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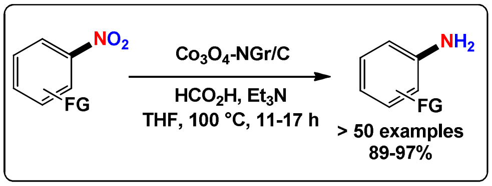
Table of Contents (TOC) graphic

Highly Selective Transfer Hydrogenation of Functionalysed Nitroarenes Using Cobalt-based Nanocatalysts

Rajenahally V. Jagadeesh, Debasis Banerjee, Percia Beatrice Arockiam, Henrik Junge, Kathrin Junge, Marga-Martina Pohl, Jörg Radnik, Angelika Brückner, Matthias Beller*

The functionalized anilines have been synthesized by the transfer hydrogenation of nitroarenes using cobalt oxide-based nanocatalysts.



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Highly Selective Transfer Hydrogenation of Functionalysed Nitroarenes Using Cobalt-based Nanocatalysts

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Anilines are important feedstock for the synthesis of variety of chemicals such as dyes, pigments, pharmaceuticals and agrochemicals. The chemoselective catalytic reduction of nitro compounds represents the most important and prevalent process for the manufacture of functionalized anilines. Consequently, the development of selective catalysts for the reduction of nitro compounds in presence of other reducible groups is a major challenge and crucial. In this regard, herein we show that the cobalt oxide (Co_3O_4-NGr@C) based nano-materials, prepared by the pyrolysis of cobalt-phenanthroline complexes on carbon constitute highly selective catalysts for the transfer hydrogenation of nitroarenes to anilines using formic acid as hydrogen source. Applying these catalysts, a series of structurally diverse and functionalized nitroarenes have been reduced to anilines with unprecedented chemo-selectivity tolerating halides, olefins, aldehyde, ketone, ester, amide and nitrile functionalities.

Introduction

Structurally diverse anilines constitute major building blocks and key intermediates for the production of pharmaceuticals, drugs, dyes, pigments and agrochemicals.[1] Generally, the selective reduction of nitroarenes represent a straightforward and versatile methodology for their synthesis.[2-4] Recently, precious metal-based nanomaterials have been used for the reduction of nitro compounds using various reducing agents.[5] However, due to high price and toxicity of these precious metals, the catalysts based on bio-relevant metals or highly preferable for this reaction. Particularly, anilines used in life science applications are substituted with various functional groups. Therefore, the chemoselective reduction of the nitro group in presence of other reducible moieties is crucial. In this respect, the development of highly selective and efficient catalysts is essential. Advantageously, heterogeneous catalysts can be easily recycled, which allows for cost-effective and sustainable synthetic processes.

Based on our experience using organometallic complexes in the presence of nitrogen ligands,[6] recently we developed novel heterogeneous catalysts by supporting metal-nitrogen complexes on solid supports through pyrolysis.[7] In our previous works,[7a,b] we demonstrated that pyrolysis of cobalt-phenanthroline complexes on carbon leads to the formation of nano-scale Co_3O_4 particles surrounded by a modified nitrogen-doped graphene layer (NGr) (Co_3O_4-NGr/C). Notably these materials are active for both hydrogenation [7a] and oxidation 7[b,c] processes. Here, for the first time we show that these materials represent excellent catalysts for the selective transfer hydrogenation of all kinds of functionalized nitroarenes to anilines using formic acid as hydrogen source.

Complementary to reductions with molecular hydrogen are transfer hydrogenations (CTH)[8] using formic acid-Et_3N or isopropanol-base systems. Advantageously, CTH reactions do not require any special experimental setup or the use of high-pressure equipment compared to conventional hydrogenation methods. Notably, formic acid or formate,[9] as hydrogen donors are abundant, inexpensive and easy to handle.

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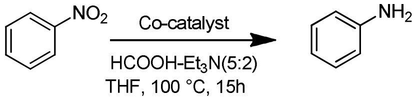
Results and Discussion

1. Preparation and activity of Co_3O_4-NGr@C materials. As developed previously,[7a,b] nanoscale Co_3O_4 catalysts were prepared by pyrolysis of in situ-generated phenanthroline-cobalt (II)-acetate on Vulcan XC72R carbon powder (see Supporting Information). Preliminary catalytic experiments were carried out applying the transfer hydrogenation of nitrobenzene as a benchmark substrate. As seen from Table 1, neither the homogeneous cobalt complex nor the supported material was active (Table 1, entries 1-3). Similarly, pyrolysis of simple cobalt acetate on carbon did not generate an active catalyst (Table 1, entry 4). However, pyrolysis of the ligated $Co(OAc)_2$ on carbon at 800 °C for 2 h under argon atmosphere led to an active catalytic material. Hence, the model reaction proceeded with complete conversion and gave aniline in 96% yield (Table 1, entry 5).

