Synthesis of platinum nano-particles in high-temperatures and high-pressures fluids

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Abstract

Colloidal dispersions of platinum nano-particles have been synthesized by the reduction of platinum ion(IV) in the high-temperature and high-pressure water, ethanol, and water–ethanol mixtures in the presence of the protective polymer of poly(N-vinyl-2-pyrrolidone) (PVP). The syntheses have been tested at various temperatures (from 100 to 300 °C) and pressures (from 5 to 25 MPa). The diameter and the composition have been examined by UV-Vis, extended X-ray absorption fine structure (EXAFS), and transmission electron micrograph (TEM), respectively. At 200 °C and 25 MPa, colloidal dispersions of platinum particles of small size (2.6 ± 0.5 nm) were synthesized from 1:1 mixture of water and ethanol within a few seconds. From the analysis of the EXAFS, it is suggested that the elementary particle size obtained under the present condition is larger than that obtained under the ambient condition. We have also succeeded in producing the colloidal dispersions in aqueous solution, although the size and its distribution were relatively larger than that of the case of water–ethanol mixture. In ethanol solution we could not synthesize a well-dispersed colloidal solution at high temperatures. The possibility of the regulation of the particle size and distribution is discussed.

Keywords: Platinum nano-particle; Supercritical fluids; High temperature and high pressure; Continuous synthesis; EXAFS

1. Introduction

Small metal particles of nanoscale are interesting materials academically and industrially [1], and the synthetic methods have widely been studied in order to make size-controlled particles. Recently much attention has been paid to the synthesis of metal nano-particles in supercritical fluids, especially in supercritical water (SCW) [2]. For example, Adschiri et al. found that various kinds of size and shape regulated metal oxide particles (Fe2O3, Co3O4, ZrO2, etc.) can be made simply by flowing the reactant aqueous solution of metal hydroxides through a high-temperature and high-pressure reactor for a few seconds [3–5]. At high temperatures such as in supercritical water, the hydrolysis proceeds very rapidly. Since the solubility of monomer oxide or the precursor of the particles is
quite low in SCW, aggregation of monomer or precursor proceeds very rapidly at the same time, which produces fine particles effectively. By these methods, metal oxides whose sizes are from 20 to 100 nm have been produced. Very recently, Ziegler et al. have succeeded in producing Cu nano-particle (average diameter of 7 nm) by adding alkanethiol (hexanethiol) as a protective agent in aqueous solution of Cu(NO$_3$)$_2$ [6]. In this case, thiol works both as the reducing agent of copper ions and as the protective agent to prevent the formation of large particles and aggregates.

Although the reaction using SCW has a lot of possibilities, several difficulties also exist because of its severe reaction conditions. Therefore other supercritical fluids have come to be investigated as solvents for the synthesis of metal particles recently [2]. For example, Pommier et al. succeeded in synthesizing TiO$_2$ and MgAl$_2$O$_4$ powders from Ti(O$i$Pr)$_4$ and Mg[Al(--OC$_4$H$_9$)$_4$]$_2$ dissolved in supercritical ethanol [7,8]. In this paper we present new results on the synthesis of platinum (Pt) metal nano-particles using high-temperature and high-pressure water, ethanol and their mixtures. It has been shown that the chemical reduction of metal ions using a polymer as a protective reagent is one of the promising ways to prepare small metal particles [9–23]. In the ordinary procedure, for example, a solution (water and ethanol mixture) of Pt ion and poly(N-vinyl-2-pyrrolidone) (PVP) is refluxed at ambient pressure and about 100 °C for 2 h, which results in colloidal dispersions of Pt metal particles of about 2–3 nm diameters. The reaction scheme is described as follows:

\[ \text{Pt}^{4+} + 2\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{Pt}^{2+} + 2\text{CH}_3\text{CHO} + 4\text{H}^+ \]

In this case, ethanol works as a reducing agent, and PVP prevents the formation of large aggregates. Miyake et al. studied this synthesis in various alcohol and water mixtures, and found that an increase of the alcohol content reduces the diameter of the particle [24]. Duff et al. also studied the reaction time, the effect of the concentration of the anion, and the effect of the annealing [17].

