

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Palm Fatty Acid Distillate (PFAD)

PFAD is a by-product from the physical refining of crude palm oil. In order to avoid the soap formation during the transesterification, the free fatty acid contained in crude palm oil was separated by physical refining process. Generally, its appearance is a light brown semi-solid at room temperature and contains more than 90 wt % of free fatty acid (Ping *et al.*, 2009). The feed analysis showed that more than 80 wt % of fatty acid in PFAD was comprised with palmitic and oleic acid (Table 2.1). Due to the low oxygen content in their molecule, non-food competitive resource, and low-cost raw material, PFAD was studied as an alternative feedstock for producing biodiesel, hydrocarbon in diesel range, and hydrogen.

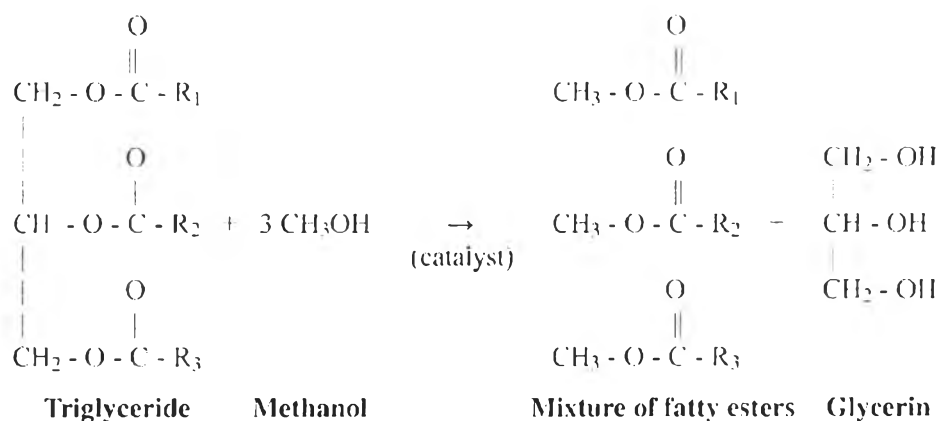
The hydrotreating of C<sub>18</sub> fatty acids to biofuels was studied in fixed bed reactor over NiW/SiO<sub>2</sub>Al<sub>2</sub>O<sub>3</sub> catalyst. The results showed that the hydrotreating temperature is the most dominant operating parameter that affects the deoxygenation activity. By varying the reaction conditions it was concluded that the hydrodeoxygenation to decarbonylation/decarboxylation ratio increases with decreasing temperature and/or increasing pressure. While, low temperature and high WHSV will promote the isomerization reaction to cause more iso-paraffins in the products (Yang *et al.*, 2013).

**Table 2.1** Free fatty acid composition of palm fatty acid distillate

PFAD composition	wt %
Myristic (C <sub>14:0</sub> )	1.2
Palmitic (C <sub>16:0</sub> )	55.1
Stearic (C <sub>18:0</sub> )	3.7
Oleic (C <sub>18:1</sub> )	34.0
Linolenic (C <sub>18:2</sub> )	6.1

## 2.2 Glycerol from Biodiesel

Glycerol has three hydroxyl groups in the molecule that are responsible for its solubility in water. Its appearance is a colorless, odorless, and viscous liquid. Nowadays, glycerol is mainly supply as a by-product from oleochemicals industry. It was estimated that every gallon of biodiesel produced approximately 1.5 pounds of glycerol (Karinen et al., 2006). The by-product glycerol was generated following the reaction in Figure 2.1. However, the rapid growing of oleochemicals industry in the last ten years resulted in the excess amount of glycerol in the market, thus lower its price. To solve this problem, many researchers have been studied on the conversion of glycerol to valuable chemicals.



**Figure 2.1** Transesterification reaction.

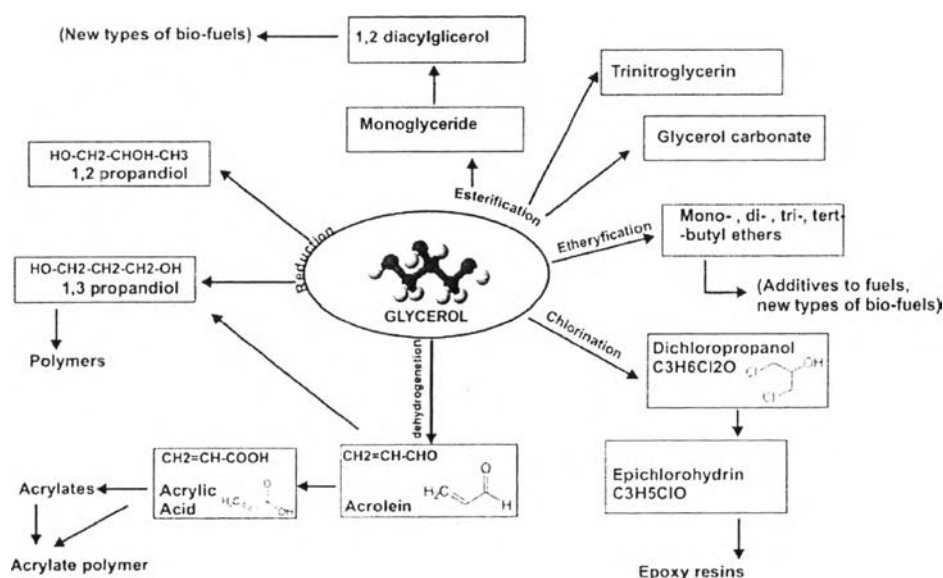
Figure 2.2 summarizes the different possible reaction pathways and products. Most of the studies focused on the dehydration of glycerol into acrolein (propenal), the synthesis of alcohols, particularly 1,2-propanediol, and the production of additives for fuels.

