

PTRF-XAFS Study of Size-Selected Pt₇ Cluster Uniformly Deposited on an Al₂O₃/NiAl(110) Substrate by Lissajour Scanning

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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 -characterizing system to clarify the relationships between the number of constitutive metal atoms and chemical properties [1]. Electronic states of Pt_n clusters on Al₂O₃ as well as on TiO₂ are, however, still unclear. In this study, we performed polarization-dependent total reflection fluorescence XAFS (PTRF-XAFS) [2] to evaluate the electronic state of a Pt₇ cluster on an Al₂O₃ layer formed on NiAl(110).

2 Experiment

$6.4 \times 10^{12} \text{ cm}^{-2}$ of Pt₇ clusters were deposited on an Al₂O₃ layer formed on NiAl(110) single crystal in the manner described in Ref. [1]. The Pt₇/Al₂O₃/NiAl(110) sample was transferred and supplied in vacuum to the PTRF-XAFS measurement system by using a portable ultrahigh-vacuum sample storage system [3]. PTRF-XAFS measurements were performed at BL-9A employing the PTRF-XAFS chamber (base pressure: 8×10^{-8} Pa) under the following three orientation conditions: the electric vector $\mathbf{E} // [1\bar{1}0]$, $\mathbf{E} // [001]$, and $\mathbf{E} // [110]$. The measured spectra were normalized using REX2000.

3 Results and Discussion

Figure 1 describes polarization dependence of a Pt *L*₃-edge XANES spectrum for the Pt₇/Al₂O₃/NiAl(110). For comparison, a Pt *L*₃-edge XANES spectrum for Pt foil, which was measured under the same condition as the Pt₇/Al₂O₃/NiAl(110), is displayed in Fig. 1 as well. There are three features regarding the Pt₇/Al₂O₃/NiAl(110). The first point is that the Pt *L*₃-edge white line for the Pt₇/Al₂O₃/NiAl(110) emerges at a higher energy than that for Pt foil does. This change, which is assigned to the shift of unoccupied 5*d* orbital of Pt to a higher energy, may be caused by nanometrization of Pt or by electronic interaction with O atoms at the surface of the Al₂O₃ support. The second point is that the integral intensity of the white line for each orientation condition of the Pt₇/Al₂O₃/NiAl(110) is high, compared to that for Pt foil. This fact means that Pt atoms in the Pt₇ cluster are slightly oxidized on average probably through electron transfer from the Pt₇ cluster to adjacent O atoms at the surface of the Al₂O₃ layer. The third point concerning polarization dependence is that the integral intensity of

the white line and the amplitude of EXAFS oscillation are higher for the condition of $\mathbf{E} // [110]$ than for the other orientations. The effective coordination number N^* is represented as functions of the angles θ_{jk} between polarization vector \mathbf{E} and bond vectors \mathbf{R}_{jk} [2].

$$N_j^* = \sum_k (0.7 + 0.9 \cos^2 \theta_{jk})$$

This relation invokes an image of relatively planar Pt₇ geometry on the Al₂O₃, parallel to NiAl(110). Such an image is consistent with the result of our previous scanning tunneling microscopy study [1].

In conclusion, the PTRF-XAFS study suggests that the Pt₇ cluster on the Al₂O₃ should have a planar structure parallel to NiAl(110). The interaction between the Pt₇ cluster and the Al₂O₃ layer formed on NiAl(110) seems to be large, which may cause the shift in the Pt *L*₃-edge white line and electron transfer from Pt atoms to adjacent O atoms. The effect of oxide support on electronic and geometric structures of Pt atoms in the Pt₇ cluster will be further discussed in the future.

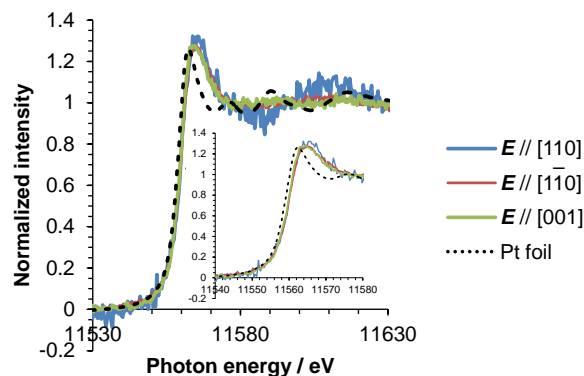


Fig. 1: Pt *L*₃-edge XANES spectra of Pt₇ clusters on Al₂O₃ formed on NiAl(110) substrate.

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References

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