Research Article

Oxidation of Alcohols to Carbonyl Compounds over Graphene Oxide Functionalized with Copper-Thiazole as a Catalyst

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ABSTRACT

The catalytic behaviour of [Cu(II)Br$_2$-BTP@MNPs] and [Cu(II)Br$_2$-BTP@GO] catalysts have been studied for the oxidation of alcohol derivatives. The comparative study indicates that the [Cu(II) Br$_2$-BTP@GO] possesses better catalytic activity over the [Cu(II)Br$_2$-BTP@MNPs] catalyst. In this reaction, we used a green solvent such as water in presence of tert-Butyl hydroperoxide (tert-BuOOH) as oxidant. The prepared catalyst was characterized by Atomic Absorption Spectrometry (AAS), X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), Transmission Electron Microscopy (TEM), Thermogravimetric Analysis (TGA), elemental analysis and Fourier Transform Infrared (FT-IR) spectroscopic techniques, also FT-IR spectroscopy and x-ray diffraction were used for characterization of recovered catalyst. The catalyst is stable and can be recovered even after five consecutive cycles of reaction with only a slight loss in its catalytic activity.

Keywords: Heterogeneous catalyst; Oxidation of alcohol; Green solvent; Graphene oxide; Thiazole ligand

INTRODUCTION

Selective oxidation of alcohols to their corresponding carbonyl compounds is one of the most important research fields in organic synthesis processes and is widely used for the production of drugs, vitamins and fragrances, perfumery and pharmaceutical industries [1-6]. Various oxidants such as NaClO, Na$_2$Cr$_2$O$_7$, KMnO$_4$ and MnO$_2$ have been used for oxidation of alcohols [7-12]. However, these oxidants are commonly hazardous or toxic and heavy-metal waste produces from these oxidants. Moreover, the reactions are often performed in undesirable solvents such as chlorinated hydrocarbons. So, for oxidation of alcohol suggested and developed ecofriendly techniques [13]. Therefore, for achieving to better condition conversion of different alcohols into corresponding aldehydes and ketones was performed with different catalyst. In this manner, variety of homogeneous catalysts has been reported for oxidation of alcohol [14-20]. But the homogeneous catalysts have disadvantages such as difficulty in the catalyst recovery and also contamination of the reaction media with metal species. Application of heterogeneous catalysts instead of homogeneous ones can solve the above mentioned problems and heterogeneous catalysts have favorable structural properties, high chemical stability, activity, selectivity and etc., [21-25]. Graphene is a one of supports among the supported catalysts. Graphene is a single atom thick sheet of carbon atoms with a two-dimensional hexagonal lattice structure material, has attracted extensive interest since the discovery of the material in 2004, because of the properties such as chemical, electrical, mechanical, optical and thermal, the grapheme has become an innovative material [26-30]. Graphene can be used in many applications such as gas sensors, biosensors, energy production, transistors, energy conversion and photocatalysis [31-36]. The lattice defects, vacancies, impurities, dopants and chemical modifications are widely considered as main objective to enhance the catalytic activity, catalytic selectivity, recovery and reusability of graphene based catalysts [37,38]. The development of new heterogeneous catalysts on various supports is necessary to search of more efficient ways to provide a promising solution taking into account environmental considerations and fabrication of an efficient catalyst [39,40]. Recently, growing interest has emerge in graphene supported metal catalysts (Au, Ag, Pd, Pt, Co, Rh)

which have been mainly applied in the liquid phase hydrogenation reactions in various applications reactions and exhibit enhanced catalytic activity [41-45].

Industrially, oxidation of alcohols is very important due to their use as starting materials for a variety of ketones, aldehydes, acids, etc., required to produce many of synthetic substances like plastics, detergents, paints, cosmetics, food additives and drug intermediates [46]. Indeed, catalytic reaction of inexpensive and widely available chemicals to produce high value added chemicals remains a significant task in many important current industrial and fine chemical processes [47]. Here we wish to report the preparation, characterization and investigation of catalytic activity of copper-thiazole supported on grapheme oxide functionalized with a 3-chloropropyl trimethoxy silane in the oxidation of alcohols with tert-BuOOH (Figure 1).

