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# Catalytic ammonolytic sol–gel preparation of a mesoporous silicon aluminium nitride from a single-source precursor

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## Abstract

A high-surface-area microporous silicon aluminum imide gel $Al_3SiN_2(NH)_w(NH_2)_x(NMe_2)_y(N^iPr)_z$ was prepared *via* catalytic ammonolysis of tetrakis(isopropylimino)bis[tris(dimethylamino)silylamino]alane $H_6Al_6(N^iPr)_4[NSi(NMe_2)_3]_2$. Pyrolysis of the gel under $NH_3$ flow at 1000 °C gave an amorphous Si–Al–N ceramic composite in which silicon is tetrahedrally coordinated with nitrogen. Aluminum is mainly present as mixed $AlN_4$ species. The Si–Al–N ceramic composite exhibits a mesoporous structure with relatively high surface area ($114 \text{ m}^2 \text{ g}^{-1}$) and narrow pore size distribution (2–8 nm).
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*Keywords:* Dimethylamino; Silylamino; Alane; Synthesis; Structure

## 1. Introduction

The preparation of micro- and mesoporous solids with a high effective surface area and a narrow-pore-size distribution has attracted considerable attention because of the potential size-selective properties of such porous materials as catalysts, catalyst supports and filters [1,2]. The sol–gel technique is an attractive approach for preparing micro/mesoporous oxide materials as powders, membranes and filters with high purity and homogeneity due to its flexibility and low temperature preparation of sols and gels [3]. A number of sol–gel processes to prepare highly porous non-oxide ceramics have also been reported, e.g., boron nitride [4–8], metal (carbo)nitrides [9–14], silicon carbonitride [15–21] and boron carbonitride [22,23]. A sol–gel process in an ammono-system has been used to prepare polymeric boron-, titano- and tantalo-silazanes by controlled co-ammonolysis of the elemental alkylamides [24]. The preparation of B/C/N xerogels by a reaction of B-trichloroborazine with bis(trimethylsilyl)carbodimide has also been reported [25]. A novel and efficient non-aqueous sol–gel process has been developed in our group to prepare high-surface-area porous silicon diimide gel by the acid-catalyzed ammonolysis of TDSA in an analogous manner to the synthesis of silica from orthosilicate esters [26]. Pyrolysis of the silicon diimide gel under $NH_3$ flow at 1000 °C gives a mesoporous silicon nitride with high-surface-area ($466 \text{ m}^2 \text{ g}^{-1}$) and narrow pore size distribution (3–7 nm) [27]. One of the authors has reported the preparation of *microporous* silicon imido nitrides with a degree of pore-size control by pyrolysis of gels prepared *via* a hot ammonolysis of TDSA in a concentrated solution of *n*-alkyl amines [2].

Microporous or mesoporous silicon nitride and its multinary or metal-doped derivatives are exceptionally attractive as porous ceramics due to a range of advantageous properties, e.g., a very high melting point, good thermal conductivity and stability, good hydrothermal and mechanical stability, high resistance to corrosion and general chemical inertness. These attributes would be especially

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advantageous in high-temperature applications, e.g., to inhibit sintering and coking due to hot-spots. Furthermore, the *basic* nature of mesoporous silicon nitride, silicon oxynitride, silicon boron nitride, silicon aluminium nitride and other multinary silicon/nitrogen derivatives induces a distinctly different physical property profile than that of the corresponding *acidic* silicates and may induce higher selectivity and activity as heterogeneous catalysts or catalyst supports in reactions where basicity promotes the reaction [28–30]. Silicon nitride has been shown to be a very useful support for catalytically active phases, e.g., the oxidation of methane using $Pd/Si_3N_4$ and $Pt/Si_3N_4$ [31–33], the selective hydrogenation of butadiene to butene using $Pd/Si_3N_4$ [29] and the dehydrogenation of propane using $Pt/Si_3N_4$ [28]. Our recent results show that nitrogen-based porous catalysts can be *superior* to commercially-available metal oxide catalysts for some gas-phase and liquid phase reactions [34,35].

