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# Heterogenized cobalt oxide catalysts for nitroarene reduction by pyrolysis of molecularly defined complexes

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**Molecularly well-defined homogeneous catalysts are known for a wide variety of chemical transformations. The effect of small changes in molecular structure can be studied in detail and used to optimize many processes. However, many industrial processes require heterogeneous catalysts because of their stability, ease of separation and recyclability, but these are more difficult to control on a molecular level. Here, we describe the conversion of homogeneous cobalt complexes into heterogeneous cobalt oxide catalysts via immobilization and pyrolysis on activated carbon. The catalysts thus produced are useful for the industrially important reduction of nitroarenes to anilines. The ligand indirectly controls the selectivity and activity of the recyclable catalyst and catalyst optimization can be performed at the level of the solution-phase precursor before conversion into the active heterogeneous catalyst.**

Catalysis is a key technology for achieving more benign processes in the chemical, pharmaceutical and material industries[1]. Owing to their stability, ease of separation and recycling, heterogeneous catalysts represent an important tool box for controlling chemical reactivity. Today, the preparation of bulk and impregnated catalysts as well as of mixed agglomerated catalysts relies mainly on classic methods, such as hydrothermal transformations, precipitation, calcination and impregnation[2,3]. More specialized methods for catalyst preparation include resin-bound complexes or complexes bound by a supported ionic liquid phase. In addition, complex organometallic precursors are used for the synthesis of heterogeneous materials, for example via metal–organic chemical vapour deposition[4–6]. Despite all these attempts, the use of defined non-volatile organometallic complexes as precursors for stable heterogeneous catalysts has been scarcely investigated[7–10].

Herein, we report a protocol to prepare novel nanoscale cobalt oxide catalysts supported on a carbon–nitrogen surface via pyrolysis of defined non-volatile organometallic amine complexes (Table 1). Depending on the organic ligands used, modification of the surface takes place and remarkable differences in catalyst activity are observed. Thereby, the ligand indirectly controls the activity and selectivity of the given reaction (Table 1).

With more than 4,000,000 tons produced per year, aniline and its derivatives represent important feedstocks in the chemical industry (www.strategyr.com/Aniline_Market_Report.asp). They are used widely for the synthesis of dyes, agrochemicals, pharmaceuticals, polymers and various other fine chemicals[1,11,12]. The common route for their preparation is the reduction of the corresponding nitro derivatives (which can be carried out using stoichiometric reducing agents such as Fe, Zn, Sn, Al and sulfur compounds), electrochemical methods or catalytic hydrogenation[1,11,13–15]. Obviously, the most environmentally benign and cost-effective reducing agent is hydrogen. Despite numerous developments of hydrogenation catalysts, there still exists a significant interest in novel inexpensive, active and selective catalysts, especially those based on non-noble metals.

Several anilines important for both organic synthesis and industry are densely substituted with a variety of different functional groups. Hence, for a generally applicable catalyst system it is essential to perform the reduction of the nitro group highly chemoselectively. Notably, such functional-group tolerance might also omit the use of protecting groups and streamline more-complex syntheses. Especially with respect to selectivity, the reduction of $-NO_2$ in the presence of other reducible substituents, such as ketones, aldehydes, alkenes or alkynes, remains challenging[12,16–28]. Most common commercially available Raney–nickel, palladium or platinum catalysts are troubled by these issues. Nevertheless, Siegrist, Blaser and co-workers achieved the selective reduction of substituted nitroarenes using commercially available platinum catalysts modified by special additives[29–33]. More recently, another important development came from the group of Corma, who disclosed a heterogeneous gold-based catalyst that can hydrogenate nitro compounds selectively in the presence of a number of functional groups[34–36]. Nevertheless, so far there exists no inexpensive non-noble metal catalyst system that allows for a general reduction of all kinds of nitroarenes.

