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Preparation of Pt dispersed porous carbon particles from polyimide particles

H. TAMAI, S. NAKATSUCHI, H. YASUDA
Graduate School of Engineering, Department of Applied Chemistry, Hiroshima University,
Higashihiroshima 1-4-1, Japan 739-8527
E-mail: tamai@hiroshima-u.ac.jp

We investigated the preparation of Pt and Pt/Ru bimetallic fine particles dispersed in polyimide particles by precipitation from various polyamic acid solutions containing Pt and Ru complexes, followed by the carbonization of the resulting polyimide particles. As Pt complexes, platinum(II) acetylacetonate [Pt(acac)$_2$], trimethylplatinum iodide [PtIMe$_3$], and (trimethyl) methylcyclopentadienylplatinum [Pt(MeCp)Me$_3$] were used. As Ru complexes, ruthenium(III) acetylacetonate [Ru(acac)$_3$], acenaphthylene heptacarbonyl triruthenium [(C$_{12}$H$_8$)Ru$_3$(CO)$_7$], and tetracarbonylbis(η-cyclopentadienyl)diruthenium [Ru$_2$(CO)$_4$Cp$_2$] were used. Bow tie-like polyimide particles containing Pt or Pt/Ru bimetallic particles could be obtained from pyromellitic dianhydride /*m*-phenylenediamine (PMDA/MPD) polyamic acid containing Pt and Ru complexes. Sheaf-like polyimide particles were obtained by using 4,4′-oxydianiline(ODA) as diamine. The morphologies of polyimide particles strongly depend on the kind and the concentration of Pt and Ru complexes. We could obtain Pt or Pt/Ru bimetallic fine particles dispersed in porous carbon particles, which morphologies are the same as the polyimide particles used as carbon precursors, by heat-treatment of the obtained polyimide particles. Pt and Pt/Ru fine particles in the range of 3∼10 nm were contained in bow tie-like or sheaf-like carbon particles. The addition of Ru complexes to polyamic acid solutions decreased the sizes of Pt particles in carbon particles.

1. Introducion

Fine metal or metal oxide particles supported on porous carbons have attracted much attention as heterogeneous catalysts [1–16] and energy devices, e.g., electrodes for electrochemical supercapacitors [17–19]. Compared with other supports, carbon materials are excellent in both thermal and chemical stabilities. Usually the supporting of metal particles is carried out by impregnation or ion-exchange methods. The amounts of metal supported by impregnation are readily controlled by impregnation time or concentration of metal ions. However, in the case of supporting by impregnation, the immobilization of metal particles is not necessarily stable. As a result, migration or elimination of metal particles from the surface of carbon often takes place during use. Furthermore, if porous carbons such as activated carbon are used as a support, pores are sometimes filled in or covered by metal particles formed by impregnation [20].

From these points of view, the authors previously investigated the simple preparation of noble metal particles dispersed in porous carbon by pyrolysis or steam activation of pitch containing noble metal complexes [21]. As a result, fine metal particles dispersed in porous carbons were obtained, and the resulting carbons presented high catalytic activity for hydrogenation reactions. In this case metal particles are supposed to be tightly fixed on carbon.

On the other hand, Burger reported porous carbon was obtained by heat-treatment of polyimide [22]. Then Nagata *et al.* reported that carbon particles which are unique and uniform in morphology are formed by heat-treatment of spherulite-like polyimide particles [23–27]. From these results, it is expected that fine metal particles dispersed in porous carbon particles containing metal complexes and that the resulting carbon particles are useful as a metal supported catalyst. From these points of view, in this work, we attempted to prepare porous carbon particles containing Pt and Pt/Ru fine particles by heat-treatment of the polyimide particles. Porous carbon particles dispersing Pt fine particles could be obtained.

2. Experimental

2.1. Materials

Pyromellitic dianhydride(PMDA) (Kanto chemical), *m*-phenylenediamine (MPD) (Kanto Chemical), 4,4′-oxydianiline(ODA) (Tokyo Chemical), *p*,*p*′-methylenedianiline (MDA)(Kanto chemical), 3,3′-sulfonyldianiline(SDA) (Wako Pure Chemical), hexamethylenediamine(HMDA) (Tokyo Chemical), octamethylenediamine(OMDA) (Tokyo Chemical), platinum(II) acetylacetonate [Pt(acac)$_2$] (Aldrich.), trimethylplatinum iodide(Me$_3$IPt)(Azumax), triruthenium dodecacarbonyl [Ru$_3$(CO)$_{12}$](Kanto chemical), acenaphthylene (Kanto Chemical), ruthenium(III) acetylacetonate [Ru(acac)$_3$](Aldrich) were purchased commercially and used without further purification. NMP (Kanto chemical) was dried over CaH$_2$ for 24 h at room temperature, and then distilled under 1.33 kPa at 80∼82°C.

(Methylcyclopentadienyl)trimethylplatinum [Pt(MeCp)Me$_3$] was prepared according to the reference [28]. 1.83 g of Me$_3$IPt suspended in 90×10^{-6} m^3 benzene was treated with 13.5×10^{-6} m^3 of THF solution of methylcyclopentadienylsodium for 2 h. After stirring, the light brown solution was evaporated to dryness under reduced pressure. The residue was recrystallized from methanol to give Pt(MeCp)Me$_3$ as light yellow crystals.

Acenaphthylene heptacarbonyl triruthenium [(C$_{12}$H$_8$)Ru$_3$(CO)$_7$] was synthesized as described below. Ru$_3$(CO)$_{12}$ (1.00 g) and 0.24 g of acenaphthylene were placed in 120×10^{-6} m^3 of heptane in a round bottomed flask and the mixture was refluxed with stirring for 24 h. Then the solvent was removed and the residue was recrystallised from CH$_2$Cl$_2$ to give (C$_{12}$H$_8$)Ru$_3$(CO)$_7$as dark brown crystals in 73% yield.

