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General and selective reductive amination of carbonyl compounds using a core–shell structured Co_3O_4/NGr@C catalyst†

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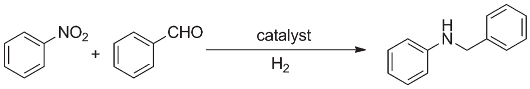
The application of heterogenized non-noble metal-based catalysts in selective catalytic hydrogenation processes is still challenging. In this respect, the preparation of a well-defined cobalt-based catalyst was investigated by immobilization of the corresponding cobalt(II)-phenanthroline-chelate on Vulcan XC72R carbon powder. The formed core–shell structured cobalt/cobalt oxide nanocomposites are encapsulated by nitrogen-enriched graphene layers. This promising cheap heterogeneous catalyst allows for an efficient domino reductive amination of carbonyl compounds with nitroarenes.

Introduction

Important catalytic methodologies in synthetic organic chemistry both on laboratory- and industrial-scale represent hydrogenation processes.[1,2] Hydrogen, notwithstanding its current mostly fossil-based production route, can be considered as an environmentally benign and clean reducing agent from an atom economy perspective. In industry, heterogeneous materials prevail for the production of bulk chemicals, materials and easy building blocks due to the beneficial stability and recycling capability of the catalysts.[3] Current challenges in heterogeneously catalyzed hydrogenations lie in the development of novel cost-effective materials and their application for structurally more complex substrates. In the latter case, especially multi-step procedures with high selectivity and activity are of importance.

In this respect, recently we became interested in the reductive amination of carbonyl compounds with nitroarenes to generate selectively secondary amines (Scheme 1). Several heterogeneous catalytic systems have been studied that enable efficient and selective N-alkylation of amines with alcohols under mild conditions.[4] Although the reported catalysts are active for such a reaction, they are significantly more expensive.



Scheme 1 Multi-step reductive amination of benzaldehyde.

Obviously, the envisioned domino transformation is scarcely known,[5] but highly attractive as it does not require prior reduction of the respective nitroarene. In general, the hydrogenation of nitroarenes to functionalized anilines is well-known with many benchmark catalytic systems.[6–9] It can be achieved with modified noble metal catalysts such as gold,[10,11] palladium or platinum onto activated carbon or alumina,[4,12–14] Pt(IV)oxide[15] as well as rhodium- or ruthenium-sulfides.[1,16] Other classical catalytic systems like RANEY® nickel,[6,17] Ni/TiO_2 [18] or Ni supported on kieselgur[19] have also been reported. However, their application is limited to activated substrates including multiple bonds or carbonyl groups. Moreover, they have practical drawbacks regarding catalyst preparation, reusability and the necessity to use modifying additives.

For some time we are interested in the replacement of precious metal complexes by non-noble metal-based catalysts, *e.g.* iron or cobalt. Especially, cobalt-based materials have been reported to be promising catalysts for Fischer–Tropsch synthesis,[20–23] NO*x* removal,[24,25] and partial oxidation of olefins.[26–28] Furthermore, cobalt catalysts are also applied for the elimination of harmful compounds from industrial and automobile emissions by combustion.[29–33] In general, the catalytic performance of these materials is controlled by specific deposition of cobalt on various supports, such as silica, titanium dioxide, alumina or zeolites.[34–36] In this respect, it is still a challenge to prepare cobalt particles with optimal size and their stabilization under the applied reaction conditions.

Recently, we synthesized novel nanostructured cobalt materials *via* immobilization of organometallic complexes onto commercially available supports.[37,38] For example, a defined complex prepared from $Co(OAc)_2$ and 1,10-phenanthroline was coated and subsequently pyrolysed onto Vulcan XC72R as

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carbon support under Ar atmosphere (M/L ratio 1 : 2). Pyrolysis at 800 °C for 2 h led to the most active hydrogenation and oxidation catalyst system (S2†).

