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Synthesis, Characterization, and Catalytic Properties of High-Surface-Area Aluminum Silicon Nitride Based Materials

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A new precursor, $[RAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2Si(NHEt)]_2$ (R = Et, Me), is proposed for the preparation of high-surface-area silicon aluminum nitride based xerogels. The conversion is carried out using ammonia gas and pentane/ammonia mixtures at low (1 bar) and high (200 bar) pressure. Materials with specific surface areas up to 800 $m^2\ g^{-1}$ are obtained under high-pressure conditions. The enrichment of aluminum in the materials obtained at low pressure indicates the formation of $Si(NHEt)_4$ as a side product that is also detected in NMR spectra. In scanning and transmission electron micrographs the materials appear with a flakelike morphology. The presence of NH groups is detected in IR spectra, and the ^{29}Si MAS NMR signal is detected at −40.5 ppm. The materials are X-ray amorphous. The composition varies with the reaction conditions. After a high-pressure transformation, the Al/Si ratio is close to 1.0 ($Al_2Si_{1.8}N_{8.7}C_{1.3}H_{11.6}$) but transformation at low NH_3 pressure only produces Al-enriched materials. The solid imides are efficient catalysts for the Michael addition of malononitrile to acrylonitrile with a high yield of 96% after 5 h.

Introduction

Sol−gel processing of inorganic nitrides has been proposed by several groups in recent years since soft chemical routes to hard ceramics give control of composition and green body shape at the preceramic stage.[1−6] Related techniques such as molecular precursor and polymer approaches have tremendous advantages because the morphology and nucleation in nanocomposites is controlled with the polymer composition.[7−12] Interrante's group has used molecular precursors for the preparation of AlN[13,14] and Si_3N_4/SiC ceramics.[15] In such processes, generally, the polymer is directly converted into the hard ceramic by pyrolysis, whereas in the sol−gel process, 1−1000-nm-sized sol particles dispersed in a liquid agglomerate with the incorporation of solvent to give a spongelike three-dimensional solid network, and the pores are filled with liquid. Xerogels are obtained by conventional drying of the wet gels to give nanoporous powders. Whereas for ceramic applications, densification is the key to obtaining high performance materials, our interest is to design such compounds as highly porous materials with high accessible surface area for catalytic transformations.[3,4,16,17]

In recent years, we have achieved porosity control in silicon nitride based materials with extremely high specific surface area up to 1000 $m^2\ g^{-1}$ and in gallium nitride based materials using template-assisted sol−gel processes and condensation reactions of amido complexes.[3,4,17−19]

Czepirski has studied the adsorption characteristics of gallium and aluminum nitride based materials and has reported surface areas up to 230 $m^2\ g^{-1}$.[20]

A key difference between silicon nitride and gallium nitride based materials is the crystallization behavior. Whereas silicon nitride based materials tend to crystallize at ambient pressure only above 1273 K, gallium nitride materials show a significant degree of crystallization already at 673 K. Thus, sintering and crystallization in such solids are responsible for a reduced surface area after template removal.

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In zeolites, stable architectures are achieved with the incorporation of aluminum into the network. The latter also introduces functional groups by charge matching requirements. Bridging OH groups are responsible for the high acidity of zeolites. Our interest was to achieve similar properties in silicon nitride based materials. The combination of silicon and aluminum in a nitride based network affords stable network architectures. In contrast to zeolites, nitride based materials are solid base catalysts with Lewis basic functional groups such as NH and NH_2. In aluminum-based networks the average Al−N bond polarity is higher as compared with that of Si−N networks. Thus, an increased performance in solid base-catalyzed reactions is expected in Si−Al−N based networks. To achieve such properties it was necessary to develop new precursors and transformation techniques that allow for a homogeneous distribution of aluminum and silicon. In the following, we describe the transformation of the tetranuclear precursor $[RAl(\mu\text{-NHEt})(\mu\text{-NEt})_2Si(NHEt)]_2$ (R = Et, Me) with gaseous and supercritical ammonia into high-surface-area silicon aluminum nitride based materials and the use of such materials in solid base catalysis.

