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Preparation of Mesoporous Carbon from Organic Polymer/Silica Nanocomposite

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A mesoporous carbon was prepared from a carbon/silica nanocomposite. The composite was obtained by mean of a sol−gel process using tetraethoxy silane (TEOS) in the presence of furfuryl alcohol (FA) as a carbon precursor and then the silica framework was removed from the composite by HF treatment. It was found that the resultant carbon is porous, and its mesoporosity depends on the sol−gel reaction conditions. For the production of mesoporous carbon, the amounts of both FA and acid catalyst (HCl) in the initial sol solution must be optimized. Under optimized conditions, the present method made it possible to develop uniform mesopores of 4 nm in diameter.

Introduction

The presence of micropore is essential for the adsorption of small gas molecules on activated carbons. However, when adsorbate is polymers, dyes, or vitamins, only mesopores allow the adsorption of such giant molecules. The importance of mesopores has been pointed out not only for giant molecule adsorption but also for new applications such as electric double-layer capacitors. Thus, the design and control of mesoporosity is very desirable for both the improvement of adsorption performance and the development of new application fields.

So far, there have been several novel approaches to the preparation of mesoporous carbon. The detailed features of these methods have been reviewed by Kyotani.[1] Among these methods, catalytic activation of carbon is the most common method. Researchers have used many types of catalysts such as iron, nickel, cobalt, rare earth metals, titanium oxide, and boron- and phosphate-containing sodium compounds.[2−8] Mesoporous carbon can also be prepared by using porous inorganic templates. For example, Knox et al.[9,10] impregnated silica gel or porous glass with phenol resin and then carbonized the resin, followed by the removal of the template. The resultant carbon was mesoporous, and it is now commercially available as a column packing material for liquid chromatography. Kamegawa and Yoshida employed a similar method to prepare mesoporous carbons which swell with an organic solvent.[11] We have previously prepared high-surface-area carbons with mesoporosity by using zeolite as a template.[12] Han et al. used silica nanoparticles as a template for the production of mesoporous carbons.[13,14] The other approaches are to carbonize either a mesoporous organic aerogel[15] or a polymer blend.[16,17] The former compound is prepared from polymer aquagel, and the mesoporosity of the aerogel can be held during its carbonization. In the polymer blend method, a nanoscale mixture of thermosetting and pyrolyzing polymers is heat-treated; the former polymer forms a carbon matrix, and the latter one leaves pore in the matrix upon the heat treatment. Despite many attempts for the preparation of mesoporous carbon, the size control of mesopore does not reach a satisfactory level and this issue is still a rewarding and challenging subject.

It is well-known that a sol−gel process is a useful technique to prepare a nanocomposite of organic and inorganic materials. For the production of the nanocomposite by the sol−gel process, tetraethoxy silane (TEOS) was often used as a silica precursor, and the shape and size of a silica obtained can be controlled by the sol−gel reaction conditions, as demonstrated by

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Bogush et al.[18] However, they did not add any carbon precursor in the silica sol. If a nanocomposite of carbon and silica is prepared with the sol–gel method and then the silica framework is removed from the composite, one can expect the formation of a carbon whose pore structure is reflected by the silica framework structure. On the basis of this idea, we prepared mesoporous carbons, and some of our results were briefly reported.[19] Here, we report more details of this method and the characteristics of the resultant carbons. We show how the sol–gel reaction conditions influence the silica structure, which in turn affects the carbon mesopore structure.

Experimental Section

A silica sol was prepared by stirring a mixture of TEOS, ethyl alcohol, deionized water, and HCl at 80 °C for 3 h. The mole ratio of TEOS, ethyl alcohol, and water was maintained constant, i.e., 1:4:2, but the ratio of HCl to TEOS was changed from 0.001 to 0.1. After the mixture was cooled in an ice bath, furfuryl alcohol (FA) as a carbon precursor was added to the silica sol with a predetermined mole ratio of FA/TEOS in the range of 0.25–4.00. This mixture was poured into a Teflon dish and then dried for 2 h at either 60 or 120 °C. During this treatment, both the gelation of TEOS and the polymerization of FA took place. Then, the poly(furfuryl alcohol) (PFA)/silica gel film was heat-treated at a rate of 2.5 °C/min to 800 °C under N_2 flow and held there for 3 h to carbonize the polymer in the composite. All of the carbon/silica composites were obtained as a film. The film was washed with stirring in an excess amount of 46% aqueous HF solution at room temperature for 24 h to dissolve the silica framework. The carbon was then obtained as an insoluble fraction. For comparison, pure PFA carbon was prepared from the mixture of FA, ethyl alcohol, and HCl (1:4:0.01) under the same carbonization conditions.

