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Copper(II)-Ethanolamine Triazine Complex on Chitosan-Functionalized Nanomaghemite for Catalytic Aerobic Oxidation of Benzylic Alcohols

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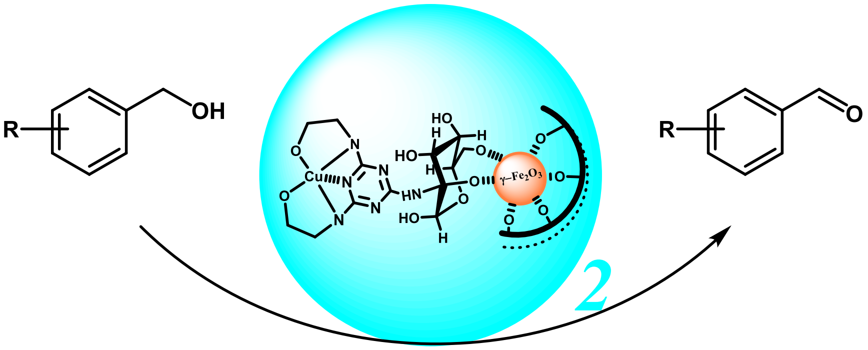
Abstract

In this study a novel, effective and recoverable Cu(II)-catalyst was synthesized by incorporating of $Cu(OAc)_2$ within ethanolamine-triazine derivative (TAETA) attached to chitosan (Chs)-functionalized γ-Fe_2O_3 nanoparticles [**MNP@Chs/TAETA-Cu(II)**]. It was characterized by different techniques such as FT-IR, EDS, ICP, TEM, TGA and VSM. The as-prepared nanocomposite demonstrated high oxidation activity and desired selectivity in the aerobic oxidation of structurally diverse set of benzyl alcohols. Spectral results and leaching experiments revealed that this magnetically recoverable heterogeneous catalyst preserved its structure after it was reused several times. This protocol offers some beneficial features such as the use of oxygen as an ideal oxidant, stability of nanocomplex, easily catalyst separation by using an external magnetic field and efficient recycling as well as the lack of by-products.

Graphic Abstract

Copper (II)-Ethanolamine Triazine Complex on Chitosan-Functionalized Nanomaghemite for Catalytic Aerobic Oxidation of Benzylic Alcohols

Benyamin Hasanpour, Maasoumeh Jafarpour,[a*] Fahimeh Feizpour, Abdolreza Rezaeifard[a*]



The magnetically separable copper (II)-ethanolamine triazine complex on chitosan-functionalized nanomaghemite demonstrated high oxidation activity and desired selectivity in the aerobic oxidation of structurally diverse set of benzyl alcohols.

Keywords Aerobic oxidation · Copper catalyst · Magnetically heterogeneous catalyst · TEMPO

Extended author information available on the last page of the article

1 Introduction

Selective alcohol oxidation to corresponding carbonyl compound is an important class of clean chemical transformations employed in synthetic organic chemistry, fine chemicals and a test bed for many fundamental concepts within the current of laboratory and chemical industry [1–3]. There are extensive diverse methods that focused on this fundamental transformation. Traditionally, many hazardous stoichiometric oxidizing reagents are performed for this conversion, which fabricate a lot of by-product and pollutants and are unsanctioned green and sustainable point of view [4–7]. Therefore, there is a strong incentive to develop new oxidation processes in this arena, owning to the industrial importance of oxidation reactions as well as development of green synthetic processes.

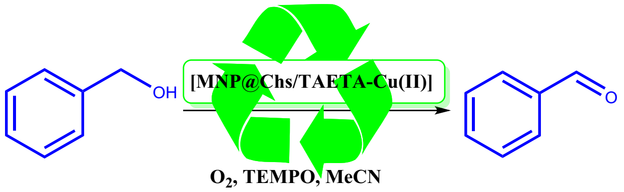
Nowadays, enormous efforts have been devoted to implement ecofriendly aerobic oxidation of alcohols [8, 9]. Selective transformation of alcohols by dioxygen can be achieved in the presence of transition metals such as V [10], Co [11], Mn [12], Fe [13], Cu [14], Mo [15], Pd [16], Au [17] and etc., which potentially lead to significant improvements over many existing systems.

Among the transition metals, copper has been the most studied metal ions. Because it is a non-noble, cheap and abundant metal and also present in nature as a catalytic active site in a variety of enzymes e.g. galactose oxidase [18–20]. The presence of copper in the active sites of different enzymes makes it an appropriate choice for the development of catalysts for oxidation reactions, a fundamental and valuable transformation both in nature and in organic synthesis.

More recently, several copper complexes combined with TEMPO have been abundantly applied in aerobic oxidation of alcohols with respect to their perfect catalytic property [21–31]. However, most of the presented catalytic processes have been performed under homogeneous conditions, which inevitably eventuated in poor recyclability and separation of the metal catalyst and therefore are inferior in the practical large scale procedures. To overcome this problem, switching from homogeneous catalysts to heterogeneous ones with keep of their inherent catalytic activity is highly favorable.

Magnetic nanoparticles have emerged as fascinating supports and have been widely studied in organic transformations because of their easy preparation and functionalization, high dispersion property and impressive separation by external magnet without need to centrifugation or filtration steps [32–34]. Further, surface modification of magnetic compound extend considerable stability as well as provide the fabrication of hybrid composite [35].

From this perspective, herein, we prepared a magnetically separable copper(II)-ethanolamine triazine complex on chitosan-functionalized nanomaghemite. The nanohybrid demonstrated high efficiency and desired selectivity toward aerobic oxidation of benzylic alcohols in the presence of TEMPO in acetonitrile (Scheme 1). The additional advantage of this catalytic system is facile and efficient reusability of the solid catalyst.



