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Room-Temperature Chemoselective Reduction of Nitro Groups Using Non-noble Metal Nanocatalysts in Water

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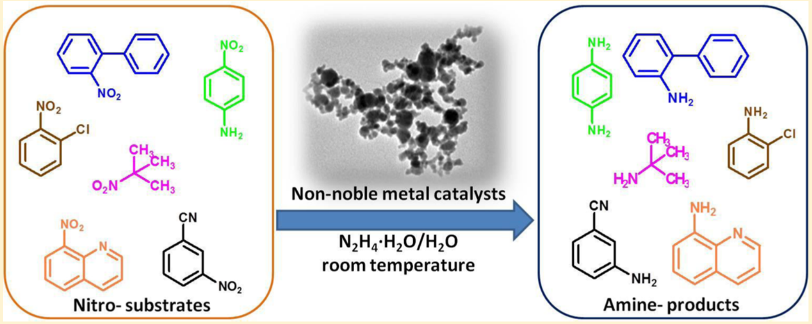
Supporting Information



ABSTRACT: Purely aqueous-phase chemoselective reduction of a wide range of aromatic and aliphatic nitro substrates has been performed in the presence of inexpensive Ni- and Co-based nanoparticle catalysts using hydrazine hydrate as a reducing agent at room temperature. Along with the observed high conversions and selectivities, the studied nanoparticle catalysts also exhibit a high tolerance to other highly reducible groups present in the nitro substrates. The development of these potential chemoselective reduction catalysts also provides a facile route for the synthesis of other industrially important fine chemicals or biologically important compounds, where other highly reducible groups are present in close proximity to the targeted nitro groups.

INTRODUCTION

Functionalized aromatic amines are important feedstocks for the synthesis of pharmaceuticals, agrochemicals, dyes, polymers, and various other industrially important fine chemicals.[1] The most commonly used method for the production of aromatic amines is the reduction of corresponding nitro substrates, using stoichiometric amounts of reducing agents (e.g., Mn, Sn, Zn), or catalytic reduction. However, the traditional noncatalytic processes are environmentally nonsustainable because of the large amount of waste generated,[2] whereas the catalytic reductions of nitro groups in the presence of metal complexes, metal sulfides, or metal powder have various practical drawbacks, such as toxic byproducts and difficulty in reuse.[3] In this context, metal nanoparticle catalysts based on noble metal (Pt, Pd, Au, Ru, and others) displayed a high potential toward the facile reduction of nitro groups using various reducing agents, such as H_2, $NaBH_4$, $N_2H_4·H_2O$, and so on.[4−6] Recently, photocatalytic reduction of nitro compounds to corresponding amines in the presence of Pd/CeO_2 and CdS has also been reported.[7] Despite high activity and selectivity achieved with noble metals, the high cost associated with the noble metals is a major hurdle and, therefore, the development of inexpensive non-noble metal-based catalysts is highly desirable. Moreover, the chemoselective reduction of nitro groups to corresponding aromatic amines is more challenging, particularly when other reducible groups are present and therefore needs special attention. Extensive progress has been observed toward the development of a more economical and chemoselective catalyst for the reduction of nitro groups to corresponding amine derivatives using low-cost non-noble metals (e.g., Ni, Co, Fe, and Cu metals or oxides).[8−12] Recent findings on catalytic systems based on $Co-Co_2B$, Fe_2O_3, Ni@Fe_2O_3, Cu, and Co_2O_3 show high activity of these catalysts,[8−12] but most reports are using harsh reaction conditions, such as elevated temperature, high pressure, and nonaqueous solvent media.[8−12] Although the Co_3O_4 catalyst by Beller et al.[8a] and the Fe_3O_4 catalyst by Kappe et al.[10] displayed high catalytic activities, reports on non-noble metal-catalyzed aliphatic nitro substrate reduction are rare.[8b,11a,12a]

It is well-known that purely aqueous-phase organic transformations are of critical importance.[13] Nevertheless, there are

