

Clarification of Reversible Low-Temperature Redox Performances of Cr and Rh-incorporated Ceria by In-situ XAFS Characterization

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1 Introduction

A Cr and Rh-incorporated ceria (denoted as $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$) was prepared and its structures were characterized by XRD, TEM/STEM-EDS/EELS, XAFS, and XPS.^[1] Reversible redox performance of $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$ by H_2/O_2 was observed at low temperatures (< 373 K).^[1] We investigated the change in oxidation states of composed metal species by *in situ* Ce L_{III}-edge, Cr K-edge, and Rh K-edge XAFS under H_2/O_2 flow and heating conditions to comprehensively clarify the behavior of each metal species in this redox performance.^[1]

2 Experimental

Ce L_{III}-edge and Cr K-edge XAFS were measured in a transmission mode at the BL-9C station. 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 XAFS was measured in a transmission mode at the AR NW-10A station. 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/ O_2 oxidation were performed as follows. $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$ 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 for 5 min, at which QXAFS measurement was started. After 5 min, the gas was exchanged to $\text{H}_2 + \text{N}_2$ (50 + 50 sccm). After 5 min, the cell was heated to 423 K (2 K min^{-1}). After keeping the temperature at 423 K for 10 min, the gas was changed to N_2 (100 sccm), and the cell was cooled to room temperature. Then, the cell was heated again to 303 K and kept for 5 min, and the QXAFS measurement was started. After 5 min, the gas was changed to $\text{O}_2 + \text{N}_2$ (50 + 50 sccm). After 5 min, the cell was heated to 573 K (5 K min^{-1}). After keeping the temperature at 573 K for 1 h, the gas was changed to N_2 (100 sccm), and the cell was cooled to room temperature.

3 Results and Discussion

Figure 1 (A-C) show *in situ* Rh K-edge, Ce L_{III}-edge, and Cr K-edge XANES spectral changes of $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$ during O_2 re-oxidation after H_2 reduction (We previously reported the XANES spectral changes during H_2 reduction,^[2] and we did not present these spectral changes here.). As we reported previously, all three species were involved in the H_2 reduction process; Rh was initially reduced at around 332 K, and both Cr and Ce were reduced until 423 K.^[2] The average Rh, Cr, and Ce oxidation state change was estimated as follows: from +3.6 to +1.4 for Rh, from +5.4 to +3.0 for Cr, and from +3.8 to +3.5 for Ce.^[1] The total oxidation state changes in the three metals were comparable to the net consumed H in the temperature-programmed reduction (TPR) experiment.^[1] As for the O_2 re-oxidation process, Rh and Ce were rapidly oxidized at 303 K; however, Cr was gradually oxidized from 350 to 550 K, and all oxidation states were back to almost original values. These results revealed the contribution of all metal species in the reversible redox performance of $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$, together with the quantitative TPR/TPO and AP-XPS experiments.^[1]

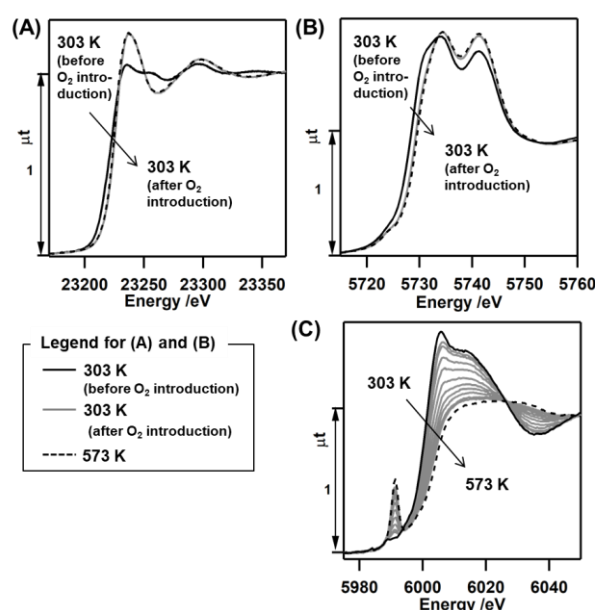


Figure 1. *In situ* (A) Rh K-edge XANES spectra (B) Cr K-edge XANES spectra, and (C) Ce L_{III}-edge XANES spectra of Cr_{0.19}Rh_{0.06}CeO_z during O₂ re-oxidation.

References

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- [2] S. Muratsugu *et al.*, *PF Activity Report 2018*, acr0183sr, (2019).

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