Rapid and facile synthesis of siliceous MCM-48 mesoporous materials†

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A rapid and facile synthesis of cubic MCM-48 mesoporous material based on the modification of Stöber synthesis in as little time as 30 minutes at room temperature is reported in this communication.

Mesoporous materials have been the focus of intense research since the discovery of the M41S class of materials in 1992 by the Mobil group.[1,2] Among the various classes of mesoporous materials, MCM-48 has an interpenetrating network of three-dimensional pores and hence is thought to possess favorable mass transfer kinetics compared to the unidimensional pores that occur in MCM-41 type of materials. The MCM-48 material is a favorable candidate for several catalytic reactions such as methanol oxidation, solid acid catalysis, hydrodesulfurization and photocatalytic decomposition of organic molecules.[3–5]

The rapid and facile synthesis of MCM-48 is still a challenge and several methods have been reported in the literature. However most of the methods reported in literature are tedious, and time consuming. Several recipes reported in literature employ hydrothermal synthesis. However, the time required for preparation is usually several hours if not several days. A reliable synthesis based on a modified Stöber synthesis has been reported by Schumacher *et al.*[6] However, the drawback of the synthesis was that the time required was relatively long, 5–24 h. Silica thin films with tailored pore morphology and narrow pore size distribution have been prepared by combining sol–gel chemistry and "evaporation-induced self-assembly.[7,8] Temperature-programmed microwave-assisted synthesis has also been reported for the rapid synthesis of ordered mesoporous materials with good thermal stability.[9]

The preparation of spherical monodisperse particles of SiO_2 was first reported by Stöber *et al.*[10] In this method, tetraalkylorthosilicate was hydrolyzed under basic and alcoholic solutions to give SiO_2 particles with diameters in the range 0.05–2 μm. Achieving uniform particle sizes and pore sizes has been a challenge. In the present study, by adopting the surfactant templating method and by carefully controlling various experimental parameters (stirring rate, aging time *etc.*) a ordered mesoporous silica material in cubic form has been synthesized in as little as 30 min at room temperature.

The synthesis of MCM-48 is dependent on a number of factors such as temperature, stirring rate, reactant ratios, type and chain length of surfactant employed, nature of solvent and Si precursor. The shortest time reported so far for the preparation of MCM-48 and metal substituted MCM-48 is 5 h. It is attractive to pursue methods to shorten the time frame of synthesis. In addition, it is better if the reported synthetic methods are carried out at ambient conditions and is fairly easy and reproducible. Here we present a method for the facile synthesis of cubic siliceous MCM-48 in as little time as 30 min at room temperature.‡ A typical gel composition is 0.41 CTAB : 11 aq. NH_3 : 1.0 TEOS : 53 EtOH : 344 H_2O. The yield of MCM-48 is in the range 0.40–0.46 g (83–96%). Fig. 1 shows the low angle powder X-ray diffraction of the calcined siliceous MCM-48 prepared using CTAB as the surfactant and stirred at various rates for 4 h at room temperature.§

It can be observed that the MCM-48 material that was not stirred (labelled as MCM-48-ns) after addition of TEOS exhibited a high level of ordering, *i.e.*, most intense d_{211} peak. The observed X-ray diffraction (XRD) patterns of calcined materials (not stirred, stirred at 300 and 600 rpm) are typical of MCM-48. The resulting diffraction peaks in these three mesoporous materials show a good correspondence to those predicted by the cubic *Ia*3*d* symmetry. These results thus indicate the existence of mesoscopic order in the materials. Furthermore, the XRD features five reflections at $2\theta < 6°$ indicating the high quality of the MCM-48 mesoporous material under these conditions. Further, the FWHM of the first peak (d_{211}) for these samples decrease as the stirring rate is increased. The full-width at half maximum (FWHM) of the d_{211} peak was found to be 0.35° for MCM-48-ns, 0.44° for MCM-48-300 and 0.52° for MCM-48-600. The XRD of the as-synthesized mesoporous materials (not shown) also showed patterns that could be indexed to cubic *Ia*3*d* symmetry. However, the intensity of the d_{211} peak was found to be about three times lower when compared with the

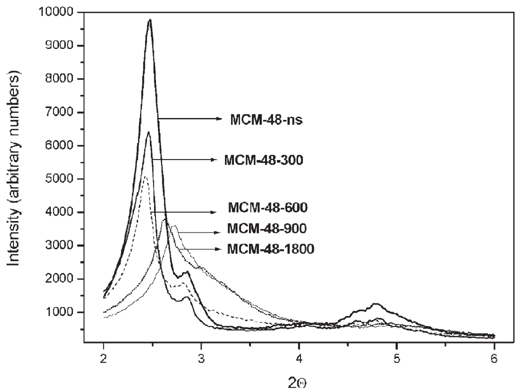

Fig. 1 Powder X-ray diffraction pattern of calcined mesoporous materials stirred at different rates for 4 h at r.t. The composition of the gel is 0.41 CTAB : 11 aq. NH_3 : 1.0 TEOS : 53 EtOH : 344 H_2O.

