



## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Catalyst for n-Octane Aromatization

The conventional catalyst for alkane aromatization is bifunctional catalyst. Although the bifunctional catalyst showed excellent activity to aromatics, but hydrogenolysis occurred at same time. This leads to the loss of aromatics selectivity. Monofunctional catalyst (has only metal site) was considered due to it can reduce this undesirable side reaction. Bernard (1980) studied the Pt support on a series of monofunctional catalyst, such as KL, NaX, NaY, Na-Omega and Na-Mordenite, for n-hexane aromatization. He founded 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. After that many researcher try to investigate the differences in the aromatization performance of Pt/KL or Pt/non-acidic catalyst.

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 to o-xylene. The dehydrogenation of the latter gave octatetraene, which, in turn to styrene. The o-xylene/ethylbenzene ratio increased at higher hydrogen pressures with platinum on alumina. He also founded effect of another 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.

Sivasanker and Padalkar (1988) experimented 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 for 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.

Zheng *et al.* (1996) compared the performance of Pt/ $\beta$  (acidic zeolite catalyst) and Pt/KL (non-acidic zeolite catalyst) to n-hexane aromatization. They found that at the calcination temperature of 300°C, Pt particles on Pt/KL zeolite were smaller than on Pt/ $\beta$  resulting in the better activity. Since n-hexane aromatization activity increased with decreasing Pt particle size, Pt/KL exhibited much superior aromatization reaction than Pt/ $\beta$ . Furthermore, in 1998, Zheng *et al.* reported that VPI was used to control the pore size of zeolite and to improve the shape-selectivity of zeolite catalyst. After investigation they found that new basic sites such as K<sub>2</sub>O appear which promoted the interaction between zeolite support and Pt metal.

Jacobs *et al.* (1999) synthesized Pt/KL catalysts by three 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 greater than unity. IE catalysts were found to have a high fraction of Pt cluster located at external surface of L zeolite and were the most sensitivity 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 catalyst 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 operate in helium atmosphere.

The recent works of Resasco *et al.* (1999,2000) also prepared catalysts for n-hexane and n-octane aromatization by impregnation method. In their works, they synthesized catalysts via two different methods, vapor phase impregnation method and incipient wetness impregnation method. The result showed the same trend as other work, VPI catalyst 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 with IWI, which showed lower selectivity and more rapid deactivation.

Many researches have accepted that Pt/KL is very suitable to n-hexane aromatization. Newer studies had tried to discover suitable catalysts 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 to n-octane aromatization (Sackamduang *et al.*, 2001). Pt/KL and Pt/CeKL catalysts were studied on n-hexane and n-octane aromatization. These catalysts were prepared by IWI and VPI methods; they founded that VPI catalysts exhibited much higher conversion, aromatic selectivity and stability than IWI catalysts for both C6 and C8 aromatization. In 2002, they observed that Pt/KL had the highest catalytic activity among the other supports and the appropriate amount of Pt loading was 1 % (Chanajaranwit *et al.*, 2002).

Commercial catalyst for n-octane aromatization is  $\text{CrO}_x/\text{La}_2\text{O}_3/\text{ZrO}_2$  catalyst. (Ehwald *et al.*, 2000). The catalyst was prepared by wet impregnation method. They performed reaction testing at 550 °C and used 0.25 g catalyst. The results showed that conversion at 2 h on stream was about 55% and aromatic selectivity was about 80%.

## 2.2 Catalyst Deactivation

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

### 2.2.1 Catalyst deactivate by sintering

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 reduction programmed (TPR) and electron microscopy (TEM) measurement showed that a high calcination 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.

### 2.2.2 Catalyst deactivation by poisoning

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 occurred. 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 causes the agglomeration of Pt metal and decreased activity after catalysts were exposed to sulfur (Vaarkamp *et al.*, 1992).

### 2.2.3 Catalyst deactivation by fouling

The most typical of fouling processes is the carbonaceous deposit or coking, those forms on most catalysts used in processing of petroleum and organic industrials. Operation under high pressure can improve carbonaceous resistance by reducing polyunsaturated coke precursor.

## **2.3 Catalyst Regeneration**

Besides the development of sulfur-resistant catalysts, the understanding of regeneration process is an important issue in industries.

