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 *et al.*, 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 *et al.*, 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 *et al.*, 1981; Dislich *et al.*, 1971; Heistand *et al.*, 1986; Lacourse *et al.*, 1986).

2.2 Sol-Gel Process in Surfactant-Templated Silica

Mesoporous silica can be synthesized in either the alkaline route (Beck, 1992) or the acid route (Huo *et al.*, 1994) both using amphiphiles as templates. In the acid route, the silica source is silicon alkoxides. The acid catalysis speeds up the hydrolysis versus the condensation rate and promotes mostly condensation at the ends of silica polymers to form linear silicate ions (Sanchez *et al.*, 1994). On the other hand, the alkaline catalysis favors both hydrolysis and condensation. Thus, the alkaline route leads to a highly condensed and compact structure, and the acid route leads to a more fuzzy and soft network (Sanchez *et al.*, 1994). The acid route is

popular for studying its rich morphology, whereas the alkaline route usually provides more stable and ordered materials because silica are highly condensed.

The second important difference is in how the in the interaction surfactant and silicate are organized. The isoelectric point of silicate is around pH = 2, below which the silicate carries a positive charge, whereas in the alkaline route the silicate is negatively charged. So in the alkaline route, surfactant and silicates organize by the strong S^+I^- electrostatic interaction. In the acid route (with pH <2), the silica species in solution are positively charged as $\equiv SiOH_2^+$ (denoted as I^+). The surfactant (S^+)-silica interaction becomes $S^+X^-I^+$ as mediated by the counterion X^- (Ozin et al., 1997). This micelle-counterion interaction is in thermodynamic equilibrium. The complex factors one needs to consider are: ion exchange equilibrium of X^- on micellar surface, surface-enhanced concentration of I^+, and proton-catalyzed silica condensation near micellar surface.

The steps in the synthesis can be roughly separated into two parts: the self-assembly of surfactant inorganic system and the inorganic polymerization of silica (Ogawa et al., 1994, Yang et al., 1997). The uncondensed silicate ions serve as the counterions in the early stage of surfactant self-assembly. This occurs quickly. The silica condensation rate is, however, slower, and extent of condensation is pH- and temperature-dependent (Renzo et al., 1999).

2.3 Surfactant Packing Parameter (g)

The classical and contemporary molecular description of surfactant organization in amphiphilic liquid-crystal arrays is described in terms of the local effective surfactant packing parameter, (Israelachvili et al., 1976) $g = V/a_0l$, where V is the total volume of the surfactant chains plus any cosolvent organic molecules between the chains, a_0 is the effective head group area at the micelle surface, and l is the kinetic surfactant tail length or the curvature elastic energy (Gruner et al., 1989). The interface surface bending energy can be written in terms of g, the actual surfactant packing parameter adopted by the aggregating chains in the phase (Hyde et al., 1992, Fogden et al., 1991). The counterion in this classical model is not explicitly included.

In classical micelle chemistry, as the g value is increased above critical values, mesophase transitions occur. The expected mesophase sequence as a function of the packing parameter is (Henriksson *et al.*, 1992)

g	Mesophase
1/3	cubic (*Pm3n*)
1/2	hexagonal (p6m)
1/2 - 2/3	cubic (*Ia3d*)
1	lamellar

Since $g = V/a_0 l$, the value of g increases as: a_0 decreases; V increases; and l decreases. These transitions reflect a decrease in surface curvature from cubic (*Pm3n*) through vesicular and lamellar. For surfactants to associate in a spherical structure, the surface area occupied by the surfactants polar head group should be large. If on the other hand the head groups are permitted to pack tightly, the aggregation number will increase, and rod or lamellar packing will be favored. The values of g (between 1/2 and 2/3) for the cubic (*Ia3d*) phase depend upon the volume fraction of surfactant chains (Hyde *et al.*, 1992).

2.4 Literature Review

Wongkasemjit *et al.* (2001) also synthesized alumatrane and silatrane using the Oxide One Pot Synthesis or 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; Phontammachai *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 TiO_2 or TS-1 for being used as photocatalysts. These materials were widely used in oxidation and photocatalysis process.

