# CHAPTER II
LITERATURE REVIEW

2.1 Alkylation of Aromatics

The catalytic alkylation of aromatic hydrocarbon is a substitution reaction wherein one or more of the hydrogen atoms on the ring or side chain is replaced by an alkyl group. Both substituted and unsubstituted aromatic structures may be so call alkylated. In general, the following reaction occurs:

$$R-\langle\ \rangle + R'CH=CHR'' \xrightarrow{\text{catalyst}} R-\langle\ \rangle-\overset{\overset{R'}{|}}{\underset{\underset{CH_2R''}{|}}{CH}}$$
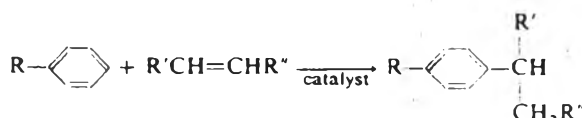
Figure 2.1 Alkylation of aromatic reaction (Mcketta, 1993).

These reactions can occur through electrophilic (acid-catalyzed), nucleophilic (base-catalyzed), or free radical mechanism. The catalyst used dictates the mechanism by which the reactions occur (Mcketta, 1993).
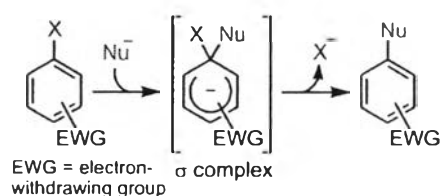
2.1.1 Electrophilic Substitutions

The most common reaction of benzene is electrophilic substitution. The typical benzene reaction has the benzene ring serving as a source of electrons, as nucleophiles. The reaction mechanism is two steps. The first step is the attack of an electrophile, E+, forming a carbocation intermediate with the aromatic ring and simultaneously destroying the aromaticity of the ring. In this structure, the positive charge is 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.
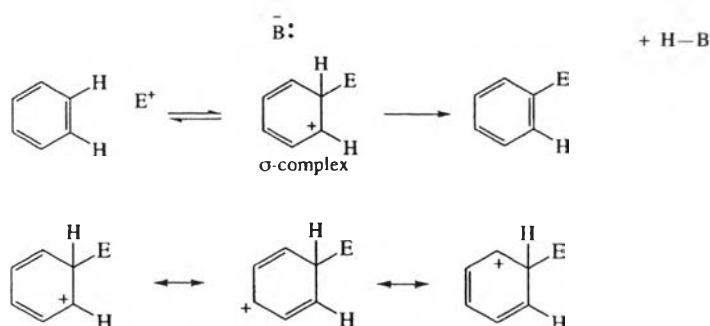
Figure 2.2 The electrophilic aromatic substitution reaction
(http://classes.uleth.ca/200201/chem2600a/notesch12.pdf).

2.1.2 Nucleophilic Substitutions

Benzene usually undergoes substitution by electrophilic attack. However in some cases, nucleophilic attack is possible. The mechanism 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).

2.2 Alkylation Catalysts

In former days such processes have been mainly carried out in the presence of homogeneous Lewis acid catalysts such as $AlCl_3$, $FeCl_3$, and BF_3. The well-known drawbacks of such homogeneously catalyzed processes have to be overcome by

applying heterogeneous catalysis. In this respect, the discovery of the shape selective acidic ZSM-5 zeolite and the development of the Mobil-Badger process for the production of ethylbenzene from benzene and ethylene have been the base for breakthrough technology in the field of aromatic alkylation reactions using solid acid catalysts (Tanabe *et al.*, 1999).

Homogeneous alkylation catalysts may be Brönsted acids such as HF and H_2SO_4. Using alkenes as alkylating agents, a proton is donated by the acid to substrate.

$$H_2C{=}CH{-}CH_3 \xrightleftharpoons{HF} \overset{+}{H_3C{-}CH{-}CH_3} \quad F^-$$
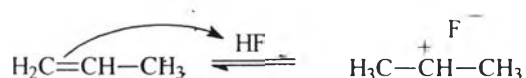
Figure 2.4 The formation of carbocation by using alkenes (Wade, 2009).

When alkenes are treated with a Lewis acid such as $AlCl_3$, a small amount of a proton acid is normally added as a co-catalyst to promote the formation of carbocation.

