A new templating method for three-dimensional mesopore networks

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A new templating method using small, inexpensive non-surfactant chemicals has been developed facilitating the synthesis of hydrothermally stable foam-like mesopore networks with high surface areas.

Porous materials are of fundamental importance in science and technology.[1] Various templates are employed to direct the synthesis of uniform micro-, meso- and macro-pores. Principally, three types of templating have been reported thus far, *i.e* templating by individual molecules giving rise to micropores, by micelles giving rise to mesopores and by emulsions or latex particles giving rise to macropores.[2–5]

Here, we report a new templating method for well defined mesoporous (siliceous) oxides (denoted as TUD-1, Fig. 1),[6] in which small, non-surfactant templates direct the formation of mesosized structural features during the polycondensation of inorganic species upon temperature increase during synthesis. The key to a successful formation of mesopores is the careful control of the intermolecular interaction among organic templates and inorganic species, *i.e.* matching the type of template molecule with the temperature regime used. With a system initially composed of three different components, (*i.e.* water, silica source and template) taking account of the change in the nature of interactions between the different constituents with temperature, we were able to synthesize a new material that is characterized by well-defined pores with an easily tunable mesopore size distribution (25–250 Å in diameter), three-dimensional connectivities (foam-type structure), high surface areas (up to *ca.* 1000 m^2 g^{-1}), and high thermal and hydrothermal stability (negligible degradation at 650 °C for 12 h or boiling in water for 2 h, little degradation after heating to 1000 °C for 2 h or boiling in water for 17 h).

The starting point of our investigation was the desire to examine whether large pores in structured silicas might be templated, not by micelles or by very large and complex organic molecules, but by aggregates of simpler molecules. Following some preliminary investigations, triethanolamine was selected as a small, inexpensive and stable organic template with a high boiling point (*ca.* 340 °C) and good miscibility towards water, alkoxysilanes (Si-source) and the silica species generated by their hydrolysis. The new methodology also allows the facile introduction of catalytic sites (acid, base, redox) as well as micropores during the initial synthesis stage.

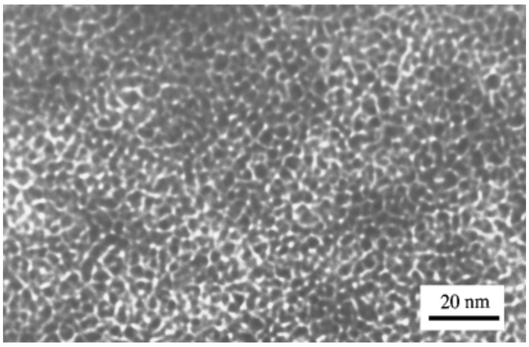

Fig. 1 High resolution transmission microscopy (HRTEM) image of the regular, mesoporous foam-like structure of TUD-1.

In the first step, a homogeneous mixture is obtained by mixing tetraethylorthosilicate (TEOS), triethanolamine (TEA) and water at room temperature.† After aging and drying in air, this mixture solidified and formed a homogeneous gel, the X-ray powder diffraction pattern of which showed no discernible peak. We interpret these data as deriving from a largely hydrogen-bonded siliceous composite polymer: the initial hydrolysis of TEOS was followed by the partial condensation of the resulting silanol species with each other and with some of the TEA, forming mixtures of mono- and oligomeric silatrane complexes and of various silica species (by ^{1}H, ^{13}C and ^{29}Si solution and MAS NMR). Hydrothermal treatment of this material changed its structure from amorphous to mesostructured. Finally, TUD-1 was obtained as a white mesoporous solid by the removal of the template either *via* Soxhlet extraction or *via* calcination. The circumstance that the mesopore range obtained is found to be directly proportional to the heating time (see Fig. 2) allowed for a very convenient, direct control of the mesopore size distributions of TUD-1. Interestingly, the porous structure can also be created without hydrothermal treatment, by employing careful calcination instead (for which a low ramp rate of *ca.* 1 °C min^{-1} is required). Hydrothermal treatment at moderately high temperature or thermal treatment (calcination) with a low ramp rate is necessary, because the condensation reactions of the various silica species are not completed after the gel formation.

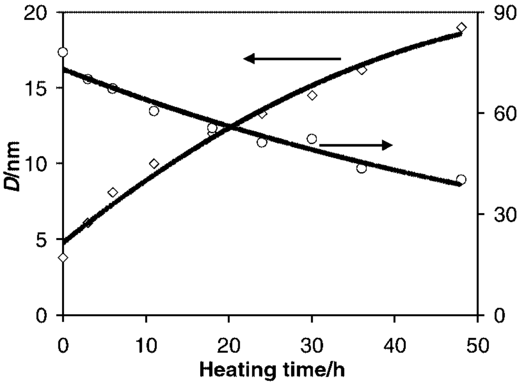

Fig. 2 Typical graph obtained when tuning the mesoporosity by variation of the heating time during hydrothermal treatment (in this case a homogeneous synthesis mixture with a molar composition of TEOS: 0.5TEA: 0.1TEAOH: 11H$_2$O was, after drying at 98 °C for 24 h, heated in an autoclave to 190 °C for different times). *D* is the mesopore diameter at maximum peak height calculated using the BJH model based on nitrogen desorption branch; *S* is the mesopore surface area calculated using the t-plot method.

