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Synthesis and properties of cobalt-dispersed carbons by pressure pyrolysis of organocobalt polymers

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Cobalt-dispersed carbons were synthesized by pressure pyrolysis of cobaltocene-divinylbenzene and phenylallylcobaltocene-divinylbenzene at 125 MPa below 700° C. The carbons resulting from cobaltocene-divinylbenzene contained uniformly dispersed fine particles, < 20 nm diameter, of metallic cobalt of lower crystallinity, which were composed of ferromagnetic and superparamagnetic particles. Metallic cobalt particles of cubic and hexagonal structures with higher crystallinity were formed during pyrolysis of phenylallylcobaltocene-divinylbenzene. Cobaltocence-divinylbenzene and phenylallylcobaltocene-divinylbenzene changed their magnetic properties from diamagnetism to paramagnetism at 250 and 200° C, respectively. The infrared absorption band of the cyclopentadienyl ring at 995 cm^{-1} disappeared at 350° C in cobaltocene-divinylbenzene and at 300° C in phenylallylcobaltocene-divinylbenzene. Superparamagnetic particles from cobaltocene-divinylbenzene aggregated and crystallized to produce larger particles of diameter 30 to 100 nm, which increased the magnetization during thermomagnetic measurement. The saturation magnetization of cobalt-dispersed carbons from phenylallylcobaltocene-divinylbenzene was higher by about 10% than that from cobaltocene-divinylbenzene. The coercive forces of cobalt-dispersed carbon from phenylallylcobaltocene-divinylbenzene and cobaltocene-divinylbenzene were 350 and 250 Oe (2.79×10^4 and $1.99 \times 10^4\, A\, m^{-1}$), respectively.

1. Introduction

Carbons with various characteristics have been synthesized by an appropriate selection of parent organic compounds and pyrolysis conditions such as temperature and pressure [1–7].

Organometallic compounds are versatile starting materials for the synthesis of carbons containing finely dispersed metallic particles of different morphologies in high yields by pressure pyrolysis. Marsh *et al.* [3] demonstrated the synthesis of anisotropic carbon spherulites by carbonization of a mixture of anthracene and ferrocene under pressure. Hirano *et al.* [6] synthesized carbon spherulites containing a dispersoid of fine metal particles by pressure pyrolysis of divinylbenzene copolymerized with vinylferrocene. Hirano *et al.* [8] reported the synthesis of carbons containing dispersed iron by pressure pyrolysis of divinylbenzene-vinylferrocene. The stabilities of the metal–carbon and carbon–carbon bonds of the organometallic polymer influence the initial stages of pyrolysis of the polymer. This explains differences in the nature of the metal particles dispersed in the resultant carbons. The presence of metal as a second phase is considered to affect the liquid–liquid microphase separations during pyrolysis, and results in the several morphologies observed in the resultant carbons.

This paper discusses the synthesis and properties of metallic cobalt-dispersed carbons by the pressure carbonization of cobalt-containing polymers. Two organocobalt compounds of cobaltocene and phenylallylcobaltocene were used as starting materials: cobaltocene has two cyclopentadienyl rings, whereas phenylallylcobaltocene has both a cyclopentadienyl and a cyclopentadiene as a four-electron donor. The pyrolysis of the cobalt-containing polymers was followed by magnetization measurements and infrared (IR) spectroscopy. The properties of cobalt-dispersed carbons were evaluated by X-ray powder diffraction a magnetic balance and a vibrating sample magnetometer.

2. Experimental procedures

Cobaltocene (dicyclopentadienylcobalt(II), abbreviated as Cp_2Co) was prepared as described by Wilkinson *et al.* [9]. Phenylallylcobaltocene (cyclopentadienyl [1-exo-(3-phenylallyl)cyclopentadiene]cobalt(I), abbreviated as PACo) was prepared according to Herberich and Bauer [10]. Comercially available divinylbenzene (a mixture of 55% *m*-divinylbenzene and *p*-divinylbenzene and 45% ethylbenzene) was used for the synthesis of the organic polymer matrix.

Pressure pyrolyses were carried out with a hydrothermal apparatus of the cold-seal type. Organocobalt compounds were dissolved in divinylbenzene (DVB).

