



## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Catalyst for n-Octane Aromatization

Paál (1980) discussed on aromatization of hydrocarbon with more than six carbon atoms. This reaction is thermodynamically even more favorable than the reaction of n-hexane, because these hydrocarbons offer more than one way of cyclization. In case of n-octane, two octatriene intermediates may be formed, via 1,3,5-octatriene would lead to ethylbenzene, and 2,4,6-octatriene would lead to o-xylene. The dehydrogenation of the latter will give octatetraene, which, in turn to styrene. The o-xylene/ethylbenzene ratio increased, with increasing the hydrogen pressure. He also founded effect of other variables, which can lead to increasing of o-xylene/ethylbenzene ratio, such as decreasing of Pt loading, increasing of tin addition, the poisoning of the catalyst with thiophene.

The conventional catalyst for octane aromatization is a bifunctional catalyst. Although the bifunctional catalyst showed an excellent activity to do aromatization, hydrogenolysis occurred at the same time. This leads to the loss of aromatic selectivity. A monofunctional catalyst (has only metal site) has been considered as it can reduce this undesirable side reactions. Bernard (1980) studied the Pt supported on a series of supports, such as KL, NaX, NaY, NaOmega and NaMordenite for n-hexane aromatization. It was found that at 733 K and 1 atm, the most active catalysts were Pt/NaX and Pt/KL. These two catalysts had a very high selectivity to aromatics. Thereafter many researchers have tried to investigate the differences in the aromatization performance of Pt/KL or Pt/support catalysts.

Zheng *et al.* (1996) compared the performances of Pt/ $\beta$  (acidic zeolite catalyst) and Pt/KL (non-acidic zeolite catalyst) on n-hexane aromatization. They found that at the calcination temperature of 300 °C, Pt particles on Pt/KL zeolite were smaller than that on Pt/ $\beta$ , resulted in the better activity. Since n-hexane aromatization activity increased with decreasing Pt particle size, Pt/KL exhibited much superior aromatization performance than Pt/ $\beta$ .

Sivasanker and Padalkar (1988) experimented the effects of acidic catalyst and non-acidic catalyst. The dehydrocyclization of n-hexane, n-heptane and n-octane were carried out over acidic and non acidic platinum-alumina catalysts. For the first two feeds, the acidic and non-acidic catalysts had nearly identical dehydrocyclization activity. However, in case of n-octane, the activity of acidic catalyst was greater than the non-acidic catalyst. As a result, the metal function was the critical parameter of a reforming catalyst valid for C<sub>6</sub> and C<sub>7</sub> alkanes, whereas both metal site and acid site were important part for n-octane aromatization.

Many researchers have accepted that Pt/KL is very suitable to n-hexane aromatization. Newer studies have tried to discover a suitable catalyst for longer alkane, such as n-octane aromatization. The recent work, conducted at the University of Oklahoma and the Petroleum and Petrochemical College, had attempted to apply Pt/KL on n-octane aromatization (Sackamduang *et al.*, 2000). Pt/KL and Pt/CeKL catalysts were studied on n-hexane and n-octane aromatization. These catalysts were prepared by incipient wetness and vapor-phase impregnation methods. They founded that VPI catalysts exhibited much higher conversion, aromatic selectivity, and stability than IWI catalysts did for both C<sub>6</sub> and C<sub>8</sub> aromatizations. Furthermore, the activity of C<sub>8</sub> aromatization was much lower than C<sub>6</sub> aromatization.

## 2.2 Existing Catalyst for n-Octane Aromatization

A commercial catalyst for n-octane aromatization is CrI<sub>x</sub>/La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> (Ehwald *et al*, 2000). The catalyst was prepared by wet impregnation method. They performed reaction testing at 550 °C and 0.25 gram catalyst was used. The results showed that the conversion at 2 hours on stream was about 55 %, and the aromatics selectivity was about 80 %.

### 2.3 Catalyst Preparation

Supported-metal catalysts are usually prepared by impregnation or ion exchange techniques on a high surface area support. Catalysts prepared by these techniques have the metal dispersed on the surface of the support as small crystallites. These crystallites are usually 8 to 100 Å in diameter, depending on the preparation method. The desirable metal loading was presented in the form of small cluster located inside pore of support. The smaller the metal cluster, the higher of catalyst activity is.

The typical techniques to load a metal are ion exchange (IE), incipient wetness impregnation (IWI), and vapor phase impregnation (VPI) methods. Each method results in different distribution size and location of metal. Catalysts prepared by VPI method were found to be more active, selective, and stable than IWI and IE catalysts.

