

# Synthesis of High-Quality MCM-48 and MCM-41 by Means of the GEMINI Surfactant Method

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Pure silica MCM-48 and MCM-41 materials were prepared using GEMINI surfactants, with the general formula  $[C_nH_{2n+1}N^+(CH_3)_2-(CH_2)_s-N^+(CH_3)_2C_mH_{2m+1}].2Br^-$ , abbreviated as GEM  $n-s-m$ . The alkyl chain length ( $n,m$ ) determines the pore size, whereas the length of the spacer ( $s$ ) influences the crystallographic phase formed. A spacer length of 10–12 C yields the cubic MCM-48; smaller spacers favor the hexagonal MCM-41 phase. A hydrothermal treatment is introduced as an intermediate synthesis step, which strongly improves the quality and stability of the calcined materials. The hydrothermal treatment reduces the synthesis time of high-quality MCM-48 to only 2 days. Both GEM 18-12-18 and GEM 16-12-16 yield excellent MCM-48, with a surface area in the range 1200–1600 m<sup>2</sup>/g and pore volumes exceeding 1.2 mL/g. The maxima of the very narrow pore size distributions are found at  $r_p = 13.1$  and 12.2 Å, respectively. The GEM 16-10-16 and GEM 18-10-18 surfactants also yield MCM-48, but the quality of these materials is lower. The GEM 16-8-16 finally yields MCM-41.

## Introduction

The engineering of porosity in common materials such as silica is emerging as a new area of great scientific and technological interest. Materials with tailor-made pore sizes and shapes are particularly important in applications where molecular recognition is needed, such as shape-selective catalysis, molecular sieving, chemical sensing, and selective adsorption.<sup>1,2</sup>

In 1992, scientists at Mobil Oil Research and Development announced the direct synthesis of the first broad family of mesoporous molecular sieves (M41S), using cationic surfactants to assemble silicate anions from solution.<sup>3</sup>

In mesoporous syntheses, the nature of the surfactant–matrix interaction is dictated by the reagents and the synthetic conditions and can affect the physical and chemical properties of the product. Six templating pathways have been identified:  $S^+I^-$ ,  $S^-I^+$ ,  $S^+X^-I^+$ ,  $S^-X^+I^-$ ,  $S-I$ , and  $S^0I^0$ , where  $S$  is the surfactant,  $I$  is the inorganic phase, and  $X$  is the mediating ion. Silicates have been synthesized by  $S^+I^-$ ,  $S^+X^-I^+$ , and  $S^0I^0$  pathways.<sup>4</sup> For the  $S^+I^-$  approach (the original Mobil approach), a cationic surfactant is chosen and the pH is set such that the inorganic precursor will be negatively charged. It is now fairly well accepted that the formation of these silica mesophases occurs via the cooperative charge density model. It assumes that when charged surfactants are used, the initial step is preferential ion exchange of the surfactant counterions (typical  $Br^-$ ) with polycharged oligomeric silicate species. This reduces the thickness of the double layer that keeps the micelles separated and allows the attractive interfacial forces to dominate the interaggregate repulsive forces. Finally, a self-assembly into a new ordered morphology is induced.<sup>5</sup> In other words, the

formation of silica mesophases is more complex and certainly more sophisticated than a simple organic template mimicking mechanism.

The three most important members of the M41S family are the hexagonal MCM-41 with a one-dimensional pore system, the cubic MCM-48 with a three-dimensional pore system, and lamellar MCM-50. Although the MCM-48 has undoubtedly the highest potential as selective adsorbent or catalytic support, it has not received too much attention over the last five years. The classic surfactants used in the synthesis of the M41S family are the alkyltrimethylammonium halides. These surfactants form preferentially hexagonal or lamellar structures, which implies that the synthesis of high-quality MCM-48 is subjected to a very narrow margin of error and a poor reproducibility.

