Template Induction of Supramolecular Structure: Synthesis and Characterisation of the Mesoporous Molecular Sieve, MCM-41.

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Amorphous silica - a radiolarian and a silica sphere.
Photograph by Roger Heady, EMU, ANU. (used with permission)

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Declaration

This dissertation is an account of research undertaken primarily in the Research School of Chemistry at the Australian National University, under the supervision of Professor John W. White. Additional experiments were performed at the ISIS Pulsed Neutron Source at the Rutherford Appleton Laboratory, Chilton, UK, the Intense Pulsed Neutron Source at Argonne National Laboratories, Illinios, USA, the Cold Neutron Research Facility at the National Institute of Standards and Technology, Washington D.C., USA and the Australian National Beamline Facility at the Photon Factory Synchrotron, Tsukuba, Japan.

All of the sample preparation required for this thesis was carried out by the candidate, except in cases where it was not possible for her to do so, in which case, detailed experimental instructions, written by the candidate, were supplied to those who carried out the work. Sample sets prepared in this fashion by Gordon Lockhart while the candidate was visiting overseas facilities for data collection purposes, are those listed in Appendix 1, Table A1.1, labelled GP, R, J, LOQ heated ordinary and LOQ heated acid. All characterisation and analysis, except where noted in the text and where indicated below, were also performed by the candidate. Gas adsorption isotherm data collection was performed by Gordon Lockhart and Dr Peter Branton, but all subsequent analysis was done by the candidate. Due to insufficient funding the overseas experiments listed below were carried out on the candidate's behalf as noted. For the shear experiments discussed in Chapter 4, section 4.3.3, one third of the data on the shear behaviour of silicate-surfactant gels was collected at the ISIS facility by Dr Philip Reynolds and Dr Tony Brown. Small angle neutron scattering contrast variation data on five samples total, on two separate occasions, was collected at the ISIS facility by Dr Jonathon Watson and Dr Tony Brown. All data processing and analysis in those cases was done by the candidate. Similarly, for the quasielastic neutron scattering experiments on hydrogen adsorbed in MCM-41 discussed in Chapter 6, section 6.7 carried out at the Argonne National Laboratories, data collection and initial data processing was carried out by Dr Philip Reynolds. For the quasielastic neutron scattering experiments on methane, Dr. Frans Trouw continued data collection and initial data reduction after the candidate returned to Australia, as funding was insufficient for her to remain to complete the experiment. Data collection and initial processing of the synchrotron X-ray patterns collected at the Australian National Beamline in Japan, were done by Dr David Cookson, and Wilfred Fullagar. All subsequent data processing was done by the candidate. All other data collection and analysis reported herein was done by the candidate. Other contributions to this work, by way of technical support and advice are acknowledged on the following pages.

None of the work presented in this thesis has been submitted to any other institution for any degree.

Karen J. Edler
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Abstract

The pure silicate mesoporous material, MCM-41 having hexagonally packed cylindrical channels with a centre to centre distance of *ca.* 45 Å may be synthesised from a preparation containing only sodium silicate solution, a surfactant template molecule, water, and some acid. The preparation was optimised initially both for heated and unheated syntheses. The effects of aging in the gel, heating time and stirring were investigated. MCM-41 materials which were stable to calcination were prepared in an ambient temperature synthesis, with stability proportional to aging time in the gel. Heated preparations proved to have highest long range order after 3 days at 100˚C in unstirred systems.

The effect of pH during synthesis was then investigated. Preparations titrated against 1 M acid to maintain a constant pH during the whole of the synthesis developed much higher long-range order, as determined by the number and intensity of the observed X-ray diffraction peaks. A small counterion effect, dependant upon the type of acid used was noted. The most highly ordered materials were prepared from preparations titrated with sulphuric acid to maintain a pH of 10 during the synthesis. Heated preparations were more ordered than those carried out at ambient temperatures, although the addition of acid also promoted order in unheated syntheses.

From these highly ordered materials X-ray diffraction patterns containing up to seven peaks were obtained using synchrotron radiation. These peaks could all be indexed to a hexagonal lattice. The intensity envelope for these peaks was modelled by the expected envelope for an array of cylinders. The data could not be fitted by a model containing only one cylinder, but required two concentric cylinders of different scattering length density. This indicates the presence of three regions in the MCM-41 framework. Firstly, a denser, continuous wall structure about 6 Å wide filling the regions between pores. Secondly, each pore is lined with a less dense silica region about 12 Å thick. The empty holes down the centre of each channel in this material have a radius of about 7 Å. The average bulk MCM-41 density calculated from the X-ray results and gas adsorption measurements was found to be low, around 0.83(5) g cm^{-3}, with the denser part of the wall being 0.99 g cm^{-3} and the less dense lining of the pores 0.87 g cm^{-3}.

This low density model with porous walls is supported by results from neutron diffraction, inelastic and quasielastic neutron scattering measurements on hydrogen adsorbed in the pores of MCM-41, and by small angle neutron scattering using contrast variation on MCM-41 materials at all stages of preparation. Other possible interpretations of the data are presented and discussed.

The behaviour of methane adsorbed in the channels of MCM-41 was also observed by quasielastic neutron scattering. Considerable alteration in the phase behaviour from that of bulk methane was observed. The melting point was depressed from 91 K in bulk methane to between 45 and 60 K for the confined methane in this system, and a liquid phase was still present in the pores at 180 K, around 70 K above the normal boiling point of the bulk material.

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Firstly, I wish to thank my supervisor, Professor John White for allowing me to work with him and his research group. His infectious enthusiasm, creativity and encouragement have made the last three years interesting and memorable. I also wish to acknowledge the invaluable co-supervisory role of Dr Philip Reynolds, whose down-to-earth advice provided an essential balance and who was always available for questions.

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The assistance of research scientists at overseas institutions must also be noted. The aid of Dr. Frans Trouw at IPNS in the collection and reduction of quasielastic neutron scattering data was deeply appreciated. Dr. Tania Slawecki at CNRF, NIST must be thanked for her enthusiasm, vegetarian cooking and all her help with the shear cell experiments on the NG-3SANS beamline. Dr. B. Hammouda is also thanked for assistance with those experiments. Dr. Richard Heenan and Dr. Steve King at ISIS, RAL gave willing and cheerful support for the small angle neutron scattering experiments on LOQ and Dr. P. Thiyagarajan did likewise for experiments at IPNS on SAD, the small angle neutron scattering machine at ANL.

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