PTRF-XAFS Study of Size-Selected Pt\textsubscript{7} Cluster Uniformly Deposited on an Al\textsubscript{2}O\textsubscript{3}/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 relationship between the number of constitutive metal atoms and chemical properties \cite{1}. Electronic states of Pt\textsubscript{7} clusters on Al\textsubscript{2}O\textsubscript{3} as well as on TiO\textsubscript{2} are, however, still unclear. In this study, we performed polarization-dependent total reflection fluorescence XAFS (PTRF-XAFS) \cite{2} to evaluate the electronic state of a Pt\textsubscript{7} cluster on an Al\textsubscript{2}O\textsubscript{3} layer formed on NiAl(110).

2 Experiment
6.4 \times 10^{12} \text{ cm}^{-2} of Pt\textsubscript{7} clusters were deposited on an Al\textsubscript{2}O\textsubscript{3} layer formed on NiAl(110) single crystal in the manner described in Ref. \cite{1}. The Pt\textsubscript{7}/Al\textsubscript{2}O\textsubscript{3}/NiAl(110) sample was transferred and supplied in vacuum to the PTRF-XAFS measurement system by using a portable ultrahigh-vacuum sample storage system \cite{3}. PTRF-XAFS measurements were performed at BL-9A employing the PTRF-XAFS chamber (base pressure: 8 \times 10^{-8} \text{ Pa}) under the following three orientation conditions: the electric vector $E$ \parallel [110], $E$ \parallel [001], and $E$ \parallel [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 Pt\textsubscript{7}/Al\textsubscript{2}O\textsubscript{3}/NiAl(110). For comparison, a Pt $L_3$-edge XANES spectrum for Pt foil, which was measured under the same condition as the Pt\textsubscript{7}/Al\textsubscript{2}O\textsubscript{3}/NiAl(110), is displayed in Fig. 1 as well. There are three features regarding the Pt\textsubscript{7}/Al\textsubscript{2}O\textsubscript{3}/NiAl(110). The first point is that the Pt $L_3$-edge white line for the Pt\textsubscript{7}/Al\textsubscript{2}O\textsubscript{3}/NiAl(110) emerges at a higher energy than that for Pt foil does. This change, which is assigned to the shift of unoccupied $5d$ 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 Al\textsubscript{2}O\textsubscript{3} support. The second point is that the integral intensity of the white line and the amplitude of EXAFS oscillation are higher for the condition of $E$ \parallel [110] than for other orientations. The effective coordination number $N^*$ is represented as functions of the angles $\theta_{jk}$ between polarization vector $E$ and bond vectors $R_{jk}$ \cite{2}.

\[ N^* = \sum (0.7 + 0.9 \cos^2 \theta_{jk}) \]

This relation invokes an image of relatively planar Pt\textsubscript{7} geometry on the Al\textsubscript{2}O\textsubscript{3}, parallel to NiAl(110). Such an image is consistent with the result of our previous scanning tunneling microscopy study \cite{1}.

In conclusion, the PTRF-XAFS study suggests that the Pt\textsubscript{7} cluster on the Al\textsubscript{2}O\textsubscript{3} should have a planar structure parallel to NiAl(110). The interaction between the Pt\textsubscript{7} cluster and the Al\textsubscript{2}O\textsubscript{3} 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 Pt\textsubscript{7} cluster will be further discussed in the future.

References
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