

Novel Synthesis of High-Quality MCM-48 Silica

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In the early nineties different periodic mesoporous silicas known as M41S¹ were synthesized using cationic surfactants as supramolecular templating materials. Since then, tremendous progress has been made in this area. This included (i) the development of syntheses using a variety of different surfactants and polymers under a wide range of pH conditions, (ii) the discovery of several new silica mesophase structures such as SBA-2, SBA-8, SBA-15, MSU-V, MSU-n, and KIT-1, and (iii) the generalization of the same synthesis strategy to non-silica materials.^{2–5} Nevertheless, the so-called MCM-41 (*p6mm*) silica whose pore structure consists of hexagonally packed cylindrical channels has been by far the most studied material. Owing to its three-dimensional pore structure, the M41S cubic mesophase, known as MCM-48 (*Ia3d*), may be more advantageous than MCM-41. However, because it is particularly difficult to synthesize, fewer investigations were devoted to MCM-48. With almost no exception, it was found that the preparation of MCM-48 silica requires the use of ethanol,^{6–10} either as additive or from tetraethyl orthosilicate. Ethanol is believed to prevent the growth of cylindrical micelles required for the synthesis of MCM-41.¹¹ Alternatively, it was possible to prepare MCM-48 using other organic polar additives such as (CH₃)₂NCH₂CH₂OH or N(CH₂CH₂OH)₃.¹² Gemini surfactant C_{16–12–16} was found to favor the formation of MCM-48 even without organic additives using fumed silica or sodium silicate. It was argued that this may be linked to the similarity between the micellar structure of the C_{16–12–16} in water and the CTAB–polar additive–water system.^{11,12} In all these cases, the pore size of MCM48 silica was found to be in the range 2–2.5 nm. More recently, MCM-48 with 3.2 nm pores was synthesized using sodium silicate and a mixture of cationic and neutral surfactants.¹³ Not only the appropriate relative amounts of surfactants depended on the nature of the neutral surfactant, but pH adjustment was required for good quality materials to be formed. The objective of the current work was to provide a novel, simple, and reproducible method for the high-yield synthesis of exceptionally good quality MCM-48 using cheap fumed silica and readily available cetyltrimethylammonium bromide (CTAB) with no organic additives.

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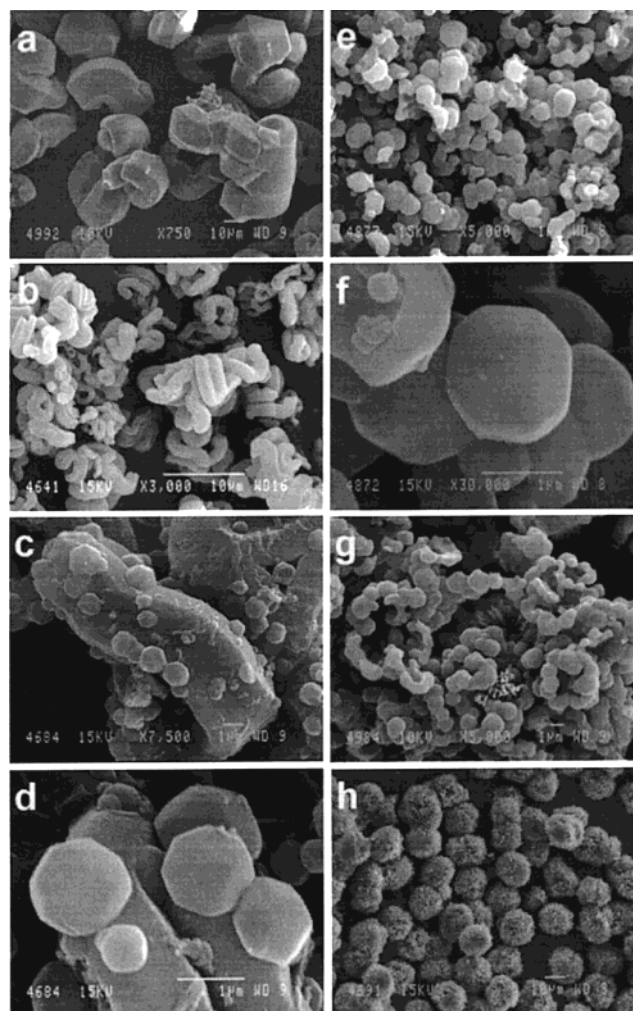


Figure 1. SEM images for samples with $x = 0.45$ and $y = 67$ prepared for 40 h at (a) 80 ($\times 750$), (b) 120 ($\times 3000$), (c) 130 ($\times 7500$), (d) 130 ($\times 20000$), (e) 132 ($\times 5000$), (f) 132 ($\times 30000$), (g) 135 ($\times 5000$), and (h) 140 °C ($\times 750$). A JEOL 840A microscope operating at an accelerating voltage of 10–15 kV was used.

Two series of samples were prepared using mixtures of Cab-O-Sil fumed silica, trimethylammonium hydroxide (TMAOH), CTAB, and water with the following composition: 1.0 SiO₂:0.317 TMAOH: x CTAB: y H₂O. The first series consisted of 12 samples with $x = 0.45$ and $y = 67$ synthesized either at 130 °C for different periods of time from 4 to 144 h or at different temperatures from 80 to 150 °C for 40 h. The other series, comprised of 34 samples, was prepared by heating synthesis mixtures with $0.042 \leq x \leq 0.67$ and $21.7 \leq y \leq 298$ at 130 °C for 40 h. In a typical preparation corresponding to $x = 0.45$ and $y = 67$, 3.85 g of TMAOH (25 w%) was diluted with 37.1 g of water before adding 5.89 g of CTAB under vigorous stirring. After 15 min, 2 g of Cab-O-Sil silica was added. The gel obtained after stirring for an additional 30 min was transferred into a Teflon-lined autoclave, and heated statically under autogenous pressure. The obtained materials were filtered, washed extensively, dried, and calcined at 540 °C, first in flowing nitrogen, then in air.

Figure 1 shows typical SEM images for samples with $x = 0.45$ and $y = 67$ prepared at different temperatures (T) for 40 h. At T between 80 and 120 °C (Figure 1a and 1b), samples exhibited MCM-41 hexagonal structure (XRD data not shown) and consisted of multifaceted tubules whose average length and thickness decreased as the temperature increased. They were

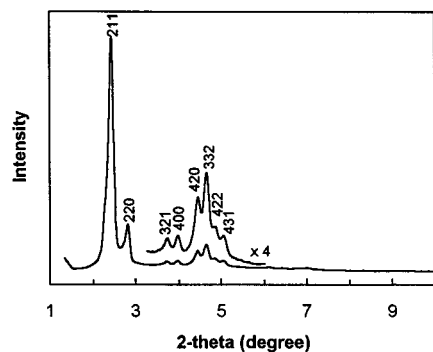


Figure 2. X-ray diffractogram for calcined sample with $x = 0.45$ and $y = 67$ prepared at $132\text{ }^{\circ}\text{C}$ for 40 h. A Siemen D5000 diffractometer was used.

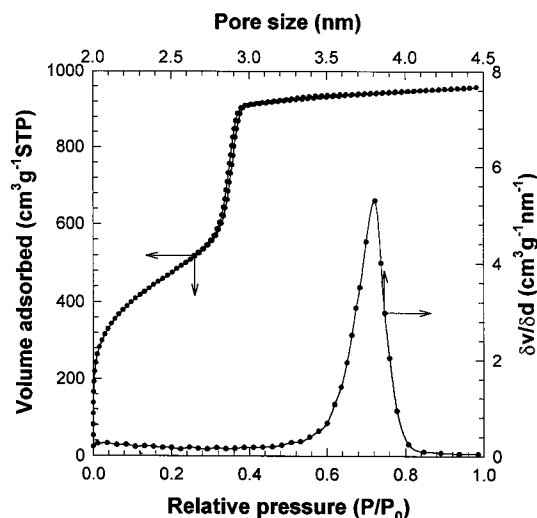


Figure 3. Nitrogen adsorption-desorption isotherm for sample with $x = 0.45$ and $y = 67$ prepared at $132\text{ }^{\circ}\text{C}$ for 40 h. Inset: Corresponding pore size distribution. A Coulter Omnisorp 100 gas analyzer was used.

endowed with 3.1–3.3 nm pores. At $130\text{ }^{\circ}\text{C}$, there was a dramatic change in the morphology of the material as ca. $1\text{ }\mu\text{m}$ truncated rhombic dodecahedral particles akin of single crystals grew out of the tubules (Figure 1c,d). On the basis of XRD data, it was inferred that this sample was comprised of a mixture of MCM-41 and MCM-48 mesophases. Moreover, the pore size distribution for this sample was bimodal with maxima at 3.4 and 3.8 nm corresponding to the hexagonal and the cubic phase, respectively. By careful control of the synthesis temperature at $132\text{ }^{\circ}\text{C}$, a sample containing only the faceted particles was obtained (Figure 1e,f). As shown in Figure 2, the XRD pattern can be indexed in a cubic MCM-48 mesophase belonging to the $Ia3d$ space group. The nitrogen adsorption-desorption isotherm for this sample (Figure 3) is typical of periodic mesoporous materials. The sharpness and height of the nitrogen condensation step and the well-defined XRD peaks provide strong evidence of the very high quality of this material. In addition, the pore size distribution was extremely narrow with a maximum at ca. 3.8 nm and a width at half height of only 0.25 nm (Figure 3, inset).¹⁴ Direct TEM observations (Figure 4) also confirmed the high degree of order of the pore system.

For synthesis temperatures of 140 and $150\text{ }^{\circ}\text{C}$, a lamellar phase ($d_{001} = 3.4\text{ nm}$) in the form of very rough $15\text{--}20\text{ }\mu\text{m}$ spheres formed (Figure 1h). As seen in Figure 1g, it was possible to “catch” the cubic to lamellar mesophase transition at $135\text{ }^{\circ}\text{C}$ as the single crystal-like particles assembled into larger spheres.

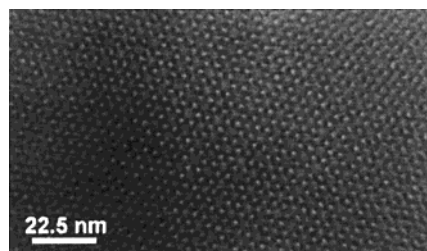


Figure 4. TEM image viewed along the [111] zone axis for sample with $x = 0.45$ and $y = 67$ prepared at $132\text{ }^{\circ}\text{C}$ for 40 h. A Philips 430 instrument operated at 100 kV was used. The specimen embedded in an epoxy resin were cut in ultrathin sections (ca. 60 nm) and examined.

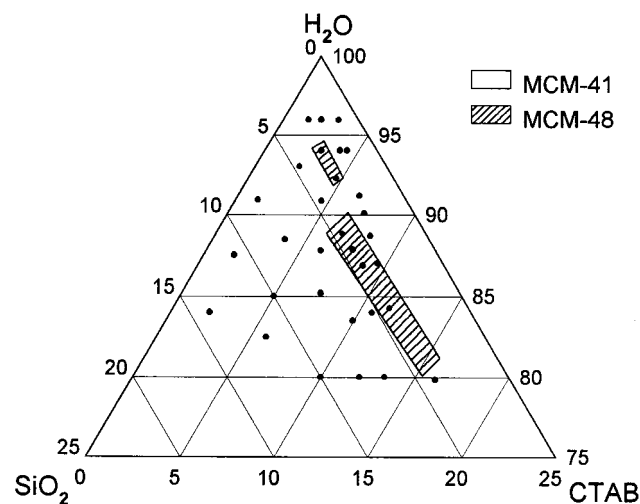


Figure 5. Phase diagram for SiO_2 -CTAB-water at $130\text{ }^{\circ}\text{C}$. For other conditions see text.

Consistent with literature data,^{7,15} a similar sequence of transformations from hexagonal to cubic then to lamellar ($\text{H} \rightarrow \text{C} \rightarrow \text{L}$) was observed when the synthesis was carried out at $130\text{ }^{\circ}\text{C}$ as a function of time. Below 40 h, and even after only 4 h, MCM-41 silica with 3.3 nm pores was generated. At 72 h, essentially pure MCM-48 faceted particles with 3.9 nm pores was formed. However, as the window of temperature to obtain the high-quality MCM-48 mesophase was very narrow, the window of synthesis time at $130\text{ }^{\circ}\text{C}$ was also too small. Almost at the same time as the $\text{H} \rightarrow \text{C}$ transition was completed, the $\text{C} \rightarrow \text{L}$ began.

To find a reasonably wide range of conditions to prepare high-quality MCM-48 reproducibly, we investigated the effect of composition at $130\text{ }^{\circ}\text{C}$. As shown in Figure 5, a sizable range of compositions afforded MCM-48 materials with the same high quality and particle morphology as described above.

It is worth mentioning that, except for their pore size (3.9 vs 2.4 nm), the crystal-like particles observed in the current work are akin to those obtained recently by Kim et al.¹⁶ However, their synthesis procedure was limited to 50% yield, and involved several steps that may be very difficult to reproduce. This included stepwise cooling from the synthesis temperature of 373 to 340 K and rapid removal of the supernatant liquid by decantation and filtration before further cooling. In contrast, our method is simple, reproducible, and routinely exceeds 85% yield.

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