Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Pyrolysis of Polymer Complexes Leading to Air-Stable Ultrafine Metal Particles Uniformly Dispersedin a Carbon Matrix

Seiichi Miyanaga[a]; Hajime Yasuda[a]; Akio Hiwara[a]; Akira Nakumura[a]; Hiroshi Sakai[b]
[a] Department of Macromolecular, Science Faculty of Science, Osaka University, Toyonaka, Osaka, Japan [b] Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Senda, Hiroshima, Japan

To cite this Article Miyanaga, Seiichi , Yasuda, Hajime , Hiwara, Akio , Nakumura, Akira and Sakai, Hiroshi(1990) 'Pyrolysis of Polymer Complexes Leading to Air-Stable Ultrafine Metal Particles Uniformly Dispersedin a Carbon Matrix', Journal of Macromolecular Science, Part A, 27: 9, 1347 — 1361

To link to this Article: DOI: 10.1080/00222339009349696

URL: http://dx.doi.org/10.1080/00222339009349696

J. MACROMOL. SCI.—CHEM., A27(9–11), pp. 1347–1361 (1990)

PYROLYSIS OF POLYMER COMPLEXES LEADING TO AIR-STABLE ULTRAFINE METAL PARTICLES UNIFORMLY DISPERSED IN A CARBON MATRIX

SEIICHI MIYANAGA, HAJIME YASUDA,*
AKIO HIWARA, and AKIRA NAKUMURA

Department of Macromolecular Science
Faculty of Science
Osaka University
Toyonaka, Osaka 560, Japan

HIROSHI SAKAI

Department of Chemistry
Faculty of Science
Hiroshima University
Higashi-Senda, Hiroshima 730, Japan

ABSTRACT

New types of air-stable metal–carbon composites which contain ultrafine metal particles (Fe, Co, Ni, Pd, Pt, Rh, Cu, etc.) uniformly dispersed in a carbon matrix were obtained by pyrolysis of a variety of soluble organometallic polymers, macromolecular–metal complexes, and blends of coal pitch with metal complexes at 400–1400°C in N_2. Some of their unique physical properties and functions are noted.

INTRODUCTION

As a part of the search for potentially new functionality in organometallic polymers and macromolecular–metal complexes, pyrolysis (calcination and sintering) of these compounds in an inert gas was explored to find a new type of metal-carbon composite. The modification of carbon fibers and carbonaceous materials by coating with metallic substances has been studied in order to improve their wettability and to endow them with new functions [1-3]. Thus far, all attempts to create iron-carbon composites by pyrolysis methods using polymers with pendant ferrocenyl groups have given unsatisfactory results since the products are either pyrophoric mixtures or simply iron carbide [4, 5]. We have recently found that pyrolysis of a series of solution-processable polymers containing transition metal complexes under appropriate conditions (650-1400°C for 1-2 day(s) in N_2 or Ar) produces highly air-stable metal-carbon composites which contain ultrafine metal particles (M = Fe, Co, Ni, Pd, Pt, Rh, Cu) of uniform diameter. Raising the temperature at a sufficiently slow rate (e.g., 0.3°C/min) is essential to obtaining the desired samples. The particles are homogeneously dispersed throughout the resulting carbon matrix, such that metal units remain well separated from each other by the carbon phase. This paper outlines our recent results on the pyrolysis of various macromolecular-metal complexes and some of unique properties of the resulting composites.

The major advantages of the present method and benefits derived from the present composites are in the following:

1) Simple preparation procedure which allows large-scale production of air-stable metal-carbon composites, especially highly graphitized composites, at relatively low heat treatment temperatures.
2) Potential to mold the resulting metal-carbon composites into various forms, i.e., thin film, fibers, powder, and pellets in various M/C ratios (variable up to ∿ 70% metal content).
3) Possible broad applications of the resulting new materials in electronic, electric, and magnetic devices (magnetic powder, electromagnetic wave absorber, electrode), oxidation/reduction catalyst (selective hydrogenation of C—C, C—O, or C—N unsaturation, and decomposition of peroxides), adsorbents (emphasized by metal), antibacterial agents, etc.

EXPERIMENTAL

General

Pyrolysis of macromolecular-metal complexes and pitch blends were conducted in an atmosphere of argon or nitrogen in a computer-controlled electric combustion tube furnace. Samples are placed in a ceramic crucible with a lid and heated to 1000°C at a rate of 0.3-0.6°C/min and maintained at 1000°C for 2 h. In those cases where the samples were molded into pellets, the precursor polymers were first calcined at 350–450°C, divided into fine powders, compressed (under 1 GPa), and then sintered at 1000°C. TEM figures were obtained on a JEOL JEM-2000FX analytical electron microscope at 120 kV, fitted with a Tracor Northern Model TN-5500 EDX analyzer. X-ray diffraction analysis was performed in a Rigaku RAD-C system using CuK_α radiation (λ = 1.5406 Å) and assignments of the resulting metal species were made based on literature data [6]. SEM and EPMA measurements were run on a JEOL JXA-733 microscope. Coercivity and saturation magnetization were measured by a dc magnetic hysteresis loop tracer at 30°C. ^{57}Fe Mössbauer spectra were taken in a standard transmission geometry at 30°C with ^{57}Co in Rh source. Isomer shift was calibrated with an α-Fe foil.

