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FULL PAPER

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Uniformly dispersed copper nanoparticles onto the modified magnetically recoverable nanocatalyst for aqueous synthesis of primary amides

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Magnetically recoverable and environmentally friendly Cu-based heterogeneous catalyst has been synthesized for the one-pot conversion of aldehydes to their corresponding primary amides. The Fe_3O_4@SiO_2 nanocomposites were prepared by synthesis of Fe_3O_4 magnetic nanoparticles (MNPs) which was then coated with a silica shell via Stöber method. Bi-functional cysteine amino acid was covalently bonded onto the siliceous shell of nanocatalyst. The Cu^{II} ions were then loaded onto the modified surface of nanocatalyst. Finally, uniformly dispersed copper nanoparticles were achieved by reduction of Cu^{II} ions with $NaBH_4$. Amidation reaction of aryl halides with electron-withdrawing or electron-donating groups and hydroxylamine hydrochloride catalyzed with Fe_3O_4@SiO_2@Cysteine-copper (FSC-Cu) MNPs in aqueous condition gave an excellent yield of products. The FSC-Cu MNPs could be easily isolated from the reaction mixture with an external magnet and reused at least 8 times without significant loss in activity.

KEYWORDS

copper nanoparticles, cysteine, heterogeneous catalyst, magnetically recoverable catalyst

1 | INTRODUCTION

The amide functional group[1] is an important organic unit in a wide range of chemical structures, including biomolecules,[2] natural products, pharmaceuticals,[3] and polymers. Csp^2–N bond as an important organic transformation[1] can be formed via oxidative amidation of aldehydes to the oximes from which nitrile intermediates converted to primary amides via dehydration-hydration process. Secondary amides can be generated through an acid-assisted Beckman rearrangement.[4] Traditionally amides are synthesized via the reaction of carboxylic acids derivatives such as acid chlorides,[5] active esters,[6] anhydrides,[7] and acyl azides[8] in the presence of coupling agents.[9] Classical name reactions such as Beckmann rearrangement[4] Staudinger ligation,[10] Ugi,[11] Schmidt-Abue rearrangement[12] have also been developed. Unfortunately, these methods often require harsh reaction conditions, hazardous and toxic coupling reagents which led to byproducts and chemical wastes. Boronic acids,[13] *N*-heterocyclic carbenes,[14] transition-metals such as ruthenium,[15] rhodium,[16] Au/TiO_2,[17] Au/DNA nanohybrids,[18] Fe,[19] Zn,[20] and Pd as catalyst[21] have been reported for amidation reactions. From the green chemistry point of view, the development of efficient catalytic systems remains a great challenge. Cu(II) salts as direct catalysts for the one-pot transformation of aldehydes to primary amides have also reported.[22] The copper catalyzed oxidative amidation of aldehydes and aliphatic amine hydrochloride salts was performed by introducing a base.[23] The conversion of aldehydes to primary amides has been studied using SBA-15 grafted ethylenediamine copper complexes.[24] Metal-free oxidative amidation of aldehydes was studied by using tert-butyl hydroperoxide (TBHP) as the oxidant.[25] The amidation of aldehydes with ammonium chloride or amine hydrochloride salts has been reported by using copper sulfate or Cu_2O and aqueous TBHP.[26]

Nevertheless, the intricacy of catalysts recovery and laborious workup procedures are the major drawback of these catalytic reactions.[27] The development of magnetic nanoparticle-supported catalysts that can be easily separated from the reaction mixture has become an important choice. The easy functionalization of magnetic nanoparticles and immobilization of various metal complexes make them a practical catalytic system with highly accessible surface area that shows enhanced efficiency than their corresponding homogeneous analogues.[28] Their insolubility and superparamagnetic nature make it possible to realize various reactions and reduce the capital and operational costs.[29,30] The EDTA functionalized magnetic nanoparticles for the removal of Cu(II) ions were reported as a magnetic nanoadsorbent.[31] In the area of magnetic catalysts, few attempts have been focused on the direct amidation of aldehydes with Cu nanoparticle-supported heterogeneous catalysts on the magnetic nanoparticles.

Herein, we report the design and preparation of an efficient heterogeneous magnetically reusable and environmentally friendly Cu-based catalyst for the mild aqueous direct conversion of aldehydes into primary amides. The use of less toxic and inexpensive copper based cysteine functionalized Fe_3O_4 catalysts has not been reported to date in the synthesis of amides. The cysteine was connected to magnetic nanoparticles previously through a sulfur-metal interaction and was used in a multi component reactions.[32] In this work, we confined copper-cysteine complexes onto the surface of silica coated magnetic nanoparticles as a highly active catalyst in the direct synthesis of amides from aldehydes.

