CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Background

Finding alternative ways to utilize toluene is an interesting way to increase the value of toluene because the direct uses of toluene are somewhat limited. In industry, toluene is widely used as solvent and feedstock for benzene and xylenes production. In this research, a new way to utilize toluene is proposed. Toluene can be utilized by alkylate with ethanol to produce *p*-ET, an important precursor for subsequent dehydrogenation and polymerization to produce poly(*p*-methyl styrene) (PPMS), a polymer which can be replace polystyrene, if required. PPMS has advantages over polystyrene such as higher flash point and glass transition temperatures and lower specific gravity. In addition, *p*-ET production from toluene would provide advantage of utilizing toluene to replace benzene in polystyrene production. In addition, *p*-ET production from ethylation of toluene with ethanol has an advantage over traditional process (such as ethylation of toluene with ethylene and methylation of ethylbenzene with methanol or methane), because ethanol can derive from renewable resources.

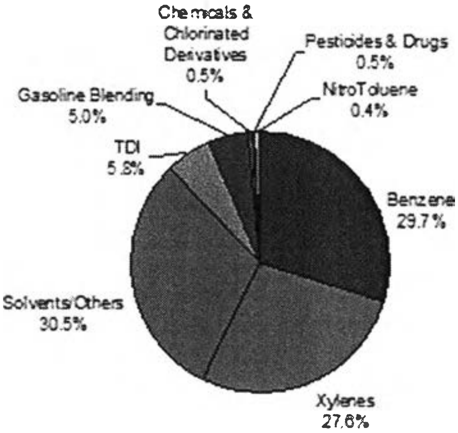


Figure 2.1 Global toluene demand by end-use segments in 2010. (http://www.giiresearch.com/press/gbi214305.shtml)

2.2 *p*-Ethyltoluene

p-Ethyltoluene (*p*-ET) is an important precursor made for subsequent dehydrogenation to *p*-methylstyrene, the monomer for poly(*p*-methylstyrene) (PPMS) production (Figure 2.2). *p*-Ethyltoluene is traditionally produced via alkylation of toluene with ethanol or ethylene in the presence of acid catalysts. The uses of poly(*p*-methylstyrene) instead of polystyrene provides new advantages of utilizing toluene to replace benzene in polystyrene production.

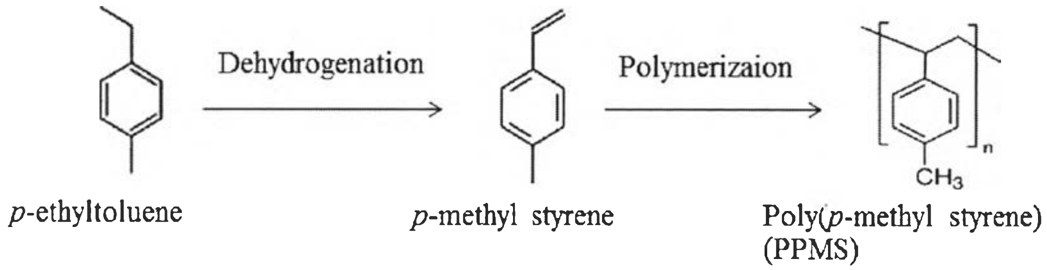


Figure 2.2 PPMS production from *p*-ET.

The properties of poly(*p*-methylstyrene) comparing to polystyrene are shown in Table 2.1. An important advantage of poly(*p*-methylstyrene) is its lower density relative to polystyrene which makes poly(*p*-methylstyrene) lighter than polystyrene. Moreover, poly(*p*-methylstyrene) has a higher glass transition temperature than polystyrene which makes poly(*p*-methylstyrene) safer for higher temperature use and storage, a higher glass transition temperature also results in a decrease in the molding cycle times, which is better for mold fill properties.

Table 2.1 Comparison between poly(*p*-methylstyrene) and polystyrene (Kaeding, 1983)

Property	Poly(*p*-methylstyrene)	Polystyrene
Specific gravity (g/ml)	1.01	1.05
Melt flow rate (condition C)	2.5	2.5
Thermal properties		
Glass transition temp (°C)	113	102
Vicat Softening (°C)	116	109
Heat distortion temp. (°C)	95	89
Mechanical properties		
Tensile strength at break (psi x 10^3)	7.0	7.6
Elongation (X)	3.0	3.0
Tensile modulus (psi x 10^{-5})	3.2	3.6
Flexural strength (psi x 10^{-5})	12	13
Hardness (Rockwell M)	82	74
Izod impact (ft·lbs./in.)	0.3	0.3

2.3 Alkylation

Alkylation is the reaction that transfers 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. The alkyl group may be transferred as an alkyl carbocation, a free radical, a carbanion or a carbine. Alkylation is an important part of organic synthesis and alkylating agents are widely used in creating medicines and industrial specialty chemicals. Alkylation with an ethyl group is known as ethylation.

2.3.1 Alkylating agent

Alkylating agent is a chemical substance that will add an alkyl group to another molecule in alkylation. Alkylating agents are classified according to their nucleophilic or electrophilic characteristic.

Nucleophilic alkylating agents deliver the equivalent of an alkyl anion (carbanion). These compounds typically can add to an electron-deficient carbon atom such as at a carbonyl group. Nucleophilic alkylating agents can also displace halide substituents on a carbon atom.

Electrophilic alkylating agents deliver the equivalent of an alkyl cation. Some of the most important electrophilic aromatic substitutions are aromatic nitration, aromatic halogenation, aromatic sulfonation, and acylation and alkylating Friedel-Crafts reactions.

