

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Zeolite

Zeolites play a very important role in the heterogeneous catalysis and have been used as adsorbents, energy storage, more recently in several emerging fields such as health and medicine, ion exchangers for their excellent thermal stability, and unique crystal structure. The properties of zeolite structure are interesting, namely:

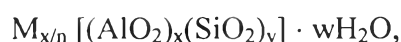
(i) They have exchangeable cations, allowing the introduction of cations with various catalytic properties.

(ii) If these cationic sites are exchanged to  $H^+$ , they can have a very high number of very strong acid sites

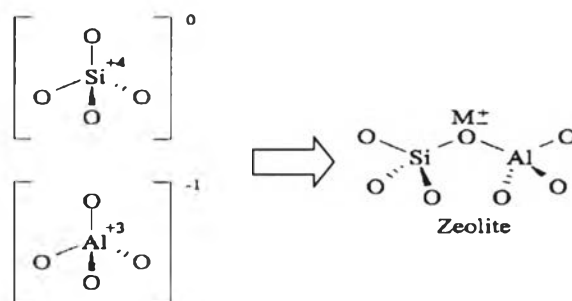
(iii) Their pore diameters are less than  $10 \text{ \AA}$  and they have pores with one or more discreet sizes.

##### 2.1.1 Zeolite Compositions

Zeolites have been described as crystalline aluminosilicates of very porous structure that contain in their natural forms ions of Group IA and Group IIA elements such as Na, K, Mg and Ca. The structure made from tetrahedral of an  $Al^{3+}$  or  $Si^{4+}$  ion surrounded by four  $O^{2-}$  ions. This tetrahedral linked to each other by the sharing of oxygen atoms. Normally, their structure built from tetrahedral  $TO_4$  units, where T is  $Si^{4+}$  or  $Al^{3+}$  ion. Each O atom shares between two T atoms. In the case of a Si tetrahedron this will give an electrically neutral unit, whereas an Al tetrahedron will give a negative charge (Figure 2.1). This charge has to be compensated to yield electrically neutral crystals. The zeolite contains cations to neutralise the charge on the Al tetrahedral. The general chemical composition of a zeolite is :

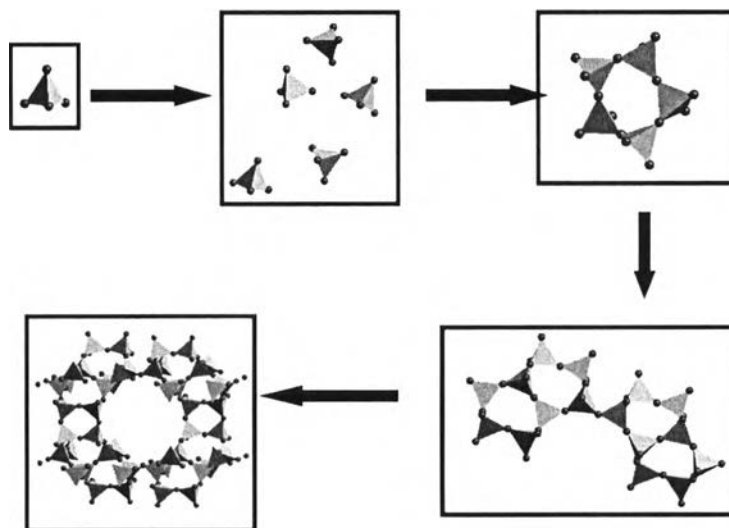


where M is an alkali or alkaline earth cation, n is the valence of the cation, w is the number of water molecules per unit cell, x and y are the total number of tetrahedral per unit cell



**Figure 2.1** Basic tetrahedron unit of aluminosilicate type zeolite  
(<http://what-when-how.com/nanoscience-and-nanotechnology/catalytic-properties-of-micro-and-mesoporous-nanomaterials-part-1-nanotechnology>).

