CHAPTER II
THEORETICAL AND LITERATURE SURVEY

2.1 Introduction to Metal Alkoxide

Metal alkoxides are used for a great variety of purpose (Harwood *et al.*, 1963). They are mainly used in catalysis with partial or complete hydrolysis, alcoholysis, transesterification, and sol-gel applications. Metal alkoxides, normally complexes with alkoxy ligands, are very useful clean oxide-precursors because alcohol groups generated from hydrolysis of metal alkoxides do not participate in subsequent processes (condensation) and can be easily removed from the solution. 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.

The atrane precursors are a kind of metal alkoxide materials containing trialkanoamine ligand. They showed a significant inertness towards hydrolysis reaction (Cabrera *et al.*, 2000), thus, it is possible to control the processes involved in the formation of the surfactant–inorganic phase composite micelles.

2.2 Microwave Synthesis

Microwaves are electromagnetic waves between infrared (IR) frequencies and radio frequency (RF), covering a broad frequency range of 0.3–300 GHz. Microwave chemistry experiments are generally conducted at 2.45 GHz (the corresponding wavelength is 12.24 cm). Materials interacted with microwaves radiation can be classified into three categories, based on (Clark *et al.*, 1996):

(1)   Reflected materials illustrating by bulk metals and alloys, e.g. copper.

(2)   Transmitted materials illustrating by fused quartz, several glasses, teflon, etc.

(3)   Absorbed materials representing the materials for microwave synthesis, e.g. aqueous solution, polar solvent, etc.

Microwave ovens offer an effective way of heating many nonconductive materials. The generated heat is determined by the specific dielectric properties of

the material itself. Microwaves cause heating within a material by exciting molecules to rotate. This rotation produces energy in the form of heat. Unlike conventional heating, this effect occurs simultaneously throughout the whole material being microwaved without any problem of heat transfer through the wall of container. The materials heated up the fastest are comprised of non-symmetrical polar molecules, which are easily rotated by microwave energy.

Advantages of microwave heating

(1)   The introduction of microwave radiation into a chemical reaction can lead to high heating rate and short processing time

(2)   Owing to the heat generated inside the materials, microwave energy leads to a more uniform heating of the synthesis mixture

(3)   It is volumetric and instantaneous (or rapid) heating with no wall or heat diffusion effects

(4)   Microwave energy enhances the dissolution of the precursor

(5)   Hot spots created within the synthesis mixture may result in a "super-heating" effect, which can be described as local overheating and is comparable to the delayed boiling of overheated liquids under conventional conditions.

2.3 The Preferential Oxidation (PROX) of CO

Hydrogen, used as a fuel for the polymer electrolyte membrane fuel cells (PEMFC), is produced by reforming of hydrocarbon. However, the obtained hydrogen contains an upper limitation of CO to be directly fed to PEMFC. The CO concentration must be reduced to value below 10 ppm to avoid poison to platinum electrode in PEMFC (Rosso et al., 2007; Jain et al., 2009). The popular method for accomplishment this process is called "preferential oxidation (PROX)" of CO. The favored reaction of the PROX of CO (Eq. (1)), and several side reactions (Eq. (2)–(5)) are presented, as followed (Sebastian et al., 2009):

$$CO + \tfrac{1}{2} O_2 \longrightarrow CO_2, \qquad \Delta H_{298K} = -284 \text{ kJ/mol} \qquad (1)$$
$$H_2 + \tfrac{1}{2} O_2 \longrightarrow H_2O, \qquad \Delta H_{298K} = -242 \text{ kJ/mol} \qquad (2)$$
$$CO_2 + H_2 \longrightarrow CO + H_2O, \qquad \Delta H_{298K} = 41 \text{ kJ/mol} \qquad (3)$$
$$CO + 3H_2 \longrightarrow CH_4 + H_2O, \qquad \Delta H_{298K} = -206 \text{ kJ/mol} \qquad (4)$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O, \quad \Delta H_{298K} = -165 \text{ kJ/mol} \qquad (5)$$

The effective catalysts for PROX of CO should illustrate (Ayastuy *et al.*, 2006) high activity for CO oxidation, high selectivity of CO, wide operation temperature to prevent precise temperature controls, and a processing temperature between two regions, the outlet temperature (200 °–300 °C) for low temperature WGSR or the operation temperature (80 °–100 °C) for PEMFC. The PROX unit is set up between them (Huang *et al.*, 2009).

