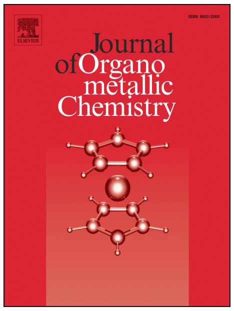

Copper (II) immobilized on magnetically separable l-arginine-β-cyclodextrin ligand system as a robust and green catalyst for direct oxidation of primary alcohols and benzyl halides to acids in neat conditions

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Copper (II) immobilized on magnetically separable L-arginine-β-cyclodextrin ligand system as a robust and green catalyst for direct oxidation of primary alcohols and benzyl halides to acids in neat conditions

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Abstract

Copper (II) immobilized on L-arginine-β-cyclodextrin-functionalized magnetite nanoparticles (nano-Fe_3O_4@L-arginine-CD-Cu(II)) was successfully synthesized and fully characterized using FT-IR, XRD, SEM, EDX, ICP, TGA and VSM techniques. The catalytic activity of these magnetically retrievable nanoparticles was evaluated in the direct oxidation of primary alcohols and benzyl halides to acids in neat conditions that was observed to proceed well and products were obtained in good yields. In addition to showing good catalytic activity, the magnetic catalyst is easy to synthesize and can be recycled at least five times with little loss in activity.

Keywords Copper (II) complex; β-cyclodextrin; L-arginine; Magnetite nanoparticles; Benzylic oxidation; Acids

1 Introduction

Oxidation is a fundamental research field in both laboratorial and industrial levels to synthesize various useful products [1,2]. Carboxylic acids are important structural motifs found in a wide range of natural products [3], pharmaceuticals and fine chemicals [4,5], they are also used as significant organic synthetic precursors to prepare esters, amides and polymers [6]. Therefore, direct oxidation of benzyl chlorides, benzyl bromides and especially alcohols to carboxylic acids is one of the most important reactions in organic synthesis [7–9]. Traditionally, acids are produced from primary alcohols by the use of toxic and hazardous strong oxidants such as manganese(VII) [10,11], chromium(VI) [12,13], hypervalent iodine [14,15] and activated DMSO [16,17], resulting in copious waste from at least stiochiometric amounts of these oxidants. Thus, it is important to develop environmentally friendly new oxidization protocols. During the last decades, most of the reported catalytic systems for the synthesis of carboxylic acid from alcohol under mild conditions are based on noble metals such as palladium, gold, ruthenium, iridium, and platinum, however the limited accessibility and high price of these noble metals constrict their application in largescale industrial production [18–21].

Non-metal catalytic systems for this oxidation transformation have also been attracted much attention and some previous studies employed DDQ, [22] thiourea, [23] and quinine-derived urea [24] as organocatalyst for the oxidation of alcohols. In the search of new aerobic oxidation procedures for alcohols, promising results have been obtained by using of catalytic systems including nitroxyl radicals, such as (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and first-row transition metals, such as Cu, Fe and Mn [25–32]. Catalysts that contain earth-abundant elements such as Co, [33] Fe, [34] Mn, [35] Cu, [36] etc. are both economically and environmentally attractive, however their efficiencies are generally low when compared with the noble metal catalysts [37] and, in most cases, a large amount of various base additives or hazardous oxidizing agents (e.g., peroxy acids, and metal oxidants) are also required to promote the activity and selectivity [38].

In recent years, many catalytic systems involving transition metal complexes with hydrogen peroxide as mild and cheap green oxidant have been investigated for the oxidation of alcohols [39–42]. In some researches, various alcohols were transformed into the corresponding carboxylic acids and ketones in good yields with *t*-BuOOH (TBHP) in the presence of Bi_2O_3 as catalyst [43]. Also, in 2013 for the first time, the use of tetra-*n*-butylammonium bromide (TBAB) as an organocatalyst with TBHP for this transformation was reported [44]. Moreover, a variety of transition metal catalysts such as Fe, Mo, Ru, Pd, V, Mn, Cu, etc. with TBHP as an oxidizing agent have been utilized for oxidation reactions of alcohols [45–52]. Among various catalytically active transition metal complexes, copper complexes bearing phosphines or nitrogen ligands have found numerous applications in organic transformations; however, there are still ongoing efforts to prepare stable copper complexes. β-Cyclodextrin (β-CD) is a water-soluble cyclic oligosaccharide consisting of seven glucose and toroidal in shape with a hydrophobic central cavity and a hydrophilic outer surface that is used as phase transfer and interface reaction catalyst. In addition, it has been shown that β-CD is capable of reversible formation of the host–guest complexes through non-covalent bondings in the cavity upon installation of transition metals and can be used effectively for catalytic organic reactions [53-55]. Host–guest interaction and metal–ligand coordination are significant noncovalent interactions to form catalytically active transition-metal complexes for organic reactions [56,57].

In the last decade, we devoted our research to develop new heterogeneous and reusable catalysts for promoting greener catalytic reactions. Magnetic nanoparticles have attracted much attention as supports for heterogeneous catalysts due to their ease of separation, recoverability, chemical stability, high surface area and ability to be functionalized [58].

