

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Alkylation of Aromatics

Alkylation means replacing an alkyl group or, sometimes aryl group into hydrocarbon compound. Therefore, the alkylation of aromatic is the substituted of an alkyl group by a hydrogen atom on the aromatic ring (Ertl *et al.*, 2008). The alkylation of aromatics widely used in the synthesis in petrochemical industries such as the production of ethylbenzene, cumene, linear alkylbenzene and alkylamine etc. In general, the following reaction (Figure2.1) occurs:



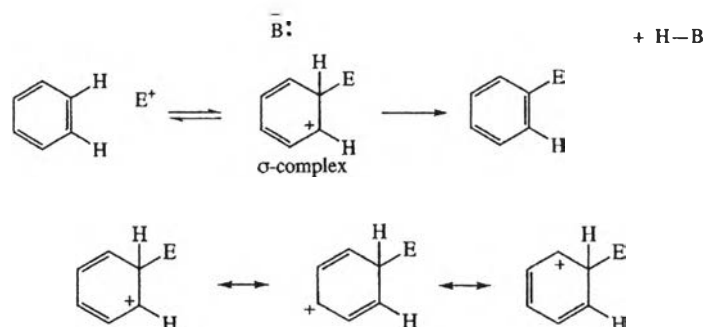
**Figure 2.1** Alkylation of aromatic compound (Mcketta, 1993).

There are several different types of alkylation. These types are classified by the character of the alkylating agent. Nucleophilic alkylating agents deliver a negatively charged alkyl group to the hydrocarbon. On the other hand, electrophilic alkylating agents deliver a positively charged alkyl group to the hydrocarbon.

##### 2.1.1 Electrophilic Substitutions

Most commercial alkylation is acid-catalyzed, including the synthesis of ethylbenzene and cumene by using benzene and ethylene as reactant. The general mechanism of all electrophilic substitution reactions that has two steps is shown in figure 2.2. The first step is the electrophile (E<sup>+</sup>) attack an aromatic ring to form a carbocation intermediate. This structure is called that  $\sigma$ -complex. The positive charge in this compound can delocalized over the molecule by resonance, making this ion more stable than an ion with a localized positive charge. During the second step a proton leaves, aromaticity is regained, and the final product is formed. The rate

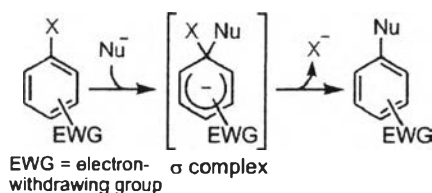
limiting step for an electrophilic aromatic substitution is the addition of the electrophile to the aromatic ring.



**Figure 2.2** The electrophilic aromatic substitution reaction (<http://classes.uleth.ca/200201/chem2600a/notesch12.pdf>).

### 2.1.2 Nucleophilic Substitutions

For the commercial base-catalyzed alkylation is the synthesis of isobutylbenzene and dimethylnaphthalene. The mechanism shown in figure 2.3 that involves an electron rich nucleophile attack on the aromatic ring to give a resonance stabilized carbanion. The leaving group, such as a halide ( $X$ ) on an aromatic ring, then departs to restore the aromaticity. Strong resonance electron withdrawing groups usually must be present in the ortho or para positions to stabilize the carbanion intermediate.

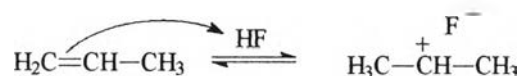


**Figure 2.3** The example of nucleophilic substitution ([http://en.wikipedia.org/wiki/Nucleophilic\\_aromatic\\_substitution](http://en.wikipedia.org/wiki/Nucleophilic_aromatic_substitution)).

## 2.2 Alkylation Catalysts

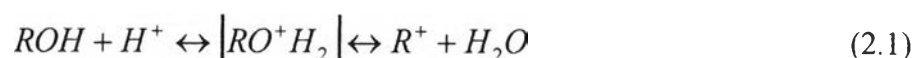
Due to stricter environmental regulations, The replacing homogeneous catalysts with heterogeneous alternatives that cause less waste disposal problems is more interest. Therefore, alkylation processes are developed that allow replacing the conventional mineral acid catalyst (namely, HF and H<sub>2</sub>SO<sub>4</sub>) with environmentally benign solid acids based on zeolites or AlPO<sub>4</sub> molecular sieves. (Hartmann, 2009)

When using alkeness are as alkylating agent, alkenes are treated with a Lewis acid such as AlCl<sub>3</sub>, a small amount of a proton acid is typically added as a co-catalyst to promote the formation of carbocation (Figure 2.4).



**Figure 2.4** The formation of carbocation by using alkenes (Wade, 2009).

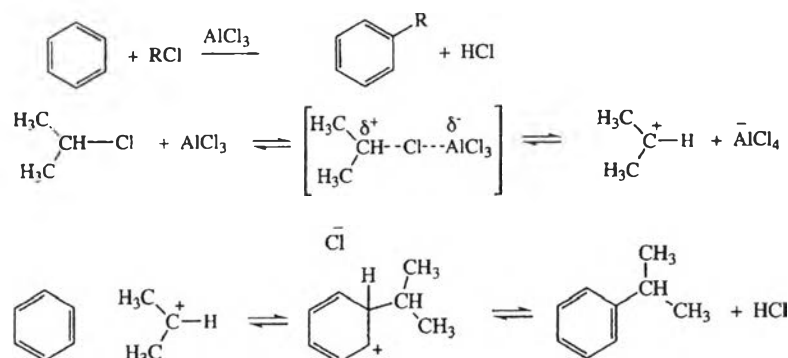
If the alkylating agents are alcohols, in the presence of Bronsted acids, they are protonated and carbocations may be formed.



In presence of Lewid acids, such as AlCl<sub>3</sub>, a complex is first formed with the alcohol and HCl is released. The complex then donates the carbocations.



In the Friedel-Crafts alkylation reaction uses an aluminum chloride (AlCl<sub>3</sub>) as the catalysts and an alkyl halide as the alkylating agent (Figure 2.5). In this reaction an alkyl halide with aluminum chloride formed the intermediate carbocation, an activated electrophile, which subsequently attacked the aromatic ring. Other sources of carbocations are alcohols, esters, ethers and olefins (Mcketta, 1993).