Synthesis of Metal-Containing Monomers and Polymers

Metal-containing monomers such as 2,4-hexadienyl[tri(carbonyl)iron] acrylate (**1**) [7] and (4-vinylpyridine)$_2$CoCl$_2$ [8] were prepared according to the procedure reported in the literature. In a similar manner, (4-vinyl pyridine)$_2$TiCl$_4$ was obtained as a yellow solid. Copolymerization of **1** with acrylonitrile (AN), styrene (ST), methyl methacrylate (MMA), or 4-vinyl pyridine (VP) was carried out in benzene at 60°C using AIBN ($2–8 \times 10^{-3}$ equivalent moles of monomer) as an initiator. The resulting polymers were precipitated in methanol or hexane. Yields of polymers ranged from 58 to 88%. The 1 : 9 copolymerization of **1** with AN gave a polymer with a monomer ratio of 1.1 : 8.9 as confirmed by elemental analysis.

Synthesis of Macromolecular-Metal Complexes

Carboxylated polystyrene was prepared according to the procedure reported by Frechet [9], and its complexation with nickel was carried out by the following procedure. Carboxylated polystyrene (10 mol% of the styrene unit was carboxylated at the *p*-position, 10.9 g) was suspended in 100 mL of THF/water (2 : 1). To this suspension was added 10 mL of 1 *N* ethanolic KOH solution. Then NiCl$_2$ (10 mmol) in water (10 mL) was added and the mixture was stirred at 60°C for 30 min. The resulting product mixture was poured into degassed water, resulting in the precipitation of a nickel containing pale green polymer.

Diphenylphosphinomethylated polystyrene (10 mol% of the styrene unit was substituted) was prepared by the known method starting from (*p*-chloromethyl)styrene [10]. The phosphinated polymer (6.5 g), dissolved in 250 mL CH_2Cl_2, was added to a CH_2Cl_2 solution of Pd(cyclooctadienyl)Cl_2 (25 mmol). A yellow polymer precipitated immediately after mixing; the polymer was washed with hexane (yield, 92%).

Pitch blends of metal complexes were prepared in the following manner. A powdered coal pitch (20.0 g) was added to poly(vinyl ferrocene) (4.0 g) in THF (250 mL). The mixture was filtered, and the solution was evaporated to dryness. Heat treatment of the resulting powdery substance at 400–1000°C in argon gave the desired metal–carbon composites.

RESULTS AND DISCUSSION

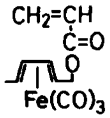
1. Synthesis of Precursor Polymers

The precursor organometallic polymers or macromolecular–metal complexes employed here may be prepared either by 1) homopolymerization of vinyl monomers containing metal complexes (e.g., 2,4-hexadienyl[tri(carbonyl)iron] acrylate) or its copolymerization with acrylonitrile (AN), styrene (ST), methyl methacrylate (MMA), or 4-vinyl pyridine (VP); 2) complexation of metal species to organic polymers with functional groups (e.g., poly(VP), poly(AN), and modified polystyrene containing COO^-, NR_2, or cyclopentadienyl ligand as a pendant group; or 3) blending of soluble macromolecular–metal complexes (e.g., poly(vinyl ferrocene) and 1,1′-bis(naphthylmethyl)ferrocene) with a pitch or organic polymers such as poly(AN) and poly(VP). (See Scheme 1.) Excellent survey monographs [11–14] should be consulted for synthesis of macromolecular–metal complexes.

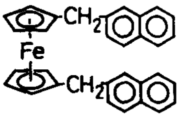
2. Carbon Composites Containing Iron Particles

2.1. Pyrolysis of Organoiron Polymers

An organoiron monomer, 2,4-hexadienyl[tri(carbonyl)iron] acrylate (**1**), is a convenient monomer with stability in air and moisture [7] which can be readily copolymerized with AN, ST, MMA, and VP in various ratios using a radical initiator, AIBN. Pyrolysis of copolymers, poly(AN/**1**) (9 : 1) and poly(ST/**1**) (9 : 1), at 1000°C for 2 h (heated to 1000°C over a period of 2 days at a rate of 0.3°C/min) under argon or nitrogen provided a new type of metal–carbon composite in 15–46% yield.