Tetracarbonylbis(η-cyclopentadienyl)diruthenium [Ru$_2$(CO)$_4$Cp$_2$] was synthesized as described below [29]. Cyclopentadiene (2 ml) was gradually added into 150×10^{-6} m^3 of heptane solution of Ru$_3$(CO)$_{12}$ (1.02 g,) and then the mixture was refluxed for 2.5 h. Air was flowed to the solution to give a dark brown suspension over night. Solvent was removed under reduced pressure and the residue was purified on alumina column (CH$_2$Cl$_2$:heptane = 2:3) to give Ru$_2$(CO)$_4$Cp$_2$ as orange powder in 20% yield.

2.2. Synthesis of polyamic acid

All operations were conducted under an argon atmosphere. A typical procedure is as follows; A NMP solution of polyamic acid (PMDA/MPD) was synthesized by adding pyromellitic dianhydride (10.40 g) to a NMP (205×10^{-6} m^3) solution of m-phenylenediamine (5.16 g) in a 500×10^{-6} m^3 three-necked flask. The solution was stirred for 1 h at 15°C, and then for 3 h at 25°C. The resulting polymer was precipitated in methanol. The product was dried in vacuum (yield: 96%).

2.3. Synthesis of polyimide particles containing Pt

A typical procedure is as follows; 1.81 g of polyamic acid (PMDA/MPD) was dissolved in 20×10^{-6} m^3 of NMP, and then 20×10^{-6} m^3 of NMP solution of Pt(acac)$_2$ (3.06 mmol) was added to the NMP solution of polyamic acid. The mixture was stirred for 3 h at 200°C. After cooling, the polyimide particles (PMDA/MPD) precipitated was separated by centrifugation, washed with NMP and pure water, and finally dried in vacuum.

2.4. Heat treatment

The carbonization of polyimide particles containing metal was conducted in argon using a combustion tube (Nippon Kagaku Togyo NC-14) and combustion furnace (Motoyama MTKW-11-1040). The sample was placed in a crucible and set in the combustion tube. Then the tube was heated up to 400°C under argon flow, kept for 1 h, and then heated at 800°C for 1 h.

2.5. Instrumental analysis

Scanning electron microscopy (SEM) was carried out on a Hitachi S-2150 instrument. X-ray diffraction (XRD) measurements were performed using a SRA M18XHF system with Cu K$_\alpha$ radiation (40 kV, 30 mA). Transmission electron microscopy (TEM) was carried out on a Topcon EM-002B electron microscope at 200 kV. Particles induced X-ray emission (PIXE) analysis was performed using a van de Graaff accelerater system with proton radiation in Hiroshima University.

3. Results and discussion

3.1. Polyimide particles containing Pt

Various polyimide particles were obtained from polyamic acids solutions containing Pt complexes. Fig. 1 shows SEM photographs of the polyimide particles precipitated from polyamic acid (PMDA/MPD) solutions containing three kinds of Pt complexes, Pt(acac)$_2$, PtIMe$_3$, and Pt(MeCp)Me$_3$. Polyimide particles obtained using Pt(acac)$_2$ are bow tie-like and uniform in size (about 1.5 μm × 1.5μm × 2.5 μm) (a in Fig. 1). In Fig. 1, the amounts of Pt complexes added to polyamic acid solutions are represented as molar ratio of Pt complex to carboxyl groups of polyamic acid (Pt molar ratio). The morphologies and sizes of these particles are similar to those synthesized from PMDA and MPD in the absence of Pt complex [23]. However, the aggregates were precipitated from polyamic acid solution of high Pt molar ratio. On the other hand, in the case of polyimide particles precipitated from polyamic acids solutions containing PtIMe$_3$, the disk-like particle morphologies were observed (b in Fig. 1), and the particles precipitated from polyamic acid solution containing Pt(MeCp)Me$_3$ were random in morphology (c in Fig. 1). These results suggest that the interaction of polyamic acid with Pt complex affects the formation of spherulite-like polyimide particles. With respect to the interaction between polyamic acid and metal complex, Bergmeister *et al.* suggested that iron acetylactonate (Fe(acac)$_3$) coordinated to individual polyamic acid chains through the acid functionality by the loss of the one acac ligand [30]. This coordination of acetylacetonate complex to individual polyamic acid chains suggests the homogeneous dispersion of metal atoms in polyamic acid.

The kind and size of the Pt component contained in polyimide particles were measured by XRD analysis and TEM, respectively. In addition, the amount of Pt incorporated into polyimide particles was determined by PIXE analysis. Fig. 2 shows XRD patterns of polyimide particles precipitated from polyamic acid