Table 1. Transfer hydrogenation of nitrobenzene with cobalt catalysts[a].

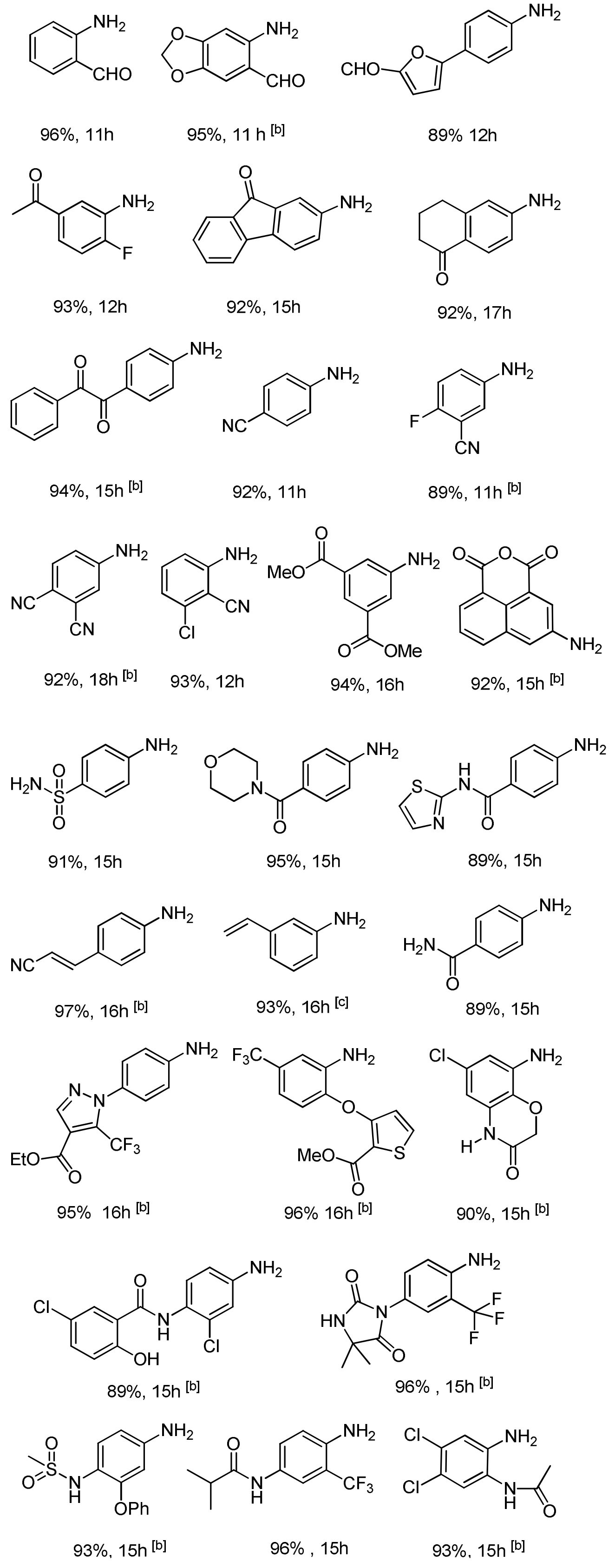


Entry	Catalyst	Pyrolysis (°C, h, Ar)	Conv. (%)	Yield (%)
1	$Co(OAc)_2.4H_2O$		2	<1
2	$Co(OAc)_2$-Phen		2	<1
3	$Co(OAc)_2$-Phen/C		2	<1
4	$Co(OAc)_2.4H_2O$/C	800 °C, 2h,	5	3
5	$Co(OAc)_2$-Phen/C	800 °C, 2h,	>99	96
6	Phen/C	800 °C, 2h,	1	<1

[a] Reaction conditions: 1 mmol nitrobenzene, 20 mg catalysts (2 mol% Co), 3.5 mmol (3.5 equiv.) of HCOOH, 1.4 mmol of Et_3N (HCOOH-Et_3N (5:2) mixture), 5 mL THF, 15 h, conversions and yields were determined by GC using n-hexadecane as internal standard.

The active catalytic material, Co_3O_4-NGr/C has been characterized by TEM, XPS, EPR and XRD spectral analysis[7a,b] (see Supporting Information). All these studies revealed the preferential formation of small (2-10 nm) Co_3O_4 particles on a nitrogen-doped carbon surface. Besides, a few larger particles of 20-80 nm and occasionally up to 800 nm size are also present, which consist of a Co and/or CoO core and a Co_3O_4 shell. These cobalt oxide particles are in close contact to the N atoms of the modified outermost layers of the graphite support.

