Magnetic CuFe₂O₄ nanoparticles as an efficient catalyst for the oxidation of alcohols to carbonyl compounds in the presence of oxone as an oxidant

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Nanomagnetic CuFe₂O₄ was used as an efficient, stable, and reusable catalyst for selective oxidation of alcohols to their corresponding carbonyl compounds using oxone (potassium hydrogen monopersulfate) as oxidant in the presence of water as solvent at room temperature. Primary and secondary alcohols gave the corresponding products in good yields. The oxidation of various primary and secondary alcohols was also examined and the corresponding products were obtained with good yields. The catalyst was investigated with XRD, SEM, ICP and IR techniques. Furthermore, the catalyst could be easily recovered and reused several times without loss of activity.

Keywords: Nanomagnetic catalyst, Copper ferrite, Oxidation, Alcohols, Carbonyl Compounds, Oxone.

INTRODUCTION

The oxidation of alcohols to their corresponding carbonyl compounds involves a basically important functional group transformation and takes a chief position in new synthetic organic chemistry [1]. They have normally been oxidized in noncatalytic ways with stoichiometric oxidants such as chromium and manganese compounds in the attendance of strong mineral acids, which produce enormous amounts of toxic metal salts as a waste [2]. Thus, the development of green oxidation systems using less poisonous catalysts, oxidants, and solvents became a crucial target for catalysis [3]. Although a variety of different catalytic systems for catalytic oxidation of alcohols has been developed, there is a growing interest in the search for new efficient metal catalysts for this concern [4-7]. Recently, sustainability and environmental friendliness are major elements in catalysis. While catalysis is an important process for the improvement of starting materials, fine chemicals and pharmaceuticals, green catalysis needs environmentally friendly catalysts which can be easily removed from the reaction media and used again many times with very high efficiency [8]. Nanoparticles display high catalytic activity and chemical selectivity under mild conditions [9]. In some reactions, the large surface area-to-volume ratio of metal oxide nanoparticles is mainly responsible for their catalytic performance [10]. In heterogeneous reactions, tedious methods like centrifugation and filtration are utilized to recover catalysts and end in loss of solid catalyst in the process of separation. Magnetic separation supplies a convenient method to remove and recycle magnetized species by utilizing an appropriate magnetic field [11–13]. Magnetic spinel ferrite nanocrystals are considered as one of the most significant inorganic materials due to their electronic, electrical, optical, magnetic and catalytic features that are significantly different from those of their bulk counterparts [14–15]. Copper ferrite nanomaterial is one such reusable catalyst which shows high catalytic activity in organic synthesis [16].

Herein, copper ferrite nanoparticles were synthesized *via* the auto-combustion assisted sol-gel method [17-18]. We showed that nanomagnetic CuFe₂O₄ is an active and reusable catalyst through magnetic separation for oxidation of alcohols with oxone in the presence of water at room temperature (Scheme 1).
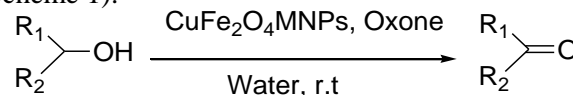
$$R_1,R_2 = \text{Aryl, Alkyl, H}$$

Scheme 1. Alcohols oxidation in the presence of nanomagnetic catalyst at room temperature

EXPERIMENTAL
General

Ferric nitrate nonahydrate Fe(NO₃)₃.9H₂O, copper nitrate trihydrate Cu(NO₃)₂.3H₂O, citric acid C₆H₈O₇, aliphatic and benzylic alcohols were

purchased from Merck (Darmstadt, Germany) and Fluka (Switzerland) and used without further purification. The IR spectra were measured on a JASCO 6300 FT-IR spectrometer (KBr disks). The structural properties of the synthesized nanoparticles were studied by X-ray powder diffraction (XRD) on an X'pert-PRO advanced diffractometer using Cu (Kα) radiation (wavelength: 1.5406 Å), operated at 40 kV and 40 mA at room temperature over the 2θ range from 20 to 70º. The particulate morphology was characterized by scanning electron microscopy (Model: 1455VP, LEO Co., England). The disc was coated with gold in an ionization chamber. Elemental analyses were performed using inductively coupled plasma optical emission spectroscopy (ICP-OES, Model: VISTA-PRO). TLC and GC were used to monitor the reactions. The aliphatic products were detected by GC-FID (VARIAN C-P-3800 with FID detector, column CP-Sil 5 CB 30m×0.32mm).

