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ORIGINAL PAPER

Magnetically nano core–shell Fe_3O_4@$Cu(OH)_x$: a highly efficient and reusable catalyst for rapid and green reduction of nitro compounds

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Abstract Magnetically separable nano core–shell Fe_3O_4@$Cu(OH)_x$ with 22 % Cu content was prepared by the addition of sodium hydroxide to a mixture of $CuCl_2{\cdot}2H_2O$ and nano Fe_3O_4 in water. Characterization of the impregnated copper hydroxide was carried out by X-ray fluorescence (XRF), X-ray diffraction (XRD) atomic absorption spectroscopy (AAS), scanning electron microscopy (SEM), value stream mapping (VSM) and Brunauer–Emmett–Teller (BET) analysis. The core–shell nanocatalyst exhibited the excellent catalytic activity toward reduction of various nitro compounds to the corresponding amines with $NaBH_4$. All reactions were carried out in H_2O (55–60 °C) within 3–15 min to afford amines in high to excellent yields. Reusability of core–shell $Cu(OH)_x$ catalyst was examined 9 times without significant loss of its catalytic activity.

Keywords Amine · Fe_3O_4@$Cu(OH)_x$ · $NaBH_4$ · Nanomagnetic · Nitro · Reduction

Introduction

Heterogeneous catalysis has become a sustainable and powerful tool for a great variety of organic transformations [1–6]. In homogeneous catalysis, however, the reagents/catalysts are often expensive and difficult to easily remove from the mixture of reactions. Therefore, their applications encounter with some rustications in academic and industrial purposes. Metal oxides [7], zeolites [8], hydrotalcites [9] ion-exchange resins [10], solid supports [11] and polyoxometalates [12–14] are the kinds of heterogeneous catalysts which are commonly used for functional group transformations.

Recently, the design and synthesis of core–shell nanoparticles, because of their potential abilities to catalyze organic reactions, has more attracted [15, 16]. The core–shell composites containing the core of Fe_3O_4 are robust and air-stable, and they can be separated by an external magnet leading to avoid traditional filtration processes [17]. It has also demonstrated that nanostructural iron catalysts are close in catalytic activity to the corresponding homogeneous catalysts. A literature review shows that impregnation of different metallic salts such as TiO_2 [18], MnO_2 [19], $Fe(OH)_3$ [20], $Co(NO_3)_2$ [21], $Cu(OH)_x$ [22, 23], $Ru(OH)_x$ [24], Pd [25, 26], Pt [27] and Rh(III)-metalloporphyrin [28] has been carried out on nanomagnetic Fe_3O_4. However, their applications in organic synthesis have quite limited.

Reduction of nitroarenes to arylamines is one of the most important organic transformations, since arylamines are versatile intermediates and precursors in the preparation of dyes, pharmaceuticals, pigments, agrochemicals and polymers [29–32]. This process is complicated when the reduction of nitro group leads to the formation of hydroxylamine or hydrazine as a side product [33, 34]. Therefore, a complete reduction of nitro group to amine is a subject of interest and various reducing agents and protocols have been introduced for this achievement [35–38]. It is known that the alone $NaBH_4$ does not reduce nitro compounds under ordinary conditions. However, the reducing power of this reagent undergoes a drastic change toward the reduction of nitro groups by a combination with metal halides or salts [39]. Although most of the reported protocols are

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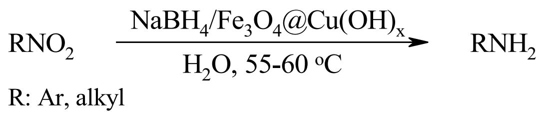


$$RNO_2 \xrightarrow[H_2O,\ 55\text{-}60\ ^{o}C]{NaBH_4/Fe_3O_4@Cu(OH)_x} RNH_2$$

Scheme 1 Reduction of nitro compounds with $NaBH_4$/nano $Fe_3O_4@Cu(OH)_x$ system

efficient and provide a useful synthetic method, however, they generally suffers from the prolonged reaction times, using expensive organic solvents, formation of side products and inability to reuse the applied catalyst.

