Synthesis of Ferrocene–Phenol Resins and Liberation of Iron Particles by Pyrolysis

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Ferrocene-phenol resin was synthesized from 1-ferrocenylethanol, phenol, and formaldehyde in the presence of an ammonia catalyst. The resin structure was elucidated by chemical and infrared analyses and then confirmed by micro Vickers hardness measurements. To liberate iron atoms from ferrocene skeletons, the resin was pyrolyzed *in vacuo* at 400 °C. The properties of the iron dispersed in a glasslike carbon matrix were investigated by magnetic susceptibility measurements, ESR, and Mössbauer spectroscopy. The iron atoms coagulated into ferromagnetic iron particles in the glasslike carbon matrix. This coagulation is discussed in connection with the resin structure.

In recent years considerable efforts have been made to prepare ultra-fine particles of metals and metal compounds. These ultra-fine particles have proven to be a powerful tool in the clarification of physical properties. Furthermore, various kinds of ultra-fine particles, from atoms to submicroscopic particles, provide important information about the mechanism of crystal growth. Several workers have reported methods for preparing the ultra-fine particles.[1–4] In previous papers[5,6] we reported an approach to the size control of ultra-fine iron particles dispersed in a glasslike carbon matrix prepared from acetylferrocene–furfural resins by heat treatment. However, it still remains obscure whether the formation of ultra-fine particles depends on the molecular structure of acetylferrocene–furfural resin or the dispersion of glasslike carbon.

This investigation has been undertaken to determine the relationship between the preparation of ultra-fine iron particles and the molecular structure of a resin. The acetylferrocene-furfural resin is synthesized from furfural and acetylferrocene. The ferrocene skeleton forms the main chain of this resin and is fixed in the resin structure.[7] On the other hand, the ferrocene skeleton of the side chain is not fixed in the resin structure. Such a resin (ferrocene–phenol resin) was synthesized from 1-ferrocenylethanol, phenol, and formaldehyde in the presence of an ammonia catalyst. The structure of ferrocene–phenol resin was elucidated by chemical analyses, infrared spectroscopic analyses, and micro Vickers hardness measurements. The ferrocene–phenol resin was pyrolyzed up to 400 °C *in vacuo* to liberate iron. The properties of iron particles dispersed in the glasslike carbon matrix were investigated by magnetic susceptibility measurements, ESR, and Mössbauer spectroscopy.

Experimental

Materials. Ferrocene was synthesized according to the method proposed by Hata *et al.*[8] Acetylferrocene[9] derived from ferrocene and acetic anhydride was reduced to 1-ferrocenylethanol using $LiAlH_4$.[10] The product was purified by recrystallization from hexane and sublimation *in vacuo*: mp 72—74 °C (Ref. 11, 73—75 °C). The other chemicals used were reagent grade.

Preparation of Resins. Ferrocene-phenol resin was synthesized in the presence of an alkali catalyst according to the method for the preparation of resole-type phenolic resin.[11] 30% aqueous ammonia was used as the alkali catalyst to avoid contamination with metal elements in the resin. 1-Ferrocenylethanol (0—1.0 mol), 1 mol of phenol, and 1.5 mol of formaldehyde (37% solution) were mixed in a three-necked separable flask. To this mixture was added aqueous ammonia amounting to 0.7 mol% of 1-ferrocenylethanol, phenol, and formaldehyde. The reaction mixture was vigorously stirred at 70 °C for 3 h, cooled to room temperature, and then neutralized with dilute hydrochloric acid. The water in the reaction product was removed to form oligomers under reduced pressure at 70 °C. Further, the oligomer was dried *in vacuo* at 70 °C for 24 h in order to remove the volatile materials. The yield of the oligomer was 70—80% The oligomer containing ferrocene was mixed with 10 wt % of hexamethylenetetramine and then heated in argon at 150 °C for 24 h. The yield of the ferrocene-phenol resin was 85—93%.

Pyrolysis. The ferrocene-phenol resin was pyrolyzed up to 400 °C *in vacuo*: 20—350 °C, 3h; 350—400 °C, 2.5 h. The heat-treated samples in the vacuum container were placed in a glovebox filled with argon gas. The following operations were carried out in the glovebox. The heat-treated resins were ground to a powder using an agate mortar and a pestle. The powdered sample for magnetic susceptibility measurements was put in the glass tube filled with anhydrous hexane, and then sealed with a rubber cap. For ESR spectral measurements, the powdered samples were put into a silica tube ($5\phi \times 200$ mm) and sealed with an epoxy resin. The powdered sample mixed with silicone grease was used for Mössbauer spectral measurements.

