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Preparation dependent stability of pure silica MCM-41

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The degradation of pure silica MCM-41 materials prepared under various synthesis conditions has been investigated. Materials from preparations titrated with acid during synthesis not only show improved long range ordering of the pore system but also greater stability. This effect is greatest in unheated preparations.

Introduction

Mesoporous silicate materials formed by the condensation of silica oligomers around self-assembled surfactant micelle templates have recently attracted much interest owing to their potential for use in catalytic or adsorbant applications.[1–8] These materials contain well organised, extremely uniform channel systems in the 20–100 Å size range, defined by the size and shape of the surfactant liquid-crystal template micelles around which the inorganic walls are formed. In MCM-41 the channel system consists of hexagonally close packed cylindrical template micelles, which form, upon removal of the surfactant, locally straight unidimensional parallel channels through which molecules may diffuse.

The stability of these materials is an important consideration for use in almost any application, and while MCM-41 has been reported to have high thermal stability in air,[9,10] it has low hydrothermal stability in water, and aqueous solutions.[11] However, incorporation of elements such as titanium or aluminium into the walls appears to decrease the thermal and hydrothermal stability of these materials.[12,13] Synthesis in the presence of various salts[11] and ion-exchange after synthesis[14] have been shown to improve the stability of pure silica MCM-41 materials. Other post-synthesis treatments with acid,[15,16] or which coat the pore interiors with further layers of silica[17,18] or alumina[19] have also been shown to improve the hydrothermal stability of these materials. Hexagonal mesoporous silica produced *via* templating with neutral surfactants has been shown to have thicker and more condensed walls than materials synthesised with cationic surfactants, and this helps to improve thermal stability.[20] Studies of the effects of pressure upon calcined MCM-41 have shown that the materials lose structure under pressure owing to hydrolysis of the Si–O–Si bonds in the walls.[21,22] Decayed MCM-41 has been shown to have excess enthalpy compared to that of bulk glass, but lower entropy than well ordered, fresh samples, owing to the incomplete hydrolysis of strained three-membered siloxane rings as the material breaks down.[23]

It is also well known that these materials will break down over the course of months when stored under ambient conditions.[24] Although the break-down of MCM-41 is known to be due to hydrolysis of siloxane bonds, the sequential effect this has on the long-range order of these materials is unusual. This present work aims to compare the stability of hexagonal phase, pure silicate materials from ‘ordinary’ alkaline preparations and materials from an alkaline preparation that has been titrated against acid during the synthesis process, and also to investigate the effect of the break-down process on the pore structure of these materials.

Experimental

Many syntheses of pure silica MCM-41 materials were carried out over a range of times and under various synthetic conditions, reported in detail elsewhere.[25–27] These syntheses were all carried out identically by adding an acidified sodium silicate solution to a cetyltrimethylammonium bromide (CTAB) solution with vigorous stirring. Synthesis gels were then treated in one of four ways. Ordinary unheated preparation gels were simply left covered at ambient temperatures to allow silica condensation to occur over extended periods of time, from days to months, before the gels were filtered off, washed, dried and calcined. Ordinary heated preparations were heated in an autoclave at 100 °C for three days without stirring before filtration, washing, drying and calcination. A typical molar gel composition for such an ordinary preparation was (CTAB 1.00/SiO_2 1.90/Na_2O 0.74/H_2SO_4 0.28/H_2O 149). Unheated acid-titrated gels were also allowed to sit, covered, at ambient temperatures for days to weeks before filtration, however these gels were titrated with 1 M acid to return the pH of the synthesis gel to a predetermined value (usually pH = 11) during this static period. Heated acid-titrated preparations were heated in the autoclave at 100 °C for three to four days and treated with 1 M acid once every 24 h to return the pH of the preparation to a predetermined pH value. These gels were then filtered off, washed, dried and calcined in the same manner as for ordinary preparation materials. The resultant molar composition for a gel titrated with acid was (CTAB 1.00/SiO_2 2.03/Na_2O 0.79/H_2SO_4 0.27/HX 0.45/H_2O 173) where HX is the acid used for the titration (acetic, hydrochloric and sulfuric acids were used in various different preparations). The effect of acid titration on the long-range order in these materials has been discussed in great detail in an earlier paper[27] and so will not be repeated here.

Calcination was carried out under several different conditions: in static conditions at 500 °C overnight, at 350 °C in flowing air for 3–4 days, and at 500 °C in flowing air overnight.

