

CHAPTER III

THEORY OF CRACKING POLYBUTENE-1

3.1 Basic Principles of Catalysis^[13]

In the study of reacting chemical system, two considerations are of importance. The first is chemical thermodynamics, the second is reaction kinetics. The thermodynamics of the system determines the maximum attainable yield of products under specified conditions. It is a fundamental principle of thermodynamics that changes in Gibbs free energy G , enthalpy H and entropy S depend only upon the initial and final states of the system, and not upon the path taken to move from one to the other. The kinetic parameters, rate coefficient k , activation energy E , order of reaction. These parameters depend sensitively on the path followed, and the introduction of a catalyzed pathway changes not only the values of these parameters, but also their significant. Classical kinetics based on collision theory is then really on little help, and theoretical discussion has necessarily to be based on the absolute rate theory. It must first be emphasized, and this is another implication of our definition, that a catalyst can increase the rate only of a reaction that is already thermodynamically as are unanalyzed reactions. Catalyst decreasing the activation energy of a reaction. This must mean that catalyzed reaction proceeds by a new and energetically more favorable partway.

It is possible to divide catalytic systems into two distinct categories, homogeneous catalysis and heterogeneous catalysis. With heterogeneous catalysis, concerns with the specific chemical properties of the surface of the chosen substance. These of course reflect the chemistry of the bulk solid, and some useful insight into the catalytic activities of surfaces is gained from knowledge of the bulk properties of the solid.

Table 3.1 presents a preliminary classification of solids into group. This table may be in part interpreted using the qualitative concept of compatibility between catalyst, reactants, and products.

Table 3.1 Classification of heterogeneous catalysts

| Class | Functions | Examples |
|-------------------------------------|---|--|
| Metals | hydrogenation dehydrogenation hydrogenolysis | Fe, Ni, Pd, Pt, Ag |
| Semiconducting oxides and sulphides | oxidation dehydrogenation desulphurization | NiO, ZnO, MnO ₂ , Cr ₂ O ₃ , Bi ₂ O ₃ -MoO ₃ , WS ₂ |
| Insulator oxides | dehydration | Al ₂ O ₃ , SiO ₂ , MgO |
| Acids | polymerization isomerization cracking alkylation | H ₃ PO ₄ , H ₂ SO ₄ , SiO ₂ -Al ₂ O ₃ , zeolites |

This table also shows that transition metals are especially good catalyst for reaction involving hydrogen and hydrocarbon. This is because these substances readily adsorb at the surfaces of metals, in a manner to be described in more detail below, and except in a few cases the reaction does not proceed below the surface.

3.2 Metal Catalysis^[14]

For a molecule to react catalytically at a metal surface, it must first be chemisorbed. When two molecules so react, at least one and probably both must be chemisorbed. Chemisorption is an essential step in the preparation of a molecule for reaction. : indeed a chemisorbed molecule sometimes resembles the product into which it will be transformed more than does the free molecule. The effect of chemisorption can

also be very like that of raising a molecule to its first electronically excited state; physical adsorption on the other hand has little direct relevance to catalysis.

For metals, relationships have been sought between collective properties and catalytic behavior. The metallic state was generally described by the simple band model or the Pauling valence structure theory, in metal the valence shell is formed by s or d band. The main-group elements with their s bands are typical electron donors and form strong bonds with electron acceptors such as sulfur or oxygen; stable sulfides and oxides are formed. These metals are therefore not suitable as catalysts. In contrast the transition metals with their d bands are excellent catalysts. It is noted worthy that both hydrogenations and oxidations can be carried out with d-block elements.

Let us now describe the electronic structure of the transition metals with the aid of the band model. According to this model the metal is a collective source of electrons and electron holes (Figure 3.1). In a row of the periodic table, the metals on the left have fewer d electrons to fill the bands. There are two regions of energetic states, namely, the valence band and the conduction band with mobile electrons or position holes. The potential energy of the electrons is characterized by the Fermi level, which corresponds to the electrochemical potential of the electrons and electron holes.

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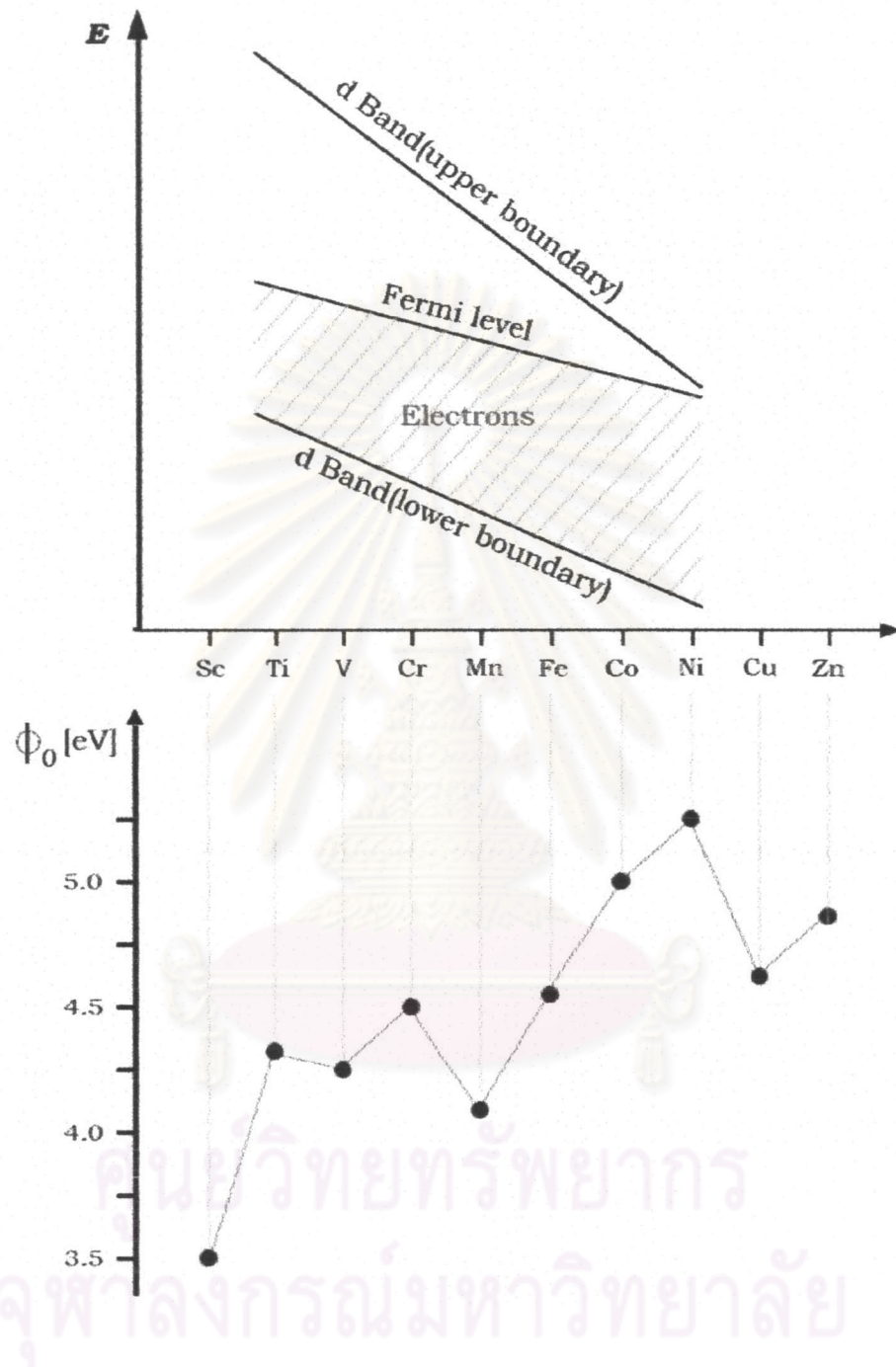


