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“Nanorust”-catalyzed Benign Oxidation of Amines for Selective Synthesis of Nitriles

Rajenahally V. Jagadeesh, Henrik Junge, and Matthias Beller*^[a]*Dedicated to Bharat Ratna Professor C. N. R. Rao on the occasion of his 80th birthday.*

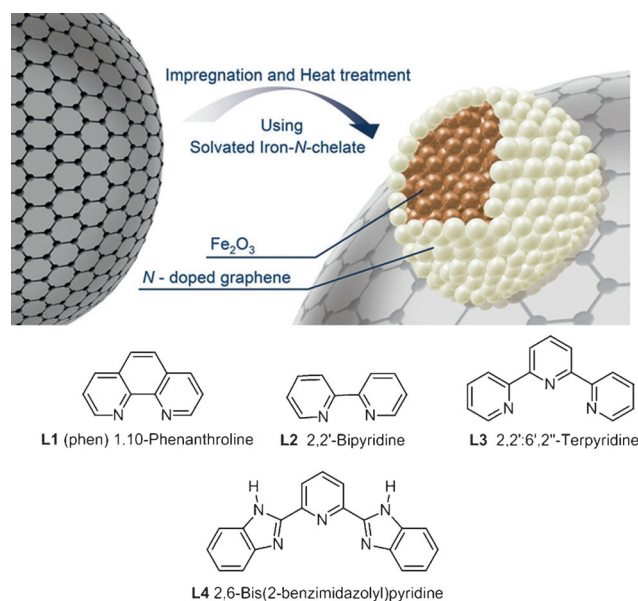
Organic nitriles constitute key precursors and central intermediates in organic synthesis. In addition, nitriles represent a versatile motif found in numerous medicinally and biologically important compounds. Generally, these nitriles are synthesized by traditional cyanation procedures using toxic cyanides. Herein, we report the selective and environmentally benign oxidative conversion of primary amines for the synthesis of structurally diverse aromatic, aliphatic and heterocyclic nitriles using a reusable “nanorust” (nanoscale Fe₂O₃)-based catalysts applying molecular oxygen.

The amino group is an omnipresent motif found in many classes of chemical compounds, including numerous industrial fine and bulk chemicals as well as agrochemicals and pharmaceuticals.^[1] Nowadays, many chemical transformations and biotransformations are routinely applied for the valorization of amines.^[2] Among these reactions, selective oxidations are less explored.^[3] On the other hand, the selective conversion of primary amines to nitriles or imines is interesting. In general, nitriles constitute important building blocks and key intermediates for organic synthesis. They also play a vital role as integral part of pharmaceuticals and agrochemicals.^[4] Traditionally, nitriles are synthesized by nucleophilic substitutions of alkyl and aryl halides using highly toxic cyanides (HCN; metal cyanides).^[5] On a larger scale, ammoxidation is the preferred method to produce acrylonitrile, methacrylonitrile, and simple benzonitriles.^[6] Notably, most of these ammoxidations are performed under drastic conditions and consequently they are restricted to nonfunctionalized substrates. Alternatively, for the conversion of amines to nitriles mainly ruthenium^[7] and copper-based^[8] catalyst systems have been applied under milder conditions. Nevertheless, most of the known catalyst systems cannot be used for the synthesis of functionalized and structurally diverse nitriles. In addition, poor catalyst activity is observed for challenging aliphatic substrates. Hence, more general methodologies for improved synthesis of advanced nitriles from amines using cost-effective and reusable catalysts are highly desirable. Regarding the potential catalysts for such reactions, obviously the use of more-abundant metals, especially iron-based systems, is preferred.^[9,10] Generally, iron-based

catalysts offer significant advantages compared to classical noble metal complexes: 1) Iron is the second-most abundant metal in the earth's crust (4.7%), 2) it constitutes the active center in numerous biocatalysts, and 3) the environmentally benign nature and low toxicity makes it an ideal metal for industrial catalysts. Due to ease of isolation and recyclability, the development of heterogeneous iron catalysts for advanced organic synthesis constitutes a prime topic and may be crucial for the advancement of cost-effective and sustainable industrial processes. Finally, it is worth mentioning that the use of air or molecular oxygen in oxidation processes is highly desired.^[11]

