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ORIGINAL PAPER

CuO supported 1-methyl-3-(3-(trimethoxysilyl) propyl) imidazolium chloride (MTMSP-Im/Cl) nanoparticles as an efficient simple heterogeneous catalysts for synthesis of β-azido alcohols

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Abstract

In the present study, CuO supported 1-methyl-3-(3-(trimethoxysilyl) propyl) imidazolium chloride (MTMSP-Im/Cl) is synthesized as a novel, efficient and eco-friendly heterogeneous nanocatalyst. This nanocatalyst was applied for selective ring opening of epoxides with azide anion in water. Structure and morphology of the obtained catalyst were investigated by FT-IR spectroscopy, XRD, TGA, FE-SEM, and EDX techniques. All the results confirmed that MTMSP-Im/Cl is grafted on to CuO nanoparticles. The synthesized nanohybrid can be easily separated after completion of the reaction and reused for four cycles without any significant reduction of its catalytic activity.

Keywords Heterogeneous nanocatalyst · Ring opening of epoxides · β-azido alcohols · CuO nanoparticles

Introduction

Nowadays, many organic reactions are carried out in the presence of catalysts. Heterogenization of homogeneous catalysts has been an interesting area of research from the industrial point of view; this combines the advantages of homogeneous catalysts (high activity and selectivity, etc.) with the engineering advantages of heterogeneous catalysts such as easy catalyst separation, long catalytic life, easy catalyst regenerability, thermal stability, and recyclability [1].

Among heterogeneous catalysts, CuO nanoparticles' (NPs) materials containing high surface area and reactive morphologies have been used widely as an efficient catalyst for organic synthesis due to good chemical and thermal stability, low cost, low toxicity, ease of handling, and high catalytic activity reusability [2–4]. Copper oxide nanoparticles are of special interest, because CuO has been shown to be an industrially important material that can be widely used in various applications such as gas sensor, magnetic storage media, battery, diode, solar energy transformation, nanofluid, semiconductor, and heterogeneous catalysis [5–12].

β-azido alcohols are remarkably versatile class of compounds which are very important in organic chemistry due to their pharmaceutical and industrial applications and useful precursors for the synthesis of oxazolines, lactames, amino sugars, and carboxylic nucleosides [13]. Various catalysts have been reported for the synthesis of β-azido alcohols in the presence of azide anion under mild conditions [14–29]. Although some of the reported catalysts give good yields under mild conditions, for the ring opening of epoxides, most of them are not environmentally friendly and suffer from high toxicity, tedious work up, used of expensive metals, or the need for large amounts of catalyst and difficulty in recovery and reusability of it [30–34]. Therefore, the development of clean, high-yielding, and environmentally friendly approaches is still a challenge for organic chemists in the synthesis of β-azido alcohol derivatives.

Based on the above introduction, in this work, we reported a new functionalized CuO nanoparticle with 1-methyl-3-(3-trimethoxysilylpropyl)-imidazolium chloride to obtain a heterogeneous catalyst for the regioselective formation of a variety of β-azido alcohols from epoxides under mild conditions.

