

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Platinum clusters in alkaline LTL zeolite are very efficient for the direct dehydrocyclization of *n*-hexane into benzene. However, they have not been as effective when the feed is *n*-octane. The product distribution obtained from the *n*-octane conversion yielded benzene and toluene as the dominant aromatic compounds, with small quantities of ethylbenzene (EB) and *o*-xylene (OX), which are the expected products of 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 preferentially convert to benzene and toluene before escaping from the pore of zeolite.

To improve the catalytic performance of Pt/KL catalyst for *n*-octane aromatization, using the KL zeolite with the short channel length as the support can improve the diffusion rate of the product out of the pore and inhibit the hydrogenolysis reaction which is occurred inside the pore of KL zeolite. Furthermore, the addition of tin (Sn) which is an inactive metal into the Pt/KL catalyst enhanced the activity and selectivity to the desired products and decreased the undesired hydrogenolysis reaction.

It was found that the particle size of KL zeolite affected the diffusion of the C8-aromatics products through of the pores. That is the larger the particle size, the higher the EB/OX ratio due to the enhanced restriction to the diffusion of OX through the zeolite channels. Moreover, it was observed that the morphology and the channel length of KL zeolites have important effects on the performance of Pt/KL catalysts used for the aromatization of *n*-octane. The effects can be interpreted in terms of the following aspects:

1. The distribution of aromatic products (ethylbenzene, orthoxylene, toluene, and benzene) is greatly affected by secondary hydrogenolysis reactions. In this regard, zeolites with longer channels and with irregular pore mouth structure prolong the residence time of C8 aromatics and increase the concentration of

benzene and toluene in the products. As a result, catalysts with very small crystal size (e.g. NCL) are preferred for producing higher C8 aromatics. In addition, the high selectivity to C8-aromatics can be obtained from the Pt/KL zeolite having more Pt located near the pore mouth.

2. The metal dispersion and distribution of metal clusters inside and outside of the zeolite channels are greatly affected by the zeolite morphology. In turn, the location of metal clusters and Pt dispersion has an important effect on the activity and stability of the catalyst. That is, the catalytic activity increases with Pt dispersion. Furthermore, catalysts with a larger fraction of small metal clusters inside the pores are more active for a longer time. The metal distribution in the zeolite is optimum with intermediate zeolite crystal size. When the crystal is too long, Pt particles can be transported outside of the zeolite during the pretreatments (i.e. reduction). In contrast, when the crystal is too small, the outer surface area dominates and a large fraction of metal particles can be deposited outside the pores.

The addition of the inactive metal (Sn) into the Pt/KL catalyst is effective for decreasing the hydrogenolysis reaction and the improvement of the activity of the Pt/KL catalyst for n-octane aromatization. The bimetallic Pt-Sn/KL catalysts exhibited the high activity, stability, and selectivity to C8-aromatics compared to the monometallic 1Pt catalyst. The activity of the bimetallic Pt-Sn/KL catalysts corresponded to the fraction of PtSn alloy phase. That is, the bimetallic Pt-Sn/KL catalyst prepared by vapor phase co-impregnation (Co1Pt1Sn) exhibited good activity compared to that prepared by sequential method because it gave the high fraction of PtSn alloy phase. Moreover, tin increased the stability of bimetallic Pt-Sn/KL by inhibition the adsorption of dehydrogenates species which are the intermediate for coke formation. The hydrogenolysis reaction which is occurred inside the pore of KL zeolite was inhibited due to the geometric and electronic effects. In case of geometric effect, the addition of tin decreases the Pt ensembles; as a result, the hydrogenolysis reaction which is occurred on the large Pt ensembles was inhibited. By electronic effect, the hydrocarbon cannot be strongly adsorbed on the metal surface; consequently, the C-C bond hydrogenolysis does not occur. In addition, it was found that the electrons transformation from tin atoms to Pt atoms causes the high selectivity of C8-aromatic products, especially for OX molecules.

In the case of using SiO_2 as a support, the addition of tin into the Pt/ SiO_2 also improved the activity and selectivity for n-octane aromatization due to the effect of the formation of PtSn alloy phase.

7.2 Recommendations

In this work, we observed that using KL zeolite having the short channel length and the addition of tin into the Pt/KL catalysts can improve the activity and the C8-aromatics selectivity for n-octane aromatization. Therefore, the combination of the short channel length with the addition of tin is an interesting study in the future. Moreover, the study of the sulfur tolerance of the bimetallic Pt-Sn/KL for n-octane aromatization is also interesting.