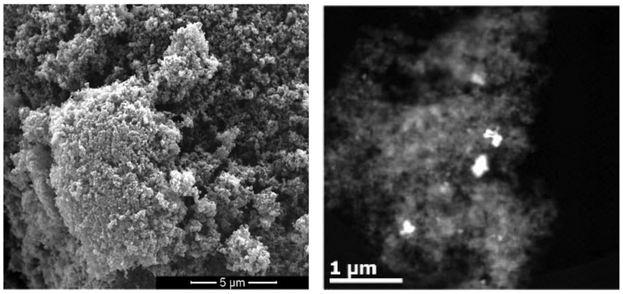


Fig. 1 SEM (left) and HAADF-TEM (right) images of the carbon supported cobalt catalyst.

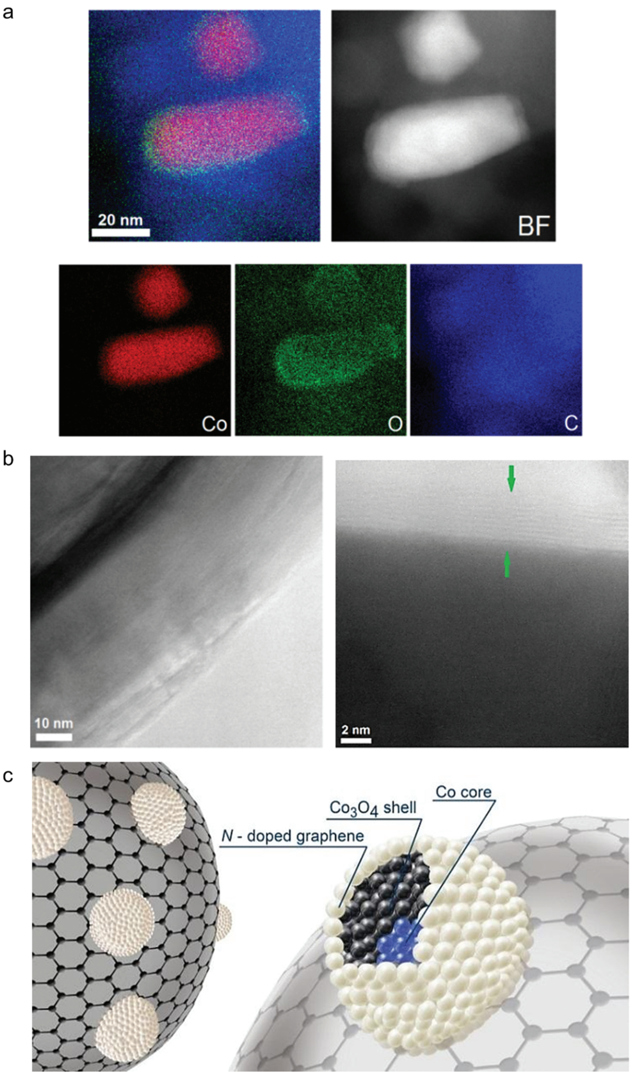


Fig. 2 (a) EDXS-mapping of Co/Co_3O_4 crystallites; cobalt (red), oxygen (green) and carbon (blue) of Co_3O_4/NGr@C. (b) Bright field TEM images to illustrate formed graphene layers. (c) Illustration of multi core–shell structured Co-Co_3O_4/NGr@C nanoparticles.

As a result, we observed fractions of well pronounced cobalt-based nanoparticles with varying sizes of 2–20 nm as well as particles and agglomerates in the range of 20–200 nm. To image the complete size spectra of these particles, a bright field (BF) and high-angle annular dark field (HAADF) at a spherical aberration (Cs)-corrected transmission electron microscope was used (Fig. 1 and 2a). In Fig. 1 the chemical constitution of the catalyst surface (scanning electron microscopy, SEM) is shown and a high contrast imaging of unequally distributed particles against the background (HAADF).

