



CHAPTER II

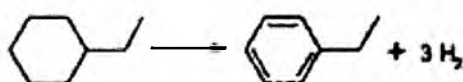
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Catalytic Reforming

Catalytic reforming of hydrocarbons is an important industrial process for producing aromatics and increasing the octane number of hydrocarbons in the gasoline boiling range. The catalytic reforming process consists of a number of reactions which takes place on bifunctional catalysts for converting the hydrocarbons contained in naphtha fractions to monocyclic aromatics.

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.

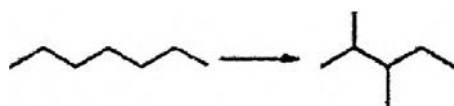
(a) Dehydrogenation of naphthenes



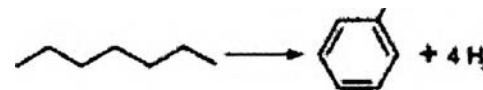
(b) Dehydroisomerization of naphthenes



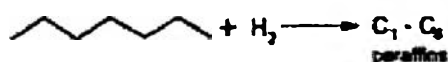
(c) Isomerization of paraffins



(d) Dehydrocyclization of paraffins



(e) Hydrocracking and hydrogenolysis



(f) Coke formation



Figure 2.1 Major reactions in catalytic reforming of naphtha

There are two ways in which catalytic reforming may be used. One option is to process the heavy fractions of straight run naphtha in order to increase their octane rating by 40-50 units. The other way is to process a narrow fraction of gasoline such

as C₆-C₈ or C₇-C₈. From the obtained reformat (called in this case BTX) is then separated the aromatic hydrocarbons (mainly benzene, toluene and xylenes), for the petrochemical industry. This second process is also called aromatization which is important process in order to increase the production of those hydrocarbons that present a higher interest for the petrochemical industry. Both processing options are performed in the same units, working under similar operating conditions. The presentation that follows will be referring to both options at the same time (Raseev *et al.*, 2003).

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 expected products of this reaction are ethylbenzene (EB) and *o*-xylene (OX) from a direct six-membered ring closure which are widely used in petrochemical industry as an intermediate compound for the production of plastics (Trakarnroek *et al.*, 2006); nevertheless, the product distribution shows benzene and toluene as major aromatics products with small quantities of EB and OX. The applications of *o*-xylene and ethylbenzene are explained briefly below (Chenier, 2002).

2.1.1 *o*-Xylene

The xylenes can be used as a mixture or separated into pure isomers, depending on the application. The mixture is obtained from catalytic reforming of naphtha and separated from benzene and toluene by distillation. Pure *o*-xylene is converted into phthalic anhydride. About 53% of phthalic anhydride is an intermediate in the synthesis of plasticizers, substances that make plastics more flexible. A common plasticizer is dioctyl phthalate. Phthalic anhydride is also used to make unsaturated polyester resins (21%) and alkyd resins (15%).

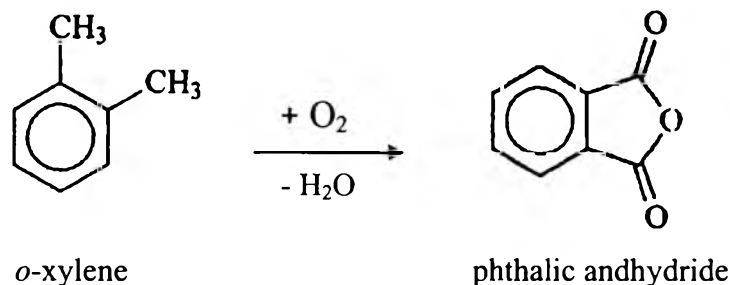


Figure 2.2 Schematic of *o*-xylene oxidation to phthalic anhydride

2.1.2 Ethylbenzene

Ethylbenzene is an organic chemical compound which is an aromatic hydrocarbon. Its major usage is in the petrochemical industry as an intermediate compound for the production of styrene, which in turn is used for making polystyrene, a commonly used plastic material. Although often present in small amounts in crude oil, ethylbenzene is produced in bulk quantities by combining the petrochemicals benzene and ethylene in an acidically-catalyzed chemical reaction. Catalytic dehydrogenation of the ethylbenzene then gives hydrogen gas and styrene, which is vinylbenzene.

