



## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Catalytic Reforming

The catalytic reforming process consists of a number of reactions which take place on bifunctional catalysts for converting the hydrocarbons contained in naphtha fractions to monocyclic aromatics.

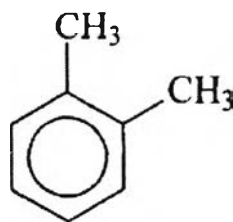
Naphthene with six carbon atom rings is subjected to dehydrogenation. Naphthenes with five carbon atom rings are subjected to isomerization followed by dehydrogenation, usually called dehydroisomerization. The alkenes go through cyclization followed by dehydrogenation, usually called dehydrocyclization. Simultaneously, the hydrocarbons and especially the alkanes undergo parallel, competing reactions of isomerization and hydrocracking with conversions sometimes comparable to the reactions producing aromatics

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 C<sub>6</sub>-C<sub>8</sub> or C<sub>7</sub>-C<sub>8</sub>. From the obtained reformate (called in this case BTX) are 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, 2003)

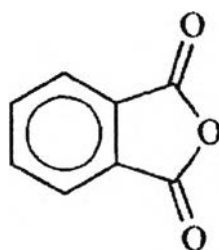
The aromatization of *n*-alkane is an important reaction to obtain high value-added products from a naphtha feedstock that is abundant in refinery operations (Trakarnroek *et al.*, 2007). The application of ethylbenzene and *o*-xylene is explained briefly below (Chenier, 2002).

### 2.1.1 *o*-Xylene



**Figure 2.1** Schematic of *o*-Xylene.

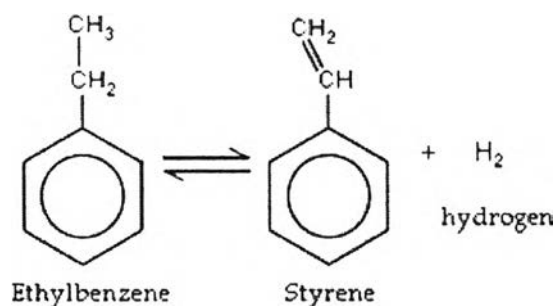
The xylenes can be used as a mixture or separated into pure isomers, depending on the application. The mixture is obtained from catalytic reforming of naphtha and separated from benzene and toluene by distillation. Pure *o*-xylene is converted into phthalic anhydride. About 53% of phthalic anhydride 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 phthalic anhydride.

### 2.1.2 Ethylbenzene

Ethylbenzene is an organic chemical compound which is an aromatic hydrocarbon. Its major use 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 dehydrogenation of ethylbenzene.

## 2.2 Catalysts for Aromatization of *n*-Alkane

In 1980, it was reported that Pt clusters in alkaline LTL zeolite are highly active and selective for the dehydrocyclization, of *n*-hexane into benzene (Bernard, 1980). Since Pt/KL catalyst has the Uniqueness for aromatization which is outlined briefly below (Davis, 1993):

### 2.2.1 Molecular Die (geometric) Effects

The *n*-hexane would preferentially adsorb onto the Pt cluster at a terminal carbon, which would favor ring closure to form benzene.

### 2.2.2 Preorganization of *n*-Hexane for Ring Closure

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. Therefore, the resulting transition state would put the free terminal carbon in close proximity with the active Pt cluster. This preorganization of the *n*-hexane molecule favored ring closure, and was responsible for the high activity and selectivity of Pt/KL for aromatization.

### 2.2.3 Electronic Effects

The high activity and selectivity of Pt/KL catalysts for aromatization derived from a unique electronic structure. Larger, softer, cations like Ba<sup>+2</sup>, with diffuse charge, would allow greater donation of electron density from zeolite oxygen anions to the Pt metal, whereas smaller, harder, cations like Mg<sup>+2</sup>, would interfere with this transfer. As a test, the competitive hydrogenation of benzene and toluene

was used. Since toluene is a better electron donor than benzene, hydrogenation of toluene was expected to be hindered with increased electron donation from the support.  $K_{\text{toluene}}/K_{\text{benzene}}$  increased with Lewis acidity ( $\text{Mg} > \text{Ca} > \text{Ba}$ ).

#### 2.2.4 Inhibition of Bimolecular Pathway

The uniqueness of Pt/KL catalysts with the ability of KL's microporous structure to inhibit bimolecular reactions leads to the formation of coke on the surface of the Pt clusters.

#### 2.2.5 Stabilization of Small Pt Clusters

The exceptional reactivity for Pt/KL resulted from the ability of the ellipsoid cages making up the channels of the KL zeolite, to stabilize small clusters.

