

Tailoring the pore-size distribution of high surface area microporous silicon imidonitriles by control of precursor composition

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Abstract

High surface area, microporous, amorphous silicon imidonitrile, characterized by infrared spectroscopy, MAS ²⁹Si NMR, surface area and porosity measurements has been prepared by thermal ammonolysis of both co-oligomers of methylsilazane and dimethylsilazanes and of block copolymers of butadiene and methylsilazane. Variation of the organic content of the silazane is a means of controlling the surface area of the resulting solid and tailoring the pore-size distribution of the final silicon imidonitrile. The resulting materials have pore-size distributions showing a maximum in the range associated with wide-pore zeolites. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Imidonitriles; Pore-size distribution; Thermal ammonolysis

1. Introduction

Shape-selective and size-selective micro- and mesoporous solids are under continuing intense scrutiny for application as catalysts, catalyst supports and membrane materials. Virtually all of the materials which have found application in this area are oxides, and are usually based on silicates. Examples of such materials include aluminosilicates (including zeolites), pillared clays, amorphous mixed-metal oxides and mesoporous silicates and their derivatives. The

tetrahedral SiO₄ units which make up these materials have analogs in the SiN₄ units which are the basis for the structural chemistry of silicon nitride, and the development of microporous nitridosilicates, and nitride analogs of other main group metal oxides, is thus an interesting and potentially useful goal.

The nitridosilicate analog to silica would be silicon diimide, Si(NH)₂, which is known only as an amorphous phase [1], but perhaps a more useful silica analog is silicon imidonitrile, Si₂N₂NH, which has been prepared as a crystalline phase by the reaction between ammonia and silicon at 600°C and 6 kbar pressure [2]. Such a material contains both potential reactive base sites (SiNH) and structural framework units

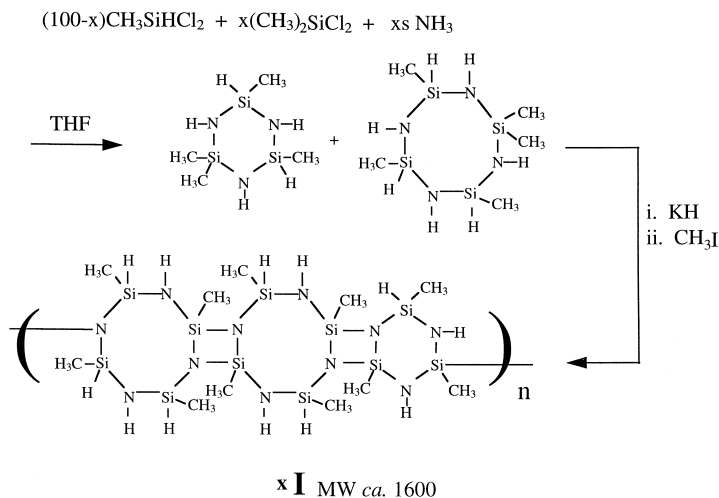
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(SiN). Nitridosilicate analogs to zeolites are rare, but the synthesis of a crystalline nitridosilicate, $\text{Ba}_2\text{Nd}_7\text{Si}_{11}\text{N}_{23}$, with a zeolitic Si–N framework structure, has also recently been accomplished [3], and crystalline nitridosilicates have recently been reviewed [4].

The preparation of nitridosilicates by substitution of oxygen in main group oxides by nitrogen has been reported by the partial nitrating of high surface area silica [5,6] and aluminosilicates [7–9]. Aluminum phosphates [10,11] have also been nitrated by treatment of the parent oxide with ammonia at elevated temperatures. In the resulting materials, nitrogen is present in the form of basic NH groups on the parent oxide surface, and these and related materials thus have the potential for interesting properties as solid base catalysts.

