

## CHAPTER II

### LITERATURE REVIEWS

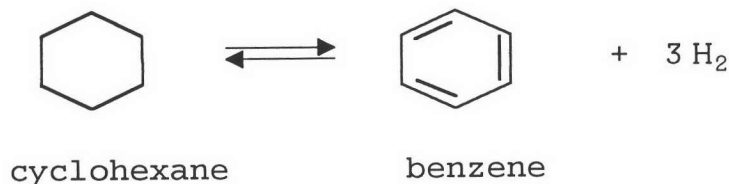
#### 2.1 Catalytic Reforming Reaction

There are four major reactions that take place during reforming. They are (1) dehydrogenation of naphthenes to aromatics, (2) dehydrocyclization of paraffins to aromatics, (3) isomerization of paraffins to isoparaffins and C<sub>5</sub>-ring naphthenes to C<sub>6</sub>-ring naphthenes and (4) hydrocracking of hydrocarbons to lower molecular weight hydrocarbons. The first two of these reactions involve dehydrogenation and will be discussed together. Typical examples of these reactions are given below. (Ciapetta and Wallace, 1972; Gary and Handwerk, 1991)

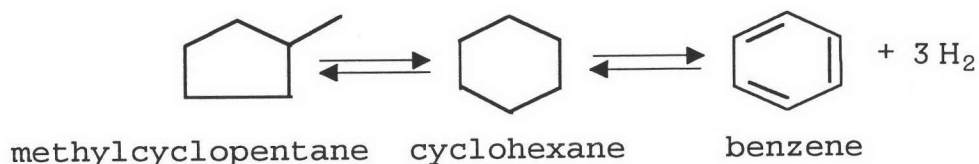
#### Dehydrogenation Reactions

The dehydrogenation reactions are highly endothermic and cause a decrease in temperature as the reaction progresses. In addition, the dehydrogenation reactions have the highest reaction rates of the reforming reactions which necessitates the use of the interheaters between catalyst beds to keep the mixture at sufficiently high temperatures for the reactions to proceed at practical rates. The major dehydrogenation reactions are:

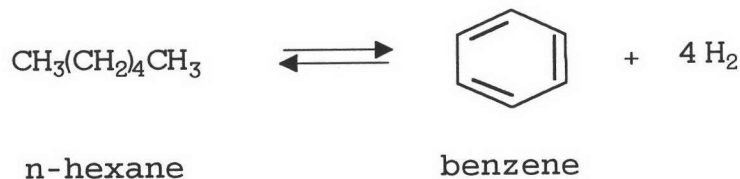
(a) Dehydrogenation of cyclohexanes to aromatics.



(b) Dehydroisomerization of alkylcyclopentanes to aromatics:



(c) dehydrocyclization of paraffins to aromatics:



The dehydrogenation of cyclohexane derivatives is a much faster reaction than either the dehydroisomerization of alkylcyclopentanes or the dehydrocyclization of paraffins, however all three reactions are necessary to obtain the high aromatic concentration needed in the product to produce a high octane number. Aromatics have a higher liquid density than paraffins or naphthenes with the same number of carbon atoms so one volume of paraffins produces only 0.77 volumes of aromatics and one volume of naphthenes approximately 0.87 volume. In addition, conversion to aromatics increases the gasoline end point because the

boiling points of aromatics are higher than the boiling points of paraffins and naphthenes with the corresponding number of carbons.

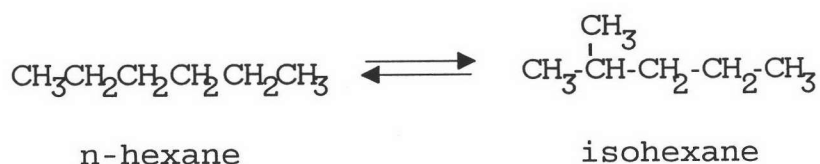
The yield of aromatics is increased by:

1. High temperature (increases reaction rate but adversely affects chemical equilibrium)
2. Low pressure (shifts chemical equilibrium "to the right")
3. Low space velocity (promotes approach to equilibrium)
4. Low hydrogen-to-hydrocarbon mole ratios (shifts chemical equilibrium "to the right", however, a sufficient hydrogen partial pressure must be maintained to avoid excessive coke formation)

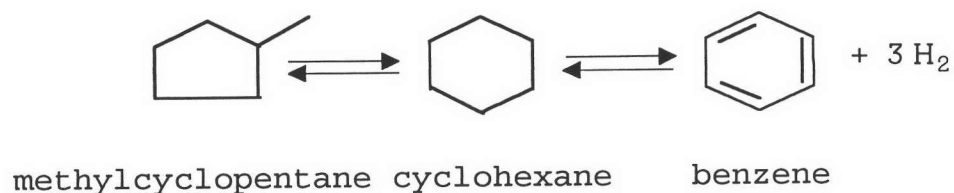
#### Isomerization Reactions

Isomerization of paraffins and cyclopentanes usually results in a lower octane product than does conversion to aromatics. However, there is substantial increase over that of the unisomerized materials. There are fairly rapid reactions with small heat effects.

(a) Isomerization of normal paraffins to isoparaffins.



(b) Isomerization of alkylcyclopentanes to cyclohexanes, plus subsequent conversion to benzene.



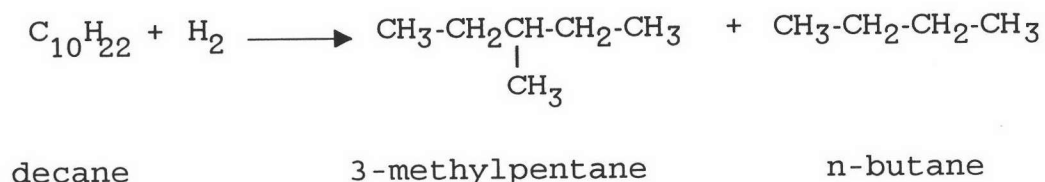
Isomerization yield is increased by:

1. High temperature (which increases reaction rate)
2. Low space velocity
3. Low pressure

There is no isomerization effect due to the hydrogen to hydrocarbon mole ratios but high hydrogen to hydrocarbon ratios reduces the hydrocarbon partial pressure and thus favor the formation of isomers.

### Hydrocracking Reactions

The hydrocracking reactions are exothermic and result in the production of lighter liquid and gas products. They are relatively slow reactions and therefore most of the hydrocracking reactions involve the cracking and saturation of paraffins.





2. For paraffins the following moles of aromatics are produced from one mole of paraffins having the indicated number of carbon atoms:

1 mole P <sub>6</sub>	yields	0.05 moles A <sub>6</sub>
1 mole P <sub>7</sub>	yields	0.10 moles A <sub>7</sub>
1 mole P <sub>8</sub>	yields	0.25 moles A <sub>8</sub>
1 mole P <sub>9</sub>	yields	0.45 moles A <sub>9</sub>
1 mole P <sub>10</sub>	yields	0.45 moles A <sub>10</sub>

As in any series of complex chemical reactions, reactions occur which produce undesirable products in addition to those desired. Reaction conditions have to be chosen that favor the desired reactions and inhibit the undesired ones. Desirable reactions in a catalytic reformer all lead to formation of aromatics and isoparaffins as follows:

1. Paraffins are isomerized and to some extent converted to naphthenes. The naphthenes are subsequently converted to aromatics.
2. Olefins are saturated to form paraffins which then react as in (1).
3. Naphthenes are converted to aromatics.
4. Aromatics are left essentially unchanged.

Reactions leading to the formation of undesirable products include:

1. Dealkylation of side chains on naphthenes and aromatics to form butane and lighter paraffins.
2. Cracking of paraffins and naphthenes to form butane and lighter paraffins.

Product distribution and reaction intermediates during catalytic reforming reaction have been thoroughly reviewed in several papers, for example, Krane et al. (1959) studied kinetic model of reforming n-heptane. A relatively simple kinetic model has been developed to describe the reaction steps between n-heptane, isoheptane, naphthene intermediate, crack products and aromatic product. The reaction patterns are indicated in Figure 2.1. n-Heptane isomerizes to isoheptane, cyclizes to a naphthene and hydrocracks. Isoheptane isomerizes to n-heptane, and also cyclizes to the naphthene and hydrocracks. The naphthene dehydrogenates to an aromatic and hydrodeacyclizes to both normal and isoheptane. The aromatic hydrogenates to the naphthene.

