

### Si(NHMe)<sub>4</sub> synthesis and characterisation

All procedures carried out under dry N<sub>2</sub>. SiCl<sub>4</sub> (18 cm<sup>3</sup>, Aldrich, 99%) was dissolved in n-pentane (90 cm<sup>3</sup>, distilled from Na/benzophenone) and cooled to -78 °C. Methylamine (100 cm<sup>3</sup>, Fluka, >99%) was passed through a column of dried molecular sieves and into the solution. The solution was allowed to warm to room temperature and filtered to remove the MeNH<sub>2</sub>.HCl by-product. Solvent was removed *in vacuo* to yield the crude product as a clear oily solid. Vacuum sublimation at 50 °C resulted in the low melting but crystalline product. Microanalysis C 31.8%, H 11.0%, N 36.7% (32.4, 10.9, 37.8 for Si(NHMe)<sub>4</sub>). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K) δ = 2.58 (d, 3H), 0.36 (broad, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K) δ = 28 (s). IR ν = 3378 (s), 2887 (s), 2806 (s), 1379 (s), 1204 (m), 1101 (s), 1049 (m), 952 (s), 809(s) cm<sup>-1</sup>.

### Gel formation

These experiments were carried out in thick walled glass pressure tubes. Attached to this was a graduated sidearm so that ammonia could be measured as liquid at -78 °C, distilled into the main reaction tube and sealed with a 12 mm PTFE tap. The system was designed to withstand the ~14 bar pressure that could be exerted on them if liquid ammonia were present at room temperature but obviously if one of these glass tubes were to become pressurised it could burst, so suitable safety precautions are essential.

Gels were prepared by exposing a solution of Si(NHMe)<sub>4</sub> (0.5 g) in THF (6 cm<sup>3</sup>) to dried ammonia (0.16 cm<sup>3</sup> at -78 °C). The ammonia was dried as a Na/NH<sub>3</sub> solution and stored in a steel pressure vessel. The solution was allowed to warm slowly overnight and once at around -20°C a single drop of trifluoromethanesulfonic acid (Aldrich, >99%) was added. Translucent gels developed over ~40 min. A glass tube was placed in the reaction mixture before gelation so that a monolithic sample could be extracted from the gel body.

### Gel drying

Ambient pressure drying was achieved by placing a gel in a glass jar in the glove box and loosening the top of the jar so that the solvent could slowly evaporate.

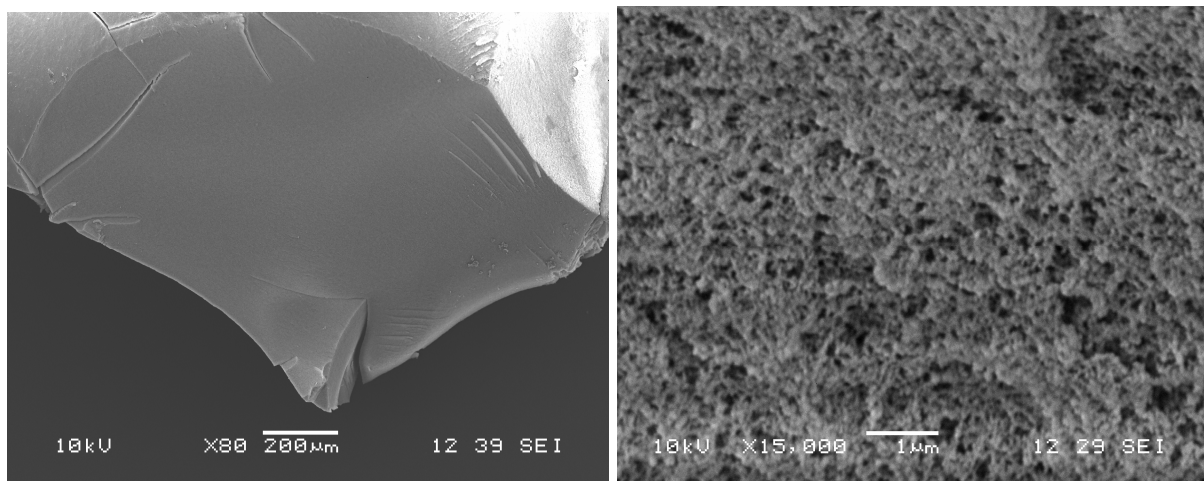
For supercritical drying, diethylamine was dried by distillation from BaO and saturated with ammonia by bubbling the dry gas through it for 2 h. Gel samples were loaded into a 3/4" diameter steel tube in the glove box, the compression fittings sealed inside the glove box before being placed inside a tube furnace (Lenton Furnaces LTF-12/38/130). Copper heating blocks were used to maintain even temperature. The pre-heater was constructed by coiling 6 m of 1/8" tubing around a band heater/Al block; the assembly and connecting pipe-work was then suitably lagged with glass wool and aluminium foil. The cooling coil was constructed from 2m of 1/16" tubing immersed in cold water. The high-pressure apparatus was set up as follows:

Solvent Flask → HPLC pump (Jasco PU-2080) → Pre-heater Coil → Heated Reactor Tube → Cooling Coil → Back-Pressure Regulator (Jasco BP-2080-81).

The pressure was set at 80 bar (8 MPa) and the system pumped, whilst slightly tilted until this pressure was reached. The vessel was then laid flat. The pre-heater was then set to 250 °C and the sample furnace at 300 °C. Solvent was pumped at 2 cm<sup>3</sup>/min for 2½ h. The system was then depressurised from 80 to 5 bar over a 30 min period. Dry NH<sub>3</sub> was flushed through the system from

a pressurised bomb at 5 bar for 20 min. The system was sealed and allowed to cool to room temperature. Samples were removed from the tube in the glove box and stored under N<sub>2</sub>.

*It should be noted that the use of such high-pressure high-temperature equipment should be attempted by trained individuals, especially whilst employing ammonia saturated diethylamine, which is particularly corrosive at even at RTP.*



**Fig. S1** SEM images of silicon imidonitride aerogel. These show the fracture surface where a piece of aerogel was broken from the monolith body for analysis. The larger pores are clearly visible in the surface of the right-hand image.

## Instrumentation

Infrared spectra were recorded on a Perkin Elmer Spectrum 1 spectrometer as pressed CsI disks in an airtight housing with CsI windows. NMR spectra were recorded in C<sub>6</sub>D<sub>6</sub> on a Bruker AV300 spectrometer. Microanalysis (C, H, N) was performed by Medac Ltd, Egham, Surrey, UK. Thermogravimetric analysis was carried out using a Mettler Toledo TGA851e housed in a glove box, under flowing high purity nitrogen (Air Products BiP grade). Powder X-ray diffraction measurements used a Siemens D5000 diffractometer with monochromated Cu-K<sub>α1</sub> radiation and a cell with plastic film windows to maintain the nitrogen sample atmosphere. SEM used a Jeol JSM-5910 with carbon coated samples. TEM (Jeol JEM-3010) samples were made up by gently crushing a piece of aerogel and suspending in dry toluene using ultrasound, then placing a drop onto a carbon grid and allowing to evaporate. Solid state <sup>29</sup>Si MAS-NMR data were collected at ambient temperature at the EPSRC service at Durham University using a Varian Unity Inova spectrometer operating at 59.56 MHz referenced to tetramethylsilane. The somewhat noisy spectra for the aerogel samples even with long collection times (42 hours for the sample in Fig. 3) are due to the long relaxation time (a 900 s recycle delay was needed) combined with the low density of the samples. Surface area analyses were undertaken by MCA Services, Cambridge, by nitrogen adsorption/desorption on a Micromeritics Tristar analyser.