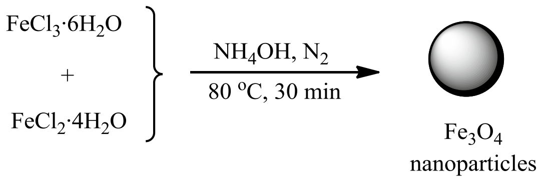
In line with the outlined strategies, herein, we wish to introduce nanomagnetic core–shell $Fe_3O_4@Cu(OH)_x$ with 22 % Cu content as a highly efficient and reusable catalyst for $NaBH_4$ reduction of nitro compounds to amines in water as an easily available and eco-friendly safe solvent (Scheme 1).

Results and discussions

Synthesis and characterizations of nano core–shell iron oxide@copper hydroxide

Nowadays, nanoparticles (NPs) exhibit high catalytic activity and chemical selectivity under mild conditions. The extreme small-sized particles maximize the surface area and allow more reactions to occur at the same time. In this context, nanomagnetic Fe_3O_4 due to nanosized particles, high reactivity, magnetic specification and reusability has been found in some useful applications in organic synthesis [17]. The literature review shows that though the synthesis and application of impregnated copper hydroxide, $Cu(OH)_x$, on nanomagnetic Fe_3O_4 with 1.37–1.62 % Cu content have been reported for addition of alkoxy diboranes to alkenes [22] and preparation of propargylamines [23], however, synthesis of this type of nanocatalyst with 22 % Cu content as well as its application in organic transformations has not been investigated yet. These subjects and continuation of our research program directed to $NaBH_4$ reduction of nitro compounds to amines [39–44] prompted us to prepare nano core–shell $Fe_3O_4@Cu(OH)_x$ with 22 % Cu content. In addition, we encouraged to investigate the catalytic activity and reusability of the prepared NPs to the titled transformation under green reaction conditions.

Synthesis of $Fe_3O_4@Cu(OH)_x$ NPs with 22 % Cu content was carried out in a two step procedure: 1) preparation of nanomagnetic Fe_3O_4 by a chemical co-precipitation of $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ in aqueous ammonia (Scheme 2) and 2) addition of nano Fe_3O_4 to aqueous solution of $CuCl_2 \cdot 2H_2O$ followed by alkali-making (pH ~ 13) the resulting suspension with NaOH (Scheme 3).

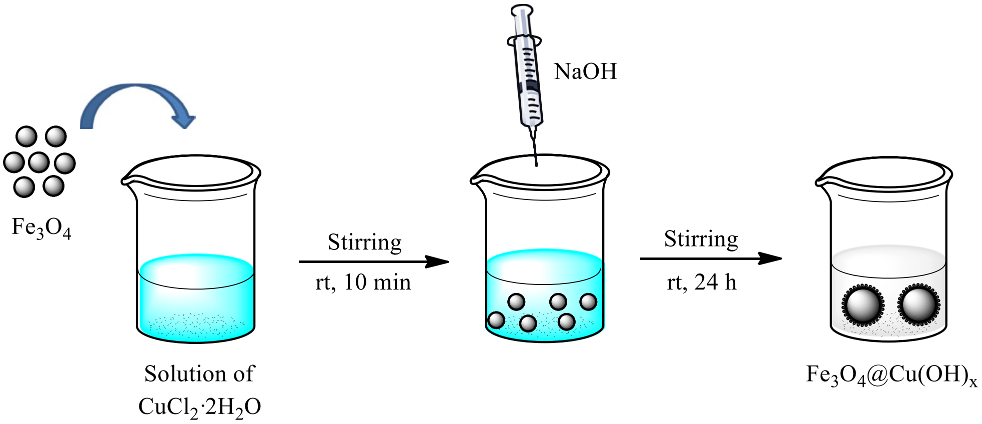


Scheme 2 Synthesis of nanomagnetic Fe_3O_4

The morphology and size distribution of the prepared core–shell $Fe_3O_4@Cu(OH)_x$ was then investigated by scanning electron microscopy. The SEM image indicates that the catalyst is as granule nanoparticles with the size distribution ranged from 13 to 30 nm. The SEM approved the nanostructure of the catalyst. The particles are agglomerated to some extent (Fig. 1).

