Carbon-coated material with bimodal pore-size distribution

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Carbon-coated material was prepared by impregnation of a polymer and successive thermal treatment. Polymers such as phenol resin, polyacrylonitrile, polyvinylchloride and polivinylidene dichloride were used for impregnation and inorganic oxides such as SiO_2, Al_2O_3, ZrO_2 and TiO_2 were used as supports. The amount of carbon coating was varied arbitrarily by changing the amount of polymer dissolved in the solvent for impregnation. Carbon-coated materials were characterized by TG/DTA, N_2 adsorption, mercury porosimetry and elemental analysis. Properties and structure of carbon-coated materials were discussed. © *2002 Kluwer Academic Publishers*

1. Introduction

Active carbon is an interesting material for catalyst support, because of its high surface area, peculiar electronic properties and functional groups on its surface. However, pore size of active carbon is generally smaller than 2 nm, which occasionally causes diffusional and pore-blocking problems.

To overcome these problems, supports having larger pore size and regulated pore size distribution with characteristics of active carbon have been investigated [1–3]. For example, Vissers *et al*. [1] showed carbon-coated Al_2O_3 could be synthesized by cracking of cyclohexene. Colin and Guiochon [2] used benzene vapor for the preparation of carbon-coated SiO_2.

So far, there are only limited numbers of papers and patents which reported preparation of the carbon-coated material using a polymer as a source of carbon, although carbon-coating using polymer has some merits; simple and safe synthesis procedure and high reproducibility. Comolli and Ganguli [4] reported carbon coating on hydrodesulfurization catalyst with polymerized furfuryl alcohol. Liu *et al*. [5] studied carbon coating with polyacrylonitrile. Sakata *et al*. [6] modified SiO_2 with phenol resin and discussed its pore structure. Kita *et al*. [7] prepared carbon membranes by coating thin layers of phenolic resin on the outer surface of a porous Al_2O_3 and then carbonizing the polymer under nitrogen atmosphere. However, investigation on properties of carbon-coated materials was not sufficient.

In this study, carbon-coated materials were prepared using polymers as a carbon source and characterization of materials obtained was investigated in detail.

2. Experimental
2.1. Preparation
Typical preparation procedure: a 1.08 g portion of phenol resin (Hitachi Kasei; HP-309NS) was dissolved in 12×10^{-6} m^3 ethanol. Properties of the phenol resin are melting point of 83–88°C and number-average molecular weight of 700–800. Into this solution, a 6.0 g portion of SiO_2, Al_2O_3, ZrO_2 or TiO_2 support predried at 600°C (TiO_2; 450°C) was introduced and settled for more than 1.5 hours so that the solution could be sufficiently impregnated. Then, ethanol was evaporated stepwise; at 40°C for 1 hour, and then at 50°C and 60°C for 25 minutes respectively and finally at 80°C overnight. Thus obtained material was placed in a tubular glass and carbonized under N_2 flow (135×10^{-6} m^3/min). For carbonization, temperature was controlled as follows: $20 \rightarrow 180$ by 5°C/min and held at this temperature for 1 hour and then $180 \rightarrow 600$ by 5°C/min and held at this temperature for 4 hours. In case of TiO_2 support, the final temperature was 450°C. The carbon loading by this typical procedure was about 8 wt%.

Surface areas of parent supports are listed in Table I. Average pore sizes of SiO_2-1, -2, TiO_2 and ZrO_2 are 50, 30, 25 and 31 nm, respectively. Al_2O_3-1 has bimodal pore-size distribution at 11 and 50 nm.

Similarly, using polyacryronitrile (PAN) in N,N-dimethylformamide, polyvinylchloride (PVC) in tetrahydrofurane and poly(vinylidene dichloride) (PVDC) in tetrahydrofurane, carbon-coated materials were prepared.

2.2. Characterization
Specific surface area and pore size distribution of micro- and meso-pore region were calculated by the analysis of N_2 adsorption isotherm with Shimadzu Asap 2400 system. Analysis of micropore region was conducted by the t-plot program equipped with the system. Pore size distribution of meso- and macro-pore region was measured by mercury porosimetry on Shimadzu Poresizer 9310. Pore volume was obtained by mercury porosimetry and by measuring the amount of water impregnated into the support and the carbon-coated

TABLE I Surface area of carbon coated SiO$_2$

Amount of carbon (wt%)	Surface area (m^2/g)[a]		
	Total	Micro	Δ[b]
0	69	8	–
1.2	72	5	3
4.5	93	27	24
8.3	120	52	51
13.9	191	99	122
23.4	305	161	236

[a]Total: Total surface area. Micro: Surface area of micropore region.
[b]Difference in total surface area from parent support.

material. Thermal analysis to measure the carbon remaining on a support was conducted on Seiko Instrument TG/DTA 220 system. Content of nitrogen and chlorine was measured by ion-chromatography after burning the coated carbon and collecting the effluent gas into a trap.

