Influence of pH on performance of sodium phosphinate for decreasing the particle size

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\textbf{ABSTRACT}

To clarify the influence of pH on performance of sodium phosphinate (NaPH\textsubscript{2}O\textsubscript{2}) for decreasing particle size of Pt nanoparticles, carbon-supported Pt nanoparticles that contained phosphorus (P–Pt/C) were synthesised by an electron-beam irradiation reduction method (EBIRM) under four different pH conditions (pH = 3, 6, 9, and 12) and under five different NaPH\textsubscript{2}O\textsubscript{2} concentrations (0.0, 0.5, 1.0, 3.0, and 5.0 mM). The relationship among pH, NaPH\textsubscript{2}O\textsubscript{2} concentration, average particle size of Pt nanoparticle, and Pt loading weight was investigated in this study. The average particle size of Pt nanoparticles was in the range of 0.8–3.4 nm and lower in the order; pH\textsubscript{12} > pH\textsubscript{3} > pH\textsubscript{6} > pH\textsubscript{9}; for example, under the same NaPH\textsubscript{2}O\textsubscript{2} concentrations of 3.0 mM, the particle size of P–Pt/C prepared at pH = 12 and pH = 9 was 1.5 and 0.8 nm, respectively. In addition, Pt loading weight was also lower in the order; pH\textsubscript{12} > pH\textsubscript{3} > pH\textsubscript{6} > pH\textsubscript{9}. In summary, these results indicated that the pH in the precursor solution affected the performance of NaPH\textsubscript{2}O\textsubscript{2}. These findings would be useful for controlling the particle size of monometallic Pt and Pt-based bimetallic nanoparticles supported on carbon particles for fuel cell applications.

\textbf{1. Introduction}

Monometallic Pt nanoparticles or bimetallic Pt–M nanoparticles (M = Ru, Cu, Co, etc.) supported on the support materials such as carbon particle, carbon nanotube, silica, and alumina are used as various catalysts. In the catalyst industry, decrease in the size of Pt nanoparticles can achieve the low usage of Pt raw materials. In general, various surfactants and polymers are added as stabilisers to the precursor solution to disperse the nanoparticles and to inhibit their growth.\cite{1–7} However, the stabilisers remained on the surface of the nanoparticles, which resulted in a decreased electrochemically active surface area (ECSA). Effective techniques for the removal of the stabilisers had not been established. To decrease the size of Pt nanoparticles without the use of stabilisers, Daimon et al. proposed a novel method using sodium phosphinate (NaPH\textsubscript{2}O\textsubscript{2}) as the P precursor, and realised the decrease in the size of PtRu nanoparticles through a polyol process with adding NaPH\textsubscript{2}O\textsubscript{2}, which resulted in improvement of catalytic activity for methanol oxidation.\cite{8}

Using an electron beam irradiation reduction method (EBIRM), various metal nanoparticles supported on the particle supports have been synthesised for use as catalysts.\cite{9–12} The EBIRM is considered to be better suited than polyol process for mass production. We have combined the EBIRM
with a method to decrease the particle size based on the use of NaPH2O2.[13,14] In addition, we prepared carbon-supported Pt nanoparticles that contained phosphorus (P–Pt/C) using an EBIRM under different NaPH2O2 concentrations and reported the relationships among the NaPH2O2 concentration, average particle size, ECSA, and Pt loading weight.[15] In the report, we demonstrated that the addition of NaPH2O2 to the precursor solutions was capable of decreasing the particle size of Pt without decreasing the points of catalytic activity. However, the pH value was maintained at three in the report. To expand the application field of this method to decrease the particle size based on the use of NaPH2O2, the relationship between pH condition and decreased particle size should be investigated because precursor solutions for the preparation of metal nanoparticles in a wet process are controlled to be various pH. In this study, we prepared P–Pt/C using an EBIRM under different pH conditions and under different NaPH2O2 concentrations. The relationships among the pH, NaPH2O2 concentration, average particle size, and Pt loading weight were investigated to provide a guideline for the preparation of smaller metal nanoparticles immobilised on a support material in a liquid phase through the addition of NaPH2O2.

