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Liquid Crystal Templating of Mesoporous Materials

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There is currently great interest in the use of lyotropic liquid crystals as templates for the production of mesoporous inorganic or metallic materials having uniform pore sizes in the range 20–100 Å or greater. Such materials have potential applications as catalysts, molecular sieves or electrodes, and can accommodate molecules which are too large to fit within the pores of conventional zeolites. We have investigated the structure and alignment of mesoporous materials produced using the True Liquid Crystal Templating (TLCT) method. In TLCT, the surfactant forms a lyotropic liquid crystal phase of well defined geometry and dimensions at the start of the synthesis. We have been able to produce hexagonal mesoporous coatings within capillaries, having a specific alignment of the 2-D hexagonal lattice, as probed by X-ray diffraction. We have also followed the structural kinetics of the alignment process. These TLCT mesoporous materials may be functionalized for catalytic applications.

Keywords: lyotropic liquid crystal; surfactant templating; mesoporous materials; X-ray diffraction; catalysis

MESOPOROUS MATERIALS AND TEMPLATING

Materials containing networks of uniform pores on the *mesoscopic* length scale (nanometre to micron) have many potential applications in diverse areas such as catalysis, separation technology, biomimetic structures and environmental remediation. Conventional zeolites are *microporous*, that is the pore diameter is restricted to less than approximately 12 Å, and there is therefore a restriction on the size of molecule which can enter the pores, ruling out many macromolecules, proteins, etc. Mesoporous materials on the other hand, where the pore

size can reach hundreds of ångströms, have no such restriction. Unlike conventional zeolites, which are fully crystalline materials, mesoporous materials such as silicates or alumino-silicates are generally amorphous.

The breakthrough in producing such materials came in 1992 when Beck, Kresge and co-workers mixed low concentrations of cationic surfactant template with an alkaline solution of a colloidal silica precursor, leading to formation of translationally-ordered composite organic / inorganic phases [1,2]. Subsequent calcination removed the organic material, leaving mesoporous silica containing 2-D or 3-D periodic lattices of pores, the family of materials being termed M41S. The process was termed "liquid crystal templating" since it was believed to involve formation of a liquid crystal phase by the cationic surfactant / silicate anion mixture during the condensation and polymerisation of the silica. X-ray powder patterns of MCM-41 (2-D hexagonal) and MCM-48 (cubic, spacegroup Ia3d) showed very similar X-ray patterns to those from the corresponding liquid crystal phases of the pure surfactant in water. The fact that sharp low-angle reflections were observed indicated a well-defined periodicity in the structure; the observation of a diffuse peak in the wide-angle region indicated that the local packing was amorphous, not crystalline.

The early work in this area already demonstrated how control of pore diameter (15 - 100 Å) and wall thickness (13 - 27 Å) could be achieved by varying the surfactant chainlength, by addition of organic solvents such as mesitylene (1,3,5-trimethylbenzene) or *n*-alkanes, or by variation of synthesis temperature (70 - 200 °C) and/or reaction time (up to one week). Subsequent work showed that alkoxysilanes such as TMOS (teramethoxysilane) could be used as the silica precursors and that nonionic surfactants such as polyoxyethylene surfactants could serve as the template [3].

The above approaches were all based upon a dilute solution regime, where the surfactant on its own would not form a liquid crystal phase. It could clearly be advantageous if the synthesis were carried out actually within a liquid crystal phase. This "true liquid crystal templating" (TLCT) approach was introduced by Attard and co-workers [4]. They used the nonionic polyoxyethylene surfactant $C_{12}EO_8$ (see Figure 1), with TMOS as the silica precursor. The components were mixed in mildly acidic solution conditions at a concentration so as to form the desired liquid crystal phase. The TMOS hydrolysed and polymerised within the liquid crystal phase to form the mesoporous silica product. The advantage of this approach is that it

should allow the symmetry and structure of the mesoporous product to be predicted from the known surfactant phase diagram (which is liable to be altered by the reaction conditions), and it may allow the formation of mesoporous monoliths or even monodomains.

The explosive growth in the last seven years in the area of liquid crystal templating has already been reviewed a number of times [5-18].

NONIONIC SURFACTANT TEMPLATING

We have investigated the possible use of a range of nonionic surfactants for TLCT (true liquid crystal templating) of mesoporous materials. The compounds we chose to study initially, shown in Figure 1, were the alkyl glucosides and the polyoxyethylene surfactants (denoted C_nEO_m, where n is the number of carbon atoms in the hydrophobic alkyl chain, and m is the number of oxyethylene groups in the polar headgroup).