2.3.2 Alkylation mechanism

For the example of an electrophilic alkylation, which in the simplest case is benzene as shown in Figure 2.3, in the first step of the reaction the electron-rich aromatic ring attacks the electrophile A. This step leads to the formation of a positively-charged cyclohexadienyl cation which is unstable, owing both to the positive charge on the molecule and to the temporary loss of aromaticity. However, the cyclohexadienyl cation is partially stabilized by resonance, which allows the positive charge to be distributed over three carbon atoms. In the second stage of the reaction, a Lewis base B donates electrons to the hydrogen atom at the point of electrophilic attack, and the electrons shared by the hydrogen return to the pi system, restoring aromaticity.

An example of nucleophilic substitution mechanism is shown in Figure 2.4. The mechanism involves an electron rich nucleophile attack on the aromatic ring to give a resonance stabilized carbanion. The leaving group, such as a halide (X) on an aromatic ring, then departs to restore the aromaticity. Strong resonance electron withdrawing groups usually must be present in the ortho or para positions to stabilize the carbanion intermediate.

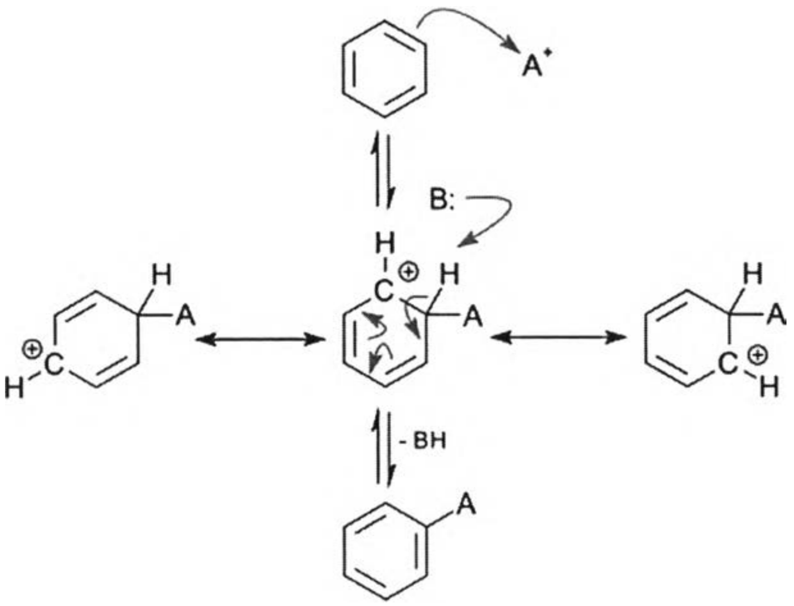


Figure 2.3 The electrophilic aromatic substitution reaction. (http://en.wikipedia.org/wiki/Electrophilic_aromatic_substitution#Reaction_mechanism)

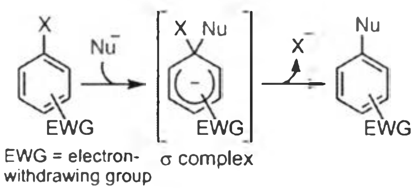


Figure 2.4 The example of nucleophilic substitution. (http://en.wikipedia.org/wiki/Nucleophilic_aromatic_substitution)

2.4 Disproportionation

Disproportionation is an important side reaction in alkylation of toluene. The disproportionation is taken place at higher temperatures compared with the alkylation due to higher activation energies for the transfer of methyl groups at the transition state with two toluene molecule and acid sites (Voloshina *et al.*, 2009).

Voloshina *et al.* (2009) reported the disproportionation mechanism of toluene on pentasil zeolites, the primary conversion products of toluene disproportionation are *p*-xylene and ethylbenzene. Form Figure 2.5, first step in toluene disproportionation is the protonation of toluene at the methyl groups, carbocation with a penta coordinate carbon atom is formed. The carbocation of first step most likely reacts with the CH group of the next toluene molecule found in the para position and also bearing some negative charge to form a binuclear activated complex or transition state. The Substantial difference between the carbocation moiety in the activate complex and the initial carbocation will involve the weakening of the bond between the -CH_4^+ group and the benzene ring, which will promote realization of a step of α- scission of this complex. The carbocation in step 3 is converted to xylene product by returning the proton to the catalyst.

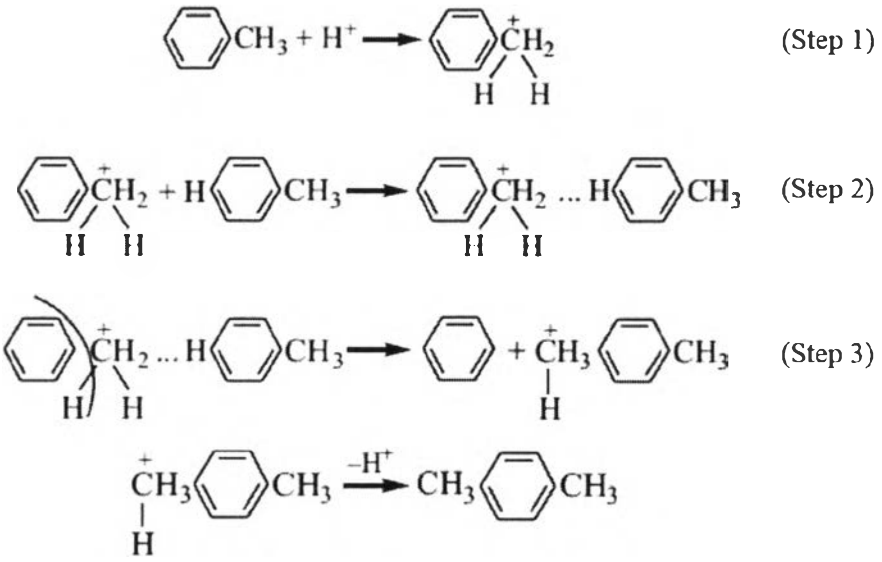


Figure 2.5 Disproportionation mechanism of toluene to *p*-xylene. (Voloshina *et al.* 2009)

In the case of the opposite orientation of the second toluene molecule in step 2 in the pentasil channel, ethylbenzene is formed instead of *p*-xylene (Figure 2.6).

