CHAPTER II
LITERATURE REVIEW

2.1 *p*-Xylene

p-Xylene is an aromatic hydrocarbon, based on benzene with two methyl substituents. The "*p*" stands for para, identifying the location of the methyl groups as across from one another. It is an isomer of xylene. Other isomers include *o*-xylene and *m*-xylene. It is used primarily for the production of polyester fibers, films and resins, such as PET (polyethylene terephthalate)

A significant fraction of the demand for *p*-xylene has been driven by use of PET for packaging of carbonated beverages and bottled water. PET resin has gas barrier properties making it particularly well suited for these applications. Other major uses of polyester are in the production of textile fibers and engineering thermoplastics. This broad applicability in polyester utilization is due to its impact resistance and superior performance as a gas barrier material. Prior to polymerization, *p*-xylene is first oxidized to terephthalic acid (TA) or dimethyl terephtalate (DMT). These diacid or dimethyl ester monomers are then polymerized via a condensation reaction with ethylene glycol to form the polyester.

Since the early 1970s *p*-xylene has grown to become a large volume petrochemical. Demand for *p*-xylene has increased tenfold since 1970 to about 26 × 10^6 t/year. Almost all of this additional production has been by the UOP Parex ™ process as shown in Figure 2.1.

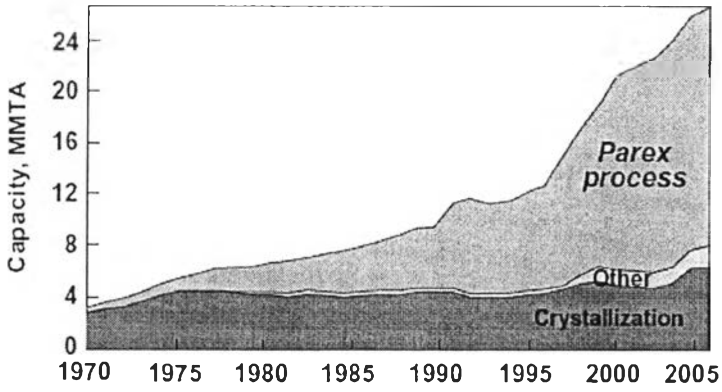

Figure 2.1 Worldwide *p*-xylene production capacity (Kulprathipanja, 2010).

2.2 UOP Aromatics Complex Process (Kulprathipanja, 2010)

The commercial production of *p*-xylene begins with petroleum naphtha, as does the production of the other mixed xylene components, benzene and toluene. Naphtha is chemically transformed to the desired petrochemical components and the individual components are recovered at required purity in what is known in the industry as an aromatics complex. A generic aromatics complex flow scheme is shown in Figure 2.2. The process block is labeled according to the corresponding UOP process units.

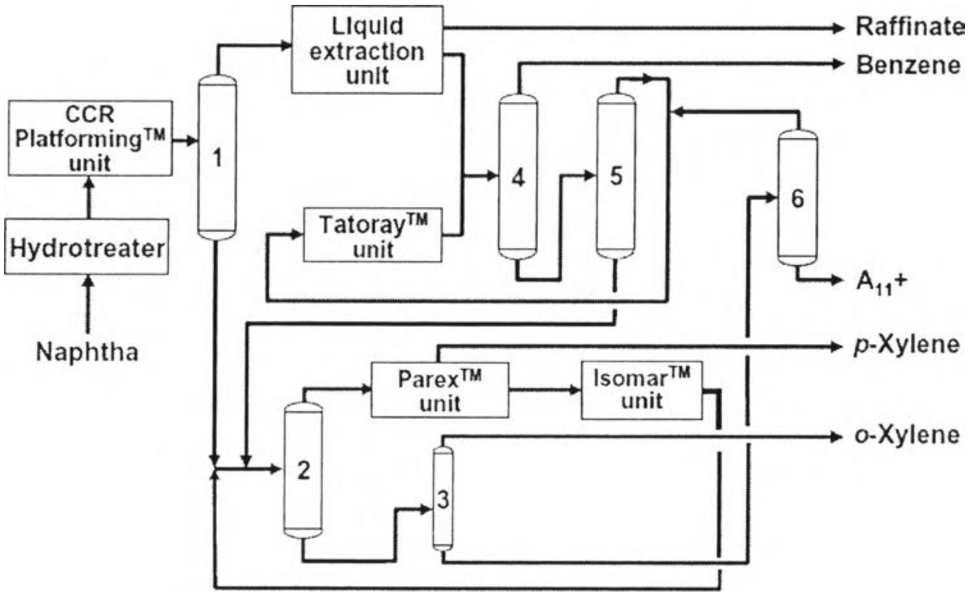

Figure 2.2 Typical aromatics complex with UOP technology.

