

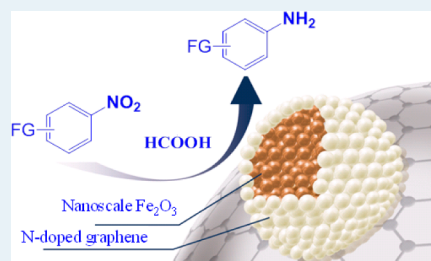
Nitrogen-Doped Graphene-Activated Iron-Oxide-Based Nanocatalysts for Selective Transfer Hydrogenation of Nitroarenes

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S Supporting Information

ABSTRACT: Nanoscaled iron oxides on carbon were modified with nitrogen-doped graphene (NGr) and found to be excellent catalysts for the chemoselective transfer hydrogenation of nitroarenes to anilines. Under standard reaction conditions, a variety of functionalized and structurally diverse anilines, which serve as key building blocks and central intermediates for fine and bulk chemicals, were synthesized in good to excellent yields.



KEYWORDS: iron nanocatalysis, transfer hydrogenation, nitroarenes, anilines, formic acid

The development of efficient and selective catalysts for modern organic synthesis continues to be a major challenge and noteworthy task. In recent years, there exists an increasing interest in the use of earth-abundant non-noble metal-based catalysts. In this regard, iron-based materials have been shown to be a viable alternative to replace existing precious-metal-based catalysts.¹ Comparing molecular-defined iron complexes with nanostructured heterogeneous catalysts, the latter are in general preferred due to easier recycling, which are crucial for cost-effective industrial processes.^{2,3} Although many simple iron-based catalysts have been developed for different chemical processes,² most of these materials have limited applications, especially for the refinement of complex substrates. In general, all these catalysts have been prepared by classic pyrolysis of iron salts on solid supports.²

In 2013, we described the pyrolysis of defined amine-ligated iron complexes. For example, the pyrolysis of phenanthroline-iron acetate on solid supports (Vulcan XC72R) at 800 °C furnished the formation of nanoscaled Fe₂O₃ particles, which are surrounded by nitrogen-doped graphene layers (Figure 1).³ Although simple pyrolyzed iron salts on carbon and homogeneous iron-amine complexes are not active for activation of hydrogen and oxygen at low temperature (<130

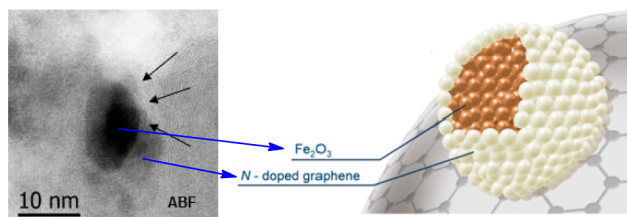
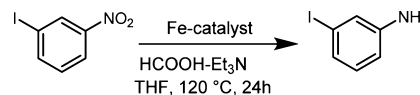


Figure 1. Nanoscaled Fe₂O₃ particles surrounded by nitrogen-doped graphene layers.

Table 1. Transfer Hydrogenation of 3-Iodonitrobenzene with Fe Catalysts^{a,b}



entry	catalyst	conv. [%] ^c	yield [%] ^c
1 ^a	-	<2	<1
2 ^a	Fe(OAc) ₂	3	<2
3 ^a	Fe(OAc) ₂ L1	3	<2
4 ^b	Fe(OAc) ₂ /C	4	2
5 ^b	Fe(OAc) ₂ L1/C	5	2
6 ^b	Fe(OAc) ₂ /C-800	8	6
7 ^b	Fe(OAc) ₂ L1/C-800	>99	94
8 ^b	Fe(OAc) ₂ L2/C-800	25	18
9 ^b	Fe(OAc) ₂ L3/C-800	50	44
10 ^b	Fe(OAc) ₂ L4/C-800	60	52