The composition percentage of Cu in nano $Fe_3O_4@Cu(OH)_x$ NPs was then determined by atomic absorption (AAS) and X-ray fluorescence (XRF) analyses. Both techniques exhibited that the Cu content in nanocatalyst was 22 %. Characterization of the core–shell nanocatalyst was more carried out by X-ray diffraction (XRD) analysis. The XRD patterns of superparamagnetic Fe_3O_4 and $Fe_3O_4@Cu(OH)_x$ NPs are shown in Fig. 2. In XRD pattern of Fe_3O_4, the peaks at 30.2°, 35.5°, 43.3°, 53.7°, 57.2° and 62.9° are attributed to the (220), (311), (400), (422), (511) and (440) crystal planes of a pure Fe_3O_4 with a spinal structure (JCPDS card no. 65-3107) [45, 46]. These peaks are corresponded to a cubic unit cell, characteristic of a cubic spinel structure. In the case of XRD pattern of $Fe_3O_4@Cu(OH)_2$, all the peaks of Fe_3O_4 are observed. The peaks at 16.5°, 23.6°, 34°, 38°, 39.6°, 54.1°, 62.9°, 63.5°, 67.3° and 72.4° are corresponded to orthorhombic copper hydroxide which is in good agreement with standard card of JCPDS No. (35-0505) [47]. The peaks at 35.8° and 53.06° for copper hydroxide overlap with the 35.5° and 53.7° peaks of Fe_3O_4.

The plots of magnetization versus applied magnetic field (VSM) for Fe_3O_4 and $Fe_3O_4@Cu(OH)_x$ NPs were also illustrated in Fig. 3. The plots show that these two kind of nanoparticles exhibited superparamagnetism and no obvious remanence or coercivity was recorded when the applied magnetic field was removed. The magnetization saturation (MS) values of Fe_3O_4 and $Fe_3O_4@Cu(OH)_x$ were 66.976 and 39.891 emu g^{-1}, respectively. The high magnetization represents the fast responsivity of the nanocatalysts in the magnetic separation. After the coating process, the Ms value of the nano Fe_3O_4 was reduced clearly which indicates the coating of copper hydroxide layer. By comparing the Ms values before and after coating of $Cu(OH)_x$, the Cu content in nano $Fe_3O_4@Cu(OH)_x$ was estimated to be 27 % [48].



Scheme 3 Synthesis of nanomagnetic $Fe_3O_4@Cu(OH)_x$

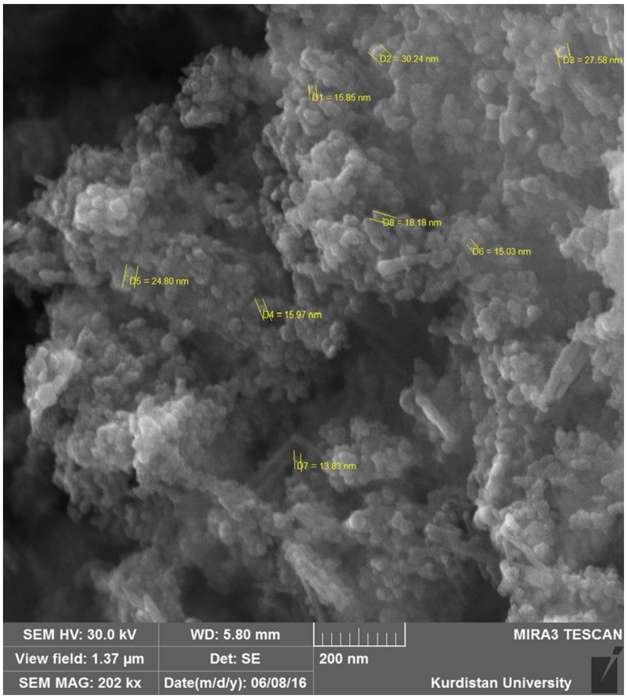


Fig. 1 SEM image of nano $Fe_3O_4@Cu(OH)_x$

Brunauer–Emmett–Teller (BET)

Nitrogen sorption was used to study the pore properties of the synthesized microspheres. The calculated specific surface area using the BET for $Fe_3O_4@Cu(OH)_x$ NPs was 68.059 $m^2\ g^{-1}$. The pore volume was 0.349 $cm^3\ g^{-1}$ (Fig. 4). The corresponding pore size distributions of the nanocatalyst were determined to be 20.559 nm using the Barrett–Joyner–Halenda (BJH), indicating that nano $Fe_3O_4@Cu(OH)_x$ is mesoporous ($2 < D_v < 50$ nm).