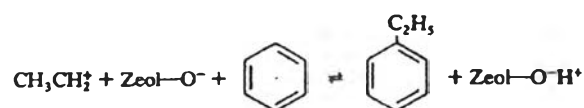
**Figure 2.5** The Friedel-Crafts reaction (<http://classes.uleth.ca/200201/chem2600a/notesch12.pdf>).

However, The Friedel-Crafts alkylation has some limitations. The product of this alkylation is more reactive than benzene, so polyalkylation can occur. Moreover, carbocation rearrangement can occur. Thus primary alkyl chlorides typically give secondary alkylbenzenes as the major product. The Friedel-Crafts alkylation is not a suitable way to make primary alkyl-substituted benzene derivatives.

Another alkylation with heterogeneous catalysts is alkylation between benzene and ethylene on a zeolite catalyst. Ethylene is protonated at a Bronsted acid site on the catalyst surface forming an ethylcarbonium ion.



The carbocation then attacks the benzene ring giving ethylbenzene and the proton is regained by zeolite (Figure 2.6).



**Figure 2.6** The carbocation attacks the benzene ring (Matar *et al.*, 1989).

Matar *et al.*, (1989) found zeolites were more suitable alkylation catalysts than the amorphous types because of their activities and selectivity toward certain reactions.

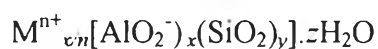
Ganti *et al.*, (1994) studied benzene alkylation with ethanol over HZSM-5 catalysts with Si/Al ratio from 30 to 280. This experiment studied in the temperature range of 548-648 K at atmospheric pressure over HZSM-5 at W/F values between 30 and 80 gcat/gmol/hr at benzene/ethanol ratio of 3/1 to 6/1. The activity and selectivity of the catalyst showed maximum conversion at a particular silica/alumina ratio of the HZSM-5 catalyst. Both ethylbenzene and diethylbenzene selectivities were found to decrease with increasing temperature. At higher benzene/ethanol molar ratios, the selectivity towards ethylbenzene decreased.

### 2.3 Zeolite

More than 200 years ago, in 1756 Baron Axel F. Cronstedt Swedish mineralogist discovered the first zeolite mineral, stilbite. He recognized zeolites as a new class of minerals consisting of hydrated aluminosilicates of the alkali and alkaline earths. Because the crystals exhibited intumescence when heated in a blowpipe flame, Cronstedt called the mineral a "zeolite". The name zeolite signifies boiling stone; the meaning is derived from the Greek word "zein" and "lithos" meaning "to boil" and "rock" respectively. Many new types of natural minerals have been discovered and a large number of synthetic zeolites have been developed for specifically commercial purposes. The synthetic zeolite was interested in application of shape selective zeolite catalyst in the petrochemical companies such as Union Carbide and Mobil. Union Carbide companies discovered a number of great economic significance zeolite, type A, X and Y during the 1950s and early 1960s by Milton and Breck of the Linde division of the company. In 1967-1969 Mobil Oil reported the synthesis of the high silica zeolites beta and ZSM-5. In 1974 Henkel introduced zeolite A in detergents as a replacement for the environmentally suspect phosphates. By 1977 industry-wide 22,000 tons of zeolite Y was in use in catalyst cracking. In 1977 Union Carbide introduced zeolite for ion-exchange separations.

Generally, Zeolites are crystalline, micro-porous, hydrated alum-silicate minerals that contain alkali and alkaline earth metals. The regular framework formed by  $\text{SiO}_4$  and  $\text{AlO}_4^-$  or other  $\text{TO}_4$  tetrahedral. These tetrahedral are linked together by corner sharing of Si or Al atoms in various ways, form several different secondary building units (SBU). A SBU consists of selected geometric groupings of those tetrahedral, which can be used to describe all of known zeolite structures. The various types of zeolites are built up from different composition and framework to generate different pores and channels which demonstrate the ability to prevent or allow the program of a reaction (Figure 2.7).

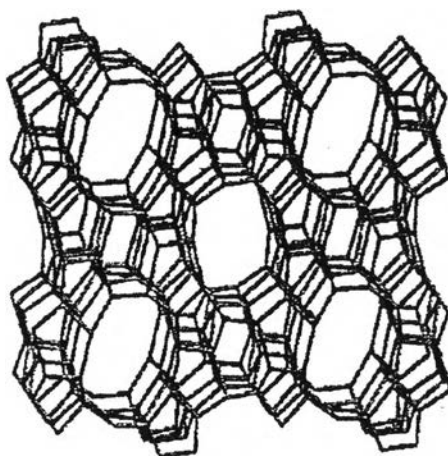
A general formula for the composition of a zeolite is:



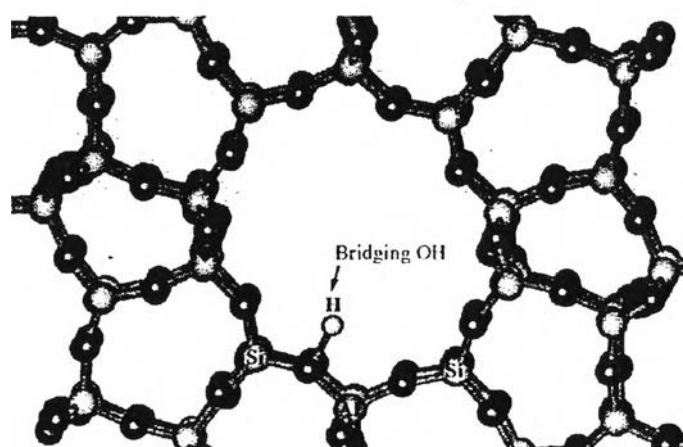
where M represent the exchangeable cation of valence n;  $y/x$  represent the Si/Al molar ratio, and is equal to or greater than 1 because  $\text{Al}^{3+}$  does not occupy adjacent tetrahedral sites, otherwise the negatively charged units next to each other will be obtained; and z represent the number of water molecules located in the channels and cavities inside a zeolite.

