

CHAPTER II



LITERATURE REVIEWS

2.1 Purpose of Reforming

Reforming was a process that increase the octane number of naphtha fraction. The final product of the reformer ("Reformate") was used as the following purpose;

- A. To used as high octane gasoline.
- B. Feed to an aromatics plant.

In producing high octane reformate, many of the compounds in the reformer feed were converted to aromatics, and thus, reformate was used as a feed to an aromatics plant. In this case, aromatics yield is more interest than octane, octane being used only as a guide by which to judge relative aromatics production. Aromatics production generally rises as octane incresses.

2.2 Reforming Catalyst

The reforming catalyst is a bifunctional catalyst which has a metal component (such as platinum) for the hydrogenation-dehydrogenation activity and an acidic component (such as alumina) for isomerization, ,hydrocracking, etc.

2.2.1 Metal Functions

The platinum catalyst was utilized in a fixed-bed reactor and was introduced in 1949 by the Universal Oil Products Co.(UOP) based on work by Haensel and his coworkers. Hydrogen, formed in the process, was recycled through the reactor to maintain a sufficiently high hydrogen partial pressure so that coke forming reactions could be minimized.

Beginning in about 1967 an improved catalyst consisting of a mixture of platinum and rhenium, a

bimetallic catalyst, supported on an acidic alumina came to replace much of the commercial use of the earlier platinum/alumina catalyst. The newer catalysts maintain their activity at lower hydrogen pressures over long periods of time. The lower hydrogen pressure also allows an increased degree of dehydrocyclization of paraffins to aromatics and generally a higher yield of C_5^+ -product and hydrogen (Satterfield, 1980).

Recently Bertolacini and Pellet (1980) demonstrated that a mechanical mixture of Pt/ Al_2O_3 and Re/ Al_2O_3 monometallic catalysts was as active and stable as the co-supported Pt-Re/ Al_2O_3 catalysts. The role of rhenium was to remove volatile coke precursors as C_5 -ring compounds, by selective hydrogenolysis. More recently Burch and Mitchell (1983) found that, under reforming conditions, the role of rhenium was selectively hydrogenated dienes to alkanes.

Margitfalvi et al. (1984) studied the role of the second metal in bimetallic catalysts. The behavior of a Pt/ Al_2O_3 catalyst was studied in n-hexane reaction by means of dilution of the catalyst bed with Re/ Al_2O_3 . The activity of the Re/ Al_2O_3 diluted by quartz was about half of the Pt/ Al_2O_3 but its hydrogenolysis activity was higher. The yield of hydrogenolysis products was 36% on the Re/ Al_2O_3 , while these values were 27.9, 29.3 and 43.4% after dilution of the Pt/ Al_2O_3 catalyst with quartz, alumina and Re/ Al_2O_3 , respectively. The dilution with Al_2O_3 resulted in a slight increase in the isomerization and hydrogenolysis selectivities due to the increase in the number of acidic sites. While dilution with Re/ Al_2O_3 only increased in the selectivity of hydrogenolysis.

The role of rhenium due to the increase in the amount of the overall hydrogen pool available for hydrogen consuming reactions as hydrogenolysis, hydrogenation of unsaturated hydrocarbons and, including hydrodepolymerization of the carbonaceous surface

overlayer. Rhenium decreased the rate of coke formation by hydrogenation of coke precursors on the catalyst surface. Platinum was the catalytically active metal in the reforming reactions, whereas, rhenium was primarily a coke or deactivation inhibitor.

2.2.2 Acidic Functions

The support of catalyst was an alumina base needed to be acidic. More recently developed reforming catalysts have crystallites of a metal such as Pt on an acidic support such as alumina, and the two functions are present in separate phases. The metal provides the hydrogenation-dehydrogenation activity, and the promoted acidic alumina provides the isomerization activity.

The acidic component of reforming catalysts plays a very important role in the overall chemical transformations that occur during catalytic reforming.

Satterfield (1980) proposed that the alumina support may have been acidified by the incorporation into the structure of about 1% chloride or fluoride during the catalyst preparation. The use of chloroplatinic acid for impregnation leads to the natural incorporation of chloride into the alumina during preparation. Acidity is gradually lost during reaction. This had poor tolerance to low concentrations of water vapour, which removed halogen from the support. The halogen could be replaced and may be restored by adding small amounts of an organic chloride or fluoride to the feed stock. Presumably this decomposes to release a halogen acid, which is adsorbed by alumina.

Further details on the process are provided in the concise reviewed by Limido et al. (1987). The alumina must be chlorinated to enhance its acidity. The ideal precursor was an aqueous solution of an anion containing chlorine ions by chloroplatinic acid in aqueous solution.

These solutions were stable only in an acid medium such as can be obtained by adding hydrochloric

acid. The amount hydrochloric acid added depends on the surface of the support to be impregnated. The exchange reaction involved on the surface of the alumina shows in Figure 2.1.

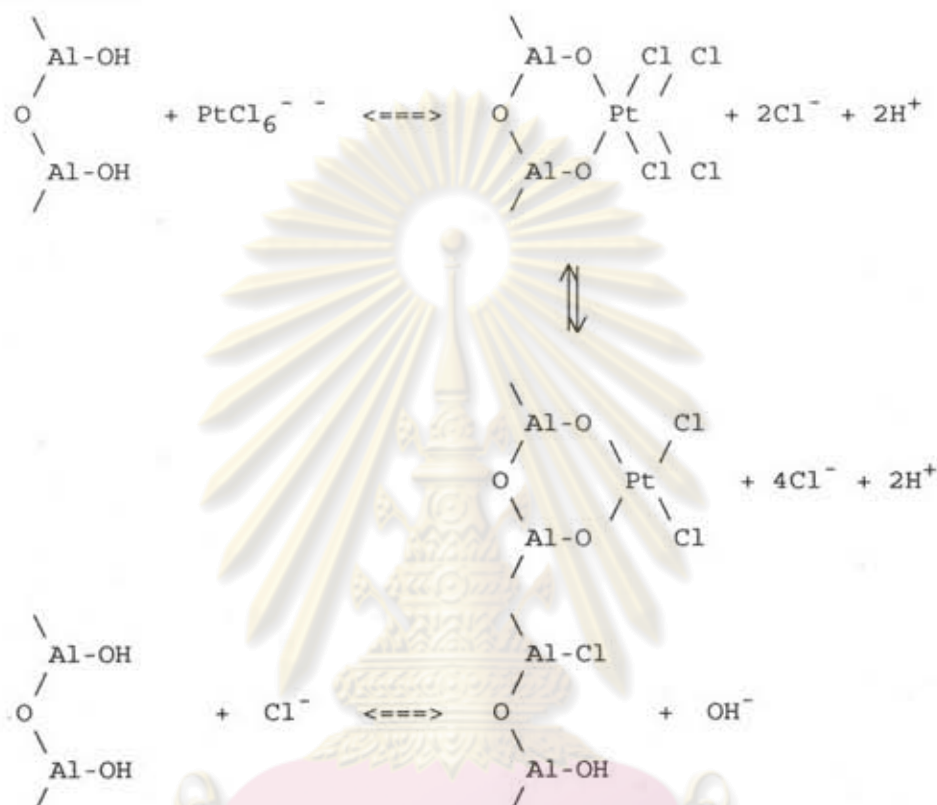


Figure 2.1 Exchange Reactions that Occur During the Platinum-Impregnation of Alumina. (From Limido et al., 1987)

These explain the competition as well as the fixation of chlorine that contributed by the chloroplatinic acid.

