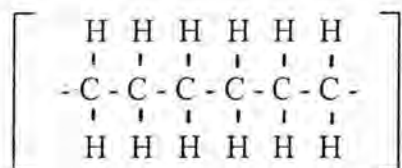


## CHAPTER II

### THEORETICAL CONSIDERATION

#### 2.1 Polyethylene [1, 9-11]

Polyethylene is the major member of a group of chemical compounds known as polyolefins. It is one of the most widely used polymers of any of the thermoplastic materials. To make polyethylene, it is necessary to use high-purity ethylene gas. The ethylene gas can be made from natural gas or obtained as a by-product of a petroleum refinery. Through addition polymerization, the resulting polymer has the following basic structure.



Polyethylene initially was a homopolymer of ethylene, but today most polyethylenes are copolymers of ethylene with 1 to 10% of  $\alpha$ -olefins, such as 1-butene, 4-methylpentene, 1-hexene and 1-octene. LDPE and some HDPE grades are ethylene homopolymers. LDPE is a branched polymer

with only 40 to 60% crystallinity. The other polyethylene grades are predominantly linear, with small amounts of branching caused by the comonomer. The linear polyethylenes are produced using Ziegler-Natta catalysts or other transition metal catalysts. The densities of polyethylene range from 0.880 to 0.957 g/cm<sup>3</sup> as shown in Table 2.1.

**Table 2.1** Types of Polyethylene

PE	Density (g/cm <sup>3</sup> )	Crystallinity	Melting Point (°C)
ULDPE	0.880-0.915	Low	
LLDPE	0.918-0.940	High	130
LDPE	0.910-0.955	40-60%	107-120
HDPE	0.941-0.954	High	130-138
HMW-HDPE	0.944-0.954	High	
UHMW-HDPE	0.955-0.957	High	

### 2.1.1 Characteristics

Polyethylene appears in its natural form as a milky white, waxy feeling material. In general, as the density increases, the stiffness, hardness, strength, heat distortion point and ability to transmit gasses increases. As density decreases, impact strength and stress crack resistance increases. Stress cracking is a surface change that polyethylene, and some other

plastics, undergo when exposed to oils, gasoline and other hydrocarbons. It appears on the material as a flaky, cracked surface.

The general properties of polyethylene are very tough at low temperatures, excellent chemical resistance, high permeability to air and gasses, low in water vapor transmission, fairly high mold shrinkage, very flexible, fairly weather ability, excellent electrical insulating properties, easily colored in transparent (film), odorless and tasteless.

### **2.1.2 Application**

Polyethylene not only finds many product applications due to its properties but also because of the many forms in which it is produced as a resin. It may be obtained in granules, powders, film, rod, tube and sheet form and molded through such processes as injection molding, fluidized bed coating, blow molding, extrusion, vacuum forming, casting and calendering. Polyethylene is used for many purposes, including: containers, electrical insulation, housewares, chemical tubing, toys, freezer bags, flexible ice cube trays, snap-on lids and battery parts. Two major applications of polyethylene are films for packaging soft goods and other nonperishables and blow molded bottles. Squeeze bottles from low density polyethylene and detergent bottles from high density are typical products.

