Versatility of magnetic Fe_3O_4 supported copper nanocomposite catalyst towards reduction of carbonyl and nitro compound

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Ferrite supported copper nanocomposite catalyst has been synthesized and characterized by TEM, SEM-EDS mapping, XRD, XPS and ICP-AES analysis. This nanocomposite is found to be more efficient and versatile towards carbonyl and nitro reduction under mild reaction condition with very good yield and turn over number. The catalyst is magnetically recoverable and also reusable for a minimum of four catalytic cycles.

Keywords: Nanocomposite, Catalysis, Carbonyl/Nitro Reduction, Magnetic separation

Among the various important processes of organic synthesis, the processes involving the reduction of substrates such as azido, nitro and carbonyl compounds are one of the most important fundamental processes due to their significant role in the pharmaceuticals and biological synthesis[1]. Although a number of metal catalysts have been reported for hydrogenation reaction, yet they have lack of applicability due to their high cost[2]. Nowadays, nanoparticles (NPs) especially iron nanoparticles (FeNPs), emerge as one of the important catalysts for this purpose due to their non-toxicity, economy and effectiveness[3]. This iron nanoparticle can also be used as precursors to seed, reduce and support another metal. Again, these NPs are magnetically recoverable which makes them unique for easy and environmental friendly recovery of the catalyst[4]. When FeNPs are used as precursor to another metal such as palladium nanoparticles, it results in hybrid nanoparticles which were proven to be active and recyclable catalysts for Suzuki coupling[5].

In this context, we report here a magnetically recyclable and versatile ferrite supported copper nanocomposites for reduction of carbonyl and nitro compound.

Materials and Methods

All chemical reagents like $FeCl_3.H_2O$, $FeSO_4.7H_2O$, $Cu(OAc)_2$, NaOH and KOH were purchased from Ranbaxy and solvents like EtOH, MeOH, ^{i}PrOH, Toluene *etc.* were obtained from Merck and used without further purification.

In our study, we have adopted a number of methodologies which are summarized as follows:

Preparation of Fe_3O_4 nanoparticles

5.41 g $FeCl_3.H_2O$ and 3.6 g urea were dissolved in water (200 mL) at 85 to 90 °C for 2 h and it turned to brown colour. Then it was cooled to room temperature. To this mixture, $FeSO_4.7H_2O$ (2.78 g) was added followed by the addition of 0.1 M NaOH solution until its pH becomes 10. Then it was ultrasonicated at 30-35 °C for 30 min. After aging for 5 h, black crystalline powder was obtained[6].

Preparation of Fe_3O_4-Cu nanocomposite

Fe_3O_4 (2 g) and $Cu(OAc)_2$ (10 wt% of Cu on Fe_3O_4) were stirred at room temperature in aqueous solution for 1 h. pH was then adjusted to 12 by adding 0.5 M NaOH solution and stirred for 10-12 h. Then it was washed with distilled water and reduced by adding 0.2 M $NaBH_4$ solution dropwise under gentle stirring in an ice-water bath for 30 min until no bubble was observed in the solution. The resulting Fe_3O_4-Cu nanoparticle suspension was subjected to ultrasonication for 10 min and then washed with distilled water and subsequently with ethanol followed by centrifugation[6].

General method for the reduction of carbonyl compounds

The carbonyl reduction reaction was performed by taking 15 mg Fe_3O_4-Cu catalyst, 1 mmol ketone, 2 mmol KOH and 3 mL solvent in a 50 mL round bottom flask. The mixture was stirred at 50 °C up to the required time. The progress of the reaction was monitored by taking thin layer chromatography (TLC). After completion of the reaction, the reaction mixture was extracted with ethyl acetate and the catalyst was separated magnetically. To this filtrate 10 mL ether was added and the product was extracted with ether. The resultant organic phases were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was subjected to silica gel column chromatography (ethyl acetate-hexane, 2:8) to obtain the desired products.

