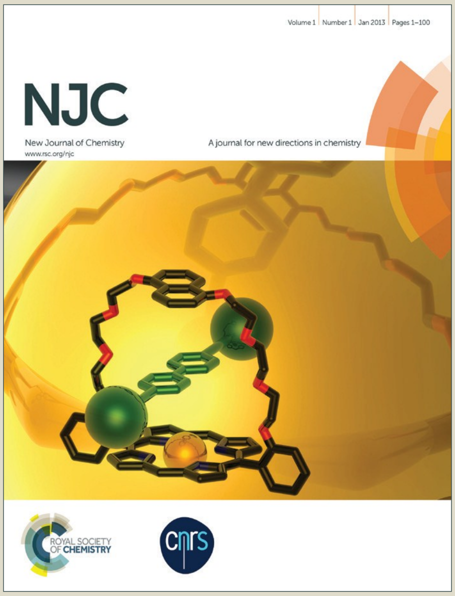


Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Graphene oxide immobilized Cu(II) complex of 1,2-*bis*(4-aminophenylthio)ethane: An efficient catalyst for epoxidation of olefins with *tert*-butyl hydroperoxide

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ali Zarnegaryan, Majid Moghadam,* Shahram Tangestaninejad,* Valiollah Mirkhani,* and Iraj Mohammdpoor-Baltork

In this work, a new, recoverable and heterogeneous catalyst was prepared by covalent attachment of the Cu(II) complex of 1,2-*bis*(4-aminophenylthio)ethane onto graphene oxide via the amide linkages. The structural and chemical nature of the catalyst was characterized by a variety of techniques such as Fourier transform infrared and diffuse reflectance UV-visible spectroscopies, X-ray diffraction, thermogravimetric analysis, transmission electron microscopy, field emission scanning electron microscopy and inductively coupled plasma atomic emission spectroscopy. The catalytic activity of this catalyst was investigated in the epoxidation of olefins with *tert*-butyl hydroperoxide. The catalyst is of great reusability and stability in the epoxidation reactions.

Introduction

Alkene epoxidation is a very useful reaction in industrial organic synthesis because the resultant epoxides are essential precursors in the synthesis of various important substances like plasticizers, cosmetics, perfumes and epoxy resins and pharmaceuticals.[1] In the last few decades, soluble transition metal salts and transition metal complexes as conventional epoxidation catalysts have been extensively used for homogeneous epoxidation of organic substrates such as cyclohexene, cyclooctene and styrene due to their high catalytic performance.[2,3] However, most of the existing methods suffer from drawbacks such as difficult recovery and recycling of the catalyst, lower catalytic activity, tedious synthesis of catalysts, harsh reaction conditions, and lower yields of the products.

In recent years, to overcome these problems, heterogenization of homogeneous catalysts has attracted much attention because they combine the best properties of both homogeneous and heterogeneous counterparts.[4] Among the various approaches for immobilizing soluble catalysts, covalent attachment has been the most frequently used strategy, as the resulting heterogeneous catalysts have good stability during the course of catalytic reactions. In this approach, the catalyst leaching from the support is minimized and thus, provides a way to prepare site isolated catalysts. In this manner, different soluble complexes have been immobilized on various supports such as silica, organic polymers, carbon nanotubes, metal-organic frameworks and etc.[5-19]

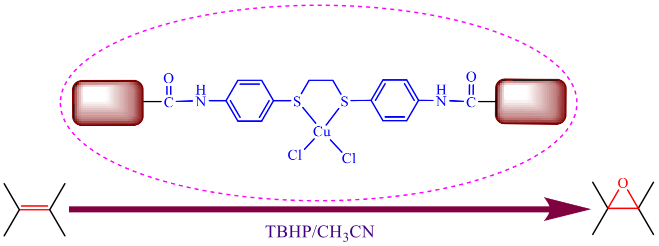
Graphene, a monolayer of carbon atoms packed into a two dimensional (2D) honeycomb lattice, is the basal building block in all graphitic materials.[20-22] Graphene oxide (GO), obtained by oxidation of graphene, is a layered material with oxygen-containing groups, such as hydroxyl, epoxide, carboxyl and carbonyl functional groups. This material is hydrophilic and readily disperses in water to form a stable colloidal suspension,[23-26] Concurrently, GO has emerged as an important material due to its unique nanostructure and a variety of fascinating characteristics such as very high specific surface area with intrinsic low mass, ample oxygen carrying functionalities, and excellent mechanical strength.[27-29] GO has been used as excellent supporting material. This is due to the presence of plenty oxygenic functional groups on the surface which can be used for immobilization of various homogeneous materials as active sites. Scheuermann et al. reported the application of GO supported Pd nanoparticles in the Suzuki-Miyaura coupling reaction with high activity and low palladium leaching.[30] Mungse et al. prepared oxo-vanadium Schiff covalently anchored onto graphene oxide sheets for the

---

[a]*Department of Chemistry, Catalysis Division, University of Isfahan Institution, Isfahan, 81746-73441 (Iran) Fax: (+98) 031-36689732.*
E-mail: moghadamm@sci.ui.ac.ir, stanges@sci.ui.ac.ir, mirkhai@sci.ui.ac.ir

oxidation of alcohols.[31] Su et al. reported GO supported transition metal Schiff base complexes as efficient and recyclable catalysts for epoxidation of styrene.[32] Nasseri et al. prepared GO supported Mn(II) Schiff base complex for epoxidation of different alkenes.[33]

In this work, the copper complex of 1,2-*bis*(4-aminophenylthio)ethane was immobilized on graphene oxide nanosheets to obtain a novel heterogeneous Cu catalyst for epoxidation of olefins with *tert*-butyl hydroperoxide (TBHP) (Scheme 1).

