

Preparation of Pt-Rh bimetallic colloidal nanoparticles by photochemical reduction and alcohol reduction

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Introduction

Supported metal nanoparticles are one of the key materials in the field of catalysis sciences. We have reported that the synthesis of colloidal metal particles and their deposition on supporting materials is one of the promising routes to obtain highly-dispersed supported metal catalysts. Recently, we obtained the Pt nano-catalysts by photochemical reduction of H_2PtCl_6 complex in ethanol-water solution and deposition of the Pt particles on TiO_2 .

This method is also useful for the preparation of supported bimetallic nano-particle catalysts. It has been reported that bimetallic particles Pt-Rh can be prepared by alcohol reduction under reflux conditions [1]. In this study, we combined photochemical reduction method with alcohol reduction method to prepare bimetallic nanoparticles which have the various metal distribution and analyze their structures by using EXAFS analysis.

Experimental

Colloidal dispersions of Pt/Rh bimetallic particles were synthesized by combination of photochemical reduction and alcohol reduction methods. Hexachloroplatinic (IV) acid (0.066 mmol) was dissolved in 100 mL of ethanol-water solution containing poly(N-vinyl-2-pyrrolidone) (Wako Pure Chemical Ind., K-30, M.W. 40,000, 5.28 mmol of monomeric units). The solution was photo-irradiated for 3 h after N_2 gas bubbling. Then rhodium(III) chloride (0.066 mmol) was added to the solution, and it was refluxed for 1 h. The solution was concentrated to 1/30 to 1/50 by vacuum evaporation before EXAFS measurements.

Pt L3- and Rh K-edge EXAFS spectra were measured in a transmission mode at BL-7C and NW10A stations, respectively. The data reduction was carried out by using REX2000 ver.2.5.9 program. The range of Fourier transformation from the k space to r space was 3-16 \AA^{-1} .

Results and discussion

Figure 1 shows the Pt L3- and Rh K-edge EXAFS spectra of Pt-Rh colloidal metal particles, compared with those of Pt and Rh particles. The main peak of Pt-Pt was observed at $R=2.6 \text{ \AA}$ for Pt particles and foils (Fig. 1(a)). The peak was not shifted but the peak intensity decreased for the Pt-Rh bimetallic particles. On the other hand, the peak shift and the decrease of peak intensity were observed for Rh EXAFS spectra of Pt-Rh particles (Fig. 1(b)). The spectra were much different from those of the spectra obtained for Pt-Rh bimetallic colloids prepared by

$NaBH_4$ reduction, in which the particles were composed of Pt- and Rh- clusters [2]. These findings indicate that Pt-Rh bond was formed in the metal particles, and implied that the particles mainly composed of Pt-core/Rh-shell structures. In the separate experiments using FTIR measurement for supported Pt-Rh particles thus prepared, CO was mainly adsorbed on Rh sites of the catalysts, confirming that metal particles were mainly composed of Pt-core/Rh-shell clusters.

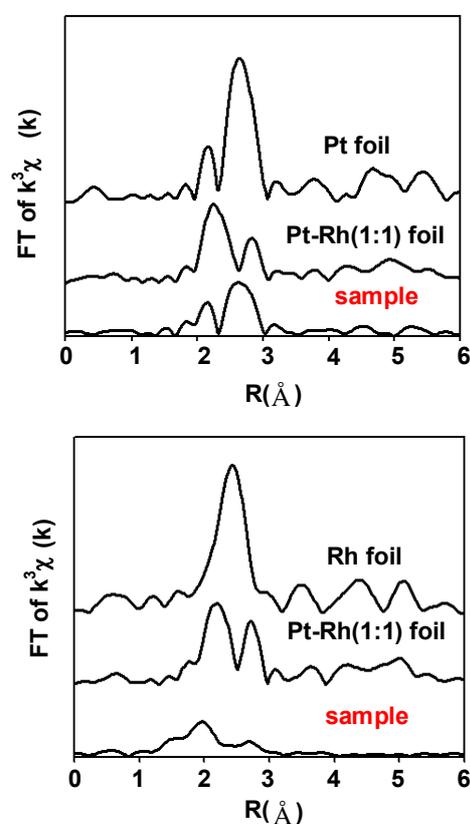


Figure 1 EXAFS spectra of Pt-Rh bimetallic particles prepared by photoreduction and alcohol reduction. (a) Pt L3-edge; (b) Rh K-edge spectra.

References

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