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Low-Cost Synthetic Route to Mesoporous Carbons with Narrow Pore Size Distributions and Tunable Porosity through Silica Xerogel Templates

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Silica xerogels synthesized by the sol−gel process were used as templates to fabricate mesoporous carbons. The silica was prepared in a two-step process, under acid pH conditions, at a high H_2O/Si molar ratio of 194 and at different HCl/Si molar ratios. Two sources were used as silica precursors: tetraethoxysilane (TEOS) and sodium silicate. The resulting silica xerogels have surface areas of >500 $m^2 \cdot g^{-1}$, pore volumes of >0.4 $cm^3 \cdot g^{-1}$, and a tunable mesopore size of between 2 and 10 nm, depending on the HCl/Si molar ratio. The mesoporous carbons obtained as inverse replicas of silica xerogel templates have large pore volumes (in the 1.5−2.1 $cm^3 \cdot g^{-1}$ range), large BET surface areas of up to 2200 $m^2 \cdot g^{-1}$, and narrow pore size distributions (PSD) in the mesopore range. The mesopore size of the carbons can be tuned between 3 and 4.5 nm depending on the type of silica xerogel selected as template. Carbons prepared in this way have structural characteristics comparable to those of mesoporous carbons made by templating mesostructured silica materials synthesized by using expensive surfactants as structure-directing agents. The procedure also allows unimodal or bimodal mesoporous carbons to be obtained from the same silica xerogel template. This is achieved by varying the amount of carbon precursor allowed to infiltrate into the silica porosity.

1. Introduction

Porous carbons are widely used in air and water purification, catalysis, and gas separation. Depending on the pore size distribution (PSD), two types of porous carbons are currently available: (i) carbons that have very narrow PSD in the micropore range (<1 nm) (i.e., carbon molecular sieves) and (ii) carbons with a wide PSD extending over the micropore−mesopore range (0−50 nm) (i.e., active carbons). Both kinds of materials are synthesized following well-established methods. Thus, active carbons are currently obtained by the carbonization of organic precursors (natural or synthetic), followed by physical or chemical activation.[1] For certain emergent applications, such as those that involve molecules of a large size, i.e., adsorption of bulky species,[2] or those that require the enhanced transport of species within the pore network, i.e., catalytic reactions involving large molecules or energy storage in double layer capacitors,[3] carbons with a porosity formed almost exclusively by mesopores with sizes in a narrow range are more effective than active carbons with a wide PSD in the micropore−mesopore range. However, carbons with these characteristics cannot be synthesized by means of the classical methods used for preparing active carbons. For this reason, the synthesis of mesoporous carbons represents a challenge, which has recently attracted much attention. One way of preparing carbons with the previously outlined characteristics involves the use of inorganic materials as templates. This approach allows mesoporous carbons to be obtained as inverse replicas. The technique consists of the following: (a) impregnation of the inorganic porous structure (template) with the carbon precursor (generally a polymer or prepolymer), (b) carbonization of the nanocomposite formed, and (c) elimination of the template. Mesostructured silica materials (MSM) synthesized by using surfactants as structure-directing agents[4−6] have, until now, been the most frequently used inorganic templates. Several mesoporous carbons with different structural characteristics (i.e., ordered or disordered pore networks, pore size, unimodal or bimodal porosity, etc.) have been obtained in this way.[7−16] This techniqueen-

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(1) Derbyshire, F.; Jagtoyen, M.; Thwaites, M.; Activated carbons − Production and Applications. In *Porosity in carbons: Characterisation and Applications*; Patrick, J. W., Ed.; Edward Arnold: London, 1995; Ch. 9.

(2) Han, S.; Sohn, K.; Hyeon, T. *Chem. Mater.* **2000**, *12*, 3337.

(3) Yoon, A.; Lee, J.; Hyeon, T.; Oh, S. M. *J. Electrochem. Soc.* **2000**, *147*, 2507.

(4) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. C. *Nature* **1992**, *359*, 710.

(5) Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242.

(6) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, D. G. *J. Am. Chem. Soc.* **1998**, *120*, 6024.

(7) Ryoo, R.; Joo, S. H.; Jun, S. *J. Phys. Chem. B* **1999**, *103*, 7743.

(8) Jun, S.; Jo, S. H.; Ryoo, R.; Kruk, M.; Jaroniec, M.; Liu, Z.; Oshuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 10712.

(9) Kim, S. S.; Pinnavaia, T. J. *Chem. Commun.* **2001**, 2418.

(10) Lee, J.; Yoon, S.; Oh, S. M.; Shin, S.; Hyeon, T. *Adv. Mater.* **2000**, *12*, 359.

(11) Yang, H.; Shi, Q.; Liu, X.; Xie, S.; Jiang, D.; Zhao, D. *Chem. Commun.* **2002**, 2842.

(12) Kruk, M.; Jaroniec, M.; Kim, T.; Ryoo, R. *Chem. Mater.* **2003**, *15*, 2815.

(13) Che, S.; Garcia-Bennet, A.; Liu, X.; Zhao, D.; Terasaki, O.; Tatsumi, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 3930.

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tails the use of expensive surfactants as templating agents for the synthesis of MSM. A low-cost route for manufacturing mesoporous carbons could be provided by using porous silica templates synthesized without the aid of surfactants (i.e., silica gels). The literature offers some examples of the application of porous silica gels as templates for obtaining porous carbons.[17−20] However, carbons obtained in this way have poorer mesoporous characteristics than those derived from MSM.