1

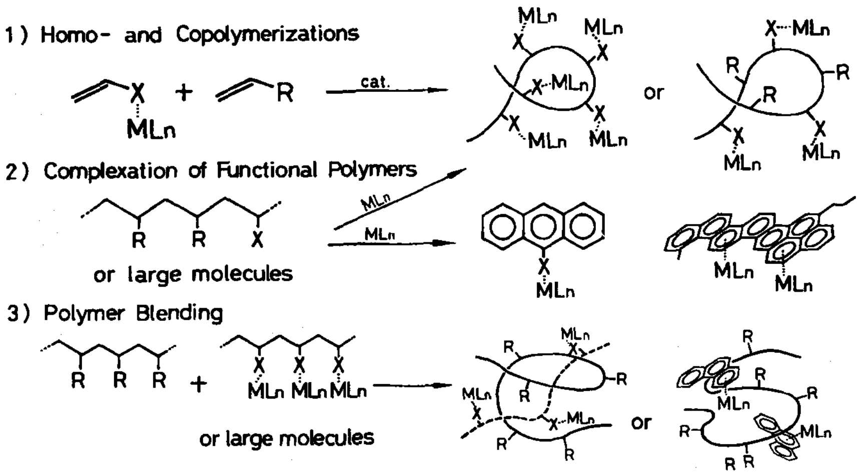


2

Ultrafine particles of α-Fe (diameter, 70–170 nm) are dispersed uniformly in the resulting carbon matrix as confirmed by transmission electron microscopic measurement (TEM) (Fig. 1), energy dispersive x-ray analysis (EDX) (Fig. 2), power x-ray diffraction (XRD) measurement (Fig. 3), and Mössbauer spectroscopic analysis [15]. The scanning electron microscopic (SEM) measurement of pelletized samples shows smooth surfaces, and the electron probe microanalysis (EPMA) reveals that metal particles are dispersed isotropically (Fig. 4).

Size and shape (polyhedron) of the resulting iron particles does not vary significantly by changing the concentration of iron component in the precursor polymer, i.e., the homopolymer of **1** yielded upon heat treatment a composite with ultrafine iron particles (Fe, 63; C, 36; H, 0.01%), the diameter of which (70–180 nm) is similar to those obtained from copolymers such as poly(AN/**1**) and poly(ST/**1**).

The BET specific surface area of the composite (C, 83.9; N, 0.3; H, < 0.01; Fe, 15.8%) resulting from poly(AN/**1**) (9 : 1) is 103–140 m²/g, indi-



MLn : mono-, di- or polynuclear complexes

SCHEME 1.

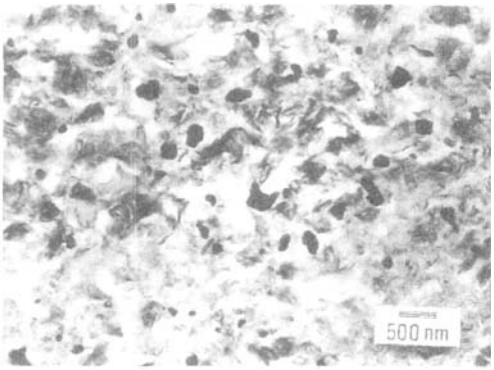


FIG 1. Transmission electron micrograph of the carbon/Fe composite prepared by pyrolysis of poly(AN/1) (9:1) at 1000°C.

cating the material is microporous. The composite is electrically conducting (σ = ∿10^3 S/cm) and exhibits fairly good magnetic properties. The coercive force, *Hc*, is 110 Oe, and the saturation magnetization, *Im*, is 19 emu/g.

2.2. Pyrolysis of Pitch Blends of Iron Complexes

The coal pitch used here is composed of a mixture of polyaromatic compounds with a softening point of 80°C (C, 92.0; H, 4.8; N, 0.3; S, 0.1%) and is soluble in benzene and THF. Pyrolysis of blends, prepared

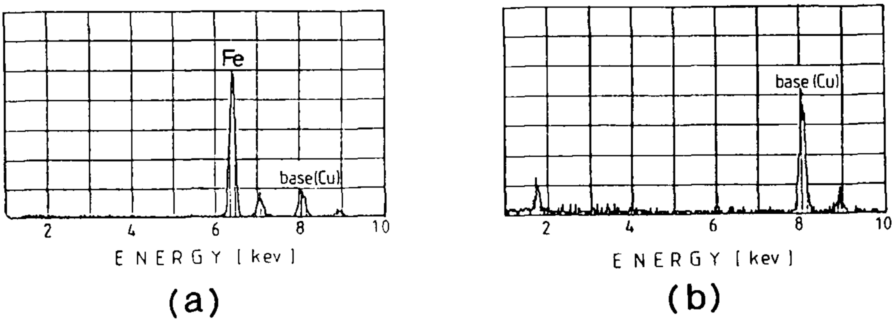


FIG. 2. EDX spectra of the pyrolytic product of poly(AN/1) (9:1): (a) particle region and (b) carbon matrix.