Exceptions of type of zeolites, the active site region also shows the dramatic effect in the properties of zeolites. The difference of oxidation state of  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  in zeolites is the crucial reason for the active site occurring. The charges imbalance occurs when the  $\text{Si}^{3+}$  substituted by  $\text{Al}^{4+}$ , and to maintain the system natural, each  $[\text{AlO}_4]^{5-}$  tetrahedral center needs a balancing positive charge such as proton or monovalence cation (Figure 2.8). These composition specific active sites of zeolite in various applications. If the charge compensating cation is  $\text{H}^+$ , a bridged hydroxyl group,  $(\text{Si}-\text{O}(\text{H})-\text{Al})$ , is formed, which function as a strong Bronsted acid site. Due to these acid sites, zeolites are solid acids and are used as catalysts. The catalytic activity of zeolites is often related to strength of the acid sites, which depends on chemical composition and topology of zeolite frameworks. These are numerous naturally occurring and synthetic zeolite. However, most zeolites used commercially are produced synthetically, each with a unique structure. Zeolites have void and space (cavities or channels) that can host cations, water or other molecules.

In the petrochemical industry, Zeolites are widely used as catalysts for a variety of reactions and separation processes, for example, in fluid catalytic cracking hydrocracking and alkylation. Zeolites confine molecules in small spaces, which causes changes in their structure and reactivity. The hydrogen form of zeolites is powerful solid-state acids, and can facilitate a host of acid-catalyzed reactions, such as isomerisation, alkylation, and cracking.



**Figure 2.7** ZSM-5zeolite pores and channels (Saenharn, 2007).



**Figure 2.8** Active sites of zeolite structure (Saenharn,2007).

### 2.3.1 Shape and Size Selectivity

In 1960 the world of catalysis obtained a new perspective. Weisz and Frillette have found unexpected intrinsic catalytic activity on synthetic zeolite. They can demonstrate molecular shape selectivity catalysis with large pore faujasite zeolites. The shape selectivity has three principle types shown as in Figure 2.9.

First, reactant shape selectivity results from the limited diffusion of some of reactants, which cannot effectively enter and diffuse inside the crystal. And the second, product selectivity occurs when only certain products that are of the proper size and shape are able to diffuse out of the channels. And the last, transition state selectivity occurs when the corresponding transition state of a certain reaction requires more space than available in the framework of the zeolite.

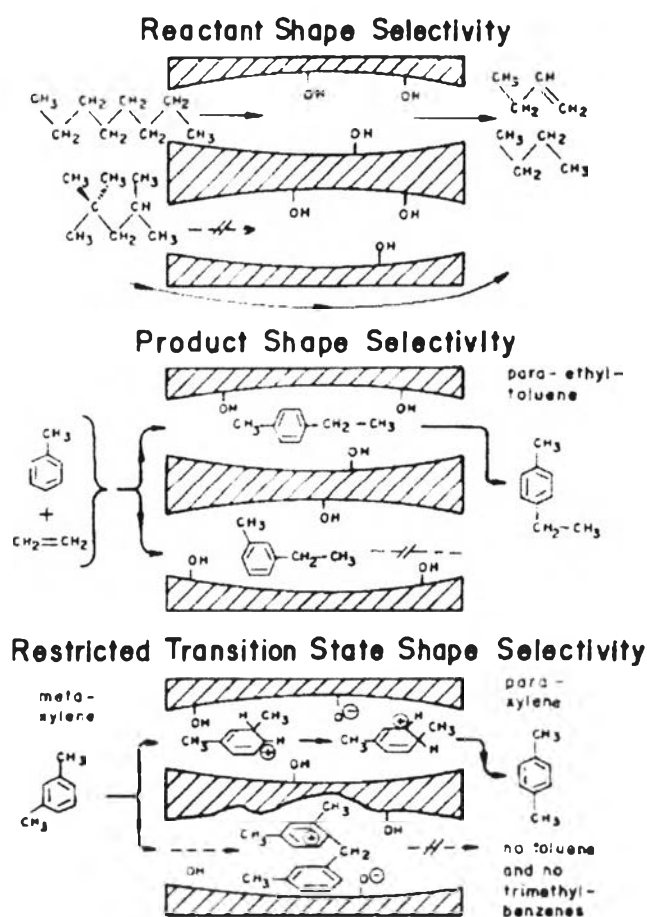


Figure 2.9 The three types of shape selectivity (Wallau, 1995).



The critical diameter (as opposed to the length) of the molecules is important in predicting shape selectivity. However, molecules are deformable and can pass through smaller opening than their critical diameter. Hence not only size but also the dynamics and structure of the molecule must be taken into account.

Matar *et al.* (1989) said that some zeolites are highly selective catalysts, and this has been correlated with the ability of the molecules to diffuse into, and the ability of the product molecules to diffuse out of the supercage, where is the locus of the catalytic activity of zeolite catalysts.

Raj *et al.* (2006) studied shape-selective reactions of alkylation of benzene, toluene and ethylbenzene with ethanol, 2-propanol, methanol and t-butanol over MnAPO-5 and MnAPO-11. The vapour phase alkylation reactions show that if carbon chain and bulkiness of the alkylating agents increase lead to rapid deactivation of the catalyst. At higher temperatures (350 and 400 °C) the catalyst was very active, while at the same time deactivation was also faster. And the liquid phase t-butylation of ethylbenzene and dodecylation of benzene at 200 °C showed good conversion and greater para and 2-phenylalkane selectivity. The catalyst also showed extended life. All these studies suggest that MnAPO-5 is a good catalyst for short chain and long chain alkylation.

