Chapter 2:

Synthesis of MCM-41

“Good questions outrank easy answers.”

Paul A. Samuelson

The principle of surfactant liquid crystal templating has been applied to many different systems, to create mesophase structures with very different characteristics. Some of these are referred to below. In this work however, the emphasis is on the simpler, pure silica hexagonal phase templated by a single surfactant species.

2.1 Introduction

The synthesis of the hexagonal mesoporous silicate known as MCM-41 is possible via a number of methods. The initial paper by Beck et al.\(^1\) cites a number of representative syntheses, using silica sources ranging from colloidal silica to tetraethyl orthosilicate (TEOS), alkyltrimethylammonium templates with varying carbon chain lengths, and counterions and other ingredients such as alumina, to affect the wall properties and mesitylene, to alter pore size. Other workers have investigated the addition of catalytically active elements such as vanadium,\(^2\)-\(^4\) titanium,\(^5\)-\(^11\) zirconium,\(^12\) iron,\(^13\) manganese,\(^14\) chromium,\(^15\) nickel\(^16\),\(^17\) and tin.\(^18\),\(^19\) Gallosilicate\(^20\)-\(^22\) and borosilicate\(^23\)-\(^26\) MCM-41 materials have also been prepared. The use of surfactant templating methods has been expanded to create porous materials from other oxides including transition metals, such as niobium,\(^27\),\(^28\) tungsten,\(^29\) vanadium,\(^29\),\(^30\) zirconium\(^31\)-\(^33\) and tantalum\(^34\) which contain no silica at all. Mesostructured aluminophosphates\(^35\),\(^36\) and tin sulphides\(^37\) have also been made. Similar mesoporous materials, designated FSM-16, can also be formed from the surfactant-modified layered polysilicate clay kanemite.\(^38\)-\(^42\) These materials have similar pore sizes and hexagonal structure to that of MCM-41 and debate continues over whether the FSM-16 derived from kanemite and MCM-41 are the same material.\(^43\)

The initial aim of the synthetic work described here was to discover the mechanism of MCM-41 formation. Later, the aim also became to optimise the preparation method, so as to create materials with the highest possible long range order, in order to investigate
the structure of the MCM-41 formed. A pure silica version of MCM-41 was used, in an attempt to reduce the number of variables in the system. Also, although versions of the preparation of MCM-41 in acidic media have been published by other workers\textsuperscript{44-49} this work has been restricted to an alkaline preparation, also for the sake of simplicity.

### 2.2 Materials

The simplest form of the MCM-41 preparation requires only four ingredients: a silicate source, a template molecule, some acid, to increase the rate of silica condensation, and water. In this work the silica source used was sodium silicate solution (Aldrich, \textasciitilde14\% NaOH, \textasciitilde27\% SiO\textsubscript{2}, density = 1.390 g cm\textsuperscript{3}) a dissolved form of silica comprised of oligomeric and monomeric species.\textsuperscript{50-52} Sodium silicate solution was used as the silica source as it was a convenient, pre-dissolved form of silica which preliminary work\textsuperscript{53} had shown to give MCM-41 structures. The template molecule was cetyltrimethylammonium bromide (CTAB, C\textsubscript{16}H\textsubscript{33}N(CH\textsubscript{3})\textsubscript{3} Br, Fluka, 98%), a surfactant with well known aggregation behaviour.\textsuperscript{54,55} The acid used was sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, Univar, Analytical Reagent, 98\%). These chemicals were used without further purification. Water was purified by a Millepore filtration system to a resistivity of 18 M\textasciitilde cm.

![Graph showing diffraction pattern](image)

**Figure 2.1** Diffraction pattern from pure crystalline CTAB (top), and from a 28 wt\% CTAB in water solution at 27\textdegree C (bottom). The solution pattern has been multiplied by a factor of 10. Intensities are on an arbitrary, but consistent scale.