## Results and discussion

For some time, we have been interested in developing molecularly defined organometallic catalysts for the selective reduction of nitroarenes[37]. Based on this work, we started a programme to develop similar heterogeneous systems. More specifically, we had the idea to prepare novel nanostructured catalysts via deposition of defined organometallic complexes onto commercially available inorganic supports with subsequent pyrolysis. According to this concept, ultimately the formation and size of the metal particles should be controlled by the precatalyst and the surrounding ligands. Notably, the plethora of organic ligands available adds another dimension of possibilities for the generation of new heterogeneous catalytic materials.

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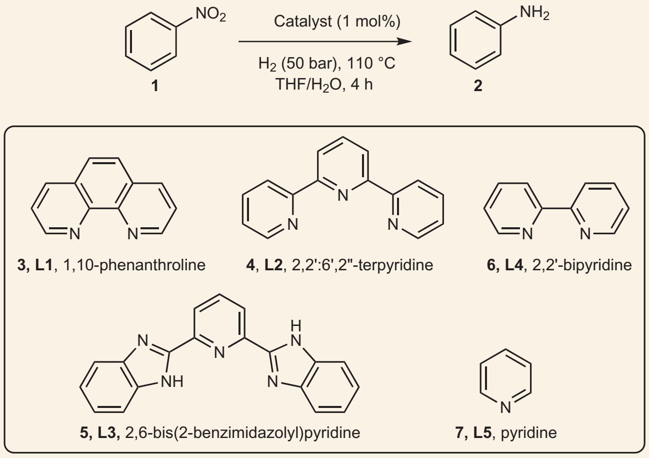
**Table 1 | Hydrogenation of nitrobenzene: comparison of selected supported cobalt oxide catalysts.**



| Entry | Catalyst | Conversion (%)* | Yield (%)* |
|---|---|---|---|
| 1 | Co/carbon | 5 | 0[†] |
| 2 | **L1**/carbon | 1 | 0[†] |
| 3 | Carbon[‡] | 6 | 0[†] |
| 4 | Co-**L1**/carbon[§] | >99 | 95/99[‖] |
| 5 | Co-**L2**/carbon | 8 | 5 |
| 6 | Co-**L3**/carbon | 26 | 19 |
| 7 | Co-**L4**/carbon | <1 | 0 |
| 8 | Co-**L5**/carbon | <1 | 0 |
| 9 | Fe-**L1**/carbon | 15 | 1[†] |
| 10 | Co-**L1**[¶] | 4 | 0 |
| 11 | Ni-**L1**[¶] | <1 | 0 |

L, ligand. Reaction conditions 110 °C, 4 h, 0.5 mmol nitrobenzene, 1 mol% catalyst (3 wt% Co-**L**/C), 50 bar hydrogen, 2 ml THF, 100 μl $H_2O$. *Determined by GC using *n*-hexadecane as an internal standard. [†]Reaction time 16 h. [‡]Pyrolysed carbon. [§]Metal/ligand ratio 1:2. [‖]Conducted in $H_2O$ (3 ml). [¶]Homogeneous catalyst.

**Catalyst synthesis and catalytic experiments.** In a preliminary catalyst screening, biorelevant and abundant metal–amine complexes based on iron, cobalt, manganese and nickel pyrolysed on carbon were tested for the industrially important benchmark of hydrogenation of nitrobenzene. Among the different metals used, cobalt(II)–amine acetate complexes showed significant activity. This was surprising to us as cobalt catalysts are scarcely used for such transformation[29–31]. Therefore, we prepared a variety of catalysts from different cobalt precursors and nitrogen ligands (Table 1) by adsorbing a solution of the respective cobalt complex onto commercially available carbon (Vulcan XC72R) and subsequent pyrolysis under inert conditions (Fig. 1). In doing so, cobalt oxide particles were expected to form that interact with the nitrogen-enriched carbon surface.

The exact preparation of the catalyst material is crucial to generate highly active species. For example, optimization of the pyrolysis step showed that the temperature gradient and the heating time at the maximum temperature significantly influence the activity and selectivity of the catalyst. The best system (see below) was obtained by performing the calcinations at 800 °C for two hours.

