Preparation of Co and Ni dispersed porous carbon from metal naphthenate-phenolic and furan resin hybrid

Takahiro TAKEI,[†] Satoshi INOUE, Qiang DONG, Yoshinori YONESAKI,
Nobuhiro KUMADA and Nobukazu KINOMURA

Center for Crystal Science and Technology, Faculty of Engineering, University of Yamanashi, 7–32 Miyamae, Kofu 400–8511

Metal-dispersed porous carbon was prepared from phenolic or furan resin mixed with Co or Ni naphthenate. The formed metal particles in these metal-dispersed porous carbons are apparently smaller than those in the metal-carbon composite prepared from metal nitrate. In the case of the metal-dispersed porous carbon prepared from phenolic resin and Co naphthenate, graphite phase was formed above 800°C around Co nanoparticles. XRD patterns and TEM micrographs confirm that metal naphthenate works as a metal source from which dispersed nanosize metal particles formed. The porous carbons prepared from phenolic or furan resin with Co or Ni naphthenate have specific surface area of approx. 400 m²/g. For the porous carbon from phenolic resin, mesopore was formed within the sample by cracking or breaking up the large particles. These results indicate that mixing of phenol monomer and the naphthenate before polymerization results in development of mesopore.

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1. Introduction

Carbon materials are generally classified into two groups; soft and hard carbon. Coke and pyrolytic carbon belong to the soft carbon,^{1,2)} and the carbon derived from phenolic and furan resin, and carbon black to the hard carbon.^{3,4)} At very high temperature of approx. 2500°C without non-additives, the soft carbon generally tends to graphitize, whereas the hard carbon can not graphitize. For the hard carbon, the structure is generally regarded as amorphous and some distinctive materials have been provided as follows. Activated carbon has many micropores between stacked small graphene sheets which have some defects, like agglomerate of non-oriented small graphite crystalloids. Carbon black is usually composed of very small turbostratic graphite which have 5- and 6-membered ring. For these carbonaceous phases, crystallinity and defect are generally examined by Raman spectroscopy using G and D band, respectively.^{5–7)}

For carbon phase, sometimes metal introduction plays an important role as a catalyst to form pore, graphitization and so on. For example, Ago et al. reported that Fe, Co or Ni/MgO catalyst works for formation of nanotube.⁸⁾ Oya et al. reported that dispersion of Ni or Co nanoparticles results in formation of turbostratic graphite from phenolic resin.^{3,9)} In addition, metal inclusion affects adsorption properties. Especially activated carbon, adsorption properties are very important because the activated carbon generally use as a adsorbent due to its very high surface area. Metal in carbon matrix affects the adsorption properties by two mechanisms as follows.^{10,11)} One is chemically catalyzed reaction during adsorption such as spill over of hydrogen into the carbon body, and another is control of pore structure during formation of the material. For the formation of pore texture, metal and carbon source are possibly very important. Oya et al. reported that mesopore formation during

carbonization from phenolic fiber with Co acetylacetonate.³⁾ However, phenolic polymer chain and Co acetylacetonate seemed to be not mixed at molecular level. There, metal naphthenates can be candidate for metal additive into carbon for the following reason. The metal naphthenate is composed of metal cation and relatively long organic chain (mainly alkyl and aromatic carboxylate). This naphthenate is insoluble in water and is soluble in nonpolar solvent. Therefore, homogeneous blend of the resin and metal naphthenate molecules may be attained by mixing monomer of the resin and the metal naphthenate before polymerization. We examine phenolic and furan resin as a carbon source and Co- or Ni-naphthenates as a metal source for preparation of organized metal and resin hybrid to form metal-dispersed carbon and also examine their pore structure and porous properties.

2. Experimental

2.1 Sample preparation

The activated carbon was prepared by two processes, polymerization of phenol and furfuryl alcohol and their decomposition. In these experiments mentioned as follows, Co and Ni naphthenates (DIC Corp.) or Co and Ni nitrates were used as metal source.

For phenolic resin, Co or Ni sources were at first put into phenol solution including trimolar formaldehyde and equimolar octylamine. The molar ratios of metal and phenol were 0.01, 0.1 and 1.0. The solution was stirred at 60°C for 6 h and then at 230°C for 24 h to polymerize. For the polymerization of furfuryl alcohol, metal source was put into furfuryl alcohol with molar ratio of 0.01. The solution was stirred at 80°C for 24 h. Then, it was heated at 150°C for 24 h to form furan resin.

