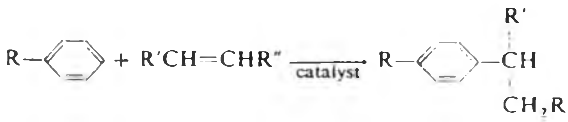
CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

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 called alkylated. In general, the following reaction (Scheme 2.1) occurs :

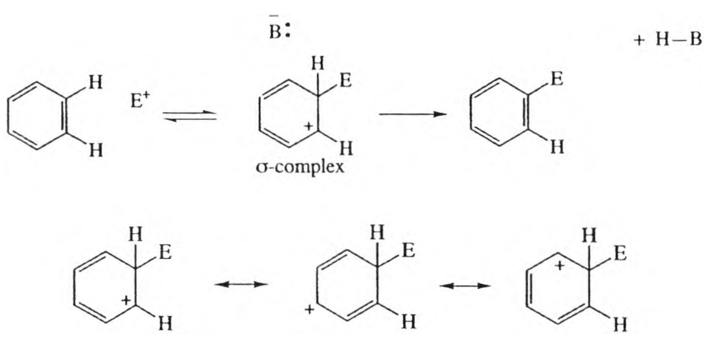


Scheme 2.1 Alkylation of aromatic reaction (Mcketta, 1993).

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

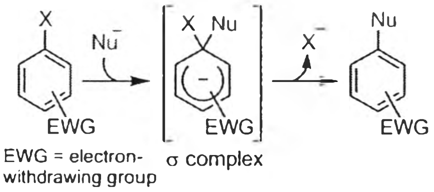
The most common reaction of benzene is electrophilic substitution. The typical benzene reaction has the benzene ring serving as a source of electrons, as nucleophiles. The reaction mechanism possesses two steps as shown in Scheme 2.2. The first step is the attack of an electrophile, E+, forming a carbocation 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.



Scheme 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 as shown in Scheme 2.3.



Scheme 2.3 The example of nucleophilic substitution (http://en.wikipedia.org/wiki/Nucleophilic_aromatic_substitution).

2.2 Free Radical Mechanism

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. In Scheme 2.4, using alkenes as alkylating agents, a proton is donated by the acid to substrate.

$$H_2C{=}CH{-}CH_3 \xrightarrow{HF} H_3C{-}\overset{+}{C}H{-}CH_3 \quad F^-$$

Scheme 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.

$$ROH + H^+ \leftrightarrow \left[RO^+H_2\right] \leftrightarrow R^+ + H_2O$$

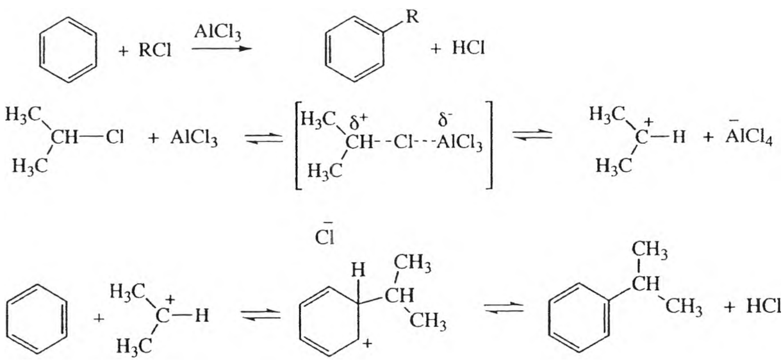
In presence of Lewis acids, such as $AlCl_3$, a complex is first formed with the alcohol and HCl is released. The complex then donates the carbocations.

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

$$ROAlCl_2 \leftrightarrow R^+ + {}^-OACl_2$$

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 $AlCl_3$ gave a maximum benzene conversion with catalyst containing 15% $AlCl_3$. Moreover, the results indicated no deactivation of $AlCl_3$ by hydrolysis with water generated by the reaction.

Alkyl halide has been extensively used to alkylate aromatic compounds. When $AlCl_3$ is used as the catalyst, the reaction is normally referred to as Friedel-Crafts reaction (Scheme 2.5).



Scheme 2.5 The Friedel-Crafts reaction (http://classes.uleth.ca/200201/chem2600a/notesch12.pdf).

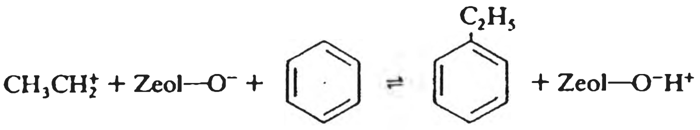
In this mechanism an alkyl halide with aluminum chloride formed the intermediate carbocation, an activated electrophile, which subsequently attacked the aromatic ring. Other sources of carbocations are alcohols, esters, ethers and olefins (Mcketta, 1993).

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. Depending on 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.

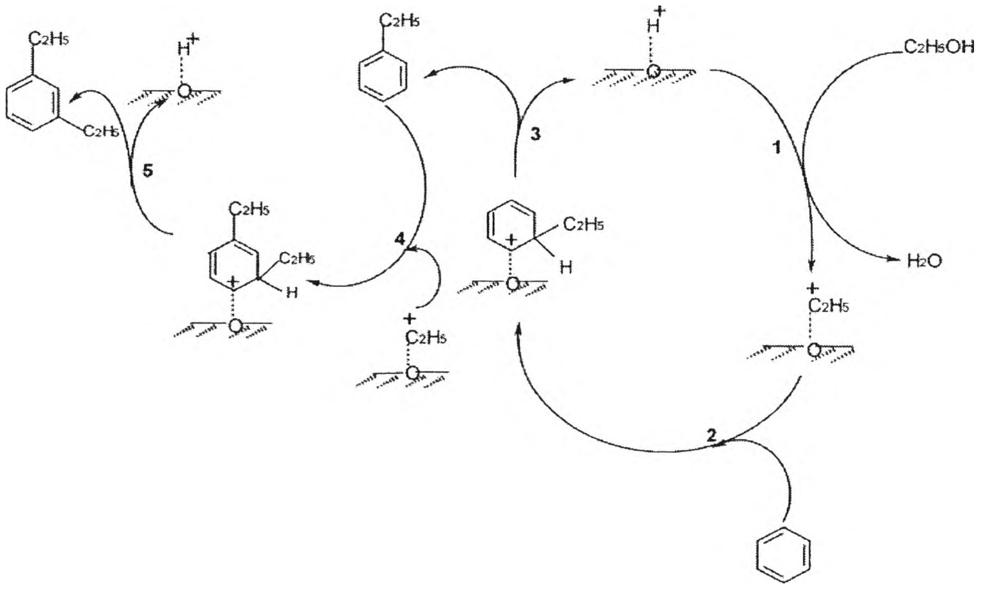
$$Zeol - O^{-}H^{+} + CH_2 = CH_2 \rightarrow CH_3 - CH_2^{+} + Zeol - O^{-} \qquad (4)$$

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



Scheme 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)



Scheme 2.7 A possible mechanism of the ethylation of benzene with ethanol over ZSM-5 (Odedairo *et al.*,2010).