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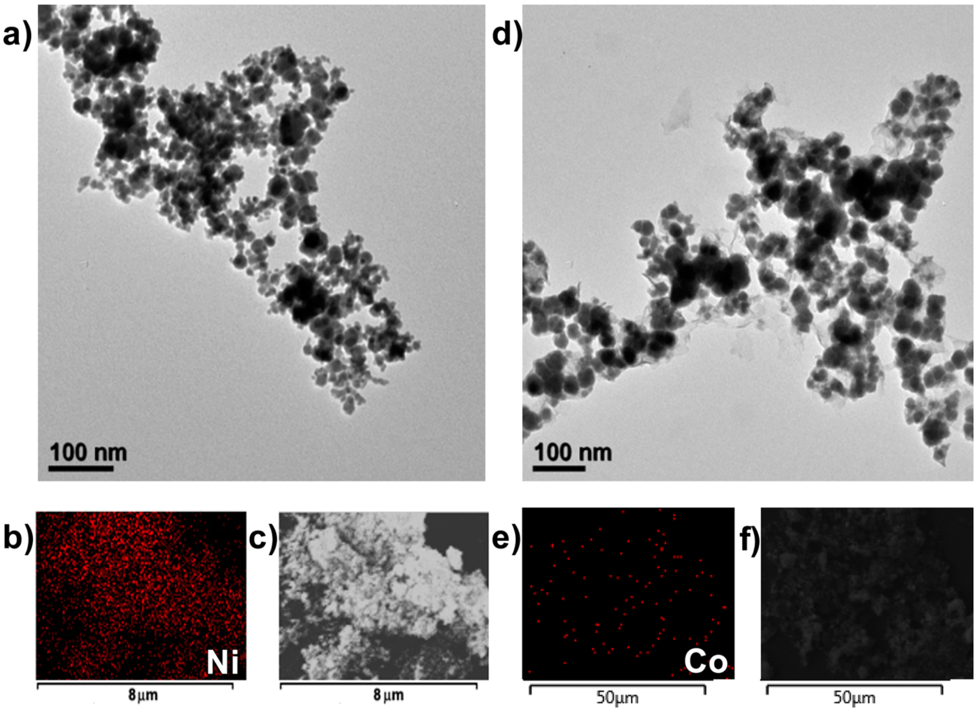


Figure 1. (a and d) TEM images and (b and e) electron mapping corresponding to the respective (c and f) SEM images of (a−c) Ni and (d−f) Co nanoparticles.

seldom any reports on inexpensive non-noble metal catalysts that can promote selective reduction of a nitro group *in both aqueous solutions and at room-temperature* conditions. We remain interested in the development of inexpensive or low-cost catalytic systems for other aqueous-aerobic reactions under mild reaction conditions and hydrazine hydrate for hydrogen generation.[14] Furthermore, unlike H_2 (requiring high pressure) or the nonselective $NaBH_4$ (nonselective reduction), the liquid hydrous hydrazine could be a better choice because it can be easily handled, mostly facilitates selective reduction, and advantageously generates only environmentally benign N_2 as a byproduct.[3−6,8−12]

Herein, we report nanoparticle catalysts (nanocatalysts) based on inexpensive non-noble metals, Ni, Co, and Cu, for aqueous-phase chemoselective reduction of nitro substrates to the respective amines using hydrazine hydrate as the reducing agent at room temperature.

EXPERIMENTAL SECTION

General Procedures. High-purity metal salts were used for the experiments. NMR spectra were recorded on a Bruker Avance 400 spectrometer. Chemical shifts are referenced to internal solvent resonances and reported relative to tetramethylsilane (TMS). Transmission electron microscopy (TEM) experiments were performed with a JEM-1400 microscope (JEOL) operated at 100−120 kV. Scanning electron microscopy (SEM) images and energy-dispersive spectrometry (EDS) analysis were collected on Carl Zeiss supra 55 and field-emission JSM-7001F (JEOL) operated at 15 kV. For TEM and SEM analysis, a few droplets of the nanoparticle suspension in ethanol were deposited onto amorphous carbon-coated 400-mesh copper grids (for Ni and Co) and a nickel grid (for Cu) and eventually air-dried. Powder X-ray diffraction (XRD) measurements were performed on the dried particles on a Shimadzu XRD-6000 Labx diffractometer at 40 kV and 30 mA using Cu Kα radiation (λ = 1.5418 Å). UV−visible spectral studies were performed on a Varian Cary 100 Bio UV−visible spectrophotometer.