Sterba and Haensel (1976) examined in more detail how this activation occur. The mentioned earlier that chlorine and fluorine act as suitably acidic components of the catalyst. 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:



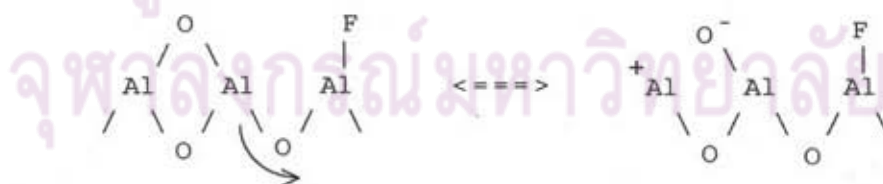
The effect of halogen on acidity was believed to be an inductive effect:



A succession of studies threw some doubt on the validity of this picture. In this picture the acid sites are oxygen bridges formed by dehydration of neighboring OH groups during calcination. These bridges can open heterolytically to provide paired acid base sites:



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



The exposed Al^+ ions will normally react as Lewis acids although in the presence of HCl or H_2O 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.

Moreover, they examined how this change in acidity effects the conversion of methylcyclopentane which much undergo a carbon-carbon break on the way of benzene. In the first instance, they have converted methylcyclopentane with catalysts containing 0.3% platinum on alumina, but variable amounts of fluorine. The condition were 260 psig, 4 liquid hourly space velocity and a hydrogen:hydrocarbon ratio of 6 and a temperature of 500°C. They observed that at very low acidity, which could be considered as the intrinsic acidity of the alumina, a small amount of benzene was formed. Furthermore, as the fluorine content was increased. The conversion increased linearly with fluorine content. At fluorine contents in excess of 1% no further increased occurs since an equilibrium value was reached with respect to benzene formation.

Moreover, they examined the effect of platinum concentration at a fixed fluorine content. The conversion at that point was limited by the fluorine content. It was amazing that such a low level of platinum can induced the transformation. The data on the fluorine effect and platinum effect clearly indicated the remarkable cooperative action of a dual function catalyst, and began to give an idea of the course of the reaction when methylcyclopentane was converted to benzene.



So, metal and acid activity must be kept high and in proper balance for the reformer to operate properly

2.3 Reactions in Reforming

The typical feedstocks to catalytic reformers were heavy straight-run (HSR) gasolines and naphthas (180°F to 375°F) generally contains the whole range of C₆ through C₁₁ hydrocarbons. These were composed of the four major hydrocarbon groups: paraffins, olefins, naphthenes, and aromatics. The paraffins and naphthenes undergo two

types of reactions in being converted to higher octane components by cyclization and isomerization. Table 2.1 showed the representative catalytic reforming reactions (Satterfield C.N., 1980).

Table 2.1 Representative Catalytic Reforming Reactions

Reaction	K	DH, kJ/mol
1. Dehydrogenation of naphthenes to aromatics	6×10^5	+221
 $\text{C}_6\text{H}_{12} \longrightarrow \text{C}_6\text{H}_6 + 3\text{H}_2$		
2. Dehydrogenation of paraffins to olefins	$\sim 4 \times 10^{-2}$	$\sim +130$
$\text{C}_6\text{H}_{14} \text{ ----> } \text{C}_6\text{H}_{12} + \text{H}_2$		
3. Isomerization of alkylcyclopentanes	8.6×10^{-2}	-15.9
 $\text{C}_6\text{H}_{12} \longrightarrow \text{C}_6\text{H}_{12}$		
4. Isomerization of n-paraffins to isoparaffins	~ 1	~ 5
$\text{n-C}_6\text{H}_{14} \text{ ----> } \text{iso C}_6\text{H}_{14}$		
5. Dehydrocyclization of paraffins to aromatics		
$\text{n-C}_6\text{H}_{14} \text{ ----> } \text{C}_6\text{H}_6 + 4\text{H}_2$		
6. Hydrocracking of paraffins		
$\text{C}_6\text{H}_{14} + \text{H}_2 \text{ ----> } \text{olefins and paraffins}$		

Reaction conditions have to be chosen that favor the desired reactions and inhibit the undesired reaction. Desirable reactions in a catalytic reformer all lead to the formation of aromatics and isoparaffins.

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 yield is increased by:

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

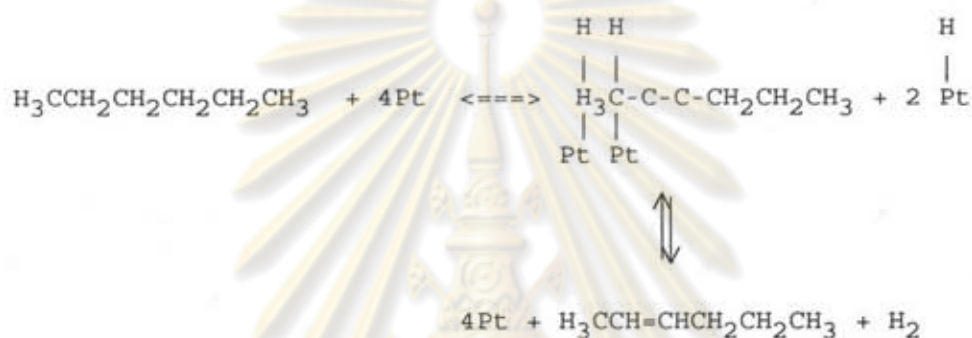
There is no isomerization effect due to the hydrogen-to-hydrocarbon mole ratios but high hydrogen-to-hydrocarbon mole ratios reduces the hydrocarbon partial pressure and thus favor the formation of isomers (Gary, 1984).

Gates, Katzer, and Schuit (1979) discussed the reactions related to catalytic reforming in some detail. Reforming involved reactions of hydrocarbons on the surface of the metal and on the promoted (acidic) alumina. The alumina-catalyzed reactions involved mainly the carbonium-ion chemistry. In this case surface catalyzed reaction mechanisms were inferred from a large body of well-established carbonium-ion chemistry for acid solutions. In the case of reactions on metal surfaces, there was no separated body of chemical information to draw on to infer the relevant surface reaction mechanisms.

2.3.1 Metal-Catalyzed Reactions

a. Hydrogenation-dehydrogenation reactions

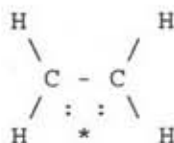
When paraffin adsorption on the metal surface involves two adjacent carbon atoms, the paraffin can split off two hydrogen atoms and adsorb as an olefinic species. Desorption without readdition of the hydrogen atoms gives a gas-phase olefin:



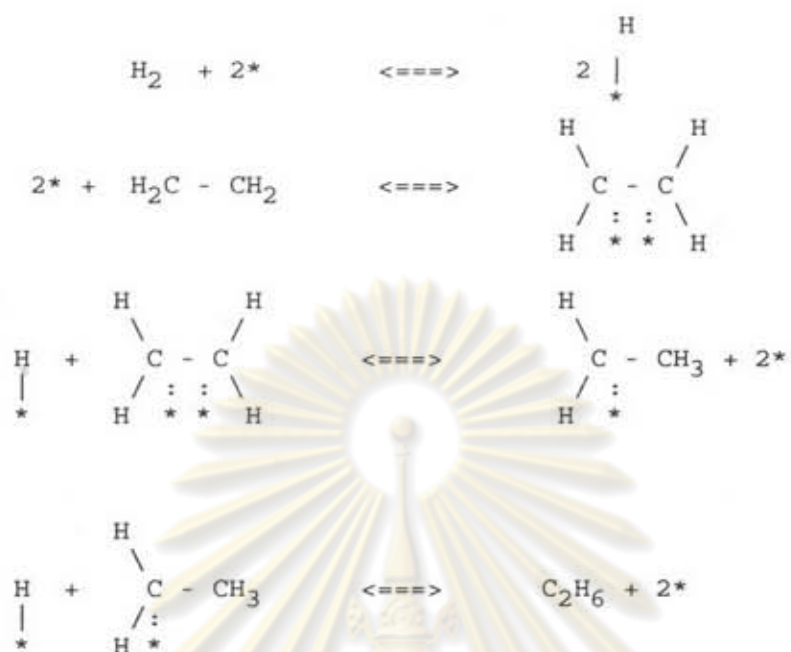
Hydrogenation-dehydrogenation of hydrocarbons on metals was exemplified by the reaction