Figure 1: Alcohol oxidation reaction with [Cu(II)Br$_2$-BTP@GO] catalyst.
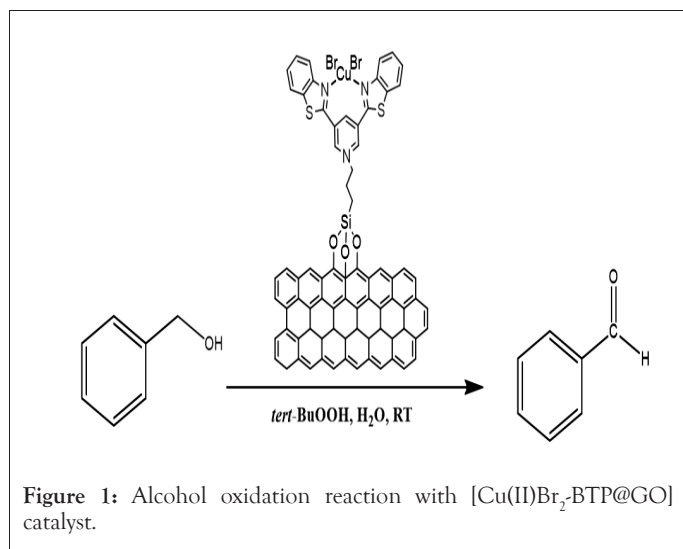
MATERIALS AND METHODS

All the reagents used were obtained from Fluka and Merck chemical companies. The FT-IR spectra were confirmed by a Bruker Vector 22 spectrometer. The SIGMA VP-500 Field Emission Scanning Electron Microscope (FE-SEM) was used for achieving the morphological features and also used from Energy Dispersive X-ray Analysis (EDXA) detector. Elemental analysis was performed on a LECO, CHNS-932 analyzer. The amount of copper in catalyst was determined by double beam Atomic Absorption Spectrophotometer (AAS), Varian AA 240, USA. The Thermal Gravimetric Analysis (TGA) curve was approved on the STA 1500 instrument at a linear heating rate of 5°C/min^{-1} from 30°C to 800°C. XRD pattern was verified using a PANalytical X-Pert diffractometer. Gas Chromatography (GC) investigates was achieved with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m.

Synthesis of Graphene Oxide-Chloropropyltrimethoxysilane (GO-CPTMS)

Synthesis of Graphene Oxide (GO) was achieved by the Hummers method [48]. After that, the graphene oxide (2.0 g) was dispersed in 40 mL of toluene and then 3-chloropropyltrimethoxysilane (CPTMS) (10 ml) was gradually added into the prepared mixture.

The reaction suspension was refluxed for 24 h. After end of the reaction, the achieved GO-CPTMS was filtrated and dried under vacuum at 110°C for 12 h.

Preparation of catalyst

The GO-CPTMS (500 mg) was dispersed in 60 ml of N,N-Dimethylformamide (DMF) with stirring for 30 min. Then, the prepared 3,5–bis(2-benzothiazolyl) pyridine (BTP ligand) (80 mg) was added to the resulting sample and refluxed for 24 h [49]. Then, the resulting solid was filtrated and washed carefully with DMF and Et$_2$O. Finally, the GO-CP-BTP (200 mg) was dispersed in methanol (20 mL) and CuBr$_2$ salt (100 mg) was added to this solution. The mixture was refluxed for 24 h. After stirring, the catalyst was filtered and washed with methanol to remove unreacted CuBr$_2$ and dried at 60°C (Figure 2).