2. Experimental

2.1. Synthesis of P–Pt/C

The P–Pt/C samples were synthesised by an EBIRM in aqueous phase. The mechanism and procedure of this radiochemical method have been described elsewhere.[4,15,16] Hexachloroplatinic acid hexahydrate (H2PtCl6·6H2O, Wako Pure Chemical Industries) was used as the Pt precursor, and pure water (15 MΩ cm) produced by Direct-Q system (Millipore) was used as the solvent. Aqueous 50-mL solutions that contained 0.5 mM H2PtCl6 were prepared in 100-mL glass vials. As a support material, 66.6 mg of carbon black powder (Vulcan XC-72R, Cabot) was added to the solutions. All Pt loading weights were adjusted to be approximately 6.8 wt%. As a reduction enhancer, 2-propanol (IPA, Wako Pure Chemical Industries) was added to the solutions, and the IPA concentration was controlled to be 1 vol%. As a pH modifier, DL-tartaric acid (C4H6O6, Wako Pure Chemical Industries) and sodium hydroxide (NaOH, Wako Pure Chemical Industries) were added to the solution. To investigate the influence of pH, four kinds of precursor solutions under different pH conditions (pH = 3, 6, 9, and 12) were prepared by controlling the amount of C4H6O6 and NaOH added to the precursor solutions. To investigate the relationship between pH condition and particle size decreased using NaPH2O2 (Wako Pure Chemical Industries), five kinds of precursor solutions under different NaPH2O2 concentrations (0.0, 0.5, 1.0, 3.0, and 5.0 mM) were prepared by controlling the amount of NaPH2O2 added while maintaining the H2PtCl6 concentration at 0.5 mM. In summary, a total of 20 kinds of precursor solutions were prepared in this study. The glass vials that contained the precursor solution were sealed after being bubbled with argon to remove oxygen dissolved in the precursor solution; the sealed vials were subsequently sonicated using an ultrasonic cleaner (2510J-MT, Yamato Scientific) to disperse the carbon particles in the precursor solution prior to the irradiation step. The precursor solutions were then irradiated with a high-energy electron beam of 4.8 MeV using the dynamitron accelerator (RDI) at Japan Electron Beam Irradiation Service (EBIS), Osaka, Japan, to reduce the Pt ions. The surface dose was controlled to be 20 kGy, and the dose rate of 3 kGy/s was fixed. In fact, the irradiation of each glass vial required 6–7 s. The surface dose was measured with radiochromic dosimeters pasted onto the walls of the glass vials. Radiation-induced radicals reduced the Pt ions in the precursor solution, and the Pt nanoparticles were stabilised on the carbon particles. After the irradiation step, the solutions were divided into the powder and supernatant solution by suction filtration using Omnipore™ hydrophilic PTFE membrane filters (JGWP04700, 47 mm diameter, 0.2 μm pore size, Millipore). After being washed with ultrapure water, the powders were subsequently dried at 70 °C for one night. All the obtained sample IDs are shown in Table 1 and the subscript values denote the input NaPH2O2 and H2PtCl6 millimolar concentrations used in the precursor solution, respectively.
2.2. Characterisation

The chemical compositions and Pt loading weights of the obtained P–Pt/C samples were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES, ICPE-9000, Shimadzu). To dissolve Pt and P in the obtained samples, aqua regia (volume ratio HCl/HNO3 3/1) was used. The diluted solutions that contained Pt and P were sprayed into a plasma torch through a nebuliser. The amounts of Pt and P in the obtained samples were calculated on the basis of a calibration curve.