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

$$ROH + H^+ \leftrightarrow \left[RO^+H_2\right] \leftrightarrow R^+ + H_2O$$
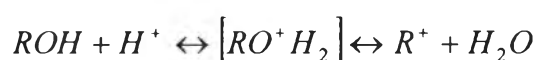
In presence of Lewid acids, such as $AlCl_3$, a complex is first formed with the alcohol and HCl is released. The complex then donates the carbocations.

$$ROH + AlCl_3 \rightarrow ROAlCl_2 + HCl$$

$$ROAlCl_2 \leftrightarrow R^+ + {}^-OAlCl_2$$
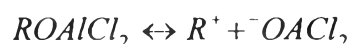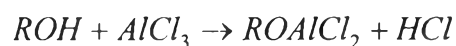
Sridevi *et al.* (2001) studied the alkylation of benzene with ethanol on $AlCl_3$ impregnated 13X zeolite to determine the kinetics of benzene alkylation, to develop a kinetic model, and to estimate the unknown parameters of the kinetic model so as to obtain an intrinsic rate expression. The experiments carried out with different

amounts of AlCl₃ gave maximum benzene conversion with catalyst containing 15% AlCl₃. Moreover, the results indicated no deactivation of AlCl₃ by hydrolysis with water generated by the reaction.

Alkyl halide has been extensively used to alkylate aromatic compounds. When AlCl₃ is used as the catalyst, the reaction is normally referred to as Friedel-Crafts reaction.
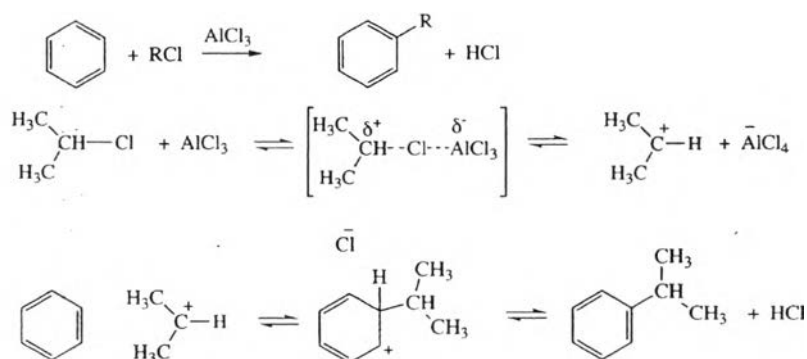
Figure 2.5 The Friedel-Crafts reaction

(http://classes.uleth.ca/200201/chem2600a/notesch12.pdf).

In this mechanism 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).

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.

Alkylation with heterogeneous catalysts has been carried out using a variety of acidic oxides such as Al_2O_3 and Al_2O_3/SiO_2. These catalysts also promote carbonium ion typed reactions. Depended the method of preparation, silica/alumina catalysts may be amorphous or crystalline. These compounds have both Brönsted

and Lewis acid sites. When alkylating benzene with ethylene, on a zeolite catalyst for example, adsorbed ethylene is protonated at a Brönsted acid site on the catalyst surface forming an ethylcarbonium ion.

$$Zeol - O^- H^+ + CH_2 = CH_2 \rightarrow CH_3 - CH_2^+ + Zeol - O^- \qquad (4)$$

The carbocation then attacks the benzene ring giving ethylbenzene and the proton is regained by zeolite.
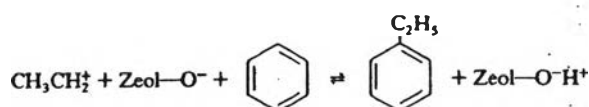
Figure 2.6 The carbocation attacks the benzene ring (Matar *et al.*, 1989).

