Supplementary material (ESI) for Journal of Materials Chemistry

This journal is © The Royal Society of Chemistry 2008

Electronic Supplementary Information

A Systematic Study of the Formation of Mesostructured Silica using Surfactant Ruthenium Complexes in High- and Low-Concentration Regimes

Katherine E. Amos[a], Nicholas J. Brooks[b], Nicola C. King[†a], Songhai Xie[c], Jesús Canales-Vázquez[c], Mark J. Danks[a], Helen B. Jervis[a], Wuzong Zhou[c], John M. Seddon[b]* and Duncan W. Bruce[d]*

a *Department of Chemistry, University of Exeter, Stocker Road, EXETER EX4 4QD, UK*

b *Department of Chemistry, Imperial College London, South Kensington, LONDON SW7 2AZ, UK (Email: j.seddon@imperial.ac.uk)*

c *School of Chemistry, University of St Andrews, ST ANDREWS, KY16 9ST, UK*

d *Department of Chemistry, University of York, Heslington, YORK, YO10 5DD, UK (Email: db519@york.ac.uk)*

[†] Present address: School of Biosciences,Geoffrey Pope Building, University of Exeter, Stocker Road, Exeter, UK, EX4 4QD.

CTAB templated silica

Mesoporous silicates were prepared using cetyltrimethylammonium bromide (CTAB) as a template, following a procedure identical to that used for the TLCT of ruthenium-based surfactants. Thus, at 50 wt% of surfactant to water and at 40 °C, CTAB forms a hexagonal H_1 mesophase (**Figure S1**) which then acts as a template to fabricated mesostructured silica. LCT was also carried out by a method directly analogous to that used in the ruthenium systems. The silicates so produced were then subjected to a variety of template-removal procedures similar to those used for the ruthenium-based analogues.

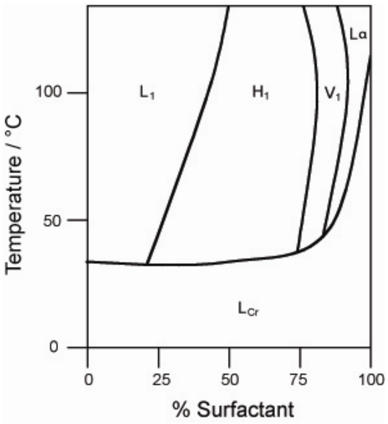


Figure S1 Binary phase diagram of CTAB in water[1]

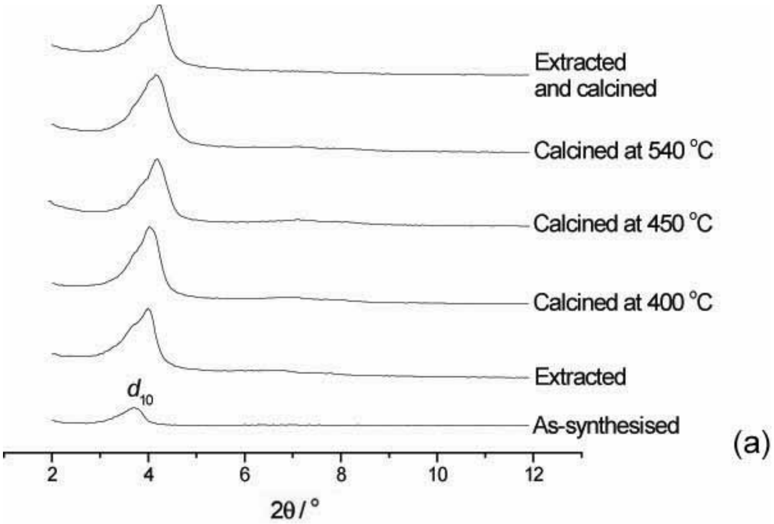
The X-ray diffraction patterns for these materials are collected in Figure S2, where it can be seen that a higher calcination temperature was required for complete removal of the template (540 °C), as indicated by previous work.[2]

The patterns for the TLCT samples exhibit the same traits as their ruthenium-templated analogues with the reflections of the as-synthesised sample being the least intense; the materials also exhibit a significant contraction in their lattice parameters as exemplified by decreasing values of d_{10}. The X-ray data do not allow the silicate to be identified as hexagonal, but by analogy with all other work on TLCT systems, we are confident this is so as we templated on a pre-formed H_1 mesophase, and because the as-synthesised material showed a birefringent texture, characteristic of a hexagonal H_1 mesophase.