Figure 3.1 Electron density of the 3d band and work function ϕ_0 of the transition metals of the fourth period

The position of the Fermi level also indicates the number density of electrons in the band model. The energy required to transport an electron from the edge of the Fermi

level into vacuum corresponds to the work function ϕ_0 (Figure 3.3a). For the d-block metals, the work function is around 4 eV and therefore in the UV range. A certain number of free levels or d-holes are available for bonding with adsorbates. The lower the Fermi level, the stronger the adsorption. How do donors and acceptors function in the band model. In the surface layer, the free electrons or holes allow molecules to be bound to the surface, whereby the strength of binding depends on the position of Fermi level. An acceptor removes electron density from the conduction band of the metal as a result of which the Fermi level drops to E_F and the work function $\phi_A > \phi_0$ (Figure 3.3b). A donor donates electrons to the conduction band of the metal, and the work function becomes corresponding lower : $\phi_A < \phi_0$ (Figure 3.3c)

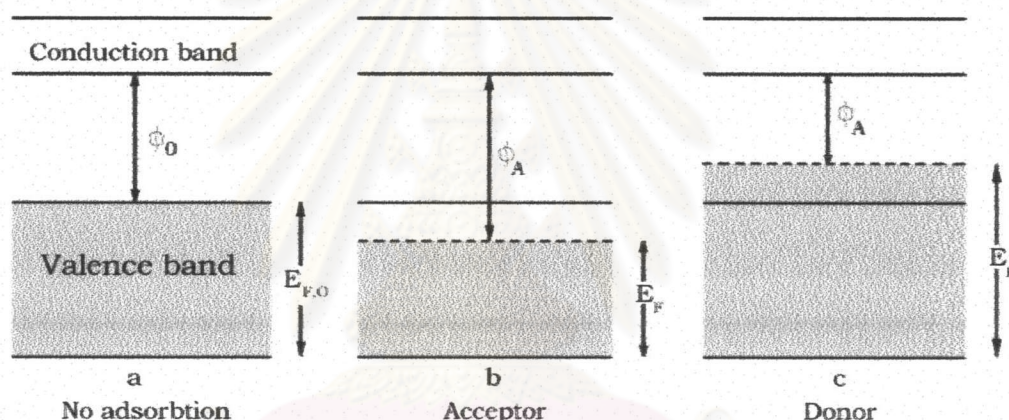


Figure 3.2 Acceptor and donor function according to the band model

a) No adsorption ; b) Acceptor ; c) Donor

$E_{F,0}$ = Fermi level ; E_F = Fermi energy

Metals normally have a narrow d band. The catalytic properties are strongly influenced by the occupational density of the electrons in this band. In many cases a direct relationship has been found between the catalytic activity of transition metals and the electronic properties of the unfilled d bands. This is shown by the general trend of the rate of adsorption along the transition metal rows. For molecular species strong binding is observed on the left-hand side of a row. For molecular species it was found that the rate of dissociative adsorption on the noble metals increases from right to left as

a function of the d-band occupation. Besides the electron occupation of the d bands, another description can be used for obtaining correlations, namely, the valence bond theory of metals. The bonding in transition metal is partially due to unpaired electrons in bonding d orbitals. The contribution of these d electrons to the valence bonding was termed "percentage d character" of the metallic bonding by Pauling, who made a distinction between three types of d orbitals in transition metals :

- Bonding d orbitals involved in covalent d s p hybrid bonds
- Metallic (free) d orbitals
- Atomic d orbitals

3.3 Catalyst Preparation and Manufacture ^[14]

Most catalyst are either a finely divided metal supported on a carrier such as alumina or silica, or a compound, more or less complex, either on a carrier or unsupported. Metal-sulfide catalysts are prepared first as the oxide and then treated with hydrogen sulfide or another sulfur compound in the presence of hydrogen to convert it to the sulfide. Either of two types of processes, generally termed the precipitation method and the impregnation method, is commonly used for making catalysts. The first involves in its initial stages the mixing of two or more solutions or suspensions of material, causing precipitation; this is followed by filtration, washing, drying, forming, and heating. Simple wet mixing without precipitation is occasionally used, but it may not provide the degree of intimate contact between species that is usually desired. High temperatures can subsequently be applied to provide homogeneity and compound formation by thermal diffusion and solid-state reaction, but this usually causes an undesired degree of sintering and consequent loss of surface area. Sometimes the desired degree of mixing can be achieved by kneading.

If a carrier is to be incorporated in the final catalyst, the original precipitation is usually carried out in the presence of a suspension of the finely divided support, or a compound or suspension that will eventually be converted to the support may be initially

present in solution. The final size and shape of the catalyst particles are determined by the forming process, which may also affect pore size and pore size distribution. Larger pores can be introduced into a catalyst by incorporating into the mixture 5 to 15 percent of wood flour, cellulose, starch or other material that can subsequently be burned out. Final catalyst material rejected for chemical or physical reasons may in some cases be recycled without harm to product specifications by powdering it and incorporating it into the catalyst mixture. Such incorporation, however, may change the pore size distribution of the final catalyst. With a gelatinous precipitate, mechanical manipulation may have a significant effect on the ultimate pore size distribution. After it is dried and formed, the precursor catalyst is activated; that is, it is converted into its active form through physical and chemical changes. This typically involves heating to cause calcination or decomposition, followed by reduction if a metallic catalyst is desired. In some cases a supported metal catalyst is pyrophoric, and reduction is carried out in the plant reactor rather than by the catalyst manufacturer to avoid hazards upon shipping and reactor loading. Some advantages of the precipitation method are that it generally provides more uniform mixing on a molecular scale of the various catalyst ingredients, the distribution of active species through the final catalyst particle is uniform, and the ultimate sizes and shapes are not limited to the forms in which desired carriers are available.