Upon upscaling the catalyst preparation to 10 g-scale, we obtained defined crystallites, which contain active single nanoparticles as core–shell structured Co/Co_3O_4 nanocomposition. The presence of such composite is supported by XRD powder diffraction and EPR measurements (S4 and 5†). An EDX-mapping with the selection of the corresponding elements confirms also this proposal (Fig. 2a). Additionally, the metal-based particles are encapsulated by individually nitrogen-enriched graphene-type layers (NGr), which were formed through the carbonization of the nitrogen ligand (Fig. 2b).[39] XPS (X-ray photoelectron spectroscopy) revealed three distinct nitrogen species: pyridinic and pyrrolic nitrogen as well as quaternary amine species. Deconvolution showed that around 64% of all N atoms are bound to the metal ions (S3†). However, the electronic influence of the nitrogen-doped graphene layers on the catalytic activity of the particles is not well understood yet.

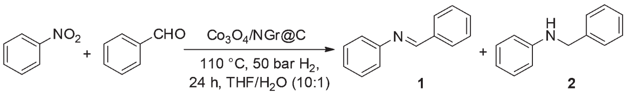
Based on spectroscopic studies, a simple 3D-model was designed to get a general idea about the core–shell structured catalyst (Fig. 2c).

Results and discussion

At the start of our project the catalyst was evaluated for the model reaction of nitrobenzene with benzaldehyde using different ratios (1 : 1, 1 : 1.5 and 1 : 2) (Scheme 2). In general, 2 mol% of the catalyst powder related to nitrobenzene was used in a THF–H_2O (10 : 1)-mixture at 110 °C and 50 bar hydrogen pressure for 24 h.

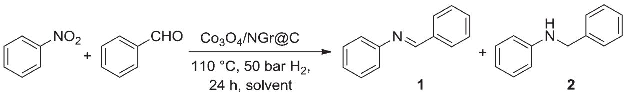
Applying the Co_3O_4/NGr@C nanoparticles nitrobenzene respectively aniline was quantitatively converted into the imine intermediate after condensation with 2 equivalents of benzaldehyde. The desired product was formed after reduction of the imine intermediate in 95% yield.

Next, the variation of the catalyst concentration was addressed. However, no significant change of the imine conversion was observed for 20 h by increasing the amount of the catalyst (>2 mol%) (Table S1,† entries 3–5).



Scheme 2 Benchmark reaction.

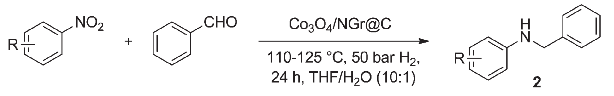
Table 1 Reductive amination of benzaldehyde with nitrobenzene: influence of the solvent

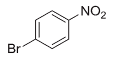
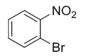
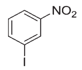
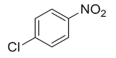
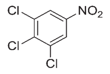
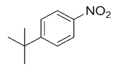
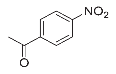
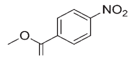
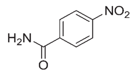


Entry[a]	Solvent	Yield imine **1**[b]	Yield amine **2**[b]
1	THF	7	78
2	Dioxane	55	39
3	H_2O	—	16
4	THF–H_2O (1 : 1)	18	64
5	THF–H_2O (5 : 1)	8	75
6	THF–H_2O (10 : 1)	—	95
7	Dioxane–H_2O (1 : 1)	31	48
8	Dioxane–H_2O (5 : 1)	12	77
9	Dioxane–H_2O (10 : 1)	8	84
10	Toluene–H_2O (10 : 1)	9	65

[a] Reaction conditions: 0.5 mmol of nitrobenzene, 1.0 mmol of benzaldehyde, 2 mol% Co_3O_4/NGr@C related to nitrobenzene, 2.75 mL solvent. [b] Determined by GC using *n*-hexadecane as an internal standard.

