

## XAFS characterization of Cu and Ru-incorporated ceria ( $\text{Cu}_{0.18}\text{Ru}_{0.05}\text{CeO}_z$ ) for alcohol ammoxidation

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### 1 Introduction

A Cu and Ru-incorporated ceria (denoted as  $\text{Cu}_{0.18}\text{Ru}_{0.05}\text{CeO}_z$ ) was prepared and its structures were characterized by XRD, TEM/STEM-EDS, XAFS, and XPS.<sup>[1]</sup>  $\text{Cu}_{0.18}\text{Ru}_{0.05}\text{CeO}_z$  showed reversible redox performance at low temperatures (<423 K).<sup>[1]</sup> We investigated the change in oxidation states of composed metal species by *in situ* Ce  $L_{\text{III}}$ -edge, Cu  $K$ -edge, and Ru  $K$ -edge XAFS with  $\text{H}_2/\text{O}_2$  flow while increasing the temperature to comprehensively clarify the behavior of each metal species during the redox performance.<sup>[1]</sup>

### 2 Experiment

Ce  $L_{\text{III}}$ -edge and Cu  $K$ -edge XAFS were measured in a transmission mode at the BL-9C station. Ionization chambers filled with pure  $\text{N}_2/\text{He}$  (30/70 v/v) and pure  $\text{N}_2/\text{Ar}$  (8.5/1.5 v/v) were used to monitor incident and transmitted X-rays for Ce  $L_{\text{III}}$ -edge, respectively. Ionization chambers filled with pure  $\text{N}_2$  and pure  $\text{N}_2/\text{Ar}$  (7.5/2.5 v/v) were used to monitor incident and transmitted X-rays for Cu  $K$ -edge, respectively. Ru  $K$ -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 for Ru  $K$ -edge, respectively.

*In situ* QXAFS measurements during  $\text{H}_2$  reduction/ $\text{O}_2$  oxidation were performed as follows.  $\text{Cu}_{0.18}\text{Ru}_{0.05}\text{CeO}_z$  was placed in an *in situ* temperature-controlled gas flow cell. After flushing with  $\text{N}_2$  (100 sccm) for 10 min, the cell was heated to 303 K and kept for 5 min, and then QXAFS measurement was started. After 5 min, the gas was switched to  $\text{H}_2 + \text{N}_2$  (50 + 50 sccm). After 5 min, the cell was heated to 473 K (2 K  $\text{min}^{-1}$ ). After keeping the temperature at 473 K for 10 min, the gas was changed to  $\text{N}_2$  (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 switched to  $\text{O}_2 + \text{N}_2$  (50 + 50 sccm). After 5 min, the cell was heated to 573 K (5 K  $\text{min}^{-1}$ ). After keeping the temperature at 573 K for 1 h, the gas was changed to  $\text{N}_2$  (100 sccm), and the cell was cooled to room temperature.

### 3 Results and Discussion

Figure 1(a-c) showed *in situ* Ru  $K$ -edge, Cu  $K$ -edge, and Ce  $L_{\text{III}}$ -edge XANES spectral changes of  $\text{Cu}_{0.18}\text{Ru}_{0.05}\text{CeO}_z$  during  $\text{H}_2$  reduction. Figure 1(d) showed the oxidation

states changes of each metal species during  $\text{H}_2$  reduction. It was found that Ru was initially reduced at 333 K, followed by Cu reduced at 353 K and finally Ce reduced at 373 K. The average oxidation states of Ru, Cu, and Ce were estimated as follows: Ru changed from +4.37 to +1.06, Cu changed from +2.00 to +0.30 and Ce changed from +3.85 to +3.62, respectively. The total oxidation states change of Ru, Cu and Ce were comparable to the net  $\text{H}_2$  consumption by TPR measurements.<sup>[1]</sup> After  $\text{O}_2$  re-oxidation, all the metal species were recovered to almost original values. These results revealed the behavior of all metal species in the reversible redox performance of  $\text{Cu}_{0.18}\text{Ru}_{0.05}\text{CeO}_z$ .  $\text{Cu}_{0.18}\text{Ru}_{0.05}\text{CeO}_z$  showed high conversion of benzyl alcohol (95%) with high selectivity (95%) to produce benzonitrile in the ammoxidation of benzyl alcohol.<sup>[1]</sup> The enhanced redox performance of  $\text{Cu}_{0.18}\text{Ru}_{0.05}\text{CeO}_z$  also suggested that the reduced structure of  $\text{Cu}_{0.18}\text{Ru}_{0.05}\text{CeO}_z$  was active for the ammoxidation.

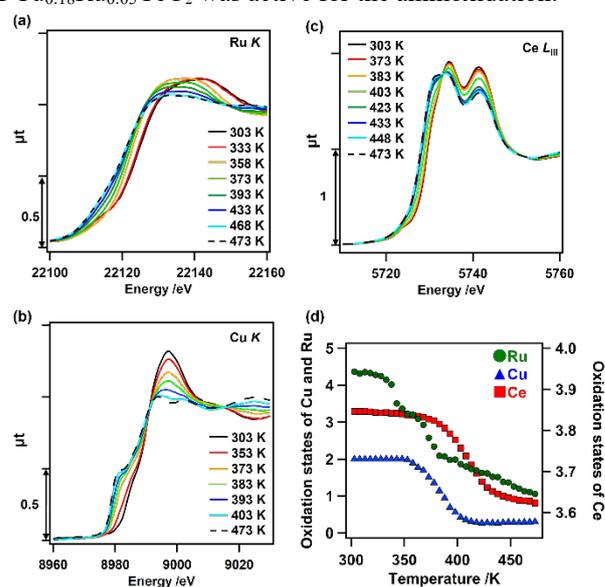


Figure 1 (reproduced from Ref. [1]): *In situ* (a) Ru  $K$ -edge XANES spectra (b) Cu  $K$ -edge XANES spectra, and (c) Ce  $L_{\text{III}}$ -edge XANES spectra of  $\text{Cu}_{0.18}\text{Ru}_{0.05}\text{CeO}_z$  during  $\text{H}_2$  reduction. (d) The changes of the oxidation states for Ru, Cu and Ce during  $\text{H}_2$  reduction.

### References

[1] C. Chen *et al.* *Phys. Chem. Chem. Phys.* **26**, 17979-17990 (2024).

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