Our interest is to develop new micro- and mesoporous non-oxide materials with high-surface-area accessible for applications in heterogenous catalysis, membranes and filters, e.g., for solid-state semiconductor gas sensors with improved performance in terms of sensitivity and selectivity [34–38]. Composite mesoporous ceramics consisting of two or more binary nitrides may be expected to have improved properties compared with single-component nitrides [39]. The most attractive approach to mesoporous ceramic composite nitrides involves the use of single-source molecular precursors possessing heterogeneous linkages such as M–N–M′, since an atomic level homogeneity of the ceramic components is present in suitable single-source precursors [40]. TDSA and its lithium salt are versatile reaction intermediates due to reactive $SiNH_2$ or SiNHLi groups in the preparation of a wide range of multinary silylamides, which contain, in addition to peripheral $Si(NMe_2)_3$ groups, Si–N–M backbones (M = Al, B, Ti, Zr, etc.). In such compounds each of the ceramogenic metal centres is in an exclusively $MN_n$ environment, which renders them particularly attractive as single-source precursors to multinary silicon-based nitride ceramics. Also, the presence of peripheral $Si(NMe_2)_3$ groups in the molecules allows the use of 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. Three single-source precursors containing boron have been prepared in our group so far, i.e., $B[NHSi(NMe_2)_3]_3$ [41], $B_3[NHSi(NMe_2)_3]_3N_3H_3$ [42,43] and $(NMe_2)B_3[NHSi(NMe_2)_3]_2N_3H_3$ [43], which were converted to mesoporous silicon boron nitride with different molar ratios by a non-aqueous ammonolytic sol–gel process [41,43]. The single-source precursor $\{Ti[NHSi(NMe_2)_3]_2[\mu\text{-}NSi(NMe_2)_3]\}_2$ was prepared and converted to mesoporous Si–Ti–N ceramic powder by a new ammonothermal process [44]. A mesoporous silicon aluminum nitride with Si:Al molar ratio of 3:1 was also prepared *via* a non-aqueous ammonolytic

sol–gel process using $(C_4H_8O)Al[HNSi(NMe_2)_3]_3$ as a precursor derived from aluminium trichloride [45,46]. This was the first example of the preparation of high-surface-area porous silicon aluminum nitride via a sol–gel route [46], although there is much previous work on the preparation of dense silicon aluminum nitride powders [47,48]. However, the content of aluminum in this composite is low, which effected the sensor selectivity and sensitivity to mixtures of polar and apolar gases. Since increasing the content of aluminum may increase the polarity and hydrophilicity of the composite ceramics, high-surface-area mesoporous silicon aluminum nitride ceramics with high aluminium to silicon ratios are expected.

In this paper, we will report the preparation of a new high-surface-area mesoporous silicon aluminum nitride with a high aluminum to silicon ratio *via* a non-aqueous ammonolytic sol–gel process using tetrakis(isopropylimino)bis[tris(dimethylamino)silylamino]alane $H_6Al_6(N^iPr)_4[NSi(NMe_2)_3]_2$, as a single-source precursor. The cage complex $H_6Al_6(N^iPr)_4[NSi(NMe_2)_3]_2$ was prepared in our group by reaction of TDSA with poly(isopropyliminoalane) $(HAlN^iPr)_6$ [49]. The silicon aluminum imide gel and its pyrolyzed product are characterized by FTIR, solid state NMR and nitrogen physisorption analysis.

## 2. Results and discussion

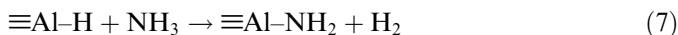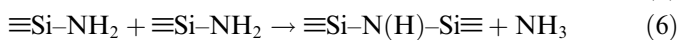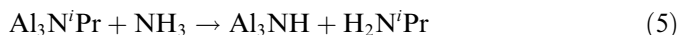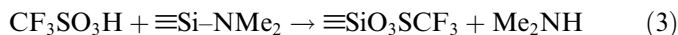### 2.1. Preparation of silicon aluminium imide gel

The silicon aluminum imide gel precursor molecule tetrakis(isopropylimino)bis[tris(dimethylamino)silylamino]alane $H_6Al_6(N^iPr)_4[NSi(NMe_2)_3]_2$, **1**, was prepared by a reaction between TDSA and poly(isopropyliminoalane) $(HAlN^iPr)_6$ according to our previous report (reaction (1)) [49]. The structure of the resultant white solid intermediate had been confirmed previously by $^1H$, $^{13}C$, $^{29}Si$ NMR, IR and single crystal X-ray analysis [49].