Low-cost mesoporous carbons with structural characteristics (i.e., surface area, pore volume, pore size, and narrow PSD) comparable to those of carbons obtained from MSM could be prepared by selecting as templating agents silica gels that have structural properties similar to those of MSM. The structural characteristics of silica gels mainly depend on the size of the primary particles. Iler[21] showed that the size to which the particles grow before they form the gel is a function of the pH used during the hydrolysis−condensation processes. Thus, for low pH the size of the primary particles is very small and consequently the silica gels obtained have a large surface area ($>$500 $m^2 \cdot g^{-1}$), large pore volumes ($>$0.5 $cm^3 \cdot g^{-1}$), and a porosity made up mainly of pores in the mesopore range with sizes below 20 nm. These structural properties are in the range of those of the MSM used as templates to fabricate mesoporous carbons. In principle, therefore, the use of acid pH to synthesize silica gels might serve to obtain templates with the appropriate structural properties.

The purpose of this work was to synthesize mesoporous carbons by means of inexpensive mesoporous silica templates obtained without the aid of surfactants. It will be shown that the mesoporous carbons thus prepared have structural characteristics (i.e., pore volume, surface area, PSD, etc.) comparable to those obtained by using MSM templates. The method employed is based on the use of inexpensive silica xerogels as templating agents. These xerogels are obtained from a synthesis mixture formed exclusively by a silica source, HCl, and water. Furthermore, it is shown that the mesoporous carbons derived from silica xerogels obtained by using inexpensive sodium silicate as the silica source have characteristics comparable to those prepared by templating silica xerogels obtained from expensive organosilica precursors (i.e., TEOS). Finally, the procedure described shows that unimodal or bimodal mesoporous carbons can be obtained from the same silica xerogel template, by simply varying the amount of carbon precursor allowed to infiltrate into the silica porosity.

2. Experimental Section

2.1. Synthesis of Silica Xerogel Templates. The synthesis of silica xerogels was carried out in a two-step process to allow separation of the hydrolysis and condensation mechanisms. The first step was performed at room temperature in an acid medium, the hydrolysis of silica precursor occurring rapidly in contrast to the condensation reactions which were slow.[22] Under these conditions, no precipitate appeared even after several days at room temperature. In a second step, the synthesis mixture was heated to 100 °C. The condensation reactions were accelerated and consequently after a few hours a consistent gel was formed.

Two types of silica source were used to synthesize the silica xerogels; i.e., TEOS (Aldrich) and sodium silicate (Aldrich, 27% SiO_2 + 14% NaOH). In a typical synthesis, the silica source was added under stirring to an aqueous solution containing HCl. The synthesis with TEOS was carried out at a high H_2O/Si molar ratio of 194 and at different HCl/Si molar ratios (x) ranging from 0.04 to 8. When the xerogel was prepared from sodium silicate as silica precursor, the molar composition of the synthesis mixture was TEOS/HCl/H_2O = 1:6:194. In the first stage, the solution was stirred in a closed Teflon vessel for 20 h at room temperature. In the second stage, the mixture was maintained for 2 days at 100 °C. The resulting gel was filtered, washed several times with water and then with acetone, dried at room temperature, and calcined in air to 600 °C (2 °C/min, 4 h).

2.2. Preparation of Templated Carbons. The carbons were synthesized according to a procedure reported elsewhere.[23] Two types of carbons were prepared in this way, i.e., unimodal and bimodal. In a typical synthesis of unimodal carbon, the silica was impregnated with paratoluenesulfonic acid (0.5 M in ethanol). Afterward, furfuryl alcohol was added to the silica until incipient wetness was achieved. The impregnated sample was cured in air for 12 h at 80 °C to polymerize the furfuryl alcohol and convert it into poly(furfuryl alcohol), which was then carbonized under N_2 at 800 °C (2 °C/min, 1 h). The porous carbon was obtained after dissolution of the silica framework in 48% HF at room temperature.

The procedure used to fabricate the bimodal carbons is identical to that employed for unimodal materials, except that in this case the silica porosity was not completely filled with the carbon precursor. Thus, only around 80% of the silica pore volume was impregnated with furfuryl alcohol.

2.3. Sample Characterization. Nitrogen adsorption and desorption isotherms were performed at 77 K in a Micromeritics ASAP 2010 volumetric adsorption system. The BET surface area was deduced from the isotherm analysis in the relative pressure range of 0.04 to 0.20. The total pore volume was calculated from the amount adsorbed at a relative pressure of 0.99. The primary mesopore volume and external surface area were estimated using the α_s-plot method. The reference adsorption data used for the α_s analysis of the silica and carbon samples correspond to a macroporous silica sample[24] and a nongraphitized carbon black sample,[25] respectively. The PSD was calculated by means of the Kruk−Jaroniec−Sayari method[26] applied to the adsorption branch. The micropore volume of the carbon samples was estimated from the CO_2 adsorption isotherm measured on a gravimetric system (CI Electronics) at 20 °C. The Dubinin−Radusckevitch method was used to analyze the CO_2 adsorption data.[27] The structure of the silica and carbon materials was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The silica xerogels obtained from TEOS and sodium silicate were identified as S−T-x (x = HCl/TEOS molar ratio) and S−S, respectively, and the corresponding carbons were denoted as C−T-x and C−S.