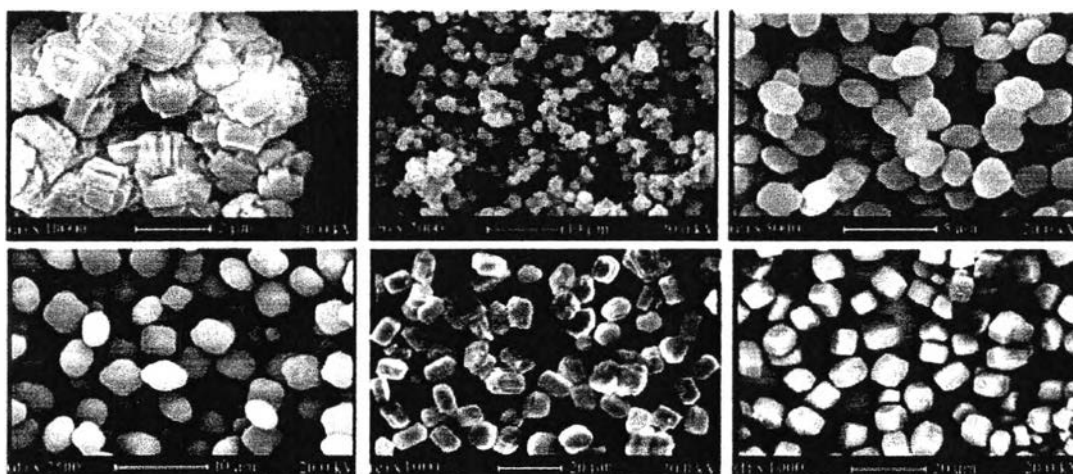
Sugi *et al.* (2006) studied shape-selective alkylation and related reaction of monocyclic aromatic hydrocarbon over  $\text{La}_2\text{O}_3$  and  $\text{CeO}_2$  modification of HZSM-5 zeolites. In the ethylation of ethylbenzene (EB), the  $\text{La}_2\text{O}_3$  modification enhanced the selectivities of p-DEB more effectively than the  $\text{CeO}_2$  modification. The improvement of the selectivities over these oxides is due to the prevention of the isomerization of p-DEB at external acid sites. The para-selectivity for  $\text{La}_2\text{O}_3$ -modified H-ZSM-5 zeolites is improved due to “product selectivity” resulting from the preferential diffusion of p-DEB by the adjustment of pore entrance as well as by the deactivation of external acid sites.

### 2.3.2 Si/Al Ratio

The Si/Al ratio is an important parameter for the application of zeolites. It is responsible for their thermal and hydrothermal stability and also for their acidity (Lechert, 2000). The Si/Al ratio refers to the change of the number of

neighboring Al atom around the bridging Hydroxyl group. If the number of neighboring Al atom around the bridging Hydroxyl group increases, the Si/Al ratio will be decrease.

Shirazi *et al.* (2008) studied the effect of Si/Al ratio of ZSM-5 zeolite on its morphology, acidity and crystal size of the synthesis ZSM-5 with different Si/Al molar ratios from 10 to 50. They found that by increasing the aluminum content of the sample, crystal size was decreased. The crystal sizes were in the range from 1 to 10  $\mu\text{m}$ . According to XRD results the intensities of the peaks increase slightly with Si/Al ratios from 10 to 50, indicating that the formation of the ZSM-5 zeolite can form easier as the Si/Al ratios increase in the gel. The scanning electron micrographs (Figure 2.17) show convincingly that the size and morphology of the crystals depended on the Si/Al molar ratio used. SEM images of the samples showed that, the morphology of the synthesized zeolites was of cubical, hexagonal and ellipsoidal in shape. In case with Si/Al molar ratio of 10, highly intergrowth and twinning with highly aggregation had occurred. The surface areas also increased with increasing Si/Al molar ratio of the samples.  $\text{NH}_3$ -TPD results showed that different Si/Al molar ratios affect the acidity of the samples and the total acid sites of ZSM-5 decreased with increasing the Si/Al molar ratio.



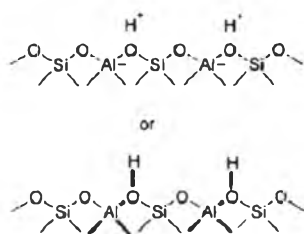
**Figure 2.10** Scanning electron micrographs of the as-synthesized zeolites with different molar ratios of Si/Al (a) 10, (b) 20, (c) 25, (d) 30, (e) 40 and (f) 50 (Shirazi *et al.*, 2008).

Li *et al.* (2009) studied the synthesis of ethylbenzene by alkylation of benzene with diethyl oxalate (DEO) over HZSM-5. This study shows that the alkylation of benzene with DEO over HZSM-5 is a convenient route for the synthesis of EB. The catalysts that have highest benzene conversion and EB selectivity is HZSM-5 with Si/Al ratio of 200 because of the proper strength of acidity. Side reactions, such as EB cracking and DEB isomerization, can be suppressed with decreases in the strength and number of acidic sites.

### 2.3.3 Acid Sites (Acidity)

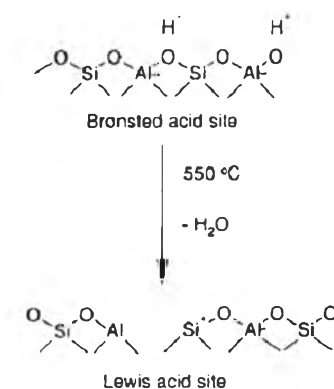
Acidity is one of the most important characteristics of zeolites which make them very useful in acid catalysis. The catalytic properties, such as activity and selectivity, depend not only on the number of the acid sites but also on their specific activities (Costa *et al.*, 2000).

Acid site in zeolite can be divided into Bronsted and Lewis acid sites. In catalysis, the definitions of Bronsted and Lewis acid sites is the site of catalyst that can donate proton ( $H^+$ ) and the site of catalyst that can accept electron pair respectively. The formation of Bronsted acid sites arising from the creation of “bridging hydroxyl groups” within the pore structure of the zeolites. These “bridging hydroxyl groups” are usually formed either by ammonium or polyvalent cation exchange followed by a calcinations step. The “bridging hydroxyl groups”, which are protons associated with negatively charged framework oxygens linked into alumina tetrahedral, are the Bronsted acid sites, as shown in Figure 2.10.



**Figure 2.11** Bronsted acid sites (“bridging hydroxyl groups”) in zeolites (Stocker, 2005).

The protons are quite mobile at higher temperatures, and at 550°C they are lost as water molecules followed by the formation of Lewis acid sites, as shown in Figure 2.11. For zeolites, it can be stated that the concentration of aluminum in the lattice is directly proportional to the concentration of acid sites (Stocker, 2005).



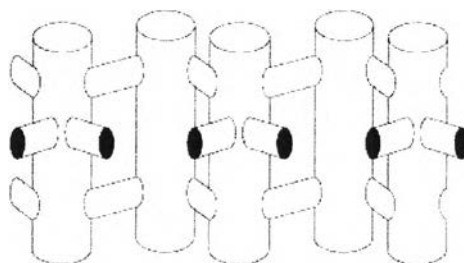
**Figure 2.12** Formation of Lewis acid sites in zeolites (Stocker, 2005).