Materials were pyrolyzed at 800 °C for 2 h under argon, Fe/L = 1:3, Fe = 3 wt %, L1 = 1,10-phenanthroline, L2 = bipyridine, L3 = terpyridine, and L4 = pyridinebisbenzimidazole. ^aHomogeneous catalysis conditions: 0.5 mmol 3-iodonitrobenzene, 1.75 mmol formic acid (3.5 equiv as a HCOOH-Et₃N (5:2) mixture (HCOOH-Et₃N = formic acid/triethylamine), 0.025 mmol Fe(OAc)₂, 0.075 mmol ligand, 5 mL tetrahydrofuran (THF). ^bHeterogeneous catalysis conditions: 0.5 mmol 3-iodonitrobenzene, 1.75 mmol formic acid (3.5 equiv as a HCOOH-Et₃N (5:2) mixture), 50 mg catalyst (5 mol % Fe), 5 mL tetrahydrofuran. ^cDetermined by gas chromatography (GC) using 100 μL of *n*-hexadecane as standard.

°C), the resulting nanocatalysts showed much better activity.³ Notably, the size of Fe₂O₃ particles and the formation of nitrogen-doped graphene layers (NGr) control the activity of

Received: December 1, 2014

Revised: January 13, 2015

Published: January 14, 2015

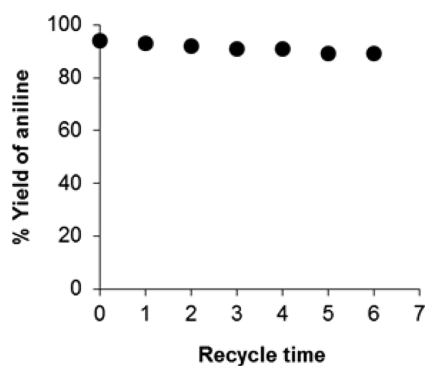


Figure 2. Reduction of 3-iodonitrobenzene: recycling of $\text{Fe}_2\text{O}_3/\text{NGr}@C$ catalysts. Reaction conditions: 1.0 mmol 3-iodonitrobenzene, 3.5 mmol formic acid (3.5 equiv. as a $\text{HCOOH}\text{-Et}_3\text{N}$ (5:2) mixture), 100 mg of catalyst (5 mol % Fe), 24 h, 6 mL THF, 120 °C, Yields were determined by GC using 100 μL of *n*-hexadecane as standard.

the material. Hence, by using different nitrogen ligands, the performance of the heterogeneous catalyst can be tuned. So far, these $\text{Fe}_2\text{O}_3/\text{NGr}@C$ -based nanomaterials have been found to be active for precious hydrogenation and green oxidation processes.³ In this work, we demonstrate for the first time that these materials also exhibit remarkable activity for the activation of formic acid in the transfer hydrogenation of nitroarenes to anilines. The resulting anilines represent important building blocks and central intermediates in the synthesis of dyes, pigments, agrochemicals, polymers, herbicides, and pharmaceuticals.⁴

Complementary to the direct hydrogenation,^{3a,5} transfer hydrogenations (CTH)^{6,7} using formic acid or formates⁷ as hydrogen donors are interesting, because the latter processes can be performed in a convenient manner without the requirement of any high-pressure equipment.

Initial catalytic experiments have been carried out with highly sensitive 3-iodonitrobenzene as the model substrate using formic acid as hydrogen source. As expected, the homogeneous iron–phenanthroline (**L1**) complex (Table 1, entries 2–3), the pyrolyzed iron acetate on carbon, and the immobilized iron–phenanthroline complex on carbon (Table 1, entries 4–6) were not active in this benchmark reaction. However, the pyrolysis of N-ligated iron acetate on carbon gave active catalysts with varying catalytic activity depending on the nature of the ligand (Table 1, entries 7–10). Again, the most active system is obtained from the pyrolysis of Fe–phenanthroline (**L1**) complex on carbon (Fe-phen/C-800). With this material, 3-iodonitrobenzene was reduced to the corresponding aniline in excellent yield without any dehalogenation (94%, Table 1, entry 7). Although the catalyst based on bipyridine (**L2**) gave poor activity (Table 1, entry 8), the use of terpyridine (**L3**) and pyridinebisbenzimidazole (**L4**) ligands also produced active catalysts (44–50%; Table 1, entries 9–10). Apparently, this difference in the catalytic activity is due to the formation of different structural features.

