# CHAPTER II
# BACKGROUND AND LITERATURE REVIEW

## 2.1 Zeolites

Zeolites are highly crystalline aluminosilicate minerals of natural or synthetic origin. It has uniform pore geometry with minimum apertures (pore opening) of from 0.3 to 10 nm. The size depends on the type of zeolite, the binding cations, and the nature of treatments. The structure of a zeolite is composed of a three-dimensional framework of $SiO_4$ and $AlO_4^-$ tetrahedra, each of which contains a silicon or aluminum atom in the center. They are sometimes termed $TO_4^-$ tetrahedra where T is silicon or aluminum. The oxygen atoms are shared between adjoining tetrahedra, which can be present in various ratios and arranged in a variety of ways. Zeolites may be represented by the empirical formula

$$M_{2/n} \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$
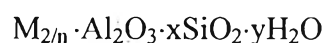
where M is a cation (Satterfield, 1991)

Zeolites can be synthesized from alkaline aqueous mixtures of aluminum and silicon compounds. The crystallization of a particular zeolite can be carefully controlled by the concentration of the reaction mixtures, temperature, and the stirring rate. The syntheses of some types of zeolites, such as pentasils, mainly utilize an organic cation as a template to form their open structure. Zeolite structure can also be modified after synthesis to obtain desire properties for their applications. For example, the extra-framework species can be simply exchanged, the Si/Al ratio can be modified by dealumination procedures (streaming and acid treatment), and other atoms (Ti, Ga, and Fe) can be replaced in zeolite framework.

The pore structure and shape in a zeolite may affect the selectivity of a catalytic reaction in three different ways as follows;

1. *Reactant Selectivity* takes place when the size of zeolite pore geometry allows only certain smaller molecules to penatrate into the zeolite pore and excludes larger molecules. Only the smaller molecules undergo a reaction inside the zeolite pore.

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2. *Product Selectivity* arises when only products of a certain size can diffuse out from the pore channel. If bulkier molecules are formed, they are converted to smaller one. They might be also converted to carbonaceous compounds, eventually leading to the pore blocking.

3. *Restricted transition-state selectivity* allows only the intermediate having a geometrical fit to the zeolite structures can be formed during the catalytic reaction.

The advantages of high shape selectivity combined with high densities of catalytic active sites, and stability at high temperatures make the utilization of zeolite so much potential for a wide variety of petrochemical processes and applied catalysis. (Hagen, 2006)

## 2.2 Zeolite ZSM5 (MFI)

### 2.2.1 The Structure of ZSM5 Zeolite

The crystalline ZSM5 (MFI) zeolite was firstly discovered by Mobil Oil Corporation (Argauer *et al.*, 1972). The ZSM5 zeolite is one of the pentasil family of zeolite. It contains two-dimensional 10-membered ring medium pore structure consisting of two intersecting channel systems. One channel system is zigzag having a cross section of 5.1 x 5.5 Å. The other channel system has 5.3 x 5.6 Å opening which run straight and perpendicular to the first channel system as shown in Figure 2.1. Typically, the aluminosilicate with the ZSM5 (MFI) structure is considered a zeolite at Si/Al ratio between 10 and 190 (Szostak, 1952).
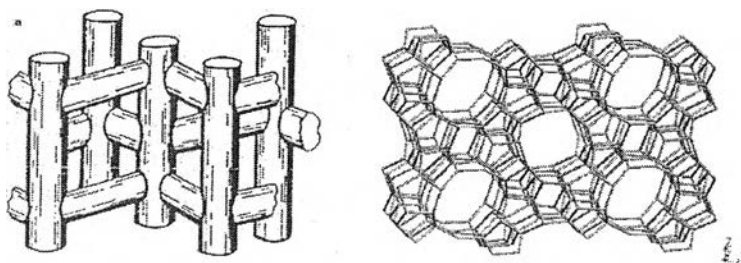