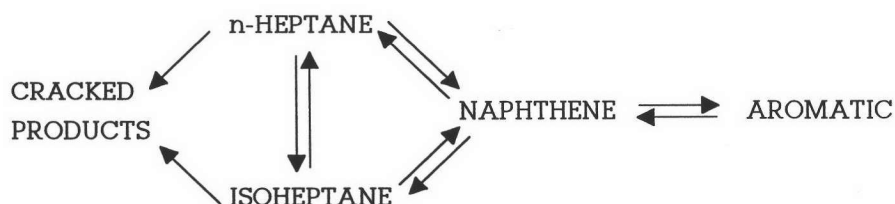


Figure 2.1 Reaction Patterns for Kinetic Model of reforming n-Heptane (from Krane et al., 1959)

Further studies of catalytic reforming reaction was reported by Kugelman (1976). He studied the effects of operating conditions on the equilibrium compositions of C<sub>6</sub> through C<sub>9</sub> hydrocarbons and found that equilibrium composition of aromatics decreased with decreasing temperature and increasing hydrogen pressures for all carbon number. For given temperature and hydrogen pressure, aromatic yield increased with increasing carbon

number. The kinetic model for catalytic reforming was shown in Figure 2.2.

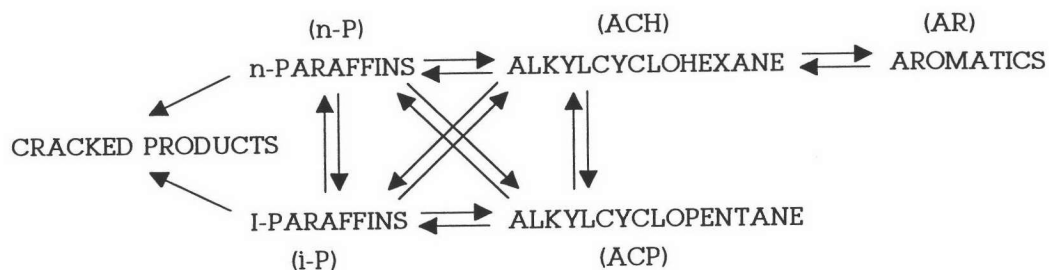


Figure 2.2 Kinetic Model for Catalytic Reforming  
(from Kugelman, 1976)

In addition, the other catalytic reforming reaction patterns will be discussed in more detail in a subsequent section (catalytic reforming reaction of n-hexane)

## 2.2 Reforming Catalyst

The first commercial catalytic reforming process in the United States was introduced in 1939, stimulated by the wartime demand for high-octane gasoline for propeller-driven aircraft and for aromatics chemicals such as toluene for use in making trinitrotoluene (TNT). A molybdena/alumina catalyst was utilized in a fixed-bed reactor operated under a high pressure of hydrogen. It was soon followed by processes utilizing a similar catalyst in a moving-bed or fluidized bed reactor. The catalyst became coked rapidly, thus requiring frequent regeneration, and these processes gradually became uneconomic during the 1950s upon the development of a catalyst consisting of platinum on an acidic alumina.

The platinum catalyst was utilized in a fixed-bed reactor and was introduced in 1949 by the Universal Oil Products Co. (UOP Platforming Process)



based on work by Haensel and his co-workers. Hydrogen, formed in the process, was recycled through the reactor to maintain a sufficiently high hydrogen partial pressure so that coke-forming reaction could be minimized. Thus the reactor could be operated for periods of many months before regeneration was needed. This was the first use of a precious metal catalyst in the petroleum industry, and it was followed rapidly by a number of related processes utilizing platinum that differed primarily in the nature of the support.

Hundreds of patents have been issued on catalyst compositions. All commercially used catalysts contain platinum, either alone or in a combination with another metal. In monometallic forms platinum content is typically 0.35 to 0.6 wt%. Bimetallic catalyst with rhenium usually contains approximately 0.3 wt% platinum and 0.3 wt% rhenium. The minimum content is set by an excessive rate of coking and is also affected by the nature of the feedstock. Diolefins, for example, cause more rapid coking which can be counteracted by a higher platinum content. For maximum utilization of a very expensive material, the platinum is spread out in as finely divided form as possible. A large fraction of the total platinum atoms present are on the surface.

The support is an alumina, in the  $\gamma$  or  $\eta$  form, which may have been acidified by the incorporating into the structure of approximately 1% chloride or fluoride during catalyst preparation. The use of chloroplatinic acid for impregnation leads to the natural incorporation of chloride into alumina during preparation. Acidity is gradually lost during reaction and may be restored by adding small amounts of an organic chloride or fluoride to the feedstock. Presumably this compound decomposes to release a halogen acid, which is adsorbed by alumina

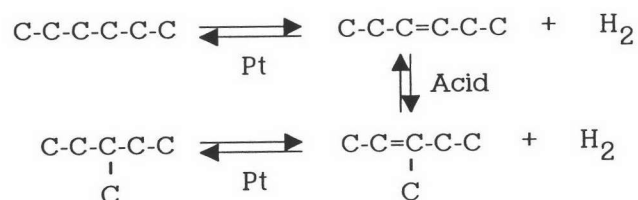
(Satterfield, 1980).

Reforming reactions typically proceed through a number of elementary steps. For example, the isomerization of, e.g., a n-paraffin to an isoparaffin, is not proceed directly but a n-paraffin is converted into an isoparaffin by first being converted into an olefin which is isomerized to an isoolefin and then converted into an isoparaffin. Correspondingly, the catalyst has two functions (sites), a hydrogenation-dehydrogenation function (metallic sites, e.g., platinum) for the paraffin-olefin conversions and an isomerization function (acidic sites) which is associated with the catalyst acidity (Satterfield, 1980).

Nowadays, typical reforming catalysts are Pt/Re on  $\text{Al}_2\text{O}_3$  and Pt/Ir on  $\text{Al}_2\text{O}_3$ . Both metals and the support play key roles in the catalysis. The role of platinum is to catalyze dehydrogenation-hydrogenation reactions. Chlorided alumina acts as an acid and catalyses carbon skeletal rearrangement through carbonium ion mechanisms. Proper acid activity is generally made by injecting trace amount of a chloride compound with the feed. The second metal, either rhenium or iridium, acts as a stabilizer and suppresses catalyst deactivation. It can also affect reaction selectivity. The role of the second metal in catalyst stabilization is not fully understood and is the subject of current industrial and academic research.

Except for naphthene dehydrogenation, which only requires a Pt site for catalysis, all the other major reactions require an interactions between sites. Ring and paraffin isomerization require the platinum function for dehydrogenation to olefin, the acid function for carbon skeletal rearrangement, and the metal function again for hydrogenation of the olefin (Ramage et al.,

1987).



Similar results were reported by Hindin et al. (1958). They studied the dehydroisomerization of methylcyclopentane to benzene. The used catalysts were mechanical mixtures of inert supported platinum and silica-alumina. The results of these experiments indicated that the above mentioned reactions can be proceeded via gas phase intermediates (olefins), which diffused from one type of catalytic site to the other. Thus, it appeared that a reaction like isomerization or dehydroisomerization of a saturated hydrocarbon can be proceeded satisfactorily by a succession of steps involving dehydrogenation to an olefins on platinum sites, followed by desorption and subsequent diffusion through the gas phase to acidic sites, where the isomerization step taken place. The isomerized olefin can be then diffused through the gas phase to a platinum site, where it can be undergone hydrogenation or dehydrogenation to form the final reaction products.

Furthermore, similar results were reported by Jenkins and Thomas (1970), and Thomas (1971). They determined the kinetics of the reactions of methylcyclopentane and of each of its products in the presence of Pt/SiO<sub>2</sub> and of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> in a differentially operated, isothermal-flow reactor. The reaction network was shown in Figure 2.3 and indicated that metal function was used for dehydrogenation to olefin and diolefins, and the metal function again for hydrogenation of the olefin to paraffins. The acid function was used for carbon

skeletal rearrangement, and only in this scheme, acid function was also used for hydrogenation of the olefin to paraffins.

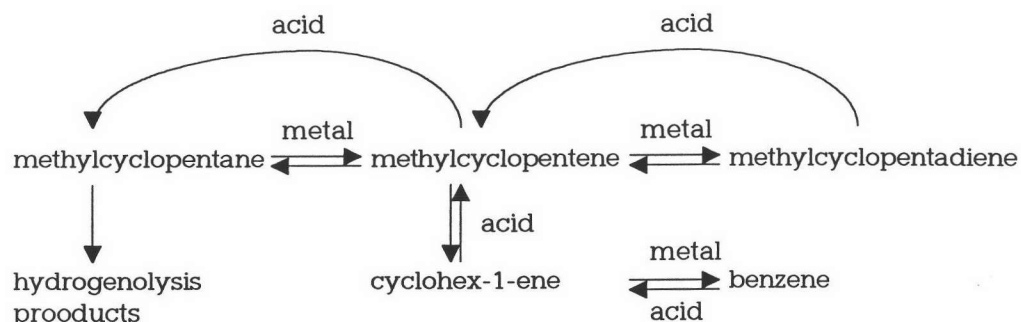
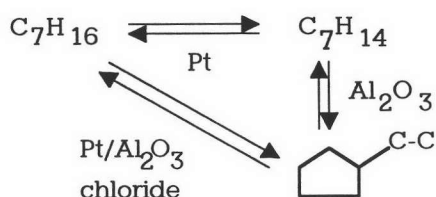


Figure 2.3 Reaction network for methylcyclopentane conversion catalysed by a mixture of large, monofunctional catalyst particles. (from Jenkins and Thomas, 1970)

Ring closure can proceed through dehydrogenation of the paraffin on a platinum site followed by carbon skeletal rearrangement on an acid site. However, there is also evidence that it can proceed directly on a single site composed of Pt, alumina, and chloride.