General method for the reduction of nitroarene

A 50 mL round bottom flask was charged with 1 mmol of the nitroarene, 2 mL of the solvent, catalyst (15 mg) and 2 mL hydrazine hydrate. Then the mixture was stirred at a temperature 60 °C using magnetic stirrer upto appropriate time. The progress of the reaction was monitored by thin layer chromatography using alumina coated TLC plates under visible light. After completion of the reaction (monitored by TLC), the reaction mixture was extracted with ethyl acetate and the catalyst was separated magnetically. Then the organic solvent was evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel using *n*-hexane and ethyl acetate as eluent.

Results and Discussion

Characterization of the catalyst

The characterization of the prepared catalyst was carried out by several analytical methods such as TEM, XRD, XPS, SEM-EDX mapping, ICP-AES analysis.

The X-ray diffraction pattern for Fe_3O_4-Cu nanocomposite (Fig. 1) shows characteristics peaks at 43.5°, 50.9° and 74.3° due to metallic Cu, corresponding to the (111), (200) and (220) crystal planes of Cu cubic structure. The diffraction peaks at $2\theta=30.5°$, 35.4°, 57.5° and 63.1° can be indexed to (220), (311), (511) and (440) planes of cubic Fe_3O_4 suggesting the formation of Fe_3O_4 particles. No other peaks arising from Cu_2O, $Cu(OH)_2$ or CuO are observed in this XRD pattern of Fe_3O_4-Cu nanocomposite [JCPDS No. 4-0836 (for metallic Cu); JCPDS 19-0629 (for Fe_3O_4)][7,8]. Using Debye-
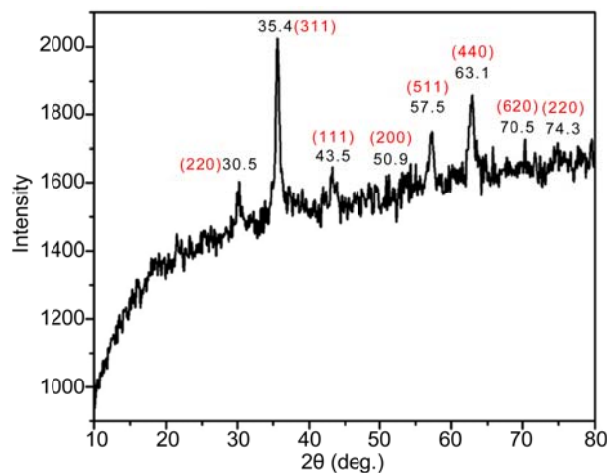

Fig. 1 — XRD pattern of Fe_3O_4-Cu

Scherrer formula, the approximate size of the crystallites was calculated and is about 25 nm based on the plane (311) at $2\theta = 35.4°$.

Fig. 2 and Fig. 3 show the TEM analysis of Fe_3O_4 and Fe_3O_4-Cu, respectively. These TEM images clearly reflect the particle size, shape and morphology of these nanocomposite materials. These indicate the nanorod and spherical shape of Fe_3O_4 and Fe_3O_4-Cu nanoparticles, respectively. The SAED patterns depicted in Fig. 2b and Fig. 3b confirm the polycrystalline nature of the nanocomposites. From the histogram (Fig. 2c and Fig. 3c) the particle diameters for Fe_3O_4-Cu is found to be in the range of 4-16 nm and that for Fe_3O_4 composite is in the range of 0-50 nm[9].

