

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.

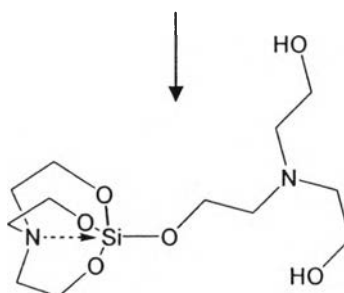
Metal alkoxides are used for a great variety of purposes (Harwood *et al.*, 1963), especially, adding a metal into an organic solution for a homogeneously catalyzed reaction. They are mainly used in catalysis with partial or complete hydrolysis, alcoholysis, transesterification and sol-gel application. 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 Synthesis of Metal Alkoxides

The metal alkoxide precursors for catalyst synthesis are of interest in this work. Apparently, the synthesis of new metal alkoxides possessing unique structures and properties is of great significance for the investigation of sol-gel process as well as the evolution of metal alkoxide chemistry. However, there are a few drawbacks of metal alkoxides that make it difficult to study their structures and properties thoroughly, such as, the extreme moisture sensitivity and the tendency to form mixtures of structurally complex species upon hydrolysis. Many scientists thus tried to improve the properties of metal alkoxides (Grainsford *et al.*, 1995; Wang *et al.*, 1999).

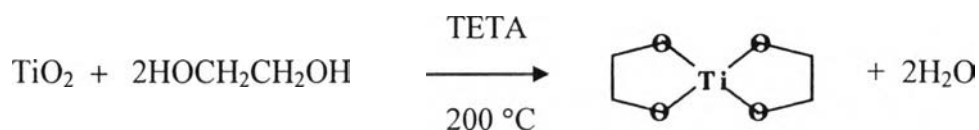
Laine *et al.* (1991) investigated a straightforward and low-cost synthesis of metal alkoxide precursor. The synthetic method used inexpensive metal oxide precursor to react with ethylene glycol in one step called “Oxide One Pot Synthesis Process (OOPS)” to successfully produce a group I metal alkoxide (Laine, 1995; Blohowiak, 1992).

Wongkasemjit *et al.* (2001) also synthesized silatrane using SiO_2 and triethanolamine/triisopropanolamines (Scheme 2.1). The precursor exhibited outstanding high stability not only in alcohol, but also in water.



Scheme 2.1 The preparation of silatrane complexes by Wongkasemjit’s method.

Not only atrane complexes, but also many metal glycolates were synthesized, especially, Ti, Zr, Ce, Sn and Mo (Ksapbutr *et al.*, 2001; Phonthammachai *et al.*, 2003; Junin *et al.*, 2004; Sadtayanon *et al.*, 2004).



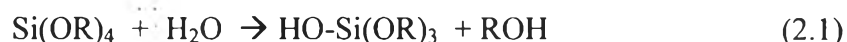
Scheme 2.2 The preparation of titanium glycolate complex (Phonthammachai *et al.*, 2003)

These precursors obtained are highly pure and suitable for studying optimal conditions of the sol-gel process for high surface porous metal oxides suitably used as a catalyst or a catalyst support.

2.3 Sol –Gel Processing

Sol-gel technique has been extensively used to prepare amorphous and crystalline materials. In general, the sol-gel process of metal oxides/alkoxides is the synthesis of an inorganic network at low temperature. This technique involves the transition characterized by a relatively rapid change from a liquid (solution or colloidal solution) into a solid (gel-like state).

Metal alkoxides are a member of metal organic compounds containing an organic ligand attaching to a metal or metalloid atom. Metal alkoxides are popular precursors for the sol-gel process because they react readily with water via hydrolysis reaction to form metal hydroxide, as shown in the following reaction.



where R represents an alkyl ligand (then OR is an alkoxy group), and ROH is an alcohol. Depending on the amounts of water and catalyst in the system, hydrolysis may go to completion, meaning that all of the OR groups are replaced by OH), or partially occur, $\text{Si(OR)}_{4n}(\text{OH})_n$. Moreover, the molar ratio of $\text{H}_2\text{O}:\text{Si(OR)}_4$ should be at least 2:1 to approach complete hydrolysis of the alkoxide (Nicolaon and Teichner, 1968).

