

## Macro-cellular silica foams: synthesis during the natural creaming process of an oil-in-water emulsion

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The room-temperature synthesis of a macro-mesoporous silica material during the natural creaming process of an oil-in-water emulsion is reported. The material has 3-dimensional interconnected macropores with a strut-like structure similar to meso-cellular silica foams<sup>1</sup> with mesoporous walls of worm-hole structure. The material has very high surface area ( $\sim 800 \text{ m}^2 \text{ g}^{-1}$ ) with narrow mesopore size distribution.

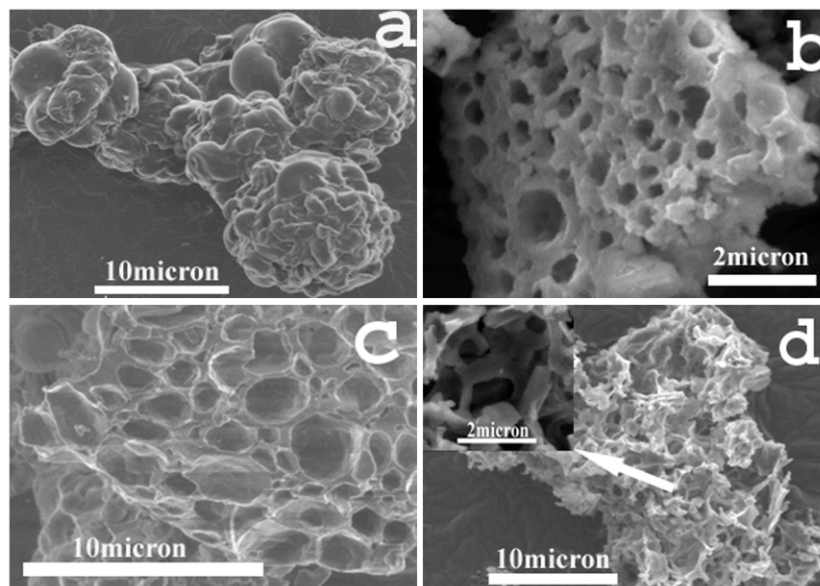
The discovery of ordered M41S-type mesoporous materials by Mobil researchers<sup>2</sup> was a breakthrough in that it filled the gap between the two existing natural porous materials *i.e.* microporous ( $< 2 \text{ nm}$ ) and macroporous ( $> 50 \text{ nm}$ ). However, the pores of the surfactant templated silicate materials are at the lower end of the mesoporous regime (2–4 nm). Stucky and co-workers<sup>3</sup> reported a series of silica materials (SBAs) where the mesoporosity was extended to 30 nm by using polymeric surfactants. An important observation of the same group was another useful material called a meso-cellular silica foam (MCFs).<sup>1</sup> The accidental discovery of MCF, consisting of spherical voids (22–42 nm in diameter) interconnected by “windows” of  $\sim 10 \text{ nm}$  occurred while synthesising SBA-15. The formation of MCFs was explained based on the phase transition from a hexagonally packed arrangement of cylindrical pores (6–12 nm in diameter) to spherical voids of MCFs. It was reported that 1,3,5-trimethylbenzene (mesitylene) could be useful as a “swelling agent” in order to swell the pores of surfactant-templated MCM-41 materials by preferential solubilisation of additives in the micelle core.<sup>4</sup> The swelling process increases the pore diameter from 4 nm to 10 nm without altering the hexagonal structure of MCM-41. The role of

mesitylene during the SBA-15 synthesis is not only as a swelling agent but also helps to generate MCFs by a templating mechanism.<sup>5</sup> The presence of spherical cells and windows in the MCFs is described based on the TEM results and theoretical calculations. In this report we show that the role of mesitylene is not only to form meso-cellular foams but also to generate new macroporous materials we name UMIST Macro-Cellular Foams (UMCF).

The synthesis of meso- and macro-cellular silica foams was carried out using a cationic surfactant (cetyltrimethylammonium bromide, CTAB), water, mesitylene, and tetraethyl orthosilicate (TEOS) in strongly acidic conditions. A typical synthesis batch composition (wt%) is as follows:

3.6 TEOS : 4.2 CTAB : 2–40 Mesitylene : 58.4 Water : 2.8 HCl

In the actual synthesis, cetyltrimethylammonium bromide (CTAB) was dissolved in water under stirring. The required amount of hydrochloric acid was added to the stirred solution giving a colourless solution. Finally a mixture of mesitylene and tetraethyl orthosilicate was added slowly for a period of 30 minutes under stirring at 800 rpm. During addition, the mixture turned opaque. The whole mixture was then stirred for 1 hour using a mechanical stirrer (stainless steel, three blades, propeller shaped). The opaque solution was transferred into a gas jar and the jar kept at 25 °C overnight. In all the synthetic batches, two layers were observed. A thick white layer floated on the top and a clear pale blue solution on the bottom. A thin white precipitate was also observed on the bottom of the jar when the mesitylene concentration was low. The white solid from the bottom layer and the white thick solid from the top layer were filtered out. The separated solids were washed with de-ionised water several