Elemental Analysis and Measurement of Properties. Iron determination was carried out with a Hitachi-207 atomic absorption spectrophotometer. IR spectra were measured with a Jasco IR-S grating spectrometer using potassium bromide disks. Micro Vickers hardness was measured with an Akashi model MVK type D instrument with a load of 200 g. The magnetic susceptibility was recorded on a Shimadzu MB-10A magnetic balance at temperatures of 77 to 293 K. Number-average molecular weights were determined by a Hitachi model-117 vapor pressure osmometer using dimethyl sulfoxide as a solvent. ESR spectra were taken on a Hitachi model 771-0061 spectrometer at 77 K. Mössbauer spectra were measured with an automechanical acceleration spectrometer at 4.2 K using a ^{57}Co-in-Cu source. All of the isomer shifts were obtained with respect to the centroid of iron metal at 293 K.

Results and Discussion

Polycondensation Reaction and Resin Structure. 1-Ferrocenylalkanols are polycondensed in the pre-

Table 1. Polycondensation Reaction and Elemental Analysis of Resins

Resin No.	Starting material[a)]		Elemental analysis of resins (wt%)				
	1-Ferrocenylethanol (mol)	Fe (wt%)	C	H	Fe	N	O[b)]
1	0.010	0.40	76.5	5.77	0.65	0.59	16.49
2	0.017	0.67	76.3	5.82	1.14	0.74	16.00
3	0.025	0.97	75.8	5.84	1.56	0.76	16.04
4	0.050	1.86	76.0	5.88	3.33	0.87	13.92
5	0.10	3.46	74.9	5.61	6.23	0.84	12.42
6	0.20	6.05	73.3	5.91	9.53	1.89	9.37
7	0.40	9.24	72.6	5.83	13.5	1.74	6.33
8	0.60	12.1	71.0	5.87	14.8	1.75	6.58
9	0.80	13.9	70.8	5.99	15.2	1.80	6.21
10	1.00	15.2	70.6	5.96	15.3	1.78	6.36
11	0	0	76.0	5.67	0	0.19	18.14

a) Phenol: 1 mol; formaldehyde: 1.5 mol. b) O=100−C−H−Fe−N.

sence of an acid and a Lewis acid. However, a base does not catalyze the polycondensation. The polycondensation reaction of aldehydes and cyclopentadienyl rings of ferrocene is catalyzed by a Lewis acid, but not by a base.[12)] A resole-type oligomer is synthesized from 1 mol of phenol and 1.5 mol of formaldehyde in the presence of an alkali catalyst. Cured resole-type phenolic resins are obtained by the thermosetting of a resole-type oligomer.[11)]

1-Ferrocenylethanol, phenol, and formaldehyde were polycondensed to make ferrocene–phenol oligomers, using aqueous ammonia as a catalyst. The curing of the ferrocene–phenol oligomer was not achieved in the absence of hexamethylenetetramine. The larger the amount of ferrocene skeletons in the oligomer was, the less the thermosetting reaction took place. The elemental analyses of the cured resins are shown in Table 1, together with the molar ratios of the starting materials. The nitrogen in the resin arose from hexamethylenetetramine, since no nitrogen is contained in any oligomer. The reactivities of 1-ferrocenylethanol and formaldehyde with phenol have not been investigated. Nevertheless, it is possible to estimate the reactivity and the structure of ferrocene–phenol resin from the data of elemental analyses. As shown in Table 1, the iron contents in the starting materials were less than those in resins 1 to 9. This relation was not valid for resin 10. The result of elemental analysis of resin 9 was identical with that of resin 10. Thus, the rate of reaction of 1-ferrocenylethanol and phenol was much faster than that of formaldehyde and phenol. The maximum quantity of 1-ferrocenylethanol allowed to react with phenol seemed to be restricted by a stoichiometric reaction. The stoichiometric reaction of 1-ferrocenylethanol, phenol, and formaldehyde should be an intermediate reaction between resins 8 and 9. From the elemental analysis of resins 9 and 10, the structural unit of the resin was calculated to be $C_{46}H_{47}O_3Fe_2N$. The number-average molecular weight of the oligomer of resin 9 was 650, which was close to the molecular weight of the structural unit of the resin. It was obvious that two ferrocene units ($C_{12}H_{13}Fe$) were contained in the structural unit. If three phenols (C_6H_6O) were bonded in it, four carbons and a nitrogen constituted the structure of the resins as the crosslinking unit. The above results suggest the resin structure shown in Fig. 1. The structure of the oligomer of resin 9 would be similar to this structure. On the initial step in the polycondensation reaction of the resin, 2 mol of phenol react with 2 mol of 1-ferrocenylethanol and the hydroxymethylation of phenol (1 mol) takes place. The ferrocenyl phenol (2 mol) reacts with 1 mol of the hydroxymethylated phenol to form the oligomer. The structure of the oligomer is classed as a novolac-type oligomer, because the cure reaction does not proceed sufficiently in the absence of hexamethylenetetramine.

