The ultrafast sonochemical synthesis of mesoporous silica MCM-41

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High quality silica MCM-41 has been synthesized in as little as 5 min using cetyltrimethylammonium bromide (CTMABr) as a template under basic conditions with the aid of ultrasonic irradiation.

Mesoporous silica MCM-41 has attracted considerable interest because of its high surface area, regular pore structure, specific pore volume and high thermal stability, all of which make it suitable for many catalytic applications.[1–3] Attention has been paid to increasing the quality of silica MCM-41 by shortening the self-assembly reaction time, since the conventional hydrothermal procedure for its synthesis usually takes 1–7 days,[4] which severely hampers its practical applications. Moreover, the large scale production of silica MCM-41 is quite unfavorable. For many catalytic applications, it would be more desirable to have an economically feasible method to prepare silica MCM-41 in a short synthesis time. Numerous methods have been developed for the synthesis of ordered mesoporous silicas, aiming at the reduction of time and energy without sacrificing the quality of the material. In this respect, microwave irradiation is considered to be an effective method for the synthesis of silica MCM-41 that offers several distinct advantages in reducing crystallization time over the conventional synthesis.[5,6] Unlike some reports of syntheses at room temperature that do not require specialized equipment,[7] the microwave method is most likely not to be applicable for large scale production. Recently, Celer and Jaroniec investigated the synthesis of ordered mesoporous silicas by a temperature-programmed microwave-assisted synthesis (TPMS) method.[8] The disadvantage associated with TPMS is that special care must be taken when operating the vessels under high pressure and high temperature conditions. In addition, it is necessary to allow the reactor to cool down for a long time after the reaction is complete.

To reduce the synthesis time for economic benefits, the use of ultrasound irradiation is now a subject of growing interest for the preparation of a variety of nanomaterials.[9] Although ultrasound does not cause chemical reactions directly, it has acoustic cavitation effects that create high local temperatures, pressures and cooling rates, giving sonicated solutions unique properties. These effects may enhance the rates of chemical reactions. Tang *et al.* have used this technique for the preparation of mesoporous silica MCM-41.[10] However, they sonicated the gel for 3.5 h, followed by aging its solution with and without heating for 28 h. Attempts have been made to prepare mesoporous silicas that are analogous to hexagonal silica MCM-41 under acidic conditions by using ultrasonic irradiation within a short synthesis time of about 20 min and a further quiescence time of 5 h.[11] Recently, the rapid sonochemical synthesis of periodic mesoporous organosilicas (PMOs) with methane and ethane bridging groups using cationic and triblock copolymer Pluronic P123 as templates, respectively, were reported.[12] Lee *et al.*[13] reported the synthesis of SBA-15 and Ti-SBA-15 silicas with ultrasonic irradiation for 1 h, followed by gelation for 1–3 h. Recently, our group achieved the synthesis of SBA-15 by a temperature-assisted sonochemical method.[14] By using the advantages associated with the sonochemical method, we report herein, for the first time, a successful synthesis of highly ordered silica MCM-41 under basic conditions *via* ultrasonic irradiation for only 5 min, which represents a significant time reduction in comparison to the conventional synthesis method. We also systematically investigate the effects of the synthesis time of sonication.

Mesoporous silica materials were prepared under ultrasonic irradiation with various time intervals. The samples are denoted as MCM-41-x, where x-represents the synthesis time in minutes of sonication.

The powder X-ray diffraction (XRD) patterns of both as-synthesized and calcined samples (Fig. 1) exhibited four diffraction peaks, which could be indexed as (100), (110), (200) and (210), characteristic of the hexagonally-ordered silica MCM-41 mesostructure. The XRD peak positions shifted to lower 2θ values when the synthesis time was increased. After calcination, the peaks shifted to higher 2θ values due to pore size contraction. The XRD results revealed that the formation of highly ordered mesoporous silica analogous to hexagonal silica MCM-41 could be achieved in as little time as 5 min under basic conditions with the aid of ultrasound irradiation.

The nitrogen adsorption–desorption isotherms of MCM-41-x are shown in Fig. 2, and the corresponding structural properties are listed in Table 1. The isotherms of MCM-41-x samples can be classified as type IV according to IUPAC nomenclature, indicating that the samples retain their hexagonal mesophases with a narrow pore size distribution after template removal. The BET surface areas and pore volumes of MCM-41-x are in the range 1260–1662 $m^2\ g^{-1}$ and 0.81–0.89 $cm^3\ g^{-1}$, respectively. The surface areas obtained are significantly higher than those of conventional silica MCM-41.[2] It has been reported that the NH_4OH-containing medium favors the formation of longer micelles.[15] This might be the reason for the higher surface areas in the present MCM-41-x samples. A small hysteresis was observed for MCM-41-50, which indicates the presence of porosity formed from the accumulation of silica particles. This might