Raimondo *et al.* (1997) studied the influence of the acidity and the pore dimension of a range of mid-pore zeolites using HZSM-5, mordenite, USY, Theta-1, BP-PILC and ATOS on the yield and selectivity of the products of benzene alkylation using methanol, ethanol, ethene, isopropanol and octanol as alkylating agents. They stated that the catalytic reactivity and selectivity of a solid acid depends not only on the physicochemical properties of the active sites but also on the dimensions and shape of the pores. From the experiments, the pore dimension plays an important role than acidity. Thus, HZSM-5 shows the higher activity because its small pore size allows formation of a bulky intermediate which would result from the electrophilic attack of this charged species at the benzene ring.

#### 2.3.4 ZSM-5 Zeolite

Zeolite Sieve of Molecular porosity or Zeolite Socony Mobil – 5 which has structure type MFI (mordenite framework inverted) is currently of more interest industrially. It is the second most used zeolite catalyst after zeolite Y. There

are more than 50 processes that use zeolite ZSM-5 as one of the main components of the catalysts. (Tanabe *et al.*, 1999) The chemical formula of ZSM-5 developed by Mobil oil is  $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192}\cdot 16\text{H}_2\text{O}$  ( $0 < n < 27$ ). The structure that rings consisting of five oxygen atom called pentasil. ZSM-5 is composed of several pentasil units linked together by oxygen bridges to form pentasil chains. The pentasil chains are interconnected by oxygen bridges to form 10-membered oxygen ring. These are importance because they provide openings in the structure large enough for passage of even rather large molecules (Gates, 1992). ZSM-5 is a highly porous material and throughout its structure it has an intersecting two-dimensional pore structure. The pore structure is shown in Figure 2.13. There is a set of straight, parallel pores intersected by a set of perpendicular zigzag pore (Gates, 1992).

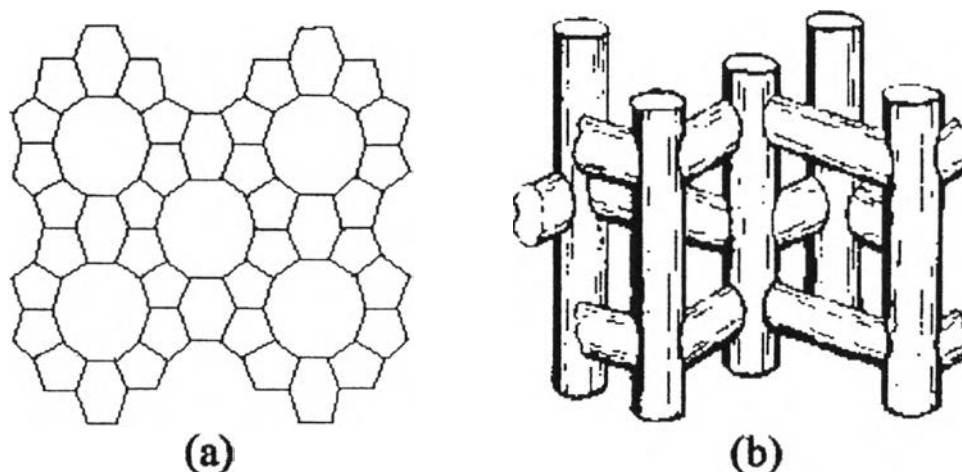


**Figure 2.13** The pore structure of ZSM-5 (<http://chemelab.ucsd.edu/methanol/memos/ZSM-5.html>).

The aluminium sites in ZSM-5 are very acidic. The substitution of  $\text{Al}_3^+$  in the place of the tetrahedral  $\text{Si}_4^+$  silica requires the addition of positive charge. When  $\text{H}^+$  is the positive charge, the acidity of the zeolite is very high. The reaction and catalysis chemistry of the ZSM-5 is due to this acidity. It is a shape-selective catalyst with remarkable catalytic properties and high thermal stability. The ZSM-5 zeolite catalyst is widely used in the petroleum and petrochemical industry for hydrocarbon isomerization and alkylation of hydrocarbon.

ZSM-5, which is compensated negative charge by  $\text{H}^+$ . The dimensions of the pore and channels are of the order of nanometer ( $1 \text{ nm} = 10\text{\AA}$ ). In some cases, the channel of the internal surface form intersections that are considerably larger than their channels. For example, the diameter of the roughly cylindrical pores and

channel of zeolites having the MFI topology as ZSM-5 are about  $5 \text{ \AA}$  (figure 2.14), but the diameter of roughly spherical intersection is about  $9 \text{ \AA}$  which act as nanoscopic catalytic reactors. ZSM-5 has two types of channel, both formed by 10-membered oxygen rings. The first of these channel is straight channel and elliptical in cross section ( $5.1 \times 5.5 \text{ \AA}$ ), the second pore is zigzag or sinusoidal channels and are circular ( $5.4 \times 5.6 \text{ \AA}$ ) in cross section. The intersection of both channels is called intersection channel.



**Figure 2.14** The structure of ZSM-5 showing two different channel structures: (a) framework, (b) channel system (the straight channel and the zigzag channels) (Saenham, 2007).

Yuan *et al.*, (2004) studied alkylation of benzene with ethanol over ZSM-5 catalyst with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios from 34 to 331 including modified ZSM-5 by Boron and magnesium. The experiment have been done at the different reaction temperatures using different catalysts in the reactor to study the change of activity and selectivity of the desires product. The results show that ethylbenzene is the primary product. The highest activity for ethylbenzene formation is ZSM-5 with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios around 100. B- and Mg- modidified enhance selectivity of ethylbenzene.

Li *et al.* (2009) studied the catalytic synthesis of ethylbenzene by alkylation of benzene with diethyl carbonate (DEC) over HZSM-5 with Si/Al ratio from 50 to 250. The results showed the alkylation of benzene with DEC over HZSM-5 is a convenient route for the synthesis of EB. In this experiment, HZSM-5 with a Si/Al ratio of 200 is the highest benzene conversion and EB selectivity due to its optimal acid strength. Strongly acidic sites may lead to excessive decomposition of DEC. Catalyst activity increases significantly as the temperature is increased from 613 to 653 K and the highest benzene conversion was obtained at 653 K. With increase in feed ratio (benzene:DEC) and WHSV the selectivity for EB can be improved.