Tsukuda and co-workers studied the synthesis of acrolein from glycerol. The aim of the study was to optimize the composition of the catalyst. It was found that by using the highest temperature and Q10-SIW-30 ( $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 24\text{H}_2\text{O}$ ) catalyst the highest acrolein was obtained (Tsukuda *et al.*, 2007). 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 %) while the higher temperatures favor the conversion into acetaldehyde (Corma *et al.*, 2008).

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 approximately 42 % (Guo *et al.*, 2009). 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<sub>2</sub>O<sub>3</sub>) (Akiyama *et al.*, 2009).

Frusteri and co-worker studied the etherification of glycerol with *tert*-butyl alcohol by using modified solid acids catalysts. The results showed that the more accessible acid sites and large pore of catalysts play a key role in promoting the catalytic activity, thus glycerol conversion and selectivity were exceeded 93 % (Frusteri *et al.*, 2009).



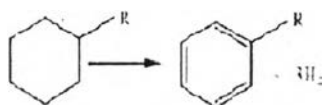
**Figure 2.2** Methods for the conversion of glycerol into useful products (Stelmachowki *et al.*, 2011).

## 2.3 Production of Aromatics

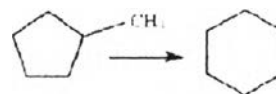
### 2.3.1 Catalytic Reforming

The aromatic hydrocarbons are mainly produced from crude oil by catalytic reforming or hydroreforming of heavy naphtha, naphtha pyrolysis, and catalytic cracking FCC (Topsøe *et al.*, 1988). The use of Catalytic naphtha reforming as a process to produce high-octane gasoline is as important now as it has been for about half century of its commercial use. The catalytic reformer occupies a key position in a refinery, providing high value-added reformat for the gasoline pool; hydrogen for feedstock improvement by the hydrogen-consuming hydrotreatment processes; and frequently benzene, toluene, and xylene aromatics for petrochemical uses. Naphtha is transformed into reformat by catalytic reforming. This process involves reconstruction of low-octane hydrocarbons in the naphtha into more valuable high octane gasoline components without changing the boiling point range. Naphtha and reformat are complex mixtures of paraffins, naphthenes, and aromatics in the C<sub>5</sub>-C<sub>12</sub> range. The reactions take place on bifunctional catalysts for converting the hydrocarbons contained in naphtha fractions to monocyclic aromatics. To achieved that the FCC catalyst contains four important components; crystalline zeolite, matrix, binder, and filler. Normally, FCC catalyst was zeolite with faujasite topology because its strong Brønsted acid sites was required for the hydrocarbon cracking. Moreover, the matrix component, containing amorphous alumina also provided the mild catalytic active site and form a diffuse medium (larger pores) that allow larger hydrocarbons to enter. As a result, a large number of reactions occur in catalytic reforming over bifunctional catalysts, such as dehydrogenation and dehydroisomerization of naphthenes to aromatics, dehydrogenation of paraffins to olefins, dehydrocyclization of paraffins and olefins to aromatics. All reactions are desirable except hydrocracking, which occurs to a greater extent at high temperature and converts valuable C<sup>+</sup> molecules (reformat) into light gases, and coke formation that will eventually deactivate the catalyst. Some examples of these reactions are shown in Figure 2.3.

