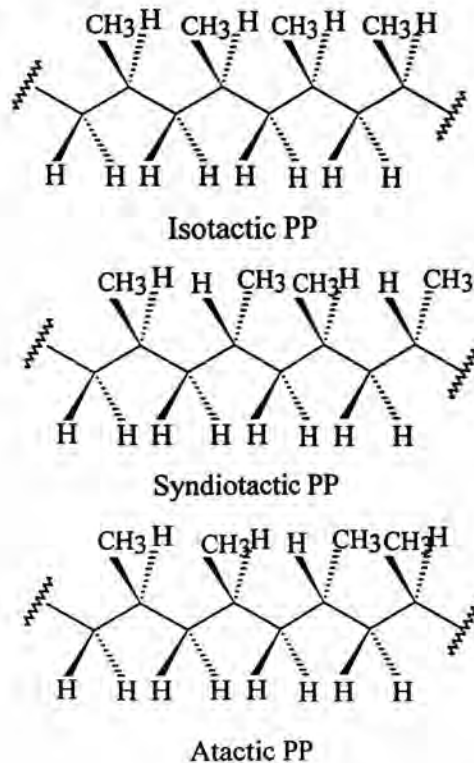


## CHAPTER II

### THEORETICAL

#### 2.1 General description of PP

The production of PP is made by polymerization of propylene in the presence of Ziegler catalysts. Recently, the used of metallocene catalysts in the production of PP has increased due to the capability of control and design of the structure of PP. [14] There are three structural types of PP (Figure 2.1) depending on the stereochemistry of the methyl groups in the macromolecule. : [15]



**Figure 2.1** Schematic Molecular Structures of Polypropylene

In isotactic PP, the methyl groups are on the same side of the carbon chain.

In syndiotactic PP: the methyl groups are alternated on the carbon chain.

In atactic PP, the methyl groups are randomly distributed in their spatial relationship to the main chain.

There are three distinct classes of PP copolymer having different application areas. Random copolymers, obtained by copolymerization of mixtures of propene and the other  $\alpha$ -olefins such as 2-6% of ethylene, have lower melting point and improved clarity. Impact (Block) copolymers, made in a two-stage polymerisation process are high-impact strength grades that contain 10-40 %wt. of dispersed propene-ethylene elastomers. One use of impact copolymers is for the battery case. On the other hand, polymer blends are PP toughened by blending with 10%wt. of PIB elastomer or ethylene-propene rubber. [16]

### **2.1.1 Physical properties**

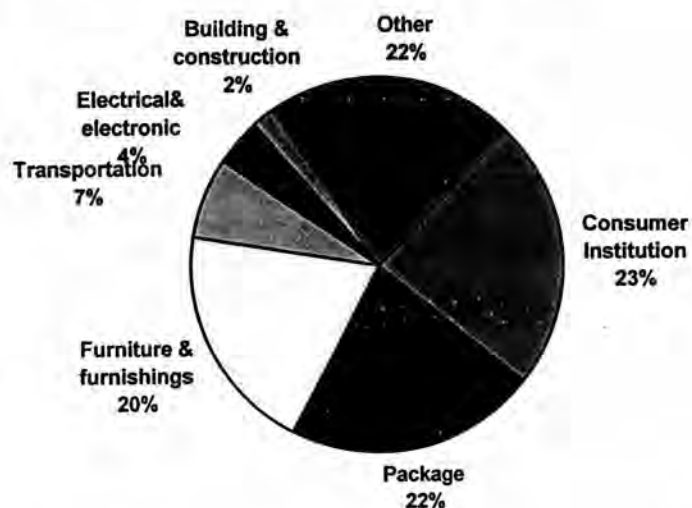
Polene 2300 NCA is a commercial type of PP that is used to produce battery cases. It composes of ethylene 5.5-7% and it has an average molecular weight ranging from 200,000 to 540,000. The molecular mass distribution (MMD) is 5-10. The other physical properties are shown in Table 2.1