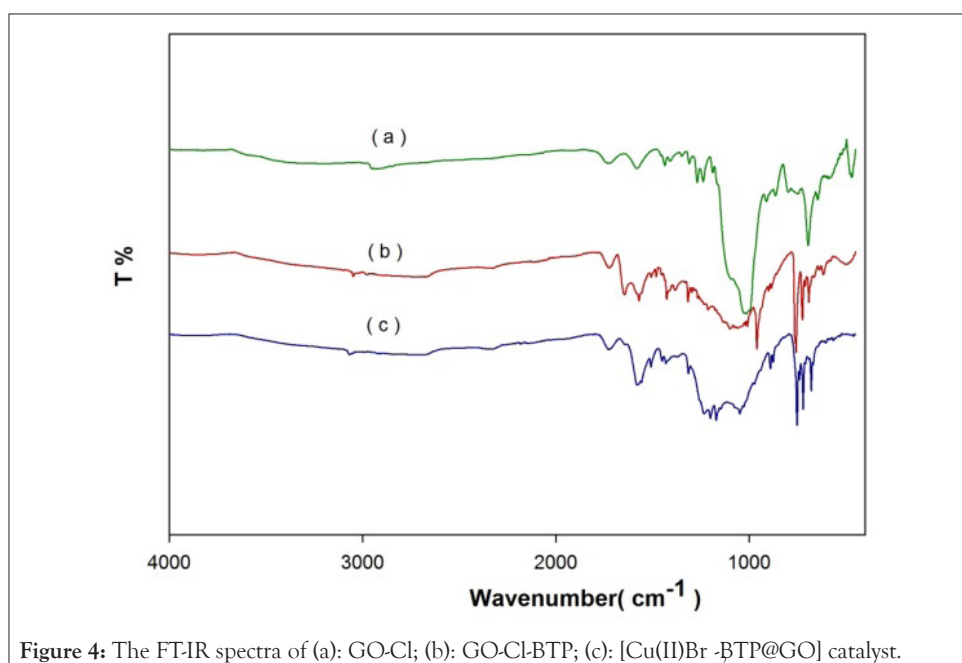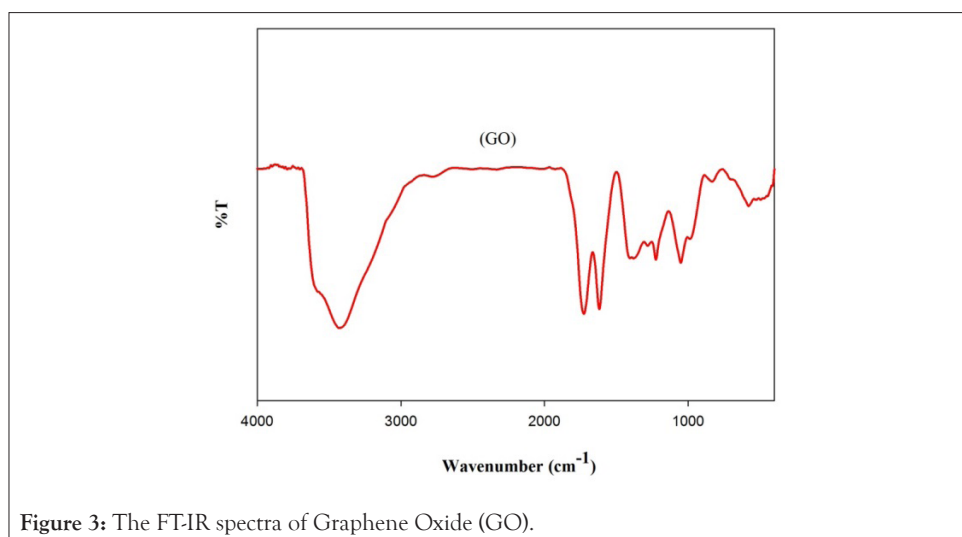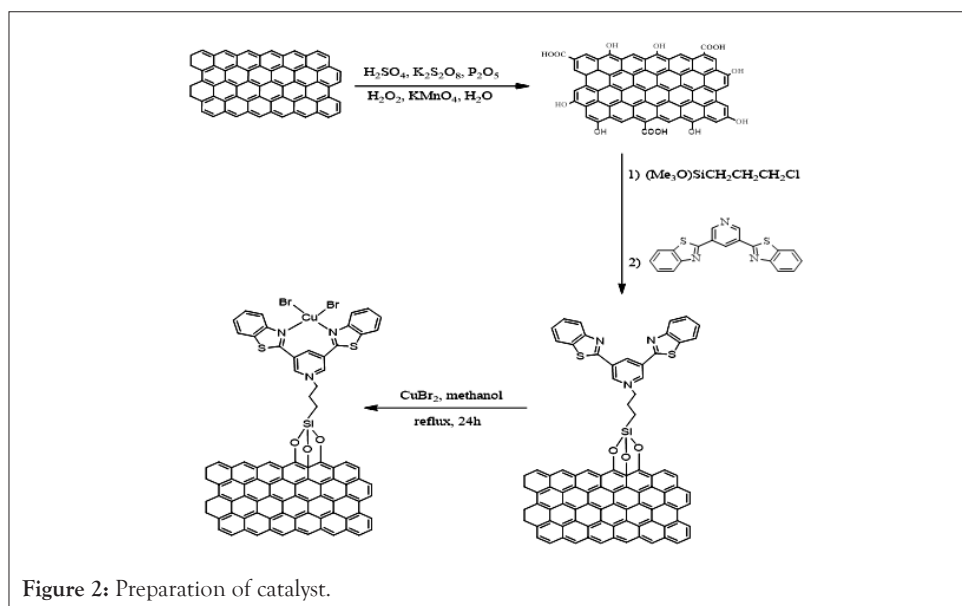### Catalytic studies of catalyst for oxidation of alcohols

