Synthesis and properties of carbons dispersed with α-iron particles from divinylbenzene–vinylferrocene

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α-Iron-dispersed carbon was synthesized, through pressure pyrolysis of divinylbenzene–vinylferrocene above 750° C, and by reduction of magnetite-dispersed carbon. Divinylbenzene–vinylferrocene copolymer was pyrolysed at 125 MPa above 750° C to yield carbons dispersed with α-iron accompanied by cementite. Magnetite in the carbon matrix was reduced to α-iron after heat treatments at 500° C in a flow of hydrogen. Carbons synthesized by the pressure pyrolysis of divinylbenzene–vinylferrocene at 800° C and 125 MPa contained iron-compound particles up to 200 nm, whereas the median diameter of α-iron particles in the carbon matrix after reduction treatments was 20 nm. α-Iron-dispersed carbon had a Curie temperature of 770° C. The saturation magnetization of iron-dispersed carbon increased with increasing the pyrolysis temperature of divinylbenzene–vinylferrocene copolymer, and reached a constant value of 183 e.m.u. g^{-1} at 800° C. The saturation magnetization of α-iron-dispersed carbon after the reduction treatment revealed practically the theoretical value of α-iron. Carbons finely dispersed with only α-iron particles were synthesized successfully by reduction of magnetite-dispersed carbons.

1. Introduction

Metal-dispersed carbons have been synthesized by pressure pyrolysis of organometallic polymers in high-carbon yields [1–8].

One of the most important objectives for the synthesis of such metal–carbon composites is the control of both the morphology of matrix carbon and the properties of metal dispersoid. Hirano et al. [3] synthesized cementite-dispersed carbon from divinylbenzene copolymerized with vinylferrocene by pressure carbonization below 680° C. The morphology of cementite-dispersed carbon was found to depend upon the concentration of iron in the starting polymer as well as pyrolysis conditions. Hirano et al. [4] demonstrated that the crystallinity of cobalt particles in the carbon reflects the thermal stability of the cobalt–carbon bond of the parent organocobalt compounds. The particle size of cementite in the carbon has been found to be controlled by the selection of the carbon–carbon bond of the starting polymer matrix and the carbon–carbon bond between ferrocene and polydivinyl-benzene [7, 8].

This paper describes the synthesis of α-iron-dispersed carbon, by pressure pyrolysis of divinylbenzene–vinylferrocene above 750° C, and from magnetite-dispersed carbon by the reduction treatment. Attempts were made to disperse α-iron particles in the carbon matrix in order to increase the saturation magnetization of carbons dispersed with iron compounds, because α-iron has the highest saturation magnetization among iron-triad metals and iron compounds.

The oxidation state of iron in the carbon should also be controlled when iron-dispersed carbon is applied to catalysts for organic synthesis. The properties of α-iron particles and accompanying phases were investigated in order to elucidate two kinds of synthesis method. The reduction method was found to be superior to the direct high-temperature pyrolysis as a synthesis method for carbons finely dispersed with α-iron particles.

2. Experimental procedure

2.1. Starting materials

Vinylferrocene (VF) was prepared according to Arimoto and Haven [9]. Commercially available divinylbenzene (a mixture of 55% m- and p-divinylbenzene and 45% ethylbenzene) was employed as the organic copolymer for the carbon matrix.

2.2. Synthesis of iron-dispersed carbon

Pressure pyrolyses were carried out in a hydrothermal apparatus of the cold-seal type as described previously [2].

2.2.1. Direct synthesis through pyrolysis above 700° C

The mixture solution of vinylferrocene (VF), divinylbenzene (DVB) was sealed into a thin-walled gold capsule of 3.0 or 5.0 mm diameter and 50 mm length. The solutions of DVB containing VF were polymerized at 300° C and 100 MPa for 2 h and then pyrolysed at temperatures from 700 to 850° C and 125 MPa

for 3 h. The heating rate was $10°C\,min^{-1}$ at 125 MPa. The pressure was kept constant by releasing water as the pressure-transporting medium during heating. The pressure was measured with a calibrated Heise gauge and the temperature was measured with a calibrated sheathed thermocouple set inside the pressure vessel. The sample was quenched after each experimental run.

2.2.2. Reduction method of magnetite-dispersed carbon

The solution of DVB containing 10.5 mol % VF and water was sealed into a gold capsule and then polymerized at 300° C and 100 MPa for 2 h as described in Section 2.2.1. The organoiron copolymers thus prepared were successively pyrolysed at 550° C and 125 MPa for 3 h in the presence of water in a gold capsule.