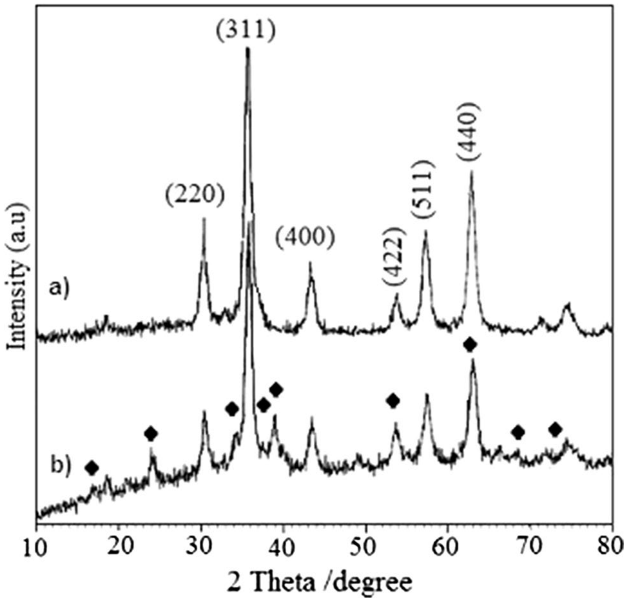


Fig. 2 XRD patterns of *a* Fe_3O_4 and *b* $Fe_3O_4@Cu(OH)_x$ NPs

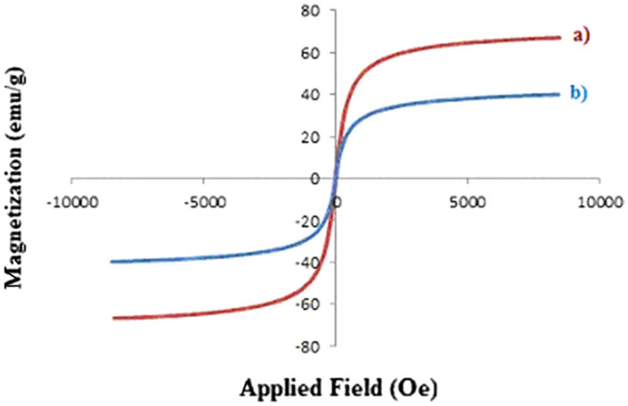


Fig. 3 Hysteresis loops of nano *a* Fe_3O_4 and *b* $Fe_3O_4@Cu(OH)_x$

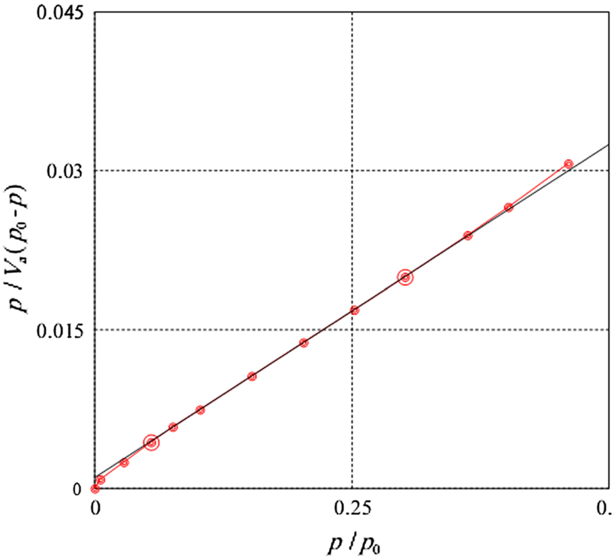


Fig. 4 BET-plot for Fe_3O_4@$Cu(OH)_x$ NPs (adsorption temperature 77 [K])

Reduction of nitro compounds with $NaBH_4$/Nano Fe_3O_4@$Cu(OH)_x$ system

After synthesis and characterization of Fe_3O_4@$Cu(OH)_x$ NPs, we turned our attention to study the influence of nanocatalyst on reducing capability of $NaBH_4$ toward the reduction of nitro compounds. In order to optimize reaction conditions, reduction of nitrobenzene with $NaBH_4$ as a model reaction was examined under different reaction conditions.

