

Magnetic nanoparticles supported Cu²⁺ and Ce³⁺ complexes: toward the chemical and electrochemical oxidation of alcohol and sulfide derivatives

Taiebeh Tamoradi, et al. [full author details at the end of the article]

Received: 15 February 2019 / Accepted: 28 April 2019 © Springer Nature B.V. 2019

Abstract

Heterogeneous catalysts are more prominent rather than homogenous catalysts since they are simply separated from products. To improve and develop heterogeneous catalysts, two core–shell magnetic nanocatalysts are prepared by anchoring of Cu and Ce complexes on the surface of Fe_3O_4 , then the efficiency of the obtained catalysts are tested toward both chemical and electrochemical oxidation of sulfide and alcohol derivatives. Characterization of mentioned catalysts was performed by using FT-IR, XRD, EDX and SEM. The obtained results confirm that the reported method has outstanding advantages such as short reaction time, high yield, easy operation, easy separation, inexpensive and non-toxic material and chemical and thermal stability.

Graphical abstract



Keywords $Fe_3O_4 \cdot Cu \cdot Ce \cdot Sulfide \cdot Alcohol \cdot Chemical oxidation \cdot Electrochemistry$

Introduction

In the last decade, vast research interest has lead to performing oxidation reactions because of their applications in many pharmaceutical, biological active molecules and chemical synthesis. On the other hand, oxidation of sulfides and alcohols are an important class of oxidation reactions in organic synthesis because of their properties and applications in many biological active molecules, chemical synthesis and pharmaceuticals such as lansoprazole, fipronil, acetaminophen, and pantoprazole. Therefore, there is a great interest to synthesis of abovementioned compounds with an economic and simple pathway [1–4]. In connection with this topic, heterogeneous catalysts contain various metal complexes (Fe, Co, Ni) supported on nanoparticles and the mesoporous were recently employed for the oxidation of sulfides and alcohols [5–10]. In line with this, there are reports of metal-based catalysts for oxidation of alcohols and sulfides using H_2O_2 as the oxidant.

Among the enormous variety of oxidizing reagents, H₂O₂ is suggested as a sustainable green because traditional reagents have disadvantages such as the use of stoichiometric amounts of oxidant, the formation of toxic waste products, and rendering impossible the reusability of the catalyst. Also, among various supports, magnetic nanoparticles are considered as ideal supports because of their simple recovery [11-13]. In recent years, attention focused on the Fe₃O₄ because such nanoparticles have much better magnetic properties than other magnetic nanoparticles. Notably, transfer of electrons between Fe²⁺ and Fe³⁺ on octahedral sites in Fe₃O₄ inverse cubic spinal structure caused unique electrical and magnetic properties in these nanoparticles. It should be mentioned that properties of Fe₃O₄ arise from their size and structure of particles. These nanoparticles are widely studied because of their application in the field of biomedical, corrosion protective, catalyst, as anticancer agent, pigments in paints and coating [14–17]. In spite of the great attention to the oxidation reactions in recent years, oxidation of alcohol and sulfide have rarely been done in the presence of the catalyst heterogeneous based on Cu [18-21]. Also, up to date, the reports about oxidation of alcohol and sulfide were not done in the presence of heterogeneous catalysts based on Ce. On the other hand, electrocatalytic conversion of organic compounds to useful chemicals is the eco-friendly vision in the green and low-cost synthesis approach [22]. Herein, we have simply immobilized Cu and Ce complexes on the surface of coated Fe₃O₄ magnetic nanoparticles with aspartic acid as the green and available ligand. Then, prepared catalysts were characterized by physical techniques and tested in the oxidation of alcohols and sulfides. The offered protocol has outstanding advantages such as easy separation of catalyst from mixed reaction, high yield, reaction short time, the use of green and available materials, etc.

Experimental

Materials

Used materials in this work such as metal ions, aspartic acid, all reagents and all solvents are purchased from Merck, Flucka or Aldrich and used without further purification.

