

CHAPTER II

THEORETICAL CONSIDERATION

Bifunctional Catalysts [4,5]

1. Generation of Isomerization Catalysts

During the first years after the discovery of paraffin isomerization, many catalysts capable of promoting the reaction were discovered and are described. They include molybdenum trisulfide, molybdenum disulfide, molybdenum trioxide, silica, copper, alumina, nickel-alumina, nickel-zinc oxide on charcoal, platinum on charcoal, and sulfuric acid. Generally, these are all less active than Friedel-Crafts catalysts.

It was found that nearly all Friedel-Crafts salts catalyze paraffin isomerization in varying degrees. Among these are aluminium chloride, aluminium bromide, ferric chloride, copper chloride, zinc chloride, calcium chloride, boron fluoride and hydrogen fluoride with or without metallic nickel present, tin chloride, and zirconium chloride. The aluminium halides are the most active.

These processes, called "First Generation", were plagued by corrosion, plugging, and high catalyst consumption, which resulted in poor on-steam efficiency and high costs.

The "Second Generation" processes supplanted the earlier ones during the middle and late 1950s, used bifunctional or dual-functional catalysts. These processes can eliminate many of the shortcomings of the first generation Friedel-Crafts systems.

The bifunctional catalysts of most interest consist of a hydrogenation-dehydrogenation component, the noble metals of Group VIII, platinum, palladium, or nickel, supported on an acidic component, such as alumina or silica-alumina. They are termed bifunctional, since they are found to promote simultaneously such reactions as the hydrogenation-dehydrogenation and the isomerization of saturated hydrocarbons, as was disclosed by Haensel [6] and by Ciapetta [7].

Later, the catalysts that greatly enhanced acidity, are prepared by treating a platinum-alumina composite with a polyhalide, such as carbon tetrachloride, chloroform, methylene chloride, aluminium chloride, etc., or impregnated of the platinum-alumina catalysts with monohalide, such as fluoride (from ammonium fluoride solution). The processes that use these high activity catalysts are collectively called "Third Generation". These three catalyst types are represented in Table 2.1.

Nowadays, the "Third Generation" which being the most active catalysts are used in many plant processes of isomerization.

Table 2.1 Three Generations of Paraffin Isomerization Catalysts

Order of Generations	Type of Catalysts
1. First Generation	Friedel-Crafts Catalysts : AlCl_3 + Hydrocarbon complex AlCl_3 on Bauxite or Al_2O_3 AlCl_3 + SbCl_3 + HCl AlBr_3 + HBr
2. Second Generation	Hydroisomerization Catalysts : Platinum on Al_2O_3 Platinum on $\text{Al}_2\text{O}_3/\text{SiO}_2$ Platinum on $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$ Platinum on Y-type Zeolite Platinum on Mordenite
3. Third Generation	Hydroisomerization Catalysts : Platinum on Al_2O_3 reacted with Organic chlorides Platinum-Fluoride on Al_2O_3 Platinum-Chloride on Al_2O_3

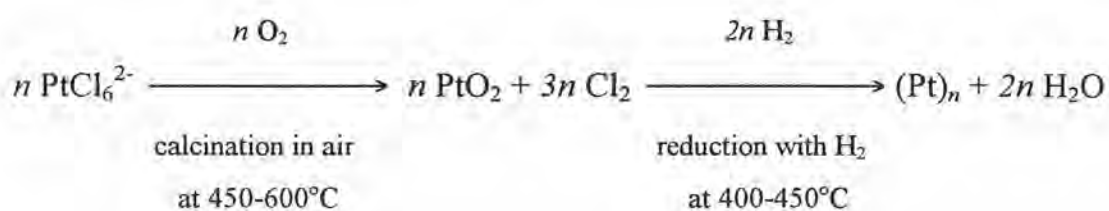
Source : represented from reference number [4]

2. Metallic Component

One common method of preparing the bifunctional catalysts involves impregnation of alumina with chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), followed by calcination in air at high temperatures in the range of 450 to 600°C [8,9]. Other catalysts have been considered. Among these are certain metal

oxides on alumina, e.g., chromia (chromium oxide) and molybdena (molybdenum oxide) on alumina. However, these catalysts are much less active than platinum on alumina catalyst.