All novel catalytic materials were tested in the model reaction at 110 °C under hydrogen (50 bar). The plain cobalt oxide/carbon catalyst and materials in which the organic ligands were immobilized on carbon material revealed no product at all (Table 1, entries 1–3). On pyrolysis of cobalt nitrogen complexes on carbon the catalytic activity is improved (Table 1, entries 4–6). Among the different amine ligands tested, phenanthroline (**L1**) was found to give the most-active system (Table 1, entry 4).

It is important that this catalyst exhibited superior reactivity even in comparison with similar nitrogen ligands such as terpyridine (**L2**) or bis(benzimidazolyl)pyridine (**L3**) (Table 1, entries 4–6). Hence, comparably small changes in the organic ligand cause extensive loss of reactivity and selectivity. The model reaction does not occur to any extent in the presence of the homogeneous precatalyst (Table 1, entry 10), even when using a tenfold amount of cobalt(II) acetate and phenanthroline. In addition, a related iron-based catalyst showed insignificant formation of aniline (Table 1, entry 9).

**Catalyst characterization.** To understand the nature of the active metal species, electron paramagnetic resonance (EPR) measurements of the supported pyrolysed cobalt catalyst were performed. The different EPR spectra were recorded in the X-band at 88 K and 290 K on a Bruker EMX CW-microspectrometer equipped with an ER 4119HS-WI high-sensitivity cavity and a variable-temperature control unit (microwave power 6.64 mW, modulation frequency 100 kHz, modulation amplitude 1 G). The EPR spectrum of the active catalyst contains a broad signal at $g = 2.12$, the intensity of which increases slightly with rising temperature (Fig. 2a). This is characteristic for antiferromagnetic $Co_3O_4$ particles. The Neel temperature, $T_N$ (above which bulk $Co_3O_4$ becomes paramagnetic), is below 40 K (refs 38,39). Thus, according to the Curie–Weiss law, a decrease of the magnetic susceptibility and, consequently, also of the EPR signal intensity would be expected on increasing the temperature from 88 to 290 K, which is not the case in Fig. 2a. However, it was found that the temperature dependence of the EPR signal intensity reflected very sensitively the onset of antiferromagnetic ordering in $Co_3O_4$ and also in other antiferromagnetic oxide materials already well above $T_N$ (ref. 40). In bulk $Co_3O_4$, the EPR intensity increased gradually up to 150 K and then remained constant up to 250 K before it started to decrease.

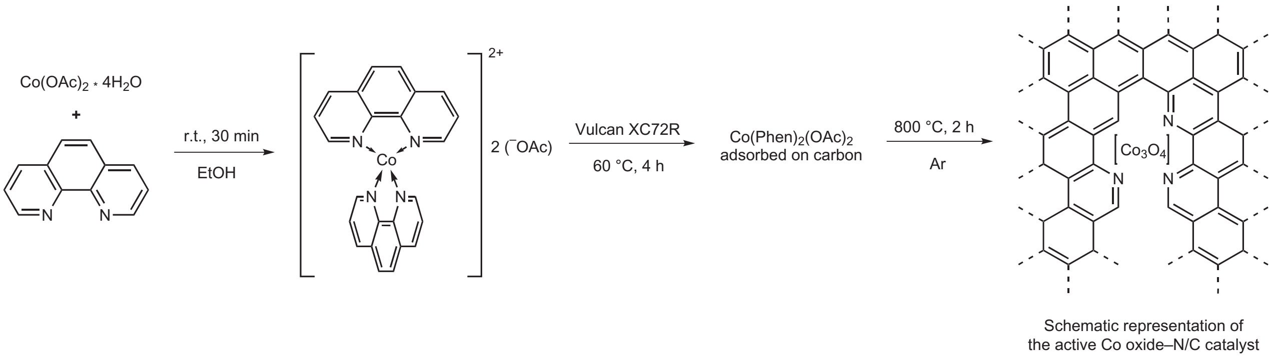


**Figure 1 | Synthesis of an active cobalt oxide-nitrogen/carbon catalyst by pyrolysing a cobalt(II) acetate-phenanthroline complex on carbon.** r.t. = room temperature.

