CHAPTER I

INTRODUCTION

One of the most important reactions in the refinery to obtain high value-added products from naphtha feedstock is the aromatization of paraffins to aromatics. In 1980, Bernard found the exceptionally high activity of platinum supported on alkaline LTL zeolite (Pt/KL) for the aromatization of n-hexane that is very efficient for the direct dehydrocyclization of n-hexane into benzene (Bernard, 1980). However, the unique behavior observed for n-hexane in terms of selectivity and catalyst life was not presented for n-octane (Huang et al., 1992). The selectivity for n-octane aromatization was still low and quickly dropped after a few hours on stream due to coke plugging in the pore of KL zeolite (Jongpatiwut et al., 2003). The expected products of this reaction are ethylbenzene (EB) and o-xylene (OX) from a direct six-membered ring closure; nevertheless, the product distribution showed benzene and toluene as major aromatic products with small quantities of EB and OX. To increase the desired products, the modification of the Pt catalyst with a second metal like Re, Ir, W, and in particular with Sn as a promoter in the zeolite provided better catalytic activity, stability, and higher product selectivity for aromatization of n-alkanes (Rangel et al., 2000; Hoang et al., 2007). In addition, it was observed that the bimetallic PtSn/KL catalyst prepared by vapor-phase co-impregnation for n-octane aromatization showed that the added tin improved the stability and selectivity to C8-aromatics products, including a decreasing the secondary hydrogenolysis reaction which occurred inside the pore of KL zeolite leading to conversion of benzene and toluene (Trakarnroek et al., 2006).

Although Pt/KL catalyst has many benefits hereinbefore, one of the important drawbacks is its sensitivity to sulfur poisoning. It is considerably more susceptible to sulfur than the conventional reforming catalysts such as Pt/Al_2O_3 and $PtRe/Al_2O_3$ (Meriaudeau et al., 1997). Several authors have found that the high sensitivity of Pt on the non-acidic support catalyst to poisoning by very low levels of sulfur is attributed to the loss of active platinum surface by adsorption of sulfur and the growth of the platinum clusters leading to catalyst deactivation (Vaarkamp et al., 1992; Lee et al., 1998). Moreover, as the metal size grows; larger ensembles and also coke forma-

tion are formed, favoring hydrogenolysis over dehydrocyclization and effecting to the reaction selectivity resulting in lower product selectivity (Vaarkamp et al., 1992; Kao et al., 1993; Paal et al., 1996). As a result, one possible approach to increase sulfur tolerance could be the addition of rare earth elements as promoters. They may act as anchoring sites for Pt particles, thus preventing their growth. They may also act as sulfur getters, thus protecting Pt, albeit temporarily, from sulfur poisoning (Jacobs et al., 1999). For example, in the case of n-hexane aromatization, heavy rare earth (e.g. Tm, Gd, Yb, Dy) elements added to Pt/KL catalyst have effect to electronic donation to Pt particles and blocking the accumulation of active Pt particles, and thus can remarkably increase the ability of resistant sulfur poisoning and the aromatic selectivity of n-hexane conversion on the Pt/KL catalyst. In the presence of sulfur, the Ce-promoted Pt/KL catalyst showed a higher tolerance to metal agglomeration and a lower rate of coke formation than the unpromoted Pt/KL for n-hexane aromatization (Jongpatiwut et al., 2001). Furthermore, addition of Tm onto the KL catalyst results in an increase of the number of active site, that is, an increase of the dispersion of the active Pt particles, which results in a much slower loss of the catalytic activity of the PtTm/KL catalyst (Fang et al., 1996).

This research aims to study 1) the sulfur tolerance of PtSn/KL for n-octane aromatization reaction 2) the improvement of sulfur tolerance of PtSn/KL after adding rare earth elements (Tm and Ce). The catalysts were prepared by vapor-phase impregnation method in which all metals were loaded on the KL zeolite by co-impregnation and sequential impregnation methods. All the fresh (reduced) samples were tested at 500°C under atmospheric pressure and characterized by a combination of techniques including hydrogen chemisorption. Transmission electron microscopy (TEM) analysis was also performed on the fresh catalyst to estimate the metal dispersion. Furthermore, temperature programmed reduction (TPR) was used to test the metal interaction. While temperature programmed oxidation (TPO) was employed to analyze the amount of coke deposits on the spent catalysts during reaction.