

# Synthesis of Large Pore Disordered MSU-Type Mesoporous Silicas through the Assembly of $C_{16}(EO)_{10}$ Surfactant and TMOS Silica Source: Effect of the Hydrothermal Treatment and Thermal Stability of Materials

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Decaoxyethylene cetyl ether [ $C_{16}(EO)_{10}$ ] has been employed as templating agent for large pore disordered MSU-type mesoporous silicas synthesis. The effect of the hydrothermal treatment (heating time and temperature) on the textural properties, in particular, pore diameter of materials has been investigated. The obtained materials have been characterized by different techniques such as X-ray diffraction, scanning and transmission electron microscopy and nitrogen adsorption–desorption analysis. The thermal stability of the compounds is also evaluated. Our results show that the pore diameter depends strongly on the heating time and temperature. This is the result of a competition between the stretching of the surfactant chains, which can lead to the breakdown of the walls separating adjacent pores, and the reorganization of micelles with heating time and temperature. At higher temperature or for longer durations, a more extended surfactant molecular conformation can be obtained, which leads to materials with larger pore sizes. A reorganization of the micellar solution during the hydrothermal treatment in autoclave can also simultaneously occur to give materials with smaller pore diameter. It is found that compounds prepared with the nonionic surfactant exhibit an enhanced thermal stability compared to those synthesized with cetyltrimethylammonium bromide (CTMABr) as templating agent. This higher stability is related to the synthesis pathway and the structure of materials.

## 1. Introduction

The synthesis of highly ordered mesoporous materials MCM (Mobil Crystalline Materials)<sup>1,2</sup> has opened a wide field of potential applications including catalysis,<sup>3</sup> separation processes,<sup>4</sup> or use as supports for transition metal complexes<sup>5</sup> or amines.<sup>6</sup> For example, Kageyama et al.<sup>7</sup> reported that Ti–MCM-41 could be used as a host matrix for the polymerization of ethylene. The synthesis called “extrusion polymerization” produces polyethylene fibers with a diameter varying between 30 and 50 nm after assembly at the outflow of these oriented nanoreactors. In the context of treatment of large molecules, many efforts are devoted to enlarge the pore size of mesoporous materials. Different methods can be employed to reach this goal. With the use of cetyltrimethylammonium bromide (CTMABr) as templating agent, hydrothermal postsynthesis treatment,<sup>8,9</sup> and the addition of swelling agents, such as tetralkylammonium cations ( $TAA^+$ ),<sup>10</sup> amines,<sup>11</sup> 1,3,5 trimethylbenzene (TMB),<sup>12–13</sup> alkanes,<sup>14–16</sup> or jointly decane and TMB,<sup>17</sup> in the micellar solution have been shown to be quite efficient ways. Another route is to perform the synthesis with a surfactant that is able to form bigger size micelles in solution than CTMABr. Triblock copolymers, such as poly(ethylene oxide)–polypropylene oxide–poly(ethylene oxide) (PEO–PPO–PEO),<sup>18–19</sup> or polyoxyethylene alkyl ethers [ $C_m(EO)_n$ ]<sup>20–26</sup> are excellent candidates for this purpose. PEO–PPO–PEO surfactants lead to the formation of SBA (Santa Barbara) materials, whereas in the case of  $C_m(EO)_n$  samples are called MSU (Michigan State University),<sup>20</sup> SBA,<sup>8</sup> or CMI-1 (Chimie des Matériaux Inorganiques)<sup>27</sup> depending on the synthesis conditions.

Because of their wide application field which is related to the hydrophile–lipophile-balance number (HLB),<sup>28–29</sup> the behavior of polyoxyethylene alkyl ethers in solution has been extensively studied in the literature and phase diagrams were well-established.<sup>30–31</sup> They can be used as emulsifiers ( $3 \leq HLB \leq 6$ ), wetting agents ( $7 \leq HLB \leq 8$ ), detergents ( $13 \leq HLB \leq 15$ ), or solubilizers ( $15 \leq HLB \leq 18$ ). With this kind of surfactant, the synthesis of mesoporous materials can be achieved via a neutral pathway ( $N^0I^0$ ), which involves hydrogen bonding between the oxygen atoms of the ethoxy headgroup ( $N^0$ ) and hydrogen atoms of the neutral inorganic precursor ( $I^0$ ). The first syntheses of mesoporous molecular sieves achieved by using this kind of surfactants were reported by Attard et al.<sup>32</sup> Then Stucky et al.<sup>19</sup> reported new cubic ( $Pm\bar{3}m$ ) and hexagonal ( $P6_3/mmc$ ) mesoporous silica structure respectively denoted SBA-11 and SBA-12, which were synthesized in strong acid media ( $pH \ll 1$ ) at room temperature with decaoxyethylene cetyl ether [ $C_{16}(EO)_{10}$ ] for SBA-11 and decaoxyethylene oleyl ether [ $C_{18}(EO)_{10}$ ] for SBA-12. The surfactant concentration in aqueous solution was in the range of 4–6 wt %. The assembly of the inorganic and organic entity occurs by a hydrogen bonding ( $S^+H^+$ ) ( $X^-I^+$ ) pathway. Pinnavaia et al.<sup>20–24</sup> also used the same surfactant and synthesized successfully wormlike-structured MSU mesoporous silica in near neutral conditions with surfactant concentration of 25 or 50 wt %. Very recent works by present authors showed that well-organized mesoporous silica with hexagonal arrangement of channels, labeled as CMI-1, can be prepared under mild acidic ( $pH = 2$ ) conditions at 80 °C, the surfactant concentration in aqueous solution being in a wide range of around 10–25 wt %.<sup>27</sup> If the surfactant concentration is raised greater than 30%, for example from 30 to 60 wt %, both mild acidic or basic media conduct to the

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formation of MSU-type mesoporous materials<sup>25,27</sup> as reported by Pinnavaia in neutral pH media.<sup>20–24</sup> MSU-type materials were reported to be very interesting for catalysis applications.<sup>24</sup>

Our previous results obtained with  $C_{13}(EO)_n$  ( $n = 6, 12, 18$ )<sup>26</sup> and  $C_{18}(EO)_{10}$ <sup>25</sup> showed that the structural and textural properties of final compounds were strongly affected by the physicochemical parameters such as surfactant/silica molar ratio, pH value of the micellar solution, stirring time, and, in particular, by the time and temperature of the hydrothermal treatment. The present paper reports a systematic study dealing with the effect of hydrothermal treatment conditions, which are less well studied, on large pore molecular sieve synthesis using  $C_{16}(EO)_{10}$  as the template. All the syntheses were driven with a surfactant concentration of 50 wt % in aqueous solution. Previous work showed that this surfactant concentration would lead to the formation of disordered mesoporous materials.<sup>27</sup> However, the study was carried out for a given hydrothermal temperature (80 °C) and time (1 day). The present study has therefore been made in order to follow closely all the steps of the synthesis. We try to better understand the determining factors others than chemical ones on the formation of materials with relatively high surfactant concentration to find some correlations between the pore size and hydrothermal conditions and to shed some light on the molecule level on effect of the hydrothermal treatment on the synthesis mechanism. The thermal stability of final compounds has also been evaluated.