The pore structure of the samples was examined at −196 °C with an automatic volumetric sorption analyzer (Autosorb-1, Quantachrome Co.) using N_2 as the adsorbent. The specific surface area (S_{BET}) and the total pore volume (V_{total}) were, respectively, determined from the BET equation and the volume of N_2 adsorbed at a relative pressure of 0.95. To evaluate the mesoporosity, the mesopore surface area (S_{meso}) and mesopore volume (V_{meso}) were determined. The former parameter was calculated using the Barrett–Joyner–Halenda (BJH) method,[20] and the latter one was derived from the difference between the pore volume (V_{total}) and the micropore volume determined from the Dubinin–Radushkevich equation.[21] In the present study, the following two parameters, the ratios of $S_{\mathrm{meso}}/S_{\mathrm{BET}}$ and $V_{\mathrm{meso}}/V_{\mathrm{total}}$, were adopted to evaluate the mesoporosity.

The microscopic features of the samples were observed with a scanning electron microscope (SEM, Hitachi: S900).

Results

Elemental Analysis. Table 1 shows the carbon content in the carbon/silica composites prepared in this work, together with their preparation conditions. The carbon content was determined from the amount of the combustible part in each carbon/silica composite. As a matter of course, the carbon content increases with the increase in the FA/TEOS mole ratio. At the same FA/TEOS ratio, the carbon content of the sample gelled at 60 °C was always slightly smaller than the corresponding sample obtained at 120 °C. The effect of the HCl/TEOS ratio was examined at 120 °C with a FA/TEOS ratio of 2.00. When the HCl/TEOS ratio was reduced from 0.01 to 0.001, the carbon content was greatly decreased despite the high FA/TEOS ratio. When the HCl/TEOS ratio was increased to 0.1, the carbon content did not change.

Table 1. Carbon Content in the Carbon/Silica Composite and Results of Elemental Analysis for the Carbons after Acid Washing

gelation temp (°C)	FA/TEOS mol ratio	HCl/TEOS mol ratio	wt % C in C/Si	elem. anal. for C (wt %) C	H	O (diff.)
60	0.25	0.01	4	90	2	8
60	0.50	0.01	10	92	2	6
60	1.00	0.01	25	94	2	4
60	2.00	0.01	42	95	2	3
60	4.00	0.01	45	99	1	0
120	0.25	0.01	6	92	2	6
120	0.50	0.01	13	95	2	3
120	1.00	0.01	28	90	2	8
120	2.00	0.01	44	96	2	2
120	4.00	0.01	47	97	2	1
120	2.00	0.001	15	98	2	0
120	2.00	0.1	45	96	2	2

The last three columns of Table 1 summarizes the results of the elemental analysis for the carbon samples obtained after the acid washing. For every sample, about 5 wt % of ash remained unremoved. Thus, the weight percentage of each element in the columns was calculated on an ash-free basis. Generally, the carbon percentage increased with the FA/TEOS ratio and the oxygen percentage decreased. The effect of the HCl/TEOS ratio on the elemental analysis was not significant.

SEM Observation. Figure 1 shows SEM photographs for some of the carbon samples prepared at a gelation temperature of 120 °C. A noticeable difference in morphology can be seen between the samples prepared under the conditions at FA/TEOS ratios of 0.25 and 0.50 and the ones at the ratios of 1.00 and 2.00. The former samples look as if many particles were agglomerated, whereas such agglomerated features are not observed in the latter samples, and they are characterized by the presence of a flat plane with several fine particles on it. Such a flat morphological feature was also observed in the carbon samples prepared at a FA/TEOS ratio of 4.00. A similar morphological change with FA/TEOS ratio was observed for the carbons prepared at a gelation temperatures of 60 °C (their SEM images were not shown here).

