Chapter1

INTRODUCTION

Introduction

Catalytic cracking is the premier conversion process found in the refinery. Nearly 20% of all distilled crude oil is processed in catalytic cracking units. An average size-cracking unit processes 50,000 barrels a day, although some units exceed 120,000 barrels per day. These units process an extremely wide variety of feedstocks. The feeds used include molecules with carbon numbers from simple C_7 to C_8 molecules to complex structure of 100 or more carbon atoms. Molecular types present are predominantly paraffins, cycloparaffins (naphthenes), and aromatics. Many of aromatic contains multiple fused rings (rings directly joined). The easiest feeds to crack consist of more paraffins and naphthenes, with minimal quantities of aromatics. Feedstock quality determines to a very large degree the value of the products that come from catalytic cracking. Product from the unit are fuel gases (H_2, C_1, C_2), liquefied petroleum gas or LPG (C_3, C_4), and gasoline-range naphtha (C_5 through C_{10}). They also include diesel range light cycle oil (LCO) (C_{11} through C_{18}), heavy cycle oil (HCO) (C_{19+}), and coke.

Catalytic cracking is *endothermic*, meaning that heat is absorbed by the reactions. The temperature of the reaction mixture declines as the reactions proceed. Heat to drive the process comes from combustion of coke formed in the process. Coke is a necessary product of cracking. It is solid, black material that is rich in carbon and low in hydrogen; chemists call this condition " highly unsaturated". Coke forms on the surface and in the pores of the catalyst during the cracking process, covering active sites and deactivating the catalysts. During regeneration, this coke is burned off from the catalyst to restore its activity. Like all combustion processes, regeneration is *exothermic*, liberating heat. Many improvements have been made to enhance the unit mechanical reliability and its ability to crack heavier,

lower-value feedstocks.(Magee and Dolbear, 1998). FCC unit utilizes a microspherodial catalyst which fluidizes when properly aerated. The main purpose of the unit is to convert high-boiling petroleum fractions called gas oil to high-value, high-octane gasoline and heating oil. Gas oil is the portion of crude oil that boils in the 650-1050°F (330-550°C) range and contains a diversified mixture of paraffins, naphthenes, aromatics, and olefins.

The laboratory evaluation of Fluid Catalytic Cracking (FCC), catalyst has evolved into a very common method for measuring performance characteristics of experimental and commercial catalyst sample. The most method employed within virtually every laboratory, makes use of the Microactivity Test Unit or MAT Unit. The MAT Unit used as the primary tool for the laboratory evaluation of FCC Catalyst.

Literature review

The cracking process takes place in a fluid catalytic cracking unit, schematically shown in Figure 1-1. The three main components of the FCC unit (FCCU) are the *riser reactor*, the *stripper* and the *regenerator*. Such a unit operates as follows:

The hot catalyst is mixed with preheated feedstock at the base of the riser reactor. Steam is also injected to facilitate the dispersion of the feedstock. While the feedstock-catalyst mixture rises in the reactor at temperatures varying from 510 to 527 $^{\circ}$C, the cracking of the feedstock take place. The reactor products enter the cyclone vessel, where cyclone separate the gaseous components (cracked products and unreacted feedstock) from the coked catalyst. The product are sent from the cyclone vessel to the fractionator, where gasoline and other fractions are separated by distillation. The catalyst is contacted with steam in the steam stripping, the coke catalyst enters the regenerator, where the coke is oxidized to CO_2, CO and steam in a stream of hot air injected through nozzles in the bottom of the regenerator. The temperature in the regenerator can vary from 650 to 790 $^{\circ}$C The resulting gases (flue gases) are routed into an overhead flue gas circuit and eliminated,

while the regenerates catalyst is returned to the riser reactor. Fresh catalyst is added periodically to the unit, to compensate for catalyst losses and gradual catalyst deactivation.
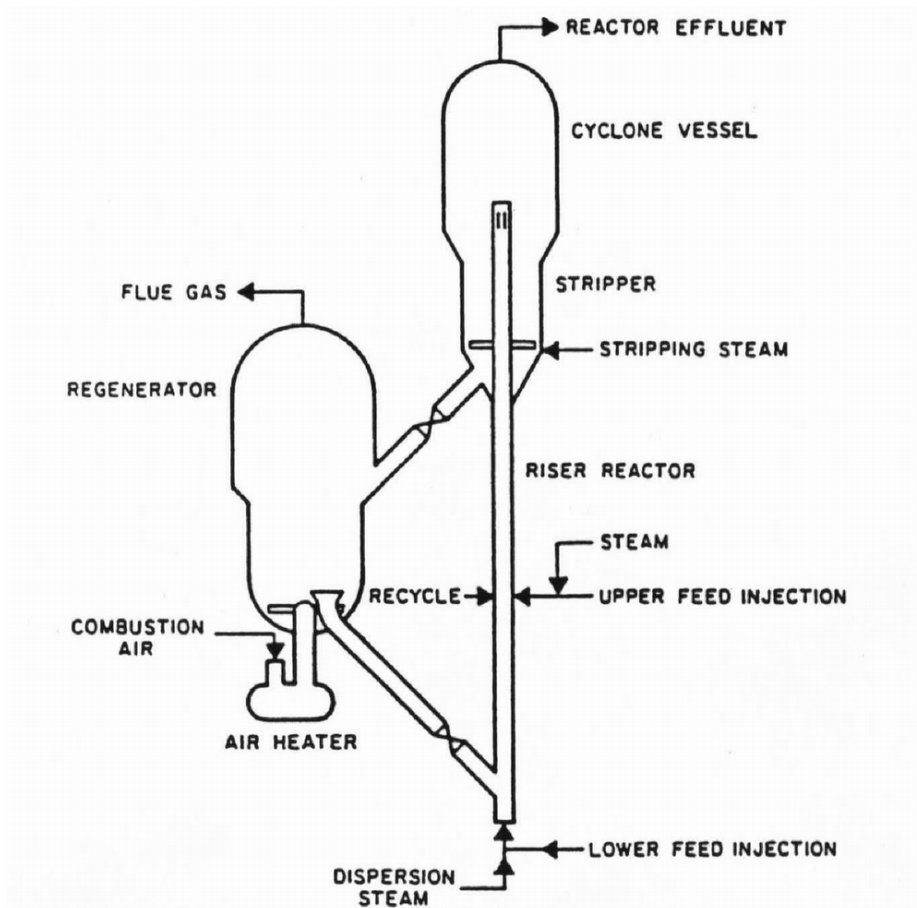
Figure 1-1. Schematic of FCC unit

Source: Magee and Dolbear, 1998: 56

In the FCC process, the entire catalyst inventory is continually circulated through the three part of the FCCU. Catalyst residence time in the riser reactor section is typically 1-3 second (with current trends to even shorter residence time). The entire reactor / stripper / regenerator cycle is less than 10 minutes. To achieve cycle time of this order, catalyst circulation rates as high as 1 ton/second in large unit are not uncommon.

Catalyst loss from the unit caused by poor resistance can be a serious problem, since the quantity loss must be replaced by fresh catalyst additions to maintain constant unit performance. Catalyst manufacturer work hard to prevent inordinate losses due to attrition, and refineries keep a close watch catalyst quality to be sure the product conforms to their specifications. Faulty unit operation can also lead to catalyst losses, even with well-made attrition-resistance catalysts (Scherzer, 1990; Magee and Dolbear, 1998; Avidan, 1993).

1. FCC Feed Characterization (Sadeghbeigi, 1995; Magee and Dolbear, 1998)

FCC feed characterization is one of the most important requirements of cat cracking. Feed characterization is a mean of relating feed quality to product yield and qualities. The effect of feedstock on unit yield, a refiner can purchase the feedstock would maximize profitability. It is not uncommon for many refiners to purchase raw crude oil or FCC feedstock without knowing their impact on unit operation.

Refiners are faced with processing many different type of crude oil. As market conditions and crude quality fluctuate, so do cat cracking feedstock properties. Feed characterization is the process of determining physical and chemical properties of the feed.

The hydrocarbon types in the FCC feed are broadly classified as paraffins, olefins, naphthenes, and aromatics.

1.1 Paraffins

Paraffins are straight or branched chain hydrocarbon having the chemical formula C_nH_{2n+2}. The name of member end with *–ane* ; example propane, isopentane, and normal heptane.

In general, FCC feeds are predominantly paraffinic. The paraffin content is typically between 50 %wt and 65 %wt of the total feed. Paraffinic stocks are easy to crack and normally yield the greatest amounts of total liquid products, the most gasoline, the lowest fuel gas, and the least octane number.

1.2 Olefins

Olefins are unsaturated compounds with a formula of C_nH_{2n}. The name of these compounds ends with –*ene*, such as ethene (ethylene) and propene (propylene). Compared to paraffins, olefins are unstable and can react with themselves or with other compounds such as oxygen and bromine solution. Olefins do not occur naturally; they show up in the FCC feed as result of preprocessing the feeds elsewhere. These processes include thermal cracking and other catalytic cracking operations.

Olefins are not the preferred feedstocks to the FCC unit. They usually crack to form undesirable products, such as slurry and coke. Typical olefin content of FCC feed is less than 5 %wt unless charging unhydrotreated thermally produced gas oils.

1.3 Naphthenes

Naphthenes (C_nH_{2n}) have the same formula as olefins, but their characteristics are significantly different. Unlike olefins that are straight-chain compounds, naphthenes are paraffins that have been "bent" into a ring or a cyclic shape. Naphthenes, like paraffins, are saturated compounds. Example of naphthenes are cyclopentane, cyclohexane, and mehtyl-cyclohexane

Naphthanes are desirable FCC feedstocks because they produce high-octane gasoline. The gasoline derived from the cracking of naphthenes has more aromatics and is heavier than the gasoline produced from the cracking of paraffins.

1.4 Aromatics

Aromatics (C_nH_{2n-6}) are similar to naphthenes, but they contain a stabilized unsaturated ring core. Aromatics are comppounds that contain at least one benzene ring. The benzene is very stable and do not crack to smaller components. Aromatics are not preferable as FCC feedstocks because most of the molecules will not crack. The cracking of aromatics mainly involves breaking off the side chains, and this can result in excess fuel gas yield. In addition, some of the aromatic compounds contain serveral rings (polynuclear aromatics) that can "compact" to form what is commonly called "chicken wire". Some of these compacted aromatics will end up on the catalyst as carbon residue (coke), and some

will become slurry product. In comparison to paraffins, the cracking of aromatic stocks results in lower conversion, lower gasoline yield, and less liquid volume gain with higher gasoline octane.

2. Catalytic Cracking

Catalytic cracking gets its name from the fact that the principal reaction catalyst involves the cleavage of large molecules into two or more smaller pieces. In addition, molecular shape changes when molecules being cracked undergo isomerization. In catalytic cracking, we consider two main kinds of reaction, called primary and secondary. Examples of the primary reactions involved in catalytic cracking are:

- Paraffins are cracked to give olefins and smaller paraffins

- Olefins are cracked to give to smaller olefins

- Naphthenes (cycloparaffins) are cracked to olefins, except the cyclohexane ring is not opened

- Alkyl aromatics lose their side chains as olefins, leaving benzene, or they lose their side chain as a paraffin, leaving a substituted benzene with an olefinic side chain

Important secondary reactions occur rapidly and include:

- Isomerization of olefins to iso-olefins

- Hydrogen transfer between naphthenes and olefins, forming aromatics and paraffins; this also leads through aromatic condensation reactions to coke formation

Thermal cracking also occurs at temperatures much higher than $1,100^{\circ}$F. This is cracking that takes place without benefit of the catalyst and proceeds by free radical mechanism. The intermediates are uncharged but highly reactive molecular fragments. Thermal cracking also causes C-C bond rupture, but the products of thermal cracking are substantially different from those formed in catalytic cracking (see Table 1-1). High yields of ethylene and small amounts of methane and alpha olefins (double bond between carbon 1

and 2) are typically. Cat cracking, in contrast, requires the catalyst and operates by carbenium ion mechanism. The reaction intermediates are charged species generated by hydrocarbon interaction with the strong acid sites on the catalyst.

Table 1-1 Catalytic vs. Thermal cracking

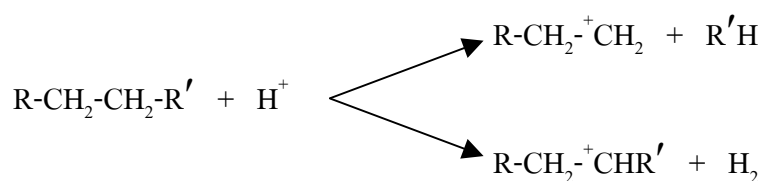Source: Magee and Dolbear, 1998: 60

Hydrocarbon cracked	Thermal cracking products	Catalytic cracking products
n-hexadecane	C_2 is the major product C_1 produced in large amounts C_4 to C_{15} olefins in products No Branched-chain products	C_3 to C_6 are the major products No olefins larger than C_4 Branched-chain paraffins present in products
Aliphatics	Little aromatization at 500 $^\circ$C	Significant aromatization at 500 $^\circ$C
Alkyl aromatics	Cracking occurs within the side chain	Dealkylation is the dominant cracking reaction
n- Olefins	Slow double-bond isomerization Little skeletal isomerization	Rapid isomerization of double-bond Rapid skeletal isomerization
Naphthenes	Cracking is slower than that of paraffins	Cracking rates comparable to those of paraffins

**2.1 Chain initiation-generation of carbenium ion**

1) Lewis acid site on catalyst abstracts hydride ion (H^-) from saturated hydrocarbon forming carbenium ion:

$$R\text{-}CH_2\text{-}CH_2\text{-}R' + L^+ \longrightarrow R\text{-}{}^+CH\text{-}CH_2\text{-}R' + LH$$
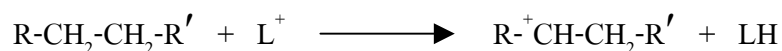
2) Bronsted acid site on catalyst protonates saturated hydrocarbon yielding a carbenium ion and or a molecule of hydrogen, e.g.:

$$R\text{-}CH_2\text{-}CH_2\text{-}R' + H^+ \begin{cases} \longrightarrow R\text{-}CH_2\text{-}{}^+CH_2 + R'H \\ \longrightarrow R\text{-}CH_2\text{-}{}^+CHR' + H_2 \end{cases}$$

3) Bronsted acid site on catalyst protonates an olefin to form carbenium ion, e.g.:

$$R\text{-}CH=CH_2 + H \longrightarrow R\text{-}{}^+CH\text{-}CH_3$$
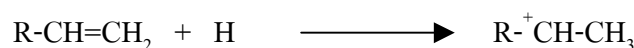
Once the initiation reaction occurs on the acid catalyst surface, the remainder of the primary and secondary reactions of carbenium ion follow. Carbenium ion formation is followed (see Figure 1-2) by the rupture (breaking) of a carbon-carbon bond in a secondary position to the positive charge. This reaction is called *beta scission*. The name comes from a practice of referring to the nearest position as alphla, the second position as beta, and so on. Beta scission is the primary way molecular weight is reduced in catalytic cracking. In the Figure 1-2, we illustrate this using cetane n-hexadecane, $C_{16}H_{34}$. The cetane carbenium ion was free to crack between either the 4 to 5 carbon position or the 7 to 8 carbon position when the positive charge is on the #6 carbon. Actually, the catalyst acid site could interact with any of the carbon in the cetane chain, but the bond cracking always occurs between the second and third carbon from the charge.
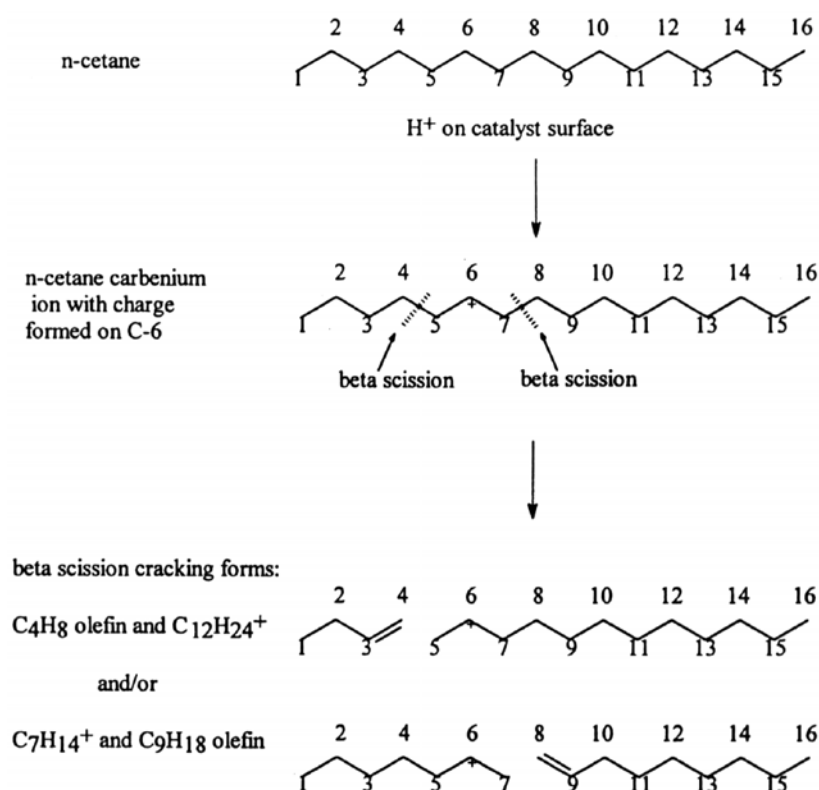
Figure 1-2 Beta scission cracking of n-cetane

Source: Magee and Dolbear, 1998: 62
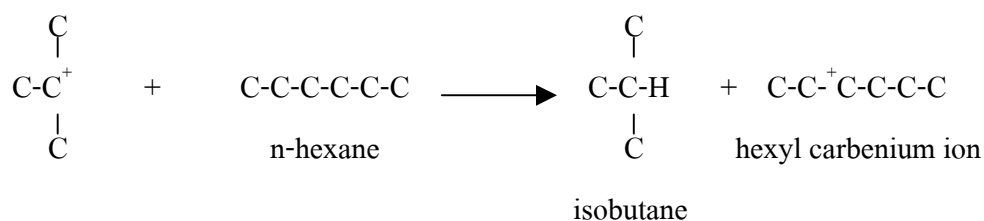
2.2 Isomerization

After this part of the reaction, we are left with an olefin and a new carbenium ion. Like the initial cetane carbenium, this new carbenium ion called *secondary* carbenium, since the charge is located on a carbon atom connected to two other carbon atom ($-C-C^+-C-$) is free to isomerize to a more stable carbenium ion. In fact, this isomerization reaction is highly favored and quite rapid. We can expect the secondary C_7 carbenium ion to isomerize rapidly to a tertiary carbenium ion. This puts the positive charge on a carbon atom surrounded by three other carbon atoms:

$$C-\overset{+}{C}-C-C-C-C$$
$$|$$
$$C$$
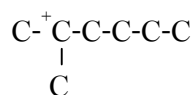
This, in turn, is free to crack beta to the charge, forming propylene and a tertiary butyl carbenium ion.

$$
\begin{array}{c}
C \\
| \\
C-\overset{+}{C} \\
| \\
C
\end{array}
\qquad + \qquad C\text{-}C\text{=}C
$$

*t*-butyl carbenium ion   propylene
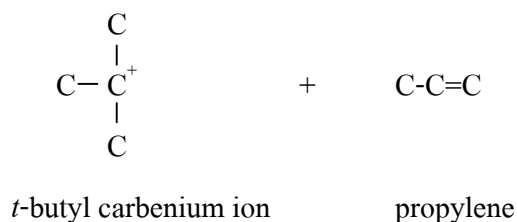
This favored rearrangement of carbenium ions trending to form tertiary carbenium ions is largely responsible for the large numbers of isomers observed in catalytic cracking. For example, the simplest tertiary carbenium ion, *t*-butyl, would react with another hydrocarbon to form a new carbenium ion plus isobutane:

$$
\begin{array}{ccccc}
\overset{C}{\underset{|}{C\text{-}\overset{+}{C}}} & + & C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}C & \longrightarrow & \overset{C}{\underset{|}{C\text{-}C\text{-}H}} \quad + \quad C\text{-}C\text{-}\overset{+}{C}\text{-}C\text{-}C\text{-}C \\
C & & \text{n-hexane} & & C \quad\quad\text{hexyl carbenium ion}
\end{array}
$$

isobutane

In these, the carbenium ion transfer a proton (H^+) to the catalyst and regenerate a Bronsted acid site; the hydrocarbon desorbs as an olefin. Another kind of termination occurs when the carbenium encounters a hydride (H^-), generating a Lewis acid site; the hydrocarbon atom then desorbs as a parafin.

2.3 Hydrogen transfer

After the primary reaction of cracking and secondary reaction of isomerization, hydrogen transfer can be considered of nearly equal importance in determining product selectivities of modern cracking catalysts. The basic reaction occurs between olefins and cycloparaffins (naphthenes), and yields parafins and aromatic as products. Since naphthenes are a major constituent of most FCC feeds, all that is needed is an olefin from the primary cracking reactions to initiate hydrogen transfer reactions. For example, bytylene can react with cyclohexane to make butane and benzene:

C=C-C-C   +   ⬡   ⟶   C-C-C-C   +   ⬡◯   + 2H$_2$

butylene   cyclohexane   butane   benzene
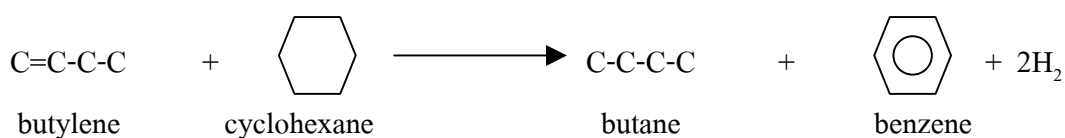
This reaction has used up a valuable light olefin (butylene) to make a light gas and an aromatic whose use in gasoline is now carefully regulated. In today's gasoline market place, this product is not particularly desirable. Such hydrogen transfer reactions occur readily in type Y zeolite catalysts. Further, hydrogen transfer also favors the formation of condensed aromatic rings, which lead to increased coke formation and a reduction of olefins in the product. In addition, the molecular weight distribution of the products are increased by hydrogen transfer, since carbenium ions are converted to paraffins by hydrogen transfer before they undergo further cracking. None of these effects is desired.

Modification of the catalyst's zeolite structure has been found to be an effective way to control hydrogen transfer reactions. Lower levels of hydrogen transfer will give lower gasoline yields, low coke yield (desirable), and high olefin yield from C$_3$ and C$_4$ right through the gasoline range. Olefins help enhance gasoline octane, as do isoparaffins and aromatics.

In summary, cat cracking leads to molecular weight reduction, usually measured as a change in the boiling range:

- The heaviest product, heavy cycle oil (HCO), distills above 640°F and may be recycled or used in heavy fuel oil

- The intermediate fraction, light cycle oil (LCO), distills from 430°F to 640°F, giving stocks that end up in jet fuel, kerosene, diesel, and home heating oil

- The lightest liquid, naphtha, distills from 100-430°F. It provides a major amount of the component of gasoline and may be split into two fractions: light (boiling from 100-230°F) and heavy (boiling from 230-430°F)

- Gases, ranging from hydrogen to butanes, which are separated and used as alkylation feeds (the olefins), petrochemical feeds (propylene, sometimes ethylene) and refinery fuel gas

In today's economic climate, HCO is the least valuable product obtained in catalytic cracking. Gasoline and lighter products are the most valuable. LCO fractions are intermediate but much closer to gasoline in value than to HCO. The importance of these economic " rule-of-thumb" is that they drive the entire catalytic cracking field, both in catalyst research and development and manufacturing, and in unit operation and design.
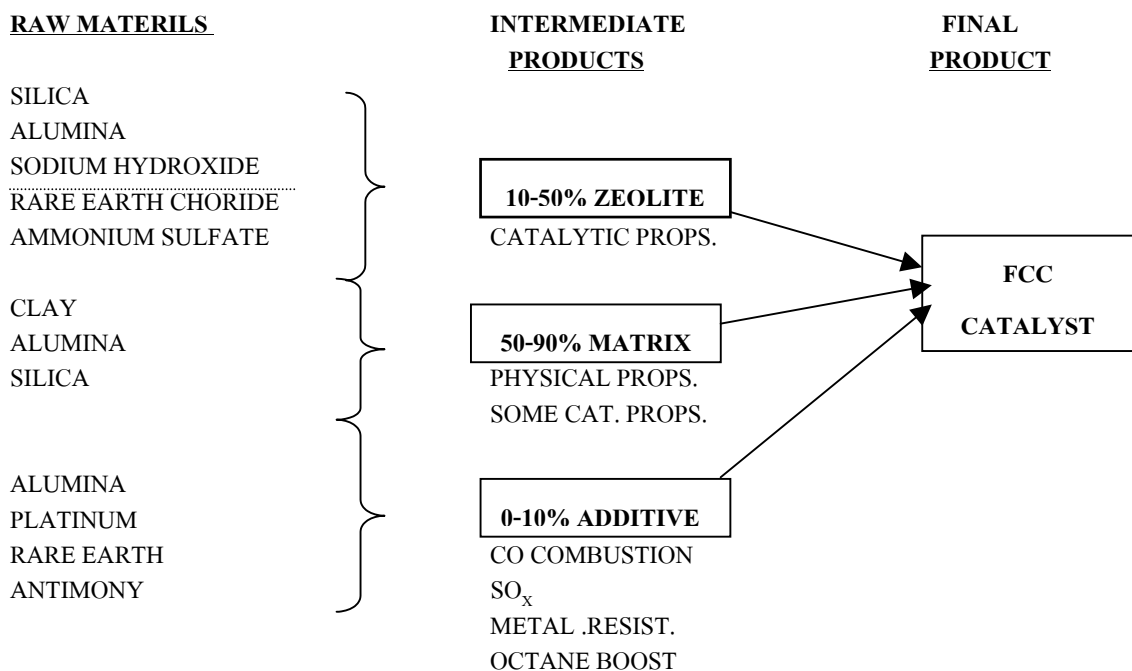
3. Composition of FCC Catalysts (Scherzer, 1993)

Modern FCC catalyst consists, in general, of two major components: zeolite and matrix. Some catalysts also contain a third component: one or several additives, designed to boost gasoline octane, increase catalyst metal resistance, reduce SO_X emissions, or facilitate CO oxidation. The additive can be incorporated into the catalyst particle or be used as a distinct physical particle.

The zeolite used in the FCC catalysts are most synthetic, faujasite type zeolite: Y and high silica Y zeolites. In the part, X zeolites have also be used, but have been replaced by more stable Y zeolite. Some commercial catalysts contain mixtures of Y and high-silica Y zeolites. The zeolites are being used mostly in the rare earth or ammonium exchanged form. Most commercial FCC catalyst contains between 15 and 40 percent zeolite, which is the major contributor to the catalytic activity and selectivity of the FCC catalyst.

The catalyst matrix consists usually of a synthetic and natural component. The synthetic component in most commercial catalyst is amorphous silica, alumina or silica alumina, while the natural component is clay. Thermally and/or chemically modified clays are also used. The matrix is responsible primarily for the physical properties of the catalyst For example, FCC catalyst used for cracking heavy feedstock (e.g., resid) usually catalytically active matrices.

The additives show a wide variation in composition, depending on their role. For example ZSM-5 zeolite is used as an octane-boosting additive. Antimony, bismuth and tin compounds are used for the passivation of heavy metal, such as nickel and vanadium, deposited on the catalyst during the cracking of metal-containing feedstocks. Certain metal oxide (Al_2O_3, MgO) or mixed metal oxides such as magnesia-alumina, mixed rare earths oxides-alumina or ceria-spinel are used to control SO_X emissions from the regenerator. Platinum is used as a CO combustion promoter. The compositions of FCC catalysts, as well as the raw material used in their manufacture, are shown schematically in Figure 1-3.

RAW MATERILS

SILICA
ALUMINA
SODIUM HYDROXIDE
RARE EARTH CHORIDE
AMMONIUM SULFATE

CLAY
ALUMINA
SILICA

ALUMINA
PLATINUM
RARE EARTH
ANTIMONY

INTERMEDIATE PRODUCTS

10-50% ZEOLITE
CATALYTIC PROPS.

50-90% MATRIX
PHYSICAL PROPS.
SOME CAT. PROPS.

0-10% ADDITIVE
CO COMBUSTION
SO_X
METAL .RESIST.
OCTANE BOOST

FINAL PRODUCT

FCC CATALYST

Figure 1-3 Composition of FCC Catalyst

Source : Scherzer, 1993 : 147

3.1 Zeolite

Zeolite, or more properly, faujasite, is the key ingredient of the FCC catalyst. Its role in the catalyst is to provide product selectivity and much of the catalytic activity. The catalyst's performance depends largely on the nature and quality of the zeolite. Understanding the zeolite structure, types, cracking mechanism, and properties are essential in choosing the " right " catalyst to produce the desired yield.

3.1.1 Zeolites Structure

Zeolite, sometimes called molecular sieve, has a well-defined lattice structure. Its basic building blocks are silica and alumina tetrahedra. Each tetrahedron (Figure1-4) consists of a silicon or aluminum atom at the center of tetrahedron, with oxygen atom at the corners.

Zeolite lattices have an organized network of very small pores. The pore diameter of nearly all of today's FCC zeolite is approximately 8.0 angstroms (Å). These small openings, with an internal surface area of roughly 600 square meters per gram, do not readily admit hydrocarbon molecules with a molecular diameter greater than 8.0 Å to 10 Å

The elementary building block of zeolite is called a unit cell. These basic building blocks combine at their oxygen atoms to form a cage structure that has well defined pores of a specific diameter. The unit cell size (UCS) is the distance between the repeating cell in the zeolite structure. One unit cell in a typical fresh Y–zeolite lattice contains 192 framework atomic positions: 55 atom of aluminum and 137 atom of silicon. This corresponds to a silica (SiO_2) to alumina (Al_2O_3) molal ratio (SAR) of 5. The unit cell size (UCS) is an important parameter in characterizing the zeolite structure. (Sadeghbeigi, 1995).
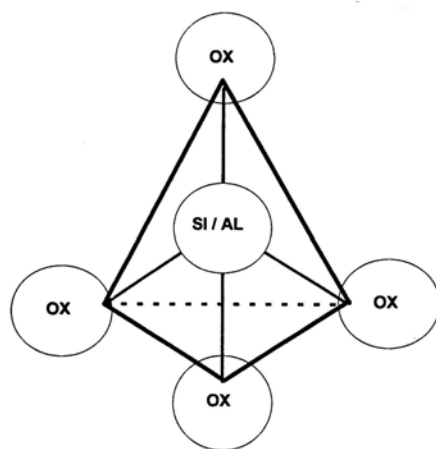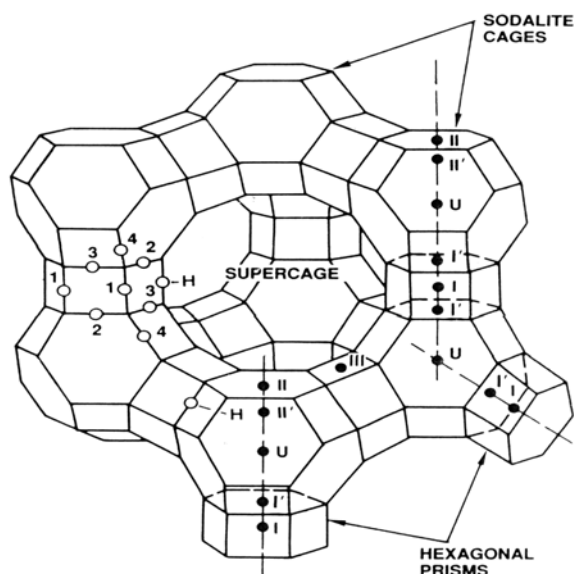
Figure 1-4 Silicon/aluminum-oxygen tetrahedron.

Source: Sadeghbeigi, 1995: 81

The structure of Y zeolites consists of a negatively charged, three-dimensional framework of SiO_4 and AlO_4 tetrahedral, joined to form an array of truncated octahedral. These truncated octahedral (β-cages or sodalite cages) are joined at the octahedral faces by hexagonal prisms resulting in tetrahedral stacking. This type of stacking creates large cavities (α-cages or supercages) with a diameter of ∼ 13 Å. The supercages can be entered through any of four tetrahedral distributed opening (12-membered rings), each having a diameter of 7.4 Å. The supercages, connected through 12-membered rings, form the large-pore system of the zeolite as shown in Figure1-5. The structure comprises also a small - pore system, made up of sodalite cages and the connecting hexagonal prisms. The six-member rings of the sodalite cages have a diameter of ∼ 2.4 Å.

Each tetrahedral coordinated aluminum atom in the framework carries a negative charge. These negative charges in the framework are compensated by cations located in specific non-framework positions, as shown in Figure 1-5. In the dehydrated form, charge-balancing protons occupy certain preferred positions in the zeolite and form two types of acidic hydroxyl groups: α-cages hydroxyls, which are very acidic and are directly accessible to adsorbates: and β-cages hydroxyls, which are less acidic but sufficiently

mobile to interact with α‑cage restricted adsorbates. In the hydrated form, the ions and the water molecules in the supercages have considerable freedom of movement, which permits ion exchange, as well as reversible dehydration and sorption (Scherzer,1990).

Figure 1‑5 Faujasite framework showing oxygen type (O) nonframework locations (●) and

Bronsted acid sites

Source : Scherzer, 1990: 23

3.1.2 Zeolite chemistry

The typical zeolite consists of silicon and aluminum atoms that are tetrahedrally joined by four oxygen atoms. Silicon is in a +4 oxidation state, therefore, a tetrahedral containing silicon is neutral in charge. In contrast, aluminum is in a +3 oxidation state. This indicates that each tetrahedron containing aluminum atom has a net charge of −1 which must be balanced by a positive ion. This ionic site accounts for the catalytic activity of zeolite.

Solutions containing sodium hydroxide are commonly used in synthesizing the zeolite. The sodium ion is used to balance the negative charge of aluminum tetrahedral. This zeolite is called soda Y or NaY. The NaY zeolite is not hydrothermally stable because of

the high sodium content. Ammonium ion is frequently used to displace the sodium. Upon drying the zeolite, ammonium is vaporized . The resulting acid sites are both the Bronsted and Lewis types. The Bronsted acid sites can be further exchanged with rare earth material such as cerium and lanthanum to enhance their strengths. The zeolite activity comes from these acid sites. (Sadeghbeigi, 1995)

3.1.3 Zeolite type

Zeolite employed in the manufacture of the FCC catalyst are a synthetic versions of naturally occurring zeolite called faujasites. There are about 40 known natural zeolites and over 150 zeolites which have been synthesized. Of this number, only a few have found commercial applications. Table 1-2 shows properties of the major synthetic zeolites.
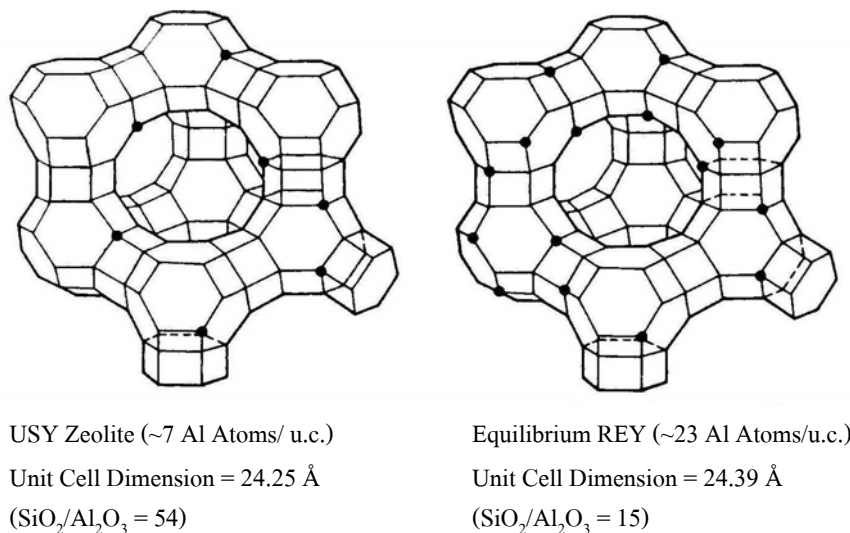
Table 1-2 Properties of the major synthetic zeolites

Source: Sadeghbeigi, 1995: 82

	Pore size Dimension (Å)	Silica to Alumina ratio	Process
Zeolite A	4.1	2 – 5	Detergent manufacturing.
Faujasite	7.4	3 – 6	Catalytic cracking and hydrocracking.
ZSM – 5	5.2 x 5.8	30 – 200	Xylene isomerization, Benzene alkylation, Catalytic cracking.
Mordenite	6.7 x 7.0	10 – 12	Hydro – isomerization, Dewaxing.

The zeolites with applications to FCC are Type X, Type Y, and ZSM – 5. Both X and Y zeolites have essentially the same crystalline structure. The major difference is that the X zeolite has a lower silica to alumina ratio than the Y zeolite. The X zeolite also has a lower thermal and hydrothermal stability than Y zeolite. Some of the earlier FCC zeolite catalysts contained X zeolite, however, virtually all of today 's catalysts contain Y zeolite or variations thereof (Figure 1-6).

USY Zeolite (~7 Al Atoms/ u.c.)   Equilibrium REY (~23 Al Atoms/u.c.)

Unit Cell Dimension = 24.25 Å   Unit Cell Dimension = 24.39 Å

$(SiO_2/Al_2O_3 = 54)$ $(SiO_2/Al_2O_3 = 15)$

Figure 1-6 Geometry of USY and REY zeolite

Source: Sadegbeigi, 1995: 83

Until the late 1970s, the NaY zeolite was mostly ion exchanged with rare earth components such as lanthanum and cerium which were used to replace sodium in the crystal. The rare-earth element, being trivalent, simply formed a " bridge" between two or three acid sites in the zeolite framework. The bridging basically protects the acid sites from being ejected from the framework and thus stabilizes the zeolite structure. Consequently, the rare earth exchange adds to the zeolite activity and thermal and hydrothermal stability.

The reduction of lead in motor gasoline in 1986 created the need for a higher FCC gasoline octane. Catalyst manufacturers responded by adjusting the zeolite formulations, an alteration that involved expelling a number of aluminum atoms from the zeolite framework. The removal of aluminum increased silica oxide to alumina oxide ratio (SAR), reduced unit cell size (UCS), and in the process, lowered the sodium level of the zeolite. These changes increased the gasoline octane by raising its olefinicity. This aluminum – deficient zeolite called *Ultrastable Y*, or USY, or simply USY, because of its higher stability than the conventional Y (Sadegbeigi, 1995).

3.1.4 Zeolite properties

The properties of the zeolite play a significant role in the overall performance of the catalyst, and familiarity with these properties increases our ability to predict catalyst response to continual changes in unit operation. From its inception in the catalyst plant, the zeolite must withstand and retain its catalytic properties under the hostile conditions of the FCC operation. The reactor/regenerator environment can cause significant changes in the chemical and structural composition of the zeolite. In the regenerator, for instance, the zeolite is subjected to thermal and hydrothermal treatments. The zeolite must also retain its crystallinity against feedstock contaminants such as vanadium and sodium.

Various analytical tests can be carried out to determine zeolite properties. These tests should supply information about the strength, type, number, and distribution of acid sites. Additional tests can also provide information about surface area and pore size distribution. The three most common parameters governing zeolite behavior are as follow:
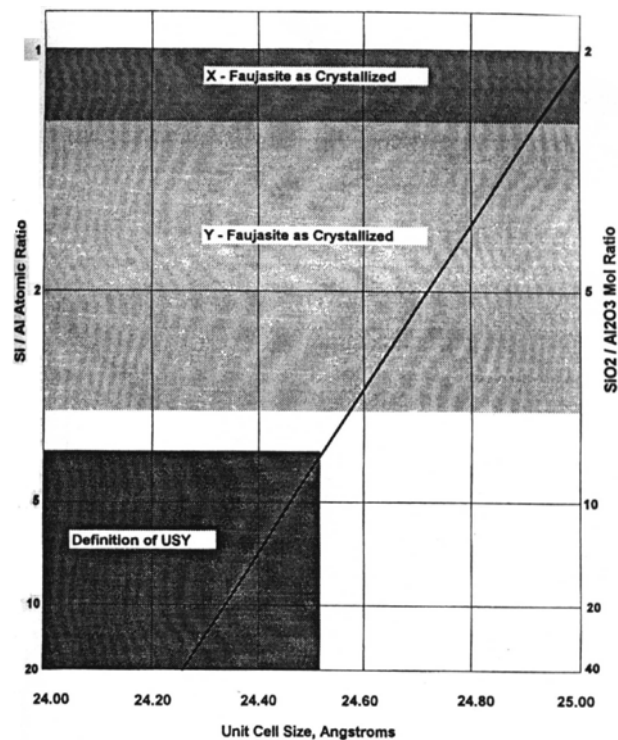
    A. Unit Cell Size

    B. Rare Earth Level

    C. Sodium Content

A. Unit Cell Size (UCS) is a measure of aluminum sites or the total potential acidity per unit cell. The negatively charged aluminum atoms are a source of active site in the zeolite. Silicon atoms do not posses any activity. The UCS is related to the number of aluminum atoms per cell (N_{Al}) by

$$N_{Al} = 111 \times (UCS - 24.215)$$

The number of silicon atoms (N_{Si}) is: $N_{si} = 192 - N_{Al}$

The SAR of the zeolite can be determined either from the above two equations or from a correlation such as the one shown in Figure 1-7.

Figure 1-7 Silica – alumina ratio versus zeolite unit cell size
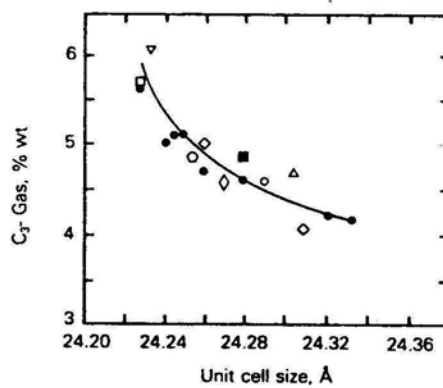
Source: Sadeghbeigi, 1995: 85

The unit cell size (UCS) is also an indicator of zeolite acidity, because the aluminum ion was larger than the silicon ion, as the UCS decreases, the acid site become further apart. The strength of the acid site is determined by the extent of their isolation from the neighboring acid sites. The close proximity of these acid sites causes destabilization of zeolite structure. Acid distribution of the zeolite is a fundamental factor affecting zeolite activity and selectivity. Additionally, the UCS measurement can used to indicate octane potential of the zeolite. A lower UCS presents fewer active sites per unit cell size. The fewer acid site are farther apart and therefore inhibit hydrogen transfer reactions, which in turn increase gasoline octane as well as production of C_3 hydrocarbon and lighter components (Figure 1-8). The octane increase is due to a higher concentration of olefins in the gasoline.
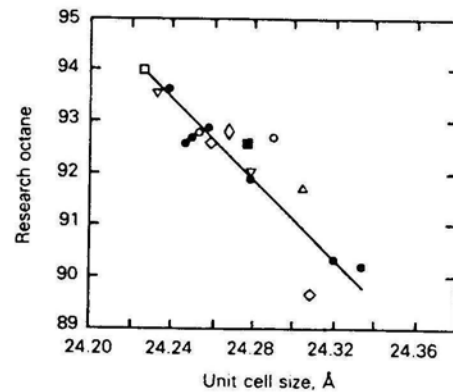
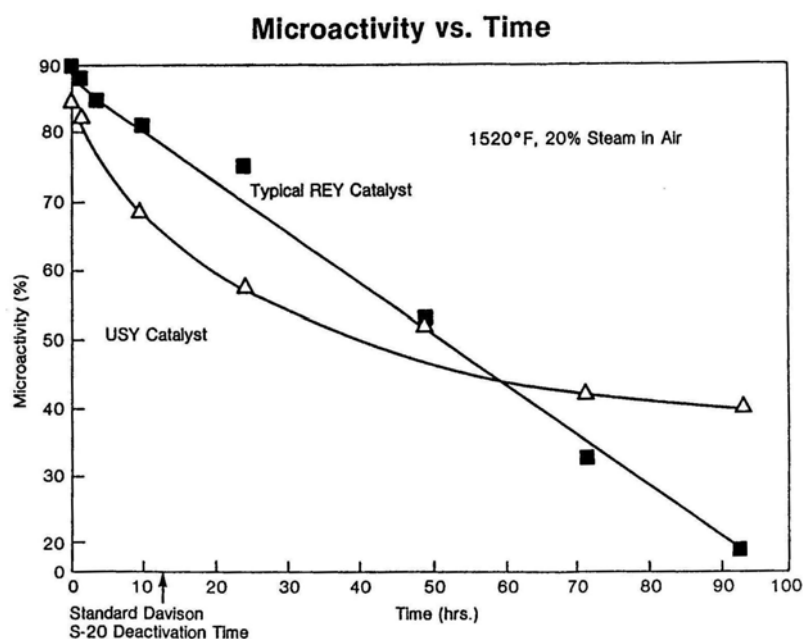Dependence of research octane number on zeolite unit cell size
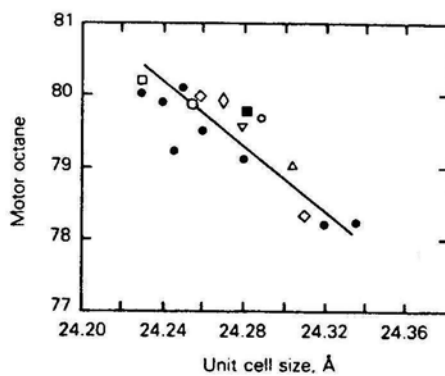
Dependence of motor octane number on zeolite unit cell size

Dependence of light gas yield on zeolite unit cell size

Figure 1-8 Effect of unit cell size on octane and C_3^- gas production

Source: Sadeghbeigi, 1995: 86

Microactivity vs. Time

Figure 1-9 Comparison of activity retention between rare earth exchanged zeolite versus
USY zeolite

Source: Sadeghbeigi, 1995: 87

Zeolite with lower unit cell size (UCS) are initially less active than conventional
rare earth exchanged zeolites (Figure 1-9). However the lower UCS zeolites tend to retain a
greater fraction of their activity under severe thermal and hydrothermal treatments, hence
the name Ultrastable Y (USY).

A freshly manufactured zeolite has a relatively high UCS in the range of 24.50 Å to
24.75 Å. The thermal and hydrothermal environmental of the regenerator extracts alumina
from the zeolite structure and therefore reduces its UCS. The final UCS level depend on the
rare earth and sodium level of the zeolite. The lower the sodium and rare earth content of
the fresh zeolite, the lower UCS of the equilibrium catalyst (E-cat.).

B. Rare Earth Level. Rare earth element serve as a " bridge " to stabilize
aluminum atoms in the zeolite structure. They prevent the aluminum atoms from separating

from the zeolite lattice when the catalyst is exposed to high temperature steam in the regenerator.

A fullly rare earth exchanged zeolite equilibrates at a high UCS, whereas a non rare earth zeolite equilibrates at a very low UCS in the range of 24.25. All intermediate level of rare earth exchanged zeolite can be produced. The rare earth increases zeolite activity and gasoline selectivity with a loss in octane (Figure 1-10). The octane loss is due to promotion of hydrogen transfer reactions. The insertion of rare earth maintains more and closer acid sites, which promotes hydrogen transfer reactions. In additions, rare earth improves thermal and hydrothermal stability of the zeolite. To improve the activity of a USY zeolite, the catalyst suppliers frequently add some rare earth to the zeolite(Sadegbeigi, 1995; Sousa-Aguiar, et.al., 1996: 267-271).
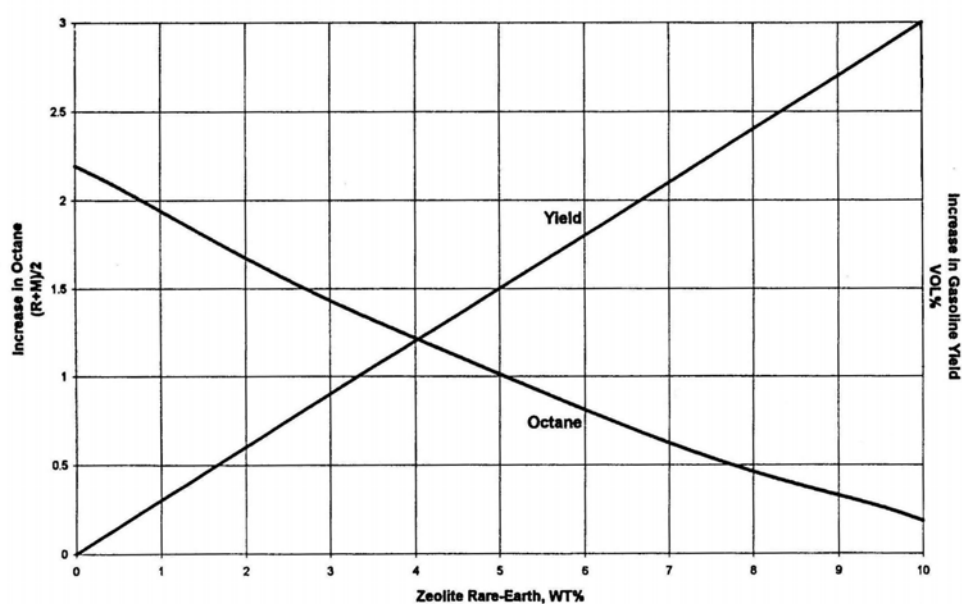

Figure 1-10 Effect of rare earth on gasoline octane and yield

Source: Sadeghbigi, 1995: 89

C. Sodium content. The sodium on the catalyst originates either from zeolite during its manufacture or from the FCC feedstock. It is important for the fresh zeolite to contain a very low amount of sodium. Sodium decreases the hydrothermal stability of the zeolite. It also reacts with the zeolite acid sites to reduce the catalyst activity. In the regenerator, sodium is mobile. Sodium ions tend to neutralize the strongest acid sites. In a dealuminated zeolite where the UCS is low (24.22 Å to 24.25 Å), the sodium can have an adverse effect on the gasoline octane (Figure1-11). The loss of octane is attributed to the drop in the number of strong acid sites.

FCC catalyst vendors are now able to manufacture catalysts with a sodium content of less than 0.2 wt %. Sodium is commonly reported as the weight percentage of sodium or soda (Na_2O) on catalyst. The proper way to compare sodium is the weight fraction of sodium in the zeolite. This is because FCC catalysts have different zeolite concentrations.

UCS, rare earth, and sodium are just three of the parameter that are readily available to characterize the zeolite properties. They provide valuable informational about catalysts behavior in the cat cracker. If required, additional tests that can be conducted to examine other zeolite properties.

MOTOR OCTANE VS. SODIUM OXIDE

RESEARCH OCTANE VS. SODIUM OXIDE
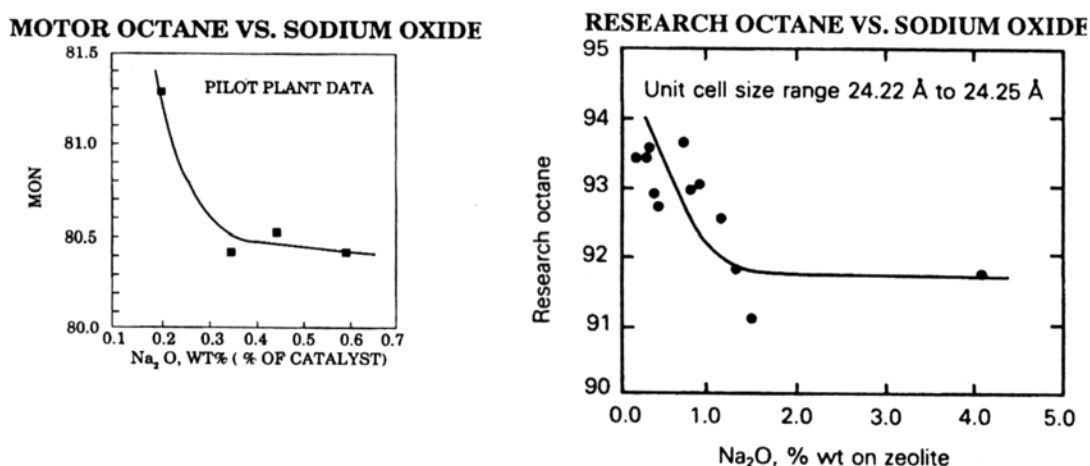
Figure 1-11 Effect of a soda motor and research octanes

Source: Sadeghbigi, 1995: 90

3.2 Matrix, Filler and Binder

The term *matrix* has different meanings to different people. For some, matrix refers to components of catalysts other than the zeolite. For others, matrix is a component of the catalyst aside from zeolite having catalyst activity. Yet for others, matrix refers to the catalyst binder. In this report *matrix* means components of the catalyst other than zeolite and the term "active matrix" means the component of the catalyst other than zeolite having catalyst activity.

Alumina is the source for an active matrix. Most active matrices used in FCC catalysts are amorphous. However, some of the catalyst suppliers incorporate a form of alumina that also has a crystalline structure. The active matrix contributes significantly to the overall performance of the FCC catalyst. The zeolite pores are not suitable for the cracking of the large hydrocarbon molecules generally having and end point $>900^{\circ}$F; they are too small to allow diffusion of the large molecules to the cracking sites. An effective matrix must have a porous structure to allow diffusion of hydrocarbons into and out of the catalyst.

An active matrix provides the primary cracking sites. The acid sites located in the catalyst matrix are not as selective as the zeolite sites but are able to crack larger molecules that are hindered from entering the small zeolite pores. The active matrix precracks heavy feed molecules for further cracking at the internal zeolite sites. The result is a synergistic interaction between matrix and zeolite in which the activity attained by their combined effect can be greater than the sum of their individual effects.

An active matrix can also serve as a trap to catch some of vanadium and basic nitrogen. The high boiling fraction of the FCC feed usually contains metals and basic nitrogen that poison the zeolite. One of the advantages of an active matrix is that it guards the zeolite from becoming deactivated prematurely by these impurities.

The *filler* is a clay incorporated into the catalyst to dilute its activity. Kaolin [$Al_2(OH)_2 \bullet Si_2O_5$] is the most common clay used in the FCC catalyst. One FCC catalyst manufacturer uses kaolin clay as a skeleton to grow the zeolite in situ.

The *binder* serves as a glue to hold the zeolite, the matrix, and the filler together. The binder may or may not have catalytic activity. The importance of the binder becomes more prominent with a catalysts that contains a high concentration of zeolite.

The functions of the filler and binder are to provide physical integrity (density, attrition resistance, particle size distribution, etc.), a heat transfer medium, and a fluidizing medium in which the more important and expensive zeolite component is incorporated.

Zeolite will affect activity, selectivity and product quality. An active matrix can improve bottoms cracking and resist vanadium and nitrogen attacks. But a matrix containing very small pores can suppress strippability of the spent catalyst and increase hydrogen yield in the presence of nickel. Clay and binder provide physical integrity and mechanical strength. (Sadeghbigi, 1995; Woltegmann, 1993)

3.3 Additives

FCC additives with a cracking or non-cracking function can be incorporated into the catalyst by the manufactures, or can be added separately by the refiner. The main benefits to these additives (catalyst and feed additives) are to alter the FCC yields and to reduce the amount of pollutants emitted from the regenerator. The additives most frequently used in FCC catalysis are: Octane-boosting additives; SO_x reducing additives; Metal passivators and traps; and CO combustion promoters.

3.3.1 Octane-boosting Addition

The most frequently used additive consists of ZSM-5 zeolite embedded in a matrix, and is commonly used as a distinct physical particle in conjunction with a FCC catalyst. ZSM-5 is a member of the pentasil family of high-silica zeolites and has relatively small pore opening ($\phi \approx 5.5$ Å). It increases gasoline octane primarily by shape selectivity cracking of low-octane, straight chain and monomethyl aliphatics to lighter products. This

results in the enrichment of gasoline in higher-octane branched paraffin, olefins and aromatics.

In addition to cracking gasoline range low-octane components, steamed or equilibrated ZSM-5 also favors the isomerization of cracking products, such as n-olefins to higher-octane branched olefins. The additive represents only small percentage (usually 1 to 3 percent) of catalyst inventory in the unit and increases both RON and MON at low concentrations.

