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On the extended recrystallisation of mesoporous silica: characterisation of restructured pure silica MCM-41

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Mesoporous silica MCM-41 may be restructured by performing secondary synthesis (*i.e.*, recrystallisation) in which *calcined* MCM-41 is used as silica source. The influence of a number of factors on the recrystallisation has been investigated. The factors investigated are, (1) the time allowed for hydrothermal recrystallisation at 150 °C, (2) the amount of amorphous silica available during recrystallisation and (3) the use of large pore MCM-41 as silica source. Increasing the time allowed for recrystallisation (from 48 to 212 hours) has little effect on the basal (d_{100}) spacing but results in a gradual and considerable increase in the pore wall thickness. The pore size therefore decreases slightly while both pore volume and surface area undergo more significant reductions. These textural changes are accompanied by restructuring of the particle morphology from the small *sphere* shaped particles of the original MCM-41 to much larger particles that are both *elongated* and *sheet (plate)-like*. Restructuring to the larger particles (for 48 hours recrystallisation) is most effective when there are only limited amounts of amorphous silica available in the recrystallisation gel. By using large pore MCM-41 materials as silica source it is possible to show that the structural and morphological transformations observed are consistent with a recrystallisation mechanism in which a significant proportion of the original MCM-41 particles are preserved and act as seeds for the restructuring.

1 Introduction

Mesoporous materials prepared *via* a mechanism in which supramolecular assemblies of surfactant micelles act as template for the organisation of inorganic silicate precursors are currently the focus of a great deal of research interest.[1,2] The mesoporous materials, first reported about a decade ago,[3,4] have the potential to extend the use of well ordered porous solids beyond the microporous (zeolite) range and into the mesoporous regime. The most studied of these materials is MCM-41, which is made up of hexagonally packed one-dimensional pore channels. The diameter of the pores can be varied in the range 15–100 Å.[1–4] Pure silica MCM-41 may be prepared *via* a wide range of methods and it is now known that materials with a variety of properties may be prepared by careful control of the synthesis conditions.[1,2] There have been several reports dealing with the post-synthesis modification of pure silica MCM-41.[5–10] In general post-synthesis treatments can be used to modify the pore size and morphology. Post-synthesis hydrothermal treatment (of as-synthesised MCM-41) in the mother liquor at 150 °C was used by Khushalani *et al.* to increase pore size from 40 to *ca.* 70 Å.[5] A later study found that such treatment leads to initial improvement of the MCM-41 ordering accompanied by small increases in pore size and that larger pore sizes were only obtained after extended treatment, which also resulted in poorer quality materials.[8] Post-synthesis restructuring of as-synthesised MCM-41 in water at 150 °C has also been shown to yield materials with improved long-range ordering and larger pore size.[9]

Many reports on the post-synthesis restructuring of pure silica MCM-41 have involved treatments on the as-synthesised (surfactant containing) material.[5–10] We on the other hand have recently been studying the post-synthesis restructuring of MCM-41 which involves the use of calcined (surfactant free) MCM-41 as 'silica source' in a secondary synthesis (or recrystallisation) step.[11–13] Our results to date suggest that the calcined MCM-41 particles can be preserved during the secondary synthesis and that they appear to undergo a morphological transformation from sphere shaped particles to larger *sheet* or *plate like* domains.[12] We have also more recently shown that the particle morphology of MCM-41 may be modified by extending the time allowed for high temperature (150 °C) crystallisation during *direct* synthesis.[14] Morphological transformation from *sphere* shaped particles to elongated *rod* or *rope-like* particles is achieved by extending the crystallisation time in an otherwise normal/*direct* MCM-41 synthesis procedure under basic conditions.[14]

It is now generally accepted that the use of longer 'crystallisation' periods during the high temperature *direct* synthesis of MCM-41, results in materials with larger basal spacing and pore size.[7,8,14] However, although long synthesis times (or post-synthesis treatments of the as-synthesised material) have certain advantages with respect to increase in basal spacing and pore size, the structural ordering of the resulting MCM-41 materials tends to decrease at the point where the largest pore sizes are obtained.[8] Consequently the resulting large pore materials generally have reduced surface area and pore volume due to poorer structural ordering.[8] Early work on recrystallisation of calcined MCM-41, however, indicated that the presence of MCM-41 crystallites/particles can inhibit pore size expansion when the time allowed for crystallisation during secondary synthesis is slightly extended from 48 to 96 hours.[12] It was thought that the re-used MCM-41 particles provide a fairly rigid backbone for further particle growth thereby inhibiting extensive pore size expansion which would normally occur at long crystallisation time.[7,8,14]