A small angle diffraction pattern for pure, solid CTAB is shown in Figure 2.1, as intensity versus momentum transfer, Q where $Q = \frac{4\lambda \sin \theta}{\lambda}$, \(\lambda\) is the wavelength of the radiation used (in this case \(\lambda = 1.54\ \text{Å}\)) and \(\theta\) is half of the scattering angle (see Chapter 3 for further details concerning small angle scattering). The pattern for a water solution of 28 wt\% CTAB at 27\textdegree C is also shown. This CTAB concentration corresponds to the hexagonal phase concentration regime for this surfactant at this temperature,\textsuperscript{54} however the double peak visible in that pattern suggests the presence of two phases in the
solution. From the \( d \)-spacings, there is probably a rod-like micelle phase present as well as the hexagonal phase.\(^{55} \) The CTAB concentration used in the MCM-41 preparations in this work, 11.5 wt\%, is within the rod-like micelle region of the phase diagram at 27\(^\circ\)C, but in the spherical micelle region at temperatures above 50\(^\circ\)C.\(^{54} \)

In order to increase the long range order of the MCM-41 materials, a number of preparations were treated with additional acid (1 M in water) as the synthesis progressed. The acids used in these syntheses were acetic acid (\( \text{CH}_3\text{COOH}, \text{BDH, Analar} \)), sulphuric acid (Univar, analytical reagent grade, 98\%), hydrochloric acid (HCl, Univar, analytical reagent grade, 36\%) and ammonium bromide (\( \text{NH}_4\text{Br}, \text{BDH, laboratory reagent grade, 99\%} \)). One preparation was titrated with equivalent amounts of sodium acetate (\( \text{Na CH}_3\text{CO}_2, \text{Univar, analytical reagent grade, 99.0\%} \)) to observe the effects of the acetate ion on the synthesis.

In the Langmuir trough work discussed in Chapter 4, an insoluble surfactant (\( \text{C}_{18}\text{H}_{37}\))\(_2\)N(CH\(_3\))\(_2\) Br was prepared by Dr Tim Senden, and used as received. Surfactant solutions were prepared in distilled chloroform (Univar, analytical reagent grade, 99.8\%).

In the neutron scattering work discussed in Chapter 5, D\(_2\)O (AEC Canada, 99\% and Cambridge Isotope Laboratories, 99.9\%) was partially substituted for the water in the synthesis gels. In other experiments potassium bromide (KBr, Aldrich, FTIR grade 99+\%) was used to alter the behaviour of the gels under shear. Nitrogen, hydrogen and methane used for gas adsorption isotherms and quasielastic neutron scattering experiments were 99.99\%, 99.95\% and 99.99\% pure, respectively.

### 2.3 Preparative Method

The synthetic method used in this work was essentially that of Beck et al.\(^{1} \) Outlines of typical preparations for the three reactions studied; unheated, heated and acid-titrated, are provided here. Further synthetic details are discussed in Chapter 4, and quantities of reagents for all preparations are given in Table A1.1 in the Appendix. Other preparative information can be found in Chapter 4, Tables 4.9 and 4.10. Compositions of preparations made for shear experiments can be found in the Appendix at Table A1.2.

For each preparation, two solutions were initially prepared. A solution of 16.4 g of CTAB in 49.2 g water was made by heating to 75\(^\circ\)C to dissolve the CTAB. An acidic sodium silicate solution was also prepared, by diluting 19.0 g of sodium silicate with 40.6 g of water and adding 1.2 g of sulfuric acid with rapid stirring. The hot CTAB solution was then added into this at room temperature, and the resulting gel stirred for a further 15 minutes, during which time it cooled to ambient temperature. 20.0 g of water was then added and stirring continued for 30 minutes. Unheated MCM-41 preparations were set aside at this point in sealed containers, and allowed to age in the synthesis gel for various periods. These were then filtered, washed, dried and calcined in the same manner as described below, for heated samples.
Otherwise, this mixture was then heated to 100°C in an autoclave for three days. This heating time was found to give materials with the greatest long range order.56 The reaction gel was usually not stirred during heating. For the larger preparations a teflon-lined Berghoff autoclave with a capacity of ca. 250 ml was used. This had a teflon coated thermocouple to monitor the solution temperature directly, and an internal magnetic stirring mechanism. This autoclave had a delay time of about 30 minutes in reaching the set temperature of 100°C and often overshot the set temperature on initial heating by up to 20°C for around 30 minutes. For smaller preparations, (25-30 ml) a set of five small autoclaves made at the RSC were used. These were heated in an oven maintained at 100°C, so the solution temperature could not be directly monitored in this case. Some later preparations, following the method of Ryoo and Kim,57 were titrated with various dilute acids in order to further improve the long range order of the MCM-41 product. These are referred to as the ‘acid-titrated’ preparations. In these preparations, three times during heating, at 24 hour intervals, the autoclave was cooled to a comfortable handling temperature, opened and titrated with one molar acid, to return the whole gel system to a predetermined pH. Each titration required about one hour from the beginning of initial cooling of the autoclave. This procedure and its effects are discussed in greater detail in Chapter 4. Preparations which were not treated with acid are referred to as the ‘ordinary’ syntheses.

