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Pore structure and swelling character of porous carbon beads prepared from esterified silica gels

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Porous carbon beads have been prepared by a replica method using five silica gels with surface areas ranging from 70 to 765 m^2 g^{-1}. The replica method consists of esterification of silica gel with 4-phenyl-1,2-dihyroxybenzene, pyrolysis of the esterified silica gel, dissolution of the silica gel, and drying of the porous carbon from water or, in some cases, from benzene. Porous carbon beads, at maximum, shrank to about 33% of the size of silica gel beads used as a substrate during drying in the preparation. The extent of shrinkage was increased with decreasing surface area of the silica gels. The porous carbons prepared from different silica gels showed a similar pore size distribution, although the distribution became somewhat broader when a silica gel with a small surface area was used. The percentage of expansion of porous carbon beads on adsorbing benzene varied to some extent with the kind of silica gel, and the porous carbon prepared from the silica gel with the surface area of 470 m^2 g^{-1} showed a maximum expansion, 31%. Porous carbon beads dried from benzene showed about 10% higher percentages of expansion on average compared with that from water. Furthermore, in the carbon beads from benzene, a small number of carbon beads showed enormously large expansion, and the expansion was found to be related to the extent of shrinkage during drying in the preparation.

1. Introduction

Porous carbon materials have been prepared by replica methods. Knox *et al.* prepared porous carbon with the surface area of 590 m^2 g^{-1} by a replica method [1, 2], and named it “porous grassy carbon”. This replica method is composed of impregnation of phenol resin into pores of silica gel, pyrolysis of the resin in the silica gel, and dissolution of the silica gel. Kyotani *et al.* provided other replica methods [3–5]. Authors have devised a new replica method whose feature is introduction of esterification to produce silica/organic-compound composites as precursors of porous carbon materials. The porous carbon beads made by this replica method possess several advantages; that is, they possess comparatively sharp pore size distributions over a range from 2 to 8 nm and high surface area of ca. 2000 m^2 g^{-1}. Furthermore, the porous carbons also have a quite unique property that their apparent volumes change largely on adsorbing vapors. Authors offered a mechanism for the dimensional change of the porous carbon beads [6]. The present paper reports an influence of the sort of silica gel used as substrate on the pore structures and the swelling characters of resulting porous carbon beads.

2. Experimental

2.1. Materials

Five silica gels (Fuji Silysia Chemical; Microbeads silica gel 3A, Microbeads silica gel 4B, Cariact 15, Cariact 30, Cariact 50) were used as substrates and abbreviated as follows: Silica 3A, Silica 4B, Silica 15, Silica 30, and Silica 50, respectively. Their surface area and pore width are given in Table I. They were sieved to a size ranging from 100 to 200 mesh and air-dried at 393 K before usage.

2.2. Preparation of porous carbon beads

Porous carbon beads were prepared by a replica method. Silica gel beads were at first impregnated with 4-phenyl-1,2-dihydroxybenzene (PB) by mixing the silica gel beads (10 g) with a 50 wt/vol% PB acetone solution (20 cm^3) at room temperature and air-drying them at 333 K. The silica beads with PB loading (ca. 50 wt %) were heated at 573 K for 1 h in a nitrogen atmosphere to esterify the silica surface. The resulting silica gel beads were washed repeatedly with acetone to remove unreacted PB and dried at 333 K under vacuum. The esterified silica gel beads were heated at 1273 K for

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TABLE I Surface area and pore width of silica gels

Substrate	Surface area ($m^2\ g^{-1}$)	Pore width (nm)
Silica 3A	765	2
Silica 4B	470	7
Silica 15	205	22
Silica 30	122	39
Silica 50	70	68

1 h under vacuum (<5 Pa), resulting in carbon-coated silica gel beads. These beads were subsequently treated with HF aqueous solution (1 : 1) at room temperature, and the carbon beads thus formed were washed with water repeatedly. The porous carbon beads in water were dried in two different manners: (1) the carbon beads were filtered and air-dried at 393 K, and (2) the water was replaced by benzene via methanol by decantation, and the porous carbon beads were filtrated and air-dried at 393 K. With reference to the name of silica gels used, we call the porous carbons as follows: Carbon 3A, Carbon 4B, Carbon 15, Carbon 30, Carbon 50 with the letter of W or B representing the solvent, water or benzene, in drying process. For further details of the preparation of the carbon-coated silica gel beads, previous papers should be consulted [7, 8].