2. Chemo-selective transfer hydrogenation of functionalized and challenging nitroarenes. The general applicability of the transfer hydrogenation process using the active Co_3O_4-NGr/C has been demonstrated applying structurally diverse functionalized nitro compounds under optimized conditions. As seen from Schemes 1 and 2 more than 50 functionalized and challenging nitroarenes have been reduced to the corresponding anilines in excellent yields and selectivities.



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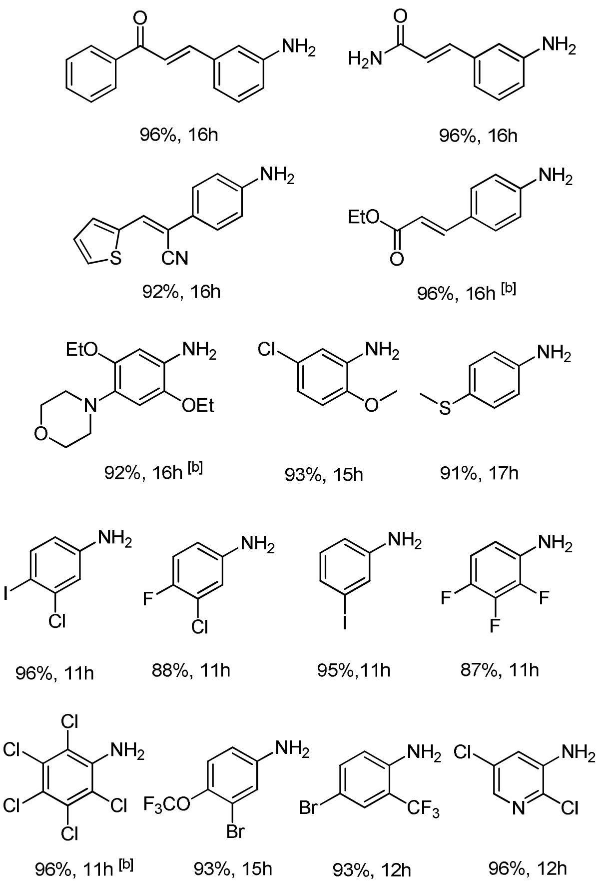
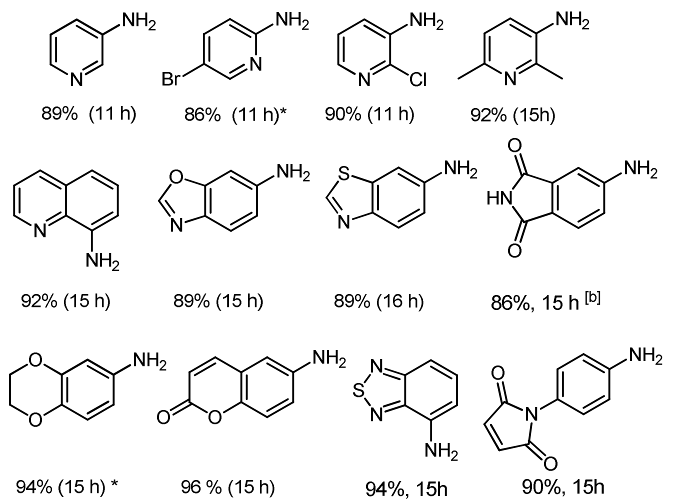


Scheme 1. Co_3O_4-NGr/C-catalyzed transfer hydrogenation of functionalized nitroarenes[a]. [a]Reaction conditions: 1 mmol nitroarene, 20 mg catalyst (2 mol% Co). 3.5 mmol (3.5 equiv.) of HCOOH, 1.4 mmol of Et_3N (HCOOH-Et_3N (5:2) mixture), 5 mL THF, 100 °C. Conversions and yields were determined by GC using n-hexadecane as internal standard. [b]Isolated yields. [c]Same as [a] at 110 °C.

From a synthetic point of view it is important to note that this cobalt-based catalyst system is highly selective for the transfer hydrogenation of nitro groups in the presence of many other easily reducible moieties. Functional groups such as aldehyde, ketone, nitrile, ester, amide, and olefins are well tolerated without being significantly reduced. Notably, amino-substituted benzonitriles common building blocks for the chemical industry are obtained in up to 93 % yield (Scheme 1). Interestingly, various ester-, amide- and sulphonamide based anilines, which constitute subunits of biologically and pharmacologically important compounds are obtained in 89-98% yields (Scheme 1). Likewise, halogenated anilines, which are used as precursors for agrochemicals, were obtained in good to excellent yields. Noteworthy, the sensitive iodo-nitroarenes were hydrogenated to the corresponding anilines in high yields (95-96 %), too, and even di-, tri- and penta-halogenated nitroarenes produced the corresponding halogenated anilines in 86-97 % (Scheme 1).

