

Synthesis of Mesoporous Manganosilicates: Mn-MCM-41, Mn-MCM-48 and Mn-MCM-L

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Mesoporous manganosilicate materials Mn-M41S, having hexagonal, cubic and lamellar structures, are synthesized with a low surfactant:Si ratio (0.12:1) at various temperatures and acid/base contents and are characterized by X-ray powder diffraction and Q-band EPR spectroscopy.

Recently a novel family of silica-based mesoporous molecular sieves, designated as M41S, was synthesized by Mobil researchers.¹⁻² The M41S family contains several members: MCM-41, having a hexagonal arrangement of unidimensional pores, MCM-48, displaying a cubic structure, and other members that have lamellar and cubic octamer structures.^{2,4-7} Variations in the composition of these materials are expected to expand the scope of their catalytic applications. Modified compositions of the silica based M41S materials have been so far limited to the incorporation of aluminium, vanadium and titanium into MCM-41.^{3,7-8} Similar substitutions have not yet been reported for the silica base cubic phase MCM-48, which has been synthesized with a high surfactant:Si ratio of 1:2.^{2,4} Here we describe the synthesis of mesoporous manganosilicate materials, Mn-M41S, having hexagonal (Mn-MCM-41), cubic (Mn-MCM-48), and lamellar (Mn-MCM-L) structures. We show that the addition of Mn ions induces the formation of the cubic phase also at a low surfactant:Si ratio (0.12) and that by variations of the base or acid content of the gel at a fixed surfactant:Si ratio, one can control the structure formed.

Two synthetic procedures, using different silica sources, were employed.² In the first method, an NaOH solution (15–30 ml, 2 mol dm⁻³) was added under constant stirring to a solution of cetyltrimethylammonium chloride (14.5 ml, 25% *m/m*; Aldrich, C₁₆H₃₃Me₃NCl, CTAC) or bromide (Aldrich, C₁₆H₃₃Me₃NBr, CTAB). This solution was then combined with an MnCl₂ solution (0.4 mol dm⁻³) and tetraethyl orthosilicate (20.5 ml; Aldrich). The composition of the resultant gel was: SiO₂·xMnO·yNa₂O·zCTAC(CTAB)·wH₂O where 0.0004 < x < 0.09, 0.16 < y < 0.49, z = 0.12 and 115 < w < 150. In the second method, sodium silicate (21 g; N brand, 27% silica, Merck) was combined with a 2 mol dm⁻³ HCl solution (5–20.5 ml) or a 2 mol dm⁻³ NaOH solution under constant stirring (*ca.* 10 min). Then, MnCl₂ (0.1–20 ml, 0.4 mol dm⁻³) and CTAC or CTAB solutions were added. The composition of the resultant gel was SiO₂·xMnO·yNa₂O·zCTAC(CTAB)·vHCl·wH₂O where 0.0004 < x < 0.09, 0.3 < y < 0.65, z = 0.12 and 0.11 < v < 0.45, 118 < w < 160. The gels obtained using these procedures were then stirred for 30 min at room temperature. High temperature (≥100 °C) syntheses were carried out in an autoclave for 72 h, otherwise the gel was left under stirring at room temperature. The solid product was recovered and calcined as described previously.² Pure silica derivatives were synthesized according to the procedures described above without the addition of MnCl₂.

Using the above procedures all three structures, Mn-MCM-41, Mn-MCM-48 and Mn-MCM-L could be generated with a wide range of Mn:Si molar ratios (0.0004–0.09) in the reaction gel. The Mn:Si ratio in the final product was usually similar to or higher than that of the corresponding reaction gel. X-Ray diffraction (XRD) powder patterns of typical as-synthesized Mn-MCM-41, Mn-MCM-48 and Mn-MCM-L materials are depicted and indexed in Fig. 1. Owing to the long range order of the pores they show diffractions in the 2θ range of 2–8°, similar to XRD patterns previously reported for M41S materials with hexagonal, cubic and lamellar structures.^{2,4} The XRD patterns of calcined Mn-MCM-41 and Mn-MCM-48 were similar to those of the as-synthesized materials although they showed a reduction in the pore size. The BET surface areas of Mn-MCM-41 and Mn-MCM-48 after calcination were 1340 and 950 m² g⁻¹ respectively, in good agreement with previously

reported values.² Calcination of Mn-MCM-L caused the collapse of the structure, as expected.²

