A non-oxide sol–gel route to synthesise silicon imidonitride monolithic gels and high surface area aerogels†

Shereen Hassan,[a] Andrew L. Hector,*[a] Jason R. Hyde,[b] Ali Kalaji[a] and David C. Smith[b]

Received (in Cambridge, UK) 18th June 2008, Accepted 6th August 2008
First published as an Advance Article on the web 12th September 2008
DOI: 10.1039/b810317h

Monolithic gels have been produced by reaction of $Si(NHMe)_4$ with ammonia in THF solution and converted to high surface area aerogels by critical point drying with ammonia saturated diethylamine solvent.

Aerogels are 3-dimensional materials with extraordinary properties derived from their very low density and highly porous structures.[1] SiO_2 aerogels are the most studied and are useful thermal insulators, optical materials, radiation detectors, sensors and catalyst supports. These are usually produced by using a supercritical fluid to exchange the solvent, then depressurising above the critical temperature of the fluid directly to the gas phase, thus avoiding any destructive surface tension effects. There is also extensive work on aerogels made from other oxides,[2] carbon[3] and recently II–VI semiconductor materials.[4]

There are few examples of nitride aerogels. Hexagonal BN aerogel monoliths have been prepared by CO_2 critical point drying of gels produced from $[(BCl)(NH)]_3$ and $(Me_3Si)_2NH$.[5] Ammonolysis of vanadium oxide aerogels or foams have also been shown to result in catalytically active vanadium oxynitrides that retain some of their porous structure.[6] However, high temperature ammonolysis of oxides requires forcing conditions and is not viable as a general route to nitride aerogels as either the aerogel framework will disintegrate, or the pores will close during the reaction.

One of the major sources of interest in forming aerogels of nitride materials is the possibility of using them in catalysis, since nitrides exhibit useful activities for hydroprocessing and a range of other reactions.[7] For silicon nitride, catalytic work has focussed on precursor derived materials that contain residual imide and/or amide groups. Porous silicon imidonitride powders have been shown to be more active than MgO for the Knoevenagel condensation to produce benzylidene malonitrile.[8] Potassium impregnation of a similar material with KNH_2 results in a superbase catalyst with close to 100% selectivity for isomerisation of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene.[9] Non-oxide sol–gel derived microporous silicon imidonitride powders, with pore sizes tuned by long chain amine templates, show enhanced activity for alkylation of styrene with ethane.[10]

Whilst synthetically more difficult than with oxides, sol–gel chemistry has the potential to produce nitrides in forms that cannot currently be accessed, and hence increase the technological potential of these materials.[11–14] Jansen and co-workers used $Si(NHMe)_4$ with transition metal amides to produce metal doped silicon nitride amorphous powders.[12] Bradley and co-workers developed $Si(NH_2)(NMe_2)_3$ as a precursor to silicon (imido)nitride,[13] acid catalysed condensation of this precursor followed by exposure to ammonia resulted in translucent monolithic gels, though these fragmented on drying and powders were the main products of this work. Kroke and co-workers have used NCN^- to crosslink Me_3SiCl resulting in monolithic silicon carbodiimide gels that can be pyrolysed to carbonitride.[14] Porous membranes have been produced from these gelation processes,[15,16] but there are no reports of drying the gels to produce bulk monoliths.Monolithic gels were produced by reacting $Si(NHMe)_4$ with two molar equivalents of NH_3 in THF solution followed by the addition of an acid catalyst.‡ The clear solution rapidly showed signs of turbidity and could maintain its shape when the vessel was tilted after 40 min. At this point the gel was white and translucent. No further changes in appearance were observed even over a period of 4 weeks. These gels do not undergo syneresis as reported by Bradley and co-workers[13] and Kroke and co-workers[14] for related systems.