To investigate the oxidation states of Cu and Fe in the nanocomposite, we performed XPS measurement using X-ray photoelectron spectrometer (Model: PHI Versa Probe II with AES) where source of X-ray is Al Kα (1486.6 eV). The XPS spectrum for Fe (Fig. 4a) exhibit two peaks at 711.12 eV and 714.00 eV correspond to Fe^{2+} $2p_{3/2}$ and Fe^{3+} $2p_{3/2}$, respectively. Along with these two characteristics peaks, there are two satellite peaks observed at 733.88 eV and 718.23 eV which confirm the divalent state of Fe in this composite[10,11]. In Fig. 4b, the main and the satellite peaks of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are shown. In this spectrum, there are two prominent peaks at 933.28 eV and 953.03 eV which are assigned to Cu(0) $2p_{3/2}$ and Cu (0) $2p_{1/2}$, respectively. The shakeup peaks for Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are observed at 943.22 eV and 963.01 eV, respectively and it indicates open d^9 shell corresponding to Cu(II). Presence of shake up peaks for Cu(II) may be due the oxidation of Cu(0) during the XPS sampling[4]. The SEM-EDX results of
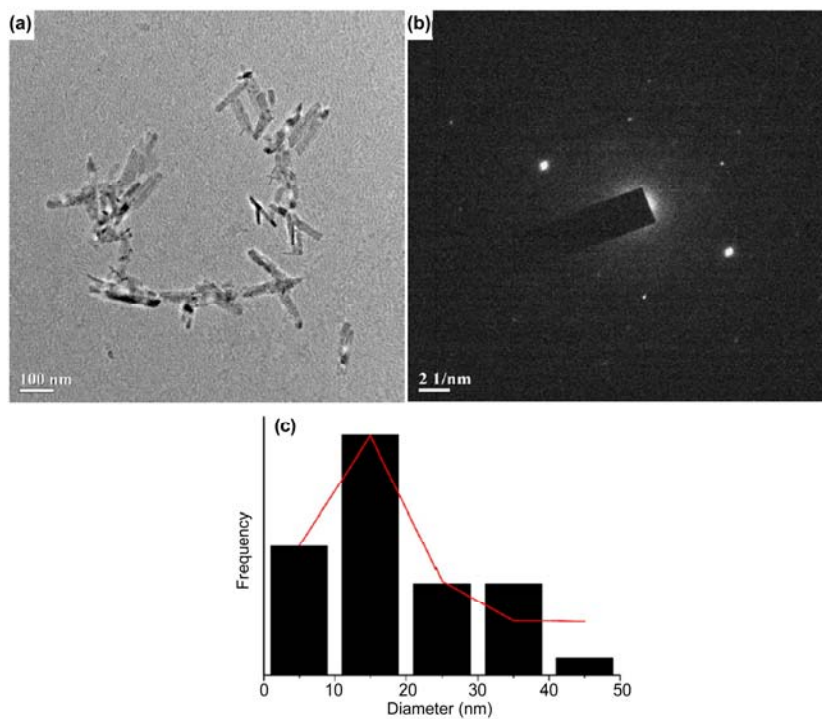
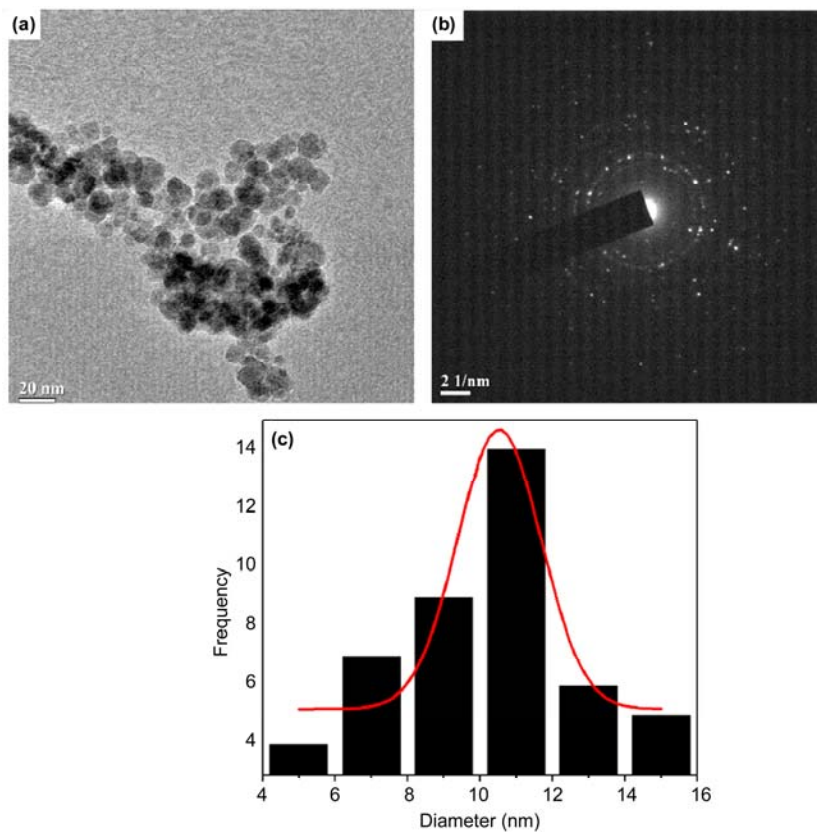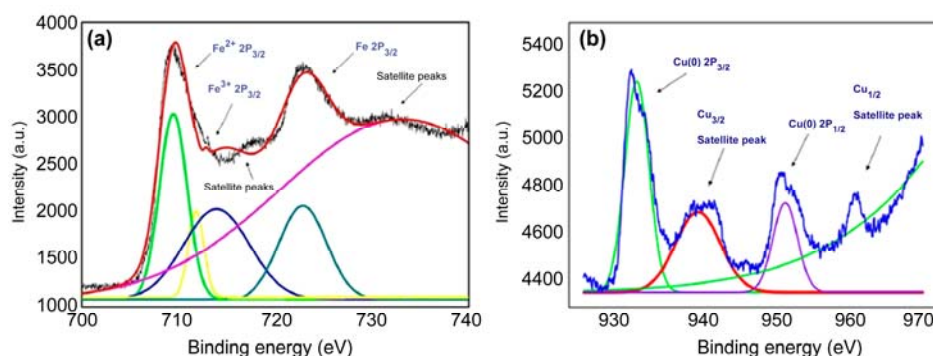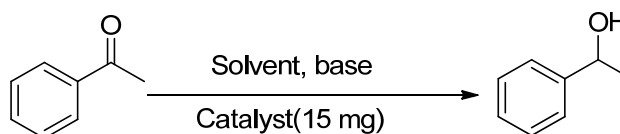Fig. 2 — (a) TEM image of Fe_3O_4, (b) SAED pattern of Fe_3O_4 and (c) histogram

