



CHAPTER 3

THEORY OF REFORMING REACTIONS

Catalytic reforming for BTX entails a number of reactions, the most important of which are dehydrogenation of naphthenes and dehydrocyclization of paraffins. The general nature of the reactions occurring over reforming catalyst are well known. Many sets of reaction data have been published from runs with pure components by Emmett (1958).

Modern reforming catalysts are extremely sensitive to heavy metals such as lead and copper; to arsenic, sulfur, and nitrogen compounds; and to excessive water. They are protected by hydrotreating the feed naphtha.

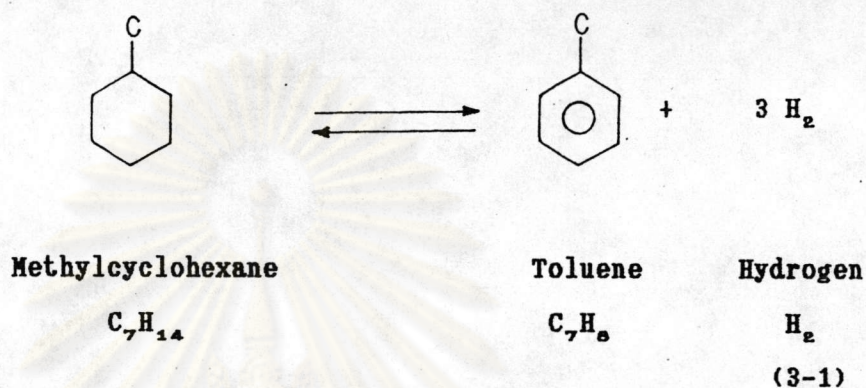
This chapter proceeds with the reforming reactions, reaction rate, rate equations and reforming catalyst.

3.1 Reforming Reactions

Until the advent of catalytic reforming, refining processes were non-selective (except a few like alkylation, polymerization, and isomerization) - that is, the feedstock was indiscriminately converted or cracked with little attempt to control specific chemical reactions. Catalytic reforming catalyst and operating conditions are designed to promote certain reactions and to inhibit others. Reactions most prevalent in catalytic reforming are dehydrogenation, isomerization, dehydrocyclization, and hydrocracking (Little, (1985)).

(1) Dehydrogenation

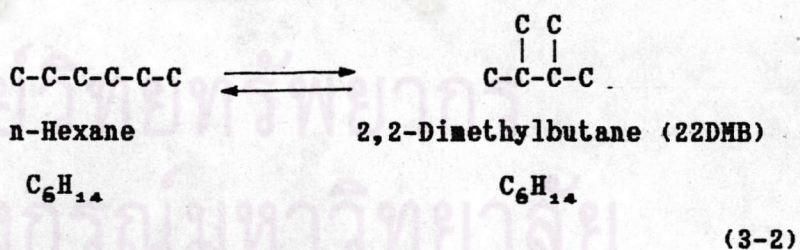
A principal reforming reaction is dehydrogenation because it produces aromatics that have high octane numbers or are valuable petrochemicals:



Dehydrogenation reactions are strongly influenced by temperature and by hydrogen partial pressure, the extent of reactions increasing as temperature increases and hydrogen partial pressure decreases (Emmett, (1958)).

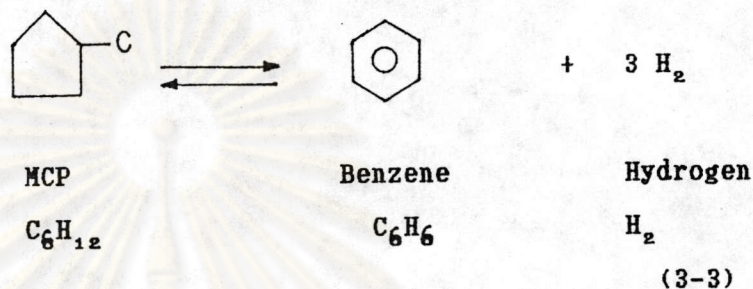
(2) Isomerization

Paraffins are isomerized at reforming conditions:



Isomerization of a paraffin rearranges the molecule with essentially no change in volume but with a marked increase in octane number.

