

CHAPTER II

THEORETICAL CONSIDERATION

2.1 Important Intermediates and Chemicals from Aromatics [5]

Aromatic hydrocarbons are important commodity chemicals in the petroleum industry. The most commercially valuable aromatics are the BTX compounds (benzene, toluene, ethylbenzene and xylenes) [6]. BTX aromatics are important raw materials for the chemical industry. For example, styrene based plastics, phenolic polymers, nylon and biologically degradable detergents are produced from benzene. Benzene is the most widely used aromatic. Many chemicals and intermediates are derived from it. As an active compound, benzene can be alkylated by many alkylating agents. It can be chlorinated, nitrated, oxidized and hydrogenated. It is not polymerized, however derivative of benzene, such as styrene, are polymerized to useful products. About 50 % of chemical benzene is used for producing ethylbenzene, which is mainly utilized to obtain styrene. Figure 2.1 shows the most important chemicals based on benzene.

Although toluene is available in a much larger amount than benzene in the reformat gasoline, its use is limited to fewer products. The petrochemical industry uses toluene is less than 5 % of the total product in the reformat. Almost 50 % of the total toluene in the United States is dealkylated to benzene; the rest is used as a solvent or as a gasoline additive. Toluene can be nitrated to trinitrotoluene, or to 2,4- and 2,6-dinitrotoluene as important intermediates in polyurethane production (Figure 2.2).

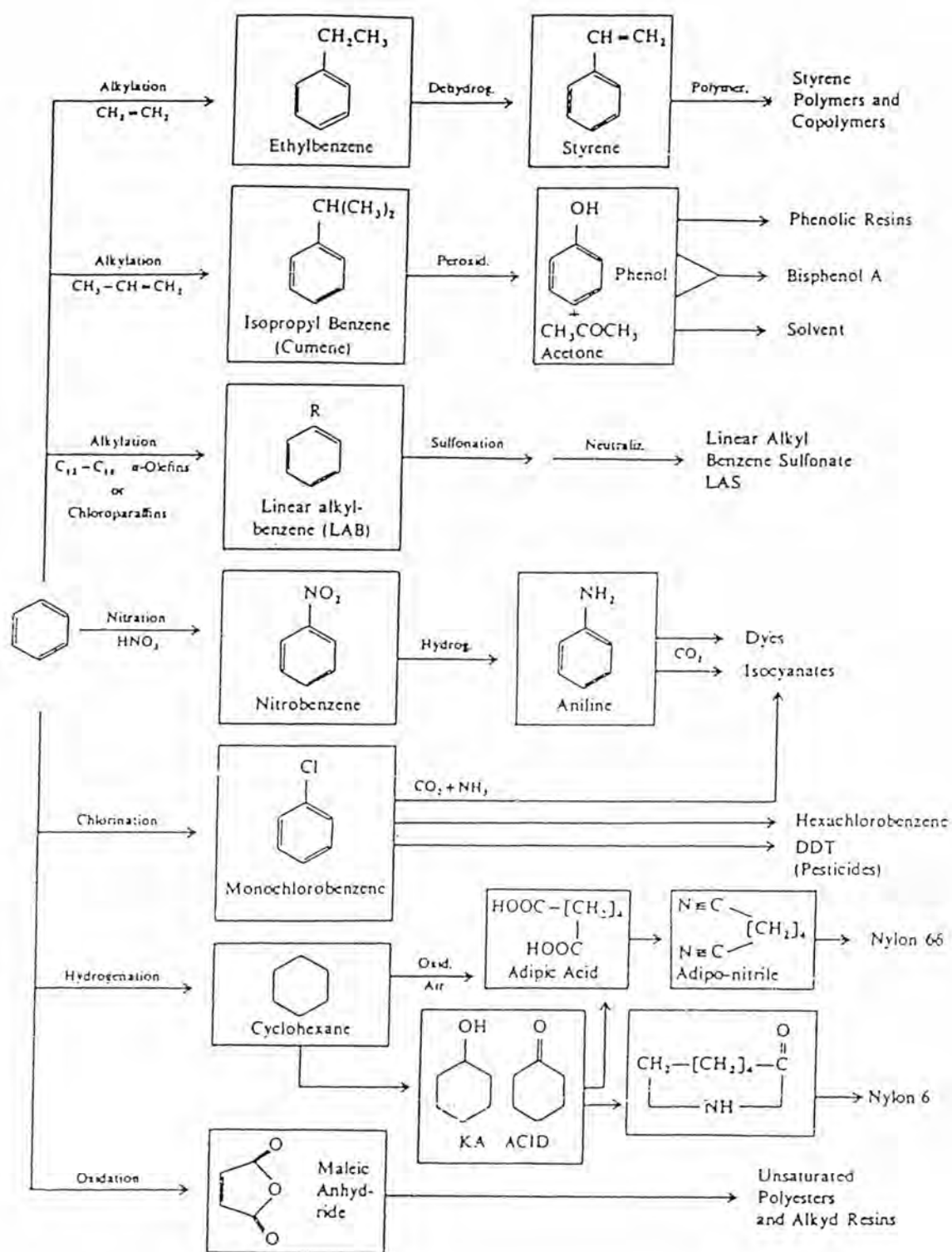


Figure 1.1 Important intermediates and chemicals from benzene [5].