Experimental Section

In all experiments, ultrahigh-purity ammonia (Messer) was used. Reactions of the precursor $[RAl(\mu\text{-NHEt})(\mu\text{-NEt})_2Si(NHEt)]_2$ (R = Et (**1**), Me (**2**)) with ammonia at ambient pressure were carried out under argon.

The precursor was dissolved in pentane and reacted with ammonia gas at room temperature for 2 h under vigorous stirring. Precursor **1** gave a turbid colloidal solution after 5−10 min that was not filterable even after 2 h reaction. The concentrated solution had a gel-like consistency. Precursor **2** gave a white flocculent solid after 1 min that was recovered by filtration and washed several times with pentane. EA Calcd. for $Al_2(CH_3)_3(NH)(NH_2)$: Al, 37.09 (41.47); C, 24.23 (27.7); H, 8.51 (9.31); N, 22.35 (21.53); Si, 2.30 (0).

For high-pressure conversions, 1.3 g of **1** was dissolved in 50 mL of pentane and filled in a 100-mL autoclave. Ammonia was condensed into the autoclave and the mixture was heated to 413 K ($P = 170$ bar) for 12 h. After the reactor had been cooled, the solid was filtered out, washed several times with pentane, and dried in a vacuum. EA: Al, 39.88; Si, 7.55; C, 11.81; H, 4.19; N, 28.78. IR(KBr): $\tilde{\nu} = 3262\ \mathrm{cm}^{-1}$, 1554 (N−H), 2942, 2903, 2863 (C−H), 936 (Si−N), 712, 656 (Al−N).

The conversion without pentane was carried out in a 36-mL autoclave that was filled with 400 mg of **1** and 15.3 g of ammonia. The autoclave was heated to 393 K for 3 d. The solid product was washed with pentane and dried in a vacuum. EA, %: C, 6.49; H, 5.10; N, 30.38; Al, 26.07; Si, 19.02.

High-surface-area silicon aluminum nitride based materials were prepared in a high-pressure ammonia reaction bomb using 300 mg of the precursor and 600 mL of NH_3 gas that was condensed into the bomb. The design of the autoclave is described elsewhere.[21] Elemental analysis, %: C, 6.32; H, 4.63; N, 47.93; Al, 21.26. Si, 19.66.

Physisorption Measurements. For nitrogen physisorption measurements at 77 K, a Micromeritics 2000 instrument was used. The pore size distribution was derived from the desorption branch of the isotherm using the BJH method.[22]

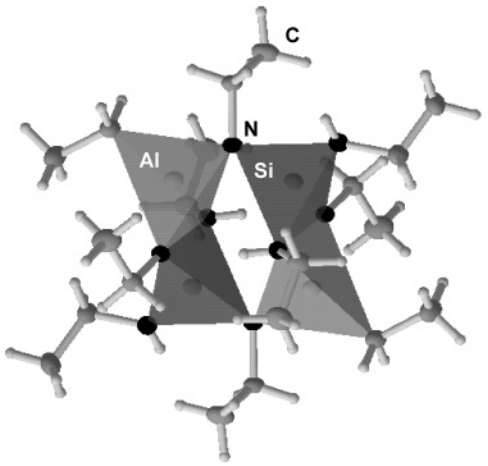

Figure 1. Molecular structure of $[EtAl(\mu\text{-NHEt})(\mu\text{-NEt})_2Si(NHEt)]_2$, **1**.

Table 1. Conversion of $[RAl(\mu\text{-NHEt})(\mu\text{-NEt})_2Si(NHEt)]_2$ under Ammonothermal Conditions

no.	temp./K	pressure/time	dilution	$S_g{}^a$ (m^2g^{-1})	Al:Si ratio
1	298	1 bar/2 h	pentane	291	16.1
2	413	170 bar/12 h	pentane	795	5.3
3	423	130 bar/72 h	pentane	n.d.	1.9
4	388	170 bar/72 h		627	1.4
5	423	200 bar/50 h		760	1.1

[a] S_g = BET surface area.

TEM. The TEM samples were prepared in a glovebox on a Gatan (type 647) vacuum transfer sample holder and analyzed on a Hitachi HF2000 or H7500 microscope. The powders were directly spread on a carbon foil without using solvents.

Results and Discussion

The synthesis and characterization of $[RAl(\mu\text{-NHEt})(\mu\text{-NEt})_2Si(NHEt)]_2$ (R = Et (**1**), Me (**2**)) has been described elsewhere.[23] The precursor is easily accessible in the reaction of trialkylaluminum, AlR_3, and tetrakis-(ethylamino)-silane, $Si(NHEt)_4$, in high yield. The tetranuclear molecule contains aluminum and silicon in tetrahedral coordination and bridging and terminal ethylamino groups (Figure 1). One residual ethyl-ligand per aluminum is also present.

We have investigated the ammonolytic transamination of **1** and **2** under ambient and high-pressure conditions. When **1** is diluted with pentane and reacted with gaseous ammonia at 293 K under vigorous stirring, a sol formation is observed after 5−10 min. After 2 h, only very small amounts of product can be recovered as a solid by filtration (Table 1, entry 1). The filtrate is still turbid, indicating the presence of ultrafine sol particles in solution. However, by means of NMR and GC techniques, $Si(NHEt)_4$ is also detected in the filtrate, indicating a preferential reaction of the aluminum center which generates tetrakis-(ethylamino)-silane. A possible reaction mechanism is outlined in Scheme 1. The reason

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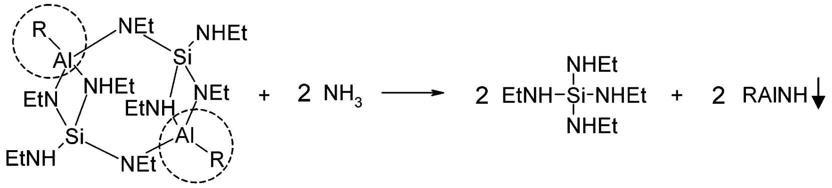
Scheme 1. Probable Transformation Pathway for the Transamination of $[RAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2Si(NHEt)]_2$



for the higher reactivity of the Al center is probably the high polarity of the Al−N bond.

Similar results are obtained with **2** in pentane at 293 K, but the solid formation is observed already after 1 min reaction with ammonia. After 2 h, the solid product is recovered by filtration and the filtrate is clear. The specific surface area of the product is 291 m^2 g^{-1}. However, $Si(NHEt)_4$ is detected in the filtrate by means of ^1H NMR spectra and the Al/Si ratio in the solid is 16.1, clearly demonstrating that the silicon center is not reactive enough to be converted under these mild reaction conditions. The composition of the product is close to the idealized formula $Al_2(CH_3)_3(NH)(NH_2)$.

To achieve complete conversion of the precursor, we have treated **1** in pentane solution with ammonia under static autothermal pressure (170 bar) for 12 h at 413 K. The resulting solid had a very high surface area (795 m^2g^{-1}) but according to elemental analysis data and NMR spectra of the filtrate the conversion was still incomplete. The Al/Si ratio in the solid was as high as 5.3, indicating a higher degree of transformation. A prolonged heat treatment (423 K) for 3 d under isostatic pressure (130 bar) gave better results and an Al/Si ratio of 1.9, which means that 50% of the silicon is incorporated in the gel.

In pentane, the sequential enrichment with silicon under more severe conditions or with prolonged treatment implicates that a sequential precipitation occurs i.e., in the first stage of the gel formation only the aluminum imides form as sol, gel, or solid particles, whereas $Si(NHEt)_4$ is reformed as a liquid in the solution. The latter is converted into $Si(NH)_2$ in the second stage of the ammonolysis at much higher pressures and temperatures. The sequential formation of the solid in this sol−gel process implies that a regular distribution of aluminum and silicon on an atomic scale is not attained. The high surface area (291 m^2g^{-1}) of Al-rich materials obtained at ambient pressure corresponds to a particle size of 7−10 nm for a nonporous powder (assuming a density of 2−3 gcm^{-3}).