2 | EXPERIMENTAL

2.1 | Synthesis of Fe_3O_4@SiO_2

The Stöber method was utilized for the synthesis of core-shell Fe_3O_4@SiO_2MNPs.[33] An aqueous dispersion of Fe_3O_4 nanoparticles (6 ml, 0.05 g ml^{-1}) were dissolved into a mixture of absolute ethanol (400 ml), and deionized water (100 ml). Ammonia solution (28 wt%, 10 ml) was then added and the mixture sonicated for 30 min. Then, 8.0 ml tetraethyl orthosilicate (TEOS) was dropped into the mixture under vigorous stirring for 12 h. After separation of the Fe_3O_4@SiO_2MNPs (FS) using an external magnet, catalyst washed with water and ethanol 4 times and dried at 60°C in oven.

2.2 | Synthesis of Fe_3O_4@SiO_2@Cycteine-Cu nanoparticles

0.1 g of FS MNPs and 0.4 g cysteine in 20 ml deionized water was mixed and sonicated for 30 min. The mixture transferred into Teflon lined autoclave and kept at 150°C for 3 h. After cooling to room temperature, the magnetic Fe_3O_4@SiO_2@Cysteine nanoparticles (FSC) were collected with a magnet and washed 6 times with water and ethanol and dried at 50°C. In the next step, FSC MNPs (0.4 gr) were dispersed in 25 ml deionized water, and mixed with $CuCl_2$ (0.2 gr in 5 ml EtOH), after sonication for 30 min, the mixture was refluxed for 4 h. Then, an aqueous solution of $NaBH_4$(15.0 ml, 0.2 M) was added dropwise to the mixture and stirred under N_2 atmosphere for 2 h. FSC-Cu nanocatalyst collected by an external magnet, washed with EtOH and water 6 times and dried under reduced pressure.

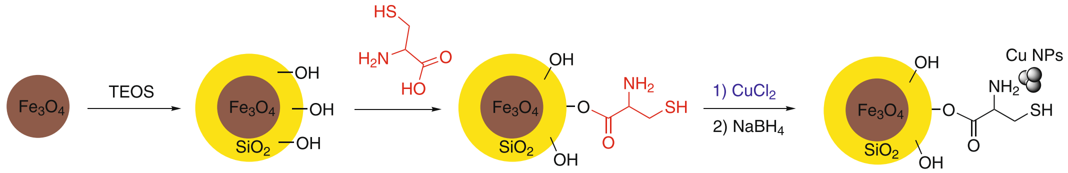
2.3 | General procedure for FSC-Cu MNPs catalyzed amide synthesis

Benzaldehyde (1.0 mmol), hydroxylamine hydrochloride (1 mmol), sodium carbonate (1.1 mmol) and FSC-Cu MNPs (1 mol%) were added to 2 mL of water. The reaction mixture was stirred at 80°C for 24 h. Completion of reaction was monitored by TLC, and the FSC-Cu MNPs were separated with an external magnet. The reaction mixture was quenched with CH_2Cl_2, residual purified by column chromatography using silica gel (n-hexane/ethyl acetate).^{1}H and ^{13}C NMR spectra were measured ($CDCl_3$) with a Bruker DRX-300 AVANCE spectrometer at 300 and 75 MHz, respectively for all products (see supporting information).

3 | RESULTS AND DISCUSSION

The efficiency of copper loaded Fe_3O_4@SiO_2-Cysteine nanocatalyst on the catalytic amidation of aromatic aldehydes was studied. The Fe_3O_4@SiO_2 MNPs were first prepared using Stöber method, in the next step cysteine in one step was covalently bonded to the surface of siliceous shell, and the Cu(II) ions was then loaded on SH and NH_2 functional groups of FSC MNPs. The FSC-Cu MNPs were characterized by transmission electron microscopy (TEM), Scanning electron microscopy (SEM), energy dispersive X-ray (EDS), ICP-OES, X-ray diffractometry (XRD), Thermal gravimetric analysis (TGA), Vibration Sampling Magnetometer (VSM), and Fourier transform infrared spectroscopy (FTIR). The effect of several environmental parameters including catalyst amount, solvents and reaction temperature have been studied. Scheme 1 show a schematic pathway of FSC-Cu MNPs synthesis procedure.