A possible mechanism to represent the ethylation of benzene with ethanol over zeolite, ZSM-5, is illustrated in Scheme 2.7. Surface proton attacks ethanol to form water and surface ethyl cation (ethoxycation). An ethyl cation attacks benzene molecule to form protonated ethylbenzene on the surface. The protonated ethylbenzene returns a proton to the surface and forms ethylbenzene. Thereafter, surface ethyl cation (ethoxy cation) attacks ethylbenzene ring carbon atom at ortho, meta or para position atom to form a surface protonated diethylbenzene. The surface protonated diethylbenzene returns a proton to the surface and forms diethylbenzene.

2.3 Zeolites

Zeolite was discovered in 1756 by the Swedish mineralogist, Boron Axel F. Cronstrdt, as the natural minerals. The word “Zeolite” is Greek in original, derived from the 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 proposes. The synthetic zeolite was interesting in applications of shape selectivity to the petrochemical companies such as Union Carbide and Mobil. In the 1950s and early 1960s, Union Carbide company 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” (USY). Between 1967 and 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 alumino-silicate 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 (Figure 2.1). A representative unit cell formula for the composition of a zeolite is:

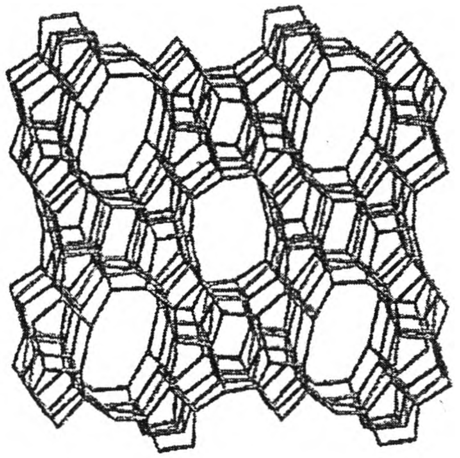
$$M^{n+}_{x/n}[AlO_2^{-})_x(SiO_2)_y].zH_2O$$

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 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 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 (Figure 2.2). These composition specific active sites of zeolite in 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.

In $AlPO_4$ type microporous materials the framework structure consists of a strictly alternating Al–O–P sequence (Al^{3+} and P^{5+}, balanced by four oxygen atoms with each 2^{-}charge, however, belonging to two tetrahedral), resulting in a completely neutral lattice as well, like in the case of pure silica zeolites. Depending on the combinations of the metal cation in the lattice, frameworks with positive or negative charges are in principal possible; however, so far only cation exchanged microporous materials are known. Vijayaraghavan *et al.* (2004) studied the activity of large pore $AlPO_4$-5 molecular sieves substituted with Mg, Mn and Zn in the vapor-phase ethylation of benzene with ethanol. They found that MAPO-5, ZAPO-5 and MnAPO-5 give higher conversion than $AlPO_4$-5 due to isomorphous substitution of metal in the frame work of the catalyst. Among the catalyst, MnAPO-5 is more active than others because of the presence of unpaired electrons in the d-subshell.

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.



ZSM-5(MFI)
Channels:
10 (5.3 x 5.6 A^{o})
10 (5.1 x 5.5 A^{o})

Figure 2.1 ZSM-5 zeolite pores and channels (Saenharn, 2007).

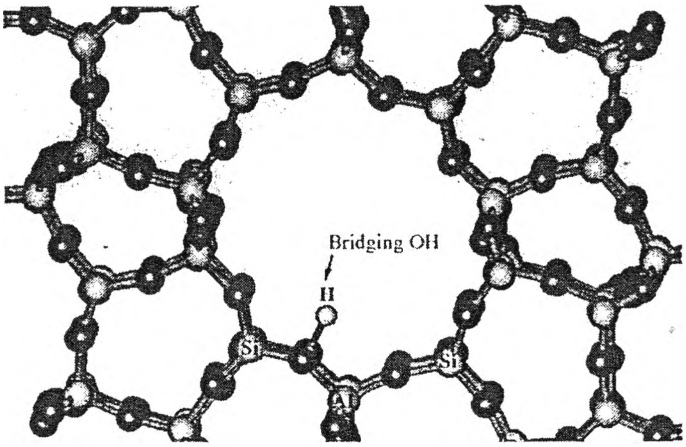


Figure 2.2 Active sites of zeolite structure (Saenharn, 2007).

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

2.3.2.1 Shape and Size Selectivity

Shape and size selectivity plays 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 selectivity, product shape selectivity, and transition-state shape selectivity. These types of selectivity are depicted in Figure 2.3. Reactant shape selectivity results from the limited diffusion 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 equivalent 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 configuration approach 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 extreme reactivity.