Fig. 3 — (a) TEM image of Fe_3O_4-Cu, (b) SAED pattern of Fe_3O_4 -Cu and (c) histogram

Fig. 4 — Deconvoluted X-ray photoelectron spectra of Fe$_3$O$_4$-Cu for (a) Fe and (b) Cu

Table 1 — Optimization of reaction condition for reduction of carbonyl compound[a]

Entry	Catalyst (mg)	Solvent	Base	Time (h)	Yield[b] (%)
1	-	H$_2$O	KOH	2	-
2	Fe$_3$O$_4$ (15)	H$_2$O	KOH	2	Trace amount
3	Fe$_3$O$_4$-Cu (15)	H$_2$O	KOH	0.5	89
4	Fe$_3$O$_4$-Cu (15)	MeOH	KOH	2	65
5	Fe$_3$O$_4$-Cu (15)	^{i}PrOH	KOH	2	78
6	Fe$_3$O$_4$-Cu (15)	DMF	KOH	2	60
7	Fe$_3$O$_4$-Cu (15)	CH$_3$CN	KOH	2	58
8	Fe$_3$O$_4$-Cu (15)	^{i}PrOH:H$_2$O	KOH	0.5	96
9	Fe$_3$O$_4$-Cu (10)	^{i}PrOH:H$_2$O	KOH	0.5	90
10	Fe$_3$O$_4$-Cu (20)	^{i}PrOH:H$_2$O	KOH	0.5	96
11	Fe$_3$O$_4$-Cu (15)	DMF:H$_2$O	KOH	2	66
12	Fe$_3$O$_4$-Cu (15)	^{i}PrOH:H$_2$O	K$_2$CO$_3$	2	68
13	Fe$_3$O$_4$-Cu (15)	^{i}PrOH:H$_2$O	Et$_3$N	2	64
14	Fe$_3$O$_4$-Cu (15)	^{i}PrOH:H$_2$O	NaOH	2	66
15	Fe$_3$O$_4$-Cu (15)	^{i}PrOH:H$_2$O	KOH	2	96[c]
16	Fe$_3$O$_4$-Cu (15)	^{i}PrOH:H$_2$O	KOH	2	90[d]
17	Fe$_3$O$_4$-Cu (15)	^{i}PrOH:H$_2$O	-	3	45

[a]Reaction condition: acetophenone (1 mmol), Catalyst, solvent (4 mL), base (0.2 mmol) at 30 °C temperature. [b]isolated yield; [c]1 mmol KOH, [d]0.1 mmol KOH

Fe$_3$O$_4$-Cu nanocomposite catalyst are given in Supplementary data. The amount of Cu loading in this Fe$_3$O$_4$-Cu catalyst was determined by ICP-AES analysis and found to be 3.8 (wt%).

