

## CHAPTER II

### LITERATURE REVIEW

Jet fuel is a type of aviation fuel designed for use in aircraft powered by gas-turbine engines. It is colorless to straw-colored in appearance. There are basically two type of fuels used in commercial aviation:

- Jet A (used mainly in the USA)
- Jet A-1 used worldwide

Jet A and Jet A-1, both are kerosene type fuels the only relevant difference between them is the freezing point ( $-40\text{ }^{\circ}\text{C}$  for Jet A and  $-47\text{ }^{\circ}\text{C}$  for Jet A-1) and the other jet fuel commonly used in civilian turbine-engine powered aviation is Jet B which is used for its enhanced cold-weather performance.

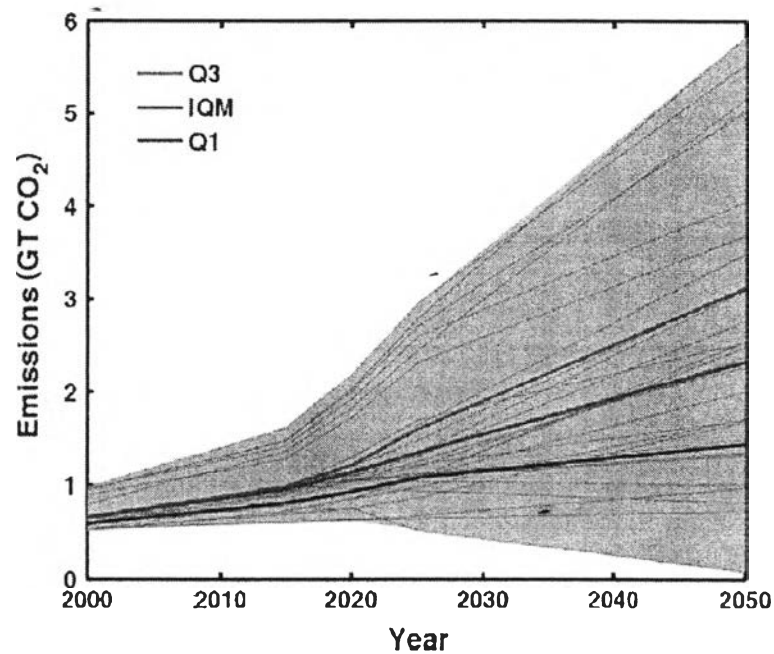
Jet fuel is a mixture of a large number of different hydrocarbons. The range of their molecular weights or carbon numbers is restricted by the requirements for the product, for example, freezing point or smoke point. Kerosene-type jet fuel (including Jet A and Jet A-1) has a carbon number distribution between about 8 and 16 carbon numbers; wide-cut or naphtha-type jet fuel (including Jet B), between about 5 and 15 carbon numbers.

#### **2.1 Environmental Issues of Jet Fuel**

Aircraft emissions, in conjunction with other anthropogenic sources are impacting Greenhouse Gases (GHG) and hence inducing climate change, though the extents of such impacts are very difficult to predict and are heavily debated. Atmospheric changes from aircraft result from three kinds of processes: i) direct emission of radioactively active substances such as  $\text{CO}_2$  or water vapor, ii) emission of chemical species that produce or destroy radioactively active substances such as  $\text{NO}_x$ , which modifies  $\text{O}_3$  concentration, and iii) emission of substances that trigger the generation of aerosol particles or lead to changes in natural clouds.

There is no real consensus outlining how much commercial aviation is contributing to total global carbon emissions, but general estimates are between 2-6%. However, there is a consensus that this would increase significantly if current

growth trends continue and if no major improvements are made e.g. introduction of renewable sustainable biofuels, technological improvements in aircraft materials, etc. The public and political pressure on the sector to decrease its GHG emissions is increasing, particularly in Europe. For this reason, the aviation industry has committed itself to achieve carbon-neutral growth by 2020, and a 50% reduction in CO<sub>2</sub> emissions by 2050 compared with 2005 levels (IATA, 2010). Several studies have investigated the development of the aviation related global CO<sub>2</sub> emissions (Figure 2.1). In the majority of those scenarios the suggested CO<sub>2</sub> reduction cannot be found – so additional efforts have to be taken to change the currently expected trends (Rosillo-Calle *et al.*, 2012).



**Figure 2.1** Inter-quartile meta-estimates for global aviation CO<sub>2</sub> emissions. IQM, Q1 and Q3 are the proposed mid, low and high global aviation CO<sub>2</sub> meta estimates adjusted to exclude military aviation (Gudmundsson *et al.*, 2012).

Due to concerns with the environmental problem, the demand for using renewable feedstocks, such as vegetable oils and animal fats to produce biojet fuel has increased.

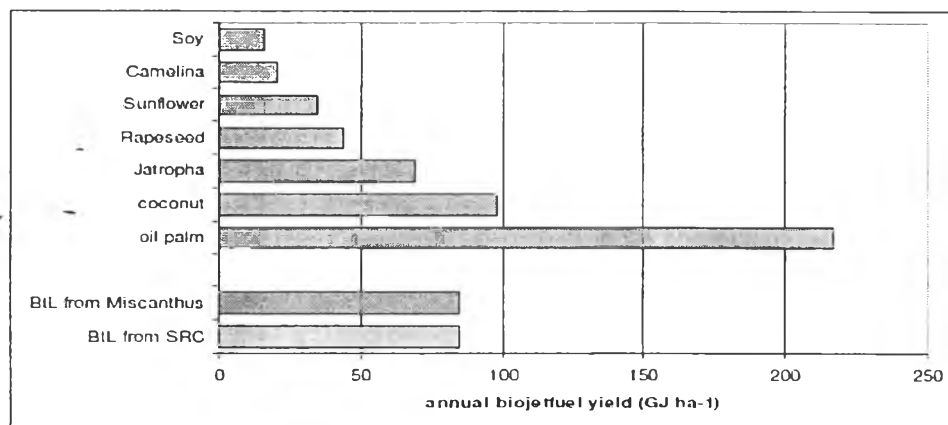
## 2.2 Bio-jet Fuel

Bio-jet fuel is a renewable fuel that can be used instead of jet fuel derived from petroleum. Similar to biodiesel, vegetable oils and other biomass derived oils can be used as feedstock for biojet fuel production. Among the vegetable oils, sources are soybean, canola, palm, jatropha, and rape. Biojet fuel usually blends with petroleum-based Jet A/Jet A-1 fuel and 50 percent sustainable biofuels.