The primary building units of the zeolite lattice are the silica and alumina tetrahedral. When these tetrahedral units combine to secondary building units (SBUs) which occurred simple polyhedral and come together to form either an array of interconnecting channels or a system of cage-like voids (Figure 2.2).



**Figure 2.2** The formation of zeolite  
(<http://www.bza.org/Bursary04/Sarwar.html>).

Channels or cages of zeolites are occupied by cations and water molecules. Counter ions (cations) are present in order to compensate for the negative framework charge created by aluminium substitution. The counter ions are from the IA and IIA groups of the periodic table which sit in the pores and voids, and are usually mobile. The results of substitution cations are narrow pore diameter of the zeolite channels. One measure of the porosity is the amount of adsorbed water. The water molecules are also present in the pores and voids, and may (in many cases) be removed by heating and re-adsorbed at lower temperatures.

### 2.1.2 Pore Structures

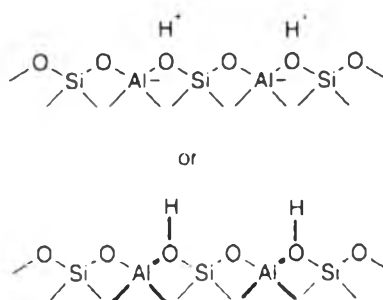
Applications of zeolite have been occurred by molecular diffusion pass through pore of zeolite. The pore of zeolite were obtained from aperture which linked to  $TO_4$  tetrahedral. Pore diameters in molecular sieves depend on the number of tetrahedral in a ring. The smallest of aperture consist of T 8 unit (8T) or 8-membered ring (8MR). The zeolite framework can be divided by pore structure as shown in Table 2.1. Besides, It was found that zeolites have ultralarge pore structure such as Cloverite (20MR). The actual pore size also depends on the type of cation present. Molecules like ammonia, hydrogen, oxygen, and argon can go through the pores of practically every type of molecular sieve. Cations, however, occupy positions which block part of the pores. Ability of substances to diffuse through pore of zeolite depend on pore size and temperature.

**Table 2.1** Classification of zeolite by pore structure (Guisnet and Gilson, 2002)

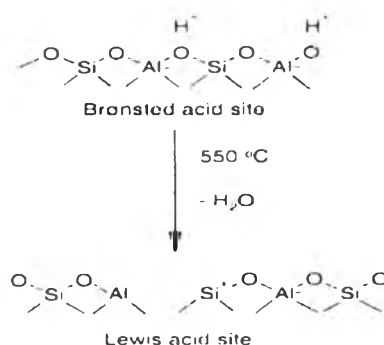
Small Pore Zeolite	Middle Pore Zeolite	Large Pore Zeolite
8-membered ring	10-membered ring	12-membered ring
3.0-4.5 °A	4.5-6.0 °A	6.0-8.0 °A
Zeolite A	Zeolite ZSM-5	Zeolite L
Erionite	ZSM-11	Faujasite (X, Y)
Chabazite	Ferriete	Mordenite
Gismonite	Stibite	ZSM-12
Phillipsite	ZSM-23	Zeolite Beta

### 2.1.3 Acid Sites (Acidity)

The acidity of ZSM-5 zeolite used as a catalyst has significant effect on reaction path and product distribution in reaction. Chemical reaction and functional groups of hydrocarbon compound can only occur on acid site of zeolites. There are classified acid sites to two types in heterogeneous catalyst, they are: i) Brønsted acid sites that an acid is a substance that gives up a proton as the bridging hydroxyl group in Si(OH)Al which is linked to tetrahedrally coordinated or framework aluminum atoms and the strength of an acid is depends on its tendency to give up a proton (Figure 2.3). ii) Lewis acid sites that an acid is a substance that can take up an electron pair to form a covalent bond (Figure 2.4).