$$(1)$$
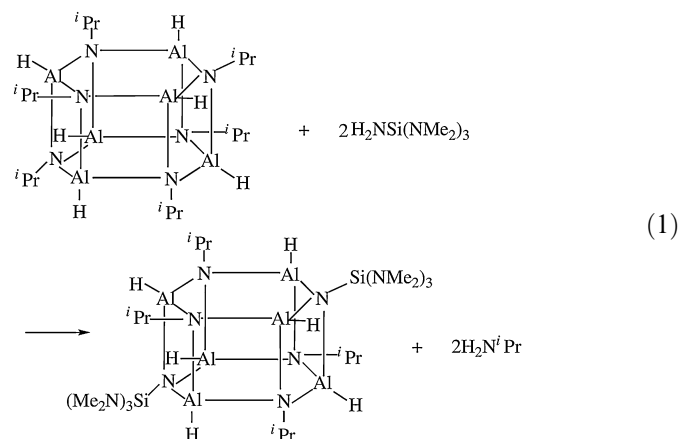
Gelation of compound **1** was carried out by ammonolysis in a tetrahydrofuran solution in the presence of a catalytic amount of trifluoromethane-sulphonic acid. An ideal reaction can be expressed by Eq. (2).

$$H_6Al_6(N^iPr)_4(NSi(NMe_2)_3)_2 + 16NH_3$$
$$\rightarrow (NH_2)_6Al_6(NH)_4(NSi)(NH_2)_3)_2 + 4H_2N^iPr$$
$$+ 6H_2 + 6HNMe_2 \qquad (2)$$
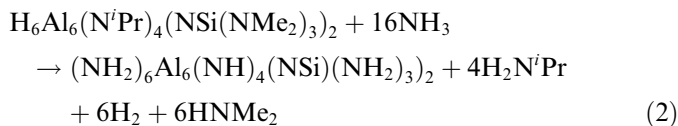
The IR spectrum of the gel and compound **1** are shown in Fig. 1. Compared to the IR spectrum of compound **1**, the intensity of $v$(CH) bands from 2790 to 2973 cm$^{-1}$ of the gel decreases greatly, but a considerable amount of alkyl groups remain. The dimethylamino groups in compound **1** can be removed easily by ammonia via reaction 3 and 4 as shown in the ammonolytic gelation of TDSA [27]. Removal of isopropylamino groups from the molecule on reaction with ammonia may be also possible (reaction (5)), but the fact that the N$^i$Pr groups are coordinated with three aluminum atoms makes the amine-exchange reaction difficult. The loss of adsorption bands at 1882 and 1873 cm$^{-1}$ is due to the reaction of AlH groups with ammonia to form a ≡Al–NH$_2$ species (reaction (7)). The broad $v$(N–H) band at 3367 cm$^{-1}$ and a low intensity band at 1570 cm$^{-1}$ (due to the presence of NH$_2$) suggest the presence of NH groups with different environments such as Si–NH–Al, Si–NH–Si, AlNH$_2$ and SiNH$_2$.

$$CF_3SO_3H + \equiv Si–NMe_2 \rightarrow \equiv SiO_3SCF_3 + Me_2NH \qquad (3)$$
$$\equiv SiO_3SCF_3 + NH_3 \rightarrow \equiv Si–NH_2 + CF_3SO_3H \qquad (4)$$
$$Al_3N^iPr + NH_3 \rightarrow Al_3NH + H_2N^iPr \qquad (5)$$
$$\equiv Si–NH_2 + \equiv Si–NH_2 \rightarrow \equiv Si–N(H)–Si\equiv + NH_3 \qquad (6)$$
$$\equiv Al–H + NH_3 \rightarrow \equiv Al–NH_2 + H_2 \qquad (7)$$
$$\equiv Al–NH_2 + \equiv Al–NH_2 \rightarrow \equiv Al–N(H)–Al\equiv + NH_3 \qquad (8)$$
$$\equiv Al–NH_2 + \equiv Si–NH_2 \rightarrow \equiv Al–N(H)–Si\equiv + NH_3 \qquad (9)$$

