Development of *In-Situ* XAFS Cell for Conversion Electron Yield Detection and Application to Shape-Controlled Al_2O_3-Supported Cuprous Oxide

Toshiki Watanabe, Misaki Katayama, and Yasuhiro Inada

Department of Applied Chemistry, Graduate School of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan

Abstract

The *in-situ* XAFS cell was developed for the conversion electron yield (CEY) detection for the characterization of active metal species under reaction gas atmosphere. The probe depth was estimated to be about 9 nm at the Cu K edge. The *in-situ* CEY cell was applied to the shape-controlled γ-Al_2O_3-supported Cu_2O catalyst. The reduction to Cu(0) by H_2 of octahedral Cu_2O particles proceeded at lower temperature than cubic particles, indicating that the surface atomic arrangement affects to the redox reaction of solid particles.

1. Introduction

The X-ray absorption fine structure (XAFS) spectroscopy is a powerful tool to analyze the local structure and electronic state of a target element containing in a large amount of coexisting materials. The utility to dilute samples is quite useful to understand the chemical state of active species of heterogeneous metal catalysts. The electron yield detection for the XAFS spectroscopy achieves the surface sensitive analysis on solid particles. In addition, the applicability under various conditions is a great advantage for the *in-situ* characterization at the operational environment. In this study, we have aimed to combine the electron yield detection with *in-situ* XAFS measurements by developing the *in-situ* XAFS cell for conversion electron yield (CEY) detection. Although a carrier gas of pure He is usually used for the sample atmosphere, the mixing with H_2 and the sample heating have been attempted to achieve the CEY detection under reductive gas atmosphere at elevated temperature.

2. Experimental

2.1. Development of *In-Situ* CEY Cell

Figure 1(A) shows a design of the newly developed *in-situ* CEY cell for surface sensitive XAFS measurements. The cell body is made of silica glass. A Kapton film (25 μm thickness) was used as the X-ray window, and an O-ring made of Viton was used to seal between the Kapton film and the cell body. The window was cooled by circulating water to prevent the damage of the O-ring and the Kapton film. A pair of electrodes made of Al to measure sample current was set in a ceramics holder. The sample powder was put on a tilted electrode, and the

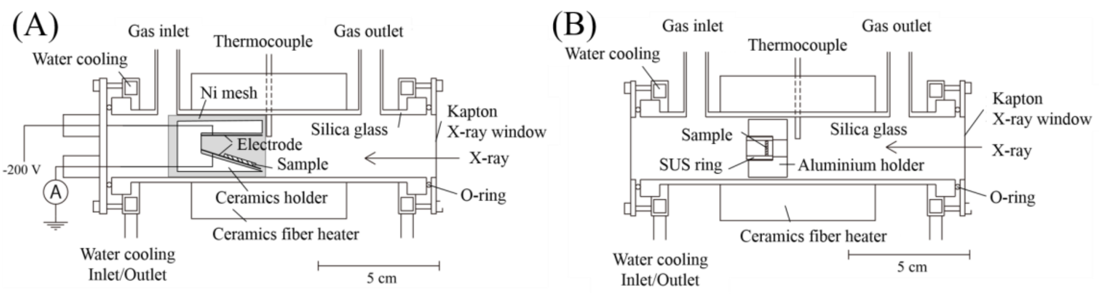

Figure 1. The schematic diagram of the developed *in-situ* XAFS cell for CEY detection (A) and in transmission mode (B).

bias voltage (*ca.* 200 V) was applied to the other electrode. The highest temperature of the current cell is limited to about 600 °C because of the melting point of Al. The CEY unit can be replaced with the sample holder for transmission measurements, as shown in Figure 1(B).

2.2. Preparation of Shape-Controlled Cu_2O Particles

The shape-controlled Cu_2O particles supported on γ-Al_2O_3 were prepared by the liquid phase reduction method [1]. An aqueous solution of ascorbic acid was dropped into an aqueous solution of $CuCl_2$, in which the γ-Al_2O_3 powder was suspended. The octahedral Cu_2O particles were available with the average particle size of 325 nm by adding PVP as a surface-active reagent. The cubic particles with the average size of 349 nm were obtained without the addition of PVP. The composition of Cu_2O was confirmed by the XRD measurements, and the particle size was estimated by the SEM measurements.

2.3. XAFS Measurements

The *in-situ* XAFS measurements were carried out at BL-3 of the SR center (Ritsumeikan University), BL-12C of the Photon Factory (KEK), and BL01B1 of SPring-8 (JASRI) at the Cu K edge by using the developed *in-situ* CEY cell. The Si(111) double-crystal monochromator was detuned to remove higher-order harmonics for the measurements at BL-12C, and the Rh-coated double-mirror system was used. The quick-scanning mode was applied for all measurements. The dilute H_2 gas (10 vol% balanced by He, 100 cm^3/min) was flowed in the CEY cell, and the powder sample was heated up to 200 °C with the increasing rate of 10 °C/min.

