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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 H_2 reduction process were investigated by *in situ* Ce L_{III}-edge, Cr K-edge, and Rh K-edge XANES to clarify which elements are responsible for the low-temperature reduction.

2 Experimental

Ce L_{III}-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 N_2/He (70/30 v/v) and pure N_2 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 H_2 reduction were performed as follows. The sample was placed in an *in situ* temperature-controlled gas flow cell. After flushing with N_2 (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 H_2 + N_2 (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 N_2 (100 sccm), and the cell was cooled to room temperature.

XANES spectra were analysed using ATHENA and ARTHEMIS programs.

3 Results and Discussion

Figure 1 (A-C) show *in situ* Ce L_{III}-edge, Cr K-edge, and Rh K-edge XANES spectral changes of ceria-based mixed oxide with Cr and Rh during H_2 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 L_{III}-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.

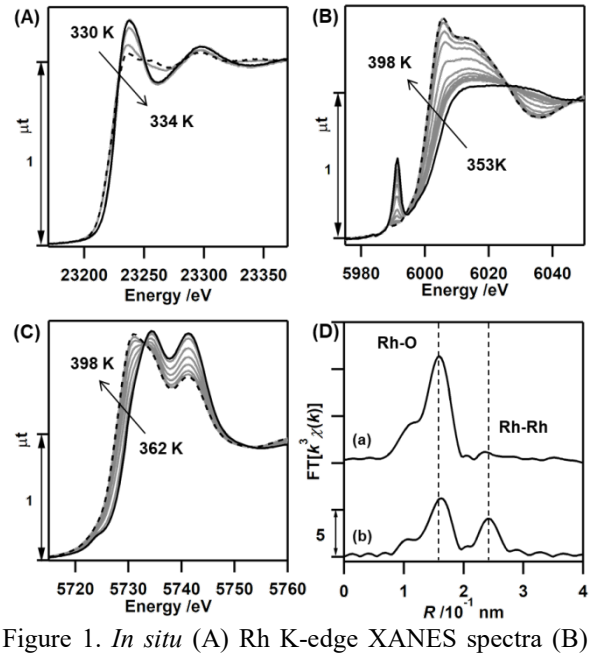

Figure 1. *In situ* (A) Rh K-edge XANES spectra (B) Cr K-edge XANES spectra, and (C) Ce L_{III}-edge XANES spectra of ceria-based mixed oxide with Cr and Rh during H_2 reduction. (D) k^3-Weighted Rh K-edge EXAFS Fourier transforms (k = 30–140 nm^{-1}) of ceria-based mixed oxide with Cr and Rh (a) before and (b) after the reduction.

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