It was found that the carbon samples prepared at higher FA/TEOS ratios (1–4) kept their filmlike shape even after the acid washing, whereas this was not the case for the carbons at lower ratios (0.25 and 0.50). They were obtained as a powder upon washing. This difference in macroscopic form corresponds to the morphological difference in the SEM images as observed in Figure 1. Such difference in carbon form indicates that at the high FA/TEOS ratios carbon is present as a rigid continuous phase in the stage of a carbon/silica composite, whereas such a continuous carbon phase was not

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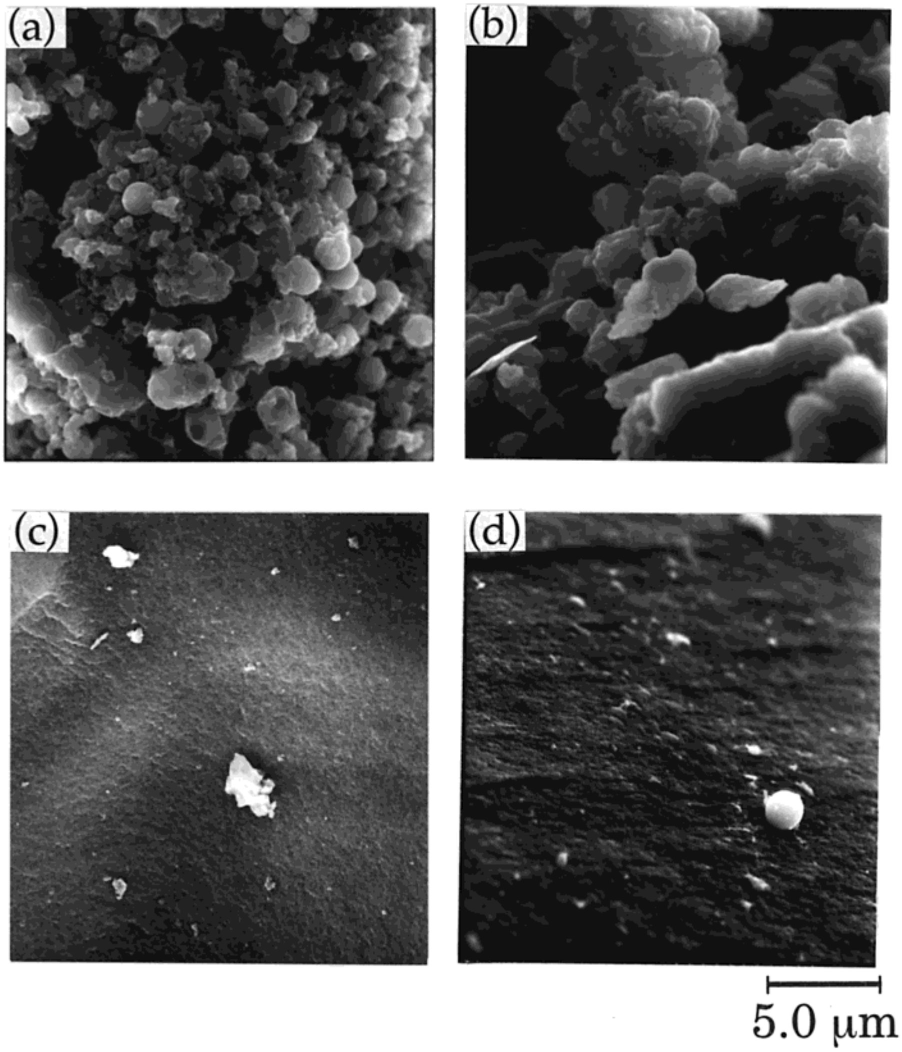

Figure 1. SEM photographs of the carbons extracted from the carbon/silica nanocomposites prepared at different FA/TEOS ratios (gelation temperature, 120 °C; HCl/TEOS, 0.01). The FA/TEOS ratios of parts a−d are 0.25, 0.50, 1.00, and 2.00, respectively.

formed in the composites prepared at the lower ratio. Thus, the latter composites lost their filmlike shape upon the removal of the silica framework by the acid washing.