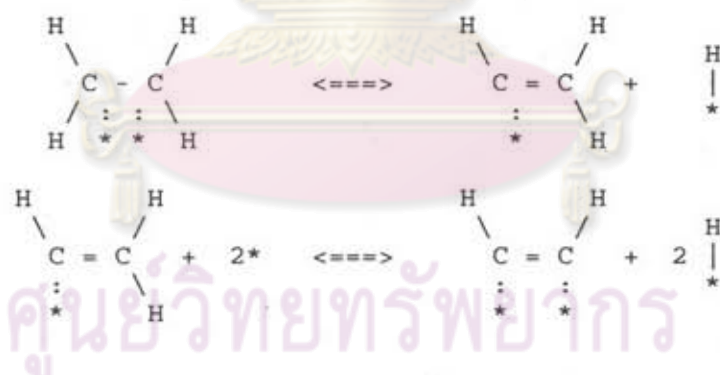
In the mechanism, a hydrogen molecule adsorbs on two surface sites (presumably single metal atoms), undergoing fission of the H-H bond. The C_2H_4 molecule adsorbs associatively on two sites by forming σ bond between each carbon atom and a metal atom.



The elementary steps are reversible and forms the basis of the following proposed reaction mechanism:



Here there is further C-H bond scission, leading to what is essentially and adsorbed acetylene molecule.



There is the cause of a self-poisoning of the catalyst, particularly when the hydrogen partial pressure was relatively low.

b. Aromatization reactions

The aromatization of cyclohexane and alkylcyclohexanes to give aromatics is specific type of dehydrogenation reaction and is important in catalytic reforming, occurring rapidly enough for equilibrium to be closely approached. Aromatization occurs almost

exclusively on the metal component.

The mechanism of cyclohexane dehydrogenation involves the adsorption of cyclohexane, with either simultaneous or rapid subsequent dissociation of six hydrogen atoms. Dehydrogenation results in the formation of an aromatics structure bonded through p-electron interaction with metal d-orbitals. Germain (1969) proposed stepwise mechanism in which all intermediate steps were rapid is in Figure 2.2.

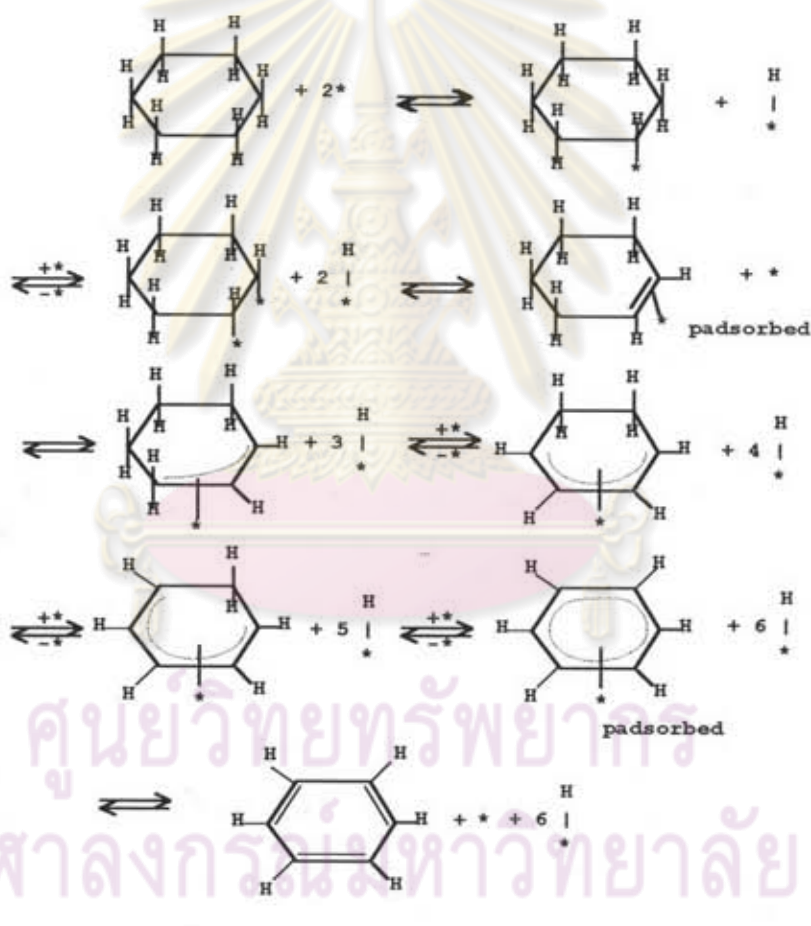


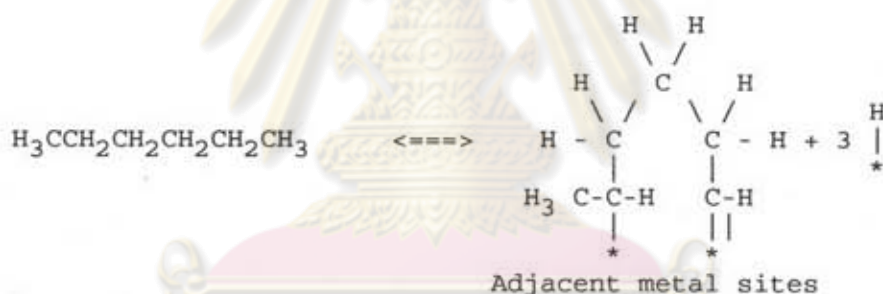
Figure 2.2 Stepwise Mechanism in Which all Intermediate Steps of Aromatization Reaction

Small quantities of gas-phase dienes and cyclohexene were observed in the product evidently the hydrogenation reaction occurs stepwise, and small amounts of the intermediates were desorbed.

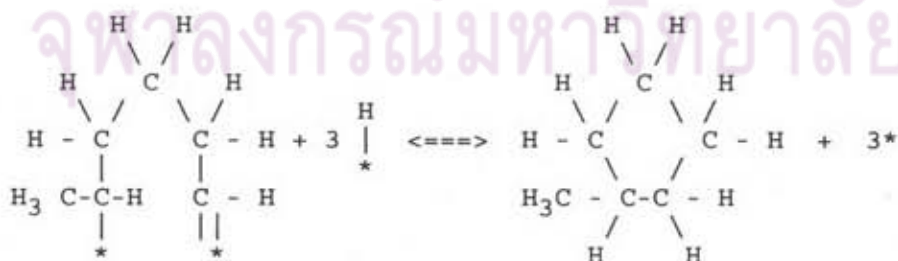
c. Isomerization and Dehydrocyclization

The paraffin adsorbs through carbon atoms which are not adjacent, one alternative to desorption is the formation of a new C-C bond leading to a five- or six-membered ring species. It is particularly evident on Pt and appears to involve the formation of intermediate five- and six-membered ring hydrocarbons and the subsequent opening at another C-C bond position. The reaction sequence in the isomerization is given as follows:

1. Two C-H bonds which are not contiguous are broken, and the hydrocarbon adsorbs on the surface with the C atoms bonded to neighboring metal sites. For example,