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

Li *et al.* (2008) are studied catalytic synthesis of ethylbenzene by alkylation of benzene with diethyl carbonate over HZSM-5. As a result, HZSM-5 with a Si/Al ratio of 200 and a temperature of 653 K has the best benzene conversion and EB selectivity due to its optimal acid strength. With increase in feed ratio (benzene:DEC) and WHSV the selectivity for EB can be improved

2.3 Zeolite

Zeolite was discovered in 1756 by the Swedish mineralogist, Boron Axel F. Cronstrdt, as the naturals minerals. The word "Zeolite" is Greek in original, derived from the word "zein" and "lithos" meaning "to boil" and "rock". Many new types of natural minerals have been discovered and a large number of synthetic zeoites have been developed for specifically commercial proposes. The synthetic zeolite was interested in application of shape selective zeoite catalyst in the petrochemical companies such as Union Carbide and Mobil. In the 1950s and early 1960s, Union

Carbide companies made several discoveries which proved to be of great economic significance and propelled them to the forefront of zeolite science. Milton and Breck of the Linde division of the Union Carbide company, over a period of 5 years, developed and characterized three novel zeolites classified as types A, X and Y. which have become 3 of the most profitable synthetic zeoites. In 1969 Grace described the first modification chemistry based on steaming zeolite Y to form an "ultrastable" Y. 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.

2.3.1 Structure of Zeolites

Zeolite are three-dimensional, microporous, crystalline aluminosilicate materials constructed from tetrahedral units, TO_4, such as $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$. Each of tetrahedral centers is connected via oxygen atom formed Si-O-Si and Si-O-Al bridges. These tetrahedral are linked together by corner sharing of Si or Al atoms in various ways, form several different SBU. A secondary building unit 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. A representative unit cell formula for the composition of a zeolite is:

$$M^{n+}_{x/n}[AlO_2^-)_x(SiO_2)_y].zH_2O$$
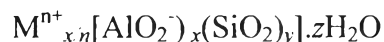
where M is the exchangeable cation of valence n; y/x is the Si/Al molar ratio, and is equal to or greater than 1 because Al^{3+} does not occupy adjacent tetrahedral sites, otherwise the negatively charged units next to each other will be obtained; and z is the number of water molecules located in the channels and cavities inside a zelite.

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 Si^{4+} and Al^{3+}

in zeolites is the crucial reason for the active site occurring. The charges imbalance occurs when the Si^{3+} substituted by Al^{4+}, and to maintain the system natural, each $[AlO_4]^{5-}$ tetrahedral center needs a balancing positive charge such as proton or monovalence cation (Fig. 2.7). These composition specific active sites of zeolite various applications. If the charge compensating cation is H^+, a bridged hydroxyl group,(Si-O(H)-Al), is formed, which function as a strong Brönsted 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 zeolite 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.

Zeolites are widely used industrially as a catalyst for a variety of reactions and separation processes. The active site of zeolite also plays a crucial role in catalyzing the reactions.
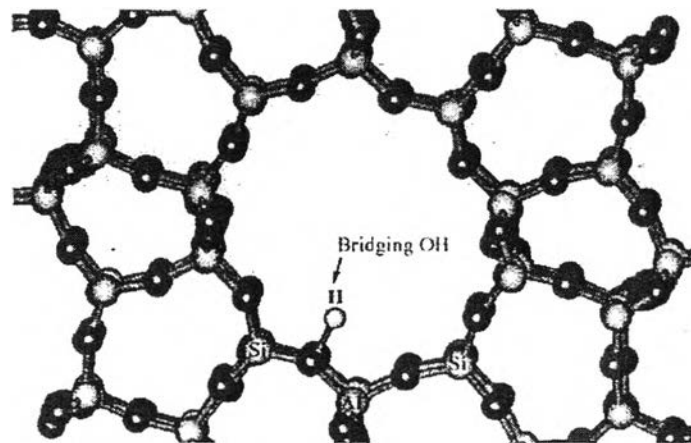
Figure 2.7 Active sites of zeolite structure (Saenharn, 2007).

2.3.2 Properties of Zeolite (Breck, D. W., 1984)

2.3.2.1 Shape and Size Selectivity

Shape and size selectivity are a very important role in catalysis. Highly crystalline and regular channel structures are among the principal features that molecular sieves used as catalysts offer over other materials.

There are three types of shape selectivity: reactant shape seletivity, product shape selectivity, and transition-staye shape seletivity. These types of selectivity are depicted in Fig. 2.8. Reactant shape selectivity results from the limiteddiffusion of some of reactants, which cannot effectively enter and diffuse inside the crystal. Product shape selectivity occurs when slowly diffusing product molecules cannot rapidly escape from the crystal, and undergo secondary reactions. Restricted transition-state shape selectivity is a kinetic effect arising from the local environment is reduced if the necessary transition state is too bulky to form readily.