**Table 2.1** Typical properties of Polene 2300 NCA. [17]

Typical Data	Unit	Value	Test Method
MFI 2.16 kg/230°C	g/10min	10	ASTM D 1238
Tensile strength at yield	N/mm <sup>2</sup>	28	ASTM D 638
Charpy notched impact strength at -20°C	mJ/mm <sup>2</sup>	3.8	DIN 53453
Shear modulus	N/mm <sup>2</sup>	680	DIN 53457
Ball indentation hardness	N/mm <sup>2</sup>	76	DIN 53456
Heat distortion temperature at 0.45 N/mm <sup>2</sup>	°C	120	ASTM D 648

### 2.1.2 Applications

In 1993 in the U.S.A, the classification of PP products, totalling 3.69 billion kg. is represented in Figure 2.2

**Figure 2.2** The applications of PP in 1993 in the U.S.A. by weight.

### **2.1.3 Environmental Aspects**

#### ***Recycling***

Lower grade PP and used PP are recycled into useful materials by blending and recompounding.

#### ***Pyrolysis***

PP can be cracked to liquid hydrocarbons by thermal pyrolysis at 400-550°C . In a recent process developed in Japan, zeolite catalysts enable this temperature to be reduced to 200-420°C using a two-stage heating process. [4]

#### ***Incineration***

Modern incineration technology, with energy recovery in the form of electricity generation, can take advantage of the high calorific value of thermoplastics. PP has the same calorific value as fuel oil.

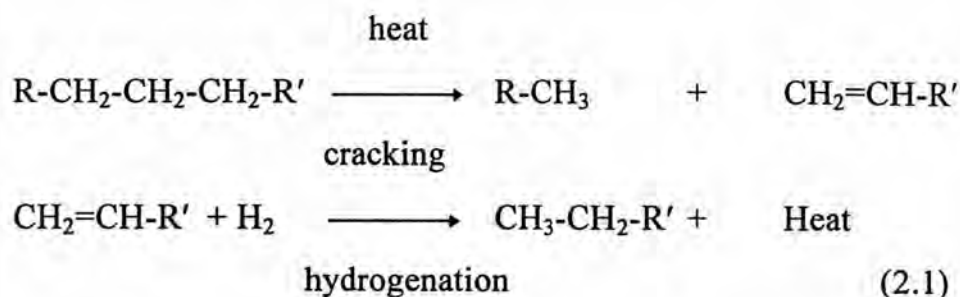
## **2.2 Hydrocracking Reaction and Dual Function Catalyst.**

### **2.2.1 Catalytic Hydrocracking**

The Hydrocracking process is defined as the decomposition of hydrocarbons over a solid catalyst at temperatures above 300°C and at hydrogen pressures between 1,200-2,000 psig. The aim is the cracking of high boiling fractions such as heavy oils and coke in the petroleum industry or polyolefins in plastic waste into lower boiling components such as hydrocarbon gases and fuel oils that have a higher API gravity and octane number than the feed. [19]

There are two main reactions involved in the hydrocracking process, catalytic cracking which is the scission of carbon-carbon single

bonds and hydrogenation which is the addition of hydrogen to carbon-carbon double bonds. Those reaction are shown in 2.1. [20]