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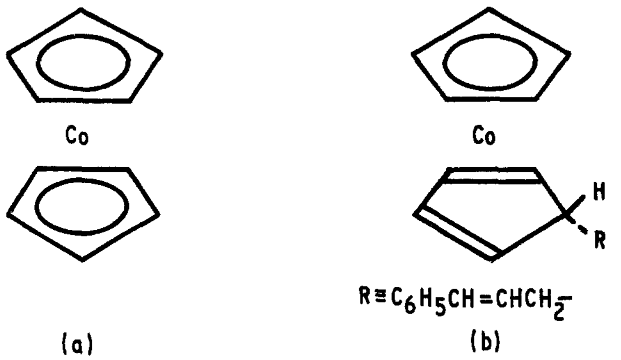

Figure 1 Starting organocobalt compounds: (a) dicyclopentadienylcobalt(II) (cobaltocene), (b) cyclopentadienyl[1-exo-(3-phenylallyl)-cyclopentadiene]cobalt(I) (phenylallylcobaltocene).

The solution was then sealed under nitrogen in a thin-walled gold capsule of diameter 3.0 or 5.0 mm and length 50 mm [4, 5].

The cobaltocene or phenylallylcobaltocene solution of divinylbenzene was polymerized at 300° C for 2 h under a pressure 100 MPa and then heat treated at temperatures from 350 to 700° C for 3 h under 125 MPa. The pressure was measured with a calibrated Heise gauge and the temperature was controlled with a calibrated sheathed thermocouple set inside the pressure vessel. The temperature was raised at 10° C min^{-1} and quenched after the heat treatment for 3 h.

The magnetization of the cobalt-containing polymers was evaluated using a magnetic balance at room temperature. The relative magnetization was calculated using gold and Mohr's salt $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, respectively, dependent upon the magnitude of magnetization. IR spectra of the polymers, including the organocobalt compounds, were measured by the KBr disc method.

Yields of carbon were as high as 80% by this pressure carbonization. The cobalt-dispersed carbons were characterized by X-ray diffraction, scanning electron miroscopy (SEM), transmission electron microscopy (TEM) and electron diffraction. The thermomagnetization curve of cobalt-dispersed carbon was measured with a magnetic balance from room temperature to 780° C. Specimens were desorbed under vacuum for several hours at 250° C prior to the thermomagnetization measurement. Both the saturation magnetization and the coercive force of cobalt-dispersed carbons were elucidated with a vibrating sample magnetometer (VSM).

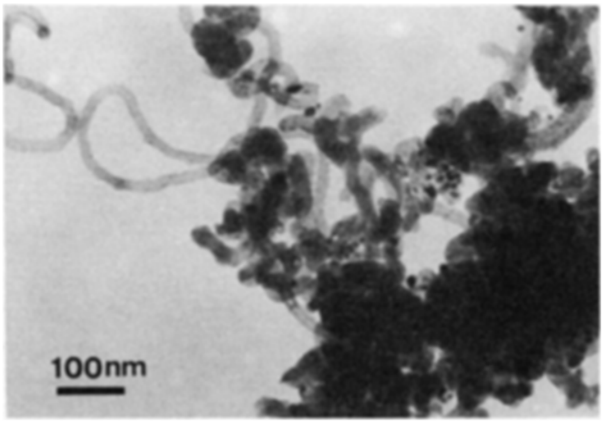

Figure 2 Microstructure of fibrous carbons with dispersed black particles of cobalt prepared from DVB–21.5 mol % Cp_2Co (5.5 wt % Co) by pyrolysis at 700° C and 125 MPa.

3. Results and discussion

3.1. Synthesis of cobalt-dispersed carbons

The molecular structures of cobaltocene (Cp_2Co) and phenylallylcobaltocene (PACo) are shown in Fig. 1. Divinylbenzene (DVB) was employed as a parent organic compound; and because of its thermal stability below 350° C, it is suitable in order to compare the thermal stabilities of the cobalt–carbon bonds of the organocobalt compounds.