Two further heated preparations, one ordinary and one titrated with acetic acid to maintain a pH of 11, were made to investigate the effect of template content upon the stability of the hexagonal mesoporous silicate materials. These materials were prepared as described above, however after filtration, washing and drying these preparations were divided into five parts. One part was left ‘as-prepared’, three of the other parts were treated to extract the surfactant template by soaking, at room temperature, overnight in water at the ratio of 40 g water to 3 g MCM-41. This slurry was then heated to *ca.* 50 °C for 5 min and immediately filtered off to remove the dissolved CTAB. This treatment was extremely mild, removing only dissolved surfactant from the MCM-41 materials. As most of the pore system was still filled with surfactant and therefore inaccessible to the water we do not believe that this treatment significantly altered the wall structure of the materials so treated. We did not attempt to remove all of the surfactant in the pores by this method, only to create materials with different silica/surfactant ratios from an identical starting material. One part of the initial material was treated in this way once, one part twice and one part three times and each was then filtered off and dried, and kept so for the subsequent aging period. The remaining part was calcined at 500 °C overnight in air, under static conditions. Small amounts of the other four parts were calcined gravimetrically to determine the amount of CTAB remaining in each. The surfactant/silica ratios for the materials resulting from this washing process are given in Table 1.

The structure of each of these ten dry samples was followed at monthly intervals by small angle X-ray scattering (SAXS) using the small angle scattering camera at the Research School of Chemistry, ANU, which has been described elsewhere.[28] Samples for small angle scattering were prepared by loading the dry powder into 1 mm Lindemann glass (lithium borate) X-ray capillaries, sealed with a high vacuum glue, which was not in contact with the powdered materials. In periods between measurements, samples were stored under ambient conditions in a drawer. Small angle X-ray scattering was also used to monitor the break-down behaviour of the other silicate MCM-41 materials described above, as were nitrogen adsorption isotherms, taken on a Sartorius microbalance. The materials were degassed at elevated temperature overnight before the isotherms were measured.

Results and discussion

Initial SAXS patterns for the calcined parts of the heated preparations described immediately above are shown in Fig. 1. The acid-titrated sample, as is typical of such materials, shows five sharp diffraction peaks from the well organised, hexagonally packed cylindrical pore system. The sample from the ordinary heated preparation shows three broader and less intense peaks, indicating a lower degree of long-range order. Uncalcined materials from these two preparations show similar SAXS patterns. Materials which are 'as prepared' and parts washed only once, from both preparations, also show sharp peaks at *ca.* 27 and 13.5 Å which may be assigned to the lamellar phase of free, crystalline CTAB, present in excess in these samples. Materials washed two or more times do not show peaks from excess template.

Template-containing MCM-41 materials from all of the syntheses carried out for this work were never observed to break-down, even over periods of up to 30 months. Low stability in CTAB-containing siliceous mesoporous materials has previously been observed by Khushalani *et al.*[29] who observed degradation in materials over periods of days to weeks, which caused gradual loss of intensity and decrease in the *d*-spacing of the first order peak in powder X-ray diffraction patterns. This was attributed to incomplete polymerisation of the siliceous framework. However no such degradation was noted in template-containing samples in this work, even for unheated preparations which would be expected to have a lower degree of condensation in the silicate walls than would be so for materials heated during synthesis. The three washed parts of the heated preparations described above also did not show any alteration in the *d*-spacing or intensity of the SAXS patterns taken over a 22 month period, despite the lower template concentration in these materials than in 'as-prepared' samples.

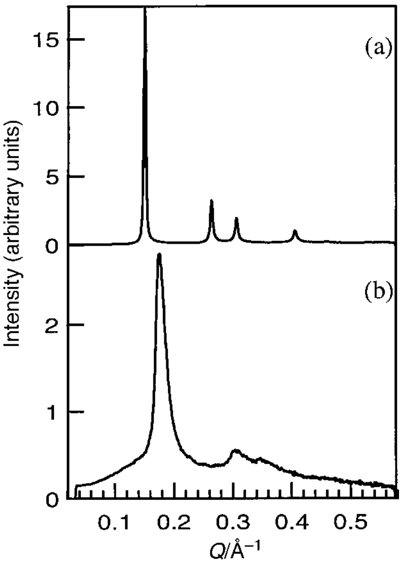

Fig. 1 SAXS patterns of (a) the freshly prepared acetic acid-titrated sample and (b) the freshly prepared untreated MCM-41 sample.

