Well-Ordered Spherical Mesoporous Materials CMI-1 Synthesized via an Assembly of Decaoxyethylene Cetyl Ether and TMOS

J. L. Blin, A. Léonard,† and B. L. Su*

Laboratoire de Chimie des Matériaux Inorganiques (CMI), ISIS, The University of Namur, 61 rue de Bruxelles, 5000 Namur, Belgium

Received October 11, 2000

Well-ordered spherical CMI-1 mesoporous materials with a hexagonal arrangement of channels, analogous to MCM-41, have been directly synthesized by variation of the weight percentage of decaoxyethylene cetyl ether [$C_{16}(EO)_{10}$] in aqueous solution. XRD, TEM, SEM, and nitrogen adsorption−desorption results led us to propose two different synthesis pathways for surfactant concentrations higher and lower than 30 wt %, respectively. For samples obtained with an elevated surfactant concentration (>30 wt %), in addition to the possible perturbation induced by methanol released in low amount during the hydrolysis of TMOS, other factors such as the interactions of the silica source with hydrophilic chain heads of surfactant molecules should also disturb the preformed hexagonal micelle array, and disordered wormhole mesostructured materials (DWM), analogous to MSU, are obtained. For the synthesis with a $C_{16}(EO)_{10}$ concentration less than 30 wt %, a cooperative mechanism, which involves the polymerization of silica source and the interface interactions between the hydroxyl groups of silica source produced from the hydrolysis of TMOS and hydrophilic chain heads of surfactant molecules which are present in the single rod micelle form, has been evidenced, leading to well-ordered CMI-1 materials with hexagonal arrangement of their channels.

1. Introduction

The synthesis scheme of mesostructured mesoporous molecular sieves is similar to that of microporous zeolites (i.d. ≤ 1.5 nm), but instead of using a structure-directing agent such as short chain amines, ether crowns, mineral cations, etc., as for zeolite synthesis, these materials are formed by supramolecular templating. Amphiphilic surfactant molecules, possessing a hydrophilic head and a long hydrophobic tail of variable length, can form first isolated, spherical, and cylindrical micelles and finally well-organized liquid crystal structures depending on the weight percentage of surfactant and preparation temperature. When the inorganic precursor such as silica is added to the micellar solution, its condensation and polymerization around the preformed single or organized micelles of template build the framework of the compound. The final mesoporous material is recovered after calcination or solvent extraction to remove surfactant and free the channels. The assembly of the first mesostructure made by Mobil researchers in 1992[1,2] is based on electrostatic interactions between a positively charged surfactant (S^+), cetyltrimethylammonium bromide [(CTMA)Br], and a negatively charged inorganic precursor (I^-). Interactions between the inorganic precursor (I) and the surfactant (S) can however occur between other entities and so several synthesis pathways can lead to the formation of mesoporous compounds. The electrostatic assembly has been extended to include charge-reversed (S^-I^+) and counterion-mediated $S^+X^-I^+$ ($X^- = Cl^-, Br^-$), $S^-M^+I^-$ ($M^+ = Na^+, K^+$) systems.[1−6] The synthesis can also be achieved through a neutral S^0I^0 [7−9] pathway, in which hydrogen bondings are responsible for the cohesiveness between the surfactant (S^0) and the inorganic precursor (I^0). Different kinds of mesoporous materials called M41S,[1,2] HMS,[9] SBA,[10] TUD,[11] or MSU[12] have been obtained via an electrostatic route for M41S and a

---

* Corresponding author. Phone: 32-81-72-45-31. Fax: 32-81-72-54-14. E-mail: bao-lian.su@fundp.ac.be.

† FRIA Fellow (Fonds National de la Recherche Scientifique, Belgium).

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

(2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlender, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(3) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky G. D. *Nature* **1994**, *368*, 317.

(4) Chen, C. Y.; Li, H. Y.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 17.

(5) Chen, C. Y.; Li, H. Y.; Burkett, S. L.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 27.

(6) Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176.

(7) Sayari, A. *Stud. Surf. Sci. Catal.* **1996**, *102*, 1.

(8) Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.

(9) Tanev, P. T.; Pinnavaia, T. J. *Chem. Mater.* **1996**, *8*, 2068.

(10) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

(11) TUD-1: Shen, Z.; Jansen, J. C.; et al. Mesoporous amorphous silicate materials and process for the separation therof. Patent application, EU4741, 1998.

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

10.1021/cm0011965 CCC: $20.00

Table 1. Comparison of Synthesis Conditions of Different Structured Materials Synthesized with Deca- or Octaoxyethylene Cetyl Ether and Neutral Silica Precursor

	materials synthesized under different conditions by				
	present authors[a]	Pinnavaia et al.[19]	Stucky et al.[20]	this work	Attard et al.[16]
surfactant	$C_{16}(EO)_{10}$	$C_{16}(EO)_{10}$	$C_{16}(EO)_{10}$	$C_{16}(EO)_{10}$	$C_{16}(EO)_8$
silica source	TMOS	TEOS	TEOS, TMOS, TPOS	TMOS	TMOS
incorporation of cation	–	transition metals	–	–	–
wt percentage of surfactant (%)	30–60	1.8	4–6	10–25	50
surfactant/silica molar ratio	0.25–3.5	0.04–0.07	<0.60	1.5	0.115
T (°C) of micellar soln preparation	70	25–65	RT	70	
acidity	pH = 2	neutral pH	$pH \ll 1$	pH = 2	pH = 2
hydrothermal treatment	2 days at 60 °C			1 day at 80 °C	
channel array	disordered	hexagonal	hexagonal	hexagonal	hexagonal[b]
label	DWM	MSU	SBA-11	CMI-1	

[a] Present work and ref 23. [b] A gentle removal of the large amount of methanol produced during the hydrolysis of TMOS was performed. They used $C_{16}(EO)_8$ as surfactant instead of $C_{16}(EO)_{10}$ used by Pinnavaia et al., Stucky et al., and the present authors.

neutral way for the others. For MSU and some SBA compounds, the system is denoted N^0I^0 instead of S^0I^0, since the template employed belongs to the family of polyoxyethylene alkyl ether [$C_m(EO)_n$], which are cheaper, more biodegradable, and less toxic than ionic templates. Moreover, the removal of the surfactant can easily be achieved by solvent extraction, using ethanol for instance, because of the less strong interactions between the entities (H-bonds). The synthesis of mesostructured oxides that is difficult or impossible by electrostatic assembly can be performed through this N^0I^0 process.[13] Very recently, wormhole MSU-type structures have been synthesized using polyoxyethylene alkyl ether with sodium silicate as wall builder to reduce the synthesis costs.[14,15] The synthesis pathway proposed was $N^0(M^+)I^-$. In these studies, various parameters such as pH value have been well investigated.

The first syntheses of mesoporous molecular sieves achieved with [$C_m(EO)_n$] surfactants were reported by Attard et al.[16] with $C_{12}(EO)_8$ and $C_{16}(EO)_8$ in 1995 using a surfactant concentration of 50 wt % and surfactant/TMOS molar ratio of 0.115. The obtained ordered materials with hexagonal arrangement of channels exhibit pore sizes up to 3.0 nm. Then, using this type of templating agent, Pinnavaia et al. have investigated the synthesis of a series of wormhole like MSU-X materials using a surfactant concentration of around 7 and 25 wt %.[12,17,18] The main difference between the work made by Attard et al.[16] and that by Pinnavaia et al.[17,18] consists of the different experimental conditions, i.e., acidic media by Attard et al. and nearly neutral environment in the latter case, which lead to different synthesis mechanisms, i.e., confinement of the aqueous framework for Attard et al. and an assembly mechanism for Pinnavaia et al. However, the regular mesoporous obtained by Attard et al.[16] were only owing to the gentle removal of the large amount of methanol released from the hydrolysis of the TMOS used as silica precursor since they found that the methanol played a role of liquid crystal breaker destroying the H_1 phase formed by the surfactant molecules in aqueous solution. Nevertheless, recently, via a new pathway [$(N^0M^{n+})I^0$] which involves the formation of hydrogen bonds between a cationic metal ($M^{n+} = Li^+, Co^{2+}, Mn^{2+}, Zn^{2+}$) complex form of a nonionic polyoxyethylene surfactant (N^0) and the neutral inorganic precursor (I^0), Pinnavaia et al.[19] have successfully oriented the structure of the final silica compounds using a very low concentration of around 1.8 wt % still under neutral media. Concerning ordered SBA-11 and SBA-12 the syntheses were performed in strong acid media ($pH \ll 1$) at room temperature with $C_{16}(EO)_{10}$ for SBA-11 and $C_{18}(EO)_{10}$ for SBA-12 with a surfactant concentration of 4–6 wt %.[20] We have also successfully obtained disordered wormhole mesostructures (DWM) analogous to MSU materials with the weight percentage of surfactant of 50 using $C_{18}(EO)_{10}$,[21] $C_{13}(EO)_n$ (n = 6, 12, 18),[22] or $C_{16}(EO)_{10}$[23] as surfactant. All the works using neutral polyoxyethylene alkyl ether surfactants and neutral silica precursors discussed above are summarized in Table 1 for a better comparison.