Scheme 1 Aerobic oxidation of benzyl alcohols in the presence of **[MNP@Chs/TAETA-Cu(II)]**

2 Experimental

2.1 General Remarks

All chemicals were purchased from Chemical Companies. The FT-IR spectra were recorded on NICOLET system. The TGA measurements were obtained by a TGA-50 (Shimadzu) at the heating rate of 10 °C min^{-1} under 20 mL/min flowing air. TEM images were obtained by TEM instrumentation (Philips CM 10). Inductively coupled plasma (ICP) atomic emission spectroscopy was conducted with an OPTIMA 7300DV. EDX analysis was carried out using TESCAN Vega Model. Progresses of the reactions were monitored by TLC using silica-gel SIL G/UV 254 plates and also by GC-FID on a Shimadzu GC-16A instrument using a 25 m CBP1-S25 (0.32 mm ID, 0.5 µm coating) capillary column. The magnetic properties of nanoparticles were recorded in a vibrating sample magnetometer (VSM, Lakeshore model 7400). NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument.

2.2 Preparation of γ-Fe_2O_3 (MNP)

γ-Fe_2O_3 nanoparticles were synthesized by a previously reported co-precipitation method with slight modifications [36]. To 75 mL solution of $FeCl_3.6H_2O$ (4.25 g, 15.8 mmol) in deionized water, 75 mL aqueous solution of $FeCl_2.4H_2O$ (1.84 g, 9.25 mmol) was added at ambient temperature under Ar atmosphere. Then, NH_4OH solution (25% v/v, 50 mL) was added dropwise (drop rate = 1 mL.min^{-1}) to the stirring mixture such that the reaction pH reached 11. The resulting black dispersion stirring was continued for 1 h and then heated to reflux for 1 h. The resulting nanoparticles were isolated by an external magnetic field and washed repeatedly with bidistilled water to neutral. The as-prepared material was heated at 2 °C min^{-1} up to 200 °C and then kept in a furnace for 3 h to give a reddish brown powder.

2.3 Preparation of Chitosan-Coated γ-Fe_2O_3 (MNP@Chs)

To 1.0 g of γ-Fe_2O_3 nanoparticles dispersed in 100 mL of bidistilled water, an aqueous solution of chitosan (1 g) was gradually added under ultrasonic agitation at 50 °C, which was then kept for 1 h under this condition. Afterwards, the precipitated products (MNP@Chs) were separated by an external magnetic field, washed with water and dried at ambient temperature [37].

2.4 Preparation of Triazine Derivative of MNP@Chs [MNP@Chs/TA]

To a 0.2 g of MNP@Chs dispersed in 5 mL of dry THF, a solution of cyanuric chloride (2 mmol in 5 mL dry THF) was gradually added under ultrasonic agitation at 60 °C, which was then kept for 2 h under this condition. Afterwards, the resulted mixture was heated to reflux for 8 h. Finally, the precipitated products were separated by an external magnetic field, washed with dry THF and dried at 50 °C in vacuum oven.

2.5 Preparation of Ethanolamine Derivative of MNP@Chs/TA [MNP@Chs/TAETA]

To 0.2 g of [MNP@Chs/TA] dispersed in 5 mL of dry THF, a solution of ethanolamine (5 mmol in 5 mL dry THF) was added under ultrasonic agitation at 60 °C. Then, 1 mmol of K_2CO_3 was gradually added and kept for 2 h under this condition. Afterwards, the resulted mixture was heated to reflux for 12 h. Finally, the precipitated products were separated by an external magnetic field, washed with EtOH and dried in vacuum oven.

2.6 Preparation of Cu(II) Complex [MNP@Chs/TAETA-Cu(II)]

To 0.2 g of [MNP@Chs/TAETA] dispersed in ethanol (5 mL) was gradually added 1 mmol $Cu(OAc)_2$ dissolved in ethanol at 60 °C under ultrasonic agitation and was kept for 3 h under this condition. Afterwards, the products were refluxed for 12 h. Finally, magnetically Cu(II) nanocomplex separated by an external magnetic field, washed with EtOH and dried in vacuum oven.

2.7 General Procedure for Aerobic Oxidation of benzyl alcohols

To a mixture of benzyl alcohol (0.125 mmol) and **[MNP@Chs/TAETA-Cu(II)]** nanocomplex (0.003 g) in MeCN (0.5 mL) was added TEMPO (12 mol %) and the reaction mixture was stirred under O_2 stream (5–7 mL min^{-1}) at 80 °C for the required time. The reaction progress was monitored by TLC and the yields of products were determined by GC analysis. The pure product was secured by plate silica chromatography using *n*-hexane/EtOAc (10:3).

