COMMUNICATION

Preparation of a mesoporous silicon boron nitride *via* a non-aqueous sol–gel route

Fei Cheng,[a] Berangere Toury,[a] Frédéric Lefebvre[b] and John S. Bradley*[a]

[a] Department of Chemistry, University of Hull, Cottingham Road, Hull, UK HU6 7RX.
E-mail: j.s.bradley@hull.ac.uk

[b] Laboratoire de Chimie Organométallique de Surface, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne Cedex, France

A silicon boron imide based gel $Si_3B(NH)_x(NH_2)_y(NMe_2)_z$ was prepared *via* catalytic ammonolysis of tris[tris(dimethylamino)silylamino]boron $B\{HNSi[N(CH_3)_2]_3\}_3$; pyrolysis of the gel under ammonia at 1000 °C gives a mesoporous silicon boron nitride with high surface area and narrow pore size distribution.

Preparation of micro- and mesoporous solids has attracted considerable attention because of their potential size-selective properties in applications such as catalysis, catalyst supports, and membrane materials.[1,2] The overwhelming majority of these materials are oxides prepared from flame pyrolysis or aqueous sol–gel techniques.[3] Recently, non-oxidic sol–gel processes have been developed with the goal of producing novel porous non-oxide solids. Paine and co-workers reported the preparation of a microporous boron nitride aerogel by reaction between 2,4,6-trichloroborazine and 1,1,1,3,3,3-hexamethyldisilazane.[4] A sol–gel process in ammono-system was reported by Jansen and co-workers to prepare polymeric boron-, titano- and tantalo-silazanes by controlled coammonolysis of the elemental alkylamides.[5] In our group, a high surface area mesoporous silicon diimide gel, a precursor for high purity silicon nitride,[6] has been prepared in a non-oxide sol–gel process by the reaction of tri(dimethylamino)silylamine (TDSA) with ammonia in the presence of an acid catalyst.[7]

Since ceramic composites consisting of two or more binary nitrides often show improved properties compared with single-component ceramics,[8] we are attempting to extend this non-aqueous sol–gel technique to the preparation of ternary imidosilicate gels which would be promising precursors for multinary silicon-based nitride materials in high surface area porous form. The synthetic strategy we have adopted uses TDSA as a starting material to assemble single source precursor molecules containing, in addition to peripheral $Si(NMe_2)_3$ groups, Si–N–M backbones (M = Al, B, Ti, Zr…). The peripheral $Si(NMe_2)_3$ groups in the molecules allow us to use the proven ammonolytic chemistry of TDSA to produce multinary imidosilicate gels with high atomic level homogeneity as precursors to micro- and mesoporous homogenous ternary nitride-based materials.

Here we report the successful preparation of a mesoporous silicon boron nitride by pyrolysis of a silicon boron imide based gel which was prepared *via* a non-aqueous sol–gel technique using tris[tris(dimethylamino)silylamino]boron $B\{HNSi[N(CH_3)_2]_3\}_3$ **1** as the precursor.

All procedures were performed under a protective nitrogen atmosphere using standard Schlenk techniques or in nitrogen filled glove box. Solvents were distilled over appropriate drying agents.

Tris[tris(dimethylamino)silylamino]borane $B\{HNSi[N(CH_3)_2]_3\}_3$ **1** was prepared as a colourless oil from the reaction of boron trichloride BCl_3 with TDSA,[7] in the presence of triethylamine as shown in eqn. (1).[9]

$$BCl_3 + 3H_2NSi(NMe_2)_3 + 3Et_3N$$
$$\xrightarrow{pentane} B[HNSi(NMe_2)_3]_3 + 3Et_3H \cdot HCl \quad (1)$$
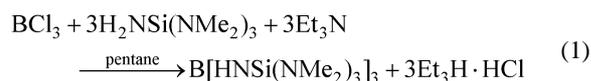
Gelation of compound **1** was carried out by ammonolysis in tetrahydrofuran solution in the presence of a catalytic amount of trifluoromethanesulfonic acid (eqn. (2)):