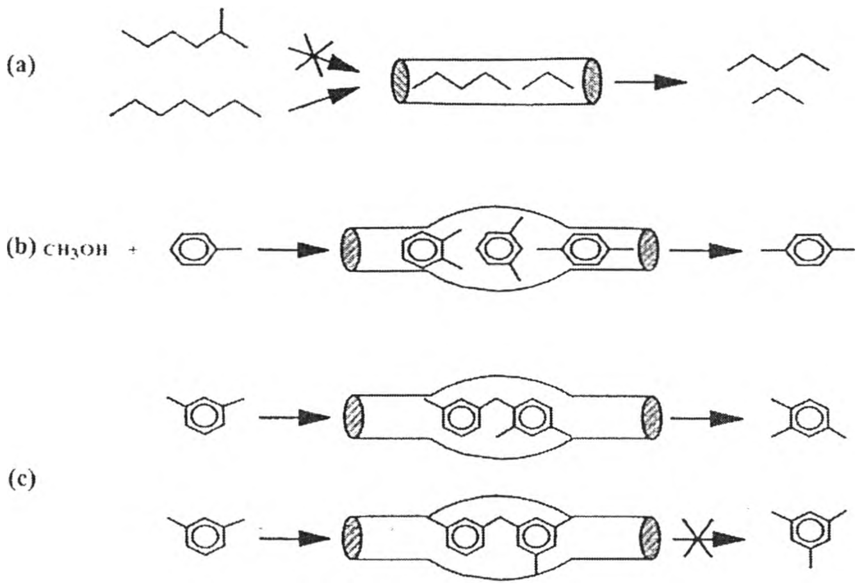


Figure 2.3 Diagram depicting the three types of selectivity: (a) reactant, (b) product and (c) transition state shape selectivity (Saenharn, 2007).

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.* (2006) 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 vapor and liquid phase alkylation of various reactions are studied over MnAPO-5 and MnAPO-11. The vapor 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) also 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 out of the pore faster.

2.3.2.2 Acid Sites (Acidity)

An important property relating to the activity of zeolites is their acidity. The activity requested is based on the formation of Brönsted 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 Brönsted acid sites, as shown in Figure 2.4.

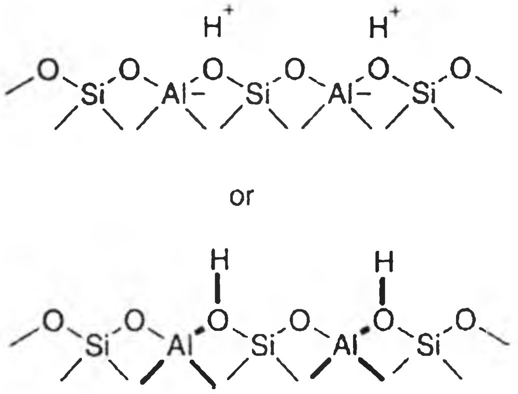


Figure 2.4 Brönsted acid sites (“bridging hydroxyl groups”) in zeolites (Stocker, 2005).

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 2.5. 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).

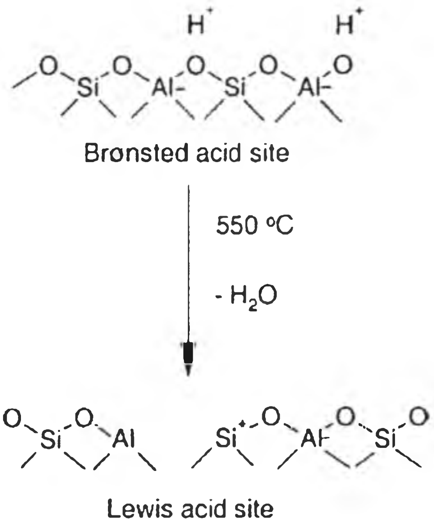


Figure 2.5 Formation of Lewis acid sites in zeolites (Stocker, 2005).

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. Figure 2.6 depicts a zeolite structure with Brönsted and Lewis acid sites.

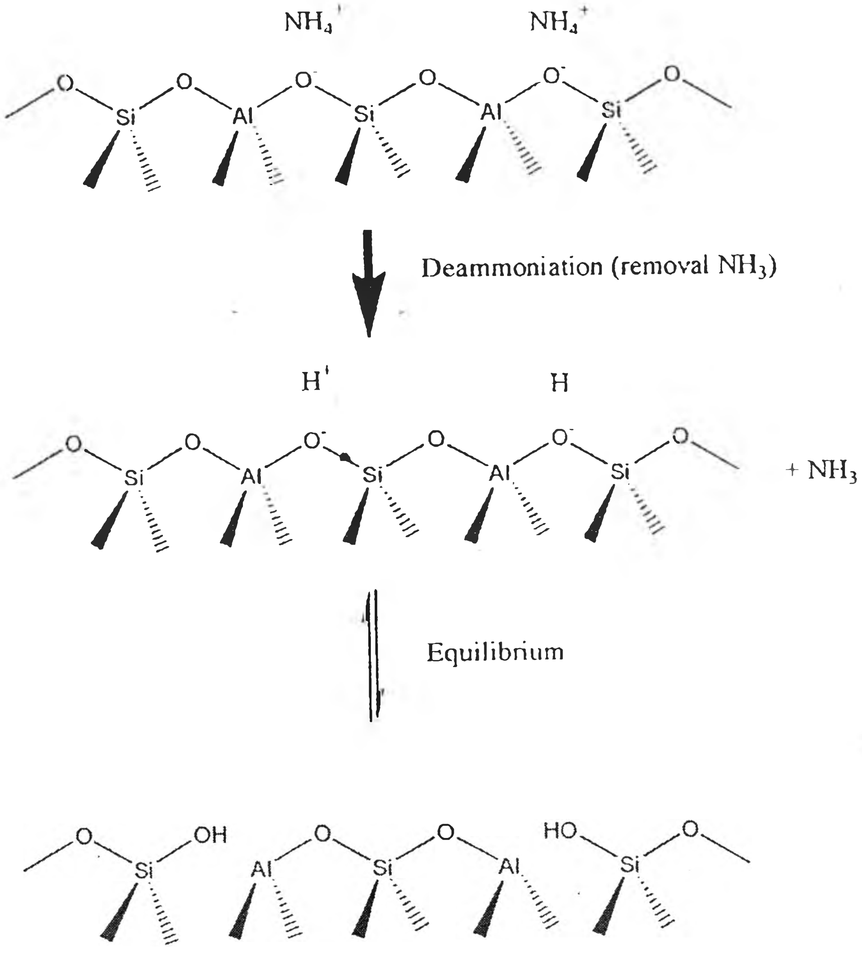


Figure 2.6 Diagram of the "surface" of a zeolite framework (Saenharn, 2007).