In 201, Air Transport Action Group (ATAG) showed the use of biojet fuels in commercial aviation has received considerable in recent years, as it is currently seen as one of the best short to medium term options to answer the challenges. Consequently almost all major commercial airlines and also some military are heavily involved in testing and developing.

### 2.2.1 Raw Material in Hydrotreated Renewable Jet Production

There are many biomass feedstocks that can be used to produce jet fuel. However, the options are limited to a handful of feedstocks. Oily feedstock can be produced on cropland and shows a wide range of area specific yields on the Figure 2.2.



**Figure 2.2** Typical biojetfuel yields from different feedstock (Addison, 2001).

Vegetable oils are considered as raw materials for biojet fuel production because they are broadly available from a variety of sources and they are renewable. The example of vegetable oils used in bio-jet fuel production are palm oil, sunflower oil, corn oil, coconut oil, jatropha oil, olive oil, canola oil, cottonseed oil, castor oil, soybean oil, etc., There are many benefits of bio-jet fuel including domestic feed-stock, decreased greenhouse gas emissions, decreased dependence on fossil fuels, improvement of rural economies and increased national security (Huber *et al.*, 2007).

One of the feedstocks receiving the greatest attention at the moment is *Jatropha curcas*. This major concern is the limitations of feedstock quantity and quality, since only a few feedstocks meet the requirements to create the strict physical and chemical characteristics of jet fuel. The benefit is these can grow on marginal land and as a hedge and the drawback is un-predictable yield.

Recently, jatropha production has been much promoted as an option for biodiesel-like production. *Jatropha* is a rapidly developing area but detailed knowledge of yields. Each seed produces 30 to 40% of its mass in oil. *Jatropha* can be grown in a range of difficult soil conditions, including arid and otherwise non-arable areas, leaving prime land available for food crops. The seeds are toxic to both humans and animals and are therefore not a food source (Berchmans *et al.*, 2008).

Some physical properties of the most common fatty acids in vegetable oils and animal fats are shown in Table 2.1. Besides these fatty acids, numerous other fatty acids occur in vegetable oils and animal fats, but their abundance usually is considerably lower and Table 2.2, that summarizes the fatty acid composition of the *jatropha curcus* oil.

**Table 2.1** Selected properties of some common fatty acids (Gerhard *et al.*, 1997)

Trivial (Systematic) name <sup>a</sup> ; Acronym <sup>b</sup>	MW	m.p. (°C)	b.p. <sup>c</sup> (°C)	Formula	Heat of Combustion
Caprylic acid (Octanoic acid); 8:0	144.22	16.5	239.3	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	-
Capric acid (Decanoic acid); 10:0	172.27	31.5	270	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	1453.07 (25°)
Lauric acid (Dodecanoic acid); 12:0	200.32	44	131 <sup>1</sup>	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	1763.25 (25°)
Myristic acid (Tetradecanoic acid); 14:0	228.38	58	250.5 <sup>100</sup>	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	2073.91 (25°)
Palmitic acid (Hexadecanoic acid); 16:0	256.43	63	350	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	2384.76 (25°)
Stearic acid (Octadecanoic acid); 18:0	284.48	71	360d	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	2696.12 (25°)
Oleic acid (9Z-Octadecenoic acid); 18:1	282.47	16	286 <sup>100</sup>	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	2657.4 (25°)
Linoleic acid (9Z,12Z- Octadecadienoic acid); 18:2	280.45	-5	229-30 <sup>16</sup>	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	- -
Linolenic acid (9Z,12Z,15Z- Octadecatrienoic acid); 18:3	278.44	-11	230-2 <sup>17</sup>	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	- -
Erucic acid (13Z-Docosenoic acid); 22:1	338.58	33-4	265 <sup>15</sup>	C <sub>22</sub> H <sub>42</sub> O <sub>2</sub>	-

a) Z denotes cis configuration.

b) The numbers denote the number of carbons and double bonds. For example, in oleic acid, 18:1 stands for eighteen carbons and one double bond.

c) Superscripts in boiling point column denote pressure (mm Hg) at which the boiling point was determined.

**Table 2.2** Fatty acid composition in vegetable oils (Berchmans *et al.*, 2008)

Fatty acid	Formula	Systemic name	Structure <sup>b</sup>	wt%
Myristic	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	Tetradecanoic	14:00	0-0.1
Palmitic	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	Hexadecanoic	16:00	14.1-15.3
Palmitoleic	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	cis-9-hexadecenoic	16:1	0-1.3
Stearic	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	Octadecanoic	18:00	3.7-9.8
Oleic	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	cis-9-Octadecanoic	18:1	34.3-45.8
Linoleic	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	cis-9,cis-12-Octadecenoic	18:2	29.0-44.2
Linolenic	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	cis-6,cis-9,cis-12-Octadecatrienoic	18:3	0-0.3
Arachidic	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	Eicosanoic	20:00	0-0.3
Behenic	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	Docosanoic	22:00	0-0.2

<sup>b</sup> xx:y indicates xx carbon in the fatty acid chain with y double bonds.

### 2.2.2 Biojet Fuel Production

The main essential process for producing renewable bio-jet is hydrocracking of hydrogenated biodiesel because this process for the conversion of middle and heavy distillates and residuals into more valuable products. Moreover, it is easy to equilibrate the supply and demand of fuels such as gasoline, diesel and jet fuel (Arroyo *et al.*, 2000). Therefore, it is desirable to be able to convert biodiesel fuel into bio-jet fuel. In addition, the branching isomerization, hydrogenation and hydrodeoxygenation are desirable reactions to improve the quality of Renewable biojet.

#### 2.2.2.1 Hydrocracking

Hydrocracking is a process combining catalytic cracking and hydrogenation of middle or heavy feedstock, which is cracked in the presence of hydrogen to produce lighter products such as gasoline, diesel and jet fuel. The process takes place in a hydrogen-rich atmosphere at elevated temperatures (260 °C to

425 °C) and pressures (35 to 200 bars). Figure 2.3, which illustrate a hydrocracking reaction.



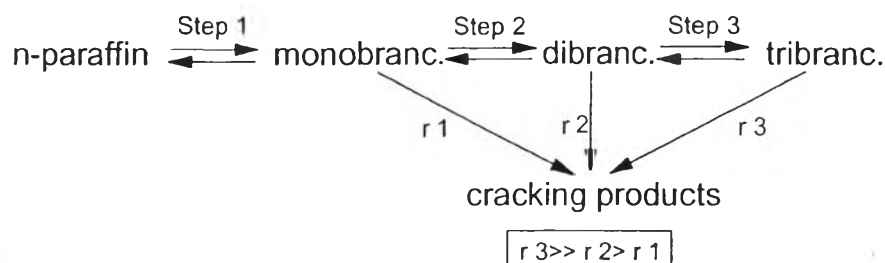
**Figure 2.3** Schematic of hydrocracking reaction.