The process of disintegration in calcined materials also occurred in quite a different manner than that described by Khushalani *et al.*[29] Fig. 2 shows the gradual break-down of the calcined part of the ordinary preparation synthesised for the degradation experiment. The patterns are vertically offset for clarity, however it can be seen that there is no change in *d*-spacing of the first order peak during the break-down process. The first order peak decreases in intensity, but it does not broaden. The higher order peaks likewise decrease in intensity and become lost in the background. The other notable feature of these SAXS patterns is the increase in intensity at low scattering angles indicating an increase in the amount of rough, amorphous silica present.

The fact that the *d*-spacing of the first order peak does not decrease indicates that the pore size of remaining, intact pores in the MCM-41 material is unaltered by the degradation process. There is no evidence of wall-collapse between two or more pores to produce larger pores, resulting in a spread of *d*-spacings, as was seen, by others, in hydrothermal restructuring

Table 1 Surfactant/silica ratios for samples from acid treated and ordinary preparations after washing, calculated by gravimetric calcination

Sample	Treatment	Surfactant/silica (wt/wt)	Surfactant/silica (mol/mol)
Acid-titrated preparation			
1.1	As prepared	2.68	0.442
1.2	One wash	1.13	0.186
1.3	Two washes	1.04	0.171
1.4	Three washes	0.93	0.153
1.5	Calcined	0	0
Ordinary preparation			
2.1	As prepared	2.12	0.349
2.2	One wash	1.51	0.254
2.3	Two washes	1.35	0.223
2.5	Three washes	1.27	0.209
2.5	Calcined	0	0

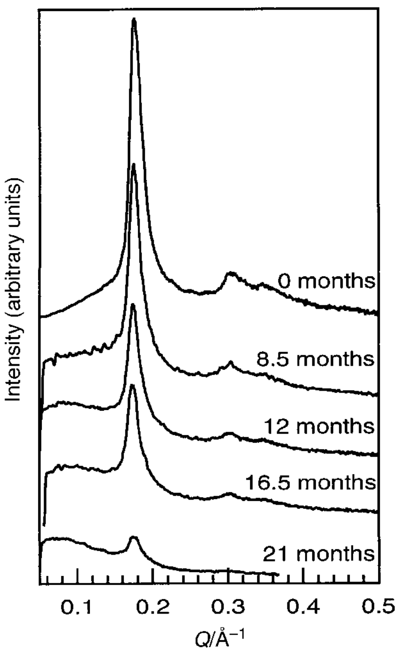

Fig. 2 Selected SAXS patterns from the break-down of the calcined sample from the ordinary MCM-41 preparation.

Table 2 Porod slopes from ln(I) *vs.* ln(Q/Å^{-1}) plots for selected new and aged samples[a]

Synthesis conditions	Slope (new)	Slope (aged)
Unheated, 7 months	−2.38(3)	−2.58(1)
Heated ordinary 3 days	*−1.61(2)*	−2.37(2)
Heated ordinary 2 days	−1.88(3)	−2.07(3) −4.06(2)
Heated ordinary 3 days	−2.00(7)	−2.26(2) −4.15(1)
Heated ordinary 6 days	−2.3(1)	−1.08(1) −2.28(1)
Heated CH_3CO_2H (pH 11)	*−2.74(2)*	*−2.89(2)*
Heated CH_3CO_2H (pH 11)	−1.93(3)	−2.05(2) −2.98(2)
Heated HCl (pH 11)	−1.69(4)	−2.12(1)
Heated H_2SO_4 (pH 11)	−2.02(6)	−2.97(2)
Heated H_2SO_4 (pH 10)	−2.76(2)	−1.85(4) −3.17(2)
Heated H_2SO_4 (pH 9)	−3.03(2)	−2.95(2)

[a] Samples above the thick line are from an ordinary preparation, whereas samples below the thick line are from acid-titrated preparations. Italicised samples are the calcined pair prepared for the monitored degradation experiment. The acid-titrated sample still showed peaks in the final measurement and it can be seen that its Porod slope has not altered greatly over the monitored period.

processes carried on to the point of break-down of structure.[29,30] Similarly, there is no overall increase in *d*-spacing, as is observed in hydrothermal restructuring processes. The absence of peak broadening observed in these materials indicates that there is no appreciable change in the domain size of the regions of ordered channels. Thus degradation cannot be occurring *via* the break-down of channels at the edge of a particle first, leaving ever smaller regions of intact channels in the centre of particles. This indicates that break-down is a nucleated process, occurring relatively quickly for each individual particle, leaving no residues of enlarged channels or local ordering that are sufficiently significant to appear in the SAXS patterns.

