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-EXAFS) 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 aceatate 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-thiopheneacetic acid [5]. We also have reported the preparation 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$_2$O 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 [100] 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$_2$O precovered TiO$_2$(110) (Ac$_2$Ot/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$_2$O at 300 K, and then 0.18 ML of Cu was deposited on the Ac$_2$O/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$_\alpha$ 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].

In conclusion we have successfully demonstrated that monoatomic Cu can be prepared by the effective blocking of Cu diffusion on an Ac$_2$O precovered TiO$_2$(110) surface. This new route can be a step towards the single-atom precise preparation of metal clusters.

REFERENCES