## 2.2 Hydrocracking Reaction and Dual Functional Catalyst

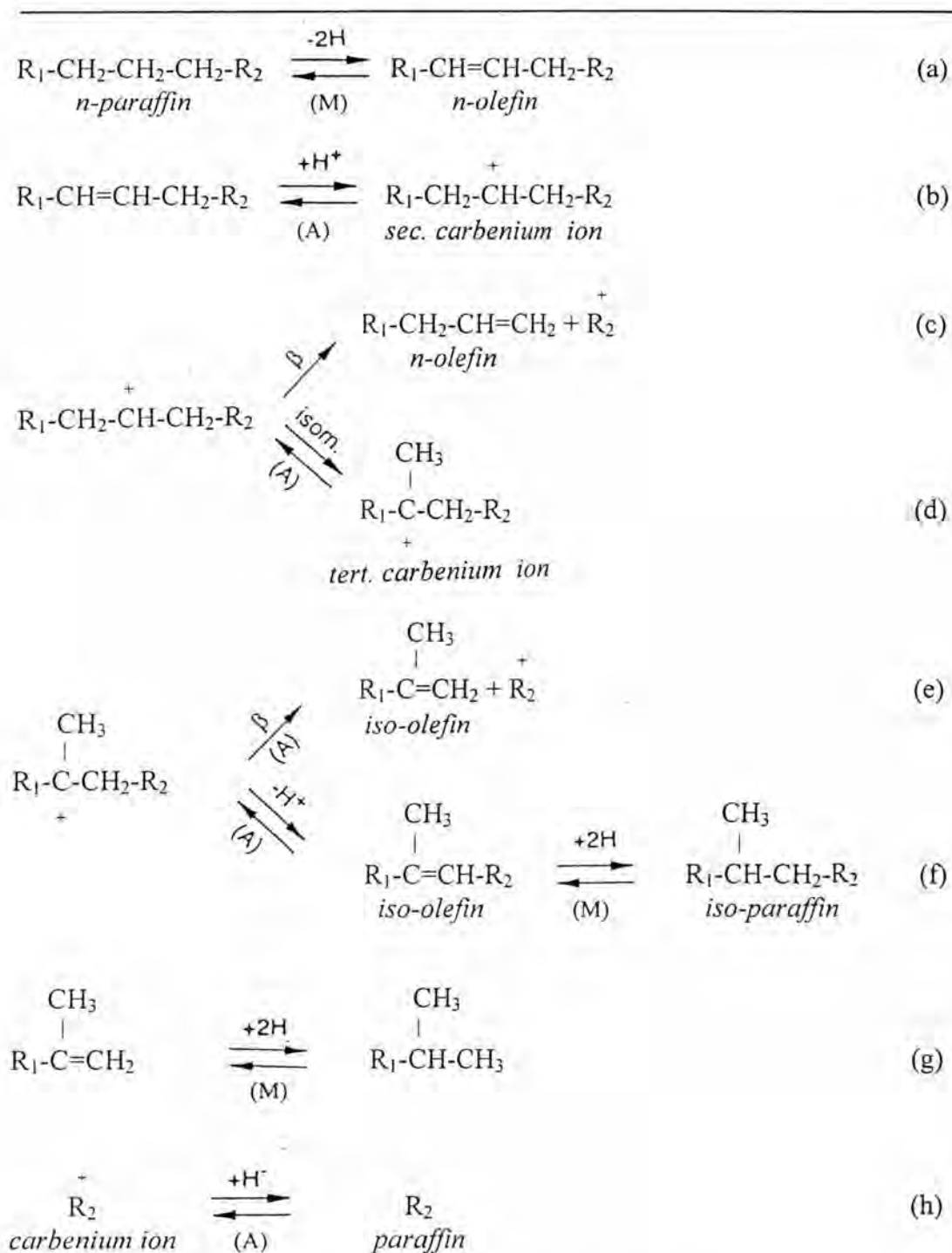
### 2.2.1 Dual Functional Catalytic Hydrocracking [12]

Hydrocracking catalysts have a cracking function and a hydrogenation - dehydrogenation function. The cracking function is provided by an acidic support, whereas the hydrogenation - dehydrogenation function is provided by metals. The acidic support consists of an amorphous oxide, a crystalline zeolite, or a mixture of crystalline zeolite and amorphous oxides. Cracking and isomerization reactions take place on the acidic support.

Hydrocracking of n-paraffins over a dual functional catalyst goes through the following steps:

- (1) Adsorption of n-paraffins on metal sites
- (2) Dehydrogenation with formation of n-olefins
- (3) Desorption from metal sites and diffusion to acid sites
- (4) Skeletal isomerization and / or cracking of olefins on the acid sites through carbenium ion intermediates
- (5) Desorption of formed olefins from acid sites and diffusion to metal sites
- (6) Hydrogenation of these olefins (n- and iso-) on metal sites
- (7) Desorption of resulting paraffins

The elementary reactions corresponding to the reaction path described are shown in Table 2.2. Product analysis has shown that whenever several reaction pathways are possible, the one leading to the formation and subsequent cracking of a tertiary carbenium ion is preferred (reactions (d) and (e) in Table 2.2). While the hydrogenation / dehydrogenation and isomerization reactions are reversible, the cracking reactions are irreversible.