We recently reported the synthesis of a high surface area microporous form of silicon imidonitride by the temperature programmed ammonolysis of oligomeric methylsilazanes [12]. This material can be seen as being based on amorphous silicon nitride in which a significant but variable proportion of the nitrogen is in the form of imide (N–H) groups, and it is thus the

nitridosilicate analog to the amorphous microporous silicas reported by Maier et al. [13,14]. As prepared by this method, the silicon imidonitride compositions, $\text{Si}_3\text{N}_{(4-2x)}(\text{NH})_{3x}$ have high surface areas (350–500 m^2/g), and show narrow pore-size distributions with maxima near 0.6 nm, in the wide-pore zeolite range. The precursors we used in that study were oligo(methylsilazanes), $(\text{MeSiHNNH})_x(\text{MeSiN})_y(\text{MeSiHNHMe})_z$, **I**, originally developed by Seyferth and Wiseman [15], Seyferth and Schwark [16] and Han et al. [17] for use as precursors in the preparation of silicon nitride and carbonitride ceramics. It had previously been reported that the controlled temperature ammonolysis of the commercial oligomeric methylsilazanes NCP100 and NCP200 (manufactured by Chisso [18,19]) at temperatures up to ca. 700°C yields microporous silicon nitride with an approximate mean pore size of 2.0 nm [20–23]. The source of microporosity in the product is the evolution of gaseous thermolysis products (methane and ammonia) between 300 and 700°C, during the time that the preceramic oligomer is transformed into a rigid amorphous matrix. A similar suggestion was made to account for the



(After Seyferth et al., *J. Am. Ceram. Soc.* **1983**, 66, C-13)

Scheme 1.

(closed) porosity in Nicalon® (silicon carbide) and silicon carbonitride fibers prepared from organometallic polymeric precursors [24].

Since the evolution of gases during ammonolysis of **I** is the mechanism by which the micropores form in the final solid, it may be possible to tailor the microporosity of amorphous silicon imidonitride by regulating the alkyl content of the oligomeric precursor alkylsilazanes. In particular, we are seeking methods by which the pore size can be increased into the mesoporous range. In this paper, we report the results of varying the organic content of the silazane precursor on the porosity of the silicon imidonitride produced by ammonolysis. This was accomplished by two methods. In the first, shown in Scheme 1, the methyl content of the oligo(methylsilazane) precursor **I** was varied by adjusting the dimethyldichlorosilane/methyldichlorosilane ratio used in its preparation. In the second, shown in Scheme 2, a copolymer, **II**, of butadiene and oligo(methylsilazane) was synthesized by the H_2PtCl_6 catalyzed hydrosilation of polybutadiene (20% 1,2-addition) with meth-

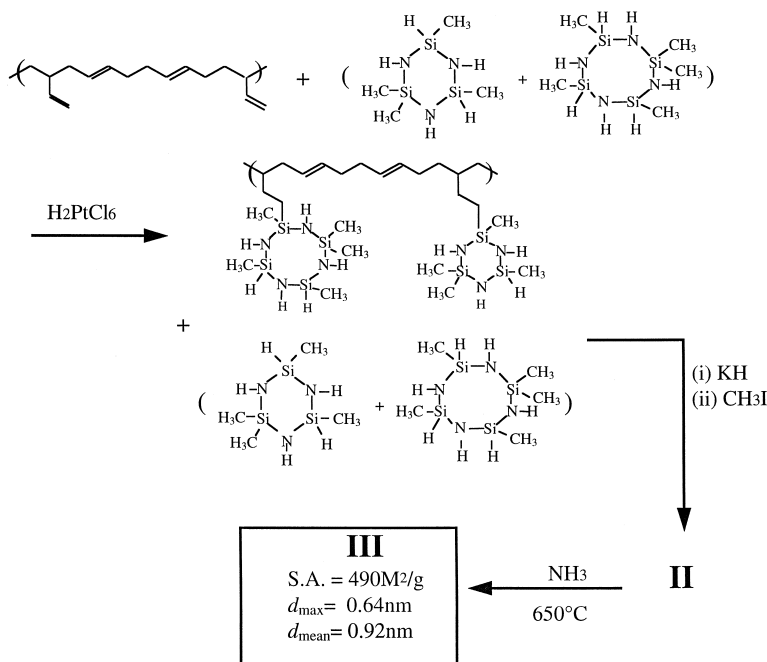
ylsilazane trimers and tetramers, using the procedure of Iraqi et al. [25].