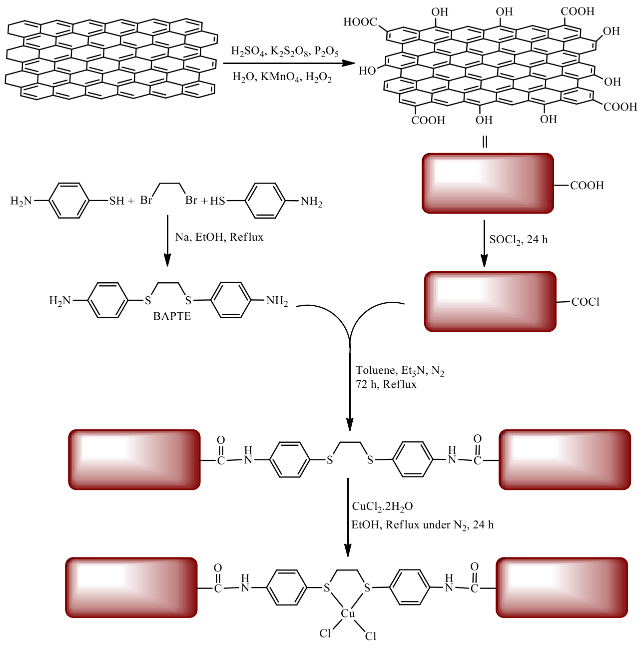


Scheme 1. Alkene epoxidation with TBHP catalyzed by Cu^{II}(BAPTE)Cl$_2$@GO

Results and discussion

Preparation and characterization of catalyst

In brief, graphene oxide (GO) was prepared from oxidation of graphene powder by modified Hummers method.[34] Prior to the immobilization of the copper catalyst, the GO was treated with SOCl$_2$ to convert the –COOH groups into –COCl groups. The GO-COCl was reacted with 1,2-*bis*(4-aminophenlythio)ethane (BAPTE) in the presence of triethylamine and the ligand was attached on GO-COCl via amide linkages. The final catalyst, Cu^{II}(BAPTE)Cl$_2$@GO, was prepared by the reaction of BAPTE@GO with CuCl$_2$ (Scheme 2).



Scheme 2 Schematic preparation of Cu^{II}(BAPTE)Cl$_2$@GO

Covalent attachment of the Cu^{II}(BAPTE)Cl$_2$ to GO support provided a catalyst which is not soluble in common organic solvents.

The structural and chemical nature of the catalyst was characterized by FT-IR and UV-vis spectroscopies, FE-SEM and TEM microscopic techniques, XRD, TGA and ICP-AES analyses.

The FT-IR spectra of GO, BAPTE, BAPTE@GO and Cu^{II}(BAPTE)Cl$_2$@GO are shown in Fig. 1. In the pure GO (Fig. 1a), the strong band at 1726 cm^{-1} represents carboxylic acid groups and the bands at 1051, 1223 and 1618 cm^{-1} are attributed to the C–O (epoxy), C–OH and C=C bonds in graphene oxide, respectively. In addition, a broad band at 3429 cm^{-1}, attributed to the stretching mode of O–H bonds, reveals the presence of many hydroxyl groups.[31] In the FT-IR spectra of BAPTE@GO and Cu^{II}(BAPTE)Cl$_2$@GO, the band at 1566 cm^{-1} is due to the N–H bending vibration. On the other hand, a new band at 1711 cm^{-1} is attributed to amide (-NH-CO-) groups (Fig. 1c and 1d).[35] The vibrational bands correspond to the –NH$_2$ groups in BAPTE (Fig. 1b) is disapperared in the BAPTE@GO and Cu^{II}(BAPTE)Cl$_2$@GO compounds. These observations confirmed the covalent attachment of BAPTE to GO *via* amide bond formation.

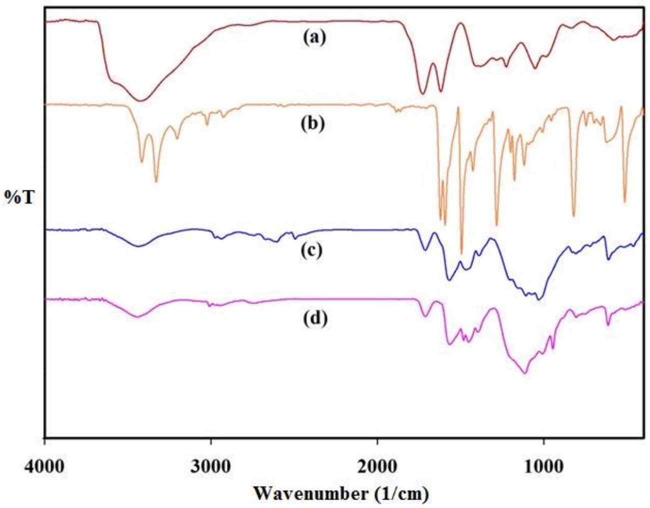


Fig. 1. FT-IR spectrum of: (a) GO, (b) BAPTE, (c) BAPTE@GO and (d) Cu^{II}(BAPTE)Cl$_2$@GO

The UV-Vis absorption spectra of GO, BAPTE@GO and Cu^{II}(BAPTE)Cl$_2$@GO are shown in Fig. 2. The UV-vis spectrum of GO shows a strong absorption peak at 230 nm which can be attributed to the π-π* transition of graphitic C–C bonds (Fig. 2).[36] The BAPTE@GO and Cu^{II}(BAPTE)Cl$_2$@GO catalyst exhibit a broad absorption at 274 nm which are completely different from the parent GO.