In this study we have tested the above synthetic method at high temperatures and high pressures. By using the high-temperature conditions of dense fluids, it may be possible to change the rate limiting process of the nucleation of the nano-particles, and offers another possibility to control the particle size. Under the ambient condition there is a long induction period for enough Pt atoms to be accumulated for a nucleation [17]. With increasing the reaction temperature, the induction period is expected to be much shortened, and the aggregation of atoms may become rate limiting. Further, at high-temperatures polymer conformation may be different from that under the ambient condition, which gives another chance to make a different regulation of the particle size. In this paper, we present the results of the synthesis in different solvent fluids (water, ethanol, and their mixtures). The colloidal solutions are analyzed by UV-Vis absorption spectrum, transmission electron micrograph (TEM), and extended X-ray absorption fine structure (EXAFS).

2. Experimental

2.1. Materials

The colloidal solution of Pt particle was synthesized by the reduction of Pt ion (Pt(IV)) with the protective polymer (PVP). As the source of Pt(IV), we tested hydrogen hexachloroplatinate(IV) hexahydrate and sodium hexachloroplatinate(IV) hydrate. The average molecular weight of PVP used here was 40,000. The solvents were water, ethanol, and their mixtures (volume fractions of water–ethanol were 1:1, 1:9). Hydrogen hexachloroplatinate(IV) hexahydrate (Guaranteed Reagent), sodium hexachloroplatinate(IV)hydrate (Guaranteed Reagent), PVP (K-30), ethanol (Guaranteed Reagent, 99.5%), and distilled water were purchased from Nacalai Tesque, and used without further purification.

2.2. Synthesis

A schematic drawing of the apparatus is shown in Fig. 1. Sample solution (a mixture of Pt ion solution and PVP solution) was pumped by a HPLC pump (JASCO Co., PU-1580) into a high-pressure optical cell (made of SUS 316) whose temperature was regulated by heat blocks (not shown in Fig. 1) within ±2 K. Another HPLC pump (JASCO Co., PU-1586) was used to flush the cell with pure solvent in order to do successive syntheses under different experimental conditions. UV-Vis absorption spectra were
measured in-situ using a xenon lamp and a multi-channel detector (Otsuka Electronics, MCPD-1000) concurrently in pouring the sample solution into the cell. The inner volume of the cell was about 0.3 cm³. The details of the high-pressure cell are given elsewhere [25]. The sample solution passed through the cell was immediately cooled down in a water/ice bath, and collected without filtering to get the colloidal dispersions. The system pressure was monitored by a strain gauge (Kyowa, PGM-500KD), and regulated by a hand-operated pressure-regulating valve within ±2 MPa or a back-pressure regulator (JASCO, SCS-BPG) within ±0.1 MPa.

We examined four different solvents: water, ethanol, and their mixtures (volume ratio = 1:1, and 1:9 of water:ethanol). In most cases, experiments were performed at 25 MPa. The highest temperature studied was 300 °C. According to ref. [26], the critical temperature of the 1:1 mixture of water and ethanol is 313 °C (Tc of pure water and ethanol are 374 and 243 °C, respectively). An empirical equation of state suggests that the mixture of water and ethanol is in liquid phase under the experimental conditions mainly used here [27].

2.3. Characterization of nano-particles

The UV-Vis absorption spectrum of the product solution was measured by a Shimadzu UV-2500PC. We evaluated the s-value which is defined as follows:

\[ s = \frac{\partial \log \text{Abs}}{\partial \log \lambda} \]

where Abs is the absorbance of colloidal dispersion and \( \lambda \) is the wavelength, respectively. It has been suggested that the s-value characterizes the size and shape of the Pt particle [17]. When the s-value is large, nano-particles are small and spherical. When the s-value is small, particles are non-spherical and relatively large. We evaluated the s-value from the absorption spectrum between 400 and 800 nm. As is presented in the later section, in our case the s-value gave a rough estimate of the extent of aggregation of nano-particles.

