

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 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.

2.1.1 Electrophilic Aromatic Substitution

The substitution of benzene by an electrophilic reagent (E^+) is schematically presented in Figure 2.1. 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.

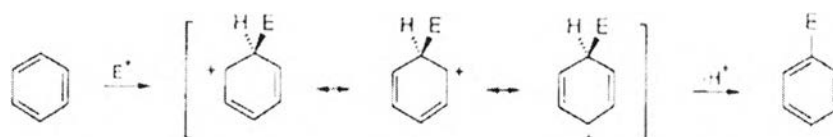


Figure 2.1 The electrophilic aromatic substitution reaction (Norman *et al.*, 1993).

Electrophilic aromatic substitution is the most common method used to synthesize substituted aromatic compounds. The reaction directly introduces functional groups onto the benzene ring and works with a variety of electrophilic reagents. All these reactions are shown below (Figure 2.2 – Figure 2.5).

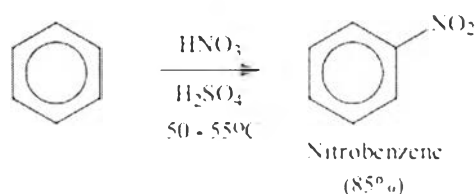


Figure 2.2 Nitration of benzene (Daley *et al.*, 2005).

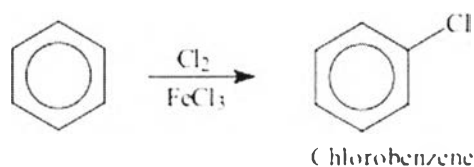


Figure 2.3 Chlorination of benzene (Daley *et al.*, 2005).

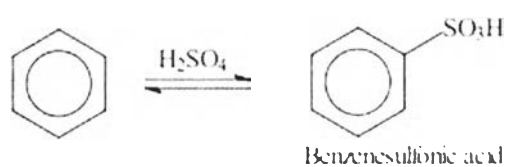


Figure 2.4 Sulfonation of benzene (Daley *et al.*, 2005).

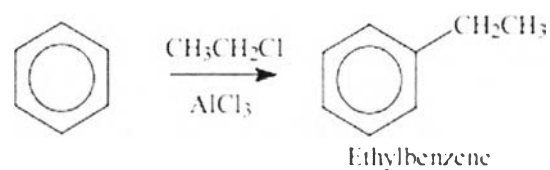


Figure 2.5 Ethylation of benzene (Daley *et al.*, 2005).

2.1.2 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 $\text{C}=\text{C}$ 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 2.6)

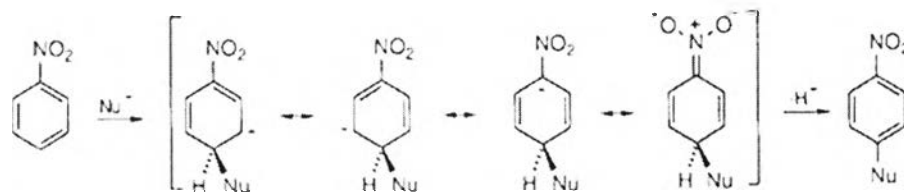


Figure 2.6 Nucleophilic aromatic substitution reaction (Norman *et al.*, 1993).

2.2 Alkylation Catalysts

Catalysts for alkylation reaction used essentially to be of the homogeneous type. However, due to the discovery that certain molecular sieves (Zeolites) are not only acidic enough to promote carbonium ion or ion-pair formation, but are also more selective than homogeneous catalysts, they are now being used in some new alkylation processes

Homogeneous alkylation catalysts may be Brønsted acid such as HF and H₂SO₄. Using alkenes as alkylating agent, a proton is donated by the acid to the substrate as shown in Figure 2.7.

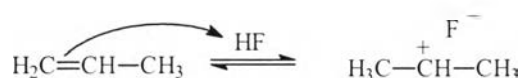
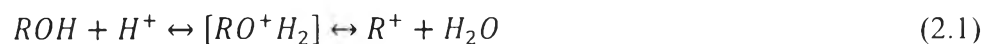


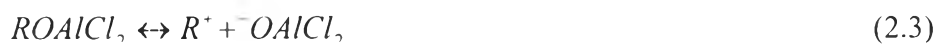
Figure 2.7 The formation of carbocation by using alkenes (Wade, 2009).

When alkenes are treated with a Lewis acid such as AlCl₃, a small amount of a proton acid is normally added as a co-catalyst to promote the formation of carbonium ions.

If alcohols are the alkylating agents in the presence of Brønsted acid, they are protonated and carbonium ions may be formed.



In the presence of Lewis acids, such as AlCl₃, a complex is first formed with the alcohol and HCl is released. The complex then donates the carbocations.



Alkyl halides have been extensively used to alkylate aromatic compounds when $AlCl_3$ is used as the catalyst, the reaction is normally referred to as Friedel-Crafts alkylation. The first step in alkylating aromatics, is the formation of a carbonium ion as shown in Figure 2.8.