2.3. Characterization

2.3.1. Surface area, pore size distribution, and pore volume

The specific surface area and the pore size distribution of the silica gels and the porous carbon beads were determined by means of the BET and the Cranston-Inkley methods, respectively, on the basis of data on nitrogen adsorption at 77 K. The pore volume was calculated from the adsorption amount of nitrogen at the relative pressure of 0.93.

2.3.2. Dimensional change of carbon beads

The percentages of shrinkage of beads during dissolution of silica gel and drying were calculated from mean diameters of 100 carbon-coated silica gel beads and the corresponding 100 carbon beads.

The changes in the sizes of carbon beads caused by adsorption of vapors were measured as follows. Carbon beads were placed in a glass cell connected to a constant-volume adsorption apparatus equipped with a optical microscope and a video recorder. The system was maintained at 303 K. The sample was previously evacuated at ca. 0.01 Pa for 1 h at 333 K, allowed to cool, and then contacted with benzene vapor at the saturated vapor pressure. Dimensional change of the carbon beads on adsorbing the vapor was recorded by the video recorder through the optical microscope. Change in the size before and after adsorption was measured for 30 beads. The upper and lower each three values were eliminated, and the mean of the residual values was adopted for calculating the extent of the dimensional change. The percentage of expansion was defined as 100 $(d - d_0)/d_0$, where d_0 and d are mean diameters of carbon beads before and after adsorption, respectively.

3. Results and discussion

3.1. Yield and morphology

Carbon contents of esterified and subsequently pyrolyzed silica gels (carbon-coated silica gels), yield of porous carbons from carbon-coated silica gels, and shrinkage of carbon beads are given in Table II. The shrinkage was independent of the kind of solvent from which the porous carbon beads were dried, and their percentages show the mean of those for water and benzene. The carbon contents of esterified silica gels depended on the sort of the silica gels and are roughly proportional to the surface areas of the silica gels. This is because PB molecules reacted with silanol groups on the silica gel surface. The yields of porous carbon was nearly equaled to the carbon content of the corresponding carbon-coated silica gel. Fig. 1 shows SEM images of Silica 4B and porous carbons. The former was shown as a representative silica gel for comparing the size with those of the porous carbons; other four silica gels used have similar size and shape to those of Silica 4B in Fig. 1a. The images clearly show a tendency that the carbon beads shrank more largely with decreasing the carbon content of carbon-coated silica gel; in other word, the smaller the surface area of silica gel used as substrate, the smaller the size of carbon beads obtained. Their spherical shape was, however, unchanged.

The elemental compositions of the porous carbons showed no dependance on the sort of silica gel. The compositions were: C; 91.9–92.4%, H; 0.8–1.1%, O; 5.7–6.4%, Ash; 0.7–1.3%.

3.2. Pore structure

Table III represents the surface area and pore volume of porous carbons. They are markedly high compared with other replica carbons [1, 2] and decreased as the

TABLE II Carbon content of modified silica gels, yield of porous carbons, and shrinkage of carbon beads

Substrate	Carbon content (%)		Yield of carbon (%)	Shrinkage (%)
	Esterified	Pyrolyzed		
Silica 3A	—	—	20.1	21
Silica 4B	20.0	14.6	15.6	41
Silica 15	11.0	9.3	9.9	50
Silica 30	7.2	6.0	6.1	59
Silica 50	4.1	3.3	3.6	67

TABLE III Surface area and pore volume of porous carbons

Porous carbon	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
Carbon 3AW	2010	1.51
Carbon 4BW	1990	1.46
Carbon 15W	1860	1.34
Carbon 30W	1770	1.33
Carbon 50W	1500	1.20

