MICROPOROUS AND
MESOPOROUS MATERIALS

Microporous and Mesoporous Materials 44–45 (2001) 147–152

www.elsevier.nl/locate/micromeso

Fine tuning of the interaction between Pluronic surfactants and silica walls in SBA-15 nanostructured materials

Y. Bennadja [a], P. Beaunier [a], D. Margolese [b], A. Davidson [a,*]

[a] *Laboratoire de Réactivité de Surface, UMR 7609-CNRS, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cédex 05, France*

[b] *Department of Chemistry, University of California at Santa Barbara, CA 93106, USA*

Received 16 February 2000; accepted 20 September 2000

Abstract

Recent efforts made to understand the nature of the interactions between Pluronic surfactants and silica walls in SBA-15 materials and to modify these interactions by post-synthesis hydrothermal treatments are summarized. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hexagonal structure; Mesoporosity; Microporosity; SBA-15

1. Introduction

Organic surfactants which form rod-like aggregates in aqueous solutions can be used to direct the polymerization of easily hydrolyzed silica precursors such as tetraethylorthosilicate (TEOS). By calcination, organic surfactants can be further eliminated to reveal a mesoporosity of uniform pore size. Based on this principle, MCM-41 materials were obtained by Mobil researchers in 1992 using cationic surfactants such as cetyltrimethylammonium [1]. MCM-41 solids have large pore sizes, which can be typically varied within the range 20–100 Å, and are therefore potentially interesting for both separation and catalytic reactions involving large molecules [2]. However, their silica walls are thin (generally less than 15 Å) resulting in a low stability in the presence of water [3,4]. More recently (in 1998), the so-called SBA-15 materials, characterized by thicker silica walls, have been prepared by using neutral triblock copolymers (Pluronic, triblock copolymer, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), $EO_xPO_yEO_x$, $BASF^R$) [5,6]. In the present work, we study the nature of the interaction between Pluronic surfactants and silica walls in SBA-15 materials and their post-synthesis modifications. We show that, by fine tuning these interactions, SBA-15 matrices of given pore sizes, wall thicknesses and unit-cell dimensions can be prepared.

2. Experimental

2.1. Synthesis

The synthesis of hexagonally ordered SBA-15 was performed as described in Refs. [5,6] with three Pluronics (P_{123}, P_{103} and L_{64} – Table 1). In a

---

[*] Corresponding author.

PII: S1387-1811(01)00178-0

Table 1
Main characteristic of Pluronic surfactants and summary of synthesis conditions

	Surfactant		Synthesis	
	Molecular weight ($g\,mol^{-1}$)	Formula	Temperature of synthesis (°C)	Weight of surfactant (g)
P_{123}	5838	$EO_{20}PO_{70}EO_{20}$	30–35	4.0
P_{103}	4994	$EO_{17}PO_{60}EO_{17}$	35–43	4.4
L_{64}	3518	$EO_{13}PO_{30}EO_{13}$	68–73	5.0

typical synthesis, an aqueous solution of Pluronic, acidified to $pH = 1$ by adding HCl, was mixed with TEOS under constant stirring. For given amounts of water (6.46 mol), TEOS (0.0409 mol) and HCl (0.24 mol), the amount of Pluronic (3–6 g) and the temperature of reaction (30–80°C) were varied. Temperatures of synthesis were selected as precognized in Ref. [5]. The amount of Pluronic was first selected in order to maintain the ratio between EO units and silicate precursors constant. This amount was further adjusted in order to obtain hexagonally well ordered SBA-15 materials, as characterized by TEM (see below). The mixture, initially homogeneous, became heterogeneous after less than 15 mn of reaction. This heterogeneous mixture was maintained 24 h at the reaction temperature and then split into two fractions. White solids (one for each Pluronic, labelled A type hereafter) were recovered by filtration of the first fraction (no washing). The second fraction was submitted to hydrothermal treatment at 100°C for three days before recovering other solids, labelled B type. A and B type solids were both calcined in air at 400°C (4 h) in order to remove the Pluronic surfactants. Calcined solids are hereafter labelled AC and BC respectively.

