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Chemical Synthesis of Mesoporous Carbon Nitrides Using Hard Templates and Their Use as a Metal-Free Catalyst for Friedel–Crafts Reaction of Benzene***Frederic Goettmann, Anna Fischer, Markus Antonietti, and Arne Thomas**

Carbon nitride is presumably the most promising (and the most sought after) candidate to complement carbon in materials applications. Diamond-like β - C_3N_4 is predicted to be of similar hardness as diamond but less compressible.^[1,2] However, it is assumed that like carbon, at ambient conditions a graphitic- C_3N_4 allotrope (g- C_3N_4) is the most stable form. Accordingly, the attempted bulk synthesis of this material is the subject of an even larger number of reports in the literature.^[3] Historically, the synthesis of g- C_3N_4 derivatives started with the observations of Berzelius described by Liebig^[4] in 1834. They reported the first synthesis of a less defined, hydrogen-containing, polymeric precursor (“melon”), which however already had the correct connectivity patterns and an approximately correct C/N ratio. g- C_3N_4 is a potentially useful substitute for amorphous and graphitic carbon in a variety of applications, for example, as a catalytic support and for gas storage.^[5] Therefore, novel procedures yielding more defined carbon nitrides, in particular mesoporous forms with large accessible areas, are eagerly awaited. Vinu et al. recently reported the synthesis of mesoporous carbon nitride by nanocasting techniques.^[6] Their material featured a large surface area; however, the C/N molar ratio (≈ 5) indicated the loss of the vast majority of nitrogen, while X-ray diffraction measurements showed low crystallinity of the pore walls.

In this paper we employ a recently developed^[7] synthetic scheme based on the self-condensation of cyanamide, dicyandiamide, or melamine accompanied by elimination of ammonia to generate mesoporous g- C_3N_4 materials with high local order. As C_3N_4 synthesis is a high-temperature procedure, appropriate templates that withstand 600 °C for at least 12 h are needed for the scaffolding of the mesoporous system. Recently, porous silicas were used successfully as templates for the generation of g- C_3N_4 nanoparticles.^[8] Herein, a

[*] Dr. F. Goettmann, A. Fischer, Prof. Dr. M. Antonietti, Dr. A. Thomas
Max-Planck-Institute of Colloids and Interfaces
Department of Colloid Chemistry
Research Campus Golm, 14424 Potsdam (Germany)
Fax: (+49) 331-567-9502
E-mail: arne.thomas@mpikg.mpg.de

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similar, but inverted, template approach is applied to the carbon nitride system, using so-called hard templates, that is, inorganic nanoparticles, which can be removed after condensation. Silica nanoparticles, which have already been used successfully for the generation of mesoporous carbon,^[9] are found to act as suitable templates.

Ideally, these silica nanoparticles could be dispersed homogeneously in the starting monomers, that is, in cyanamide. In our case, such a dispersion is favored by appropriate surface interactions between the silica surface and the amine and, later, aromatic nitrogen groups. Condensation of the monomers at elevated temperatures (two condensation procedures were applied; see the Experimental Section) resulted in carbon nitride/silica hybrids, in which the silica nanoparticles remain well-dispersed in a solid C₃N₄ matrix. The silica template was dissolved with ammonium hydrogen fluoride solution and removed to yield various mesoporous materials of the type mpg-C₃N_{4/r}. (In the following the “g” is omitted when the first heat treatment was used, in other words, when the material is not sufficiently graphitic; *r* refers to the initial silica/cyanamide mass ratio (0.5, 1, 1.6).) These materials were fully characterized by using transmission electron microscopy (TEM), nitrogen adsorption, wide- and small-angle X-ray scattering, elemental analysis, and FTIR spectroscopy.

