9208 *J. Am. Chem. Soc.* **2001,** *123,* 9208−9209

Colloidal Imprinting: A Novel Approach to the Synthesis of Mesoporous Carbons

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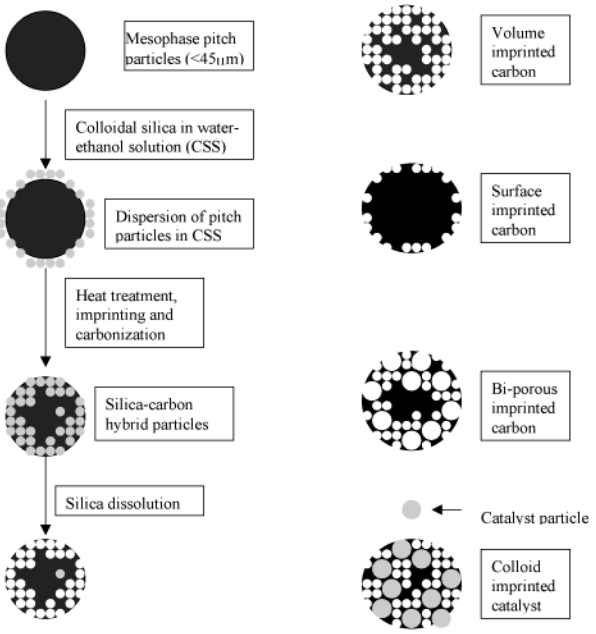
Received June 28, 2001

Although porous carbons have been in use for thousands of years and have become adsorbents of great industrial importance,[1] many important methods to design their porous structures have appeared just recently.[2] One of such methods employs the ordered mesoporous silicas (OMS), e.g., MCM-48[3] and SBA-15,[4] as templates and involves the pore filling with a carbon precursor followed by carbonization and silica dissolution.[2c−f] The resulting carbons exhibited ordered mesopores of size below $\sim$7 nm arising from the dissolved silica framework. Another method, which is more appropriate for preparation of macroporous materials, involves colloids as templates. The colloidal crystal templating has become very popular for designing novel porous materials.[5] Thus, it is not surprising that colloidal silica particles[6] as well as colloidal crystals[2a,b] were used for preparation of porous carbons. The synthesis route, which involved mixing of colloidal silica particles with carbon precursor to obtain a composite, its subsequent carbonization, and silica dissolution, gave a carbon with disordered pores resembling the initial colloidal aggregates.[6] In contrast, the colloidal crystal templating afforded carbons with ordered macropores or mesopores of size greater than 30 nm.[2a,b] This templating route involves the formation of colloidal crystals, infiltration of the crystal's interstitial space with a fluid-type carbon precursor, and its solidification followed by removal of the template. Several of the templated carbons contain disordered micropores present in the walls of ordered mesopores or macropores.[2e] These micropores are formed during carbonization of many common carbon precursors.[7]

This work reports a novel approach to the synthesis of carbonaceous materials, which involves creation of mesopores in carbon precursor particles by imprinting with colloidal silica particles. In contrast to the colloidal templating, which involves a fluid-type carbon precursor, the colloid-imprinted carbons (CIC) are synthesized by imprinting solid particles of the mesophase pitch used as carbon precursor with colloidal silica particles. As can be seen in Scheme 1, the colloidal imprinting (CI), depending on the synthesis conditions, allows the creation of spherical pores in the volume of precursor particles as well as on their surface. Also, the use of colloidal particles of different sizes and/or chemical nature in the CI process allows one to design the pores of different sizes in the CIC materials as well as to tailor their sorption and catalytic properties. An important advantage of using the mesophase pitch is its easy carbonization, which lead to almost nonmicroporous carbons.[1,7] This pitch is a common precursor for carbon fibers, which are nonporous materials.[8]

Scheme 1. Synthesis of Colloid-Imprinted Carbons



The synthesis of CIC was performed by using a synthetic Mitsubishi mesophase pitch (H/C ratio = 0.6 and softening point = 237 °C). The powdered (particles <45 μm) mesophase pitch was dispersed in ethanol, mixed with an excess of colloidal silica solution in a closed flask, and stirred at about 50 °C for 5 h. Next, the flask was opened allowing a slow evaporation of solvent under stirring (about 3−5 h). The resulting mixture was kept at 260 °C, which is slightly higher than the softening point of this pitch, for 30 min under nitrogen. During this short time, the colloidal particles were able to penetrate pitch particles and form the colloidal silica-pitch composite, which was heated at a rate of 2−5 °C/min and carbonized at 900 °C for 2 h under nitrogen followed by dissolution of silica with 3 M NaOH solution at about 95 °C. Thermogravimetric analysis of the CIC samples up to 1000 °C in flowing air revealed less than 1% of residue, indicating that almost all silica was dissolved. The Ludox AS-30 ($\sim$230 m^2/g) and AS-40 ($\sim$135 m^2/g) colloidal silicas were used to prepare CIC-13 and two CIC-24A&B samples, respectively (13 and 24 refer to the mean pore diameter estimated from nitrogen adsorption). In addition, two CIC-24C&D samples were synthesized using the Ludox AS-40 colloidal silica and the pretreated pitch particles, which were obtained by heating them in silicone oil for 30 min at 250 °C and washing with toluene and acetone at room temperature.