3. Results and Discussion

3.1. Performance of Developed *In-Situ* CEY Cell

The measured XAFS spectra, the EXAFS oscillation functions, and the Fourier transform functions of Cu foil measured by the developed *in-situ* CEY cell are shown in Figure 2 by comparing the results of the transmission mode and the CEY detection. The obtained data by the CEY detection is perfectly in agreement with that of the transmission mode.

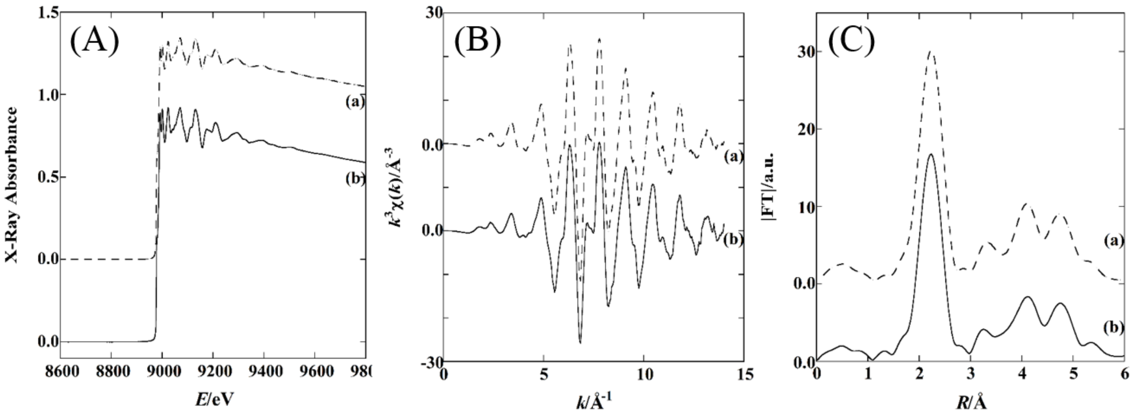

Figure 2. XAFS spectra (A), the EXAFS oscillation functions (B), and the Fourier transform functions (C) of Cu foil measured in transmission mode (a) and by CEY detection (b).

3.2. Reduction of Supported Cu_2O Particles

An example of XANES spectral change is shown in Figure 3 for the reduction process of octahedral Cu_2O particles supported on γ-Al_2O_3 measured by using the *in-situ* CEY cell. The temperature was changed from 25 to 200 °C. The initial and final XANES spectra were respectively consistent with those of Cu_2O and Cu foil measured independently. The XANES spectrum was changed from Cu_2O to Cu(0) by increasing temperature under dilute H_2 atmosphere. Some isosbestic points were clearly observed, indicating that the chemical transition from Cu_2O to Cu(0) proceeded with no other species. All results indicate that the supported Cu_2O particles are reduced for both octahedral and cubic shapes.

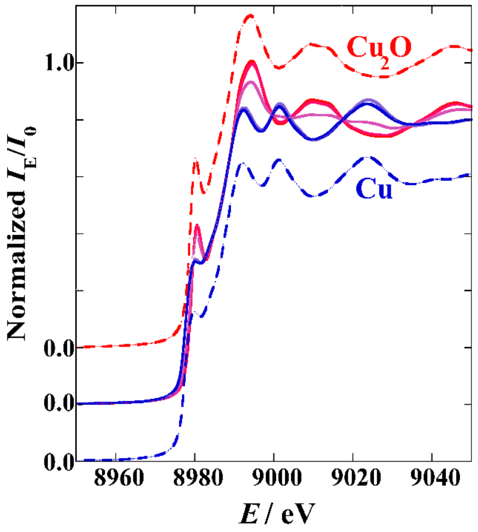

Figure 3. XANES spectral change of octahedral Cu_2O particles supported on γ-Al_2O_3 measured by using the developed *in-situ* CEY cell.

The sample composition was analyzed by the pattern fitting of the XANES spectrum, and the calculated values of mole fraction are plotted in Figure 4 as a function of temperature. In Figure 4(A), the temperature dependence of the composition in the surface region of the particle is compared between octahedral and cubic particles on the basis of the results measured by the *in-situ* CEY technique. The octahedral particles reduced at around 130 °C, whereas the reduction of cubic particles proceeded at slightly higher temperature of about 160 °C. The lower reduction temperature for the octahedral particle indicates that the (111) facets of the octahedral particle have higher affinity with H_2 than the (100) facets of the cubic particle.