TEM images were taken mainly by JEM-2000FX with the help of Prof. S. Ioda and Dr. T. Nemoto (Institute for Chemical Research, Kyoto University). The high-resolution carbon-supported copper mesh was used to support the samples of colloidal dispersions. The diameter of each particle was determined from enlarged photographs. The histogram of the particle size distribution and the average diameter were obtained by measuring about 400 particles in arbitrarily chosen areas.

2.4. EXAFS measurement

The EXAFS measurements of Pt-L III edge of Pt colloidal dispersions were performed at the Photon Factory, High Energy Accelerator Research Organization (KEK-PF), using the BL-10B, BL-7C, BL-12C stations. The experimental details are described elsewhere [13]. Briefly, the measurements were carried out in a transmission mode using the 10 mm path length cell with polyimide film windows (KAPTON-200IL, 50 μm of thickness).
In the EXAFS analysis, the raw EXAFS data in energy space \(\log (I_0 / I)\) versus \(E\), where \(I_0\), \(I\), and \(E\) are the incident beam intensity, transmitted beam intensity, and the X-ray energy, respectively, were reduced to the photoelectron wave vector \((k)\) space described elsewhere [28] with the threshold energy \(E_0\), where \(k = \left(2m(E - E_0)/\hbar^2\right)^{1/2}\) (\(\hbar\) is the Planck constant). The EXAFS spectra were extracted using a cubic spline method and normalized to the edge height. The \(k^3\chi(k)\) 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 [29]. The typical range of Fourier transformation from the \(k\) space to the \(r\) space was 30–160 nm\(^{-1}\). For the purpose of the curve-fitting, the high-frequency noise was removed by a Fourier filtering technique, and the inverse Fourier transformation to the \(k\) space was employed [28].

\[
k^3\chi(k) = \sum_j N_j F_j(k) k_j^2 \exp\left(-2\sigma_j^2 k_j^2\right) \\
\times \sin[k_j r_j + \phi_j(k)]
\]

where \(N_j\) denotes the coordination number, \(r_j\) the bond distance, \(\Delta E_0\) the difference between the theoretical and experimental threshold energies, and \(\sigma_j\) the Debye–Waller factor of the \(j\)th coordination shell. The resulting filtered data were fitted with empirically-derived phase shift \(\phi_j(k)\) and amplitude functions \(F_j(k)\) evaluated from the reference sample (Pt foil) [30].

3. Results and discussion

We have tested the syntheses in different four solvent systems, 1:1 mixture of water and ethanol, water, ethanol, and 1:9 mixture of water and ethanol. We found significant dependence on the solvent species. In the followings, we will show the results in different solvent species, respectively.

3.1. 1:1 mixture of water and ethanol

Fig. 2(a) shows the UV-Vis absorption spectra of the colloidal dispersions synthesized from the 1:1 mixture (0.75 mM Pt and 1.5 g/dm\(^3\) PVP) at 200 °C and 25 MPa at various flow rates. The ratio of polymer unit to metal ion concentration \((R \equiv [PVP \text{unit}]/[Pt(IV)])\) is about 20. When the flow rate was low (near 0.1 cm\(^3\) min\(^{-1}\), in which the residence time in the cell is about 180 s), a low-absorbent solution was obtained. The color of the solution was black–brown and somewhat metallic. On the other hand, when the flow rate was high (e.g., 3 cm\(^3\) min\(^{-1}\), 6 s residence time), a high-absorbent yellow–brown solution was obtained. The absorption spectrum measured in situ is also in the figure. The larger absorption of the spectrum in situ is mainly due to the longer optical path length (about twice of other cases). This spectrum indicates that Pt metal particles were produced at high temperature before cooling. The flow rate dependence of the \(s\)-value is shown in Fig. 2(b). Larger
Fig. 3. (a) UV-Vis absorption spectra of the Pt colloidal solutions produced at different temperature and at 25 MPa for the 1:1 solution (15 mM Pt ion and 15 g dm\(^{-3}\) PVP) \((R = 10)\). (b) Temperature dependence of \(s\)-values of the Pt colloidal solutions produced from various concentrations of Pt ion and PVP.

