Synthesis of direct templated aligned mesoporous silica coatings within capillaries

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Mesoporous liquid-crystal templated silica forms intact coatings with channels adopting a curious alignment, when synthesised within thin capillaries.

The design of tailor-made mesoporous structures, templated by assemblies of surfactant molecules, has attracted a great deal of interest from materials scientists and chemists alike. The synthesis and structural characterisation of one particular family of silica-based mesoporous materials, denoted M41S, is now well documented.[1,2] These materials are templated under alkaline conditions, at elevated temperatures, in the presence of cationic quaternary ammonium surfactants. Several other synthetic procedures employing different surfactant templates, silica precursors and/or reaction conditions to prepare similar mesoporous products, have been described in the literature.[3–6] Most of the synthetic procedures use low surfactant concentration regimes, and rely on a co-precipitation process whereby the surfactant micelles are trapped within the silica, providing a structure-directing environment for the mesostructured solid.

By contrast, in our work gels containing relatively high concentrations of a non-ionic polyoxyethylene surfactant are used as a ‘direct’ templating medium for the formation of hexagonal mesoporous silica. The synthetic method was first described by Attard *et al.*,[7] and is termed true liquid crystal templating (TLCT). Their calcined products, templated using octaethylene glycol monododecyl ether ($C_{12}EO_8$) consisted of hexagonal arrays of 28 Å diameter channels, as seen by transmission electron microscopy, with a *d*-spacing of 34 Å (seen by powder X-ray diffraction). The arrays of pores in the TLCT materials strongly resembled those seen for MCM-41, the hexagonal M41S analogue. N_2 BET adsorption measurements showed that the calcined mesoporous silica had a specific surface area of 1400 $m^2\ g^{-1}$. Our synthetic mixtures were closely analogous to those used by Attard *et al.*,[7] consisting of an *n*-alkyl, octaoxyethylene surfactant template in an acidic TLCT system with tetramethylorthosilicate (TMOS) as the silica precursor. Two different surfactants were used as templates: octaethylene glycol monododecyl ether ($C_{12}EO_8$) and octaethylene glycol monodecyl ether ($C_{10}EO_8$). The weight ratio of the components in both synthetic mixtures was 1 $C_nEO_8 : 1\ H_2O$ (pH 2) : 2.11 TMOS (n = 10 or 12), and the hydrolysis/polymerization reaction was carried out overnight under vacuum at room temperature. The mesoporous product obtained from these mixtures was transparent, with the same characteristic optical texture under the polarising microscope as previously observed by Attard *et al.*[7]

The synthesis of a single, monolithic mesoporous structure, containing aligned pores, is a particularly exciting goal. A material of this kind would have potential applications in nanoscale engineering, separation technology, microelectronics, biomaterials engineering and catalysis. In biological systems, control of hierarchical ordering in biomineralization processes is achieved by the use of organic templates and confinement by surfaces such as membranes. Various attempts at aligning MCM-41 type materials with a view to producing monoliths (monodomain samples) have been described in the literature; such work could lead to an extension of the applications of the powder-like products usually obtained.[8–11] The alignment of these mesoporous films relied on heterogeneous nucleation of the surfactant/inorganic precursor onto the aligning surface being favoured over precipitation (homogeneous nucleation) within the bulk solution.

To produce alignment of the TLCT material, we inserted the synthesis gel into a 0.5 mm (internal diameter) glass or quartz capillary by capillary action. The capillary was left with one end dipping into the synthesis gel and the assembly was placed under vacuum overnight, coating the inside walls of the capillary with birefringent mesoporous material which was stable to removal of the template by calcination at 500 °C. Polarising microscopy on the calcined quartz capillary gave similar optical textures to the as-synthesized material, with enhanced colours. A void in the centre of the capillary was clearly visible and the coating was continuous. No discernible difference between coatings on glass and quartz walls was observed, indicating that the precise atomic arrangement of the silica within the capillary walls does not influence the alignment.

Very well aligned six-spot patterns were systematically obtained by X-ray diffraction, employing an image intensified CCD-based X-ray detector of our own design,[12] when the beam was passed at right angles to the capillary axis through the top or bottom edges of the coated capillary before calcination. The orientation of the reciprocal lattice shows that in real space the channels are arranged on a hexagonal lattice, one face of which is parallel to the capillary wall [Fig. 1(*a*)]. After calcination these six-fold spots [corresponding to the (10) reflections] were more intense, and two higher orders [the (11) and the (20) reflections] of the hexagonal diffraction pattern became visible. This implies that calcination results in increased local ordering of the mesoporous product. Both the X-ray diffraction and the polarising microscopy results suggest that the channels of the as-synthesised and calcined products are arranged in rings, or a tight coil, as depicted in Fig. 1(*a*).

When the X-ray beam was passed through the capillary at positions marginally closer to its centre, the diagonal spots in the six-fold pattern spread into arcs, suggesting that the hexagonally packed channels twist and/or bend within their coiled arrangement, *cf.* Fig. 1(*b*). When the beam was passed centrally through the capillary, no diffraction spots were observed. The alignment experiment was found to be reproducible using both C_{10} and C_{12} POE surfactant systems. The *d*-spacings of the materials were 40 and 45 Å before calcination, and 35 and 38 Å after calcination, respectively, for the two chain lengths. The corresponding lattice parameters for the two templated materials were respectively 46 and 52 Å before calcination, and 40.5 and 44 Å after calcination.

