

Preparation and Characteristics of Ultrafine Metal Particles Immobilized on Fine Polymer Particles

HISASHI TAMAI,* HIROYUKI SAKURAI, YOSHIFUMI HIROTA, FUMITAKA NISHIYAMA, and HAJIME YASUDA

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashihiroshima 724, Japan

SYNOPSIS

Ultrafine metal particles immobilized on fine copolymer particles were produced by reduction of copolymer particles–metal ion complexes. Submicrometer-size copolymer particles containing nitrogen, prepared by emulsifier-free emulsion polymerization, were applied. Transmission electron microscopy (TEM) observation and X-ray diffraction analysis indicated that ultrafine noble metal particles with diameter below 10 nm were formed and uniformly immobilized on the surface of copolymer particles. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Ultrafine metal particles immobilized on various materials have attracted considerable interest since these composites exhibit wide application as active catalysts in various chemical reactions such as hydrogenation and hydrogenolysis. Ultrafine metal particles supported on inorganic materials are generally prepared by impregnation and ion-exchange methods.^{1–3} In these methods, formation of ultrafine metal particles occurs by reduction of inorganic salts. We chose here fine polymer particles possessing high surface area and fluidity as supporting materials since these should exhibit anomalous reactivity. However, there have been few investigations on the preparation of ultrafine metal particles supported on polymer particles, although Warshawsky et al.⁴ reported the production of metal-covered polymer particles by chemical metal deposition.

On the other hand, there have been a large number of reports on the formation of ultrafine metal particles by reducing metal ion in solution. Rampino et al.^{5,6} reported the formation of palladium particles with an average diameter of 70 nm, by reducing aqueous Pd(II) hydroxide in an aqueous solution of poly(vinyl alcohol). Hirai et al.^{7,8} reported the production of noble metal particles with particle size of 10–50 Å by reducing the corresponding metal salts

with primary or secondary alcohols or ether in an aqueous solution of poly(*N*-vinyl-2-pyrrolidone). They found that palladium particles, prepared by reduction of Pd(II) chloride with methanol in the presence of poly(*N*-vinyl-2-pyrrolidone) catalyze partial hydrogenation of cyclopentadiene and methyl esters of unsaturated fatty acid to the corresponding monoenes.⁹

Regarding the preparation of fine polymer particles, emulsifier-free emulsion polymerization is well known to produce submicrometer-size fine polymer particles. One of the characteristics of this method lies in the formation of polymer particles which are monodispersed in size and highly spherical. Therefore we have used this type of polymer particle as supporting material for ultrafine metal particles.

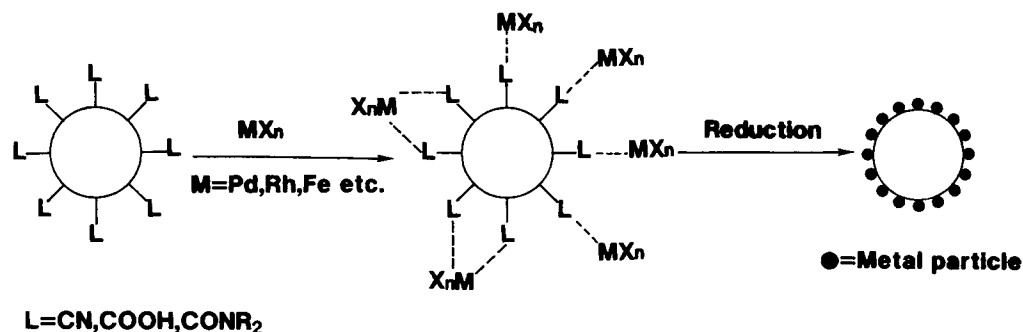
Scheme I illustrates the outline of the present synthesis of ultrafine metal particles by reduction of metal ion on the surface of fine polymer particles.

EXPERIMENTAL

Materials

Styrene (St), acrylonitrile (AN), and divinylbenzene (DVB) from Wako Pure Chemical are purified by distillation under reduced pressure. *N*-vinylimidazole (Vlz) from Aldrich was distilled under a reduced Ar atmosphere. Acrylamide (AAM) from Wako was recrystallized from benzene. Metal chlorides, viz.,

* To whom correspondence should be addressed.



Scheme 1 Preparation of ultrafine metal particles immobilized on fine polymer particles.

Co(II) chloride, Rh(III) chloride, Cu(II) chloride, and Ni(II) chloride from Wako were used without further purification. Silver nitrate, hexachloroplatinic acid (H_2PtCl_6) and sodium palladium chloride (Na_2PdCl_4) were also used without further purification. Other chemicals were all analytical grade.

Styrene/acrylonitrile copolymer [poly(St-co-AN)], styrene/acrylamide copolymer [poly(St-co-AAm)], styrene/vinylimidazole copolymer [poly(St-co-VIz)], and styrene/vinylimidazole/divinylbenzene copolymer [poly(St-co-VIz-co-DVB)] fine particles were prepared by copolymerizing styrene with functional monomers such as AN, AAm, VIz, and DVB by emulsifier-free emulsion polymerization using potassium persulfate (KPS) or 2,2-azobis-amidinopropane hydrochloride (AAP) as initiators. The preparation conditions are shown in Table 1. The sizes of particles obtained ranges of 300–350 nm in diameter, essentially monodisperse in size. The resulting copolymer particles were purified by repeating serum replacement of the dispersions.