A graphite crucible was filled with the as-pyrolysed product and then heat-treatment was carried out at temperatures between 500 and 700° C in a flow of hydrogen.

The as-prepared specimen was also heat-treated between 700 and 900° C under nitrogen and vacuum (about 10 Pa), respectively.

2.3. Characterization of iron-dispersed carbon

The yield of carbon was as high as 80% by weight.

The carbonized product was analysed by X-ray diffraction analysis. The iron-dispersed carbon was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron diffraction analysis. The particle diameter of α-iron in a carbon matrix was measured by TEM.

The thermomagnetization curve of iron-dispersed carbon was measured with a magnetic balance from room temperature to 850° C. The specimen was outgassed under vacuum for several hours at 250° C and then sealed into a quartz capsule under vacuum prior to the thermomagnetic measurement. The saturation magnetization of iron-dispersed carbon was evaluated using a vibrating sample magnetometer at room temperature.

3. Results and discussion

3.1. Synthesis of iron-dispersed carbon

3.1.1. Pressure pyrolysis of organoiron polymer above 700° C

Divinylbenzene (DVB)–10.5 mol % vinylferrocene (VF) was pyrolysed at temperatures between 700 and 850° C under 125 MPa for 3 h, and the XRD profiles of pyrolysis products are shown in Fig. 1.

The XRD profile of the product pyrolysed at 700° C consisted of two broad diffractions as shown in Fig. 1a. The broad diffraction centred at $2\theta = 25.5°$ (Cu$K\alpha$) is attributable to turbostratic carbon. The diffraction from $2\theta = 41.0°$ to $46.5°$ corresponds to cementite (Fe$_3$C). As the pyrolysis temperature increased from 700 to 750° C, the sharp reflection at $2\theta = 44.6°$ due to α-iron appeared. However, the broad diffraction from $2\theta = 41.0°$ to $46.0°$ superimposed on the reflection of α-iron in Figs 1c and d
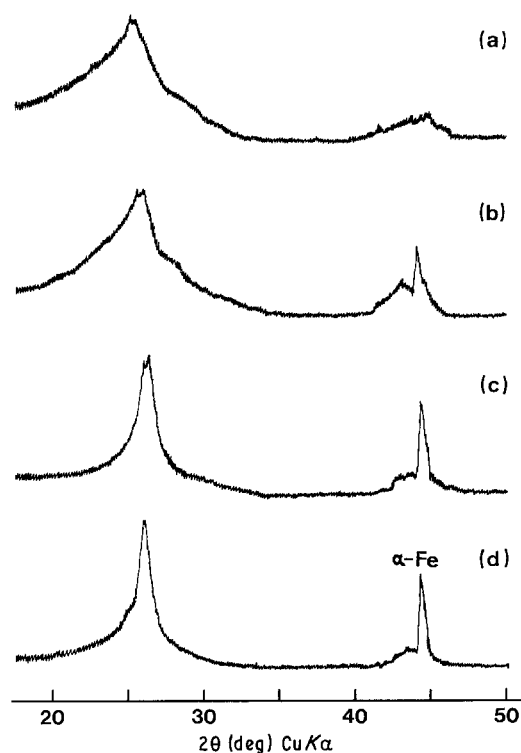

Figure 1 X-ray diffraction profiles of iron-dispersed carbons formed by pyrolysis of DVB–10.5 mol % VF at temperatures from 700 to 850° C under 125 MPa: (a) 700° C; (b) 750° C; (c) 800° C; (d) 850° C.

suggests the coexistence of cementite in the specimen pyrolysed even at 800 and 850° C.

On increasing the pyrolysis temperature from 700 to 850° C, the 0 0 2 diffraction of turbostratic carbon at 25.5° sharpens its half-value width with a shift of peak maximum from 25.5° to 26.3°. This fact suggests the alignment of an hexagonal layer increased in order with increasing pyrolysis temperature in the presence of catalyst iron, as reported [10].

3.1.2. Synthesis of α-iron-dispersed carbon through reduction of magnetite-dispersed carbon

Magnetite-dispersed carbon was synthesized by pressure pyrolysis of DVB–10.5 mol % VF and 17.6 wt % water at 550° C and 125 MPa for 3 h [3]. The formation of magnetite in the carbon was confirmed by XRD analysis.

Magnetite-dispersed carbon was heat-treated in a flow of hydrogen at temperatures from 500 to 700° C. The XRD profiles of the specimen after heat treatment are shown in Fig. 2. The specimen heat treated at 500° C for 1 h showed the diffractions of α-iron at $2\theta = 44.6°$ and würstite at 41.9° (Fig. 2a). Only α-iron particles were dispersed in the carbon matrix after heat treatment at 500° C for 2 h as shown in Fig. 2b. However, cementite began to form at 700° C even in a flow of hydrogen (Fig. 2c).

