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Recyclable Cu(II)-(MAA-EGDMA) catalyst for selective oxidation of alcohols to aldehydes using sodium hypochlorite

Roya Ranjineh Khojasteh * and Mitra Maleki

Department of Inorganic Chemistry, Faculty of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, 1651153311, Iran
r_ranjinehkhojasteh@iau-tnb.ac.ir (R.R.K.), maleki123@hotmail.com (M.M.)

* *Corresponding author at: Department of Inorganic Chemistry, Faculty of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, 1651153311, Iran.*
e-mail: r_ranjinehkhojasteh@iau-tnb.ac.ir (R.R. Khojasteh).

RESEARCH ARTICLE

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ABSTRACT

Copper(II) α-benzoin oxime complex was synthesized by the reaction between copper(II) benzoate and α-benzoin oxime. The poly methacrylic acid-ethylene glycol dimethacrylate (MAA-EGDMA) was applied as support of copper complex catalyst for oxidation of alcohols to aldehydes using NaClO. The structure and morphology of immobilized Cu(II)-benzoin oxime have been studied by using different analysis including Fourier Transform Infrared (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM) and Thermal Gravimetric Analysis (TGA). The yield of aldehydes was determined by Gas Chromatography (GC) analysis. The immobilized Cu(II)-benzoin oxime indicated a high catalytic activity compared to its absence for the alcohol oxidation with sodium hypochlorite. The effect of the reaction time and temperature, the solvent type, the amounts of catalyst and NaClO were optimized to obtain maximum yield. The prepared catalyst had various benefits such as being inexpensive, environmentally friendly manner, recyclable, reducing the reaction time and increasing the yield. A reaction mechanism is proposed for oxidation of alcohols in the presence of the catalyst.

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1. Introduction

The selective oxidation of alcohols to their corresponding aldehydes is an important process. Aldehydes are valuable compounds, act as intermediate in chemical synthesis and several catalytic reactions [1-3]. It is also important to note that the oxidation of alcohol groups to carbonyl groups indicates a principal step in the degradation of fats during the human metabolism [4-7]. In recent years, research efforts were focused on increasing selective activity and reducing the cost in the catalytic processing of compounds in various fields such as fuels, fine chemicals, and pollution reduction [8-13]. The development of highly active catalyst for the selective oxidation of alcohols with air in aqueous media plays an essential role in the heterogeneous catalytic process [14-17].

Although an appropriate improvement was observed in the oxidation of alcohols using transition metal catalysts, the existence of different challenges cannot be ignored in the progress of these systems [18-22]. In fact, only a few examples of cheap and green copper catalysts with O_2 or H_2O_2 have been reported so far and no reports on the Cu(II)-(MAA-EGDMA) catalyst have been discussed yet. Marko *et al.* first reported the efficient use of CuCl(Phen-DEADH$_2$) (Phen: 1,10-Phenanthroline; DEADH$_2$: Diethyl hydrazinodicarboxylate) catalytic system for the oxidation of primary and secondary alcohols under dioxygen at 90°C [23].

Velusamy and Punniyamurthy reported oxidation of alcohols to carboxylic acid analogues and ketones catalyzed by a salen-type Cu(II) complex with H_2O_2 as the source of oxygen, at 80 °C in acetonitrile [24]. Ragagnin *et al.* developed catalyst systems CuCl-TEMPO (TEMPO: 2,2,6,6-Tetramethyl-1-piperidinyloxy) for the oxidation of alcohols under dioxygen at 90 °C under conditions of fluorous biphasic [25]. The key obstacles of the mentioned processes are safety risks, toxic by-products and high temperature. Moreover, over-oxidation of aldehydes to carboxylic acids is often unavoidable side reaction. In this regard, design of new and less polluting oxidation procedures in low temperature is considered to be a priority for the new chemistry. The stabilization of complexes using polymers is a novel method in the synthesis of organic chemistry, in which the catalyst can easily be recovered after the completion of the reaction. The MAA-EGDMA polymer has this ability to form hydrogen or covalent bond using its functional groups in order to immobilize a complex.

In order to develop environmentally benign methods, we found that the immobilized copper(II) benzoin oxime has a reasonably good catalytic activity and selectivity for the alcohol oxidation with sodium hypochlorite at room temperature.