\(s\)-values near 3 were obtained for the flow rate higher than 0.3 cm\(^3\) min\(^{-1}\). The trend is almost independent of the Pt concentration.

Fig. 3(a) shows the UV-Vis absorption spectra of the solutions obtained at different temperatures with the flow rate of 3 cm\(^3\) min\(^{-1}\). As is shown in the figure, no reaction occurred at 100 °C during this short reaction time [9]. With elevating the temperature up to 150 °C, however, a reaction proceeded to some extent, and at 200 °C a high-absorbent yellow–brown solution was obtained. Fig. 3(b) shows the effect of the temperature on the \(s\)-value with different metal and PVP concentrations. Larger \(s\)-values were observed for the solutions produced between 150 and 260 °C. At 300 °C, the \(s\)-value became small again. At this temperature there were a lot of small bubbles in the solution coming out of the cell. The high excess amount of PVP did not affect the \(s\)-value of colloidal dispersions, although in the case of \(R = 1\) the \(s\)-value was relatively small. In the case of \(R < 1\), aggregations of the metal particles were obtained as in the case of the ambient condition [9].

Fig. 4 shows the Fourier transforms of the Pt-L III-edge EXAFS spectra for Pt solutions shown in Fig. 3(a). The solution after passing through the cell at 100 °C showed the same peak position and intensity as the reactant solution, whose peak is assigned to the bond of Pt\(^{4+}\)-Cl\(^-\). With increasing the temperature to 150 °C, the peak due to the bond of Pt\(^{4+}\)-Cl\(^-\) vanished and another peak ranging from 2 to 3 Å increased due to the metallic bond of Pt–Pt. The coordination number of Pt atom around the Pt atom was 9.2 ± 0.3 on the average, which was almost constant above 200 °C. If we assume a spherical and fcc structure for this colloidal particle, the average diameter estimated from this coordination number is 2.1 nm.

Fig. 5 shows typical TEM images of Pt particles produced at 25 MPa, 200 and 260 °C, respectively. As is shown in the image, the distribution of the diameter was narrow, and the solution was well dispersed. The average diameter was not strongly different from that obtained by the ordinary method, and was not strongly dependent on the temperature in the case of 15 mM solution. On the other hand, the diameter was rela-
Fig. 5. TEM images and distributions of diameter extracted from the corresponding image for the 1:1 mixture. (a) 15 mM Pt ion and 15 g dm⁻³ PVP (corresponding to \( R = 10 \)) with a flow rate 3 cm³ min⁻¹ at 200 °C and 25 MPa. (b) Histogram from the image (a). (c) Almost the same condition as (a) except the temperature (260 °C). (d) Histogram from the image (c).

Figures 5 (a), (b), (c), and (d) respectively small at 200 °C in the case of 1.5 mM solution in comparison with that at 260 °C.

These results are summarized in Table 1. The pH value of the reactant solution did not affect the reaction products, since we got a similar result for the solution of sodium hexachloroplatinate. We did not detect notable pressure effect from 5 to 25 MPa either, probably because the density of the solvent does not drastically change at this temperature in this pressure region.

