

Surface Structure of Au species on the Premodified TiO₂(110) with Acetic anhydride acid

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Introduction

The control of metal-oxide interface structure is a key technology for developing a new catalyst because the metal-oxide interface structure governs the active site structure and chemical properties. As an approach we have successfully prepared atomically dispersed Cu species on the TiO₂(110) surface by a premodified surface method. In the study we have reported that Polarization-dependent Total Reflection Fluorescence XAFS (PTRF-XAFS) showed that the monoatomic Cu species were stabilized on the surface by two chemical interactions through the formation of Cu-O or Cu-S (adsorbate) and Cu-O (bridging surface oxygen) bonds [1-2].

In this work we challenge to prepare monoatomic Au species on the TiO₂(110) surface by the premodified surface method. We have expected that the precovered TiO₂(110) surface with acetic anhydride may provide a stable adsorption structure for Au and prevent the diffusion of Au species. The surface structure of Au species on the pre-modified TiO₂(110) by adopting acetic anhydride was determined by the 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 cleaned surface was modified by adsorbing acetic anhydride with saturation coverage at room temperature. Au (6.5 × 10¹³ Au atoms/cm²) was deposited on the modified surface by vacuum evaporation of Au. The prepared sample was designated as Au/AcOAc/TiO₂(110) hereinafter. PTRF-XAFS measurement was carried out with an in-situ PTRF-XAFS measurement chamber (a base pressure of ca. 8 × 10⁻⁸ Pa)[3]. The Au L₂ edge XAFS was measured in a fluorescence mode using a 19-element Ge solid state detector (SSDGL0110S, Canberra, USA) to avoid small amount of impurity fluorescence coming from holder materials. EXAFS analysis was carried out by REX 2000 (Rigaku Co., Japan) and FEFF8.02 code[4].

Results and Discussion

Fig. 1(a) shows the observed Au L₂-edge XANES spectra of Au/AcOAc/TiO₂(110) with Au foil. First, there

was no difference in all orientations. It indicates the surface structure should be a symmetric structure. Second, the characteristic peaks observed in Au foil were observed in all XANES spectra, but the intensity was weaker than that of Au foil. It suggests that small Au particles should be formed on the TiO₂(110) surface.

In EXAFS region (Fig.1 (b)), all spectra showed similar features. The χ^2 test showed no polarization dependency in all orientation. It is in agreement with the XANES result. Curve fitting analysis showed the presence of Au-Au interaction for all orientations at 0.270 nm which is 0.14 nm shorter than that of Au bulk. It indicates the presence of small Au particles on TiO₂(110) surface.

XAFS results described that the premodified TiO₂(110) with acetic anhydride is not strong enough preventing Au diffusion. We are now performing the premodified surface method with 3-thiophene carboxylic acid possessing a sulfur atom which can coordinate to Au for obtaining monoatomic Au species.

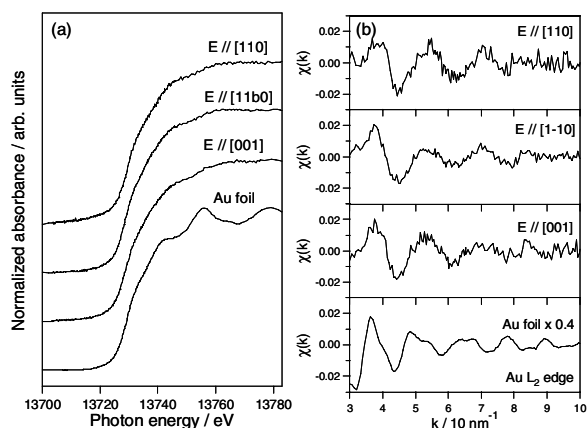


Fig. 1 The PTRF-XAFS spectra of Au/AcOAc/TiO₂(110). (a) XANES; (b) EXAFS.

References

- [1] W.-J. Chun et al., *Chem.Phys.Lett.* **433** (2007) 345.
 - [2] W.-J. Chun et al., *PF Activity Reports* **23** (2006)62.
 - [3] W.-J. Chun et al., *J. Synchrotron Rad.*, **8** (2001) 168.
 - [4] A. L. Ankudinov et al., *Phys. Rev. B* **58** (1998)7565.
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