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 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 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, 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.

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 H_2O on the Brönsted and Lewis acidities of two sulfated zirconia (SZ) catalysts. TPD results of all basic probes on SZ-I 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 Sieve of Molecular porosity – 5 developed by Mobil oil, is an aluminosilicate zeolite which chemical formula is $Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$ ($0<n<27$). In ZSM-5, the tetrahedral are linked to form the chain type building block. The chain can be connected to form a layer (Gates, 1992). ZSM-5 is composed of several pentasil units linked together by oxygen bridges to form pentasil chains. A pentasil unit consists of five oxygen atom in this structure. 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 2.7. There is a set of straight, parallel pores intersected by a set of perpendicular zigzag pore (Gates, 1992).

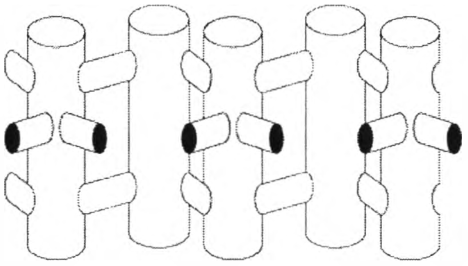


Figure 2.7 The pore dimensions of ZSM-5 (http://chemelab.ucsd.edu/methanol/memos/ZSM-5.html).

The aluminium sites in ZSM-5 are very acidic. The substitution of Al_3^+ in the place of the tetrahedral Si_4^+ silica requires the addition of positive charge. When 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 wildly used in the petroleum and petrochemical industry for hydrocarbon isomerization and alkylation of hydrocarbon.

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 A^o). 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 A^o (figure 2.8), but the diameter of roughly spherical intersection is about 9 A^o 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 A^o), the second pore is zigzag or sinusoidal channels and are circular (5.4 x 5.6 A^o) in cross section. The intersection of both channels is called intersection channel.

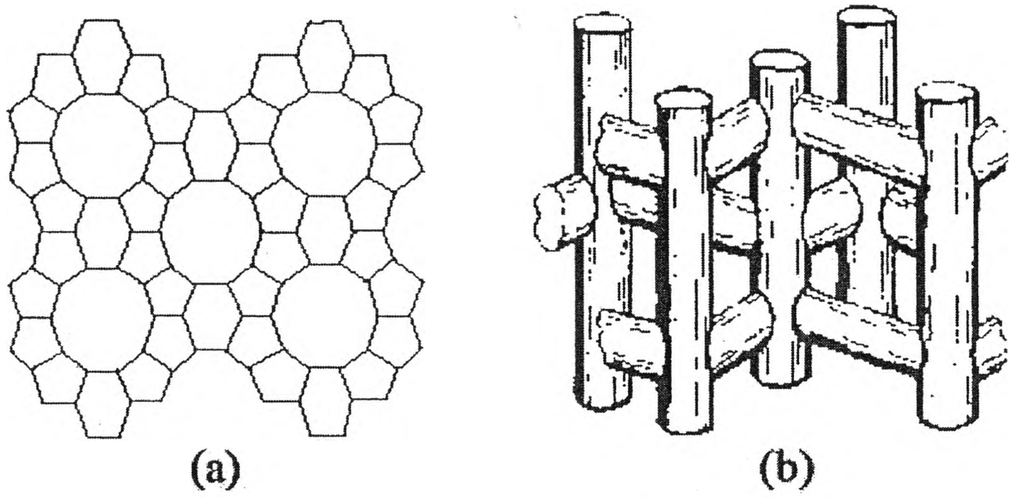


Figure 2.8 Structure of ZSM-5 showing two different channel structures: (a) framework, (b) channel system (the straight channel and the zigzag channels) (Saenharn, 2007).

Li *et al.* (2009) studied the synthesis of ethylbenzene by alkylation of benzene with diethyl carbonate (DEC) over HZSM-5. As a result, the alkylation of benzene with DEC over HZSM-5 was a convenient route for the synthesis of EB. Of all the catalysts tested, HZSM-5 with a Si/Al ratio of 200 has the best benzene conversion and EB selectivity due to its optimal acid strength. Strongly acidic sites may lead to excessive decomposition of DEC. Catalyst activity increased significantly as the temperature was 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.

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

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.

Honda *et al.* (2008) studied the preparation of highly active binder-added MoO_3/HZSM-5 catalyst for the non-oxidative dehydroaromatization of methane. They compared three different procedures (a) impregnation of MoO_3 over a wet mixture of HZSM-5 and a binder SiO_2 or Al_2O_3 followed by calcination, (b) impregnation of MoO_3 on HZSM-5 followed by a wet mixture of the resulting sample with one binder and then calcination, and (c) carburization of MoO_3 pre-impregnated on HZSM-5 followed by a wet mixture of the carburized MoO_3/HZSM-5 with one binder, respectively. They observed that the procedure (c) certainly allowed a successful localization of MoO_3 on its primary support HZSM-5 and therefore presented an applicable way of preparing highly active binder-added Mo/HZSM-5 catalysts for the non-oxidative dehydroaromatization of methane.

Berthos *et al.*(2007) studied the aromatization of methanol and methylation of benzene over Mo_2C /ZSM-5 catalysts. They found that the deposition of Mo_2C on ZSM-5 markedly enhanced the formation of aromatics. The highest yield of the formation of aromatics was measured for 5% Mo_2C /ZSM-5 ($SiO_2/Al_2O_3 = 80$) at 773 K.

2.5 Hydrothermal 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 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 Bronsted acidity after hydrothermal treatment (Topsoe *et al.*,1988 ,Datka *et al.*,1996 , and Kumar *et al.*,2000).

Guo *et al.* (2003) also found the 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 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. 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 the 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 the 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 fomation of coke during the methane dehydroaromatization reaction.

Lertjiamratna *et al.* (2009) studied the modification of acid properties and catalytic properties of $AlPO_4$ by hydrothermal pretreatment for methanol dehydration to dimethyl ether. They observed that 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 Bronsted acid sites). However, a hydrothermal pretreatment at 100 °C may 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 indicated 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 resulting in the improvement of catalytic stability.

2.6 Zeolite Synthesis

Zeolite synthesis can be performed 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 Figure 2.9. 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.*, 2009).