Huo et al.<sup>6,7</sup> rationalized the MCM-48 synthesis by carefully selecting surfactants that favor this cubic mesophase. This strategy was based on the surfactant packing parameter within an amphiphilic liquid-crystal array,  $g = V/a_0l$ , where  $V$  equals the total volume occupied by the alkyl tailgroup,  $a_0$  is the effective headgroup area at the micelle surface, and  $l$  is the kinetic length of the alkyl chain. The cubic mesophase ( $Im3d$ ) forms for  $g$ -values in the interval 0.5–0.65, whereas the hexagonal phase ( $p6m$ ) forms at  $g$ -values below 0.5.

One of the first surfactants, favoring the MCM-48 formation, was the CBDAC surfactant (CBDAC represents cetyl benzyl dimethylammonium chloride,  $C_{16}H_{33}(CH_3)_2N^+(CH_2)(C_6H_5)Cl$ ).<sup>8</sup> It contains a phenyl ring attached to the quaternary nitrogen atom which folds over into the hydrophobic region, decreasing the headgroup area and increasing the value of  $V$ . Using this surfactant, MCM-48 could be produced over a wide range of surfactant-to-silica mole ratios, as low as 0.1.

The most groundbreaking surfactant discovered for the consistent synthetic preparation of MCM-48 was the GEMINI surfactant, with formula  $[C_nH_{2n+1}N^+(CH_3)_2-(CH_2)_s-N^+(CH_3)_2C_mH_{2m+1}].2Br^-$ , denoted as GEM  $n-s-m$ .<sup>6</sup> Alami et al.<sup>9</sup> noticed that the headgroup area  $a_0$  changes significantly with

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the length of the spacer ( $s$ ). At  $s$ -values below 10, the spacer is in contact with the water, lying more or less stretched at the air–water interface. At  $s$ -values above 10, the spacer becomes too hydrophobic to remain in contact with the water and folds to the air side of the interface. Therefore, GEMINI surfactants with a spacer of 12 C favor the formation of the cubic MCM-48 phase, since this spacer is long enough to penetrate the hydrophobic core of the micelle (decreasing  $a_0$  and increasing  $V$ ), but also stays at the outer portion of the micelle, since it is bonded to the headgroup. In this respect, its micellar structure is similar to the  $C_{16}$ TMABr–polar additive–water mixture.

In this article, we will discuss the formation of MCM structures, using the GEM 18-12-18, GEM 16-12-16, GEM 18-10-18, GEM 16-10-16, and GEM 16-8-16 surfactants, evaluating the effect of the spacer and the chain length on the type of mesophase formed. Within the same surfactant, also the effects of pH, synthesis temperature, and synthesis time will be evaluated. The benefits of a hydrothermal post-treatment in pure water on the stability of these materials will be discussed.

### Experimental Section

The surfactants are prepared by refluxing stoichiometric amounts of  $\alpha,\omega$ -dibromoalkane ( $s$ ) and  $N,N$ -dimethyl alkylamine ( $n,m$ ), respectively, in ethanol or acetone for 1–4 days, followed by several recrystallizations from acetone. To synthesize MCM-48, the surfactant is dissolved in water, NaOH is added, and after a few minutes TEOS ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) is added. The molar gel composition is (GEM/NaOH/ $\text{H}_2\text{O}$ /TEOS = 0.06/0.6/150/1). The solution is stirred for 2 h at room temperature, after which the pH has dropped to approximately 12. Subsequently, the entire solution is put in an autoclave at 100 °C for several days. The resulting white solid is obtained by vacuum filtration. Fresh water (20 g) is added per gram of product and returned to the autoclave at 100 °C for an additional period of time. Finally, the product is calcined in ambient air, heating the precursor from room temperature to 550 °C with a heating rate of 5 °C/min.