**Figure 2.1**   Schematic of ZSM5 zeolite structure.

## 2.2.2 The Catalytic Applications of ZSM5 Zeolite

ZSM5 zeolite was found board applications, for instance, in cracking process, in methanol conversion to gasoline, and in aromatic processing. ZSM5 zeolite is a kind of superacid catalyst. Therefore, the acid sites of H-ZSM5 zeolite are strong enough at high temperatures to protonate paraffins and thereby initiating catalytic cracking, which is one of the important processes for producing raw materials for the petrochemical industry, such as ethane and propylene (Gates, 1992). The cracking reaction of the paraffins over H-ZSM5 takes place through the carbonium ion chemistry. The carbonium ion can be generated by proton transfer from $\alpha$, then undergo $\beta$-scission to form a smaller paraffin and a smaller cerbenium ion. On a Lewis site, transfer of a proton from an alkane can form a carbenium ion that then undergoes $\beta$-scission. Parraffin cracking is much slower than olefin cracking (Satterfield, 1991). The olefin cracking can take place through the carbenium ion, which is formed by the protonation of adsorbed olefins on the Brønsted acid site. The overall catalytic cracking mechanism consists of various combinations of protonation, $\beta$-scission, hydrogen transfer, and isomerization. Many other reactions are catalyzed by acidic H-ZSM5 zeolite catalyst. They also proceed through the carbenium ion intermediate chemistry. The adsorbed carbenium ion reacts with forthcoming aromatic molecule from the environment of the zeolite pore, leading to alkylation. Ga modified H-ZSM5 has shown to be an effective catalyst for alkylation of benzene with propane (Bigey and Su, 2004). Toluene and ethylbenzene are formed as major products. Cumene and $n$-propylbenzene are also produced at low reaction temperatures in small amounts. Furthermore, the industrial process use the H-ZSM5 in xylene isomerization for obtaining high concentration of $p$-xylene in $C_8$ aromatics cut. The reaction is carried out at 400 °C in the presence of hydrogen (Hagen, 2006).

In 1970s, Mobil Oil completely developed a new synthetic fuel process, known as MTG process, for the conversion of methanol to gasoline range hydrocarbons using H-ZSM5 zeolite catalyst. In a primary reaction, the methanol is dehydrated to dimethyl ether (DME). Subsequently, a complex series of reaction

takes place. DME is further dehydrated to yield light olefins, such as ethylene and propylene. These olefins would undergo oligomerization and cracking reactions, resulting in a variety of hydrocarbons obtained in this reaction ($C_4$-$C_{10}$). Also, substantial amounts of aromatics were yielded (Chang, 1977; Chang, 1984).

ZSM5 zeolite is uniquely suited as a catalyst for the alkane aromatization because of its unique characteristic in shape selective behavior, its high resistance to deactivation at high temperature, and its high acid strength. The studies on propane aromatization over H-ZSM5 catalyst indicated that the decomposition of propane into methane and $C_2H_5^+$ via the C-C bond cleavage of propane is the primary reaction. The reaction pathway of propane aromatization on H-ZSM5 was proposed that it takes place through a complicated sequential reaction network of β-scission, dehydrogenation, oligomerization, and cyclization (Biscardi and Iglesia, 1998). For butane aromatization on H-ZSM5 catalysts, propane is the major product and the yield of aromatization is very small (Ono, 1992). Ishaq et al. (1998) reported that only 23 wt% selectivity of aromatics from 83 % conversion was yielded from the aromatization of n-butane over H-ZSM5.

