

Characterization of rare earth-doped CeO₂-ZrO₂ as oxygen storage materials by IR and isotopic transient kinetic analyses

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Abstract: The coordination state of surface cations of rare earth-doped CeO₂-ZrO₂ materials was evaluated by IR spectroscopy following methanol adsorption. The OSC properties of rare earth-doped CeO₂-ZrO₂ estimated by CO pulse method was increased with an increase in the proportion of the coordinatively unsaturated surface (*cus*) Ce³⁺ sites on the surface. Isotopic oxygen exchange reaction revealed that rare earth additive can alter the mobility of oxygen species on the surface of CeO₂-ZrO₂, resulting in the different OSC properties.

Keywords: CeO₂-ZrO₂, FT-IR spectroscopy, Isotopic transient kinetic analysis.

1. Introduction

Over the last few decades, CeO₂-based materials have received extensive attraction as a catalyst and support.¹ This is because of their unique oxygen release/sorption properties, so-called “oxygen storage capacity (OSC)”. Among the reactions effectively catalyzed by CeO₂-based materials, oxidation reactions such as CO oxidation, diesel soot combustion and VOCs abatement are strongly related with the OSC properties. Since structural defects are favorable for the mobility of charged species such as electrons or oxygen anions in the solid materials, the doping of cations into CeO₂-ZrO₂ is effective strategy to improve the OSC properties. On the other hand, oxygen release/sorption process takes place on the surface of CeO₂-ZrO₂ material, so that the surface properties related to OSC should be characterized. Methanol is known to be dissociatively adsorbed on cation sites, giving the IR bands at different wavenumbers depending on the coordination state of cations. Daturi et al.^{2,3} proposed the effectiveness of methanol adsorption by IR spectroscopy for the surface characterization of CeO₂-based materials. However, they did not well investigate the relationship between OSC values and coordination state of surface cations. In this study, we have evaluated the coordination state of surface cations of rare earth-doped CeO₂-ZrO₂ materials by IR spectroscopy following methanol adsorption, and then investigated the correlation with the OSC properties estimated by CO pulse method. We have also examined the mobility of oxygen species on the surface of CeO₂-ZrO₂ by isotopic oxygen exchange reaction.

2. Experimental

Rare earth-doped CeO₂-ZrO₂ materials were prepared by coprecipitation method, where the contents of rare earth additive and CeO₂ were fixed at 5 and 40 wt%. *In situ* FT-IR spectra following methanol adsorption were measured to identify the surface coordination state of CeO₂-ZrO₂. Before adsorption of methanol at room temperature, a self-supporting sample disk was pretreated with O₂ at 600 °C and then evacuated at the same temperature. The ¹⁶O/¹⁸O isotopic exchange reaction was carried out using a fixed-bed flow reactor. A reaction gas of 1% ¹⁸O₂/He was fed to the catalyst bed while the temperature was linearly increased from room temperature to 600 °C at a rate of 10 °C/min. The masses of 32 (¹⁶O₂), 34 (¹⁸O¹⁶O) and 36 (¹⁸O₂) were continuously monitored by the mass spectrometer.

3. Results and discussion

Figure 1 shows the IR spectra of methanol adsorbed on rare earth (La, Y, Pr, Nd) doped CeO₂-ZrO₂, as typical results, after evacuation at 100 °C. No great difference in the features of IR bands between un-

doped and rare earth-doped $\text{CeO}_2\text{-ZrO}_2$ was observed. In Fig. 1(B) is shown the deconvolution spectrum observed on $\text{CeO}_2\text{-ZrO}_2$. The IR bands at 1102 (marked I), 1066 (II) and 1017 cm^{-1} (III) are attributed to the $\nu(\text{OC})$ stretching vibration of on-top, doubly and triply bridged methoxy species, respectively, coordinated to Ce^{4+} ions and the 1155 cm^{-1} (I^*) is due to on-top methoxy species coordinated to Zr^{4+} ions. As seen in Fig. 1(B), a well-defined band at 1040 cm^{-1} (II') was detected. According to the literature,³ this band would be due to the methoxy species coordinated to heterocationic $\text{Ce}^{4+}/\text{Zr}^{4+}$ pairs.