The increase in small angle scattering with increasing break-down of the material indicates the formation of a highly divided form of amorphous silica with many void spaces. In samples where no diffraction peaks remain, the scattering shows a fall-off in Q ($Q = 4\pi \sin \theta/\lambda$, where θ is the half scattering angle), at low angles reminiscent of that of aerogels, another form of highly porous, amorphous silica.[31] The slope from Porod plots for scattering from MCM-41 materials prior to and after break-down can give some information on the surface structure in these materials. Slopes around -4 are characteristic of smooth particles whereas slopes between -1 and -3 indicate mass fractal structures (with Porod slope equal to the fractal dimension, D), while slopes between -3 and -4 are characteristic of fractally rough surfaces (with $D = 6 - |\text{slope}|$).[32] Table 2 gives Porod slopes for some representative samples studied for this work. Fig. 3 shows Porod plots for one sample from an ordinary preparation, prior to, and after breakdown.

The Porod slopes for all samples are mostly in the region between -1 and -3 indicating mass fractal structures on large length scales ($>$40 Å), in both fresh and degraded materials, with fractal dimension equal to the slope. As degradation proceeds, the Porod slope usually increases, except where two regions with different slopes develop as degradation occurs. In these broken-down materials, the two regions with different slopes indicate changes in the structure at different length scales. The second region, at higher Q (smaller length scales) occurs in the region of the first order diffraction peak in these materials and so may be related to the residual pore structure in the broken-down materials, or simply masked by the peak in the fresh samples. Van den Bossche *et al.*[33] measured similar Porod slopes for freshly calcined surfactant templated materials in which the pore structure did not survive calcination. These unstable materials were found to exhibit surface fractal behaviour, in contrast to uncalcined, template containing materials, which had smooth surfaces. These heat degraded samples had Porod slopes of -3.2 to -3.4, (*i.e.* $D = 2.6$–2.8) indicating the development of a rough divided surface during breakdown. At least one sample in that study also showed two regions of fractal behaviour, a mass fractal region (between 210 and 30 nm) with slope -2.55, and a surface fractal region (between 28 and 2.6 nm) with slope -3.48. In that study, samples from a preparation that did retain hexagonal structure upon calcination, showed Porod slopes of -3.4, also indicating a rough surface. The surface fractal dimension D, of the interior of the MCM-41 pore surface (where $D = 6 - |\text{slope}|$ for surface fractals) has also been evaluated for fresh MCM-41 samples by gas adsorption studies to be 1.78.[34]

Nitrogen isotherms on decayed materials [Fig. 4(b)] are significantly altered from those of ordered MCM-41 samples [Fig. 4(a)]. The type II shape[35] suggests the development of micropores along with a considerable loss of adsorptive capacity compared to freshly prepared MCM-41 samples. In

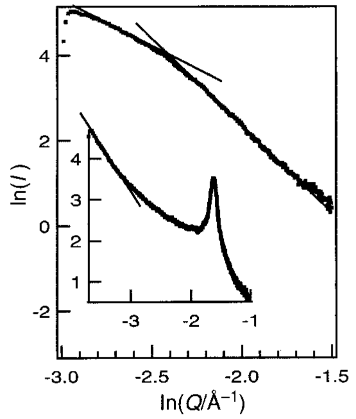

Fig. 3 Porod plot for a sample from a heated, ordinary MCM-41 synthesis which showed complete degradation of the diffraction peaks, inset is the Porod plot for the fresh material.

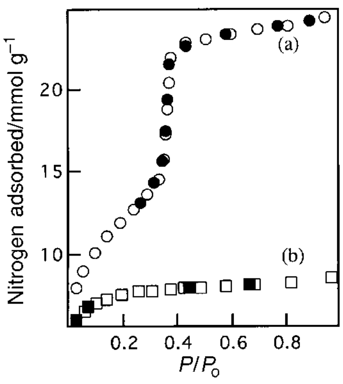

Fig. 4 Nitrogen adsorption and desorption isotherm run at 77 K on (a) a freshly calcined MCM-41 sample from a preparation titrated against sulfuric acid to maintain a pH of 11 (circles) and (b) a degraded MCM-41 sample from an acetic acid-titrated preparation, synthesised at pH = 11 (squares). Open symbols indicate adsorption, filled ones indicate desorption.

Fig. 4(a) the fresh MCM-41 material adsorbed 24 mmol g^{-1} at complete filling. For the decayed material however, the maximum adsorption is only 8.2 mmol g^{-1}. Comparison plots also indicate significant development of micropores in the broken down MCM-41 material, consistent with the SAXS data showing rough, divided surfaces. The isotherm of hydrothermally degraded material looks very different to the type I nitrogen isotherms resulting from MCM-41 materials in which the pore structure has been destroyed by applied pressure, where the compressed material is no longer porous.[21] High angle synchrotron diffraction patterns of broken-down MCM-41 do not show diffraction peaks at high angles, only a large broad hump characteristic of amorphous silica which is also present in fresh, well ordered materials.