Table 2 Hydrogenation of different nitroarenes with benzaldehyde



Entry[a]	Substrate	T (°C)	Mole ratio imine/amine **2**	Yield amine **2**[b] (%)
1		110	1 : 4	71[c]
2		110	1 : 3	55
3		110	1 : 4	68
4		110	1 : 5	76
5		125	1 : 1	48[c]
6		110	1 : 15	93
7		110	1 : 5	59
8		125	1 : 1	57
9		125	1 : 1	54

[a] Reaction conditions: 0.5 mmol of nitroarene, 1.0 mmol of benzaldehyde, 2 mol% Co_3O_4/NGr@C related to nitroarene, 2.75 mL solvent. [b] Determined by GC using *n*-hexadecane as internal standard. [c] Isolated yield by flash chromatography.

As shown in Table 1, the most suitable polar-aprotic solvent for this reaction is tetrahydrofuran (THF) (Table 1, entries 1 and 2). Interestingly, the addition of small amounts of H_2O is beneficial for the overall reductive amination process (Table 1, entry 6). The increased catalytic activity with/without water might be explained by the promotion of hydrophobic association of carbonyl compounds and amines and suppression of the catalyst poisoning.[40,41] However, by increasing the ratio of water in THF, the activity of the catalyst significantly decreases (Table 1, entries 4–6).[42] In general, the hydrogenation of the imine intermediate should be the rate-determining step in this reductive amination sequence. Other solvents such as dioxane or toluene also in combination with water did not show similar effects (Table 1, entries 7–10).

Complete hydrogenation of the imine intermediate took place within 24 h. Nevertheless, trace amounts (<2%) of the tertiary amine were formed. In previous reports the formation of these minor side products should occur *via* hemiaminals or *gem*-diamines.[43,44] Moreover, a catalytic experiment with an excess of benzaldehyde, gave also traces of benzyl alcohol.

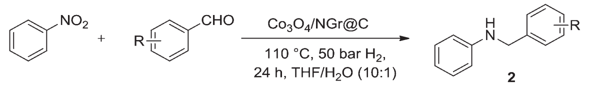
To demonstrate the general applicability of the optimized catalytic system, the reductive coupling reaction with various nitroarenes and aromatic aldehydes was investigated (Tables 2–4). As a general trend, the reaction is facilitated by either electron-rich aromatic aldehydes or electron-rich nitroarenes. Hence, alkyl- and alkoxy-substituted nitroarenes or aromatic aldehydes are reduced in good to excellent yields to give the desired secondary amines (Table 2, entry 4; Table 3, entries 1, 2, 7 and 8). The presence of an electron-withdrawing substituent led to less reactive anilines and the subsequent hydrogenation of the imine intermediate is interfered to the secondary amine (Table 2, entries 5, 7–9). Even by increasing the temperature up to 130 °C and using longer reaction times, the imine conversion did not significantly changed (Table 2, entries 7–9).

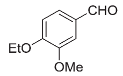
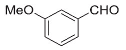
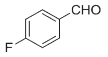
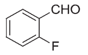
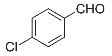
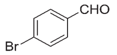
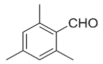
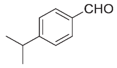
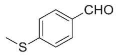
Furthermore, various halogenated substrates gave the corresponding amines with 47–80% yield (Table 2, entries 1–3; Table 3, entry 4). The reaction with the *ortho*-isomers compared to *para*- or *meta*-isomer is slightly slower due to the steric effect (Table 2, entry 2; Table 3, entries 3–6). Di- and tri-halogenated nitroarenes exhibit reactivity similar to that of *ortho*-halogenated derivatives (Table 2, entry 5). In this latter case a mixture of the imine and the desired product was obtained due to the slow final hydrogenation step. Analogues results were observed with the different substituted aromatic aldehydes (Table 3, entries 4–6). Among the various tested substrates *p*-fluorobenzaldehyde showed the best performance (Table 3, entry 3). In case of the bromo-substituted substrate, trace amounts of dehalogenated products were obtained, too.