Although H-ZSM5 catalyst shows high conversion, its total aromatics selectivity is quite low. The high conversion on H-ZSM5 may be achieved as a result of the acidic properties of the catalyst. However, the low dehydrogenation capability of H-ZSM5 catalyst may lead to the low selectivity to total aromatics. Therefore, the addition of dehydrogenating metal (Pt, Zn, and Ga) into H-ZSM5 was added to improve the selectivity of aromatics. The study on the aromatization of propane (Meriaudeau et al., 1997) indicated that the highest aromatics selectivity was observed on Ga/H-ZSM5 or Zn/H-ZSM5 catalysts. Nevertheless, Pt/HZSM-5 yielded less aromatic selectivity than H-ZSM5. This might be due to the fact that the hydrogenolysis activity of Pt leads to the production of greater amount of lower alkanes, especially ethane. Furthermore, it was demonstrated that the role of Ga, Zn, and Pt is to improve the rate of propane dehydrogenation, hence facilitating oligomerization. The aromatization took place through the formation of dienes, trienes over the metal sites, followed by cyclization on the acid sites. Also, it was reported that Zn cation catalyzes the dehydrogenation of n-hexane and cyclics intermediates into corresponding aromatics leading to higher selectivity of aromatic

compounds (Smiešková *et al.*, 2004). Besides, Zn species not only enhance the dehydrogenation activity, but also alkene conversion rate from the oligomerization /β-scission reactions leading to the production of aromatics (Biscardi and Iglesia, 1999). Moreover, it was proposed that Zn species possibly catalyzed the direct dehydrocyclization as observed in the enhanced selectivity of toluene from n-heptane aromatization (Viswanadham *et al.*, 1996).

## 2.3 Zeolite X (Fuajasite)

### 2.3.1 The Structure of X Zeolite

The zeolite family of faujasites, including zeolite X, is found the largest scale applications in catalysis processes. The framework geometry of zeolite X is much similar to that of zeolite A. It has a network of three-dimensional intersecting pore channels, consisting of an array of cavities (know as a "*supercage*") with a diameter about 1.2 nm. The entrance to each supercage is through six bridging oxygen ions (called a hexagonal prism), linking of sodalite cages with a diameter of about 0.74 nm (12-membered oxygen rings) as shown in Figure 2.2. This aperture admits large hydrocarbon molecules, such as naphthalene to penetrate. However, the pore diameter of 0.74 nm is small enough to restrict the transportation of some molecules. Zeolite X has been utilized in catalytic cracking of petroleum for the production of gasoline range hydrocarbons.
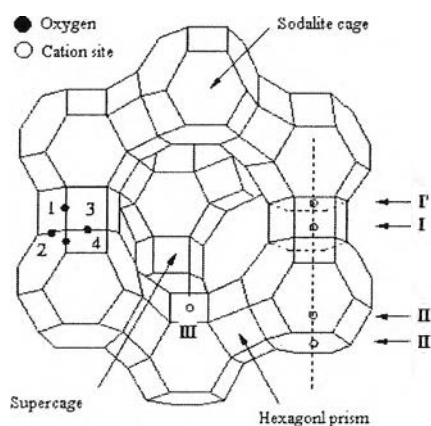


**Figure 2.2** Structure of Faujasites.

2.3.2 The Catalytic Application of X Zeolite

Zeolite X has been studied as a catalyst for aldol condensation, which is an important reaction for the production of fine chemicals. The aldol condensation of acetone was investigated over the alkali containing X and Y zeolites at 350 °C (Dartt and Davis, 1994). It was found that the major products were mesityl oxide and isophorone with 80 % selectivity at 8-15 % conversion. Another aldol condensation that has been shown to be catalyzed by the alkali exchanged X zeolite is the condensation of methyl propanoate with formaldehyde for the synthesis of methyl methacrylate (Wierzchowski and Zatoski, 1991). The catalyst provided up to 70 % conversion of formaldehyde and 74 % selectivity of methyl methacrylate.

Another interesting reaction taking place in the presence of the cesium exchanged X zeolite is the side chain alkylation of toluene with methanol for the styrene and ethylbenzene productions (Dartt and Davis, 1994). It was found that the dehydrogenation of methanol to formaldehyde, alkylating agent, is a primary reaction of the side chain alkylation. Furthermore, the second step involved the addition of formaldehyde in the methyl group. However, the decomposition of methanol to carbon monoxide, catalyzed by the strong base sites, is a main side reaction during the reaction between toluene and methanol.