Measurement

Fourier transform infrared (FTIR) spectra and powder X-ray diffraction (XRD) measurements of samples were recorded using with a Bruker VERTEX 80 v model using the KBr pellets and Co radiation source with a wave length=1.78897 Å, 40 kV, respectively. TGA measurement and elemental analysis of all samples were performed by a Shimadzu DTG-60 instrument and energy-dispersive X-ray spectroscopy (EDAX, TSCAN), respectively. The amount of metals (Cu and Ce) and the external morphology of catalyst were investigated by inductively coupled plasma-optical emission spectrometry (ICP-OES) and FESEM-TESCAN MIRA3.

Preparation of Fe_3O_4 @Aspartic-M (M = Cu and Ce)

The 1 g of Fe_3O_4 nanoparticles were synthesized by the reported methods in the literature and then reacted with 1.5 mL of (3-Chloropropyl)trimethoxysilane in hexane under reflux conditions for 24 h. The obtained back powder was separated with an external magnetic field and dried at 60 C and then reacted with 1.5 g of aspartic acid in 50 mL of toluene under a reflux reaction for 24 h. Finally, Fe_3O_4 @Aspartic was separated from a mixed reaction by an external magnetic field. Then, in order to have synthesis of Fe_3O_4 @Aspartic-M (M=Cu and Ce) catalyst, 2.5 mmol metal ions (Cu or Ce) was added to 1 g of Fe_3O_4 @Aspartic in ethanol for 16 h. Finally, prepared Fe_3O_4 @Aspartic-M (M=Cu and Ce) was separated from a mixed reaction by an external magnetic field and washed with ethanol.

General procedure for the oxidation of sulfides

A mixture containing sulfide (1 mmol), H_2O_2 (0.5 mL) and catalyst (0.007 g) was stirred at room temperature under solvent-free conditions. After completion of the reaction (tested by TLC), catalyst was easily separated by an external magnet and sulfoxide derivatives were extracted with ethyl acetate to give the pure products.

General procedure for the oxidation of alcohols

A mixture containing of 1 mmol aromatic alcohols (1 mmol), H_2O_2 (0.7 mL) and catalyst (0.015 g) in acetonitrile solvent was stirred at room temperature. After

completion of the reaction (tested by TLC), catalyst was easily separated by an external magnet and aldehyde derivatives were extracted with acetonitrile to give the pure products.

Electrocatalytic oxidation of sulfide and benzyl alcohol

The electrocatalytic oxidation of sulfide and alcohols was tested by μ Autolab type III in an electrochemical cell containing a three electrode system, an Ag/AgCl as reference electrode, a platinum wire as counter electrode and glassy carbon electrode (GCE) as working electrode for support of nanocatalyst. The electrochemical reactions were tested in both acetonitrile and aqueous 1 M KOH solutions.

Results and discussion

Catalyst preparation

In order to design a recoverable catalyst system for oxidation sulfides and alcohols, according to Scheme 1, magnetic nanoparticles were coated with Cu and Ce complexes.

Catalyst characterization

The successfully immobilization of Cu and Ce complexes on the surface of Fe_3O_4 was confirmed by using Fourier transform infrared spectroscopy, scanning electron



Scheme 1 General route for the fabrication of $M@Fe_3O_4$ (M=Cu and Ce)

microscopies, X-ray diffraction, energy-dispersive X-ray spectroscopy, and a vibrating sample magnetometer.

In order to investigate the morphology of prepared samples, we used SEM analysis in which prepared nanoparticles have spherical and homogeneous morphology in these images (Fig. 1).

The energy-dispersive X-ray spectroscopy (EDX) analysis of $Cu@Fe_3O_4$ (a) and $Ce@Fe_3O_4$ (b) indicated the presence of N, O, C, Si, Cu species and N, O, C, Si, Cu, Ce species in the mentioned catalysts in which was confirmed the immobilization Cu and Ce complexes on the surface of Fe_3O_4 (Fig. 2).

FT-IR spectra of Fe_3O_4 , chloro-functionalized Fe_3O_4 , Cu@Fe_3O_4 and Ce@ Fe_3O_4 is a confirmation for the synthesis of the mentioned compounds (Fig. 3).



