Synthesis of Pt/Rh and Pt/Pd bimetallic particles under high-temperatures and high-pressures and the analysis of the structure

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Colloidal dispersions of Pt/Rh and Pt/Pd nanoparticles have been synthesized by the reduction of Pt(Ⅳ)/Rh(Ⅲ) and Pt(Ⅳ)/Pd(Ⅱ) ionic solutions, respectively, under the high-temperatures (from 100 to 300 ºC) and high-pressures (at 25 MPa) in the presence of protective polymer reagent, poly(N-vinyl-2-pyrrolidone). The size and the structure of the synthesized particles have been examined by extended X-ray absorption fine structure (EXAFS) and transmission electron micrograph. At 260 ºC and 25 MPa, we have succeeded in producing the bimetallic particles (Pt/Rh and Pt/Pd). The distribution of different metallic species tended to be random in particle, in contrast to the bimetallic particle synthesized under ambient condition which have a core-shell structure.

1. Introduction

Noble metal nanoparticles have been of importance in both academic and industrial fields, because of their uniqueness of size-dependent optical, catalytic, magnetic, and electronic properties[1]. In order to synthesize nanoparticles efficiently and effectively, various methods have been developed such as photochemical reduction, laser ablation, chemical vapor method, plasma heating method, and so on[1]. Recently, synthesis of metal nanoparticles in supercritical fluids has attracted increasing attention[2,3]. Since supercritical water and supercritical carbon dioxide are relatively stable and environmentally harmless, much attention has been paid to them as reaction fields to prepare nanoparticles. For example, Adschiri et al. found that various kinds of size and shape controlled metallic oxide nanoparticles can be formed simply by flowing the metal hydroxides through a high-temperature and high-pressure reactor for a few seconds[4-6].

In this paper we present the study on the synthesis of bimetallic particles of noble metals. We have applied a chemical reduction method in the high-temperature and high-pressure fluids using a polymer as a protective reagent[7-16]. We have already demonstrated that the chemical reduction of platinum (Ⅳ) ion (Pt(Ⅳ)) under the existence of poly(N-vinyl-2-pyrrolidone) (PVP) in water and ethanol mixture could produce a colloidal dispersion of Pt nanoparticles of 2.6±0.5 nm within a few seconds by using a flow reactor system operating under the high-temperature and high-pressure[17]. The same method has also been applied successfully to the synthesis of Rh nanoparticles [18]. Here we applied the same flow reactor system to the synthesis of the bimetallic particles composed of platinum and rhodium (Pt/Rh), and of platinum and palladium (Pt/Pd), respectively. It has been reported that two hour reflux of water-ethanol mixture containing Pt 4+ and Rh3+ in the presence of PVP under ambient pressure produces bimetallic particles of Pt/Rh whose average diameter is 4.0±1.3 nm[15]. A similar method produces the Pt/Pd bimetallic particle of diameter 1.6±0.3 nm[19]. For both bimetallic particles, measurements of extended X-ray absorption fine structure (EXAFS) have been applied in order to specify the distribution of atoms within a particle. According to their results, both bimetallic particles have a core-shell structure of Pt core. In the present study we have succeeded in synthesizing bimetallic particles using the high-pressure flow reactor system. The analysis of EXAFS suggests that the atom distribution within a bimetallic particle produced under the high-
temperature and high-pressure condition is different from that expected from the core-shell structure.

2. Experimental methods

2.1. Materials Colloidal dispersions of Pt/Rh and Pt/Pd particles were synthesized by the reduction of solutions which contain original ionic species with a protective polymer, poly(N-vinyl-2-pyrrolidone) (PVP). As sources of metallic ions, we used hexachloroplatinate(IV) hexahydrate, sodium hexachloroplatinate(IV) hydrate, rhodium chloride(III), and palladium chloride(II) (guaranteed reagent), respectively. Average molecular weight of PVP used here was about 40,000. Ethanol (guaranteed reagent, 99.5%) was used without further purification. Water purified by a Milli-Q system (>10 MΩ cm, Millipore, Milli-Q SP UF) was used.