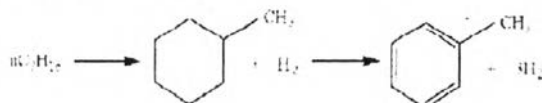
## Dehydrogenation of alkylcyclohexanes



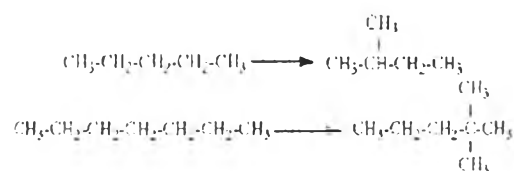
## Isomerization of alkylcyclopentanes



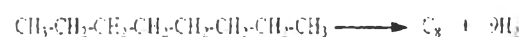
## Dehydrocyclization of paraffins



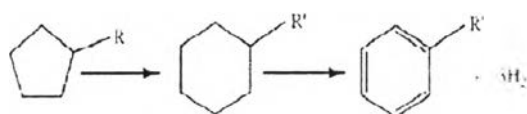
## Isomerization of paraffins



## Coke formation



## Dehydroisomerization of alkylcyclopentanes



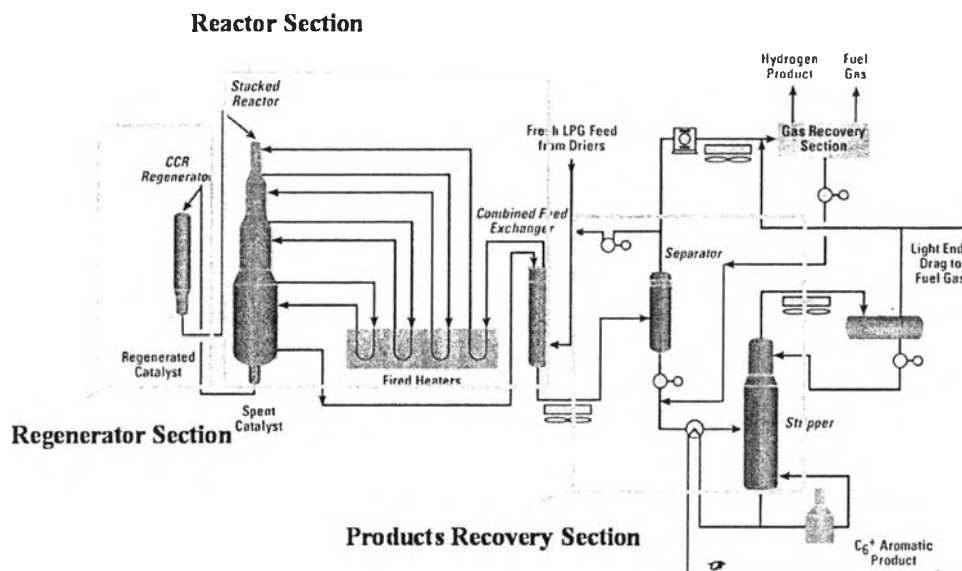
## Hydrocracking of paraffins



**Figure 2.3** Major reactions in catalytic reforming of naphtha.

### 2.3.2 Cyclar Process

Cyclar catalytic process is one of the most important processes for producing aromatics. This process was based on Universal Oil Production (UOP) continuous catalyst regeneration (CCR) technology and a catalyst formulation established by BP. Due to the propose of convert the light alkanes (by-product from FCC unit) to BTX aromatics, the catalyst have to available in oligomerization, cracking, and aromatization. There are three main components namely zeolite, gallium, and binder. It was reported that the Brønsted acid site of zeolite was responsible for the cracking, oligomerization, aromatization while the promoted Ga play a key role as a dehydrogenation metal, converting light alkanes to alkenes, precursor for producing aromatics. The binder component provides mechanical integrity and spherical shape to the catalyst.



**Figure 2.4** Schematic representation of UOP Cyclar Process.

The Cyclar process can be divided into three main sections; (i) Reactor, (ii) Regenerator, and (iii) Products Recovery. Because the net reaction is endothermic, the interstate reheating was applied to achieve high per pass conversions while maintaining high aromatics selectivity. The limitation of the catalyst is the fast deactivation, thus requiring it to be regenerated continuously. To solve this problem, the Cyclar process use UOP's Continuous Catalyst Regeneration (CCR) technology. The catalyst regeneration is performed by burning off the coke in the fluidized bed and moving the deactivated catalyst to the regenerator and the re-activated catalyst to the reactor. As a result, the aromatic yield is stable in long term operation.

## 2.4 Aromatization

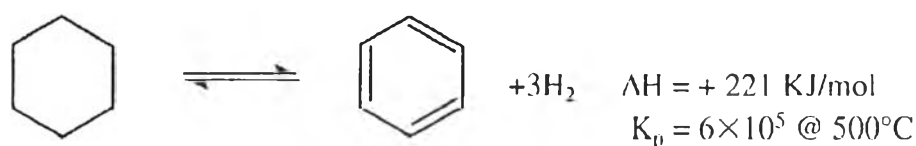
One of the most important reactions to obtain high value added products from naphtha feedstock is the aromatization of *n*-alkane which is of considerable theoretical and industrial importance. This reaction is highly complex reaction which involves transformation of various hydrocarbons into different reaction steps. The aromatization of *n*-alkanes over solid acid catalyst such as ZSM-5 can be explained

via a two-step mechanism which first includes dehydrogenation and cracking of paraffins to form an olefinic intermediate and then dehydrocyclization of the olefinic intermediate to form aromatics.

The two reactions directly responsible for enriching aromatics are the dehydrogenation of naphthenes and the dehydrocyclization of paraffins.

#### 2.4.1 Dehydrogenation

The first reaction can be represented by the dehydrogenation of cyclohexane to benzene in Figure 2.5.



**Figure 2.5** Schematic of cyclohexane dehydrogenation to benzene.

This reaction is fast; it reaches equilibrium quickly. The reaction is also reversible, highly endothermic, and the equilibrium constant is quite large. It is evident that the yield of aromatics (benzene) is favored at higher temperatures and lower pressures. The effect of decreasing  $\text{H}_2$  partial pressure is even more pronounced in shifting the equilibrium to the right. However,  $\text{H}_2$  is still needed to retard the coke formation.