After removal of solvent under vacuum, which resulted in total fragmentation of the gel body, IR spectra showed ν_{C-H} ($\sim$2900 cm^{-1}) and a broad ν_{N-H} ($\sim$3400 cm^{-1}) feature plus two further bands at $\sim$900 and $\sim$1200 cm^{-1}. This is similar to spectra of $Si(NH)_x(NH_2)_y(NMe_2)_z$ gels reported by others,[15] of course the difference here is that NHMe groups are present rather than NMe_2. TGA under nitrogen showed a stepped mass loss of $\sim$40% by 400 °C followed by a gradual loss of a further 10% by 900 °C. These features correspond to rapid initial condensation with loss of any of the small, volatile oligomers $MeNH_2$ and NH_3, followed by slower condensation as the polymeric xerogel becomes a rigid ceramic.

Slow drying of gels under nitrogen at ambient pressure resulted in massive shrinkage of the monolith body to around 10% of its original dimensions. However, flushing with supercritical diethylamine at 300 °C and 8 MPa pressure followed by controlled depressurisation yielded aerogel monoliths with very little dimensional change (*approx*. 2 mm shrinkage in the length of a 30 mm sample). A xerogel and an aerogel produced by these two processes are shown in Fig. 1. CO_2 is commonly used as the supercritical fluid in such processes, but was not used here due to concerns about reactivity with these gels. Since the mass loss in the TGA data under nitrogen was so

---

[a] *School of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ. E-mail: A.L.Hector@soton.ac.uk; Fax: +44(0)23 8059 3781; Tel: +44(0)23 8059 4125*
[b] *School of Physics and Astronomy, University of Southampton, Highfield, Southampton, UK SO17 1BJ*

† Electronic supplementary information (ESI) available: Full experimental information and SEM images of the aerogels. See DOI: 10.1039/b810317h

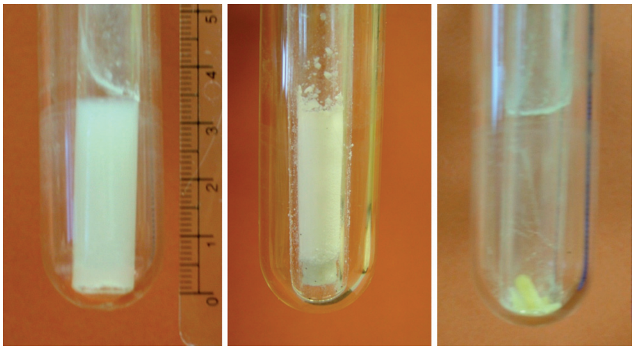

Fig. 1 Photographs of a wet gel (left), a SCF dried aerogel (centre) and a xerogel dried at ambient temperature under dry nitrogen (right).

significant, the Et_2NH solvent was saturated with ammonia in a bid to crosslink the gel during the drying process and hence minimise loss of any small oligomers or monomeric species. This may also have the effect of reducing the number of organic amide substituent groups remaining in the gel since these should be readily replaced by NH_2 groups.

Powder X-ray diffraction showed the aerogels to be amorphous. IR spectra, Fig. 2, showed $\nu_{N–H}$ at 3370 cm^{-1} with a weak shoulder at 3470 cm^{-1} corresponding to ν_{NH2}, $\nu_{C–H}$ at 2960–2800 cm^{-1}, δ_{NH2} at 1545 cm^{-1} and 2 $\nu_{Si–N}$ bands at 1210 and 925 cm^{-1}. This is similar to powdered gels pyrolysed under nitrogen at the same temperature[17] except that no $\nu_{C\equiv N}$ stretch due to pyrolysis of amide groups ($\sim$2250 cm^{-1}) was observed. Microanalysis varied somewhat from sample to sample with typically 8% C, 4% H and 36% N. Si_3N_4 contains 40% N but these gels contain NH, NH_2 and NHMe groups, so the nitrogen content should be higher. It can be difficult to obtain good nitrogen analysis because Si_3N_4 has high oxidation resistance. This was tested with a commercial Si_3N_4 sample (Aldrich, $<$50 nm particle size) which showed a nitrogen content of 35%. TGA under nitrogen showed a mass loss of around 16% between 400 and 600 °C, giving some indication of the proportion of the mass due to condensable groups. ^{29}Si MAS-NMR showed a broad resonance at -41 ppm (Fig. 3). Crystalline Si_3N_4 has signals at -47 to -49 ppm[18] but a broad resonance at -41 ppm has previously been observed in gel derived silicon imidonitride samples and ascribed to SiN_4 tetrahedra containing a significant number of amide/imide groups,[17] which produced Si_3N_4 when pyrolysed at higher temperature.