The CTAB-templated materials also exhibited a large degree of lattice contraction when extracted prior to calcination, due to the absence of template to act as a scaffold during calcination (Table S1).

The most evident difference in the X-ray patterns of the LCT materials is the shoulder found to low angle of the d_{10} reflection of the hexagonal lattice, for which we believe there to be two possible explanations. The first is that there are two, incommensurate hexagonal pore structures. The nature of low concentration templating is such that the mesophase that forms arises from the alkylammonium salt of a condensing polyoxosilicate that forms during the reaction. It is likely that there is a dispersity in the size of these large anions, which could lead to mesophases of different dimensions around which the silicate eventually forms. The second possibility is that there are, in co-existence, both a H_I and a *Pm3n* cubic arrangement. There is literature evidence for an epitaxial transformation from cubic to hexagonal phases on drying,[3] the d_{211} reflection of the cubic lattice being coincident with the d_{10} reflection of the hexagonal system (the reflection to lower angle is the d_{210} of the cubic system). Others have reported a similar phenomena whereby the initial synthesis gel consists of a cubic mesostructure, again *Pm3n*, which transforms to hexagonal over time; the transformation being monitored *via* a number of *in situ* techniques.[4]

Beyond this difference, the more intense reflections of the calcined samples compared with the as-synthesised material are seen again, although it is interesting to note that in these systems, apparently the best developed hexagonal morphology was present in the extracted material prior to calcination.



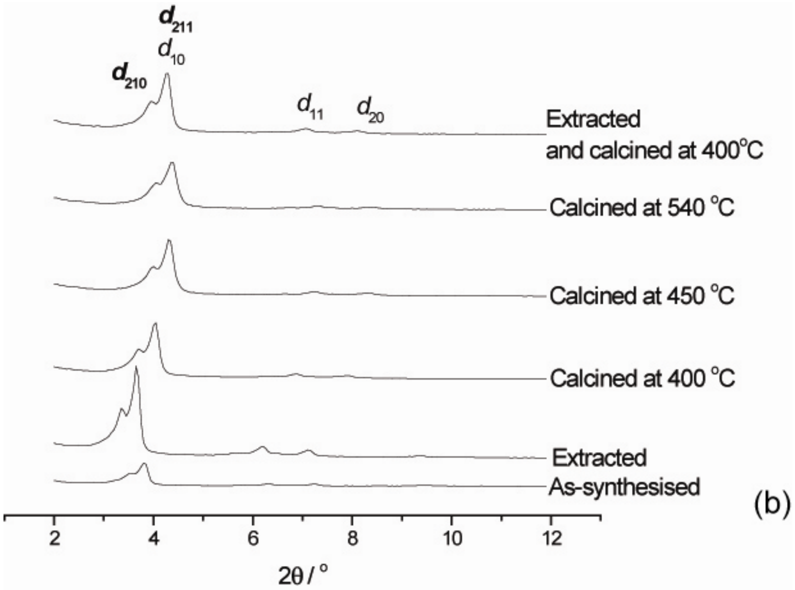
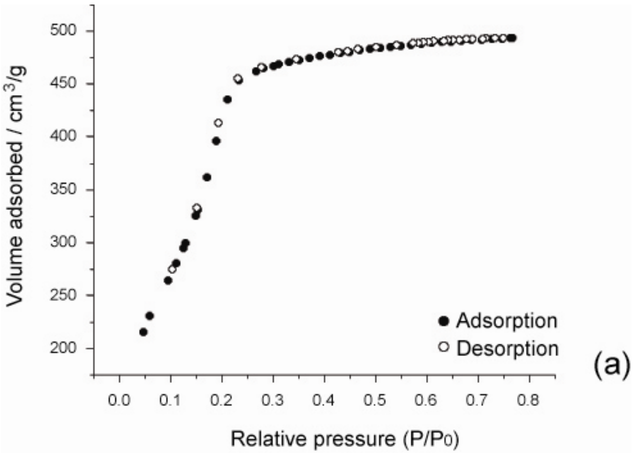