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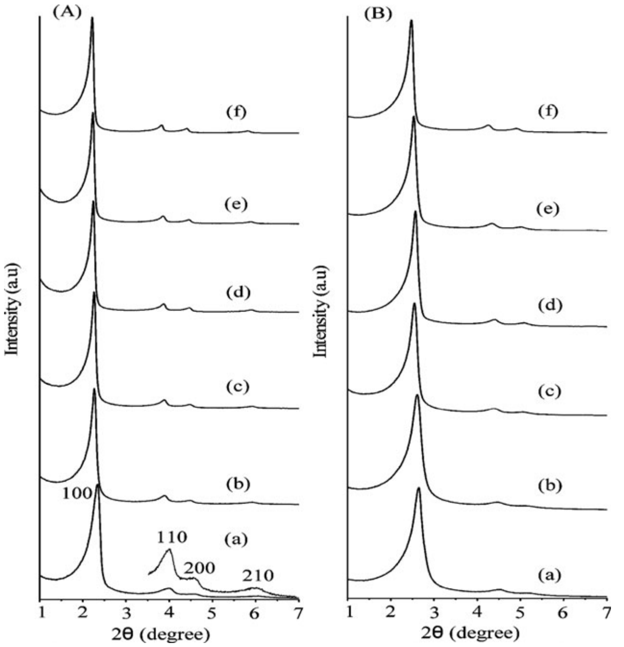

Fig. 1 XRD patterns of (A) as-synthesized and (B) calcined MCM-41-x, where x = (a) 5, (b) 10, (c) 20, (d) 30, (e) 40 and (f) 50.

account for the gradual decrease in surface area and the increase in pore size when the synthesis time is prolonged. In addition, the temperature of the water in the sonication bath increased approximately 5 °C every 10 min. After 50 min, the temperature had reached 58 °C, which might also have had some influence on the textural properties of the MCM-41-x materials. The results demonstrate that extension of the sonication time is unfavorable to the textural properties of the resulting MCM-41-x materials. Nevertheless, all the MCM-41-x samples exhibited high surface areas and large pore volumes.

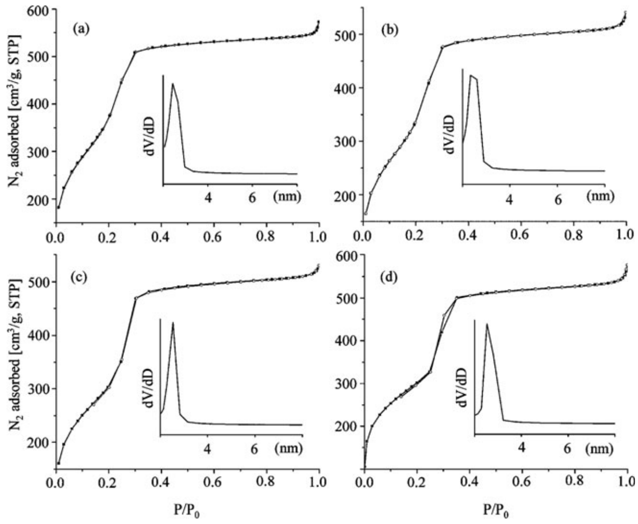

Fig. 2 N_2 adsorption–desorption isotherms of calcined MCM-41-x, where x = (a) 5, (b) 10, (c) 30 and (d) 50.

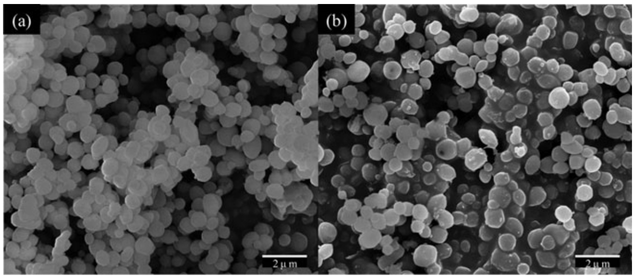

Fig. 3 SEM images of MCM-41-x, where x = (a) 5 and (b) 50.

