CHAPTER 2

LITERATURE SURVEY

2.1 HYDROCRACKING PROCESS

Because of the interesting roles of the developed catalysts, the old process, thermal cracking, has been replaced by the more efficient catalytic process. One of them is hydrocracking, a cracking operation with hydrogenation of heavy hydrocarbon molecules to yield lighter and more useful hydrocarbons. Improved catalysts have been developed which permit operations at relatively low pressures, and the world-wide demand for high octane gasoline and the decrease in demand for distillate fuels has caused a necessity for converting higher boiling point petroleum materials to gasoline and jet fuels.

The original hydrocracking process was developed in Germany in 1927 and the first modern commercial hydrocracking unit was operated in 1961. Since then commercial hydrocracking has developed rapidly with hydrocracking feedstocks ranging from naphtha to residue and products ranging from liquefied petroleum gas to lubricating oil.

The interest in the use of hydrocracking has been caused by several factors ; among them are (18 : 121)

1. The demand for petroleum products has shifted to high ratios of gasoline compared with the usages of middle distillates.

2. Byproduct hydrogen at low costs and in large amounts has become available from catalytic reforming operations in recent years.

Hydrocracking process has more advantages than the others in petroleum refining ; some of them are :

1. Better balance of gasoline and distillate production.

2. Greater gasoline yield .

3. Improved gasoline pool octane quality and sensitivity .

4. Production of relatively high amounts of isobutane in the butane fraction.

5. Supplements catalytic cracking to upgrade heavy cracking stocks, aromatics, cycle oils, and coker oils to gasoline, jet fuels and light fuel oils. (18 : 121-141)

2.1.1 Early Hydrocracking

The hydrocracking process was first commercially developed by I.G. Farben Industrie in 1927 for converting brown coal or lignite into liquid fuels, mainly gasoline, and was first brought to U.S.A. by Esso Research and Engineering Company in the early 1930s. for use in upgrading petroleum feedstocks and products, especially in

the production of lubricating oil, diesel fuel and gasoline.

Because of some disadvantages of this early process, high pressure equipment being required and hydrogen consumed in the process having to be manufactured, the process was economically unattractive and was abandoned during the end of the World War II.

The early hydrocracking, one of the oldest catalytic processes in petroleum refining, was fixed bed non-regenerative process. The reactor was operated in the temperature range of 600 - 1000 °F the pressures of 200 atmospheres or greater to inhibit coking reactions that would destroy catalyst activity. Because the chemical reaction is exothermic, make-up hydrogen was added at several points down the catalyst bed to serve as a cooling medium and to supply some of the hydrogen required for the hydrocracking reaction.

The earliest hydrocracking catalysts, found to be high in activity, were tungsten disulfide and molybdenum disulfide. These catalysts were promoted to use against sulfur containing hydrocarbon compounds. These catalysts gave high gasoline yields but low in octane number.

The next catalysts, replaceing disulfides of tungsten and molybdenum, was the supporting of these disulfides on a natural clay, such as montmorillonite clay treated with

hydrofluoric acid, which gave much higher octane number in gasoline yield.

2.1.2 Modern Hydrocracking

Because of development of improved catalysts, hydrocracking is possible at less severe conditions than the earlier processes. And fortunately, cheaper hydrogen has been produced as a by-product of catalytic cracking process, and also can be manufactured by an improved methane steam reformation process. Therefore, hydrocracking has been chosen to meet the increasing demand for better and more liquid hydrocarbon fuels.

The first modern hydrocracking operation was placed on stream in 1959 by the Standard Oil Company of California. Most of the modern processes are fixed bed of catalyst, downward flow of reactants, similar to the early version, but operation has been done at about half of the total pressure of the early one, as in table 2.1. Exceptions are H. Oil and LC - Fining processes, which are expanded or ebullating bed processes. Most of the processes are single or double stages. Single stage processes are used when the reactants are lighter hydrocarbons and the desired products are middle distillates, liquefied petroleum gas or gasoline. If feedstocks are heavy hydrocarbons, double stage processes are used instead.

Table 2-1   List of Hydrocracking Processes Available for
             License (18, 19)

| Process	Company
Isocracking / Isomax	Chevron Research and UOP
Unicracking / JHC	Union Oil of California and Esso Research and Engineering Co.
HDC Unibon	UOP
H-G Hydrocracking	Gulf Oil Co. And Houdry Process and Chemical Co.
Ultracracking	Standard Oil Co. (Indiana)
BP	British Petroleum Trading Ltd.
BASF - IFP	Ba dische Anilin-und Soda-Fabrik and Institut Francais du Petrole
BOC	UOP
H - Oil	Hydrocarbon Research Inc./Texaco
LC - Fining / Hy - C	Cities Services / Lummus
Shell	Shell Development Co.
VARGA	Hungarian People's Republic and German Democratic Republic

Modern hydrocracking catalysts are dual function having both cracking and hydrogenating activity. A typical catalyst comprises one or more of group VIB or group VIII metal of the periodic table on an acidic support, such as silica-alumina or silica-magnesia or treated zeolite. The cracking activity is supplied by the acidic support, and the hydrogenating activity is supplied by the metal, metal oxides or metal sulfides.

In the U.S.A, the most important application of hydrocracking is to convert gas oils into high quality gasoline. In the other regions, the application seems to convert high boiling point distillates or residue to middle distillates. And there are other uses of the hydrocracking process, for example, to produce jet fuel from gas oils and liquefied petroleum gas (L P G) from low octane naphtha.

2.2 HYDROCRACKING MECHANISM.

The reactions of catalytic cracking are highly complex and its pattern can be interpreted in terms of the carbonium - ion theory following the original suggestions of Whitmore in the interpretation of certain hydrocarbon reactions in solution. The theory of catalytic cracking was developed by many investigators, including Greensfelder et al., C.L. Phomas, Hansford, and others. It is reviewed by Oblad et.al., Emmett, and more recently by Gates et. al.

There are many ways that a carbonium ion can be formed such as attraction by an olefin of a proton from a Bronsted acid (12 : 162) :

$$H_2C = CHR + H^+ \longrightarrow CH_3C^+HR$$
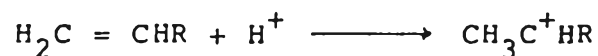
Modern commercial hydrocracking catalysts are dual function type, containing both hydrogenation-dehydrogenation component and acidic component. Reactions on a dual functional catalyst are characterized by extensive isomerization and skeletal rearrangement. With shape selective zeolite catalysts, the molecules reacting and the products forming are primarily determined by the geometrical characteristics of the catalyst pores. (31 : 4)

2.2.1 Paraffin Hydrocracking

The Carbonium ions, the intermediates in catalytic cracking reactions, are electron - deficient entities comprising a positively charged carbon atom with three monovalent atoms or the equivalent attached. These ions can be formed in many different ways but the simplest steps are the addition of a proton to an olefin or an aromatic, or the removal of a hydride ion from a saturated hydrocarbon.

The rate of hydrocracking of paraffins is slower than that of olefins, which can be explained that the slower step is involved in the formation of the

steps have been proposed, but further studies are required to decide which come closest to the truth. Some proposals are :

1) A small amount of olefin is formed by thermal cracking, and converted to carbonium ions.

2) Removal of a hydride ion is effected by means of a proton of the catalyst.

3) Dehydrogenation of a small amount of paraffins to form olefins, which can be further converted to carbonium ions.

4) A catalyst proton attacks a paraffin to cause splitting into a smaller paraffin and a carbonium ion.

5) Addition of a proton to form a complex CR_4H^+ which then breaks into a smaller paraffin and a carbonium ion (32 : 78)

6) An electron is transferred from a hydrocarbon to the catalyst to form a positive molecule ion, which may then react to form a carbonium ion. This has been proposed by Franklin and Nicholson on the basis of a carrelation between activation energy for cracking and ionization potential for C_3 to C_6 n- paraffins. The correlation does not hold for branched paraffins or cyclohexane. (16 : 3)

Though carbonium ions can be formed in different ways, as said above, there is a reasonable

mechanism for normal paraffin hydrocracking which have been proposed by Flinn, Beuther and Larson and Archibald, Greenfelder, Holzman and Rowe Ref (33 : 745). The mechanisms are as follow :

1. Secondary carbonium ion can be formed by the normal paraffin reactions at any secondary carbon atom in the molecule, or by hydrogen transferal.
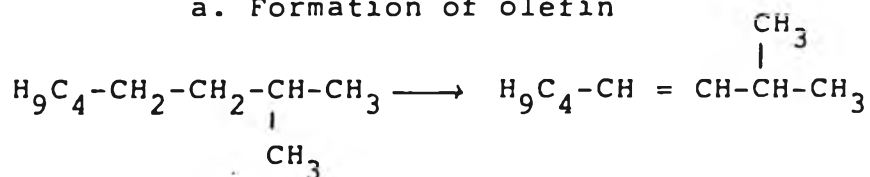
2. The carbonium ion can isomerize to form a more stable ion, crack at a carbon - carbon bond in the beta position of the carbonium ion carbon atom to form an olefin and a smaller secondary or tertiary carbonium ion, or desorb as a normal olefin.

3. The isomerized carbonium ion can undergo further isomerization, crack or desorb.

4. Olefinic products are saturated by hydrogenation or hydrogen transfer reactions.

The example reactions concerning the hydrocracking reaction mechanisms are as follows :

a. Formation of olefin

$$H_9C_4-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \longrightarrow H_9C_4-CH = CH-\underset{\overset{|}{CH_3}}{CH}-CH_3$$

b. Formation of carbonium ion

$$R-CH_2-CH_2-CH_3-H^- \longrightarrow R-CH_2-CH_2-\overset{+}{CH_2}$$
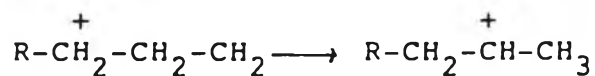
Paraffin   Carbonium ion

Carbonium ions can be formed in the presence of an acidic catalyst, either by the removal of a hydride ion from a saturated hydrocarbon or by the addition of a proton to an olefin or aromatic nucleus. Therefore, the catalyst system must be capable of either accepting an electron pair, or donating a proton.

Carbonium ions are highly reactive and have only a transient existence, but are responsible for almost all of the reactions which occur in the catalytic cracking process. The ease with which they are formed depends on their relative stability which decreases in the order (19:395)

tertiary > secondary > primary > ethyl > methyl

c. Isomerization of carbonium ion to a more stable ion, such as primary carbonium ion isomerizes to form secondary carbonium ion or further isomerizes from secondary carbonium ion to tertiary carbonium ion.
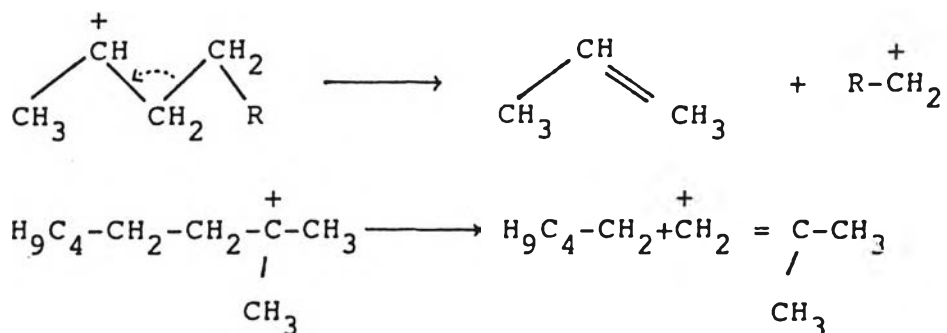
$$R-CH_2-CH_2-\overset{+}{CH_2} \longrightarrow R-CH_2-\overset{+}{CH}-CH_3$$

Primary carbonium ion   Secondary carbonium ion

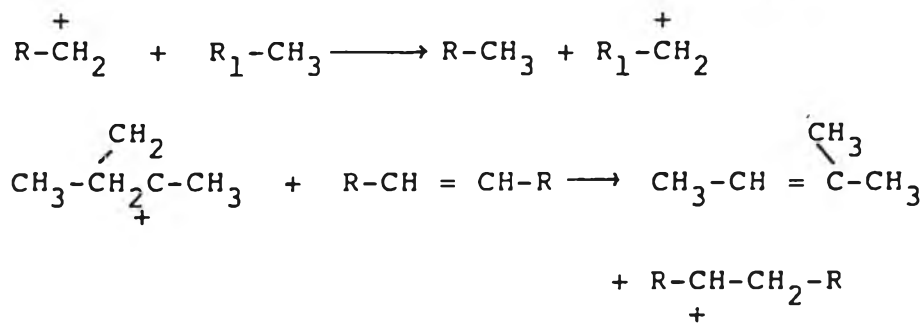$$R-\overset{+}{CH}-CH_2-CH_3 \longrightarrow R-\overset{+}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$
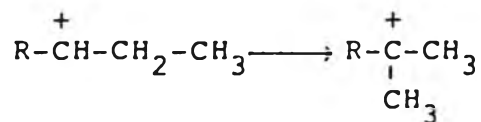
Secondary carbonium ion Tertiary carbonium ion

d. Beta scission or cracking of carbonium ions at beta position of C-C bond

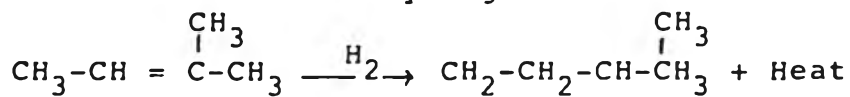$$\text{CH}_3\text{-}\underset{\text{CH}_2}{\overset{+}{\text{CH}}}\text{-}\underset{\text{CH}_2}{\text{CH}_2}\text{-R} \longrightarrow \underset{\text{CH}_3}{\text{CH}}=\underset{\text{CH}_3}{\text{CH}} + \overset{+}{R\text{-CH}_2}$$

$$\text{H}_9\text{C}_4\text{-CH}_2\text{-CH}_2\text{-}\underset{\underset{\text{CH}_3}{|}}{\overset{+}{\text{C}}}\text{-CH}_3 \longrightarrow \text{H}_9\text{C}_4\text{-}\overset{+}{\text{CH}_2} + \text{CH}_2 = \underset{\underset{\text{CH}_3}{/}}{\text{C}}\text{-CH}_3$$

e. Hydrogen transfer

$$\overset{+}{\text{R-CH}_2} + \text{R}_1\text{-CH}_3 \longrightarrow \text{R-CH}_3 + \overset{+}{\text{R}_1\text{-CH}_2}$$

$$\text{CH}_3\text{-}\underset{\overset{|}{+}}{\underset{\text{CH}_2}{\text{CH}_2}}\overset{\text{CH}_2}{\text{C}}\text{-CH}_3 + \text{R-CH} = \text{CH-R} \longrightarrow \text{CH}_3\text{-CH} = \overset{\text{CH}_3}{\text{C}}\text{-CH}_3$$

$$+ \underset{+}{\text{R-CH-CH}_2\text{-R}}$$

Naphthene + olefin ⟶ Aromatic + Paraffin

Aromatic coke precursor + olefin ⟶ coke + Paraffin.

f. Olefin Hydrogenation (17 : 2)

$$\text{CH}_3\text{-CH} = \overset{\overset{\text{CH}_3}{|}}{\text{C}}\text{-CH}_3 \xrightarrow{\text{H}_2} \text{CH}_2\text{-CH}_2\text{-}\overset{\overset{\text{CH}_3}{|}}{\text{CH}}\text{-CH}_3 + \text{Heat}$$

g. Olefins are cracked to give smaller
olefins.

$$\text{C}_n\text{H}_{2n+1} \longrightarrow \text{C}_m\text{H}_{2m} + \text{C}_p\text{H}_{2m} \text{ where } n = m + p$$
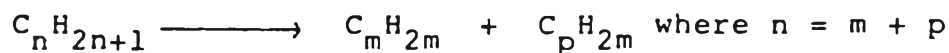
h. Alkyl aromatics undergo dealkylation.

$$\text{ArC}_n\text{H}_{2n+1} \longrightarrow \text{A}_r\text{H} + \text{C}_n\text{H}_{2n}$$
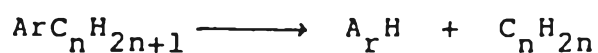
Aromatic H.C.

i. Instead of the foregoing dealkylation reaction, aromatic side-chain scission may occur

$$ArC_nH_{2n+1} \longrightarrow ArC_mH_{2m-1} \quad + \quad C_pH_{2p+2} \quad \text{where } n = m + p$$
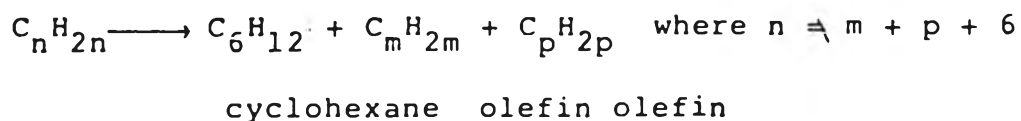
Aromalic with   paraffin

Olefinic   side-chain

Unsubstituted aromatics undergo relatively slow cracking under typical industrial reaction conditions because of the stability of the aromatic ring

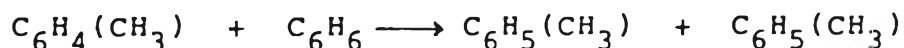j. Naphthenes (cycloparaffins) are cracked to give olefins.

$$C_nH_{2n} \longrightarrow C_mH_{2m} \quad + \quad C_pH_{2p} \quad \text{where } n = m + p$$
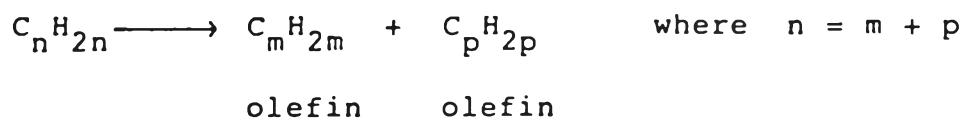
olefin   olefin

If the cycloparaffin contains a cyclohexane ring, however, the ring is not opened.

$$C_nH_{2n} \longrightarrow C_6H_{12} + C_mH_{2m} + C_pH_{2p} \quad \text{where } n = m + p + 6$$

cyclohexane   olefin olefin

k. Isomerization

Olefin $\longrightarrow$ Isoolefin

l. Alkyl - group transfer

$$C_6H_4(CH_3) \quad + \quad C_6H_6 \longrightarrow C_6H_5(CH_3) \quad + \quad C_6H_5(CH_3)$$

m. Condensation reaction

$$\text{(benzene)}\overset{CH_2 = CH_2}{} + R_1CH = CHR_2 \longrightarrow \text{(naphthalene)}\overset{R_2}{\underset{R_1}{}} + 2H$$
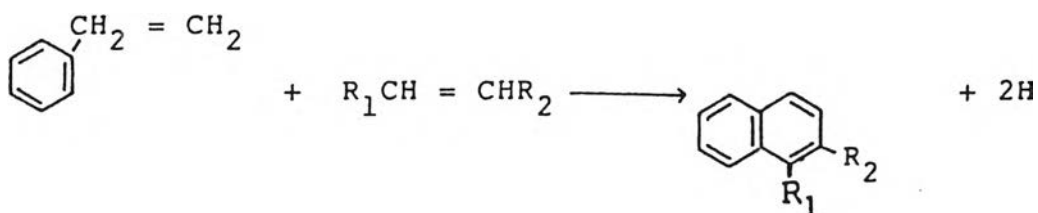
n. Disproportionation of low-molecular-
weight olefin

$$2 \; H_2C = CHCH_2 \longrightarrow H_2C = CHCH_3 + H_2C = CHCH_2CH_2CH_3$$
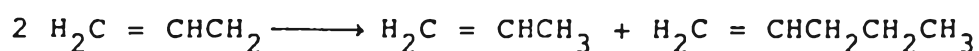
2.2.2 Hydrocracking Reaction Using Zeolites.

A number of studies on hydrocracking using zeolite catalysts have been made not only with olefins but also paraffins, naphtha and naphthenes whose mechanism followed a carbonium ion mechanism. Because shape selective character of zeolite catalysts, only certain size of reactant molecules can diffuse through the pores and react. And in the same way, certain size of products can diffuse out of the pores.

Clement and co - workers concluded that the more acidic catalyst was more reactive for hydrocracking and that hydrocracking followed a carbonium ion mechanism, after they had studied the reactions of cyclohexane and benzene using several types of X synthetic zeolite (Na-X, Ca-X, Mg-X, Ce-X) in which the major hydrocracked products were propane and butanes.

Weisz and co-workers studied the hydrocracking of a mixture of n- paraffins and branched paraffins. They found that only n- paraffins were hydrocracked by using proper shape selective zeolite catalysts. (34 : 154)

Beecher, Voorhies and Eberly (35 : 203) worked on the hydrocracking of decane and decahydronaphthalene (decalin) over two types of synthetic mordenite catalysts. One type of the catalysts was palladium on H - mordenite and the other was palladium on alumina defecient H - mordenite. They have reported that acid-leached, alumina - deficient mordenite has higher catalytic activity because of lower diffusion resistance. And they also found that decalin had a lower reaction rate than decane when hydrocracked in pure compound, and that decalin was preferentially converted in a decane-decalin mixture.

Osipov and Khavkin indicated that hydrocracking over a nickel impregnated zeolite catalyst was a first order reaction (31 : 1)

Hatcher and Voorhies studied the hydrocracking of n- hexane and cyclohexane over zeolites (Pd-H-faujasite and Pd-H-mordenite). They have found that the model was first order with respect to the hydrocarbon. And similar to Beecher and co-workers, the synergistic effects of cyclohexane hydrocracking have been found. Further

more studies have been made on hydrocracking over zeolites and also hydroisomerization concerning hydrocracking reactions. (15 : 361, 27 : 366)

2.3 ZEOLITE CATALYSTS

2.3.1 General

The catalysts originally used for hydrocracking are sulfides of tungsten, nickel or molybdenum, which are unsupported catalysts. Now they are replaced with catalysts supported on acid treated clay and/or zeolite.

The name zeolite was first used by Baron Cronstedt in 1756 and the so-called "molecular sieve" by Mcbain. Zeolites were initially used as ion exchange resins' in water softening plants and adsorbers. Shape selectivity is an attractive property which make zeolites one of the most important catalysts.

The structural formula of a zeolite natural and synthetic is based on the crystal unit cell, the smallest unit of structure, represented by

$$M_{x/n} \left[(AlO_2)_x (SiO_2)_y \right] . wH_2O$$
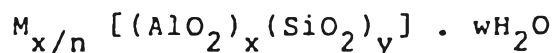
Here n is the valence of cation M, w is the number of water molecules per unit cell, x and y are total number of tetrahedral per unit cell, and y/x usually has value of 1-5. However, recently high silica zeolites

have been prepared in which y/x is 10 to 100 or even higher
and, in one case, a molecular-sieve silica has reportedly
been prepared.

All zeolite crystal structures have a
pyramid or tetrahedron as the basic building block of a unit
to zeolite. The tetrahedron is formed with four oxygen atoms
surrounding a central silicon atom, which can be substituted
with aluminium atom (Fig. 2-1)

2.3.2 Classification of Zeolites

The molecular-sieve zeolite may be divided
into two groups. One is mineral (natural) zeolite and the
other is synthetic zeolite.

Mineral zeolite (Table 2-2)

Mineral zeolites or natural zeolites occur in
nature in vesicles of basaltic lava (in such areas as
Hawaii, Iceland, and Nova Scotia), in specific, kinds of
rocks subjected to moderate geologic temperature and
pressure (the metamorphic zeolite facies), and in altered
and reacted volcanic ash deposits. (29 : 26-27)

Synthetic zeolites (Table 2-3)

Most of commercial zeolites used today are
synthetic products made in high purity using organic
preparative methods at temperatures in the range of 100 °C
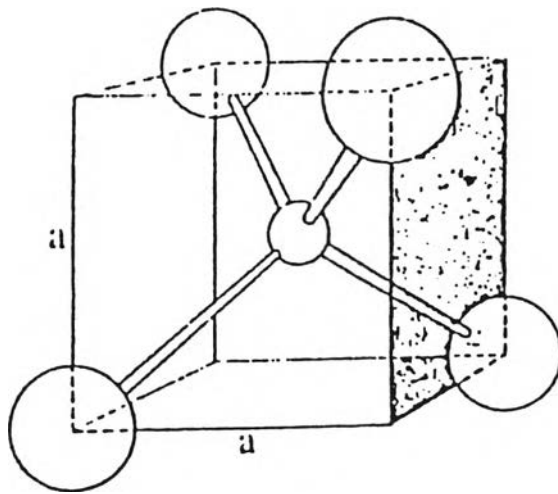to 160 °C. However, much of the pre - 1960 synthetic zeolite

Figure 2-1   The Tetrahedron Formed of a Basic Building

Unit of Zeolite.

Table 2-2 Mineral Zeolite (4 : 4)

No.	Name	Structure Group	Year Discovered	Typical Occurrence in Igneous Rocks	Occurrence in Sedimentary Rocks
1	Analcime	1	1784	Ireland, New Jersey, etc.	Western U.S.,deep sea floor
2	Bikitaite	6	1957	Rhodesia	
3	Brewsterite	7	1822	Scotland	
4	Chabazite	4	1772	Nova Scotia, Ireland, etc.	Arizona, Nevada, Italy
5	Clinoptilolite	7	1890	Wyoming	Western U.S.,deep sea floor
6	Dachiardite	6	1905	Elba	
7	Edingtonite	5	1825	Scotland	
8	Epistibite	6	1823	Iceland	
9	Erionite	2	1890	Rare ; Oregon	Nevada, Oregon
10	Faujasite	4	1842	Rare ; Germany	
11	Ferrierite	6	1918	Rare ; British Columbia	Utah
12	Garronite	3	1962	Ireland, Iceland	
13	Gismondine	1	1816	Rare ; Italy	
14	Gmelinite	4	1807	Nova Scotia	
15	Gonnardite	5	1896	France, Italy	
16	Harmotome	1	1775	Scotland	
17	Herschelite	4	1825	Sicily	Arizona
18	Heulandite	7	1801	Iceland	New Zealand
19	Kehocite	1	1893	Rare ; South Dakota	
20	Laumontite	1	1785	Nova Scotia, Faroe Islands	New Zealand, U.S.S.R., Calif.
21	Levynite	2	1825	Iceland	
22	Mesolite	5	1813	Nova Scotia	
23	Mordenite	6	1864	Nova Scotia	U.S.S.R., Japan, Western U.S.
24	Natrolite	5	1758	Ireland, New Jersey	
25	Offretite	2	1890	Rare ; France	
26	Paulingite	1	1960	Rare ; Washington	
27	Phillipsite	1	1824	Ireland, Sicily	Western U.S.,Africa, deep sea floor
28	Scolecite	5	1801	Iceland, Colorado	
29	Stellerite	7	1909		
30	Stilbite	7	1756	Iceland, Ireland, Scotland	
31	Thomsonite	5	1801	Scotland, Colorado	
32	Viseite	1	1942	Rare ; Belgium	
33	Wairakite	1	1955	New Zealand	
34	Yugawaralite	1	1952	Japan	

Table 2-3 Some Synthetic Zeolites (4:6, 1:51)

Name	Composition	Structure
ZSM-2	$Li_2O \cdot Al_2O_3 \cdot 3.3\text{-}4.0$ $SiO_2 \cdot H_2O$	Tetragonal a = 27.4, c = 28.1A Adsorbs cyclohexane
ZSM-3	$0.3\text{-}0.8 \ Li_2O \cdot 0.7\text{-}0.2$ $Na_2O \cdot Al_2O_3 \cdot 2.8\text{-}4.5$ $SiO_2 \cdot 9H_2O$	Faujasite-type Adsorbs cyclohexane
ZSM-4	$0.5\text{-}0.01 \ TMA \cdot 0.5\text{-}0.99$ $Na_2O \cdot Al_2O_3 \cdot 6.15$ $SiO_2 \cdot 5H_2O^a$	Cubic a_o = 22.2A Adsorbs cyclohexane
ZSM-5[e]	$(TPA,Na)_2O \cdot Al_2O_3 \cdot 5\text{-}100 \ SiO_2 \cdot YH_2O$	Tetragonal a = 23.2, c = 19.9
ZSM-10[f]	$(R,K_2)O \cdot Al_2O_3 \cdot 5\text{-}7SiO_2 \cdot 9H_2O$	- -
Zeolite N	$0.83 \pm 0.05 \ Na_2O \cdot 0.03 \pm 0.01$ $TMA \cdot Al_3O_3 \cdot 1.8\text{-}2.2$ $SiO_2 \cdot YH_2O$	Cubic a_o = 37.2A Small pore
Zeolite Ω	$0.07 \ TMA \cdot 0.5\text{-}1.5$ $Na_2O \cdot Al_2O_3 \cdot 6\text{-}12$ $SiO_2 \cdot 10H_2O$	Hexagonal a = 18.1, c = 7.59 Large pore size 11A
Zeolite α	$0.2\text{-}0.5 \ TMA \cdot 0.5\text{-}0.8$ $Na_2O \cdot Al_2O_3 \cdot 4.0\text{-}7.0$ $SiO_2 \cdot YH_2O$	Cubic, A-Type a_o = 12.04A Adsorbs n-hexane
Zeolite β	$XNa(1.0 \pm 0.1\text{-}X) \ TEA \cdot$ $AlO_2 \cdot 5\text{-}100 \ SiO_2 \cdot$ $4H_2O^b$	Cubic a_o = 12.04 Adsorbs cyclohexane
Zeolite N-A	$TMA \cdot Al_2O_3 \cdot 2.5\text{-}6.0$ $SiO_2 \cdot 7H_2O$	A-Type Cubic a_p = 12.12 Adsorbs n-hexane
Zeolite Li-A	$Li_2Al_2Si_2O_8 \cdot 4H_2O$	Orthorhombic
Zeolite F	$K_{11}[(AlO_2)_{11}(SiO_2)_{11}] \cdot 16H_2O$	Tetragonal a = 10.4, c = 13.9
Zeolite Z	$K_2Al_2Si_2O_8 \cdot 3H_2O$	-
Zeolite H	$K_{14}[(AlO_2)_{14}(SiO_2)_{14}] \cdot 28 \ H_2O$	Hexagonal a = 13.4, c = 13.2

Table 2-3 Some Synthetic Zeolites (Continued)

Name	Composition	Structure
Zeolite Li-H	$Li_2Al_2Si_8O_{20} \cdot 5H_2O$	Tetragonal
Zeolite J	$K_7[(AlO_2)_7(SiO_2)_7 \cdot 4H_2O$	Tetragonal a = 9.45, c = 9.92
Zeolite E	$(K,Na)_2Al_2Si_2O_8 \cdot 3.3\ H_2O$	-
Zeolite M	$K_{14}[(AlO_2)_{14}\ (SiO_2)_{14}] \cdot 12\ H_2O$	Tetragonal a = 13.1, c = 10.5
Zeolite Q	$K_{40}[(AlO_2)_{40}(SiO_2)_{44}] \cdot 86\ H_2O$	Tetragonal a = 13.5, c = 35.2
Zeolite W	$K_{42}[(AlO_2)_{42}(SiO_2)_{76}] \cdot 107\ H_2O$	Cubic, a = 20.1
ZK-19	$(Na_2O,K_2O) \cdot Al_2O_3 \cdot$ $3.0\text{-}6.25\ SiO_2 \cdot 5\ H_2O$	Phillipsite-type Absorbs H_2O
ZK-20	$(0.1\text{-}0.2)R_2O \cdot (0.8\text{-}0.9)$ $Na_2O \cdot Al_2O_3 \cdot 4\text{-}5$ $SiO_2 \cdot YH_2O^c$	Levynite-type Adsorbs CH_4
ZK-21	$1.0\pm\ Na_2O \cdot Al_2O_3 \cdot$ $YSiO_2 \cdot ZP_2O_5^d$ Y = 1.9 to 4.5, $Z = 0.01$ to $\frac{Y+2}{48}$	A-type Cubic a_0 = 12.14 - 12.21 Adsorbs n-hexane
ZK-22	$(TMA,\ NA_2O)^d$	A-type Adsorbs n-hexane

[a] TMA = teramethylammonium.

[b] TEA = tetraethylammonium.

[c]

R =
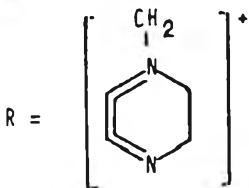
[d] Intercalated phosphate-up to 1 P/ β cage. Thus, if Y = 4, Z = 1/8 unit cell; contents are $Na_8[(AlO_2)_8(SiO_2)_{16} \cdot 1.0\ PO_2$

[e] TPA = tetrapropylammonium.

[f] R = $[1,4\text{-dimethyl-1,4-diazoniabicyclo }(2,2,2)\text{ octane}]^{2+}$

chemistry sought to mimic the geochemical environments of the known mineral forms and thought to be necessary for zeolite formation, -200 °C to 400 °C and several tens of atmospheres water pressure. In 1957 when chemists were beginning to successfully make zeolites at low temperatures (< 100 °C) on a commercial scale, ore-body-sized zeolite deposits also were recognized in low-temperature-altered volcanic ash deposits.

Synthetic zeolites are high-purity specialty chemicals that serve a wide range of applications, from fluid catalytic cracking of over 20 million barrels (3180 ML) a day of crude oil to drying the laboratory jar of solvent. Most synthetic zeolites are thermodynamically metastable products in their preferred synthesis conditions. They are prepared not only under closely controlled conditions of temperature, pressure, and time, but with specific reactants and physical reaction environments, particularly ones that control levels of homogenization and nucleation conditions. All of the controlled conditions depend on the process and composition required for specific reaction (29 : 26-28).

Another interested classification of zeolites is based on its structure and divided into 7 groups. This structural classification, shown in Table 2-4 (1 : 48), have been proposed by Smith and Fischer and Meier. It is based on the frame work topology of the zeolites, for which the

Table 2-4 Classification of Zeolites (1 : 48-50)

Name	Typical Unit Cell Contents	Type of Polyhedral Cage[a]	Framework Density, g/cc[b]	Void Fraction[c]	Type of Channels[d]	Free Aperture of Main Channels, Å[e]
Group 1 (S4R)						
Analcime	$Na_{16}[(AlO_2)_{16}(SiO_2)_{32}] \cdot 16\ H_2O$		1.85	0.18	One	2.6
Harmotome	$Ba_2[(AlO_2)_4(SiO_2)_{12}] \cdot 12\ H_2O$		1.59	0.31	Three	4.2 x 4.4
PHillipsite	$(K,Na)_{10}[(AlO_2)_{10}(SiO_2)_{22}] \cdot 20\ H_2O$		1.58	0.31	Three	4.2 x 4.4, 2.8 x 4.8
Gismondine	$Ca_4[(AlO_2)_8(SiO_2)_8] \cdot 16\ H_2O$		1.52	0.46	Three	3.1 x 4.4
P	$Na_6[(AlO_2)_6(SiO_2)_{10}] \cdot 15\ H_2O$		1.57	0.41	Three	3.5
Paulingite	$(K_2,Na,Ca,Ba)_{76}[(AlO_2)_{152}(SiO_2)_{520}] \cdot 700\ H_2O$	$\alpha,\beta,\gamma,\delta$(10-hedron)	1.54	0.49	Three	3.9
Laumonite	$Ca_4[(AlO_2)_8(SiO_2)_{1.6}] \cdot 16\ H_2O$		1.77	0.34	One	4.6 x 6.3
Yugawaralite	$Ca_2[(AlO_2)_4(SiO_2)_{12}] \cdot 8\ H_2O$		1.81	0.27	Two	3.6 x 2.8
Group 2 (S6R)						
Erionite[f]	$(Ca,Mg,K_2,Na_2)_{45}[(AlO_2)_{27}] \cdot 27\ H_2O$	ϵ,23-hedron	1.51	0.35	Three	3.6 x 5.2
Offretiti[f]	$(K_2,Ca_2)_{2.7}[(AlO_2)_{5.4}(SiO_2)_{12.6}] \cdot 15\ H_2O$	ϵ,14-hedron (II)	1.55	0.40	Three	3.6 x 5.2, lla 6.4, llc
T	$(Na_{1.2}K_{2.8}[(AlO_2)_4(SiO_2)_{14}] \cdot 14\ H_2O$	ϵ,23,14-hedron	1.50	0.40	Three	3.6 x 4.8
Levynite[m]	$Ca_3[(AlO_2)_6(SiO_2)_{12}] \cdot 18\ H_2O$	Ellipsoidal 17-hedron	1.54	0.40	Two	3.2 x 5.1
Omega[g]	$Na_{6.8},TMA_{1.6}[(AlO_2)_8(SiO_2)_{28}] \cdot 21\ H_2O$	14-hedron (II)	1.65	0.38	One	7.5
Sodalite Hydrate	$Na_6[(AlO_2)_6(SiO_2)_6] \cdot 7.5\ H_2O$		1.72	0.35	Three	2.2
Losod	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 19\ H_2O$	ϵ,β,17-hedron	1.58	0.33	Three	2.2

Table 2-4 Classification of Zeolites (continued)

Name	Typical Unit Cell Contents	Type of Polyhedral Cage[a]	Framework Density, g/cc[b]	Void Fraction[c]	Type of Channels[d]	Free Aperture of Main Channels, Å[e]
Group 3 (D4R)[n]						
A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27\ H_2O$	α, β	1.27	0.47	Three	4.2
N-A	$Na_4TMA_3[(AlO_2)_7(SiO_2)_{17}] \cdot 21\ H_2O$	α, β	1.3	0.5	Three	4.2
ZK-4	$Na_8TMA[(AlO_2)_9(SiO_2)_{15}] \cdot 28\ H_2O$	α, β	1.3	0.47	Three	4.2
Group 4 (D6R)						
Faujasite	$(Na_2,K_2,Ca,Mg)_{29.5}[(AlO_2)_{59}(SiO_2)_{133}] \cdot 235\ H_2O$	β, 26-hedron (II)	1.27	0.47	Three	7.4
X	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264\ H_2O$	β, 26-hedron (II)	1.31	0.50	Three	7.4
Y	$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}] \cdot 250\ H_2O$	β, 26-hedron (II)	1.25-1.29	0.48	Three	7.4
Chabazite	$Ca_2[(AlO_2)_4(SiO_2)_8] \cdot 13\ H_2O$	20-hedron	1.45	0.47	Three	3.7 x 4.2
Gmelinite	$Na_8[(AlO_2)_8(SiO_2)_{16}] \cdot 24\ H_2O$	14-hedron (II)	1.46	0.44	Three	3.6 x 3.9, lla 7.0, llc
ZK-5[o]	$(R,Na_2)_{15}[(AlO_2)_{30}(SiO_2)_{66}] \cdot 98\ H_2O$	α, γ	1.46	0.44	Three	3.9
L[h]	$K_9[(AlO_2)_9(SiO_2)_{27}] \cdot 22\ H_2O$	ϵ	1.61	0.32	One	7.1
Group 5 (T_5O_{10})[i]						
Natrolite	$Na_{16}[(AlO_2)_{16}(SiO_2)_{24}] \cdot 16\ H_2O$		1.76	C.23	Two	2.6 x 3.9
Scolecite	$Ca_8[(AlO_2)_{16}(SiO_2)_{24}] \cdot 24\ H_2O$		1.75	0.31	Two	2.6 x 3.9
Mesolite	$Na_{16}Ca_{16}[(AlO_2)_{48}(SiO_2)_{72}] \cdot 64\ H_2O$		1.75	0.30	Two	2.6 x 3.9
Thomsonite	$Na_4Ca_8[(AlO_2)_{20}(SiO_2)_{20}] \cdot 24\ H_2O$		1.76	0.32	Two	2.6 x 3.9
Gonnardite	$Na_4Ca_2[(AlO_2)_8(SiO_2)_{12}] \cdot 14\ H_2O$		1.74	0.31	Two	2.6 x 3.9

Table 2-4 Classification of Zeolites (continued)