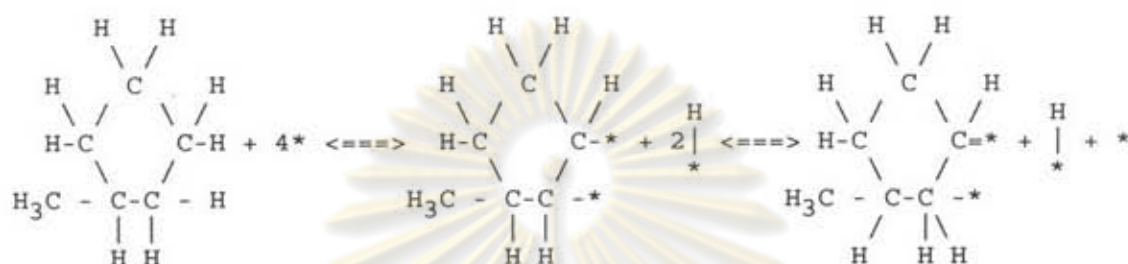


2. A C-C bond forms between the two C-* carbon atom, resulting in the formation of a cyclopentane or cyclohexane ring:

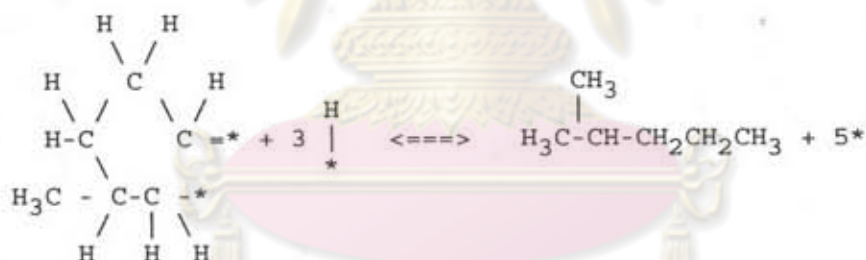


Desorption of a five-membered ring species (methylcyclopentane) or six-membered ring species (cyclohexane) can occur.

3. The ring species can readsorb on the surface or change the carbon atoms which are actually bound to the surface without desorbing, and the C-C bond between the adsorbed atoms (difference from those adsorbed during ring closure) can be broken:



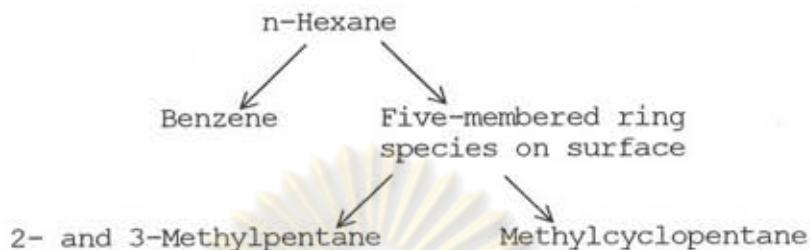
4. Hydrogen-atom addition to the adsorbed species and desorption without remaking the C-C bond leads ultimately to skeletal isomerization; ie., the overall reaction is n-hexane \rightarrow 2-methylpentane:



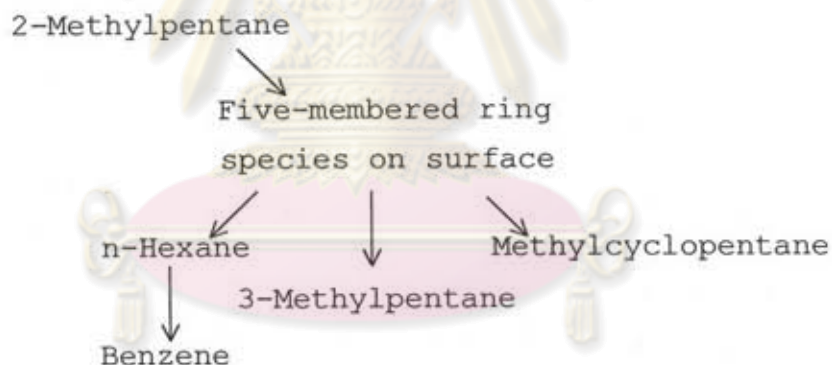
For the isomerization of C_6 -paraffins on a metal surface, six-membered-ring closure also occurs but does not lead to isomerization, only cyclization. Once the six-membered ring is formed on the metal, dehydrogenation to an aromatic occurs very rapidly unless the hydrogen partial pressure is high enough to suppress the reaction.

The reaction network for isomerization and dehydrocyclization of n-hexane and 2-methylpentane are catalyzed by Pt on nonacidic alumina as follow, n-Hexane is readily converted into 2- and 3-methylpentane and methylcyclopentane. Both five- and six-membered ring closure occurred as parallel reactions. The following

network was proposed for the Pt-catalyzed reactions of n-hexane under reforming conditions:



The reactions of branched paraffins contained only five carbon atoms in the chain, involved the formation of five-membered ring species, which then gave isomerized products, including n-hexane. The n-hexane can then react to give a six-membered ring, as indicated below:



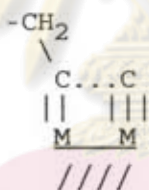
The benzene formation rate was zero near the origin, indicating that benzene was a secondary product. Hydrogen atoms were readily available on the metal surface to hydrogenate any of the C-C bonds which might open to give an isomer from the cyclic C_5 species. Dimethylbutanes were not observed experimentally, in accordance with the proposed scheme. If an $i-C_6$ paraffin was used as a feed, benzene appeared as a secondary rather than a primary because of the need to form n-hexane first.

d. Hydrogenolysis

A common form of C-C bond scission occurs with formation of CH₄ along with smaller amounts of C₂H₆. In its simplest form, 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 carbons appear to have undergone further dehydrogenation, forming multiple carbon-metal bonds and leading to almost complete dehydrogenation of the carbon atoms in some cases.



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 was broken, rehydrogenation of the fragments occurs, leading to CH₄ and a paraffin from the other fragment.

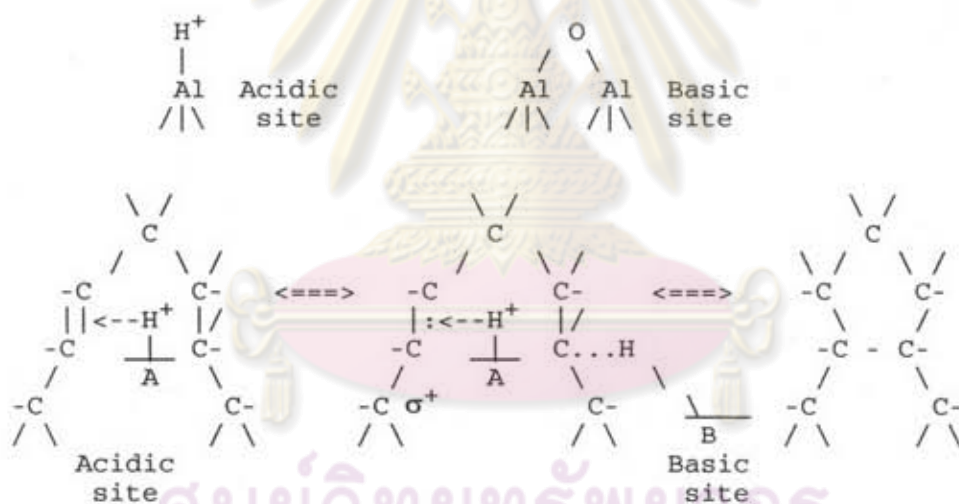
Hydrogenolysis reactions require high temperatures and strong bonding of reactants to the catalyst and are therefore difficult to accomplish; they are demanding compared with hydrogenation reactions, which occur much more readily. They appear to require at least a pair (and possibly a more complex ensemble) of metal atoms.