A mixture of 0.25 mmol of alcohol and 0.5 mmol of tert-butyl hydroperoxide in H$_2$O (3 ml) at room temperature was prepared. Then, the adequate amount of catalyst (100 mg of catalyst, 0.17 mol% Cu) was added to the solution. The progress of the reaction was monitored by Gas Chromatography (GC). At the end of the reaction, the catalyst was separated by simple filtration, washed with H$_2$O and dried in the oven.

RESULTS AND DISCUSSION

Synthesis and characterization of [Cu(II)Br$_2$-BTP@GO] catalyst

FT-IR spectroscopy: The FT-IR spectra of GO, GO-CP, GO-CP-BTP, [Cu(II)Br$_2$-BTP@GO] and reused catalyst are presented in Figures 3 and 4a. The FT-IR spectrum of GO shown in Figure 3, exhibited a strong band in the region of 1726 cm^{-1} is revealed to carboxylic acid (C=O) group, and the C-O (epoxy), C-OH and C=C groups were shown at 1051, 1223 and 1618 cm^{-1} respectively [50,51]. Also, a broad band in the region of 3429 cm^{-1} attributed to O-H stretching absorption. Figure 4a exhibited characteristic bands at 1108 and 1025 cm^{-1} for Si-O-Si and Si-O-C bonds, respectively. Aliphatic C-H bonds presented at 2890 and 2937 cm^{-1} due to the GO modification. The FT-IR spectra of GO-CP-BTP exhibited a peak at 1648 cm^{-1} which is attributed to stretching vibration of imine group. This band imine group in Figure 4b at 1670 cm^{-1} shifted to lower frequency (1514 cm^{-1}) in [Cu(II)Br$_2$-BTP@GO] catalyst, which confirmed that coordination of copper was successfully completed onto the surface of GO-CP-BTP. Additionally, the FT-IR spectrum of recovered catalyst was shown in Figure 4a. As can be seen the structure of the catalyst does not change after the 5th reaction run (Figures 3 and 4a-4c).