DVB solution, mixed with an organocobalt compound, was polymerized at 300° C and 100 MPa for 2 h, yielded dark-brownish hard polymers. The PACo–DVB copolymer showed no characteristic IR absorption band due to the olefinic carbon–carbon double bond of PACo at 1649 cm^{-1} after such copolymerization. Several systems including organocobalt compound from 1.4 to 5.5 wt % as cobalt metal were successively pyrolysed in a sealed gold capsule at the temperatures 550 to 700° C and 125 MPa. Carbons thus formed had the morphology of coalescing polyhedra. When polymers containing more than 5.0 wt % cobalt were pyrolysed above 650° C at 125 MPa, the resultant carbons had polyhedral and fibrous morphologies. Fig. 2 shows the microstructure of fibrous carbon with finely dispersed metallic cobalt particles synthesized from the DVB–21.5 mol % Cp_2Co polymer including 5.5 wt % Co at 700° C and 125 MPa for 3 h. Black particles in an electron micrograph, < 20 nm diameter, were confirmed to be cubic metallic cobalt by using electron diffraction.

X-ray diffraction of the product from the pressure pyrolysis of DVB–13.5 mol % Cp_2Co (3.5 wt % Co) are shown in Fig. 3a, and are composed of two broad diffraction lines with maxima at $2\theta = 25.5$ and 44.5° (Cu$K\alpha$) which are independent of the initial concentration of cobalt. Cobaltocene itself behaves similarly. The former diffraction band is ascribed to the 0 0 2 diffraction of the turbostratic carbon, the latter to metallic cobalt with low crystallinity.

On the other hand, cobalt particles dispersed in the carbon formed from PACo–DVB copolymer (3.5 wt % Co) under the same conditions showed the strong diffraction lines of cubic and hexagonal cobalt at $2\theta =$ 44.2 and 47.5°, respectively, as shown in Fig. 3b. As the concentration of cobalt in the PACo–DVB polymer increased from 3.5 to 6.5 wt %, the intensity of the diffraction lines of cubic and hexagonal cobalt became stronger. There also appeared other diffraction lines at $2\theta = 41.7°$ (hexagonal cobalt) and 51.5° (cubic) as shown in Fig. 3c.

When the organoiron copolymer was pyrolysed under pressure, iron carbide was dispersed in the resultant carbon and could be converted to α-iron [8]. In contrast, cobalt carbide was only formed in traces during pyrolysis but was not observed in formed carbons, as it is unstable above 260° C [11].

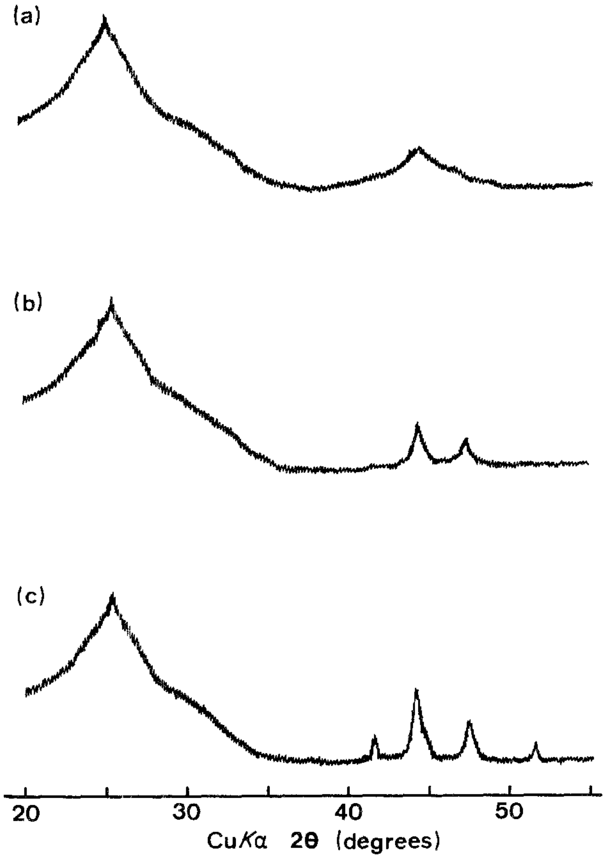

Figure 3 X-ray diffraction profiles of cobalt-dispersed carbons formed by pyrolysis of organocobalt polymers at 650° C and 125 MPa. Starting material (a) Cp_2Co–DVB (3.5 wt % Co), (b) PACo–DVB (3.5 wt % Co), (c) PACo–DVB (6.5 wt % Co).

3.2. The pyrolysis process of cobalt-containing polymers

3.2.1. Changes in magnetization

DVB solutions with 3.0 wt % Co as organocobalt compound were pyrolysed under pressure at several heat treatment temperatures (HTT). The magnetization of the carbon formed was measured with a magnetic balance at room temperature. Variations of magnetization with HTT are summarized in Fig. 4.