**Table 2.2** Typical Reaction Path in Hydrocracking of n-Paraffins

β: beta scission, A: acid site, M: metal site

### 2.2.2 Preparation and Structure of Dual Functional Catalyst

The metal on support is prepared by a process called impregnation. Impregnation is done by depositing a metal salt on a porous support, converting this salt to an oxide and then reducing it to the metallic state. [13]

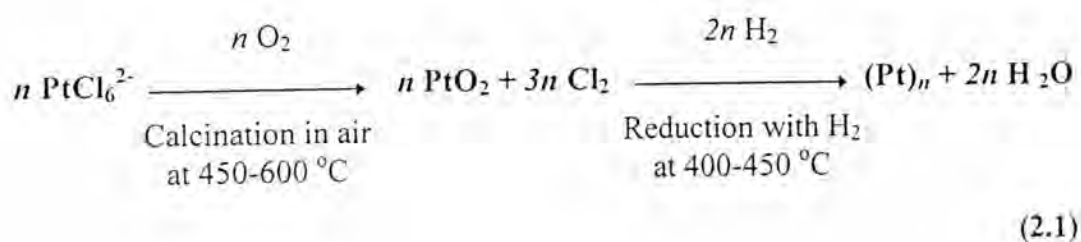
Tin, transition metals (e.g. Pt, Ni, Co or Fe) and fluoride are impregnated on the support. Table 2.3 gives the basic quantities of elements that are impregnated on the support.

**Table 2.3** The basic quantity of the impregnated element on support [14]

Element	Quantity (%wt)
Pt	0.01-2
Fe	5-10
Co	5-10
Ni	5-10
Sn	0.01-5
F	0.1-3.5

Finally, the impregnated catalysts are reduced at hydrogen pressure of 400 psig and temperature of 400 °C for 6 hours.

The preparation of metal impregnated alumina supported by hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) is shown in the equation 2.1. [15]



### 2.2.3 Metallic Component

Transition metals are the hydrogenation / dehydrogenation sites because they have vacant d-orbitals in their atoms, accepting electrons for sharing into chemisorption bands. Either molecular hydrogen or alkanes tend to be dissociatively chemisorbed to atomic hydrogen. On the other hand, chemisorption of alkenes involves the sharing of one pair of electrons from the multiple bond into the vacant d-orbital. The general predictions for chemisorption on transition metals are summarized as follows.

(a) the strength of the M-H bond decreases with the increase in atomic number of the metal (M) along a particular transition series in the periodic table;

(b) the number of M-H bonds per unit area of metal surface at maximum surface coverage increases with increasing atomic number.



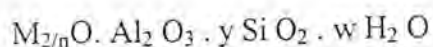
The effectiveness of tin is greatly enhanced by the addition of halogen acid or ammonium halide. Due to the effectiveness of tin, the development of catalyst is impregnated tin with group VIII metals. [16]

#### 2.2.4 Acidic Component

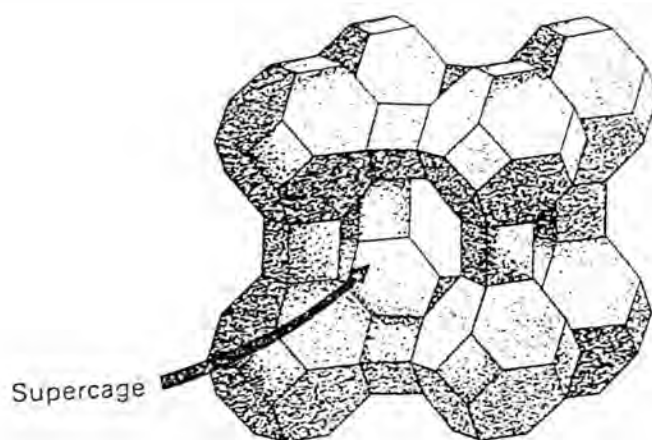
The molecular sieve support used in dual functional catalyst has been shown to be acidic in nature.

##### *Molecular Sieve*

Molecular-sieve zeolites [17] are crystalline aluminosilicates of Group IA and Group IIA elements such as sodium, potassium, magnesium and calcium. Chemically, they are represented by the empirical formula :