$$B[HNSi(NMe_2)_3]_3 + 9NH_3$$
$$\xrightarrow{CF_3SO_3H} BSi_3(NH)_3(NH_2)_9 + 9HNMe_2 \quad (2)$$
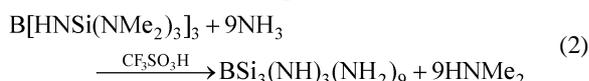
To a solution of **1** (2.66 g, 4.96 mmol) in dry THF (150 mL) was added trifluoromethanesulfonic acid (27.8 μL, 0.31 mmol) at room temperature. After 30 min, a solution of ammonia (50 mmol) in THF (10 mL) was added, and the mixture was left quiescent at room temperature for a further 3 days, at which point a slight opalescence was observed. The solution was re-saturated with ammonia by addition of liquid ammonia solution (10 mL) and the resulting mixture was left to stand at 50 °C for 3 days, giving a translucent semi-rigid gel. Evaporation of the solvent and evolved dimethylamine in a stream of nitrogen followed by drying under reduced pressure at 50 °C for 6 h yielded a translucent white solid.

The IR spectra of the gel and pyrolyzed product, as well as compound **1** are shown in Fig. 1. Compared to the IR spectrum of **1**, the ν(N–H) band at 3347 cm^{-1} became broad and a low intensity band at 1571 cm^{-1} (due to the presence of NH_2) was observed, suggesting that the NH groups are present with different environments such as Si–NH–B, Si–NH–Si and SiNH$_2$. The intensity of the ν(CH) bands from 2796 to 2993 cm^{-1} decreases greatly, but significant amounts of dimethyamino groups are still present in the gel. Thermogravimetric analysis in combination with mass spectrometry showed that dimethylamine and ammonia are the principal gases evolved below 700 °C, as expected for the elimination of the –NMe_2 and –NH_x groups of the gel as further condensation occurred, consistent with the IR results. These spectral features indicated that ammonolysis of **1** leads to the formation of a silicon boron imide based gel containing residual dimethylamino groups: $Si_3B(NH)_x(NH_2)_y(NMe_2)_z$. Nitrogen adsorption analysis showed that the dried gel exhibited a mesoporous structure (type IV physisorption isotherm) with a BET surface area of 260 m^2 g^{-1}.
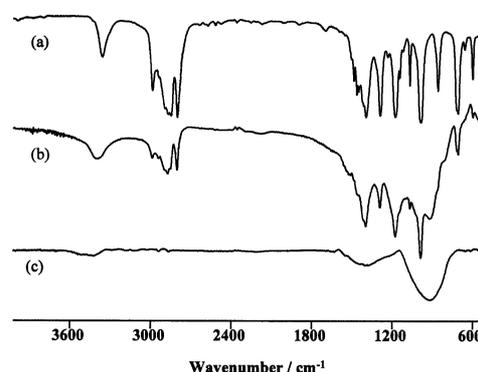
Fig. 1 IR spectra of (a) the precursor compound **1**, (b) the gel from **1**, and (c) the product pyrolyzed from the gel at 1000 °C under NH$_3$ flow.

Pyrolysis of the gel was performed under an NH_3 flow using a tube furnace. An X-ray amorphous white solid was obtained after pyrolysis at 1000 °C for 2 h. Inductively coupled plasma emission analysis showed that the molar ratio of silicon to boron in the pyrolyzed product was 2.89:1, close to that in the precursor compound **1**. The IR spectrum of the solid (Fig. 1) showed two broad absorbances at 1409 and 954 cm^{-1}, which can be ascribed to $\nu(B–N)$ and $\nu(Si–N)$, respectively.[10] The presence of a small amount of residual hydrogen in the final product is suggested by low intensity infrared absorptions in the $\nu(NH)$ region (Fig. 1(c)).The absence of any resonances in the ^{13}C CP-MAS NMR spectrum and the absence of any colour in the product confirmed that the pyrolyzed product is carbon free. ^{29}Si NMR CP-MAS NMR showed a single broad resonance at −44 ppm ascribable to the presence of Si_3N_4.[11] The ^{11}B MAS NMR spectrum was characterized by a powder pattern indicative of a second order quadrupolar interaction. Simulation of the line shape gave the following parameters: isotropic chemical shift δ = 30 ppm, quadrupolar coupling constant C_Q = 3.6 MHz, asymmetry facter η = 0.13, which can be ascribed to the presence of hex-BN.[12] X-Ray powder diffraction revealed no evidence of crystallinity and no ordering of the pores. On the basis of these results the white amorphous solid is identified as a Si_3N_4/BN composite.