· 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.

An equivlent to activation energy exists for the diffusion of molecule inside the molecular sieve because the temperature-dependent translation energy of molecule (as move through the force fields in the pores) must increase significantly as the dimensions of the molecular configulation appoach the void dimensions of the crystal. It should be noted that the effective diffusivity varies with molecular type; adsorption affinity affects diffusivity, and rapidly reacting molecules (such as olefins) show diffusion mass transfer limitations inside the structure due to their ectreme reactivity.
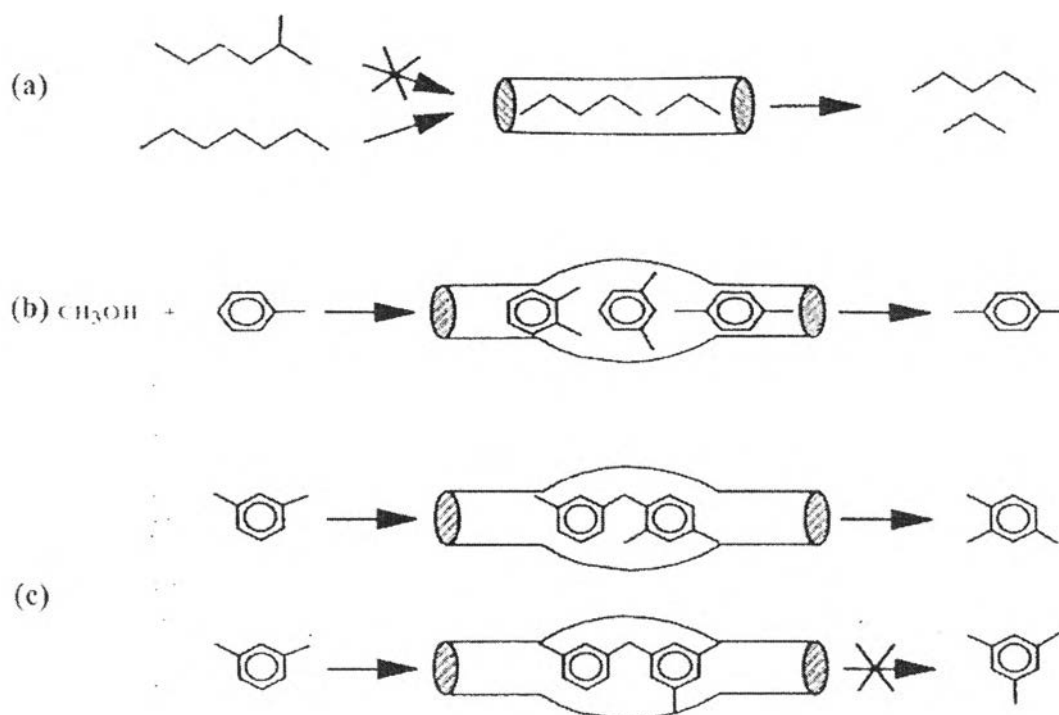
Figure 2.8 Diagram depicting the three types of selectivity: (a) reactant, (b) product and (c) transition state shape selectivity (Saenharn, 2007).

The effective size and relative accessibility of the pore and cavities can be altered by partially blocking the pore and/or by changing the molecular sieve crystal size. The effect of shape selective are especially induced by the above two methods when the diffusivities of these species differ significantly.

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 (Matar *et al.*, 1989).

Romannicov *et al.*, (1994) indicated that ZSM-5, small pore zeolite, promotes the formation mainly of para isomer products while wide-pore beta zeolite contains all three isomer products (para, meta and ortho). The ratios among them depend on the ratios of partial substitution rates.

Raj *et al.* (2005) studied shape-selective reactions with AEL and AFI type molecular sieves alkylation of benzene, toluene and ethylbenzene with

ethanol, 2-propanol, methanol and t-butanol. The vapour and liquid phase alkylation of various reactions are studied over MnAPO-5 and MnAPO-11. The vapour phase alkylation reactions show that increase in carbon chain and bulkiness of the alkylating agents 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.

