



CHAPTER II

LITERATURE REVIEW

2.1 Catalysts for Aromatization of n-Alkane

In 1980, it was reported that Pt clusters in alkaline LTL zeolite are highly active and selective for the dehydrocyclization of n-hexane into benzene (Bernard, 1980). Since Pt/KL catalyst has the uniqueness for aromatization which is outlined briefly below (Davis, 1993):

2.1.1 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.

2.1.2 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.

2.1.3 Electronic Effects

The high activity and selectivity of Pt/KL catalysts for aromatization derived from a unique electronic structure. Larger, softer, cations like 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 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 ($\text{Mg} > \text{Ca} > \text{Ba}$).

2.1.4 Inhibition of Bimolecular Pathways

The uniqueness of Pt/KL catalysts with the ability of KL's microporous structure to inhibit bimolecular reactions leads to the formation of coke on the surface of the Pt clusters.

2.1.5 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.

As well as aromatization of n-octane, it was observed that high dispersion of Pt clusters inside the channel of KL zeolite is the important factor for the aromatization performance (Jongpatiwut *et al.*, 2003). To prepare a Pt/KL catalyst with high dispersion of Pt clusters inside the channel of KL zeolite, vapor phase impregnation (VPI) is the best preparation methods compared to both incipient wetness impregnation (IWI) and ion-exchange method (IE). The Pt/KL catalyst prepared by ion exchange method resulted in high fraction of Pt particle external to the L zeolite and rapid deactivation by coke formation. IWI method will provide the Pt/KL catalyst with Pt clusters inside the channels; however, at high temperature reduction treatment, the growth of Pt clusters inside the channel was displayed. For Pt/KL catalyst prepared by VPI method, the Pt clusters are located inside the channel and more resistant to agglomerate at high temperature (Jacob *et al.*, 2001; Jacob *et al.*, 1999).

Although Pt/KL catalysts prepared by vapor phase impregnation (VPI) provide very high Pt dispersion located inside the channels of the zeolite, the activity for n-octane aromatization was still low and quickly dropped after a few hours on stream (Jongpatiwut *et al.*, 2003; Jongpatiwut *et al.*, 2005). The product distribution obtained from the reaction showed benzene and toluene as major aromatic products, with small quantities of ethylbenzene (EB) and o-xylene (OX) which are the expected products from a direct six-membered ring closure. Since the pore size of the KL zeolite is 0.71 nm, larger than the critical diameter of EB but smaller than that of OX, OX diffuses much slower than EB. As a result, OX would preferential convert to benzene and toluene before escaping from the pore of zeolite. In the study, it was proposed that pore length of the zeolite should have a great impact on product distribution and catalyst life. The idea of short channel KL zeolite has been previously discussed by Treacy (1999) to minimize the problem of Pt

entombment due to Pt agglomeration and coking. Furthermore, the zeolite with small particle size provides advantages over the zeolite with large particle size by enhancing the ratio of surface area to mass, diffusion rates, and resistance to deactivation by pore plugging.

2.2 The Structure of LTL Zeolite

The crystal structure of zeolite L was determined initially by Barrer and Villiger (Barrer and Villiger, 1969). The structure of zeolite L is hexagonal (space group P6/mmm) with unit cell constants $a=18.4 \text{ \AA}$ and $c=7.5 \text{ \AA}$. The linkages of the cancrinite cages (ϵ -cages) by double 6-rings (D6R) led to the formation of column in the c-direction. And thus give rise to 12-membered rings with a free diameter of 7.1 \AA of one dimensional pores leading to cavity of about $0.48 \times 1.20 \times 1.07 \text{ nm}$ as shown in Figure 2.1. Typically, Si/Al ratio in the framework is 3.0 (KO and Ahn, 1999; Tsapatsis *et al.*, 1994)