In continuation of our laboratory interests in developing environmentally procedures [59], now we have focused on β-CD as a greener supramolecular compound and L-arginine as a nucleophilic natural amino acid. Copper (II) immobilized on L-arginine-β-cyclodextrin-functionalized magnetite nanoparticles were successfully synthesized and fully characterized, then these synthesized magnetic nanoparticles were employed as a highly efficient and recoverable green catalyst for direct oxidation of primary alcohols and benzyl halides to acids in neat conditions.

2 Experimental

2.1 Materials and Instrumentation

All reagents and solvents were purchased from reputable commercial suppliers and used without further purification. All reactions were carried out in the air. All reported yields are isolated yields. FT-IR spectra were obtained over the region 400−4000 cm^{-1} using a Nicolet IR100 FT-IR with spectroscopic grade KBr. The X-ray diffraction pattern was obtained at room temperature using a Philips X-pert 1710 diffractometer with Co Kα (α = 1.78897 $\mathring{A}$), 40 kV voltage, 40 mA current and in the range 100- 900 (2θ) with a scan speed of 0.020/s. SEM (Philips XL 30 and S-4160) was utilized to study the catalyst morphology and size. Magnetic saturation of the catalyst was obtained using a vibrating magnetometer/ alternating gradient force magnetometer (VSM/AGFM, MDK Co., Iran). Thermal gravimetric analysis was recorded using a thermal analyzer with a heating rate of 20 $^{\circ}C\ min^{-1}$ over a temperature range of 25-1100 $^{\circ}C$ under flowing nitrogen. ICP analyse was performed using a Varlan Vista-Pro ICP-OE spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance (DRX 250 MHz and DRX 500 MHz) in a pure deuterated $CHCl_3$ solvent with tetramethylsilane (TMS) as an internal standard.

2.2 Preparation of Fe_3O_4@L-arginine

5 mmol $FeCl_3.6H_2O$ and 2.5 mmol $FeCl_2.4H_2O$ salts were dissolved in 50 ml water under vigorous stirring. An aqueous ammonia solution (28 %w/w, 30 ml) was then added to the stirring mixture to reach the reaction pH about 11, followed by adding 1.5 mmol of L-arginine. This

mixture was refluxed at 100 °C for 8 h. The resulting nanoparticles were collected magnetically and washed several times with water and ethanol and dried in an oven at 80 °C.

2.3 Preparation of Fe_3O_4@L-arginine-CD-Cu(II)

At first tosylation of CD was performed according to the former procedure [53]. Typically, p-toluenesulfonyl chloride (5mmol) was added to a solution of pyridine containing 10 mmol CD, the suspension was cooled to 0 °C and kept for 24 h. Upon completion, cold water was added to the mixture in order to afford a white precipitate. The resulting precipitate was filtered and dried in oven. To synthesize the Fe_3O_4@L-arginine-CD, β-cyclodextrin-OTS (0.25 gr) was dispersed in dry toluene under stirring conditions. The resulting mixture was added to the suspension of Fe_3O_4@L-arginine (0.5 gr) in dry toluene. After that, the mixture was refluxed for 18 h. The resulting nanoparticles were concentrated by magnetic decantation and washed several times with toluene (2× 100 mL), ethanol (2× 100 mL) and finally diethyl ether, followed by drying in an oven.

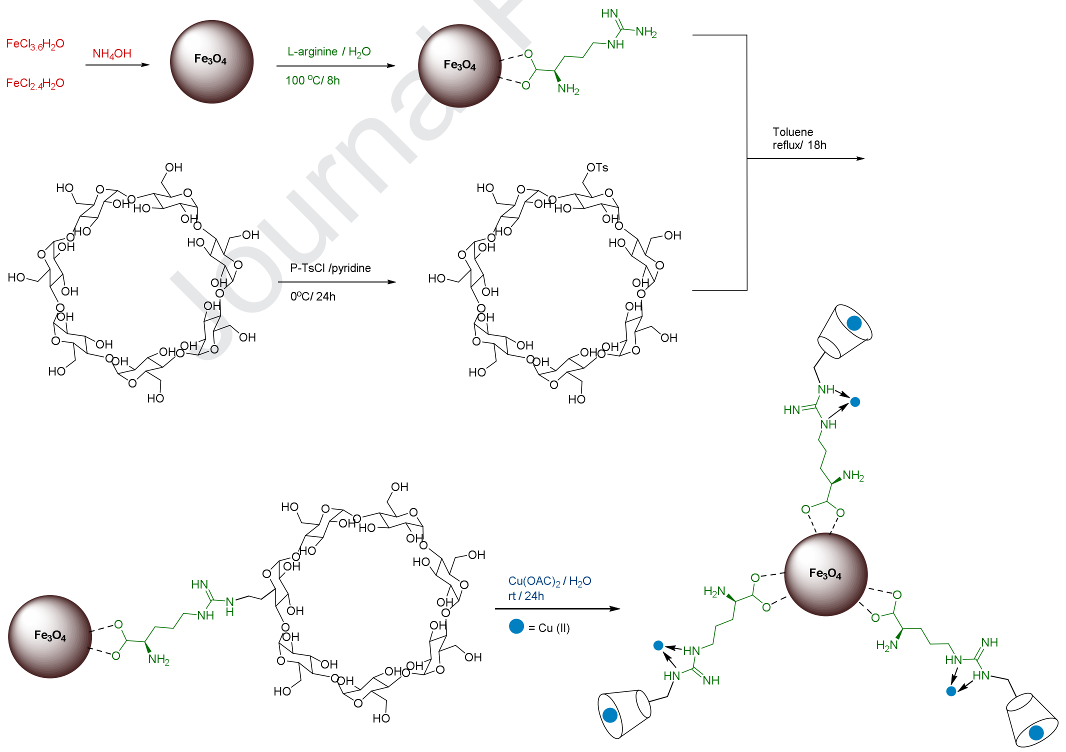
The resultant nanoparticles were dispersed in 20 mL of water and then 2 mmol of $Cu(OAC)_2.2H_2O$ in 30 ml of water was added, the resulting suspension was stirred at room temperature. After 24 h, nanoparticles were separated using an external magnet and washed several times with water and ethanol and dried in an oven overnight.