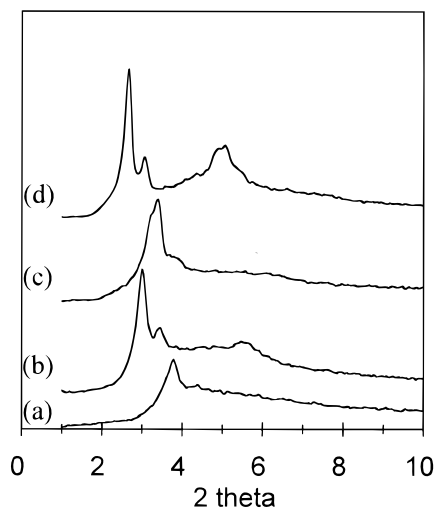
X-ray diffraction patterns were collected on a Philips PW1840 powder diffractometer (45 kV, 25 mA), using a Ni-filtered Cu  $K_\alpha$  radiation. Porosity and surface area studies were performed on a Quantachrome Autosorb-1-MP automated gas adsorption system. The calcined samples were degassed for 17 h at 200 °C. Gas adsorption occurred using nitrogen as the adsorbate at liquid nitrogen temperature. Surface areas were calculated using the well-known BET method, and pore size distribution was calculated using the method of Barret, Joyner, and Halenda.<sup>10</sup> TGA measurements were recorded on a Mettler TG50 thermobalance.

### Results and Discussion

**The Cubic Directing Surfactants: GEM 18-12-18 and GEM 16-12-16.** In the optimization of the synthesis procedure, we have included both the cooking time (autoclaving the gel in its original basic environment at 100 °C) and the hydrothermal post-treatment time (autoclaving the filtrate in pure water at 100 °C).

Hydrothermal post-treatment was introduced by Huo et al.,<sup>6</sup> mainly as a means to enlarge the pore sizes of the obtained MCM materials. They noticed that the unit cell parameter  $a$  of a MCM-41, prepared by  $C_{18}\text{TMA}^+$ , expands from 5.45 to 7.96 nm after a hydrothermal treatment in pure water at 100 °C for 4 weeks.

We have noticed that this type of hydrothermal treatment also (and mainly) improves the long-range ordering of the pores,

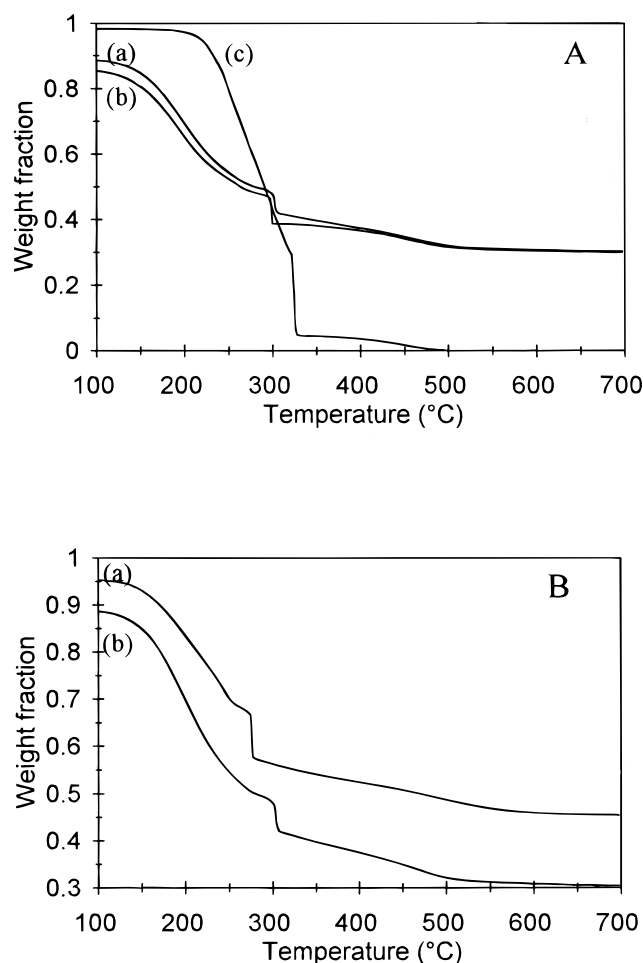


**Figure 1.** X-ray diffractograms of MCM-48, prepared by the GEM 16-12-16 surfactant. (a) 1 day in base, (b) 1 day in base and 1 day in water, (c) 10 days in base. Diffractogram (d): MCM-48, prepared by GEM 18-12-18 after 1 day in base and 1 day in water.

hereby drastically reducing the synthesis time of high-quality MCM materials from several weeks to a few days.

