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Redirecting the assembly of hexagonal MCM-41 into cubic MCM-48 from sodium silicate without the use of an organic structure modifier

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In contrast to earlier methods requiring the presence of organic modifiers for the preparation of cubic MCM-48 mesostructures from low cost sodium silicate, we show that this three dimensional framework structure can be readily assembled in the absence of co-surfactants simply by using the overall SiO_2/OH^- ratio as a means of controlling the surfactant packing parameter.

In comparison to the one dimensional channel network of hexagonal MCM-41 mesostructures,[1,2] the three dimensional pore structure of cubic MCM-48 is potentially more desirable for applications in adsorption and catalysis because of more favorable mass transfer kinetics. Moreover, owing to its branched channel system, MCM-48 is an excellent inorganic template for the synthesis of other nanostructures, particularly well ordered mesocarbons.[3] However, the materials applications of MCM-48 have been limited in part by the relatively high costs of the reagents needed to assemble this mesophase.

Initial studies of MCM-48 assembly indicated that with quaternary ammonium salts as the structure director (*e.g.* cetyltrimethylammonium bromide, CTAB) the presence of ethanol as a co-surfactant was essential, whether formed *in situ* through hydrolysis of a tetraethylorthosilicate precursor or added separately when sodium silicate was used as the silica source.[4–7] It was suggested that ethanol increases the surfactant packing parameter ($g = V/(a_oL)$)[8–11] and redirects mesostructure assembly from hexagonal MCM-41 to cubic MCM-48. The need for an organic co-surfactant was further supported by the observation that other polar organic additives, such as $(CH_3)_2NCH_2CH_2OH$, $(C_2H_5O)_3N$[10] and ethylene oxide oligomers,[12,13] also favored the formation of the cubic phase from quaternary ammonium ions and sodium silicate. However, Corma *et al.*[14] and, more recently, Sayari[15] demonstrated that MCM-48 could be prepared from fumed silica, tetramethylammonium hydroxide (TMAOH) and CTAB without the need for a co-surfactant. These latter results, though achieved through the use of cost-intensive reagents, suggested to us that it should be possible to use the silicate precursor itself to alter the CTAB packing parameter. This strategy would allow for the direct assembly of MCM-48 from low cost sodium silicate without the need for an organic modifier.

Accordingly, we have surveyed the assembly of mesostructures from CTAB and sodium silicate under hydrothermal conditions in the absence of co-surfactants and have found that the assembly of hexagonal MCM-41 can be redirected to cubic MCM-48 by adjusting the overall SiO_2/OH^- molar ratio to a value between ~2.3 and 2.9. Most commercially available sodium silicate solutions are prepared at much lower SiO_2/OH^- ratios, which may explain why this region of synthesis space based on sodium silicate reagents has gone unexplored. However, the SiO_2/OH^- ratio can be readjusted through the addition of sulfuric acid while retaining a basic pH, thus altering ion pair interactions at the surfactant head group and favoring a surfactant packing parameter suitable for MCM-48 assembly.

In a typical synthesis, a commercially available sodium silicate solution with an initial overall SiO_2/OH^- molar ratio of 1.29 (Aldrich) was added to a stirred aqueous solution of CTAB, bringing the composition of the solution to molar ratios of $CTAB/SiO_2 = 0.20$ and $H_2O/SiO_2 = 120$. An amount of H_2SO_4 was then added to bring the overall SiO_2/OH^- ratio to the desired value. The resulting mixture was sealed in a Teflon-lined autoclave and heated at 150 °C for 6–36 h. The solid products were recovered in nearly quantitative yield by filtration, washing with water, drying at ambient temperature overnight, and then calcining at 550 °C for 4 h to remove the surfactant.

Table 1 summarizes the unit cell dimensions and textural properties of the products formed at selected overall SiO_2/OH^- stoichiometries between 2.38 and 3.57 after a reaction time of 36 h at 150°C. At overall SiO_2/OH^- ratios above ~3.0, only hexagonal MCM-41 was formed. At ratios below 3.0, however, MCM-48 with cubic *Ia*3*d* symmetry appeared and became the dominant phase down to a ratio of 2.38. The most highly ordered cubic product, as judged from the widths of the X-ray diffraction peaks, occurred at an overall SiO_2/OH^- ratio near 2.6. As shown by the XRD patterns in Fig. 1, reducing the reaction time from 36 h to 18 h at this stoichiometry still afforded cubic MCM-48, but the higher order peaks were less resolved, indicating a lower degree of long range order. Decreasing the reaction time to 6 h resulted in a disordered phase. Table 1 also provides the textural properties for the products formed at these lower reaction times.