3. Results and discussion
3.1. Thermal properties of phenol resin
Weight decrease of phenol resin on heating in N$_2$ stream is shown in Fig. 1. Exothermal curing with no substantial weight change occurred at about 155°C, and total weight decrease up to 540°C was 28 wt%. Melting point was not observed clearly.

3.2. Characterization of carbon-coated material
Loading of remaining carbon was easily varied by changing the amount of phenol resin dissolved in the solvent for impregnation (Table I). Thus, carbon loading of 1, 4, 8, 14 and 23 wt% was possible. In case of 23 wt%, because of the limitation of solubility of phenol resin, the coating procedure was repeated twice. The color of the carbon-coated material was black throughout the support even for 1 wt% coating, though the color became less black.

Assuming the density of coated carbon to be 2000 kg/m^3 (cf. 2260 for graphite and <2000 for amorphous carbon) and homogeneous carbon coating of the surface, the thickness of carbon on the silica surface was calculated to be 1.07 nm for 15 wt% of carbon. This means 4 graphite-carbon layers on the silica surface
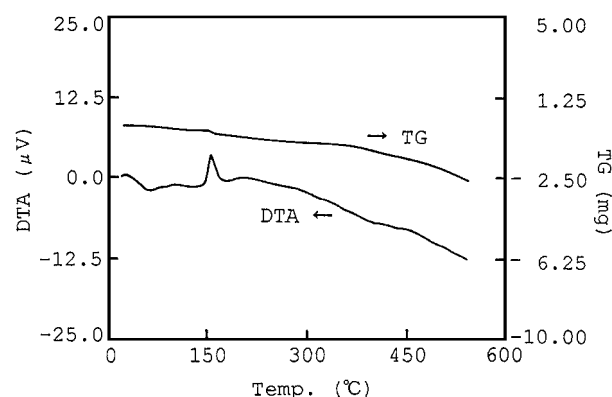

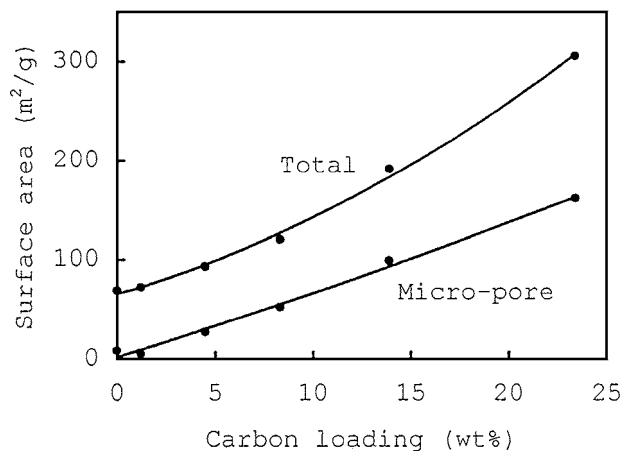*Figure 1* TG/DTA analysis of phenol resin. Condition: by 10°C/min in N$_2$ stream

Figure 2 Influence of carbon-loading on total surface area and the surface area of micropore region.

since the interplanar distance of graphite is 0.335 nm [8]. When the loading is one fourth of 15 wt%, a monolayer of carbon might be expected. If this is correct, the silica support having 1.2 wt% of carbon might not be covered with carbon homogeneously. It must be taken into consideration that this discussion depended on the assumption that the density of carbon is 2000 kg/m^3. Therefore, if the carbon covering the surface of SiO$_2$ is not like graphite but like an amorphous carbon, the critical value for monolayer coverage is less than ca. 3.75 wt%.

If carbon is covering the surface of SiO$_2$ homogeneously, the surface area should have resulted in nearly the same as before the carbon coating. However, as was clearly indicated in Table I, increase of total surface area was apparently observed.

In Table I is also shown the surface area of the micropore region calculated by so-called t-plot and the relation between total surface area and the surface area of the micropore region is shown in Fig. 2. Considering the difference between total surface area and the surface area of the micropore region, it can be said that an increase in the surface area up to ca. 8 wt% of carbon is related to that of the micropore region. Thus, the pore-size distribution was considered to be bimodal; namely the original mesopore and the newly appeared micropore. For the loading higher than ca. 10 wt%, the increase is not only from micropore but also from mesopore region. This phenomenon may indicate that up to ca. 8 wt%, rather homogeneous surface coverage occurred and micropores existed in this carbon layer. On the other hand, for the higher carbon-loaded SiO$_2$, carbon existed not only as the homogeneous surface layer with micropores but also as a sponge-like porous carbon [9].

