

Preparation of Ultrafine Metal Particle-Supported Fine Carbon Particles

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SYNOPSIS

Ultrafine metal particle-supported carbon particles were synthesized by pyrolysis of polymer particle-metal ions such as Co(II), Ni(II), Cu(II), Ag, Pd(II), and Rh(III) complexes. The sizes of metal particles increased with increasing pyrolysis temperature. Pd and Rh particles were on the whole smaller than were Co, Ni, and Cu, even though the amounts of Pd and Rh ions immobilized were higher. Rh particles supported on carbon particles exhibited high catalytic activity for the decomposition of hydrogen peroxide. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Ultrafine metal particle-supported on carbon materials are of considerable interest due to their high catalytic activity for various chemical reactions and the high heat resistance of carbon. In general, ultrafine metal particles supported on carbon are produced by the impregnation method, where ultrafine metal particles are formed by the reduction of inorganic salts on the surface of carbon. On the other hand, Hirano et al. reported the synthesis of metal-dispersed carbon by pressure pyrolysis of an organometallic polymer^{1,2} or a divinylbenzene-vinylferrocene copolymer.^{3,4} Honda et al.⁵ described the preparation of relatively large (>20–30 μm) carbon microbeads containing fine platinum particles using a mesophase pitch. However, there have been few reports on the direct preparation of ultrafine metal particle-supported fine carbon particles from carbon precursors.

We previously reported that ultrafine metal particles immobilized on fine polymer particles are prepared by the reduction of metal ion immobilized on the surface of fine polymer particles.^{6,7} In addition, we reported that fine carbon, in some cases hollow, particles with uniform size were produced by the

pyrolysis of submicron-size polystyrene-polyacrylonitrile composite particles, which were prepared by emulsifier-free emulsion polymerization.⁸ On the basis of these results, in this work, we attempted the preparation of ultrafine metal particle-supported carbon particles by pyrolysis of polymer particle-metal ion surface complexes.

EXPERIMENTAL

Styrene, acrylonitrile, and acrylic acid purchased from Wako Pure Chemical Co. were purified by distillation under reduced pressure in an argon atmosphere. Potassium peroxodisulfate (KPS) was recrystallized from water and then dried in a vacuum. Silver nitrate, sodium tetrachloropalladate(II) trihydrate, rhodium(III) chloride, cobalt(II) chloride, nickel(II) chloride, and copper(II) chloride (Wako Pure Chemical Co.) were used without further purification. Water was used after distillation and deionization throughout the experiments.

Styrene/acrylonitrile copolymer [poly(St-co-AN)] particles and styrene/acrylic acid/acrylonitrile copolymer [poly(St-co-AA-co-AN)] particles were prepared by emulsifier-free emulsion polymerization using KPS as an initiator. The reaction was carried out in an argon atmosphere at 70°C. The polymerization recipes and the sizes of obtained particles are shown in Table I. The poly-

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Table I Preparation of Fine Polymer Particles

		Poly(St- <i>co</i> -AN)	Poly(St- <i>co</i> -AA- <i>co</i> -AN)
Styrene	(mol/L)	0.10	0.10
Acrylic acid	(mol/L)	—	0.10
Acrylonitrile	(mol/L)	0.90	0.80
KPS	(mol/L)	10 ⁻³	10 ⁻³
Particle size	(nm)	285	306

KPS: potassium peroxydisulfate.

mer particles were centrifuged and the sedimented particles were redispersed in water using an ultrasonic vibrator. This purification procedure was repeated twice.

A typical preparation of metal complexes of copolymer particles was as follows: A copolymer dispersion of 25 mL (polymer content 1.0 g) was mixed with an aqueous solution of a metal compound (0.001 or 0.01 mol in 25 mL). The mixture was stirred for 2 h at room temperature. The resulting copolymer particles were centrifuged and then redispersed in water. This procedure was repeated twice to remove residual ions.

Pyrolysis of metal ion-immobilized copolymer particles was conducted in an argon atmosphere in a cylindrical combustion furnace. Samples were heated to 400–1000°C at a rate of 100°C/h and maintained there for 4 h.

TEM observation was conducted with a Topcon EM-002B electron microscope at 200 kV. The amounts of metal immobilized on copolymer and carbon particles were measured by particle-induced X-ray emission (PIXE) analysis. PIXE analysis was performed using a van de Graaff accelerator. The intensity of the characteristic X-ray generated by irradiation of H⁺ was measured and the concentrations of metal were calculated using authentic samples of various amounts of metals.