FTIR spectrum of silica coated Fe_3O_4@SiO_2 MNPs (FS) showed a broad peak around 475 cm^{-1} due to the stretching vibration of Fe-O bond which can be an evidence for Fe_3O_4 existence. Asymmetric vibration of Si-O-Si bond and the symmetric stretching of Si-OH bond were located at 1100 cm^{-1} and 947 cm^{-1}, respectively (Figure 1a). These results can be attributed to silica coating of Fe_3O_4 surface.[34]



SCHEME 1 Schematic representation of the FSC-Cu MNPs preparation

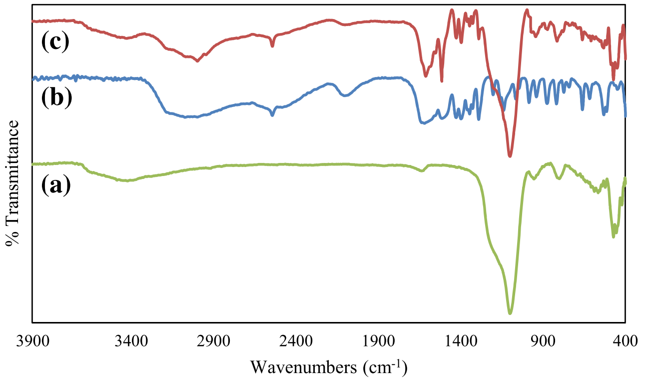


FIGURE 1 IR spectra of (a) $Fe_3O_4@SiO_2$, (b) Cysteine, (c) $Fe_3O_4@SiO_2$-cysteine

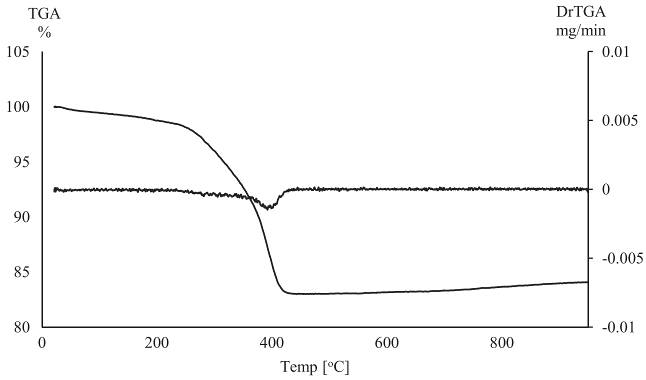


FIGURE 2 Thermogravimetric (TG) analysis curve of FSC MNPs

Cysteine amino acid show characteristic peaks at 1610 cm^{-1} and 1397 cm^{-1} which attributed to the asymmetric and symmetric stretching of carboxylic group. A very broad peak of NH_3^+ stretch is observed between 3000 and 3500 cm^{-1}. A weak peak at 2541 cm^{-1} is due to the presence of S-H groups of cysteine (Figure 1b). Cysteine functionalized FS MNPs exhibit several changes in characteristic peaks in comparison with Figure 1a due to high concentration of grafted cysteine units. The peak located at 2541 cm^{-1} is related to the presence of S-H groups onto the FS MNPs. Also, two peaks due to asymmetric and symmetric N-H stretching were located at 3400 cm^{-1} and 3220 cm^{-1} respectively. (Figure 1c), which confirms the functionalization of surface with cysteine molecules.[35]

To examine the thermal stability of FSC-Cu MNPs the thermogravimetric (TG) analysis was used. As shown in Figure 2 the initial weight loss up to 200°C was probably related to the loss of absorbed water molecules[35] The weight loss in the temperature range of 200-600°C was attributed to the evaporation and subsequent decomposition of surface grafted cysteine groups of FSC MNPs.[35] Therefore, these results confirm that the ligand grafting had been successfully achieved.

The crystal structure of Fe_3O_4 and FSC-Cu MNPs were characterized by XRD. Six diffraction peaks at $2\theta = 30.31°$, 35.64°, 43.31°, 53.86°, 57.24°, 62.83° attributed to the (220), (311), (400), (422), (511), (440) crystal planes of the Fe_3O_4 crystal[34] with cubic phase according to the JCPDS card no. 19–0629 (Figure 3a). As shown in Figure 3b, no remarkable changes occurs in the number of peaks, but due to the heavy atom effect of Cu the characteristic peaks of Fe_3O_4 becomes weak in curve 3b. These results indicate that crystal structure of Fe_3O_4 core after immobilization of Cu nanoparticles retain unchanged. Also, new peaks which were located at $2\theta = 43.65°$, 50.84° and 74.26° attributed to the (111), (200), and (220) planes of the fcc structure of Cu nanoparticles in the catalysis matrix according to the JCPDS card no. 04–0836.[36] The ICP and EDS analyzes confirm the presence of Cu units in the FSC-Cu matrix.