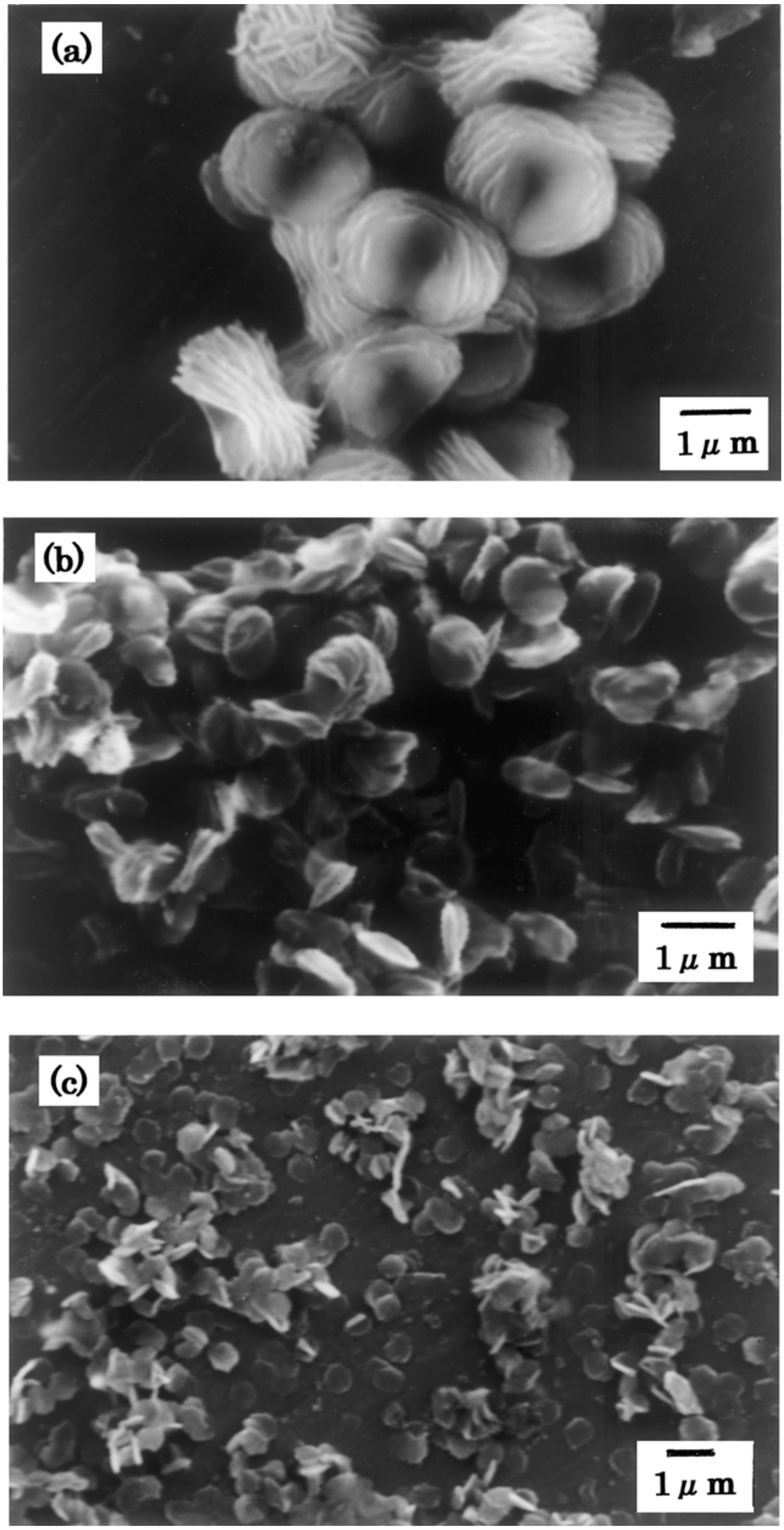

Figure 1 SEM images of polyimide particles precipitated from polyamic acid (PMDA/MPD) solutions containing Pt complexes (Pt/carboxyl groups of polyamic acid molar ratio = 0.1): (a) Pt(acac)$_2$, (b) PtIMe$_3$, and (c) Pt(MeCp)Me$_3$.

(PMDA/MPD) solution containing various concentrations of Pt(acac)$_2$. The peaks assigned to polyimide crystals and Pt crystals were observed. These XRD patterns indicate that fine Pt particles were incorporated into bow tie-like polyimide particles. The sizes of Pt particles formed in polyimide particles were independent on the concentration of Pt(acac)$_2$, because the peak widths of Pt particles were scarcely changed with the change of concentration of Pt(acac)$_2$. Similarly, XRD patterns of polyimide particles obtained using other Pt

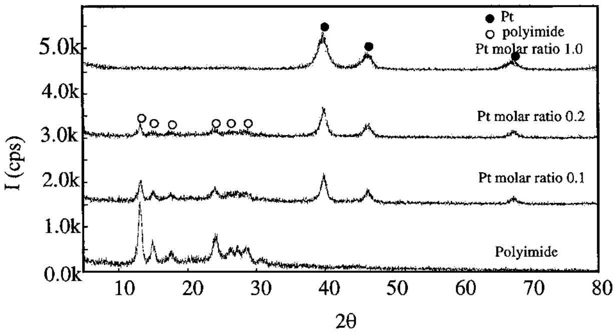

Figure 2 XRD patterns of polyimide particles precipitated from polyamic acid (PMDA/MPD) solutions containing $Pt(acac)_2$.

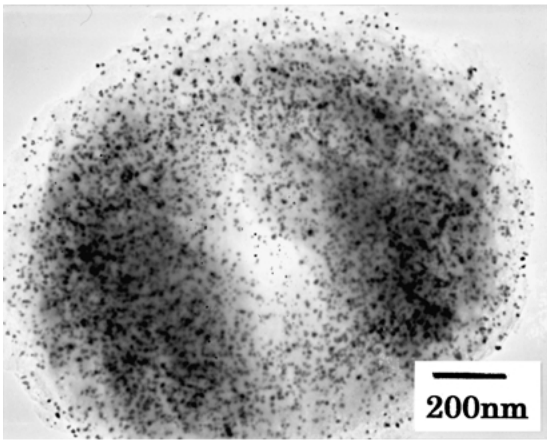

Figure 3 TEM image of polyimide particles precipitated from polyamic acid (PMDA/MPD) solution containing $Pt(acac)_2$(Pt/carboxyl groups of polyamic acid molar ratio = 0.1).

complexes, viz., $PtIMe_3$ and $Pt(MeCp)Me_3$, indicated the formation of Pt particles in polyimide particles. Pt is supposed to be formed from Pt complexes throughout the thermal imidization of polyamic acid. On the other hand, the peaks assigned to polyimide crystals were weakened with increasing the amount of Pt complex, as shown in Fig. 2. The increase in coordination of the Pt complex to individual polyamic acid chains is supposed to interfere the imidization of polyamic acid, namely, the formation of spherulite-like polyimide particles.

