

Mesoporous Carbons Synthesized by Imprinting Ordered and Disordered Porous Structures of Silica Particles in Mesophase Pitch

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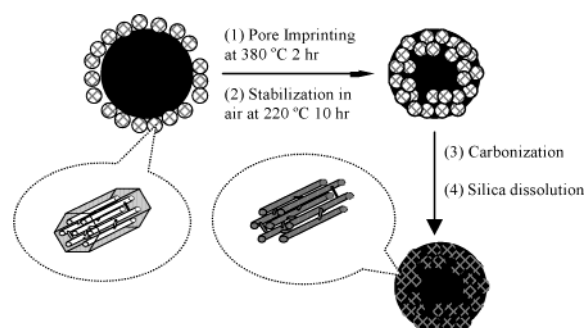
A novel method for imprinting porous silica particles with ordered and disordered structures in mesophase pitch particles is proposed. It is shown that the particle-imprinted carbons may possess ordered or disordered porous domains depending on the porous structure of the silica particles used in the imprinting process.

Adsorbents for large molecules, chromatographic separations, electric double layer capacitors, photonic devices, and lithium batteries require carbons with controlled mesoporous structures. Mesoporous carbons can be obtained by using catalytic activation, sol–gel processing, carbonization of mesostructured block copolymers of different thermal properties, and templating methods, which employ ordered mesoporous silicas (OMS) and colloidal silicas.^{1–4} So far, templating is the most efficient method to prepare ordered mesoporous carbons (OMC).⁴ The availability of various OMS templates, e.g., MCM-48, SBA-15, SBA-16, and FDU-1 provides vast opportunities for the synthesis of OMC in the form of interconnected nanorods, nanopipes, and nanospheres.^{4,5} The main idea of this method is to fill the ordered silica template with a fluid carbon precursor, e.g., sucrose or furfuryl alcohol, carbonize the resulting composite and dissolve the silica template. Although the templating method affords high quality OMC, it has also some limitations. For instance, the template structure limits the range of achievable mesopores to 2–6 nm in the case of OMS and above 50 nm in the case of colloidal crystals.⁶ In addition, the use of the aforementioned carbon precursors is responsible for the formation of irregular micropores in the pore walls of OMC.

Recently, we reported⁶ a promising colloidal imprinting (CI) method for the synthesis of carbons with uniform spherical pores in the range from ~6 to 60 nm, which fills the pore size gap between carbons prepared by using OMS and colloidal silica crystals as templates. The main concept of this method was to incorporate spherical silica colloids into mesophase pitch particles at controlled temperature, carbonize silica-pitch composite particles, and dissolve the colloidal silica. The ease of penetration of silica colloids into mesophase pitch particles is intriguing. It was shown that the degree of this penetration can be easily controlled by introducing air stabilization before the carbonization step⁷ and the resulting colloid-imprinted carbons (CIC) withstand graphitization at 2400 °C in argon.⁸ Soon after the first report on CIC, their spherical mesopores were used to synthesize spherical particles of zeolites.⁹ Although the porous structure in CIC consists of uniform and spherical mesopores, no pore ordering was observed.^{6,9}

While colloidal imprinting involved nonporous silica colloids, here we demonstrate the possibility to imprint porous silica particles with ordered or disordered structures in large me-

SCHEME 1: Illustration of the Imprinting Process of Porous Silica Particles with Ordered Structures in Mesophase Pitch Particle