After heating, the materials were filtered while still warm and washed with 70°C Millepore filtered water to remove any unincorporated CTAB. The material was dried in an oven at 100°C for up to one hour and stored in glass vials sealed with a screw cap, usually in the dark, although no special precautions were taken to exclude light or atmospheric moisture from these materials.

2.4 Removal of Template

The organic template molecule, CTAB, was removed from the silicate lattice by one of two techniques, calcination or washing. Calcination is the burning out of the template under conditions which do not greatly affect the integrity of silicate structure. This has the advantage of ensuring the removal of all carbonaceous material, but also causes a significant shrinkage in the MCM-41 lattice parameter which is discussed further in Chapter 4. In an attempt to avoid this, template removal by washing was also considered, although in this work, complete template removal by this method was never achieved. The development of the acid-titrated preparation reduced the need for mild methods of template removal, as calcination had a much smaller effect on the lattice parameter of acid-treated samples.

Other investigators have reported calcination at temperatures up to 540°C under oxygen.1,58,59 The temperature used for calcination does not appear to affect the quality of the product greatly. A shrinkage of up to 25% in the lattice constant has been observed occur on calcination,60 depending on the synthesis conditions, although pore collapse occurs only after heating to temperatures of 900°C in dry air.59 Washing out of the template by boiling in HCl/ethanol mixtures has also been reported as effective for template removal and as causing less lattice shrinkage than the burning out methods.59,61 Template removal by washing in acidic ethanol has been shown to be
more successful in mesoporous silicates made via neutral templating routes than by ionic templating.62 There is however, debate as to whether some template remains in the structure after such treatments.63 Ionic template recovery has also been reported. That technique requires the use of exchange ions or ion pairs which replace the charged template molecules during the extraction process.61 Template removal by supercritical extraction or oxygen plasma treatment has also been suggested.60

Calcination was performed in either a tube furnace or a muffle furnace. In the small tube furnace the product was dried and then slowly heated under a stream of pure nitrogen, over a period of several hours to 350°C. The sample was maintained at this temperature for one day and then calcined further at 350°C under a stream of dry air for four days. Samples calcined in the muffle furnace or a larger tube furnace were heated to 500°C over about 30 minutes and were maintained at this temperature overnight. The large tube furnace allowed a stream of dry air to be passed over the samples during calcination, but the muffle furnace did not. Calcined samples were also stored in sealed glass vials. Calcination at higher temperatures for shorter times appeared to be most successful in eliminating the template, judged by the final, pure white colour of the product, but did not appear to significantly affect the stability (see Tables 4.9 and 4.10 below) or the pore size of the product.

Table 2.1  Surfactant/silica ratios for samples from acid treated and ordinary preparations after washing, calculated by gravimetric calcination.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Surfactant/Silica wt/wt</th>
<th>N/Si mol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Titrated</td>
<td>as prepared</td>
<td>2.68</td>
<td>0.442</td>
</tr>
<tr>
<td>Prep 1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>1 wash</td>
<td>1.13</td>
<td>0.186</td>
</tr>
<tr>
<td>1.3</td>
<td>2 washes</td>
<td>1.04</td>
<td>0.171</td>
</tr>
<tr>
<td>1.4</td>
<td>3 washes</td>
<td>0.93</td>
<td>0.153</td>
</tr>
<tr>
<td>1.5</td>
<td>calcined</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ordinary Prep</td>
<td>as prepared</td>
<td>2.12</td>
<td>0.349</td>
</tr>
<tr>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>1 wash</td>
<td>1.51</td>
<td>0.254</td>
</tr>
<tr>
<td>2.3</td>
<td>2 washes</td>
<td>1.35</td>
<td>0.223</td>
</tr>
<tr>
<td>2.5</td>
<td>3 washes</td>
<td>1.27</td>
<td>0.209</td>
</tr>
<tr>
<td>2.5</td>
<td>calcined</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