Figure S2 X-Ray diffraction patterns of silicates prepared (a) by TLCT on the H_1 phase of CTAB and (b) using an LCT approach

All of the above materials exhibited Type IV isotherms, characteristic of mesoporosity; Figure S3 shows a typical isotherm for each system and it can be seen clearly that there is no hysteresis loop and a sharp inflection in the curve, indicating narrow pore distribution and a uniform pore structure. Pore sizes calculated from the desorption curve using the BJH method,[5] are in the range of 22.3 to 26.2 Å depending upon the method employed to remove the surfactant template. A full set of data is presented in Table S1, where it can be seen that the materials have very high surface areas (>1000 $m^2\ g^{-1}$) and thick pore walls, although the surface areas are systematically higher in the TLCT materials. It is also noteworthy that the surface area for the LCT material calcined at 400 °C is very low and indicates incomplete removal of the template. We believe that these data reflect the larger domain size obtained under TLCT (it is prepared as a monolith) where the pores are generally more accessible.



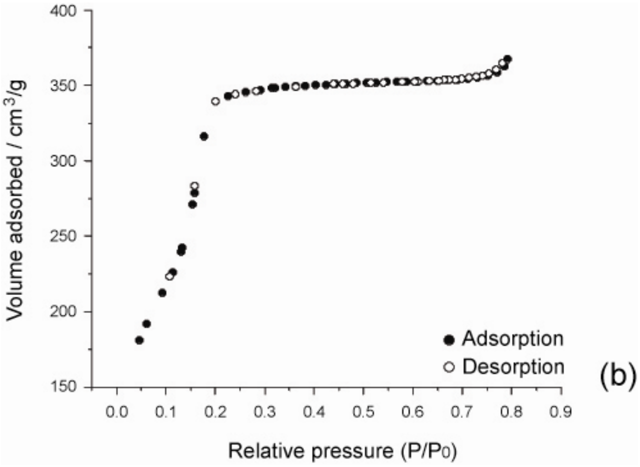


Figure S3 BET isotherm detailing the sorption behaviour of N_2 on (a) a TLCT-templated and (b) an LCT-templated silicate

Table S1 Results combining BET and XRD data for TLCT-CTAB silica

Conditions	d_{10}/Å	a/Å	BET surface area / m2 g^{-1}	Average pore diameter/ Å	Average wall thickness/ Å	Pore volume /cm3 g^{-1}
TLCT						
As-synthesised	35.5	41.1	–	–	–	–
Calcined at 400 °C	32.5	37.5	1456	25.6	11.9	0.99
Calcined at 450 °C	31.6	36.5	1390	24.8	11.7	0.84
Calcined at 540 °C	31.7	36.6	1342	22.3	14.3	0.58
Extracted with methanol	33.3	38.5	1418	23.6	14.9	0.91
Extracted and calcined (400 °C)	30.9	35.7	1400	22.3	13.4	0.57
LCT						
As-synthesised	34.6	39.9	–	–	–	–
Calcined at 400 °C	32.5	37.5	598	26.2	11.3	0.40
Calcined at 450 °C	30.9	35.7	1048	24.9	10.8	0.63
Calcined at 540 °C	30.6	35.3	1222	24.2	11.1	0.72
Extracted with methanol	36.0	41.6	1089	24.8	16.8	0.97
Extracted and calcined (400 °C)	30.9	35.7	1163	24.6	11.1	0.83

^{29}Si{^{1}H} MAS-NMR spectra (Figure S4) were largely identical in their general nature when compared with those of the ruthenium systems, namely that calcined materials showed exclusively Q^3 and Q^4 signals due to the degree of condensation, although there was appreciably more Q^2 in the as-synthesised materials obtained using CTAB.