3 Results and Discussion

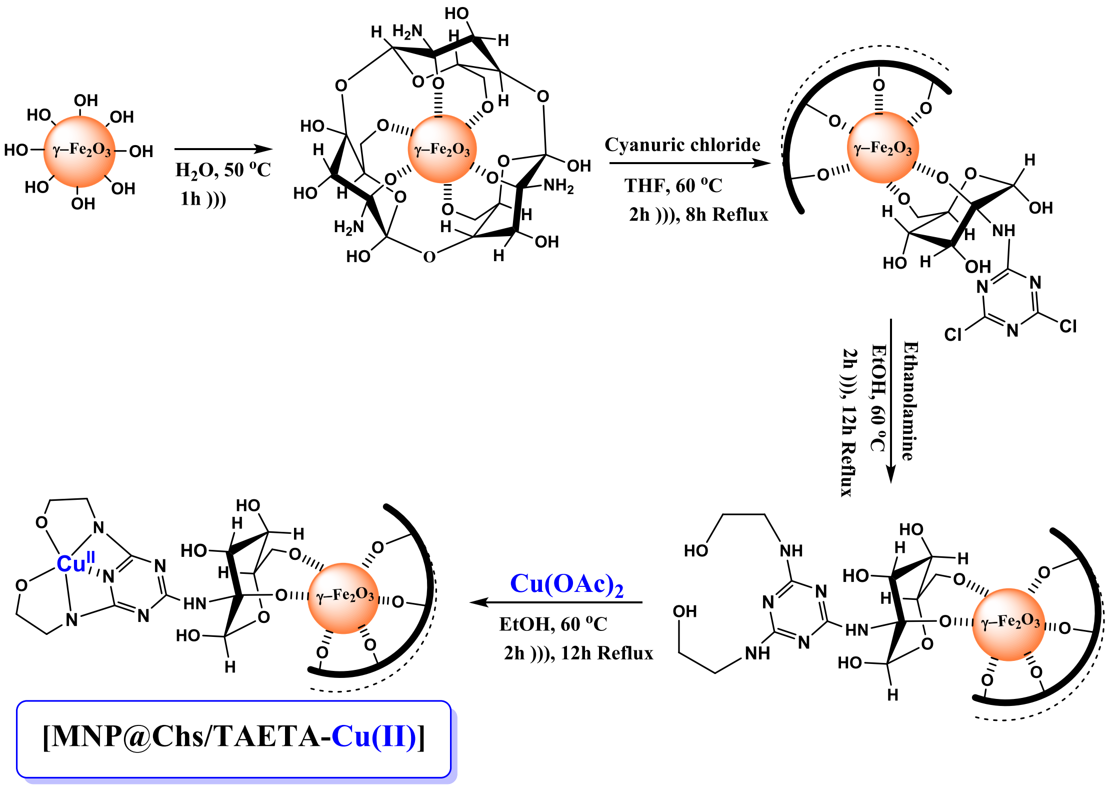
3.1 Fabrication and Structural Characterization of the Catalyst

As shown in scheme 2, as-prepared magnetic nanoparticles by co-precipitation method were coated with chitosan layer under ultrasonic agitation. Next, chitosan-coated magnetic nanoparticles were reacted with the cyanuric chloride and ethanolamine, respectively.

Afterward, the copper complex was obtained by incorporating of $Cu(OAc)_2$ into as-prepared [MNP@Chs/TAETA] under ultrasonic agitation and then, reflux condition.

The FT-IR spectroscopy was applied to identify the bonding structure and composition of **[MNP@Chs/TAETA-Cu(II)]** nanocomplex (Fig. 1). The comparison of the FT-IR spectra of MNP (a), MNP@Chs (b), [MNP@Chs/TAETA] (c) with **[MNP@Chs/TAETA-Cu(II)]** nanohybrid (d) depicted in Fig. 1 confirmed the successful fabrication of the as-prepared catalyst. The typical bands at 582 and 634 cm^{-1} can be clearly observed in all spectra attributed to the stretching vibrations of Fe–O groups. Moreover, the corresponding C–H and O–H bands are also observed at 2900 and 3400 cm^{-1} regions. Strong peaks at 3435, 3361 cm^{-1} and 1633 cm^{-1} rationalized to N–H stretching and bending vibrations in the chitosan fragment, respectively (Fig. 1b) [38]. In the spectrum for [MNP@Chs/TAETA)] (Fig. 1c) the absorption band at 1605 cm^{-1} can be ascribed to the C=N stretching vibration mode which suggests that the reaction of cyanuric chloride with amine group of chitosan is dominant. Besides, because of overlapping peaks, the presence of ethanolamine is not clear. It can be evidently shown that all of the main characteristic peaks appeared in Fig. 1a–c, are present in the as-prepared **[MNP@Chs/TAETA-Cu(II)]** nanohybrid (Fig. 1d).

Transmission electron microscopy (TEM) images of **[MNP@Chs/TAETA-Cu(II)]** nanohybrid depicted in Fig. 2, clearly show that the particles are approximately spherical in shape, with size ranging between 16 and 20 nm (Fig. 2).



Scheme 2 Preparation of **[MNP@Chs/TAETA-Cu (II)]** nanohybrid

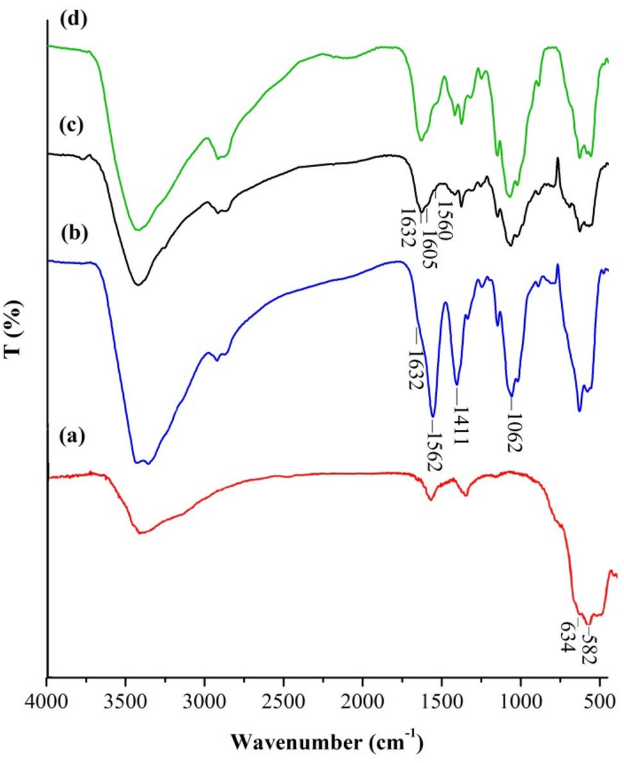


Fig. 1 FT-IR spectra of (a) MNPs, (b) MNP@Chs, (c) [MNP@Chs/TAETA], (d) **[MNP@Chs/TAETA-Cu (II)]** nanohybrid

The energy-dispersive X-ray spectroscopy (EDX) indicated that the nanohybrid is composed of Cu, Fe, N and O, as expected (Fig. 3).