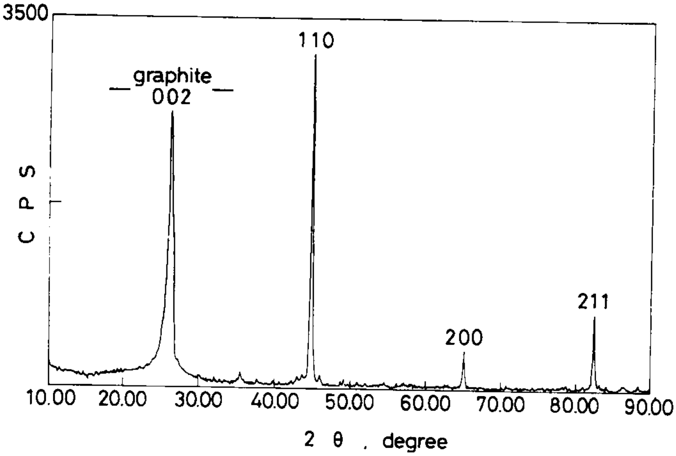


FIG. 3. XRD profile of the powdered carbon/Fe composite derived from poly(AN/1) (9:1).

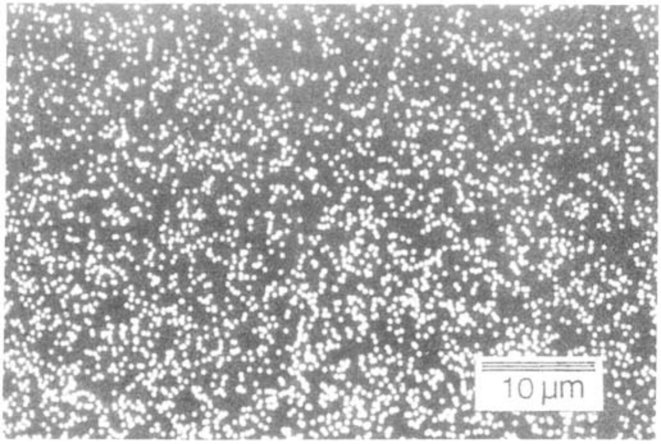


FIG. 4. EPMA image of the carbon/Fe composite obtained by pyrolysis of poly(AN/1) (9:1) at 1000°C.

by mixing ferrocene or vinyl ferrocene (∿5–40 wt%) with pitch in benzene followed by flash evaporation of solvent, does not produce the desired material containing an iron component because these iron complexes sublime. The use of poly(vinyl ferrocene) or less volatile 1,1′-bis(naphthylmethyl)ferrocene (2) provided the solution to this problem. Pitch blends containing these complexes (5–20 mol%) yielded air-stable ultrafine particles of α-Fe (∿20 nm) dispersed in carbon by heat treatment even at 450°C, although pyrolysis of poly(vinyl ferrocene) itself gave a pyrophoric complex mixture in low yield (<5%). Further heating to 900°C resulted in growth of the pure α-Fe particles with a diameter of 120–159 nm. Heat treatment at 1400°C brings about contamination by Fe_3C (18%) and γ-Fe (11%) in α-Fe as analyzed by Mössbauer studies (Fig. 5). Blending of $Fe(acac)_3$ or $Fe_2(CO)_9$ also provided a convenient route for synthesis of the iron–carbon composites. Although pyrolysis at 400°C produced undesired Fe_3O_4 (magnetite) particles as a major product, subsequent heat treatment at 800°C successfully gave rise to the formation of desired α-Fe particles (diameter, ∿50 nm) dispersed in car-

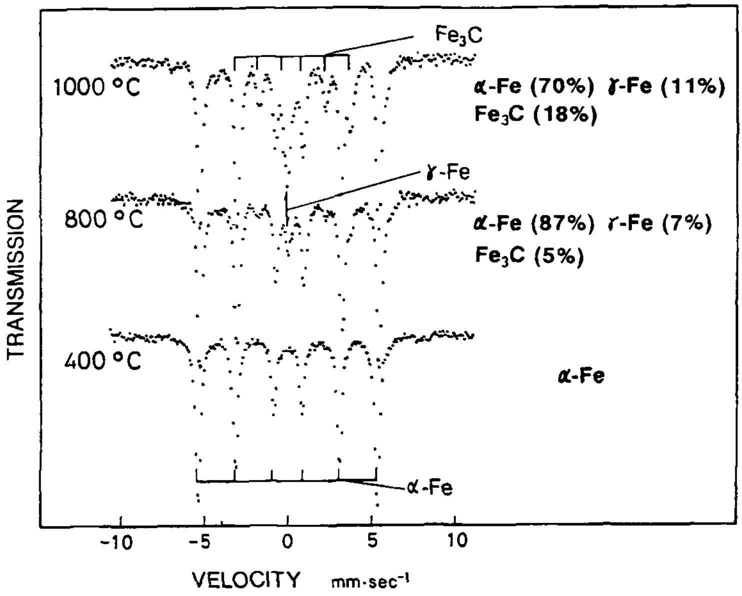
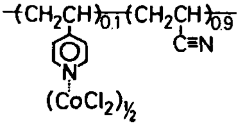


