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Original Research Article

Superparamagnetic core-shell metal-organic framework (Fe3O4@Ni-Co-BTC NPs): an efficient and magnetically retrievable nanostructured catalyst for the reduction of nitro compounds to amines

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ABSTRACT

Herein, a highly efficient and chemoselective strategy was developed for the reduction of nitro compounds in the presence of a bimetallic nanocatalyst. Thanks to inimitable structure of Fe3O4@Ni-Co-BTC NPs, this catalyst exhibits superior catalytic performance for the reduction of electron-donating and electron-withdrawing aromatic, heteroaromatic, heterocyclic and aliphatic nitro compounds. Interestingly, the aforesaid nanocatalyst showed high chemoselectivity for the reduction of the nitro group in the presence of other reducible functional groups such as COOH, CHO, COCH3, CN, NHAc and OCOCH3. Furthermore, Fe3O4@Ni-Co-BTC NPs could be easily separated from the reaction mixture and reused for at least seven consecutive recycle runs.

Keywords: Superparamagnetic core-shell metal-organic framework (Fe3O4@Ni-Co-BTC NPs), Nitro compounds, Amines, Nanostructured catalyst, Reduction.

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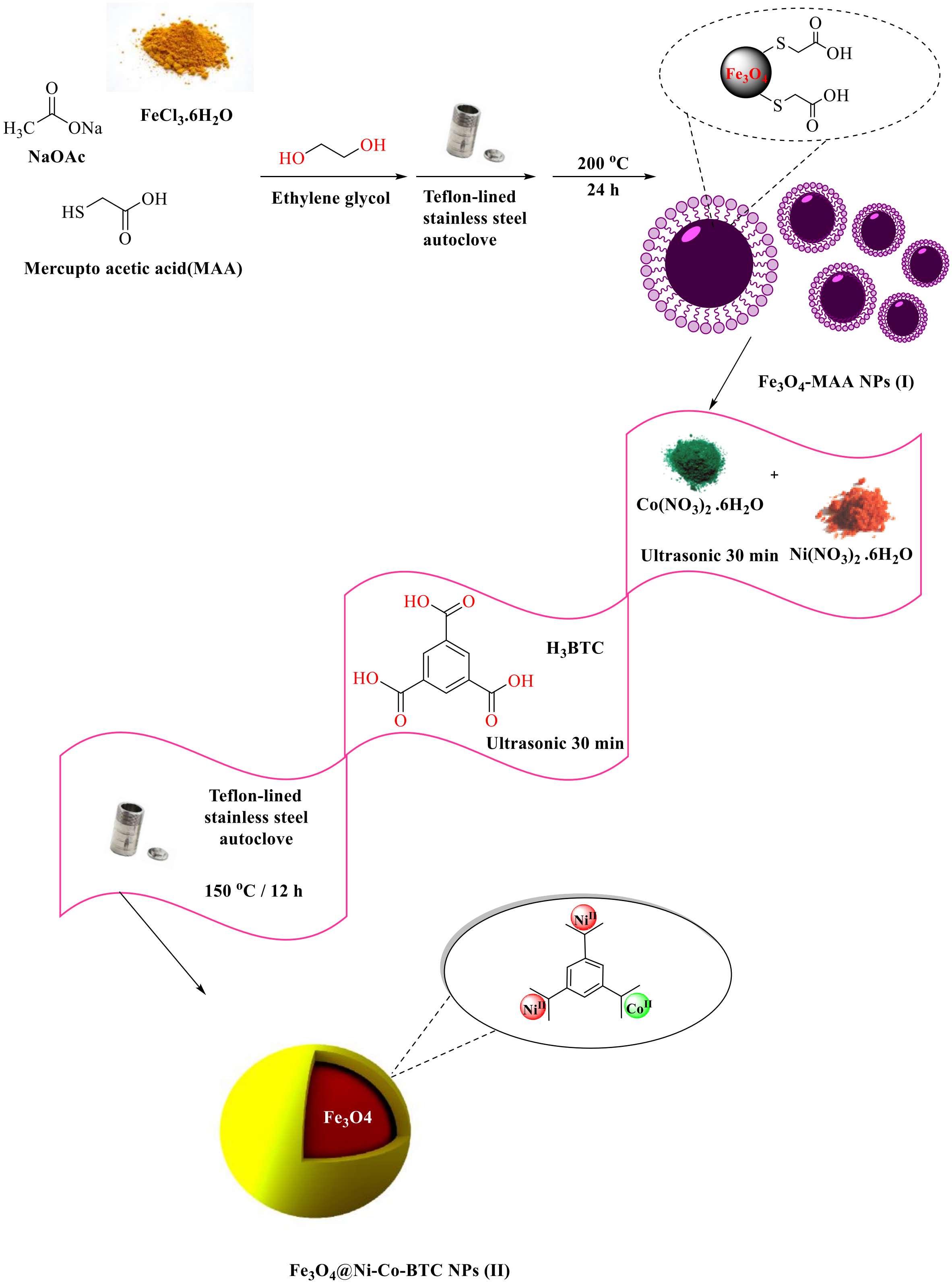
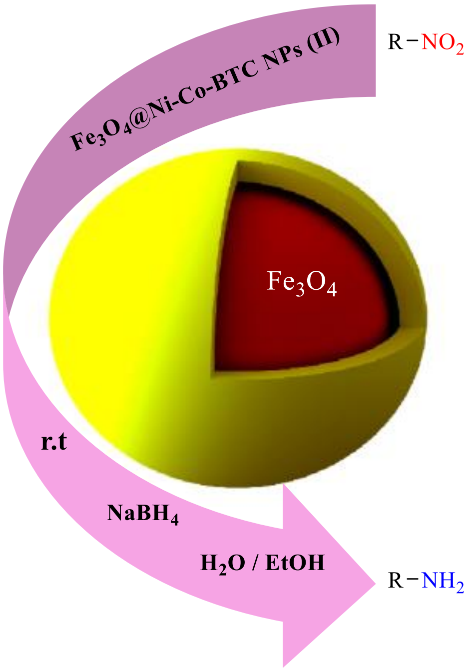
Introduction

