Controlled Synthesis of Microporous Ceramic Materials from Organolithic Macromolecular Precursors

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Microporous Si–C–O ceramic materials with high surface areas are prepared by treating a pyrolysed organolithic macromolecular material with hydrofluoric acid.

Microporous ceramic materials prepared from polymer precursors are potentially useful as components of ultrafiltration membranes,[1] chemical sensors[2] and composite catalysts.[3] We report here the successful synthesis of one such material using the four-step sequence outlined in Fig. 1.

The argon adsorption isotherm of this material at 87 K,[4]‡ Fig. 2(*a*), is of Type I and when replotted to emphasise the region of low relative pressures, Fig. 2(*b*), shows that the pore sizes are comparable to those of crystalline ALPO-5 (8 Å)[5] and VPI-5 (12.1 Å)[6]§. However, the pore size distribution is broad as expected for an amorphous material. The total pore volume¶ is *ca.* 0.19 ml g^{-1} which corresponds to a surface area¶ of 594 m^2 g^{-1}.

The first step in the synthesis of the material described above is the preparation of the vinyl-functionalised spherosilicate, $[Si_8O_{20}][Si(Me)_2CHCH_2]_8$, **1**, which has been described

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‡ Measured on an Omnisorb 100 dynamic flow adsorption apparatus.

§ The adsorption isotherms of ALPO-5 and VPI-5 are superimposed for comparison.

¶ Calculated at $p/p_0 = 0.4$ using $\rho = 1.46$ g ml^{-1} for liquid Ar at 87 K and assuming[4] that a single argon atom covers 14.2 $Å^2$.

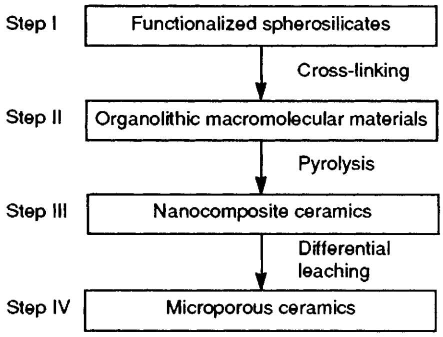

Fig. 1 Outline of the synthetic procedure used to synthesize microporous ceramic materials.

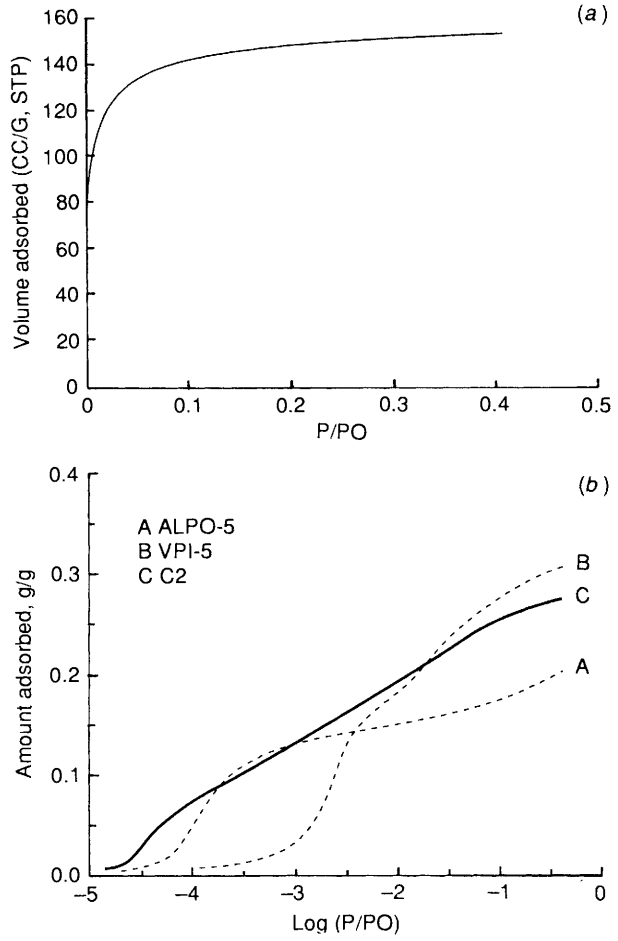

Fig. 2 (*a*) Argon adsorption isotherm of the product **C2**, at 87 K showing Type I behaviour, characteristic of microporous materials. (*b*) Isotherm replotted to emphasize region of low relative pressure. The dotted lines which are isotherms of ALPO-5 and VPI-5.

in detail elsewhere[7–10] and whose structure is shown in Fig. 3. The repeat unit, $[O_{3/2}SiOSi(Me)_2CH_2CH_2Si(Me)_2C_6H_4O_{1/2}]$ of the organolithic macromolecular material (OMM) prepared from compound **1** and the bifunctional compound $[HSi(Me)_2C_6H_4O_{1/2}]_2$, **2**,|| is exactly the same as the repeat unit of the OMM reported previously.[11] The ^{29}Si and ^{13}C CPMAS NMR spectra** of this new OMM are shown in Fig. 4(*a*) and