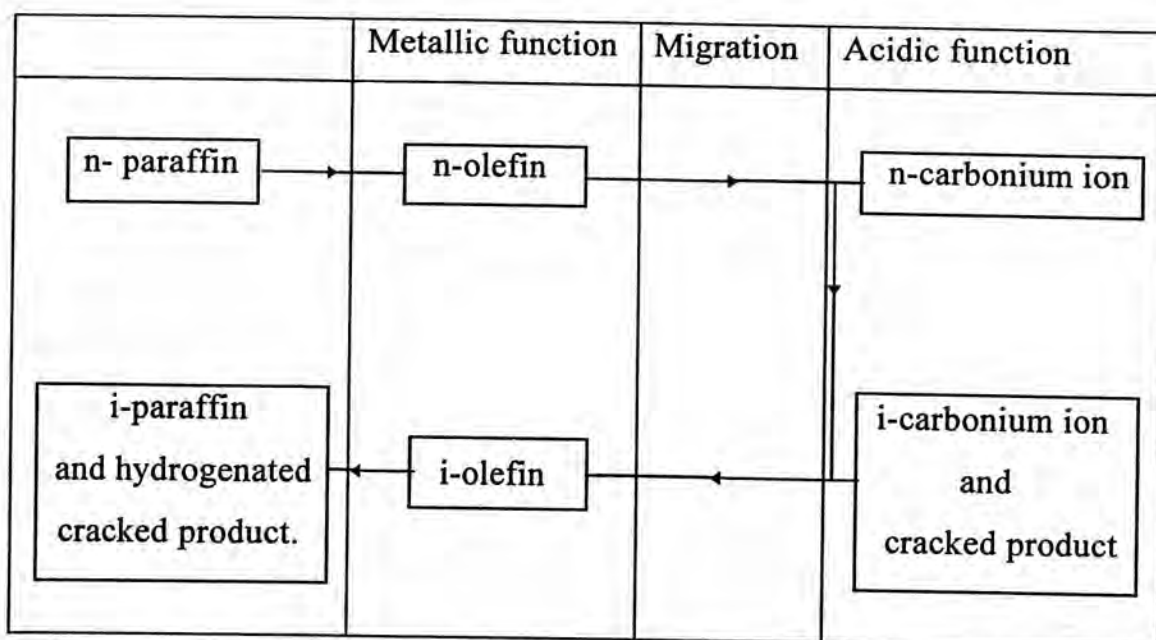


The reaction actually provides an excess of heat (exothermic). This heat causes the reactor temperature to increase and accelerate the reaction rate. The temperature can be controlled by injecting cold hydrogen into the reactor.

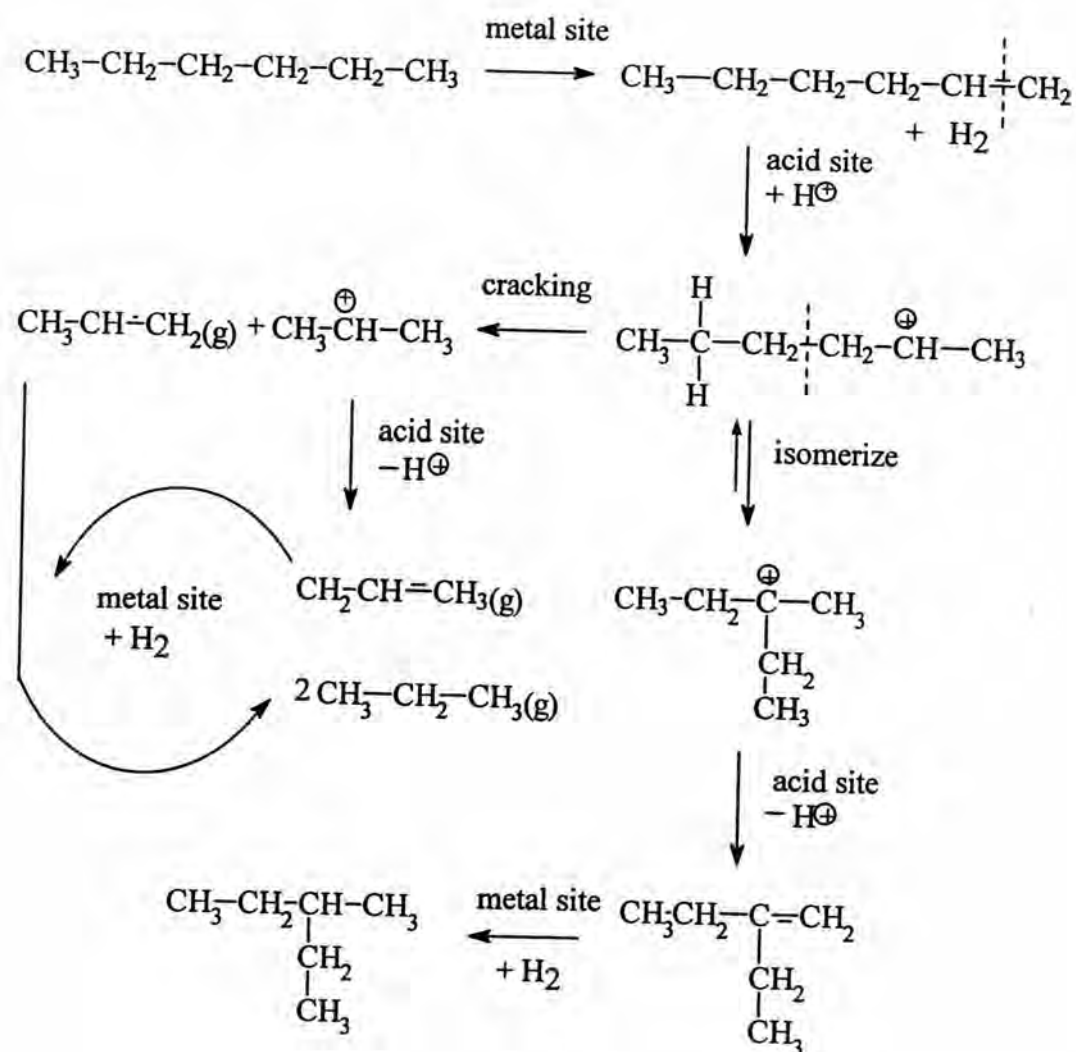
The catalysts used in hydrocracking reaction are dual function catalysts consisting of an aggregation of metal dispersed on a support. These catalysts are characterised by providing cracking sites and hydrogenation/dehydrogenation sites.