**Figure 2.3** Brønsted acid sites (“bridging hydroxyl groups”) in zeolites (Stocker, 2005).



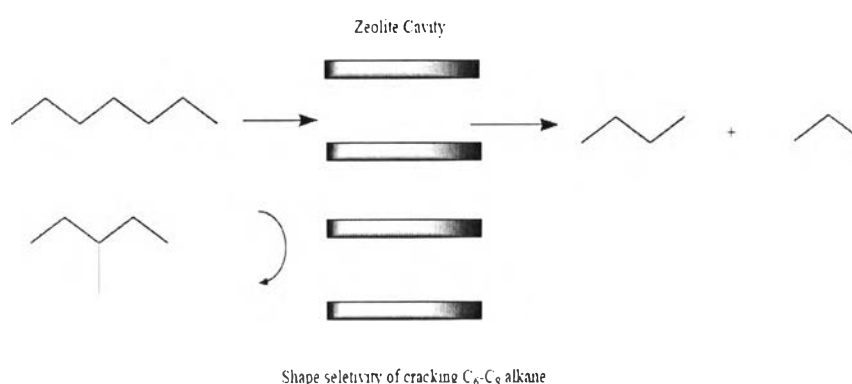
**Figure 2.4** Lewis acid sites in zeolites (Stocker, 2005).

### 2.1.4 Shape Selectivity

Shape selectivity is a unique feature of heterogeneous catalysis by zeolite. Almost all of the active sites are confined within the pores of zeolite and if the pores are small, the reactant molecules have to pass through those the pores and react chemical reaction at active sites. After that the products molecules to diffuse through those the pores. Only molecules whose dimensions are less than a critical size can enter the pores and can leave appear in the final product. Therefore, the pore size is important factor often imposes a strong influence on the selectivity of zeolite-catalyzed reactions. Shape selectivity effects are usually classified into the three different types.

#### 2.1.4.1 *Reactant Shape Selectivity*

Reactant selectivity occurs when only part of the reactant molecules are small enough to diffuse through the catalyst pores. Consequently, the reaction is selective toward the conversion of suitable size reactant molecules (Figure 2.5).

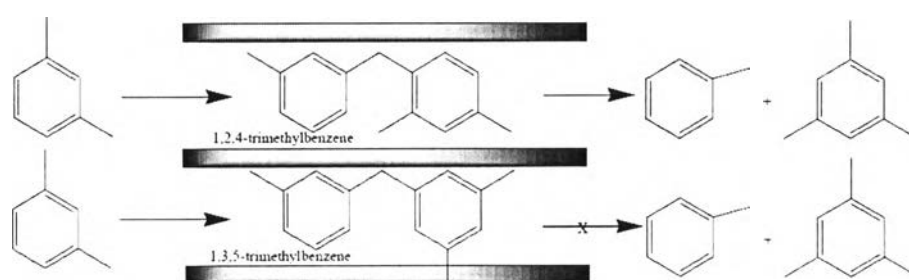


**Figure 2.5** Reactant Shape Selectivity of cracking C<sub>6</sub>-C<sub>8</sub> alkane

(<http://chem.flas.kps.ku.ac.th/01403443/01403443-REPORT-CATYLSIS-ZEOLITE.pdf> ).

### 2.1.4.2 Restricted Transition State Shape Selectivity

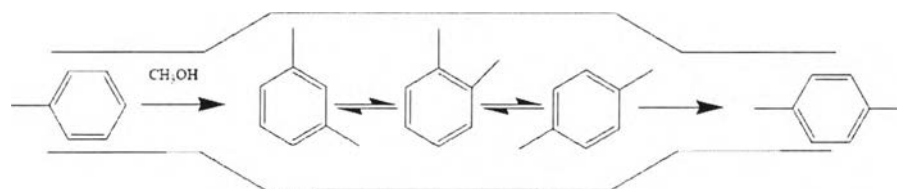
Restricted transition state selectivity is depicted in Figure 2.6. This selectivity occurs when the reactions are prevented because the corresponding transition state would require more space than available in the cavities. Neither reactant nor potential product molecules are prevented from diffusing through the pores. Reactions requiring smaller transition states proceed unhindered.