Figure 1a–c clearly illustrates this effect. The GEM 16-12-16 surfactant was stirred for 2 h with NaOH and TEOS (in the above-mentioned molar concentration) and autoclaved in this medium for an additional 24 h at 100 °C. The white solid was then cut in two; one fraction was calcined without further treatment (diffractogram (a)), and the other fraction was subjected to an additional hydrothermal treatment of 24 h at 100 °C (diffractogram (b)). Diffractogram (b) shows that after a synthesis time of only 48 h (1 day in a basic medium and 1 day in pure water), already a very high degree of pore-ordering emerges, showing a typical XRD pattern for MCM-48, with two intense cubic reflections in the region  $2\theta = 2$ –4, assigned to the 211 and the 220 reflection, respectively. A more diffuse pattern can be observed in the region  $2\theta = 4$ –7, which is in fact a superposition of the 321, 400, 420, 332, 422, 431, 521, 611, 541, 631, and 543 reflections. The cubic unit cell parameter is easily calculated by the formula:  $a = d(h^2 + k^2 + l^2)^{1/2}$  with  $d$  the interplanar spacing, as calculated by Bragg's law. Diffractogram (c) shows the XRD pattern after an autoclaving time in basic medium of 10 days, without further hydrothermal treatment. Although the synthesis times is 5 times longer, the resolution of the diffractogram is obviously poorer (inferior long-range ordering of the pores) and the peak maxima occur at higher angles, which means that the cubic unit cell is smaller. Exactly the same sequence was found for the GEM 18-12-18 surfactant. The X-ray pattern of a MCM-48, prepared by GEM 18-12-18 after 1 day in base and 1 day hydrothermal treatment is shown in diffractogram (d), again confirming the high degree of crystallinity, obtained by a synthesis procedure of only 2 days. The improvement of the long-range pore ordering upon hydrothermal treatment suggests that the silicate framework condenses and undergoes reconstruction under mild hydrothermal conditions. During the condensation, the framework negative charge density decreases, hereby inducing changes in the packing of the surfactant, to maintain the charge matching.

TGA measurements provide further confirmation for the favorable effects of a hydrothermal treatment. The TGA measurements were recorded as follows: a sample was heated from 30 to 100 °C in flowing nitrogen and kept isothermally at this temperature for 1 h. Then, the sample was heated from

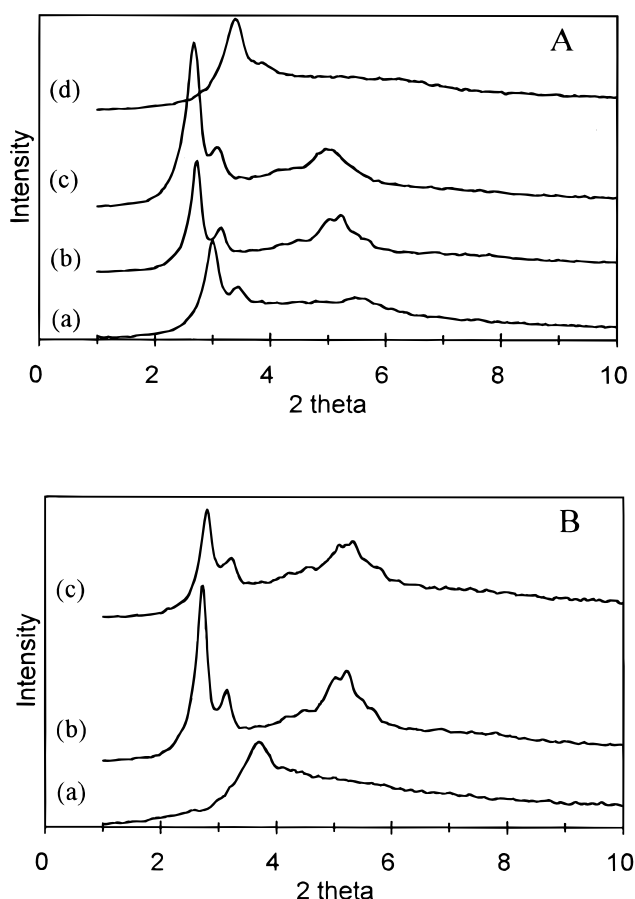


**Figure 2.** (A) Thermograms of the silicate precursor with GEM 16-12-16 surfactant after 1 day (a) and 5 days (b) in basic medium. Thermogram (c): pure GEM 16-12-16. (B) Thermograms of the silica precursor with GEM 16-12-16 surfactant after 5 days (a) and 1 day (b) hydrothermal treatment.