Further support for such a mechanism was obtained by Mill and co-workers (1953) who made experiments on three types of catalysts, the first containing only an acidic function, the second only a dehydrogenation function, and the third containing both functions. Data were obtained from conversion of C<sub>6</sub>-cycloparaffins (cyclohexane, methylcyclopentane, cyclohexene and methylcyclopentene). 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, Mill and co-workers proposed the scheme shown in Figure 2.4 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. According to the mechanism, the conversion of methylcyclopentane to benzene, for example, first involves dehydrogenation to methylcyclopentene on hydrogenation-dehydrogenation centers of the catalyst, followed by isomerization to cyclohexene on acidic centers. The cyclohexene then returns to hydrogenation-dehydrogenation centers where it can either be hydrogenated to cyclohexane or further dehydrogenated to benzene, the relative amounts of these products depending on reaction conditions.

In the reaction scheme in Figure 2.4, the dehydrocyclization of n-hexane is indicated to proceed via formation of n-hexene on dehydrogenation centers, followed by cyclization of the n-hexene to methylcyclopentane on acidic centers. The methylcyclopentane then is converted to benzene in the manner just described.

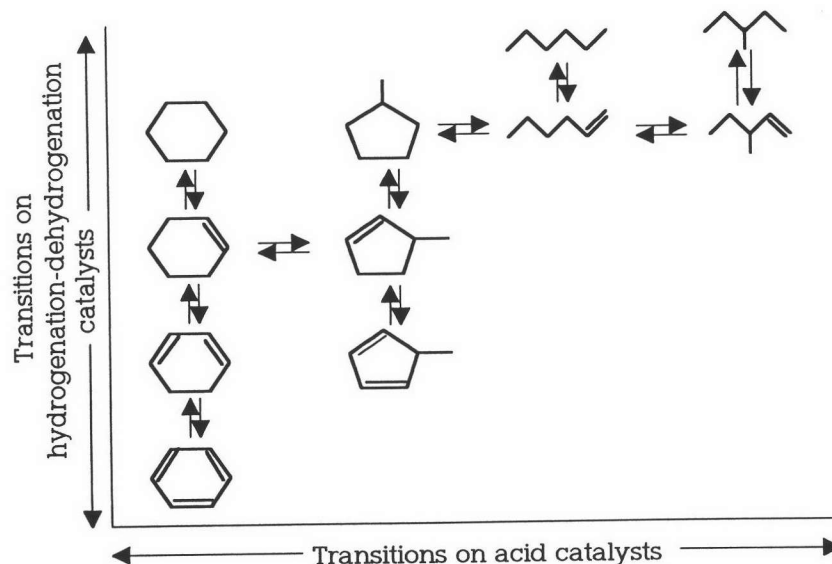


Figure 2.4 Reforming  $C_6$  Hydrocarbons with Dual Function Catalyst (from Mills et al., 1953)

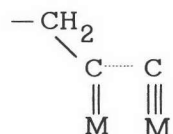
Cracking reactions can take place on either the acid site or the platinum site. Acid cracking is characterized by the formation of the  $C_3$  and  $C_4$  paraffin due to the carbonium ion mechanism. Metal cracking (hydrogenolysis), as shown by Sinfelt (1964), is random and forms more  $C_1$  and  $C_2$  gases relative to acid cracking.

In hydrogenolysis, a common form of C-C bond scission with formation of  $CH_4$  along with smaller amounts of  $C_2H_6$ . The mechanism of hydrogenolysis proceeds as follows on metal surfaces:



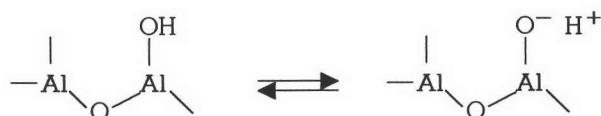
The mechanism of hydrogenolysis appears to involve adsorption of adjacent carbon atoms on adjacent metal sites, with breaking of C-H bonds. For the C-C bond rupture to occur, the carbon appear to have to

undergo further dehydrogenation, forming multiple carbon-metal bonds and leading to almost complete

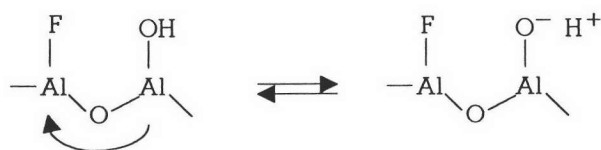


dehydrogenation of the carbon atoms. The strength of the metal-carbon bonds appears to be crucial to the rate of breaking the C-C bond. Once the C-C bond is broken, rehydrogenation of the fragments occurs, leading to CH<sub>4</sub> and a paraffin from the other fragment. However, since hydrogenolysis reactions require a site ensemble of two or more atoms, there must be a lower limit of crystallite size or cluster size below which the specific rate of hydrogenolysis decreases (Gates et al., 1979).

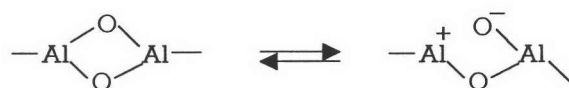
Sterba and Haensel (1976) mentioned that chlorine and fluorine act as suitably acidic components of the catalyst. The catalyst surface was largely that of a high surface  $\gamma$ -alumina, a polymeric structure with an occasional hydroxyl group. It was originally assumed that the acid sites on alumina were protonic (Bronsted) sites localized on the hydroxyl groups that were known to remain on an alumina surface even after calcination:



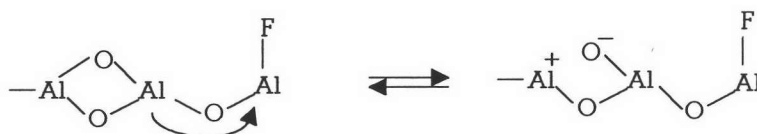
The effect of halogen on acidity was believed to be an inductive effect:



The previous studies also indicated that most of the acid sites on alumina were lewis acids. The evidence by no means rules out the presence of some protonic sites. In this picture the acid sites are oxygen bridges formed by dehydration of neighbouring OH groups during calcination. These bridges can open heterolytically to provide paired acid base sites:



The presence of a neighbouring halogen would enhance this polarization by an inductive effect:

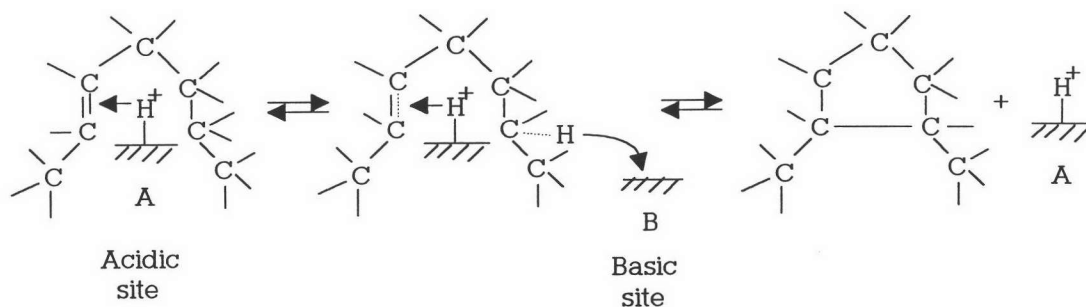


The exposed  $\text{Al}^+$  ions will normally react as Lewis acids although in the presence of  $\text{HCl}$  or  $\text{H}_2\text{O}$  it is conceivable that protonic sites can be formed. There is some evidence that the oxygen bridges remain in a closed (neutral) form until a reactive molecule actually approaches the site.