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[14] Taguchi, A.; Smatt, J.; Linden, M. *Adv. Mater.* **2003**, *15*, 1209.
[15] Kleitz, F.; Choi, S.; Ryoo, R. *Chem. Commun.* **2003**, 2136.
[16] Fan, J.; Yu, C.; Gao, F.; Lei, J.; Luo, Q.; Tu, B.; Zhao, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 3146.
[17] Knox, J. H.; Gilbert, M. T. Preparation of porous carbons. U.S. Patent 4,263,268, April 21, 1981.
[18] Kamegawa, K.; Yoshida, H. *Carbon* **1997**, *35*, 631.
[19] Kawashima, D.; Aihara, T.; Kobayashi, Y.; Kyotani, T.; Tomita, A. *Chem. Mater.* **2003**, *12*, 3397.
[20] Han, S.; Kim, M.; Hyeon, T. *Carbon* **2003**, *41*, 1525.
[21] Iler, R. K. *The Chemistry of Silica*; John Wiley Sons: New York, 1979.
[22] Brinker, C. J. *J. Non-Cryst. Solids* **1988**, *100*, 31.
[23] Fuertes, A. B.; Nevskaia, D. *Microporous Mesoporous Mater.* **2003**, *62*, 177.
[24] Jaroniec, M.; Kruk, M.; Oliver, J. P. *Langmuir* **1999**, *15*, 5410.
[25] Kruk, M.; Jaroniec, M.; Gadkaree, K. P. *J. Colloid Interface Sci.* **1997**, *192*, 250.
[26] Kruk, M.; Jaroniec, M.; Sayari, A. *Langmuir* **1997**, *13*, 6267.
[27] Roquerol, F.; Roquerol, J.; Sing, K. *Adsorption by Powders and Porous Solids*; Academic Press: London, 1999; Chapter 8.

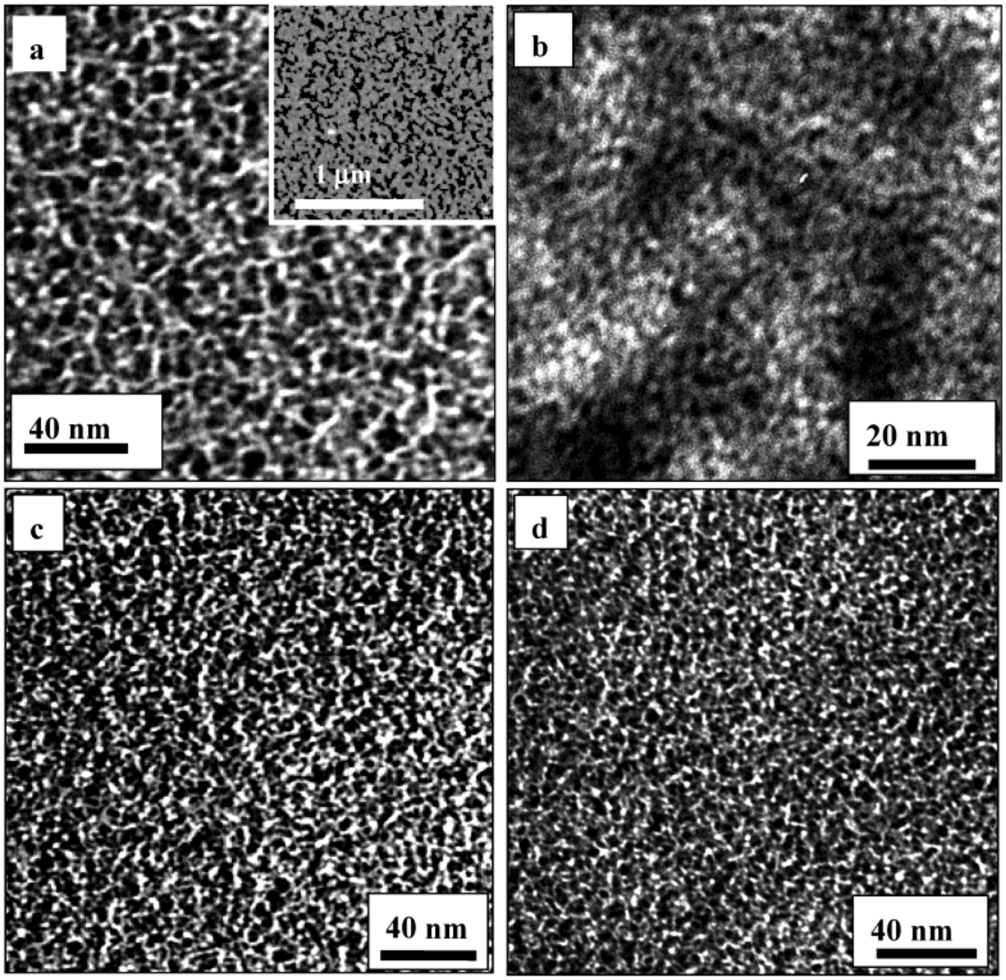

Figure 1. TEM images of silica xerogels (a, S−T-6; b, S−S) and templated carbons (c, C−T-6; d, C−S). SEM microphotograph of S−T-6 is given in Figure 1a (inset).