Fig. 3 shows the TEM image of polyimide particles precipitated from polyamic acid (PMDA/MPD) solution containing $Pt(acac)_2$. Pt fine particles were dispersed in polyimide particles. This result suggests that the Pt complex is dispersed in polyamic acid. The mean sizes of Pt particles determined from TEM photographs are shown in Table I. Pt particles of about 10 nm were dispersed in the polyimide particles. The size of the Pt particles in polyimide particles decreased with increasing the concentration of $Pt(acac)_2$ in polyamic acid solutions. The effect of concentration of Pt complex on particle size of Pt is not consistent with the effect of metal ion concentration on metal particle size in convenient precipitation of metal particles from metal ion solutions.

The yields and Pt contents of polyimide particles are shown in Table I. The yields of polyimide particles from polyamic acid solutions containing Pt complexes depend on the kind of Pt complex. The addition of $Pt(MeCp)Me_3$ lowered the yield compared with other complexes. The coordination of $Pt(MeCp)Me_3$ to polyamic acid chain is tighter than those of other complexes, and consequently the formation of polyimide particles seems to be inhibited. Regarding Pt content, the calculated amounts of Pt were determined presuming that Pt added in polyamic acid solutions is completely incorporated into polyimide particles. As shown in Table I, the measured amounts of Pt in polyimide particles are slightly lower than those calculated. A very small amount of Pt complex is supposed to remain in solvent. Pt contents increased with increasing concentration of Pt complexes added in polyamic acid solutions. Therefore most Pt complexes added in polyamic acid solutions are incorporated into polyimide particles. This also suggests that the coordination of Pt complex to individual polyamic acid chains, which is suggested by Bergmeiater *et al.* [30], plays an important role in the formation of polyimide particles containing fine Pt particles and the dispersion of Pt particles.

The preparation of polyimide particles from polyamic acids prepared with ODA, SDA, HMDA, and OMDA as diamine components was investigated. Fig. 4 shows the SEM image of polyimide particles precipitated from polyamic acid (PMDA/ODA) solution containing $Pt(acac)_2$. Sheaf-like polyimide particles with uniform size were obtained with ODA. Their shapes were different from that of polyimide (PMDA/MDA) particles containing Pt. On the other hand, uniform particles were not obtained from SDA, HMDA, and OMDA.

3.2. Polyimide particles containing Pt and Ru

We investigated the influence of the addition of other metal complexes in addition to Pt complex on the

TABLE I Polyimide particles precipitated from polyamic acid (PMDA/MPD) solutions containing Pt complex

Run	Pt complex	Pt molar ratio (Pt/PAA[a])	Yield (%)	Particle morphology	Pt content (mg/g) calcd.	Pt content (mg/g) found	Pt particle size (nm)
1	–	–	70.2	Bow tie-like	–	–	–
2	$Pt(acac)_2$	0.1	83.5	Bow tie-like	67	54	10.5
3	$Pt(acac)_2$	0.2	67.0	Bow tie-like	134	82	10.1
4	$Pt(acac)_2$	1.0	73.2	Aggregate	402	333	4.8
5	$PtIMe_3$	0.1	81.5	Bow tie-like	63	57	Aggregate
6	$Pt(MeCp)Me_3$	0.1	50.0	Disc-like	63	57	10.0

[a] Carboxyl groups of polyamic acid.

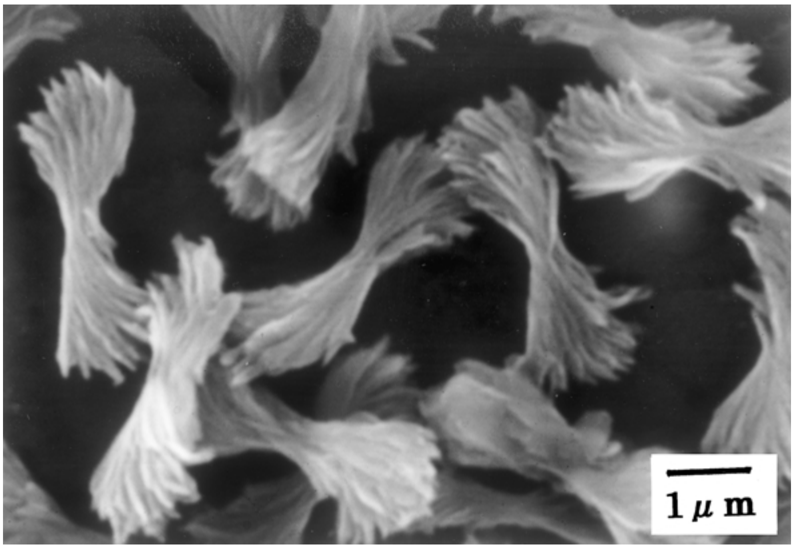

Figure 4 SEM image of polyimide particles precipitated from polyamic acid (PMDA/ODA) solution containing $Pt(acac)_2$ (Pt/carboxyl groups of polyamic acid molar ratio = 0.1).

precipitation of polyimide particles and the formation of metal particles. In this work, the preparation of polyimide particles from polyamic acid solution containing Ru complex in addition to Pt complex was investigated. Fig. 5 shows SEM images of polyimide particles precipitated from polyamic acid(PMDA/MPD) solution containing $Pt(acac)_2$ and $Ru(acac)_3$ or $(C_{12}H_8)Ru_3(CO)_7$ as Ru complexes. Uniform bow tie-like particles were obtained from these procedures. On the other hand, small disc-like particles were precipitated from polyamic acid solution containing $Ru_2(CO)_4Cp_2$. No particle was precipitated at high concentration of Ru complexes in polyamic acid solutions. The kind and the concentration of Ru complexes strongly affected the morphologies of precipitated polyimide particles. The coordination of Ru complex in addition to Pt complex to individual polyamic acid chains through the acid functionality, which was suggested by Bergmeister *et al.* [30], is supposed to influence the formation of polyimide particle.