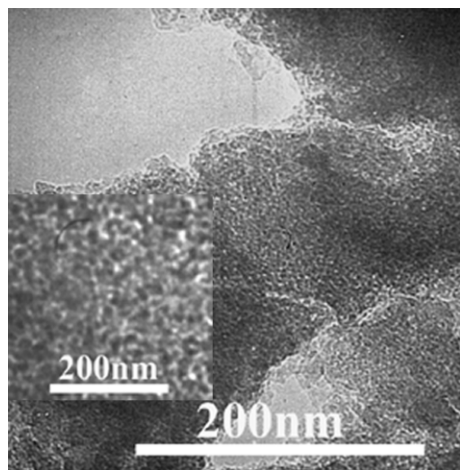
**Fig. 1** Scanning electron micrographs of samples synthesised with different mesitylene concentrations: (a) 2 wt%, no macropores (b) 15 wt%, macropores with thick walls (c) 26 wt%, macropores with thin walls (d) 31 wt%, a strut-like structure.

times. Both materials (top and bottom) were dried at 40 °C for 6 hours. The dried materials were white in colour. These materials were then calcined for a period of 10 hours at 650 °C in air. The temperature of the furnace was increased at the rate of 1 °C min<sup>-1</sup>. All materials were characterised by powder XRD, SEM, TEM, N<sub>2</sub> adsorption, Hg porosimetry and solid state <sup>29</sup>Si NMR.

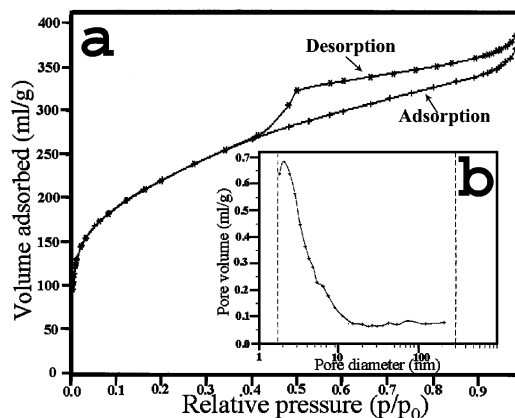
All materials exhibited a broad XRD peak ( $d \cong 4.5$  nm) in the low angle region both before and after calcination, a strong indication of the presence of mesoporosity without any long range ordering. However, observation by SEM showed different morphologies depending on the mesitylene concentration (Fig. 1). Synthesis at low mesitylene concentration (2%) produced a cauliflower morphology (Fig. 1a) similar to meso-cellular foams (MCFs)<sup>1</sup> whereas macroporous solids were obtained by increasing the mesitylene concentration from 2% to 31%. Synthesis using 31% mesitylene in the reaction produced a unique macroporous solid (Fig. 1d) similar to the strut-like structure of MCFs<sup>1</sup> but at a different length scale. The cell openings are around 4 micron with interconnecting windows of size 1 micron. The strut-like structure disappears and forms a simple disordered macroporous solid with thicker walls by decreasing the mesitylene concentration from 31% to 15%.

The wall structure of UMCF was characterised by TEM and N<sub>2</sub> adsorption. TEM (Fig. 2) of the material exhibited disordered mesopores with worm-hole structure<sup>6</sup> and the size of the mesopores is around 4 nm. In agreement with this, the N<sub>2</sub> adsorption isotherms of UMCF shows a type IV isotherm (Fig. 3). The presence of hysteresis at  $p/p_0 > 0.4$  clearly indicates the presence of mesoporosity and the upturn at  $p/p_0$  close to 1.0 is indicative of macroporosity. The presence of macroporosity was also identified by Hg porosimetry with a peak at 1 micron due to Hg intrusion through the windows into the cells of UMCF. The BET surface area of the material is very high with a value of 796 m<sup>2</sup> g<sup>-1</sup>.

The various Si environments Q<sup>n</sup> {where Q<sup>n</sup> represent Si(OSi)<sub>n</sub>(OH)<sub>4-n</sub> and 4 ≥ n ≥ 1} can be identified due to the distinct chemical shift values in <sup>29</sup>Si single pulse MAS NMR spectrum. (Q<sup>2</sup> + Q<sup>3</sup>)/Q<sup>4</sup> of the uncalcined form of UMCF is 0.59



**Fig. 2** Transmission electron micrograph image of sample synthesised with 31 wt% mesitylene concentration.



**Fig. 3** Nitrogen adsorption isotherm of UMCF synthesised with 31 wt% oil concentration (a) and the mesopore size distribution (b).

compared to 1.31 of MCFs indicating that the walls of the UMCF are more condensed. Upon calcination, the value remains the same in the case of UMCF whereas it reduces to 0.39 for MCFs. This result indicates that the walls of the MCFs are more strained due to the transformation of Q<sup>3</sup> to Q<sup>4</sup> by calcination. Further <sup>29</sup>Si-<sup>1</sup>H CPMAS results indicate that the Q<sup>4</sup> in UMCF is more remote from the proton pool than in MCF materials.

The formation of macro-cellular foams is explained based on a very simple natural phenomenon of oil-in-water emulsion known as “creaming”. The macroporosity is generated due to the condensation of silica around the oil droplets during the creaming process of emulsion. The surfactant CTAB has a dual use (i) as an emulsion stabiliser and (ii) as a template for mesopore formation. Similarly mesitylene acts as a dispersed phase in an oil-in-water emulsion at high concentration but also as a swelling agent for the phase transformation from hexagonal to meso-cellular foams at low concentration as described previously.<sup>5</sup>

In conclusion, we demonstrate a simple method to generate a series of porous silica materials from meso-cellular foams to macro-cellular foams with various pore sizes and pore structure. This is the first report regarding the synthesis of macro-cellular foams of silica (UMCF). The high surface area of this material with hierarchically ordered porous structure could be a useful support material for enzyme catalysis and bio-molecular sieving.

## Notes and references

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