The synthesis mechanism, proposed by Mobil's scientists, involves that silica species interact with rod micelles of surfactant to form the mesoporous compound and explains how the synthesis of highly organized mesoporous materials[1] can be achieved via a cooperative mechanism even with a weight percentage of (CTMA)Br in aqueous solution less than cmc2 [critical micelle concentration at which rod micelles of (CTMA)Br pack together to give a hexagonal array (H_1 phase)]. This revealed that the concentration of surfactant is one of key factors in the mesoporous materials synthesis. As discussed above, the polyoxyethylene alkyl ethers were often used in two extreme conditions, i.e., at very low concentration (less than 7 wt %) leading to the synthesis of regularly organized SBA-11 and SBA-12 (4–6 wt %)[20] or to MSU (7 wt %) and ordered materials (1.8 wt %).[12] The organization of the channels was obtained in the last case by adding transition metal cations to the micellar solution. Higher concentrations (25 or 50 wt %) lead to the preparation of wormlike MSU mat-

---

(13) Bagshaw, S. A.; Pinnavaia, T. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *10*, 1102.

(14) Sierra, L.; Guth, J. L. *Microporous Mesoporous Mater.* **1999**, *27*, 243.

(15) Boissière, C.; Larbot, A.; Prouzet, E. *Chem. Mater.* **2000**, *12*, 1937.

(16) Attard, G. S.; Glyde, J. C.; Göltner, C. G. *Nature* **1995**, *378*, 366.

(17) Prouzet, E.; Pinnavaia, T. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 516.

(18) Prouzet, E.; Cot, F.; Nabias, G.; Larbot, A.; Kooyman, P.; Pinnavaia, T. J. *Chem. Mater.* **1999**, *11*, 1498.

(19) Zhang, W.; Glomski, B.; Pauly, T. R.; Pinnavaia, T. J. *Chem. Commun.* **1999**, 1803.

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

(21) Blin, J. L.; Herrier, G.; Su, B. L. *Stud. Surf. Sci. Catal.* **2000**, *129*, 67.

(22) Blin, J. L.; Becue, A.; Pauwels, B.; Van Tendeloo, G.; Su, B. L. *Microporous Mesoporous Mater.* **2000**, *44–45*, 41.

(23) Léonard, A.; Blin, J. L.; Su, B. L. *Chem. Mater.*, submitted for publication.

erials[17,18,21−23] or to regular mesophases[16] if a supplementary step to remove from the reaction system the methanol produced during hydrolysis of TMOS was performed (Table 1). The variation of this kind of surfactant concentration on the synthesis of structured porous materials, however, has not been reported yet in the literature.

The present work reports a systematic study on the synthesis of well-ordered mesoporous silica in a wide but nonexplored range of surfactant concentrations under mild acidic conditions. This work has been carried out in order to shed some light on the molecular level on the synthesis mechanism using polyoxyethylene alkyl ether as surfactant and to correlate the final phase of inorganic network with the initial phase of micelles in aqueous solution. We also try to understand how the interface hydrogen-bonding type interactions between the silica source and the outer micelles can disturb the micellar array and further the final structure of mesoporous materials.

2. Experimental Section

2.1. Syntheses. A micellar solution with a weight percentage of $C_{16}(EO)_{10}$ (Brij 56) varying from 10 to 60 was prepared by dissolving the surfactant at 70 °C in an aqueous solution during 3 h. The pH value of the micellar solution was then adjusted with H_2SO_4 to 2.0. The obtained medium was stirred for 3 h at 70 °C before adding drop by drop the silica source: tetramethoxysilane (TMOS). The surfactant/silicium molar ratio is fixed to 1.5, according to our previous work[23] which consisted in studying systematically the effect of the molar ratio on the compounds prepared. The obtained gel was sealed in Teflon autoclaves and heated for 1 day at 80 °C. The final products were recovered after ethanol extraction with a Soxhlet apparatus during 30 h[23] and calcination under nitrogen and then air atmosphere at 500 °C for 18 h to remove all the surfactant and impurities.

2.2. Characterization. The XRD patterns were obtained with a Siemens D 5000 diffractometer equipped with a copper anode producing X-rays with wavelength equal to 1.54178 Å. The TEM micrographs were taken using a 100 kV Philips Technaï microscope. Samples powders were embedded in an epoxy resin and then sectioned with an ultramicrotome. The thin films were supported on copper grids previously coated by carbon to improve stability and reduce the accumulation of charges. The morphology of the obtained solide phases was studied using a Philips XL-20 scanning electron microscope (SEM) with conventional sample preparation and imaging techniques. Nitrogen adsorption−desorption isotherms were obtained at −196 °C over a wide relative pressure range from 0.01 to 0.995 with a volumetric adsorption analyzer ASAP 2010 or TRISTAR 3000 manufactured by Micromeritics. The samples were degassed further under vacuum for several hours at 320 °C before nitrogen adsorption measurements. The pore diameter and the pore size distribution were determined by the BJH (Barret, Joyner, Halenda) method.[24] Although it is well-known that this method gives an underestimated pore size and that some new methods have been developed,[25] we use it here for the sake of simplicity, and this mathematical algorithm will not affect significantly our systematic comparison. Moreover, at present, from our knowledge, there is no method that can give an accurate calculation of pore sizes superior to 5 nm.

3. Results and Discussion

3.1. Structural Investigations. 3.1.1. X-ray Diffraction Analysis. Figure 1 depicts the variation of the XRD pattern with the surfactant weight percentage in the aqueous solution. It has been reported[26] that X-ray diffractograms of powdery hexagonal mesoporous materials exhibit a typical four peaks pattern with a very strong feature at a low angle (100 reflection line) and three other weaker peaks at higher angles (110, 200, and 210 reflection lines). These four reflection lines can be indexed on a hexagonal unit cell ($a_0 = 2d_{100}/(3)^{1/2}$) which is the sum of the pore diameter and the thickness of the pore wall. The absence of the last three peaks suggests a disordered structure of the mesoporous molecular sieves with wormholelike channel systems, analogous to MSU-type materials. The broad peak that is observed on the XRD pattern is normally an indication of the average pore to pore separation in the disordered wormhole framework, which presents a lack of long-range crystallographic order.

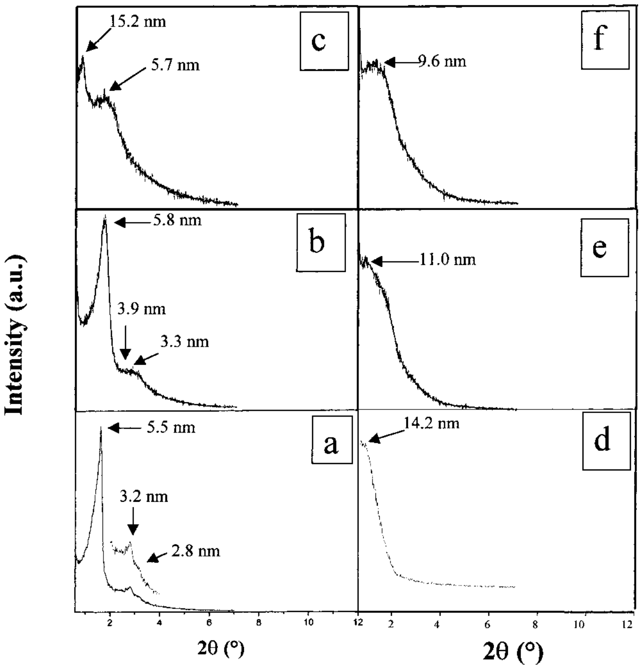

Figure 1. XRD diffraction patterns of compounds synthesized with a weight percentage (%) of $C_{16}(EO)_{10}$ of (a) 10, (b) 20, (c) 30, (d) 40, (e) 45, and (f) 60.