The dispersibility and particle sizes of the Pt nanoparticles supported on the carbon particles were investigated using transmission electron microscope (TEM, H-8100, Hitachi, 200 kV). For the representative P–Pt/C samples (P0.0–Pt0.5/C, P0.5–Pt0.5/C, and P3.0–Pt0.5/C samples), the particle size distributions were obtained by measuring the sizes of more than 100 metal particles. The average particle sizes of the Pt nanoparticles were then obtained as a geometric mean.

3. Results and discussion

3.1. ICP-AES

Table 1 shows the input and actual weights and P/Pt ratios for the P–Pt/C samples synthesised by an EBIRM under different pH conditions and under different NaPH2O2 concentrations. Platinum was detected in all of the P–Pt/C samples, and a small amount of P was also detected in most of the P–Pt/C samples except for P0.5–Pt0.5/C_pH12, P1.0–Pt0.5/C_pH12, and non-NaPH2O2-containing samples; P0.0–Pt0.5/C_pH3, P0.0–Pt0.5/C_pH6, P0.0–Pt0.5/C_pH9, and P0.0–Pt0.5/C_pH12. The P/Pt ratios of the P–Pt/C samples prepared at pH = 12 have a tendency to be lower than those of the P–Pt/C samples prepared at other pH. At high pH condition, phosphinic acid is easily oxidised, and therefore the reaction of P precipitation (PH2O2 + 2H+ + 2e− → P + 2H2O) would be suppressed.

Table 1. Input and actual weights and P/Pt ratios for the P–Pt/C samples synthesised by an EBIRM under different pH conditions and under different NaPH2O2 concentrations.

| Sample ID | Input | Actual |
|-----------|-------|--------|
|           | P [mg] | Pt [mg] | P/Pt ratio |
|           |       |       | P [mg] | Pt [mg] | P/Pt ratio |
| P0.0–Pt0.5/C_pH3 | 0.00 | 4.88 | 0 | 0.00 | 4.43 | 0.0 |
| P0.5–Pt0.5/C_pH3 | 0.77 | 4.88 | 1 | 0.17 | 3.65 | 0.3 |
| P1.0–Pt0.5/C_pH3 | 1.55 | 4.88 | 2 | 0.14 | 1.38 | 0.7 |
| P3.0–Pt0.5/C_pH3 | 4.65 | 4.88 | 6 | 0.09 | 0.55 | 1.0 |
| P5.0–Pt0.5/C_pH3 | 7.74 | 4.88 | 10 | 0.10 | 0.5 | 1.3 |
| P0.0–Pt0.5/C_pH6 | 0.00 | 4.88 | 0 | 0.00 | 4.14 | 0.0 |
| P0.5–Pt0.5/C_pH6 | 0.77 | 4.88 | 1 | 0.12 | 2.7 | 0.3 |
| P1.0–Pt0.5/C_pH6 | 1.55 | 4.88 | 2 | 0.06 | 1.1 | 0.3 |
| P3.0–Pt0.5/C_pH6 | 4.65 | 4.88 | 6 | 0.02 | 0.52 | 0.3 |
| P5.0–Pt0.5/C_pH6 | 7.74 | 4.88 | 10 | 0.03 | 0.47 | 0.4 |
| P0.0–Pt0.5/C_pH9 | 0.00 | 4.88 | 0 | 0.00 | 4.18 | 0.0 |
| P0.5–Pt0.5/C_pH9 | 0.77 | 4.88 | 1 | 0.10 | 1.89 | 0.3 |
| P1.0–Pt0.5/C_pH9 | 1.55 | 4.88 | 2 | 0.05 | 1.04 | 0.3 |
| P3.0–Pt0.5/C_pH9 | 4.65 | 4.88 | 6 | 0.03 | 0.59 | 0.4 |
| P5.0–Pt0.5/C_pH9 | 7.74 | 4.88 | 10 | 0.03 | 0.47 | 0.5 |
| P0.0–Pt0.5/C_pH12 | 0.00 | 4.88 | 0 | 0.00 | 4.63 | 0.0 |
| P0.5–Pt0.5/C_pH12 | 0.77 | 4.88 | 1 | 0.00 | 3.81 | 0.0 |
| P1.0–Pt0.5/C_pH12 | 1.55 | 4.88 | 2 | 0.00 | 3.38 | 0.0 |
| P3.0–Pt0.5/C_pH12 | 4.65 | 4.88 | 6 | 0.02 | 2.13 | 0.1 |
| P5.0–Pt0.5/C_pH12 | 7.74 | 4.88 | 10 | 0.05 | 0.94 | 0.3 |