2.2. Characterization

A and B solids were characterized by chemical analysis (Centre de microanalyse du CNRS, Solaize, France). The rather large values of the hexagonal lattice parameter (around 10 nm) of the SBA-15 solids described here make it necessary to record X-ray diffraction lines at rather low scattering angles. Such X-ray scattering experiments were performed using a laboratory set-up (rotating anode) described elsewhere [7]. Powder samples were held in Lindemann glass capillaries (usually 1 mm in diameter). The $\underline{a}$ unit-cell parameter was estimated from the position of the (10) diffraction line. AC and BC solids were also characterized by transmission electronic microscopy and by nitrogen sorption isotherms. Pore size distributions were calculated based on the desorption branch of the nitrogen sorption isotherms using the BJH formula (Barrett-Joyner-Halenda formula, BJH [8]). In Table 2, the diameter of mesopores for each

Table 2
Main characteristics of the SBA-15 solids described in the present work

Pluronic surfactant	Solid	$Si/EO/Cl^-$ (molar ratios)	$\underline{a}$ (XRD, Å)	D_{BJH} (Å)	$t = \underline{a} - D_{BJH}$ (Å)	t/D_{BJH}
$P_{123}(x/y) = 0.3$	$P_{123}AU$	1/0.5/0.3	118.5	–	–	–
	$P_{123}BU$	1/0.4/0.4	118.5	–	–	–
	$P_{123}AC$	–	94.5	40.0 (+)	54.5	0.9
	$P_{123}BC$	–	110.8	60.0	50.8	–
$P_{103}(x/y) = 0.3$	$P_{103}AU$	1/0.5/0.6	106.8	–	–	–
	$P_{103}BU$	1/0.4/0.2	108.7	–	–	–
	$P_{103}AC$	–	87.0	40.0 (+)	47.0	1.2
	$P_{103}BC$	–	103.5	50.0	53.5	–
$L_{64}(x/y) = 0.4$	$L_{64}AC$	–	47.3	30.0	17.3	0.6

D_{BJH}: mesopore diameter as obtained by BJH formula for relative (P/P^0) pressures greater than 0.31. The (+) symbol indicates an increase in the pore size for relative (P/P^0) pressures lower than 0.31, attributed to micropores; $\underline{a}$: unit-cell parameter as determined by XRD; t: approximate wall thickness.

calcined solid, D_{BJH}, corresponds to the maximum of the pore size distribution. Pore wall thickness, t, was assessed by subtracting D_{BJH} from the $\underline{a}$ unit-cell parameter which corresponds to the distance between the centers of adjacent mesopores. Although the BJH analysis underestimates pore sizes [9–11], yielding an overestimate of wall thickness, relative changes should be accurately portrayed.

3. Results

3.1. Characterization of uncalcined SBA-15 solids

The diffractograms of P_{123}AU and P_{123}BU solids are similar (not shown): a sharp Bragg peak, indexed as (1 0) is associated with three weaker peaks, indexed as (1 1), (2 0) and (3 0). These peaks indicate a long range hexagonal mesoscopic organization with a unit-cell parameter $\underline{a}$ of 118.5 Å.

The amount of chlorine ions trapped in a given uncalcined A type SBA-15 increases from P_{103} to P_{123}. No chlorine could be detected in L_{64}AC. With both P_{123} and P_{103}, some Pluronic and Cl^- anions are eliminated upon the hydrothermal treatment used to transform AU type solids into BU type ones.