Naphtha enters the aromatics complex and is hydrotreated to remove sulfur, oxygen and nitrogen. The naphthenes and paraffins in the treated naphtha are then reformed to aromatics in the UOP CCR Platforming ™ process unit, producing a C_5+ stream referred to as reformate. The reformate is then sent to Column 1 where toluene and lighter boilers (A_7–) are split from mixed xylene and heavier components (A_8+). The A_8+ components go to Column 2 where they are sent along with an A_8 recycle stream from the UOP Isomar ™ process unit and an A_{8+} stream from the UOP Tatoray ™ process unit. A portion of the *o*-xylene and all the A_9+ leaves the bottom of Column 2.

The mixed xylenes go overhead and on to the UOP Parex ™ process unit. The Parex unit extracts the *p*-xylene in the stream at 99.7 – 99.9% purity at a recovery in excess of 97%. The other stream exiting the Parex unit contains the unextracted mixed xylene components. This Parex raffinate stream is sent to the Isomar unit where the mixed xylenes are reacted in the presence of hydrogen over a zeolite catalyst to an equilibrium mixture of mixed xylenes containing about 22% *p*-xylene. The equilibrated xylenes are recycled to Column 2 to remove trace A_9+ by product formed in the xylene isomerization reaction.

Some *o*-xylene is recovered in Column 3 from the bottoms stream of Column 2 to produce a > 98.5% purity *o*– xylene product. The A_9+ from Column 3 is rerun in Column 4 so that the A_{11+} components are removed before sending the A_9 – A_{10} components to the Tatoray unit. Meanwhile, the A_7–aromatics from the Column 1 overhead are extracted by extractive distillation using Sulfolane solvent in the UOP Sulfolane ™ process unit.

The non-aromatics in the C_5–C_8 range are rejected as raffinate for use as gasoline or feed to a naphtha steam cracker for ethylene and propylene production. The extracted benzene and toluene are sent to Column 4 along with A_6+ produced in the Tatoray unit. A > 99.9% benzene product is produced from the overhead of Column 4. The bottoms of Column 4 are sent to Column 5 where the toluene is taken overhead and returned to the Tatoray unit to be transalkylated over a zeolite catalyst in the presence of hydrogen with the A_9 – A_{10} material from Column 6, to produce more benzene and mixed xylenes. The A_{8+} material from the bottom of Column 5 is sent to Column 2 for recovery of the mixed xylenes produced in the Tatoray unit.

2.3 Glycerol from Biodiesel

Biodiesel is mainly produced through a process known as transesterification, as shown in Figure 2.3. Biodiesel production will generate about 10% (w/w) glycerol as the main byproduct. In other words, every gallon of biodiesel produced generates approximately 1.05 pounds of glycerol.

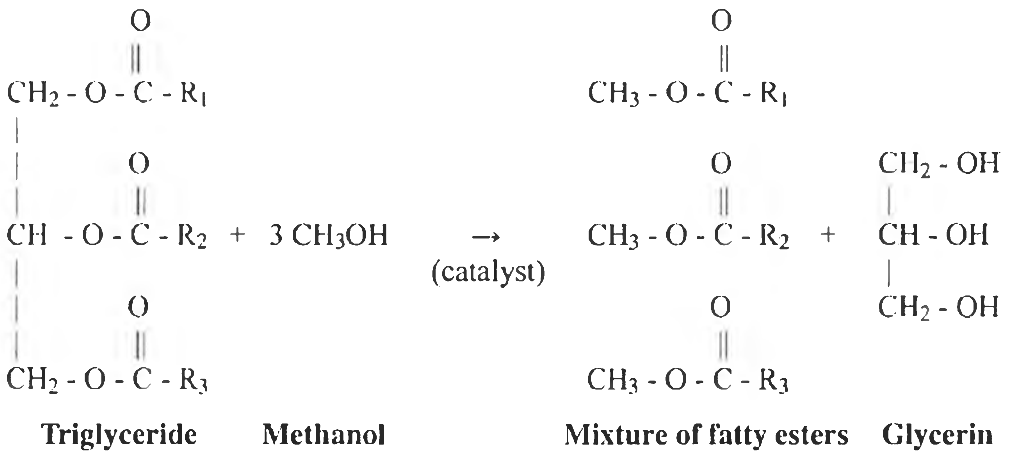

Figure 2.3 Transesterification reaction.

Where R_1, R_2, and R_3 are long hydrocarbon chains, sometimes called fatty acid chains. There are only five chains that are most common in soybean oil and animal fats (others are present in small amounts).

2.4 Conversion of Glycerol into Other Chemical Products

Figure 2.4 summarized the different possible reaction pathways and products. Most of the studies focused on the dehydration of glycerol into acrolein (propenal), the synthesis of alcohols, particularly 1,2-propanediol, and the production of additives for fuels.

Tsukuda and co-workers studied the synthesis of acrolein (propenal) from glycerol. The aim of the study was to optimize the composition of the catalyst. The best results were obtained with the highest temperature and a Q10-SIW-30 ($H_4SiW_{12}O_{40}$•$24H_2O$) catalyst. Corma also studied the conversion of glycerol to acrolein in two different reactors: a fluidized bed reactor similar to an FCC and a fixed-bed reactor. It was found that lower temperatures favor the conversion into acrolein (yield of 55 to 62%) and higher temperatures favor the conversion into acetaldehyde.

