

Controlled Surface Structure of Cu species by Modified TiO₂(110) Surface with Chemisorbed Acetic acid

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Introduction

The control of metal-oxide interface structure is indispensable to develop a new catalyst because the metal-oxide interface structure governs to determine the active site structure and chemical properties. Our group have recently revealed that surface structures of metal species which are bound to the surface anions such as bridging oxygen atoms of TiO₂(110) and are strongly correlated with the interface anion structures. [1-2] These results suggest that the modification of the surface anion structure may control the structures of the surface metal species.

Onishi et al. reported that carboxylic acids such as formic acid and acetic acid form ordered (2×1) overlayers on TiO₂(110) at their saturation coverages.[3] We presume that the well defined chemisorbed carboxylic acids on TiO₂(110) can be used as an organic modifier to control the structures of metal clusters. The present work describes a novel method for the control of Cu species a on modified TiO₂(110) surface and its surface structures determined by Polarization-dependent Total Reflection Fluorescence XAFS (PTRF-XAFS) technique.

Experimental

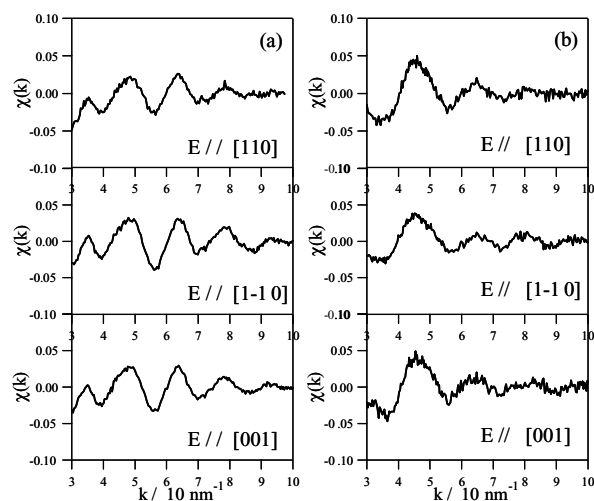
TiO₂(110) crystals were cleaned by Ar ion sputtering at room temperature, followed by annealing at 1000 K until a sharp (1 × 1) LEED pattern was obtained. The clean surface was modified by adsorbing acetic acid with saturation coverage at room temperature. 0.01 ML Cu was loaded to the modified surface 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.

Results and Discussion

Figure 1 shows the PTRF-XAFS oscillations of 0.01 ML Cu on the clean TiO₂(110) and the modified surface with acetic acid. 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 TiO₂(110) even at

0.01 ML. Chen et al., also reported that Cu is easily aggregated to Cu metal particles when it is deposited on the clean TiO₂(110) surface by STM.[4]

On the other hand, Cu deposited on the modified surface showed different behavior. The oscillations damped monotonically. Note that the oscillations at around 30 nm⁻¹ were completely different from those of Cu on the clean surface. It indicates that the modified surface by CH₃COOH hindered deposited Cu atoms to form Cu clusters. Considering the fact that the metal atoms are preferably located at the virtual cation position,[1] we are proposing a model structure where Cu atom adsorbed at the atop site of a bridging oxygen atom and it bound to the adsorbed CH₃COO molecules located by the side of the Cu atom through Cu-O (carboxyl group) bonds. Further analysis is in progress.



References

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