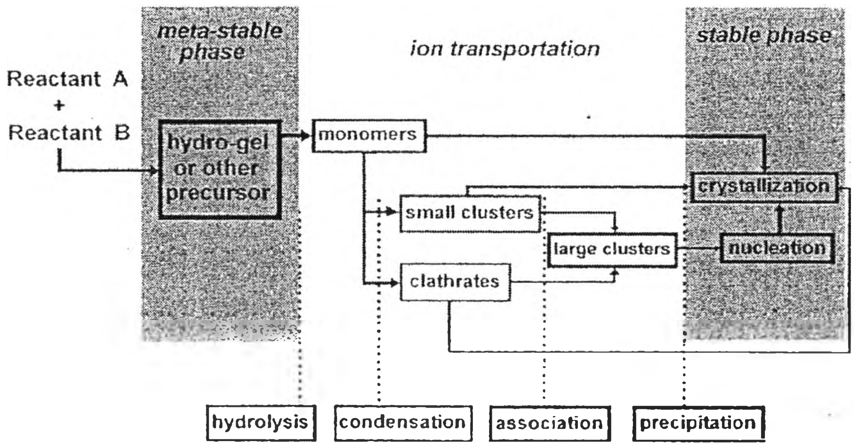


Figure 2.9 A schematic representation of zeolite crystallization process (Barrer, 1978).

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 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.

Considering that there are more than 100 frameworks, each with multiple synthetic procedures, it is important to ask what is the optimal way to learn about zeolite synthesis. 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 (Liu *et al.*, 1999). ZSM-5 typically crystallizes in the Para orthorhombic space group with lattice constants $a = 20.1$, $b = 19.9$, and $c = 13.4$ A^o. the framework density of Si+Al atoms is 17.9 per 1000 A^{o3}. Figure 2.10(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. Figure 2.10(b) shows the channel running parallel to (010) with 10-ring openings of 5.4 x 5.6 A^o , and sinusoidal channel parallel to the (100) axis with 10-ring openings of dimension 5.1 x 5.5 A^o (Seidal *et al.*, 1999; Smith, 1998). The O-T-O bond angles vary between 105^o and 113^o with an average value of 109 ± 2^o. among the T-O-T angles, two almost linear bonds are observed at 176.2^o and 178^o (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).

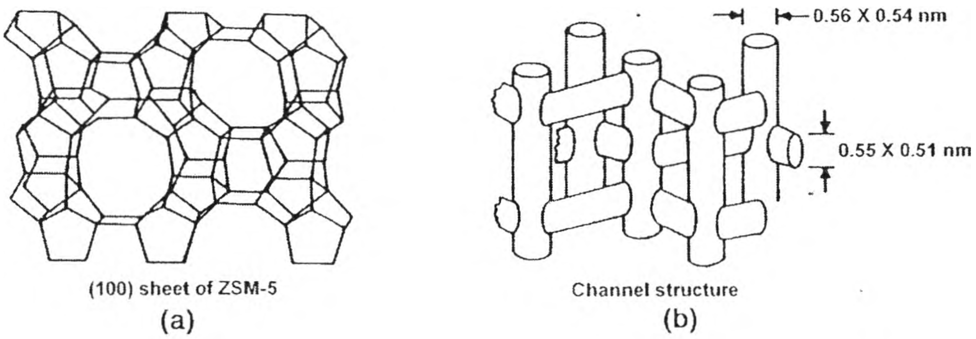


Figure 2.10 Structure of ZSM-5: (a) Skeletal diagram of the (100) face of ZSM-5, (b) Channel structure of ZSM-5 (Scott *et al.*, 2003).

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.

The mechanism of crystal growth from the macroscopic to the molecular level was revealed in several reviews regarding synthesis of zeolites and molecular sieves (Veldman *et al.*, 1997; 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).

2.6.1 Effect of Si/Al Ratio

The catalytic and sorption properties of the zeolite are often influenced by their crystal size. The acidity of ZSM-5 zeolite used as a catalyst has significant effect on reaction path and product distribution in reaction. According to the important role of surface area and diffusional path in the catalytic behavior, zeolites with small crystal size having high external surface area and short diffusional path can have significant effect on product distribution in catalytic reaction. The morphology, surface area, acidity and crystal size distribution are influenced by Si/Al ratio in the zeolite structure (Shirazi *et al.*, 2008).

Shirazi *et al.* (2008) studied the effect of Si/Al ratio of ZSM-5 zeolite on its morphology, acidity and crystal size. The gel composition and synthesis conditions for ZSM-5 synthesis with different Si/Al molar ratios : 10, 20, 25, 30, 40 and 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 μm. 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 became easier as the Si/Al ratios increase in the gel. The scanning electron micrographs (Figure 2.11) 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. It was also observed that the surface areas increased with increasing Si/Al molar ratio of the samples. 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.

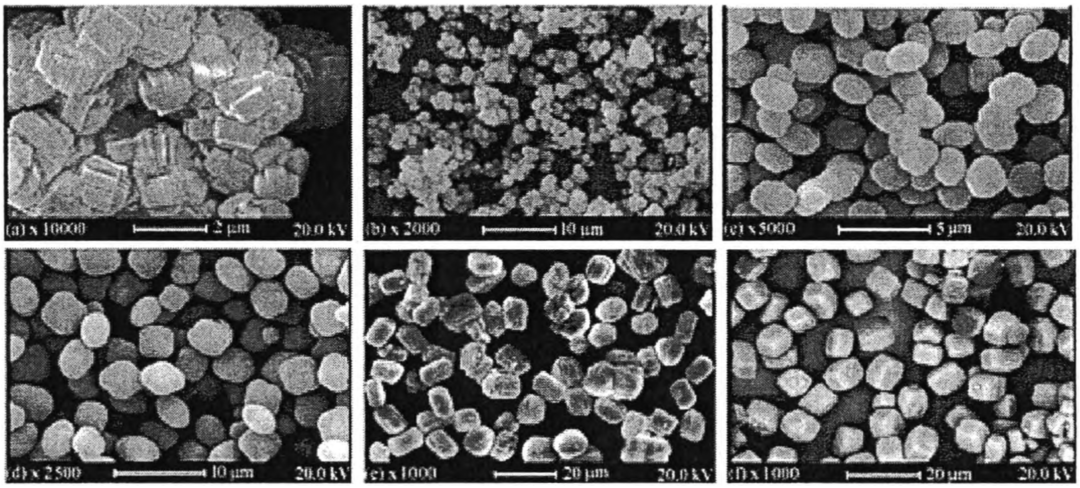


Figure 2.11 Scanning electron micrographs of the as-synthesized zeolites with different molar ratios of Si/Al (a) 10, (b) 20, (c) 25, (d) 30, (e) 40 and (f) 50 (Shirazi *et al.*, 2008).