XRD patterns of the obtained polyimide particles indicated that Pt or Pt/Ru alloy crystals generated in polyimide particles. However, because the peaks derived from Pt or Pt/Ru alloy are weak, the distinction between Pt and Pt/Ru alloy could not be done. The formation of fine particles which are Pt or Pt/Ru alloy in polyimide particles was also observed by TEM. The sizes of Pt or Pt/Ru alloy particles determined by TEM and the amounts of Pt and Ru incorporated in polyimide particles determined by PIXE analysis are shown in Table II. As shown in Table II, when the concentrations of Pt and Ru complexes added to polyamic acid solutions are low, Pt and Ru were quantitatively incorporated in polyimide particles. On the other hand, the addition of Ru complexes makes the sizes of Pt or Pt/Ru alloy particles small, that is, the size of Pt particles decreased from about 10 nm to below 7 nm, especially 2.6 nm in the case of $(C_{12}H_8)Ru_3(CO)_7$. Pt and Ru contents are affected by the kind of Ru complex. Pt and Ru contents measured in polyimide particles precipitated from polyamic acid containing $(C_{12}H_8)Ru_3(CO)_7$ and $Ru_2(CO)_4Cp_2$ are lower than those calculated. It is supposed that the incorporation of Pt and Ru into polyimide particles seems to be lowered due to the weak coordination of these Pt complexes to polyamic acid compared with $Pt(acac)_2$.

3.3. Carbonization of polyimide particles containing Pt

Polyimide particles containing Pt fine particles were heat-treated first at 400°C for 1 h and then 800°C for 1 h. Fig. 6 shows SEM and TEM images of

TABLE II Polyimide particles precipitated from polyamic acid (PMDA/MPD) solutions containing Pt $(acac)_2$ and Ru complex

Run	Pt molar ratio (Pt/PAA[a])	Ru complex	Ru molar ratio (Ru/PAA[a])	Yield (%)	Particle morphology	Pt content (mg/g) calcd.	Pt content (mg/g) found	Ru content (mg/g) calcd.	Ru content (mg/g) found	Metal particle size (nm)
1	0.1	$Ru(acac)_3$	0.01	61.7	Bow tie-like	63	54	3	3	7.6
2	0.1	$Ru(acac)_3$	0.05	–[b]	–[b]	–	–	–	–	–
3	0.1	$Ru(acac)_3$	0.10	–[b]	–[b]	–	–	–	–	–
4	0.1	$(C_{12}H_8)Ru_3(CO)_7$	0.03	47.3	Bow tie-like	61	22	32	14	2.6
5	1.0	$(C_{12}H_8)Ru_3(CO)_7$	1.00	–[b]	–[b]	–	–	–	–	–
6	0.1	$Ru_2(CO)_4Cp_2$	0.05	51.6	Disc-like	61	26	32	24	4.5

[a] Carboxyl group of polyamic acid.

[b] No particle.

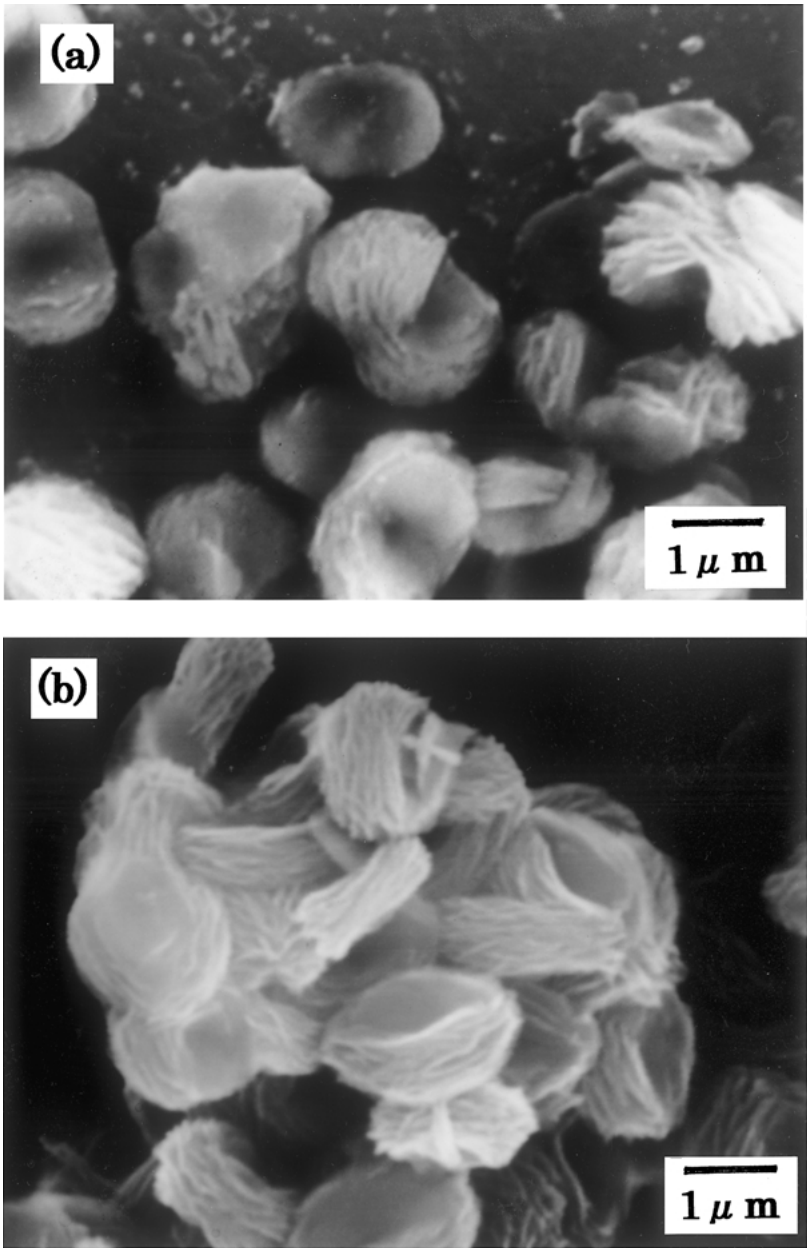

Figure 5 SEM images of polyimide particles precipitated from polyamic acid (PMDA/MPD) solutions containing Pt(acac)$_2$and Ru complexes (Pt/carboxyl groups of polyamic acid molar ratio = 0.1): (a) Ru(acac)$_3$, (Ru/Pt ratio = 0.1) and (b) (C$_{12}$H$_8$)Ru$_3$(CO)$_7$(Ru/Pt ratio = 0.3).

the carbon particles obtained by heat-treatment of polyimide (PMDA/MPD) particles containing Pt. The morphology of the carbon particles was bow tie-like, similar to that of polyimide particles. The carbon particles obtained from other polyimide particles containing Pt were almost the same in shape as the polyimide particles used as precursors. Throughout the heat-treatment the shapes of polyimide particles are scarcely changed.