At its simplest level, sol-gel chemistry with metal alkoxides can be described in terms of two main reactions:



where X can be either H or R (an alkyl group).

The most important characteristic of the sol-gel preparation of catalytic materials is its ease to control the reaction rate, leading to the following advantages:

- (i) The ability to maintain high purity (because of purity of starting materials);

- (ii) The ability to change physical characteristics, such as pore size distribution and pore volume;
- (iii) The ability to vary compositional homogeneity at a molecular level;
- (iv) The ability to prepare samples at low temperatures;
- (v) The ability to introduce several components in a single step;
- (vi) The ability to produce samples in different physical forms.

The M-O-M network product is formed by polycondensation reactions, as shown in Reaction 2.3 in which alcohol and water are produced as by-products. Further extent of the condensation of the sol results in the formation of gel. There are many parameters affecting gel properties, such as temperature, pH, type of precursor, and solvent. Varying the temperature is the most effective when it can alter the relative rate of competing reactions. Solvent can change the nature of an alkoxide precursor through solvent exchange or directly affect the condensation reaction. It is also possible to prepare gel without solvent as long as another mean, such as ultrasound irradiation, is used to homogenize. Furthermore, pH of the solution, which can be changed by the addition of either acid or base catalyst, is also the most important parameter in obtaining gel because the rate and content of the hydrolysis reaction are influenced by the change in pH (Aelion *et al.*, 1950).

In general, the sol-gel process gives high surface area, pore structure, homogeneous property of the products, and moreover, it is a low-temperature method for converting metal alkoxide to metal oxide. Many works investigated the sol-gel process using various types of precursors for certain properties.

2.4 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 interaction surfactant and silicate are organized. The isoelectric point of silicate is around $\text{pH} = 2$, 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 $\text{pH} < 2$), the silica species in solution are positively charged as $\equiv\text{SiOH}_2^+$ (denoted as I^+). The surfactant (S^-)-silica interaction becomes $\text{S}^+\text{X}^-\text{I}^+$ as mediated by the counterion X^- (Ozin *et al.*, 1997). This micelle-counterion interaction is in thermodynamic equilibrium. For 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).

2.5 Literature Review

Zhao *et al.* reported that the use of TEOS as silica source and amphiphilic triblock copolymers to direct the organization of polymerizing silica species have resulted in the preparation of well-ordered hexagonal mesoporous silica structure (SBA-15) with uniform pore size up to approx. 300 Å. The SBA-15 material is synthesized in acidic media produces highly ordered, two-dimensional hexagonal (space group $p6mm$) silica-block copolymer mesophases. Calcination at 500 °C gives porous structures with large interlattice d spacings of 74.5 to 320 Å, pore sizes from 46–300 Å, pore volume fraction up to 0.85 and silica wall thicknesses of 31–64 Å. SBA-15 can be readily prepared over a wide range of uniform pore sizes and pore wall thicknesses, using a variety of poly(alkylene oxide) triblock copolymers such as

poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) and by the addition of cosolvent organic molecule such as 1,3,5-trimethylbenzene (TMB). SBA-15 is formed in acidic condition with HCl, HBr, HI, HNO₃, H₂SO₄ or H₃PO₄ acids, above the isoelectric point of silica (pH 2), no precipitation or formation of silica gel occurs. At neutral (pH 7), only disordered or amorphous silica is obtained (Zhao *et al.*, 1998). Lin *et al.* also found that when the pH is adjusted to 5, fast silica condensation rate leads to the formation of irregular particles rather than crystals (Lin *et al.*, 2008).

Zhao *et al.* also found that the pore size of hexagonal mesoporous SBA-15 can be increased to more than 300 Å by increasing the hydrophobic volume of the self-assemble aggregates. This can be achieved by changing the copolymer composition or block sizes, or by adding cosolvent organic molecule such as TMB (Zhao *et al.*, 1998).