3.2. Physical characterization of calcined SBA-15 solids

Four diffraction peaks ((1 0), (1 1), (2 0) and (3 0)), corresponding to a $\underline{a}$ parameter of 94.5 Å are observed on the diffractogram of the P_{123}AC solid (Fig. 1). The diffractogram of P_{103}AC (not shown) displays similar features, associated with a smaller unit-cell parameter ($\underline{a} = 87$ Å). The diffractogram of L_{64}AC only shows the (1 0) diffraction (Fig. 1) corresponding to $\underline{a}$ unit-cell dimension of 47.3 Å. The structural ordering of mesoporous SBA-15 materials therefore strongly depends upon the number of EO groups in Pluronic surfactants and, in our experimental conditions, the L_{64}AC solid exhibits a structural ordering clearly lower than P_{123}AC and P_{103}AC solids.

Furthermore, the lattice parameter $\underline{a}$ of SBA-15 solids strongly decreases upon calcination. The observed unit cell shrinkage differs significantly for A and B type solids. With P_{123}, unit-cell contractions of 20% between A and AC samples but limited to less than 10% between B and BC samples are observed. Similarly, with P_{103}, unit-cell contractions of nearly 20% between A and AC samples but limited to less than 5% between B and BC samples are observed. The limited contractions observed for B type solids reveal that, in these materials, the polymerization degree of silica precursors is larger than in A type ones.

Under the synthesis conditions summarized in Table 1, SBA-15 matrices of excellent structural ordering are observed by MET (Fig. 2). Curved cylinders of relatively uniform size (typically 200–400 nm diameter, 1–3 μm long) presenting a well ordered hexagonal array of mesopores when the electron beam is parallel to their main axis are observed. Interestingly, we have observed that when the amount of Pluronic used during the

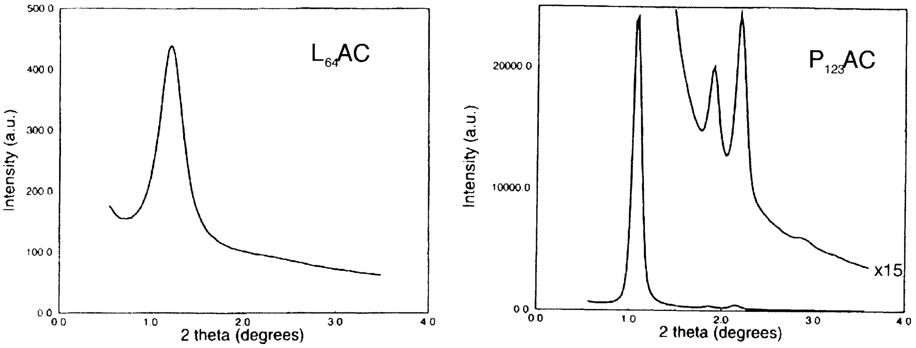

Fig. 1. SAXS results on L_{64}AC and P_{123}AC samples.

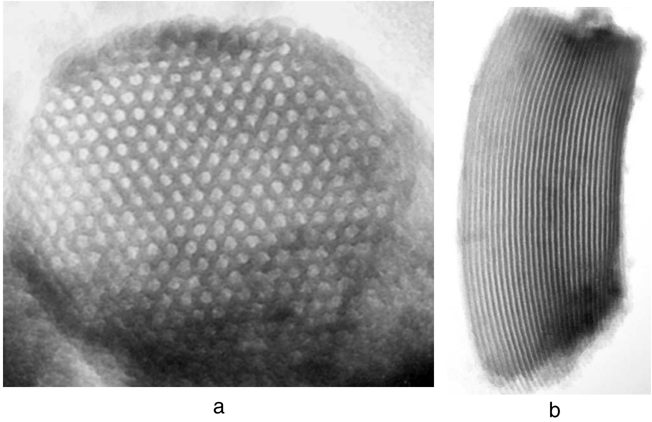
a
b

Fig. 2. MET images of P_{123}BC: (a) along the C_6 axis; (b) perpendicular to this axis (length of the grain around 1 μm).

synthesis is decreased, the curved cylinders typical of the hexagonal SBA-15 phase progressively transform into porous spheres (illustrated for P_{103} in Fig. 3). For a given Pluronic, the ratio between the spheres and the curved cylinders regularly increases on decreasing Pluronic overall concentration.