Amines are very important functional derivatives in synthetic chemistry, material science and many other fields [1]. They are known as antioxidants and ubiquitous building blocks in the synthesis of various organic compounds such as pharmaceuticals, polymers, dyestuffs, agricultural chemicals, photographic and rubber materials, chelating agents and other industrially important products [2-5]. So, the particular immense interest has been devoted to the preparation of amines by various methods including reductive amination of carbonyl compounds, alkylation of ammonia, and reduction of azides, amides, nitriles, oximes as well as nitro compounds [6-9]. Generally, the chemoselective reduction of nitro compounds in the presence of a catalyst and a reductant (as an important route in environmental applications and organic synthesis operations) represents the most fundamental, straightforward and indispensable process in chemical, petrochemical, pharmaceutical and food industries to prepare amines [10-13]. In modern organic synthesis, various reductants such as H_2 [14], NH_2NH_2 [15], NH_4Cl [16], alcohols [17], acids [18], $NaHSO_3$ [19], $NaBH_4$ [20], $LiAlH_4$ [21], and ammonia-borane [22], in association with highly active and expensive metal catalysts such as Pt [23], Pd [24], Au [25], and Ir [26] have already been successfully employed for catalytic hydrogenation processes. However, the widespread applications of some of the aforementioned methods are limited due to low selectivity and reaction rates (using alcohols as the hydrogen source) and low availability or high cost of some reductants as well as low earth abundance, high price and toxicity of metal catalysts. In this context, application of $NaBH_4$ as a most popular and mild reducing agent reductant (commercially available and cheap) has gained much recent interests [27-33], while much attention has been transferred to the research of effective catalysts based on earth-abundant metal elements (such as Fe, Co, Ni) too [34-43]. The literature review shows that different homogeneous/heterogeneous catalysts have often been employed for reduction of easily available and in-expensive nitro compounds into amines [44-52], In the last decade, reduction of nitro compounds into their corresponding amines using metal nanoparticles (as a bridge between homogeneous and heterogeneous catalysis) has gained a considerable attention to overcome the problems associated to both homogeneous and heterogeneous catalysis such as separation and recycling of catalyst, catalytic poisoning and low contact of reactant molecules with catalyst. Recently, bimetallic nanoparticles are generally used as catalysts for such kind of transformations [53-59]. In this line, and in continuation of our continued interests in development green synthetic methodologies [60-74] the catalytic activity of the recent fabricated superparamagnetic core-shell metal-organic framework (Fe_3O_4@Ni-Co-BTC NPs) [75] (Scheme 1) as bimetallic nanoparticles was tested in chemoselective reduction of nitro compounds to the corresponding amines (Scheme 2).



Scheme 1. The schematic pathway for the synthesis of the superparamagnetic core-shell metal-organic framework (Fe_3O_4@Ni-Co-BTC NPs) **(II)**



R = C_6H_5 , 2-$HOOCC_6H_4$, 3-$HOOCC_6H_4$, 4-$HOOCC_6H_4$, 4-$HOCC_6H_4$, 4-AcC_6H_4 , 4-NCC_6H_4 , 2-$O_2NC_6H_4$, 3-$O_2NC_6H_4$, 2-Cl 5-$O_2NC_6H_3$, 3-O_2N 5-$HOOCC_6H_3$, 4-IC_6H_4 ,3-Cl 4-$H_2NC_6H_3$, 3-NC 4-$H_2NC_6H_3$, 3-H_2N 4-HOC_6H_3 , 2-HOC_6H_4 , 4-HOC_6H_4 , 2-$H_2NC_6H_4$, 4-$H_2NC_6H_4$, 4-$AcHNC_6H_4$, 2-$H_3COC_6H_4$, 4-$AcOC_6H_4$,4-$H_3CC_6H_4$, 4-$HOH_2CC_6H_4$,4-$BrH_2CC_6H_4$, 4-$ClH_2CC_6H_4$, 1-Naphthyl , 2-Chloro 4-Amine 6-Methyl Pyrimidine , Cyclohexyl

Scheme 2. Reduction of different nitro compounds catalyzed by Fe_3O_4@Ni-Co-BTC NPs

Experimental

General

All chemical reagents and solvents were purchased from Merck chemical company and were used as received without further purification. The progress of the reactions was accomplished by thin layer chromatography on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization, in m/z (rel %). The NMR spectra were recorded on a 400 MHz Bruker Avance instrument in acetone-d_6 or $CDCl_3$. The superparamagnetic core-shell metal-organic framework (Fe_3O_4@Ni-Co-BTC NPs) were prepared using a method previously reported in the literature.[76] All yields refer to the isolated products after purification by recrystallization or short column chromatography.