2.3.2 Alumina-Catalyzed Reaction

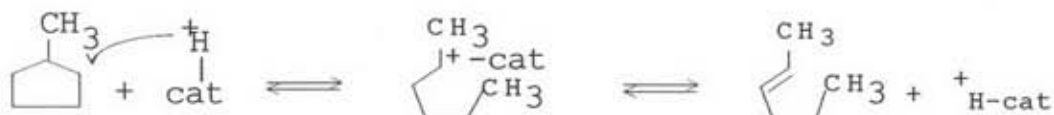
Isomerization reactions on the alumina support proceed by carbonium-ion mechanisms.

For isomerization of straight-chain paraffins, it is desirable first to dehydrogenate them to straight-chain olefins, to isomerize the olefins on the acid centers of the catalyst, and then to rehydrogenate the branched olefins to give isoparaffins. This reaction scheme is the heart of the catalytic reforming process.

Olefin isomerization reactions occur readily on acid catalyst and can be cyclized on acid centers by reaction mechanisms which have to be firmly established. It is 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 on an adjacent pair of acid-base sites on the catalyst surface:



The acid-catalyzed ring opening of methycyclopentane occurs directly by protonation of the ring structure with formation of an acyclic carbonium ion (Brandenberger, Callender, and Meerbott, 1976).



Hydrocracking is desired in measured amounts to split long-chain paraffins of low octane number to give shorter-chain, higher-octane species. Hydrocracking occurs on the acidic centers of the catalyst. Hydrocracking is facilitated by dehydrogenation of paraffins to olefins on the metal. The major characteristics of hydrocracking are that (1) all cracked species are saturated, (2) the process involves bifunctional catalysis, and (3) catalyst deactivation is much less rapid than in catalytic cracking.

2.3.3 Bifunctional Catalysis of Reforming Reactions

The reaction scheme 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 are the key intermediates in the reaction network. The original statement of a reaction scheme for reforming, due to Mills et al. (1953), is shown in Figure 2.3.

According to this scheme, the reactant (n-hexane) is first dehydrogenated on the metal to give straight-chain hexene. The hexene migrates to a neighboring acid center. It is 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.

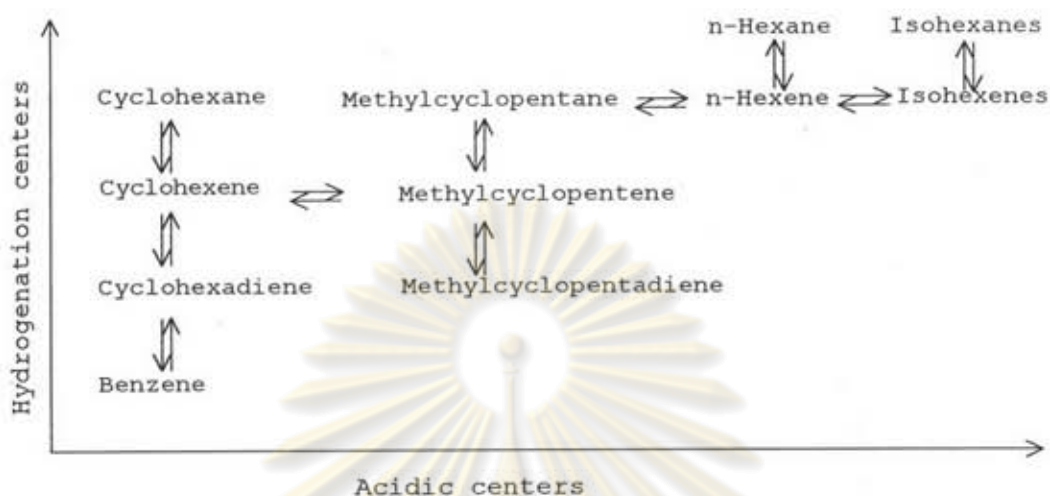


Figure 2.3 Reaction Network for Reforming of C_6 -Hydrocarbons According to Mills et. al. (1953)

Product distribution and reaction intermediates during catalytic reforming reaction have been thoroughly reviewed in several papers, for example, Blue and Gould (1979) purposed the main reactions of catalytic reforming. Because of the wide range of paraffins and naphthenes included in the platformer feed and because the reaction rates varied considerably with the carbon number of the reactant, these reactions occurred in series and in parallel to each other, forming the rather complicated overall reaction indicated in Figure 2.4. Similar results were reported by Kmak et al. (1973), Kleelman (1976), Kugelmann (1976) and Mayers (1986).

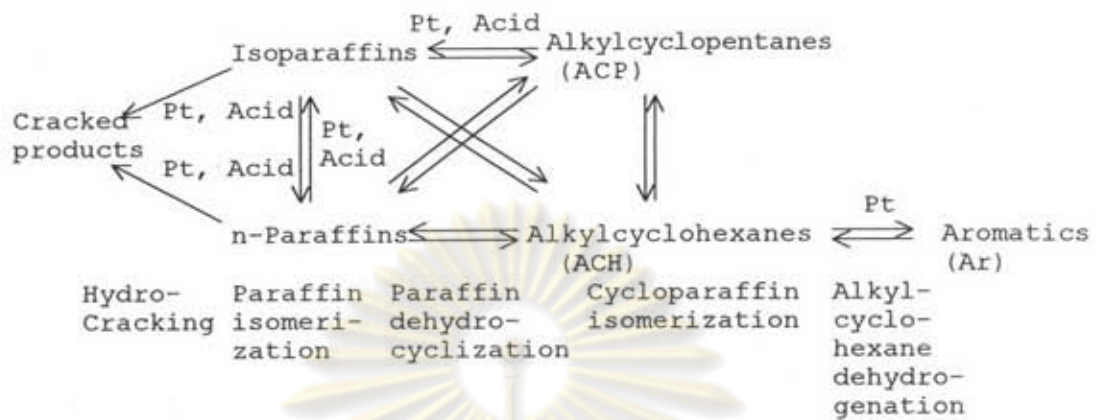


Figure 2.4 Main Reaction of Catalytic Reforming.
(from Blue and Gould, 1979)

Most of reactions were reversible indicating the importance of reaction equilibrium. The alkylicyclopentanes (ACP) to aromatics process (ACP \rightleftharpoons ACH \rightleftharpoons Ar) was less efficient than ACH dehydrogenation, owing to slowness of the first step and ACP ring opening, and required an acidic platinum catalyst. Cyclohexane was converted to benzene in close to 100% efficiency, whereas only 50-75% of methylcyclopentane is converted to benzene.

In the case of isomerization of n-hexane, similar results were obtained by Christoffel (1979). He described the interconversion of five hexane isomers and their hydrocracking to crack products. The reaction pattern is shown below:

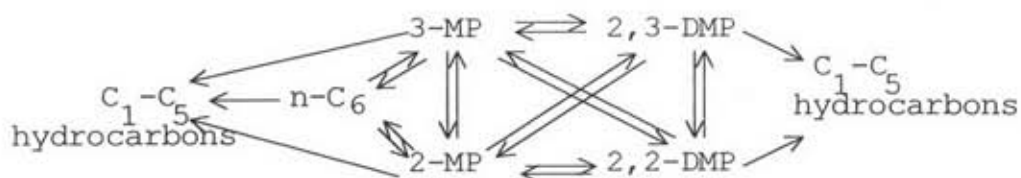


Figure 2.5 Reaction Pattern of Isomerization and Cracking of the Five Hexane Isomers.
(from Christoffel, 1979)

In the relative reaction rate, the primary reaction for the C_6 and C_7 paraffins proceed at significantly different rates. The rate of dehydrocyclization for hexane is only one-third of that of hydrocracking, so the fraction of the n-hexane converted to benzene is relative low. Normal heptane hydrocracks at about the same rate rate as n-hexane, so the faster rate of dehydrocyclization (about 4 times that of hexane) leads to significantly greater fractional conversion to aromatics for n-heptane in comparison with hexane. Both paraffins are converted rapidly to the various possible isomers (Mayer, 1986).