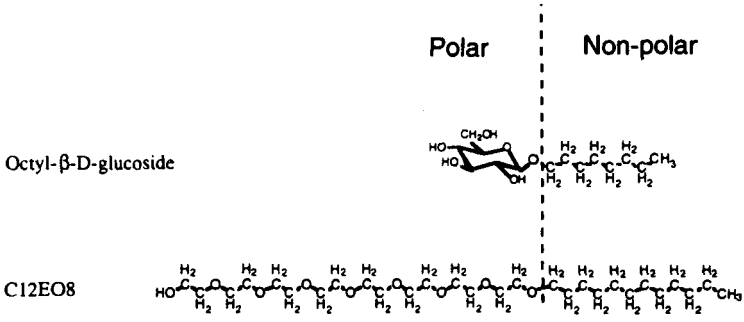

FIGURE 1 Alkyl glucosides and polyoxyethylene surfactants.

We have previously determined phase diagrams for a range of alkyl glucosides [19, 20], and phase diagrams have been published for many of the polyoxyethylene surfactants [21]. These nonionic surfactants form various type I (oil-in-water) fluid lyotropic phases, such as the L_α lamellar phase, the 2-D hexagonal H_1 phase, and the type I bicontinuous cubic phase Ia3d (also known as the gyroid cubic phase). Certain of the

C_nEO_m surfactants also exhibit micellar cubic phases. These latter phases are based upon discontinuous packings of micelles, and tend to form when the system requires greater interfacial mean curvature than can be attained in the hexagonal H_1 phase. So far three different cubic packings, of spacegroups Pm3n, Fm3m and Im3m have been observed [22]. It has recently been found for $C_{12}EO_8$ that the mesophase region adjacent to the micellar solution actually contains both a micellar cubic phase, of spacegroup Pm3n, and a 3-D hexagonal micellar phase, of spacegroup $P6_3/mmc$ [23].

A particularly attractive feature, from the templating viewpoint, of these two nonionic surfactant systems is that they tend to spontaneously form large monodomain samples [19, 22, 24]. This could clearly be advantageous in the production of mesoporous monoliths.

Our initial attempts at templating mesoporous silica using alkyl glucosides were largely unsuccessful, for a number of technical reasons, and so we focussed our efforts on the polyoxyethylene surfactants as templates. For these experiments we followed essentially the TLCT procedure previously described [4], mixing together 0.05 g of C_nEO_m, 50 µl of 0.01 M HCl, and 105.5 µl of TMOS.

Methanol is evolved during the reaction:

$$Si(OCH_3)_4 + 2\,H_2O \;\dashrightarrow\; SiO_2 + 4\,CH_3OH$$

and was removed by applying a light vacuum; the liquid-crystalline phase was first destroyed by the methanol, but then reforms and sets to a mesoporous gel. The gel was then calcined to remove residual water, methanol and surfactant, using the following program:

1. Heat from 25 °C - 550 °C at 5 °C / min (under nitrogen flow);
2. Leave 1 hr at 550 °C (under nitrogen flow);
3. Leave a further 8 hr at 550 °C (under oxygen flow);
4. Cool back to 25 °C at 10 °C / min (under oxygen flow).

We carried out phase identification and determination of phase structure of the templated materials using X-ray diffraction and transmission electron microscopy. We found that we were able to successfully

template 2-D hexagonal mesoporous silica using a wide range of C_nEO_m surfactants. The optical textures of these transparent templated materials were very similar to those of lyotropic liquid crystalline hexagonal phases. The lattice parameters were determined by X-ray diffraction for both the as-synthesized gels, and the calcined materials. They were found to depend as expected upon both *n* and *m* in a more-or-less consistent way, as shown in Table 1.

Surfactant	a / Å (as-synthesized)	a / Å (calcined)
$C_{16}EO_4$	52.5	45.4
$C_{12}EO_5$	45.4	40.1
$C_{12}EO_6$	47.3	41.0
$C_{14}EO_6$	51.8	44.2
$C_{16}EO_6$	55.2	47.3
$C_{18}EO_6$	57.4	49.0
$C_{10}EO_8$	46.2	40.4
$C_{12}EO_8$	52.0	43.9
$C_{16}EO_8$	57.4	49.0
$C_{12}EO_{12}$	53.2	50.1

TABLE 1 Lattice parameters of hexagonal mesoporous silica templated using a range of polyoxyethylene surfactants.

After calcination, there was a 5 – 15% shrinkage of the lattice parameters. This occured without any disordering of the hexagonal packing of the pores; on the contrary, the ordering tended to increase, as shown by an increase in the number of low-angle Bragg peaks typically observed [25].

Transmission electron microscopy (data not shown) of the calcined material showed sub-micron domains within which the cylinders were regularly stacked in parallel straight lines across the domain (the usual orientation of the cylinders was lying in the plane of the microscope grid).

Nitrogen adsorption BET measurements yielded type IV isotherms, typically (for $C_{12}EO_8$) giving a surface area of 1,033 $m^2\ g^{-1}$; BJH (Barrett-Joyner-Halenda) analysis gave a (desorption) pore diameter of 24.3 Å.

