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[18] More than 50000 mutants can be screened per day, if the analysis time can be reduced to about 1 min per test and faster pipetting steps are possible.

Pore-Size Engineering of Silicon Imido Nitride for Catalytic Applications**

David Farrusseng, Klaus Schlichte, Bernd Spliethoff, Annette Wingen, Stefan Kaskel,* John S. Bradley, and Ferdi Schüth

Microporous and mesoporous materials with high internal surface area and pore volume play a key role in the development of new heterogeneous catalysts and solid membranes.[1] The strategy in the synthesis of materials with well defined pore structure is to direct the networking of molecular or ionic precursors by a templating agent, which can be a molecule, an ion, a polymer, or a supramolecular assembly.[2] Removal of the occluded template produces materials with patterns of characteristic pore size, shape, and structure. Although there is a growing interest in expanding these templating routes to materials other than oxides, only in the case of sulfides and some super-Prussian-blue compounds have micro- and mesoporous inorganic nonoxide materials been synthesized.[3] Nitrido-sodalites with very small pores, probably inaccessible to organic substrates, were obtained from the solid-state reaction of HPN_2 and divalent metal salts.[4]

Several methods for the synthesis of dense silicon nitride starting from elemental silicon, silicon chloride, or even carbodiimide have been reported.[5] However, the first microporous silicon imido nitrides with a mean pore size of 0.7 nm were synthesized by Bradley and Dismukes in pyrolysis reactions of polysilazanes.[6] Mesoporous silicon imido nitride with a narrow pore-size distribution ($d_{av} = 5.6$ nm) and a high specific surface area (up to 1000 $m^2 g^{-1}$) was obtained recently using the ammonolysis of silicon tetrachloride in organic solvents.[7]

We describe herein a template-assisted method which allows, for the first time, tailoring the pore size of microporous silicon nitride materials in a wide range from primary to secondary micropores. In this procedure, tris(dimethylamino)silylamine $[(CH_3)_2N]_3SiNH_2$ **1**[8] is ammonolyzed in a concentrated solution of $CH_3(CH_2)_nNH_2$ ($n = 11-17$) in hot acetonitrile. The ammonolysis can be considered as an analogue of silicon oxide manufacture by sol–gel methods using prehydrolyzed tetramethoxysilane and water. After cooling to room temperature, a gel forms which is dried and heated slowly to 823 K in flowing ammonia. According to nitrogen physisorption experiments (Figure 1), such materials prepared using alkylamines of different chain length

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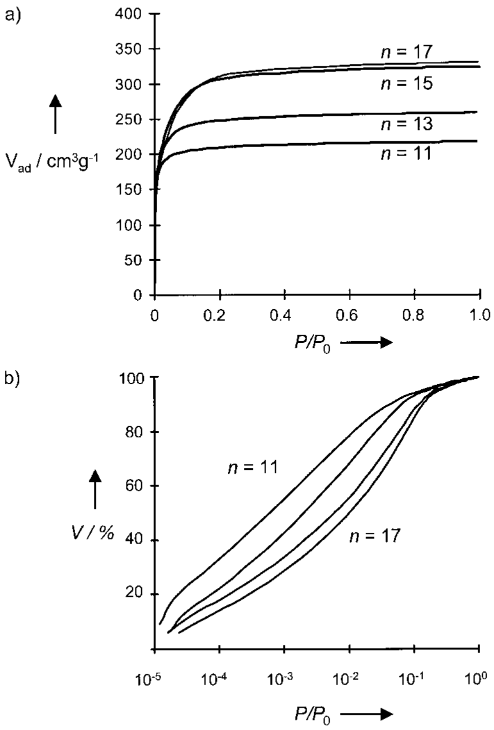


Figure 1. a) Nitrogen physisorption isotherms of microporous silicon imido nitrides prepared using $CH_3(CH_2)_nNH_2$ ($n = 11-17$) as templates, b) logarithmic plot (V = volume adsorbed normalized to volume at $P/P_0 = 1$).