The hydrogenation/dehydrogenation components are usually metals or a mixture of metals from group VI or VIII, preferably group VIII. The cracking sites or acid sites are provided by alumina, silica/alumina combinations or by zeolites.

The reaction mechanism of dual function catalyst and an example are shown in Figure 2.3. and Figure 2.4 respectively.



**Figure 2.3** Reaction mechanism of dual functional catalyst. [21]



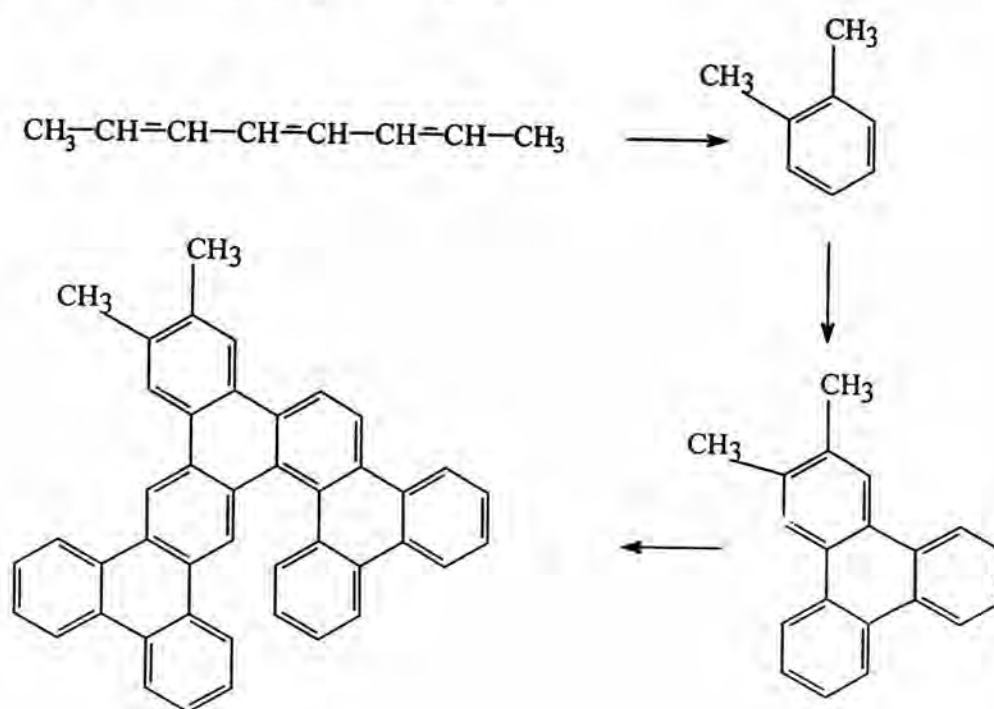
**Figure 2.4** Reaction mechanism of catalytic hydrocracking of hexane [22]

Alkanes will be strongly chemisorbed and dehydrogenated readily to olefins on a transition metal. Diffusion will take the olefin to an alumina acidic site, where it will be chemisorbed as a carbonium ion and undergo cracking and/or polymerization. In turn, the new olefin products will contact with metal sites after diffusion, where rehydrogenation tends to occur, releasing new alkane species. Many isomerization reactions occur under the conditions of catalytic cracking such as skeleton or double bond isomerization, dehydrocyclization and aromatization. These isomerizations



take place during the cracking to produce isomerized olefins that are rapidly hydrogenated. A carbocation will undergo rearrangement of the carbon skeleton to form a more stable carbocation, a primary carbocation may rearrange to form a secondary carbocation or a tertiary carbocation. Depending on the conditions, principally temperature, carbonium ions can be precursors to polymerised or cracked derivatives of the original reactant. The control factor is mainly thermodynamic. Low temperatures favour polymerization but high temperatures favour cracking.

A side reaction includes coking, the formation of high molecular weight aromatic or highly unsaturated carbonaceous solids on the surface of the catalyst, taking place simultaneously with the isomerization. Cokes usually contain polycyclic aromatic structures. The mechanism of the process is represented in Figure 2.5. [23]



**Figure 2.5** Reaction mechanism of coke formation



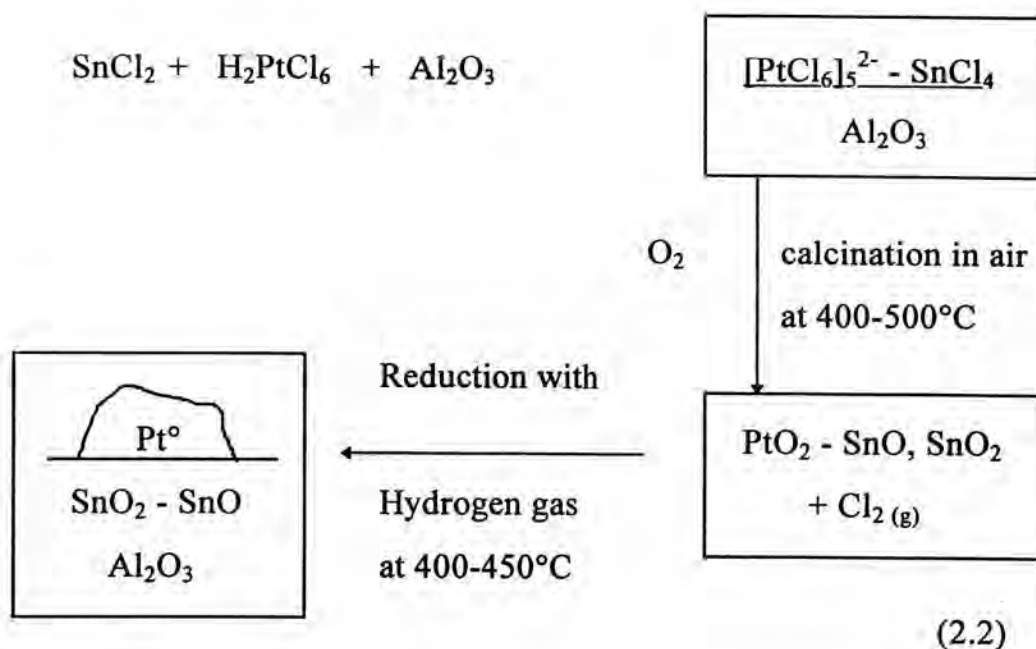
Coking is undesirable because the coke can plug the pores or occlude the surface of the catalyst, reducing or destroying the activity of the catalyst. The catalyst surface can be regenerated by carefully burning off the coke. Other products from side reactions are lower molecular weight hydrocarbons, lower alkenes, dienes and acetylene.

### **2.2.2 Preparation and Structure of Dual Functional Catalyst.**

The metal on support catalyst is prepared by a process called impregnation. Impregnation is done by depositing a metal salt on a porous support, converting this salt to oxide and then reducing it to the metallic state. [24]

In multimetallic catalytic composites, the various metals may be deposited in any desired order but in most methods, the platinum group metal is deposited after tin. The catalysts are prepared by impregnation of stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ), 0.01-5 wt.%, impregnation of a metal chloride from group VIII such as iron (III) chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) 5-10 wt.%, cobalt (II) chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) 5-10 wt.%, nickel (II) chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) 5-10 wt.% or chloroplatinic acid 0.01-2 wt.%, and then impregnation of ammonium fluoride ( $\text{NH}_4\text{F}$ ) 0.1-3.5 wt.%. Finally, the impregnated catalysts are reduced at a hydrogen pressure of 400 psig and a temperature of  $400^\circ\text{C}$  for six hours.

