

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Ceria-zirconia mixed oxides were prepared using sol-gel method. The study was performed in stages. Firstly, the mixed oxides were prepared by varying amount of zirconia in the solution. It was found that on the basis of the XRD and FT Raman results, the most homogeneous samples are in the ceria-rich compositions. The monoclinic phase is present only in the case of pure zirconia after calcination at 900°C. For zirconia content in the range of 50-90 mol%, the dissolution of ZrO₂ into the CeO₂ lattice was observed with the formation of a fluorite structured with a partial tetragonalization for higher zirconium loading. Surface area increases with the increased ceria content up to 90 mol%, and an increase of zirconia increases the surface area stability up to 40 mol%. Reciprocal substitution of the two oxides enhances the thermal stability of the single oxide, especially in the Ce-rich region. TPR results show that an increase in the amount of zirconium molar content results in a decrease in the reduction temperature for mixed oxides, which have zirconia molar content between 10-40 mol%. The CO oxidation activities of mixed oxides were found to be related to its composition. The cubic phase mixed oxides could be reduced easier than the tetragonal phase. It can be speculated that a solid solution of ceria-zirconia in a cubic phase is a good catalyst for CO oxidation.

Secondly, the influences of various synthesis parameters are investigated. The highest surface area (205.6 m²/g) was achieved from sample using Ce:Zr equal to 6:4 and aged for 10 days. It was also observed that aging time causes significant effect to textural and structure of mixed oxides. Calcinations of the mixed oxide gels at 500° and 900°C crystallizes the mixed oxide domains and strongly affects the porosity and surface areas for these pore-solid nanoarchitectures. Heat treatment reduces the void volume, changes the pore-size distribution, and increases the average grain size. The mixed

oxides show a good compositional homogeneity and thermal stability, which is an important requirement in these materials for applications in the formulation of catalysts for auto-exhaust treatment.

Thirdly, copper was added into mixed oxides to enhance the catalytic activity. Various amounts of coppers were added into mixed oxides, which have been prepared via the surfactant-aided sol-gel process at ambient temperature and were tested for CO oxidation reaction. Three different CuO species, which are highly dispersed CuO, copper ion in the solid solution, and bulk CuO species, were distinguished by UV-DRS, XRD and TPR results. The highly dispersed CuO species are the active phase for CO oxidation, as was observed by the declined in catalytic activity after the removal of the highly dispersed CuO species by acid treatment.

Lastly, copper-ceria-zirconia-alumina catalysts with various amounts of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ have been prepared via the surfactant-aided sol-gel process at ambient temperature. The introduction of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ mixed oxides into alumina causes a decelerating effect on its phase transformation and retains a certain surface area for a long period of time at elevated temperature beyond initial quick loss of surface area. When the $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ content is less than 20%, it shows a slightly suppressing effect on the transformation temperature. When 20% $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ is added, the mixed powders maintain an optimized stability, with an acceptable specific surface area after calcinations at 1100°C for 24 h. When more $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ is further added, the surface area of the mixed powders decreases again due to the much lower surface area of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ itself after such a long period of time at elevated temperature. This phenomenon may be expressed by the decomposition of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ mixed oxides and the formation of CeO_2 or CeAlO_3 on the surface of the alumina, which may decrease the surface diffusion and rate of sintering of alumina. Furthermore, the introducing of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ additives causes less particle-to-particle contacts in the alumina bulk, which also may retard the grain growth and finally the transformation.

7.2 Suggestions for Further Works

The suggestions for further works are:

1. Development of higher oxygen storage capacity (OSC) catalysts to achieve the zero emission catalysts. This could be achieved by employment of X-Ray absorption fine structure (XRFS) to determine the optimum molecular structure for cation-cation-oxygen network for OSC.
2. Investigate on various support materials at higher reduction temperature as a preparation for future generation TWC catalysts.