Immobilization of Metal Ions

Immobilization of metal ions was conducted by stirring fine copolymer particles in aqueous or ethanol

solution of metal compounds. Typical procedures are as follows.

The aqueous dispersion of poly(St-co-AN) particles (0.55 g/5 mL) was added to the aqueous Na_2PdCl_4 solution (0.24 g/55 mL) and the mixture was stirred for 1 h at 60°C. Pd ion immobilized on poly(St-co-AN) particles were separated by centrifugation and redispersed in water. After repeating the centrifugation–redispersion procedure, the particles were dried under reduced pressure.

Poly(St-co-AAm) fine particles dispersed in water–ethanol (volume ratio = 1 : 5) (0.24 g/30 mL) were added to the ethanol solution of RhCl_3 (0.15 g/20 mL). The mixture was stirred for 1 h at room temperature. Further purification of Rh ion immobilized on poly(St-co-AAm) particles was conducted in essentially the same manner as described for Pd ion.

Poly(St-co-VIz) (1 g) or poly(St-co-VIz-co-DVB) (1 g) fine particles was stirred in 50 mL of metal ion aqueous solutions of $2 \times 10^{-2} M$ in the case of CuCl_2 , CoCl_2 , and NiCl_2 and of $4 \times 10^{-2} M$ in the case of H_2PtCl_6 , Na_2PdCl_4 , and RhCl_3 for 3 h at room temperature. The purification was carried out in a similar manner as described for Pd ion immobilized on poly(St-co-AN) particles.

Table I Preparation of Fine Polymer Particles^a

	Poly(St-co-AN)	Poly(St-co-AAm)	Poly(St-co-VIz)	Poly(St-co-VIz-co-DVB)
Styrene, mol/L	0.82	0.86	1.0	1.0
Acrylonitrile, mol/L	0.82	—	—	—
Acrylamide, mol/L	—	0.35	—	—
N-vinylimidazole, mol/L	—	—	0.30	0.30
Divinylbenzene, mol/L	—	—	—	—
KPS, mol/L	2.0×10^{-3}	2.0×10^{-3}	—	0.067
AAP, mol/L	—	—	5.0×10^{-3}	5.0×10^{-3}
Particle diameter, nm	330	287	354	331

^a Polym. temp., 70°C; polym. time, 6 h; KPS: potassium persulfate; AAP: 2,2-azobis-(2-amidinopropane) dihydrochloride.

Table II Amount of Metal Ions Immobilized on PS and Poly(St-co-VIz) Fine Particles^a

Polymer Particle	Metal Compounds	Metal Conc. (mol/L)	Immobilized Amounts (mg/g Particle)	
PS	FeCl ₂	0.1	0.07	
		0.2	0.09	
		0.4	0.13	
		0.8	0.58	
	CoCl ₂	0.02	0.13	
		NiCl ₂	0.02	0.17
		CuCl ₂	0.06	0.08
		AgNO ₃	0.06	0.56
		H ₂ PtCl ₆	0.002	0.08
		Poly(St/VIz)	FeCl ₂	0.02
0.1	4.1			
0.2	6.0			
0.4	8.1			
0.8	21.1			
CoCl ₂	0.02		0.21	
	0.4		0.54	
NiCl ₂	0.02		0.40	
	0.4		3.3	
CuCl ₂	0.02		3.9	
	0.06		4.0	
	0.2		4.5	
	0.4		5.5	
	0.6		5.8	
AgNO ₃	0.06		5.8	
Na ₂ PdCl ₄	0.016		5.9	
H ₂ PtCl ₆	0.002		8.7	
	0.004		16.8	
	0.006		29.0	

^a Particle concentration: 20 g/L.

Reduction of Copolymer Particles–Metal Ion Complexes

Fine copolymer particles treated with metal compounds were reduced using NaBH₄ or NH₂NH₂. For example, 0.4 g of metal ion immobilized on particles were suspended in ethanol solution (50 mL) of

NaBH₄ (0.2 mol/L) or ethanol solution (50 mL) of NH₂NH₂ (0.28 mol/L). The mixture was refluxed for 3 h, and then fine copolymer particles were separated by centrifugation.

Table III Amount of Metal Ions Immobilized on Poly(St-co-VIz-co-DVB) Fine Particles

Metal Compounds	Particle Conc. (g/L)	Metal Conc. (mol/L)	Immobilized Amounts (mg/g Particle)
CoCl ₂	20	0.2	1.05
NiCl ₂	20	0.2	2.95
CuCl ₂	20	0.2	5.87
H ₂ PtCl ₆	20	0.004	35.7
Na ₂ PdCl ₄	20	0.004	31.3
RhCl ₃	20	0.004	9.7

Catalytic Activity

Catalytic activities of ultrafine metal particles immobilized on poly(St-co-VIz-co-DVB) particles were tested for the hydrogenation reaction of 1-hexene. Noble metal particles immobilized on poly(St-co-VIz-co-DVB) particles were dried under reduced pressure for 1 h at room temperature and aged in hydrogen atmosphere for 1 h. After the addition of an *n*-heptane solution of 1-hexene to these metal particles immobilized on copolymer particles, a part of the reactant was taken out to examine the compositional analysis of the reactant by gas chromatography.