Generally, a hydrothermal treatment time of 11–72 h at 100 °C was needed to yield well-ordered mesoporous structures of high surface area (690 m²/g), uniform pore diameter (47 Å) and volume (0.56 cm³/g). Subsequently, Newalkar *et al.* introduced microwave-assisted syntheses to shorten reaction time (2 h) while obtaining materials of similar quality to those prepared in the autoclave. The microwave method proves superior as volumetric heating favors homogeneous nucleation, and fast dissolution and supersaturation of precipitated gels promotes shorter crystallization times (Park *et al.*, 1998; Komarneni *et al.*, 1994).

For titanium-substituted SBA-15, Zhang *et al.* (2002) successfully prepared Ti-SBA-15 using TMOS and titanium isopropoxide as silicon and titanium sources, respectively. Since the hydrolysis of titanium alkoxide is fairly instantaneous, whereas the hydrolysis of silicon precursor much slower, certain amount of fluoride (F/Si = 0.03–0.05) was added to accelerate the hydrolysis of TMOS; and pH value was adjusted to below 1.0 to obtain high quality of Ti-SBA-15.

Chen *et al.* (2004) successfully synthesized Ti-SBA-15 under acidity hydrothermal conditions using titanium trichloride (TiCl₃) and TEOS as titanium and silicon sources, respectively. They pre-mixed H₂O₂ with a certain amount of TiCl₃ before adding into the gel-solution to improve the ordered structure of the Ti-SBA-15. At the maximum Si/Ti ratios, only the samples prepared in the presence of H₂O₂

could maintain their ordered structure. In addition, the products synthesized by adding H_2O_2 tended to have higher surface area, larger pore size and pore volume than those synthesized without adding H_2O_2 .

In order to synthesize Ti-containing SBA-15, almost all researchers used either titanium isopropoxide or TiCl_3 as titanium source. Both compounds are expensive, moisture unstable and relatively high reactivity. Wongkasemjit and coworkers (2003–2006) successfully prepared titanium glycolate using inexpensive and widely available titanium oxide (TiO_2) and ethylene glycol as starting materials via the OOPS process. The resulting moisture stable titanium glycolate could be effectively used to synthesize many types of materials, such as high surface area anatase TiO_2 (Phonthammachai *et al.*, 2003), sillenite ($\text{Bi}_{12}\text{TiO}_{20}$) (Thanabodeekit *et al.*, 2005), titanium loaded TS-1 zeolite (Phonthammachai *et al.*, 2006), and highly ordered mesoporous Ti-SBA-1 (Tanglumlert *et al.*, 2008).

Li *et al.*, (2005) reported that the Fe-SBA-15 could be successfully synthesized using a simple direct hydrothermal method under weak acid condition in the presence of fluoride, using TMOS and iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) as silicon and iron precursors, triblock copolymer surfactant $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ as a template. They found that when the pH value of the solution was lower than 2.0, the highly isolated framework iron species (Fe^{3+}) were obtained. Besides, adding more iron precursor could improve the order of the mesostructure because of the salt effect. Moreover, different iron species were produced by changing the pH value of the solution, and, for all of the calcined samples, the iron ions exhibited tetrahedral coordination in the silica framework with Fe/Si molar ratio below 0.0022 at pH 1.5.

Melero *et al.* (2007) have reported the preparation of molybdenum-containing SBA-15 using co-condensation technique under acidic condition using non-ionic surfactant as a template, TEOS and ammonium molybdate tetrahydrate $[(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}]$ as silica and molybdenum sources. They prehydrolyzed molybdenum precursor for at least 3 h to depolymerize heptamolybdate species to form monomeric soluble molybdenum(VI) species before adding silica and molybdenum precursor into the template solution. After stirring at 40 °C for 20 h the mixture was aged at 100 °C for 24 h and further calcined. The resultant product from

this method showed good mesoscopic ordering, narrow pore size distribution and high dispersion of molybdenum species.

Wongkasemjit *et al.* (2009) have been successful to use molybdenum glycolate to prepare Mo-SBA-1 in dilute acidic condition at room temperature using silatrane as a silica source and C₁₆TMAB as a template. The mesoporous Mo-SBA-1 obtained from this method maintained a well-order mesostructure and high surface area. The amount of molybdenum that could be incorporated into the SBA-1 framework was relatively high (up to 5%mol) without any extraframe work.