ordered mesoporous oxide using atrane route. This atrane precursor, namely, silatrane and alumatrane, are alkoxide precursors and have superior properties. Silatrane and alumatrane become possible to control the processes involved in the formation of the surfactant inorganic phase composition micelle.

Silatrane was prepared by using Vekade's (1993) synthetic method. Both MCM-41 and metal loaded MCM-41 were prepared based on the inertness of the aqueous solution of the atrane complex, without prejudice to their inherent thermodynamic instability. Chemically homogeneity in microstructure and texture of all the mesostructures and mesoporous materials were also reported in this work.

Because MCM-41 exclusively contains mesopores it can both provide access to large molecules and alleviate diffusion problems, which are frequently encountered in microporous materials, such as, zeolites (Barton *et al.*, 1999; Xiu *et al.*, 1996). It should be noted, however, that the one-dimensional nature as well as the relatively large length of the mesopores (usually extending over several hundreds of nanometers) could also give rise to transportation limitations.

Many researchers have tried to introduce a second cation, such as, a transition metal, into the silica-based MCM-41 framework and used them as effective catalysts for various kinds of reactions. The deposition of an oxide over another high surface area oxide involves phenomena comparable to wetting, with some of the host-guest complexes wielding monolayers (Gao *et al.*, 1998). In principle, the supported systems often give more thermally and hydrothermally stable. Vanadium-substituted MCM-41 materials were found to be very active catalysts in the selective oxidation of hydrocarbons using H_2O_2 in liquid phase reaction, especially for larger molecules (Smarsly *et al.*, 2001). Ti-MCM-41 was also prepared to be used as an oxidation catalyst with peroxide or as photocatalysts. Doping with Fe, Mn or V instead of Al suppressed completely the photocatalytic activity. Ti-MCM-41 was prepared by either grafting titanium precursor onto silanol surface via the post-synthetic procedure or depositing titanium precursor on MCM-41 from the sol obtained by controlled hydrolysis of titanium alkoxide precursor followed by calcination (Trong *et al.*, 2003). Amaros *et al.* (2001) synthesized very high titanium content mesoporous silicas using silatrane and titanatrane. In their work, the minimum Si/Ti ratio is as low as 1.9 (Haskouri *et al.*, 2002).

Many researchers reported the synthesis, characterization, the location and coordination of titanium in titanasilicate molecular sieve MCM-41 using NMR and XANES (Maria *et al.*, 1996). Maria *et al.* (2000) reported the synthetic method of Ti-MCM-41 using novel one-pot procedures based on liquid crystal templating. Both

soluble (titanocene dichloride) and insoluble (titanium acetylacetonate) Ti sources were used. The nature of the transition metal precursor, hydrophobicity or hydrophilicity, determines whether the catalytic species will be accessible within the mesopores or buried in the silica walls. The results showed that Ti from soluble source existed mainly as isolated tetrahedral Ti(IV) oxide. Extraframework was not presented for soluble source whereas insoluble Ti source was presented. Marchese *et al.* (1997) synthesized mesoporous titanosilicate using TEA as template. They reported that TEA was found to act not only as template, but also a director of positioning Ti-site to form isolated tetrahedrally coordinated Ti species.

Ikeue *et al.* (2002) studied Ti-containing silica thin films with two different mesostructures by solvent evaporation method. The catalysts were tested for the photocatalysis of CO₂ with H₂O. They found that porous silica thin film exhibited higher photo catalyst activity than Ti-MCM-41 powder, making these thin films be candidates as efficient photocatalysts for various reactions. The same reactivity results were also showed in the study of Shioya *et al.* (2003). They synthesized Ti-containing mesoporous silica thin film, exhibiting higher photocatalytic activity than Ti-MCM-41 powder even with the same pore structure.

Not only Ti containing mesoporous that has been widely used, large transition metal, i.e. Mo and W, has been reported to disperse onto mesoporous molecular sieve due to the incorporated in rigid framework of zeolite limiting the insertion. In contrast, the high dispersion of molybdenum can be achieved by incorporating in much flexible framework of MCM-41 (Louis, 1993). Molybdenum loaded onto silica is of importance in hydrodesulfurization and hydrodenitrogenation processes in petroleum industry (Reddy *et al.*, 1998; Song *et al.*, 1999). High dispersion of supported Mo was reported to exhibit high catalyst activity for not only thermal reactions, such as, hydrogenation, dehydrogenation, oxidation and metathesis, but also photocatalytic reaction, such as, partial oxidation of hydrocarbon.

Piquemal *et al.* (1999) reported the preparation of high dispersion of high molybdenum content onto mesoporous silica. They used MoO₃ to react with H₂O₂ to form molybdenum peroxo complexes in acidic condition. This synthesis gives the Mo/Si (mol/mol) ratio of 0.04. High dispersion of MoO₃ onto mesoporous silica

MCM-41 was also reported using thermal spreading (Li *et al.*, 2002). It was found that the dispersion capacity was strongly influenced by the surface area of the supports at the dispersed temperature. The critical dispersion capacity of MoO₃ on the surface of MCM-41 is 0.26g/g.

Morey *et al.* (2000) synthesized molybdenum grafted of MCM-48, using a water sensitive metal alkoxide to react with surface silanols within the pores to generate isolated metal centers. They found that metal alkoxide can generate isolated molybdenum species onto the support via Mo-O-Si bond. The prepared catalysts were tested for catalytic peroxide activity.

Umabal *et al.* (2000) synthesized bismuth titanate from co-precipitated stoichiometric bismuth nitrate and potassium titanyl oxalate at pH 5 to obtain pure phase of Bi₄Ti₃O₁₂. Yao *et al.* (2003a, b, 2004) synthesized perovskite bismuth titanate using chemical solution decomposition (CSD) of bismuth nitrate and titanium butoxide, and tested for the photocatalytic property. This material showed high photocatalytic activities to degrade methyl orange solution in 4 hr. They also synthesized selenite bismuth titanate, Bi₁₂TiO₂₀, which contains piezo-electrical properties. This material was reported to have high photocatalytic activity under UV irradiation (Yao *et al.*, 2002, 2003).