Typical procedure for reduction of nitrobenzene to aniline in the presence of Fe_3O_4@Ni-Co-BTC NPs

In a round-bottomed flask (10 ml) equipped with magnetic stirrer, nitrobenzene (1 mmol, 0.123 g), EtOH/ H_2O (1/1 v/v, 4 mL) and Fe_3O_4@Ni-Co-BTC NPs (0.008 g, 2.56 mol% Ni: 1.25 mol% Co) were added successively. To the resulting mixture, $NaBH_4$ (5 mmol, 0.189g) as a fine powder was added slowly at room temperature and a fine black precipitate was immediately deposited. The mixture continued to be stirred for 15 min and the progress of the reaction was monitored by TLC (eluent; EtOAc/*n*-hexane: 1/2). After completion of the reaction, Fe_3O_4@Ni-Co-BTC NPs was recovered with an external magnet, and washed with EtOAc and water three times and dried in an oven at 60 ˚C overnight. Thereafter, distilled water (5 mL) was added to the reaction mixture and the mixture stirred for 10 min. Then the reaction mixture was extracted with EtOAc (3 × 5 ml) and dried over Na_2SO_4. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel (eluent; EtOAc/*n*-hexane: 1/2) gave the pure liquid aniline (0.088 g, 95 %).

Results and Discussion

Nowadays, the large amount of "auxiliary waste" in most chemical processes focused attention on green chemistry. Industries have also begun to use green chemistry by using environmentally benign reagents and conditions such as new heterogeneous catalysts and less toxic solvents (aqueous solvents), which often lead to clean and eco-friendly protocols and waste prevention through the simplified workups and offsetting the costs [76-81]. In accordance with specified strategies, the catalytic performance of the Fe_3O_4@Ni-Co-BTC NPs (**II**) in reduction of nitro compounds has been systematically investigated by performing the reduction of nitrobenzene as a model compound with $NaBH_4$ under different reaction conditions. The results are presented in Table 1. To carry out any study, the role of each element involved in the process should be evaluated. In order to elucidate the role of either $NaBH_4$ or Fe_3O_4@Ni-Co-BTC NPs (**II**), a set of control reactions was set up at room temperature. (Table 1, entries 1-2) Observation of the results showed that no reasonable yield of aniline was obtained in the absence of $NaBH_4$ and Fe_3O_4@Ni-Co-BTC NPs (**II**). (Table 1, entry 1) Also, the reaction is not carried out in the presence of $NaBH_4$ alone or Fe_3O_4@Ni-Co-BTC NPs (**II**) alone even after prolonged reaction time. (Table 1, entry 2,3) However, the influence of Fe_3O_4@Ni-Co-BTC NPs (**II**) as catalyst on reducing capability of $NaBH_4$ was noteworthy. (Table 1, entry 4) Then, we optimized the reaction conditions using various molar ratios of $NaBH_4$ as well as testing different catalyst loading at room temperature. Primarily, H_2O was used as an ecologically safe and easily available solvent. With respect to the importance of green chemistry legislations and to improve the product yield as well as the reaction rate, the model reaction was conducted in EtOH and different binary mixtures of H_2O and EtOH. (Table 1, entries 5-10) After careful investigations, it was observed that, the reaction proceeded more efficiently in H_2O: EtOH (1:1) than the other media. Having found the best solvent, we address next optimization in terms of the molar ratios of $NaBH_4$ as reducing agent. (Table 1, entries 11-14) As seen from Table 1, 5 equivalents of $NaBH_4$ is required to accelerate the reduction. As the reaction does not proceed in the absence of $NaBH_4$ (Table 1, entry 3), the released hydrogen from $NaBH_4$ during the catalytic process immediately utilized for reduction of starting material and additional amounts get liberated to the atmosphere. Next, we have studied the effect of catalyst loading on the product yield and reaction rate as well. (Table 1, entries 15,16) It was shown that the reaction rate was dramatically slowed down with decrease of catalyst loading while additional amounts of Fe_3O_4@Ni-Co-BTC NPs (**II**) does not have any influence on product yield. Finally, to confirm the superior catalytic performance of Fe_3O_4@Ni-Co-BTC NPs (**II**), the model reaction was performed in the presence of Fe_3O_4@MAA NPs (**I**), Fe_3O_4@Ni-BTC NPs and Fe_3O_4@Co-BTC NPs under the optimized reaction conditions. (Table 1, entries 17-19) No reduction was happened after reacting for 24 h using Fe_3O_4@MAA NPs (**I**). Comparatively, the reaction in the presence of Fe_3O_4@Ni-BTC NPs and Fe_3O_4@Co-BTC NPs was sluggish and no reasonable yield of aniline was afforded. Therefore, it can be concluded that the strong synergistic effect between Co and Ni is decisive in the reduction of the nitro group.

