Reduction Property of Cu Catalyst Supported on SiO_2 under CO Atmosphere

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The supported Cu catalyst is used for various reactions to convert the CO molecule, such as methanol synthesis form syngas, water gas shift, and CO oxidation. The supported Cu species is exposed by reactants and products under the reaction conditions, and the chemical state of the Cu species is changed by the reactions with those gasses. It is necessary for the catalyst design to understand the chemical state conversion of the Cu species under the reaction conditions. Moreover, the Cu particle size is one of the key parameters to optimize the catalytic performance. The purpose of this research is clarification of the particle size effects on the chemical state conversion of the SiO_2-supported Cu species during the temperature-programmed reduction (TPR) process under the CO atmosphere.

The SiO_2-supported Cu catalyst was prepared by the impregnation method. The citric acid was added into the precursor solution to control the Cu particle size. The Cu particle size was estimated to be 10 nm (citric acid) and 16 nm (no additive) by the TEM observations. The *in-situ* XAFS measurements using the flow-type cell made of SiO_2 glass were performed at BL-3 of SR center (Ritsumeikan Univ.) and BL-9C of Photon Factory (KEK). The Cu catalyst was heated up to 500 °C under the gas flow of 10 vol% CO/He (100 cm^3/min).

The observed XANES change during the TPR process under the CO atmosphere demonstrated the quantitative reduction of CuO to Cu(0) for both samples. The composition of the Cu species was analyzed by the linear combination fitting based on the XANES spectrum. Figure 1 shows the fraction changes of the Cu species as a function of temperature. The reduction temperature of the small CuO particle is lower than that of large CuO particle. The particle size dependence on the reduction temperature agrees with the case of the corresponding reduction under the H_2 environment [1]. It is considered that the lower shift for the small particle is caused by the larger surface area and the shorter oxygen migration path. It is expected that the lower reduction temperature can utilize the catalytic reaction driven by the redox reactions of the Cu species, such as the CO oxidation and the NO-CO reaction.

The fraction of Cu_2O during the TPR process is clearly dependent on the particle size. The Cu_2O species for the large particle appeared between 200 °C and 400 °C. On the other hand, there is no Cu_2O species in the case of the small particle, although a trace amount of Cu_2O is observed during the TPR process under H_2 [1]. These results suggest that the small Cu_2O species is highly reactive against CO, and it may achieve to proceed the CO oxidation reaction at lower temperature. This is the useful information to improve the catalytic performance.

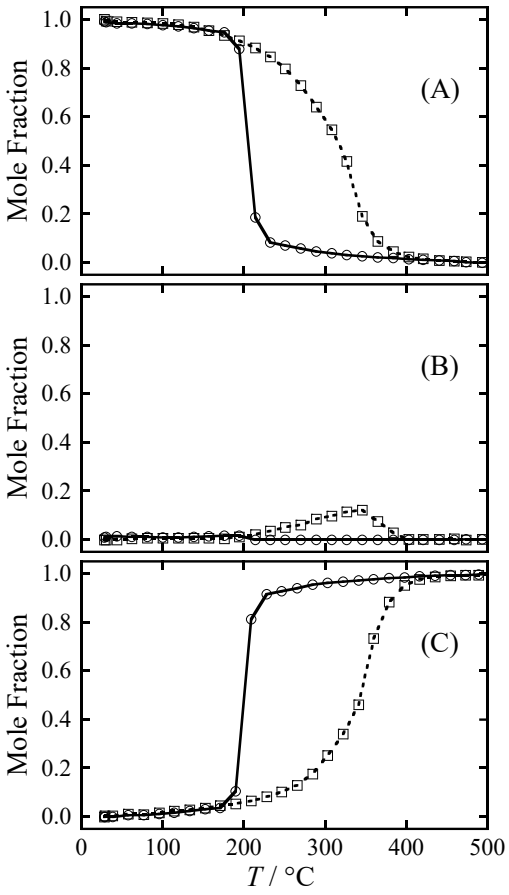

Fig. 1 The composition changes of the Cu species supported on SiO_2 during the TPR process under CO atmosphere. The mole fraction of CuO species (A), Cu_2O species (B), and metallic Cu species (C) is plotted as a function of temperature. The solid and dashed line shows the small particle (10 nm) and large particle (16 nm), respectively.

References

[1] S. Yamashita, S. Chotiwan, Y. Yamamoto, M. Katayama, and Y. Inada, *J. Vac. Soc. Jpn.*, **2016**, *59*, 293.