The high surface area (S_g = 795 m^2g^{-1}) of composites obtained at higher pressure is remarkable and comparable to that of very high surface area silicas such as MCM-41 (typically 1000 m^2g^{-1}) or high-surface-area silicon imide prepared from halide precursors (700−1000 m^2g^{-1}).[3,17] The nitrogen physisorption measurement (Figure 2) clearly indicates a significant uptake in the mesopore regime with an average pore diameter of 5.8 nm. However, the pore size distribution is rather broad as expected for such nontemplated materials in which nucleation and growth in solution govern the evolution of the nanometer-sized pores.

The IR spectrum of the solid shows N−H stretching and deformation frequencies at 3262 and 1554 cm^{-1}, respectively. In addition, C−H stretching frequencies are present and in agreement with the residual carbon content found via elemental analyses, whereas Si−N and Al−N stretching vibrations give rise to broad absorptions at 936, 712, and 656 cm^{-1}.

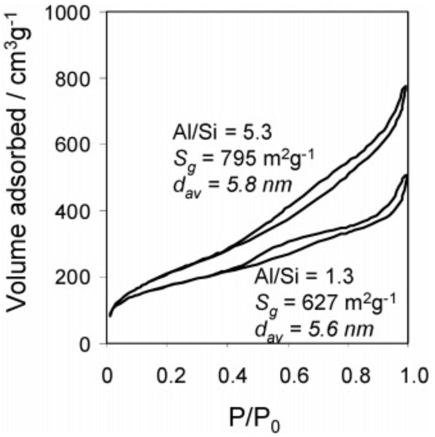


Figure 2. Nitrogen physisorption isotherms (77 K) of aluminum silicon nitride materials synthesized via high-pressure ammonolysis in pentane solution.

The morphology of the powder is comparable to that of layered silicates such as clays (Figure 3) and differs significantly from the morphology of high-surface-area silicon imide obtained in pentane from $SiCl_4$ or $Si(NHEt)_4$.[17] Such a platelike amorphous structure could be related to a nucleation mechanism in which the morphology of Al−NH networks forming initially determines the morphology of the product. Another reason could be the formation of local structures that are analogues of clay. However, since the products are completely amorphous there is no proof for a clay-like structure of the high-surface-area materials.

To achieve complete conversion of the precursor we have also used the ammonothermal conversion without pentane dilution (Table 1). Thus, the reaction of **1** at 388 K in an autoclave (36 mL) filled with 15.3 g of liquid ammonia gives almost complete conversion and an Al/Si ratio of 1.3. The resulting solid has a high specific surface area (S_g = 627 m^2 g^{-1}) and a low carbon content (6.5%).

Even better results are obtained in a high-pressure autoclave at 423 K in supercritical ammonia. The composition of the product is $Al_2Si_{1.8}N_{8.7}C_{1.3}H_{11.6}$. ^{29}Si and ^{27}Al MAS NMR spectra show broad signals centered at −40.5 and 113.5 ppm, respectively. They are characteristic for the less regular coordination in amorphous inorganic nitride based materials.[17] The ^{29}Si MAS signal is close to that of materials obtained using the transamination of halides described earlier,[17] a material that is typically named $Si(NH)_2$ (silicon diimide) in the literature, even though it probably contains also amido and nitride groups.