General Procedure for the Preparation of Non-noble Metal (Ni, Co, and Cu) Nanoparticles. Ni nanoparticles were prepared using a poly(vinylpyrrolidone) (PVP)-stabilized aqueous-phase coreduction process. In a typical synthesis, 5 mL of an aqueous solution of $NaBH_4$ (0.040 g) was added dropwise to an aqueous solution (5 mL) containing $NiCl_2 \cdot 6H_2O$ (0.20 mmol, 0.047 g) and PVP (0.100 g) at room temperature. The content of the flask was sonicated for 10 min to obtain Ni nanoparticles as a black suspension. Co and Cu nanoparticles were also prepared analogously using $CoCl_2 \cdot 6H_2O$ (0.20 mmol, 0.047 g) and $CuCl_2 \cdot 2H_2O$ (0.20 mmol, 0.034 g), respectively, in place of $NiCl_2 \cdot 0.6H_2O$.

General Procedure for the Reduction of Nitroarenes Using Hydrazine Monohydrate at Room Temperature. To a reaction flask containing an aqueous suspension of freshly prepared nanoparticle catalysts (0.2 mmol based on the metal salt used to prepare the particles) was added 1.0 mmol of nitro substrate, and the contents was stirred for 5 min. A total of 0.2 mL of hydrazine monohydrate was then added to the mixture, and the reaction contents was stirred at room temperature. Progress of the reaction was monitored by thin-layer chromatography. After completion, the reaction mixture was centrifuged at 15000 rpm to separate out the catalysts. The reaction mixture was extracted by dichloromethane (3 × 10 mL), the organic layer was dried over anhydrous $NaSO_4$ and filtered off, and the solvent was evaporated at reduced pressure. All of the products were characterized by ^1H NMR (400 MHz with TMS as the standard).

Purification and Characterization of Nanocatalysts. Before and after the catalytic reactions, the nanoparticle suspension was centrifuged (15000 rpm, 10 min, 298 K) to separate the solution and nanocatalyst, which was washed twice with 5 mL of water and ethanol, dried in a vacuum, and then used for SEM, TEM, EDS, and powder XRD measurements.

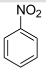
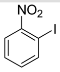
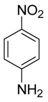
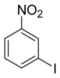
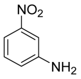
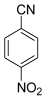
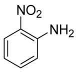
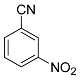
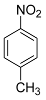
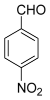
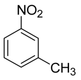
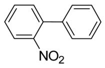
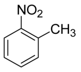
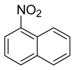
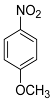
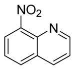
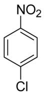
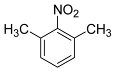
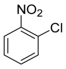
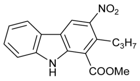
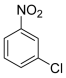
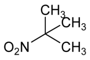
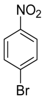
RESULT AND DISCUSSION

In a typical process, Ni nanoparticle catalysts (nanocatalysts) were prepared using aqueous-phase reduction of $NiCl_2 \cdot 6H_2O$ by $NaBH_4$, as a reducing agent, in the presence of PVP. Co and Cu nanocatalysts were also prepared analogously using the method for the preparation of Ni nanoparticles.

Table 1. Catalytic Reduction of Nitroarenes to the Corresponding Anilines

$$R-NO_2 \xrightarrow[\substack{N_2H_4.H_2O,\ rt \\ H_2O}]{\substack{\text{non-noble metal nanocatalyst} \\ \text{(PVP stabilised)}}} R-NH_2$$