The morphology of the synthesized products was characterized by SEM and TEM. The Fe_3O_4 MNPs are multifaceted cubic particles with average diameters of about 40 nm

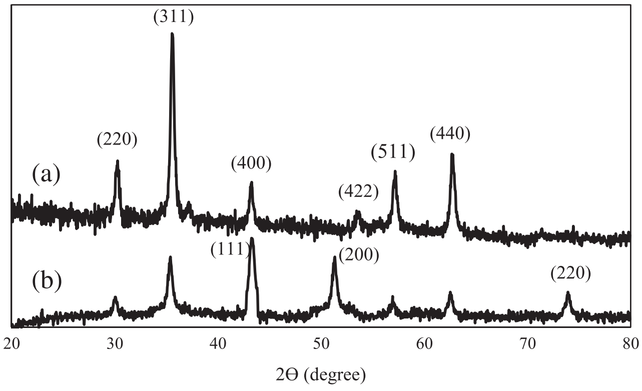


FIGURE 3 XRD patterns of (a) Fe_3O_4 and (b) FSC-Cu MNPs

(Figure 4a). Silica coated surface of Fe_3O_4 MNPs were showed in Figure 4b, which in contrast to the Figure 4a show a Fe_3O_4 MNPs within a siliceous shell. Figure 4c show a high dispersity of Cu NPs onto the surface of FSC MNPs, which indicates core-shell structure has not influenced after immobilization of Cu nanoparticle on the surface of FS MNPs. As shown in Figure 4d the SEM image of FSC-Cu nanocatalyst showed a spherical morphology. The content of Cu in the sample was confirmed by inductively coupled plasma/optical electron microscopy (ICP-OES). The amount of loaded Cu onto the FSC was 14.981 wt. %. In addition, the attendance of Fe, Si and Cu elements are shown in Figure 4e. These results confirmed the existence of Fe_3O_4, $SiO_2$and Cu elements in this catalyst.

As shown in Figure 5 the magnetic hysteresis loops of the Fe_3O_4 and FSC-Cu MNPs exhibit a ferromagnetic behavior at the room temperature. The magnetic saturation value (Ms) of the Fe_3O_4 and FSC-Cu MNPs is 65 and 35 emu/g, respectively. This decrease in the Ms value of FSC-Cu MNPs is due to disordered structure of silica shell at interfaces which provide less magnetic moment per unit mass than that of ferromagnetic core regions. These results demonstrated that the core-shell particles possess magnetic properties.

The catalytic performance of the FSC-Cu as a magnetically recoverable nanocatalyst was investigated through the synthesis of primary amides from aromatic aldehydes. The reaction of benzaldehyde and hydroxylamine hydrochloride carried out under aqueous condition as a model reaction. Different reaction conditions have been studied which is summarized in Table 1. For comparative purposes, SiO_2-Cu was prepared and its effect was compared with FSC-Cu. The SiO_2-Cu catalyst showed lower yield than FSC-Cu. Also hot filtration test for SiO_2-Cu revealed the leaching of Cu units after 4 recycle. The FSC-Cu could be reused 8 run without any significant decrease in activity (Figure 6). Hot filtration tests for FSC-Cu showed negligible Cu leaching up to 6 run. Various solvents and bases were tested in the model reaction which based on Table 1 results water was found to be the optimum solvent (Table 1, entries 10–15). No amide product was obtained without any base. Cs_2CO_3 was effective base and up to 99% of benzamide was formed (Table 1, entry 15), which was in good agreement with previously reported results[37] Because of low price and availability, Na_2CO_3 was selected as a base for optimized condition. The amount of the Cu units had a critical effect on the yields and time of reaction. Model reaction conducted with 0.5 mol% catalyst could provide 70% yield of benzamide after 30 h at 100°C (Table 1, entry 13). Based on these results, 1 mmol of aldehyde, 1 mmol of hydroxylamine hydrochloride, 1 mol% FSC-Cu, 1.1 mmol of Na_2CO_3 and 2 ml of water were chosen as optimized conditions.

