CHEMCOMM
Communication
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Hydrothermally stable restructured mesoporous silica

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Received (in Cambridge, UK) 20th February 2001, Accepted 17th April 2001
First published as an Advance Article on the web 2nd May 2001

Pure silica mesoporous materials that exhibit remarkable hydrothermal stability may be prepared by restructuring calcined MCM-41 *via* secondary synthesis involving extended recrystallisation.

Mesoporous silicas, such as MCM-41, are potentially useful as sorbents, heterogeneous catalysts and as hosts for the preparation of composite materials for advanced applications.[1] The preparation of mesoporous silicas which exhibit good hydrothermal stability (in hot water and under steaming conditions) is one of the most important requirements with respect to their use. To date, most of the work reported on the hydrothermal stability of mesoporous silicas has dealt with stability in boiling water.[2–6] This is mainly because stability in hot aqueous solutions is considered essential to ensure succesful post-synthesis modifications such as grafting and ion-exchange. Recent advances indicate that the hydrothermal stability of pure silica MCM-41 in boiling water can be improved by a variety of methods which include repeated pH adjustment and/or stabilisation *via* salt effects during synthesis,[2,5,7] restructuring of the as-synthesised material,[3,6] or the preparation of materials with thicker and more polymerised pore walls.[4] Stabilisation *via* a pore wall thickening approach appears to be the most straightforward, but no appropriate synthesis strategies for the control of wall thickness have so far been reported. Here we report on the remarkable steam and boiling water stability of restructured pure silica MCM-41 materials that are prepared *via* a seeded crystallisation route. The restructured materials are prepared *via* a route which involves the use of calcined MCM-41 as 'silica source' for secondary synthesis which is performed over extended periods of time. By extending the time allowed for high temperature recrystallisation during the secondary synthesis step it is possible to systematically increase the pore wall thickness. We believe that the remarkable stability observed here is due to a combination of thicker pore walls and a less strained silica framework. Restructuring during the extended 'recrystallisation' may act to heal any defects and relieve strains in the parent MCM-41 framework.

The parent MCM-41 was prepared using a normal procedure 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 h 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 h at room temperature following which the gel was transferred to a Teflon-lined autoclave and heated at 150 °C for 48 h. 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 h to yield the parent MCM-41. For restructuring, a synthesis gel of molar ratio as above was assembled except that the parent MCM-41 was used as the 'silica source'.[8–10] The experimental procedures were exactly as described above except that during the secondary synthesis the heating at 150 °C was performed for 96, 140 or 168 h. The restructured samples were designated MCM-41(RX) where X is the crystallisation time in hours, *i.e.* MCM-41(R96), MCM-41(R140) and MCM-41(R168) for 96, 140, 168 h, respectively. Hydrothermal stability was tested by heat treatment at 900 °C in a flow of nitrogen saturated with water vapour at room temperature.

The textural parameters of the parent and restructured MCM-41 materials before and after hydrothermal treatment are given in Table 1. First we note that the basal spacing of the restructured materials remains much the same despite the differences in the time allowed for recrystallisation. This is in contrast with previous results, which show that increasing the crystallisation time during high temperature (⩾150 °C) synthesis of MCM-41 favours larger basal spacing.[13,14] The most likely explanation for the non-changing basal spacing observed here is that the structural backbone of the parent MCM-41 is maintained during the recrystallisation.[8–10] The main event during the recrystallisation may therefore involve further growth or linking of the existing parent MCM-41 particles as previously described.[4,9] We note that this is a strong indication of the previously proposed seeding mechanism.[8–10] The surface area and pore volume of the restructured materials gradually decrease with increasing recrystallisation time. The decrease in surface area and pore volume is presumably due to the formation of thicker pore walls; it is envisaged that the wall thickening occurs within the existing pores of the parent MCM-41.[4,9] This then causes the pore size to decrease as shown in Table 1. The pore wall thickness calculated for the materials increases by more than 50% from 10.0 Å for the parent MCM-41 to 11.4, 13.9 and 15.2 Å for MCM-41(R96), MCM-41(R140) and MCM-41(R168), respectively. This clearly represents a systematic increase in pore wall thickness of pure silica MCM-41 by simply changing the recrystallisation time. It is worth pointing out that the emphasis here is on the increase (*i.e.* > 50%) rather than the actual pore wall thickness values, which can vary depending on the calculation method.[4] Powder XRD patterns of the parent and restructured MCM-41 materials are shown in Fig. 1A. In all cases well ordered materials were obtained as indicated by the XRD patterns which show an intense (100) diffraction peak and at least two higher order peaks. In contrast to extended direct synthesis, no significant

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
MCM-41	47.3	943	0.95	44.6
Steamed	37.6	131	0.17	
Refluxed		231	0.33	
MCM-41(R96)	48.1	806	0.83	44.1
Steamed	45.1	626	0.55	
Refluxed		669	0.83	
MCM-41(R140)	49.8	690	0.68	43.6
Steamed	47.4	650	0.63	
Refluxed		639	0.69	
MCM-41(R168)	49.2	613	0.59	41.6
Steamed	47.0	546	0.53	
Refluxed		552	0.62	

[a] Pore size was determined by applying a geometric model.[11] 1.6 g cm^{-3} was used as density of the silica walls.[12]

