

## CHAPTER II

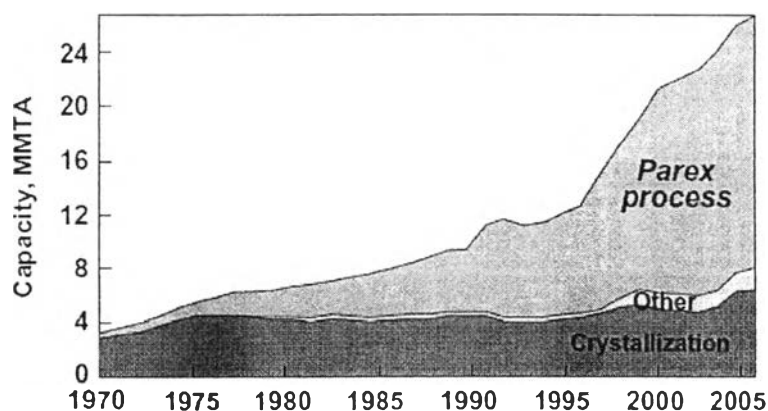
### LITERATURE REVIEW

#### 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 terephthalate (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  $26 \times 10^6$  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).



The mixed xylenes go overhead and on to the UOP Parex <sup>TM</sup> 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<sub>9+</sub> 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<sub>9+</sub> from Column 3 is rerun in Column 4 so that the A<sub>11+</sub> components are removed before sending the A<sub>9</sub> – A<sub>10</sub> components to the Tatoray unit. Meanwhile, the A<sub>7</sub>-aromatics from the Column 1 overhead are extracted by extractive distillation using Sulfolane solvent in the UOP Sulfolane <sup>TM</sup> process unit.

The non-aromatics in the C<sub>5</sub>–C<sub>8</sub> 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<sub>6+</sub> 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<sub>9</sub> – A<sub>10</sub> material from Column 6, to produce more benzene and mixed xylenes. The A<sub>8+</sub> material from the bottom of Column 5 is sent to Column 2 for recovery of the mixed xylenes produced in the Tatoray unit.

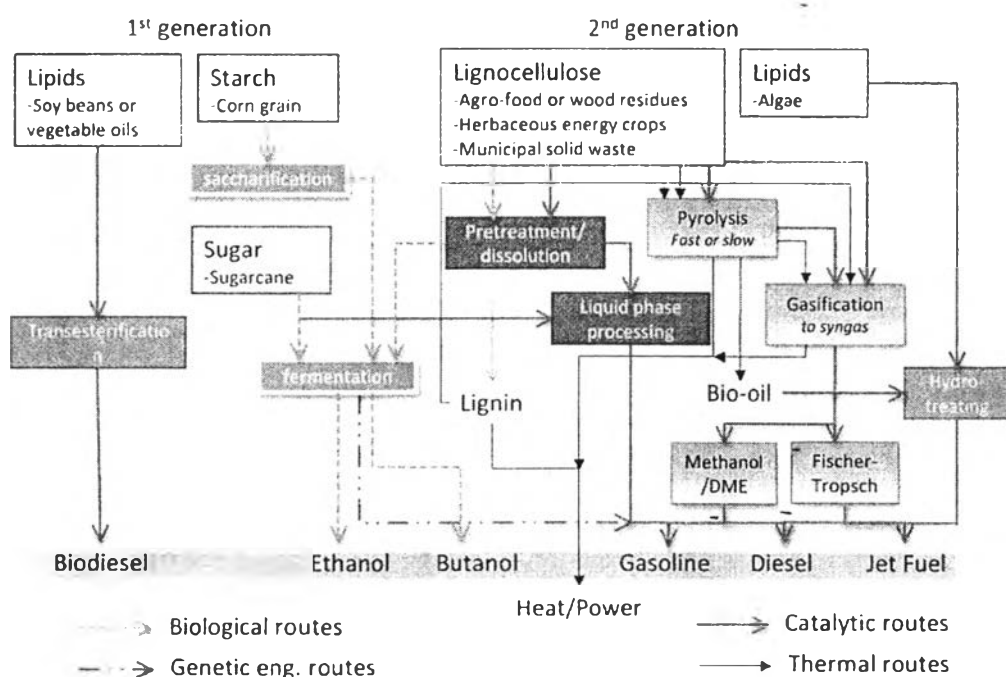
### 2.3 Biomass as a Feedstock (Stefaan Stevens, 2010)

Biomass used for the production as energy source of organic basic block can be divided into two main “generations”. In the first generation is biomass in competition with the food industry (sugarcane, corn, and cassava) which is not the case for second generation biomass. Two types of second biomass types can be distinguished: lignocellulosic biomass (corn stover, switch grass) and microalgae.

The first generation biomass contains starch, sugars and lipids. Sugarcane can after a physical pretreatment directly be transformed through fermentation to bio ethanol. Starch containing bio ethanol requires an additional preliminary saccharification step. Lipids can through catalytic transesterification be converted into biodiesel.

Converting processes starting from second generation biomass are not commercially attractive yet but offers, as mentioned before great advantages compared to the first generation biomass. There are three main routes for the conversion of lignocellulosic materials into biofuels: thermo chemical, bio chemical and chemo catalytic.