The DVB solution mixed with Cp_2Co was diamagnetic at room temperature because of the contribution of excess diamagnetic DVB over the paramagnetic Cp_2Co. Since PACo is diamagnetic, the DVB solution mixed with PACo shows diamagnetism at room temperature.

The PACo–DVB copolymer became paramagnetic at HTT $>$ 200° C at 100 MPa and increased gradually as the HTT increased from 200 to 300° C. The development of paramagnetic species and their aggregation in the PACo–DVB matrix proceeded concurrently with the polymerization of DVB, even at 200° C. The magnetization of PACo–DVB copolymer was about three times that of Cp_2Co–DVB polymer (HTT 250° C).

On the other hand, the magnetization of the Cp_2Co–DVB polymer changed from being diamagnetic to paramagnetic at 250° C and remained constant to 330° C, rapidly increasing between 330° C and 350° C.

The temperature of rapid change of magnetization in the Cp_2Co–DVB polymer takes place 50° C lower than with the vinylferrocene–DVB copolymer. This agrees with the difference in dissociation energies, that of the iron–carbon bond of ferrocene being 304 kJ mol^{-1} and that of cobaltocene being 270 kJ mol^{-1} [12]. Similarly, the cyclopentadienyl–cobalt bond of Cp_2Co is known to be thermally more stable than the bond between cyclopentadiene and cobalt in phenylallylcobaltocene.

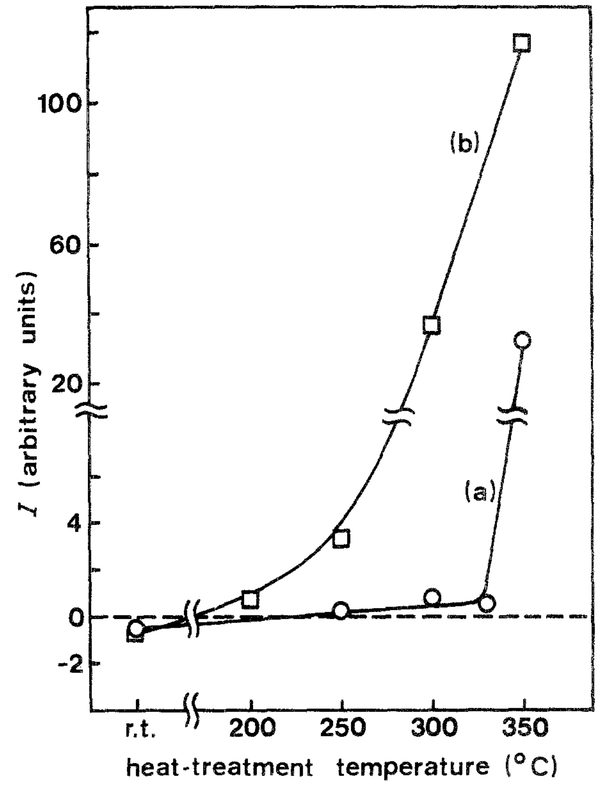

Figure 4 Magnetization of polymers containing 3.0 wt % Co treated at various temperatures for 2 h and 100 MPa: (a) cobaltocene-divinylbenzene, (b) phenylallylcobaltocene-divinylbenzene.

3.2.2. IR spectroscopy

The thermal degradation of the polymer containing 3.0 wt % Co was followed by IR spectroscopy. The intenstiy of the absorption band at 995 cm^{-1} of Cp_2Co–DVB and PACo–DVB polymers (characteristic of the cyclopentadienyl ring [13]) decreased as the pyrolysis temperature increased from 200 to 350° C. The weak absorption band at 995 cm^{-1} of the Cp_2Co–DVB polymer was observed at 300° C, and then disappeared at 350° C. However, no absorption at 995 cm^{-1} was observed by the pyrolysis of the PACo–DVB copolymer even at HTT 300° C.

This analysis of IR spectroscopy supports the fact that the PACo–DVB copolymer showed a remarkable increase in the magnetization compared with the Cp_2Co–DVB polymer between 200 and 350° C.

