Further Improvements in the Long-Range Order of MCM-41 Materials

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Synthetic methods for making an all-silica MCM-41 mesoporous silicate of high long-range order are reported. The product shows up to seven orders of X-ray diffraction and good stability under calcination conditions. The greatest improvement in structure occurs when the pH is held between 9 and 10 during synthesis and the sulfate anion is present.

Introduction

MCM-41 is a silicate molecular sieve formed from close-packed silica-coated micelles of a surfactant template. Removal of the template via calcination leaves mesoporous parallel channels in a hexagonal array. The formation mechanism is not settled;[1,2] however most evidence appears to point to individual cylindrical surfactant micelles becoming coated with silica and then condensing to form the hexagonal array of channels. In previous papers we have discussed some methods for optimizing the quality of the MCM-41 product[3] as well as synthesis at room temperature.[4] The further improvements to the synthesis discussed here have allowed a more detailed elucidation of the wall structure of this material.[5]

In previous experiments[3] we found that heating the cetyltrimethylammonium bromide (CTAB)/silicate gel system at 100 °C for periods of the order of 3 days, produces material with three orders of the 35 Å spacing on the X-ray diffraction patterns but that longer heating gives no better long-range order. An improvement to this method reported by Ryoo and Kim[6] took account of the rise in the pH of the system during synthesis and that this might well be inimical to the crystallization process.

Ryoo's method of titrating the mixture in the reaction vessel from time to time with acetic acid kept the pH of the system at about pH 11 during the hydrothermal synthesis. The effect of this on the diffraction pattern was to produce more orders of diffraction indicating higher long-range order of the MCM-41 tube structure, although not necessarily in the silica wall crystallinity. We report here further development of this method by optimizing the mineral acid used and performing the synthesis at a number of different pH values to best define the conditions for the maximum number of orders of the X-ray diffraction and the highest intensity of these peaks.

Experimental Section

The synthesis gels were made up as previously described[7] using sodium silicate solution (∼14% NaOH, ∼27% SiO_2) from Aldrich, cetyltrimethylammonium bromide (CTAB, 98%) from Fluka, sulfuric acid from Univar (analytical reagent grade, 98%) and Millipore-treated water. One synthesis mix was carried through to completion without addition of acid, as described in the earlier paper, to provide a control for the acid-titrated preparations. Aliquots from it were taken for small-angle X-ray scattering (SAXS) analysis at each step of the process. An acetic acid titrated synthesis gel, directly following the method of Ryoo et al.,[6] was followed in the same way for a direct comparison of the two methods.

To compare the effects of different acids, two further preparations were made and titrated against various acids during the heating process. These had typical compositions 1.00 CTAB/1.89 SiO_2/0.738 Na_2O/0.267 H_2SO_4/0.123 HX/160 H_2O, where HX is the acid used as titer in each case. The initial pH of these synthesis gels was measured to be about 11.5 before the first hydrothermal treatment at 100 °C. Despite the high pH, no acid was added at this time. In one series of experiments, the start gel was divided into parts to be heated in separate autoclaves, so that the effects of the addition of various acids could be compared while avoiding differences in surfactant and silica concentrations.

For the second series, the start gel was similarly divided to study the effects of conducting the synthesis at pH values between 7 and 11, using sulfuric acid as the titer since the previous experiment showed it to be most efficacious in increasing the crystallinity of the final calcined product. The acids used in these syntheses were acetic acid (BDH, Analar), sulfuric acid (Univar, analytical reagent grade, 98%), hydrochloric acid (Univar, analytical reagent grade, 36%) and ammonium bromide (BDH, laboratory reagent grade, 99%) all made up to 1 M solutions. One preparation was titrated with equivalent amounts of sodium acetate (Univar, analytical reagent grade, 99.0%) to observe the effects of the acetate ion on the synthesis.

After heating the start gels at 100 °C for 24 h, each autoclave was cooled to a comfortable handling temperature and opened, and a titration performed with 1 M acid so as to bring the pH of the whole gel system back to a predetermined value. At each stage of the titration a small amount of the gel was removed so as to monitor the small-angle X-ray scattering from the system. Heating was continued for subsequent 24 h periods, and it was found that the acid titer

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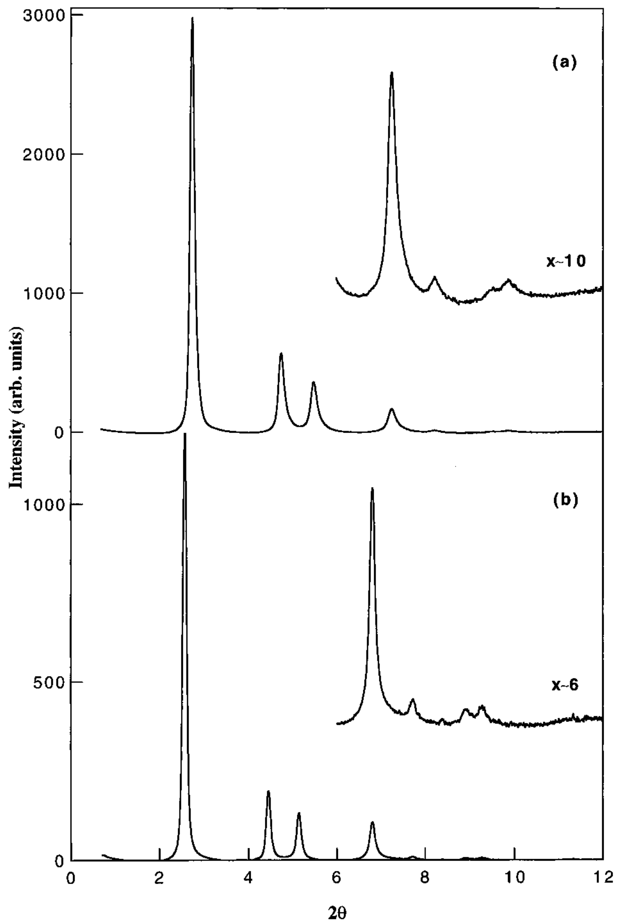