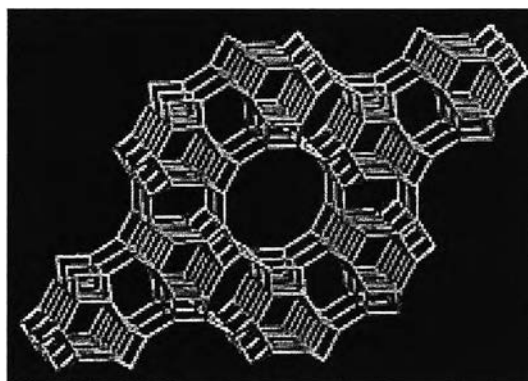


Figure 2.1 Schematic of L zeolite structure.

The formula in terms of oxide is $0.9 \text{ to } 1.3\text{M}_{2/n}\text{O} : \text{Al}_2\text{O}_3 : 5.2 \text{ to } 6.9\text{SiO}_2 : y\text{H}_2\text{O}$, when M represents an exchangeable cation of valence n, and y represents a value within the range from 0 to 9 (Breck and Nancy, 1965).

2.3 Synthesis of KL Zeolites

The most often observed shape of zeolite L crystal is cylindrical with the channels running parallel to the central axis and it was found that using cylindrical shape of KL zeolites as a base of catalyst for alkane aromatization showed a remarkable improved activity life time over extended periods of time, much greater than that achieved with catalysts using the clam-shaped KL zeolite. The typical composition of gel mixture for synthesis KL zeolite with cylindrical shape having the particle size of 2 to 2.5 micron is $2.62\text{K}_2\text{O} : \text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 160\text{H}_2\text{O}$. The sources of the starting material are potassium hydroxide, aluminium hydroxide, Ludox HS-40, and water. Using the crystallization temperature at $150\text{ }^\circ\text{C}$ for 72 h to bring about the crystallization. In addition, the different morphologies of KL zeolites were obtained by adjusting the gel composition. For example, increasing the amount of K_2O up to 3.5 moles resulted in the clam-shaped KL zeolite or increasing or decreasing the amount of K_2O to 2.21 moles gave the long channel length of KL zeolite (Wortel, 1985; Ruiz et al., 2002; Ko and Ahh, 1999).

Verduijn (1987) showed that adding of small amount of added metal such as magnesium, calcium, barium, cobalt, zinc, chromium, manganese or nickel can reduce the crystal size of KL zeolite and result in zeolite L with flat basal planes. Moreover, these metals can suppress unwanted zeolite W or erionite formation during the crystallization. After that, Verduijn found that typical ratio of $2.62\text{K}_2\text{O} : 0.5\text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 160\text{H}_2\text{O}$ with a suitable quantity of divalent cation can give the L zeolite in which crystals are very flat cylinders of hockey puck or coin shape. The crystals are coin or hockey puck shaped and have a relatively large diameter and short length. The length of a crystal is a measurement of the outer edge of the crystal perpendicular to the basal plane containing the diameter. When the length/diameter ratio is 0.2-0.5 the crystal shape is termed as hockey puck as shown in Figure 2.2. When the length/diameter is less than 0.2 the shape is termed as coin. The results from the catalytic testing by aromatization of mixed C6 showed that the 0.6 wt% Pt supported on zeolite having a short channel length gave a better yield and selectivity of benzene, and also enhanced cycle length compared with the zeolite having a long channel length (Verduijn, 1991; Verduijn, 2001).

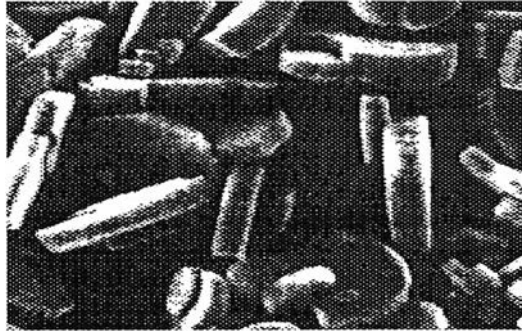


Figure 2.2 SEM image of hockey puck KL zeolite with the size of 40,000 times (Verduijn *et al.*, 2001).