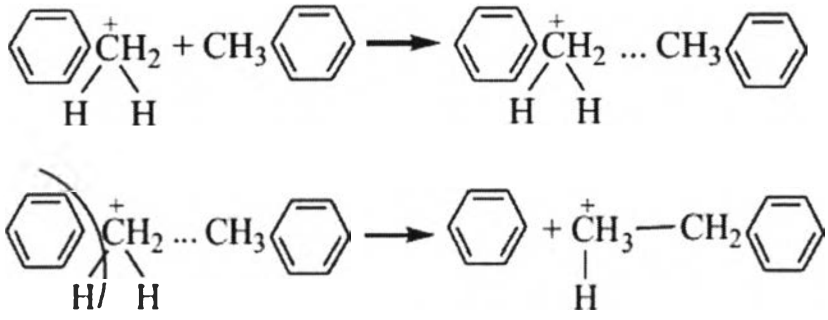


Figure 2.6 Disproportionation mechanism of toluene to ethylbenzene. (Voloshina *et al.* 2009)

2.5 Alkylation catalysts

Traditional acid catalysts used in alkylation such as $AlCl_3$, HCl, have considerable corrosion of apparatus, large catalyst consumption, environmental problems, when these catalysts are used, a large amount of non-desired isomer and products are formed, which is very undesirable and have an adverse effect on the quality of the products. Furthermore, separation of isomers is difficult due the similar boiling points of the isomer products.

Homogeneous alkylation catalysts may be Brönsted acids such as HF and in Figure 2.7, using alkenes as alkylating agents, a proton is donated by the acid to substrate.

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

In the 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.

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

$$ROAlCl_2 \leftrightarrow R^+ + {}^-OAlCl_2$$

An important reaction in aromatic akylation is known as the Friedel–Crafts reactions, developed by Charles Friedel and James Crafts to attach substituents to an aromatic ring. There are two main types of Friedel–Crafts reactions: alkylation reactions and acylation reactions, both proceeding by electrophilic aromatic substitution.

Friedel–Crafts alkylation involves the alkylation of an aromatic ring with an alkyl halide using a strong Lewis acid catalyst. With anhydrous ferric chloride as a catalyst, the alkyl group attaches at the former site of the chloride ion. The general mechanism is shown in Figure 2.8.

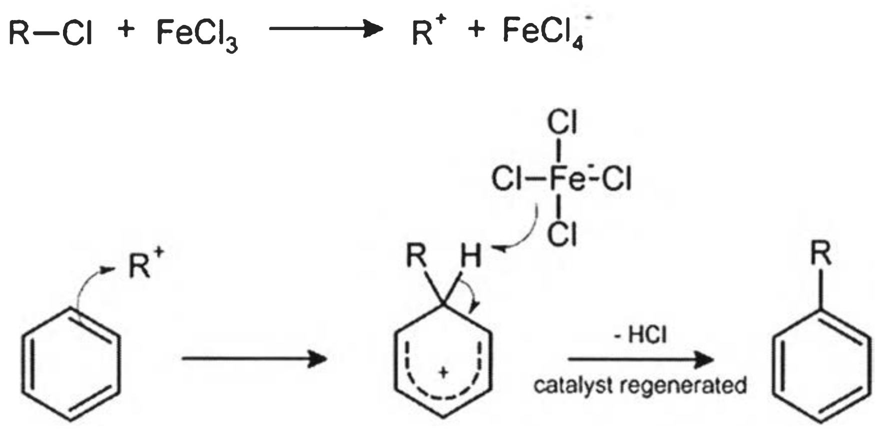


Figure 2.8 Friedel–Crafts alkylation.
(http://en.wikipedia.org/wiki/File:Friedel_Crafts_mechanism.png)

Friedel–Crafts acylation (Figure 2.9) is the acylation of aromatic rings with an acylchloride using a strong Lewis acid catalyst, also possible with acid anhydrides. Reaction conditions are similar to the Friedel–Crafts alkylation. This reaction has several advantages over the alkylation reaction due to the electron-withdrawing effect of the carbonyl group, product is always less reactive than the original molecule, so multiple acylations do not occur.

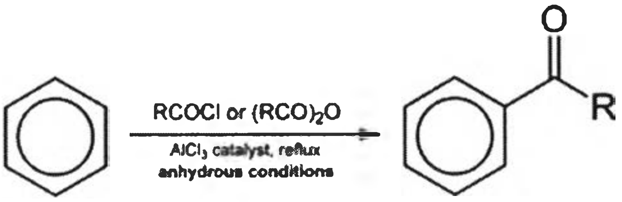


Figure 2.9 Friedel–Crafts acylation.
(http://en.wikipedia.org/wiki/File:Friedel-Crafts-acylation-overview.png)

Advances in the synthesis, zeolites have made it possible to develop a new process for the selective production such as selective isomers due to its shape selectivity and acidity.