3. Results and Discussion

3.1. Structural Characteristics of Silica Xerogel Templates. SEM inspection of the silica xerogel surface (Figure 1a, inset) reveals the existence of a very open structure made up of interconnected clusters with the macropores corresponding to the inter-cluster voids. This structure is typical of silica xerogels prepared by a two-step process.[28] The porosity in the calcined xerogels is hierarchically arranged on two length scales, i.e., macroporosity between the clusters and mesoporosity within the clusters. The internal structure of the clusters is illustrated by means of the TEM images shown in Figure 1a for the S−T-6 sample obtained from TEOS and Figure 1b for the S−S sample prepared by using sodium silicate. They reveal a highly disordered 3-D interconnected porous network. The clusters are the result of the aggregation of very small primary particles (<10 nm) and the porosity can be ascribed to the spaces between these particles.[21,29]

The porous structure of the silica xerogels is significantly influenced by the HCl/Si molar ratio used during their synthesis. Thus, increasing the HCl/Si molar ratio provokes significant modifications in the porosity of the silica samples. This is evidenced from the nitrogen sorption isotherms (Figure 2a) and PSDs (Figure 2b) corresponding to the silica xerogels prepared using TEOS as the silica source. The silica samples obtained at low HCl/Si molar ratios (i.e., S−T-0.04 and S−T-0.12) exhibit nitrogen sorption isotherms of type I (Figure 2a), which are characteristic of materials with narrow porosity. The PSDs of these samples (Figure 2b) prove that this porosity is made up of pores with sizes of around 2 nm, i.e., at the limit of the micropore−mesopore ranges. For higher HCl/Si molar ratios (i.e., ≥0.5), the nitrogen sorption isotherms of the silica xerogels are type IV and exhibit hysteresis loops associated with capillary condensation on the mesopores.[30] The PSDs shown in Figure 2b clearly indicate that the pores in silica xerogels shift to larger sizes, from 2.2 to 10.1 nm (Table 1), as the HCl/Si ratio increases from 0.04 to 8. This provides us with a tool for tuning the structural characteristics of silica xerogels. This tool will be very useful when these materials are employed as templates to prepare porous carbons. Bearing in mind that the structural characteristics of templates are transferred to the synthesized carbons, it is reasonable to assume that by selecting the appropriate template, the porosity of carbons can be tailored.

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[28] Fidalgo, A.; Rosa, M. E.; Ilharco, L. M. *Chem. Mater.* **2003**, *15*, 2186.

[29] Brinker, C. J.; Scherer, G. W. *Sol−Gel Science*; Academic Press: New York, 1990.

[30] Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, Academic Press: London, 1982; Chapter 3.