Inspired by the “noble” features of our recently developed nano-metal oxides (e.g. Fe₂O₃/NGr@C; “nanorust” and Co₃O₄/NGr@C) and our continuing interest in sustainable organic synthesis,^[12] recently we became attracted to the dehydrogenation of amines. Here, we show for the first time that nanometer-scale Fe₂O₃ materials are excellent catalysts for the selective oxidation of primary amines to diverse aliphatic, aromatic, and heterocyclic nitriles.

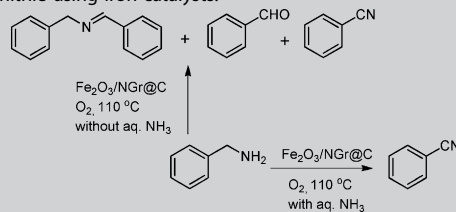
The used Fe₂O₃-based nanocatalysts (Fe₂O₃/NGr@C) were prepared by pyrolysis of in situ-generated nitrogen-ligated iron acetate complexes on carbon support at 800 °C for 2 h under argon atmosphere (Scheme 1).^[12a]



Scheme 1. Preparation of Fe₂O₃/NGr@C-catalysts using different nitrogen ligands (Fe = 3 wt%, Fe/L = 1:3 mole ratio).

[a] Dr. R. V. Jagadeesh, Dr. H. Junge, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e. V. an der Universität Rostock
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
E-mail: matthias.beller@catalysis.de

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Table 1. Synthesis of benzonitrile using iron catalysts.^[a]

Entry	Carbon	Iron complex ^[b]	Pyrolysis conditions		gas	Yield of benzonitrile ^[c] [%]
			T [°C]	t [h]		
1 ^[a]	–	–	–	–	–	< 1
2 ^[a]	–	Fe(OAc) ₂	–	–	–	< 2
3 ^[a]	–	Fe(OAc) ₂ -L1	–	–	–	< 2
4 ^[d]	Vulcan XC72R	Fe(OAc) ₂	–	–	–	2
5 ^[d]	Vulcan XC72R	Fe(OAc) ₂ -L1	–	–	–	2
6 ^[d]	Vulcan XC72R	Fe(OAc) ₂	800	2	Ar	5
7 ^[d]	Vulcan XC72R	Fe(OAc) ₂ -L1	800	2	Ar	97
8 ^[d]	Vulcan XC72R	Fe(OAc) ₂ -L2	800	2	Ar	20
9 ^[d]	Vulcan XC72R	Fe(OAc) ₂ -L3	800	2	Ar	60
10 ^[d]	Vulcan XC72R	Fe(OAc) ₂ -L4	800	2	Ar	79
11 ^[d]	Vulcan XC72R	–	800	2	Ar	< 1

[a] Homogeneous catalysis reaction conditions: 0.5 mmol benzylamine, 0.02 mmol Fe(OAc)₂, 0.06 mmol ligand, 200 μL aq. NH₃ (28–30% NH₃ basis), 3 bar O₂, 4 mL *t*-amyl alcohol. [b] L = ligand. [c] Determined by GC. [d] Heterogeneous catalysis reaction conditions: 0.5 mmol benzylamine 40 mg catalyst (4 mol% Fe), 200 μL aq. NH₃ (28–30% NH₃ basis), 3 bar O₂, 4 mL *t*-amyl alcohol.