Many routes exist for converting biomass to biochemical/fuels. An overview of the main routes of biomass to biofuels is illustrated in Figure 2.3. Depending of the type of biomass different conversion routes are possible.



**Figure 2.3** Main routes to biofuels (Stefaan Stevens, 2010).

Reactions of methanol and higher alcohols over H-ZSM-5 were studied as a function of time, temperature, total pressure and H<sub>2</sub> partial pressure in a batch reactor. The observed yields were compared to the theoretical yields of C<sub>8</sub> species (typical gasoline species) based on the number of carbon atoms to give the

percentage of theoretical yield as to show that longer chain alcohols produce more C8-type hydrocarbons (Gujar *et al.*, 2009).

### 2.3.1 Ethanol

Ethanol is an alcohol-based fuel made by fermenting and distilling starch crops, such as corn and cassava. It can also be made from "cellulosic biomass" such as trees and grasses. The use of ethanol can reduce our dependence upon foreign oil and reduce greenhouse gas emissions.

Ethanol has been made since ancient times by the fermentation of sugars. All beverage ethanol and more than half of industrial ethanol is still made by this process. Simple sugars are the raw material. Zymase, an enzyme from yeast, changes the simple sugars into ethanol and carbon dioxide. The fermentation reaction, was represented by the simple equation.



In 2006, global production of bioethanol reached 13.5 billion gallons, up from 12.1 billion gallons in 2005. Bioethanol currently accounts for more than 94% of global biofuel production, with the majority coming from sugar cane. About 60% of global bioethanol production comes from sugar cane and 40% from other crops. Brazil and the United States are the world leaders, which exploit sugar cane and corn, respectively, and they together account for about 70% of the world bioethanol production. Thailand also produces a lot of ethanol. The top ten bioethanol producers are presented in Table 2.1 (Balat *et al.*, 2008).

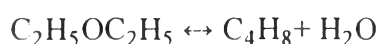
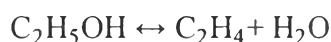
**Table 2.1** The top ten bioethanol producers (billion gallons)

Country	2004	2005	2006
USA	3.54	4.26	4.85
Brazil	3.99	4.23	4.49
China	0.96	1.00	1.02
India	0.46	0.45	0.50
France	0.22	0.24	0.25
Germany	0.07	0.11	0.20
Russia	0.20	0.20	0.17
Canada	0.06	0.06	0.15
South Africa	0.11	0.10	0.10
Thailand	0.07	0.08	0.09

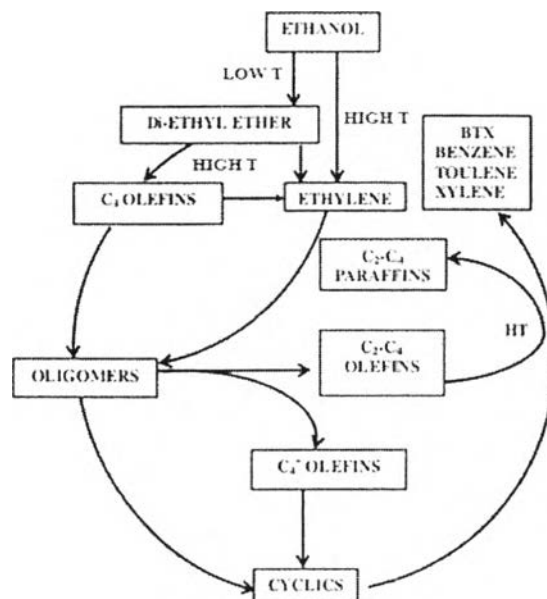
### 2.3.1.1 Reaction Mechanism of Ethanol

At low temperatures, the preferable formation of diethylether by intermolecular dehydration between two ethanol molecules occurs.

However, the formation of ethylene by intramolecular dehydration of ethanol or diethylether exclusively occurs at higher reaction temperature. It appears that diethylether can be converted to C<sub>4</sub> olefins as well as to ethylene by dehydration,



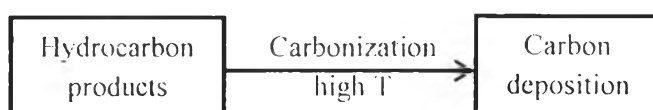
Ethylene and C<sub>4</sub> olefins, formed by dehydration, could undergo further reactions such as oligomerization, aromatization(cyclization), H transfer or cracking, to give higher hydrocarbons (olefins, paraffins,BTX and other aromatic products such as ethylbenzene and C<sub>9+</sub>). These reactions are enhanced by using solid acid catalyst especially H-ZSM-5 zeolite and some metals supported on zeolites can enhance the formation of BTX (Inaba *et al.*, 2006).



**Figure 2.4** Reaction pathway of ethanol to hydrocarbon.

Moreover, benzene and toluene in aromatics can be produced from dealkylation reaction of ethylbenzene and  $C_{9+}$  with hydrogen (Choudhary *et al.*, 1984).