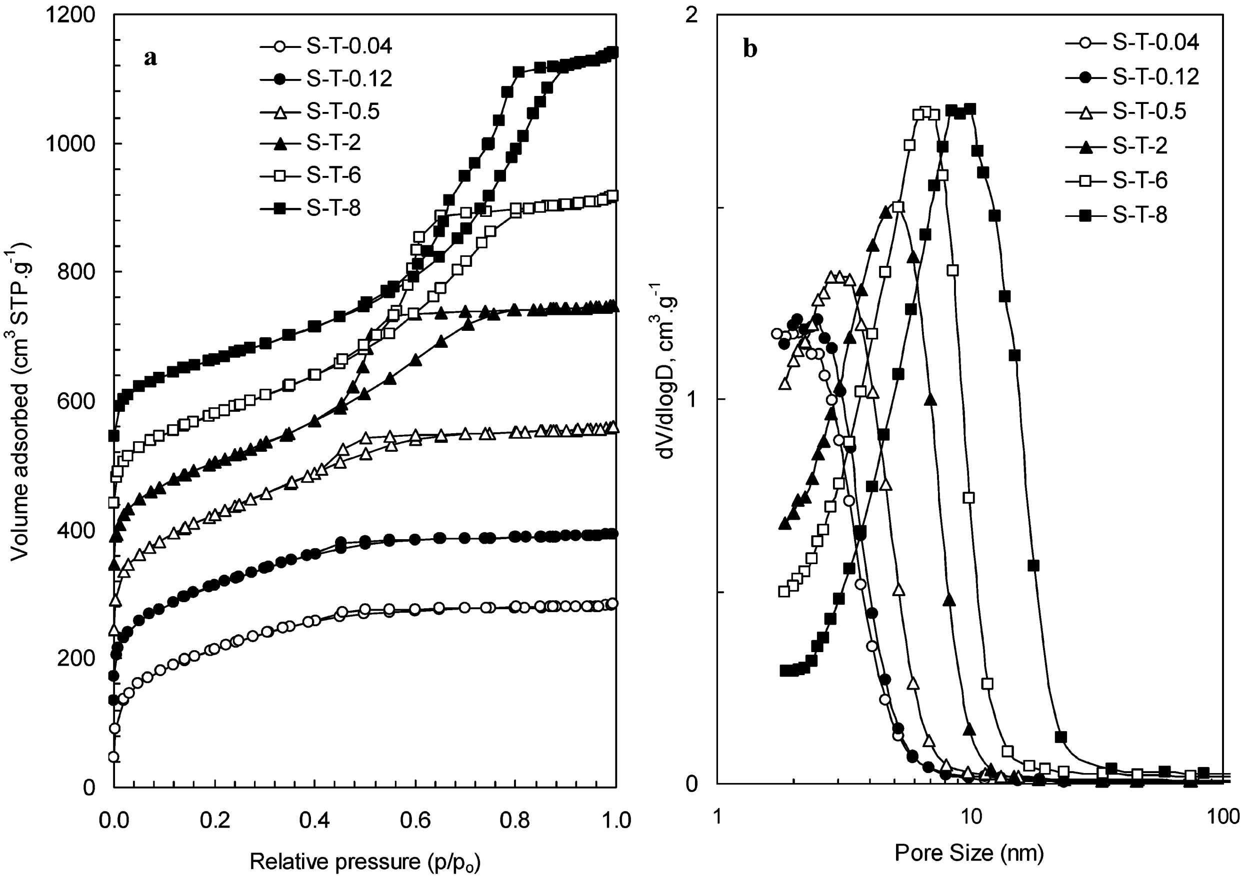

Figure 2. Nitrogen sorption isotherms (a) and pore size distributions (b) of silica xerogels prepared at different HCl/TEOS molar ratios. In Figure 2a, isotherms of S−T-0.12, S−T-0.5, S−T-2, S−T-6, and S−T-8 are vertically shifted for 100, 200, 300, 400, and 500 cm^3·g^{-1} respectively, for clarity.

Table 1. Structural Characteristics of Silica Xerogels

			α_s-plot results			
code	S_{BET} (m^2·g^{-1})	V_p (cm^3·g^{-1})[a]	V_{mesop} (cm^3·g^{-1})[b]	S_{ext} (m^2·g^{-1})	δ_{KJS} (nm)[c]	fwhm (nm)[d]
S−T-0.04	770	0.44	0.41	14	2.2	-
S−T-0.12	770	0.45	0.44	12	2.4	-
S−T-0.5	810	0.56	0.53	17	2.8	-
S−T-2	740	0.69	0.67	14	5.2	5.3
S−T-6	660	0.80	0.76	22	6.7	6.3
S−T-8	600	0.99	0.92	40	10.1	11.9
S−S	510	0.80	0.77	17	8.6	7.4

[a] Total pore volume from N_2 adsorption at p/p$_o$= 0.99. [b] Volume of primary mesopores. [c] Maximum of PSD. [d] Full width at half-maximum (fwhm).

Table 1 summarizes the structural characteristics of the silica xerogels. The BET surface area of the samples obtained at HCl/Si ≤ 2 is around 750−800 m^2·g^{-1}, but for higher ratios a drop in the specific surface area is observed. The total pore volume increases uniformly with the HCl/Si ratios from 0.44 cm^3·g^{-1} (S−T-0.04) to 0.99 cm^3·g^{-1} (S−T-8). From the α-plot analysis of the N_2 isotherms, it was found that these materials have a low external surface area and no appreciable microporosity, with the pore volume being mainly ascribed to the primary mesopores (V_{mesop} in Table 1). Therefore, the internal structure of the clusters that make up these materials can be viewed as a 3-D disordered mesoporous network connected on three dimensions and nonporous primary silica particles.

From an economical point of view, it makes sense to use a cheap silica source rather than expensive organosilica compounds (i.e., TEOS). Sodium silicate is a very cheap silica source and has been widely used in the synthesis of MSM.[31−33] We observed that the silica xerogels synthesized with sodium silicate have structural properties comparable to those obtained by using TEOS. This is evidenced from Figure 3 where the nitrogen sorption isotherms and PSDs (inset) of the silica xerogels derived from sodium silicate (denoted as S−S) are compared to those obtained by using TEOS (S−T-6). The S−T-6 sample was selected for comparison because the composition of the synthesis mixture (i.e., Si/HCl/H_2O) used in its preparation is similar to that employed for S−S. The isotherms of both samples are type IV with a condensation step at p/p$_o$~0.6−0.8, which clearly indicates a mesoporous structure. This is confirmed by the PSD displayed in Figure 3 (inset). The pore sizes are slightly larger for S−S (maximum of PSD, δ_{KJS}= 8.6 nm) with respect to S−T-6 (δ_{KJS}= 6.7 nm). Both materials have relatively broad PSD with fwhm (full width at half-maximum) values in the 6−7 nm range (see Table 1). The structural properties of S−S and S−T-6 are given in Table 1. Both materials show similar pore volumes (0.8 cm^3·g^{-1}), with the BET surface area being larger for S−T-6 silica (660 m^2·g^{-1}) than for S−S (510 m^2·g^{-1}).

It should be noted that the structural characteristics (i.e., pore volume, pore size distribution, and specific

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(31) Sierra, I.; Lopez, B.; Guth, J. *Adv. Mater.* **1999**, *11*, 307.
(32) Kim, J. M.; Stucky, G. D. *Chem. Commun.* **2000**, 1159.
(33) Boissiere, C.; Larbot, A.; Prouzet, E. *Chem. Mater.* **2000**, *12*, 1937.

