

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Sol-gel Process

Traditional ceramic and glass processes need high temperature to transform inorganic powders into dense objects by melting or sintering. The high temperatures and agglomeration of powders often limit control of the microstructure, properties, shape, and surface feature obtained. The goal of sol-gel technology is to use a low temperature chemical process to produce net-shape, net-surface objects, or composites that can be used commercially after a minimum of additional processing step.

Sol-gel technology is the preparation of ceramic, glass, or composite materials by the preparation of a sol, gelation of the sol, and removal of the solvent. Potential advantages of the sol-gel process include:

1. the ability to maintain high purity,
2. the ability to vary compositional homogeneity at a molecule level,
3. low temperature of processing that leads to energy saving,
4. preparation of new crystalline phases and new non-crystalline solids,
5. the ability to produce samples in different physical forms,
6. ultrastructure control of materials by manipulating network formation from early stages of sol formation, and
7. preparation of materials having improved physical properties.

The handling of precursor by heat treatment is the factor needed to be considered. In general, the sol-gel process is the synthesis of an inorganic 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 colloidal solution) into a solid (gel-like state).

Sol-gel technology can be divided into 2 types. Firstly, colloidal method involves the suspension of solid particles in a liquid from a sol (Schmidt, 1994). Secondly, polymeric method involves the polymerization of organometallic compounds, such as alkoxides that provide 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 cation.

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

Sol-gel process involves the following steps:

1. Hydrolysis of precursor,
2. Polycondensation,
3. Gel formation, and then
4. Organic pyrolysis by heat treatment.

The first step, starting materials (metal alkoxides) are mixed in a 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 alkoxides precursor. Many factors influence the rate of hydrolysis and condensation because both processes often occur simultaneously. The most important variables are temperature, nature and concentration of electrolyte, nature of solvents, and types of alkoxides precursor. The following step, calcination, is necessary to convert gel into a useful form.

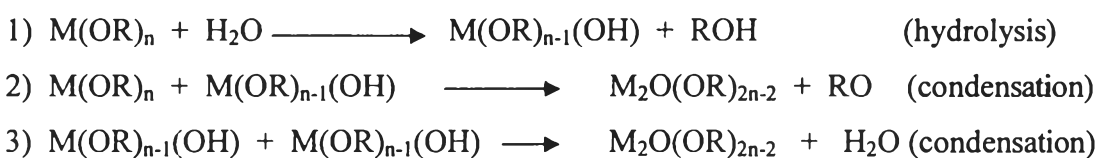
Sol-gel process can be done at the ambient condition (a vacuum is not needed). Another advantage of this process is inexpensive as compared to other deposit techniques. Materials can be produced in a variety of forms, such as fine powders, thin films, monoliths and fiber. However, some disadvantages of the sol-gel process are excessive shrinkage that can cause cracking.

At present, metal alkoxides are used as precursors for polymeric gel in sol-gel processing. These precursors are readily used with a suitable organic solvent, which is usually alcohol. The metal alkoxides bond is in general extremely susceptible to hydrolytic reaction leading to metal hydroxides or hydrated oxide. The choice of alkoxides can be considered by many factors including metal content, reactivity, availability, cost, and sensitivity to moisture and decomposition temperature.

A compound with less organic content and high metal content is a proper precursor. Less organic solvent causes in less volumetric shrinkage during drying

and annealing. Therefore, film has fewer tendencies to crack. However, a compound with high metal content is usually much more reactive, it may be difficult to prepare a stable solution. For alkoxides with different alkyl groups, the reactivity usually increases in the order of metal > ethyl > propyl > butyl > higher order alkyl groups.

There are two important reactions in polymeric gel formation. These reactions are partially hydrolysis, followed by condensation polymerization. Polymerization steps via hydrolysis and condensation reaction are illustrated in reactions 1 – 3.



The M-O-M network product is formed by polycondensation reactions as in reactions 2 and 3 which alcohol and water are produced as the by-products. There are many applications of controlled hydrolysis to obtain a desired molecular structure.

Other parameters that need to be considered are aging of gel along with 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 continue to occur after the gel point. The process can actually be desirable because it leads to a more cross-linked network that is mechanically stronger and easier to handle.

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

Calcination/sintering is often done in the presence of a reactive gas (e.g. flowing air, oxygen, or hydrogen) in order to burn off any residue organics or to oxidize (or reduce) a sample. Exposing the sample to a high temperature over an extended period of time leads to sintering and a decrease in surface area, respectively. The process can also cause the material to crystallize into different

structure forms. Thus, the physical characteristics of the product depend on parameters, such as temperature, heating rate, time, and gaseous environment.

