Microscopic Observation for Reduction Process of Octahedral Cu_2O Particle

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Improving the activity and selectivity of supported metal catalysts is important for saving resources and reducing costs. Methods for improving catalytic performance include reducing the particle size of active metal species to increase their surface area and controlling the particle shape [1]. Cu_2O particles, which are active in environmental purification, can be controlled into various shapes. Depending on the conditions of the synthesis reaction, it is possible to control the shape to polyhedrons, cubes, octahedrons, etc [2-4]. The performance of a catalyst is significantly affected by the chemical state of the active species exposed on the particle surface. A change in the chemical state of surface species can cause the catalyst to lose activity, or conversely, the change can dominate the catalytic cycle. Understanding the details of the reduction process on the surface of Cu_2O particles will be an important factor in understanding the source of the catalytic activity. In this study, we have performed *in situ* XAFS and SEM analysis for the temperature-programmed reduction (TPR) process of octahedral Cu_2O particles.

The octahedral Cu_2O particles were synthesized by the hydrothermal method using an aqueous solution of copper(II) chloride as a precursor and tartaric acid in a basic solution as a reducing agent. The obtained Cu_2O particles were heated to 400 °C under a 10 vol% He-diluted H_2 atmosphere, and *in situ* XAFS measurements for the TPR process were performed at BL-3. In addition, SEM measurements were carried out on the Cu_2O particles reduced at 285 °C and 325 °C.

The change in the XANES spectrum during the TPR process is shown in Fig. 1. The initial spectrum was identical to that of Cu_2O, and it was clarified that reduction of Cu_2O to Cu(0) proceeded in the temperature range from 275 °C to 325 °C. The shapes of Cu_2O particles that were reduced at various temperatures within the temperature range were observed using SEM. The results are given in Fig. 2. For the Cu_2O particle reduced at 285 °C, microparticles were observed on the surfaces of the {111} faces. Such a situation has not been observed in as-synthesized particles. When the reduction temperature was increased to 325 °C, the microparticles disappeared, and instead a lot of hollows were observed on the particle surface. Because *in situ* XAFS measurement revealed that the reduction to Cu(0) completed at 325 °C, it is considered that Fig. 2(b) is the formed Cu(0) particle.

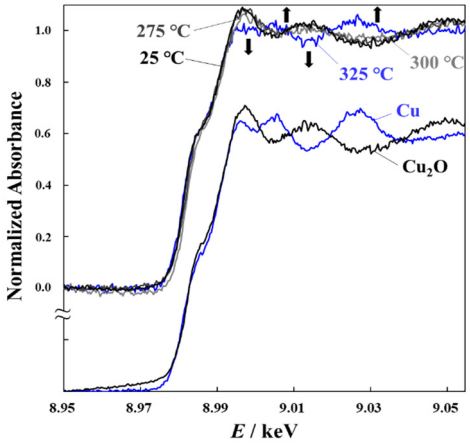

Fig. 1. XANES change measured at Cu K edge for the TPR process of octahedral Cu_2O particles. XANES spectra of bulk Cu_2O and Cu metal are shown for comparison.

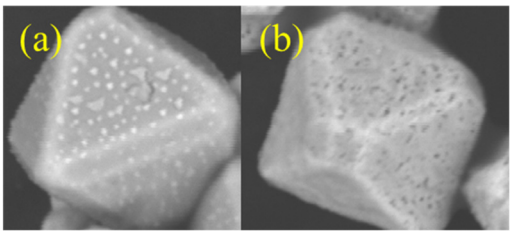

Fig. 2. The SEM images of octahedral Cu_2O particle reduced at 285 °C (a) and 325 °C (b).

The particle shape seems to be maintained after reduction to Cu(0), but due to the difference in volume between Cu_2O and Cu(0), the octahedral Cu(0) particles have many vacancies.

The chemical state analysis of the microparticles observed on the {111} plane of the Cu_2O particle during reduction is essential for understanding the reduction mechanism. It will be clarified by microscopic XAFS analysis of a single particle.

References

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