2.4 General procedure for oxidation of primary alcohols and benzyl halides using Fe_3O_4@L-arginine-CD-Cu(II)

An appropriate primary alcohol (1.0 mmol) or benzyl halide (1.0 mmol) was added into a test tube containing 40 mg catalyst and 4 mmol of tert-butyl hydroperoxide (TBHP 70 wt%) under solvent free conditions. Then the suspension was magnetically stirred for 5 h at 90 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, an aqueous solution of potassium hydroxide was added to the resulting mixture followed by separation of the catalyst from the mixture by an external magnet. After separation of the catalyst, it was washed with ethanol (2× 10 mL) and dried in an oven for reuse in subsequent reactions under the same conditions. Then the resulting solution was extracted with ethyl acetate and aqueous phase was separated, then hydrochloric acid was added dropwise to the aqueous solution to reach the mixture pH about 11 and finally the obtained mixture was extracted with ethyl acetate. The organic phase was separated and evaporated to afford the desired product in pure form.

3 Results and Discussion

The procedure for the synthesis of the catalytic system is shown in Scheme 1. Fe_3O_4 nanoparticles were prepared according to conventional co-precipitation method of ferrous and ferric ions in alkali solution. The abundant surface hydroxyl groups of Fe_3O_4 provide this possibility for grafting of arginine on these magnetic nanoparticles. Subsequently, the reaction of modified magnetic nanoparticles with β-CD–OTS, obtained from the treatment of β-CD (β-cyclodextrin) and TsCl (*p*-toluenesulfonylchloride), led to the desired magnetic nanoparticles-supported organocatalyst. Finally, treatment of L-arginine-β-CD-functionalized magnetite nanoparticles with $Cu(OAc)_2$ in MeOH for 24h provided Fe_3O_4@L-arginine-CD-Cu(II). According to the previous reports [56,57], and by considering the presence of β-cyclodextrin and L-arginine functional groups that can act respectively as good host and active ligand for immobilizing copper species, it can be expected that there are two coordinated Cu(II) ions on each chain.



Scheme 1. Preparation of nano-Fe_3O_4@L-arginine-CD-Cu(II).

The synthesized catalyst was fully characterized using various instrumental techniques such as FT-IR, XRD, SEM, EDX, TGA, ICP and VSM. The FT-IR spectra of the magnetic nanoparticles show the peaks that confirm the successful synthesis of the catalyst [60]. The FT-IR spectra of Fe_3O_4, Fe_3O_4@L-arginine, Fe_3O_4@L-arginine-CD-Cu(II) are shown in Figure 1. The typical peak of Fe-O stretching vibration in 567 cm^{-1} demonsrate the formation of magnetite nanoparticles. In the spectrum for arginine-functionalized magnetic nanoparticles, the peak appearing at 1626 cm^{-1} is ascribed to the COO stretching vibrations. It means that the L-arginine was supported on the magnetite surface. The bands at 2922 cm^{-1} and 3414 cm^{-1} can be attributed to the stretching vibrations of $–CH_2$ and –OH groups in β-CD. Meanwhile, the successful attachment of β-CD on the surface of Fe_3O_4@arginine can be clearly confirmed by the observed characteristic peaks at 1026, 1153 and 1219 cm^{-1}, which could be attributed to the antisymmetric glycosidic C–O–C vibration and the coupled C–C/C–O stretching vibration.