These polymerized samples were heated at 800°C for 1 h in N₂ gas for carbonization. Activation treatment was carried out by heat treatment at 900°C in steam carried by N₂ flow for 6 h. These samples are designated as C-*n*M (C: P and F, *n*: 0.01, 0.1 and 1.0, M: Co and Ni for Co- and Ni-naphthenate, Co^{Nit} and Ni^{Nit} for Co

[†] Corresponding author: T. Takei; E-mail: takei@yamanashi.ac.jp

Fig. 1. XRD patterns of the metal-dispersed porous carbon with metal/carbon ratio of 0, 0.01, 0.1 and 1.0 prepared from phenolic resin as a carbon source and Co- or Ni-naphthenate as a metal source.

and Ni nitrate and M for any metal), where C indicates variety of resin, n concentration of loaded metal and M kind of metal. For example, P-0.01Co means the metal-dispersed porous carbon derived from phenolic resin including Co with loading ratio of 0.01, and F- n M means the carbon from furan resin with any ratio of Co or Ni metal.

2.2 Characterization

Components of the sample were identified by X-ray diffraction with monochromated CuK α radiation (RINT2000, Rigaku). The porous properties, specific surface area, pore size distribution and pore volume were measured by N₂ porosimeter (Belsorp-mini, Nippon BEL) at -196°C . A chemical state of carbon was examined by Raman spectroscopy (inVia Raman Microscope, RENISHAW). The texture of the metal-dispersed porous carbon was observed by transmission electron microscopy (JEM-2000FXII, JEOL).

3. Results

3.1 Carbonization of resin including Co and Ni naphthenates

Co and Ni-dispersed porous carbon were at first prepared from phenol and metal naphthenates. Figure 1 shows the XRD patterns of phenol resin-derived carbonized samples including metal with various Co and Ni ratio from the naphthenates. For P- n Co, halos at the range from 15 to 30° diminished and a new diffraction peak emerged at around 26° . These peaks seem to be attributed to a graphite phase. On the other hand, XRD patterns confirm that the graphite phase did not crystallize in P- n Ni samples. All samples show 111 diffraction peak of metal which

Fig. 2. XRD patterns of the metal-dispersed porous carbon with metal/carbon ratio of 0.01 prepared from phenolic and furan resin as a carbon source and Co- or Ni-naphthenate and nitrate as a metal source.

have FCC with a lattice constant of approx. 0.35 nm. The peak drastically grew at more than 0.01 of the concentration of loaded metal. Such a precipitous growth suggests that there is a threshold of metal-dispersible concentration between 0.01 and 0.1. Hereafter, we use the metal of 0.01 to investigate effect of carbon and metal sources.

Figure 2 shows XRD patterns of carbonized samples from a phenolic and furfuryl resin including Co or Ni naphthenates, P- and F-0.01M. The patterns of carbonized resins with Co or Ni nitrates were also showed for comparison in the same figure. These patterns confirm that Co and Ni metals were crystallized for not only the metal-dispersed porous carbon obtained from the naphthenates but also metal nitrates. For the carbons prepared from the phenolic resin, crystallinity of Co and Ni metal from the nitrates seems higher than that from the naphthenates. For only P-0.01Co, the diffraction line attributed to interlayer spacing between graphene sheets is observed at approx. 26° . On the other hand, for the carbons obtained from the furfuryl alcohol, the crystallinity of Ni was extraordinary high in the F-0.01Ni sample. For F-0.01Co^{Nit}, a very small amount of graphite was possibly crystallized.

Figure 3 shows TEM micrographs of P-, F-0M, P- and F-0.01M. For P- and F-0M, no tumor is observed. For P-0.01Co, Co particles with ten or several tens nanometer in size are observed. Fine fragments are also observed at around Co particles. These fragments are probably graphite particles. For P-0.01Ni, very fine Ni particles are observed. Since the particle size seems to be approx. 10 nm, these particles are possibly composed of one crystallite. For P-0.01Co^{Nit}, very large Co particles of approx. 500 nm are observed. These particles are apparently agglomerates composed of some crystallites. Similar structure with smaller agglomerates can be observed in the P-0.01Ni^{Nit}. For F-0.01Co, Co particle is approx 50–100 nm in size. Therefore, the particle must be composed of several crystallites. On the other hand, Ni crystallites were dispersed in F-0.01Ni. The F-0.01Co^{Nit} and F-0.01Ni^{Nit} have Co and Ni agglomerates with several tens or hundreds nanometer in size within themselves. These micrographs confirm that agglomerate tends to be formed by using Co or Ni nitrate.