2.4 Thermodynamic and Kinetic Datas

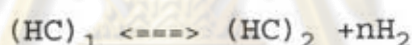
2.4.1 Thermodynamic Considerations

Sinfelt (1964) discussed the thermodynamics of the more important reactions in catalytic reforming by referring to the equilibria involved in the various interconversions among certain of the C_6 -hydrocarbons. Some thermodynamic equilibrium constants at 500°C , a typical temperature in catalytic reforming, and heat of reaction are given in Table 2.2. The equilibrium constants in this table apply when the partial pressures of the various components are expressed in atmospheres.

Table 2.2 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 \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 3-methylpentane	0.76	-1.1
n-Hexane \rightleftharpoons 1-hexene + H ₂	0.037	31.0

^a For the reaction



the equilibrium constant is defined as

$$K_p = \frac{P(CH)_2 P^n(H_2)}{P(CH)_1}$$

The dehydrogenation of cyclohexane and the dehydrocyclization of n-hexane to yield benzene were 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 was 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 dehydrogenation of paraffins to olefins, while it does not take place to a large extent at typical reforming conditions. At equilibrium only very small concentrations of olefins can exist with paraffins, is nevertheless of considerable importance, since olefins appear to be intermediates in some of the reactions. The thermodynamics of olefin formation can play an important role in determining the rates of those reactions which proceed via olefin intermediates, since thermodynamics sets an upper limit on the attainable concentration of olefin in the system.

The equilibria in the case of isomerization reactions are much less temperature sensitive than in the case of dehydrogenation reactions. Furthermore, it is seen that the equilibrium between methylcyclopentane and cyclohexane favors the former, indicating that the five-membered ring structure is more stable than the six-membered ring. In the case of equilibria between n-hexane and the methylpentanes, it can be seen that the 2-methylpentane is the favored isomer over 3-methylpentane, which is reasonable from the simple statistical consideration that the substituent methyl group can occupy either of two equivalent positions in the former molecule as compared to one in the latter.

2.4.2 Kinetic Analysis

Gates, Katzer, and Schuit (1979) reported the behavior of reforming and the influence of heat effects. A qualitative summary of the rate behavior of the important reaction classes catalysed by a modern bifunctional catalyst is given in Table 2.3 with statements of the heat effects. Naphthene and paraffin dehydrogenation reactions are so rapid that they are essentially in equilibrium, and rate need not be considered explicitly. Similarly, the equilibrium between n-paraffins and isoparaffins is usually closely

approached. In contrast, the rates of cyclization and hydrocracking are typically low and in need of explicit consideration.

Table 2.3 Rate Behavior and Heat Effects of Important Reforming Reactions (From Gates, Katzer, and Schuit, 1979)

Reaction Type	Relative Rate	Effect of Increase in Total Pressure	Heat Effect
1. Naphthene Dehydrogenation	Most rapid	Decreases Conversion	Very Endothermic
2. Paraffin Dehydrogenation	Very Rapid	Decreases Conversion	Endothermic
3. Naphthene Isomerization	Rapid	Decreases Rate	Mildly Exothermic
4. Isomerization of Paraffins	Rapid	Decreases Rate	Mildly Exothermic
5. Dehydro cyclization	Slow	Small Decrease in Rate	Endothermic
6. Hydrocracking	Slowest	Increased Rate	Quite Exothermic

Hydrogen partial pressure is an important variable since it strongly affects the conversion to aromatics and the rate of hydrocracking. Since reforming reactions which produced hydrogen, especially aromatization, predominate over those which consume hydrogen, the process is a net hydrogen producer.

Conversion of paraffins to aromatics is the slowest reaction and is the principal reaction in the latter part of the reformer. This reaction provides the final portion of octane generation needed to meet the specified octane. It should be noted that this reaction is the most dependent on space velocity or catalyst

resident time. That is, it requires a larger amount of catalyst than the other principle reactions. For this reason the initial reactors in the reformer are smaller in volume than the terminal reactors.

2.5 Deactivation of Catalyst

The deactivation of catalysts is a phenomenon of considerable importance in catalysis because many catalytic agents show a loss of activity with time. Research activity on this subject has been concerned primarily with chemical, kinetic and modelling aspects. Knowledge and research into the chemical aspects of the deactivation of catalysts are necessary in order to formulate more stable catalytic systems.

2.5.1 Type of Deactivation

The deactivation processes can be subdivided into four general classes.

a. Fouling: the loss of activity caused by species present in the fluid phase or originating from surface reactions which deposit physically on the surface and cote or block sites which would otherwise be available for catalysts. The formation of the coke is a natural by product occurring in all catalytic reforming operations. The coke accumulates on the catalyst and retards the catalyst's ability to produce desired products. Eventually the coke buildup reaches the point where operation of the unit cannot be properly maintained. At that point, the catalyst is regenerated by burning off the coke in an inert atmosphere containing a small amount of oxygen. The regeneration procedure brings the catalyst back to essentially fresh catalyst conditions. The maximum temperature is around 550°C, beyond which the supports loss surface and mechanical resistance (Mayers, 1986).

After coke combustion the catalyst generally contains 0.6-0.8 wt% chlorine compared to .0.9-1.3 for new

catalysts. Reloading with chlorine is done with chlorine compounds such as free chlorine, hydrochloric acid or organic chlorine derivatives like carbontetrachloride or dichloropropane. The reaction with alumina can be carried out at around 250°C, but is carried out industrially at around 450°C in the presence of air. The exact mechanism is not very well known but the principal reactions can be represented by the equations in Figure 2.6 (Limido et al. 1987).

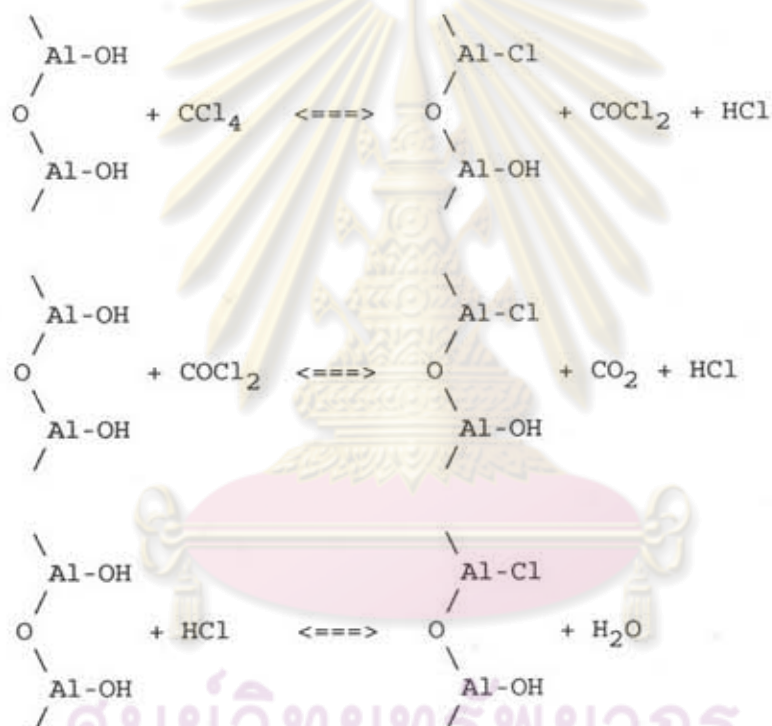


Figure 2.6 Reaction Mechanism for the Chlorination of Alumina with CCl_4

b. Sintering: the loss of activity caused by a reduction of the surface area as a result, for example, of local increases of temperature.

c. Solid-state reactions: the loss of activity caused by changes in the chemical nature and/or composition of the constituents of the catalyst.

d. Poisoning: the loss of activity caused by the chemisorption of impurities which are present in the

feed, and which thereby occupy the active sites of the catalyst which would otherwise be available.