Inductively coupled plasma atomic emission (ICP-AES) analysis of the title catalyst revealed a Cu content of 16 wt% consistent with 2.5 mmol Cu per gram of catalyst.

Thermal stability of the **[MNP@Chs/TAETA-Cu (II)]** nanohybrid was measured using a thermal gravimetric analysis (TGA) under air with heating rate of 10 °C/min up to 800 °C. As seen in Fig. 4, the small weight loss at lower temperature below 170 °C is probably corresponding to evaporation of physically absorbed water. There are three weight loss stages at 180–220, 220–400, and 400–670 °C, respectively. The first step is ascribed to the decomposition of the ethanolamine and two later steps are rationalized to the decomposition of residual organic groups.

The magnetic properties of **[MNP@Chs/TAETA-Cu(II)]** nanohybrid were characterized by VSM at room temperature (Fig. 5). No coercivity or remanence could be observed for the all samples, testifying their typical superparamagnetic behaviors. The saturation magnetization value of the as-prepared nanohybrid was lower than that of pristine MNP nanoparticles due to the existence of shell materials. However, the magnetization of nanohybrid was adequate to

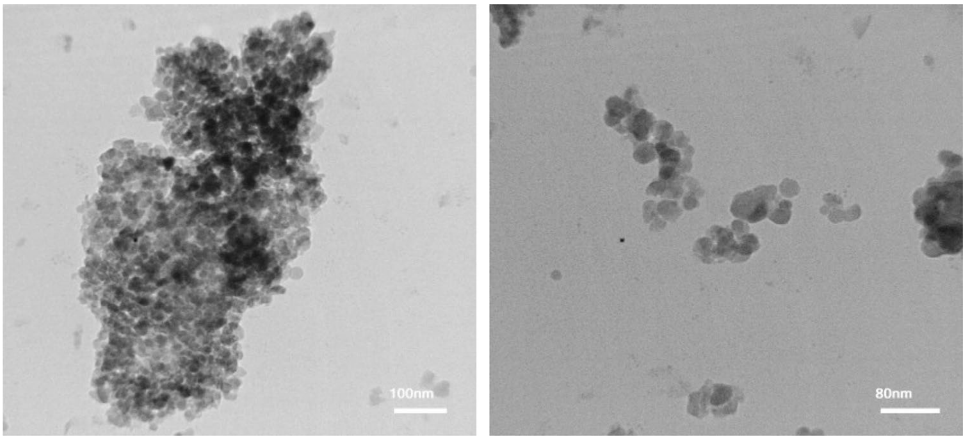


Fig. 2 TEM images of **[MNP@Chs/TAETA-Cu (II)]** nanohybrid

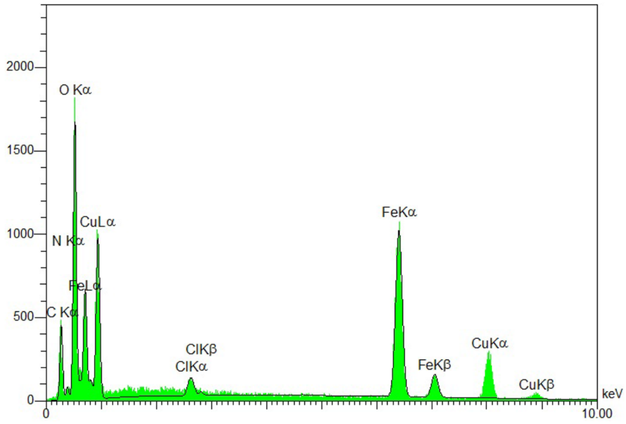


Fig. 3 EDX analysis of **[MNP@Chs/TAETA-Cu (II)]** nanohybrid

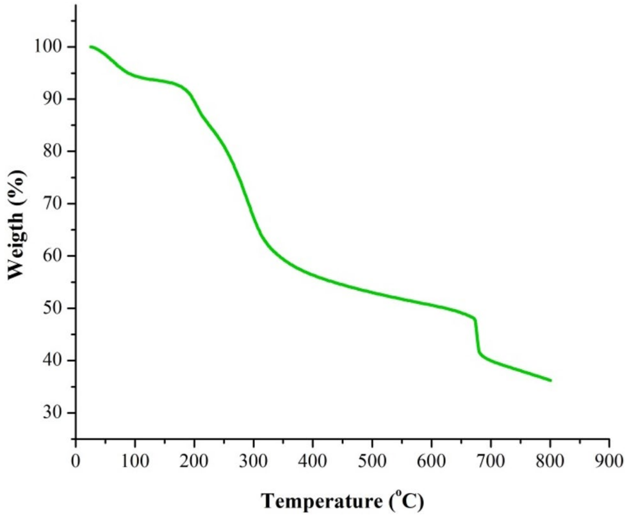


Fig. 4 TGA curve of **[MNP@Chs/TAETA-Cu (II)]** nanohybrid

achieve complete separation of the catalyst with a magnet bar within a short time at the end of reaction.