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(a) α-Benzoin oxime

(b) Copper(II) α-benzoin oxime

Figure 1. (**a**) Chemical structure of α-benzoin oxime ligand and (**b**) the crystallographically coordination mode of copper(II) α-benzoin oxime [25].

Using sodium hypochlorite as a cheap and accessible oxidant, which produces benign byproducts, should be beneficial. In this paper, we accomplished a convenient, effective and simple method for the oxidation of alcohols to their corresponding carbonyl compounds using NaClO catalyzed by recyclable polymer supported copper complex in aqueous media. The yields of oxidation products are reasonable without further oxidation of aldehydes to carboxylic acids. Experimental procedure can be performed without the use of high volumes of additives and without the using of multi-separation processes. The effect of different factors affecting on the reaction yield was discussed. The MAA-EGDMA particles can be regarded as novel supports for immobilization of copper(II) benzoin oxime and the aim of this research is to develop the heterogeneously supported catalysts used in the oxidation of alcohols.

2. Experimental

2.1. Materials and physical measurements

All chemicals and solvents were purchased from Merck and Sigma-Aldrich Companies and used without further purification. The FT-IR spectra (KBr discs) were recorded using a Spectrum One, Perkin Elmer spectrometer. Elemental analyses (C, H, and N) were carried out on a Heraeus instrument (Vario EL). Thin-Layer chromatography (TLC) was performed for determination of purity of the synthesized compounds using *n*-hexane/ethyl acetate (3:17, *v*:*v*) mixture. The yield of aldehydes was determined by Gas Chromatography analysis; carried out with a HP 6890 AGILENT, Flame ionization detector (FID) instrument equipped with a CP Sil 5-CB column (50 m×0.53 mm) using decane as internal standard. A Perkin Elmer model AAnalyst 100 Atomic Absorption spectrometer was used for determining Cu value desorption of the Cu(II)-(MAA-EGDMA) catalyst. Scanning Electron Microscopy (SEM) image was observed with EM 3200-KYKY. Thermal gravimetric analysis (TGA) was performed on a BAHR STA 503 in air with a heating rate of 5 °C/min.

2.2. Preparation of complex

The complex was synthesized as described earlier [26]. The complex was prepared by adding copper(II) benzoate (1.0 mmol, 0.35 g) with α-benzoin oxime as ligand (1.0 mmol, 0.23 g) to dichloromethane (30 mL). The mixture was heated to reflux for about 60 min. The green crystals were recovered by filtration and dried after six days (Figure 1). The green crystals were extracted with Et_2O (60 mL) of the reaction mixture and dried after six days (Figure 1). Color: Green crystals. Yield: 66%. M.p.: 165-168 °C. FT-IR (KBr, ν, cm^{-1}): 3057 (C-H) (aromatic), 29201 (C-H) (aliphatic), 1679 (C=N), 1087 (C-O), 1070 (N-O), 1443 (C=C), 601 (Cu-C), 495 (Cu-O). Anal. calcd. for $C_{140}H_{110}Cu_{10}N_{10}O_{20}$: C, 58.23; H, 3.84; N, 4.85. Found: C, 58.11; H, 3.68; N, 4.95%.

2.3. Preparation of Cu(II)-(MAA-EGDMA) catalyst

The poly methacrylic acid-ethylene glycol dimethacrylate was prepared according to the method [21]. A solution was prepared by dissolving of copper(II) α-benzoin oxime (0.416 mmol, 0.1 g) in anhydrous chloroform (6 mL). Then, methacrylic acid (1.5 mmol, 0.129 mL), ethylene glycol dimethacrylate (14 mmol, 2.6 mL) and 2,2'-azo-*bis*-(2-methylpropionitrile) (0.146 mmol, 24 mg) were added into the prepared solution. The mixture was degassed under vacuum in a sonicating water bath being purged with nitrogen for 5 min. While maintaining flow of nitrogen, the reaction flask was removed from the sonicating bath, sealed and placed inside a water bath at 60 °C so as to allow the starting of the reaction. Under these conditions, the reaction was continued for 20 h. A rigid structure product was obtained after drying in air overnight. The product was grounded into fine particles using mortar and pestle. The polymer particles were washed with methanol three times and with distilled water twice.

