# CHAPTER II
LITERATURE REVIEW

2.1 Catalytic Reforming

The aim of this process is to improve the octane number of a naphtha feeds-tock by changing its chemical composition. In general, aromatics have higher octane ratings than paraffins and cycloparaffins. Similar to aromatics, branched paraffins have high octane ratings. (Matar *et al.*, 1994; Antos *et al.*, 2004)

2.1.1 Reforming Reactions

These are major reforming reactions of naphtha as shown below in Figure 2.1. In fact, four reactions of (a) – (d) are used to beneficially obtain an increase in the octane number of products; in contrast, hydrocracking and hydrogenolysis (carbon-carbon scissions), which result in low molecular weight paraffins and coke formation that will eventually deactivate the catalyst.
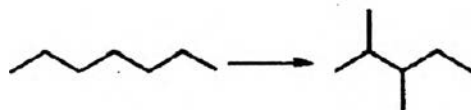
(a) Dehydrogenation of naphthenes
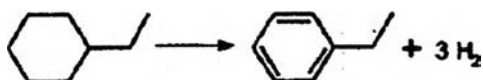
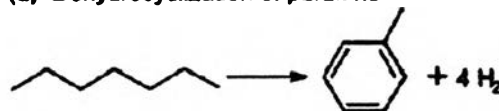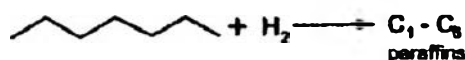**(b) Dehydroisomerization of naphthenes**

(c) Isomerization of paraffins

(d) Dehydrocyclization of paraffins

(e) Hydrocracking and hydrogenolysis

(f) Coke formation

Figure 2.1 Major reactions in catalytic reforming of naphtha.

2.1.1.1 Aromatization

One of the most common-important reactions to obtain high value added products from naphtha feedstock is the aromatization of n-alkane which is of considerable theoretical and industrial importance. Aromatization is believed to proceed via a two-step mechanism which first includes dehydrogenation and cracking of paraffins to form an olefinic intermediate and then dehydrocyclization of the olefinic intermediate to form aromatics (Harandi *et al.*, 1991).

The two reactions directly responsible for enriching naphtha with aromatics are the dehydrogenation of naphthenes and the dehydrocyclization of paraffins. The first reaction can be represented by the dehydrogenation of cyclohexane to benzene as shown in Figure 2.2.

$$+3H_2 \quad \Delta H = +221 \text{ KJ/mol}$$
$$K_p = 6 \times 10^5 \ @ \ 500°C$$
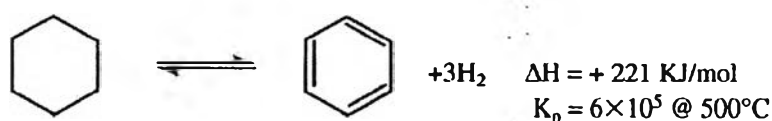
Figure 2.2 Schematic of cyclohexane dehydrogenation to benzene.

This reaction is fast; it reaches equilibrium quickly. The reaction is also reversible, highly endothermic, and the equilibrium constant is quite large. It is evident that the yield of aromatics (benzene) is favored at higher temperatures and lower pressures. The effect of decreasing H_2 partial is even more pronounced in shifting the equilibrium to the right.

The second aromatization reaction is the dehydrocyclization of paraffins to aromatics. For example, if n-hexane represents this reaction, the first step would be to dehydrogenate the hexane molecule over the platinum surface, giving 1-hexene (2- or 3-hexenes are also possible isomers, but cyclization to a cyclohexane ring may occur through a different mechanism). Cyclohexane then dehydrogenates to benzene as shown in Figure 2.3.

$$CH_3(CH_2)_3CH=CH_2 \rightleftharpoons \bigcirc \rightleftharpoons \bigcirc +3\,H_2 \quad \begin{array}{l} \Delta H = +266\ KJ/mol \\ K_p = 7.8\times10^4\ @\ 500°C \end{array}$$

**Figure 2.3** Schematic of n-hexane dehydrocyclization to benzene.

This is also an endothermic reaction, and the equilibrium production of aromatics is favored at higher temperatures and lower pressures. However, the relative rate of this reaction is much lower than the dehydrogenation of cyclohexanes.

Figure 2.4, a stepwise dehydrocyclization with gradual loss of hydrogen to form a conjugated triene followed by ring closure and further dehydrogenation may account for aromatics formation: (Olah and Molnár, 2003)
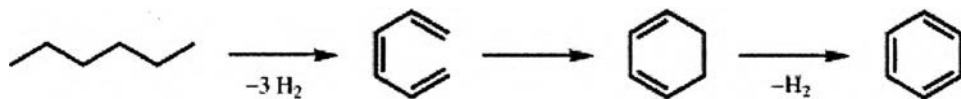
**Figure 2.4** A stepwise dehydrocyclization of n-hexane.

Dehydrocyclization of n-octane can produce ethylbenzene and o-xylene by a mechanism that involves the direct formation of a six-member carbon ring as shown in Figure 2.5 (Shi and David, 1995):
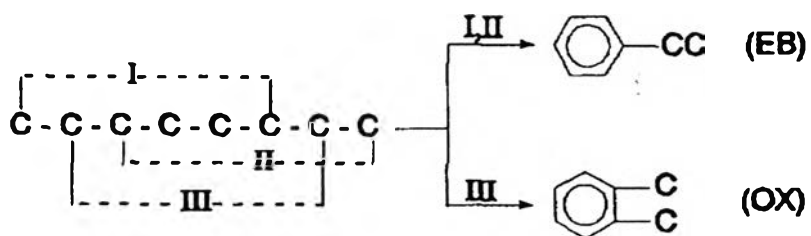
Figure 2.5 A mechanism of n-octane dehydrocyclization.