**Figure 2.6** Intermediate shape selectivity of Disproportionation m-xylene (<http://chem.flas.kps.ku.ac.th/01403443/01403443-REPORT-CATYLSIS-ZEOLITE.pdf>).

### 2.4.1.3 Product Shape Selectivity

Product selectivity occurs when some of the product formed within the pores are too bulky to diffuse out as observed products show in Figure 2.7. They are either converted to less bulky molecules (e.g., by equilibration) or eventually deactivate the catalyst by blocking the pores.

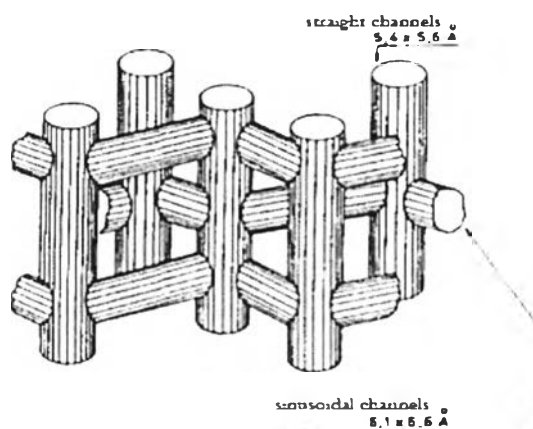


**Figure 2.7** Product shape selectivity of alkylation toluene with methanol (<http://chem.flas.kps.ku.ac.th/01403443/01403443-REPORT-CATYLSIS-ZEOLITE.pdf>).

## 2.2 ZSM-5 Zeolite

Zeolite ZSM-5 is a special type of zeolite. It is a "high-silica" zeolite, which gives it most of its special properties. Zeolite ZSM-5 is moderately hydrophilic to highly hydrophobic (depending on the Si/Al ratio), whereas zeolites like the types A, X and Y are very hydrophilic. The number and type of cations compensating the lattice charge are an important factor as to this property. Zeolite ZSM-5 has a very high temperature (>1000°C) and acid stability (down to pH=3). The last property makes it possible to obtain the hydrogen form directly by exchanging the zeolite in a dilute hydrochloric acid solution without large Al-losses.

The zeolite ZSM-5 consists of a two dimensional network of channels having a structure as shown in Figure 2.8. They have two special pore type intersecting each other and both are formed by 10 membered oxygen ring. The pore type straight channel ellipsoidal ring has varies diameter from 5.1x5.5 Å and other zig-zags has circular opening of 5.4x5.6 Å. Therefore, the average diameter pore is 5.5 Å with a Si/Al ratio ranging between 10 and 500.



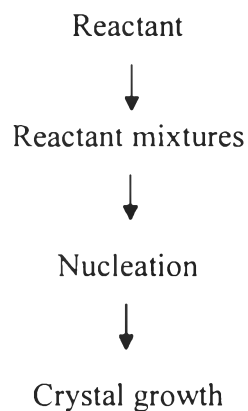
**Figure 2.8** ZSM-5 three dimensional structure and channel system (Valverde *et al.*, 1991).

### 2.2.1 Zeolite Syntheses

H-ZSM-5 zeolite was synthesized by hydrothermal method from a source of alumina, source of silica and an alkali such as NaOH, and/or a quaternary ammonium compound. An inhomogeneous gel is produced which gradually crystallizes, in some cases forming more than one type of zeolite in succession.

Synthetic zeolites are generally made by mixing solutions of aluminates and silicates, often with the formation of a gel, and by maintaining the mixture at temperatures of 100 °C or more for selected periods temperatures of 100 °C or more for selected periods.