Hydrochloric acid (10 %, 25 mL) was added to the Cu(II)-(MAA-EGDMA) catalyst (1 g) and the solution was stirring for 10 min at room temperature. The precipitate was filtered off and the solution was used for copper desorption. The amounts of copper desorption from the Cu(II)-(MAA-EGDMA) catalyst was determined by atomic absorption spectrometer. After eight times washing, the amount of copper in the solution was reached zero.

(MAA-EGDMA) polymer: Color: White. Yield: 83%. M.p.: 386-398 °C. FT-IR (KBr, ν, cm^{-1}): 1455 (CH_3) (aliphatic), 1725 (C=O), 1157 (C-O-C), 1638 (C=C).

Cu(II)-(MAA-EGDMA) catalyst: Color: Light green. Yield: 78%. M.p.: 575-580 °C. FT-IR (KBr, ν, cm^{-1}): 1730 (C=O), 1263 (C-O-C), 1661 (C=C), 3451 (O-H), 2959 (C-H) (aromatic), 1456 (C=C), 623 (Cu-N), 588 (Cu-O).

2.4. General procedure for the oxidation of alcohols

Due to the optimization examinations of the amounts of catalyst and NaClO, the solvent type, the reaction time and temperature, the general method of oxidation of the alcohols is described as follows: Alcohol (0.9 mmol) was added to a mixture of Cu(II)-(MAA-EGDMA) catalyst (0.01 g) in dichloromethane (0.3 mL). The solution was magnetically stirred and cooled to 0 °C in an ice bath. Then, sodium hypochlorite (3%, 6 mL) was added, and the solution was stirred for 2 h at 0 °C, following by another 2 h at room temperature (25 °C). The catalyst was filtered and sodium sulfate (0.02 g) was added to the solution in order to dry. Sodium sulfate hydrated was filtered after one day. The reaction products were investigated by TLC (Thin Layer Chromatography). The yield of aldehydes was determined by GC analysis. The reaction products were determined by comparing with the commercially available carbonyl compounds.

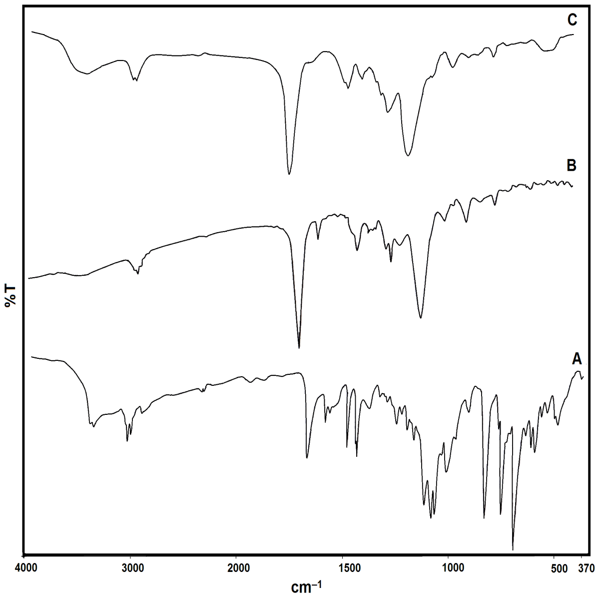


Figure 2. IR spectra of the (**a**) copper(II) α-benzoin oxime complex, (**b**) (MAA-EGDMA) polymer (**c**) and Cu(II)-(MAA-EGDMA) catalyst.

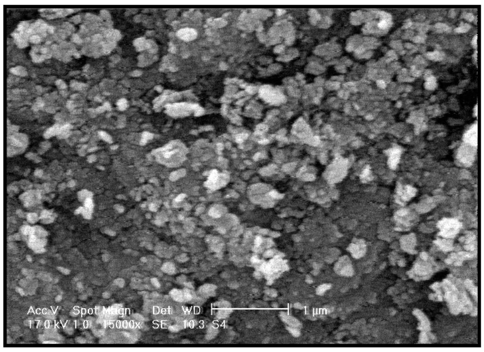


Figure 3. SEM image of the Cu(II)-(MAA-EGDMA) catalyst.