Table 1. Preliminary catalytic tests for the reduction of nitrobenzene to aniline with $NaBH_4$/ Fe_3O_4@Ni-Co-BTC NPs (**II**) system.

$$R{-}NO_2 \longrightarrow R{-}NH_2$$

Entry	Catalyst (mol% of Ni:Co)	Molar ratio of Nitrobenzene/$NaBH_4$	Solvent	Time (h)	Isolated Yield (%)
1	-	1/0	H_2O	24	0
2	-	1/2	H_2O	24	0
3	2.56 : 1.25	1/0	H_2O	24	0
4	2.56 : 1.25	1/2	H_2O	3/24	35/35
5	2.56 : 1.25	1/2	EtOH	3/24	35/35
6	2.56 : 1.25	1/2	H_2O : EtOH (1:1)	1.5	50
7	2.56 : 1.25	1/2	H_2O : EtOH (2:1)	1.5	20

8	2.56 : 1.25	1/2	H_2O : EtOH (1:2)	1.5	40
9	2.56 : 1.25	1/2	H_2O : EtOH (1:3)	1.5	20
10	2.56 : 1.25	1/2	H_2O : EtOH (1:4)	1.5	15
11	2.56 : 1.25	1/3	H_2O : EtOH (1:1)	1	60
12	2.56 : 1.25	1/4	H_2O : EtOH (1:1)	40 (min)	70
13	**2.56 : 1.25**	**1/5**	**H_2O : EtOH (1:1)**	**15 (min)**	**>95**
14	2.56 : 1.25	1/6	H_2O : EtOH (1:1)	15 (min)	>95
15	2.24 : 1.04	1/5	H_2O : EtOH (1:1)	60 (min)	80
16	2.88 : 1.34	1/5	H_2O : EtOH (1:1)	15 (min)	>95
17[a]	0.009 (g)	1/5	H_2O : EtOH (1:1)	24	0
18[b]	2.56	1/5	H_2O : EtOH (1:1)	6	50
19[c]	1.25	1/5	H_2O : EtOH (1:1)	6	45

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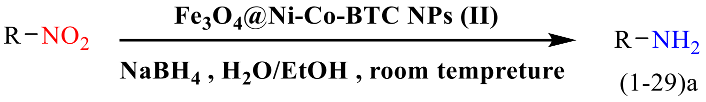
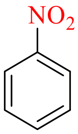
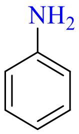
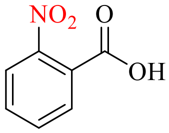
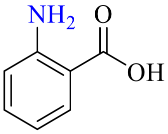
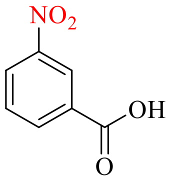
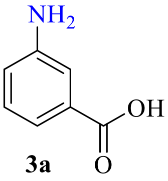
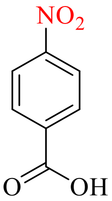
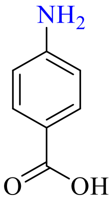
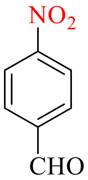
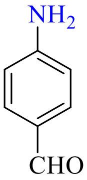
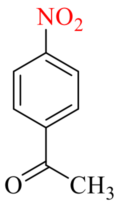
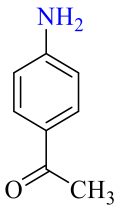
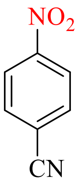
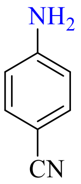
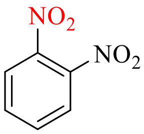
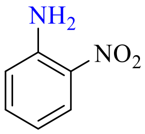
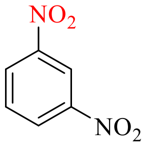
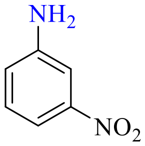
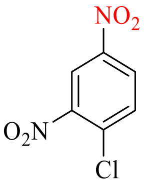
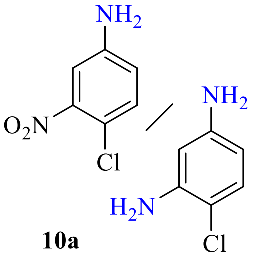
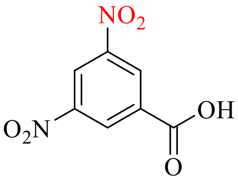
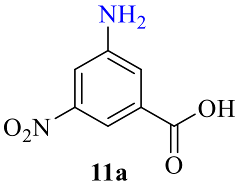
[a] The reaction was performed in the presence of Fe_3O_4@MAA NPs (**I**). [b] The reaction was performed in the presence of Fe_3O_4@Ni-BTC NPs. [c] The reaction was performed in the presence of Fe_3O_4@Co-BTC NPs.