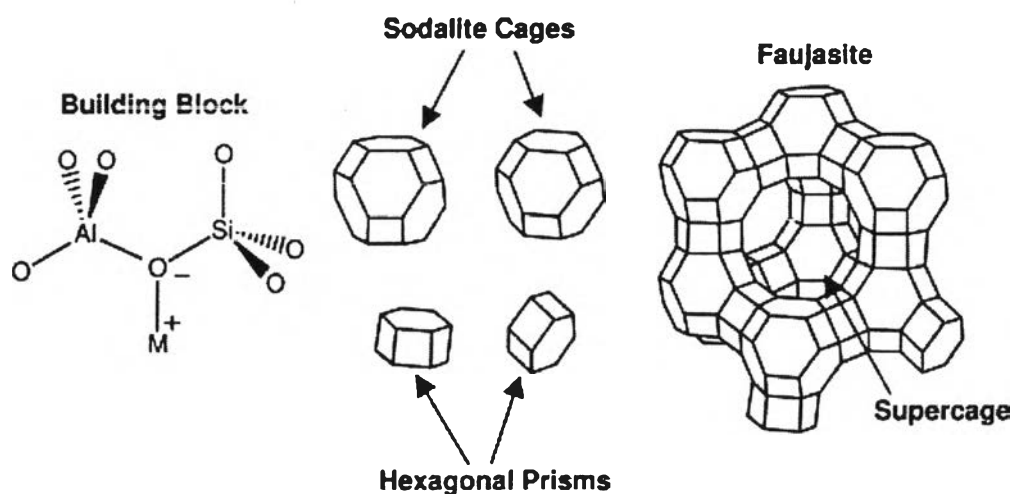
Other critical parameters need to be considered are viscosity, and rheological properties of the solutions. Therefore, many applications of controlled hydrolysis to obtain a desired molecular structure and appropriate viscosity of the solution are used to improve spinning and coating ability. In addition, the solution concentration, viscosity, surface tension of the solution and the deposition technique determine the film thickness and uniformity (Thanabodeekij *et al*, 2003).

## 2.2 Zeolite

Molecular sieve zeolites are crystalline aluminosilicates in which the aluminum atoms and the silicon atoms are present in the form of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra. Consequently, the zeolite framework has net negative charge which is produced when the alumina tetrahedra are present, which must be balanced by associated cations, e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{H}^+$ ,  $\text{NH}_4^+$ , etc. On the other hand, the silica tetrahedra do not need to have any balancing cations due to the silica tetrahedra have no net charge. The alumina tetrahedra in the lattice must be adjacent to silica tetrahedra, while the silica tetrahedra may have adjacent alumina or silica tetrahedra as neighbors. The connection of silica and alumina tetrahedra causes myriad of lattice architectures which consist of channels and cages that are occupied by the cations and water molecules. Figure 2.1 illustrates the highly porous nature of faujasite and the need for charge balancing cation.

The arrangement of tetrahedra (primary building units) can be classified into various types of secondary building units (SBUs), which may be simple polyhedral, such as cube, hexagonal prisms, or truncated octahedra. The unit cell is formed from the connection of each polyhedral. Hence, there are many unit cells formed. The porosity is mostly generated only when the polyhedra are connected to form a unit cell. The pores can be classified as cages and channels. High aluminium content zeolites tend to be a cage structure framework while high silica content zeolites tend to be a channel structure framework. The window is a pore aperture of the

framework structure. The classification of zeolites based on size of window is illustrated in Table 2.1.



**Figure 2.1** Schematic diagram of a faujasite-type zeolite.  $M^+$  is a charge-balancing cation (Davis, 2002).

**Table 2.1** Classification of zeolites based on size of windows (Kanchanachinto *et al*, 2004)

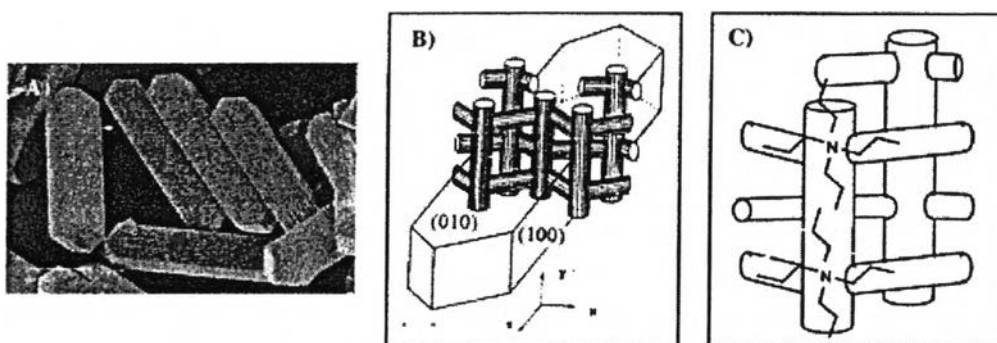
Small	Medium	Large	Extra Large		Mesoporous
4-5A°	5-6A°	7-8A°	12A°	13A°	16-100A°
8-T ring	10-T ring	12-T ring	18-T ring	20-T ring	Variable
Zeolite A Chabazite ZK-5 Rho Erionite	ZSM-5 Theta-1 Rerrierite ZSM-48	Faujasite Mordenite Offretite Beta Zeolite L	VPI-5	Cloverite	MCM-41 MCM-48