In general, catalysts yielding hydrocarbon product (olefins, paraffins and aromatics) can be deactivated by depositing of carbon from hydrocarbon products via carbonization reaction at high temperature.



**Figure 2.5** Deposition of carbon.

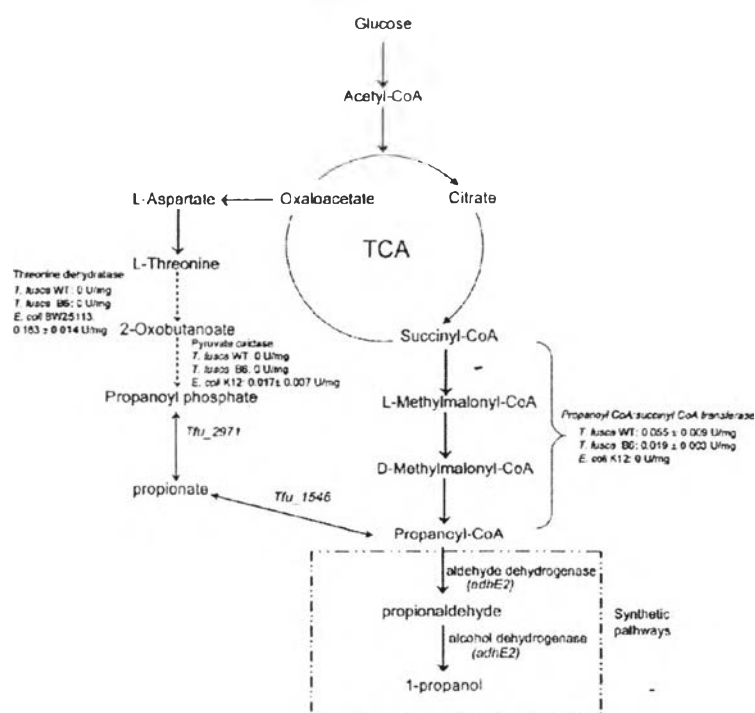
### 2.3.2 Propanol

Propanol is a secondary alcohol that is commonly used as a solvent. It can be found in most paints and wood stains as well as cleaners, cosmetics, and adhesives. The alcohol also finds use in industrial processes as a dehydrating agent. Its most commonly known domestic use is in rubbing alcohol at generally a mixture of 70% isopropanol and 30% water. Isopropanol, or isopropyl alcohol, is a clear, flammable liquid which smells of acetone. The structure of isopropanol consists of a

three carbon chain with the alcohol attached at the middle carbon. Its formula is  $C_3H_8O$ .

Due to its dehydrating nature, propanol has been used as a biological specimen preservative. This allows for a non-toxic alternative to formaldehyde while still accomplishing proper preservation. In regards to safety concerns, propanol is a volatile liquid which is highly flammable. Therefore, caution should be exercised when using the solvent near heat sources.

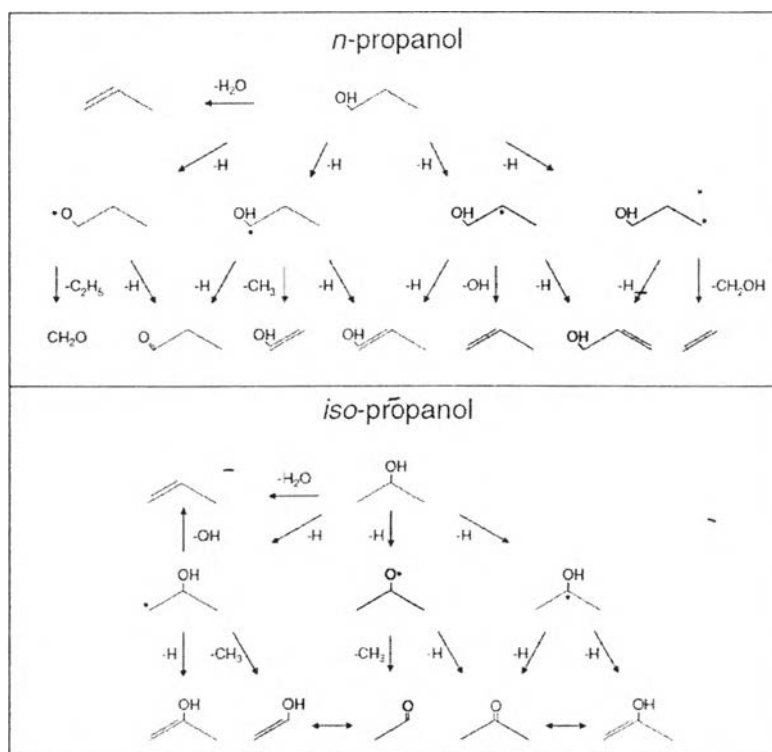
Biopropanol can be derived from *E. coli* bacteria via fermentation the direct conversion of untreated plant biomass to 1-propanol in aerobic growth conditions using an engineered strain of the actinobacterium, *Thermobifidafusca*. (Yu Deng *et al.*, 2011).



**Figure 2.6** Schematic illustration of 1-propanol production via the threonine and succinyl-CoA:propanoyl-CoA path way the genetically engineered *T. fusca*.