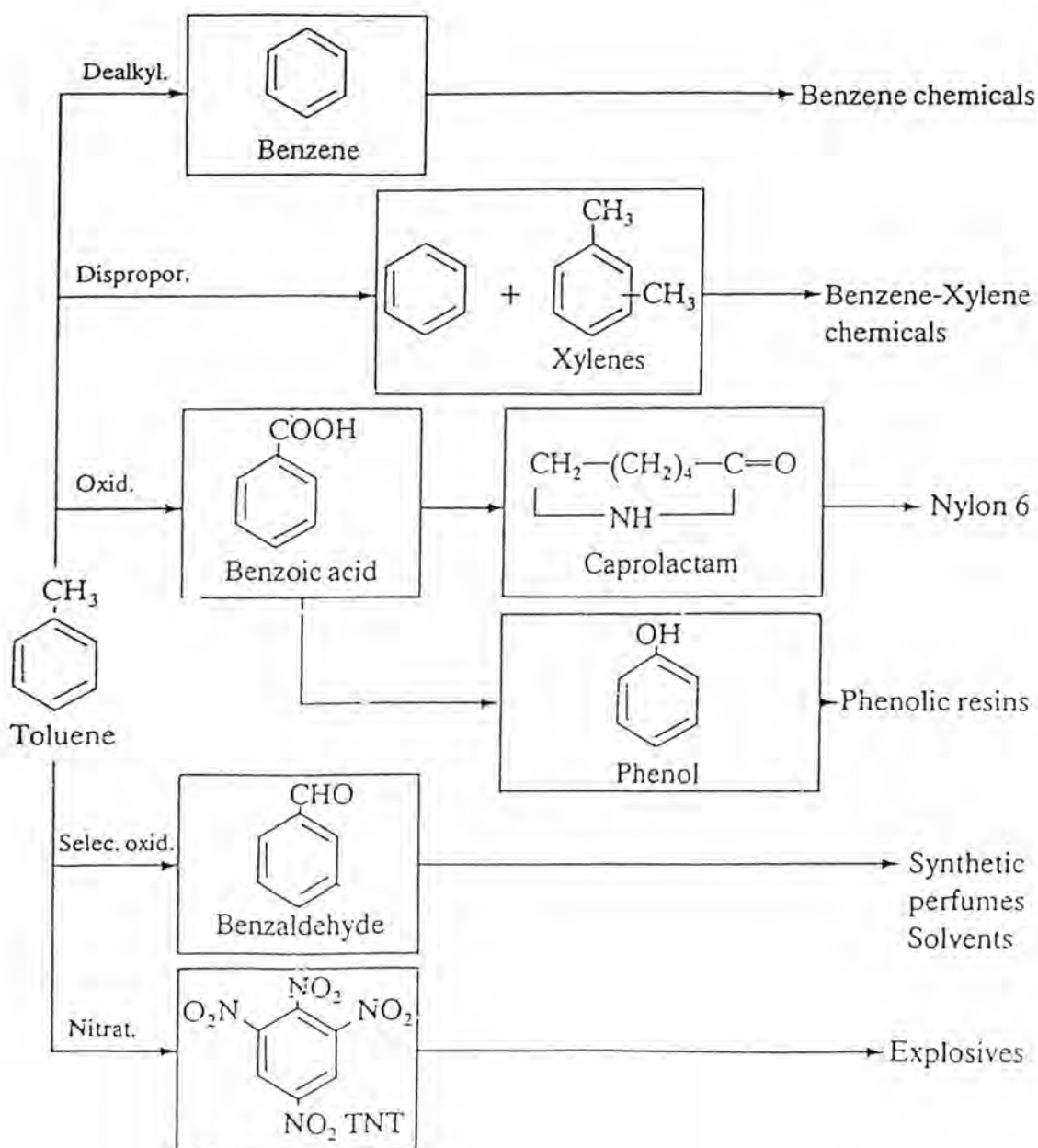


Figure 2.2 Important intermediates and chemicals from toluene [5].

The mixture of xylenes from the reformates has three isomer: ortho-, para- and meta. The most valuable isomer is p-xylene. It is the most important intermediate for producing terephthalic acid, which is used for production of polyesters. And the polyester are most important synthetic fiber raw materials. Figure 2.3 shows the most important chemicals based on xylenes