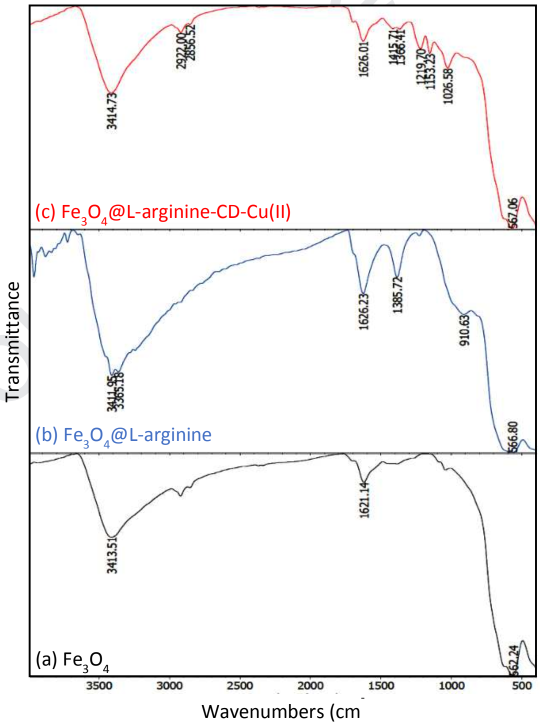
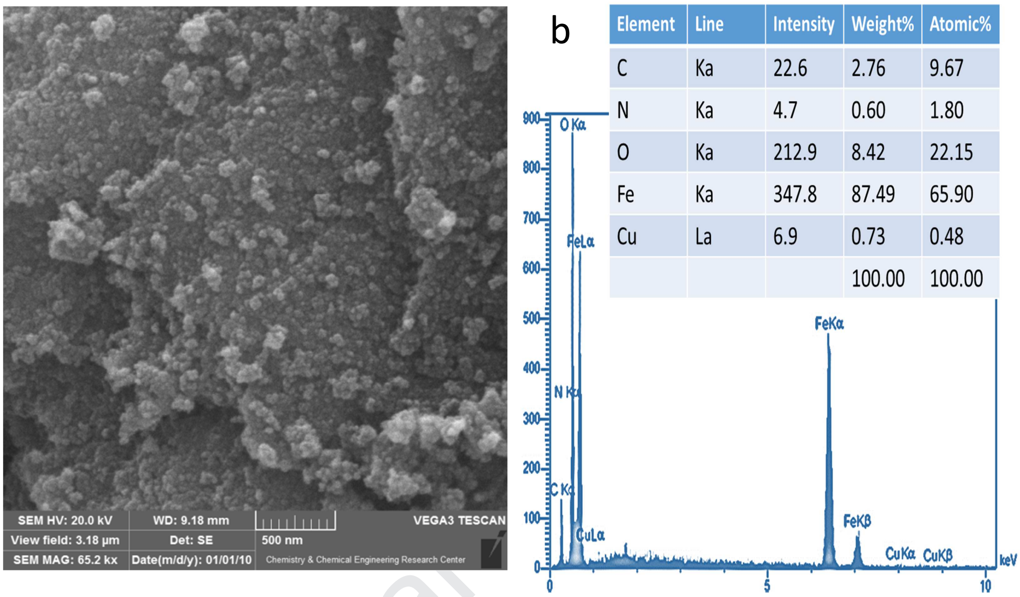


Figure 1. The FT-IR spectra of the Fe_3O_4 (a), Fe_3O_4@L-arginine (b) and Fe_3O_4@L-arginine-CD-Cu(II) (c).

The surface morphology of the prepared catalyst was evaluated by scanning electron microscopy (SEM). The SEM image of the catalyst showed that the particles of the catalyst were obtained in nano scale and these magnetic nanoparticles in the presence of L-arginine-cyclodextrin-Cu(II) have a nearly spherical shape (Figure 2a). Energy-dispersive X-ray (EDX) spectrum of the obtained nanomaterials (Figure 2b) confirmed the presence of the expected elements in the structure of Fe_3O_4@L-arginine-CD-Cu(II), namely iron, oxygen, nitrogen and copper with wt% of 87.49, 8.42, 0.60 and 0.73, respectively.



Element	Line	Intensity	Weight%	Atomic%
C	Ka	22.6	2.76	9.67
N	Ka	4.7	0.60	1.80
O	Ka	212.9	8.42	22.15
Fe	Ka	347.8	87.49	65.90
Cu	La	6.9	0.73	0.48
			100.00	100.00

Figure 2. a) SEM and b) EDX analysis of the catalyst.

To determine the crystalline structure of the magnetic nanoparticles, X-ray diffraction (XRD) pattern was studied in a domain of 10–90° (Figure 4). It can be observed that the diffraction peaks at around 35.17°, 41.53°, 50.53°, 63.61°, 67.77°, and 74.61° corresponding to (220), (311), (400), (422), (511), and (440) are quite identical to characteristic peaks of the standard spinel cubic magnetite (JCPDS card no. 19–0629) and any other characteristic peaks due to the impurities of other oxides of iron were not detected.