100 to 700 °C in flowing oxygen at 5 °C/min. The first point of the thermogram is the residual weight fraction of the sample after the isothermal treatment at 100 °C.

Figure 2A shows the thermograms of the pure GEM 16-12-16 surfactant and of the surfactant/silicate precursors after a treatment in base for 1 and 5 days. The samples were not subjected to a hydrothermal treatment. The thermograms of the two precursor samples are very similar: condensation and dehydration in the region 100–200 °C, an important weight loss in the region 200–300 °C due to the decomposition and oxidation of the surfactant, followed by a much slower dehydroxylation in the region 300–500 °C. No significant weight loss is observed above 500 °C. We have shown in a previous publication<sup>11</sup> that at this temperature the MCM is exclusively covered with isolated silanols (0.9 OH/nm<sup>2</sup>) which are very difficult to dehydroxylate.

Figure 2B shows the thermograms for a precursor, autoclaved in base for 5 days, followed by a hydrothermal treatment of 1 and 5 days. It is obvious from this figure that the hydrothermal treatment has a huge impact on the thermal behavior of the samples. First of all, the residual weight fraction of the hydrothermally treated samples increases from 30% to almost 50%. So, the inorganic fraction of the precursor almost doubles during the hydrothermal treatment because of silica condensation and pore-wall thickening. Second, close inspection of the thermograms reveals that the weight loss at 300 °C (surfactant

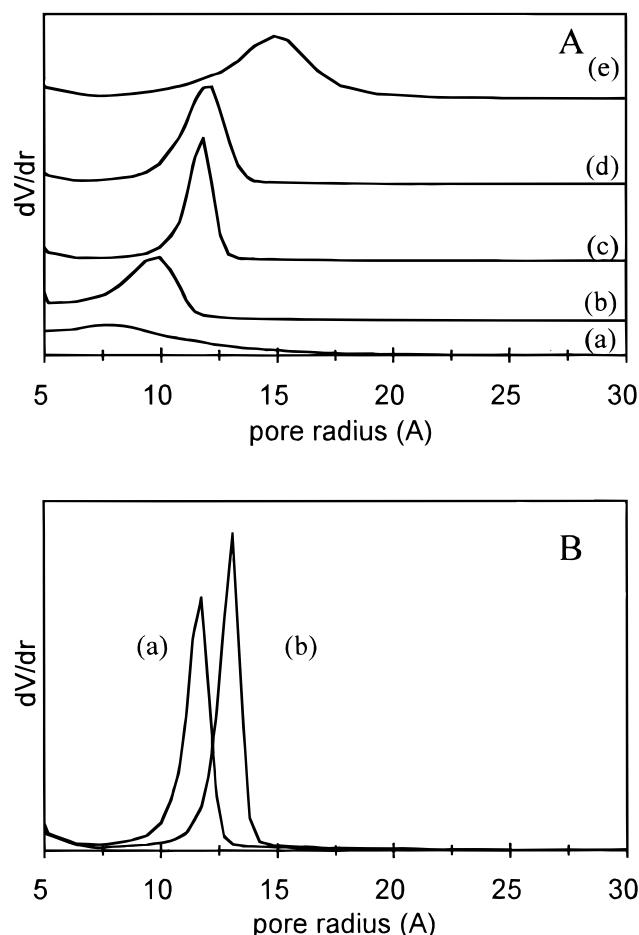


**Figure 3.** (A) X-ray diffractograms of MCM-48, prepared by the GEM 16-12-16 surfactant. Samples were prepared by a treatment in base for 1 day (a), 5 days (b), 10 days (c), and 21 days (d), followed by a hydrothermal treatment of 1–3 days. (B) X-ray diffractograms of MCM-48, prepared by the GEM 16-12-16 surfactant. Samples were prepared by a treatment in base for 5 days, followed by a hydrothermal treatment for 1 day (a), 3 days (b), and 5 days (c).

decomposition) shifts to a slightly lower temperature. This shift suggests that the surfactant–silicate interactions change upon hydrothermal treatment. The exact decomposition/oxidation mechanism, however, has not yet been revealed.