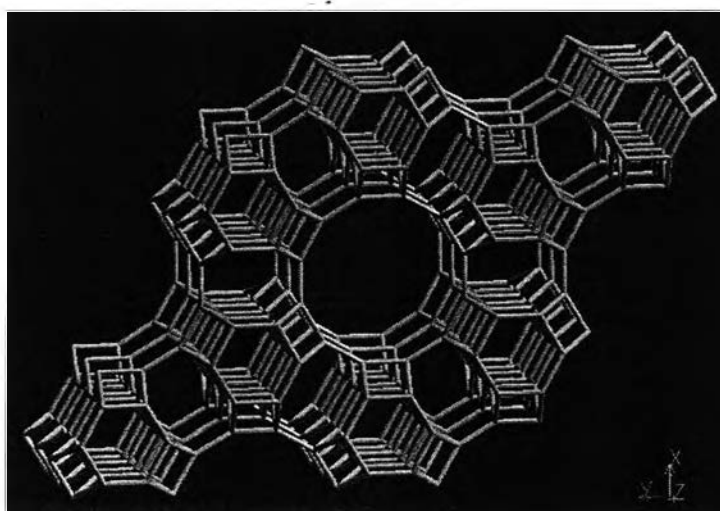
As well as aromatization of *n*-octane, it was observed that high dispersion of Pt clusters inside the channel of KL zeolite is the important factor for the aromatization performance (Jongpatiwut *et al.*, 2003). To prepare a Pt/KL catalyst with dispersion of Pt clusters inside the channel of KL zeolite, vapor phase impregnation (VPI) is the best preparation methods compared to both incipient wetness impregnation (IWI) and ion-exchange method (IE). The 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. IWI method will provide 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. For Pt/KL catalyst prepared by VPI method, the Pt clusters are located inside the channel and more resistant to agglomerate at high temperature (Jacob *et al.*, 2001; Jacob *et al.*, 1999).

Although Pt/KL catalysts prepared by vapor phase impregnation (VPI) provide very high Pt dispersion located inside the channels of the zeolite, the activity for *n*-octane aromatization was still low and quickly dropped after a few hours on stream (Jongpatiwut *et al.*, 2003; Jongpatiwut *et al.*, 2005). The product distribution obtained from the reaction showed benzene and toluene as major aromatic products, with small quantities of ethylbenzene (EB) and *o*-xylene (OX) which are the expected products from a direct six-membered ring closure. Since the pore size of the KL zeolite is 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 preferential 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 entomment 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.

### 2.3 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 ( $\epsilon$ -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  $7.1 \text{ \AA}$  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  $0.9$  to  $1.3M_{2/n}O$ :  $Al_2O_3$ :  $5.2$  to  $6.9SiO_2$ :  $yH_2O$ , when  $M$  represents an exchangeable cation of valence  $n$ , and  $y$  represents a value within the range from  $0$  to  $9$  (Breck and Nancy, 1965).

## 2.4 Synthesis of KL Zeolites

The most often observed shape of zeolite L crystal is cylindrical with the channels running parallel to the central axis and it was found that using cylindrical shape of KL zeolite as a base of catalyst for alkane aromatization showed a remarkable improved activity life time over extended periods of time, much greater than that achieved with catalysts using the clam-shaped KL zeolite. The typical composition of gel mixture for synthesis KL zeolite with cylindrical shape having the particle size of  $2$  to  $2.5$  micron is  $2.62K_2O$ :  $Al_2O_3$ :  $10SiO_2$ :  $160H_2O$ . The sources of the starting material are potassium hydroxide, aluminium hydroxide, Ludox HS-40, and water. Using the crystallization temperature at  $150^\circ C$  for  $72$  h brings about the crystallization. In addition, the different morphologies of KL zeolites were obtained by adjusting the gel composition. For example, increasing the amount of  $K_2O$  up to  $3.5$  moles resulted in the clam-shaped KL zeolite or increasing or decreasing the amount of  $K_2O$  to  $2.21$  moles gave the long channel length of KL zeolite (Wortel, 1985; Ruiz *et al.*, 2002; Ko and Ahh, 1999).

Verduijn (1987) showed that adding of small amount of added metal such as magnesium, calcium, barium, cobalt, zinc, chromium, manganese or nickel can reduce the crystal size of KL zeolite and result in zeolite L with flat basal planes. Moreover, these metals can suppress unwanted zeolite W or erionite formation during the crystallization. After that, Verduijn found that typical ratio of  $2.62K_2O$ :  $0.5Al_2O_3$ :  $10SiO_2$ :  $160H_2O$  with a suitable quantity of divalent cation can give the L zeolite in which crystals are very flat cylinders of hockey puck or coin shape. The crystals are coin or hockey puck shaped and have a relatively large diameter and short length. The length of a crystal is a measurement of the outer edge of the crystal perpendicular to the basal plane containing the diameter. When the length/diameter ratio is  $0.2$ - $0.5$ , the crystal shape is termed as hockey puck as shown in Figure 2.5. When the length/diameter is less than  $0.2$ , the shape is termed as coin. The results

from the catalytic testing by aromatization of mixed C6 showed that the 0.6 wt% Pt supported on zeolite having short channel length gave a better yield and selectivity of benzene, and also enhanced cycle length compared with the zeolite having a long channel length (Verduijn, 1991; Verduijn, 2001).