## 2.4 Acidity -Basicity of Zeolites

Zeolites in the proton form ($H^+$) are solid acids whose the acid strength can be adjusted by modification of the zeolites, for instance, ion exchange, variation of Si/Al ratio, and dealuminaition. The acidity of the zeolites depends on the framework Si/Al ratio because the proton exchange capacity is equal to the concentration of $Al^{3+}$ ions in the zeolites. Hence, the structure containing low Si/Al ratios can have higher concentration of acid sites than the others. The zeolites with high concentration of protons are hydrophilic, having strong affinties for polar small molecules to diffuse in the pore. The zeolites with low $H^+$ concentrations, such as silicalite, are hydrophobic and take up organic compounds (Gates, 1992).

To understand the acidity of zeolites, it is helpful to consider a simplified scheme of the interior structures of the pores, where the reaction takes place. The hydrogen form zeolite is represented in Figure 2.3. It should be recognized that the proton is mobile within the structure.
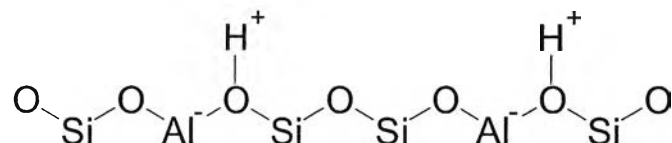


**Figure 2.3** The representation of acid sites in the zeolite.

Infrared investigation on the zeolites, for example, A, X, and Y zeolites has shown the evidence of –OH group as silanol in various positions with a neighboring $SiO_4$ tetrahedra. The interactions of the –OH groups with bases like pyridine demonstrate that the –OH groups located near $AlO_4^-$ have a strong Brønsted acid character, which are generally the active sites of H-zeolites. When the zeolites have low densities of proton donor group, which is exhibited by the zeolites with the low concentration of $AlO_4^-$ tetrahedra (H-ZSM5 and USY zeolites), the proton donor strength are high. They are superacids that can even protonate the alkane at high temperatures. When an H-zeolite is heated at high temperature, water is driven off and coordinatively unsaturated $Al_3^+$ ions are formed, leading to the formation of Lewis acid (Figure 2.4). As shown in Figure 2.4, one Lewis acid sites is generated from two Brønsted acid sites. Bases like pyridine are more strongly bound to Lewis acid than to Brønsted acid.
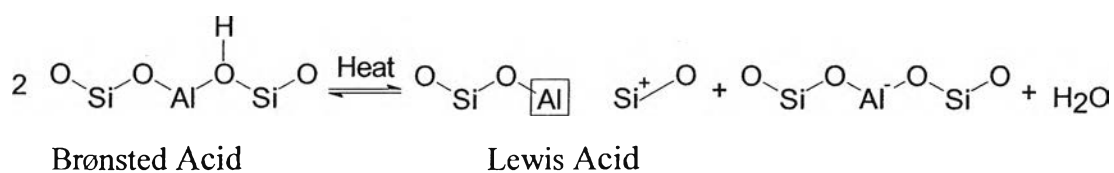


**Figure 2.4** The formation of Lewis acids (Hagen, 2006).

It is surprising that so little is known about the zeolites also acting solid base. The basicity in zeolites can be generated either from the framework oxygen or from the incorporated basic cation species (alkali cation). Actually, alkali cation exchanged zeolites contain both acidic and basic sites. The alkali cations behave as Lewis acids and the lattice oxygens ($AlO_4^-$) tetrahedral that are paired with the alkali cations are basic sites. In the zeolites, Brønsted basic sites (framework basic –OH groups) do not exist. The hydroxyl group with basic properties may take place in the form of non-framework multivalent cations. Hence, in the zeolites exchanged with alkali cations, the negative framework charge compensated by cations with a low electronegativity and delocalized over the framework oxygens is high enough to generate Lewis base properties (Ertl, 1997). Generally, the basic strength of the alkali exchanged zeolites is gradually changed by the size of the exchanged alkali cations; for instance,

