Redox Property of Cu/SiO₂ Catalysts
Prepared under the Existence of Organic Additives

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1. Introduction
The particle size of active metal species is a key factor for the catalytic activity of supported metal catalysts. It is important for the catalyst design to reveal the chemical state conversion of small metal species. In fact, the chemical state conversion of SiO₂-supported Co, Ni, and Cu species is affected by their particle size. Recently, it is found that the organic additives at the preparation process control the size of active metal species. This study will clarify the relationship between the chemical state conversion and the Cu particle size.

2. Experimental
The Cu/SiO₂ catalysts were prepared by the impregnation method under the existence of an organic additive with the Cu loading of 10 wt.%. A stoichiometric amount of organic additive, such as citric acid, succinic acid, and alanine, was added into the copper nitrate solution to control the Cu particle size.

The in-situ XAFS experiments were conducted at BL-3 of the SR center (Ritsumeikan Univ.) and at BL-9C of the Photon Factory (KEK). The XAFS measurements were carried out at the Cu K edge during the temperature-programmed reduction (TPR) and oxidation (TPO) processes under the dilute H₂ or O₂ gas flow.

3. Results and Discussion
The CuO crystallite size was estimated using the Scherer equation for the CuO(111) line. The crystallite size of 49 nm for CuO/SiO₂ prepared without any organic additives was reduced to 27 nm, 17 nm, and 11 nm when succinic acid, citric acid, and alanine was added during the preparation process, respectively. It has been demonstrated that the organic additive can control
the particle size of the supported Cu species.

The composition changes for the Cu/SiO₂ catalyst during the TPR and the TPO processes are given in Figure 1. The CuO was reduced to metallic Cu(0) via Cu₂O during the TPR process, and the three components also exited in the TPO process.

Figure 1. The composition change for the Cu/SiO₂ catalyst prepared with succinic acid during the TPR (A) and the TPO (B) process.

Figure 2 shows the mole fraction changes of the metallic Cu(0) species as a function of temperature during TPR and TPO processes. In the both cases, the reaction temperature was shifted lower with the diminishing the particle size. It is considered that the lower shift is resulted from the easy migration of oxide ion in the cupper particle. It should be noted that the reduction temperature of the smallest CuO particle (11 nm) is shifted higher. This suggests that the interaction at the interface between the CuO and SiO₂ particle stabilizes the CuO state especially for the small CuO particle because of the increased contact area.

Figure 2. The composition of the metallic Cu(0) species as a function of temperature during the TPR (A) and the TPO (B) process.