2.6 Zeolite

Zeolites are microporous, aluminosilicate, crystalline minerals with unique 3-D lattices of Si, Al and O that make up silica and alumina tetrahedral, was discovered in 1756 by Swedish mineralogist Axel Fredrik Cronstedt. There are currently 176 unique zeolite framework types, and each is assigned a three-letter code by the Structure Commission of the International Zeolite Association.The chemical composition of a zeolite can be represented by a following formula (Weitkamp, 2000).

$$A^{m+}_{y/m}[(SiO_2)_x \cdot (AlO_2^-)_y] \cdot zH_2O$$

Where A is a cation with the charge m, (x+y) is the number of tetrahedra per crystallographic unit cell and x /y is the so-called framework silicon /aluminum ratio. Lowenstein's rule precludes that two contiguous tetrahedra contain aluminum on tetrahedral positions, i.e. Al–O–Al linkages are forbidden. Silicon and aluminum in aluminosilicate zeolites are referred to as the T-atoms.

Zeolites have a porous structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive ions are loosely held and can be exchanged for others in a contact solution. Zeolites have the ability to sort molecules based on size due to the regular pore structure. These dimensions are on a molecular level and can be used to control the molecules that can enter/leave the zeolite channel.

In petrochemical industry, zeolites are used as catalysts for fluid catalytic cracking, hydrocracking and alkylation. Zeolites confine molecules in small spaces, which cause changes in their structure and reactivity. The hydrogen form of zeolites is powerful solid-state acids, and can use for acid-catalyzed reactions, such as isomerization, alkylation, and cracking.

Weitkamp. (2000) showed the structures of four selected zeolites with their respective void systems and pore dimensions are shown in Figure 2.10. In these commonly used representations, the T-atoms are located at the vertices, and the lines connecting them stand for T–O–T bonds. If 24 tetrahedra are linked together as shown in the top line, it can be referred as a sodalite unit. The structure of the mineral faujasite came from the connecting of sodalite units. Zeolite X and Y are identical with the structures, but zeolite X has n_{Si}/n_{Al} between 1 and 1.5 and zeolite Y has n_{Si}/n_{Al} more than 1.5. Zeolite Y is an important catalyst for fluid catalytic cracking. Its pore system is relatively spacious and consists of spherical cages, with a diameter of 1.3 nm connected tetrahedrally with four neighboring cages through windows with a diameter of 0.74 nm formed by 12 TO_4-tetrahedra. Zeolite Y is classified to possess a three-dimensional, 12-membered-ring pore system. ZSM-5 is built from the pentasil unit. The first of these channels is straight channel and elliptical in cross section 0.56 x 0.53 nm, the second pore are zigzag or sinusoidal channels in cross section 0.55 x 0.51 nm. The intersection of both channels is called intersection channel. ZSM-5 is suitable for the synthesis of ethylbenzene, the isomerization of xylenes, the disproportionation and alkylation of toluene, due to the shape selectivity for mono-aromatic products.

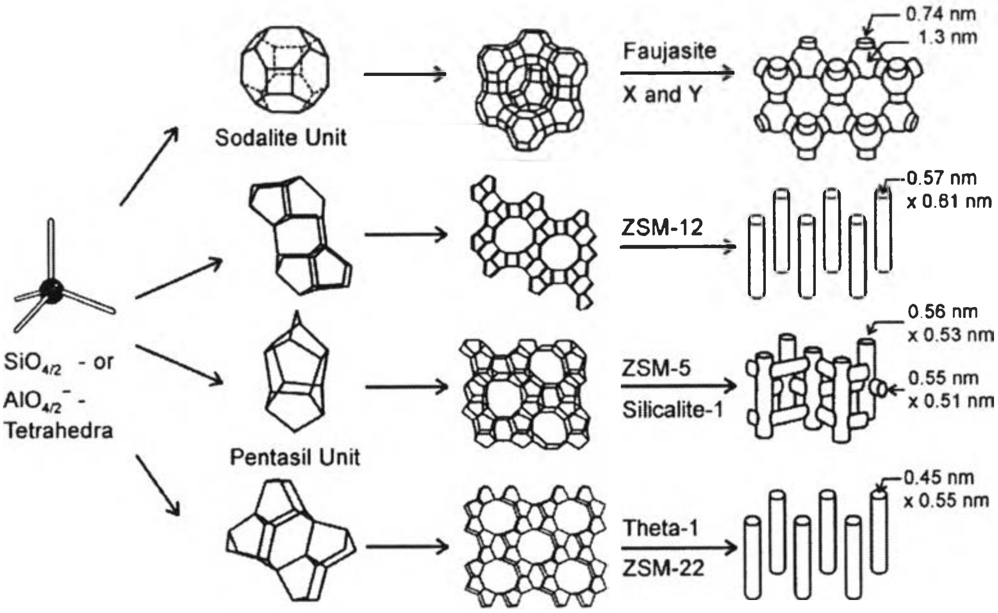


Figure 2.10 Structures of selected zeolites (from top to bottom: zeolites X and Y; zeolite ZSM-12; zeolite ZSM-5; zeolite ZSM-22), their micropore systems, and dimensions. (Weitkamp, 2000)

2.6.1 ZSM-5

ZSM-5 (Zeolite Socony Mobil–5) which has structure type MFI (mordenite framework inverted) is composed of several pentasil units linked with oxygen bridges to form pentasil chains. The pore structure is shown in Figure 2.15. The first of these channels is straight channel and elliptical in cross section 0.56 x 0.53 nm. the second pore are zigzag or sinusoidal channels in cross section 0.55 x 0.51 nm. The intersection of both channels is called intersection channel (Weitkamp. 2000). The pore structure of ZSM-5 is shown in Figure 2.11.