The aim of the present work was threefold, (1) to characterise the structural ordering of MCM-41 materials prepared *via extended* (*up to 212 hours*) recrystallisation, (2) to establish the morphology (in particular whether rod-like or sheet-like particles are formed) of extensively recrystallised MCM-41 materials and (3) to find out whether extended recrystallisation can afford MCM-41 materials with thick pore walls while still retaining the good structural ordering of the original material. The hope was that variations in the recrystallisation time could be used to systematically increase the wall thickness without affecting the structural ordering. The ability to tailor the wall thickness in such a manner is desirable and the formation of

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thick pore walls would afford some advantages with respect to structural stability (thermal and hydrothermal). With regard to particle morphology, it was of interest to find out the effect of extended recrystallisation given that *secondary synthesis*, involving short recrystallisation periods (48 hours), gives rise to sheet or plate-like particles[12] while extended *direct synthesis* on its own results in elongated rod-like particles.[14] By varying the nature (pore size and basal spacing) of the MCM-41 used as silica source during recrystallisation, this work also provided a simple test for the previously suggested seeding mechanism.[12] This test was based on the assumption that if total dissolution of the re-used MCM-41 particles occurred during recrystallisation, the recrystallised materials would not only be the same in all cases (regardless of the MCM-41 used as silica source) but also would be similar to MCM-41 products obtained from direct synthesis using conventional amorphous silica sources. In a seeding mechanism, the presence of MCM-41 particles is expected to prevent the formation of large pore MCM-41 materials regardless of the time allowed for recrystallisation.

2 Experimental

2.1 Synthesis of materials

The parent MCM-41 was prepared as follows: tetramethylammonium hydroxide (TMAOH) and cetyltrimethylammonium bromide (CTAB) were dissolved in distilled water by stirring at 35 °C to give a clear solution. The silica source, fumed silica (Sigma), was then added to the template solution under stirring for 1 hour. After further stirring for 1 hour to allow the silica to be fully dispersed, the resulting synthesis gel of composition SiO_2 : 0.25CTAB : 0.2TMAOH : $40H_2O$ was left to age for 20 hours at room temperature following which the gel was transferred to a Teflon-lined autoclave and heated at 150 °C for 48 hours. The solid product was obtained by filtration, washed with distilled water, dried in air at room temperature and calcined in air at 550 °C for 8 hours to yield the parent MCM-41. For recrystallisation, a synthesis gel of molar ratio as above was assembled except that the (calcined) parent MCM-41 was used as the 'silica source'. The experimental procedures were exactly as described above except that, during the recrystallisation, the heating at 150 °C was performed for 96, 140, 168 or 212 hours. The recrystallised samples were designated MCM-41(R*X*) where *X* is the recrystallisation time in hours, *i.e.*, MCM-41(R96), MCM-41(R140), MCM-41(R168) and MCM-41(R212) for 96, 140, 168 and 212 hours respectively.

2.2 Characterisation

Powder X-ray diffraction (XRD) patterns were recorded using a Philips 1830 powder diffractometer with Cu-Kα radiation (40 kV, 40 mA), 0.02° step size and 1 s step time. Textural properties were determined at −196 °C using nitrogen in a conventional volumetric technique by a Coulter SA3100 sorptometer. Before analysis the previously calcined samples were evacuated overnight (14 hours) at 200 °C under vacuum. The surface area was calculated using the BET method based on adsorption data in the partial pressure (P/P_0) range 0.05 to 0.2, the total pore volume was determined from the amount of N_2 adsorbed at a P/P_0 = *ca.* 0.99. The pore size was calculated based on a geometric model detailed elsewhere,[15,16] according to the equation: pore size $= cd(\rho Vp/1 + \rho Vp)^{1/2}$, where $c = 1.213$, ρ is the density of silica walls, d is basal spacing (d_{100}) and Vp is mesopore volume. Scanning electron microscopy (SEM) images were recorded using a JEOL JSM-820 scanning electron microscope. Samples were mounted using a conductive carbon double-sided sticky tape. A thin (*ca.* 10 nm) coating of gold sputter was deposited onto the samples to reduce the effects of charging. Transmission electron microscopy (TEM) images were recorded using a JEOL 2000-FX electron microscope operating at 200 kV. Samples for analysis were prepared by spreading them on a holey carbon film supported on a grid.

3 Results and discussion

3.1 Effect of extended recrystallisation on textural properties

The powder X-ray diffraction (XRD) patterns obtained for the calcined parent MCM-41 and the recrystallised materials are shown in Fig. 1. The pattern of the parent MCM-41 is typical of a relatively well ordered material and shows an intense (100) diffraction peak and three higher order (110), (200) and (210) peaks. The patterns of the recrystallised MCM-41 samples indicate that in all cases well ordered materials were obtained. This observation is particularly significant for materials recrystallised for 140 hours or longer in that it contrasts with what has been observed for extended direct synthesis where significant diminution of structural ordering is known to occur.[7,8,14] Indeed, the XRD patterns indicate that materials recrystallised for between 96 and 168 hours possess better structural ordering compared to the parent MCM-41 material. It is also noteworthy that for all recrystallised samples, there is very little shift in the 2*θ* value of the (100) peak, indicating that recrystallisation time does not have a significant effect on the final basal (d_{100}) spacing of the calcined recrystallised samples.