Reforming catalysts are deactivated by various poisons. The most common poisons are sulfur, lead, and other heavy metals, organic or combined nitrogen, and water.

Sulfur is a very common poison which deactivates the metal sites on the catalyst. This deactivation results in higher temperature requirements and decrease liquid yields. Sulfur is a temporary poison and much of the excess sulfur deposited can be removed by continued operation with low sulfur feeds or by special stripping procedures.

Organic nitrogen (not elemental) deactivates the chloride sites on the catalyst by converting to ammonia in the reformer.

Water in large quantities can be a serious problem since it washes chloride from the catalyst.

2.5.2 Sensitivity to Impurities (Limido et al. 1987).

The platinum on alumina catalyst is shown to be relatively sensitive to poisoning. The acid function is inhibited by bases present in the feed either as ammonia or as nitrogen compounds that are transformed into ammonia on the catalyst. The inhibition proceeds through neutralization by forming volatile ammonium chloride. Figure 2.7 shows inhibition of the acid function and the leaching of chlorine through the formation of ammonium ion chloride. The action of nitrogen on the catalyst is revealed by a strong inhibition of the isomerization and a reduction in the dehydrocyclization activity.

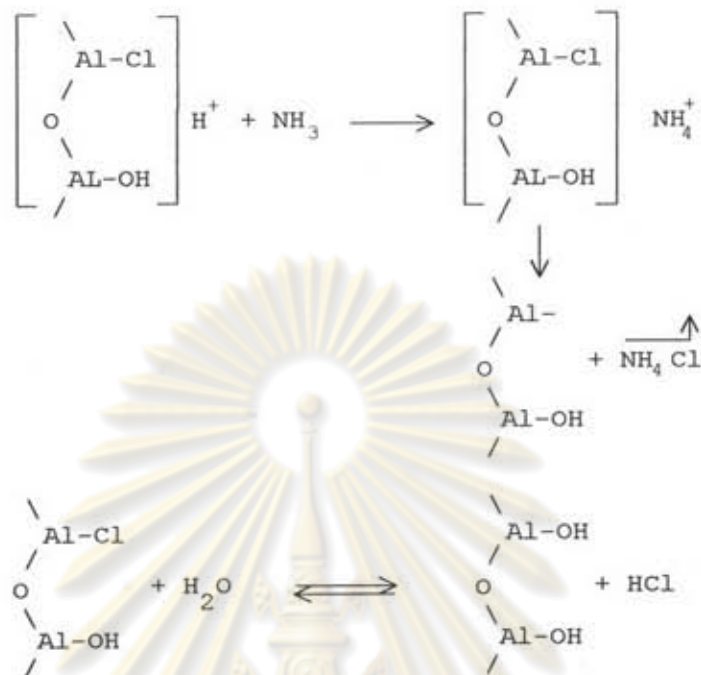


Figure 2.7 Reaction Mechanism for Reforming Catalyst Inhibition by Ammonia and Water

Any water introduced to the feed either as free water or as dissolved oxygen causes the same reaction of chlorine leaching and leads to the rapid decline in catalytic activity.

The metal function is inhibited by sulfur compounds, which are transformed into hydrogen sulfide on the catalyst. Sulfur actually acts as a platinum sulfidation agent. At operating temperatures and hydrogen partial pressures the following equilibrium is established:



Thus the reforming catalyst exhibits a sensitivity to the conventional impurities of straight-run heavy gasolines including water, sulfur

compounds, nitrogen compounds, certain metal compounds containing arsenic, as well as possible pollutants from refinery operations, such as lead compounds or copper compounds, or even construction materials of the unit, such as iron.

In summary, for best use this catalyst should be protect against inhibitors and permanent poisons, and operate within the thermodynamic and kinetic constraints of the process.

2.5.3 Nitrogen Compounds

The effects of nitrogen compounds on catalytic reforming are one of important effects. Although some crude oils are free of nitrogen, others have as much as 1.0%. In crude oils, nitrogen is present largely in the form of heterocyclic compounds having five or six-membered rings, mostly unsaturated. The nonheterocyclic compounds include anilines, aliphatic amines, and nitriles. Some of these are easier to denitrogenate than the heterocyclic nitrogen compounds. The heterocyclic and other nitrogen compounds are often grouped into strong bases (quinolines, pyridines, acridines) versus weak bases or nonbasic compounds (indoles, pyrroles, carbazoles). Some representative heterocyclic nitrogen compounds are shown in Table 2.4. These can be either basic or nonbasic. The strong basic compounds are of particular concern in acid-catalyzed reaction, such as catalytic cracking, since they will poison acidic sites.

The pKa values (solution basicity) and proton affinities for nitrogen compounds are reported in Table 2.5.

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 (Gates, Katzer, and Schuit (1979)).

Table 2.4 Representative Heterocyclic Nitrogen Compounds (From Cocchetto and Satterfield, 1976).



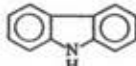






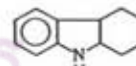



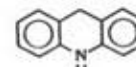
Name	Formular	Structure
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	
Pyridine	C_5H_5N	
Quinoline	C_8H_7N	
Isoquinoline	C_8H_7N	
Acridine	$C_{13}H_9N$	
Pyrrolidine	C_4H_9N	
Indoline	C_8H_9N	
Hexahydrocarbazole	$C_{12}H_{15}N$	
Piperidine	$C_6H_{11}N$	
1,2,3,4-Tetrahydroquinoline	$C_8H_{11}N$	
1,2,3,4-Tetrahydroisoquinoline	$C_8H_{11}N$	
9,10-Dihydroacridine	$C_{13}H_{11}N$	

Table 2.5 The pKa Values and Proton Affinities for Nitrogen Compounds (From Chantalaka, 1993).

Compounds	pKa	Proton affinities (kcal/mol)
Ammonia	9.24	207
Aniline	4.63	213.5
2,6-Dimethylpyridine	6.71	231.5
Pyridine	5.29	222
1,2,3,4-Tetrahydroquinoline	--	225 (a)
Piperidine	11.12	229.7
Quinoline	4.80	227.6

Less is known about the hydrodenitrogenation (HDN) of heterocyclic ring compounds than of the analogous reactions with heterocyclic sulfur compounds. Aliphatic amines react readily, but aromatic amines are less reactive. With pyridine, the ring is first hydrogenated to piperidine, which forms, in turn, pentylamine and pentane plus ammonia (McIlvried, 1971). With quinoline, analogous reactions occur but a greater variety of intermediate compounds are formed. These include 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, and decahydroquinoline, followed by hydrocracking to form aromatic and saturated cyclic amines, and then cyclic hydrocarbons. The overall reaction network is relatively complex.

Cocchetto and Satterfield (1976) concluded that, in general, hydrodenitrogenation of heterocyclic nitrogen compounds was first saturated, followed by ring fracture at a carbon-nitrogen bond. Nitrogen was then removed from the resulting amine or aniline as ammonia.

Speight (1991) concluded that organic nitrogen compounds were converted into ammonia under reforming conditions, and this neutralizes acid sites on the catalyst and thus represses the activity for isomerization, hydrocracking, and dehydrocyclization reactions, that was supported by Ciapetta (1972).