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Experimental part

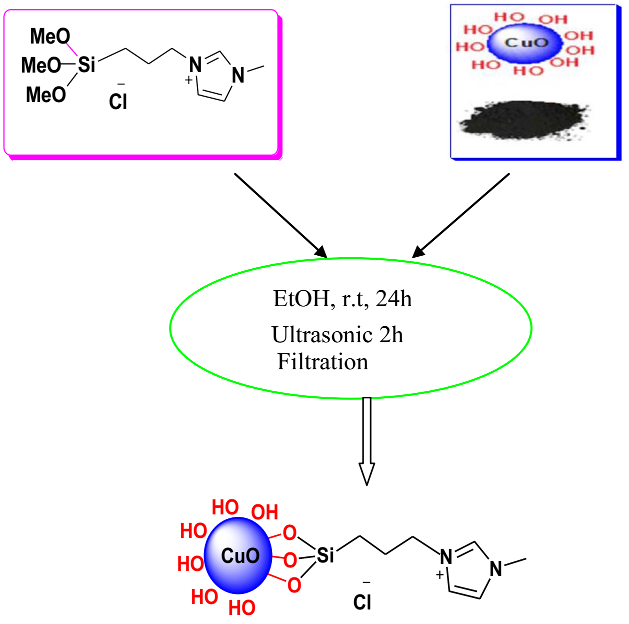
General

Nano-CuO powder was purchased from Alborz Chemical Co. (Tehran, Iran). Nano-size CuO powder had average particle size of < 50 nm and specific surface areas > 80 m^2 g^{-1}. Other chemical reagents in high purity were purchased from Merck and Aldrich and were used without further purification. Products were characterized by comparison of their physical data, FT-IR, ^{1}H, and ^{13}C NMR spectra with the known samples [21, 35–38]. The purity of the compounds synthesized was monitored by TLC on silica gel polygram SILG/UV 254 plates.

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance DPX 400 MHz spectrometer, respectively. An FT-IR spectrum of the CuO-np@MSP-Im/Cl nanocatalyst and products were recorded in the range 400–4000 cm^{-1} on a Perkin-Elmer 550 spectrometer. The particle size, external morphology of the particles, and elemental analysis of the nanocatalyst were characterized by field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray (EDX) spectroscopy, model Mira 3-XMU. X-ray diffraction (XRD) patterns of the samples were taken on a Philips X-ray diffractometer Model PW1840. The thermal gravimetric analysis (TGA) curve of the heterogeneous nanocatalyst was recorded on BAHR SPA 503 at heating rates of 10 °C min^{-1}. Modification CuO (NPs) was carried out on ultrasonic liquid processor. Ultrasound was wave of frequency 2.25×10^4Hz and power of 100W.

Preparation of CuO-np@MSP-Im/Cl catalyst

In the first step, 1-methyl-3-(3-(trimethoxysilyl) propyl) imidazolium chloride (MTMSP-ImCl) was prepared according to the reported method valizadeh [39]. The product was identified through the spectroscopic data, which were confirmed by comparison with those reported in the literature [40]. In the second step, MTMSP-Im/Cl was dissolved in deionized water and stirred at room temperature for15 min, and then, the mixture was ultrasonicated for 15 min (A). In the following, CuO nanopowders were suspended in the deionized (DI) water and the obtained mixture was ultrasonicated for 15 min (B). Then, solutions A and B were mixed and immersed in ethanol and slowly stirred at room temperature for 24 h, and then ultrasonicated for 2 h. Finally, the reaction mixture was filtered using Whatman filter paper and, subsequently, was washed with deionized water two times to remove the unattached coupling agent compound. The functionalized CuO nanoparticles were dried under vacuum for 24 h and were grounded with a mortar and pestle before use (Scheme 1). The presence of organic groups on the surface of functionalized nanoparticles was confirmed by FT-IR, TGA, XRD, EDX, and FE-SEM analysis.



Scheme 1 Surface-functionalized CuO nanoparticles

General procedure for the regioselectivity of ring opening of epoxides by CuO-np@MSP-Im/Cl heterogeneous nanocatalyst

A mixture of epoxide (1 mmol), sodium azide (2 mmol), and catalyst (0.08 g) in water (5 ml) was stirred at 80 °C for the time as shown in Table 4. The completion of the reaction was followed by TLC using *n*-hexane/ethyl acetate (5/1) as eluent. The reaction mixture was filtrated, and separated catalyst dried and regenerated. Then, the product was extracted with diethyl ether (3 × 5 mL), and the organic phase was concentrated and dried using $MgSO_4$. After evaporation of the solvent under reduced pressure with a rotary evaporator, the β-azido alcohols were obtained with high yields. The desired pure product(s) were identified on the basis of their IR, ^{1}H NMR, and ^{13}C NMR.

Selected spectral data

1-Azido-3-phenoxy-2-propanol (Table 4, entry 1): **IR** (neat): ν_{max} N_3 (2110), OH (3395). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.45–3.54 (m, 2H), 3.89 (m, 1H), 3.97–4.03 (m, 2H), 4.18 (s, 1H), 6.95-7.00 (m, 2H), 7.02–7.06 (m, 1H), 7.27–7.36 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 52.3, 67.1, 68.3, 112.7, 120.1, 128.8, 157.9.