**Figure 2.5** SEM image of hockey puck KL zeolite with the size of 40,000 times (Verduijn *et al*, 2001).

To reduce the particle size of zeolite, crystallization conditions and composition-dependent parameters which are alkalinity, dilution, ratio between Si and other tetrahedron-forming elements, template concentration, ionic strength, and presence to crystallization poisons were concerned (Renzo, 1998). In 1996, Gontier and Tuel showed that applying the aging period to crystallization decreases the crystal size of titanium silicalite-1 (TS-1) to about 6-7  $\mu\text{m}$  compared to no applying ageing period that resulted in the crystal size about 17-18  $\mu\text{m}$ . Moreover, it was observed that stirring the gel during crystallization strongly decreases the particle size of TS-1. In 2001, Li *et al* found that ageing process can decrease the crystal size of TPA-silicalite-1 by enhancing the rate of nucleation and produce a larger number of nuclei. Moreover, it was reported that incorporation of colloidal L zeolite seed into the gel before crystallization can also reduce the product particle size (Verduijn *et al*, 2001).

Normally, many research groups synthesized KL zeolite by conventional hydrothermal treatment. In this method, it takes a long crystallization time because the heat transfer is from an oil bath or an electrical oven to the reagents and resulted

in lower heating rate. Employing microwave radiation was found to be useful in manufacturing of microporous crystalline materials because it gives a higher heating rate due to volumetric heating, resulting in homogeneous nucleation and providing crystalline materials in a short crystallization time (Chu and Dwyer, 1988). Furthermore, it is a clean and economical heating system (Romero *et al.* 2004). Slang *et al.* (1997) found that aging is prerequisite for the successful rapid synthesis of NaA in microwave synthesis and this is contrast to the conventional synthesis. When the synthesis mixture has been aged sufficiently, the synthesis of NaA can be done in 1 min by microwave heating, leading to small crystals with a relatively homogeneous crystal size distribution. In addition, Park and Komarneni (1998) reported that  $\text{AlPO}_4\text{-11}$  and cloverite was successfully synthesized by microwave-hydrothermal heating. The crystallization time of these molecular sieves was greatly shortened by using the microwave heating system compared with the conventional heating system.

## 2.5 The Effect of Additional Promoter into Pt/KL Catalyst

In naphtha reforming, a number of promoter metals have been used as additives for Pt catalysts to increase catalyst lifetime by hampering coking and to improve selectivity of desired products. The most frequently used catalysts in naphtha reforming processed are Pt-Re, Pt-Ir, and Pt-Sn. Re and Ir are the promoters having catalytic properties on their own, whereas Sn is catalytically inactive. The addition of Sn to monometallic catalysts can change in selectivity, inhibit hydrocracking, hydrogenolysis, hydrogenation, isomerization and coke deposition on the catalyst surface, and improve dehydroisomerization and dehydrocyclization reaction (Paal *et al.*, 1997).

Since undesirable processes in the alkane aromatization such as hydrogenolysis reaction and coke formation are known to require relatively large clusters or ensembles of adjacent metal atoms whilst desirable reaction which is aromatization can occur on single isolated atoms (Biloen *et al.*, 1977; Coq and Figueras, 1984). 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/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared by simultaneous impregnation showed a better catalytic behavior toward C8-aromatics formation than Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. 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 Sn in the catalyst was due to an alternation to favor the weaker C-H bonds in the -CH<sub>2</sub>-group rather than the stronger bonds of the -CH<sub>3</sub> groups. Therefore, the remarkable increase in catalytic activity and selectivity of the dehydrocyclization are 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/Al<sub>2</sub>O<sub>3</sub> and also beneficial changed in selectivity during *n*-C8 dehydrocyclization. The results showed that Sn is the best modifier of the metallic function, because it decreases hydrogenolysis and modifies the acid function, tuning and balancing it in order to produce more cyclization to C6 ring closure and to decrease cracking to C3-C5 and condensation to carbonaceous deposits. On the other hand, tungsten (W) increases 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 Sn 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, Sn in metallic form (in solid solution, in small bimetallic clusters, alloyed with Pt, or as Sn<sup>2+</sup> 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 Sn (lower than the detection limit) should affect the properties of platinum. In fact, 15 atom% of Sn is 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 Sn 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 reactions 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 PtSn-SiO<sub>2</sub> catalyst whereas irreversible adsorption applies for the Pt-SiO<sub>2</sub> 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 PtSn nanoparticles supported on KL zeolite (SnPt/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 PtSn nanoparticles was formed inside the KL zeolite channel, since the amount of xenon adsorption per unit cell for the PtSn/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 PtSn/KL catalyst seems to be Sn<sup>2+</sup> 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 PtSn/KL catalyst over *n*-hexane aromatization was improved with mainly the Pt ensemble effect by an incorporation of Sn 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.