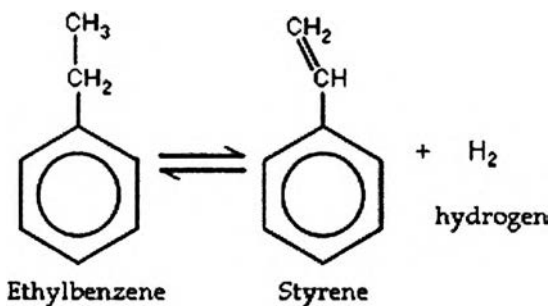


Figure 2.3 Schematic of ethylbenzene dehydrogenation to styrene

2.2 Catalysts for Aromatization of *n*-Alkane

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 dimensional-zeolite channels, which limits the extent of the alkane hydrogenolysis,
- The size and morphology of the zeolite channels, which inhibit bimolecular and hydrogen transfer reactions generally involved in the mechanism of coke formation,
- The stabilizing effect of KL support against the sintering of Pt crystallites due to the dimensions of the channels and possibly to the interaction 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 interactions. This preorganization of the *n*-hexane molecule favored ring closure, and was responsible for the high activity and selectivity 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 aromatization performance (Jongpatiwut *et al.*, 2003). To prepare a Pt/KL catalyst with dispersion of Pt clusters inside the channel of KL zeolite, vapor phase impregnation (VPI) is the best preparation methods compared to both incipient wetness impregnation (IWI) and ion-exchange method (IE). 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 (Ja-

cobs *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). 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 zeolite 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.

2.2 The Structure of LTL Zeolite

The crystal structure of zeolite L was determined initially by Barrer and Villiger (Barrer and Villiger, 1969). The structure of zeolite L is hexagonal (space group P6/mmm) with unit cell constants $a=18.4 \text{ \AA}$ and $c=7.5 \text{ \AA}$. The linkages of the cancrinite cages (ϵ -cages) by double 6-rings (D6R) led to the formation of column in the *c*-direction. And thus give rise to 12-membered rings with a free diameter of 7.1 \AA of one dimensional pores leading to cavity of about $0.48 \times 1.20 \times 1.07 \text{ nm}$ as shown in Figure 2.4. Typically, Si/Al ratio in the framework is 3.0 (KO and Ahn, 1999; Tsapatsis *et al.*, 1994).

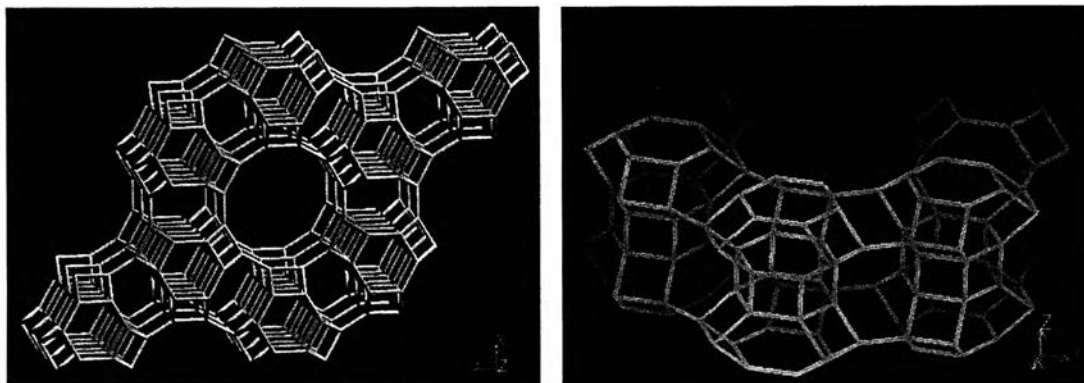


Figure 2.4 Schematic of L zeolite structure

The formula in terms of oxide is $0.9 \text{ to } 1.3\text{M}_{2/n}\text{O} : \text{Al}_2\text{O}_3 : 5.2 \text{ to } 6.9\text{SiO}_2 : y\text{H}_2\text{O}$, when M represents an exchangeable cation of valence.