Preparation of CuFe₂O₄ MNPs in aqueous solution

Copper ferrite nanoparticles were synthesized *via* the auto-combustion assisted sol-gel method from Cu^{2+} and Fe^{3+} ions (molar ratio 1:2) in ammonia solution [17,18]. Briefly, $Fe(NO_3)_3.9H_2O$, $Cu(NO_3)_2.3H_2O$ and the chelating agent were dissolved in distilled water. The molar ratio of metal nitrate to citric acid was 1:1. The pH value was adjusted to 7 by dropwise adding ammonia solution (28%) to the reaction mixture under constant stirring. Then, the solution was evaporated on a water bath (60 ºC) to form a sticky gel. The temperature was increased to 80 ºC in order to obtain a thick gel. The gel was kept on a hot plate for auto-combustion and the temperature was increased to *ca.* 200 ºC. A large amount of gases (CO_2, H_2O, and N_2) was released and auto-combustion occurred giving rise to a black ferrite powder. The powder was washed three times with distilled water and acetone and was isolated in a magnetic field.

General procedure for the oxidation of alcohol

Alcohol (1 mmol), water (2 mL) and 6 mol % of nanomagnetic CuFe₂O₄ (14 mg) were added to a round-bottomed flask. The mixture was stirred for two minutes. Then, oxone (0.7 mmol) was added in three portions for 15 min. The mixture was stirred at room temperature. The reaction was followed by TLC (EtOAc-cyclohexane, 2:10). After the completion of the reaction, the product was extracted in dichloromethane. The solvent was evaporated under reduced pressure to give the corresponding pure aromatic products. Purification of the residue using flash column chromatography (silica gel) provided the pure carbonyl compounds. The products were identified by IR spectra. The aliphatic products in dichloromethane were dried using anhydrous MgSO₄ and were detected by GC-FID by comparison with standard samples of the corresponding alcohols and carbonyl compounds. The GC yields of the aliphatic products were calculated based on their gas chromatograms.

RESULTS AND DISCUSSION

Characterization of the catalyst

The FT-IR spectrum of the CuFe₂O₄ MNPs is presented in Fig. 1. A broad absorption band at about 3440 cm⁻¹ represents a stretching mode of H₂O molecules and indicates that a large number of OH groups are present on the surface of the MNPs [19]. In the range of 1000–400 cm⁻¹, two broad metal–oxygen bands are observed. A metal–oxygen absorption band typical for the spinel structure of the ferrite at ~580 cm⁻¹ was observed. This band strongly suggests intrinsic stretching vibrations of the metal (M ↔ O) at the tetrahedral site [20-21], whereas the lowest band, usually observed in the range 450–400 cm⁻¹, is assigned to octahedral metal stretching [22-24]. Fig. 2 shows the XRD pattern of the CuFe₂O₄ MNPs. Generally, XRD can be used to characterize the crystallinity of nanoparticles, and it gives the average diameters of all nanoparticles. The results indicate that the discernible peaks in Fig. 2 [18, 25] correspond to a cubic spinel structure of copper iron oxide (JCPDS card No. 01-077-0010). The diameter of the CuFe₂O₄ MNPs determined by the Debye-Scherrer equation using XRD data (D = 0.94 λ / B Cos θ) was 57.9 nm. From the ICP- OES results, the atomic ratio of Cu-Fe was found to be 0.57, which is close to that of CuFe₂O₄ and 26.5% w/w is copper. The SEM analysis suggests that the CuFe₂O₄ MNPs are nanocrystalline and their shape is irregular spherical (Fig. 3). These results are in good agreement with the XRD analyses.