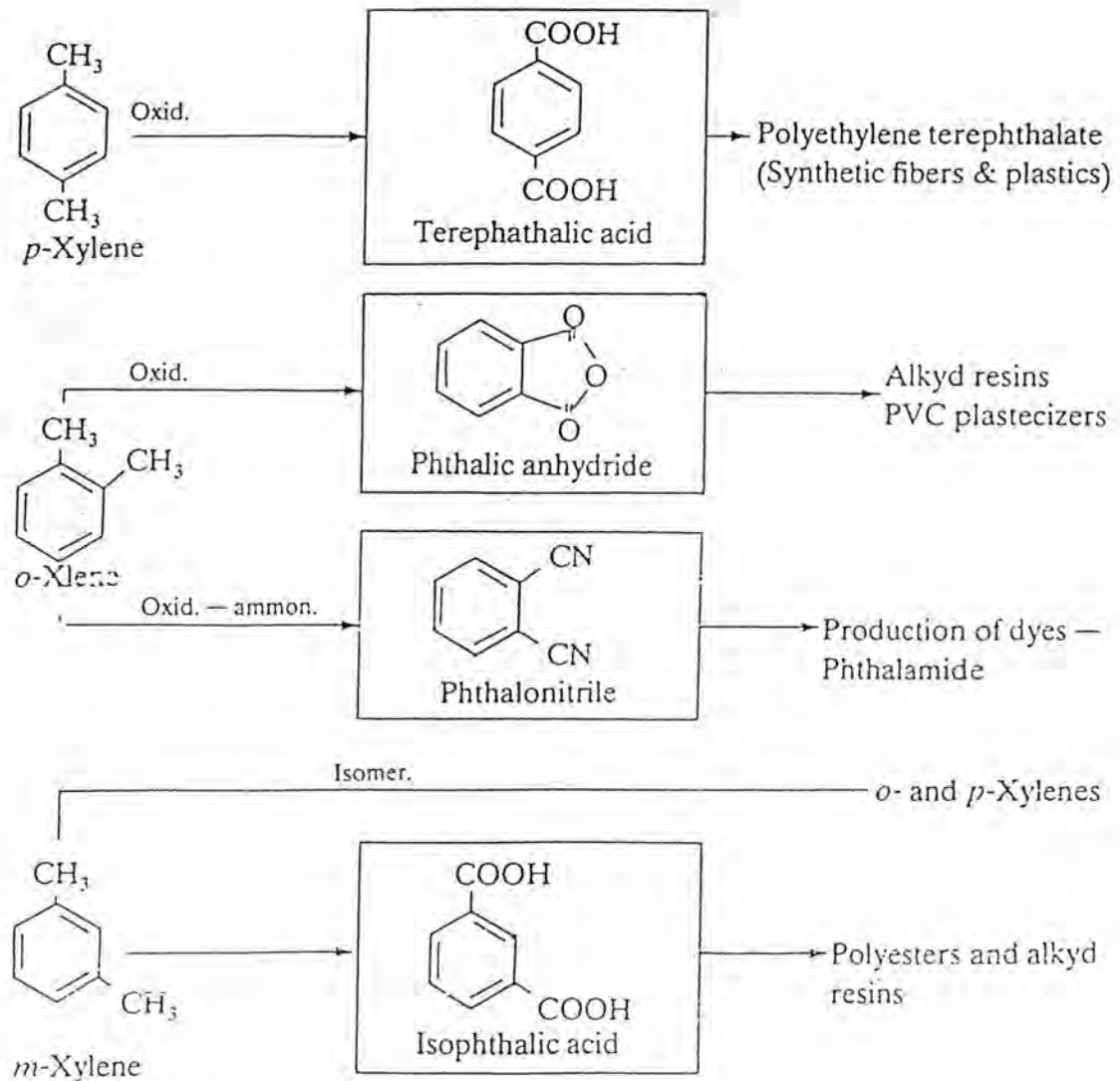


Figure 2.3 Important chemicals from xylenes [5].

2.2 Catalysts [7]

Catalysts play major role in catalytic reforming. Since severe conditions were needed to obtain aromatics from other hydrocarbons without the use of catalysts and since the yields were relatively low, dehydrogenation catalysts were used to improve yield and reaction conditions. The leading

commercial catalysts were platinum on alumina, platinum on silica-alumina, chromia on alumina, and molybdena on alumina.

The catalyst base was alumina, the dehydrogenating element was platinum, and the percentage platinum was between 0.3-0.6. Other elements that may be present were halides in percentages from 0-1.

The most desired catalyst was the one that promotes the production of aromatics and depresses the hydrogen cracking process. A bimetallic catalyst was produced containing platinum and other metal promoters, such as rhenium. The activity was improved, and the selectivity of such a catalyst allowed catalytic reforming to occur at lower pressures and higher temperatures with moderate regeneration cycles. Selectivity was governed by the relative rates of competing reactions, namely, dehydrogenation to yield aromatics and hydrocracking to yield lighter paraffins. Although activity was determined by the magnitude of the rate constant, platinum catalysts were generally the most active. They were also very expensive.

Such catalysts have a dual function. The platinum acts as a dehydrogenating agent. An acid substance, such as fluorine or chlorine, acts as the agent for isomerization. Enough platinum was used commercially to ensure that dehydrogenation activity was large when compared to the activity experienced for isomerization

(1) The Catalyst Supports [5]

The selection of a carrier depended on its having certain desirable characteristics. These characteristics include:

- Inertness.
- Desirable mechanical properties, including attrition resistance, hardness, and compressive strength.