In 1972. ZSM-5 was first synthesized by Argauer and Landolt with three different solutions. The first solution is the alumina source, sodium ions, and hydroxide ions. Alumina will form soluble $Al(OH)_4$ ions in the presence of excess base. The second solution has the tetrapropylammonium cation as a templating agent. The third solution is the silica source. Mixing the three solutions produces supersaturated tetrapropylammonium ZSM-5, which can be heated to recrystallize and produce a solid.

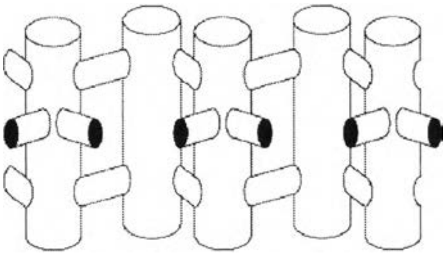


Figure 2.11 The pore structure of ZSM-5.
(http://chemelab.ucsd.edu/methanol/memos/ZSM-5.html)

ZSM-5 has high silica to alumina ratio. Whenever an Al^{3+} cation replaces a Si^{4+} cation, an additional positive charge is required to neutralize the charge. With proton (H+) as the cation, the material becomes very acidic. Thus the acidity is proportional to the Al content. The structure and the acidity of ZSM-5 are suitable for acid-catalyzed reactions such as hydrocarbon isomerization and the alkylation of hydrocarbons. An example is the isomerization of m-xylene to *p*-xylene. Within the pores of ZSM-5, *p*-xylene which has a much higher diffusion coefficient than *m*-xylene can diffuse out of the catalyst very quickly, allows the isomerization occur with high yield of the selective products.

2.6.2 Acidity

Zeolites consist of a 3-D network of metal–oxygen tetrahedra 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 devided into Brönsted acid sites and Lewis acid sites. 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 (Stocker, 2005). The Brönsted acid sites, is shown in Figure 2.12.

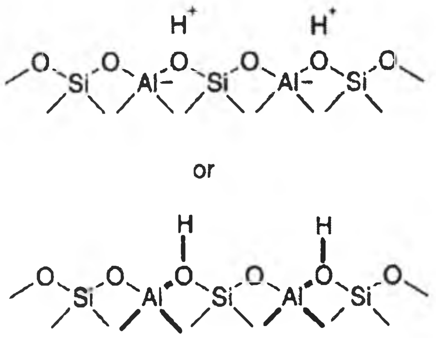


Figure 2.12 Brönsted acid sites ("bridging hydroxyl groups") in zeolites. (Stocker, 2005)

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 (Figure 2.13).

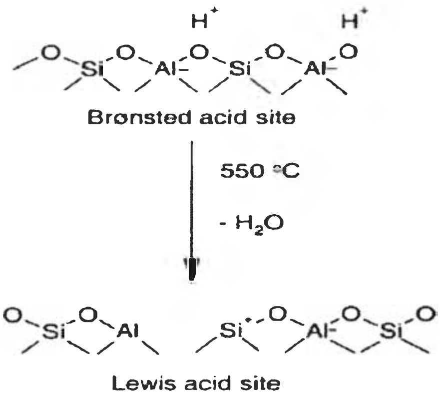


Figure 2.13 Formation of Lewis acid sites in zeolites. (Stocker, 2005)

2.6.3 Shape selectivity

The molecular shape-selective mechanisms of zeolites can be divided into reactant, product and restricted transition state-type selectivity as shown in Figure 2.14 (Stöcker, 2005).

Reactant selectivity describes the phenomenon of microporous catalysts acting as molecular sieves and excluding bulky molecules from entering the pore while allowing only the smaller molecules enter. The critical exclusion limit can be varied over a wide range of different zeolites.

Product selectivity refers to discrete diffusivities of the reaction products formed in zeolites with respect to the microporous pore structure. Small product molecules may easily leave the zeolite pore, while larger product molecules stay much longer in the cavities of the zeolites.

Restricted transition state-type selectivity occurs when the spatial configuration around a transition state or a reaction intermediate located in the intra-crystalline volume is such that only certain configurations are possible. This means the formation of reaction intermediates and/or transition states is sterically limited due to the shape and size of the microporous lattice allowing the access of the species formed to interact with the active sites.