Table IV Amount of Noble Metals Immobilized on Poly(St-co-VIz-co-DVB) Fine Particles after Reduction

Copolymer Particle	Metal Ion	Reducing Agent	Immobilized Amount (mg/g)
Poly(St-co-VIz-co-DVB)	Pt	—	35.7
		NaBH ₄	24.3
		NH ₂ NH ₂	30.8
Poly(St-co-VIz-co-DVB)	Pd	—	31.3
		NaBH ₄	18.0
		NH ₂ NH ₂	18.5
Poly(St-co-VIz-co-DVB)	Rh	—	9.7
		NaBH ₄	6.1
		NH ₂ NH ₂	5.2

Characterization

The size and morphology of ultrafine metal particles immobilized on copolymer particles were investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis. TEM observation was conducted using an Akashi ABT 002B (Akashi Electron Beam Technology) and XRD patterns were measured by an X-ray diffractometer (Rigaku RDA IB).

The amounts of immobilized metal ions and metal particles were measured by particle-induced X-ray emission (PIXE) analysis. PIXE analysis was performed using a van de Graaff accelerator system.

Electron spectroscopy chemical analysis (ESCA) spectra were obtained using the ULVAC-PHI ESCA 5000 with a MgK_α X-ray source radiation generated

at 15 keV and 30 mA. Gas chromatographic analysis was performed on a Hitachi 163 gas chromatograph equipped with a flame ionization detector.

RESULTS AND DISCUSSION

Amount of Metal Immobilized

Immobilization of metal ions is greatly dependent on the capability of chemical and physical adsorption on the surface of particles. Affinity of metal ions on the polymer surface due to physical adsorption is generally weak, and most metal ions deposited on the surface of polystyrene (PS) particles are readily removed by repeated serum replacement. Thus, the amounts of metal ions im-

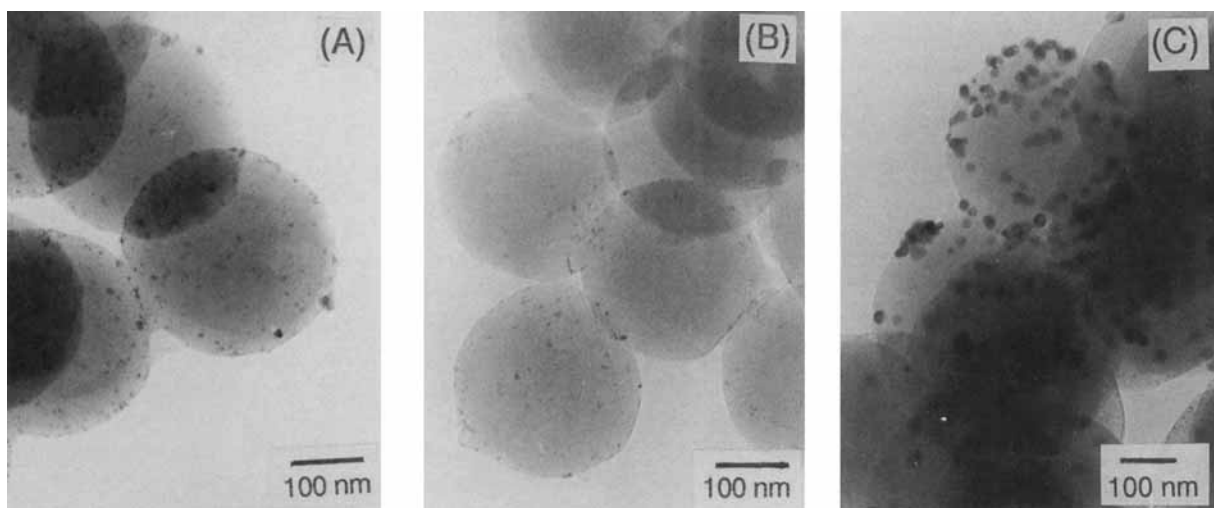


Figure 1 TEM images of fine copolymer particles-metal ion complexes reduced by NaBH₄: (a) poly(St-co-AN)-Pd(II) ion complex; (b) poly(St-co-AAm)-Rh(III) ion complex; (c) poly(St-co-VIz)-Pd(II) ion complex.