Also more control may be available over pore size and pore size distribution. If two or more metal compounds are present, in a batch-type operation they may precipitate at different rates or in sequence rather than simultaneously, thus affecting the final structure of the solid. Both the ultimate physical and chemical structure of the catalyst are frequently very sensitive to the pH of the precipitation, in which case precipitation is carried out continuously in a well-mixed vessel with careful control of pH. Impregnation is the easiest method of making a catalyst. A carrier, usually porous, is contacted with a solution, usually aqueous, of one or more suitable metallic compounds. The carrier is then dried, and the catalyst is activated as in the case of precipitated catalysts. The size and shape of the catalyst particles are that of the carrier. The impregnation technique requires less equipment since the filtering and forming steps

are eliminated and washing may not be needed. It is the preferred process in preparing supported noble metal catalysts, for which it is usually economically desirable to spread out the metal in as finely divided a form as possible. The noble metal is usually present in the order of 1 wt% or less of the total. This makes maximum use of a very expensive ingredient; in a precipitated catalyst some of the active ingredient may be enclosed by other material present and thus unavailable for reaction.

3.3.1 Precipitation Method of Catalysts

3.3.1.1 Precipitation

In a common procedure an aqueous metal salt solution is contacted with an aqueous alkali, ammonium hydroxide or ammonium carbonate, to cause the precipitation of an insoluble metal hydroxide or carbonate. These can be readily converted to oxides by heating. The starting compounds are generally chosen because of their availability and high water solubility, and in some cases to avoid introducing elements that may be deleterious in the final catalyst or that may cause difficulties in subsequent processing. Control of air and water pollution is also an important factor. NO_x from nitrates must be removed, for example by scrubbing with aqueous alkali; many heavy metals are more or less toxic and cannot be simply discharged. If the final catalyst is to be a supported metal, sulfate may be undesirable, since it can be reduced to a sulfide, which is a common poison for metal catalysts, the metal nitrate salt is often preferred because it usually is highly water soluble, generally available, and cheap, but NO_x control is required. An organic compound such as a formate or oxalate may be used, although these are more expensive and organic fragments from their decomposition on heating may adsorb on the catalyst to cause partial inactivation. Also, the average ultimate metal particle size may be considerably different if it is formed by decomposition of a compound rather than by reduction of an oxide. Sulfates and chlorides are generally water-soluble, but the anions must usually be removed by washing, and disposal of waste water may be a problem. A preferred base is usually

ammonium hydroxide since it leaves no cation residue, but it may complex with some metals and keep them in solution.

If a relatively crystalline precipitate is formed, the size of crystals may affect the ultimate particle size of a supported metal catalyst. Thus, fine crystals may be desired to produce high surface area of a supported metal catalyst, but crystals that are too fine may be difficult to filter. The size of such crystals may be controlled by a variety of techniques. In a multi component catalyst, crystals may be smaller if the metals are truly coprecipitated rather than precipitated in sequence. Crystal size may also be affected by temperature and by stirring, since this affects nucleation and the degree of supersaturating. Ripening, in which a precipitated is allowed to stand for a period, can allow for re-crystallization in which small and/or amorphous particles dissolve and crystalline particles grow. This may convert a gelatinous precipitate to a more crystalline and filterable solid.

Silicic acid and a number of metal hydroxides, e.g., those of aluminum, iron, and titanium, form gelatinous colloids, this can make them extremely difficult to filter or to purify by washing. Such gels may be coagulated by electrolytes, but the process of washing to remove electrolyte impurities may cause them to re-disperse into colloidal solution, termed peptization. Hence, a silicic acid gel may be washed with dilute hydrochloric acid, or an aluminum hydroxide gel with aqueous ammonium nitrate, to maintain an ionic environment and hence the coagulated form. The additives can be subsequently removed by heating, gels readily occlude ionic impurities, which may be difficult to remove by washing. The possibility of reaction between carrier and reagents should also be considered in this step. Thus, acidic solutions of reagents may react with basic carriers, and vice versa.

3.3.1.2 Forming operations

The nature of the forming operations is determined by a balance among several factors, including rheological properties of the mixture, and the necessity to

achieve satisfactory strength, an open-pore structure, and high activity in the ultimate catalyst, in addition to economics. Relatively hard materials, which typically have high melting points, cannot be made into pellets without suitable additives. Operations causing an increase in crushing strength usually also decrease pore volume and average pore size, and hence may cause diffusion limitations. Typically, commercial catalysts have a void fraction of about 0.5 cm^3 of voids per cubic centimeter of porous pellet.

3.3.1.3 Calcination

This may have several purposes. One is to eliminate extraneous material such as binders and die lubricants, as well as volatile and unstable anions and cations that have been previously introduced, but are not desired in the final catalyst. Second, a substantially elevated temperature is usually needed to increase the strength of the final pellet or extruded by causing incipient sintering. Excessive sintering will reduce the catalyst activity by reducing surface area, and it may also cause diffusion limitations by reduction of pore size, so an optimum is desired. If a metallic catalyst is the ultimate goal, conversion to the oxide form is frequently sought prior to reduction. If a complex catalyst is the goal, a substantially elevated firing temperature may be required to cause mixing by diffusion of individual species to form a desired compound or crystal phase. In any event, the catalyst should be heated under controlled conditions to a temperature at least as high as will be encountered in the plant reactor to removed bound water, carbon dioxide, etc. If these decompositions occur to a significant extent in the plant, they may cause structural weakness in pellets, leading to breakup, dusting, and so on, that may cause excessive pressure drop and premature reactor shutdown.

For small production runs, conventional batch-type multi tray dryers and calciners are common, but labor costs are high. For larger production runs, a continuous rotary, kiln may be used. More precise temperature control is achievable with a continuous tunnel kiln. This may be heated electrically with numerous zones so that temperature rise can be programmed. Trays may be fastened onto a stainless steel

mesh belt and automatically loaded and dumped, or trays may be placed and removed manually.

Upon heating pellets in a tray calciner, an exothermic reaction may develop that can lead to excessively high temperature locally, affecting the catalyst adversely. The effect can stem from an exothermic decomposition reaction, as in the thermal decomposition of an ammonium copper chromate to form a "copper chromite" catalyst or by reactions among pellet ingredients, such as that between a metal nitrate and organic admixtures such as cellulose, graphite, or stearates. Combustion in air of these organic substances or of remaining organic solvents may also occur. The effect is most pronounced with thick layers of pellets from which heat generated internally cannot easily escape. It may be controlled by using a slower rate of heat up or using thinner layers of pellets, although it may be necessary to use layers as thin as 1/8 inch or so.

3.3.1.4 Reduction to the metal

Most commonly, a metal is formed by reduction of the oxide at an elevated temperature by contact with flowing hydrogen or hydrogen diluted with nitrogen, the latter for safety reasons. A considerable excess of hydrogen may be required to sweep away the product water. If present in too high a concentration, water vapor may accelerate the sintering of an oxide, and it can also retard the rate of the reduction reaction by forming a hydroxylated surface.

Some metal compounds can be reduced by chemical reagents, such as formaldehyde, formic acid, or hydrazine, but these methods are usually more expensive. Alternately, the metal may be formed by decomposition of an organic compound, as by decomposition of nickel formate to yield deposited nickel. In this case, however, organic fragments may become adsorbed onto the metallic catalyst, possibly giving rise to considerably different properties than that of a catalyst reduced in hydrogen. Moreover, the ultimate metal particle size is determined by the sintering characteristics of the metal produced, whereas in oxide reduction, particle size may be determined in part, in a

rather complicated way, by the formation of metal nuclei and their growth from the oxide particles.