3.1.3. Heat treatment of magnetite-dispersed carbon under nitrogen and vacuum

Magnetite was found to disperse without any change after heat-treatments in a flow of nitrogen at 700° C for 1 h. The lowest temperature at which magnetite particles reacted with carbon matrix was 750° C, at
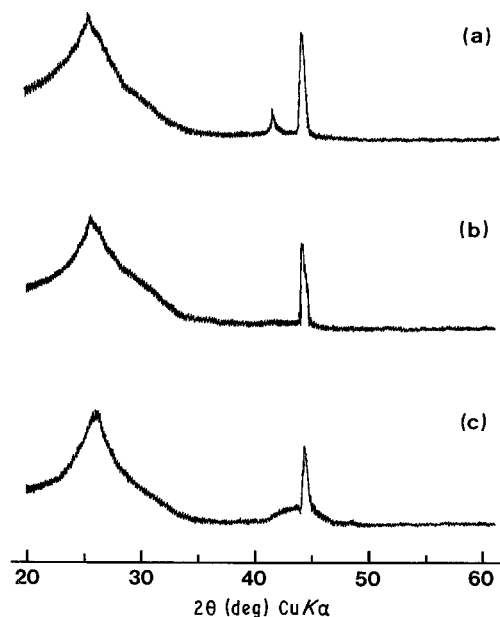
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Figure 2 X-ray diffraction profiles of iron-dispersed carbons synthesized by reduction of magnetite-dispersed carbons at various temperatures under hydrogen: (a) 500° C, 1 h; (b) 500° C, 2 h; (c) 700° C, 1 h.
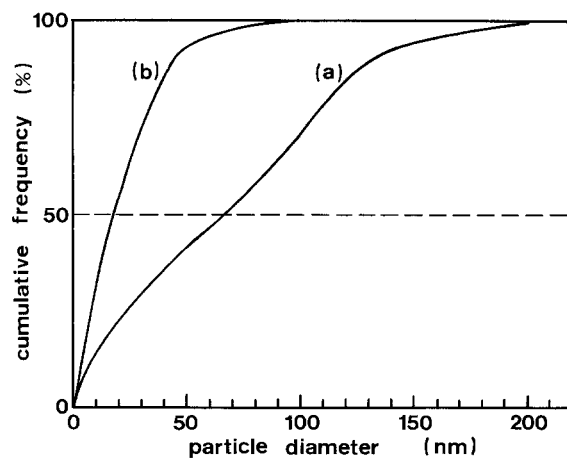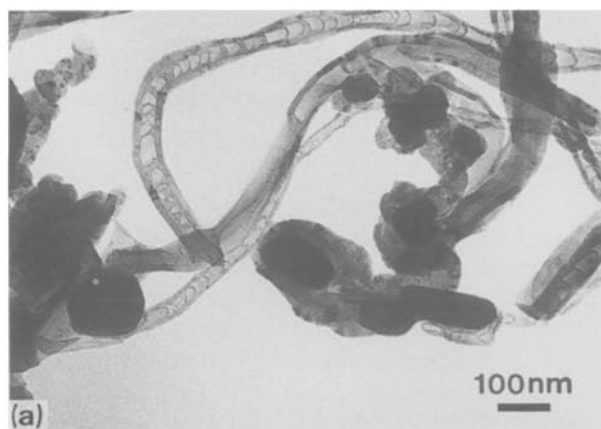

Figure 4 Size cumulative curves of α-iron particles dispersed in the carbon formed from organoiron copolymer including 3.0 wt % iron: (a) by pyrolysis of DVB–VF at 800° C and 125 MPa for 3 h; (b) through the reduction of magnetite-dispersed carbon at 500° C for 2 h under hydrogen.

which magnetite particles were not converted to α-iron but to a mixture of cementite and magnetite.

The heat treatment of magnetite-dispersed carbon under a vacuum of about 10 Pa gave a similar result to that obtained in a flow of nitrogen. The iron compound in the carbon matrix after heat treatment at 750° C and 10 Pa for 1 h was a mixture of magnetite and cementite. Magnetite was completely reduced to cementite after heat treatment at 800° C and 10 Pa for 3 h. No α-iron was formed in the specimen by heat treatment up to 900° C under 10 Pa.

Hydrogen does reduce magnetite completely to α-iron at about 500° C before α-iron reacts with carbon to form cementite, because hydrogen is a more powerful reducing agent than carbon.