Rajeev *et al.*, (2008) studied the method for obtained jet fuel from diesel fuel, the method comprised subjecting the diesel fuel to hydrocracking to convert at least a portion of the diesel fuel into a mixture of light hydrocarbon, kerosene, naphtha and a liquefied petroleum gas, and then recovered jet fuel from the kerosene. The result shown hydrocracking was carried out at pressure between 6-17 MPa and temperature between 200 and about 400 °C and palladium on zeolite was a catalyst for cracking.

The hydrocracking of light cycle oil (LCO) over a Pt–Pd/HY zeolite catalyst was studied by Gutiérrez *et al.* (2012). This work studied The effect of space velocity (WHSV) has been studied in the single-step hydrocracking of the LCO obtained as by product in catalytic cracking (FCC) units, over a-bifunctional catalyst of Pt–Pd supported on a high acidity HY zeolite. Accordingly, the hydrocracking and hydrodesulphurization conversions and yields of product fractions (medium distillates, naphtha, LPG and dry gas) have been determined. The reaction conditions have been 350 °C, 45 bar, H<sub>2</sub>/LCO molar ratio of 10. In results shown the decrease of space velocity to 1 h<sup>-1</sup> has a significant effect on the yield of medium distillates, naphtha and aromatic products, which evidences that the study should be extended by using more severe conditions (higher temperatures, pressures and/or H<sub>2</sub>/LCO ratios in the feed) in order to explore the industrial interest of noble metal catalysts for LCO hydrocracking in a single-step.

Reaction pathway of the *n*-alkane is first isomerized into its monobranched isomers and subsequently into di- and tri-branched isomers. According to the Figure 2.4, the cracking products are formed mainly through β-scission of di- and tri-branched isomers since they can crack through a more energetically

favourable  $\beta$ -scission mode not allowed for the monobranched and linear molecules (Calemma, V. *et al.*, 2000).



**Figure 2.4** Reaction scheme for the formation of feed isomers and cracked products (Calemma *et al.*, 2000).

#### 2.2.2.2 Hydroisomerization

The hydroisomerization of heavy linear alkanes is of a great interest in petroleum industry. Indeed, the transformation of long chain *n*-alkanes into branched alkanes allows to increase the octane number of gasoline and to improve the low temperature performances of diesel or lubricating oils. However, while a selective isomerization of light *n*-alkanes is easy to perform, that of heavy *n*-alkanes is much more difficult to obtain, the cracking of long chain alkanes being very rapid. Thus, the catalytic systems used for the transformation of long chain alkanes must have a very high selectivity for isomerization rather than for cracking (Soualah *et al.*, 2008).

In 2001, Boskovic and co-worker studied the effect of hydroisomerization on Pt/HY catalyst. Catalysts containing 0.5 wt% of Pt on Na(H)Y zeolite were prepared by ion-exchange and wetness impregnation. The acidity was altered by calcined temperature and by the order of calcination. The reaction was run with different reaction temperature and different calcination temperature. The reaction was carried out at temperature from 200 to 350 °C at atmospheric pressure in a fixed-bed reactor containing 1 cm<sup>3</sup> of catalyst. The catalysts were prepared by ion-exchange and wetness impregnation and calcined temperatures were varied in different final temperature. All of the products were transferred to a gas chromatograph in order to measure component in products. From the result, the catalyst which



was prepared by ion-exchange had the lowest activity and the selectivity at the optimum temperature of 250 °C is considerable but due to low activity the isomer yield is the lowest. The cause of poor activity and selectivity of the catalyst which was prepared by ion-exchange is balanced metallic function. It can be either in low metal loading or in low dispersion of Pt. When the applied procedures of calcination and reduction should give a highly dispersed catalyst. Then, the problem of poor activity and selectivity of catalyst which was prepared by ion-exchange is more likely that load metal(Pt). Among catalysts obtained by wetness impregnation with 400 °C calcined temperature give the highest activity and very high selectivity which equal to 62.81 % isomerization yield. The optimal activity and selectivity represent through low cracking and high isomer yield. At the higher reaction temperature, the reaction generate acid sites and then we need to very balance between acidic and metal function so that will get balance of hydrocracking and hydroisomerization.

#### 2.2.2.3 Hydrogenation and Dehydrogenation

Hydrogenation is the chemical reaction that can obtain from the addition of hydrogen until becoming saturated substances, and dehydrogenation is pulled hydrogen out and reverted to unsaturated substances. Hydrogenation of the carbon-to-carbon double bonds in triglycerides, especially of vegetable oils, is a major industry in many parts of the world. Principal products, obtained by catalytic hydrogenation, include oleomargarines, shortening, soap stock and industrial greases and oils. However, hydrogenation mechanism is not completely clarified, until now. The chemistry of triglycerides partial hydrogenation process is complicated. Both mono- and poly-unsaturated acid groups in the oil hydrogenate at various rates, depending on the operating conditions. Furthermore, the geometrical and positional isomerization of the double bonds in mono- and poly-unsaturated acid groups occurs in significant numbers during the hydrogenation (Jovanović *et al.*, 2000).

#### 2.2.2.4 Hydrogenolysis

Hydrogenolysis is a chemical reaction whereby a carbon-carbon or carbon-heteroatom single bond is cleaved or undergoes "lysis" by hydrogen. The heteroatom may vary, but it usually is oxygen, nitrogen, or sulfur. A related reaction is hydrogenation, where hydrogen is added to the molecule, without

cleaving bonds. Usually hydrogenolysis is conducted catalytically using hydrogen gas (Connor, R. *et al.*, 1932). The following represents a hydrogenolysis reaction:

