Atomically Dispersed Cu on a TiO_2 (110) Surface Precovered with Acetic Anhydride

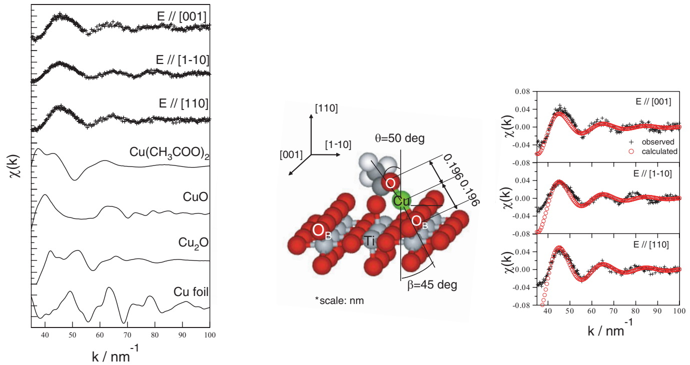
A new route for preparing highly dispersed monoatomic metal species on metal oxide surfaces is proposed. We have successfully obtained monoatomic Cu on a TiO_2(110) surface precovered with an acetic anhydride layer. Polarization-dependent total-reflection fluorescence X-ray absorption fine structure (PTRF-XAFS) spectra revealed that the three-dimensional structures of the monoatomic Cu species on the surface were stabilized by two Cu-O bonds, namely the Cu-O (acetate) and Cu-O (bridging surface oxygen) bonds. These results suggest that Cu diffusion is effectively blocked by the two acetate species, which originate from the dissociative adsorption of acetic anhydride onto the TiO_2(110) surface.

Controlling the size of metal clusters on oxide surfaces is an important issue for preparing catalysts, fuel cells, and sensors etc. For understanding the governing factors in the size control metal clusters on TiO_2(110) as a model system have been intensively explored [1]. Many Scanning Tunnel Microscopy (STM) studies have highlighted that self-regulated clusters with sizes of a few nm are formed when Cu and Ni are deposited on the surface. These studies, however, concluded that it is difficult to obtain monoatomic metal species on the terrace sites of TiO_2 (110) due to small stabilization energies, and also small activation energies for diffusion [2-4].

Despite these problems, we have successfully prepared monoatomic Cu species anchored by the S atoms of a thiophene moiety on a TiO_2(110) surface precovered with 3-thiophenecarboxylic acid [5]. We also have reported the prepartion of monoatomic Cu on TiO_2 (110) by surface reaction with an organometallic compound $Cu(DPM)_2$ [6]. These approaches indicate that increasing the diffusion energy barrier on the oxides can effectively block metal diffusion.

In this study we have attempted to raise the diffusion energy barrier by blocking directly the diffusion path on the TiO_2(110) surface. Previous High Resolution Electron Energy Loss Spectroscopy (HREELS) and STM studies have shown that Ac_2O is dissociatively adsorbed on the surface [7, 8]. Noteworthy is the acetate species termed type B which has the O–C–O plane parallel to the $[1\bar{1}0]$ direction. We expected that the acetate species would block the metal diffusion path on the TiO_2(110) surface. The surface structure of Cu on Ac_2O precovered TiO_2(110) (Ac_2O/TiO_2(110)) was determined using PTRF-EXAFS.

All procedures were conducted in a PTRF-EXAFS Ultra High Vacuum chamber [2, 5, 6]. A cleaned TiO_2(110) surface was fully covered with Ac_2O at 300 K, and then 0.18 ML of Cu was deposited on the Ac_2O/TiO_2(110) surface by metal evaporation. Cu coverage was estimated using XPS, and XAFS measurements were performed at BL-9A. Considering the anisotropic surface structure of TiO_2(110), EXAFS measurements were carried out at three orientations with respect to the electric vector of the incident X-rays [2, 5, 6]. The Cu K_α fluorescence was detected using a 19-element Ge Solid State Detector. EXAFS analyses were carried out using the REX 2000 software and the FEFF8.02 code [9].



(a)

(b)

Figure 1
(a) PTRF-EXAFS spectra of Cu on Ac_2O/TiO_2(110) and reference compounds in three orientations, (b) calculated PTRF-EXAFS spectra based on the proposed model.

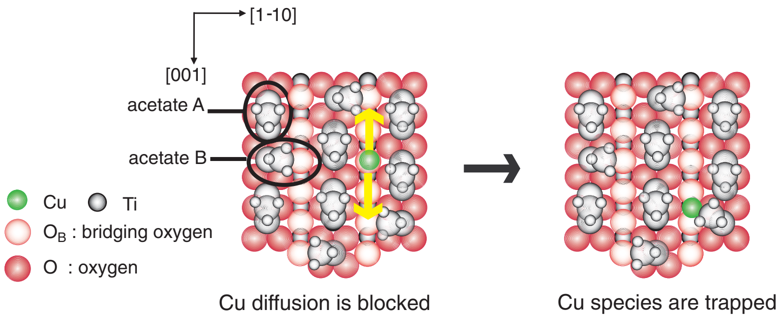


Figure 2
Proposed mechanism of absorption of Cu on Ac_2O/TiO_2(110).

Figure 1(a) shows the PTRF-EXAFS spectra of the sample and also of reference compounds. All PTRF-EXAFS spectra show different features from that of the Cu foil, with envelopes damped more quickly than those of CuO and $Cu(CH_3COO)_2$. Preliminary curve fit results indicate that the main contribution is the Cu-O interaction, with Cu-Ti and Cu-Cu bonding being less likely. To derive a detailed structure, an iteration method using the FEFF code and a real-space structural model was employed [2, 5, 6]. The calculated EXAFS oscillations based on the model structure in Fig. 1 (b) provided good fit results for the PTRF-EXAFS spectra of [001], $[1\bar{1}0]$, and [110], with residues of 0.73, 1.05 and 0.98, respectively. In the model Cu is bonded with two oxygen atoms. One Cu-O bond comes from the bridging surface oxygen, and the other from the adsorbed acetate. The Cu-O bond length is estimated to be 0.196 nm, and the O-Cu-O bond angle to be 166°, which is close to 180°, indicating that the Cu is in a monovalent state. A proposed mechanism is illustrated in Fig. 2. Theoretical calculations [10] have suggested that metals interact with bridging oxygen atoms on the stoichiometric TiO_2(110) surface, and the diffusion energy barrier along the [001] direction parallel to the bridging oxygen row is small [3, 4]. In addition, the type B acetate of the Ac_2O/TiO_2(110) surface lies on the bridging oxygen or the diffusion path. Consequently Cu diffusion is strongly blocked by the type B acetate.

In conclusion we have successfully demonstrated that monoatomic Cu can be prepared by the effective blocking of Cu diffusion on an Ac_2O precovered TiO_2(110) surface. This new route can be a step towards the single-atom precise preparation of metal clusters.

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