### 2.3.2.1 Reaction Mechanism of Propanol



**Figure 2.7** Reaction mechanism of *n*-propanol and iso-propanol decomposition.

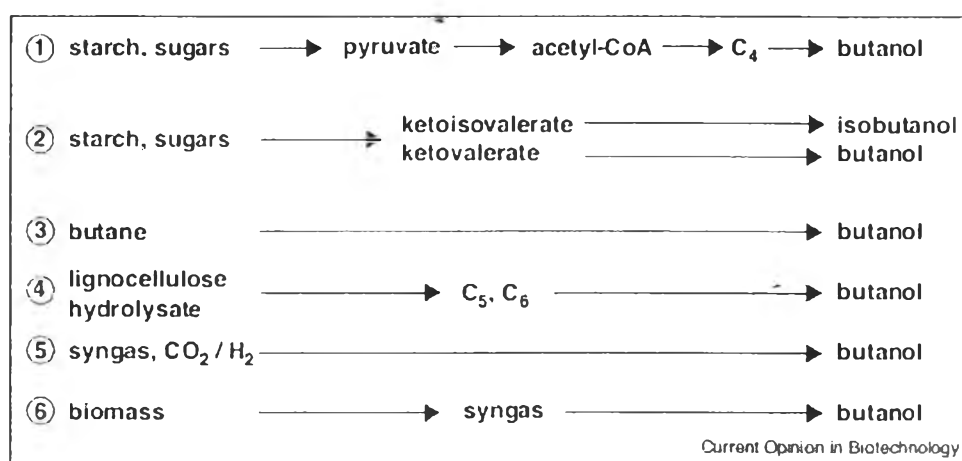
From Figure, 2.7 H-abstraction reactions form three different intermediate radicals  $\text{C}_3\text{H}_7\text{O}$  whose major decomposition product is acetone. *n*-propanol is the most reactive of the two isomers (*n*-propanol and isopropanol) due to the larger importance of radical pathways with the significant formation of propanal ( $\text{C}_2\text{H}_5\text{CHO}$ ). As usual, H-abstraction reactions of OH and H radicals are the dominant ones. On the contrary, molecular dehydration of iso-propanol is the main source of propylene. The formation of 1-propyl radical and the successive demethylation reaction.

### 2.3.3 Butanol

Butanol ( $\text{C}_4\text{H}_{10}\text{O}$ ) or butyl alcohol is an alcohol that can be used as a solvent or fuel. Biobutanol refers to butanol that has been produced from biomass. Biobutanol is produced by a microbial fermentation, similar to ethanol and can be made from the same range of sugar, starch or cellulosic feedstocks. Biobutanol

production is currently more expensive than ethanol so it has not been commercialized on a large scale. However, biobutanol has several advantages over ethanol and is currently the focus of substantial research and development.

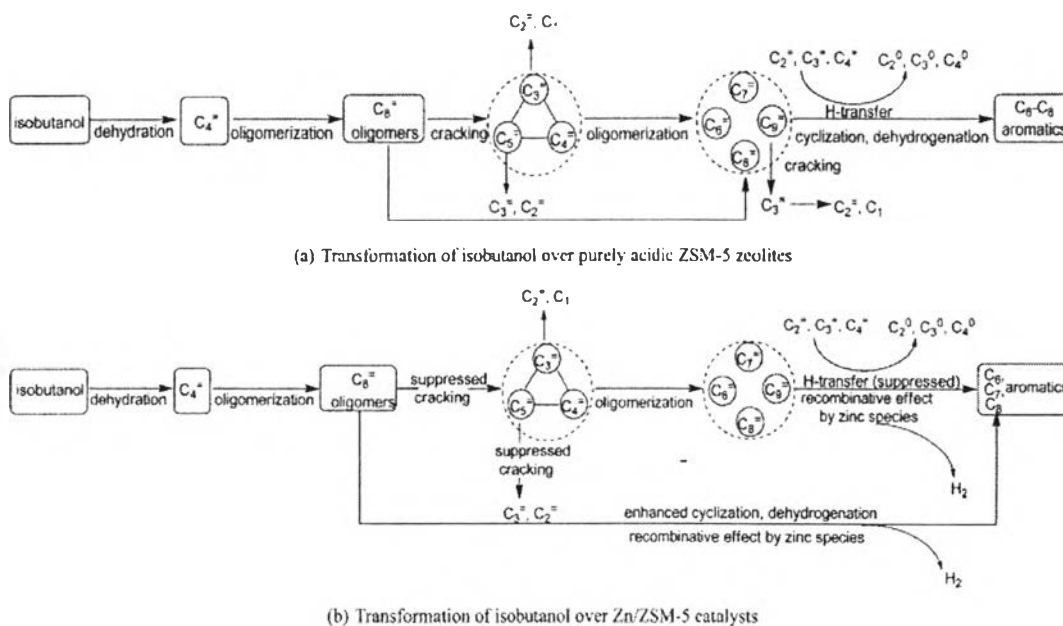
Metabolic and engineered pathways leading to butanol show in Figure 2.8 Starch or sugars are degraded by glycolysis to pyruvate, which is converted to acetyl-CoA,  $\text{CO}_2$ , and reduced ferredoxin by pyruvate: ferredoxin oxidoreductase. Two molecules of acetyl-CoA are then combined to acetoacetyl-CoA, which in turn is formed into 3-hydroxybutyryl-CoA, crotonyl-CoA, butyryl-CoA, butyraldehyde, and finally butanol (Fermentative production of butanol — the academic perspective Peter Durre)