2.1.1.2 Isomerization

Reactions leading to skeletal rearrangement of paraffins and cycloparaffins in a catalytic reactor are also important in raising the octane number of the reformate product. Isomerization reactions may occur on the platinum catalyst surface or on the acid catalyst sites. In the former case, the reaction is slow. For example, methylcyclopentane isomerizes to cyclohexane and then dehydrogenate to benzene as shown in Figure 2.6:
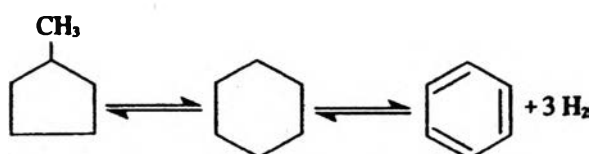
Figure 2.6 Schematic of methylcyclopentane conversion to benzene.

2.1.1.3 Hydrocracking

Hydrocracking is a hydrogen-consuming reaction that leads to higher gas production and lower liquid yield. This reaction is favored at high temperatures and high hydrogen partial pressure. Figure 2.7 represents a hydrocracking reaction:

$$RCH_2CH_2CH_2R' + H_2 \longrightarrow RCH_2CH_3 + R'CH_3$$

Figure 2.7 Schematic of hydrocracking reaction.

Bond breaking can occur at any position along the hydrocarbon chain. Because the aromatization reactions mentioned earlier produce hydrogen and are favored at high temperatures, some hydrocracking occurs also under these conditions. However, hydrocracking long-chain molecules can produce C_6, C_7, and C_8 hydrocarbons that are suitable for hydrodecyclization to aromatics.

2.1.1.4 Hydrodealkylation

Hydrodealkylation is a cracking reaction of an aromatic side chain in presence of hydrogen. Like hydrocracking, the reaction comsumes hydrogen and is favored at a higher hydrogen partial pressure. This reaction is particularly important for increasing benzene yield when methylbenzenes and ethylbenzene are dealkylated. Although the overall reaction is slightly exothermic, the cracking step is favored at higher temperatures. Hydrodealkylation may be represented by the reaction of toluene and hydrogen as shown in Figure 2.8.

$$CH_3\text{-}C_6H_5 + H_2 \longrightarrow C_6H_6 + CH_4$$
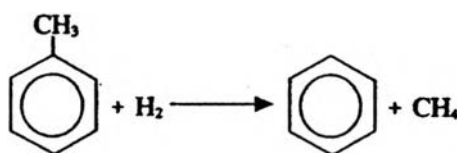
Figure 2.8 Schematic of hydrodealkylation reaction.

2.1.2 Reforming Products

Catalytic reforming is considered the key process for obtaining benzene, toluene, and xylene (BTX). These aromatics are important intermediates for the production of many chemicals.

2.1.2.1 Benzene

Benzene (C_6H_6) is the simplest aromatic hydrocarbon and by far the most widely used one. Before 1940, the main source of benzene and substituted benzene was coal tar. Currently, it is mainly obtained from catalytic reforming. Other sources are pyrolysis gasolines and coal liquids. Benzene is an important chemical intermediate and is the precursor for many commercial chemicals and polymers such as phenol, styrene for polystyrenic, and caprolactom for nylon 6.

Monosubstitution can occur at any one of the six equivalent carbons of the ring. Most of the monosubstituted benzenes have common names such as toluene (methylbenzene), phenol (hydroxybenzene), and aniline (aminobenzene). When two hydrogens in the ring are substituted by the same reagent, three isomers are possible. The prefixes ortho, meta, and para are used to indicate the location of

the substituents in 1,2-: 1,3-: or 1,4-positions. For example, there are three xylene isomers as shown in Figure 2.9:

o-Xylene	m-Xylene	p-Xylene
(1,2-Dimethyl-benzene)	(1,3-Dimethyl-benzene)	(1,4-Dimethyl-benzene)
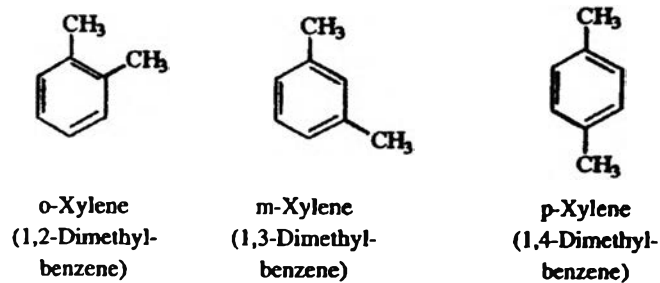
Figure 2.9 Identified xylene isomers.

2.1.2.2 Ethylbenzene

Ethylbenzene ($C_6H_5CH_2CH_3$) is one of the C_8 aromatic constituents in reformates and pyrolysis gasolines. Most ethylbenzene is obtained by alkylation of benzene with ethylene. It was used for production of styrene.

2.1.2.3 Methylbenzenes (Toluene and Xylenes)

Methylbenzenes occur in small quantities in naphtha and higher boiling fractions of petroleum. Those presently of commercial importance are toluene, o-xylene, p-xylene, and to a much lesser extent m-xylene. Currently, the largest single use of toluene is to convert it to benzene. p-xylene is mainly used to produce terephthalic acid for polyesters. o-xylene is mainly used to produce phthalic anhydride for plasticizers.

2.2 Catalyst Deactivation for Reforming

The mechanisms of catalyst deactivation can be grouped into six intrinsic mechanisms of catalyst decay (Bartholomew et al., 2001):

1. poisoning
2. fouling
3. thermal degradation
4. vapor compound formation accompanied by transport

5. vapor–solid and/or solid–solid reactions

6. attrition/ crushing

The causes of deactivation are basically three-fold: chemical, mechanical and thermal. Each of the six basic mechanisms is defined briefly in Table 2.1.