*The data of P–Pt/C_pH3 samples are the same as in our previous report.*[15]
Figure 1 shows the Pt loading weight for each input NaPH2O2 concentration. At each pH condition, the actual Pt loading weights for all the Pt/C0 samples decreases as the NaPH2O2 concentration is increased. However, only Pt/C0 pH12 samples have different behaviour on decrease in Pt loading weight although Pt/C0 pH3, Pt/C0 pH6, and Pt/C0 pH9 samples have similar behaviour. For Pt/C0 pH3, Pt/C0 pH6, and Pt/C0 pH9 samples, the Pt loading weights drastically decrease and the actual/input ratios of the Pt weights become less than 30% as the NaPH2O2 concentration is controlled to be greater than 1.0 mM. These results imply that NaPH2O2 prevents the reduction of Pt ions and/or prevents the formation of Pt clusters on the Pt nanoparticles supported on the carbon particles, thereby blocking the growth of the Pt nanoparticles. In contrast, for only Pt/C0 pH12 samples, mild decrease in the Pt loading weight is seen in Figure 1. In the absence of NaPH2O2, the Pt loading weights are almost equal. In the case that NaPH2O2 is added to the precursor solutions, it finds that the Pt loading weight is lower in the order: Pt/C0 pH12 > Pt/C0 pH3 > Pt/C0 pH6 > Pt/C0 pH9 samples. These different behaviours on Pt loading weight imply that the change in pH affects the performance of NaPH2O2.

3.2. TEM

Figure 2 shows the TEM images of the representative Pt/C samples synthesised by an EBIRM under different pH conditions and under different NaPH2O2 concentrations: Pt/C0.5/C, Pt/C0.5/C, and Pt/C0.5/C samples. The larger grey grains represent the carbon particles and the smaller black grains with diameters less than 10 nm represent the Pt particles. The Pt particles are clearly supported on the carbon particles regardless of pH condition, as shown in Figure 2. However, the dispersibility of Pt particles on the carbon particles is different due to pH condition. For the Pt/C samples synthesised at pH ≤ 9, many Pt particles are well dispersed on the surface of the carbon particles (Figure 2(a)–2(ii)). Whereas, for the Pt/C samples synthesised at pH = 12, some Pt particles are agglomerated on the surface of the carbon particles (Figure 2(j)–(l)). In fact, it finds that the pH in a precursor solution affects the dispersibility of the Pt particles supported on the carbon particles. Similar behaviour based on pH is seen in the previous report in AuPd system [12] and in PtRu system [17] although the reason remains under review. In addition, the effect of the use of NaPH2O2 as the P precursor on the size of the Pt nanoparticles is also evident in Figure 2. At each pH condition, the average particle size of the Pt nanoparticles decreases as the NaPH2O2 concentration is increased. Table 2 shows the Pt loading weights and average particle sizes of the Pt nanoparticles supported on the carbon particles for the representative Pt/C samples. In the case of the same NaPH2O2 concentration, each average particle size of the Pt/C pH12 sample is larger than those of other Pt/C samples. Seeing more about the relationship among pH, NaPH2O2
concentration, and average particle size, it finds that the average particle size is smaller in the order; $P_{0.0}/C0\text{Pt}_0.5/C_{\text{pH}3} > P_{0.5}/C0\text{Pt}_0.5/C_{\text{pH}6} > P_{3.0}/C0\text{Pt}_0.5/C_{\text{pH}9}$ samples. This tendency on average particle size agrees with the tendency on Pt loading weight. In summary, these results on average particle size also indicate that pH in a precursor solution affects the performance of NaPH$_2$O$_2$.