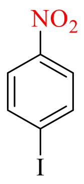
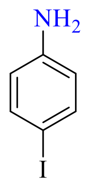
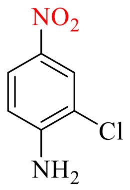
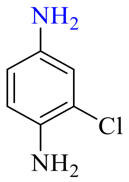
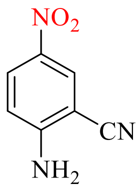
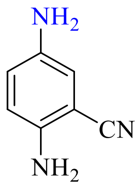
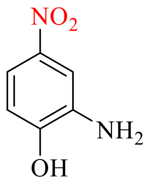
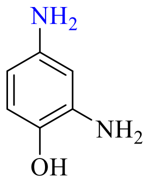
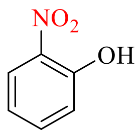
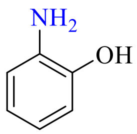
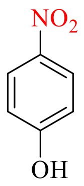
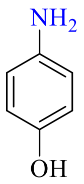
Next, synthetic utility of $NaBH_4$/ Fe_3O_4@Ni-Co-BTC NPs (**II**) system was further studied by reduction of structurally different nitro compounds to corresponding amines. Table 2 summarizes the results of this investigation. As it is seen, (Table 2) all reactions were carried out successfully in H_2O /EtOH (1/1) using 5 molar equivalents of $NaBH_4$ at room temperature. The corresponding amines were obtained in high to excellent yields within 5-40 min. The catalytic system has ability to successfully convert nitro aromatic compounds containing electron-withdrawing or electron-releasing groups as substituents to their corresponding amines. Electron-donating groups as well as electron-withdrawing groups did not have a significant influence on the reaction rate and all the nitro aromatic compounds were reduced rapidly in excellent yields under the optimized conditions. $NaBH_4$/ Fe_3O_4@Ni-Co-BTC NPs (**II**) system catalyzed chemoselective reduction of nitro aromatic compounds with COOH, CHO, $COCH_3$, CN, NHAc and $OCOCH_3$ functionalities and the corresponding amines were obtained in the range of 75-95% depending on the position of the functional group with respect to NO_2 group to be reduced. (Table 2, entries 2-7, 11, 14, 20 and 22) It means that the current protocol reduces nitro groups in high reactivity and chemoselectivity versus COOH, CHO, $COCH_3$, CN, NHAc and $OCOCH_3$ functionality. The catalytic system was found to be effective for reduction of nitro aromatic compounds having Cl, I, OH, NH_2, OCH_3 and CH_3 functionalities and the corresponding amines were successfully obtained with good to excellent yields. (Table 2, entries 10, 12-19, 21 and 23) Comparatively, the catalytic reduction of *ortho*-substituted nitro aromatic compounds (COOH, NO_2, OH and NH_2) was sluggish than that of *meta* or *para* isomers or gave relatively lower yield under similar reaction conditions, which may be attributed to steric hindrance or intra-molecular hydrogen bonding among NO_2 and the other groups which are close to each other on the benzene ring. (Table 2, entry 2 *vs* entries 3,4, entry 8 *vs* entry 9, entry 16 *vs* entry 17 and entry 18 *vs* entry19) A more examination exhibited that the present method was also efficient for reduction of dinitro compounds using 10 molar equivalents of $NaBH_4$ in the presence of Fe_3O_4@Ni-Co-BTC NPs (**II**). (Table 2, entry10) The protocol also tolerates nitro aromatic compounds with other functional groups (CH_2OH, CH_2Cl and CH_2Br) and other aromatic, heteroaromatic and heterocyclic nitro compounds under the optimized reaction conditions. (Table 2, entries 24-28) It was found that the reactions were completed smoothly within 15-35 min with excellent yields of corresponding amines. The reducing capability of $NaBH_4$/ Fe_3O_4@Ni-Co-BTC NPs (**II**) system toward reduction of aliphatic nitro compounds was also studied by the reduction of nitrocyclohexane. The result showed that, as nitro aromatic compounds, aliphatic nitro compound is compatible with the applied conditions and the corresponding aliphatic amine was obtained successfully. (Table 2, entries 29)

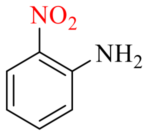
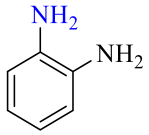
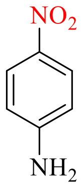
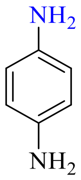
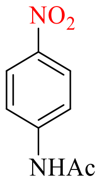
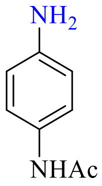
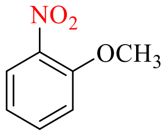
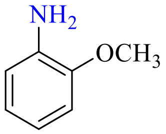
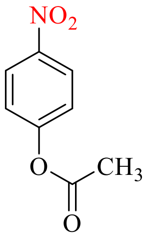
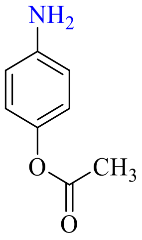
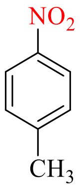
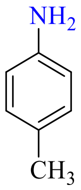
Table 2. Reduction of nitro compounds with $NaBH_4$/ Fe_3O_4@Ni-Co-BTC NPs (**II**) system

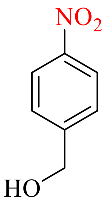
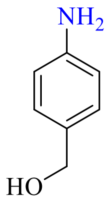
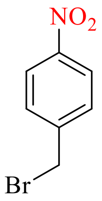
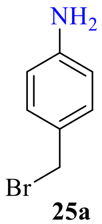
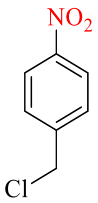
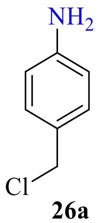
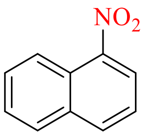
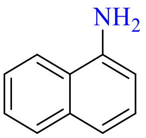
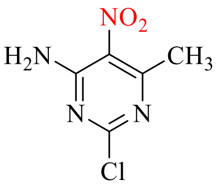
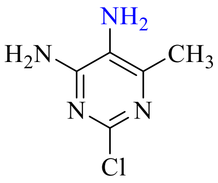
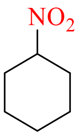
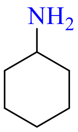


Entry	Nitro compound	Product	Time (min)	Isolated yield (%)
1		 **1a**	15	95
2		 **2a**	15	75
3		 **3a**	15	85
4		 **4a**	10	95
5		 **5a**	15	75