To assay the scope of the optimized conditions, a wide range of aromatic aldehydes were tested and the results are

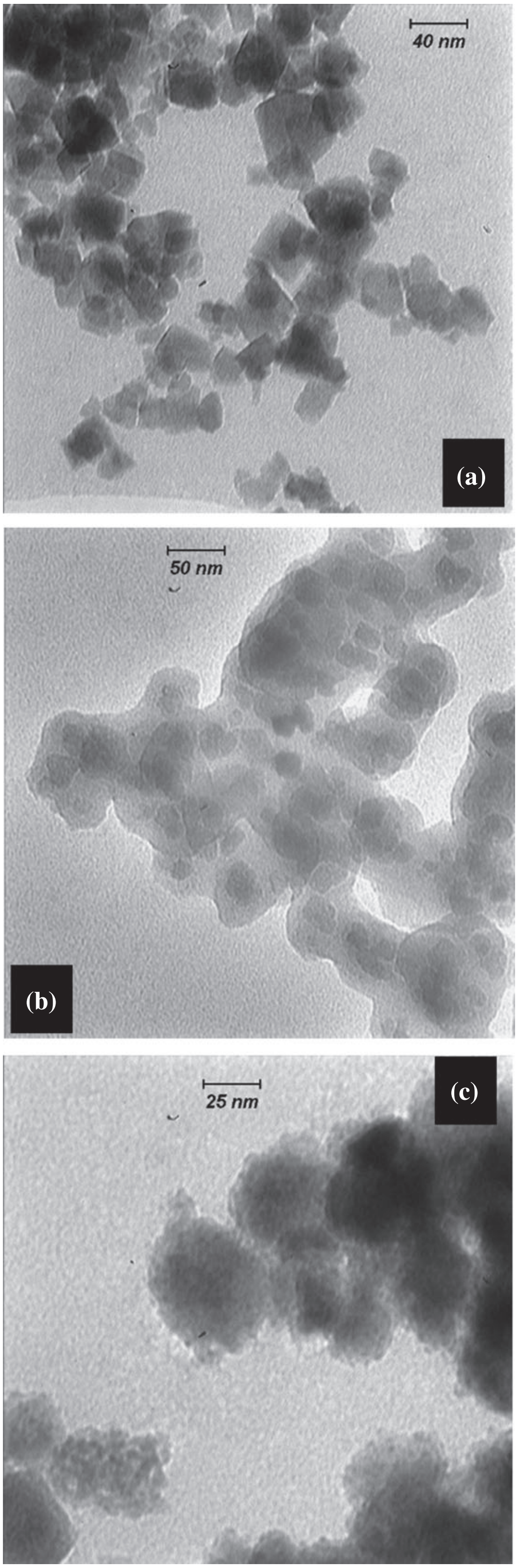


FIGURE 4 TEM images of (a) Fe_3O_4 MNPs, (b) Fe_3O_4@SiO_2 MNPs, (c) FSC-Cu MNPs. SEM image of (d) FSC-Cu MNPs. EDS analyzes of (e) FSC-Cu MNPs

