

## CHAPTER II

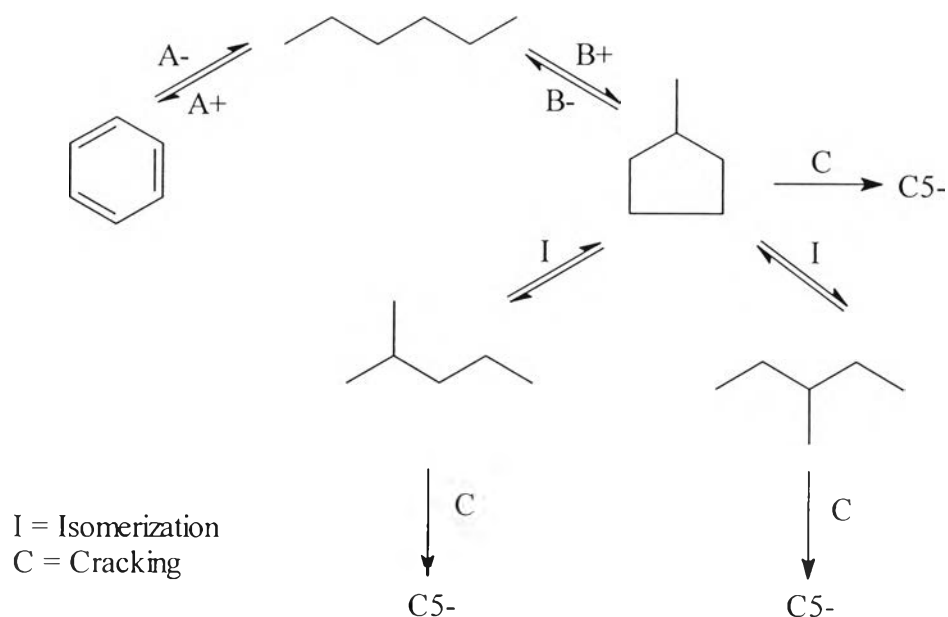
### LITERATURE SURVEY

#### 2.1 Catalytic Reforming

This research related to the reforming catalyst that is Pt supported on nonacidic potassium L-zeolite (Pt/KL) catalysts. The exceptional high catalytic activity and selectivity of Pt/KL was accepted in several years for the conversion of n-hexane to benzene. The catalytic reforming is used in refinery to improve the octane number of distillates in the gasoline boiling range, and in chemical manufacture for the production of aromatic hydrocarbons.

Catalytic reforming involves reacting feed vapor over a catalyst at temperature in the range of 450 to 550 °C and pressure in the range of 10 to 50 atm, in the presence of hydrogen. The conventional catalysts used are dual function catalysts (Satterfield, 1991), that is, they have both the acidic and hydrogenation-dehydrogenation properties. Almost invariably they are Pt on alumina catalysts, Pt is the hydrogenation-dehydrogenation component while the alumina which is generally treated with chlorides or fluorides is the acidic component.

Although a dual function catalyst, Pt/Al<sub>2</sub>O<sub>3</sub>, drives the equilibrium reactions to the right. But hydrogenolysis, particularly of the C<sub>6</sub> fraction, can lower the benzene yield. Nevertheless, Pt/KL, the monofunctional catalyst could reduce this undesirable side reaction (Tamm *et al.*, 1987). Considering the general reaction network of Figure 2.1, the main features of the AROMAX process are the promotion of steps A<sup>+</sup> and B<sup>-</sup> and the minimization of all the reaction steps.



**Figure 2.1** Reaction pathway for monofunctional reforming catalysts using n-hexane as the reactant (Tamm *et al.*, 1987).

## 2.2 Catalytic Performance of Pt/KL

Since Bernard (1980) found that Pt/KL exhibits the best activity and selectivity over the other nonacidic zeolite catalysts. There are several research works investigated the distinguishing in the aromatization performance of Pt on KL-zeolite and Pt on the other supports.

Manninger *et al.* (1989) found that Pt/KL promoted aromatization, isomerization, and hydrogenolysis on n-hexane with a selectivity pattern similar to Pt/SiO<sub>2</sub> in EUROPT-1. Nevertheless, in 1990, Tauster and Steger revealed that Pt/KL contrast with Pt/SiO<sub>2</sub> in having:

- 1) Pt/KL show much greater selectivity for aromatization than Pt/SiO<sub>2</sub>.
- 2) A strong preference for cracking the terminal carbon-carbon bond as opposed to interior bonds. These properties enhanced terminal adsorption of the hexane molecule at the Pt surface. They believe the fact that Pt in both

these zeolite is accessible only through pore holes of  $\sim 7.3$  Å is a critical feature which leads to these unusual properties.

