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Synthesis of amorphous, microporous silica with adamantanamine as a templating agent

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Amorphous, microporous silica with a spherical particle morphology has been prepared with adamantanamine, and its unusual structural properties suggest a non-zeolitic templating synthesis pathway.

Templating agents have been widely used in directing the formation of porous inorganic structures.[1,2] Traditionally, small organic molecules have been used as individual *molecular* templates in constructing the pore openings and cage-like cavities in microporous zeolites (pores < 20 Å).[2] In contrast, long-chained surfactant molecules are used as *supramolecular* templating agents in the preparation of amorphous mesoporous M41S-type silicates (pores > 20 Å).[3–6] The amphiphilic molecules interact with inorganic precursors and organize into micellar domains to form mesostructured metal oxide/surfactant composites. Mesoporous materials are produced after removal of the organic templating agents. Microporous transition metal oxide analogues prepared with short-chain surfactant-like molecules[7] and bifunctional surfactants[8] have recently been reported.

Here, we describe the formation of amorphous microporous silica using adamantanamine. Adamantanamine is a small, bulky molecule (axial length of *ca.* 5.9 Å) used as a molecular template in the preparation of zeolites, *e.g.* deca-dodecasil 3R (DD3R).[9]

In the synthesis of silicate/adamantanamine composites, 120 mol equivalents of water were added to an ethanolic solution consisting of 4 g of tetraethylorthosilicate and adamantanamine with an adamantanamine/Si molar ratio of 0.4. After stirring the reaction mixture at room temperature for 48 h, the white precipitate obtained was collected by filtration and washed with water. The resulting solid powder, designated as Si-TMS7, gave the X-ray diffraction (XRD) pattern shown in Fig. 1(a). Upon calcination at 540 °C for 3 h in air to remove the adamantanamine from the inorganic/organic composite, Si-TMS7 retained its XRD pattern [Fig. 1(b)]. The resulting silicate has an effective BET surface area of 737 $m^2\ g^{-1}$ and a pore volume of 0.35 $cm^3\ g^{-1}$. The type I nitrogen adsorption isotherm in Fig. 2 clearly illustrates the microporous nature of Si-TMS7.

The XRD patterns of Si-TMS7 (Fig. 1) have an intense low-angle diffraction peak, with *d*-spacings of 21.5 and 20.4 Å before and after calcination at 540 °C, respectively. The patterns resemble more closely those of surfactant-templated mesoporous materials than those of any zeolites. The lack of higher-order diffraction peaks indicates the absence of long-range pore ordering. The lone diffraction peak represents a common distance between the pore walls, as is usually observed in supramolecular-templated mesoporous materials with local pore ordering, *e.g.* KIT-1,[10] MSU-1[6] and L_3-phase silica gels.[11]

The particle morphology of calcined Si-TMS7 is predominated by *ca.* 1 μm spheres, as shown by transmission electron microscopy (TEM) [Fig. 3(a)]. These spheres are very monodisperse in size, as also confirmed by scanning electron microscopy. The morphology of Si-TMS7 is similar to the 200–500 μm spherical particles of MCM-41 prepared through surfactant–templating within butanol-in-water emulsions.[12] An emulsion-like system of adamantanamine, ethanol and water could be responsible for the spherical shapes of Si-TMS7 particles.

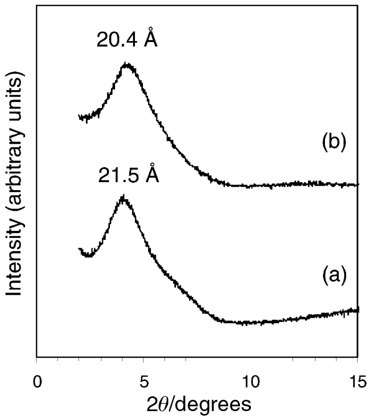

Fig. 1 XRD patterns of Si-TMS7 synthesized with adamantanamine templates at room temperature: (a) as-synthesized and (b) after calcination at 540 °C. The XRD patterns were obtained with a Siemens D5000 θ–θ diffractometer with Cu-Kα radiation (λ = 1.5406 Å).