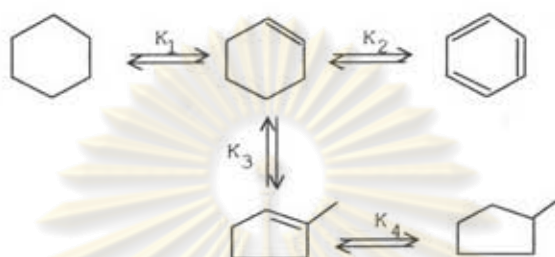
Hettinger, Keith, Gring and Teter (1955) investigated the specific effects of such temporary poisons as water, sulfur, and nitrogen on hydroforming reactions. The data showed that water tends to impair catalyst selectivity by decreasing dehydrocyclization and increasing hydrocracking activity. Some benzene, as well as C_8 , C_9 and C_{10} aromatics were usually founded in n-heptane reformat. In the presence of water there was a small but real increased in the ratio of C_8 , C_9 and C_{10} aromatics relative to benzene. A modest amount of water promotes hydrocracking, inhibits dehydrocyclization, and has no apparent effect on dehydrogenation. The conclusion was that only acidic sites were modified in the presence of water. Sulfur, as H_2S increased hydrocracking, and decreases dehydrocyclization and dehydrogenation activity.

Moreover, the effect of nitrogen (such as NH_3) was also studied on n-heptane, and n-nonane hydroforming. In the presented of nitrogen, it decreased mole% conversion of n-heptane to aromatics from 37% to 16% and decreased mole% conversion of n-nonane to aromatics from 63% to 24%.

The effect of NH_3 was similar water in some respects, in that neither has any effect on the dehydrogenation reaction. Hydrocracking, isomerization, and dehydrocyclization were all adversely affected in the presence of ammonia.

Sterba and Haensel (1976) investigated the sulfur poisoning on the rate of conversion of cyclohexane to benzene. The slowing down of reaction of cyclohexane to

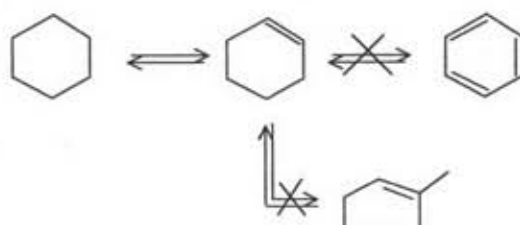
benzene accentuated the participation of an otherwise slower reaction, that was the conversion of cyclohexane to methylcyclopentene (MCP⁺) and then to methylcyclopentane (MCP). The reaction networks were:



The unpoisoned relative rate were $K_2 \gg K_1 \gg K_3 < K_4$ and the poisoned relative rate were $K_2 < K_1$, $K_3 > K_4$, $K_3 > K_2$. This reaction pointed out was acid catalyzed.

The experiments were carried out to poison the acid function in the presence of 50 ppm of sulfur poisoning. The acid-catalyzed reaction of cyclohexane was completely upressed by 10 ppm of nitrogen, added as pyridine. The experiments no longer observe the substantial formation of MCP⁺ and MCP despite the presence of sulfur.

The result showed that cyclohexene concentration to build up by blocking the acid catalyzed reaction by nitrogen poison, and blocking of the cyclohexane conversion to benzene by the sulfur poison as following network:



Pary (1963) and Robschlager et al. (1984) studied that the injection of pyridine into the feed suppressed the activity of catalyst. The decrease in activity was only temporary. When the administration of pyridine stopped. The activity reached almost the original level. It showed that pyridine poisons the metal sites reversibly while the acidic sites of alumina are poisoned irreversibly.

Recently Das, Srivastava and Saraf (1988) studied the reforming of naphtha over Pt-Sn/Al₂O₃ and Pt-Re/Al₂O₃ catalysts. The experiments were conducted at 763 K and one atmosphere pressure. Weight hourly space velocity of 2.5 g naphtha/g catalyst/hour was used. Nitrogen was introduced during reaction to accelerate the catalyze deactivation. A naphtha:hydrogen:nitrogen mole ratio of 1:7:7 was used for reforming reaction. They showed that, in the presence of nitrogen in the stream resulted in a significant activity decline by the total aromatic yield. The individual benzene, toluene, and xylene yields were consideration.

Xylene production decreased with time on stream due to lose in activity of catalyst, after 20 hours operation the xylene production declined by 19.8% and total aromatics declined by 11.9% whereas benzene declined by 57%. Toluene showed a reverse trend and its production increased by 121.5% over the same time period.

They suggested that presence of N₂ seems to promoted dealkylation of C₇ hydrocarbons to produced more benzene. This dealkylation activity decreases with coke formation.

More recently, Dees, Hartog and Ponec (1991) studied of active sites of reforming catalysts by poisoning. They purposed that, the injection of pyridine into the feed made it possible to distinguish between the metal and acidic site activity. The experiments were conducted over a series of 1 weight% Pt, Ir, Pt-Ir, Ru,

Re on γ -alumina Catalysts that were prepared in laboratory, and commercial catalysts were investigated; the CK 303 (0.3 wt% Pt/ γ -Al₂O₃) catalyst, the CK 455 (1 wt% Pt-Re(1:1)/ γ -Al₂O₃) catalyst, and Euro Pt-1 (6.3 wt% Pt/SiO₂).

A continuous flow of H₂/n-hexane was 18/1 at total pressure 1 bar passed the catalyst at a constant temperature 620 Kelvin. The experiments were performed by stabilization of the catalyst, after achieving a rather constant activity and selectivity for 20 hours. The total added amount of pyridine 0.08 mmole injected into the feed 8 times in 4 hours. Then a period of 4 hours was allowed for recovery of activity.

The experiments with n-hexane over several catalysts, lead to the data which were plotted as a function of time. The injection of pyridine into the feed results in a sharply decreasing conversion, with all alumina-supported systems.

After the addition of pyridine had been stopped, catalysts show a recovery of activity. However, there was a difference in behavior of the various catalysts. Both alumina supported platinum catalysts did not restored the activity completely and recovered also slowly.

The selectivity patterns of the catalysts changed drastically by the presence of pyridine. A small decreased in selectivity to hydrogenolysis was accompanied by an increasing selectivity to cyclization. Both monometallic platinum catalysts show a strong decrease in selectivity to isomerization upon pyridine poisoning. This is accompanied by an increasing selectivity to cyclization (methylcyclopentane).

2.6 Literature Summary

1. The reforming catalyst is a bifunctional catalyst which has a metal component an acidic component

present on the catalyst surface.

2. The alumina support may have been acidified by the incorporation with chloride or fluoride. The effect of chloride or fluoride on acidity is believed to be an inductive effect.

3. The case of reaction on metal surfaces which proceed through the surface reaction mechanisms as follows:

- 3.1 Hydrogenation-dehydrogenation reactions
- 3.2 Aromatization reactions
- 3.3 Isomerization and dehydrocyclization
- 3.4 Hydrogenolysis

4. The alumina-catalyzed reactions proceed mainly through carbonium-ion mechanisms as follows:

- 4.1 Isomerization
- 4.2 Cyclization
- 4.3 Hydrocracking

5. The desired products in catalytic reforming which lead to the formation of aromatics and isoparaffins.

6. The yield of aromatic and isomerization are increased by:

- 6.1 High temperature
- 6.2 Low pressure
- 6.3 Low space velocity
- 6.4 Low $H_2:H/C$ mole ratio

7. The effects of nitrogen compounds on catalytic reforming are important effects. Organic nitrogen compounds are converted into ammonia under reforming conditions and this neutralizes acid sites on the catalyst thus the reactions which proceed on acid site are suppressed.