Exploratory catalytic experiments were performed using benzyl amine as model substrate, applying molecular oxygen (Table 1). Although the heterogeneous iron catalyst proved to be active, the corresponding secondary imine was obtained as major product. In addition, a mixture of benzaldehyde and benzonitrile also formed in minor amounts. It is assumed that an initial iron oxide-catalyzed dehydrogenation of benzyl amine to the corresponding imine occurs. This reactive intermediate undergoes further dehydrogenation to give the desired product or alternatively forms the more stable secondary imine by addition of benzyl amine and elimination of ammonia. Trace amounts of benzaldehyde are explained by hydrolysis of the imine.

In order to suppress the formation of the secondary imine, aqueous ammonia was added to the reaction mixture. Indeed, this led to a highly selective formation of benzonitrile. Therefore, all of the following experiments were performed in the presence of aqueous ammonia. As expected, homogeneous iron-phenanthroline complexes were not active in the benchmark reaction (Table 1, entries 2–3). Similarly, pyrolyzed iron acetate on carbon and iron-phenanthroline complex immobilized on carbon under non-pyrolyzed conditions were not active (entries 4–6). However, pyrolysis of *N*-ligated iron acetate on carbon gave active catalysts with varying catalytic activities (entries 7–10). The most active system was obtained from pyrolysis of Fe-phenanthroline (L1) complex on carbon (Fe-phen/C-800). With this material benzyl amine was completely converted to benzonitrile in excellent yield (97%, entry 7). While, the catalyst based on bipyridine (L2) gave poor activity (entry 8), terpyridine (L3) and pyridinebisbenzimidazole (L4)

gave also active catalysts (60–79% yield of benzonitrile; entries 9–10).

As previously described the catalytic materials were systematically characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), and Mössbauer spectroscopy (see the Supporting Information).^[12a] Specifically, the Fe-phenanthroline/C-800 catalyst is characterized by the formation of nano-scale Fe₂O₃ particles (2–5 and 20–80 nm), which are surrounded by 3–5 layers of nitrogen-doped graphene (see Figure S1A). In contrast to this most active material, the Fe₂O₃ particles in Fe-bipyridyl/C-800 are much larger and consist of several crystallites (Figure S1B). In the latter case, the Fe₂O₃ particles are not surrounded by gra-

phene layers. In case of simple pyrolyzed iron-acetate (Fe(OAc)₂/C-800), the Fe₂O₃ particles occur in well-faceted big particles of 100–800 nm size (Figure S1C), which are also not surrounded by graphene layers. From all these results, we propose the formation of the nitrogen-doped graphene layers to be crucial for activity and we represent the active catalyst Fe-phen/C-800 as Fe₂O₃/NGr@C. This catalyst system is highly stable and can be conveniently recycled and re-used up to 5 times (Figure 1). For industry, catalyst re-usability is a major issue, which is also important for the advancement of cost-effective processes.

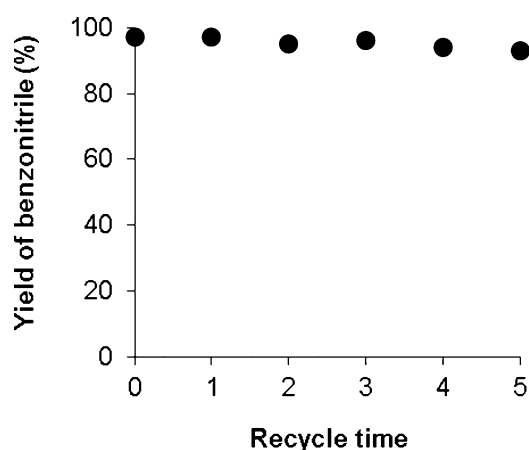


Figure 1. Synthesis of benzonitrile: recycling of Fe₂O₃/NGr@C-catalysts. Reaction conditions: 1 mmol benzylamine, 80 mg catalyst (4 mol% Fe), 400 μL aq. NH₃ (28–30% NH₃ basis), 3 bar O₂, 4 mL *t*-amyl alcohol, 110 °C, 15–20 h. Yields were determined by GC using *n*-hexadecane standard.