FIG. 5. ^{57}Fe Mössbauer spectra of the pyrolytic product of pitch/1,1′-bis(naphthylmethyl) ferrocene, heat treated at 1000°C (top), 800°C (middle), and 400°C (bottom).

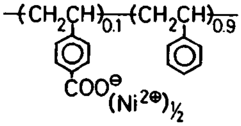
bon in ∿78% carbonization yield (the oxide was reduced to the metal by the effect of carbon). The exceedingly high stability of these iron-carbon composites in aerobic conditions (>2 months at room temperature) may be ascribed to the encapsulation of the iron particle by the surrounding carbon. The BET specific surface areas of the present pitch system (1000°C treatment) are rather small (5–10 m^2/g) unless otherwise activated by steam or CO_2 treatment. The electrical conductivity (σ) is $\sim 10^2$ S/cm.

3. Carbon Composites Containing Cobalt and Nickel Particles

Highly air-stable ultrafine particles of pure β-Co (cubic) and nickel (cubic) can be produced quite readily using the present method. For example, heat treatment of poly[AN/$(VP)_2CoCl_2$] (18 : 1) (**3**) at 1000°C provided ultrafine particles (diameter, 30 nm) of pure β-Co, while pyrolysis of poly[ST/$(VP)_2CoCl_2$] gave a 4 : 1 mixture of β- and α-Co particles (Fig. 6). In a similar manner, poly[ST/$(CH_2CHC_6H_4CO_2)_2Ni$] (**4**) (18 : 1) and poly[AN/$(AN)_2NiCl_2$] (18 : 1) were converted into a carbon composite containing Ni particles (diameter, 120–160 nm) (Fig. 7). Thus the use of organocobalt or organonickel polymers as precursors is not always required. This finding is of significant importance because the air- and moisture-sensitive organometallic polymers are inconvenient to handle in the synthesis of composites. Noteworthy are the blends of pitch with air-sensitive cobaltocene or nickelocene which decompose smoothly upon heating to 450°C to produce the desired carbon-cobalt (diameter of Co, 80 nm) and carbon-nickel composites (diameter of Ni, 30 nm) as confirmed by TEM and XRD analyses.



3



4

More remarkable is the progressive catalytic effect of iron, cobalt, and nickel in graphitization of the carbon composites. Poly(AN), poly(ST), and poly(VP) with pendant Fe, Co, and Ni complexes noted above were converted into highly graphitized materials upon heating to 1000°C (the extent of graphitization calculated based on Warren's p-value [16] is 75–82%), while graphitization does not occur when pitch blends of these

