



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

MICROPOROUS AND
MESOPOROUS MATERIALS

Microporous and Mesoporous Materials 79 (2005) 269–273

www.elsevier.com/locate/micromeso

Preparation of ordered carbon/silica hybrid mesoporous materials with specific pore size expansion

Xianbin Liu, Fuxiang Chang, Lei Xu, Yue Yang, Peng Tian, Lihong Qu, Zhongmin Liu*

Applied Catalysis Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

Received 22 September 2004; received in revised form 12 November 2004; accepted 15 November 2004

Available online 7 January 2005

Abstract

A hybrid carbon/silica mesoporous material with unexpected pore size expansion was prepared using directly carbonized surfactant method. At the given conditions of treatment, the resultant product had expanded d -spacings ($d = 19.6$ nm) and a pore diameter of up to 8.8 nm could be achieved, suggesting a pore diameter expansion of 54% compared with the conventionally calcined mesoporous silica in air. PXRD, nitrogen adsorption measurement and TEM investigations show that the mesoporous structure was preserved perfectly after the carbonization treatment. The distinct advantage over conventional expanded pore techniques is that the treatment did not affect the hexagonal ordering of the parent silica.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Hybrid carbon/silica material; Expanding pore size; Mesopore; Template; Mesoporosity

1. Introduction

Because mesoporous materials possess uniformly sized mesopores (1.5–10.0 nm), high surface areas and large pore volumes, they have extensive potential applications as catalysts, supports and advanced materials. In particular, mesoporous materials with controllable pore sizes are very important for industrial catalytic applications for tailoring substrate selectivity and reactivity. The precise tuning of pore sizes is among the many desirable properties that have made such materials the focus of great interest.

At present, many methods have been reported for controlling the periodic unit cell and pore size of mesoporous materials. Firstly, the researchers in Mobil Corporation [1] found that the pore diameter of MCM-41 molecular sieves was increased from 1.8 nm to 3.8 nm

by increasing the length of alkyl groups ($n = 8, 9, 10, 12, 14, 16$). Other researchers [3–6] have reported similar results too. Secondly, the use of organic swelling agents is an effective way to control pore sizes of mesoporous materials. Beck et al. [2] reported their pioneering work that the pore size of mesoporous MCM-41 materials could be tailored by the addition of 1,3,5-trimethylbenzene as a swelling agent. Subsequently, alkanes [7,8], triisopropylbenzene [9] and amines [10] were used as swelling agents. Although the introduction of these swelling agents had been shown to lead to pore expansion by up to 30%, all of information obtained showed that the long-range order of the mesoporous structure was gradually lost. Thirdly, the unit cell of the mesoporous structure was substantially enlarged by the post synthesis hydrothermal treatment under the conditions of appropriate treatment parameters in water, or mother synthesis liquors or amine suspensions [11–14]. Huo et al. [11] found the unit cell of MCM-41 increased initially with time and then reached a maximum with a lattice expansion of approximately 25–35%. When a

* Corresponding author. Tel.: +86 411 84685510; fax: +86 411 84691570.

E-mail address: zml@dicp.ac.cn (Z. Liu).

certain upper limit of the pore size was reached, a further hydrothermal treatment led to a decrease of product quality. As a result, the hydrothermal restructuring method was a restricted way to synthesise mesoporous materials with a tailored pore size. Lastly, Hanrahan et al. [15] recently reported a novel method of tailoring the pore size of mesoporous silica using supercritical carbon dioxide. Pore diameters can be up to 10 nm under reasonably adjusted operation pressures, and the pore size can be expanded by 54%. The advantage of the method was that the treatment did not affect the hexagonal ordering of the host.

In this paper, we have prepared hybrid carbon/silica materials with pore size expansion using direct carbonization of the structure-directing agent. The ordering of the hybrid product is retained perfectly as that of the parent SBA-15. The distinct advantages over the traditional pore-expanding technique are the absence of pore ordering decrease and complicated procedures.