3.2. Particle size of α-iron dispersed in carbon matrix

Figs 3a and b show the microstructures of α-iron-dispersed carbon synthesized by pyrolysis of DVB–10.5 mol % VF at 800° C and 125 MPa, and of the

reduction product of magnetite-dispersed carbon containing the same number of iron atoms, respectively.

The black particles were confirmed to be α-iron by electron diffraction analysis.

Fig. 4 summarizes the particle diameter distribution of α-iron in the carbon matrix synthesized by high-temperature pyrolysis and the reduction method. The carbon formed through the high-temperature pyrolysis contained particles up to 200 nm, whereas the particle sizes of α-iron by the reduction method were less than 100 nm. The median diameter of α-iron particles obtained by the high-temperature pyrolysis is about 65 nm, which is three times larger than that obtained by the reduction method.

The size of α-iron particles increased on thermal diffusion by the pressure pyrolysis at higher temperatures of 800° C. On the other hand, the original magnetite-dispersed carbon formed at 550° C and 125 MPa had a particle size of magnetite, less than 100 nm, which did not increase much in size through reduction to α-iron at 500° C for 2 h in a flow of hydrogen. The growth of α-iron particles by diffusion at 500° C does not proceed so markedly as that at 800° C. Therefore, the high-temperature pyrolysis of DVB–VF copolymer at 800° C gave larger particles of
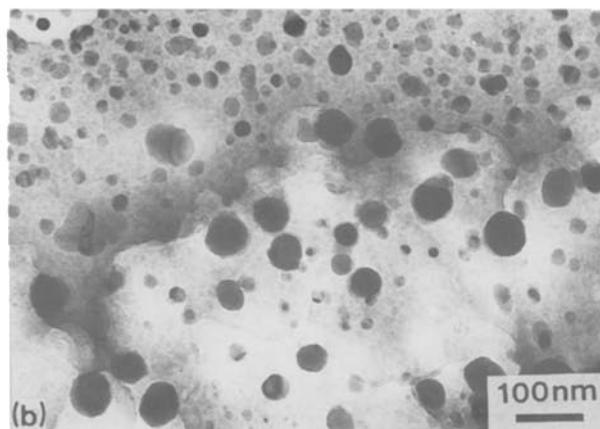

Figure 3 Microstructures of carbons dispersed with black particles of α-iron: (a) carbon including 3.0 wt % iron prepared from DVB–VF copolymer by pyrolysis at 800° C under 125 MPa; (b) carbon synthesized by reduction of magnetite-dispersed carbon containing 3.0 wt % iron at 500° C for 2 h under hydrogen.
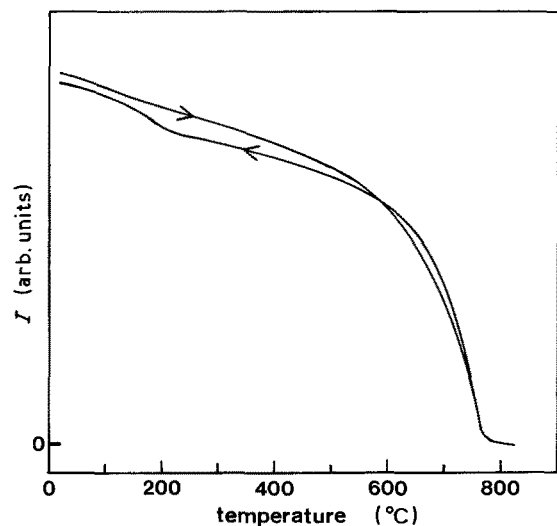
Figure 5 Thermomagnetization curve of α-iron-dispersed carbon formed by reduction of magnetite-dispersed carbon containing 1.5 wt% iron.

Figure 6 Saturation magnetization of carbons synthesized from DVB-10.5 mol% VF at temperatures between 700 and 850°C under 125 MPa.

α-iron than those formed by the reduction of magnetite particles at 500°C.

3.3. Magnetic properties of iron-dispersed carbon

3.3.1. Thermomagnetic behaviour

Fig. 5 shows the thermomagnetization curve of iron-dispersed carbon from room temperature to 850°C. The specimen was prepared through the reduction of magnetite-dispersed carbon formed by pyrolysis of DVB-5.1 mol% VF-10.0 wt% water at 550°C and 125 MPa as described in Section 3.1.2.

On heating, the magnetization of the specimen decreased and reached zero at 770°C, which is in good agreement with the Curie temperature of α-iron itself. No other Curie points of iron compounds except α-iron were observed in the thermomagnetization curve during heating. However, the thermomagnetization curve showed a Curie point of cementite at 210°C on cooling, and recovered almost the original magnetization.