- Stability under reaction and regeneration conditions.
- Surface area. High surface was usually desirable, but not always.
- Porosity, including average pore size and pore-size distribution. High area implies fine pores, but relatively small pores (for example, <5 nm) may become plugged in catalyst preparation, especially if high loading were sought.
- Low cost.

The Alumina Support [8,9,10]

The term “alumina” was used to describe various hydrate and anhydrous aluminium oxides. Most commercially available aluminas were prepared from the mineral bauxite (a mixture of hydrated aluminas and several non-alumina impurities) by the Bayer process, and were available at > 99% purity. Thermally stable high-surface-area forms of alumina can be prepared with acidic or basic surfaces. These may be used as acid or base catalysts for other catalytic materials (e.g. metals, oxides, sulphides, etc.).

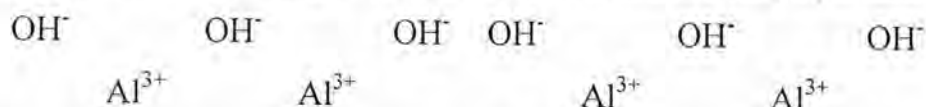
γ -alumina has a thermally stable high surface area, large mesopore volume and strong surface acidity. It was used as a bifunctional support for platinum in platforming (platinum reforming) the catalyst. Platforming catalysts were used to convert low-octane hydrocarbons to higher-octane species. Catalysts typically contain 0.25-0.5 wt. % platinum on high-purity γ -alumina, promoted with 0.5-1.0 wt. % Cl^- or F^- to increase surface acidity. Platinum provides sites for hydrogenation/ dehydrogenation. Promoted alumina provides acid sites to catalyst isomerization and cyclization reactions.

The most important alumina for use as a carrier was $\gamma\text{-Al}_2\text{O}_3$ or $\eta\text{-Al}_2\text{O}_3$, which have high area and were relatively stable over the temperature range of interest for most catalytic reactions. Their surface area can be

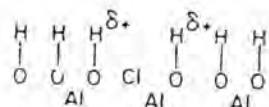
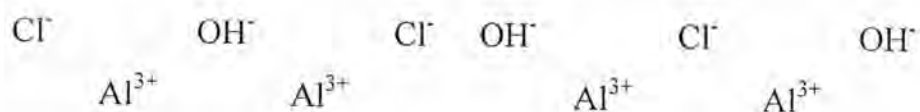
controlled [11]. The η form was inherently more acidic than the γ form, which makes it more active for many acid-catalyzed reactions such as olefin isomerization.

Acidity of Alumina

Fully hydrated aluminas may have some surface Brønsted acidity since their surface contain OH^- groups. In the η - and γ -aluminas, both Brønsted and Lewis acidity may be present, but they were weakly acidic. The acidity of OH^- group present on the surface can be markedly enhanced by the proximity of Cl^- ions: the development of surface acidity on alumina may be similar to that for silica-alumina, for which the electronic asymmetry set up by the proximity of the different species draws electrons from the O-H bond, increasing the acidity of the group. Partial conversion of a fully hydrated



alumina surface to a surface consisting of Cl^- and OH^- group (for example, by treating the surface with HCl) enhances the acidity of the remaining OH group markedly.



Electrons were pulled toward chlorine atoms and away from O-H bond, marking the OH group more acidic.

Fig 2.1 Acidity enhancement in alumina [11].

It would appear that the acidity of a group on the alumina surface can be progressively increased as more of the OH groups surrounding it were replaced by Cl^- ions. Thus both amount of acidity and the acid-site strength can be controlled on alumina

Alumina-supported bimetallic reforming catalyst have also been investigated with rhenium additions improved the thermal stability of 0.5 % $\text{Pt}/\text{Al}_2\text{O}_3$ but had little effect on activity, unlike 0.01-0.1 % $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts where activity was increased. Iridium additions improved thermal stability and resistance to poisoning by sulfur compounds. However, it was also reported that the very high dehydrogenation activity of unsulfided bimetallic reforming catalysts leads to easy production of coke on the metal surface [12].

The Molecular Sieve [13,14]

The commercial molecular sieves produced by Union Carbide were the Linde Molecular sieve 3A, 4A and 5A, the small pore synthetic zeolite. The sodium form (as synthesized) was 4A which can be modified by introducing the potassium cation (3A) or the calcium cation (5A), via ion exchange. Again cations have a specific role in controlling effective pore dimension. The unit cell of zeolite A contains 24 tetrahedral, 12 AlO_4 and 12 SiO_4 . When fully hydrate, there were 27 water molecules.

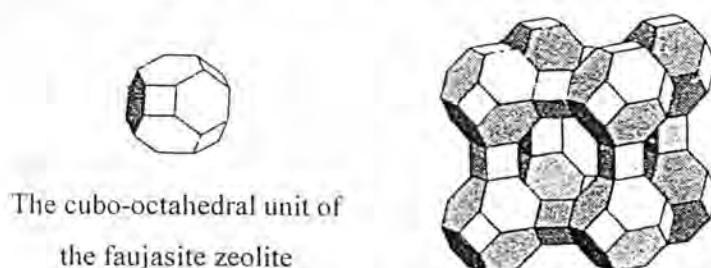


Figure 2.2 Structure of A zeolite [15].

