

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The objective of this research is to develop a catalyst for tar elimination with superior resistance to carbon formation in biomass gasification process. The catalysts used in this work are based on CeO₂-ZrO₂-based and Ni supported on CeO₂-ZrO₂-based mixed oxides catalysts. The activities and stabilities of the catalysts are tested for total oxidation and steam reforming reactions. Benzene, toluene and naphthalene are selected as the model tar compound for the investigation of biomass-derived tar reforming.

For total oxidation reaction, it can be concluded that the catalytic activity for the naphthalene oxidation over CeO₂-ZrO₂ mixed oxide catalysts is directly relative to the catalyst redox properties. The optimal composition of the CeO₂-ZrO₂ mixed oxide catalyst that gives the highest activity is attained with Ce_{0.75}Zr_{0.25}O₂. Furthermore, the incorporation of Fe, Mn and V cations into CeO₂-ZrO₂ mixed oxide, Ce_{0.75}Zr_{0.15}Me_{0.10}O₂ (Me = Fe, Mn and V), is able to modify the redox properties of the mixed oxide catalyst resulting in the improvement of catalytic activity for benzene, toluene and naphthalene oxidations. The Mn-doped CeO₂-ZrO₂ mixed oxides catalyst, Ce_{0.75}Zr_{0.15}Mn_{0.10}O₂, was found to exhibit the highest activity toward complete oxidation of the three studied tar compounds. The catalytic activity was related to the redox properties of the mixed oxide catalysts.

Based on kinetic studies, the reaction rate of catalytic oxidation of naphthalene depends on both the naphthalene and oxygen concentrations. The reaction mechanism can be expressed by the Mars-van Krevelen mechanism, with oxygen of the metallic oxides acting as the active oxygen, being consumed during the naphthalene oxidation and restored by oxygen from the gas-phase. The oxidation step is identified as the rate-determining step with its activation energy of ca. 90 kJ/mol.

For steam reforming reaction, it can be concluded that the use of reducible supports, in particular Ce_{0.75}Zr_{0.15}Me_{0.10}O₂ (Me = Cr, Fe, Mn and V) and Ce_{0.75}Zr_{0.25}-

Mn_xO_2 ($x = 0, 0.10, 0.20, \text{ and } 0.25$), showed an advantage for steam reforming of both naphthalene and toluene with a resistance to carbon formation. In the case of steam reforming of toluene, the transition metal oxide-doped $\text{CeO}_2\text{-ZrO}_2$ supported nickel catalysts, $\text{Ni/Ce}_{0.75}\text{Zr}_{0.15}\text{Me}_{0.10}\text{O}_2$ ($\text{Me} = \text{Cr, Fe, Mn and V}$), exhibit high activities and stabilities for toluene steam reforming with no sign of deactivation. In particular, the incorporation of Mn into ceria-zirconia mixed oxide is able to modify the redox properties of the mixed oxide support resulting in the improvement of the catalytic properties of the $\text{Ni/Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ mixed oxide catalyst and maintains the catalytic activity for the steam reforming of both naphthalene and toluene. The $\text{Ni/Ce}_{0.75}\text{Zr}_{0.25-x}\text{Mn}_x\text{O}_2$ ($x = 0, 0.10, 0.20, \text{ and } 0.25$) mixed oxide catalysts also exhibit high activities and stabilities for naphthalene steam reforming. Moreover, the presence of Mn results in the dramatic decrease in carbon deposition due to the reduction of filamentous carbon by retarding the solubility of carbon in Ni particles as well as promoting the oxidation of intermediates or precursor of deposited carbon.

8.2 Recommendations

Since, the Mn-doped $\text{CeO}_2\text{-ZrO}_2$ mixed oxide ($\text{Ce}_{0.75}\text{Zr}_{0.15}\text{Mn}_{0.10}\text{O}_2$) finds attractive as an alternative material for tar elimination in biomass gasification systems, with either oxidation or steam reforming reactions, however, the details about the oxidation states and the interaction between Ni and $\text{Ce}_{0.75}\text{Zr}_{0.15}\text{Mn}_{0.10}\text{O}_2$, are still not clearly understood now. Therefore, studies in surface sciences of such catalysts relevant to the activity, stability as well as the carbon formation resistance should be further investigated. Additionally, in order to comprehend the mechanisms of the steam reforming of tar compounds over the transition metal oxide-doped $\text{CeO}_2\text{-ZrO}_2$ mixed oxide catalysts, the reaction kinetic analysis should also be investigated.