The structural features of the materials have been identified by systematic characterization using transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), and Mössbauer spectroscopy (see the Supporting Information). All these characterization studies revealed that in the active material (Fe-phenanthroline/C-800), mainly Fe_2O_3 particles of size 2–5 and 20–80 nm have been formed and which are surrounded by 3–

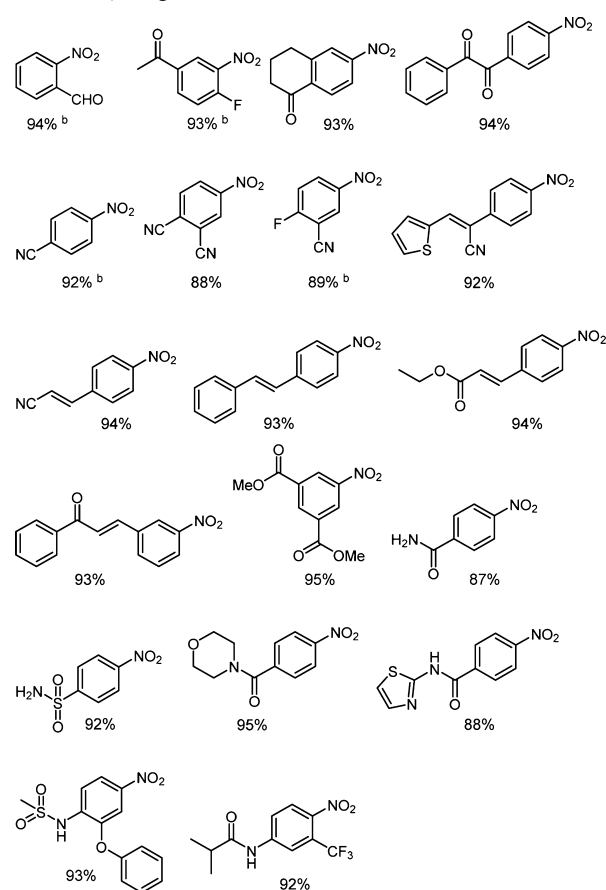
Table 2. $\text{Fe}_2\text{O}_3/\text{NGr}@C$ -Catalyzed Transfer Hydrogenation of Halogenated Nitroarenes^a

Entry	Nitroarene	Yield (%) ^c
1		95
2		90 ^d
3		95
4		94
5		93
6		90
7		89 ^d
8		92 ^d
9 ^[b]		93
10 ^[b]		88
11 ^[b]		93 ^d
12 ^[b]		89 ^d

^aReaction conditions: 0.5 mmol substrate, 1.75 mmol formic acid (3.5 equiv as a $\text{HCOOH}\text{-Et}_3\text{N}$ (5:2) mixture), 50 mg catalyst (5 mol % Fe), 20 h. ^bSame as “a” for 24 h. ^cIsolated yields. ^dGC yields using 100 μL of *n*-hexadecane as standard.

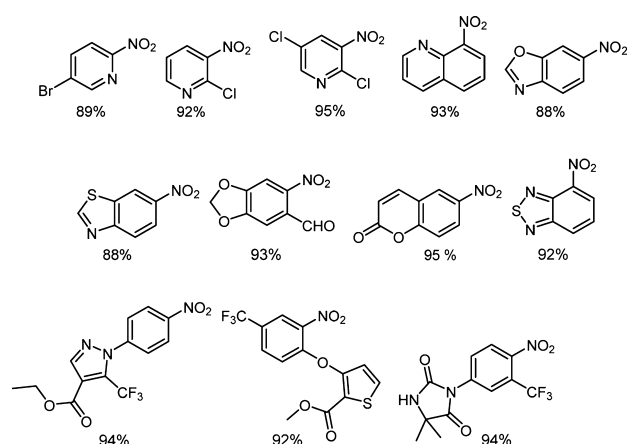
5 nitrogen-doped graphene layers (see Figure S1A). In contrast to this most active material, in the case of Fe-bipyridine/C-800, the resulting Fe_2O_3 particles are much larger and consist of several crystallites (Figure S1B). Moreover, these particles are not surrounded by graphene layers. The pyrolysis of simple iron-acetate ($\text{Fe}(\text{OAc})_2/\text{C-800}$) leads to well-faceted Fe_2O_3 particles of 100–800 nm size (Figure S1C), which are also not surrounded by graphene layers. Apparently, the formation of “smaller” Fe_2O_3 particles and the formation of nitrogen-doped graphene layers are both crucial to form active catalysts.