The TGA curve of pure GO and heterogeneous catalyst were shown in (Fig. 3). Graphene oxide shows a low weight loss below 100 °C, evidently owing to evaporation of water molecules which are held in the material. The second significant weight loss is observed in the range of 190–220 °C, due to thermal decomposition of oxygen carrying functionalities. The TGA curve of heterogeneous catalyst shows a low weight loss at 75-300 °C due to the decomposition of the residual oxygen containing groups. Compared with the thermogram of GO, the weight loss of $Cu^{II}(BAPTE)Cl_2@GO$ below 300 °C is lower, indicating that the main oxygen-containing functional groups of GO has been converted after reacting with BAPTE.

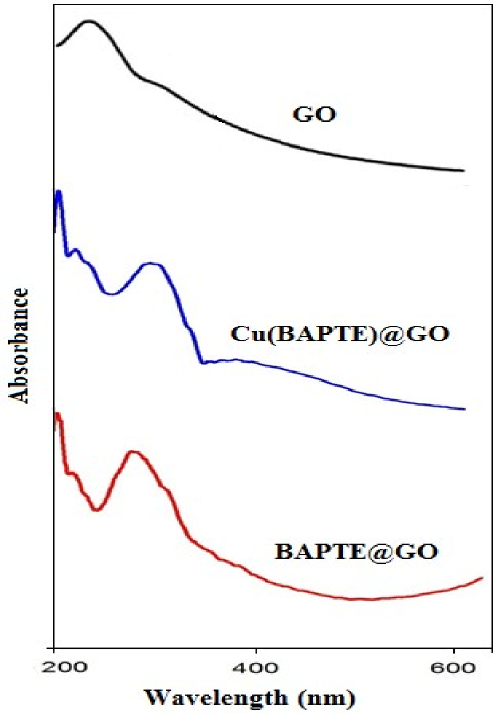


Fig. 2. UV-vis absorption spectrum of: a) graphene oxide, (b) BAPTE@GO and (c) $Cu^{II}(BAPTE)Cl_2@GO$ catalyst.

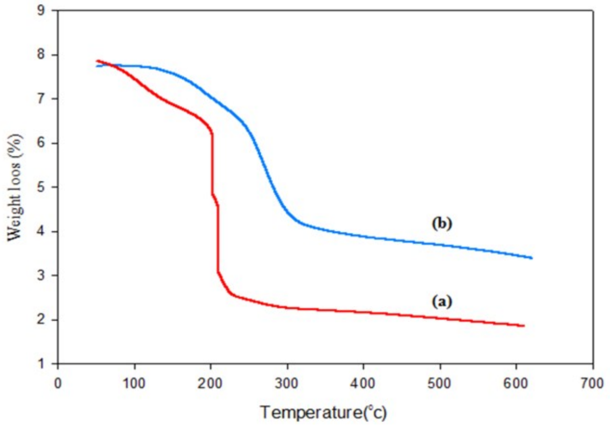


Fig. 3. Thermogram of: (a) graphene oxide; (b $Cu^{II}(BAPTE)Cl_2@GO$ catalyst

The XRD patterns are used to study the changes in structure (Fig. 4). For GO, two peaks at 2θ = 11.3° and 24.26° correspond to (001) and (002) reflections of GO and graphite powder, respectively (Fig. 4a).[31] The presence of various oxygen carrying functionalities on the basal planes of graphene oxide layers and the trapped water molecules between these layers increased the d-spacing in graphene oxide.[27,37,38] By immobilization of BAPTE, the intense (001) peak is almost disappears, whereas the appearance of diffraction peaks of pure BAPTE in the supported catalyst at around 2θ =14-28° indicates the immobilization of 1,2-*bis*(4-aminophenylthio)ethane (BAPTE) on the GO (Fig. 4b and 4c).

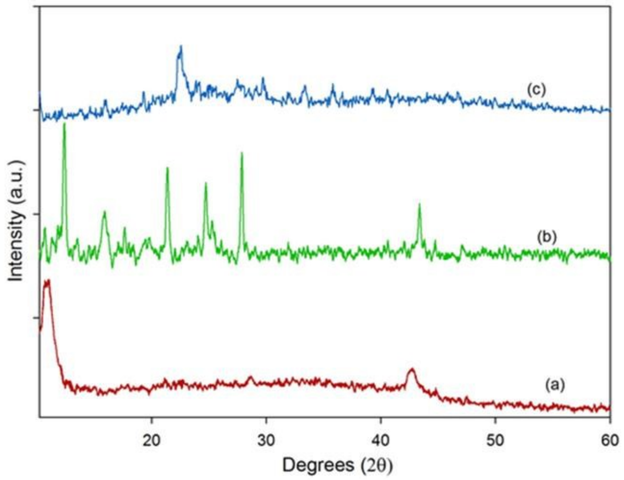


Fig. 4. XRD pattern of: (a) graphene oxide, (b) BAPTE@GO, and (c) $Cu^{II}(BAPTE)Cl_2@GO$ catalyst.

The surface morphologies of GO and $Cu^{II}(BAPTE)Cl_2@GO$ were studied using field emission scanning electron microscopy (FE-SEM). As shown in Fig. 5a, there are large flakes of GO with macroscopic wrinkling. Compared to GO sheets, the FE-SEM image of $Cu^{II}(BAPTE)Cl_2@GO$ (Fig. 5b) exhibited an agglomerated layered structure incorporating copper complex moieties between the sheets.