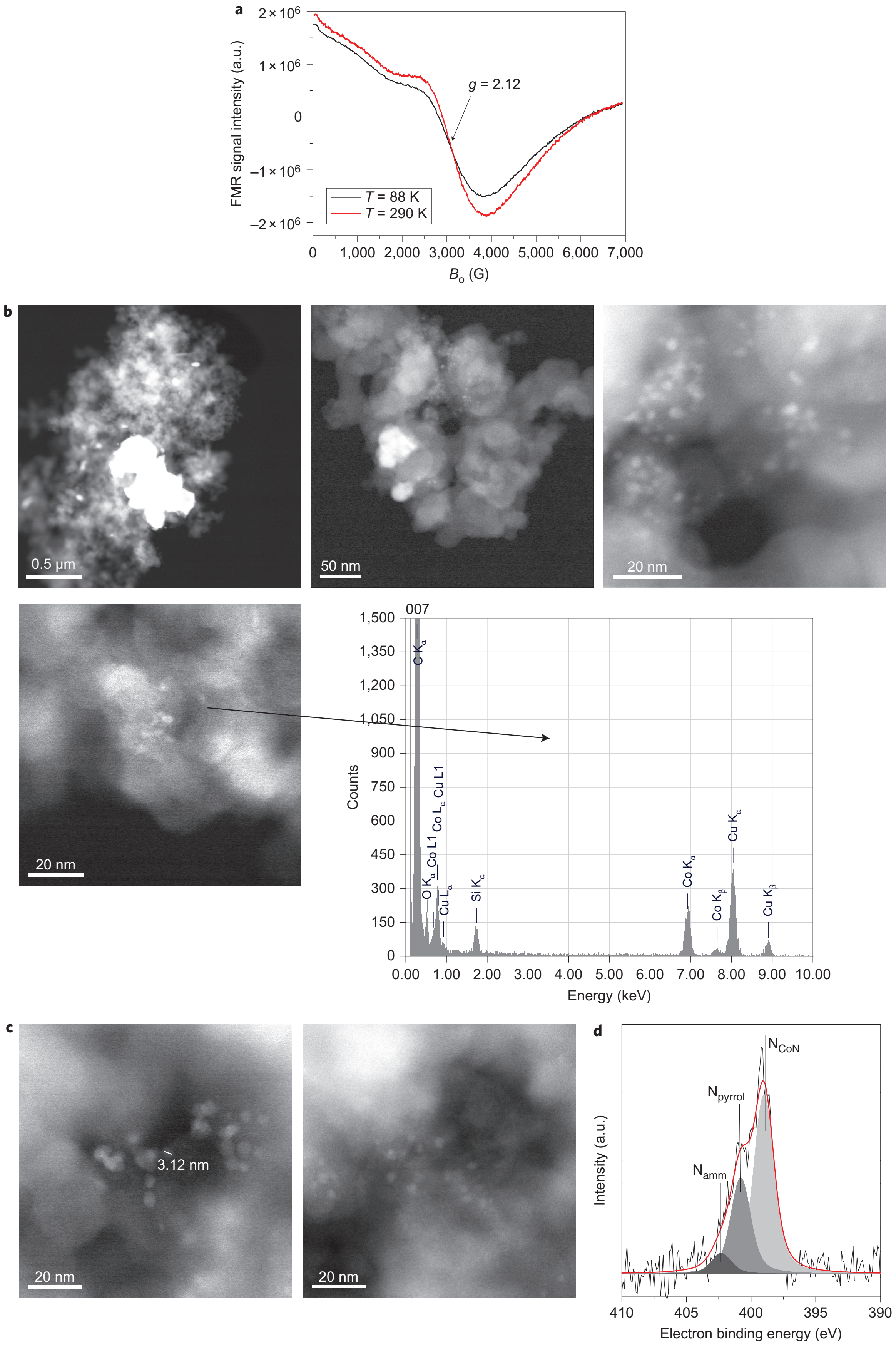


**Figure 2 | Catalyst characterization.** **a**, EPR spectra of the active cobalt catalyst recorded at 88 and 290 K. **b**, HAADF images and EDXS (bottom right) of $Co_3O_4$-**L1**/C. **c**, HAADF images of $Co_3O_4$-**L2**/C. **d**, XPS N1s spectrum of $Co_3O_4$-**L1**/C. The different N1s states are labelled as $N_{CoN}$ for nitrogen bound to cobalt, $N_{pyrrol}$ for pyrrolic N and $N_{amm}$ for nitrogen of quaternary amine species. a.u. = arbitrary units.