Daturi et al.^{2,3} investigated the effect of oxidation/reduction pretreatment on the features of IR bands due to methoxy species, and concluded that the 1066 (II) and 1040 cm^{-1} (II') bands are ascribed to the presence of “coordinatively unsaturated surface (*cus*) cation”. Coordinatively unsaturated surface cation sites are known to be accompanied with oxygen defect sites on which oxygen release/sorption process would take place. Therefore, it can be expected that the proportion of the *cus* Ce^{3+} sites on the surface of $\text{CeO}_2\text{-ZrO}_2$ materials is responsible for high OSC properties. Figure 2 shows the relationship between the proportion of the *cus* Ce^{3+} sites on the surface and the OSC values estimated at 600 °C by pulsing CO. Here, the proportion of the *cus* Ce^{3+} sites on the surface was evaluated by the peak area ratio of “ $(\text{II} + \text{II}')/\text{I}$ ”. A good correlation between the surface proportion of the *cus* Ce^{3+} sites and the OSC values was observed, suggesting that the surface *cus* Ce^{3+} sites on $\text{CeO}_2\text{-ZrO}_2$ materials are related to the evolution of oxygen release/sorption properties.

The mobility of oxygen species on the surface of $\text{CeO}_2\text{-ZrO}_2$ was evaluated by $^{16}\text{O}/^{18}\text{O}$ isotopic exchange reaction. The decrease in $^{18}\text{O}_2$ and an evolution of $^{16}\text{O}^{18}\text{O}$ were observed at the temperatures above 350 °C. The temperature at which the decrease in $^{18}\text{O}_2$ started was different depending on the rare earth additive. Rare earth doped $\text{CeO}_2\text{-ZrO}_2$ with high OSC catalyzed $^{16}\text{O}/^{18}\text{O}$ isotopic exchange reaction at lower temperatures, suggesting that oxygen mobility estimated by this method correlates with the OSC property.

4. Conclusions

We found that the use of methanol as an IR molecular probe is effective technique to investigate the coordination state of surface cations related to the evolution of oxygen release/sorption properties on $\text{CeO}_2\text{-ZrO}_2$ materials. The mobility of oxygen species on the surface of $\text{CeO}_2\text{-ZrO}_2$ estimated by $^{16}\text{O}/^{18}\text{O}$ isotopic exchange reaction was found to correlate with the OSC property.

References

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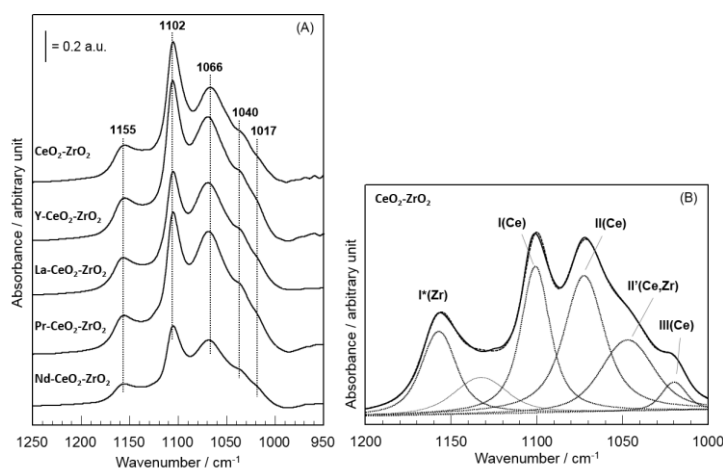


Figure 1. FT-IR difference spectra of methoxy species adsorbed on rare earth-doped $\text{CeO}_2\text{-ZrO}_2$.

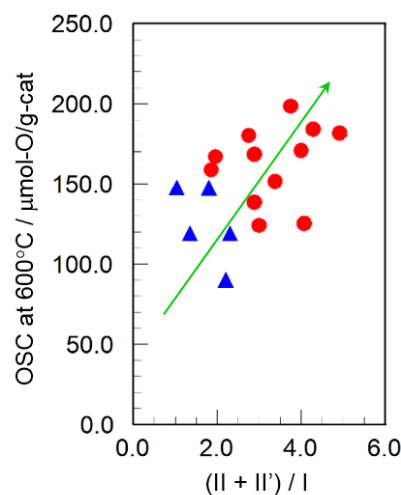


Figure 2. Relationship between the proportion of the *cus* Ce^{3+} sites on the surface and the OSC values at 600 °C