Mesoporous graphitic carbon nitride as a versatile, metal-free catalyst for the cyclisation of functional nitriles and alkynes†‡

Frédéric Goettmann, Anna Fischer, Markus Antonietti and Arne Thomas*

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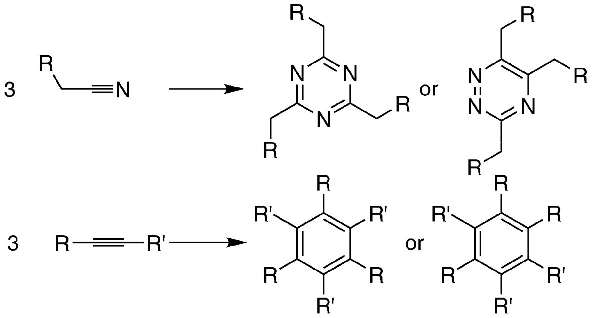
Mesoporous graphitic C_3N_4 was successfully employed as an effective catalyst for the cyclotrimerisation of various nitriles into triazine derivatives and the cyclisation of functional alkynes.

Introduction

Cyclotrimerisations of triple bonds are usually very exothermic reactions because they result in the formation of aromatic rings. Their practical realisation, however, is hindered by very high activation energies. This can be exemplified by the archetypical case of ethyne, where the activation energy of the concerted mechanism was estimated to be around 250 kJ mol^{-1}.[1] Nevertheless, such reactions are of great synthetic significance because they permit access to functional aromatic systems, such as benzene and triazine derivatives. Functional benzene rings are ubiquitous chemical commodities.[2] Triazines, formally resulting from the trimerisation of nitriles (Scheme 1), are important building blocks for supramolecular chemistry,[3] polymer syntheses[4,5] and have been used as crop protecting agents.[6]

Due to the increased attention paid to the environmental sustainability of chemical processes,[7–9] concerns about the usual syntheses of such compounds have arisen. The main syntheses of functional triazines rely either on the wasteful substitution of chlorine in cyanuric chloride[3] or on the alkali promoted trimerisation of nitriles,[10] the latter being incompatible with numerous functionalities. Recently, de la Hoz *et al.* reported on a catalytic synthesis of substituted s-triazine derivatives that relies on silica-supported Lewis acids.[11] In the case of benzene derivatives, the use of transition metals, for which cost, availability and toxicity are main issues, is regarded as unavoidable.[2]



Scheme 1 Formal representation of the syntheses of triazines from nitriles, and benzene derivatives from alkynes.

Here, we report on a heterogeneous metal-free catalytic system, which turned out to be effective for these cyclisations. An "ideal" catalyst[12,13] should be a solid (*i.e.* easy to handle and to separate); it should also be as simple as possible in terms of chemical composition (*i.e.* easy to synthesise), mesoporous (exhibiting high surface areas and good accessibility[14–17]) and, of course, highly catalytically active. A "metal-free" catalyst (like, for instance, graphite[18] or the proline systems used for homogeneous organocatalysis[19,20]) would provide additional benefits to the synthetic process, considering cost, toxicity and environmental sustainability.

In previous studies, we have shown that mesoporous graphitic carbon nitride, named mpg-C_3N_4, is such a potent metal-free heterogeneous catalyst, as it catalysed Friedel–Crafts type aromatic substitutions on benzene,[21,22] as well as the reaction of benzene and CO_2 to form phenol and CO.[23] Herein, we report on the catalytic activity of this purely organic material in the cyclisation of nitriles and alkynes.