2. Experimental

2.1. Preparation of samples

Silica SBA-15 was synthesized according to the procedure reported by Zhao et al. [16]. The triblock copolymers in the process of preparing SBA-15, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, were directly used as carbon precursors. The as-synthesized SBA-15 was first impregnated with concentrated sulfuric acid for 12 h and then the obtained brown sample was put into a tubular oven. The sample was held at 523 K for 2 h under N_2 flow (purity 99.999%), and then heated at 823 K for 4 h to carbonize the structure-directing agent completely. In the process of carbonization, the volume of the sample was expanded to some extent. After cooling down to ambient temperature under nitrogen flow, a black product was obtained and designated as S15N. In comparison, S15A was prepared by calcining the as-synthesized SBA-15 in air to eliminate the surfactant (at 823 K for 4 h). A portion of S15N was calcined in air to eliminate the carbon, and the sample was designated as S15NA.

2.2. Characterization

Powder X-ray diffraction patterns were recorded on a Philips X'Pert Pro diffractometer using $\text{CuK}\alpha$ radiation of wavelength $\lambda = 0.15406$ nm (40 kV, 40 mA). Diffraction data for all samples were recorded between 0.2° and 6.0° (2θ). Infrared spectra of samples were recorded on a Bruker EQUINOX55 FTIR spectrometer. Powder samples were dispersed in KBr pellets for IR analysis. The spectra were acquired in the range between 400 and 4000 cm^{-1} at 4 cm^{-1} resolution and 32 scans. Nitrogen adsorption isotherms were measured at 77 K on a

Micromeritics ASAP 2010 volumetric adsorption analyzer. Before the measurements, all powder samples were outgassed under vacuum for 6 h at 523 K in the degassing port of the adsorption apparatus. The BET specific surface area [17] was calculated using data in a relative pressure range from 0.05 to 0.25 by the Brunauer–Emmett–Teller (BET) method. The total pore volume [17] was determined from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution was calculated from desorption branches of nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) model [17]. Transmission electron microscopy (TEM) images were taken with a JEOL JEM2000EX electron microscope with an accelerating voltage of 100 kV. Weight change curves were recorded under flowing oxygen on a Perkin–Elmer TGA high-resolution thermogravimetric analyzer.

3. Results and discussion

Fig. 1 shows the Fourier transform infrared (FTIR) spectra of as-synthesized SBA-15, S15A and S15N. The presence of an adsorption peak for the C–H bonds ($2900\text{--}3000\text{ cm}^{-1}$) in the spectrum of as-synthesized SBA-15 indicates the surfactant used as the template exists in the sample. But the C–H bonds are no longer observed in samples S15A and S15N, indicating the surfactant in the as-synthesized SBA-15 silica is completely removed or converted into other matter such as carbon. In general, the bands at 1090 cm^{-1} and 800 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of the Si–O–Si framework, respectively. The bands at 1090 cm^{-1} and 800 cm^{-1} for S15N samples become narrower and weaker than those of S15A. The phenomenon can be observed in mesoporous

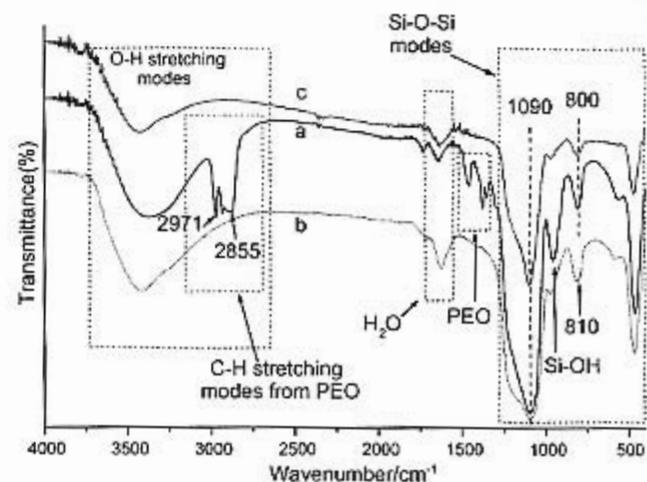


Fig. 1. The FTIR spectra of the samples: (a) as-synthesized SBA-15, (b) S15A and (c) S15N.

