

## CHAPTER IX

### CONCLUSIONS AND RECOMMENDATIONS

The pyrolysis of waste tire using various noble metals loaded on different supports as catalysts has been studied. The roles of metal and the effects of metallic nature, such as metal loading, metal particle sizes, and the addition of a second metal, and pyrolysis condition, i.e. pyrolysis temperature and catalyst temperatures were investigated.

During the thermal pyrolysis of waste tire, a considerable amount of polar-aromatics was produced. Increasing pyrolysis temperature led to an increment of polar-aromatic content and also a shift of polar-aromatic distribution to the higher carbon number. A set of possible polar-aromatic formation pathways were proposed. The use of acid zeolites (HMOR and HBETA) decreased polar-aromatics dramatically, and the introduction of Pt on the zeolites even caused a further decrease. Pt clusters enhanced the hydrogenation reactions, resulting in the conversion of polar-aromatics and their precursors to saturated HCs. Consequently, these compounds might undergo the cracking reactions catalyzed by the acid function of the catalysts, thus reducing the amount of the polar-aromatics.

The influences of metallic natures were investigated by using different noble metals (Rh, Re, Ru, Pt) supported on HMOR catalysts. Except Re/HMOR, all noble metal-supported catalysts increased light oil production, and simultaneously decreased poly- and polar-aromatics in the derived oils. And, it was revealed that among these noble metals, Ru was the most active metal for the reduction of poly- and polar-aromatics and simultaneous light oil production. The best catalytic performance of ruthenium catalyst was ascribed to its metallic nature; that is it has a low metal electronic heat capacity constant ( $\gamma$ ) and high hydrogenation activity.

The roles of ruthenium were subsequently elucidated by studying the activity of Ru/SBA-1 catalysts since SBA-1 was proven to be catalytically inactive and its structure retained after reaction. Ruthenium clusters were the active sites for poly- and polar-

aromatic hydrocarbons (PPAHs) reduction. The conversion of these PPAH and saturated compounds to the lighter one with the presence of ruthenium sites resulted in the greater light oil production as well as the increment of the yield of gaseous products. Ruthenium particle sizes in the tested range (2.5 nm - 4.5 nm) strongly influenced the catalytic activity of Ru-supported catalysts. Poly- and polar-aromatic contents decreased whereas naphtha and kerosene increased with decreasing ruthenium particles.

Catalyst temperatures considerably affected the product distribution and the nature of the products obtained from the MCM-41 catalyzed-pyrolysis of waste tire. The oil yield first decreased, and then increased with catalyst temperature. And, under the highest studied catalyst temperature, the highest poly- and polar-aromatics were produced. In addition, increasing catalyst temperature decreased the yield of naphtha in accordance with the increment of heavier fractions. The incorporation of Ru on the surface of MCM-41 was found to have promotion effects on the catalytic activity, i.e. enhancing light oil production as well as poly- and polar-aromatic reduction. And the catalytic activity increased with increasing Ru loading. That was explained by the promotion in the hydrogenation of both poly- and polar-aromatics, as Ru loading increased, followed by ring-opening and/or cracking producing lower molecular weight hydrocarbons.

Significant synergistic effects of two metals on the RuNi/HMOR catalysts were observed on both aromatic reduction and naphtha production in the tire-derived oil. And the synergy factor  $\zeta$  was found to strongly depend on the metal composition of the catalysts,  $\alpha$  ( $\alpha = \text{Ru}/(\text{Ru}+\text{Ni})$ ). And  $\zeta$  first increased with increasing  $\alpha$ , reached a maximum at  $\alpha = 0.36$ , and then decreased with further increasing  $\alpha$ . Catalyst characterization results indicated that the close interaction between ruthenium and nickel, leading to the formation of bimetallic RuNi particles, was the cause for the observed synergistic effects. The stronger the interaction between ruthenium and nickel, the greater synergistic effect was obtained.

Although we have mentioned some points related to the properties of the spent catalysts, however it is recommended that the life cycle of the catalysts be determined,

and optimized catalyst be prepared in the industrial form in the future work. The parameters, e.g. pellet diameter, type of binder, type of matrix, catalyst composition, etc may be studied to obtain a good industrial catalyst for catalytic pyrolysis of waste tire. Finally, the obtained oil may be refined and tested for its combustion properties in an engine.