$$Li < Na < K < Rb < Cs$$

and

$$Y\ (Si/Al = 2.5)\ <\ X\ (Si/Al = 1.2)$$

These changes in the Lewis basic strength can be observed by that O1s binding energy of the framework oxygen investigated by X-ray photoelectron spectroscopy (Okamoto, 1988). It was found that the O1s binding energy for the alkali cation exchanged X and Y zeolites increased with increasing the electronegativity of the cations. This indicates that the large exchangeable cation could donate more electrons to the framework oxygen than the smaller cations. Then, the electron density localized on the framework oxygen, where Lewis basicity is generated, becomes more concentrated. Therefore, the low value of O1s binding energy is observed when the zeolite contains high electron density.

## 2.5 Catalytic Production of Fuels and Chemicals from Renewable Resources

Recently, the growth of energy demand with the limited availability of petroleum reserves leads to a shortage in the petroleum-derived fuels, resulting in an increase in oil price. Much attention has been drawn to the utilization of renewable

sources for the production of liquid transportation fuels and chemicals. Potential feedstock for the synthesis of biofuels as replacements of fossil fuels includes biomass, vegetable oil, and animal fat.

Biodiesel (Fatty Acid Methyl Esters, FAMEs) from trans-esterification of vegetable oil and animal fat with alcohol becomes more attractive as an alternative fuel. Although the biodiesel provides high cetane number and is burned cleanly, its thermal and oxidative instabilities are major problems. Thus, the catalytic deoxygenation has been proposed to improve the properties and the utilization potential. The conversions of methyl stearate, stearic acid, and tristearine were carried out in semi-batch reactor at 573-633 K under high pressure (0.6-4.0 MPa) in hydrogen and helium atmosphere (Kubickova et al., 2005). It was shown that Pd/C is an effective catalyst for decarboxylation. In the flow of helium, the ethyl stearate was firstly converted to stearic acid as an intermediate. Subsequently, it was further reacted to form n-heptadecane. However, in the presence of hydrogen, the ethyl stearate was directly transformed to n-heptadecane through decarbonylation /decarboxylation. Furthermore, the decarboxylation reaction was also studied with model compounds, methyl heptanoate and methyl hexanoate over hydrotreating catalysts (sulfided NiMo- and CoMo- supported $\gamma Al_2O_3$) under moderate conditions (Senol et al., 2005). It has been proposed that the decarboxylation of methyl esters to hydrocarbons could proceed through three main routes. The first path involved the dehydration of alcohol to hydrocarbons. The second path yielded the hydrodcarbons from the deesterification to produce an alcohol and a carboxylic acid. The carboxylic acid would further transformed to hydrocarbons directly through decarboxylation or with alcohol intermediate. The direct decarboxylation of the esters leading to hydrocarbons took place in the third path. They found that the water suppressed the decarboxylation reaction, inhibiting the formation of $C_6$ hydrocarbons (Senol et al., 2005). Recently, Phuong et al. has reported that 1% $Pt/\gamma Al_2O_3$ successfully provided high activity and high selectivity to diesel range hydrocarbons from the deoxygenation of methyl octanoate and methyl stearate, a model compound of biodiesel and real vegetable oil feedstock, respectively (Phuong et al., 2009). The reaction was carried out in a flow reactor for the gas phase reaction of methyl octanotate and in a semibatch reactor for the liquid phase reaction of methyl stearate.

The main products from the reaction of the methyl octanoate were a mixture of $C_7$ hydrocarbons, obtaining from the decarbonylation of the methyl ester. Only small amount of $C_8$ hydrocarbons were formed. Similarly, high selectivity of heptadecane was obtained from the reaction of methyl stearate on 1% $Pt/\gamma Al_2O_3$. However, it was found that the carrier gas played an important role in the catalytic activity in the semibatch reactor. That is hydrogen as a carrier gas yielded higher conversion and selectivity than helium did.

