

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Catalyst for n-Octane Aromatization

Ever since the discovery of Pt/KL in 1980 by Bernard, controversy has arisen as to if and why Pt/KL is unique for the aromatization of n-hexane reaction. Here are roughly five different possible explanations attesting to the uniqueness of Pt/KL for aromatization, and these explanations offer either geometric or electronic interpretations:

- (a) *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.
- (b) *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.
- (c) *Electronic Effects*: The high activity and selectivity of Pt/KL catalysts for aromatization derived from a unique electronic structure. Larger, softer, cations like  $\text{Ba}^{+2}$ , with diffuse charge, would allow greater donation of electron density from zeolite oxygen anions to the Pt metal, whereas smaller, harder, cations like  $\text{Mg}^{+2}$ , 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 ( $\text{Mg} > \text{Ca} > \text{Ba}$ ).
- (d) *Inhibition of Bimolecular Pathways*: The uniqueness of Pt/KL catalysts with the ability of KL's microporous structure to inhibit bimolecular reactions leading to the formation of coke on the surface of the Pt clusters.

(e) *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.

For the high activity and selectivity, most authors agree that an effective catalyst should have as much Pt as possible inside the channels of the zeolites.

Jacobs *et al.* (2001) Pt/KL catalysts were synthesized 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 to investigate the sensitivity of each catalyst to thermal treatment. All catalysts showed high dispersion and H/Pt ratio greater than unity. And from 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 sensitivity to thermal treatment. These catalysts deactivated easily 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 difference VPI method were studied, including moderate vacuum and a helium flow. Both of them showed similar result as including high vacuum. Therefore, the possible scaling up process is deal with VPI technique including moderate vacuum or operate in helium atmosphere.

Jacobs *et al.* (1999) also prepared catalysts for n-hexane and n-octane aromatization by impregnation method. In theirs works, they synthesized catalysts via two different method, 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.

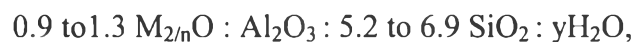
Although vapor phase impregnation (VPI) method was found to result in the highest Pt dispersion and maximum incorporation of Pt inside the channels of the zeolite compared to any other method. Jongpatiwut *et al.* (2003) showed that on the Pt/KL catalyst prepared by the VPI method (optimum performance in n-hexane

aromatization) the activity for n-octane aromatization at 500 °C and 1 atm was low and it quickly dropped after a few hours on stream. The product distribution obtained from the n-octane conversion showed benzene and toluene as the dominant aromatic compounds, with small quantities of ethylbenzene (EB) and o-xylene (OX), which are the expected products from the direct closure of the six-member ring. The analysis of the product evolution as a function of conversion indicated that the benzene and toluene are secondary products resulting from the hydrogenolysis of ethylbenzene and o-xylene. Diffusional effects play a significant role in determining this product distribution. Since ethylbenzene and o-xylene are produced inside the channels of the zeolite, they are hydrogenolysed before they can escape. By contrast, on the Pt/SiO<sub>2</sub> catalyst used for comparison, ethylbenzene and o-xylene were the dominant aromatic products, although the overall aromatization activity was much lower than on the Pt/KL catalyst. The rapid deactivation found in the aromatization of n-octane on Pt/KL compared to that of n-hexane can also be explained in terms of the diffusional effects. The C<sub>8</sub>-aromatics produced inside the zeolite diffuse out of the system with much greater difficulty than benzene. Therefore, they form coke and plug the pores to a greater extent than benzene. Temperature programmed oxidation and sorption studies on spent samples demonstrate that the degree of pore blocking is much higher during n-octane aromatization than during n-hexane aromatization.

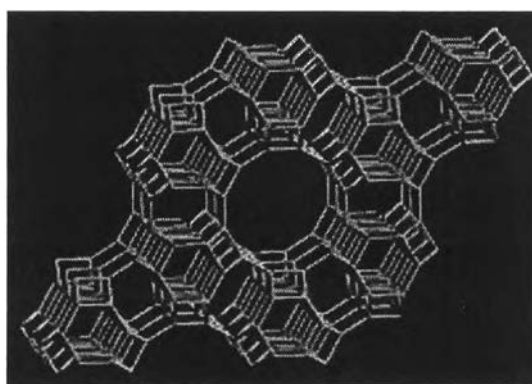
Therefore, the idea of enhancing life, activity, and selectivity of catalysts in n-octane aromatization has been discussed. Catalysts of a small particle size have advantages over larger particle size, such as those produced for reactions involving hydrocarbon conversions because of their enhanced ratio of surface area to mass, high diffusion rates and reactivities, and resistance to deactivation by pore plugging and surface contamination.

## **2.2 Structure of L Zeolite and Synthesis Method**

The crystal structure of L zeolite was determined initially by Barrer and Villiger. It has a 12 membered ring structure, one-dimensional pore of about 0.71 nm aperture leading to cavities of about 0.48×1.24 ×1.07 nm, and its Si/Al ratio is typically 3.0. The formula in terms of oxide is



where M represents an exchangeable cation of valence n, and y represents a value within the range from 0 to 9. As shown in Figure 2.1, the framework of L zeolite can be visualized as a linear assembly of corrugated four-ring ribbons aligned parallel to the c-axis, which cross-link to produce parallel 12-ring and 8-ring channels (Treacy, 1999).