The nitrogen adsorption–desorption isotherms of calcined SBA-15 materials have been described elsewhere as irreversible type IV isotherms with a H1 hysteresis loop [5]. For (P/P^0) greater than 0.31, a single maximum (with a full width at half maximum lower than 10 Å) is observed on the pore size distribution of each sample. The ratio between the thickness of silica walls and the diameter of mesopores in A type calcined SBA-15 materials directly corresponds to the x/y ratio of the Pluronic used to synthesized them. Furthermore, smaller D_{BJH} values are observed for AC solids than for BC ones, indicating that the hydrothermal treatment induces an increase of mesopore diameter associated with a decrease of wall thickness. For (P/P^0) lower than 0.31, the pore size distribution curves of AC and BC type materials are also different. In this low relative pressure range, the pore size distributions of BC solids are indeed flat whereas those of AC materials are characterized by an increase revealing the presence of micropores (pore size lower than 20 Å). The presence of such micropores has been confirmed in three recent publications [12–14].

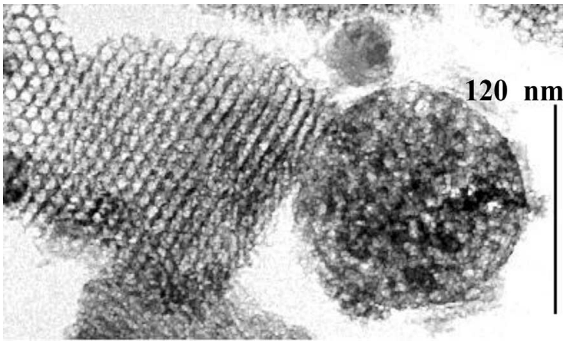

Fig. 3. Coexistence of particles presenting an hexagonal array of mesopores and of porous spheres.

4. Discussion

4.1. Organization control through interaction between Pluronic and silicate precursors

The general route producing a silica-based SBA-15 material is a templating scheme where an aqueous acidic solution containing an amphiphilic Pluronic surfactant is reacted with a silicate source such as tetraethoxysilicate. Using different Pluronic surfactants in such conditions, we could achieve control of the morphology by adjusting the relative concentrations of Pluronic and inorganic precursors. In this way, we observed that a cylinder > sphere sequence of morphologies can be induced. This sequence closely mimics experimental results obtained on block copolymer/homopolymer [15] and copolymer/epoxy resin blends [16]. This sequence implies that the interaction between the organic precursors and the EO units of the Pluronic surfactant is responsible for the curvature of the EO/PO interface. The silicate precursors increase the overall hydrophilic volume defined by EO units whereas the volume occupied by PO chains remains essentially constant. This implies that, as indicated in a recent NMR study [17], the chains formed by EO units penetrate deeply within the silica walls of SBA-15 solids.

4.2. Post-synthesis modifications

At pH close to 1, positively charged protonated silica species are expected to interact, via electrostatic interactions involving chlorine anions, with Pluronics [6]. Chemical analysis suggests that these interactions are not operating during the synthesis of the L_{64}AU solid. At the high temperature necessary for the synthesis of this solid, the EO units of L_{64} can be expected to be hydrophobic and therefore to remain out of the silica walls. By contrast, these electrostatic interactions are involved during the formation of P_{123}AU and P_{103}AU solids, in which Cl^- ions are detected.

Upon the post-synthesis hydrothermal treatment used to obtain B type solids, these Cl^- anions are partially eliminated. The nature of the interactions between Pluronics and silica walls is therefore clearly modified.