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

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).

2.6.2 Effects of Crystallization Temperature and Time

The crystallization process consists of two major events, nucleation and crystal growth. The pathway of the crystallization process as well as the morphology and singular properties (crystal size and distribution) of the MFI-type zeolite are influenced by different variables: the silicon and aluminum source, the aluminum content, the template / silicon ratio, the nature of the cations present in the synthesis medium, the alkalinity, the presence of seeds, the water contents, and crystallization temperature and time, etc. The control of the crystal size is crucial to monitor adequately the activity and selectivity of the ZSM-5 samples (Jacobs *et al.*, 1981; Haag *et al.*, 1980). However, the effects of time and temperature are most interesting to investigate because crystallization can lead to different both physical and chemical properties of the final product.

Khatamian *et al.* (2009) studied the preparation and characterization of nanosized ZSM-5 zeolite using gaolin and investigation of crystallization time and temperature changes on the size and crystallinity of products. They found that the highest crystallinity was obtained at 180 °C and increasing temperature from 120 to 180 °C resulted in catalysts with higher crystallinity. The sample crystallized at 168 h (longest time) showed the highest crystallinity. By increasing the temperature and time, a larger crystal size was obtained.

Chareonpanich *et al.* (2004) studied the direct synthesis of ZSM-5 zeolite using the Mae-Moh lignite fly ash as the main raw material. However, they focused on the factors affecting the ZSM-5 zeolite yield, crystallization temperature and time. SEM photographs of the products at 150 and 180 °C are shown in Figure 2.12. At the temperature of 150 °C, the unknown amorphous solids of irregular shape and crystalline were found. It was noticed that the ZSM-5 zeolite could not be produced under this low temperature. At 210 °C, only ZSM-5 zeolite was found (43 wt. %). The SEM photograph of the product at 180 °C indicated the presence of the cubic crystals of ZSM-5 zeolite and the needle-like crystals of zeolite P, while only the cubic crystals of the ZSM-5 zeolite were found at 210 °C. They explained according to Break *et al.* (1974) that the formation of metastable phases of zeolites depend on temperature, and then the most stable phase will continue to grow and be detected finally. Not only the temperature, but the holding time also plays an important role on the formation of the specific metastable phase of zeolite. For the study on the effect of the holding time, the synthesis temperature was fixed at 210 °C and the holding time was varied at 0, 1, 2, 3 and 4 h. On the yields of the product crystals, they found that the longer the holding time, the greater the yield of ZSM-5 crystalline zeolite.

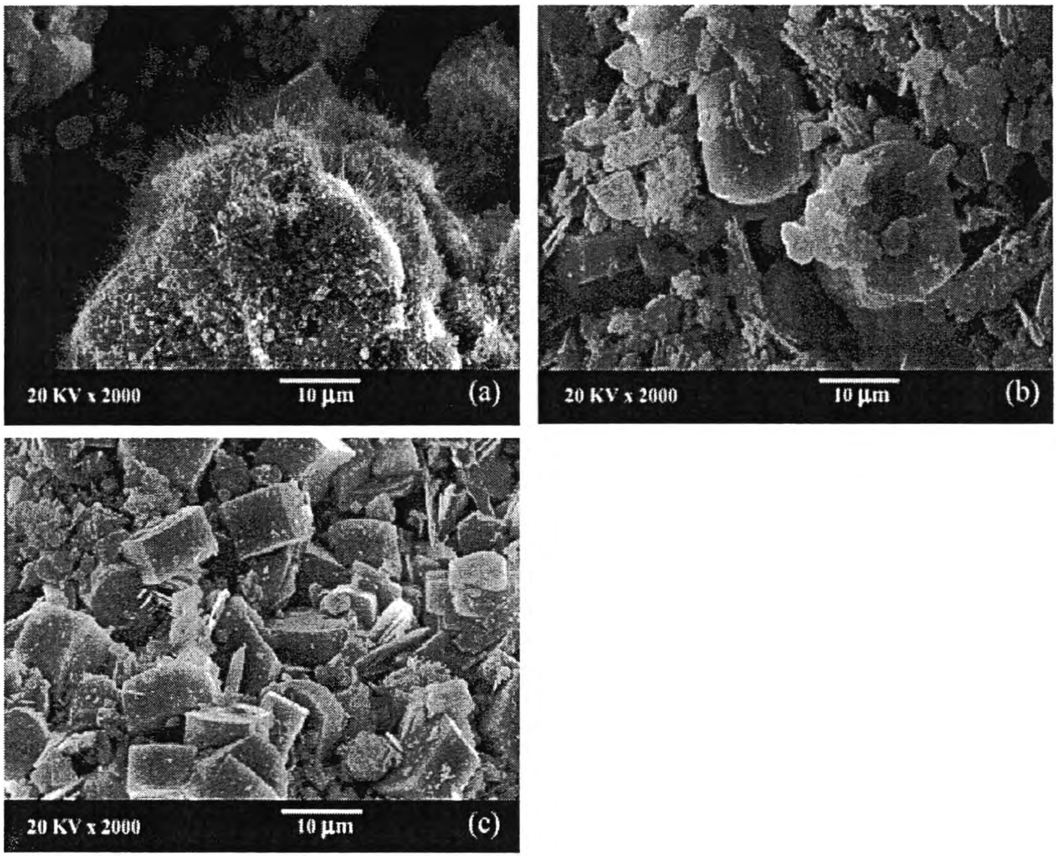


Figure 2.12 SEM photographs of treated products obtained from synthesis at holding temperatures of (a) 150 °C, (b) 180 °C, and (c) 210 °C (SiO_2/Al_2O_3 mole ratio: 40, initial pressure: 3 bar, holding period: 2 h) (Chareonpanich *et al.*, 2004).