The general applicability of the Fe₂O₃/NGr@C catalyst is demonstrated in the synthesis of a large variety of structurally diverse nitriles. Benzonitriles, which constitute subunits of pharmaceuticals and agrochemicals, were obtained in good to excellent yields (Table 2). Interestingly, the halogenated benzonitriles, which are precursors for agrochemicals, pesticides and

Table 2. Fe₂O₃/NGr@C-catalyzed synthesis of substituted and functionalized benzonitriles.^[a]

Entry	Benzonitrile	Yield [%] ^[b]
1		98, 96 ^[c]
2		96
3		92
4		96
5		97, ^[d] 94 ^[c]
6		97, ^[d] 95 ^[c]
7		94 ^[d]
8		97, 93 ^[c]
9		96
10		95 ^[d]
11		97, 93 ^[c]
12		98, 95 ^[c]
13		97, 94 ^[c]
14		92 ^[d]
15		83 ^[c,e]
16		98

Table 2. (Continued)		
Entry	Benzonitrile	Yield [%] ^[b]
17		97
18		94, ^[f] 93 ^[c]
19		92 ^[f]
20		97

[a] Reaction conditions: 0.5 mmol amine, 40 mg catalyst (4 mol% Fe), 200 μL aq. NH₃ (28–30% NH₃ basis), 3 bar O₂, 4 mL *t*-amyl alcohol, 110 °C, 15 h. [b] Determined by GC. [c] Isolated yields. [d] For 24 h. [e] 300 μL aq. NH₃, 30 h. [f] 50 mg catalyst, 300 μL aq. NH₃, 130 °C 24 h.

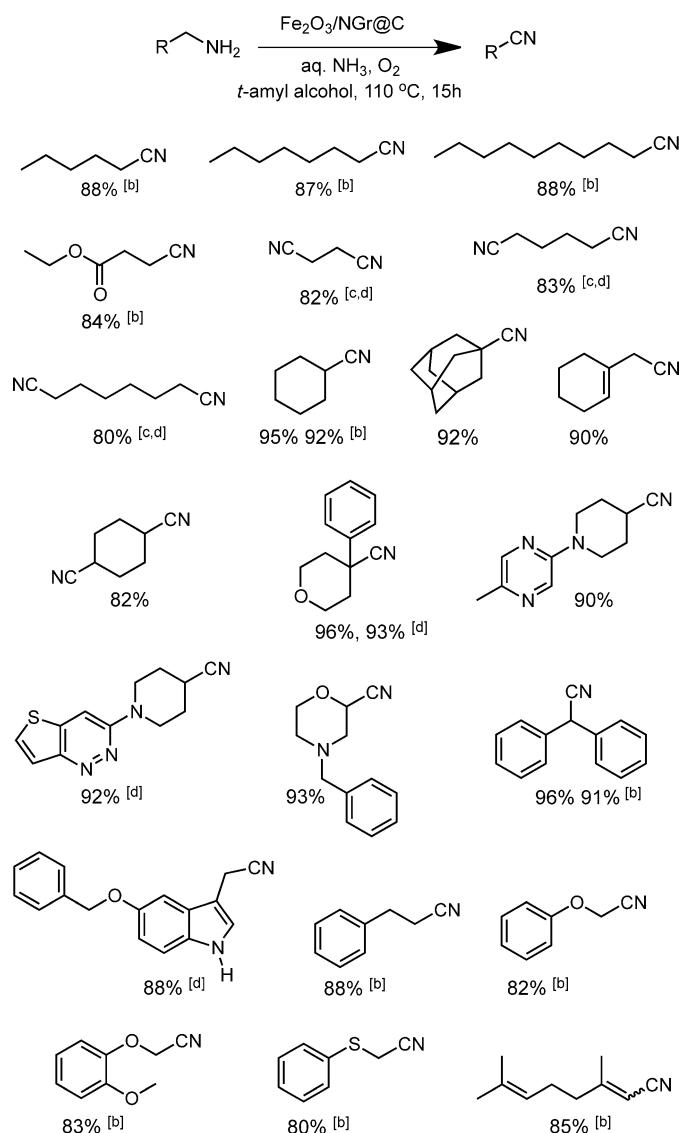
engineering materials, were prepared in 93–97% yields (entries 3–11). Notably, functionalized benzonitriles, which are difficult to prepare by classic ammoxidation, have been successfully synthesized in up to 97% (entries 13–20).