Preparation of platinum metal impregnated on alumina received from chloroplatinic acid solution can be represented as the hexachloroplatinate ion being a precursor which does not react with the support as :



On the metallic component (usually platinum), hydrocarbons can undergo hydrogenation or dehydrogenation reactions in the presence of hydrogen (H_2) pressure. It is however evident that platinum catalysts are more active in hydrogenation-dehydrogenation reactions than other metals. The activity in the dehydrogenation reactions is generally established by extent of dehydrogenation of cyclohexane over the catalyst sample. Table 2.2 gives a comparison of the activities of some catalysts in the dehydrogenation of cyclohexane [10].

Table 2.2 Rate of the Dehydrogenation of Cyclohexane over different catalysts (temperature 427 °C, pressure 7 atm)

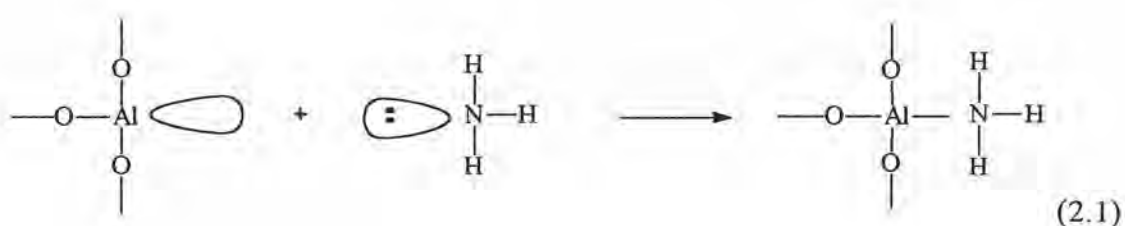
Catalyst	Dehydrogenation activity, mmoles benzene / g of catalyst sec ⁻¹
34% Cr ₂ O ₃ on Al ₂ O ₃	0.5
10% Mo ₂ O ₃ on Al ₂ O ₃	3
5% Ni on Al ₂ O ₃	13
5% Co on Al ₂ O ₃	13
0.5% Ir on Al ₂ O ₃	190
1% Pd on Al ₂ O ₃	200
5% Ni on SiO ₂	320
1% Rh on Al ₂ O ₃	890
0.5% Pt on Al ₂ O ₃	1,400-4,000

Source : represented from reference number [10]

3. Acidic Component

The alumina or silica-alumina supports used in bifunctional catalysts have been shown to be acidic in nature. A Lewis acid is defined as a species that can accept a pair of electrons from a base. This is a very general definition of an acid proposed by G.N. Lewis in 1923 [11]. In the case of structure in equation 2.1, the aluminium atom is not completely coordinated, i.e., it is bonded to three oxygen atoms instead of four. The aluminium atom thus has a total of six valence electrons instead of the maximum eight. It therefore has the potential of accepting a pair of electrons from another species to complete a stable octet.

The acidic properties are readily demonstrated by the affinity of these solids for adsorption of basic compounds, such as ammonia, trimethylamine, n-butylamine, pyridine, and quinoline [12,13]. Furthermore, adsorption of certain acid-base indicators, such as butter yellow gives a coloration similar to that observed in acid media [14,15]. To illustrate the interaction of a Lewis acid and a Lewis base, can be represented in which a molecule of ammonia could bond with the aluminium atom in structure of equation 2.1.



The ammonia molecule donates a pair of electrons to the electron-deficient aluminium atom in the above reaction, thus completing a stable octet of electrons. This example is a pertinent one, since adsorption of ammonia has been used as a way of measuring the acidity of solid catalyst surfaces.

Treatment of alumina with halogens, such as chloride or fluoride tends to make the acidic properties of alumina more pronounced, in the sense that it increases the activity of alumina for the catalysis of typical acid catalyzed reactions, such as the skeletal isomerization and various cracking reactions of hydrocarbons [16-18]. The enhancement of acidic properties is then attributed to the halogens having higher electron affinities than oxygen, thus causing the residual hydrogen atoms on the surface to become more acidic.