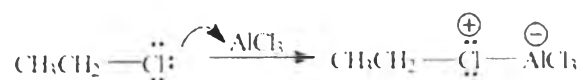
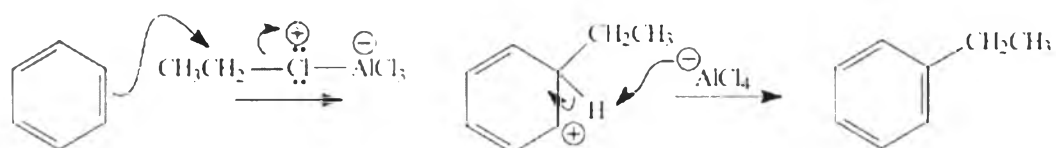


Figure 2.8 Friedel-Crafts alkylation (Daley *et al.*, 2005).

The benzene ring then undergoes electrophilic attack by the complex to form a σ complex—completing the first step of the electrophilic aromatic substitution reaction. Immediately following the first step, the σ complex undergoes



the second step and loses a proton to form the alkyl benzene as shown in Figure 2.9.

Figure 2.9 Friedel-Crafts alkylation (Daley *et al.*, 2005).

Alkylation with heterogeneous catalysts has been carried out using a variety of acidic oxides such as Al_2O_3 and Al_2O_3 and Al_2O_3/SiO_2 . These catalysts also promote carbonium ion-type reactions. Depending on the method of preparation, silica/alumina catalysts may be amorphous or crystalline. These compounds have both Brønsted and Lewis acid sites. When alkylating toluene with methanol, on a zeolite catalyst for example, adsorbed methanol is protonated at a Brønsted acid site on the catalyst surface forming a protonated form of methanol.

Protonated form of methanol then attacks the toluene ring giving xylene

isomer and the proton is regained by zeolite as shown in Figure 2.10.

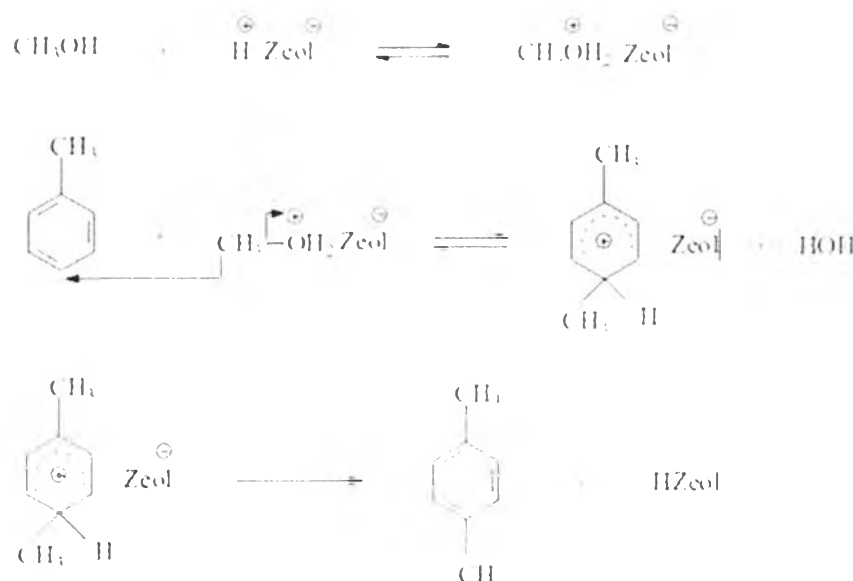
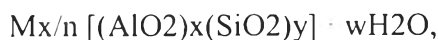


Figure 2.10 Mechanism of toluene alkylation with methanol using H-zeolite (Aboul-ghheit *et al.*, 2011).

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

2.3 Zeolites

Zeolites are crystalline, micro porous, hydrated aluminosilicates that are built from an infinitely extending three dimensional network of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral linked to each other by the sharing of oxygen atoms [1]. Generally, their structure can be considered as inorganic polymer built from tetrahedral TO_4 units, where T is Si^{4+} or Al^{3+} ion. Each O atom is shared between two T atoms. The structure formula of zeolite is based on the crystallographic unit cell (Bekkum *et al.*, 1991).



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.

The primary building unit of zeolites as shown in Figure 2.11 is the tetrahedron and the secondary building units (SBUs) are the geometric arrangements of tetrahedral (Breck *et al.*, 1974). The SBUs may be simple polyhedral such as cubes, hexagonal prisms, or cube-octahedral (Bekkum *et al.*, 1991). The structures can be formed by repeating SBUs and according to them zeolites can be classified into eight groups. In Figure 2.12 are presented components of the structure zeolite.

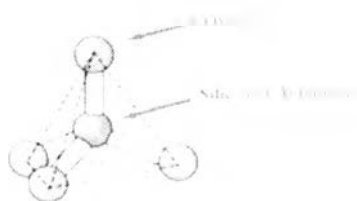


Figure 2.11 Primary building unit of zeolite structure

(http://www.sustz.com/Proceeding09/Papers/Technical%20studies/D_GEORGIEV.pdf).