2. Experimental

Methyldichlorosilane, dimethyldichlorosilane and polybutadiene (20% 1,2- and 80% *cis*- and *trans*- 1,4-addition, MW 5000) were purchased from Aldrich and used as received. Solvents were dried and distilled under argon according to literature methods. Thermogravimetric analysis and TGA–mass spectrometry were performed on a Netzsch TG 209 instrument under argon coupled to a Balzers Thermostar quadrupole mass spectrometer. FTIR spectra were obtained in KBr pellets on a Nicolet Magna 550 instrument. Solid state NMR spectra were obtained on a Bruker MSL 300 spectrometer.

2.1. Oligomeric methyl / dimethylsilazanes **I**

A series of $CH_3SiHCl_2/(CH_3)_2SiCl_2$ derived oligosilazanes was prepared by the method



Scheme 2.

of Seyferth and Wise [15] and Seyferth and Schwark [16], in which the proportion of $(\text{CH}_3)_2\text{Si}$ groups (and thus the quantity of methane evolved during ammonolysis) was varied. Three such materials were prepared in which the ratio of $\text{CH}_3\text{SiHCl}_2$ to $(\text{CH}_3)_2\text{SiCl}_2$ was varied by using 14%, 28% and 36% $(\text{CH}_3)_2\text{SiCl}_2$. These materials prepared from $x\%$ $(\text{CH}_3)_2\text{SiCl}_2$ and $(100 - x)\%$ $\text{CH}_3\text{SiHCl}_2$ are hereafter designated ^xI . Ammonia was reacted with the mixtures of methylchlorosilane and dimethylchlorosilane in tetrahydrofuran to yield a mixture of low molecular weight trimeric and tetrameric silazanes. After filtration of the precipitated ammonium chloride, the resulting mixture was treated with a catalytic quantity of KH to yield oligomeric silazanes in a cross-linking reaction, which was terminated by addition of methyl iodide (Scheme 1). Filtration and evaporation of the solvent yielded the product oligomeric methyl/dimethylsilazanes as white solids. ^{14}I and ^{28}I were powders, while ^{36}I was a waxy solid. IR for ^{28}I (KBr pellet): 3409 cm^{-1} ($\nu(\text{N-H})$), 2958 cm^{-1} ($\nu(\text{C-H})$), 2127 cm^{-1} ($\nu(\text{Si-H})$), 1259 cm^{-1} (δCH_3), $1160\text{--}900\text{ cm}^{-1}$ (br, $\nu(\text{Si-N})$). CP-MAS ^{29}Si NMR (60 MHz): $\delta = -20.4\text{ ppm}$ ($>\text{Si}(\text{H})\text{CH}_3$) and 2.9 ppm ($>\text{Si}(\text{CH}_3)_2$).

2.2. Copolymers of butadiene and methylsilazane **II**

A solution of oligo(methylsilazane) trimers and tetramers was prepared by passing a stream of dry ammonia (30 l/h) through a solution of methylchlorosilane (58.2 ml, 69.5 g, 0.6 mol) in dry toluene (700 ml) and stirring vigorously for 3 h. The resulting precipitate of ammonium chloride was removed by filtration. GLC analysis of the filtrate showed a mixture of cyclic trimeric and tetrameric methylsilazanes. To the solution was added 32.4 g polybutadiene (20% 1,2 polymer), and H_2PtCl_6 (25 mg). The suspension was stirred at 80° for 20 h. Evaporation and extraction into dichloromethane (150 ml), followed by filtration and evaporation of the

solvent and drying under reduced pressure (10^{-2} Torr 25°C) resulted in a gummy viscous solid (50.4 g).

