Bimodal pore systems in non-ionically templated [Si]-MSU-X mesoporous silica through biomimetic synthesis in weakly ionic solutions

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Non-ionically templated [Si]-MSU-1 mesoporous silicas have been prepared in weakly ionic sodium salt solutions from a non-ionic silica precursor and exhibit highly symmetric bimodal mesopore systems and demonstrate the immense flexibility of the non-ionic templating system.

Innovation in the synthesis of inorganic structures with novel and improved synthesis routes and structures is an area of intense international scientific and technological research. Ever since the disclosure of the M41S family of materials[1] in 1992, a veritable explosion of research effort has occurred in the area of macromolecular and micelle templating syntheses of mesostructured materials.[2] A considerable number of different synthesis approaches have now been developed, all of which possess strong philosophical similarities but are both chemically and mechanistically diverse.[3]

One of the major post M41S advances has been the discovery that non-ionic alkyl polyethylene oxide (PEO) surfactants and block co-polymers can template regular inorganic structures.[4–9] The N^0I^0,[4,5] $N^0/N^+X^-I^+$[6,7] and $N^0M^+I^-$[6] non-ionic templating routes appear to offer significant advantages over other assembly pathways. These include reproduction of structures reported in cationic systems[7] and novel structures, thicker pore walls and economic and environmental cost benefits of near ambient temperature, neutral pH and low cost, non-toxic and recoverable templates.

Biomimetic vesicular structures can form when the ionic strength of the non-ionic surfactant solution is raised from that of the pure aqueous solution through modification of the PEO–H_2O hydrogen bonding. To date such structures have only been exploited for inorganic phase formation through the application of diamine bolaform surfactants.[10] Here, we have simultaneously created biomimetic vesicle structures along with regular micelles from non-ionic alkyl-PEO surfactants in dilute electrolyte solutions† and thereby used these to direct the assembly of novel mesostructured silicas. We report, for the first time, the synthesis of inorganic silica structures that exhibit bimodal pore systems with pore diameters in the size range 3.0–9.0 nm.

Powder X-ray diffraction patterns (XRD) of a hydrothermally treated [Fig. 1(a)] and then calcined [Fig. 1(b)] sample synthesised in the presence of NaCl can be compared to XRD patterns of regular MSU-X materials.[5] The latter generally display single d_{100} reflections indicative of uniform worm-like mesopores with no long range periodicity. Two strong major reflections are observed in conjunction with a number of minor reflections at higher angles. An initial hypothesis was that these reflections were due to reflections from a novel two- or three-dimensional pore structure. Further analysis however modified this hypothesis and suggested a structure simultaneously possessing two distinct pore arrangements.

The formation of a novel structure type was supported by N_2 sorption isotherms (Fig. 2) which clearly display two distinct capillary condensation steps.[11] BJH model analysis of a material prepared in NaCl solution provides two pore diameter maxima at 3.4 and 5.2 nm (Table 1). Hysteresis is observed in the desorption branch which also exhibits two distinct, but less well separated, desorption steps. The suggestion is therefore, that two interconnected pore systems are present and that the desorption hysteresis suggests a three-dimensional pore structure.

Scanning electron micrographs (SEM) indicate elementary particles of *ca.* 0.5 μm that exhibit a general spherical morphology and some evidence for the formation of rounded extrusion-like particles. Secondary particles are aggregates of *ca.* 10–15 μm diameter. Confirmation of a double pore system was obtained from transmission electron micrographs (TEM) (Fig. 3). The micrographs show regions of extended lamellar-like features with low curvature, regions of highly ordered pores in hexagonal symmetry and regions of less ordered worm-like pore symmetry. This suggests that both vesicular and micellar aggregation types co-exist in these systems.