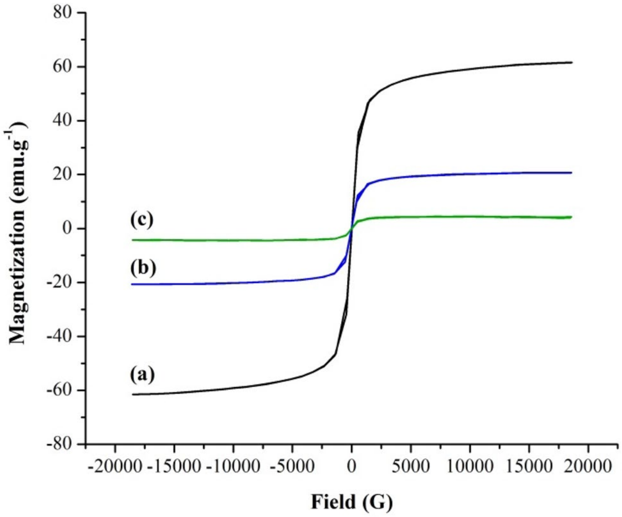


Fig. 5 VSM curves for (a) MNPs, (b) MNP@Chs, (c) **[MNP@Chs/TAETA-Cu (II)]** nanohybrid

3.2 Catalytic Activity

Initial experiments were conducted to screen the solvent nature, temperature and the TEMPO and catalyst amounts. For this, 4-cholorobenzyl alcohol was selected as the model substrate to optimize the aforementioned reaction conditions under air (Fig. 6). No oxidation product was detected in the absence of catalyst or TEMPO, testifying that both of them are indispensable for the reaction to trigger.

The progress of the reaction in different solvents such as EtOAc, H_2O, MeCN, EtOH (0.5 mL) as well as solvent free condition were investigated (0.05 mol% of the catalyst and 10 mol% TEMPO 0.125 mmol of 4-cholorobenzyl alcohol) and MeCN showed to be the best, under air at 80 °C (Fig. 6i,ii).

The screening of the nature of the additive revealed a strong influence of TEMPO on the catalytic performance, while, the *N*-hydroxyimidester (NHPI or NHSI),