To 17.0 g of this material was added a solution of cyclic trimeric and tetrameric methylsilazanes prepared from 25.7 g methylchlorosilane in tetrahydrofuran (500 ml). To the mixture was added KH (300 mg), which resulted in immediate gas evolution. The mixture was heated under reflux for 2 h, cooled to room temperature, and methyl iodide (1 ml) was added. After stirring for 24 h the reaction mixture was filtered through a $1\text{ }\mu\text{m}$ glass filter and evaporated to give an off white waxy solid, **II**, 39.5 g.

2.3. Preparation of silicon imidonitride, **III**

Silicon imidonitride, **III**, was prepared from each of the ^xI materials and from **II** by the method previously reported [12,23]. For example, a sample of ^{28}I was heated at a rate of $5^\circ\text{C}/\text{min}$ from room temperature to 650°C in a stream of ammonia (10 l/h), and then cooled in a stream of argon, yielding a white, X-ray amorphous solid. IR (KBr pellet): 3370 cm^{-1} ($\nu(\text{N-H})$), $1000\text{--}800\text{ cm}^{-1}$ (br, $\nu(\text{Si-N})$). Samples of **II** prepared from the various ^xI and **II** precursors had similar IR spectra. MAS ^{29}Si NMR for a sample of **III** prepared from ^{28}I (60 MHz, Bloch decay): -42.6 ppm (shifting to $(-44.2\text{ ppm}$ in the CP-MAS spectrum)).

3. Results and discussion

3.1. Oligomeric methyl/dimethylsilazanes ^xI

The infrared spectra of the various precursor oligomethyl/dimethylsilazanes ^xI were very similar, differing essentially in the relative intensity of C-H bands (due to SiCH_3 and $\text{Si}(\text{CH}_3)_2$) and N-H and Si-H bands. CP-MAS ^{29}Si NMR (60 MHz) of the various ^xI materials showed resonances at ca. -20 ppm ($>\text{Si}(\text{H})\text{CH}_3$) and ca. 3.0 ppm ($>\text{Si}(\text{CH}_3)_2$), similar to those observed for the NCP materials [26]

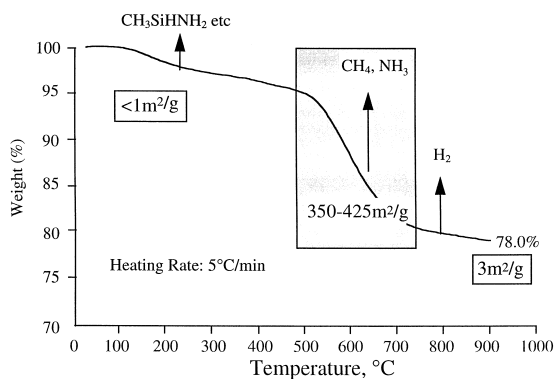


Fig. 1. TGA/MS data for ^{28}I , showing gases evolved and the development of surface area with temperature. Heating rate $5^\circ\text{C}/\text{min}$, under flowing argon.

with relative intensities consistent with the ratio of $\text{CH}_3\text{SiHCl}_2$ to $(\text{CH}_3)_2\text{SiCl}_2$ used in the synthesis.

Thermogravimetric analysis of various ^xI samples under flowing argon showed weight losses at $150\text{--}200$ and $450\text{--}600^\circ\text{C}$, followed by a gradual weight loss up to 800°C , similar to those reported for the commercial oligomeric silazanes NCP100 and NCP200 [23,26]. TGA-MS confirmed the elimination of low molecular weight silicon containing fragments, ($150\text{--}200^\circ\text{C}$), ammonia and methane ($450\text{--}600^\circ\text{C}$), and methane and hydrogen ($> 700^\circ\text{C}$) (Fig. 1) as has been established for the NCP oligomers and other oligo(methylsilazanes) [17,26]. ^{28}I (MW 1600), gave the highest ceramic yield (78%) when pyrolysed in argon at $10^\circ\text{C}/\text{min}$ to 700°C (this compares with 79% for NCP200 [26]). TGA-MS of a sample of ^{28}I under flowing ammonia gas (kindly carried out by H.W. Thoms, Bayer, Leverkusen) showed the same major weight loss at $400\text{--}600^\circ\text{C}$, with concomitant evolution of methane, and a final ceramic yield of 82.5%.

