

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Compositions in Tire-derived Oil

Tire-derived oil (TDO) is a dark brown/black colored, medium viscosity oil with sulphur or aromatic odor. This liquid is very complex, containing more than 100 compounds in majority (Cunliffe *et al.*, 1998). Among those, they were saturated hydrocarbons, olefins, and aromatics, for examples. Dai *et al.* used  $\text{SiO}_2/\text{Al}_2\text{O}_3$  liquid column chromatography to separate a TDO, and analyzed by using GC/MS. They reported that the hydrocarbon species in TDOs was 26.77 wt.% alkanes, 42.09 wt.% aromatics, 26.64 wt.% non-hydrocarbon, and 4.05 wt% asphaltene, and found that the aromatics were the mixture of mono-aromatics, di-aromatics, and poly-aromatics (Dai *et al.*, 2001). William and Bottrill used  $\text{SiO}_2/\text{Al}_2\text{O}_3$  liquid column chromatography to separate sulfur-polycyclic aromatic hydrocarbons, and then analyzed by using a normal GC/MS. They found that these compounds were 2-methylthiophene, 3-methylthiophene, 2-ethylthiophene, 2,5-dimethylthiophene, 2,4-dimethylthiophene, 2,3-dimethylthiophene, 3-ethylthiophene, 2-isopropylthiophene, 2-tert-butylthiophene and their derivatives (Williams *et al.*, 1995). Pakdel *et al.* studied the production of *dl*-limonene by vacuum pyrolysis of used tire using a normal GC/MS, and found that *dl*-limonene was mixed in alkane, alkene, and poly-aromatics fractions. However, the peaks were not easy to be resolved because they came out nearly at the same retention time and had similar boiling point (Pakdel *et al.*, 2001). Moreover, Lagesgoiti *et al.* characterized the liquid product in TDO by using a normal GC/MS. They found that the chromatograms of poly-aromatics and polar-aromatics were not explicitly separated from one another, and it was difficult to interpret the results (Laresgoiti *et al.*, 2004). Boxiong *et al.* revealed hydrocarbon species in TDOs by using a normal GC/MS to investigate the influence of zeolite USY catalyst, and found 38 hydrocarbon species of aromatic hydrocarbons in the light fraction that are the mixtures of saturated hydrocarbons (with aliphatic and branch chain), olefins, naphthenes, and aromatics. They also found that the

chromatograms showed some of saturated hydrocarbons and olefins that could not be identified because they evolved at the same retention time (Boxiong *et al.*, 2007).

## 2.2 Sulfur Compounds in Tire-derived Oil and Their Reactivity

Tire-derived oil (TDO) contains approximately 0.8 – 1.1 % wt sulphur (Roy *et al.*, 1990; William *et al.*, 1995). The S-compounds in TDO may give rise to toxic and corrosive SO<sub>x</sub>. Moreover, S-compounds are a group of refractory compounds that need a specific process for treatment, like hydrodesulfurization (HDS). Several studies showed that the reactivity of S-compounds in HDS decreased in the order: thiophenes > benzothiophenes > dibenzothiophenes > alkyldibenzothiophene (Kilanowski *et al.*, 1978; Houalla *et al.*, 1980; Andari *et al.*, 1996). For the alkyldibenzothiophenes, 2,8-dimethyldibenzothiophene was more reactive than 4-methyldibenzothiophene. The one with the lowest reactivity in the alkylbenzothiophenes is 4,6-dimethyldibenzothiophene due to steric hindrance (Andari *et al.*, 1996; Gutiérrez and Klimova, 2011). Therefore, the structure of S-compounds in TDO should be accounted for, in consideration of the reactivity in HDS. William and Brotrill (1995) studied the sulphur-polycyclic aromatic hydrocarbons in tire pyrolysis oil. They used liquid column chromatography to separate sulfur-polycyclic aromatic hydrocarbons and that were then analyzed by using a normal GC/MS. They found that 10 S-compounds existed in TDO; however, the chromatograms were not explicitly resolved. Moreover, Lagesgoiti *et al.*, (2004) characterized the components in TDO by using a normal GC/MS. They found that the chromatograms of poly-aromatics and polar-aromatics were not explicitly separated from one another, and it was difficult to interpret the results. In conclusion, it is not easy to resolve overlapped peaks from the chromatograms of TDOs using a normal GC/MS; therefore, the separation of a complex mixture of TDOs requires highly-advanced technology with high chromatogram resolution.

### 2.3 Reactions for Basic Catalysts

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.