Fig. 3. TEM micrographs of the metal-dispersed porous carbon with metal/carbon ratio of 0.01 prepared from phenolic and furan resin as a carbon source and Co- or Ni-naphthenate and nitrate as a metal source.

3.2 Adsorption isotherms of metal-dispersed porous carbons

Figures 4(a) and 4(b) show N_2 isotherms of these samples measured at -196°C . From these curves, pore structures are found to be different by carbon and metal source as follows. For the metal-dispersed porous carbon obtained from phenolic resin, P-0M, P-0.01Co^{Nit} and P-0.01Ni^{Nit} show type I isotherm. Such isotherm generally results from microporous material because micropore filling occurs. For P-0.01Co and P-0.01Ni, adsorption volume steeply increases at very high relative pressure of approx. 1.0. Apparent hysteresis emerged in these isotherms. Such hysteresis loop represents existence of mesopore. On the other hand, for the carbon from furan resin (polymerized furfuryl alcohol), F-0M shows the increase of adsorbed volume at high relative pressure, while F-0.01M carbons show the type I isotherms. These isotherms confirm that carbon sources and metal sources significantly affect pore structure.

Table 1 shows specific surface area (Sa) and pore volume (Vp). For P-*n*M, the Sa of P-0.01M of around $360\text{--}450\text{ m}^2/\text{g}$ are half as large as that of P-0M. However, Vp of P-0.01Co and -0.01Ni shows similar to that of P-0M while those of P-0.01Co^{Nit} and -0.01Ni^{Nit} are around half as the trend of Sa. For F-*n*M, the Sa of F-0.01Co and Ni are around $200\text{ m}^2/\text{g}$. These are smaller than those of P-0.01M. In addition, ratios of the Sa and the Vp are almost constant in spite of the differences on metal source for F-*n*M. These results indicate that mean pore radii are changed in P-*n*M using metal naphthenates, whereas those are almost constant at least in F-*n*M.

4. Discussion

4.1 Co and Ni nanoparticles and graphitization in the metal-dispersed porous carbon from hybrid resin

In Fig. 2, XRD patterns confirm that crystallization of metals in all samples and graphitization in P-0.01Co. Table 2 shows Co

and Ni crystallite sizes in the metal-dispersed porous carbons. General trend is smaller metal crystallites formed in phenolic resin than those in furan resin. This trend possibly results from the structure of resin. Phenolic resin polymerized in base condition generally tends to form 3-dimensional structure by cross-linkage. On the other hand, furfuryl alcohol is generally polymerized with cross-linkage in acidic circumstance.¹²⁾ Therefore, the cross-linkage in the phenolic resin is possibly developed more than that in the furan resin in this study. The cross-linked resin with 3-dimensional structure may isolates molecule of metal source within the 3-dimensional network to form metal nanoparticle. On using metal naphthenate, the naphthenate chain might snaggle with the 3-dimensional structure to be dispersed better. Actually, for the P-*n*M samples, metal crystallite which was derived from metal naphthenate was smaller than that from metal nitrate. Especially for P-0.01Co, broad diffraction line of Co at around $40\text{--}45^\circ$ seems to be composed of two peaks; a peak at 44.2° and a broad peak at 43.5° . Both two peaks are probably derived from slight different Co metal phases, α -Co and carbon-stabilized Co, respectively. On the other hand, for F-*n*M, inverse tendency is confirmed. The reason of such tendency may result from weak acidity of metal nitrate. That is, the weak acidity of metal nitrate may cause some cross linkages of furan resin with introducing small amount of metal cation. These crystallite sizes in Table 2 are coarsely coincident with the size of observed by TEM as shown in Fig. 3.

The XRD patterns in Fig. 2 confirm that apparent graphitization in P-0.01Co. The diffraction line exists at 0.345 nm which is slightly larger by around 0.01 nm than that of general graphite. Such large interlayer spacing possibly confirms that the slightly turbostratic structure generally showed in typical catalytic graphitization.³⁾ The diffraction line can be regarded as supporting evidence for fine dispersion of Co nanoparticles. In fact, we examined graphitization temperature for Co naphthenate phenolic resin hybrid. XRD patterns omitted in this paper confirm

Fig. 4. N_2 isotherms at -196°C of the metal-dispersed porous carbon with metal/carbon ratio of 0.01 prepared from phenolic and furan resin as a carbon source and Co- or Ni-naphthenate and nitrate as a metal source.

