Chapter 2

THEORY

1. **Fluid Catalytic Cracking Unit**

Catalytic cracking is endothermic reaction meaning that heat is absorbed by the reaction. The temperature of the reaction mixture declines as the reaction proceeds. Heat to drive the process comes from combustion of coke formed in the process. Coke is a necessary product of cracking. It is a 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 the catalyst to restore its activity. Like all combustion process, regeneration is exothermic, liberating heat.

The three main components of a Fluid Catalytic Cracking (FCC) unit are the riser reactor, the stripper and the regenerator. Their process can be described as follows:

1. The riser reactor. The predominately endothermic cracking processes take place, forming products that include coke. In the riser, as the name implies, the catalyst, the feed and product hydrocarbon rise up the reactor pipe. Since the reactions are endothermic, reaction temperature decline from bottom to top. At top, the mixture enter a sold-gas separator and the product vapors are led away.

2. The stripper. The steam is added and unreacted-reacted hydrocarbons adsorbed on the catalyst are released. The stripped catalyst is then directed into the regenerator.

3. The regenerator. The air is added and the combustion of coke on the catalyst occurs with the liberation of heat. Regenerator temperature are typically $1,300^{o} - 1,400^{o}F$. Heat exchanges and the circulating catalyst capture the heat evolved during regeneration to be used in preheating the reactor feed to appropriate cracking temperatures ($950^{o} - 1,020^{o}F$).

In the FCC process the entire catalyst inventory is continually circulated through the three parts of the FCC unit. A typical plant is shown in Figure 2-1. The cracking

process is carried out in a 'fluidised' bed of catalyst in which pre-heated crude oil (370 ^{o}C) meets a catalyst bed in a 'riser'. The reacted slurry is then passed into a reaction zone (480-520 ^{o}C) and the resulting products pass into a further zone where the catalyst is separated from the products. The catalyst is then steam-treated to recover sorbed hydrocarbons, and then finally regenerated to be re-used as a hot catalyst to pre-heat the crude oil entering the reaction zone. The products then pass on to a fractionator to separate the major products of Cl-C3 gas, petrol, light cycle oil, heavy gas oil and recycle (resid) oil. The regeneration stage is designed at 590-730 ^{o}C as an air purge to remove coke from the catalyst (coke content is critical, reactors are designed to keep coke content on zeolite to < 0.1 %wt.). Catalyst residence time in the riser reactor section is typically 1-3 seconds (with current trends to even shorter residence times). 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.
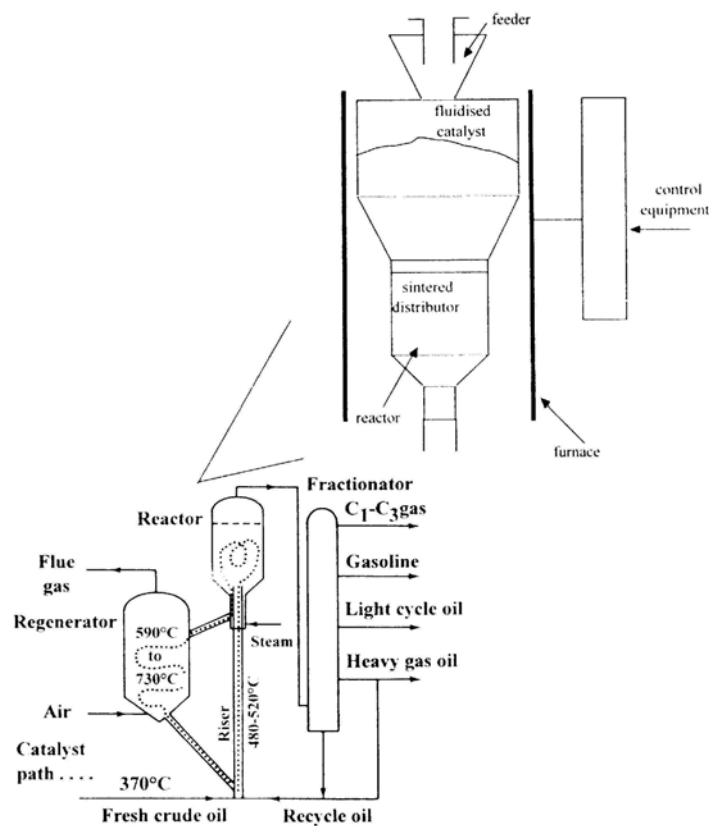

Figure 2-1 Conventional fluidised-bed catalytic cracking unit.

Source: Tomlinson, 1998: 40

One of the truly important properties of FCC catalysts can be intuitively presumed from this brief description of operation the catalyst must be robust to withstand the obvious stresses of operation.Temperatures are high and fluctuate. Coke is repeatedly deposited and burned off. Furthermore, the tiny catalyst particles are moving at high speed through steel reactors and pipes, where wall contacts and interparticle contacts are impossible to avoid.

All catalyst manufacturers carefully control the "robustness" of the FCC catalyst. The measurement of FCC particle breakdown with time in special lab sized units puts a semiquantilative evaluation on attrition resistance. This is broadly related to breakdown with time in commercial units.

Catalyst loss from the unit caused by poor attrition resistance can be a serious problem, since the quantities lost must be replaced by fresh catalyst additions to maintain constant unit performance. Catalyst manufacturers work hard to prevent inordinate losses due to attrition, and refineries keep a close watch on catalyst quality to be sure the product conforms to their specifications. (Magee and Dolbear, 1998; Tomlinson, 1998)

2. **Catalyst** (Wilson, 1997)

Fluid cracking catalysts are microspheroidal particles having a particle size distribution between 10 – 150 microns. The primary active ingredient in catalysts is a synthetic zeolite. This component can be between 15 – 50 %wt. of the catalyst.

A second active ingredient found in many catalysts today is some form of alumina. This is generally referred to as active matrix and is added to improve the heavy oil or bottoms conversion activity of the catalyst. The active alumina content of FCC catalyst is generally between 0 – 20 %wt.

The non-active remainder of the catalyst consists of fillers, generally kaolin clay and binders. The fillers contribute to physical properties of the catalyst such as density, pore volume and surface area. The binders serve to hold the various constituents together in the catalyst particle.

Most catalysts available today use silica compounds as the primary binder. Other materials used as binders in certain catalysts include various aluminum compounds or clays.

In operation, fresh catalyst must be added to the unit to make up for losses and to maintain the catalyst activity. Make-up rates for units processing gas oil feeds are typically 0.15 – 0.20 pounds of catalyst per barrel of feed. For units processing resid feeds, the make up rate must be higher to control the metals levels on the catalyst. For these units, the make-up rate may be as high as 1.5 pounds per barrel. When the catalyst make up rate required for activity maintenance or metals control is higher than the catalyst loss rate, equilibrium catalyst must be withdrawn from the unit to balance the fresh catalyst make-up rate.

In addition to the primary cracking catalyst, there are a number of additives which can be added to the unit catalyst inventory. Typical additives are combustion promoter (often referred to as just "promoter") which is used to accelerate the combustion of CO to CO_2 in the regenerator; ZSM-5 which is used to increase the gasoline octane and the yield of light olefins and SO_x adsorption additives which are used to reduce the sulfur oxides in the regenerator flue gas.

3. Hydrocarbon Classification

The hydrocarbon types in the FCC feed are broadly classified as paraffins, olefins, napthenes and aromatics (PONA) (Sadeghbeigi, 1995) Each of these types represents a specific molecular arrangement. When the processed in an FCC unit, each of these types will produce a different slate of products. When mixtures of these types are processed, the net product produced and their properties will be determined by the composition of mixture. (Wilson, 1997)

3.1 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 hexane.Typical paraffins are show in Figure 2-2.

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.
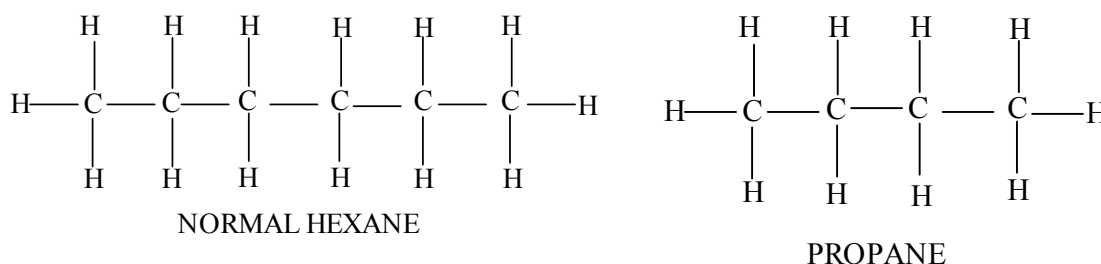
Figure 2-2 Paraffins.

Source: Wilson, 1997: 54 ; Sadeghbeigi, 1995:38

3.2 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). Typical olefins are show in Figure 2-3.
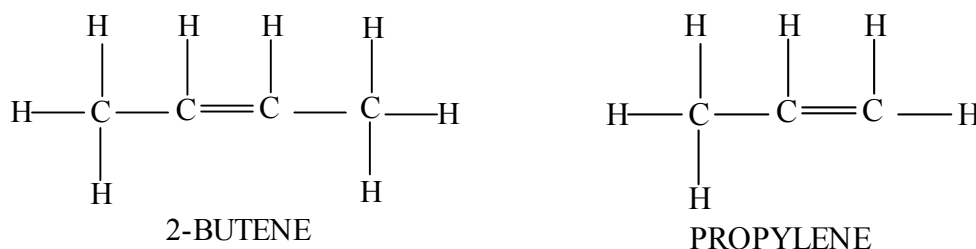

Figure 2-3   Olefins.