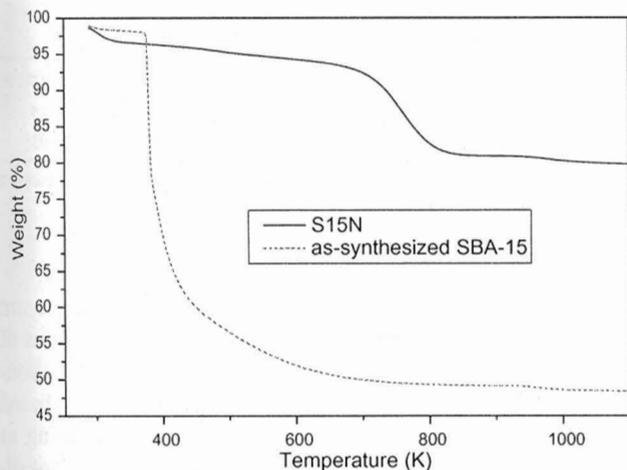


Fig. 2. Weight change curves under air atmosphere for as-synthesized SBA-15 and S15N.

silicas by chemically modified organic ligands or supported metal particles. The possible reason is that the coating materials such as organosilanes or metal precursors change the infrared activity of the matrix [18,19]. This result indicates that the carbon in S15N possibly existed in the form of a coating of the mesopores.

From the weight losses between 373 and 1173 K in the TG profiles of the samples (Fig. 2), the as-synthesized SBA-15 exhibited about 39 wt.% weight loss at temperatures between 373 and 473 K. This weight loss can be attributed to the decomposition and desorption of structure-directing agent. The main weight loss with 15 wt.% for S15N sample centered at 800 K may be related to the oxidation of carbon resulted from pyrolysis of the triblock copolymers. This is, about 39 wt.% surfactant and 15 wt.% carbon existed in as-synthesized SBA-15 and S15N respectively. However, if the as-synthesized SBA-15 was not impregnated with concentrated sulfuric acid and calcined directly in N_2 , only 8 wt.% carbon in the sample was observed. These results indicate that it is very crucial to pretreat the as-synthesized mesoporous silica with concentrated sulfuric acid for obtaining the higher carbon amount in the resulting hybrid material.

The XRD patterns of the three samples are depicted in Fig. 3. The as-synthesized SBA-15 shows three clear diffraction peaks with $d = 9.88$, 5.85 and 5.09 nm (Fig. 3a). These peaks can be indexed to (100), (110) and (200) reflections associated with P6mm hexagonal symmetry. The presence of three diffraction peaks indicates the as-synthesized SBA-15 has a high degree of hexagonal mesoscopic organization. The XRD patterns of S15A shows that the P6mm morphology is preserved, although the first peak appears at slightly larger 2θ value with $d(100) = 9.5$ nm due to the condensation of silanol groups of silica wall [16]. Surprisingly, the diffraction peaks of S15N shift to the lower 2θ value. The S15N

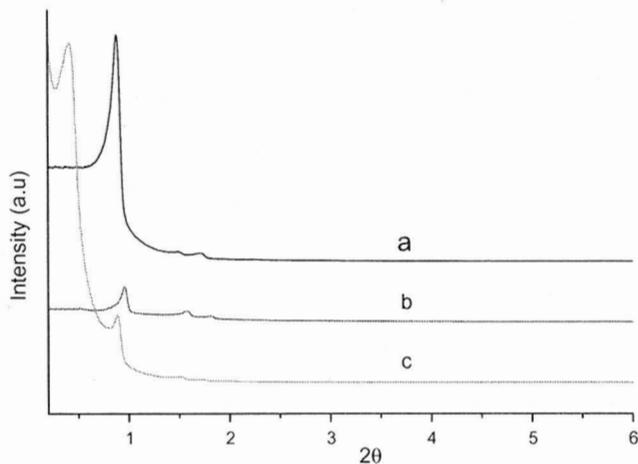


Fig. 3. X-ray diffraction patterns of the three samples: (a) as-synthesized SBA-15, (b) S15A and (c) S15N.