The N_2 sorption isotherms for all the MCM-41 materials are shown in Fig. 2 and Table 1 gives the corresponding textural properties. All the samples exhibit *adsorption* isotherms with a well-developed step in the relative pressure (P/P_0) range 0.35 to 0.45 characteristic of capillary condensation (filling) into uniform mesopores. The *adsorption* isotherms therefore indicate that the structural ordering and narrow pore size distribution of the parent MCM-41 is maintained in the recrystallised samples regardless of the time allowed for recrystallisation. The *adsorption* isotherms are therefore in excellent agreement with the XRD patterns in Fig. 1 and confirm that all the recrystallised materials possess good structural ordering. The *sorption* (adsorption/desorption) isotherms of the parent sample and sample MCM-41(R96) exhibit some hysteresis which is characteristic of MCM-41 materials with pores larger

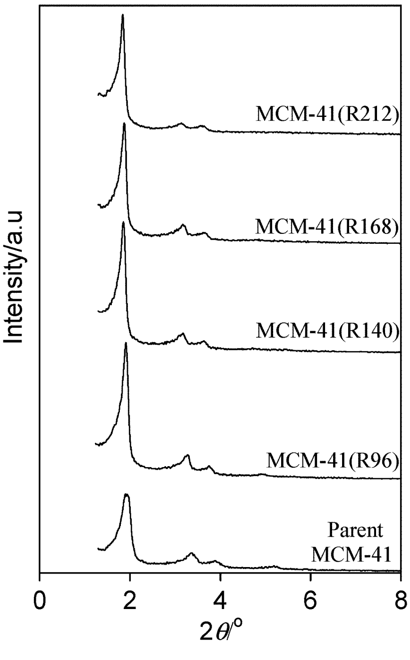

Fig. 1 Powder XRD patterns of MCM-41 (bottom) and MCM-41(R*X*) materials prepared *via* recrystallisation, where *X* is the time allowed for hydrothermal recrystallisation.

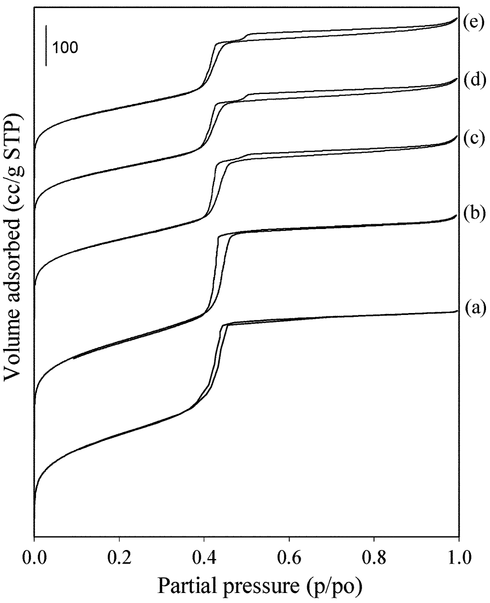

Fig. 2 Nitrogen sorption isotherms of (a) parent MCM-41 and MCM-41(R*X*) materials prepared *via* recrystallisation, (b) MCM-41(R96), (c) MCM-41(R140), (d) MCM-41(R168) and (e) MCM-41(R212).

than 40 Å.[16] However as the recrystallisation increases beyond 96 hours, the hysteresis exhibited by the *sorption* isotherms of the materials progressively changes. The *sorption* isotherms of samples MCM-41(R140), MCM-41(R168) and MCM-41(R212) exhibit a hysteresis loop, at $P/P_0 > 0.45$, which can be attributed to the presence of aggregates made up of platy particles.[17] This high partial pressure hysteresis loop is typical of slit pore widths created by the aggregation of platy particles.[17] This is an indication that the particle morphology changes during recrystallisation (platy particles are formed) and that the extent of the change (formation of platy particles) is greatest at longer recrystallisation time.