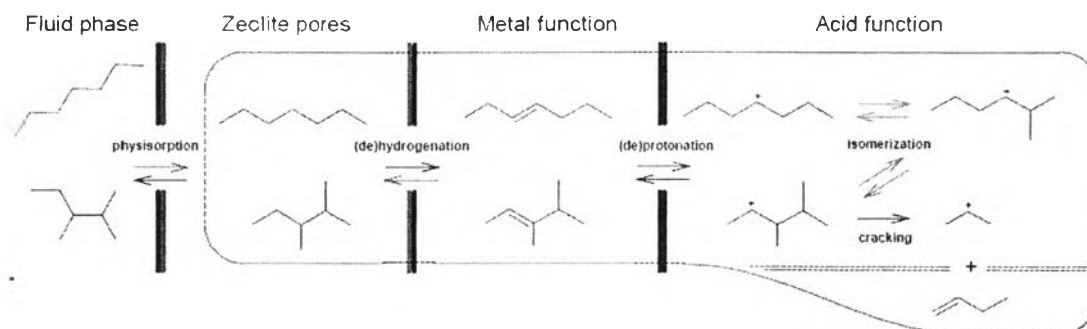


**Figure 2.5** Schematic of hydrogenolysis reaction (Connor, R. *et al.*, 1932).

### 2.3 Catalyst for Biojet Production

Bifunctional zeolite catalysts are currently used in refinery processes like hydrocracking or hydroisomerization. These catalysts have two types of active : hydrogenating sites (metal site) to dehydrogenate saturated reactant molecules to alkenes and to hydrogenate olefin intermediates desorbed from the acid sites and acid sites for isomerization and cracking. Usually hydrogenating sites result from group VIII metals like palladium or platinum. So bifunction catalysts, which contain metal and supports, are used particularly for Hydroteated Renewable Jet production (Guerin *et al.*, 1988).

The formation of cracked products generally involves two successive reaction steps: the hydroisomerization step and the actual hydrocracking step. These two competing reaction via the same carbonium intermediate species. A long chain hydrocarbon from fluid phase enters the catalyst through physisorption to a metal function. On the metal function, the elimination of a single H<sub>2</sub> molecule takes place resulting in an olefin. This olefin is desorbed by the metal sites and chemisorbs on an acid site for protonation yielding a carbenium ion. This carbenium ion can isomerize through alkyl shift and/or protonated cyclopropane (PCP) and/or cyclobutane (PCP) branching. Cracking occurs through scission of the C-C bond in β-position of the charge-carrying carbon atom (Van der Borgh K., 2010).



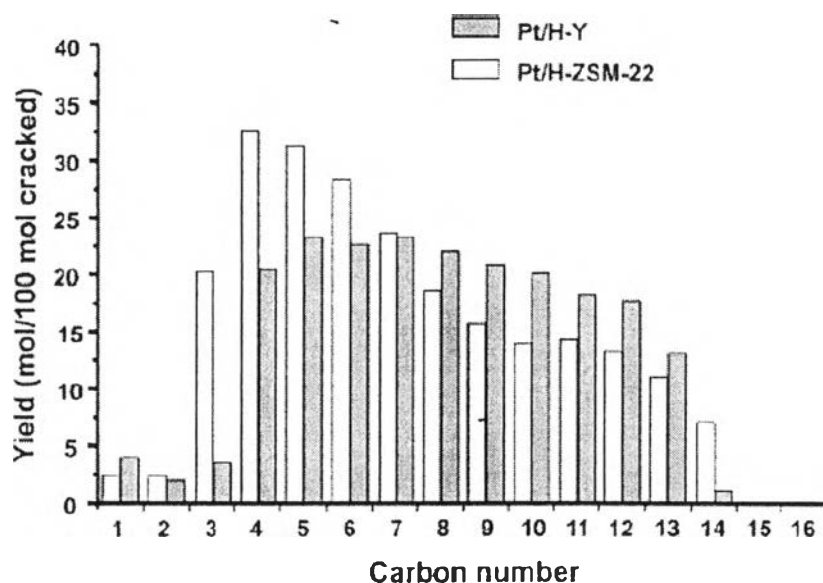
**Figure 2.6** Bifunctional reaction mechanism of hydroconversion (Van der Borgh K., 2010).

In 1965, Lin and co-worker had proposed a series of rule that have proved to be guidelines for the preparation of tailored hydroisomerization and hydrocracking catalysts for hydrocarbon processing. These rules were designated as the “hybridization rules of electronic and acidic interactions”, and the main aim is as follows.

- The metal (i.e., the electronic component) and the support (i.e., the acidic component) of the catalyst interact with each other to form a hybridized active center. The catalytic properties of the hybridized centers depend on the nature of the precursor components as well as the interaction between the two components.
- The stronger the acidity of the support, the higher the cracking activity, and the lower the isomerization selectivity. However, the acidity of the support with the electronic action of the metal component, the hydrogenation activity will be strengthened, whilst the cracking activity will be weakened, and this hybridizing effect will in turn enhance the isomerization activity of the catalyst.

Zeolites are widely used as acid support and play an important role in the catalysts used in hydrocracking process because they improve catalytic activity, selectivity, or stability by imparting shape selectivity. Zeolites have been successful because of their crystallinity, high surface area, adsorption capacity, and uniform size distribution which enable shape selectivity (A.M. Alsobaai *et al.*, 2007).

In 1998, Souverijns and co-worker studied the hydrocracking of isoheptadecanes on Pt/H-ZSM-22 and Pt/HY. The catalytic experiments were conducted in a tubular down flow reactor. The catalysts were activated in situ in the reactor by calcination under flowing oxygen at 673 K, followed by a reduction under flowing hydrogen at the same temperature. The n-C17 and hydrogen partial pressures at the entrance of the reactor were 900 Pa and 350 kPa, respectively. The constant space time,  $W/F_0$  is equal to  $0.5 \text{ h kg mol}^{-1}$ . In Figure, the result shows that Pt/HY catalyst gets carbon distribution in range from C4 to C13 but Pt/H-ZSM-22 catalyst gets lighter carbon range.



**Figure 2.7** Yield of cracked product fractions per carbon number at 25% cracking yield of n-C17 on Pt/HY and Pt/H-ZSM-22 (Souverijns *et al.*, 1998).