To reduce the particle size of zeolite, crystallization conditions and composition-dependent parameters which are alkalinity, dilution, ratio between Si and other tetrahedron-forming elements, template concentration, ionic strength, and presence to crystallization poisons were concerned (Renzo, 1998). In 1996, Gontier and Tuel showed that applying the aging period to crystallization decreases the crystal size of titanium silicalite-1 (TS-1) to about 6-7 μm compared to no applying ageing period that resulted in the crystal size about 17-18 μm . Moreover, it was observed that stirring the gel during crystallization strongly decreases the particle size of TS-1. In 2001, Li *et al.* found that ageing process can decrease the crystal size of TPA-silicalite-1 by enhancing the rate of nucleation and produced a larger number of nuclei. Moreover, it was reported that incorporation of colloidal L zeolite seed into the gel before crystallization can also reduce the product particle size (Verduijn *et al.*, 2001).

Normally, many research groups synthesized KL zeolite by conventional-hydrothermal treatment. In this method, it takes a long crystallization time because the heat transfer is from an oil bath or an electrical oven to the reagents and resulted in lower heating rate. Employing microwave radiation was found to be useful in manufacturing of microporous crystalline materials because it gives a higher heating rate due to volumetric heating, resulting in homogeneous nucleation and providing crystalline materials in a short crystallization time (Chu and Dwyer, 1988). Furthermore, it is a clean and economical heating system (Romero *et al.*, 2004).

Slang *et al.* (1997) found that aging is prerequisite for the successful rapid synthesis of NaA in microwave synthesis and this is contrast to the conventional synthesis. When the synthesis mixture has been aged sufficiently, the synthesis of NaA can be done in 1 min by microwave heating, leading to small crystals with a relatively homogeneous crystal size distribution. In addition, Park and Komarneni (1998) reported that AlPO₄-11 and cloverite were successfully synthesized by microwave-hydrothermal heating. The crystallization time of these molecular sieves was greatly shortened by using the microwave heating system compared with the conventional heating system.

2.4 The Effect of Additional Promoter into Pt/KL Catalyst

In naphtha reforming, a number of promoter metals have been used as additives for Pt catalysts to increase catalyst lifetime by hampering coking and to improve selectivity of desired products. The most frequently used catalysts in naphtha reforming processed are Pt-Re, Pt-Ir, and Pt-Sn. Re and Ir are the promoters having catalytic properties on their own, whereas Sn is catalytically inactive. The addition of Sn to monometallic catalysts can change in selectivity, inhibit hydrocracking, hydrogenolysis, hydrogenation, isomerization and coke deposition on the catalyst surface, and improve dehydroisomerization and dehydrocyclization reaction (Paal *et al.*, 1997).

Since undesirable processes in the alkane aromatization such as hydrogenolysis reaction and coke formation are known to require relatively large clusters or ensembles of adjacent metal atoms whilst desirable reaction which is aromatization can occur on single isolated atoms (Biloen *et al.*, 1977; Coq and Figueras, 1984). Therefore, to inhibit the hydrogenolysis reaction and improve the catalyst resistance to deactivation, the particle size of Pt clusters must be decreased. The active platinum surface can be diluted into smaller ensembles by the addition of an inactive species such as Sn, Au, or Pb. In 1994, Lee and Lee found that Pt-Sn/ γ -Al₂O₃ prepared by simultaneous impregnation showed a better catalytic behavior toward C₈-aromatics formation than Pt/ γ -Al₂O₃. The added Sn did not affect electronically on Pt because the mole ratio of o-xylene/ethylbenzene over various Pt-

Sn catalytic with different mole ratio of Sn/Pt was shown to be almost constant. Since it has been proposed that the alternation of the EB:OX ratio by the presence of tin in the catalyst was due to an alternation to favor the weaker C-H bonds in the -CH₂-group rather than the stronger bonds of the -CH₃ groups. Therefore, the remarkable increase in catalytic activity and selectivity of the dehydrocyclization are by the structure change of Pt by adding Sn. That is, the existence of Sn around Pt leads to the increase of the number of small ensembles composed of Pt, which causes rapid change in activity and selectivity of the catalyst.

