

3D structure determination of metals on a TiO₂ single crystal surface: Effect of premodification with a mercapto compound on single metal dispersion

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Abstract

Precise size control of the metal species on oxide surfaces, especially in the range of <1 nm, is now highly important to develop the next-generation catalysts, sensors, and electronic devices. However this is not easy since metal atoms are easily aggregated to form large particles on oxide surfaces. This is due to the small stabilization energy and/or the small activation energy for the metal diffusion. If one can obtain a monatomic metal species on the TiO₂(110), it can be a building block of the metal cluster and helps us to control the cluster size in one-atom precision. Our group has developed the “premodified surface method” to obtain a highly dispersed metal species. In the premodified surface method, an oxide surface is precovered with a functional organic molecule possessing a substituent atom which can strongly coordinate to a metal atom before metal deposition. We have determined the precise 3D structures of such metal species by polarization-dependent total reflection fluorescence (PTRF) XAFS technique [1-5].

Figure 1 shows the 3D structure of atomically dispersed Cu species which were prepared by vacuum deposition of Cu metal atoms on a TiO₂(110) surface precovered with *o*-mercaptobenzoic acid (*o*-MBA) [2,3]. The 3D structure was determined by fitting the observed PTRF-XAFS spectra with FEFF-simulated spectra. The monomeric Cu species was stabilized by forming chemical bonds with sulfur of the adsorbed *o*-MBA and oxygen of the substrate TiO₂ although in the absence of *o*-MBA Cu was aggregated to form clusters. The XANES results clearly suggested that the Cu species was monovalent. We also applied the premodified surface method to other metals such as Au, Ni and Pt. Au and Ni were atomically dispersed by bond formation with sulfur and oxygen as similar with Cu in Figure 1, but Pt was aggregated to form clusters [1, 4]. We will discuss the factors that govern single metal dispersion based on the energy difference between sulfur–metal–oxygen and metal–metal bond formations.

References

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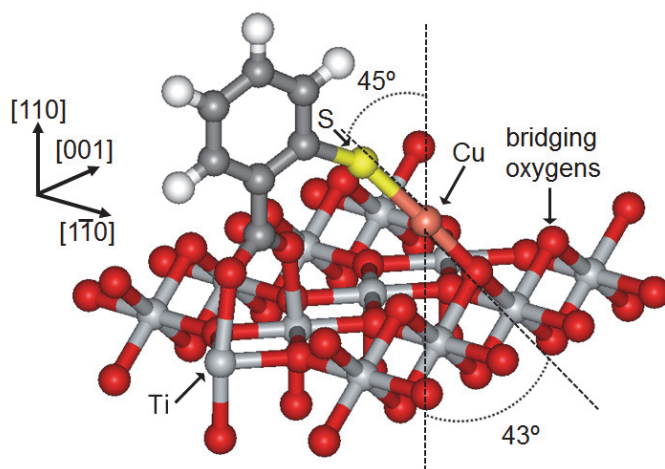


Figure 1. 3D structure of Cu/*o*-MBA/TiO₂(110). Cu-S and Cu-O bond distances are 0.219 nm and 0.185 nm, respectively.