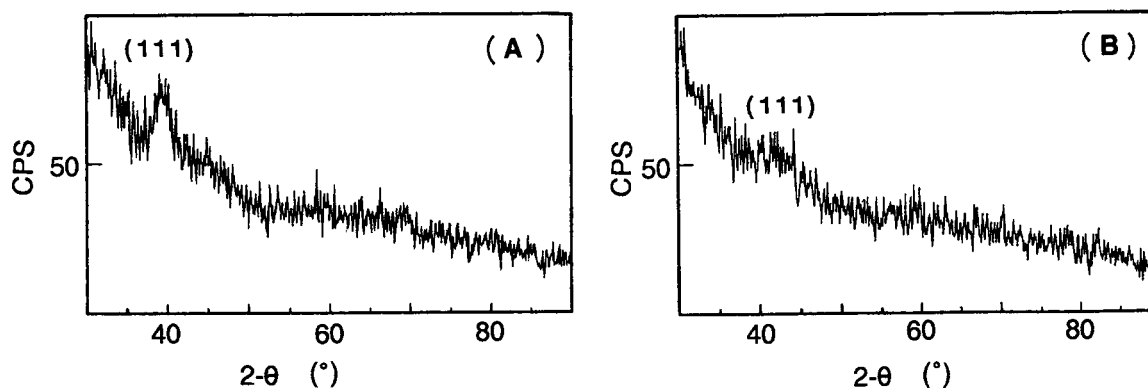


Figure 2 XRD patterns of fine copolymer particles–metal ion complexes reduced by NaBH_4 : (a) poly(St-co-AN)-Pd(II) ion complex; (b) poly(St-co-AAm)-Rh(III) ion complex.

mobilized on PS particles are very low, as shown in Table II. On the other hand, the poly(St-co-VIz) particles exhibit much higher adsorption than those on PS particles. Especially, noble metal ions such as Pd(II) and Pt(IV) ions are rapidly fixed on the surface of poly(St-co-VIz) particles, and the immobilized amounts increase with increasing concentration of metal ions. As shown in Table III, the amounts of Pd(II), Pt(IV), and Rh(III) ions immobilized on poly(St-co-VIz-co-DVB) particles are slightly higher than those on poly(St-co-VIz) particles.

The comparisons of the amounts of metal ions immobilized on poly(St-co-VIz) and poly(St-co-VIz-co-DVB) particles with those on PS particles indicate that the metal ions on poly(St-co-VIz) and poly(St-co-VIz-co-DVB) particles immobilize by complex formation of metal ions with nitrogen atoms of imidazole groups present on the surface of particles. With respect to complex formation with poly(VIz), Lippert et al.¹⁰ reported that the stoichiometry of the complex formed in a solution containing excess Ni^{2+} was $[\text{imidazole}]/[\text{Ni}^{2+}] = 6 : 1$ in aqueous solution and $4 : 1$ in aqueous 1M KNO_3 when a poly(VIz) solution was added to a Ni^{2+} solution. Geraty and Vos¹¹ found that, from spectroscopic and electrochemical studies, different types of ruthenium–poly(VIz) complex form depending upon the reaction condition. Additionally, Chen and Challa¹² described a Cu^{2+} complex of poly(St-co-VIz) that existed in a monomeric structure of $[\text{imidazole}]/[\text{Cu}^{2+}] = 4 : 1$ in solution at high ligand–copper ratio, as revealed by the electron paramagnetic resonance spectra of the complexes. These results indicate that the immobilization of metal ions occurs by complex formation on the surface of copolymer particles where

nitrogen-containing polymer such as poly(VIz), poly(AN), and poly(AAm) are present.

Table IV shows the amounts of noble metals immobilized on the surface of poly(St-co-VIz-co-DVB) fine particles after reduction with NaBH_4 and NH_2NH_2 . The amounts of metal immobilized lowered slightly as compared with those before reduction. This fact suggests that only a small part of the metal ions are removed from the surface of fine copolymer particles through the reducing process.

TEM Observation

Figure 1 shows typical TEM photographs of poly(St-co-AN) and poly(St-co-VIz) particles–Pd ion complexes and poly(St-co-AAm) particles–Rh ion complex after reduction by NaBH_4 . In the case of poly(St-co-AN)–Pd and poly(St-co-AAm)–Rh particles, the formation of ultrafine metal particles with diameter below 10 nm is observed, and these ultrafine metal particles are uniformly immobilized on the surface of fine copolymer particles. Poly(St-co-VIz) particles–Pd ion complex produced relatively large metal particles. Figure 2 shows the XRD profiles of the reduction products from poly(St-co-AN) particles–Pd ion complex and poly(St-co-AAm) particles–Rh ion complex, respectively. In both cases, weak and broad diffractions at $2\theta = \text{about } 40^\circ$ exist in the diffraction pattern. This is ascribable to the formation of highly ultrafine particles. These diffractions corresponding to Pd (2θ of main diffraction = 40.1°)¹³ and Rh (2θ of main diffraction = 41.1°)¹³ indicate that ultrafine Pd or Rh particles are formed on the surface of fine copolymer particles by reduction of fine copolymer particles–metal ion complexes. The resulting

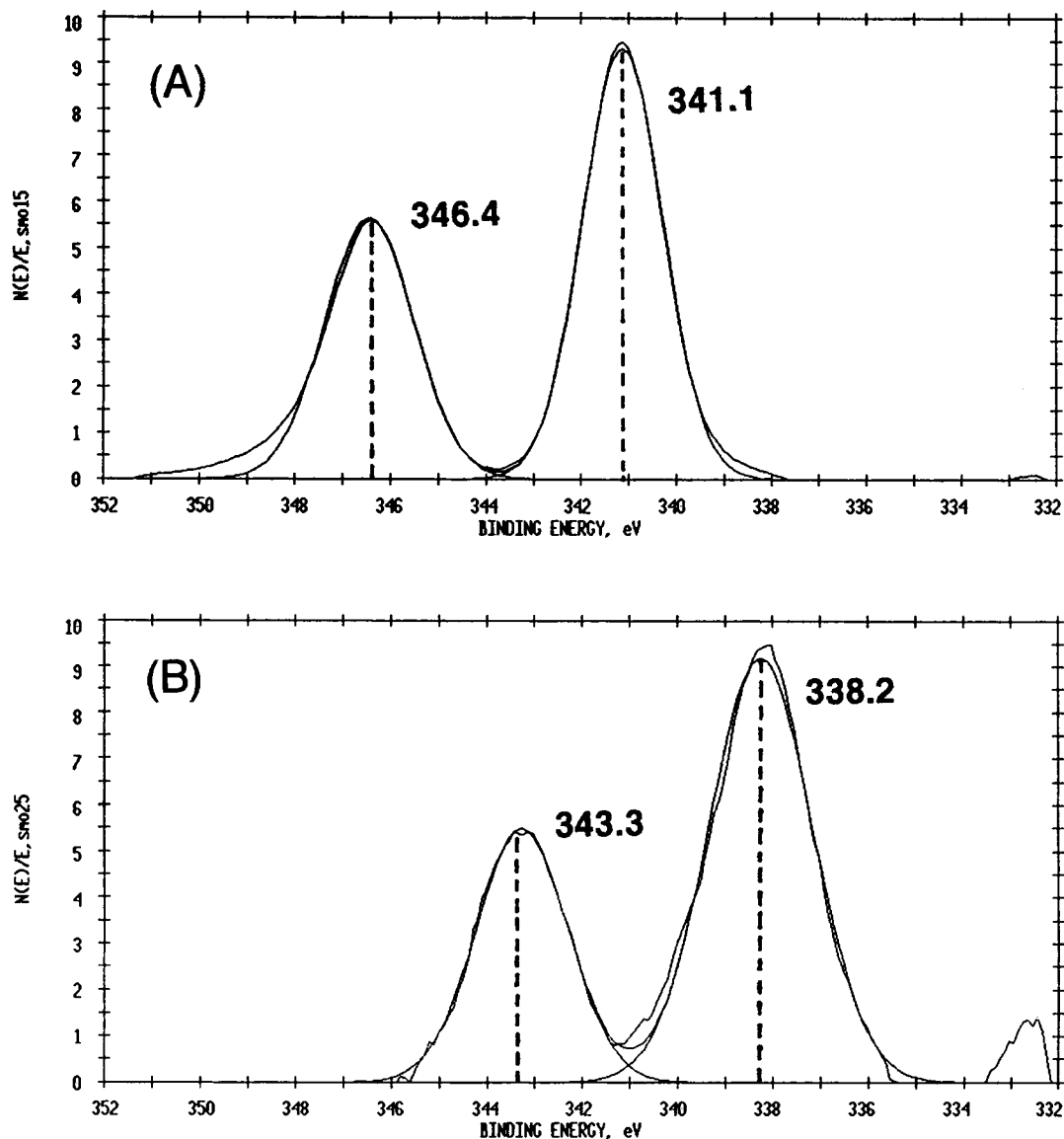


Figure 3 ESCA spectra of poly(St-co-VIz-co-DVB) particles-Pd(II) ion complex: (a) before reduction; (b) after reduction by NH_2NH_2 .

amounts of immobilized metal are shown in Table IV and indicate that a large portion of ultrafine metal particles are fixed stably on the surface of fine copolymer particles. In previous work^{14,15} on the characteristics of fine copolymer particles prepared by emulsifier-free emulsion polymerization, we reported that copolymerization of hydrophilic monomers such as acrylamide and 2-hydroxyethyl methacrylate resulted in a water-soluble polymer layer on the surface of particles. From this result, we can imagine the presence of flexible polymer chains protruding from the surface of these copolymer particles.

On the other hand, the generation of ultrafine

metal particles was not observed in the case of the poly(St-co-VIz) particles-Co(II), -Ni(II), or -Cu(II) ion complexes after reduction by NaBH_4 . As shown in Table II, the amounts of these metal ions immobilized on poly(St-co-VIz) fine particles are low. Therefore, it is supposed that there is no formation of ultrafine metal particles or the particles are too small to be observed by TEM analysis. The results on metal immobilization on polystyrene particles (shown in Table II) suggest that the low immobilization of metal ions such as Co(II), Ni(II), and Cu(II) should be attributed to poor complex formation between these metal ions and poly(VIz). However, complex formation between imidazole units on the

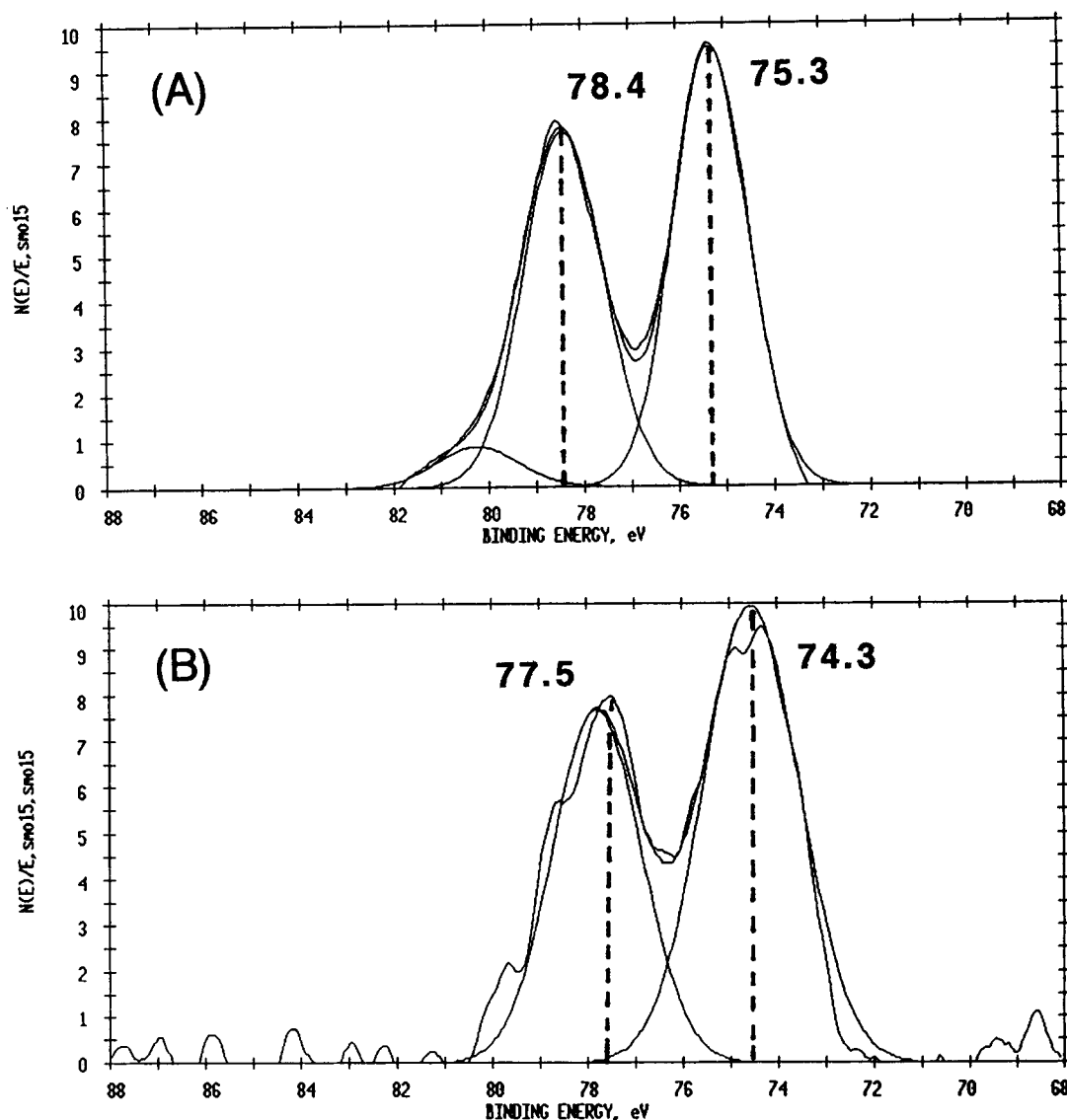


Figure 4 ESCA spectra of poly(St-co-Vlz-co-DBV) particles-Pt(IV) ion complex: (a) before reduction; (b) after reduction by NH_2NH_2 .

surface of poly(St-co-Vlz) particles and metal ions is not clear.

ESCA Analysis

The reduction products from poly(St-co-Vlz-co-DVB) particles-metal ion complexes were investigated by ESCA analysis. The results on poly(St-co-Vlz-co-DVB) particles-Pd(II), -Pt(IV), and -Rh(III) ion complexes are shown in Figures 3-5, respectively. As shown in Figure 3, the electron binding energy of Pd_{3d} of poly(St-co-Vlz-co-DVB) particles-Pd ion complex before reduction is 341.1 eV. This binding energy is close to that of PdCl_2 ($\text{Pd}_{3d} = 337.8$ eV).¹⁶ The electron binding energy of Pd_{3d} after reduction

with NH_2NH_2 is 338.2 eV. This binding energy is comparable to that of PdO_2 ($\text{Pd}_{3d} = 337.9$ eV)¹⁷ rather than that of Pd ($\text{Pd}_{3d} = 335.2$ eV).¹⁸ Similarly, the binding energy of $\text{Pt}_{4f} = 75.3$ eV of poly(St-co-Vlz-co-DVB) particles-Pt(IV) ion complex before reduction resembles that of K_2PtCl_6 ($\text{Pt}_{4f} = 75.4$ eV),¹⁹ whereas the binding energy of $\text{Pt}_{4f} = 74.3$ eV after reduction is almost consistent with that of PtO_2 ($\text{Pt}_{4f} = 74.2$ eV).²⁰ These results suggest that Pd(II) or Pt(IV) ions existing on the surface of poly(St-co-Vlz-co-DVB) particles are reduced to Pd(0) and Pt(0) by reduction treatments, and ultrafine metal particles are formed. Then, spontaneous oxidation of the resulting ultrafine metal particles in air produced PdO_2 and PtO_2 . On the other hand, the elec-

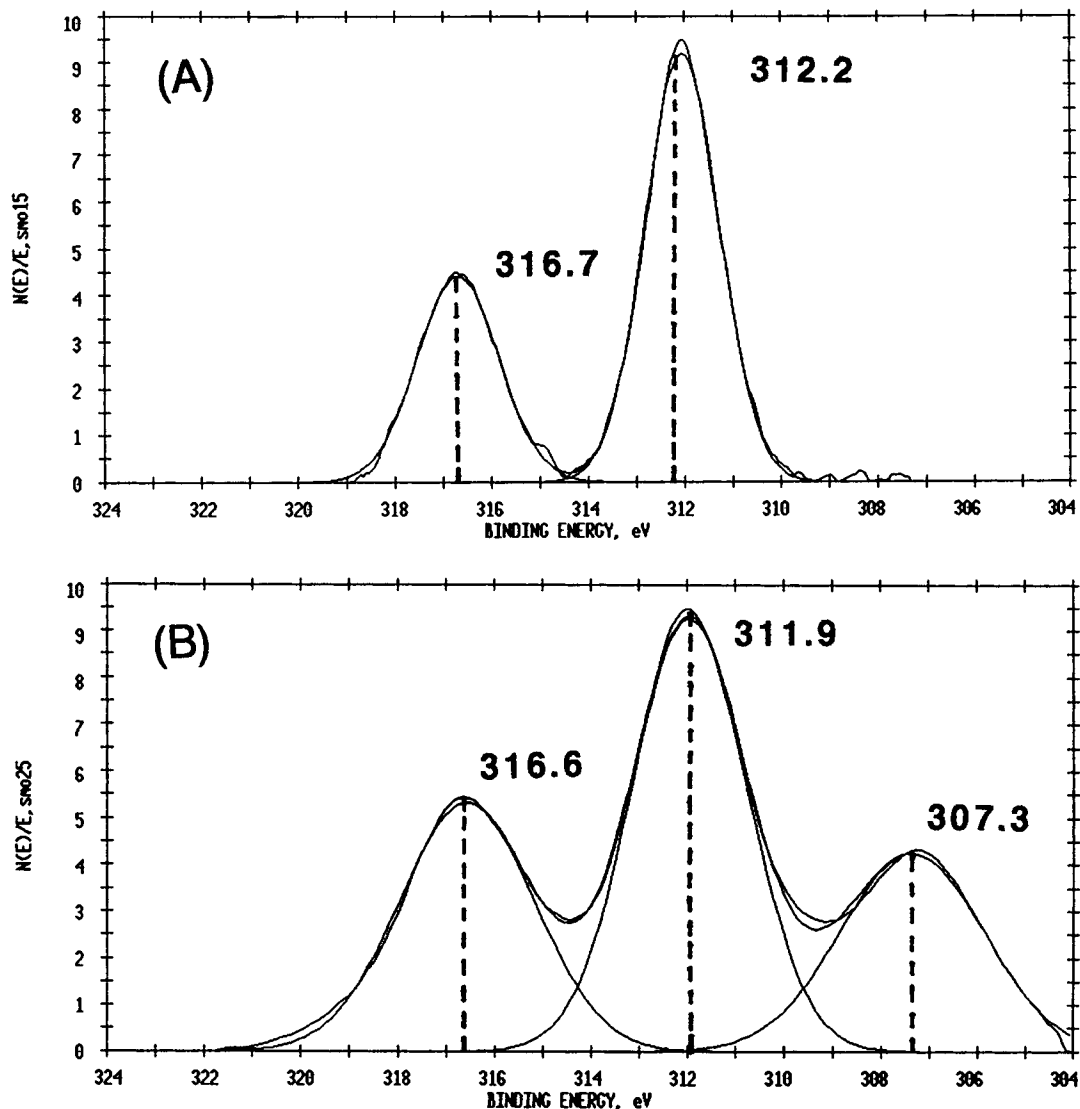


Figure 5 ESCA spectra of poly(St-co-Vlz-co-DBV) particles-Rh(III) ion complex: (a) before reduction; (b) after reduction by NaBH_4 .

tron binding energy of $\text{Rh}_{3d} = 312.2$ eV of poly(St-co-Vlz-co-DVB) particles-Rh(III) ion complex before reduction is close to that of RhCl_3 ($\text{Rh}_{3d} = 310.1$ eV).²¹ In the case of poly(St-co-Vlz-co-DVB) particles-Rh(III) ion complexes after reduction by NaBH_4 , an electron binding energy of 307.3 eV is newly observed in addition to the binding energies of 311.9 and 316.6 eV. The binding energy of 307.3 eV is almost consistent with that of $\text{Rh}_{3d} = 307.2$ eV of Rh.²² This result indicates that, under the conditions tested in this work, ultrafine Rh particles are formed together with imidazole-Rh(III) complex

on the surface of poly(St-co-Vlz-co-DVB) particles-Rh(III) ion complexes even after reduction.

Catalytic Activity

Figure 6 shows the results on the hydrogenation of 1-hexene using the reduction products from poly(St-co-Vlz-co-DVB) particles-noble metal ion complexes. A comparison of the relative rates of hydrogenation indicates that ultrafine Rh particles produced by reduction with NaBH_4 exhibited the highest activity, whereas other poly(S-co-/Vlz-co-

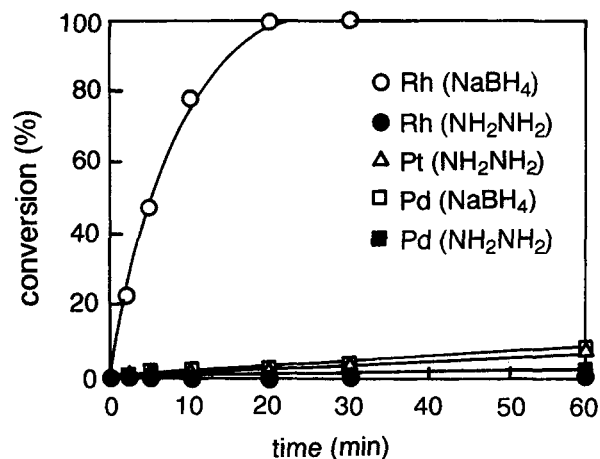


Figure 6 Hydrogenation of 1-hexene catalyzed by reduced poly(St-co-VIz-co-DVB) particles-metal ion complexes at mole ratio of 1-hexene/metal = 5×10^2 and metal concentration = 3.2×10^{-4} mol/L.

DVB) particles-metal (Pt, Pd) complexes gave lower activity presumably due to autooxidation with air.

REFERENCES

1. D. C. Koningsberger, J. B. A. D. van Zon, H. F. J. vant Blik, G. J. Visser, R. Prins, A. N. Mansour, D. E. Sayers, and D. R. Short, J. R. Katzer, *J. Phys. Chem.*, **89**, 4075 (1985).
2. R. J. Emrich, A. N. Mansour, D. E. Sayers, S. T. Mcmillan, and J. R. Katzer, *J. Phys. Chem.*, **89**, 4261 (1985).
3. M. A. Baltanas, J. H. Onuferko, S. T. Mcmillan, and J. R. Katzer, *J. Phys. Chem.*, **91**, 3772 (1987).
4. A. Warshawsky and D. A. Upson, *J. Polym. Sci., Part A, Polym. Chem.*, **27**, 2963 (1989).
5. L. D. Rampino and F. F. Nord, *J. Am. Chem. Soc.*, **63**, 2745 (1941).
6. L. D. Rampino, K. E. Kavanagh, and F. F. Nord, *Proc. Natl. Acad. Sci., U.S.A.*, **29**, 246 (1943).
7. H. Hirai, Y. Nakao, and N. Toshima, *J. Macromol. Sci., Chem.*, **A12**, 1117 (1978).
8. H. Hirai, Y. Nakao, and N. Tpsima, *J. Macromol. Sci., Chem.*, **A13**, 727 (1979).
9. H. Hirai, H. Chawanya, and N. Toshima, *Nippon Kagaku Kaishi*, 1027 (1984).
10. J. L. Lippert, J. A. Robertson, J. R. Havens, and J. S. Tan, *Macromolecules*, **18**, 63 (1985).
11. S. M. Geraty and J. G. Vos, *J. Chem. Soc. Dalton Trans.*, 3073 (1987).
12. W. Chen and G. Challa, *Polymer*, **31**, 2171 (1990).
13. W. F. McLune, Ed., *Powder Diffraction File. Inorganic Volume*, JCPDS International Center for Diffraction, Swarthmore, PA, 1988.
14. H. Tamai, T. Murakami, and T. Suzawa, *J. Appl. Polym. Sci.*, **30**, 3857 (1985).
15. H. Tamai, M. Hasegawa, and T. Suzawa, *J. Appl. Polym. Sci.*, **38**, 403 (1989).
16. G. Kumar, J. R. Blackburn, R. G. Albridge, W. E. Moddemann, and M. M. Jones, *Inorg. Chem.*, **11**, 296 (1972).
17. K. S. Kim, A. F. Gossmann, and N. Winograd, *Anal. Chem.*, **46**, 197 (1974).
18. R. J. Bird and P. Swift, *J. Electron. Spectrosc. Relat. Phenom.*, **21**, 227 (1980).
19. L. E. Cox and D. M. Hercules, *J. Electron. Spectrosc. Relat. Phenom.*, **1**, 193 (1972).
20. J. Escard, B. Pontviane, M. T. Chenebaux, and J. Cosyns, *Bull. Chim. Soc. Fr.*, 2400 (1972).
21. Y. Okamoto, N. Ishida, T. Imanaka, and S. Teranishi, *J. Catal.*, **58**, 82 (1979).
22. R. M. Friedman, J. Hudis, M. L. Perlman, and R. E. Watson, *Phys. Rev.*, **B8**, 2434 (1973).

Received July 12, 1994

Accepted September 6, 1994