Sun *et al.* (2009) studied ethylation of coking benzene over nanoscale HZSM-5 zeolite including hydrothermal treatment, calcinations and La<sub>2</sub>O<sub>3</sub> modification on the performance of nanoscale HZSM-5 zeolite. As a result, these post-treatments reduce of the total acidity and B/L ratio due to dealumination and transformation of framework Al, and change pore structure from the single micropores to coexistence of micropores and mesopores. The decrease in the acidity, especial the Bronsted site, suppress the carbon deposit formation resulting in the improvement of catalytic stability. The result showed that La-C-HT-HZSM-5 exhibited higher stability in the ethylation of coking benzene under industrial reaction conditions with the coking benzene conversion of 14.5% and the total ethylbenzene selectivity of 98.8%.

Odedairo *et al.* (2010) studied the effect of zeolite acidity and structure in benzene ethylation reaction with ethanol over the ZSM-5, TNU-9, mordenite and SSZ-33 catalyst. SSZ-33 catalyst gave the highest benzene conversion, which the result of high acidity of this zeolite and large pores. The benzene conversion follows the order: SSZ-33>TNU-9>ZSM-5>mordenite. On the other hand, EB selectivity follows the order: ZSM-5>TNU-9>SSZ-33>mordenite.

Odedairo *et al.* (2010) also studied the kinetic analysis of benzene ethylation over ZSM-5 based catalyst in a fluidized-bed reactor. Benzene conversion, ethylbenzene yield and diethylbenzene yield were found to increase with reaction temperature and time for the different temperatures. If the effect of feed ratio (B/E) increases, the selectivity for EB can be increase too.

## 2.4 Zeolite Synthesis

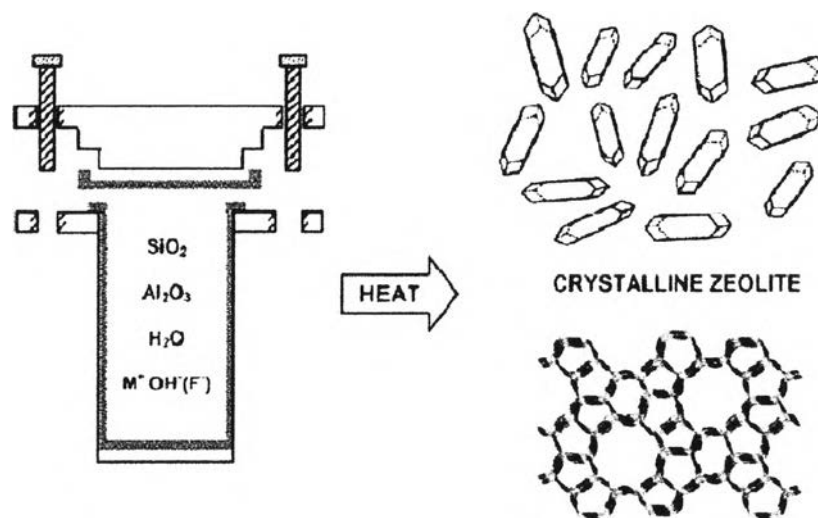
In 1958 several literatures report by under Milton's leadership, the Linde Division of Union Carbide has successfully synthesized nearly all the important commercial zeolite (Milton,1989; Rabo and Schoonover, 2001; Cundy et al., 2003). From Cundy and Cox (2005), a summary of principal proposal for zeolite synthesis mechanism since 1959 to 2004 is listed in Table 2.1.

**Table 2.1** Summary of principal proposals for zeolite synthesis mechanism, 1959-2004 (Cundy and Cox, 2005)

Author(s)	Principle system studied	Main feature of mechanism
Barrer	Various low-silica phase	Condensation polymerization of polygonal and polyhedral anions
Flanigen and Breck	Na-A, Na-X	Linkage of polyhedra (formed by $M^+$ -assisted arrangement of anions): crystal growth mainly in the solid phase
Kerr	Na-A	Crystal growth from solution species
Zhdanov	Na-A, Na-X	Solid $\leftrightarrow$ liquid solubility equilibrium, nuclei from condensation reactions, crystal growth from solution
Derouane, Detremmerie, Gabelica and Blom	Na, TPA-ZSM-5	Synthesis "A": liquid phase ion transportation. Synthesis "B": solid hydrogel phase transformation
Chang and Bell	Na, TPA-Si-ZSM-5	Embryonic clathrate TPA-silicate units, ordered into nuclei through $OH^-$ -mediated Si-O-Si cleavage/recombination
Burkett and Davis	TPA-Si-ZSM-5	Pre-organised inorganic-organic composites, nucleation through aggregation, crystal growth layer-by-layer
Leuven Group	TPA-Si-ZSM-5	Oligomers $\rightarrow$ precursor "trimer"(33 Si) $\rightarrow$ $\times 12 \rightarrow$ "nanoslabs", growth by aggregation



Synthetic zeolites are typically synthesized under hydrothermal conditions with reagents being a silica source, an alumina source, a mineralizing agent such as  $\text{OH}^-$  or  $\text{F}^-$ , and organic molecule as structure directing agents (SDA) at high temperature and pressures. Sources of silicon and aluminum are dissolved or suspended in water along with a structure directing agent and an alkali hydroxide is added as a mineralizer to catalyze the breaking and formation of T-O-T bonds. The homogenized zeolite gel is transferred to an autoclave as presented in Figure 2.15. The gel is heated and the zeolite crystallizes from the amorphous substrates typically within days.