The synthesis of zeolites involves several steps, as shown below:



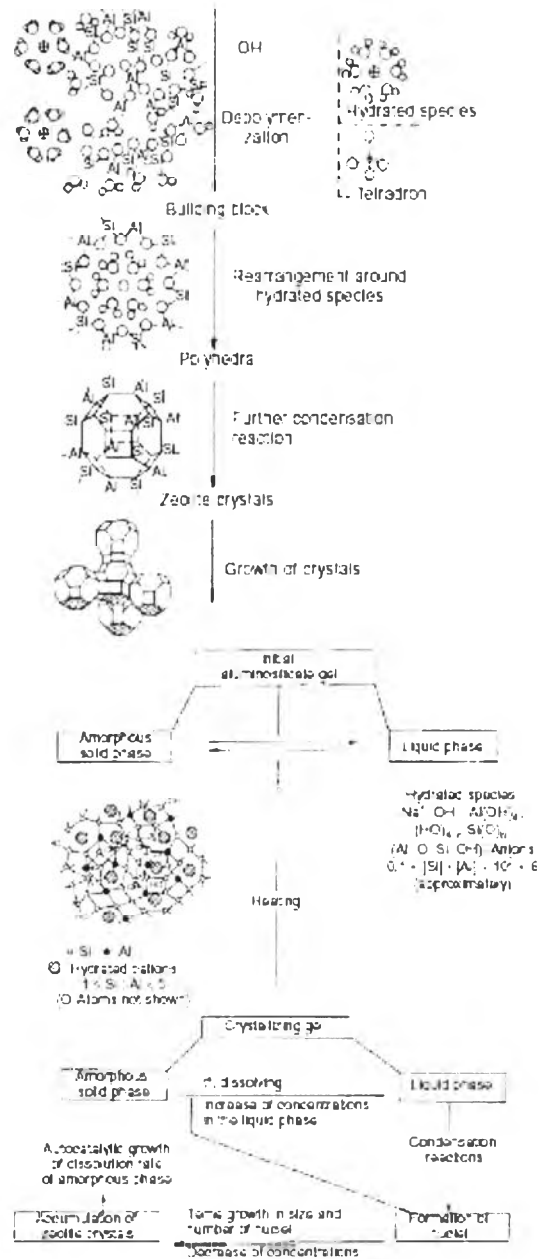


The mechanisms of zeolite formation are very complex due to the plethora of chemical reactions, equilibrium, and solubility variations that occur through the heterogeneous synthesis mixture during the crystallization process. The process of zeolitization is thermally activated and usually takes place at elevated temperatures in order to achieve a high yield of crystals in an acceptable period of time. The variables in the synthesis of zeolites are temperature, alkalinity (pH), and chemical composition of the reactant mixtures. These variables do not necessarily determine the products obtained in hydrothermal reactions because nucleation appears to be kinetically rather than thermodynamically determined and controlled. The kinetic variables include the treatment of reactants prior to crystallization, their chemical, and physical nature.

With reference to the source materials, one would hope that a mole of  $\text{SiO}_2$  would be equivalent to another  $\text{SiO}_2$ , from whatever source, when compounded into agel. Experience teaches us that this is not the case;  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are to some degree polymeric before gelation. Any reagent contains some unsuspected impurities, which can be active on the synthesis. To duplicate the work, one has to repeat with the same source material. The starting material cannot be just silica, but precipitated silica, fumed silica, or silica sol, from a designated supplier. For very high silica phases, the alumina content of the silica source may be very important. Besides, one has to carefully prepare the gel and the step-by-step procedure has to be followed as noted. These steps include the order of mixing, the device used to mix, the aging time and temperature, nucleation, and batch composition. For example, the ingredients are not added sequentially, but combined into two (or three) subgroups that are blended to make the final gel. After a careful preparation of the precursor, a suitable reaction vessel has to be selected to provide the desired temperature, pressure, agitation, and the facility to withdraw an occasional sample. Several companies from the United States of America, Japan, and Germany manufacture autoclaves with all such facilities for the synthesis of zeolites.

The mechanism of zeolite synthesis was divided into two extremes: (i) the solution-mediated transport mechanism, and (ii) the solid-phase transformation mechanism are shown in Figure 2.9. The first one involves the diffusion of aluminate,

silicate, and/or aluminosilicate species from the liquid phase to nucleation site for crystal growth.