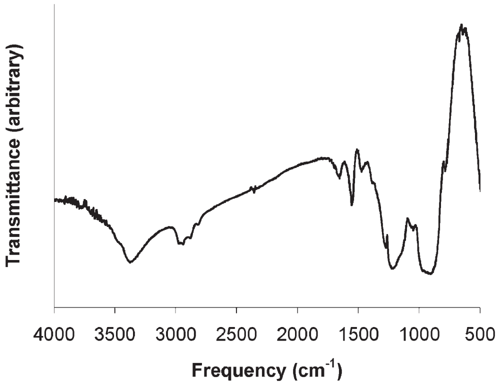

Fig. 2 IR spectrum of a silicon imidonitride aerogel (CsI disc).

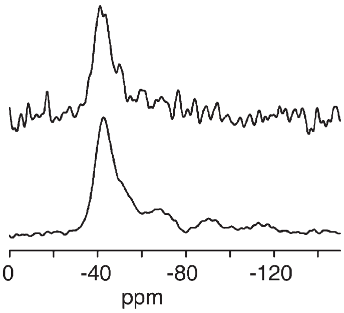

Fig. 3 ^{29}Si MAS-NMR spectra of two silicon imidonitride samples prepared under different conditions: an aerogel (top) and a xerogel heated at 300 °C under NH_3 (bottom).

For comparison, a xerogel recovered by removing the solvent *in vacuo* was heated to 300 °C under NH_3. This xerogel was also amorphous. The IR spectrum closely resembled that in Fig. 2 except that the $\nu_{C–H}$ bands were absent and a $\nu_{C\equiv N}$ peak was observed at 2230 cm^{-1} suggesting that organic substituent groups had decomposed under these conditions. TGA under nitrogen showed a mass loss of $\sim$13% at 400 °C followed by a further gradual loss of $\sim$12% up to 900 °C, a similar profile to the gel itself but with smaller mass losses. ^{29}Si MAS-NMR (Fig. 3) showed a similar resonance to that of the aerogel at -43 ppm, with weaker peaks at around -50, -69 and -90 ppm.

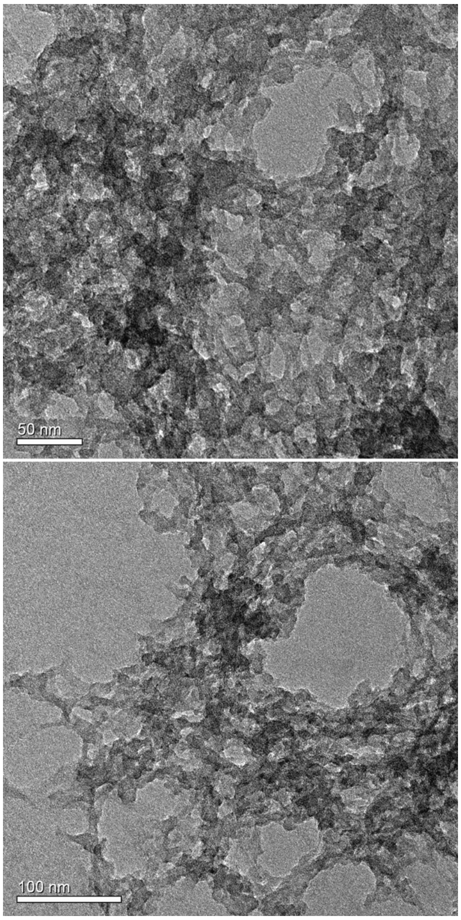

Fig. 4 TEM images of a silicon imidonitride aerogel sample. The scale bar is 50 nm in the top image and 100 nm in the bottom.