Naphthene hydrocarbons may also isomerize in reforming reactors. When this happens, they almost immediately undergo dehydrogenation to an aromatic. For example, a naphthene isomerization is the conversion of methylcyclopentane (MCP) to benzene:

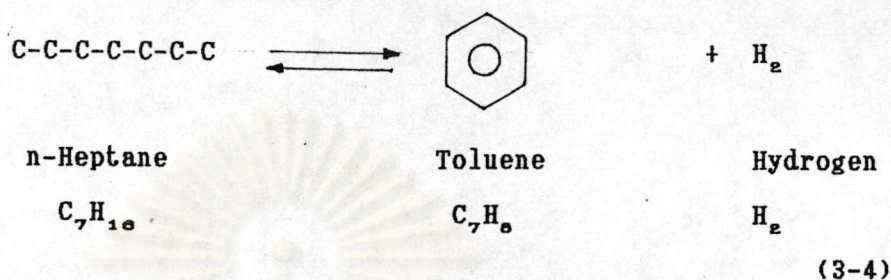


MCP is generally acknowledged to isomerize first to cyclohexane, which then dehydrogenates to benzene. Volume decreases, but octane number increases. Apparently this reaction involves ring opening, with a likelihood of forming paraffins as well as aromatics. On the other hand, paraffins can be cyclized to aromatics by what is known as dehydrocyclization.

(3) Dehydrocyclization

Probably the most difficult reaction to promote in reforming is dehydrocyclization. It is a required reaction for production of a satisfactory yield of high-octane-number reformate. Most reforming feedstocks contain a substantial quantity of low-octane-number paraffins. The dehydrogenation and isomerization reactions of paraffins alone cannot produce enough aromatics and isoparaffins to yield high-octane-number reformate.

A typical dehydrocyclization is:

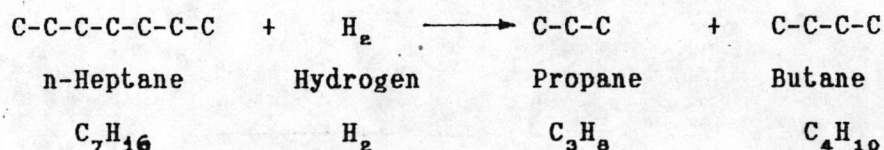


As with naphthene isomerization, there are intermediate steps between the paraffin and the aromatic. The reaction is favored by high temperature and low pressure; it predominantly takes place in the last reactor in the train.

For cyclization, a paraffin with at least a six-carbon straight chain is needed. Consequently, n-pentane does not cyclize, nor does 2-methylpentane nor 2,2-dimethylpentane. However, n-heptane will cyclize to benzene. The longer straight-chain paraffins will dehydrocyclize more readily than the shorter chains.

(4) Hydrocracking

The breaking of the C-C bond in reforming operations is called hydrocracking. Hydrocracking can break a paraffin molecule into two molecules of lower molecular weight or can open the ring of a naphthene. Aromatics present in the feed or produced in the reactors do not normally undergo ring opening at reforming temperatures and pressures. Examples of hydrocracking reactions are:



(3-5)

These paraffins are the result of hydrocracking close to the outlet of the last reactor where no time is left for hydrogenation. High temperature and high pressure accelerate hydrocracking. It usually takes place on the acidic sites of the catalyst but can also cause pyrolysis (chemical decomposition by heat) at temperatures above 1,100 °F. Hydrocracking produces coke precursors that cover active catalyst sites.

Hydrocracking is not all bad. For example, n-decane can split into n-heptane and propane. The n-heptane can then dehydrocyclize to toluene, a high-octane-number aromatic. Although a refiner usually likes to operate a reformer with a minimum amount of hydrocracking - to maximize C_8^+ output - a reformer can be operated at a higher than necessary octane to yield more propane and butanes.

3.2 Reaction Rate

All the above reactions occur in reforming, but all do not proceed at the same rate. For the most part, an engineer assigned to a reforming unit will think more about relative rates of reactions of broad classes of hydrocarbons rather than the reaction rates of individual components. It is well known in reforming that naphthene dehydrogenation is a relatively fast reaction, is endothermic, and is favored by low hydrogen partial pressure.

A general characterization of relative reaction rates is:

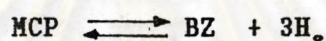
Reaction	Relative Rate	Comments
Dehydrocyclization	1	Endothermic; promoted by low pressure and high temperature
Hydrocracking	4	Exothermic; promoted by high pressure and high temperature
Isomerization	12	Mildly exothermic; promoted by high temperature, only slightly affected by pressure
Naphthene dehydrogenation	100 ⁺	Endothermic; promoted by low pressure and high temperature

The above relative rates are broad generalizations. For example, the rate of dehydrocyclization of n-heptane is much faster than that of n-hexane. In general, the higher the number of carbon atoms per molecule, the more rapid the rates for the above reactions.

3.3 Rate Equations

In order to develop the kinetics, an expression is required that related the rate and amount of adsorption to the concentration of the component of the fluid in contact with surface for complex reactions by Hougen and Watson (1947) rate equations. An attempt to formulate a rate equation for solid-catalyzed reactions start from the basic laws of chemical kinetics encountered in the treatment of homogeneous reactions.