Mn-MCM-41 could be produced over a wide range of temperatures (21–100 °C). At room temperature it was detected after only 5 min reaction time. The first structure observed was Mn-MCM-41; we did not detect a precursor lamellar phase at earlier times, as reported by Monnier *et al.*⁵ for MCM-41. At low surfactant:Si ratios, Mn-MCM-48 could be synthesized only at high temperatures (100–120 °C) and the synthesis of a pure lamellar phase required either a high temperature (> 130 °C) or a high surfactant:Si ratio. At a fixed gel composition the structure of the Mn-M41S material obtained depends on the temperature. The following order was observed with increasing temperatures: hexagonal → mixture hexagonal, lamellar mixture → cubic → lamellar, *i.e.* at room temperatures pure Mn-MCM-41 was produced and an increase in the temperature transformed it to a lamellar or a cubic phase. This indicates that the temperature plays an important role both in terms of template organization and silanol condensation. This supports the basic liquid crystal templating mechanism proposed earlier for the M41S materials.^{2,6} Furthermore, the transformation observed above suggests that the precursor to the M41S structures is a collection of individual silicated surfactant micellar rods.

At fixed temperature and surfactant:Si ratio the structure formed could be controlled by varying the base or acid content of the gel. The structures formed, however, were a function of the silica source used. When tetraethyl orthosilicate was used, increasing the NaOH concentration and keeping the tem-

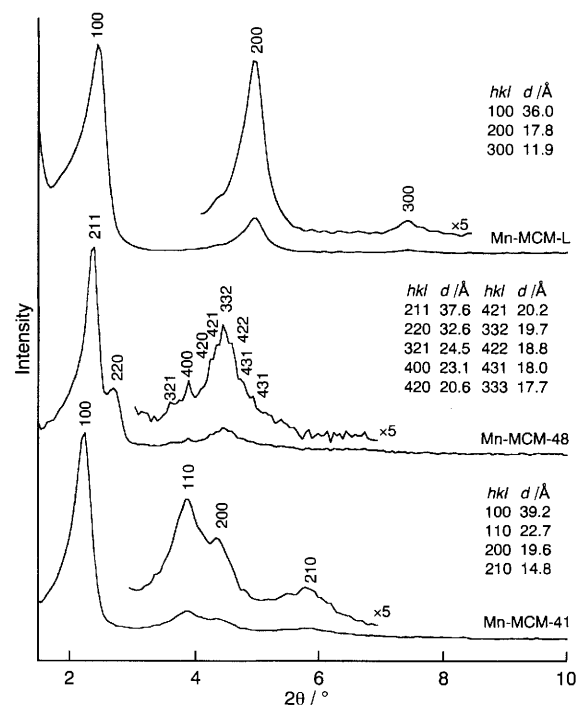


Fig. 1 Powder X-ray diffraction pattern of as-synthesized Mn-MCM-41, Mn-MCM-48 and Mn-MCM-L. The gel composition of all three samples was: 92SiO₂·0.4MnO·22.5Na₂O·11CTAC and the synthesis temperatures were room temp., 100 °C and 150 °C, respectively.

perature (100 °C) and the concentration of all other components constant resulted in the trend hexagonal → lamellar → cubic → hexagonal (in different samples). In contrast, when sodium silicate was used the cubic phase was not produced and the order observed with increasing NaOH concentration was hexagonal → lamellar. This difference may arise from a faster silicate hydrolysis rate in sodium silicate than in tetraethyl orthosilicate, resulting in enhanced silanol condensation and the formation of a thicker amorphous silica wall that inhibits the transformation to the cubic phase.

Mn-MCM-41 could be generated within a relatively large range of base concentrations ($0.16 < y < 0.27$ or $0.35 < y < 0.49$), whereas only a narrow range ($0.30 < y < 0.34$) produced Mn-MCM-48. Moreover, while Mn-MCM-48 could be synthesized with a wide range of Mn:Si, it did not form under the same conditions in the absence of MnCl₂. Increasing the NaOH concentration, however, did produce MCM-48, indicating that the addition of Mn ions or NaOH induces the formation of the cubic phase.

To characterize the location of Mn ions, in the products (important for understanding their role in the synthetic mechanism, X- and Q-band EPR measurements were carried out on

the M41S materials before and after calcination. All as-synthesized materials besides those synthesized at room temperature with HCl did not show any EPR signals either at room temperature or at -120 °C. We attribute the absence of the EPR signal to the presence of Mn^{III} species, rather than Mn^{II}, since the latter is oxidized to Mn^{III} in basic media in air.⁹ Calcination of these materials, however, did produce a typical spectrum of Mn^{II} indicating that during calcination at least part of the Mn^{III} was reduced to Mn^{II}. In contrast, in as-synthesized Mn-containing aluminophosphate molecular sieves, synthesized under acidic conditions, typical spectra of Mn^{II} were readily observed.¹⁰

The Q-band EPR spectrum of Mn-MCM-41 synthesized at room temperature in the presence of HCl exhibits a typical Mn^{II} spectrum with a hyperfine coupling, *a*, of 81 G and *g* ≈ 2.00, as shown in Fig. 2(a). Low intensity forbidden transitions are evident in both the room temperature and the low temperature spectra, indicating that the Mn^{II} species are rather immobilized. Upon calcination, the hyperfine coupling changed to 91 G and the forbidden transitions apparent in the low temperature spectrum of the calcined sample, became averaged out in the room temperature spectrum. This indicates that the Mn^{II} species are more mobile after calcination. The same spectrum was obtained from calcined Mn-MCM-41 which did not exhibit Mn^{II} EPR signals prior to calcination. The spectrum of calcined Mn-MCM-48, shown in Fig. 2(c), is very similar to that of a MnCl₂ solution in 1:1 water-glycerol at both room temperature and -120 °C [Fig. 2(d)] indicating that fully mobile, hydrated Mn²⁺ ions are present.

The greater immobility of the Mn^{II} species in as-synthesized Mn-MCM-41 at room temp. can be attributed either to its location within the wall or in the interface region of the polar head groups of the template and the silica walls. In the calcined samples of both Mn-MCM-41 and Mn-MCM-48, however, their high mobility indicates that they are not located within the inorganic wall but are within the pores.

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References

- 1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- 2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D.H. Olson, E. W. Shepard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
- 3 R. Schmidt, D. Akporiage, M. Stocker and O. H. Ellestad, *J. Chem. Soc. Chem. Commun.*, 1994, 1493.
- 4 Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth and G. D. Stucky, *Nature*, 1994, **368**, 317.
- 5 A. Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299.
- 6 C. Y. Chen, H. X. Li and M. E. Davis, *Microporous Mater.*, 1993, **2**, 17; 27.
- 7 P. T. Taner, M. Chibwe and T. J. Pinnavaia, *Nature*, 1994, **368**, 321.
- 8 K. M. Reddy, I. Moudrakovski and A. Sayari, *J. Chem. Soc., Chem. Commun.*, 1994, 1059.
- 9 R. D. W. Kemmit, in *Comprehensive Inorganic Chemistry*, Pergamon, Oxford, 1973, vol. 3, p.771.
- 10 Z. Levi, A. M. Raitsimring and D. Goldfarb, *J. Phys. Chem.*, 1991, **95**, 7831.

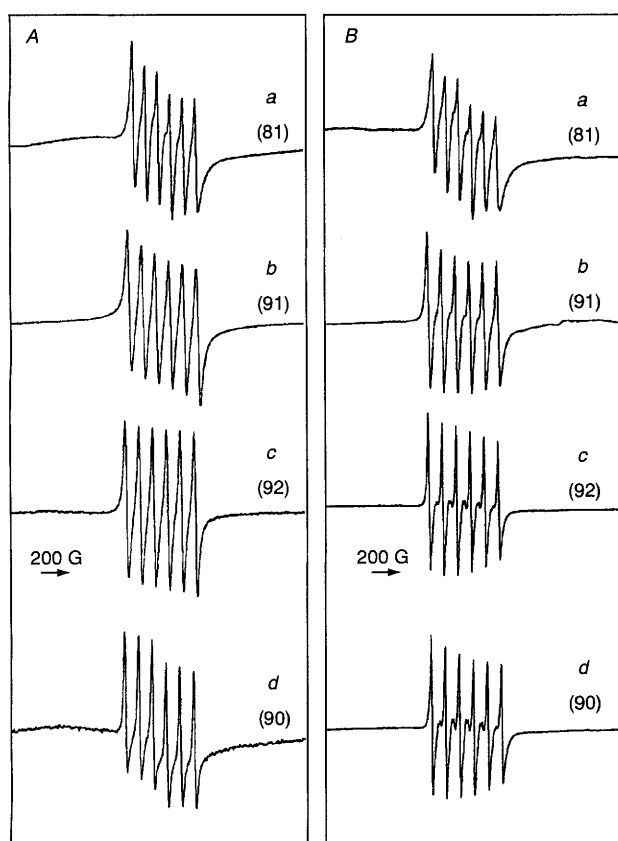


Fig. 2 Q-band EPR spectra (ca. 34 GHz), recorded at (A), room temp., (B) 150 K of (a) as-synthesized Mn-MCM-41, synthesized with HCl at room temp.; (b) same after calcination; (c) calcined Mn-MCM-48 (same sample as in Fig. 1); (d) 0.1 mmol dm⁻³ MnCl₂ solution in water-glycerol (1:1). The numbers in parentheses represent the hyperfine splittings in Gauss.