## 2. Experimental Section

**2.1. Preparation of the Micellar Solution: Weight Percentage and Temperature.** The cloud point values of the  $C_{16}(EO)_{10}$ , which arises from a balance of intermicellar van der Waals attractions and hydration repulsion, is 77 °C.<sup>33</sup> For a good solubility of surfactant in water, the temperature for the micellar solution preparation was 70 °C. Mesoporous materials synthesis takes profit of the supramolecular assemblies of surfactant molecules as framework templates. In aqueous solution, these molecules pack together to form first isolated spherical, then cylindrical micelles and finally highly ordered phases, depending on preparation conditions. The synthesis of pure siliceous mesoporous molecular sieves consists of the condensation and polymerization of an inorganic source of silica around the micelles of surfactant. If the interactions between the surfactant and the inorganic precursor do not disturb the array of the micelles in solution, we can expect that the organization of the micelles will determine the structure of the final compounds. Considering the phase diagram of  $C_{16}(EO)_8$  and  $C_{16}(EO)_{12}$ , established by Mitchell et al.,<sup>30</sup> we can deduce for  $C_{16}(EO)_{10}$  that from 15 to 85 °C a hexagonal  $H_1$  phase is present in aqueous solution for a weight percentage of surfactant located between 30 and 65%. However, we showed that with surfactant concentration between 30 and 65% only disordered mesoporous materials were obtained for a hydrothermal temperature and time of 80 °C and 1 day. To study the effect of hydrothermal conditions on the synthesis of MSU-type mesoporous materials, a surfactant concentration of 50 wt % was chosen in the present work.

**2.2. Syntheses. Disordered MSU-Type Mesoporous Materials.** The micellar solution with 50% (wt) of  $C_{16}(EO)_{10}$  surfactant was prepared by dissolving the surfactant at 70 °C in an aqueous solution. The pH value of the micellar solution was then adjusted with  $H_2SO_4$  to 2.0. The obtained solution was stirred for 3 h at same temperature before adding drop by drop the silica source: tetramethoxysilane (TMOS). The surfactant/silicium molar ratio is fixed at 1.5, according to our previous work.<sup>34</sup> The obtained gel was sealed in Teflon autoclaves and heated. Heating time

and temperature vary respectively from 0 to 15 days and from 60 to 100 °C. The final products were obtained after ethanol extraction with a Soxhlet apparatus during 30 h. The further calcination at 550 °C was made as follows: The first step was accomplished under a nitrogen atmosphere. The samples were heated to 150 °C at a rate of 2 °C/min and remained during 1 h at this temperature. Then, the same program was applied to reach 350 °C and the final desired calcination temperature (550 °C). When final temperature was attained, the flow of oxygen was introduced and the calcination at this step was maintained for 12 h. For the thermal stability study of the samples, the calcination was performed identically, only the final temperature was different (550, 600, 700, 800, 900, and 1000 °C).

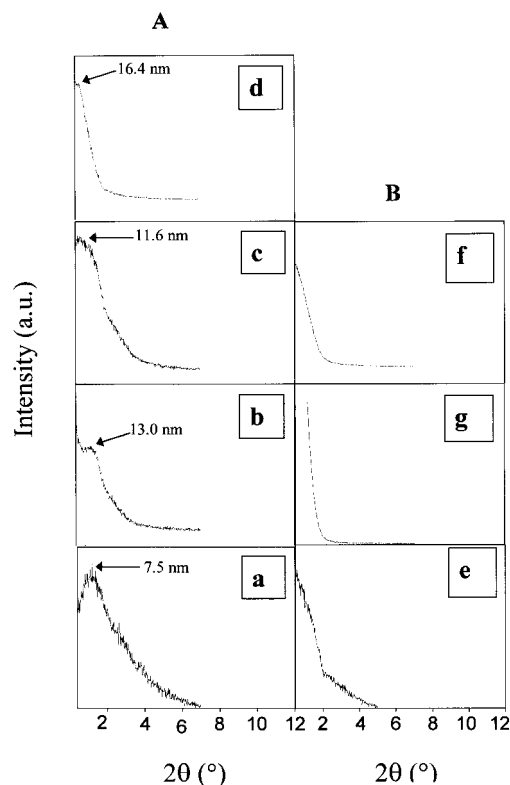
**Large Pore MCM-41.** Cetyltrimethylammonium bromide was dissolved in water at 40 °C to obtain a clear micellar solution, in which the two swelling agents (decane and TMB) were introduced drop by drop. Then sodium silicate was added to this solution and the pH value was adjusted with sulfuric acid. The pH value and the surfactant/silica molar ratio were fixed at 10 and 0.62. After it was stirred for several hours at room temperature, the homogeneous gel with the following composition 1.0 CTMABr, 0.63  $SiO_2$ , 2  $C_{10}H_{22}$ , 1.5 TMB, 102  $H_2O$  was sealed in Teflon autoclaves and heated. The synthesis temperature and time were respectively 80 °C and 1 day according to our previous work.<sup>17</sup> The solid phase was obtained after ethanol extraction and calcination in the same conditions as that for MSU-type materials.

**2.3. Characterization.** The XRD patterns were obtained with a Siemens D 5000-Matic diffractometer equipped with a copper anticathode producing X-rays with wavelength equal to 1.54178 Å. The morphology of the obtained intermediate and final phases was studied using Philips XL-20 Scanning electron microscope (SEM) using 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 in a vacuum for several hours at 320 °C before nitrogen adsorption measurements. The pore diameter and the pore size distribution were determined by the BJH method,<sup>35</sup> although it is well-known that this method gives underestimated pore size values and some new interesting methods have been developed recently by Jaroniec et al.<sup>36</sup> From our knowledge and discussions with different researchers<sup>37</sup> who work on the establishment of new calculation method for pore size distribution, until now, no method can give an accurate determination for materials with pore sizes larger than 5 nm. Moreover, the treatment of adsorption data with this method will not affect significantly our systematic comparison.

## 3. Results and Discussion

**3.1. Kinetic Study of Large Pore Mesoporous Materials Synthesis.** The physical properties of the obtained compounds are found to be dependent on several factors such as pH value of the micellar solution, surfactant/silica molar ratio, and weight percentage of surfactant, but also the heating time and temperature. Here, we have thus investigated the effect of hydrothermal treatment, i.e., heating time and temperature on the formation of large pore mesoporous materials.