The observed intensity behaviour in Fig. 2a is exactly in line with the previous results and also with the fact that a considerable fraction of rather large particles (20–80 nm) was observed by transmission electron microscopy (TEM) (see below). The EPR signal at $g = 2.12$ is superimposed on a second very broad anisotropic signal, the positive lobe of which is cut off at $B = 0$. This suggests that the magnetic properties are not exactly the same for each particle. The reason may be different particle sizes (see below) and/or replacement of oxygen by nitrogen in the coordination of cobalt (as observed by X-ray photoelectron spectroscopy (XPS), see below). The presence of metallic cobalt and/or cobalt oxide can be ruled out because their magnetic properties are not in line with the observed EPR intensity behaviour. Indeed, cobalt is ferromagnetic but cobalt oxide is antiferromagnetic, with $T_N \approx 293$ K (ref. 41).

To understand in more detail the remarkable activity difference of the carbon-supported $Co_3O_4$–**L1** material compared to that of the other catalysts, scanning transmission electron microscopy investigations of $Co_3O_4$–**L1**/C and $Co_3O_4$–**L2**/C were conducted. To image the complete size spectra of cobalt oxide particles, a high-angle annular dark field (HAADF) at a spherical aberration (Cs)-corrected microscope was used. With a conventional TEM it was not possible to image the smallest particles because of the weak contrast.

As shown in Fig. 2b,c, for the different materials the cobalt oxide particle size varies significantly. To our surprise, in the active catalyst system $Co_3O_4$–**L1**/C the particle sizes had a wide size distribution with a fraction of particles of 2–10 nm, and particles and agglomerates in the range 20–80 nm. Occasionally, even larger structures up to 800 nm were present. As shown by energy-dispersive X-ray spectroscopy (EDXS) analysis, both the very small particles and the larger ones contained cobalt. Also, we observed some cloudy structures with weak contrast even in the HAADF (Fig. 2b) that contained $Co_3O_4$ as well. However, when the less-reactive **L2**–Co(II) acetate complex adsorbed onto carbon was analysed (Fig. 2c), the size of the well-defined particles rarely exceeded the range 2–10 nm. In the latter case, larger elements were not present. In addition, cloudy cobalt-containing structures with weak contrast were absent. Although in most catalytic reactions smaller nanoparticles exhibit higher activity, apparently in this catalytic reaction the best performance is achieved with larger particles, although we cannot rule out the activity of the observed cloudy cobalt structures[42–44].

To obtain further insight into the structure of the catalyst and especially the role of nitrogen from the organic ligand, XPS investigations on the bonding of nitrogen and cobalt were carried out. Interestingly, three distinct peaks are observed in the N1*s* spectra of $Co_3O_4$–**L1**/C with an electron-binding energy of 399.0 eV, 400.8 eV and 402.3 eV (Fig. 2d). The lowest binding-energy peak can be attributed to a pyridine-type nitrogen, which is bound to a metal ion[45]. The electron-binding energy of 400.8 eV is characteristic of a pyrrole-type nitrogen that contributes two electrons to the carbon matrix. It is bound to a hydrogen atom. Such types of nitrogen are found after the carbonization of nitrogen-containing organic materials[46]. Finally, the small peak at 402.3 eV is typical for quaternary amine species ($NR_4^+$)[47]. The ratio between all cobalt atoms and all nitrogen atoms in the near-surface region was 1:4.7. Deconvolution revealed that around 64% of all nitrogen atoms are bound to the metal ions and therefore, statistically, three nitrogen atoms are bound to one cobalt atom.