Here we have developed a magnetic Fe$_3$O$_4$ supported copper nanocomposite catalyst and studied the versatile catalytic activity of the same. At first, we have taken acetophenone as model substrate, water as solvent and KOH as base (Table 1) in order to observe its catalytic activity. Initially, the reaction was performed by using KOH alone as well as with the mixture of KOH and Fe$_3$O$_4$, but the transfer hydrogenation reaction did not occur under these conditions even at 100 °C (Table 1, entries 1, 2). However, when the mixture of KOH and Fe$_3$O$_4$-Cu was used, it resulted in the quantitative conversion of acetophenone to the corresponding alcohol (Table 1, entry 3). The effect of different bases such as K$_2$CO$_3$, Et$_3$N, NaOH *etc*. and that of different solvents such as MeOH, ^{i}PrOH, DMF, CH$_3$CN *etc*. (Table 1, entries 4-14) has also been observed throughout our study. It revealed that a mixture of H$_2$O: ^{i}PrOH as solvent with KOH as base gave the highest yield of the product (Table 1, entry 8). When the reaction was carried out with catalyst using ^{i}PrOH: H$_2$O as solvent in absence of a base, then it is observed that the reaction took
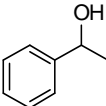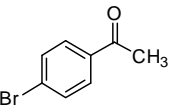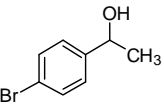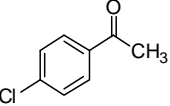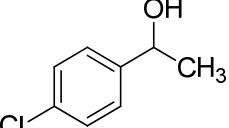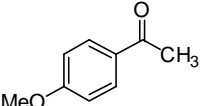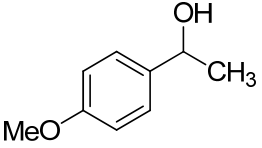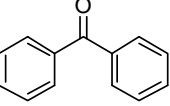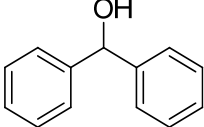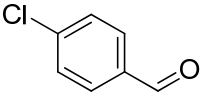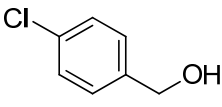
longer time and the product yield is also low which indicates the crucial role of the base in the reaction. Since the reaction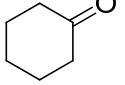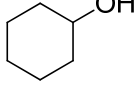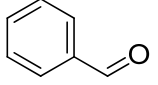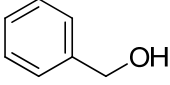 proceeds to some extent in absence of base, it can be concluded that ^{i}PrOH acts as a hydrogen source in this reaction[12] (Table 1, entries 17).

On optimizing the amount of catalyst (entries 9, 10) and amount of base (entries 15, 16), it was observed that 0.2 mmol KOH and 15 mg of this solid catalyst was sufficient for this good conversion (Table 1, entry 8).We have chosen a wide range of carbonyl compound for observing the catalytic activity of the catalyst as shown in Table 2.

In order to check the versatility of our catalyst, we have studied the efficiency of the catalyst for reduction of aromatic nitro compounds. Initially the reaction did not proceed satisfactorily when we have used a mixture of H_2O: ^{i}PrOH as solvent, KOH as base and 4-chloro nitrobenzene as model substrate (Table 3, entry 1). The effect of some bases (Table 3, entries 3, 13) and some solvents (Table 3, entries 3-7) have also been studied in this context. From this study, it was found that the reaction cannot occur in absence of base and satisfactory results have been observed in solvents with higher polarity. Table 3 showed that the reaction proceeds very well to provide the desired product with water as solvent and $H_2N-NH_2.H_2O$ as hydrogen source (Table 3, entry 4).

