

EXAFS studies of Pt-Rh bimetallic colloidal particles prepared by chemical reduction with sodium borohydride

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Introduction

Noble metal nanoparticles have attracted much attention in the field of catalysis sciences, because the catalytic properties strongly depend on the particle sizes and shapes. Colloidal metal nanoparticles can be easily synthesized by chemical reduction using H_2 , $NaBH_4$, alcohols, and hydrazine as reducing agents in the presence of protecting polymers and ligands. The reduction methods and reduction conditions along with the dispersions of metal precursors affect the size and shape of the metal nanoparticles.

Harada et al. have reported that bimetallic particles Pt-Rh can be prepared by alcohol reduction under reflux conditions [1]. EXAFS studies revealed that the metal particles were mainly composed of Pt-core/Rh-shell clusters. In this study, we prepared Pt-Rh metal particles by chemical reduction with $NaBH_4$ in aqueous solutions and examined the composition of the particles by using EXAFS measurements. The main objective of this study is to investigate the effect of preparation method on the contribution of Pt-Rh bimetallic particles.

Experimental

Colloidal dispersions of Pt/Rh bimetallic particles were synthesized by borohydride-reduction method. Hexachloroplatinic (IV) acid (0.33 mmol) and rhodium(III) chloride (0.33 mmol) were dissolved in 500 mL of water containing poly(N-vinyl-2-pyrrolidone) (Wako Pure Chemical Ind., K-30, M.W. 40,000, 1.51 g, 13.6 mmol of monomeric units). The molar ratio of Pt(IV) to Rh(III) in the aqueous solution was 1:0, 1:1, and 0:1. The total amount of both metals was kept at 0.66 mmol in 500 mL of the aqueous solution. The mixed solution was stirred at 70°C until the temperature does not change. An aqueous solution dissolving $NaBH_4$ (0.32 mol/L) was poured drop by drop in the mixed solution, and then stirred for 10 min. The samples were 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-9C and NW10A stations, respectively. The data reduction was carried out by using REX2000 ver.2.3.3 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 shifted to 2.8 \AA and decreased in its intensity for Pt-Rh particles. The peak shift and the decrease of peak intensity were also observed for Rh EXAFS spectra of Pt-Rh particles (Fig. 1(b)). These findings indicate that Pt-Rh bond was formed in the metal particles. The spectra were much different from those of the spectra obtained for Pt-Rh bimetallic colloids prepared by alcohol reduction [1], and resembled the feature of cluster-in-cluster structures, in which the particles were composed of Pt and Rh clusters [2].

The chemical reduction with $NaBH_4$ can rapidly reduce Pt and Rh ions in aqueous solution as compared with alcohol reduction. Thus, our results suggest that the distribution of Pt and Rh in the metal particles strongly depends on the reduction rate of Pt and Rh metals.

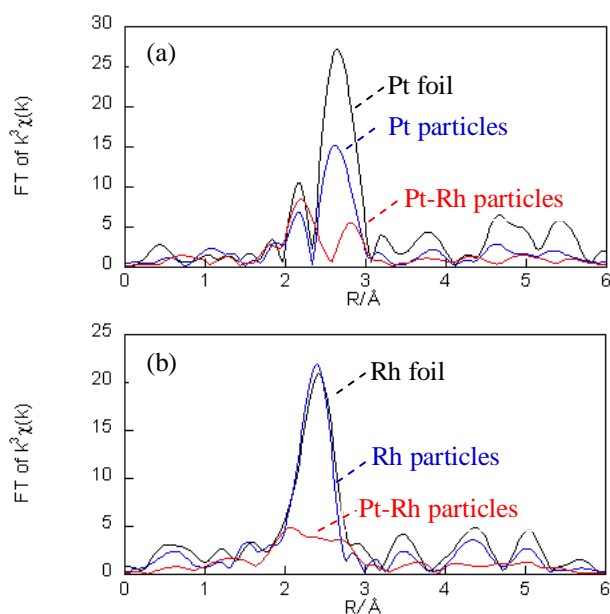


Fig. 1 Pt L3- and Rh K-edge EXAFS spectra of Pt-Rh bimetallic particles prepared by $NaBH_4$ reduction. (a) Pt L3-edge; (b) Rh K-edge spectra.

References

- [1] M. Harada et al., *J. Phys. Chem.* 98, 2653 (1994).
- [2] M. Harada and H. Einaga, *J. Colloid. Interf. Sci.* 308, 568 (2007).

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