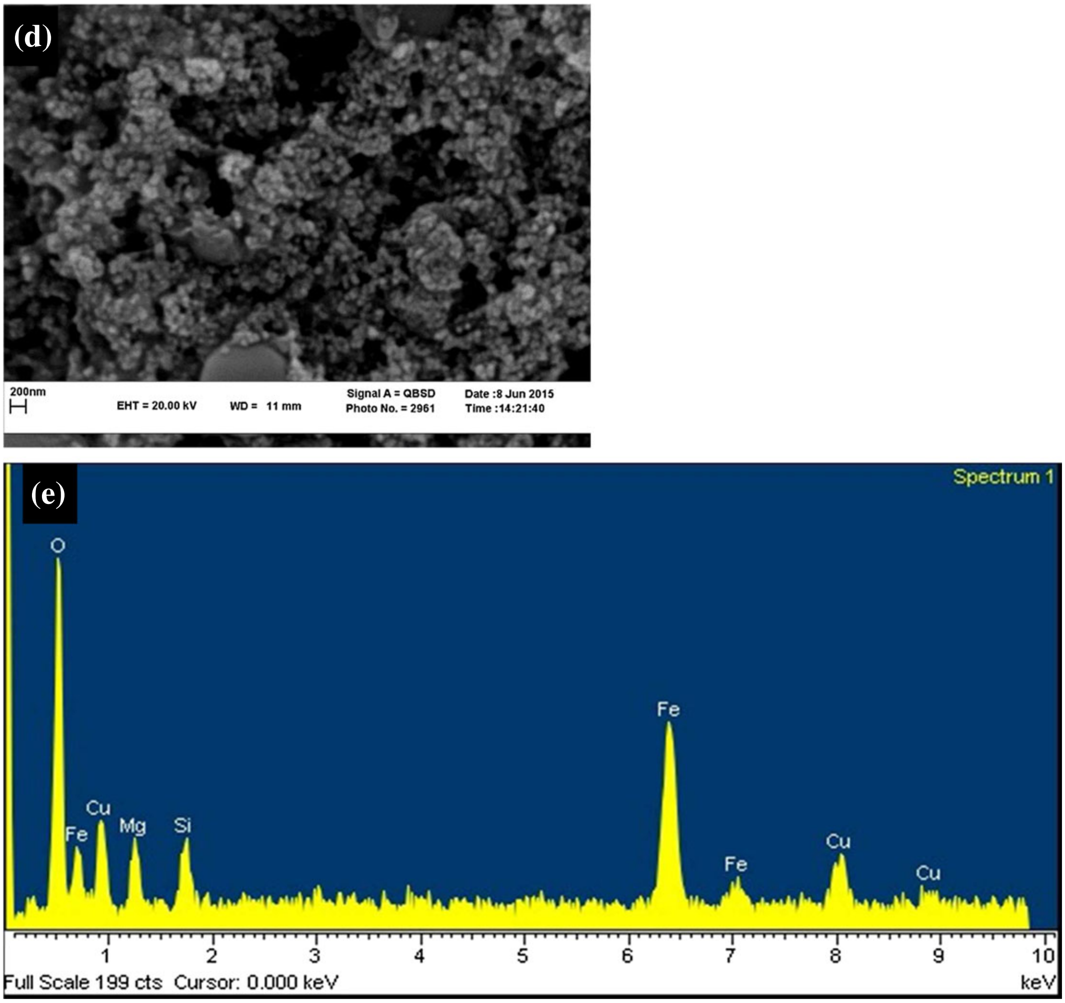


FIGURE 4 (Continued)

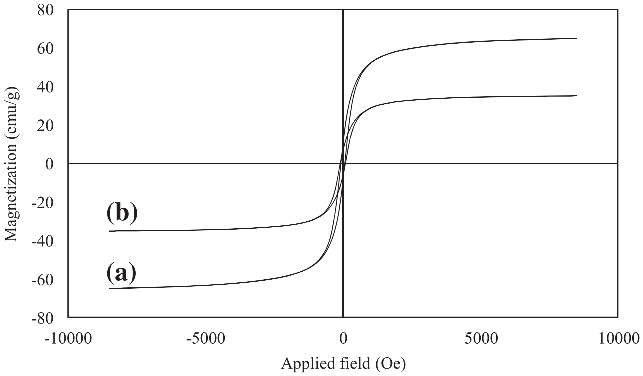


FIGURE 5 Magnetization hysteresis loops measured at room temperatures: (a) Fe_3O_4, (b) FSC-Cu MNPs

summarized in Table 2. The reaction gave an excellent result for aryl aldehydes either with electron-withdrawing or electron-donating groups. Ortho substituted aryl aldehydes showed lower yield and required extended reaction time which can be attributed to steric effects (Table 2, entries 3, 5, 8, 12).

A hot filtration test[38] was performed to determine the activity of catalyst from the Cu leaching point of view under optimized reaction conditions. The catalyst was removed by an external magnet after 10 h reaction (~35% conversion). No further increase in product yield was observed even after 50 h upon catalyst removal. These results indicated that Cu ions are strongly coordinated with cysteine and showed the heterogeneous nature of the FSC-Cu MNPs.

Reusability of the catalyst was evaluated in the model reaction (Figure 6). In terms of copper leaching, our study showed that apart from being highly stable under the optimized conditions. After completing the reaction the FSC-Cu MNPs were separated from reaction mixture easily by an external magnet, washed with water and ethanol 3 times, then dried at 60°C for 2 h. The FSC-Cu catalyst could be reused at least 8 times without a significant loss of its activity Figure 6. (Reaction conditions: benzaldehyde (1 mmol), hydroxylamine hydrochloride (1 mmol), 1.1 mmol of Na_2CO_3 (1.1 mmol), FSC-Cu MNPs (1 mol %), water (2 ml). As shown in Figure 6b the powder XRD data of

TABLE 1 Optimization of reaction conditions[a]

Entry	Catalyst	Base	Solvent	Cu (mol%)	T (°C)	Time (h)	Yield[b] (%)
1	FSC-Cu	Na_2CO_3	EtOH	4	80	36	52
2	FSC-Cu	Na_2CO_3	EtOH	2	80	36	52
3	FSC-Cu	Na_2CO_3	EtOH	1	80	48	50
4	SiO_2-Cu	Na_2CO_3	MeOH	5	80	48	33
5	FSC-Cu	Na_2CO_3	MeOH	2	80	48	55
6	FSC-Cu	Na_2CO_3	MeOH	1	80	48	49
7	FSC-Cu	Na_2CO_3	Toluene	1	80	55	60
8	FSC-Cu	Na_2CO_3	DMF	1	100	36	55
9	FSC-Cu	Na_2CO_3	DMSO	1	100	36	58
10	FSC-Cu	K_3PO_4	H_2O	1	80	40	65
11	FSC-Cu	K_2CO_3	H_2O	1	80	30	80
12	FSC-Cu	NaOAc	H_2O	1	80	48	75
13	FSC-Cu	Na_2CO_3	H_2O	0.5	100	30	70
14	FSC-Cu	Na_2CO_3	H_2O	1	80	24	97
15	FSC-Cu	Cs_2CO_3	H_2O	1	80	24	>99