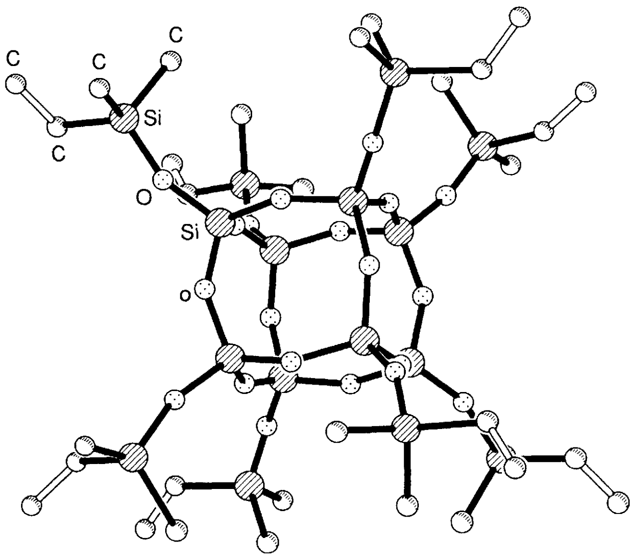

Fig. 3 Ball and stick representation of the structure of the functionalised spherosilicate $[Si_8O_8](OSi(Me)_2CHCH_2)_8$, **1**. Only one unit of this oligomeric molecule is labelled.

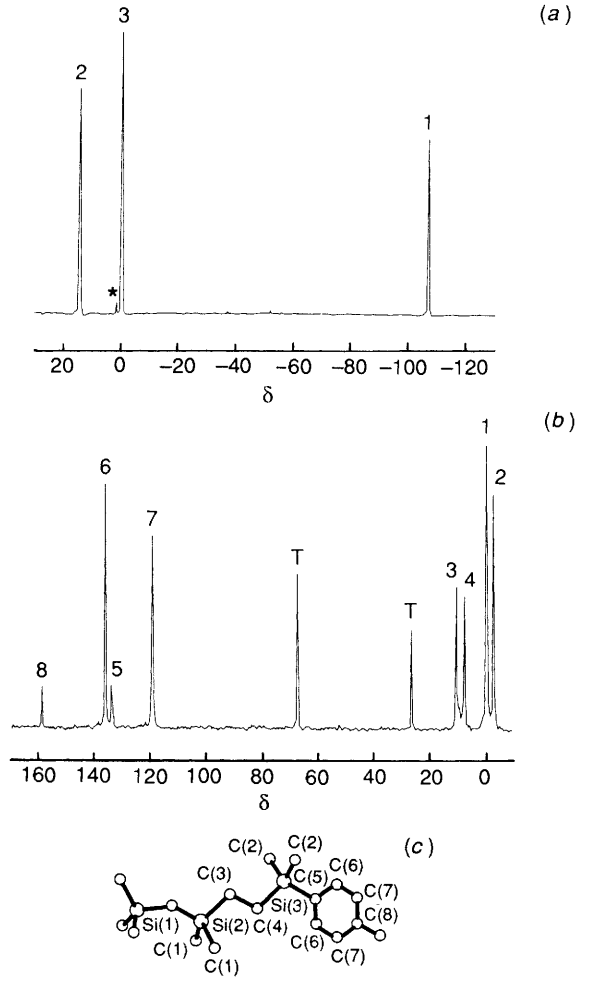

Fig. 4 (*a*) ^{29}Si CPMAS NMR spectrum of the OMM derived from **1**, after it is saturated with tetrahydrofuran (*ca*. 50% w/w); (*b*) ^{13}C CPMAS NMR spectrum of the same OMM. The peaks labelled T are assigned to tetrahydrofuran. (*c*) Ball and stick drawing of the repeat unit of the OMM. The atom numbers correspond to peak numbers in (*a*) and (*b*).

|| Reaction procedure is as follows: **1** (1.53 g) + **2** (1.46 mL) + THF (1.8 ml) + catalyst solution [1.2 ml of $PtCl_2(C_6H_5CN)_2$ in THF, 250 μg Pt ml^{-1}]: reaction time, 2 days under N_2.