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† Electronic supplementary information (ESI) available: Fig. S1: Transmission electron microscopy image of MCM-48-300-20. Fig. S2: Scanning electron microscopy image of a representative siliceous MCM-48 mesoporous material. See DOI: 10.1039/b706633c

calcined sample. Further, the d_{211} reflection was found to exist as a shoulder rather than a distinct peak. There is a shrinkage of 0.2–0.4 nm (3–6%) of the unit-cell parameter upon calcination. FT-IR spectra (not shown) of the calcined materials indicate the complete removal of the surfactant molecules. Calcination at heating rates of 5 °C min^{-1} or higher usually led to the collapse of MCM-48 framework and hence the samples were calcined at a rate of 3 °C min^{-1}. The cubic unit cell parameter (*a*), of the calcined mesoporous materials (calculated from the 211 reflection) was also found to slightly increase from 87.2 Å for MCM-48-ns to 87.9 Å for MCM-48-300 and 89.4 Å for MCM-48–600. Stirring at rates, 900 rpm and higher in contrast lead to the formation of a poorly ordered mesophase. In case of MCM-48-900 and MCM-48-1800, the XRD results showed only two peaks at $2\theta < 6°$ reflecting the poor quality of the mesophase. The first intense peaks for the samples stirred at 900 and 1800 rpm are very broad and the FWHM of the peaks are considerably larger, *i.e.* $>1°$. The XRD patterns of these two samples could not be indexed to a hexagonal phase since the reciprocal spacing $1/d_{hk}$ ratios were found to be 1 : 1.84. This is in contrast to the expected ratios of 1 : $\sqrt{3}$ for a hexagonal phase. Thus, an optimum stirring rate is essential for the formation of a high quality cubic phase.

In a series of experiments designed at finding the optimum conditions for the synthesis of MCM-48, several experimental conditions were varied systematically, one at a time. Among the conditions that were varied were stirring time, amount of the surfactant, nature of the alcohol, chain length of the surfactant molecules, nature of the silica precursor, pH of the sol, amount of water in the reaction mixture, temperature and aging time. It was found that for samples (with the gel composition as indicated previously) stirred at 300 rpm, a stirring time of 4 h or longer was essential for the formation of good quality cubic MCM-48 phase. Stirring (at 300 rpm) for 2 h was found to form only a poorly structured cubic phase and the XRD results showed a shoulder at $\sim 2\theta = 2.8°$ instead of a well-defined peak. Stirring for times longer than 4 h was essentially found to give a cubic MCM-48 mesoporous material with no appreciable loss in the quality of the material. In general there was an increase in the unit cell parameter (a_0) with increase in time of stirring. The a_0 value increased from 87.9 Å for the sample stirred (at 300 rpm) for 4 h to 90.1 Å for the sample stirred at 300 rpm for 1 day at r.t.

The amount of surfactant was also found to affect the formation of the cubic phase. At [CTAB]/[TEOS] ratios of 0.2 and less, no cubic phase was formed. Instead, the XRD results (not shown) indicate the reciprocal spacing $1/d_{hk}$ ratios to be 1 : 1.77 : 2.04. This is in very close agreement with the expected ratio of 1 : $\sqrt{3}$: 2.00. Thus, at low [CTAB]/[TEOS] ratios, a hexagonal phase is formed rather than a cubic phase. At [CTAB]/[TEOS] ratios of 0.8 and higher, no improvement in the quality of the cubic phase was discerned, excepting a very slight decrease in the FWHM of the peak d_{211} to 0.30° from 0.35°. A [CTAB]/[TEOS] ratio of 0.41 was used for further studies since this ratio was found to be sufficient for the formation of the cubic phase.

A series of alcohols were used instead of ethanol and the XRD results suggest that when no alcohol was used, or when methanol, propanol and butanol were used, a poorly structured mesoporous material was formed. The broadening of the peaks in these instances suggest that the network of pores in these materials consist of short worm like tubular channels.