An attempt was also made to remove the template by a succession of washings in water. In one experiment two bulk samples, one from an ordinary preparation and one from an acetic acid titrated preparation were separated into four parts. Each was washed by being mixed in 13.3 g of water per gram of unwashed MCM-41 at room temperature
overnight, then heated in an oven at 100°C for 10-15 minutes before the supernatant water was removed with a pipette. This was repeated up to three times for each sample. On the final wash each sample was filtered while still warm, then dried in the oven for two hours. Gravimetric calcination of small amounts of these washed samples showed that successive washings did reduce the CTAB to silica ratio (shown in Table 2.1), however significant amounts of template remained in these samples. Chen et al. have previously reported the N/Si ratio in as-synthesised MCM-41 to be 0.294 for a pure silica sample synthesised in a preparation which initially contained 14 wt% CTAB. The preparations discussed here initially contained 11.5 wt% CTAB.

A similar washing experiment was carried out on an uncalcined ordinary MCM-41 specimen (Argonne Prep 2). In this case the 0.0990 g of uncalcined MCM-41 was successively washed with 20 g water and the conductivity of this suspension monitored from the addition of the water until 2-3 hours after the addition. The water was removed after 24 hours, the sample dried in the oven, the water replaced with an equal mass and the conductivity followed for the first couple of hours. This was repeated 5 times. A similar experiment was performed using only 0.01 g of the same uncalcined MCM-41 in 18 g of water. The conductivity of the water removed from both experiments after standing overnight is shown in Figure 2.2 above and the change in conductivity of the water upon addition in each case is shown in Figure 2.3 below.

Figure 2.2 and 2.3 show that the most CTAB is removed by the first wash, although the rising trend in conductivity for subsequent washes indicates that the surfactant is still diffusing out from within the structure. An equilibrium state, with the surfactant partitioned between the MCM-41 structure and the solution, was therefore never reached on the time scale of these measurements. A change in the behaviour of the MCM-41 particles as the surfactant was washed out was noted. The particles began to be suspended in the solution and eventually to float on the surface of the solution after
about the third washing of the samples. This indicates that the overall density of the re-hydrated, washed particles must be slightly less than that of the solution, so some air must be trapped in the structure.

The conductivity data indicate that although washing with water successfully removed some CTAB from the MCM-41 structure, there was still a significant amount of template trapped inside even after five successive washings. Calcination was therefore used to remove the template from all further samples discussed in this work.
2.5 Physical Description of MCM-41 Materials

The MCM-41 materials produced by this method were white powders. The density of the unpacked powder for a material from an acid-titrated preparation was 0.098(5) g cm$^{-3}$. The uncalcined materials tended to be coarser and slightly sticky owing to the hydroscopic nature of the CTAB template. Calcined materials varied from a light brown in colour to pure white, depending on the method of calcination. The smaller tube furnace with its lower calcination temperature often produced darker specimens, however the colour did not noticeably affect other properties of the material. Samples produced using the acid-titration method had a much finer texture and were more friable than those produced using the initial method outlined above.

The grain size of these materials as determined by optical microscopy is around 3-10 µm for materials from ordinary preparations and 2-5 µm for acid-titrated materials, although both types of MCM-41 also contain many larger, aggregated particles. Scanning electron micrographs of the acid-titrated materials show particles of between 5 and 10 µm across with smooth surfaces. Micrographs of the ordinary preparation materials show much larger, rougher masses of coiled, intertwined tubes. These are discussed in greater detail in Chapter 4.

2.6 References