3.2. Copolymers of butadiene and methylsilazane **II**

The infrared spectrum of the butadiene-methylsilazane copolymer, **II**, showed CH stretching absorptions ($3075, 3007, 2951, 2918$ and 2846 cm^{-1} (KBr Pellet)) with intensities reflecting

the high hydrocarbyl content of the material. A comparison of the relative intensities of the $\nu(\text{N-H})$ band (3402 cm^{-1}) and $\nu(\text{Si-H})$ band (2107 cm^{-1}) in **II** with those in a sample of **I** showed changes consistent with the partial consumption of the silane functionality in the hydrosilation reaction, as shown in Fig. 2.

TGA analysis of the initial product of hydrosilation of poly(butadiene) with mixed cyclic trimeric and tetrameric methylsilazanes (Scheme 2) (before cross-linking with further silazanes) showed significant weight loss below 300°C and complete volatilization of the material below 500°C (zero ceramic yield) consistent with the lack of cross-linking between silazane species in the material. The thermal cracking of Si-C bonds in poly(methylsilazanes) is well established, and in this case would result in the formation of volatile, free, low molecular weight silazane species. Catalytic cross-linking of the initial hydrosilation product resulted in the formation of **II** in which polybutadiene and polysilazane moieties interpenetrate on the molecular scale (Scheme 2) and TGA analysis of **II** under argon up to 900°C gave only minor weight losses ($< 5\%$) at 162 and 355°C , followed by a major weight loss ($> 30\%$) at 442°C . A final weight loss of ca. 5% was observed at 630°C .

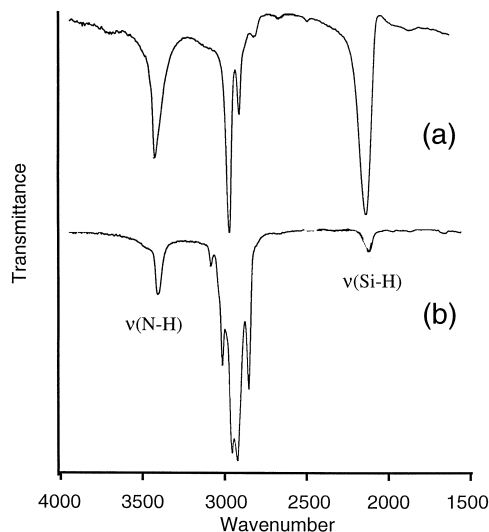


Fig. 2. Infrared spectra of (a) oligo(methyl/dimethylsilazane) ^{28}I and (b) co(polybutadiene-methylsilazane), **II**.

The ceramic yield was 49%. TGA of a physical mixture of poly(butadiene) and **I** showed essentially a superimposition of the TGA trace for **I** with a further sharp weight loss at 427°C due to poly(butadiene) thermolysis.

3.3. Silicon imidonitride, **III**

The infrared spectra of each of the **III** samples (KBr pellet) prepared from the various ^x**I** and **II** precursors showed the absence of CH modes, consistent with the complete ammonolysis of the precursors. The intense absorbance at 3370 cm⁻¹ characteristic of NH vibrational modes, and other bands in the range 1000–800 cm⁻¹, are consistent with the formulation of all of the **III** materials prepared from ^x**I** and **II** as silicon imidonitride. Samples of **III** prepared from **II** by heating in ammonia to 650°C showed similar spectra with the addition of a low intensity $\nu(\text{Si-H})$ band at 2173 cm⁻¹. Heating to 1000°C caused the disappearance of this band. These IR spectra are similar to that reported for silicon diimide, (Si(NH)₂)_n, a polymeric analog of **III** [1].