The effects on the synthesis of [Si]-MSU-1 materials in the presence of Na^+ electrolytes can be separated into two different effects. In the case of H^+ cation addition[6,7] some authors have proposed that the template becomes protonated and should thus

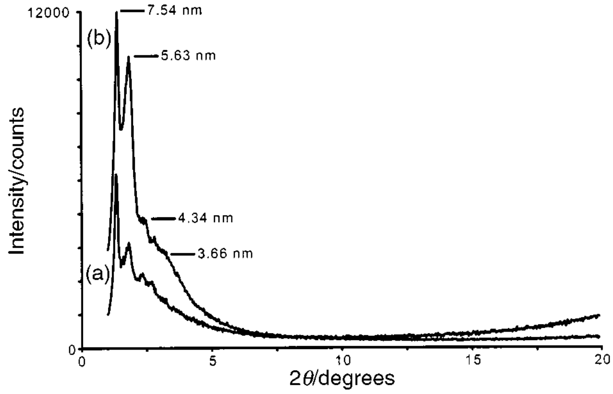

Fig. 1 XRD patterns of Brij 97 templated [Si]-MSU-1 prepared in the presence of NaCl: (a) hydrotreated at 100 °C for 72 h and (b) hydrotreated and calcined at 600 °C for 4 h.

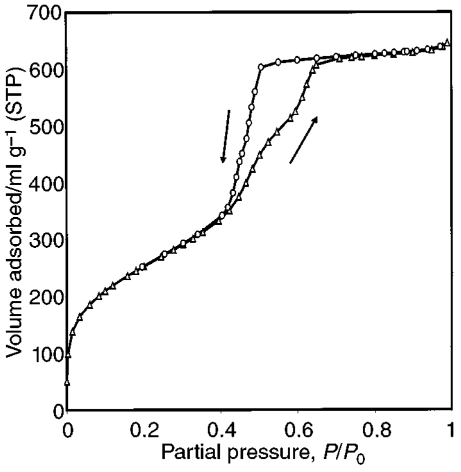

Fig. 2 Nitrogen adsorption–desorption isotherms of hydrotreated and calcined [Si]-MUS-1 prepared in the presence of NaCl.

Table 1 Properties of [Si]-MSU-1 silica samples prepared in the presence of dilute electrolytes

[Si]MSU-1 sample[a]	Electro-lyte[b]	d_{h00}[c]/nm	Pore diameter[d]/ nm	Surface area[e]/ m^2 g^{-1}	Pore volume[f]/ ml g^{-1}
1	NaF	9.2, 5.3	8.7	520	1.2
2	NaCl	7.5, 5.6	5.2, 3.4	900	1.0
3	NaBr	7.9, 5.8	5.6, 3.6	810	1.1
4	NaI	8.7, 5.8	8.0	500	1.3
5	$NaSO_4$	8.5, 6.0	6.2, 3.8	880	1.2
6	$NaNO_3$	7.8, 6.0	5.8, 4.5	730	1.1
7	NaOAc	8.5, 4.9	6.7	900	1.4

[a] All samples templated with Brij 97 oleyl-EO_{10} non-ionic surfactant. [b] Sodium salts added at 5 mol% w.r.t Si. [c] ±0,1 nm [d] Pore diameters (±0.1 nm) calculated using the BJH cylinder model. (This model has recently been shown to underestimate pore diameters by up to 20%).[13] [e] Surface areas (±10 m^2 g^{-1}) calculated with the BET model. [f] Pore volumes (±0.1 ml g^{-1}) calculated from $P/P_0 = 0.98$.

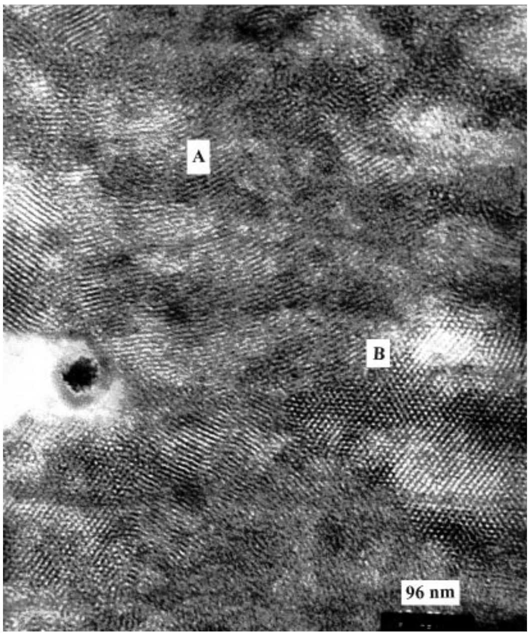

Fig. 3 Representative TEM of hydrotreated and calcined [Si]-MSU-1 prepared in the presence of NaCl showing (A) extended curved lamellar and (B) hexagonally ordered mesopores.