3.3.2 Impregnation

Two methods of contacting may be distinguished. The support is sometimes dipped into an excess quantity of solution, whereupon the uptake is the sum of solution occluded in the pore plus material adsorbed on the pore surfaces. If two or more compounds are present, they are frequently adsorbed on the support surface in a ratio different from that in the solution and solution concentrations also change with continued contacting. Additions to the solution must take these effects into account. Moreover, material may be dissolved from the support into the treating solution. More precise control is achieved by a technique termed dry impregnation, or impregnation to incipient wetness, which is commonly used industrially. A batch of the support is tumbled and sprayed with a solution of appropriate concentration, corresponding in quantity to the total known pore volume of the support, or slightly less. This allows accurate control of the amount of the active ingredient that will be incorporated into the catalyst, but the maximum loading obtainable in a single impregnation is limited by the solubility of the reagent. The resulting catalyst is then usually dried and calcined.

In a few cases, the active ingredient may be fixed inside the catalyst by immersing the impregnated catalyst in a reagent to cause precipitation to occur. Oxide supports such as alumina and silica are readily wet by aqueous solutions, as are most activated carbons, which have a layer of chemisorbed oxygen on them. Capillary forces then ensure that liquid is sucked into the entire porous structure. Because of capillary pressure, even pores closed at one end are nearly filled, and the solution of gas in the liquid assists the process. If the support is not readily wetted, e.g., a carbon that is highly graphitized or without chemisorbed oxygen, an organic solvent may be used or the support may be impregnated under vacuum. These procedures are somewhat more costly to use in the plant than incipient impregnation.

3.3.2.1 Distribution through pellet

Most metal reagents are adsorbed to varying degrees on most supports, but the characteristics of the process are complicated since various types of adsorption are possible. Silica and zeolites are acidic and adsorb cations. Alumina is amphoteric. Titania is also amphoteric, but more acidic than alumina. For these adsorbents the relative adsorption of cations and anions can be controlled by adjusting pH. Metal ions may be cation-exchanged with a surface containing hydroxyl groups or containing alkali or alkaline earth-metal ion, or they may be held by coordination. The surface structure of the carrier may also be altered by the impregnation procedure, thus changing its adsorption characteristics. The ultimate degree of dispersion of metal through the catalyst pellet is also determined by the interplay of a large number of factors whose relative importance varies with circumstances. These include the method of impregnation, the strength of adsorption, the extent to which the metal compound is present as occluded solute (that in the bulk liquid in the pores) in contrast to adsorbed species on pore walls, and the chemical reactions that occur upon heating and drying.

The situation may be further complicated by attack on the support. Silica gel is attacked at high pH, and alumina, which is amphoteric, is attacked at a pH that is either too high or too low. Indeed, during the impregnation of an alumina support with an acidic liquid, some solution of alumina may first occur, followed by precipitation as the pH increases. It may be desirable to control this effect by using a buffer. It is also possible to control the deposition by competitive adsorption, e.g., by adding a citrate to the impregnation solution. This procedure has been used to embed a catalytically active layer slightly inside a catalyst particle. Such a structure may be desired for prolongation of catalyst life in an application in which poisons are deposited on the outside surface of a porous catalyst support. An example is supported platinum catalysts for oxidation of pollutants in automobile engine exhaust. In general, use of the dipping method with a great excess of solution should lead to an essentially uniform deposit of adsorbed material if sufficient time is allowed for diffusion of reagent species to the interior and if

side reactions are unimportant. If adsorption is initially non uniform and not too strong, redistribution continues even after the pellet is removed from solution, leading to a more uniform distribution. The dry process can also effect the distribution of an active ingredient. The crystallite size of a resulting supported metal catalyst may also be altered if a considerable portion of the soluble metal is occluded rather than adsorbed. Again, the effects are complex, and little can be said of general guidance. Initially, evaporation occurs at the outer surface of the particle, but liquid evaporated from small pores will be replaced by liquid drawn from large pore by capillarity. The places where crystallization begins and the ultimate distribution of metal depend on such factors as the initial degree of saturation of the liquid, the rate of nucleation, the rate of heating, connectivity (the degree of connection of liquid paths between pores) at the time of crystallization, and the possibility of surface migration. Commercially available impregnated catalysts are usually found to have a higher concentration of metal at the outside than at the center, even when a more or less uniformly deposited catalyst is desired.

3.4 Catalyst Support^[14]

The early concept of a support or a carrier was of an inert substance that provided a means of spreading out an expensive catalyst ingredient such as platinum for its most effective use, or a means of improving the mechanical strength of an inherently weak catalyst. However, the carrier may actually contribute catalytic activity, depending on the reaction and reaction conditions, and it may react to some extent with other catalyst ingredients during the manufacturing process. It can also help stabilize the catalytically active structure. The carrier may be used as pellets or powders to be impregnated, a powdered incorporated into a mixture to be precipitated, or the carrier may itself be precipitated from solution in the manufacturing process. Some substances such as colloidal alumina or colloidal silica may play a double role, acting as a binding agent in catalyst manufacture and as a carrier in the ultimate product. Alumina in the γ form is intrinsically weakly acidic, but such a substance may be a truly inert carrier for many reactions. In other cases it can be used by itself as a catalyst, as in dehydration of

an alcohol. High-area carriers are sometimes loosely referred to as active carriers in contrast to low -area inert carriers, but this usage may be misleading.

The selection of a carrier is based on its having certain desirable characteristics. In addition to possible chemical effects certain physical properties are important:

1. Inertness to undesired reaction.
2. Desirable mechanical properties, including attrition resistance, hardness, and compressive strength.
3. Stability under reaction and regeneration conditions.
4. Surface area (high surface area is usually, but not always, desirable).
5. Porosity, including average pore size and pore-size distribution (high area implies fine pores, but relatively small pores, such as < 2 nm, may become plugged in catalyst preparation, especially if high loading are sought).
6. Low cost.

3.3.1 Activated carbon ^[15]

If a carbonaceous material such as coal, lignite, wood, or petroleum pitch is heated in the absence of air, much of the substance devolatilizes, leaving behind a porous structure of carbon that usually also contains some hydrogen. This may then be activated by controlled oxidation with steam or carbon dioxide to further open up the pores and increase total surface area. The activated carbon may contain up to about 10% by weight of oxygen, which may cover a large fraction of the surface as chemisorbed oxygen in the form of ketones, hydroxyls, or carboxylic acids. These can cause its adsorptive properties to be considerably different than a carbon heated in inert gas or under reducing conditions. The surface area can range up to $1,200 \text{ m}^2/\text{g}$.