Guo and co-workers investigated the reduction of glycerol into 1,2-propanediol with a bifunctional Co/MgO catalyst. The maximum glycerol conversion was about 55% and the selectivity for the desired product did not exceed 42%.

Akiyama also studied the conversion of glycerol into 1,2-propanediol (1,2-PDO). A glycerol conversion of 100% was obtained with copper catalysts (Cu/Al_2O_3).

Frusteri and co-worker prepared fuel additives by etherification of glycerol with *tert*-butyl alcohol. Both the glycerol conversion and the selectivity were high and exceeded 93%. Kijenski also studied the conversion of glycerol into its *tert*-butyl ether derivative. A glycerol conversion of 50% was achieved and a high selectivity to ethers was obtained for long reaction times

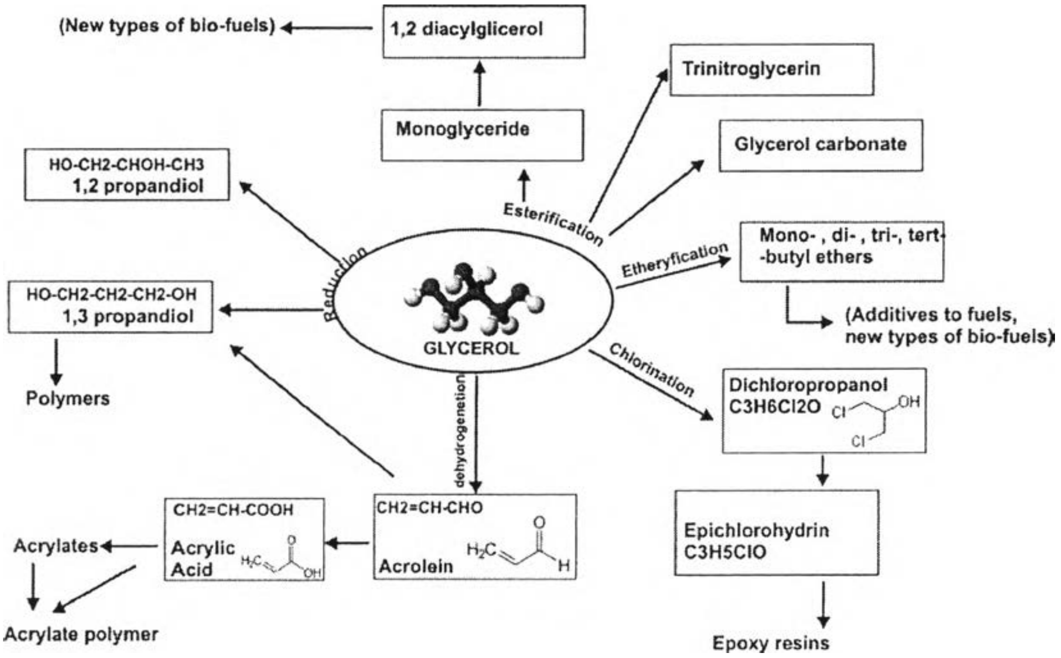

Figure 2.4 Methods of conversion of glycerol into useful products (Marek Stelmachowski, 2011).

2.5 Structure of Zeolite

Zeolites are water-containing crystalline aluminosilicates with highly ordered structures consisting of SiO_4 and AlO_4 tetrahedron unit. Actually aluminum has a stable coordination number of three. In order to force aluminum to have tetrahedron structure or coordination number of four, the AlO_4 tetrahedrons come to have the oxidation number of -1.

The SiO_4 and AlO_4 tetrahedron unit are connected each other through common oxygen atoms to give a three-dimensional network. Negative charges from AlO_4 tetrahedrons usually compensated by protons, metal cations, or NH_4^+. The interior of the pore system, with its atomic-scale dimensions, is the catalytically active surface of the zeolites. The inner pore structure depends on the composition, the zeolite type, and the cations.

Advantages of zeolite structure over other solid material:

- Well defined crystalline structure, good reproducibility in production.
- Well define inner pores in which active species can be resided.
- Adjustable framework composition and cations associated with different acid properties and stability.
- Various structures that can be used as shape-selectivity catalysts for different reactions.
- Zeolite catalysts are thermally stable in high temperature and can be regenerated by combustion of carbon deposits.