The application of graphitic C_3N_4 as a catalyst for activating aromatic six-membered rings was motivated by the hexagonal symmetry of the tri-s-triazine units in its connectivity pattern (the structure of the graphite-like sheets of g-C_3N_4 was initially proposed by Kroke *et al.* and is now widely accepted,[24] Fig. 1) and the assumption that the p_z orbitals or the lone pairs of its aromatic nitrogens could interact with π^*-orbitals of aromatic rings. For the same symmetry reasons, graphitic C_3N_4 was thought to be able to stabilise one of the transition states of cyclotrimerisations, even though their aromaticity is still a matter of debate.[25,26]

Experimental

The chemicals that were used were employed as received. For the catalytic tests, we used the previously described mesoporous graphitic C_3N_4, mpg-C_3N_4.[21] In a typical synthesis, 2.5 g of a water dispersion of 12 nm silica spheres (Ludox® HS40, Aldrich) were added to 1.0 g of melted cyanamide (99%, Aldrich). The mixture was subsequently heated to 550 °C in

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Max-Planck-Institute of Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, D-14424 Potsdam, Germany. E-mail: arne.thomas@mpikg.mpg.de; Fax: +49 331-567-9502; Tel: +49 331-567-9509

† Electronic supplementary information (ESI) available: FT-IR spectra of the used powders; computational details. See DOI: 10.1039/b618555j.

‡ The HTML version of this article has been enhanced with colour images.

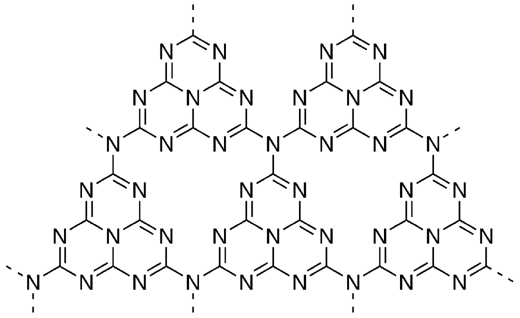


Fig. 1 Structure proposed by Kroke *et al.* for g-C_3N_4 (ref. 24).

a closed ceramic crucible for 4 h. After an additional heat treatment at 600 °C for 10 h and removal of the silica with NH_4HF_2 (Riedel de Haën), the resulting powder exhibited a specific surface area of 140 m^2 g^{-1} and an average pore diameter of 12 nm, as measured from nitrogen adsorption (measured with a Micromeritics Tristar 3000 system).

For a reference test, we also synthesised a heat treated mpg-C_3N_4 (mpg-C_3N_4-ht). For that, 500 mg of the previously described mesoporous powder was heated at 550 °C for 1 h in a closed iron autoclave fitted with a glass vessel. The specific surface area and the mean pore size of the resulting powder were not significantly different from those of mpg-C_3N_4. FT-IR measurements, however, showed that the amount of uncondensed amino groups at the surface of the pores was strongly decreased:† the broad band around 3130 cm^{-1}, corresponding to the N–H stretching modes, is noticeably weaker, while a strong peak at 725 cm^{-1}, present in the primary mpg-C_3N_4, which could be attributed to NH_2 bending modes according to Wang *et al.*,[27] almost vanished. A strong peak at 2162 cm^{-1}, which was attributed to uncondensed cyano moieties, is also reduced by this additional step.

In typical catalytic experiments, 50 mg of mpg-C_3N_4 was suspended in 5 ml of either the pure nitrile or alkyne, or a solution of nitrile in hexane (95%, Aldrich), or a solution of alkyne in xylenes (mixed isomers, extra pure, Merck). The resulting suspension was then placed in a 50 ml stainless steel autoclave fitted with a Teflon mantle (Samplatec Company) and heated to 150 or 180 °C for the planned reaction time. Acetonitrile (hyper grade, Merck) was used as the reactant and solvent. For the other nitriles, 10 mmol were dissolved in hexane, corresponding to 550 mg propionitrile (99%, Aldrich), 1 g benzonitrile (98%, Fluka), 1 g pyrazinecarbonitrile (99%, Aldrich), 760 mg chloroacetonitrile (99%, Aldrich) and 890 mg 3-chloropropionitrile (98%, Aldrich). Phenylacetylene (97%, Fluka) and propargyl alcohol (98%, Alfa Aesar) could be used as the reactant and solvent, as well. When working with xylenes as the solvent, 1 g of diphenylacetylene (98%, Aldrich), 500 mg of dimethyl acetylenedicarboxylate (99%, Aldrich) or 200 mg of propargyl alcohol (98%, Alfa Aesar) were used.