Table 2.1 Mechanisms of catalyst deactivation

Mechanism	Type	Brief definition/description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
Thermal degradation	Thermal	Thermally induced loss of catalytic surface area, support area, and active phase–support reactions
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapor–solid and solid–solid reactions	Chemical	Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase
Attrition/crushing	Mechanical	Loss of catalytic material due to abrasion Loss of internal surface area due to mechanical-induced crushing of the catalyst particle

2.2.1 Poisoning

Poisoning is the strong chemisorption of reactants, products or impurities on sites otherwise available for catalysis. Thus, poisoning has operational meaning; that is, whether a species acts as a poison depends upon its adsorption strength relative to the other species competing for catalytic sites. In addition to physically blocking of adsorption sites, adsorbed poisons may induce changes in the electronic or geometric structure of the surface. Mechanisms by which a poison may affect catalytic activity are multifold as illustrated by a conceptual two-dimensional model of sulfur poisoning of ethylene hydrogenation on a metal surface shown in Figure 2.10.
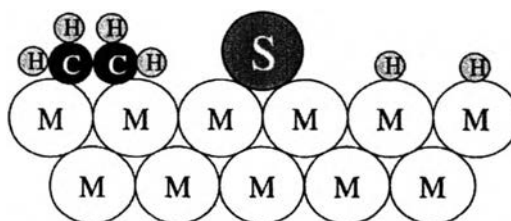
Figure 2.10 Conceptual model of poisoning by sulfur atoms of a metal surface during ethylene hydrogenation.

The adsorbed poison can affect the catalyst in the following manner:

(i) A strongly adsorbed atom of sulfur physically blocks at least one three- or four-fold adsorption/reaction site (projecting into three dimensions) and three or four topside sites on the metal surface.

(ii) It electronically modifies its nearest neighbor metal atoms and possibly its next nearest neighbor atoms by virtue of its strong chemical bond.

(iii) The restructuring of the surface by the strongly adsorbed poison, possibly causing dramatic changes in catalytic properties, especially for reactions sensitive to surface structure.

(iv) The adsorbed poison blocks access of adsorbed reactants to each other.

(v) Prevents or slows the surface diffusion of adsorbed reactants.

Since a number of common poisons such as coke, sulfur and arsenic compounds are strongly and irreversibly adsorbed, poisoning is best prevented through purification of the reactant stream by means of scrubbers or guard beds, rather than attempting to remove the poison from the catalyst after the fact.

Catalysis of feed containing several hundred ppm sulfur, was also of interest because: (1) aromatization activity is decreased with sulfur bearing feeds regardless of the method of catalyst manufacture, (2) about half of the refineries worldwide do not hydrodesulfurize the n-pentane/n-hexane (C₅/C₆) fraction of the gasoline pool, and (3) little is known about the effects of catalyst pretreatment on the catalyst deactivation by sulfur poisoning (Jao et al., 1995).

Poisoning selectivity is illustrated in Figure 2.11, a plot of activity (the reaction rate normalized to initial rate) versus normalized poison concentration.
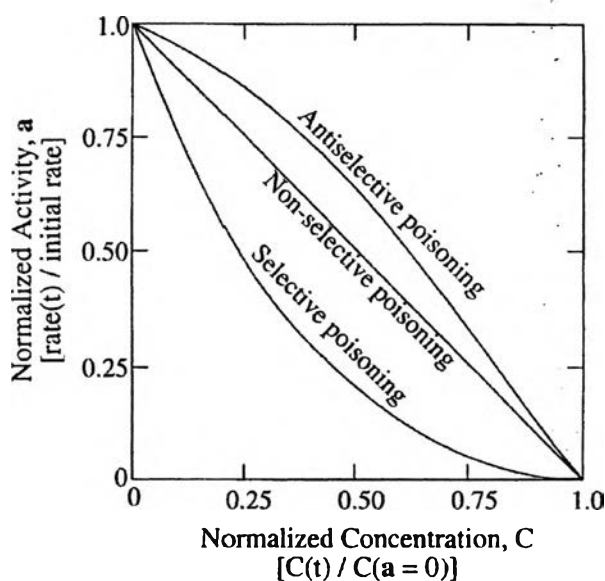
Figure 2.11 Three kinds of poisoning behavior in terms of normalized activity vs. normalized poison concentration.

(i) *Selective poisoning:* occurs when the activity of the catalyst decreases rapidly in the beginning with increasing surface coverage by the poison and the deactivation rate slow down at higher coverage.

(ii) *Non-selective poisoning:* the activity loss is proportional to the con-

centration of adsorbed poison.

(iii) *Anti-selective poisoning*: occurs when the initial loss in activity is less and the loss becomes more pronounced with increasing surface coverage by the poison.

2.2.2 Fouling, Coking and Carbon Deposition

Fouling is the physical (mechanical) deposition of species from the fluid phase onto the catalyst surface, which results in activity loss due to blockage of sites and/or pores. In its advanced stages it may result in disintegration of catalyst particles and plugging of the reactor voids. Important examples include mechanical deposits of carbon and coke in porous catalysts, although carbon- and coke-forming processes also involve chemisorption of different kinds of carbons or condensed hydrocarbons which may act as catalyst poisons. The definitions of carbon and coke are somewhat arbitrary and by convention related to their origin. Carbon is typically a product of CO disproportionation while coke is produced by decomposition or condensation of hydrocarbons on catalyst surfaces and typically consists of polymerized heavy hydrocarbons. Nevertheless, coke forms may vary from high molecular weight hydrocarbons to primarily carbons such as graphite, depending upon the conditions under which the coke was formed and aged. The chemical structures of cokes or carbons formed in catalytic processes vary with reaction type, catalyst type, and reaction conditions.