Fig. 6 shows TEM image of the carbon particles. Pt fine particles are dispersed in the carbon particles. The mean sizes of Pt particles were determined from TEM photographs. Table III shows the carbonization yields,

TABLE III Carbonization of polyimide particles obtained from polyamic acid (PMDA/MPD) solutions containing Pt complex

Run	Pt complex	Pt molar ratio (Pt/PAA[a])	Carbonization yield (%)	Particle morphology	Pt content (mg/g) calcd.	Pt content (mg/g) found	Pt particle size (nm)	BET surface area (m^2/g)
1-C	–	–	50.5	Bow tie-like	–	–	–	440
2-C	Pt(acac)$_2$	0.1	51.9	Bow tie-like	86	97	12.7	390
3-C	Pt(acac)$_2$	0.2	53.5	Bow tie-like	134	142	11.3	370
4-C	Pt(acac)$_2$	1.0	67.4	Aggregate	493	395	6.0	170
5-C	PtIMe$_3$	0.1	50.5	Bow tie-like	112	100	Aggregate	332
6-C	Pt(MeCp)Me$_3$	0.1	53.7	Disc-like	108	65	10.4	85

Heat-treatment: 400°C 1 h, 800°C 1 h.

[a] Carboxyl groups of polyamic acid.

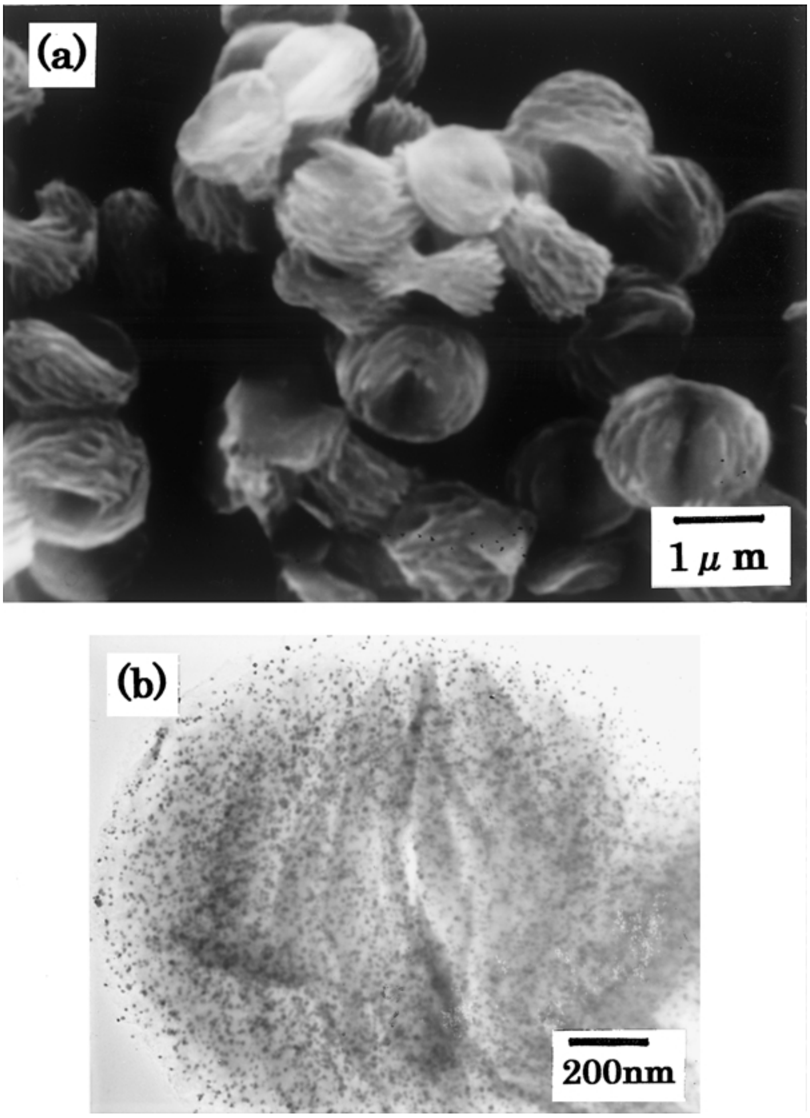

Figure 6 SEM(a) and TEM(b) images of carbon particles obtained by heat-treatment of polyimide particles containing Pt (Pt/carboxyl groups of polyamic acid molar ratio = 0.1).

Pt contents, and Pt sizes of the obtained carbon particles. Calculated Pt contents in carbon particles were determined from Pt contents in polyimide particles and carbonization yields. In the case of Pt(acac)$_2$, the carbonization yields and Pt contents in the carbon particles increased with increasing the amounts of Pt(acac)$_2$ added in polyamic acid solutions. It is supposed that Pt added into polyamic acid is incorporated into carbon particles and the increase in carbonization yield is due to the increase in Pt amount contained in carbon particles. On the other hand, Pt contents in carbon particles depend on the kind of Pt complex. That is, Pt content of the carbon particles prepared from polyamic acid containing Pt(MeCp)Me$_3$ is lower than that from polyamic acid containing Pt(acac)$_2$. It is supposed that the Pt complex partly disappears from the polyimide particles during heat-treatment in the case of Pt(MeCp)Me$_3$. The mean sizes of the Pt particles are in the range of $6 \sim 13$ nm. These sizes are almost unchanged compared with the sizes of the Pt particles in the polyimide particles. That is, the growing of fine Pt particles with aggregation of Pt particles seems not to take place during carbonization of polyimide particles.

