

Synthesis of highly ordered MCM-41 by micelle-packing control with mixed surfactants

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The mesoporous silica molecular sieve MCM-41 can be obtained in a highly ordered form with various pore diameters if micelle packing is suitably controlled with a mixture of *n*-alkyltrimethylammonium bromide and *n*-alkyltriethylammonium bromide according to the length of the C₁₂–C₂₂ alkyl groups.

The periodic assemblage between surfactant micelles and inorganic layers is a versatile route to the synthesis of molecular sieves with uniform pore diameters in the mesopore range.^{1–6} Previous work on the synthesis of such mesoporous silica molecular sieves referred to as MCM-41 and SBA-15 has revealed that the mesopore diameters can be controlled by using surfactants with different tail lengths and expanding the micelles with suitable organic additives.^{2,6–8} Here, we point out that the structural order of the resultant mesoporous materials decreases with changing pore diameter, due to mismatches in the surfactant's head-to-tail packing ratio. We demonstrate that the structural order can be improved remarkably if mixed surfactants of *n*-alkyltriethylammonium bromides [C_{*n*}H_{2*n*+1}NEt₃Br (*n* = 12, 14, 16, 20 and 22), ATEABr for brevity] and *n*-alkyltrimethylammonium bromides (C_{*n*}H_{2*n*+1}NMe₃Br, ATMABr) are used for the synthesis of MCM-41. The optimum mixing ratio can be tuned according to the length of the alkyl groups.

The ATEABr and ATMABr surfactants used for the synthesis of MCM-41 were received from Aldrich or synthesised in our laboratory. The synthesis of ATEABr was carried out by the reaction of 1-bromoalkane with triethylamine in acetonitrile solution under reflux.⁹ ATMABr surfactants were synthesised similarly using 1-bromoalkane and trimethylamine, but the reaction was performed in a pressure vessel in order to prevent loss of trimethylamine. Synthesised surfactants were purified twice *via* dissolution in chloroform and subsequent recrystallisation by the addition of ethyl acetate.

The synthesis of the MCM-41 silica was performed in a manner similar to that reported in our previous work,^{10,11} except for the use of ATEABr–ATMABr mixtures. An aqueous solution of sodium silicate with Na/Si = 0.5 (2.4 mass% Na₂O, 9.2 mass% SiO₂, 88.4 mass% H₂O) was used as the silica source. The silica source was added dropwise to an aqueous solution of an ATEABr–ATMABr mixture at a given temperature while the solution was stirred vigorously. After continuously stirring for 1 h, the resultant gel mixture was heated for 24 h at 373 K. The mixture after heating was cooled to the same temperature as before the initial mixing, and the pH of the mixture was adjusted to 10 with acetic acid. The mixture after the pH adjustment was heated again for 48 h at 373 K. pH adjustment and subsequent heating was repeated once more before the precipitated MCM-41 product was finally filtered off. The product was washed with EtOH–HCl–H₂O (84.1:1.0:14.9 mol/mol) and calcined in air at 823 K. The structural order of the product was estimated by its XRD pattern obtained on a Rigaku Miniflex (0.5 kW) instrument using Cu-K α radiation with 0.01° 2 θ step size and 1 s step time.

Fig. 1 shows highly resolved XRD patterns for the C_{*n*}MCM-41 samples obtained after optimisation of the starting compositions and mixing temperatures as listed in Table 1. C_{*n*} indicates

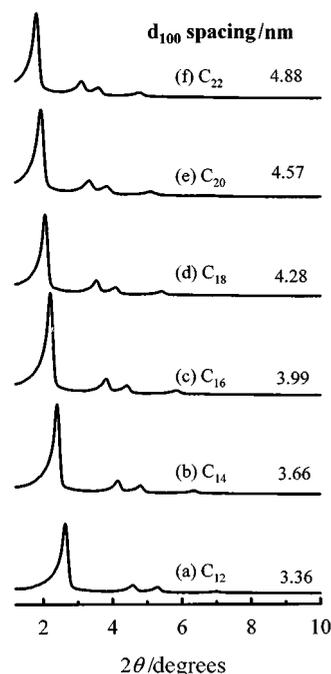


Fig. 1 XRD patterns for high-quality C_{*n*}MCM-41 samples obtained by the optimum synthesis conditions given in Table 1: (a) C₁₂, (b) C₁₄, (c) C₁₆, (d) C₁₈, (e) C₂₀ and (f) C₂₂MCM-41. Samples were calcined in air at 823 K.

the number of carbon atoms in the alkyl chain of the surfactants. These results show that the optimum ATEABr/ATMABr ratio increased with increasing alkyl chain length in the surfactant. For the synthesis of C₁₂ and C₁₄MCM-41, the addition of ATEABr was not beneficial and led to XRD line broadening and loss of intensity. The synthesis of C₁₆–C₂₀MCM-41 by the addition of ATEABr showed a significant improvement of the structural order up to an optimum ATEABr/ATMABr ratio, after which the structural order was progressively lost. The optimum ratio for ATEABr/ATMABr increased from C₁₆ to C₂₂MCM-41 so that ATEABr was used as the single surfactant for C₂₂MCM-41. As reported in Table 1, the surfactant concentration and the mixing temperature were also optimised

Table 1 Optimum conditions for synthesis of MCM-41

Sample ^a	ATMABr ATEABr H ₂ O			Mixing temp/K
	<i>x</i>	<i>y</i>	<i>z</i>	
C ₁₂ MCM-41	1.0	0.0	400	293
C ₁₄ MCM-41	1.0	0.0	400	293
C ₁₆ MCM-41	0.80	0.20	400	303
C ₁₈ MCM-41	0.66	0.34	400	328
C ₂₀ MCM-41	0.10	0.90	500	333
C ₂₂ MCM-41	0.0	1.0	500	338

^a C_{*n*}MCM-41 denotes MCM-41 samples synthesised using a mixture of C_{*n*}H_{2*n*+1}NMe₃Br and C_{*n*}H_{2*n*+1}NEt₃Br. The composition of the starting mixture was 4 SiO₂:*x* C_{*n*}ATMABr:*y* C_{*n*}ATEABr:1 Na₂O:*z* H₂O.

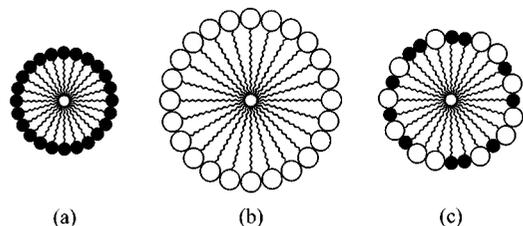


Fig. 2 Schematic models for the cross section of surfactant micelles. (a) The small NMe₃ head group is suitable for short alkyl tails, for the formation of the hexagonal C₁₂MCM-41 mesophase. (b) The large NEt₃ head group for C₂₂MCM-41. (c) The micelle packing in an intermediate case can be controlled with mixed surfactants.

according to the decrease in the solubility of the surfactants as the alkyl group size increases.

An explanation for the change in the optimal ATEABr/ATMABr ratio is depicted in Fig. 2. As Fig. 2(a) shows, small head groups are necessary to form a cylindrical micelle with short alkyl tails in the case of the C₁₂ and C₁₄MCM-41 synthesis. If the tail length increases with the same head group, the resultant micelle structures are likely to be those with smaller surface curvatures such as for the cubic *Ia3d* and eventually the lamellar phase. Hence lamellar mesophases are most easily obtained when C₂₂ATMABr is used as a single surfactant for the synthesis of silica-surfactant mesostructures. The head group size should be increased by the substitution with C₂₂ATEABr in order to synthesise the hexagonal mesostructure [Fig. 2(b)]. The highly ordered XRD patterns for C₁₆–C₂₀ MCM-41 in Fig. 1 indicate that the use of the ATMABr–ATEABr mixtures is an effective way for controlling the surface curvature of micelles for the hexagonal mesophase [Fig. 2(c)] and probably for the synthesis of other mesophases.

Highly ordered C₂₂MCM-41 can also be obtained using ATMABr as the single surfactant and sodium silicate as the silica source if the pH of the starting mixture is carefully adjusted to 8 before heating, as reported by Namba *et al.*¹² A lamellar or disordered mesophase is obtained if the pH is not adjusted at all, or adjusted after heating. The effect of the pH adjustment is evidence for the mesophase-formation mechanism that takes place co-operatively by the silica source and surfactants.¹³ In this mechanism, the silicate anion participates as a part of the head-group moiety of the micelle. The size of the silicate species increases with decreasing pH, and consequently at low pH, the combination of the large silicate species with the small head of the ATMABr surfactant leads to the formation of a large head group that is suitable for the hexagonal mesophase. Thus, the optimum ATEABr/ATMABr ratio for MCM-41 synthesis depends not only on the length of the surfactant tails but also on the pH of the reaction mixture (Fig. 3). The reversibility of the formation of the silica-surfactant mesostructure is another important factor that affects MCM-41 synthesis. The formation of the hexagonal mesophase at pH 8 is not easily reversed and consequently the synthesis becomes very sensitive to the timing and temperature for the pH adjustment during the silicate polymerisation. On the other hand, the synthesis using C₂₂ATEABr can be performed more easily at sufficiently high pH where the formation of the hexagonal mesostructure is reversible.

The surface curvature of micelles can also be controlled using other mixed surfactant systems such as cationic–neutral¹⁴ and cationic–anionic.¹⁵ For example, it has been reported that the use of ATMABr and poly(oxyethylene) alkyl ethers produced the cubic mesoporous silica molecular sieve MCM-48 in high yield [4.2 SiO₂/surfactant (mol/mol)] by hydrothermal synthesis at atmospheric pressure.¹⁴ Mixed surfactants may be considered for finding mesoporous silica molecular sieves with

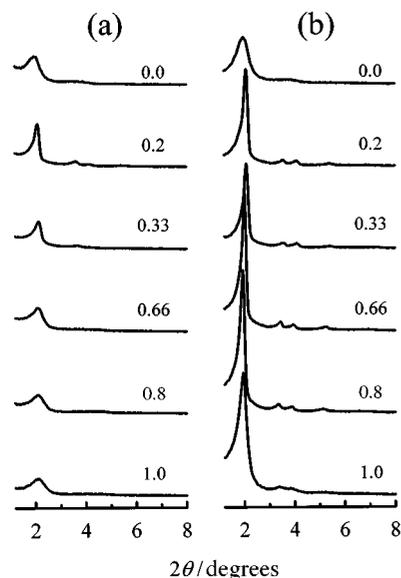


Fig. 3 XRD patterns for MCM-41 synthesised with 4 SiO₂:*x* C₁₈ATMABr:(1–*x*) C₁₈ATEABr:1 Na₂O:400 H₂O (mol/mol). Numbers denote the mole number *x* for C₁₈ATMABr. (a) Product, filtered and dried, after the starting mixture was heated for 24 h at 373 K. (b) Product, filtered and dried, after the pH of the heated mixture in (a) was adjusted to 10 and heated again for 48 h at 373 K.

new structures, as well as improving synthesis procedures for known materials. In addition, the same idea may be used to adjust the surfactant's head group size proportionally to the increase in the diameter of the micelle, when organic additives are used to increase the pore diameter.

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