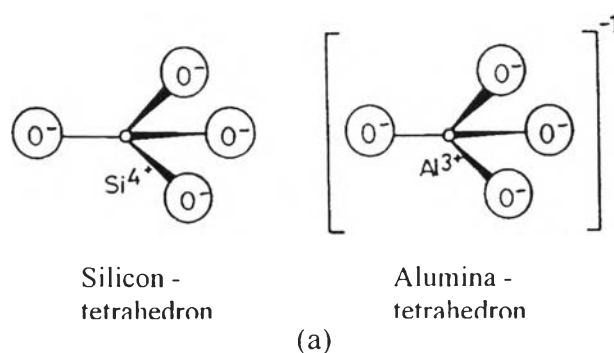
#### 2.4 HY Zeolite

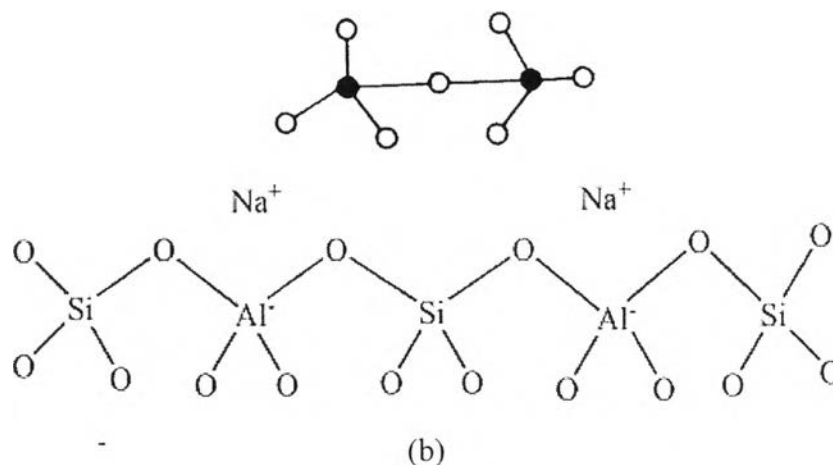
Zeolites were first recognized as a new type of minerals in 1756 by a Swedish mineralogist. He called this mineral is “zeolite” (Greek word: meaning boiling stone) as it seemed to boil at high temperature due to high water content. Since then, many types of naturally occurring zeolites have been found, such as: chabazite,

erionite, faujasite, mordenite, etc. Zeolites consist of microporous crystalline aluminosilicates and possess properties of adsorption, reaction, and ion-exchange (Weitkamp, J., 1999). Today, these and other zeolites structures are of great interest in catalysis, yet their naturally occurring forms are of limited value, because

- They almost always contain undesired impurity phases.
- Chemical composition varies from one deposit to another and even from one stratum to another in the same deposit.
- Nature did not optimize their properties for catalytic applications.

and have only a few are of commercial importance such as, type A, X, Y, Z, L, ZSM-5 etc (Corma *et al.*, (1985). The primary building block of all zeolites is a tetrahedron of four oxygen anions that surround a silicon or aluminum ion, as shown in Figure 2.8(a). These tetrahedra are arranged in such a way that each of the four oxygen anions is further shared by another silica or alumina tetrahedron. The crystalline framework extends in three dimensions; therefore the  $-2$  oxidation state of each oxygen is accounted for. The  $+4$  charge on each silicon ion is balanced by the four tetrahedral oxygen making the silica tetrahedral electrostatically neutral. On the other hand, the  $+3$  charge on aluminum is not balanced by the surrounding four tetrahedral oxygens, leaving a residual charge of  $-1$  on each alumina tetrahedron. Thus each alumina tetrahedron requires a  $+1$  charge from a cation in the structure to be electrostatically neutral, as shown in Figure 2.8(b). The cations providing electric stability to alumina tetrahedron are commonly sodium in the zeolite where they occupy non-framework positions.

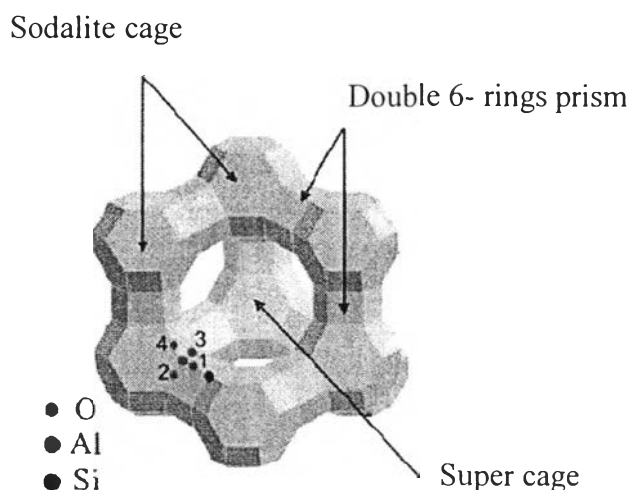




**Figure 2.8** (a) Primary building blocks of zeolites, (b) simplified surface structure of zeolite.

One of the main functions of zeolite is in the petroleum and petrochemical field. Hydrocracking and hydroisomerization of hydrocarbons are the basic processes in the petroleum refining industry which produce a broad range of highly valuable chemicals, diesel oil, petrol, and gasoline. They proceed over bi-functional catalysts with two quite different components representing metallic and acidic functions. Different zeolites, zeolite-like solid acids, and also acidic oxides are used as the acidic components (Kuznetsov *et al.*, 2003). One of the most commercially used zeolites for petroleum refining is Zeolite Y because of its high concentration of active acid sites, its high thermal stability and high size selectivity (Htay *et al.*, 2008).

Zeolite Y is a faujasite molecular sieve with 7.4 Å diameter pores and a three-dimensional pore structure. The basic structural units for zeolites Y are the sodalite cages, which are arranged so as to form supercages that are large enough to accommodate spheres with 1.2 nm (Song *et al.*, 2005).



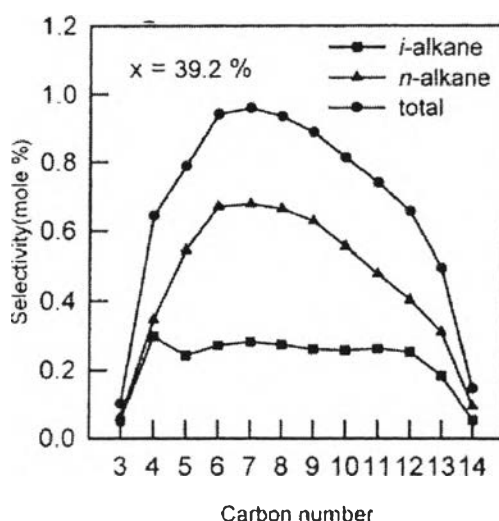
**Figure 2.9** Perspective view of Y zeolite structure. The silicon or aluminum ions are located at the corners and the oxygen ions near the edges.

From Figure 2.9, that showed Y zeolite structure. Each supercage contains four windows of 12-membered Al or Si rings with a diameter of 7.4 Å. while the diameters of the sodalite cage and the double 6-ring are 6.6 and 2.6 Å respectively.