X-ray Diffraction analysis (XRD): The XRD patterns of GO, prepared catalyst and reused catalyst are shown in Figure 5. For graphene oxide as shown in Figure 3, has a sharp peak at $2\theta=10.86°$ resultant to (001), which is due to the oxidation of graphite powder. In Figure 3, a new broad peak represented at around $2\theta=23°-28°$, which is related to the major oxygen functional groups of graphene oxide have been effectively functionalized (Figures 5a-5c).
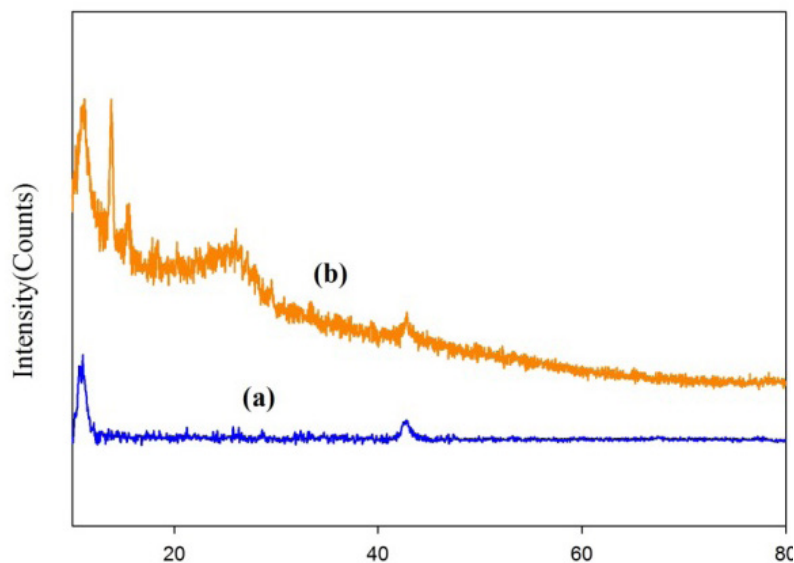
Figure 2: Preparation of catalyst.

Figure 3: The FT-IR spectra of Graphene Oxide (GO).

Figure 4: The FT-IR spectra of (a): GO-Cl; (b): GO-Cl-BTP; (c): [Cu(II)Br $_2$-BTP@GO] catalyst.

Figure 5: XRD of (a): Graphene oxide; (b): [Cu(II)Br$_2$-BTP@GO] catalyst.

Thermogravimetric Analysis (TGA): TGA curve of grapheme oxide and copper catalyst were examined in the range of 25°C-600°C temperature. For the catalyst two degradation phases were displayed in Figure 6a between 25°C-235°C first loss (about 17%) was related to water adsorbed on graphene oxide and unreacted supporting material. Between 235°C and 414°C the second loss (about 24%) belonged to the decomposition of organic groups (Figures 6a and 6b).
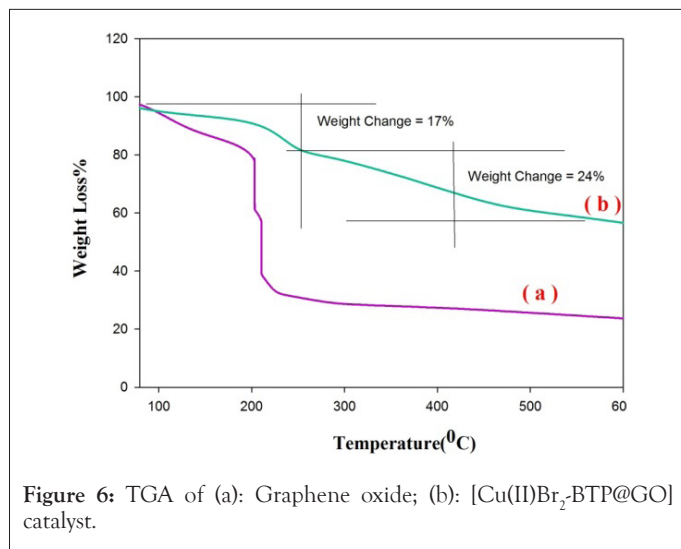

Figure 6: TGA of (a): Graphene oxide; (b): [Cu(II)Br$_2$-BTP@GO] catalyst.