The products of the reactions were analysed using GC-MS (Agilent Technologies, GC 6890N, MS 5975) and, after isolation of the products, using ^1H and ^{13}C NMR spectroscopy (Bruker DMX 400).

FT-IR analyses of the catalysts were undertaken with a BioRad FTS600 spectrometer.

All computations were performed using the Gaussian 03 suite of programs[28] and gradient-corrected density functional theory by using the B3LYP functional.[29] Optimisations were carried out using the 6-311G basis set.

Results

The results of our experiments are summarised in Table 1. The conversion rates were calculated as the molar ratio of products and initial amount of reactant as determined from GC with an internal standard. The turnover frequencies (TOFs) were calculated as the number of mols of product formed per day and per theoretical number of mols of tri-s-triazine units in the catalyst. As only the tri-s-triazine units at the surface of the catalyst are likely to be accessible and can thus be active, our TOFs are thus largely underestimated. Nevertheless, these values are a useful tool for comparing the reactivities of our substrates as it can be assumed that the TOF is underestimated in the same way for each test.

Within the series of tested cyano compounds, acetonitrile showed the highest turnover frequency (Table 1, entry 1 with a TOF of 55 d^{-1}), while reference tests without catalyst (Table 1, entry 3) or with adenine as a catalyst (as nitriles are known to be able to react in basic media, Table 1, entry 4) failed to yield any detectable reaction products. It is worth noticing that molecules with comparable steric hindrance but different polarity exhibit very different reactivities. In the cases of propionitrile, chloropropionitrile and chloroacetonitrile (Table 1, entries 6, 11, 10), which are comparable from a steric point of view, the reactivities decrease according to the polarity of the C–N triple bond (which can, for instance, be evaluated from tabulated IR data[30]). Carbonitriles with aromatic moieties, however, behave differently; pyrazinecarbonitrile (Table 1, entry 8), for example, is one of the most reactive nitriles (TOF = 8.9 d^{-1}), while benzonitrile (Table 1, entry 7) does not react at all.

For alkynes, the expected cyclotrimerisation products are obtained in modest to good yields with dimethyl acetylenedicarboxylate (TOF = 0.2 d^{-1}) and propargyl alcohol (TOF = 33 d^{-1} at 5% conversion and TOF = 18 d^{-1} at 70% conversion). As seen from Table 1, phenyl- and diphenylacetylene also yielded Diels–Alder products (1-phenylnaphthalene and 1,2,3-triphenylnaphthalene).

Discussion

For the experiments in which alkynes are the reactants, the formation of trimerisation products is indeed catalysed, possibly through a mechanism that relies on the same electron transfer mechanism as the one postulated for the activation of benzene. Nevertheless, when the reactants can also act as dienes, Diels–Alder reactions are an alternative for the reaction pathway, which is indeed also observed, in part, for phenylacetylene and as the main reaction channel for diphenylacetylene. As reference tests without the catalyst showed no detectable conversion, these Diels–Alder reactions are apparently also catalysed by mpg-C_3N_4.

This is consistent with the results of Katritzky *et al.*, who showed that higher temperatures and pressures were required