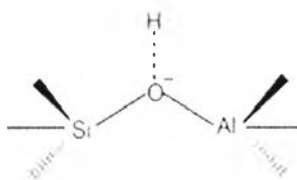


Figure 2.12 Chemical structure of zeolite

(http://www.sustz.com/Proceeding09/Papers/Technical%20studies/D_GEORGIEV.pdf).

Zeolite open-structure framework consists of many channels and/or interconnected voids of discrete size (in the range 0.3-20 Å) which are occupied by cations and water molecules. Each AlO_4 tetrahedron in the framework bears a net

negative charge which is balanced by a cation. Typically, these counter ions are elements from the IA and IIA groups of the periodic table. The cations can reversibly be exchanged for other ions possessing the same sign charge when aqueous passed through channels and voids. This replacement results in the narrowing of the pore diameter of the zeolite channels. The water may be removed reversibly by the application of heat. The SBUs can be simple arrangements of tetrahedral such as four, six, eight, ten or more complicated membered ring. Other factors such as the location, size and coordination of the extraframework cations can also influence the pore size. Some simple zeolite SBUs and their shorthand notations are given in Table 2.1 (Breck, 1974).

Table 2.1 Classification of zeolite structures (Breck ,1974)

| Number of linked tetrahedral | SBU created | Shorthand description |
|------------------------------|------------------|-----------------------|
| 4 | 4oxygen ring | S4R |
| 5 | 5oxygen ring | S5R |
| 6 | 6 oxygen ring | S6R |
| 8 | 8 oxygen ring | S8R |
| 8 | 4-4 oxygen rings | D4R |
| 12 | 6-6 oxygen rings | D6R |
| 16 | 8-8 oxygen rings | D8R |

One of the main properties that make zeolites attractive catalysts for a broad spectrum of chemical conversions is their high thermal stability. While most zeolites remain intact at temperature up to ca. 650 °C, structural collapse of some high-silica zeolites only occurs at temperatures above 1000 °C (Basaldella *et al.*, 1995). In the following, three further key properties of zeolite catalysts, namely acidity, shape selectivity and the Si/Al ratio effect, will be briefly addressed.

2.3.1 Acidity

Zeolites consist of a 3-D network of metal–oxygen tetrahedral which provide the microporous structure, in which the active sites are part of the structure. Acid sites result from the imbalance of the metal and the oxygen formal charge in the primary building unit. Acid sites in zeolites can be divided into Brønsted acid sites and Lewis acid sites. The formation of Brønsted 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 Brønsted acid sites are shown in Figure 2.13.

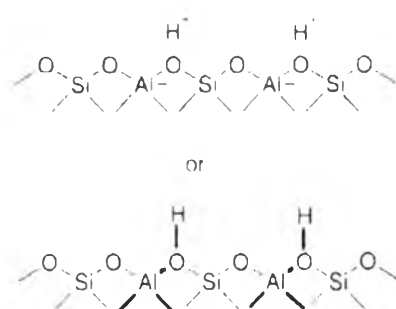


Figure 2.13 Brønsted acid sites (“bridging hydroxyl groups”) in zeolites (Stocker, 2005).

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 (Figure 2.14).

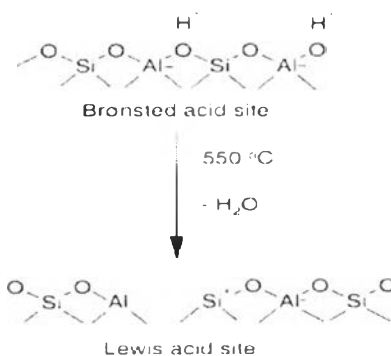


Figure 2.14 Formation of Lewis acid sites in zeolites (Stocker, 2005).

2.3.2 Shape Selectivity

The dimensions of the species involved in chemical reactions are of the same order of magnitude as those of the pores and cavities of zeolites often imposes a strong influence on the selectivity of zeolite-catalyzed reactions. A catalytic reaction proceeds in a shape-selectivity manner, if its selectivity depends unambiguously on the pore width or pore architecture of the solid catalyst. Shape selectivity is a unique feature of heterogeneous catalysis by zeolite.

The shape selectivity does not only depend on the pore system zeolite catalyst but also on the dimension of the species involved, i.e., the reactant molecules, the products molecules, the reaction intermediates and the transition states. After the classical concept of Weisz *et al.* (1980) and Csicsery *et al.* (1986) shape selectivity effects are usually classified into the three different types.

2.3.2.1 Reactant Shape Selectivity

It describe the phenomena, only those reactants can be converted that are of proper size to enter the intrazeolitic pores as shown in Figure 2.15. Consequently, the reaction is selective toward the conversion of suitable size reactant molecules.