Fig. 1 SEM images of $Cu@Fe_3O_4$ (a) and $Ce@Fe_3O_4$ (b)



Fig. 2 EDX spectrum of $Cu@Fe_3O_4$ (a) and $Ce@Fe_3O_4$ (b)



Fig. 3 FT-IR spectra of Fe_3O_4 (a), chloro-functionalized Fe_3O_4 (b), $Fe_3O_4@Aspartic$ (c) $Ce@Fe_3O_4$ (d) and $Cu@Fe_3O_4$ (e)

The presence of a sharp peak at approximately 578 cm⁻¹ at all samples is dependent to the Fe–O band of the spinel structure. The characteristic absorption band at 2850–2965 cm⁻¹ is assigned to C–H stretching vibration in Fig. 3b–e, which could



Fig. 4 The XRD patterns of $Cu@Fe_3O_4(a)$ and $Ce@Fe_3O_4(b)$

due to functionalization of Fe_3O_4 with 3-choloropropyl) trimethoxysilane. Also, the connection of aspartic ligand of the surface of Fe_3O_4 was confirmed by the presence of the C=O strong absorption at approximately 1600 cm⁻¹.

The structure of cubic inverted spinal of the immobilized chloro-functionalized Fe_3O_4 with Cu and Ce complexes was confirmed by XRD patterns (Fig. 4) and the presence of diffraction peaks of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) in the mentioned catalysts is due to green degredation of Fe_3O_4 nanoparticles [23].

Catalytic studies

In order to test catalytic activity of prepared catalysts, we decided to examine the catalyst in the oxidation reactions such as oxidation of sulfide and alcohol derivatives (Scheme 2). Firstly, the amount of catalyst is optimized for the oxidation of methyl phenyl sulfide (Table 1). We selected the $Cu@Fe_3O_4$ catalyst for the synthesis of methyl phenyl sulfoxide in the presence of 0.5 mL of H_2O_2 in the solvent-free conditions. It should be noted that solvent-free conditions were usually selected as optimization conditions in the synthesis of sulfoxide derivatives. Also, in order to extend the scope of this work, we synthesized many sulfide derivatives in the presence of the obtained optimization conditions (Table 2).

In order to have optimization of conditions for the oxidation of alcohol derivatives, various amounts of $Cu@Fe_3O_4$ catalyst were optimized for the oxidation of 1 mmol benzyl alcohol in the presence of H_2O_2 (0.7 mL) as green oxidant in



Table 1 Optimization of reaction conditions for the synthesis of methyl phenyl sulfoxide in the presence of $Cu@Fe_3O_4$

Entry	Solvent	Type of catalyst	Amount of cata- lyst (mg)	Time (min)	Yield ^a (%)
1	Solvent-free	Fe ₃ O ₄	7	120	Trace
2	Solvent-free	Aspartic@Fe ₃ O ₄	7	120	Trace
3	Solvent-free	Cu@Fe ₃ O ₄	3	100	74
4	Solvent-free	Cu@Fe ₃ O ₄	5	80	80
5	Solvent-free	Cu@Fe ₃ O ₄	7	45	97
6	Solvent-free	Cu@Fe ₃ O ₄	9	40	97

^aIsolated yield

acetonitrile. Then, various solvents were tested on the reaction results. Finally, observation results are summarized in Table 3. It should be noted that many aldehyde derivatives were also synthesized in the presence of the obtained optimization conditions (Table 4).

After the investigation of catalytic activity of $M@Fe_3O_4$ (M=Cu and Ce), the reusability of mentioned nanoparticles was tested in the synthesis of methyl phenyl sulfoxide and benzaldehyde in which the results of this study are shown in Figs. 5 and 6.

