CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The catalytic dehydration reaction of bio-ethanol to hydrocarbons was performed over the modification of SAPO-34 by using supported and sunsupported SnO_x and Sb_2O_x in the isothermal fixed bed reactor at 400 C° under atmospheric pressure. The pure form of Sn and Sb; namely, metallic Sn, SnO, SnO_2, metallic Sb, Sb_2O_3 and Sb_2O_5, were tested to observe the effect of a sole metal oxide. In addition, the metal-doped SAPO-34 was treated under the H_2 atmosphere at 400 C° for 2 h, and then tested to observe the synergistic effect of metal and support on product distribution. Moreover, the changes of surface species on metal oxide-doped SAPO-34 catalysts were investigated as a function of time on stream. The loading percentage of metal oxide and calcination temperature were varied, which are 5 and 7 wt%, and 400 C° and 700 C°, respectively.

For the effect of individually unsupported catalysts, metallic Sn and Sb have hydrogenation properties, especially metallic Sn, resulting in high selectivity of cooking gas. SnO_2 enhanced oligomerization and hydrogenation reaction of light olefins to form hexane, and cyclization and aromatization to form cyclohexane and benzene. On the other hand, SnO showed less acid property, compared to SnO_2, resulting high selectivity of oxygenate compounds. For antimony oxides with different oxidation states, the selectivity of propylene, cooking gas and butylenes from using Sb_2O_5 is higher than those in Sb_2O_3. In addition, the hydrogenation property of metallic tin and antimony corresponded to the results using $5Sn^0$SAPO-34 and $5Sb^0$SAPO-34, which promoted the selectivity of cooking gas significantly.

For the effect of loading percentage on the surface species of tin oxide-doped SAPO-34 with the calcination temperature 400 C°, tin oxide was found to have interaction between metal oxide and support, and be highly dispersed on SAPO-34. SnO_2 (Sn^{+4}) was found to enhance propylene, cooking gas, benzene and even C+10 aromatics. With increasing the calcination temperature, the oxidation state of tin oxide was +2 on SnSAPO34 calcined at 700 C° due to the basic property, rather resulting in high selectivity of oxygenates.

The effects of various loading percentages of antimony oxide and calcination temperature were observed on the product distribution. With increasing the loading percentage from 5 wt% to 7 wt% antimony oxide, the surface Sb_2O_3 increases, resulting in lower selectivity of propylene, cooking gas and butylenes than those obtained from 7 wt% antimony oxide-doped SAPO-34. The increase of calcination temperature was found to promote the agglomeration of Sb_2O_3, and it behaves like unsupported one. At calcination temperature 700 C°, Sb_2O_3 (Sb^{+3}) was observe to promote oxygenate formation, while Sb_2O_5 (Sb^{+5}) enhance the formation of non-aromatics and benzene.

It can be concluded that changes of oxidation state of surface components are responsible for the product distribution when the loading percentage and calcination temperature were varied. Moreover, bigger hydrocarbons were formed because of high dispersion of metal oxides and the interaction between the loading and the support.

5.2 Recommendations

For the future work, the modified SAPO-34 with pure oxidation of metal shall be invented in order to obtain the targeted products. In addition, different supports shall be used in order to enhance the valuable oils.