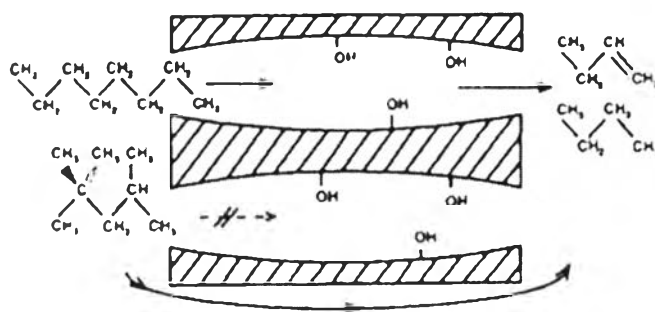


Figure 2.15 Reactant shape selectivity (Baerns *et al.*, 2004).

2.3.2.2 Product Shape Selectivity

When a chemical reaction inside a zeolite leads to products of different molecular size, the diffusion of the smaller product molecules out of the zeolite pores will be preferred, and only this product may be detected in the reactor effluent. The other product which is too bulky to leave the zeolite pores may undergo

consecutive reactions to either smaller molecules or to higher molecular species that remain adsorbed in the zeolite as shown in Figure 2.16, eventually leading to catalyst deactivation by pore blockage. Product shape selectivity may be viewed as the reverse of reactant shape selectivity.

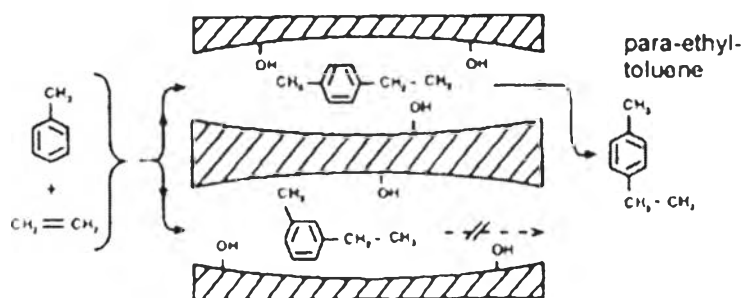


Figure 2.16 Product shape selectivity (Baerns *et al.*, 2004).

2.3.2.3 Restricted Transition State Shape Selectivity

Under the local constraints inside a zeolite pore one reaction may be favored over other parallel or consecutive reactions, if the corresponding transition state (or intermediate) is less bulky. For instance, the pores of a zeolite may provide sufficient space for the transition state of the intramolecular isomerization of *m*-xylene, while the transition state of the bimolecular transalkylation reaction is too bulky to be accommodated inside the pores and hence, no disproportionation products can be formed as shown in Figure 2.17.

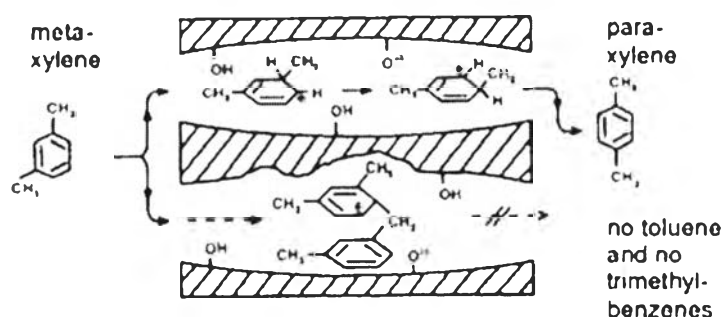


Figure 2.17 Restricted transition state shape selectivity (Baerns *et al.*, 2004).

ZSM-5 zeolites have made it possible to develop a new process for the selective production of *p*-xylene due to shape of ZSM-5, which is suitable for mono-aromatic selective reactions.

2.4 Zeolite Si/Al molar ratio

When the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio decreased, Zeolite acidity increases in strength due to the increase in AlO_4^- sites, which strengthens the electro-static field in the zeolite and increases the number of acid sites. However, the wide array of cage and channel arrangements and electrochemical properties that result from various crystalline structures and different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios also affect zeolite acid strength. In certain conditions, a high density of AlO_4^- in the zeolite framework could actually lower the acid strength of the adsorbent the reverse in acid strength can be explained by the dipolar repulsion of the AlO_4^- Groups outweighing the increase in polarizability. For the reasons stated, an increase in zeolite activity as the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ increases is normally observed. Manipulating both the exchanged cations and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio offers a great flexibility in tailoring adsorbents for a specific application. However, the more variables that are altered, the more difficult the adsorption behavior becomes to predict (Kulprathipanja, 2010).

2.5 ZSM-5 zeolite

A primary unit cell of zeolite ZSM-5 is shown in Figure 2.18. The secondary building unit for ZSM-5 is the $T_{12}O_{20}$ block and the ZSM-5 unit cell contains 96 T-atoms also shown in Figure 2.18.