Table 2. Pt loading weights and average particle sizes for the representative Pt–P/C samples synthesised by an EBIRM under different pH conditions and under different NaPH$_2$O$_2$ concentrations.

| Sample ID          | Loading weight [wt%] | Particle size [nm] |
|--------------------|----------------------|--------------------|
| $P_{0.0}/C0\text{Pt}_0.5/C_{\text{pH}3}$ | 6.2                  | 3.4                |
| $P_{0.5}/C0\text{Pt}_0.5/C_{\text{pH}3}$ | 5.2                  | 2.0                |
| $P_{3.0}/C0\text{Pt}_0.5/C_{\text{pH}3}$ | 0.8                  | 1.2                |
| $P_{0.0}/C0\text{Pt}_0.5/C_{\text{pH}6}$ | 5.9                  | 3.3                |
| $P_{0.5}/C0\text{Pt}_0.5/C_{\text{pH}6}$ | 3.9                  | 2.0                |
| $P_{3.0}/C0\text{Pt}_0.5/C_{\text{pH}6}$ | 0.9                  | 1.1                |
| $P_{0.0}/C0\text{Pt}_0.5/C_{\text{pH}9}$ | 5.9                  | 3.3                |
| $P_{0.5}/C0\text{Pt}_0.5/C_{\text{pH}9}$ | 2.8                  | 1.6                |
| $P_{3.0}/C0\text{Pt}_0.5/C_{\text{pH}9}$ | 0.9                  | 0.8                |
| $P_{0.0}/C0\text{Pt}_0.5/C_{\text{pH}12}$ | 6.5                  | 3.9                |
| $P_{0.5}/C0\text{Pt}_0.5/C_{\text{pH}12}$ | 5.4                  | 2.3                |
| $P_{3.0}/C0\text{Pt}_0.5/C_{\text{pH}12}$ | 3.1                  | 1.5                |

*The data of $P_{0.0}/C0\text{Pt}_0.5/C_{\text{pH}3}$ samples are the same as in our previous report.[15]*
4. Conclusion

We prepared the P–Pt/C samples by an EBIRM under different pH conditions and under different NaPH$_2$O$_2$ concentrations, and investigated the relationship among the pH, NaPH$_2$O$_2$ concentration, average particle size, and Pt loading weight. The average particle size was lower in the order; P–Pt/C$_{pH12}$ > P–Pt/C$_{pH3}$ > P–Pt/C$_{pH6}$ > P–Pt/C$_{pH9}$ samples; for example, the particle size of P$_{3.0}$–Pt$_{0.5}$/C$_{pH9}$ decreased to 0.8 nm due to P addition, while decrease in the particle size of P$_{3.0}$–Pt$_{0.5}$/C$_{pH12}$ stopped at 1.5 nm. In addition, the Pt loading weight was lower in the same order; P–Pt/C$_{pH12}$ > P–Pt/C$_{pH3}$ > P–Pt/C$_{pH6}$ > P–Pt/C$_{pH9}$ samples; for example, the Pt loading weight of P$_{3.0}$–Pt$_{0.5}$/C$_{pH9}$ drastically decreased from 5.9 to 0.9 wt% due to the addition of an excess of NaPH$_2$O$_2$ while the Pt loading weight of P$_{3.0}$–Pt$_{0.5}$/C$_{pH12}$ stopped at 3.1 wt%. In summary, the pH in the precursor solution affected the performance of NaPH$_2$O$_2$. This information on relationship between pH and the performance of NaPH$_2$O$_2$ would be a good guideline for the preparation of smaller metal nanoparticles deposited onto the support materials using a wet process with the addition of NaPH$_2$O$_2$, then pH condition should be carefully selected.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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