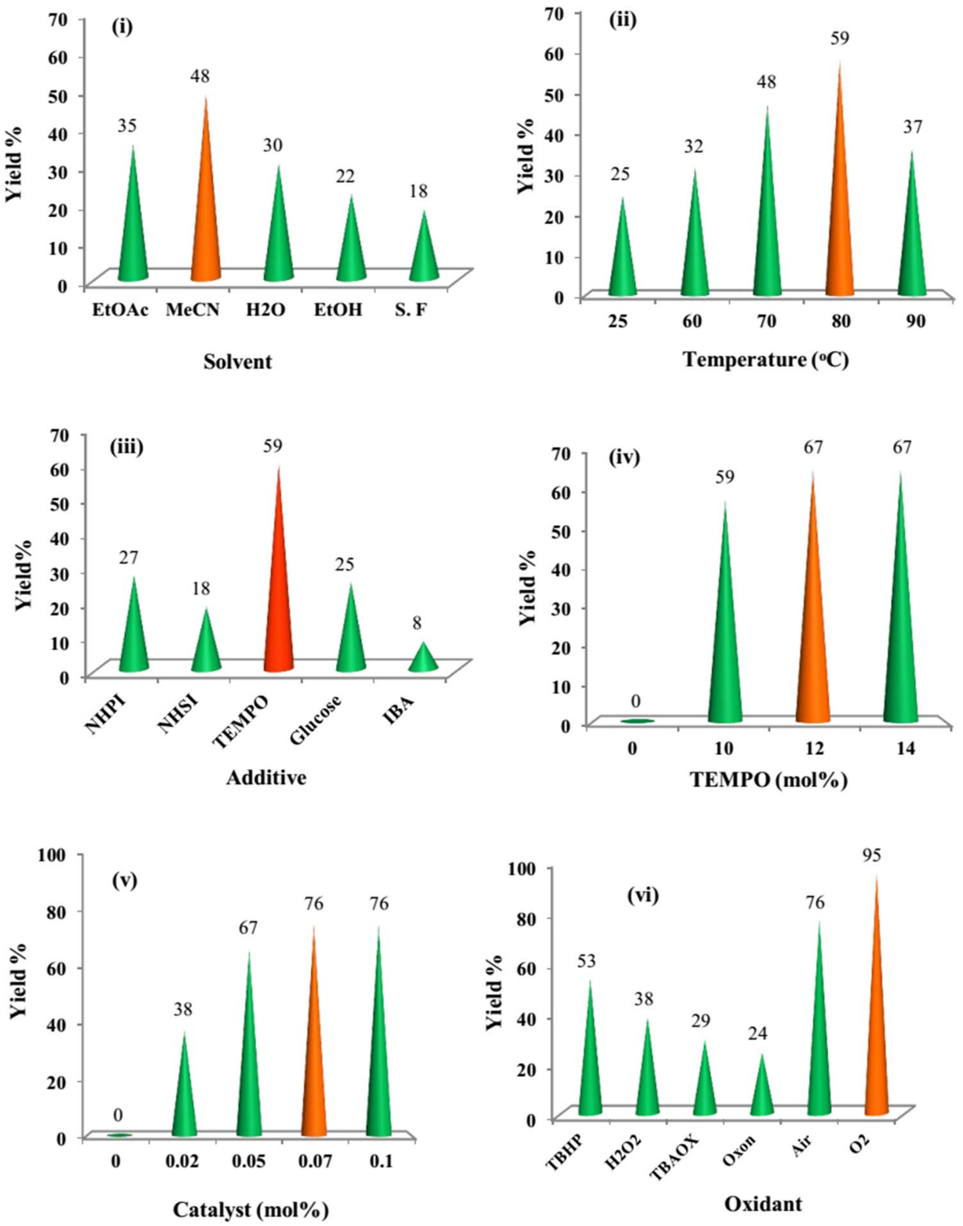


Fig. 6 The screening of **i** solvent nature **ii** temperature **iii** additive nature **iv** TEMPO **v** catalyst amount under air, after 6 h and **vi** oxidant after 6 h, except O_2 (yield reported after 3 h) in the oxidation of 4-chlorobenzyl alcohol (0.125 mmol) catalyzed by **[MNP@Chs/TAETA-Cu(II)]** nanohybrid. The yields were reported based on GC analysis

iso-butyraldehyde (IBA) and glucose were inferior additives for this oxidation system (Fig. 6iii, iv).

A survey of the results for the effect of catalyst amount presented in Fig. 6v, revealed that the reaction proceeded well with low catalyst loading of 0.07 mol%, meanwhile, more catalyst did no effect on the reaction performance. Finally, the effect of different common oxidants, such as O_2, H_2O_2, TBHP, TBAOX and Oxon® was assessed. Based on the data given in Fig. 6vi, the reaction rate and yield of oxidation product improved by using molecular oxygen (1 atm) instead of air, while, other oxidants used in this study, decreased the conversion and yield. As a result, the optimized reaction conditions were identified as 0.07 mol% of **[MNP@Chs/TAETA-Cu(II)]** catalyst, 12 mol% of TEMPO in 0.5 mL MeCN at 80 °C under oxygen stream (1 atm).

It should be noted that, the parent materials including MNPs, MNP@Chs, [MNP@Chs/TA] nanohybrid, [MNP@Chs/TAETA] nanohybrid as well as copper acetate exhibited poor activity toward alcohol oxidation under this condition confirming the superior catalytic activity of the as-prepared **[MNP@Chs/TAETA-Cu (II)]** nanohybrid (Fig. 7).

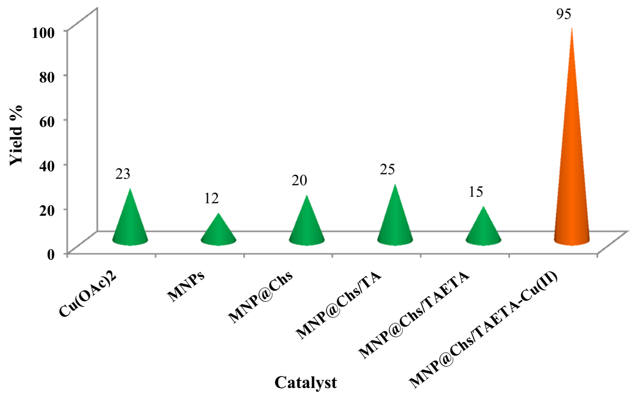


Fig. 7 Comparison of catalytic activity of **[MNP@Chs/TAETA-Cu (II)]** with parent materials in the oxidation of 4-chlorobenzyl alcohol (0.12 mmol) in the presence of TEMPO (12 mol%) in MeCN (0.5 mL) at 80 °C, under O_2 (1 atm) after 3 h

The general applicability of the title catalytic system was assessed by oxidation of various benzylic alcohols under the optimized conditions. As shown in Table 1, all the examined substrates produced the corresponding aldehydes and ketones in good to high yields. The selectivity of the procedure was notable, so that, no over-oxidation to the carboxylic acids and esters was observed for primary and secondary alcohols, respectively. The reactions affected by the stereoelectronic features of the substrates. Compared with bare benzyl alcohol, the molecules containing electron releasing groups on the phenyl ring such as –Me, $–CMe_3$ and –OMe demonstrated a slightly increased conversion rate (Table 1, entries 2, 3, 5). While, hindered *ortho* substituted benzyl alcohols (entry 4) as well as those substituted with electron withdrawing groups such as $–NO_2$ retarded the reaction and required longer reaction time to complete this transformation (Table 1, entries 8, 9). Secondary benzylic alcohols could also be converted to the desired ketones, successfully (Table 1, entries 10–13). To investigate the chemoselectivity of the method, cinnamyl alcohol and 4-methylsulfanylbenzyl alcohol were subjected to oxidation reaction (Table 1, entries 14, 15). The results indicated that the olefin moiety and sulfide group remained intact at both cases and related carbonyl compounds were obtained as sole products. It should be noted that a modest yield was observed in the oxidation of 2-adamantanol (Table 1, entry 16). Meanwhile, the attempts to oxidize linear aliphatic alcohols under different conditions failed.

3.3 Mechanism Study

The suggested mechanism is depicted in Scheme 3. Initially, the benzyl alcohol binds to the Cu(II) center of catalyst through hydroxyl group followed by deprotonation to form complex **B**. The coordination of TEMPO to complex **B** give rise to hydrogen abstraction from benzylic position of coordinated alcohol, generating active complex **C.** Releasing benzaldehyde from active complex **C**, produces Cu(I) counterpart of catalyst (**D**) which could be oxidized to Cu(II) complex as starting catalyst to restart new cycle.

