

Chapter 7:

Conclusion

“A conclusion is simply the place where you got tired of thinking.”

Martin H. Fischer

The two major foci of this thesis have been the synthesis of MCM-41 hexagonal phase, pure silicate materials, showing high long range order and the determination of a detailed structural model for these materials. A simplified preparation containing only sodium silicate solution, CTAB and some acid was chosen, with the aim of reducing the number of variables in the system with the attendant possibility of investigating the formation mechanism for this material.

The synthetic work, reported in Chapters 2 and 4 concerned four major variations on the preparation. The first two were the heated and unheated ordinary MCM-41 preparations, which were optimised in relation to heating or aging time in the gel, and the use of stirring during the synthesis. The other two were the heated and unheated acid titrated preparations. These were optimised in relation to the type of acid used for the titration and the pH level maintained during the heating or aging in the gel. The syntheses were followed experimentally through all stages of preparation - wet synthesis gels, washed and dried MCM-41 materials which still contained template, and the calcined materials in which the CTAB had been removed by burning out at high temperatures.

Of these preparations, the acid titrated materials prepared using four days of heating, with three acid titrations, using 1M sulphuric acid to maintain a pH of 10, had the highest degree of long-range order, as revealed by the number and intensities of the observable X-ray diffraction peaks. The pH at which the system was maintained during heating was shown to have an important effect upon the long-range order of the MCM-41 formed. The order appeared greatest for pH values around 10, with diffraction peak intensity decreasing with deviations from this value.

Other acids proved to have a similar, though less marked effect upon the long-range order of the product. The order in which the acid counterions were effective in

increasing the order was shown to be the reverse of the lyotropic series for CTAB, the surfactant template. The lyotropic series measures binding strengths of a counterion with the surfactant headgroup. The result here therefore indicates that more ordered materials are produced in systems where the other anions in solution bind least strongly to the surfactant headgroups, enabling enhanced ion-exchange with the silicate polyanions during synthesis. Unheated materials were shown to be stable to isolation from the synthesis gel, and retained their structure on calcination, although their stability appears to be proportional to the length of aging time in the gel. The long range order of these materials also benefited from the acid titration method used for the heated materials.

Despite the formation and observation, in Langmuir trough experiments, of a silicated surfactant species, under conditions where no micelles had formed, no final conclusions could be drawn on formation mechanisms. The templated structures in the preparation under study formed too quickly to be directly observed using the methods available, and showed no further gross structural evolution with time. Shear experiments on freshly prepared, unheated synthesis gels showed that the initial structure formed in the reaction mixture retained its neutron diffraction signature at shear rates up to $10\,000\text{ s}^{-1}$. These gels must therefore contain hexagonal phase material with a high degree of connectivity between individual cylindrical silicated micelles from an early stage of the preparation.

The manufacture of MCM-41 materials with high-long range order enabled X-ray diffraction patterns showing up to seven orders of diffraction to be obtained. The data from these patterns was fitted by a model for the scattering from cylinders. These calculations showed that the MCM-41 material contained two distinct density regions in the walls. These were identified as a denser, continuous wall region, and a less dense material lining the inside of each channel. The central empty hole in these materials appears to be smaller than has previously been reported for other MCM-41 materials which have been characterised using gas adsorption isotherms. The wall density of MCM-41 was also shown from these calculations to be very low, being about 40% silica by volume, even in the dense, continuous part of the structure.

Data from neutron diffraction, small angle neutron scattering, and inelastic and quasielastic neutron scattering experiments have been shown to be consistent with the three region model which contains highly porous walls. Since the X-ray data only gives structural information projected onto two dimensions, a second possible model for the MCM-41 material, consistent with the X-ray data has also been proposed. In this case the material could contain smooth-walled channels with high degree of tortuosity and connectivity, which give the two dimensional projection of differing density regions. This may approach a highly defective MCM-48 structure, however the resources available were not able to model this possible structure.

Finally, the MCM-41 material prepared in this work was used in a study of the behaviour of methane and hydrogen condensed into the channel system. The confinement in the silicate channels resulted in a raised temperature for the onset of rotational diffusion in methane, but a decreased temperature for the melting point transition compared to that of bulk methane. A persistent fluid in the pores at

temperatures up to 180 K shows also a smearing in the boiling point of the confined methane. Hydrogen was shown to exist in two sites within the MCM-41 channels. The proportion of molecules in each site was dependent upon filling. The more hindered site, which filled first was identified as a site adjacent to the silica wall, while the less hindered site, which filled at higher gas loadings corresponded to a site within the pore region.

The final conclusion for this work therefore, is that it is possible to create more highly ordered MCM-41 materials by means of pH control during synthesis. These materials show up to seven peaks in the X-ray diffraction pattern, enabling the construction of a detailed structural model. The two-dimensional projection of the wall structure contains two density regions in the silica, as well as a small central pore. The low overall wall densities indicate highly porous silica frameworks within these walls.