The reduction temperature is compared for the octahedral Cu_2O particle between the CEY and transmission detections. The surface-sensitive CEY detection showed the lower reduction temperature by about 40 °C than the bulk reduction probed by the transmission measurement. It is found that the surface region of the octahedral particle is easily reduced because of the existence of the unsaturated Cu atoms on the (111) facet, which strongly interact with the H_2 molecule. Because the O atom migration is necessary for the bulk reduction, the higher temperature detected by the transmission measurement means that the O atom migration occurs at about 170 °C in the octahedral particle.

In contrast, the reduction temperature of the bulk region was almost consistent with that of the surface region in the case of the cubic particle, as shown in Figure 4(C). Both measurements showed the comparable temperature of reduction around 170 °C. The surface reduction is not facilitated for the cubic particle because of the lack of the unsaturated Cu atoms on the (100) facet. The O atom migration in the Cu_2O particle thus controls the reduction temperature of the whole particle. This motion is independent on the particle shape, and thus the comparable reduction temperatures are reasonable between the octahedral

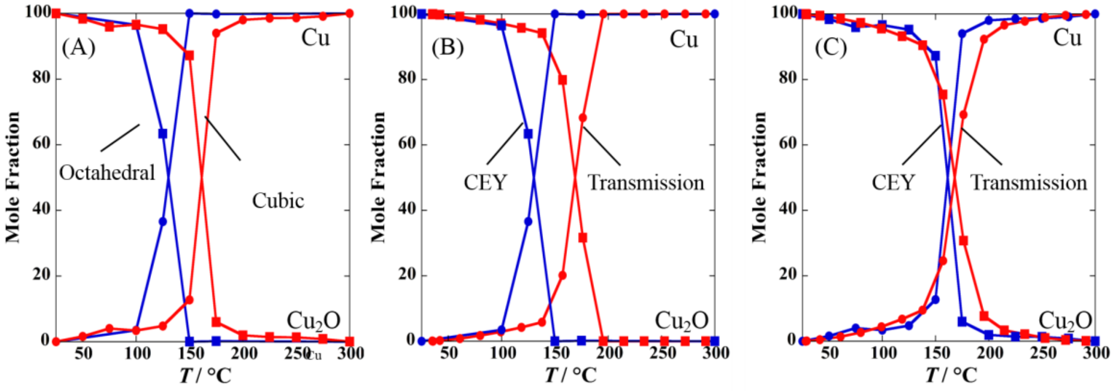

Figure 4. The mole fraction of Cu_2O and Cu(0) as a function of temperature for octahedral and cubic particles measured by the CEY detection (A). In B and C, the results of octahedral and cubic particles are respectively compared between the CEY and transmission detection.

particles with the unsaturated Cu atoms on the surface and the cubic particles with no such Cu atoms.

3.3. Probe Depth of the CEY Detection

The CEY measurements revealed that the reduction process of the surface region of octahedral particles was completed at 150 °C as seen in Figure 4. At this temperature, the reduction of about 15 percent of whole Cu_2O particle completed according to the transmission measurement. Because the average size is 325 nm for the octahedral particles, the 15 percent of the particle volume corresponds to the shell depth of 8.9 nm (see Figure 5). This means that the probe depth by the CEY detection is about 9 nm at the X-ray energy of 9 keV. In the case of the cubic particle, the composition is considered to be homogeneous for all parts of the particle until the reduction is completed, and thus the same reduction temperature was observed for both the transmission and CEY detections.

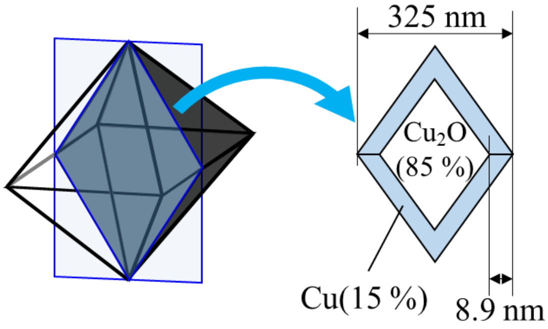

Figure 5. The probe depth of the CEY measurement.

4. Conclusion

In this study, we have succeeded in developing *in-situ* XAFS cell for the CEY detection with the probe depth of about 9 nm at 9 keV to observe chemical reactions proceeded in the surface region of supported particles in heterogeneous catalysts. The facilitated surface reduction was observed for the octahedral Cu_2O particles, which is supported by the existence of the unsaturated Cu atoms on the (111) facet of octahedral particles. The *in-situ* CEY technique is expected to become a new and useful analysis tool for heterogeneous catalysts.

Acknowledgment

XAFS measurements were carried out under the approval of the Photon Factory Program

Advisory Committee (Proposal Nos. 2011G531 and 2013G596) of High Accelerator Research Organization and the approval of the Japan Synchrotron Radiation Research Institute Program Advisory Committee (Proposal No. 2013B1294).

Reference

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