2.2. Synthesis of the colloidal dispersion A schematic drawing of apparatus is shown in Fig. 1. Sample solution (mixture of metallic ion solution and PVP solution) was pumped by a HPLC pump (JASCO Corp., PU1580) into a high pressure optical cell (made of SUS316) whose temperature was regulated by heat blocks within ±2K. The inner volume of the cell was about 0.3 cm³. The sample solution passed through the high pressure cell was cooled down in a water/ice bath, and collected without filtering to get the colloidal dispersion. The system pressure was monitored by a strain gauge (Kyowa, PGM-500KD), and regulated by a back pressure regulator (JASCO Corp., SCF-BPG) within ±0.1MPa. Three kinds of solvent were examined: water, ethanol, and their mixture (1:1 by volume). In the most cases, the synthesis was performed at 25 MPa and the flow rate was typically 3 cm³ min⁻¹.

2.3. Characterization of the colloidal dispersion The particle size was estimated from a TEM image taken by JEM-2000FX (JEOL, acceleration voltage: 200 kV). The high-resolution carbon-supported copper mesh was used to support the colloidal dispersion. The histogram of the particle size was obtained by measuring about 300 particles each in arbitrarily chosen areas on the enlarged photograph.

2.4. EXAFS measurement EXAFS was measured in a transmission mode at Photon Factory, High Energy Accelerator Research Organization in Japan (KEK-PF), using BL-10B and BL-7C station. The experimental details are described elsewhere[17].

2.5. EXAFS analysis In the EXAFS analysis, the raw data in energy space (log(I/I₀) versus E, where I₀, I, and E are the incident beam intensity, transmitted beam intensity, and the X-ray beam energy respectively, were reduced to the photoelectron vector space described elsewhere[20] with the threshold energy E₀, where k = [2m(E-E₀)/h²]¹/² (h = h/2π, where h is the Planck constant). The EXAFS spectra were extracted using Cubic Spline method and normalized to the edge height. The k²χ(k) function versus k data and the corresponding Fourier transforms were obtained using Hanning window function with 1/10 FT ranges in the same way as before[20]. The typical range of Fourier transformation from the k space to the r space was 30-160 nm⁻¹. For the purpose of curve-fitting, the noise seen on high-frequency was removed by the Fourier filtering technique, and the inverse Fourier transformation to the k space was employed[20].

\[
k^2 \chi(k) = \sum_j N_j F_j(k_j) \exp(-2\sigma^2 k^2) \sin[2k r_j + \phi_j(k_j)] \frac{r_j^2}{r_j^2}
\]

where \(N_j\) denotes the coordination number, \(r_j\) the bond distance, \(\Delta E_{ij}\) the difference between theoretical and experimental threshold energies, and \(\sigma_j\) the Debye-Waller factor of the \(j\)-th coordination shell, respectively. The resulting filtered data were fitted with empirically derived phase shift (\(\phi_j(k)\)) and the amplitude function (\(F_j(k)\))
evaluated from the reference sample (foils of alloy between Pt and Rh, and between Pt and Pd)[15,21].

3. Results and Discussion

We have tried the synthesis under various experimental conditions, and succeeded in producing bimetallic particles of Pt/Rh and Pt/Pd. From the analysis of EXAFS data, we found that both particles have different internal atomic distribution from those prepared under the ambient condition.

3.1. Pt/Rh bimetallic particles

A typical example of a TEM image of colloidal dispersion of particles synthesized from the mixture solution of 15 mM [Pt^4+] and [Rh^3+] with 30 g dm^-3 PVP at 25 MPa and 260 °C is shown in Fig. 2(a). Here the solvent is water and ethanol mixture. The ratio of polymer unit of PVP to the concentration of metallic ion (R = [PVP]/[M(n)], M(n) : metallic ion) was about 9. From this image, the diameter of particles is estimated to be 2.4±0.5 nm (Fig. 2(b)). The diameter and its distribution are quite smaller than those prepared under the ambient condition (4.0±1.3 nm)[15].

Figure 3 shows the Fourier transforms of the Pt LIII-edge and Rh K-edge EXAFS spectra for the solutions obtained at various molar ratios of concentrations between [Pt] and [Rh], together with the spectra for the reference foils. In both absorption edges, we could observe the contributions from two metallic species, which clearly indicates that particles are alloyed.

Table 1 lists the coordination numbers obtained from the fitting of the EXAFS spectrum for the colloidal dispersion synthesized from the equimolar solution of Pt and Rh at 25 MPa and 260 °C in the water and ethanol 1:1 mixture. In the table, the results for the particle produced under ambient condition are also listed[15]. It can be readily seen from the table, the atomic distribution within a metallic particle is quite different depending on the synthetic conditions.