3.3. Magnetic properties of cobalt-dispersed carbon

3.3.1. Themomagnetic behaviour

Fig. 5 illustrates thermomagnetization curves of the cobalt-dispersed carbons from Cp_2Co–DVB and PACo–DVB polymers (5.5 wt % Co), pyrolysed at 700° C and 125 MPa for 3 h.

The magnetization of cobalt-dispersed carbons decreased with increase in temperature (the Curie temperature of cobalt itself is 1121° C [14]). The magnetization of the carbons formed from Cp_2Co–DVB polymer increased remarkably at about 500° C on the

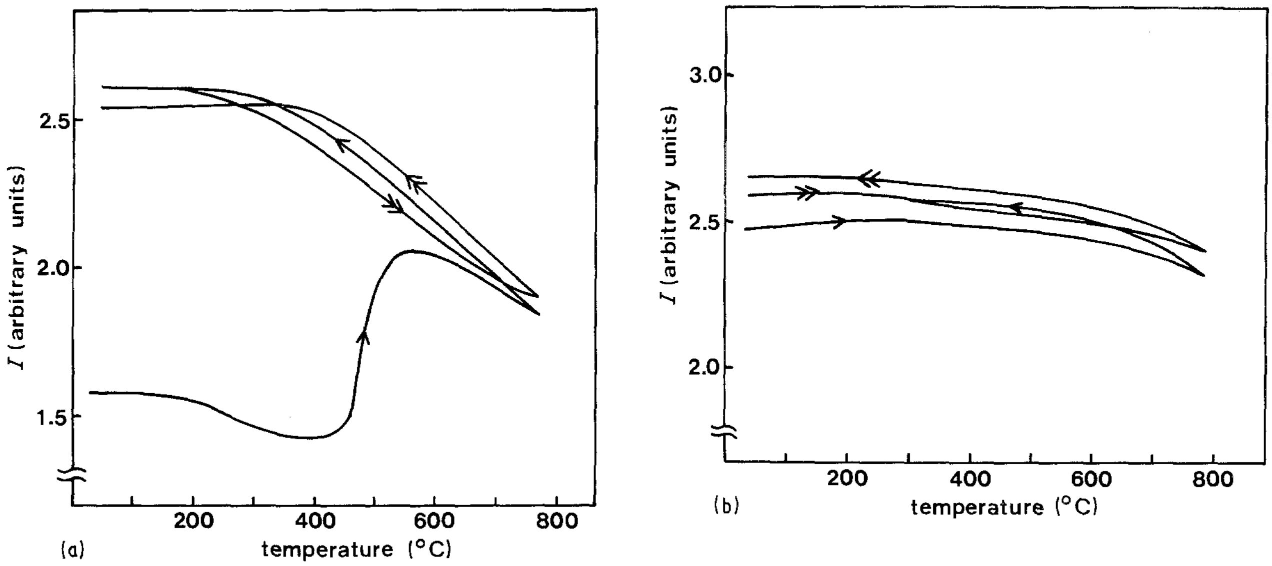

Figure 5 Thermomagnetization curves of cobalt-dispersed carbons formed by pyrolysis of polydivinylbenzene containing 5.5 wt % Co at 700° C and 125 MPa: (a) cobaltocene-divinylbenzene, (b) phenylallylcobaltocene-divinylbenzene.

first heating as shown in Fig. 5a, while no similar increase of magnetization was observed on heating and cooling (Fig. 5b). The as-prepared carbon from the Cp_2Co–DVB polymer contained both ferromagnetic and superparamagnetic cobalt particles. The growth and crystallization of superparamagnetic, fine metallic cobalt particles on the first heating increased the magnetization as shown in Fig. 5a, in agreement with the result that the marked crystallization into cubic and hexagonal cobalt was confirmed by X-ray diffraction after the thermomagnetization measurement. In contrast, no remarkable increase of crystallinity of dispersed cobalt in carbons formed from the PACo–DVB copolymer was detected by X-ray diffraction.

Cobalt particles, < 20 nm diameter, in the carbon from the Cp_2Co–DVB polymer shown in Fig. 2 grew to larger particles of 30 to 100 nm in diameter as shown in Fig. 6 during the thermomagnetic measurement. On the other hand, the as-prepared carbon from PACo–DVB copolymer includes the larger size of cobalt particles of around 100 nm in diameter.

3.3.2. Saturation magnetization and coercive force

Fig. 7 shows the relation of the saturation magnetization (σ_s) to the concentration of cobalt in cobalt-dispersed carbon formed from Cp_2Co–DVB and PACo–DVB polymers at 550° C and 125 MPa for 3 h.