Many preparation chemical analyses of zeolite A have indicated a Si/Al ratio of slightly less than 1 [16]. Zeolites of interest to shape selective catalysis may be divided into five major groups according to their pore/channel systems. There were 8-Membered Oxygen Ring System, Medium pore systems, Dual pore systems, large pore systems and Mesopore systems. The 8-membered Oxygen Ring Systems include most of the earliest known shape selective small pore zeolites, such as Linde Type A, erionite, and chabazite. The dimension of the pore opening also varies accordingly. For example, Linde Type A and ZK-4 have circular openings. Members of the group sorb straight chain molecules such as n-paraffins and olefins and olefins and primary alcohol [13].

(2) The Metal [11,17]

A conceptual advance was made by Sterba and co-workers [18] when they discovered the use of a support for the platinum that provided a separate catalytic function acidity to the isomerization. A summary of the dehydrogenation activity of several supported metals was given in Table 2.1, The most active metal was Pt because of its high activity and its unique selectivity characteristic. It was desirable to have it on the alumina in the highly dispersed form.

Table 2.1 Dehydrogenation of ethylcyclohexane with suspended noble metal catalyst [17].

Catalyst	H ₂ /mmol	Ethylbenzene/mmol
Pt/Al ₂ O ₃	13.04	4.15
Pd/Al ₂ O ₃	3.67	1.25
Rh/Al ₂ O ₃	1.96	0.78
Ru/Al ₂ O ₃	0.04	0.02

The catalytic dehydrogeno-aromatization of ethylcyclohexane indicated that the activity order was Pt>Pd>Rh>Ru as shown in table above.

The catalyst containing less than 1 wt. % platinum on alumina were characterized and expressed a very high dispersion of the metal. For a fresh catalyst containing 0.6 wt. % platinum, the ratio platinum atom to adsorbed hydrogen atoms was almost equal to unity. This showed that the metal was very highly dispersed on the support [19].

(3) Preparation Technique[20,21]

Support-metal catalysts were usually prepared by impregnation or ion exchange (ion adsorption) on a high-surface-area support such as silica or alumina. The methods were discussed here for Pt/Al₂O₃ especially, but they also apply to many other catalyst.

In the first method, the porous support, Al₂O₃ was saturated with a solution of a salt such as H₂PtCl₆. If only a shell of metal around the outside of the catalyst particle was desired, as it may be when pore diffusion affects the catalyst performance, sufficient solution was used to coat only the outside of the porous particles. H₂PtCl₆ was adsorbed very quickly from aqueous solution, resulting in a layer on the outer surface of an alumina pellet. This disadvantage could be overcome by the addition of HCl to the impregnation solution. [PtCl₆]²⁻ was adsorbed more slowly from acidic solution, resulting in more highly dispersed Pt, distributed homogeneously through out the alumina [24]. Then, it was calcined in air to convert the metal salt into a metal oxide. The oxide was reduced by hydrogen to give zero-valent metal.

After calcination the catalyst can advantageously undergo an activation treatment under hydrogen and at high temperature, e.g., 300° to

500° C, in order to obtain a more active metallic phase. The procedure of this treatment under hydrogen consists of a slow temperature rise under a hydrogen stream until the maximum reduction temperature was, for example, between 350° to 450° C and this was maintained for 1 to 6 hours [22].

2.3 Catalytic Reforming of Naphtha

The petroleum industry uses catalytic reforming to improve gasoline antiknock quality.[5] Catalytic naphtha reforming was especially a dehydrogenation process. Historically, naphtha reforming was developed to obtain a high octane gasoline by thermally changing the molecular structure of the hydrocarbon mixture. Catalytic naphtha reforming soon replaced the thermal process for the same purpose. The catalyst used was metal oxide, which was unstable. Platforming was first introduced by UOP, when it was discovered that platinum was more stable and active than catalysts previously used. Bimetallic and multimetallic catalysts, which were developed later, provided even more stability and activity than monometallic platinum catalysts. However, all these catalysts contain platinum with one or more other metals.

Platinum reforming is the reforming process which has the widest current use. It brought the significance of dual function catalyst into both prominence and importance. These catalysts, which were 0.3 - 1.0 % Pt well disperse on an acidic alumina (γ or η), have dehydrogenation sites on the Pt and isomerization sites on the alumina. Cl⁻, F⁻, or both may be added to the alumina to get the desired acidity [23]. The first catalysts used in catalytic reforming were chromium oxide or molybdenum oxide supported on alumina. These catalysts were unstable and produced large amounts of coke, which deactivated the catalysts after short periods. UOP was the first company which

introduced a platinum-alumina catalyst in 1949. This catalyst system was proved more active and selective than the oxides previously used. Platforming was a naphtha reforming process using 0.3-0.7 weight percent platinum on an alumina carrier. In catalytic reforming two catalytic sites were needed : hydrogenation-dehydrogenation sites, and acid sites which promoted reactions by a carbonium ion intermediate. Platinum was the best known hydrogenation-dehydrogenation catalyst. Acid sites were provided by the alumina carrier. Both these sites were necessary for aromatization and isomerization reactions [5]. In some respects these two functions seem to operate completely independent of one another, e.g., methylcyclohexane dehydrogenates on the Pt as if the alumina were not there. The cyclopentane homologs isomerize on the alumina almost as if the Pt were not there, yet the two must cooperate in the same way in keeping the catalyst clean.