($CH_3(CH_2)_nNH_2$, $n = 11$, 13, 15, 17) are all microporous and the isotherms are of type I. The micropore volume increases with the length of the amine alkyl chain (Table 1). Logarithmic plots (Figure 1 b) show that for the longer amines used as templates the nitrogen adsorption predominately occurs at higher relative pressures corresponding to secondary micropores. The actual calculation of the pore size using Horvath–Kawazoe or density functional theory (DFT) methods is difficult, since the principal interaction potentials of the adsorbate and the adsorbent are unknown and assumptions have to be made about the pore morphology.[9] The numerical values of the pore diameters calculated from the DFT method (Table 1) are therefore not fully accurate but, more importantly, allow a comparison among members of a class of similar materials which presumably have the same interaction potentials.

Table 1. Nitrogen physisorption results for high surface-area silicon imido nitrides prepared using linear aliphatic amines $CH_3(CH_2)_nNH_2$ as templates.

Template chain ength *n*	Micropore volume [cm^{3}g^{-1}]	Average pore diameter [Å]
11	0.32	11.8
12	0.34	12.4
13	0.37	13.6
14	0.38	13.7
15	0.42	15.7
17	0.48	16.5

The nanometer-sized micropores are easily discerned in high-resolution TEM pictures (Figure 2). They reveal the uniform channel-like pore structure of the air-sensitive nitrides. Crystallization of the inorganic network was neither observed in TEM pictures nor in XRD powder patterns even after annealing the gels at 1273 K in a stream of gaseous ammonia. Samples treated thusly maintained their high micropore volume (0.35 cm^{3}g^{-1}) as well as the pore structure. This surprisingly low sintering tendency is an attractive feature and reveals the promising potential of the material as a support in high temperature catalysis under nonoxidizing conditions.

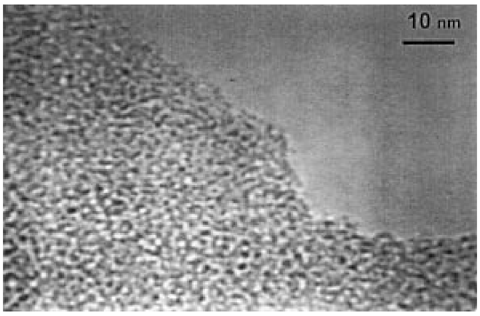
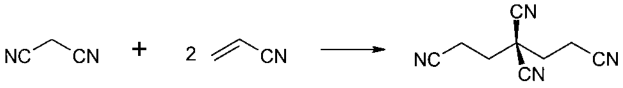


Figure 2. TEM picture of microporous silicon nitride (template: octadecylamine, $d_{av} = 1.7$ nm).

The pore evolution mechanism is still unknown. The size of the pores is of the same order as the size of the templating molecules, and therefore a micellar templating mechanism—in any case unlikely because of the low dielectric constant of the organic solvent—can be excluded. In fact, we believe that the amines are occluded in the first condensation step and released after thermal consolidation of the network during the heat treatment at about 673 K.

IR spectroscopy of the heat-treated samples was used to identify silicon imido nitride [$\tilde{\nu} = 3408$ (v(NH)), 1549 ($\delta(NH_2)$), 1182 (δ(NH)), 891 cm^{-1} ($\nu_{as}(Si_2N)$)].[8] The ^{29}Si MAS NMR spectrum consists of a broad line with a maximum at $\delta = -41$ and a shoulder at about $\delta = -50$. The line covers a region between $\delta = -35$ and -55. Such a broadening originates from the amorphous character of preceramic silicon nitride powders, in which various different coordination spheres are present.[10]

Silicon imido nitride with high accessible surface area can be used as a solid base catalyst in Michael addition reactions due to the presence of basic sites. For example, moderately acidic substrates like malononitrile ($pK_a = 11$) are activated to form addition products with substrates like acrylonitrile (Scheme 1).



Scheme 1.