#### 2.4.2 Dehydrocyclization

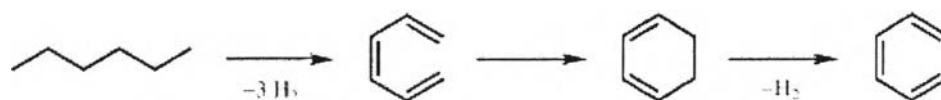
The second process is the dehydrocyclization of paraffins to aromatics. For example, if *n*-hexane represents this reaction, the first step would be the dehydrogenation of hexane molecule over the platinum surface, giving *l*-hexene (2- or 3-hexenes are also possible isomers) after that passed through the cyclization to cyclohexane ring then dehydrogenates to benzene in Figure 2.6.



**Figure 2.6** Schematic of *n*-hexane dehydrocyclization to benzene.

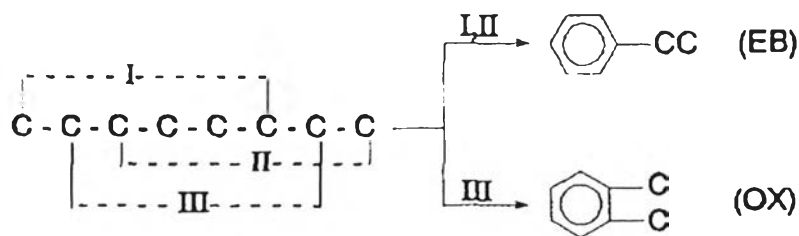
This is also an endothermic reaction, and the equilibrium production of aromatics is favored at higher temperatures and lower pressures. However, the relative rate of this reaction is much lower than the dehydrogenation of cyclohexanes.

From Figure 2.7, a stepwise dehydrocyclization with gradual loss of hydrogen to form a conjugated triene followed by ring closure and further dehydrogenation may account for aromatics formation.



**Figure 2.7** A stepwise dehydrocyclization of *n*-hexane.

Dehydrocyclization of *n*-octane can produce ethylbenzene and *o*-xylene by a mechanism that involves the direct formation of a six-member carbon ring as shown in Figure 2.8.

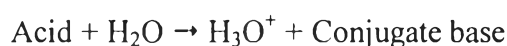


**Figure 2.8** A mechanism of *n*-octane dehydrocyclization.



## 2.5 Lewis and Brønsted Acid Concepts

Generally, three types of definition have been proposed to classify the acid properties. The first definition was explained by Arrhenius, An Arrhenius acid is a substance that increases the concentration of hydronium ions when added to water, resulting in  $\text{H}_3\text{O}^+$  ions.



More general concept was later developed by Brønsted and Lowry. The Brønsted acid is a proton donor and a Brønsted base is a proton acceptor. The third definition was defined by G.N. Lewis. Due to the fact that there are several reactions that seem to be of the acid–base nature without involving in proton transfer. The key phenomenon in this theory became the interaction of a pair of electrons of one moiety with an empty orbital of another. The Lewis acid is defined as an electron–pair acceptor and Lewis base is an electron–pair donor. As agree with Brønsted and Lowry definition, any substance that acts as a proton donor should be classified as an acid and any substance that accepts a proton should be classified as a base.

In zeolites both Lewis and Brønsted acid can exist. Due to the compensation of negative charge lattice Al atom with proton, Brønsted acid site is formed inside the zeolite voids. Normally, the negative charge could be compensated by introducing metal cations in the extraframework position of zeolites. The cations metal could bind to one or more oxygen atoms close to the zeolite framework  $\text{Al}^{3+}$  and may act as an electron–pair acceptor, in other words as a Lewis acid site.

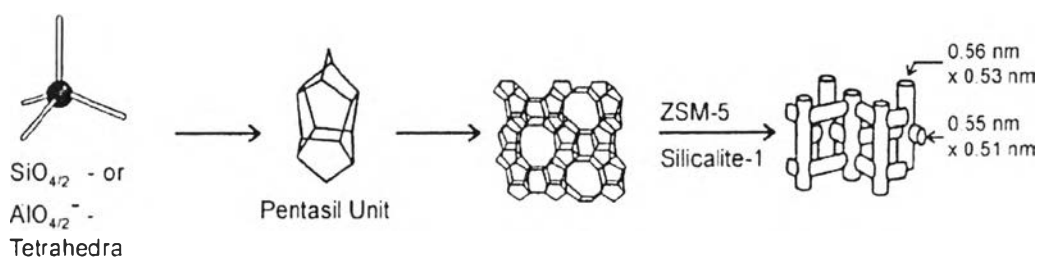
## 2.6 Zeolite

Zeolite 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. However within the zeolite structure, the presence of  $\text{AlO}_4$  tetrahedra in the fully siliceous zeolite framework resulted in a negative charge on the oxygen atoms surrounding the lattice Al ion. Normally, the negative charge will be compensated by protons, metal cations, or  $\text{NH}_4^+$ . The advantage of zeolite structure over other solid material was illustrated as follows;

- 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 reaction.
- Zeolite catalysts are thermally stable in high temperature and can be regenerated by combustion of carbon deposits.