Optimization of alcohol oxidation conditions

We tried to convert 2-chlorobenzyl alcohol (1 mmol) to 2-chlorobenzaldehyde, as a model reaction in the presence of CuFe₂O₄ as a nanomagnetic catalyst (12 mg) and oxone (1 mmol added in three steps) in various solvents (2mL) at r.t. and the results are given in Table 1. The best result was achieved in the presence of water (Table 1, entry 4).
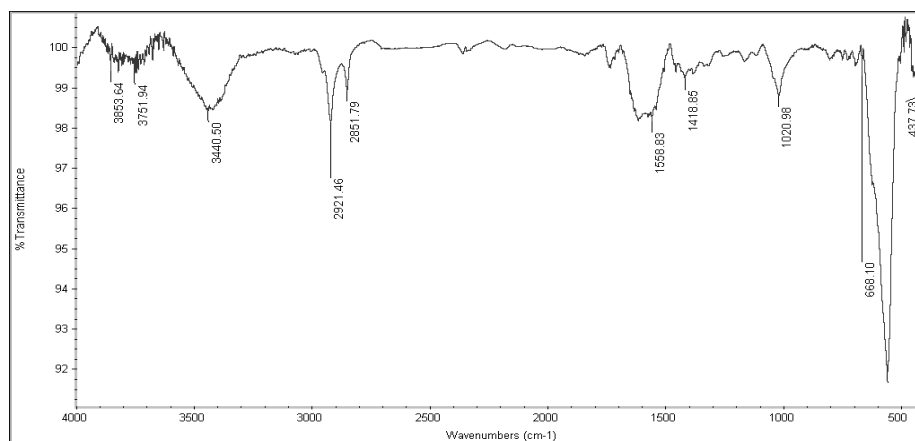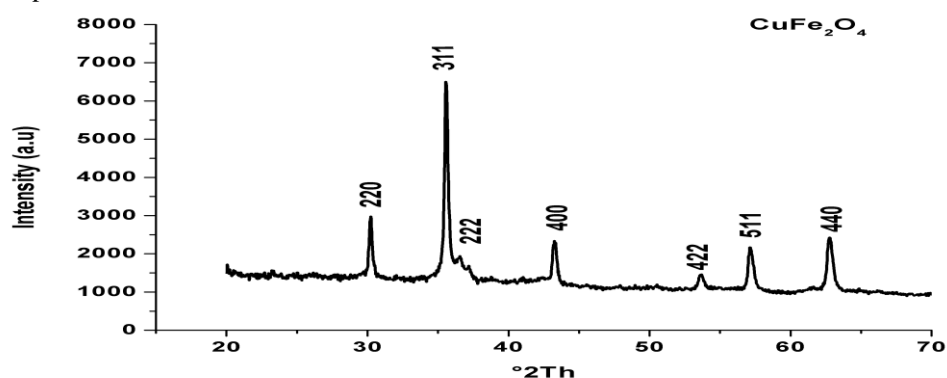
Fig. 1. FT-IR spectrum of the CuFe$_2$O$_4$ MNPs

Fig. 2. XRD pattern of the CuFe$_2$O$_4$ MNPs
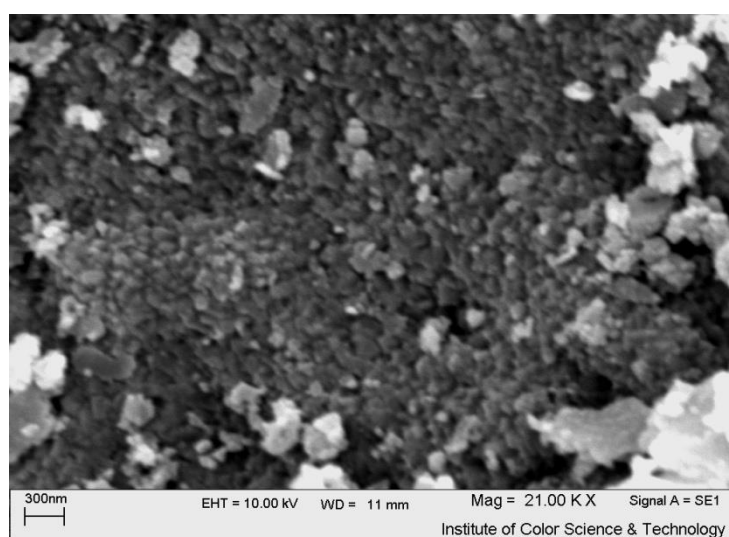

Fig. 3. SEM image of the CuFe$_2$O$_4$ MNPs

Table 1. Conversion of 2-chlorobenzyl alcohol to 2-chlorobenzaldehyde in different solvents with oxone in the presence of CuFe$_2$O$_4$ MNPs catalyst at r.t.

