CHAPTER II
LITERATURE REVIEW

Atrane was evolved in the middle of last century. Due to the ball shaped molecules and a transannular bond it has unexpected properties. Three major structures are shown in Figure 2.1. Verkade in 1993 summarized its properties and reactivity depending on substitution of the Z and steric properties of the E. Y substituent strongly affected the properties of atrane, as well.

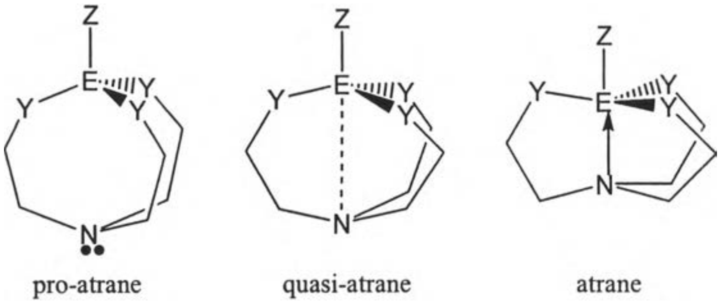

Figure 2.1 Structures of Atrane Compounds.

Many atrane compounds were synthesized in the last decade, for example, E is Co, Mo, Ni, Cu, Zn, Cd and etc. Several works were studied on the thermal stability, as reported by Yilmaz *et al.* in 2000, 1996 and 1995.

Frye *et al.* had reported on silatrane synthesis (where E = Si) since 1971, mainly emphasizing on enhancement of solvolytic stability due to the presence of transannular bond of N→Si, generating more electron density on silicon atom to prevent the nucleophilic displacement. In general, about 34% of silatrane were nucleophilically displaced under boiling aqueous solution. Considerably, this is more stable than conventional orthosilicate. It can be explained that, firstly, the bridge-head (Z group) of silicon precludes backside attack, secondly, if the cage was decorated by alkyl substituted (Y group), the peripheral group may impede the nucleophile to attack. The last reason is as a result of 3d orbital of the silicon atom was partially occupied, and resultant of negative charge discouraged an attack by nucleophile. Various kinds of ligand (Y goup) and the end cap Z group were studied.

Wongkasemjit *et al.* in 2001 successfully synthesized the tris(alumatranyloxy-i-propyl)amine from aluminum hydroxide and triisopropanolamine. This method has an advantage over others in terms of using inexpensive starting materials and simple oxide one pot synthesis (OOPS) process. This novel material gives polymeric form determined using FAB^+-MS.

Many attempts to apply atranes for some specific purpose were carried out, such as, combining silatrane to ferrocene, as reported by Calhorda *et al.* (1997) and Pedersen *et al.* (1999). Due to the inertness towards hydrolysis, Cabrera *et al.* (2000) used silatrane and alumatrane, as precursors, to synthesize mesoporous by assistance of surfactant, and found that atrane complexes are good precursors for synthesis of ordered mesoporous mixed oxides, therefore, might give good performance for nanoporous materials.

Sathupunya *et al.* (2002-2003) successfully synthesized zeolites type GIS, ANA, and LTA from alumatrane and silatrane. By microwave technique, the zeolite was synthesized within few hours. This combination of novel atrane chemistry and microwave technique dominantly gives a new route to zeolite synthesis. The hydrolysis behavior of the silatrane and alumatrane mixture was studied under sodium salt and sodium hydroxide condition, and showed that using FTIR it takes only few hours to hydrolyze these atrane compounds. Crystallization condition was studied and found the transformation of GIS to ANA by extending the microwave heating time.

In this work, MFI zeolite which was first discovered by Socony Mobil Oil Company by using 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. Generally, tetrapropyl ammonium (TPA) template molecule is used for MFI synthesis. Another relative structure of MFI due to the same pentasil structure is MEL that can be synthesized by using tetrabutyl ammonium salt (TBA). Both structures were shown in the appendix part. Many kinds of starting materials were used for MFI synthesis, namely, silicic, fumed silica, colloidal silicate and organometallic, such as, tetraethoxysilane (TEOS). Different starting material gives different approach of MFI formation.

De Moor *et al.* (1999) proposed a nucleation and growth mechanism for the formation of MFI from a mixture of silicic acid and tetrapropylammonium hydroxide (TPAOH) using small angle X-ray scattering technique and found that nanometer-scale primary units ("nanoblocks") containing a specific MFI topology were formed. Nucleation involves the aggregation (~ 10 nm) unit, which comes from primary particles (2.8 nm) aggregate. Crystal growth occurs via stepwise addition of primary particles throughout the reaction period. They studied the effect of base concentration on the concentration of aggregates and rate of crystal nucleation. They found that the primary unit was exiting through the reaction period and became constant at the point of crystal growth; however, the aggregation of the nucleation was consumed all in the early period of reaction. The nucleation concentration is depended on the Si/OH ratio. Extended work on gelating system was studied and reported at the same year. Trimethylene-bis(N-hexyl,N-methyl-piperidinium) was used as template. They found that the primary unit was the same as the previous work (2.8 nm) for both gelating and nongelating system. They summarized that the large gel structure or heterogeneous gel had no meaning for zeolite nucleation and growth. In the year 2000, they used dimer and trimer of TPA to study using the same technique. The primary size was also the same but the aggregation was a bit bigger, ranging from 10-15 nm, which is the essential for nucleation. The result shows step growth via the addition of the primary units.