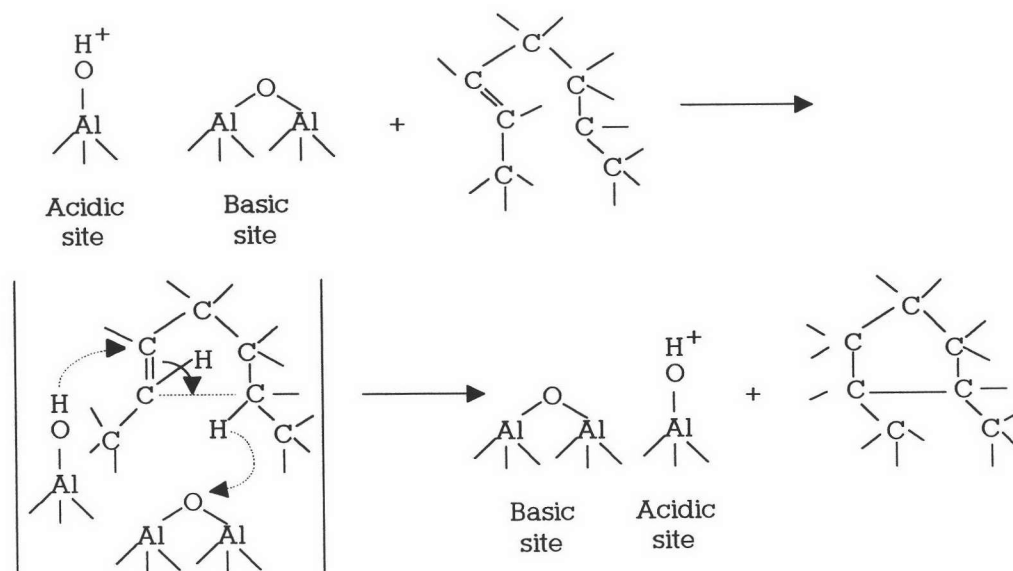
Gate et al. (1979) studied the alumina-catalysed reactions such as isomerization. They proposed that the cyclization of olefins, e.g., of heptene-2 to give a 5-carbon ring structure, does not appear to occur via a normal carbonium-ion mechanism on promoted alumina, since this would involve a cyclopentyl carbonium ion, which could desorb as cyclopentene or abstract a hydride ion and desorb as cyclopentane, cyclopentenes are not observed under reforming conditions. It was more probable that a concerted reaction occurs, involving



double-bond protonation by a Bronsted acid site and simultaneous proton abstraction from a carbon atom along the chain. Ring closure could occur by reaction of the two polar centers, as follows:



This reaction might be expected to occur on an adjacent pair of acid-base sites on the catalyst surface:



### 2.3 Deactivation of catalyst

A catalyst may lose its activity or its selectivity for a wide variety of reasons. The causes may be grouped loosely into:

- 1) Poisoning
- 2) Fouling
- 3) Sintering
- 4) Loss of active species

(McKetta and Cunningham, 1978, Satterfield, 1980)

#### Poisoning

Small quantities of impurities in reactants which decrease the catalyst activity are known as poisons. Poisons slow down the reaction and eventually stop it altogether. Inhibitors are not considered as poisons. Reactant, products, and undesired products such as soot, coke, and wax are also not considered poisons. Poisons are only the substances present in reactants as impurities which destroy the catalytic activity.

Most poisoning is due to surface effect, and the strong bond formations make it permanent and irreversible. In a complex reaction it may affect one reaction step more than another, hence the selectivity towards a desired reaction may be improved by deliberately adding a poison. It adsorbs on active sites of the catalyst, and if not adsorbed too strongly, it is gradually desorbed when the poison is eliminated from the feed stream. The phenomenon is then temporary. If adsorption is strong, the effect is permanent. The desorption may be enhanced by reaction with the fluid. Thus in a hydrogenation reaction a metallic catalyst may be poisoned by adsorption of a sulfur compound, but desorption may be enhanced by its conversion to  $H_2S$  by reaction with  $H_2$ . If a reaction product is strongly adsorbed, the reaction may be termed self-poisoned or

self-inhibited.

### **Fouling**

Fouling is the term applied to the formation of carbonaceous deposits (non volatile) on the catalyst in the course of many reactions of hydrocarbons and other organic substances. These deposits result from the reaction of organic substances at higher temperatures. They are usually some form of carbon or heavy tars adsorbed on the surface and within the bare structure of the catalyst. These deposits eventually cover the surface, causing a decrease in the activity. These materials can be easily removed by regeneration, by combustion, or by reducing the catalyst in  $H_2$ , if required.

### **Sintering**

The surface of a catalyst often decreases during use due to crystal growth. This occurs more rapidly at higher reaction temperatures. This phenomenon is called sintering. Due to the rapid decrease in surface, there is an irreversible loss in activity of the catalyst. This is a common phenomenon in high temperature catalysis. It may consist of growth of metal crystallites on a support or of a decrease in area of nonsupported catalyst.

### **Loss of Active Species**

The particular active species may also be converted to another form less active or selective, as is the case with certain complex metal oxides used in partial oxidation reactions. A complex metal oxide crystal may also decompose into other compounds, sometimes caused by loss of a particular element via

volatilization of a compound. A somewhat amorphous catalyst may crystallize, or a compound active in one crystal habit may be converted into a less active crystalline form. A supported metal catalyst may be reduced in activity or selectivity by becoming alloyed with a metallic impurity or by reaction with the support, for example, a nickel/alumina catalyst may be converted to a nickel aluminated.

#### **2.4 Deactivation of Reforming Catalyst**

In reforming with a paraffinic feed, poisoning begins on the metal with the formation of the olefinic species and aromatics. These can slowly form coke on the metal, but they can also be transported by gas-phase diffusion and surface migration to the acid sites, where they slowly form more resistant coke, as shown schematically in Figure 2.5. The long term deactivation in reforming is probably due to this second type of coke formation.

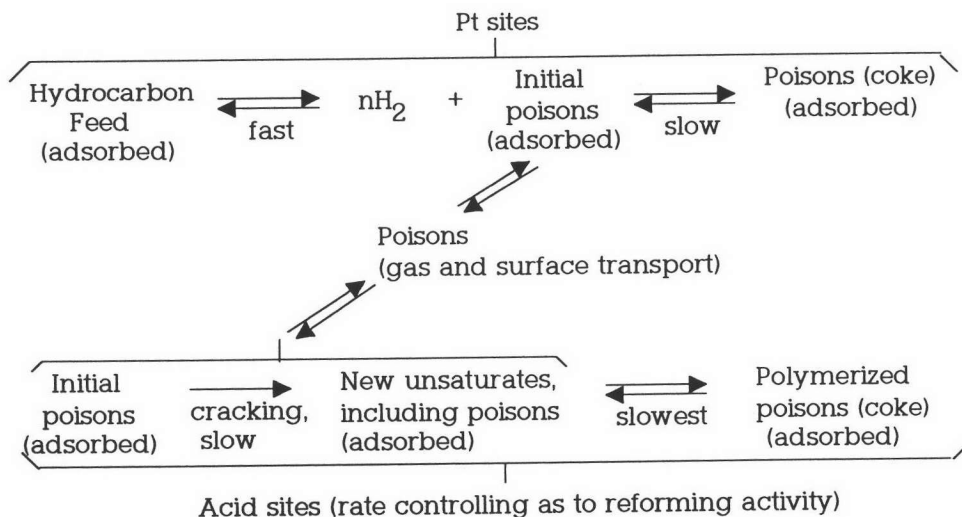
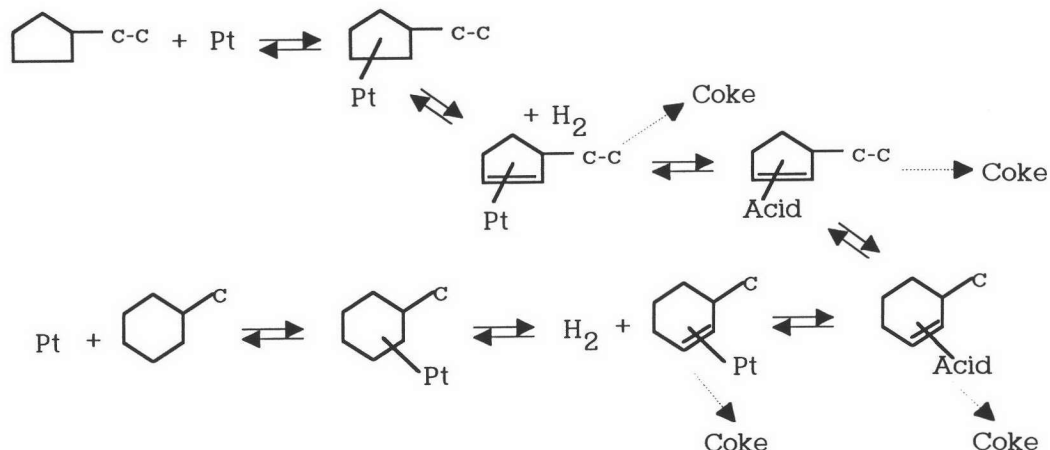


Figure 2.5 Schematic representation of deactivation processes involving coke formation on reforming catalysts (Ciapetta and Wallace, 1972, partly from Gates et al., 1979)

Ramage et al. (1987) studied the naphthene isomerization of  $C_5$ -ring naphthene to  $C_6$ -ring naphthene. They concluded that a platinum catalysed dehydrogenation-hydrogenation reactions while an acid catalysed carbon skeletal rearrangement. Furthermore, They found that the catalyst deactivated because of coke formation on the Platinum and acid sites. The overall scheme for ethylcyclopentane is shown here. It also thought that the second metal, Re or Ir, lower the formation rate of these coke precursor.



## 2.5 Catalytic Reforming of n-Hexane

The kinetics of simultaneous isomerization and cracking of normal and isohexane on a bifunctional 0.35 wt% Pt-Al<sub>2</sub>O<sub>3</sub> catalyst has been studied at 435°C, a total pressure of 10.5 bar and a hydrogen/hydrocarbon partial pressure ratio of 20 in a fixed bed reactor. The isomerization and cracking rate constants were evaluated by Christoffel (1979). Reaction pattern in Figure 2.6 is used to describe simultaneous cracking and isomerization of normal and isohexanes.