The change in the structure of carbon may be considered from the viewpoint of interaction between the surface of the support and the phenol resin impregnated. When the amount of phenol resin used was small, it had a relatively strong interaction with the surface of the support and the carbon derived from this kind of phenol resin had covered the inner surface of the support as layer after thermal treatment. Whereas for the higher carbon loading, in addition to the carbon covering the surface the glassy carbon developed in the pore

TABLE II Properties of Carbon-coated materials prepared with phenol resin

Support	Parent support			Carbon-coated material			
	Area[a] (m^2/g)	Vp (H$_2$O)[b] $(\times 10^{-3}m^3/kg)$	Vp (Hg)[c] $(\times 10^{-3}m^3/kg)$	Carbon (wt%)	Area[a] (m^2/g)	Vp (H$_2$O)[b] $(\times 10^{-3}m^3/kg)$	Vp (Hg)[c] $(\times 10^{-3}m^3/kg)$
SiO$_2$-1	69(8)	1.05	0.99	8.3 (7.5)[d]	120(52)	0.90	1.07
SiO$_2$-2	98(15)	1.05	0.97	7.9 (7.9)[d]	155(50)	0.90	0.83
Al$_2$O$_3$-1	205(21)	0.89	0.99	8.2	207(25)	n.d.	0.78
TiO$_2$	40(3)	0.33	0.30	5.5[e]	55(15)	n.d.	0.22

[a]Total surface area. Surface area of the micropore region is in the parenthesis.
[b]Pore volume measured by water-impregnation.
[c]Pore-volume measured by mercury porosimetry.
[d]Second batch to confirm reproducibility.
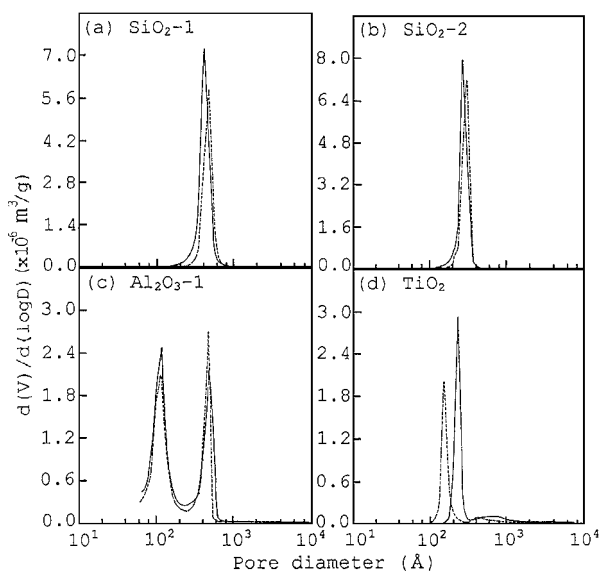[e]Carbon-coating procedure was repeated twice.

Figure 3 Pore-size distribution of carbon-coated materials measured by mercury porosimetry. ——: parent, ·········: carbon-coated.

Figure 4 Pore-size distribution of carbon-coated materials by nitrogen adsorption analysis.

of the support due to the weak interaction between the support and the phenol resin impregnated.

In Table II, properties of carbon-coated materials prepared from two kinds of SiO$_2$, Al$_2$O$_3$ and TiO$_2$ are indicated. It is clear that the reproducibility of preparation is very good in spite of a very simple preparation method. Pore volume measured by two methods agreed well with each other. Decrease in pore volume by carbon coating was indicated, and this would be the result of existing carbon inside of the mesopores of the supports.

In the former section, we estimated the interaction between the phenol resin and the surface of SiO$_2$. Considering the data in Table II, changes in the surface area are very similar among the supports and therefore the interaction with the phenol resin seems not very different among the supports.

