Rapid synthesis of high quality MCM-41 silica with ultrasound radiation†

Xianghai Tang,‡ Suwen Liu, Yanqin Wang, Weiping Huang, Elena Sominski, Oleg Palchik, Yuri Koltypin and Aharon Gedanken*

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel. E-mail; gedanken@mail.biu.ac.il

High quality MCM-41 silica with thick walls and a very narrow distribution of mesopore size has been synthesized in a relatively short time *via* ultrasound radiation.

Recently, great efforts have been dedicated to improving the synthesis of mesoporous MCM-41 silica[1] by lowering the temperature, shortening the crystallization time as well as controlling the particle size.[2] However, due to the amorphous nature within the pore wall,[3,4] the products synthesized in alkaline media at low temperature have been much less stable than those obtained at higher temperatures,[5] which imposes a strict limitation on their applications. To achieve highly stable MCM-41 silica, a number of papers have focused on thickening the pore wall in order to obtain a more condensed and longer range ordered framework, either by modifying the assembly pathways[6] or by post-synthesis treatments.[7] The drawbacks of these procedures obviously lie within the time-consuming and complicated processing strategies. Therefore it is more desirable to synthesize stable MCM-41 silica by a quick and direct way.

Ultrasound has been introduced to a variety of material syntheses[8,9] owing to its sonochemical effects based on acoustic cavitation, a property which results from the continuous formation, growth and implosive collapse of bubbles within a liquid.[10] We have found it possible, for the first time, to quickly synthesize MCM-41 silica with small particle size and enhanced pore wall thickness by a sonochemical process.

To synthesize all-silica MCM-41 in the present work, a mixture with initial molar ratio of 1.0 Na_2SiO_3 : 0.33 CTAB : 1.86 EtAc : 450 H_2O was first prepared in the following manner; CTAB and EtAc are cetyltrimethylammonium bromide and ethyl acetate, respectively. Typically, to an aqueous solution containing 4.90 g CTAB, 11.65 g $Na_2SiO_3 \cdot 9H_2O$ and 325 mL distilled water, 6.70 g EtAc was quickly injected under either vigorous stirring or sonication. A white precipitate appeared after *ca.* 1 min. The slurry was then divided into six parts for further treatment, the synthesis conditions of which are summarized in Table 1.

Powder X-ray diffraction (PXRD) shows differences among the as-synthesized as well as the calcined products. Except for the calcined sample A, all samples exhibit at least three well resolved reflections in the 2θ range between 2 and 10°. The patterns can be indexed to an ordered hexagonal lattice typical of MCM-41.[1] Interestingly, the full width at half maximum height (FWHM) of the (100) reflections of the samples synthesized with ultrasound is slightly narrower than those obtained without ultrasound (Table 2). It is well known that both structural disorder and a decrease in particle size may result in diffraction line broadening. In fact, under TEM the particles of samples A and F are much smaller and poorly

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Table 1 Synthesis conditions used to prepare samples A–F and their crystalline phases[a]

| Sample	Synthesis conditions	Sample	a_0[b]/Å
A	Aged for 4.5 h without stirring under ambient conditions	MCM-41	44.1
B	Sonicated for 3.5 h under ambient conditions	MCM-41	46.4
C	Heated at 358 K for 28 h then sonicated for 3.5 h under ambient conditions	MCM-41	47.6
D	Aged for 28 h then sonicated for 3.5 h under ambient conditions	MCM-41	47.5
E	Heated at 358 K for 56 h without stirring	MCM-41	47.4
F	Aged for 56 h under ambient conditions without stirring	MCM-41	47.5

[a] Sonication is carried out in a 50 mL sonication cell with a high-intensity ultrasonic horn (Sonic and Materials, model VC-600, 0.5 in Ti horn, 20 kHz, 100 W cm^{-2}). [b] Unit cell constant of the as-synthesized sample, $a_0 = 2d_{100}/\sqrt{3}$, where d_{100} is the d-spacing of (100) reflection.

Table 2 Textural properties of samples A–F after calcination in air at 823 K for 4 h and further at 923 K for 1 h

Sample	Solid	FWHM[a]/°	a_0[b]/Å	S_{BET}[c]/ m² g^{-1}	V_T[d]/ mL g^{-1}	V_F[e]/ mL g^{-1}	V_{Tx}[f]/ mL g^{-1}	D[g]/Å	W[h]/Å	V_F/V_T	W/a_0
A	Amorphous	—	—	833	0.386	—	—	—	—	—	—
B	MCM-41	0.16	44.9	853	0.794	0.656	0.138	24.8	20.1	0.827	0.448
C	MCM-41	0.16	43.4	835	0.783	0.611	0.172	23.3	20.1	0.780	0.463
D	MCM-41	0.18	42.5	931	0.920	0.660	0.260	22.6	19.9	0.717	0.468
E	MCM-41	0.20	42.5	1041	1.264	0.771	0.493	23.5	19.0	0.610	0.447
F	MCM-41	0.28	40.9	1042	1.109	0.776	0.433	23.5	17.4	0.700	0.425