Recently, Y zeolite has been found to exhibit a good catalytic performance for catalytic process because of its unique properties, for instance the main pore structure is uniform three-dimension with widely pore opening enough to admit the large molecules, excellent flexibility structure to control Al content of the structure for possible to optimize active catalyst, high thermal and hydrothermal stability in order to withstand regenerate conditions. However, the synthesis of Y zeolite is a complex process, due to the complexly growth of pure crystal of Y zeolite is very sensitive to preparation condition. Furthermore the poor crystal has negative effect to the performance of Y zeolite catalyst.

Park *et al.*, (2000) studied the Pt/zeolite catalysts for n-hexadecane. The catalytic conversion of n-hexadecane was carried out in a batch reactor of 300 ml. A 0.5 g aliquot of catalyst was loaded in the reactor and then hydrogen was introduced with 50 mL/min to reduce platinum at 350 °C and 500 rpm for 2 h. The reactor was cooled down to room temperature, fed with 50 ml of n-hexadecane and pressurized

to 34.5 bar with hydrogen. The reactor was gradually heated at a rate of 5 °C/min to 350 °C and the pressure was set to 103 bar. In Figure 2.10, the results on Pt/HY from this experiment showed that the most cracked products (*n*-alkane) have carbon numbers in the range between C<sub>4</sub> and C<sub>13</sub> more than the isomerized products (*i*-alkane) for conversion 40 %.



**Figure 2.10** Molar distribution in the cracked products on Pt/HY during *n*-hexadecane isomerization at 350 °C and 103 bar (Park *et al.*, 2000).

#### 2.4.1 Synthetic of Y Zeolite

In the mid late 1940's inspired of the Linde Division of Union Carbide Co.th, to initiate studies in zeolite synthesis in search of new approaches for separation and purification of air. Between 1949 and 1954 R.M. Milton and co-worker D.W. Breck discovered a number of commercially significant zeolite, type A, X, and Y.

In 1954 Union Carbide commercialized synthetic zeolites as a new class of industrial material for separation and purification. The earliest applications were the drying of refrigerant gas and nature gas. In 1955 T.B. Reed and D.W. Breck reported the structure of synthesis zeolite A.

In 1959 Union Carbide marketed the "ISOSIV" process for normal-isoparaffin separation, representing the first major bulk separation process using true



molecular sieving selectivity. Also in 1959 a Y zeolite catalyst was marketed by Carbide as an isomerization catalyst.

Bauer and co-workers in the early 1960s developed the use of reaction mixtures containing quaternary ammonium ions or other cations to direct the crystallization process. In their work and succeeding studies, a primary motivation was to attempt to synthesize zeolites with large apertures than X and Y. This did not occur, but instead organic species were found to modify the synthesis process in a variety of ways that led to the discovery of many new zeolites, and new methods of synthesizing zeolite with structures similar to previously known zeolite.

In 1962 Mobil Oil introduced the use of synthetic of zeolite X as a cracking catalyst. In 1969 Grace described the first modification chemistry based on steaming Y zeolite to form an "ultrastable" Y. In 1967-1969 Mobil Oil reported the synthesis of the high silica zeolites beta and ZSM-5. In 1974 Henkel introduced zeolite detergents as a replacement for the environmentally suspect phosphates. By 1977 industry-wide 22,000 tons of Y zeolite was in use in catalytic cracking. In 1977 The Union Carbide introduced zeolite for ion-exchange separation. (P.A. Jacobs et al., 2001).

Exactly, zeolites are generally synthesized by a hydrothermal process from a source of alumina (sodium aluminate or aluminum sulfate) and of silica (a silica sol, fumed silica, or sodium water glass) and an alkali such as NaOH, and/or a quaternary ammonium compound. An inhomogeneous gel is produced which gradually crystallizes, in some cases forming more than one type of zeolite in succession. Nucleation effects can be important, and an initial induction period at near ambient temperature may be followed by crystallization temperature that may range up to 473 K or higher. The pressure is equal to the saturated vapor pressure of the water present.

After synthesis the zeolite are washed, dried, heated to remove water of crystallization, and calcined in air, e.g., at about 823 K. Organic species are also thus removed. For most catalytic purpose, the zeolite is converted into acidic form. For some zeolites this can be achieved by treatment with aqueous HCl without significantly altering the framework structure. For other zeolites Na<sup>+</sup> is replaced with NH<sub>4</sub><sup>+</sup> via an ammonium compound such as NH<sub>4</sub>OH, NH<sub>4</sub>Cl or NH<sub>4</sub>NO<sub>3</sub>. Upon

heating  $\text{NH}_3$  is driven off, leaving the zeolite in the acid form. For some reaction a hydrogenation component such as platinum or nickel is introduced by impregnation or ion-exchange (Satterfield, C.N., 1996).

Several researchers have devoted their efforts to improve the batch process for preparation method of Y zeolite. Many zeolite synthesis operating variables have been identified and optimized to improve the quality of zeolites and reduce the synthesis time.

Although hydrothermal (liquid-state) processing is a well-established technique for synthesis of many materials, the kinetics are slow owing to the low temperatures used, and for this reason, we started using microwave field to accelerate the kinetics of reaction. The combination of microwave field with the hydrothermal method was named the “microwave hydrothermal” (M-H) process.

Arafat *et al.*, (1993) studied the preparation of Y zeolite and ZSM-5 using microwave method and shown the advantages of applying microwave heating in the zeolite synthesis. Both of zeolite type were prepared in very short crystallization time, Y zeolite crystallites were prepared in a microwave oven in 10 min, whereas 10-50 h are required by conventional heating techniques and ZSM-5 could also be synthesized in 30 min at 140 °C using this technique.

Katsuki *et al.*, (2001) studied on the synthesis of NaY zeolite crystals by using microwave-hydrothermal (M-H) processing. NaY zeolites were synthesized from colloidal silica, sodium aluminate, sodium hydroxide and deionized water at  $100\pm C$ , and some properties were studied, then compared to the formation of NaY zeolite via conventional hydrothermal (C-H) treatment. The results on the NaY synthesis showed the M-H treatment led to increased rate of formation by 3 to 4 times. NaY zeolite could be prepared in 1 to 2 h and the yield of the zeolite was 40% in 1 h and 96% in 2 h via M-H method because not only fast heat up to the treatment temperature but also apparently because of increased kinetics.

