9A/2004G285

Surface Structure of Cu Species by Modified TiO_2(110) Surface with Acetic Anhydride Acid

Wang-Jae Chun[1, 2], Yuichiro Koike[5], Kaoru Ijima[4], Keisuke Fujikawa[3], Hidenori Ashima[2], Masaharu Nomura[5], Yasuhiro Iwasawa[6], and Kiyotaka Asakura[1]
[1]Catalysis Research Center Hokkaido University, Sapporo 001-0021, Japan, [2]CREST, JST, Saitama 332-0012, Japan, [3]Department of Quantum Science and Engineering, Hokkaido University, Sapporo 060-8628, Japan, [4]Department of Electronic Engineering, Yamanashi University, Kofu 400-8510, Yamanashi, Japan, [5]Photon Factory, Institute of Materials Structure Science, Tsukuba 305-0801, Japan, [6]Department of Chemistry, Graduate School of Science, The University of Tokyo, Tokyo 113-0081, Japan

Introduction

The control of metal-oxide interface structure is a key technology for developing a new catalyst because the metal-oxide interface structure governs the active site structure and chemical properties.

As an approach we have successfully prepared highly dispersed Cu_3 trimer and Cu_6 prism clusters on the TiO_2(110) surface using an organometallic compound.[1-2] In the study, we have suggested that the DPM ligands play an important role in preventing the Cu aggregation and creating the unique clusters. From the knowledge we have expected that if the TiO_2(110) surface is covered with an organic molecule possessing a substituent atom which can covalently bound to Cu, the adsorbed organic molecule layer on the surface may provide a stable adsorption structure for Cu and prevent the diffusion of Cu species.

In this work we report the successful preparation of monoatomic Cu species on the pre-modified TiO_2 (110) by adopting acetic anhydride and the Cu species surface structure determined by Polarization-dependent Total Reflection Fluorescence XAFS (PTRF-XAFS) technique.

Experimental

TiO_2(110) crystals were cleaned by Ar ion sputtering at room temperature, followed by annealing at 1000 K until a sharp (1 × 1) LEED pattern was obtained. The cleaned surface was modified by adsorbing acetic anhydride with saturation coverage at room temperature. 0.18 ML Cu was loaded to the modified surface by vacuum evaporation of Cu wire. The prepared sample was designated as Cu/AcOAc/TiO_2(110) hereinafter. PTRF-XAFS measurement was carried out with an in-situ PTRF-XAFS measurement chamber (a base pressure of ca. 8×10^{-8} Pa) and a Canberra 19-element SSD in a fluorescence mode at BL9A. XAFS analysis was performed with REX 2000 and FEFF 8.0.

Results and Discussion

Fig. 1(a) shows the observed Cu *K*-edge PTRF-EXAFS spectra of Cu/AcOAc/TiO_2(110) in three orientations with reference compounds. First, there was no difference in amplitude intensity at three orientations. Second, the envelopes of all EXAFS oscillations damp quickly compared to that of Cu foil. It indicated that the nearest neighbourhoods of Cu could be oxygen atoms. The curve fitting analysis assuming Cu-O interaction showed that the Cu-O bond distances in all orientations were determined about 0.194 nm. For the [110] direction, Cu-Ti interaction was also evaluated because the direction corresponds to the electric vector pointing to TiO_2 substrate direction. But the contribution of Cu-Ti bond did not found. The effective coordination numbers of all orientations, N, were found in the range of 2 ~ 3. No significant difference in the ratio of N describes that the structure of Cu species will be a symmetrical structure.

For deriving a detailed structure, an iteration method using FEFF code and a real-space model structure was employed. Fig. 1(b) shows the proposed model structure. The Cu-O bond distance was found at 0.196 nm. The bond angles of the Cu-O interaction to the surface normal were $\theta = 54.7$ and $\beta = 42.6$ degree. The nearest Cu-Ti bond distance found at 0.364 nm proposed that the contribution of Cu-Ti interaction in the observed EXAFS is negligible. These results indicate that our new approach (surface-pre-modified method) can successively block the diffusion of metal species and provide monoatomic metal species without elaborate chemical syntheses.

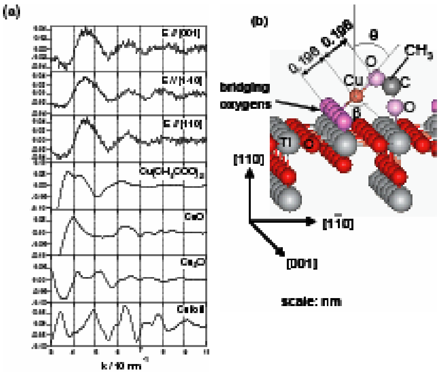

Figure1 Observed Cu K-edge PTRF-EXAFS of Cu/AcOAc/TiO_2 (110)(a) and the proposed model structure (b)

References

[1] Y. Tanizawa et al., *J. Phys. Chem. B* **107** (2003) 12917.
[2] Y. Tanizawa et al., *J. Synchrotron.Rad.* **8** (2001) 508.

*wchun@cat.hokudai.ac.jp