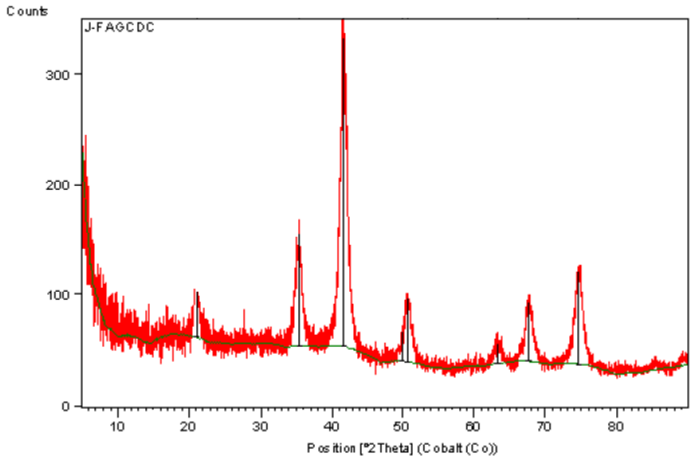


Figure 4. X-ray diffraction pattern of Fe_3O_4@L-arginine-CD-Cu(II).

Thermogravimetric analysis (TGA) was performed to investigate the thermal behavior of the catalyst. The TGA result of Fe_3O_4@L-arginine-CD-Cu(II) is presented in Figure 3. The weight loss observed in TGA curve below 200 °C can be mainly attributed to the water desorption from the magnetite surface (1.76%). Two degradation steps can be detected over the range of 220–550 °C, which can be attributed to the subsequent decomposition of organic moieties, L-arginine and β-CD, grafted on the surface of the magnetite nanoparticles. Using TGA analysis, the content of organic moiety in Fe_3O_4@L-arginine-CD-Cu(II) was estimated to be about 12.52 w/w%. Moreover, the Cu content of the prepared catalyst was 0.086 mmol per gram of Fe_3O_4@L-arginine-CD-Cu(II) using ICP-AES.

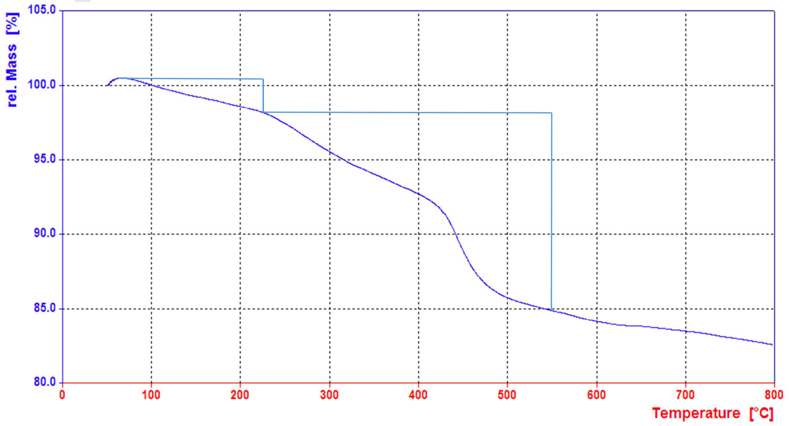


Figure 3. TGA curve of Fe_3O_4@L-arginine-CD-Cu(II).

Magnetic hysteresis measurements of the nanoparticles were explored in an applied magnetic field at room temperature, with the field sweeping from −10000 to +10000 Oe using a vibrating sample magnetometer (VSM). As shown in Figure 5, the saturation magnetization (Ms) value of nanoparticles is 60.15, demonstrating that the catalyst is superparamagnetic. Some decreasing of the value of Ms in compare to pure Fe_3O_4 is attributed to the organic layer on the surface of Fe_3O_4 [61].

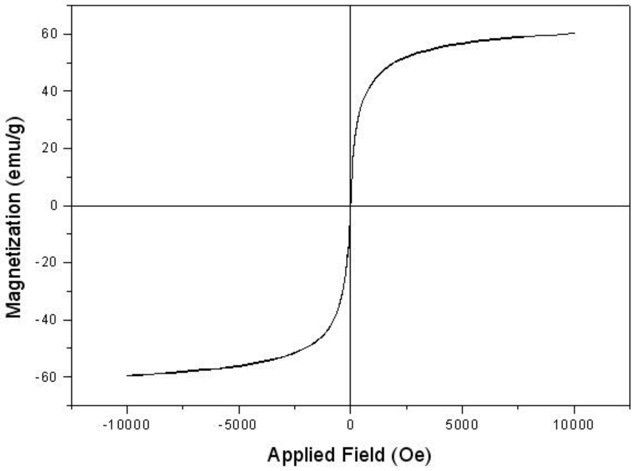
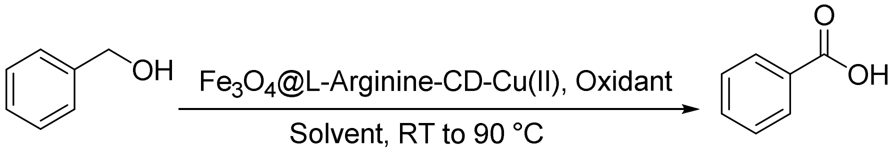


Figure 5. Magnetization curve of Fe_3O_4@L-arginine-CD-Cu(II).