Figure 1. Synchrotron X-ray diffraction pattern from (a) calcined MCM-41 derived from a preparation titrated with sulfuric acid during synthesis and (b) uncalcined MCM-41 derived from the same preparation.

necessary to bring the gel back to a chosen pH value dropped by nearly a factor of 10 over a 3 day period (e.g., for a nominally constant pH = 11 preparation). This indicates that the release of alkali into the synthesis gel drops considerably as the synthesis proceeds and is in line with our previous observation of the most efficacious time for synthesis.

After 4 days of heating, the synthesis gel was filtered, washed, and dried to give a product which was used for physical measurements. The effects of the different mineral acids and the chosen pH value of the synthesis were thus compared. The products were also compared after calcination to remove the surfactant template.

The samples were characterized using the small-angle X-ray scattering (SAXS) camera at the Research School of Chemistry at the Australian National University.[8] The SAXS patterns presented in this paper were taken using X-rays of wavelength 1.54 Å and are shown as plots of intensity against the momentum transfer, $Q = 4\pi/\lambda \sin \theta$, where θ is half of the scattering angle. Data were also taken at the Australian National Beamline, Photon Factory, Tsukuba, Japan on calcined and uncalcined specimens from preparations treated with sulfuric and acetic acids to maintain a pH of 11. Figure 1 is a plot of the scattered intensity as a function of 2θ, the scattering angle, for an X-ray wavelength $\lambda = 1.8963(1)$ Å , for the sulfuric acid treated preparation. The peak positions, their indexation, and intensities are shown in Table 1. All samples for X-ray pattern determination were run in Lindeman glass (lithium borate) X-ray capillary tubes. Nitrogen adsorption isotherms at 77 K were also run on some of the calcined materials using a Satorius microbalance to allow the determination of BET surface areas.

Table 1. Observed X-ray Intensities and Indexation after Background Fitting and Subtraction, from Template Containing and Calcined MCM-41, Produced from Sulfuric Acid Titrated, Controlled pH Synthesis Conditions

	calcined		uncalcined	
reflection	intensity	2θ	intensity	2θ
10	26.683	2.741	10.082	2.573
11	6.576	4.741	1.637	4.463
20	4.465	5.475	1.335	5.146
21	2.436	7.244	1.245	6.804
30	0.124	8.209	0.119	7.729
22	0.030	9.525	0.059	8.935
31	0.141	9.857	0.065	9.277

Results

A comparison of the acid-treated and the ordinary, untitrated preparation shows that the beneficial effects of acid treatment on the diffraction pattern from the material are already apparent after the first acid addition (second heating). Figure 2 shows a comparison between the average peak intensities from SAXS patterns of two acid-treated (CH_3COOH and H_2SO_4) preparations and an ordinary MCM-41 preparation. There is clearly an increase in the peak heights in the wet gels as a result of the acid titration procedure. The increase in intensity upon washing and drying is probably due to the increase in contrast occurring with the removal of water from the system, and the further increase in intensity upon calcination is due to the removal of template from the pores which again increases the contrast. This intensity increase due to the increasing difference in contrast upon washing, drying, and calcination occurs in all preparations studied. The effect appears to be smaller in the untitrated preparation since the total peak intensities are smaller; however, the proportional increase in intensity is much the same as for the acid-treated preparations. The sulfuric acid treated systems retain the higher orders of diffraction upon calcination better than those treated with acetic acid.

Figure 3 compares diffraction data from non-acid-treated (a) and acid-treated (b) preparations at some stages of MCM-41 synthesis. In a non-acid-treated MCM-41 preparation up to four hexagonal (*hk*0) MCM-41 peaks may be seen in the wet synthesis gel at all stages of heating. Often these are accompanied by two sharp peaks from the lamellar phase of crystalline CTAB (e.g., at $Q = 0.24$ Å^{-1} and $Q = 0.48$ Å^{-1} in Figure 3a). Upon washing and drying this material may still show up to four peaks, and the CTAB peaks may also still be visible. Calcination removes all signs of the CTAB crystals, but also reduces the number of MCM-41 peaks to three and causes considerable peak broadening, indicating a decrease in crystallite size and, possibly, order. Figure 3a shows such a progression of diffraction patterns through these preparation stages.

In an acid-titrated synthesis gel the number and sharpness of MCM-41 peaks increases with the amount of acid added and the heating time. Figure 3b shows the progression in diffraction patterns for some of the stages of the acid-titrated preparation. A small increase in peak intensity is observed to occur merely with the acid addition. This effect is augmented by a factor of 2−4 by heating (see also Figure 2). The CTAB lamellar phase peaks (although present in the initial synthesis

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[8] Aldissi, M.; Henderson, S.; White, J. W.; Zemb, T. *Mater. Sci. Forum* **1988**, *27/28*, 437.