The surfactant chain length was found to influence the formation of the mesoporous phase. At [surfactant]/[TEOS] ratios of 0.41, stirred at 300 rpm for 4 h, only the samples that contained CTAB, was found to form the cubic phase. As expected the *d* value of the highest intense peak increased from 26.4 Å for C_{10}, 28.3 for C_{12}, 33.4 for C_{14}, to 35.9 Å when CTAB was used as the surfactant. When the chain length was very short, *i.e.* C_{10}, only one peak in the low angle region was found. In contrast with C_{12} as the surfactant, two peaks in the low angle region ($2\theta < 6°$) with *d* values respectively of 28.3 and 16.2 Å were observed. When the surfactant chain length was $C_{14,}$ three peaks were observed, with d_{100} = 33.4 Å, d_{110} = 18.8 Å and d_{200} = 16.2 Å. The reciprocal spacing $1/d_{hk}$ ratios were found to be 1 : 1.76 : 2.06, which is in close agreement with the expected ratios for a hexagonal, *p*6*m* phase. Use of TMOS instead of TEOS under similar conditions led to the formation of a hexagonal phase. The amount of ammonia too was found to have a profound influence in the nature of the mesoporous phase. At ratios of $[NH_3]/[TEOS] = 0.09$ as shown in Fig. 1 a cubic phase is formed. However, at $[NH_3]/[TEOS] = 0.045$ and lower, only one peak in the low angle region was found, with a *d* value of 33.9. At $[NH_3]/[TEOS] > 0.1$, a hexagonal phase is formed. Another factor that was found to influence the formation of the cubic phase was the amount of water in the initial gel composition. At ratios of $[H_2O]/[TEOS]$ of less than 100, a hexagonal phase was formed whereas at ratios of $[H_2O]/[TEOS]$ of less than 200, only a weakly structured cubic phase was formed. Also, at ratios of [EtOH]/[TEOS] = 25 and lower, only a hexagonal phase was formed. No significant improvement in the quality of the cubic phase was observed when the temperature of the initial gel was increased to 60 ± 5 °C.

In another set of experiments, designed to reduce the processing time required for the synthesis of cubic MCM-48, the gel composition was maintained at 0.41 CTAB : 11 aq. NH_3 : 1.0 TEOS : 53 EtOH : 344 H_2O as previously and the stirring (300 rpm) time (after addition of TEOS) was maintained at 10 min. This was determined from our observations that it took at least 10 min for the silica to start precipitating under the reaction conditions employed. After 10 min of stirring at 300 rpm, the gel was aged for further periods ranging from 20 to 110 min. The solids obtained were, washed, dried and calcined as described previously. Fig. 2 shows the powder XRD of the calcined MCM-48 samples that

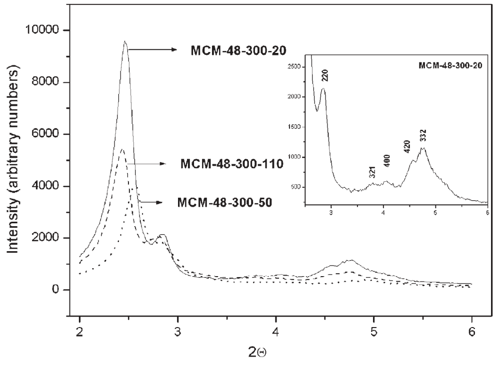

Fig. 2 Powder X-ray diffraction pattern of calcined MCM-48 mesoporous materials aged statically for different periods at r.t. MCM-48-300-20 refers to sample stirred at 300 rpm for 10 min and then aged for additional 20 min.

Table 1 Textural properties of calcined MCM-48 materials

Material	Surface area[a]/ $m^2\ g^{-1}$	Pore volume[b]/ $cm^3\ g^{-1}$	Pore diameter[c]/Å	Unit cell parameter[d]/Å	
MCM-48-ns	1567	0.98	22.2	89.7	87.2
MCM-48-300	1339	0.96	22.2	93.2	87.7
MCM-48-300-20	1527	0.96	22.2	92.0	87.7
MCM-48-300-50	1532	0.85	22.2	93.5	84.5
MCM-48-300-110	1437	0.84	22.3	92.1	88.1

[a] Determined by applying Brunauer–Emmett–Teller (BET) equation to a relative pressure (P/P_0) range of 0.05–0.35 in the adsorption isotherm. [b] Calculated from the amount of N_2 adsorbed at the highest relative pressure of 0.99. [c] Calculated from the Barrett–Joyner–Halenda (BJH) equation using the desorption isotherm. [d] Calculated using the formula $a = \sqrt{6}d$, where d represents the d_{211} reflection. The left and right columns refer to the a values of uncalcined and calcined samples, respectively.