The broad bands at 950 and 710 cm$^{-1}$ are ascribable to the presence of $v$(SiN) and $v$(AlN), respectively [50]. All these spectral features indicate that ammonolysis of **1** produces a slightly inhomogeneous silicon aluminum imide gel containing residual dimethylamino and isopropylimino groups $Al_3SiN_2(NH)_w(NH_2)_x(NMe_2)_y(N^iPr)_z$. The presence of residual dimethylamino and isopropylimino groups suggests that the transamination reactions were not yet complete by the time of semi-rigid gel formation.
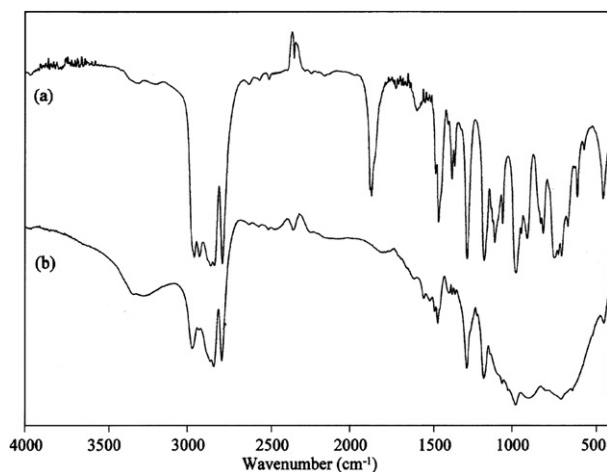
The formation of the gel should be attributed to the structure of the precursor molecule. The Si(NMe$_2$)$_3$ periphery of compound **1** undergoes a gelation process similar to that of H$_2$NSi(NMe$_2$) [27]. Trifluoromethane-sulfonic acid will react with Si(NMe$_2$)$_3$ groups to form a silyltriflate (Eq. (3)) [51], which is a very good leaving group [27,51] and can be easily substituted by NH$_3$ forming a reactive Si–NH$_2$ unit (Eq. (4)). One Si–NH$_2$ unit will then react with another Si–NH$_2$ unit to form a crosslinked network consisting of a Si–N(H)–Si backbone (Eq. (6)). Moreover, the ≡Al–NH$_2$ species formed from the reaction of AlH with NH$_3$ will also react with another ≡Al–NH$_2$ or Si–NH$_2$ unit to form a network consisting of Al–NH–Al and Al–N(H)–Si backbones (Eqs. (8) and (9)). Nitrogen adsorption analysis of this new gel shows a typical physisorption isotherm of type I, indicating the formation of microporous structure, see Fig. 2. The BET surface area is 442 m$^2$ g$^{-1}$.

## 2.2. Pyrolysis of the silicon aluminum imide gel

The TG analysis under Ar flow (Fig. 3) indicates that the ceramic yield of the gel up to 1000 °C is 56.2%. However, the residue after heating to 1000 °C was black, suggesting that carbon may have been retained in the pyrolyzed residue as free carbon or as a mixture of free carbon and carbide [52]. In order to reduce the degree of contamination by carbon the pyrolysis was carried out under active NH$_3$ flow [53].

Pyrolysis of the gel under an atmosphere of ammonia at temperature up to 1000 °C gave a white solid with a ceramic yield of 49%. ICP emission analysis shows that the molar ratio of the silicon to aluminum in the product is 1:2.9, the same ratio as that present in the precursor



Fig. 1. IR spectra of: (a) H$_6$Al$_6$(N$^i$Pr)$_4$[NSi(NMe$_2$)$_3$]$_2$, **1** and (b) the gel from **1**.
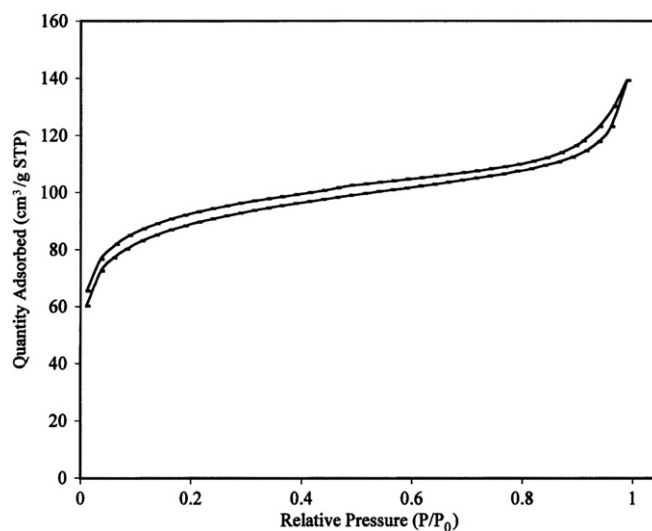