R = aromatic and aliphatic

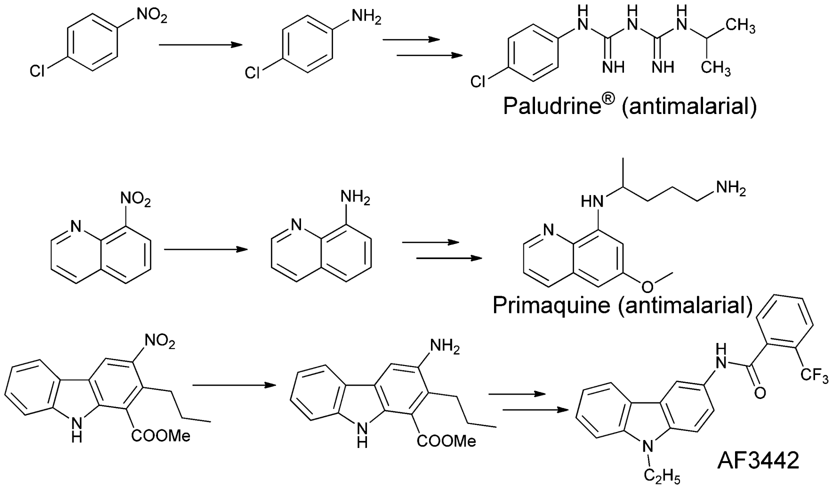
entry	substrate	Ni catalyst sel./conv.(%)[b] (time)	Co catalyst sel./conv.(%)[b] (time)	entry	substrate	Ni catalyst sel./conv.(%)[b] (time)	Co catalyst sel./conv.(%)[b] (time)
1		>99/>99 (75 min)	85/50 (300 min)	13		75/>99 (60 min)	>99/>99 (120 min)
2		>99/>99 (30 min)	>99/>99 (30 min)	14		83/>99 (60 min)	>99/>99 (30 min)
3		>99/95 (15 min)	>99/50 (120 min)	15		77/85 (240 min)	91/30 (120 min)
4		>99/94 (300 min)	>99/>99 (120 min)	16		60/92 (240 min)	93/30 (120 min)
5		>99/>99 (35 min)	>99/>99 (25 min)	17		>99/>99 (90 min)	>99/>99 (90 min)
6		>99/>99 (70 min)	>99/70 (120 min)	18		>99/>99 (60 min)	92/>99 (60 min)
7		>99/>99 (40 min)	>99/>99 (45 min)	19		>99/96 (60 min)	>99/97 (90 min)
8		>99/95 (60 min)	>99/66 (120 min)	20		77/80 (240 min)	96/93 (240 min)
9		>99/>99 (120 min)	>99/>99 (120 min)	21		>99/>99 (40 min)	>99/>99 (45 min)
10		>99/>99 (40 min)	>99/>99 (25 min)	22		>99/>99 (360 min)	n.d
11		>99/>99 (110 min)	10/n.d (120 min)	23		>99/>99 (45 min)	>99/95 (60 min)
12		>99/95 (30 min)	>99/>99 (20 min)	24	CH_3NO_2	80/>99 (60 min)	70/>99 (60 min)

[a] Reaction conditions: room temperature, 1 mmol of nitro substrate, 20 mol % catalyst, 0.2 mL of $N_2H_4 \cdot H_2O$, and 10 mL of H_2O. [b] Determined by ^1H NMR.

The synthesized nanoparticles were identified as face-centered-cubic (fcc)-structured Ni (JCPDS 65-0380), Co (JCPDS 01-1255), and Cu (JCPDS 04-0836) nanoparticles by their powder XRD patterns, where the major diffraction peak can be indexed to the (111) diffraction plane (Figures S1, S2, S4 and S6 in the Supporting Information, SI).The TEM images (Figures 1 and S1, S2, S4, and S5 in the SI) obtained for Ni, Co, and Cu nanoparticles revealed average particle sizes of ~10 nm with irregular shape for all of the nanoparticles. EDS analysis from several points and elemental mapping investigations of the Ni, Co, and Cu nanoparticles revealed the presence of the respective elements (Figures 1 and S3, S5, and S7 in the SI).