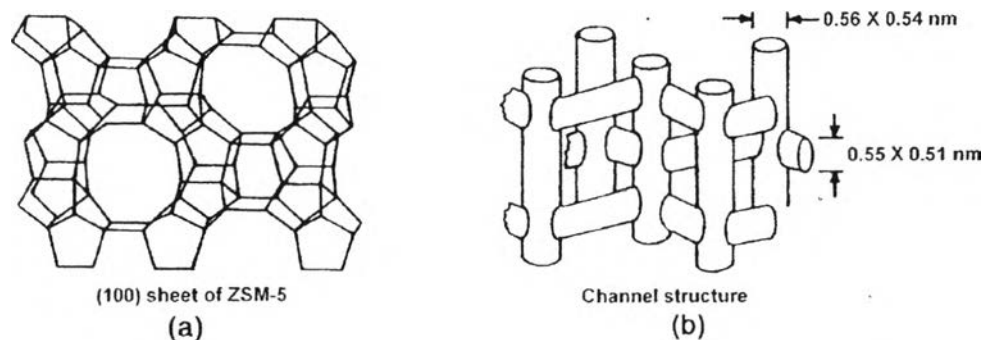
**Figure 2.15** Schematic presentation of hydrothermal zeolite synthesis (Cundy and Cox, 2005).

The final product depends on a complex interplay between many variables including  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the starting medium, nucleating agents, temperature, pH, water content, aging, stirring, and the presence of inorganic and organic cation. These parameters have an influence on the resulting zeolite crystallization. One way to think about zeolite crystallization is to view it as a process with multiple pathways. Pathways for a specific framework may be intervened with another path that leads to a different zeolite framework. Thus, minor perturbations can lead to “lane switching” and formation of unanticipated crystal topologies. Such path

overlap and multiple pathways make it difficult to carry out designed zeolite synthesis routes. Most of the advances have come in this field from trial-and-error discoveries, and development of important empirical information has been the basis of further development. In order to investigate whether or not the expected zeolite is really obtained, XRD need to be confirmed on the obtained sample, and its then compared with that of the reference ([www.iza-structure.org/databases](http://www.iza-structure.org/databases)).

Focusing on a single framework, MFI, and examining the literature related to its crystallization, has been taken. Arguably, this framework is the most studied of all zeolites, and examining its growth from difference perspectives provide a comprehensive picture of zeolite crystallization. Obviously, some of the specific details are peculiar to MFI-type frameworks and not readily extendable to other systems. Yet the conclusions that can be drawn from the data should be more generally applicable.

The crystallization of ZSM-5 was first reported in 1978 (Liu *et al.*, 1999). ZSM-5 typically crystallizes in the Para orthorhombic space group with lattice constants  $a = 20.1\text{Å}$ ,  $b = 19.9\text{Å}$ , and  $c = 13.4\text{Å}$ . The framework density of Si+Al atoms is 17.9 per  $1000\text{Å}^3$ . Figure 2.16 (a) shows the skeletal diagram of (100) face of ZSM-5, where the 10-membered ring apertures are the entrances to the sinusoidal channels. Figure 2.10 (b) shows the channel running parallel to (010) with 10-ring openings of  $5.4 \times 5.6\text{Å}$ , and sinusoidal channel parallel to the (100) axis with 10-ring openings of dimension  $5.1 \times 5.5\text{Å}$  (Seidal *et al.*, 1999; Smith, 1998). The O-T-O bond angles vary between  $105^\circ$  and  $113^\circ$  with an average value of  $109 \pm 2^\circ$ . Among the T-O-T angles, two almost linear bonds are observed at  $176.2^\circ$  and  $178^\circ$  (Davison, 1999). The tetrapropylammonium ion (TPA), typically used for synthesizing the MFI framework, is located in the intersection of the two channels, with a conformation different from that in TPABr (Colella, 1996).



**Figure 2.16** (a) Skeletal diagram of the (100) face of ZSM-5, (b) Channel structure of ZSM-5 (Scott *et al.*, 2003).

The completely siliceous form of ZSM-5, silicalite, exhibits hydrophobicity and can extract organic molecules from water streams. The defect hydroxyl groups in silicalite cause residual hydrophilicity, which can be completely absent in fluoride-silicalite, and exhibits extreme hydrophobic behavior, adsorbing < 1 wt% water at 20 Torr at 25 °C. These crystals of density 1.7 g/ml will float on water (Haidouti C., 1997; Ricke *et al.*, 1995).

In the previous work, the researchers examine how reactant composition influences crystallization, with particular focus on the role of inorganic and organic cations as well as organic molecules, and discussed about the role of physical conditions, such as temperature and crystallization in the presence of seeds. Synthesis in the presence of fluoride ions and organic solvents in contrasted with conventional hydrothermal synthesis. This section demonstrates that for ZSM-5 synthesis, inorganic cations define a very narrow composition field, which can be significantly expanded by the use of organic species.

The diversity of the crystals can be synthesized. Besides a wide range of chemical compositions, MFI can be obtained as nanocrystals, single crystals, intergrowths, membranes, and thin films, and morphology of the crystals and how it is influenced by variation of the synthesis parameters.

Udomsin (2010) studied on alkylation of benzene with ethanol to ethylbenzene by using commercial HZSM-5 catalyst. In this research has three type

of commercial HZSM-5 catalysts which have a different in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio (23, 45 and 195). The result shows that HZSM-5 catalyst with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio 195 has the highest ethylbenzene selectivity at the condition of reaction temperature  $300\text{ }^\circ\text{C}$ , B/E feed ratio = 1, and  $\text{WHSV} = 8\text{ h}^{-1}$ .

Duang-udom (2011) studied on alkylation of benzene with ethanol to ethylbenzene by using synthesized HZSM-5 catalyst with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio 195 in different synthesized temperature ( $150\text{ }^\circ\text{C}$  and  $180\text{ }^\circ\text{C}$ ) and time (24, 48 and 72 h). This experiment tested in fixed-bed reactor including different reaction temperature ( $300$  to  $600\text{ }^\circ\text{C}$ ), B/E feed ratio (1 to 4). The alkylation of benzene with ethanol to ethylbenzene by using HZSM-5 catalyst that obtained from synthesized temperature  $150\text{ }^\circ\text{C}$  for 48 h has the highest ethylbenzene selectivity at the optimal condition of reaction temperature  $500\text{ }^\circ\text{C}$  and B/E feed ratio = 4.