Sárkany *et al.*, (1984) proposed two possible pathways for the formation of coke on metal sites, one involving adsorbed single C-atom entities, and the other occurring by polymerization of polyolefins. The first mainly occurs on metallic sites and the second pathway corresponds to the metallic-support interface. Deposition of coke occurs through progressive dehydrogenation, condensation, polymerization, and cyclization of hydrogen-deficient hydrocarbon species on the surface of the catalyst and the coke precursors are mostly olefins and aromatics. Coke formation is a bi-functional reaction, requiring the dehydrogenating capacity of the metallic function and the condensation–polymerization capacity of the acidic function (Sahoo *et al.*, 2003).

Possible effects of fouling by carbon (or coke) on the functioning of a supported metal catalyst are illustrated in Figure 2.12.
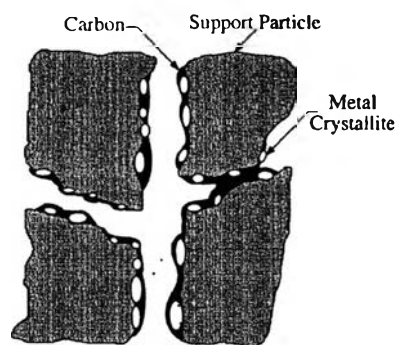
Figure 2.12 Conceptual model of fouling, crystallite encapsulation and pore plugging of a supported metal catalyst due to carbon deposition.

(i) Carbon may chemisorb strongly as a monolayer or physically adsorb in multilayers and in either case block access of reactants to metal surface sites.

(ii) Carbon may totally encapsulate a metal particle and thereby completely deactivate that particle.

(iii) Carbon may plug micro- and mesopores such that access of reactants is denied too many crystallites inside these pores.

(iv) In extreme cases, carbon may strong carbon filaments may build-up in pores to the extent that they stress and fracture the support material, ultimately causing disintegration of catalyst pellets and plugging of reactor voids.

Keys to preventing carbon deposition and coke formation include:

(a) Operating under conditions that minimize formation, e.g. at sufficiently high H_2/CO ratios in FT synthesis.

(b) Optimizing catalyst design, e.g. in the case of zeolites optimizing acidity to minimize coke formation.

(c) Purifying the feed to remove precursors that accelerate carbon or coke formation, e.g. removal of polynuclear aromatics from the feed of a hydrocracking or hydrotreating process which otherwise react readily on acid sites to form coke.

2.2.3 Thermal Degradation and Sintering

Thermally-induced deactivation of catalysts results from

(i) Loss of catalytic surface area due to crystallite growth of the catalytic phase.

(ii) Loss of support area due to support collapse and of catalytic surface area due to pore collapse on crystallites of the active phase.

(iii) Chemical transformations of catalytic phases to non-catalytic phases.

Sintering processes generally take place at high reaction temperatures (e.g. > 500 °C) and are generally accelerated by the presence of water vapor. Three principal mechanisms of metal crystallite growth have been advanced:

(1) Crystallite migration

(2) Atomic migration

(3) Vapor transport (at very high temperatures)

The processes of crystallite and atomic migration are illustrated in Figure 2.13.

Metal
Crystallite

B

A
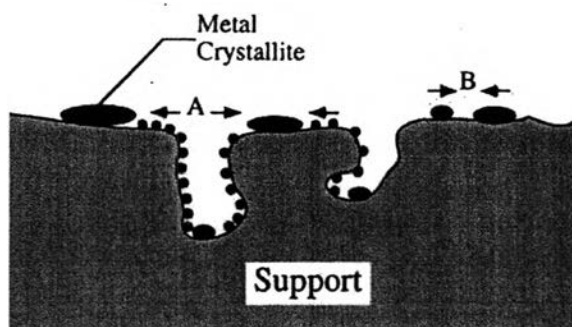
Support

Figure 2.13 Two conceptual models for crystallite growth due to sintering by (A) atomic migration or (B) crystallite migration.

Crystallite migration involves the migration of entire crystallites over the support surface followed by collision and coalescence. Atomic migration involves detachment of metal atoms from crystallites, migration of these atoms over the support surface and ultimately, capture by larger crystallites. In general, sintering processes are kinetically slow (at moderate reaction temperatures) and irreversible or

difficult to reverse. Thus, sintering is more easily prevented than cured; the key is to maximize catalytic activity enough to enable operation at temperatures low enough that sintering rates are negligible.

2.2.3.1 Sintering of Metals

Sintering occurs because small crystallites always tent to lower their surface free energies by minimizing their specific surface areas. Factors affecting metal particle growth and redispersion in supported metals are temperature, atmosphere, metal type, metal dispersion, promoters/impurities and support surface area, texture and porosity. Sintering rates increase exponentially with temperature. Metals sinter relatively rapidly in oxygen and relatively slowly in hydrogen, although depending upon the support, metal redispersion can be facilitated by exposure at high temperature (e.g. 500–550 °C for Pt/Al_2O_3) to oxygen and chlorine followed by reduction. Water vapor also increases the sintering rate of supported metals. Normalized dispersion (percentage of metal exposed at any time divided by the initial percentage exposed) versus time data in Figure 2.14 show that at temperatures of 650 °C or higher, rates of metal surface area loss (measured by hydrogen chemisorption) due to sintering of Ni/silica in hydrogen atmosphere are significant, causing 70% loss of the original metal surface area within 50 h at 750 °C. In reducing atmosphere, metal crystallite stability generally decreases with decreasing metal melting temperature, i.e. in the order Ru > Ir > Rh > Pt > Pd > Ni > Cu > Ag, although this order may be affected by relatively stronger metal–support interactions, e.g. the observed order of decreasing stability of supported platinum in vacuum is Pt/Al_2O_3 > Pt/SiO_2 > Pt/C. In oxidizing atmospheres, metal crystallite stability depends on the volatility of metal oxides and the strength of the metal oxide–support interaction. For noble metals, metal stability in air decreases in the order Rh > Pt > Ir > Ru; formation of volatile RuO_4 accounts for the relative instability of ruthenium.
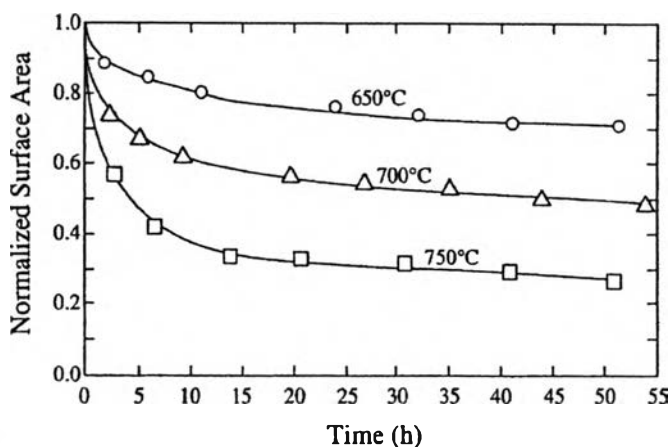
Figure 2.14 Normalized nickel surface area (based on H_2 adsorption) vs. time data during sintering of 13.5% Ni/SiO_2 in H_2 at 650, 700 and 750 °C.