Reactions Occurring over Bifunctional Catalysts [3,5,21]

1. General Aspects of Reaction Mechanisms

Indications of the mechanism of isomerization reactions of saturated hydrocarbons were obtained by Ciapetta [19], who observed that olefins were isomerized over the nickel-silica-alumina catalyst at appreciably lower temperatures than were the corresponding saturated hydrocarbons, suggesting that olefins were intermediates in the reaction. Ciapetta also suggested that the rearrangement of the carbon skeleton took place via a carbonium ion mechanism. Further support for such a mechanism was obtained by Mills and co-workers [20], who made experiments on three different types of catalysts, the first containing only an acidic function, the second only a dehydrogenation function, and the third containing both functions. It was found that the conversion of cyclohexane to benzene proceeded as well over the dehydrogenation catalyst as it did over the bifunctional catalyst but did not take place over the catalyst which contained only an acidic function. The isomerization-dehydroisomerization of methylcyclopentane to cyclohexane and benzene was found to occur to a significant extent only in the case of the bifunctional catalyst. Isomerization of cyclohexene to methylcyclopentene was found to require only an acidic function. Based on these observations, Mills and co-workers proposed the scheme in Figure 2.1 [21] to describe the reforming of C_6 hydrocarbons over a bifunctional catalyst.

The vertical reaction paths in the figure take place on the hydrogenation-dehydrogenation centers of the catalyst and the horizontal reaction paths on the acidic centers. The relative amounts of these products depending on reaction conditions.

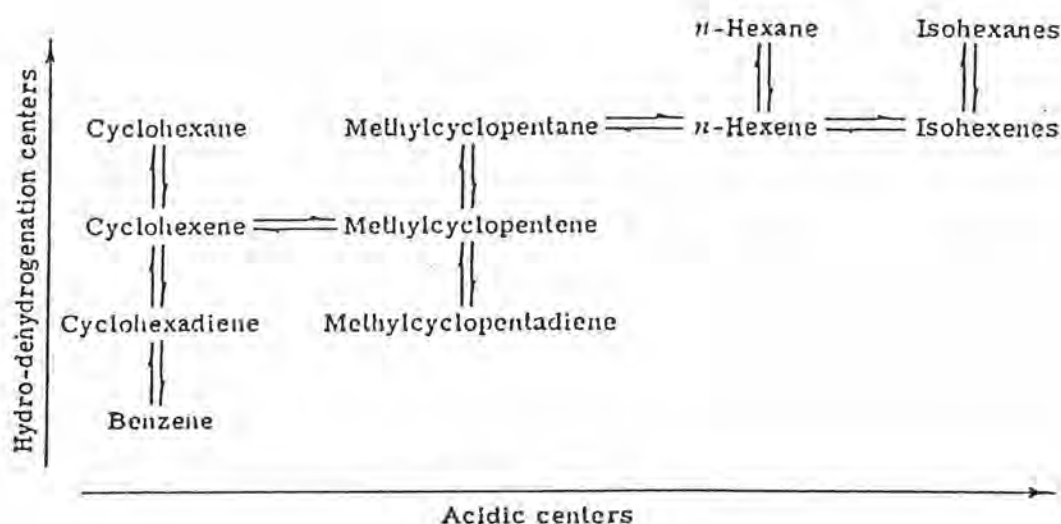


Figure 2.1 Reaction pathways in reforming C₆ hydrocarbons

Hydrocracking reaction over bifunctional catalysts are quite complex. Thus, over platinum-alumina catalysts both cracking on platinum metal sites and acid-catalyzed cracking can occur [16]. It has been suggested that olefins formed on platinum sites were intermediates in hydrocracking, in a manner similar to isomerization [16]. However, it has been found that appreciable hydrocracking of saturated hydrocarbons can also take place over alumina or halogenated alumina [18,22], although no active dehydrogenation component is present.

In the case of bifunctional platinum-acidic oxide catalysts, it has been demonstrated that the platinum sites and acidic sites can act independently. Thus, Weisz and Swegler [23] have shown that mechanical mixtures, in which the dehydrogenation and acidic functions were present on separate particles, were active for the isomerization of *n*-paraffins.