### 2.3 MFI Zeolite

In this work, MFI zeolite, first discovered by Secony Mobil Oil Company by using an industrial microwave oven, is our focus. It can be synthesized by using template, acting as a structure-directing agent to occupy the channel space of the zeolite. Normally, tetrapropyl ammonium (TPA) template molecule is used for MFI.

Two main components constitute the MFI structure (MFI for Mobil Five): ZSM-5, where the Si/Al ratio varies between 10 and 500, and silicalite-1, a pure siliceous form (Si/Al > 500). MFI structure is characterized by the presence of two types of interconnected channels, the opening of which is delimited by 10 tetrahedral units (Figure 2.2). Silicalite-1 can be obtained in the presence of the great variety of organic template species. However, the pure phase can be obtained only by performing the synthesis in the presence of tetrapropylammonium cations ( $\text{TPA}^+$ ).

In the as-synthesized solids, four  $\text{TPA}^+$  per unit cell are occluded within the inorganic framework, at the intersection of both systems of channels as illustrated in Figure 2.2. It is clear that there is a geometrical turning between these cations and the channel system, as only one cation per intersection is present.



**Figure 2.2** Structure-type MFI: (A) crystals of silicalite-1; (B) overview of the channel system; (C) scheme of the location of the  $\text{TPA}^+$  cations at the channel intersection (Soler-Illia *et al.*, 2002).

The MFI zeolite synthesis directly from silatrane via sol-gel process and microwave technique was studied by Phiriyawirut *et al.* (2003). Silatrane was synthesized from the reaction of  $\text{SiO}_2$  and triethanolamine using ethylene glycol as a solvent. In their work, the effects of  $\text{Na}^+$ ,  $\text{OH}^-$ , and tetrabutyl ammonium hydroxide concentration in the reaction mixture were investigated. The results showed that the rate of MFI formation decreased with increasing  $\text{Na}^+$ , decreasing  $\text{OH}^-$ , or lower tetrabutyl ammonium hydroxide. The reaction temperature and aging time were also varied. It was found that a longer aging time was more important to achieve high

crystallinity than heating time. The shape of MFI crystals appeared to depend on the level of water.

Phiriyawirut *et al.* (2003) prepared silatrane and alumatrane via the oxide one-pot process, and used as precursors for MFI synthesis. Two types of template, tetrabutyl ammonium hydroxide (TBA) and Tetrapropyl ammonium bromide (TPA) were studied to compare their effect on the MFI morphology. They found that morphology obtained from TPA and TBA was different due to the steric hindrance of the template during crystal formation. They also investigated the influence of aging time, and of the sodium and hydroxide content of alumatrane. It was found that increasing in alumatrane loading caused more difficulty for MFI crystal formation. Moreover, they concluded that the tendency for MFI formation was improved by increasing the aging and heating time.

#### 2.4 Fe-MFI Zeolite

There are four means to introduce iron into MFI zeolite as the followings: direct synthesis, post synthetic modification of borolite, ion exchange in solid or liquid state, and by impregnation. Generally, iron ions may have two kinds of emplacements when present in MFI lattices. The first is a framework iron in the tetrahedral oxygen co-ordination which belongs to the lattice of MFI. Another one is situated in extra-framework position as iron oxide, -hydroxide and usually has octahedral co-ordination. Brabec *et al.* (1998) found that iron in the zeolite framework was obtained only from direct synthesis method. On the other hand, ion exchange of iron in solution or in solid phase always results in extra-framework iron species sitting with unknown position (either charge-balancing position and/or in the voids of zeolite as -oxide/hydroxide).

The iron containing of MFI catalysts plays the important role in selective redox reduction, like biomimetic oxidations, or selective catalytic reductions of pollutants, dangerous for the environment. During the catalytic processes, iron in the framework and extra-framework plays the different functions. As Phu *et al.* (2001) used a synthesized Fe-ZSM-5 zeolites to study the reaction of phenol oxidation by using  $H_2O_2$  as a reducing agent. The results showed that this reaction can be

catalyzed by both of framework and extra-framework iron in aqueous solution. However, the framework iron can catalyze more completely phenol oxidation than the extra-framework iron does.