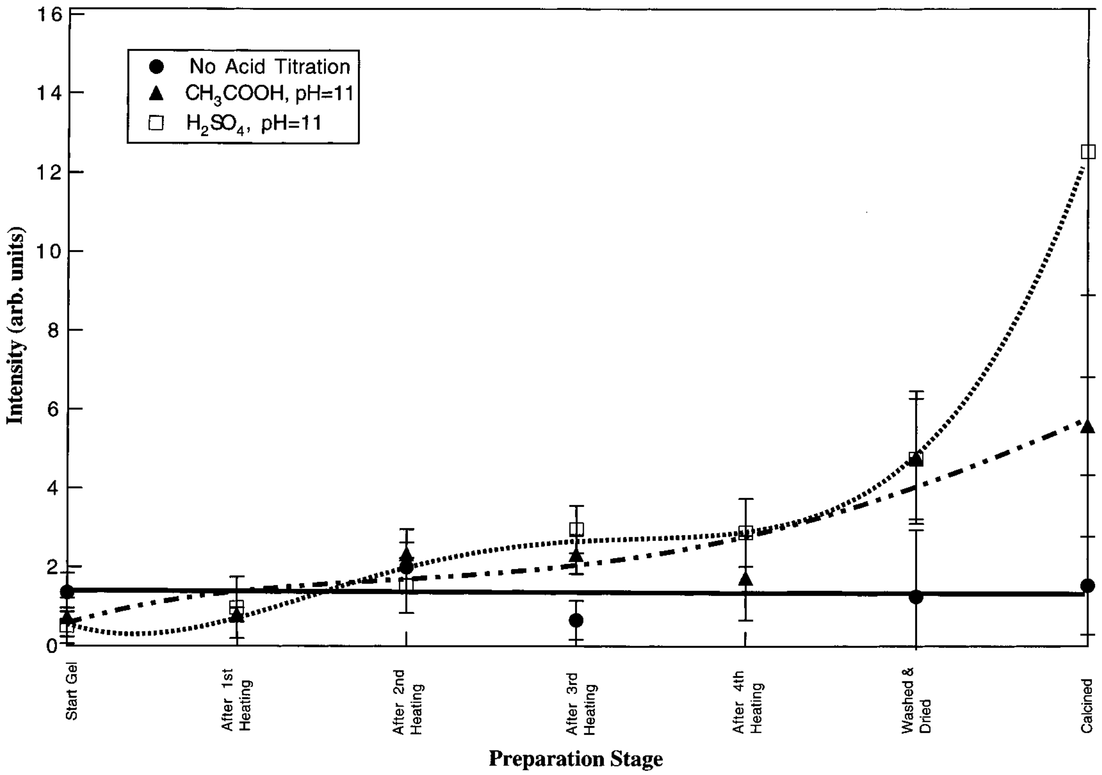

Figure 2. Peak intensity for various stages of preparation of an ordinary MCM-41 preparation (—) compared with preparations titrated with acetic acid (- - —) and sulfuric acid (- - -). The lines drawn through the points are merely guides to the eye. The error bars correspond to the greatest deviation from the mean.

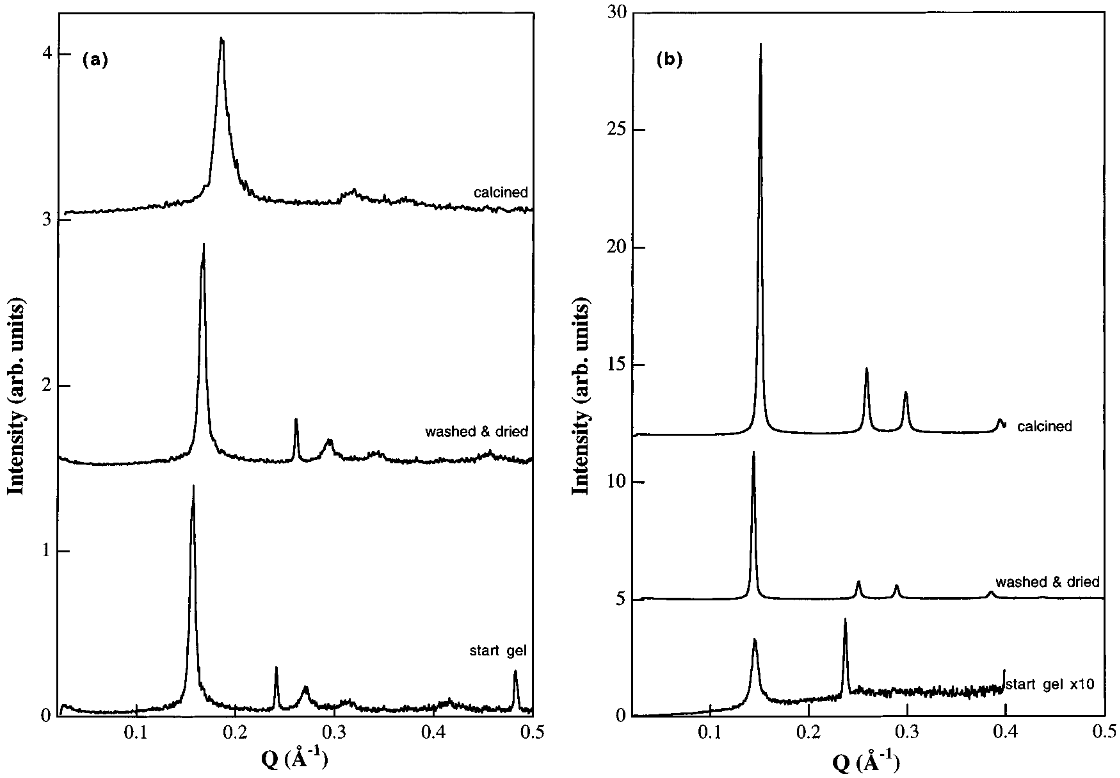

Figure 3. Diffraction patterns for the wet synthesis gels, washed and dried material and calcined material from (a) an ordinary MCM-41 preparation and (b) a sulfuric acid-titrated preparation.