Trakarnroek (2007) studied on *n*-octane aromatization on monofunctional Pt-Sn/KL catalyst prepared by different preparation methods, including the various Sn/Pt ratios. They were observed that the addition of Sn improved the stability and selectivity to C<sub>8</sub>-aromatics products, including a decreasing the secondary hydrogenolysis reaction which occurred inside the pores of KL zeolite. The stability of the

catalysts and the decrease of the undesired hydrogenolysis reaction were improved by geometric and electronic effects. The addition of Sn decreased the particle size of metal; consequently, the coke formation and hydrogenolysis reaction is inhibited. In addition, Co1Pt1Sn prepared by vapor phase co-impregnation, yield a high fraction of alloy phase compared to Seq1Pt1Sn and Seq1Sn1Pt, which were the catalysts prepared by vapor phase sequential impregnation. This PtSn alloy formation causes the electron transfer from Sn to Pt atoms as observed from the XPS data. From this electronic effect, OX molecules were more produced as compared to those obtained without the addition of Sn. Consequently, the EB/OX ratio is lower than unity.

It is shown that the addition of Sn to Pt has the following effects on aromatization reaction:

- i) Increases the catalyst stability and decreases the rate of deactivation (Vázquez-Zavala *et al.*, 1998)
- ii) Changes the selectivity by inhibiting hydrocracking, oligomerization and coke formation on the catalyst surface due to a geometrical effect (Stagg *et al.*, 1997; and Sharma *et al.*, 1998;).
- iii) The metallic crystallites show high degree of dispersion and higher resistance to aging (Vázquez-Zavala *et al.*, 1998).

The accurate nature of supported PtSn system is very complicated. There are numerous factors that can affect the properties of catalysts such as the acidity of the support, preparation procedure, nature of the precursor compounds, impregnation sequence of metal loading, activation of the solid (Siri *et al.*, 1997), dispersion of the active metallic species (Sharma *et al.*, 2002) and particle size of the support (Merlen *et al.*, 1996). Nowadays, several studies are being carried out to evaluate the modification of the stability, selectivity and activity of metallic catalysts by the addition of some alkali metals such as Li, Ba, K, Ca and others (Rombi *et al.*, 2003; Siri *et al.*, 1997; and Cortright *et al.*, 2000). The use of alkaline ions has been reported for Pt/Al<sub>2</sub>O<sub>3</sub> and PtSn/SiO<sub>2</sub>, Ni/SiO<sub>2</sub> (Praliauf *et al.*, 1986), Pd/SiO<sub>2</sub> (Poutsma *et al.*, 1978) and Cr/Al<sub>2</sub>O<sub>3</sub> (Rombi *et al.*, 2003). Siri *et al.* (1997) studied isobutene dehydrogenation in a series of Pt and Pt–Sn catalysts, modified by the Li addition, prepared by incipient wetness impregnation and surface organometallic chemistry on

metal (SOMC/M) techniques. The incorporation of Sn and Li improved light-paraffin dehydrogenation and inhibited isomerization and cracking reactions.

The effect of potassium on Pt and Pt–Sn supported on silica, prepared by ion-exchange method, was studied by Cortright *et al.* (2000) for isobutane dehydrogenation. They found that the addition of Sn and potassium diminishes the size of the surface platinum ensembles, suppressing the hydrogenolysis, isomerization and coking reactions. In K–Sn–Pt/SiO<sub>2</sub> catalyst, dehydrogenation rate increased either due to an increase in the number of sites available for hydrogen removal from adsorbed isobutane or to the stabilization by potassium of molecular adsorbed isobutane. In the same manner, Rodríguez (2005) also studied on the effect of tin and potassium addition on the nature of platinum supported on silica, prepared by incipient wetness co-impregnation and sequential impregnation. They observed that the proximity between the Pt and Sn species favors the formation of Pt–Sn ensembles or alloys after the reduction treatment that provides stability and selectivity for the isobutane dehydrogenation. The addition of potassium to Pt–Sn/SiO<sub>2</sub> did not have a marked effect in the Pt dispersion nor the activity of the fresh catalysts; however, this improved the dehydrogenation selectivity, which reached values of almost 100%. Potassium is deposited mainly on the support, affecting reactions there. The surface Pt–Sn species were affected by the calcinations, causing the segregation of Pt and Sn oxide species. In addition, there was a decrease of the CO/Pt ratio, activity and selectivity of the Pt–Sn catalysts. The low values of conversion for the calcined Pt–Sn catalysts, in comparison with the fresh catalysts, emphasize the effect of the calcination treatment on the distribution and interaction of Pt and Sn. In the calcined Pt–Sn–K catalysts, the activity is related to the K–Pt–Sn interactions.