From a synthetic point of view, it is noteworthy that reducible functionalities such as ketones, esters, amides, and nitriles are well tolerated by the cobalt-based catalyst to give the corresponding amines in good yield (Table 2, entries 7–9; Table 3, entry 9, Table 4, entry 3). As expected the reaction of substituted anilines with substituted benzaldehydes proceeded well (Table 4, entries 1–3).

The reductive amination using aliphatic nitro compounds and aldehydes is more challenging. To our delight the desired products were obtained in 60–68% isolated yields. Linear,

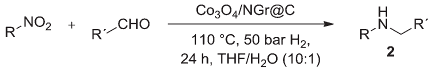
Table 3 Hydrogenation of aromatic aldehydes with nitrobenzene

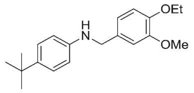
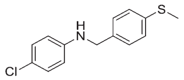
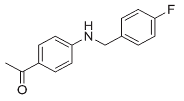
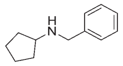
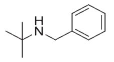
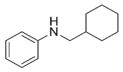
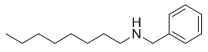
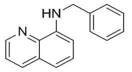
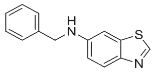


Entry[a]	Substrate	Mole ratio imine/amine **2**	Yield amine **2**[b] (%)
1		1 : 4	75
2		1 : 3	71
3		1 : 3	80[c]
4		1 : 3	65
5		1 : 4	69
6		1 : 10	67
7		1 : 5	84
8		1 : 20	94[c]
9		1 : 6	64[c]

[a] Reaction conditions: 0.5 mmol of nitrobenzene, 1.0 mmol of benzaldehyde, 2 mol% Co_3O_4/NGr@C related to nitroarene, 2.75 mL solvent. [b] Determined by GC using *n*-hexadecane as internal standard. [c] Isolated yield by flash chromatography.

Table 4 Hydrogenation of diverse nitro compounds with aldehydes

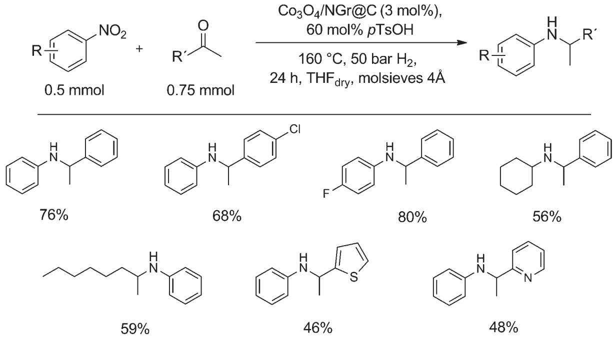


Entry[a]	Product	Mole ratio imine/amine **2**[b]	Yield amine **2**[b] (%)
1		1 : 4	75
2		1 : 3	71
3		1 : 4	80
4		1 : 3	65
5		1 : 4	60
6		1 : 10	64[c]
7		1 : 5	68
8		1 : 20	79
9		1 : 6	65[c]

[a] Reaction conditions: 0.5 mmol of nitrobenzene, 1.0 mmol of benzaldehyde, 2 mol% Co_3O_4/NGr@C related to nitroarene, 2.75 mL solvent. [b] Determined by GC using *n*-hexadecane as internal standard. [c] Isolated yield by flash chromatography.

cyclic as well as branched nitro alkanes were used (Table 4, entries 4–7). Next, to generate N-heterocyclic amines, nitro-substituted heteroarenes were tested. The best results have been found for quinoline and benzothiazole (Table 4, entries 8 and 9). Finally, we tested the coupling reaction of 1-vinyl-4-nitrobenzene, citral and citronellal. Unfortunately, in these cases an isomeric mixture of imines and amines was obtained. Here, the hydrogenation of the double bonds was dominant or at least competitive with the imine reduction.