The particle size, particle morphology and distribution of the MCM-41-x samples were investigated by using scanning electron microscopy (SEM), as shown in Fig. 3. The MCM-41-x samples displayed a spherical shape with a relatively uniform size of around 1 μm, which is basically identical to that of conventional silica MCM-41.[2] No significant difference in particle size or shape was observed upon increasing the synthesis time of sonication. Transmission electron microscopic (TEM) images (Fig. 4) clearly show that MCM-41-5 exhibits an ordered hexagonal mesostructure that is consistent with previous reports of silica MCM-41 synthesized under basic media.[15]

The degree of condensation of the silica framework was estimated by performing ^{29}Si MAS (magic angle spinning) NMR spectroscopy on the as-synthesized samples prepared in different time intervals (Fig. 5). The spectra reveal three broad resonance peaks corresponding to the structural units $Si(OSi)_2(OH)_2$ (Q^2) at −92 ppm, $Si(OSi)_3OH$ (Q^3) at −102 ppm and $Si(OSi)_4$ (Q^4) at −110 ppm, respectively. The percentages of the Q^n species were calculated by deconvolution of the spectra. The MCM-41-5 sample exhibited more Q^2 and Q^3 species than the other samples, indicating a rather incomplete condensation of the silica in such a short reaction time. However, such a short reaction time does not seem to harm the structure formation, as confirmed by XRD and nitrogen sorption measurements. When the sonication time was increased, the intensities of the Q^2 and Q^3 species decreased and the $Q^4/(Q^3 + Q^2)$ ratio increased progressively, suggesting that a longer sonication time is helpful for the formation of a more condensed silica framework. Upon calcination, the spectrum (Fig. 6) exhibited only a broad unresolved signal that could be ascribed to the overlap of Q^3 and Q^4. A higher Q^4/Q^3 ratio was observed for the calcined samples as compared to those of the as-synthesized samples, indicating that further condensation of the silica occurred upon calcination. Since both calcined samples exhibited nearly the same Q^4/Q^3 ratio, the degree of cross-linking of the silica framework remained unaltered after calcination.

Solvent extraction procedures, following reported methods,[12] were also attempted in this study to remove the template by using various concentrations of HCl in acetone. However, the XRD results showed a disordered structure for the sample after such a solvent extraction treatment. This suggests that the pure MCM-41-x material is not stable towards solvent extraction compared to PMOs, with which the silica framework is composed of organic linkers. Without applying sonication, a time of at least 2 h was required for the preparation of the silica MCM-41 materials in the presence of an ammonia solution, which acts as a catalyst for the faster

Table 1 Textural properties of MCM-41-x, where x represents the synthesis time in min

x	d_{100}	a_0/nm[a]	A_{BET}/m^2 g^{-1}[b]	V_{p}/cm^3 g^{-1}[c]	Pore size/nm
5	3.33 (3.76)[d]	3.84 (4.34)	1662	0.89	2.6
10	3.38 (3.88)	3.90 (4.49)	1554	0.84	2.6
20	3.46 (3.90)	4.01 (4.50)	1592	0.89	2.6
30	3.44 (3.93)	3.97 (4.54)	1424	0.81	2.6
40	3.49 (3.95)	4.02 (4.56)	1361	0.85	2.7
50	3.56 (3.98)	4.12 (4.59)	1260	0.87	2.9

[a] Lattice parameters a_0 were calculated based on the formula $a_0 = 2d_{100}/\sqrt{3}$. [b] A_{BET} = BET surface area. [c] V_{p} = total pore volume. [d] The numbers in parentheses are for as-synthesized samples.

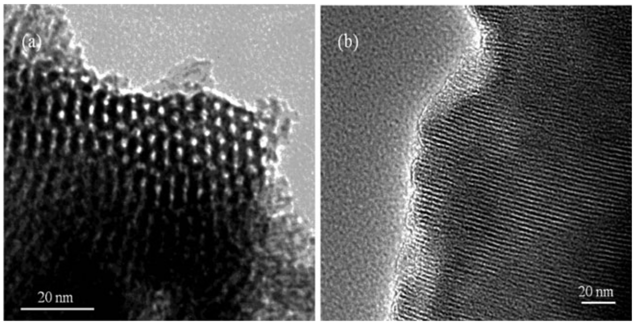

Fig. 4 TEM images of MCM-41-5 in a direction (a) parallel and (b) perpendicular to the pore axis.

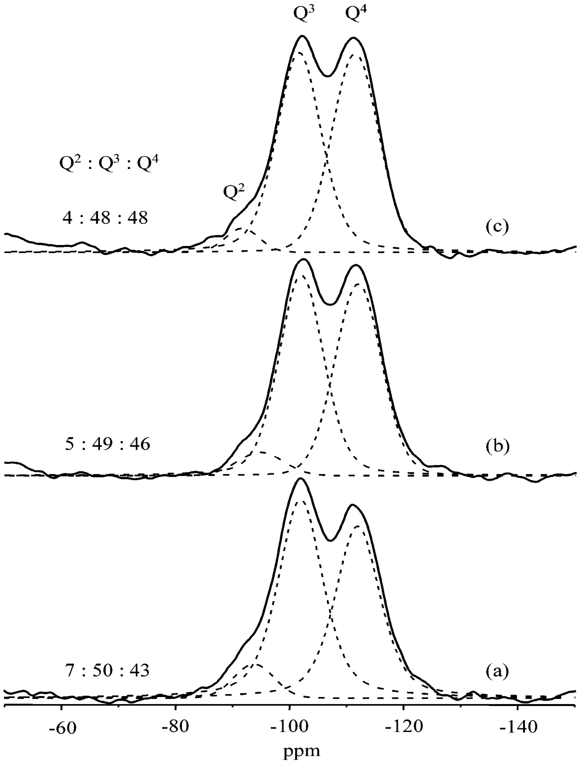

Fig. 5 ^{29}Si MAS NMR spectra of as-synthesized MCM-41-x, where x = (a) 5, (b) 20 and (c) 50. The dashed lines are the components used for spectral deconvolution.

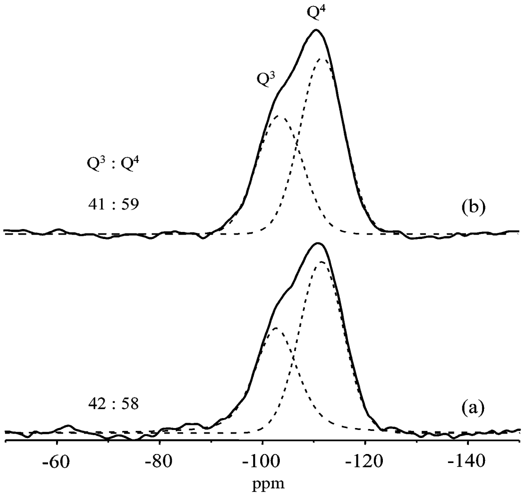

Fig. 6 ^{29}Si MAS NMR spectra of calcined MCM-41-x, where x = (a) 5 and (b) 50. The dashed lines are the components used for spectral deconvolution.

condensation of TEOS.[15] This study reveals that ultrasonic irradiation reinforces the rapid hydrolysis and condensation of silicon precursors, and makes the small silica oligomers more homogeneous in the mixture, which is slow and rate-limiting under normal conditions. As a result, the fabrication of the mesostructure can be achieved more efficiently with the aid of ultrasonic irradiation. On the contrary, the conventional hydrothermal synthesis route generally requires much longer reaction times for both the condensation and crystallization of the silica precursors. In the present work, the whole synthesis took as little as 5 min, which is substantially less than the previously reported methods.

In summary, we have demonstrated that the formation of highly ordered silica MCM-41 mesostructures can be achieved in a few minutes with the aid of ultrasonic irradiation. The present sonochemical synthesis pathway not only allows high quality silica MCM-41 to be obtained in a more economical way, *i.e.* in a much shorter reaction time, but also opens up new opportunities for the large scale industrial production of mesoporous silica materials.

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Experimental section

Preparation of mesoporous silica MCM-41 materials

A base-catalyzed route was used to synthesize silica MCM-41. In a typical synthesis, 0.3 g of CTMABr was dissolved in a mixture of 16 g of NH_4OH (35 wt%) and 63 g of water under sonication for 1 min. After a homogeneous solution had been obtained, 1.36 g of TEOS (tetraethoxysilane) was added dropwise with vigorous stirring. The resulting solution was then subjected to sonication using an ultrasonic generator, type D200H (Delta Co. Ltd), with a frequency of 43 kHz and a power of 200 W for times ranging from 5 to 50 min. The molar composition of the reaction mixture was 1 TEOS : 0.125 CTMABr : 69 NH_4OH : 525 H_2O. The resulting precipitate was then filtered, washed with de-ionized water, dried in an oven at ambient temperature and followed by calcination in air with a heating rate of 3 °C min^{-1} from room temperature to 550 °C, being kept at 550 °C for 4 h. A calcined sample of about 0.2 g was thus obtained.

Characterization methods

XRD patterns were collected on a PANalytical X'Pert Pro diffractometer using Cu-K_α radiation (λ = 0.15406 nm) at 45 kV and 40 mA. N_2 adsorption–desorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 analyzer. Specific surface areas were calculated by using the Brunauer–Emmett–Teller (BET) method. The pore size distribution was obtained from an analysis of the adsorption branch of the isotherm by the Barrett–Joyner–Halenda (BJH) method. Solid-state ^{29}Si NMR spectra were recorded on a Varian Infinityplus-500 NMR spectrometer equipped with 5.0 and 7.5 mm Chemagnetics probes. SEM was performed on a Hitachi S-800 field-emission scanning microscope. TEM was carried out on a JEOL JEM2100 microscope operating at 200 kV.

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