DOI: 10.1039/b101665m

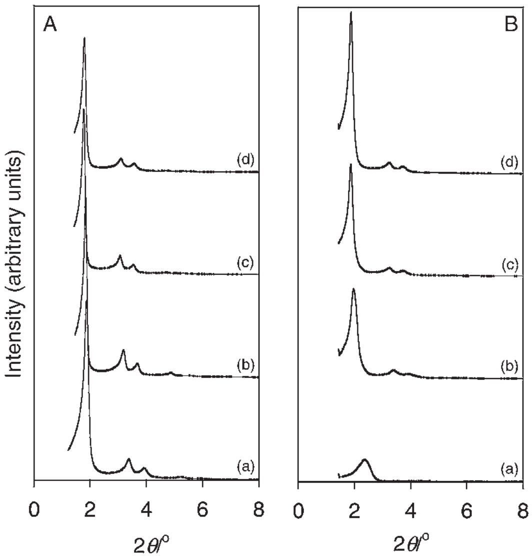

Fig. 1 Powder XRD patterns of (a) parent pure silica MCM-41, and restructured (b) MCM-41(R96), (c) MCM-41(R140) and (d) MCM-41(R168) materials before (A) and after (B) hydrothermal treatment at 900 °C under a flow of N_2 saturated with water vapour at room temperature. The intensity scales are the same for A and B.

diminution of structural ordering is observed even after recrystallisation for 168 h.[14]

Fig. 1B shows the powder XRD patterns of the parent MCM-41 and restructured materials after hydrothermal treatment at 900 °C. The parent sample is severely degraded after the hydrothermal treatment at 900 °C; the XRD pattern of the steamed parent sample exhibits only a weak (basal) 100 peak and no higher order peaks. The N_2 sorption isotherm of the steamed parent MCM-41 (not shown) exhibited virtually no mesoporous character and its surface area and pore volume reduced by more than 80% as shown in Table 1. We note that these observations are consistent with previous results on the steam stability of pure silica MCM-41 materials. For example, Chen *et al.* observed degradation of conventionally synthesised Si-MCM-41 after treatment at 850 °C in water vapour (8 Torr)[15] while materials prepared *via* repeated pH adjustment were severely degraded after 2 h at 800 °C in a flow of O_2 saturated with water vapour at room temperature.[7] In the present study steam stability was remarkably improved after restructuring. Fig. 1B indicates a much higher steam stability for the restructured samples compared with the parent MCM-41. It is also apparent from Fig. 1 that the stability of the restructured samples is higher for materials that have been recrystallised for longer periods of time. Indeed, for sample MCM-41(R168) there is virtually no change in the XRD pattern after the hydrothermal treatment at 900 °C. The N_2 sorption isotherms of the restructured samples (not shown) exhibit a sharp mesopore filling step characteristic of well ordered MCM-41 materials. The restructured samples are able to retain much of their original surface area and pore volume after steaming as indicated in Table 1. Sample MCM-41(R96) retains 78 and 66% of its original surface area and pore volume, respectively. Samples recrystallised for 140 and 168 h retain *ca.* 90% of their surface area and pore volume. These small reductions in surface area and pore volume observed for the steamed, restructured samples contrast sharply with the $>80\%$ decrease for the parent MCM-41 material. Furthermore, the stability of the restructured framework is illustrated by the small lattice contractions observed for MCM-41(R140) and MCM-41(R168), *i.e.* only *ca.* 5% reduction in basal spacing compared with 20% contraction for the parent MCM-41.

We also investigated the stability of the restructured MCM-41 samples in boiling water. This was performed by refluxing the samples for 24 h in distilled water at a solid : liquid ratio of 1 g per litre. The trends observed in 'boiling water' stability were similar to those discussed above for steamed samples; the restructured samples retained their structural integrity while the parent MCM-41 sample was severely degraded. The surface area of the refluxed parent sample decreased by 75% compared with a reduction of typically $< 17\%$ for the restructured samples (see Table 1). Interestingly, the pore volume of the restructured samples was virtually unchanged after refluxing. (It is worth noting that MCM-41 materials prepared *via* repeated pH adjustment undergo severe degradation after 12 h in boiling water.[2] Restructuring of as-synthesised MCM-41 in the mother-liquor or water can yield slightly more stable materials which are nevertheless considerably degraded after 22 h in boiling water).[3] We also note that the restructured materials exhibit good thermal stability in static air; after calcination at 1000 °C for 6 h the parent MCM-41 was completely destroyed (its surface area reduced to 24 $m^2\ g^{-1}$) while MCM-41(R96) and MCM-41(R168) retained some structural ordering and surface area of 244 and 401 $m^2\ g^{-1}$ respectively. It appears therefore that the restructured materials reported here are exceptionally stable and in any case more hydrothermally stable than any previously reported MCM-41 with the possible exception of those stabilised with the addition of salts during synthesis.[5] Stabilisation in the present case is achieved *via* thicker and more polymerised pore walls which provide a silica framework which has fewer defects compared with that of the parent MCM-41. A higher extent of silica condensation in the restructured materials was confirmed by the proportion of fully condensed silica species in the as-synthesised samples; $Q^4 : Q^3$ ratios obtained from ^{29}Si MAS NMR analysis were in the range 3.5–4.5 for the restructured samples, compared with 1.5 for the parent MCM-41 material. It is likely that the restructuring, in addition to increasing pore wall thickness and silica condensation, also serves to heal any defects present in the parent material. The restructured materials therefore undergo little forced silica condensation during calcination thereby resulting in stabilised and less strained silica frameworks. This is consistent with the observation that on calcination, the restructured samples undergo virtually no lattice contraction, compared with a 9% decrease in the lattice size of the parent MCM-41 sample. It is also possible that the large particle size of the restructured materials contributes to their hydrothermal stability.[9]

The author is grateful to the EPSRC for an Advanced Fellowship.

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