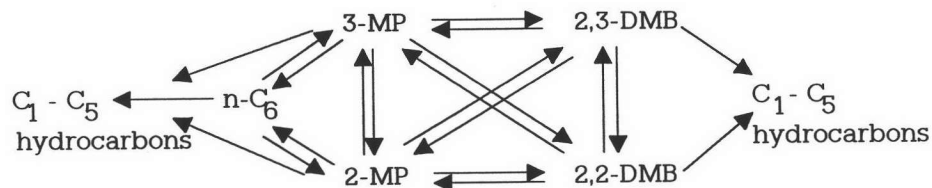


Figure 2.6 Reaction Pattern of Isomerization and Cracking of the Five Hexane Isomers (Christoffel, 1979).

The kinetics of hexane isomerization has been described on the basis of different kinetic models.

Evering and Waugh (1951) postulated that the hexanes isomerize in a stepwise manner according to Figure 2.7.

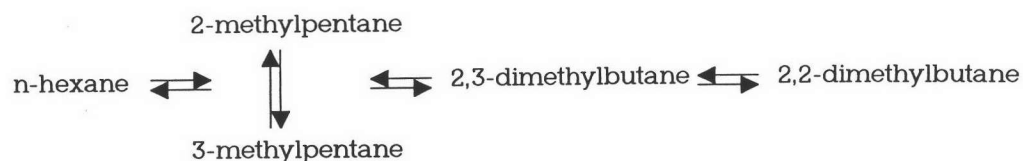


Figure 2.7 Reaction Pattern of Isomerization of the Five Hexane Isomers (Evering and Waugh, 1951).

In 1982, Marin and Froment studied the isomerization, dehydrocyclization and hydrocracking of  $C_6$  hydrocarbons on a commercial reforming Pt- $Al_2O_3$  catalyst in a tubular reactor. The temperature was varied from 420°C to 500°C, the pressure from 1.6 to 16 bar, the molar  $H_2$ /hydrocarbon inlet ratios from 1.5 to 20 (units:  $10^{-3}$  kmol/kg cat.hr.bar). Their considerations led to the reaction network shown in Figure 2.8.

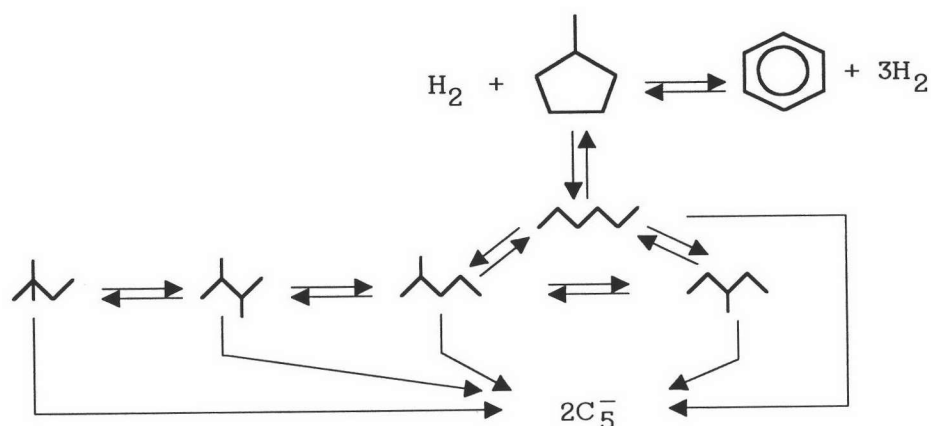


Figure 2.8 Reaction network of  $C_6$  at 420°C, 10 bar and molar  $H_2$ /hydrocarbon inlet ratio of 10 (from Marin and Froment, 1982)

In 1975, Blue and Gould purposed the main reactions of catalytic reforming. Similar results were reported by Henningsen et al. (1970), Kmak et al. (1973), Kleelman (1976) and Mayers (1986). Because of the wide range of paraffins and naphthenes included in the platformer feed and because the reaction rates vary considerably with the carbon number of the reactant, these reactions occur in series and in parallel to each other, forming the rather complicated overall reaction indicated in Figure 2.9.

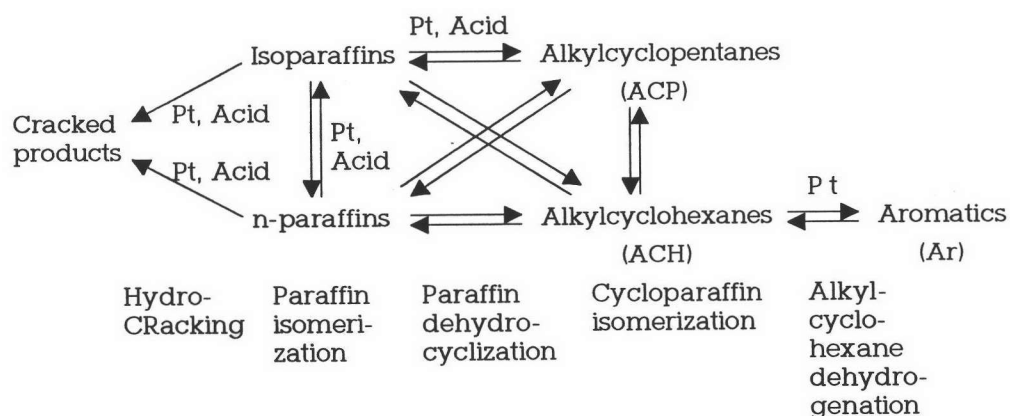


Figure 2.9 Main Reaction of Catalytic Reforming  
(from Kirk-othmer, 1982)

Most of reactions are reversible indicating the importance of reaction equilibrium. In the alkylcyclohexane to aromatic equilibrium,  $ACH \rightleftharpoons Ar$ , aromatics are favored by high temperatures and low pressures. Reforming conditions promote rapid ACH dehydrogenation with conversion to aromatics.

The alkylcyclopentane (ACP) to aromatics process is less efficient than ACH dehydrogenation ( $ACP \rightleftharpoons ACH \rightleftharpoons Ar$ ), owing to slowness of the first step and ACP ring opening, and its requires an acidic platinum catalyst. Cyclohexane is converted to benzene in close to 100%



efficiency, whereas only 50-75% of methylcyclopentane is converted to benzene. Reformer feeds of high aromatics-plus-cycloparaffins content produce high-octane reformates using only the cycloparaffins-to-aromatics reactions. Cyclization of paraffins is generally more difficult.

## 2.6 Effects of Process Variables

Temperature, pressure, space velocity, hydrogen to feed mole ratios, and composition of feed are the principal operating variables in fixed-bed catalytic reforming.

### Reactor Temperature

In general, reactor temperatures range from about 850 to 975°F (454 to 524°C). Temperature increases are most effective in increasing the octane number of the products through increasing both the aromatization and hydrocracking reactions. Ciapetta et al. (1958) suggested that too high temperatures cause serious losses in product yield through promoting excessive hydrocracking. Too low temperatures, on the other hand, gave too little aromatization of naphthenes and paraffins to permit production of high octane gasolines. In practice, the effects of decline catalyst activity with time on stream were compensated for by gradual increased in the operating temperatures up to the limits described above.

Gates et al. (1979) indicated that reaction temperatures are chosen to balance the advantage of increased catalytic activity and disadvantage of increased deactivation rate as temperature is increased. The values range from 460 to 525°C and are usually between 482 and 500°C. Low-pressure processes are

operated at slightly higher temperatures than the others to optimize conversion to high-octane-number products. As, catalysts lose activity in operation, reactor temperature is gradually increased to maintain a constant octane number in the product reformat.

### **Reactor Pressure**

The effects of the reactor pressure have been extensively discussed. Ciapetta et al. (1958) suggested that high pressure operation tended to inhibit aromatization and to promote hydrocracking. A more volatile reformat is produced and hydrogen production was low. Low pressure operation, on the other hand, repressed hydrocracking and significantly increased the amount of aromatics formed. Higher gasoline yields are obtained and the hydrogen production is maximized. However, coking of the catalyst is increased owing to the lower hydrogen partial pressures, and the processes which employ low pressure (200-300 psig) are equipped with facilities for regular regeneration of the activated catalyst.

Aromatics formation as a function of pressure and temperature, for a C<sub>6</sub>-370 K Mid-Continent naphtha, the temperature ranges are 452-527°C and the pressure range are 6.8-40.4 atm (100-600 psi). Ramage et al. (1987) indicated that high yields of aromatics are favored by low pressures and high temperatures. Pressure below 6.7 atm (98.63 psi) were not yet feasible in commercial operation because of rapid catalyst deactivation.