Entrv	Substrate	Product	Time	Time (min)		Yield (%) ^a	
			Cu	Ce	Cu	Ce	
1	S ^s	2a	45	40	97	95	
2	~~~	2b	75	85	89	91	
3	\bigcirc	2c	65	75	92	93	
4		2d	60	75	88	85	
5		2e	50	60	90	92	

Table 2 Oxidation of sulfide using H_2O_2 in presence of M@Fe₃O₄ (M=Cu and Ce)

^aIsolated yield

Table 3 Optimization of reaction conditions for the synthesis of benzaldehyde in the presence of Cu@ $\rm Fe_3O_4$

5 1					
Entry	Solvent	Type of ctalyst	Amount of catalyst (mg)	Time (min)	Yield ^a (%)
1	Acetonitrile	Fe ₃ O ₄	15	110	26
2	Acetonitrile	Aspartic@Fe ₃ O ₄	15	110	29
3	Acetonitrile	Cu@Fe ₃ O ₄	15	110	67
4	Acetonitrile	Cu@Fe ₃ O ₄	18	110	69
5	Acetonitrile	Cu@Fe ₃ O ₄	13	110	52
6	Acetonitrile	Cu@Fe ₃ O ₄	11	110	33
7	Solvent-Free	Cu@Fe ₃ O ₄	15	110	Trace
8	H ₂ O	Cu@Fe ₃ O ₄	15	110	21
9	Dichloromethane	Cu@Fe ₃ O ₄	15	110	18

^aIsolated yield

Electrocatalytic studies

As mentioned above, electrochemical conversions of chemical compounds at heterogeneous catalysts into desired materials can be a good candidate on the way to lowcoast and rapid synthesis approaches, where it not required to have the additional

Entry	Substrate	Product	Yield (%) ^a	
			Cu	Ce
1	ОН	4a	67	62
2	СІ	4b	61	63
3	Н3СО	4c	48	45

Table 4 Oxidation of alcohol using H_2O_2 in presence of M@Fe₃O₄ (M=Cu and Ce)

^aIsolated yield



Fig. 5 Reusability of $Cu@Fe_3O_4(a)$ and $Ce@Fe_3O_4(b)$ in the synthesis of methyl phenyl sulfoxide

homogenous reagent (such as H_2O_2 that we have used for chemical conversions of sulfide and alcohols) in the progress of catalytic reaction. Herein, the usability of asprepared catalysts toward oxidation of sulfide and non-aliphatic alcohols via electrochemistry was also investigated. Figures 7 and 8 show the comparison of cyclic voltammograms recorded by glassy carbon electrodes modified by pristine Fe₃O₄ and Cu/Ce-loaded on Fe₃O₄ nanoparticles in the absence (dark line) and presence (pink line) of 50 µM benzyl alcohol (Fig. 7) or 50 µM sulfide (Fig. 8). In the case of benzyl alcohol, it is oxidized by pristine Fe₃O₄ in acetonitrile (CAN) and a catalytic current ca. ~3 A per gram of catalyst (A g⁻¹) can be seen. After modification of Fe₃O₄ by



Fig. 6 Reusability of $Ce@Fe_3O_4$ (a) and $Ce@Fe_3O_4$ (b) in the synthesis of benzaldehyde



Fig.7 Electrocatalytic (cyclic voltammogram with scan rate 0.05 V s⁻¹) oxidation of benzyl alcohol by Fe_3O_4 nanoparticles and after loading of Cu⁺² and Ce⁺³ on it, in acetonitrile (containing 0.01 M ammonium hexafluorophosphate as electrolyte) and water (1 M KOH) solvents

a complex containing Cu⁺², the catalytic current is slightly increased. In the meantime, Ce⁺³ complex @Fe₃O₄ exhibits a higher current density rather than Cu⁺² complex @Fe₃O₄. On the contrary, Cu⁺² complex @Fe₃O₄ displays the catalytic activity also in aqueous solution, while it cannot be seen for the Ce⁺³ complex @Fe₃O₄, indicating that the higher activity of Ce⁺³ complex is in organic solvent rather than aqueous solution, and it is completely vice versa in the case of Cu⁺² complex.