In 1998 Zheng *et al.* reported that VPI technique was used to control the pore size of zeolite and improve the shape-selectivity of zeolite catalyst. They used VPI technique to modify supported KL zeolite for n-hexane aromatization. After the investigation, he founded new basic sites such as K<sub>2</sub>O appeared, and these sites promoted the interaction between the zeolite support and Pt metal. In addition, these new basic sites also improved catalyst activity and enhanced sulfur tolerance.

Jacobs *et al.* (1999) synthesized Pt/KL catalysts by different methods including IE, IWI and VPI, and investigated the effect of metal loading. The catalysts were pretreated at two different reduction temperatures at 400 and 500 °C in order to investigate the sensitivity of each catalyst to thermal treatment. All catalysts showed high dispersion, and H/Pt ratio was greater than unity. And FTIR of adsorbed CO showed the characteristic dispersion and location of Pt cluster by each method. IE catalysts were found to have a high fraction of Pt cluster located at external surface of L zeolite, and were the most sensitive to thermal treatment. These catalysts were easily deactivated by coke formation. IWI and VPI catalysts showed a majority of Pt cluster located inside channel of zeolite L. After thermal treatment, IWI catalysts were damaged by half of their activity, while the performance of VPI catalysts maintained. Furthermore, different VPI methods were

studied, including under moderate vacuum and a helium flow. Both of them showed similar results as when high vacuum was applied. Therefore, the possible scaling up process would involve VPI technique with the combination of including moderate vacuum or operating in helium atmosphere.

Lertrojanochoosit and Thongsrikate (2000) also deliberated about n-hexane aromatization on Pt/KL. In their works, they synthesized catalysts via two different methods: vapor phase impregnation method and incipient wetness impregnation method. The results showed the same trend as other works, that is, VPI catalysts had a high dispersion with a majority of small Pt clusters inside the L zeolite channels. This morphology resulted in high catalyst stability and selectivity to aromatic formation, even in the presence of sulfur, in contrast to IWI, which displayed lower aromatics selectivity and deactivated very rapidly in the presence of sulfur.

## 2.4 The Addition of Rare Earth

Though the Pt/KL showed the excellent performance to n-hexane aromatization, it is highly sensitive to sulfur. Rare earth addition can enhance the sulfur tolerance of the catalysts (Fang *et al.* 1996). The Pt/KL catalysts were modified by  $Tm_2O_3$ . The catalysts containing thulium ranging from 0.05 to 0.2 wt % showed higher aromatization activity and higher stability when compared to the unmodified Pt/KL catalysts. However, they also concluded that high content of thulium might block up the channels of L-zeolite.

Not only was Thulium studied, but series of rare earth were also prepared on L-zeolite in order to investigate the sulfur tolerance enhancement. Gd, Tb, Dy, Tm, Yb and Lu loaded catalysts were prepared by impregnation on the L-zeolite support. Their results revealed that those added rare earth elements affected the electron donation of Pt particles, and blocked the accumulation of active Pt particles. Thus, rare earth addition can remarkably increase the ability of sulfur resistance, and also increase aromatics selectivity of catalysts (Fang *et al.* 1997).

## 2.5 Catalyst Deactivation

In general, the catalyst can be deactivated in 3 ways: sintering, poisoning and fouling.

### 2.5.1 Catalyst Deactivation by Sintering

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

Powerful tools were used to study the morphological change in catalyst resulting for thermal treatment ( Alvarez and Resasco, 1996). The series of Pt/L zeolites and Pt/Mg(Al)O had been investigated. The combination of temperature programmed reduction (TPR) and transmission electron microscopy (TEM) measurement showed that a high calcination temperature 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. It was indicated that during the catalyst preparation, a large fraction of Pt species was trapped inside the bulk of the support and came out to the surface after a oxidation/reduction cycle at only high temperature. Corresponding to Lertrojanochoosit and Thongsrikate (2000), it was 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.

### 2.5.2 Catalyst Deactivation by Poisoning

The most usual type of catalyst poisoning is caused by an impurity, which presents in the feed stream. The impurity can interact with catalyst faster than the feed, so the loss of active site occurred. This phenomenon is so called fall-off in activity of the catalysts. Poisoning can occur in both permanent and temporary conditions. Operation, without poisoning required a sophisticate removing impurity

process, is not suitable for industrial processes. Therefore, the impurity tolerance enhancement of catalyst is widely concerned.

Vaarkamp *et al.* (1992) studied the effect of sulfur poisoning on Pt/KL catalyst. The fresh and spent catalysts were characterized by EXAFS and H<sub>2</sub> chemisorption. The results showed the agglomeration of Pt metal after catalyst were exposed to sulfur. Furthermore, the activity of catalysts was greatly decreased.

### 2.5.3 Catalyst Deactivation by Fouling

The most typical fouling process are the carbonaceous deposit or coking occurred in processing of petroleum and organic industrials. Operation under high pressure can improve carbonaceous resistance by reducing polyunsaturated coke precursor.