Table 1 Results of the cyclotrimerisation tests catalysed by mpg-C_3N_4

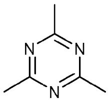
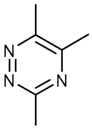
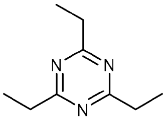
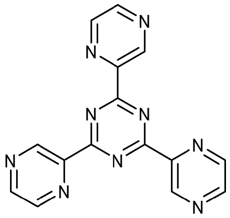
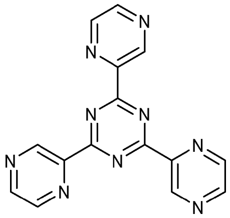
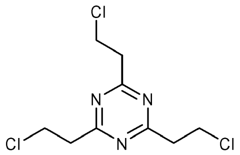
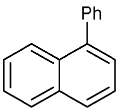
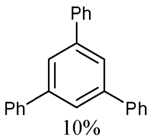
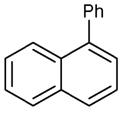
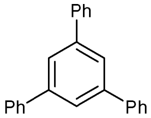
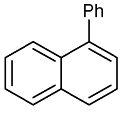
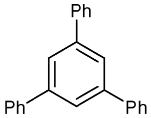
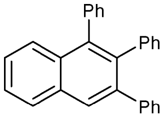
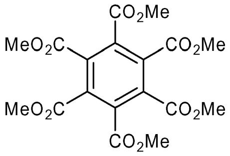
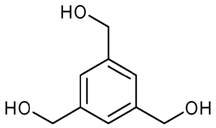
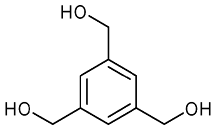
Entry	Reactant	Solvent	Temperature/ °C	Reaction time/h	Conversion rate (%)[a]	TOF[b]/ day^{-1}	Products[c]
1	Acetonitrile	—	180	80	20	55	 100%
2	Acetonitrile	—	150	48	1	1.2	 100%
3	Acetonitrile[d]	—	180	80	<0.5	—	—
4	Acetonitrile[e]	—	180	48	<0.5	—	—
5	Acetonitrile[f]	—	180	80	<0.5	—	—
6	Propionitrile	Hexane	180	48	15	2.4	 100%
7	Benzonitrile	Hexane	180	48	<0.5	—	—
8	Pyrazinecarbonitrile	Hexane	180	48	100	8.9	 100%
9	Pyrazinecarbonitrile[f]	Hexane	180	48	45	4.0	 100%
10	2-Chloroacetonitrile	Hexane	180	48	<0.5	—	—
11	3-Chloropropionitrile	Hexane	180	48	10	1.2	 100%
12	Phenylacetylene	—	140	24	8	13	 90%  10%

Table 1 (*continued*)

Entry	Reactant	Solvent	Temperature/ °C	Reaction time/h	Conversion rate (%)[a]	TOF[b]/ day^{-1}	Products[c]
13	Phenylacetylene	—	180	24	75	126	 41%  32%
14	Phenylacetylene[f]	—	180	24	99.5	166	 31%  44%
15	Phenylacetylene[d]	—	180	24	<0.5	—	—
16	Diphenylacetylene	Xylenes	150	60	100	4.3	 100%
17	Dimethyl acetylenedicarboxylate	Xylenes	120	48	10	0.2	 100%
18	Propargyl alcohol	—	120	24	5	33	 100%
19	Propargyl alcohol	Xylenes	120	24	70	18	 100%

[a] The conversion rates were calculated as the molar ratio of products and initial amount of reactant as determined from GC. [b] The turnover frequencies (TOFs) were calculated as the number of mols of product formed per day and per theoretical number of mols of tri-s-triazine units in the catalyst. [c] The percentages indicated below each product reflect the relative amount of this species among the other reaction products, as determined from GC. [d] Reference test without catalyst. [e] Reference test with adenine as a nitrogen rich soluble organic base. [f] Reference test with heat-treated mpg-C_3N_4.

to allow the non-catalytic Diels–Alder condensation of such alkynes to take place,[31] *i.e.* the role of the mpg-C_3N_4 would be, in part, to generate close-packed surface states by adsorption. Thermal [2 + 4] cyclisations are known to proceed *via* a concerted mechanism involving the π-system of both reactants. It is thus not surprising that mpg-C_3N_4 also activates those reactions, which are similar to the trimerisation reactions. In the case of diphenylacetylene, the Diels–Alder condensation is observed exclusively, probably because of steric effects. In the case of phenylacetylene, a change in temperature allows tuning of the ratio between the two different reaction products. 1-Phenylnaphthalene remains, however, the main product.