6		 **6a**	15	80
7		 **7a**	5	95
8		 **8a**	12	70
9		 **9a**	15	95
10		 **10a**	15/17	85/90
11		 **11a**	10	95

12		 **12a**	15	75
13		 **13a**	20	90
14		 **14a**	18	85
15		 **15a**	30	80
16		 **16a**	40	95
17		 **17a**	30	95

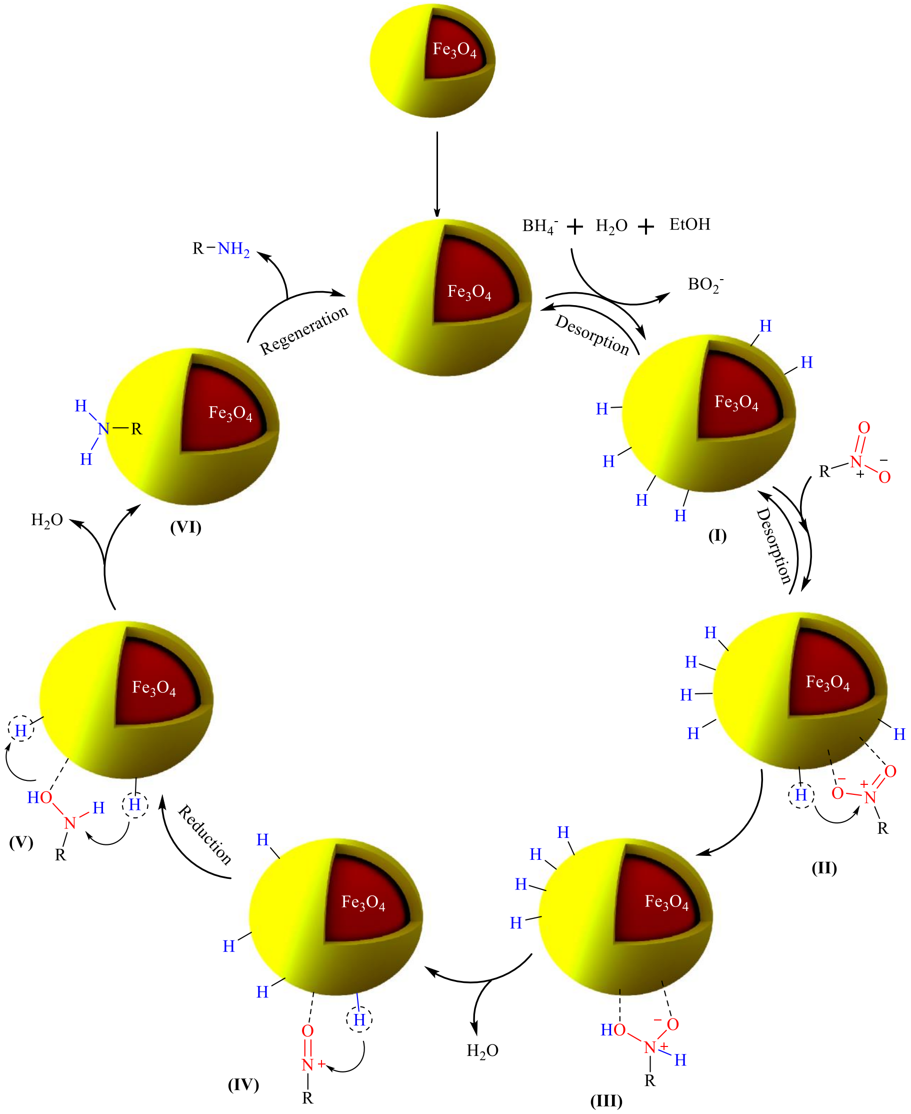
18		 **18a**	35	90
19		 **19a**	25	95
20		 **20a**	20	95
21		 **21a**	20	75
22		 **22a**	15	90
23		 **23a**	30	85

24		 **24a**	35	90
25		 **25a**	18	90
26		 **26a**	20	90
27		 **27a**	15	90
28		 **28a**	15	95
29		 **29a**	20	95

The product of each catalytic reaction was separated, purified and characterized by investigation on their FT-IR spectrum or comparison of their melting points with those reported in the literature. Additionally, the structures of some selected compounds (2a ,4a , 7a ,9a ,17a ,18a ,19a ,20a ,23a

,28a) were further recognized by ^{1}HNMR, ^{13}CNMR and mass spectrometry. The common spectral feature of all prepared amines is the presence of amino group in the FT-IR spectra. Two sharp absorption bands at 3477-3219 and 3387-3009 cm^{-1} correspond to -NH_2 functional group due to N-H *str*. vibrations (asymmetric and symmetric). The characteristic absorption bands at 1274-1160 cm^{-1}established the presence of C-N bond of primary amine. In the ^{1}H NMR spectra, a broad resonating signal in the range of δ 3 to 4.24 attributed to two hydrogens of -NH_2 group. (see "Supporting Information" file)

