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Structure analysis of Pt cluster on highly oriented pyrolytic graphite

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Introduction

Understanding the interface interaction between metal nano-clusters and the surfaces of graphite-related material is indispensable for many industrial applications such as catalysis. It has been found that Pt monolayer clusters, with a width of 2-3 nm, on a highly oriented pyrolytic graphite (HOPG) surface promote catalytic activity for the H_2-D_2 exchange reaction [1]. The origin of this enhancement has been attributed to the interface interaction between the Pt atoms and the graphite surface which leads to a shift in the d-band center of the Pt away from the Fermi level. The scanning tunneling microscopy (STM) observation of the monolayer Pt cluster on HOPG suggests that the Pt-Pt distance of the Pt cluster is shorter than that of the crystalline Pt as much as about 13 %. In this work, to investigate the Pt-Pt distance of the Pt cluster more in detail by the macroscopic and spectroscopic method, X-ray absorption fine structure (XAFS) measurements have been conducted.

Experimental

The experiments were performed at BL-7C under ultrahigh vacuum condition (~3.0 $\times 10^{-8}$ Pa). XAFS spectra were obtained around Pt-L_{III} edge for following four samples: (1) as-deposited Pt/HOPG surface (θ_{Pt} = 0.1, having a higher catalytic activity, refer to as "active Pt/HOPG"), (2) annealed Pt/HOPG surface at 400 K under hydrogen atmosphere with 24 Torr (θ_{Pt} = 0.1, having a normal catalytic activity, refer to as "normal Pt/HOPG"), (3) the pristine HOPG surface and (4) the reference sample of Pt particles on a graphite tape. The XAFS signal was obtained by collecting fluorescence intensity at the specific energy related to the X-ray absorption by the solid-state detector (SSD) during the scan of incident X-ray energy. In each sample, 10-13 scans were measured to obtain better S/N ratio.

Results and Discussion

The XAFS results are shown in Fig. 1a. In every case, large background signals appear and inhibit the direct analysis of the results. This is probably due to the inclusion of the elastic scattering intensity of incident X-ray beam into the measured fluorescence intensity. Such an elastic intensity is known to be negligible for the typical sample with enough thickness. Due to the small amount of Pt in our sample (θ_{Pt} = 0.1), the effect is probably not negligible. To distinguish the fluorescence intensity from the background signal, the XAFS result of the pristine HOPG is subtracted from each result for Pt/HOPG as shown in Fig. 1b. By subtracting the background signal, the absorption by Pt-L_{III} edge at ~11.5 keV appears as observed by the reference Pt sample. However, the Fourier transformed XAFS signals do not indicate a reasonable Pt-Pt distance as shown in Fig. 2 (1-2 Å is extremely short), possibly due to the incomplete subtraction of the background signal.

As a future work, by accumulating the fluorescence signals in the wide energy range with multi-channel-scalar, clear distinction of the fluorescence intensity from background signal will be done to investigate the Pt-Pt distance of Pt cluster even at sub-monolayer Pt coverage.

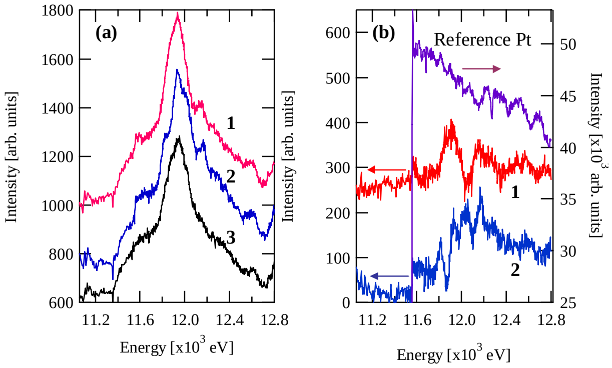

Fig. 1 (a) XAFS results (b) XAFS results subtracted by the signal from pristine HOPG. The notation numbers 1, 2 and 3 indicate the sample of active Pt/HOPG, normal Pt/HOPG and pristine HOPG, respectively. The reference Pt result is also shown in (b).

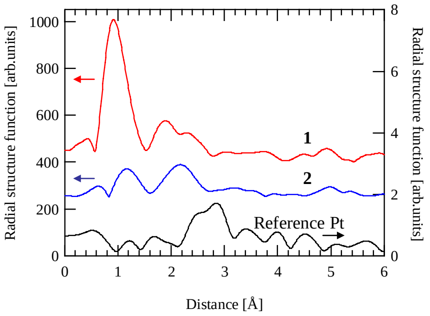

Fig. 2 Fourier transformed XAFS results. The notation numbers 1 and 2 indicate the sample of active Pt/HOPG and normal Pt/HOPG, respectively. The reference Pt result is also shown.

Reference

[1] T. Kondo, K. Izumi, K. Watahiki, Y. Iwasaki, T. Suzuki, J. Nakamura, J. Phys. Chem. C **112** (2008) 15607.

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