**Figure 2.8** Metabolic and engineered pathways leading to butanol.

### 2.3.3.1 Transformation of Isobutyl Alcohol

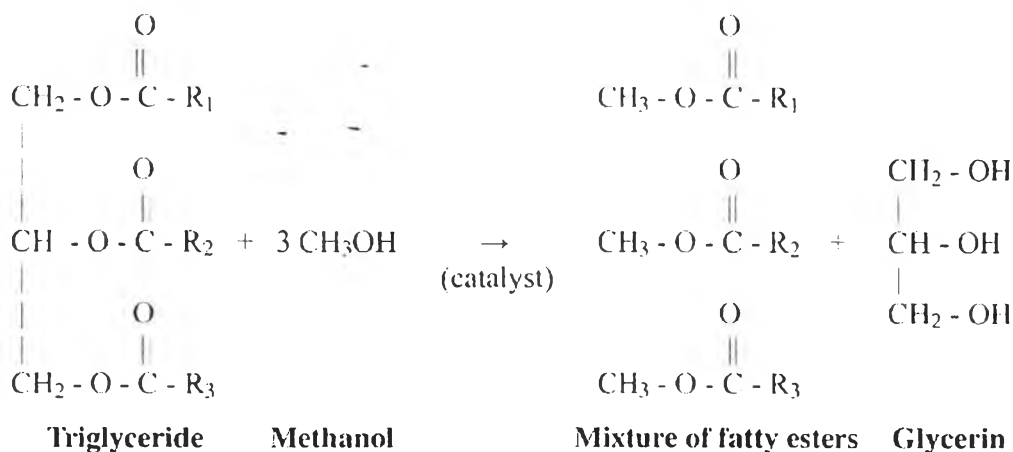
Figure 2.9 describes the major reaction pathways for the conversion of isobutyl alcohol to aromatics over the ZSM-5 zeolites. Starting from isobutyl alcohol, aromatics are formed through the steps of dehydration, oligomerization, cyclization, and the parallel hydrogen transfer reactions. Butane isomers are generated at the expense of isobutene and butene isomers as the balanced products of aromatics due to the hydrogen transfer reactions. Another major balanced product of propane is generated through the combined oligomerization–cracking and hydrogen transfer of  $\text{C}_6$ – $\text{C}_9$  oligomers.



**Figure 2.9** Transformation pathways of isobutyl alcohol over ZSM-5 and Zn/ZSM-5 Catalysts.

### 2.3.4 Glycerol

Biodiesel is mainly produced through a process known as transesterification, as shown in Figure 2.10 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 2.10** Transesterification reaction.

Where R1, R2, and R3 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).

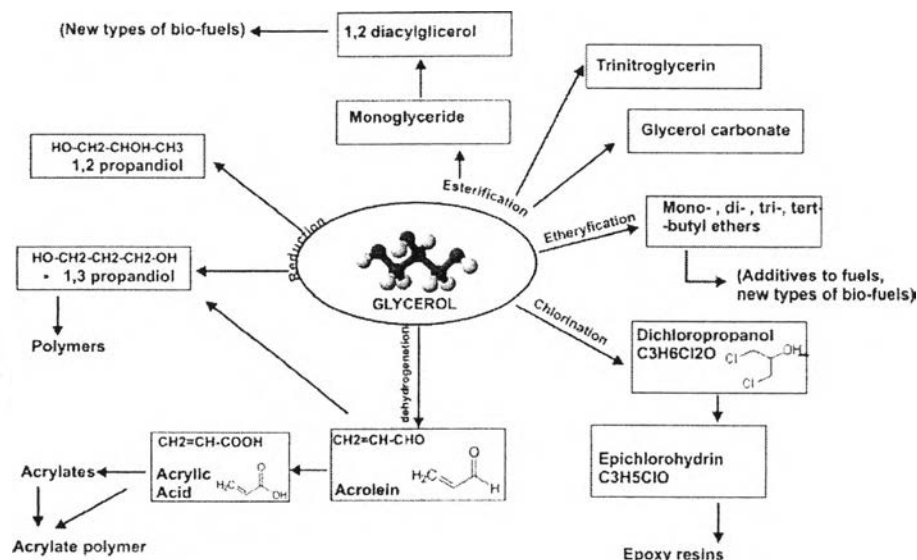
#### 2.3.4.1 Conversion of Glycerol into Other Chemical Products

Figure 2.11 summarizes 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-worker studied the synthesis of acrolein 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 ( $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ ) 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 ( $\text{Cu}/\text{Al}_2\text{O}_3$ ).

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 2.11** Methods of conversion of glycerol into useful products (Marek Stelmachowski, 2011).