Similar results were reported by Gates et al. (1979). In processes operated at the relatively high pressures of 34 to 50 atm, the high partial pressure of hydrogen resulted in high rates of hydrocracking, limited degrees of conversion to aromatics, low rates of catalyst

deactivation, and low yields of hydrogen. In contrast, low-pressure operation (8.5 to 20.5 atm) gave high conversion to aromatics, low hydrocracking conversions, and high hydrogen yields, however, it also led to rapid deactivation of the catalyst by coke formation.

### **Space Velocity**

The space velocity of the liquid can frequently be used to control reforming severity. Low space velocities increase hydrocracking (at constant temperature) but have little effect on the aromatization, since this reaction is quite rapid under normal operating conditions with platinum catalysts. Higher space velocities tend to inhibit hydrocracking. To make a high octane product, temperature must be increased at the faster feed rates. This tends to cancel the beneficial effects on yield of the repressed hydrocracking. The relatively slow isomerization and cyclization reactions are likewise hindered by high space velocities. In general operation, space velocities range from 1 to 5 liquid hourly space velocity, with 2 to 3 being the preferred range. (Ciapetta et al., 1958)

Gates et al. (1979) indicated that space velocity ranges from 0.9 to 5 vol of liquid feed per volume of catalyst per hour, with 1 to 2 most common. The choice represented a compromise between allowable hydrocracking and desirable dehydrocyclization. Aromatization and isomerization are not affected by changes in space velocity, since these reactions approach equilibrium even at high space velocities.

### **Hydrogen to Hydrocarbon Mole Ratio**

Hydrogen/fresh feed mole ratios of 3 to 10 are most frequently used, with 5 to 8 being the preferred

range (Ciapetta et al., 1958, Gates et al., 1979). High hydrogen-to-hydrocarbon ratio adversely affects aromatization, increases hydrocracking and reduced catalyst deactivation rates because of coke lay down on the catalyst. There is an equilibrium established between hydrogen recycle and carbon deposited on the catalyst in the reactors. Coke is being continuously laid down on the catalyst and removed by the hydrogen in the recycle gas. In practice, with higher boiling stocks, it is often desirable to increase the partial pressure of hydrogen. High pressure, however, tend to repress aromatization at constant conditions. Low partial pressures of hydrogen usually lead to too rapid deactivation of the catalyst through increased coke deposition and lower limits of pressure are governed by the desired amount of hydrocracking and the maximum allowable lay down of coke on the catalyst.

#### **Composition of Reformer Feed**

Catalytic reformer feeds are saturated (not olefinic) materials, in the majority of cases the feed may be a straight-run naphtha, but other by-product low-octane naphthas (e.g., coker naphtha) can be processed after treatment to remove olefins and other contaminants. Feed which have an appreciable concentration of unsaturated hydrocarbons must usually be hydrotreated before reforming in order to prevent undue hydrogen consumption in the reformer and excessive catalyst deactivation (Gates et al., 1979). Hydrocarbon naphtha that contains substantial quantities of naphthenes is also a suitable feed. The yield of gasoline of a given octane number and at given operating conditions depends on the hydrocarbon types in the feed. For example, high-naphthene stocks, which readily give

aromatic gasolines, are the easiest to reform and give the highest gasoline yields. Paraffinic stocks, however, which depend on the more difficult isomerization, dehydrocyclization and hydrocracking reactions, require more severe conditions and give lower gasoline yields than the naphthenic stocks. The end point of the feed is usually limited to about 190°C (375°F) (Speight, 1991).

The concentrations of impurities in the feed that can act as catalyst poisons must also be rigorously controlled. Sulfur poisons the metal function of the catalyst and must be maintained at concentrations less than about 1 ppm in the feed contacting the newer catalysts. Fuels with higher sulfur content must be catalytically hydrodesulfurized before being reformed. Organic nitrogen compounds are converted into ammonia and poison the acid function of the reforming catalyst. Their concentrations must also be kept below about 2 ppm, nitrogen compounds are usually removed in a catalytic hydrotreating step, which simultaneously leads to hydrodesulfurization. Water and chlorine-containing compounds are undesirable feed components because they alter the acidity of the support and thus upset the balance between the reactions occurring. Since these compounds are not easily eliminated, their concentrations are carefully controlled to maintain the proper catalyst acidity. Metals such as As, Pb, and Cu must be kept at extremely low concentrations, since they alloy with the Pt component or otherwise deactivate it. Severe poisoning by As has been reported with 30 parts per billion of As in the feed (Gates et al., 1979).

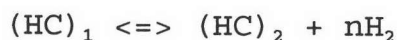
## 2.7 Thermodynamic Considerations

The thermodynamics of the more important reactions in catalytic reforming can be discussed conveniently by referring to the equilibria involved in the various interconversions among certain of the C<sub>6</sub> hydrocarbons. Some thermodynamic equilibrium constants at 500°C, a typical temperature in catalytic reforming, and heat of reaction are given in Table 2.1. The equilibrium constants in this table apply when the partial pressures of the various components are expressed in atmospheres.

Table 2.1 Thermodynamic Data for Typical Reforming Reactions (from Sinfelt, 1964)

Reaction	$K_p^a$ at 500 °C, $P_i$ in atm	$H_r$ , kcal/mol of hydrocarbon
Cyclohexane $\rightarrow$ benzene + 3H <sub>2</sub>	$6 \times 10^5$	52.8
Methylcyclopentane $\rightarrow$ cyclohexane	0.086	-3.8
n-Hexane $\rightarrow$ benzene + 4H <sub>2</sub>	$0.78 \times 10^5$	63.6
n-Hexane $\rightarrow$ 2-methylpentane	1.1	-1.4
n-Hexane $\rightarrow$ 3-methylpentane	0.76	-1.1
n-Hexane $\rightarrow$ 1-hexene + H <sub>2</sub>	0.037	31.0

<sup>a</sup> For the reaction



the equilibrium constant is defined as

$$K_p = \frac{P_{(HC)2} P_{H_2}^n}{P_{(HC)1}}$$

Sinfelt (1964) reported that the dehydrogenation of cyclohexane and the dehydrocyclization of n-hexane to yield benzene are seen to be strongly endothermic, so that increasing temperature has a marked effect on improving the extent of conversions to aromatics. Hydrogen partial pressure obviously has a marked effect on the extent of formation of benzene, and from the viewpoint of equilibria alone, it is advantageous to operate at as high temperature and as low a hydrogen partial pressure as possible to maximize the yield of the aromatics. However, other considerations, such as catalyst deactivation due to formation of carbonaceous residues on the surface, place a practical upper limit on temperature and a lower limit on hydrogen partial pressure in catalytic reforming operations.

The thermodynamic considerations in the formation of aromatics from higher molecular weight paraffins and cycloparaffins was qualitatively the same as for formation of benzene, but it should be noted that the equilibrium tends to shift more in favor of the aromatics as the molecular weight increases. Thus, for example, the formation of toluene from methylcyclohexane is thermodynamically more favorable than the formation of benzene from cyclohexane, as shown in Table 2.2.

Table 2.2 Thermodynamic Data for Formation of Benzene and Toluene (from Sinfelt, 1964)

Reaction	k at 500°C
Cyclohexane $\rightarrow$ benzene + 3H <sub>2</sub>	6 X 10 <sup>5</sup>
Methylcyclohexane $\rightarrow$ toluene + 3H <sub>2</sub>	2 X 10 <sup>6</sup>

The dehydrogenation of paraffins to olefins, while it does not take place to a large extent at typical reforming conditions, is nevertheless of considerable importance, since olefins appear to be intermediates in some of the reactions. The formation of olefins from paraffins, similar to the formation of aromatics, is favored by the combination of high temperature and low hydrogen partial pressure.

From the previous reviews, it is necessary to change the process operating conditions to maintain the reaction severity and to suppress undesired reactions. Some basic relationships in catalytic reforming are shown in Table 2.3.

Thus the most useful operating conditions for desired products (aromatics) are (1) high temperature, (2) Low pressure, (3) Low space velocity, and (4) low hydrogen-to-hydrocarbon mole ratios.



Table 2.3 Some Basic Relationships in Catalytic Reforming  
(from Gary and Handwerk, 1987)

Reaction	Hydro cracking	Isomeri- zation	Cycli- zation	Naphthene isomeri- zation	Naphthene dehydro- genation
Reaction rate	Slowest	Rapid	Slow	Rapid	Vary fast
Heat effect	Exothermic	Mildly exother.	Mildly exother.	Mildly exother.	Quit endothermic
Effect of High pressure	Aids	None	Hinders	None	Hinders
Effect of High temp.	Aids	Aids	Aids	Aids	Aids
Effect of High space velocity	Hinders	Hinders	Hinders	Hinders	Hinders
Effect on hydrogen production	Absorb	None	Evolves	None	Evolves
Effect on density	Decrease	Slight Decrease	Increase	Slight Increase	Increase
Effect on volumetric yield	Varies	Slight Increase	Decrease	Slight Increase	Decrease
Effect on octane	Increase	Increase	Increase	Slight decrease	Increase

## 2.8 Effects of Sulfur Compounds on Catalytic Reforming

Sulfur compounds in petroleum products are not necessarily the same as those found in crude oil. Radical changes in structure occur on distillation, chemical refining and, particularly, on cracking. New sulfur compounds are formed by the interaction of sulfur compounds present in the crude oil with hydrocarbon and other petroleum constituents. In chemical refining, hydrogen sulfide and mercaptans may react with the unsaturated hydrocarbons.