The illustrated results in Table 1 shows that reduction of nitrobenzene with $NaBH_4$ in the presence of Fe_3O_4@$Cu(OH)_x$ NPs in protic and aprotic solvents was not efficient. However, using H_2O as the sole solvent dramatically accelerated the rate of reduction (entries 3–5). These observations revealed that H_2O was the best solvent of choice, and the molar equivalents of 1:2:0.06 for $PhNO_2$, $NaBH_4$ and Fe_3O_4@$Cu(OH)_x$ were the requirements to complete reduction of nitrobenzene. Subsequently, aniline was obtained as a sole product within 3 min at 55–60 °C (Table 1, entry 5). The scope and generality of this synthetic protocol was then studied with the reduction of various aromatic nitro compounds at the optimized conditions (Table 2).

The summarized results in Table 2 show that reduction of nitroarenes having electron-releasing or withdrawing functionalities was carried out successfully using 2–3 molar equivalents of $NaBH_4$ and 6–15 mol % Fe_3O_4@$Cu(OH)_x$ within 3–12 min (H_2O, 55–60 °C) (entries 1–15). It is also noteworthy that in the case of nitroarenes containing formyl group, both of nitro and formyl groups were reduced with the same reactivity. Subsequently, higher molar equivalents of $NaBH_4$ and the nanocatalyst were required to complete reduction of nitroaldehydes to their amino alcohols (Table 2, entries 16–18). In the case of nitro compounds containing ketone functionality, a perfect chemoselectivity was observed when the controlled amounts of $NaBH_4$ were supplied in reduction reactions: with the molar equivalents of 2:0.2 for $NaBH_4$/nano Fe_3O_4@$Cu(OH)_x$, the reduction of nitro group was carried out in a perfect selectivity. However, the successful reduction of both functional groups can be obtained when four molar equivalents of $NaBH_4$ were used in reduction reactions (entries 19–22). It means that the current protocol reduces nitro groups in high reactivity and chemoselectivity versus ketone functionality. However, this chemoselectivity between nitro and formyl

Table 1 Optimization experiments for reduction of nitrobenzene to aniline with $NaBH_4$/nano Fe_3O_4@$Cu(OH)_x$ system under different conditions

Entry	$NaBH_4$ (mmol)	Fe_3O_4@$Cu(OH)_x$ (mmol)	Solvent (mL)	Condition	Time (min)	Conversion (%)
1	2	–	H_2O	55–60 °C	300	30
2	–	1	H_2O	55–60 °C	300	10
3	2	0.5	H_2O	rt	40	90
4	2	0.1	H_2O	55–60 °C	3	95
5	2	0.06	H_2O	55–60 °C	3	95
6	2	0.1	MeOH	Reflux	120	50
7	2	0.1	MeOH–H_2O	Reflux	120	75
8	2	0.1	EtOH	Reflux	120	50
9	2	0.1	EtOH–H_2O	Reflux	120	75
10	2	0.1	CH_3CN	Reflux	120	0
11	2	0.1	CH_3CN–H_2O	Reflux	120	50
12	2	0.1	THF	Reflux	120	50
13	2	0.1	THF–H_2O	Reflux	120	75

All reactions were carried out with 1 mmol of nitrobenzene in 3 mL solvent

Table 2 Reduction of nitro compounds with $NaBH_4$/nano Fe_3O_4@$Cu(OH)_x$ system