Entry	Solvent	Yield (%)	Time (min)
1	Dichloromethane	15	90
2	Cyclohexane	trace	90
3	Acetonitrile	22	90
4	Water	65	90
5	Ethanol	trace	90
6	Dry toluene	trace	90
7	Ethyl acetate	10	90

We also studied the oxidation of 2-chlorobenzyl alcohol to 2-chloro benzaldehyde with other oxidants in the presence of nanomagnetic CuFe$_2$O$_4$ catalyst in water at room temperature. These results showed that a higher yield was achieved with oxone as oxidant (Table 2, entry 3). We observed that in the absence of oxidant (in nitrogen atmosphere), 2-chlorobenzyl alcohol was not oxidized with this system, even for a long reaction time.

Catalyst and oxidant amounts were also optimized. The results showed that 14 mg of catalyst (6 mol%) and 0.7 mmol of oxidant were the best amounts for the oxidation of 1 mmol of alcohol (Table 3 and 4). In these reactions, the aldehyde selectivity was very high (>99%). No competing reaction such as overoxidation of aldehydes to the corresponding carboxylic acids was observed in any of the cases under the above conditions, but the reaction produced a byproduct (carboxylic acid) at high temperatures (>40 °C).

Application scope

The reaction conditions, which were optimized for 2-chlorobenzyl alcohol, can be easily applied to various primary and secondary alcohols. As indicated in Table 5, the CuFe₂O₄ MNPs catalyst showed high activity/selectivity and excellent reusability in oxidation processes. In most cases, the aldehyde selectivity was quite high (>99%). The oxidation of various benzylic alcohols gave carbonyl compounds in high yields and short reaction times. The electron withdrawing groups dramatically reduced the reaction rate (entry11) and the electron donor substituted group in the benzene ring of benzylic alcohols accelerated the reaction rate (entry14).

The oxidation times for aliphatic alcohols were fairly long (entries 17-19). No competing reaction such as overoxidation of aldehydes to the corresponding carboxylic acids was observed in any of the cases under the above conditions.

Table 2. Oxidation of 2-chlorobenzyl alcohol using various oxidants in water in the presence of CuFe₂O₄ MNPs catalyst at r.t.

Entry	Oxidizing agent (1mmol)	Yield (%)	Time (min)
1	H_2O_2	20	90
2	O_2 atmosphere	trace	90
3	Oxone	65	90
4	-	0	90

Table 3. Oxidation of 2-chlorobenzyl alcohol with oxone (1mmol) and different amounts of CuFe₂O₄ MNPs in water at r.t

Entry	Amount of nanomagnetic CuFe₂O₄ catalyst (mol%)	Yield (%)	Time (min)
1	10	86	90
2	7	85	90
3	6	86	90
4	5	65	90
5	4	48	90
6	0	20	90

Table 4. Oxidation of 2-chlorobenzyl alcohol (1mmol) in water with different amounts of oxone in the presence of CuFe₂O₄ MNPs catalyst (6 mol%) at r.t

Entry	Amount of oxone (mmol)	Yield (%)	Time (min)
1	1	86	90
2	0.7	86	90
3	0.5	77	90
4	0.3	52	90
5	0.1	20	90

The catalyst was easily separated from the products by exposure of the reaction vessel to an external magnet and decantation of the reaction solution. The remaining catalyst was washed with acetone and water to remove residual products and dried. This catalyst could be reused in 6 further iterative cycles without obvious reduction in activity (Fig. 4). Measurements by ICP-OES showed that 26.3% of the catalyst weight in the 6th recycling was copper. Hence, there was no obvious decrease in the copper content of the catalyst in the 6th recycling. The XRD pattern of the CuFe₂O₄ MNPs in the 6th recycling showed no obvious difference in comparison with its first XRD pattern.

Proposed mechanism for the oxidation

Based on our experimental results and the related literature [26-28], we propose the following reaction mechanism for the oxidation of alcohols by oxone in water in the presence of CuFe₂O₄ MNPs catalyst (Scheme 2). Initially alcohol and catalyst were stirred and alcohol was grafted on the catalyst (Stage I). Then, oxone was added and was dissolved in water and HSO_5^- took electrons (Stage II). The procedure was followed byelimination of H^+ (Stage III). It seems that a large number of OH groups are present on the surface of the catalyst (Fig. 1, absorption band at 3440 cm⁻¹). The OH groups cause some interactions in the water phase. Since the catalyst is present in the water phase, HSO_5^- takes electrons fairly rapidly. When the catalyst resides in the organic phase, HSO_5^- forms a separate aqueous phase, thus Fe(II) cannot donate an electron.

Table 5. Oxidation of various alcohols using $CuFe_2O_4$ MNPs as catalyst (6 mol%) in the presence of oxone (at r.t.) in water
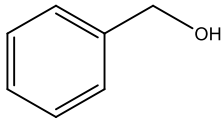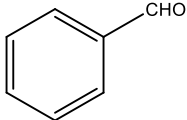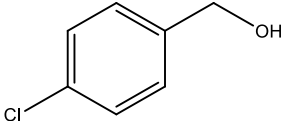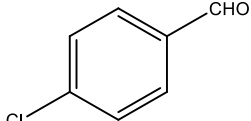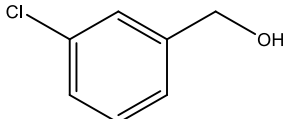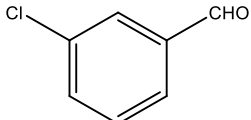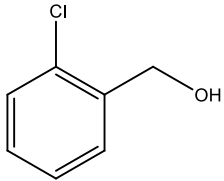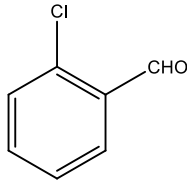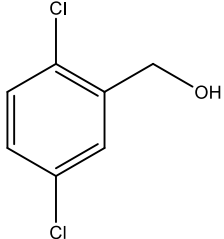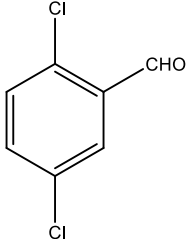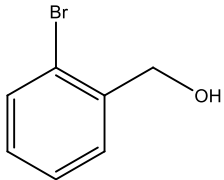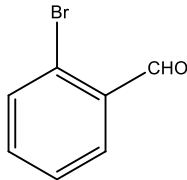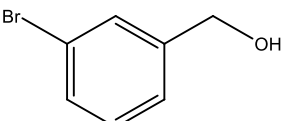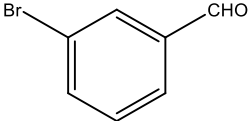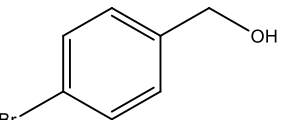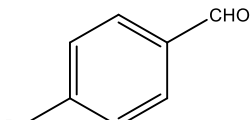
Entry	Substrate	Product	Yield[a] (%)	Time (min)
1	2	3	4	5
1			90	90
2			87	85
3			86	90
4			83	95
5			84	90
6			86	85
7			88	95
8			85	90