Physisorption analysis (Fig. 2) showed that the white solid displays a type IV nitrogen adsorption isotherm typical of a mesoporous material with a narrow pore size distribution and a BET surface area of 243 m^2 g^{-1}, suggesting a potentially useful mesoporous material with good selectivity.[13]
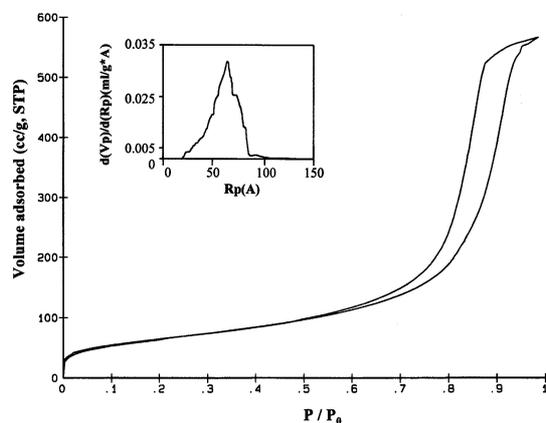
In summary, a mesoporous silicon boron nitride with high surface area and narrow pore size distribution has been prepared by pyrolysis of a silicon boron imide based gel, prepared *via* catalytic ammonolysis of tris[tris(dimethylamino)silylamino-]boron B{HNSi[N(CH$_3$)$_3$]$_2$}$_3$.

Notes and references

1 J. M. Thomas and W. J. Thomas, *Heterogeneous Catalysis*, VCH, Weinheim, 1997.
2 D. Farrusseng, K. Schlichte, B. Spliethoff, A. Wingen, S. Kaskel, J. S. Bradley and F. Schüth, *Angew. Chem., Int. Ed.*, 2001, **40**, 4204.
3 C. J. Brinker and G. W. Schere, *Sol–Gel Science*, Academic Press, London, 1990.
4 D. A. Lindquist, T. T. Borek, S. J. Kramer, C. K. Narula, G. Johnston, R. Schaeffer, D. M. Smith and R. T. Paine, *J. Am. Ceram. Soc.*, 1990, **73**, 757.
5 J. Löffelholz, J. Engering and M. Jansen, *Z. Anorg. Allg. Chem.*, 2000, **626**, 963.
6 K. S. Mazdiyasni and C. M. Cooke, *J. Am. Ceram. Soc.*, 1973, **56**, 628.
7 R. Rovai, C. W. Lehmann and J. S. Bradley, *Angew. Chem., Int. Ed.*, 1999, **38**, 2036.
8 K. K. Chawla, *Ceramic Matrix Composites*, Chapman & Hall, London, 1993.
9 Preparation and characterization of **1**: to a solution of TDSA (10.4 g, 59.0 mmol) in pentane (170 mL) was added triethylamine (9.62 g, 95 mmol) and boron brichloride BCl$_3$ (19.7 mmol) in pentane (60 mL) at −80 °C. After stirring at −80 °C for 1 h, the reaction mixture solution was allowed to return to room temperature and react for another 2 h. The resulting Et$_3$N·HCl was removed by filtration, and the filtrate concentrated under reduced pressure to give a liquid. ^1H NMR: δ 2.60 (s, 54H, N(CH$_3$)$_3$), 2.2 (s, 3H BNHSi); ^{13}C NMR: δ 37.9 (s, Si(N(CH$_3$)$_2$)]$_3$); ^{11}B NMR: δ 25.9 (s, BNH); ^{29}Si NMR: δ −34.4 (s, Si[N(CH$_3$)$_2$]$_3$); MS (*m/z*, EI): 536 [**1**]$^+$. IR (neat, cm^{-1}): 3347 (m, $\nu(NH)$); 2976 (s), 2856 (s), 2841 (s) 2790 (s), ($\nu(CH)$); 1395 (s), 1299 (s), 1172 (s), 992 (s), 871 (m), 717 (s).
10 K. Nakamoto, *Infrared and Roman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, Inc., New York, 1997.
11 K. R. Carduner, C. S. Blackwell, W. B. Hammond, F. Reidinger and G. R. Hatfield, *J. Am. Chem. Soc.*, 1990, **112**, 4674.
12 C. Gervais, F. Babonneau, J. Maquet, C. Bonhomme, D. Massiot, E. Framery and M. Vaultier, *Magn. Res. Chem.*, 1998, **36**, 407.
13 L. V. Wüllen and M. Jansen, *J. Mater. Chem.*, 2001, **11**, 223.

Fig. 2 Nitrogen adsorption isothem for the product pyrolyzed at 1000 °C under NH_3 flow.