Source: Wilson, 1997: 54; Sadeghbeigi, 1995: 38

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.

3.3 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. Examples of naphthenes are cyclopentane, cyclohexane, and mehtyl-cyclohexane. Typical naphthenes are show in Figure 2-4.

CYCLOPENTANE   CYCLOHEXANE

Figure 2-4 Naphthenes.
        Source: Wilson, 1997: 55; Sadeghbeigi, 1995: 40

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.

3.4 Aromatics

Aromatics (C_nH_{2n-6}) are similar to naphthenes, but they contain a stabilized unsaturated ring core. Example of aromatics are benzene, toluene and aniline. Typical aromatics are show in Figure 2-5.

CH3

BENZENE   TOLUENE

Figure 2-5 Aromatics.
        Source: Wilson, 1997: 55; Sadeghbeigi, 1995: 40

Aromatics are compounds 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 feedstock 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 several 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 (Sadeghbeigi, 1995).

3.5 Hybrid Molecules (Wilson, 1997)

Naphthene and aromatic compounds often contain paraffinic side chains (Figure 2-6). These side chains are subject to the same reaction as parafinic molecules. Thus, an alkyaromatic molecule, while classified as an aromatic compound, undergo cracking reaction on the alkly side chain. The result of these reactions would be an olefin and an alkyl aromatics with a reduce side chain.

Similarly, an alkyl cycloparaffin could undergo both cracking of the naphthene ring or of the alkyl side chain. This molecules could also be convert to an alkyl aromatic by hydrogen transfer involving the naphthenic ring. Figure 2-7 illustrates some of the possible reaction of these hybrid molecule.
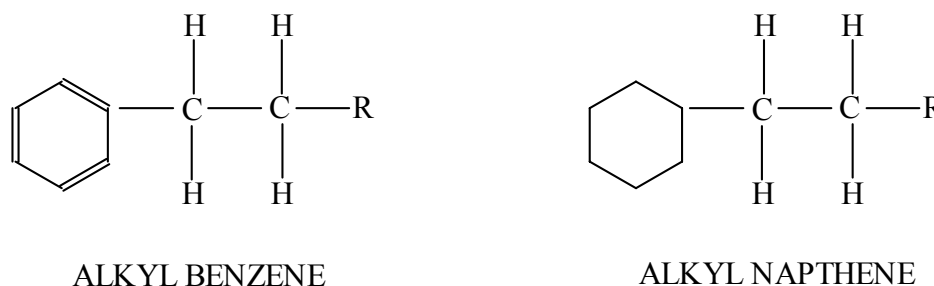
ALKYL BENZENE   ALKYL NAPTHENE

Figure 2-6 Hybrid molecules.

Source: Wilson, 1997: 57

Figure 2-7 Hybrid molecules side chain cracking.

Source: Wilson. 1997: 57

4. Gasoline Octane

The octane rating of a gasoline blend is primarily a function of the relative concentration of different hydrocarbon in the blend. Aromatic have the highest octane rating and n-paraffins the lowest. Olefins naphthenes and branced paraffins have higher octane ratings than the n-paraffins. The octane rating of FCC gasoline is affect by three major factors 1. Feedstock composition and properties 2. Process variables 3. Catalyst

4.1 Feedstock.

The aromatics have high octane number an increase in aromaticity of the feedstock will result in an increase in gasoline nuumber (Scherzer, 1990). Generally feeds with higher API gravities are less aromatic and produce a lower octane gasoline. As a rule of thumb, a one number increase in API gravity will result in 0.25 number decrease in the RON and 0.15 decrease in the MON. In a commercial unit these changes may be offset by the increased conversion that normally results from changing to a lower density feed (Wilson, 1997).

4.2 Process Variables

Process changes can result in octane gain of up to 3 RON and 1 MON. The following variables have been identified as having an effect on the octane rating of FCC gasoline.

- Conversion
- Reaction temperature
- Regenerator bed temperature
- Carbon on regenerated catalyst
- Oil partial pressure
- Oil residence time (contact time)
- Recycle ratio
- Process steam
- Gasoline boiling range

Among these variables, conversion and reaction temperature have the most significant impact on octane numbers. In general, increased operating severity result in higher octane numbers.

4.3 Catalyst

In addition to the type of feedstock and operating conditions of the unit, the octane rating of FCC gasoline is also affected by the type of catalyst used in the cracking process. Catalysts designed to boost the octane rating of FCC gasoline are called octane-boosting, octane-enhancing or in short. octane FCC catalysts. In general, such catalysts can enhance octane by about 3 RON and $1 - 1.5$ MON. depending on the base catalyst and octane level.

Similar to gasoline FCC catalysts, octane FCC catalysts consist of two major components: zeolite and matrix. Some octane catalysts contain a third component: an octane-boosting additive, either incorporated into the catalyst matrix or added as a separate particle. While both the zeolite and matrix components affect the octane rating of FCC gasoline, it is the zeolite component that plays the major role.

According to their composition, most octane FCC catalysts can be classified as follows:

1. Catalysts containing an octane-boosting Y zeolite in a catalytically inert matrix.
2. Catalysts containing an octane-boosting Y zeolite in the catalytically active matrix.

3. Catalysts containing an octane-boosting or a conventional. rare earth-exchanged Y zeolite and an octane-boosting additive, such as ZSM-5 zeolite.

Catalysts in the first and second category can also contain in addition to the octane-boosting Y zeolite, a conventional, rare earth-exchanged Y zeolite (Scherzer, 1990).

5. Zeolite (Dyer, 1988)

In 1756 a Swedish mineralogist, Cronstedt, recognized a new mineral species which he call 'zeolite' on the basis of its intumescence.He found zeolites in relatively small cavities in rock of volcanic origin a classical zeolite occurrence.

At present some 39 naturally occurring zeolite species have been recorded and their structures determined. In addition more than 100 synthetic species with no known natural counterparts have been confirmed as new zeolite and the majority await full structural determination.

5.1 Zeolite Structure

The zeolite have three-dimensional structures arising from a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedra (Figure 2-8.)
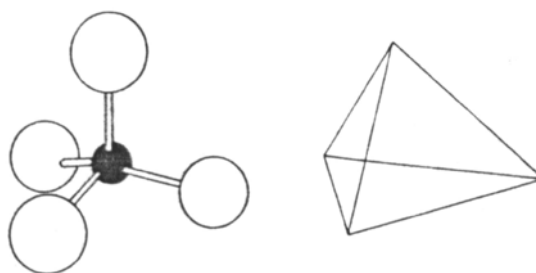

Figure 2-8 Representations of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra.
Source: Dyer, 1988: 1

By definition these tetrahedra are assembled together such that the oxygen at each tetrahedral corner is shared with that in an identical tetrahedron (Si or Al), as

shown in Figure 2-9. This corner sharing creates infinite lattice comprised of identical building blocks (unit cells) in a manner common to all crystalline materials (Dyer, 1988).
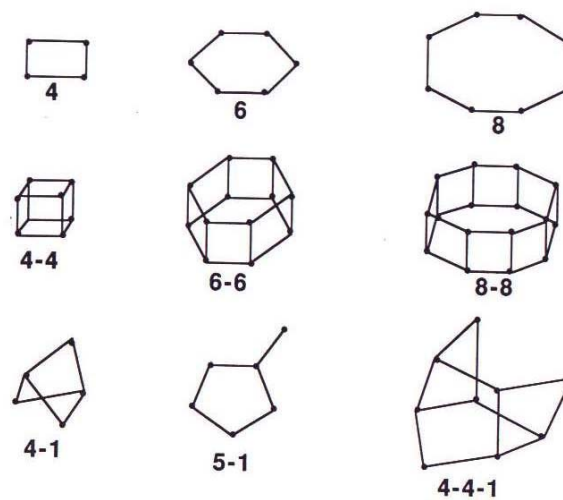

Figure 2-9 Tetrahedra linked together to create a three-dimensional structure.

Source: Dyer, 1988: 12

The structures are commonly discussed in term of levels of organization the basic tetrahedral units known as secondary building units (SBU), comprising single or double ring structures as shown in Figure 2-10, which in turn are linked together to generate the structure of the zeolite. Higher subsidiary levels of structural organization can be identified in polyhedral building blocks, for example the 'sodalite unit' (or β cage) shown in Figure 2-11, which comprises both four and six rings linked together to from a cubo-octahedron; each of the 'vertices' of this truncated octahedron has a four-ring of T atoms, while the eight face are six-rings as shown in the figure. The cage has an internal free diameter of ~6 Å assuming a conventional van der Waals radious for oxygen sufficient to encapsulate small molecules.

Figure 2-10 Secondary building units (SBU) in zeolites.

Source: Catlow, 1992: 2

Different modes of linking of sodalite units generate some of the commonest zeolite structures. By fusing the unit together via their four-rings generate the structure of sodalite itself, which is both a naturally occurring mineral and a widely synthesized industrial material One of the most celebrated vanants based on the sodalite structure is the beautiful blue dye ultramarine in which S_3^- radicals (which adsorb in the red region of the visible spectrum) are trapped within the sodalite cage.