Lane *et al.* (1991) displayed the reaction pathways of the monofunctional catalysts. They indicated that benzene is formed as a primary product via one-six-ring closure and methylcyclopentane is formed as a primary product via one-five-ring closure. Pt/KL has two times greater in the one-six to one-five ring closure ratio than the others Pt catalysts. The increased selectivity and activity for one-six-ring closure observed for the L-zeolite catalyst is consistent with an influence of the zeolite geometry on the transition state, i.e., the confinement (conformation) model. In L-zeolite, adsorption forces between n-hexane and the zeolite channel may lead to preorganization of the transition state for direct benzene formation.

Many types of supports (e.g., Pt/KL, Pt/BaKL, Pt/KBaL, Pt/NaY, PtCsNaY, Pt/NaFAU, Pt/hex, Pt/SSZ-24, Pt/Silica and Pt/Carbon) were varied to study the n-hexane aromatization reaction by Mielczarski *et al.* (1992). They concluded that Pt/KL showed the best performance because the lack of any acidity in the support and the ability of L-zeolite to stabilize the formation of extremely small Pt clusters. In agree with the Davis (1994) who summarized the reasons in the excellent performance of Pt/KL over the other supports. He revealed that the metal cluster supported on basic L-zeolite are more electron-rich than that supported on silica, L-zeolite stabilized small Pt clusters and the micropore structure of zeolite inhibited the bimolecular reactions that deactivate the catalyst.

Miller *et al.* (1996) also considered the geometric effects in L-zeolite dehydrocyclization catalysts. They found that for most catalysts, including zeolite and amorphous supports (i.e. K-FER, K-MFI, K-MTW, K-BEA, K-MAZ, and K-FAU), have the ratio of 1-6 to 1-5 ring closure lower than Pt/KL. Pt/K-MAZ, which has a pore geometry similar to that of L-zeolite, was not quite as selective as Pt/KL for 1-6 to 1-5 ring closure (0.89) but exhibits the

higher ring closure ratio than the other catalysts. Their experiment results are most consistent with the preorganization model, in which the reactant molecule is adsorbed in the zeolite channel in a cyclic conformation similar to the transition state, thereby reducing the entropy of activation leading to a preference for 1-6 ring closure. The zeolite geometry of LTL is the best suited for this adsorption.

They also studied the addition of alkali on Pt/KL resulting in a small increase in the ring closure selectivity and in reduction of C1-C5 hydrogenolysis selectivity. So they concluded that the optimum catalyst is one with small Pt particles support on KL-zeolite that has been modified with a small excess of alkali.

Moreover, the computer simulations demonstrated that at high conversion a high 1-6 to 1-5 ring closure ratio led to a high apparent activity. In addition, the ultimate benzene selectivity was substantially higher at high conversion leading to almost double the benzene yield at constant C1-C5 yield.

However the high performance of Pt/KL was still interesting. In 1998, Jacobs *et al.* investigated the n-hexane aromatization on Pt/SiO<sub>2</sub>, Pt/KL and PtMg(Al)O. They found that Pt/KL catalyst exhibits much higher aromatization activity and selectivity than Pt/Mg(Al)O and Pt/SiO<sub>2</sub>. They assumed that the basicity of the support alone couldn't explain the high performance of Pt/KL catalysts. Benzene is the main product on Pt/KL and hexenes and lighter compounds are the principal by-products, in contrast with Pt/Mg(Al)O that has hexenes as the main product. Since hexenes are primary products and benzene is a secondary product, the exceptional aromatization activity of Pt/KL is explained in terms of its ability to convert hexene into benzene. Furthermore they summarized that the most important role of the zeolite is to inhibit bimolecular interactions that lead to coke formation.

## 2.3 Catalyst Deactivation

In generally, the catalysts can be deactivated in 3 ways i.e., sintering, fouling and poisoning.

1. *Sintering* is a physical process associated with the loss of area of the catalyst when it operated above the normal range of temperature.

2. *Fouling* is a process of catalyst deactivation that may be either physical or chemical in nature. The most typical of fouling processes is the carbonaceous deposition or “coke” that forms on the most catalyst used in the processes of petroleum fractions or other organic chemical feedstock.