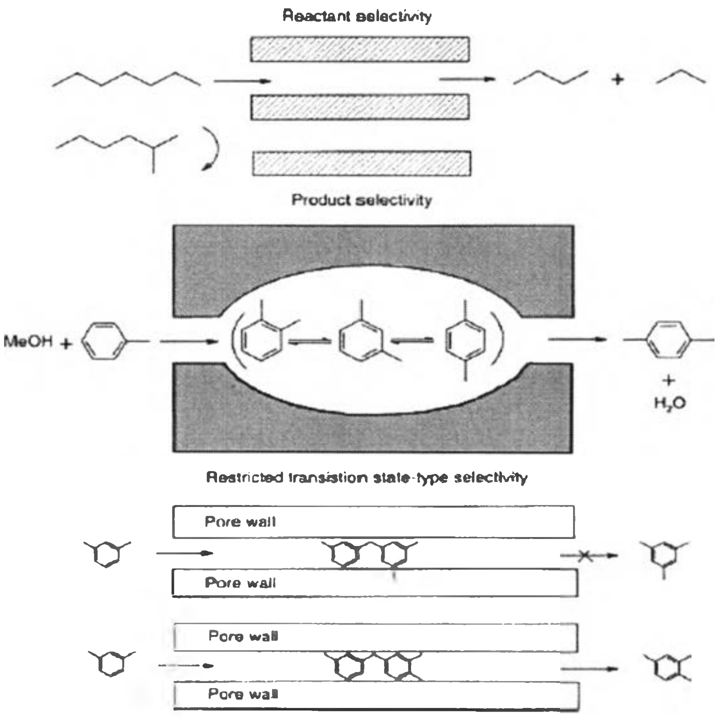


Figure 2.14 Schematic representation of the three types of shape selectivity. (Stocker, 2005)

2.6.4 Si/Al Ratio

Shirazi *et al.* (2008) studied the effects of Si/Al ratio of ZSM-5 zeolite on the morphology, acidity and crystal size of ZSM-5 by synthesized ZSM-5 with different Si/Al molar ratios from 10 to 50. They found that an increasing the aluminum content of the sample results in the decreasing in crystal size in the range from 1 to 10 μm. From XRD results the intensities of the peaks increase slightly when increasing Si/Al ratios from 10 to 50, indicating that ZSM-5 zeolite can form easier as the Si/Al ratios increase. The size and morphology of the crystals also depended on the Si/Al molar ratio. SEM images 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 aggregation had occurred. Surface areas of zeolites 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 zeolites. Total acidity of ZSM-5 decreased with increasing the Si/Al molar ratio.

2.7 Ethylation of toluene using ZSM-5 catalysts

Paparatto *et al.* (1986) studied the effects of structural and morphological features of the ZSM-5 and ZSM-11 on the activity and selectivity to *p*-ET in toluene alkylation with ethanol. Catalysts were prepared with the different Si/Al ratios and organic cations such as tetrapropylammonium (TPA), triethanolamine (TEA) and tetrabutylammonium (TBA). They found that the *p*-ET selectivity rises on increasing the primary particle as shown in Table 2.2, and the best performance was obtained on TEA samples. They summarized the behavior of ZSM-5 catalysts by the two-step mechanism. The first reaction is the shape selective alkylation on the acid sites inside the zeolite channels, where the formation of *p*-isomer is favored. When the *p*-isomer passes through the ZSM pores, it comes into contact with the acid sites on the external surface and isomerizes toward *m*- and *o*-ET. An increase in particle size results in lower the external surface area, undesired side reactions such as isomerization are less favorable.

Chen and Feng (1992) studied the effects of preparation method on activity of catalyst in toluene alkylation with ethanol. Non-skeletal boron-containing zeolite catalyst (BZSM-5) was prepared by using ion impregnation of boric acid on ZSM-5. The skeletal boron-containing zeolite catalyst (SB) was prepared by introducing boron during the synthesis. Partial dealuminated boron-containing zeolite catalyst (WBZ) was prepared by the treatment of ZSM-5 zeolite with boric acid solution in a flow condition at high temperature. They found that BZSM-5 has high *p*-selectivity but low stability. For SB, *p*-selectivity increases with the increase of skeletal boron. For WBZ, the *p*-selectivities and stabilities are higher than SB catalyst. They conclude that because of the effect of modifiers, the amount of strong acid sites is reduced and some undesired side reactions such as isomerization are prohibited. Such a result is in favor of *p*-selectivity.

Table 2.2 Summary of the characteristics of the catalysts in comparison with their performances in m-Xylene isomerization and Toluene Alkylation with Ethanol (Paparatto *et al.*, 1986)

Organic cation	SiO_2/Al_2O_3 Molar ratio	Structure	d_{XRD} (nm)	d_{SEM} (μm)	d_S (nm)	S_{ex} (m^2/g)	Conversion (%)	*p*-ET selectivity (%)
TPA	25	ZSM-5	34	0.5	36	88	74	31
TPA	25	ZSM-5	64	1-2	640	5	44	85
TPA	58	ZSM-5	87	1-4	160	20	65	41
TPA	63	ZSM-5	90	1-4	320	10	61	48
TEA	25	ZSM-5	83	1	145	22	71	46
TEA	25	ZSM-5	63	1	400	8	65	57
TEA	25	ZSM-5	145	3-7	460	7	61	57
TEA	25	ZSM-5	77	3-7	530	6	55	75
TEA	48	ZSM-5	300	4-8	750	4	50	87
TEA	63	ZSM-5	300	4-8	700	4-5	46	92
TBA	40	ZSM-11	50	1	35	90	54	33
TBA	80	ZSM-11	58	1	40	80	45	45

Where

d_{XRD}	is the crystallite size
d_{SEM}	is the shape and the dimension range of the crystals or their aggregates,
d_S	is the size of the primary particles
S_{ex}	is the surface area outside the zeolitic pores

Bhandarkar and Bhatia (1994) studied the selective formation of *p*-ET using toluene and ethanol between unmodified and modified shape-selective HZSM-5 catalysts. They found that HZSM-5 modified with phosphorus, boron, and magnesium yielded better selectivity (around 90%) as compared to unmodified HZSM-5 catalyst (around 50%) under identical conditions. They concluded that with modification, the strength of the strong Brönsted acid sites decreases and more weak Lewis acid sites are formed.

