Photon Factory Activity Report 2013 #31 (2014) **B**

9A/2013G123

PTRF-XAFS Study of Atomically Precise Pt$_n$ Clusters on TiO$_2$(110) Surface

Yusaku F. Nishimura[1], Yoshihide Watanabe[1]*, Hiromitsu Uehara[2], Noritake Isomura[1],
Ryo Suzuki[1], Atsushi Beniya[1], Kiyotaka Asakura[2] and Satoru Takakusagi[2]
[1]Toyota Central R&D Labs., Inc., Aichi 480-1192, Japan
[2]Hokkaido University, Hokkaido 001-0021, Japan

1. Introduction

Demand for supported noble metals as automotive catalysts has been increasing year by year, caused by tightened emission regulations throughout the world. It is crucial to improve specific catalytic activity and reduce the use of noble metals, taking finite availability of these metals into account. To this end, one possibility is to utilize noble metal clusters consisting of several atoms.

So far, we have developed atomically precise cluster-producing and cluster-characterizing system to reveal the relationships between the number of constitutive metal atoms and chemical properties [1]. However, structures of Pt$_n$ clusters on the whole TiO$_2$(110) surface are still unclear. In this study, we performed polarization-dependent total-reflection fluorescence X-ray absorption fine structure (PTRF-XAFS) [2] to evaluate the structure of Pt$_4$ cluster on TiO$_2$(110) surface.

2. Experiment

A clean TiO$_2$(110) single crystal surface was prepared by repeated Ar$^+$ ion sputtering and annealing cycles at 980 K. Pt$_4$ clusters were deposited onto the TiO$_2$(110) surface in the manner described in Ref [1]. The amount of Pt$_4$ clusters was adjusted to 2×10^{13} clusters cm^{-2} based on the Pt cluster ion current.

PTRF-XAFS measurements were performed at BL9A employing a PTRF-XAFS chamber (base pressure: 8×10^{-8} Pa) for the following three orientation conditions: the electric vector ***E*** // $[1\bar{1}0]$, ***E*** // [001], and ***E*** // [110]. XAFS analysis was performed with REX2000, ATHENA, ARTEMIS, and FEFF9.05.

3. Results and Discussion

The observed Pt L_3-edge PTRF-XAFS spectra of Pt$_4$/TiO$_2$(110) in three orientations are indicated by black dots in Fig. 1. Difference in the spectral shape is rather small among these three spectra even though polarization dependence is generally weak at L_3-edge [2]. This implies a symmetric structure as an average Pt$_4$/TiO$_2$(110) structure. Preliminary curve fitting analysis suggests that there should be two contributions from Pt–O (1.85 ± 0.05 Å) and from Pt–Pt (2.67 ± 0.05 Å). The above information invokes the average structural model in which a regular tetrahedral Pt$_4$ cluster is stabilized by forming Pt–O bonds with the oxygen atoms at the TiO$_2$(110) surface. EXAFS oscillations were calculated for this model in three orientations as the first step. The red lines shown in Fig. 1 correspond to the EXAFS oscillations calculated for the tetrahedral model in which the average distances of Pt–O and Pt–Pt are 1.85 Å and 2.64 Å, respectively.

In our previous STM study [3], a Pt$_4$ cluster appeared to have a planar structure on the TiO$_2$(110), differently from the result of this PTRF-XAFS analysis. Further analysis will be performed to discuss this difference and refine the structural model of a Pt$_4$ cluster on the TiO$_2$(110). Pt$_7$ and Pt$_{10}$ clusters on the TiO$_2$(110) will also be analyzed in the same manner to discuss the relationship between the number of Pt atoms in a cluster and the cluster structure.

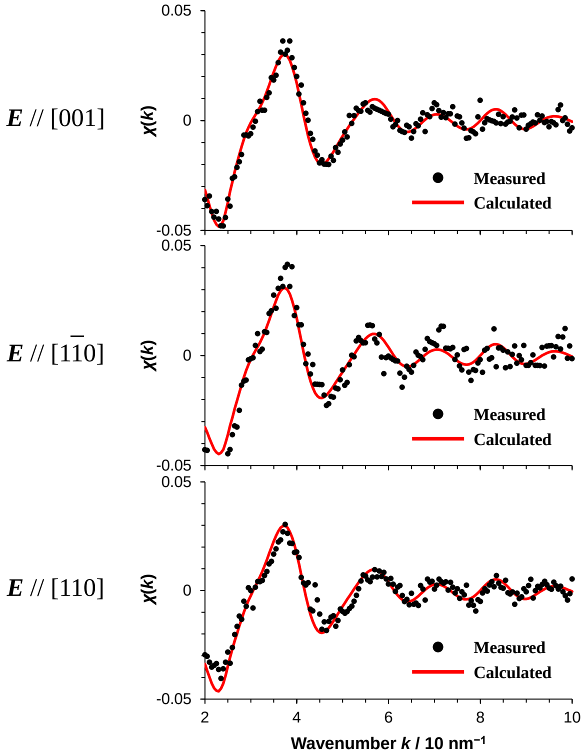

Figure 1. PTRF-XAFS spectra of Pt$_4$/TiO$_2$(110) at the Pt L_3-edge (indicated by black dots). Red lines correspond to the EXAFS oscillations calculated for a regular tetrahedral structure model.

References

[1] Y. Watanabe and N. Isomura, *J. Vac. Sci. Technol. A*, **27**, 1153 (2009).

[2] K. Asakura, S. Takakusagi, H. Ariga, W.-J. Chun, S. Suzuki, Y. Koike, H. Uehara, K. Miyazaki, and Y. Iwasawa, *Faraday Discuss.*, **162**, 165 (2013).

[3] N. Isomura, X. Wu, and Y. Watanabe, *J. Chem. Phys.*, **131**, 164707 (2009).

* e0827@mosk.tytlabs.co.jp