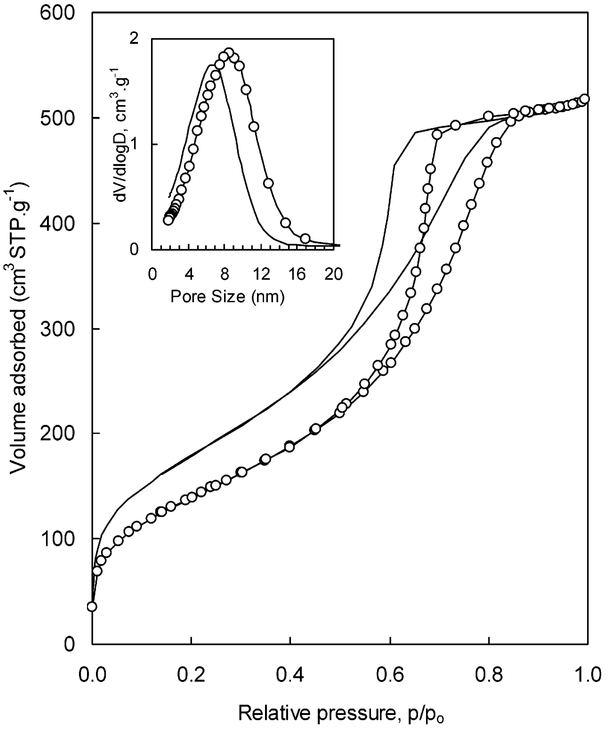

Figure 3. Nitrogen sorption isotherms and pore size distributions (inset) of silica xerogels prepared by using TEOS (S−T-6, −−) and sodium silicate (S−S, −○−) as silica precursors.

surface area) of the silica xerogels synthesized in this work, especially of those obtained at HCl/Si ≥ 0.5, are comparable to those of the MSM usually employed as templates to prepare mesoporous carbons (i.e., MCM-48, SBA-15, HMS, MSU, etc).[4−6] This suggests that silica xerogels with these characteristics may serve as suitable templates for synthesizing mesoporous carbons.

3.2. Templated Carbons. The silica xerogels were used as templates to make mesoporous carbons. The structure of the templated carbons obtained after the dissolution of the silica framework is illustrated in the TEM images shown in Figure 1c for the C−T-6 sample and in Figure 1d for the C−S carbon derived from sodium silicate−silica xerogel. It can be observed that both samples exhibit a highly disordered pore structure, as might be expected for an inverse replica of the silica xerogel frameworks displayed in Figure 1a and b. Clearer evidence of the porous structure of the mesoporous carbons is obtained from the N_2 sorption isotherms (Figure 4a) and the PSDs (Figure 4b) corresponding to the carbons derived from the silica xerogels formed at different HCl/Si molar ratios. These figures reveal that templated carbons have a structural porosity (i.e., derived from the removal of the silica framework) made up of mesopores. They exhibit narrow PSD, with the fwhm values being <2.5 nm and in most cases <1.5 nm (see Table 2). The structural characteristics of the templated carbons obtained from the silica xerogels derived from TEOS are presented in Table 2. They have very large BET surface areas of up to 2200 m^2•g^{-1} (C−T-0.12) and large pore volumes of up to 2.07 cm^3•g^{-1} (C−T-6). The porosity in both carbons is made up almost exclusively of structural mesopores, as can be deduced from the low amount adsorbed beyond the condensation step. The pore volumes assigned to the structural mesopores were calculated from the α-plot analysis and they are indicated in Table 2. The micropore volume (<1 nm) for the carbon samples was estimated by CO_2