We evaluated the catalytic activities of the freshly prepared nanocatalysts for the reduction of nitro groups by the addition of a suitable nitro substrate and hydrazine hydrate, as a reducing agent, in the reaction flask containing an aqueous suspension of nanocatalyst. Reaction products were analyzed after the reaction contents was stirred for a specified time at room temperature and under aerobic conditions. The efficacies of the synthesized Ni, Co, and Cu metal nanoparticles were first evaluated for the reduction of a model nitro substrate, *p*-

Scheme 1. Selective Reduction of Nitro Substrates to Industrially Relevant Amino Compounds



nitroaniline (Table S1 in the SI). Experiments revealed that high conversions and selectivity could be achieved in 30 min in the presence of Ni and Co nanoparticles (Table 1, entry 2). The catalytic reaction was also monitored by UV–visible spectroscopy (Figure S8 in the SI), where a gradual decrease in the intensity of the characteristic absorbance peak of *p*-nitroaniline at 367 nm was observed, along with the development of new absorbance peaks at 239 and 305 nm corresponding to the formation of *p*-phenylenediamine by the reduction of *p*-nitroaniline. The time-dependent ^{1}H NMR spectra (Figure S9 in the SI) of the catalytic reduction reaction of *p*-nitroaniline to *p*-phenylenediamine measured at regular intervals of 5, 10, and 15 min of the reaction reveal that ~78% conversion could be achieved within the first 5 min of the catalytic reaction. High conversions were also observed with 10 and 5 mol % Ni nanocatalysts with >99% selectivity but needed relatively longer reaction time (Table S1 in the SI). Notably, either in the absence of catalyst or in the absence of hydrazine hydrate, no reaction was observed. It is worth mentioning that using even a small amount of organic solvent, such as ethanol, prolonged reaction times required to achieve full conversion (Table S2 in the SI). This behavior is presumable due to the instant agglomeration of nanoparticles induced by ethanol.[15] Therefore, we performed all of our experiments in water only, without the addition of any organic solvent, which is the most desirable reaction condition for any process.

Under optimal catalytic reaction conditions, room-temperature reaction in water under aerobic conditions, the general scope of the most active Ni and Co nanocatalysts was extensively evaluated for the reduction of various functionalized aromatic and aliphatic nitro substrates to the respective amines, including many industrially and biologically relevant aromatic amines, such as chloro-substituted anilines or biphenylamines (Table 1). Full-to-high conversions of the nitro substrates with excellent selectivity (>99% for most of the cases) toward the respective amines were achieved in all of the catalytic reactions under aerobic-aqueous conditions at room temperature. It is worth mentioning here that most of the reports with non-noble metals are performed under high temperature or using nonaqueous solvents, but our reported Ni and Co catalysts show high catalytic performance under room temperature and in water. Earlier reports with Ni/SiO$_2$ catalysts show that catalytic reduction of nitrobenzene can only be performed at high temperature (90 °C) in ethanol.[12d] Along with the high conversions obtained with the catalytic reduction of nitrobenzene (Table 1, entry 1), the substituted nitrobenzene having amino (Table 1, entries 2–4), methyl (Table 1, entries 5–7), or methoxy (Table 1, entry 8) groups also displayed high conversions and selectivities with Ni and Co nanocatalysts. Moreover, the studied nanocatalysts also showed impressive chemoselective reduction of the most-challenging nitroarene substrates bearing other easily reducible groups (Table 1).

To our delight, bromo- and iodo-substituted nitroarenes, which can undergo facile dehelogenation, were selectively reduced to the respective haloaromatic amines (Table 1, entries 12–14) without showing any sign of dehalogenation. Furthermore, the position (ortho, meta, or para) of the halide substituents did not induce any significant differences in catalytic reactivity (Table 1, entries 9–14). Moreover, *p*-chloroaniline, obtained by the facile reduction of *p*-chloronitrobenzene (Table 1, entry 9), is an important ingredient for the synthesis of an antimalarial drug, paludrine (Scheme 1).[16] Nitro groups in aromatic nitro substrates, having other reducible functional groups, such as nitrile (Table 1, entries 15 and 16) and aldehyde (Table 1, entry 17), could be selectively reduced to the respective aromatic amines in good yields. In addition, the reduction of the nitro group in a biphenyl (Table 1, entry 18) or heterocyclic system (Table 1, entry 20) could be achieved with high selectivity and conversion to the corresponding amines. 8-Aminoquinoline, obtained from 8-nitroquinoline (Table 1, entry 20), is also an important ingredient for the synthesis of antimalerial drugs primaquine (Scheme 1), tafenoquine, and pamaquine.[17] The 3-nitrocarbazole derivative (Table 1, entry 22) could be effectively and selectively reduced to the corresponding 3-aminocarbazole derivative, an important intermediate in the preparation of a pharmaceutical, AF3442, which is useful for the treatment of prostaglandin E2 mediated disorders or diseases, such as inflammatory processes, Alzheimer's, asthma, etc. (Scheme 1).[18]