**Figure 2.9** Schematic illustrations of the solution-mediated transport (Byrappa *et al.*, 2001).

Rugwong, (2012) studied ethylation of benzene with ethanol to ethylbenzene using synthesized HZSM-5 catalysts. It was demonstrated that the synthesized HZSM-5 catalysts with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 195, which used NaOH and  $\text{NH}_4\text{F}$  as a mineralizing agent and various synthesized temperature and time. The results show that catalyst synthesized by  $\text{NH}_4\text{F}$  were not suitable used for characterization and the catalytic activity because its ratios has not approach to the target of 195. Therefore, HZSM-5 synthesized by NaOH at 120 °C for 72 h provided high EB selectivity. Moreover, at high temperature synthesis (140 °C) gave higher benzene conversion than other conditions.

Karimi *et al.* (2012) studied of the effect of synthesis parameters on ZSM-5 nanocrystalline material during template-hydrothermal synthesis in the presence of chelating agent. ZSM-5 zeolite was synthesized via hydrothermally and using TPABr and TPAOH were as templates. The obtained results are indicated that the average particle size increases with increase of crystallization time. Based on the crystallinity and morphology of the final products, it is obvious that TPAOH is a suitable template for ZSM-5. Crystallization temperature was performed crystallization temperature at 125, 150, 175 and 200 °C and at 175 °C a highly crystalline ZSM-5. Finally, the effect of template concentration that TPA/Si 0.058 was synthesized zeolite with smooth surfaces and high crystallinity.

## 2.2.2 Modification of Catalysts

### 2.2.2.1 *Dealumination*

Dealumination is removal of aluminum from zeolite structure that can generate intracrystalline mesopore and modify its acidic property.

Cesteros *et al.* (2011) studied the dealumination of zeolite beta, mordenite and zsm-5 using acid treatment under microwave irradiation. Dealumination experiments were used Na-Mordenite (Si/Al = 6.5), Na-Beta (Si/Al = 10) and Na-ZSM-5 (Si/Al = 20) treated with HCl 6 M under microwave irradiation at 373 K for 15 min. These zeolite compared with zeolite were acid-treated by autoclaving in a conventional oven at the same temperature and time. The results showed that all zeolite acid-treated under microwaves were faster dealuminated than conventional

heating. Besides, the use of microwaves treated zeolite showed higher mesoporosity, higher Si/Al ratio, higher surface area, and Bronsted acid sites than zeolite treated by conventional heating. When compared with zeolite, beta zeolite was easier to dealuminate than mordenite whereas ZSM-5 was dealuminated vary low. Because each zeolite was different flexibility of framework and approach of aluminium atoms depending on the pores arrangement and sizes.

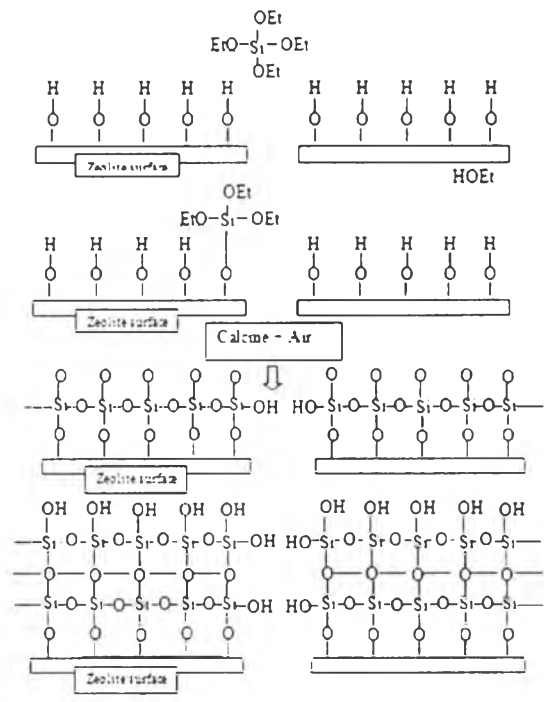
Hu *et al.* (2011) improved dealumination method for modify acidity of HZSM-5 by using self-adsorbed water in HZSM-5. There were two dealumination method. The first, named as “dry steaming dealumination” (DSD) was carried out making full use of self-adsorbed water in the HZSM-5 and then heat from 25-400 °C with a heating rate of 4 °C/min in N<sub>2</sub> flow. The other method, dealumination by traditional hydrothermal method at 500 °C for 4 h. The results showed that HZSM-5 dealumination by DSD method increased Si/Al ratio and produced extra-framework Al (EFAl) when compare parent HZSM-5. The total surface area and Brosted acid sites decrease when compare parent HZSM-5. From the dealumination by DSD method it was found the effect of adsorbed water in the zeolite. When high flow rate of N<sub>2</sub>, HZSM-5 adsorbed water decrease. So the amounts of acid site increase. Compared with the traditional steaming dealumination, DSD method is more effective than the traditional because it is very simple, convenient, efficient, controllable, no additional steam and without using addition or removal of water in zeolite.

