

Preparation of Precisely Size-controlled Au Nanoclusters on Oxide Single Crystal Surface with Wet Chemical Methods

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Introduction

Gold has been regarded as an inert metal for catalytic applications before Haruta et al. have reported that Au particles below 10 nm in size supported on TiO₂ have unique catalytic properties in low temperature CO oxidation reaction [1]. However, there is still no clear picture with respect to the origin of the size-dependent catalytic activity and the role of metal-support interaction. Therefore it is important to prepare precisely size-controlled Au nanoclusters on TiO₂ single crystal surface and examine the catalytic activity of the Au nanoclusters with extremely narrow size distribution.

In this work, deposition of [Au₁₁(PPh₃)₈Cl₂]Cl on TiO₂(110) surface from solution phase was performed and the structure of the deposited Au species was investigated by the Polarization-dependent Total Reflection (PTRF) XAFS technique.

Experimental

Nb doped (0.05wt%) TiO₂(110) surface was cleaned by HF etching and annealing in air at 1000 K. A sharp (1x1) LEED pattern was observed. The cleaned surface was immersed in 1mM *p*-mercaptobenzoic acid (MBA) to modify the TiO₂(111) surface with *p*-MBA monolayer. The modified surface was then immersed in dichloromethane solution containing 50 μM [Au₁₁(PPh₃)₈Cl₂]Cl. Adsorption of the Au clusters was confirmed by the existence of Au 4f peak in the XPS measurements. The Au coverage was estimated to be ca. 1.6 ML by XPS. PTRF-XAFS measurements were carried out with in-situ PTRF-XAFS chamber (base pressure: 8 x 10⁻⁸ Pa) [2]. XAFS analysis was carried out using REX 2000 and FEFF8.0.

Results and Discussion

Fig. 1 shows Au L₃-edge EXFAS spectra of the deposited Au clusters on TiO₂(110) surface premodified with *p*-MBA. There were no significant differences in the spectra for the three polarization directions. It indicates that the structure of the Au species should be a symmetric one. The characteristic oscillation due to Au-Au

interaction observed in the spectrum of Au foil was observed for all the spectra, but the periodicity and amplitude were longer and smaller, respectively, than those of Au foil. These results indicate that the average bond length and coordination number of Au-Au interaction were shorter and smaller, respectively, than those of bulk Au, clearly suggesting the successful deposition of the Au nanoclusters without aggregation even at such a high coverage (1.6 ML).

Theoretical simulation of the EXAFS oscillation of Au₁₁(PPh₃)₈Cl₂ was performed using FEFF software based on the structural model proposed by powder XRD analysis, and the result was compared with the observed spectra. However a well-fitted result was not obtained. This is probably because the structure of the Au nanoclusters was modified by the ligand exchange reaction when they were attached to the surface.

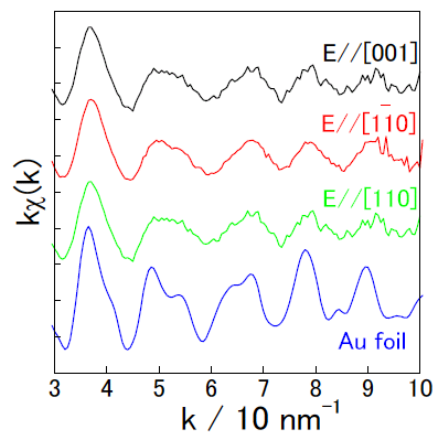


Fig. 1 PTRF-EXAFS spectra of Au nanoclusters ([Au₁₁(PPh₃)₈Cl₂]Cl) deposited on TiO₂(110) surface.

References

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- [2] W.-J. Chun et al., *J. Synchrotron Rad.* **8** (2001) 168.

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