Table 2 — Reduction of carbonyl compound[a]

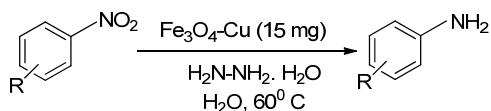| Entry	Substrate	Product	Time (h)	Yield[b] (%)	TON	TOF
1			0.5	96	168.42	336.84
2			1	90	157.89	157.89
3			2	85	149.12	74.56
4			1	89	156.14	156.14
5			1	88	154.38	154.38
6			1	92	161.40	161.40
7			2	88	154.38	77.19
8			0.5	90	157.89	317.8

[a]Reaction condition: substrate (1 mmol), Catalyst (15 mg), solvent (4 mL), base (0.2 mmol) at 30 °C temperature. [b]isolated yield, **TON** = mole of product/mole of catalyst; TOF=TON/time

Table 3 — Optimization of reaction condition for reduction of nitro compound[a]
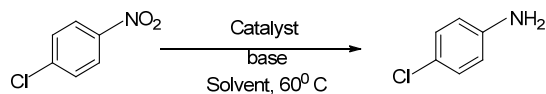
Entry	Catalyst (mg)	Solvent	Base	Time (h)	Yield[b] (%)
1	Fe$_3$O$_4$-Cu (15)	^{i}PrOH:H$_2$O	KOH	2	-[c]
2	Fe$_3$O$_4$-Cu (15)	^{i}PrOH:H$_2$O	KOH	2	-
3	Fe$_3$O$_4$-Cu (15)	^{i}PrOH:H$_2$O	H$_2$N-NH$_2$. H$_2$O	2	78
4	Fe$_3$O$_4$-Cu (15)	H$_2$O	H$_2$N-NH$_2$. H$_2$O	2	91
5	Fe$_3$O$_4$-Cu (15)	MeOH	H$_2$N-NH$_2$. H$_2$O	2	48
6	Fe$_3$O$_4$-Cu (15)	EtOH	H$_2$N-NH$_2$. H$_2$O	2	56
7	Fe$_3$O$_4$-Cu (15)	Toluene	H$_2$N-NH$_2$. H$_2$O	2	-
8	Fe$_3$O$_4$-Cu (10)	H$_2$O	H$_2$N-NH$_2$. H$_2$O	2	80
9	Fe$_3$O$_4$-Cu (20)	H$_2$O	H$_2$N-NH$_2$. H$_2$O	2	91
10	Fe$_3$O$_4$-Cu (15)	H$_2$O	H$_2$N-NH$_2$. H$_2$O	2	91[d]
11	Fe$_3$O$_4$-Cu (15)	H$_2$O	H$_2$N-NH$_2$. H$_2$O	2	88[e]
12	Fe$_3$O$_4$-Cu (15)	H$_2$O	-		-
13	Fe$_3$O$_4$-Cu (15)	H$_2$O	NaBH$_4$	2	43

[a]Reaction condition: 4-chloronitrobenzene (1 mmol), Catalyst, solvent (2 mL), base (0.5 mL) at 60 °C temperature
[b]isolated yield; [c]at 30 °C temperature; [d]0.6 mL base used; [e]0.3 mL base used

Table 4 — Reduction of nitro compound[a]

Entry	Substrate	Product	Time (h)	Yield[b] (%)	TON	TOF
1			2	91	159.64	79.82
2			5	80	140.35	28.07
3			4	87	152.63	38.15
4			6	89	156.00	26.02
5			5	62	108.77	21.75
6			4.5	80	140.35	31.18
7			3	83	145.61	48.53
8			5	85	149.12	29.842

[a]Reaction condition: substrate (1mmol), Catalyst (15 mg), solvent (2 mL), base (0.5 mL) at 60 °C temperature.
[b]isolated yield; TON = mole of product/mole of catalyst; TOF=TON/time

With the above optimized reaction condition, the efficiency of our developed catalyst has been tested for different aromatic nitro compounds whose results are shown in Table 4. It was observed that all the nitroarenes were reduced in excellent yields affording a single product. From Table 2 and Table 4, we can compare the turn over number and turn over frequency of the two reactions. Our comparison revealed that reduction of carbonyl compounds to their corresponding alcohols is comparatively faster than that of nitro compounds to the corresponding amines.