Thiophenes may be absent in the charge but appear in the distillation products and reduce an octane number. Hydrogen sulfide is normally associated with crude oil and additional quantities are produced on distillation. It is easily eliminated because its acidic properties and low boiling point ( $-72.9^{\circ}\text{F}$ ). Mercaptans, also known as thio-alcohols or thiols, are the most advertised petroleum constituents. Their presence in the light petroleum fractions is easily detected by odor and by simple chemical tests. Sulfides or thioethers are relatively stable compounds. They are removed in order to meet specifications for total sulfur content of petroleum products. Disulfides are obtained by oxidation of mercaptans and are the ultimate products in the sweetening processes. With the exception of odor, the disulfides may be more offensive than the mercaptans in the finished oils. Modern refining processes remove the mercaptans instead of converting to disulfides. Polysulfides are formed on oxidizing mercaptans in the presence of excess sulfur. They are more objectionable than the disulfides. Corrosiveness of polysulfides increases with the increase in the number of sulfur atoms in the molecule. (Kalichevsky and Kobe, 1956)

Because sulfur adsorbs very strongly on metals and prevents or modifies the further adsorption of reactant molecules, its presence on a catalyst surface usually effects substantial or complete loss of activity in many important reactions, particularly in hydrogenation reactions. Where the reaction network leads to two or more products, adsorbed sulfur can markedly affect the selectivity by reducing the rate of one of the reactions more than the others (Bartholomew, 1982). A number of sulfur compounds known to poison catalysts include  $\text{H}_2\text{S}$ ,  $\text{CS}_2$ ,  $\text{MeSH}$ ,  $\text{Et}_2\text{SH}$ ,  $\text{Me}_2\text{S}$ ,  $\text{Et}_2\text{S}$ ,

thiophene, COS, SO<sub>2</sub>, and SO<sub>3</sub>. These sulfur compounds have unshared electron pairs which can lead to very strong chemisorption on the metal surface. Maxted (1951) suggested that sulfur compounds chemisorb on transition metals by forming bonds in which previously unshared electrons in the sulfur atom are donated into the d orbitals of the metal.

Bickle and his co-workers (1990) studied the role of sulfur in catalytic reforming of hydrocarbons on platinum-rhenium/alumina. They studied cyclohexane reforming and n-heptane reforming on 0.3-0.3% Pt-Re/Al<sub>2</sub>O<sub>3</sub> 0.95% Cl catalyst in the presence of sulfur. The experimental conditions (T = 480°C, P = 10 atm, WHSV = 5 h<sup>-1</sup>, hydrogen/hydrocarbon ratio = 10) were used. In the case of n-heptane reforming, they found that toluene production levels around 15% were achieved. Introduction of 10 ppm (by weight) sulfur (thiophene) saw a gradual decrease in the toluene production to 5% over 400 min. Corresponding increases in isomer production and unconverted n-heptane occurred over this time. The yield of crackates was difficult to monitor accurately due to the "resonating" nature of gas production during normal operation, however, it appeared that the yield also increased during sulfidation with 10 ppm sulfur-doped liquid feed. Despite the resonating nature of gas production found in all n-heptane reforming experiments, liquid yield were stable and accurately reproducible. Returning to a pure feed saw a slight increase in toluene production, while isomerization and unreacted n-heptane remained constant. Introduction of 500 ppm sulfur severely attenuates dehydrocyclization. Cracking and isomerization also decreased but not so drastically. The level of unconverted n-heptane correspondingly increased.

They suggested that for lined out Pt-Re/Al<sub>2</sub>O<sub>3</sub> (first 200 minutes of the experiment), a coke overlayer of reversible coke exists over the metal surface with a small fraction of graphitic coke. Graphitic coke was formed on platinum face atoms. Due to the ensemble dilution effect of rhenium in the platinum matrix and the high independent hydrogenolysis activity of uncapped rhenium, graphitic coke formation would be at a distance from the rhenium atoms. When sulfur was first introduced to the system, preferential adsorption to rhenium will occur. The capped Re-S produced acted as an inert dilutant. The geometric effect decreased the platinum ensemble size on the bimetallic catalyst. Until all surface rhenium atoms were capped. The adsorption of sulfur then occurred on the platinum face atoms (as irreversible sulfur, S<sub>i</sub>) that were free of any electronic interaction with rhenium until this saturation level was reached. Any further sulfur adsorption would be via reversible sulfur (S<sub>r</sub>) to the platinum low-coordination sites. The combined effect of Re-S and Pt-S<sub>i</sub> that modified the platinum ensemble size and the electronic interactions caused the hydrogenolysis and dehydrocyclization activities to decrease. Pt-Re(S)/Al<sub>2</sub>O<sub>3</sub> has a 50% lower crackate yield than does lined out Pt-Re/Al<sub>2</sub>O<sub>3</sub> with gas selectivity, indicating the distribution of crackates has changed drastically away from hydrogenolysis gases to acid site crackates due to the capping of the rhenium atoms.

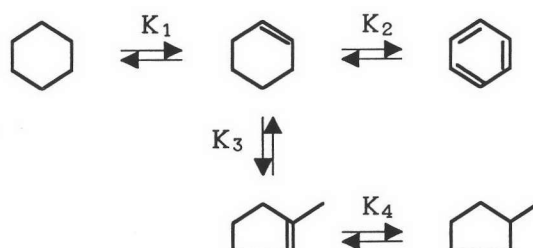
The effect of sulfur on hydroforming (reforming) reactions has been investigated and reported. Hettlinger et al. (1955) studied the effect of sulfur (H<sub>2</sub>S) on the reactions of n-heptane containing 0.8% sulfur. They found that the dehydrocyclization is considerably reduced, while hydrocracking is appreciably accelerated.

The effect of sulfur on dehydrogenation of methylcyclohexane was also studied. The results showed that at a high sulfur concentration (5% sulfur as thiophene), dehydrogenation is almost completely eliminated. At 0.16% sulfur, dehydrogenation is partially reduced. Further processing with sulfur-free methylcyclohexane restored catalyst activity.

Further studies of reforming reaction was reported by Meerbott et al. (1954) and, they studied the effect of sulfur on Platforming of East-West Texas feed. It was observed in these experiments that an increase in sulfur concentration in the feedstock has two principal effects-initial inhibition of aromatics formation, and accelerated catalyst activity decline rate. The inhibition of Platforming catalyst by sulfur appears to be a reversible reaction. Furthermore, whether the deactivation of the platinum on the catalyst is caused by the formation of a chemical compound between platinum and sulfur or by a chemisorption of hydrogen sulfide on the platinum surface, it was felt that an additional increase in hydrogen partial pressure would be beneficial in suppressing the effect of higher sulfur concentrations on the Platforming catalyst. Increased pressure, however, is thermodynamically less favorable for methylcyclopentane conversion to benzene at constant temperature. Consequently, to offset the loss in aromatics yield due to higher pressure, a higher reactor temperature is required.

Sterba and Haensel (1976) investigated the effect of sulfur on the rate constants in the reaction as shown below. In the dehydrogenation of cyclohexane to benzene, the formation of benzene from the intermediate cyclohexene was rapid. In the conversion of methylcyclopentane to benzene, cyclohexene was also

expected to the intermediate between methylcyclopentene and benzene. And it has not been found in the product. The results shown that the unpoisoned relative rates are:  $K_2 \gg K_1 \gg K_3 < K_4$ . However, the poisoned relative rates may be quite different. The presence of only 50 ppm of sulfur poison in the form of thiophene has changed the course of the reaction.



The poisoned relative rates were:  $K_2 < K_1$ ,  $K_3 > K_4$ ,  $K_3 > K_2$ . The reasoning was as follows: the sulfur poisoning of the reaction involving cyclohexane does produce a substantial reduction in the rate of conversion of cyclohexane and, in particular, slows down the conversion of cyclohexene to benzene. The slowing down of this last reaction accentuates the participation of an otherwise slower reaction, that is the conversion of  $CH^{\ominus}$  to  $MCP^{\ominus}$  and then to MCP. This reaction is acid catalysed. They noted that low levels of sulfur cause striking changes in activity and selectivity, for example, in experiments at high space velocity the addition of 50 ppm sulfur decreased overall conversion of cyclohexane by a factor of 10, whereas conversion to benzene decreased from 97 to 0% and conversion to methylcyclopentane increased from 0.9 and 0% to 44 and 35%, respectively. Thus the presence of only 50 ppm sulfur changed the entire course of the reaction.