Fig.8 Electrocatalytic (cyclic voltammogram with scan rate 0.05 V s⁻¹) oxidation of sulfide by Fe_3O_4 nanoparticles and after loading of Cu^{+2} and Ce^{+3} on it, in acetonitrile (containing 0.01 M ammonium hexafluorophosphateas electrolyte) and water (1 M KOH) solvents

Entry	Substrate	Catalyst	Time (min)	Yield (%) ^a
1	Methylphenylsulfide	O(IV)-MCM-41	240	95 [<mark>2</mark> 4]
2	Methylphenylsulfide	VO-salen-MCM-41	120	95 [25]
3	Methylphenylsulfide	Ni-salen-MCM-41	156	90 [26]
4	Methylphenylsulfide	$VO_2F(dmpz)_2$	300	95 [27]
7	Methylphenylsulfide	Cu@Fe ₃ O ₄	45	97 [This work]
8	Methylphenylsulfide	Ce@Fe ₃ O ₄	40	95 [This work]
9	Benzaldehyde	MOF-253-Ru7	180	90 [2]
10	Benzaldehyde	AuCl	600	100 [28]
11	Benzaldehyde	FS-4	480	79.8 [19]
14	Benzaldehyde	Cu@Fe ₃ O ₄	110	69 [This work]
15	Benzaldehyde	Ce@Fe ₃ O ₄	110	67 [This work]

Table 5 Comparison of $Cu@Fe_3O_4$ and $Ce@Fe_3O_4$ in the oxidation of methylphenylsulfide and benzaldehyde with previously reported procedure

^aIsolated yields

The above explanations are also seen in electrocatalytic oxidation reaction of sulfide. As can be seen in Fig. 8, in ACN solvent Cu^{+2} complex@Fe₃O₄ display about 2.2 and 2.9 times higher catalytic activity rather than Cu^{+2} complex@Fe₃O₄ and pristine Fe₃O₄, respectively. Whereas, in KOH aqueous solution, Cu^{+2} complex@Fe₃O₄ has displayed two fold higher catalytic current than Cu^{+2} complex@Fe₃O₄ and Cu^{+2} Fe₃O₄. One reason for these observations may be referred to

soft and hardness of metal ions. Ce^{+3} and OH^- are classified as hard ions, while Cu^{+2} ions have a borderline soft and hardness properties. Consequently, Ce^{+3} ions strongly interact with OH^- in aqueous solution, and its catalytic activity is decreased. On the contrary, organic or aqueous solution may have a similar solvation effect on the prepared Cu^{+2} complex, and consequently, the catalytic activity is just slightly changed in KOH aqueous or ACN solutions.

Comparison of the catalyst

In order to show the high efficiency of prepared catalyst, catalytic activity of Cu@ Fe_3O_4 and Ce@Fe_3O_4 in the synthesis of methyl phenyl sulfoxide and benzaldehyde compared with other catalysts in the literature in which this comparison shows advantages such as easy separation of catalyst from mixed reaction, high yield, high thermal and mechanical stability, short reaction time, easy operation, the use of green and available materials, etc (Table 5).

Conclusion

In summary, two nanocatalysts were designed by anchoring of Cu^{2+} and Ce^{3+} complexes on the surface of Fe_3O_4 as a magnetic support. The oxidation of alcohol and sulfide derivatives was tested in the presence of designed catalysts in which high catalytic activity was shown for the mentioned catalysts. The perspective of electrochemical oxidation of these substances can be solvent-free in a two electrode system.

Also, the use of non-toxic and available materials, the use of short procedure and high yield, recoverable catalyst and simple operation are outstanding benefits of the proposed protocol.

Acknowledgements The authors are deeply grateful to University of Kurdistan University for financial support of this research project.

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Affiliations

Taiebeh Tamoradi^{1,3} · Aso Navaee¹ · Abdollah Salimi¹ · Seyedeh Masoumeh Mousavi² · Mohammad Ghadermazi¹ · Hojat Veisi³

- ⊠ Taiebeh Tamoradi t.tabss@yahoo.com
- Aso Navaee aso.navaee@gmail.com
- ¹ Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj, Iran
- ² Department of Environmental Planning, Tehran University, Tehran, Iran
- ³ Department of Chemistry, Payame Noor University, Tehran, Iran