[a] Reaction conditions: benzaldehyde (1 mmol), $NH_2OH \cdot HCl$ (1 mmol), base (1.1 mmol) in 2 ml of solvent.

[b] Isolated yield.

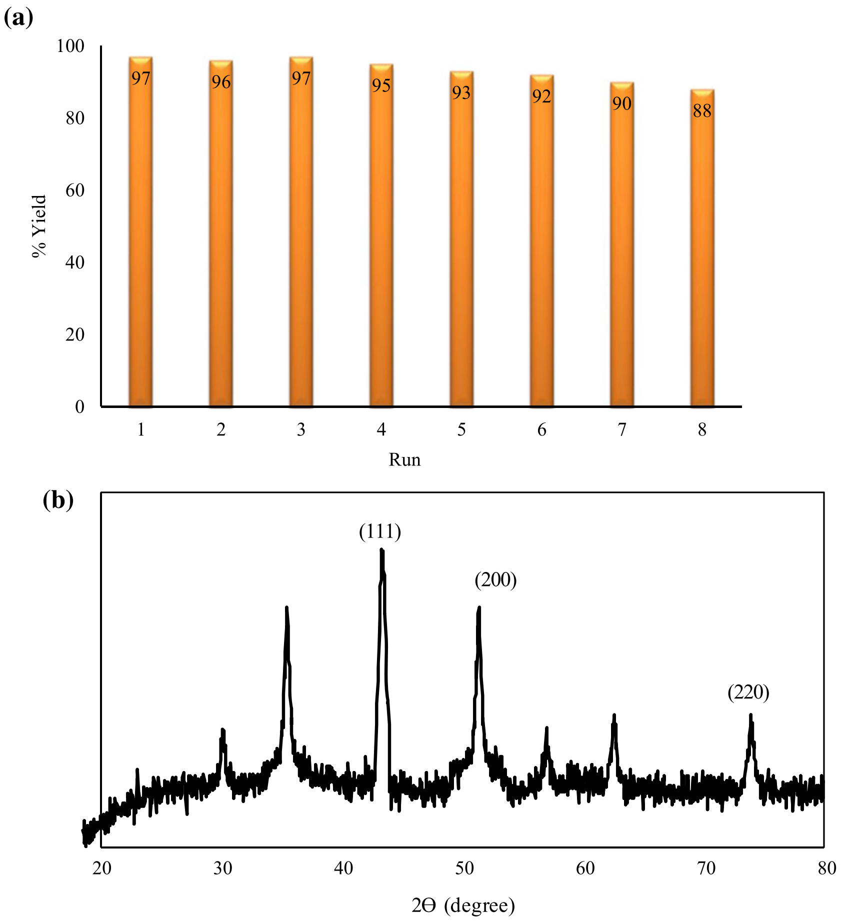
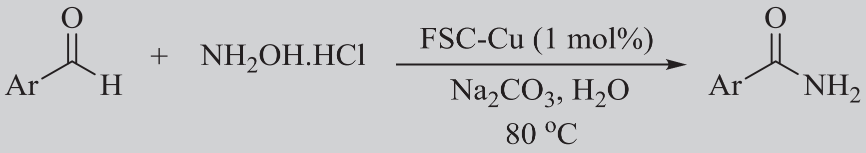
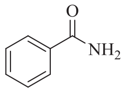
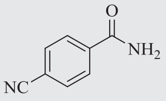
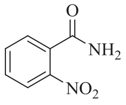
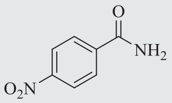
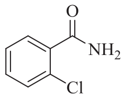
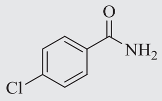
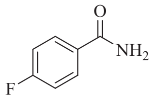
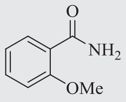
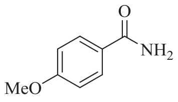
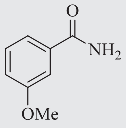
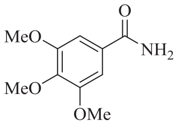