### 2.6.1 ZSM-5 Zeolite

ZSM-5, Zeolite Socony Mobil-5 (MFI Framework) is one of the most important zeolite used in petroleum and petrochemical industry. The ZSM-5 structure is shown in figure 2.9, 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 type of channels: straight channels ( $5.3 \times 5.6 \text{ \AA}$ ) and sinusoidal channels ( $5.1 \times 5.5 \text{ \AA}$ ). These two channels are perpendicular to each other and generate intersections with diameters of  $8.9 \text{ \AA}$ . The absence of large cages with small windows leads to the special coke-resistant properties of HZSM-5 zeolite (Chen *et al.*, 1979).



**Figure 2.9** Structure of ZSM-5 zeolite.

### 2.6.2 Zeolite Acidity

The acid properties of zeolite resulted from the presence of  $\text{AlO}_4$  tetrahedra in the fully siliceous zeolite framework. Its negative charge on the oxygen atoms surrounding the lattice Al ion can be compensated by exchangeable cations

such as (e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , etc). However, the positive ions can readily be displaced by contacting with solution or other chemical treatments. These ions are usually referred to as extraframework cations. The important form, H forms zeolite, in which the negative charge is compensated by framework-bound protons, give rise to very high acidity of zeolite materials. The acid strength of zeolite mainly depends 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.

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-calorimeter, 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 *et al.*, 1995).

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 (Weber *et al.*, 1998).

### 2.6.3 Shape Selectivity of HZSM-5 Zeolite

It is believed that the active site of the zeolite mostly located in the pores of the zeolite. Generally, there are seven fundamental steps, involved in the gas phase reaction using zeolite catalyst.

- i) Diffusion of the starting materials through the boundary layer to the catalyst surface.
- ii) Diffusion of the starting materials into the pores (pore diffusion).
- iii) Adsorption of the reactants on the inner surface of the pores.
- iv) Chemical reaction on the catalyst surface.
- v) Desorption of the products from the catalyst surface.
- vi) Diffusion of the products out of the pores.
- vii) Diffusion of the products away from the catalyst through the boundary layer and into the gas phase.

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; reactant selectivity, product selectivity, and restricted transition state selectivity.

#### 2.6.3.1 Reactant Selectivity

In this case only starting materials with certain size and shape can penetrate into the pore of the zeolite and undergo reaction at the catalytic active sites. The bulkier reactant which is larger than the diameter of the zeolite pore will be limited. Hence the term molecular sieve is justified. Table 2.2 showed the pore diameter of some zeolites with the kinetic molecular diameters of some reactant. From this data, one can justify a suitable zeolite for a particular starting material.

However, it should be noted that the molecules are not rigid objects and that the kinetic diameter gives only a rough estimate of the molecular size.

**Table 2.2** Kinetic diameters of some reactants and pore sizes diameter of zeolite (Cybulski *et al.*,2001).

Molecule	Kinetic diameter [nm]	Zeolite, pore size [nm]	
He	0.25	KA	0.3
NH <sub>3</sub>	0.26	LiA	0.40
H <sub>2</sub> O	0.28	NaA	0.41
N <sub>2</sub> , SO <sub>2</sub>	0.36	CaA	0.50
Propane	0.43	Erionite	0.38 × 0.52
<i>n</i> -Hexane	0.49	ZSM-5	0.54 × 0.56/0.51 × 0.55
Isobutane	0.50	ZSM-12	0.57 × 0.69
Benzene	0.53	CaX	0.69
<i>p</i> -Xylene	0.57	Mordenite	0.67–0.70
CCl <sub>4</sub>	0.59	NaX	0.74
Cyclohexane	0.62	AlPO-5	0.80
<i>o</i> -, <i>m</i> -Xylene	0.63	VPI-5	1.20
Mesitylene	0.77		
(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	0.81		

Generally, to study the catalytic characterization of zeolite, the test reaction is carried out. The constraint index CI is the parameter, presented the relative rate of cracking of a 1:1 mixture of *n*-hexane (kinetic diameter of 0.49 nm) and 3-methylpentane (kinetic diameter of 0.56 nm). This value is strongly dependent on the pore size of the zeolite. The zeolite with large pore diameter, which is little or no shape selectivity, will result in low CI number, between zero and two. While the medium pore zeolite possesses approximately two to 12, and values higher than 12 represent the high shape selectivity zeolite (small pore zeolite).