Activated carbon is a processed carbon material with a highly developed porous structure and a large internal specific surface area. If you take a look

at a cross section of an activated carbon particle, it looks like a beehive. It consists, principally of carbon (87 to 97%) but also contains such element as hydrogen, oxygen, sulfur and nitrogen, as well as various compounds either originating from the raw material used in its production or generated during its manufacture. Activated carbon has the ability to absorb various substances both from the gas and liquid phases. It is widely used for adsorption of pollutants from gaseous and liquid steam, for recovery of solvent and as a catalyst or catalyst support. In the nuclear industry, activated carbon is used for adsorption of iodine and nobles gases from gaseous effluents. One of the most important fields in terms of consumption is in water and waste water treatment. To obtain these activated carbons from cheap and readily available raw materials for the production of activated carbon such as wood, peat, coconut, shell, coal.

3.3.1.1 Production of activated carbon

Activated carbon is usually produced by the carbonization and activation of carbonaceous materials.

- Carbonization (or pyrolysis)

The carbonaceous material that constitutes the basis for the production of activated carbon by the steam-gas method must meet certain requirements among which the most important are: (i) low content of volatile matter, (ii) high content of elemental carbon, (iii) definite porosity and (iv) sufficient strength of attrition. Of course, raw materials do not meet all these requirements simultaneously and therefore they require carbonization.

This is one of the most important steps in the production process of activated carbons since it is in the course of carbonization that the initial porous structure is formed. During carbonization most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting material, and the freed atoms of elementary carbon are grouped into organized

crystallographic formations known as elementary graphitic crystallites. The mutual arrangement of the crystallites is irregular, so that free interstices remain between them and apparently as the result of deposition and decomposition of tarry substances, these becomes filled or at least blocked by disorganized ("amorphous") carbon. These are three clear stages in the carbonization process: (a) loss of water in the 27-197 °C range: (b) primary pyrolysis in the 197-497 °C range with evolution of most gases and tars with formation of the basic structure of the char: (c) consolidation of char structure at 497-847 °C with a very small weight loss.

The resulting carbonized product has only a very small adsorption capacity. Presumably, at least for carbonization at lower temperature (400-600 °C), part of the tar remains in the pores between the crystallites and on their surface. A carbon with a large adsorption capacity, however, can be produced only by activating the carbonized material under such conditions that the activation agent (steam, carbon dioxide, etc.) reacts with the carbon.

- Activation

There are two main types of production of activated carbon:

a) By carbonizing material with the addition of activating agents (ZnCl_2 , CaCl_2 , H_3PO_4). This method is generally known as "chemical activation".

b) By allowing the inactive carbonized product (prepared by the usual methods of carbonization) to react with oxidizing gases (steam, carbon dioxide, oxygen). This method is generally known as "physical activation".

a) Chemical activation

The common chemicals used are dehydrating agent such as ZnCl_2 , CaCl_2 , MgCl_2 and some acid such as H_3PO_4 and H_2SO_4 . The activated agent influences the pyrolytic processes so that the formation of tar is restricted to minimum and the amount of the aqueous phase in the distillate is also less than that in the normal

carbonization. The activation agent also changes the chemical nature of the cellulose substrate by dehydration, which decomposes the organic substances by the action of the action of heat and prevents the formation of tar.

Chemical activation is usually carried out at temperatures from 400-600 °C. These temperatures are lower than those needed for activation with gaseous agent (physical activation). An important factor in chemical activation is the degree (coefficient) of impregnation; this is the weight ratio of the anhydrous activation salt to the dry starting material. The effect of the degree of impregnation on the resulting product is apparent from the fact that the volume of salt in the carbonized material equals the volume of pores which are freed by its extraction. For small degree of impregnation the increase in the total pore volume of the product which increases in the degree of impregnation is due to the increase in the number of small pores. When the degree of impregnation is further raised, the number of large-diameter pores increases and the volume of the smallest decreases.

b) Physical activation

The basic method of activating coal-based granules consists of their treatment with oxidizing gases (steam, carbon dioxide, oxygen) at elevated temperatures. In the activation process, carbon reacts with the oxidizing agent and the resulting carbon oxides diffuse from the carbon surface. Owing to the partial gasification of the granules or grains, a porous structure builds up inside them. The structure of the carbonization product consists of a system of crystallites similar to those of graphite bonded by aliphatic type bonds to yield a spatial polymer. The spaces between the neighboring crystallites constitute the primary porous structure of the carbon. The pores of the carbonized granules are often filled with tar decomposition products and are blocked with amorphous carbon. This amorphous carbon reacts in the initial oxidation step, and as a result the closed pores open and new ones are formed.

In the process of further oxidation, the carbon of the elementary crystallites enters into reaction due to which the existing pores widen. Deep oxidation leads to a reduction in the total volume of micropores due to the burning off of the walls between the neighboring pores, and in consequence the adsorptive properties and mechanical strength of material decrease. In the first stage of activation, when burn-off is of not higher than 10% (which occurs at low reaction times), this disorganized carbon is burnt out preferentially and the closed and clogged pores between the sheets are freed. In the course of further activation at the second stage, carbon of the aromatic sheet is burnt. When the burn-off is less than 50%, a microporous activated carbon is obtained, when it is large than 75% (which occurs at high reaction times) a macroporous product is obtained; and when the burn-off is between 50 and 75%, the product is of mixed structure and contains both micropores and macropores. Development of macropores due to coalescence or widening of micropores under fast reaction conditions. Carbon oxidation is a complex heterogeneous process encompassing the transport of reagents to the surface of the particles, their diffusion into the pores, chemisorption on the pore surface, reaction with carbon, desorption of the reaction products, and diffusion of these products to the particle surface. The concentration profile of the oxidizing agent of the granule volume, and hence the formation of the carbon porous structure, depends of the rate of the particular steps of the process.

At low temperatures the rate of the chemical reaction of carbon with the oxidizing agent is slow, so it is this reaction that limits the overall rate of the process. This results in a dynamic equilibrium becoming established between the concentration of the oxidizing agent in the pores and that in the interparticle spaces. In such a case the activation process yields a homogeneous product with a uniform distribution of the pores throughout the whole volume of the granule, with increase of the oxidation temperature.

The rate of the chemical reaction increases much faster than that of diffusion, and then the overall rate of the process becomes limited by the rate of transport of the oxidizing agent into the granule. At very high temperatures the oxidation

reaction rate becomes so high that the whole oxidizing agent reacts with carbon on the external surface of the granule. In such a case significant losses of the material occur due to superficial burn-off, and the porous structure is not formed. The rate of the oxidation process is limited by the reactivity of the initial carbonaceous material towards the oxidizing agent. The greater is the reactivity of the substrates, the lower the optimal temperature of the process at which uniform formation of pores in the granule.

- Pyrolysis and steam activation

Normally the production of activated carbons involves two stages: the carbonization of the raw materials followed by high temperature activation, at 800-1,000 °C, of the resulting chars. The method used in this study combines the two stages into a single one, while the treatment temperature is considerably lower, 600-800 °C. This method is preferable to the two-stage treatment from an economic point of view. During the pyrolysis and steam activation of carbon-containing materials the following main processes take place:

- Oxidation-thermolytic conversion of the carbon material leading to the accumulation of oxygen containing groups.
- A thermal destruction process including the decomposition of the oxygen-containing groups accompanied by the formation of carbon oxides and water.
- Condensation processes.
- Deeper penetration of the water molecules and opening up of the initially closed pores into the structure of the carbon materials.

