

Structure of Atomically Dispersed Ni Species Formed on a TiO₂(110) Surface Premodified with Mercaptobenzoic Acid

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1 Introduction

Precise size control of 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. Our group has developed the “premodified surface method” to obtain a highly dispersed metal species, where before metal deposition an oxide surface is precovered with an organic molecule possessing functional groups which can strongly coordinate to a metal atom and fix to oxide surface [1-3]. We have already succeeded in preparing atomically dispersed Cu and Au species on the TiO₂(110) surfaces premodified MBA (mercaptobenzoic acid) molecules [2,3]. In this study, we applied the premodified surface method to another metal that is Ni, and the structure of the Ni species on a TiO₂(110) surface premodified with *ortho*-MBA (*o*-MBA) was determined by polarization dependent total-reflection fluorescence (PTRF) EXAFS. This method allows us to deposit 10 times larger amount of atomically dispersed Ni than on a bare TiO₂ (110) surface [4].

2 Experimental

Nb-doped (0.05 wt%) TiO₂(110) surface was cleaned by HF etching and annealing in air at 973 K. The cleaned surface was immersed in 2 mM *o*-MBA ethanol solution to modify the TiO₂(110) surface with *o*-MBA monolayer. Ni was vacuum-deposited on the *o*-MBA-modified surface, and the coverage was estimated to be 0.27 ML by XPS measurements (1 ML=5.2×10¹⁴/cm²).

PTRF-XAFS measurements were carried out at BL9A with *in-situ* PTRF-XAFS chamber (base pressure 8 × 10⁻⁸ Pa). XAFS analysis was carried out using REX2000 and FEFF8.40.

3 Results and Discussion

Fig. 1(a)-(c) shows the observed Ni K-edge PTRF-EXAFS spectra (black curves) of Ni/*o*-MBA/TiO₂(110) in three orientations. The envelopes of the PTRF-EXAFS oscillations damped quickly compared with the EXAFS spectrum of Ni foil. This means that the nearest neighbor atom of Ni is not Ni, but a lighter atom like sulfur or oxygen. Curve fitting analysis indicated contribution from Ni-S interaction (2.20±0.05 Å) and Ni-O interaction (1.89±0.05 Å) and no Ni-Ni interaction, showing that Ni was atomically dispersed. There was no significant

difference in the effective coordination numbers for the Ni-S bond in the three orientations, indicating that the Ni-S bond was directed close to the magic angle (~55°) with respect to [110] and to ~45° with respect to [001] and [1 $\bar{1}$ 0].

To determine a detailed structure of the Ni species, an iteration method using a FEFF code and a real space model structure was employed. Fig. 1(d) shows the proposed model structure, and polarization dependent FEFF simulation using this model structure is illustrated in Fig. 1(a)-(c) (red curves) together with the experimental spectra (black curves) showing a good agreement with the observed ones.

We have succeeded in preparing a large amount of monatomic Ni species on a TiO₂(110) surface by using the premodified surface method.

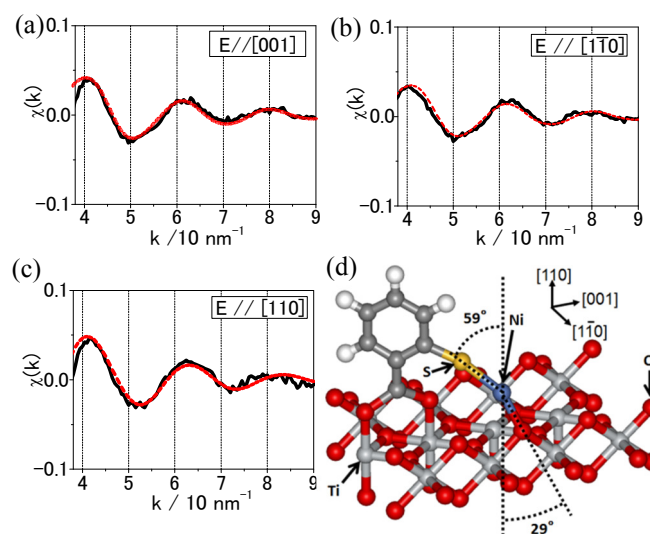


Fig. 1: (a)~(c) PTRF-EXAFS spectra (black curves) and simulated spectra (red curves) of Ni/*o*-MBA/TiO₂(110), respectively; (a) E// [001], (b) [1 $\bar{1}$ 0], (c) [110]. (d) Structure model of the Ni/*o*-MBA/TiO₂(110).

References

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