Prins *et al.* (2000) studied the dealumination of mordenite using nitric acid is compared with using oxalic acid. The dealumination was remove by acid leaching of mordenite mixed with 60 ml of solution of nitric or oxalic acid at 100 °C. Using three different concentration of each acid: 6, 2 and 1 M of nitric acid, 2, 1 and 0.5 M of oxalic acid and treatment time up to 2 h. The results showed that Si/Al ratio increase to 120 were reached using low concentration of oxalic acid. Whereas Si/Al ratio increase limit to 70 were reached using highest concentration of nitric acid. External surface area (ESA) remained constant at about 14 m<sup>2</sup>/g when using oxalic acid. On the other hand, when used nitric acid was the ESA increase with increasing acid strength and dealumination time. It was found that oxalic acid

was more effective than nitric acid because of dual nature of oxalic acid. Oxalic acid related both as a hydrolyzing and as a chelating agent.

2.2.2.2 *Silylation*

Silylation uses modify the external acid site of zeolite which can be deposited of an inert silica layer from the group of alkoxy silane and polysiloxane such as tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS) and polysiloxane. The modify can be achieved by chemical vapor deposition (CVD) or chemical liquid deposition (CLD) as the molecular diameter of CLD agent is larger than the micropore opening of zeolites. After CLD coating and calcination, silica deposition at the external surface will decompose and leave coating of inactive SiO<sub>2</sub> on the external surface of zeolite, results in deactivation of the active sites and reducing the pore size on external surface. The silylation process is shown in Figure 2.10.



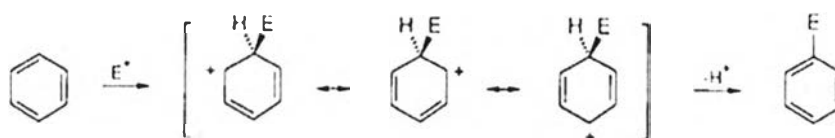
**Figure 2.10** Silylation process  
 (<http://www.slideboom.com/presentations/279497/Silylation-And-Metal-oxide-on-solid-Acids>).

## 2.3 Alkylation of Aromatics

Alkylation of aromatic is a substitution that removes an alkyl group from one molecule to another molecule, one or more of the hydrogen atoms on the ring or side chain is replaced by an alkyl group. This reaction can occur through electrophilic reagent, nucleophilic reagent, or freeradical mechanism.