For example, ring expansion of methylcyclopentane (MCP) to benzene (Marin et al., (1982)):



From this example, the kinetic equation for reactions catalyzed by solid based on the chemisorption mechanism may always be written as a combination of three groups (Yang and Hougen (1950)):

In general form of the overall rate is :

$$r_A = \frac{(\text{kinetic factor}) (\text{driving-force group})}{(\text{adsorption group})^n} \quad (3-6)$$

Where n is the exponent of adsorption group.

From Appendix B in Table B-1, driving force groups is

$$\frac{(p_{\text{MCP}} - p_{\text{BZ}} p_{\text{H}_2}^3)}{K_{\text{MCP-BZ}}}$$

and kinetic groups (rate constant), and n = 2.

Where K_{MCP-BZ} and k_{MCP-BZ}° is equilibrium constant and rate constant of this reaction. p_{MCP} , p_{BZ} and p_{H_2} are partial pressure of methylcyclopentane, benzene and hydrogen, respectively.

Thus, the rate equation in term of partial pressure of hydrocarbon/partial pressure of hydrogen is written as

$$r_{MCP-BZ} = k_{MCP-BZ}^{\circ} \left(p_{MCP} - \frac{p_{BZ} p_{H_2}^2}{K_{MCP-BZ}} \right) / (p_H \mathcal{T})^2 \quad (3-7)$$

where \mathcal{T} is the adsorption term accounting for the coverage of the catalyst sites by the reacting species, and

$$\mathcal{T} = 1 + \frac{K_{H_2O} p_{DMB} + p_{MP} + p_{nH}}{p_H} + \frac{K_{MCP} p_{MCP}}{p_H}$$

Where K_{H_2O} , and K_{MCP} are really products of adsorption constants.

In model discrimination and parameter estimation in heterogeneous catalysis, the form of the rate equation (of the model) is not known a priori, although physico-chemical insight and several formalisms limit the spectrum of possible models. Also unknown, of course, are the values of the rate coefficients and of the adsorption coefficients K_A , K_R , K_S , or in other words, the parameters of the model. The estimation of parameters should be accompanied by extensive statistical testing. In kinetic analysis the equations are often rearranged to permit estimation of the parameters by linear regression, a practice that violates some of the premises of the

statistical analysis. Thus, a kinetic investigation consists mainly of two parts: model discrimination and parameter estimation. The methodology of kinetic analysis, by both the differential and the integral method, has been discussed in detail by Froment (1975).

3.4 Catalysts

An outstanding feature of reforming catalyst, even from the beginning, is the incorporation of more than one function in a single catalyst. For this reason, reforming catalysts have been termed dual functional, bifunctional and, recently, multifunctional (Little, (1985)).

Technologists involved in the development of reforming catalysts recognize that the reforming reactions require at least two different functions. One is a metal to catalyze the dehydrogenation of naphthenes to aromatics and to hydrogenate olefins formed by dehydrogenation and hydrogenolysis of paraffins. It is generally acknowledged that the metal component also contributes to dehydrocyclization and isomerization. The second function needed is an acid to catalyze isomerization, cyclization, and hydrocracking. The contribution of catalyst components to reactions that occur in reforming and the effect of environmental variables, although the subjects of vast research, are still not well understood. The general consensus is that the catalyst-metal function and the acid function are both necessary and both contribute, sometimes individually and sometimes collectively.

One of the better visualizations of the dual function of reforming catalyst and reforming reactions is presented in Figure 3-1. This figure has appeared in a number of reforming articles and was first published by Mills et al., (1953). In this simplified representation of reforming reaction network, reactions indicated by vertical arrows are catalyzed by the metal function of the catalyst. Reactions indicated by horizontal arrows are catalyzed by the acid function of the catalyst. For example, the mechanism for producing benzene from n-hexane is dehydrogenation to n-hexene on a metal site, isomerization of n-hexene to methylcyclopentane on an acid site, dehydrogenation to methylcyclopentene on a metal site, isomerization to cyclohexene on an acid site, then dehydrogenation on a metal site to cyclohexadiene, and, finally, benzene.

Catalyst Poisons

Reforming catalyst poisons are classified as either temporary or permanent. Temporary poisons are those which can be removed from the catalyst without a shutdown, and the catalyst is restored to proper activity and selectivity. A classic temporary poison is sulfur which causes a significant activity loss (octane number decrease) with a bimetallic catalyst.