2. Description of Catalytic Reforming Reactions

Some of the typical reforming reactions catalyzed by the bifunctional, metal-acidic oxide catalysts, along with a specific example of each, are listed in equations 2.2-2.5 below : [5]

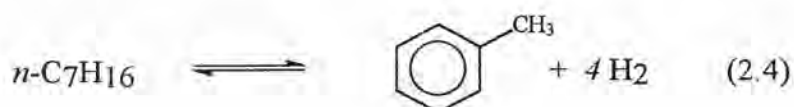
(a) Dehydrogenation of cyclohexanes (cycloparaffins) to aromatics



(b) Skeletal isomerization of n-paraffins to branched-chain paraffins



(c) Aromatization or Dehydrocyclization of paraffins to aromatics



(d) Hydrocracking to low molecular weight paraffins



Early reported studies on the application of bifunctional catalysts to the foregoing reactions were those of Haensel and Donaldson [24], Ciapetta and Hunter [25,26,27], Heinemann and co-workers [28], and Hettinger and coworkers [29].

The major part of the antiknock improvement obtained in the catalytic reforming of petroleum naphthas is due to the formation of aromatics. Lesser contributions result from the isomerization of straight-chain paraffins to branched-chain paraffins and hydrocracking of high molecular weight components to lower molecular weight components in the gasoline boiling range.

Of all the reactions taking place in catalytic reforming, the dehydrogenation of cycloparaffins to aromatics occurs the most readily. Skeletal isomerization reactions also occur readily, but not nearly so fast as the dehydrogenation of cycloparaffins. The limiting reactions in most catalytic reforming operations are hydrocracking reaction and aromatization reaction (dehydrocyclization reaction), which generally occur at much lower rates.

3. Thermodynamic Considerations [5,21]

The thermodynamics of the more important reactions in catalytic reforming can be discussed conveniently by referring to the equilibria involved in various interconversions among C_6 hydrocarbons. Some thermodynamic equilibrium constants at 500°C , a typical temperature in catalytic reforming, and heats of reaction are given in Table 2.3. The equilibrium constant K in Table 2.3 is defined in terms of the partial pressures of the reactants and products expressed in atmospheres.

Table 2.3 Thermodynamic Data on Reactions of C₆ Hydrocarbons

Reaction	K	ΔH_f , kcal/mole
Cyclohexane \rightarrow Benzene + 3 H ₂	6×10^5	52.8
<i>n</i> -Hexane \rightarrow Benzene + 4 H ₂	0.78×10^5	63.6
<i>n</i> -Hexane \rightarrow 2-Methylpentane	1.1	-1.4
<i>n</i> -Hexane \rightarrow 3-Methylpentane	0.76	-1.1

Source : from reference number [5]

The dehydrogenation of cyclohexane and the dehydrocyclization or aromatization of *n*-hexane to yield benzene are strongly endothermic, so that increasing temperature markedly improves the extent of conversion to benzene. It is advantageous to operate at as high a temperature as possible to maximize the yield of the aromatic hydrocarbon.

The thermodynamic considerations in the formation of aromatic hydrocarbons from higher molecular weight paraffins and cycloparaffins are qualitatively the same as for the formation of benzene from *n*-hexane and cyclohexane. Quantitatively, the equilibrium favors the aromatic hydrocarbon to a greater extent as the molecular weight increases.

The equilibria for the skeletal isomerization reactions are much less temperatures sensitive than those for dehydrogenation reactions, since the heats of formation of reaction are relatively small. In the equilibria between *n*-hexane and the methylpentanes, 2-methylpentane is the favored isomer over 3-methylpentane. This is reasonable from the simple statistical consideration that the substituent methyl group can occupy either of two equivalent positions in the former molecule, compared to one in the latter.

Hydrocracking reactions involve rupture of carbon-carbon bonds followed by hydrogenation. Such reactions are very exothermic and are highly favorable from a thermodynamic point of view. Thermodynamic considerations

are not important in determining the extent to which these cracking reactions occur in catalytic reforming. Practically speaking, the reactions are limited solely by kinetic factors.

4. Role of Hydrogen in Isomerization Reactions [3,5]

The effect of hydrogen pressure has been observed for both the isomerization of *n*-heptane to methylhexanes [30] and the aromatization (dehydrocyclization) of *n*-heptane to toluene [30] over similar platinum on alumina catalysts. In both of these cases it has been found that reaction does not take place in the complete absence of hydrogen (H_2) as indicated in Figure 2.2 for *n*-heptane skeletal isomerization and in Figure 2.3 for *n*-heptane aromatization.

