

Pd K-edge XAFS study on palladium-polymer micelle catalyst

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Introduction

Colloidal metal particles and metal clusters have attracted much interest because of their unique properties and potential applicability to microelectronics, chemical sensing, data storage, catalysts, etc.

In this paper, we describe the formation of stable, subnanometer Pd clusters contained within micelles produced from random copolymers using a novel method. To the best of our knowledge, the Pd clusters formed in this work are the smallest reported to date (average cluster diameter ~ 0.7 nm). The clusters were stabilized in several micelle morphologies, and exhibited efficient catalytic activity in hydrogenation and Heck reactions.

Experimental Section

The cross-linking of palladium-polymer micelles was prepared as described elsewhere.[1] X-ray absorption experiments of the palladium-polymer micelles catalysts were carried out on the beam line 10B at Photon Factory in High Energy Accelerator Research Organization Institute of Materials Structure Science (KEK-PF), Tsukuba Japan, with a ring energy of 2.5 GeV and stored current of 450-380 mA. X-ray absorption spectra were recorded in a transmission mode at room temperature with a Si(311) channel cut monochromator. The intensities of the incident and transmitted X-ray were measured with 17-cm ion chamber with a Ar gas flow and a 62-cm ion chamber with a Ar gas flow, respectively. Energy calibration was carried out using Pd K-edge of Pd foil.

Results and Discussion

Fig. 1 shows the radial structure function (RSF) of PdO, Pd catalyst and Pd metal, which were obtained by Fourier transforming of k^3 -weighted Pd K-edge EXAFS spectra of these samples. A peak observed at 2-4 Å shows the presence of the second-neighboring Pd atoms. It is noteworthy that the peaks due to second neighboring Pd atoms for Pd catalyst (Fig. 1b) and reference Pd metal (Fig. 1c) appeared at the same position. This confirms that the Pd was in metallic environment. However, the peak magnitude for Pd catalyst was much lower than that for the reference Pd metal. This result demonstrates the decrease in the number of second-neighboring Pd atoms, supporting the formation of small Pd metal particles in Pd catalyst. On the other hand, the RSF peaks appearing around 1.6 Å are due to the backscattering from the

adjacent carbon or oxygen atoms. In the RSF of PdO, the peak around 1.6 Å is assignable to Pd-O shell. In the RSF of Pd catalyst, very small peak can be noticed in the similar position, which is probably due to carbon atoms of polymer coordinated with Pd atoms (Pd-C shell) or oxygen atoms on the surface of Pd metal particles (Pd-O shell), in our opinion. In any case, this would be minor fraction.

We also performed nonlinear curve-fitting analyses of the Fourier-filtered EXAFS of the first and the second shells, corresponding Pd-C(or Pd-O) and Pd-Pd shells, by a least-squares. From this analysis for Pd catalyst the distance of the Pd-Pd shell was estimated 2.76 Å, which was almost consistent with that of the reference Pd metal. The coordination number (CN) was calculated to be 4.4, which was much lower than that in reference Pd metal, suggesting that the size of the palladium metal in Pd catalyst was extremely small like small clusters.

The sphere-like particle of fcc structure was considered as a stable model cluster to estimate the cluster size of Pd metal from the coordination number as plotted in Fig. 2. The cluster whose coordination number was 4.4 would be larger than 4-atom tetrahedra and less than 13-atom cuboctahedron; the estimated number of Pd was around 9 and diameter was around 0.8 nm, indicating the formation of nano-size palladium metal cluster in Pd catalyst.

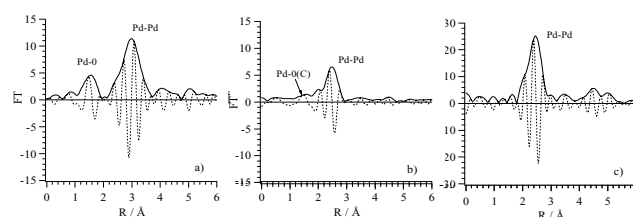


Fig.1 FT of k^3 -weighted Pd K-edge EXAFS of a) PdO, b) Pd catalyst and c) Pd foil.

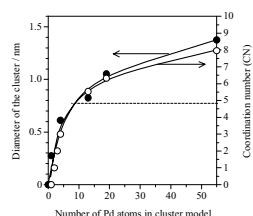


Fig. 2 Geometrical calculation of diameter of small sphere Pd cluster and the average coordination number in the cluster.

References

[1] K. Okamoto, R. Akiyama, H. Yoshida, T. Yoshida and S. Kobayashi, *J. Am. Chem. Soc.*, 127, 2125 (2005)