2.2.3.2 Sintering of Supports

A supported metal catalyst can also deactivate due to the sintering of the support. When the support sinters, the supported metal particles come closer making easier to sinter. Besides when supports sinter, the nature of the surface can undergo modifications resulting in weakened metal support interactions. Sometimes the sintering support may also trap metal particles inside their closed pores preventing their accessibility to the reactants.

Supports can sinter through one or more of the following mechanisms:

1. Surface diffusion,
2. Solid-state diffusion,
3. Evaporation/condensation of volatile atoms/molecules,
4. Grain boundary diffusion, and
5. Phase transformation.

2.2.4 Gas/vapor–solid and Solid–state Reactions

In addition to poisoning, there are other chemical routes leading to catalyst deactivation:

(1) Reactions of the vapor phase with the catalyst surface to produce

(a) Inactive bulk and surface phases (rather than strongly ad-

sorbed species).

(b) Volatile compounds which exit the catalyst and reactor in the vapor phase.

(2) Catalytic solid–support or catalytic solid–promoter reactions.

(3) Solid–state transformations of the catalytic phases during reaction.

Examples of these four phenomena include: 1) oxidation of Co metal supported on silica by product water to Co surface silicates during FT synthesis at high conversion, 2) loss of Pt by formation of volatile PtO_2 during ammonia oxidation on Pt–Rh gauze catalysts. These forms of chemical deactivation can be prevented or moderated in large part through careful control of reaction conditions and appropriate design of the catalyst.

2.2.5 Mechanical Failure of Catalysts

Mechanical failure of catalysts is observed in several different forms, including

(1) Crushing of granular, pellet or monolithic catalyst forms due to a load,

(2) Attrition, the size reduction and/or breakup of catalyst granules or pellets to produce fines, especially in fluid or slurry beds, and

(3) Erosion of catalyst particles or monolith coatings at high fluid velocities.

2.3 Prevention of Catalyst Deactivation

As the catalyst is the heart of a process, it is necessary to keep it working for as long as it is possible. Though some catalysts may be regenerated through burning (or washing with solvents) of the coke or poison, frequent regeneration entail loss of productivity and a slow decline in the performance of the catalyst with each regeneration. It is necessary, so, to maximize the cycle length (active period) of the catalyst before resorting to regeneration. The prevention of catalyst deactivation will depend on the identification of the reasons for deactivation. Some typical reasons for deactivation and methods for prevention of catalyst activity loss are showed in Table 2.2.

Table 2.2 Reasons for deactivation and methods for prevention of catalyst activity loss

Cause	Solutions
Poisoning	Purity feed; use guard beds; use additives which selectively react with/deactivate the poison; change reaction conditions
Coking	Avoid coke precursors in feed; avoid free radical reaction; avoid free space; passivate metal surfaces; add water, hydrogen; use shape selective zeolities; add promoters; change operating conditions.
Sintering	Use promoters/stabilizers; lower reaction temperature; avoid specific impurities
Loss of catalytic phase	Avoid impurities which can cause volatilization; alter operating conditions; add promoters
Mechanical failure	Improve mechanical strength of catalyst; alter reaction conditions; improve catalyst formation

2.4 Catalysts for Aromatization of *n*-Alkane

The aromatization of *n*-alkane can be performed on both bifunctional—metal and acid—(dehydrogenation, hydrogenolysis, isomerization, cyclization, and hydrocracking) and monofunctional—only metal—(dehydrogenation and hydrogenolysis) catalysts (Antos *et al.*, 2004). The advantage of using monofunctional catalysts is the elimination of the isomerization paths, which result in lower selectivity to aromatic (Trakarnroek *et al.*, 2006). The zeolite such as MFI, BEA, MOR, LTL, and MTT is made non-acidic catalyst by being base-exchanged with an alkali metal or alkaline earth metal, such as cesium, potassium, sodium, rubidium, barium, calcium, magnesium, and mixtures thereof, to reduce acidity (Stevenson *et al.*, 2008).