The *sorption* isotherms also indicate that extended recrystallisation causes a slight shift to lower pore size (pore filling step shifts to lower P/P_0) for the recrystallised samples and that the extent of the shift increases with the time allowed for recrystallisation. This is confirmed in Table 1 by the trend in calculated average pore size. The total change in pore size is however limited and in any case less than 10%. The decrease in pore size (as recrystallisation time increases) is accompanied by a small and apparently gradual increase in basal (d_{100}) spacing which therefore results in thicker pore walls for the recrystallised MCM-41 materials. The pore wall thickness of the recrystallised samples therefore gradually rises as the recrystallisation time is increased. It is worth noting that the trend observed here means that recrystallisation can be used to systematically tailor the pore wall thickness of MCM-41 materials.[18] The thicker walls of seeded MCM-41 materials are, as expected, accompanied by lower surface area and pore volume. From the textural data in Table 1 and the XRD patterns in Fig. 1 it is clear that the basal spacing of the seeded materials remains much the same despite the large variation in the time allowed for recrystallisation. This sharply contrasts with what is observed for extended direct synthesis using amorphous silica sources. The most likely explanation for the largely non-changing basal spacing observed here, is that the structural backbone of the parent MCM-41 is maintained even after extended recrystallisation. The main event that occurs during the recrystallisation may therefore involve further growth or linking of the existing parent MCM-41 particles as previously described.[11,12,19] The main textural change, *i.e.*, decrease in surface area and pore volume as recrystallisation time is increased can be attributed to the formation of thicker pore walls; it is envisaged that the wall thickening occurs within the existing pores of the parent MCM-41 without any significant change to the basal spacing.

3.2 Effect of extended recrystallisation on particle morphology

Typical scanning electron microscopy (SEM) micrographs obtained for the parent MCM-41 and the recrystallised MCM-41 samples are shown in Fig. 3 and Fig. 4 respectively. As shown in Fig. 3, the parent MCM-41 is made up of submicrometer sized free standing or aggregated *sphere* shaped particles which is the typical morphology of normal MCM-41 synthesised under basic conditions. However, the morphology of the seeded samples (Fig. 4) significantly departs from sphere

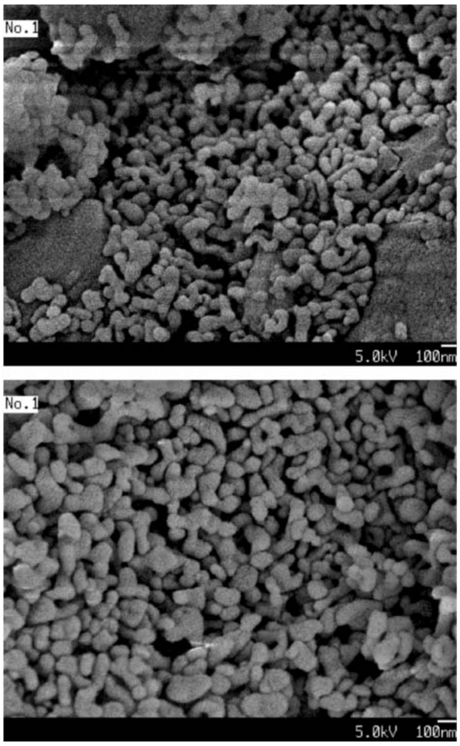

Fig. 3 Representative SEM micrographs obtained for parent MCM-41.

Table 1 Textural properties of the study materials

Sample	d_{100}/Å	Surface area/ m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Pore size[a]/Å	a_o[b]/Å	Wall thickness[c]/Å
MCM-41	47.3	943	0.95	44.6 (47.2)	54.6	10.0 (7.4)
MCM-41(R96)	48.1	806	0.83	44.1 (46.9)	55.5	11.4 (8.6)
MCM-41(R140)	49.8	690	0.68	43.6 (46.8)	57.5	13.9 (10.7)
MCM-41(R168)	49.2	613	0.59	41.6 (44.9)	56.8	15.2 (11.9)
MCM-41(R212)	50.2	540	0.51	40.8 (44.3)	58.0	17.2 (13.7)

[a] Pore size was determined by applying a geometric model;[15,16] 1.6 g cm^{-3} was used as density of the silica walls.[20] [b] a_o = The lattice parameter, from the XRD data using the formula $a_o = 2d_{100}/\sqrt{3}$. Values in parentheses are obtained for a silica wall density of 2.2 g cm^{-3}. [c] Wall thickness = a_o − pore size. Values in parentheses are obtained for a silica wall density of 2.2 g cm^{-3}. .