Along with the excellent conversions obtained for the reduction of aromatic nitro substrates, the studied nanoparticle catalysts also displayed high selectivity and conversion for the reduction of aliphatic nitro substrates. High conversion and selectivity was achieved for the reduction of 2-nitro-2-methylpropane (Table 1, entry 23) and nitromethane (Table 1, entry 24) to isopropylamine and methylamine, respectively. The aliphatic amines were obtained in their hydrochloride salts because of their relatively low boiling point. It is worth noting that, to date, only Fe_3O_4 was found to catalyze the reduction of aliphatic nitro substrates,[11a] whereas Ni- or Co-based catalysts were seldom reported.[8b,12a] The studied Ni and Co nanoparticle catalysts represent the first examples for room-temperature facile reduction of aliphatic nitro substrates in water.

Unlike the high catalytic activities shown by Ni and Co nanocatalysts, Cu nanocatalysts displayed moderate-to-low catalytic activity for the reduction of nitro substrates to the corresponding amines (Table S3 in the SI). After the reaction, Co nanoparticles were retrieved from the reaction mixture using an external magnet (Figure S10 in the SI), whereas Ni and Cu nanoparticles were retrieved by centrifugation. Notably, using *p*-nitroanilne as the model substrate, Ni nanoparticles can be recycled in up to five consecutive catalytic reactions (Figure 2). However, a decline in the activity for the fourth and fifth catalytic cycles was observed, which is primarily due to the agglomeration of Ni nanoparticles. Moreover, with prolonged reaction time, these reactions lead to complete conversion for the fourth, fifth, and even sixth cycles.

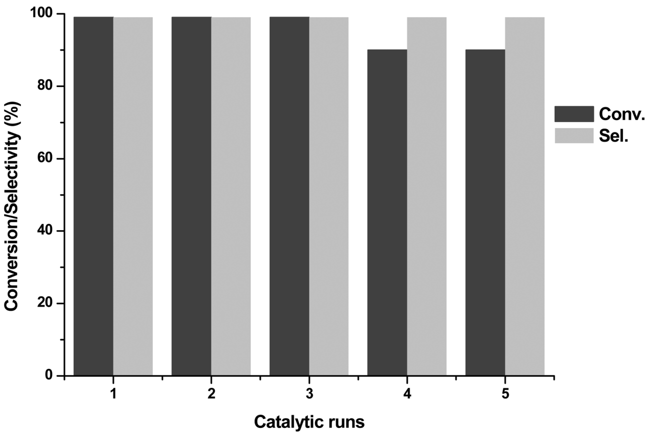


Figure 2. Recyclability test for the catalytic reduction of *p*-nitroaniline to *p*-phenylenediamine in the presence of Ni nanocatalysts.

To investigate the catalytic reduction pathway, we monitored the reaction progress and identified different possible intermediates by using UV–visible (Figure 3), ^{1}H NMR (Figure S11 in the SI), and mass spectrometry (Figure S12 in the SI) for the catalytic reduction of nitrobenzene to aniline in the presence of Ni nanocatalysts. The UV–visible spectrum recorded in water (Figure 3) after several minutes showed the formation of a nitrosobenzene intermediate (276 and 301 nm), but we could not find any absorbance for phenylhydroxylamine or diazobenzene.