Raj *et al.* (2006) studied the para selectivity compared to meta and ortho in the vapor and liquid phase alkylation of various reactions over MnAPO-5 and MnAPO-11. They indicated the distribution of the reaction products for para, meta and ortho isomers is strongly influenced by the channel geometry and the transport of individual isomers into channel structure. From the results, the para isomer shows the greatest selectivity. The critical diameter of para isomer is smaller than meta so the para isomer diffuse oot of the pore faster.

2.3.2.2 Acid Sites (acidity)

All of the variation pretreatment conditions as well as synthesis and post-treatments (hydrothermal, thermal and chemical), affect the ultimate acidity an acidity observed in the zeolite molecular sieves. Both Brönsted and Lewis acid sites are exhibited in these materials, with assertions by various investigations that:

1. Brönsted acid sites are the active center.

2. Lewis acid sites are the active center.

3. Brönsted and Lewis acid sites together act as the active centers.

4. Cations or the other types of sites in small concentrations act in the conjunction with the Brönsted/Lewis acid sites to function as the active center.

Strong electric fields in the zeolites arise from the various charge species. This is Brönsted/Lewis acidity model usually employed to describe

the active sites of molecular sieves. Fig. 2.9 depocts a zeolite structure with Brönsted and Lewis acid sites.
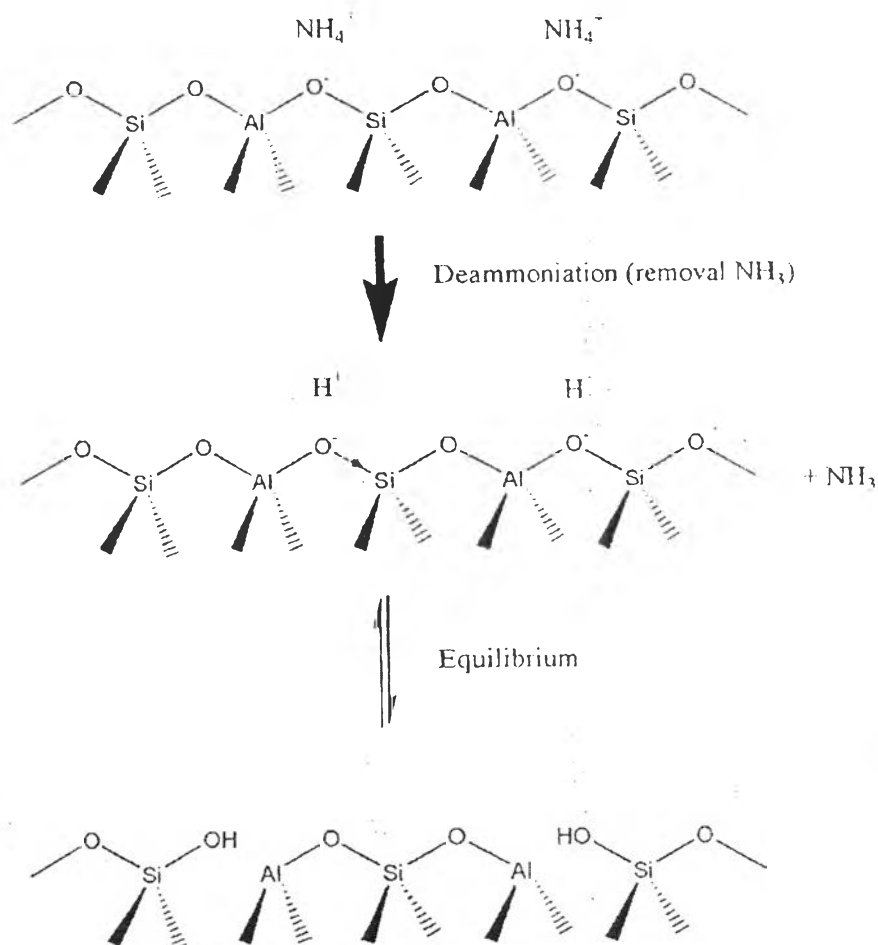
Figure 2.9 Diagram of the "surface" of a zeolite framework (Saenharn, 2007).

