

Improved Long-range Order of Silicious MCM-41 by Gradual Heating of Synthesis Gel

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Mesoporous MCM-41 with fiber-like morphology and a high degree of long-range internal order in micrometer range, could be prepared by very gradual heating of the precursor gel to the crystallization temperature.

Ordered mesostructured inorganic solids have acquired immense importance in material science research, in application to catalysis, molecular separation, and in optoelectronics because of the possibility to tailor their nanostructure and morphology.¹ So, the preparation of surfactant-templated mesoporous silica, which is ordered at both the nanoscale and micrometer/millimeter length scale, has attracted considerable research interest.²⁻⁶ Well-ordered MCM-41 ropes, fibers or rods are of particular interest especially for the fabrication of silica-based nanotube materials such as conducting wires.⁷ Crystallization of ordered mesoporous materials^{8,9} from a liquid crystalline structure comprised of complex mixture of surfactant and silicates is highly sensitive to the synthesis condition. The rigidity and curvatures of the interfaces in the gel could be modified by inducing mesoscopic structural changes by varying parameters such as temperature, alkalinity and by addition of counterions and alcohols.¹⁰⁻¹⁴ Thus it may be possible to control and form higher degree of internal ordering of the mesoporous channels.

We report here a simple approach to the preparation of elongated MCM-41 fibers with a high degree of long-range internal ordering of the pores (ordered at micrometer-range). Morphological transformation from sphere-shaped particles to elongated rod-like particles was achieved by gradually heating the synthesis gel to the crystallization temperature in an otherwise normal MCM-41 synthesis procedure under basic conditions.

The MCM-41 materials were prepared using a synthesis procedure similar to that described earlier¹⁵ as follows: Cetyltrimethylammonium bromide (CTAB) (Acros, 99%) was dissolved in distilled water at 35 °C under stirring. To it a solution of sodium silicate (Aldrich, 14% NaOH and 27% SiO₂) was added and stirred for 20 min. The pH of the solution was then immediately adjusted to 10 with dilute (1 M) sulfuric acid. The molar composition of the gel mixture was 1.00 SiO₂/0.35 CTAB/100 H₂O. The gel mixture was further stirred for 1 h. The resulting mixture was transferred to a Teflon-lined autoclave and was aged by gradually raising the temperature to the desired crystallization temperature (100–125 °C) at a ramp rate of 0.5 °C/min and then heated at constant temperature for 48–96 h in a programmable oven. The final solid product obtained after filtration, was washed with distilled water, dried in air and calcined at 560 °C for 6 h to remove the template molecules. Standard samples were also prepared using similar gel composition but directly heating the gel to 100 °C for 48 h (MCM-41(a)) and 125 °C for 96 h (MCM-41(b)).

All the materials exhibit 4–5 sharp XRD peaks, which re-

fect a well-aligned MCM-41 structure with high long-range internal ordering of the mesopores. A comparison of XRD patterns of the MCM-41 samples and the analyses of their corresponding peak intensities for the various diffraction peaks summarized in Table 1 show some very prominent differences. The samples prepared by gradually raising the temperature of the synthesis gel to 125 °C (MCM-41(e) and MCM-41(f)) exhibit enhanced XRD scattering intensities of the higher order diffraction peaks. For example, the sample MCM-41(e) shows nearly 29, 58, and 100% increase in d_{110} , d_{200} and d_{210} diffraction peaks when compared with MCM-41(a) sample synthesized by conventional procedure. Such a large increase in higher order diffraction peaks has not been reported so far and is indicative of a very high degree of long-range ordering within the mesoporous silicas.

Nitrogen adsorption/desorption analysis showed type IV isotherm with virtually no hysteresis, for the samples MCM-41(a), MCM-41(e) and MCM-41(f) (isotherms not shown). Table 1 summarizes the surface properties and pore structure obtained from nitrogen sorption data and XRD results. Slow heating of the synthesis gel results in large increase in wall thickness and decrease in the average pore size. High pore wall thickness implies higher stability for these samples. In fact the samples were found to be thermally stable up to 900 °C with little loss in crystallinity and long-range order unlike conventional sample which showed considerable (25–35%) loss in crystallinity after heating to 900 °C. All the samples exhibit very high surface areas and pore volumes and very narrow pore size distribution. It is worth noting that depending on the crystallization condition the pore size of the samples varied between 25–30 Å.