2.4 The Effect of Sulfur on Pt/KL Catalyst

It is also known that one of the most serious drawbacks exhibited by the Pt/KL catalysts is their low sulfur tolerance which are 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). To achieve aromatization, the feed has to be reduced the amount of sulfur to extremely low levels. Therefore, the development 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 (Tamm *et al.*, 1988; Jacobs *et al.*, 1999, 2000). The obvious results of the studies demonstrated that 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; Kao *et al.*, 1993; Paal *et al.*, 1996). On the other hand, other authors have proposed that the K cations directly participate in the aromatization process and they, rather than Pt, are preferentially poisoned by sulfur (Fukunaga and Ponec, 1995).

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

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; Carvalho *et al.*, 2004). 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 (Coq *et al.*, 1995; Ponec *et al.*, 1995). 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 and Figueras, 1984; Vogelzang *et al.*, 1981)). Therefore, to inhibit the hydrogenolysis reaction and improve the catalyst resistance to deactivation, the particle size of Pt clusters must be decreased. The active platinum surface can be diluted into smaller ensembles by the addition of an inactive species such as Sn, Au, or Pb. In

1994, Lee and Lee found that Pt-Sn/ γ -Al₂O₃ prepared by simultaneous impregnation showed a better catalytic behavior toward C₈-aromatics formation than Pt/ γ -Al₂O₃. The added Sn did not affect electronically on Pt because the mole ratio of *o*-xylene/ethylbenzene over various Pt-Sn catalytic with different mole ratio of Sn/Pt was shown to be almost constant. Since it has been proposed that the alternation of the EB:OX ratio by the presence of tin in the catalyst was due to an alternation to favor the weaker C-H bonds in the -CH₂-group rather than the stronger bonds of the -CH₃ groups. Therefore, the remarkable increase in catalytic activity and selectivity of the dehydrocyclization is by the structure change of Pt by adding Sn. That is, the existence of Sn around Pt leads to the increase of the number of small ensembles composed of Pt, which causes rapid change in activity and selectivity of the catalyst.

For *n*-octane reforming over alumina-supported Pt, Pt-Sn and Pt-W catalysts, it was found that the addition of Sn and W increased in the activity and stability to Pt/Al₂O₃ and also beneficial changed in selectivity during *n*-C₈ dehydrocyclization. The results showed that tin was the best modifier of the metallic function, because it decreased hydrogenolysis and modifies the acid function, tuning and balancing it in order to produce more cyclization to C₆ ring closure including to decrease cracking to C₃-C₅ and condensation to carbonaceous deposits. On the other hand, tungsten (W) increased the activity in hydrogenolysis of the catalyst. This can occur through the formation of hydrogen-tungsten compounds, being favored hydrogenolysis, hydrocracking and other hydrogenation reactions (Rangel *et al.*, 2000).

However, it was found that not only does tin modify the stability and selectivity of the Pt function by ensemble effect, but also does it modify the Pt function by an electronic effect. By this way, tin in metallic form (in solid solution, in small bimetallic clusters, alloyed with Pt, or as Sn²⁺ ions in intimate contact with Pt atom) gives its electron to the holes of the 5d band of platinum atoms. Of this is the case, small amounts of tin (lower than the detection limit) should affect the properties of platinum. In fact, 15 atom% of tin was sufficient to fill the hole of the 5d band of platinum. On the basis of the electronic effect, it is possible to explain the promotion effect of tin by assuming that coke precursors are not adsorbed on the surface of the doped platinum crystals, but rather they move to the support, avoiding deactivation of the active site. A lower coke formation can also occur because condensation reac-

tions are inhibited, and lower amount of polymers are formed. For the same reason, C-C bond hydrogenolysis does not occur, again because the hydrocarbon cannot be strongly adsorbed on the catalyst (Ertl *et al.*, 1997). In 1995, Shi and Davis showed that tin alters the property of the platinum for alkane dehydrocyclization by applying reversible alkane adsorption/desorption for the Pt-Sn-SiO₂ catalyst whereas irreversible adsorption applies for the Pt-SiO₂ catalyst. The data shown that tin causes the alkane to be bound to the metal surface less tightly than when tin is absent.