sample shows four diffraction peaks with lattice spacings of $d = 19.6$, 9.83, 5.81 and 5.07 nm. The XRD patterns of S15N can be indexed as the P6mm symmetry. Upon carbonization treatment in nitrogen flow, the main diffraction peak of S15N shows expanded d -spacings. In addition, the above-mentioned observation suggests that the framework ordering of the mesopore channels in hybrid carbon/silica material is unchanged.

Fig. 4 presents the nitrogen adsorption–desorption isotherms of S15A and S15N and structural properties of composites are shown in Table 1. Both of them were type IV and their hysteresis loop showed the characteristics of ordered mesoporous materials with capillary condensation phenomenon [17]. Interestingly, this observation clearly reveals that steep capillary condensation step in the isotherm of S15N shifted to a higher relative pressure compared with that of the S15A sample. The relative pressure at which the capillary condensation occurs increases significantly from 0.6 to 0.7,

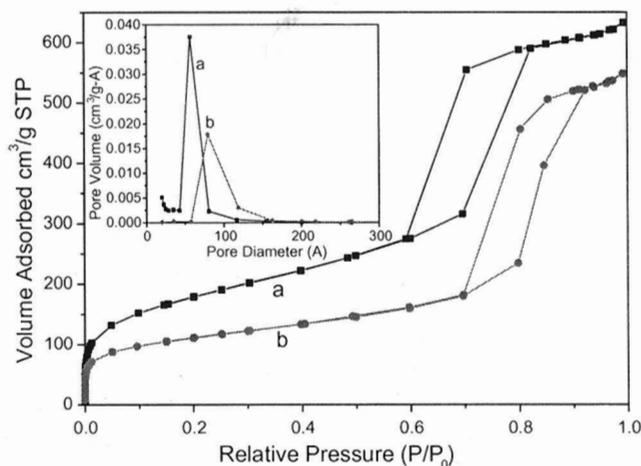


Fig. 4. Nitrogen adsorption–desorption isotherms and pore-size distribution curves for two samples: (a) S15A and (b) S15N.

Table 1
Structural properties of composites^a

Sample	2θ (100)	d (nm)	a (nm)	S_{BET} (m ² /g)	V_p (cm ³ /g)	P_{PSD} (nm)	b (nm)
S15A	0.97	9.15	10.57	639	1.0	5.7	4.87
S15N	0.45	19.6	22.63	388	0.86	8.7	13.93

^a 2θ , main (100) peak position; d , XRD (100) interplanar spacing; $a = 2d/1.732$; S_{BET} , the BET specific surface area; V_p , primary mesopore volume; P_{PSD} , the pore diameter calculated using the BJH method; b , the thickness of wall, $b = a - P_{\text{PSD}}$.

indicating that the value of the pore diameter increases markedly with the treatment conditions since the P/P_0 of the inflection point is related to the pore diameter. The increase of pore diameter in S15CN agrees well with the results of XRD. The pore size distribution is calculated from the desorption branch by the BJH method. The maximal pore diameters for S15A and S15N are 5.7 and 8.8 nm, respectively (see Fig. 2 inset). Upon carbonization treatment, the shape of the hysteresis loop of S15N is identical to that of S15A. This indicates the surfactant-derived carbon is present as a coating on the pore walls rather than in the form of particles that would block the pore system of SBA-15.

