

## CHAPTER III

### THEORY

#### 3.1 Catalyst preparation and manufacture

Most catalysts 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; filtration, washing, drying, forming, and heating follow this. 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.

### **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 onto the pore surfaces. If two or more compounds are present, they are frequency

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, occur oxide supports such as alumina and silica are readily wet by aqueous solutions. Most of 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.

#### 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 impregnating 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 pallet is removed from solution, leading to a more uniform distribution. The dry process can also affect 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.<sup>[4]</sup>

### **3.2 Catalyst support**

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 carrier may be incorporated into a mixture to be precipitated, or the carrier may itself be precipitated from solution in the manufacturing process.

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

### 3.2.1 Activated carbon

#### Activated carbon from palm-oil shell

Palm-oil or *Elaeis guineensis* Jacq is the same family as the coconut. Palm-oil is extracted from the mesocarp, and kernel oil is obtained from the kernel after the endocarp has been removed. It grows well in hot zone where has plentiful and regular rainfall throughout the year, the southern part of Thailand is ideal for it. It is grown mostly in Krabi, Suratthani, Chumphon and Satun. The plantation areas in these provinces where it is sporadically planted are Trang, Prachuab Khiri Khan, Puket and Yala. Palm-oil strains include the following :

- *Macrocaya strain*

It is an old strain, gives low yield and therefore is not often grown.

- *Dura strain.*

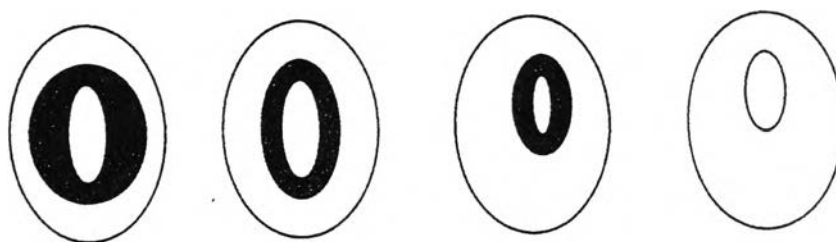
It is similar to the old strain. The skin of the fruit is rather thick. It is commonly grown, it is preferred as a breeding strain for the improvement of new strains.

- *Pisifera strain.*

It has thick outer flesh (mesocarp) and high oil yield. However it is not commonly used in cultivation, though preferred as a breeding strain for the improvement of new strain.

- *Tenera strain.*

It is a cross between Dura and Pisifera strains, with outstanding characteristics. It gives a high yield of large fruits with thick outer flesh, thin inner flesh, thin skin and high oil content. This strain is therefore widely planted.



	DURA	TENERA	PISIFERA
	<u>African</u>	<u>Deli</u>	
	Thick shell	Medium shell	Thin shell
	45 % pulp	60 % pulp	75 % pulp
	40 % shell	30 % shell	15 % shell
	15 % kernel	15 % kernel	10 % kernel
			No shell
			92 % pulp
			0 % shell
			8 % kernel

Figure 3.1 Palm-oil strains in Thailand <sup>171</sup>

Palm-oil cultivation in Thailand has shown increasing economic significance with its expanding market demand at an average growth rate of 15% a year. Estimates of the bank of Thailand put palm oil plantation areas in Thailand at 957,600 rai (1991), mainly concentrated in the southern part of Thailand. It was followed by the generation of enormous amounts of by-products at plantation grounds, oil press and refineries. It estimates that the pressing process produces about 292,367 tons of palm mesocarp fiber , 157,428 tons of palm oil shell and 742,163 tons of empty fruit bunches as waste in 1997. <sup>[13]</sup>

The superior adsorption properties of palm-oil shell activated carbon are due to the nature characteristics of the palm-oil shell.

- High porosity
- Large surface area
- Favourable pore size
- High mechanical strength
- Low impurity

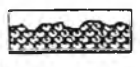
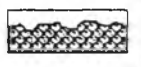
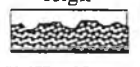
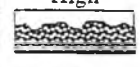

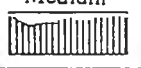
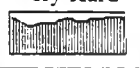
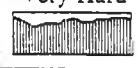


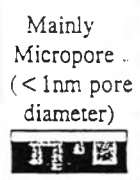
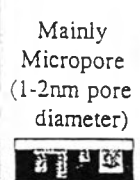



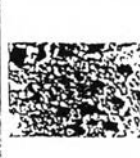
	Wood	Coal	Coconut	Palm shell
Density	Low 	Low 	High 	High 
Hardness	Soft 	Medium 	Very Hard 	Very Hard 
Pore Diameter	Macropore & Mesopore 	Macropore & Mesopore 	Mainly Micropore (< 1nm pore diameter) 	Mainly Micropore (1-2nm pore diameter) 
Morphology (x 10,000 times magnification)				

Figure 3.2 Some comparisons of raw materials for activated carbon <sup>[17]</sup>

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 streams, for recovery of solvent and as a catalyst or catalyst support. In the nuclear industry, activated carbon is used for adsorption of iodine and noble gases from gaseous effluents. One of the most important fields in terms of consumption is in water and wastewater treatment. To obtain these activated carbons from cheap and readily available precursors. Raw materials for the production of activated carbon such as wood, peat, coconut, shell, coal.