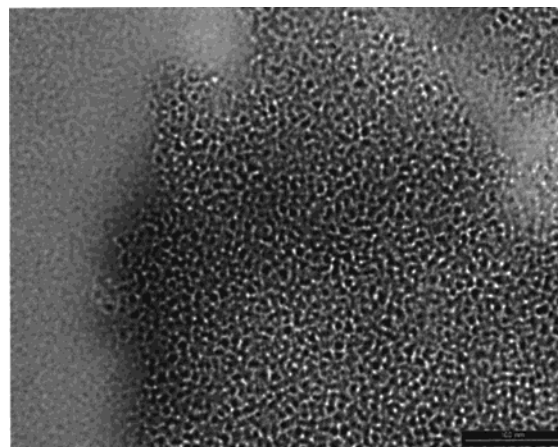
**3.1.1. XRD Analysis.** Figure 1 reports the XRD patterns of materials obtained at 60 °C (a, b, c, d of Figure 1A), 80 °C (e and f of Figure 1B), and 100 °C (g of Figure 1B) at different synthesis times. It has been reported<sup>38</sup> that X-ray diffractograms of high quality powder hexagonal mesoporous materials exhibit



**Figure 1.** XRD diffraction patterns of compounds synthesized at 60 °C for (a) 0, (b) 2, (c) 3, (d) 11 days; at 80 °C for (e) 1, (f) 8 days; at 100 °C for (g) 2 days.

patterns with at least four peaks with a very strong feature at a low angle of  $2\theta$  (100 reflection line) and other peaks at a higher angles (110, 200, 210, ... reflection lines). These reflection lines can be indexed on a hexagonal unit cell ( $a_0 = 2d_{100}/(3)^{1/2}$ ). The presence of the only first peak suggests a disordered structure of the compound.

From Figure 1 it is observed that, at low temperature (60 °C), only one peak located at 13.0, 11.6, and 16.4 nm for heating times of 2 (Figure 1b), 3 (Figure 1c), and 11 days (Figure 1d) respectively, is detected. This indicates that the samples do not have the hexagonal structure. However, according to the phase diagram, a hexagonal structure of micelles is indeed present in aqueous solution before adding the silica source. Thus, in agreement with our previous observations,<sup>27,34</sup> we can conclude that the interaction between TMOS and hydrophilic head of decaoxyethylene cetyl ether disturbs the array of the micelles formed in solution. The presence of only one reflection line indicates that the compounds belong to the MSU family. As discussed in introduction part, these molecular sieves have a structure of regularly sized wormlike channels. The diffractograms exhibit only a broad peak, arising from the average pore to pore separation in the disordered wormhole framework, which present a lack of the long-range crystallographic order. The TEM picture of one of our samples reported in Figure 2 confirms the wormhole-like structure of our materials and its adherence to MSU family. If the heating temperature is increased to 80 (Figure 1e,f) or 100 °C (Figure 1g), no peak is detected any more after 2 days of hydrothermal treatment. This first results from the fact that the quite large pore size makes the reflection line, typical of MSU-type materials, appeared at so small angle that no peak characteristic of the MSU-type material structure can be detected by our conventional XRD diffractometer. On the other hand, as we will discuss below, for some samples, the pore size distribution is relatively broad and it becomes more



**Figure 2.** TEM micrograph of a typical sample.

or less inhomogeneous, meaning that the regular size of the channels could be very likely partly lost.

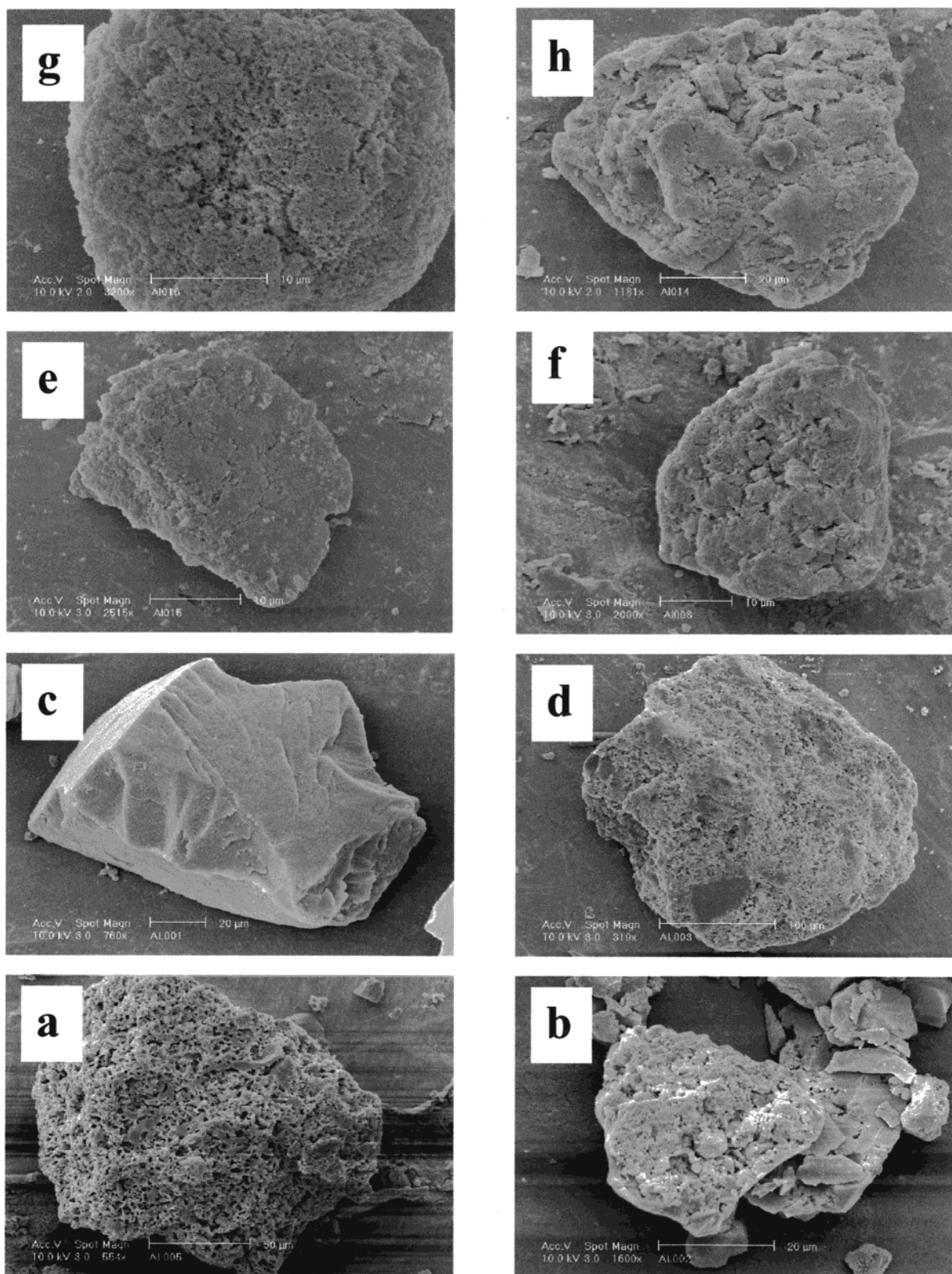
It should be noted that for the sample which has not been subjected to a hydrothermal treatment, one reflection situated at 7.5 nm (a of Figure 1A) is present on the XRD pattern. So, when tetramethoxysilane is added to the prepared micellar solution and pH is adjusted, the condensation and polymerization of the silica take place around the micelles of surfactant. This is suggestive of the formation of mesoporous materials even before the hydrothermal treatment. Moreover, the hydrothermal treatment will affect the textural properties and in particular the pore diameter of final compounds.