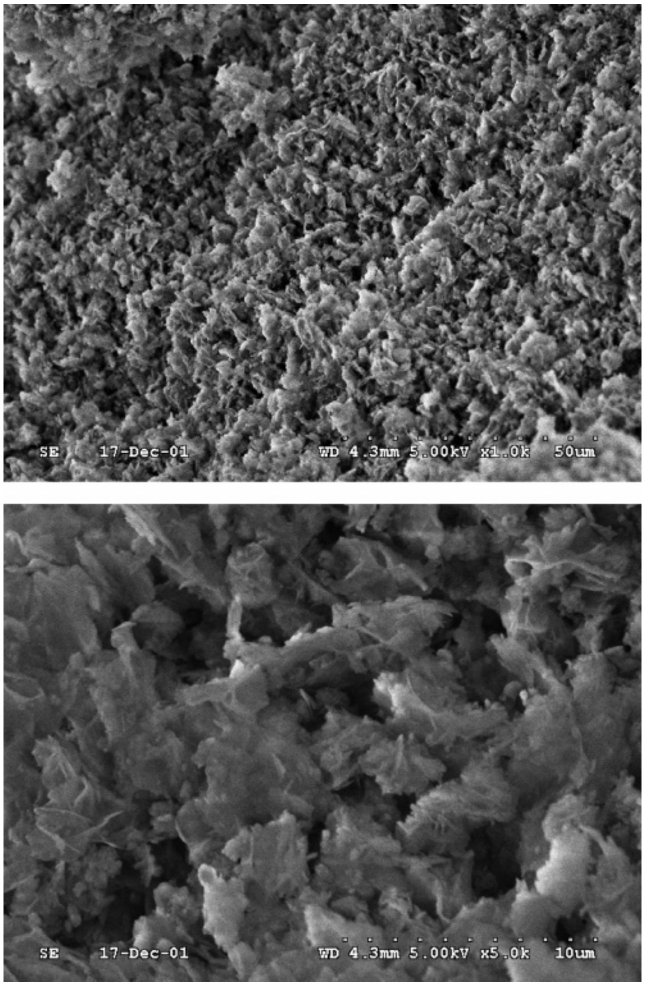


Figure 3. Scanning electron micrograph of high-surface-area aluminum silicon nitride.

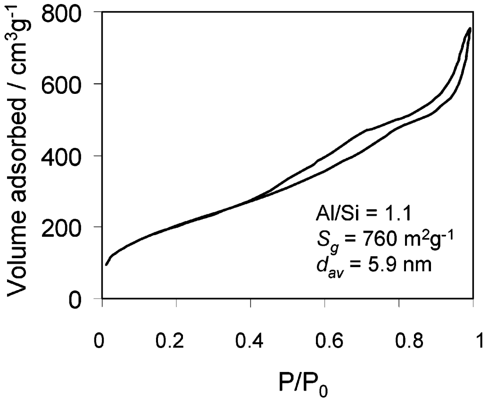


Figure 4. Nitrogen physisorption isotherm (77 K) of aluminum silicon nitride materials synthesized via high-pressure ammonolysis without pentane dilution.

The specific surface area after transformation in supercritical ammonia is as high as 760 $m^2\ g^{-1}$, comparable to materials obtained in pentane. However, a regular pore size distribution is not obtained but the material has some porosity in the mesopore regime and a broad pore size distribution (Figure 4).

Transmission electron micrographs also reveal a platelike morphology with a plate thickness in the range of 5−10 nanometers (Figure 5). Tube-like morphologies can be discerned in the micrographs. Thus, the sheets probably roll up to form tubes, similarly to that observed for other inorganic nanotubes made of layered materials such as WS_2. By EDX, the Al:Si ratio in these materials is close to 1.0, in agreement with bulk elemental analyses. Since the low pressure conversion with ammonia, especially in dilution with pentane, favors the precipitation of aluminum-rich materials, the formation of a material with an Al/Si ratio close to one could again be the result of a sequential reaction of the precursor, in which first solid $Al_2(NH)_3$ and liquid $Si(NHEt)_4$ are formed, and only at higher pressure and longer reaction periods is $Si(NHEt)_4$ converted into solid $Si(NH)_2$. The latter should lead to a micro-segregation and regions in the amorphous material that are aluminum-rich and silicon-rich. However, EDX analyses in the electron microscope with spot sizes of 3−5 nm do not show an enhanced abundance of one of the elements in certain domains. Thus, a homogeneous distribution on the nanometer scale is obtained using the single source precursor and an ammonothermal conversion in supercritical ammonia.