N_2 Adsorption. The N_2 isotherms for the carbon samples at −196 °C are illustrated in Figure 2, where for both parts a and b a remarkable difference in isotherm shape is observed between the samples prepared at the FA/TEOS ratios (1.00 and 2.00) and at the lower ratios (0.25 and 0.50). The former samples show an increase in the slopes of the isotherms and a clear hysteresis loop in the pressure range of 0.4−0.8. These are typical features of Type IV isotherm,[22] which occurs on a mesoporous adsorbent. On the other hand, the amounts of N_2 adsorbed in the latter samples are smaller, and their isotherms do not show a clear hysteresis loop, indicating poor development of mesoporosity. For the carbon samples prepared at a FA/TEOS ratio of 4.00, their isotherms are intermediate between the above two cases.

From the isotherms, we determined the BET surface area, pore volume, and mesoporosity, which are summarized in Table 2. The two parameters ($S_{\text{meso}}/S_{\text{BET}}$ and $V_{\text{meso}}/V_{\text{total}}$) are put in this table as a measure of mesoporosity. The former parameter, $S_{\text{meso}}/S_{\text{BET}}$, has often been used as a mesopore ratio of activated carbons.[5,23] In the table, the maximum value of $S_{\text{meso}}/S_{\text{BET}}$ at a gelation temperature of 60 °C is equal to 1.00, and at 120 °C, the value reaches more than one. Sakata et al. also found such a large ratio when they used $S_{\text{meso}}/S_{\text{BET}}$ to determine the mesopore ratio of carbon/iron composite prepared from bamboo.[24] Values of more than one are unreasonable in view of the definition of a mesopore ratio, as pointed out by Sakata et al.[24] Thus, in the present study we used $V_{\text{meso}}/V_{\text{total}}$ rather than $S_{\text{meso}}/S_{\text{BET}}$ as a measure of mesoporosity.

Table 2 clearly indicates that the carbons obtained have porosities with different degrees. Since the surface area of the pure PFA carbon prepared without silica was almost zero, the mixing with silica at the nanometer level endowed the resultant carbons with their porosity. The values of both the surface area and the pore volume increase with an increase in the FA/TEOS ratio and reach a maximum at a ratio of 2.00, followed by their

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Table 2. Pore Structure of the Carbons Prepared from the Carbon/Silica Nanocomposites.

gelation temp. (°C)	FA/TEOS mol ratio	HCl/TEOS mol ratio	BET surf. area S_{BET} (m^2/g)	total pore vol. V_{total} (cm^3/g)	S_{meso}/S_{BET}	V_{meso}/V_{total}
60	0.25	0.01	220	0.15	0.33	0.35
60	0.50	0.01	460	0.32	0.44	0.41
60	1.00	0.01	580	0.74	1.00	0.71
60	2.00	0.01	910	0.79	0.96	0.63
60	4.00	0.01	740	0.42	0.55	0.49
120	0.25	0.01	150	0.14	0.50	0.48
120	0.50	0.01	350	0.26	0.40	0.40
120	1.00	0.01	1060	1.06	1.09	0.69
120	2.00	0.01	1170	1.27	1.11	0.67
120	4.00	0.01	890	0.63	0.74	0.55
120	2.00	0.001	1030	0.80	0.54	0.54
120	2.00	0.1	200	0.17	0.53	0.53