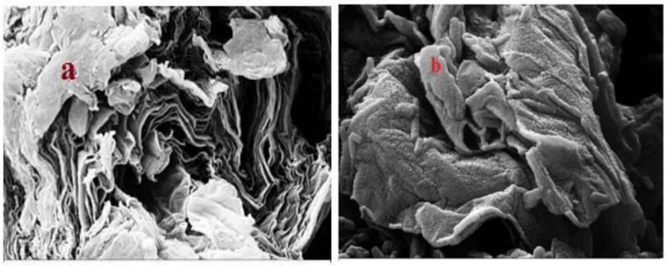
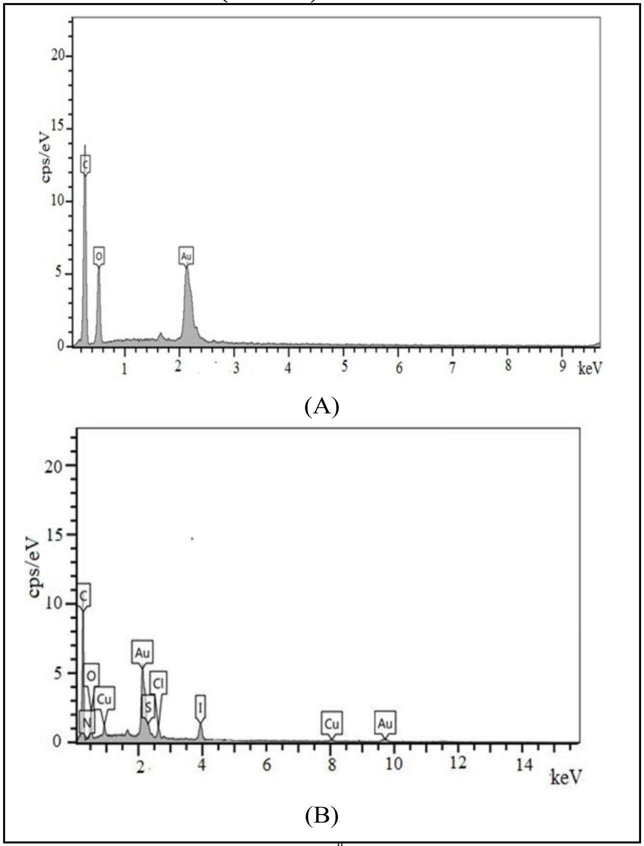


Fig. 5. FE-SEM image of: (a) GO; (b) $Cu^{II}(BAPTE)Cl_2@GO$

Energy dispersive (X-Ray spectroscopy) analyses of GO and $Cu^{II}(BAPTE)Cl_2@GO$ were shown in (Fig. 6). As can be seen, the in the EDX spectrum of GO, the major elements are carbon and oxygen (Fig. 6a). In the EDX spectrum of $Cu^{II}(BAPTE)Cl_2@GO$ (Fig. 6b), the presence of Cu, N and S peaks originates from $Cu^{II}(BAPTE)Cl_2$ is a good indication in for attachment of $Cu^{II}(BAPTE)Cl_2$ on GO sheets.

TEM image of $Cu^{II}(BAPTE)Cl_2@GO$ showed twisted nanosheets (Fig. 7). In the TEM image of

$Cu^{II}(BAPTE)Cl_2$@GO the appearance of dark spots is due to the attachment of Cu^{II}(BAPTE) molecules on the GO surface.[39]



(A)

(B)

Fig. 6. EDX spectrum of: (a) GO and (b) $Cu^{II}(BAPTE)Cl_2$@GO

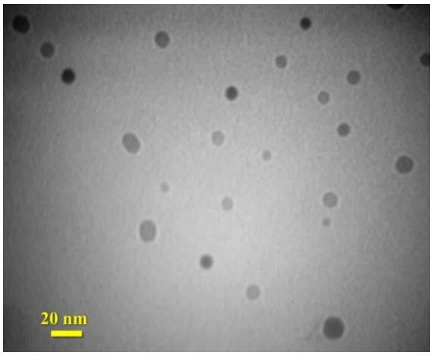


Fig. 7. TEM images of $Cu^{II}(BAPTE)Cl_2$@GO catalyst

Investigation of catalytic activity of $Cu^{II}(BAPTE)Cl_2$@GO in the epoxidation of olefins with TBHP

Initially, the catalytic activity of the prepared catalyst was investigated in the epoxidation of cyclooctene using TBHP as a model reaction under different conditions. To find optimum reaction conditions, the influence of different factors that may affect the conversion and selectivity of the cyclooctene epoxidation was investigated.

For choosing the reaction media, the model reaction was carried out in different solvents such as acetonitrile, 1,2-dichloroethane (DCE), methanol, ethanol, tetrahydrofuran (THF) ethanol–water and water using 0.7 mol% of the heterogeneous Cu(II) catalyst, (Table 1, entries 1-8). The best yield was obtained in acetonitrile. The effect of reaction temperature was also investigated in the model reaction. The temperature showed remarkable effect on the epoxide yield. Amongst the tested temperatures, the 80 °C was the optimum temperature for obtaining the highest conversion (Table 1, entries 1 and 9-13).

For optimization of the catalyst amount, different amounts of catalyst were used in the model reaction and the best results were obtained in the presence of 25 mg (0.7 mol%) of heterogeneous $Cu^{II}(BAPTE)Cl_2$@GO catalyst after 8 h. Increasing the catalyst amount did not affect the reaction rate. Note that in the absence of catalyst, no product was detected in the reaction mixture (Table 1, entries 1 and 14-17).