Next, we performed the oxidative conversion of primary aliphatic amines to nitriles. Noteworthy, most of the known catalytic systems are less active towards aliphatic substrates and therefore reaction of these substrates is less studied compared to benzylic amines. Remarkably, this iron-based catalyst is effective and highly selective for such amines oxidation. When applying Fe₂O₃/NGr@C as catalyst, aliphatic mono- and dinitriles, which constitute precursors and key intermediates for polymer and electronic materials, could be synthesized in good to excellent yields (Scheme 2). Further, we carried out the synthesis of heterocyclic nitriles, which are valuable precursors and intermediates for active life science products. Again, we obtained the corresponding cyanoheterocycles with excellent yields using our iron-based catalyst system (Scheme 3). Finally, we showed the synthetic utility of this method by performing reactions on scale of 2 gram. Here also we obtained good to excellent yields of nitriles (Scheme 4).

In summary, we showed that the simple nanoscale Fe₂O₃ (“nanorust”) constitutes an efficient and selective catalyst for the environmentally benign oxidation of amines. This synthesis of nitriles makes use of molecular oxygen and aqueous ammonia. Notably, our catalyst system is stable, easily recycled, and can be re-used. The general applicability of this methodology is demonstrated by the synthesis of around 60 structurally diverse and interesting nitriles in good to excellent yields.

Experimental Section

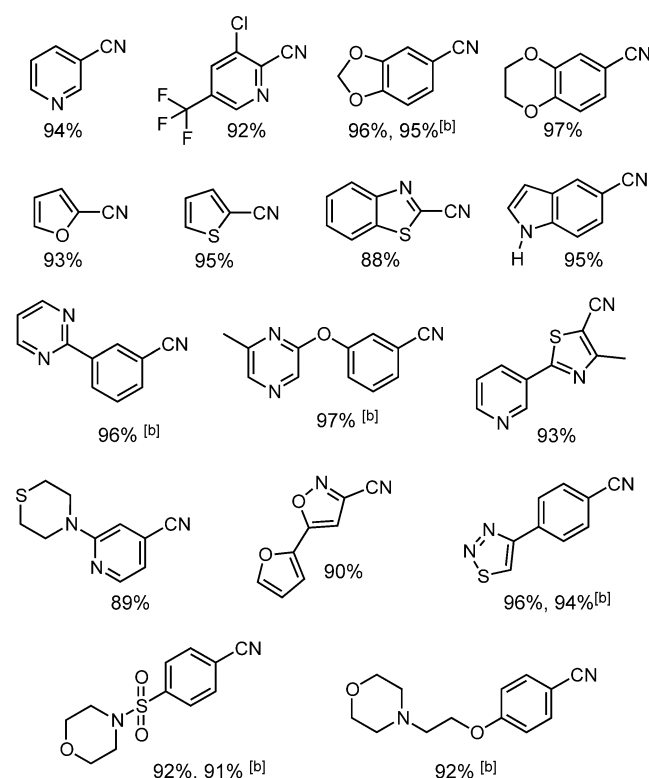
General procedure for the synthesis of nitriles: A magnetic stirring bar and the corresponding amine were transferred to a glass vial (7 mL) and then the solvent was added. Next, the catalyst was added followed by addition of aqueous NH₃. Then, the vial was fitted with septum, cap, and needle. The reaction vials (8 vials) were placed into a 300 mL autoclave and the autoclave was pressurized with 3 bar of oxygen. The autoclave was placed into an alu-