Table 1. Specific surface area and pore volume of the metal-dispersed porous carbon

Sample	Sa/ $\text{m}^2\cdot\text{g}^{-1}$	Vp/ $\text{mL}\cdot\text{g}^{-1}$
P-0M	841	0.43
P-0.01Co	375	0.41
P-0.01Ni	445	0.51
P-0.01Co ^{Nit}	421	0.24
P-0.01Ni ^{Nit}	361	0.19
F-0M	577	0.37
F-0.01Co	195	0.11
F-0.01Ni	222	0.13
F-0.01Co ^{Nit}	312	0.17
F-0.01Ni ^{Nit}	283	0.18

that graphite phase could be crystallized at 800°C or above. The crystallite size seems to be very small of approx. 5 nm estimated from FWHM of the diffraction line.

Figure 5 shows the Raman spectra of P- and F-0.01M samples. Basing on the previous literature,⁵⁾ the Raman spectra were deconvoluted to five bands, I, D, D', G and D'. From the paper, I, D' and D' bands were fixed at 1170, 1500 and 1618 cm^{-1} , and the peaks were fitted with Gaussian (I and D'

bands) and Lorentzian (others) functions. Sharma et al. have been reported that in-plane crystallite size of graphite can be calculated from the intensity ratio, I_D/I_G .¹³⁾ This in-plane crystallite size can be applicable to size of graphene sheet (D_{graphene}) in this paper. The I_D/I_G and calculated graphene size are shown in **Table 3**. From this table, D_{graphene} seems to be almost constant for P-*n*M; however, weak trend seems to be larger Sa with smaller D_{graphene} . For F-*n*M, D_{graphene} are slightly larger for that those for P-*n*M. For F-0.01Ni^{Nit}, the calculated graphene sheet is apparently large in spite of no graphitization. From these results, addition of metal naphthenate did not affect graphene size or crystallographic defect of graphitic structure, for even P-0.01Co in which graphitization occurred.

4.2 Formation of porous structure

Isotherms with N_2 of the metal-dispersed porous carbon in Fig. 4 indicate different pore structures by different carbon and metal source. Generally *t*-plot brings in some informations of pore structure. **Figures 6(a)** and **6(b)** show *t*-plots of these carbons prepared from phenolic and furan resin, respectively. In the *t*-plot, the slopes in the initial stage (small *t* range) and second stage (large *t* range) express area of all pore surfaces and of outer surface of the particles, respectively. When the *t*-plot go off the

Table 2. Crystallite size of metal (Co or Ni) in metal-dispersed porous carbon prepared from Co or Ni naphthenates or nitrates

Sample	P-0.01Co	P-0.01Ni	P-0.01Co ^{Nit}	P-0.01Ni ^{Nit}	F-0.01Co	F-0.01Ni	F-0.01Co ^{Nit}	F-0.01Ni ^{Nit}
$D_{\text{metal}}/\text{nm}$	12	10	13	19	32	42	29	30

Fig. 5. Raman spectra of the metal-dispersed porous carbon with metal/carbon ratio of 0.01 prepared from phenolic and furan resin as a carbon source and Co- or Ni-naphthenate and nitrate as a metal source.

Table 3. Intensity ratio of D and G band, and graphene sheet size calculated from the ratio

Sample	I_D/I_G	$D_{\text{graphene}}/\text{nm}$
P-0M	2.93	1.5
P-0.01Co	2.27	1.9
P-0.01Ni	2.90	1.5
P-0.01Co ^{Nit}	2.51	1.7
P-0.01Ni ^{Nit}	2.52	1.7
F-0M	2.22	1.9
F-0.01Co	2.32	1.9
F-0.01Ni	2.20	1.9
F-0.01Co ^{Nit}	2.01	2.1
F-0.01Ni ^{Nit}	1.32	3.2

linear line on the upper side in the second stage, capillary condensation of the N_2 gas must occur within inside of mesopore. For P-0M and P-0.01M^{Nit}, the t -plots indicate an existence of only micropore because the slopes in the second stage are very small. Usually, micropore can be formed during carbonization and activation from phenolic or furan resins between the stacked graphene grains to transform itself into hard carbon. For P-0.01Co, the micropore also exists and outer surface area is extraordinary larger than the other samples; however, there are little mesopore in the samples. The larger outer surface area is the collateral evidence for crystallization of graphite. The crystallization results in local change of density and then carbon particles are dissected out to increase surface area. For P-0.01Ni, the t -plot shows the capillary condensation of mesopore above t of approx. 1 nm. Therefore, the t -plot indicates micropore and mesopore formation in the sample. On the other hand, for F- n M samples, the t -plots confirm that a significant textural change was

not occurred. For these samples, the t -plots confirm that micropore and no mesopore exist while outer surface area seems to be slightly different.