FIGURE 6 (a) Reusability of FSC-Cu MNPs in the conversion of benzaldehyde to benzamine, (b) XRD analyze of recycled FSC-Cu MNPs

recycled FSC-Cu MNPs after 8 runs clearly illustrate that the catalyst still remains as crystalline. The content of Cu in the sample was confirmed by ICP-OES. The ICP-OES analysis of catalyst resulted in a value of about 14.896 wt. % of Cu. In comparison with as-synthesized FSC-Cu MNPs with 14.981 wt. % of Cu, only 0.085 wt. % of Cu was leached

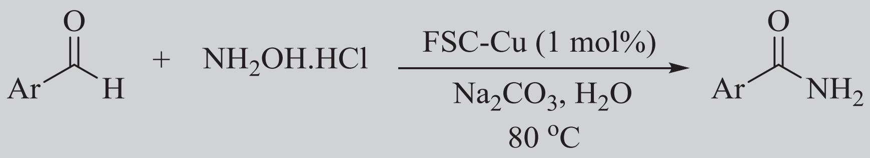
TABLE 2 Aqueous conversion of aldehydes to primary amides using FSC-Cu

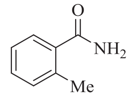
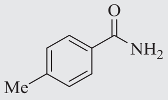


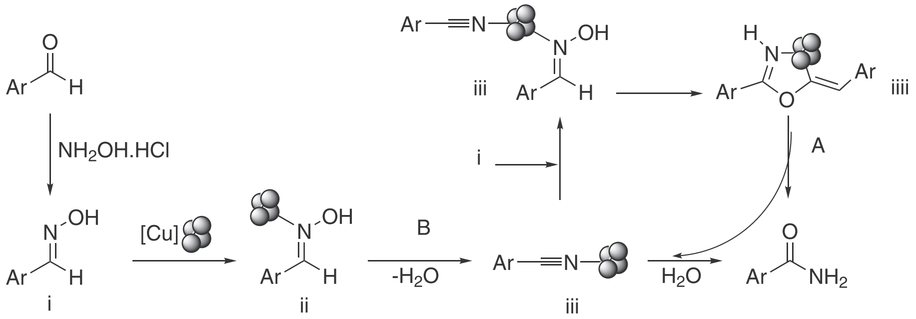
Entry	Product	Time (h)	Yield (%)
1		24	97
2		22	95
3		26	90
4		22	92
5		23	89
6		23	90
7		24	87
8		25	89
9		24	91
10		24	95
11		24	94

(Continues)

TABLE 2 (Continued)



Entry	Product	Time (h)	Yield (%)
12		25	90
13		23	95



SCHEME 2 Proposed mechanisms for the catalytic conversion of aldehydes to amides

after 8 runs which is negligible and confirm that catalyst is really heterogeneous.

The proposed mechanism for amidation of aldehydes is shown in Scheme 2. Two different metal catalyzed pathways have been previously reported.[37] The pathway A involves five-membered cyclic intermediate, which decomposes into the amide product. The pathway B involves dehydration/hydration process with a rearrangement to the amide product.[37] We believe that pathway B seems to be the most plausible on the basis of obtained results and previously reported Cu activities in chemical processes.[39]

TABLE 3 Comparison of catalytic performance of different systems

Catalyst	Cat. (mol%)	Solvent	T (°C)	Yield (%)	Ref
$Pd(OAc)_2$	5	$DMSO-H_2O$	100	98	[37b]
$Cu(OAc)_2$	2	H_2O	110	99	[22a]
$CuSO_4.5H_2O$	2	Solvent free	110	95	[22b]
$TerpyRu(PPh_3)Cl_2$	1	Toluene	110	88	[37e]
$[RuCl(CO)(PPh_3)(TAC)]$	1	Toluene	110	95	[40]
SBA-15/En-Cu	2	H_2O/48 h	80	95	[24]
FSC-Cu	1	H_2O/24 h	80	97	This work

The catalytic activity of FSC-Cu MNPs was comparable to those of reported homogeneous Cu systems (Table 3).

4 | CONCLUSION

In summary, we have developed the magnetically recoverable Cu-based catalyst for direct amidation of aromatic aldehydes with $NH_2OH.HCl$ under aqueous conditions. The mild reaction conditions, broad substrate scope make FSC-Cu MNPs efficient and environmentally friendly for the synthesis of primary amides. Cysteine was used as a ligand for modification of silica coated magnetic nanoparticles which used for generation of Cu NPs. This catalyst can be reused for at least 8 consecutive runs without significant loss of catalytic activity.

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