9A/2003G093

Cu Structure on Modified TiO$_2$(110) Surface by Chemisorbed Carboxylic Acid

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Introduction

Metal-oxide interfaces play a major role in electronic structure related to the many technological development of heterogeneous catalysts, electronic devices, and sensors. We have revealed that surface structures of metal species which are bound to the surface anions such as bridging oxygen atoms of TiO$_2$ (110) and are strongly correlated with the interface anion structures.[1-3] Therefore the modification of the surface anion structure, which can be coordinated to metal species, will control the structures the surface metal species.

Onishi et al. and Guo et al. reported that carboxylic acids such as formic acid, acetic acid, and benzoic acid form ordered (2 × 1) overlayers on TiO$_2$ (110) at saturation coverage.[4-5] We presume that the spatial form and the periodicity of chemisorbed carboxylic acids on TiO$_2$ (110) can be used as a template for controlling the structures of metal clusters on single-crystal metal oxide surfaces if the carboxyl adsorbates have the particular substitutes which can be coordinated to metal species. In this paper, we report that the surface structure of Cu on 3-thiophenecarboxlyic acid (TCA) modified TiO$_2$ (110) by means of 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 showed no other elements on the surface than Ti and oxygen by XPS. We modified the clean surface by adsorbing 3-Thiophenecarboxylic acid with saturation coverage at room temperature. Cu was evaporated to the modified surface by vacuum evaporation of Cu wire. The Cu coverages were monitored by XPS. PTRF-XAFS 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. For comparison, we also measured PTRF-XAFS spectra of Cu species on a clean TiO$_2$ (110) surface.

Results and Discussion

Figure 1 shows the PTRF-XAFS oscillations of 0.1 ML Cu on the clean TiO$_2$ (110) and the modified surface with TCA. For the clean surface all spectra were identical and showed oscillations characteristic to 3 dimensional Cu particles. It indicates that 3-dimensional Cu particles are formed on the clean TiO$_2$ (110) even at 0.1 ML. On the other hand, Cu deposited on the modified surface showed different behavior. The oscillations damped monotonically. In addition, the structures in the parallel directions of surface i.e. E // [001] and E // [1-10] at 30 nm^{-1} were different from that in the perpendicular direction. These results suggested the presence of asymmetric Cu surface structure on the modified surface. The preliminary analysis suggested the presence of Cu-S bonding in the perpendicular direction. We assumed that the difference might arise from the surface modifications with chemisorbed TCA which avoids the nucleation of particles. These results demonstrate the possibility to synthesize a new surface metal species using modified single crystal metal oxide surfaces. Detailed analysis is in progress.

References

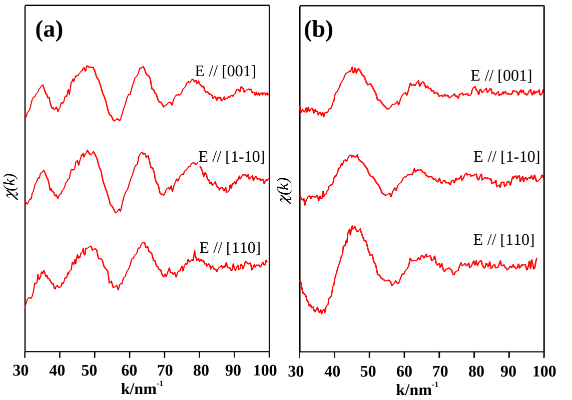

Fig.1 Observed PTRF-EXAFS oscillation of 0.1 ML Cu on the clean TiO$_2$(110) surface (a) and on the modified TiO$_2$(110) by TCA(b).

[1] W. –J. Chun et al., *J. Phys. Chem. B* **102** (1998) 9006.
[2] K. Ijima et al., *Chem. Phys. Lett.* **384** (2004) 134.
[3] Y. Tanizawa et al., *J. Phys. Chem. B* **107** (2003) 12917.
[4] H. Onishi et al., *Chem. Phys. Lett.* **226** (1994) 111.
[5] Q. Guo et al., *Surf. Sci.* **433-435** (1999) 322.

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