Modification of [M]-MSU-X mesoporous silicate pore morphology by post-synthesis treatment

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[M]-MSU-X mesoporous silicates prepared from selected low concentration non-ionic polyethylene oxide surfactants have been subjected to post synthesis hydrothermal treatment which significantly modifies the pore morphologies forming stable hexagonal or lamellar structures through an internal dissolution-redirection mechanism.

The development of synthetic methods to improved templated mesostructured materials[1–3] for catalytic and molecular sieving applications is attracting considerable attention. The search for inexpensive and environmentally benign routes to specialised materials and fine chemicals is also an area of considerable scientific and technological interest. Recent work has shown that mesostructured silica,[4] metallo-silicates[5] and alumina[6] may be templated by inexpensive and non-toxic non-ionic polyethylene oxide (PEO) and tri-block co-polymer surfactants under near ambient reaction conditions.[4]

The pore architectures of these so-called MSU-X molecular sieve materials were described as three-dimensional interconnecting networks of 'worm-like' channels.[7,8] Hexagonal mesoporous silicas have previously been reported[9,10] from very high alkyl-PEO surfactant concentrations (50 wt%) and strongly acidic reaction media. Here we describe an improved yet very simple, inexpensive and environmentally benign synthesis route to [M]-MSU-X mesoporous silicates that exhibit worm-like, hexagonal and lamellar pore architectures. A possible mechanism for the pore rearrangement is briefly discussed.

[M]-MSU-X mesostructures have been prepared from selected members of the Brij® series of commercially available alkyl-PEO surfactants. These materials have been found to consistently exhibit greater lattice regularity than any of the Tergitol 15-S®, Triton® or Pluronic® series of surfactants that have been previously employed at low surfactant concentration (Fig. 1).[4–6,7] If any [M]-MSU-1 material with worm-like pore morphology was dried and treated in water at 373 K under autogenous pressure for approximately 72 h its pore symmetry became significantly reordered and thermally induced lattice contraction upon calcination became almost negligible. Only when high regularity [M]-MSU-1 materials prepared from the Brij® series of surfactants were treated however, were lamellar and hexagonally symmetric structures observed.

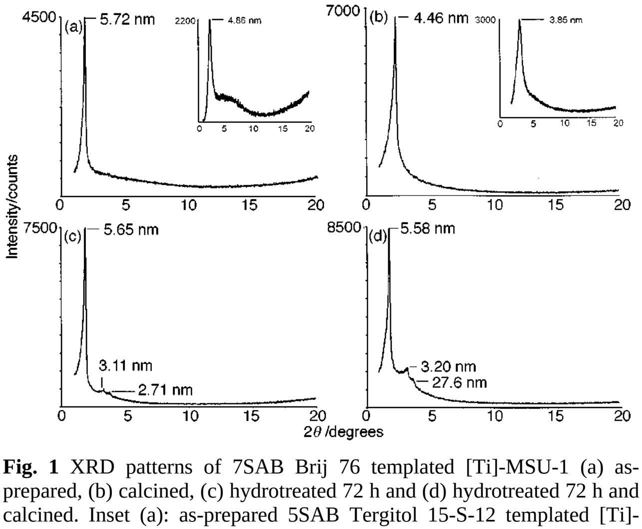

Fig. 1 XRD patterns of 7SAB Brij 76 templated [Ti]-MSU-1 (a) as-prepared, (b) calcined, (c) hydrotreated 72 h and (d) hydrotreated 72 h and calcined. Inset (a): as-prepared 5SAB Tergitol 15-S-12 templated [Ti]-MSU-1, (b) calcined 5SAB-C. (λ = 0.179026 nm.)

[Si]-, [Al]-, [Zr]- and [Ti]-MSU-1 silicates were prepared according to a method previously reported utilising the $N^0(N^+)X^-I^+$ assembly route.[5] Reordered [M]-MSU-1 materials were then prepared by treating the dried samples in distilled water (1 g sample per 30 mL water) at 100 °C in a sealed container for predetermined times.[11] The samples were recovered, dried in air and, in this instance, calcined at 600 °C for 4 h to remove the template. A Tergitol 15-S-12 templated [Ti]-MSU-1 sample is labeled 5SAB and a Brij 76 templated [Ti]-MSU-1 sample is labeled 7SAB, with suffixes HT-3 for 72 h hydrothermal treatment and C for calcination.

