

CHAPTER I

INTRODUCTION

Several research articles in waste tire pyrolysis reported the uses of many catalysts to improve the quality of tire-derived oil. As in our previous work, Pinket (2010) studied the 1%Rh/KL for waste tire pyrolysis, and found that the Rh/KL catalyst significantly decreased the yield of di-aromatics (DAHs), poly-aromatics (PAHs), and polar-aromatics (PPAHs) in conjunction with a significant increase in mono-aromatics (MAHs). However, no detail on chemicals in MAHs, DAHs, PAHs, and PPAHs was reported, and the surface activity or the relative changes of hydrocarbons in the oil on the surface of KL and Rh/KL was not explained clearly.

The KL zeolite is a solid basic catalyst that contains K^+ as a cation. It has basic property and one dimensional channel of 12-membered rings with a pore size of 0.71 nm (Sato *et al.*, 1999). KL has been employed as a support of Ru for the hydrogenation of unsaturated aldehyde (Álvarez-Rodríguez *et al.*, 2005). Azzam *et al.* (2010) studied the aromatization of hexane over Pt/KL catalyst, and they found that L-zeolite channels inhibited the coke formation and catalyst deactivation. Moreover, A basic catalyst that has a K^+ as a cation such as potassium tert-butoxide ($K^+(CH_3)_3CO^-$) and K/Al_2O_3 can provide both hydrogenation and aromatization. Stapp and Kleinschmidt (1965) studied the isomerization of cyclooctadienes to cis-Biscyclo[3.3.0]oct-2-ene, and reported that potassium tert-butoxide can hydrogenate linear dienes, like 1,5-hexadiene, to hexane. Moreover, Slaugh (1967) studied metal hydrides as hydrogenation and isomerization catalysts, and found that potassium hydride (KH) appeared to be several hundred times more active than sodium hydride. In addition, Slaugh (1968) studied the hydrogenation of benzene to phenylcyclohexane using supported alkali metal catalysts, and found that the catalytic properties of alkali metals could be changed drastically by depositing them on certain supports. Furthermore, Friedman *et al.* (1971) found that alkali metals and alkali metal alloys can be used as catalysts for the hydrogenation of poly-aromatic hydrocarbons to products containing an isolate aromatic ring. In addition, a basic catalyst can also provide aromatization of hydrocarbon compounds. Pines and Eschinazi (1955) studied sodium-catalyzed double bonds migration and

dehydrogenation of *d*-limonene and phellandrene, and found that the base catalyst can aromatize *d*-limonene to *p*-cymene. Moreover, Brown (1973) revealed potassium hydride with amine can provide aromatization of *d*-limonene to *p*-cymene at room temperature.

Rhodium was found to be one of the most active noble that showed higher yields in hydrogenation and the ring opening of naphthalene than Pt and Ir for diesel upgrading (Jacquin *et al.*, 2003). Nurunnabi *et al.* (2006) reported that the addition of 0.035% Rh on NiO-MgO resulted in the most effective catalyst to improve catalytic activity and inhibit carbon deposition in methane steam reforming. Jacquin *et al.* (2008) found that bimetallic PdRh showed the activity and selectivity in hydrogenation and the ring opening of poly-aromatic compounds. Moreover, Gault *et al.*, (1981) revealed the mechanism over metal catalysts. They found that the metal surfaces were suitable for driving some reactions of five-membered ring and six-membered ring. The reactions of the saturated five-membered ring compounds took place via multiplet mechanism whereas the unsaturated five-membered ring compounds took place via dicarbene mechanism.

The study on the surface activity of the catalyst is very important for a researcher who wants to develop the catalyst that can provide a specific reaction. Since the Rh/KL catalyst was found to significantly enhance the formulation of mono-aromatic compounds in TDOs, the surface activity on the KL and Rh/KL was studied. The changes of chemical components in tire-derived oils were revealed by using a comprehensive 2D gas chromatograph with time-of-flight mass spectrometry (GC × GC- TOF/MS), which were categorized into seven groups; that are, saturated hydrocarbons (SATs), olefin hydrocarbons (OLEs), terpene hydrocarbons (TERs), mono-aromatic hydrocarbons (MAHs), di-aromatic hydrocarbons (DAHs), poly-aromatic hydrocarbons (PAHs), and polar-aromatic hydrocarbon (PPAHs), including sulfur compounds. The changes of chemical components abundantly found in each group were confirmed by using the Two-dimension Heteronuclear Single-Quantum Correlation-Nuclear Magnetic Resonance (HSQC-NMR) technique.