

## CHAPTER II

### LITERATURE SURVEY

#### 2.1 The Aromatization on the Pt/KL Catalyst

Naphtha reforming involves reacting feed vapor over a catalyst at temperature in the range of 450-550 °C and pressure in the range of 10-50 atm, in the presence of hydrogen. The conventional catalysts used are bifunctional catalysts having both the acidic and metallic active sites (Satterfield, 1991). Almost invariably, they are Pt on alumina catalysts, Pt is the hydrogenation-dehydrogenation component while the alumina is the acidic component.

Tamm *et al.* (1987) reported that although the bifunctional catalyst, Pt/Al<sub>2</sub>O<sub>3</sub>, drives the equilibrium reaction to higher conversion, but hydrogenolysis, particularly of the C<sub>6</sub> fraction, can lower benzene yield. Therefore, a new catalyst, Pt supported on the potassium form of zeolite was reported in 1980 by J.R. Bernard (Bernard, 1980).

In 1991, Lane and co-workers demonstrated that the nonacidic, L-zeolite reforming catalyst differs from conventional, bifunctional, having only a metal (platinum) function. The L-zeolite catalyst, therefore, benefits from the absence of acid-catalyzed hydrocracking resulting in higher liquid yields. Monofunctional reforming catalysts form aromatic products via one-six-ring closure and are unable to directly convert methylcyclopentane into benzene.

Since Bernard discovered the remarkably high selectivity of Pt/KL zeolite catalysts for the aromatization of n-hexane to benzenes in 1980, much attention has been directed to these catalyst systems (Bernard, 1980). Bernard studied the Pt clusters supported on a series of alkaline zeolites which are KL, NaX, NaY, Na-omega and Na-mordenite, for n-hexane aromatization in dihydrogen at 733 K and atmospheric pressure. They reported that most active

catalyst for n-hexane conversion was Pt/NaX, and the most selective catalyst for aromatization was Pt/KL. Therefore, much attention has been directed to Pt/KL catalyst systems. In contrast, catalysts currently used in reforming processes and basically consisting of platinum and alumina, are effective for producing xylenes and other aromatics from C<sub>8+</sub> paraffinic hydrocarbons, but are much less effective for producing benzene and toluene. Therefore, from an industrial as well as from scientific point of view, the Pt/KL zeolite catalyst systems have attracted considerable attention (Buss and Hughes, 1984).

The reasons why the Pt/KL catalysts are effective for n-hexane aromatization are still not perfectly clear. Among them, Besoukhanova *et al.* (1981) proposed that the platinum particles encaged in the L zeolite channels are activated by the interaction with the walls of the alkaline L zeolite. In n-hexane aromatization, the conversions and selectivity for benzene increased in the order of Li < Na < K < Rb < Cs. As the results of carbon monoxide adsorption and infrared spectroscopy showed the electron-deficiency of platinum on these alkaline L zeolites decreased in the same order as n-hexane aromatization, they concluded that the electronic states of platinum was one of the most important factors for the catalytic activities. Larsen and Haller (1989) have studied competitive toluene/benzene hydrogenation, and hydrogenation of carbon monoxide over alkaline earth cation exchanged L zeolites. Mchugh *et al.* (1990) conducted X-ray absorption measurements of these catalysts to evaluate the change in the electronic state of platinum as a result of its interaction with the walls of L zeolites. They also concluded that the selectivity to aromatics increased with decreasing electron deficiency of the platinum particles.

Tauster and Steger (1990) suggested that the L zeolite possessed channels suitable for collimation the flux of n-hexane molecules and for confining n-hexane molecules and pre-organizing them as pseudo-cyclic molecule. They also speculated that a linear orientation of the alkanes in the

channels of zeolite L favored adsorption of n-hexane on a Pt cluster at a terminal carbon. They reasoned that, if n-hexane preferentially adsorbed on the catalytically active Pt cluster at a terminal carbon, then 1,6 ring closure to form benzene must also be favored. Their results exhibited that Pt/KL catalyst gave both higher benzene selectivity and terminal hydrogenolysis than Pt/silica, which was consistent with the idea that terminal adsorption was enhanced on zeolite L catalysts as compared to non-acidic catalysts. They used the term 'molecular die catalysis' to describe the collimation effect that influenced the zeolite channels. Alvarez and Resasco (1991) also found that in the hydrogenolysis of methylcyclopentane over Pt/KL, the production of 3-methylpentane was significant and they concluded that the channel structure of L zeolite was one of the most important factors for its catalytic activities as well as the electronic state of platinum.