Reusability Test

Reusability is one of the very important factors for the effectiveness of a catalyst. The reusability of our

catalyst has been studied by using nitro reduction reaction with nitrobenzene and carbonyl reduction with acetophenone upto 4th cycle (Table 5). Since the catalyst is magnetic in nature, so it is easily recoverable by using an external magnet after completion of the reaction and that can be reused in new coupling reaction after thoroughly washing with water and ethyl acetate and drying.
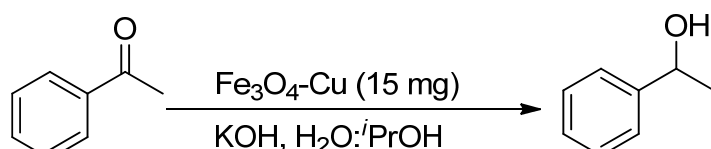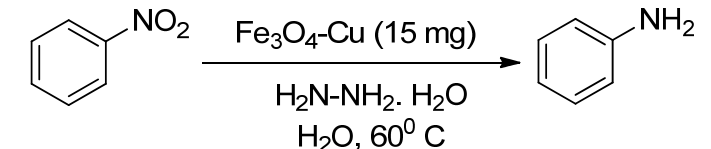
The ICP-AES analysis studied at the end of 4th cycle indicates that there is detection of a very negligible amount (below detection limit) of metal in the solution suggesting the robust nature as well as heterogeneity of the catalyst. However, since there is no significant leaching of metal during the catalysis, the slight gradual decrease in product yield and increase of time after successive reuse may be due to physical loss of the amount of the catalyst. The TEM

image and SAED pattern of the Fe3O4-Cu catalyst after 4th cycle is depicted in Fig. 5 which indicates no significant change in the surface morphology of the catalyst. Again, the SAED pattern indicates that the catalyst retains its polycrystalline nature even after 4th catalytic cycle.

Mechanism

Here we have proposed a general pathway for the reduction of nitroarenes. In this proposed mechanism, nitrosoarene and aryl hydroxylamines may be formed as intermediates, and then aryl hydroxylamines are rapidly reduced into anilines by hydrazine. It is possible that the supported electron rich Cu(0) species activates hydrazine hydrate as a reducing agent in the transfer hydrogenation of nitro compounds into the corresponding amines[13] (Scheme 1).