The catalytic performance of Fe_3O_4@L-arginine-CD-Cu(II) was investigated in the oxidation of benzyl alcohol to benzoic acid as a model reaction (Table 1). As seen in entry 1, using TBHP as oxidant in the absence of the catalyst no product was observed, also in the presence of pure Fe_3O_4 we observed that only a trace amount of benzyl alcohol was oxidized (Table 1, entry 2). Using 40 mg catalyst in the presence of H_2O_2 and meta-chloroperoxybenzoic acid (MCPBA) as oxidant gave 20% and 10% yield of benzoic acid, respectively (Table 1, entry 3,4). In the next step, when the reaction was performed in the presence 40 mg of the catalyst in neat conditions at 90 °C, we observed the formation of the most amount of the desired product, (Table 1, entry 5). We optimized the catalyst amount and according to the obtained results (Table 1, entries 5-8) 40 mg (0.34 mol%) of the catalyst was chosen as the best catalyst amount. Subsequently, the model reaction was performed in different temperatures (Table 1, entries 9-12) and the optimized temperature was obtained (90 °C). To examine the effect of different solvents, the model reaction was performed in the presence of various solvents such as: acetonitrile, ethanol, H_2O, DMF, DMSO, toluene and xylene affording desired product in good to excellent yields (Table 1, entries 13-20). As shown in Table 1, the best result was obtained by carrying out the reaction using 40 mg (0.34 mol%) of Fe_3O_4@L-arginine-CD-Cu(II) at 90 °C in neat conditions (Table 1, entry 5).



Scheme 2. Oxidation reaction of benzyl alcohol.

Table 1. Optimization of reaction conditions for oxidation of benzyl alcohol.

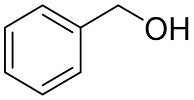
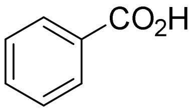
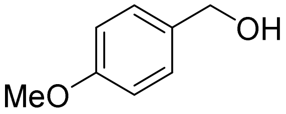
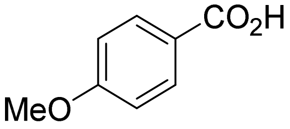
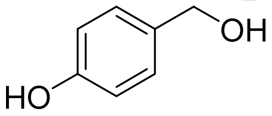
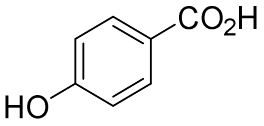
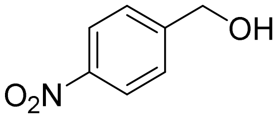
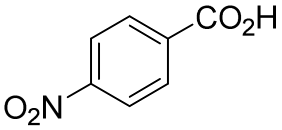
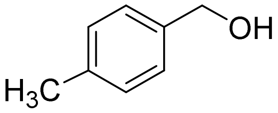
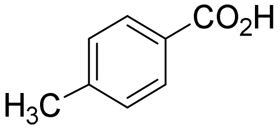
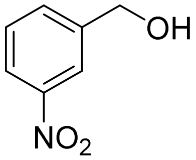
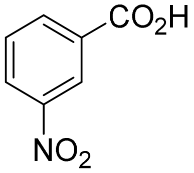
Entry	Catalyst (mg)	Copper content (mol%)	Oxidant	Solvent	Temperature (°C)	Yield (%)[a]
1	None	None	TBHP	Neat	90	N.R
2	Fe_3O_4	None	TBHP	Neat	90	N.R
3	40	0.34	H_2O_2	Neat	90	20
4	40	0.34	MCPBA	Neat	90	Trace
5	40	0.34	TBHP	Neat	90	92
6	45	0.39	TBHP	Neat	90	92
7	20	0.17	TBHP	Neat	90	35
8	30	0.26	TBHP	Neat	90	60
9	40	0.34	TBHP	Neat	RT	Trace
10	40	0.34	TBHP	Neat	70	55
11	40	0.34	TBHP	Neat	80	80
12	40	0.34	TBHP	Neat	100	93
13	40	0.34	TBHP	acetonitrile	90	60
14	40	0.34	TBHP	Ethanol	90	60
15	40	0.34	TBHP	H_2O	90	40
16	40	0.34	TBHP	DMF	90	Trace
17	40	0.34	TBHP	DMSO	90	Trace
18	40	0.34	TBHP	Toluene	90	20
19	40	0.34	TBHP	xylene	90	15
20	40	0.34	TBHP	mesitylene	90	15