3. Results and discussion

3.1. Physical measurements

The IR spectra of the prepared compounds are presented in Figure 2. Based on the observed spectrum of complex, a sharp band appeared at 1678 cm^{-1} is assigned to the azomethine ν(C=N). The C-H (aromatic) stretching band is observed at 3057 cm^{-1}. In the 700-900 cm^{-1} region, the sharp bands are attributed to C-H (out of plane) bending vibrations. These bands decreased in the Cu(II)-(MAA-EGDMA) catalyst due to coordination with the MAA-EGDMA polymer. The band related to the C-H (aromatic) stretching in the Cu(II)-(MAA-EGDMA) catalyst is shifted to a lower wave number. Also, the bands assigned to OH groups in the complex and Cu(II)-(MAA-EGDMA) catalyst appeared at 3378 and 3451 cm^{-1}, respectively; however, these bands disappeared in the MAA-EGDMA polymer. Absorption patterns of the complex and Cu(II)-(MAA-EGDMA) catalyst indicate the bands at 600 and 623 cm^{-1} assigned for the ν(Cu-N) and 495 and 587 cm^{-1} related to the ν(Cu-O), however, these bands disappeared in the MAA-EGDMA polymer.

Morphology of the Cu(II)-(MAA-EGDMA) catalyst is shown in Figure 3. Based on the SEM image recorded at magnification of 15000, the catalyst particles are spherical.

Figure 4 exhibits the TG analysis of the Cu(II)-(MAA-EGDMA) catalyst. According to the TGA spectrum, two decomposition states are observed. The first mass loss (13% weight loss), between 198 and 323 °C, which represents the decomposition of the copper(II) α-benzoin oxime. The second mass loss (44% weight loss), which appears between 355-530 °C, is related to the (MAA-EGDMA) polymer decomposition. It should be noted that the Cu(II)-(MAA-EGDMA) catalyst was fully decomposed prior to reaching the temperature of 580 °C.

3.2. Optimization

The reaction conditions for the catalytic oxidation of alcohols by the NaClO/Cu(II)-(MAA-EGDMA) system were optimized. The yield of catalytic oxidation of alcohols depends on various factors such as time, solvent, catalyst, etc. In this paper, the reaction model was investigated by changing the reaction time and temperature, the solvent type, the amounts of NaClO and catalyst. Benzyl alcohol was selected as a probe substrate during optimization. This simple aromatic compound is particularly activated toward oxidation.

3.2.1. Solvent effect

At first, the effect of *n*-hexane, acetone, dichloromethane, acetonitrile, tetrahydrofuran and chloroform solvents on the reaction yield in the presence (Yield I, Table 1) and the absence (Yield II, Table 1) of the catalyst were investigated.

Table 1. Influence of solvent on the reaction yield [a,b].

Entry	Solvent	Yield I (%)	Yield II (%)
1	Dichloromethane	66	40
2	Acetone	37	15
3	Tetrahydrofuran	25	10
4	Acetonitrile	47	25
5	Chloroform	35	15
6	*n*-Hexane	23	10

[a] GC yield.
[b] Condition of reaction: solvent (0.3 mL), catalyst (0.01 g), benzyl alcohol (0.9 mmol), NaClO (3%, 6 mL), time (120 min), temperature (25 °C).

Table 2. Influence of the NaClO amount on the reaction yield [a,b].

Entry	NaClO (3%) (mL)	Yield I (%)	Yield II (%)
1	4	41	30
2	6	66	45
3	9	67	55
4	12	67	58

[a] GC yield.
[b] Condition of reaction: dichloromethane (0.3 mL), catalyst (0.01 g), benzyl alcohol (0.9 mmol), time (120 min), temperature (25 °C).

Table 3. Influence of the catalyst amount on the reaction yield [a,b].

Entry	Catalyst (g)	Yield (%)
1	0.010	66
2	0.013	62
3	0.017	63

[a] GC yield.
[b] Condition of reaction: dichloromethane (0.3 mL), benzyl alcohol (0.9 mmol), NaClO (3 %, 6 mL), time (120 min), temperature (25 °C).

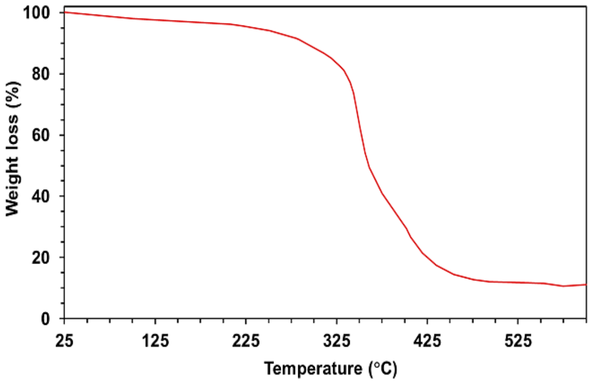


Figure 4. The TG analysis of the Cu(II)-(MAA-EGDMA) catalyst.