The preparation of metal impregnated alumina by hexachloroplatinic acid is shown in the equation 2.2 [25]



Impregnation with  $\text{NH}_4\text{F}$  enhances both acidic activities of  $\text{SnO}$  and  $\text{SnO}_2$  by forming  $\text{SnF}_2$  or  $\text{SnF}_4$  and of alumina by inductively withdrawing electrons from the aluminium atom.[26] Because fluoride has higher electronegativity than oxygen, the residual hydrogen atom on the surface becomes more acidic.

### 2.2.3.1 Metallic component

Transition metals are the hydrogenation/dehydrogenation sites because they have vacant  $d$ -orbitals in their atoms, accepting electron 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;

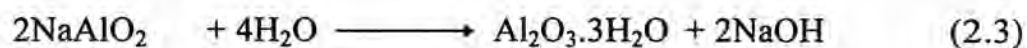
(b) the number of M-H bonds per unit area of metal surface at maximum surface coverage increases with increasing atomic number.

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 metal. [27]

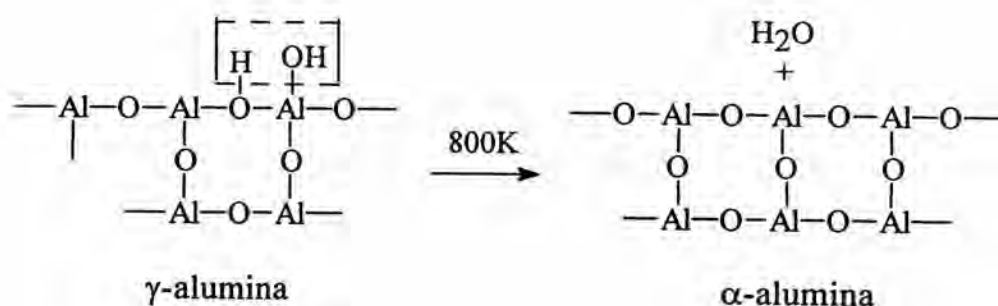
### 2.2.3.2 Acidic Component.

#### *Alumina*

Alumina ( $\text{Al}_2\text{O}_3$ ), the acidic component in dual function catalyst, exists in several distinct forms: the gamma form or the alpha form, depending on the method of preparation and subsequent treatment. A typical mode of preparation involves the hydrolysis of sodium aluminate to yield a trihydrate (equation 2.3).

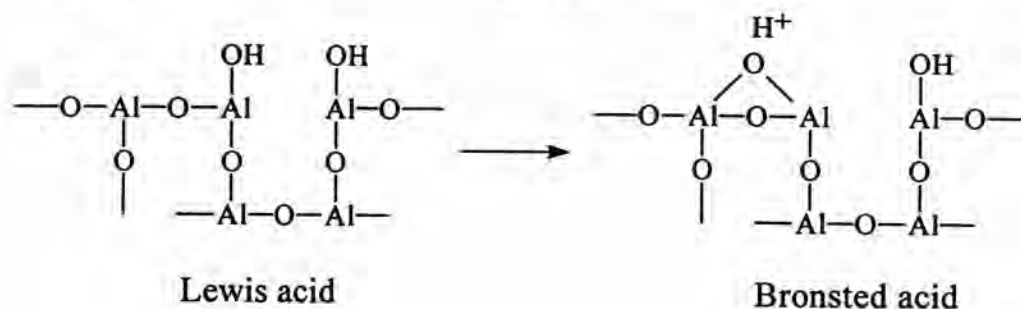


When the trihydrate is heated to 700K, most of the water is driven off and the product, known as  $\gamma$ -alumina, retains about 0.5% of the original water. As shown in Figure 2.6, if  $\gamma$ -alumina is heated above 800K, the residual water is driven off to generate a catalytically inactive form known as  $\alpha$ -alumina.