The Si-TMS7 spheres were microtomed to reveal their amorphous, microporous structure [Fig. 3(b)]. Highly packed, randomly ordered pores appear throughout the particle. The pore size is estimated to be in the 13–17 Å range, more than twice the size of a single adamantanamine molecule (*ca.* 5.9 Å). We speculate that aggregates of adamantanamine may be directing the formation of the pores, distinct from the surfactant micellar domains prominent in mesoporous materials synthesis.

The temperature was found to be a very important parameter in the synthesis of Si-TMS7. Mesostructured Si-TMS7 could only be derived under ambient conditions; hydrothermal treatment at elevated temperatures resulted in amorphous, non-

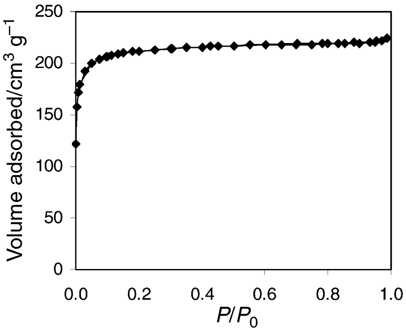

Fig. 2 N_2 adsorption isotherm of Si-TMS7 after adamantanamine removal by calcination at 540 °C in air. The isotherm was collected on a Micromeritics 2010 Gas Adsorption Analyzer after degassing the sample at 150 °C and 10^{-3} mmHg for 6 h.

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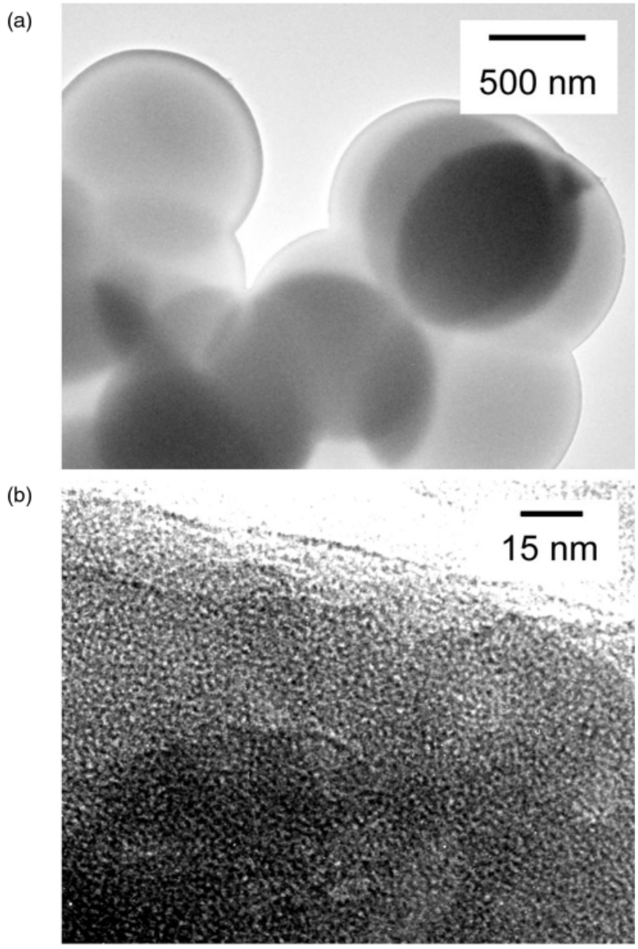

Fig. 3 TEM images of calcined Si–TMS7 (a) before and (b) after microtoming. The thinned sections were prepared by setting the calcined powder in acrylic resin. The microscopy was performed on a JEOL 2010 operating at 200 kV with a LaB_6 gun.

mesostructured materials. The interaction between the adamantanamine and the silicon alkoxide is most likely characterized by hydrogen bonding, which would be too weak to be sustained at high temperatures.[5,13] Other important factors that determine the templated inorganic structure are solubility and hydrophobicity of the templates, as shown by the fact that linear amines with only hydrocarbon chain length of > 6 are capable of leading to porous silicas with self-assembled templating structures.[13]

In conclusion, adamantanamine was used to prepare silicate/organic composites and was successfully removed without structural collapse of the resulting microporous silica. The unique structure and large 13–17 Å micropores provide evidence for collective templating of the small rigid adamantanamine molecules. Through such a synthesis pathway, other non-zeolitic microporous metal oxides can be attained.

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