Pore-size distributions measured by mercury porosimetry and N$_2$ adsorption are shown in Figs 3 and 4, respectively. From the pore size distribution of SiO$_2$ and Al$_2$O$_3$ by porosimetry, it seems that carbon coating did not influence the pore size distribution. However, considering the increase of BET surface area in Table I, it should be said that micropore was not detected because of the instrumental limitation (5.5 nm). In the case of TiO$_2$, the peak position shifted to the
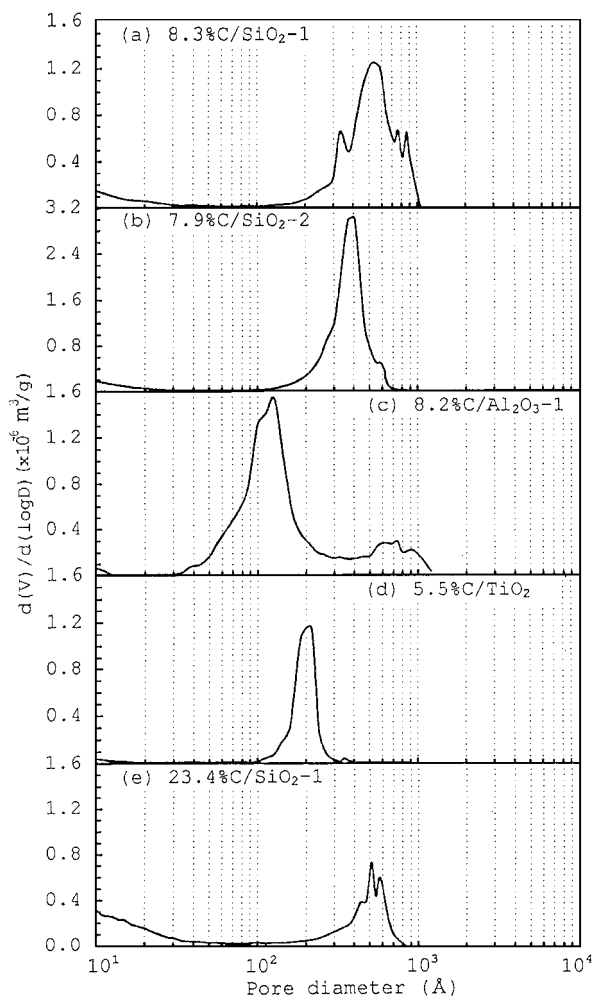
smaller pore size and this might have been caused by the repeated coating procedure. The pore-size distribution measured by N$_2$ adsorption coincided with that measured by porosimety as a whole, although the peak top is not well demonstrated. Here, it should be stressed that occurrence of micropore and the bimodal pore-size distribution are observed in Fig. 4e.

As is indicated in Table III, carbon-coated materials could be prepared not only from phenol resin but also from other polymers. It should be emphasized that by adopting polymers including heteroatom such as

TABLE III Carbon-coated materials prepared with PAN, PVC and PVDC

Carbon source	Carbon (wt%)	N or Cl (wt%)	Surface area (m²/g)[a]	
			Total	Micro
PAN-C/SiO$_2$-1[b]	3.8	0.11	78	7
PVC-C/SiO$_2$-1[b]	3.0	<0.05	83	6
PVDC-C/SiO$_2$-1[b]	3.6	0.37	113	30
PVC-C/ZrO$_2$[c]	1.0	0.83	49	4
PVDC-C/ZrO$_2$[c]	1.2	0.43	49	5
PAN-C/Al$_2$O$_3$-2[d]	5.2	0.10	120	3
PVDC-C/Al$_2$O$_3$-2[d]	4.2	1.03	136	20
PAN-C/TiO$_2$[e]	1.1	0.04	44	2

[a]Total: Total surface area. Micro: Surface area of micropore region.
[b]SiO$_2$-1 : 69 m²/g.
[c]ZrO$_2$: 53 m²/g.
[d]Al$_2$O$_3$-2: 118 m²/g.
[e]TiO$_2$: 40 m²/g.

nitrogen and chlorine, carbon-coated material having these heteroatoms could be obtained when a proper temperature for heating was adopted [5]. These carbon-coated materials containing a heteroatom might become a useful bifunctional support material.

What should be pointed out is the carbon coating with PVDC. When PVDC was used as a carbon source, development of micropores was eminent compared to PAN and PVC. This may be concerned with dehydrochlorination of PVDC [10]. The double bond or triple bond caused by dehydrochlorination might have bonded each other and this could have resulted in a microporous matrix. On the other hand, carbon-coated materials of similar properties were obtained from PAN and PVC except that the remaining element differed.

4. Conclusions

Carbon-coated SiO$_2$ having different carbon loading was easily prepared by changing the amount of phenol resin dissolved in a solvent for impregnation.

It was estimated that when the amount of phenol resin was small, it interacted with the surface of the support and homogeneous coverage of the inner surface of the support by a carbon layer resulted. It seemed that in the layer the micropore was developed and surface area increased. On the other hand, when the loading was high, both the covering of the support as layer and filling of the support pore with a sponge-like carbon occurred. Thus, the pore-size distribution of the carbon-coated materials was considered to be bimodal.

Carbon coating was also possible on other supports such as Al$_2$O$_3$, ZrO$_2$ and TiO$_2$ with other polymers such as PAN, PVC and PVDC. From these polymers, carbon-coated materials having heteroatom were obtained and it was expected that these materials might be used as a bifunctional support material.

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