CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

This work studied the effect of Cu- and Zn-modified catalysts on waste tire pyrolysis products, especially the effect of metal-support interaction on tire-derived oil, petrochemicals, and sulfur removal. Copper-loaded catalysts have been widely used in selective hydrogenation process, and copper-exchanged zeolite adsorbents have been used for sulfur removal from liquid fuels. Zinc is widely used not only as catalysts in light alkane aromatization process but also as adsorbents for sulfur reduction of liquid fuels. So, Cu- and Zn-supported catalysts were expected to exhibit their abilities in catalytic pyrolysis of waste tire as well. The metals were added onto four types of zeolites (HBETA, HY, HMOR and KL) for studying their abilities on each support.

The selected zeolites were used to compare the effects of Si/Al ratio (HBETA and HY), pore structure (HY and HMOR) and acid/base properties (HMOR and KL). As a result, the higher acid density catalyst (HY zeolite) exhibited higher cracking, ring-opening and hydrogenolysis activities than the lower acid density catalyst (HBETA zeolite). The 3D pore structure catalyst (HY zeolite) showed higher cracking and hydrogenolysis activities than 1D pore structure catalyst (HMOR zeolite). Furthermore, the 3D pore structure catalyst has higher open space (pore size and architecture), resulting in higher total aromatic production. The acid and basic catalysts (HMOR and KL zeolites) exhibited cracking ability. Furthermore, the acid catalyst can also exhibit hydrogenolysis ability. The petroleum valuable products were differently produced in each zeolite case. HBETA highly produced benzene and ethylbenzene. HY highly produced benzene and toluene. HMOR largely produced for styrene production while KL did not produce any outstanding species at all.

Copper can exhibit sulfur removal ability on the zeolites (HBETA, HY and HMOR). Furthermore, the effect of metal-support interaction significantly affected the sulfur removal ability of the Cu-loaded catalysts. The copper-loaded catalyst with strongest metal-support interaction is the best catalyst for sulfur removal from the pyrolysis oils. Some sulfur-containing compounds in tire-derived oils that were found were classified into six groups: thophenes (Th), benzothiophenes (BT), dibenzothiophenes (DBT), naphthothiophenes (NT), benzothiazoles (BTz), and isothiocyanates (ITC). The sulfur-containing compounds can be converted into valuable petrochemical products such as ethylbenzene, styrene, toluene, xylenes, benzene, cumene, and cyclohexane. Furthermore. the petrochemical valuable products produced in high amount were benzene, ethylbenzene and cyclohexane in Cu/HY case, and benzene, toluene and ethylbenzene in Cu/HMOR case, whereas benzene and cumene were highly produced in the Cu/KL case.

Acid density of Zn loaded on zeolites (HBETA. HY. and HMOR) strongly affected sulfur removal from tire-derived oils. The best zinc-loaded catalyst was the one with the highest acid density. The major species of sulfur-containing compounds were similar to those reported in Chapter VI. Furthermore, zinc-loaded catalysts can also convert sulfur-containing compounds into petrochemicals as well. All Zn-loaded catalysts can produce a high selectivity of cumene and ethylbenzene in gasoline. Moreover, Zn/HBETA highly produced cyclohexane while the other zinc-loaded catalysts also highly produced styrene.

Basicity of KL-supported catalysts is highly increased when Cu or Zn was loaded on the support. Moreover, Cu- or Zn-loaded basic support (KL zeolite) can also increase sulfur removal ability of the catalyst because the catalysts can adsorb sulfur-compounds on potassium ions and Cu or Zn sites. The increase of basicity in Cu/KL and Zn/KL catalysts can cause the high decrease of the amount of benzothiophenes and dibenzothiophenes in oils. Furthermore. the Cu-KL interaction was lower than Zn-KL interaction causing hydrodesulfurization activity promoted in the Cu-loaded KL case, resulting in higher sulfur removal from tire-derived oil (lower sulfur content in the oil). Cu/KL can give higher petrochemical productivity than Zn/KL as well. The petrochemical valuable products were highly produced in the species of benzene and cumene in the Cu/KL catalyst case, and ethylbenzene and cumene in the Zn/KL case.

Even though the catalyst characterizations were enough for explanation of results, it is recommended that some techniques should be used to determine some properties of catalysts for studying the effect of them in terms of the specific abilities. For more clear explanation of the results, the pyrolysis products and spent catalysts should be analyzed/characterized for the amounts of carbon, hydrogen, oxygen, and nitrogen by using CHSNO Analyzer.