Duang-udom, (2011) studied the Alkylation of Benzene with Ethanol to Ethylbenzene using Synthesized HZSM-5 Catalysts. It was demonstrated that the synthesized HZSM-5 catalysts with SiO_2/Al_2O_3 ratios of 180 provided high selectivity to EB for the alkylation of benzene with ethanol. It was observed that the catalyst hydrothermally synthesized at 150 °C for 48 h provided a relatively suitable crystallinity, surface characteristic, and Brönsted acid sites, resulting in a higher catalytic activity in terms of ethanol conversion and selectivity to EB. For reaction temperature 500 °C gave the highest selectivity to EB and benzene conversion because at suitable high temperature, bulkier molecules can diffuse more quickly, and other products cannot occur due to exothermic reaction. Moreover, increasing the B/E feed ratio resulted in decreasing the benzene conversion, but increasing the selectivity to EB. It was suggested that for alkylation of benzene with ethanol when using the synthesized HZSM-5 catalyst obtained from synthesized temperature 150 °C for 48h, the optimal parameters be a temperature of 500 °C, and a B/E feed molar ratio of 4:1.

2.6.3 Effect of H_2O/SiO_2 Molar Ratio

In the synthesis of zeolite, water provides an indispensable medium for the dissolution and diffusion of aluminosilicate (Suzuki *et al.*, 1987). The low ratios of H_2O/SiO_2, the short distance between nutrients in the aqueous solution should have enhanced the nucleation and thus crystallization.

Gu *et al.* (2009) studied the In situ assembly of ZSM-5 nanocrystals into micro-sized single-crystal-like aggregates via acid-catalyzed hydrolysis of tetraethylorthosilicate using TPABr as a structure directing agent. The role of water content in the synthesis was a major factor that they considered. Herein, H_2O/SiO_2 molar ratio was adjusted from 5 to 80. By XRD results, they found that highly crystallized ZSM-5 was achieved in the range 20–40 of H_2O/SiO_2 ratio. However, when the H_2O/SiO_2 ratio is too low, less than 20, the viscosity of the aluminosilicate gel was too dense for substrates to diffuse freely and/or interact to each other, leading to the failed formation of ZSM-5 crystalline.

Mochizuki *et al.* (2011) studied the Facile control of crystallite size of ZSM-5 catalyst for cracking of hexane. However, they focused on the factors affecting the ZSM-5 zeolite size. They found that the molar ratio of the H_2O/SiO_2 in the gel hardly affected the morphology. In the molar composition of water, 8.3, 30, 40 and 100, the crystallites were mono-dispersed in every case. The average sizes were found to be 106, 253, 380 and 935 nm for the H_2O/SiO_2 ratio of 8.3, 30, 40 and 100. The crystallite size was decreased with a decrease in the molar composition of water. Therefore, they concluded that the role of water content in the synthesis was a major factor affecting to the crystal size.

2.7 Nanoscale Zeolites

Zeolites possess well-defined crystalline structures with molecular-sized pores, ion exchangeable sites and high hydrothermal stability, making them being widely used as catalysts in petrochemical processing and fine chemical industry. However, due to their low diffusion efficiency which often leads to the low availability of active sites and/or fast deactivation, the optimization of catalytic performance is still an inherent challenge for zeolites. The reduction of the zeolite crystals to nanometer is an effective way to reduce the mass transport limitations of guest molecules in the micropores by shortening the diffusion pathlength. Therefore, the exploration of the catalytic application of the nanozeolites has become the top concern in the research on their applications (Sugimoto *et al.*, 1987).

Sugimoto *et al.* (1987) investigated the effect of crystal size on the catalytic properties of nanocrystalline HZSM-5 in the conversion of methanol to gasoline (MTG reaction), and a good correlation was observed between crystal size and their catalytic properties. In contrast to large crystallites, the aggregated HZSM-5 consisting of small crystallites showed long catalytic life and high selectivity for hydrocarbon and aromatics.

Yamamura *et al.* (1994) studied the relationship between external surface area of nanosized ZSM-5 and catalytic performance for ethylene oligomerization. It was found that the lifetime of ZSM-5 nanozeolite in the oligomerization of ethylene absolutely depended on their external surface area or crystal size.

Schwarz *et al.* (1998) have synthesized ZK-5 zeolites with various crystal sizes from 0.4 to 2.0 μm and found that the small-sized zeolites were more active than the large sized ones in the methylamine synthesis reactions.

Loenders *et al.* (1998) found that the intracrystalline diffusion limitation of zeolite BEA would be negligible in the alkylation of isobutane with 1-butene when the size of zeolite BEA crystals was smaller than 14 nm, corresponding to the external surface areas larger than ca. 280 m^2 g^{-1}.

The alkylate yield obtained is proportional to the number of Brönsted acid sites of the zeolite catalysts in the absence of diffusion limitation. Additionally, the nanosized zeolite BEA has been used as solid acid catalyst in Friedel–Crafts alkylation of aromatics and heteroaromatics as well. (Botella *et al.*, 2000; Derouane *et al.*, 2004; Sartori *et al.*, 2006; Kantam *et al.*, 2005) It was found that the zeolite crystallite size played an important role on the improvement of the reactivity and catalyst decay, and the nanosized zeolite showed the most promising reactivity accompanying with the minimizing of the coke deposition (Sartori *et al.*, 2006; Kantam *et al.*, 2005).

Notably, the reduction of zeolite size leads to more accessible catalytic active sites, and thereby ensures its high reactivity in the bulky molecule participated catalytic reactions, such as cracking of polyolefins with the molecular sizes larger than those of the zeolitic micropores.