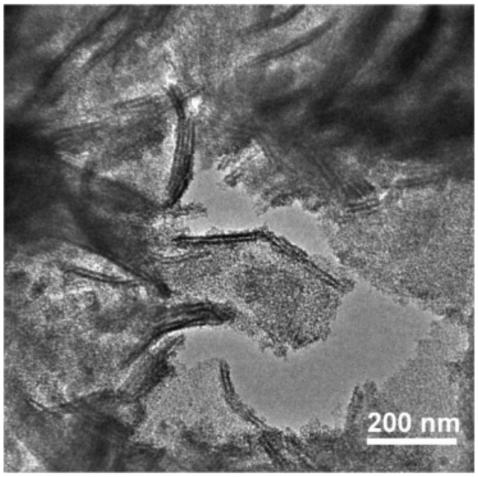


Figure 5. Transmission electron micrograph of high-surface-area aluminum silicon nitride.

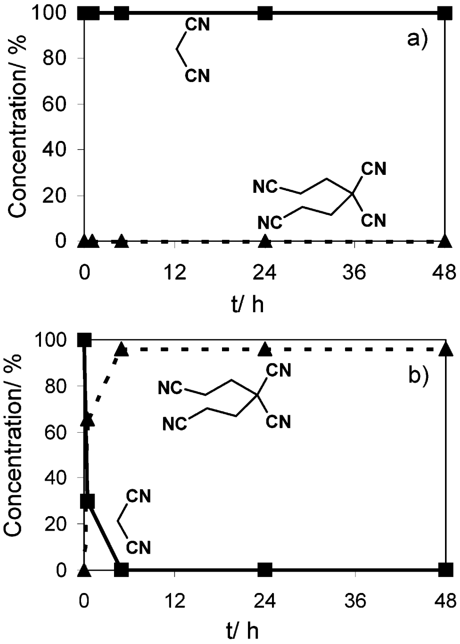
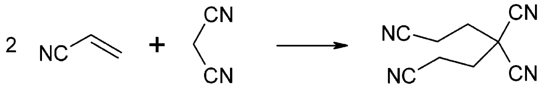


Figure 6. Concentration of malononitrile and the Michael-addition product without catalyst (a), and with the use of high-surface-area aluminum silicon nitride (b).

Catalytic Properties. High-surface-area nitrides are excellent supports and active components in heterogeneous catalysis.[4,16,24] A high accessible surface area is necessary to achieve a high conversion at low temperature. The introduction of aluminum into the framework enhances the basic properties of the catalyst. As compared with molecular catalysts, solid powders are easily recovered by filtration and are therefore economic and environmentally friendly.

We have used high-surface-area aluminum silicon nitride based materials as catalysts in the Michael-addition reaction of malononitrile to acrylontrile at 333 K (Scheme 2).

Scheme 2. Michael-Addition Reaction of Malononitrile to Acrylonitrile



To ensure that the conversion is zero when the catalyst is omitted, blank experiments were carried out and the concentration of the educt and product were followed by GC analyses (Figure 6a). No conversion was detected.

In contrast, when the catalyst (Table 1, entry 5) is added (5%), the malononitrile is completely consumed after 5 h and a yield of up to 96% is detected (Figure 6b) demonstrating the high catalytic activity of the new solid base material.

Conclusion

The ammonolytic conversion of a novel Al−Si precurser, $[RAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2Si(NHEt)]_2$ (R = Et, Me), was studied at ambient temperature and pressure conditions and at high temperature and pressure up to 200 bar. X-ray amorphous high-surface-area materials (xerogels) are obtained with specific surface areas ranging from 300 to 800 $m^2\ g^{-1}$ depending on the reaction conditions. The products have a broad pore size distribution and a lamellar morphology. Imidonitrides with an Al/Si ratio close to 1.0 are obtained only at higher pressure. In particular, in the presence of the organic solvent pentane, the formation of $Si(NHEt)_4$ leads to a sequential integration of Al and Si into the solid, whereas in supercritical ammonia, the Al/Si ratio is 1.1 and a microsegregation cannot be detected.

The novel nitrides containing aluminum have a high catalytic activity and can be used as solid base catalysts in the Michael addition reaction.

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