Yu and Tan (2006) studied the para-selective HZSM-5 crystals prepared by the chemical liquid deposition (CLD) with tetraethyl orthosilicate (TEOS) as the catalyst for alkylation of toluene with ethylene in supercritical carbon dioxide. They concluded that an enhancement of *p*-ET selectivity results from the reduction of pore opening and the lower external acidity due to the selective silica deposition near pore mouth and external surface of the crystals by chemical liquid deposition.

Liu *et al.* (2010) reported that HZSM-5 with Si/Al = 150 shows both high selectivity and catalytic activity for alkylation of toluene with ethylene. In addition, they studied the effects of modified catalysts on the shape-selectivity for *p*-ET production with alkylation of toluene and ethylene. Modified catalysts were prepared by chemical liquid deposition of silica (SiO_2-CLD), chemical vapor deposition of silica (SiO_2-CVD) and impregnation with La_2O_3 and MgO. The results are shown in Table 2.3.

Table 2.3 Catalytic performance for toluene alkylation over modified HZSM-5 (Si/Al = 150). (Liu *et al.*, 2010)

Sample	Toluene conversion %	Ethylene conversion %	Total ET selectivity %	Total *p*-ET selectivity %
Unmodified HZSM-5	29.4	95.5	91.2	74.9
SiO_2-CLD/HZSM-5	27.9	93.5	91.3	90.7
SiO_2-CVD/HZSM-5	26.1	91.0	89.7	87.2
SiO_2-CLD&MgO/HZSM-5	25.0	90.7	95.1	98.6
SiO_2-CLD&La_2O_3/HZSM-5	25.6	91.3	94.8	98.2

They concluded that SiO_2-CLD/HZSM-5 shows higher catalytic activity as SiO_2-CVD/HZSM-5 loses more acidic sites in channels during modification.

Because two side reactions that lower the *p*-selectivity such as disproportionation of toluene and dealkylation of methyl ethylbenzene required the stronger acidic sites. In order to reduce the side reactions of both disproportionation and dealkylation, metallic oxides were added to decrease HZSM-5 acidic strength. The acid characterization is shown in Table 2.4. Moreover, the further La_2O_3 or MgO modification reduces coking deactivation from ethylene polymerization over HZSM-5 catalyst, improving its stability

Table 2.4 Results of NH_3-TPD characterization for the acidity of modified ZSM-5 (Liu *et al.*, 2010)

Sample	Weak acidic sites		Strong acidic sites	
	Temperature K	Desorbed NH_3 mmol/g	Temperature K	Desorbed NH_3 mmol/g
Unmodified HZSM-5	529	0.67	778	0.31
SiO_2-CLD/HZSM-5	528	0.53	775	0.25
SiO_2-CVD/HZSM-5	526	0.48	773	0.20
SiO_2-CLD&MgO/HZSM-5	525	0.50	750	0.11
SiO_2-CLD&La_2O_3/HZSM-5	529	0.51	754	0.12

2.8 Zeolite modification

Although zeolite is a suitable catalyst for many processes, modification of zeolite is still necessary to obtain the higher product selectivity. The following literature reviews are the related HZSM-5 modification that can applies for ethylation of toluene with ethanol.

Y. Sugi *et al.* (2005) deactivate external acid sites for alkylation and related reactions of mononuclear aromatic hydrocarbons over H-ZSM-5 by impregnation of H-ZSM-5 with La_2O_3 and CeO_2 which are larger than zeolite pore size. They founded that the external acid amount decreased with an increase in loading amount of La_2O_3, but no such decrease is observed by the CeO_2 modification and found that the La_2O_3 modification causes the adjustment of pore entrance.

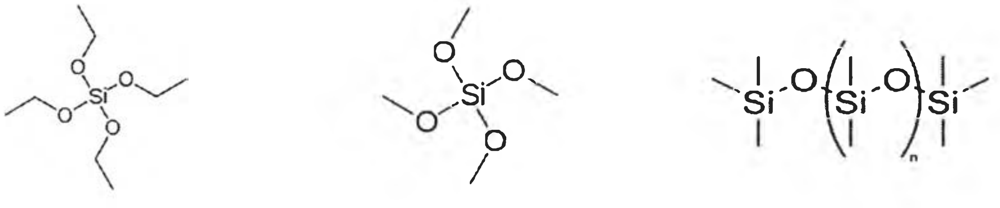
X. Guan *et al.* (2006) deactivate acid sites for ethylation of ethylbenzene with ethanol by nitridation by treating HZSM-5 with ammonia at elevated temperature.

They found that the strong acid sites of zeolites reduced dramatically while the structures still had high crystallinity and high specific surface areas.

To prevent the undesired reaction that occurs at external surface, external surface modification is necessary. Many surface modification techniques were studied to improve catalytic selectivity such as impregnation of metallic or non-metallic compounds and pre-coking. Although large molecular size organic base compounds could deactivate the external acidic sites but organic compounds are not stable at high reaction temperatures, an impregnation of metallic or non-metallic compounds such as H_3PO_4, CaO, MgO also could eliminate the external acidic sites, but greatly decreasing the acidic sites in channels. The pre-coking modification is difficult to be operated, and has to be conducted again after regeneration of zeolite catalyst. To replace the pre-coking modification, the chemical liquid deposition (CLD) and chemical vapor deposition (CVD) are another method to modify external acidity of catalysts. The difference between CLD and CVD is the phase of the deposition agents. Compared with CVD, CLD may be more easily operated and transferred to an industrial scale preparation. An introduction of a substituted silyl group to a molecule is known as Silylation.