**3.1.2. Particles Morphology.** Figure 3 shows scanning electron micrographs, representing the variation of morphologies with synthesis time and temperature at 60 °C (Figure 2a–d), 80 °C (Figure 2e and f) and 100 °C (Figure 2h). The particles morphology is not significantly influenced by the hydrothermal treatment. For all compounds, irregular edge-shaped large particles with variable sizes and forms are obtained. At the microscopic scale, i.e., micrometer range, the surface of most of samples appears to be very porous. This suggests that in addition to the mesopores some macropores could be present.

**3.1.3. Nitrogen Adsorption–Desorption Analysis.** Both nitrogen adsorption and desorption branches of one of our samples (Figure 4A) are represented. For the sake of clarity, Figure 4B compares only the nitrogen adsorption branches of three samples obtained at 60 (Figure 4Ba), 80 (Figure 4Bb), and 100 °C (Figure 4Bc) for a heating time of 4 days. Figure 4C depicts the nitrogen adsorption branches of samples obtained at 60 °C with different heating time. Except materials obtained at 60 °C with a heating times inferior to 2 days (Figure 4Ca,b), a type IV nitrogen isotherm, characteristic of mesoporous compounds according to the BDDT<sup>39</sup> classification, is observed for all of the synthesized samples, whatever the heating time and temperature may be.

A hysteresis loop similar to  $H_2$  type is observed for all of our samples (Figure 4A). This type of hysteresis loop has a strong steep desorption branch and a more or less sloping adsorption branch. It may arise from the same types of open capillaries as are responsible for  $H_1$  type hysteresis, characteristic of MCM-41 kind of materials. This indicates that the effective radii of the bodies of the pore of our samples are more or less inhomogeneously distributed but the effective radii of narrow entrances are all of equal size.  $H_2$  type hysteresis loop is typical for wormhole structured MSU-type materials. The nitrogen adsorption study confirms once again that our present samples are MSU-type compounds.

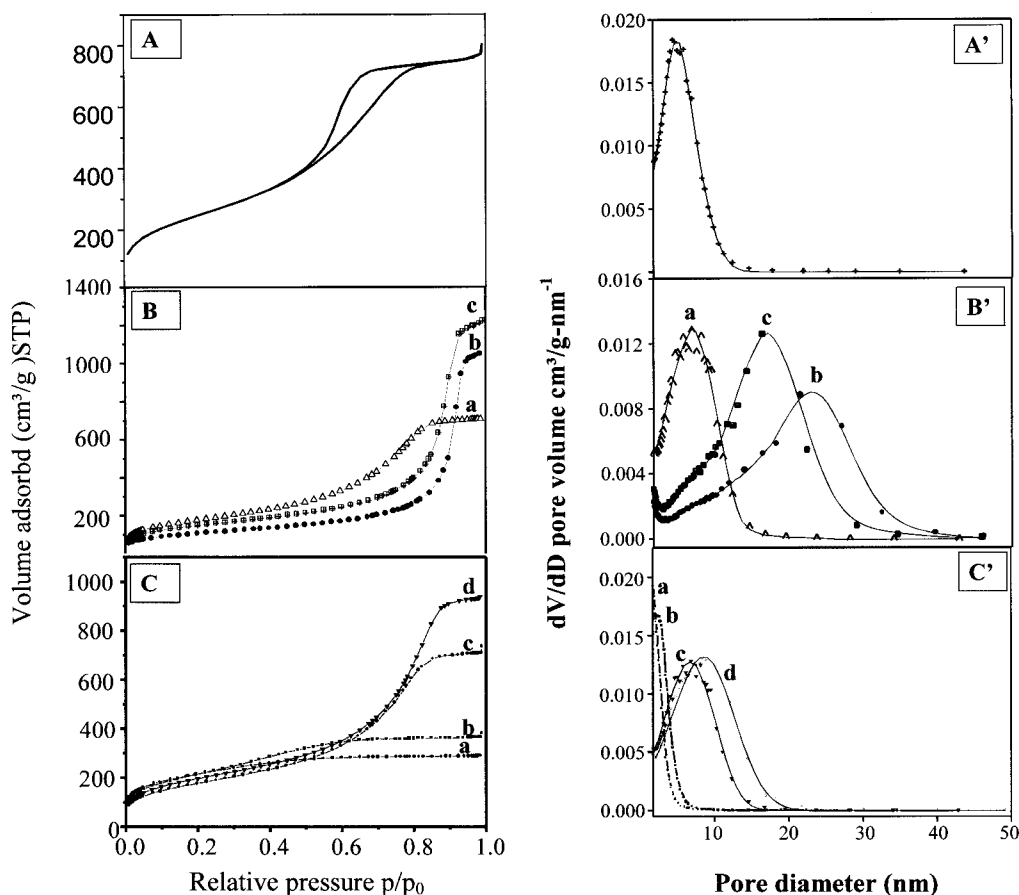




**Figure 3.** Variation of the particles morphology with synthesis time and temperature (a) 0.5, (b) 2, (c) 4, (d) 8 days at 60 °C; (e) 0.5, (f) 6 days at 80 °C; and (g) 1, (h) 8 days at 100 °C.

A relatively sharp increase in the adsorbed volume of nitrogen due to the capillary condensation is noted for all these materials at high  $p/p_0$  values (superior to 0.5). This indicates that the pore size of the molecular sieves is rather large since the  $p/p_0$  position of the inflection point is related to the pore size according to the Kelvin equation.<sup>39</sup> However, it should be noted that for a given time, if the temperature is raised, the capillary condensa-

tion takes place at higher values, for example, it varies from  $p/p_0 = 0.75$  to 0.90 if the heating temperature is increased from 60 to 100 °C for a heating treatment of 4 days (Figure 4B). This suggests that materials obtained at lower temperature have lower pore diameter. Increasing the temperature of the hydrothermal treatment favors thus the formation of channels with larger size. We will discuss this observation in detail below.



**Figure 4.** Nitrogen adsorption isotherms (A, B and C) and pore size distribution (A', B', and C') of compounds synthesized. A and A': 1 day at 80 °C. B and B': 4 days at (a) 60 °C, (b) 100 °C, and (c) 80 °C. C and C': at 60 °C for (a) 0, (b) 1, (c) 4, and (d) 2 days.

The nitrogen adsorption isotherm of compounds synthesized at 60 °C with a heating time less than 2 days (Figure 4Ca,b) is not well-defined in the way that it exhibits a linear region from  $p/p_0 = 0.1$  to 0.4 before reaching a plateau. This kind of isotherm is situated between the type I, related to microporous materials, and the type IV, characteristic of mesoporous materials. The analysis of the pore size distribution (Figure 4C'a,b) shows that these materials possess supermicropores, i.e., pore sizes centered at round 1.7 nm. According to Dubinin,<sup>40</sup> these materials belong to supermicroporous family. Jaroniec et al.<sup>41</sup> have recently observed and evaluated the microporosity present in mesoporous materials using different methods. Certainly,  $\alpha$ ,  $v$ ,  $t$ -plots, Dubinin–Astakhov or Dubinin–Radushkevich methods can also be utilized to evaluate quantitatively the supermicroporosity. Here we just want to draw an attention that supermicroporous materials with very high surface area can be obtained by controlling the hydrothermal conditions. Anyway, the supermicroporous materials form an interesting category of materials, between microporous materials, such as zeolites, and mesoporous, for example, M41S materials, which can open a wide field of applications such as the treatment of molecules requiring only the compounds containing supermicroporosity. Our present study reveals also an important observation that the progressive elevation of the heating temperature and/or time induces the transition of materials from a supermicroporous structure to a mesoporous one.