Figure 3A shows the diffractograms of the calcined samples, prepared by the GEM 16-12-16 surfactant, as a function of the cooking time in basic media. All samples were subjected to a hydrothermal post-treatment of 1–3 days. It clearly shows that the crystallinity of the MCM-48 samples goes through an optimum. It is noticeable that the increase in peak intensity is accompanied by a shift of the 211 cubic reflection toward lower diffraction angles, i.e., toward larger cubic unit cells, as calculated by the formula:  $a = d(h^2 + k^2 + l^2)^{1/2}$ . Also the postsynthesis hydrothermal treatment time has an optimum, as illustrated in Figure 3B. Usually, the long-range ordering of the pores increases during the first 1–3 days of hydrothermal treatment, after which the crystallinity decreases. During such a treatment, the silicate network further condenses, hereby reducing continuously the charge density interaction with the cationic surfactant. The phase formation has a distinct optimum, after which the silicate–surfactant interaction further reduces to the point where amorphous silica is formed.

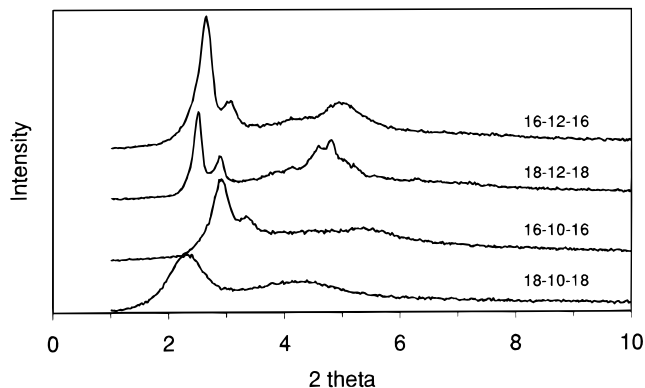
Figure 4 shows selected pore size distributions of the obtained MCM-48 materials. All samples in Figure 4A were prepared by the GEM 16-12-16 surfactant. It again confirms the gradual improvement of the pore size distribution, accompanied by a shift toward larger pore sizes, as a function of the combined



**Figure 4.** (A) Pore-size distribution of MCM-48, prepared by the GEM 16-12-16 surfactant. Treatment: 5 days base, 1 day water (a), 1 day base, 1 day water (b), 5 days base, 3 days water (c), 10 days base, 1 day water (d) and 10 days base, 5 days water (e). (B) Pore size distributions of MCM-48, prepared by GEM 16-12-16 (a) and GEM 18-12-18 (b).

effect of the two autoclaving steps. The steep optimum in the synthesis again becomes obvious. An autoclaving time, which is too long (especially in neutral media), results in a broadening of the pore size distribution and an amorphization of the MCM material, although the total pore volume remains reasonably constant. The effect of the tail length on the pore radius is shown in Figure 4B. This figure evidences that it is very well possible to make tailor-made MCM-48 materials: the actual average pore size can be tuned by changing the surfactant chain length.

**The Intermediate Surfactants: GEM 16-10-16 and GEM 18-10-18.** Theoretically, the MCM-41 phase could be formed, using GEMINI surfactants with spacer lengths in the region of 6–10 carbon atoms.<sup>6</sup> Shorter spacers would yield lamellar structures and longer spacers would yield cubic MCM-48 structures, as evidenced in the previous section. Using the same optimization sequence as in the previous section, we found that the GEM 16-10-16 and the GEM 18-10-18 yield MCM-48, rather than MCM-41. This preference for formation of the cubic phase was independent of the surfactant/silica ratio and independent of the pH (varied between 10.5 and 13). The best MCM-48 materials were obtained by a surfactant/silica molar ratio of 0.06/1 and by abstaining from pH control during the synthesis. Variations in these parameters reduced the crystallinity of the materials, but did not result in the formation of MCM-41.



**Figure 5.** X-ray diffractograms of MCM-48, prepared by different GEMINI surfactants. GEM 16-12-16: 10 days in base, 1 day in water; GEM 18-12-18: 4 days in base, 2 days in water; GEM 16-10-16: 7 days in base, 5 days in water; GEM 18-10-18: 3 days in base, 5 days in water.

**TABLE 1: Survey of the Most Important Characteristics of Pure Silica MCM-48 Materials<sup>a</sup>**

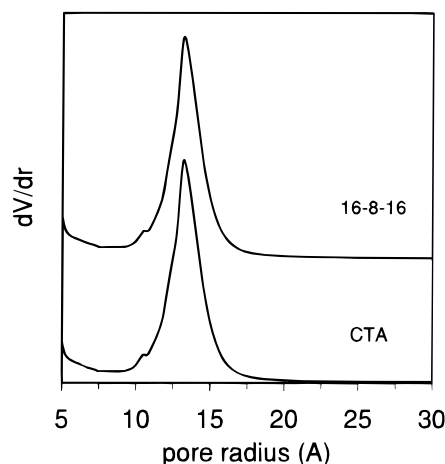
surfactants	days base; days water	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_p$ (mL/g)	$r_p$ (Å)	$a$ (nm)
18-12-18	1, 1	1400	1.3	12.0	8.2
	4, 2	1600	1.4	13.1	8.6
16-12-16	1, 1	1200	1.0	9.8	7.3
	1, 3	1300	1.0	9.5	7.3
	5, 3	1300	1.0	11.8	8.0
	10, 1	1500	1.2	12.2	8.1
18-10-18	3, 5	900	1.0	11.5	n.a.
16-10-16	7, 1	1200	0.9	9.4	7.4
CTA <sup>+</sup> 12		1000–1200	0.9–1.1		7.5–8.5
CTA <sup>+</sup> 13		1150	1.1		8.4
CBDAC <sup>8</sup>		n.a.	n.a.		8.5
CBDAC <sup>14</sup>		1150	1.0		8.3

<sup>a</sup> CTA: cetyltrimethylammonium, CBDAC: cetylbenzyltrimethylammonium chloride, n.a.; not available.

Figure 5 shows the XRDs of the optimized materials, prepared by the four different surfactants. The best diffractograms are obtained using the GEM 18-12-18 and the GEM 16-12-16. Although the intensity of the peaks is higher for the GEM 16-12-16, the best resolution is obtained using the GEM 18-12-18 surfactants. The GEM 16-10-16 surfactant yields undoubtedly MCM-48, but the resolution of the bands is rather poor. The long-range ordering of the pore is not as good as for the surfactants with a spacer of 12 C. Also, the cubic unit cell is smaller: 7.4 nm, compared to 8.2 and 8.6 for the GEM 16-12-16 and the GEM 18-12-18, respectively. The GEM 18-10-18 yields an ambiguous XRD pattern: the resolution is too poor to really assign a crystallographic phase. The actual position of the broad bands suggests a very poorly resolved cubic MCM-48 phase. In any case, the GEM 16-10-16 and GEM 18-10-18 surfactants do not produce high-quality MCM-41 nor MCM-48 in any straightforward manner and they do not seem to add any surplus to the use of the GEM 16-12-16 and GEM 18-12-18 surfactants.

Table 1 summarizes the pore volume, surface area, and average pore size of a few characteristic MCM-48 materials, prepared by the GEMINI surfactants, and compares these values with literature data. It should be emphasized that high-quality MCM-48 is obtained after only 2 days ( $S_{\text{BET}} > 1200 \text{ m}^2/\text{g} > 1.0 \text{ mL/g}$ ). The classical procedures often require several weeks to obtain a good MCM-48.