#### **3.2.1.1 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 become 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 temperatures (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**

Generally, there are two main types of production of activated carbon:

- a) By carbonizing material with the addition of activating agents ( $\text{ZnCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{H}_3\text{PO}_4$ ). 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**

For chemical activation, the common chemicals used are dehydrating agent such as  $\text{ZnCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and some acid such as  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$ . 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 activated is usually carried out at temperatures from 400-600 (C. These temperature 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 increase 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 neighbouring 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 micro-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 small, 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 a 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.

### **3.2.1.2 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 (-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. Thus sets o 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

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 m<sup>2</sup>/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 radii  $\geq 100-200$  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 cm<sup>3</sup>/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 m<sup>2</sup>/g are negligibly small when compared with the surface of the remaining type of pore, Consequently macropores are not of great importance in the process of adsorption as they merely act as transport arteries rendering the internal parts of the carbon grains 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 cm<sup>3</sup>/g and their specific surface area in the range of 20-100 m<sup>2</sup>/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 cm<sup>3</sup>/g. The energy of adsorption in micropores is substantially greater than that for adsorption in mesopores

or at the non porous surface, which causes a particularly 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.

### **3.2.1.3 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 heteroatoms 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.

### **3.2.1.4 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'

Federations (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 für 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 *Bruneuer, Emmett, and Teller* (BET) *classification*. In all cases the amount of vapor adsorbed increased as its partial pressure is increasing, 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.

#### **Physical test**

- *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 tests

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 a carbon. Thus the properties of activated carbons are estimated by comparing the result of measurements for different adsorbates, e.g. by comparing the adsorptions 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 0.007-0.03N, 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 a 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 surface 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 molecules is significant.<sup>[13]</sup>

- *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.

### 3.3 Mechanism of cracking processes

Cracking processes were assigned to two fundamental classes;

#### 3.3.1 Thermal cracking

Thermal cracking<sup>[11]</sup>, where free radicals (lacking one hydrogen atom on carbon atom in the hydrocarbon molecule) are intermediate species which cracked by a  $\beta$ -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:

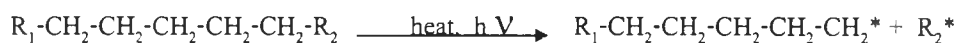
The normal paraffin molecule loses a hydrogen atom by collision and reaction with a small free hydrocarbon radical or a free hydrogen atom, thereby becoming a free radical itself. This radical may immediately crack or may undergo radical isomerization prior to cracking. Radical isomerization presumably 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 ( position to the carbon atom lacking one hydrogen atom. Cracking at the ( 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 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.

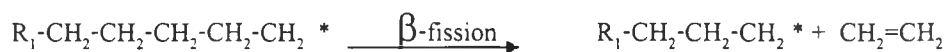
A schematic representation of polypropylene cracking is as follows;

### 1. Initiation Step

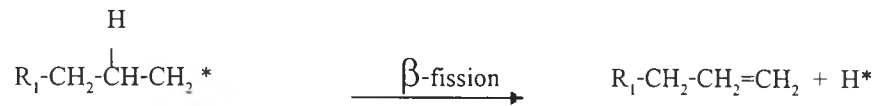


### 2. Propagation Step

#### 2.1 $\beta$ -fission



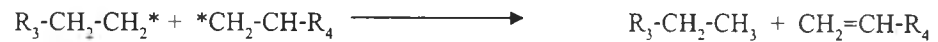
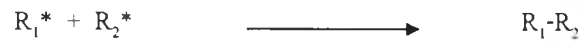




## 2.2 Chain Transfer



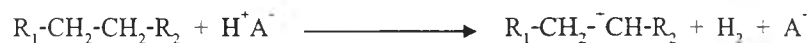
## 3. Termination Step



### 3.4.2 Catalytic cracking

Catalytic cracking<sup>[12]</sup> is the most important and widely used refinery processes 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.

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



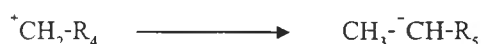
Chain propagation involves an exchange reaction in which a carbonium ion reacts with a polypropylene to give a new hydrocarbon and a carbonium ion of the polypropylene to be cracked (hydride transfer).



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.  $\beta$ -scission:



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



Subsequent step involve further  $\beta$ -scission and hydride transfer and proceed until the chain becomes so short that cracking at the  $\beta$  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:

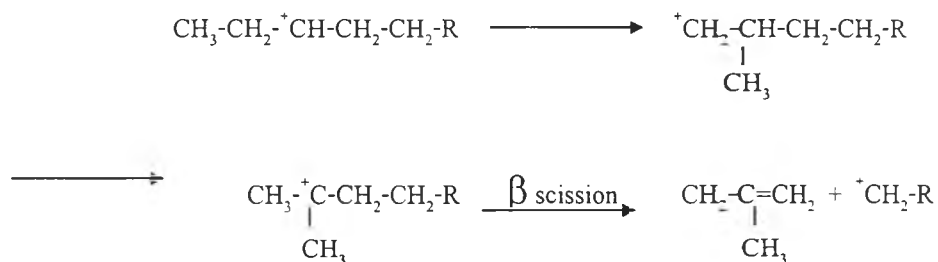


Figure 3.3 Role of Fe/AC in PP cracking.<sup>[8]</sup>