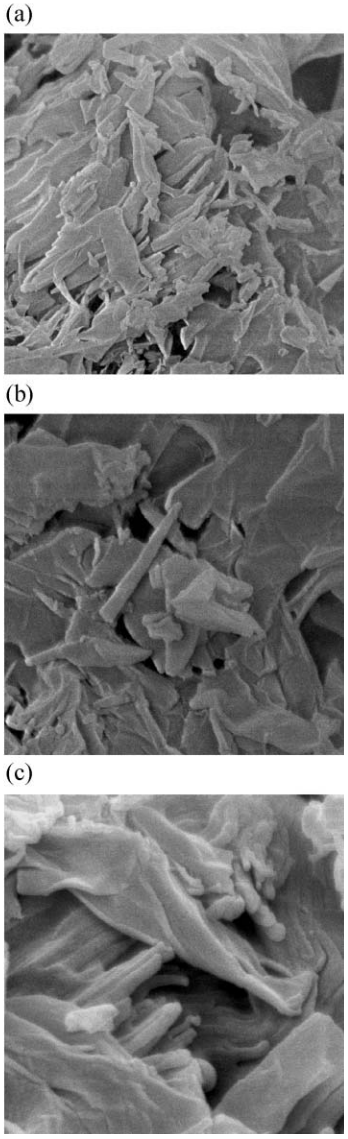

Fig. 4 Representative SEM micrographs of MCM-41 materials prepared *via* recrystallisation. The width and height of the micrographs are (a) 6 μm, (b) 2.5 μm and (c) 2.5 μm.

shaped particles. In all cases we observed *elongated sheet-like* (or *platy*) particles. In some cases the particles appeared to be continuous (joined) as shown in Fig. 4c. It is noteworthy that the particle morphology observed here differs from that which we have previously reported for (i) MCM-41 materials *recrystallised for 48 hours only*[12,13] or (ii) materials *directly* synthesised for extended periods.[14] The former exhibit extended sheet-like particles[12] while the latter show elongated rod or rope-like particles.[14] The present materials therefore appear to present an intermediate morphology; the particles are sheet-like but in most cases appear elongated in a particular direction (see for example Fig. 4a). The morphology observed here is therefore consistent with the fact that extended seeded synthesis combines both recrystallisation and long synthesis. Another significant observation is that the particle morphology of the recrystallised samples, shown in Fig. 4 (*i.e.*, the presence of aggregates of platy particles), is consistent with the interpretation of the sorption isotherms in Fig. 2. Both N_2 sorption and SEM analysis therefore point to the formation of platy particles. It is also noteworthy that no sphere shaped particles (similar to those of the parent MCM-41) are observed for the recrystallised samples which clearly indicates that the original MCM-41 is extensively restructured during the extended recrystallisation.

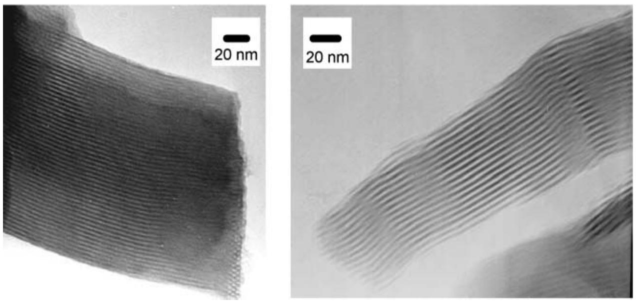

Fig. 5 TEM micrographs of elongated particles obtained for (left) MCM-41(R96) and (right) MCM-41(R168) indicating good pore ordering.

The transmission electron microscopy (TEM) micrographs in Fig. 5 show that the elongated/platy particles of the recrystallised MCM-41 materials posses good pore ordering. In certain instances (Fig. 4c) it is also possible to observe individual rod-like (rather than platy) particle ends. These rod-like particle ends, which appear to be sealed or bent, are similar to those we have previously observed for MCM-41 *directly* synthesised for extended periods.[14] The presence of particles with rounded ends is more clearly shown in Fig. 6. When these particles are viewed from the top (see Fig. 6) they appear 'rounded' suggesting that the pore channels that run along the axis of the particles are also rounded. This is confirmed in Fig. 7, which shows that individual particle ends are sealed and that the pore channels 'bend' round the particle end.

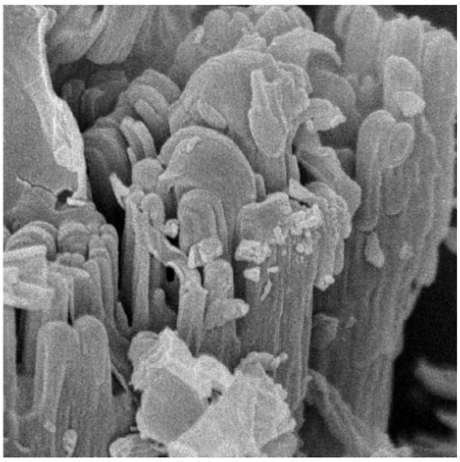

Fig. 6 Representative SEM micrograph of unusual 'rounded' particle morphology. The width and height of the micrograph is 4.8 μm. This particle morphology showing aggregates of elongated/platy particles was observed for MCM-41(R140), MCM-41(R168) and MCM-41(R212).