The ammonium-from zeolite was converted to the hydrogen-from one by calcinations at elevated temperature. The thermal treatment causes removal of NH_3 from the cation sites and leaves protons as the balancing cations. The aluminum sites with its associated bridged Si-O-H are a classical Brönsted acid. The Brönsted acid site has been proposed to exist in equilibrium with the so call Lewis acid site, the trigonally coordinated aluminum.

Raimondo *et al.* (1997) studied the influence of the acidity and the pore dimension of a range of mid-pore zeolites using H-ZSM-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 akylating 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, H-ZSM-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.

Loveless *et al.* (2008) studied discrepancy between TPD- and FTIR-based measurements of Brönsted and Lewis acidity for sulfated zirconia. They used TPD and FTIR to determine the effect of H2O on the Brönsted and Lewis acidities of two sulfated zirconia (SZ) catalysts. TPD results of all basic probes on SZ-1 showed that water displaces previously adsorbed molecules from weak Lewis sites. DRIFTS experiments agreed generally, but not exclusively, with the traditional interpretation of conversion of Lewis sites to Brönsted sites with hydration.

2.3.3 ZSM-5 (Zeolite Socony Mobil-5)

ZSM-5 (Zeolite Soncony Mobil-5 is discovered by Mobil Oil Company) is a comermcial name of MFI zeolite with high silica to alumina ratio, and H-ZSM-5 is ZSM-5, which is compensated negative charge by H^+. the dimensions of the pore and channels are of the order of nanometer (1 nm = 10 Å). 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, but the diameter of roughly spherical intersection is about 9 Å 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 x 5.5 Å), the second pore is zigzag or sinusoidal channels and are circular (5.4 x 5.6 Å) in cross section. The intersection of both channels is called intersection channel.

Li *et al.* (2009) studied the synthesis of ethylbenzene by alkylation of benzene with diethyl oxalate (DEO) over HZSM-5. As a result, HZSM-5 with a Si/Al ratio of 200 at temperature of 653 K exhibits the highest benzene conversion

and EB selectivity due to the proper strength of acidity. The selectivity for EB was improved obviously with an increase in the feed ratio of benzene to DEO.

Another factor that affects the catalytic activity of zeolites is the type of cations on zeolites. The metal exchange into the HZSM-5 catalysts, using NaZSM-5, CoZSM-5, and CuZSM-5, for the methylation of benzene with methanol was observed by Adebajo et al, (2000). The results showed that the conversion and selectivity to toluene are higher when these catalysts were used at low temperatures (250-350°C).

2.4 Aromatization

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 process are well documented in several excellent reviews (Berthos *et al.*, 2007).

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

Honda *et al.* (2008) studied preparation of highly active binder-added MoO3/HZSM-5 catalyst for the non-oxidative dehydroaromatization of methane. They compare with three different procedures (a) impregnation of MoO3 over a wet mixture of HZSM-5 and a binder SiO2 or Al2O3 followed by calcination, (b) impregnation of MoO3 on HZSM-5 followed by a wet mixture of the resulting sample with one binder and then calcination, and (c) carburization ofMoO3 pre-impregnated on HZSM-5 followed by a wet mixture of the carburized MoO3/HZSM-5 with one binder, respectively. As a result, procedure (c) certainly allows a successful localization of MoO3 on its primary support HZSM-5 and therefore

presents an applicable way of preparing highly active binder-added Mo/HZSM-5 catalysts for the non-oxidative dehydroaromatization of methane.

And Berthos et al.(2007) studied aromatization of methanol and methylation of benzene over Mo2C/ZSM-5 catalysts. They found that the deposition of Mo_2C onZSM-5 markedly enhanced the formation of aromatics. The highest yield of the formation of aromatics was measured for 5% Mo2C/ZSM-5 (SiO2/Al2O3 = 80) at 773 K

2.5 Hydrothermal Pre-treatment

Hydrothermal treatment is often employed to adjust the acidity of zeolites (Triantafillidis et al., 2001) and to improve its stability in many reactions. The effect of hydrothermal treatment on the activity and catalytic stability can be attributed to the change in zeolites' acidity.

Many other 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 nonframe-work Al-oxide species and Brönsted acidity after hydrothermal treatment (Topsoe et al.,1988 ,Datka et al.,1996 , and Kumar et al.,2000).