The effectiveness of reforming catalysts comprising a non-acidic L-zeolite and a platinum-group metal for dehydrocyclization of paraffins is well known in the

art. In 1980, Bernard found the exceptionally high activity of platinum supported on alkaline LTL zeolite (Pt/KL) for the aromatization of n-hexane that is very efficient for the direct dehydrocyclization of n-hexane into benzene (Bernard, 1980). Since properties of Pt/KL catalysts are responsible for their high aromatization efficiency as following (Davis, 1993; Meriaudeau *et al.*, 1997):

- The nonacid character of Pt-KL, which suppresses every possible cracking reactions,
- The extremely small size of Pt particles within the one dimensio-nalzeolite channels, which limits the extent of the alkane hydroge-nolysis,
- The size and morphology of the zeolite channels, which inhibit bi-molecular and hydrogen transfer reactions generally involved in the mechanism of coke formation,
- The stabilizing effect of KL support against the sintering of Pt crys-tallites due to the dimensions of the channels and possibly to the in-teraction between the Pt particles and the zeolite channels,
- And, the space inside the L-zeolite was similar to that of a cyclic, six carbon species. Therefore, the adsorbed hexane curls around on itself in the zeolite cage in order to maximize its Van der Waals in-teractions. This preorganization of the n-hexane molecule favored ring closure, and was responsible for the high activity and selectivi-ty of Pt/KL for aromatization.

As well as aromatization of n-octane, it was observed that high dispersion of Pt clusters inside the channel of KL zeolite is the important factor for the aromatiza-tion performance (Jongpatiwut *et al.*, 2003). However, Jacobs *et al.* (2000) specified, VPI catalysts give more finely dispersed Pt clusters than both conventional incipient wetness impregnation (IWI) and ion-exchange method (IE). Therefore, the catalyst prepared by the VPI method was more active and selective than that prepared by the other method. The reasons supporting this statement were as follows: 1) IWI method provided the Pt/KL catalyst with Pt clusters inside the channels; however, at high temperature reduction treatment, the growth of Pt clusters inside the channel was

displayed and Pt/KL catalyst prepared by ion exchange method resulted in high fraction of Pt particle external to the L zeolite and rapid deactivation by coke formation 2) as for the catalyst prepared by VPI method, the Pt clusters were located inside the channel and more resistant to agglomerate at high temperature (Jacobs *et al.*, 1999; Jacobs *et al.*, 2001).

However, the unique behavior exhibited for *n*-hexane in terms of selectivity and catalyst life were not presented for *n*-octane (Huang *et al.*, 1992) because the selectivity for *n*-octane aromatization still lowered and quickly dropped due to pore plugging after a few hours on stream (Jongpatiwut *et al.*, 2003, 2005). The expected products of this reaction are ethylbenzene (EB) and *o*-xylene (OX) from a direct six-membered ring closure; nevertheless, the product distribution shows benzene and toluene as major aromatics products with small quantities of EB and OX. Since the pore size of the KL zeolite is approximately 0.71 nm, larger than the critical diameter of EB but smaller than that of OX, OX diffuses much slower than EB. As a result, OX would preferentially convert to benzene and toluene before escaping from the pore of zeolite. In the study, it was proposed that pore length of the zeolite should have a great impact on product distribution and catalyst life. The idea of short channel KL zeolile has been previously discussed by Treacy (1999) to minimize the problem of Pt entombment due to Pt agglomeration and coking. Furthermore, the zeolite with small particle size provides advantages over the zeolite with large particle size by enhancing the ratio of surface area to mass, diffusion rates, and resistance to deactivation by pore plugging. Trakarnroek *et al.* (2006) found that the catalysts with shorter channel length exhibited improved activity, selectivity, and catalyst life. It favored a high dispersion of Pt inside the zeolite.

2.5 The Structure of LTL Zeolite

The crystal structure of zeolite L was determined initially by Barrer and Villiger (Barrer *et al.*, 1969). The zeolite L has one-dimensional pores of about 0.71 nm aperture leading to cavities of about $0.48 \times 1.24 \times 1.07$ nm and its Si/Al ratio is typically 3.0 (KO *et al.*, 1999). The framework structure (Figure 2.15) consists of 12-ring channels (Baur *et al.*, 2006).
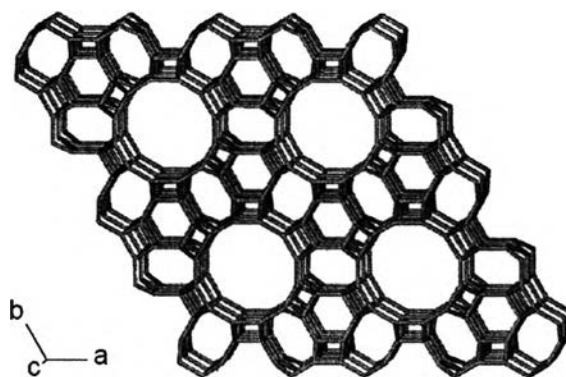
Figure 2.15 The framework structure of LTL-type compounds in the highest possible topological symmetry $P\ 6/mmm$. View parallel [001] rotated by 5° about [100] and [120].

2.6 The Effect of Sulfur on Pt/KL Catalyst

The susceptibility to poisoning by sulfur arises from the fact that there is strong metal–sulfur chemisorption. Thus, even small amounts of sulfur present in the reactants can lead to saturation of the metal surface. The sensitivity to sulfur poisoning varies greatly with the particular application and catalyst. For example, Pt/LTL zeolite aromatization catalysts are extremely sensitive to sulfur poisoning, requiring feed sulfur levels below 0.05 ppm for adequate catalyst life. In contrast, conventional Pt/alumina naphtha reforming catalysts operate with feed sulfur levels up to about 20 ppm, while bimetallic distillate aromatic saturation catalysts (PtPd/acidic zeolite) can tolerate up to 1000 ppm sulfur. (Miller *et al.*, 1996)

It is also known that one of the most serious drawbacks exhibited by the Pt/KL catalysts is their low sulfur tolerance which is very sensitive to even traces of sulfur (e.g. parts per billion) in the aromatization reforming catalysts (Hughes *et al.*, 1986; Meriaudeau *et al.*, 1997). During the operation, the activity of any catalyst is gradually decreased. In particular, sulfur poisoning of platinum-based naphtha reforming catalysts takes place under industrial condition in the presence of simultaneous deactivation by coking (Borgna *et al.*, 2000). To achieve aromatization, the feed has to be reduced the amount of sulfur to extremely low levels. Therefore, the devel-

opment of Pt/KL catalysts which is able to withstand higher sulfur concentrations than those used to day appears as an attractive goal (Jacobs *et al.*, 1998).