Bridging (rather than fusing) of sodalite units via four-rings generates the structure of zeolite A also shown in Figure 2-11. The structure, which does not occur naturally, is very extensively synthesized owing to its use in ion exchange, gas separation and drying. An alternative mode of bridging, via six-rings, generates what is probably the single most important zeolite structure, illustrated in Figure 2-11, and referred to as zeolite X or Y depending on the Si/Al ratio, as discussed below. The structure is also adopted by the rare mineral faujasite. The most intriguing feature of this framework is that the mode of linkage of the sodalite units generates very large voids, known as 'supercages', also shown in Figure 2-11. Access to these voids is via large 'windows', also evident in the figure, whose molecular diameter is 7.44. This allows organic molecules to diffuse both in and out of the supercages, and the zeolite is indeed one of the most important catalytic systems, being widely used in the cracking of long to shorter chain molecules in the gasoline range.
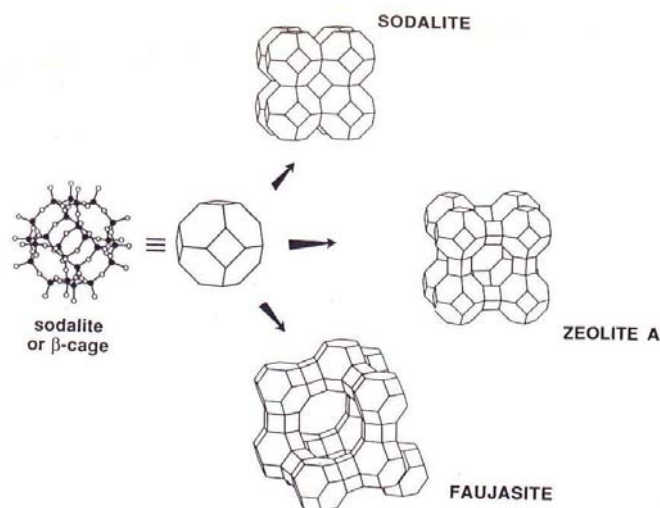
Figure 2-11 The sodalite or cage, linked to create the structures of sodalite, zeolite A
and Faujasite (zeolite X/Y).

Source: Catlow, 1992: 3

6. Application of Zeolite (Catlow, 1992)

Zeolites are routinely used in three main areas of industrial chemistry. The largest
is heterogeneous catalysts. Older but important applications are in ion exchange and gas
separation.

6.1 Catalysis

Zeolites catalyst several types of reaction involving organic molecules. The
most important are cracking, isomerization and hydrocarbon synthesis, but there is an
increasing application in the field of synthesis of organic fine chemicals.There are two
fundamental considerations in zeolite catalysis. The first refers to the basic reaction
mechanism and the second to the way in which the products are controlled by the
geometry and topology of the microporous crystal structure.

6.2 Reaction Mechanisms

Bronsted acid mechanisms are most important in zeolite catalysis. Bridging hydroxyl groups (see Figure 2-12) are, as noted, the commonest type of acid site. As discussed above, these may be considered as protonated oxygens, the protons being present as charge compensators for the negatively charged framework aluminium. The Coulombic interaction between the tetrahedral aluminium and the protons means that Si-OH-Al bridges provide the dominant type of acid species although acid sites associated with defects are thought to contribute to catalytic processes. The variation of acidity with aluminium content is one of the most fascinating aspects of zeolite science and is one where theoretical technique can make an important contribution.

Bronsted acid catalysis within zeolites is essentially conventional. The acidic hydroxyl groups protonate unsaturated organic molecules, or basic groups such as OH and NH_2. The fate of the protonated species may, however, depend strongly on other acid-base properties of the zeolite, including Lewis acidity and basicity of the framework oxygen ions. Moreover, as we have argued, the nature of the product is controlled by the structure of zeolite pores. A simple but important example is the catalytic conversion of metaxylene to paraxylene. The isomers can be interconverted by acid catalysis. However, if the isomerization is undertaken within the pores of the zeolite ZSM-5 the para-isomer has a much higher diffusion coefficient as, unlike metaxylene, it can migrate along the pores of this zeolite. It thus diffuses rapidly out of the catalyst, which therefore effects the required isomerization with high yield.
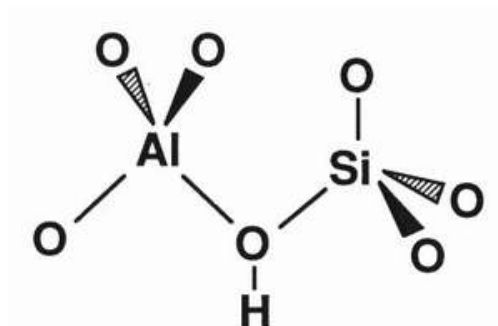

Figure 2-12 Bridging hydroxyl group in aluminium substituted zeolites.
Source: Catlow, 1992: 6

Lewis acidity is known to be important in zeolites. Indeed it has been speculated that it plays an important role in hydrocarbon cracking reactions. Fluid bed catalytic cracking which employs zeolite Y and in which the heavy components of crude oil are broken down into hydrocarbons in the gasoline range remains the single most important application of zeolites. Although the technology of this complex process is well developed, our understanding of the reaction pathways is far from complete. The process of coking, whereby the pores of the zeolite become blocked with carbon, is also poorly understood, and there is a clear need for better knowledge at the atomic level of the reaction mechanisms involved.

6.3 Ion Exchange

Hydrated cations within zeolite pores are loosely bound and they will readily exchange with other cations in surrounding aqueous media. The study of ion exchange is a mature subject and the thermodynamics of ion exchange equilibria are well understood. The traditional application is in water softening and increasing use of zeolites is made in the detergent industry. Topical recent applications have concerned the removal of radioactive ions from contaminated water.

6.4 Gas Separation

The obvious fact that different molecules have different equilibrium constants for sorption and different diffusion coefficients within the pores enables zeolites to be used to effect gas separation – a phenomenon which has been widely explored. Understanding of the relative thermodynamics and kinetics of the different sorbed species is crucial for predicting these important technological processes. More specifically, the pore structure of zeolites may be exploited to 'sieve' molecules with the required dimensions to enter the pores. This sieving may be fine tuned by altering the sizes and numbers of the cations present in the pores.

7. NaY Zeolite

NaY zeolite (faujasite) is produce by digesting a mixture of silica, alumina and caustic for serveral hours at prescribed temperature until crystallization occurs. A typical NaY zeolite contains approximately 13 %wt. Na_2O. To enhance activity, thermal and hydrothermal stability of NaY, the sodium level must be reduced. This is normally done by the ion exchanging of NaY with a medium containing rare-earth cations and/or hydrogen ions. Ammonium sulfate solution are frequently employed as a source for hydrogen ion. (Sadeghbeigi, 1995.)

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 Figure 2-13. 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.
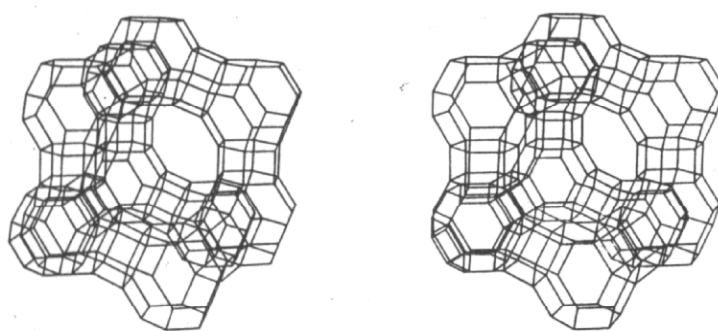

Figure 2-13 Stereodiagram of framework topology of faujasite.

Source: Rabo, 1976:17

8. USY Zeolite

USY (ultrastable Y) zeolite was prepared from NaY zeolite. NaY zeolite is ammonium exchange with a solution of the ammonium salt in order to reduce the sodium content to 3 or 4% Na_2O. The partially ammonium exchange zeolite is then calcined at high temperature (about 760 ^{o}C) under steam, in order to stabilize the zeolite and move the remaining sodium ions into exchange positions. In commercial operations, the calcination is usually done in rotary calciners.

Subsequent ammonium exchanges remove most of remaining sodium ions. In its final form, the zeolite contain less than 1% Na_2O and has unit cell site of about 24.55$\pm$0.02 Å, as shown in Figure 2-14. A high framework silica-to-alumina ratio, low unit cell size and low sodium content are essential in making these zeolite effective in octane enhancing catalysts.
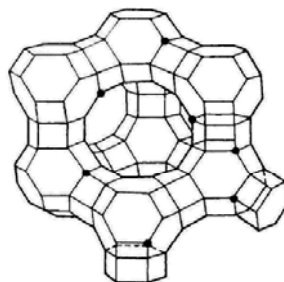
USY Zeolite (~7 Al Atoms/ u.c)
Unit Cell Dimension = 24.25 Å (SiO_2/Al_2O_3 = 54)

Figure 2-14 Geometry of USY zeolite.
Source: Sadegbeigi, 1995:83

9. REY Zeolite

REY (rare-earth Y) zeolite was prepared from NaY zeolite by ionic exchange with rare earth in solution. It was used primarily to boost the gasoline yield, especially where maximizing octane-barrels rather than gasoline octane is the major objective. Partially, rather than fully, rare earth exchange Y zeolite are used mainly to reduce coke and dry gas formation during the cracking process. As the rare earth content of

REY decrease, their contribution to octane enhancement increases while gasoline make decrease.

The commercial rare earth salts are a mixture of lanthanum and cerium salts, with smaller amount of neodymium and praseodymium. The ionic exchange occurs primarily with super cage sodium ions, due to the inability of hydrated rare earth ions ($\varnothing$~7.9 Å) to penetrate the 6-membered ring of the sodalite cage ($\varnothing$~2.4 Å). Figure 2-15 show geometry of REY zeolite.
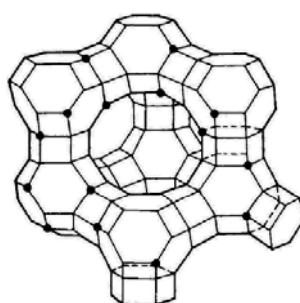
Equilibrium REY (~ 23 Al Atoms/u.c.)