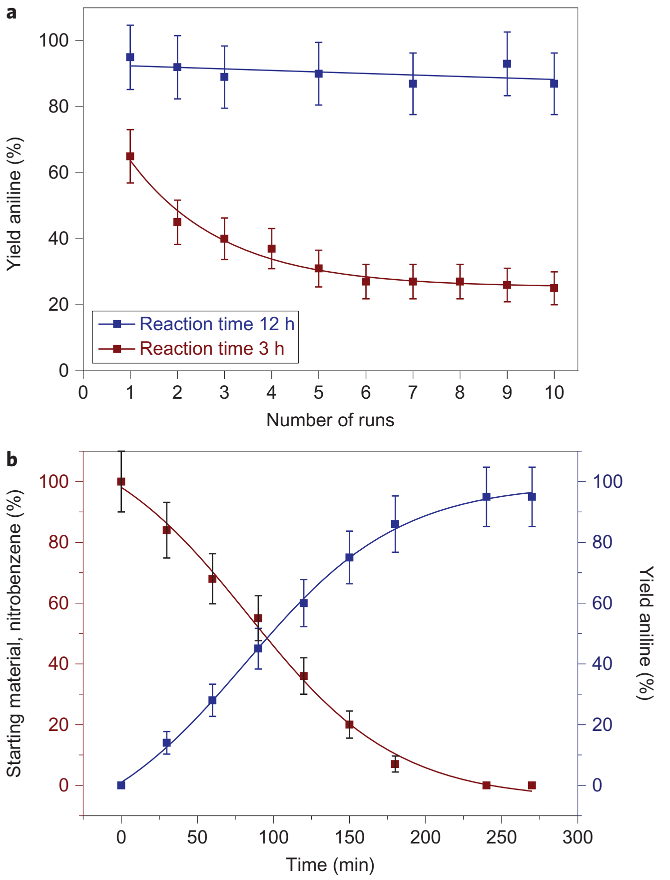
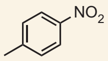
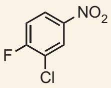
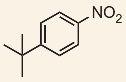
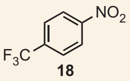
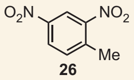
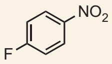
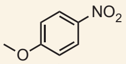
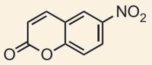
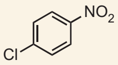
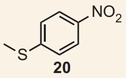
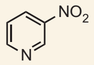
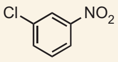
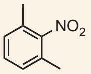
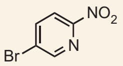
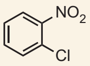
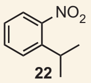
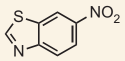
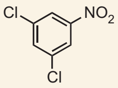
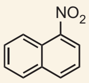
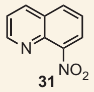
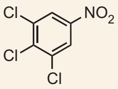
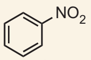
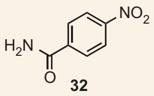
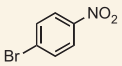
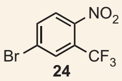
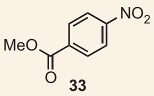


**Figure 3 | Catalyst recycling and kinetic data of the hydrogenation of nitrobenzene catalysed by cobalt oxide. a**, Recycling experiments over ten runs with different reaction times (three and 12 hours). **b**, Kinetic profile of the reduction of nitrobenzene to aniline using the cobalt catalyst. Reaction conditions: 110 °C, 0.5 mmol nitrobenzene, 1 mol% catalyst (3 wt% Co-**L1**/C), 50 bar hydrogen, 2 ml THF, 100 µl $H_2O$. Conversion and yields were determined by gas chromatography (GC) using *n*-hexadecane as an internal standard. The error bars were calculated using Origin 8.

**Catalytic experiments.** As shown in Fig. 3 the catalyst is recycled up to ten times with little loss of activity, which shows the potential applicability of this system. Selectivity and yield of aniline remained constant through all cycles when the reaction was run for 12 hours. However, when the activity of the reused catalyst was evaluated after three hours an initial loss of activity was observed. After the fifth run the activity started to level off and yields remained at around 30% until the tenth run (Fig. 3a). The kinetic profile of the reaction reveals that nitrobenzene was converted smoothly into aniline without a significant formation of dangerous intermediates, for example hydroxylamine, being detected (Fig. 3b). Interestingly, the reaction rate of the hydrogenation is dependent on the amount of water present. When we used dry organic solvents, for example tetrahydrofuran (THF), the reaction times had to be prolonged to achieve full conversion. This stimulated us to perform the reaction simply ‘on water’ without any additional organic solvent present. To our delight, the catalyst activity was even higher in pure water compared to that in THF[48,49].