FE-SEM, EDX and mapping analysis: The surface morphology of the copper catalyst was investigated by Field Emission Scanning Electron Microscopy (FE-SEM) as shown in Figure 7. Scanning Electron Microscopy (SEM) images showed rod-like shapes with uniform structures. The FE-SEM images approve the presence of copper nanoparticles. The Energy Dispersive X-ray (EDX) analysis of catalyst confirmed the presence of copper and other atoms on the surface of obtained catalyst as shown in Figure 8. Additionally, the elemental mapping showed all of the atoms have been distributed regularly in the surface of the catalyst as shown

in Figure 9. For measured of the amount of copper on the surface of the catalyst used from Atomic Absorption Spectrophotometer (AAS) analyzer and the amount of copper was 0.087 mmol g^{-1}. Moreover, CHNS analysis determined the nitrogen content and the amount of ligand on the grapheme oxide is 1.03 mmol g^{-1} (Figures 7-9).

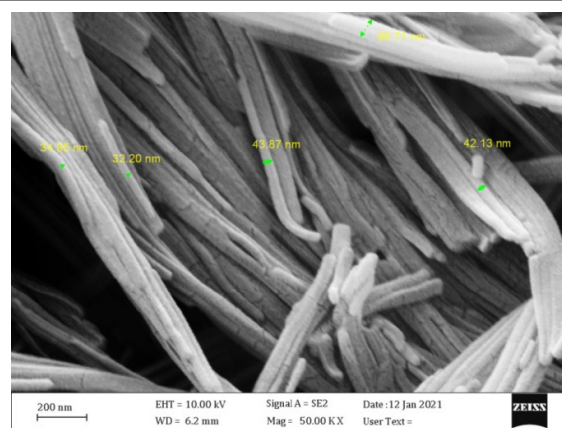**Figure 7:** SEM images of [Cu(II)Br$_2$-BTP@GO] catalyst.
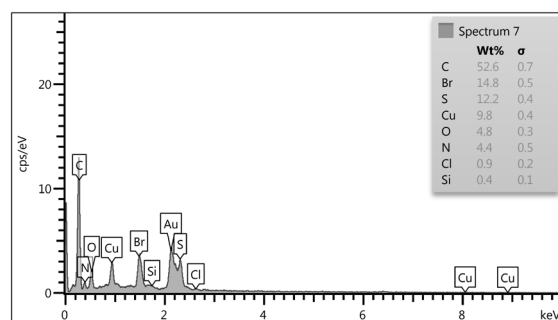
Figure 8: EDX spectrum of [Cu(II)Br$_2$-BTP@GO] catalyst. **Note:** C: Carbon; Br: Bromine; S: Sulphur; Cu: Copper; O: Oxygen; N: Nitrogen; Cl: Chlorine; Si: Silicon

Figure 9: Elemental Mapping of [Cu(II)Br$_2$-BTP@GO] catalyst.
Note: ( ): Bromine (Br); ( ): Cu (Copper); ( ): Cl (Chlorine); ( ): S (Sulphur); ( ): N (Nitrogen); ( ): C (Carbon); ( ): O (Oxygen); ( ): Si (Silicon)
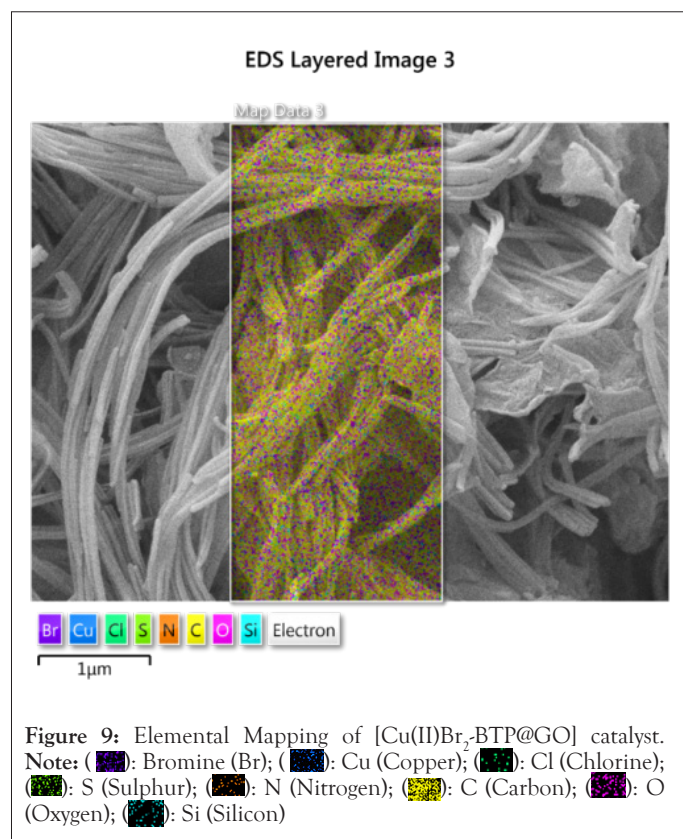
Catalytic studies