Based on the data obtained in the optimization experiments, the efficiency of the title aerobic oxidation reaction was crucially dependent on the presence and amount of TEMPO, so that the reaction did not proceed in the absent of TEMPO. Moreover, radical scavengers such as 2,6-di-*tert*-butyl-4-methylphenol retarded the oxidation of 4-chlorobenzyl alcohol. Therefore, a radical mechanism maybe suggested for this aerobic oxidation system [39–41] (Scheme 3).

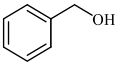
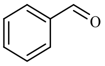
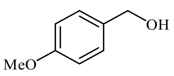
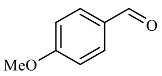
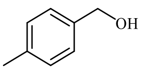
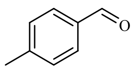
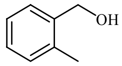
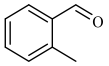
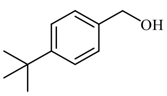
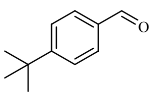
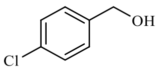
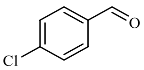
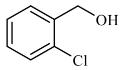
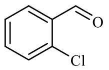
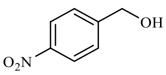
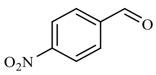
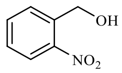
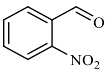
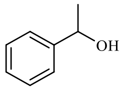
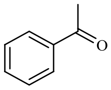
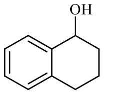
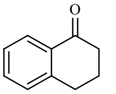
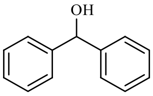
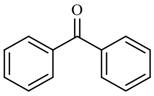
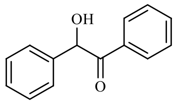
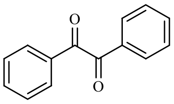
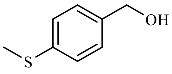
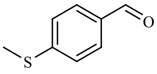
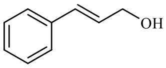
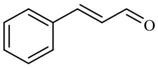
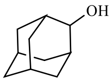
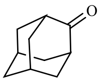
3.4 The Catalyst Reuse and Stability

The level of reusability and the catalytic activity are important factors for the application of heterogeneous systems. To this end, the recovery of the **[MNP@Chs/TAETA-Cu(II)]** nanohybrid was examined in the oxidation of 4-chlorobenzyl alcohol as model reaction. After completion of the reaction, the reaction mixture was cooled to ambient temperature and the nanohybrid was separated magnetically, washed with ethanol and dried under vacuum oven. In order to test the activity and the stability, the catalyst was recovered at least five times. The catalyst showed remarkable results without significant loss in catalytic activity (Fig. 8).

Next, we investigated the leaching of metal from the solid host. Based on the ICP-AES analysis, no leached Cu was observed after five consecutive runs. Moreover, a comparison of the FT-IR spectra of the fresh and reused catalyst revealed that the **[MNP@Chs/TAETA-Cu(II)]** nanohybrid preserved its structure during oxidation reaction (Fig. 9).

Table 2 shows the merit of this operationally protocol in comparison with previously reported Cu-based catalysis methods in the aerobic oxidation of benzyl alcohol as a model substrate. This comparison revealed the strong points of the presented catalytic oxidation system in terms of catalyst loading, reaction time, yield and especially, reaction conditions. A further notable advantage is easy recoverability by a simple magnet, eliminating the need of

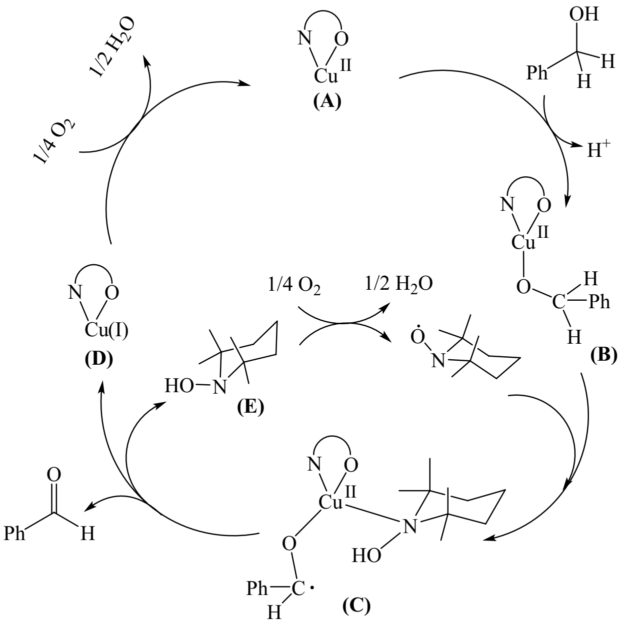
Table 1 Oxidation of benzylic alcohols using TEMPO/O_2 oxidative system catalyzed by **[MNP@Chs/TAETA-Cu(II)]** nanohybrid

Entry	Alcohol	Product[a]	Time (h)	Yield (%)[b]
1			2.45	90
2			2.30	95
3			2.30	92
4			3.15	75
5			2.45	93
6			3	95
7			3.20	100
8			7	68
9			6	49
10			3.40	100
11			5.30	82
12			4.30	92
13			5	78
14			4.40	89
15			6.50	78
16			8	31

The reactions were run with substrate (0.12 mmol), TEMPO (12 mol%) and cat (0.07 mol%) under O_2 (5–7 mL min^{-1}) at 80 °C in MeCN (0.5 mL)

[a] The products were identified by comparison with their authentic samples retention times of GC analysis and NMR spectra

[b] The selectivity of products were > 99% based on GC analysis



Scheme 3 Proposed mechanism for the aerobic oxidation of benzylic alcohols in the presence of **[MNP@Chs/TAETA-Cu (II)]** nanohybrid and TEMPO