It was reported that the carbon materials prepared from polyimide are porous [20]. We measured the pore characteristics of the resulting carbon particles. BET specific surface areas of the carbon particles obtained from polyamic acid containing Pt(acac)$_2$ decreased with increasing the amount of Pt(acac)$_2$ added. Additionally the BET surface area of the carbon particles from polyimide particles containing Pt(MeCp)Me$_3$ is very low. From these results, it is suggested that Pt particles formed from Pt complexes inhibit the pore formation or destroy the pore structure. However the carbon particles are still porous and have BET surface area of about 400 m^2/g in the case of polyimide particles precipitated from polyamic acid (PMDA/MPD) solution containing 0.1 molar ratio of Pt(acac)$_2$ to carboxyl groups of polyamic acid. The pore radius distributions are shown in Fig. 7. Micro- and meso-pores of about 1.2 nm and 3 nm in diameter were contained in the carbon particles.

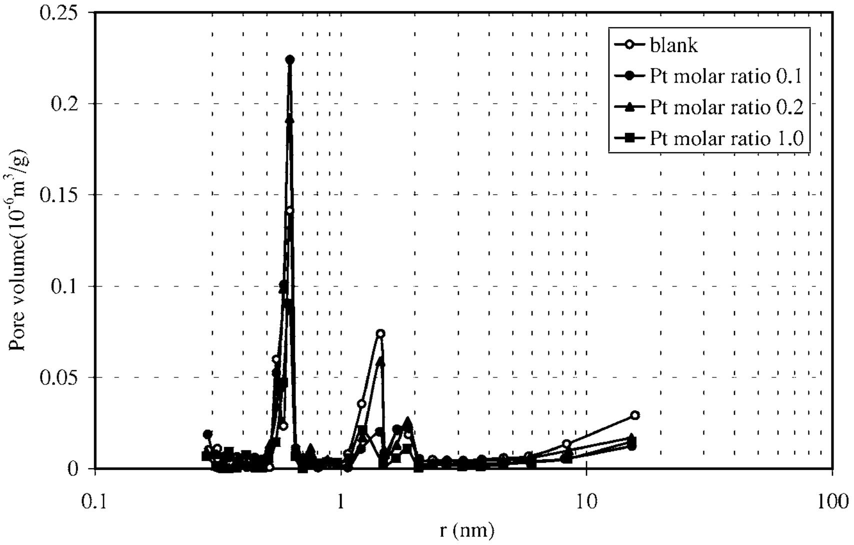

Figure 7 Pore radius distributions of carbon particles obtained from polyimide particles precipitated from polyamic acid (PMDA/MPD) containing Pt(acac)$_2$.

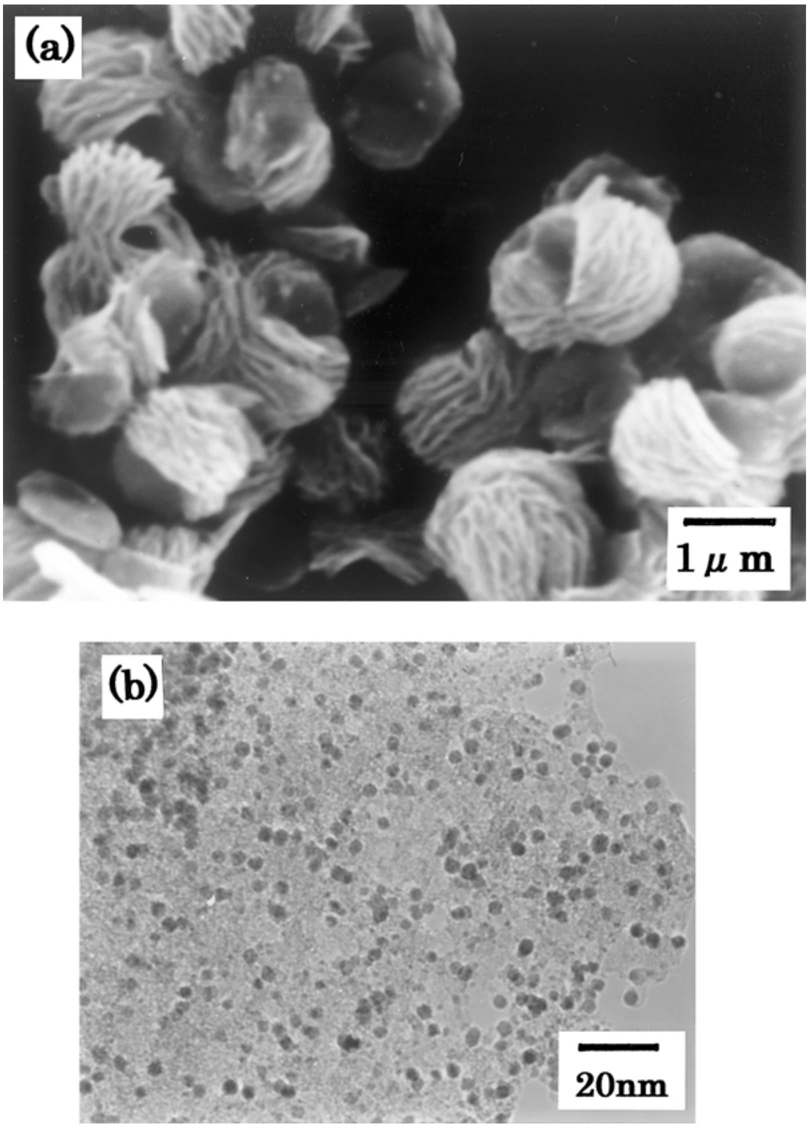

Figure 8 SEM(a) and TEM(b) images of carbon particles obtained from polyimide particles containing Pt and Ru(Pt/carboxyl groups of polyamic acid molar ratio = 0.1) Ru:$(C_{12}H_8)Ru_3(CO)_7$, Ru/Pt ratio = 0.3.