3. Synthesis of amino-heterocycles. Finally, transfer hydrogenations of heterocyclic nitro compounds were performed. The amino-substituted N-heterocycles, which are important intermediates in pharmaceutical and agrochemical industries, were also obtained in good to excellent yields (Scheme 3).



Scheme 2. Co_3O_4-N/C catalyzed transfer hydrogenation of nitro-heterocycles. Reaction conditions: 1 mmol nitro compound, 20 mg catalyst (1 mol% Co). 3.5 mmol (3.5 equiv.) of HCOOH, 1.4 mmol of Et_3N (HCOOH-Et_3N (5:2) mixture), 5 mL THF, 100 °C, isolated yields, *GC yields using n-hexadecane as internal standard.

4. Catalyst recycling. In a final set of catalytic experiments, we examined the stability and reusability of the Co_3O_4-NGr/C catalysts. Indeed the catalyst has been easily recycled and reused up to 6 cycles without significant loss of catalytic activity. In addition, to prove the stability of the material, 20 mg of catalyst along with THF was heated at 100 °C. Then, the hot suspension was quickly filtered. Performing standard catalytic tests (1 mmol nitrobenzene) using the hot filtrate solution and HCOOH/Et_3N (5:2) did not result in any activity and the formation of aniline was not observed. This clearly, indicates that, the active metal species have not been leached out from the support during the reaction and remains bound to the support.

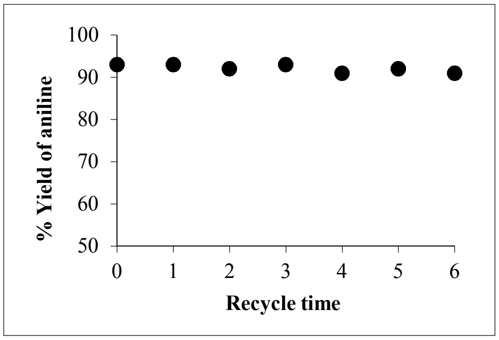


Figure 1. Transfer hydrogenation of nitrobenzene to aniline: Recycling of Co_3O_4-NGr@C. Reaction conditions: 5.0 mmol nitrobenzene, 3.5 mmol (3.5 equiv.) of HCOOH, 1.4 mmol of Et_3N (HCOOH-Et_3N (5:2) mixture), 100 mg catalyst (2 mol% Co), 13-15h, 10 mL THF, yields were determined by GC using n-hexadecane as internal standard.

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Experimental Section

20 mg Co_3O_4-NGr/C-catalyst (2 mol% Co) and 5 mL dry THF were added to oven dried pressure tube (ACE). Then, corresponding nitro compound (1 mmol), 3.5 mmol (3.5 equiv.) of HCOOH, 1.4 mmol of Et_3N (HCOOH-Et_3N (5:2) mixture) and 100 μL n-hexadecane as internal standard were added sequentially. The pressure tube was flushed with argon, fitted with screw cap and the reaction was allowed to progress at 100 ^{0}C for desired time. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with ethyl acetate. Then, catalyst was filtered off, and the sample of the mixture was directly subjected to GC analysis. Conversion and yields were determined by GC-FID (HP6890 with FID detector, column HP530 m x 250 mm x 0.25 μm). Quantitative and qualitative analysis of anilines were made by GC, GC–MS analysis. For isolation of anilines, the reactions were performed without adding n-hexadecane. After completion of the reaction, the catalyst was filtered off, washed with ethyl acetate and the filtrate containing reaction product was concentrated. The corresponding aniline was purified by column chromatography (silica; n-hexane-ethyl acetate mixture). The collected fractions were dried over anhydrous Na_2SO_4. Then, solvent was removed in vacuo and finally the product was dried.

Conclusions

In conclusion, stable, inexpensive and reusable cobalt oxide-based nano-materials are found to be highly active and selective catalysts for the chemo-selective transfer hydrogenation of nitroarenes to anilines. The active Co_3O_4-NGr/C nanocatalysts have been prepared by pyrolysis of amino-ligated cobalt (II) acetate on commercial Vulcan XC72R. Excellent chemo-selectivity was demonstrated applying nitroarenes with olefin, aldehyde, keto, ester, amide and nitrile functionalities.

Acknowledgements

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