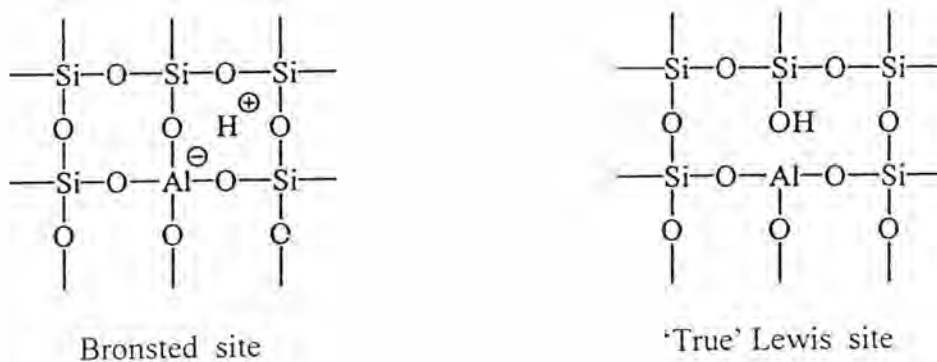


where y is 2 or greater, n is the cation valence and w represents the water contained in the voids of the zeolite. Structurally, zeolites are complex, crystalline inorganic polymers based on an infinitely extending framework of  $AlO_4$  and  $SiO_4$  tetrahedra linked to each other by the sharing of oxygen ions, produce a three-dimensional framework with highly regular channels, often referred to as “supercages” as seen in Figure 2.1.



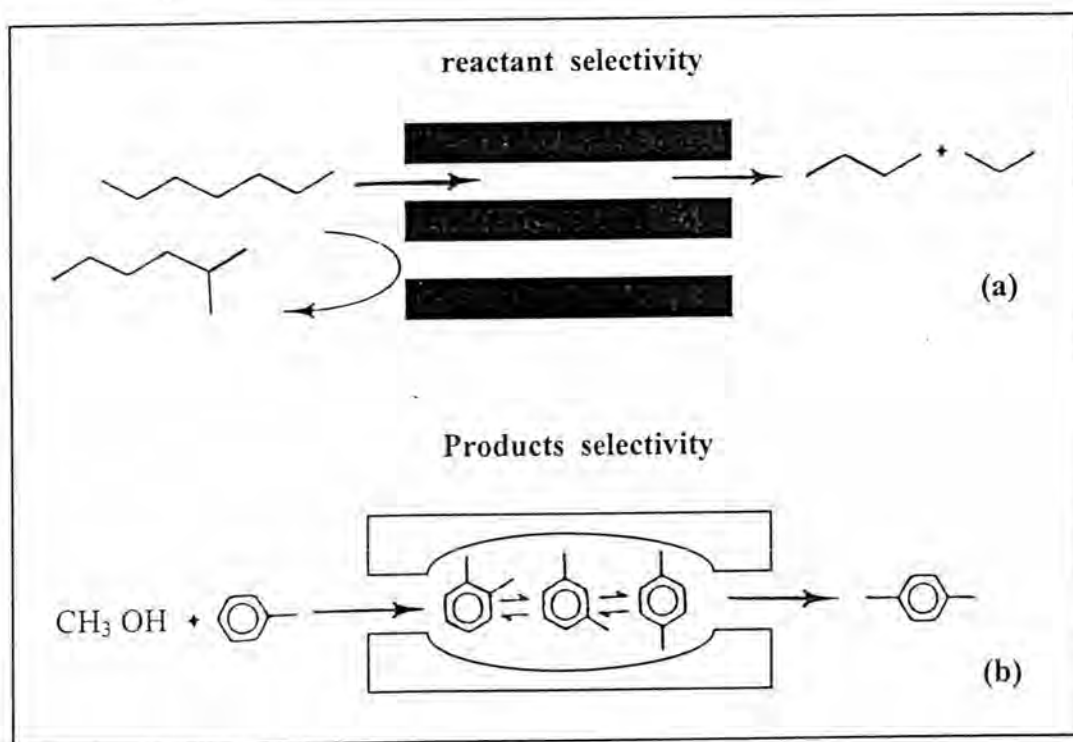
**Figure 2.1** The basic structure unit of molecular sieve

The alumina is bonded to three oxygen atoms whereas the silica atoms in silica are bonded to four oxygen atoms, so there are two main microscopic structures of silica-alumina. (Figure 2.2)



**Figure 2.2** Representation of the Bronsted and Lewis sites in silica-alumina

Catalytic hydrocracking take place largely within zeolite frameworks. The zeolites have very special practical advantages over the more traditional catalysts, in that they will admit only certain reactant molecules and that this can be potentially tailored to produce selected products. This selectivity is known as “shape-selective catalysis” and is controlled by “configurational diffusion”. The catalytic reactions are promoted by virtue of a matching of size, shape and orientation of the reactant and product molecules to the geometry of the zeolite framework. (Figure 2.3)



**Figure 2.3** Representation of (a) reactant shape selectivity in zeolite channel (rejection of branched chain hydrocarbons) and (b) product shape selectivity (*p*-xylene diffuses preferentially out of the channel) [18]