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. Platinum supported on alkaline LTL zeolite (Pt/KL) 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 dispersion of Pt clusters that remain inside the channels of the zeolite (Jacob *et al.*, 1999; Jacob *et al.*, 2001), the selectivity for *n*-octane aromatization is still low and quickly drops after a few hours on stream (Jongpatiwut *et al.*, 2003). The product distribution shows benzene and toluene as major aromatic products with small quantities of ethylbenzene (EB) and *o*-xylene (OX), which are the only two expected products from a direct six-membered ring closure. The pore size of the KL zeolite is 0.71 nm, that is, larger than the critical diameter of EB but smaller than that of OX, thus OX diffuses though the zeolite crystals much more slowly than EB. As a result, OX is preferentially converted to benzene and toluene before escaping from the pore of zeolite (Jongpatiwut *et al.*, 2003).

There are two possible factors affecting the selectivity of C8-aromatic products. The first one is the pore length of KL zeolite (Jongpatiwut *et al.*, 2005). Accordingly, using the shorter channel length KL zeolite might decrease the residence time of both EB and OX inside the zeolite pore. By that experiment, the hydrogenolysis reaction can be inhibited. In previous study (Trakarnroek *et al.*, 2007), it was found that zeolite with longer channels and irregular pore mouth structures 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. nano-crystalline) are preferred for producing higher C8-aromatics. It means that the catalysts with shorter channels have a much lower extent of secondary hydrogenolysis. The second one is the particle size of the platinum clusters. Over platinum, the hydrogenolysis of alkanes is strongly dependent on the metal particle size. It is now well recognized that the hydrogenolysis activity of Pt decreases substantially

when the dimension of the Pt particle is less than 1-2 nm and also when Pt is alloyed with a nonactive metal, such as Au, Sn, Pb (Meriaudeau *et al.*, 1997; Antos *et al.*, 1995). For many reactions in the petrochemical industries, such as naptha reforming, alkane dehydrogenation, *n*-alkane dehydrogenation, etc., tin (Sn) was used as a promoter to improve the catalytic activity for such reactions (Rangel *et al.*, 2000). For example, in the naphtha reforming, Sn is added to Pt/Al_2O_3 catalyst and acts as the promoter metal. In the case of using the Pt/KL as the catalyst in *n*-hexane aromatization, it has been found that catalytic performance of the Pt/KL catalyst can be improved with mainly the Pt ensemble effect by an incorporation of Sn (Cho *et al.*, 2004). In addition, on Pt-Sn/KL, it was observed that the bimetallic Pt-Sn catalyst prepared by vapor phase co-impregnation for *n*-octane aromatization showed that the addition of Sn improved the stability and selectivity to C8-aromatics products, including a decrease in the secondary hydrogenolysis reaction which occurred inside the pored of KL zeolite (Trakarnroek *et al.*, 2007). Sn modifies the stability and selectivity of the Pt function in two ways, ensemble and electronic effects. By an ensemble effect, Sn decreases the number of contiguous platinum atoms and then the multipoint adsorption of hydrocarbon molecules on the surface is hampered. Consequently, the hydrogenolysis and deactivation can be reduced. In addition to the purely geometric, ensemble dilution, Sn modifies Pt electronically by giving its electron to the holes of 5d band of platinum atom (Ertl *et al.*, 1997; Pall *et al.*, 1997; Macleod *et al.*, 1998). By this electronic effect, C-C bond hydrogenolysis does not occur because the hydrocarbon cannot be strongly adsorbed on the catalyst surface.

During reforming, Pt-Sn/KL deactivates due to accumulation of coke depositions on the catalyst, and agglomeration of fine catalytic metal particles disperses in the catalyst into larger particles. Therefore, regeneration of deactivated catalysts is of great interest. However, the catalyst regeneration has been less studied than catalysts deactivation because the mechanism is not always simple and reversible. Only a few studies have been reported. Attention is focused on Pt-Sn catalysts because they are widely used in reforming reactions. In addition, regeneration only makes sense where deactivation can be reverted, as in the case of coke deposition (Afonso *et al.*, 1997). Regeneration of a spent catalyst is influenced by a great number of parameters. For instance, time necessary to remove coke and temperature,

which is probably the most critical parameter in a regeneration process because it influences directly the stability of the metallic phase and of the support. In addition, work has also been done on Pt-Sn alloys, and it has been shown that the alloy is completely destroyed when heated in air which has an impact on catalyst properties. Therefore, the activity is recovered by burning-off coke with diluted air, and in this process it is very important to maintain the Pt-Sn interaction (Pieck *et al.*, 2005).

The aims of this research are to study 1) the catalytic performance of Pt-Sn supported on the synthesis nano-crystalline KL zeolite (NCL) and the ratio of Pt/Sn in the *n*-octane aromatization reaction, 2) the effect of Pt-Sn catalyst regeneration as supported on the commercial KL zeolite which has an impact on catalyst properties by changing the interaction between Pt-Sn. First of all, NCL was synthesized by microwave-hydrothermal treatment, followed by the X-ray diffraction (XRD) in order to characterize the zeolite properties. Secondly, Pt was incorporated in the NCL and commercial KL zeolites (COM) by the vapor phase co-impregnation (Trakarnroek *et al.*, 2007). The fresh catalysts was characterized by hydrogen chemisorption while transmission electron microscopy (TEM) analysis was performed on the fresh catalyst to estimate the metal dispersion. Furthermore, temperature programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS) were used to test the Pt-Sn interaction. The activity and selectivity of the catalysts for *n*-octane aromatization were carried out at 500°C under atmospheric pressure. Temperature programmed oxidation (TPO) was employed to analyze the amount of coke deposits on the spent catalysts during reaction. From the previous experiment, it has been found that the addition of Sn improved the stability and activity in catalytic performance in the conversion of *n*-octane.