The reactivity of the various nitriles can be correlated neither to their bulkiness nor—over the whole set of examined starting products—directly to the polarity of their triple bond. The strong differences in the observed TOFs could thus rely on the way these molecules interact with the catalyst. FT-IR

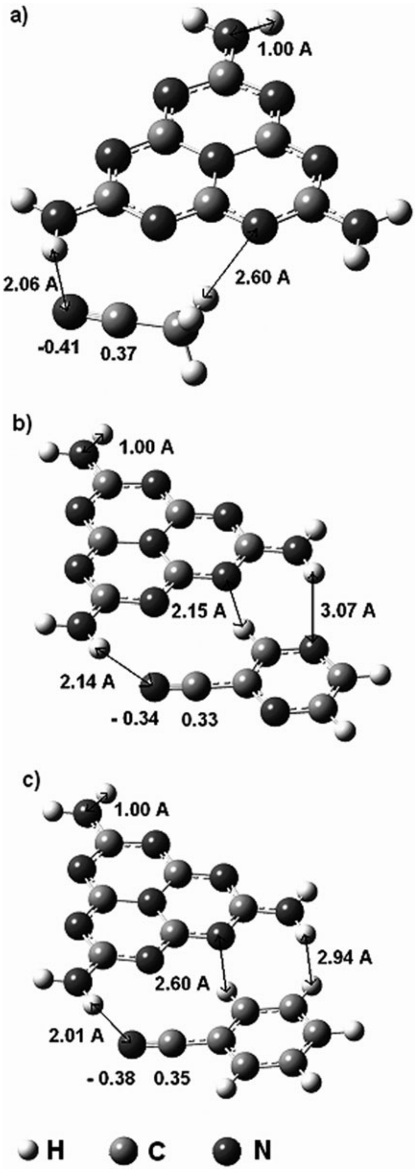


Fig. 2 Optimised structures of the adducts of a model triamino tri-s-triazine (melem) unit and (a) acetonitrile, (b) pyrazinecarbonitrile and (c) benzonitrile. Some typical bond lengths and NBO charges on the cyano group are given.

measurements on acetonitrile adsorbed on mpg-C_3N_4 show a weak bathochromic shift in the C–N asymmetric stretching vibration of the cyano moiety (from 2293 to 2290 cm^{-1}), consistent with a weakening of this bond.†

DFT modelling was undertaken to illustrate further details on how nitriles could interact with the active centres in mpg-C_3N_4, here modelled by the triamino tri-s-triazine (melem) molecule. These calculations are not meant to be a full investigation of the actual reaction mechanism, which would require a better theoretical model and expensive transition state optimisations. We investigated the geometries, relative thermodynamic stabilities and charge repartitions (in a natural bond orbital, NBO, population analysis[32]) of adducts of various nitriles and melem. Geometric parameters of the optimised molecules are reported in the ESI.† Fig. 2 displays some of the optimised adducts. Important features of the calculated structures are summarised in Table 2.

Interestingly, while benzene and tri-s-triazine units in mpg-C_3N_4 are probably interacting face-to-face through π-stacking,[21,23] stable adducts of nitriles with the melem unit were found to occur through H-bonding with the amino groups (Fig. 2). The adduct formation is always exothermic, up to about -50 kJ mol^{-1} in the case of pyrazinecarbonitrile. This molecule interacts with the melem unit through three H-bonds (Fig. 2b), comparable to the lock–key pattern interaction between substrate and reactant found for many enzymes[33,34] and known in supramolecular chemistry.[35] The complexation of the nitriles does not noticeably affect the lengths of their N–C bonds or the corresponding N–C–C angles. On the other hand, the dipole moment of the N–C triple bond is strongly modified by the H-bond formation. For example, while the non-complexed acetonitrile features a N–C dipole moment of 3.48 D, the adduct reaches 4.39 D. The observed polarisation of the N–C triple bond originates mainly from the electrostatic deformation of its electronic cloud by the nearby proton involved in the H-bond and could be involved in the mechanism of the trimerisation. This would be consistent with experimental evidence from early reports on the use of strong acids as suitable solvents for the cyclotrimerisation of nitriles.[36,37]