Cho and Ryoo (2004) prepared Pt-Sn nanoparticles supported on KL zeolite (Pt-Sn/KL) by ion exchange method and controlled the Sn/Pt ratio at 0.1, 0.2, and 0.4, respectively. They found that no pore blockage was observed when Pt-Sn nanoparticles were formed inside the KL zeolite channel, since the amount of xenon adsorption per unit cell for the Pt-Sn/KL catalyst was the same as that of KL zeolite. Furthermore, from EXAFS, incorporation of Sn into Pt nanoparticle could not cause an increase of particle size of Pt corresponding with no increase of the coordination number of the Pt-Sn. The chemical state of Sn in the Pt-Sn/KL catalyst seems to be Sn²⁺ referred from the obtained Pt-Sn distance which is around 0.279 nm. The results of the XANES analysis suggested that electron transfer occurred from Sn to Pt and resulted in the significant change in the d band structure. Catalytic performance of the Pt-Sn/KL catalyst over n-hexane aromatization was improved with mainly the Pt ensemble effect by an incorporation of tin because the formation of dehydrogenated species required for isomerization, hydrogenolysis and coke formation was suppressed, resulting in the high selectivity to benzene. Also, the change of electronic structure of the nanoparticles may affect the adsorption characteristics of reactants such as hydrogen and similarly benzene.

There have been several attempts to increase the sulfur tolerance of the Pt/KL catalysts. One possible approach to increase sulfur tolerance could be the addition of promoters. 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 (Jacobs *et al.*, 1999). 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.*, 2001). 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.* demonstrated that one of the considerable effects of Tm is to capture sulfur, hence guarding the Pt particles from poisoning (Fang *et al.*, 1996; Jacobs *et al.*, 1999). However, adding only the rare earth element onto the catalyst does not ensure a good performance, it has to include method of preparation and pretreatment. 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.

2.6 Catalyst Deactivation for Reforming

A catalyst is defined as a substance, which accelerates the rate of a chemical reaction without itself getting “affected” or “changed”. This definition suggests an infinite life for the catalyst. In practice, this is really not true. All catalysts deactivate, though at different rates, and have finite lives. The deactivation is often a result of side or parallel reactions or poisoning. We will now examine the deactivation of catalysts in detail (Viswanathan, 2002). Causes for catalyst deactivation at least five main reasons for catalyst deactivation are recognized.

1. Poisoning (Chemical effect)
2. Fouling, coking, carbon deposition etc. (Mechanical effect)
3. Thermal damage (Thermal effect)

4. Loss of catalytic phases (Chemical effect)
5. Attrition (Mechanical effect)

2.6.1 Poisoning

Poisoning of catalytic sites occurs from strong chemisorption of impurities, reactants, products or by products. Catalyst poisons from strong adsorptive bonds with the catalyst surface, blocking active centers. Therefore, even very small quantities of catalyst poisons can influence the adsorption of reactants on the catalyst. The term catalyst poison is usually applied to foreign materials in the reaction system, e.g. sulfur, nitrogen, oxygen. 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 and (2) little is known about the effects of catalyst pretreatment on the catalyst deactivation by sulfur poisoning (Jao et al., 1995).

Poisoning effects are very specific. A reactant in one reaction can be a poison for another reaction over a different catalyst; e.g., CO is a reactant in Fischer-Tropsch catalysis (iron oxide catalyst) and is a poison in NH_3 synthesis.

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

- (i) physically block the active center
- (ii) electronically modify the adjacent active centers
- (iii) restructure the surface
- (iv) block interaction between two adsorbed species and
- (v) prevent diffusion of the adsorbed species.

