

XAFS Analysis on Reduction Process of Copper(II) Oxide Supported on Ceria and Silica

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Introduction

Knowledge of the chemical state of supported active metal species is important to understand the catalytic activity, and the chemical state conversion is a key process to understand the degradation mechanism of the heterogeneous catalysis system. The systematic investigation on the chemical state conversion of the metal species supported on oxide materials provides useful information to design catalysis systems with the improved performance. In this study, the reduction process of CuO supported on CeO₂ has been analyzed using *in-situ* XAFS technique, and the reduction property of CuO/CeO₂ has been compared with CuO/SiO₂ to clarify the contribution from supporting CeO₂, which has the oxygen storage/release ability.

Experimental Methods

CuO/CeO₂ and CuO/SiO₂ were prepared by the impregnation method. An aqueous solution of Cu(NO₃)₂ was mixed with the powder of CeO₂ or SiO₂. The suspension was dried and the obtained powder was subject to the calcination in air at 600 °C. The *in-situ* XAFS measurements at the Cu K and Ce L₃ edge were carried out at BL-9C and BL-9A of Photon Factory (KEK, Japan), respectively, during the temperature-programmed reduction (TPR) process under the gas flow of H₂ (10 vol%) diluted by He from room temperature to 900 °C. The *in-situ* XRD measurements were also performed to observe the change of the crystal phase.

Results and Discussion

The Ce L₃ XAFS measurement during the TPR process revealed that CeO₂ was converted to an intermediate valence state at *ca.* 350 °C and further reduced to Ce₂O₃ at *ca.* 850 °C. The *in-situ* XRD observation showed the lattice expansion at the same temperature where the intermediate state was generated. According to the edge shift of the XANES spectrum, the intermediate state was assigned to a non-stoichiometric oxide with the composition of CeO_{1.74}. The composition analysis during the TPR process clarified that the supported CuO species was reduced to Cu(0) via Cu₂O at *ca.* 300 °C. The composition of Cu₂O was suppressed to less than 20 % because of the relative stability of the Cu(0) state under the H₂ gas atmosphere. A similar composition change was observed for CuO/SiO₂, but the reduction temperature of CuO was lower by *ca.* 70 °C. The *in-situ* XAFS study also revealed that the composition of CeO₂ was not changed at all at the reduction temperature of CuO, suggesting the independent reduction of CuO and CeO₂.

Conclusion

The present *in-situ* XAFS studies clarified the formation of a non-stoichiometric oxide of CeO_{1.74} during the reduction treatment of CuO/CeO₂, whereas the reduction of supported CuO to Cu(0) via Cu₂O is found to be independent from the intermediate valence state.