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Preparation of Pt/Rh bimetallic colloidal particles using borohydride reduction

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Introduction

In this paper we present the preparation of Pt/Rh bimetallic particles by borohydride-reduction method in the presence of poly(N-vinyl-2-pyrrolidone) in water. For the Pt/Rh bimetallic particles, measurements of EXAFS have been applied in order to specify the distribution of atoms within a bimetallic particle. The analysis of EXAFS suggests that the distribution of atom within a bimetallic particle produced by borohydride-reduction is different from that expected from the core-shell structure.

Experimental

Colloidal dispersions of Pt/Rh bimetallic particles were synthesized by the borohydride-reduction method. Hexachloroplatinic acid (0.033 mmol) and rhodium chloride (0.033 mmol) was dissolved in water. PVP as a protecting polymer (1.36 mmol of monomeric units) was added in an aqueous solution (50 mL) containing various molar ratio of Pt : Rh = 1:1. The mixed solution was stirred at 50°C at 150 rpm until the temperature did not change. After stirring for ca. 30 min, an aqueous solution (5 mL) dissolving $NaBH_4$ (1.6 mmol) was poured drop by drop in the mixed solution, and then stirred at 50 °C for more than 2 h under air, which resulted in the dark brown solution of the Pt/Rh colloidal dispersions.

Results and discussion

Table 1 shows the curve fitting results (coordination number (C.N.)) for the colloidal dispersions of the Pt/Rh(1/1) bimetallic particles obtained from EXAFS analysis of the particles. The C.N.s of Pt and Rh atoms around the Pt atom are determined as 8.0 ± 1.0 and 3.2 ± 0.6, respectively. The C.N.s of Rh and Pt atoms around the Rh atom are determined as 6.7 ± 1.0 and 3.0 ± 1.0, respectively. The bond distances of Pt-Pt, Rh-Rh, and Pt-Rh are 0.272, 0.270, and 0.271 nm, respectively. These values are consistent with the bond distances of Pt, Rh and Pt/Rh alloy foils [1]. Here the average diameter (d^{EXAFS}) is estimated from the average coordination number of the EXAFS analysis on the assumption that the particle has a spherical shape and fcc structure. The value of d^{EXAFS} is 2.9 ± 0.4 nm (corresponding to the C.N. of 10.5 ± 0.9) in the case of the borohydride-reduction, and larger than that in the case of the alcohol-reduction (1.3 ± 0.2 nm), which is estimated from the C.N. of 6.9 ± 0.8 [1]. This finding implies that the borohydride-reduction causes the aggregation of metal particles and the formation of larger particles compared with the alcohol-reduction.

In the case of the Pt/Rh(1/1) bimetallic particles prepared by the borohydride-reduction, the average particle size (d^{TEM}) has been determined from TEM to be 2.8 nm. Thus, the Pt/Rh(1/1) bimetallic particles consists of the centered six atoms and the four layered atoms with fcc structure around the six atoms, totally containing 470 atoms. One can take three types of models for the Pt/Rh(1/1) bimetallic particles. The first one is the Pt single core model, which occupies the Rh monolayer surface consisting of 236 atoms and the Pt single core consisting of 234 atoms (Pt single core model). The second one is the cluster-in-cluster model, which consists of 236 Pt atoms forming 10 cores and 234 Rh atoms locating around the 10 Pt cores and combining the Pt cores. The third one is the random model, which both Pt and Rh atoms are randomly located in a particle.

Table 1 also summarizes the C.N.s of these model structures expected from the average size (about 2.8 nm) of the Pt/Rh(1/1) bimetallic particles. The consistency between the experimental C.N.s and those calculated for the core model or the random model is not appropriate for the model of Pt/Rh(1/1) bimetallic particles prepared by the borohydride-reduction. On the other hand, the C.N.s calculated for the cluster-in-cluster model are nearly the same as those obtained from EXAFS analysis, suggesting that the cluster-in-cluster model is appropriate for the model of Pt/Rh(1/1) bimetallic particles.

Table 1. Coordination numbers obtained from EXAFS analysis of Pt/Rh bimetallic particles.

Bond	Coordination Number	
	Borohydride -reduction	Calc. Cluster-in-cluster
Pt-Pt	8.0 ± 1.0	7.7
Pt-Rh	3.2 ± 0.6	2.7
Rh-Rh	6.7 ± 1.0	6.8
Rh-Pt	3.0 ± 1.0	2.7
average	10.5 ± 0.9	(9.9)

Reference

[1] M. Harada et al., J. Phys. Chem. 98, 2653 (1994).

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