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Development of *in-situ* XAFS cell for simultaneous measurement of conversion-electron-yield and transmission detections

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1 Introduction

The particle surface of metal species supported on oxide materials is an active field for many catalytic reactions, and such heterogeneous catalysts are utilized for a lot of chemical processes to achieve the high activity and the selectivity. It is thus important to evaluate the chemical state of the surface species of active metal particles under the reaction gas environment, at which the catalytic reactions proceed. The *in-situ* X-ray absorbance fine structure (XAFS) method is powerful to analyze selectively the chemical state and the local structure for a target metal species. In addition, the conversion-electron-yield (CEY) detection of the XAFS measurement is useful to observe the surface region of the solid particles. Therefore, the CEY observation under the reaction gas atmosphere can provide crucial aspects for the active species of the working catalysts. In this study, we have developed the *in-situ* XAFS cell for simultaneous measurement of the CEY and transmission detections under gas flow environment at elevated temperature.

2 Experiment

Fig. 1 shows a design of the developed *in-situ* XAFS cell. The cell body is made of silica glass, and a pair of electrodes (50 μm thickness) made of Al is set in a ceramics holder. The sample powder is put on the slanted electrode, and the bias voltage (*ca.* +500 V under dilute H_2) is applied to another electrode. Because of the melting point of Al, the highest temperature of the present cell is limited to *ca.* 600 °C.

The sample powder of shape-controlled Cu_2O particle supported on γ-Al_2O_3 was prepared according to the liquid phase reduction method reported previously [1]. The reduction reaction of the cubic Cu_2O particles were observed using the developed cell. The *in-situ* XAFS measurements were carried out at BL-9C of Photon Factory (KEK). The sample was heated up to 320 °C with the increasing rate of 10 °C/min under the dilute H_2 gas flow balanced by He (10 vol%, 200 cm^3/min).

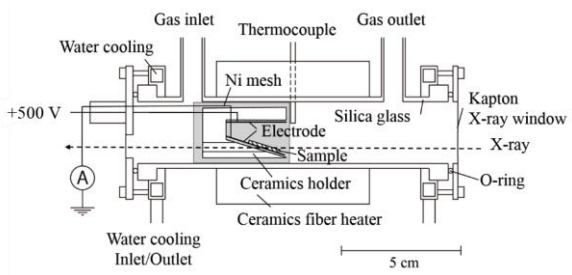

Fig. 1: Schematic diagram of the developed *in-situ* XAFS cell for simultaneous measurement of CEY and transmission detection.

3 Results and Discussion

The sample composition was analyzed by the pattern fitting of the XANES spectrum, and the calculated values of mole fraction were plotted in Fig. 2 as a function of temperature. The transmission data revealed that the bulk region of the cubic Cu_2O particle was reduced to Cu(0) at *ca.* 250 °C, whereas the CEY data indicated that the surface region was reduced at slightly higher temperature of *ca.* 270 °C. The XANES spectra measured at 260 °C are clearly different between the CEY and transmission detections (Fig. 2(B)). The difference suggests that the reduction of the inner part precedes the surface reduction for the cubic Cu_2O particle. It is considered that the removed O atoms by H_2 at the particle surface are supplied by the O atom migration from the inner part of the particle, and that the surface Cu_2O shell is finally reduced to Cu(0).

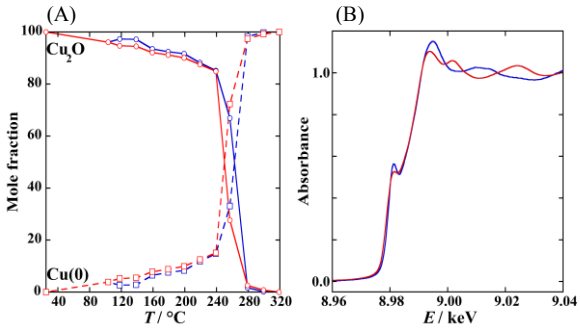

Fig. 2: The mole fraction of Cu_2O and Cu(0) as a function of temperature for the supported Cu_2O particles (A). The XANES spectra measured at 260 °C (B). The blue lines and the red lines show the result for the CEY and transmission detections, respectively.

Reference

[1] D.-F. Zhang, H. Zhang, L. Guo, K. Zheng, X.-D. Han, and Z. Zhang, *J. Mater. Chem.*, **19**, 5220–5225 (2009).

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