In this work, the [Cu(II)Br$_2$-BTP@GO] catalyst's performance was examined by oxidation of benzyl alcohol to benzaldehyde. The best conditions for the amount of catalyst, time of reaction, type of oxidant and solvent were measured. The effect of the catalyst amount [Cu(II)Br$_2$-BTP@GO] were investigated on the oxidation procedure of benzyl alcohol, after than the room temperature was selected as best temperature. In the absence of the catalyst the yield was negligible and when the amount of the catalyst was increased from 0.02 g to 0.03 g the yield did not change. The best result was attained with 0.17 mol% (0.02 gr) of the catalyst as shown in Table 1, entry 5. In this reaction the effect of time was studied and the best time was 3 hour. For investigation of the effect of solvent, different solvents were examined such as acetonitrile; acetonitrile/H$_2$O and H$_2$O, amongst them the water was are found an appropriate solvent for achieving the best reaction condition. Various oxidants such as Na$_2$CO$_3$, tert-BuOOH, H$_2$O$_2$, K$_2$CO$_3$, Et$_3$N and NaIO$_4$ were investigated for the oxidation of benzyl alcohol and tert-BuOOH was showed the best results (Table 1).

Table 1: Optimization of conditions in the oxidation of benzyl alcohol catalyzed with Cu(II)Br2-BTP@MNPs.

Entry	Catalyst (mol%)	Oxidant	Time (h)	Solvent	Yield (%)
1	0.17	NaIO$_4$	12	H$_2$O	60
2	0.17	Na$_2$CO$_3$	12	H$_2$O	20
3	0.17	K$_2$CO$_3$	12	H$_2$O	15
4	0.17	H$_2$O$_2$	12	H$_2$O	65
5	0.17	TBHP	3	H$_2$O	90
6	0.17	TBHP	3	CH$_3$CN	50
7	0.17	TBHP	3	CH$_3$CN/H$_2$O	75
8	0.087	TBHP	3	H$_2$O	65
9	0.26	TBHP	3	H$_2$O	90
11	-	TBHP	12	H$_2$O	Trace
12	GO	TBHP	12	H$_2$O	Trace
13	Fe3O$_4$	TBHP	12	H$_2$O	Trace

Finally, under optimized reaction conditions, oxidation of different alcohol was evaluated with tert-BuOOH as oxidant at 25°C in water and with the use of Cu(II)Br2-BTP@MNPs catalyst, and results show that the [Cu(II)Br$_2$-BTP@GO] catalyst was better than Cu(II)Br2-BTP@MNPs catalyst. Various alcohols reacted to their corresponding aldehydes and obtained results showed that the nature of substituent on the phenyl ring has no obvious effect on the yield of the product. And linear and cyclic alcohols were successfully oxidized to their corresponding carbonyl compounds (Table 2).

Table 2: Optimization of conditions in the oxidation of benzyl alcohol catalyzed with Cu(II)Br2-BTP@MNPs.