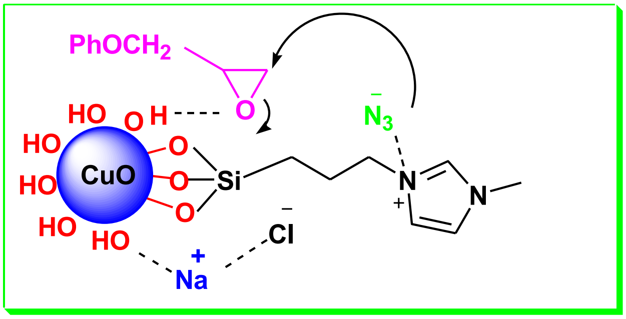
1-Azido-3-allyloxy-2-propanol (Table 4, entry 2): **IR** (neat): ν_{max} N_3 (2100), OH (3400). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.41–3.49 (m, 2H), 3.8 (m, 1H), 3.96–4.04 (m, 2H), 4.18 (s, 1H), 3.5 (m, 2H), 5.2 (dd, 1H), 5.5 (dd, 1H), 5.9 (dd, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 53.39, 69.85, 71.30, 72.09, 117.33, 134.35.

1-azido-2-octanol (Table 4, entry 5): **IR** (neat): ν_{max} N_3 (2104), OH (3404). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.78 (t, J = 6.2 Hz, 3H), 1.20 (s, 7H), 1.35 (s, 3H), 1.95 (s, 1H), 3.16–3.32 (m, 2H), 3.65 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 12.12, 20.01, 23.45, 27.21, 30.56, 33.41, 55.17, 69.74.

2-Azido-2-phenyl-1-ethanol (Table 4, entry 11**): IR** (neat): ν_{max} N_3 (2096), OH (3405). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.60 (s, 1H), 3.72–3.84 (m, 2H), 4.64 (t, 1H *J* = 6.7 Hz), 7.30–7.61 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 65.5, 67.5, 125.6, 126.9, 128.8, 136.1.

Results and discussion

The application of CuO nanoparticles for organic reactions has attracted much attention in the recent years [41–46]. However, since, the bare CuO NPs are not soluble in organic solvents or water and easily aggregated, the presence of organic groups within the inorganic materials helps effectively to increase the hydrophobicity and hydrothermal behavior of these materials as well as decrease their tendency to agglomerate [47, 48]. Considering these facts, herein, we reported the synthesis of a new nanocatalyst of CuO NPs that are modified with an ionic liquid-containing imidazolium group (Scheme 1). This new catalyst which is easily dispersed in the water or polar organic phase is a solid acid and was used to promote the epoxides azidolysis under very mild condition (Scheme 2). The chemical structure of CuO-np@MSP-Im/Cl nanohybrid was characterized using FT-IR, TGA, XRD, EDX, and FE-SEM analysis.



Scheme 2 Postulated roles of CuO-np@MSP-Im/Cl nanohybrid in the β-azido alcohol synthesis

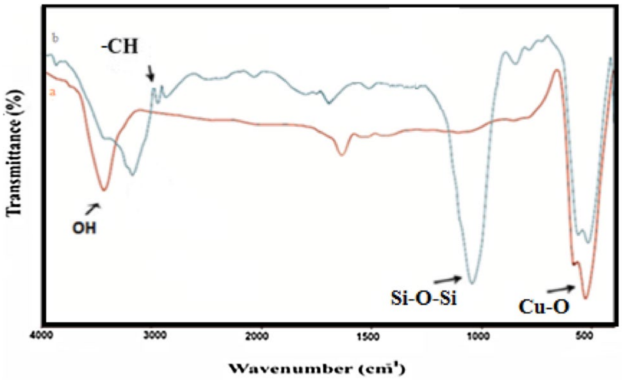


Fig. 1 FT-IR spectra of **a** bare CuO and **b** CuO-np@MSP-Im/Cl nanohybrid

FT-IR analysis was employed to study the formation of the heterogeneous catalyst. Figure 1 shows FT-IR spectra of pure CuO and CuO-np@MSP-Im/Cl nanoparticles.