The susceptibility of MCM-41 materials to degradation is highly preparation dependent. The degradation data for the calcined samples from the two preparations studied in detail are presented as plots *vs.* time of the area under the first order peak for the calcined materials, normalised by the area under the first order peak from the as-prepared MCM-41 material from the same preparation (see Fig. 5). This normalisation against a material which did not appear to change with time (the ratios between silicate and crystalline surfactant peak intensities are constant) accounts for instrumental variation over the almost two year time scale of the experiment. For the material from the acid-titrated preparation, the peak intensities in both the calcined, and the three times washed sample are roughly constant over the duration of the experiment. From Fig. 5 there is an indication of a drop in peak intensity in the calcined material, occurring within the first month of aging. This may correspond to some initial rehydrolysis of strained siloxane bridges formed during calcination, as seen by Zhao *et al.*[24] when they studied calcined MCM-41 samples rehydrated overnight. However, after this first loss of peak intensity, which gives all of the downward trend in the line of best fit, the remaining material retained order over the time period considered. The similar best fit for material from the ordinary preparation shows a clear, continuous decline in intensity over the period investigated, at a rate of loss of relative intensity of 0.04 per month, indicating a greater susceptibility of this material to degradation.

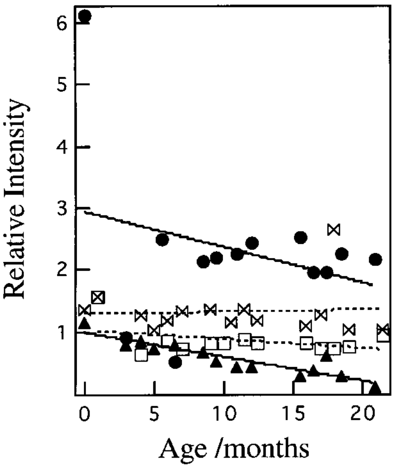

Fig. 5 Progression of first order peak intensity normalised against the as-prepared pattern with aging time for calcined (filled circles) and three times washed (open squares) samples from an acid titrated preparation and for calcined (filled triangles) and three times washed samples (open bowties) from the ordinary preparation.

From the other materials studied it appears that the most stable materials are prepared from *unheated* preparations, which have been titrated with acid during preparation. There is a startling increase in stability after only one acid addition, even though the long range order in such materials can be further improved by continued pH adjustments during the course of preparation. The less ordered materials from unheated, acid-titrated preparations did not show any greater degree of degradation after 20 months than more well ordered materials from the same preparation. In heated preparations the type of acid used for the pH adjustments may affect break-down behaviour. Samples prepared using sulfuric acid are more susceptible to break-down in shorter time than those prepared using acetic acid, despite the greater degree of long range order observed for sulfuric acid-titrated materials.[27] Stability to degradation is also favoured by aging of the dry, template containing MCM-41 materials prior to calcination. Materials from the same batch, calcined at a later time proved to be more stable than those calcined soon after preparation. The calcination temperature and use of static or flowing air during calcination do not appear to affect the stability of the materials studied.

The general observations outlined above appear to agree with the findings of Zhao *et al.*,[24] who observed hydrolysis causing break-down to be promoted by strained siloxane bonds in the walls of MCM-41 materials. In the materials studied here, those prepared under the most mild conditions, at room temperature proved to be as, or more stable, than those heated during preparation, provided that the pH of the preparation was lowered slightly to allow silica condensation to occur. Under these conditions, at ambient temperature and pH of 11, the walls of MCM-41 appear to be able to attain a high degree of condensation with a lower number of the strained bonds, promoting stability. Stability is also enhanced by allowing aging of the materials with the template still present. Presumably in this case there is some slow reforming of bonds within the silica walls to remove strain. From these arguments it can be predicted that materials subjected to extended hydrothermal restructuring after synthesis should be similarly resistant to break-down upon template removal, as these systems have a much greater ability to reform bonds to relieve strain.

Conclusion

MCM-41 materials from alkaline preparations where the pH was repeatedly lowered during synthesis to maintain a constant pH value are more stable to hydrolysis than MCM-41 materials from ordinary preparations. Stability does not, however, appear to be correlated to the degree of long range order present in the material. The stability of these materials is probably related to the extent to which the preparation conditions create strained siloxane bonds, which are susceptible to hydrolysis within the silicate walls.

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