### 2.3.1 Electrophilic Aromatic Substitution

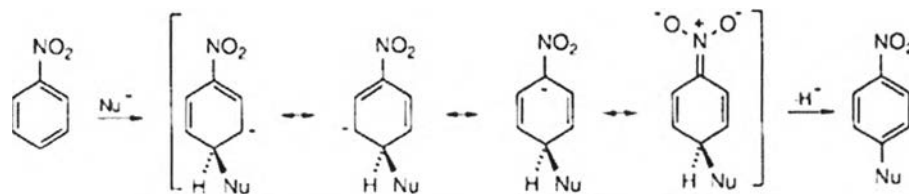
The substitution of benzene by an electrophilic reagent ( $E^+$ ) is schematically presented in Figure 2.11. The reaction occurs in two stages, the reagent adds to one carbon atom of nucleus, giving a carbocation in which the positive charge is delocalized over three carbon atoms, and a proton is then eliminated from this adduct.



**Figure 2.11** The electrophilic aromatic substitution reaction (Norman *et al.*, 1993).

### 2.3.2 Nucleophilic Aromatic Substitution

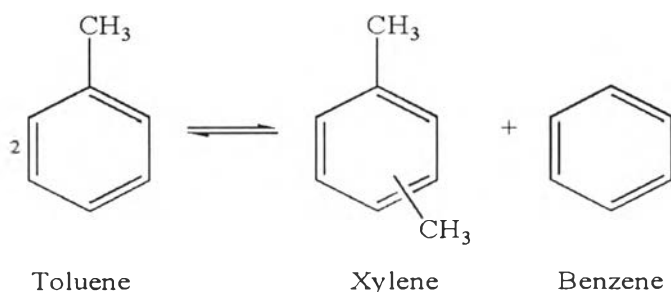
Although benzene is moderately reactive towards electrophiles, it is inert to nucleophiles. However, just as the attachment of a group of  $-M$  type to the  $C=C$  bond in alkene activates that bond to nucleophiles, so the attachment of such substituent to the benzene ring activates the ring to nucleophiles. The mechanism of this, and most other, nucleophilic aromatic substitution is similar to that of electrophilic aromatic substitutions except that an anionic rather than a cationic intermediate is involved. The nucleophile adds to the aromatic ring to give a delocalized anion from which a hydride ion is eliminated (Figure 2.12)



**Figure 2.12** Nucleophilic aromatic substitution reaction (Norman *et al.*, 1993).

## 2.4 Disproportionation

The process of disproportionation is shown in Figure 2.13. This process occurs at higher temperature when compared with the alkylation due to higher activation energies for the transfer of methyl group at the transition state with two toluene molecule and acid sites (Voloshina *et al.*, 2009)



**Figure 2.13** The process of disproportionation (Hilary *et al.*, 2007).

## 2.5 Production of Xylenes

The conventional *p*-xylene process converts toluene to *p*-xylene (and its isomers) in the presence of methanol over a heated catalyst bed of ZSM-5 zeolite. The process follows the following highly exothermic reaction:



The ratio of the isomers, para: ortho : meta is approximately 1:1:2, which is very close to the thermodynamic equilibrium values for the three isomers at the reforming temperature as shown in Table 2.2.

**Table 2.2** Thermodynamic equilibrium values for xylene isomers at three temperatures (Matar *et al.*, 1989)

Component	Amount (wt%) at Reforming Temperature		
	200 °C	300 °C	400 °C
<i>p</i> -xylene	21.8	21.1	18.9
<i>o</i> -xylene	20.6	21.6	23.0
<i>m</i> -xylene	53.5	51.1	47.1
Ethylbenzene	4.1	6.2	11.0

Zhao *et al.* (2010) studied effect of metal modification of HZSM-5 on catalyst stability in the shape-selective methylation of toluene. Modification catalysts by TEOS with 3% SiO<sub>2</sub> show 84-90 % *p*-xylene in the xylene products and high stability. With increasing SiO<sub>2</sub> content enhanced the para selectivity significantly up to 99.5% due to SiO<sub>2</sub> from TEOS was only deposited on the acidic sites of the external surface, which effectively prevented the product *p*-xylene from isomerization and improved the selectivity. The modification with Pt, Pd, Co and Ni metal on nano-scale HZSM-5 were obtain the results that inhibited the formation of coke from alkenes and significantly improved the stability at the condition of high *p*-selectivity.