**Figure 6.** Pore-size distributions of MCM-41, prepared by the GEM 16-8-16 surfactant and by the CTABr surfactant.

**TABLE 2: Summary of Relevant Characteristics of MCM-41 Materials, Prepared by the CTABr and the GEM 16-8-16 Surfactant**

surfactant	pH	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$r_p$ (nm)	$V_p$ ( $\text{cc/g}$ )	$a$ (nm)
CTABr	12	1190	1.3	0.96	4.3
CTABr	11	1110	1.45	1.06	4.6
16-8-16	11.5	1200	1.3	0.98	4.6

**The Hexagonal Directing Surfactants: GEM 16-8-16.** As the GEMINI surfactant with a spacer length of 10 C still yields MCM-48 materials, a surfactant with a spacer length of only 8 C was synthesized. A chain length of 16 C was selected, to allow comparison with MCM-41, prepared by the commonly used  $\text{CTA}^+$  (cetyltrimethylammonium) salt.

Contrary to the synthesis of MCM-48 materials, we found that the best results are obtained by a very careful pH control. During the stirring period of 2h, the pH was kept constant by adding a NaOH solution dropwise to the synthesis mixture.

Some relevant characteristics of the obtained MCM-41 materials are summarized in Table 2. The CTA samples were autoclaved in base for 1 day, followed by a hydrothermal treatment of 2 days. The 16-8-16 sample was autoclaved for 3 days, followed by a hydrothermal treatment of 1 day. These periods were chosen after a thorough optimization and yield the best results.

The hexagonal unit cell constant  $a$  was calculated from the 100 (and 110, 200, and 210) reflections, using the following formula:

$$d = \frac{1}{\sqrt{4(h^2 + hk + k^2) + 3a^2 + \frac{1}{c^2}}}$$

The cell constant  $c$ , representing the size of the unit cell according to the  $z$ -axis, is trivial for the one-dimensional MCM-41 materials.

Close inspection of the pore size distributions of these three materials in the region  $r_p = 5\text{--}30 \text{ \AA}$  (Figure 6) shows that the GEMINI MCM-41 has a less resolved pore-size distribution than the one prepared by the CTABr. The same observation can be made for the XRDs (not shown). These data lead to the conclusion that the GEM 16-8-16 surfactant yields MCM-41 materials that are comparable to the materials prepared by the  $\text{CTA}^+$  surfactant, but it does not seem to offer a superior

alternative for the synthesis of MCM-41 with respect to the existing synthesis routes. Studies on the direct hydrothermal incorporation of transition metal ions into the silicate wall are now being pursued, to compare the on-stream stability and the catalytic characteristics of materials, prepared by  $\text{CTA}^+$  and by GEMINI surfactants.

## Conclusions

The use of GEMINI surfactants  $[(\text{C}_n\text{H}_{2n+1}\text{N}^+(\text{CH}_3)_2-(\text{CH}_2)_s-\text{N}^+(\text{CH}_3)_2\text{C}_m\text{H}_{2m+1}]\cdot 2\text{Br}$  and the introduction of a hydrothermal post treatment have facilitated the synthesis of MCM-48 and have greatly improved the quality of the obtained materials. The spacer length ( $s$ ) of the GEMINI surfactants determines the crystallographic phase that is formed, whereas the chain length ( $n, m$ ) determines the average pore size.

The GEM 18-12-18 and GEM 16-12-16 surfactants yield already good-quality MCM-48 after a synthesis time of 2 days (1 day in an autoclave at  $100^\circ\text{C}$  in the original mixture and 1 day in an autoclave at  $100^\circ\text{C}$  in pure water). Slightly increasing the synthesis time improves the MCM-48 materials until an optimum is reached. MCM-48 materials can thus be prepared with surface areas  $> 1500 \text{ m}^2/\text{g}$  and pore volumes of  $1.4 \text{ cm}^3/\text{g}$ . The pore-size distributions are very narrow, and their maximum can be tuned by an appropriate choice of GEMINI surfactant. Secondary tuning of the pore maximum and the width of the distribution can be achieved by changing the synthesis times.

The GEMINI surfactants with a spacer length of 10 C also yield MCM-48, but the quality of these materials is lower. The GEM 16-8-16, finally, produces MCM-41. Its quality is comparable to that of the materials synthesized by the CTABr surfactant.

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