Unit cell dimension = 24.39 Å ($SiO_2/Al_2O_3 \approx 15$)

Figure 2-15 Geometry of REY zeolite.

Source : Sadegbeigi, 1995:83

Some of the zeolite sodium ions are exchanged by hydrogen ions present in the acidic rare earth salts solution. Calcination of partially rare earth exchange zeolite results in stripping of the hydrate shell from the rare earth ions and migration of the hydrated ions into the sodalite cages. At the same time, most of the remaining sodium ions move into supercage positions and are subsequently removed by ammonium exchange. During calcination, some of the cerium ions present in the rare earth mixture are oxidized to the tetravalent state. Furthermore, the rare earth ions that migrate into the sodalite cages form cationic polynuclear hydroxy complexes. Upon calcination, RE is converted in to REY zeolite.

10. ZSM-5 Zeolite

The synthesis of ZSM-5 was first described by Argauer and Landolt from Mobil Oil Co. in 1972. ZSM-5 is member of the pentasil family of high-silica zeolite and, due to unusual properties, has found a wide application as a catalytic material. ZSM-5 is used commercially in synthetic fuels (conversion of methanol to gasoline), petroleum refining (dewaxing of distillates) and petrochemical for examples xylene isomerization, toluene disproportrionation and ethylbenzene manufacture (Scherzer, 1990). The pore size of ZSM-5 is smaller than that of Y-zeolite (5.1 Å to 5.6 Å versus 8 Å to 9 Å). In addition, the pore arrangement of ZSM-5 is different than Y-zeolite as shown in Figure 2-16. The shape selectivily of ZSM-5 allows preferential cracking of long-chain, low-octane normal paraffins as well as some olefins in the gasoline fraction.

Y FAUJASITE
7-8 Å CAGE OPENING

ZSM-5
5.1-5.6 Å CHANNEL OPENING

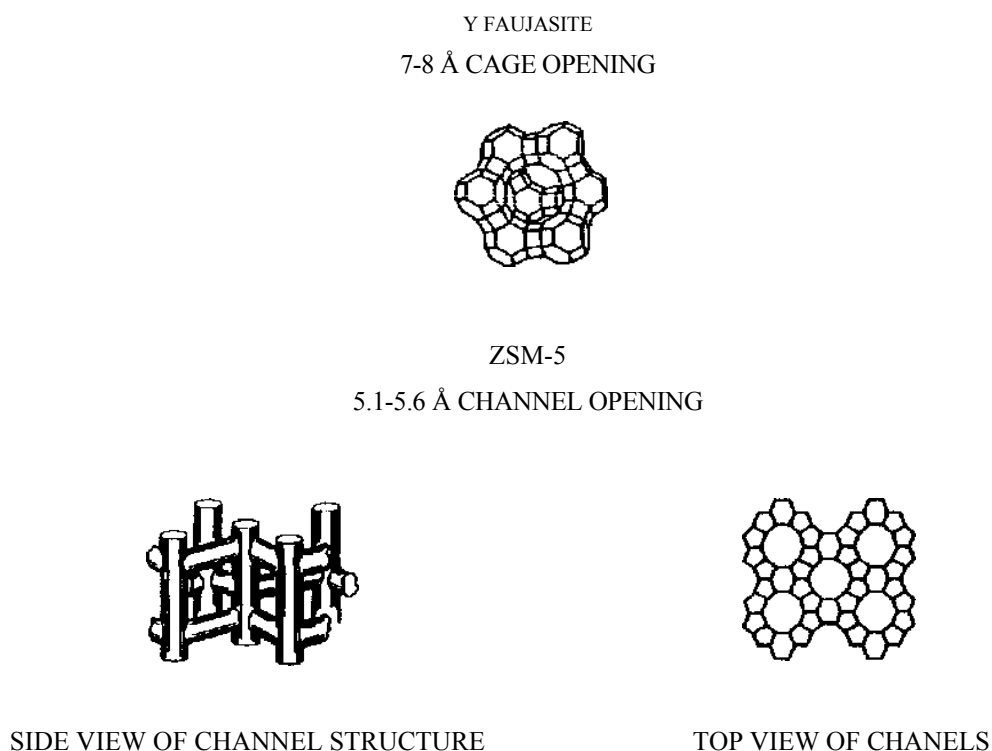SIDE VIEW OF CHANNEL STRUCTURE   TOP VIEW OF CHANELS

Figure 2-16 Comparison of Y faujasite and ZSM-5 zeolite.

Source: Sadeghbeigi, 1995: 117

ZSM-5 additive is added to the unit to boost gasoline octane and to increase light olefin yields. ZSM-5 accomplishes this by upgrading low-octane

components in the gasoline boiling range (C_7 to C_{10}) into light olefins (C_3, C_4, C_5). ZSM-5 inhibits paraffin hydrogenation by cracking the C_7+ olefins.

ZSM-5 effectiveness depends on several variables. The cat crackers that process highly paraffinic feedstock and have lower base octane will receive the greatest benefits of using ZSM-5. ZSM-5 will have little effect on improving gasoline octane in units that process naphthenic feedstock or operate at a high conversion level.

When using ZSM-5, there is almost an even trade-off between FCC gasoline volume and LPG yield. For a one-number increase in the research octane of FCC gasoline, there is a 1 to 1.5 vol% decrease in the gasoline and almost a corresponding increase in the LPG. This again depends on feed quality, operating parameters, and base octane.

The decision to add ZSM-5 depends on the objectives and constraints of the unit. ZSM-5 application will increase load on the wet gas compressor, FCC gas plant, and other downstream units. Most refiners who add ZSM-5 do it on a seasonal basis, again depending on their octane need and unit limitations.

The concentration of the ZSM-5 additive should be greater than 1 percent of catalyst inventory to see a noticeable increase in the octane. An octane boost of 1 RON will typically require 2% to 5% ZSM-5 additive in the inventory. It should be noted that the proper way of quoting percentage should be by ZSM-5 concentration rather than the total additive, because the activity and attrition rate can vary from one supplier to another supplier. There are new generations of ZSM-5 additives which have nearly twice the activity of the earlier additives.

In summary, ZSM-5 provides the refiner the flexibility to increase gasoline octane and light olefins. With the introduction of reformulated gasoline, ZSM-5 could play an important role in producing isobutylene, use as the feedstock for production of methyl tertiary butyl ether (MTBE) Sadeghbeigi, 1995).

11.   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 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:

1. Unit Cell Size
2. Rare Earth Level
3. Sodium Content

11.1 Unit Cell Size

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 (silica-alumina ratio) of the zeolite can be determined either from the above two equations or from a correlation such as the one shown in Figure 2-17.
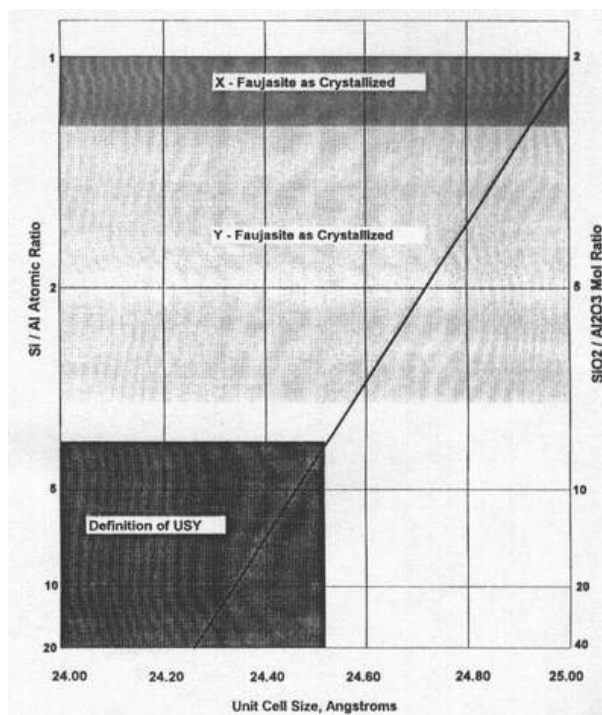
Figure 2-17 Silca-alumina ratio versus zeolite unit cell size.

Source: Sadeghbeigi, 1995:85

The unit cell size 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. Zeolite with lower UCS are initially less active than conventional rare earth exchanged zeolites. 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.

11.2 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 fully 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. 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.

11.3 Sodium Content

Sodium content is detrimental to zeolite stability, activity and its octane-enhancing capability. The lower activity and octane-enhancing capacity is attributed to the partial neutralization of strong Broensted acid sites by sodium ions. In commercial FCC catalysts, the sodium content of the zeolite is minimized, usually below 1 percent Na_2O. This is accomplished by ionic exchange of the zeolite with solutions of ammonium and/or rare earth salts. However, there are report that the presence of small amounts of sodium in the zeolite may have a beneficial effect on stability and selectivity (Magee and Mitchell, 1993). 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. The loss of octane is attributed to the drop in the number of strong acid sites.

Fluid catalytic cracking 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 (Sadeghbeigi, 1995).

12.   Matrix

The other constituent of the catalyst is the nonzeolitic portion or matrix. This consists of binders, fillers, and nonzeolitic active ingerdients.

Binder act to hold the particle together. The most frequently used binder is silica base. This binder is catalytically neutral. Other binders include natural or treated clays and various aluminum compounds. In addition to acting as a binder, most of these materials also have some catalytic activity.

Kaoline clay is the filler that is used to contain the active ingredients. The filler serves to provide the catalyst with its gross physical properties such as hardness, density and size.