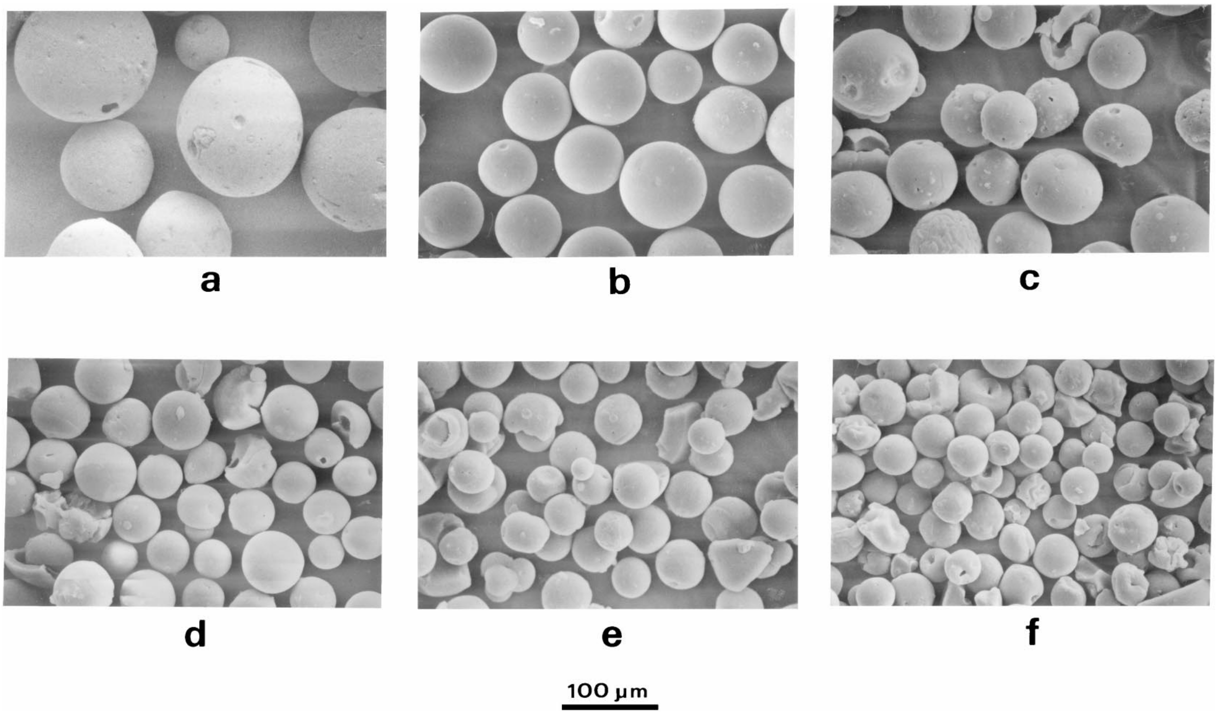

Figure 1 SEM images of silica 4B and porous carbons. (a) Silica 4B; (b) Carbon 3AW; (c) Carbon 4BW; (d) Carbon 15W; (e) Carbon 30W; (f) Carbon 50W.