For the sample obtained with 10 wt % $C_{16}(EO)_{10}$ (Figure 1a), in addition to a sharp peak at $2\theta = 2.35°$ (5.5 nm), two peaks at $2\theta = 4.08°$ (3.2 nm) and $2\theta = 4.71°$ (2.8 nm) are detected. The presence of these two last peaks is suggestive of a hexagonal organization of the channels in our material. According to Bragg's rule, the unit cell dimension (a_0) can be deduced and is about 6.5 nm. With increasing surfactant concentration in the micellar solution, the position of the sharp peak remains almost constant (Figure 1b,c), indicating that a_0 does not vary. Nevertheless, the (110) and (200) reflections become less resolved and their intensity decreases (Figure 1b) and disappear completely for a surfactant weight percentage equal to 30 (Figure 1c). This suggests that the channel array is not very regular any more and the hexagonal symmetry is lost. Simultaneously a new peak located at $2\theta = 0.58°$ (15.2 nm) is detected, which means that the disorganization of the mesoporous

---

[24] Barret, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 37.

[25] Jarionec, C. P.; Kruk, M.; Jarionec, M. *J. Phys. Chem. B* **1998**, *102*, 5503.

[26] Chen, C. Y.; Xiao, S. O.; Davis, M. E. *Microporous Mater.* **1995**, *4*, 20.

Table 2. *d* spacing Values, Specific Surface Area Pore Volume, and Pore Diameter of the Samples Obtained at Different Surfactant Weight Percentages [$C_{16}(EO)_{10}$/TMOS Molar Ratio = 1.5; Hydrothermal Treatment Temperature = 80 °C; Time = 1 day]

surfactant wt %	*d* spacing (nm)	S_{BET} (m^2/g)	pore vol [$cm^3/(g\ STP)$]	pore diameter (nm)
10	5.5	920	1.32	4.3
20	5.8	1058	1.63	4.7
25		1042	1.21	4.1
30	15.2/5.7	885	1.39	4.3
40	14.2	833	0.98	4.5
45	11.0	766	1.04	4.9
50		878	1.08	4.6
60	9.6	840	0.77	3.6

molecular sieve occurs. The occurrence of two reflection lines at $2\theta = 0.58$ and 2.35° might be suggestive of the presence of two different phases. With increasing surfactant weight percentage from 30 to 60 (curves d−f of Figure 1), no significant change is noted. Only the position of the reflection line at very low angle moves slightly toward higher angle and it becomes broader and broader. The (110) and (200) reflections, arising from the hexagonal structure, are not observed any longer, and as just discussed above, the presence of a single reflection indicates the formation of the disordered structure. Since our synthesis conditions are quite different from those used for MSU materials by Pinnavaia et al.,[12,17,18] here we label the disordered wormhole mesostructured materials obtained from our present work as DWM (disordered wormhole mesostructure). According to Pinnavaia et al.,[17] the position of broader reflection line in DWM compounds is related to the sum of the pore diameter and the thickness of the pore wall, so when the $C_{16}(EO)_{10}$ concentration in the micellar solution is varied from 30 to 60 wt %, we notice a slight decrease of either the pore diameter or the wall thickness or both. However, our results obtained by nitrogen adsorption−desorption analysis show that the pore diameter remains almost constant (Table 2). So we can conclude that the wall thickness slightly decreases when the surfactant weight percentage of the surfactant is raised to 60. For the sake of better comparison, the values of *d*-spacing of all the samples obtained at different weight percentage of surfactant are given in Table 2. Above results demonstrate clearly that, with a weight percentage lower than 30, well-ordered silicas are obtained, whereas, with a weight percentage higher than 30, disordered structures are formed. A mixture of these two phases could be present if a surfactant weight percentage of 30 is used.

The above results indicate that the formation of well-ordered mesoporous molecular sieves can be achieved in a wide range of the weight percentage of $C_{16}(EO)_{10}$ in the micellar solution from 10 to 25. Even if highly ordered mesoporous materials have already been obtained[19,20] using same templating agent, the direct formation of such materials without any additives and supplementary steps and in a wide but not explored concentration range of surfactant with a very high surfactant/TMOS molar ratio and a mild pH value of synthesis gel has not been reported yet in the literature. Attard et al. obtained the regular inorganic network owing to a supplementary removal of methanol by using $C_{16}(EO)_8$ (50 wt %) instead of $C_{16}(EO)_{10}$ used by Stucky et al.,[20] Pinnavaia et al.,[19] and the present authors. We name therefore the compounds obtained in our present conditions CMI-1 (Chimie des Matériaux Inorganiques). [**CMI-2**: same structure as CMI-1 but synthesized with $C_{16}(EO)_{10}$ as the surfactant with the presence of a series of transition metal ions (surfactant concentration: 10−60 wt %). Léonard, A.; Blin, J. L.; Su, B. L., to be published. **CI-3 and 4**: same structure as CMI-1 but synthesized with $C_{18-1}(EO)_{10}$ as the surfactant with (CMI-4) and without (CMI-3) the presence of a series of transition metal ions (surfactant concentration: 10−25 wt % for CMI-3 and 10−60 wt % for CMI-4). Herrier, G.; Su, B. L. *Stud. Surf. Sci. Catal.* **2001**, in press. **CMI-5**: large-pore mesoporous silicas with a cubic structure (fcc) synthesized with CTMABr as the surfactant and decane and TMB as double swelling agents. Blin, J. L.; Pauwels, Van Tendeloo, Su, B. L., to be published.] As evidenced from Table 1, concerning SBA-11, for a typical preparation, Stucky et al.[20] employed a surfactant weight percentage in the range from 4 to 6, with a $C_{16}(EO)_{10}$/silica molar ratio lower than 0.6. Indeed, beyond this value, a poorly ordered unstable mesophase was formed as they clearly pointed out.[20] Moreover, the synthesis was performed at room temperature under strong acidic conditions ($pH \ll 1$). They found that if the acid concentration was in the range of pH 2−6, no precipitation of silica could take place. But, under a neutral media with similar concentration of around 7 wt % of this surfactant, the disordered materials were obtained.[12] The synthesis method of an ordered mesostructure reported by Pinnavaia et al.[19] with this surfactant involves also a very low weight percentage of $C_{16}(EO)_{10}$ (1.8) with $C_{16}(EO)_{10}$/silica molar ratio between 0.04 and 0.07 but with the incorporation of transition metal salts into the micellar solution in order to generate the mesoporous formation through an electrostatic pathway at neutral pH value. Still using the same pH value, but with surfactant concentration of 25 wt %, Pinnavaia et al. obtained only disordered MSU-type materials. These results indicate that under neutral media with $C_{16}(EO)_{10}$ without incorporation of transition metal ions, whatever the surfactant concentration is used, a low (7 wt %) or a medium (25 wt %) in aqueous solution, the obtained materials have a disordered structure with wormhole like channels. In contrary, the synthesis of CMI-1 is achieved with a surfactant concentration located between 10 and 25 wt % in the micellar solution, at a pH value of 2 and a $C_{16}(EO)_{10}$/silica molar ratio of 1.5. The hydrothermal treatment is performed at 80 °C during 1 day. Our present results show clearly that under the experimental conditions, which were considered by some researchers[20] to be impossible for the synthesis of highly ordered mesoporous materials, we could however successfully synthesize well-organized mesoporous silica with the regular hexagonal arrangement of their channels without using transition metal cations.[19] The elevation of synthesis temperature and the manner of micellar solution preparation could be some of the key factors of successful synthesis under mild acidic conditions. The appellation of CMI-1 for our materials is thus well justified.