3.3.1.2 Molecular, crystalline and porous structure of activated carbon

The graphite-like microcrystalline structure is the basic structural unit of activated carbon, as in the case of carbon black. The ordering of carbon atoms in an elementary microcrystallite indicates considerable similarity to the structure of pure graphite, the crystals of which consist of parallel layers of condensed regular hexagonal

ring space 0.335 nm. apart. Such interlayer spacing is diagnostic of interaction by means of Van Der Waals forces. The length of the carbon-carbon bond in individual layers is 0.142 nm. Each carbon atom bonds with the three adjoining ones by means of covalent bonds, and the fourth delocalized π -electron may move freely in a system of conjugated double bonds of condensed aromatic ring. The scheme of arrangement of the carbon atoms in crystal of graphite. The formation of the crystalline structure of activated carbon begins early during the carbonization process of the starting material. Then sets a condensed aromatic ring of various numbers, which are the nascent center of graphite-like microcrystallites, are formed. Although their structure resembles that of a crystal of graphite there exist some deviations from that structure. Thus, among other things, the interlayer distances are unequal in crystals of activated carbon and range from 0.34 to 0.35 nm. Again, the orientations of the respective layers generally display deviations. Such deviations from the ordering characteristic of graphite, called a turbostratic structure. Disordering of the crystal lattice may be caused to a considerable degree both by its defects (vacant lattice sites) and by the presence of built-in heteroatoms. It is resulted from the kind of the raw material used, the nature and quantity of its impurities as well as the methods and conditions of the production processes of the active carbon. The average activated carbons have a strongly developed internal structure (the specific surface often exceeds 1000 and sometimes even 1500 m²/g), and they are usually characterized by a polydisperse capillary structure, featuring pores of different shapes and sizes. Bearing in mind the values of the effective radii and the mechanism of adsorption of gases, Dubinin proposed three main types of pore, namely macropores, mesopores and micropores.

Macropores are those having effective radius ≥ 100 -200 nm and their volume is not entirely filled with adsorbate via the mechanism of capillary condensation (it may occur only for a relative pressure of adsorbate of nearly one). The volumes of macropores are usually in the range 0.2-0.8 cm³/g and the maximum of volume distribution curves according to the radii are usually in the range 500-2000 nm. The values of their specific surface area not exceeding 0.5 m²/g are negligibly small when compared with the surface of the remaining type of pore. Consequently macropores are

most of great important in the process of adsorption as they merely act as transport arteries rendering the internal parts of the carbon grains as accessible to the particles of adsorbate.

Mesopores, also known as transitional pores, have effective radii falling in the range of 1.5-1.6 nm to 100-200 nm. The process of filling their volume with adsorbate take place via the mechanism of capillary condensation. For average activated carbons, the volumes of mesopores lie between the limits 0.1-0.5 cm³/g and their specific surface area in the range of 20-100 m²/g. The maximum of the distribution curve of their volume versus their radii is mostly in the range of 4-20 nm. Mesopores, beside their significant contribution to adsorption, also perform as the main transport arteries for the adsorbate.

Micropores have sizes comparable with those of adsorbed molecules. Their effective radii are usually smaller than 1.5-1.6 nm and for average activated carbons their volumes usually lie between 0.2-0.6 cm³/g. The energy of adsorption in micropores is substantially greater than that for adsorption in mesopores or at the non porous surface, which cause a particular large increase of adsorption capacity for small equilibrium pressure of adsorbate. In micropores, adsorption proceeds via the mechanism of volume filling. For some activated carbon, the microporous structure may have a complex nature, e.g. two overlapping microporous structure: firstly one for effective pore radii smaller than 0.6-0.7 nm and termed specific micropores, and the secondly one exhibiting pore radii from 0.6-0.7 to 1.5-1.6 nm termed supermicropores.

3.3.1.3 Chemical nature of the surface of activated carbon

The chemical nature of activated carbons significantly influences their adsorptive, electrochemical, catalytic, acid-base, redox, hydrophilic-hydrophobic, and other properties. It is determined decisively by type, quantity and bonding of various heteroatoms, especially oxygen. Heteroatoms may be combined both with peripheral carbon atoms at the corners and edges of crystallites and in intercrystalline spaces and

even in defect zones of particular planes constituting the crystallites. Most heteroatoms are grouped at the surface of activated. Apart from their different locations, the heterotoms are strongly differentiated in terms of their chemical reactivity. Surface-bound heteroatoms are believed to adopt the character of the functional groups typical for aromatic compounds. The surface functional groups often consist of more than one type of heteroatom, e.g. oxygen and hydrogen together as -OH or -COOH. Surface functional groups can originate from the starting material from which a particular activated carbon is produced.

Substantial quantities of oxygen can be introduced during the production process itself, e.g. during activated carbonaceous materials by oxidizing gases, such as water vapor and air. Activated carbon used predominantly for practical purposes generally includes some percentage by weight of chemically-bond oxygen and usually much smaller quantity of hydrogen combines with surface carbon atoms either directly or through oxygen.

3.3.1.4 Estimation of the properties of activated carbon

The commercial use of activated carbons, their transport, storage and sales require knowledge of the properties of these materials. The methods for estimating these properties are approved by the members of the activated carbons sector group of the European Council of Chemical Manufactures' Federation (CEFIC). The tests require highly professional laboratories and advanced equipment. Most of the testing methods have been developed and by approved such organizations as the American Society for Testing Material (ASTM), the American Water Works Association (AWWA), the Deutsches Institute for Normung e.V. (DIN), or the International Organization for Standardization (ISO).

- B.E.T. Surface area

To measure total surface area, nonspecific physical adsorption is required, but even with physical adsorption the isotherm varies somewhat with the nature of the adsorbent (the solid). Most physical adsorption isotherms may be grouped into five types, as originally proposed by Frunauer, Deming, Deming and Teller (BDDT). More recently, the grouping has generally been termed the Brunauer, Emmett, and Teller (BET) classification. In all cases the amount of vapor adsorbed increase as its partial pressure is increased, becoming at some point equivalent to a monolayer, but then increasing to a multilayer, which eventually merges into a condensed phase as the relative pressure, P/P_0 approaches unity.

- Bulk density. The bulk density is defined as the mass per unit volume of the activated carbon sample in air including both the pore system and the void between the particles. The bulk density of activated carbon, depending on the shapes, sizes and densities of the individual particles is indispensable for determining the size of unit packages.

- Adsorption test

The adsorption properties of activated carbons are generally estimated by determining the isotherms of adsorption from the liquid phase. The determination of the adsorption of one test substance from an aqueous solution is often insufficient for characterizing the adsorption properties of carbon. Thus the properties of activated carbons are estimated by comparing the result of measurements for different adsorbates, e.g. by comparing the adsorption of fairly large molecules of methylene blue or iodine.