To evaluate the oxidizing potential of other common oxidants, cyclooctene was subjected to the oxidation using different oxidants such as H_2O_2, TBHP and $NaIO_4$. The highest epoxide yield was obtained with TBHP while in the absence of oxidant; no conversion was observed (Table 1, entries 1 and 18-20).

Table 1. Optimization of reaction conditions in the epoxidation of cyclooctene catalyzed by $Cu^{II}(BAPTE)Cl_2$@GO.[a]

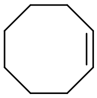
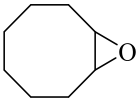
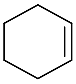
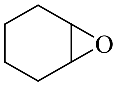
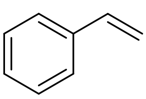
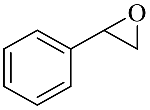
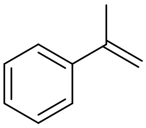
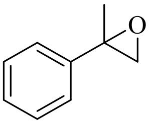
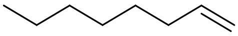
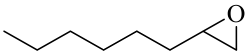
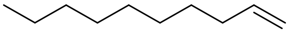
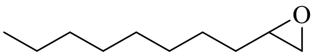
Entry	Catalyst amount (mol%)	T (°C)	Solvent	Oxidant	Yield (%)[b]
1	0.7	80	CH_3CN	TBHP	97
2	0.7	80	EtOAc	TBHP	80
3	0.7	80	$C_2H_4Cl_2$	TBHP	62
4	0.7	80	MeOH	TBHP	35
5	0.7	80	EtOH	TBHP	26
6	0.7	80	THF	TBHP	45
7	0.7	80	EtOH-H_2O	TBHP	22
8	0.7	80	H_2O	TBHP	14
9	0.7	25	CH_3CN	TBHP	18
10	0.7	40	CH_3CN	TBHP	33
11	0.7	60	CH_3CN	TBHP	58
12	0.7	70	CH_3CN	TBHP	75
13	0.7	90	CH_3CN	TBHP	97
14	0	80	CH_3CN	TBHP	0
15	0.25	80	CH_3CN	TBHP	31
16	0.5	80	CH_3CN	TBHP	63
17	1.0	80	CH_3CN	TBHP	97
18	0.7	80	CH_3CN	H_2O_2	70
19	0.7	80	CH_3CN	$NaIO_4$	42
20	0.7	80	CH_3CN	-	0

[a] Reaction conditions: Cyclooctene (1 mmol), oxidant (3 mmol), solvent (5 mL) and catalyst after 8 h.

[b] GC yield based on the initial cyclooctene.

Under the optimized reaction conditions, the scope of this protocol was further investigated in the epoxidation of different olefins with TBHP. The results are summarized in Table 2. Cyclooctene was converted selectively to its corresponding epoxide in 97% yield. Cyclohexene was oxidized in 95% yield with 92% epoxide selectivity and trace amount of cyclohex-2-ene-1-one was produced. In the epoxidation of styrene and α-methylstyrene, benzaldehyde and acetophenone were produced as minor products. 1-Octene and 1-decene as linear alkenes were epoxidized efficiently by this catalyst in high yields and selectivity.

Table 2. Epoxidation of alkenes with *tert*-BuOOH catalyzed by heterogeneous Cu(II) complex under reflux conditions.[a]

Entry	Olefin	Product	Epoxide Selectivity (%)	Yield (%)[b]	TOF (h^{-1})
1			100	97	17.3
2			92[c]	95	16.9
3			88[d]	93	16.6
4			90[e]	96	17.1
5			92	94	16. 8
6			90	91	16.3

[a]Reaction conditions: Alkene (1 mmol), TBHP (3 mmol) and catalyst (0.7 mol% based on Cu) in acetonitrile at 80 °C after 8 h.

[b]Determined by GC based on starting alkene.

[c]The by-product is cyclohex-2-ene-1-one.

[d]The by-product is benzaldehyde.

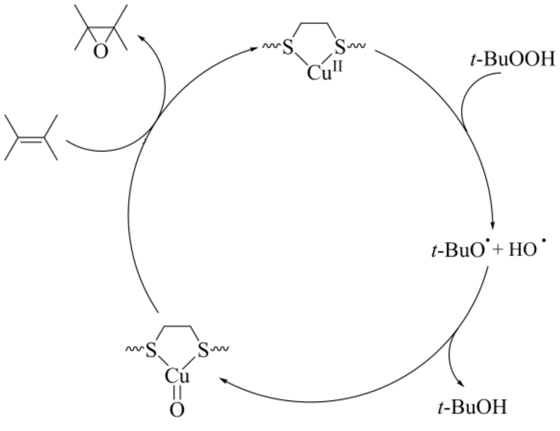
[e]The by-product is acetophenone.

The results obtained by $Cu^{II}(BAPTE)Cl_2$@GO in the epoxidation of cyclohexene was compared with the results reported for some other copper(II) catalysts. As can be seen, our reported method is superior in terms of reaction times, yields or epoxide selectivity (Table 3). Also, in most cases, the higher TOF has been obtained by our reported method.

Table 3. Comparison of the catalytic activity of $Cu^{II}(BAPTE)Cl_2$@GO with other reported copper(II) catalysts in the epoxidation of cyclohexene.