The resonance at -42.6 ppm in the MAS ²⁹Si NMR (60 MHz, Bloch decay) of **III** prepared from ²⁸**I** is similar to that found for Si₃N₄, and also for the porous materials previously reported by Dismukes et al. [23]. The resonance is a convolution of resonances due to

a range of ²⁹Si environments ranging from SiN₄ at higher field to ²⁹Si in an environment which includes varying proportions of ²⁹Si-NH_x, at lower field with intensities reflecting their actual abundance. This is confirmed by the relative enhancement of the -42.6 ppm resonance in the CP-MAS spectrum of **III**, and a shift to lower field (-44.2 ppm), due to the selective enhancement in the CP spectrum of a lower field ²⁹Si-NH_x resonance. A similarly interpreted but larger shift of ca. 3 ppm has been observed in the Bloch decay and CP spectra of samples of amorphous silicon nitride prepared from SiH₄ and NH₃ by laser pyrolysis [27].

The goal of the research described in this paper is to attempt to tailor the porosity of microporous silicon imidonitride by varying the amount of gaseous thermolysis products released during thermal treatment by varying the alkyl content of the preceramic materials. Both the variation of Si(CH₃)₂ content in ^x**I** and the inclusion of poly(butadiene) chains in **II** will result in a corresponding variation in the volume of gases evolved during thermal treatment of **I**.

We will use as a basis for comparison the properties of **III** prepared from ²⁸**I**. This material displays a type I argon isotherm typical of microporous materials, as shown in Fig. 3a with a micropore volume of 0.14 ml/g and a surface area of 403 m²/g. The pore-size distribution,

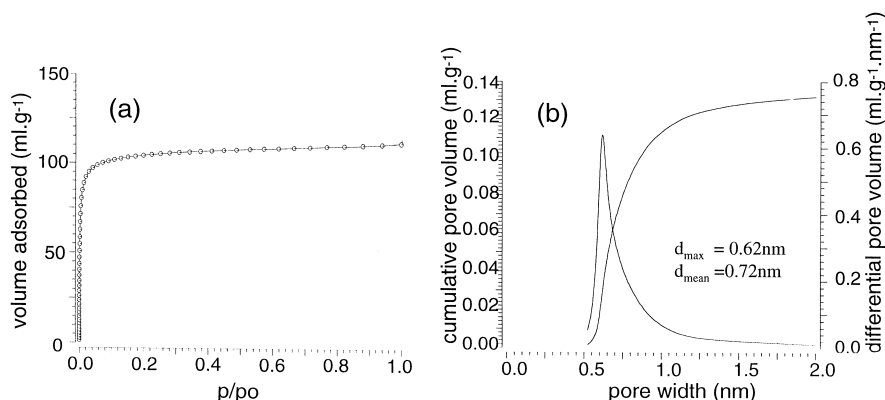


Fig. 3. (a) Argon adsorption isotherm at 77 K for silicon imidonitride **III** prepared from ²⁸**I** by heating under ammonia at 10°C/min to 650°C. (b) Pore-size distribution. ¹

Table 1

Oligo (methyl/dimethylsilazane (CH ₃) ₂ SiCl ₂ :CH ₃ SiHCl) in synthesis mixture	Final temp. <i>T_f</i> (°C)	Surface area (m ² /g)	Pore-size dist. (max/mean; nm)
14:86 ¹⁴ I	700	368	0.61/0.70
28:72 ²⁸ I	650	403	0.62/0.72
36:64 ³⁶ I	650	420	0.62/0.83
28:72 ²⁸ I	600	360	0.62/0.70
28:72 ²⁸ I	700	367	0.62/0.70
28:27 ²⁸ I	900	3	–
poly(butadiene/methylsilazane) II	650	494	0.64/0.92
II	1000	450	0.67/1.2

(NH₃, 10 l/h, 1 bar, 25°C – *T_f* at 5°C/min, 1 h at *T_f*, *T_f* – 25°C at 5°C/min under Ar.)