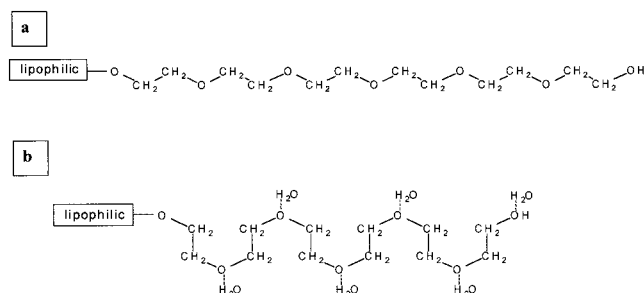
**Variation of the Pore Diameter with Hydrothermal Treatment.** Homogeneous mesoporous materials, showing pore size from 4.0 nm up to 15.8 nm with very high specific surface areas of around 950 m<sup>2</sup>/g have been synthesized (Figure 4B',C' and Table 1). The higher the pore diameter, the broader the

**TABLE 1: Variation of the Pore Diameter Determined by the BJH Method with Synthesis Heating Temperature and Time**

heating time (days)	pore diameter (nm) after heating		
	60 °C	80 °C	100 °C
0	1.7	<i>a</i>	<i>a</i>
0.5	1.7	5.2	7.5
1	1.7	4.7	8.0
2	9.4	4.0	13.4
3	6.7		
4	5.8	12.9	15.8
5	5.2	<i>a</i>	<i>a</i>
6	4.5	9.9	17.1
8	4.8	12.1	14.6
11	7.9	12.1	<i>a</i>

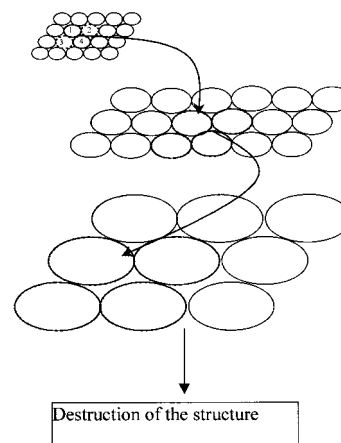
<sup>a</sup> No data.

pore size distribution. It is observed that the pore diameter depends strongly on the heating time and temperature (Table 1). This is in agreement with results reported previously concerning polyoxyethylene (6) tridecyl ether<sup>26</sup> and decaoxyethylene oleyl ether<sup>25</sup> and observed by Pinnavaia et al.<sup>21</sup> Two main tendencies can be drawn from Table 1. First, with increasing temperature, the pore diameter grows as revealed above. Second, for a given temperature, in particular for 60 and 80 °C, the pore diameter increases sharply at first and then decreases when hydrothermal treatment is prolonged. The first tendency can be explained as follows. We have reported<sup>34</sup> that decaoxyethylene cetyl ether can be solubilized in water in different ways. Under acidic conditions, large amount of protons is present. Because of the hydrogen-bonded water molecules present around the hydrophilic heads of surfactant (Figure 5a),



**Figure 5.** Schematic representations of different polyoxyethylene alkyl ether conformations at a, high temperature; b, low temperature.

the equilibrium between the contracted and extended conformation of  $C_{16}(EO)_{10}$  is strongly shifted toward the contracted form (Figure 5b). While, if the pH value is increased above the neutrality, large amount of hydroxyl anions present in the solution provokes a break of the hydrogen bonds between oxygen atoms of the ethoxy headgroup and hydrogens of the tetramethoxysilane. Thus, a part of the micelle adopt a more extended conformation (Figure 5a), which leads to the formation of materials with bigger pore diameter. In the present work, the variation of the pore size is dependent also on the change of the surfactant conformation with the synthesis temperature. At low heating temperature, the hydrophilic part of the decaoxyethylene cetyl ether surfactant adopts a more contracted conformation because of large number of the hydrogen-bonded water molecules present around the hydrophilic heads of surfactant. Contacts and interaction of the ethoxy oxygens with the silanol groups of the silica are not favored by this configuration. The effective cross-sectional area of the hydrophilic headgroup of the surfactant is important. According to Kunieda et al.,<sup>42</sup> micelles with a high curvature and a small diameter are therefore formed. If the heating temperature is raised, due to the thermal agitation, the water molecules bonded around ethoxy oxygen through hydrogen bonds disappear progressively and a more extended conformation is expected. The curvature of the micelle will thus decrease. This conformation allows more interactions with silica but needs a larger area on the silica walls to be achieved. This results in an increase in the pore diameter. Finally, if the heating temperature is further raised, the surfactant-silica interface becomes less important and the size of the mesopores increases with the stretching of the surfactant molecules. This increase in length of surfactant chain or size of micelles can induce a breakdown of the wall separating two adjacent pores. A channel with a bigger size is therefore formed. This phenomenon of wall breakdown was previously reported by Sayari et al.<sup>11</sup> to explain the process of pore size enlargement of pure siliceous mesoporous materials during a postsynthesis treatment, using an amine as swelling agent. As illustrated in Figure 6, pairs or triplets of adjacent pores can transform into single pores in a similar way. However, the second tendency, drawn from Table 1 that for a given temperature, the pore diameter increases first and then decrease with increasing thermal treatment duration, cannot be explained in this way. It is observed that between 2 and 6 days of hydrothermal treatment at a heating temperature of 60 °C, the pore diameter decreases from 9.4 to 4.5 nm instead of increase as expected. The possibility of reorganization of the micelles should be considered. Some molecules leave the formed micelles and, to maximize the hydrogen bonding interactions between the molecules of surfactant and water molecules or silica source, a rearrangement of the micellar system in the gel occurs, which leads to the formation of more micelles, but with a smaller size,



**Figure 6.** Schematic illustration of the breakdown of the wall separating two adjacent pores.

as shown in Figure 7. For times less than 6 days, the materials result from a compromise between the reorganization of the formed micellar phase to get more stable micelles and the stretching of the surfactant molecules with increasing hydrothermal time.