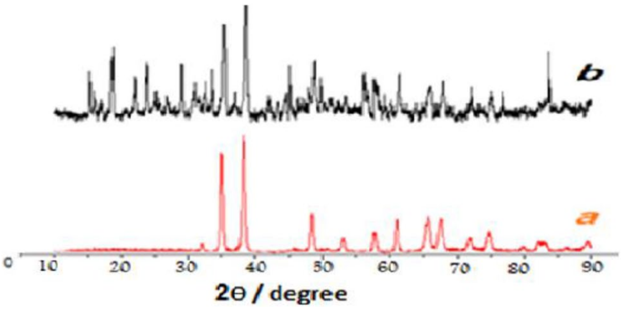


Fig. 2 XRD pattern **a** pure CuO NPs and **b** CuO-np@MSP-Im/Cl nanohybrid

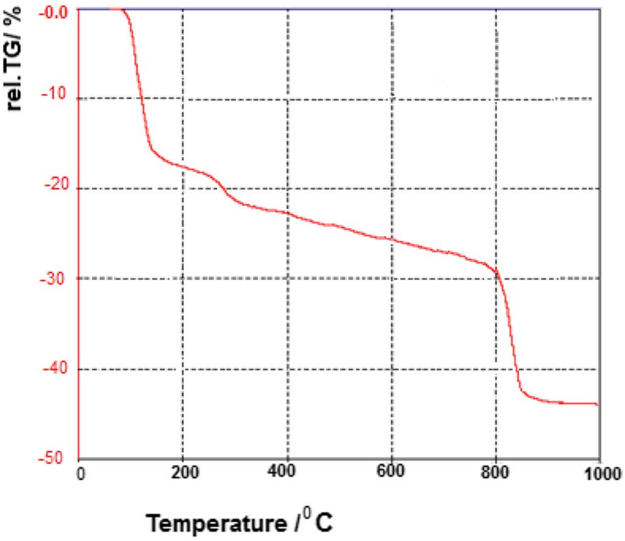


Fig. 3 TGA curve CuO-np@MSP-Im/Cl nanocatalyst

In the spectrum of bare CuO nanoparticles (Fig. 1a), the peak at 529.48 cm^{-1} is attributed to Cu–O bond stretching. The broadband peak in region 3431 cm^{-1} shows the O–H-stretching vibration of surface hydroxyls. The band at 1621 cm^{-1} is the O–H-bending vibrations. The spectrum (Fig. 1b) shows the modified CuO NPs with ionic liquid (MTMSP-Im/Cl). The hydroxyl stretching and bending bands are shifted to 3416 and 1635 cm^{-1} respectively. The new bands at 1383 and 1059 cm^{-1} can be attributed to the attached IL on the surface of CuO NPs. The strong peak appeared at 525.48 cm^{-1} was assigned to Cu–O-stretching vibration. The broadband at 1059 cm^{-1} refers to the presence of (Si–O–Si) stretching vibration. The two broad peeks at 1683.09 $cm^{-1}$and 1507.39 cm^{-1} are related to C=N and C=C vibrations, the new band at 2885 cm^{-1} attributed to the presence of C–H vibration, and the absorption at 3077.37 cm^{-1} is due to remaining hydroxyl groups on NPs' surface. These results provided the evidences that MTMSP-Im/Cl (coupling agent) were successfully attached to the surface of CuO NPs.

The crystalline structures of samples at room temperature were examined using a Philips X-ray diffractometer equipped with a Cu Kα anode ($\lambda = 1.540$ Å) for 2θ, in the range of 10°–90°. The XRD patterns of bare CuO and CuO-np@MSP-Im/Cl nanohybrid are presented in Fig. 2. The diffraction lines in Fig. 2a can be assigned to single-phase CuO with a monoclinic structure [49]. In the XRD pattern of Fig. 2b, the presence of MTMSP-Im/ Cl is observed in addition to CuO, and reflections of monoclinic CuO phase were clearly observed in surface-modified NPs. This observation