As poisons function through strong chemisorption, they are very selective. It is worth enough to know that different catalysts are poisoned by different agent.

Types of Poisoning

Poisoning can be classified into three types, viz., selective and anti-selective poisoning. The three types of poisoning are classified based on the relationship between catalyst activity loss and the concentration of the poison in the feed or the relative surface coverage by the poison (Figure 2.5).

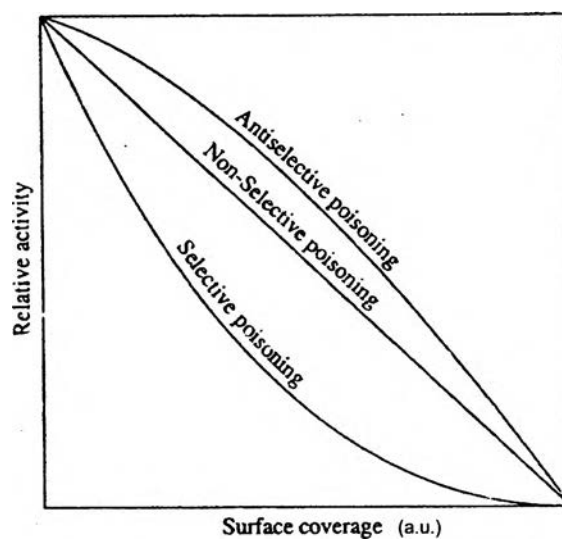


Figure 2.5 Three different types of poisoning generally observed in the case of heterogeneous catalysts

(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*: Occurs when the loss in catalyst activity is proportional to poison coverage.

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

2.6.2 Fouling

Fouling of a catalyst takes place when carbonaceous material or extraneous metal oxides are deposited on the catalyst. Carbonaceous materials are the major causes of deactivation in most reactions. These can be coke (polynuclear aromatics or large oligomeric molecules; $C/H > 0.5$) or carbon. Coke deposits lower the activity of catalysts by one or more of the following effects:

- (1) adsorb strongly on the active sites (metal, acid centres),
- (2) physically envelope the active centre (a metal crystallite),
- (3) plug the micro and meso pores of the catalysts and

- (4) damage the physical texture or shape of the catalyst through growth of the carbonaceous materials.

The major effects of fouling noticed during the reaction are:

- (i) activity loss; temperature of reactor is continuously increased to compensate for loss in activity and
- (ii) increase in pressure drop across the bed.

2.6.2.1 Coking

The mechanism of coke formation will depend on the type of catalyst, the reactants, the reaction conditions and the reactor feed composition. In addition, Matín *et al.* (2005) also show that the characteristics of the coke depend on the deactivation process, and that coke on the industrial catalyst could be successfully described and defined. Generally, two types of nature of coke have been recognized. The soluble coke extracts of spent catalysts is rich in alkylated mono- and diaromatics with low percentage of polyaromatics whereas the nature of insoluble coke is highly polyaromatic (aromaticity, $f_a > 0.95$) (Sahoo *et al.*, 2003). A soluble coke can be extracted using solvent ($C/H = 0.5$ to 1) and an insoluble coke ($C/H \Rightarrow 1$) which is not soluble in organic solvents. Both types of coke are burnt off into CO_2 at elevated temperatures. Catalysts, like those used in HDS, have long cycle length (cycle length = period of operation between two successive regeneration) of 1 to 5 years due to the mild operating conditions (H_2 atmosphere, high pressures and moderate temperature of $< 400^\circ C$). On the other hand, cracking catalysts deactivate in seconds due to the heavy nature of the feed and severe operating conditions (atmospheric pressure $> 500^\circ C$). Many factors influence the formation of coke on catalysts. Because of pore filling by the coke, the pore volume of the catalyst decreases faster than its surface area. Possible effects of fouling by carbon (or coke) on the functioning of supported metal catalyst are illustrated in Figure 2.6 (Bartholomew, 2001).