Entry	Catalyst	Time (h)	Conversion (%)	Epoxide Selectivity (%)	TOF (h^{-1})	Ref.
1	$Cu^{II}(BAPTE)Cl_2$@GO	8	95	92	16.9	This study
2	PS-Cu-Sal	7	74	30	17.6	40
3	Cu-S-$AMSiO_2$	12	32.4	1.3	2.2	41
4	Cu-S-AM(PS)	12	57.4	2.9	4.0	41
5	Cu(salen)	12	30	1.4	2.1	41
6	$[Cu_4(O)(\mathbf{L}^{1})_2(CH_3COO)_4]$	24	78	90	12.0	42
7	$[Cu_4(O)(\mathbf{L}^{2})_2(CH_3COO)_4]CH_3CN$	24	85	87	13.3	42
8	$[Cu_4(O)(\mathbf{L}^{3})_2(CH_3COO)_4]$	24	88	92	17.0	42
9	$[Cu_4(O)(\mathbf{L}^{4})_2(CH_3COO)_4]$	24	90	87	12.0	42
10	$[Cu_2Ni(L^1)(2,2'\text{-bpy})_2(NO_3)_2][ClO_4]_2$	24	46	74	88.0	43
11	$[Cu_2L(\mu_{1,1}, -N_3)(\mu_{1,3}-N_3)(\mu_{1,1,1}-N_3)]$	24	76	84	12.1	44
12	PS–Cu–amp-Cl	6	61	79	49.8	45
13	Cu(salen)−f− GO	12	75	66	99.3	46
14	$[Cu(H_2btec)(bipy)]$	24	65	73	79.0	47
15	$[Cu_2(bipy)_2(btec)]\infty$ MOF	6	20	6	13.0	48

A plausible mechanism for this reaction is shown in Scheme 3. According to this mechanism, homolytic cleavage of O-O peroxy bond produces the *t*-BuO• and •OH radicals. Addition of 2,6-di-*tert*-butylphenol as a radical scavenger stopped the reaction and no product was produced. Upon reaction of these radicals with Cu catalyst, a metal oxo was formed which can transfer its oxygen to alkene to produce the epoxide.



Scheme 3 The proposed mechanism for epoxidation of alkenes with TBHP

The reusability of catalyst was investigated in the sequential epoxidation of cyclooctene with TBHP. In this manner, after each run, the catalyst was separated from the reaction mixture by simple filtration and washed with acetonitrile and ethanol, dried at 40 °C and used with fresh cyclooctene and TBHP. The results, which are summarized in Fig. 8, showed that the catalyst could be reused four consecutive times without loss of its catalytic activity. The amount of Cu leached was determined by ICP which showed a value of about 1% in the first run and 0.4 % in the second run. No Cu was detected in the filtrates of third and fourth run.

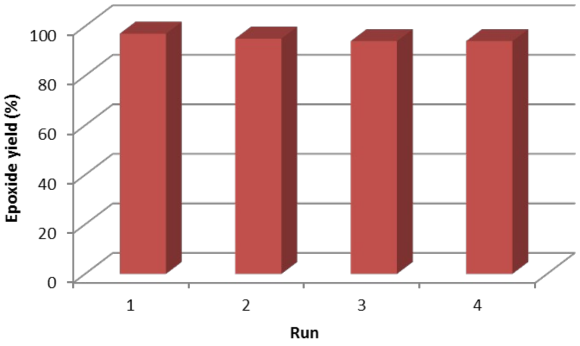


Fig. 8. Investigation of catalyst reusability in the epoxidation of cyclooctene with TBHP

Conclusion

The surface of graphene oxide is rich of different functional groups which can be used for supporting of various catalysts. The Cu(II) complex of 1,2-*bis*(4-aminophenylthio)ethane, $Cu^{II}(BAPTE)Cl_2$, supported on graphene nanosheets was prepared by covalent interaction between amino groups of 1,2-*bis*(4-aminophenylthio)ethane and acyl groups on the graphene oxide followed by reaction with $CuCl_2$. The prepared heterogeneous catalyst was used as a highly efficient catalyst in the epoxidation of various olefins with TBHP. Moreover, the catalyst was recovered easily and reused without significant loss in its catalytic activity.

Experimental

General remarks

Materials and methods

All chemicals were purchased from Merck and Sigma-Aldrich chemical companies and used without purification. FT-IR spectra were obtained as potassium bromide pellets in the range of 400–4000 cm^{-1} with a JASCO 6300D instrument. Diffuse reflectance UV–vis (DR UV–vis) spectra were obtained on a JASCO, V-670 (190-2700 nm) spectrophotometer. The ICP analyses were performed on an ICP-Spectrociros CCD instrument. The XRD measurements were carried out using a Bruker D_8-advance X-ray diffractometer with Cu K_α radiation (λ= 1.5406 Å). The TEM images were obtained using a Philips CM10 instrument. TGA analysis was performed by heating at a constant rate of 10 °C min^{-1} from 50 °C to 600 °C under argon atmosphere. The Cu content of the catalysts was determined by Shimadzu AA-6300 atomic absorption spectroscopy (AAS). The yields were determined by a Shimadzu GC-16A gas chromatograph (GC) equipped with a flame ionization detector. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) and iridium (IXRF Systems) software.

The copper loading of the catalyst was determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES). Loading of copper in the prepared catalyst was found to be 0.28 mmol g^{-1}.