Introducing high concentration of sulfur (9,800 ppm) caused a 90 % decrease in benzene production with corresponding increases in isomerization and unconverted cyclohexane [24].

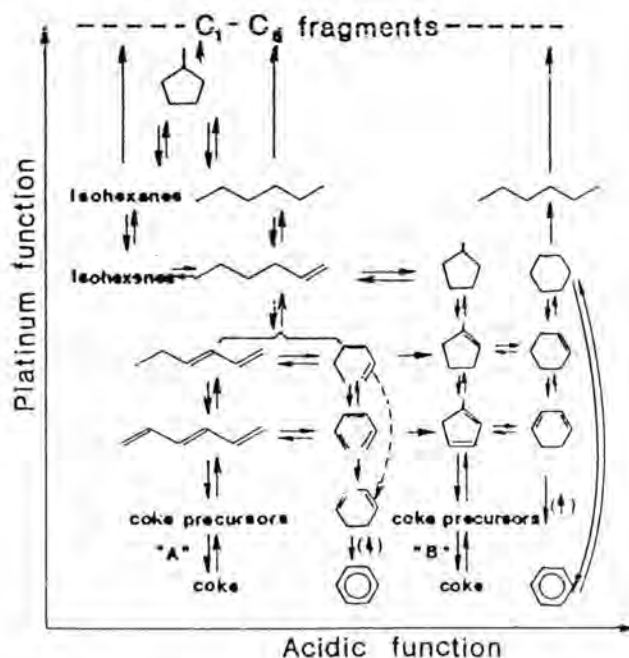
2.4 Bifunctional Catalysis of Reforming Reactions [25, 26]

The information of aromatics by dehydrocyclization of paraffins over metal-acidic oxide catalysts has been studied by several investigators. The metal-acidic oxide catalysts consist of an active dehydrogenation component, such as platinum or palladium, dispersed on an acidic support such as alumina or silica-alumina. These dualfunction catalysts are particularly active for dehydrocyclization, and this has been attributed at least in part to their high dehydrogenation activity [25].

Reforming reactions require two different functions: (1) a metal catalyzes dehydrogenation of paraffins into olefins and naphthenes into

aromatics; it also catalyzes hydrogenation of isoolefins and contributes to dehydrocyclization and isomerization, and (2) an acid function provided by the support catalyzes isomerization, cyclization, and hydrocracking through carbonium-ion mechanisms. The two functions interact through the olefins, which were the key intermediates in the reaction.

For the metal-acid Pt/alumina bifunctional catalyst, Mill et al. [26] proposed a bifunctional mechanism which was the original bifunctional mechanism for reforming reaction of n-hexane and methylcyclopentane. The mechanism was adapted by Menon and Paal [27] and showed in Scheme 2.1.



Scheme 2.1 Mechanism for reforming reaction of n-Hexane.

This mechanism attributed all dehydrogenation-hydrogenation reaction to Pt metal sites and all skeletal rearrangement steps (ring closure, ring contraction, and enlargement) to carbonium ion reactions occurring at the acidic sites on alumina [27].

An alternative pathway for aromatization would be stepwise dehydrogenation of the open-chain feed followed by ring closure of some of the polyunsaturated intermediates, e.g., hexatriene. Originally, the formation of dienes during aromatization was observed over Chromia catalysts by Pines and Csicsery [28].

According to this scheme, the reactant (*n*-hexane) was first dehydrogenated on the metal to give straight chain hexene. The hexene migrates to a neighboring acid center; there it was protonated to give a secondary carbonium ion, which can then isomerize and desorb as isohexene and migrate to the metal function, where it can be adsorbed and hydrogenated to give isohexane. Alternatively, the secondary carbonium ion can react to form methylcyclopentane, which can react further to form cyclohexene and then benzene. Other routes to the aromatic also exist.

2.5 Thermodynamics [11]

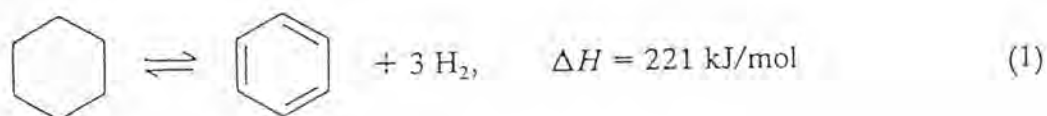
Thermodynamic data for typical reforming reactions at 500°C are given in Table 2.2. At equilibrium, cyclohexanes were substantially converted into aromatics at low hydrogen partial pressures. At equilibrium only very small concentrations of olefins can exist with paraffins. The major reforming reactions were endothermic.