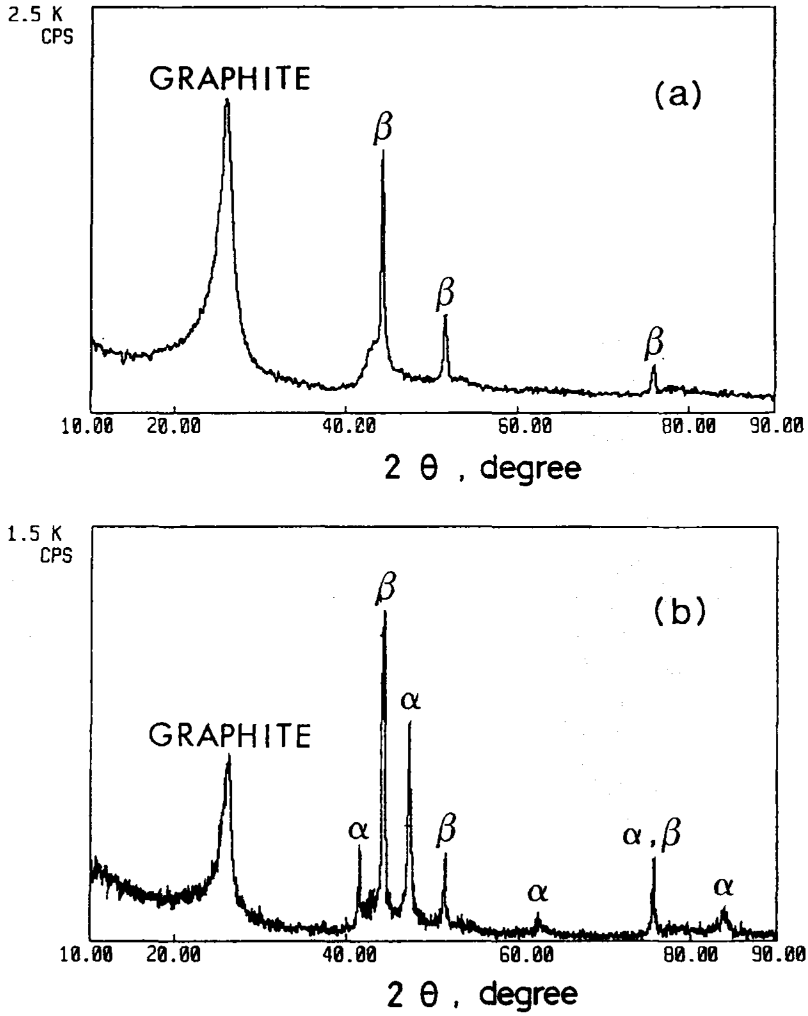


FIG. 6. XRD patterns of the carbon/Co composites derived from (a) poly[AN/(VP)$_2$CoCl$_2$] (18:1) and (b) poly[ST/ (VP)$_2$CoCl$_2$] (18:1).

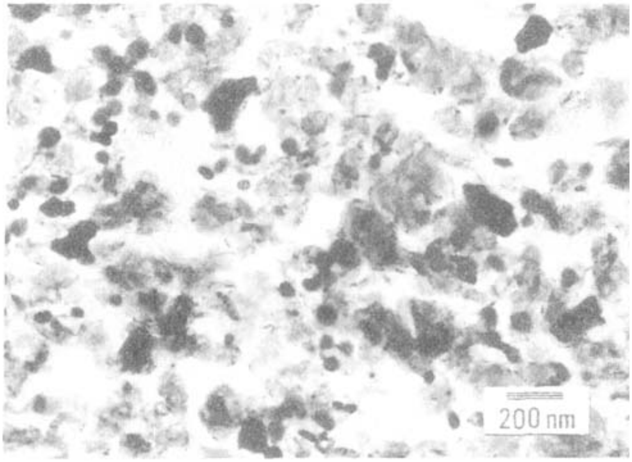


FIG. 7. Transmission electron micrograph of carbon/Ni composite obtained from poly[ST/$(CH_2CHC_6H_4COO)_2Ni$] (18 : 1).

metal complexes are treated under the same conditions. Since graphitization of conventional organic polymers generally requires a much higher temperature (>2000°C), the present method seems to offer practical applications which would lead to significant energy reduction in industrial graphitization processes. All the graphitized carbonaceous materials thus obtained exhibit good electrical conductivity irrespective of the identity of the metal ($\sigma = \sim 10^2$ S/cm), while nongraphitized samples obtained below 600°C show rather small conductivity ($\sigma = \ < 10$ S/cm).

4. Carbon Composites Containing Noble Metal Particles

The eight elements, i.e., Ag, Au, Ru, Os, Rh, Ir, Pd, and Pt, are conventionally referred to as noble metals. However, these metals are known to become pyrophoric when in a finely divided state. We could also obtain carbon composites containing ultrafine particles of these metals by starting from appropriate macromolecular-metal complexes. For example, pyrolysis of poly[AN/$(CH_2CHCOO)_2Pd$] (**5**) (18 : 1), poly[AN/$(CH_2CHCOO)_2Rh$] (18 : 1), or poly[ST/$(VP)_2AgNO_3$] (18 : 1) at 1000°C for 2 days gave rise to the formation of ultrafine particles of Pd (2–5 nm), Rh (5–20 nm) or Ag (1–5 nm) dispersed homogeneously in carbon matrices (Fig. 8).

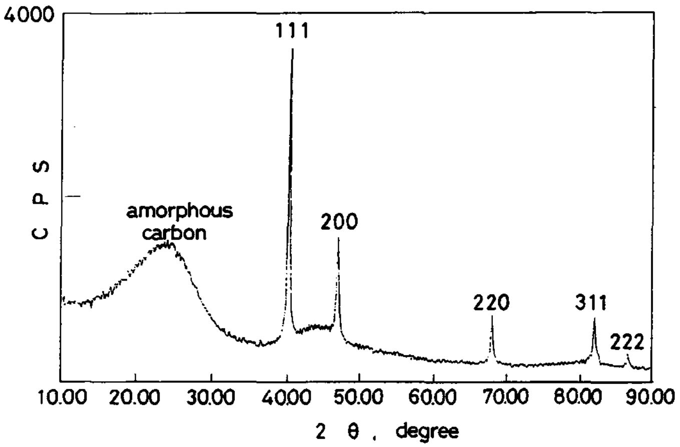
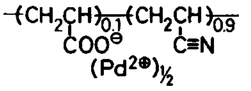


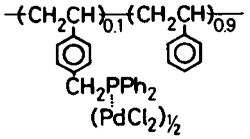
FIG. 8. XRD profile of the carbon/Pd composite obtained by pyrolysis of poly[AN/ $(CH_2CHCOO)_2Pd$] (18 : 1) at 1000°C.