Extensive studies have investigated the direct product production of diesel and chemicals from vegetable oil via direct hydrotreatment. Under the hydrogen atmosphere, the deoxygenation of unsaturated vegetable oil, for instance, methyl oleate, oleic acid, and linoleic acid was achieved with high selectivity to diesel range hydrocarbons on the Pd/C catalyst (Snare et al., 2007). Parallel to the deoxygenation, hydrogenation also takes place. Another interesting reaction is the transformation of carboxylic acid to hydrocarbons through ketonic decarboxylation (Corma et al., 2008). They have shown that the Pt, Pd, and Ru supported MgO provided a good catalytic activity for the ketonic decarboxylation of fatty acid (lauric acid). In the reaction, two molecules of the fatty acid are condensed to form a symmetric ketone, which could be used in many applications, such as ink manufacturing and dishwashing detergent. Furthermore, the second step of the reaction includes the reduction of ketones to alcohol via hydrogenation on the metal sites. Then, the dehydration of the alcohols yields the long chain hydrocarbons.

Pyrolysis of biomass and wood waste is an old technology, becoming interesting again among various processes. Typically, the pyrolysis of biomass produces three different energy products, which are coke, gas, and oil, with different quantities. The pyrolysis oil consists of two main fractions. One is an aqueous fraction containing light oxygenates and another is the organic compounds with high content of pyrolytic lignin (Gayubo et al., 2004). Considerable attention has been paid to the transformation of oxygenates compounds in the aqueous fraction for the quality improvement of pyrolysis oil. The operating conditions and reactivity for the transformation of oxygenate components, such as alcohol, phenol, aldehyde, ketone and acid was investigated on H-ZSM5 catalyst (Gayubo et al., 2004). It is demonstrated that alcohol could be dehydrated rapidly to olefins at temperature

around 200 °C. Moreover, iso-alcohols are even more rapidly dehydrated than the linear alcohols. Then, the olefins produced from the dehydration would further react to form high olefins and aromatics at the temperature higher 350 °C. The study also shows that phenol provided low reactivity and yielded small amount of hydrocarbons (propylene and butenes). Moreover, acetone is less reactivity than alcohol and requires high space time to achieve high conversion. Acetone is dehydrated to $i$-butene, then is turned to $C_{5+}$ hydrocarbons and aromatics. Aldehyde has low reactivity with rapid deactivation on H-ZSM5 and produced small amount of $C_{6+}$ hydrocarbons. In the case of acid, the decarboxylation is a favorable route for deoxygenation around 400 °C. In addition, the conversion of the model pyrolysis oil occurs though a complex combination of reaction pathways (Adjaye and Bakhshi, 1995). It has been proposed that the primary reactions involve in cracking and deoxygenation, the secondary reactions include secondary cracking, olefin formation, oligomerization, and cyclization, and the terminating reactions include akylation, isomerization, diproportionation, polymerization, and condensation.

Recent studies by Corma and Huber have shown that H-ZSM5 is an effective catalyst for the conversion of glycerol and sorbitol, which are a by-production from transesterification and biomass-derived sugar (Corma et al., 2007). The oxygen is removed from glycerol and sorbitol in the form of $H_2O$, $CO_2$, and CO. Moreover, glycerol and sorbitol gave similar product distributions. The production of olefins, paraffins, and coke can be obtained through the repeated dehydration and hydrogen transfer. Aromatics (about 20 mol %) are formed via Diels-Alder and condensation reaction of olefins and dehydrated species. In additions, they also investigated the catalytic conversion of glycerol/water mixture over H-ZSM5 (Corma et al., 2008). In the reaction, acrolein was found as a dominant product. Short olefins, aromatics and other oxygenates were also formed. They demonstrated that the products from the reaction of glycerol were obtained from a series of reactions, dehydration, cracking and hydrogen transfer, which are catalyzed by the acid sites of the zeolite.