The flow rate dependence can be explained by rapid reduction of the Pt ion at the high temperature. At the elevated temperature (e.g., 200 °C), the reduction of the Pt ion to the Pt atom by ethanol proceeds very rapidly. Therefore, when the flow rate is high, the concentration of Pt atom becomes larger than the critical concentration for the nucleation within a few seconds, and the nucleation occurs immediately. When the flow rate is low, a new Pt ion is supplied before the particle goes out of the cell. Then the new Pt atom may aggregate to the particles already exist. Furthermore, in our system using the SUS316 stainless steel, the product nano-particle easily adheres to the surface of the stainless steel, which also decreases the number of Pt particles coming out of the cell. These explain low-absorption and small s-value for the low flow rate.

The optimum temperature of operation is determined by the flow rate and the stability of the polymer. The former factor is dominated by the reaction time. The latter factor limits the highest operating temperature. At 300 °C the productivity of colloidal solutions becomes worse. We consider that this is due to the effects of the decompositions of the polymer and ethanol at high temperature. At this temperature, there were bubbles in the product colloidal solutions coming out of the cell. We analyzed the gas for the
Table 1
Results of s-values and coordination numbers of Pt particles synthesized at the flow rate of 3 cm$^3$ min$^{-1}$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>T ($^\circ$C)</th>
<th>Pt(IV) (mM)</th>
<th>PVP (g dm$^{-3}$)</th>
<th>P (MPa)</th>
<th>s$^a$</th>
<th>s$^b$</th>
<th>d$^c$ (nm)</th>
<th>$\sigma$ (nm)</th>
<th>N$^d$</th>
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<tbody>
<tr>
<td>H$_2$O–C$_2$H$_5$OH (1:1)</td>
<td>100</td>
<td>0.66</td>
<td>3</td>
<td>0.1</td>
<td>–</td>
<td>–</td>
<td>2.7</td>
<td>0.5</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>15</td>
<td>15</td>
<td>25</td>
<td>–</td>
<td>2.9</td>
<td>2.6</td>
<td>0.5</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>15</td>
<td>15</td>
<td>25</td>
<td>–</td>
<td>3.2</td>
<td>2.8</td>
<td>0.5</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>1.5</td>
<td>15</td>
<td>25</td>
<td>–</td>
<td>2.8</td>
<td>3.4</td>
<td>1.0</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>1.5</td>
<td>15</td>
<td>10</td>
<td>–</td>
<td>2.9</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>15 (Na$^f$)</td>
<td>15</td>
<td>25</td>
<td>–</td>
<td>2.3</td>
<td>2.7</td>
<td>–</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>15 (Na$^f$)</td>
<td>15</td>
<td>10</td>
<td>2.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>9.3</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>200</td>
<td>15</td>
<td>15</td>
<td>25</td>
<td>1.5</td>
<td>1.8</td>
<td>3.2</td>
<td>0.9</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>15</td>
<td>30</td>
<td>25</td>
<td>–</td>
<td>2.5</td>
<td>1.9</td>
<td>0.9</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>15 (Na$^f$)</td>
<td>15</td>
<td>25</td>
<td>–</td>
<td>2.2</td>
<td>–</td>
<td>–</td>
<td>7.3</td>
</tr>
<tr>
<td>C$_2$H$_5$OH$^g$</td>
<td>150</td>
<td>1.5</td>
<td>1.5</td>
<td>25</td>
<td>–</td>
<td>0.8</td>
<td>3.0 (agr.$^i$)</td>
<td>0.7</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.5</td>
<td>1.5</td>
<td>25</td>
<td>–</td>
<td>0.9</td>
<td>3.0 (agr.$^i$)</td>
<td>0.4</td>
<td>–</td>
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<td></td>
<td>260</td>
<td>1.5</td>
<td>1.5</td>
<td>25</td>
<td>–</td>
<td>1.5</td>
<td>agr.$^i$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.5</td>
<td>10</td>
<td>–</td>
<td>1.3</td>
<td>agr.$^i$</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>200$^h$</td>
<td>3.5</td>
<td>1.5</td>
<td>25</td>
<td>1.1</td>
<td>0.9</td>
<td>3.0 (agr.$^i$)</td>
<td>0.4</td>
<td>10.1</td>
</tr>
<tr>
<td>H$_2$O–C$_2$H$_5$OH (1:9)</td>
<td>150</td>
<td>15</td>
<td>15</td>
<td>25</td>
<td>–</td>
<td>1.2</td>
<td>sed.$^j$</td>
<td>–</td>
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<tr>
<td></td>
<td>200</td>
<td>15</td>
<td>15</td>
<td>25</td>
<td>–</td>
<td>0.6</td>
<td>sed.$^j$</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ s-value from the absorption spectrum in situ.