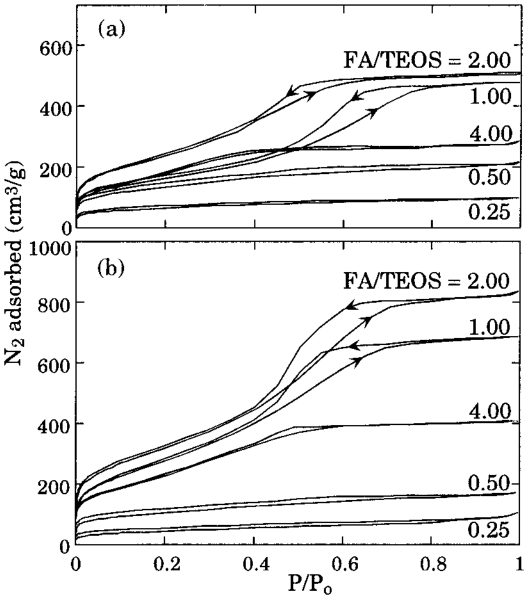

Figure 2. N_2 isotherms for the carbons prepared at different FA/TEOS ratios at gelation temperatures of (a) 60 and (b) 120 °C (HCl/TEOS, 0.01). Numerical values in the figure indicate FA/TEOS ratio.

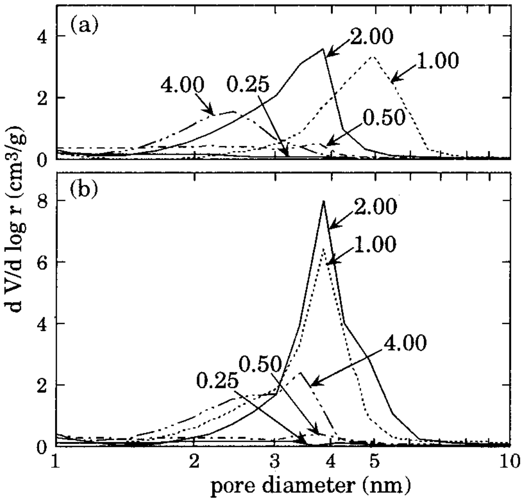

Figure 3. Effect of FA/TEOS ratio on pore size distribution for the carbons prepared from the carbon/silica nanocomposites at gelation temperatures of (a) 60 and (b) 120 °C (HCl/TEOS, 0.01). Numerical values in the figure indicate FA/TEOS ratio.

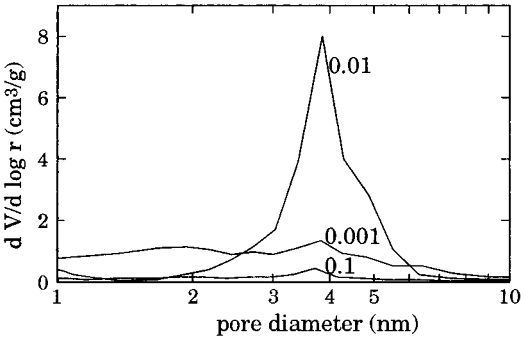

Figure 4. Effect of HCl/TEOS ratio on pore size distribution for the carbons prepared from the carbon/silica nanocomposites at gelation temperature of 120 °C and FA/TEOS of 2.00. Numerical values in the figure indicate HCl/TEOS ratio.

slight decrease at 4.00. A similar change with FA/TEOS ratio is observed for the mesoporosity expressed by the parameter V_{meso}/V_{total}; i.e., the mesoporosity shows a maximum around a FA/TEOS ratio of 1 or 2. However, the mesoporosity is small when the HCl/TEOS ratio was set to either 0.001 or 0.1. Specially for the latter sample, not only the mesoporosity but also both the surface area and the pore volumes are low.

Pore Size Distribution. The variation of mesopore with the FA/TEOS ratio will more clearly be presented by the mesopore distribution curves, as shown in Figure 3, where the curves were determined by the BJH method. As was revealed in Figure 2, Figure 3 also shows that no substantial mesopore is present in the samples at FA/TEOS ratios of 0.25 and 0.50, whereas all of the other samples have a clear peak in each distribution curve in the mesopore range. Their peak position and broadness change with the sol−gel reaction conditions. At a gelation temperature of 60 °C, the peak position is shifted from 5 to 2.5 nm with increasing the FA/TEOS ratio. At 120 °C, the samples at the ratios of 1.00 and 2.00 show a very sharp pore distribution centered at 4 nm. The effect of the HCl/TEOS ratio on the pore distribution curve is illustrated in Figure 4. Although the sample prepared at a HCl/TEOS ratio of 0.01 shows a sharp peak at around 4 nm, almost no peak is observed when the HCl/TEOS ratio was changed to either 0.001 or 0.1.