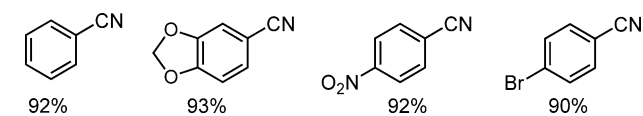
Scheme 2. Fe₂O₃/NGr@C-catalyzed synthesis of aliphatic nitriles. Reaction conditions: 0.5 mmol amine, 40 mg catalyst (4 mol% Fe), 100–200 μL aq. NH₃ (28–30% NH₃ basis), 3 bar O₂, 4 mL *t*-amyl alcohol, 110 °C, 15 h. Yields were determined by GC using *n*-hexadecane as standard. [b] in 4 mL *n*-heptane or *t*-amyl alcohol. [c] 60 mg catalyst, 300–400 μL aq. NH₃, 4 mL *n*-heptane or *t*-amyl alcohol. [d] Isolated yield.

minum block (placed 30 min before counting the reaction time in order to attain reaction temperature) preheated at 120 °C and the reactions were stirred for the required time. During the reaction, the inside temperature of the autoclave was measured to be 110 °C and this temperature was taken as the reaction temperature. After completion of the reaction, the autoclave was cooled to room temperature. The remaining oxygen was discharged and the samples were removed from the autoclave. To the individual vials, 100 μL *n*-hexadecane as standard was added and the reaction product was filtered through a plug of silica and then analyzed by GC and GC-MS. Qualitative and quantitative analysis of all products were made using GC and GC-MS analysis.

Procedure for product isolation: Under similar experimental conditions as described above, after completion of the reaction, the autoclave was cooled to room temperature and remaining oxygen was discharged. The catalyst from the reaction mixture was filtered



Scheme 3. Fe₂O₃/NGr@C-catalyzed synthesis of heterocyclic nitriles. Reaction conditions: 0.5 mmol amine, 40 mg catalyst (4 mol% Fe), 200 μL aq. NH₃ (28–30% NH₃ basis), 3 bar O₂, 4 mL *t*-amyl alcohol, 110 °C, 15 h. Yields were determined by GC using *n*-hexadecane standard. [b] Isolated yields.



Scheme 4. Gram-scale reactions. Reaction conditions: 2 g substrate, weight of catalyst corresponds to 4 mol% Fe, 200 μL aq. NH₃ for every 0.5 mmol substrate, 110 °C, 50–100 mL *t*-amyl alcohol, 20–34 h. Isolated yields

off and washed with ethyl acetate. The solvent from the filtrate containing the reaction product was removed in vacuo. The corresponding nitrile was purified by column chromatography (silica; *n*-hexane/ethyl acetate mixture). All products were analyzed by GC and GC-MS analysis.

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Keywords: amines · catalysis · iron · nitriles · oxidations

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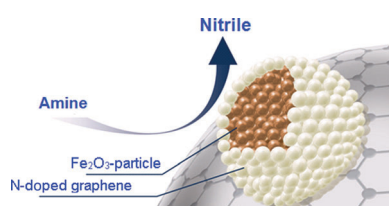
COMMUNICATIONS

R. V. Jagadeesh, H. Junge, M. Beller*

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"Nanorust"-catalyzed Benign Oxidation of Amines for Selective Synthesis of Nitriles



Next steps towards an iron age in catalysis: A "nanorust"-based material is produced by the pyrolysis of iron acetate-phenanthroline complex on carbon. The material, comprising nanoscale iron oxide covered by layers of nitrogen-doped graphene on carbon ($\text{Fe}_2\text{O}_3/\text{NGr@C}$), is a stable, active, and reusable catalyst system for environmentally benign oxidation processes. The selective synthesis of structurally diverse nitriles from amines using molecular oxygen is performed.