The primary purpose of this active matrix is to crack the larger molecule present in the FCC feed. Most of the active sites in the zeolite are enclosed in the crystal supercage. The pores in the zeolite crystal have a uniform diameter and will not pass molecules larger than about 8 Å units in diameter. Larger molecule must be precracked either on the external surface of the zeolite or by an active ingredient with large pores (Wilson, 1997).

Early attempts to used pure zeolite in the catalytic cracking of gas oil met with failure. Because of the high surface area, site density of the zeolite, and generally long catalyst-oil contact times involved in bed cracking in early FCC units, the product stream was high in undesirable secondary reaction product such as coke and light gas. Clearly, overcracking and coke rapidly deactivated the pure zeolite catalyst. A simple dilution of the zeolite in a matrix reduced over cracking and coke poisoning and produced a zeolite containing FCC catalyst that was far superior to exiting amorphous silica-alumina or acidified clay base catalysts.

12.1 Binder

The oil industry has gradually increased demands for attrition resistant FCC catalyst. These demands have arisen from the need to reduce particulate air pollution from catalyst fines and to prevent the loss of expensive catalyst. Hence, the binder has become an increasingly critical component of the catalyst matrix. Commercial FCC catalyst producers have devoted substantial time and effort to improving catalyst binding. At present, four binder systems are used in the commercial production of FCC catalyst, and an extraordinary number have been examined in laboratory preparations. Table 2-1 shows the four binder types and their main characteristics.

Table 2-1 Commercial FCC binders.

Type	Surface area	Activity
Silicasol	20 m^2/g	Very low
Aluminum chlorhydrol (ACH)	60-80 m^2/g	Moderate
Peptized alumina	300 m^2/g	High
Self-binding (In situ)	-	High

Source: Magee and Mitchell, 1993: 117

12.1.1 Silica Sol

The acidified silica sol binder was introduced commercially in the mid-1970's. The binder was attractive for its low activity, ease of manufacture, and dispersibility. The sol is produced by an intimate mixture of sodium silicate and acidified aluminum sulfate solution. A clear, low-viscosity silica sol results. Because silicate gels rapidly in the pH range from 11.0 to 3.5, the silicate and acid alum must be mixed rapidly to prevent local pH excursions and micro gelatin of the sol. Thus extremely effective local mixing is required.

Furthermore, gel tune is also strongly affected by reactant concentrations and solution temperature. Consequently, the sols are made at relatively low silica solids (10 %wt.) and cooling of the components is required. Mediocre mixing, elevated temperatures (>100 ^{o}F), or high silicate concentrations cause the

formation of turbid sol or gel particles with poor binding characteristics. Once formed, the sol is in a metastable state. Particle growth is dependent on temperature, pH, and silica concentration. Even sol formed under conditions known to impart good binding can form microgel within one hour of synthesis and form a clear silica gel within several hours at a pH equal to 2.5 to 2.7. Although producing the sol from the interaction of silicate with sulfuric acid is possible, the sol product is unstable with respect to changes m pH and rapidly gels when mired with other FCC catalyst components. The presence of aluminum (III) offers some buffering capacity to the sol and prevents rapid gelation of the spray dryer feed slurry. When the sol is mixed with the other components, it rapidly disperses throughout the slurry. When spray dried, the sol rapidly gels, binding the components together.

12.1.2 Aluminum Chlorhydrol

The aluminum chlorhydrol (ACH) binder was introduced commercially in the late 1970's. The binder is a hydroxylated aluminum based sol containing chloride as the counter ion. Aluminum chlorhydrol can be produced by reacting aluminum metal with hydrochloric acid to get a clear solution at pH 3.0 to 4.0. The aluminum-chloride ratio can be varied and determines the amount of various molecular weight alumina oligomers in the sol. Likewise, the material can be produced by the slow hydrolysis of $AlCl_3$ solution with base. Addition rate of the base to the $AlCl_3$ solution is critical as is mixing to prevent the formation of $Al(OH)_3$ gel.

Although the equilibria of alumina species in the sol are complex, it is better understood than that of silica sol in the same pH range. The predominant species seems to be $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. Compared to silica sol with average particle sizes of 5 to 10 nm, the size of the aluminum oligomers is relatively small. Thus dispersion throughout the FCC matrix would thus be expected to be superior.

Unlike silica sol, the solution structure of ACH is not particularly sensitive to time or temperature but is sensitive to pH. Because of its high chloride content (12%), ACH m also considerably more corrosive, especially at elevated temperature, to stainless steel catalyst preparation equipment than is silica sol. The ACH remains stable indefinitely at constant pH and can be refluxed without gelling and without any other noticeable change in sol properties.

In practice, ACH is mixed with other FCC components, and the resulting slurry is spray dried. The spray dried microspheres, unlike the spheres bound by silica sol, show little green strength. They must be directly calcined at temperatures high enough to cause dehydroxylation of the alumina in order to be slurried without damage to the microsphere or to gain attrition resistance. The spray dried microspheres cannot be slurried in water and maintain physical integrity prior to firing, as is true with acidified silica sol bound microspheres. Because the calcination of ACH-bound catalysts produces dehydroxylated alumina species, the binder does possess some surface area and cracking activity. Whether the active sites are Lewis or Bronsted acids is not clear.

12.1.3 Peptized Alumina

Another commonly used alumina based binder is prepared by peptizing pseudoboehmite alumina (PBA), usually with formic acid. The action of the acid on the reactive alumina produces an alumina so1 with particle size in the range of several hundred nanometers. The opaque, milky-white color of the sol testify to its significantly larger particle size compared with silica sol or ACH. Other monobasic acids such as HCl and HNO_3 can also be used to peptize the alumina, but formic seems to be the commercial choice, because of fewer problems in terms of stack emissions or corrosion. Pseudoboehmite alumina cannot be pepped with di- or tri-basic acids, such as sulfuric acid. After acidification, the peptized alumina is mixed with the other FCC components and spray dried. Like ACH, the spray dried microspheres have little green strength and cannot be slurried in water without significant damage. The sol itself is somewhat unstable with respect to pH, time, and temperature. Depending on alumina concentration and pH, the sol will gel within ten minutes to several hours. Unlike silica sol, the gel particles seem to be only weakly bound, and whether gelation affects the binding properties of the sol is unclear.

The spray dyer feed slurry prepared with peptized alumina is noticeably more viscous than corresponding slurries using silica sol or ACH as binders. In practice a small amount (3 to 5%) of stabilized polysilicic acid (PSA) is added to the spray dryer feed to improve overall binding. Stabilized PSA can be prepared by passing dilute sodium silicate solution through an acid ion exchange

column to remove most of the sodium ions. Subsequent stabilization is affected with minimal amount base, usually ammonia. Pseudoboehmite possesses surface areas of more than 300 m²/g and undergoes a phase change to gamma alumina at FCC unit regenerator temperatures. The acidity of gamma alumina is well documented. Hence, this binder is active for gas oil cracking and serves a dual purpose as an active bottoms cracking component and binder. Bottoms are the large high-molecular weight components in the FCC feed. Usually their size makes them too large for diffusion into the zeolite pores (diameter = 7.4 Å)

12.1.4 In Situ Binding

The in situ type of FCC catalyst preparation introduced by Engelhard contains no added binder. The first preparative step calls for forming kaolin microspheres. However, clay-to-clay particle binding after spray drying is quite weak, and the particles cannot be slurried in water without complete breakdown. After high temperature calcination (approximately 1800 °F) the particles develop significant attrition resistance and maintain their microspherical shape during the second step of the in situ crystallization process in caustic solution at 180 °F.

The crystallization step imparts even more hardness to the microsphere and forms intrastructural NaY. Hydroxyls on the surface of the clay platelets react with one another at high temperature to eliminate water and form oxygen-bridged bonds between the particles.

During crystallization, significant silica is removed from the particle to leave macropores which are filled by the intrastructural zeolite particle growth. Significant porosity in the 30 to 100 A range results. The remaining matrix is higher in alumina than the starting kaolin because of the silica removal and possesses significant acidity. The combination of acidity and high surface area make this material an active matrix for bottoms cracking. The large matrix surface area and exposure of contaminant metal present in the clay can lead to high coke and gas make. Retaining some of the silica (as described by Brown) reduces some of this undesirable matte activity by reducing overall surface area. Recent technology using combinations of metakaolin and seed technology seems to reduce the porosity and surface area to an even greater extent.

12.2 Clay

Clay is added to most FCC catalysts as an inert densifier, that is, to improve the apparent bulk density (ABD) of the catalysts with out having the effect on catalyst activity and selectivity. In all known FCC catalysts, the clay of choice is kaolin. Its ability to form high solids pumpable slurries, low fresh surface area, and ease of packing as a result of its platelet structure make kaolin particularly suitable. Most manufacturers purchase the kaolin as a 60 to 65 %wt. slurry (usually dispersed with sodium silicate or tetrasodiumpyrophosphate) and use it without further processing.

Some parameters of the kaolin are critical for FCC manufacturing. Specifically, the kaolin particle size must be small to ensure that the resulting FCC catalyst possesses good ABD add attrition resistance. Average particle size (by sedigraph) of 0.3 to 0.4 μ with a 90% point of approximately 1 μ are normal for FCC use. The iron and titania content of the clay can also be important. High iron or titania levels can lead to undesirable secondary reactions, such as gas and coke formation and increased CO combustion in the regenerator, when such clays are used in the manufacture of cracking catalysts. Titania levels below 3.0 %wt. and an iron content of 0.4 to 0.8 %wt. are considered acceptable. Because of environmental concerns, the crystalline silica content of the clay has also become an important parameter. Although crystalline silica is present in very small concentration in clay, recent government regulations have increased the importance of minimizing its presence.