Entry	Alcohol	Carbonyl compound	Yield (%)	TOF (h^{-1})
1	Benzyl alcohol	Benzaldehyde	88	172.5
2	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	90	176.4
3	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	90	176.4
4	2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	86	168.6
5	3-Nitrobenzyl alcohol	3-Nitrobenzaldehyde	85	166.6
6	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	86	168.6
7	1-Octanol	1-Octanal	70	137.2
8	Cinnamyl alcohol	Cinnamaldehyde	79	154.9

Reusability of catalyst: Recyclability and reusability are two main advantages for heterogeneous catalyst. These parameters are important from environmental, economic and industrial points of view. Therefore, the reusability of the [Cu(II)Br$_2$-BTP@GO] catalyst was investigated in oxidation of benzyl alcohol with tert-BuOOH under the optimized reaction conditions. After each catalytic run, the catalyst was separated by centrifugation and then washing with H$_2$O and Et$_2$O, and drying in an oven at 60°C, and then used in the next run. The results are shown in Figure 10, exhibited that the catalyst could be reused several times in catalytic reactions without noticeable loss of activity. The copper content of the catalyst after fourth run was measured by Atomic Absorption Spectrophotometer (AAS), which showed a value of about 0.075 mmol/g (about 95% of the initial Cu content), for the catalyst was used in the oxidation of benzyl alcohol (Figure 10 and Table 3).

Figure 10: The results of catalyst recovery in the oxidation of benzyl alcohol with tert-BuOOH.
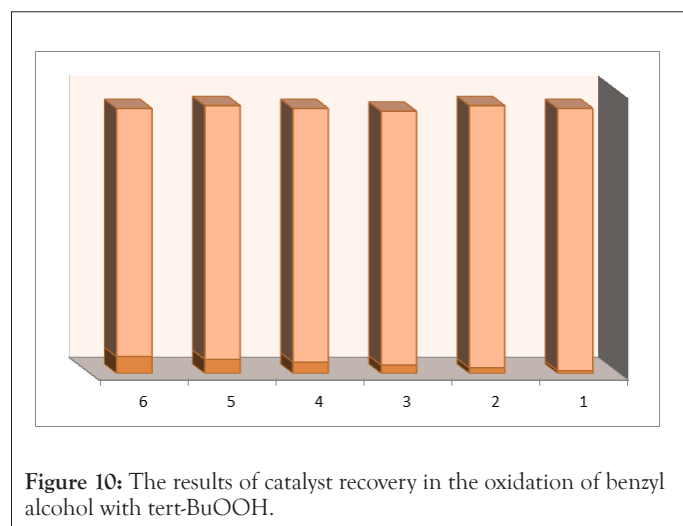
Table 3: Comparison of this work with other published works.

Entry	Catalytic system	Time (h)	Yield (%)
1	(L3=(2-C$_5$H$_4$N)CH$_2$N)Cu(OAc)	2	90
2	Cu^{II} (8-hydroxyquinoline-imine) complex	8	90
3	N-heterocyclic carbene complex (Cu-NHC@Pyrm-OMS)	8	97
4	Cu(I)-iodide-2,2'-dipyridylamine (dpa) catalyst	24	99
5	Cu^{II} (4-bromobenzoate/2,2-dipyridylamine) complex	24	100

CONCLUSION

In this study, we have synthesized a catalyst from thiazole ligand by immobilization of CuBr$_2$ onto the surface of graphene oxide. Graphene oxide was used as supporting material to increase the catalytic properties of copper. The XRD indicates the presence of copper (cu) and graphene oxide in the synthesized samples. Moreover, the SEM and TEM results confirmed that the Cu nanoparticles strongly deposited on the surface of GO nanosheets. Additionally, the present work shows that the oxidation of benzyl alcohol to benzaldehyde can be achieved with a [Cu(II)Br$_2$-BTP@GO] (0.02 g weight, RT and TBHP as the oxidant). Finally, the catalyst recovered and reused at least six times.

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