The composite containing ultrafine particles of Cu (<2 nm) is also available by heat treatment (1000°C) of a polymer containing copper carboxylate as the pendant group. Thus, pyrolysis of polymers with pendant noble metal complexes gave the desired pure metal particles, suppressing the formation of metal oxides or metal nitrides, regardless of the presence of $(COO)_2M$, COOH, amine, or CN group in polymers. However, the polymers containing phosphine ligands show a markedly different behavior. A typical example is seen in the pyrolysis of poly[ST/ $(CH_2CHC_6H_4CH_2PPh_2)_2PdCl_2$] (**6**) (18 : 1) at 1000°C, which yields only fine particles of phosphide (Fig. 9) (diameter, ∿20 nm) composed of Pd_5P_2 (60%) and PdP_2 (40%) as confirmed by XRD analysis [6]. It should be noted that the resulting carbon matrices were amorphous when polymers containing noble metal complexes were used. These materials exhibit relatively small electrical conductivity (σ = <10 S/cm).



$$-(CH_2\underset{\underset{(Pd^{2\oplus})_{1/2}}{COO^{\ominus}}}{CH})_{0.1}(CH_2\underset{C\equiv N}{CH})_{0.9}-$$

5



6

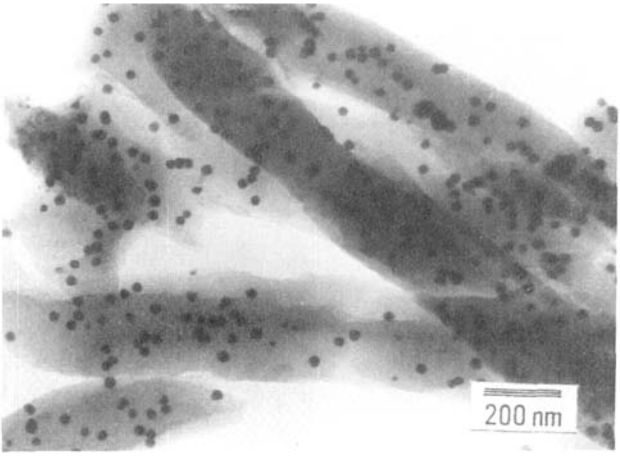
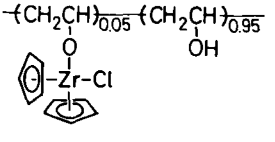


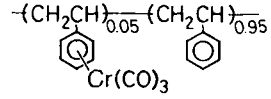
FIG. 9. Transmission electron micrograph of the pyrolytic product of poly[ST/ $(CH_2CHC_6H_4CH_2PPh_2)_2PdCl_2$] (18 : 1). Particles are palladium phosphide.

5. Pyrolysis of Polymers Containing Early Transition Metals

Polymer complexes containing early transition metals generally produce ultrafine particles of metal nitrides, metal oxides, or metal carbides in place of metal particles. For example, pyrolysis of poly[ST/ $(VP)_2TiCl_4$] (18 : 1) and poly(vinyl alcohol/$ZrClCp_2$) (**7**) (20 : 1) at 1000°C led to the formation of TiN (diameter, 20–160 nm) and ZrO_2 (∿2 nm), respectively. Poly[ST/$(CH_2CHC_6H_5)Cr(CO)_3$] (**8**), which is prepared by the reaction of $Cr(CO)_6$ with polystyrene, gave Cr_3C_2 particles of ∿30 nm. The carbon phase is amorphous in all cases.



7



8

6. Reaction Pathways for the Formation of Ultrafine Particles

The dependency of particle size and chemical constitution of the product on the heat treatment temperature was analyzed by TGA, XRD, and