Iglesia *et al.* (1993) reported the unique feature of L-zeolite that it can inhibit the coke formation. They observed that the aromatization of n-heptane was initially high on Pt/SiO<sub>2</sub>, but after a few minutes on stream, the catalyst became unselective. On the other hand, the selectivity on Pt/KL zeolite did not change with time. Therefore, they concluded that selectivity of n-alkanes aromatization is an intrinsic property of clean Pt particles, and under reaction conditions, Pt particles can remain clean within the channels of the L-zeolite. The TEM of spent Pt/KL showed that the Pt outside the zeolite was coked, but the one inside still clean which should retain high activity and selectivity. This idea also supported the observation by Rollman (1977) that the intracrystalline coke formation is a shape-selective reaction. The channel structure inhibits bimolecular transition states required for polymerization which can lead to coke formation. Similar arguments have been used for ZSM-5.

The effect of various additives to platinum catalysts was studied by Fukunaga and Ponec (1997). They found that the presence of K<sup>+</sup> or Mg<sup>2+</sup> on various Pt supported catalysts increased the catalytic activity of n-hexane

aromatization when compared to cation-free Pt catalyst. The role of the  $K^+$  or  $Mg^{2+}$  was two-fold that were neutralization of acidic OH groups and influence on the reaction of platinum.

Despite the great disparity in the possible explanations offered by several authors, most of them agreed in the uniqueness of Pt/KL catalysts to promote high aromatization of n-hexane. There are not much studies in the open literature related to the aromatization of large alkanes, such as n-octane ( $C_8$ ) but these reactions would indeed have very important industrial application. From the new environmental regulations require a decrease in the concentration of benzene in the gasolines, but in order to keep the octane number high, the concentration of other aromatics such as xylenes should be increased. Therefore, it would be highly desirable to find effective catalyst for aromatization of  $C_8$  alkanes.

There has been a study of n- $C_8$  reforming by using Pt, Pt-Sn and Pt-W supported on  $\gamma-Al_2O_3$ , which was the bifunctional catalyst. It was proposed that dehydrocyclization of paraffins is one of the main reactions during naphtha reforming because it increases the octane number and produces valuable aromatic hydrocarbon (benzene, toluene and xylenes). The reaction rate is favored at high temperature and at low pressure. Conditions under which catalyst deactivation is important, therefore being necessary for the use of stable catalysts. Different formulations were proposed in order to achieve a better stability and to increase the selectivity to aromatics of the traditional Pt/ $Al_2O_3$  catalyst. The catalyst using in this work are Pt, Pt-Sn and Pt-W supported on  $\gamma-Al_2O_3$  and characterized by  $H_2$  chemisorption, TEM, TPR, test reaction of n- $C_8$  reforming (Rangel *et al.*, 2000).

## 2.2 Catalyst Deactivation

Although the exceptionally high activity and selectivity exhibited by Pt/KL zeolite catalysts for the aromatization of n-hexane to benzene are well established, however a major shortcoming for these catalysts is their extremely high sensitivity to even very small amounts of sulfur (e.g. parts per billion) in the feed has limited their industrial applications.

For example, researchers at Chevron, Buss *et al.* (1984) showed that a Pt/BaKL catalyst, which was able to maintain for 12 months a high yield of aromatics when a sulfur-free feed employed, totally lost its activity in a few days when 1 ppm of sulfur was added in the feed. Similarly, researchers at Exxon clearly demonstrated what a potent poison sulfur is for these catalysts (McVicker *et al.*, 1993). Both the feed conversion and the selectivity to benzene greatly decreased when 0.2 ppm of sulfur were added to the feed. A run that was conducted with a sulfur-free feed at 510°C, exhibited a decrease in conversion from 90 to 83% during the first 100 hrs on stream. By contrast, a run conducted in the presence of only 0.2 ppm of S added as thiophene showed a decrease from 90 to 30% during the same period. A similar behavior was obtained when changes in selectivity were compared. For the first run, the selectivity only dropped from 75 to 68% while for the second run, it went down to 30%. Therefore it would be of great interest to find a way to make these Pt/L zeolite catalysts more tolerant to the presence of sulfur in the feed.

The fundamental reason behind the high sensitivity of these catalysts to sulfur is still a subject of controversy. By analyzing the amount of sulfur deposited and the corresponding drop in activity, Exxon researcher, McVicker *et al.* (1993) concluded that the deactivation by sulfur was due to a progressive loss of Pt active sites by blocking of the zeolite channels rather than to a modification of the catalytic (electronic) nature of the catalyst. In fact, they observed metal agglomeration to a size that roughly corresponds to the size of

the pore mouth. In a similar, but independent work conducted on Pt/BaKL catalysts, Vaarkamp *et al.* (1992) also investigated the effects of minute amounts sulfur in the n-hexane feed. They observed that when the aromatization rate decreased to 30% of its original value, the size of the Pt clusters, as measured by EXAFS analysis, increased from 5-6 atoms in the fresh sample to 13 atoms. They proposed that sulfur was located at the metal-zeolite interface, thus deanchoring the particle and promoting sintering. Therefore, it is important to realize that if deactivation by sulfur occurs it will be necessary not only to remove the sulfur, but also to redisperse the Pt particles and relocated inside the channels of the zeolite. Very recently, a different explanation has been proposed. It has been postulated that the high aromatization activity of Pt/KL catalysts is due to a direct participation of the  $K^+$  sites in the ring closure. Accordingly, the sulfur deactivation would be due to a direct interaction of the  $K^+$  ions with sulfur, thus losing their ability to promote the aromatization (Fukunaga and Ponec, 1995)

