

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In order to decrease aromatics contents and to improve fuel properties, the saturation of aromatics alone might not be able to achieve the fuel specifications of the near future. Thus, selective ring opening is introduced as a potential reaction to achieve the requirements. In this contribution, the hydrogenation of tetralin and the ring opening of 1,3-dimethylcyclohexane were investigated. In the first section, the hydrogenation of tetralin was carried out on Pt/Al₂O₃, Pd/Al₂O₃, and Ni/Al₂O₃ catalysts. The aim of this work was to study the role of metal catalysts in the hydrogenation of tetralin towards cis-decalin since such an isomer facilitates the ring opening products in the subsequent process. It was found that the evolutions of trans/cis-decalin ratios on catalysts prepared depended on tetralin conversion. Besides the hydrogenation of tetralin, the isomerization of cis- to trans-decalin, which has a negative effect on the yield of the cis-decalin product, was also observed at high tetralin conversions. The hydrogenation rates of tetralin on catalysts prepared were increased in the following order: Pt > Ni > Pd. The order of the rates of isomerization of cis- to trans-decalin of the three catalysts are also followed the same trend as observed from the hydrogenation rates. However, the isomerization of cis- to trans-decalin was not observed at low tetralin conversions since the adsorption of cis-decalin to isomerize to trans-decalin was inhibited with the adsorption of tetralin. As a result, the intrinsic properties of tetralin hydrogenation towards cis- and trans-decalin of each catalyst were revealed at low tetralin conversions. It was found that the trans/cis decalin ratio on Pd is around two times higher than that on Ni and Pt catalysts. The results may be due to the difference in the hydrogenation rate of $\Delta^{1,9}$ -octalin intermediate. Thus the yield of cis-decalin in the hydrogenation of tetralin can be maximized using the catalysts with high selective towards cis-decalin product with a low rate of cis- to trans-decalin isomerization.

In the second part, the ring opening of 1,3-dimethylcyclohexane (1,3-DMCH) was investigated on unpromoted Ir and promoted Ir catalysts with K or Ni.

At low W/F ratio, the primary products (2-methylcycloheptane, 4-methylcycloheptane, and 2,4-dimethylcyclohexane) were mainly obtained then, in turn, subsequently cracked to secondary products with lower molecular weight at higher W/F ratios. The addition of K on Ir/SiO₂ at appropriate Ir to K ratio resulted in the decrease in Ir cluster. As a consequence, active sites for the breaking of the C-C bonds at the substituted positions were promoted. Interestingly, the addition of Ni on Ir/Al₂O₃ may form Ir-Ni alloy or the modified alumina to nickel aluminate. It was observed that the Ir-Ni/Al₂O₃ (Ir to Ni molar ratio equal 1:3) catalyst preferred to produce alkane products with high degrees of branching when compared to Ir/Al₂O₃. The calculated octane number from mixtures of ring opening products as a function of W/F was first introduced to clearly observe the improvement of octane number. It was obviously shown that even though the naphthenic rings were opened, it might not guarantee that the octane number would be increased. Only on Ir/SiO₂ and Ir-Ni/Al₂O₃ catalysts, the octane number from ring opening products was continuously increased as a function of W/F. In the cases of Ir/Al₂O₃ and Ir-K/Al₂O₃ catalysts, the octane number of ring opening products was decreased at the front end of the reactor these catalysts were selective to produce alkane products with low degrees of branching. Although the increase in octane number could be achieved at high W/F ratios, the secondary products attained are undesirable due to the lost in carbon number. It is proposed here that the selectivity of the catalysts to improve the fuel properties on Ir catalysts can be adjusted using a promoter such as K or Ni at optimum Ir/K or Ir/Ni ratios.

7.2 Recommendations

The ring opening reaction is well known as a promising reaction for cetane or octane number improvement. However, further research is required to provide the ring opening reaction as a potential alternative. There are many challenging issues to consider, as the following:

- Typically, the products from the ring opening reaction are classified into two groups, which are the primary and secondary products. At high ring opening conversion (high W/F), the extensive hydrogenolysis of primary

products to secondary products causes an economical unfeasible solution due to the loss of carbon number compared to the original feed. Therefore, the extensive cracking in ring opening reaction should be controlled.

- Aromatic compounds typically present in real feed. However, the study of site competition between the ring opening of naphthenes and aromatic compounds is still limited. Therefore, the selectivity and activity of ring opening in the presence of aromatics should be clarified.
- Generally, the noble catalysts are easily poisoned from trace amounts of sulfur. Therefore, catalyst designs with high selectivity, catalytic activity and high sulfur tolerance are necessary to approach the requirement.