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Atomic-scale Structure of a Pt_4 Cluster on TiO_2(110) Surface Investigated by the PTRF-XAFS Method

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1 Introduction

Size-selected noble metal clusters are expected to improve catalytic activities and thus to reduce the use of noble metals, especially for automotive catalysts. So far, we have developed size-selected cluster-producing and cluster-characterizing system to clarify the relationships between the number of constitutive metal atoms and chemical properties [1]. Atomic-scale structures of Pt_n clusters on TiO_2(110) surface are, however, still unclear. In this study, we performed polarization-dependent total reflection fluorescence XAFS (PTRF-XAFS) [2] to evaluate the structure of a Pt_4 cluster on TiO_2(110) surface.

2 Experiment

2×10^{13} cm^{-2} of Pt_4 clusters were deposited on a cleaned TiO_2(110) single crystal in the manner described in Refs [1,3]. The Pt_4/TiO_2(110) sample was supplied in vacuum to PTRF-XAFS measurements at BL-9A employing the PTRF-XAFS-dedicated system. Procedures of PTRF-XAFS measurement and analysis are represented in Ref [3]. The goodness of fit between the observed ($\chi_{obs}(k)$) and the calculated ($\chi_{cal}(k)$) EXAFS oscillations, R, was evaluated by using the reduced chi square expressed as follows

$$R = \sqrt{\frac{1}{N-P-1}\sum_{30\le k/\mathrm{nm}^{-1}\le 90}\left(\frac{\chi_{cal}(k)-\chi_{obs}(k)}{\sigma_{\overline{\chi_{obs}(k)}}}\right)^2}$$

where N, P, and $\sigma_{\overline{\chi_{obs}(k_1)}}$ stand for the number of data points, the number of fitting parameters, and the standard deviation of average $\chi_{obs}(k)$ at $k = k_1$, respectively.

3 Results and Discussion

In our previous STM study [4], Pt_4 clusters deposited on TiO_2(110) surface appeared to have a pseudo-square-shaped planar structure. Preliminary PTRF-XAFS analysis [3] indicated that a Pt_4 cluster on the TiO_2(110) surface might have a regular tetrahedral structure stabilized by Pt–O bonds formed with the O atoms at the TiO_2(110) surface. We compared three expected structures for Pt_4 clusters consistent with STM results, as shown in Fig. 1: (a) a regular tetrahedron (tetrahedron), (b) a square in which a diagonal was parallel to the [001] direction (diamond shape), and (c) a square in which a side was parallel to the [001] direction (square). Here, Pt–Pt bond length in these model structures was fixed to the value estimated by curve fitting analysis (0.2645 nm). Relative position of a Pt_4 cluster to the TiO_2(110) surface was determined as follows. Thousands of Pt_4 positions against the TiO_2(110) surface were systematically calculated. For each position, FEFF calculations were performed to evaluate the values of R. Finally, the models with minimum R values were selected as the most appropriate models for the above three structures, as depicted in Fig. 2.

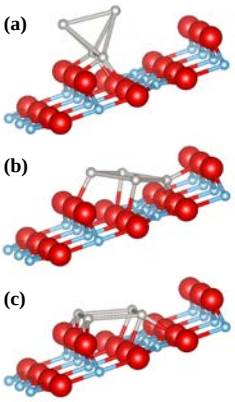

Fig. 1: Model structures of Pt_4/TiO_2(110).

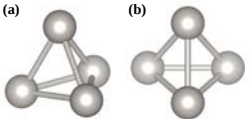

Fig. 2: 2D views of a regular tetrahedron.

The R values for three structures in Fig. 2 are listed in Table 1. Based on the R values, a regular tetrahedral structure is considered to be the most likely structure for Pt_4 clusters on the whole. It would be possible that a regular tetrahedron (Fig. 1a) looks like a pseudo-square in the 2D view from the direction as shown in Fig. 1b.

Further investigation and analysis will be required to obtain compatible structure model with the STM results.

Table 1: R values for EXAFS oscillation fits.

Structure	E // [001]	E // [1$\bar{1}$0]	E // [110]
(a) Tetrahedron	**0.97**	**0.93**	**0.95**
(b) Diamond shape	1.11	0.96	1.23
(c) Square	1.15	1.41	1.29

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