** Measured on a Bruker MSL-300 instrument. ^{29}Si NMR (59.6 MHz) external standard = M_8Q_8.

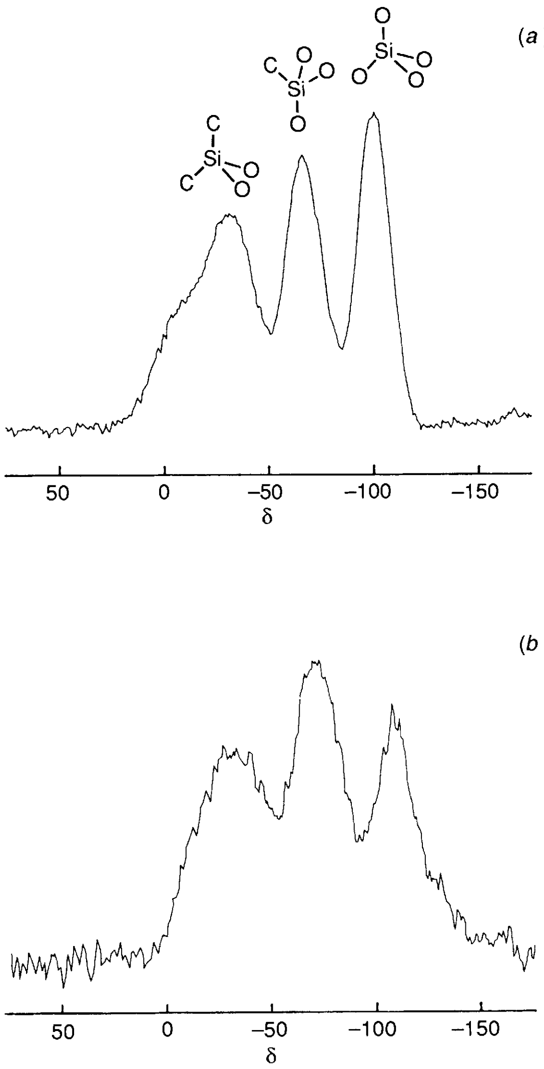

Fig. 5 (*a*) ^{29}Si MAS NMR spectrum of the black Si–C–O ceramic material, **C1**, obtained by pyrolysis of the OMM at 800 °C under N_2 for 2 h. (*b*) ^{29}Si MAS NMR spectrum of the microporous ceramic material, **C2**, obtained by leaching out the SiO_2-rich phase in **C1** with hydrofluoric acid.

Fig. 4(*b*), respectively, and the structure of the repeat unit is shown in Fig. 4(*c*), with the atoms labelled to show the peak assignments in the two spectra. The three large peaks in the ^{29}Si CPMAS spectrum at *ca.* −107.9, −0.7 and 14.0 are assigned to silicon atom environments, which can be described†† as SiO_4^{Si}, SiC_3O^{Si} and SiC_4, respectively. The small peak, marked with an asterisk is assigned to residual vinyl-substituted silicon atoms and its intensity relative to the two adjacent peaks shows that the network is >95% complete.

The pyrolysis‡‡ of this OMM in an inert atmosphere (N_2) at 800 °C gives a high yield[12]§§ (*ca.* 75%) of a black ceramic material, **C1**. The ^{29}Si MAS spectrum of **C1**, Fig. 5(*a*), shows three broad peaks at *ca.* −103.2, −69.2 and −33.2 with a shoulder on the last peak at *ca.* − 5. Comparison of these values with the ones observed in the ^{29}Si CPMAS NMR spectrum of the starting OMM, Fig. 4(*a*), clearly shows that pyrolysis results in extensive changes in the number of oxygen or carbon atoms bonded to the silicon atoms.[13] In the OMM the silicon atom environments can be described as SiO_4^{Si}, SiC_3O^{Si} and SiC_4, while in **C1** they are best described as $SiO_4^{C,Si}$, $SiCO_3^{C,Si}$, $SiC_2O_2^{C,Si}$, and SiC_4 on the basis of the ^{29}Si MAS NMR spectrum, Fig. 5(*a*).

When **C1** is leached with HF it undergoes no visible change but a weight loss of ca. 42% is observed.¶¶ The ^{29}Si MAS NMR spectrum, Fig. 5(*b*), of the black product, **C2**, shows that the intensity of the peak assigned to SiO_4 is diminished relative to the other peaks when compared to the ^{29}Si MAS NMR spectrum of **C1**. Since **C2** has been found to be microporous with pore sizes in the nanometre range, **C1** must be a nanocomposite material consisting of an amorphous SiO_2-rich phase which is derived from the spherosilicate moieties in the starting OMM and dispersed in an amophous Si–C–O phase derived from the cross-linking groups.

The synthetic procedure described above is potentially a general one applicable to a wide variety of OMMs. In addition to the spherosilicate based OMMs, one could conceivably prepare OMMs based on tubular silicates[15] and lamellar silicates.[16] The microporous ceramic materials derived from these various OMMs would exhibit differences that reflect the differences in the structures of the starting OMMs thus affording a certain degree of control over the properties of these novel materials.

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†† $SiC_mO_n^{X,Y}$, $m + n = 4$; denotes a silicon atom in a tetrahedral environment consisting of *m* carbon atoms and *n* oxygen atoms where the oxygen atoms may be linked to atoms of type X or Y.

‡‡ Quartz tube reactor placed in a vertical tube furnace. Heated from 100 to 800 °C in 1 h, held at 800 °C for 2 h.

§§ Determined from TGA trace of pyrolysis under N_2.

¶¶ **C1** (0.86 g) was leached twice with 48% aqueous HF (5 ml) for a total of *ca.* 30 h in a Teflon beaker and washed with distilled H_2O. The air-dried weight was 0.59 g. The TGA trace of this material shows a 14.76% weight loss around 100 °C, which agrees well with the value determined from the Gurvitsch rule[14] for the amount of H_2O adsorbed. The yield of **C2** is therefore only 0.5 g (58%).