gel), decrease rapidly in size with heating and acid addition, and are rarely seen after the second titration and heating step. This may indicate a more efficient use of the CTAB present in the synthesis gel. It may have been incorporated into the mesoporous structure rather than remaining as “excess” unused template in its crystalline form. Washing and drying the acid treated MCM-41 results in a material with up to seven peaks in the synchrotron X-ray diffraction patterns (see also Figure 1) and usually no visible CTAB peaks. These peaks are retained upon calcination and undergo very little broadening. The structure is thus consider-

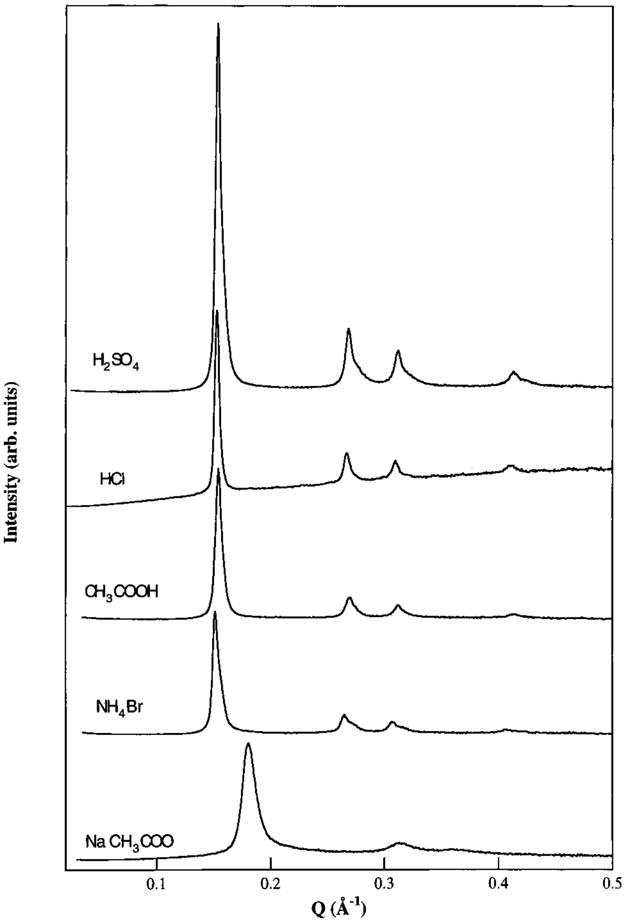

Figure 4. Small-angle diffraction patterns for calcined MCM-41 materials treated to maintain pH = 11.0 during preparation using a variety of different acids.

ably more stable to the calcination process as well as having greater inherent long-range order than materials from the ordinary preparation.

All of the acids used were found to be effective in producing an improvement in the X-ray diffraction pattern along the lines reported by Ryoo.[6] The addition of sodium acetate as a control experiment had little effect on the diffraction pattern. The increase in crystallinity is therefore obviously the result of the acid addition. The relative efficacy of the various acids can be seen by comparison of the small-angle diffraction patterns from calcined materials produced from acid-titrated preparations shown in Figure 4. The effect of maintaining the synthesis gel at various approximately constant pH values during synthesis can be seen in Figure 5. Figure 1 shows the synchrotron X-ray diffraction patterns from an uncalcined and calcined specimen produced when the titrations were done with sulfuric acid to a constant pH = 11.0. This material had a total of 4 days heating with three titrations with the acid to maintain the pH at 11. It is the best result obtained so far. The BET surface area of this material is 990 m^2/g compared with 750 m^2/g for the material titrated with acetic acid.

Crystallite Size. The resolution functions of the X-ray instruments used are much narrower than the observed peak widths, which may thus be used to estimate crystallite size. Materials from the ordinary preparation have much broader peaks than those from acid-treated preparations and so much smaller crystallites in the basal plane directions. Crystallite sizes calculated using the Scherrer equation[9] are shown in Figure 6 for various stages of preparations treated with acids to maintain a pH of 11 throughout the synthesis. For untitrated preparations there is a 3-fold increase in crystallite size following the first heating for 24 h at 100 °C. In this preparation the crystallite size continues to slowly increase throughout the heating process up to the third heating but decreases again after the fourth heating—behavior consistent with our earlier finding that 3 days of heating is optimum for this preparation. It then decreases upon washing and decreases still further on drying and calcination. In the acid preparations the same sudden increase following the first heating is also observed. After this there is a small further increase in crystallite size over that of the ordinary preparation after the first acid addition and second heating. Crystallite size then stays roughly constant until the washing, drying, and calcination steps.

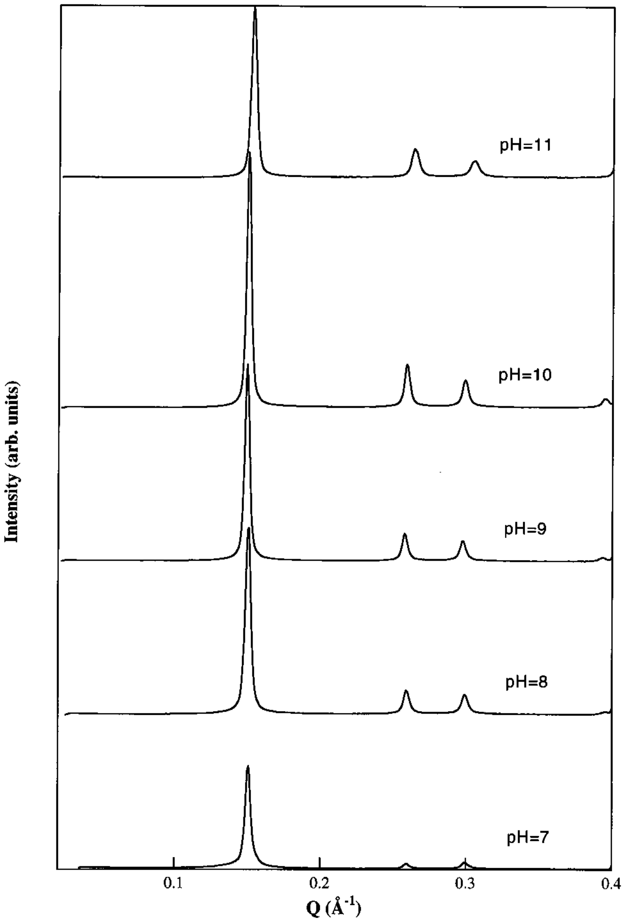

Figure 5. Small-angle X-ray diffraction patterns for MCM-41 materials treated with sulfuric acid to maintain various pH values during synthesis.

These results are consistent with an equilibrium having been reached for that pH, and with the crystallites dissolving and reforming during the heating process to form the more highly crystalline materials. In the ordinary preparation such an equilibrium situation is never reached, and the crystallites once grown, begin to redissolve during the observed period of heating.

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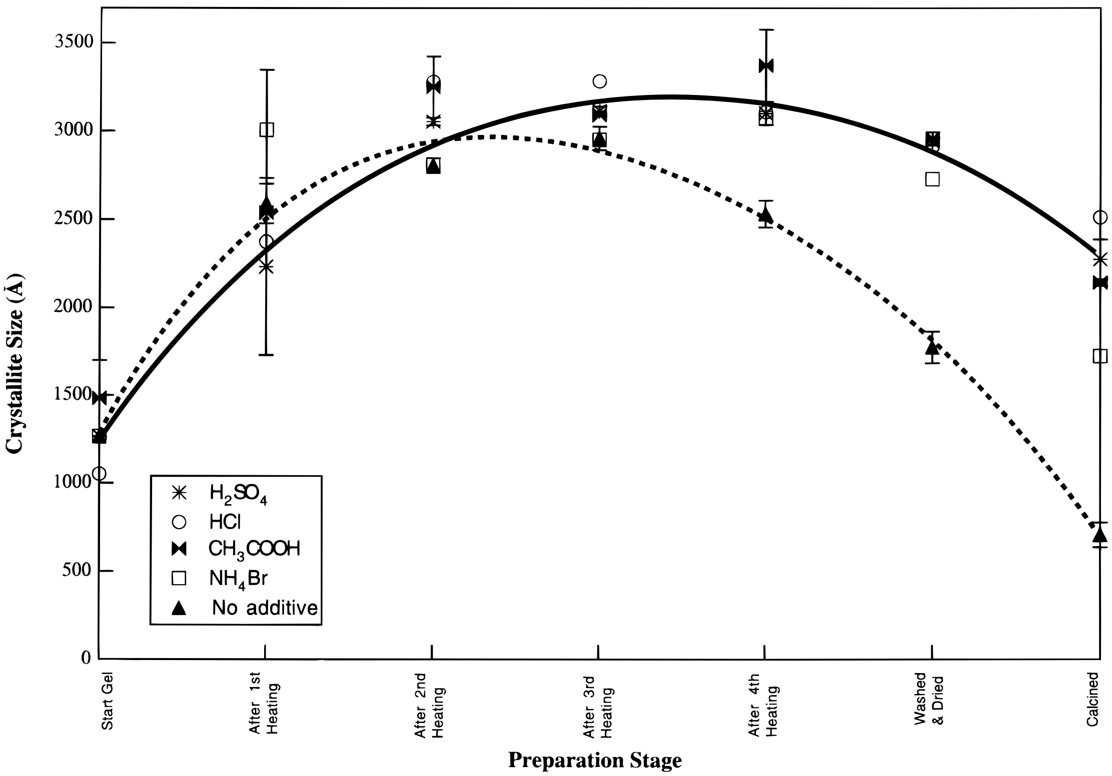

Figure 6. Crystallite size determined from the width of the 10 Bragg reflection for various synthesis stages for preparations treated with various acids to a pH of 11. The lines drawn through the points are merely guides to the eye: the solid line indicates trends in the acid titrated preparations, while the dotted line follows the untreated preparation. The errors correspond to the greatest deviation from the mean, in those preparations that were repeated.

The crystallite size in the acid-treated materials decreases upon drying and then again upon calcination, but this decrease is much less significant than in the materials from the untreated synthesis. We conclude, therefore, that the acid-treated materials are much more stable to calcination than those from the ordinary preparation. This is consistent with a higher degree of silicate polymerization having occurred during the synthesis of the acid-treated materials. Among the acid-treated materials, hydrochloric acid produces the largest crystallite sizes in the calcined materials, followed by sulfuric acid, acetic acid, and ammonium bromide. The addition of sodium acetate to the preparation has no beneficial effect on crystallite size and may even have a detrimental effect.

Shrinkage on Calcination. The other major difference in behavior between acid-titrated and ordinary MCM-41 preparations is the degree of shrinkage in the *d* spacing that occurs during synthesis. In the ordinary preparation, an initial synthesis gel with a *d* spacing of 44.2(5) Å has a *d* spacing of 42.7(5) Å by the final stage of heating. This contracts further upon drying and washing to 39.9(5) Å and again upon calcination to 33.8(5) Å. However in the acid-titrated preparations the initial synthesis gel *d* spacing (e.g., of 43.6(5) Å for a preparation titrated with sulfuric acid to maintain a pH of 11) is retained through all of the acid titration and heating steps. There is no decrease in *d* spacing on drying and washing (43.6(5) Å) and only a small decrease during calcination (to 41.0(5) Å, in this case). We attribute these differences to a much higher flexibility in the wall structure of the untreated materials. The increasing peak width as the ordinary synthesis proceeds indicates that the shrinkage does some damage to the preexisting crystallites. This again points to a higher degree of siloxyl condensation in the synthesis for the acid-titrated case.

A plot of 10 Bragg peak intensity against moles of acid added to the synthesis gel during preparation (Figure 7) showing leveling off of the peak intensity with time closely reflects the decreased amount of acid titer needed to bring the pH of the gel back to the desired value as the synthesis proceeds and hence the completeness of siloxyl condensation. The fact that at each step in the procedure the pH creeps up again during heating after titration shows that the condensation reaction proceeds until an equilibrium is reached between condensing and dissolving silica. Heating under such equilibrium conditions probably aids the observed increase in long-range order by allowing a certain degree of annealing of the structure to occur.

Discussion

MCM-41 Structure and Stability. The improved long-range order obtained by the methods described above has allowed us to model the wall structure of MCM-41,[5] and this contributes to understanding the mechanism of formation. The data from Figure 1 allow a form factor to be fitted to obtain information about the wall structure and thickness. This shows that the walls of hexagonal MCM-41 may have two components—a denser, continuous phase forming the boundary between the hexagonally close-packed cylindrical channels and a significantly less dense phase lining the inside of the pores. The average values obtained for the total wall thicknesses, 15.6(3) Å, for the calcined and 17.5(2) Å for the uncalcined materials are much larger than those estimated from high-resolution electron microscopy (8 Å)[10] and combined analysis of nitrogen adsorption

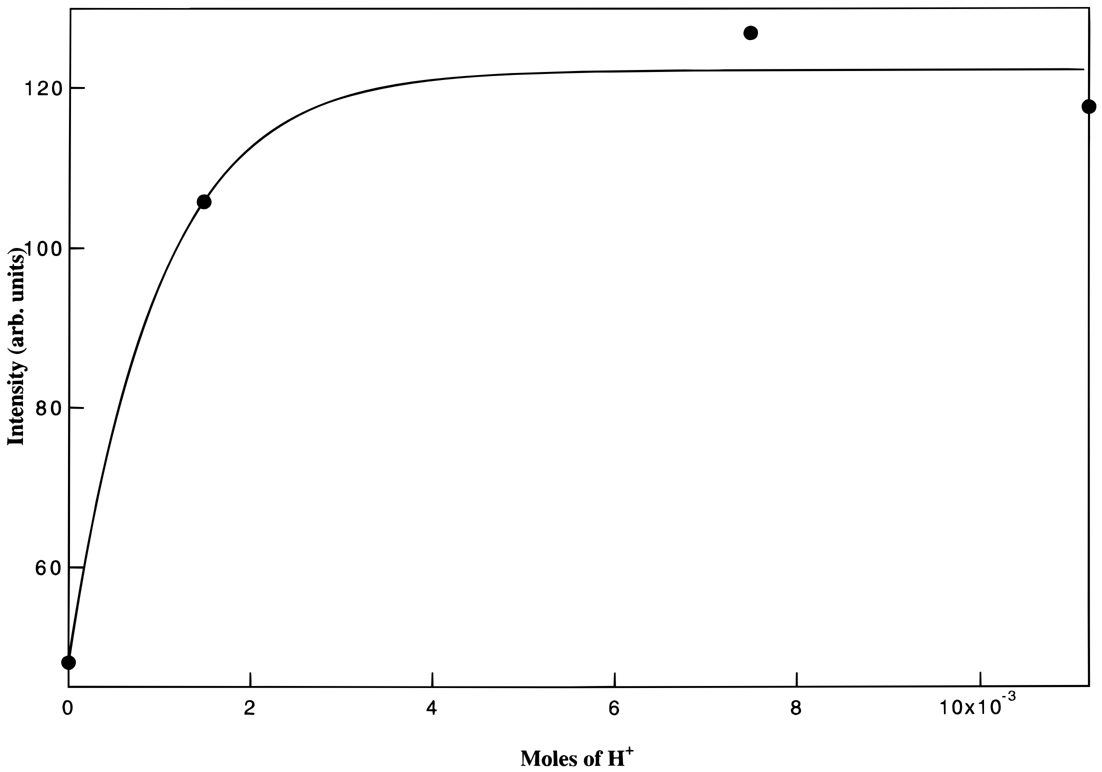

Figure 7. Peak intensity plotted against acid concentration in the wet synthesis gel for a MCM-41 preparation titrated against acetic acid to maintain a pH of 11.

isotherms and X-ray diffraction data (12.5 Å).[11−13] These earlier methods measured only an average wall thickness, since they assume a two-region (hole/wall) model. In our case, the calcined MCM-41 from the preparation titrated against acetic acid has a slightly thinner dense wall (5.7(4) Å), than the similarly calcined sulfuric acid sample (6.39(5) Å), but in the uncalcined materials the trend is reversed with dense walls of 5.92(5) Å for the sulfuric acid treated and 7.22(5) Å for the acetic acid treated materials respectively. When these materials are calcined, the less dense silicate layer has a thickness of around 12.6 Å, whereas in the uncalcined materials it is about 14.2 Å.

The acid-titrated materials appear to be much more hydrothermally stable than those from the ordinary MCM-41 preparation[14] and so may well have thicker or more densely polymerized walls than materials from the ordinary preparation to achieve this stability. The completely empty central channel indicated by our work is also considerably smaller than that observed by others (ca. 7 Å diameter in the calcined materials) but nitrogen isotherms on this material indicate pore diameters of 28−35 Å.[15] Thus the silicate forming the lining of the channels is possibly highly divided and dendritic, a condition that allows adsorbed molecules to penetrate into the walls. Inelastic scattering data[15] show that in hydrogen-filled MCM-41 at 15 K, about half of the absorbed hydrogen is in the more or less bulk state—the rest being absorbed in a more or less uniform wall site.

The form factor data[5] also show that the walls of MCM-41 have very low densities compared to that of colloidal silica. Data from gas adsorption isotherms indicate that the mean density of calcined MCM-41 is about 0.83(5) g cm^{-3}, 0.99 g cm^{-3} for the denser continuous walls and 0.87 g cm^{-3} for the less dense lining of the channels. These values have errors of 4−5% in the absolute values, but the difference has an error of less than 1%. These low densities indicate a large amount of void space in the walls. This may be due to counterions binding to the CTAB micelles, as discussed below, causing the silicate polymerization process to form a loose highly interwoven network rather than dense colloidal silica.

Many factors may influence the density of the silica forming the walls. As the polymerized silica chains are neutral or have low charge, they may be quite hydrophobic and so able to penetrate the CTAB micelle by forcing their way between the surfactant molecules. Work on pure surfactant systems has shown that water molecules may penetrate the micelle surface to distances of 3−6 carbon atoms,[16] so silicate monomers and oligomers could also occupy such regions. Micellar surfaces are known to be rough, and in organic reactions catalyzed by cationic micelles, solutes may occupy voids at the surface thereby stabilizing the micelle.[17] Neutral polymerized silicate may behave similarly to these hydrophobic organic molecules. As the presence of the

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surfactant, even in the absence of acid, is known to catalyze silicate polymerization in MCM-41[1] an accelerated reaction may also result in looser networks of silica than is typical of the colloidal silicates. Other workers[18] have also noted an increase in the crystallization rate of a variety of zeolites, including pure silicate structures, templated with quaternary ammonium ions when promoter ions such as PO_4^{3-}, NO_3^-, SO_4^{2-}, and CO_3^{2-} were added to the synthesis gel before heating. Liquid-state ^{29}Si NMR experiments showed that the promoter ions dramatically accelerated the formation of soluble Q^4 species and their rapid condensation into crystalline silicate units. They conclude that the presence of ionic species with greater polarizing ability enhances the process of crystallization dramatically by speeding up condensation processes between silica-enclatherated template moieties. By analogy, in the formation of mesoporous silicate MCM-41 materials in the presence of acids similar mechanisms may operate and the presence of such ions may also increase the rate of condensation in the synthesis gels of these materials.

Acid addition may also have other effects. Adsorption data for hydrogen in MCM-41 show that a single, well-defined boiling point is observed for all hydrogen contained in the pore system.[14,15] This indicates that the pores of the MCM-41 material must be interconnected to some extent. Small-angle neutron scattering from water-filled calcined MCM-41 materials indicates that all of the void space is accessible to water[19] and nitrogen adsorption isotherms show no evidence of micropores.[15] The interconnectedness of the pores may be due to the low densities and highly dissected nature of the walls; however, the absence of micropores in such a system seems unlikely. An alternate model for this material is, therefore, also discussed in a previous paper.[15] This model posits that MCM-41 may be a defective MCM-48 cubic structure where the smooth-walled channels are largely hexagonally close-packed cylinders but have interconnections which resemble the infinite periodic minimal surface which has been postulated as the structure of MCM-48.[20] In the [111] projection of a cubic gyroid minimal surface of symmetry $Ia3d$, (Figure 9 in Larsson et al.[21]), there is a distinct resemblance between MCM-48 and the MCM-41 structure observed in transmission electron micrographs[10] and diffraction patterns.[5,6] Interconversion between MCM-41 and MCM-48 has recently been reported by Stucky et al.[22] Acid addition may in this case also effect changes in the silicate/surfactant phase diagram, promoting the intermediate states.

Counterion Effects. The reasonably similar results from the various acids confirm the value of Ryoo's method, but the differences, shown in Figure 4, do suggest an effect of the counteranion which should be explored further. The suggestion from our results is that the sulfate ion has had the most beneficial effect in improving the quality of the diffraction pattern. The order in which the various acids enhance long range order in the calcined material is $SO_4^{2-} > C_2H_3O_2^- > Cl^- > Br^-$. From this it would seem that as well as the direct effect of H^+ on the silicate equilibrium, properties of the anion will also affect the synthesis.