be labelled $N^+X^-I^+$.[7] In the system presented here, the pH of the reaction medium remains neutral and thus the assembly pathway is a true ion mediated non-ionically templated $N^0X^{+/-}I^0$ pathway. We suggest that the Na^+ cations induce the formation of vesicular systems through 'coordination' of PEO head groups, conformation extension and surface curvature decrease thereby forming vesicles. As the Na^+ concentration is 40 mol% with respect to R-PEO and each R-PEO contains 10 EO groups, only 4–8 mol% of the R-PEO surfactant will be fully Na^+ coordinated (assuming one Na^+ per one or two EO groups). Thus the remaining 96–92 mol% R-PEO surfactant will be in the normal state with regular PEO conformations forming regular micelles with greater surface curvature.

The second electrolyte effect is that of the anion which modifies not only the interaction of the tetraethyl orthosilicate (TEOS) silica precursor with the template head-group, but also the rate of hydrolysis and condensation of the TEOS. The effect of different anions in the $N^0X^{+/-}I^0$ pathway is to cause subtle changes to the final form of the mesostructures beyond the template aggregation modification caused by the cation. Fluoride addition has been previously reported[5] and remains a special case. The F^- ion possesses special chemistry that leads to very rapid TEOS condensation,[11] very small elementary particles, decreased micelle curvature and hence larger pore diameters.[5] The strong F^-/TEOS interaction appears to override any cation effects and a single pore system is formed. The other halides Cl^-, Br^- and I^- show decreasing rates of TEOS hydrolysis with increasing ionic radius. The oxy-anions SO_4^{2-}, NO_3^- and OAC^- show varying separation of the diameters of the two pore systems again with increasing ionic radius and decreasing ionisation (Table 1). ^{29}Si MAS NMR spectra indicate that anions with greater ionisation constant (*e.g.* F^-, Cl^-, SO_4^{2-}) induce more extensive hydrolysis of the TEOS and therefore more condensed and stable silica structures. Possible coordination effects by oxy-anions have not as yet been fully considered.

The results briefly outlined here provide further indications of the immense flexibility of the non-ionic alkyl-PEO templating system. They show that simple engineering of the chemistry in the synthesis medium can have profound effects on the templating mechanism and resultant porous products. This is further indication that the technological future of mesoporous materials development will lie within the PEO templating system. The exact nature of the templating system remains to be established. An investigation of the complete mechanisms through which different electrolytes (*i.e.* hard and soft cations and anions) modify the templating process is currently under investigation and will be discussed in a future contribution.

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Notes and references

† *Experimental*: In a typical $N^0X^-I^0$ [Si]-MSU-X synthesis, a non-ionic polyethylene oxide surfactant was dissolved in distilled water at 7.5 wt%. In this study, Brij 97 (oleyl EO_{10}) surfactant was used exclusively. The temperature of the surfactant solution was raised to 40 ± 2 °C and TEOS was added under stirring to an Si: surfactant molar ratio of 8 : 1 and stirred for a predetermined time. The electrolyte, dissolved in a minimum of water was then added to the surfactant–TEOS solution at 5 mol% with respect to Si (*i.e.* 0.4 mol% w.r.t. PEO, 0.04 mol% w.r.t EO). The mixture was stirred at moderate rate, while the temperature was held at 40 ± 2 °C, over 36 h ensuring that the total aqueous volume was maintained. The white precipitate obtained was recovered by filtration, washed with distilled water and dried in air at room temperature. The dried samples were then hydrothermally treated by dispersing in distilled water and heating in a sealed polypropylene bottle at 100 °C for 72 h. The hydrothermally treated samples were recovered by filtration and dried in air at room temperature. The template was removed from the products by calcination at 600 °C in air over 4 h at a heating rate of 2 °C min^{-1}.

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