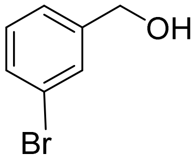
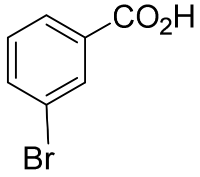
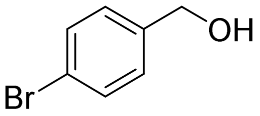
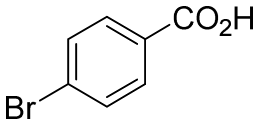
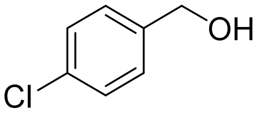
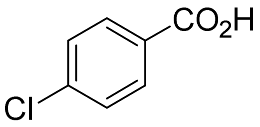
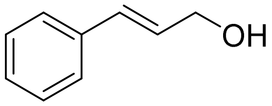
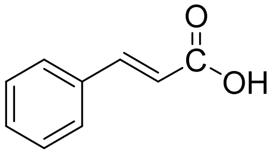
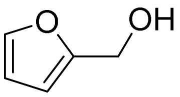
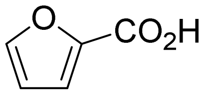
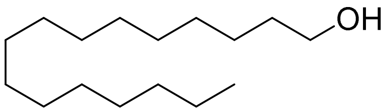
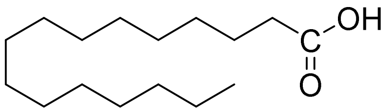
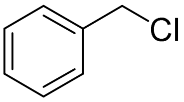
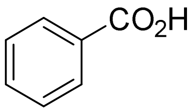
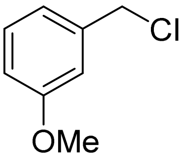
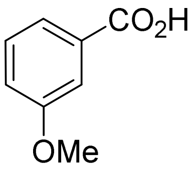
Reaction conditions: benzyl alcohol (1.0 mmol), Oxidant (4.0 mmol), Catalyst (40 mg), 5 h in neat conditions.

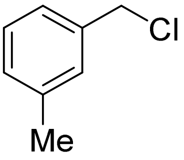
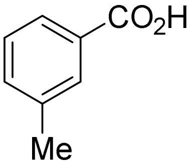
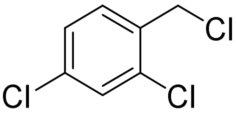
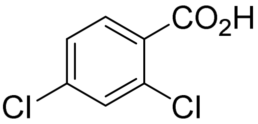
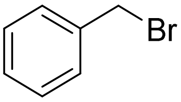
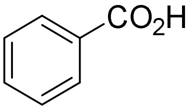
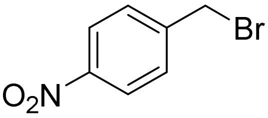
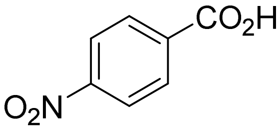
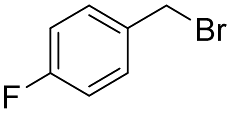
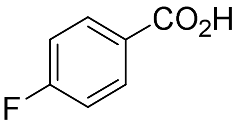
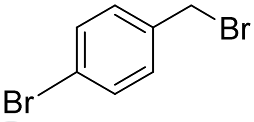
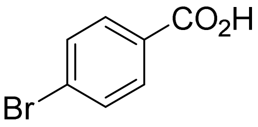
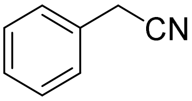
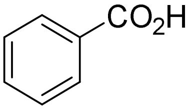
[a]Isolated yields.

To demonstrate the generality of this protocol, the scope of the reaction was investigated under the optimized conditions and the results are summarized in Tables 2. We found that these conditions are useful for a wide range of primary alcohols and benzyl halides. Different benzylic alcohols, including those with either electron-withdrawing or electron-donating groups, were oxidized to the benzoic acids in quantitative yield (Table 2, entries 1-9). When allylic and furfuryl alcohols were employed as substrate, the corresponding acids were generated in high yields (Table 2, entries 10, 11). Aliphatic alcohol was oxidized slower than the others (Table 2, entry 12). When various benzyl halides were employed in the reaction, the corresponding acids were obtained in good to excellent yields (Table 2, entries 13-20). Following the same procedure as described above, when benzyl cyanide was used, the corresponding acid was obtained in excellent yield (Table 2, entry 21).

Table 2. Oxidation reaction of primary alcohols and benzyl halides.

