CHAPTER I

INTRODUCTION

One of the most important reactions in the refinery to obtain high value-added products from naphtha feedstock is the aromatization. In 1980, Bernard found that 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 (Hunges 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). Trakarnroek et $al.$ (2006) 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.

Although Pt/KL catalyst is exceptionally high activity and selectivity for the aromatization of n-hexane to benzene, one of the most serious drawbacks exhibited by the Pt/KL catalysts is their extremely high sensitivity to even minute concentrations of sulfur (e.g., parts per billion) (Jacobs et $al.$, 1998). The main problems of catalyst deactivation in the presence of sulfur is attributed to the loss of active platinum surface by adsorption of sulfur and the growth of the platinum clusters (Vaarkamp et $al.$, 1992; Lee et $al.$, 1998). Moreover, as the metal size grows; larger ensembles and also coke formation are formed, favoring hydrogenolysis over dehydrocyclization and effecting to the reaction selectivity resulting in lower product selectivity (Vaarkamp et $al.$, 1992; Paal et $al.$, 1996). One possible approach to increase sulfur tolerance of the catalyst could be the addition of a second metal as a promoter. There are a number of ways in which these promoters could operate (Resasco et $al.$, 1994). They may act as anchoring sites for Pt particles, thus preventing their growth. They may also act as sulfur getters, thus protecting Pt, even though temporarily, from sulfur poisoning.

A number of bimetallic systems have been introduced including Pt–Re, Pt–Ir, Pt–Sn, and Pt–Ge over Al_2O_3, all of which have improved activity and stability

compared to monometallic Pt/Al$_2$O$_3$ (Macleod *et al.*, 1998). The overall deactivation rate—deactivation by coke and sulfur—for *n*-hexane conversion increased in the order Pt–Ge < Pt << Pt–Sn ≤ Pt–Re. Pt–Ge/Al$_2$O$_3$ was the most stable catalyst essentially because of its high thiotolerance for *n*-hexane transformation reactions by weakening the strength of the sulfur platinum bond and also because it showed low activity for dehydrogenation reactions leading to the formation of coke precursors (Borgna *et al.*, 2000). Moreover, the addition of Ge on Pt–Re/Al$_2$O$_3$ or Pt–Ir/Al$_2$O$_3$ increases the formation of *o*-xylene and toluene which are the important petrochemical feedstock (Santos *et al.*, 2005; Boutzeloit *et al.*, 2006). However, at high Ge contents a drastic decrease of the toluene yield is observed due to a strong poisoning of the metal phase and the formation of isolated Ge species (Benitez *et al.*, 2007).

The purposes of this research are to study sulfur tolerance of bimetallic (Pt–Sn and Pt–Ge) over KL zeolite catalysts for *n*-octane aromatization reaction and to optimize the amount of the second metal (Ge). The activities and selectivities of the catalysts will also be evaluated. The catalysts were prepared by vapor-phase impregnation method in which all metals were loaded on the KL zeolite by co-impregnation method. 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 and spent catalysts to estimate the metal dispersion. The size and location of the Pt clusters in the KL were examined by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of Adsorbed CO. Furthermore, temperature programmed reduction (TPR) was used to investigate the catalyst reducibility. The oxidation states of the metal phased were investigated by X-Ray Photoelectron Spectroscopy (XPS). While temperature programmed oxidation (TPO) was employed to analyze the type and amount of coke deposits on the spent catalysts.