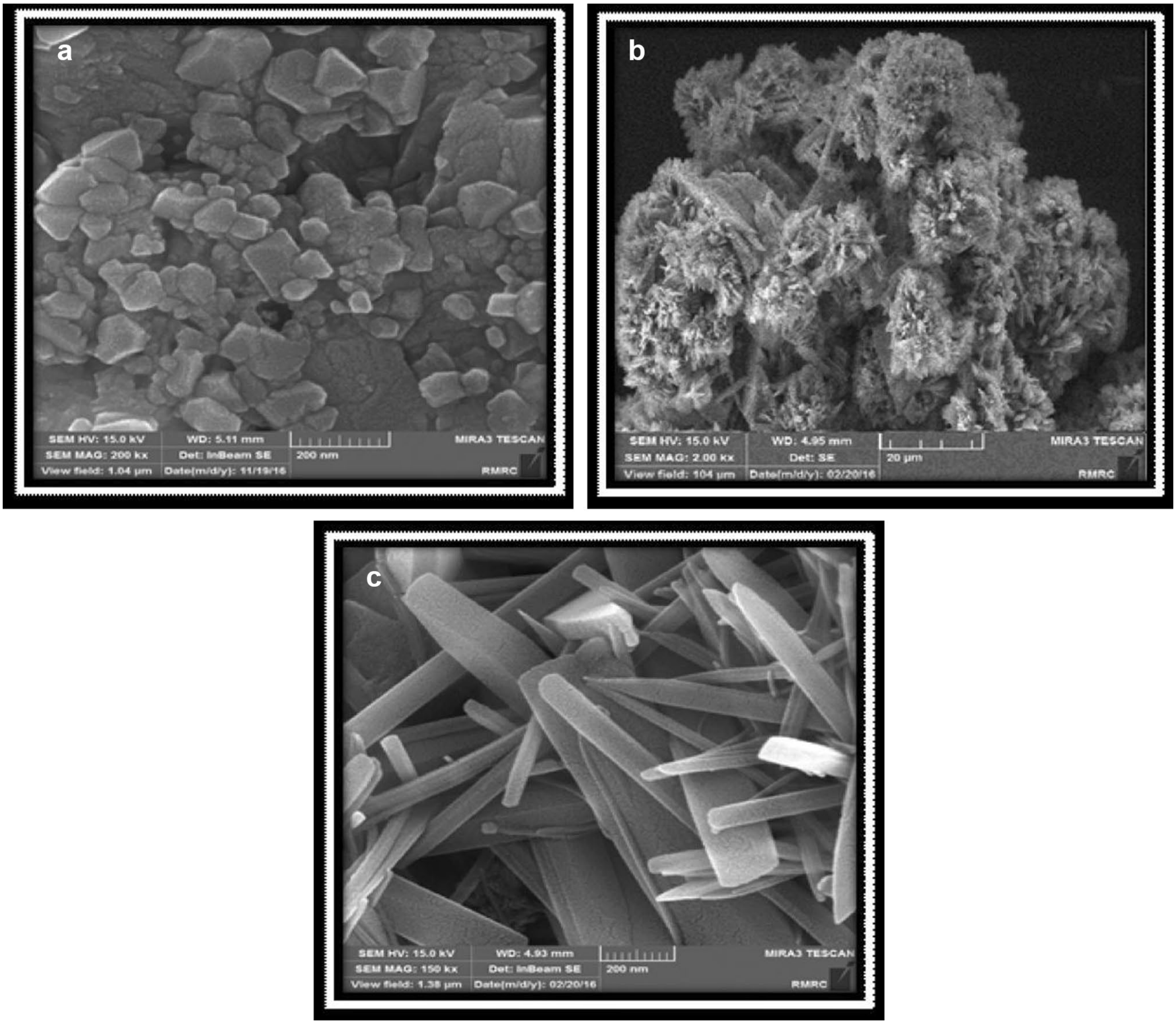


Fig. 4 FE-SEM image of **a** original CuO NPs and **b, c** CuO-np @MSP-Im/Cl nanocatalyst

confirms the nanohybrid formation of interaction between MTMSP-Im/Cl and CuO nanoparticles. The crystal size of nanohybrid is 18–45 nm as determined by Debby-Sherrer's formula.

TGA of solid acidic CuO-np@MSP-Im/Cl heterogeneous catalyst and the amount of the loading MTMSP-Im/Cl were investigated by thermal gravimetric analysis (Fig. 3) and Volhard's method. The 17% weight loss below 150 °C might be due to the loss of the adsorbed water as well as dehydration of the surface –OH groups. At higher temperature around 246–800 °C, it seems that the organic part is decomposed by a mass loss of about 12%. Thus, the TGA curves also convey the obvious information that the MTMSP-Im/Cl molecules are successfully immobilized onto CuO NPs. The amount of chloride that is equal by imidazolium units was also determined by Volhard's method [50] (0.38 mmol g^{-1}).