#### 2.6.3.2 Product Selectivity

Product selectivity corresponds to the cavity of the zeolite, only the certain size and shape that can exit from the pore system. One of the most widely studied is the methylation and the disproportion of toluene over HZSM-5

zeolite. Both reactions lead to the formation of *o*-, *m*-, and *p*-xylene. Under the thermodynamic equilibrium, a *p*-xylene fraction is limited to only 24%. This is explained by the fact that for the smaller molecule *p*-xylene has diffusion rate higher than  $10^4$  as compared with other two isomers. Due to the high demand of *p*-xylene, its selectivity over HZSM-5 catalyst can be increased by, for example;

- Increasing the size of the zeolite crystals
- Incorporation of cations or other organic materials in the pore structure
- Closing some of the pore apertures

#### 2.6.3.3 Restricted Transition State Selectivity

This form of shape selectivity depends on the chemical reaction often proceed via intermediates. Due to the zeolite cavity, only the intermediates that have a geometrical fit to the zeolite pore can be formed during the reaction. This selectivity occurs preferentially when both monomolecular and bimolecular rearrangements are possible. An example is the disproportionation of *m*-xylene to toluene and trimethyl-benzenes in the large pored zeolite Y. In case of large pore system, the diphenylmethane carbenium ion transition states can be formed as precursors for methyl group rearrangement. Thus the reaction product consists mainly of the unsymmetrical 1,2,4-trimethylbenzene rather than mesitylene. On the contrary, over medium pore sized HZSM-5, monomolecular xylene isomerization dominates and the former mentioned disproportionation is not observed as a side reaction.

#### 2.6.4 Production of Zeolites

The synthesis of zeolite was achieved in alkaline aqueous mixtures of aluminum and silicon compounds. The reaction could take place both under atmospheric pressure and high pressure autoclave. The crystallization of a particular zeolite was carefully controlled by concentration of the reactants, the temperature, and the shearing energy of the stirrer. The mixing of liquid phase resulted in the formation of gel, a transition of the gel phase into the liquid aqueous phase occurs, whereby crystalline zeolites are formed from the amorphous particles. Templates such as tetrapropylammonium hydroxide are used in the synthesis of silicon rich

petasil zeolite. The C, H, and N of the tertiary ammonium cation is removed in the subsequent calcination of the microcrystalline product.

The modification of the zeolite could be done after the synthesis. The simplest method is the exchange of extra-framework species. The Si/Al ratio can be adjusted by dealumination method, involving steaming, acid treatment, and ammonium exchange. The introducing of other metals such as B, Ga, Fe and Ti into the zeolite frameworks has been widely published. For example, Titanium-Silicate (TS-1), synthesized hydrothermally from the mixing of tetraethyl orthotitanate, tetraethyl orthosilicate with Si:Ti ratio of 30–50, tetrapropylammonium hydroxide, and water. The reaction was carried out at 160–180 °C and calcined at 550 °C. To ensure that Ti atoms occupy lattice sites with no near neighbour Ti atoms, the high Si:Ti ratios is recommended.

## 2.7 The Catalytic Activity of HZSM-5 Catalysts

The reaction pathway for catalytic cracking of palm oil over HZSM-5 catalyst was proposed by Leng and co-workers (Leng *et al.*, 1999). Firstly, palm oil undergoes thermal and catalytic cracking on the external surface of catalyst to produce heavy hydrocarbons and oxygenates. It was assumed that the heavy hydrocarbon was cracked by the external acid site resulting in light paraffins and olefins, diffused in to the pore of HZSM-5. While the deoxygenation of the oxygenates formed water, carbon dioxide, and carbon monoxide. Light olefins passed through the oligomerization to produce heavier alkenes and alkanes in the range of gasoline, diesel, and kerosene fractions. The aromatics hydrocarbons was formed by the aromatization, alkylation and isomerization of heavier olefins and paraffins.

The conversion of glycerol to gasoline-range alkyl-aromatics has been studied over a series of zeolites (HY, Mordenite, HZSM-22, and HZSM-5) by Trung and co-workers. The results showed that the pore structure of the zeolite plays a key role on the final product distribution. While using one-dimensional zeolite Mordenite and HZSM-22, the main products was oxygenates (propenal and acetol) without the formation of aromatics. In contrast, over three dimensional HY and

HZSM-5 catalysts, it was found that glycerol can be converted to high yield of C<sub>8</sub>-C<sub>10</sub> aromatics. By varying the contact time, temperature, and pressure, they summarized that the longer contact time, higher temperature, and pressure favor the aromatics formation (Hoang *et al.*, 2010).

The effect of HZSM-5 acidity to the aromatization of alcohol was studied by varying Si/Al ratios. Vasant and co-workers concluded that as Si/Al ratios decreased, the conversion of ethanol and methanol to aromatics are increased. It was reasonable to conclude that the aromatization activity was depended on the acidity of the catalyst (Choudhary *et al.*, 1985). Eventhough, the effect of Si/Al ratios was also reported to the hydrophobicity of the catalyst. As reported by Yong and co-workers, by studying the dehydration of glycerol, the decrease in Si/Al ratios resulted in the strong absorption of water, blocked the acid sites from being accessible for reactants, thus lower the catalytic acitivity (Kim *et al.*, 2011).

In 2008, Corma 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 (Corma *et al.*, 2008). They 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-workers (Zakaria *et al.*, 2012). They proposed that, over HZSM-5 catalyst, glycerol was first dehydrated to form 3-hydroxypropanal. Eventhough the dehydration of glycerol can precede via the formation of acetol, 3-hydroxypropanal is a more feasible option due to 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 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 the catalyst deactivation.