Low-angle powder X-ray diffraction (XRD) analyses (Fig. 1) show the single and multiple reflection patterns of [Ti]-MSU-1 samples in the as-prepared, hydrothermally treated and calcined forms. The as-prepared samples [Fig. 1(a)] exhibit intense first-order d_{100} reflections indicative of mesostructures possessing non-ordered worm-like pore structures with no long-range symmetry. It is however, immediately apparent from comparison of the peak widths and intensities, that the relations between structural repeat units are considerably more regular in the Brij 76 templated sample (Fig. 1) than in the Tergitol 15-S-12 templated sample (Fig. 1 inset). Calcination produced lattice contractions in the order of 20% and intensity increases of the d_{100} reflections that have been previously well documented.[1–10] Hydrothermal treatment of the as-prepared 7SAB sample for 72 h however, results in the appearance of two additional reflections [Fig. 1(c)]. The d spacings are not simple multiples, which would be expected for a lamellar system so are therefore probably best described by a hexagonal symmetry or at the very least, to pore symmetry similar to that observed for hexagonal MCM-41 type materials.[1,2] The appearance of additional XRD reflections were not observed for materials prepared from other non-ionic surfactant templates, such as Tergitol 15-S-12, although there is evidence for improvement in the pore ordering of all [M]-MSU-X materials.[12]

An important consequence of the hydro-treatment is that calcination of the treated samples results in negligible lattice contractions. This result indicates that the hydro-treatment causes hydrolysis and condensation of the silicate structure beyond that caused during the initial formation reaction.

Nitrogen adsorption isotherms of the various samples reflect important differences between [M]-MSU-X mesostructures prepared with Brij® surfactants, over other surfactants, and hydrothermally treated samples. The isotherm of 7SAB-C is characteristic of a material with pore diameter in the small mesoporous region exhibiting a shallow step with a definite point of inflexion at P/P_0 = 0.25 and no hysteresis of the desorption branch. Samples prepared with other PEO surfactants (*e.g.* 5SAB-C) generally exhibit no point of inflexion in the same region, indicating slightly smaller pore diameters

Table 1 Textural properties of worm-like and hexagonally symmetric[Ti]-MSU-1 mesoporous metallo-silicates

[Ti]-MSU-1 sample	d_{100} lattice spacing[a]/ nm	Lattice contraction[b] (%)	BET surface area[c]/ $m^2 g^{-1}$	Pore diameter[d]/nm	Pore volume[e]/ $cm^3 g^{-1}$	Wall thickness[f,g]/nm
5SAB	4.85					
5SAB-C	3.85	21	800	1.8[h]	0.35	2.0
5SAB-HT-3	4.55					
5SAB-HT-3C	4.50	0.7	970	2.4[i]	0.70	2.1
7SAB	5.70					
7SAB-C	4.45	22	920	2.2[a]	0.50	2.3
7SAB-HT-3	5.65					
7SAB-HT-3C	5.60	1.2	970	3.6[b]	1.10	2.0

[a] ±0.05 nm. [b] ±0.1%. [c] 10 $m^2 g^{-1}$. [d] ±0.5 nm. [e] ±0.05 $cm^3 g^{-1}$. [f] ±0.5 nm. [g] Wall thicknesses calculated by subtracting pore diameter from d_{100} lattice spacing value assuming that the d_{100} value is equivalent to the distance between adjacent pore centres. [h] Average pore diameter calculated from adsorption isotherm using HK model for cylindrical pores. This model tends to over-estimate pore diameters if pores are above 2.0 nm diameter. [i] Average pore diameter calculated from adsorption isotherm using BJH model for cylindrical pores. This model tends to under-estimate pore diameters.