12.3 Active Ingredient

A modern FCC catalysts require active stable matrices capable of converting heavy oil molecule to lighter products and minimizing the effects of contaminant metals. Three such matrix components have been used in commercial FCC catalysts, whereas others have shown large promise in laboratory testing.

12.3.1 Alumina

By far the most common material added to commercial FCC catalysts to accomplish heavy oil conversion is alumina in various forms and amounts. Alumma has long been used as an active support in reforming and hydrotreating

catalysts. In FCC catalysts, some silica is included with the alumina either in the form of added silica (polysilicic acid), silica binder or is present naturally in the day based in situ process. Silica also forms tetrahedrally coordinated silica-alumina species on the alumina surface to produce Bronsted acidity and a more active cracking surface.

Commercial manufacturers use PBA, amorphous alumina, and aluminum chlorhydrol sols to add alumina to the FCC catalysts. The amount and type of alumina added to the catalyst formulation depends on the FCC unit severity and the feedstock being processed. In the case of PBA, the material is generally peptized prior to addition. Because of the small particle size achieved by peptizing the PBA, no additional mechanical particle size reduction is required. Amorphous aluminas are necessarily subjected to some form of mechanical particle reduction prior to inclusion in the catalyst matrix.

12.3.2 Silica-Alumina

Amorphous silica-alumina, in which aluminum is tetrahedrally coordinated to silicon through oxygen bridges, was the active cracking component in many FCC catalysts before the discovery of zeolite as an active FCC catalyst component. Even though the active sites thus formed were similar to those in zeolite X and Y, the amorphous silica-aluminas were much less gasoline and coke selective than the zeolite containing catalysts and were much less active. In the early years after the introduction of zeolite cracking catalysts, amorphous silica-alumina matrices were used in conjunction with the zeolite. However, because of thier relatively non-selective cracking characteristics and the fact that they were poor binders, their use was abandoned in favor of better binders (Magee and Mitchell, 1993).

13. Active Site

The active sites in cracking catalysts are acid sites, for example they are proton donors (called Bronsted acid sites) or electron pair (two electrons) acceptors (called Lewis acid sites). Both types can initiate the carbenium ion cracking chain described in Figure 2-18. Acid sites in all conventional cracking catalysts are formed by interactions of silica and alumina, SiO_2 and Al_2O_3. Under appropriate reaction conditions, these two materials (or other materials containing sources of SiO_2 and

Al$_2$O$_3$) interact to form a solid acid of the following simplified structure (Magee and Dolbear, 1998).
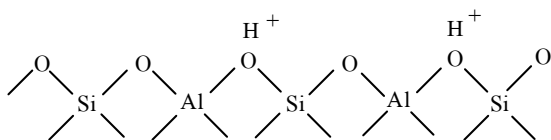

Figure 2-18 Formation of Bronsted site.

Source: Dyer, 1988: 121

In high-silica zeolite these 'protonated' zeolites can be made by direct exchange with mineral acid. Ideally the 'protonnated' form contains hydroxyls which are protons associated with negatively charged framework oxygens link into alumina tetrahedra. The protons have great mobility when the temperature is above 200 $^{\circ}$C, and at 550 $^{\circ}$C they are lost as water with the consequent formation of Lewis sites, as show in Figure 2-19.
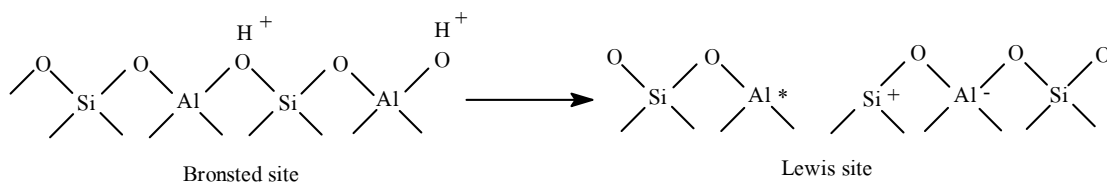

Figure 2-19 Formation of Lewis site.

Source: Dyer, 1988: 122

The Lewis sites in turn are unstable, especially in the continued presence of water vapor and an annealing process stabilizes the structure. This produces called 'true' Lewis site by ejecting Al species from the framework, as show in Figure 2-20 (Dyer, 1988).
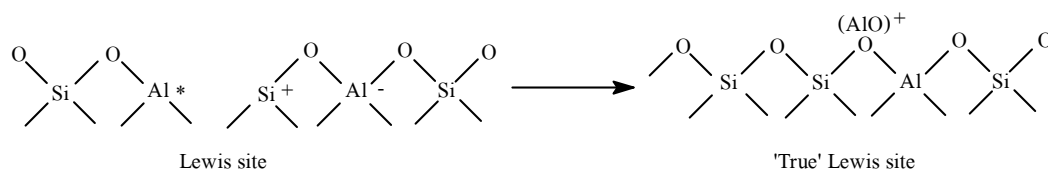
Figure 2-20 Formation of 'true' Lewis site.

Source: Dyer, 1988: 122

14. Composition and Classification of Fluid Catalytic Cracking Catalyst

The modern fluid catalytic cracking catalysts 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 zeolites used in FCC catalysts are mostly synthetic, faujasite type zeolites: Y and high-silica Y zeolites. In the past, X zeolites have also been used but have been replaced by the more stable Y zeolites. 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 catalysts contain 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 a natural component. The synthetic component in most commercial catalysts 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, although it can also have a catalytic role. For example, FCC catalysts used for cracking heavy feedstocks (e.g., resid) usually have catalytically active matrices.

Regarding their main applications, commercial FCC catalysts can be broadly classified in three categories: (1) gasoline FCC catalysts, (2) octane FCC catalysts, and (3) resid FCC catalysts. Gasoline catalysts are used when the major objective is to maximize gasoline yields. Octane catalysts are used when the objective is to

maximize gasoline octane or octane-barrels (the product between gasoline yield and octane number). Resid catalysts are used to crack resid feedstocks.

The zeolite component of the gasoline catalysts is commonly a rare earth, hydrogen Y zeolite (REHY), with a rare earth content between 10 and 13 percent RE_2O_3. Such zeolites will give high gasoline yields. However, they will also generate high coke yields. The matrix usually plays a minor catalytic role in these catalysts and is therefore catalytically inactive (e.g., silica/clay matrix) or of moderate activity, as show in Figure 2-21.

Octane catalysts contain mostly high-silica Y zeolites in rare earth or hydrogen exchanged form as show in Figure 2-22. They can also contain rare earth, hydrogen Y (REHY) zeolites with a lower rare earth content. Furthermore, an octane-boosting additive, such as ZSM-5 zeolite, is sometimes present in such catalysts. The matrix is catalytically active and usually contains amorphous alumina or silica-alumina, in addition to clay.

```
                    ┌──────────────────────┐
                    │ Gasoline FCC catalyst │
                    └──────────────────────┘
              ┌──────────────┴──────────────────┐
   ┌─────────────────────────┐        ┌──────────────────┐
   │   Zeolite component     │        │ Matrix component │
   │ Large pore FAU (Ø ~ 8 Å)│        └──────────────────┘
   └─────────────────────────┘          ┌──────┴──────┐
                                   ┌───────────┐  ┌─────────┐
                                   │ Synthetic │  │ Natural │
                                   └───────────┘  └─────────┘
```

-RE, HY (10-13%RE_2O_3)   -SiO_2 -Clay
-REY (%RE_2O_3 > 13)   -Al_2O_3 -Modified clay
-(REX)   -SiO_2-Al_2O_3
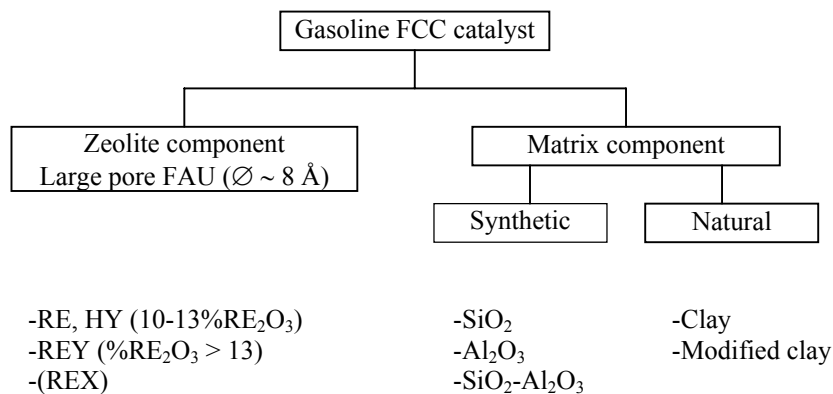
Figure 2-21 Composition of gasoline FCC catalyst.