3. *Poisoning* is the deactivation of catalyst due to small amount of material, associated with the adsorption of the poison on the active sites of the catalyst.

For Pt/KL, the selective dehydrocyclization and terminal adsorption properties of clean Pt sites within or outside L-zeolite can inhibit the deactivation of Pt clusters. However only Pt clusters within the protected environment of L-zeolite channels that favor dehydrocyclization thermodynamics (Iglesia and Baumgarner, 1992).

Hexenes were almost exclusive primary products. The low amount of cis-2-hexene may indicate its enhanced reactivity in aromatization (Manninger *et al.*, 1991). Moreover, Jacobs *et al.*(1998) found that the presence of hexenes as products, which are generated in the reaction as precursors for benzene, is an indicator of the loss of aromatization activity.

According to Menacherry and Haller (1998)'s work, in the absence of sulfur impurities, the deactivation appears to be due to two types of coke formation:

- The effect of the deposition of carbon atoms on the surface of the metal particles
- The pore blockage from coking

Furthermore, the increase in reaction time could increase the number of channel blockage by Pt that showed the distribution of Pt particle size by a transmission electron microscopy (TEM). This problem is exacerbated by long L-zeolite channel lengths (Treacy, 1999).

Since the L-zeolite was discovered to play an important role in the inhibit bimolecular interactions that lead to coke formation (Jacobs *et al.*, 1999). The main cause in the deactivation of Pt/KL is sulfur poisoning (Vaarkamp *et al.*, 1992). This problem was very concerned in much research. Not only Pt will lose their characteristic after sulfur attached but also resulted in the pore blockage.

## **2.4 Catalyst Preparation**

The approximate metal loading method has affected on the catalytic performance and the stability of Pt/KL. There are several preparation methods i.e., incipient wetness impregnation (IWI) method, ion exchange (IE) method and chemical vapor deposition (CVD) method that were used to load Pt precursors into L-zeolite. The favorable method in the recent years is the CVD method (Jacobs *et al.*, 2000).

### **2.4.1 Incipient Wetness Impregnation and Ion Exchange Method**

For IWI that is the conventional effective method more than IE, the solid is impregnated with a nonsolvent liquid, usually water or hydrocarbons, necessary to fill the pores completely. Addition of liquid must be stopped when the solid tends to become sticky or large excess has been used, the liquid can be removed by centrifugation. In that condition the pore volume is equal to the volume of the liquid adsorbed by the solid (Leofanti *et al.*, 1998).

The Pt/KL catalysts prepared by ion exchange (IE), incipient wetness impregnation (IWI) and coimpregnation with KCl (IWI+KCl) have been characterized by Ostgard *et al.* (1991). The results showed that, after reduction the IWI catalysts contain smallest Pt particles located inside the zeolite channels, while the IE samples has large particles, some of which are on the external surfaces. At high temperature, excess KCl reacts with zeolite protons, forming HCl, which escapes. In comparison to the IE samples, the IWI catalysts are less acidic, more selective for dehydrocyclization, but less selective for hydrogenolysis that requires large Pt ensembles, then IWI produced less C1-C5 compounds and less coke.

The Pt has to reduce before the reaction testing. Manninger *et al.* (1990) found that NaBH<sub>4</sub> reduction results in a less stable catalyst than H<sub>2</sub> reduction, but the formation could be stabilized by heating in H<sub>2</sub>. In the reduction step ion-exchange catalysts creates additional acid centers; these can be eliminated by after-treatment with KNO<sub>3</sub>. However the acid centers in IE catalysts is not considered, this is the weak point of IE method. Although IWI method was accepted for several years, but the catalysts from IWI method have platinum cluster that close proximity to each other and will sintering in the high thermal treatment.

Therefore there are many research works tried to prepared Pt/KL to achieve the highly disperse Pt particles inside the zeolite channels more than IWI method.

#### 2.4.2 Chemical Vapor Deposition Method

Most acetylacetonate (AcAc) forms of divalent and trivalent metal cations can be easily sublimed below their decomposition temperature under low pressure. Hong *et al.* (1992) developed a novel Pt-incorporation procedure that involves sublimation of Pt(AcAc)<sub>2</sub> into dehydrated L-zeolite.

Highly dispersed, non acidic L-zeolite were produced by thermal treatment of vapor phase impregnated samples (Mielczarski *et al.*, 1992).