## 2.4 Structure of Zeolite

Zeolites are water-containing crystalline aluminosilicates with highly ordered structures consisting of  $\text{SiO}_4$  and  $\text{AlO}_4$  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  $\text{AlO}_4$  tetrahedron come to have the oxidation number of -1.

The  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedron unit are connected each other through common oxygen atoms to give a three-dimensional network. Negative charges from  $\text{AlO}_4^-$  tetrahedrons usually compensated by protons, metal cations, or  $\text{NH}_4^+$ . 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:

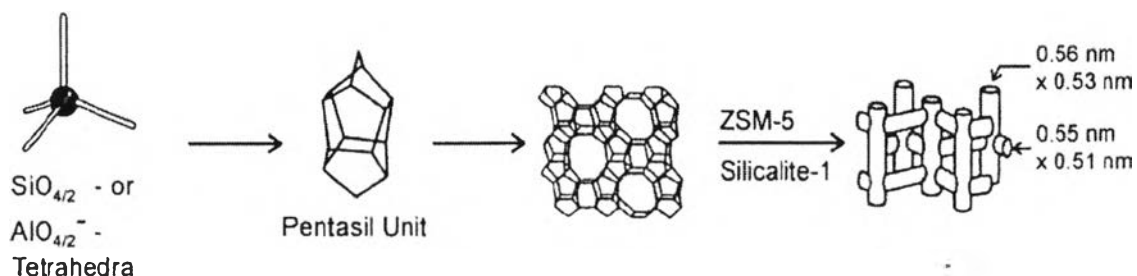
- Well defined crystalline structure, good reproducibility in production.
- Well define inner pores in which active species can be resided.
- Adjustable framework composition and cations associated with different acid properties and stability.

- 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 2.2** Structure of zeolite (Tsai, *et al.*, 1999)

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

ZSM-5 zeolite or MFI is one of the most important zeolites used in petroleum and petrochemical industry. The structure of ZSM-5 zeolite, shown in Figure 2.12, 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 2.12** Structure of ZSM-5 zeolite.

## 2.5 Acidity of Zeolite

HZSM-5 is the protonic type of ZSM-5 zeolite that have 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  $\text{NH}_4\text{NO}_3$  solution to be  $\text{NH}_4^+$  form
- iii) Calcination of  $\text{NH}_4^+$  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 depend 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.

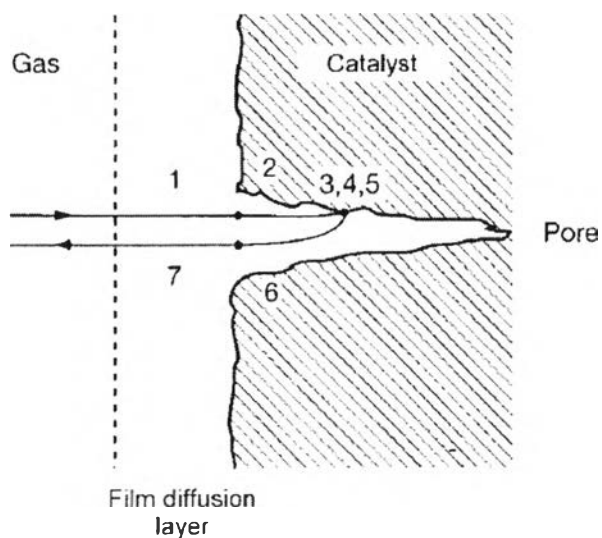
In 1998, Weber *et al.* measured the concentration of the acid sites of silylated HZSM-5 zeolites using temperature programmed desorption (TPD) of 4-methyl-quinoline. As the kinetic diameter of 4-methyl-quinoline (7.3 Å) is larger than the pore openings of HZSM-5 zeolites ( $5.6 \times 5.3$  Å), this 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.

## 2.6 Mechanisms of the Shape Selectivity

Zeolite usually shows specific selectivity in some reactions due to their well-defined pore structure. It is generally believed that the majority of active sites are 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.



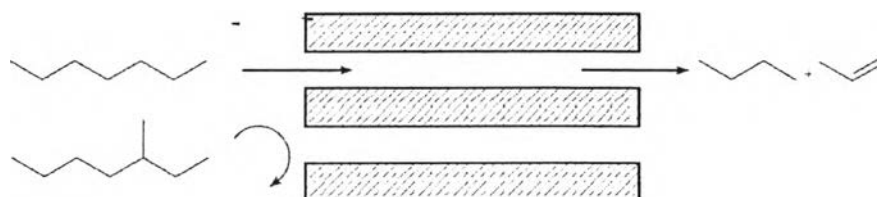


**Figure 2.13** Individual steps of a heterogeneously catalyzed gas-phase reaction (Hagen, *et al* 2006).

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 ;

