DEFECT STRUCTURE AND TRANSPORT PROPERTIES OF CERIA-ZIRCONIA-BASED OXIDES

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CeO_2-ZrO_2 based oxides (CZ) showing excellent oxygen storage capacity (OSC) are widely used in three-way catalysts. To further improve their storage capacity and kinetics at low temperatures, defect structural analysis appears to play an important role. In this study, ^{89}Y NMR spectroscopy is performed to probe the preference sites of oxygen vacancies in CZ under not only oxidizing but also reducing atmospheres. Figure 1 shows the ^{89}Y NMR spectra taken for $(Ce_{1-x}Zr_x)_{0.8}Y_{0.2}O_{2-d}$ annealed under (a) air and (b) Ar-5%H_2 atmospheres. 7- and 8-coordinated environments are clearly observed for both cases. Based on their integrated intensities as a function of Zr content (Fig. 1 (c)), the oxygen vacancies appear to favor Zr rather than Y and Ce; the same trend has been reported for various fluorite-type oxides [1, 2]. This suggests that doping of smaller cations is effective to enhance their OSC. Furthermore, OSC and kinetics of $CoFe_2O_4$-added CZ at around 400°C are evaluated. The spinel-type oxides such as $CoFe_2O_4$ has been well known to enhance oxygen transport properties of ceria-based oxides [3, 4]. In this study, $CoFe_2O_4$-added CZ were prepared by the Pechini and solid-state reaction methods. 5 vol% $CoFe_2O_4$-added $Ce_{0.5}Zr_{0.5}O_{2-d}$ shows higher OSC and faster kinetics at 400°C than $Ce_{0.5}Zr_{0.5}O_{2-d}$ itself. The microstructure including the distribution of $CoFe_2O_4$ was analyzed by TEM; their morphology was found to strongly depend on the volume fraction of $CoFe_2O_4$ and fabrication techniques. Their surface exchange kinetics is also discussed based on pulse isotope exchange results for powder samples.

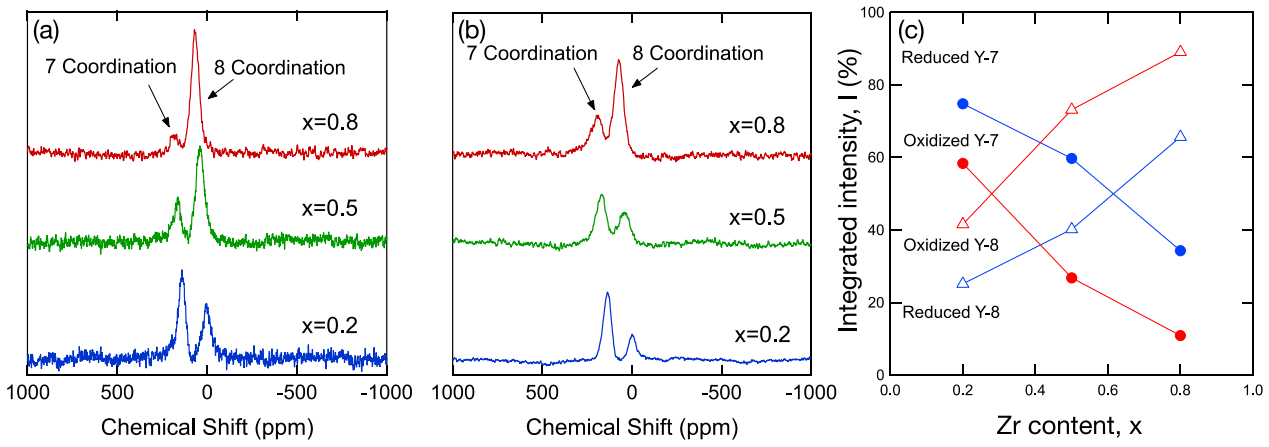

Figure 1 ^{89}Y NMR spectra of $(Ce_{1-x}Zr_x)_{0.8}Y_{0.2}O_{2-d}$ annealed under (a) air and (b) Ar-5%H_2 atmospheres, and (c) integrated intensities of 7- and 8-coordinated Y environments.

References

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