Mössbauer studies by using poly[AN/2,4-hexadienyl[tri(carbonyl)iron] acrylate (**1**) (9 : 1) as a typical precursor. Heat treatment of the sample at 250–280°C *in vacuo* shows a weight loss of 15% as analyzed by TGA. This may be ascribed to the evolution of CO from the iron complex. The weight loss reaches ∿55% upon subsequent heating to 800°C *in vacuo*. The formation of Fe_3C is predominant at this temperature as revealed by TEM, XRD, and Mössbauer measurements. The average particle size is 30 nm. Prolonged heating at 1000°C resulted in a significant loss of H and N components and conversion of Fe_3C into α-Fe. Thus the particles grow larger (120–170 nm) during this procedure and the carbon phase is graphitized. We can therefore estimate that the Fe atoms or clusters generated by reductive decomposition of Fe_3C at around 850–950°C catalyze by both carbonization and graphitization and gradually coagulate to α-Fe particles, presumably via the liquid state (ultrafine metals generally show remarkably lower melting point as compared to bulk metals). A similar catalytic effect of Fe, Co, and Ni metals is reported in gas-phase whisker formation [17–19]. The poor thermal stabilities of cobalt and nickel carbides are responsible for the predominant formation of Co and Ni metal particles in pyrolysis at relatively lower temperatures (450–600°C). Although magnetite (Fe_3O_4) generated in the initial stage of pyrolysis of pitch-Fe(acac)$_3$ is able to be reduced to α-Fe particles at 800°C by the action of the surrounding carbon, particles such as Cr_3C_2, ZrO_2, and TiN remain unreacted under similar conditions.

7. Characteristic Properties of the Present Metal/Carbon Composites

Since the present composites containing Fe, Ni, and Co particles are conducting with fairly large magnetic susceptibilities (Hc = 100–500 Oe), they may serve as good electromagnetic shielding devices or absorbers. Indeed, composites derived from pitch/poly(vinyl ferrocene) showed sufficient S-parameter and permittivity for high frequency waves (200 m–2 GHz). The carbon composite containing Pt–Fe alloy (PAN system) revealed especially high catalytic activity in the hydrogenation of 1-hexene leading to hexane (13.0 H_2 mol/metal mol·h). The pyroproduct from **1** and PAN also exhibits good catalytic activity in the decomposition of aqueous 5–30% H_2O_2 (evolution of O_2, 9.8 mol/mol metal · min), and Pt fine particles (diameter, 1–2 nm) dispersed homogeneously in activated carbon (steam-treated pitch system) and also showed excellent activity (985 mol/mol metal · min). Bacteriostatic activities were especially found in cases of Ag- and Co-dispersed carbon composites.

Their activities are nearly the same as that of colloidal silver deposited on the surface of activated carbon. These may therefore serve as a convenient long-life sterilizer.

Further applications of a series of the present metal composites are now in progress.

REFERENCES

[1] R. Warren, C. H. Anderson, and M. Carlsson, *J. Mater. Sci., 13*, 178 (1978).
[2] R. Ehrburger, A. Mongilardi, and J. Lahaye, *Colloid. Interface Sci., 91*, 151 (1983).
[3] M. S. Dresselhaus and G. Dresselhaus, *Adv. Phys., 30*, 139 (1981).
[4] S. Yajima and M. Omori, *Chem. Lett.*, p. 277 (1974).
[5] S. Hirano, T. Yogo, H. Suzuki, and S. Naka, *J. Mater. Sci., 18*, 2811 (1983).
[6] W. F. McClume (ed.), *Powder Diffraction File. Inorganic Volume*, JCPDS International Center for Diffraction, 1988.
[7] C. U. Pittman Jr., O. E. Ayers, and S. P. McManus, *J. Macromol. Sci.–Chem., A7*, 1563 (1973).
[8] N. H. Agnew and L. F. Larkworthy, *J. Chem. Soc.*, p. 4669 (1965).
[9] M. J. Farrall and M. J. Frechet, *J. Org. Chem., 41*, 3877 (1976).
[10] R. H. Grubbs and L. C. Kroll, *J. Am. Chem. Soc., 93*, 3062 (1971).
[11] J. E. Sheats, C. E. Carraher Jr., and C. U. Pittman Jr. (eds.), *Metal Containing Polymeric Systems*, Plenum, New York, 1985.
[12] C. Carraher Jr., J. Sheats, and C. Pittman Jr. (eds.), *Advances in Organometallic and Inorganic Polymers*, Dekker, New York, 1982.
[13] N. K. Mathur and R. E. Williams, *J. Macromol. Sci.–Rev. Macromol. Chem., C15*, 117 (1976).
[14] E. Tsuchida and H. Nishide, *Adv. Polym. Sci., 24*, 1 (1977).
[15] N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall, London, 1971.
[16] B. E. Warren, *Proceedings of 1st Conference on Carbon*, Buffalo, 1956, p. 49.
[17] R. T. K. Baker, P. S. Harris, R. B. Thonas, and R. J. Waite, *Catalyst, 30*, 86 (1973).
[18] T. Baird, J. R. Fryer, and B. Grant, *Carbon, 12*, 591 (1974).
[19] F. Bensadd, P. Gadelle, M. Coulon, and L. Bonnetei, *Ibid., 26*, 61 (1988).