

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

The MFP process has been optimized in order to obtain high H₂ purity and very low CO contamination at low-temperature reaction under the Au-based catalysts. First, the optimization process started with the SRM unit, varying many parameters associated with the Au/CeO₂-Fe₂O₃ catalysts e.g. support selection, support composition, Au content, gas pretreatment, calcination temperature, H₂O/CH₃OH feed molar ratio, and stability test. The results revealed that the 3 wt% Au/CeO₂-Fe₂O₃ (Ce:Fe = 1:1) calcined at 400 °C exhibited the complete CH₃OH conversion, 75.5 % H₂ selectivity, and 5 % CO selectivity at 400 °C. However, this catalyst deactivated rapidly at this high reaction temperature because of coke formation and the unstable CeO₂-Fe₂O₃ solid solution which led to the Fe³⁺ segregation of the Ce⁴⁺ lattice in the support site. The use of O₂ pretreatment reduced the amount of coke on the surface of the spent catalyst; conversely, it negatively affected the non-uniform solid solution of the fresh catalyst via complex mechanisms.

As previously stated, the use of CeO₂-ZrO₂ (Ce:Zr = 3:1) support provided more thermal stability due to the uniform Ce_{0.75}Zr_{0.25}O₂ solid solution. Afterward, the co-addition of Cu with Au metal to form the bimetallic catalyst significantly improved the low-temperature catalytic activity in the range of 200–300 °C. The appropriate bimetallic catalyst preparation—pH 7 of depositing condition, 7 wt% total metal loading, Au/Cu atomic ratio = 1/3, and calcination temperature = 300 °C—resulted in the formation of a homogeneous Au-Cu alloy, being the active site for the SRM activity. The combination of the alloy metal and solid solution support obviously provided the long catalyst life-time with complete CH₃OH conversion, 82 % H₂ selectivity, and 1 % CO selectivity at low temperature of 300 °C, which was suitable to continually send to the PROX unit to reduce CO gas.

To achieve the overall optimization, the CO in the rich H₂ reformat was minimized by using the double-stage PROX reactors under the use of 1 wt% Au/CeO₂ catalyst. In comparison to the single-stage PROX, the addition of the second stage significantly enhanced the CO conversion and O₂ conversion up to 98 % and 100 %, respectively. From all studied parameters, the highest PROX performance was found under the optimum conditions—unity O₂/CO feed ratio, O₂ split ratio = 50:50, total amount of catalyst use = 500 mg, catalyst weight split ratio = 0.35:0.15, T_{1st stage} = 110 °C, and T_{2nd stage} = 100 °C—that minimized the CO concentration at the reformat stream to 300 ppm. Nonetheless, the concentration of CO output was still too high for the use of PEM application. Further development of MFP must be carried out in the future work.

9.2 Recommendations

To fulfill the experiment of the MFP process, the Au catalyst used in the PROX reactor should be considered as another effective parameter in lowering the CO concentration in the reformat stream to be less than 10 ppm. The variation of GHSV in both SRM and PROX units should be optimized since this can be related to the size and efficiency of the MFP, being one of the important hurdles, which will obviously help to simplify the fuel processor designs and show promises in lifting the foregoing drawbacks. For the PROX unit, the condenser should be installed between the SRM and PROX units in order to trap water and other liquid products which contaminated in the reformat stream since these liquid products caused the negative effect on the Au catalyst surface by blocking its active site.

According to the use of Au–Cu bimetallic catalyst in the SRM unit, the CO chemisorption and high resolution transmission electron microscope (HRTEM) characterizations should be used to help identify the structure of the metal surface and to support the hypothesis of the core-shell model. The addition of another precious metal, such as Ag, with Au to form bimetallic catalyst should be also investigated on the SRM activity since these metals have the similar lattice constant that can form the alloy easily, and this alloy may be active for both H₂ production and CO reduction in the SRM unit.