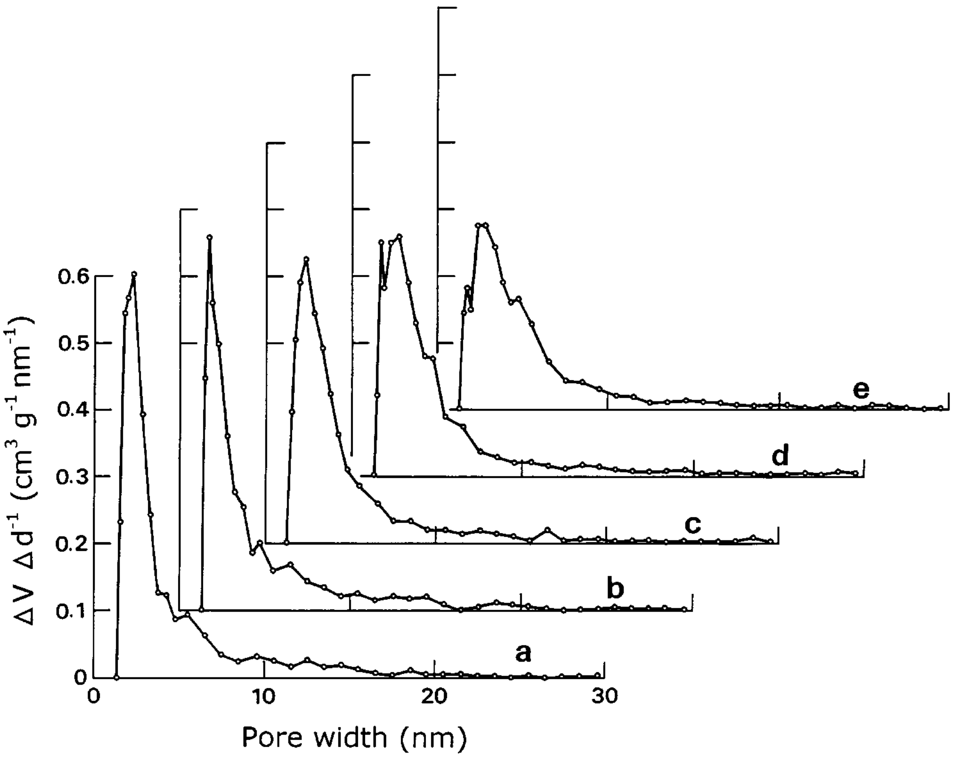

Figure 2 Pore size distributions of porous carbons. (a) Carbon 3AW; (b) Carbon 4BW; (c) Carbon 15W; (d) Carbon 30W; (e) Carbon 50W.

surface area of silica gels decreased. Fig. 2 shows pore size distribution curves for the porous carbons. Despite a wide range of the mean pore size (from 2 to 68 nm) of the silica gels, the mean pore size of the resulting carbon beads was 3 nm, which was calculated from the surface area and the pore volume listed in Table III. The pore size of Carbon 50W is about one-twentieth that of Silica 50. This large decrease in the pore width was caused by large contraction of the carbon beads on drying. Additionally, the pore size distribution became somewhat broader when carbon beads contract largely. As described in the preceding paper [6], pyrolysis of esterified silica gel forms carbon films on the silica surface, and the films consist of disordered carbon and graphitic carbon layers some of which accumulate each other. The carbon films are about 1 nm in thickness and cover the silica surface partially. Dissolution of the silica gel with HF solution did not change the

TABLE IV Expansion of porous carbons on adsorbing benzene

Porous carbon	Expansion (%)
Carbon 3AW	17
Carbon 4BW	31
Carbon 15W	28
Carbon 30W	28
Carbon 50W	26
Carbon 3AB	22
Carbon 4BB	40
Carbon 15B	39
Carbon 30B	37
Carbon 50B	37

appearance of the beads, but during dryness the carbon beads contracted largely. The fact that carbon beads from silica gels with a variety of surface areas showed similar pore size distribution offers a following view. When the silica gels of carbon-coated silica gels are dissolved, a silica gel with a small surface area leaves a loose carbon structure comprised of carbon films, and a silica gel with a large surface area contrary leads to a tight one in water. On drying carbon beads with the loose structure contract largely compared with the tight ones, resulting in porous carbon beads with a similar pore size distribution to that for the tight one.

3.3. Swelling character

The extent of expansion of carbon beads on adsorbing benzene are listed in Table IV. The carbon beads made from Silica 4B showed the largest expansion, and the porous carbons dried from benzene showed about 10% higher percentages than those from water. Furthermore, in the carbon beads dried from benzene a minute number of beads showed enormously large expansion except for Carbon 3A and Carbon 4B which showed small shrinkage in their preparation (Table II). A few carbon beads of Carbon 15 expanded about 85% (shrinkage, 50%); Carbon 30, 120% (shrinkage, 59%) and Carbon 50, 150% (shrinkage 67%). This large expansion means that the expansion of carbon beads on adsorption is closely associated with the contraction during drying in their preparation although the large expansion was not observed in the carbon beads dried from water and the reason is not still clear.

Authors offered a mechanism for the dimensional change of carbon beads during adsorption on the basis of balance of three forces: strain force generated on shrinkage of carbon beads during drying as the force to expand carbon beads, capillary force arising at menisci of condensed adsorbate in pores of the carbon beads and interfacial energy of carbon layers constructing the carbon beads as the forces to contract [6]. The enormously large expansion of carbon beads dried from benzene is probably due to remaining of the large strain force in the carbon beads. Moreover, the fact that the enormously large expansion was not obserbed when carbon beads were dried from water suggests that benzene is preferable to remain large strain in the carbon structure compared with water.

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