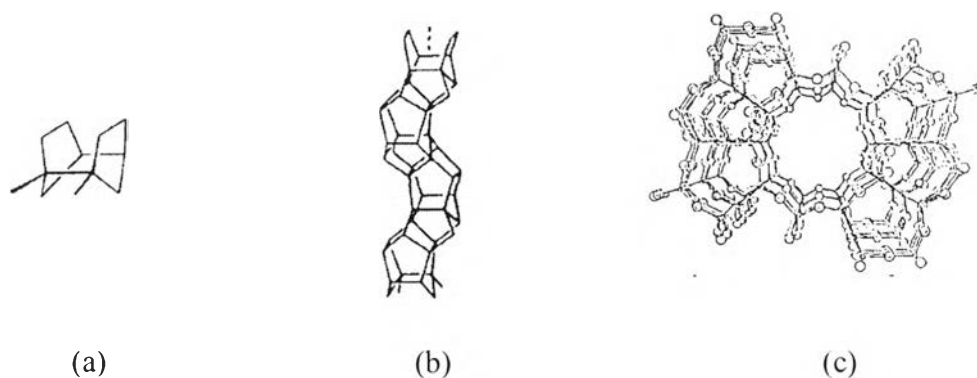


Figure 2.18 (a) A Primary unit cell of ZSM-5 (b) The secondary building unit of ZSM-5 (c) Unit cell of ZSM-5 (Breck ,1974).

The complete zeolite structure does not fill the complete space. It contains cavities in the form of cages and channels. These pores will contain the adsorbed species when the zeolite is filled with an adsorbate. The intracrystalline space is substantial: a zeolite can have a void volume of up to 0.48 ml/ml (0.31 ml/g for H_2O adsorption in CaA zeolite, (Breck, 1974). Zeolite ZSM-5 has a pore system as shown in Figure 2.19, it consists of a system of intersecting straight and sinusoidal channels. For clarity, the channels in the schematic drawing in Figure 2.18 are drawn with a smaller diameter than actually is the case. In the photograph the channels are shown in the right scale. The void volume of this zeolite is 0.17 ml/g, so this zeolite has a higher structural density than for instance zeolite A. The channels in ZSM-5 have a diameter of 0.50 to 0.56 nm, leaving enough space to allow passage of aromatic nuclei like benzene, *p*-xylene and pyridine(s).

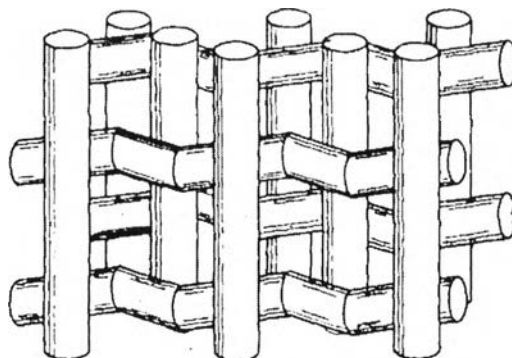


Figure 2.19 Channel structure of ZSM-5 (Breck, 1974).

2.6 Modification of Catalyst

As the commercial HZSM-5 zeolite which show the low selectivity to *p*-xylene. It was suggested that the selectivity to *p*-xylene could be improved by the catalyst modification with various methods such as impregnation of metallic or nonmetallic compounds, coke deposition, dealumination, chemical liquid deposition (CLD), chemical vapor deposition (CVD), etc. Deposition of an inert silica layer onto the external surface of the HZSM-5 catalyst by CLD has been demonstrated to be effective for obtaining a high *p*-xylene selectivity due to the deactivated external acid sites which can cause an isomerization of *p*-xylene to *o*- and *m*-xylene resulting in decreasing the selectivity to *p*-xylene (Cejka *et al.*, 1996). In addition, the acid properties and resultant catalytic activity of zeolite materials are known to be related to the degree of substitution of aluminum for silicon in the framework. As the dealumination with acid agent which have molecular diameters larger than zeolite pore openings, they could be used to selectively remove the framework aluminum at the external surface of HZSM-5 catalyst as well.

2.6.1 Dealumination

The term dealumination generally refers to the removal of aluminum from the zeolite framework, even though the overall aluminum content of the zeolite may not drastically change. Alumina may still reside in the pores either on cation positions or as deposits of other compounds like amorphous silica-alumina of

aluminum salts which is all referred to as “extra-framework aluminum”. Many procedures for framework dealumination are known which may be subdivided into thermal treatments, hydrothermal treatment, extraction of framework aluminum with acid and replacement of framework aluminum with silicon from silicon halides or hexafluorosilicate (Weitkamp *et al.*, 1999). In Figure 2.20 show dealumination via hydrothermal treatment and acid leaching. Due to the sometimes harsh conditions applied, creation of secondary pores (mesopores) and production of crystal defects with partial, but considerable loss of crystallinity can occur during dealumination.