$^b$ s-value of the product solution. In the case of smaller s-values (below ca. 2), there is distribution of values at different experimental runs ($\pm$0.5).

$^c$ Average diameter (d) and standard deviation ($\sigma$) of the particle counted from TEM images.

$^d$ Coordination numbers of Pt atom around Pt atom from EXAFS. An error bar of 10%.

$^e$ Ref. [13].

$^f$ The Pt solution was made from sodium hexachloroplatinate.

$^g$ Only the dilute solution was examined. When the solutions of 30 mM [Pt]/ethanol and of 30 g dm$^{-3}$ PVP/ethanol were mixed to make the concentrated Pt solution, sedimentation occurred, and the solution became gel-like.

$^h$ The flow rate was 2.1 cm$^3$ min$^{-1}$.

$^i$ The flow rate was 1.5 cm$^3$ min$^{-1}$.

$^j$ Sedimentation of metal particles were observed for the collected solutions.

existence of carbon dioxide by using the gas detector (Gastec, GVC-100 with the detection unit of carbon dioxide (2H)). We found nearly 20% of carbon dioxide in the bubbles. We also analyzed the bubbles from the solution without Pt ion and PVP, and found that similar amount of carbon dioxide is in it. This suggests that the decomposition of ethanol occurs together with the decomposition of PVP. These side reactions reduce the productivity of Pt atom, and also reduce the ability of protection of aggregation.

Finally we consider the average diameter estimated from the EXAFS. The Pt particle produced under the ambient condition has a coordination number around 8, which gives a much smaller estimate of the diameter (1.4 nm) than that estimated from the TEM image (2.7 nm) [13,18]. In order to explain the discrepancy between the diameters from the TEM image and from the EXAFS spectrum, Harada et al. proposed that the larger size particle observed by TEM is composed of a cluster of small elementary particle. The EXAFS measures this elementary particle size. In the present case, the TEM size of the particle is relatively larger than that estimated by EXAFS. However, the difference is not so evident as in the case of ambient solution. This means that the elementary particle produced at high pressure and high temperature is larger than that produced at ambient pressure. This is probably due to the larger concentration of the precursor produced in a short time due to the high-temperature reduction.
Fig. 6 shows typical UV-Vis spectra for the aqueous solution together with other solutions tested here. It is surprising that the reduction occurs without ethanol. In aqueous solution, however, the reaction hardly proceeded at 150°C in contrast to the case of the 1:1 mixture. As is shown in Fig. 6(b), s-values of the aqueous solution also took maximum around 200–260°C, although the value was relatively smaller than those of the 1:1 mixture. Above 260°C there were bubbles in the solution coming out of the cell.

What is the reducing agent in the case of water solution? Considering the existence of bubbles in the product solution, the most probable candidate is PVP. If PVP is decomposed during the reaction process, there should be not a small amount of carbon dioxide in the bubbles. To ensure this hypothesis, we analyzed the bubbles and found nearly 4% of carbon dioxide. This strongly suggests the decomposition of PVP.

TEM images from this solution are shown in Fig. 7(a) and (c). The average diameter (3.2 nm) was relatively larger than that of the 1:1 mixture. More notably the distribution was quite large (±0.9 nm). At lower concentration, although the average diameter became small, the distribution was still large. This large distribution should be related to the reduction of the protecting ability of PVP by the decomposition.

