

EXAFS analysis of Pt-core/Rh-shell bimetallic nanoparticles prepared by multi-step reduction processes

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1 Introduction

Preparation of supported metal nanoparticles with high dispersion is one of the important topics in the research field of catalysis science and technology. Our preparation methods involve the formation of colloidal nanoparticles by the reduction of metal ions in alcohol-ethanol solution in the presence of protecting polymers. We have reported that highly-dispersed Pt/TiO₂ catalysts were obtained by this method [1]. This method is also effective for obtaining bimetallic nanoparticles composed of two kinds of noble metals, such as Pt and Rh [2]. We herein report the EXAFS studies of Pt-core/Rh-shell bimetallic nanoparticles prepared by multi-step reduction processes using photoirradiation and refluxing in aqueous ethanol solution.

2 Experimental

Pt nanoparticles were prepared by photoreduction of PtCl₄²⁻ to Pt in EtOH-H₂O solution in the presence of poly-N-vinylpyrrolidone (PVP). An aqueous ethanol solution containing RhCl₃ and PVP was added to the Pt-containing colloidal dispersion and the mixed solution was refluxed for 1h. EXAFS measurements were performed in transmission mode and fluorescence mode at room temperature, using BL-NW10A and BL-7C at KEK-PF.

3 Results and Discussion

Pt-Rh bimetallic nanoparticles prepared by the photoirradiation-refluxing steps have the average particle sizes with ca. 3.0 nm. Fig. 1 shows the EXAFS spectra of the samples where the atomic ratio of Pt-Rh was 4:1, 1:1, 1:4, along with reference alloy foils. The Pt L3-edge spectra show that the bands due to Pt-Pt bonds were mainly present in the sample with the Pt-Rh ratio of 1:1 and 4:1. On the other hand, no obvious Rh-Rh bonds were observed for these samples, as shown in the Rh-K edge spectra, indicating that Pt-Rh bonds were formed in these samples.

When the Pt-Rh ratio was changed to 1:4, the bands due to Rh-Rh bonds appeared for the Rh-K spectra and the bands were split to two peaks due to the phase shift caused by the formation of Pt-Rh bonds.

On the basis of the findings described above, we proposed the models for Pt-Rh bimetallic nanoparticles. For the particles with lower Rh/Pt ratio than that corresponding to monolayer coverage, Rh metals were highly dispersed on Pt nanoparticles, whereas Pt nanoparticles were fully covered with Rh metals for high Rh/Pt ratio. Thus, Pt-core/Rh-shell bimetallic

nanoparticles were obtained by our preparation methods. In addition, the particles were deposited on TiO₂ by liquid phase adsorption processes. FTIR studies for the samples after CO adsorption revealed that the particles retained Pt-core/Rh-shell structures.

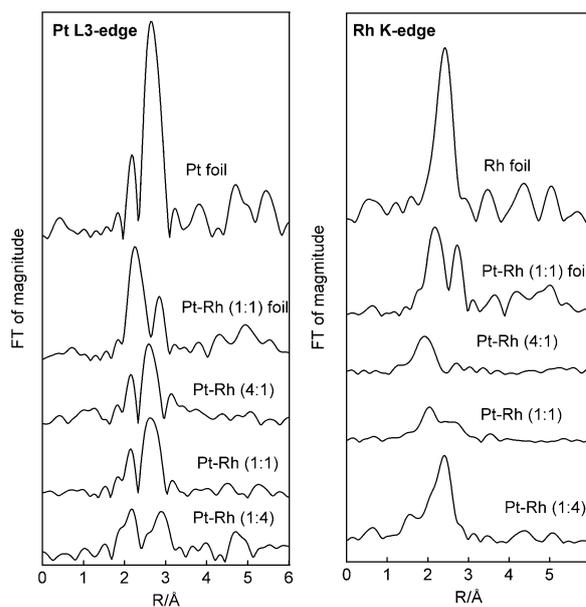


Fig. 1: EXAFS spectra of Pt-Rh bimetallic nanoparticles and reference foils.

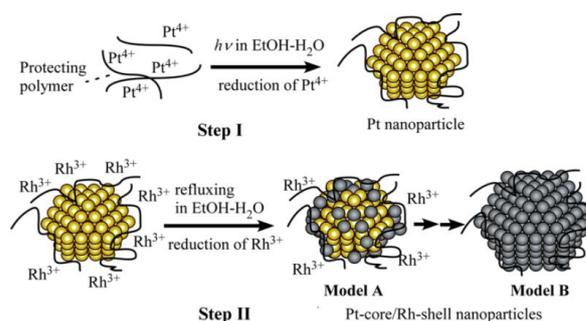


Fig. 2: Proposed models for Pt-core/Rh-shell bimetallic nanoparticles.

References

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