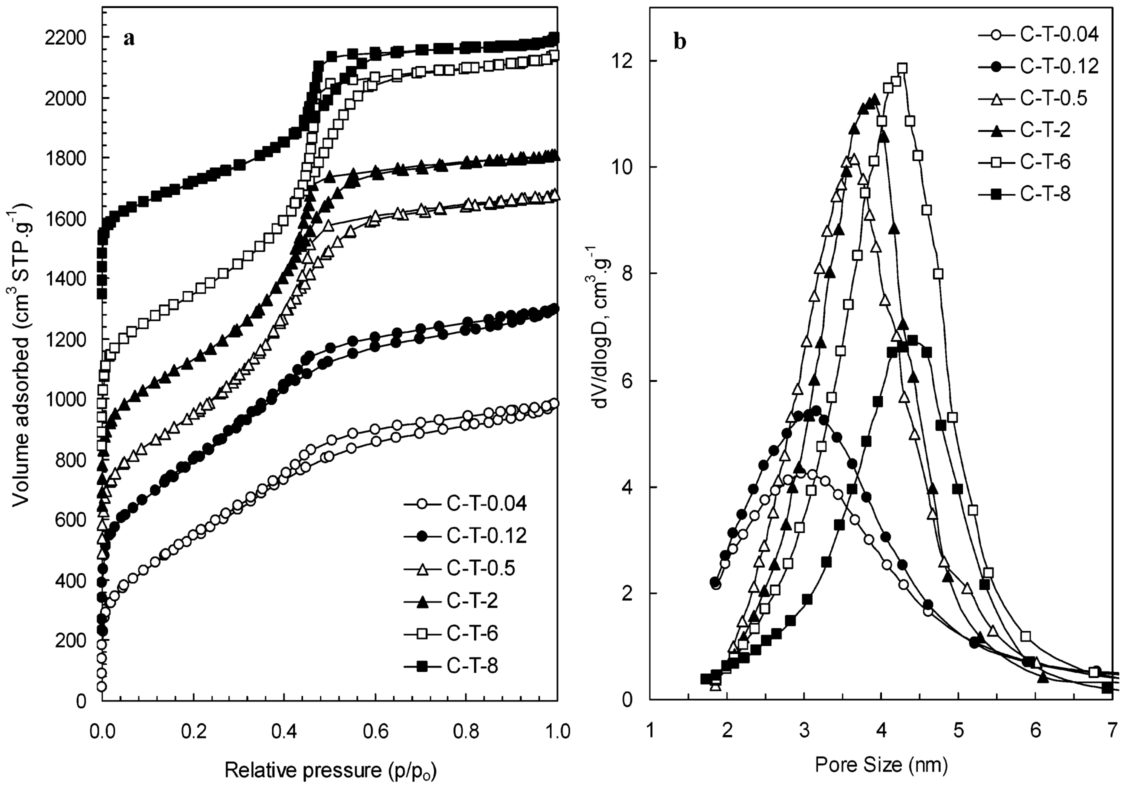

Figure 4. Nitrogen sorption isotherms (a) and pore size distributions (b) of carbons fabricated by using silica xerogel templates prepared at different HCl/TEOS molar ratios. In Figure 4a, isotherms of C−T-0.12, C−T-0.5, C−T-2, C−T-6, and C−T-8 are vertically shifted for 200, 400, 600, 800, and 1300 cm^3.g^{-1} respectively, for clarity.

Table 2. Structural Characteristics of Templated Carbons

code	S_{BET} ($m^2 \cdot g^{-1}$)	V_p ($cm^3 \cdot g^{-1}$)[a]	α_s-plot results V_{mesop} ($cm^3 \cdot g^{-1}$)[b]	 S_{ext} ($m^2 \cdot g^{-1}$)	δ_{KJ} (nm)[c]	fwhm (nm)[d]
C−T-0.04	1980	1.53	1.27	74	3.0	2.5
C−T-0.12	2190	1.70	1.43	105	3.2	2.2
C−T-0.5	2040	1.98	1.90	36	3.7	1.6
C−T-2	1940	1.88	1.82	25	3.9	1.4
C−T-6	2000	2.07	1.94	23	4.3	1.5
C−T-8	1480	1.39	1.29	16	4.4	1.6
C−S	1610	1.74	1.67	27	5.0	3.0
C−S-b[e]	1700	2.10	1.45 (0.57)[f]	27	4.9 (24)[g]	2.1

[a] Total pore volume from N_2 adsorption at p/p_o= 0.99. [b] Volume of structural mesopores (i.e., derived from the silica skeletal removal). [c] Maximum of PSD. [d] Full width at half-maximum (fwhm) of structural mesopores. [e] Bimodal carbon from silica xerogel S−S. [f] The pore volume for complementary mesopores is given in parentheses. [g] The size of larger mesopores is given in parentheses.

adsorption at 20 °C and for all samples was in the range of 0.25−0.30 cm^3−g^{-1}, which are typical values for glassy carbons.[34] It can be assigned to the intrinsic porosity of the carbon framework rather to the connection between adjacent mesopores. The PSDs displayed in Figure 4b show that the pores shift to larger sizes for silica templates obtained at higher HCl/Si molar ratios. Thus, the maximum in the PSD (δ_{KJS}) varies from 3.0 nm (HCl/Si = 0.04) to 4.4 nm (HCl/Si = 8) (Table 2). This variation occurs in parallel with the change observed in the pore size of the corresponding silica xerogel templates (see Figure 3b and Table 1). The modification of the pore size of the templated carbons confirms the previous hypothesis and shows that the porosity of carbons derived from silica xerogel templates can be tuned to within certain limits.

Table 2 contains the main physical properties of the C−S carbon obtained from a silica xerogel prepared by using sodium silicate (S−S). This carbon has structural properties which are close to those measured for carbons derived from TEOS−silica xerogel templates (i.e., S−T-6). The most remarkable differences are a somewhat lower specific surface area (1610 $m^2 \cdot g^{-1}$ for C−S vs 2000 $m^2 \cdot g^{-1}$ for C−T-6), a larger mesopore size (δ_{KJS} = 5.0 nm for C−S vs 4.3 nm for C−T-6), and a wider PSD (fwhm = 3.0 nm for C−S vs 1.5 nm for C−T-6). Figure 5 shows the nitrogen sorption isotherm and PSD (inset) for the C−S carbon. As with the carbons obtained from TEOS−silica xerogels, the porosity in the C−S sample corresponds almost exclusively to the structural mesopores.

Table 3 gives the structural properties of several representative mesoporous carbons fabricated from MSM templates as reported by different authors. A comparison of these values with those corresponding to the carbons reported here (Table 2) shows that mesoporous carbons obtained from silica xerogel templates have comparable or even better (in terms of surface area and pore volume values) porous characteristics than the materials derived from MSMs.