Besides the direct reduction of nitrobenzene to aniline, as indicated by UV–visible experiments, the intermediates of this direct reduction pathway, nitrosobenzene and phenylhydroxylamine, may undergo condensation to form azoxybenzene, which may be further converted to aniline. To further investigate this, we performed the catalytic reduction of nitrobenzene in an ice bath to slow down the reaction. The ^{1}H NMR spectra of the reaction mixture examined after 15 min of reaction inferred the formation of phenylhydroxylamine (7.2%), nitrosobenzene (1.2%), and azoxybenzene (18%) intermediates. The formation of phenylhydroxylamine (m/z 110.0602) was also confirmed by mass spectral analysis. Furthermore, the occurrence of azoxybenzene also suggested a possible azoxybenzene mechanism for the reduction of nitrobenzene to aniline. However, diazobenzene was not observed at any stage of the investigation. Moreover, we also examined the direct reduction of pure diazobenzene to aniline, but even after prolonged reaction time, almost no conversion was observed. These observations further support the theory that the direct reduction of nitrobenzene to aniline, via nitrosobenzene and phenylhydroxylamine, is the most favored pathway (Figure 4).

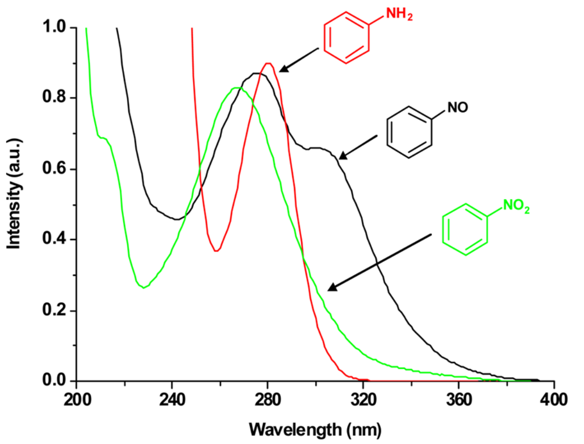


Figure 3. UV–visible spectra for the catalytic reduction of nitrobenzene to aniline in the presence of Ni nanocatalysts, showing the appearance of a nitrosobenzene intermediate.

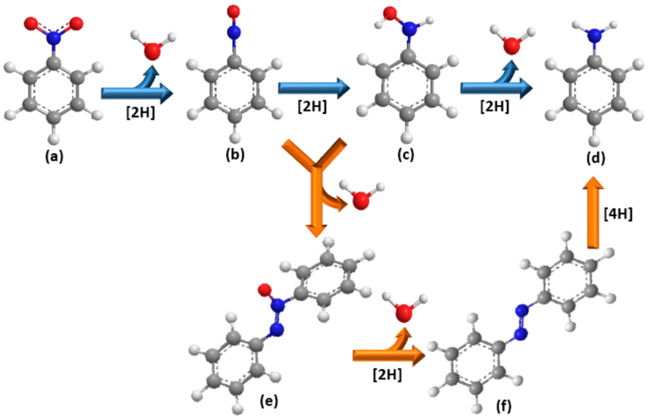


Figure 4. Proposed mechanism for the catalytic reduction of (a) nitrobenzene to (d) aniline in the presence of Ni nanocatalysts, where (b) nitrosobenzene, (c) phenylhydroxylamine, (e) azobenzene, and (f) diazobenzene are reaction intermediates.

■ CONCLUSIONS

In conclusion, the studied inexpensive non-noble metal-based nanocatalysts represent a most active catalyst system for extremely efficient aqueous-phase room-temperature chemoselective reduction of a wide range of nitro substrates into the respective amines. Along with general functional group tolerance, it also provides high tolerance toward numerous other highly reducible functional groups. Most importantly, the studied catalysts also effectively facilitate aliphatic nitro substrate reduction, which was not reported earlier with any form of Ni or Co catalysts. Moreover, high-temperature organic solvents and an inert atmosphere are not necessary for the catalytic reactions. Advantageously, water and nitrogen are the only byproducts from the catalytic reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data of the amine products, catalytic reduction of nitroarenes to corresponding *p*-nitroaniline, catalytic reduction of nitro substrates to corresponding amines, characterization of nanoparticle catalysts including TEM and SEM images, EDX mapping, powder XRD patterns, time-dependent UV−visible and ^{1}H NMR spectra, separation of cobalt nanoparticles from the reaction mixture, and proposed mechanism and identification of reaction intermediates, and spectra of the amine products obtained from the catalytic reduction of nitro substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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