ALIGNMENT OF TEMPLATED MESOPOROUS SILICA

A number of recent attempts have been made within the dilute synthesis regime to produce aligned films of 2-D hexagonal mesoporous silica [26-28]. Growth on mica led to an alignment of the cylinders in the plane of the mica surface, but the direction of the cylinders tended to meander on the surface. On a graphite substrate, the cylinders again lay in the plane, but were straight and were aligned along one of the three symmetry axes of the underlying graphite lattice. On an amorphous silica substrate, however, the cylinders appeared to point out of the plane of the surface, towards the solution. Some degree of alignment was also induced when films were grown at the air-water interface [29] or at the oil-water interface in an emulsion system [30]. Further approaches to producing alignment have involved the use of shear [31, 32], electric fields [33] or magnetic fields [34, 35].

The problem with aligning hexagonal mesoporous films on a substrate is that the mesopores tend to lie parallal to the surface of the substrate. This means that access from the bulk solution into the pores and across the film is severely restricted, and limits the potential usefulness in separation and sensor applications. In principle bicontinuous cubic mesoporous materials should not have this restriction and should be more suitable. However, the most promising result so far has employed a 3-D hexagonal (spacegroup $P6_3/mmc$) mesoporous material templated using a double-headed surfactant [36]. This result is surprising, because the lyotropic surfactant phase of this spacegroup is based upon a 3-D hexagonal packing of discrete micelles, and would be expected to yield a closed-cell silica foam, rather than a mesoporous material.

We have explored a number of approaches to induce alignment of mesoporous silica produced by the TLCT approach. For example, we tried using directionally-rubbed, polyimide-coated 10 μm liquid crystal display cells. The cell was first confirmed to produce the expected alignment of a low molar mass liquid crystal sample (8-OCB,

octyloxycyanobiphenyl). However, it was found not to produce a specific alignment of the surfactant hexagonal phase. Confining 50 wt% $C_{10}EO_8$ / 0.01 M HCl between mica plates was found to produce considerable alignment of the H_I phase, as indicated by a striated optical texture between crossed polarizers. However, when the synthesis gel was confined, although some alignment of the mesoporous material was observed, the results were not reproducible. The most successful way of producing alignment was found to be to introduce the synthesis mixture into 0.5 mm quartz capillaries by capillary action, and allow the hydrolysis / polymerisation reaction to proceed in the confined environment. This led to a highly reproducible alignment, which was preserved after calcination [25]. Passing the X-ray beam through the edge of the capillary, with the capillary axis perpendicular to the beam, yielded a six-spot low-angle diffraction pattern, whose alignment showed that the hexagonal lattice lies with the face of the hexagon parallel to the wall of the capillary, and with the cylinders spiralling around the capillary axis. A slight distortion of the hexagonal lattice was observed, presumably due to interaction with the wall of the capillary.

The kinetics of phase formation and alignment was followed by carrying out an *in-situ* X-ray diffraction experiment, monitoring the intensity of one of the six primary low-angle X-ray peaks as a function of time. It was found that the self-assembly of the mesoporous gel occurs over a 15 minute time interval, and that the aligned hexagonal phase forms directly, without any intermediate structures / alignments occurring.

INCORPORATION OF CATALYTIC SITES

A number of attempts have been made to functionalize mesoporous materials synthesised in the dilute regime by the incorporation of catalytic sites. Transition metals such as titanium, platinum, vanadium, etc. can be incorporated into the mesoporous silica framework, or grafted onto the walls of the mesopores (see various references in [18]).

We have demonstrated that titanium catalytic sites can be introduced into TLCT mesoporous silica by a "one-pot" method [37]. The titanium precursor was dissolved either in the aqueous region (titanium acetyl acetonate) or the hydrophobic region (titanocene dichloride) of the surfactant H_I phase of $C_{12}EO_8$. The calcined

hexagonal mesoporous material had a pore diameter (from nitrogen adsorption measurements) of 25 Å. The titanocene-based material was found to be catalytically-active in the epoxidation of octene (84 mol epoxide per mol Ti per hour, at 80 °C using *tert*-butylhydroperoxide as the source of oxygen). The nature of the catalytic sites was probed by uv-vis diffuse reflectance spectroscopy. The observation of an intense maximum absorbance, centred at 220 nm, indicated the presence of isolated tetrahedral Ti(IV) sites. The accessibility of these sites to external gaseous probe molecules was checked by carrying out photoluminescence measurements, and it was found that a partial quenching of the photoemmission signal was induced by 0.3 bar oxygen.

A novel approach for direct incorporation of metals into mesoporous structures is to use surfactant templates with organometallic complex headgroups [38, 39]. We have been investigating the use of the TLCT approach for the direct incorporation of ruthenium catalytic sites into mesoporous silica [H. B. Jervis, M. E. Raimondi, R. Rajad, T. Maschmeyer, J. M. Seddon and D. W. Bruce, unpublished observations]. A surfactant ruthenium complex was used both as the template, and as the source of catalytically-active ruthenium sites in the mesoporous silica. The calcined mesoporous material was found to selectively catalyse the hydrogenation of 1-hexene to *n*-hexane.

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