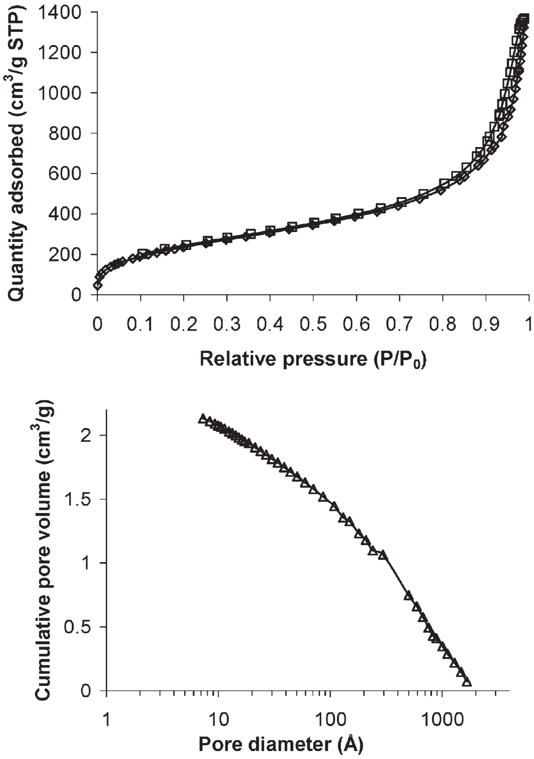

Fig. 5 Adsorption–desorption isotherms (top) and pore volume calculation (bottom) of a silicon imidonitride aerogel.

These resemble signals seen in oximide gels and attributed to SiN_3O, SiN_2O_2 and $SiNO_3$ groups.[19] The ammonia used for the pyrolysis was dried over a column of molecular sieves and this data shows how moisture sensitive the gels are during heating. The lack of these resonances in the NMR spectra of the aerogels demonstrates that these contain very low levels of oxygen.

SEM images of the aerogels (see ESI†) showed sheer faces where the fragment studied had been fractured from the monolith body with large (100–200 nm) pores visible from the surface. TEM showed a network of small ($\sim$20 nm) pores separated by thin walls, Fig. 4, with the large pores running through this structure. EDX showed strong silicon and nitrogen signals plus some oxygen (samples were handled in air prior to analysis). Pores were not observed by electron microscopy in xerogels heated under NH_3 at 300 °C.

Nitrogen adsorption–desorption experiments revealed the aerogels to be mesoporous with a type IV profile, Fig. 5. The BET surface area is 883(3) m^2 g^{-1}. The BJH pore volume calculation reveals a wide range of pore sizes from 0.7 to 170 nm, with around 50% of the pore volume due to pores greater than 10 nm in size. The high proportion of larger pore sizes is also reflected in the relatively tight hysteresis loop.

In view of the previous work on catalytic activity of similar compositions, it can be assumed that these aerogels will provide useful catalysts. A broad range of possibilities also exists to modify the pore structure or surface properties (*e.g.* concentration of NH_2 and NHMe groups) of these materials through changes to the gelation, aging or drying procedure. It is also potentially useful to make these materials in this monolithic form rather than very low density powder since they could potentially be used for catalysis in a gas- or supercritical fluid-phase flow process.[20]

In summary, silicon imidonitride aerogels are produced by critical point drying of $Si(NHMe)_4$-based monolithic gels. These have an open pore structure and high surface area and are potentially useful catalytic materials.

The authors thank the Royal Society for a University Research Fellowship (ALH), the Egyptian government for a study scholarship (SH) and RCUK for support under EP/C006763/1 (JRH). Thanks also to David Apperley for recording solid-state NMR spectra at the EPSRC Service in Durham and to Barbara Cressey for collecting TEM data.

Notes and references

‡ $Si(NHMe)_4$ was produced from $SiCl_4$ and H_2NMe, then purified by sublimation.[16] Gels were prepared by exposing a solution of $Si(NHMe)_4$ (0.5 g) in THF (6 cm^3) to dried ammonia (0.16 cm^3 at −78 °C). The solution was allowed to warm slowly overnight by sublimation of a dry ice bath. At ~ -20 °C a drop of trifluoromethanesulfonic acid was added and the tube removed from the cold bath. Gelation occurs over a period of around 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. At −78 °C the $Si(NHMe)_4$ starting material is partially precipitated, so it is important to warm the solution before acid addition. However, when the solution is close to 0 °C it becomes turbid and at room temperature some precipitation is observed. To obtain translucent gels, the acid must be added at low temperature.