The scanning electron microscopy (SEM) micrograph for the standard sample MCM-41(a) (Figure 1a) and that for sample MCM-41(f) crystallized by gradually heating the synthesis gel to 125 °C (Figure 1b) reveal entirely different morphologies. The standard MCM-41(a) sample (Figure 1a) is comprised of submicrometer-size free, intergrowing or aggregated sphere-like particles, which is the typical morphology of normal MCM-41 synthesized under basic conditions. The morphology of MCM-41(f) (Figure 1b) differs from that of the standard MCM-41 sample in that it consists of elongated well-separated particles 200–400 µm in length and with ≈75 µm in thickness. Figure 1c shows the nature of walls of the long particles. At higher magnifications (Figures 1c and 1d) it can be observed that individual particles consist of bundles of silica fibers arranged coaxially along the particle's long axis. These silica fibers have a ribbon-like morphology (Figure 1d). These fiber-like MCM-41 with long-range order are essentially different from the MCM-41 materials reported earlier.^{2-6,10-14} The controlled heating protocol is responsible for this difference.

Further evidence for the presence of highly ordered, long-range periodic mesoporous structure is obtained by TEM analysis (Figure 2). Sample MCM-41(f) showed a hexagonal array of

Table 1. Pore structure properties and XRD intensities of MCM-41 samples

Sample	Surf. area /m ² g ⁻¹	Pore vol /cm ³ g ⁻¹	Pore ^a size /Å	a ₀ ^b /Å	Wall ^c Å	XRD Intensity/arb unit			
						d ₁₀₀	d ₁₁₀	d ₂₀₀	D ₂₁₀
MCM-41(a)	1205	1.80	38	46	8	6.7	1.4	1.2	0.7
MCM-41(b)	914	1.48	37	49	12	4.8	1.2	1.0	0.6
MCM-41(c)	921	0.95	27	43	16	3.2	1.3	1.4	1.1
MCM-41(d)	886	1.09	25	45	20	3.6	1.6	2.0	1.3
MCM-41(e)	1170	1.6	28	44	16	4.4	1.5	1.9	1.5
MCM-41(f)	1012	1.5	26	44	18	3.2	1.8	1.9	1.4

Crystallization conditions: MCM-41(a), 100 °C static (48 h); MCM-41(b), 125 °C static (96 h); MCM-41(c), 100 °C (0.5 °C/min., 48 h); MCM-41(d), 100 °C (0.5 °C/min, 96 h); MCM-41(e), 125 °C (0.5 °C/min., 48 h); MCM-41(f), 125 °C (0.5 °C/min. 96 h).

^aPore size from BJH analysis of adsorption data. ^blattice parameter, from the XRD data using the formula $a_0 = 2d_{100}/\sqrt{3}$. ^cWall thickness = a_0 – pore size.

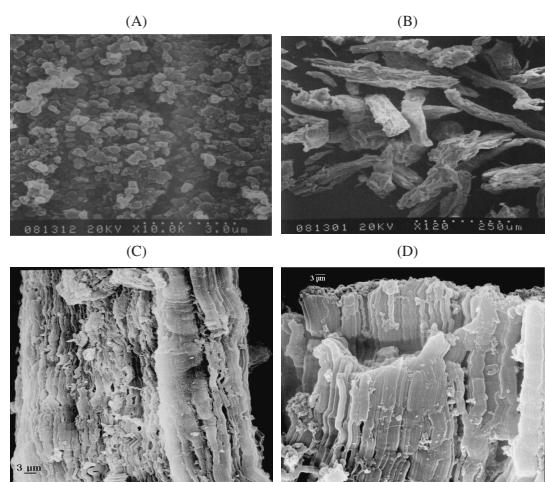


Figure 1. SEM micrographs of calcined MCM-41 samples. (A) MCM-41(a); (B) MCM-41(f); (C), (D) higher magnification images of sample MCM-41(f).

