

Synthesis of mesoporous silicon imido nitride with high surface area and narrow pore size distribution

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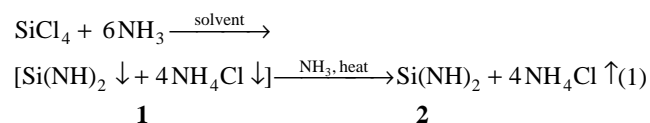
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Silicon imido nitride with a specific surface area up to 1000 $\text{m}^2 \text{g}^{-1}$ is obtained by ammonolysis of silicon tetrachloride in organic solvents and subsequent NH_4Cl removal at elevated temperatures in a stream of anhydrous ammonia. The material has a remarkably narrow pore size distribution and a mean pore size of 5.7 nm. TEM investigations reveal the spherical macromorphology and uniform dendritic mesostructure of the micrometer sized particles. A high number of Si-NH_2 groups on the inner surface of the material is indicated from IR measurements. ^{29}Si MAS NMR indicates the presence of SiN_4^{8-} tetrahedra.

Tailoring inorganic solids is a key feature in the search for purpose-built high-performance materials. High specific surface area and control of pore size and pore morphology are especially needed in heterogeneous catalysis.¹ For oxide materials a wide range of methods has been developed such as flame pyrolysis and sol gel techniques.² Due to our recent interest in the development of porous non-oxide ceramics as heterogeneous catalysts we have investigated the synthesis of silicon imido nitride as a high surface area material under various conditions. Even though this material has been widely studied as a precursor to obtain Si_3N_4 for structural applications,³ sinterability and densification have mainly been stressed, whereas only few attempts have been made to systematically tailor its surface area and pore structure and only recently has its potential in heterogeneous catalysis become apparent.^{4–6}

In order to achieve easy access to highly porous materials we have used SiCl_4 (Arkos, 99.8%) in various solvents (4% solution) such as pentane, toluene, tetrahydrofuran and polyethyleneglycol dimethyl ether and precipitated the diimide with anhydrous ammonia gas (UHP, Messer).[†] After filtration, the coprecipitated NH_4Cl was removed by sublimation in a dynamic (40 ml min^{-1}) ammonia atmosphere (1 bar) at elevated temperature [eqn. (1)]



The composition of the product **2** depends on the heat treatment. According to wet chemical analysis of the powder the N:Si ratio is 1.60 for a sample calcined at 873 K, and 1.50 at 1073 K. The formula $\text{Si}_2\text{N}_2(\text{NH})$ instead of $\text{Si}(\text{NH})_2$ is often assigned to intermediates during the technical process of decomposing $\text{Si}(\text{NH})_2/x\text{NH}_4\text{Cl}$ to prepare Si_3N_4 for structural ceramics. We have therefore adopted the rather unspecific nomenclature 'high surface area silicon imido nitride' (HSA-SIN) for **2**. It is obtained with a BET surface area up to 1000 $\text{m}^2 \text{g}^{-1}$ as a white, X-ray amorphous powder if pentane is used as the solvent and the initial precipitation is carried out at room temperature followed by heating the resulting solid to 723 K for 2 h with a rate of 5 K min^{-1} . This is the highest surface area so far reported for $\text{Si}(\text{NH})_2$ and comparable to that for MCM-41-like materials.⁷ Even though the pores do not form an ordered array according to small-angle X-ray measurements, the adsorption

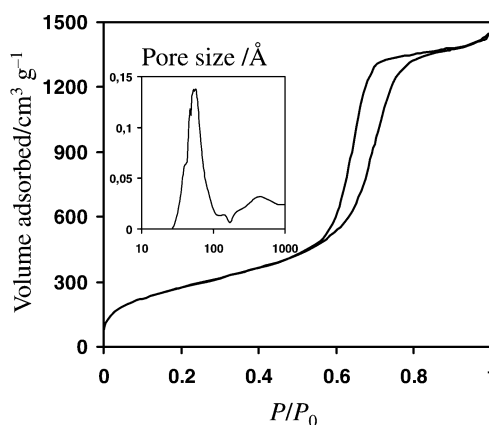


Fig. 1 Nitrogen adsorption isotherm for HSA-SIN synthesized in pentane after calcination in ammonia and its pore size distribution.

isotherm[†] (Fig. 1) indicates the presence of mesopores with a narrow pore size distribution, a sharp maximum at 5.1 nm and a mean pore diameter of 5.7 nm. No percolation effect due to ink bottle pores is observed. For applications in heterogeneous catalysis ordering of the pores is not necessary but high surface area, narrow pore size distribution and homogeneity of the inner surface are highly desirable to obtain high performance materials with good selectivity.