Firstly we have calculated the averaged diameter \( d_{\text{EXAFS}} \) 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 \( d_{\text{EXAFS}} \) is 1.3 nm for the ambient one, and 3.2 nm for the high temperature one. Since \( d_{\text{EXAFS}} \) changes significantly with a small change of N at the larger N region (more than 10), the error of \( d_{\text{EXAFS}} \) becomes large with increasing N. Therefore we can consider that at the high temperature condition \( d_{\text{EXAFS}} \) is almost similar to the diameter estimated from the TEM (\( d_{\text{TEM}} \)), while under the ambient condition \( d_{\text{EXAFS}} \) is much smaller than \( d_{\text{TEM}} \). This means that the elementary cluster size[16] is enlarged in the metallic particle synthesized at the high temperature.

Another interesting point is the difference in the distribution of coordination numbers. The most probable model which explains the coordination number for the ambient results is the Pt-core and Rh-shell model[15]. On the other hand, the results
for the high-temperature and the high-pressure can be better explained as a model which has nearly random distribution.

We have also tried the synthesis in other solvents; water and ethanol. For both solvents, we could synthesize the bimetallic particles of Pt/Rh, which was ensured by the EXAFS spectra. The coordination structure synthesized in water was similar to those obtained for the water and ethanol mixture.

3.2. Pt/Pd bimetallic particles Pt/Pd bimetallic particles were synthesized in a similar manner with Pt/Rh bimetallic particles, although the concentrations of both metallic ions and PVP were reduced to 1/10 due to the low solubility of PdCl₂ in water. A typical example of a TEM image of Pt/Pd bimetallic particles produced at 25 MPa and 200 ºC in the water and ethanol mixture is shown in Fig. 4(a). According to the TEM image, an average particle diameter and its distribution is estimated to be 4.4±0.9 nm (Fig. 4(b)). In contrast to the case of Pt/Rh bimetallic particles, it is found that particles produced in the high-pressure and high-temperature fluid have the larger size and wider distribution than those produced under the ambient condition (1.6±0.3 nm).

Figure 5 shows the Pt LIII-edge and Pd K-edge EXAFS spectra for the colloidal dispersions obtained from the solutions with Pt/Pd (1/1) molar ratio of concentration in water and ethanol mixture at different temperatures, together with the spectra for the reference foils (Pt/Pd =1/1 alloyed foil).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Coordination Number</th>
<th>25MPa</th>
<th>200 ºC</th>
<th>random</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Pt</td>
<td>6.3</td>
<td>6.6</td>
<td>5.9</td>
<td>5.2</td>
</tr>
<tr>
<td>Pt-Rh</td>
<td>1.7</td>
<td>2.9</td>
<td>4.6</td>
<td>5.2</td>
</tr>
<tr>
<td>Rh-Rh</td>
<td>2.6</td>
<td>3.1</td>
<td>4.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Rh-Pt</td>
<td>3.1</td>
<td>3.0</td>
<td>5.8</td>
<td>5.2</td>
</tr>
<tr>
<td>average</td>
<td>7.8</td>
<td>10.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Coordination numbers(Ns) obtained from EXAFS analysis of Pt/Pd bimetallic particles. The average coordination numbers [N = 0.5(N₁₄-P₄₋₁₄ + N₁₄-P₄₋₁₄) + 0.5(N₁₄-P₄₋₁₄ + N₁₄-P₄₋₁₄)] are calculated on the last line. For the comparison, Ns calculated from the fcc model of particles which best matches the experimental data are shown.
of the EXAFS spectra. As is the case of Pt/Rh, the value of \( d_{\text{EXAFS}} \) at the higher temperature is similar to the diameter estimated from the TEM (\( d_{\text{TEM}} \)), in contrast to the result for the ambient condition. Moreover, the alloyed structures have tendency to hold random structure in a particle.

4. Conclusions

We have succeeded in synthesizing Pt/Rh and Pt/Pd nanoparticles stabilized by PVP as a protective reagent under the high-temperatures and the high-pressures. Although Pt/Rh and Pt/Pd bimetallic particles prepared under the ambient condition are known to have the Pt-core structure, it is found that neither of the nanoparticles produced in the present condition has the Pt-core structure. Instead, it is most likely that the bimetallic particles have random structure. From the TEM observation, the particle size of Pt/Rh particle (2.4±0.5 nm) was smaller than that of Pt/Rh aggregates (4.0±1.3 nm) prepared under ambient pressure, and that of Pt/Pd particle (4.4±0.9 nm) was relatively larger than that (1.6±0.3 nm) of Pt/Pd elementary particle. That is, regulation of particle size was achieved by adjusting the reaction temperature and pressure.

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References and Notes