(Table 1).[7] After hydrothermal treatment the shallow step is replaced by a well defined, high volume step in the upper capillary condensation region of the isotherm (P/P_0 = 0.55) indicative of well defined mesopores. Some hysteresis of the desorption branch becomes evident which may be a result of necking of the pores but is also possibly a consequence of the high adsorption partial pressure given that hysteresis is generally observed in mesostructured materials where the adsorption step is above P/P_0 = 0.45.

Selected area transmission electron micrograph (TEM) of the as-prepared materials (not presented) display the worm-like pore architecture previously reported for MSU-X materials.[4] Fig. 2 suggests that as a result of the hydrothermal treatment, the worm-like pore morphology has largely been replaced by a structure exhibiting ordering in two dimensions. In the present image the most obvious new feature appears as a lamellar phase coincident with the preexisting worm-like structure. When this evidence is combined with XRD data and the fact that the samples are calcined it seems reasonable to conclude that regular pores exist both parallel and perpendicular to the electron beam and that areas of hexagonal symmetry are being observed.

We suggest that hydrothermal treatment of templated silicate mesostructures causes structural modification through a dissolution/reprecipitation mechanism. Initially a diffuse inner layer of silica at the pore/template interphase, as invoked by Edler and White,[13] dissolves at the elevated temperature of the treatment. This dissolved silica reaches supersaturation within the interphase and then reprecipitates into a more dense phase on the pore wall. Only when the template is retained within the pore void can this dissolved silica be redirected to form on the pore walls. Such behaviour is observed for S^+I^- MCM-41 materials[11,13] but not for $S^+X^-I^+$ nor $S^\circ I^\circ$ templating.[12] It is by no means obvious that it would be observed in $N^+X^-I^0$ or N^0 I^0 templated systems.

The data presented here however show definite beneficial effects of hydrothermal treatment on the non-ionically templated silicate systems. The exact mechanism whereby the worm-like pore morphology transforms into the more regular arrangement is currently under investigation. We are also currently investigating possible improvements in the molecular sieving and catalytic properties of the modified samples over regular MSU-X materials in the isomerisation of terpene substrates.

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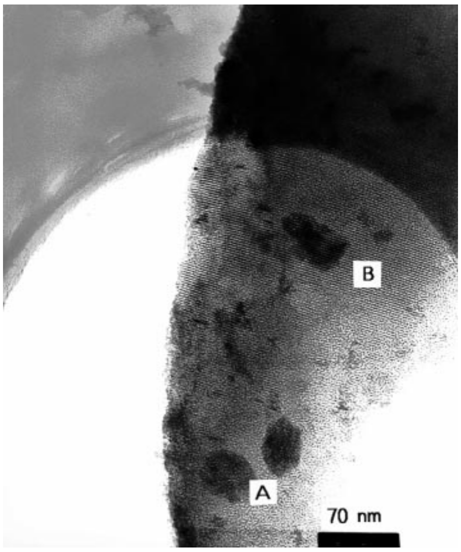

Fig. 2 Representative transmission electron micrograph of sample 7SAB-HT-3C displaying areas of (A) worm-like and (B) and hexagonal/lamellar symmetries.

Notes and references

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 G. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth and G. D. Stucky, *Nature*, 1994, **368**, 317.
3 P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 865.
4 S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242.
5 S. A. Bagshaw, T. Kemmitt and N. B. Milestone, *Microporous Mesoporous Mater.*, 1998, **22**, 419.
6 S. A. Bagshaw and T. J. Pinnavaia, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1102.
7 E. Prouzet and T. J. Pinnavaia, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 516.
8 R. Richer and L. Mercier, *Chem. Commun.*, 1998, 1775.
9 G. S. Attard, J. C. Glyde and C. S. Gottner, *Nature*, 1995, **378**, 366.
10 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Freidrikson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
11 Q. Huo, D. I. Margolese and G. D. Stucky, *Chem. Mater.*, 1996, **8**, 1147.
12 S. A. Bagshaw, *Stud. Surf. Sci. Catal.*, 1998, **117**, 381.
13 K. J. Edler, P. A. Reynolds, J. W. White and D. Cookson, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 199.

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