Chemical State Analysis of Cu Nanoparticles on MgO (001)

Takeru Yagi, Kei Mitsuhashi, and Masaru Takizawa

Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

Cu based catalysts exhibit strong catalytic activities for the water-gas shift reaction, methanol oxidation, methanol synthesis and others [1, 2]. However, their performance is not fully understood and is highly dependent on the synthesis conditions or the nature of the oxide support. MgO(001) is of interest as a substrate for various thin metal films, e.g. Ag/MgO(001) [3] and epitaxially grown Fe/MgO(001) [4]. MgO(001) is also used as a substrate for model catalysts [5]. Because gas phase redox reactions on oxide surfaces progress via transfer of an electronic excess charge, it is important to understand surface electronic properties. In this study, we analyzed the electronic properties of Cu nanoparticles deposited on MgO(001) surfaces by X-ray absorption fine structure (XAFS) measurement using synchrotron-radiation (SR) light.

The experiment was carried out at the BL-8 of SR Center, Ritsumeikan University. The mirror-finished MgO(001) substrates were sonicated in organic solvents and then annealed at 1000 °C for 6 hours in ultrahigh vacuum (UHV) of ~1 × 10^4 Pa. The clean (1×1) surfaces were checked by Reflection High Energy Electron Diffraction (RHEED). Then, Cu was deposited on the clean surfaces at RT with a Knudsen cell at a rate of 0.08 ML/min under UHV condition. Here, 1 ML means 1.77×10^15 atoms/cm², corresponding to the areal density of Cu(111). The XAFS measurements were carried out at room temperature under UHV of ~1 × 10^7 Pa. XAFS spectra of the samples were simultaneously collected by total electron yield (TEY) and partial electron yield (PEY) through a sample drain current and a micro-channel plate detector with retarding grids, respectively. The retarding voltage was set to −350 V for O K-edge.

Figure 1 shows O K-edge TEY XAFS spectra for clean MgO(001), Cu/MgO(001) at several Cu coverage, CuO, and Cu$_2$O powders. The structures are very different among MgO, CuO, and Cu$_2$O, that is, the first absorption peak appears around ~530 eV for Cu$_2$O, ~532 eV for CuO, and ~537 eV for MgO. With increasing Cu coverage on MgO, the TEY spectra hardly change, maybe due to the large probing depth.

Figure 2 shows O K-edge PEY XAFS spectra measured for clean MgO(001), Cu/MgO(001) at several Cu coverage, CuO, and Cu$_2$O powders. The structure around 537 eV was identified to that of the MgO(001). Interestingly, the structure around 532 eV appears at Cu coverage of 0.5 ML. This structure is coincident with that of CuO powder. These results suggest that Cu nanoparticles react with oxygen of the MgO(001) surface and then Cu nanoparticles is oxidized. C. S. Chen et al. [6] report that CuO species created at Cu/TiO$_2$ interface. For MgO substrate, the similar reaction may be occurring and this species may be potentially responsible for catalysts activities.

References


Fig. 1 O K-edge TEY XAFS spectra measured for clean MgO(001), Cu (0.2ML, 0.5ML)/MgO(001), CuO, and Cu$_2$O powders.

Fig. 2 O K-edge PEY XAFS spectra measured for clean MgO(001), Cu (0.2ML, 0.5ML)/MgO(001), and CuO powder.