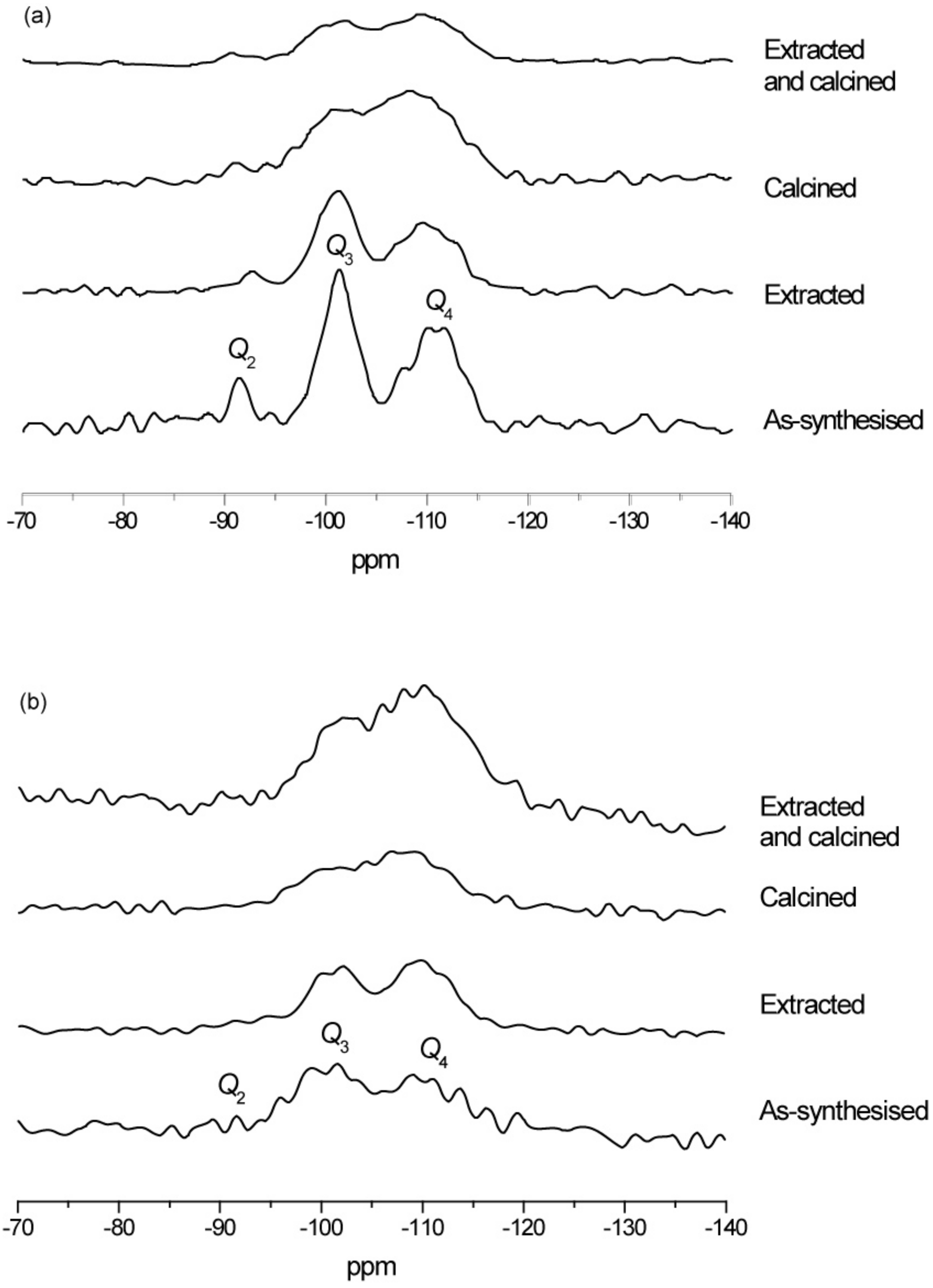


Figure S4 29Si MAS-NMR spectra recorded for (a) TLCT and (b) LCT silica formed using CTAB as the structure directing surfactant

TEM images obtained for these materials (Figure S5) reveal details of their mesostructure and also provide evidence to resolve the origin of the two, low-angle reflections in the X-ray pattern. Thus, the micrographs display areas of both hexagonal (Figure S5a) and cubic (Figure S5b) pore morphology and so suggest that the origin of the lower-angle reflection belongs in the cubic material found by electron microscopy.