In previous works, Pt/KL catalysts poisoned by sulfur have been characterized by TEM (Jacobs *et al.*, 1998; McVicker *et al.*, 1993), EXAFS (Jacobs *et al.*, 1998; Vaarkamp *et al.*, 1992), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed CO (Jacobs *et al.*, 1999; Jacobs *et al.*, 2000). The obvious results of the studies demonstrated that Pt particle growth is accelerated in the presence of sulfur, leading to zeolite pore plugging and significant losses in catalytic activity due to the loss of active platinum surface by adsorption of sulfur (Jongpatiwut *et al.*, 2002). Consequently, these deactivate the catalyst after prolonged operation (Lee *et al.*, 1998). By mechanisms which are not fully understood, sulfur promotes Pt crystal growth and movement of Pt out of the zeolite channels; hence, sulfur behaves as a structure blocker. Moreover, as the particle size grows, larger ensembles are formed, favoring hydrogenolysis over dehydrocyclization and effecting to the reaction selectivity resulting in lower product selectivity (Vaarkamp *et al.*, 1992; Paal *et al.*, 1996). On the other hand, other authors have proposed that the presence of K^+ can be related to both the high aromatization activity/selectivity and the high sulfur sensitivity in *n*-hexane conversion (Fukunaga *et al.*, 1995; Ponec *et al.*, 1995) and Miller *et al.* (1996) showed that there is a rapid loss in activity due to coke formation in sulfur poisoned, alkaline LTL, while rate of deactivation by coke in the sulfide, acidic LTL is much lower. The coadsorption of carbonaceous deposits on platinum may change both the sulfur poisoning and thermodynamics of sulfur adsorption (Apesteguia *et al.*, 1982; Pradier *et al.*, 1988).

2.7 The Effect of Second Metals (Promoters) on Pt/KL Catalyst

Promoters are substances that are themselves not catalytically active but increase the activity of catalysts. The function of these substances, which are added to catalysts in amounts of a few per cent, has not been fully elucidated. There are four types of promoters: (Hagen, 2006)

- **Structure promoters** increase the selectivity by influencing the catalyst surface such that the number of possible for the adsorbed mole-

cules decreases and favored reaction path dominates. They are of major importance since they are directly involved in solid-state reaction of the catalytically active metal surface.

- **Electronic promoters** become dispersed in the active phase and influence its electronic character and therefore the chemical binding of the adsorbate.

- **Textural promoters** inhibit the growth of catalyst particles to form larger, less active structures during the reaction. Thus they prevent loss of active surface by sintering and increase the thermal stability of the catalyst.

- **Catalyst-poison-resistant promoters** protect the active phase against poisoning by impurities, either present in the starting materials or formed in side reactions.

Promoters are the subject of great interest in catalyst research due to their remarkable influence on the activity, selectivity, and stability of industrial catalysts.

In the reforming process, it was observed however that catalyst comprising a second metal in addition to platinum as a promoter (so-called bimetallic catalyst) had better catalytic properties (Furcht *et al.*, 2001). The extensive academic studies were performed to clarify the role of the different modifying metals such as Re, Sn, Ir, and Ge which are frequently used in naphtha reforming process. These bimetallic catalysts seem to be more stable (Bruch and Mitchell, 1983; Lanh *et al.*, 1984), more selective, more resistant to coking (Bertolaccini and Pellet, 1980; De Jongste and Ponec, 1980), and sintering (Charosset *et al.*, 1979), and apparently they have better activity (Passos *et al.*, 1998) than the monometallic, only Pt, ones.

Bimetallic catalyst is often regarded as alloys, although alloying would mean an intimate mixing of all components, which would create new phases. In another approach, two ideas have been put forward to account for properties of bimetallic catalysts: the 'geometrical' and 'electronic' theories (Ponec *et al.*, 1995; Macleod *et al.*, 1998). In the geometrical theory, since undesirable processes in the alkane aromatization such as hydrogenolysis reaction and coke formation were known to require relatively large clusters or ensembles of adjacent metal atoms whilst desirable

reaction which aromatization can occur on single isolated atoms (Biloen *et al.*, 1977; Coq *et al.*, 1984). Therefore, to inhibit the hydrogenolysis reaction and improve the catalyst resistance to deactivation, the particle size of Pt clusters must be decreased. The inactive second component such as Sn or Ge can divide the active surface to smaller units ('ensemble' effect). 'Structure-insensitive' reactions (like cyclohexane dehydrogenation) would then exhibit almost the same rate up to rather high additive concentration, whereas 'structure-sensitive' processes are hampered at lower amounts of second, inactive metal (Biloen *et al.*, 1980; Macleod *et al.*, 1998).

Burch and Mitchell summarized the various viewpoints presented by different groups regarding the origin of these improvements related to the second metal: (1) the formation of an alloy like Pt–Sn, and Pt–Re, which exhibit different properties either as a result of ensemble or of electron modifications; (2) stabilization against sintering; (3) interaction with metal ions of the second element stabilized in the surface of the support; (4) increasing the hydrogenolysis activity; (5) decreasing the hydrogenolysis activity; (6) suppression of surface carbiding; (7) improving hydrogenation activity; and (8) hydrogenation of coke residues. These conclusions are all directly or indirectly related to coking or decoking processes. Coleto *et al.* (2007) showed, the platinum dispersion and metal active surface of the catalysts decreased in the following order: Pt–Sn/Al$_2$O$_3$ > Pt–Re/Al$_2$O$_3$ > Pt–Ge/Al$_2$O$_3$ > Pt/Al$_2$O$_3$. Therefore, the introduction of the second metal also increased the dispersion of platinum on the catalyst surface.