Table 5 continued
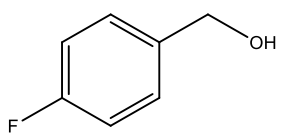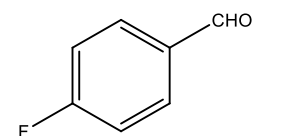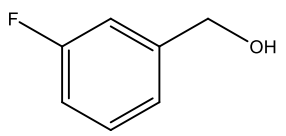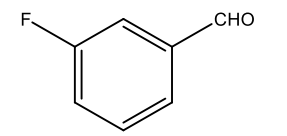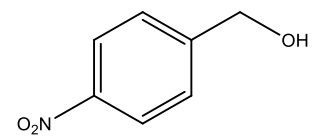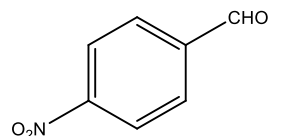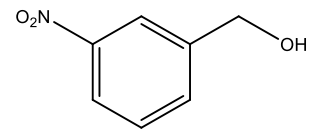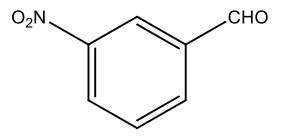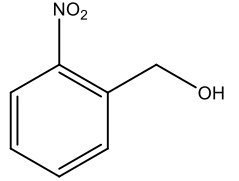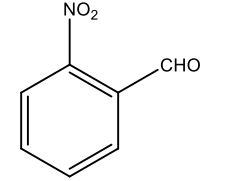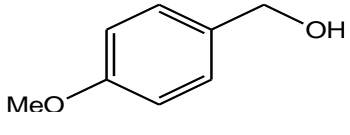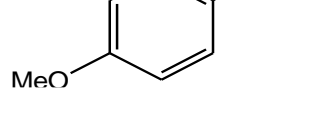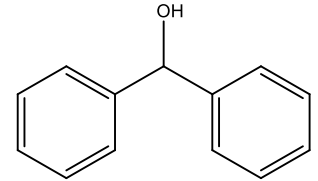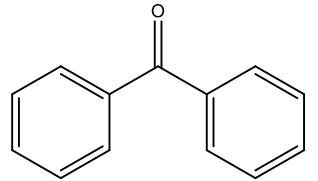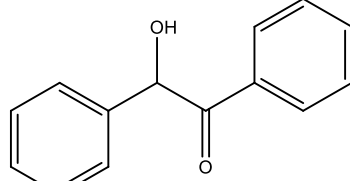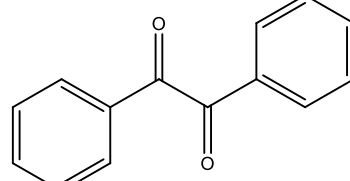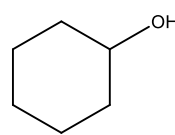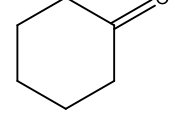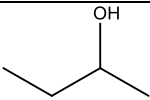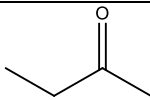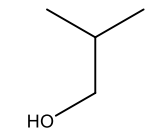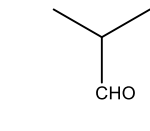
1	2	3	4	5
9			88	90
10			86	85
11			84	120
12			84	120
13			80	120
14			91	90
15			85	95
16			70	120
17[b]			99.84	150

Table 5 continued

1	2	3	4	5
18[b]	(structure: 2-butanol, OH)	(structure: 2-butanone, O)	99.50	150
19[b]	(structure: isobutanol, HO)	(structure: isobutyraldehyde, CHO)	99.16	150

a- Yields refer to isolated products. The products were characterized by their spectral data (IR) and compared with authentic samples. b-The yields refer to GC analysi