Syntheses of supported catalyst, $Cu^{II}(BAPTE)Cl_2@GO$

Synthesis of Graphene Oxide

Graphene oxide (GO) was oxidized from graphite powder by a modified Hummer method.[34] Three gram of graphite power (Sigma-Aldrich), 12 mL of H_2SO_4 was added and mixed with 2.5 g of $K_2S_2O_8$ and P_2O_5 at 80 °C for 4.5 h. Then, the mixture was cooled to room temperature and washed with deionized water (500 mL). After then, the mixture was stirred overnight at room temperature and then filtered and washed with deionized water and ethanol, subsequently and dried. The collected powder was added to H_2SO_4 (120 mL) with $KMnO_4$ (15 g) in a two-neck flask placed in an ice bath and stirred slowly until the contents were completely dissolved. Then, deionized water (250 mL) was added into the mixture with stirring for 2 h at 35 °C. Finally, deionized water (250 mL) was added along with 20 mL of H_2O_2, and the reaction was terminated via stirring for 30 min in an ice bath. The resulting mixture was washed until reaching pH= 7, and then a brown powder was collected after drying in a vacuum oven.

Synthesis of BAPTE

In a round-bottom flask, 4-aminothiophenol (2.5 g, 20 mmol) was added to absolute EtOH (20 ml) containing Na (0.46 g, 20 mmol). Then, 1,2-dibromoethane (0.86 ml, 10 mmol) in EtOH (5 ml) was added dropwise with constant stirring to the refluxing solution. The mixture was cooled and poured into H_2O (300 ml). The solid was filtered off, washed with H_2O and dried. The product was recrystallized from EtOH, and a yellowish residue was obtained. Yield: 68%, m.p. 79 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm)= 7.19 (2H, d), 7.21 (2H, m), 6.60 (2H, m), 6.62 (2H, d), 3.73 (4H, m), 2.89 (4H, m). FT-IR (KBr) (cm^{-1}): 3416 (s), 2932 (w), 2280 (w), 1620 (w), 1592 (m), 1493 (s), 1283 (s), 1176 (m), 1117 (m), 819 (s).

Synthesis of GO-COCl

The obtained GO (3.0 g) was suspended in thionyl chloride (40 ml) and the mixture was at stirred at 60 °C under nitrogen atmosphere for 6 h. Then, the resultant solid was filtered, washed with anhydrous toluene at least 5 times to remove the residual thionyl chloride and dried at 40 °C for 24 h in a vacuum oven.

Preparation of $Cu^{II}(BAPTE)Cl_2$@GO catalyst

The GO-COCl (1 g) was dispersed in anhydrous toluene (80 ml) using an ultrasonic bath. Then, 1,2-*bis*(4-aminophenylthio)ethane (100 mg) and triethylamine (4 ml) were added to this mixture and the resulting mixture was refluxed for 48 h under nitrogen atmosphere. After the reaction was completed, the mixture was filtered and washed with anhydrous toluene (4×10 mL) to remove the non-reacted BAPTE. In the final step, the prepared powder was dispersed in ethanol (60 ml), $CuCl_2.2H_2O$ (250 mg) was added and the mixture was stirred under reflux conditions for 24 h. At the end of the reaction, $Cu^{II}(BAPTE)Cl_2$@GO was filtered and washed with ethanol several times to remove the unreacted $CuCl_2.2H_2O$.

General procedure for catalytic epoxidation of olefins

In a round bottom flask, a mixture of alkene (1 mmol) and $Cu^{II}(BAPTE)Cl_2$@GO (25 mg, 0.007 mmol) in acetonitrile (5 ml) was prepared. TBHP (3 mmol) was added drop-wise to the reaction vessel and the mixture was stirred under reflux conditions. Progress of the reaction was monitored by GC. After completion of the reaction, the catalyst was separated by centrifugation, washed with acetonitrile and ethanol, and dried at 50 ºC. The recovered catalyst was used for investigation of the catalyst reusability.

Acknowledgements

The authors are grateful to the Research Council of the University of Isfahan for financial support of this work.

Notes and references

1 L. Hu, L. Shi, H. Hong, M. Li, Q. Bao, J. Tang, J. Ge, J. Lu, X. Cao and H. Gu, *Chem. Commun*., 2010, **46**, 85912

2 G. Grivani, G. Bruno, H. A. Rudbari, A. D. Khalaji and P. Pourteimouri, *Inorg. Chem. Commun.*, 2012, **18**, 15.

3 M. G. Topuzova, S. V. Kotov and T. M. Kolev, *Appl. Catal. A: Gen.*, 2005, **281**, 157.

4 G. A. Barf and R. A. Sheldon, *J. Mol. Catal. A: Chem.*, 1995,**102**, 23.

5 S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork and K. Ghani, *Catal. Commun.*, 2009, **10**, 853.

6 S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork and K. Ghani, *Inorg. Chem. Commun.*, 2008, **11**, 270.

7 M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and S. Gharaati, *J. Mol. Catal. A: Chem.*, 2011, **337**, 95.

8 Grivani, S. Tangestaninejad, M. H. Habibi, V. Mirkhani and M. Moghadam, *Appl. Catal. A: Gen.*, 2006, **299**, 131.

9 M. Hatefi, M. Moghadam, I. Sheikhshoaei, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Baltork and H. Kargar, *Appl. Catal. A: Gen.*, 2009, **370**, 66.

10 B. Bahramian, V. Mirkhani, M. Moghadam and S. Tangestaninejad, *Catal. Commun*., 2006, **7**, 289.

11 M. Tavassoli, A. Landarani-Isfahani, M. Moghadam, S. Tangestaninejad, V. Mirkhani and I. Mohammadpoor-Baltork, *Appl. Catal. A: Gen.*, 2015, **503**, 186-195.

12 F. Esnaashari, M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Baltork, A. R. Khosoropour, M. Zakeri and S. Hushmandrad, *Polyhedron*, 2012, **48**, 212–220.