Figure 1 shows TEM pictures of a sample with an initial cyanamide/silica mass ratio of 1:1 that was condensed for 4 h at 550 °C and freed of the template. The TEM pictures indicate that the pore size and connectivity of those powders

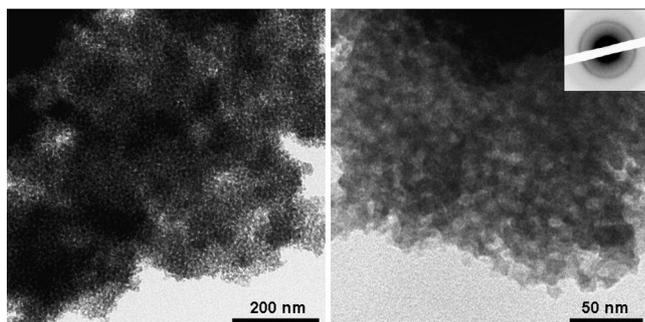


Figure 1. TEM images and an electron diffraction pattern of mp-C₃N_{4/1} after removal of the silica nanoparticles.

exactly reflect the geometric properties of the original template. The disordered pore system of spherical pores with a mean diameter of 12 nm can be regarded as a direct image, or more appropriately, a negative image of the structure of the silica sol. In addition, electron diffraction of a selected area proves the high partial crystallinity of the pore walls, which is revealed by one intense diffraction ring corresponding to the stacking distance of g-C₃N₄ (*d* = 0.33 nm).

Figure 2 shows nitrogen adsorption/desorption isotherms of three mp-C₃N₄ samples prepared with different silica/cyanamide ratios. The curves show a small hysteresis typical for the existence of randomly connected spherical pores, only

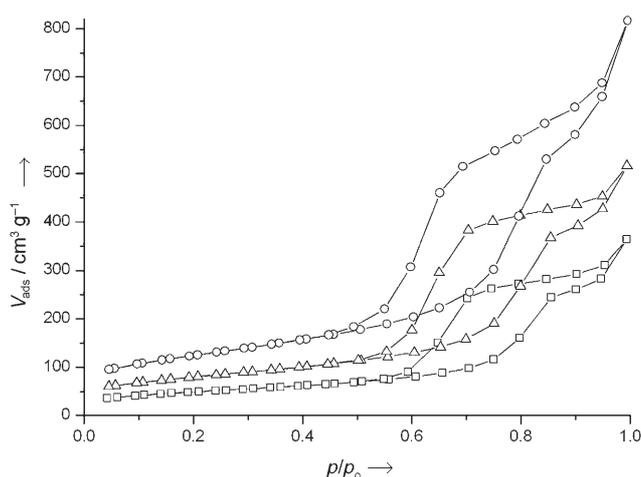


Figure 2. Nitrogen gas adsorption isotherms for different mp-C₃N₄ samples reflecting different template concentrations. □ mp-C₃N_{4/0.5}, △ mp-C₃N_{4/1}, ○ mp-C₃N_{4/1.6}.

weak microporosity, and surface areas between 86 and 439 m² g⁻¹, depending on the template content.

To evaluate the degree of condensation and the structure of the pore walls, we performed wide-angle X-ray scattering (WAXS) measurements and elemental analysis. The data along with those of an appropriately condensed bulk g-C₃N₄ are shown in Figure 3. The X-ray diffraction patterns reveal

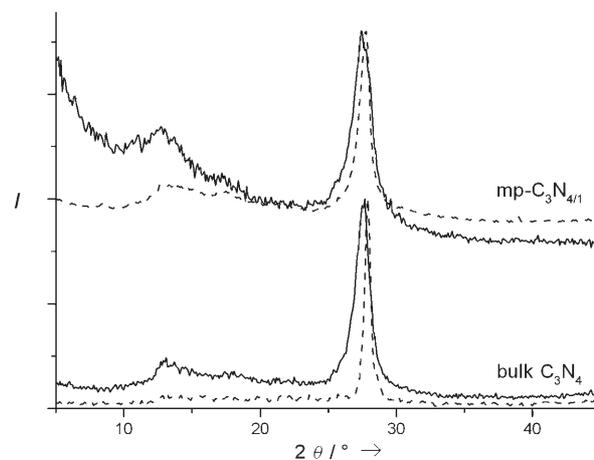


Figure 3. Comparison of the WAXS diagram of mp-C₃N_{4/1} with that of the corresponding nonporous material after two different heat treatments: 550 °C for 4 h in closed but unsealed quartz tubes (—); additional heating at 600 °C for 10 h in sealed quartz ampules (----).