Porosity measurements: Omnisorp 360, Ar adsorption 87 K, static dosage.

Micropore distribution: Horvath–Kawazo method, ADP 3.03 (Porotec).

determined by the Horvath–Kawazo method [28,29] is narrow and monomodal, with a maximum at 0.62 nm and a mean pore diameter of 0.71 nm, Fig. 3b. ¹ Changes of ±50°C in the final ammonolysis temperature resulted in a reduction in the final surface area to ca. 360 m²/g, but the mean pore diameter remained the same. Heating to 900°C caused a complete loss of surface area (ca. 3 m²/g) and microporosity without inducing crystallization.

Variation of the (CH₃)₂Si content in a series of oligomeric silazanes prepared using different (CH₃)₂SiCl₂:CH₃SiHCl₂ ratios resulted in ammonolysis products with surface areas dependent on the (CH₃)₂Si content of the silazane oligomer. Thus, using (CH₃)₂SiCl₂:CH₃SiHCl₂ ratios of 0.16, 0.39 and 0.56 gave microporous products with surface areas of 368, 403 and 420 m²/g. As we reported earlier, the maxima in the pore-size distributions of all these materials, when they were prepared under the same conditions, were identical, but contrary to our preliminary analysis the mean pore diameter increased slightly with increasing methyl content in the precursor, i.e., the pore-size distribution broadened slightly. These data are summarized in

Table 1. Thus, the influence of varying the volume of methane evolved during thermal treatment is to increase the surface area of the silicon imidonitride produced and to broaden the pore-size distribution.

The incorporation of a much larger quantity of hydrocarbyl residues into the precursor, accomplished by the hydrosilation of poly(butadiene) with a mixture of trimeric and tetrameric methylsilazanes to give **II**, also, has an impact on the porosity of **III**. In this case, there was even greater influence of precursor composition on the properties of the product. Samples of **III** prepared from **II** were microporous, with a micropore volume of 0.20 ml/g, but with a broader pore-size distribution than that observed for **III** prepared from **I**, showing a similar maximum at 0.64 nm but a mean value of 0.92 nm, as shown in Fig. 4. Thus, the greater volume of gaseous hydrocarbon released during heat treatment of **II** under ammonia has expanded to a considerable degree the pore structure of the product silicon imidonitride. However, a further improvement in the properties of **III** produced in this way is seen by comparing the thermal stability of the product prepared from **I** and that prepared from **III**. The pore structure of the former collapses when the material is heated above 750°, and after treatment at 900°C for 1 h the surface area is reduced to 3 m²/g. However, a sample of **III** produced from **II**, which after heating in ammonia to 450°C for 1 h, has a surface area of 420 m²/g, which actually in-

¹ Argon adsorption isotherms were performed at 87 K on an Omnisorp 360 instrument (Coulter). Surface areas were determined derived from BET analysis of the low pressure part of the isotherm. Micropore-size distribution was determined by the Horvath–Kawazo model using ADP software, version 3.03, (Porotec, Frankfurt) using a nitrogen on carbon potential at 77 K.

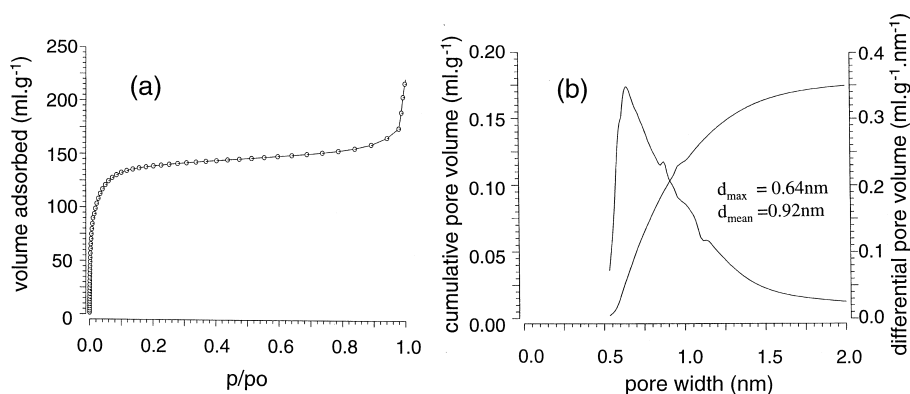


Fig. 4. (a) Argon adsorption isotherm at 77 K for silicon imidonitride **III** prepared from **II** by heating under ammonia at 10°C/min to 650°C. (b) Pore-size distribution. ¹