The reaction yield was higher in the presence of dichloromethane solvent (Table 1). This is probably due to the coordination of dichloromethane molecules during the catalytic cycle which enhances the activity.

3.2.2. The amount of NaClO

In order to examine how the amount of sodium hypochlorite affects, benzyl alcohol was oxidized with different volumes of sodium hypochlorite in dichloromethane solvent in the presence (Yield I, Table 2) and the absence (Yield II, Table 2) of the catalyst. According to these results, 6 mL of 3% solution of sodium hypochlorite was considered as an appropriate volume because the reaction yield increased from 45 to 66 % in the presence of the catalyst.

3.2.3. The amount of catalyst

In order to optimize the amount of catalyst, the oxidation of benzyl alcohol with sodium hypochlorite in dichloromethane solvent was investigated with different amounts of the catalyst. Based on the obtained results, the reaction time decreased with increasing of the catalyst amount, however the reaction yield did not change significantly. In this regard, the amount of 0.01 g was selected as the optimum value (Table 3).

3.2.4. Temperature effect

In order to optimize the temperature, the oxidation reaction was carried out at different temperatures 0, 25 (room temperature) and 80 °C. Benzoic acid was obtained at 95% yield from the reaction of benzyl alcohol with sodium hypochlorite at 80 °C. Based on the obtained results, it was observed that the two temperatures of 25 and 0 °C were considered as the best temperatures (Table 4).

3.2.5. Time effect

To improve the yield, the reaction was performed at 0 °C for 15, 45 and 120 minutes and the results are shown in Table 5. On the basis of the collision theory, reactions should be conducted in an effective manner; at low temperature, particles have low energy and less mobility and as a result the number of collisions and interactions diminish, on the other hand, selectivity decrease at boiling temperature. Thus, the conversion reaction of alcohols to aldehyde was performed for 2 h at two different temperatures of 0 and 25 °C.

In conclusion, the reaction conditions for the catalytic oxidation of alcohols were optimized by using 6 mL of sodium hypochlorite (3%) in the presence of catalyst (0.01 g) and in dichloromethane solvent. An efficient procedure to obtain maximum yield was achieved when solution was stirred for 2 h at 0 °C, followed by another 2 h at room temperature (25 °C).

Table 4. The effect of temperature on the reaction yield [a,b].

Entry	Temperature (°C)	Time(min)	Benzyl alcohol (%)	Benzoic acid (%)	Benzaldehyde (%)	Benzaldehyde selectivity (%)
1	80	15	5	95	0	0
2	25	60	48	0	52	100
3	0	90	41	0	59	100

[a] GC yield.

[b] Condition of reaction: dichloromethane (0.3 mL), catalyst (0.01 g), benzyl alcohol (0.9 mmol), NaClO (3 %, 6 mL).

Table 5. The effect of time on the reaction yield [a,b].

Entry	Time (min)	Benzyl alcohol (%)	Benzaldehyde (%)
1	15	68	32
2	45	57	43
3	120	36	64

[a] GC yield.

[b] Condition of reaction: dichloromethane (0.3 mL), catalyst (0.01 g), benzyl alcohol (0.9 mmol), NaClO (3 %, 6 mL), temperature (0 °C).