Entry	Substrate	Product	Yield (%)[a]
1			92
2			90
3			89
4			68
5			85
6			90

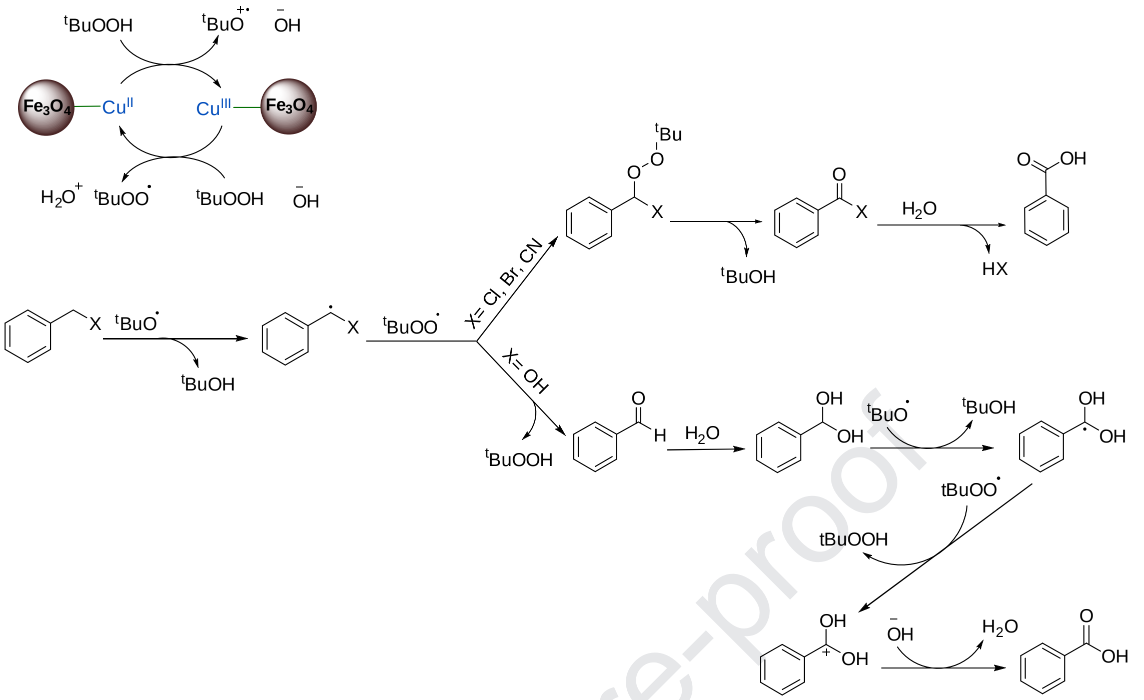
7			80
8			89
9			85
10			87
11			91
12			55
13			92
14			85

15			87
16			80
17			85
18			65
19			80
20			75
21			90

Reaction conditions: benzyl alcohol or benzyl halide or benzyl cyanide (1.0 mmol), (TBHP 70 wt%) (4.0 mmol), Fe_3O_4@L-arginine-CD-Cu(II) (40 mg), 5 h in neat conditions.

[a]Isolated yields.

The plausible mechanism for the oxidation of benzyl halides and benzyl alcohols in the presence of catalyst is shown in scheme 2. In the first step by using of Cu and TBHP, activated benzyl halide produced carbonyl group and *tert*-butanol. In the second step, carbonyl group was activated and oxidized to benzoic acid.



Scheme 3. Proposed mechanism for oxidation of benzyl alcohol, benzyl halide and benzyl cyanide using Fe_3O_4@L-arginine-CD-Cu(II).

The recyclability and reusability are very important points for heterogeneous catalysis systems. In order to examine the reusability of the catalyst in oxidation reaction of primary alcohols to acids, the model reaction was repeated under optimized conditions. In each cycle, after completion of the reaction, the catalyst was magnetically concentrated and washed with ethanol several times, dried and was used in the next cycle. We found that the catalyst was recovered for five runs without considerable loss of its activity, as shown in Figure 6.

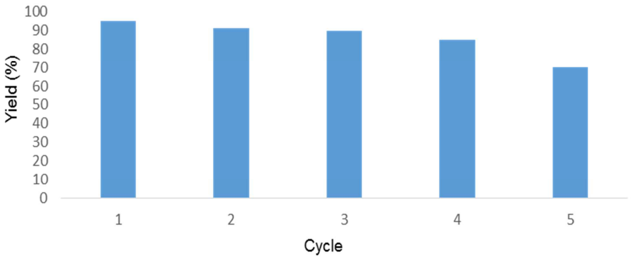


Figure 6. Recyclability of the synthesized catalyst.

In this research, we also measure the amount of leaching of copper from the heterogeneous catalyst in the oxidation reaction by ICP analysis. For this purpose, the catalyst was removed by magnetic decantation after the oxidation reaction of benzyl alcohol to benzoic acid was completed and the copper content of the filtrate after the first reaction was determined to be only 0.34%. Moreover, the copper loading amount before and after recycling of the catalyst was checked by ICP analysis and it was observed that the copper content of this catalyst did not decrease appreciably after the reaction.

4 Conclusions

In conclusion, we have developed a highly efficient, robust and recoverable green catalyst, copper immobilized on magnetically separable L-arginine-β-cyclodextrin ligand system, for direct oxidation of primary alcohols, benzyl halides and benzyl cyanide to acids in neat conditions that was observed to proceed well and products were obtained in good yields. In addition, recovery and reusability of the catalyst have been investigated in oxidation reaction of benzyl alcohol to benzoic acid and the catalyst was reused in at least five cycles without a significant loss of activity.

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Compliance with Ethical Standards

Conflict of interest We declare that no conflict of interest exists.

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Highlights

- Cu (II) immobilized on L-arginine-β-CD-functionalized magnetite nanoparticles was well synthesized
- The synthesized catalyst was fully characterized by using various analytical techniques
- The catalyst was used in the oxidation of primary alcohols and benzyl halides to acids
- The reactions were carried out in neat conditions to obtain products in good yields
- The catalyst was simply recycled and reused at least five times with little loss in activity

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: