A method for the synthesis of high quality large crystal MCM-41

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Preparation of large crystal MCM-41 has been achieved by using calcined small crystallite MCM-41 as seeds in a multistage synthesis method. The possible formation mechanism is discussed. We believe that the newly discovered method is particularly important in making high quality thin films of mesoporous materials.

Following the discovery of the M41S family of ordered silica materials,[1,2] considerable attention has been focused on tailoring their pore structures.[3–6] For example, the diameter of hexagonally packed one-dimensional channels in MCM-41 can be tailored from 15 to over 100 Å[2–6] by a variety of methods which include using templating surfactant molecules with different alkyl chain lengths,[2] adding auxiliary organic molecules (which are solubilised in the hydrophobic region of the templating aggregates thus increasing micellar size)[2] or hydrothermal restructuring in the mother liquor over longer crystallization time or at higher reaction temperature.[3–6] The pore size uniformity or long range structural ordering can also be improved by careful choice and control of synthesis conditions.[7,8] However, there are very few reports on the control or increase in crystal size of MCM-41 despite the fact that crystal size is crucial to the fabrication and use of this material in thin film applications (such as in separation membranes) and in making molecular wires.[9] This is not surprising because, compared to the three-dimensional MCM-48, the formation of large crystals of MCM-41 would be difficult due to the one-dimensional channel structure which is subject to bending and fracture. Here we report on a new synthetic approach which involves the use of calcined MCM-41 as the seeds for further synthesis. The resulting material (herein referred to as secondary MCM-41) shows significantly improved long range structural ordering and a marked increase in crystal size.

The parent MCM-41 material (herein referred to as the primary MCM-41) was prepared following a normal procedure.† For secondary synthesis a synthetic gel of the same molar ratio was assembled except that the primary MCM-41 was used as 'silica source' instead of the fumed silica. The experimental procedures were exactly the same as described for the primary synthesis.† The MCM-41 yield, based on silica recovery, was *ca.* 60% for the primary synthesis and > 90% for the secondary synthesis.

The powder X-ray diffraction (XRD) patterns obtained from the calcined primary and secondary MCM-41 are shown in Fig 1. The pattern of the primary MCM-41 is typical of a well ordered specimen and shows an intense (100) diffraction peak and three higher order (110), (200) and (210) peaks. The pattern of the secondary MCM-41 shows an increase in the intensity of the (100) peak along with an increase in intensity and improvement in the resolution of the higher order peaks. In addition we were able to observe the (300) peak and a diffuse (220, 310) peak; these peaks are seldom observed even in the 'best' quality MCM-41 reported previously.[8] The presence of these higher order peaks indicates an improvement in long range ordering while the increase in peak intensities and associated reduction in full width at half maxima (FWHM) is a reflection of larger scattering domain (or crystal) size. The secondary synthesis does not however have any significant effect on the d_{100} spacing of the calcined samples. We note that doubling the primary synthesis time from 48 hours to 96 hours results in an increase in d_{100} spacing and a decrease in long range ordering with no apparent change in crystal size. Preliminary porosity data indicate that the surface area and pore volume of the secondary MCM-41 are slightly lower than those of the primary MCM-41. The average pore diameter (APD) is also lower for the secondary MCM-41. The lower APD taken together with the unchanging basal spacing is an indication that secondary synthesis results in a material with thicker pore walls. Thicker pore walls are expected to impart greater thermal and hydrothermal stability; indeed we have found that the secondary MCM-41 is relatively more stable to refluxing in boiling water compared to the primary material.

Transmission electron microscopic (TEM) images and selected area electron diffraction (SAED) patterns of the samples were obtained from a Jeol JEM-200CX electron microscope. The crystal size of the primary MCM-41 is in the range 400–600 Å range and no crystallites larger than 1000 Å were observed. This is similar to other normal MCM-41 specimens presented in previous reports.[10] On the other hand, the crystal size of the secondary MCM-41 is from 4000 to 8000 Å and crystallites smaller than 1000 Å were never observed. A typical TEM image together with a corresponding SAED pattern is shown in Fig. 2. It is clearly demonstrated that the secondary synthesis results in an increase in the crystal size of MCM-41 and crystallinity of the specimen has been significantly improved as indicated by

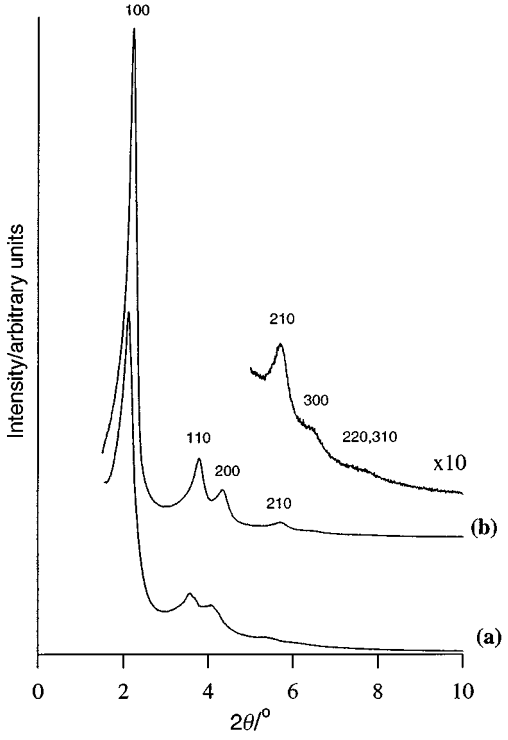

Fig. 1 Powder XRD patterns of calcined (a) primary MCM-41 and (b) secondary MCM-41.

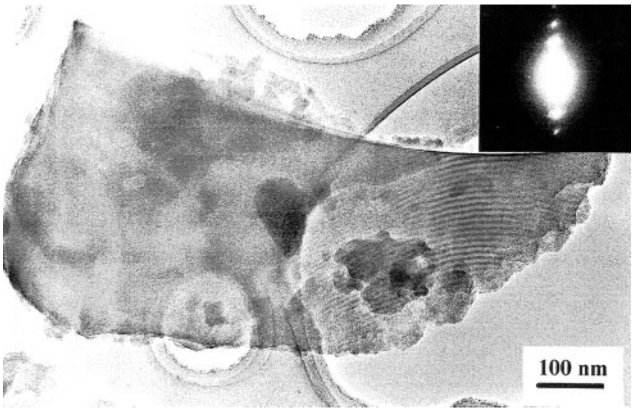

Fig. 2 TEM image and corresponding SAED pattern of a large crystal of MCM-41.

SAED patterns where four or more pairs of diffraction spots appear along the [100] direction, while only one or two pairs can been seen from the primary MCM-41 crystallites.

Thermogravimetric analysis (TGA) of the as-synthesized samples indicate that the amount of template occluded by the secondary MCM-41 is *ca.* 18% lower than in the primary MCM-41. This indicates that less amine is required during the secondary synthesis which would be the case if the primary MCM-41 (which is the silica source) remains largely intact with its crystallites acting as seeds or starting points for further MCM-41 formation. In this scenario the real source of silicate ions for crystal enlargement is amorphous silica which is usually part of any MCM-41 yield.

The extension of the MCM-41 framework is preceded by the dissolution (which is made possible by the presence of OH^- ions from TMAOH) of the 'silica source'.[11] The OH ions are used up during the dissolution and therefore the extent to which the concentration of OH ions (or pH) reduces during the crystallization period is a measure of the amount of dissolution.[11] For the primary synthesis we observed a decrease in pH from 12.4 to 11.5 after ageing for 20 hours at room temperature and a further decrease to 10.7 after heating at 150 °C for 48 hours. In contrast the gel for secondary synthesis had a pH of 11.5 which remained largely unaffected by aging at room temperature and reduced only slightly to 11.2 after heating for 48 hours at 150 °C. We attribute this smaller reduction in pH to the fact that there was much less dissolution during the secondary synthesis. In other words, if the MCM-41 particulates had dissolved extensively (to the same extent as the dissolution of fumed silica during the primary synthesis) we would have observed a larger pH decrease similar to that observed for the primary synthesis. These results along with the higher silica recovery are a strong indication that the primary MCM-41 is preserved during the secondary synthesis and that the slight decrease in pH is due to the dissolution of amorphous silica phase.

The TGA of the as-synthesized primary and secondary samples also indicated that the weight loss attributable to dehydroxylation of silanol groups (between 350 and 800 °C)[3,12] was 35% less for the secondary sample. This is a clear indication that the as-synthesized secondary MCM-41 is at a much higher level of silicate polymerization compared to its primary precursor and agrees with our suggestion that the primary MCM-41 remains largely intact during the secondary synthesis. This is further supported by our observation that on calcination the basal spacing of the primary MCM-41 reduced by 8.0% compared to a reduction of 2.5% for the secondary MCM-41. It is generally accepted that a higher extent of contraction is an indication of a less polymerized or cross-linked framework which therefore undergoes greater dehydroxylation.[11] Indeed ^{29}Si MAS NMR of the as-synthesized samples indicates that the Q4/Q3 ratio is higher for the secondary MCM-41.

According to a recent report,[13] during the preparation of MCM-41, the cylindrical surfactant and the silica aggregates are simultaneously formed. The silicate ions enter the particles from the surface perpendicular to the *c* axis of the aggregates and the molecules of the surfactant must enter along the aggregate cylinders until the density of the surfactant approaches its maximum value. In the present work, when the calcined MCM-41 crystallites were used as seeds during the secondary synthesis, it is possible that the template molecules attach themselves at the mouth of the pore channels of the primary MCM-41 and encourage crystal growth parallel to the channels and, consequently, growth of larger crystals becomes possible. This method can be applied in future preparation of large single crystals and high quality thin films of MCM-41.

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Notes and references

† *Preparative procedure of the primary MCM-41*: tetramethylammonium hydroxide (TMAOH) and cetyltrimethyammonium bromide (CTAB) were dissolved in distilled water by stirring at 35 °C. The silica source, fumed silica (Sigma), was added to the solution under stirring for 1 hour. After further stirring for 1 hour the resulting synthetic gel of composition $SiO_2 : 0.25$ CTAB : 0.2 TMAOH : 40 H_2O was left to age for 20 hours at room temperature following which the mixture 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 at 550 °C for 8 hours.

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