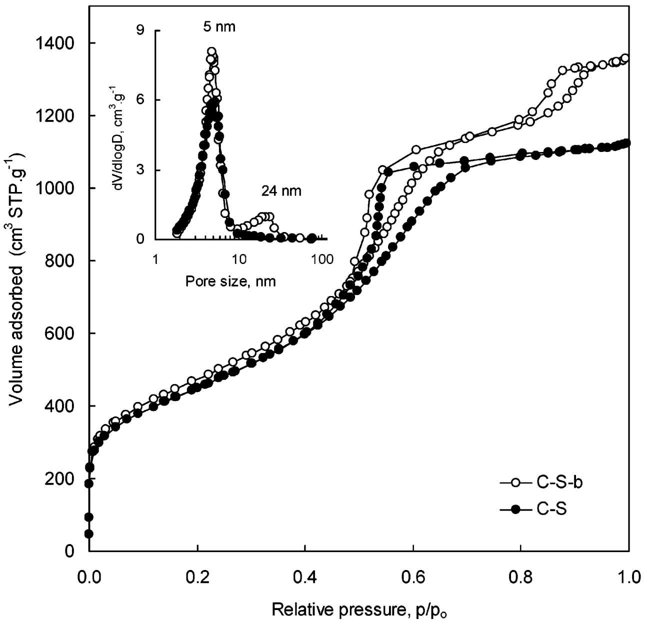

Figure 5. Nitrogen sorption isotherms and pore size distributions (insets) of unimodal (C−S) and bimodal (C−S-b) porous carbons prepared by templating silica xerogels obtained by using sodium silicate.

Table 3. Structural Characteristics of Several Representative Mesoporous Carbons Fabricated by Templating MSMs

carbon code	MSM template	S_{BET} ($m^2 \cdot g^{-1}$)	V_p ($cm^3 \cdot g^{-1}$)	δ_{KJS} (nm)	fwhm (nm)	ref
CMK-1	MCM-48	1400	1.3	3.5	~1.5	7
CMK-3	SBA-15	1520	1.3	4.5	~1.5	8
SNU-2	HMS	1060	0.7	2.0	>1.5	10
C-MSU−H	MSU−H	1230	1.3	3.9	~1.6	9

3.3. Bimodal Templated Carbons. Mesoporous carbons with two pore systems are of great practical interest because enhanced accessibility to active sites can be expected compared that of to unimodal carbons. The synthesis of bimodal carbons using MSM templates has recently been reported by our group[23,35] and other authors.[36] In this work we have set out to show that mesoporous bimodal carbons can be easily obtained from silica xerogel templates. Thus, in addition to the synthesis of unimodal carbons such as those shown in Figure 4, it is possible to prepare mesoporous carbons with two (bimodal) pore systems by controlling the amount of carbon precursor allowed to infiltrate into the porosity of the silica xerogels. Figure 5 shows the N_2 sorption isotherm and the PSD (inset) of a carbon (denoted as C−S-b) with two pore systems. This sample was obtained by templating a silica xerogel synthesized with sodium silicate. As described in the Experimental Section, to obtain the bimodal carbon the silica porosity was not completely filled with carbon precursor as in the case of C−S. The C−S-b carbon contains, in addition to structural mesopores, a complementary porosity composed of large mesopores. The structural pores of C−S-b are centered at around 4.9 nm (Figure 5, inset), fwhm being 2.1 nm (Table 2). When comparing the PSDs for the structural mesopores obtained for C−S and C−S-b (Figure 5, inset), it can be seen that they are very similar. The complementary porosity of C−S-b is made up of mesopores with sizes in the 10−30 nm range, whose maximum size is centered around 24 nm (Figure

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(34) Fitzer, E.; Schaefer, W.; Yamada, S. *Carbon* **1969**, *7*, 643.

(35) Fuertes, A. B.; Nevskaia, D. *J. Mater. Chem.* **2003**, *13*, 1843.

(36) Lee, J.; Kim, J.; Hyeon, T. *Chem. Commun.* **2003**, 1138.

5, inset). These mesopores are originated by coalescence of the nonfilled silica pores with those resulting from the removal of the silica walls.[23,35] The size of these large pores depends on the number of adjacent nonfilled silica pores involved. This fact explains why these pores exhibit a relatively wide PSD, in the 10−30 nm range. The size of these complementary mesopores increases concomitantly with that of the structural mesopores as has been recently evidenced for mesoporous carbons fabricated by templating MSU-1 silica.[37] The bimodal C−S-b carbon has a large BET surface area (1700 $m^2 \cdot g^{-1}$) and a very large pore volume of 2.10 $cm^3.g^{-1}$ (Table 2). From the α-plot analysis of the N_2 isotherm the pore volume of the structural mesopores was estimated to be 1.45 $cm^3 \cdot g^{-1}$, whereas that of the complementary mesopores was 0.57 $cm^3 \cdot g^{-1}$ (Table 2).

4. Conclusions

In summary, mesoporous carbons with large surface areas and pore volumes have been successfully synthesized by using silica xerogels as templates. The synthesized carbons have structural characteristics (i.e., pore size, pore volume, surface area, and PSDs), which are comparable to those of templated carbons synthesized from MSM that were obtained using expensive surfactants as structure-directing agents. The replacement of MSM by silica xerogels will make it possible to produce mesoporous carbons for practical applications at low cost. This claim is supported by the fact that silica xerogels can be prepared from inexpensive sodium silicate. Porous carbons with tunable pore sizes can be obtained by modifying the HCl/Si molar ratio used in the synthesis of the silica xerogel template. In addition, it has been shown that mesoporous carbons with unimodal or bimodal pore size distributions can be obtained from the same silica xerogel template by varying the amount of carbon precursor allowed to infiltrate into the silica porosity.

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(37) Alvarez, S.; Fuertes, A. B. *Carbon* **2004**, *42*, 437.