Because of requiring very expensive and complicated sulfur-removal operations, therefore, it has been strong interest in finding catalysts able to effect the aromatization reaction in the presence of sulfur. To increase sulfur tolerance of Pt/KL catalysts, researchers at Sun Company, Larsen *et al.* (1996) patented a composition of matter that includes the addition of Ni to Pt/KL catalysts and results in a material that reduces the rate of Pt particle growth in the presence of sulfur and exhibits a moderate improvement in rate of deactivation by sulfur as compared to the Pt/KL catalyst.

Fang *et al.* (1996) had the study which try to increase sulfur tolerance by addition of rare earths (RE) as promoter. They tested the Pt/KL catalyst modified by  $Tm_2O_3$  for the n-hexane, methycyclopentane and cyclohexane conversion reaction. These Pt/KL modified catalysts exhibit aromatization activity and sulfur resistance, which are higher than those of unmodified Pt/KL catalysts. Also, the capacity of the sulfur poisoning resistant and the

stability of the catalysts are increase when adding an appropriate amount of Tm. Furthermore, Fang *et al.* (1997) indicated that it may have a positive effect on the aromatization activity and the sulfur resistances of Pt/KL catalysts. They prepared catalyst by using co-impregnation of Pt and the rare earth with aqueous solution. They have examined a series of Pt-RE-KL catalysts containing 0.2 wt % of different kinds of rare earth (i.e. Gd, Tb, Dy, Tm, Yb and Lu) and sighted the surface behavior and catalytic properties of the catalysts. It appeared that addition of a suitable amount of some heavy rare earth elements to Pt-KL catalyst was very beneficial to increase the aromatic as well as the hydrocracking selectivity. In addition, the adding of heavy RE elements into KL catalyst also gave rise to an increase in the active site number, that was, an increase in the dispersity of active Pt particles, therefore, the sulfur sensitivities of the Pt-RE-KL catalysts were decreased.

For recent studied, Jacobs *et al.* (1999) investigated the effect of Pt/KL zeolite catalysts preparation method, by using incipient wetness impregnation (IWI), ion exchange (IE) and vapor-phase impregnation (VPI) method. It was observed that IWI and VPI methods provide the majority of Pt particles located inside the channels of the L zeolite. However, the VPI catalysts yield smaller Pt particles than those in the catalysts prepared by the IWI method. So the preparation methods of catalysts can greatly influence the size and morphology of the Pt particles inside the channels of the zeolite. These morphology variations have strong effects on the stability of the catalyst under both sulfur-free and sulfur containing feeds. Therefore, VPI is an effective preparation method to enhance aromatization performance. They also studied the additional of rare earth as promoter, by adding Tm as promoter had important consequences on the aromatization performance of Pt/KL catalysts (which determine by EXAFS analysis and DRIFTS of adsorbed CO), where Tm resulted in a catalyst with higher Pt dispersion, increased the activity of catalysts and Tm acts as a sulfur getter, so it delays the poisoning of Pt.

Anyhow, other preparation methods such as co-impregnation of Pt, it can be found that Tm will hinder dispersion of Pt, demonstrated by DRIFTS of adsorbed CO. Tm can caused blocking of L zeolite channels, so cause a higher deactivation rate under reaction.

Beside the deactivation due to the sulfur poisoning is the main cause of the decrease in activity and selectivity of the Pt/KL catalysts for the aromatization of the n-alkane. The effect of water vapor to the Pt/KL catalysts is also interesting to study.

It has been observed by the Japanese group that the Pd-zeolite catalysts for selective catalytic reduction of nitrogen monoxide by methane can be deactivated by the water vapor (Ohtsuka and Tabata, 1999). They investigated the gradual decrease in NO<sub>x</sub> conversion in the presence of water vapor. The CO adsorption measurement revealed that Pd-ZSM-5 tested in the presence of water suffered the severest decrease in Pd dispersion. Raman measurement clearly indicated the PdO is formed on the deactivated samples. These results suggested that deactivation of Pd-zeolite is caused by Pd agglomeration to form PdO and water vapor promotes the agglomeration.