Supplementary Material (ESI) for Chemical Communications

Growth limits in platinum oxides formed on Pt-skin layers on Pt-Co bimetallic nanoparticles

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electronic suppulementary information

Experimental details

Carbon-supported Pt_3Co nanoparticles were obtained from Tanaka Kikinzoku Kogyo (TKK). The chemical composition of the bimetallic Pt-Co alloy was determined to be Co 22 at% through energy-dispersive x-ray analyses. The loading of the metallic components was 42 wt% relative to the carbon support. The average particles size was estimated to be approximately 4.2 nm in diameter determined by transmission electron micrography.

Platinum catalysts (50wt %, supported on Ketjen black) were prepared with the standard platinum-oxide colloidal method. The average particles size was 2.0 nm. Since larger Pt particles are generally more stable than smaller Pt particles especially below 5 nm[1], we carefully compared the oxidation behavior between Pt_3Co (4.2 nm) and Pt (2 nm). Although no systematic studies have been done to date, the surface oxidation rate could be faster for smaller nanoparticles, due to modifications to the surface energy or electronic states, similar to enhanced specific activity in smaller Pt nanoparticles.[2]

The catalyst electrode was prepared by spreading a suspension of carbon-supported Pt_3Co nanoparticles dispersed in Nafion® solution onto a thin carbon electrode (thickness: 120 μm). The electrochemical cell was designed for x-ray absorption spectroscopy (XAS) in a transmission configuration.[3] The electrochemical cell consisted of the sample, counter, and reference electrodes, like a standard three-electrode electrochemical cell, except for a very thin electrolyte region along the x-ray pathway. The inert atmosphere in the cell was maintained by purging it with ultra-pure nitrogen gas.

Prior to the XAS measurements, the catalysts were electrochemically cleaned by repeating cyclic voltammetry scans (10–20 times) between 0.05 and 1.2 V. After the experiments on potential-step oxidation, the form of CV was exactly identical, indicating that the present Pt_3Co nanoparticles were stable at least under these experimental conditions.

X-ray absorption spectroscopy measurements and data analyses

XAS analyses were carried out with standard procedures using REX2000. The k^3-weighted χ(k) data ranging from 2.5 to 14.0 Å was Fourier-transformed into *r*-space for non-linear curve fitting. The backscattering amplitudes and phase shifts for all atom pairs were theoretically calculated with FEFF8 code.[4]

Structural model for nominal Pt_3Co nanoparticles with Pt-skin layers

Figure S1 plots the EXAFS data (EXAFS oscillation and Fourier transform) for the electrochemically cleaned Pt_3Co (taken at 0.4 V vs. RHE). The fitting parameters are listed in Table S1.

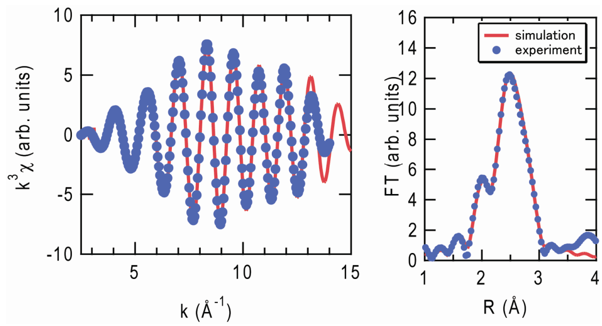

Fig. S1. EXAFS spectra in *k*-space and *r*-space for Pt_3Co (0.4 V vs. RHE) Simulation was done assuming Pt-Pt and Pt-Co bonds.

	CN	R	E_0	DW
Pt-Pt	9.0(9)	2.72(1)	-2.2(6)	0.08(0)
Pt-Co	1.6(3)	2.63(9)	0.57(4)	0.07(9)

Table S2 Fitting parameters for electrochemically cleaned Pt_3Co nanoparticles. CN and DW stand for Coordination Number and Debye-Waller factor.

To obtain an average structure of Pt_3Co nanoparticles with Pt-skin layers (inset of Fig. 1(a)), we assumed a simple spherical model that consisted of a Pt_3Co inner-core and a Pt shell with a diameter of 4.2 nm. For the Pt_3Co core with a diameter of approximately 3.5 nm, we obtained a number of Pt-Pt and Pt-Co bonds and the coordination numbers listed in Table S2, which almost agree with the experimental data.

If Co atoms partly segregate in the inner core, the Pt-skin layers should become thinner, because the coordination number for Pt-Pt in the core part increases; consequently, the Pt-Pt coordination number for the Pt-skin layers decreases.

Bonds	Number of bonds (model)	Coordination number (model)	Coordination number (experiments)
Total	29172	10.75	10.72
Pt-Pt	24504	9.03	9.09
Pt-Co	4668	1.72	1.63

Table S2 Numbers of Pt bonds and coordination numbers for Pt_3Co model and those obtained from experiments.

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