sophase pitch particles (see Scheme 1). The resulting particle-imprinted carbons (PIC) may possess ordered or disordered porous domains depending on the porosity of silica particles used. As in the previous work,⁶ the AR synthetic mesophase pitch (Mitsubishi) was used as the carbon precursor. Two types of the PIC samples were prepared by employing OMS particles of SBA-15 and silica particles with disordered porosity. The PIC-SBA15 sample was synthesized by using particles of SBA-15, which exhibit 2D hexagonally ordered cylindrical mesopores interconnected by complementary micropores. The SBA-15 sample, prepared by using the triblock copolymer EO₂₀PO₇₀EO₂₀ (Pluronic P123, BASF) as the template and tetraethoxysilane as the silica source, was described elsewhere.¹⁰ Its surface area, pore volume, and pore width were equal to 845 m²/g, 1.10 cm³/g, and 10.6 nm, respectively. 0.22 g of this sample was thoroughly mixed with 0.37 g of mesophase pitch particles (<20 μm) in 20 mL ethanol under vigorous stirring at ~50 °C until solvent evaporated. The resulting mixture was heated at 380 °C in nitrogen atmosphere for 120 min followed by air stabilization at 220 °C for 10 h. Carbonization of the resulting pitch/silica composite was carried out under nitrogen protection at 850 °C for 60 min, and the silica dissolution was performed using aqueous HF solution.

During the imprinting process at 380 °C in nitrogen the mesophase pitch softened, which facilitated the penetration of small SBA-15 particles into large pitch particles and resulted in the formation of the pitch/SBA-15 composite. After oxidation at 220 °C in air and carbonization in nitrogen at 850 °C, the carbon/SBA-15 composite shows very small adsorption of nitrogen in comparison to that on SBA-15 (see the Supporting

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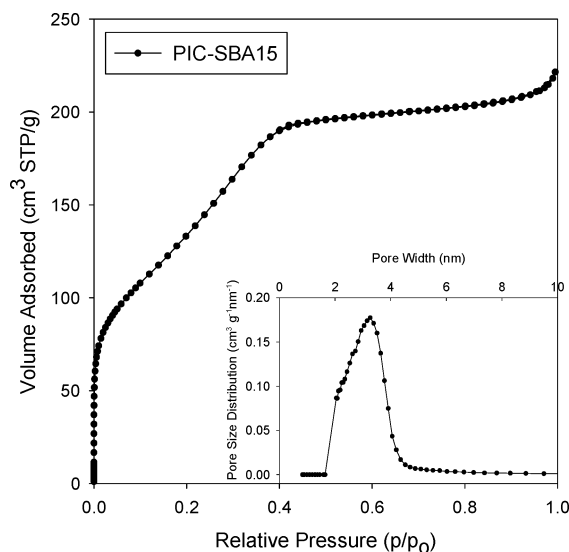


Figure 1. Nitrogen adsorption isotherm at $-196\text{ }^{\circ}\text{C}$ on the PIC-SBA15 sample and the corresponding pore size distribution.

Information, Figure 1S). The BET surface area and pore volume for this composite, $32\text{ m}^2/\text{g}$ and $0.048\text{ cm}^3/\text{g}$, were very small in comparison to the corresponding values for SBA-15 given above. A significant decrease in the surface area and porosity of the pitch/SBA-15 composite indicates that the interpenetration of SBA-15 and mesophase pitch particles was effective because only less than 5% of the SBA-15 porosity was accessible for nitrogen adsorption. Also, the use of mesophase pitch as carbon precursor in comparison to commonly used precursors is advantageous because of high carbonization yield (65–70%), low shrinkage of the structure, and small microporosity in the resulting carbons.

Figure 1 shows the nitrogen adsorption isotherm and the corresponding pore size distribution for the SBA-15 imprinted carbon. The latter was calculated from the adsorption branch of the isotherm using the KJS method¹¹ with the statistical film thickness calibrated for nitrogen on a reference Cabot BP280 carbon black.¹² This adsorption isotherm exhibits a distinct condensation step in the relative pressure range from 0.1 to 0.4, which levels off at higher relative pressures indicating a relatively low external surface area and uniform pore structure of the PIC-SBA15 sample. The BET surface area and pore volume of this carbon are equal to $491\text{ m}^2/\text{g}$ and $0.34\text{ cm}^3/\text{g}$, respectively. The pore size distribution is narrow and has a maximum at 3.4 nm (see inset in Figure 1). This pore size is about 1.5 times smaller than that for the carbon synthesized by using SBA-15 as the template and sucrose as the carbon precursor.¹³ This difference is due to the high carbonization yield and rather small shrinkage of the mesophase pitch during carbonization, which results in a smaller distance between carbon nanorods after removal of SBA-15. Although the adsorption study showed a narrow distribution of pores in the entire PIC-SBA15 sample, transmission electron microscopy (Figure 2) and powder X-ray diffraction (Supporting Information, Figure 2S) proved that these pores are ordered.

