

In situ XAFS characterization of Cr and Rh-incorporated Ceria ($\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$) during NO reduction with CO

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1 Introduction

The Cr and Rh-incorporated ceria (denoted as $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$)^[1] showed an NO reduction activity at 373 K. It afforded >99% NO conversion at 393 K and >99% N_2 selectivity at 473 K, which were superior to $\text{Rh}_{0.04}\text{CeO}_2$, $\text{Cr}_{0.17}\text{CeO}_2$, and CeO_2 , respectively. (conditions: NO (0.5%), CO (1.0%), Ar (5.0%), and He (balance) with a total flow rate of 100 mL min^{-1} (GHSV = 6500 h^{-1})).^[2] We investigated the change in the oxidation states of composed metal species in $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$ by *in situ* Ce L_{III}-edge, Cr K-edge, and Rh K-edge XAFS under NO/CO flow and heating conditions to comprehensively clarify the behavior of each metal species in the NO reduction performance with CO.^[2]

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 under NO flow/CO flow 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 pretreatment with N_2 (100 mL min^{-1}) at 573 K for 1 h, the cell temperature was decreased to 473 K under N_2 flow (100 mL min^{-1}) for 60 min. After 10 min, the QXAFS measurement was started. After 5 min, the gas was changed to CO + N_2 (5 + 95 mL min^{-1}) and the gas flow was held for 30 min. After 10 min, the cell was flushed with N_2 (100 mL min^{-1}) for 20 min. Secondly, the gas was changed to NO + N_2 (5 + 95 mL min^{-1}) and the gas flow was held for 30 min. The gas was finally changed to N_2 (100 mL min^{-1}), and the cell was cooled to room temperature.

3 Results and Discussion

Figure 1 (A(a), B(a), C(a)) show *in situ* Rh K-edge, Ce L_{III}-edge, and Cr K-edge XANES spectral changes of $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$ under CO flow.^[2] The

Rh and Cr K-edge XANES spectra rapidly changed within 5 min, suggesting that oxygen species in the Cr component was consumed by the reaction with CO. On the other hand, the Ce L_{III}-edge XANES spectra gradually changed over 30 min. Figure 1 (A(b), B(b), C(b)) show *in situ* Rh K-edge, Cr K-edge, and Ce L_{III}-edge XANES spectral changes of $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$ under NO flow.^[2] All XANES spectral change showed that all metal species were oxidized, suggesting that the reduced Rh species and Cr components and CeO_2 surface were re-oxidized by NO.

Together with *in situ* FT-IR spectral analyses of $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$ under CO and NO treatments and kinetic analysis, Rh species acted as adsorption sites for both NO and CO, and chromium oxides played a role to the oxygen transfer from the cleaved NO to CO on the CeO_2 surface. This effect would promote the efficient NO reduction with CO on $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$ at low temperature.

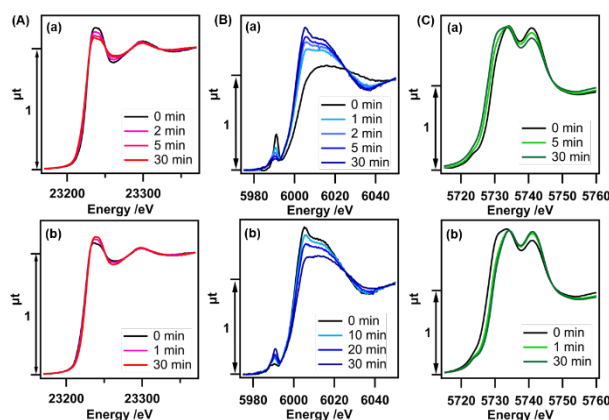


Figure 1. *In situ* (A) Rh K-edge XANES, (B) Cr K-edge XANES, and (C) Ce L_{III}-edge XANES spectra of $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_2$ (a) under CO flow and (b) under NO flow at 473 K.

References

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