X-ray diffraction analysis was performed in a Rigaku RDA-IB system using CuK α radiation and the assignments of the resulting metal species were made based on literature data. The catalytic activity of ultrafine metal particles immobilized on carbon particles was tested for the decomposition reaction of hydrogen peroxide. Ultrafine metal particle-supported carbon particles were dried in a Schlenk tube under reduced pressure for 1 h at room temperature. After the addition of 200 mL of water and 2 mL of 30 wt % H₂O₂ aqueous solution, the volume of generated O₂ gas was measured at room temperature.

RESULTS AND DISCUSSION

Amount of Metal Ion Immobilized

We previously reported that ultrafine metal particle-immobilized fine copolymer particles are produced by reduction of copolymer particle–metal ion complexes, and the generation of ultrafine metal particles is dependent on the amounts of metal ions immobilized on the surface of copolymer particles before reduction. Similarly, the amounts of metal ions immobilized on the surface of copolymer particles may play an important role in the generation of ultrafine metal particles by the pyrolysis of copolymer particle–metal ion complexes. The amounts of metal ions immobilized on poly(St-*co*-AN) and poly(St-*co*-AA-*co*-AN) particles are shown in Table II. The immobilized amounts of noble metal ions, viz., Ag(I), Pd(II), and Rh(III), are relatively high even though the concentrations of metal ions are lower, compared with those of transition-metal ions such as Co(II), Ni(II), and Cu(II). Additively, the amounts of metal ions immobilized on poly(St-*co*-AA-*co*-AN) particles are roughly 10 times higher than those on poly(St-*co*-AN). Regarding the immobilization of various metal ions on the surface of polymer particles which were prepared by emulsifier-free emulsion polymerization, we reported that metal ions such as Fe(II), Co(II), Cu(II), and Pt(IV) were scarcely immobilized on polystyrene particles without any functional groups, and, on the other hand, a high amount of such metal ions was immobilized on a styrene/acrylic acid copolymer⁷ and styrene/*N*-vinylimidazole copolymer⁶ particles. In addition, the amount of Pd ions immobilized on styrene/acrylic acid copolymer particles was generally higher than those of other metal ions. Warshawsky and Upson⁹ reported the production of metal-covered polymer particles using polymer particles containing functional groups which can bind Pd ions by coordinate or ionic bonds. These results suggest that the high amounts of metal ions immobilized on

Table II Amounts of Metal Immobilized on Fine Copolymer Particles

Copolymer Particle	Metal Compounds	Metal Ion Concentration (mol/L)	Immobilized Metal Amounts (mg/g)
Poly(St-co-AN)	CoCl ₂	0.2	0.18
	NiCl ₂	0.2	0.14
	CuCl ₂	0.2	0.24
	AgNO ₃	0.02	2.78
	PdCl ₂	0.02	3.34
	RhCl ₃	0.02	1.32
Poly(St-co-AA-co-AN)	CoCl ₂	0.2	9.1
	NiCl ₂	0.2	15.6
	CuCl ₂	0.2	11.4
	AgNO ₃	0.2	23.8
	PdCl ₂	0.02	39.2
	RhCl ₃	0.02	11.5

poly(St-co-AA-co-AN) particles are due to complex formation with carboxyl groups derived from acrylic acid.

Carbon Particle

Figures 1 and 2 show TEM photographs of fine carbon particles obtained by pyrolysis of a poly(St-co-AN) particle-Rh(III) ion complex and poly(St-co-AA-co-AN) particle-Pd(II) ion complexes, respectively, at 800 and 1000°C for 4 h. In both copolymer particle-metal ion complexes, the formation of ultrafine metal particles in carbon particles was observed. The sizes of these metal particles formed at

low pyrolysis temperature (800°C) are below 5 nm and increased with increasing pyrolysis temperature. XRD analysis of the obtained carbon particles indicated the formation of ultrafine metal, i.e., Rh or Pd crystals. As shown in Figure 3, the carbon particles obtained by pyrolysis at 600°C exhibited no obvious diffraction peak in the XRD pattern. From these results, it is suggested that very small crystal-like clusters are generated by pyrolysis of copolymer particle-metal ion complexes at an early stage of pyrolysis or low pyrolysis temperature, and these clusters grow to crystal with increasing pyrolysis temperature. Similarly to ultrafine Rh or Pd particles immobilized carbon particles, Co or Ni particle-