creases to 490 m²/g after 1 h at 820°C, and even after 1 h at 1000°C, the sample retains a surface area of > 400 m²/g. The pore-size distribution is also affected by high temperature treatment, and after 1 h at 1000°C the maximum in the pore-size distribution is found at 0.67 nm, and the mean value is 1.2 nm.

Other materials with a similar composition to **III** have been reported. The reaction between ammonia and silicon at 600°C and 6 kbar pressure yields the crystalline phase Si₂N₂NH [2]. Amorphous silicon nitride has been prepared from laser pyrolysis of silane–ammonia mixtures [27,30]. Silicon imidonitrides with the stoichiometries (Si₃N₂(NH)₃)_n and (Si₂N₂(NH))_n, arising from the thermolysis of (Si(NH)₂)_n, have been reported [31,32], and the materials we report here are related to these compositions (for which there are no reports of microporosity).

A material identified as high surface area amorphous silicon nitride has been reported by Dismukes et al. from the temperature programmed ammonolysis of NCP silazane precursors, and by Han et al. in their extended studies of the thermal chemistry of oligosilazanes [17]. In the latter work, N–H containing products were identified by infrared spectroscopy. The microporosity and surface area of the materials prepared by Dismukes et al. depended critically

on heating rate during ammonia treatment, with heating rates of rate of ≤ 10°C/min being necessary to avoid a complete loss of porosity and surface area [23]. However, in the present work, we find the formation of a high surface area microporous product from the precursors prepared in-house even at heating rates as high as 20°C/min. These differing observations are almost certainly due to the fact that the oligomeric silazanes which we prepared possess a degree of cross-linking to that found in the commercial materials [26].

By virtue of its microporosity and the presence of Si–NH groups, **III** is a solid base with potential for size selective catalytic properties. We have shown previously [12] that **III** is a solid catalyst for the Knoevenagel condensation reaction between benzaldehyde and a series of active methylene compounds. We are continuing our evaluation of the catalytic properties of **III** with particular focus on the possibility of size-selectivity.

We have also prepared analogous high surface area microporous materials related to silicon aluminium oxynitrides (SiAlONs) [33], which, as nitridoaluminosilicate analogues to aluminosilicates, provide the possibility of acidic and basic sites, and these materials will be described in detail separately. The acid–base properties of these materials are of special sig-

nificance, due to the ever increasing demands for environmentally benign chemical processes in which inorganic solids with useful acidic and/or basic properties can serve as alternatives for the potentially environmentally threatening liquid acid and base catalysts used in more mature chemical technological processes. Solid acid catalysts such as zeolites have been developed to a significant degree in the petrochemical and fine chemical industries [34,35] but the application of solid bases is relatively undeveloped [36,37].

4. Summary

Amorphous silicon imidonitride is a nitridosilicate analogue to the amorphous silica-based mixed metal oxides reported by Maier et al. [13,14], with similar pore-size distributions and surface areas. The putative analogy between the oxide and nitride chemistry of silicon is extended to the domain of amorphous nitridosilicates. By changing the composition of the precursor compounds, we have shown that the pore-size distribution of amorphous silicon imidonitride can be tailored, thus opening the way for the exploration of useful size-selectivity in its catalytic properties. The presence of substantial amounts of N–H groups in the silicon imidonitride materials, together with their sharply defined microporosity and their previously demonstrated activity in catalyzing the Knoevenagel condensation reaction demonstrates that they constitute a new class of microporous solid bases.

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