13 M. Nooraeipour, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and N. Iravani, *J. Coord. Chem.* 2012, **65**, 226.

14 M. Zakeri, M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, A.R. Khosrpour and M. Alizadeh, *Transition Met. Chem.* 2012, **37**, 45.

15 S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork and M.S. Saeedi, *Appl. Catal. A: Gen.*, 2010, **381**, 233.

16 M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, H. Kargar and N. Zeini-Isfahani, *Polyhedron*, 2009, **28**, 3816.

17 M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and N.S. Mirbagheri, *Appl. Organomet. Chem.*, 2010, **708**, 2014.

18 F. Zadehahmadi, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, A. R. Khosropour and R. Kardanpour, *Appl. Catal. A: Gen.*, 2014, **477**, 34.

19 F. Zadehahmadi, F. Ahmadi, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork and R. Kardanpour, *J. Mol. Catal. A: Chem.*, 2015, **398**, 1.

20 X. Fan, W. Peng, Y. Li, X. Li, S. Wang, G. Zhang and F. Zhang, *Adv. Mater.*, 2008, **20**, 4490.

21 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183.

22 G. Wang, J. Yang, J. Park, X. Gou, B. Wang, H. Liu and J. Yao, *J. Phys. Chem. C*, 2008, **112**, 8192.

23 N. A. Kotov, *Nature*, 2006, **442**, 254–255.

24 G. H. Chen, D. J. Wu, W. U. Weng and C. L. Wu, *Carbon*, 2003, **41**, 619.

25 G. H. Chen, C. L. Wu, W. G. Weng, D. J. Wu and W. L. Yan, *Polymer*, 2003, **44**, 1781.

26 G. H. Chen, W. G. Weng, D. J. Wu, C. L. Wu, J. R. Lu, P. P. Wang and X. F. Chen, *Carbon*, 2004, **42**, 753.

27 D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen and R. S. Ruoff, *Nature*, 2007, **448**, 457.

28 D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228.

29 O. C. Compton and S. T. Nguyen, *Small*, 2010, **6**, 711.

30 G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth and R. Mulhaupt, *J. Am. Chem. Soc.*, 2009, **131**, 8262.

31 H. P. Mungse, S. Verma, N. Kumar, B. Sain and O. P. Khatri, *J. Mater. Chem.*, 2012, **22**, 5427.

32 H. Su, Z. Li, Q. Huo, J. Guan and Q. Kan, *RSC Adv.*, 2014, **4**, 9990.

33 M. A. Nasseri, A. Allahresani and H. Raissi, *RSC Adv.*, 2014, **4**, 26087.

34 W. S. J. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, 1957, **80**, 1339

35 P. Kumar, G. Singh, D. Tripathi and S. L. Jain, *RSC Adv.*, 2014, **4**, 50331.

36 V. H. Pham, T. V. Cuong, S. H. Hur, E. W. Shin, J. S. Kim, J. S. Chung and E. J. Kim, *Carbon*, 2010, **48**, 1945.

37 S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558.

38 D. Pan, S. Wang, B. Zhao, M. Wu, H. Zhang, Y. Wang and Z. Jia, *Chem. Mater.*, 2009, **21**, 3136.

39 B. Li, H. Cao, G. Yin, Y. Lu and J. Yin, *J. Mater. Chem*., 2011, **21**, 10645-1648.

40 S. M. Islama, P.Mondal, S. Mukherjee, A. S. Roya and A.Bhaumik, *Polym. Adv. Technol.* 2011, **22**, 933.

41 P. Karandikar, K. C. Dhanya, S. Deshpande, A. J. Chandwadkar, S. Sivasanker, M. Agashe, *Catal. Commun.* 2004, **5**, 69.

42 P. Roy, M. Nandi, M. Manassero, M. Ricc´o, M. Mazzani, A. Bhaumik and P. Banerjee**,** *Dalton Trans.* 2009, 9543.

43 S. Biswas, A. Dutta, M. Dolai, I. Bhowmick, M. Rouzières, R. Clérac, A.m. Panjad and M. Alia, Dalton Trans., 2015,**44**, 9426..

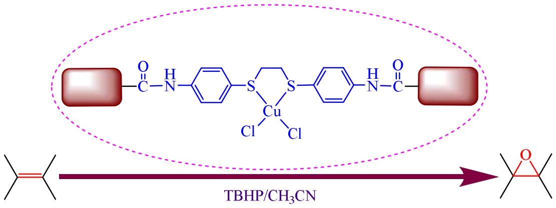
44 P. Roy , K.Dhara , M. Manassero , P. Banerjee, *Inorg. Chem. Communi.* 2008, **11**, 265.

45 S. M. Islam , A. S. Roy , P. Mondal , N. Salam , J .Inorg. Organomet. Polym. 2012, **22**,717.

46 Q. Zhao, C. Bai, W. Zhang, Y. Li, G. Zhang, F. Zhang, and X. Fan, *Ind. Eng. Chem. Res.* 2014, **53**, 4232.

47 K**.**Brown, S. Zolezzi, P. Aguirre, D. Venegas-Yazigi, V.Paredes-Garc ´ ıa,, R. Baggio, M.A. Novak f and E. Spodine**,** Dalton Trans., 2009, 1422.

48 P. Cancino, V. P.García, P. Aguirre and E. Spodine, *Catal. Sci. Technol.*, 2014, **4**, 2599.



Alkene epoxidation with *tert*-butyl hydroperoxide catalyzed by Cu(II) dithiol complex supported on graphene oxide is reported