The only ferromagnetic dispersoid in the specimen was α-iron before the thermomagnetic measurement. However, the reaction of α-iron particles with excess carbon during heating resulted in the formation of a small amount of cementite.

3.3.2. Saturation magnetization of iron-dispersed carbon

Fig. 6 correlates the saturation magnetization of the specimen synthesized from DVB-10.5 mol% VF above 700°C and the pyrolysis temperature of copolymer. The saturation magnetization of the specimen was converted to the value per gram of metal. The saturation magnetization increased with increasing pyrolysis temperature from 700 to 750°C, and reached a constant value of 183 e.m.u. g^{-1} at 800°C. The formation of α-iron in the specimen shown in Fig. 1 is responsible for the rapid increase of the saturation magnetization at 750°C, because the saturation magnetization of α-iron is about 1.7 times higher than that of cementite.

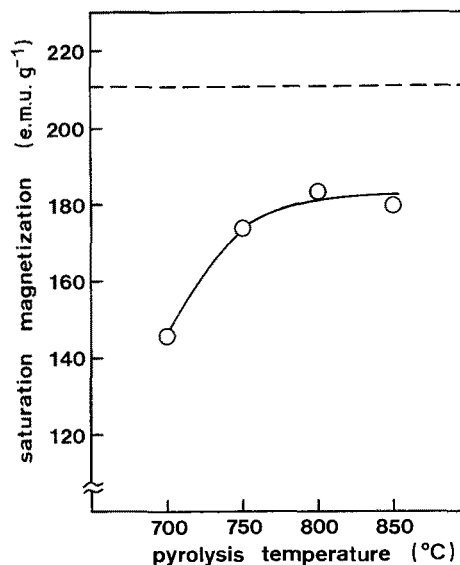The dashed line in Fig. 6 shows the saturation magnetization of carbon dispersed with α-iron produced through the reduction method containing the same concentration of iron atoms. The saturation magnetization of iron-dispersed carbon formed by the reduction method is higher than that obtained by the high-temperature pyrolysis of copolymer, because the iron phases of the latter comprise α-iron and cementite. The saturation magnetization of the specimen by the reduction method was 211 e.m.u. g^{-1}, which revealed about 97% of the theoretically calculated value based upon α-iron itself.

4. Conclusions

Carbons dispersed with α-iron particles were synthesized using divinylbenzene–vinylferrocene copolymer. The properties of iron-dispersed carbon formed through the pressure pyrolysis of divinylbenzene–vinylferrocene were compared with those synthesized by the reduction of magnetite-dispersed carbon. The results are summarized as follows:

1. Only α-iron particles were dispersed in the carbon matrix formed by the reduction method, while α-iron was accompanied by cementite in the specimen synthesized by pyrolysis of divinylbenzene–vinylferrocene above 750°C.

2. The median diameter of α-iron particles in the carbon matrix formed through the reduction method was 20 nm, which was one-third of that formed by the pyrolysis at high temperature.

3. The saturation magnetization of the specimen obtained by the reduction method was 97% of the theoretical value of pure α-iron, and was higher than that obtained by the high-temperature pyrolysis.

The reduction method was found to be better than the high-temperature pyrolysis for the synthesis of carbon finely dispersed with α-iron particles.

References
1. H. MARSH, F. DACHILLE, J. MELVIN and P. L. WALKER Jr, *Carbon* **9** (1971) 159.

2. S. HIRANO, F. DACHILLE and P. L. WALKER Jr, *High Temp. High Press.* **5** (1973) 207.
3. S. HIRANO, T. YOGO, H. SUZUKI and S. NAKA, *J. Mater. Sci.* **18** (1983) 2811.
4. S. HIRANO, T. YOGO, N. NOGAMI and S. NAKA, *ibid.* **21** (1986) 225.
5. T. YOGO, E. TAMURA, S. NAKA and S. HIRANO, *ibid.* **21** (1986) 941.
6. S. HIRANO, T. YOGO, K. KIKUTA and S. NAKA, *ibid.* **21** (1986) 1951.
7. T. YOGO, H. YOKOYAMA, S. NAKA and S. HIRANO, *ibid.* **21** (1986) 2571.
8. T. YOGO, S. NAKA and S. HIRANO, *ibid.* **22** (1987) 985.
9. F. S. ARIMOTO and A. C. HAVEN Jr, *J. Amer. Chem. Soc.* **77** (1955) 6295.
10. D. B. FISCHBACH, in "Chemistry and Physics of Carbon", edited by P. L. Walker Jr, Vol. 7 (Marcel Dekker, New York, 1971) p. 1.