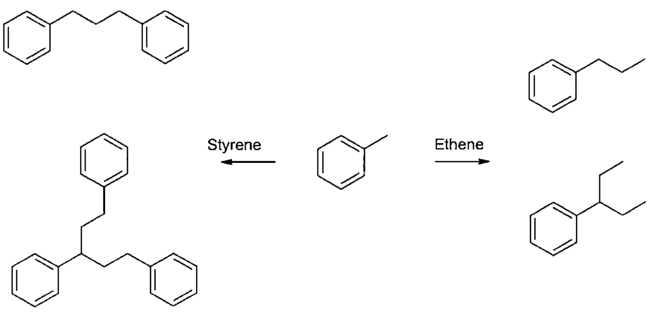
Due to the basicity of the inner surface and its high thermal and chemical stability, silicon nitride can be used as a solid superbase catalyst ($pK_a > 26$) after potassium impregnation.[11] Solid superbases like alkali metal promoted oxides are used in industry for the isomerization of polycyclic alkenes or in side-chain alkylations of alkylbenzenes.[12] In the case of silicon nitride, the covalent network is advantageous to achieve shape selectivity through pore-size engineering, as opposed to nonporous basic oxide supports like MgO or Al_2O_3. Zeolites are less suitable for such reactions due to a high number of acidic sites. However, the catalytic isomerization of 1-butene has been reported over sodium metal clusters located in high-alumina zeolites.[13]

The educt and product selectivity of our nitrides is demonstrated by comparing the performance of microporous ($d_{av} = 1.7$ nm) and mesoporous ($d_{av} = 5.6$ nm) silicon nitride catalysts (Table 2). The side-chain alkylation of toluene with styrene (Scheme 2) proceeds within minutes with the mesoporous catalyst and produces also higher addition products. In contrast, the microporous catalyst gives no conversion due to the bulky character of the products. The alkylation reaction with ethene on the other hand (Scheme 2) proceeds smoothly with both catalysts, and at higher ethene pressures (30 bar) the dialkylation product forms even over the microporous catalyst since both propylbenzene and (1-ethylpropyl)benzene fit in the secondary micropores.

Table 2. Conversion [%] over potassium-promoted micro- and mesoporous silicon imido nitride (reaction time in parentheses).

Reaction	Microporous catalyst ($d_{av} = 1.7$ nm)	Mesoporous catalyst ($d_{av} = 5.6$ nm)
toluene + ethene[a]	74.0 (60 h)[c]	25.0 (96 h)[d]
toluene + styrene[a]	0.0 (48 h)	100.0 (10 min)
1-hexene[b]	99.3 (18 h)	95.5 (2 min)
1-hexadecene[b]	0.0 (18 h)	80.8 (2 min)

[a] Scheme 2. [b] Double bond shift. [c] 30 bar. [d] 20 bar.



Scheme 2.

Similar differences between micro- and mesoporous nitrides are observed in alkene isomerization reactions. Using the mesoporous catalyst, isomerization of 1-hexene and 1-hexadecene (1:1 mixture) to the more stable alkenes with inner double bonds proceeds within minutes for both substrates. The microporous solid converts instead only the shorter substrate 1-hexene, and the pure 1-hexadecene can be recovered from the mixture. These selectivity differences confirm the results of the nitrogen adsorption measurements. Probably the calculated pore radii are a little to high as compared to the size of the substrates and products, which is due to the limitations of the pore size analysis.

Summarizing, we have demonstrated that pore-size tailoring of silicon imido nitride is possible. The compounds described here represent a new class of shape-selective solid superbase catalysts.

Experimental Section

All operations were performed using an argon-filled glove box or a vacuum line and dry solvents. Alkylamines (Merck, Aldrich) were dried in vacuum prior to use. Tris(dimethylamino)silylamine was prepared according to a procedure previously reported and characterized by GC/MS.[8] Typically, the liquid precursor (1.00 mmol) was added to a solution of $CH_3(CH_2)_nNH_2$ (2 g, $n = 11-17$) in boiling acetonitrile (20 mL, saturated with gaseous ammonia). After 1 h stirring, the reaction mixture was cooled to room temperature and a gel formed at the bottom of the flask. After washing with hot acetonitrile, the gel was dried in vacuum and heated slowly to 823 K in a dynamic ammonia atmosphere (1 bar) to give a yellowish, X-ray amorphous silicon imido nitride powder.

Nitrogen physisorption measurements were performed on a Micromeritics 2000 apparatus. The micropore volume was deduced from the total amount nitrogen adsorbed at $P/P_0 = 0.2$. The Micromeritics DFT program was used to estimate absolute pore sizes.[14] For ^{29}Si MAS NMR experiments, a Bruker Avance 500WB instrument was used. The spectra were recorded using a single-pulse excitation ($\pi/2$, 4.5 μs) with a repetition time of 60 s and a MAS frequency of 5.0 kHz.