Name	Typical Unit Cell Contents	Type of Polyhedral Cage[a]	Framework Density, g/cc[b]	Void Fraction[c]	Type of Channels[d]	Free Aperture of Main Channels, A[e]
Edingtonite	$Ba_2[(AlO_2)_4(SiO_2)_6]$. 8 H_2O		1.68	0.36	Two	3.5 x 3.9
Group 6 (T_8O_{16})[j]						
Mordenite	$Na_8[(AlO_2)_8(SiO_2)_{40}$. 24 H_2O		1.70	0.28	Two	6.7 x 7.0, 11c 2.9 x 5.7, 11b
Dachiardite	$Na_5[(AlO_2)_5(SiO_2)_{19}]$. 12 H_2O		1.72	0.32	Two	3.7 x 6.7, 11b 3.6 x 4.8, 11c
Ferrierite	$Na_{1.5}Mg_2[(AlO_2)_{5.5}(SiO_2)_{30.5}]$. 18 H_2O		1.76	0.28	Two	4.3 x 5.5, 11c 3.4 x 4.8, 11b
Epistilbite	$Ca_3[(AlO_2)_6(SiO_2)_{18}]$. 18 H_2O		1.76	0.25	Two	3.2 x 5.3, 11a 3.7 x 4.4, 11c
Bikitaite	$Li_2[(AlO_2)_2(SiO_2)_4]$. 2 H_2O		2.02	0.23	One	3.2 x 4.9
Group 7 $(T_{10}O_{20})$[k]						
Heulandite	$Ca_4[(AlO_2)_8(SiO_2)_{28}]$. 24 H_2O		1.69	0.39	Two	4.0 x 5.5, 11a 4.0 x 7.2, 11c
Clinoptilolite	$Na_6[(AlO_2)_8(SiO_2)_{30}]$. 24 H_2O		1.71	0.34	?	? 4.1 x 6.2, 11a
Stilbite	$Ca_4[(AlO_2)_8(SiO_2)_{28}]$. 28 H_2O		1.64	0.39	Two	2.7 x 5.7, 11c
Brewsterite	$(Sr,Ba,Ca)_2[(AlO_2)_4(SiO_2)_{12}]$. 10 H_2O		1.77	0.26	Two	2.7 x 4.1 11c 2.3 x 5.0 11a

[a]Of the five space-filling solids of Federov, three (cube, hexagonal prism, and truncated octahedron) are found as polyhedral units in zeolite frameworks. The cube is the double 4-ring (D4R) as shown here. The double 6-ring (D6R) is the hexagonal prism or 8-hedron. The α -cage is the Archimedean semiregular, soild, truncated cuboctahedron referred to also as a 26-hedron, type I. The β -cage is the truncated octahedron or 14-hedron, type I. The ϵ -cage is the 18-hedron and the γ -cage the 11-hedron. Other polyhedral units are as given by Barrer.

[b]The framework density is based on the dimensions of the unit cell of the hydrated zeolite and framework contents only. Multiplication by 10 gives the density in units of tetrahedra/1000 A^3.

[c]The void fraction is determined from the water content of the hydrated zeolite.

[d]Refers to the network of channels which permeate the structure of the hydrated zeolite. Considerable distortion may occur in the group 5 and 7 zeolites upon dehydration.

[e]Based upon the structure of the hydrated zeolite.

[f]Erionite and offretite may also be considered to consist of double 6-rings linked ty single 6-rings.

[g]Zeolite Ω may be considered to consist of single 6-rings linked by double ·2-rings.

[h]Zeolite L consists of double 6-rings linked by single 12-rings.

[i]The T_5O_{10} refers to the unit of 5 tetrahedra as given by Meier for the 4-1 type of SBU.

[j]The T_8O_{16} unit refers to the characteristic configuration of tetrahedra.

[k]The $T_{10}O_{20}$ unit is the characteristic configuration of tetrahedra.

[l]Synthetic zeolites classified in group 1 include ZK-19, W and P-W related to phillipsite, and various synthetic phases related to analcite.

[m]The synthetic zeolite, ZK-20, is reported to have the levynite-type structure.

[n]Other zeolites with the A-type structure include zeolite α , ZK-21 and ZK-22.

[o]R = [1,4-dimethyl-1,4-diazoniabicyclo (2,2,2) octane]$^{2+}$

structures are known and their composition shown in Table 2-5.

2.3.3 Zeolites as Hydrocracking Catalysts.

Several types of zeolites are used in the studies of catalytic hydrocracking because of its selective property. The first patent of zeolite as catalyst was issued in 1917 [U.S. 1,215,391] which concerned a palladium-exchanged chabasite for use in the hydrogenation reactions. And now there are many patented zeolite catalysts available commercially. Many zeolite catalysts can be modified by exchanging the sodium ion in the aluminum tetrahedron for other cations : for example, ammonium ions may be substituted for the sodium. Then the ammonia can be driven off by calcining and the final ions are hydrogen, resulting in the so-called acidic form. The hydrogen form of zeolites have been found to be extremely active catalysts by numerous investigators.

Other cations can also be exchanged for the sodium in zeolites, such as calcium. Some zeolites were impregnated with a metal or mixture of metal, for example, platinum or palladium to give more activity in hydrogenation-dehydrogenation reactions.

Many zeolites used in catalytic cracking belong to type 5A, type X, natural and synthetic faujasite,

Table 2-5 Zeolite Compositions (7 : 639)

Zeolite	CAS Registry No.	Typical formula
Natural		
chabazite	[12251-32-0]	$Ca_2[(AlO_2)_4(SiO_2)_8] \cdot 13\ H_2O$
mordenite	[12173-98-7]	$Na_8[(AlO_2)_8(SiO_2)_{40}] \cdot 24\ H_2O$
erionite	[12150-42-8]	$(Ca,Mg,Na_2,K_2)_{4.5}[(AlO_2)_9(SiO_2)_{27}] \cdot 27\ H_2O$
faujasite	[12173-28-3]	$(Ca,Mg,Na_2,K_2)_{29.5}[(AlO_2)_{59}(SiO_2)_{133}] \cdot 235\ H_2O$
clinoptilolite	[12321-85-6]	$Na_6[(AlO_2)_6(SiO_2)_{30}] \cdot 24\ H_2O$
Synthetic		
zeolite A		$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27\ H_2O$
zeolite X		$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264\ H_2O$
zeolite Y		$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}] \cdot 250\ H_2O$
zeolite L		$K_9[(AlO_2)_9(SiO_2)_{27}] \cdot 22\ H_2O$
zeolite omega		$Na_{6.8}TMA_{1.6}[(AlO_2)_8(SiO_2)_{28}] \cdot 21\ H_2O$[a]
ZSM-5	[58339-99-4]	$(Na,TPA)_3[(AlO_2)_3(SiO_2)_{96}] \cdot 16\ H_2O$[b]

[a] TMA = tetramethylammonium.

[b] TPA = tetrapropylammonium

mordenite type ZK-5', gmelinite, chabazite, stilbite and offretite. These catalysts are also used in another important reaction, for example, isomerization. The zeolite catalysts used for hydrocracking reactions are either impregnated or not impregnated.

2.4 HYDROCRACKING REACTION IN THE PRESENT STUDY

2.4.1 Reactants Used

The main reactants used consist of n-hexane (which is liquid at room temperature) and hydrogen gas. The liquid n-hexane reactant was Baker analyzed reagent whose density at 25 °C is 0.664 g/ml. and 96.33 % in purity with its isomer as impurities consisted of 1.25 % of 2MP and 1.57 % 3-MP. Hydrogen was 99.999 % purity and contained oxygen less than 3 ppm., and was supplied in cylinder container by Thai Industrial Gas Company. The hydrogen reactant is used for the hydrogenation of cracked olefins to paraffins or saturated hydrocarbons. By the way, nitrogen gas was used to purge the system before and after each experiment.