the graphite-like stacking of C₃N₄ layers in both the bulk and the mesoporous material. The (002) peaks correspond to interlayer distances of *d* = 0.326 nm (material prepared at 550 °C) and *d* = 0.319 nm (material prepared at 600 °C). The X-ray patterns recorded for the mesoporous materials do not differ significantly from those of the nonporous materials, except for a slight broadening of the (002) peak and a decrease in the overall intensity. This can be attributed to a reduced correlation length introduced by the spherical

porogens. The ordering in the pore walls is significantly increased by the second tempering step (600 °C/10 h) prior to the removal of the silica template. For the bulk and the mesoporous materials, a pronounced additional peak is found at $2\theta = 13.1^\circ$, corresponding to a distance $d = 0.675$ nm, which can be attributed to an in-plane structural packing motif, for example, the hole-to-hole distance of the nitride pores (Figure 4). For the mesoporous materials this peak is broadened, again reflecting the effect of the geometric confinement in the nanosized pore walls.

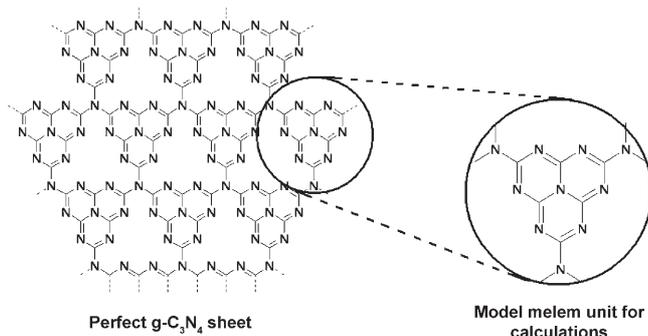


Figure 4. Representation of a perfect graphitic C_3N_4 and of the melem unit used for modeling purposes.

Elemental analyses were performed several times on different batches of the prepared material. An average value of 0.71 was determined for the C/N ratio (theoretical value of C_3N_4 : 0.75). We attribute the additional small amounts of hydrogen (1.5%) to (minor) structural defects, surface termination effects by uncondensed amino functions (which is supported by the fact that the H content increases with surface area), and adsorbed water (as evidenced by FTIR spectroscopy). Although this material does not exhibit perfect crystallinity, its X-ray diffraction pattern indicates an organization level that differs strongly from Liebig's "melon".

For a long time the field of mesoporous materials was restricted to inorganic solids^[10] and resulted in their numerous applications especially as catalysts and catalytic supports.^[11] Based on its unique electronic properties and large surface area, mpg- C_3N_4 should be an alternative catalyst complementary to the high-surface-area metal oxides usually used. According to Kroke et al.^[12] the basic motifs of a g- C_3N_4 sheet are melem rings linked by nitrogen bridges. We performed DFT calculations using the Gaussian O3 package with the B3LYP functional on a model melem unit to gain insight into the local electronic structure of g- C_3N_4 . The optimized geometry is shown in Figure 5. It is worth noticing that even in the uncondensed form the amino groups are planar, indicating sp^2 hybridization. In this case the lone pairs of these atoms interact with the π system of the arene. The three highest occupied molecular orbitals feature π symmetry, whereas HOMO-3 is an antibonding combination of the atomic orbitals describing the lone pairs of the "aromatic" nitrogen atoms. These results are in good qualitative agreement with results reported by Le Breton et al. in 1984;^[13] the HOMO consists exclusively of the p_z orbitals of the hetero-

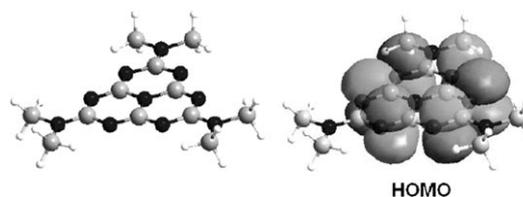


Figure 5. Optimized geometry (DFT) of the model melem ring (left) and a representation of the HOMO (right).

cyclic nitrogens, which is exactly the symmetry of the highest unoccupied π -type orbital in the Hückel model of benzene. It should thus be possible for the melem units to transfer electron density to arenes through overlapping of those orbitals, resulting in a very unusual arene activation.