One possible approach to increase sulfur tolerance could be the addition of promoters. There are a number of ways in which these promoters could operate (Resasco *et al.*, 1994). They may act as anchoring sites for Pt particles, thus preventing their growth. They may also act as sulfur getters, thus protecting Pt, albeit temporarily, from sulfur poisoning. The overall deactivation rate—deactivation by coke and sulfur—for *n*-hexane conversion increased in the order Pt–Ge < Pt << Pt–Sn ≤ Pt–Re. Pt–Ge/Al$_2$O$_3$ was the most stable catalyst essentially because of its high thiotolerance for *n*-hexane transformation reactions by weakening the strength of the sulfur platinum bond and also because it showed low activity for dehydrogenation reactions leading to the formation of coke precursors (Borgna *et al.*, 2000). Miller *et al.* (1990) recommended that the addition of rhenium to conventional platinum reforming cata-

lysts substantially increases catalyst life in the reforming process and has no effect on the catalyst selectivity, but it also makes the catalyst more sensitive to sulfur poisoning. So, the advantages of the lower deactivation rate can be negated by the sulfur poisoning effects when the feedstock sulfur levels exceed a few parts per million.

Beltramini *et al.* (1988) suggested that the existence of Pt–Ge cluster on alumina. It is possible that part of the Ge is present as GeO_2 form, controlling the acid sites of alumina. The results clearly show that the main effect of added germanium is increase stability is enhanced dehydrocyclization, and keeping metal sites free of deactivation. Similarly, the strong depression of hydrogenolysis that occurred when germanium was added to an iridium catalyst suggests that a very strong geometric interaction occurred, even though the percentage of germanium present as Ge^0 may have been small. This geometric effect may have been produced by GeO_x species (Macleod *et al.*, 1998). The intermetallic phase of PtGe formed on the external surface of HZSM-5 would have the high activity for the dehydrogenation of butane and alkylcyclohexene, which are the key steps for the formation of aromatic hydrocarbons from butane. Dehydrogenation activity of PtGe, however, would be slightly lower than that of Pt particles. This will control the coke formation on PtGe to attain the longer catalyst life, keeping the selectivity to aromatics higher than that of HZSM-5. The activity of PtGe for the hydrogenolysis of butane and various products into methane would be also lower than that of the Pt particles. It is concluded that these catalytic properties make PtGe a favorable catalyst for the selective formation of aromatic hydrocarbons in cooperation with the acid sites inside the pores of HZSM-5. Moreover, Pt–Ge intermetallic compounds with Pt/Ge molar ratio of 1.0 supported on HZSM-5 showed the highest selectivity to aromatic hydrocarbons (Komatsu *et al.*, 2000).

Few authors have studied the addition of rare earth elements (e.g. Dy, Tm, Ce, Yb) as promoters (Li *et al.*, 1994; Fang *et al.*, 1997; Grau *et al.*, 1998; Jongpatiwut *et al.*, 2002). Li *et al.* have indicated that the addition of rare earth elements may have a positive effect on the aromatization activity and the sulfur resistance of Pt/KL catalysts. To support this idea, there were some results reported that adding rare earth (RE) element in the Pt/KL zeolite is better than that on the catalyst without RE in term of selectivity.

For example, in the case of *n*-hexane aromatization, heavy rare earth elements added to Pt/KL catalyst have effect to electronic donation to Pt particles and blocking the accumulation of active Pt particles, and thus can remarkably increase the ability of resistant sulfur poisoning and the aromatic selectivity of *n*-hexane conversion on the Pt/KL catalyst. In the presence of sulfur, the Ce-promoted Pt/KL catalyst showed a higher resistance to metal agglomeration and a lower rate of coke formation than the unpromoted Pt/KL for *n*-hexane aromatization (Jongpatiwut *et al.*, 2002). Furthermore, addition of Tm onto the KL catalyst results in an increase of the active site number, that is, an increase of the dispersion of the active Pt particles, which results in a more slowly loss of the catalytic activity of the Pt–Tm/KL catalyst. More importantly, Jacobs *et al.* (2000); and Fang *et al.* (1996) demonstrated that one of the considerable effects of Tm is to capture sulfur, so it delays the poisoning of Pt. However, adding only the rare earth element onto the catalyst does not ensure a good performance, it has to include method of preparation and the amount of Tm. In agreement of previous studies, the resulting parameters showed that the VPI method is the best preparation due to the fact that it gave the highest metal dispersion. While the sequential vapor-phase impregnation method with a small amount of Tm (0.15%) yielded a catalyst with improved catalytic properties, other methods such as coimpregnation of Pt and Tm hindered the dispersion of Pt, causing blocking of the L-zeolite channels and a higher deactivation rate in the reaction. Moreover, a high content of thulium in the catalysts may block up the channels of the L-zeolite; so a too high content of thulium in Pt–Tm/KL catalysts is not beneficial to the catalytic properties of the catalysts and results in a decrease of the aromatization selectivity of the catalysts.

Resasco *et al.* (2000) showed that In the presence of 600 ppb sulfur, Tm-containing catalyst exhibited at the same activity for *n*-hexane conversion as the sulfur free run and the selectivity profile of the Pt–Tm/KL catalyst is practically flat as a function of time on stream. Fang *et al.* (1997) revealed, the addition of heavy rare earth elements (Gd, Tb, Dy, Tm or Yb) to Pt/KL catalyst can greatly increase the ability of resistant sulfur poisoning and the aromatic selectivity of catalyst due to electronic donation to Pt particles and blocking the accumulation of active Pt particles.