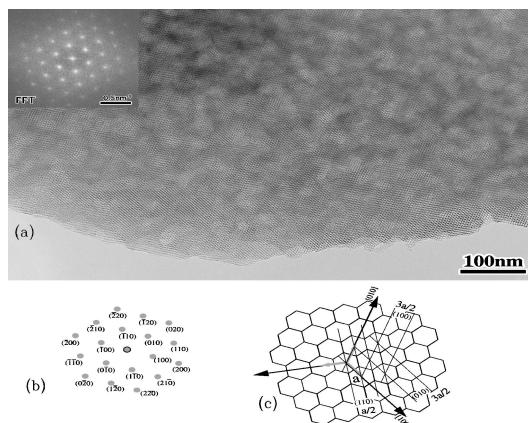


Figure 2. (a) TEM micrograph of calcined MCM-41(f) sample showing long-range order of hexagonal mesopores, insert shows the diffraction pattern; (b) schematic diffraction pattern and (c) real space configuration.

regularly sized mesopores separated by thick silica walls due to the hexagonal repeating tubules. The TEM clearly shows the presence of hexagonal arrays of mesopores ordered in micrometer range without any defects, and it supports the XRD observation of the presence of long-range order in these samples. The formation of MCM-41 with tubular morphology is found to be dependent on the gradual heating of the synthesis gel to the required crystallization temperature.

A sequential liquid crystal phase transformation mechanism for crystallization similar to that proposed by Monnier et al.,¹⁶ and Lin et al.² can be invoked to account for the formation of highly ordered elongated MCM-41 samples. The initial gel in the form of a clear solution of monomers or low oligomers of silicates and spherical micelles turn into a thick gel due to condensation of silica polyanions which have strong electrostatic interaction with surfactant cations and form layers consisting of hexagonal micelle cylinders. Gradual heating of the synthesis gel thermally favors the sequential organization process from layered, lamellar mesostructure to hexagonal mesostructure.

In conclusion, it has been possible to synthesize mesoporous MCM-41 materials with a high degree of long-range internal order in micrometer range, by very slowly heating the precursor gel to the crystallization temperature. This synthesis method offers the potential of fabricating monoliths of periodic mesoporous materials with a high degree of control over the long-range order, phase structure and pore size. Such materials would provide a perfect host for conductive carbon wires as well embedded and oriented metal and semiconductor nanorods and play an important role in the development of catalysts and nanometer-sized electronic devices. Further work on application of this method in synthesis of other mesoporous metal oxides is underway.

References and Notes

- 1 J. Y. Ying, C. P. Mehnert, and M. S. Wong, *Angew. Chem., Int. Ed.*, **38**, 56 (1999).
- 2 H.-P. Lin and C.-H. Mou, *Science*, **273**, 765 (1996).
- 3 H. Yang, N. Coombs, and G. A. Ozin, *Nature*, **386**, 692 (1997).
- 4 H.-P. Lin, S.-B. Liu, C.-Y. Mou, and C.-Y. Tang, *Chem. Commun.*, **1999**, 583.
- 5 L.-Z. Wang, J.-L. Shi, F.-Q. Tang, J. Yu, M.-L. Ruan, and D.-S. Yan, *J. Mater. Chem.*, **9**, 643 (1999).
- 6 P. Schmidt-Winkel, P. Yang, D. I. Margolese, B. F. Chmelka, and G. D. Stucky, *Adv. Mater.*, **11**, 303 (1999).
- 7 C.-G. Wa and T. Bein, *Chem. Mater.*, **6**, 1109 (1994).
- 8 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).
- 9 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olsen, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992).
- 10 M. Ogawa, *J. Am. Chem. Soc.*, **116**, 7941 (1994).
- 11 P. T. Tanev and T. J. Pinnavaia, *Science*, **271**, 1267 (1996).
- 12 S. Oliver, A. Kuperman, N. Coombs, A. Lough, and G. A. Ozin, *Nature*, **378**, 47 (1995).
- 13 A. Firouzi, D. Kumar, L. M. Bull, T. Besier, P. Sieger, Q. Huo, S. A. Walker, J. A. Zasadzinski, C. Glinka, J. Nicol, D. Margolese, G. D. Stucky, and B. F. Chmelka, *Science*, **267**, 1138 (1995).
- 14 C. A. Fyfe and G. Fu, *J. Am. Chem. Soc.*, **117**, 9709 (1995).
- 15 D. W. Hwang, A. K. Sinha, C.-Y. Cheng, T.-Y. Yu, and L.-P. Hwang, *J. Phys. Chem. B*, **105**, 5713 (2001).
- 16 A. Monnier, F. Schüth, Q. Huo, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurthy, P. Petroff, A. Firouzi, M. Janicke, and B. F. Chmelka, *Science*, **261**, 1299 (1993).