Next, the general scope of our supported cobalt catalyst was demonstrated in the reduction of more than 30 functionalized nitroarenes (some of these compounds are toxic, for example entry 20 in Table 2, and should be handled with appropriate caution). As shown in Table 2, a variety of industrially relevant anilines such as chloro- and fluoroanilines were prepared in good to excellent yields (83–99% (Table 2, entries 3–10)). Even sterically demanding nitroarenes (Table 2, entries 14 and 15) and substrates bearing more-labile bromide substituents or sulfur were hydrogenated smoothly (Table 2, entries 9 and 13).

**Table 2 | Cobalt-catalysed hydrogenation of substituted nitroarenes.**

| Entry | Substrate | Time (h) | Yield (%)* | Entry | Substrate | Time (h) | Yield (%)* | Entry | Substrate | Time (h) | Yield (%)* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 |  <br>**8** | 4 | 91/93[†] | 10 |  <br>**17** | 6 | 83 | 19 |  <br>**25** | 4 | 78 |
| 2 |  <br>**9** | 4 | 99/99[†] | 11 |  <br>**18** | 6 | 93 | 20 |  <br>**26** | 12 | 83[†,‡,§] |
| 3 |  <br>**10** | 6 | 92 | 12 |  <br>**19** | 6 | 78 | 21 |  <br>**27** | 12 | 85[†] |
| 4 |  <br>**11** | 6 | 95 | 13 |  <br>**20** | 6 | 85/83[†] | 22 |  <br>**28** | 12 | 53[‡] |
| 5 |  <br>**12** | 6 | 95/93[†] | 14 |  <br>**21** | 12 | 96 | 22 |  <br>**29** | 12 | 58[†] |
| 6 |  <br>**13** | 4 | 99/99[‖] | 15 |  <br>**22** | 12 | 97/99[†] | 24 |  <br>**30** | 12 | 75[†] |
| 7 |  <br>**14** | 6 | 97 | 16 |  <br>**23** | 4 | 99 | 25 |  <br>**31** | 12 | 73 |
| 8 |  <br>**15** | 6 | 93/96[†]/98[§] | 17 |  <br>**1** | 12 | 91 | 26 |  <br>**32** | 12 | 73 |
| 9 |  <br>**16** | 6 | 94/98[§] | 18 |  <br>**24** | 4/12 | 78/88[†] | 27 |  <br>**33** | 4 | 89 |

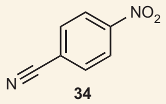
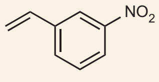
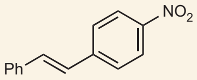
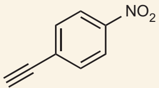
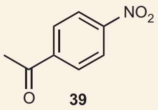
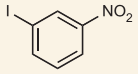
Reaction conditions: 110 °C, 0.5 mmol nitroarene, 1 mol% catalyst (3 wt% Co-L1/C), 50 bar hydrogen, 2 ml THF, 100 μl $H_2O$; >99% conversion observed in all cases. *Determined by GC using *n*-hexadecane as an internal standard. [†]Conducted in $H_2O$ (3 ml). [‡]Reduction selectively yields the diamine. [§]Isolated yield (5 mmol scale). [‖]Isolated yield (50 mmol scale), 0.2 mol% catalyst, 48 h, 10 ml THF, 1 ml $H_2O$.

Moreover, both electron-deficient substituents, such as trifluoromethyl, and electron-rich groups, for example methoxy and amino, were tolerated well. In addition to anilines, heteroaromatic amines are valuable building blocks for the preparation of a variety of agrochemicals and pharmaceuticals[50]. Therefore, five different nitroheteroarenes were subjected to the standard hydrogenation conditions. Without further optimization all the substrates were reduced in moderate-to-good yields (53–85% (Table 2, entries 21–25)).