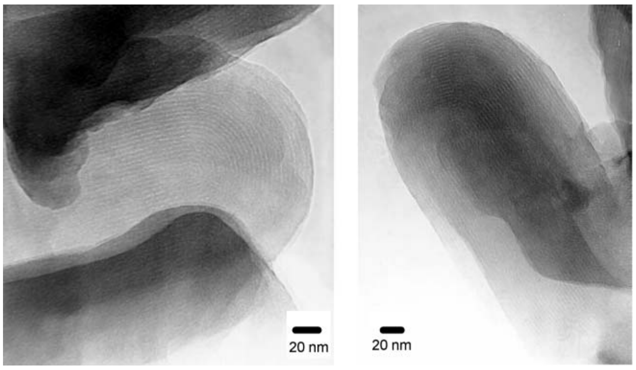

Fig. 7 TEM micrographs of 'rounded' particles shown in Fig. 6.

3.3 Effect of extended recrystallisation on stability

We have recently reported on the hydrothermal (steam and boiling water) stability of seeded pure silica MCM-41 materials.[18] The materials were found to exhibit remarkable hydrothermal stability in boiling water and at high temperature (steaming) conditions.[18] Stabilisation was thought to occur *via* thicker and more polymerised pore walls which provide a silica framework which has fewer defects compared to that of the parent MCM-41. A greater extent of silica condensation for the seeded materials was indeed confirmed by ^{29}Si MAS NMR analysis which gave Q^4/Q^3 ratios in the range 3.5 to 4.5 compared to 1.5 for the parent MCM-41 material. The recrystallisation (or restructuring) that occurs during the seeded synthesis may therefore, in addition to increasing pore wall thickness and silica condensation, also act to heal any defects present in the parent material thus creating a more stable silica framework. Indeed when subjected to severe thermal treatment, 6 hours at 1000 °C, the recrystallised/restructured materials can, remarkably, still retain a well-ordered structure. This is illustrated in Fig. 8 which shows the XRD pattern of the parent MCM-41, MCM-41(R96) and MCM-41(R168) after calcination at 1000 °C for *6 hours*. The parent MCM-41 is virtually destroyed while the recrystallised materials still exhibit a significant amount of hexagonal pore ordering. The textural properties (surface area, m^2 g^{-1}, and pore volume, cm^3 g^{-1}) for the samples after heat treatment at 1000 °C, are, 401 and 0.31 for MCM-41(R168), 244 and 0.18 for MCM-41(R96), 24 and 0.05 for the parent MCM-41. The improvement in thermal stability is therefore greatest at longer recrystallisation time. On a more general note, Pauly *et al.* have recently shown that pure silica MCM-41 materials prepared from fumed silica in the absence of Na ions (*i.e.*, materials similar to the parent MCM-41 used here) exhibit higher hydrothermal stability compared to materials prepared in the presence of Na ions.[21] It is likely that restructuring of such Na-free materials, as described here, leads to pure silica MCM-41 materials that are even more stable compared to materials prepared *via* other routes.[18]

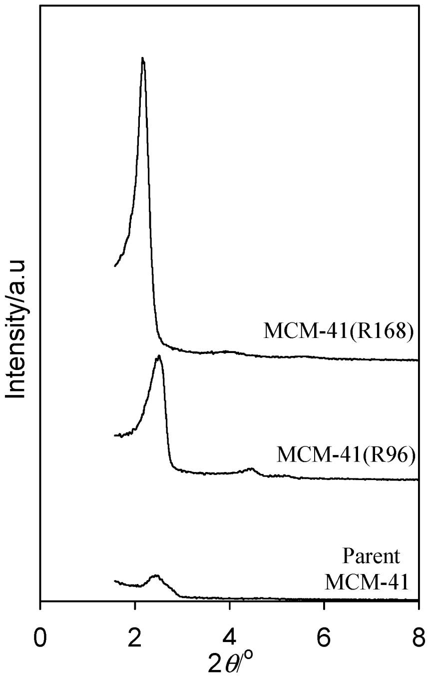

Fig. 8 Powder XRD patterns of MCM-41 (bottom) and MCM-41(R*X*) materials after calcination at 1000 °C for *6 hours*.