Huo *et al.* (1994, 1996) reported that silica mesophases of the SBA-1 can be formed using a combination of cationic surfactant (S^+), halogen anion (X^-) and cationic silicate species (I^+), through the acidic route. Large head-group surfactants,

such as, alkyltriethyl ammonium $C_nH_{2n+1}(C_2H_5)_3N^+$ (n = 12, 14, 16 and 18) favored the SBA-1 cubic $Pm3n$ mesophase. Highly ordered mesophases can be formed over a wide range of strongly acidic conditions. They found that HCl favors the formation of SBA-1 cubic mesophase. Kim and Ryoo (1999) mentioned that the 3d-cubic SBA-1 could be synthesized using cetyl trimethylammonium chloride (CTMACl) as a surfactant, and found that low temperatures were favorable in the formation of high-quality cubic mesophase. Kruk et $al.$ (1999) reported that nitrogen adsorption showed that highly ordered SBA-1 materials exhibited broad steps of capillary condensation, suggesting that relatively broad pore size distributions might be related to a cage-like pore structure of these materials. Che et $al.$ (2001) studied the effect of counter ion on mesophase formation, succeeding in the synthesis of highly ordered SBA-1 materials with 54 or 74 crystal faces. They found that the formation of mesophase was affected by counter anion and that the SBA-1 cubic $Pm3n$ phase was formed from the lower curvature 2d-hexagonal $p6mm$ mesophase. Later on, (2002) they found that the mesostructure formation greatly depended on the concentration of acid, and also presented the procedure for synthesizing SBA-1 using cetyltrimethylammonium bromide (CTMABr) as a template. Chao et $al.$ (2005) introduced a new concept to synthesize the SBA-1 mesoporous silica in a dilute solution. They found that the high-quality SBA-1 could be conveniently prepared using commercially available alkyltrimethylammonium surfactant and sodium silicate. Kao et $al.$ (2005) studied the effect of synthesis approach by adding the short-chain alcohols such as methanol, ethanol and polyols as cosolvents. They found that, the alcohol additives can serve as phase controllers during the high-temperature synthesis of SBA-1. The hydrophobic/hydrophilic character of the alcohol molecules determines the role of the alcohol, either cosolvent or cosurfactant, played in the phase transformation of the cubic $Pm3n$ mesophase. Soon after, (2006) they successfully synthesized well-ordered SBA-1 materials over a broad temperature range, by using CTPABr, a bulky headgroup surfactant, as the templating agent under strongly acidic condition with HCl. The tightly packed CTPABr surfactants not only make the spherical micelle more stable against the temperature change, but also are sensitive to HCl concentrations at high temperatures.

The inclusion of guest molecules in mesoporous materials is one of focused subjects in this study instead of incorporating aluminum or other heteroatoms into mesoporous silica materials using the silatrane precursor for catalytic functions, as studied by our groups (Wongkasemjit *et al.*, 2001). Diaz *et al.* (2003) studied a novel type of redox-active materials by incorporating dendritic guest molecules, (poly(propyleneimine) dendrimers) containing amidoferrocenyl moieties, into a mesoporous silica hosts (MCM-41) with highly ordered channels. Larsen *et al.* (2000) used poly(propyleneimine) tetrahexacontaamine dendrimers (DAB-Am-64) as a single molecule template to produce mesoporous silicas from tetraethyl orthosilicate (TEOS), and found that X-ray diffraction (XRD) patterns revealed the occurrence of mesostructure, but transmission electron microscopic (TEM) analysis of a stained product showed the images of "globular" and "disordered filaments". The 4.0th generation (G4) poly(amido amine) (PAMAM) dendrimer was also used as a template for the sol-gel reaction of TEOS. The silica gels were characterized using XRD and nitrogen adsorption.

Mitra *et al.* (2004) characterized PAMAM dendrimer-templated, TEOS-based mesoporous silica using TEM, and after the removal of dendrimers by calcination, nanopores were disorderly maintained in the silica matrix. The PAMAM dendrimer was also utilized as a single molecule template to synthesize nanopores in iron phosphate mesostructures (Mitamura *et al.*, 2007).

It has been found that noble metals, such as V, Co, Cr, Ti and Fe, can be grafted onto siliceous frameworks of SBA-1 using the metal-implantation method (Dai *et al.*, 2001, Vinu *et al.*, 2002-2004, Ji *et al.* 2003). In recent years, a series of titanium-containing mesoporous molecular sieves, such as Ti-MCM-41 (Thanabodeekij *et al.*, 2005), Ti-HMS, Ti-MSU have been synthesized. Due to the cubic structure of three-dimensional mesopores of SBA-1, it is much more desirable for catalytic application than one-dimensional mesopore materials. Ji *et al.* (2005) investigated that Ti-SBA-1 materials showed relatively high activity and selectivity in the epoxidation of styrene with aqueous hydrogen peroxide as oxidant, due to the presence of high dispersion and isolation of Ti in the SBA-1 framework.

In addition, iron incorporate mesoporous materials have received much attention in past decades because of their unique catalytic properties in various

reactions, such as hydrocarbon oxidation, selective catalytic reduction, acylation and alkylation reaction. Vinu *et al.* (2005-2006) successfully synthesized Fe-SBA-1 by simply adjusting the molar hydrochloric acid to surfactant ratio and used these materials in applications like acylation of toluene and butylation of phenol.