These calculations do not allow the building of a whole model to account for the observed activation of nitriles by mpg-C_3N_4, but suggest that H-bonding is playing an important role. The ability of mpg-C_3N_4 to form such H-bonds is strongly dependent on the amount of uncondensed amino functionalities at its surface. Indeed, Schnick and Lotsch recently showed, by means of solid state ^{15}N NMR spectroscopy, that bulk graphitic C_3N_4 features such uncondensed amino groups to a large extent.[38] We showed that these amino groups also play a predominant role in the activation of CO_2 by mpg-C_3N_4.[23] As a cross-testing experiment, we tried to reduce the number of those amine groups by a heat treatment step at the borderline of mpg-C_3N_4 stability. Indeed, a so-treated material showed no catalytic activity in the cyclotrimerisation of acetonitrile (Table 1, entry 5) and a much lower activity with pyrazinecarbonitrile (Table 1, entry 9), but it proved even more effective in catalysing the cyclisation of phenylacetylene (Table 1, entry 14, TOF = 166 d^{-1}). In our opinion, this experiment supports the idea that activation of nitriles, at least partly, relies on appropriate H-bonding patterns involving free amino functionalities, while the cyclisation of alkynes (also of the Diels–Alder type) is presumably due to aromatic charge-transfer interactions, as described for the metal-free catalysis of Friedel–Crafts reactions.

Conclusion

In this contribution, we have shown that mpg-C_3N_4 is a versatile, functionality-tolerant catalyst for the cyclotrimerisation of triple bonds. Numerical investigations also showed that the activation of nitriles is likely to proceed *via* H-bonds, whereas activation of alkynes presumably progresses *via* π-stacking, as is assumed for the activation of benzene. The simultaneous presence of different activation mechanisms in one structure (“multifunctional catalysis”) renders the

Table 2 Some geometric and electronic parameters of the optimised adducts[a]

Adduct of melem with	Formation enthalpy/kJ mol^{-1}	C–N distance in the cyano bond/Å	H-bond length between the cyano and amino group/Å	N–C–C angle of the cyano function/°	NBO charges in the cyano group		
					N	C	Dipole moment/debye
Acetonitrile	−38.9	1.164 *(1.165)*[b]	2.063	176.9 *(180.0)*	−0.42 *(−0.33)*	0.37 *(0.29)*	4.39 *(3.48)*
Propionitrile	−38.1	1.165 *(1.165)*	2.060	177.0 *(179.3)*	−0.42 *(−0.33)*	0.37 *(0.25)*	4.38 *(3.48)*
Pyrazinecarbonitrile	−49.9	1.165 *(1.166)*	2.139	176.8 *(178.4)*	−0.39 *(−0.26)*	0.33 *(0.27)*	4.03 *(2.98)*
Benzonitrile	−37.8	1.167 *(1.168)*	2.013	178.1 *(180.0)*	−0.38 *(−0.30)*	0.35 *(0.28)*	4.10 *(3.26)*

[a] All computations were performed using the Gaussian 03 suite of programs[28] and gradient-corrected density functional theory by using the B3LYP functional.[29] Optimisations were carried out using the 6-311G basis set. Evaluation of the charge repartition was achieved using the natural bond orbital (NBO) population analysis.[32] [b] For comparison, the corresponding lengths, angles and charges in the non-complexed nitriles are given in brackets.

different carbonitrides a very promising class of functional solid-state structures, particularly to explore the possibilities of a metal-free coordination chemistry and a coupled "green" group-efficient heterogeneous catalysis.

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