Scheme 1. Fe₂O₃/NGr@C-Catalyzed Chemoselective Transfer Hydrogenation of Nitroarenes^a



^aReaction conditions: 0.5 mmol substrate, 1.75 mmol formic acid (3.5 equiv as a HCOOH-Et₃N (5:2) mixture), 50 mg catalyst (5 mol % Fe), 20–24 h, isolated yields. ^bGC yields using 100 μ L of *n*-hexadecane as standard.

Scheme 2. Transfer Hydrogenation of Nitro Heterocycles Using Fe₂O₃/NGr@C Catalysts^a



^aReaction conditions: 0.5 mmol substrate, 1.75 mmol formic acid (3.5 equiv as a HCOOH-Et₃N (5:2) mixture), 50 mg catalyst (5 mol % Fe), 24 h, isolated yields.

Gratifyingly, the active catalyst system is highly stable and can be conveniently recycled and reused up to 6 times (Figure 2). For industry, such catalyst reusability is very important.

After the successful transfer hydrogenation of the benchmark reaction, we tested the scope and selectivity of the Fe₂O₃/NGr@C (Fe-L1/C-800)-catalyst for the transfer hydrogenation of structurally diverse and functionalized nitroarenes (Table 2 and Schemes 1 and 2).

As shown in Table 2, sensitive halogenated and substituted nitroarenes can be selectively reduced to the corresponding anilines in good to excellent yields (89–95%). It is noteworthy that no dehalogenation occurred in any of these cases.

After having demonstrated successfully the reduction of halogenated nitroarenes, we started to apply the procedure for the chemoselective transfer hydrogenation of demanding functionalized nitroarenes. Interestingly, the catalyst, Fe₂O₃/NGr@C allows for the selective transfer hydrogenation of nitro group in the presence of functional groups such as aldehyde, ketone, cyano, carbonyl, amide, and ester groups as well as C–C double bonds (Scheme 1). Notably, in all cases, the reduction of these reducible moieties was not observed, and the corresponding amines have been obtained in up to 95% yield (Scheme 1).

Next, we examined the reduction of nitro heterocycles to the corresponding amines, which represent important intermediates for life science molecules. Here, also the catalyst allows for the selective synthesis of amino heterocycles in 88–95% yields (Scheme 2). All these results confirm that the catalyst Fe₂O₃/NGr@C is remarkably selective for nitro transfer hydrogenation under the prevailed experimental conditions.

In summary, for the first time, the transfer hydrogenation of functionalized and structurally diverse nitro arenes to anilines has been performed using durable and reusable iron oxide-based nanocatalysts. This Fe₂O₃/NGr@C catalyst shows a unique selectivity for the nitro group reduction in the presence of diverse functional groups.

■ ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501916p.

Catalyst preparation; procedure for the transfer hydrogenation; EPR TEM, XPS, XRD analyses; and NMR spectral data and spectra ([PDF](#))

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the analytical department of Leibniz-Institute for Catalysis, Rostock for their excellent analytical service, and we are grateful to Prof. A. Brückner and Dr. J. Radnik and Dr. M.-M. Pohl for catalyst characterization. This work has been supported by the State of Mecklenburg-Vorpommern, and the BMBF (Bundesministerium für Bildung und Forschung).

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