The addition of alkaline metals was employed not only Potassium but also Lithium, Sodium, Calcium etc. Recently, many researches are being carried out on different catalyst, alkaline metals etc. to improve the catalytic performance and acidity of the supports of Pt–Sn catalysts. An example to illustrate the influence of acidity and basicity of the supports can be found in the work of Siri (2005), who carried out the modifying effect of alkaline metals (Li, Na and K) which is studied on the acid properties of the support and on the behavior of PtSn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalytic systems, in the isobutane dehydrogenation. The isopropyl alcohol transformation rate decreases

sharply with the addition of alkaline metals, according to the sequence  $\text{Li} < \text{Na} < \text{K}$ . For the dehydrogenation reaction, the addition of K improves the stability level of the catalyst, and, as a result, PtSnK1.7 catalyst presents the best performance activity/selectivity/stability (Siri *et al.*, 2005). Moreover, there was another research that corresponds with this result. They found that the presence of both K and Li in the catalysts resulted in higher activity and stability of the catalyst for the dehydrogenation of iC4 to isobutene. The amount of  $\text{Pt}_x\text{Sn}_y$  alloy and the percentage of Sn reduced to the metallic state were higher in those Pt–Sn/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts, in which, higher quantities of  $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$  complex were formed during the impregnation. The results suggested the existence of a relationship between the amount of  $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$  complex deposited on the alumina after the impregnation step, tin reducibility and PtSn alloy formation (Cortright *et al.*, 1986). Pt–Sn–K supported catalyst used in this study showed higher selectivity than Pt–Sn–Li. Its remarkable performance for the dehydrogenation of iC4 was associated with the structural and electronic properties. Suitable and sufficient weight percentage of Sn and the use of K as the promoter for reducing undesired production and acidity of the support caused the highest selectivity to isobutene. The addition of K resulted in better selectivity toward isobutene. It was observed that alkali and alkaline earth metals are basic in character and could suppress the strong acidity responsible for the reaction chain to propagate further from isobutene such as cracking, oligomerization, cyclization and coke formation (Tasbihi *et al.*, 2007)

## 2.6 Catalyst Deactivation

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. The effect of the poison will depend on its adsorption strength (at the active centre) relative to that of the reactants, the larger the strength of adsorption, the stronger the poisoning effect.

Poisoning effects are very specific. A reactant is one reaction which 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  $\text{NH}_3$  synthesis.

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

- (i) physically block the active centre
- (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.

The most usual type of catalyst poisoning is caused by an impurity, which present in the feed stream. The impurity can interact with catalyst faster than the feed, so the loss of active site occurs. These phenomena so called fall-off in activity of the catalysts. Poisoning can occur in both permanent and temporary. Operating, without poisoning required an effective removing impurity process, is not suitable for industrial process. Therefore, the impurity tolerance enhancement of catalyst is widely concerned. For instance, the effect of impurity such as sulfur greatly caused the agglomeration of Pt metal and decreased activity after catalysts were exposed to sulfur (Vaarkamp *et al.*, 1992).

### 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

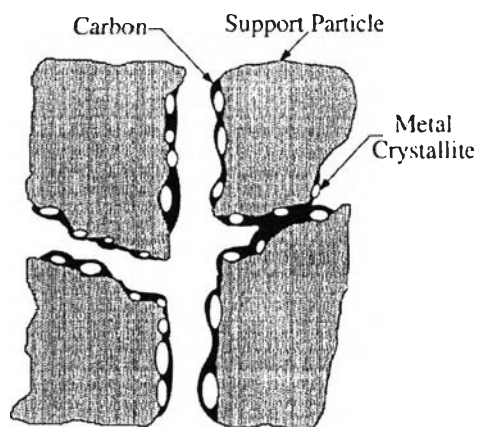
The major effects of fouling noticed during the reaction are:

- (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 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 regenerations) of 1 to 5 years due to the mild operating conditions ( $H_2$  atmosphere, high pressure 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

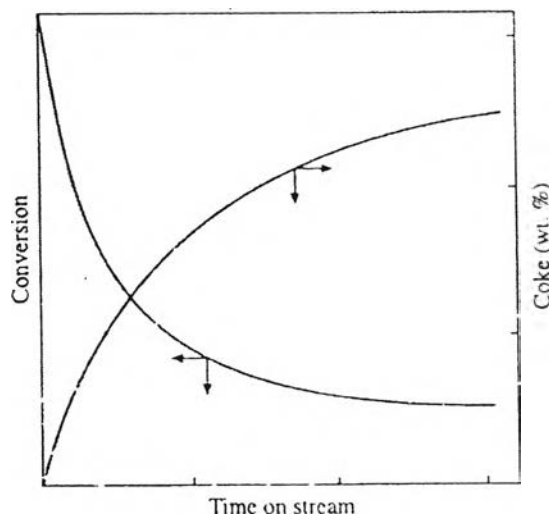
(atmospheric pressure; > 500°C). Many factors influence the formation of coke on catalysts. Because of pore filling by the coke, the pore volume of the catalyst decreases faster than its surface area. Possible effects of fouling by carbon (or coke) on the functioning of supported metal catalyst are illustrated 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.

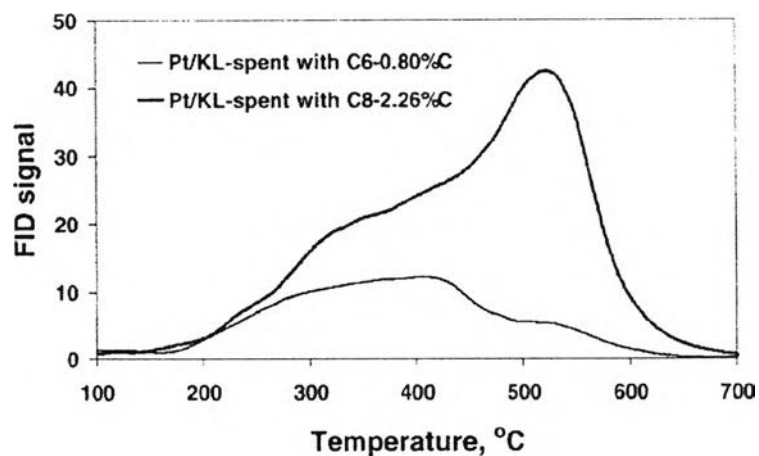
The activity loss itself is more rapid in the beginning and becomes slower after some time. In some catalyst with long lives, the activity may decrease asymptotically with time after the initial rapid loss (Figure 2.7).





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

The deactivation for *n*-alkane aromatization has been studied on Pt/KL by two methods, incipient wetness (IWI) and vapor phase impregnation (VPI) with different feeds, being *n*-hexane and *n*-octane during 9 h on stream (Jongpatiwut *et al.*, 2003). On the VPI Pt/KL catalyst, more than twice as much coke was deposited during the *n*-octane aromatization as during the *n*-hexane aromatization, which parallels the faster rate of deactivation observed with *n*-octane. The corresponding TPO profiles are shown in Figure 2.8. Not only the overall oxygen consumption, but the relative size of the peaks is clearly different. The large oxidation peak appearing at high temperature after *n*-octane reaction is possibly due to the plugging of zeolite pores, which would retard the oxidation of the coke deposits. On the IWI catalyst, the difference between the amount of coke deposited with *n*-octane and with C6 was not as great, but it must be noted that the IWI catalyst already had twice as much coke as the VPI catalyst after the *n*-hexane reaction.



**Figure 2.8** Temperature programmed oxidation (TPO) profiles of coke deposits left over the Pt/KL-VPI catalyst after 9 h on stream during *n*-hexane (thin line) and *n*-octane aromatization (heavier line). Reaction condition: 500°C, H<sub>2</sub>/*n*-C<sub>6</sub> (or *n*-C<sub>8</sub>) molar ratio 6:1, WHSV 5 h<sup>-1</sup>.

#### 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<sub>2</sub>S 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 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<sub>2</sub> 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 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<sub>2</sub>O<sub>3</sub>, Ni-Al<sub>2</sub>O<sub>3</sub> etc.) and oxide catalysts with large surface areas (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, 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

Sintering is a physical process associated with a loss of surface area of the catalysts when operated above the suitable range of temperature. The typical reduction temperature for Pt/KL is 400-500°C. Sintering may result on all surface areas of catalyst or may cause a loss only in the metal crystallite parts.

The powerful tool is used to study the morphological change in catalyst resulting for thermal treatment (Alvarez and Resasco 1996). Two catalyst

series, Pt/L zeolites and Pt/Mg (Al) O, had been investigated. Combination of temperature programmed reduction (TPR) and electron microscopy (TEM) measurement showed that a high calcinations temperature treatment on Pt/L zeolites resulted in a migration of the Pt species outside the channels of zeolites. Similarly, the analysis of TPR and the methylcyclopentane ring opening selectivity to *n*-hexane over the Pt/Mg(Al)O zeolite indicated that, during preparation of catalyst, a large fraction of Pt species became trapped inside the bulk of the support and came out to the surface only after cycle of oxidation/reduction at relatively high temperature. In agreement with Resasco *et al.* (1999), they confirmed that the thermal treatment caused the change of the catalyst active site. The catalysts were more stable at a lower temperature even in the presence of sulfur.

#### 2.6.3.2 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.

#### 2.6.3.3 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 bi-metallic catalysts)
3. Metal or carrier transitions (e.g.,  $\gamma$ -alumina to  $\alpha$ -alumina) and
4. Reaction of the carrier with the reactants etc. (e.g.,  $\text{SiO}_2$  or  $\text{TiO}_2$  are used in SCR catalysts and not  $\text{Al}_2\text{O}_3$  as the latter support reacts with  $\text{SO}_3$  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  $\text{NH}_3$  to NO (temp  $> 900^\circ\text{C}$ ), loss of Pt occurs as Pt-oxide. In fact, addition of Rh decreases Pt loss besides decreasing 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.

### **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 regeneration. 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** Prevention of catalyst deactivation

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 zeolites; 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/Al<sub>2</sub>O<sub>3</sub> 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-Al<sub>2</sub>O<sub>3</sub> catalysts. Besides, these promoters also keep the catalyst active at higher coke contents than possible with Pt-Al<sub>2</sub>O<sub>3</sub>. 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 Brönsted acidity in the catalysts.

## 2.8 Regeneration of Deactivated Catalysts

In several refinery and petrochemical processes the catalyst deactivates by coke formation, e.g. during cracking of heavy oil, hydrodesulphurization and reforming of naphtha into high octane gasoline. The catalyst must be regenerated by continuous or periodic coke combustion (Kern and Jess, 2005). Although regeneration of the spent catalysts is of great interest, it has been less studied than deactivation because the mechanisms of deactivation are not always simple and reversible. Regeneration of a coked particle involves both chemical reaction and transport processes, since oxygen must be transported by external mass transfer and pore diffusion to the internal coked surface. As already outlined by Weisz (Weisz and Goodwin, 1963, 1966), pore diffusion strongly influences the effective rate of burn-off, at least for particle diameters and temperatures relevant for industrial (fixed bed) processes (> 1mm, > 400°C). Several groups (Arteaga *et al.*, 1986; Yoshimura *et al.*, 1988) have used deactivated catalysts under laboratory and industrial conditions in order to study their regeneration with steam and/or oxygen under several experimental conditions. Characterization of the metallic phase was made by physicochemical and spectroscopic methods. In the previous interest, either on

industrial or fundamental aspects, of the regeneration of metallic catalysts increased. In spite of that, only a few studies have been published. Attention is focused primarily on Pt-based catalysts (Pt, Pt-Re, Pt-Ir) because they are widely used in reforming reactions (Afonso *et al.*, 1997).

### 2.8.1 Regeneration Parameters

Regeneration of a spent catalyst is influenced by three great numbers of parameters. These are related to the mechanisms of deactivation, experimental regeneration conditions, and textural properties of the catalysts and the nature of the metallic phase. Therefore, the regeneration of a given catalyst must be treated as a particular case, and must take into account the history of the sample (purity, composition of feedstock, industrial conditions of use, etc.). Furthermore, regeneration only makes sense in cases where deactivation can be reverted, as in the case of coke deposition (Bartholomew, 1984).

#### 2.8.1.1 *Temperature*

Temperature is probably the most critical parameter in a regeneration process because it influences directly the stability of the metallic phase and of the support. In addition to destructuring of the metallic phase (agglomeration, crystallization, volatilization), sinterization of the support and reaction of the catalytic phases themselves or with the support (thus forming inactive species) may occur (Bartholomew, 1984). The catalytic reforming reactions normally take place at high temperatures (above 500°C) and are accelerated by steam (Bartholomew, 1984). In addition, one must keep in mind the possibility of coke ignition if temperature is not properly controlled. Stagg *et al.* (1997) were also found that the high-temperature reduction/oxidation treatments usually employed to regenerate spent catalysts can have a detrimental effect on the activity and selectivity of the Pt–Sn/SiO<sub>2</sub> catalysts. It is postulated that such thermal treatments lead to the disruption of the Pt–Sn alloys causing an increase in the fraction of unalloyed surface Pt. As a result, the rates of coke formation and deactivation drastically increase. The monometallic (Pt only) catalysts are also affected by the high-temperature reduction/oxidation processes. The oxidation treatment results in an increased rate of coke formation and



deactivation, while the regeneration process results in a much smaller effect. This difference may be due to carbon residues left on the surface. These residues may disrupt Pt ensembles and cause a decrease in the rate of undesired reactions, such as hydrogenolysis and coking, which require a large ensemble of Pt.

Since the regeneration at high temperature is completely destroyed Pt-Sn alloys, it is better to start the regeneration at lower temperature. Therefore, several research groups have found the strategy for regeneration of the spent catalyst at lower temperature to maintain Pt-Sn interaction. It means that the initial activity and selectivity was regained after regeneration. Pieck *et al.*, (2005) compared the combustion of coke deposits of Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with O<sub>2</sub> and O<sub>3</sub>. They found that the preparation of Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts by co-impregnation produced a good Pt-Sn interaction. A fast drop of the dehydrogenating capacity occurs upon increasing the Sn content, due to the increase of the Pt-Sn alloying and the decrease of free non-alloyed Pt. The TPO of coked catalysts with O<sub>2</sub> and with O<sub>3</sub> showed that O<sub>3</sub> was able to burn coke at near room temperature with a maximum rate at 150–160°C that was a balance between the growth of the oxidation rate and the O<sub>3</sub> decomposition at higher temperatures. The TPO with O<sub>2</sub> started at about 350°C, and had a sharp maximum at 520°C and ends at 550°C. The regeneration of the coked catalyst with O<sub>2</sub> at 450°C produced metal segregation, with an increase of the concentration of unalloyed Pt and of the metal catalytic activity. The regeneration with O<sub>3</sub> at 125°C preserved better the Pt-Sn interaction. In this case, the coke was oxygenated step by step producing intermediates that were easier to burn with O<sub>3</sub> or O<sub>2</sub>. The coke elimination with O<sub>2</sub> started on the metal function while the coke elimination with O<sub>3</sub> started on the alumina support.

In addition, Ma *et al.* (2004) studied the regeneration of the Mo/HZSM-5 catalyst used for methane aromatization at 1023 K with a small amount of NO addition to air (NO/air = 1/50 vol/vol). They reported that one can eliminate the entire deposited hydrocarbon at 823 K by using pure air. With a small amount of NO addition to air (1/50 vol/vol), the coke removing ability was strongly promoted. The deposited hydrocarbon on the used catalyst started to be removed above 603 K, and the total coke removing temperature was 723 K. Much lower regeneration temperature suppressed the migration and sublimation of Mo species during the

regeneration, preventing any structure change of the Mo active sites, which resulted in the very stable methane dehydro-aromatization performance on the regenerated Mo catalyst. As a result, the benzene formation rates of the catalyst started to decrease after the eighth regeneration cycle with NO addition to air, while the benzene formation rates of the catalyst regenerated with pure air started to decrease only after the fourth regeneration cycle.

### 2.8.1.2 Heating Rate

Heating rate on regeneration processes is the critical step which seems to be the initial coke burning rate (Klusacek, 1985). Pretreatment, control of oxygen content in the oxidant mixture, and slow heating rate are usually employed to better control the coke combustion (Klusacek, 1985). Therefore, low heating rates ( $1\text{-}5^\circ\text{C min}^{-1}$ ) were usually maintained in some regeneration processes (Arteaga *et al.*, 1986; Yoshimura *et al.*, 1988; and Marécot *et al.*, 1990). Fast dissipation of the heat generated by coke burning is another alternative to reduce the possibility of coke ignition (Furimsky *et al.*, 1988). This is especially true when the H/C atomic ratio is high (Pieck *et al.*, 1989a).

### 2.8.1.3 Time

Time necessary to remove coke depends on the regeneration temperature. A short regeneration cycle (ca. 1 h at ca.  $400^\circ\text{C}$ ) allows a partial recovery of the catalytic activity only (Gallezot *et al.*, 1989; Pieck *et al.*, 1989b; Pieck *et al.*, 1991 and Rickard *et al.*, 1990). Essentially, only coke associated with the metallic phase is removed.

Afonso *et al.* (1997) studied on the influence of heating rate ( $2\text{-}15^\circ\text{C/min}$ ), temperature (coke oxidation,  $350\text{-}600^\circ\text{C}$ ) and time ( $2\text{-}15$  h) on the catalytic and structural properties of a regenerated Pt-Sn/ $\text{Al}_2\text{O}_3$  catalyst (pretreated with  $\text{H}_2$  at  $350^\circ\text{C}$ ). They reported that slow heating rates have increased the catalytic activity of regenerated samples and the best regeneration temperature was  $450^\circ\text{C}$ . They also observed that the relevant properties of regenerated catalysts reached a final state after treatment for 8 h under an oxidant atmosphere. At higher temperatures, data seemed to indicate that the effect of Sn over Pt is basically of geometric nature,

which was destroyed when catalyst overheating occurred. Preliminary studies on the regeneration of an industrial deactivated Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst (Afonso *et al.*, 1995) have indicated that pretreatment with H<sub>2</sub> was an important procedure for the regeneration process and with H<sub>2</sub>, regeneration was enhanced. The results can be interpreted by physical meaning due to the partial recovery of textural properties, and by chemical effects due to the reduction (at least partially) of the metallic phase, incipient coke gasification and desorption-cracking processes of coke fragments. Pretreatment with H<sub>2</sub> was an important procedure for the regeneration process due to the partial recovery of textural properties and the reduction (at least partially) of the metallic phase, incipient coke gasification and desorption-cracking processes of coke fragments (Afonso *et al.*, 1995).

Lerkijcharoenwong *et al.* (2003) found that Pt/KL catalyst prepared by Vapor Phase Impregnation method was known to be an effective catalyst for *n*-octane aromatization. However, during the reaction, catalysts deactivated due to coke formation. Consequently, it was common practice to regenerate the catalysts to recover their activity. Hence, the attempt of this work was to investigate the influences of air flow rate, temperature and time of regeneration by coke oxidation in air to determine the optimal regeneration conditions of such catalysts. In addition, oxychlorination treatment was also studied to redisperse Pt particles after regeneration in air. It was found that the optimal regeneration temperature, time and air flow rate was 250°C, 0.5 h and 100 ml/min/g of catalyst, respectively. Moreover, it was clearly seen that regeneration with oxychlorination treatment can restore Pt redispersion as close as that of the fresh catalysts.