Recently, the synthesis of Y zeolite with small particle size has received much attention, because the use of such Y zeolite can noticeably improve catalytic cracking selectivity with reduce coking. In additional, Nano crystalline zeolites are zeolites with discrete, uniform crystals with dimensions of less than 100 nm that have unique properties relative to conventional micrometer-sized zeolite

crystals. Nanocrystalline zeolite have higher external surface areas and reduced diffusion path lengths relative to conventional micrometer-sized zeolites, the synthesis of small or nanocrystalline zeolite has been reported by several groups (Song *et al.*, 2005).

#### 2.4.2 Control of Zeolite Crystal Size

The sensitivity of zeolite catalysts to crystal-size effects derives from the same properties that account for their selectivity. Slow configurational diffusion in molecular size micropores justify the preferential adsorption of small reagents and the selective desorption of small products, but this property can also severely impair the effectiveness of the catalyst. Shape-selective catalytic reactions on zeolites and diffusion in zeolites have been the object of recent reviews. In any case, shape selectivity is higher for larger crystals. The optimum particle size for shape-selective catalysis is the result of a compromise between selectivity and effectiveness.

Several parameters influence the choice of the optimum size of zeolite crystals: (a) shape-selective catalysis requires larger crystals; (b) catalyst effectiveness is larger for smaller crystals; (c) in bifunctional catalysts, particle size can influence the average distance between acidic and metallic sites, and modify the product distribution; (d) coke deactivation can be more severe for larger crystals; (e) diffusion of matrix components is easier in the case of smaller crystals; (f) template extraction, cation exchange, even distribution of metal functions are more easily performed for smaller crystals; (g) regeneration of used catalysts can be more difficult for larger crystals; (i) filtration and recovery of very small crystals is a technological challenge (Di Renzo *et al.*, 1998).

The crystal size of zeolites is determined by the relative rates of the two competing phenomena occurring during synthesis, namely, nucleation and crystal growth. The higher the nucleation rate, the smaller the zeolite crystals obtained. Several parameters take part in the establishment of the relative rates of nucleation and crystal growth. Varying these parameters may lead to changes in the sizes of zeolite crystals (Jülide Köroğlu *et al.*, 2002). The Example of key parameters governing zeolization are hydrogel molar composition, alkalinity (pH), aging time (time to

form gel network), crystallization time (time for crystal growth), and templates molecules (Jitkarnka, J., 2012).

#### 2.4.2.1 Effect of Gel Aging Time

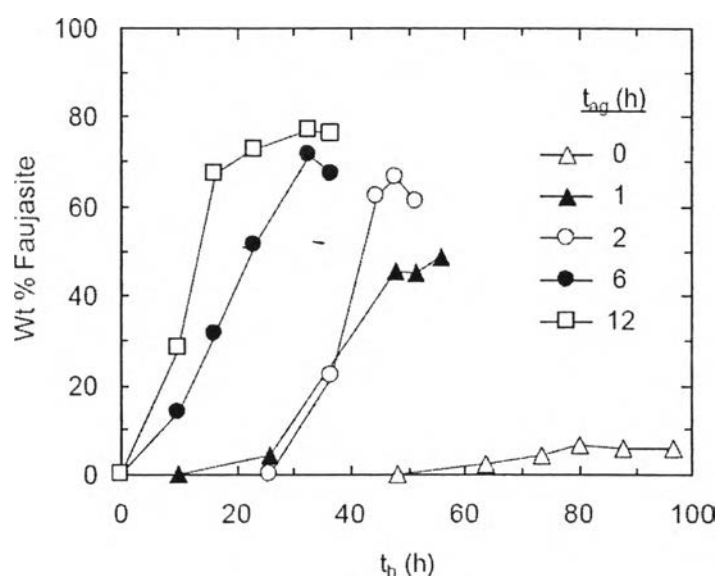
Aging the synthesis mixture prior to crystallization is a common method used to tailor the size of zeolite crystals. Aging, especially at room temperature, may favor the process of nucleation significantly. It is generally hypothesized that the nucleation rate is significant at room temperature while the growth rate is negligible and nuclei lie dormant until the temperature is raised. Thus, aging at relatively low temperatures may allow for an increase in the number of nuclei or nuclei precursors, which in turn allows the preparation of smaller zeolite crystals.

Jülide Köroğlu *et al.*, (2002) studied the effect of low-temperature gel using on the synthesis of zeolite Y. It was determined that both the particle sizes and the span of the size distribution may be decreased further by aging the aging temperature below room temperature. The alkalinity of the gel composition seemed to play a significant role in determining the magnitude of the effects of lowering the aging temperature on particle size and the size distributions of the aged zeolite sample. The Si/Al ratio of Y zeolite was enhanced when the lower aging temperature and less alkaline gel composition were used.

In 2004, Larlus and co-worker studied effecting of the chemical composition of the starting gel, aging time, and crystallization temperature on the crystal size and morphology of zeolite L. The result shown he crystal size and morphology of zeolite L were also influenced by the variation of the aging time and crystallization temperature, long aging of the gel (1-4 weeks) under ambient conditions provided nanosized crystals with narrow particle size distribution.

Ginter *et al.*, (1992) studied the ageing of the starting gel as another feature, which is related to the nucleation step in the synthesis of zeolites. They performed two different studies; to quantify the physical and chemical transformations occurring during the ageing of aluminosilicate gel produced from colloidal silica, and to investigate the effects of ageing on the synthesis of NaY zeolite. For both studies, they used colloidal silica and sodium aluminate solutions as starting materials. In the first study, they found that upon mixing of colloidal silica sol and

sodium aluminate solutions, a gel was immediately formed due to the flocculation of silica particles in the sol. By mixing, the gel was homogenized into small granules in the order of 1 mm in diameter. However, no chemical transformation was observed upon mixing, but during ageing, the silica particles were slowly dissolved and released silicate anions into the surrounding solution. These species reacted with aluminate anions and formed aluminum silicate species, which precipitated due to their low solubility. The solid amorphous aluminosilicate thus formed was rich in Al and hydrated  $\text{Na}^+$  cations. The precipitation of aluminosilicate consumed the dissolved Al and prevented the accumulation of Si in solution. When the entire dissolved Al was consumed in aluminosilicate formation, the remaining colloidal silica started to dissolve in the solution, which decreased the basic pH and started to release silicate anions in the solution. The aluminosilicate slowly reacted with the silicate anions in solution, which resulted in an increase in Si/Al ratio and a decrease in Na/Al ratio. In their second study, as shown in Figure 2.11, they found that room-temperature ageing of colloidal silica gel strongly affected the kinetics of NaY crystallization at 100 °C. With ageing, the crystallization was accelerated and the final crystal size was decreased, especially ageing up to 12 h.