2.9 Silylation

Silylation is a process in which zeolite was treated with silicon compounds selected from the group of alkoxysilane 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. An example structure of silylation agents are shown in Figure 2.15.



(a) (b) (c)

Figure 2.15 Silylation agents (a) Tetraethyl orthosilicate, (b) Tetramethyl orthosilicate, 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 Silylation process is shown in Figure 2.16.

Zhu *et al.* (2007) studied the effects of chemical liquid deposition (CLD) with polysiloxane on acidity and catalytic properties of the HZSM-5 catalyst (Si/Al = 24). HZSM-5 was mixed with hexane solution of polysiloxane compound at 10 wt % of polysiloxane. They found that the acidic amount of the modified ZSM-5 decreased with increasing extent of the modification, but the acidic strength distribution of the modified ZSM-5 was almost unchanged compared to parent ZSM-5. After the four-cycle modification, the external surface of the modified ZSM-5 may be regarded to be almost non-acidic due to coverage of deposition silica.

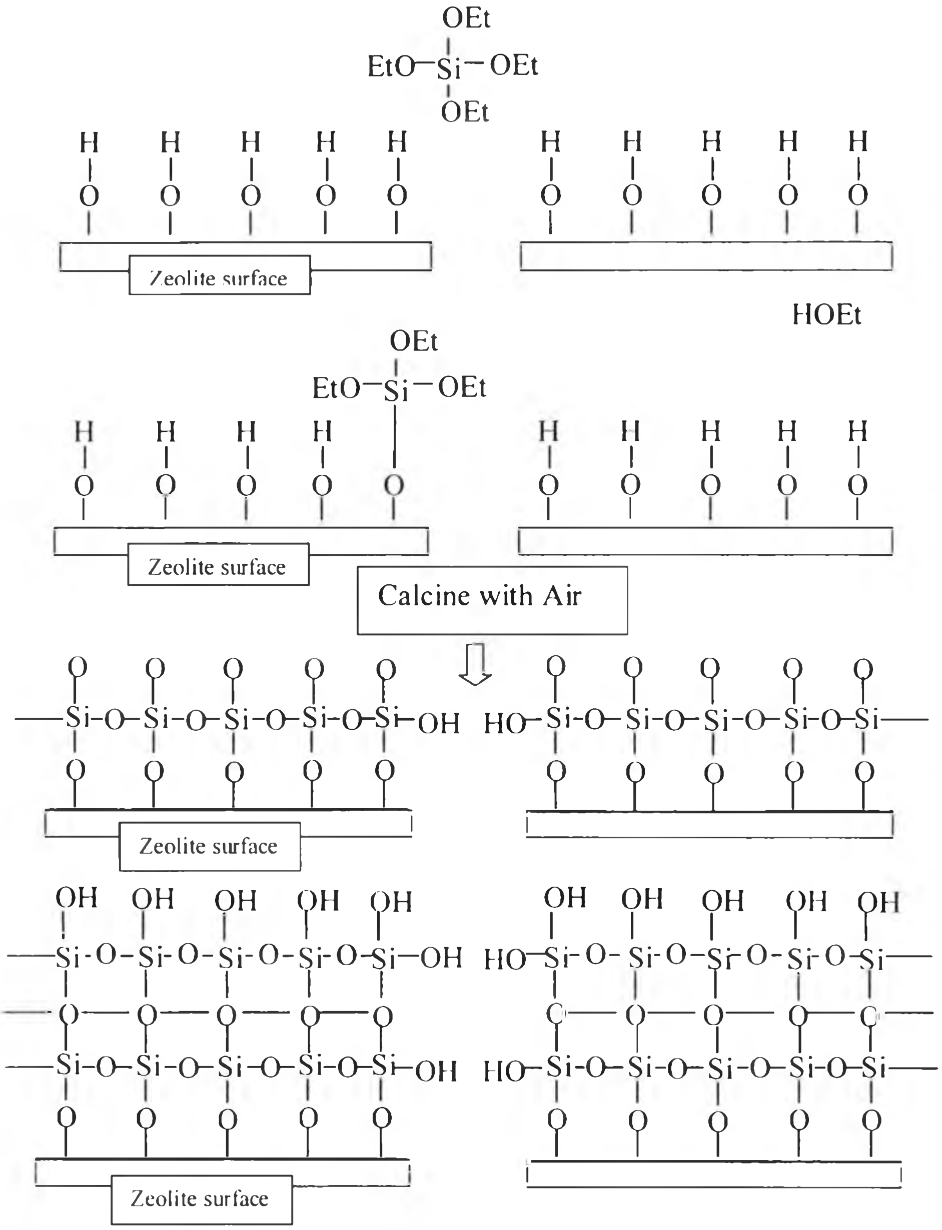


Figure 2.16 Silylation process.
(http://www.slideboom.com/presentations/279497/Silylation-And-Metal-oxide-on-solid-Acids)

Hui *et al.* (2011) studied the disprotionation of toluene by modified ZSM-5 catalysts (Si/Al = 19) with chemical liquid deposition with tetraethyl orthosilicate (TEOS). HZSM-5 was mixed with cyclohexane containing TEOS. They found that the disproportionation of toluene more favored at low Si/Al ratio. Among of the tested CLD agents and solvents, TEOS with cyclohexane as a solvent showed the highest activity. They also found that doing organic acid treatment before CLD, improve the activity of CLD modified catalysts, and the best activity obtained from treatment with citric acid.