

Reduction Property of CuO Particle Supported on Mesoporous Silica

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Supported Cu particle is used as an excellent catalyst for CO₂ hydrogenation reaction. One of the key parameters of the catalytic performance is the particle size of the active Cu species. It is thus important to understand the particle size effect on chemical state conversion of the Cu species. In this study, the particle size of the supported Cu species was controlled by the addition of citric acid into the impregnation solution and by the utilization of mesoporous silica (KIT6) as the supporting material. The chemical state of the Cu species was analyzed by the *in situ* XAFS measurements during the reduction process at elevated temperatures.

The supported Cu catalysts were prepared by the impregnation method. SiO₂ (specific surface area: 185 m² g⁻¹) and KIT6 (395 m² g⁻¹) was used as the support. The citric acid was added into the impregnation solution. The *in situ* XAFS experiments were performed at BL-3 of the SR center (Ritsumeikan Univ.) and BL-9C of the Photon Factory (KEK). The XAFS measurements carried out at the Cu K edge during the reduction process under 10 vol% H₂/He atmosphere up to 400 °C.

The average particle size of the supported Cu species was estimated by the transmitted electron microscopy (TEM) observation. The particle size (10 nm) prepared with citric acid was smaller than that (15 nm) without the addition on standard SiO₂. In the same way, the average particle size prepared with citric acid on KIT6 was 5 nm. On the other hand, it was found that two different size distributions (6 nm and 27 nm) existed for the sample prepared without citric acid on KIT6.

The mole fraction of the CuO species during the reduction process was shown in Fig. 1 determined by the composition analysis using the XANES spectrum. The reduction temperature of CuO/SiO₂ prepared with citric acid (250 °C) was by *ca.* 80 °C lower than that (330 °C) of no additive sample. It is considered that the lower shift of the reduction temperature is caused by the decrease in the particle size. The small particle supported on KIT6 prepared with citric acid was reduced at the same temperature (250 °C).

The reduction of CuO/KIT6 prepared without any additives proceeded at two temperatures, 250 °C and 380 °C. The lower temperature is consistent with that of the small CuO particles,

and the existence of such particles is supported by the TEM measurement. The small particles are considered to form in the pore of KIT6. The higher temperature is assigned to the reduction of the larger particle, which is reasonably considered to exist at the outside of the pore. Our previous research reveals that the XANES spectrum of the small metallic Cu particle disagrees with the large particle [1]. The composition analysis estimates the fraction of small Cu particle to be 73%. It corresponds to the fraction of the CuO species reduced at lower temperature.

This study indicates that the particle size affects the reduction property of the CuO species. Two sizes of the CuO particle were formed on KIT6, and this study revealed that the mixed CuO and Cu(0) states can be coexisted by its reduction at 260 °C.

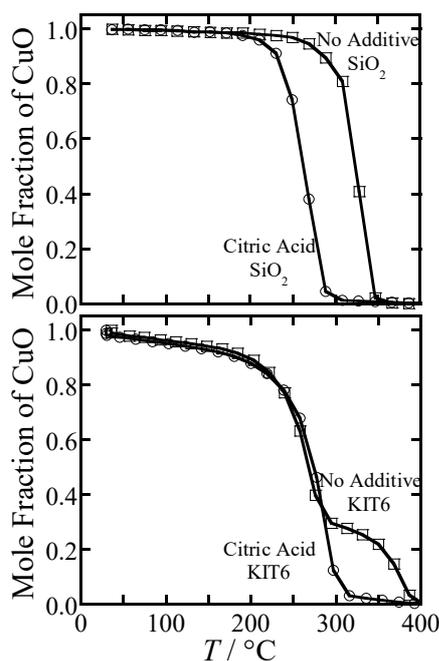


Fig. 1 The mole fraction changes of supported CuO species during the reduction process.

Reference

- [1] N. Afiza, Y. Yamamoto, K. Maruyama, K. Nakamura, S. Yamashita, M. Katayama, and Y. Inada, *Adv. X-ray Chem. Anal.*, **2016**, 47, 301.