Guo et al. (2003) also found hydrothermal treatment following HCl leaching improved the stability of HZSM-5 zeolites in the methylation of 4-methylbi-phenyl with methanol, which was ascribed to dealumination after hydrothermal treatment.

Choudhary et al. (2005) studied influence of hydrothermal pretreatment on acidity and activity of H-GaAlMFI zeolite for the propane aromatization reaction. They vary in different hydrothermal (HT) pretreatments. Each of the HT pretreatment parameters showed a profound influence on the propane aromatization activity. The product selectivity was, however, only mildly affected by the HT pretreatments. The following factors were found to be important for high propane aromatization activity (a) strong zeolitic acidity and (b) optimal content/dispersion of the extra-framework Ga species which are formed in situ during the HT pretreatments.

Song *et al.* (2005) found that hydrothermal treatment reduced both strong and weak acid sites of ZSM-5 zeolites, and thus reduced the carbon deposit during olefin aromatization.

Song *et al.* (2006) studied hydrothermal post-synthesis of a commercial HZSM-5 zeolite in $Al(NO_3)_3$ 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 fornation of coke during the methane dehydroaromatization reaction.

Lertjiamratna *et al.* (2009) studied modification of acid properties and catalytic properties of AlPO4 by hydrothermal pretreatment for methanol dehydration to dimethyl ether. As a result, the catalysts pretreated at 200–300°C exhibited higher methanol conversion than the non-treated catalyst while the one treated at a lower temperature of 100°C showed lower activity because there was an increase of lattice hydroxyls on the hydrothermally treated catalysts in the form of P-OH group (weak Brönsted acid sites). However, hydrothermal pretreatment at 100°Cmay result in catalyst poisoning by weakly bonded water molecules instead so that lower catalyst activity was obtained.

Sun *et al.* (2009) studied some post-treatment effects, including hydrothermal treatment, calcination and La_2O_3 modification, on the catalytic performance of a nanoscale HZSM-5 zeolite for ethylation of coking benzene with ethylene and ethanol. This study indicate these post-treatments of the catalyst can reduce both the total number of acid sites and the Brönsted/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 Brönsted acidity, suppressed the carbon deposit formation result in the improvement of catalytic stability. The results 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%.

2.5 Zeolite Synthesis

Zeolite synthesis occurs by a hydrothermal process with reagents being a silica source, an alumina source, a mineralizing agent such as OH⁻ or F⁻ , and organic molecule as structure-directing agents. A schematic of zeolite growth process is shown in Fig. 2.10. The complexity of the process makes the synthesis susceptible to physical effects such as stirring, aging, and order of reagent addition (Flanigen, 1980). Several independent processes are occurring in the medium crystallization as well as dissolution of metastable phase. It is commonly observed that the conversion of the composition to crystals is rapid as the crystallization process gets started. This suggests that nucleation is the rate-limiting step and is consistent with studies reporting that the addition of seed crystals decreases the induction time (Flanigen, 1980). At least four subsystems can be considered. First is the formation of simple polymeric aluminosilicates. Second is the aggregation of these complexes to from embryo. Third is the nucleation as aggregate formation with a well ordered core and micelle formation (primary particles). And forth is the aggregation of primary particle via oriented aggregation (Mumpton, 1999). Flanigen has elaborated on these concepts further (Li *et al.*, 1998).
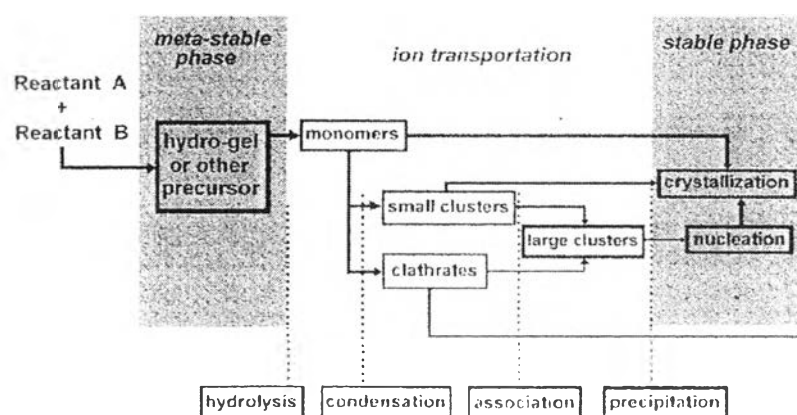
Figure 2.10 A schematic representation of zeolite crystallization process (Barrer, 1978).

