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EXAFS studies on the spr Pt/Al_2O_3 catalyst prepared from Pt-PVA colloid

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Introduction

Colloidal clusters can provide a controlled small metal particles. Particle sizes were easily controlled between 0.7 to 5 nm by selecting reduction time, the kind and the amount of stabilizer, and so on. Although the colloidal clusters are very small, the polymer stabilizer remained on the metal surfaces and lead to lowering the metal surface area. Thus, the method of stabilizer removal from the colloidal clusters on the catalysts was one of the problems.

Sprayed catalysts were prepared by rapid heating process at the high temperature, such as 1073 K. It seems that the rapid heating process can remove the polymer stabilizer and prevent the aggregation of metal particles. In this study, we prepared Pt/Al_2O_3 catalyst from Pt-PVA (polyvinyl alcohol) colloidal clusters by spray reaction technique. Pt cluster size was characterized by EXAFS analysis.

Experimental

Pt-PVA colloidal cluster was prepared from $H_2PtCl_6{\cdot}6H_2O$ and PVA aqueous solution with molar ratio of 1:100 to 1:300. Methanol (equivalent amount to H_2O) was added and refluxed for 1 h at 338 K, resulting dark brown solution including Pt colloid. Spr 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 heated in a quartz tube at 1073 K under an ambient condition within a second. Sprayed catalysts were calcined in the air at 673 K for 1 h to remove the residual stabilizer. Catalysts were designated with PVA molar ratio, as PVA100. Calcined catalysts were designated as PVA100c.

Pt L_3-edge EXAFS spectra were measured at BL-10B of the Photon Factory with Si(311) channel cut monochromator. The powder samples were transferred into 10 mm length of 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 collected 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 spr Pt/Al_2O_3 catalysts can be attributed Pt-Pt bond in the Pt metal. Coordination number (CN) of Pt-Pt was reduced from 9.5 to 7.6 as increasing PVA ratio as shown in Table 1. So the particle size growth during spraying process was suppressed by the PVA stabilizer. Although the amount of PVA with the molar ratio of 100 is not enough for preventing the Pt aggregation, there exists the polymer stabilizer residue. To remove the residual carbon contaminant, catalysts were further calcined in air. CN of calcined catalyst was not changed from that of original sprayed one as shown in Table 1. Additional calcinations at 673 K did not lead the serious aggregation for all catalysts. The diminishment of the residue was confirmed by Raman spectroscopy.

It can be said that the spraying method by using Pt-PVA colloid can provide the small Pt clusters on the alumina support, and further calcinations effectively remove the residual carbon without change the particle size.

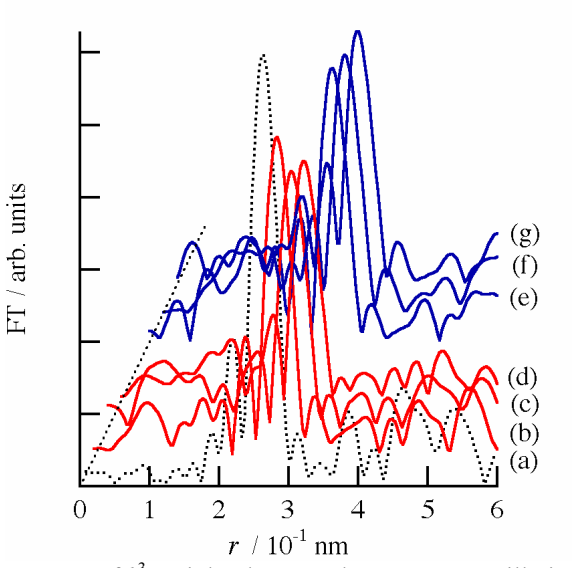

Fig. 1. FT of k^3-weighted Pt L_3-edge EXAFS oscillation; (a) Pt foil, (b) PVA100, (c) PVA200, (d) PVA300, (e) PVA100c, (f) PVA200c, (g) PVA300c.

Table 1: Curve fitting results for Pt-Pt coordination

sample	N	r / nm	dE / eV	DW / nm
PVA100	9.5	0.277	-1.282	0.0061
PVA200	8.8	0.278	2.146	0.0064
PVA300	7.6	0.277	0.577	0.0063
PVA100c	10	0.277	0.855	0.0067
PVA200c	8.7	0.276	-1.277	0.0064
PVA300c	7.6	0.276	-2.927	0.0062
bulk Pt	12	0.2774	0.0	0.006

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