Clearly, the most-challenging substrates are those that bear other easily reducible moieties (Table 3). In this respect, the supported gold catalyst from Corma and Serna showed impressive chemoselectivity, even in the presence of olefinic bonds[34]. However, even with the gold catalyst no examples with demanding substituents, such as alkynes, iodides or heteroarenes, were reported. In this respect, we were pleased to find that the novel cobalt catalyst is not only able to reduce nitro groups in the presence of alkenes, but also alkynes with full conversion and without any detectable concurrent reduction of the unsaturated unit (88–96% (Table 3, entries 2–4)). Compared to well-known noble metal catalysts (Supplementary Table S6), clearly our novel catalyst performs in a superior manner. For example, applying nitrosubstituted aryl iodides in general facile dehalogenation is observed with current commercially available catalysts based on precious metal, but using the cobalt-based catalyst the reaction proceeds efficiently in 92% yield (Table 3, entry 7).

To our delight, substrates that contained sensitive aldehyde or keto substituents were also converted smoothly and selectively into the corresponding anilines (79–97% (Table 3, entries 5 and 6)). Furthermore, carboxylic acid derivatives, such as nitriles, were tolerated well.

**Table 3 | Selective cobalt-catalysed hydrogenation of nitroarenes that bear easy-to-reduce functional groups.**

| Entry | Substrate | Time (h) | Yield (%)[*] |
|---|---|---|---|
| 1 |  **34** | 4 | 83 |
| 2 |  **35** | 6 | 91 |
| 3 |  **36** | 6 | 96/97[†] |
| 4 |  **37** | 4 | 88[‡] |
| 5 |  **38** | 4 | 97 |
| 6 |  **39** | 4 | 79 |
| 7 |  **40** | 6 | 92/99[†] |

Reaction conditions: 110 °C, 0.5 mmol nitroarene, 1 mol% catalyst (3 wt% Co-**L1**/C), 50 bar hydrogen, 2 ml THF, 100 μl $H_2O$; >99% conversion observed in all cases. [*]Determined by GC using *n*-hexadecane as an internal standard. [†]Isolated yield (5 mmol scale). [‡]2 mol% cobalt catalyst.

## Summary and conclusion

We have developed novel cobalt-based catalysts for the hydrogenation of nitroarenes into the corresponding anilines. The most-active catalyst is prepared via adsorption of a cobalt–phenanthroline complex onto a commercially available carbon support and subsequent pyrolysis. Depending on the amine ligands used, different cobalt particles form on a carbon–nitrogen surface. Although the control of the active metal centre by organic ligands is well established in homogeneous catalysis[51,52], such concepts are less investigated in heterogeneous catalysis. In contrast to known examples of ‘ship-in-the-bottle’ surface organometallic or immobilized homogeneous catalysts, in our approach the overall catalyst performance is controlled indirectly by the ligand[53–55].

The optimal catalyst system constitutes one of the most general, functional-group tolerant, inexpensive and environmentally benign catalysts known to date for the industrially important reduction of nitroarenes. It tolerates numerous other reducible functional groups and can be reused several times without loss of activity. Advantageously, during catalysis protective gas techniques or dry solvents are not necessary and reactions can be performed at an increased rate on water.

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## Author contributions

M.B., F.A.W. and R.V.J. planned and developed the project, F.A.W. performed and designed the experiments and co-wrote the paper, R.V.J. developed, designed and prepared the catalysts and was involved in writing the paper, G.W. conducted catalytic experiments and performed the analytics, M.N. was involved in discussions and contributed to the writing of the paper, K.J. participated in discussions and contributed to the writing of the paper, H.J. was involved in the development of the catalyst, A.E.S. performed electrochemical studies of the catalyst and was involved in the catalyst development, J. Radnik did the XPS experiments, M.M.P. performed the TEM experiments, J. Rabeah and A.B. were responsible for EPR experiments, M.B. directed the project, participated in the design of catalytic experiments and in the design of the catalyst, and co-wrote the paper.

## Additional information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.B.

## Competing financial interests

The authors declare no competing financial interests.