Source: Magee and Mitchell, 1993: 148

```
                        ┌─────────────────────┐
                        │  Octane FCC catalyst │
                        └──────────┬──────────┘
              ┌────────────────────┴────────────────────┐
      ┌───────────────┐                         ┌────────────────┐
      │ Zeolite component │                     │ Matrix component │
      └───────┬───────┘                         └───────┬────────┘
        ┌─────┴─────┐                            ┌───────┴───────┐
┌─────────────┐ ┌──────────────────┐      ┌───────────┐ ┌───────────┐
│ Large pore  │ │ Medium and small │      │ Synthetic │ │  Natural  │
│ (∅ ~ 8 Å)   │ │ pore (additive)  │      └───────────┘ └───────────┘
└─────────────┘ │ (∅ < 6 Å)        │
                └──────────────────┘
```

-HSY (RE or H-form)   -ZSM-5   -SiO$_2$ -Clay
-RE, HY   -ZSM-11   -Al$_2$O$_3$ -Modified Clay
                         -SAPO-11   -SiO$_2$-Al$_2$O$_3$
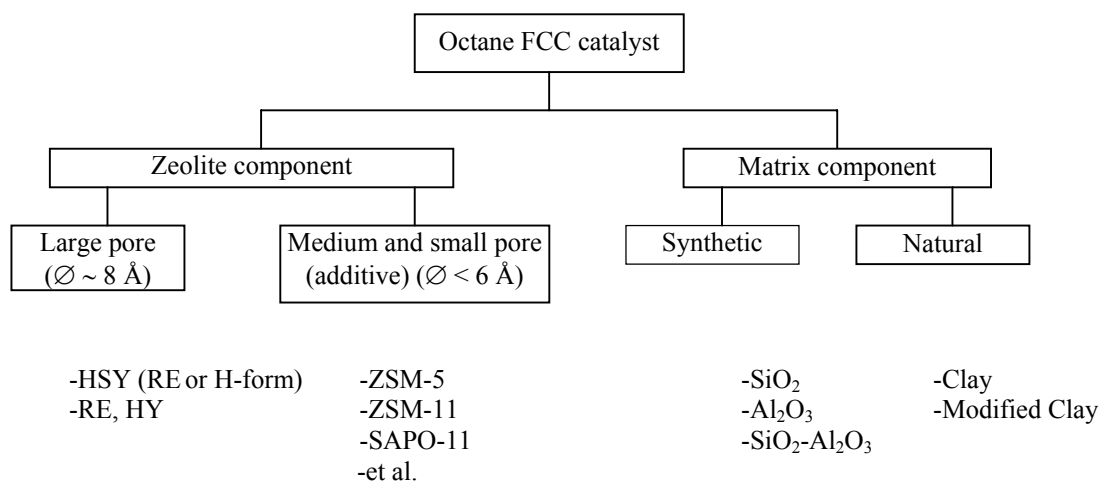   -et al.

Figure 2-22 Composition of octane FCC catalyst.

Source: Magee and Mitchell, 1993: 148

Resid catalysts usually contain zeolites similar to those present in octane catalysts: rare earth exchanged, high-silica Y and rare earth, hydrogen Y zeolites. The rare earth content of these zeolites is often high. The catalysts contain a large pore, active matrix, in which the active component is amorphous alumina, silica-alumina and, in some instances, modified clay. Furthermore, such catalysts contain metal passivators or traps, SO$_x$ abatement additives and CO combustion promoters. The metal passivators, additives and combustion promoters are generally blended with the FCC catalyst, as show in Figure 2-23 (Magee and Mitchell, 1993).
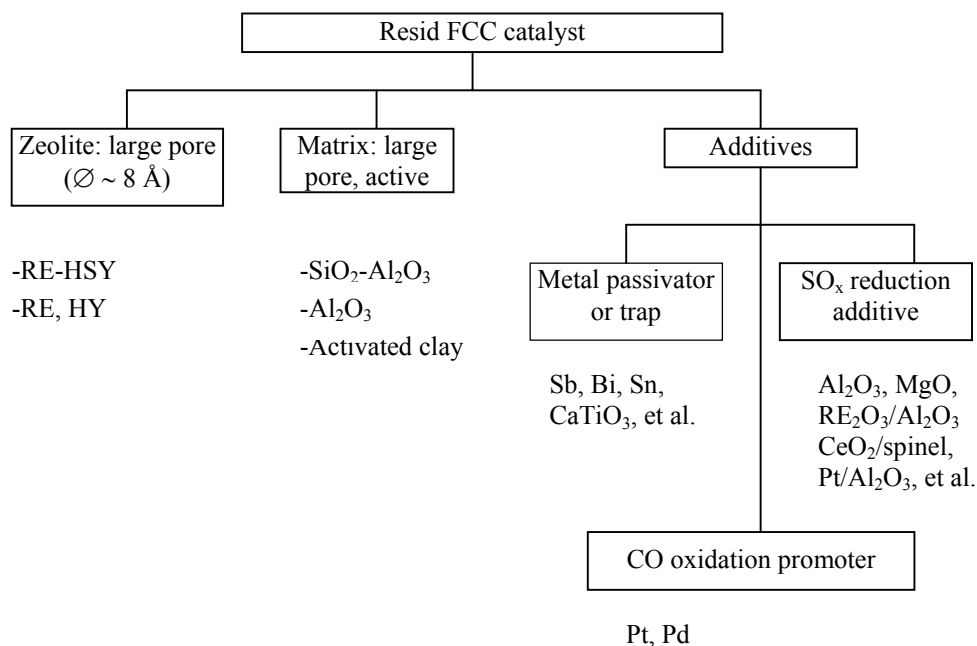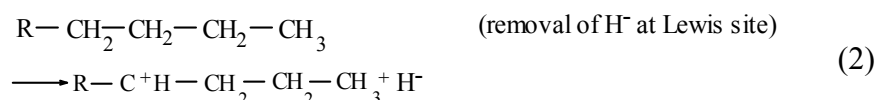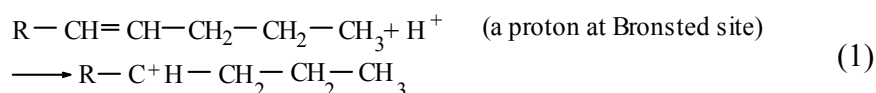
Figure 2-23 Composition of resid FCC catalyst.

Source: Magee and Mitchell, 1993: 149

15. Mechanism of Catalytic Cracking Reaction

The reaction that occur when a hydrocarbon molecules reacts on the solid surface of a catalyst all involve positively charged organic species, usually carbenium ions. The first step is the vaporization of the feed by the catalyst. The next step is formation of positive-charged carbon atoms called 'carbocations'. Carbocation is a generic term for a positive-charged carbon ion. Carbocation can further be subdivided into carbenium and carbonium ions.

A carbenium ion, $R\text{-}CH_2^+$, comes either from adding a positive charge to an olefin and/or from removing a hydrogen and two electrons from a paraffin molecule (Equations 1 and 2).

$$R-CH=CH-CH_2-CH_2-CH_3 + H^+ \quad \text{(a proton at Bronsted site)}$$
$$\longrightarrow R-C^+H-CH_2-CH_2-CH_3 \tag{1}$$

$$R-CH_2-CH_2-CH_2-CH_3 \quad \text{(removal of } H^- \text{ at Lewis site)}$$
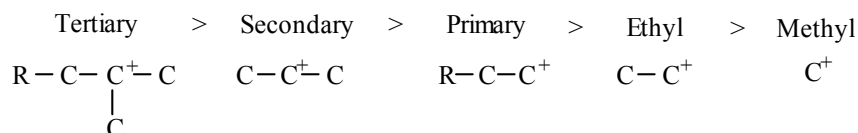$$\longrightarrow R-C^+H-CH_2-CH_2-CH_3 + H^- \tag{2}$$

The Bronsted and Lewis acid sites on the catalyst are responsible for generating carbenium ions. The Bronsted site donates a proton to an olefin molecule and the Lewis acid site removes electrons from a paraffin molecule. In commercial units, olefins are either in the feed or are produced through thermal cracking reactions.

A carbonium ion, CH_5^+, is formed by adding a hydrogen ion (H^+) to a paraffin molecule (Equation 3). This is accomplished via direct attack of a proton from the catalyst Bronsted site. The resulting molecule will have a positive charge with 5 bonds to it.

$$R-CH_2-CH_2-CH_2-CH_2-CH_3 + H^+ \qquad \text{(proton attack)}$$
$$\longrightarrow R-C^+H-CH_2-CH_2-CH_2-CH_3 + H_2$$
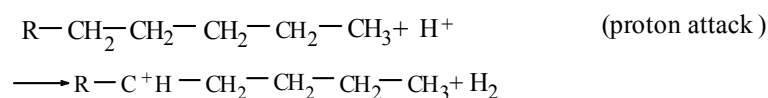
The carbonium ion's charge is not stable and the catalyst acid sites are probably not strong enough to form a lot of carbonium ions. Consequently, nearly all the cat cracking chemistry is carbenium ion chemistry. The stability of carbocations depends on the nature of alkyl groups attached to the positive charge. The relative stability of carbenium ions is as follows:

$$
\begin{array}{ccccccccc}
\text{Tertiary} & > & \text{Secondary} & > & \text{Primary} & > & \text{Ethyl} & > & \text{Methyl} \\
R-C-\overset{+}{C}-C & & C-\overset{+}{C}-C & & R-C-C^+ & & C-C^+ & & C^+ \\
\quad\ \ \vert & & & & & & & & \\
\quad\ \ C & & & & & & & &
\end{array}
$$

One of the benefits of catalytic cracking is that the primary and secondary ions tend to rearrange to form a tertiary ion (a carbon with three other carbon bonds attached). As will be discussed later, the increased stability of tertiary ions accounts for the high degree of branching associated with cat cracking.