For both as-synthesised and calcined products, a slight distortion away from hexagonal symmetry, presumably induced by the surface alignment interactions, was observed. A similar distortion has recently been observed for films of mesoporous silica aligned on mica and graphite surfaces.[9] The fact that the coating remained intact after calcination suggests that the channels in the coating must have outlets through which the organic phase can escape, without disturbing the structure. We

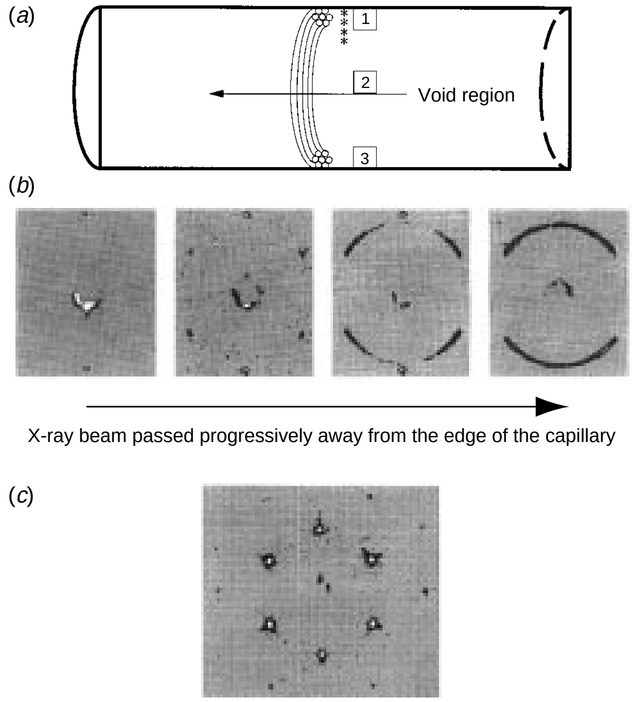

Fig. 1 (*a*) Schematic longitudinal section of a coated capillary showing hexagonally packed channels of mesoporous SiO_2/C_nEO_8 product lining the capillary walls (n = 10 or 12). Six-spot patterns were obtained when the X-ray beam was passed perpendicularly through the capillary at positions (1) and (3); no diffraction pattern was obtained when the X-ray beam was passed through the centre of the capillary (2). (*b*) Sequence of X-ray diffraction patterns obtained for the aligned $SiO_2/C_{10}EO_8$ composite coating when the X-ray beam crossed the capillary at positions shown by asterisks in (*a*). (*c*) Pattern obtained for the calcined sample when the X-ray beam was passed through the edge of the capillary.

propose that the channels are in fact spiralling in tight coils from one end of the coating to the other, with an outlet at either end, rather than consisting of individual closed rings.

When the alignment experiment was carried out using capillaries treated with phenyltrimethoxysilane (to render the surfaces hydrophobic), both polarising microscopy and X-ray diffraction suggest that the alignment of the product was severely disturbed. The nature of the supporting surface is therefore important for successful alignment. However, it should be noted that the alignment effect is not observed when the synthesis mixtures were spread in a thin layer on a flat piece of glass or quartz and allowed to react under vacuum, under identical conditions to those used for the capillary alignment experiments. This indicates that the alignment is predominantly due to confinement within the capillaries.

The kinetics of self-assembly were followed using *in situ* X-ray diffraction. The intensity of the X-ray diffraction *versus* time is plotted in Fig. 2 for one of the six spots of the aligned pattern (obtained when passing the beam through the edge of the capillary). An exposure was taken every five minutes over a period of 3 h, and a 'box integration' was made on the same area of each pattern (containing the diffraction spot) to obtain the intensity data. The data show that the self-assembly occurs over a period of about 15 min. Interestingly, there were no patterns other than the aligned six-fold spot pattern observable throughout the experiment, indicating the observed alignment to be both the kinetically and thermodynamically favoured arrangement.

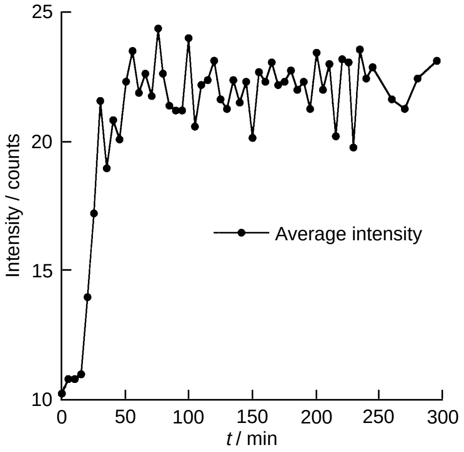

Fig. 2 Plot of average diffraction spot intensity *versus* time for an *in situ* X-ray diffraction experiment to probe the kinetics of the alignment process

In this work, TLCT has been found to be a suitable method for producing aligned mesoporous siliceous materials. The results obtained show that macroscopically aligned coatings can be made from TLCT systems, simply by confining the synthesis mixtures in a capillary. The coatings, which are systematically and reproducibly obtained, contain coils of aligned mesopores, lining the walls of the capillary. The aligned coatings of composite product are stable to calcination (removal of the organic template) at 500 °C. The kinetic investigations of the system show that there are no detectable intermediate structures between gel hydrolysis and the final aligned coating.

M. E. R. thanks the EPSRC for a studentship and T. M. thanks the EU for a TMR Fellowship. Helpful discussions with Professor C. R. A. Catlow are gratefully acknowledged.

Footnotes and References

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Received in Bath, UK, 3rd June 1997; 7/03964F