Table 5 — Reusability of the Fe$_3$O$_4$-Cu nanocomposite

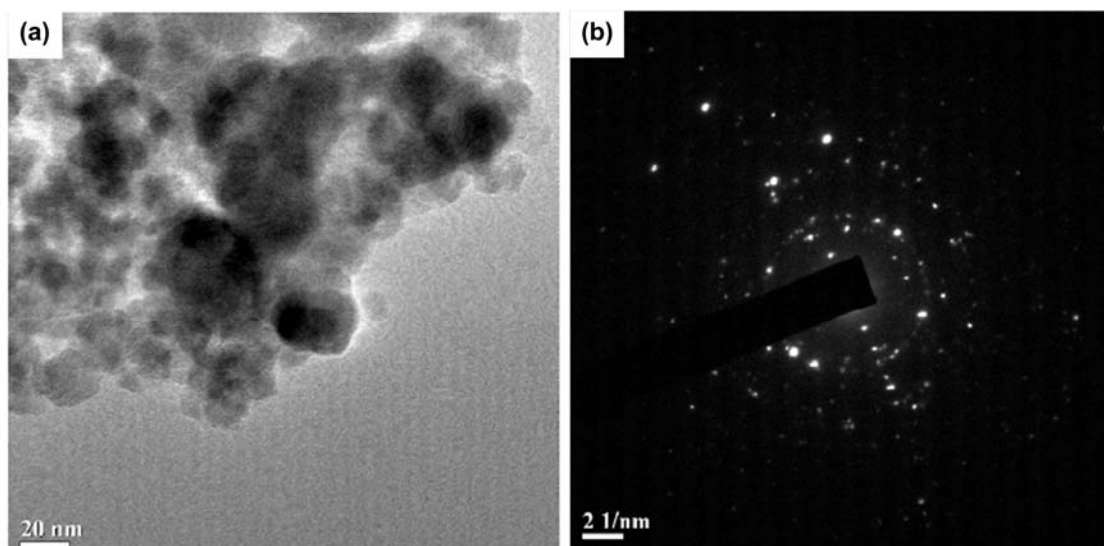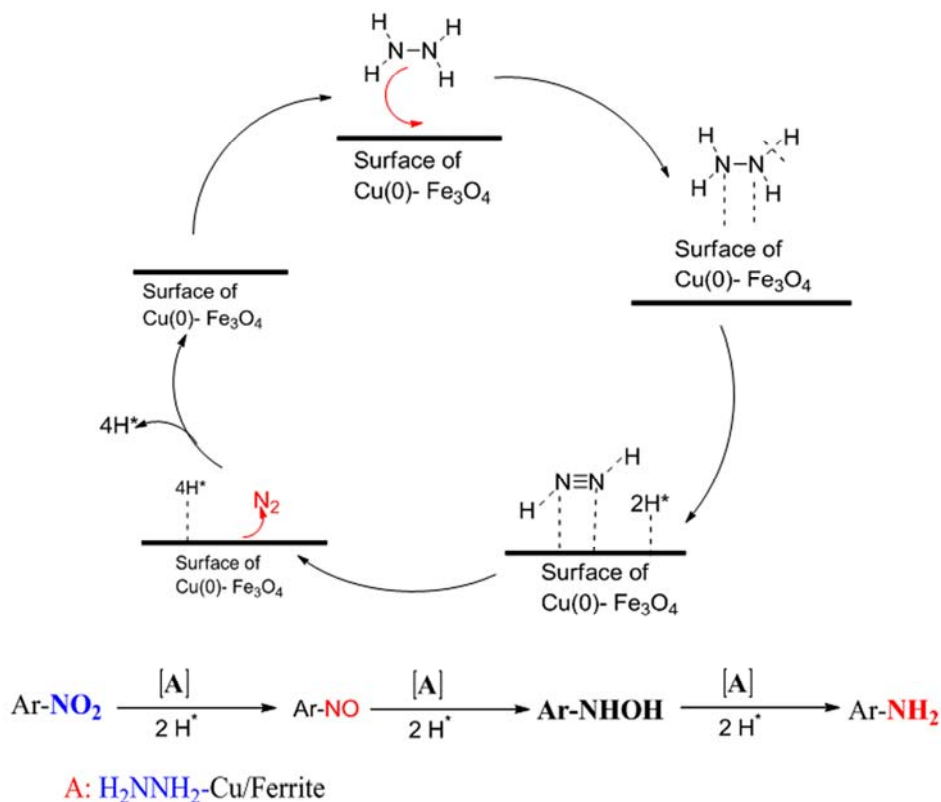| Reduction Reaction	No. Cycle	Time (h)	Yield[a] (%)
(acetophenone → 1-phenylethanol) Fe$_3$O$_4$-Cu (15 mg), KOH, H$_2$O:^{i}PrOH	1	0.5	96
	2	0.5	92
	3	1	90
	4	1	88
(nitrobenzene → aniline) Fe$_3$O$_4$-Cu (15 mg), H$_2$N-NH$_2$. H$_2$O, H$_2$O, 60^0 C	1	4	87
	2	4	85
	3	4	73
	4	4	70

[a]Isolated Yield

Fig. 5 — (a) TEM image and (b) SAED pattern of Fe$_3$O$_4$-Cu catalyst after 4th cycle

Scheme 1 — Schematic for the general pathway for the reduction of nitroarenes

Conclusions

In conclusion, it is observed that Fe₃O₄-Cu nanocomposite catalyst is robust, magnetically recoverable and versatile towards reduction of both aromatic nitro compound and carbonyl compound. We have avoided the use of expensive precursors and resources to linkers or ligands throughout the preparation of the nanocomposite. Due to the heterogeneity and magnetically recoverable nature of the catalyst, it banishes the necessity for a traditional filtration process for the separation of the catalyst.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(01)10-18_SupplData.pdf.

Acknowledgement

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