3.3.2 SO_x Reducing Additives

Such additives are used in conjunction with FCC catalysts when cracking high sulfur feedstocks, in order to reduce SO_x emissions from the regenerator below acceptable limits. The additives are mostly inorganic oxide (e.g. Al_2O_3, MgO) or mixed oxides (e.g. spinels, rare earth oxide mixtures, vanadia-alumina, ceria-promoted spinels). The additive promotes the oxidation of SO_2 to SO_3 in the regenerator, followed by the formation of metal sulfate type compounds on the additive. In the reactor (and stripper) the metal sulfates are reduced to hydrogen sulfide, which leaves the FCC unit with the cracked products and is subsequently removed with an amine scrubber. The additive represents usually a few percent of catalyst inventory and is often added by the refiner shortly before catalyst utilization.

3.3.3 Metal Passivators and Metal Traps

These additives are used primarily in resid cracking and are designed to minimize the deleterious effect on catalyst and its performance by the heavy metals present in the feedstock, such as nickel, vanadium, iron and copper. In the absence of such additives, nickel deposited on the catalyst causes a significant increase in coke and hydrogen make, while vanadium causes partial destruction of the zeolite under steam, in addition to increasing coke and hydrogen make. Nickel is often passivated with antimony or bismuth containing additives, while vanadium is passivated with tin compounds. Metal traps are usually physically distinct particles that trap the contaminant metal. Numerous metal oxides (e.g. Al_2O_3, TiO_2) mixed oxides (e.g. $BaTiO_3$, $CaZrO_3$) and natural clays (e.g. metakaolin,

sepiolite) have been recommended as metal traps. These materials are usually mixed with binder and spray dried. The resulting microspheroidal particles are blended with the catalyst.
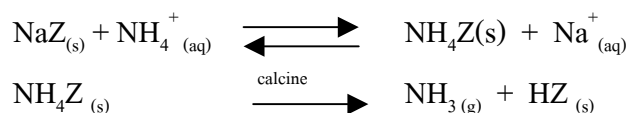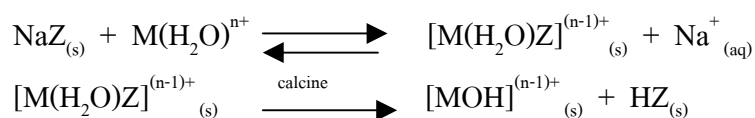
3.3.4 CO Combustion Promoters

To facilitate the oxidation of CO to CO_2 in the dense phase of the regenerator, platinum-or palladium-based combustion promoters are being used. Maximizing CO oxidation in the dense phase of the regenerator prevents uncontrolled CO oxidation (after burning) in the dilute phase, which can cause metallurgical damage to the equipment. Furthermore, the heat generated during maximized CO oxidation in the dense phase is transferred to the circulating catalyst, thus providing additional heat for the endothermic cracking reaction in the riser. Maximizing CO oxidation also minimizes flue gas CO emissions. (Scherzer, 1993)

4. Catalyst Properties

Catalyst properties are determined by a micro activity test (MAT). A sample of the decoke equilibrium catalyst is placed in a laboratory reactor, a typical FCC feed is passed over the catalyst at cracking condition and the result is analyzed.

4.1 Active Site

Most industrial applications of zeolite are based upon technology adapted from the acid silica alumina catalysts originally developed for the cracking reaction. This means that the activity required is based upon the production of Bronsted sites arising from the creation 'hydroxyls' within the zeolite pore structure. These hydroxyls are usually formed either by ammonium or polyvalent cation exchange followed by a calcination (Dryer, 1988; Humphries, et.at, 1993; Williams et.al., 1999: 161-175).

Ammonium ion exchange

$$NaZ_{(s)} + NH_4^+{}_{(aq)} \xrightleftharpoons{\qquad} NH_4Z(s) + Na^+{}_{(aq)}$$

$$NH_4Z_{(s)} \xrightarrow{\text{calcine}} NH_{3(g)} + HZ_{(s)}$$

Polyvalent ion exchange

$$NaZ_{(s)} + M(H_2O)^{n+} \xrightleftharpoons{\qquad} [M(H_2O)Z]^{(n-1)+}{}_{(s)} + Na^+{}_{(aq)}$$

$$[M(H_2O)Z]^{(n-1)+}{}_{(s)} \xrightarrow{\text{calcine}} [MOH]^{(n-1)+}{}_{(s)} + HZ_{(s)}$$

The tetrahedrally coordinated aluminium atoms in the zeolite framework each carry a negative charge. The compensating cations, however, are not of the structural framewoke and are located in several different sites throughout the pores and cavities of the zeolite. Cation occupancy in zeolite Y is confined to the small (sodalite) cage and the hexagonal prism. They are easily exchanged by contacting the solid zeolite with solutions of ammonium and/ or rare earth salts and this the key to changing the acidity of the active site on the material. An obvious goal for zeolite Y is to substitute protons for sodium ions, a prerequisite for carbocation formation. This cannot be easily achieved directly, however, since acidic solutions effect the removal of aluminium from the zeolite framework through hydrolysis and the structure collapses. A relatively easy route to HY, shown in Figure 1–12, involves treatment with ammonium salts, followed by calcination above 600°F to decompose the NH_4^+ ion into NH_3 gas and H^+, which maintains the structure. The protons bond with oxygen atoms in the lattice to form -OH group. In this form, HY zeolite has the ability to transfer a proton to an adsorbed hydrocarbon and the active sites are known as Bronsted acid sites.
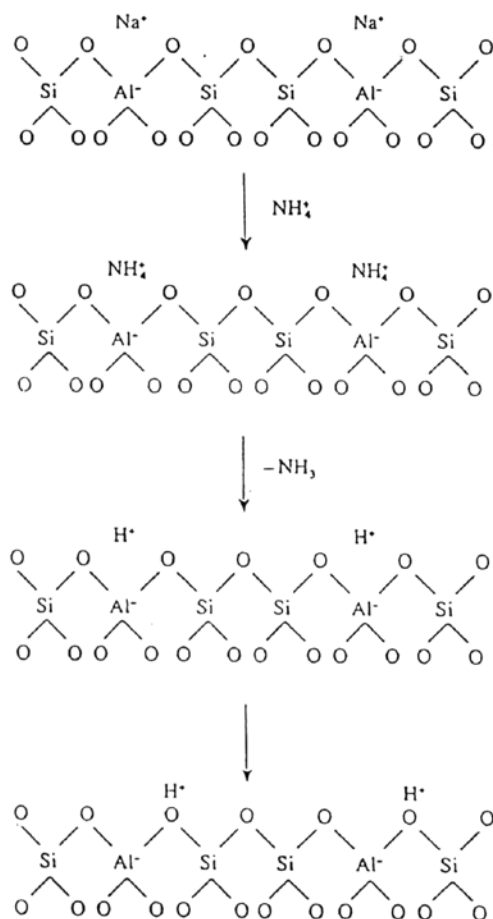
Figure 1−12 Formation of Bronsted Acid Sites.
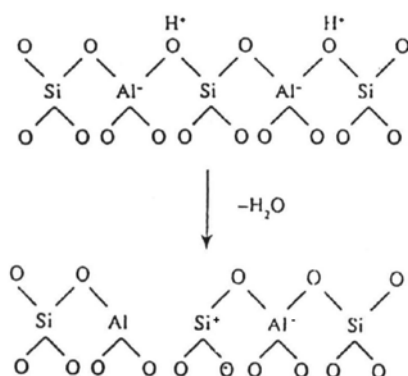
Source: Humphries, Harris and Connor, 1993: 46

In addition to direct proton exchange and the calcination of ammnium exchanged Y zeolite, Bronsted acidity can also be introduced by the hydrolysis of ion exchanged polyvalent cation, followed by partial dehydration. For example, a Y zeolite in its native sodium form can be treated with a commercial rare earth salt solution (typical a mixture of lanthanum, cerium, neodymium and praseodimium chlorides) to replace most of sodium

ions, with polyvalent rare earth ions. The highly charged rare earth ions quickly hydrolyze, creating acid sites as shown below:

$$La^{3+} + H_2O \longrightarrow La(OH)^{2+} + H^+$$

$$La(OH)^{2+} + H_2O \longrightarrow La(OH)_2^+ + H^+$$
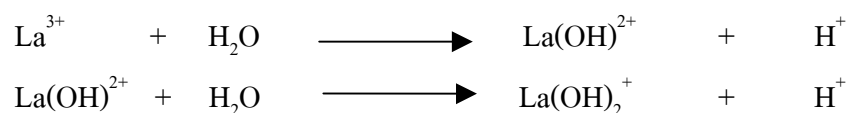
The rare earth hydroxy ions occupy site in the zeolite framework that increase the thermal and hydrothermal stability.

Bronsted acid sites formed by any of these methods can be further dehydroxylated at temperatures in excess of about $750^{\circ}F$ to form Lewis acid sites as shown in Figure 1-13. Lewis acid sites have the ability to accept an electron pair from an adsorbed hydrocarbon to create a carbon (e.g. via hydride abstraction).

Figure 1-13 Formation of Lewis acid site

Source: Humphries, Harris and Connor, 1993: 47

The elimination of water by dehydroxylation should lead to the creation of one Lewis acid site from every two Bronsted acid sites. Nevertheless, the number of Bronsted acid sites converted to Lewis site increases with temperature until about $1500^{\circ}F$, when only the latter remain (see Figure 1 –14). However, if the calcination temperature is kept below $1100^{\circ}F$ most of the Lewis acid site can be rehydrated to restore the Bronsted sites.
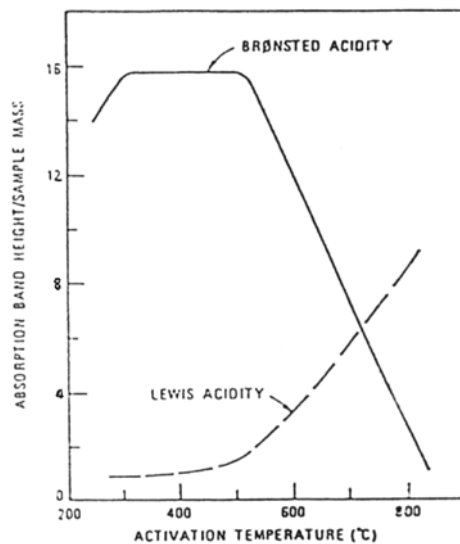
Figure 1-14 Relation between Bronsted and Lewis acid sites as measured by pyridine

adsorption.

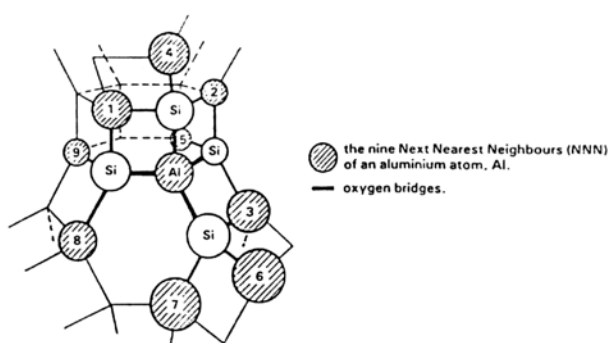Source: Humphries, Harris and Connor, 1993: 48

The concept of Lewis acid sites readily forming donor–acceptor complex with, for example, H^-, is the basis for Lewis site characterization as well as dehydrogenation reactions with paraffins.

Factors influencing the acid properties of zeolites include the method preparation, temperature of dehydration and silica to alumina ratio and distribution of the framework atoms. For example the strength of the Lewis sites created by the thermal procedure described above is higher than that of Bronsted sites.

Correlation between the acidity of a zeolite and its catalytic properties is a difficult task. However, three factors are important here: the total number of acid sites, the ratio of Bronsted to Lewis sites, and the acid strength distribution (and density) of each type of site. For Y zeolite, a maximum in strong acid site and cracking activity occurs at silica to alumina ratios (SAR) from 7 to 15. In contrast, for ZSM–5, hexane cracking ability increases linearly with increased aluminium content, leading to the conclusion that the

maximum in acidity is a function not only of the zeolite structure but also the surrounding of the individual aluminum atoms in the framework.

The concept of "Next Nearest Neighbors" was proposed in order to provide a reasonable estimate of the acidic behavior of zeolites. The acid strength of the zeolite was related to the distribution of aluminium atoms in the framework. Each framework atom (Si or Al) in the zeolite is in the tetrahedral coordination with oxygen and each aluminium atom has four silicon atoms as "Nearest Neighbors", this is Lowenstein's Rule. The four silicon sites in zeolite Y are connected to nine other framework atom sites and these are the "Next Nearest Neighbor" (Figure 1-15). The strongest Bronsted acid sites were associated with those framework aluminium atoms which had no "Next Nearest Neighbor" (O-NNN) framework aluminum atoms. Next strongest acidity is associated with 1 - NNN sites, with a steady decline in acid strength through the 9 – NNN sites.

Figure1-15 Next Nearest Neighbors.

Source: Humphries, Harris and Connor, 1993: 49

Thus as the aluminum framework atoms are removed from Y zeolite, stronger, more isolated O – NNN acid sites are generated. As soon as all the acid sites are due to isolated O – NNN framework aluminum atoms, a maximum acidity is achieved (SAR of 9-12). The activity will then decrease linearly with the removal of more framework aluminum of similar strength (Humphries, et.al., 1993; Ino and Al-khattaf, 1996).

Studies using model compounds to look at the reactions of hydrocarbon with a solid surface have concluded that both carbenium and carbonium ion intermediates are involved. Bronsted sites can form both, whereas Lewis sites produce only cabenium ions. Therefore, for many reactions, the activity of a catalyst should depend essentially on its Bronsted acidity, since Lewis sites alone do not appear to be active in most hydrocarbon reactions. However, Lewis sites are believed to play a significant role in reaction such as double bond shifts and cis/trans isomerization of olefins. This anomaly has been rationalized through the concept of "super acid" sites, which are believed to arise from a coupling of Lewis and Bronsted sites resulting in a considerable increase in activity of the latter. Other that the super acid acidity can arise from the interaction of Bronsted sites with extra framework aluminum generated after ultrastabilization with steam.

Stabilization to a lower unit cell size reduces the number of acid sites on the zeolite since the latter are associated with the framework aluminium atoms. In addition to the increased hydrothermal stability, dealuminate Y zeolites are observed to have stronger acid sites than their higher cell size parents

4.2 Cracking selectivities

**Activity.** Activity is defined as the % conversion of the feed to gasoline and lighter products or:

$$Conversion = 100 - \text{the quantity of LCO} - \text{the quantity of HCO}$$

The actual kinetic activity of a catalyst is defined as

$$Activity \quad = \quad \frac{Conversion}{100 - Conversion}$$

For our purpose here, we can understand that USY is much less active than REY. This is because any given weight of USY contains fewer active sites than REY (and the others, REHY and REUSY, are intermediate). However, in actual practice, USY catalysts are made at approximately the same activity levels as REY catalysts by simply adding more

USY to the catalyst formulation. A factor of 2-3 is about right. In other words, to match the activity of a REY catalyst with 10% REY, the catalyst supplier would need 20% to 30% USY (lesser quantities of REUSY and even less for REHY). However, the selectivity differences show in table1-3 are determined at basically constant activity and thus show us the direction taken in catalyst formulation to emphasize various yields.
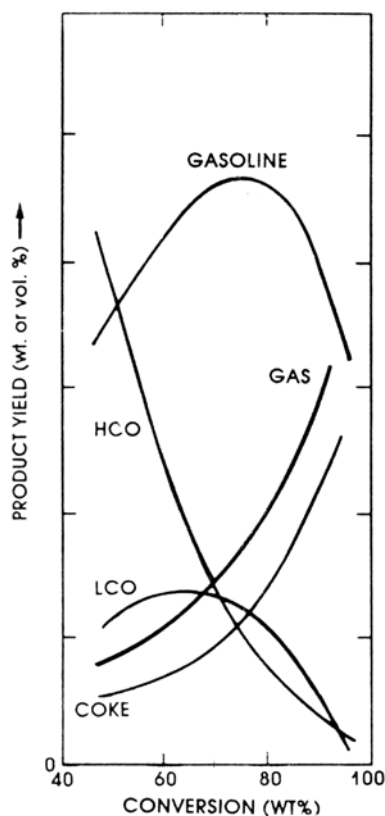
Figure 1-16 General correlation between product yield and conversion

Source: Scherzer, 1990: 112

The general correlation between product yield and conversion obtained with FCC catalysts is show in Figure 1-16. As conversion increase, the gasoline yields go through a maximum and then decline due to overcracking. The change in LCO yields with conversion shows a similar pattern. Coke and dry gas yield increase while HCO yields decrease with increased conversion.

Table1-3 Cracking selectivity of different Y zeolite and of active matrix

Source: Magee and Dolbear, 1998: 71

	USY	REUSY	REHY	REY	Active Matrix
Unit cell size	◄——————— decrease ————————				
Framework Si/Al	◄——————— increase ————————				
RE content	◄——————— decrease ————————				
Dry yield	Low	Low	Low	Low	High
C_3/C_4 yield	High	Moderate	Moderate	Low	High
C_3/C_4 olefins	high	Moderate	Moderate	Low	High
Coke/conversion	Very Low	Very Low	Low	Moderate	High
Gasoline selectivity	Moderate	High	High	High	Low
Octane potential	high	Moderate	Low	Low	High
LCO selectivity	Moderate	Moderate	Low	Low	High
DO selectivity	Moderate	Moderate	High	High	Low

Active matrix. The "pre-zeolite" FCC catalyst clearly shows the advantages of using any of the zeolites as far as gasoline yield and coke selectivity is concerned. But the active matrix also gave high olefin yields, albeit at relatively low conversion levels. It did crack HCO oil molecules into the LCO or light range, thus minimizing the yields of low value HCO. This assures the active matrix a place in FCC catalyst production.

Coke selectivity. USY and REUSY are the best candidates for the moderating coke yield at constant conversions.

Gasoline selectivity. Here, REHY and REY are the choices because of the large concentration of active sites that limit olefin formation (because of increased levels of hydrogen transfer). On average, they also terminate carbenium chains by eliminating olefins (which readily form carbenium ions to continue the chain cracking reactions and lower gasoline yield).

LCO and HCO selectivity. The most profound influences on these molecular range are the matrix structure and activity. In this case, the large pores of the matrix easily accommodate large HCO molecules and crack them into the LCO (or lighter) range, both

reducing the HCO yield and increasing LCO. However, LCO products may be further cracked by the zeloite, since the matrix cracking of HCO could reduce the size enough to fit in the zeolite and further crack.

Objectives

1. To study the procedure for prepared USY, REHY and REY zeolites catalyst.
2. To compare the performance of USY, REHY, REY and their composites in the catalytic cracking process.

Possible Achievement

The possible achievement is to reproduce USY, REHY and REY catalysts previously studied by a former master degree students of the Department of Chemical Engineering, PSU. These catalysts and their composites were used to study the performance on catalytic cracking process.

Contents of Research

1. Synthesis of NaY zeolite
2. Preparation of USY, REHY and REY zeolites
3. Preparation of catalysts
   3.1 Preparation of USY, REHY and REY zeolites catalysts
   3.2 Preparation of mixed zeolites catalysts
4. Characterization and evaluation of catalysts