**Figure 2.6** Dehydration of  $\gamma$ -alumina to  $\alpha$ -alumina.

$\gamma$ -Alumina shows both high catalytic activity for dehydration and high effective surface area,  $300 \text{ m}^2 \text{ g}^{-1}$ . Figure 2.7 shows that Bronsted acid structure occurs from the donation of a lone pair electrons from O atom in OH group to Al atom with releasing a proton.



**Figure 2.7** Diagrammatic representations of the function as Lewis acid and Bronsted acid of  $\gamma$ -alumina [23]

In the hydrocracking reaction, a carbocation can be generated in two ways, the first is by protonation of a double bond by a Bronsted acid : (equation 2.4)

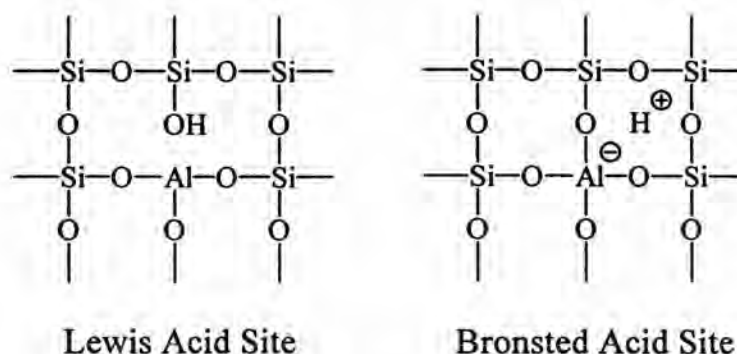


and the second is heterolytic bond cleavage in the presence of Lewis acid:



### *Molecular sieve*

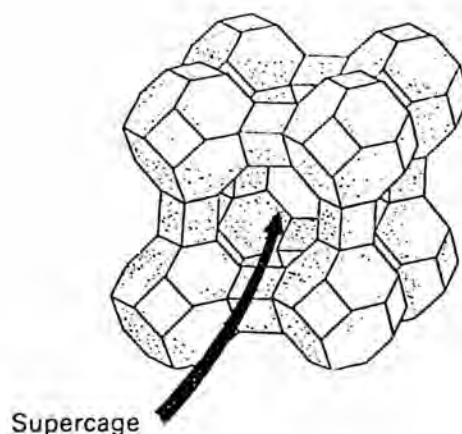
The structure of silica-alumina is a silica tetrahedral lattice in which some of the silicon atoms have been replaced by aluminium atoms. The aluminium atoms are bonded to three oxygen atoms whereas the silicon atoms in silica are bonded to four oxygen atoms.



**Figure 2.8** Representations of the Lewis and Bronsted acid sites in silica-alumina. [28,29]

In the Lewis structure, oxygen atom from -OH group bonded with Si atom can share a lone pair of electrons with Al atom to form a fourth bond of Al with a proton to unsaturated hydrocarbons in the process of its chemisorption to obtain carbonium ion.

Molecular sieves, one type of silica-alumina, has the empirical formula  $(M^{n+})_{x/n}(AlO_2)_x(SiO_2)_y \cdot mH_2O \cdot M^{n+}$  when  $M^{n+}$  is a  $Na^+$ ,  $m$  is the number of water molecules of crystallization and  $(x+y)$  is the number of tetrahedral in the unit cell. The  $AlO_4^-$  and  $SiO_4$  tetrahedra, linked through share oxygen atoms, produces a three-dimensional framework with highly regular channels, often referred to as 'supercages' as seen in Figure 2.9.



**Figure 2.9** The basic structure unit of molecular sieve

The aperture is bounded by 8 silicon or aluminium atoms and 8 oxygen atoms and has a diameter of about 0.4 nm. These supercages can enhance cracking activities for hydrocarbons by up to four orders of magnitude because there are localized regions of high electrostatic fields associated with the presence of cations to induce the diffusion of molecules through the pore system. These pores cause the size selectivity of the molecular sieve. Since the most active surface are within the pore structure, only those molecules diffusing through the supercages can undergo the reaction.