Table 2-2 Thermodynamic data for typical reforming reactions.

Reaction	K_p at 500°C	ΔH_f kcal/mol of hydrocarbon
Cyclohexane \rightleftharpoons benzene + 3H ₂	6×10^5	52.8
Methylcyclopentane \rightleftharpoons cyclohexane	0.086	-3.8
n-Hexane \rightleftharpoons benzene + 4H ₂	0.78×10^5	63.6
n-Hexane \rightleftharpoons 2-methylpentane	1.1	-1.4
n-Hexane \rightleftharpoons 1-hexene + H ₂	0.037	31.0

(1) Aromatization Reactions [5]

Aromatization reactions were those leading to the formation of an aromatic compound from a nonaromatic hydrocarbon. Important aromatization reactions were the hydrogenation of naphthenes (saturated cyclic hydrocarbons) and the dehydrocyclization reaction of alkanes. The first was fast and reached equilibrium in a short time. The reaction was a dehydrogenation of cyclohexane or a substituted cyclohexane on the dehydrogenation sites of a metal such as a platinum. Substituted cyclopentanes require an additional step, isomerization, to be changed into a cyclohexane followed by dehydrogenation. Equation(1) illustrates the dehydrogenation of cyclohexane to benzene.

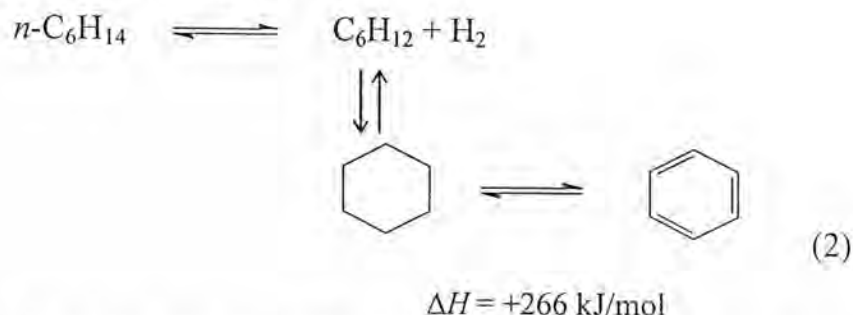


$$K_p = \frac{P_{Ar} \cdot P_{H_2}^3}{P_{naph}} = 6 \times 10^5 @ 500^\circ\text{C}$$

The reaction was reversible and highly endothermic. From the balanced equation, the equilibrium constant was 6×10^5 at 500°C (pressure in atmospheres).

It was clear that the yield of benzene was favored at higher temperatures and lower pressures. The effect of pressure varies dramatically with the change in H_2 partial pressure. Reforming units were normally run within the temperature and pressure ranges $500\text{-}530^\circ\text{C}$ and $14\text{-}25 \text{ kg/cm}^2$ respectively.

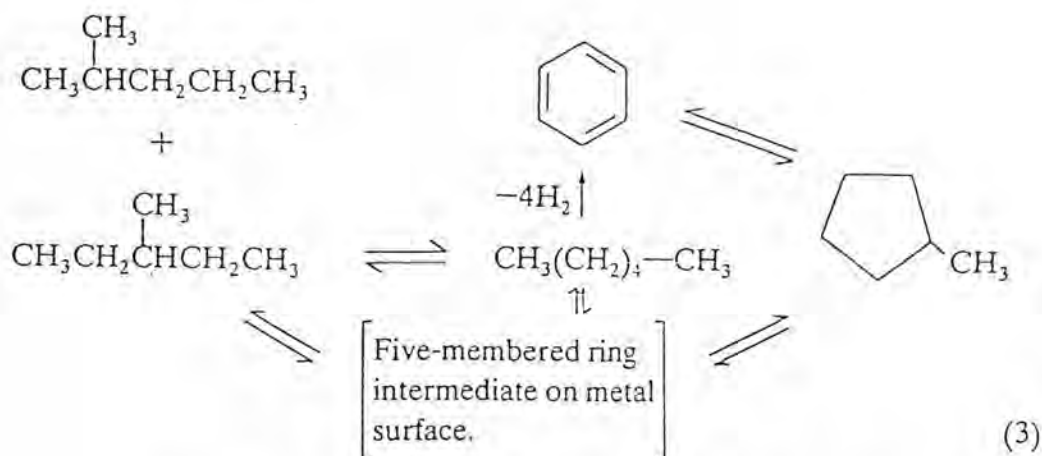
The second important reaction was dehydrocyclizing alkanes. Dehydrocyclization of alkanes involves consecutive reactions. The first step was dehydrogenation to an alkene. Other steps follow which may involve the formation of a carbonium ion. Using *n*-hexane as an example, the reaction could be represented by Equation (2).