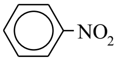
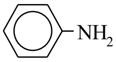
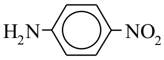
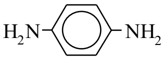
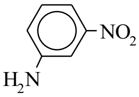
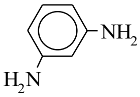
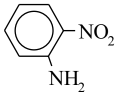
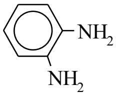
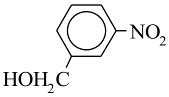
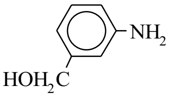
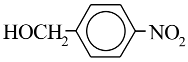
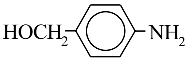
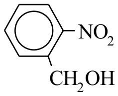
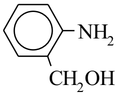
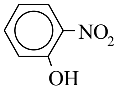
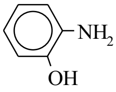
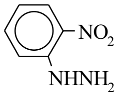
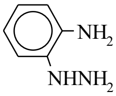
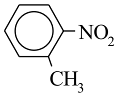
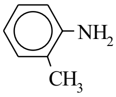
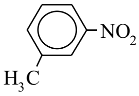
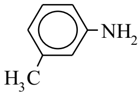
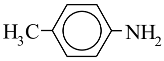
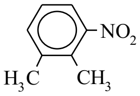
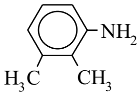
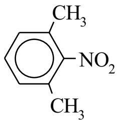
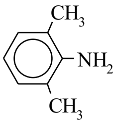
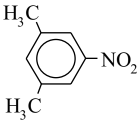
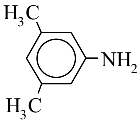
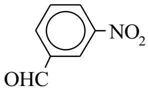
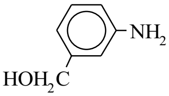
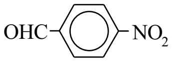
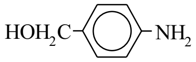
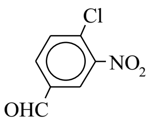
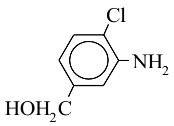
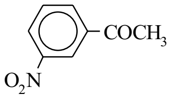
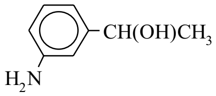
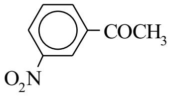
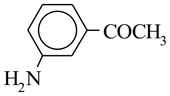
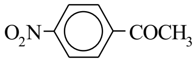
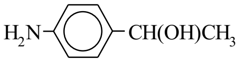
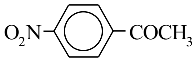
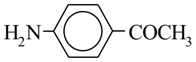
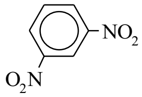
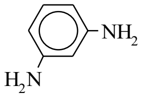
Entry	Substrate	Product	Molar ratio subs./$NaBH_4$/cat .	Time (min)	Yield (%)[a]
1			1:2:0.06	3	95
2			1:2:0.06	4	92
3			1:2:0.1	5	94
4			1:2:0.1	5	91
5			1:2:0.1	6	93
6			1:2:0.06	4	91
7			1:2:0.06	6	91
8			1:3:0.1	5	91
9			1:3:0.15	12	89
10			1:2:0.06	6	95
11			1:2:0.06	5	95
12			1:2:0.06	4	94
13			1:2:0.06	4	93
14			1:2:0.06	7	93
15			1:2:0.06	7	95
16			1:4:0.2	15	91

Table 2 continued

17			1:3.5:0.15	12	93
18			1:3.5:0.15	12	92
19			1:4:0.2	12	94
20			1:2:0.2	12	94
21			1:4:0.2	15	89
22			1:2:0.2	12	94
23			1:3.5:0.2	12	92
24	1-Nitrohexane	1-Hexylamine	1:2:0.2	8	89
25	2-Nitroheptane	2-Aminoheptane	1:2:0.2	8	91

All reactions were carried out in H_2O (3 mL, 55–60 °C)

[a] Yields refer to isolated pure products

functionality cannot accessible. A more examination exhibited that the present method was also efficient for reduction of dinitro compounds using the molar equivalents of 3.5:0.2 for $NaBH_4$/nano Fe_3O_4@Cu$(OH)_x$ system in H_2O (Table 2, entry 23).

The reducing capability of $NaBH_4$/nano Fe_3O_4@Cu$(OH)_x$ system toward reduction of aliphatic nitro compounds was also studied by the reduction of 1-nitrohexane and 2-nitroheptane with 2:0.02 molar equivalents of $NaBH_4$ and Fe_3O_4@Cu$(OH)_x$ NPs in H_2O at 55–60 °C. The results showed that as aromatic nitro compounds, this protocol was also efficient and the corresponding aliphatic amines were obtained successfully in 90–94 % yields within 10–15 min (Table 2, entries 24 and 25).

For practical purposes, the ability to easy recycle the catalyst is highly desirable. To investigate this issue, the reusability of Fe_3O_4@Cu$(OH)_x$ NPs was examined in $NaBH_4$ reduction of nitrobenzene. The obtained results exhibited that the nanocatalyst has remarkable reusability. After completion of the reaction, the nanocatalyst was separated from the reaction by an external magnet (Fig. 5). The core–shell nanocatalyst was then washed with diethyl ether to remove residual contaminants. The vessel of reaction was again charged with fresh nitrobenzene, $NaBH_4$ and water to run the reduction reaction for a second time. The examinations showed that the nanocatalyst can be reused severally without significant loss of its catalytic activity (Fig. 6).

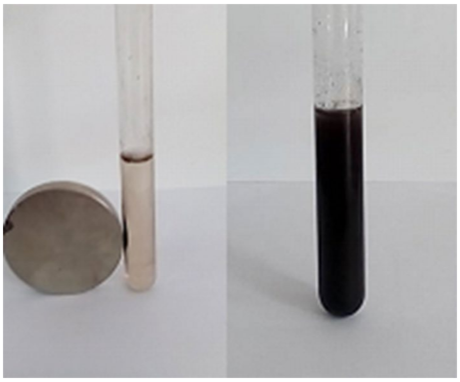


Fig. 5 Separation of Fe_3O_4@Cu$(OH)_x$ NPs by external magnet

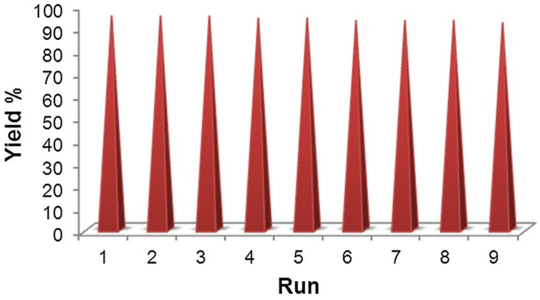


Fig. 6 Reduction of nitrobenzene with $NaBH_4$/recycled nano Fe_3O_4@$Cu(OH)_x$ system

Although we reused the nanocatalyst for nine reduction cycles, however, we believe that due to fantastic catalytic activity of the core–shell nanocatalyst, it can be reused for too much reduction cycles of nitrobenzene and consequently other nitro compounds.

The usefulness and capability of $NaBH_4$/nano Fe_3O_4@$Cu(OH)_x$ system in reduction of nitroarenes were highlighted by comparison of the obtained result for nitrobenzene with other reported systems (Table 3). A case study shows that in viewpoints of reusability of the nanocatalyst, amounts of reducing agent, reaction time and yield of the product, the present protocol shows a more or comparable efficiency than the other systems.

Conclusions

In this paper, the impregnation of copper hydroxide on nanomagnetic Fe_3O_4 with 22 % Cu content was carried out successfully. The prepared nano Fe_3O_4@$Cu(OH)_x$ was then characterized with XRD, XRF, AAS, VSM, SEM and BET analyses. The core–shell nanocatalyst exhibited the excellent catalytic activity and reusability in $NaBH_4$ reduction of various nitro compounds. All reactions were carried out in water (55–60 °C) within 3–15 min to afford amines in high to excellent yields. In addition, the nanocatalyst can be reused for nine catalytic cycles without significant loss of its catalytic activity. Remarkable reusability and easy separation of the nanocatalyst, high yields and mild reaction conditions as well as the benefits of using water as a green solvent are the advantages which make this protocol a perfect choice for reduction of nitro compounds.

Experimental

General

All reagents and substrates were purchased from commercial sources in high purity, and they were used without further purification. ^1H, ^{13}C NMR and FT-IR spectra were recorded on Bruker Avance 300 MHz and Thermo Nicolet Nexus 670 spectrometers. The products are known, and they were characterized by their ^1H, ^{13}C NMR and FT-IR spectra followed by comparison with authentic data. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F_{254} aluminum sheet. X-ray diffraction (XRD) measurements were performed with a X'PertPro. The X-ray wavelength was 1.54 Å, and the diffraction patterns were recorded in the 2θ range (10°–80°). The particle morphology was examined by measuring SEM using FESEM-TESCAN MIRA3. Magnetic properties of the samples were measured using a vibration sample magnetometer (VSM, model MDKFT) under magnetic fields up to 20 kOe. The N_2 adsorption–desorption isotherms were tested on Belsorp-max, BEL Japan. The specific surface area of samples was determined using the Brunauer–Emmett–Teller (BET) method. The pore volume and pore size distribution were derived from the desorption profiles of the isotherms using the Barrett–Joyner–Halanda (BJH) method. The elemental analysis of the nanocatalyst was carried out by atomic adsorption spectroscopy (Shimadzu AA670) and X-ray fluorescence (Philips 2404, Holland).