TEM investigations (Fig. 2) reveal the spherical morphology of the particles with typical size of 0.1 μm diameter. The radial dendritic channel-like mesostructure is independent of the size of the aggregates. We found that polar solvents such as tetrahydrofuran also give mesoporous silicon imido nitride but with considerably lower surface area (560 $\text{m}^2 \text{g}^{-1}$) and two distribution maxima at 7.6 and 40.6 nm. The effect of washing the coprecipitate **1** with liquid ammonia results in an even more drastic reduction of the surface area (*ca.* 300 $\text{m}^2 \text{g}^{-1}$) and the

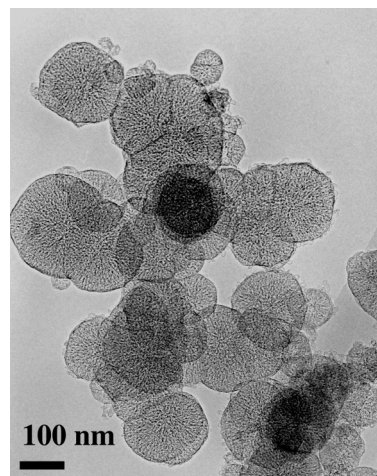


Fig. 2 Transmission electron micrograph of HSA-SIN.

narrow distribution now being completely lost, with a wide range of sizes from micro- to macro-pores being observed. While washing with liquid ammonia is often applied when sinterable Si(NH)₂ powder is needed for structural ceramics this method to remove NH₄Cl seems highly inappropriate for specific pore structure design. So far only one group has reported a specific surface area of up to 1000 m² g⁻¹ for silicon diimide using the precipitation method and toluene for dilution of SiCl₄, but the pore morphology was not discussed.⁸ In our experiments, toluene reduces the total yield of the reaction by at least a factor of 10, and is therefore less appropriate.

The particle formation mechanism is still unknown. Some intergrown spheres suggest that the large spheres might have formed by merging of smaller spheres but whether this formation has occurred in solution or during heat treatment is still not clear. However, the strong impact of the solvent on the surface properties as well as the spherical morphology of the aggregates suggests that their formation occurs in solution where surface tension and solubility govern nucleation and growth. In fact we believe that NH₄Cl nanocrystals act as a template for the surrounding Si(NH)₂. This view is supported by the fact that polar solvents cause pore collapse due to the higher solubility and recrystallization of the NH₄Cl whereas in pentane the generated ammonium chloride nuclei remain small. This is in accord with the particle size determined from the broadening of the ammonium chloride Bragg reflections in the coprecipitate **1** (ca. 8 nm).

IR spectroscopy gives similar results as earlier studies⁹ [$\nu(\text{NH})$: 3374 cm⁻¹, $\delta(\text{NH}_2)$: 1548 cm⁻¹, $\delta(\text{NH})$: 1182 cm⁻¹, $\nu_{\text{as}}(\text{Si}_2\text{N})$: 905 cm⁻¹]. The $\delta(\text{NH}_2)$ mode indicates the presence of amino groups located on the inner surface of the material in analogy to silanol groups present on the inner surface of MCM-41. This band is stronger for samples synthesized in pentane vs. tetrahydrofuran, corresponding to the higher inner surface area of the former sample; exposure to air as well as lithiation with butyl lithium reduces its relative intensity. No Si–O stretching modes were observed if the material was handled properly with exclusion of moisture or air.

The ²⁹Si MAS NMR spectrum consists of one broad peak centered at –42 ppm, the signal covering the region between –35 and –55 ppm. The broadening originates from the ill defined local structure and is characteristic for amorphous preceramic silicon nitride powders¹⁰ in which different functional groups are present. Thus in HSA-SIN, Si(NH)_{4/2} groups are most abundant but SiN_{(4-x)/3}(NH)_{x/2} (x = 0–3) groups in the bulk and Si(NH)_{(4-x)/2}(NH₂)_x (x = 1,2) groups on the inner surface of the material are also present. A shoulder at –49 ppm indicates a high abundance of SiN_{4/3} groups with a chemical shift comparable to that of β-Si₃N₄¹¹ at –48.7 ppm. A low level of silicon oxide impurities was also concluded from the absence of any significant peaks close to –100 ppm, though due to the

high background noise, such impurities could not be completely excluded. The chlorine contamination was also low (<2% by EDX).

The high temperature stability and low sintering tendency of the nitride is remarkable and reveals its promising potential as a support in high temperature catalysis: after 2 h of heat treatment at 1273 K in a dynamic ammonia atmosphere (1 bar, 40 ml min⁻¹) the high surface area is only slightly reduced (820 m² g⁻¹). The pore size distribution remains narrow with only a slightly reduced mean pore size (4.9 nm).

New compounds will become available as heterogeneous catalysts and supports if morphological syntheses of non-oxide ceramics as high surface area materials are further explored. We have demonstrated that ammonolysis of silicon tetrachloride in solution is an easy route to high surface area silicon imido nitride with uniform pore morphology—a material with potential for base-catalyzed reactions suitable for further functionalization, impregnation and high temperature applications.

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Notes and references

† All operations are performed using a vacuum line or an argon-filled glove box and dry solvents. Nitrogen physisorption measurements were performed using an ASAP 2000 (micromeritics) instrument.

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