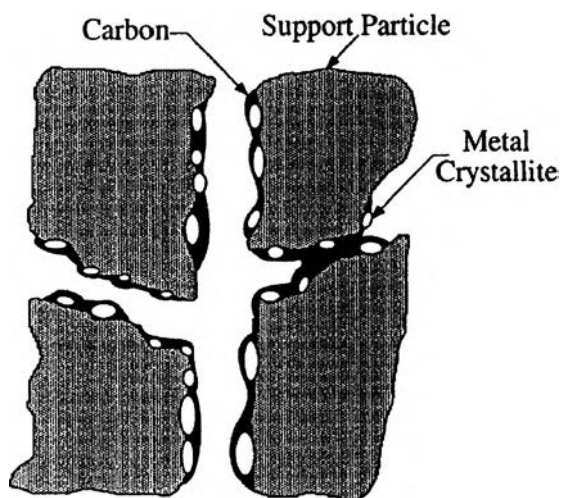


Figure 2.6 Conceptual model of fouling, crystallite encapsulation and pore plugging of a supported metal catalyst due to carbon deposition

The activity loss itself is more rapid in the beginning and becomes slower after some time. In some catalyst with long lives, the activity may decrease asymptotically with time after the initial rapid loss (Figure 2.7).

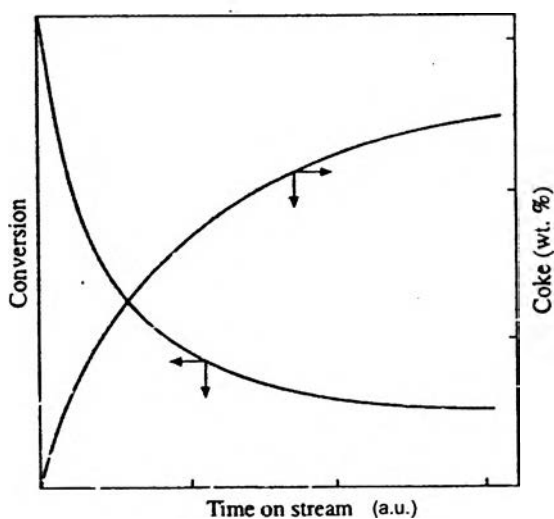


Figure 2.7 Relationship between catalyst activity loss and coke deposition with during of run

2.6.2.2 Metal Deposition

Metal deposition is a major problem in petroleum refining processes where heavy oil feeds are used. The major metallic impurities present in these oils are V and Ni, which are present as organometallics. The large metal content in the feed causes deactivation of HDS catalysts when desulfurization of residua is carried out. The metal complexes break down at the high pressures and hydrogen atmosphere, the metals react with the H_2S in the system and transform into S deposits. These deposits affect the activity of the catalyst, besides leading to plugging of the bed and causing large pressure drop across the bed.

When the metal feed containing feeds are used in FCC processes, the deposited V destroys the zeolite component of the catalyst causing again rapid deactivation. The Ni in the feed leads to excessive dehydrogenation resulting in increased H_2 in the gas and also increased coke lay down on the catalyst. Examination of the metal concentration profiles in individual particles of FCC catalysts reveals that while V is uniformly distributed throughout an individual particle, Ni is deposited mostly at the periphery.

Metal can also come from the plumbing (corrosion of pipes, tube etc.) of the reactors. These deposits are mainly iron oxide scales which deposit on the top layers of the catalyst bed. For example, in the case of HDS reactors, these are periodically skimmed off from the top of the bed to keep the pressure drop within limits.

2.6.3 Thermal Degradation

Catalyst activity loss due to thermal damage is often a serious problem in supported metal catalysts (Pt- Al_2O_3 , Ni- Al_2O_3 etc.) and oxide catalysts with large surface areas (SiO_2 - Al_2O_3 , zeolite, iron-molybdate etc.)

The major thermal damages to the catalysts are:

- (1) Loss of metal surface area due to crystallite growth (sintering of metal),
- (2) Loss of support surface area due to pore collapse (sintering of support), and
- (3) Transformation of the catalytic phase into a non-catalytic phase.