Fig. 2. Nitrogen physisorption isotherm of the silicon aluminum imide gel prepared from compound **1**.
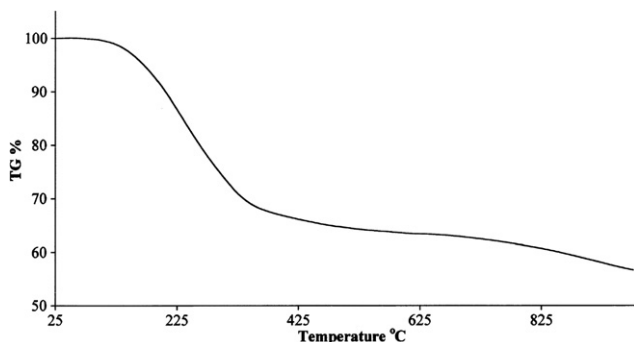
Fig. 3. TG of the silicon aluminum imide gel prepared from compound **1**.



Fig. 5. ^{29}Si CP-MAS NMR spectra of the product pyrolyzed from the silicon aluminium imide gel under $NH_3$ at 1000 °C.
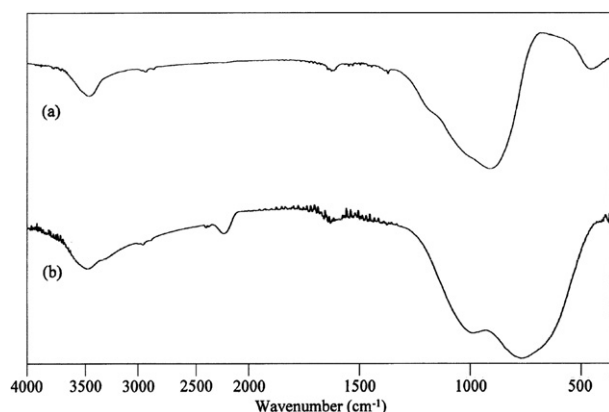


Fig. 4. IR spectra of: (a) pyrolyzed product of the silicon diimide gel prepared from TDSA and (b) pyrolyzed product of the silicon aluminum imide gel prepared from **1**.
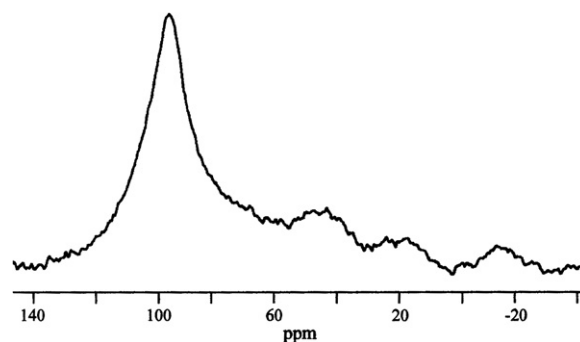


Fig. 6. ^{27}Al MAS NMR spectra of the product pyrolyzed from the silicon aluminum imide gel under $NH_3$ at 1000 °C.

compound **1** within experimental error. The IR spectra of the pyrolyzed product as well as the product pyrolyzed from silicon diimide gel formed from TDSA are showed in Fig. 4. The broad peak centered at 990 cm^{−1} is primarily attributed to $v$(Si–N) in amorphous $Si_3N_4$, which is ~40 cm^{−1} shifted from that of product pyrolyzed from silicon diimide gel [27]. The broad peak centered at 715 cm^{−1} is due to the presence of $v$(Al–N) [50]. The presence of a small amount of residual hydrogen in the final product is suggested by the low-intensity adsorption in the $v$(NH) region. A new small broad peak at ~2200 cm^{−1}, which is not present in the IR spectra of the pyrolyzed product from silicon imide gel, is probably formed during decomposition of the gel. A broad band in a similar position in the IR spectra of the pyrolyzed products (HAlN[i]Pr)$_6$ can be ascribed to the stretching vibration of C≡N groups [54,55].