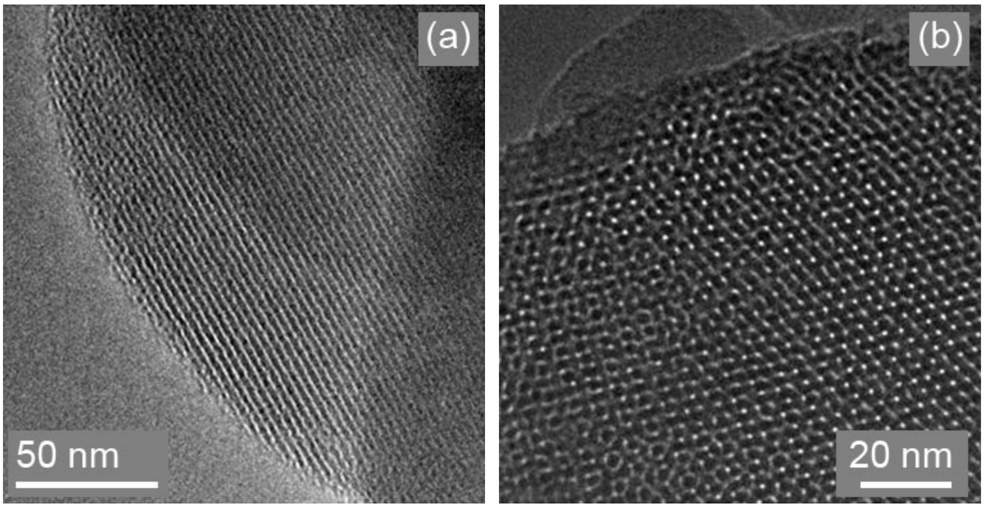


Figure S5 TEM images of silica templated at a low concentration of CTAB (LCT)

This journal is © The Royal Society of Chemistry 2008

Supplementary TEM image

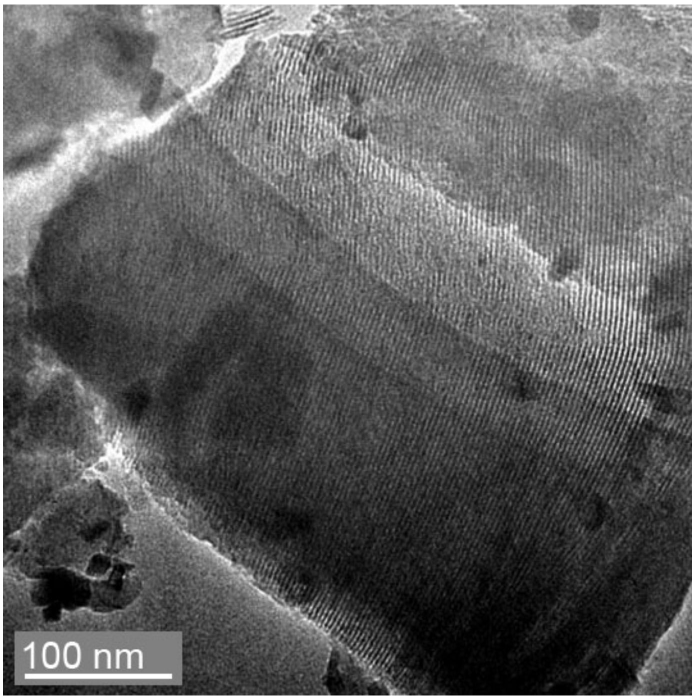


Figure S6 Micrograph illustrating the long persistence length of TLCT mesopores

Supplementary References

1. T. Warnheim and A. Jonsson, *J. Colloid Interface Sci.*, 1988, **125**, 627-633.
2. C. M. Bambrough, The Open University, 1998.
3. M. C. Liu, H. S. Sheu and S. F. Cheng, *Chem. Commun.*, 2002, 2854-2855.
4. S. N. Che, S. Kamiya, O. Terasaki and T. Tatsumi, *J. Am. Chem. Soc.*, 2001, **123**, 12089-12090.
5. E. P. Barrett, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, 1951, **73**, 373-380.