2.6.3.1 Sintering of Metals

Sintering occurs because small crystallites always tend to lower their surface free energies by minimizing their specific surface areas.

Various mechanisms have been proposed for the sintering of metals. These are:

1. Crystallite migration
2. Atomic migration
3. Spreading and splitting and
4. Vapor transport

In crystallite migration, entire (small) crystallites migrate and fuse to form bigger thermodynamically more stable crystallites. This is a likely scenario when the dispersion levels are moderately high and metal-support interactions are weak. Similarly, atoms can migrate and coalesce into small crystallites at high dispersion levels. Spreading and splitting are expected to occur when the metal-support interaction is large and the contact angle between the support and the metal is small. This can be expected in the case of low melting elements. Sintering through vapor transport will occur at high temperatures. In the case of Pt group metals; this is a major sintering pathway in oxidizing conditions when metal oxides with lower vapor pressures are formed.

The rate of sintering of supported metals depends on many parameters such as the nature of the atmosphere, the nature of the support and the presence of impurities. The rate of sintering increases with temperature. The activation energy values for sintering depend on the nature of the metal, the support and ambient atmosphere. E_a values of 13 to 97 kJ mol⁻¹ have been reported for Pt-Al₂O₃ at different sintering conditions. The typical sintering behavior of metal catalyst is presented in Figure 2.8. The surface area loss is initially rapid, but becomes progressively less at longer times reaching a nearly constant value after a certain period, the magnitude of this value being smaller at higher temperatures.

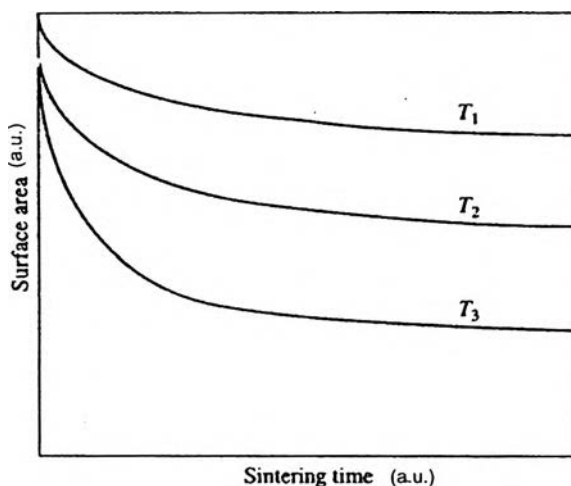


Figure 2.8 Influence of sintering temperature on metal surface area: $T_3 > T_2 > T_1$

In H_2 , the resistance to sintering of the metals is in the order: Ru > Ir > Rh > Pt > Pd > Ni > Cu > Ag. This order is found to be nearly in the order of the melting points of the elements. As for O_2 , the resistance to sintering in the case of Pt group metal is in the decreasing order: Rh > Pt > Ir > Ru. This order is related to the vapor pressure of the oxides of the above metals, the higher the vapor pressure, the faster the sintering. Thus, sintering takes place in reductive atmospheres through metal species, while it takes place via the oxide species in oxidizing atmospheres.

Supported-metal interactions also play a role in determining the sintering rate of supported catalysts. Strong metal support interaction stabilizes the supported metal from sintering. For example, the interaction of most metals (and many oxides) is stronger with an alumina surface than with a silica surface. As a result, alumina supported catalysts are generally more sinter resistant than silica supported catalysts. Sintering increases in the order: Pt- Al_2O_3 < Pt- SiO_2 < P-C.

Impurities such as Cl_2 , and S in the gas phase or support increase metal atom mobility. Other impurities such as O_2 , Ca and Cs appear to decrease metal atom mobility. Similarly, surface defects and the pore system in the support can reduce sintering rate by impeding the migration of metal particles.

2.6.3.2 Sintering of Supports

A supported metal catalyst can also deactivate due to the sinter-

ing 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.