The analysis of EXAFS also gives an interesting feature. As is shown in Table 1 the coordination number obtained from the fitting of the EXAFS spectrum was relatively small (8.8), which gives the diameter of 1.8 nm, although the average diameter estimated from the TEM image was large (3.2 ± 0.9 nm). We consider that the elementary particle size is estimated as 1.8 nm and that the TEM images represents the size of the cluster of this elementary particle, although irregular particle shape may contribute the difference to some extent. The large distribution of the particle size found in a TEM mage is due to the variation of the clustering of the elementary particles. This variation also comes from the decomposition of PVP.

3.3. Ethanol

Fig. 6 shows the UV-Vis absorption spectrum for the ethanol solution. The spectra for the ethanol were quite different from that obtained for the 1:1 solution. From Fig. 6(b) the s-value was around 1 from 200 to 300°C, being almost independent of R. Slight addition of water did not remarkably improve this tendency. In the case of 1:9 mixture of water and ethanol, the product solution was also metallic brown and the
Fig. 7. TEM images and distributions of diameter extracted from the corresponding image for (a) aqueous solution of 15 mM Pt ion and 15 g dm$^{-3}$ PVP with a flow rate 3 cm$^3$ min$^{-1}$ at 200°C and 25 MPa, (c) almost the same as (a) except for the concentrations (1.5 mM Pt ion and 30 g dm$^{-3}$ PVP), (e) ethanol solution of 1.5 mM Pt ion and 1.5 g dm$^{-3}$ PVP with a flow rate 3 cm$^3$ min$^{-1}$ at 150°C and 25 MPa. (b), (d) and (f) are the histograms from the images (a), (c) and (e), respectively.

UV-Vis absorption spectrum was similar to that for ethanol. The $x$-values were around 1 in the measured temperature region.

The TEM image from the ethanol solution is shown in Fig. 7(e). There were a lot of aggregates in the TEM image. Each aggregate was composed of particles of about 3 nm, and its distribution was not so large as in water. The diameter was larger than that in the case of the 1:1 mixture, which makes a contrast to the colloidal dispersions prepared at ambient pressure where smaller diameter of particles are obtained with less water fraction [24]. The analysis of EXAFS gave the
coordination number of 10.1 in Table 1. This gives the diameter of 2.8 nm, which is the same value obtained from the analysis of the TEM image.

Considering that the diameter of each particle is not large and its shape is almost spherical, the relatively small $\tau$ value of the ethanol solution is ascribed to the aggregation of the particles, not to the particle size and shape. We are not sure why this kind of aggregates are formed. There might be a possibility that these aggregates are produced during the process of making the sample grid for the TEM measurement. However, we ensured that there were also lager aggregates in the ethanol solution, which could not pass the membrane filter (50 µm). One possible origin of creation of aggregates is the reducing stability of ion and polymer in ethanol solution. In the concentrated solution of Pt ion in ethanol, adding the polymer makes a drastic change of the solution properties as is noted in Table 1. In the case of low-dielectric constant solution, the ionic interaction is not well shielded. Therefore, the stability of the polymer solution is strongly affected by the ionic species. This will cause the difference of the productivity of the colloidal solutions. In the case of RhCl$_3$·3H$_2$O, we can synthesize the nano-particle in the ethanol solution at high temperature in contrast to the case of Pt. This may support the above-discussion.

4. Summary

We have presented a new application of a high-temperature and high-pressure system to synthesize Pt nano-particles. We have succeeded in efficiently producing a large amount of Pt particles with a few nanometer diameter and a narrow size distribution within a few seconds. According to the analysis of the EXAFS, the elementary particle size is a little larger than that produced under the ambient condition. We also found that the reduction proceeded even in aqueous solution, where the relatively large size distribution and different particle structure were observed. In pure ethanol solution we could not synthesize a good colloidal solution at high temperatures, probably because the stability of the precursor was poor. We consider that the approach using the high-temperature fluids at high pressure will open a new way for the synthesis of nano-particles.

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