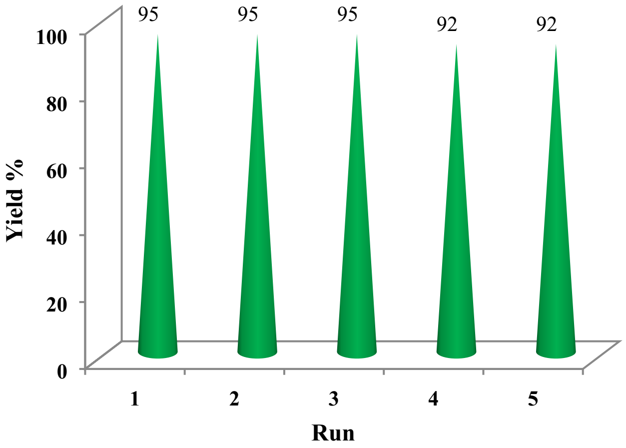


Fig. 8 Recycling of the catalytic system for the oxidation of 4-chlorobenzyl alcohol using the **[MNP@Chs/TAETA-Cu (II)]** nanohybrid, according to optimized conditions

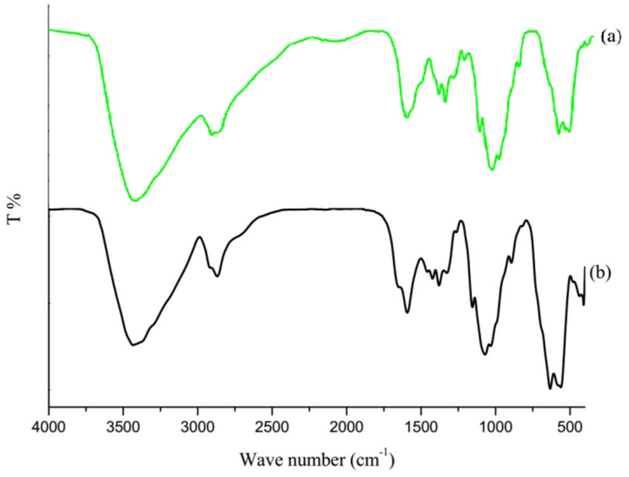


Fig. 9 Comparative FTIR spectra of fresh **[MNP@Chs/TAETA-Cu (II)]** nanohybrid (a) with used one (b) in aerobic oxidation of 4-chlorobenzyl alcohol

a large solvent volume for catalyst filtration at the end of reaction. These benefits, qualify all requirements of an efficient catalytic system for industrial implementation.

4 Conclusion

In summary, we have developed an efficient and clean protocol for aerobic oxidation of benzylic alcohols over a new magnetically recyclable **[MNP@Chs/TAETA-Cu(II)]** nanohybrid. The as-prepared catalyst displayed excellent selectivity and high catalytic activity for oxidation of primary and secondary benzylic alcohols to carbonyl compounds. The use of oxygen as an ideal oxidant, stability of nanocomplex, easily catalyst separation and recycling as well as preventing of by-products formation are salient features of this protocol, which make it cost effective and eco-friendly. Thus, our methodology could enable industrially important reactions to be carried out efficiently under safe and practically attainable conditions.

Table 2 Comparison of oxidative activity of **[MNP@Chs/TAETA-Cu (II)]** nanohybrid with other Cu-based catalysts in oxidation of benzyl alcohol

Entry	Catalyst	Catalyst (mol%)	Conditions	Time (h)	Yield (%)	Refs
1	**[MNP@Chs/TAETA-Cu (II)]**	**0.07**	**MeCN/TEMPO/O_2/80 °C**	**2.45**	**90**	**This work**
2	$CuFe_2O_4$	10	H_2O/TEMPO/O_2/100 °C	24	95	[42]
3	[Cu(II)L_2(DMF)$_2$]-HMS^a	20 mg	Toluene/TEMPO/O_2/80 °C	16	80	[43]
4	[Cu(AcO)$_2$(py)]$_2$	1.5	scCO_2/TEMPO/O_2/80 °C	12	48	[44]
5	PS^b–PEG-TD$_2$^{c}–Cu(OAc)$_2$	20	Heptan/TEMPO/air/80 °C	24	41	[45]
6	MCM-41-bpy-CuI	1	EtOH/NH_3/TEMPO/air/50 °C	22	91	[46]
7	[Cu(DPIO)$_2$(SiF$_6$)]^d	3.5	$C_2D_2Cl_4$/TBN/O_2/80 °C	24	94	[47]
8	bis(3,5-di-^{t}Bu-salicylaldimine)cu(II)	0.66	Toluene/TEMPO/O_2/60 °C	1	85	[48]
9	CuO-ZnO	70 mg	H_2O/Cs_2CO_3/O_2/100 °C	1.3	92	[49]
10	$CuCl_2$@MOF-NH_2	1	MeCN/TEMPO/air/70 °C	6	98	[50]
11	Cu-MOF-74	1.2	MeCN/TEMPO/O_2/70 °C	12	89	[51]
12	Fe_3O_4/Cu_3(BTC)$_2$^{e}	0.4	MeCN/TEMPO/Na_2CO_3/O_2/75 °C	6	99	[52]

Our work in this table is highlighted in bold

[a] 2D-hexagonal mesoporous silica

[b] Polystyrene

[c] triazine-based polyethyleneamine dendrimer

[d] 4,7-bis(4-pyridyl)-1,1,3,3-tetramethylisoindolin-2-yloxyl

[e] 1,3,5-benzenetricarboxylate

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Compliance with Ethical Standards

Conflict of interest The author declares no conflict of interest.

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