Shown in Figure 1 are nitrogen adsorption−desorption isotherms at −196 °C measured on a Micromeritics 2010 adsorption analyzer together with the corresponding pore size distributions (PSD). The latter were calculated by the BJH method[9] using the

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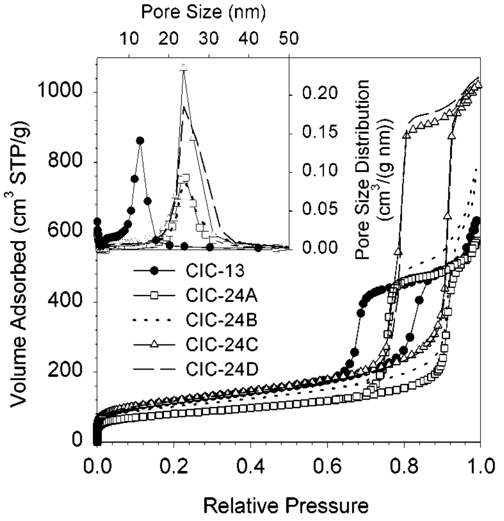

Figure 1. Nitrogen adsorption isotherms at −196 °C and the corresponding pore size distributions for colloid-imprinted carbons.

Table 1. The BET Surface Area (*S*), Total Pore Volume (*V*), and Pore Width (*w*) at the Maximum of PSD for the Colloid-Imprinted Carbons

sample	*S* (m^2/g)	*V* (cm^3/g)	*w* (nm)
CIC-13	418	0.91	12.7
CIC-24A	286	0.89	24.2
CIC-24B	362	1.07	23.8
CIC-24C	425	1.57	23.6
CIC-24D	420	1.61	23.7

statistical film thickness (*t*-curve) obtained from nitrogen adsorption data on the BP280 carbon black[10] by adjusting it to the multilayer range of the *t*-curve calibrated for the MCM-41 samples.[11] As can be seen in Figure 1, nitrogen adsorption isotherms exhibit very sharp condensation steps, which reflect narrow PSD. The pore width at the maximum of PSD exceeds about 10% the particle size of the colloidal silica estimated on the basis of the manufacturer data, which may be due to the approximate nature of the BJH method. All four syntheses of the AS-40 imprinted carbons gave very similar values of the pore size (see Table 1). Also, the synthesis employing the pretreated pitch particles seems to be highly reproducible as evidenced by the coincidence of adsorption isotherms for CIC-24C&D. The total pore volumes of these samples are much greater than those for the CIC-24A&B samples (see Table 1). Their BET surface areas are quite close to the expected maximum surface area, which is ∼500 m^2/g.

The CI process allows the control of the pore width of the resulting CIC materials up to 6 nm by using proper colloidal silica particles. In the case of silica colloids close to 6 nm some pores larger than the single particle are often formed due to the presence of coalesced colloidal aggregates. However, even in this case the primary mesopores strictly corresponding to the single colloidal particles were formed, which has not been achieved yet by the colloidal crystal templating method.[2a,b] Also, the sol−gel-type process involving colloidal silica afforded carbons with much broader PSD and without exact correspondence between the mean pore size and the diameter of the colloidal particles used.[6] Indeed, we have synthesized carbons with much more narrow PSD centered at proper pore sizes using the same colloids as those in ref 6. Another important feature of CIC is their nonmicroporous nature resulting from using the mesophase pitch as carbon precursor with no tendency to the micropore formation (microporosity was below 1−2% of the total pore volume).

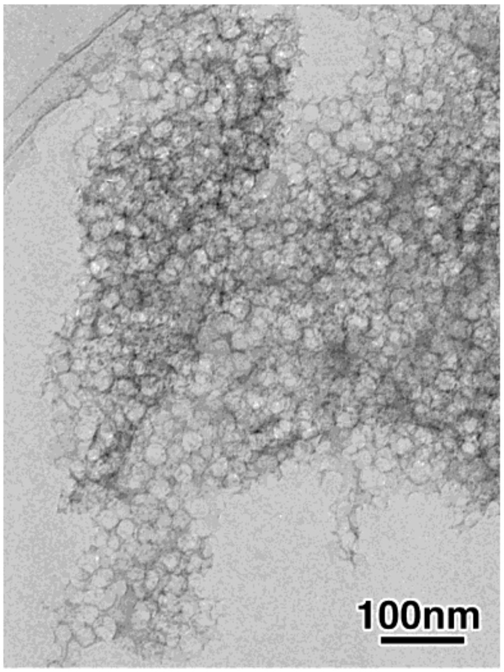

Figure 2. TEM image for the CIC-24A sample recorded with a JEM-4000 EX TEM instrument.

As can be seen in Figure 2, which shows a typical TEM image for CIC, the structure of this material consists of rather randomly distributed interconnected spherical mesopores obtained by imprinting the pitch particles with colloidal silica particles. The size of these pores is remarkably uniform, which results from monodispersity of the colloidal particles.

In summary, the imprinting of the mesophase pitch particles with colloidal silica particles provides a simple way to synthesize carbons with interconnected mesopores having diameters that correspond to the size of the colloids used. The CI process is reproducible and effective for synthesis of carbons with the desired size of mesopores, high pore volume, and relatively high surface area. Note that both starting materials, i.e., pitch and colloidal silica, are commercially available on a large scale. It is expected that this process is also suitable for tailoring adsorption and catalytic properties by adding colloidal particles of specific surface properties. In addition, the CIC materials, similarly to carbon fibers, can be oxidized under controlled conditions to create micropores and alter their surface properties as well as graphitized to introduce the graphite crystallinity. These modification opportunities extend their potential applications ranging from adsorption to catalysts supports and electrode materials.

Acknowledgment. The authors thank Drs. O. Terasaki and Z. Liu (Tohoku University, Japan) for TEM images for two CIC samples and Dr. M. Kruk (Kent State University) for valuable discussions.

JA0165178

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