#### 2.6.1 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

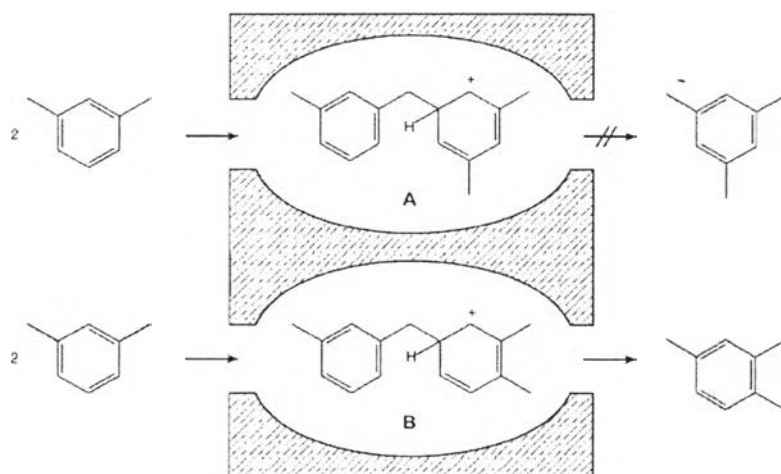


**Figure 2.14** Reactant shape selectivity of n-alkane compare with iso-alkane (Hagen, 2006).

### 2.6.2 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 fit 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).

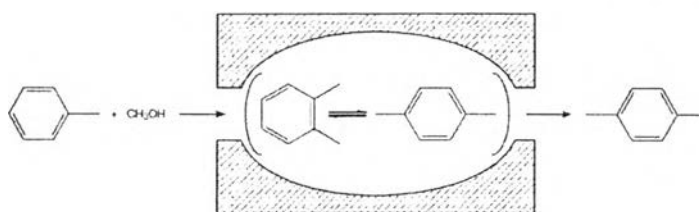


**Figure 2.15** Transition state selectivity of disproportionation of *m*-xylene (Hagen, 2006).

### 2.6.3 Product Shape Selectivity

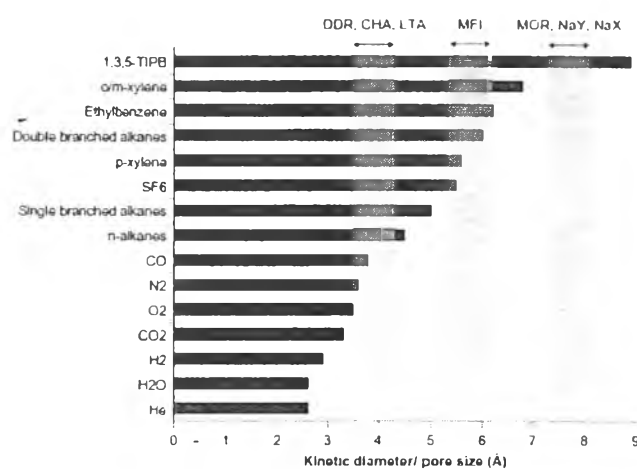
Product shape selectivity relates to the cavity size of a zeolite, only products of a certain size and shape that can exit from the pore system are formed. Deviation of product distribution from equilibrium composition can be seen in this selectivity if the products involved in the reaction are large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

For example, the methylation of toluene Figure 2.16 and the disproportionation of toluene on ZSM-5. In both reactions all three isomers *o*-xylene, *m*-xylene, and *p*-xylene are formed. The desired product *p*-xylene can be obtained with selectivities 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 2.16** 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 2.17 below.



**Figure 2.17** Kinetic diameter of common industrial molecules shown relative to the pore sizes of common zeolite structures (Kulprathipanja, 2010).

## 2.7 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/Al<sub>2</sub> =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 has 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 Dañuthai 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 acrolein 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 micro activity 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 2010, Yiwen and coworker studied the catalytic behavior of H-ZSM-5 and Zn/H-ZSM-5 for the aromatization of dimethyl ether (DME) was investigated. The increase in the number and strength of acid sites on the H-ZSM-5 zeolite was beneficial for DME aromatization. Aromatization performance was enhanced by loading Zn into H-ZSM-5. The yields of total and C8 aromatics over H-ZSM-5 at 360 °C were 50.0% and 28.6%, respectively, and over Zn/H-ZSM-5 (Zn 2% in mass) were 66.2% and 39.0%, respectively. At 480 °C, the total aromatics yield increased to 78.0% over Zn/H-ZSM-5.

In 2012, Varvarin and coworker investigated conversion of n-butanol to hydrocarbons over H-ZSM-5, H-ZSM-11, H-L and H-Y zeolites at 300–400 °C using a fixed bed flow reactor has been studied. It was shown that all studied H-zeolites provide 100% alcohol conversion at 300 °C. The conversion products are liquid hydrocarbons C5–10, gaseous hydrocarbons C<5 and water. The yield of liquid hydrocarbons over the H-pentasil is higher (52–55 wt.%) than over large pore H-L and H-Y (43–48 wt.%). The liquid fraction obtained over H-ZSM-5 includes aromatics mainly whereas on H-Y-olefins. It was shown that H-ZSM-5 (Si/Al = 20) is capable to provide the yield of liquid hydrocarbons on the level of 50–55 wt.% from spent alcohol at load on a catalyst up to 20 mmol C<sub>4</sub>H<sub>9</sub>OH g<sup>-1</sup> cat h<sup>-1</sup>.

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.