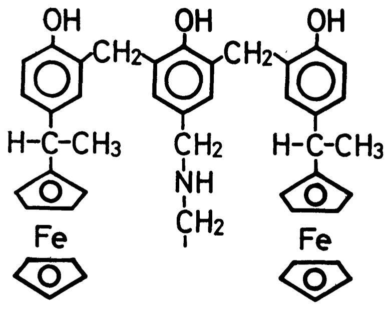

Fig. 1. The structure of ferrocene-phenol resin 9.

The amount of crosslinkage in a resin is related to its rigidity.[13)] The micro Vickers hardness of resins, which is an indication of the rigidity, decreased rapidly with the increase in iron content, as shown in Fig. 2. The amount of crosslinkages in the resins decreased with an increase in the amount of ferrocene skeletons. This result indicated that the unsubstituted cyclopentadienyl ring does not take part in the formation of the main chain.

The IR spectra of ferrocene–phenol and resole-type phenolic resins are shown in Fig. 3. The absorption bands at 480, 818, 998, 1103, and 3080 cm^{-1} were assigned to ferrocene. The 480 cm^{-1} band was due to the ring metal stretching of ferrocene.[14)] The

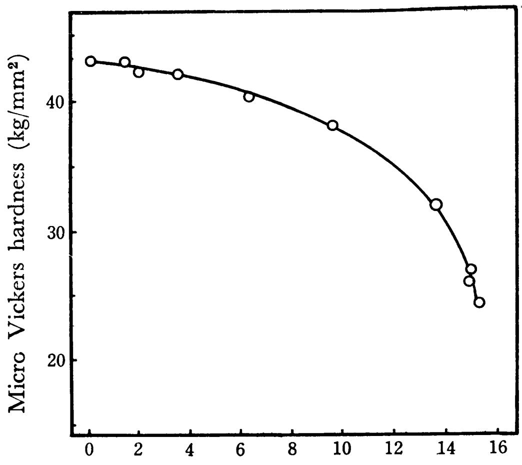

Fig. 2. Relation between micro Vickers hardness and iron contents of ferrocene-phenol resins.

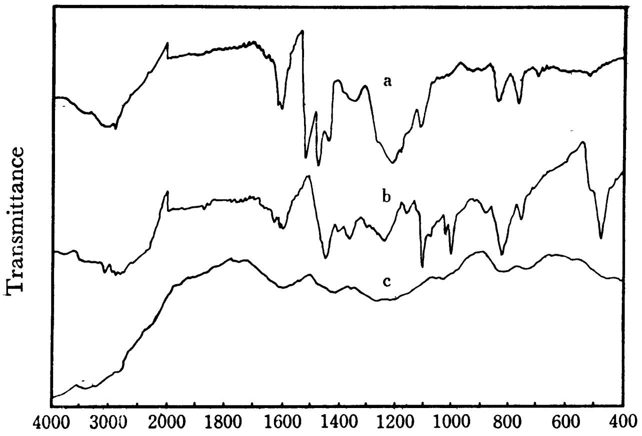

Fig. 3. IR spectra of phenolic resin and ferrocene-phenol resin, the heat-treated at 400 °C; (a) phenolic resin 11, (b) ferrocene-phenol resin 9, (c) ferrocene-phenol resin 9 heat-treated at 400 °C.

out-of-plane bending of ferrocene CH was manifested by the band at 818 cm^{-1}.[15] The presence of unsubstituted cyclopentadienyl rings was revealed by two bands at 998 and 1103 cm^{-1}.[16] The absorption band which appeared at 3080 cm^{-1} could be assigned to the stretching of ferrocenyl C–H.[14] In the IR spectrum of resole resin, the three bands at 1500—1650 cm^{-1} were assigned to the skeletal stretching mode of semi-unsaturated carbon-carbon bond. The band at 1220 cm,$^{-1}$ which was observed in both ferrocene–phenol and resole resins, corresponded to the absorption band of phenolic OH. In the IR spectrum of resole resin, two bands at 855 and 753 cm^{-1} were assigned to a 1,2,4,6-tetrasubstituted aromatic ring and a 1,2,4-trisubstituted aromatic ring, respectively. However, two bands at 753 and 874 cm^{-1} due to the 1,2,4-trisubstituted aromatic ring were strongly observed in the IR spectrum of ferrocene–phenol resin.[17] Results of IR spectral studies are in accord with the structure of ferrocene–phenol resin shown in Fig. 1.