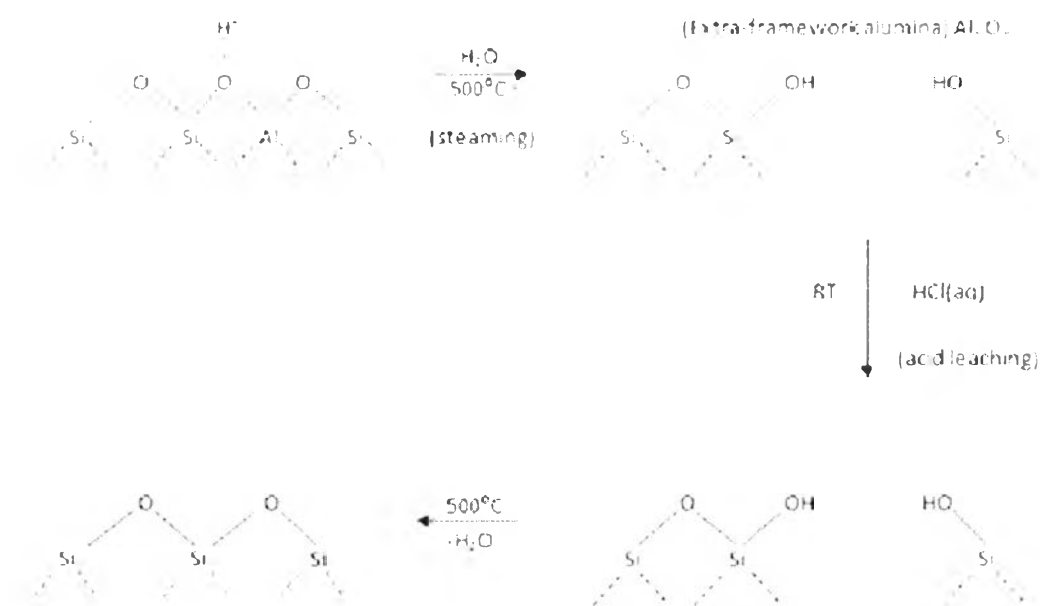


Figure 2.20 Dealumination via hydrothermal treatment and acid leaching.

Lucas *et al.* (1997) has observed the effect of steaming on acidity and aromatization activity with dealumination of HZSM-5 zeolites. The result showed that deactivation via steaming treatment produces a decrease in acid sites strength and density, which is related to coke formation. Infrared data show an increase in weak and Lewis acid sites. Furthermore, medium/strong acid sites ratio is close to unity for catalyst with the best deactivation behavior. Steam-HCl treatment also produces a decrease in the acid strength and density, leading to a similar acid strength distribution than steamed catalysts. The best deactivation behavior found in

these catalysts must be explained in terms of toxicity of coke, which is dependent on coke content, location and nature.

Mihalyi *et al.* (2012) studied the effect of extra-framework Al (EFAl) formed by successive steaming and acid leaching of zeolite MCM-22 on its structure and catalytic performance. The result showed that 1.) the present of EFAl entities causes blocking of the zeolite micropores and leads to significant reduction in their adsorption capacity and catalytic activities. This effect is assumed to be a particular feature of the steam-acid dealuminated MCM-22. 2.) the proposed by other authors selective replacement of proton sites by such steam-acid dealumination of MCM-22 Zeolite should be implied not only as definite extraction and elimination of the framework Al atoms connected to bridging protons but also as a process of burying of these acid sites inaccessible and inefficient and is the reason for the observed enhanced -xylene selectivity. 3.)The presence of residual EFAl species limits the access of the reactant molecules to the catalytically active sites, leads to reduced activity in m-xylene conversion, affects the products distribution in both reactions of m-xylene isomerization and disproportionation and determines the mode of coke formation.

2.6.2 Silylation

Silylation is a process in which zeolite was treated with silicon compounds selected from the group of alkoxy silane and polysiloxanes. Silylation can modify the external acid site of zeolites by an introduction of a silicon compounds which have a larger kinetic diameter than the pore of zeolites such as tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS) and polysiloxane. Example structures of silylation agents are shown in Figure 2.21.

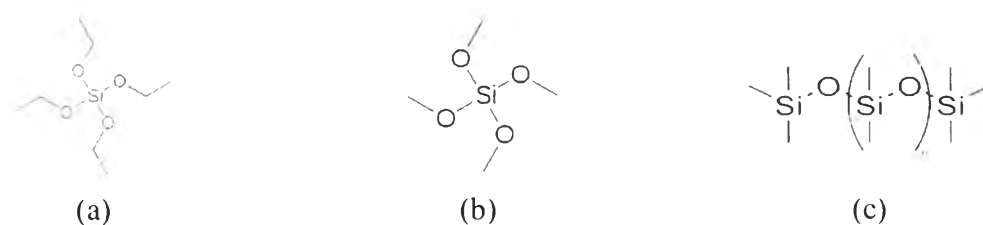


Figure 2.21 Silylation agents (a) TEOS, (b) TMOS and (c) polysiloxane.