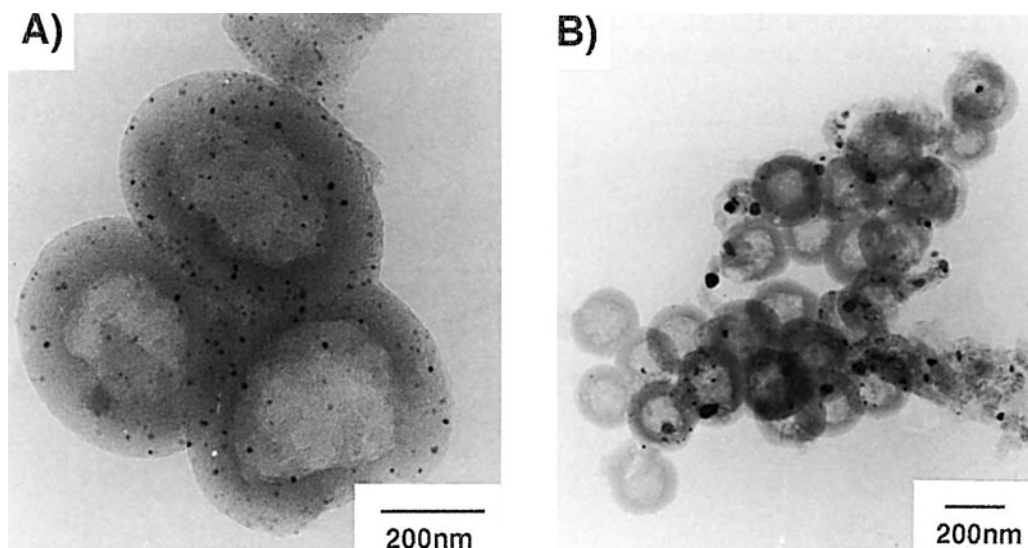


Figure 1 TEM images of poly(St-co-AN) particles-Rh(III) complexes pyrolyzed at (A) 800°C and (B) 1000°C for 4 h.

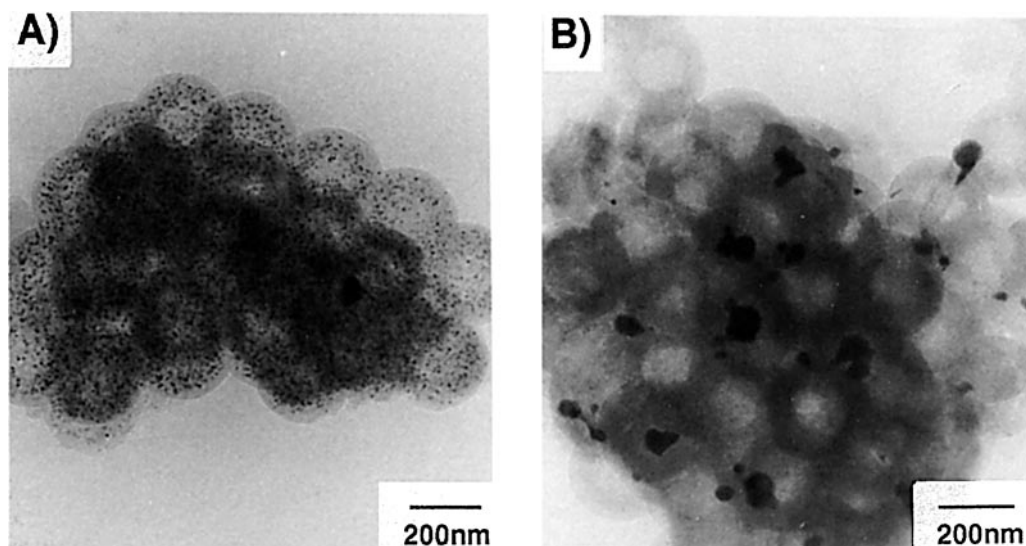


Figure 2 TEM images of poly(St-co-AA-co-AN) particle-Pd(II) complexes pyrolyzed at (A) 800°C and (B) 1000°C for 4 h.

immobilized carbon particles were obtained by pyrolysis of poly(St-co-AN) or poly(St-co-AA-co-AN) particle-Co(II) or -Ni(II) complexes. In both cases, the particle sizes of metal formed increased with increasing pyrolysis temperature.