3.1.2. TEM Investigations. The TEM micrographs, represented in Figure 2, show that materials synthesized with a weight percentage of $C_{16}(EO)_{10}$ superior or equal to 30 (Figure 2A,a−c) have a disordered structure

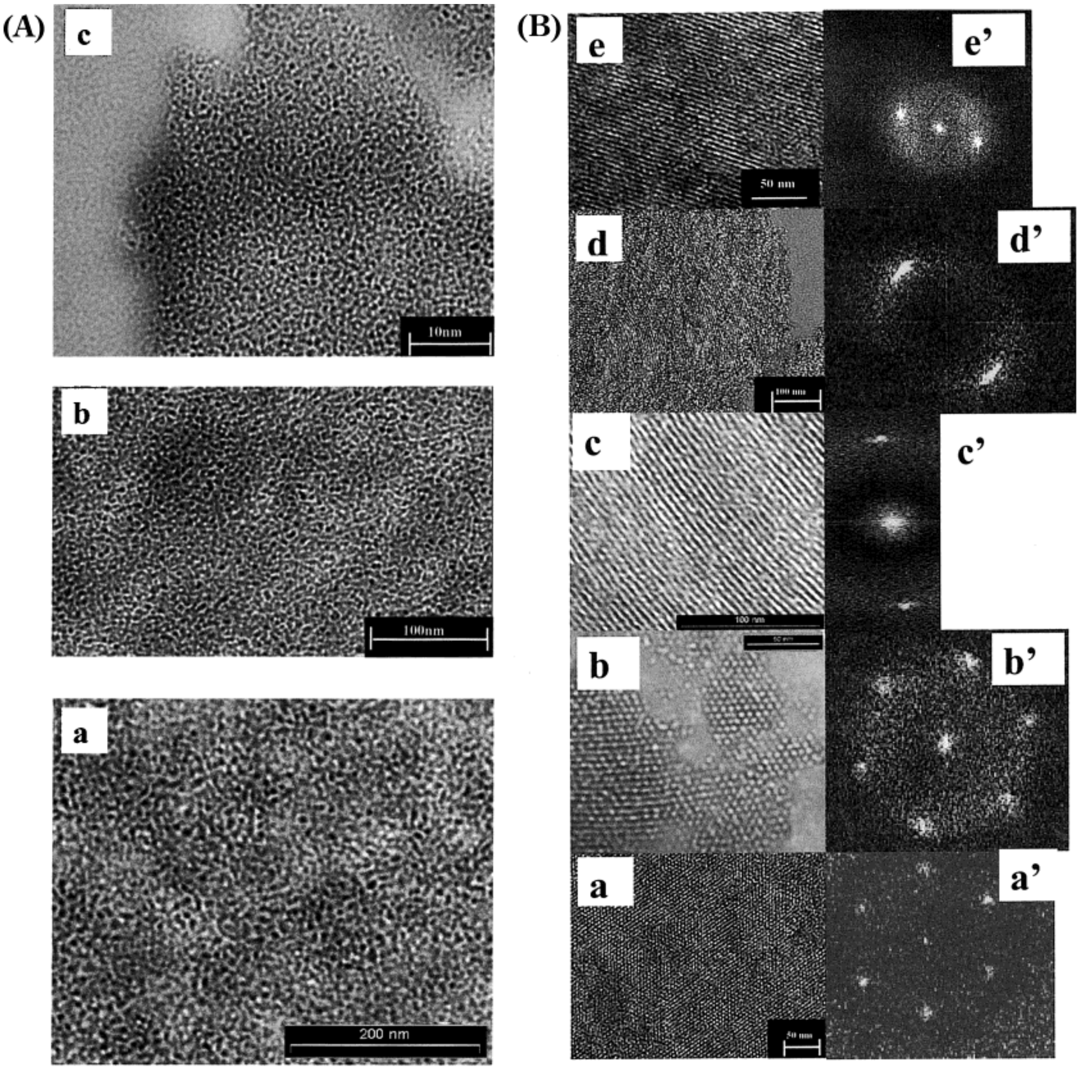

Figure 2. TEM micrographs (a−e) of materials synthesized at 80 °C for 1 day with $C_{16}(EO)_{10}$ surfactant weight percentages (%) of (A) 50 (a, b) and 40 (c) and (B) 10 (micrographs made at different zones a−d) and 20 (e). (a′)−(e′): Fourier transforms of micrographs a−e.

with a large number of wormhole-like and interconnected channels lacking a long-range packing order as observed in MSU compounds. According to the phase diagram reported by Mitchell et al.[27] for this kind of templating agents, a hexagonal H1 phase is present in aqueous solution with a weight percentage of surfactant between 30 and 65 in a temperature range of 15−85 °C. Thus, mesoporous molecular sieves possessing this structure are expected. The experimental results are contrary to our expectation. This suggests that the addition of TMOS, or the presence of some species formed in the solution after the addition of TMOS, for example the methanol produced by the hydrolysis of TMOS, disturb the array of micelles preformed in aqueous solution, which confirms the XRD results. These results are in good agreement with those obtained by Pinnavaia et al. for MSU-1−4 synthesis where they used a surfactant concentration of 25 wt %. For lower loadings of $C_{16}(EO)_{10}$ (in the range of 10−25 wt %), i.e., concerning CMI-1 compounds, the peaks characteristic of the 100, 110, and 200 reflections of the hexagonal structure with a well-ordered channel array are observed from the XRD patterns. The hexagonal arrangement of the channels is further confirmed by TEM micrographs of different samples (10 wt %, Figure 2B,a−d; 20 wt %, Figure 2B,e). It is quite interesting to see from Figure 2B,d that the pore array looks like a fingerprint. This feature could be related to the spherical morphology with particle sizes of 1−2 μm of our sample. The morphology analysis of our materials will be discussed in the following section. The Fourier transform pictures of TEM images exhibit 6-fold symmetry, and the measured angles between two bright spots are very close to 60° (Figure 2B,a′,b′). Two light spots (Figure 2B,c′−e′) are present, indicative of the parallelism of well-oriented channels. So according to these observations, we can conclude that CMI-1 materials have a hexagonal arrangement of their channels and the formation of this mesostructure is favored by the addition of the silica source as no hexagonal phase is expected for this weight percentage of template in solution.[27]

3.2. Particles Morphology. Figure 3 shows SEM pictures of the samples synthesized at different surfactant weight percentages in the micellar solution. The magnification scales used depend on the particle size

---

(27) Mitchell, D. J.; Tiddy, G. J. T.; Waring, L.; Bostock, T.; McDonald, M. P. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 975.

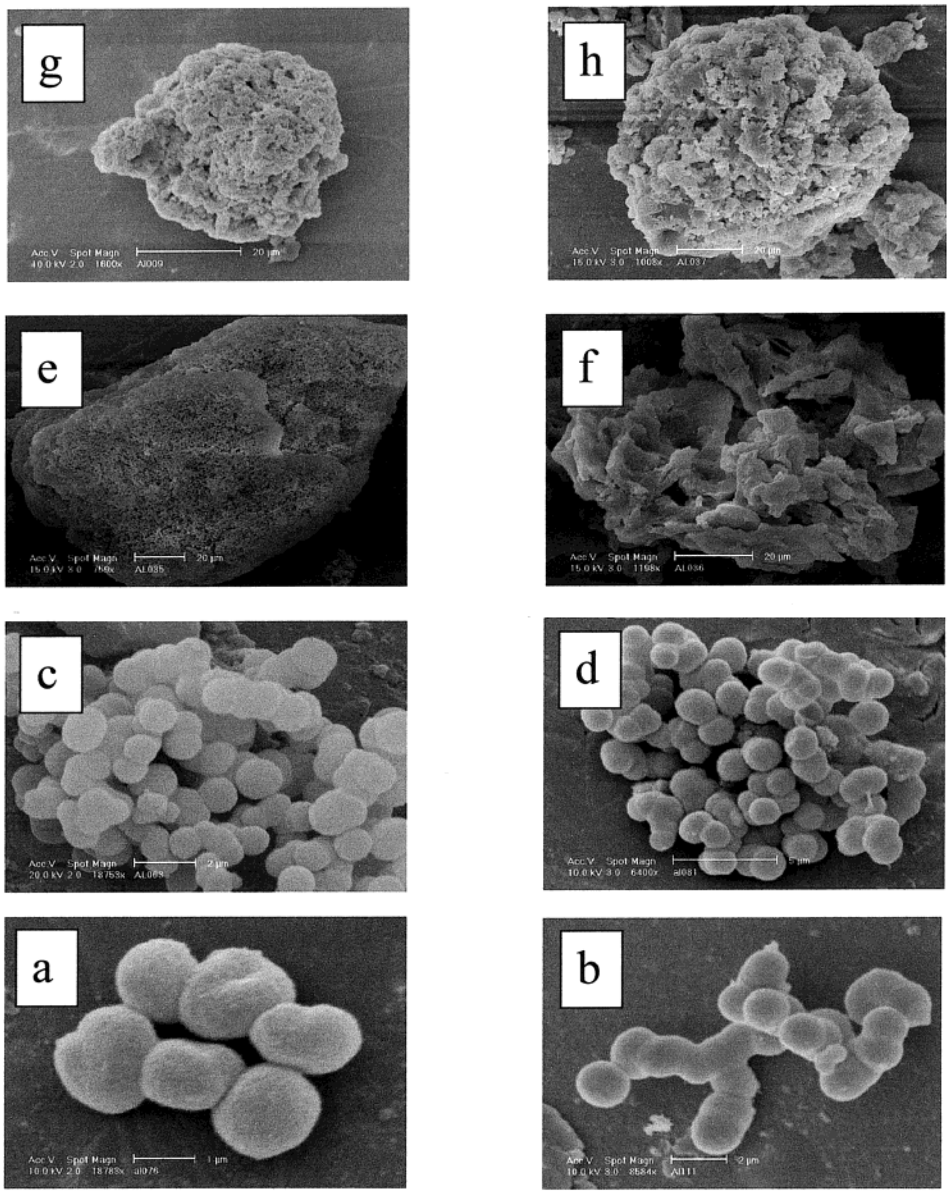

Figure 3. Variation of the particles morphology with the weight percentage of $C_{16}(EO)_{10}$ (wt %) (a) 10, (b) 15, (c) 20, (d) 25, (e) 30, (f) 40, (g) 50, and (h) 60.