Although further exploration is required to understand the mechanism details, however, based on the previous reported in literature [82, 83], a possible mechanism is depicted in Scheme 3. It is postulated that electron transfer from BH_4^- (in $NaBH_4$) to nitro compound is responsible to start this reaction. According to the proposed mechanism, it is expected that adsorbing the borohydride ions on the surface of Fe_3O_4@Ni-Co-BTC NPs can transfer a hydride ion to the surface of the catalyst, resulting in the formation of intermediate **I**. Simultaneously, due to the existence of positive sites on the surface of the catalyst (Ni^{2+} and Co^{2+}), nitro reactant can be easily adsorbed on the positively charged sites of Fe_3O_4@Ni-Co-BTC NPs (which leads to formation of intermediate **II**). In the following step, the adsorbed nitro group uptake hydrogen from the surface of the catalyst which leads to the formation of nitroso compound (intermediate **IV**). Eventually, the desired product was obtained through a reduction step along with a hydro deoxygenation process which regenerated the free surface of the catalyst for repeating this process. (Scheme 3)



Scheme 3. Proposed mechanism for the reduction of nitro compounds in the presence of Fe_3O_4@Ni-Co-BTC NPs.

A very important and significant aspect of heterogeneous catalyst in green catalytic process is its easy recovery from the reaction mixture and reusability for subsequent reactions until the catalyst is deactivated. The recoverability and reusability of the Fe_3O_4@Ni-Co-BTC NPs (**II**) in reduction of nitrobenzene to aniline were investigated under one constant set of operating conditions (nitrobenzene/ $NaBH_4$: 1/5, room temperature, time: 15 min). After each experimental run, Fe_3O_4@Ni-Co-BTC NPs (**II**) was recovered with an external magnet, and washed with EtOAc and water three times followed by drying in an oven at 60 ˚C overnight. Then, the catalyst was directly transferred to fresh reaction mixture for the next run. Figure 1 shows that similar results were obtained after the first, second, third and fourth runs in the presence of Fe_3O_4@Ni-Co-BTC NPs (**II**) and then the catalytic activity was dropped in fifth, sixth and seventh runs yielding 93% (91%), 92% (90%) and 90% (88%) conversions (isolated yields). These results confirmed the reliability and practicality of this method. Moreover, the recovered catalyst was further examined by FT-IR spectroscopy. Results clearly showed no obvious changes in intensities, frequencies and shapes of absorption bands. (Figure 2)

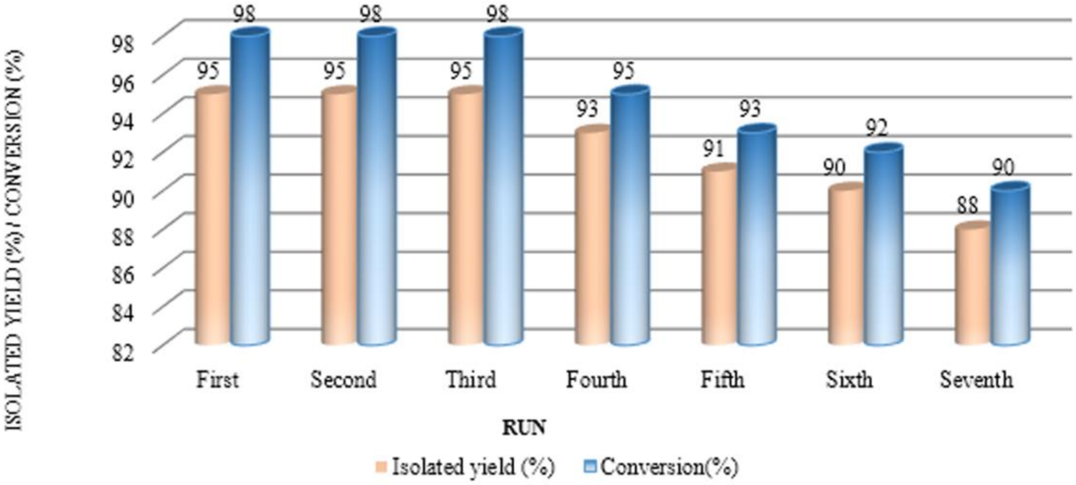


Figure 1. Reduction of nitrobenzene to aniline in the presence of reused Fe_3O_4@Ni-Co-BTC NPs (**II**)

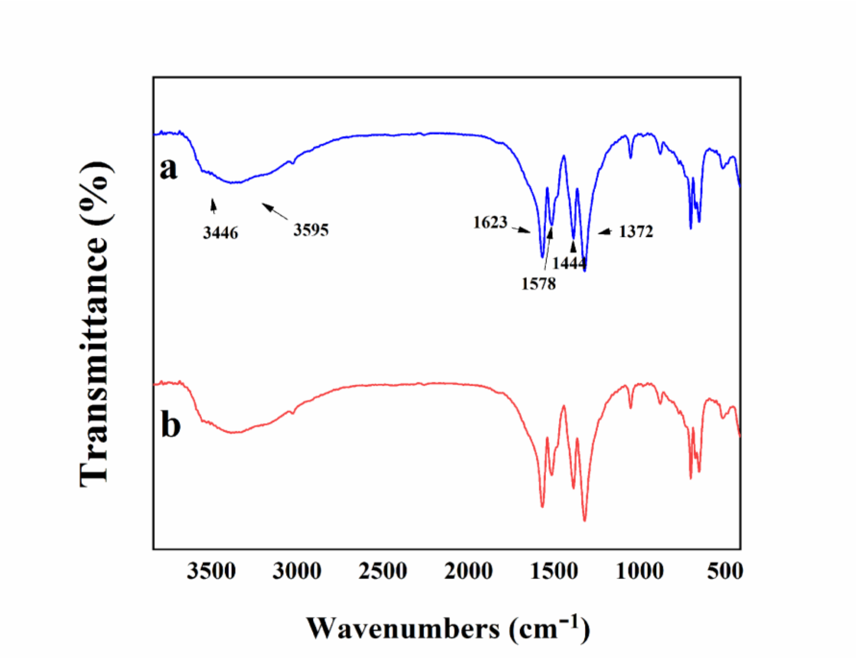


Figure 2. FT-IR spectra of (a) fresh Fe_3O_4@Ni-Co-BTC NPs (**II**) and (b) 7th reused Fe_3O_4@Ni-Co-BTC NPs (**II**)