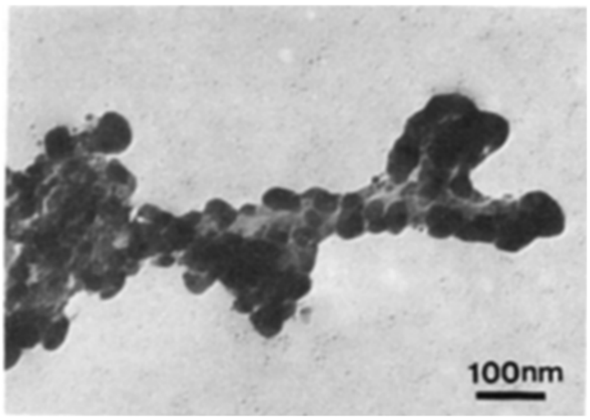

Figure 6 Microstructure of cobalt-dispersed carbons after thermomagnetization measurement of specimen of Fig. 2.

The linear relation between σ_s and the concentration of cobalt can be observed, which shows the uniform dispersion of cobalt in the carbon formed. The σ_s of cobalt-dispersed carbon form the PACo–DVB copolymer is higher by about 10% than that from Cp_2Co–DVB polymer. The coercive forces (H_c) of cobalt-dispersed carbon from PACo–DVB and Cp_2Co–DVB polymer are about 350 and 250 Oe, respectively (2.79×10^4 and $1.99 \times 10^4\,A\,m^{-1}$). The higher crystallinity of cobalt in the carbon from PACo–DVB copolymer is responsible for the higher σ_s and H_c than that from Cp_2Co–DVB polymer.

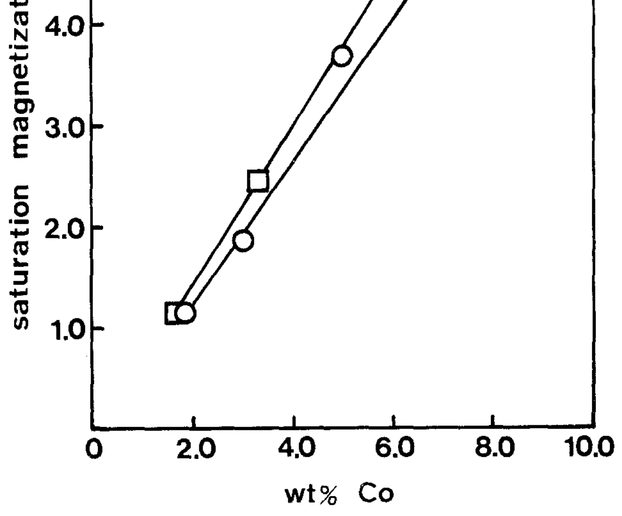

Figure 7 Saturation magnetization of cobalt-dispersed carbons formed from polydivinylbenzene containing organocobalt compounds by pyrolysis at 550° C for 3 h under 125 MPa: (a) cobaltocene-divinylbenzene, (b) phenylallylcobaltocene-divinylbenzene.

When the as-prepared carbon containing 5.0 wt % Co from Cp_2Co–DVB polymer was heat treated at 760° C for 6 h, its σ_s increased from 3.7 to 7.5 emu g^{-1} (95% of the theoretical value) with increase of H_c from 250 to 380 Oe (1.99×10^4 to $3.03 \times 10^4 A m^{-1}$). This heat treatment played a role not only in the growth and crystallization of superparamagnetic, fine cobalt particles, but also in the rearrangement of the crystal lattice of ferromagnetic metallic cobalt particles.

4. Conclusions

The properties of cobalt particles dispersed in the resultant carbon could be controlled by selection of the cobalt–carbon bond of the starting organocobalt compounds. Differences of crystallinity of cobalt in the resultant carbon originate in the different ease of the initial aggregation of paramagnetic species in polymers below 350° C. The magnetic properties of cobalt-dispersed carbon were dependent on the starting organometallic conpounds in their effect on the size and crystallinity of the resultant cobalt particles. Cobaltocene was found to be a better starting organocobalt compound than phenylallylcobaltocene for the homogeneous dispersion of fine metallic cobalt particles in the carbon formed.

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