The FE-SEM scanning electron microscopy images were used to obtain the surface morphology, size distribution, and particles shape of modified CuO NPs. Figure 4 shows the photographs of the surface bare CuO NPs and CuO-np@MSP-Im/Cl hybrid. As shown, the synthesized heterogeneous nanocatalyst has needle shape with nano-thickness ranging from 10 to 50 nm and with nano-needle length ranging from 1 to 2μm.

The corresponding energy-dispersive X-ray (EDX) spectroscopy measurements are tabulated in Table 1. The result confirmed the presence of expected elements in the structure of the catalyst, namely Cu, C, N, Si, Cl, and O. Therefore, the structure of the catalyst was completely confirmed by EDX analysis.

After successful characterization of CuO-np@MSP-Im/Cl catalyst, we have tested its catalytic activity for the synthesis of β-azido alcohols derivatives by reaction of different epoxides with sodium azide. In the beginning, a model reaction of 3-phenoxy-1, 2-epoxypropane (1 mmol) and sodium azide (2–3 mmol) in the presence of CuO-np@MSP-Im/Cl Catalyst was investigated in various conditions, and compared with the other catalysts. The results obtained

Table 1 EDX of bare CuO and CuO-np@MSP-Im/Cl samples

Sample	Compound (at%)					
	C	Cu	O	N	Cl	Si
Bare CuO NPs		31.62	68.38			
CuO-np@MSP-Im/Cl	19.89	20.48	49.53	4.30	3.71	2.09

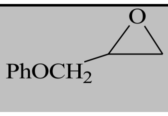
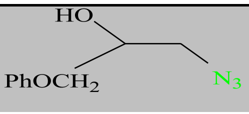
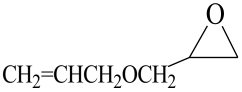
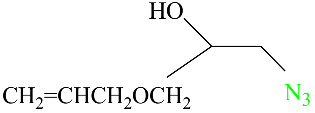
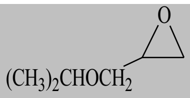
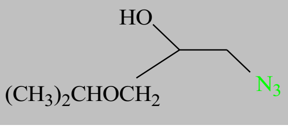
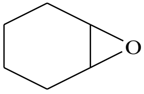
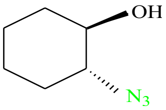
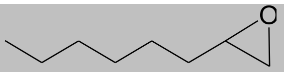
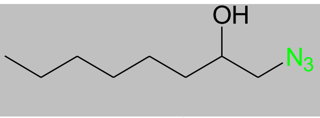
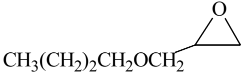
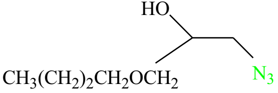
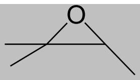
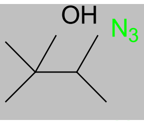
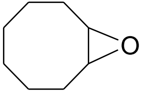
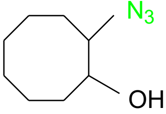
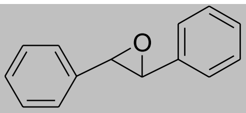
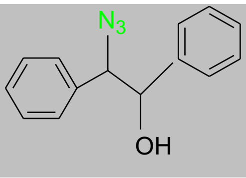
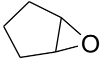
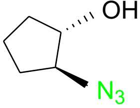
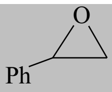
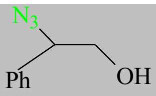
Table 2 Optimization of reaction conditions for ring-opening 3-phenoxy-1, 2-epoxypropane

Entry	Catalyst (g)	NaN_3 (mmol)	Temperature (°C)	Solvent	Time (min)	Yield%
1	–	3	80	H_2O	120	Trace
2	0.08	2	80	–	50	67
3	0.08	3	80	H_2O	20	85
4	0.08	2	80	H_2O	20	96
5	0.12	2	80	H_2O	25	88
6	0.08	2	80	CH_3OH	40	70
7	0.08	2	80	C_2H_5OH	40	73
8	0. 08	3	80	CH_3CN	30	80
9	0.08 bare CuO	2	80	H_2O	130	54

Table 3 Comparison of azidolysis of 3-phenoxy-1, 2-epoxypropane with different catalysts