For n-octane reforming over alumina-supported Pt, Pt-Sn and Pt-W catalysts, it was found that the addition of Sn and W increased in the activity and stability to Pt/Al₂O₃ and also beneficial changed in selectivity during n-C₈ dehydrocyclization. The results showed that Tin is the best modifier of the metallic function, because it decreases hydrogenolysis and modifies the acid function, tuning and balancing it in order to produce more cyclization to C₆ ring closure and to decrease cracking to C₃-C₅ and condensation to carbonaceous deposits. On the other hand, tungsten (W) increases the activity in hydrogenolysis of the catalyst. This can occur through the formation of hydrogen-tungsten compounds, being favored hydrogenolysis, hydrocracking, and other hydrogenation reactions (Rangel *et al.*, 2000).

However, it was found that not only does tin modify the stability and selectivity of the Pt function by ensemble effect but also does it modify the Pt function by an electronic effect. By this way, tin in metallic form (in solid solution, in small bimetallic clusters, alloyed with Pt, or as Sn²⁺ ions in intimate contact with Pt atom) gives its electron to the holes of the 5d band of platinum atoms. Of this is the case, small amounts of tin (lower than the detection limit) should affect the properties of platinum. In fact, 15 atom% of tin is sufficient to fill the hole of the 5d band of platinum. On the basis of the electronic effect, it is possible to explain the promotion effect of tin by assuming that coke precursors are not adsorbed on the surface of the doped platinum crystals, but rather they move to the support, avoiding deactivation of the active site. A lower coke formation can also occur because condensation reactions are inhibited, and lower amount of polymers are formed. For the same reason, C-C bond hydrogenolysis does not occur, again because the

hydrocarbon cannot be strongly adsorbed on the catalyst (Ertl *et al.*, 1997). In 1995, Shi and Davis showed that tin alters the property of the platinum for alkane dehydrocyclization by applying reversible alkane adsorption/desorption for the Pt-Sn-SiO₂ catalyst whereas irreversible adsorption applies for the Pt-SiO₂ catalyst. The data showed that tin causes the alkane to be bound to the metal surface less tightly than when tin is absent.

Cho and Ryoo (2004) prepared PtSn nanoparticles supported on KL zeolite (SnPt/KL) by ion exchange method and controlled the Sn/Pt ratio at 0.1, 0.2, and 0.4, respectively. They found that no pore blockage was observed when PtSn nanoparticles was formed inside the KL zeolite channel, since the amount of xenon adsorption per unit cell for the PtSn/KL catalysts was the same as that of KL zeolite. Furthermore, from EXAFS, incorporation of Sn into Pt nanoparticle could not cause an increase of particle size of Pt corresponding with no increase of the coordination number of the Pt-Sn. The chemical state of Sn in the PtSn/KL catalyst seems to be Sn²⁺ referred from the obtained Pt-Sn distance which is around 0.279 nm. The results of the XANES analysis suggested that electron transfer occurred from Sn to Pt and resulted in the significant change in the d band structure. Catalytic performance of the PtSn/KL catalyst over n-hexane aromatization was improved with mainly the Pt ensemble effect by an incorporation of tin because the formation of dehydrogenated species required for isomerization, hydrogenolysis and coke formation was suppressed, resulting in the high selectivity to benzene. Also, the change of electronic structure of the nanoparticles may affect the adsorption characteristics of reactants such as hydrogen and similarly benzene.