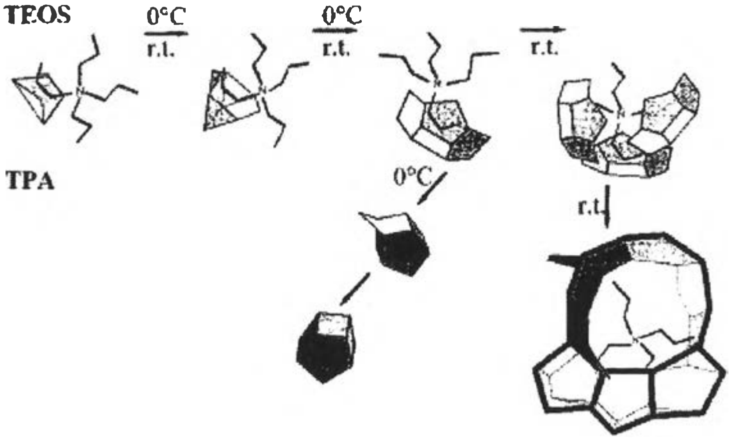

Figure 2.2 Schematic presentation of the TPA-directed polycondensation process of TEOS (Christine *et al.* in J. Phys. Chem. B 1999, 103, 4965)

The use of organosilicate compounds, such as TEOS, in MFI synthesis was demonstrated by Martens *et al.* (1999). They studied the reaction of TEOS and concentrated TPAOH, and observed the formation of MFI nanoblocks. X-ray scattering, tansmission electron microscopy, atomic force microscopy and ^{29}Si-NMR were used to determine the naonslab with dimensions of 1.3 x 4.0 x 4.0 nm. It has MFI structure with nine channel intersections per particles. They expanded work to study and explain how the MFI ring was formed before the presence of nanoslab using ^{29}Si-NMR technique. The Bicyclic pentamer is formed around the TPA and developed to pentacyclic octamer and then turned to be tetracyclic undecamer. Three tetracyclic undecamers around TPA template turn to ring structure of MFI, as shown in figure 2.2. Further work was studied on how the nanoslabs construct the MFI crystal using XRS technique to monitor the changing in size of the crystal. This work was extended to MEL zeolite, the counterpart of MFI, which gives difference of growth of the crystal.

An alternative way to synthesize MFI was introduced in 1999 with template free method by Machado *et al.* Generally, MFI topology is required template molecule, especially the high silicate zeolite; however, it can be omitted in the case of high aluminum content. The Si/Al is at around 12 to 29. However, it is possible to obtain other kind of zeolite, such as, MOR from the same synthesis of gel by only changing either temperature or crystallization time.

It has many attempts to insert heteroatom of metal which acts as catalyst into the MFI, for example, Fe, Ga, Ti and V for specific purpose. In this work, vanadium is the metal to be loaded into the MFI structure, as named VS-1.

Whittington *et al.* in 1991 prepared VS-1 by the reaction of vanadium oxytrichloride ($VOCl_3$) with H-ZSM5 and silicalite. The vanadium incorporated into the structure by removal of the silanol group in the pore structure to form $(\equiv SiO)_3\equiv VO$. For the treatment of $VOCl_3$ with H-ZSM5, the acid site was removed and the reaction was partly reversible on treatment with water. The irreversible and reversible reactions are associated respectively with dealumination and proton removal by binding vanadium species at framework of aluminum. ESR results at 293 and 77 K show that the vanadium has weak interaction with the silicatlite but strong interaction with H-ZSM5. The binding probably occurs near framework of aluminum. XPS shows that very small amount of vanadium is adsorbed at surface of zeolite.

Petras *et al.* in 1992 used V_2O_5 mill with H-ZSM-5 to compare with ion exchange method of VOC_2O_4. Using mechanical mixing, the vanadium was reduced and partly replaced the strong acid OH group (~40%) inside the channel of zeolite, while the remaining vanadium was adsorbed on OH group, the exterior of crystal. Both techniques give the same symmetry of C_{4v}. Adsorption of water or ammonia changes the ligand symmetry to square bipyramid which weakens the V=O bond.

Centi G. *et al.* in 1992 prepared by hydrothermal synthesis with VCl_3. 4 vanadium species were detected, viz. (i) polynuclear vanadium oxide removable by ammonium acetate extraction (ii) nearly octahedral vanadyl (VO^{2+}) inside channel (iii) V^{5+} with nearly tetrahedral environment and (iv) after reduction of V^{4+} in nearly tetrahedral environment. Very small amount of vanadium incorporated to the structure having Si/V at around 545, and the excess was presented in the amorphous form inside and outside channels. FTIR showed that the vanadium was present inside only after treatment with ammonium acetate if weak silanol was detected.

Sen *et al.* in 1996 studied the influence of synthetic method between fluoride and alkali methods. They found that vanadium in alkaline gel favored to incorporate to the framework, but not in acidic gel. It is known that the alkali method gives more defect than the fluoride one, which can be monitored by the presence of OH group inside the channel, and most of vanadium is present in the defect sites in the MFI framework. EPR result shows that by using the acid media the vanadium is formed polymeric species after calcination and the phase transformation occurs from orthorhombic to monoclinic which is detected using XRD, but vanadium is incorporate as V^{5+} in distorted tetrahedral environment in the alkali medium.

Some research prepared the VS-1 in the form of membrane, as reported by Tavolaro *et al.* in 2002, Louisa *et al.* in 2001 and Julbe *et al.* in 2000. For the work of Julbe, the prepared membrane on alumina tubes was tested by oxidative dehydrogenation of propane. The test was compared between MFI and V-MFI, and found that both membranes were active at 550°C, but the V-MFI led to slightly better propylene yield at very low vanadium content in V-MFI with selectivity in the range of 40-50%. The performances of both catalysts were stored after 200 hour of testing.