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Structure of Photodeposited Pt Complexes Formed on a TiO_2(110) Surface

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1 Introduction

Photodeposition has been widely used to prepare metal-supported oxide (photo)catalysts ever since Bard et al. reported it in 1978 [1]. The irradiation of a semiconductor oxide powder (e.g., TiO_2) with UV light in the solution containing metal cations having an appropriate redox potential results in the reduction of the metal cations by the photoexcited electrons, generating metal particles on TiO_2. To understand the photodeposition process at the atomic level, i.e., adsorption of metal cations on an oxide support, reduction of the metal cations and successive aggregation of metal atoms, it is important to investigate the processes on a well-defined single crystal oxide surface by using surface science techniques.

In this study, we examined structure of photodeposited Pt complexes on a TiO_2(110) surface formed at the initial stage of the photodeposition process by polarization-dependent total reflection XAFS (PTRF-XAFS).

2 Experiment

TiO_2(110) single crystal surface was cleaned by immersing in 10 % HF solution for 10 min and annealing at 600 °C in air for 12 h according to the previous reports [2]. The TiO_2 sample was then immersed in aqueous alcoholic H_2PtCl_6 solution containing 150 ml MilliQ water, 30 ml methanol and 40.2 mg $H_2PtCl_6 \cdot H_2O$ that was deaerated by passing the ultrapure Ar gas through the solution for more than 30 min. Then the sample surface was illuminated with UV light (360 nm band from a 300 W Xe lamp obtained with band-pass filters) for 10 s. After rinsing thoroughly with MilliQ water, the sample was transferred into the ultra-high vacuum (UHV) PTRF-XAFS chamber [3]. PTRF-XAFS measurements were carried out with the UHV PTRF-XAFS chamber. XAFS analysis was performed using REX 2000.

3 Results and Discussion

Fig. 1(a) shows the Pt L_3-edge PTRF-XANES spectra of the photodeposited Pt species on a TiO_2(110) surface. We observed a polarization dependence, where the white line peak for the E//[1$\bar{1}$0] direction was slightly stronger than the other two directions (E//[001] and [110]), suggesting orientation of the Pt species was not random but ordered with respect to the TiO_2(110) surface. The oxidation state of the Pt species formed on the TiO_2(110) surface was estimated to be divalent by considering the inflection point and the white line peak intensity of the XANES spectra. XPS measurements also supported that the oxidation state of the deposited Pt species was divalent. Fig. 1(b) shows the Pt L_3-edge PTRF-EXAFS spectra of the photodeposited Pt species on the TiO_2(110) surface. No significant polarization dependence was observed in the three spectra with different orientations. Preliminary curve fitting analysis revealed Pt-O (1.94 Å) and Pt-Cl (2.26 Å) bonds for all the orientations.

The obtained results suggested that $[PtCl_6]^{2-}$ species (Pt^{4+}) in the solution were reduced by irradiation of the TiO_2(110) surface with the UV light to form the divalent Pt complexes attached to the TiO_2 surface via Pt-O (lattice O of TiO_2) bonds. We are now trying to determine the three-dimensional structure of the photodeposited Pt species by FEFF simulation.

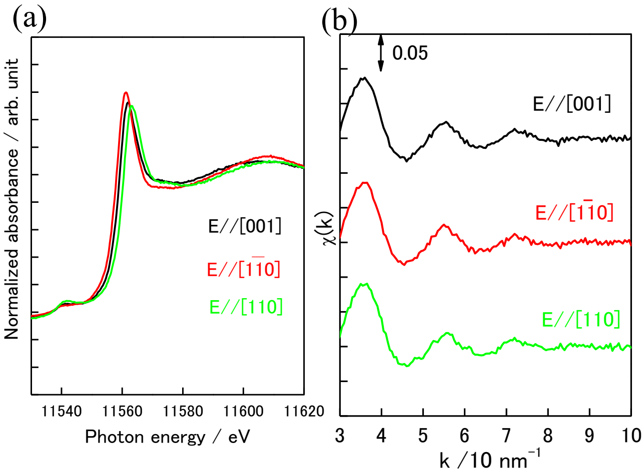

Fig. 1: (a) PTRF-XANES spectra and (b) PTRF-EXAFS spectra of the photodeposited Pt species formed on a TiO_2(110) surface by irradiation of the TiO_2(110) surface with UV light in aqueous alcoholic H_2PtCl_6 solution.

References

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