2.4 Literature Review

AlPO$_4$-5 with AFI-type framework was first synthesized from aluminophosphate gel in the presence of organic amines under conventional hydrothermal heating (Wilson *et al.*, 1982). It is known that the AFI-type can be synthesized using several types of structure-directing agents; for example TEA (Wan *et al.*, 2000), TEAOH (Du *et al.*, 1997), TPA (Gua *et al.*, 2005), TPAOH (Zhai *et al.*, 2006), and TBAOH (Jiang *et al.*, 2005). Microwave heating method was applied to the synthesis of AlPO$_4$-5 crystal from the synthesis mixture containing HF acid (Girnus *et al.*, 1995). Fang *et al.* (1997) synthesized AlPO$_4$-5 molecular sieves by microwave heating, and found that it gave smaller particle size and narrower size distribution (Kodaira *et al.*, 1999) than the ones synthesized by the conventional hydrothermal method. In addition, using the microwave technique, the morphology, orientation, and size of the AlPO$_4$-5 crystals could be controlled by varying temperature, water content, and amount of organic template (Mintova *et al.*, 1998). Jhung *et al.* (2004) reported that the aspect ratio could be increased greatly when the synthesis was carried out in dilute conditions and the fluoride was added in the synthesis mixture. Egeblad *et al.* (2007) reported that a new mesoporous AlPO$_4$-5 zeotype material could be synthesized by introducing carbon particle template in addition to triethylamine structure-directing agent into the reaction mixtures with the fluoride route for conventional synthesis.

Incorporation of a small amount of Si (Jhung *et al.*, 2004) into AFI framework can change their acidity. The microwave irradiation technique can also be used to prepare SAPO-5 and SAPO-34 molecular sieves (Jhung *et al.*, 2003),

showing selective phase formation with microwave irradiation and hydrothermal heating, respectively, of the same gel irrespective of the acidity or the type of the templates. The SAPO-5 structure may transform into the SAPO-34 structure with the increase of crystallization time probably due to the relative stability of the two phases. Jhung $et\ al.$ (2004) prepared $AlPO_4$-5 and SAPO-5 by microwave irradiation. The results showed that the addition of Si into an alkaline precursor gel hindered the crystal growth in the c-direction and the presence of fluoride ions retarded the nucleation and crystal growth. It is an advantage to synthesize SAPO with high silicon content (Zhao $et\ al.$, 2002; Wang $et\ al.$, 2003). However, due to poor crystallinity and formation of large siliceous islands at high Si concentration in the gel, the silicon content in the SAPO is limited.

Heteroatom-substituted $AlPO_4$-5 and SAPO-5 have also been investigated extensively. Various metal ions, such as VAPO-5 (Jhung $et\ al.$, 2005), [Ni]APO-5 (Jehng $et\ al.$, 2001), [Cr]APO-5 (Laha $et\ al.$, 2006), TAPO-5 (Rios $et\ al.$, 2002), have been incorporated and the resulting systems are potential catalysts. Saha $et\ al.$ (2005) synthesized metalloaluminophosphate (MAPO-5) in which $AlPO_4$ lattice is also substituted by alkaline earth metals: Mg, Ca, Sr, and Ba by varying synthesis parameters, such as gel composition, content of alkaline earth metals, amount of water, and heating time. These parameters affected crystallization of molecular sieves. Pt loaded $AlPO_4$-5 (Zhu $et\ al.$, 1997) and SAPO-5 were also prepared to test activity performance on isomerization of hydrocarbon (Xiao $et\ al.$, 1998; Kumar $et\ al.$, 2005; Roldan $et\ al.$, 2007).