A permanent catalyst poison is one that impairs catalyst performance to the point that the unit must be shut down and the catalyst replaced because there is no way to restore it to a satisfactory performance level. A classic permanent catalyst poison is arsenic, which deposits on the catalyst and causes a rapid loss in activity. A general requirement is that the maximum allowable arsenic content of the

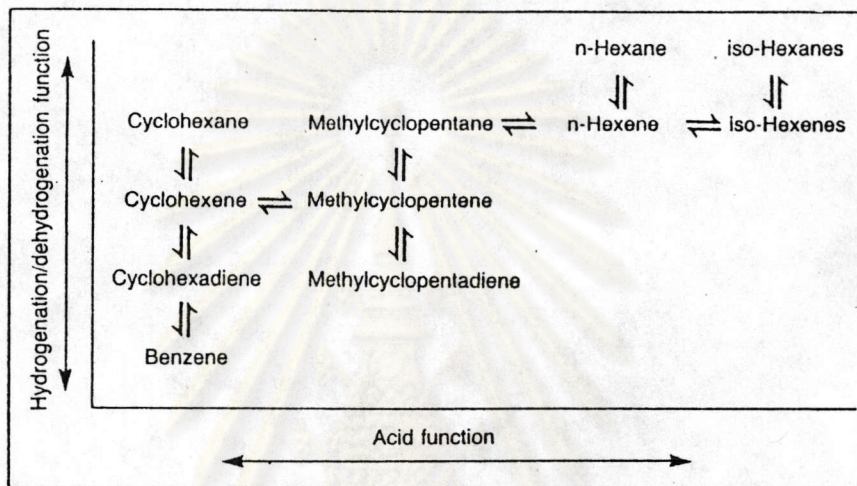


Figure 3-1 Reactions of a multifunction reforming catalyst
(Heinemann et al., (1953))

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

feedstock is 1 part per billion (ppb) wt, which is as low as analytical methods can detect arsenic in naphtha feedstocks.

The poisons of a catalyst reforming are:

Sulfur. Sulfur deactivates the hydrogenation/dehydrogenation function of the catalyst by forming metal sulfides. The reaction, however, is reversible. When sulfur is removed from the feed, the sulfur leaves the catalyst and appears as hydrogen sulfide in reformer products.

Nitrogen. Organic nitrogen compounds in reformer feed are converted to ammonia, which poisons the acid function of the catalyst. This generally means the ammonia reacts with the chloride component. When organic nitrogen is eliminated from the feed, the catalyst gives up ammonium chloride and recovers its acid function if chloride is brought up to the proper level by chloride addition. Molecular nitrogen (N_2) apparently does not react at reforming conditions and so is not a catalyst poison.

Halides. Too much chloride increases the acid function of the catalyst beyond the optimum required for balanced catalyst performance. When excess chloride is eliminated from the feed, chloride leaves the catalyst. Balance is restored by control of chloride injection. Fluoride has the same effect as chloride, except fluoride is very difficult to strip from the catalyst and makes controlling the acid-catalyzed hydrocracking reaction more difficult.

Water. It comes from moisture in the feed or from oxygenated hydrocarbons converted to water at reforming conditions. Although some moisture is required to activate the alumina support, excess water can throw the acid function of the catalyst out of balance by stripping chlorides from the

catalyst. Balance of catalyst functions is restored by elimination of the excess water source and by chloride injection.

Metals. Trace quantities of metal such as arsenic or lead can enter a reformer with reactor charge. The metals deposit nearly quantitatively on the catalyst and deactivate the metal (platinum) function of the catalyst. The effect is irreversible; the arsenic or lead cannot be removed to restore the reforming functions of the catalyst. Preventing arsenic or lead from entering the unit and replacing the poisoned catalyst are necessary to bring unit performance up to its proper level.

Carbon on Catalyst. Rapid buildup of carbon on the catalyst accelerates loss of activity and selectivity. Carbon laydown is generally attributed to condensation of aromatics into polycyclic aromatics. These polycyclic aromatics strongly adhere to the catalyst and are ultimately converted to coke. At some level of coke on the catalyst - about 7-10 wt% for platinum-only catalyst and 20-40 wt% for bimetallic catalyst - activity and selectivity are so low that the catalyst must be regenerated by burning off the coke. A high rate of carbon laydown and coking is frequently a result of high-boiling hydrocarbons in reactor charge.


Catalyst Regeneration

Catalyst regeneration of an acidic platinum or multimetallic Al_2O_3 catalyst will always involve at least the following:

- (1) Purging of hydrogen and hydrocarbons.
- (2) Burning off the coke with very dilute air at first, and then with more concentrated air.
- (3) Adjusting the catalyst acidity.

- (4) Purging all oxygen from the system.
- (5) Reducing the catalyst with hydrogen.

The above procedure may be all that is needed when regenerating a catalyst twice a year in semiregenerative operation. In this case the acidity is likely to be adjusted by circulating very dilute HCl or organic chloride through the catalyst between step (4) and (5) above.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย