

Preparation of Ultrafine Metal Particles Supported on Alumina by Pyrolysis of Polymer Complex/Alumina Composites

HISASHI TAMAI,^{1*} HIROYUKI SAKURAI,¹ TAKAYUKI YAMAGIRI,¹ FUMITAKA NISHIYAMA,¹ HIROSHI SAKAI,² and HAJIME YASUDA¹

¹Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-hiroshima, Hiroshima 724, Japan; ²Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama 1-3-1 Higashi-hiroshima, Hiroshima 724 Japan

SYNOPSIS

Ultrafine metal particles supported on alumina were prepared by pyrolysis of poly(vinylferrocene)(Poly(VFc))/alumina or sodium polyacrylate-Pd(II) (Poly(AANa)-Pd(II))/alumina precursors at 800 ~ 1200°C. α -Fe particles produced on κ -Al₂O₃ was obtained by pyrolysis of the mixture of Poly(VFc)/alumina(5/5) at 1000°C. Crystalline Pd supported on alumina was also obtained from Poly(AANa)-Pd(II)/alumina precursor. The size of metal particles formed increased with increasing mixing ratio of polymer complex with alumina. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Ultrafine metal particles supported on inorganic materials such as silica and alumina exhibit high catalytic activity for various chemical reactions such as CO₂ reducing reaction with CH₄, and hydroformylation. Catalytic activity is mainly affected by the size and the dispersion of metal particles. In general, these dispersed metals supported on inorganic materials are prepared by the impregnation method and the ion-exchange method.¹⁻³ In these methods, using inorganic metal salts or metal ions, metal particles are formed by reduction of inorganic materials. Therefore, the size and the dispersion of metal particles are highly dependent on the reduction conditions.

On the other hand, it has been reported that ultrafine metal particles supported on inorganic materials were produced by using organometallics such as metal carbonyl⁴⁻⁹ and metal alkoxide.^{10,11} Recently, it was found that fine metal particles were generated by pyrolysis of polymer complexes as

starting materials.^{12,13} Miyanaga and co-workers¹² reported the production of ultrafine metal particles/carbon composites by pyrolysis of various polymer complexes and organometallics/coal pitch composites. Micheli¹³ reported the synthesis of reactive ceramic powders such as zirconia, yttria, alumina, and lead titanate by thermal decomposition of poly(acrylic acid)-multivalent metal complexes and concluded that they formed large agglomerates composed of small uniform size particles domains. However, there are few reports on the preparation of metal particles supported on inorganic materials by using polymer complexes as starting materials.

In this work, the preparation of ultrafine metal particles supported on alumina by pyrolysis of polymer complexes/alumina precursors is described.

EXPERIMENTAL

Materials

Alumina powder, Activated Acidic Super I, was purchased from ICN Biomedicals and was used without further purification. Sodium polyacrylate (Poly(AANa)) with DP = 15,000-20,000, was purchased from Wako Pure Chemical Ind. Vinylferrocene

* To whom correspondence should be addressed.

(VFc) was synthesized from ferrocene. Palladium (II), sodium chloride (Na_2PdCl_4) and other reagents from Wako Pure Chemical Ind. were all analytical grade and used without further purification.

Preparation of Poly(VFc)

Polymerization of VFc (0.1 g) was carried out at 85°C for 20 h using AIBN (4×10^{-3} g) as initiator. The resulting polymer was dissolved in toluene and precipitated in methanol. Molecular weight M_n by gel permeation chromatography was 1.45×10^4 .

Preparation of Polymer Complex/Alumina Precursors

Alumina powder was dispersed in Poly(VFc) dissolved in chloroform at various weight ratios. Poly(VFc)/alumina precursors were obtained by evaporation of the resulting dispersion to dryness.

Na_2PdCl_4 (0.26 g) was added to an aqueous solution (25 mL) of Poly(AANa) (0.5 g). The mixture was stirred at room temperature for 1 day. To the resulting Poly(AANa)-Pd(II) complex was added the alumina ground to a powder and the dispersion was evaporated to dryness.

The resulting Poly(VFc)/alumina and Poly(AANa)-Pd(II)/alumina composites were molded into pellets at a pressure of 600 kg/cm².

Pyrolysis of Polymer Complexes/Alumina Precursors

Pyrolysis of the pellets of polymer complex/alumina composites was conducted in an atmosphere of argon in an electric combustion tube furnace. Samples were heated to 800–1200°C at a rate of 100°C/h and maintained there for 10 h.

Measurements

Metal contents supported on alumina were determined by particle-induced x-ray emission (PIXE) analysis. The intensities of characteristic x-rays generated by irradiation of H^+ were measured and the concentrations of metal in alumina were calculated using authentic samples of various amounts of metals. TEM observation was conducted with an Akashi 002B electron microscope at 200kV. X-ray diffraction analysis was performed in a Rigaku RDA-IB system using $\text{CuK}\alpha$ radiation and assignments of the resulting metal species were made based on literature data.^{14,57} ^{57}Fe Mössbauer spectra were taken in a standard transmission geometry at room tem-

perature with ^{57}Co . BET surface area was determined by the N_2 adsorption method. Catalytic activity of the Pd/alumina composite was measured for hydrogenation of 1-hexene to *n*-hexane. After the Pd/alumina composite was treated in a H_2 stream for 1 h, 10 mL of *n*-heptane (78.4 mL) solution of 1-hexene (1.6 mL) was added in a H_2 atmosphere. The reactant solution was taken out and the composition was analyzed by gas chromatography.

RESULTS AND DISCUSSION

Pyrolysis of Poly(VFc)/Alumina Precursors

The yield and Fe contents of the pyrolytic products obtained from poly(VFc)/alumina precursors are shown in Table I. The yield decreased and Fe content increased with decreasing mixing ratio of poly(VFc)/alumina and raising the pyrolysis temperature. These results suggest that most Fe atoms derived from poly(VFc) remain in the alumina matrix. On the other hand, pyrolysis of ferrocene or vinylferrocene/alumina precursors does not produce Fe/alumina composites of high Fe content. This is ascribable to the sublimation of ferrocene and vinylferrocene during heat treatment.

A transmission electron microscope (TEM) image of the pyrolytic product obtained from poly(VFc)/alumina precursor, at a mixing ratio of poly(VFc)/alumina = 8/2 (wt/wt) at 1000°C, is

Table I Pyrolysis of Poly(VFc)/Alumina Precursor

Temperature (°C)	Poly(VFc)/Alumina Mixing Ratio	Yield (%)	Fe Content in Pyrolytic Product (mg/g)
800	1/9	93	10
	5/5	70	53
	8/2	53	94
1000	1/9	88	22
	2/8	84	49
	3/7	81	57
	4/6	76	69
	5/5	67	80
	6/4	64	77
	7/3	51	86
1200	8/2	48	110
	1/9	89	12
	5/5	66	76
	8/2	41	100

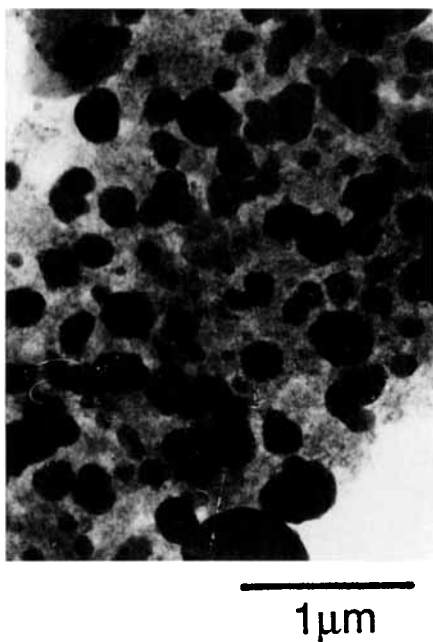


Figure 1 TEM photograph of the pyrolytic product from Poly(VFc)/alumina precursor of mixing ratio of Poly(VFc)/alumina = 8/2 (wt/wt) at 1000°C.

shown in Figure 1. Metal particles of average size of 100–200 nm disperse well in alumina matrix. Relatively large size of particles were generated from the precursor at a high mixing ratio of poly(VFc)/alumina, while pyrolysis of poly(VFc)/alumina at a low mixing ratio at lower temperature (800°C) produced small size of metal particles (about 2.5 nm). From these results, we can estimate that the

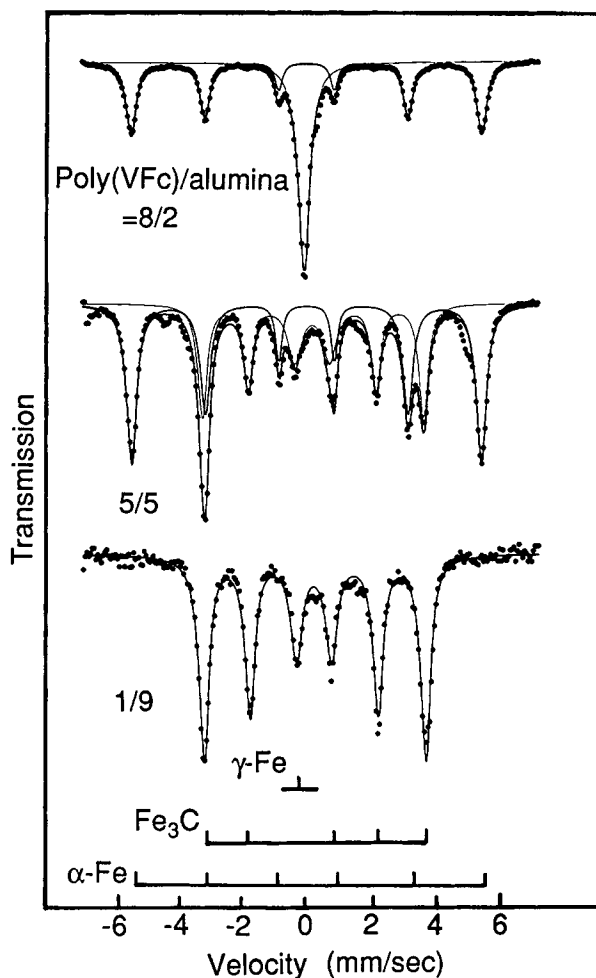


Figure 3 ⁵⁷Fe Mössbauer spectra of the pyrolytic products from Poly(VFc)/alumina precursors at 1000°C.

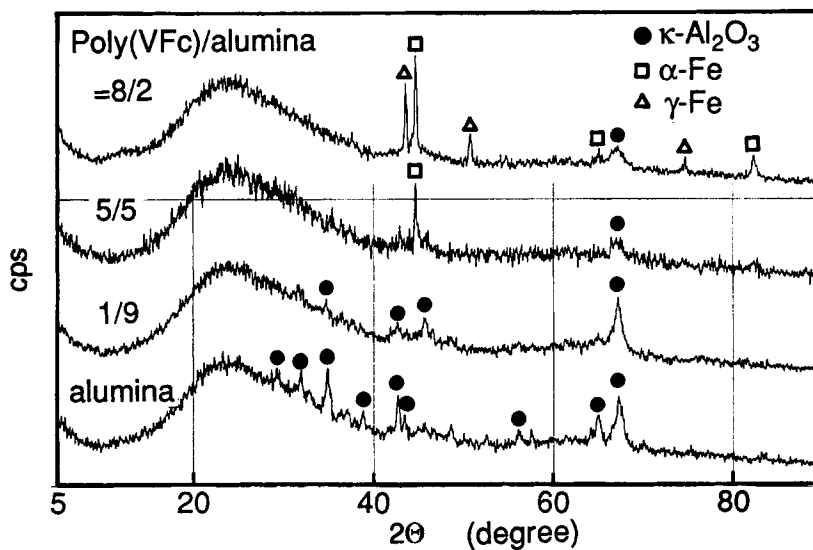


Figure 2 XRD patterns of the powdered pyrolytic products from Poly(VFc)/alumina precursors at 1000°C.

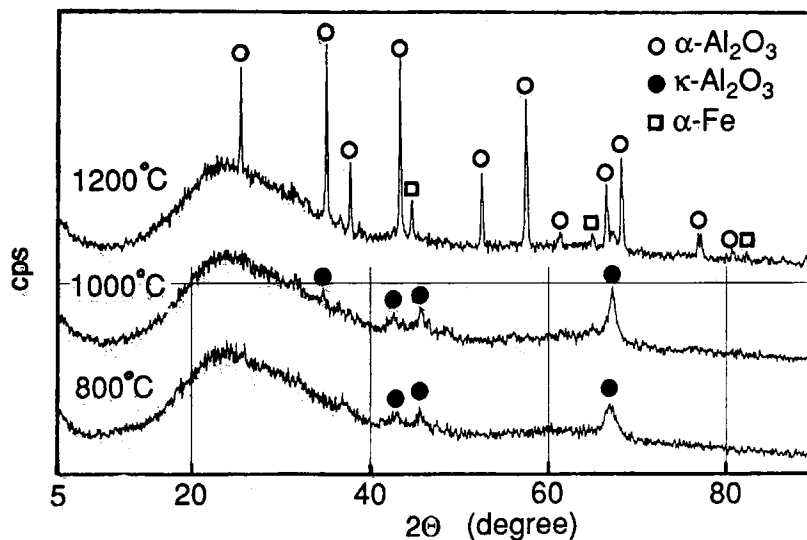


Figure 4 XRD patterns of the powdered pyrolytic products from Poly(VFc)/alumina composites of mixing ratio of Poly(VFc)/alumina = 1/9 (wt/wt).

cores of Fe particles are formed by aggregation of Fe atoms generated from the decomposition of poly(VFc) in the alumina matrix, and a high density of Fe atoms in the alumina matrix results in the formation of large particles. Concerning the variation of mixing ratio of poly(VFc) with alumina,

XRD patterns and Mössbauer spectra of metal particles/alumina composites obtained by pyrolysis at 1000°C are shown in Figures 2 and 3. XRD spectra indicate the formation of α -Fe particles in κ -Al₂O₃ matrix from the precursor of poly(VFc)/alumina = 5/5, while the increase in mixing ratio of poly(VFc) with alumina resulted in the formation of γ -Fe particles in addition to α -Fe particles as shown in the XRD pattern of the composite of poly(VFc)/alumina = 8/2 (wt/wt). On the other hand, the formation of Fe₃C from the 1/9 composite is revealed by Mössbauer spectra as shown in Figure 3. Consequently, in the pyrolytic products from the

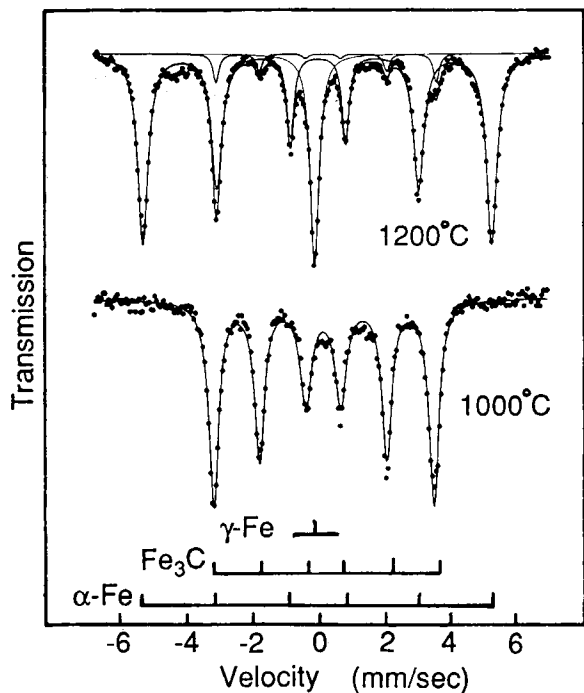


Figure 5 ⁵⁷Fe Mössbauer spectra of the pyrolytic products from Poly(VFc)/alumina composites of mixing ratio of Poly(VFc)/alumina = 1/9 (wt/wt).

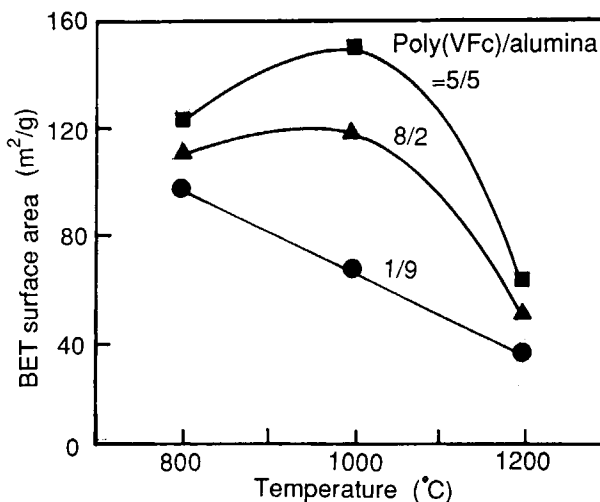


Figure 6 BET surface area of the pyrolytic products from Poly(VFc)/alumina precursors.

Table II Pyrolysis of Poly(AANa)-Pd(II) Alumina Precursors

Poly(AANa)-Pd(II) (Molar Ratio of AA Unit/Na ₂ PdCl ₄)	Poly(AANa)-Pd(II)/Alumina Mixing Ratio (wt)	Yield (%)	Pd Content in Pyrolytic Product (mg/g)
4/1	2/8	89	7
	5/5	71	19
	8/2	55	80
1/1	2/8	87	27
	5/5	65	44
	8/2	69	169
Na ₂ PdCl ₄	2/8	90	25
No Poly(AANa)	5/5	80	15
	8/2	77	4

1/9 composite, it is suggested that α -Fe particles and Fe₃C amorphous or fine particles are present as a mixture in κ -Al₂O₃ matrix. In addition, the Mössbauer spectrum shows the formation of α -Fe and γ -Fe particles from the 8/2 composite.

Concerning the effect of pyrolysis temperature, XRD patterns and Mössbauer spectra of Fe/alumina composites obtained from poly(VFc)/alumina = 1/9 are shown in Figures 4 and 5. Miyanaga et al.¹² reported the formation of Fe₃C and γ -Fe in addition to α -Fe in carbon matrix by heat treatment of coal pitch/poly(VFc) mixture at 800–1000°C, while pure ultrafine α -Fe particles are produced by pyrolysis at 400°C. Similarly to these results, α -Fe particles and γ -Fe were produced in κ -Al₂O₃ by py-

rolysis at 1200°C, and mainly Fe₃C was produced in κ -Al₂O₃ by pyrolysis at 1000°C.

Pyrolysis of pellets of poly(VFc)/alumina composite can produce either the micropore or macropore. Figure 6 shows the BET surface area of pyrolytic products from poly(VFc)/alumina composites as a function of mixing ratio of poly(VFc)/alumina and pyrolysis temperature. The results indicate all the pyrolytic products are porous (40–150 m²/g). The pyrolytic products from the composites, with a mixing ratio of VFc unit/alumina = 5/5 at 1000°C, exhibit the maximum BET surface area. A high pyrolytic temperature (1200°C) and low mixing ratio of poly(VFc) may cause the disintegration of pores generated at 1000°C.

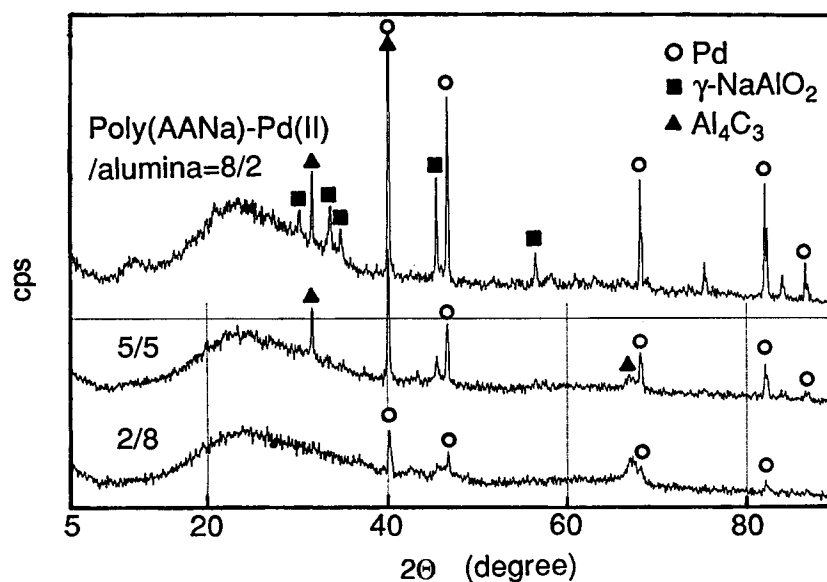


Figure 7 XRD patterns of the powdered pyrolytic products from Poly(AANa)-Pd(II)/alumina (molar mixing ratio of AA unit/Na₂PdCl₄ = 4/1) composites at 800°C.

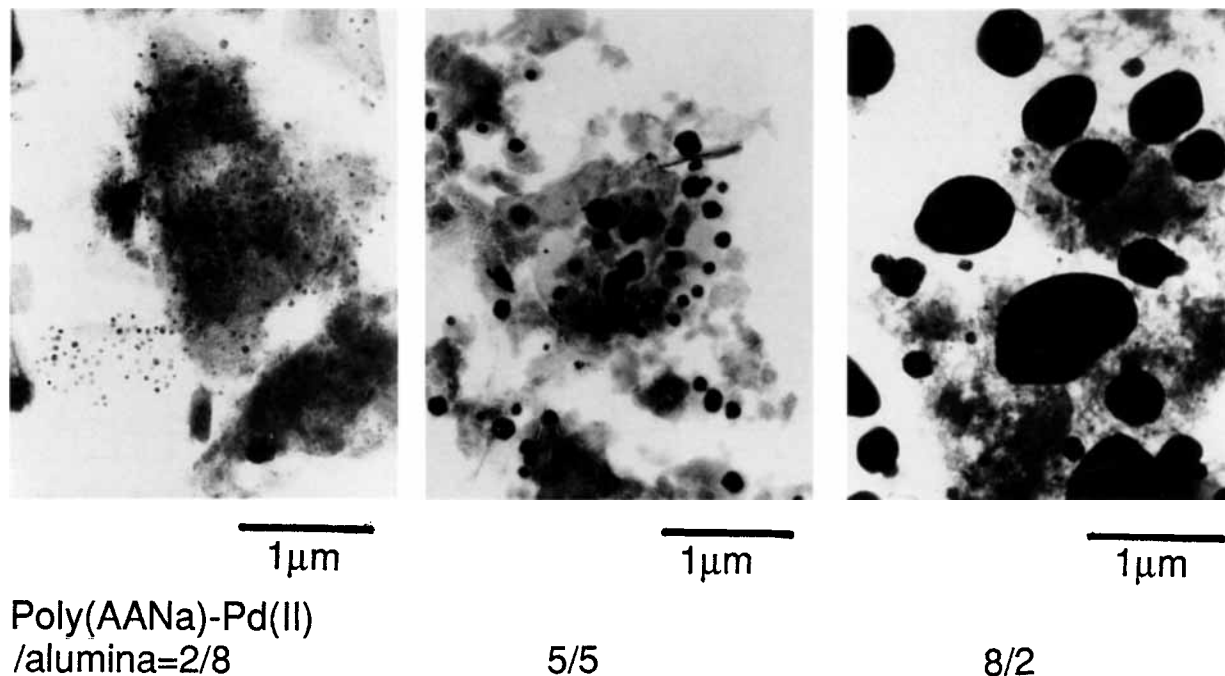


Figure 8 TEM photographs of Pd/alumina composites from Poly(AANa)-Pd(II) (molar mixing ratio of Poly(AANa)/ $\text{Na}_2\text{PdCl}_4 = 4/1$)/alumina precursors at 800°C .

Pyrolysis of Poly(AANa)-Pd(II) Precursors

For the preparation of poly(AANa)-Pd(II) complexes, molar mixing ratios of acrylic acid (AA) unit/ Na_2PdCl_4 of 4/1 and 1/1 were used as the reaction ratios of poly(AANa) with Na_2PdCl_4 . The pyrolytic yields (wt %) and Pd contents of the products from poly(AANa)-Pd(II)/alumina composites are shown in Table II. The pyrolytic yields decreased and Pd contents increased with increasing mixing ratio of poly(AANa)-Pd(II)/alumina. These results indicate that weight loss of poly(AANa)-Pd(II)/alumina composite during pyrolysis is ascribed to the decomposition of poly(AANa), and a large portion of Pd is supposed to remain in the alumina matrix. Therefore, in the case of a high mixing ratio of poly(AANa)-Pd(II) complex with alumina, a high amount of Pd was supported on the alumina matrix. This behavior is remarkable in the case of poly(AANa) unit/ Na_2PdCl_4 ratio of 1/1 (mole/mole). On the other hand, Pd content in the pyrolytic product, from a mixture of Na_2PdCl_4 with alumina [in the absence of poly(AANa)], is very low and the amount of Pd supported on alumina decreases with decreasing mixing ratio. Thus, the direct pyrolysis of Na_2PdCl_4 /alumina seems useless for production of Pd fine particles supported on alumina, because Pd metal is removed during heat treatment. These results indicate that the use of

polymer complex is effective for the formation of metal particles in an alumina matrix.

The XRD spectra of the pyrolytic products from poly(AANa)-Pd(II)/alumina (molar mixing ratio of AA unit/ $\text{Na}_2\text{PdCl}_4 = 4/1$) precursor at 800°C (Fig. 7) indicate the formation of Pd crystallites which grow during pyrolysis. The size of Pd crystallites increases with increasing mixing ratio of poly(AANa)-Pd(II) complex with alumina. On the

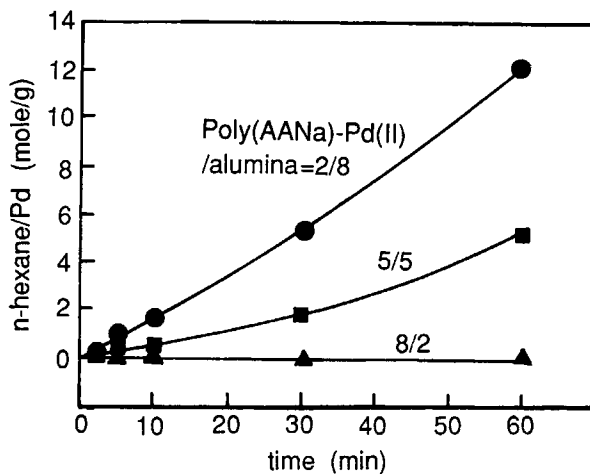


Figure 9 Catalytic activity of Pd/alumina composites for hydrogenation of 1-hexene to n-hexane.

other hand, in the case of a high mixing ratio of poly(AANa)-Pd(II) complex, the crystallites of other aluminum compounds such as γ -NaAlO₂ and Al₄C₃ are also formed.

TEM photographs of Pd/alumina composites obtained from poly(AANa)-Pd(II)/alumina composites (molar mixing ratio of AA unit/Na₂PdCl₄ = 4/1) at 800°C are shown in Figure 8. Pd fine particles disperse uniformly in the alumina matrix and the particle size increases in the order of mixing ratio of poly(AANa)-Pd(II)/alumina = 2/8 (average size 40 nm), 5/5 (125 nm), and 8/2 (500 nm).

As an application of the present composites, catalytic hydrogenation of 1-hexene to *n*-hexane was tested here. The result is shown in Figure 9. The Pd/alumina composites from the precursor of weight mixing ratio of poly(AANa)-Pd(II)/alumina = 2/8 exhibited higher activity. The composite from the precursor of mixing ratio of 8/2 has scarcely less catalytic activity for hydrogenation. This is related to the big size of the Pd particles in the composite from the precursor with mixing ratio of 8/2.

REFERENCES

1. D. C. Koningsberger, J. B. A. D. van Zon, H. F. J. van t Blik, G. J. Visser, R. Prins, A. N. Mansour, D. E. Sayers, D. R. Short, and 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. F. Hugues, J. A. Dalmon, P. Busslere, A. K. Smith, J. M. Basset, and D. Olivier, *J. Phys. Chem.*, **86**, 5136 (1982).
5. D. Ballivet-Tkatchenko and I. Tkatchenko, *J. Mol. Catal.*, **13**, 1 (1981).
6. G. B. McVicker and M. A. Vannice, *J. Catal.*, **63**, 25 (1980).
7. W. F. Graydon and M. D. Langan, *J. Catal.*, **69**, 180 (1981).
8. E. O. Odebunmi, Y. Zhao, H. Knozinger, B. Tesche, W. H. Manogue, B. C. Gates, and J. Hulse, *J. Catal.*, **86**, 95 (1984).
9. P. Bosch, D. Acosta, J. Zenith, D. M. Nicolson, and B. C. Gates, *J. Mol. Catal.*, **31**, 73 (1985).
10. A. Ueno, H. Suzuki, and Y. Kotera, *J. Chem. Soc., Faraday Trans. I*, **79**, 127 (1983).
11. K. Tohji, Y. Udagawa, S. Tanabe, and A. Ueno, *J. Am. Chem. Soc.*, **106**, 612 (1984).
12. S. Miyanaga, H. Yasuda, A. Hiwara, A. Nakamura, and H. Sakai, *J. Macromol. Sci. Chem.*, **A27**, 1347 (1990).
13. A. L. Micheli, *Ceramics Intl.*, **15**, 131 (1989).
14. W. F. McClune, ed., *Powder Diffraction File, Inorganic Volume*, JCPDS International Center for Diffraction, 1988.

Received October 14, 1993

Accepted March 25, 1994