As far as the environmental pollution is concerned, air pollutants consist of carbon monoxide, oxide of nitrogen, hydrocarbon residue, and oxide of sulphur. To solve this problem, the minimization of these toxic gases is the main way to protect the environment. In this work, the reduction of nitrogen oxide using synthesized Fe-MFI catalyst is focused.

## 2.5 Catalytic Removal of NO<sub>x</sub>

The major NO<sub>x</sub> emission sources are fuel combustion in automobile engines and coal fired power plants. Therefore, the reduction of NO<sub>x</sub> belongs to the most important tasks of environmental chemistry. The de-pollution of NO<sub>x</sub> (deNO<sub>x</sub>) can be classified into two ways as catalytic decomposition of NO and selective catalytic reduction.

The catalytic decomposition of NO is the simplest way to thermodynamically remove NO<sub>x</sub>. Kinetically, however, it is inhibited by high activation energy.

The selective catalytic reduction (SCR) of NO with various reductants such as H<sub>2</sub>, CO and hydrocarbon in the presence of a noble metal supported zeolite catalysts is an efficient way to reduce the pollutant emissions from vehicles.

Wang *et al.* (2003) studied the reduction of NO with CO in the presence of excess oxygen over different noble metal supported ZSM-5 catalysts. They found that Pt/ZSM-5 was active when H<sub>2</sub> was used as a reductant, whereas, CO was suitable for Ir/ZSM-5. The difference was due to the different mechanisms of two reactions, NO can dissociate more easily over Ir/ZSM-5 than Pt/ZSM-5, while the oxidation of CO by O<sub>2</sub> proceeded more rapidly on Pt/ZSM-5 than on the Ir/ZSM-5.

Iliopoulou *et al.* (2004) used a series of Ag-based catalysts supported on unpromoted or Ce-promoted  $\gamma$ -alumina as a catalyst in order to study the selective catalytic reduction of NO<sub>x</sub> with various reductants. C<sub>3</sub>H<sub>6</sub>, CH<sub>4</sub>, and CO were used as the reducing agents, and C<sub>3</sub>H<sub>6</sub> has the highest reducing activity. Moreover, the



various hydrocarbons were also tested as reductants. The deNO<sub>x</sub> performance was enhanced when using the higher and less saturated hydrocarbons.

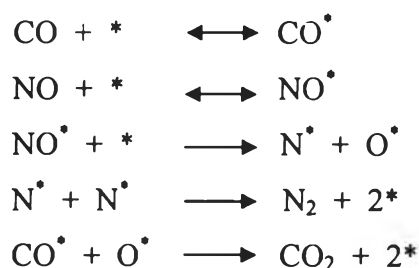
## 2.6 Selective Catalytic Reduction (SCR) by CO

Reduction of NO<sub>x</sub> is of great importance and interest in air pollution control especially in the high temperature combustion processes. Generally, NO is much abundant than other nitrogen oxides of the NO<sub>x</sub> pollutants. In addition, CO is also found in ineffective combustion processes. In the easiest case NO can react with CO forming a half of N<sub>2</sub> molecule and CO<sub>2</sub>.



Besides many other applications, this reaction is one of the key processes in automobile exhaust catalysts.

For a clean Pt(100) surface, the most realistic model explaining the autocatalytic behaviour is the vacancy requirement of the NO dissociation (Eichler and Hafner, 2001). As shown below:



(\* denotes an empty surface site, \* in superscript refers to adsorbed species)

Firstly, NO and CO are adsorbed on the surface of catalyst. This step consumes an empty surface site. The islands of adsorbed species are formed and grown until the sites are occupied and no more vacant surface sites are left. For the next step, NO dissociation does not occur until one of the adsorbed gases starts to desorb due to the requirement of an additional surface site. Then, N<sub>2</sub> desorption and

CO oxidation are occurred after the dissociation of NO can take place. At this point, these steps provide two additional vacant sites, so that the first two steps can continue until no more CO and NO are adsorbed on the vacant site. This process is called “the autocatalytic” because it produces more vacant surface sites (4\*) than it requires (1\*).

Fernández-García, *et al.* (2003) analyzed the redox and chemical processes taking place during the CO+NO+O<sub>2</sub> reaction by using a series of Pd-Cr bimetallic catalysts supported on a (Ce-Zr)O<sub>x</sub>/AL<sub>2</sub>O<sub>3</sub> mixed support. The results showed that the nature of support strongly affected the catalytic behaviour. Moreover, by using this catalytic system, the addition of Cr was less influential in terms of catalytic activity.