[a] Full width at half maximum height of (100) reflection. [b] Unit cell constant, $a_0 = 2d_{100}/\sqrt{3}$, where d_{100} is the d-spacing of (100) reflection. [c] BET surface area, calculated from the linear part of the BET plot ($p/p_0 = 0.1$–0.2). [d] Total pore volume, taken from the volume of N_2 adsorbed at $p/p_0 = 0.995$. [e] Framework pore volume, derived from the volume of N_2 adsorbed at $p/p_0 = 0.54$. [f] Textural pore volume, obtained from the difference ($V_T - V_F$). [g] Average pore diameter, estimated using the adsorption branch of the isotherm and the Barrett–Joyner–Halenda (BJH) formula. [h] Pore wall thickness, estimated from the difference ($a_0 - D$).
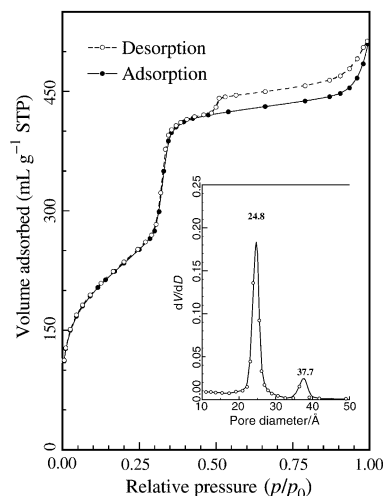
Fig. 1 N$_2$ adsorption–desorption isotherms of calcined sample B. *Inset*: the pore size distribution calculated by the use of the adsorption data.

aggregated than those of samples B–E, though samples A and F are more uniform in size. Moreover, all samples suffer a framework contraction upon calcination as indicated by the d_{100}-spacings' diminution, except for sample A whose framework collapses. This implies that the samples synthesized without ultrasound are less ordered and of lower stability than those synthesized with ultrasound.

The results from liquid N$_2$ adsorption–desorption measurements shed more light on the sonochemical effect upon the synthesis. Fig. 1 shows the N$_2$ adsorption–desorption isotherm as well as the pore size distribution of calcined sample B, and the structural features of the products are detailed in Table 2. The results indicate that samples B–F retain their hexagonal mesophase and exhibit narrow pore size distributions after removal of the organic templates. Though the BJH method may systematically underestimate the pore size by up to 1.0 nm,[11] and although many recent papers have developed more accurate methods for pore size calculation,[12] we think that the data obtained by applying the same method are comparable, and therefore the quantitative results based on these data are credible. It is quite obvious that the ultrasonic processing favors a thicker wall formation. Though acoustic cavitation etched the particles, resulting in a coarse outer surface whereas the inside channels retained the hexagonal arrangement, the electron diffraction pattern shows higher order spots, which provide evidence that both the pore array and pore walls are highly ordered. The processing time of sample B is relatively short; however, a highly ordered, stable mesostructure was fabricated. It was previously reported that MCM-41 can be prepared in a few hours under ambient conditions but, unfortunately, no data regarding the stability have been presented.[13] In our case, the pore wall thicknesses of samples B–D are larger than those of samples E and F. This is quite promising since high quality MCM-41 can be synthesized by a simpler procedure as well as in a shorter time than by the conventional methods. The unit cell constants of the samples decrease in the order B > C > D ≈ E > F after calcination *vs.* C ≈ D ≈ E ≈ F > B before calcination, which means that the frameworks of samples B–D suffer less shrinkage than those of samples E and F. This implies that the pore walls of the sonochemically prepared samples are more condensed or ordered than those of the conventionally prepared ones. The ^{29}Si MAS NMR of calcined sample D is measured and reveals that the framework consists primarily of a fully cross-linked Q^4 unit and a smaller fraction of Q^3 sites. The calculated Q^4:Q^3 ratio is 6.7:1; normally, calcined silica mesostructures prepared by conventional methods have Q^4:Q^3 values near 3.[1] The Q^4:Q^3 ratio of calcined sample D is much higher than those prepared with special treatment,[7c] and is comparable to those of MSG silicas with ratios in the range

6.2–7.4.[6d] In fact, when sample D was refluxed for 6 h in boiling water its crystallinity changed very little. It decreased by *ca.* 35% after refluxing for 12 h, while in the literature[14] the MCM-41 prepared using conventional hydrothermal methods became amorphous after refluxing for 12 h. This can be an advantage of the sonochemical effects. During the formation of the framework, despite the agitation of the ultrasound which helps to disperse the small silica oligomers more homogeneously in the mixture, the formation of hot spots within the surfactant–silicate interface may accelerate the silica polymerization which is slow and rate-limited under normal conditions. Thus the fabrication of the mesostructure can be achieved more efficiently. On the one hand, acoustic cavitation etches the surface of surfactant–silicate micelles which results in a coarse outer surface. On the other hand, hot spots accelerate the condensation of surface silanol groups among micelles, and by this way ultrasound radiation accelerates the formation of the MCM-41 framework and the growth of particles. This two-fold function of ultrasound radiation results in the particles of samples B–E being bigger and more aggregated than those of samples A and F, though samples A and F are more uniform in size.

In conclusion, a novel synthesis route has been developed to prepare high quality MCM-41 within a relatively short time by involving ultrasound. The as-prepared material, whose mesopore size shows a very narrow distribution, possesses thick and condensed wall and is therefore thermally stable.

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