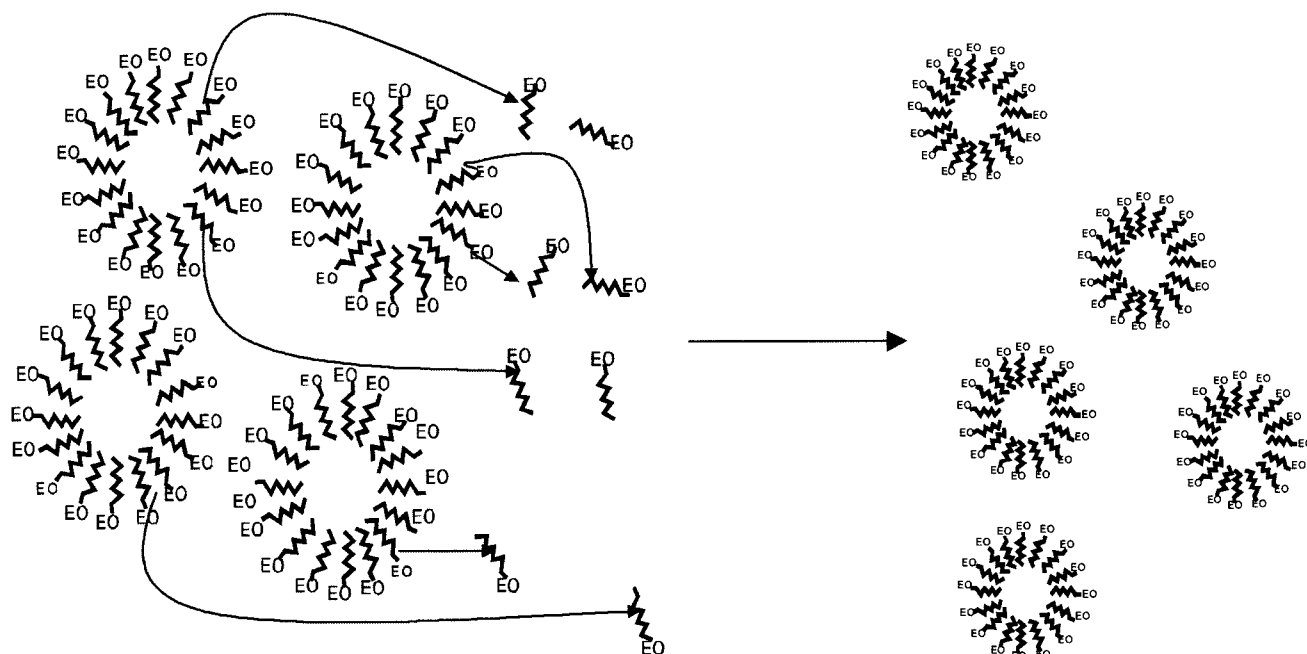
**Variation of Specific Surface Area with Hydrothermal Treatment.** Figure 8 depicts the variation of the specific surface area with heating time and temperature.

At 100 °C (Curve a of Figure 8). After 0.5 days hydrothermal treatment, the value of the specific surface area decreases sharply from 670 to 405 m<sup>2</sup>/g for 2 days, indicating the loss of the mesostructure of our materials. Referring to the typical four steps crystallization curve observed for zeolites (steps I, the nucleation; II, the growth of crystals; III, the crystallization; and IV, the amorphization)<sup>43</sup> or mesoporous molecular sieve synthesis (step I, the hydrolysis of inorganic silica source in aqueous solution; step II, the polycondensation of silica source around highly organized micelles; step III, the continuous polycondensation and the formation of mesostructures; and step IV, the destruction of the mesostructure),<sup>16</sup> this can be attributed to the destruction of the structure, i.e., the step IV. Neither step I nor step II is detected. These two steps are already achieved during the preparation of the gel. The loss of the mesostructure can be related to the heating temperature, which is higher than the cloud point value of our present surfactant. As mentioned in the Experimental Section, the cloud point of decaoxyethylene cetyl ether is found to be 77 °C. This value was determined for surfactant in aqueous solution. However, the cloud point can be changed when silica source, i.e., TMOS is added to the micellar solution. This may explain why materials with high quality were still obtained at 100 °C, but only at short hydrothermal treatment times.

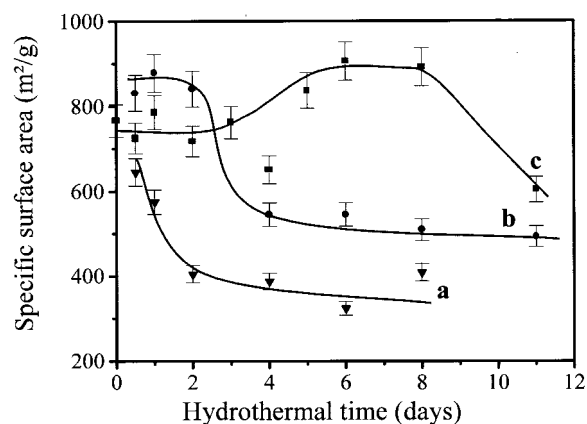
At 60 °C (Curve c of Figure 8). As mentioned above, the transition from a supermicroporous to a mesoporous material occurs suddenly after 2 days. This phenomenon is accompanied by an increase of the specific surface area from 750 m<sup>2</sup>/g for a heating time of 1 day to 900 m<sup>2</sup>/g for a 5 days heating time. This can be due to a decrease of the density of the material. Between 5 and 8 days, the value of the specific surface area remains constant, the step III of the crystallization curve is reached, it corresponds to an increase of the thickness of the wall separating two adjacent pores. After 8 days of hydrothermal treatment at this temperature, the specific surface area drops sharply to 600 m<sup>2</sup>/g for a synthesis time of 11 days.

As just mentioned from 8 to 11 days, the specific surface area drops from 900 to 600 m<sup>2</sup>/g, concurrently the value of the





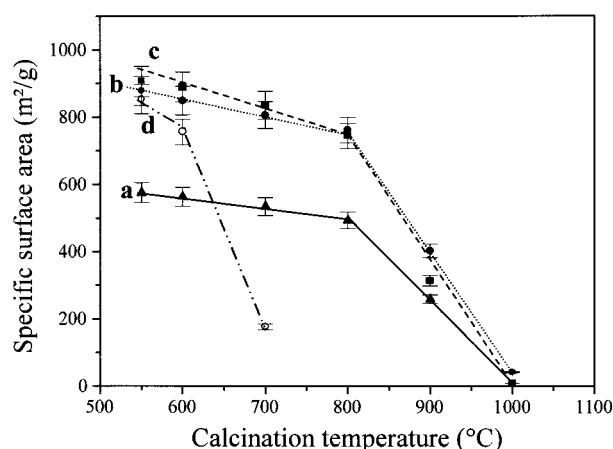
**Figure 7.** Schematic illustration of the reorganization of the micellar solution during the hydrothermal treatment.



**Figure 8.** Variation of the specific surface area of samples synthesized at (a) 100, (b) 80, and (c) 60 °C with heating time.

mean pore diameter increases from 4.8 to 7.9 nm. Because of the high value of the specific surface area, this is not attributable to the destruction of the structure. To explain this variation we have to consider again a breakdown of the wall separating two adjacent pores as represented in Figure 6. If the hydrothermal treatment is prolonged, the break of the pore walls occurs to give a channel with a larger size. Now two new formed channels can lead to the formation of a pore with higher diameter. Compounds with larger channel aperture and lower specific surface areas are thus formed. This process of pore size enlargement continues until the complete destruction of the molecular sieve is reached.

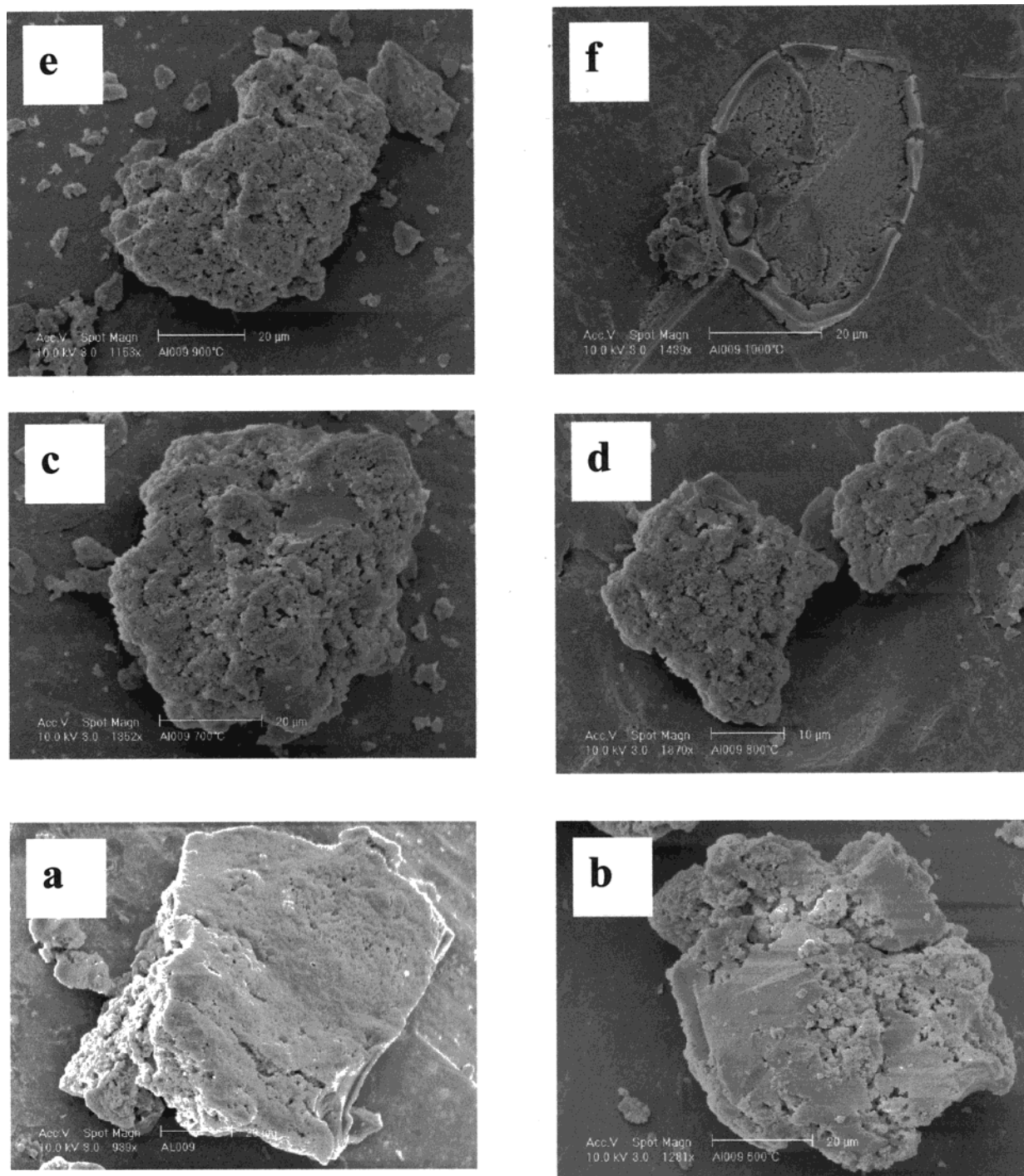
At 80 °C (Curve b of Figure 8). Besides the transition from supermicroporous to mesoporous material, the variations of the specific surface area and pore diameter with heating time are analogous to those reported for 60 °C. The phenomenon of pore wall breakdown and the decrease of the specific surface area occur after a synthesis time of 4 days, which is earlier than that at 60 °C. This can be related to the value of cloud point, as mentioned for 100 °C. However, between 0.5 and 2 days for a constant value of the specific surface area (step III of crystallization process), the mean pore diameter decreases, which is an indication of a reorganization of the micelles during the



**Figure 9.** Variation of the specific surface area of samples synthesized (a) 1 day at 100 °C (sample A), (b) 1 day at 80 °C (sample B), (c) 6 days at 60 °C (sample C), and (d) of MCM-41 (sample D) with calcination temperature. Pore diameter (nm) of sample A, 8.0; sample B, 4.7; sample C, 4.5; and sample D, 7.5.

hydrothermal treatment as described above and depicted in Figure 7. This part of results reveals clearly that the variation of pore diameter and surface area with hydrothermal temperature and time is a result of a compromise between the stretching of surfactant chain, which can lead to wall breakdown to give large pore and the reorganization of micelles to give the small size more stable micelles conducting to the small pore diameter with increasing hydrothermal temperature and time.

**3.2. Thermal Stability of the Mesoporous Materials Obtained.** This study was performed using three samples, noted A, B, and C, for which synthesis conditions, i.e., heating time and temperature are respectively 1 day at 100 °C, 1 day at 80 °C, and 6 days at 60 °C. The pore diameter of samples A, B, and C are respectively 8.0, 4.7, and 4.5 nm. To evaluate their thermal stability, these samples were calcined at different temperatures: 550, 600, 700, 800, and 1000 °C. The heating rate, time and atmosphere are described in Experimental Section. The variation of the specific surface area vs calcination temperature (Figure 9) was used to evaluate the thermal stability



**Figure 10.** Variation of the particle morphology of a sample synthesized at 80 °C for 1 day with calcination temperature (a) 550, (b) 600, (c) 700, (d) 800 °C, (e) 900 °C, and (f) 1000 °C.

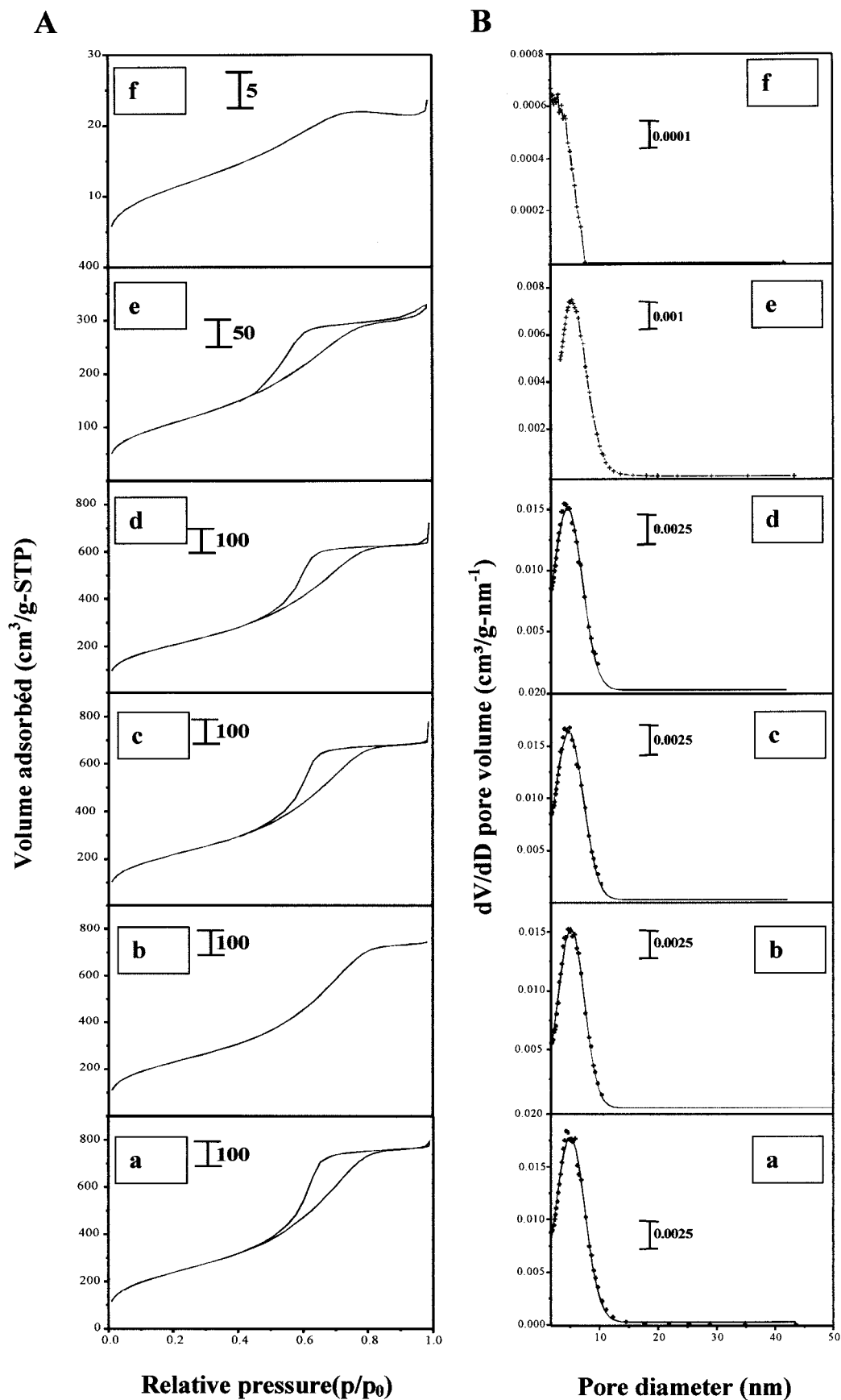
of our compounds. To compare the thermal stability of MSU-type and MCM-type materials, we also report in Figure 9 the variation of the specific surface area of a large pore MCM-41 (sample D) material with pore size of 7.5 nm used for this study.

From Figure 9, it is obvious that for MSU-type mesoporous samples, the specific surface area remains constant until calcination temperature reaches 800 °C, then its value drops dramatically. For instance, for sample B, the specific surface area decreases from 800 to 20 m<sup>2</sup>/g if the calcination temperature is raised from 800 to 1000 °C. These samples with different pore diameters but synthesized in same way only with different hydrothermal times and temperatures show similar thermal stability being independent of the pore diameter.

From 550 to 800 °C, the morphology of the particles (Figure 10) is not affected by the calcination temperature. But after treatment at 1000 °C, the crystals seem to be burst and sintered. This indicates the loss of the porosity and the sintering of the mesoporous particles.

Even after calcination at 1000 °C, all recovered materials exhibit a type IV isotherm (Figure 11A), characteristic of mesoporous compounds. A part of mesoporosity of the samples is thus retained and the pore size distribution remains quite narrow (Figure 11B). However, the maximum volume of nitrogen adsorbed at relative pressure  $p/p_0 = 1$  becomes weaker with the increasing of calcination temperature. For example, concerning sample B, its drops from 700 to 20 cm<sup>3</sup>/g-STP if





**Figure 11.** Variation of the nitrogen adsorption isotherm (A) and pore size distribution (B) of sample synthesized at 80 °C for 1 day with calcination temperature (a) 550, (b) 600, (c) 700, (d) 800 °C, (e) 900 °C, and (f) 1000 °C.

the calcination temperature is changed from 550 to 1000 °C. Thus, the porous volume has decreased dramatically. This is in

agreement with the observations obtained by scanning electron microscopy.

From Figure 9, it is interesting to note that MSU-type materials exhibit a higher thermal stability than large pore MCM-41 sample prepared by using CTMABr as surfactant together with decane and 1,3,5 trimethylbenzene as swelling agents. This structure does not resist the severe calcination superior to 600 °C. This indicates clearly that the preparation method can influence the textural properties of the samples, consequently the thermal stability. The similar thermal stability observed with samples A, B, and C (different pore sizes but similar synthesis method) confirms our suggestion. This observation gives also some information about the thickness of the wall separating two adjacent pores. As reported by Pinnavaia et al.,<sup>44</sup> the wall thickness is more important for mesoporous molecular sieves prepared via a neutral  $\text{N}^0\text{T}^0$  pathway than those prepared via an electrostatic route such as  $\text{S}^+\text{I}^-$  for hexagonal MCM-41 materials; therefore, they have higher thermal stability. Moreover the higher thermal stability of MSU compounds could be related to their disordered channel array. When the temperature of calcination is raised, the channels are only progressively destroyed and the mesostructure slowly collapses as proven by the retention of residual mesoporosity after calcination at 900 and 1000 °C.

#### 4. Conclusion

Decaoxyethylene cetyl ether can be used as templating agent for large pore silica mesoporous molecular sieve formation. The XRD patterns, TEM picture, and  $\text{N}_2$  adsorption-desorption isotherms show that the synthesized materials belong to the MSU family and have a wormlike channel array. Thus, the incorporation of the silica source into the micellar solution disturbs the array of the preformed micelles.

The kinetic study of large pore mesoporous materials formation shows that the hydrothermal treatment in the autoclave should not exceed 1 day at 100 °C due to the destruction of the structure. At 60 °C a transition from supermicroporous to mesoporous materials is observed between 0 and 2 days of hydrothermal treatment. This phenomenon is explained by considering the change in conformation of surfactant, which can induce a breakdown of the wall separating two adjacent pores. Beyond this duration, the structured micelles can simultaneously reorganize to lead to the formation of smaller ones. Thus, a decrease of the pore diameter value is noted, whereas the specific surface area remains constant. At 80 °C a reorganization of the micellar solution takes place after 2 days.

The breakdown of the walls and reorganization of the micelles depend strongly on the hydrothermal treatment and are related to the change in surfactant conformation.

Because of their structural characteristics, samples prepared with this kind of surfactant have a higher thermal stability (800 °C) than those containing a similar pore size prepared using CTMABr together with decane and 1,3,5-trimethylbenzene as swelling agents (600 °C).

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