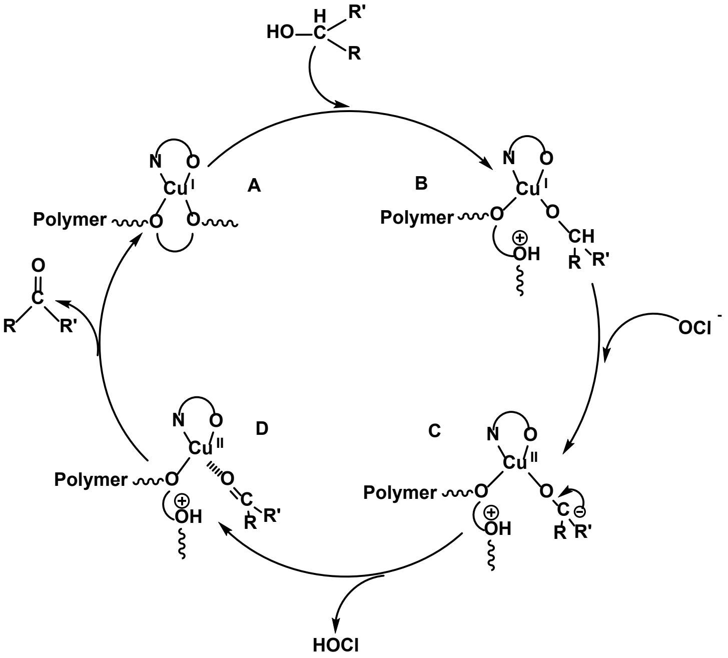


Figure 5. Proposed mechanism of Cu(II)-(MAA-EGDMA) catalyst catalyzed oxidation of alcohols to aldehydes.

3.3. The oxidation of alcohols catalyzed by Cu(II)-(MAA-EGDMA)

After determining the best conditions, the catalytic oxidation of various alcohols by the Cu(II)-(MAA-EGDMA) catalyst and NaClO in dichloromethane solvent was studied (Table 6). Under these conditions, various alcohols were quantitatively oxidized to aldehydes without any byproducts. Although electron donating groups in benzylic alcohols accelerated the reaction (Table 6, Entry 2-7) electron withdrawing groups decelerated it (Table 6, Entry 8-10). Allylic alcohols (Table 6, Entry 14,15) and benzylic diols (Table 6, Entry 21-24) were selectively oxidized to the corresponding aldehydes and ketones with reasonably good yields. However, aliphatic alcohols cannot be oxidized into corresponding carbonyls under the same reaction conditions (Table 6, Entry 17,18) whereas benzylic, and even allylic secondary alcohol were oxidized at low yield (Table 6, Entry 12,13). In contrast to conventional methods, no evidence of chlorinated product was obtained when activated benzylic alcohols were subjected to oxidation.

According to a work reported by Marko and colleagues, a series of alcohols were oxidized using CuCl, phenanthroline, di-*tert*-butyl hydrazine-1,2-dicarboxylate (DBADH$_2$), and t-BuOK. Unfortunately, this method was not effective for the oxidation of primary aliphatic alcohols [23]. On the basis of Jiang and Ragauskas method, a pyridyl based ionic liquid, 1-butyl-4-methylpryridinium hexafluorophosphate ([bmpy]PF$_6$) along with acetamido-TEMPO (a TEMPO source that can be recycled in ionic liquids) and DMAP (4-(dimethylamino) pyridine) used for the oxidation of Cu-catalyzed aerobic alcohols. At room temperature, the reactions for the chemo-selective oxidation of a wide range of primary benzylic, allylic and aliphatic benzyls were successfully performed, but no oxidation was observed for secondary alcohols [8].

3.4. Competition between alcohols

To determine the selectivity of the NaClO/Cu(II)-(MAA-EGDMA) system, the oxidation of various alcohols was studied together and the results are presented in Table 7. On the basis of the obtained results, it was found that the primary alcohols yield was higher than that of the secondary alcohols at the same time because the primary alcohols had more chemoselectivity for reaction.

According to a work conducted by Sheldon and co-workers, a reaction of 2,2'-bypyridine as a ligand with copper(II) salts in the presence of TEMPO was performed resulted in the oxidation of primary benzylic, allylic, and aliphatic alcohols to the corresponding aldehydes. Although the oxidation did not lead to acid but a base as co-catalysts required for the reaction. On the basis of their method, secondary alcohols were not oxidized also only the primary alcohol was oxidized when mixtures of primary and secondary alcohols were exposed to the reaction conditions [18].

Table 6. Oxidation of selected alcohols catalyzed by Cu(II)-(MAA-EGDMA) [a,b].

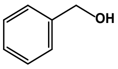
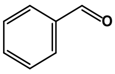
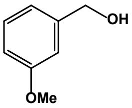
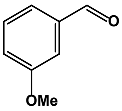
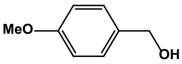
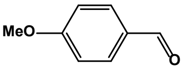
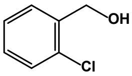
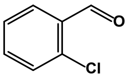
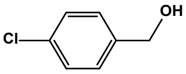
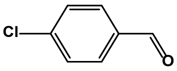
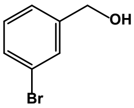
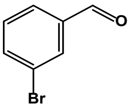
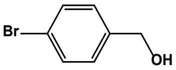
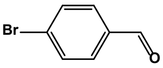
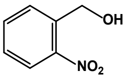
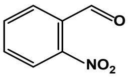
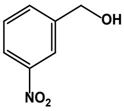
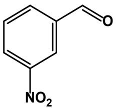
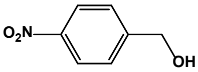
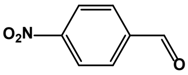
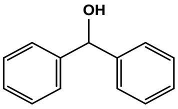
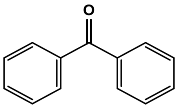
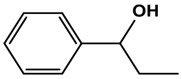
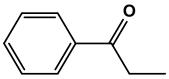
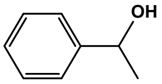
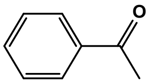
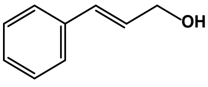
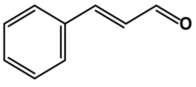
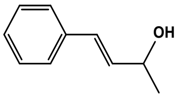
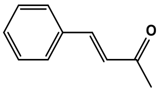
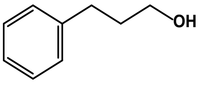
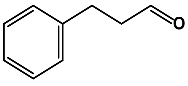
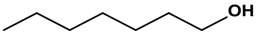
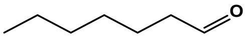
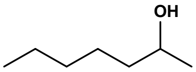
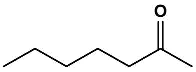
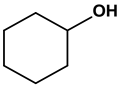
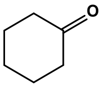
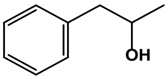
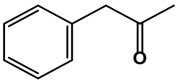
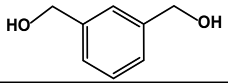
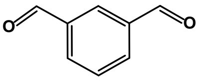
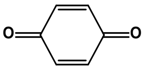
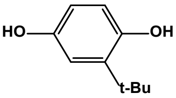
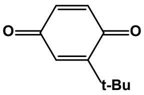
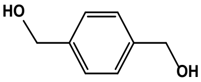
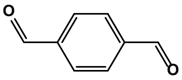
Entry	Substrate	Product	Yield (%)
1			95
2			70
3			75
4			93
5			95
6			94
7			91
8			75
9			70
10			80
11			95
12			63
13			68
14			75
15			61
16			70
17			58
18			52
19			90
20			80
21			78

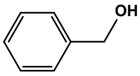
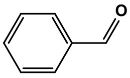
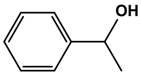
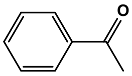
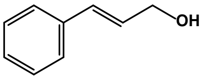
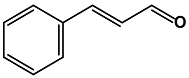
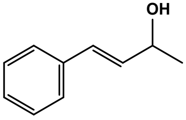
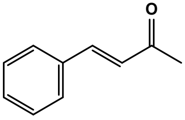
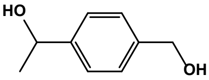
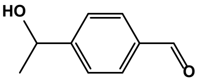
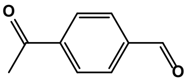
Table 6. Continued.

Entry	Substrate	Product	Yield (%)
22			82
23			80
24			65

^{a} GC yield.

^{b} Condition of reaction: dichloromethane (0.3 mL), catalyst (0.01 g), alcohol (0.9 mmol), NaClO (3 %, 6 mL), temperature (0 and then 25 °C), time (120 min at each temperature).

Table 7. The effect of competition between alcohols ^{a,b}.

Entry	Substrate	Product	Yield (%)
1			76
			54
2			60
			49
3			41
			52

^{a} GC yield.

^{b} Condition of reaction: dichloromethane (0.3 mL), catalyst (0.01 g), alcohol (0.9 mmol), NaClO (3 %, 6 mL), temperature (0 and then 25 °C), time (120 min at each temperature).

Table 8. Investigation of the catalyst recycling ^{a,b}.