To show the value, efficacy, and capability of the present protocol for the reduction of nitro compounds to the corresponding amines, the catalytic performance of Fe_3O_4@Ni-Co-BTC NPs (**II**) was compared with some previously reported methodologies. Results are summarized in Table 3 [84-92]. By considering the merits of the other catalysts it is worth noting that some of them require heating of the reaction medium (Table 3, entries 1-2 and 5-9) with using costly and high price catalyst. (Table 3, entries 1, 3, 4 and 6) More importantly, compared with other catalysts, Fe_3O_4@Ni-Co-BTC NPs (**II**) can be easily separated from the reaction mixture by means of a magnetic bar (Table 3, compare with entries 3-9) and reused at least seven times without any significant loss of its catalytic activity as well. (Table 3, entries 2, 4 and 5) Noticeably, using environmentally friendly solvent (Table 3, entries 3 and 9) and reducing agent, (Table 3, entries 5-9) and simple workup procedure are another merits of this nanostructured catalyst in reduction of nitro compound.

Table 3. Comparison of results for reduction of nitrobenzene to aniline by Fe_3O_4@Ni-Co-BTC NPs (**II**) with other reported catalysts.

Entry	Catalyst (mol %)	Solvent	Reductant	Temperature (°C)	Time (min)	Isolated Yield (%)	Reusability	Ref
1		H_2O	$NaBH_4$	80	30	98	5	84

	γ-Fe_2O_3@HAp-CD.Ag (0.09 mol% Ag)							
2	Cu-BTC@Fe_3O_4 (15 mg)	EtOH/ H_2O (3/1)	$NaBH_4$	45	3 (h)	99	-	85
3	Pd-GHJ[a] (15 mg)	H_2O/MeOH (7/3)	H_3NBH_3	RT	20	99	5	86
4	Ruthenium(II)-NNN pincer complexes[b] (18 mg)	EtOH	$NaBH_4$	RT	30	95	-	87
5	Ni-Co BMNPs[c] (0.4 mmol%)	EtOH	$N_2H_4.H_2O$	80	1(h)	99	-	88
6	Pd/NH_2-UiO-66 (0.7 mol%)	H_2O	HCOOH	60	7 (h)	99	5	89
7	Co_3O_4@Al_2O_3/SiO_2 (2 mol%)	EtOH	$N_2H_4.H_2O$	60	2 (h)	98	8	90
8	Co@ZDC@mC-700[d] (10 mg)	EtOH	$N_2H_4.H_2O$	80	10	100	6	91
9	Co@NPC-800[e] (4.8 mol% Co)	THF/H_2O (4.5/0.5)	$HCOONH_4$	120	12 (h)	100	6	92
10	Fe_3O_4@Ni-Co-BTC NPs (**II**) (2.56:1.25 mol% Ni:Co)	H_2O/EtOH (1/1)	$NaBH_4$	RT	15	95	7	present study

[a] Graphene hydrogel. [b] Ruthenium(II)-NNN pincer complexes RuL(L = 2,6-bis(morpholinomethyl)pyridine, 2,6-bis((piperazin-1-yl)methyl)pyridine, 2,6-bis((4-methylpiperazin-1-yl)methyl)pyridine and 2,6-bis(piperidin-1-ylmethyl)pyridine). [c] Bimetallic. [d] ZIF-67-derived carbon mesoporous carbon. [e] N,P-codoped carbon.

Conclusion

In this manuscript, we report a chemoselective, efficient, eco-friendly and base-free procedure for the reduction of nitro compounds in the presence of a heterogeneous bimetallic nanocatalyst. Structurally different nitro compounds (including electron-deficient and electron-rich aromatic, heteroaromatic and aliphatic nitro compounds) effectively reduced to their corresponding amines using this catalytic system in high yields. In the catalytic reaction, $NaBH_4$ was used as an electron and hydrogen source in green media at room temperature. Furthermore, it should be mention that the presence of any additives or promoters not necessary for the progress of this reaction. Moreover, based on the obtained results, we conclude that the bimetallic nature of Fe_3O_4@Ni-Co-BTC NPs gave good results compared to monometallic ones. This method has many advantages such as chemoselectivity (reduction of the nitro group in the presence of other reducible functional groups such as COOH, CHO, $COCH_3$, CN, NHAc and $OCOCH_3$), high yield of products, green solvent, fast and clean reaction process, easy work-up of products according to magnetically separation of catalyst. These features make the presented method superior to most of the reported strategy from the green chemistry point of view. Also, it is worth noting that this heterogeneous nanocatalyst could be used repetitively at least up to 7 times without a discernible decrease in its catalytic activity.

Acknowledgements

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