This order appears to be the reverse of the anionic lyotropic series observed for CTAB. The lyotropic series given in Larsen and Magid[23] on the basis of the enthalpy of transfer of the salt from water to solutions of 0.1 M CTABr is citrate $< CO_3^{2-} < SO_4^{2-} < C_2H_3O_2^- < F^- < OH^- < HCO_2^- < Cl^- < NO_3^- < Br^- < SO_3C_7H_7^-$. We would predict that titrating the synthesis mix with say carbonic or citric acid should promote even greater long-range order in the calcined material. Of course, the major ionic component of the solution is the original counterion of the surfactant, in this case, Br^-, as well as the OH^- ion. For a preparation titrated to pH = 11 the total concentration of SO_4^{2-} after addition over the course of the reaction was 8.56×10^{-2} M in an initial solution which contained 0.307 M Br^-. Larsen and Magid[23] observe that although addition of hydroxide decreased the amount of bromide bound to the micelle, no binding of hydroxide was observed in solutions with pH values of 12−13. Fluorescence quenching has also shown that OH^- does not directly displace Br^- from the surface of CTAB micelles,[17] so the relative binding strength of bromide and silicate anions will be a more important determinant of structure than the counterions from the titrant, if such effects are important. Starting with a pure cetyltrimethylammonium chloride or hydroxide surfactant will thus presumably also enhance the long-range order.

Underwood and Anaker[24] find a similar, although not identical, series for decyltrimethylammonium bromide ranked in order of cmc value. They conclude that the electrostatic headgroup repulsions which hinder assembly of the micellar surface are mitigated most effectively by the least hydrated counterions, which therefore promote the most ordering in the surfactant self-assembly process. It has also been observed for dialkyldimethylammonium surfactants that the properties of their Langmuir films depend greatly on the counterion,[25] with the monolayer being contracted by anions increasingly in the order of increasing hydration (i.e., $F^- < Cl^- < Br^-$). This means, once again, that the least hydrated ions bind strongest to the surfactant. Large hydrated ions such as fluoride, hydroxide, and acetate gave expanded monolayer compression isotherms and do not bind to the surfactant headgroups. The somewhat more hydrated CO_3^{2-} ions showed a lesser degree of binding than SO_4^{2-} ions. This alone could not explain the observed monolayer contractions which indicate that a significant lateral repulsion exists between surfactant headgroups, and it was concluded that Stern-layer effects that correlate with the size of the anion are also important. The drop in potential across the Stern layer is proportional to its thickness,[26] and the width of the Stern layer will be related to the counterion size. Presumably, the weaker the binding between the counterions in the reaction mix and the surfactant template, the easier it is for the silicate anion to displace them and so concentrate on the surface of

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the micelle to polymerize. Tightly bound anions may also become incorporated in the silicate matrix and therefore affect the continuity of the silica polymerization. The observed increase in crystallinity dependent on the counterion is small compared to the increase due to the addition of H^+; however, it may also improve other properties of the MCM-41 material that have not yet been investigated. Further work using a greater variety of counterions may elucidate this point further.

Effect of pH. The effect of the pH at which a synthesis is maintained is less strong than the effect of counteranion. Working with the sulfate ion at a lower pH appears to have been beneficial (Figure 5) and the optimum pH for this synthesis appears to be between 9 and 10. This is well below the pH of 10.5−11 at which the neat sodium silicate solution used in this synthesis is found to gel. The gel point of the synthesis mixture also occurs around pH of 11 and can be noticed during the acid addition titrations as a distinct viscosity change in the solution and by a slight buffering effect. Adding further acid once this gel point is passed does not increase the viscosity further and no further buffering occurs; however, the improvement in the long-range order of the product continues in preparations maintained at pH values below this point. It therefore seems unlikely that this crossing of the gel point is directly related to the improvement in order. Some previous work on the effect of the initial pH of the alkaline synthesis gel on wall thickness[27] found that the thickness increased with decreasing pH up to 16 Å, suggesting that a thicker silicate coat is deposited on the micelles as the silica solubility decreases. However, this pH variation did not result in highly ordered material as is the case in the preparations adjusted for pH *during* synthesis.

During the synthesis, heating the titrated reaction gels causes the pH to rise once more. Preparations titrated to maintain a pH of 10 will return to pH values above 11 during the overnight heating following at least the first two acid additions (although not after the third acid addition). Colloidal silicas have been observed to dissolve just below a pH of 11.[28] Thus by repeatedly returning the synthesis gel to a pH of 10 the reaction is crossing and recrossing this dissolution point during the course of the heating. The potential thus exists for some annealing of the structure to occur through this dissolution and reprecipitation process. It is also possible that by precipitating a substantial quantity of the silica through lowering the pH, the growth of the MCM-41 crystallites proceeds in a more ordered fashion, with silica drawn as needed from an insoluble form rather than from soluble polyanions.

Conclusion

We have prepared MCM-41 materials with a high degree of long-range order which show up to seven orders of diffraction in synchrotron X-ray studies. These materials are achieved by adjusting the pH of the reaction gel during the heating process to maintain a constant pH. Material prepared at a pH of 9−10 have the sharpest diffraction peaks, indicating larger crystallite sizes, and these remain intact to a greater degree than those in the ordinary preparation throughout the synthetic process. Our best results were achieved using sulfuric acid, although the effect of the counterion is small compared to the overall effect of the acid addition. The counterion effect may be due to the strength of the binding between the ion and the surfactant, however the reasons for the greater ordering of the overall structure remain unclear.

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