Hong *et al.*(1992) used CVD method to load Pt into aluminosilicate (KL, BaKL, NaY, CsNaY, cubic and hexagonal polytypes of faujasite, ZSM-12 and SSZ-24) and aluminophosphate (AlPO<sub>4</sub>-5 and CVD-5) molecular sieves. The characterization by XRD, TPD, elemental analysis, <sup>13</sup>C MAS NMR, TEM and H<sub>2</sub> chemisorption revealed that Pt can be loaded into the microporous of molecular sieves with both charged and neutral framework while IWI and IE method, Pt can be loaded only in the charged framework. The advantage of CVD method over IWI and IE method is CVD method could not change the acid/base properties of the molecular sieve. In addition, Pt that impregnated by CVD method does not migrate to the exterior surface at the condition of aromatization reaction.

Bellatreccia *et al.* (1995) investigated the CVD-based Pt/KL by *in-situ* extended X-ray absorption fine structure (EXAFS) spectroscopy. After *in-situ* reduction (H<sub>2</sub>, 400 °C), EXAFS results suggested the presence of small metal particles, which may be localized inside the KL-zeolite channels. After the reforming of methylcyclopentane at 500°C (and 1 atm), no coke deposition was evidenced by EXAFS, in agreement with the non-acidic character of Pt/KL. Moreover, the severe O<sub>2</sub>/H<sub>2</sub> regeneration cycle did not alter the structure and location of Pt particles inside the zeolite.

Jacobs *et al.* (1999) studied two series of Pt/KL catalysts with varying metal loading that synthesized by IWI and CVD method. The catalysts were characterized by TEM, FTIR of absorbed CO, EXAFS and pulse testing of MCP ring opening. The characteristic morphology produced by the CVD method was found to improve the performance of the catalyst under clean and sulfur poisoning conditions, enhancing the catalyst's resistance to formation of coke and decreasing the particle agglomeration rate.



However, Hong *et al.* (1992) recommended that it is necessary to  $\text{Pt}(\text{AcAc})_2$  and the molecular sieves be fully dehydrated and kept in a vacuum of better than  $10^{-4}$  Torr for the successful sublimation of  $\text{Pt}(\text{AcAc})_2$ .

The preparation under vacuum condition was not widely used because of the restriction in the cost of operation. Therefore the preparation under atmospheric pressure was selected to study. Jacobs *et al.* (2000) compared the catalysts that prepared by CVD method that was done under vacuum condition and helium flow system. They suggested that the catalysts that prepared by CVD method in the helium flow system which prefer in the industrial application showed the high catalytic performance similar to the catalysts that prepared in the vacuum system.

In addition to the improvement of Pt/KL by plenty of preparation methods, Pt/KL was modified by addition of promoters such as barium and rare earth elements. The purpose of these modifications were increasing the activity, selectivity and stability of Pt/KL.

Derouche and Vanderveken (1988) suggested that the addition of  $\text{Ba}^{2+}$  into L-zeolite attributed to the L-zeolite pore system which confines reactants within its pores in such a manner as to assist the organization of n-hexane into a “pseudocycle” and stabilized transition state complex.

Fukunaga and Ponec (1997) suggested that the presence of  $\text{K}^+$  (i.e. the cation in zeolite) can be related to both the high aromatization activity/selectivity and the high sensitivity to sulfur poisoning in n-hexane conversion. In addition, the  $\text{K}^+$  which stabilizes an intermediate of aromatization, loses this properties by its interaction with sulfur.

Fang *et al.* (1997) studied a series of Pt-RE-KL, which containing 0.8 wt% Pt and 0.2 wt% RE (RE is rare earth element such as Gd, Tb, Dy, Tm, Yb, and Lu) and prepared by IWI method. Their used proper % loading from their previous work, they found that the RE loading should in the range of

0.05 – 0.2%. The samples were prepared by IWI method and characterized by TPD, TPR and plus-CS<sub>2</sub> poisoning test. They concluded that those heavy rare earth elements added to Pt/KL catalyst donate electron to Pt particles and prevent the accumulation of active Pt particles. Thus RE can remarkably increase the ability of resistance sulfur poisoning and the aromatic selectivity of n-hexane or MCP conversion on Pt/KL catalysts.

Jacobs *et al.*(2000) focused on the addition of Tm (0.15% wt) by CVD method. They found that Tm could increase the sulfur tolerance of Pt/KL by act as sulfur getter and can increase the dispersion of small Pt particles in the zeolite.

## 2.5 Catalyst Characterization

The several characterization methods were applied to investigate the properties of Pt/KL resulting in the improvement their properties in the future.