Rugwong (2012) studied the effects of textural properties and acidity on ethylation of benzene with ethanol to ethylbenzene by using synthesized HZSM-5 catalyst with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio 195 in different synthesized temperature ( $120\text{ }^\circ\text{C}$  and  $140\text{ }^\circ\text{C}$ ) and time (24, 48 and 72 h). This experiment tested in fixed-bed reactor including different reaction temperature ( $300$  to  $600\text{ }^\circ\text{C}$ ), B/E feed ratio (1 to 4) and weight hourly space velocity ( $10$ - $20\text{ h}^{-1}$ ). The alkylation of benzene with ethanol to ethylbenzene by using HZSM-5 catalyst that obtained from synthesized temperature  $120\text{ }^\circ\text{C}$  for 72 h has the highest ethylbenzene selectivity at the optimal condition of reaction temperature  $500\text{ }^\circ\text{C}$ , B/E feed ratio = 4 and  $\text{WHSV} = 20\text{ h}^{-1}$ .

## 2.5 Hydrothermal Pre-treatment

Hydrothermal treatment has many processes to do it but the mainly hydrothermal treatment is the reaction that streams pass to the catalyst. Hydrothermal treatment can adjust the zeolite acidity since the molecule of water hydrolyzes Al in the structure to the aluminium oxide ( $\text{Al}_n\text{O}_m$ ). Moreover, hydrothermal treatment also enlarges the pore diameter.

Many researchers reported that dealumination of zeolites improved its activity in acid-catalyzed reactions due to the complex effect between Lewis acidity

that resulted from the increased non-framework Al-oxide species and Bronsted acidity after hydrothermal treatment (Sun *et al.*, 2009).

Sobrinho *et al.* (1995) studied the combination of steaming/acid leaching treatments on Zeolite Y with different framework and non-framework aluminum contents. They found that the hydrothermal dealumination produced an enrichment of aluminum at the external surface but the acid leaching removed part of these aluminum species preferentially at the external surface. Then the treatments also led to the appearance of mesopores.

Kumar *et al.* (2000) studied Influence of mild dealumination on physicochemical, acidic and catalytic properties of H-ZSM-5. The results show the activity was maximum for HCl-treated and acetylacetone-treated samples that is attributed to the increase in the overall acidity (both Lewis and Bronsted of samples) as well as to the creation of mesoporosity.

Guo *et al.* (2003) found that hydrothermal treatment following HCl leaching enhances the stability of HZSM-5 zeolites in the methylation of 4-methylbiphenyl with methanol cause dealumination after hydrothermal treatment.

Choudhary *et al.* (2005) studied the influence of hydrothermal pretreatment on acidity and activity of H-GaAlMFI zeolite for the propane aromatization reaction. They vary in different hydrothermal (HT) pretreatments (concentration of steam: 0–80%, HT temperature: 400–600 °C and time of HT pretreatment: 0–6 h) that showed a profound influence on the propane aromatization activity but only the mildly HT pretreatments that affect the product selectivity. The propane aromatization activity appears to be dependent on strong zeolitic acidity as well as content/dispersion of the extra-framework Ga species which are formed in situ during the HT pretreatments.

Song *et al.* (2006) studied the hydrothermal post-synthesis of a commercial HZSM-5 zeolite in  $\text{Al}(\text{NO}_3)_3$  aqueous solution to enhance the coke-resistance of Mo/HZSM-5 catalyst for methane dehydroaromatization reaction. As a result, the Mo/HZSM-5 catalyst showed rather high methane conversion and selectivity of aromatics by effectively inhibiting the formation of coke during the methane dehydroaromatization reaction.

Li *et al.* (2009) studied for synthesis of ethylbenzene by alkylation of benzene with diethyl carbonate over parent MCM-22 and hydrothermal-treated

MCM-22. And Sun *et al.* (2009) studied some post-treatment effects, including hydrothermal treatment, calcination and  $\text{La}_2\text{O}_3$  modification, on the catalytic performance of a nanoscale HZSM-5 zeolite for ethylation of coking benzene with ethylene and ethanol. Both studies indicated these post-treatments of the catalyst can reduce both the total number of acid sites and the Bronsted/Lewis ratio due to dealumination and transformation of framework Al, and change pore structure from the single micropores to the coexistence of micropores and large micropores. The decrease in the acidity, especial the Bronsted acidity, suppressed the carbon deposit formation resulting in the improvement of catalytic stability.

## 2.6 Aromatization

Aromatization is the reaction that converts a nonaromatic hydrocarbon structure to aromatic hydrocarbon. The aromatization of petroleum products is conducted according to the reactions discovered by Soviet chemists in 1936. The direct conversion of alkanes into aromatics is an important process for industry, and thus extensive research on this reaction has been performed. The results obtained on various catalysts and the possible mechanisms of complex processes are well documented in several excellent reviews (Berthos *et al.*, 2007).

Aromatization of light hydrocarbons into aromatics over zeolite catalysts, in particular on middle-porous ZSM-5 (MFI) has attracted much attention in the past decades. Because of the properties that make ZSM-5 critical for industrial applications are its high thermal and acid stability, high selectivity, high activity and coke resistance in many catalytic conversions (Asaftei *et al.*, 2009).

Choudhary and Nayak (1984) studied the conversion of methanol and ethanol to aromatics on HZSM-5 and found that it was dependent on the Si/Al ratio and degree of H-exchange of the zeolite. As a result, the conversion decrease with Si/Al ratio and increase with degree of H-exchange of the zeolite. They suggested that the strong acid sites be required for the aromatization and in their absence, the deposition of hydrocarbon residue in the zeolite channels occurred. A good correlation between the acidity (active acid sites) and the aromatization activity of the zeolite was obtained.

Steinberg *et al.* (2001) studied aromatization of ethane on platinum containing ZSM-5 zeolites. They found ethane convert to aromatics on Pt/H-ZSM-5 starts at 670 K and alkylaromatics that formed among the reaction at low temperature convert to benzene and C<sub>8</sub>+ aromatic above 900 K. The composition of the reaction products strongly depends on the temperature and gas space velocity (GHSV).

Barthos *et al.* (2006) studied the decomposition and aromatization of ethanol on pure and promoted ZSM-5 catalysts. The primary reaction of ethanol on pure ZSM-5 is the dehydration reaction yielding ethylene, small amounts of hydrocarbons, and aromatics. Deposition of different additives, such as Mo<sub>2</sub>C, ZnO, and Ga<sub>2</sub>O<sub>3</sub> on zeolite, enhances the aromatization of ethylene to form benzene and toluene at 773-973 K in the dehydration process of ethanol.