In addition, the one-pot synthesis of *N*-substituted amines was extended by using aromatic or aliphatic ketones as substrates. Notably, the reaction proceeded successfully in the presence of 60 mol% *p*TsOH with 3 mol% catalyst loading and 50 bar H_2 pressure at 160 °C for 24 h in dry THF. Selected substitution patterns on the aromatic core of the substrates did not have a significant influence on the catalytic activity and the desired products were obtained in good yields (Scheme 3).



Scheme 3 Hydrogenation of nitro compounds with ketones.

Finally, we demonstrated that it is easily possible to recycle the catalyst up to six times. After the first run, some decay in activity is observed (Fig. 3). Then, the selectivity and yield of *N*-benzylaniline remained constant at ~60%. The leaching of the active metal from the supported material was not observed. TEM studies also showed that the used catalyst had no observable structural change relative to the fresh one.

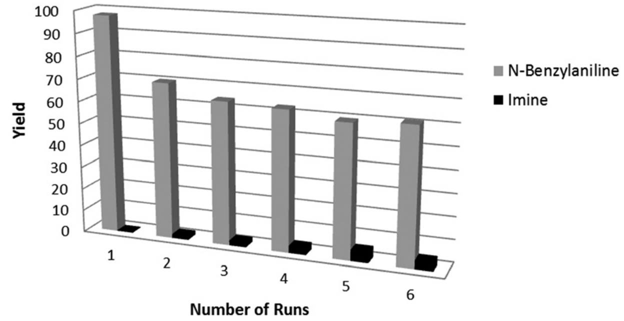


Fig. 3 Recycling experiments of the reductive amination of benzaldehyde with nitrobenzene.

Conclusion

In conclusion, we have described a nano-structured cobalt-based catalyst for the straightforward reductive amination with nitroarenes. Employing molecular hydrogen as the reductant, hydrogenation of the nitro group and the resulting imines took place to give selectively a variety of secondary amines. This atom efficient and environmentally friendly methodology is applicable to both aliphatic and aromatic nitro compounds, aldehydes and ketones.

Experimental section

The general procedure for the one-pot reductive amination is as follows: in a reaction vial (8 mL), nitroarene (0.5 mmol) and aromatic aldehyde (1.0 mmol) were dissolved in 3 mL THF–H_2O (10 : 1)-solvent mixture. Then, 2 mol% of the cobalt-based catalyst was added. The reaction vials (up to 7) were placed into a 300 mL autoclave. The autoclave was flushed with hydrogen twice (*ca.* 40 bar) and pressurized to 50 bar hydrogen. It was then placed into an aluminium block, heated up to 110 °C or 125 °C, and stirred for the indicated time (24 h). After the reaction was complete, the autoclave was cooled to room temperature and the hydrogen was released. To the crude reaction mixture was added *n*-hexadecane (52 μL) as an internal standard. Subsequently, the solution was filtered through silica gel and analysed to determine the yield by using GC.

Synthesis of 3 wt% carbon-supported cobalt-based catalyst

In a 100 mL round bottom flask, $Co(OAc)_2$ (124.5 mg, 0.5 mmol) and 1,10-phenanthroline (180.2 mg, 1.0 mmol) were dissolved in 20 mL EtOH and stirred for 1 h at 60 °C, leading to the formation of a dark yellow solution. Next, Vulcan XC72R carbon powder (700 mg) was added and the mixture was stirred overnight at room temperature. Afterwards, the solvent of the suspension was evaporated and the remained carbon powder was dried for 4 h. Finally, the catalyst was pyrolysed at 800 °C for 2 h under an argon atmosphere (elemental analysis of Co_3O_4/NGr@C (wt%): C = 92.28, H = 0.20, N = 2.70, Co = 3.50, O = 1.32).

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