XAFS Characterization of the Redox-active Ceria-based Mixed Oxides Co-introduced with the First and Second Series Transition Metals

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1 Introduction

Introduction of different metal ions to cerium dioxide is one of the promising methods to reduce the redox reaction temperature and increase oxygen storage/release capacity of cerium oxide. We prepared ceria-based mixed oxides by co-introduction of first- and second-period transition metals to ceria and achieved high redox activity at low temperatures. For example, the introduction of both Cr and Rh decreased the reduction temperature to below 373 K on ceria. The oxidation state changes of Ce, Cr, and Rh with H2 reduction process were investigated by in situ Ce LIII-edge, Cr K-edge, and Rh K-edge XANES to clarify which elements are responsible for the low-temperature reduction.

2 Experimental

Ce LIII-edge and Cr K-edge XANES were measured in a transmission mode at the BL-9C station with a Si(111) double-crystal monochromator. Ionization chambers filled with pure N2/He (70/30 v/v) and pure N2 were used to monitor incident and transmitted X-rays, respectively. Rh K-edge XANES and EXAFS were measured in a transmission mode at the AR NW-10A station with a Si(311) double-crystal monochromator. Ionization chambers filled with pure Ar and pure Kr were used to monitor incident and transmitted X-rays, respectively.

In situ QXAFS measurements during H2 reduction were performed as follows. The sample was placed in an in situ temperature-controlled gas flow cell. After flushing with N2 (100 sccm), the cell was heated to 303 K and kept at this temperature for 5 min, at which QXAFS measurement was started. After 5 min, the gas was exchanged to H2 + N2 (50 + 50 sccm) and the temperature was held for another 5 min. Then, the cell was heated to 423 K at a rate of 2 K min⁻¹. After keeping the temperature at 423 K, the gas was changed to N2 (100 sccm), and the cell was cooled to room temperature.

XANES spectra were analysed using ATHENA and ARTEMIS programs.

3 Results and Discussion

Figure 1 (A-C) show in situ Ce LIII-edge, Cr K-edge, and Rh K-edge XANES spectra of ceria-based mixed oxide with Cr and Rh during H2 reduction. All three species were involved in the reduction processes. The Rh K-edge XANES spectra firstly changed at the lowest temperature of around 332 K. (Figure 1(A)). Following the reduction of Rh, both the Cr K-edge and Ce LIII-edge XANES spectra changed remarkably (Figure 1(B, C)), which proved the oxidation state decrease in both Cr and Ce ions. These results showed that the low-temperature reduction of ceria-based mixed oxide with Cr and Rh proceeded via the multi-reduction of the three metal species, not by a single metal source in the oxide.

Figure 1(D) shows change in Rh K-edge EXAFS FT before and after the reduction. Before the reduction, there was only Rh-O bond at 0.204 ± 0.001 nm (coordination number (CN) = 5.8 ± 1.3). After the reduction, Rh-Rh bonds at 0.270 ± 0.002 nm (CN = 2.6 ± 0.7) were observed together with the Rh-O bond at 0.205 ± 0.002 nm. This result indicates that the formation of small Rh nanoclusters were also important for the acceleration of low-temperature redox process.

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