The product distribution of methylcyclopentane (MCP) ring opening can use as probe reactions (Ostgard *et al.*, 1992). The high 3-methylpentane/2-methylpentane ratio suggesting that the MCP molecule becomes oriented inside the zeolite channels. It was resulting from the small Pt particles in the channels of zeolite. This result was confirmed by H<sub>2</sub> chemisorption analysis.

The microcalorimetric measurements at 353 K of Sharma *et al.*(1994) showed that the heat of CO adsorption is the same on freshly reduced Pt/SiO<sub>2</sub> and Pt/K(Ba)L catalysts but the different were observed after the reaction testing. The carboneous species that accumulate on Pt/SiO<sub>2</sub> during n-hexane conversion decrease the total number of adsorption sites and the number of sites that adsorb CO strongly. In contrast with Pt/K(Ba)L that retained the adsorptive properties of the freshly reduced catalysts.

The NMR of  $^{13}\text{CO}$  adsorption (Sharma *et al.*, 1994) showed that the small cluster-sized Pt particles are more resistance to deactivation by self-poisoning reactions than larger Pt particles.

Chao *et al.* (1995) characterized the Pt cluster size and location on the zeolite using the chemical shift in  $^{129}\text{Xe}$  NMR spectroscopy of adsorbed xenon and the x-ray adsorption fine structure (XAFS) obtained at the Pt  $L_{III}$  edge. The results indicated that a Pt cluster consist of 5-7 Pt atoms located inside the zeolite main channel which is formed by the interconnection of cage 1.1 nm in diameter to each other in a linear way through 0.71 nm aperture. The Pt cluster in the KL-zeolite channel is so small which does not cause pore blockage for the adsorption of xenon atoms (atomic diameter 0.43 nm) and  $\text{CCl}_4$  molecules (atomic diameter 0.59 nm) severely.

The EXAFS data analysis (Mojet and Koningsberger, 1996) also showed that after reduction very small Pt metal particles are present consisting of five to six atoms.

XAFS experiments on reduced Pt/KL before and after CO admission revealed that the small Pt particles decompose upon CO exposure. This led to small  $[\text{Pt}(\text{CO})_2]_3$  entities that are stabilized by the zeolite pore walls.

The XAFS data revealed that the decreased electron density on Pt after CO admission implying  $\pi$ -backdonation from Pt to CO, a positive charge on Pt in the newly formed cluster or a combination of both.

The FTIR spectra of adsorbed CO was widely used to characterize the distribution and location of Pt particle (Lane *et al.*, 1993). All Pt catalysts showed a strong absorbance band around  $2070 \pm 20 \text{ cm}^{-1}$  due to linear-bonded CO and showed a weakly absorbance band around  $1850 \pm 20 \text{ cm}^{-1}$  due to bridge-bonded CO. Pt/KL, Pt/KMFI, Pt/KMTW and Pt/KSiO<sub>2</sub> had an additional absorbance near  $1970 \text{ cm}^{-1}$ . The additional band is not observed for Pt/silica, Pt/LaL, Pt/HL and Pt/HMFI, i.e., neutral and acidic supports.

Stakheev *et al.*(1995) investigated FTIR spectra of adsorbed CO. They presumed that the basic oxygen atoms of the zeolite framework can act as  $\delta$ -donor ligands and stabilized the Pt carbonyls

Their results reveal the existence of two groups of Pt particles in the sample group of

1. Particles that localized on the outer surface of the zeolite microcrystals and in the near surface region; they exhibit CO bands at 2060-2050  $\text{cm}^{-1}$  close to those of Pt supported on conventional supports.

2. Group of particles that are engaged inside zeolite channels and their electronic structure is presumably strongly perturbed by the zeolite framework CO band, can observed at frequencies in the range of 1960-1920  $\text{cm}^{-1}$ .

Menacherry and Haller (1998) investigated the FTIR spectra of adsorbed CO. They suggested that the increase in benzene selectivity correlate with a shift to lower stretching frequencies of the CO adsorption bands, indicating that an increase in electron density at the surface metal atoms.

They presumed that the effect of the support in the high activity and aromatization selectivity of Pt/KL can be twofold, i.e., the stabilization of extremely small metal particles of specific morphology under reaction conditions and metal support interaction involving charge transfer between the metal particles and the support resulting in an increased electron density over the metal particles.

In addition, this electronic effect can be related to the specific morphologies of the metal particles formed on different supports and on using different preparation methods.