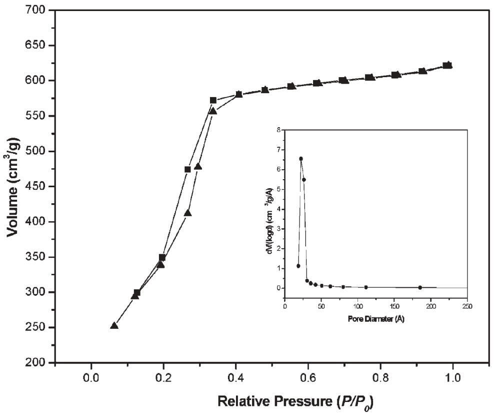

Fig. 3 Nitrogen adsorption isotherm of MCM-48-300-20. This sample was stirred at 300 rpm for 10 min and then aged for additional 20 min at r.t. The triangles represent adsorption isotherm whereas the squares represent the desorption isotherm. The inset shows the pore size distribution.

were stirred for 10 min at 300 rpm after addition of TEOS but aged (statically) for different times. The XRD results show that static aging for as low as 20 min is sufficient for the formation of the cubic phase. The inset in Fig. 2 shows the XRD pattern in the low angle region of $2\theta = 2.5$–6°. The presence of five peaks in this region is indicative of the formation of a high quality cubic phase. In case of all the samples, there is considerable shrinkage of the unit cell on calcination, from 2.8% to the sample not stirred to 9.6% to the sample stirred for 10 min at 300 rpm and then aged statically for 50 min. However, the pore diameter (determined by applying the BJH equation to the desorption isotherm) is nearly constant as shown in Table 1 below suggesting that the thickness of the silica material is altered by the synthesis conditions, however this factor needs to be examined more critically.

The textural properties of the MCM-48 materials are shown in Table 1. The nitrogen adsorption isotherms¶ of the mesoporous material that is prepared in 30 min at r.t. is shown in Fig. 3. A typical reversible type IV adsorption isotherm is observed for all the samples. At relative pressures, P/P_0 between 0.2 and 0.4, a sharp inflection due to capillary condensation within the mesopores is observed, which is characteristic of cubic MCM-48 mesoporous materials. The mesoporous materials have large surface areas (1300–1600 $m^2\ g^{-1}$) and large pore volumes (>0.8 $cm^3\ g^{-1}$).

Transmission electron microscopic studies (shown in ESI†) confirm the cubic nature of the mesoporous materials. Scanning electron microscopy image of representative MCM-48 (shown in ESI†) suggest that almost uniform spherical silica particles with no agglomeration are formed at room temperature.

In summary our results indicate that cubic (*Ia*3*d*) MCM-48 mesoporous materials can be prepared in as little time as 30 min by careful control of stirring rates and aging times. Efforts are on way to extend this method and preliminary studies suggest that Ti-MCM-48 materials can also be prepared in an analogous manner.

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Notes and references

‡ A typical preparation of siliceous MCM-48 is as follows: in a polypropylene bottle (125 mL), 1.2 g (3.3 mmol) of cetyltrimethylammonium bromide (CTAB) was first dissolved in 50 mL water and stirred at room temperature (30 ± 5 °C) until all the surfactant molecules had dissolved. Then 25 mL ethanol (200 Proof, AAPER chemicals) was added and the solution stirred for ~5 min. To this solution, 6 mL of aq. NH_3 (0.09 mol) was added and the solution stirred vigorously. Finally 1.8 mL (8 mmol) of the silica precursor, tetraethylorthosilicate (TEOS) was added and the mixture was stirred at 300 rpm for a further 4 h. The composition of the initial gel typically is 0.41 CTAB : 11 aq. NH_3 : 1.0 TEOS : 53 EtOH : 344 H_2O. The precipitate obtained was filtered off and washed with deionized water. The white powder obtained was dried in an air oven at 80–90 °C overnight. The dried powder was then ground finely and then calcined in static air at 550 °C at a heating rate of 3 °C min^{-1} to remove the surfactant molecules.

§ For XRD studies, the mesoporous samples were smeared on top of the sample holder and the sample packed tightly. A Scintag Pad V X-ray diffractometer with DSMNT data acquisition and analysis software was used. The diffractometer was operated at 40 kV and 30 mA and the low angle regions were scanned from 2 to 6° (2θ) with a step size of 0.02°.

¶ The nitrogen adsorption measurements were carried out on the mesoporous samples at 77 K using a Quantachrome Nova 2200*e* gas adsorption analyzer. The samples were outgassed for at least 1 h at 100 °C prior to the adsorption measurements.

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