As can be seen from the overall change in enthalpy, this reaction was also highly endothermic and was favored by higher temperature and lower pressures. Although reaction (2) was fast, the relative rate was far less than that of reaction (1). This could be understood on the basis that cyclization of hexane to cyclohexane was slow.

An important reaction that was indirectly related to aromatization was the isomerization of alkanes and cycloalkanes. Isomerization may take place on the surface of a non-acidic catalyst such as platinum or non-acidic alumina or by the aid of an acid catalyst. In the former case the reaction was slow. It has been found that when 2-methylpentane was reformed using Pt on

non-acidic alumina, benzene appeared as a secondary product. The dehydrocyclization of hexane may take place either directly on the catalyst surface or through the formation of a five-membered ring intermediate which isomerizes to cyclohexane. It seems that 2- and 3-methylpentanes may have to isomerize to *n*-hexane or alternatively may form a five-membered ring intermediate before dehydrogenation to benzene. This sequence of reactions is shown in Equation (3).



Acidic catalysts, on the other hand, catalyze the isomerization reaction much faster than non-acidic catalysts, through the intermediate of a carbonium ion. The isomerization step may be more significant for hydrocarbons having fewer than six carbons in the main chain such as methylpentanes and dimethylbutane. These compounds can isomerize to *n*-hexane which was able to dehydrocyclize to benzene. When acid catalysts were used it seems that the dehydrogenation of *n*-hexane to an *n*-hexene would be the first step. The alkene was then protonated to a carbonium ion intermediate followed by cyclization. Whether cyclization takes place through a methylcyclopentane intermediate followed by isomerization to cyclohexane, or by direct cyclization, was not clear.

(2) Kinetics

To understand the behavior of reforming reactors, we must understand the reaction kinetics and the influence of heat effects. A qualitative summary of the rate behavior of the important reaction classes catalyzed by the modern bifunctional catalyst is given in Table 2.3 with statements of the heat effects.

Table 2.3 Rate behavior and heat effects of important reforming reactions [11].

Reaction type	Relative rate	Effect of increase in total pressure	Heat effect
Hydrocracking	Slowest	Increases rate	Quite exothermic
Dehydrocyclization	Slow	None to small decrease in rate	Endothermic
Isomerization of paraffins	Rapid	Decreases rate	Mildly exothermic
Naphthene isomerization	Rapid	Decreases rate	Mildly exothermic
Paraffin dehydrogenation	Quite rapid	Decreases conversion	Endothermic
Naphthene gehydrogenation	Very rapid	Decreases conversion	Very endothermic

2.6 Literature Review

Many investigators have studied the processes to produce these aromatics such as:

Bournonville et al. (1993) [29] studied the process for catalytic aromatization of hydrocarbons containing 5 to 9 atoms per molecule. They use a catalyst containing a MFI zeolite containing 0.3 % of platinum and at least one additional metal chosen from the group constituted by tin, germanium, lead and indium. The support was alumina. The operating conditions were at

temperature of 480°C and at pressure of about 0.25 megapascal. The product of the aromatization contained 30 - 70 % by weight of aromatics.

Brand et al. (1996) [30] studied the catalytic reforming of naphtha which has a boiling range between 50 - 190°C. Naphtha was converted on a catalyst which contained about 0.4 % by weight of Pt and about 0.1 - 0.5 % by weight Zn under 500°C, and 10 bars of hydrogen. This research convert naphtha to an aromatic of 51.2 % by weight and percent yield of aromatics was 40.2 % by weight.

Kuchar et al.(1995) [31] studied the process for converting C₅/C₆ hydrocarbons to aromatic products. The process consisted of two reaction zone where the feedstream was contacted with zeolite at a temperature of about 300 - 500°C and a pressure of about 68 - 689 kPa. The catalyst was the same for the two reactors and comprised of zeolite composes of a gallium component and an alumina phosphate binder.

Le Van Mao et al. (1990) [6] did research on an aromatization catalyst comprising a mixture of ZSM-5 or ZSM-11 with zinc oxide/alumina co-precipitate. The major component of the feedstream were ethylene and propane. The examination took place under a temperature of about 500 - 540° C. There were about 47.3 wt. % aromatics in the product.

Bennett et al. (1988) [32] studied the process for converting C₂ - C₆ paraffin hydrocarbons to aromatic hydrocarbons over a gallium loaded zeolite. The process comprised two steps: first, ethane was contacted with catalyst at a temperature of from 500 - 650°C over a period from 10 to 50 hours; second, C₃-C₆ hydrocarbon (75 wt. % propane) were introduced at a temperature of 470 - 580°C over a period from 40 to 200 hours. Both steps carried out at a pressure about 1 to 20 bar. 90% of butane and 50% of propane was converted and 36% yield of aromatic was obtained.

Ever since the advent of catalytic reforming of naphtha or into high-octane in the 1950s, the mechanism of aromatization of alkenes and other reforming reactions have been a subject of intensive study. An added impulse to this came from the rapid growth of petrochemical industries in the following decades and the dedicated use of catalytic reforming to produce C₆-C₈ aromatics as petrochemical feedstock.