A perfect infinite g- C_3N_4 sheet, however, is likely to feature an electronic band structure (theoretical investigations are currently underway that support this idea) and thus no electron localization in the π states. The above-mentioned activation might therefore only be possible on defects, which promote electron relocalization. In the case of graphite it is well known that defects such as edges,^[14] curvature,^[15] and doping atoms^[16] can induce electron relocalization. In addition, such defects have recently been demonstrated to be catalytically active sites in the oxidative dehydrogenation of ethylbenzene.^[17,18] mpg- C_3N_4 features almost all of these structures in combination with a high surface area, which implies that this material should contain a large number of potentially catalytic active sites. For this reason we investigated the activity of mpg- C_3N_4 as a catalyst for the activation of aromatic compounds.

A typical process for the C–H activation of aromatic molecules is the Friedel–Crafts acylation. Usually the electrophile is activated, although activation of the nucleophile should, in principle, yield the same results. In fact, graphite particles have already been used to promote Friedel–Crafts reactions. However, because of the large excess of graphite required, it is not clear whether this is catalytic activation.^[19,20]

For our purpose, we analyzed six samples of mesoporous C_3N_4 with varying surface area (amount of template) and degree of organization (heat treatment; Table 1). We first

Table 1: Specific surface areas (in $m^2 g^{-1}$) of the different mesoporous nitrides synthesized for catalytic applications.

	$C_3N_{4/0.5}$	$C_3N_{4/1}$	$C_3N_{4/1.6}$
mp-	136	190	440
mpg-	86	141	327

investigated the effect of various solvents (benzene, heptane, anisole) on the acylation of benzene with hexanoyl chloride using mp- $C_3N_{4/1}$ as the catalyst. The corresponding conversion rates are listed in Table 2. In all cases, medium to high conversion was found; that is, mp- C_3N_4 indeed acts as an activation catalyst. The observed difference between reactions conducted in benzene and heptane is likely to result from passivation of the surface of mp- C_3N_4 by a large excess of benzene. We are currently examining this assumption by

Table 2: Catalytic activity of mp-C₃N_{4/1} in the Friedel–Crafts acylation of benzene with hexanoyl chloride in different solvents.

	Benzene	Heptane	Anisole
T [°C]	80	90	150
Conversion [%]	16	80	60

spectroscopy. The choice of anisole as a solvent might be surprising as it is well known to be much more reactive than benzene as a Friedel–Crafts substrate. Indeed, in mixtures of benzene and anisole the only product formed is *n*-hexanophenone. This finding indicates that anisole does not react as long as benzene is present. As the catalysis is supposed to originate from electron donation from melem units to the aromatic substrate, substrates having lower-lying molecular orbitals should interact more strongly with the C₃N₄ surface. On the other hand, substitutions on the aromatic ring alter the symmetry of the molecular orbitals, resulting in an inferior overlap with the HOMO of localized melem units. These two considerations together with steric effects make it difficult to predict the reactivity of individual arenes.

Since heptane was found to be a suitable solvent for the Friedel–Crafts acylation (Table 2), it was used in subsequent experiments. We set out to analyze the effect of the surface and crystallinity of the catalysts. The acylations were performed with hexanoyl chloride (50 mg) and benzene (150 mg) in heptane (5 g) for 20 h at 90 °C using 25 mg of the corresponding carbon nitride as the catalyst. The products of the reactions were analyzed by GC with an internal standard for quantification. Some results are summarized in Table 3. Most of the mesoporous carbon nitrides used are

Table 3: Catalytic activity of mpg-C₃N₄ in the Friedel–Crafts acylation of benzene.^[a]

Catalyst	Conversion [%]	TOF × 100 [h ⁻¹] ^[b]
mp-C ₃ N _{4/0.5}	52	3.6
mp-C ₃ N _{4/1}	80	5.5
mp-C ₃ N _{4/1.6}	52	3.6
mpg-C ₃ N _{4/0.5}	90	6.2
bulk g-C ₃ N ₄	0	–
graphite	1	–