Ordered channel-having arrays of parallel lines in as-synthesized SBA-15 and S15N were observed clearly from TEM images along the direction of the pore arrangement (see Fig. 5). Any significant buildup of external carbon phases and associated pore blockage in S15N could be excluded, which confirmed that carbonization treatment did not destroy the mesostructural regularity of the material and the resultant product kept the excellent long ordering of the pores. The centers of adjacent black lines were ≈ 10 nm, in good agreement with the value (8.8 nm) determined from the nitrogen adsorption measurement. The surface-to-surface distance (wall thickness) was 10 nm. That the S15N sample possessed the thicker wall (shown in Table 1) was the direct evidence of the presence of a carbon coating in the channels of the mesoporous materials.

The interesting question was “why was the pore diameter expanded in the hybrid carbon/silica mesoporous material obtained by carbonizing the structure-

directing agent?” Studies of the mechanisms of pore size expansion are in progress. The possible explanations of these phenomena are present as follows. The lattice contraction of the as-synthesized mesoporous silica-based materials occurred under the conditions of heating at higher temperatures in air due to the condensation of silanol groups [20,21]. If the as-synthesized SBA-15 sample was firstly treated with concentrated sulfuric acid, surfactants in the mesopores would be dehydrated and carbonized to partially cross linked materials, as evidenced by the brown color of the sample. That is, a small amount of carbon-like species would be produced and formed the supporting scaffold of carbon in the mesopores of material after this step.

In course of further high temperature carbonization under N_2 , the existing carbon scaffold possibly prevented the contraction of the silica wall. As a result, the pore diameter of the hybrid material using the novel method was larger than the sample calcined directly in air. If the S15N was calcined in air at 823 K for 4 h again, the main diffraction peak of the final product had the same d -spacing as that of the S15A sample (the XRD pattern of S15NA is identical to that of S15A in Fig. 3b). These realities suggest that the presence of carbon has a significant influence on the pore size expansion.

However, questions remain about the form of carbon and the extent of wall condensation. Compared with the carbon/SBA-15 composites in the process of prepared CMK-5 carbon, the physical properties of S15N were different. Because the surfactant in the as-synthesized SBA-15 must first be removed by calcination or solvent

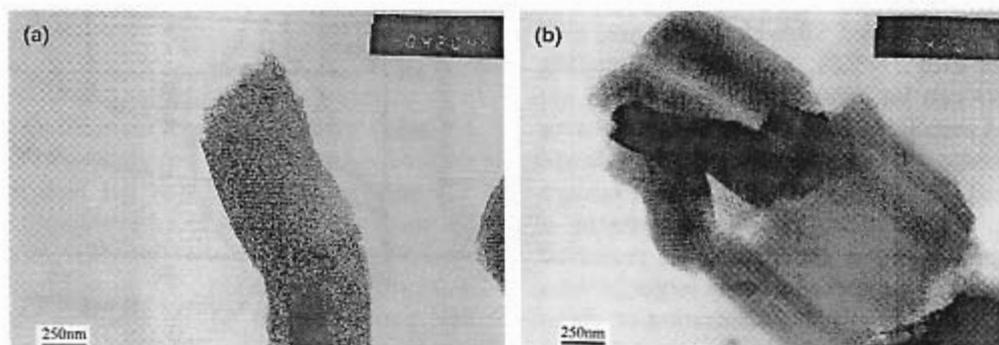


Fig. 5. TEM images of the samples along the direction of pore arrangement: (a) S15N and (b) the as-synthesized SBA-15.

extraction this operation inevitably led to a decrease of pore diameter [7]. Subsequently the introduction of carbon precursors formed the coating in the inner mesopore walls, and the carbon/SBA-15 composites were achieved after carbonization, this process would further decrease the pore diameter of carbon/SBA-15 composites [22]. The method used in this paper was entirely different from the above-mentioned method. Therefore, a different result was obtained.