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At low temperatures (up to 100 °C) and after substantial loss of volatile components (water and ethanol, up to 70 wt%), the strengths of the various interactions between TEA, the various types of silatrane complexes and the silica oligomers are similar enough to form a homogeneous mixture without mesostructure. However, at elevated temperatures the silica oligomers condense extensively and the silatrane complexes partially or fully hydrolyze due to the more labile nature of Si–alkoxy bonds as compared to Si–siloxy bonds. The TEA is then largely expelled from the silica network and separate silica and template phases begin to form. The coalescence of the resulting silica particles further separates the phases on a mesoscale. This microsyneresis (resulting in a solid–liquid mixture) gradually forces the TEA into meso-sized aggregates, templating the mesopores.

X-Ray diffraction patterns of TUD-1 show only one peak at low angle (scanning from 0.5–40° in 2θ), indicating it is a mesostructured material. Nitrogen adsorption isotherms revealed reproducible surface areas of between 500 and 1000 $m^2 g^{-1}$ and pore volumes of between 0.6 and 1.7 $cm^3 g^{-1}$, depending on the synthesis conditions. When employing hydrothermal treatment, the pore volume and wall thickness of TUD-1 increased with time, with a corresponding decrease in surface area, demonstrating that the pore formation is a dynamic process, consistent with the model proposed above.

We attempted to visualise the mesopore connectivity by HRTEM using Pt wires as a contrast agent.[7] The resulting images are consistent with a 3-D connectivity, but not sufficient to prove this. The synthesis of an inverse structure of TUD-1 out of carbon (using the methodology of Ryoo[8]) yielded a nanoscale carbonaceous network (surface area >1000 $m^2 g^{-1}$, tunable mesopore size),‡ showing a similar image of a foam-like mesopore structure (Fig. 3). This result excludes one- or two-dimensional pore connectivities in TUD-1, as otherwise the resultant carbonaceous mesopore network would collapse upon the removal of silica. Thus, we were able to show that TUD-1 contains three-dimensional pore networks.

Hence, siliceous TUD-1, with its inherent possibility of a bimodal pore distribution (*vide supra*), offers a wide scope for chemical applications as most procedures commonly employed to impart functionality on silica can be used. For example, it is very straightforward to prepare highly dispersed metal particles on TUD-1. Furthermore, ^{29}Si CP-MAS NMR measurements of a typical TUD-1 sample before and after calcination reveal the presence a substantial Q_3 signal, allowing for functionalization *via* grafting onto the pendant silanol groups lining the mesopore walls.[9]

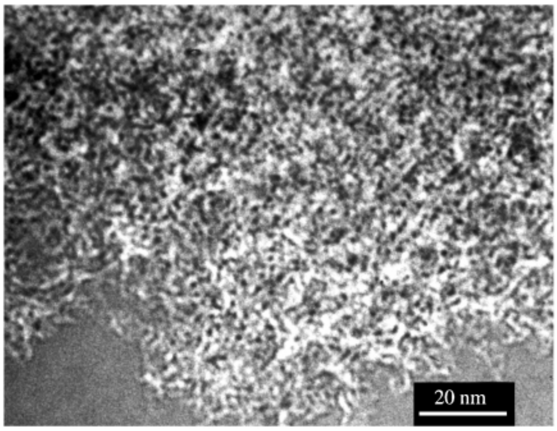

Fig. 3 Mesoporous carbon templated by TUD-1 silica, yielding an 'inverse' TUD-1 structure.

In addition, metals such as, *e.g.* titanium, zirconium or vanadium can be grafted *via* complexation with the TEA onto the surface of the mesopore wall, providing a 'one-pot' grafting methodology.[10]

In a similar vein, functionalized surfaces are easily fashioned in a one-pot procedure by the inclusion of a certain amount of functional siloxy precursor (*e.g.* $NH_2(CH_2)_3Si(OEt)_3$) into the synthesis gel.[11] Moreover, strong acid sites (by NH_3-TPD) can be prepared that are located in the micropores, whereas the mesopores can be made mildly acidic, offering a wide scope for application in acid catalyzed reactions.

Full results on acid site functionalizations, one-pot surface functionalizations, metal particle and metal oxide impregnations/immobilizations and related catalytic tests will be published shortly.

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Notes and references

† Tetraethyl orthosilicate (TEOS), triethanolamine (TEA) and water were combined at room temperature in ratios of 1 : 0.25–2 : 10–40 to obtain a homogeneous mixture. This mixture solidified after aging at room temperature for 6–24 h and subsequent heating to 96–100 °C for 12–24 h in air, forming a homogeneous gel. This gel was transferred into an autoclave and heated at *ca.* 150–200 °C for between 0 and 3 days. Finally it was calcined at 600 °C for 10 h with a ramp rate of *ca.* 1 °C min^{-1} in air, or extracted in a Soxhlet apparatus using ethanol for 3 days to obtain the final mesoprous materials. Micropores could also be introduced by addition of traditional zeolite templates, *e.g.* tetraethylammonium hydroxide, with a ratio of 0.1–0.3 with respect to Si in the final synthesis mixture.

‡ The carbonaceous network templated by TUD-1 shows a bimodal mesopore system due to structure transformation. The sizes of these two mesopores can be tuned in ranges of 3.5–5.0 and 15–25 nm, respectively, depending on the original TUD-1 sample. Full details will be published shortly.

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