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PTRF-XAFS analysis of structure of Au_{11} cluster on TiO_2(110) Surface

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Introduction

Gold nanoclusters on TiO_2 with less than 10 nm have attracted much attention as active catalysts towards CO oxidation reactions at low temperature.[1] Recent studies showed that sub-nanometer-sized Au clusters also work as highly active catalysts for CO oxidation[2] and O_2 electroreduction.[3]

Here, Au_{11} clusters ($Au_{11}(PPh_3)_8Cl_3$) with well-defined composition and structure were deposited on TiO_2(110) surface using a wet-chemical method, and the structure of the deposited Au clusters was examined by using polarization dependent total-reflection fluorescence (PTRF) XAFS.

Experimental

Nb doped (0.05wt%) TiO_2(110) surface was cleaned by HF etching and annealing in air at 1000 K. The cleaned surface was immersed in 1mM *p*-mercaptobenzoic acid (MBA) to modify the TiO_2(110) surface with *p*-MBA monolayer. The modified surface was then immersed in dichloromethane solution containing 50 μM $[Au_{11}(PPh_3)_8Cl_2]Cl$. Adsorption of the Au clusters was confirmed by the existence of the Au4f peak in the XPS measurements. The Au coverage was 0.3 ML~1.6ML depending on immersion time. PTRF-XAFS measurements were carried out at BL9A with in-situ PTRF-XAFS chamber (base pressure 8 × 10^{-8} Pa). No coverage dependence of the PTRF-XAFS spectra was observed. XAFS analysis was carried out using REX2000 and FEFF8.40.

Results and Discussion

Fig. 1(a)-(c) show the observed Au L_3-edge PTRF-EXAFS spectra of the deposited Au clusters on TiO_2(110) surface premodified with *p*-MBA. No significant polarization dependence was observed. The amplitude of the EXAFS oscillations of the Au_{11} clusters on *p*-MBA/TiO_2(110) was almost equal to that of Au_{11} powder sample, suggesting that Au_{11} clusters maintain the number of Au atoms after the surface attachment. However the periodicity of the EXAFS oscillations was shorter. The preliminary curve fitting analysis showed that the average Au-Au bond distance of the deposited Au clusters was 2.80 Å, which was longer by ca 0.1 Å than that of the Au_{11} powder (2.68Å) and shorter than that of bulk Au-Au (2.88 Å).

FEFF calculation was performed to determine a more detailed structure of the deposited Au clusters. We were not able to reproduce the observed spectra when using structural models based on simple expansion of Au-Au bond of the original Au_{11} structure determined by single crystal XRD analysis. On the other hand, a well-fitted result was obtained when structure of the Au_{11} core was relaxed and optimized by using DFT calculation after removing some of the ligands, as shown in Fig. 2. This suggests that surface attachment of the Au_{11} clusters causes removal of some protecting ligands and structural change of the Au_{11} core probably due to chemical interaction with thiol group of the adsorbed *p*-MBA on TiO_2(110) surface.

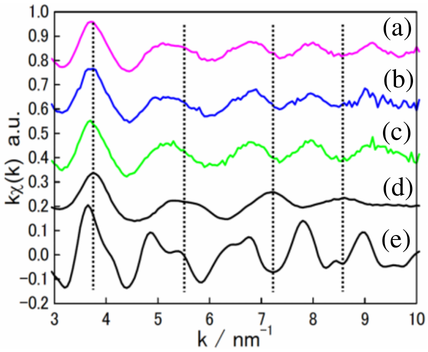

Fig.1 PTRF-EXAFS spectra of deposited Au_{11} clusters on TiO_2(110). (a) E // [001], (b) E //[1$\bar{1}$0], (c) E // [110]. (d), (e) are EXAFS spectra of Au_{11} powder and Au foil, respectively

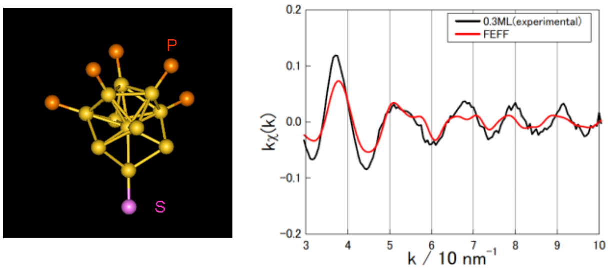

Fig. 2 FEFF calculation of a modified Au_{11} structure.

References

(1) M. Haruta, *Catal. Surveys Jpn.* **1** (1997) 61.
(2) Herzing et al., *Science* **321** (2008) 1331.
(3) Chen et al., *Angew. Chem. Int. Ed.* **48** (2009) 4386.

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