10B/2001G321

EXAFS studies on the sprayed Pt catalyst prepared from PVP-stabilized colloid

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Introduction

Sprayed catalysts show the strong interaction between supported particles and the support. However, the aggregation of the particles easily occurred, and hence, the particle size was usually larger than 10 nm.

Particle sizes of platinum colloidal clusters are easily controlled between 0.8 to 4 nm by choosing reduction time, kind of stabilizer, the method of reduction and so on. Although colloidal clusters are very small, the stabilizer, such as polymers, covered the metal surfaces and lead to low metal surface area. Thus, the effective removal of the stabilizer from the colloidal clusters on the catalysts is one of the crucial problems.

In this study, we prepared Pt/Al_2O_3 catalyst from Pt-PVP (polyvinylpyrrolidone) colloidal clusters by spray reaction technique. Pt cluster size was characterized by EXAFS analysis.

Experimental

Pt-PVP colloidal cluster was prepared from $H_2PtCl_6 \cdot 6H_2O$ and PVP aqueous solution with molar ratio of 1:40. Ethanol (equivalent amount to H_2O) was added, followed by refluxed for 1 h at 356 K, resulting dark brown solution included Pt colloid [PVP-colloid]. Sprayed Pt/Al_2O_3 catalyst was prepared from the above Pt-colloidal solution and $Al(NO_3)_3 \cdot 9H_2O$ with the molar ratio of Pt:Al = 0.5:99.5. The ultrasonicated solution was aspirated through a quartz tube situated in the electric furnace at 1073 K under an ambient condition. The reacting droplets were dried, decomposed into oxides and subsequently calcined in the furnace within a second [PVP-spr1073]. Sprayed catalysts were calcined in the air at 673 K for 1 h to remove the residual stabilizer [PVP-spr1073c].

Pt L_3-edge EXAFS spectra were collected at BL-10B of the Photon Factory with Si(311) channel cut monochromator. Colloidal solution was concentrated and dried on the felt sheet. The powder samples were transferred into Al cells with Kapton windows. Curve-fitting analyses of k^3-weighted EXAFS oscillations in the k-space were performed by the EXAFS analysis program REX2000 (Rigaku Co.). Model parameters for curve-fitting analysis (back scattering amplitude and phase shift) were extracted from an EXAFS oscillation observed for bulk Pt (N =12, r =0.2774 nm).

Results and discussions

FT of the catalysts was shown in Fig. 1. The main peak of the colloidal solution and sprayed Pt/Al_2O_3 catalysts can be attributed Pt-Pt coordination in the Pt metal. Coordination number (CN) of Pt-Pt in PVP-colloid is 7.8 as shown in Table 1. So the particle size was estimated <2 nm. Although concentration process of colloidal solution might lead the some aggregation, severe aggregation had not occurred. CN of PVP-spr1073 and PVP-spr1073c are 8.1 and 8.6, respectively. They are almost same as that of PVP-colloid, suggesting the small Pt clusters can be prepared on the Al_2O_3 support by spray reaction technique. Moreover, additional calcination at 673 K did not lead the serious aggregation. It can be said that the strong interaction between Pt and Al_2O_3 support in the sprayed catalysts can prevent the aggregation during the treatment. The effectiveness of the spray reaction technique and colloidal solution to the catalyst preparation can be presented.

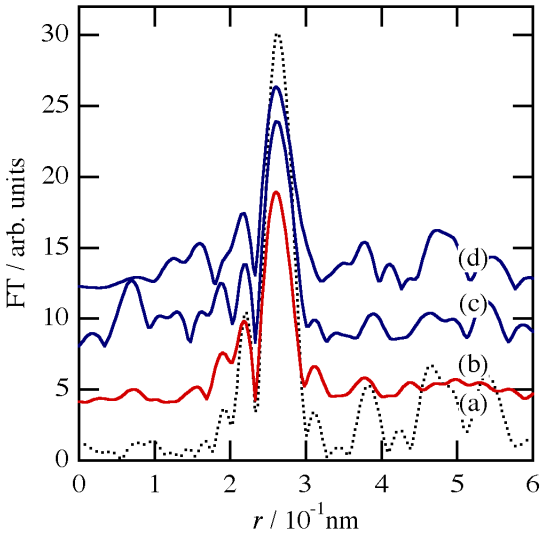

Figure 1. FT of k^3-weighted Pt L_3-edge EXAFS oscillation; (a) Pt foil, (b) PVP-colloid, (c) PVP-spr1073, (d) PVP-spr1073c.

Table 1: Curve fitting* results for Pt-Pt coordination

sample	N	r / nm	dE / eV	DW / nm
PVP-colloid	7.8	0.276	–0.885	0.0068
PVP-spr1073	8.1	0.276	–0.172	0.0066
PVP-spr1073c	8.6	0.276	–0.808	0.0071
bulk Pt	12	0.2774	0.0	0.006

*Fourier filtering range: 0.23-0.30 nm.

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