Preparation of nanomagnetic Fe_3O_4

Magnetically nano Fe_3O_4 was prepared by chemical co-precipitation of chloride salts of Fe^{3+} and Fe^{2+} [53, 54].

Table 3 Comparison of the reduction of nitrobenzene with $NaBH_4$/nano Fe_3O_4@$Cu(OH)_x$ and other reported systems

Entry	Catalyst	Reductant	Time (min)	Yield (%)	Condition	Reusability (times)	Refs.
1	Fe_3O_4@$Cu(OH)_x$ (20 mg)	$NaBH_4$ (2 mmol)	3	95	55–60 °C	9	*
2	Fe_3O_4@Ni (33 mg)	$NaBH_4$ (4 mmol)	25	95	rt	30	[49]
3	Fe_3O_4@Ni (50 mg)	Glycerol/KOH (2 mmol)	180	94	80 °C	8	[50]
4	Nano Ni (11 mg)	$N_2H_4{\cdot}2H_2O$ (0.2 mL)	75	99	rt	5	[51]
5	Nano Co (11 mg)	$N_2H_4{\cdot}2H_2O$ (0.2 mL)	300	50	rt	5	[51]
6	Co_3O_4–NGr/C (20 mg)	Formic acid (3.5 mmol)	15 h	96	100 °C	6	[52]

* Current protocol

Typically, in a two-neck round-bottom flask, a solution of $FeCl_3 \cdot 6H_2O$ (5.838 g, 0.0216 mol) and $FeCl_2 \cdot 4H_2O$ (2.147 g, 0.0108 mol) in distilled water (100 mL) was prepared. The solution was stirred vigorously by mechanical stirrer at 85 °C under N_2 atmosphere for 10 min. Aqueous NH_4OH (25 %, 10 mL) was quickly added in one portion to the prepared solution of iron salts at 85 °C. Upon the addition, the black Fe_3O_4 nanoparticles were immediately precipitated. The resulting mixture was continued to stirring at 85 °C for 30 min followed by cooling to the room temperature. The nanoparticles were then separated from the reaction mixture (by an external magnet) and washed doubly with distilled water followed by a solution of NaCl (0.02 M). Drying under air atmosphere affords the pure nanomagnetic Fe_3O_4 (size of nanoparticles: 13–30 nm).

Synthesis of Fe_3O_4@$Cu(OH)_x$ NPs with 22 % Cu content

To a solution of $CuCl_2 \cdot 2H_2O$ (0.852 g, 5 mmol) in distilled water (30 mL), nano Fe_3O_4 (1 g, 4.31 mmol) was added and the mixture was vigorously stirred for 10 min at room temperature. The mixture was then slowly basified with NaOH (1 M) up to pH ~ 13. The resulting basified mixture was stirred at room temperature for 24 h, and then the nanoparticles were separated from the reaction mixture via magnetic decantation. Collected Fe_3O_4@$Cu(OH)_x$ NPs was washed with distilled water and then dried under air atmosphere within 2 days. Atomic absorption and X-ray fluorescence analyses resulted 22 % Cu content for the prepared nanocatalyst.

A typical procedure for reduction of nitrobenzene to aniline with $NaBH_4$/Nano Fe_3O_4@$Cu(OH)_x$ system

In a round-bottom flask (10 mL) equipped with a magnetic stirrer, a mixture of nitrobenzene (0.123 g, 1 mmol) and H_2O (3 mL) was prepared. Nano Fe_3O_4@$Cu(OH)_x$ (20 mg, 0.06 mmol, $x = 2$) was then added, and the resulting mixture was stirred for 5 min. Next, $NaBH_4$ (0.076 g, 2 mmol) was added and the reaction mixture was continued to stirring for 3 min at 55–60 °C. TLC monitored the progress of the reaction (eluent, *n*-hexane/EtOAc: 5/2). After completion of the reaction, the nanocatalyst was separated by an external magnet and the reaction mixture was extracted with EtOAc (2 × 5 mL). Drying organic layer over anhydrous Na_2SO_4 and then evaporation of the solvent affords the pure liquid aniline in 95 % yield (0.088 g, Table 2, entry 1).

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