

Structural Analysis of Bimetal Nanoparticles prepared in Sub- and Supercritical Fluids by means of EXAFS

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Introduction

The synthesis of nanometer scale metal-polymer composites is of crucial importance for unique size-dependent optical, catalytic, magnetic, and electronic properties compared to their bulk counterparts. Especially bimetallic clusters of noble metals are quite interesting subjects. These kinds of bimetallic clusters can be synthesized by the thermal reduction of mixtures of noble metal ions, e.g. Pt(IV) and Rh(III) under the existence of protective polymer such as poly(N-vinyl-2-pyrrolidone)(PVP). The clusters synthesized by ordinal method have the core-shell structure, i.e., the platinum core is surrounded by the rhodium atoms. In this work, we have tried to change this structure by synthesizing under the high-temperature and high pressure condition. By using the high-temperature conditions of dense fluids which are not possible under ambient pressure, it may be possible to change the rate limiting process to create the nanoparticles, which offers another possibility to control the alloyed-structure of bimetallic cluster.

Experimental

Platinum/Rhodium bimetallic colloidal dispersions were synthesized by passing solutions of mixture of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and PVP through the high-temperature and high-pressure SUS cell. The molar ratios of Pt(IV) and Rh(III) were varied as 4/1, 1/1, and 1/4. The preparation conditions of temperature and pressure were 473-573 K and 25 MPa, respectively. As the solvent fluids, we used 1/1 mixture of water and ethanol. The obtained samples were then poured into cells for EXAFS measurements, and Pt-L_{III} and Rh-K edges' EXAFS spectra were collected at room temperature in a transmission mode at BL-10B and BL-7C to estimate the coordination numbers (C.N.s) of platinum and rhodium atoms.

Results and Discussion

Figure 1 shows the Pt-L_{III} edge EXAFS Fourier transforms for the reduced solutions of mixtures of Pt and Rh ions with 15 g/dm³ PVP. The total amount of ion concentration was adjusted to 15 mM. The synthesis was performed at 200 °C and 25 MPa. With increasing the

molar ratio of Rh to Pt, the splitting of the main peak due to Rh scattering is observed. By using the phase-shift and amplitude which were extracted from the EXAFS spectra of Pt, Rh, and Pt/Rh alloy foils, we evaluated the coordination numbers of each scattering atoms.

Table 1 lists some of our results. With increasing the temperature, the C.N. of Rh around Rh drastically increases. The analysis suggests that the alloyed structure changes from the core-shell type to the random type with increasing the temperature. The analysis for the another molar ratio is now proceeding.

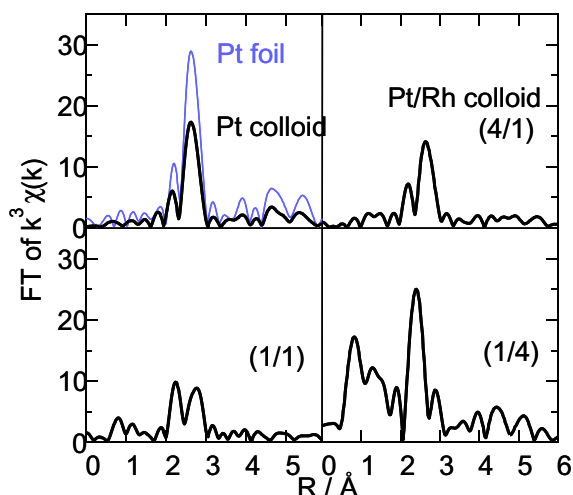


Fig. 1 Fourier transforms of Pt-L_{III} edge for Pt/Rh colloidal solutions created at different molar ratios of Pt and Rh.

Table 1. The C.N. from the EXAFS spectra for Pt/Rh(1/1) bimetallic clusters synthesized under 25 MPa.

Temp. (K)	d(nm)	absorbing atom	scattering atom	N
200°C	2.3	Pt	Pt	6.6
			Rh	3.7
		Rh	Rh	1.7
			Pt	4.3
260°C	2.4	Pt	Pt	5.9
			Rh	4.6
		Rh	Rh	4.5

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