A number of research works have been involved metal oxide with flower-like shape, viz. TiO_2 (Li $et\ al.$, 2006), CuO (Zhu $et\ al.$, 2007), ZnO (Jiang $et\ al.$, 2007). The preparation of ZnO was also obtained with a more vivid natural flower shape in the synthesis mixture containing triethanolamine (Li $et\ al.$, 2007). The synthesis of K-H zeolite with flower-like product was obtained from the use of atrane precursors (Sathupanya $et\ al.$, 2004), generating triethanolamine and triisopropanolamine from the hydrolysis reaction of silatrane and alumatrane precursors, respectively. Trialkanoamine could also act as stabilizing agent in the synthesis of zeolite materials (Wilson $et\ al.$, 1982; Coker $et\ al.$, 1998).

The PROX of CO in H_2-rich gas for PEMFC application progressively calls more attention. Among the noble metals used for PROX of CO, Pt is widely used as metal catalyst owing to its electronic structure proper to break atomic bonding of adsorbed molecules (Jo *et al.*, 2009) and its high resistance to deactivation by CO_2 or H_2O (Padilla *et al.*, 2009). Pt based catalysts are well known to be an effective catalyst for CO oxidation at high temperature (Jo *et al.*, 2009). The effect of Pt precursor types: H_2PtCl_6, $Pt(NH_3)_4Cl_2$, $Pt(NH_3)_4(NO_3)_2$, over the preparation of Pt/3A zeolite catalysts was also studied (Rosso *et al.*, 2007). The result reported that the sample produced with $Pt(NH_3)_4Cl_2$ showed the best catalytic performance as the acceptance CO conversion level in a wide operation temperature. Pt metal is generally loaded onto alumina support, showing active and selective around 200 °C on the PROX of CO reaction (Kahlich *et al.*, 1997; Kim *et al.*, 2002; Manasilp *et al.*, 2002) with less methanation (Oh and Sinkevitch, 1993). The enhancement of catalytic performance over Pt/Al_2O_3 catalysts was obtained by the addition of the modifying elements, e.g. Co, Mn, Fe, Ni, Cu, to create the Pt-promoter oxide interfacial sites (Jain *et al.*, 2009). They acted as an active oxygen provider supplying oxygen for CO oxidation on Pt. Furthermore, utilizing zeolites as support for Pt based catalysts on the PROX of CO has been investigated by several groups (Watanabe *et al.*, 1995; Igarashi *et al.*, 1997; Sebastian *et al.*, 2009) owing to the molecular sieve effects to increase selectivity. Beside, zeolites containing larger molecular weights and higher chemisorbing properties result in H_2, CO, and O_2 with longer contact time to adsorb on catalysts, as compared Al_2O_3 support (Kotobuki *et al.*, 2005). Igarashi *et al.* (1997) demonstrated Pt supported zeolite A, zeolite X and MOR on PROX of CO, and revealed that all supports did not achieve 100% CO conversion at 1% O_2 to oxidize 1% CO in gas mixture. Higher content of O_2 was needed to achieve complete CO conversion (Igarashi *et al.*, 1997); however, it is a risk for explosion. A comparison of the kinetics of CO oxidation in H_2-rich on Pt/MOR and Pt/Al_2O_3 was evaluated (Ren and Hong, 2007). Pt/MOR showed a wider operation temperature than Pt/Al_2O_3, particularly towards lower reaction temperature. Sebastian *et al.* (2009) also investigated on Pt supported on zeolites (MOR, ZSM-5, FAU and ETS-10), and Pt/FAU was the only one attaining 100% CO conversion due to its larger pore size and higher dispersion of Pt.