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In-Situ XAFS Analysis for Reduction Process of $CuCl_2$ on SiO_2

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1. Introduction

It is most important to know the chemical state of active species, when considering the performance of heterogeneous catalysts. For the active material of the rechargeable battery, assigning the chemical species in the electrode is the basis for understanding the electrode reaction. For both materials, the chemical state conversion of the metal species in the solid phase is not only directly linked to the performance but also provides a guideline for the development of new functions.

We have previously analyzed the conversion process for H_2 reduction of NiO and O_2 oxidation of Ni on SiO_2 supports.[1,2] It has been clarified that the reduction of NiO starts at a certain point of the particle surface and penetrates to the inside of the NiO particle. The conversion mechanism of the reduction process for CoO[3] and CuO[4,5] has been elucidated in the same way as NiO. In this study, oxygen was replaced with chlorine having the comparable electronegativity, and the chemical state analysis was carried out using the *in-situ* XAFS technique for the reduction process of $CuCl_2$ by H_2.

2. Experimental

An aqueous solution of $CuCl_2$ was used for the impregnation under the incipient wetness condition to prepare the $CuCl_2$ hydrates supported on SiO_2 (192 m^2 g^{-1}) with the Cu loading of 40 wt%, which was obtained by drying at 60 °C in air. *In-situ* XAFS measurement at the Cu K edge was performed at BL-3 of the SR Center for the reduction process under a He-diluted H_2 gas flow (10 vol%) at elevated temperatures to 475 °C.

3. Results and Discussion

Figure 1 shows the XANES spectral changes measured for the reduction process $CuCl_2$ hydrate supported on SiO_2. The spectrum at room temperature was consistent with that of $CuCl_2$ hydrate with a single white line, and it was changed to that of anhydrous $CuCl_2$ with double white lines by heating to 75 °C. The XANES spectrum observed at around 300 °C was characteristic of CuCl with a white line at 8984 eV, and the spectra from room temperature to 315 ˚C had an isosbestic point at 8986 eV. The XANES spectrum was further changed to that of metallic Cu at above 365 ˚C with the isosbestic points at 8979 and 8989 eV. The *in-situ* XAFS measurement clearly demonstrated two-step reduction from $CuCl_2$ to metallic Cu via CuCl.

The values of normalized X-ray absorbance are plotted as a function of temperature in Fig. 2 at 8982 and 8992 eV, that is characteristic energy for CuCl and $CuCl_2$, respectively. The anhydrous $CuCl_2$ was found to be reduced at the temperature range from 225 to 285 ˚C, and the quantitative formation of the CuCl species in the range of 310 ± 25 ˚C was clearly supported by the XANES spectrum in Fig. 1, which was consistent with that of bulk CuCl. This study revealed that the reduction of $CuCl_2$ proceeded at a lower temperature than that of CuO (*ca.* 320 ˚C).[3] Furthermore, the fact that there is a temperature range in which the CuCl state is stable is in contrast to the rapid reduction of Cu_2O to metallic Cu.

The final XANES spectra at above 365 ˚C were in agreement with that of Cu foil, and the absorbance change given in Fig. 2

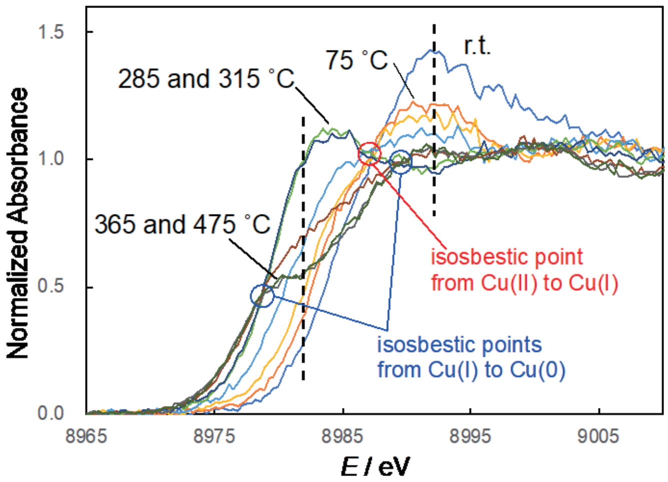

Fig. 1 XANES spectral change for the reduction process of $CuCl_2$ hydrate supported on SiO_2 under a He-diluted H_2 gas flow (10 vol%) at elevated temperature to 475 °C.

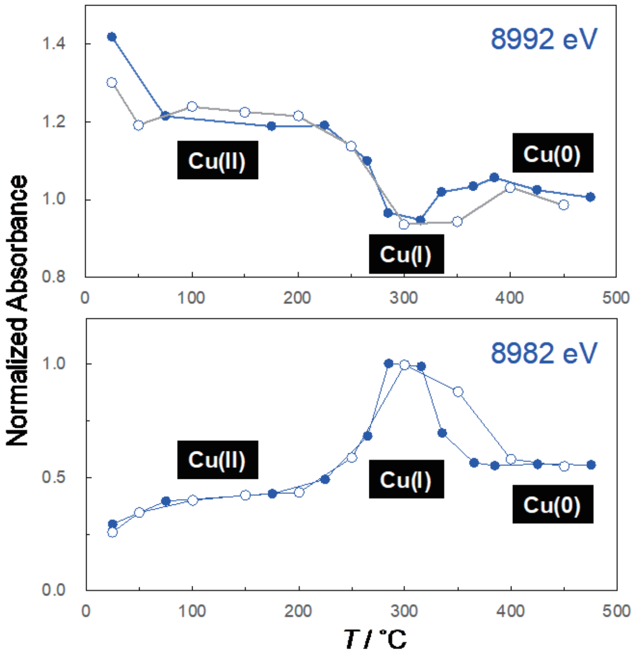

Fig. 2 Change of normalized X-ray absorbance at 8992 and 8992 eV as a function of temperature for *in-situ* XAFS measurements of the first (open circles) and second (filled circles) run.

indicated that the second reduction process from CuCl to Cu(0) proceeded in the temperature range of 350 ± 15 ˚C. The X-ray absorbance at around 350 ˚C of the second run was largely deviated from that of the first run. The increase rate of temperature of the second run was much slower than that of the first run. It is thus considered that the delayed reduction in the first run is related to the relatively slow conversion of CuCl to Cu(0). This dynamic behavior of CuCl suggesting its thermodynamic stability also contrasts with the instability of Cu_2O, which is easily reduced.

4. Conclusion

The chemical state conversion of $CuCl_2$ on SiO_2 were analyzed using the *in-situ* XAFS method during the temperature-programmed reduction process under the He-diluted H_2 gas flow. This study clarified the temperature at which the stepwise reduction from $CuCl_2$ to metallic Cu via CuCl proceeds on SiO_2. It has been pointed out that the reduction temperatures of chlorides are identical to those of oxides, whereas there is a clear difference in the thermodynamic stability of the Cu(I) state.

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