1 N. Hüsing and U. Schubert, *Angew. Chem., Int. Ed.*, 1998, **37**, 22.
2 A. M. Orlovic, D. T. Janackovic and D. U. Skala, Aerogels in Catalysis, in *New Developments in Catalysis Research*, ed. L. P. Bevy, Nova Science Publishers, Hauppauge NY, 2005, ch. 2.
3 C. Moreno-Castilla and F. J. Maldonado-Hódar, *Carbon*, 2005, **43**, 455.
4 S. L. Brock, I. U. Arachchige and K. K. Kalebaila, *Comments Inorg. Chem.*, 2006, **27**, 103; Y. P. Gao, C. N. Sisk and L. J. Hope-Weeks, *Chem. Mater.*, 2007, **19**, 6007.
5 R. T. Paine and C. K. Narula, *Chem. Rev.*, 1990, **90**, 73.
6 O. Merdrignac-Conanec, K. El Badraoui and P. L'Haridon, *J. Solid State Chem.*, 2005, **178**, 218; P. Krawiec, P. L. de Cola, R. Gläser, J. Weitkamp, C. Wiedenthaler and S. Kaskel, *Adv. Mater.*, 2006, **18**, 505.
7 For reviews see: J. S. J. Hargreaves and D. Mckay, *Catalysis Specialist Periodical Report*, Royal Society of Chemistry, London, 2006, vol. 19, p. 84; E. Furimsky, *Appl. Catal., A*, 2003, **240**, 1.
8 D. Hullmann, G. Wendt and G. Ziegenbalg, *Chem. Eng. Technol.*, 2001, **24**, 147.
9 S. Kaskel and K. Schlichte, *J. Catal.*, 2001, **201**, 270.
10 D. Farrusseng, K. Schlichte, B. Spliethoff, A. Wingen, S. Kaskel, J. S. Bradley and F. Schüth, *Angew. Chem., Int. Ed.*, 2001, **40**, 4204.
11 A. L. Hector, *Chem. Soc. Rev.*, 2007, **36**, 1745; A. W. Jackson and A. L. Hector, *J. Mater. Chem.*, 2007, **17**, 1016.
12 J. Löffelholz, J. Engering and M. Jansen, *Z. Anorg. Allg. Chem.*, 2000, **626**, 963.
13 R. Rovai, C. W. Lehmann and J. S. Bradley, *Angew. Chem., Int. Ed.*, 1999, **38**, 2036.
14 C. Balan, K. W. Völger, E. Kroke and R. Riedel, *Macromolecules*, 2000, **33**, 3304; E. Kroke, *Adv. Sci. Technol.*, 1999, **15**, 123.
15 F. Cheng, S. M. Kelly, S. Clark, J. S. Bradley, M. Baumbach and A. Schütze, *J. Membr. Sci.*, 2006, **280**, 530; R. Hauser, S. Nahar-Borchard, R. Riedel, Y. H. Ikuhara and Y. Iwamoto, *J. Ceram. Soc. Jpn.*, 2006, **114**, 524.
16 H. Andersch and M. Jansen, *Acta Crystallogr.*, 1990, **C46**, 1985.
17 F. Cheng, S. Clark, S. M. Kelly and J. S. Bradley, *J. Am. Ceram. Soc.*, 2004, **87**, 1413.
18 K. R. Carduner, C. S. Blackwell, W. B. Hammond, F. Reidlinger and G. R. Hatfield, *J. Am. Chem. Soc.*, 1990, **112**, 4676.
19 F. Cheng, S. M. Kelly, F. Lefebvre, A. F. Lee, K. Wilson, S. Clark and J. S. Bradley, *J. Mater. Chem.*, 2005, **15**, 3039.
20 K. Morley, P. Licence, J. R. Hyde, S. M. Howdle, R. Mokaya and P. Marr, *J. Mater. Chem.*, 2004, **14**, 1212.