Another carbon sample, PIC-M, was prepared using porous silica particles with disordered structure, LiChrospher Si-100 from Merck, as the imprinting agent. The imprinting temperature was $280\text{ }^{\circ}\text{C}$. The pitch stabilization in air, carbonization, and silica removal procedures were the same as those for PIC-SBA15. The nitrogen adsorption isotherm for PIC-M is shown in Figure 3S of the Supporting Information. This isotherm exhibits a rather broad capillary condensation step indicating

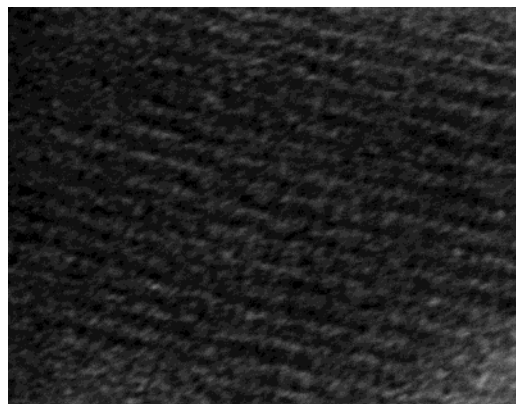


Figure 2. TEM image for the PIC-SBA15 sample.

the existence of relatively large disordered mesopores. The PIC-M sample imprinted with LiChrospher Si-100 particles has the BET surface area of $175\text{ m}^2/\text{g}$ and pore volume of $0.22\text{ cm}^3/\text{g}$.

The use of porous particles as the pore imprinting agents allows imprinting the pore wall structure in addition to the particle size and shape in large pitch particles. For the PIC samples under study, the contribution to the total specific surface area arising from imprinting the size of silica particles is negligible because their size was relatively large (in microns). Thus, the resulting surface area in these carbons arose from imprinting the pore wall structure of the silica particles. The ability to imprint the pore wall structure of silica particles in large pitch particles distinguishes this process from the colloidal imprinting, in which only the shape and size of silica colloids is imprinted. However, in this case, the surface area of colloid-imprinted carbons can be relatively high because the size of colloids is in nanometers or tens of nanometers.

The ability to control the extent of the imprinting process by air stabilization opens new possibilities in the synthesis of PIC. It is possible to prepare carbon particles with ordered porous shells/nonporous cores as well as particles having larger spherical pores interconnected by means of ordered domains, when colloids and porous particles are used as imprinting agents. In contrast to the templating method,¹⁴ in the imprinting process, the connections between mesopore channels are not so essential because the nonporous core can attach carbon nanorods. Thus, even MCM-41 can potentially be used to make imprints on the surface of pitch particles. Also, the particle size of imprinted carbons is determined by the size of pitch particles. On the contrary, the size of carbon particles obtained in the templating method is determined by the particle size of OMS templates, which are in the submicrometer or even nanometer range.

In conclusion, the imprinting of mesophase pitch particles with porous silica of ordered and disordered structures provides a simple, reproducible, and effective way to synthesize carbons with desired surface area, mesopore structure, and morphology. This method allows imprinting not only the pore wall structure of silica particles, but also their shape and size as well as it opens new avenues for designing carbon mesostructures.

Additional note: Recently, a related paper to this work appeared in the *Journal of Materials Chemistry* (2003, 13, 2535) on the template synthesis of ordered mesoporous carbons by impregnating ordered mesoporous silicas with low viscosity petroleum pitch at $302\text{ }^{\circ}\text{C}$.

Supporting Information Available: Nitrogen adsorption isotherms for SBA-15 and pitch/SBA-15 composite (Figure 1S), powder X-ray diffraction patterns for SBA-15 and PI-SBA15

samples (Figure 2S), and nitrogen adsorption isotherm for PIC-M (Figure 3S). These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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