### 2.4 KL Zeolite

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.

A highly selective catalyst in the aromatization of n-hexane was found by Barrer and Villiger (1969), who used the platinum catalyst supported on KL zeolite.

The influence of different alkali catalysts on the aromatization selectivity was investigated by Becue *et al.* (1999). The highest selectivity on Pt/KL catalyst was found, and it should promote an increase in octane number. The application of KL catalyst selective hydrogenation reaction has been studied in several researchers. Jacobs *et al.*, 2001 studied the different preparations of Pt/KL catalyst for n-hexane aromatization. They explained that the different methods affected the various results of platinum cluster distribution on the KL support. They also suggested that the vapor phase impregnation was an effective method on KL powder, but not on the extrudates whose efficiency decreased in the presence of the binder material. In 2008, Kumar *et al.*, studied the role of pore size on the aromatization activity of Pt/KL catalyst, which light naphtha was used as a feedstock. It was noted that the pore volume and dispersion was decreased at high metal loading above 0.4wt% because of the Pt agglomeration. No loss in pore volume and surface area was found at low metal loading. In addition, they suggested that the catalyst prepared by incipient wetness impregnation can be an active and stable catalyst for aromatization. The selective hydrogenation was studied by Alvarez-Rodriguez *et al.* (2005). They found selectivity and activity on the hydrogenation of unsaturated aldehyde by using ruthenium supported on KL zeolite. Later, they further studied the effect of various preparation methods of catalysts. They reported that the Ru/KL catalyst prepared by incipient wetness impregnation showed less reactive but more selective to unsaturated alcohol than catalyst prepared by treating with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ . These results related to the size and location of particles in the zeolite framework. In the other study, Alvarez-Rodriguez *et al.* (2008) reported that nickel supported on KL catalyst showed the positive relationship of catalytic activity. However, the addition of copper on Ni/KL catalysts inhibited the hydrogenation of nickel.

## 2.5 Rhodium Catalysts

Rhodium, a noble metal, provides catalytic activity and selectivity in many reactions. It has been reported in several catalytic applications. In 2000, Teschner *et al.* studied the hydrogenolytic ring opening of methylcyclopentane on  $\text{Rh/Al}_2\text{O}_3$  with different metal loading (0.3, 3 and 10%). It was observed that

different H<sub>2</sub> pressure and temperatures could affect selectivity to ring opening products and consequently towards fragmentation products (<C<sub>6</sub>) resulting from multiple C-C bond ruptures. Likewise in 2002, they suggested that the hydrogenolytic cleavage of hydrocarbon C-C bonds was found as a main reaction in the conversion of C<sub>6</sub> alkanes and methyl cyclopentane while C<sub>5</sub>-cyclization was a minor reaction. Jacquin *et al.* (2003) investigated novel supported Rh, Pt, Ir and Ru mesoporous aluminosilicates as catalysts in the hydrogenation of naphthalene. They reported that at 300°C and atmospheric pressure, rhodium exhibited higher selectivity to hydrogenolysis and/or ring-opening products than platinum-containing catalysts. Moreover, at 6 MPa supported rhodium catalyst promoted the high amount of high-molecular weight and fully hydrogenated products from naphthalene. Similarly, Albertazzi *et al.* (2003) also found an increase in catalytic activity of rhodium supported on MCM-41 catalyst in the hydrogenation of naphthalene at 6 MPa. However, low thio-tolerance resulting in catalyst deactivation in the dry reforming of methane was found on the catalysts. In 2009, Barama *et al.* found the most active catalyst for the dry reforming of methane was the Rh/Al-PILC catalyst among Pd, Ni and Ce catalysts. It was suggested that rhodium catalyst can be used in many reactions as an effective catalyst.

According to Pinklet. (2010), Rh metal on a KL support predominated the ring opening of aromatic compounds in tire-derived oil, resulting in the increases in saturated hydrocarbons and mono-aromatics with the drastic decreases in di-aromatics and poly-aromatics. At present, there has been no research to investigate the surface activity that reveals reaction pathways over the Rh/KL catalyst. The objective of this study was to examine the changes in species of components in the tire-derived products evolved from using KL and Rh/KL as a catalyst. The changes of the compounds in the products were expected to disclose the activity on the surface of KL and Rh/KL. The tire pyrolysis experiments were conducted in a bench-scaled autoclave reactor. GC x GC / TOF-MS was used to analyze the chemicals species produced by pyrolysis, and HSQC-NMR was used to confirm the chemical structures of compounds that changed upon the use of catalysts.