The general procedure for potassium promotion is described elsewhere.[11] All test reactions were carried out at 295 K. For alkene isomerizations, 1-hexene and 1-hexadecene were mixed (1:1) and 2 mL of the mixture was added to the catalyst (100 mg). The ethylation was carried out in a 50 mL steel autoclave at a pressure of 20–30 bar loaded with 10 mL toluene. The product composition was analyzed by means of GC/MS and ^{1}H NMR spectroscopy.

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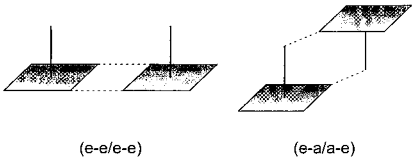
Magnetic Interactions as Supramolecular Function: Structure and Magnetic Properties of Hydrogen-Bridged Dinuclear Copper(II) Complexes**

Winfried Plass,* Axel Pohlmann, and
Jens Rautengarten

Dedicated to Professor Ernst-Gottfried Jäger
on the occasion of his 65th birthday

Hydrogen bonds play a key role in interactions in biological structures, supramolecular chemistry, and crystal engineering.[1] As such they are also important to understand the properties of relevant magnetic materials.[2] In particular for some copper(II)-containing coordination compounds it has been shown that the variation of possible supramolecular interactions can substantially influence the magnetic properties of related coordination polymers.[3]

Although copper(II) complexes have been widely studied, only two basic patterns of hydrogen bonding have been observed for dinuclear units (Scheme 1). In accord with the preferred square-planar coordination environment for copper(II) ions with the option of one or two additional apical ligands, these hydrogen bonds can be denoted as either equatorial–equatorial (e–e) or equatorial–apical (e–a) with regard to the position of the involved donor and acceptor atoms. If one considers that the magnetic orbital at each copper(II) ion is defined by the short equatorial bonds, that is basically an orbital of $d_{x^2-y^2}$ type with some possible admixture of d_{z^2} character, a qualitative magneto-structural correlation would predict antiferromagnetic coupling for (e–e/e–e) bridging patterns and weak interactions, which should be of ferromagnetic nature, for (e–a/a–e) bridging patterns. In addition, the magnitude of the magnetic coupling should also be related to the strength of the involved hydrogen bonds. This basic concept is in agreement with the observed structural and magnetic data of relevant systems.[4]



Scheme 1. Schematic representation for the hydrogen bonding patterns observed for dinuclear copper(II) complexes with square-pyramidal coordination geometry at the copper(II) centers (e: equatorial position, a: apical position).

To probe this qualitative magneto-structural relationship we synthesized the copper(II) complex with the trivalent, pentadentate Schiff base ligand *N*-salicylidene-2-(bis(2-hydroxyethyl)amino)ethylamine (H_3sabhea). The resulting self-complementary complex cation $[Cu(H_2sabhea)]^+$ can be isolated as hydrogen-bridged dinuclear complex **1**. Complex **1** can be reversibly deprotonated in aqueous solution yielding **2**, the first triply hydrogen-bridged dinuclear copper(II) complex.

$[\{Cu(H_2sabhea)\}_2](BF_4)_2$ **1**

$[\{Cu(H_2sabhea)\}\{Cu(Hsabhea)\}]BF_4$ **2**

The X-ray crystal structure analyses[5] of the isolated compounds **1** · 0.5 EtOH · 0.25 H_2O (**1a**) and **2** · H_2O (**2a**) reveal the dimeric hydrogen-bridged structure of the cationic copper(II) complexes (Figure 1). The prearranged coplanar configuration for three donor sets of the H_3sabhea ligand (O1, N1, and N2; see Figure 1) defines the orientation of the equatorial plane of the distorted square-pyramidal coordination environment of the copper(II) centers.[6] This is consistent with the observed elongation of the apical Cu–O bonds by about 25–30 pm as compared to the relevant equatorial bonds (see Figure 1). The two hydrogen bonds in **1** involve the equatorially coordinated alcohol group as donor and the phenolate oxygen as acceptor; this leads to a (e–e/e–e) bridging pattern (see Scheme 1). The observed O ··· O distance of 260 pm is within the range of strong O–H ··· O hydrogen bonds.[1f] In **1** both apical coordinated alcohol groups are oriented *cis* with respect to the hydrogen bonding

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