[a] Reaction conditions: A mixture of benzene (150 mg), hexanoyl chloride (50 mg), and (C₃N₄) in heptane (5 g) was stirred at 90 °C for 20 h. The products were analyzed by gas chromatography. [b] Turnover frequency: *n*(hexanoyl chloride) per *n*(melem units) per hour.

indeed active catalysts for the Friedel–Crafts acylation, whereas the bulk carbon nitride was inactive. As a reference, graphite particles (1 μm in diameter) were used under the same conditions and were found to be far less active.

No clear correlation can be found between the specific surface area and the catalytic activity of samples that were submitted to the same heat treatment, as the activity appears to go through a maximum. This can also indicate that only the pore walls of a certain minimal thickness have a suitable electronic structure. The second heat treatment at 600 °C and the resulting increase in organization and condensation seem

to improve the catalytic activity, and the best results were obtained for mpg-C₃N_{4/0.5} (90 % conversion).

To conclude, we have synthesized a mesoporous, high-surface-area graphitic carbon nitride by using colloidal silica nanoparticles as a template, and its catalytic properties were tested in Friedel–Crafts reactions. Remarkable activity enhancement was found for reactions with benzene as the coupling partner. We are currently trying to prove experimentally that this catalysis arises from back-donation of electron density from molecular orbitals of the catalyst to unoccupied orbitals of the arene. As defects in the graphitic layers appear to be responsible for the catalytic activity, in future work we will focus on determining the structure of the catalyst more precisely to gain better insight into the underlying activation mechanism.

Most of the solids used in heterogeneous catalysis are Lewis acids.^[21] We hope that mpg-C₃N₄ described here will pave the way for metal-free heterogeneous catalysts with Lewis-base character. This would be an important step towards metal-free coordination chemistry and catalysis. Moreover, this system is likely to be active for other C–C coupling and C–H activation reactions. It is remarkable that this was achieved with a material first described by Berzelius and Liebig, one of the first organic solid-state materials made.

Experimental Section

TEM images were recorded on a Zeiss EM91 microscope. WAXS spectra were recorded on a Bruker D8 Advance diffractometer and the SAXS spectra on a Enraf Nonius FR590. FTIR spectra were recorded on a BioRad FTS 6000 spectrometer.

Synthesis of g-C₃N₄: Molten cyanamide (1 g, 24 mmol; Aldrich) was heated and stirred at 70 °C, and different amounts of a 40 % dispersion of 12-nm SiO₂ particles (Ludox HS40, Aldrich) in water were added dropwise (1.25, 2.0, 4.0 g Ludox for the *r* = 0.5, 1, 1.6). The resulting transparent mixtures were then heated at a rate of 4.5 K min⁻¹ over 2 h to reach a temperature of 550 °C and then tempered at this temperature for another 4 h. To prepare mp-C₃N₄, the resulting brown–yellow powder was treated with a 4 M NH₄HF₂ for two days to remove the silica template. The powders were then centrifuged and washed three times with distilled water and twice with ethanol. Finally the powders were dried at 70 °C under vacuum for several hours. To prepare mpg-C₃N₄, samples resulting from the first heat treatment (without silica extraction) were heated to 600 °C for 10 h under static vacuum in a sealed quartz ampule. To remove the silica templates, the obtained light-brown powders were treated with NH₄HF₂ as described above.

All computations were performed using the Gaussian 03 suite of programs^[22] and gradient-corrected density functional theory by using the B3LYP functional.^[23] Optimizations were carried out using the 6-21G basis set.

Catalysis experiments: A sample of mesoporous C₃N₄ (25 mg, 0.5 mmol melem units) was suspended in a solution of benzene (2 mmol) and hexanoyl chloride (50 mg, 0.75 mmol) in the respective solvent (5 g). The mixture was heated to reflux. After 20 h reaction time, an aliquot of the mixture was poured into ethanol and analyzed by GC. The structure of the product was confirmed by ¹H NMR spectroscopy.

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