Coughlin et al. (1984) and Parera et al. (1986) reported that presence of sulfur lowers the hydrocracking

activity of coked Pt-Re catalyst resulting in higher liquid product. Furthermore, Van Trimpont et al. (1985) found that 0.28 mole of sulfur per mole metal exposed was sufficient to suppress hydrogenolysis activity.

Spight (1991) found that under the high-hydrogen partial pressure conditions used in catalytic reforming, sulfur compounds are readily converted into hydrogen sulfide which, unless removed, builds up to a high concentration in the recycle gas. Hydrogen sulfide is a reversible poison for platinum and causes a decrease in the catalyst dehydrogenation and dehydrocyclization activities. In the first catalytic reformers the hydrogen sulfide was removed from the gas cycle stream by adsorption in, for example, diethanolamine. Modern units usually remove sulfur from the feed by conventional desulfurization over cobalt-molybdenum catalyst. An additional benefit of desulfurization of the feed to a level of < 5 ppm sulfur is the elimination of H<sub>2</sub>S corrosion problems in the heaters and reactors.

The role of sulfur in reforming on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Re/Al<sub>2</sub>O<sub>3</sub> was investigated by Menon and Prasad (1976). They found that sulfur preadsorbed at 773 K (500°C) suppressed all of the representative metal catalysed reforming reactions including hexane and cyclohexane dehydrogenation, dehydroisomerization of methylcyclopentane, and hydrocracking. On Pt-Re, the extent of hydrocracking was reduced to a much greater extent than these other reactions, explaining why this catalyst produces less coke than Pt/Al<sub>2</sub>O<sub>3</sub>.

The sulfur is responsible for suppressing hydrocracking of organic molecules on Pt is consistent with the work of Fischer and Kelemen (1978) showing that bonding of benzene on Pt is sufficiently modified by preadsorb sulfur to enable an increasing fraction of the

adsorbed benzene to desorb at elevated temperatures rather than to dehydrogenate.

The influence of the molecular size and structure of the sulfur poison on platinum catalyst have been reported by Maxted (1951). He proposed that poisons containing sulfur as becoming anchored to the toxic part of their molecules may be regarded as becoming anchored to the catalyst surface by the sulfur atom. Accordingly, even if the remainder of the poison molecule contains no atoms or groups which normally acted as catalyst poisons, this nontoxic part of the molecule will be maintained in a preferential position for the obstructive covering or occupation of catalytic surface. In this way, the normally nontoxic portion should, by its coverage of surface, acted as if it were itself toxic. On measuring the toxicities of the alkyl thiols and sulfides, in each case up to the hexadecyl compound, it was found that the molecular toxicity, namely the toxicity expressed per gram mole of inhibitor or per gram atom of sulfur, increased continuously with the chain length. The rate of increase in toxicity with each additional  $-CH_2$  chain unit decreased however as the length of the chain become greater. Further, the sulfides, which contain two hydrocarbon chains, were more toxic than the corresponding thiols, which contain only one chain.

A point of considerable interest arises if the hydrocarbon chain has two terminal sulfur atoms in place of one. In the case of a single sulfur anchor, the maximum surface area over which there is a time-probability of adsorption of (or obstructive coverage by) the chain is a circle of radius equal to the chain length. It should however be possible to restrict this mobility of the chain, and consequently to diminish the are of influence, by providing a second sulfur anchor





diethyl disulfide,  $(C_2H_5)_2S_2$ , does not differ greatly molecular toxicity from diethyl sulfide,  $(C_2H_5)_2S$ , again in spite of doubled sulfur content.

Minachev and his associates (1960) had previously investigated the effect of thiophene on the dehydrogenation of cyclohexane over a platinum alumina catalyst. In agreement with much of the work carried out in the United States, these investigators found that the decrease in dehydrogenation activity depended on the concentration of thiophene in the feed, and after several hours on stream, a constant activity was obtained for any fixed concentration of thiophene in the feed. They had also observed that poisoned catalysts can be regenerated to the original activity by passing pure cyclohexane over them, however, the time required for regeneration was determined by the concentration of thiophene in the mixture that was used in poisoning catalysts.

Minachev et al. (1960) employed the radio active isotope  $S^{35}$  to determine, how much sulfur was on the catalyst when it reached an equilibrium value of reactivity. The catalyst used in this study contained 5% platinum on alumina. The cyclohexane feed was poisoned with 1, 2, 3, and 9% of the  $S^{35}$  labelled thiophene. The reaction was studied at  $450^\circ C$ , a hydrogen pressure of 20 atm, and a hydrogen to hydrocarbon mole ratio of 5. Catalyst regeneration was accomplished by the use of pure cyclohexane under the same reaction conditions. They studied the effect of passing thiophene-free cyclohexane over the sulfur poisoned catalyst. Radiometric analysis showed that the recovery of the activity is accompanied by the removal of sulfur from the catalyst. These results confirmed the view that there is an equilibrium between the deposition of sulfur on the catalyst and its removal under the conditions of dehydrogenation of

mixtures of cyclohexane and thiophene. However, the catalysts which had regained their original activity as a result of regeneration were found to contain appreciable amounts of sulfur. On the average, the amount was 40% of the sulfur content of the catalyst before regeneration. This sulfur apparently represents a fixed amount which is irreversibly deposited on the catalyst, since it could not be removed by regeneration with pure cyclohexane.

Bursian et al. (1966) investigated the effect of sulfur (carbon disulfide,  $\text{CS}_2$ ) on the isomerization rate of pentane over a platinum catalyst under hydrogen pressure. The isomerization reaction was studied at a temperature of  $380^\circ\text{C}$ , a pressure of 40 atm, a hydrogen to pentane mole ratio of 3, and LHSV of 1 to 4 vol of pentane per vol of catalyst. They concluded that sulfur concentrations over a fairly wide range produce comparatively little decrease in the pentane isomerization rate. They also concluded from the data that the sulfur compound poisoned the metallic sites of the catalyst rather than the acid centers of the support.

## 2.9 Literature Summary

1. The desired reactions in a catalytic reforming all lead to formation of aromatics and isoparaffins as follows:

1.1 Paraffins are isomerized and some extent converted to naphthenes. The naphthenes are subsequently converted to aromatics.

1.2 Olefins are saturated to form paraffins which then react as in (1.1).

1.3 Naphthenes are dehydrogenated to aromatics.

1.4 Aromatics are left essentially unchanged.

2. Reactions leading to the formation of undesirable products include:

2.1 Dealkylation of side chains on naphthenes and aromatics to form butane and lighter paraffins.

2.2 Cracking of paraffins and naphthenes to form butane and lighter paraffins.

3. The operating condition for catalytic reforming depends on the hydrocarbon types in the feed. The high naphthene stocks, which readily give aromatic gasolines, are the easiest to reform and give the highest gasoline yields. Paraffinic stocks, however, which depend on the more difficult isomerization, dehydrocyclization and hydrocracking reactions, require more severe conditions and give lower gasoline yields than the naphthenic stocks. In general, the operating pressures are varied in the range of 6.8-40.4 atm (100-600 psig), and the temperatures are varied from 450-527°C, the space velocities are varied from 1 to 5 liquid hourly space velocity and the hydrogen/hydrocarbon mole ratios of 3 to 10 are most frequently used.

4. All commercially used catalysts contain platinum, either alone or in a combination with another metal. Typical reforming catalysts are Pt/Re on  $\text{Al}_2\text{O}_3$  and Pt/Ir on  $\text{Al}_2\text{O}_3$ . Both metals and the support play key roles in the catalysis. The role of platinum is to catalyse dehydrogenation-hydrogenation reactions. Chlorided alumina acts as an acid and catalyses carbon skeletal rearrangement through carbonium ion mechanisms. In addition, hydrocracking is catalysed by both metal and acid sites.

5. In reforming with a paraffinic feed, the deactivation of reforming catalyst was occurred due to coke formation, poisoning begins on the metal with the formation of the olefinic species and aromatics. These can slowly form coke on the metal, but they can also be transported by gas-phase diffusion and surface migration to the acid sites.

6. Reforming catalyst was deactivated due to sulfur poisoning. When sulfur was first introduced to the system, preferential adsorption to rhenium will occur. The capped Re-S produced acted as an inert dilutant. The geometric effect decreased the platinum ensemble size on the bimetallic catalyst. Until all surface rhenium atoms were capped. The adsorption of sulfur then occurred on the platinum face atoms. It caused the dehydrogenation and dehydrocyclization activities to decrease. Isomerization and hydrocracking activity seem to be difficult to monitor accurately.

7. The influence of the molecular size and structure of the sulfur poison on platinum catalyst have been reported that the sulfides, which contain two hydrocarbon chains, were more toxic than the corresponding thiols, which contain only one chain. On the other hand, the two sulfur atoms, instead of

occupying terminal position, are adjacent to one another, little change in toxicity occurs: thus, diethyl disulfide,  $(C_2H_5)_2S_2$ , does not differ greatly molecular toxicity from diethyl sulfide,  $(C_2H_5)_2S$ .