In Silylation process the silicon compound will react with the

hydroxyl group of zeolites at the external surface which result in silica deposition on the external surface. After calcination, silica deposition at the external surface will decompose and leave coating of inactive SiO_2 on the external surface of zeolite, results in deactivation of the active sites and reducing the pore size on external surface. The schematic of silylation process is shown in Figure 2.22.

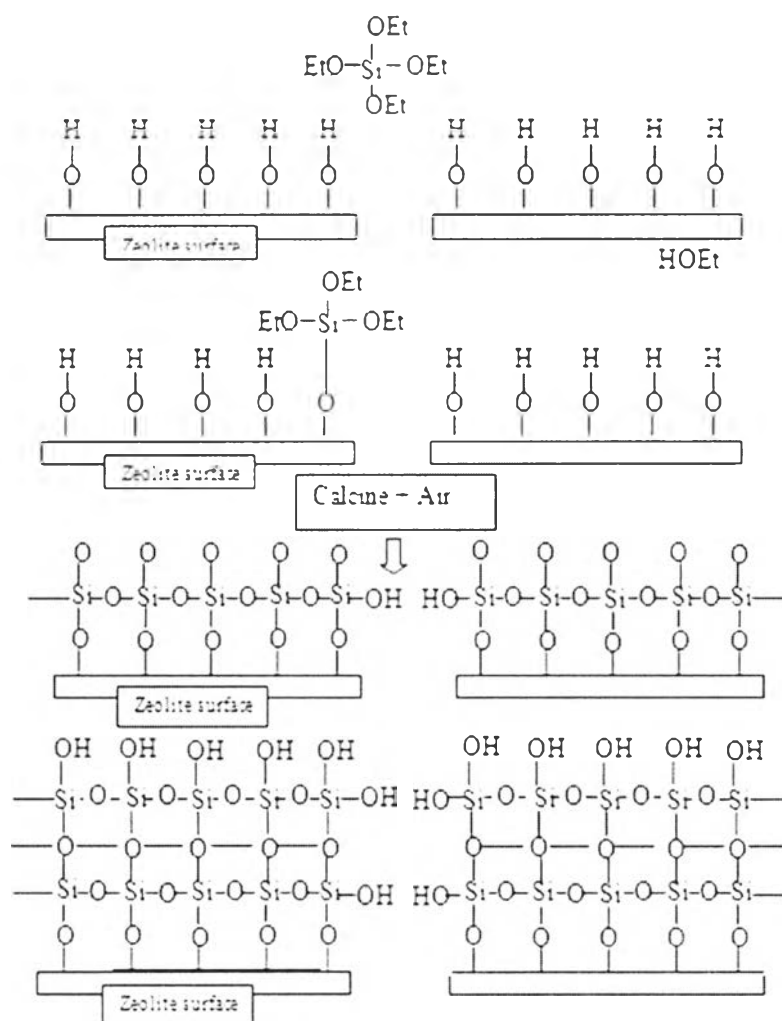


Figure 2.22 Schematic of the silylation process

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

Hui *et al.* (2011) studied the effect of modified ZSM-5 Zeolite Catalyst with using chemical liquid deposition with tetraethyl orthosilicate (TEOS) for disproportionation of toluene. The catalyst were prepared by the modification of the cylinder-shaped ZSM-5 zeolite extrudates with chemical liquid deposition with

TEOS. Various parameters for preparing catalyst were changed to investigate including $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of ZSM-5 zeolite, the type and amount of deposition agent, the type of acid-treatment for dealumination, the time and cycle of deposition treatment. The results showed that, 1.) The ZSM-5 zeolite extrudates with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 38 demonstrated the highest conversion of 48.7% 2) TEOS as CLD agent evidently behaved the best for its highest para-xylene selectivity together with a very high toluene conversion, the amount of TEOS was 0.4ml per gram catalyst. 3) The acid treatment ZSM-5 showed the same level para-xylene selectivity to the untreated sample. However, when the acid-treated ZSM-5 zeolite extrudates were further modified by CLD, the resulting catalysts showed very different activities compared with the sample without an acid-treatment para xylene selectivity over the three organic acid-treated catalysts was enhanced substantially. Moreover, oxalic acid simultaneously caused a higher conversion. 4.) The appropriate CLD time was 7-10 h with two-cycle CLD.

2.7 Production of Xylenes

2.7.1 Alkylation of Toluene with Methanol

Xylenes are mainly produced by a distillation-extraction scheme from reformed gasolines. Xylenes are important precursors for many chemicals. 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

p-Xylene is the most important of the three isomers since it is utilized for the synthesis of terephthalic acid for polyester production. A process that selectively produces *p*-xylene may be economically competitive to the currently used scheme.

p-Xylene is produced by disproportionation of toluene and *p*-xylene-oriented isomerization of mixed xylene isomer. However, these processes will produce a large quantities of benzene so the cost of isolation and purification is relatively high. The catalytic methylation of toluene is a very promising alternative method of producing *p*-xylene without any by-product. A variety of zeolites have

been used for catalyzing this reaction.