Discussion

The results of elemental analysis (wt %) for the pure PFA carbon were as follows: C, 84; H, 1; N, 1; O (diff.), 14. The presence of nitrogen may be explained from the presence of trace N_2 retained in the very narrow micropores of the PFA carbon. The details of such N_2 retention have been described elsewhere.[25] When we compare this result with those in Table 1, it can be said that the PFA carbons derived from the composites have quite low oxygen content and consequently high carbon content. This finding suggests that the presence of the silica framework in the composite facilitates carbonization of the PFA. Although we do not have a clear explanation for this phenomenon, we can conclude that the carbonization process of PFA in the nanospace confined by the silica framework is quite different from that of bulk PFA.

It was found that the carbon/silica composites had a dense structure and their surface areas were almost equal to zero. This suggests that upon the HF treatment the silica framework in the composites was converted into the pores in the carbon. In other words, the volume of the silica content in the composites would correspond to the pore volume of the carbons in Table 2. To check this hypothesis, we calculated the volume of silica in the composites from their ash contents by assuming that the ash consists of only SiO_2 and its density is 2.6 g/cm^3. For the composites prepared at the temperature of 60 °C, these values were 9.2, 3.5, 1.2, 0.5, and 0.5 cm^3/g of carbon at FA/TEOS ratios of 0.25, 0.50, 1.00, 2.00, and 4.00, respectively. The calculated values at the lower FA/TEOS ratios (0.25 and 0.50) are much larger than the actual pore volumes of the carbon samples, 0.15 and 0.32 cm^3/g, respectively. This discrepancy can be due to the structure of these composites. Since they have a large amount of the silica, their continuous phase may not be carbon but silica. If this is the case, such a silica phase cannot be converted to the mesopores in the carbon samples upon acid washing.

The above discussion suggests that the presence of a continuous carbon phase in the carbon/silica composite is essential for the production of highly porous carbon. To form such a continuous carbon phase, a FA/TEOS ratio of, at least, 1 is necessary. However, this is not a sufficient condition for the development of mesoporosity. An optimum FA/TEOS ratio is necessary, as shown in Figure 3. Furthermore, the effect of the HCl/TEOS ratio on the mesoporosity is quite important (Figure 4).

A mixing at the nanometer level of the carbon phase with the silica in the composite structure should be a key factor for the development of mesoporosity. Such a mixing could be achieved if the gelation of TEOS and the polymerization of FA take place simultaneously at almost the same rate. The high HCl content in the initial FA/silica sol solution might enhance initially the polymerization of FA, leading to aggregation of the PFA phase before the silica framework structure starts to form. As a result, this condition gave carbon with poor porosity (Table 2), although the carbon content in the corresponding composite was almost the same as that in the composite prepared at a HCl/TEOS ratio of 0.01 (Table 1). At the low HCl content, the degree of the polymerization is not high and therefore some of the FA monomers may be volatilized or decomposed during the carbonization process. This could be the reason for the very small carbon content in the composite (Table 1).

Conclusions

A nanocomposite of carbon and silica was prepared by using a sol−gel process with TEOS in the presence of FA followed by the polymerization of FA and its subsequent carbonization. The removal of the silica framework from such a nanocomposite led to the formation of porous carbon. It was found that the mesoporosity and mesopore structure (pore size and distribution) strongly depend on the sol−gel reaction conditions. For the production of carbon having mainly mesopores, the sol−gel conditions should be optimized. The mole ratio of FA/TEOS should be in the range of 1−2, and furthermore, a moderate amount of HCl as an acid catalyst should be added to the sol solution. The sol−gel process under these conditions allows the nanometer-level mixing of the PFA phase with the silica phase in the composite, resulting in the formation of mesoporous carbon upon carbonization and the subsequent removal of the silica framework. Under the above sol−gel conditions and at a high gelation temperature (120 °C), mesoporous carbon with a very narrow pore size distribution centered at 4 nm could be prepared.

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