2.4.2 Catalysts Studied

2.4.2.1 Type of Catalysts studied.

Two types of catalysts were studied to find out their effects on the hydrocracking reaction of n-hexane.
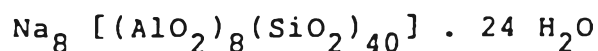
They are :

a) Na-Mordenite

b) Na-Y

Na-Mordenite

Mordenite is one of the zeolites as well as one of the most important cracking catalysts. Mordenite which has chainlike or fibrous crystal structure, one dimensional pores, occur naturally and can also be synthesized. The formula of mordenite is :

$$Na_8 \ [(AlO_2)_8(SiO_2)_{40}] \ . \ 24 \ H_2O$$

Though the first patent for zeolitic catalyst was issued in 1917, large-scale work started form 1960. Keough and Sands recognized the catalytic properties of mordenite in 1961 which was in the form of H-mordenite.

The mordenite structure can be compared to a bundle of parallel tubes and its void volume is 0.14 cc/gm, considerably less than Y-type, (Fig.2-2). Many studies have shown H-mordenite is very active in catalytic cracking

Na-Y

Synthetic zeolite type y is a well-known member of the faujasite family whose typical formula is :

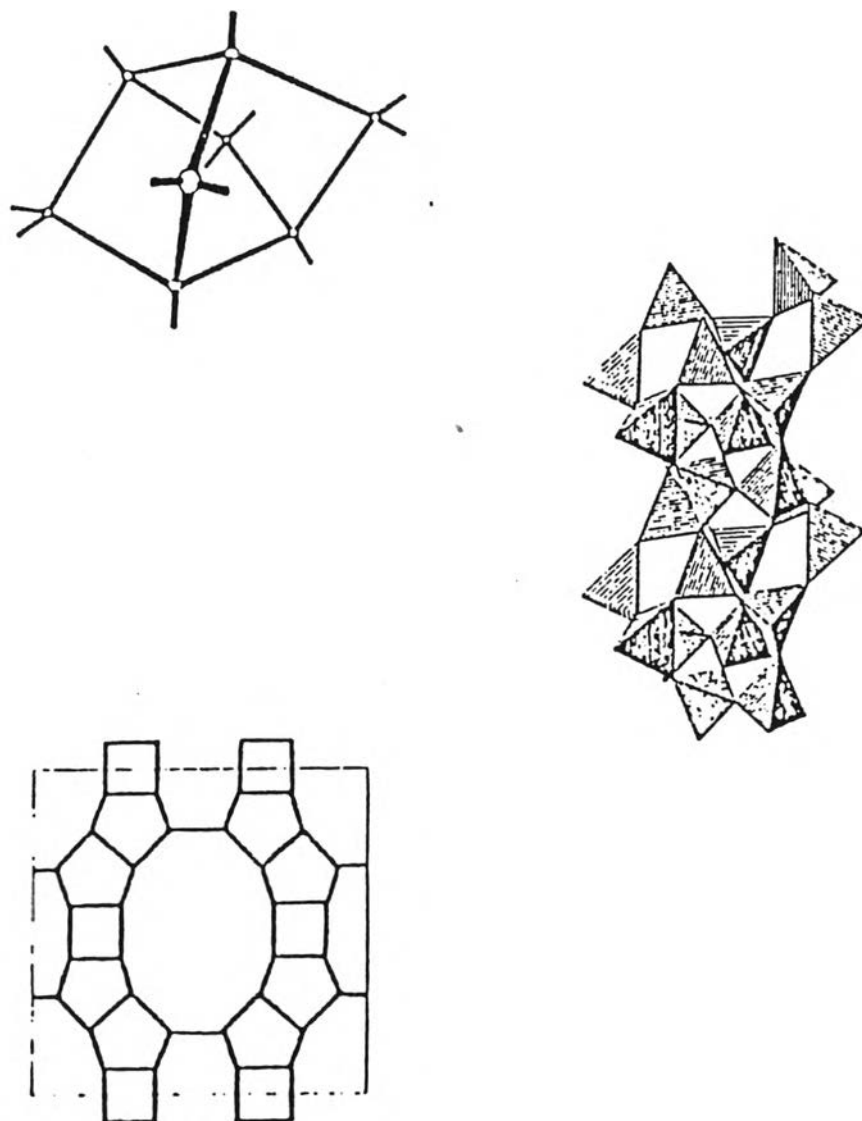$$Na_{56} \ [(AlO_2)_{56}(SiO_2)_{136}] \ . \ 264 \ H_2O$$
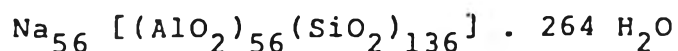
Figure 2-2   Chainlike or Fibrous Crystal Structure of
Mordenite.

Both natural and synthetic versions of this type have a void volume of 0.35 cc/gm. Its structure is a truncated octahedra, 2-dimensional, as shown in Figure 2-3. Each vortex represents a silicon or aluminum atom of the basic tetrahedron, and each edge represents a linking of oxygen atom. The sodium form can be exchanged to H-form which provides acidic active sites required for catalytic activity for many reactions, such as catalytic cracking, isomerization, alkylation and etc.

2.4.2.2 Composition

The composition of the mordenite and Na-Y zeolite catalysts used in the study is shown in Table 2-6.
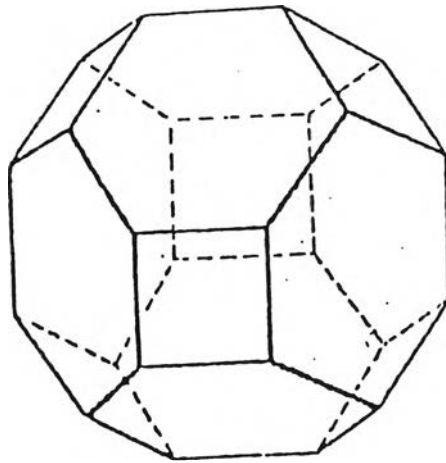
Figure 2-3   A Truncated Octahedra Structure of Na- Y.

Table 2-6   Composition   of   Zeolite   studied.

zeolite type composition	Na-Y TSZ-320 NAA	Na-Mordenite TSZ-620 NAA
SiO_2 (wt %) dry basis	66.7	84.3
Al_2O_3 (wt %) dry basis	20.3	9.4
Na_2O (wt %) dry basis	12.3	5.5
K_2O (wt %) dry basis	−	−
SiO_2/Al_2O_3 (mole ratio)	5.6	15.3
Na_2O/Al_2O_3 (mole ratio)	−	−
K_2O/Al_2O_3 (mole ratio)	−	−