In 2012, Yu and coworker Studied transformation of isobutyl alcohol to aromatics in a gas phase, fixed-bed reactor system over several purely acidic zeolites. (USY4.3,  $\beta$ 31.6, ZSM-11<sup>26.6</sup>, ZSM-5<sup>13.3</sup>, ZSM-5<sup>34.3</sup>, and ZSM-5<sup>42.7</sup>) ZSM-5 zeolites at 450 °C under atmospheric pressure give higher aromatics yields (~42 wt %) among the evaluated zeolites, and the Si/ Al ratios (Si/Al = 13–43) of ZSM-5 slightly influence their catalytic performances. The yields to benzene, toluene, and xylene reach 33–35 wt % over the purely acidic ZSM-5 catalysts; however, large amounts of propane and isobutane are also generated as the balanced byproduct. To improve the conversion to aromatics, several metal species (Zn, Ga, Mo, La, Ni, Ag, and Pt) are supported on the ZSM-5. The enhancements in aromatics yields (~60 wt %) are observed only on the Zn/ZSM-5 catalysts. With the suitable Zn loading (2.3–5.1 wt %), the yields to benzene, toluene, and xylene are increased to 49–52 wt %. Mainly the Zn species residing at exchange sites promote the transformation of isobutyl alcohol are decrease the strong-strength Brønsted acidity of the ZSM-5 zeolites and thus suppress the multiple oligomerization cracking steps for the formation of C3 fragments and facilitate the recombinative desorption of H atoms to H<sub>2</sub> and improve the dehydrogenation reactions for the formation of aromatics. Therefore, the Zn/ZSM-5 catalysts promote the formation of toluene and xylene and inhibit the generation of undesired propane and butane isomers.

Gas-phase dehydration of glycerol over ZSM-5 catalysts was studied by Kim and co-workers in 2010. The effect of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 150 showed the highest glycerol dehydration

activity at 315 °C among the various ZSM-5 catalysts. H-ZSM-5 with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 30 showed less catalytic activity than H-ZSM-5 with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 150. The amount of adsorbed H<sub>2</sub>O and its binding strength also decreased with increasing SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O 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 Youming and co-worker in 2010. For the methanol conversion, the result shown that, BTX selectivity is increased in presence of Zn in HSM-5 but Ln/HSM-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<sub>2</sub> 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 C<sub>3</sub> 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 2011. 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<sub>5+</sub> 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<sub>4</sub> hydrocarbons and alkane/aromatics and H<sub>2</sub>/aromatics mole ratios are strongly influenced by the space velocity. The results indicate that the aromatization involves H<sub>2</sub> 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.

HZSM-5 zeolite is one of the most well-known solid acid catalysts, and has been widely used in the fuel-upgrading and production of many petrochemicals. HZSM-5 zeolite is attributed to the presence of strong acid sites, which are responsible for the catalytic activity, and the intersecting 10-member ring (MR) micropores, which account for the shape-selectivity and coke resistance exhibited over this catalyst. However, the coke formation, which usually deactivates the zeolite catalyst, is still pronounced owing to the strong acid sites associated with the framework aluminum, and long diffusion pathlength of the regular micropores.

The traditional method for improving the catalytic stability of zeolite catalyst is reducing the acid sites density by dealumination. Steaming treatment and acid leaching are usually employed to lower the number of framework aluminum. In contrast to the dealumination, the desilication by alkali treatment can preferentially remove the silicon of zeolite, and is an intriguing new strategy for creating mesopores on the material without destroying the micropores.

The distribution of aromatics and C<sub>8</sub>-aromatic isomers depends strongly upon the amount (i.e. yield) of aromatics and C<sub>8</sub>-aromatics, respectively, formed in the process. The primary aromatics produced in the process are found to be mainly *p*-xylene and *o*-xylene. The aromatics distribution is controlled by the aromatics intertransformation (viz. 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*-xylene to *p*-xylene 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.

In 2007, Li and co-worker studied Aromatization and isomerization of 1-hexene over alkali-treated HZSM-5 zeolites. The results showed that new mesopores could be created and enlarged on ZSM-5 zeolite by increasing the NaOH concentration, temperature and treatment time in the alkali treatment. However, excessive high NaOH concentration induced the collapse of zeolite framework. Alkali treatment HZSM-5 were used as catalysts the reaction activity of 1-hexene was enhanced, and the stabilities of aromatization and isomerization reactions were improved, which shortened the diffusion pathlength of the feed/products and reduced the channel blockage from coke.

In 2011 Ni and co-worker studied Preparation of hierarchical mesoporous Zn/HZSM-5 catalyst and its application in MTG reaction. They found that the mesopores formed by alkali-treatment in the Zn/HZ5/0.3AT zeolite catalyst enhance the synergetic effect between Zn species and acid sites and the resistance to coke deposition. Impregnation of Zn cations onto ZSM-5 zeolite can improve the selectivity to aromatic hydrocarbons. Therefore, the preparation of hierarchical mesoporous HZSM-5 zeolite by alkali treatment and introduction of Zn cations on it are effective and facial approaches to enhance the catalytic performance of MTG reaction over HZSM-5 catalysts with only micropores.

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, 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  $\text{SiO}_2/\text{Al}_2\text{O}_3$  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.