The ^{29}Si CP-MAS NMR spectrum shows a single resonance at −49 ppm, indicating the formation of $SiN_{4/3}$ groups with a chemical shift comparable to that of β-$Si_3N_4$ [56] (Fig. 5). The ^{27}Al MAS NMR spectrum exhibits a broad signal at ~100 ppm, which can be ascribed to the $AlN_4$ environment (Fig. 6). The small broad signals at ~45 ppm, ~18 ppm and −15 ppm suggests that other aluminum environments such as $AlN_5$ units and $AlN_6$ may be present [57,58]. Formation of the mixed local chemical



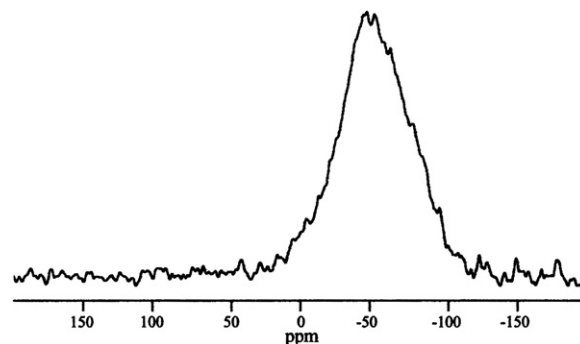Fig. 7. TEM of the product pyrolyzed from the silicon aluminum imide gel under $NH_3$ at 1000 °C.

environment of the aluminum nuclei was also reported in the pyrolysis products of aluminum-modified polysilazanes and polysilylcarbodiimides [58]. X-ray powder diffraction studies of the final ceramic material reveal no evidence of crystallinity and no ordering of the pores. TEM investigations (Fig. 7) reveal nanometer-sized pores, but without any ordered structures, which is consistent with the XRD result. On the basis of these results the pyrolyzed product

Fig. 8. Nitrogen physisorption isotherm of the product pyrolyzed from the silicon aluminum imide gel.

is identified as a amorphous Si–Al–N composite in which silicon is tetrahedrally coordinated with nitrogen and aluminum is mainly present as $AlN_4$.

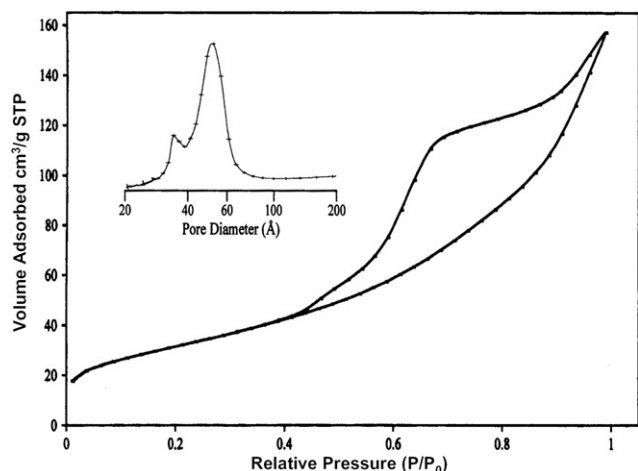Physisorption analysis (Fig. 8) shows that the white product displays a type IV nitrogen adsorption isotherm typical of a mesoporous material with a BET surface area of $114 \, m^2 \, g^{-1}$ and a pore size distribution of 2–8 nm. Compared to the silicon aluminum imide gel, the pore structure has changed from microporous to mesoporous and the surface area has decreased significantly. The expansion of pores should be due to the evolution of dimethylamine ($HNMe_2$), isopropylimine ($H_2N^iPr$) and ammonia ($NH_3$) arising from the ammonolysis and condensation reactions between $NH_3$, Si–$NMe_2$, Si–$NH_2$, Si–NH and Al–$N^iPr$ groups during the pyrolysis [42,59,60]. On the other hand, chemical reactions between these functional groups attached to the pore internal surface will generate attractive forces that bring about viscous flow of the polymer and consequent shrinkage of the pores and therefore a reduction in the effective surface area [61]. The BET surface area [$114 \, m^2 \, g^{-1}$] and pore size distribution [2–8 nm] of the silicon aluminium nitride prepared from tris(dimethylamino)silylamine as a reaction intermediate are similar to those [$190 \, m^2 \, g^{-1}$ and 2–9 nm] of the silicon aluminium nitride prepared via catalytic ammonolysis of tris[tris(dimethylamino)silylamino](tetrahydrofuran)alane, ($C_4H_8O$)Al-[$HNSi(NMe_2)_3$]$_3$ [46]. However, the Si:Al molar ratio [1:3] is much lower than that [3:1] of the corresponding mesoporous ceramic material prepared using our previous procedure [46], i.e., it should be much more polar. These facts demonstrate the versatility and utility of our sol–gel approach to mesoporous non-oxide ceramics using TDSA as a reaction intermediate with quite different sources of aluminium. The use of an atmosphere of ammonia during the pyrolysis procedure in each case leads to a complete removal of carbon from the gel precursors. The gas adsorption properties of porous membranes of these two kinds of silicon aluminium nitride with different polarity will be evaluated and compared in due course.