Researcher at British Petroleum Co. (Crowson *et al.*, 1976) patented a regeneration of platinum group metal zeolite catalysts by using chlorine. They regenerated the deactivated catalysts by using (a) a burn off at 500°C (b) a treatment with inert gas, 0.5-20% vol O<sub>2</sub> and 5-500 ppm vol Cl<sub>2</sub> at 400°-500°C (c) a purge and

(d) a reduction in a stream of  $H_2$  at  $200^{\circ}$ - $600^{\circ}C$ . They observed that the treatment with inert gas was believed to redistribute the Pt groups metal and restore catalyst activity in a way that burn-off alone cannot do.

Burbidge and Rees (1980) at the same company above patented a process for the dispersal and redispersal of a platinum group metals comprising in a stream of inert gas in order to regenerate the catalyst that become deactivated by deposition of carbonaceous material during processing.

Bernard and Breysse (1985) , researcher at Elf France Co., patented the invention related to a process for the regeneration of an aromatization catalyst containing a metal Group VIII supported on zeolite, the process being such that the catalyst is subjected to combustion, and then to oxychlorination (oxychlorination by heat treatment by mixtures of air and chlorine or, further, by chlorinated compounds such as  $CCl_4$  in the presence of air). According to the invention, the oxychlorination step is followed by a hydration step, whereby the hydration step the catalyst is cooled by an air stream containing water at temperature not exceeding  $200^{\circ}C$ , the weight proportion of said water with respect to the weight of catalyst being about 10%. The treatment according to the invention increases the selectivity of the regenerated catalyst.

Exxon researchers (Fung, 1992) patented the method of regenerating a Group VIII noble metal deactivated catalyst which has been contaminated with coke during reforming process. The method comprises (a) burning off the coke from the catalyst, (b) redispersing the noble metal on the support; (c) chemically reducing the catalyst: the redispersing step(b) being carried out by contacting the catalyst in a reaction vessel with a halogen or halide-containing gas and carbon dioxide gas, the amount of carbon dioxide being maintained at a partial pressure of at least 2 kPa in the reaction vessel substantially throughout the period in which the catalyst is in contact with the halogen or halide-containing gas. They observed that the presence of carbon dioxide in the redispersion step of the catalyst's regeneration and reactivation process enhances the activity and hence the performance of the catalyst. The method according to the invention has particular benefits for the regeneration of Group VIII containing catalysts supported by a zeolite material.

Sugimoto *et al.* (1993) found the novel regeneration method of the used Pt/KL zeolite by using the treatment of KL zeolite with chlorotrifluoromethane ( $\text{CF}_3\text{Cl}$ ) to increase the catalytic activity for the aromatization of  $\text{C}_6$  feedstock. The deactivation of the Pt/FKL was caused by sintering of the platinum particles, loss of halogen atoms and coke formation during aromatization of the  $\text{C}_6$  feedstock. It was found that the catalyst performance of the Pt/FKL was restored by decoking in flowing  $0.005\%\text{CCl}_4 + 2\%\text{O}_2 + 97.995\%\text{N}_2$  from room temperature to 773K, followed by treatment in flowing  $0.8\%\text{freon 112} + 10\%\text{O}_2 + 89.2\%\text{N}_2$  at 773K. From the results of IR spectra of chemisorbed CO and terminal OH groups, it is suggested that the most important goal of regenerating the used Pt/FKL is to disperse the platinum particles and restore their electronic state.

Recently, Exxon researchers (Fung *et al.*, 1998) observed the method of regenerating a deactivated reforming catalyst comprising a type L zeolite containing a Group VIII noble metal. The regeneration to enhance dispersion can be done by a method involving (1) contacting the catalyst with oxygen and water at elevated temperature, (2) contacting the catalyst at elevated temperature with a source of chlorine such as HCl or  $\text{Cl}_2$ , and preferably oxygen and water, (3) contacting the catalyst at elevated temperature with oxygen and optionally water, and (4) contacting the catalyst at elevated temperature with hydrogen and optionally water to reduce the catalyst. Preferably the noble metal is platinum. These inventions effectively regenerated to enhance the catalytic activity and activity maintenance properties by a process whereby coke deposits are removed from the catalyst, the dispersion of the metal is enhanced by an oxychlorination procedure. The procedure leads temporarily to excess chlorine on the catalyst surface. The excess chlorine is then removed from the catalyst and the noble metal is stabilized on the catalyst surface.

Afonso *et al.* (1997) studied on the influence of heating rate (2-15  $^\circ\text{C}/\text{min}$ ), temperature (coke oxidation, 350-600  $^\circ\text{C}$ ) and time (2-15 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. Pretreatment with  $\text{H}_2$  is 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).