Starting with the physical form of the reactants and their precise chemical composition to the synthesis condition, each of these parameters can have a profound 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 intertwined 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.

Considering that there are more than 100 frameworks, each with multiple synthetic procedures, it is important to ask what the optimal way to learn about zeolite synthesis is. Several possible options exist, for example: cataloging all the possible recipes for formation of different zeolites, defining composition fields of different zeolites, contrasting growth patterns of different zeolites, and examining a single zeolite synthesis from different perspectives.

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 (Scott *et al.*, 2003). ZSM-5 typically crystallizes in the Pnma orthorhombic space group with lattice constants $a = 20.1$, $b = 19.9$, and $c = 13.4$ Å. the framework density of Si+Al atoms is 17.9 per 1000 Å^3. Fig. 2.11(a) shows the skeletal diagram of (100) face of ZSM-5 face ZSM-5, where the 10-membered ring apertures are the entrances to the sinusoidal channels. Fig. 2.11(b) shows the channel running parallel to (010) with 10-ring openings of 5.4 x 5.6 Å, and sinusoidal channel parallel to the (100) axis with 10-ring openings of dimension 5.1 x 5.5 Å (Scott *et al.*, 2003). The O-T-O bond angles vary between 105° and 113° with an average value of 109 ± 2°. among the T-

O-T angles, two almost linear bonds are observed at 176.2° and 178° (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).

(100) sheet of ZSM-5
(a)

Channel structure
(b)

0.56 X 0.54 nm

0.55 X 0.51 nm
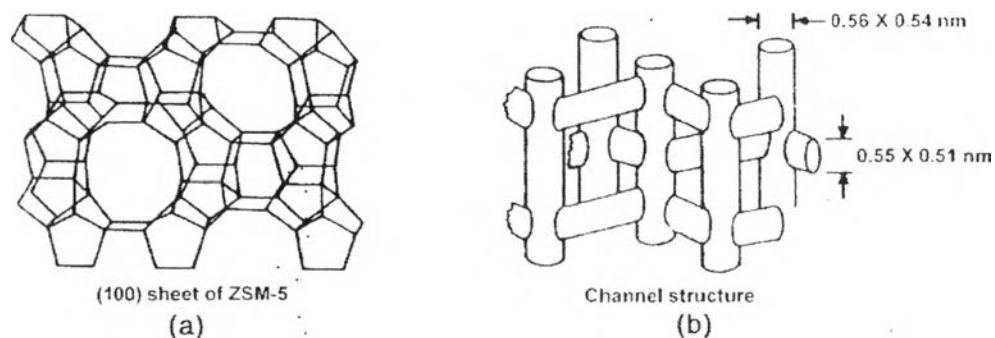
Figure 2.11 (a) Skeletal diagram of the (100) face of ZSM-5. (b) Channel structure of ZSM-5 (Scott *et al.*, 2003).

The completey 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 provious 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.

The mechanism of crystal growth from the macroscopic to the molecular level has been several reviews regarding synthesis of zeolites and molecular sieves (Poulsen, and Oksbjerg, 1995; Mojzis *et al.*, 1994; Olver, 1997). The evolution of molecular sieve zeolite technology for the period up to the early 1980s has been summarized (Haidouti, 1997).

In previous work (Udomsin, 2010) studied on alkylation of benzene with ethanol to ethylbenzene by using commercial HZSM-5 catalysts. In her research work, three types of commercial HZSM-5 catalysts which have a different in the SiO_2/Al_2O_3 (23, 45, and 195) were investigated. The highest selectivity to EB was observed with using SiO_2/Al_2O_3 of 195 at the condition of; 300 °C, B/E = 1, and WHSV = 8 h^{-1}

In this work, further study on the HZSM-5 with the SiO_2/Al_2O_3 of 195 was focused. The HZSM-5 with the SiO_2/Al_2O_3 of 195 was synthesized by using various synthesis conditions such as crystallization temperature and crystallization time. The synthesized catalysts were then being tested for its activity on the alkylation of benzene with ethanol to ethylbenzene.