## 3. Conclusions

A non-aqueous sol–gel process has been investigated to prepare mesoporous silicon aluminium nitride with a aluminium to silicon ratio of 3:1. Catalytic ammonolysis of tetrakis(isopropylimino)bis[tris(dimethylamino)silylamino] alane $H_6Al_6(N^iPr)_4[NSi(NMe_2)_3]_2$ gave a high-surface-area microporous silicon aluminum imide gel. The microporous structure of the gel has been transformed to a mesoporous structure after pyrolysis at 1000 °C due to the evolution of nitrogen-containing gases arising from the ammonolysis and condensation reactions between $NH_3$, Si–$NMe_2$, Si–$NH_2$, Si–NH and Al–$N^iPr$ groups. The resultant amorphous mesoporous silicon aluminum nitride composite has a relatively high surface area and a narrow pore size distribution.

## 4. Experimental procedure

### 4.1. General comments

All procedures were performed under an anhydrous nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled glove box. The solvent tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone prior to use. Trifluoromethanesulfonic acid and liquified ammonia were obtained from Sigma–Aldrich and Energas LTD, respectively. Tetrakis(isopropylimino)bis[tris(dimethylamino)silylamino]alane $H_6Al_6$-$(N^iPr)_4[NSi(NMe_2)_3]_2$, **1**, was prepared by a reaction of TDSA with poly(isopropyliminoalane) ($HAlN^iPr$)$_6$ according to our previous report [49]. The $^{29}Si$ CP-MAS solid NMR spectra were obtained on a Bruker DSX-300 spectrometer operating at 59.6 MHz with tetramethylsilane as a reference. The spinning rate was 5 kHz. The $^{27}Al$ solid NMR was measured at a frequency of 78.1 MHz with a single pulse sequence, using $[Al(H_2O)]^{3+}$ as a reference. A short pulse angle (less than $\pi/12$) was used with a recycle delay of 1 s. The spinning rate was 10 kHz. IR spectra were recorded on a Nicolet Magna-500 FTIR spectrometer. TG analysis was performed on a Netzsch TGA TG209 thermobalance. X-ray diffraction analysis was carried out using a SIEMENS D5000 instrument. Nitrogen adsorption isotherms were performed at 77 K using a Micromeritics Tri-Star 3000 instrument, and surface area was determined from BET analysis. Transmission electron microscopy (TEM) was performed on a JEOL 2011 electron microscope operating at an accelerating voltage of 120 kV. The sample was prepared using carbon-coated copper grids. One drop of an ethanol suspension of the sample was placed on the carbon-coated grid using a microsyringe.

### 4.2. Preparation of silicon aluminum imide gel

Trifluoromethanesulfonic acid (22.5 μL, 0.25 mmol) was added to a solution of **1** (1.9 g, 2.5 mmol) in dry tetrahydrofuran (180 mL). After stirring the reaction mixture for

30 min and standing quiescent at 50 °C for 15 h, the mixture was returned to room temperature and a cooled ($\sim -80$ °C) solution of ammonia (34 mmol) in THF (20 mL) was added. After standing quiescent at room temperature for 3 days, a translucent gel filling about half of the original volume of the reaction mixture was obtained. Evaporation of remaining solvent in the gel by a stream of nitrogen followed by drying under reduced pressure at 50 °C for 6 h yielded a translucent white gel. IR (KBr, cm$^{-1}$): 3367 (m) ($\nu$(NH)); 2975 (w), 2862 (w), 2778 (w) ($\nu$(CH)); 1570 (w) ($\delta$(NH)); 1180 (s) ($\delta$(N–C)); 950 (s) ($\nu$(Si–N)); 710 (w) ($\nu$(Al–N)).

### 4.3. Pyrolysis of the silicon aluminum imide gel

The gel was pyrolyzed in a tube furnace. About 0.5 g of the gel was placed in a BN boat, which was then introduced into a quartz tube in a glove box. The quartz tube was then taken out from the glove box and connected with NH$_3$ flow. The gel was heated to 200 °C with a ramp rate of 5 °C min$^{-1}$, held at 200 °C for 2 h, and then heated at 1000 °C for 2 h under a NH$_3$ flow.

### Acknowledgements

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