TABLE IV Carbonization of polyimide particles obtained from polyamic acid (PMDA/MPD) solutions containing Pt (acac)$_2$ and Ru complex

Run	Pt molar ratio (Pt/PAA[a])	Ru complex	Ru molar ratio (Ru/PAA[a])	Carbonization yield (%)	Particle morphology	Pt content (mg/g)		Ru content (mg/g)		Pt/Ru particle size (nm)	BET surface area (m^2/g)
						calcd.	found	calcd.	found		
7-C	0.1	Ru(acac)$_3$	0.01	61.7	Bow tie-like	138	142	5	5	7.6	70
10-C	0.1	$(C_{12}H_8)Ru_3(CO)_7$	0.03	47.3	Bow tie-like	52	47	34	32	2.6	405
12-C	0.1	$Ru_2(CO)_4Cp_2$	0.05	51.6	Disc-like	50	44	48	39	4.5	160

Heat-treatment: 400°C 1 h, 800°C 1 h.

[a]Carboxyl group of polyamic acid.

3.4. Carbonization of polyimide particles containing Pt and Ru

Fig. 8 shows SEM and TEM images of carbon particles obtained by heat-treatment of polyimide (PMDA/MPD) particles containing both Pt and Ru. Bow tie-like carbon particles (about 1.5 μm × 1.5 μm × 2.5 μm) were obtained after carbonization of polyimide (PMDA/MPD) particles. The shape of the polyimide particles was maintained after carbonization, although the weight of carbon particles decreased below half of those of polyimide particles. As shown in TEM photographs in Fig. 8, fine metal particles derived from Pt and Ru complexes are uniformly contained in carbon particles. Fig. 9 shows XRD patterns of the carbon particles obtained from polyimide(PMDA/MPD) particles containing Pt and Ru. The peaks which are supposed to be due to Pt or Pt/Ru alloy particles were observed in carbon particles. Pt or Pt/Ru alloy is supposed to be formed during heat-treatment. Similarly, the formation of Pt or Pt/Ru alloy particles by carbonization was indicated in the cases of other polyimide particles containing Pt and Ru. On the other hand, the peaks assigned to polyimide crystals in the XRD patterns disappeared.

The sizes of Pt or Pt/Ru alloy particles determined from TEM photographs are shown in Table IV. Pt and Ru contents in carbon particles are also shown in Table IV. As shown in Fig. 8 and Table IV, the sizes of Pt (Pt/Ru alloy) particles decreased by the addition of Ru comlexes in polyamic acid solutions. Especially, in the cases of $(C_{12}H_8)Ru_3(CO)_7$, small size particles less than about 4 nm in diameter were formed in carbon particles. It should be noted that the size of Pt particles decreased on adding Ru. Additionally Pt and Ru contents in carbon particles are almost the same as the calculated values determined from those in polyimide particles used as precursors. There seems to be no loss of Pt and Ru throughout heat-treatment. The carbon particles from polyimide particles obtained by the addition of $(C_{12}H_8)Ru_3(CO)_7$ have about 400 m^2/g of BET surface area and are highly porous. The addition of Ru(acac)$_3$ or $Ru_2(CO)_4Cp_2$ decreased BET surface area compared with carbon particles without Ru metal.

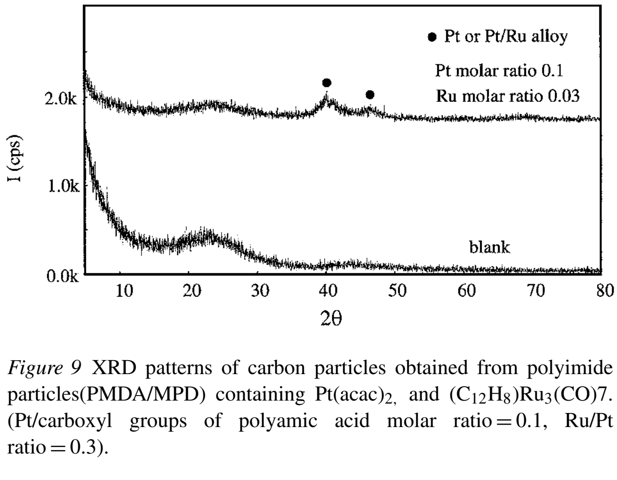

Figure 9 XRD patterns of carbon particles obtained from polyimide particles(PMDA/MPD) containing Pt(acac)$_2$, and $(C_{12}H_8)Ru_3(CO)7$. (Pt/carboxyl groups of polyamic acid molar ratio = 0.1, Ru/Pt ratio = 0.3).

4. Conclusion

Bow tie-like polyimide particles which are uniform in size and contain Pt or Pt/Ru bimetallic particles could be obtained by precipitation from polyamic acid (PMDA/MPD) containing Pt and Ru complexes. Sheaf-like polyimide particles containing Pt were obtained by using ODA as diamine. The morphologies of polyimide particles depend on the kind and the concentration of Pt and Ru complexes. These results suggested that the coordination of Pt and Ru complexes to individual polyamic acid chains played an important role in the formation of polyimide particles. Pt or Pt/Ru bimetallic fine particles dispersed in porous carbon particles, which morphologies are the same as polyimide particles used as carbon precursors, were obtained by heat-treatment of the resulting polyimide particles. Pt and Pt/Ru fine particles in the range of 3 ∼ 10 nm were homogeneously contained in bow tie-like carbon particles. The sizes of Pt particles in carbon particles decreased by the addition of Ru complexes to polyamic acid solutions.

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