TABLE 2. ELEMENTAL ANALYSIS OF RESINS HEAT-TREATED AT 400 °C

Resin No.	Elemental analysis (wt%)				
	Fe	C	H	N	O[a]
1	0.55	82.01	4.84	0.00	12.96
2	0.98	81.68	4.85	0.00	12.49
3	1.03	81.27	4.77	0.00	12.93
4	3.71	80.33	4.84	0.00	11.12
5	4.29	79.41	5.98	0.00	10.32
6	7.95	76.13	5.18	0.00	10.74
7	11.60	73.56	5.18	0.00	9.66
8	13.20	72.10	5.15	0.00	9.55
9	14.70	71.41	5.16	0.15	8.58
10	14.65	71.87	5.14	0.21	8.13
11	0.00	82.31	4.88	0.00	12.81

a) O = 100 − Fe − C − H − N.

Pyrolysis. The pyrolysis of resins was carried out by heat treatment up to 400 °C *in vacuo*. The IR spectrum of heat-treated ferrocene–phenol resin is shown in Fig. 3. All absorption bands due to ferrocene disappeared in the spectrum. This shows that the ferrocene skeleton in the ferrocene–phenol resin was destroyed, and iron was liberated by the heat treatment at 400 °C. Elemental analyses of heat-treated resins are shown in Table 2. The heat-treated resins contained carbon, hydrogen, iron, nitrogen, and oxygen. The nitrogen contents were less than those of the resins. The iron contents were 0.55—14.7%, which were close to that of acetylferrocene–furfural resin (1.00—13.2%).[5] It is well known that phenol and furan resins are converted into the hard and impervious carbon which does not contain open pores.[18] Especially, the impervious carbon prepared at 400 °C is in a completely glassy state.

Properties of Liberated Iron Particles. The measurement of magnetization is useful in determining whether the iron particles dispersed in the glasslike carbon matrix are superparamagnetic or not. Magnetic susceptibilities of heat-treated resins 1 to 10 indicated that the iron particles were ferromagnetic. The measurement of ESR spectra was carried out for all heat-treated resins. The ESR spectra of heat-treated resins

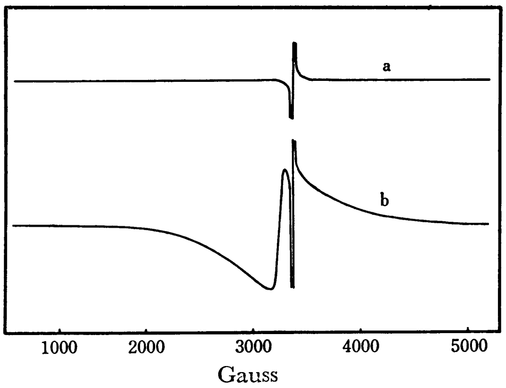

Fig. 4. ESR spectra of phenolic and ferrocene-phenol resins heat-treated at 400 °C; (a) phenolic resin 11, (b) ferrocene-phenol resin 1.

1 and 11 are shown in Fig. 4. The broad line near $g=2.09$ in resin 1 was due to the ferromagnetic resonance absorption of iron.[19] The ferromagnetic resonance absorption was common to the other heat-treated resins, 2 to 10. However, the peak intensity in the spectra increased with increase in iron contents. The sharp line at $g=2.002$, which was observed in the resins 1 and 11, corresponded to the resonance of free electrons on the carbon atom.[20] Further, the presence of ferromagnetic irons was confirmed in detail by their magnetic hyperfine splitting in the Mössbauer spectrum of the heat-treated resin 3, as shown in Fig. 5.[21] Because additional lines were not observed in the spectrum, only ferromagnetic iron was formed in the glasslike carbon matrix.

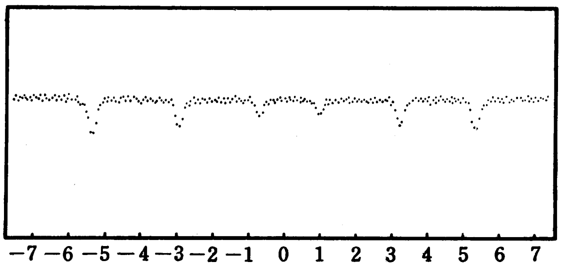

Fig. 5. Mössbauer spectrum of ferrocene-phenol resin 3 heat-treated at 400 °C.

The results of the present work lead to the following conclusions. Iron particles are formed in the glasslike carbon matrix by the heat treatment of ferrocene–phenol resins, in which the ferrocene skeleton is contained as a side chain. These iron particles are ferromagnetic and are different from the iron particles prepared from acetylferrocene–furfural resins in which the ferrocene skeleton forms the main chain of the resin. In the case of the side chain structure, the iron liberated from ferrocene skeletons is considered to coagulate to form the ferromagnetic iron because the spaces around the ferrocene skeleton are loosely surrounded by the resin structure. In this respect, it is necessary to take into account the differences between the properties of glasslike carbons prepared from ferrocene–phenol resin and acetylferrocene–furfural resin. However, these differences are considered to be small compared with the structural differences between these two resins; the details of these differences are now under investigation.

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