## 2.8 The Roles of Zn Species on Zn/HZSM-5 Catalysts

The effect of introducing Zn on HZSM-5 catalyst to the aromatization pathway of paraffin was studied by Viswanadham and co-workers (Viswanadham et al., 1996). The evident showed that over HZSM-5, the paraffins cracking was the first step, whereas over Zn/HZSM-5 catalyst it is preferentially the paraffin dehydrogenation. The resulted olefins passed through the cracking, oligomerization and dehydrocyclization to give aromatics. Due to the high concentration of olefins fragments over Zn/HZSM-5, the aromatics were ultimately improved with the presence of Zn. Moreover, the effective conversion of olefins occurring in the presence of Zn also reduced the secondary cracking, resulting in the decrease of methane and ethane. In addition, the decrease in C<sub>9</sub> aromatics and the increase in toluene was explained by the preferential in direct dehydrocyclization/ direct aromatization of *n*-heptane in stead of the cracking-and-oligomerization route.

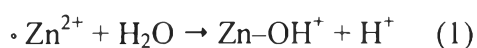
The introducing Zn on HZSM-5 catalysts was also studied in the transformation of isobutyl alcohol to aromatics (benzene, toluene, and xylene). The results showed that over HZSM-5 catalysts, the large amount of short alkanes (propane and butane) was generated. However by loading Zn on HZSM-5 catalyst, the enhancement in aromatics yields (60 wt %) was observed. As compared with other dehydrogenation metals (Ga, Mo, La, Ni, Ag, and Pt), the significant improve in aromatics was results from two maners; (i) the exchange of Zn with strong Brønsted acid suppressed the cracking to light paraffins, (ii) the Zn at exchange site

facilitate the recombinative desorption of hydrogen, hence, enhance the reactions toward aromatics (Yu *et al.*, 2012).

The effect of preparation method to the formation of Zn species was studied by Niu and co-workers (Niu *et al.*, 2014). Zn-containing HZSM-5 zeolite were prepared by four methods including impregnation, ion exchange, physical mixing with ZnO, and direct synthesis. The catalysts were tested in the process of methanol to aromatics. In the case of impregnation, zinc mainly present as  $\text{ZnOH}^+$  with a small amount of ZnO. While ion-exchange method, only  $\text{ZnOH}^+$  species was formed. The reaction results showed the linear correlation between amount  $\text{ZnOH}^+$  species and the selectivity to aromatics. The  $\text{ZnOH}^+$  species was concluded to promote the dehydrogenation of light hydrocarbons to aromatics and suppress the hydrogen transfer reaction.

In order to understand how exchanged  $\text{Zn}^{2+}$  stabilized on HZSM-5 structure, *in situ* Zn K-edge X-ray absorption was applied. The results showed that by using aqueous phase ion-exchange method, condensation reaction of  $(\text{ZnOH})^+$  species with acidic OH groups lead to the formation of the active  $\text{Zn}^{2+}$  cations interacting with two Al sites ( $\text{O}^- - \text{Zn}^{2+} - \text{O}^-$ ). The temperature programmed reduction showed that in contrast with ZnO, these Zn species did not reduce to zero-valent even at 900 °C. Exchanged Zn cations increased propane conversion turnover rates, hydrogen formation rates, and selectivity to aromatics on HZSM-5 (Biscardi *et al.*, 1998).

As is mentioned earlier, the exchange of Zn cations with Brønsted acid site resulted in the lower catalyst acidity. However, the few weaker Brønsted acid sites was regenerated after the hydrolysis of exchanged  $\text{Zn}^{2+}$  with water as shown in equation 1.



In agreement with previous work, it appears more plausible that a part of  $(\text{ZnOH})^+$  was not stable at high temperature and tended to couple with nearby OH groups to form  $\text{H}_2\text{O}$  and a  $\text{Zn}^{2+}$  cation interact with two aluminum sites through the reverse reaction 1 (El-Malki *et al.*, 1999).

In the contrast with aqueous phase ion exchange method, the exchange of HZSM-5 zeolite with Zn vapors, two types of  $\text{Zn}^{2+}$  cations are suggested to exist: (i)