Once formed in the initial step, carbenium ions can form a number of different reactions. The nature and strength of the catalyst acid sites will significantly influence the degree to which these reactions occur. The three dominant reactions of carbenium ions are:

- The cracking of a carbon-carbon bond
- Isomerization
- Hydrogen transfer

15.1 Cracking Reactions

The cracking, or beta-scission, is a key feature of ionic cracking. Beta-scission is splitting of the C-C bond at two bonds away from the positive-charge carbon atom. There is a preference for beta-scission because the energy required to break this bond is tower than that needed to break the adjacent C-C bonds. In addition, long-chain hydrocarbons are more reactive than short-chain hydrocarbons; therefore, the rate of the cracking reactions decreases with decreasing chain length to the point that it is not possible to form stable carbenium ions. The initial products of beta-scission are an olefin and a new carbenium ion (Equation 4). The newly formed carbenium ion will then continue a series of chain reactions. Small ions such as a four-carbon or five-carbon can then react with another big molecule and transfer the positive charge, and then the big molecule can crack. Cracking does not eliminate the positive charge; it stays there until two ions run into each other. The smaller ions are more stable and will not crack. They stay longer and finally transfer their charge into a big molecule.

$$R-C^+H-CH_2-CH_2-CH_2-CH_3$$
$$\longrightarrow CH_3-CH=CH_2 + C^+H_2-CH_2-CH_2R$$

$$(4)$$
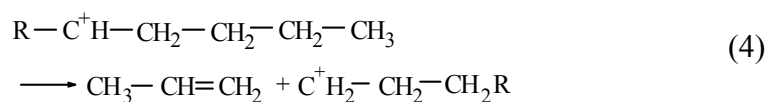
Because beta-scission is monomolecular, cracking is endolhermic. Consequently, cracking rate is favored by high temperatures; cracking is not equilibrium limited. The reactions that occur during gas oil cracking over zeolite catalysts are sumarized in Table 2-2.

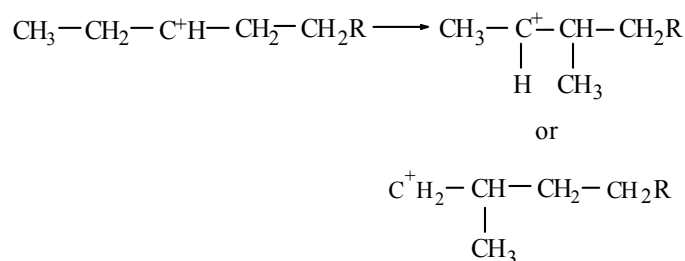**Table 2-2** Main reactions in FCC catalysis.
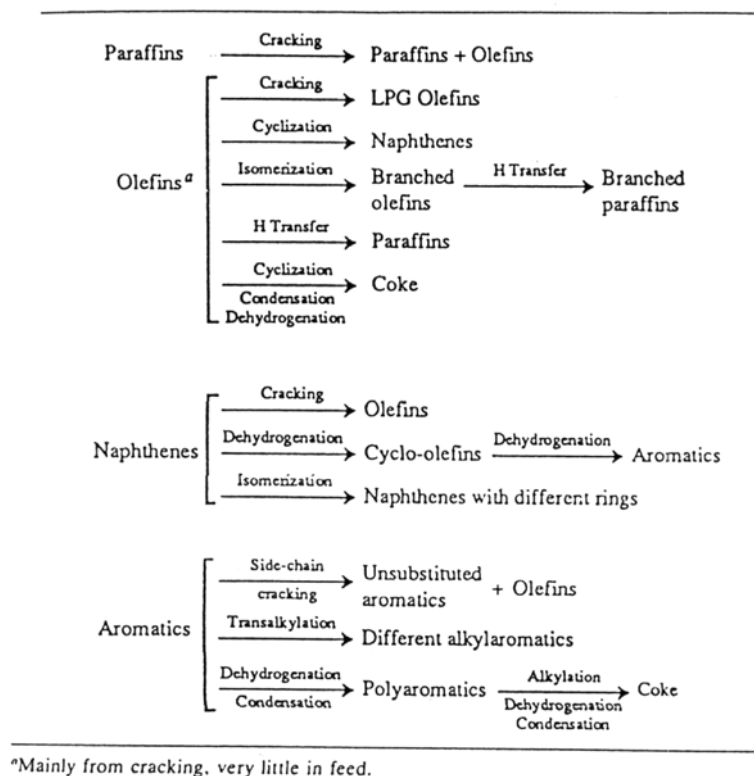
"Mainly from cracking, very little in feed.

Source: Scherzer, 1993: 90

15.2 Isomerization Reactions

Isomerization reactions occur more frequently in catalytic cracking than in thermal cracking. As discussed earlier, thermal cracking is a free-radical mechanism. Breaking of a bond in both thermal and catalytic mechanisms is via beta-scission; however, in catalytic cracking a number of carbocations tend to rearrange to form tertiary ions. Tertiary ions are more stable than secondary and primary ions; they shift around and crack to produce branched molecules (Equation 5). Free radicals do not do that; they yield normal or straight compounds. Some of the advantages of isomerization are as follows:

- Higher octane

- Higher-value chemical and oxygenate feedstocks

- Lower cloud point for diesel fuel

$$CH_3-CH_2-C^+H-CH_2-CH_2R \longrightarrow CH_3-\overset{+}{C}-CH-CH_2R$$

$$\overset{|}{H} \quad \overset{|}{CH_3}$$

or

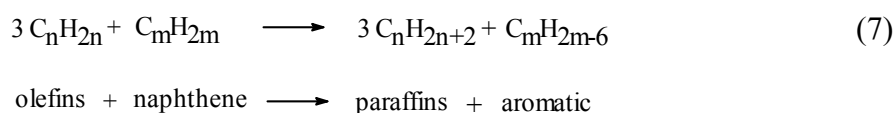$$\overset{+}{C}H_2-CH-CH_2-CH_2R$$

$$\overset{|}{CH_3}$$

The isoparaffins in the gasoline boiling range have higher octane than normal paraffins. Compounds such as isobutylene and isoamylene will be extremely valuable as the feedstocks for the production of methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME). MTBE and TAME can be blended into the gasoline to reduce auto emissions. Finally, isoparaffins in the light cycle oil boiling range improve the cloud point.

15.3 Hydrogen Transfer Reactions

Hydrogen transfer, or more correctly hydride transfer, is a bimolecular reaction in which one reactant is an olefin. An example of hydrogen transfer is the reaction of two olefins. Both olefins would have to be adsorbed on the active sites and the sites would have to be close together for these reactions to take place. One of these olefins becomes paraffin and the other becomes cyclo-olefins; so hydrogen is moved from one to another. Cyclo-olefin is now hydrogen transferred with another olefin to yield cyclodi-olefin. Cyclodi-olefin will then rearrange to form an aromatic, and aromatics are extremely stable. Therefore, hydrogen transfer of olefins converts them to paraffins and aromatics (Equation 6).

$$4\,C_nH_{2n} \longrightarrow 3\,C_nH_{2n+2} + C_nH_{2n-6} \tag{6}$$

$$\text{olefins} \longrightarrow \text{paraffins} + \text{aromatic}$$
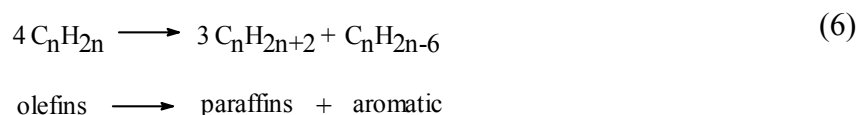
Napthenic compounds are also hydrogen donors and can read with olefins to produce paraffins and aromatics (Equation 7).

$$3\,C_nH_{2n} + C_mH_{2m} \longrightarrow 3\,C_nH_{2n+2} + C_mH_{2m-6} \tag{7}$$

$$\text{olefins} + \text{naphthene} \longrightarrow \text{paraffins} + \text{aromatic}$$

A rare-earth-exchanged zeolite increases indirectly hydrogen transfers. In simple terms, the rare earth forms bridges between two to three acid sites in the catalyst framework. In doing so, the rare earth basically protects those acid sites being ejected from the framework. Because hydrogen transfer is promoted from adjacent acid sites, bridging these sites with rare earth promotes hydrogen transfer reactions.

Hydrogen transfer reactions usually increase FCC gasoline yield and its stability. It does so by reducing reactivity of the gasoline being produced. When there is hydrogen transfer, there are fewer olefins. Olefins are the reactive species in gasoline for secondary reactions; therefore, hydrogen transfer reactions reduce indirectly 'overcracking' of the gasoline.

Cracking, isomerization, and hydrogen transfer reactions account for the majority of reactions occurring in cat cracking. There are other associated reactions that do indeed play an important role in unit operation. Two prominent reactions are dehydrogenation and coking. Under ideal conditions, i.e., a 'clean' feedstock and catalyst with no metals, cat cracking does not yield any appreciable amounts of molecular hydrogen. Therefore, dehydrogenation reactions will only proceed if the catalyst is contaminated with metals such as nickel and vanadium.

Cat cracking of gas oil molecules yields a residue called coke. Chemistry of coke formation is complex and not very well understood. Similar to hydrogen transfer reactions, catalytic coke is a 'bimolecular' reaction product and proceeds via carbenium ions or free radicals. In theory, coke yield should increase as hydrogen transfer rate is increased. It is postulated that reactions producing unsaturates and multi-ring aromatics are the principal coke-forming compounds. Unsaturates such as olefins, diolefins, and multi-ring polycyclic olefins are very reactive and can polymerize to form coke.

For a given catalyst and feedstock, catalytic coke yield is a direct function of conversion. However, there exists an optimum riser temperature in which the coke yield is minimum. For a typical cat cracker, this temperature is about 950 ^{o}F. Let's look at two extreme riser temperatures of 850 ^{o}F and 1050 ^{o}F. At 850 ^{o}F, a lot of coke is formed mainly because the carbenium ions do not desorb at this low temperature. At 1050 ^{o}F, a large amount of coke is formed largely due to olefin polymerization (Magee and Mitchell, 1993; Sadeghbeigi, 1995).