The sizes of ultrafine metal particles formed on carbon particles were estimated from the line width of the XRD profiles using Scherrer's equation. The particle sizes of metal, as a whole, increased with increasing pyrolysis temperature, and the sizes of noble metals such as Pd and Rh are smaller than those of Co, Ni, and Cu, even though the amounts of metal ions immobilized on the copolymer particles are higher in Pd and Rh (Table III). Shioyama et al.¹⁰ suggested that the size of ultrafine metal par-

ticles generated by the reduction of metal chlorides in a graphite matrix is related to the bulk melting point of the metal, i.e., the higher the bulk melting point, the smaller the metal size. The bulk melting points of Co, Ni, Cu, Ag, Pd, and Rh are 1495, 1455, 1083, 961, 1552, and 1960, respectively. The smaller size of Rh particles may be due to the high melting point. On the other hand, Potoczna-Petru and Krajczyk¹¹ suggested, from the morphology and microstructure of Co particles formed on the carbon surface by reduction treatment, that Co particles were formed as a result of migration and coalescence of smaller crystallites. From this suggestion and the changes of particle size by pyrolysis temperature, it is supposed that, in the case of Co, Ni, Cu, and Ag, metal atoms (zero-valent) generated by pyrolysis of metal complexes on copolymer particles move to re-

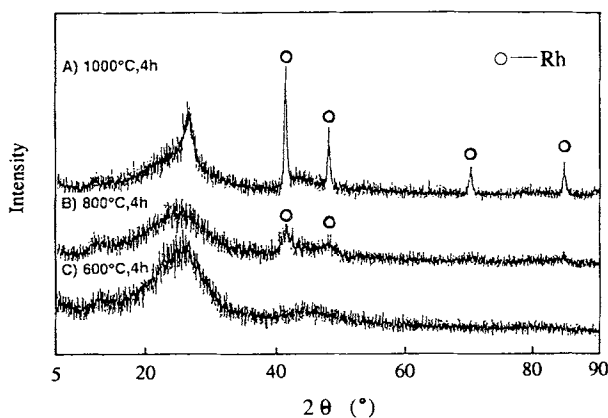


Figure 3 XRD patterns of poly(St-co-AN) particle-Rh(III) complexes pyrolyzed at 600, 800, and 1000°C for 4 h.

Table III Particle Size of Ultrafine Metal Particles Formed by Pyrolysis of Poly(St-co-AA-co-AN) Particle-Metal Ion Complexes

Metal Compounds	Metal Size (nm)		
	600°C	800°C	1000°C
CoCl ₂	nd	13	20
NiCl ₂	nd	15	18
CuCl ₂	nd	nd	16
AgNO ₃	5	16	49
PdCl ₂	nd	3	16
RhCl ₃	nd	3	15

nd: not determined.

Table IV Catalytic Activity of Ultrafine Metal Particles Immobilized on Carbon Particles for Degradation of H₂O₂

Copolymer Complexes	Pyrolysis		Activity ([O ₂]mL/g-Metal, min)
	Temp (°C)	Time (h)	
<u>Poly(St-co-AA-co-AN)</u>			
—CoCl ₂	1000	2	1607
—NiCl ₂	1000	4	807
—CuCl ₂	1000	2	357
<u>Poly(St-co-AN)</u>			
—PdCl ₂	1000	4	267
—RhCl ₃	1000	4	9030
Rh/carbon			1930
Pd/carbon			8800

sult in the formation of aggregate-like clusters and the aggregates grow to a great size.

Catalytic Activity of Ultrafine Metal Particles Immobilized on Carbon Particles

Ultrafine metal particles have wide applications as active catalysts for various chemical reactions. The catalytic activity of ultrafine metal particles immobilized on carbon particles for the decomposition reaction of hydrogen peroxide was measured. The results are shown in Table IV. The results are compared with commercially available Rh or Pd particles supported on carbon powder (Rh/C or Pd/C). All the metal particles immobilized on carbon particles obtained by pyrolysis of copolymer particle-metal ion complexes exhibited catalytic activities. However, the activities of Ni, Co, Cu, and Pd particles immobilized on carbon particles are lower than those of commercial Rh/C or Pd/C. On the other hand, Rh particles immobilized on carbon particles from the poly(St-co-AA-co-AN)-Rh ion complex gave higher activity than did Rh/C and comparable activity to commercial Pd/C. Regarding the effect of pyrolysis temperature on the catalytic activities of ultrafine metal particles, the activities of ultrafine metal particles formed by pyrolysis at 800°C was on the whole lower than that formed at 1000°C, even though the size of metal particles at 800°C is smaller than that at 1000°C. Previously, we reported that carbon particles obtained by pyrolysis of styrene-acrylonitrile copolymer particles contain a high N content from the elemental analysis of carbon par-

ticles.⁸ The catalytic activity of ultrafine metal particle-supported carbon particles obtained by pyrolysis of styrene/acrylic acid/acrylonitrile copolymer particles may be influenced by N and metal nitrides. This influence is higher than is the size of metal particles. However, this suggestion could require further examination in the future.

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Received July 31, 1995

Accepted November 29, 1995