$\text{Zn}^{2+}$  in vicinity of isolated Al center and (ii)  $\text{Zn}^{2+}$  in vicinity of two Al centers. It is widely accepted that Zn at exchange site enhances the aromatization reaction due to its ability in the recombination and desorption of  $\text{H}_2$ , hence, the understanding in dissociation and recombination processes of  $\text{H}_2$  on Zn/HZSM-5 catalyst is important for clarifying the mechanism of alkane dehydrogenation. Kazansky *et al.* studied the dissociation of  $\text{H}_2$  on Zn/HZSM-5 catalyst by assigning a signal at 1934–1936  $\text{cm}^{-1}$  to the IR vibrational frequency of Zn–H bonds. They concluded that only by using chemical vapor deposition of Zn on HZSM-5 catalyst,  $\text{Zn}^{2+}$  are located on partially charge compensated  $\text{Zn}^{2+}$  ions and this species is responsible for the dissociation of  $\text{H}_2$  (Kazansky *et al.*, 2004). In contrast, by modeling  $\text{H}_2$  adsorption on both completely and partially charge compensated  $\text{Zn}^{2+}$ , Shubin *et al.* and Yakovlev *et al.* calculated the  $\text{H}_2$  dissociation to be favorable on both zinc species. However the later evidence, studied by Aleksandrov and co-workers showed that the dissociation of  $\text{H}_2$  on  $\text{Zn}^{2+}$  cation at paired Al site has the lowest free energy of activation. The essential role of the second Al center in vicinity of the zinc cation is generating the basic framework oxygen center, participating in the reaction steps. Without the second Al center close to the zinc species, the reaction would form rather stable intermediates  $\text{ZnH}^+$  or  $\text{Zn}(\text{C}_2\text{H}_5)^+$  (Aleksandrov *et al.*, 2010).

Even though it was accepted that the exchanged  $\text{Zn}^{2+}$  species can not be completely reduced, the effect of hydrogen on the exchanged  $\text{Zn}^{2+}$  species was investigated by Pyridine-IR. An infrared (IR) showed the formation of protonic acid site by heating Zn/HZSM-5 under hydrogen atmosphere. The ease of generating protonic acid site may be due to the presence of strong Lewis sites and zinc particles. The zinc particles may play a role as an active site for the dissociation of hydrogen molecule into hydrogen atoms and the Lewis acid sites may stabilize protons by accepting electrons from hydrogen atoms. The generation of this new protonic acid site was proved to significantly enhance the isomerization of *n*-pentane (Triwahyono *et al.*, 2011).

## 2.9 Modified HZSM-5 Catalysts for Highly Selective *p*-Xylene Formation

The pore size of ZSM-5 is known to be a shape selective for the formation of *p*-xylene. Generally in the diffusion control region, the increase in crystal size of ZSM-5 will increase the diffusion resistance. As a result, the *p*-xylene selectivity will be increased with decreasing the conversion. However, it was impossible to maximize the *p*-xylene selectivity by adjusting only crystal size because acid sites present both inside and outside of the HZSM-5 crystal. Even only *p*-xylene that can diffuse out of the pore, the isomerization of *p*-xylene to *o*- and *m*-xylene also take place on the external Brønsted acid site. Consequently, the actual *p*-xylene is lower than the value without the effect of reactions on the external surface (Mirth *et al.*, 1993). Thus the idea to modify the external surfaces with an inactive layer have been interested for decades.

A post-synthesis modification by chemical vapor deposition (CVD) of tetraethylorthosilicate (TEOS) is one of the most effective methods to enhance the shape selectivity of HZSM-5 catalyst (Niwa *et al.*, 1992). Due to the larger kinetic diameter of silicon alkoxides, compared with the pore of HZSM-5, only hydroxyl groups on the external surface and near pore openings react with the silylating agents. As a result, the Si-O-Si or Si-O-Al bonds were formed as a passivation of these unselective acid site. Nevertheless, the pore of HZSM-5 are simultaneously narrowed or partially blocked.

Alternatively, chemical liquid deposition (CLD) can be used to modify the external surface of zeolite. Compared with CVD, CLD can be more easily applied to a large scale industrial preparation. However, the narrowing of pore mouth also led to the deposition of coke on the external surface of HZSM-5 catalyst, same problem was also present in the CVD method (Grundling *et al.*, 1996).

Instead of coating with silica, the surface dealumination of zeolite catalytic particles is one of the most effective ways to eliminate the external acid sites. The poisoning adsorption of external acid sites have been studied over zeolite such as pyridine (Nayak *et al.*, 1984), 4-methylquinoline (Jennings *et al.*, 1990), and 2,4-dimethylquinoline (Wu *et al.*, 1998). However the removal of strong acid sites decreased the catalytic activity of the catalyst.

Due to the fact that even by using the above mentioned method; CVD, CLD, and dealumination, it is difficult to fully remove the acid site on the external surface. The development of new composite zeolite consisting of ZSM-5 and silicalite layer was studied to solve this problem. As widely known, the acidity of zeolite came from the presence of trivalent elements, most case is Al, substituted with a trivalent negative charge. The charge is balanced by cation exchanged with proton or alkaline earth metal. The presence of proton behaves as a strong acid site both in the crystal and on the external surface. Focusing on silicalite, the framework structure is code name of MFI, same as ZSM-5. On the contrary, silicalite does not contain Al in the framework, thus shows no acidity. Coating silicalite on ZSM-5, two positive effects could be expected. Firstly, the selective permeation of *p*-xylene through the inactive silicalite layer can be expected. Secondly, the inactive silicalite layer inhibits the isomerization from *p*-xylene to other xylene isomers on the external surface. In the diffusion control region, *p*-xylene is mainly formed inside crystals. In this case, the second effect is more important to improve *p*-xylene (Vu *et al.*, 2006).