$$HSO_5^- \; + \; 2H^+ \; +2e \; \longrightarrow \; H_2O \; +HSO_4^-$$
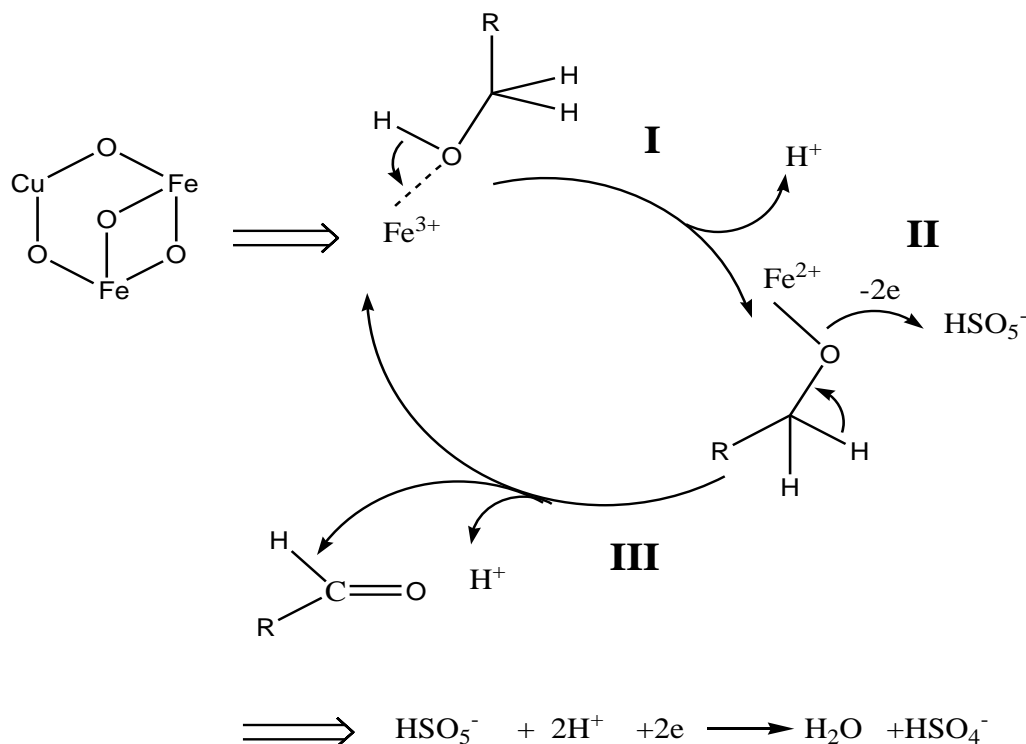
Scheme 2. Proposed mechanism for the oxidation of alcohols by oxone oxidant in the presence of CuFe₂O₄ MNPs
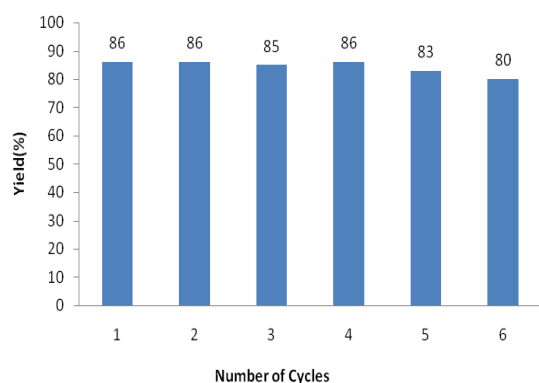
Fig. 4. Recycling of the catalyst for oxidation of 2-chlorobenzyl alcohol

CONCLUSIONS

To summarize, we have introduced a direct and effective method for the oxidation of alcohols to their corresponding carbonyl compounds using oxone in the presence of nanomagnetic CuFe₂O₄ catalyst as a reusable, non-toxic, non-corrosive, inexpensive and commercially available heterogeneous catalyst in water. The method also offers some other advantages such as stability of the oxidation system, simplicity, short reaction times, good yields of the products and mild reaction conditions. The catalyst can be subsequently reused in 6 further iterative cycles with no decrease in activity. The extension of the application of this nanocatalyst to various oxidation reactions is currently under investigation in our laboratory.

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МАГНИТНИ НАНОЧАСТИЦИ ОТ CuFe₂O₄ КАТО ЕФЕКТИВЕН КАТАЛИЗАТОР ЗА ОКИСЛЯВАНЕТО НА АЛКОХОЛИ ДО КАРБОНИЛНИ СЪЕДИНЕНИЯ В ПРИСЪСТВИЕ НА ОКСОН КАТО ОКИСЛИТЕЛ

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(Резюме)

Използвани са магнитни наночастици от CuFe₂O₄ като ефективен, устойчив катализатор за многократна употреба за селективното окисление на алкохоли до съответните им карбонилни съединения от оксон (натриев хидроген-персулфат) като окислител във водна среда при стайна температура. Първичните и вторичните алкохоли дават съответните продукти с добри добиви. Катализаторът е изследван с помощта на XRD, SEM, ICP и IR-методи. Катализаторът може лесно да се извлече и да се употребява многократно без загуба на активност.