Table 2.1 Structure of zeolite (Tsai, *et al.*, 1999)

Zeolite	Number of rings	Pore size (Å)	Pore/channel structure
8-membered oxygen ring			
Erionite	8	3.6×5.1	Intersecting
10-membered oxygen ring			
ZSM-5	10	5.1×5.6	Intersecting
		5.1×5.6	
ZSM-11	10	5.3×5.4	Intersecting
Dual pore system			
Ferrierite	10, 8	4.2×5.4	One dimensional
		3.5×4.8	10:8 intersecting
Mordenite	12	6.5×7.0	One dimensional
	8	2.6×5.7	12:8 intersecting
12-membered oxygen ring			
ZSM-12	12	5.5×5.9	One dimensional
Faujasite	12	7.4	intersecting
		7.4×6.5	12:12 intersecting
Mesoporous system			
VPI-5	18	12.1	One dimensional
MCM41-S	-	16-100	One dimensional

ZSM-5 zeolite or MFI is one of the most important zeolite used in petroleum and petrochemical industry. The structure of ZSM-5 zeolite, shown in figure 2.4, has 10-membered oxygen ring which compose of 5-rings as secondary building units. These so-called 5–1 units are structurally analogous to methycyclopentane. It has two types of channels: straight channels (5.3×5.6 Å) and sinusoidal channels (5.1×5.5 Å). These two channels are perpendicular to each other and generate intersections with diameters of 8.9 Å. The absence of large cages with small windows leads to the special coke-resistant properties of HZSM-5 zeolite (Chen *et al.*,1979).

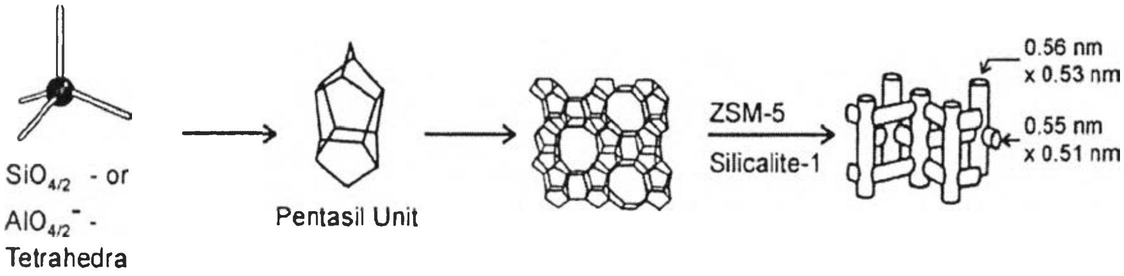

Figure 2.5 Structure of ZSM-5 zeolite.

2.6 Acidity of Zeolite

HZSM-5 is the protonic type of ZSM-5 zeolite that has been used in acid catalyzed reaction. Typically, HZSM-5 zeolite can be derived by following steps:

i) Calcination to decompose the organic amine template

ii) Ion exchange of zeolite in sodium form with NH_4NO_3 solution to be NH_4^+ form

iii) Calcination of NH_4^+ form into protonic form

In principle, the acidity and acid strength are the key properties of zeolite which play an important role in the selectivity and activity of zeolite

The acid properties of zeolites can be characterized by using alkane cracking, temperature programmed desorption, micro-calorimetry, IR spectroscopy and MAS NMR observations. Two different type of acid site are Brønsted and Lewis acid sites. Typically, IR spectroscopy of pyridine adsorption can be used to differentiate and measure ratio of Brønsted per Lewis acid sites. Brønsted acid site are related to aluminum located in the framework of zeolites. However, Lewis acid site are related to the extra-framework aluminum (EFAL) or distorted aluminum in the framework. EFAL is usually generated during the synthesis, calcination or/and ion exchange process (Farneth and Gorte., 1995).

The acid strength of zeolite is mainly depending on Si/Al ratio. As the Si/Al decrease, the number of neighboring Al atoms around the hydroxyl group increase: therefore, the acidity increase but acid strength decrease. The strongest Brønsted acid site can be obtained upon completely isolated Al in framework due to the higher electronegativity of Si compared to Al.

The concentration of the acid sites located on the external surface and in the pore mouth region of zeolites can be determined using probe molecules with larger kinetic diameters compared to the entrance of the zeolites and thus these molecules are believed to interact only with the acid sites located on the external surface and in the pore mouth region.

In 1998, Weber *et al.* measured the concentration of the acid sites of silylated HZSM-5 zeolites using temperature programmed desorption (TPD) of 4-methyl-quinoline. As the kinetic diameter of 4-methyl-quinoline (7.3 Å) is larger than the pore openings of HZSM-5 zeolites (5.6 × 5.3 Å), this molecule is incapable of completely entering into the pores and, therefore, the acid sites on the external surface of HZSM-5 can be quantitatively determined.

2.7 Mechanisms of the Shape Selectivity

Zeolite usually shows specific selectivity in some reactions due to their well- defined pore structure. It generally believed that the majority of active site is located in the pores of zeolite. Typically, seven fundamental steps are involved in an overall gas phase reaction using zeolite as catalyst

1) Diffusion of the starting materials through the boundary layer to the catalyst surface.
2) Diffusion of the starting materials into the pores (pore diffusion).
3) Adsorption of the reactants on the inner surface of the pores.
4) Chemical reaction on the catalyst surface.
5) Desorption of the products from the catalyst surface.

6) Diffusion of the products out of the pores.
7) Diffusion of the products away from the catalyst through the boundary layer and into the gas phase.

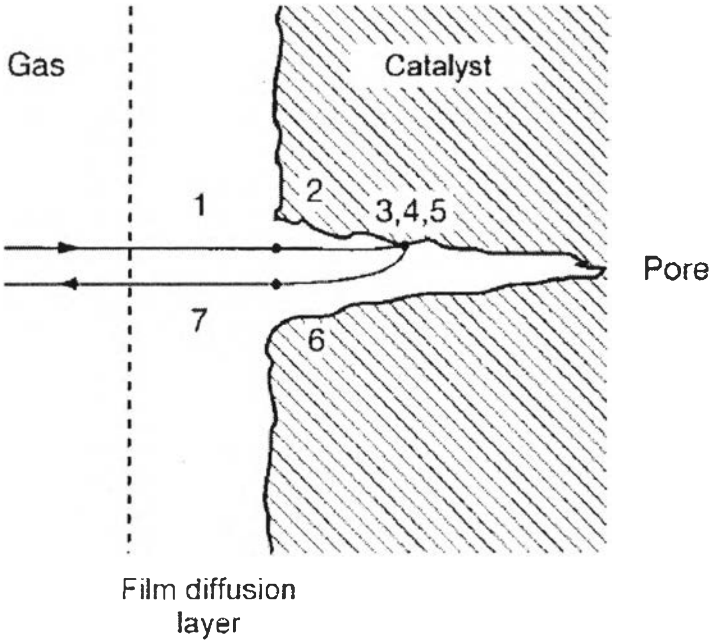

Figure 2.6 Individual steps of a heterogeneously catalyzed gas-phase reaction (Hagen, 2006).

The shape selectivity of the zeolite for a specific reaction may be involved in step 2, 4 or/and 6. Based on different controlling steps, the shape selectivity of zeolite can be classified into three types;

2.7.1 Reactant Shape Selectivity

Reactant shape selectivity can be seen in the case of different reactant molecule with bulkier and smaller size when compared to the pore mouth of zeolite. The smaller kinetic diameter can diffuse into the pore of zeolite and then approach to the active sites located inside the pore of zeolite. On the other hand, the reactant with larger kinetic diameter, cannot diffuse into the pore of zeolite

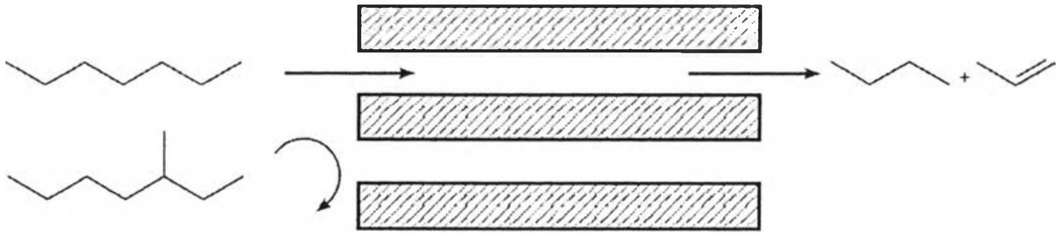

Figure 2.7 Reactant shape selectivity of n-alkane compare with iso-alkane (Hagen, 2006).

2.7.2 Transition State Selectivity

Transition state selectivity depends on the fact that the chemical reactions usually undergo via intermediates. Due to the pore system, only those intermediates which have a suitable geometrical in the cage of zeolite can be formed during catalysis reaction.

For example, disproportionation of *m*-xylene to toluene and trimethylbenzenes in the wide-pored zeolite Y. In the zeolite cavity, bulky diphenylmethane carbenium ion transition states can be formed as precursors for methyl group rearrangement, whereby the less bulky carbenium ion B is favored. Thus the reaction product consists mainly of the unsymmetrical 1,2,4-trimethylbenzene rather than mesitylene (case A).

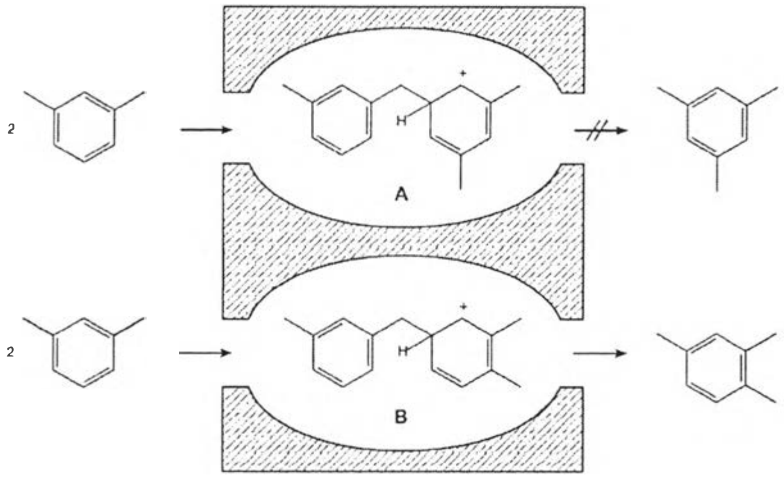

Figure 2.8 Transition state selectivity of disproportionation of *m*-xylene (Hagen ,2006).

2.7.3 Product Shape Selectivity

Product shape selectivity relate to the cavity size of a zeolite, only products of a certain size and shape that can exit from the pore system are formed. Deviation of product distribution from equilibrium composition can be seen in this selectivity if the products involving in the reaction are large difference in kinetic diameter leading to large difference in their diffusivities.

For example, the methylation of toluene (Figure 2.9) and the disproportionation of toluene on ZSM-5. In both reactions all three isomers *o*-, *m*-, and *p*-xylene are formed. The desired product *p*-xylene can be obtained with selectivity of over 90 %, although the thermodynamic equilibrium corresponds to a *p*-xylene fraction of only 24 %. This is explained by the fact that for the smaller molecule *p*-xylene has a rate of diffusion that is faster than those of the other two isomers.

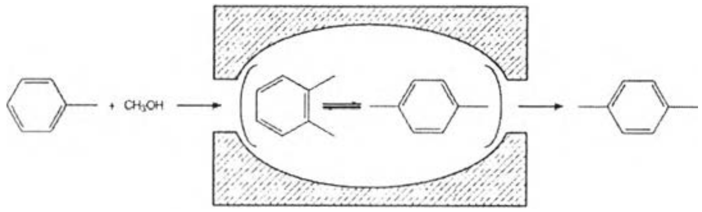

Figure 2.9 Product shape selectivity of methylation of toluene (Hagen, 2006).

There are many different zeolite structures that suitable for many petrochemical industrial products as shown in figure 10 below.

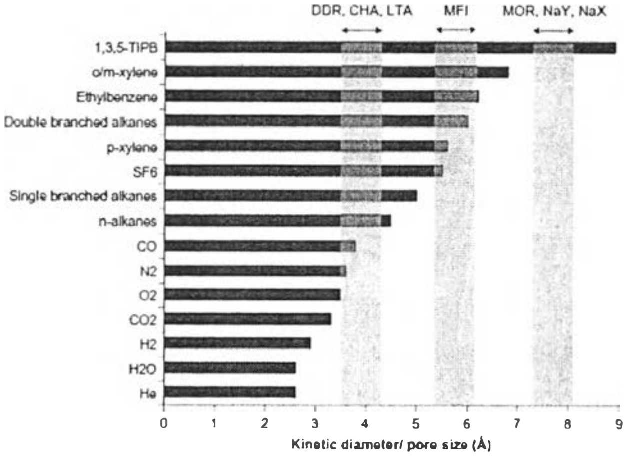

Figure 2.10 Kinetic diameter of common industrial molecules shown relative to the pore sizes of common zeolite structures (Kulprathipanja, 2010).

2.8 Modification of Zeolites

Conversion of alcohols to aromatics on ZSM-5 zeolite was studied in 1984 by Vasant and co-worker. They found that, as Si/Al ratio is decreased, the conversion of ethanol and methanol to aromatics are increased due to an increase in acid sites which are involved in the aromatization reactions. For the aromatics products distribution, in case of methanol conversion, the concentration of xylene in aromatics passes through a minimum at Si/Al ratio of 17.2, benzene and A_{9+} are increased, ethylbenzene is decreased and toluene is not significantly affected. In case of ethanol conversion, there is not significant variation in concentrations of benzene and xylenes but the concentration of ethylbenzene and A_{9+} are decreased and that of toluene is increased.

The influence of degree of cation exchange was also studied, when the degree of H^+ exchange is increased from 0.5 to 1.0 in both the methanol and ethanol conversions, the concentration of xylenes in the total aromatics passes through maximum, the concentrations of benzene and toluene increase, and that of ethyl benzene and C_{9+}-aromatics decrease. These results indicate that the distribution of aromatics is controlled to some extent by secondary reactions, particularly by dealkylation reaction. The concentrations of benzene and toluene in aromatics increase and that of ethyl benzene and C_{9+}-aromatics decrease due to an increase in the rate of dealkylation because of the increase in the strong acid sites accompanying the increase in the degree of H^+ exchange.

In 1992, Saha and Sivasanker investigate the influence of Zn and Ga doping on the conversion of ethanol to hydrocarbons over ZSM-5(82). The result indicates that incorporation of Zn and Ga not only increases the yield of the liquid products, but also increases the life of catalyst. Moreover, H-transfer reaction increases when Zn and Ga are incorporated in H-ZSM-5 due to the lower olefin product of Zn and Ga doping catalysts.

In 2005, Inaba *et al.* studied the ethanol conversion to hydrocarbons over zeolite catalysts. H-Beta(27), H-ZSM-5(29,190), USY(6.3) and H-mordenite(18.3) with no metal loaded were used. H-ZSM-5 (Si/Al2 =29) zeolite had high activity for the production of BTX compounds (benzene, toluene, xylenes), while other zeolites exclusively formed ethylene. The introduction of Ga on H-ZSM-5 support resulted in the highest selectivity of toluene, xylene and total amount of BTX. In general, the catalysts yielding BTX in high selectivity deposit large amount of carbon, However, among the zeolite alone, H-Beta(27), USY(6.3) and H-mordenite(18.3) formed no or little BTX, but were prone to heavy deposits of carbon, while H-ZSM-5(29), which gave high yield of BTX, was subject to a moderate quantity of carbon deposits, suggesting that the larger micropore structure of zeolite may encourage carbon deposition. Among the metal catalysts supported on H-ZSM-5 zeolite, Au catalysts have highest inhibition of carbon deposition and no decrease in selectivity of BTX.

In 2010, Conversion of glycerol to alkyl-aromatics over zeolites was studied by Danuthai and co-workers. They investigated on a series of zeolites (HZSM-5, HY, Mordenite and HZSM-22) at 300-400 °C and atmospheric pressure or 2 MPa. Although propenal is the major primary glycerol dehydration product over all zeolites, the pore structure of zeolite play a significant role on the final product distribution. The major products over one-dimensional zeolites Mordenite and HZSM-22 are oxygenates (propenal, acetol, and heavy oxygenates) without aromatic formation. HZSM-22 is suitable for the production of propenal with 86% yield at 100% glycerol conversion. However, it is found that glycerol can be converted to high yields of alkyl-aromatics, mainly C8-C10 over three-dimensional HY and HZSM-5. A longer contact time, higher temperatures, and higher pressures favor the formation of aromatics, with a maximum yield of 60% over HZSM-5.

A two-bed configuration with a deoxygenation/hydrogenation catalyst (Pd/ZnO) as the first bed and HZSM-5 as the second bed can further increase the alkyl-aromatic yield. The mono-functional oxygenates produced by the first bed were oligomerized and aromatized into gasoline-range alkyl-aromatics over the second bed.

In 2008, Corna and coworker investigated the reaction pathway for the catalytic conversion of glycerol to acrolein over ZSM-5 catalyst in a fixed microactivity test (MAT) reactor. The found that, acrolein was obtained by reacting gas-phase glycerol/water mixtures with zeolite catalysts. Glycerol was converted through a series of reactions involving dehydration, cracking, and hydrogen transfer and catalyzed by the acid sites of the zeolite. Acrolein was the major product; short olefins, aromatics, acetaldehyde, hydroxyacetone, acids, and acetone also were formed through a complex reaction network.

In 2012, the conversion of glycerol to olefins was studied by Zakaria and co-worker. They proposed that, the acidity of ZSM-5 resulted in glycerol to undergo dehydration process to form 3-hydroxypropanal. In actual, the dehydration of glycerol can also precede via the formation of acetol. However, 3-hydroxypropanal is a more feasible option because of its tendency to break up further to acetaldehyde and formaldehyde; and vinyl alcohol and formaldehyde. Vinyl alcohol under the catalytic reaction condition will undergo deoxygenation process, releasing oxygen to form ethylene. At the same time, other side reactions involving acetaldehyde will trigger the formation of propylene and butylene. Acetaldehyde will undergo carbonyl bond specific dissociation [TS = Ethylidene oxo-species] to form propylene. At the same time protonated acetaldehyde will couple within itself to undergo reductive coupling to form butylene. From the experiment, the production of butylene was almost negligible and this can be explained by the cracking of butylene to form ethylene. Despite the formation of ethylene, propylene and butylene, continuous heating experienced by olefin remaining in the hydrocarbon pool of zeolite network will result to gradual C–H bond eventually broken, via dehydrogenation process, thus resulted to coke formation on catalyst surface. Furthermore, coke precursors prefer to form on surface with moderate to strong acid sites, which then finally lead to catalyst deactivation.

Gas-phase dehydration of glycerol over ZSM-5 catalysts was studied by Kim and co-workers in 2010. The effect of the SiO_2/Al_2O_3 ratios in ZSM-5 on the gas-phase dehydration of glycerol was examined over Na-ZSM-5 and H-ZSM-5. H-ZSM-5 with a SiO_2/Al_2O_3 ratio of 150 showed the highest glycerol dehydration activity at 315 °C among the various ZSM-5 catalysts. H-ZSM-5 with a SiO_2/Al_2O_3 ratio of 30 showed less catalytic activity than H-ZSM-5 with a SiO_2/Al_2O_3 ratio of 150. The amount of adsorbed H2O and its binding strength also decreased with increasing SiO_2/Al_2O_3 ratio in the case of HZSM- 5. Na-ZSM-5, having moderate Lewis acid sites, showed the least catalytic activity, which may be due to its weak acid strength for this reaction and strong adsorption of H_2O on the active sites. As long as the molar ratio between water and glycerol was in the range from 2 to 11, there was no noticeable difference in the glycerol conversion but the acrolein yield increased with increasing fraction of water in the feed.

Co-impregnation of Zn and Ln on HZSM-5(50) in aromatization of alcohols and ethers was studied by Ni and co-worker in 2010. For the methanol conversion, the result shown that, BTX selectivity is increased in presence of Zn in HZSM-5 but Ln/HZSM-5 has no improvement in BTX selectivity. Obviously, Zn species has abilities of efficiently converting alkenes of alkanes to aromatics and La acts as a promoter in the co-impregnated Zn/Ln/HZSM-5 catalyst only after the pretreatment in H_2 stream at 550 °C for 3 h. Moreover, Ln also stabilizes the life time of the catalyst. In case of different feedstock (Ethanol, DEE, and DME), the product distributions are very similar, in which C3 hydrocarbon, toluene, and xylene are main products.

Porosity is another important properties of ZSM-5 that facilitates the adsorption-desorption and diffusion behavior of the molecules. The additional porosity created by inter-crystalline void in nano particle size of ZSM-5 in process of ethanol to aromatic was studied by Viswanadham and co-worker in 2012. They found that, the nano crystalline H-ZSM-5(30) catalyst having high acidity and stack order of mesoporosity give higher aromatics yield over the micro crystalline H-ZSM-5(30).

The effect of acidity was also studied, the low acidity, micro crystalline H-ZSM-5(100) yield mainly propylene due to amount of acidity not efficient even for the formation of C_{5+} olefin leading to small amount of aromatics.

In 2002, Choudhary and co-worker studied the influence of space velocity and reaction temperature at atmospheric pressure on aromatization of dilute ethylene over H-GaAlMFI zeolite catalyst. The selectivity of aromatics, propene, propane and C_4 hydrocarbons and alkane/aromatics and H_2/aromatics mole ratios are strongly influenced by the space velocity. The results indicate that the aromatization involves H_2 transfer reactions predominantly at the lower temperatures and/or higher space velocities whereas dehydrogenation reactions become predominant at higher temperatures and/or lower space velocities.

The distribution of aromatics and C_8 aromatic isomers depends strongly upon the amount (i.e. yield) of aromatics and C_8 aromatics, respectively, formed in the process. The primary aromatics produced in the process are found to be mainly *p*- and *o*-xylenes. The aromatics distribution is controlled by the aromatics intertransformation(via.isomerization,alkylation/dealkylation and disproportionation) reactions. The *p*-xylene/*m*-xylene ratio is decreased as expected, but the *p*-xylene/*o*-xylene ratio is increased with increasing both the space velocity and temperature. The increase of *p*-xylene/*o*-xylene ratio is found to be unusual, much above the equilibrium value. This indicates that, the isomerization of *o*- to *p*- and *m*-xylene most probably controlled kinetically.

HZSM-5 zeolites always show low selectivity due to the presence of the unselective acid sites, which are believed to be located on the external surface and in the pore mouth regions of zeolites. In addition, the small difference in the diffusivities between the desired products and undesired products in as-synthesized zeolites attributes to the low selectivity of zeolites.

There are several methods to eliminate the external and pore mouth acid site have been studied, including pre-coking, CVD (chemical vapor deposition) and CLD (chemical liquid deposition).

In 1995, Bhat and co-worker studied n-pentane aromatization over chemical vapor deposited MFI zeolite to enhance *p*-xylene selectivity in total xylene. They found that *p*-xylene selectivity can be enhanced to 99% when using Silica deposition 21%wt. Moreover, with increase in reaction temperature from 500 to 540 °C, *p*-xylene selectivity changed only from 99 to 93%. It can easily be extended to aromatization of any other hydrocarbons such as propane or butane.

In 2002, Zheng and co-worker studied the influence of CLD on the distribution of acid sites in HZSM-5 zeolite and concluded that the concentration of Brønsted and Lewis acid sites was markedly decreased and the enhanced modification effects could be achieved using multi-cycle silylation for zeolite with small crystals.

In 2007, Zhu and co-worker prepared shape selectivity catalysts for the disproportionation of toluene by the modification of the ZSM-5 with chemical liquid deposition using polysiloxane. The result indicate that deposition of polysiloxane to silica mainly occurs on the external surface making lower amount of acid but and does not change the acidic strength distribution of ZSM-5. After four-cycle modification, the conversion of toluene is reduced from 48.6 to 27.1% and *p*-xylene selectivity is increased from 24.3 to 96.2%. So the external surface of modified ZSM-5 may be regard to be almost inactive.

In 2011, Teng Hui and co-worker studied the high shape selectivity ZSM-5 modified by using chemical liquid deposition in toluene disproportionation. They found that the best SiO_2/Al_2O_3 ratio is 38 to obtain high toluene conversion and *p*-xylene selectivity. For the effect of CLD condition, the results indicate that TEOS is the best CLD agent, cyclohexane and oxalic acid is the appropriate CLD solvent and treatment acid respectively for TEOS. External dealumination by acid treatment can improve activity of catalyst only corporate with CLD. Multi-cycle deposition not only increased the amount of silica deposited on external surface, but also improved the uniformity of the silica layer. On the other hand, the conversion is decreased as selectivity is increased.