



## CHAPTER I

### INTRODUCTION

The aromatization of n-alkane is an important reaction to obtain high value-added products from a naphtha feedstock that is abundant in refinery operations. This reaction can be used in many industrial applications and can be carried out with both bifunctional (acid-metal) and monofunctional (only-metal) catalysts. The advantage of using monofunctional catalysts is that they are not active for isomerization paths, which typically occur on the bifunctional catalysts and result in lower selectivity to aromatics (Meriaudeau and Naccache, 1997). Platinum clusters on alkaline LTL zeolite is an efficient catalyst for the dehydrocyclization of n-hexane into benzene (Bernard, 1980) However, for n-octane aromatization, Pt/KL catalysts are not as effective as for n-hexane aromatization. Although Pt/KL catalysts prepared by vapor phase impregnation (VPI) provide very high Pt dispersion located inside the channels of the zeolite (Jacobs *et al.*, 1999; Jacobs *et al.*, 2001), the activity for n-octane aromatization was still low and quickly dropped after a few hours on stream (Jongpatiwut *et al.*, 2003). The product distribution obtained from the reaction showed benzene and toluene as major aromatics 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. Furthermore, it was found that among Pt catalysts supported on larger pore size zeolites (Pt/K-LTL, Pt/K-BEA, Pt/K-MAZ, Pt/K-FAU), the Pt/K-LTL catalyst exhibited the best performance for the aromatization of n-octane. Since Pt/K-LTL has much higher Pt dispersion inside the channel than other catalysts (Jongpatiwut *et al.*, 2005).

To improve the performance of Pt/KL catalyst for n-octane aromatization, KL zeolite having the short channel length as well as the small particle size was studied for enhancing the diffusion of EB and OX molecules out of the channel of

KL zeolite and avoiding the hydrogenolysis reaction occurring inside the channel of KL zeolite. Since the zeolite with small particle size provides the advantages over the zeolite with large particle size by increasing the ratio of surface area to mass, diffusion rates, and resistance to deactivate by pore plugging (Verduijn *et al.*, 2001). In 1991, it was found that for mixed C6 aromatization, KL zeolite having the short channel length has the advantages over that having the long channel length by improving the stability of Pt/KL catalyst and giving the greater selectivity and yield of benzene (Verduijn, 1991). Furthermore, diluting the active platinum surface into smaller ensembles by the addition of an inactive species such as Sn, Au, and Pb can decrease the hydrogenolysis activity (Macleod *et al.*, 1998). Since the hydrogenolysis reaction which is the undesired reaction in the aromatization of n-octane is the structure sensitive reaction and requires the larger metal ensembles (Miller *et al.*, 1996).

Therefore, in this contribution, the objective of this work is to improve the catalytic performance of Pt/KL catalysts for n-octane aromatization. The scopes of work are divided into two parts. The first part is to study the effect of the crystal size as well as the channel length and the morphology of the KL zeolites as shown in Chapters IV and V. The second part is to study the effect of adding of inactive metal into the Pt/KL catalysts on hydrogenolysis reaction inhibition as described in Chapter VI. The overall conclusions and recommendations are summerized in Chapter VII.