Entry	Catalyst/g	Time (min)	Yield%	References
1	Fe_3O_4@SiO_2/BNC/0.03	50	95	[51]
2	[Hmim] N_3/3 mmol	55	94	[18]
3	PEG-300/2	60	90	[52]
4	Fe_3O_4–PS–Co–[PAA–g–PEG]/0.01	35	99	[21]
5	TSIL-N_3/2 mmol	60	80	[53]
6	SiO_2–PEG/0.1	120	95	[54]
7	Network polymer/0.1	90	89	[29]
8	CuO-np@MSP-Im/Cl/0.08	20	96	This work

Table 4 CuO-np@MSP-Im/Cl catalyzed regioselective ring opening of epoxides

Entry	Epoxide	Product(s)[a]	Time(min)	Yields(%)[b]
1			20	96
2			45	91
3			20	85
4			15	93
5			28	90
6			27	81
7			40	90
8			45	25
9			120	78
10			70	90
11			25	86

[a] Products were identified by comparison of their physical and spectral data with those of authentic samples

[b] Isolated yields

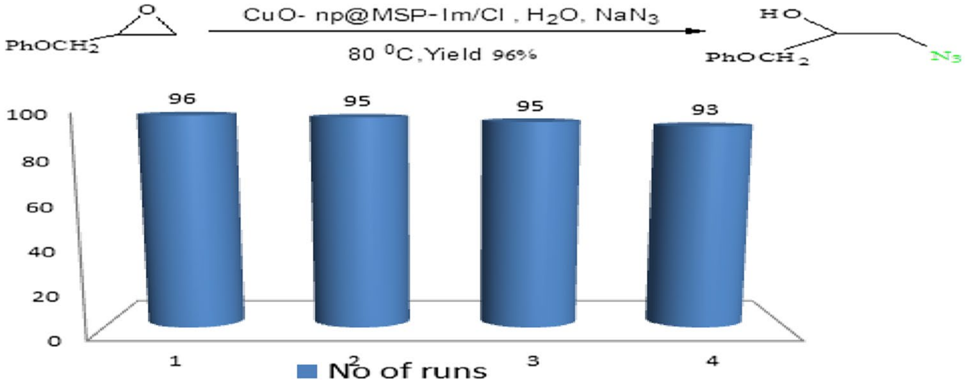


Fig. 5 Recyclability of the CuO-np@MSP-Im/Cl heterogeneous catalyst

are summarized in Tables 2 and 3. After some experiments, it was found that the use of 2 mmol of sodium azide per 3-phenoxy-1, 2-epoxypropane in the presence of CuO-np@MSP-Im/Cl (0.08 g) in water was the best condition (Table 2 entry 4). As shown in Table 2, the higher activity of the immobilized catalyst CuO-np@MSP-Im/Cl compared with its bare CuO NPs could be attributed to the participation of MTMSP-Im/Cl in the catalytic process (compared entries 4 and 9). As can be seen in Table 3, higher yield and shorter reaction time of product were obtained when CuO-np@MSP-Im/Cl was utilized as the catalyst (entry 9). Therefore, this reaction was developed with a wide range of substituted epoxides with sodium azide in the presence of synthesized heterogeneous nanocatalyst under mild conditions and the results are summarized in Table 4. These results clearly demonstrate that CuO-np@MSP-Im/Cl is an efficient catalyst for the high regioselectivity of ring opening of epoxides.

Due to the importance of green chemistry and catalyst recycling, of CuO-np@MSP-Im/Cl nanohybrid was investigated under the optimized conditions. The catalyst was reused four times in the one-pot 3-phenoxy-1, 2-epoxy propane with sodium azide in water. The recovered catalyst was reused after each run, washed with water and ethanol, and dried in an oven at 60 °C for 30 min. The results illustrated in Fig. 5 showed that the catalyst CuO-np@MSP-Im/Cl was reused with consistent activity even after the four cycles.

Conclusion

In this work, CuO supported 1-methyl-3-(3-(trimethoxysilyl) propyl) imidazolium chloride (CuO-np@MSP-Im/Cl) was successfully synthesized under ultrasonic irradiation. Then, the synthesized catalyst showed good performance in the synthesis of β-azido alcohols. The catalyst can easily be separated by simple filtration and reused for several cycles with consistent activity. Moreover, this methodology offers several advantages, including excellent regioselectivity, high yields, short reaction times, and simple workup in isolation of the products with high purity.

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