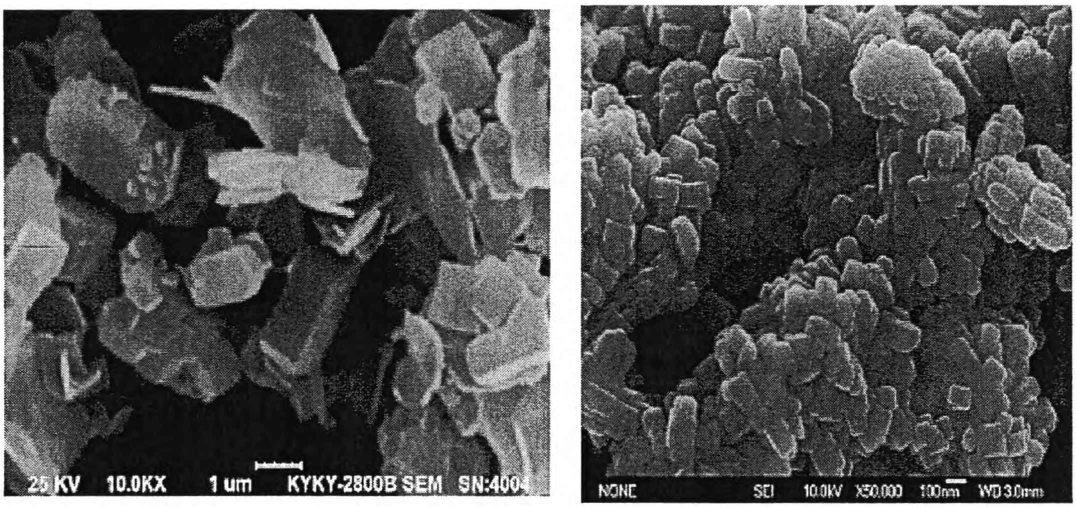
Serrano *et al.* (2005) studied the catalytic properties of nanocrystalline HZSM-5 in the catalytic cracking of polyolefins into light hydrocarbon mixtures, and the high activity and selectivity towards olefinic gases were obtained over this catalyst. The amount of external surface of the catalyst was considered as one of the main factors affecting the catalyst activity. Due to the abundant acid sites on their large external surface, the nanozeolites could crack the polyolefin with high conversion. Additionally, the small molecules generated from polyolefin cracking would then diffuse into the micropores of nanozeolite and bear secondary reactions on the acid sites in the internal surface. The decrease of the crystal size also favours internal diffusion of these small molecules.

Mastral *et al.* (2006) also employed nanocrystalline HZSM-5 in the catalytic pyrolysis of polyethylene. The use of nanocrystalline HZSM-5 allowed high yields of gas fractions and a higher selectivity to the products obtained than those achieved by thermal cracking. On the contrary, with the decrease of the crystals sizes, the shape selectivities of many reactions, such as alkylation or isomerization of aromatics, will decrease because of the increasing of external surface acidity of and the shortening of inner pore channels for the guest molecules. (Csicsery *et al.*, 1984; Kaeding *et al.*, 1985; Kim *et al.*, 1988; Shiralkar *et al.*, 1991; Hibino *et al.*, 1991; Beschmann *et al.*, 1994; Bhat *et al.*, 1996) Although, the decrease of crystals size will decrease their characteristic molecule-selectivity, their activity and lifetime could be probably increased because the shorter diffusion path and/or more pore-opening increased its coke tolerance ability. (Zhao *et al.*, 2007) The enhancement of the lifetime with the expense of the loss of selectivity becomes a dilemma for the application of nanoparticles of zeolites in catalysis. Accordingly, it is suggested that the small sized zeolite crystals should be applied with blockage or removal of their external acidic sites for these diffusion-controlled reactions (Melson *et al.*, 1997).

Wang *et al.* (2008) compared the catalytic performances on nanoscale HZSM-5 and microscale HZSM-5. The comparison of catalytic performance on nanoscale HZSM-5 and microscale HZSM-5 showed that nanoscale HZSM-5 was different from microscale HZSM-5 in catalytic performance for the larger reactant molecule such as 1,3,5-TMB and 1,2,4-TMB. The catalytic performance of toluene disproportionation and alkylation of toluene with methanol were similar because the small reactant molecule. This difference in reaction on nanoscale HZSM-5 and microscale HZSM-5 was attributed to the difference in the concentration of external acid sites and the configuration of reactant molecule. Figures 2.13 shows the fine crystals of nanoscale HZSM-5 severely conglomerate and the crystal size of nanoscale HZSM-5 was 70–100 nm.

Petushkov *et al.* (2011) conducted the synthesis of hierarchical nanocrystalline ZSM-5 with controlled particle size and mesoporosity. The mesopore volume and size distribution showed a dependence on particle size such that smaller particles lead to higher mesopore volumes and narrower pore size distributions. Increasing the specific surface area and decreasing the micropore diffusion pathlength in zeolites are important factors for improving the performance of zeolites in catalytic applications and these factors can be optimized by decreasing the zeolite particle size. Creation of a hierarchical zeolite material that possesses both micro- and mesopores with very large surface areas and improved mass transport properties is an effective solution.

Zhao *et al.* (2011) studied the effect of Pt on stability of nano-scale ZSM-5 catalyst for toluene alkylation with methanol into p-xylene. Nanoscale HZSM-5 was chosen as catalyst precursor for its advantages in activity and stability. The modification with Pt inhibited the formation of coke from alkenes and significantly improved the stability with constant para-selectivity (~98%). The Pt-modified nano-scale HZSM-5 catalysts showed excellent stability as well as para-selectivity.



(a) (b)

Figure 2.13 SEM photographs of (a) microscale HZSM-5, (b) nanoscale HZSM-5 (Wang *et al.*, 2008).

The conventional zeolites are utilized widely in both petrochemical and fine chemical catalysis. The application of nanotechnology have made significant progress in the current and lead to use in the area of catalyst. In the past decades, the effect of external surface brought by the decreasing of zeolite size have been deeply investigated on cracking bulky molecules. The rich acid sites on external surface of nanozeolites make them a major influence on a high activity for the reaction of large molecules, while their abundant pore-opening and short diffusion path would greatly enhance their tolerance to coking. However, increasing the external surface acidity with the decrease of the crystals size could also decrease the shape selectivity of catalysts in those diffusion-controlled shape-selective reactions (Zhang *et al.*, 2009). Therefore, some optimizations among the reactive activity, lifetime and shape-selectivity still are required for a definite reaction.