of the materials in order to give both a global view and a local view of the particle surface. For high $C_{16}(EO)_{10}$ loadings (≥30 wt %), the particles morphology (Figure 3e−h) is very different. The sample obtained with 30 wt % of surfactant (Figure 3e) exhibits the large and porous particles such as sponge and the surface is quite rough whereas, for the samples prepared with a surfactant concentration higher than 50 wt % (Figure 3g,h), large agglomerates are formed and irregular edge-shaped particles can be observed. The morphology of the sample obtained with a surfactant loading of 40 wt % is a bursting form of the agglomerates (Figure 3). However, at low $C_{16}(EO)_{10}$ loadings (less than 30 wt %), the morphology of particles remains practically unchanged and it can be described by an assembly of spheres of very small diameter (1−2 μm) (Figure 3a−d), and thus, the "fingerprint" of TEM micrographs (Figure 2B,d) appears to be a section of such a sphere with the channels running concentrically. The change in morphology of samples with the surfactant weight percentage will further be studied and reported elsewhere.[28] Structured mesoporous materials with spherical morphology were already synthesized with different surfactants.[29−32]

3.3. Characterization by Nitrogen Adsorption−Desorption. For the sake of clarity, Figure 4A,B depicts only the nitrogen adsorption branches of solid phases obtained with different surfactant concentrations. Both nitrogen adsorption and desorption isotherms of two samples, one obtained with surfactant concentration less than 30 wt % and another higher than 30 wt %, are given in the frame of Figure 4A,B, respectively, for demonstration. An H_1 type hysteresis loop in which adsorption and desorption branches are steep[33] is

---

(28) Léonard, A.; Blin, J. L.; Su, B. L. To be published.

(29) Grün, M.; Unger, K. K.; Matsumoto, A.; Tsutsumi, K. *Microporous Mesoporous Mater.* **1999**, *27*, 207.

(30) Boissière, C.; van der Lee, A.; El Mansouri, A.; Larbot, A.; Prouzet, E. *Chem. Commun.* **1999**, 2047.

(31) Qian Luo, L. L.; Zhiyuan, X.; Zhao, D. *Stud. Surf. Sci. Catal.* **2000**, *129*, 37.

(32) Boissière, C.; Larbot, A.; Prouzet, E. *Stud. Surf. Sci. Catal.* **2000**, *129*, 31.

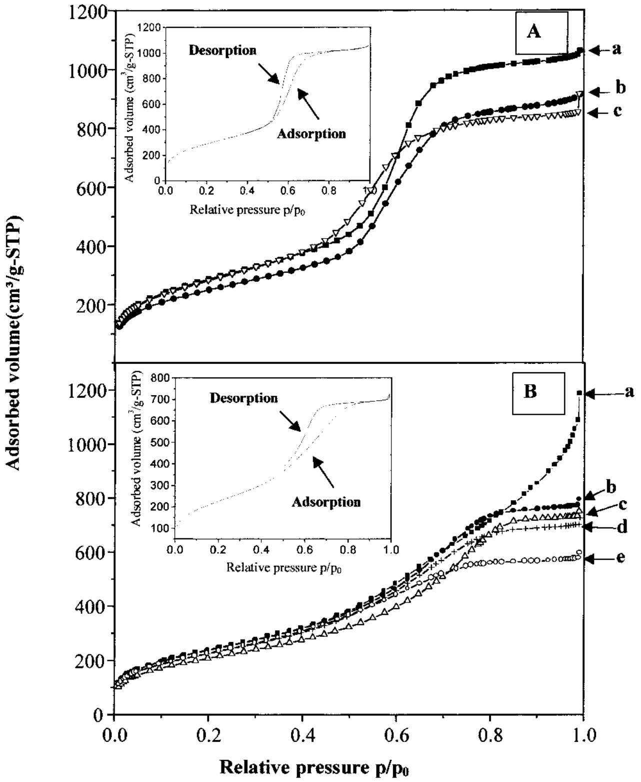

Figure 4. Nitrogen adsorption isotherms of compounds synthesized with a weight percentage of $C_{16}(EO)_{10}$ (wt %) (A) inferior to 30 [(a) 10, (b) 20, (c) 25)] and (B) superior or equal to 30 [(a) 30, (b) 40, (c) 45, (d) 50, (f) 60].

observed for the samples obtained with surfactant concentration less than 30 wt % (Figure 4A) whereas a hysteresis loop similar to H_2 type in which the desorption branch is steep but adsorption branch is more or less sloping[33] corresponds to samples prepared with a surfactant concentration higher than 30 wt % (Figure 4B). The H_2 type hysteresis loop can arise from the same type of open capillaries as are responsible for H_1 hysteresis loop which can be observed very commonly from MCM-41 type materials with a very regular arrangement of channels with very homogeneous openings. The H_2 type hysteresis loop is often encountered for disordered materials with a wormhole structure and represents that the effective radii of narrow entrances are all of equal size although an H_1 type hysteresis loop was also recently observed for MSU-type materials by Boissière et al.[15] The above observation suggests that the pore size distribution of wormholelike structured materials is relatively larger than that of MCM-41-type materials. The BJH treatment of nitrogen adsorption data will confirm our present analysis, and we will discuss further in detail below the pore size distribution of all our samples.

All the synthesized materials exhibit a type IV isotherm[34] (Figure 4A,B) except the material synthesized with a surfactant concentration of 30 wt %. The pore volume (Table 2) measured by the volume of nitrogen adsorbed in the pores of the materials obtained with surfactant weight percentages less than 30, i.e., CMI-1 materials (Figure 4A), is higher than for compounds synthesized with surfactant concentrations exceeding 30 wt %, i.e., disordered materials with wormholelike channels (Figure 4B).

For samples synthesized with a weight percentage of $C_{16}(EO)_{10}$ less than 30, i.e., CMI-1 (Figure 4A), the sharp increase of the adsorbed volume of nitrogen due to capillary condensation occurs at a relative pressure $p/p_0 = 0.50$. This part of the curve is almost vertical, indicating a high homogeneity in pore size distribution of the final product since the p/p_0 position of the inflection point is related to the pore diameter according to the Kelvin equation.[33] The pore diameter distribution determined by using the BJH method is quite narrow and approximately centered at 4.4 (±0.3) nm (Figure 5A). However, if the loading of surfactant is raised, the capillary condensation is spread out over a larger range of relative pressures, meaning that compounds become less homogeneous in pore sizes. This is confirmed by the broader pore diameter distribution (Figure 5B), reflecting the transition from a well-ordered mesoporous material, with a uniform pore diameter, labeled as CMI-1, to a disordered structure with wormlike channels. The above analysis and the observations of two types of hysteresis loops are in agreement with the XRD and TEM results, and thus, we can conclude that a weight percentage of templating agent equal to 30 is the upper limit to obtain well-ordered CMI-1 mesoporous materials.

It should be noted that, in the case of the isotherm of the sample prepared with 30 wt % of $C_{16}(EO)_{10}$, the adsorbed volume of nitrogen increases significantly at high relative pressures instead of remaining constant due to saturation. This compound contains very large secondary mesoporosity or even macroporosity, which can be clearly observed from Figure 3e. This secondary mesoporosity or macroporosity could come from the interparticle pores or the pores produced by ethanol extraction and calcination. The condensation of nitrogen in these large mesopores or macropores very likely occurs in addition to the adsorption inside the channels. This complementary textural mesoporosity and macroporosity makes the transport of reagents to framework reaction centers more efficient and thus favors the catalytic activity. In a paper dealing with applications of mesoporous molecular sieves with wormhole framework structures, Pinnavaia et al.[35] show that the catalytic activity of HMS compounds for a sterically demanding condensed phase reaction, such as the alkylation of 2,4-di-*tert*-butylphenol with cinnamyl alcohol, is strongly affected by the textural mesoporosity that facilitates the arrival of reagents to the framework mesopores. The behavior of this sample can be explained by the transition from well-ordered material CMI-1 to disordered wormhole mesostructures (DWM), with increasing the weight percentage of surfactant in aqueous solution. There is a competition between the formation of the two structures, on one hand a well-ordered hexagonal phase and on the other hand the disordered structure with a wormlike channel array. As discussed above, the morphology of the samples obtained with surfactant loadings lower or higher than 30% is quite

---

(33) Gregg, S. I.; Sing. K. S. W. *Adsorption, Surface Area and Porosity*, 2nd edition.; Academic Press: London, 1982.

(34) Brunauer, S.; Deming, L. S.; Deming, W. S.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723.

(35) Pauly, T. R.; Liu, Y.; Pinnavaia, T. J.; Billinge, S. J. L.; Riecker, T. P. *J. Am. Chem. Soc.* **1999**, *121*, 8835.

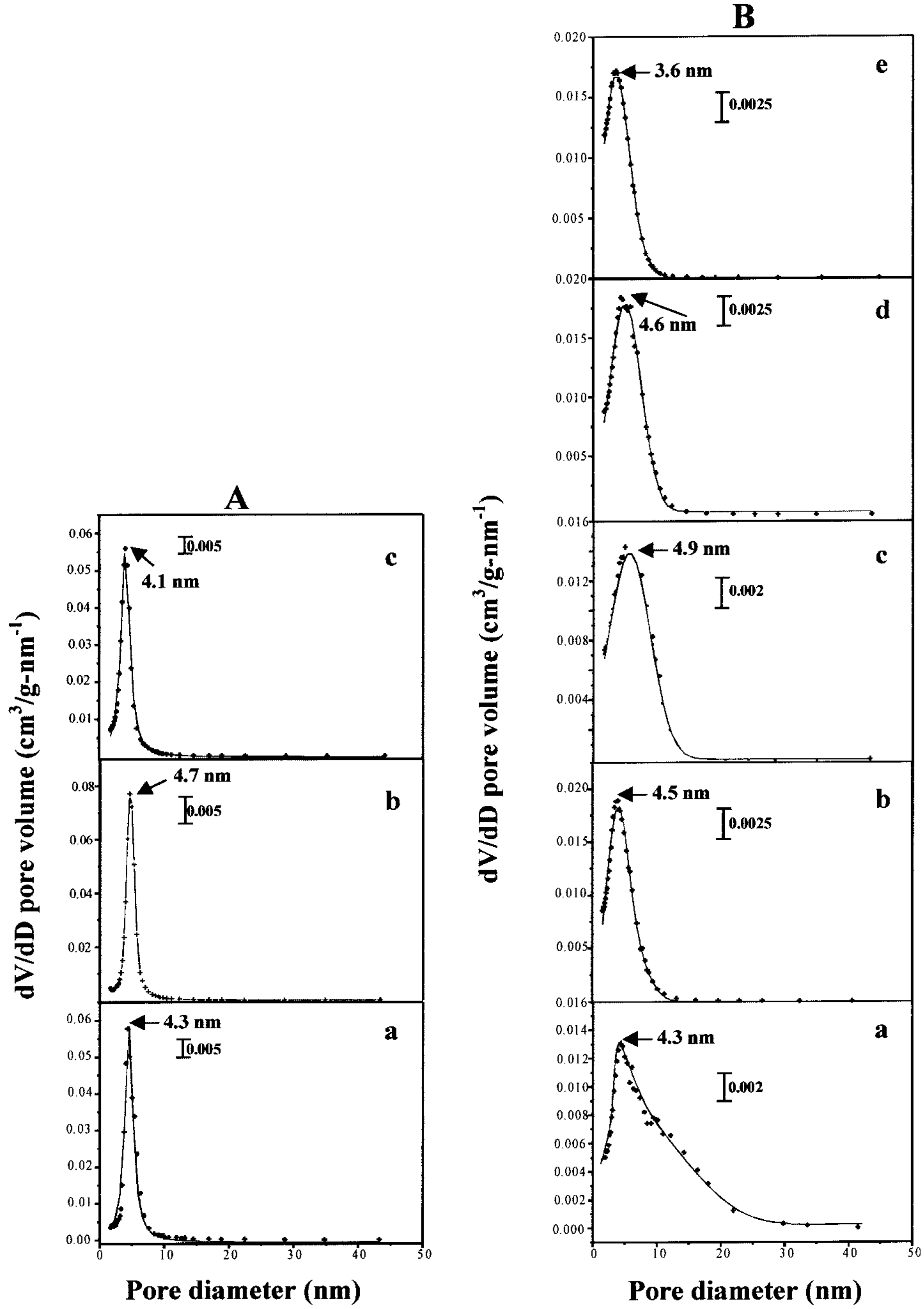

Figure 5. Pore size distribution of compounds synthesized with a weight percentage of $C_{16}(EO)_{10}$ (wt %) (A) inferior to 30 [(a) 10, (b) 20, (c) 25] and (B) superior or equal to 30 [(a) 30, (b) 40, (c) 45, (d) 50, (f) 60].

different. The former consists of agglomerates of small spheres while the latter is formed by agglomerates of irregular edge-shaped particles. The morphology of the sample obtained with 30 wt % of surfactant in aqueous solution corresponds to large porous sponge particles. This means that not only the inorganic network obtained at this surfactant loading is the result of the competition between CMI-1 and DWM compounds but also the morphology is likely to emerge from the competition between the agglomerates of spherical particles and the agglomerates of irregular edge-shaped particles. All these competitions lead to a different and special nitrogen adsorption behavior of this sample. Due to the existence of secondary mesoporosity and macroporosity in very small fractions, they are not evidenced in the pore size distribution curve obtained from BJH method.

As illustrated in Figure 6A and Table 2, the value of the specific surface area is high whatever the surfactant concentration is. Nevertheless, a slight decrease is noted beyond 30 wt %; the value varies from 1000 to 800 m^2/g with increasing the weight percentage of surfactant from 25 to 30. This confirms again that something happens at around a surfactant concentration of 30 wt %. As discussed above, at a surfactant weight percentage of 30 in aqueous solution, well-ordered CMI-1 phase and disordered wormhole structure phase coexist. This weight percentage is a border for two phases. Decreasing the weight percentage from 30 favors the formation of CMI-1 structure, while increasing the weight percentage leads to the formation of disordered wormhole structures. Concerning the pore diameter (Figure 6B and Table 2), the value remains practically constant in

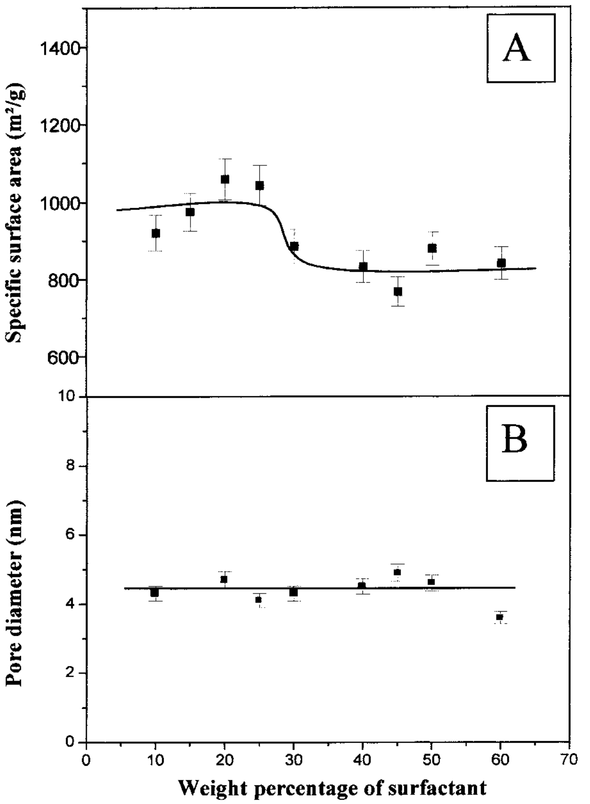

Figure 6. Variation of the specific surface area (A) and pore diameter (B) with the weight percentage of $C_{16}(EO)_{10}$.

the templating agent concentration domain investigated. However, as observed, the pore size distribution appears to be broader when the transition from CMI-1 materials to disordered wormhole molecular sieves occurs (Figure 5). The constant pore diameter observed at any surfactant weight percentage gives very important information and indicates that the size of micelles formed in aqueous solution is the same and is independent of the surfactant weight percentage while the wall thickness should be lower in the samples synthesized with surfactant concentration higher than 30 wt % as discussed in the section 3.1.1.

4. Discussion

4.1. Synthesis Pathway as a Function of Surfactant Concentration. In the present study, where $C_{16}(EO)_{10}$ is employed, two main tendencies are observed, depending on the surfactant concentration. For surfactant weight percentages superior to 30, the surfactant concentration is located in the zone of the normal hexagonal phase (H_1), so mesostuctures with this symmetry could be expected. However, the XRD, TEM, and nitrogen adsorption results show that the channel array is disordered. Whereas, for a $C_{16}(EO)_{10}$ loading less than 30%, in contrary to expectation, well-organized CMI-1 materials with the regular hexagonal arrangement of channels are prepared. We propose therefore two different mechanisms for the synthesis of CMI-1 and DWM materials.

4.1.1. Materials Synthesized with a High Weight Percentage of $C_{16}(EO)_{10}$ (>30). The schematic representation of the proposed synthesis mechanism is given in Figure 7. When the TMOS is added to the aqueous solution of micelles having a hexagonal structure (H_1), hydrogen-bonding type interactions between the oxygen atoms of the ethoxy headgroups of the surfactant and hydrogen atoms of the silica source occur. Then, when the polymerization of silica takes place, it disturbs the H_1 regular array of the formed micelles and the channels slightly move in order to minimize steric and electrostatic energies. Thus, the regular organization of the preformed micelles is lost and the obtained materials will be disordered. Only one broad peak is detected on the XRD pattern; channels with a wormlike structure are observed by TEM, and a H_2 type hysteresis loop can be noted from nitrogen adsorption, which indicates that the recovered compounds are DWM materials. The results obtained by Pinnavaia et al. using neutral pH value with TEOS as silica precursor confirm our present proposition. One may think that the important production of methanol in the course of the hydrolysis reaction of TMOS (one molecule TMOS after its hydrolysis produces 4 molecules of methanol) can disturb the preformed hexagonal micellar array in aqueous solution since Attard et al.[16] have reported the effect of methanol as a liquid crystal breaker in a 50 wt % micellar solution of $C_{12}(EO)_8$ and $C_{16}(EO)_8$. This effect can be expected to be more significant with increasing the surfactant concentration since we fixed the surfactant/TMOS molar ratio to 1.5. Increasing the surfactant weight percentage in water means the increase of TMOS amount in the gel. Table 3 gives the comparison of the estimated amount of methanol produced during the synthesis at different surfactant weight percentages. The amount of methanol increases with increasing TMOS amount and the effect of methanol as liquid crystal breaker will be enhanced. In the work performed by Attard et al.[16] with a 50 wt % micellar solution of $C_{12}(EO)_8$ (i.e. $C_{12}(EO)_8:H_2O\ (pH = 2):TMOS = 1:1:2$ by weight), the amount of methanol released from the hydrolysis of the TMOS is very high (estimated concentration: 52.63 mol/L) and the H_1 liquid crystal phase formed in micellar solution can be destroyed by the high amount of methanol released. However, in the present work, also with a 50 wt % micellar solution and surfactant/TMOS molar ratio of 1.5, the weight ratio of the gel is $C_{16}(EO)_{10}:H_2O:TMOS = 1:1:0.15$. The amount of the TMOS added is much lower than that in the work by Attard et al.;[16] the amount of methanol released (4.00 mol/L) is also much lower. For a weight percentage of 30 and 40 wt %, H_1 liquid crystals are present in solution and the amount of the released methanol becomes insignificant compared with the amount of water in solution (Table 3). However, only DWM materials are obtained and H_1 liquid crystals do not lead to the formation of hexagonal mesostructured solids. Furthermore, the liquid crystal breaker effect was not observed for ethanol. At least until now, no paper has described this effect played by ethanol, although it was reported that the addition of alcohols such as 1-butanol, 1-propanol, 1-pentanol, cyclohexanol, and phenol in the synthesis mixture for MCM-41 promotes an amorphous product.[36] Pinnavaia et al. using TEOS with 7 and 25 wt % liquid crystal solution of $C_{16}(EO)_{10}$ obtained only the disordered wormholelike mesoporous materials.

---

(36) Beck, J. S. U.S. Patent 5,057,296, 1991.

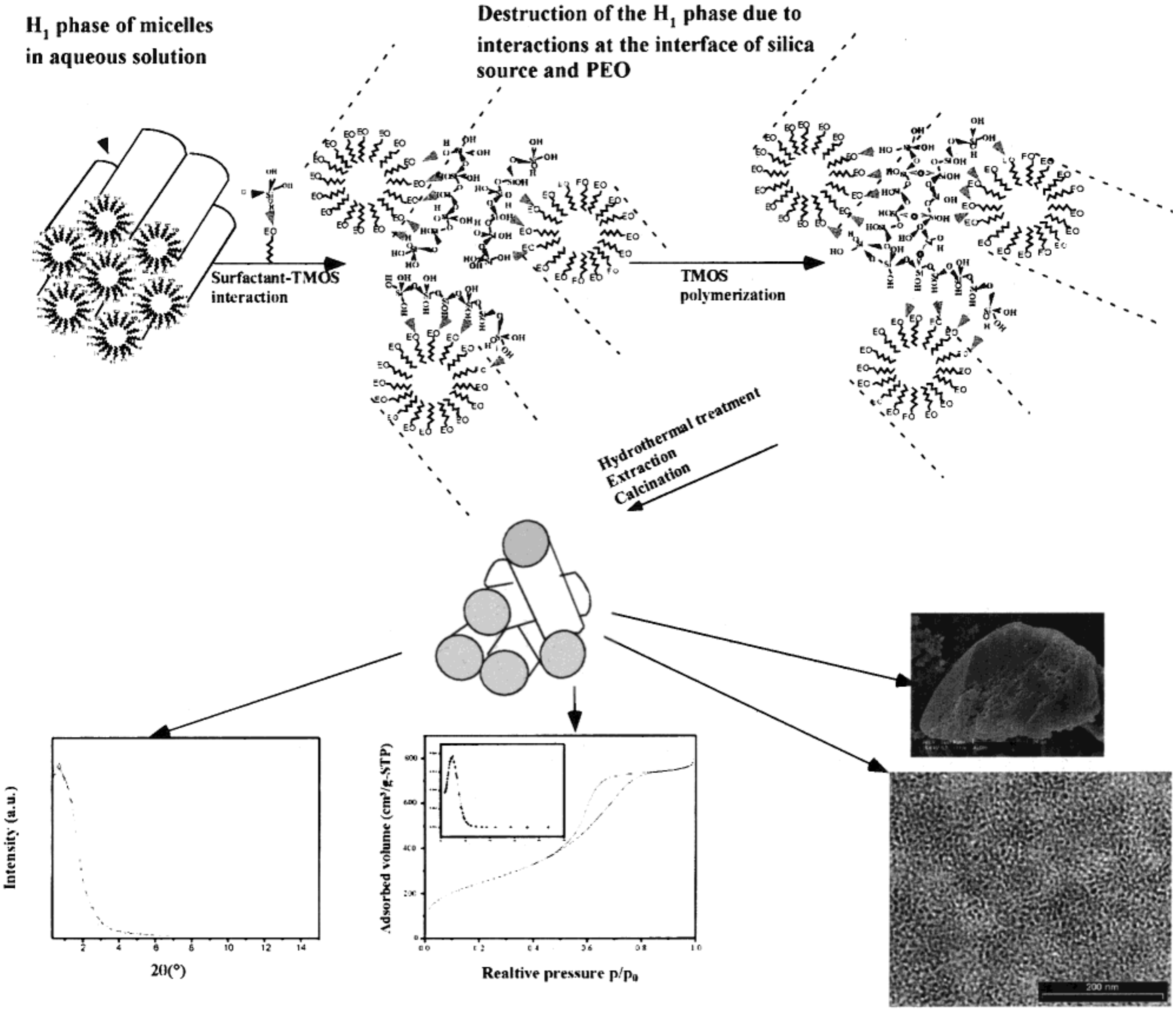

Figure 7. Schematic representation of the proposed synthesis mechanism for materials obtained with a weight percentage of $C_{16}(EO)_{10}$ > 30%.

Table 3. Estimated Amount of Methanol Produced from TMOS in Autoclave after Its Hydrolysis at Different Surfactant Weight Percentages in Water (Surfactant/TMOS Molar Ratio = 1.5)

surfactant wt percentage (wt %)	10	20	30	40	50[a]	60
surfactant concn (mol/L)	0.16	0.369	0.649	1.01	1.51	2.27
TMOS concn (mol/L)	0.112	0.252	0.433	0.67	1.00	1.51
methanol concn (mol/L)	0.448	1.08	1.73	2.68	4.00	6.05

[a] In the synthesis performed by Attard et al.[16] the methanol concentration is 52.63 mol/L with a surfactant concentration of 50 wt % [$C_{12}(EO)_8$:H_2O:TMOS = 1:1:2 by weight].

From the above discussion, we can conclude that the effect of the methanol as liquid crystal breaker can certainly not be neglected since the work performed by Attard et al. with a chemical composition by weight of 1.80 TMOS:1.0 Brij 56:0.25−5000 acidified H_2O (the amount of TMOS is very high) and which will be published soon[37] proved indeed that regular materials could be obtained by removing methanol using a rotary evaporator. However, the interface interactions between the surfactant and the hydroxyl groups of silica sources also play an even more important role in the destructuration of the H_1 liquid crystals in solution.

4.1.2. Materials Synthesized with a $C_{16}(EO)_{10}$ Loading <30%, i.e., CMI-1. The formation mechanism illustrated in Figure 8 is analogous to that developed by Mobil's scientists.[1] First, the isolated micelles of surfactant are formed since the concentration of surfactant in aqueous solution is low. When the silica is added as mentioned above, hydrogen-bonding interactions between the oxygen atoms of the ethoxy headgroup of the surfactant and hydrogen atoms of TMOS appear. To complete polymerization of tetramethoxysilane, these rodlike supramolecular assemblies (template−silica) have to pack together, which involves a highly ordered arrangement of the channels as it can be seen from the TEM micrographs. Well-organized mesoporous molecular sieves CMI-1 are thus formed. This involves a

---

(37) Attard, G. S.; et al. *Microporous Mesoporous Mater.* **2001**, in press.

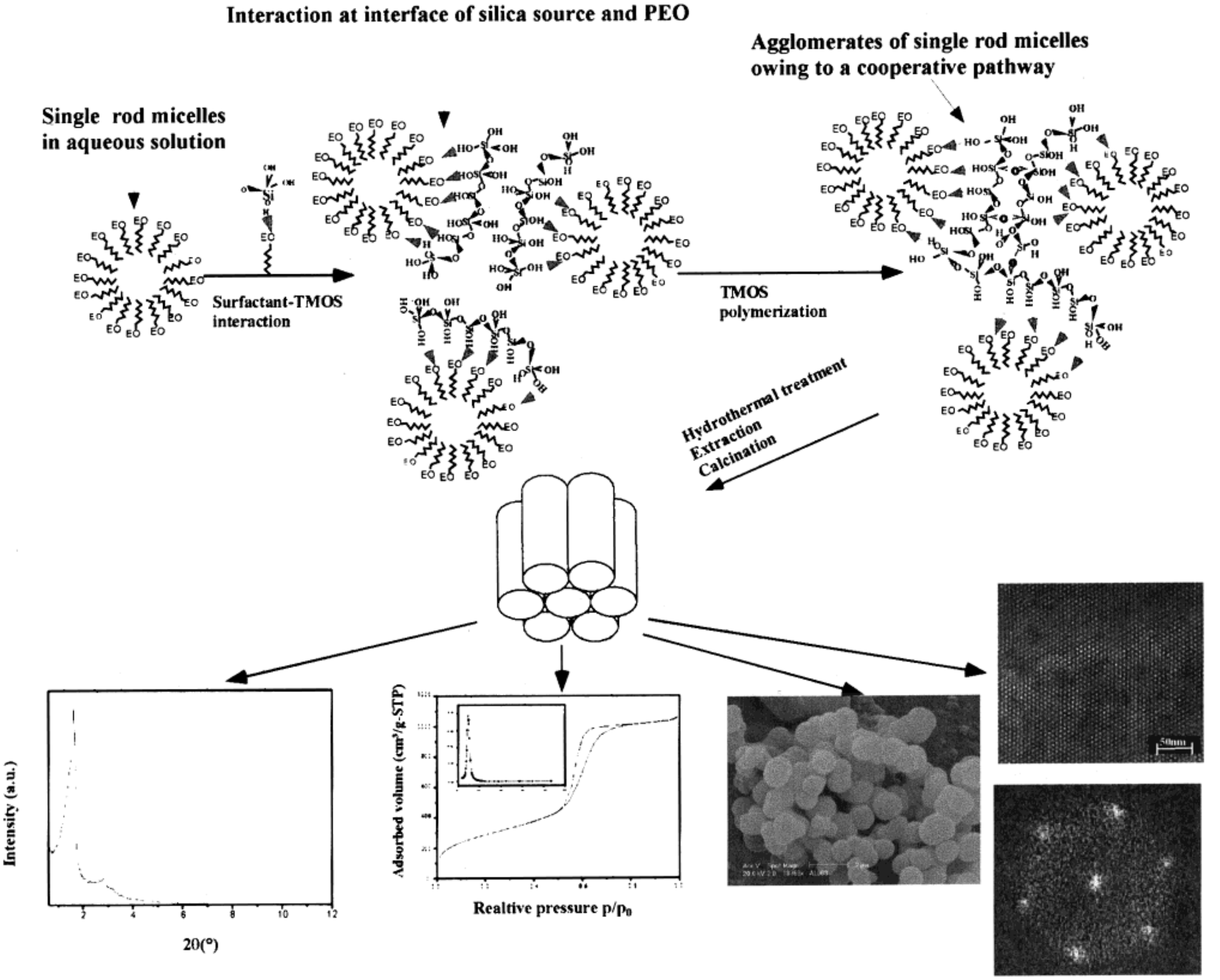

Figure 8. Schematic representation of the proposed synthesis mechanism for CMI-1 molecular sieves (surfactant weight percentage < 30%).

cooperative mechanism, which is clearly described in Figure 8; i.e., hydroxyl groups of silica source produced by the hydrolysis reaction interact with hydrophilic chain heads of surfactant molecules and the polymerization of silica species at the interface of rod micelles attracts the rod micelles covered by the silica source together to form a regular arrangement, leading to CMI-1 materials.

It should be noted that the materials obtained with surfactant weight percentage of 30 are the results of the competition of these two mechanisms. Both CMI-1 and DWM materials are simultaneously present. That is why this material has specific behavior in XRD, nitrogen adsorption, and morphology.

One may ask also why, with 7 wt % of surfactant concentration in neutral media, no ordered materials with hexagonal array of channel were obtained by Pinnavaia et al.[12] if no effect of ethanol as liquid crystal breaker was observed and since at this concentration no H_1 phase was formed? This can be explained by the difference in preparation conditions (acidic, neutral, or basic media), which affect the polymerization of silica source and, consequently, the cooperative synthesis pathway and organization of mesophases during the hydrothermal treatment. We have also shown that the preparation conditions of micellar solution can strongly influence the mesostructure and morphology formed.

5. Conclusion

Spherical CMI-1 molecular sieves with hexagonal structure have been synthesized in a relatively wide range (10−25) of weight percentage of decaoxyethylene cetyl ether in the micellar solution under mild acidic conditions with which no synthesis of ordered mesoporous materials has been reported yet in the literature.

Two synthesis mechanisms have been proposed for the synthesis of CMI-1 and DWM materials. The first one deals with high surfactant loadings. When the tetramethoxysilane molecules are added to the aqueous solution of micelles having a hexagonal structure, their interactions with surfactant molecules induce a displacement of the channels and the recovered materials have the DWM characteristics. The second one concerns CMI-1 synthesis, i.e., compounds prepared with a weight percentage of $C_{16}(EO)_{10}$ less than 30. After the addition of silica, to reach a complete polymerization of tetramethoxysilane, the supramolecular template−silica assemblies have to pack together, which conducts to a highly ordered arrangement of the channels. This is a cooperative effect of interface interactions of hydroxyl groups of silica source rod micelles and polymerization of silica source covering the outer layer of rod micelles.

Acknowledgment. This work has been performed within the framework of PAI/IUAP 4-10. We thank Prof. P. A. Jacobs and Mrs. L. Leplat of KU Leuven for XRD measurements. A.L. thanks the FNRS (Fond National de la Recherche Scientifique, Belgium) for a FRIA scholarship.

CM0011965