4. Summary

In summary, using a simple method a new hybrid carbon-silica mesoporous material was prepared. Unlike using swelling agent processes loss of mesoporous ordering was not observed in the carbon/silica material by XRD and TEM analyses. Pretreatment of the parent material with concentrated sulfuric acid could increase the carbon amount in the resultant product. Moreover, the pore size of the carbonized sample was obviously enlarged compared with that of samples calcined directly in air. From our viewpoint the method for carbonization treatment could prove more cost effective with respect to the conventional expanding pore methods. Mesoporous materials with a larger pore diameter increased their potential uses as molecular sieves for the bulky organic compound separation and catalyst supports. It is expected that this novel and simple technique could be suitable for the preparation of other carbon-containing hybrid mesoporous materials.

Acknowledgment

The author thanks Prof. Q.H. Xia in Hubei University for TEM images and useful discussions.

References

- [1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartulli, J.S. Beck, *Nature* 359 (1992) 710.
- [2] J.S. Beck, J.C. Vartulli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T. Chu, D.H. Olson, E. Sheppard, S.B. McMullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [3] J.S. Beck, J.C. Vartulli, G.J. Kennedy, C.T. Kresge, W.J. Roth, S.E. Schramm, *Chem. Mater.* 6 (1994) 1816.
- [4] H.-P. Lin, S. Cheng, C.-Y. Mou, *Micropor. Mater.* 10 (1997) 111.
- [5] M. Kurk, M. Jaroniec, R. Ryoo, S.H. Joo, *Chem. Mater.* 12 (2000) 1414.
- [6] S. Namba, A. Mochizuki, M. Kito, *Chem. Lett.* (1998) 569.
- [7] N.K. Raman, M.T. Anderson, C.J. Brinker, *Chem. Mater.* 8 (1996) 1682.
- [8] N. Ulagappan, C.N.R. Rao, *Chem. Commun.* (1996) 2759.
- [9] J.L. Blin, C. Ojjaques, G. Herrier, B.-L. Su, *Langmuir* 16 (2000) 4229.
- [10] T. Kimura, Y. Sugahara, K. Kuroda, *J. Chem. Soc. Chem. Commun.* (1998) 559.
- [11] Q. Huo, D.I. Margolese, G.D. Stucky, *Chem. Mater.* 8 (1996) 1147.
- [12] A. Sayari, P. Liu, M. Kurk, M. Jaroniec, *Chem. Mater.* 9 (1997) 2499.
- [13] S. Hamoudi, K. Belkacemi, *J. Porous. Mater.* 11 (2004) 47.
- [14] D. Khushalani, A. Kuperman, G.A. Ozin, K. Tanaka, J. Garces, M.M. Olken, N. Coombs, *Adv. Mater.* 7 (1995) 842.
- [15] J.P. Hanrahan, M.P. Copley, K.M. Ryan, T.R. Spalding, M.A. Morris, J.D. Holmes, *Chem. Mater.* 16 (2004) 424.
- [16] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.* 120 (1998) 6024.
- [17] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniowska, *Pure Appl. Chem.* 57 (1985) 603.
- [18] G. Calleja, R.V. Grieken, R. Garcia, J.A. Melero, J. Zglesias, *J. Mol. Catal. A. Chem.* 182–183 (2002) 215.
- [19] L. Li, J.-L. Shi, L.-X. Zhang, L.-M. Xiong, J.-N. Yan, *Adv. Mater.* 16 (2004) 1079.
- [20] M. Kruk, M. Jaroniec, R. Ryoo, S.H. Joo, *J. Phys. Chem. B* 104 (2000) 7960.
- [21] R. Ryoo, C.H. Ko, M. Kruk, V. Antochshuk, M. Jaroniec, *J. Phys. Chem. B* 104 (2000) 11465.
- [22] M. Kruk, M. Jaroniec, T.-W. Kim, R. Ryoo, *Chem. Mater.* 15 (2003) 2815.