As indicated by a contraction of unit-cell dimension revealed by X-ray diffraction, a restructuring of silica walls takes place upon calcination in both A and B type solids. However, this restructuring is less pronounced in B type solids than in A type ones. Furthermore, after elimination of Pluronic surfactants by calcination, both a mesoporosity and a microporosity are revealed by nitrogen sorption experiments in AC type materials whereas, in type BC ones, only a mesoporosity can be detected. These two observations suggest that, upon the hydrothermal treatment which is used to transform A type solids into B type ones, the EO units are expelled from silica walls. However, as shown by X-ray diffraction, this expulsion, is restricted to a local scale and does not disrupt the long-range order of the hexagonal lattice.

5. Conclusions

Understanding all the interactions between silicate precursors and Pluronic surfactants is important to achieve the ultimate goal of designing SBA-15 materials. As already indicated by several authors [5,13], the present work confirms, that the characteristics (wall thickness, mesopore diameter, resistance to shrinkage upon calcination) of SBA-15 solids prepared by precipitation, and their dependence on post-synthesis hydrothermal treatments, reflect changes in the number of EO units and their degree of penetration within silica walls.

With P_{123}, P_{103} and L_{64} Pluronic surfactants, we show that, at the temperatures of synthesis indicated in Ref. [5], the ratio between inorganic and organic precursors deserves a special attention. Indeed, the inorganic silicate precursors are responsible for the curvature of the EO/PO interface. A cylinder > sphere sequence of morphologies is therefore induced when this ratio is too high.

Acknowledgements

The authors are deeply indebted to Prof. G. Stucky, Prof. N. Che and Dr. N. Breysse for their constant help and support. We thank BASF for providing block copolymer Pluronic surfactants and M. Imperor-Clerc for the X-ray diffraction experiments performed at the Laboratoire de Physique des Solides, Orsay, France.

References

[1] C.T. Kresge, Leonowicz, M.E. Roth, W.J. Vartuli, J.C. Beck, Nature 114 (1992) 10834.
[2] J. Ying, C. Mehnert, M.S. Wong, Angew. Chem. Int. Ed. 38 (1999) 56.
[3] X.S. Zhao, F. Audsley, G.Q. Lu, J. Phys. Chem. B 102 (1998) 4143.
[4] J.M. Kim, R. Ryoo, Bull. Korean Chem. Soc. 17 (1996) 66.

[5] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. Fredrickson, B. Chmelka, G. Stucky, Science 279 (1998) 548.
[6] P. Yang, D. Zhao, D. Margolese, B. Chmelka, G. Stucky, Nature 396 (1998) 152.
[7] M. Imperor-Clerc, P. Davidson, Eur. Phys. J. B 9 (1999) 93.
[8] E.P. Barrett, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373.
[9] P.I. Ravikovitch, D. Wei, W.T. Chueh, G.L. Haller, A.V. Neimark, J. Phys. Chem. B 101 (1997) 3671.
[10] W.W. Lukens, P. Schmidt-Winkel, D. Zhao, J. Feng, G. Stucky, Langmuir 15 (1999) 5279.
[11] Z. Luan, E.M. Maes, P.A.W. van der Heide, D. Zhao, R.S. Czernuszewicz, L. Kevan, Chem. Mater. 11 (1999) 3680.
[12] M. Imperor-Clerc, P. Davidson, A. Davidson, J. Am. Chem. Soc. 122 (2000) 11925.
[13] M. Kruk, M. Jaroniec, C.H. Ko, R. Ryoo, Chem. Mater. 12 (2000) 1961.
[14] R. Ryoo, C.H. Ko, M. Kruk, V. Antochshuk, M. Jaroniec, J. Phys. Chem. B 104 (2000) 10448.
[15] K.I. Winey, E.L. Thomas, L.J. Fetters, Macromolecules 25 (1992) 2645.
[16] P.M. Lipic, F.S. Bates, M.A. Hillmyer, J. Am. Chem. Soc. 120 (1998) 8963.
[17] N.A. Melosh, P. Lipic, F.S. Bates, F. Wudl, G.D. Stucky, G.H. Fredrickson, B.F. Chmelka, Macromolecules 32 (1999) 4332.