Table 4 shows radius of micropore ($R_{\text{p}_{\text{micro}}}$), and fraction of surface area and pore volume derived from micropore ($F_{\text{micro}}^{\text{Sa}}$ and $F_{\text{micro}}^{\text{Vp}}$) estimated by BET and t -plots. From this table, $F_{\text{micro}}^{\text{Vp}}$ s of P-0.01Co and -0.01Ni are apparently small compared to the others. These values clearly represent existence of mesopore or extra-large outer surface. The fractions of mesopore volume of P-0.01Co and -0.01Ni are apparently larger than those within the carbon obtained from phenolic fiber with Co acetylacetonate reported by Oya et al. of 14–54 vol %.³⁾ Such development of mesopore possibly results from use of naphthenate before polymerization of phenolic resin.

Figure 7 shows schematic illustrations of hybridization and pore formation models. Consequently, there are three types of porous structure as shown in Fig. 7. In the case of F-0M, F-0.01M and F-0.01M^{Nit}, only micropores and no mesopores are formed in the metal-dispersed porous carbons because fran resin can not take in the naphthenate chain. For P-0M and P-0.01M^{Nit}, no naphthenate chain poses similar porous structure, many micropores and no mesopores. The schematic models of them are showed in Figs. 7(a) and 7(b). For P-0.01Co and P-0.01Ni, 3-dimensional network of phenol possibly takes in the naphthenate chains during polymerization. Since the large outer surface area is shown only in the combination of phenolic resin and metal naphthenate, such hybridization might make the particle somewhat fragile. In the case of P-0.01Co, the partial graphitization poses that the hybridized particles are break apart due to the partial change of density as illustrated in Fig. 7(c). In the case of P-0.01Ni, many cracks were probably generated, which works mesopore. This model is expressed in Fig. 7(d).

Fig. 6. t -plots of the metal-dispersed porous carbon with metal/carbon ratio of 0.01. (a) prepared from phenolic resin and (b) from furan resin.

Table 4. Micropore radius, fraction of surface area and pore volume derived from micropore ($F_{\text{micro}}^{\text{Sa}}$ and $F_{\text{micro}}^{\text{Vp}}$) calculated from the t -plot in the metal-dispersed porous carbon

Sample	$R_{\text{p}}^{\text{micro}}/\text{nm}$	$F_{\text{micro}}^{\text{Sa}}/\%$	$F_{\text{micro}}^{\text{Vp}}/\%$
P-0M	0.66	99.9	99.9
P-0.01Co	0.62	76.2	24.2
P-0.01Ni	0.60	86.7	34.6
P-0.01Co ^{Nit}	0.64	97.7	87.6
P-0.01Ni ^{Nit}	0.62	98.9	93.2
F-0M	0.67	92.2	68.1
F-0.01Co	0.79	97.7	89.2
F-0.01Ni	0.78	97.1	87.2
F-0.01Co ^{Nit}	0.67	99.1	95.4
F-0.01Ni ^{Nit}	0.71	93.6	74.5

5. Conclusions

Phenolic or furan resin were hybridized with Co- or Ni-naphthenate by mixing before polymerization. Metal-dispersed porous carbons were prepared from the phenolic or furan resins and were examined with the following results.

1. In the case of phenol and metal naphthenate, the 3-dimensional network probably tends to take in the naphthenate chain and consequently metal nanoparticles are well dispersed and mesopores are formed in the resultant carbon.
2. The formed metal particles in these metal-dispersed porous carbons from phenolic resin are apparently

Fig. 7. Schematic illustrations of the metal-dispersed porous carbon with metal/carbon ratio of 0.01.

smaller than those in the carbon from that with metal nitrate. Especially Ni metal particles are around 10 nm in size.

3. Existence of Co naphthenate tends to accelerate formation of graphite at low temperature above 800°C.

4. The specific surface areas of the metal-dispersed porous carbons using Co or Ni naphthenate are approx. 400 m²/g.
5. The Co and Ni naphthenates works as a mesopore former of the amorphous carbon prepared from the phenolic resin including the metal naphthenates.

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