- Iodine adsorption. The study of the process of iodine

Adsorption and also the determination of the iodine number is a simple and quick test for estimating the specific surface area of activated carbon. The iodine number is defined as the number of milligrams of iodine adsorbed by 1 g of activated carbon from an aqueous solution when the iodine concentration of the residual filtrate is 0.02 N. If the final values obtained are different from 0.02 N but lie in the range of 0.007-0.03 N, appropriate corrections are necessary. In this method it is assumed that iodine at the equilibrium concentration of 0.02 N is adsorbed on the carbon in the form of monolayer, and this is the reason why there is a relationship between the iodine number of activated carbon and its specific surface area which may be determined, for example, by the BET method. The specific areas of activated carbons with highly developed microporous structures as determined by the iodine number method are too low. This is because iodine is adsorbed chiefly on the surface of pores much larger than 1 nm, while in activated carbons with large specific surface areas the proportion of very fine pores inaccessible to iodine molecule is significant.

- Methylene blue adsorption.

The methylene blue value gives an indication of the adsorption capacity of activated carbon for molecules having similar dimensions to methylene blue, it also gives an indication of the specific surface area of the carbon which results from the existence of mesopores of dimensions greater than 1.5 nm.

- Volatile matter content.

The international standard used for determination of volatile matter in hard coal and coke is also applicable to activated carbon. A sample of powdered (< 0.1 mm.) activated carbon is heated at 950 ± 25 °C for $7 \text{ min} \pm 10 \text{ s}$. Volatile matter content is determined by establishing the loss in mass resulting from heating an activated carbon sample under rigidly controlled conditions.

- Moisture content.

A simple method of determining the water content is drying activated carbon in a dryer. The sample of powdered (1-2 g) or granule (5-10 g) carbon is dried at 150 °C to constant weight (usually about 3 hr.). The weight loss is expressed as a percentage of the weight of the original sample.

- Ash content.

The ash content in various types of activated carbon varies over a wide range, depending primarily on the type of raw material. The relative ash content also increases with increase in the degree burning of the coal during activation. Ash consist mainly of oxides and in smaller amounts, of sulfates, carbonates, and other compounds of iron, aluminum calcium, sodium, potassium, magnesium and many other metals. Depending upon the type of raw material, it may comprise different and often fairly large quantities of silicon. The commonly used method of removing ash is to leach activated carbon with acids. Due to the complex composition of ash, mixture of acids, e.g. hydrochloric or hydrofluoric acid, are often used if ash contains substantial quantities of silicon. The ash content of activated carbon can be determined by ignition of the crucible in an electric muffle furnace. Ignition is conducted at 650 ± 25 °C for 3 to 16 hr., depending on the type activated carbon and dimensions of its particles, to constant mass. The weight of the ashed carbon is expressed as a percentage of the weight of the original carbon sample.

3.3.1.5 Uses of activated carbon

The advantage of using activated carbon is that in certain circumstances a single stage of adsorption may replace several and physical separations or it may permit separation of compounds of the same boiling point. As states earlier, activated carbon are used mainly in the purification and decolorization of

liquids and as such are used mostly in powder form and derived from cellulose raw materials (about 85% of total use). Some the advantages of using activated carbon are listed below:

Dry cleaning solvent. With the increase in dry cleaning in recent years, particularly in coin-operated machines, the need has arisen for convenient on the spot method of purifying the solvent which with the passage of time become contaminated with oils and grease. These become rancid as well as dark colored and impart obnoxious odors to the cleaning liquid. The odors are reduced but not eliminated by distillation of the solvents. Activated carbon has proved to be effective in decolorizing and deodorizing.

Sugar. The main action of the carbon is in decolorization but it also removes nitrogenous substance and lyophilic colloids. By doing so it improves filtration, reduces foaming during evaporation and increase the speed of crystallization. When saturated the carbon is removed and regenerated by heating in steam and air at a red heat.

Water. Water is usually treated with chlorine to destroy bacteria but this can at times impart an unpleasant taste, which is especially marked when the chlorine has reacted with micro-organisms and with phenol. The bad taste becomes very noticeable when the supplying river is at a low level but it can be removed by treating the water with activated carbon. This should be an increasing market, particularly if the cost of activated carbon can be reduced.

Tyres. It has been found that white wall tyres retain their whiteness better if activated carbon is incorporated in the reinforcing carbon black.

Pharmaceuticals. Activated carbon has the property of concentrating the active component from a broth. The desired component can be recovered from the carbon by solvents. Penicillin was the first to be treated on a large scale by this method.

With the increasing emphasis being placed on pollution by effluents it would seem that activated carbon may play an important part in reducing this problem.

Foodstuffs. Here activated carbons are used to remove soaps and peroxides from edible fats to prevent poisoning of hydrogenation catalysts. They also improve color and flavor, e.g. in soup stocks and vinegar, and improve the storage properties of freshly distilled whisky.

Gas phase carbons. These should have the following properties : (i) high absorptive capacity; (ii) high retention; (iii) high selectivity in the presence of water vapor; (iv) low flow resistance; (v) high resistance to breakage; (vi) complete release of vapor at increased temperature and decrease pressure.

3.4 Mechanism of Cracking Processes^[13,15]

3.4.1 Thermal cracking

Thermal cracking, where free radicals (lacking one hydrogen atom on carbon atom in the hydrocarbon molecule) are intermediate species which cracked by a β -scission mechanism.

The most successful present explanation of thermal cracking of hydrocarbon is Rice free radical theory as modified by Kossiakoff and Rick. This will be called the "RK-theory" as follows to explain the cracking of normal paraffin:

The normal paraffin molecule loses a hydrogen atom by collision and reaction with a small free hydrocarbon radical or a free hydrogen atom, thereby becoming a free radical itself. This radical may immediately crack or may undergo radical isomerization prior to cracking. Radical isomerization presumably occurs through a coiled configuration of a single radical, in which the hydrogen donor and acceptor carbon atom much closely approach each other. Radical isomerization is a change of

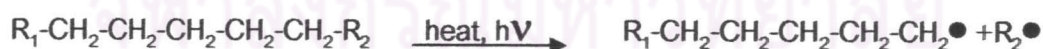
the position of hydrogen atom, usually to yield a more stable radical in order of tertiary > secondary > primary free radical.

Cracking of either the original or isomerized radical then takes place at a carbon-carbon bond located in the β position to the carbon atom lacking one hydrogen atom. Cracking at the β position gives directly an alpha olefin and a primary radical (lacking one hydrogen atom on primary carbon atom); in this step no change of position of any hydrogen atom with respect to the carbon skeleton.