**Figure 2.11** Effect of ageing of starting gel on the synthesis of zeolite NaY; wt% of NaY in the solid phase isolated from synthesis gels as a function of heating time for

aging time up to 12 h as determined by powder X-ray diffraction (Ginter *et al.*, 1992).

Their results are consistent with the generally accepted hypothesis that ageing enables the formation of nuclei from which crystals subsequently grow.

#### 2.4.2.2 *Effect of Crystallization Temperature*

Crystallization temperature is one of most frequently studied crystallization condition that influences the kinetics of crystal growth of zeolites. The synthesis of small crystals zeolite NaY was studied by Sang *et al.*, (2006). Zeolite NaY with small crystals was hydrothermally synthesized by using a two – stage variable temperature program without the presence of organic templates. In this work, the results described effect of temperature on the crystal properties and size of desired zeolite. The effect of temperature on the crystallization of zeolite NaY was examined at temperatures ranging from 313 to 393 K. Zeolite NaY could be suitably achieved at 373 and 333 K. However, the crystallization at 393 K induced the formation of zeolite P instead of zeolite Y. When the temperature was decreased to 313 K, only amorphous solid could be produced.

#### 2.4.2.3 *Effect of Organic Cation Agent*

Preparation of uniform and small crystal for formation of high quality zeolite membrane. It is well known that the addition of some organic cations can accelerates the formation of zeolites, and facilitates to prepare uniform zeolite particles. Some reports were usually synthesized in tetramethylammonium (TMA)-aluminosilicate solution. To synthesis zeolite Y nano-crystal, a variety of organic materials have been used as templating agent for the effective synthesis of nano-particles. Tetramethylammonium cation ( $\text{TMA}^+$ ) from tetramethylammonium hydroxide (TMAOH) or tetramethylammonium bromide (TMABr) is the most typical organic template (Kim *et al.*, 2009).

Huang *et al.*, (2008) studied preparation NaA zeolite membrane thought organic cation addition. This work showed the effects of TMAOH amount on membrane formation and permeation properties. By addition of suitable amount of TMAOH in the clear synthesis solution, the crystals size of NaA zeolite could be reduced from about 10  $\mu\text{m}$  to 3-4  $\mu\text{m}$  because with adding TMAOH, the

zeolite particle grew slowly with crystallization time and average zeolite particle size was remarkably reduced.

Investigation on hydrothermal synthesis parameters in preparation of nanoparticles of LTA zeolite with the aid of TMAOH was studied by Jafari *et al.* (2013). In this work, nanocrystals of LTA zeolite with crystallite sizes ranging from 30 to 70 nm were synthesized successfully and Tetramethylammonium hydroxide (TMAOH) was used as template. The result shown the the effects of organic and inorganic cation as well as crystallization conditions including aging time, synthesis time, and synthesis temperature on size of the zeolites. The obtained results showed that zeolite size decreases significantly and zeolite size distribution becomes narrow by increasing aging time, and organic cation content, addition of organic cation resulted in the reduction of particle size due to its relatively strong basic property. This basic medium enhances solubility of the silica species. Consequently, the nucleation rate of zeolite particles increases by increasing the degree of super saturation of silica species.

## 2.5 Effecting of Small Crystal Size Zeolite

The reduction of particle size from the micrometer to the nanometer scale leads to substantial changes in the properties of the materials, which have an impact on the performance of zeolites in traditional application areas such as catalysis and separation. Thus, the ratio of external to internal number of atoms increases rapidly as the particle size decreases and zeolite nanoparticles have large external surface areas and high surface activity. The external surface acidity is of importance when the zeolite is intended to be used as a catalyst in reactions involving bulky molecules. In addition, smaller zeolite crystals have reduced diffusion path lengths relative to conventional micrometer-sized zeolites.

Cambor *et al.* (1989) investigated vacuum gasoil on USY zeolite (unit cell size 24.5-24.25). It was showed that smaller crystal sizes produced more gasoline and diesel, and less coke and gas, However, smaller crystal was less hydrothermally stable than bigger crystals But, if NaY zeolite was made with silicon to alumi-

num ratio  $\geq 3.0$ , the smaller crystals were hydrothermally stable and showed a higher activity and better selectivity than bigger crystal, even streaming at 750 °C for 5 h.

Vuong *et al.*, (2010) studied the effect of crystal nanosizes on the catalytic performance of nanosized zeolite. Different crystal sizes consist of 25, 40 and 100 nm, were prepared in toluene and formamide solvents and External surface area decreased with the external surface area also. The results revealed a good correlation between the crystal size of zeolites and the activity: smaller nanozeolite-based FCC catalyst exhibits higher catalytic activity. The relationship between gasoline selectivity and conversion is a function of nanozeolite size. In general, the performance of these catalyst is in the following order FCC-25 > FCC-40 > FCC-100.

In 2012, Meng and co-workers studied the effect of crystal sizes of HZSM-5 zeolites in ethanol conversion to propylene. Three ZSM-5 zeolites with different crystal sizes were prepared in different method and characterized by SEM, XRD, and adsorption/desorption of N<sub>2</sub>, NH<sub>3</sub>-TPD, Py-IR and TG-DTA techniques. The results shown that the acidic properties of HZSM-5 catalysts are very similar, but their textual properties are strongly influenced by crystal size, it could be seen that both the micropore surface area and external surface area increase with decreasing crystal size and the volumes of mesopores and average pore diameter also increase with decreasing crystal sizes. Their catalytic performances for the ethanol conversion to propylene were investigated in a continuous flow fixed-bed micro-reactor. In comparison with the large-sized HZSM-5, the small-sized HZSM-5 shows higher propylene selectivity and better stability, which reveals that decreasing the crystal size of zeolite is of benefit to ethanol conversion to propylene due to its larger pore volume, more secondary pores, shorter channels, and reduced diffusion path lengths, which shows low formation rate of coke, low diffusion resistance and high ability to tolerate the coke.

Aguiar *et al.*, (1995) studied about the cracking of 1,3,5-TIPB carried out over two Y zeolite of 63 and 193 nm average particle sizes, revealed that much higher rates of reaction are obtained with the smaller crystallite sample. Nevertheless, when the rates of disappearance, which were at first expressed per g of zeolitic, were divided by the number of aluminum atoms on the external zeolitic surface, equal



values were obtained for both zeolites. These results confirm the assumption that the reaction is taking place on just the external surface of the crystals.