2.6.3.3 *Thermal degradation of supported catalysts*

The manner in which supported catalysts can undergo thermal damage into non (or less) –active catalyst are:

1. Reaction of the metal with the support to produce an inactive compound; e.g., Ni/alumina or Co/alumina, which form inactive spinels,
2. Segregation of the metal or carrier components (e.g., in bimetallic catalysts),
3. Metal or carrier transitions (e.g., γ -alumina to α -alumina), and
4. Reaction of the carrier with the reactants etc. (e.g., SiO₂ or TiO₂ are used in SCR catalysts and not Al₂O₃ as the latter support reacts with SO₃ in the exhaust gas).

2.6.4 Loss of Catalytic Phases by Vapor Transport

Catalytic phases can sometimes be lost through reaction with one of the reactants or products. For example, loss of Ni as Ni-carbonyl has been noticed when using Ni catalysts for reactions involving CO under reductive conditions. Similar, when Rh-Pt gauze is used in the oxidation of NH₃ to NO (temp > 900°C), loss of Pt occurs as Pt-oxide. In fact, addition of Rh decreases Pt loss besides de-

creasing surface restructuring. Another example is in the aromatization of small alkanes into aromatics over ZnO-ZSM-5. The loss in activity of the catalyst is mainly attributed to the loss of Zn.

2.6.5 Mechanical Failure of Catalysts

This is important cause of failure of industrial catalysts. Mechanical failure can happen in two ways:

1. During the reaction due to changes in the catalyst brought about by side reaction or
2. Due to the inherent low mechanical strength of the catalyst.

Stream reforming and stream cracking catalysts sometimes undergo mechanical failure due to growth of carbonaceous particles inside the pellets. Ring tables of iron molybdate used in the oxidation of methanol to formaldehyde are known to undergo mechanical failure (break-up) due to the formation of iron and molybdenum oxide phases. In the case of FCC processes abrasion between particles takes place and catalyst fines tend to be generated. These leave the system through the flue gas and along with product. The loss of catalyst is compensated by addition of catalyst (make-up) which can exceed 1 ton per day in a typical FCC unit. Besides, during attrition, the more valuable component for activity (zeolite) may be preferentially lost leading to rapid loss of catalyst activity. At the same time, if the fluidized particles are too hard, they may also damage the reactor internals by abrasion. In slurry reactors, attrition can lead to loss of the catalyst (sometimes expensive) which may also be difficult to separate from the products. In fixed-bed reactors, mechanical failure may take place through crushing of the pellets/extrudates.

2.7. **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 regen-

eration. It is necessary, therefore, 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 presented in Table 2.1.

Table 2.1 Typical reasons for deactivation and methods for prevention of catalyst deactivation

<i>Cause</i>	<i>Solutions</i>
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

Poisoning is a major cause for deactivation of metal catalysts. In the case of Pt-Al₂O₃ used in the reforming of naphtha to aromatics, S compounds in the feed are the major poisons. These are removed by hydrodesulfurization of the feed prior to contacting with the catalyst; the feed, which usually contains 10-15 ppm of S is desulfurized to < 1 ppm. In the case of methanation catalysts (supported Pd/Ni), a guard bed of ZnO is usually used to remove S to the required specifications. Additives that selectively passivate or react with the poisons are used with FCC catalysts. Ni is passivated with Sb or Bi containing additives and V is neutralized by

Sn containing additives.

Coking is a universal phenomenon in the case of heterogeneous catalysts operated at high temperatures. Coking is not easy to avoid, though it is possible to minimize it by decreasing the concentration of coke precursors like unsaturates and high boiling aromatics. Coke deposition is reported to be lowered by adding promoters like Re and Ir to Pt-Al₂O₃ catalysts. Besides, these promoters also keep the catalyst active at higher coke contents than possible with Pt-Al₂O₃. Again, the above promoters also lower the sintering rate of the active component, Pt. Chloride ions present on the support increase its acidity, besides decreasing the sintering of Pt. As moisture causes the elimination of chloride ions from the support, besides poisoning the acid centers and enhancing the sintering of the support, tight control of the moisture in the system is mandatory. However, a small amount of moisture (20 to 40 ppm) is kept in the system to create and maintain the desired Brønsted acidity in the catalysts.