The primary radical derived from this step may immediately recombine at the β bond to give ethylene and another primary radical, or it may first isomerize. In the absence of radical isomerization, only primary radicals are derived from cracking reaction of normal paraffin; primary radicals thus give only ethylene as the olefin product. Radical isomerization reduces the amount of ethylene, but it still remains the major product. By successive recombination, the radicals ultimately are reduced to methyl or ethyl fragments. These radicals then react with feedstock molecules to produce new free radicals and are themselves converted to methane or ethane. Thus, cracking is propagated as chain reaction

An example schematic representation of polyolefin cracking is as follows:

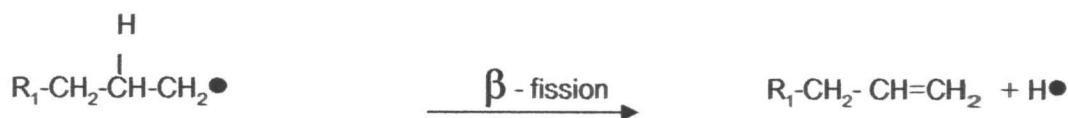
1. Initiation Step



2. Propagation Step

2.1 β -fission





2.2 Chain Transfer



3. Termination



3.4.2 Catalytic cracking

Catalytic cracking is the most important and widely used refinery process for converting heavy oil more valuable gasoline and lighter product. Originally cracking was accomplished thermally but the catalytic process has almost completely replaced thermal cracking because of more gasoline having a higher octane and less heavy oil and unsaturated gases are produced.

A major difference between thermal and catalytic cracking is that reactions through catalytic cracking occur via carbonium ion intermediate, compared to the free radical intermediate in thermal cracking. Carbonium ions are longer-lived and accordingly more selective than free radicals.

There are two possibilities for the initial step in the catalytic cracking of polyolefin. The most involves the simultaneous loss of a hydride ion from the polyolefin

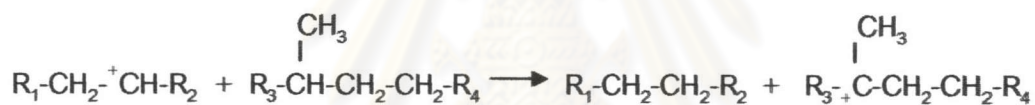
molecule and of a proton from the acidic catalyst surface. This produces a carbonium ion in combination with acid anion and molecular hydrogen:



Alternatively a small amount of olefin, created by thermal cracking could initiate the reaction:



Chain propagation involves an exchange reaction in which a carbonium ion reacts with a polyolefin to give a new hydrocarbon and a carbonium ion of the polyolefin to be cracked (hydride transfer).



The next step is the decomposition of the activated molecule. The primary rule involved is that the carbon-carbon cleavage occurs at the position one carbon atom away from the carbonium ion, i.e. β -scission:

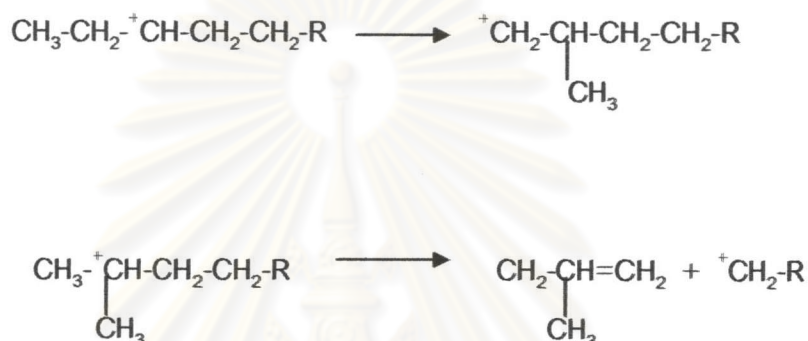


A hydride shift then converts the primary carbonium ion formed into a secondary carbonium ion:



Subsequent steps involve further β -scission and hydride transfer and proceed until the chain becomes so short that cracking at the β position is no longer a rapid reaction.

Large amounts of iso-compounds are formed in catalytic cracking. This is readily explained by the rearrangement of the secondary carbonium ion:



3.4.3 Hydrocracking

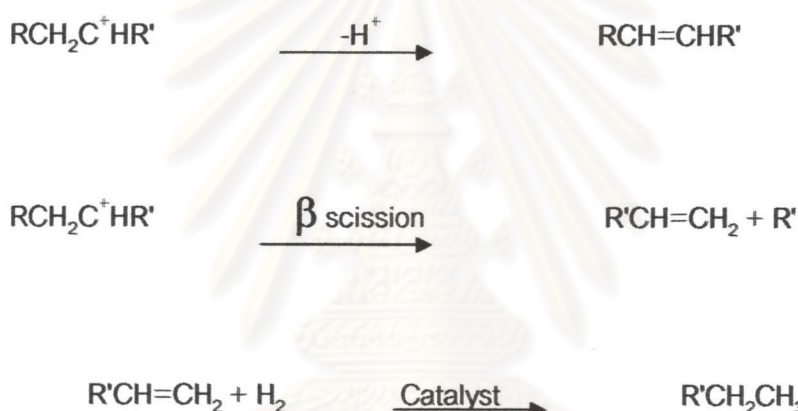
Hydrocracking is essentially catalytic cracking in the presence of hydrogen. It is one of the most versatile petroleum refining schemes adapted to process low value stocks. Generally, the feedstocks are not suitable for catalytic cracking because of their high metal, sulfur, nitrogen, and asphaltene. The process can also use feeds with high aromatic content.

The dual-function catalysts used in hydrocracking provide high surface area cracking sites and hydrogenation-dehydrogenation sites. Catalysts with strong acidic activity promote isomerization, leading to a high iso/normal ratios. The hydrogenation-dehydrogenation activity, on the other hand, is provided by catalysts such as iron, cobalt, molybdenum, tungsten, vanadium, palladium, or rare earth elements. As with catalytic cracking, the main reactions occur by carbonium ion and beta scission, yielding two fragments that could be hydrogenated on the catalyst

surface. The main hydrocracking reaction could be illustrated by the first step formation of a carbonium ion over the catalyst surface:



The carbonium ion may rearrange, eliminate a proton to produce an olefin, or crack at a beta position to yield to an olefin and a new carbonium ion. Under an atmosphere of hydrogen and in the presence of a catalyst with hydrogenation-dehydrogenation activity, the olefins are hydrogenated to paraffinic compounds. This reaction sequence could be represented as follows:



As can be anticipated, most products from hydrocracking are saturated. For this reason, gasoline from hydrocracking units have lower octane ratings than those produced by catalytic cracking units; they have a lower aromatic content due to high hydrogenation activity. Products from hydrocracking units are suitable for jet fuel use. Hydrocracking also produces light hydrocarbon gases (LPG) suitable as petrochemical feedstock.

Other reactions that occur during hydrocracking are the fragmentation followed by hydrogenation (hydrogenolysis) of the complex asphaltenes and heterocyclic compounds normally present in the feeds.

Hydrocracking reaction conditions vary widely, depending on the feed and the required products. Temperature and pressure range from 400 to 480 °C and 35 to 170 atmospheres, respectively. Space velocities in the range of 0.5 to 2.0 hr⁻¹ are applied.



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