**Figure 2.1** Schematic of L zeolite structure.

Preparations of the L zeolite have been reported mostly as patents by various investigators, with or without using organic templates, claiming different morphologies. Most of studies dealing with L zeolite synthesis so far have been conducted at relatively low temperature ranging from 270 to 403 K in a  $\text{K}^+$  ionic system and usually it took 3 to 10 days to obtain a highly crystalline product. Furthermore, careful control of the substrate mixture composition was a prerequisite to avoid coprecipitation of unwanted zeolite W or T phase.

Ko and Ahn (1999) found that substantial reduction in synthesis time was achieved for L zeolite crystallization by attempting a hydrothermal synthesis at elevated temperature of 443 K in a  $\text{Na}^+/\text{K}^+$  mixed alkali system. Highly crystalline L zeolite crystals were obtained in a reproducible manner without zeolite W or T phase impurities at the substrate gel composition of  $5.4\text{K}_2\text{O}-5.7\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-30\text{SiO}_2-500\text{H}_2\text{O}$ . L Zeolite could be obtained in high purity at the optimum  $\text{Na}_2\text{O}/(\text{K}_2\text{O}+\text{Na}_2\text{O})$  ratio of around 0.5, whilst zeolite W was formed when the

$\text{Na}_2\text{O}/(\text{K}_2\text{O}+\text{Na}_2\text{O})$  ratio was more than 0.66. The chemical analysis of the L zeolite crystals obtained showed that the most potassium hydroxide with a smaller amount of sodium hydroxide was incorporated in the structure regardless of NaOH/KOH used. The L zeolite synthesized was typical clam shaped crystals of domed basal plane with the mean diameter of 1.4 microns and structurally stable up to 1073 K, however, the surface area (BET) of the L zeolite exhibited a substantial decrease at calcination temperatures higher than 873 K. Physico-chemical properties of the L zeolite prepared as a catalyst or as a support were evaluated using the probe reactions of toluene alkylation and n-octane aromatization. In toluene alkylation, an-acid form H-L catalyst showed the fast deactivation due to one-dimensional pore structure being blocked by the coke formed at the strong acid sites, despite high catalytic activity at the beginning of the reaction. In addition, relatively high amounts of trimethylbenzene and diethylbenzene were formed due to a large 12-membered ring pore structure of the zeolite L. Pt/NaKL catalyst prepared showed a high conversion of n-hexane and high selectivity to benzene in n-hexane aromatization reaction, far exceeding the performance of Pt/mordenite.

Verduijn *et al.* (1991 and 1995) found that potassium zeolites of type L in which the crystals are very flat cylinders of “hockey puck” or “coin” shape may be prepared by adjusting the  $\text{K}_2\text{O}/\text{SiO}_2$  and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and including in the mixture from which the zeolite is crystallized a small amount of divalent cation such as magnesium or barium. The addition of these metals also suppress unwanted zeolite W formation even when synthesis conditions favour formation of other zeolites. The resulting zeolite has a short channel length and is particularly useful as a base for aromatization catalysis. It can be seen that the improved stability of the “hockey puck” catalysts give a greater selectivity and yield and also allows for greatly increased cycle length compare with the reference catalyst of KL type. In the same year they showed that processes for reforming, and in particular aromatizing, hydrocarbons from a petroleum source may be carried out by conducting the hydrocarbons with a catalyst of a zeolite KL impregnated with a metal promotor such as platinum, in which the zeolite crystals are hockey puck shape. The processes have a good yield and selectivity for the desired reformed products and the catalyst is

stable, is associated with a low rate of coke formation, and has a long catalytically active life before regeneration is required.



**Figure 2.2** SEM micrograph of hockey puck KL zeolite with the size of 40,000 times (Verduijn, 2001).

Nowadays numerous papers and patents have been published on the argument and in several conventional synthesis routes, successful use of microwaves has been proved. Microwave irradiation is more efficient for transferring thermal energy to a volume of material than conventional thermal processing which transfers heat through the surfaces of the material by convection, conduction, and radiation. The oscillating electromagnetic field, which is generated by microwaves, interacts with the dielectric properties of materials leading to rotation of molecular dipoles and subsequent energy dissipation as heat from internal resistance to that rotation.

A number of publications have recently appeared on microwave zeolite synthesis to reduce crystallization time by rapid heating of the reaction mixture. Preparation of zeolite NaA, zeolite Y, and ZSM-5 has been performed with reduction in crystallization time from several hours to few minutes by combining pressure with microwave heating in suitable autoclaves.

Slangen *et al.* (1996) found that in the microwave synthesis of zeolite NaA ageing of the synthesis mixture is a prerequisite for fast crystallization. The rapid heating in microwave synthesis requires better preparation of the synthesis mixture

compared to conventional synthesis methods. Sufficiently aged mixtures can yield NaA, with crystal size ranging from 0.1 to 0.3 micron, after 1 minute in the microwave.