Entry	Catalyst recycling	Yield (%)
1	First	95
2	Second	95
3	Third	88

^{a} GC yield.

^{b} Condition of reaction: dichloromethane (0.3 mL), catalyst (0.01 g), benzyl alcohol (0.9 mmol), NaClO (3 %, 6 mL), temperature (0 and then 25 °C), time (120 min at each temperature).

3.5. Investigation of the catalyst recycling

The benefit of this method is the reuse of the catalyst. Hence, the oxidation of benzyl alcohol was carried out with sodium hypochlorite, then the same reaction was performed 2 times with the same catalyst used at the beginning (Table 8). Based on the obtained results, it was observed that the recycled catalyst could be used at least 2 times.

Punniyamurthy and colleagues investigated the oxidation of the chemoselectively of primary alcohols by salen-type ligand on Cu [27]. Although this system had similar goals with the Sheldon's work [18], a pure O_2 atmosphere as well as a high temperature (100 °C) was required. They indicated that the catalyst could be recycled up to three times without reducing its activity. Ansari and Gree reported an aerobic alcohol oxidation catalyzed by CuCl-TEMPO which succeeded in the ionic liquid 1-butyl-3-methylimidazolium hexafluoro phosphate ([bmim]PF_6) [28]. This method was used to oxidize primary and secondary benzylic and allylic alcohols at 65 °C. Under these conditions, aliphatic alcohols which oxidized with incomplete conversion had slower rates. Despite the fact that the CuCl-TEMPO catalyst was not recyclable, the Cu(II)-(MAA-EGDMA) catalyst could be recycled and facilitated oxidation at lower temperature.

3.6. Proposed mechanism

The proposed mechanism in Figure 5 shows the oxidation of alcohols to the aldehydes using sodium hypochlorite in the presence of Cu(II)-(MAA-EGDMA) catalyst. The catalytic cycle begins with the Cu(II)-(MAA-EGDMA) catalyst **A**. The coordinated alcohol is deprotonated to alkoxide resulting in a formation of species **B**. Subsequently, the β-H is rapidly captured by OCl^- resulting in intermolecular hydrogen transfer and produces species **C**. Species **D** is reorganized by elimination of HOCl. Finally, release of the ketone (or aldehyde) regenerates the active Cu(II)-(MAA-EGDMA) catalyst **A**, and a new catalytic cycle ensues. The mechanism proposes that the chemoselectivity is related to the formation of intermediate **C**, so that even secondary alcohol can arrange to undergo hydrogen transfer. The Cu(II)-(MAA-EGDMA) catalyst is still active after the end of the oxidation reaction, and can be recycled by simple filtration and reused immediately.

4. Conclusion

In this research, the Cu(II)-(MAA-EGDMA) catalyst was synthesized in order to investigate the oxidation of alcohols with sodium hypochlorite. The synthesized catalyst possessed different advantages such as being inexpensive, environmentally friendly manner, recyclable, reducing the reaction time and increasing the reaction yield. The recycled catalyst can be used at least 2 times in another oxidation reaction. To achieve the best conditions, benzyl alcohol was used as a probe substrate. The optimum conditions were reached by five levels including the amounts of NaClO and catalyst, the solvent type, the reaction time and temperature.

Electron donating groups on benzylic alcohols increased the yield of oxidation reaction, whereas electron withdrawing groups diminished it. Allylic alcohols and benzylic diols were selectively oxidized to the corresponding unsaturated aldehydes and ketones with reasonable yields. Nevertheless, aliphatic alcohols were not oxidized into corresponding carbonyls under the same reaction conditions, and even secondary allylic alcohols were oxidized at low yield.

In conclusion, the procedure reported here could be regarded as a convenient and high-yielding method for the oxidation of primary benzylic and allylic alcohols to aldehydes with no over oxidation to carboxylic acids. Additionally, this process exhibited an unprecedented degree of chemoselectivity for the oxidation of primary hydroxy groups in the presence of its secondary. The reaction mechanism proposed the oxidation of alcohols to the aldehydes using sodium hypochlorite in the presence of Cu(II)-(MAA-EGDMA) catalyst. These features revealed their significant synthetic value.

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Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

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ORCID

Roya RanjinehKhojasteh
http://orcid.org/0000-0002-3899-8908
MitraMaleki
http://orcid.org/0000-0003-4826-1325

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