Fig. 2 illustrates the nitrogen adsorption–desorption isotherms and Horvath–Kawazoe pore size distributions for a well ordered MCM-48 phase obtained after a reaction time of 36 h. The BET surface area (1116 m^2 g^{-1}), average pore size (34 Å)

Table 1 Properties of the mesostructures assembled from sodium silicate and CTAB at 150 °C

Synthesis conditions					
Overall SiO_2/OH^- (mol/mol)	Rection time/h	Mesophase	Unit cell/Å	Surface area/m^2 g^{-1}	HK pore size/Å
3.57	36	Hexagonal	48.6	1290	34
3.33	36	Hexagonal	47.3	1070	31
2.94	36	Hexagonal + Cubic	—	1031	32
2.63	36	Cubic	98.1	1116	34
2.38	36	Cubic	98.4	937	34
2.63	18	Cubic	98.1	1127	32
2.63	6	Disordered	42.1	1380	27

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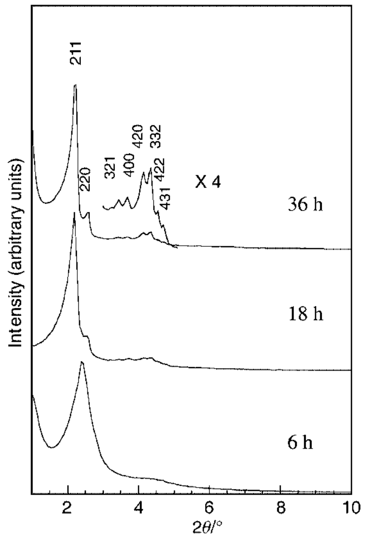

Fig. 1 XRD patterns of calcined (550 °C) mesostructures prepared from CTAB and sodium silicate at an overall SiO_2/OH^- ratio of 2.63, a reaction temperature of 150 °C and reaction times of 6, 18 and 36 h.

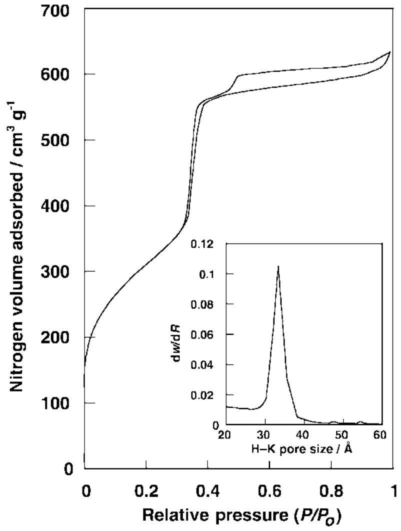

Fig. 2 Nitrogen adsorption–desorption isotherms for calcined MCM-48 prepared at an overall SiO_2/OH^- ratio of 2.63 (150 °C, 36 h). Inset: Horvath–Kawazoe framework pore size distribution.

and pore size distribution (3 Å width at half height) are in accord with those previously reported for MCM-48. In addition to the step-like uptake of nitrogen at a relative pressure near 0.35, which corresponds to the filling of framework mesopores, the isotherm in Fig. 2 exhibits a type H4 hysteresis loop at higher partial pressures indicative of secondary mesoporosity. This secondary mesoporosity may arise from intraparticle defects (voids), as observed previously for certain forms of MCM-48,[16] or from interparticle contacts.[17] TEM images, as shown in Fig. 3, indicate that the particles are monolithic and essentially free of the kind of intraparticle defects that might give rise to secondary mesoporosity. However, the particles tend to adopt a plate-like morphology. The aggregation of plate-like particles is likely to generate slit-shaped interparticle pores consistent with a type H4 hysteresis loop.[18]

The above results demonstrate that MCM-48 can be reliably assembled from cost-efficient sodium silicate and CTAB without the use of organic additives as structure modifiers. By altering the overall SiO_2/OH^- ratio we have also altered the ion pairing interactions between the silicate precursor and the surfactant head group, thereby increasing the surfactant packing parameter and redirecting the structure of the resulting mesophase. It should also be possible to use this strategy for the assembly of other mesophases and compositions without requiring the use of organic structure modifiers to achieve changes in the surfactant packing parameter.

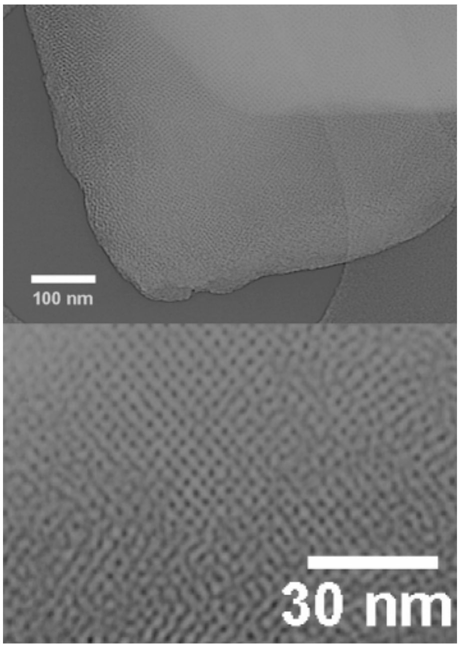

Fig. 3 TEM images of calcined MCM-48 prepared at an overall SiO_2/OH^- ratio of 2.63 (150 °C, 36 h).

It also is possible to use this chemistry for the assembly of aluminated MCM-48 derivatives simply by incorporating sodium aluminate into the initial gel. For instance, an Al–MCM-48 with a Si/Al ratio of 32 was readily prepared under equivalent SiO_2/OH^- ratios without compromising the structural integrity of the cubic phase. Thus, these improvements in MCM-48 synthesis should at least facilitate the more widespread use of this unique mesophase in materials research.

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