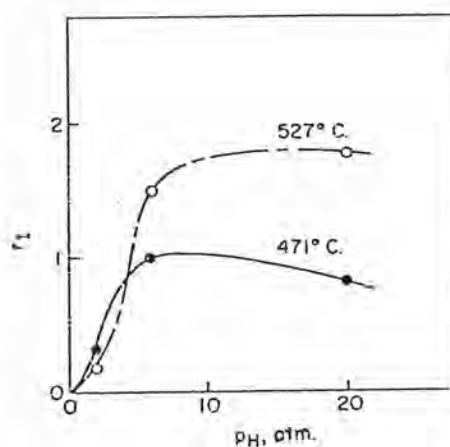


Figure 2.2 Effect of hydrogen pressure on the rate of skeletal isomerization of *n*-heptane over Pt/Al₂O₃ catalyst.

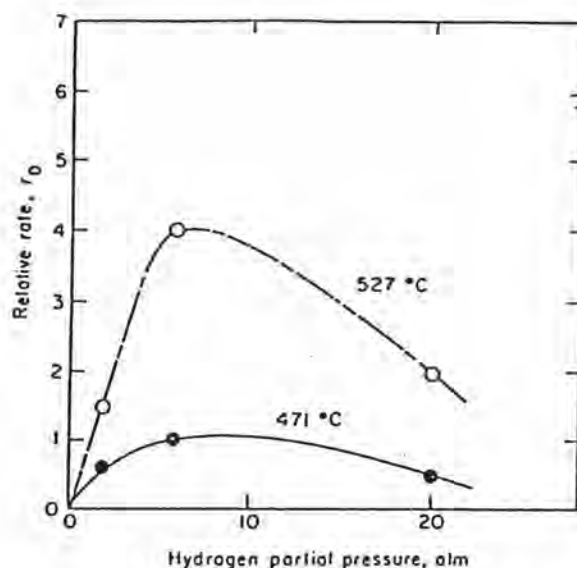


Figure 2.3 Effect of hydrogen pressure on the rate of aromatization (dehydrocyclization) of *n*-heptane over Pt/Al₂O₃ catalyst.

The hydrogen pressure effect on the rates has been interpreted as follows. In the absence of hydrogen, or at low hydrogen pressures, the platinum sites become heavily covered with hydrogen-deficient hydrocarbon residues (cokes). The role of hydrogen is then keeping the platinum sites free of these surface residues. With increasing hydrogen partial pressure, the platinum sites become partially cleaned of the carbonaceous residues or cokes.

Antiknock Quality

The tendency to knock, or “ping”, or explode on compression in internal combustion engines is quantified by the octane number. Two laboratory methods, the Research and the Motor method, have been standardized for obtaining octane numbers of motor fuels by comparing their knock tendencies in standard test engines with the reference fuel blends from *n*-heptane and isooctane. The proportion of “isooctane” in the reference fuel

knock tendencies in standard test engines with the reference fuels blends from *n*-heptane and isooctane. The proportion of “isooctane” in the reference fuel which matches the knock tendency of the fuel under test is termed its octane number [31]. Because “isooctane” has better antiknock properties than most commercial gasolines, it is arbitrarily assigned an octane number of 100. A poor fuel, *n*-heptane, is assigned an octane rating of zero. Generally, *n*-paraffins have lower octane numbers than branched paraffins, while aromatics have high octane numbers.

The Research and the Motor method use the same basic test engine but operate under different conditions. The Research Octane Number (RON) is accepted as a better guide of antiknock quality of fuels when vehicles are operated under mild conditions associated with low engine speeds. When operation is at high engine speed or under heavy load conditions, the Motor Octane Number (MON) may become of equal or greater importance.

Table 2.4 Operating Conditions for Research and Motor Methods

Conditions	Motor method	Research method
Inlet temperature	149°C (300°F)	52°C (125°F)
Inlet pressure	Atmospheric	
Humidity	0.0036-0.0072 kg/kg dry air	
Coolant temperature	100°C (212°F)	
Engine speed	900 rpm	600 rpm
Spark advance	19-26°Btc	13°Btc
Air-fuel ratio	Adjusted for maximum knock	

Source : from reference number [32]