Recent work for alkylation of toluene with methanol using HY-zeolite and ZSM-5 at a temperature range of 300-700°C has shown that over 90% selectivity for *p*-xylene could be reached. If this process proves feasible, the alkylation of toluene over shape-selective zeolites may be utilized in the future.

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

| Aromatic wt% | Reaction 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 |

2.7.2 Catalysts

The catalysts are predominantly modified ZSM-5 zeolite. In general, the modification is intended to restrict pore mouth size to promote the shape selective production of *p*-xylene within the microporous structure. The similar modification also serve to remove external acid sites and eliminate the consecutive isomerization of *p*-xylene. Methods used to modify the zeolite pore opening have included silylation, incorporation of metal oxides such as MgO, ZnO and P₂O₅, steaming and the combination of steaming and chemical modification (Kulprathipanja, 2010).

Zhu *et al.* (2005) investigated the roles of acidity and structure of zeolite for catalyzing toluene alkylation with methanol by using a variety of zeolites, including MOR, MCM-22, SAPO-34, SAPO-11, SAPO-5 and ZSM-5 with different SiO₂/Al₂O₃ ratios. The result showed that the catalytic activity of zeolite for the alkylation is approximately proportional to the number of its mid-strength acidic sites, except for SAPO-34 with small channels (8 membered-ring) and MOR with strong acidity. Moreover, the acidic sites for catalyzing toluene alkylation are weaker

in strength than those for catalyzing toluene disproportionation, but slightly stronger than those for catalyzing the reaction of methanol to hydrocarbons. On the other hand, zeolites with 12-membered ring (MOR, SAPO-5) channels may lead to the further alkylation of xylene rapid deactivation by coking. Zeolite with 8-membered ring channels restrict toluene alkylation, only favorable for forming non-aromatic hydrocarbons. As a result, zeolite with 10 membered ring channels and mid-strength acidity show high catalytic selectivity and activity for the toluene alkylation with methanol to xylene including, ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 136$), SAPO-11 and MCM-22, they show more than 70% selectivity of toluene to xylene and >30% toluene conversion.

Breen *et al.* (2007) observed the improved selectivity in the toluene alkylation reaction through understanding and optimizing the condition of process. The toluene alkylation was carried out at reaction 440 °C with HZSM-5 zeolite $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 80. The research were focused on effect of boron content of catalyst, methanol feed concentration, weight hourly space velocity (WHSV) and water concentration in the feed. The results showed that the born content of $\geq 6\%$ exhibited the highest para-xylene selectivity. Toluene conversion was increased when increasing of methanol concentration and decreasing of WHSV but no effect on para-selectivity which remain constant at > 99.9% and the highest toluene conversion and selectivity to p-xylene were observed at a molar ratio of water to methanol of 9:1.

Zhao *et al.*, 2010 studied the effect of metal modification on the catalytic performance, especially the catalyst stability. Toluene methylation was carried out in a continuous flow fixed bed reactor at 460 °C, 2.0 h^{-1} WHSV with P-MG modified nano-scale HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$). The results showed that P-Mg modified catalyst with 3 wt% SiO_2 exhibited excellent stability (more than 500h) but lowered p-xylene selectivity (less than 90%) Upon further increasing the amount of SiO_2 , the catalyst deactivated in a relatively short time on stream, although the para-selectivity was significantly increased up to 99.5%. The high p-xylene-selectivity catalyst modified further with Pt, Pd, Co, Ni, metal demonstrated excellent stability and high para-selectivity more than 98.3% with toluene conversion of 20% was achieved. Hence, loading metals with good hydrogenation properties such as Pt, Pd,

Co and Ni, was an effective method to improve the catalyst stability.

Aboul-Gheit *et al.* (2011) observed the effect of Pd loading on H-ZSM-5 catalyst for toluene alkylation with methanol. The catalytic runs were carried out in a fixed-bed down-flow reactor at temperatures between 300 °C and 500 °C, a space velocity of 2.6 h⁻¹, a series of catalysts containing 0.1, 0.2 or 0.3 Pd in HZSM-5 zeolite. The result showed that para-xylene selectivity was increase systematically with increasing the Pd content in the catalysts because Pd has tailored the pore diameter and caused more restricted diffusion of the larger isomers: (ortho- and meta-xylenes) relative to the diffusion of para-xylene. Although, para-xylene production was the highest on the 0.2% Pd/HZSM-5 catalyst. The heavy undesied trimethylbenzenes were the lowest to be formed on the 0.3% Pd containing catalyst. In Comparison of the para-xylene selectivity on the current Pd/H-ZSM-5 catalysts with that on the corresponding Pt/HZSM-5 catalysts (in a recently published investigation, Aboul-Gheit *et al.*, 2010). Evidently, the current Pd/H-ZSM-5 catalysts are more significantly para-selective than those containing platinum. This can be attributed to the difference in atomic weight of Pt and Pd.