3.4 Effect of using large pore MCM-41 or adding amorphous silica on the recrystallisation

The extended recrystallisation of mesoporous silica MCM-41 has some advantages with respect to structural ordering and stability. It was of interest to clarify whether similar well ordered MCM-41 materials could be prepared by either (1) reversing the order of crystallisation (*i.e.*, by performing the extended synthesis first followed by recrystallisation for the 'normal' 48 hours) or (2) adding both calcined MCM-41 and amorphous (fumed) silica to the recrystallisation gel. Fig. 9 shows the powder X-ray diffraction patterns obtained for an MCM-41 directly synthesised for 168 hours (designated MCM-41(168)), MCM-41 recrystallised for 168 hours (*i.e.*, MCM-41(R168)) and MCM-41(168) recrystallised for 48 hours (designated MCM-41(168R48). It is clear from Fig. 9 that sample MCM-41(R168) exhibits the best structural ordering. The directly synthesised sample (MCM-41(168) has a larger basal spacing but poorer structural ordering.[7,8,14] The XRD pattern of sample MCM-41(168R48), for which the order of crystallisation is reversed suggests the presence of two MCM-41 phases; a large basal spacing MCM-41 phase (with a basal peak at the same position as MCM-41(168)) and a phase with a low intensity peak at lower basal spacing. The lower basal spacing peak is at a position similar to that of normal MCM-41 directly prepared for 48 hours. The large basal spacing phase is clearly derived from preserved MCM-41(168) while the other phase is 'new' MCM-41 formed during the 48 hour recrystallisation. Indeed SEM analysis of sample MCM-41(168R48) clearly shows the presence of the two phases (Fig. 10). The small sphere shaped particles are the 'new' MCM-41 and the larger particles are the preserved MCM-41(168) phase. Fig. 10b also shows that intergrowth between the two phases does occur to some extent. (We note that such intergrowth can be the basis of particle enlargement/restructuring.) However, seeding into a single phase material does not occur in the case of MCM-41(168R48) indicating that MCM-41 with unusually large basal spacing is not suitable as silica source for recrystallisation

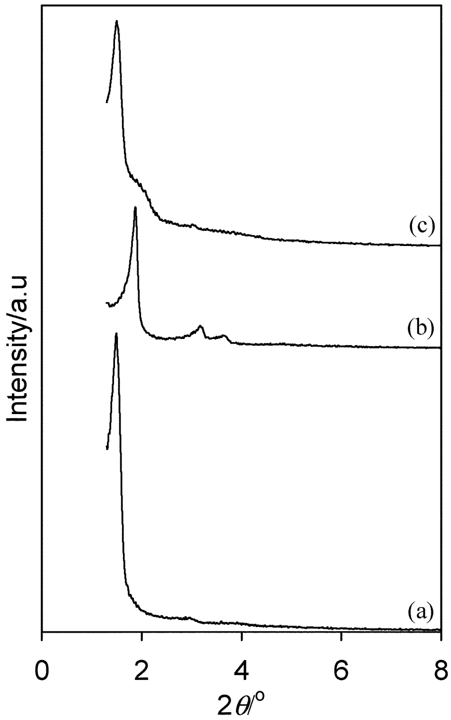

Fig. 9 Powder XRD patterns of (a) MCM-41(168), *i.e.*, directly synthesised for 168 hours, (b) MCM-41(R168), *i.e.*, 48 hours synthesis followed by (seeded) recrystallisation for 168 hours and (c) MCM-41(168R48), *i.e.*, 168 hours synthesis followed by recrystallisation for 48 hours.

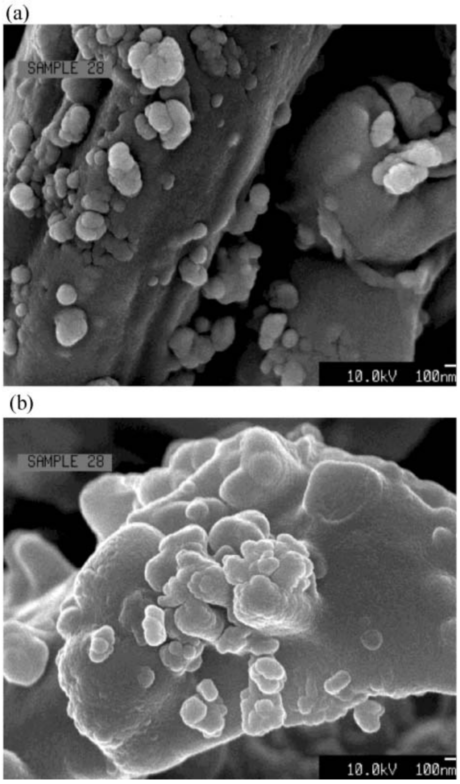

Fig. 10 Representative SEM micrographs of sample MCM-41(168R48).

to single phase materials. It is worth noting that the XRD pattern shown in Fig. 9c and the SEM micrographs in Fig. 10, confirm that calcined MCM-41 can be preserved when subjected to conditions similar to those used to prepare the MCM-41(R*X*) materials reported here.[22] This is an important observation because for a seeding mechanism to be operative, MCM-41 crystallites/particles must be preserved. The difference in structural ordering between the *directly* synthesised (for 168 hours) and *seeded* (for 168 hours) samples is confirmed by the N_2 sorption isotherms shown in Fig. 11. We further note that, in addition to better structural ordering, the *seeded* sample has higher surface area and pore volume, *i.e.*, 613 $m^2 g^{-1}$ and 0.59 $cm^3 g^{-1}$ for the *seeded* sample compared to 320 $m^2 g^{-1}$ and 0.37 $cm^3 g^{-1}$ for the *directly* synthesised sample.

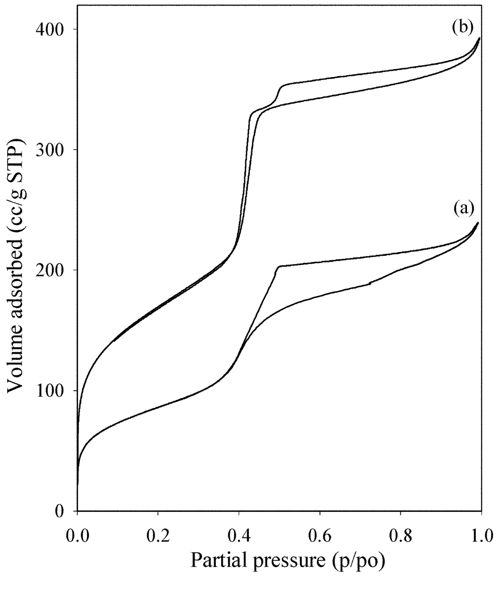

Fig. 11 Nitrogen sorption isotherm of (a) MCM-41(168), *i.e.*, directly synthesised for 168 hours compared with that of (b) MCM-41(R168), *i.e.*, 48 hours synthesis followed by (seeded) recrystallisation for 168 hours.

In an effort to further control the particle size/morphology of the recrystallised materials, we added fumed silica along with calcined parent MCM-41 (at a 50/50 wt ratio) to the recrystallisation gel and carried out the recrystallisation for 48 hours. The hope here was that the presence of both calcined MCM-41 particles and a large amount of amorphous silica would encourage the formation of even larger 'seeded' particles. SEM micrographs obtained for the resulting material are shown in Fig. 12. The micrographs show that, although large particles are formed, they are covered in smaller particles resulting in what appears to be a two-phase (with respect to particle morphology) material. This indicates that 'seeded' enlargement or restructuring of particle morphology (for 48 hour recrystallisation) is only successful when a limited amount of amorphous silica is present in the secondary synthesis (recrystallisation) gel. The presence of large amounts of amorphous silica encourages the formation of a new MCM-41 phase. We are currently investigating the effect of increasing the recrystallisation time beyond 48 hours on the 50/50 (fumed silica/MCM-41) synthesis.

4 Conclusions

In summary we have shown here that extended recrystallisation can be used to prepare purely silaceous MCM-41 materials with good long-range structural ordering and thicker pore walls. Changing the time allowed for recrystallisation can be used to vary the pore wall thickness and particle morphology. The pore wall thickness can be increased by more than 70% without any significant structural degradation. The increase in wall thickness is accompanied by lower surface area and pore volume (which reduce by up to 40% for the thickest pore walls obtained). Restructuring to larger elongated and sheet (or platy) particles is most effective when there is only a limited amount of amorphous silica available in the recrystallisation

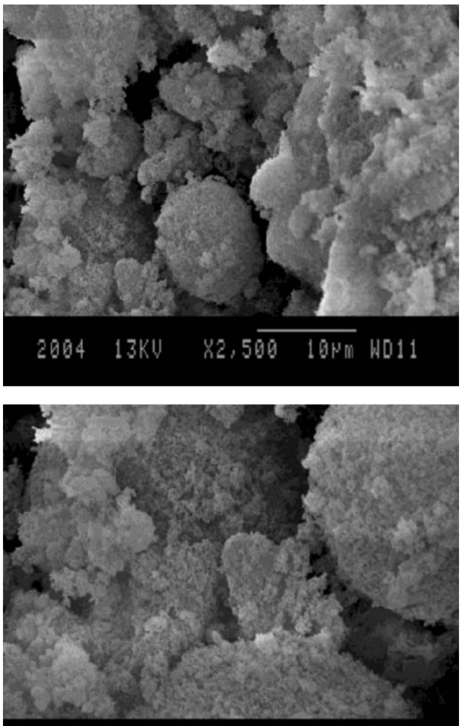

Fig. 12 Representative SEM micrographs of a recrystallised (for 48 hours) MCM-41 sample prepared from a 50/50 (fumed silica/calcined MCM-41) wt ratio gel.

gel. The recrystallisation can be used, not only to tailor the particle morphology but also to prepare highly thermally stable MCM-41 materials. The structural and morphological transformations observed are consistent with a recrystallisation mechanism in which a significant proportion of the original MCM-41 particles are preserved and can act as seeds for further particle restructuring.

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