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Guanidine complex of copper supported on boehmite nanoparticles as practical, recyclable, chemo and homoselective organic–inorganic hybrid nanocatalyst for organic reactions

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Funding information Islamic Azad University Boehmite (BO) nanoparticles (NPs) were prepared *via* the injection of aqueous NaOH solution to aqueous aluminum nitrate solution at room temperature. Afterwards, a new complex of copper was immobilized on BO-NPs (Cu-Guanidine@BO-NPs). This heterogeneous nanocatalyst was used as a practical, recyclable, chemo and homoselective nanocatalyst in the organic processes, i.e. the preparation of tetrazole five-membered heterocycles and chemoselective sulfoxidation of sulfides using H_2O_2 as oxidant. In this sense, the prepared nanocatalyst was characterized by AAS, N₂ adsorption–desorption isotherms, WDX, EDS, SEM, and TGA techniques. The reusability of this catalyst was investigated in the described organic reactions for several runs without notable loss of its catalytic activity. Moreover, all of the tetrazole and sulfoxide derivatives were isolated in high Turn Over Number (TON) and Turn Over Frequency (TOF) numbers indicating the high activity and selectivity of Cu-Guanidine@BO-NPs in the described reactions.

K E Y W O R D S

Boehmite nanoparticles, copper, guanidine, sulfoxides, Tetrazoles

1 | INTRODUCTION

The recoverability, stability, selectivity and catalytic efficiency of the catalysts are important factors in catalytic process.^[1-4] Therefore, heterogeneous catalysts have been widely applied in academic researches and industrial applications due to their easy reusability.^[5-10] Unfortunately, heterogeneous catalysts have lower activity and selectivity than homogenous catalysts.^[11] During recent years, in order to achieve the advantages of both heterogeneous catalysts (recoverability and stability) and homogeneous catalysts (catalytic efficiency and selectivity), NPs have been applied as support for the fabrication of nanocatalysts.^[4,12-14] Because of the fact that NPs have high surface area, leading to high catalysts loading capacity on NPs, we witness a sort of high catalytic efficiency.^[14,15] In this regard, various NPs were widely used in order to prepare heterogeneous catalysts. In this sense, it is worth mentioning that carbon nanotubes,^[16] polymers,^[17] silica nanomaterials,^[18,19] graphene oxide,^[20,21] Metal–organic framework,^[22] iron oxide,^[23] heteropolyacid,^[24] ionic liquids,^[25,26] boehmite NPs^[27,28] etc. were used as support for the immobilization of the homogeneous catalysts. Among them, boehmite NPs is inert in various chemical conditions, and has excellent stability.^[29] High aggregation of -OH groups on the inert surface of boehmite NPs allowed them to be used as support for the stabilization of the catalysts.^[30,31] Moreover, boehmite NPs can be obtain from inexpensive and available materials such as sodium hydroxide and aluminum nitrate in aqueous conditions.^[32] Therefore, the application of boehmite NPs has the advantage of being environment friendly.^[33,34] In addition, boehmite NPs have fundamental advantages i.e. non-toxicity, good surface area, good stability and ease of surface modification.^[35] In this sense, several experimental procedures which have been presented for the synthesis of boehmite NPs have focused on the properties of boehmite NPs.^[36-41] Despite all advantages of boehmite NPs, it was rarely used as heterogeneous support during recent years.^[42,43] Therefore, we report a complex of copper on boehmite NPs (Cu-Guanidine-@BO-NPs) as efficient and heterogeneous catalyst for the chemoselective sulfoxidation of sulfides using H₂O₂ as oxidant reagent and also for the preparation of four-membered heterocycles such as tetrazoles via [3 + 2] cycloaddition of NaN₃ to the nitriles. Tetrazoles as nitrogen rich structures of organic compounds were employed in pharmaceuticals, medicine, biochemistry, photographic agents and especially in explosives.^[44-46] Moreover, tetrazoles serve in coordination chemistry and have also been applied in several useful biochemical transformations.^[47-49] In addition, tetrazoles can be used as stable replacements for carboxvlic acid groups in drug design.^[47] Tetrazole derivatives are usually prepared by [2 + 3] cycloaddition reaction of nitriles with azides which gives 5-substituted 1Htetrazoles.^[42,47] Likewise, the selective sulfoxidation of sulfides is a great transformation in organic chemistry^[29,31] which emerged in the separation of radioactive. enzymes activation, and less common Metals.^[29,50] Among several oxidant reagents for sulfoxidation of sulfides, H₂O₂ offers excellent advantages such as being readily available and environmentally friendly with the only by-product of water.^[23,27] Therefore, to keep pace with green chemistry principles, herein, we reported copper catalyst on boehmite nanoparticles as a stable and reusable catalyst for the oxidation of sulfides using hydrogen peroxide as oxidant.

2 | EXPERIMENTAL

2.1 | Materials and instruments

Chemicals and solvents which are employed in this work were purchased from Aldrich, Fluka, or Merck companies and used without further purification. Thermogravimetric analyses (TGA) of the catalyst were recorded by a SDT Q600 V20.9 Build 20 device under air atmosphere in the temperature range of 30–800 °C and at a heating rate of 10 °C min⁻¹. The morphology and size of the catalyst were obtained by SEM images using FESEM-TESCAN MIRA3 Scanning Electron Microscopes. Besides, this Scanning Electron Microscopes was employed for the component elemental analysis (EDS and WDX) of nanoparticles. In addition, the exact content of copper in the catalyst structure was measured by AAS technique using 400p-novAA instrument from Analytik Jena Company. Nitrogen adsorption isotherms were recorded by a standard gas manifold at 77 K to the textural properties of the catalyst using a BELSORP MINI II device. Moreover, the catalyst sample was degassed at 120 °C for 2 hr using a BEL PREP VAC II device before analysis. NMR spectra of products were recorded using Bruker DRX-400 spectrometer at 100–400 MHz. Melting points were measured with an Electrothermal 9,100 apparatus.

2.2 | Preparation of cu-guanidine@BO-NPs nanocatalyst

The modified boehmite NPs by 3-choloropropyltrimtoxysilane (nPr-Cl@BO-NPs) were prepared based on the resent reported method.^[12] Afterwards, nPr-Cl@BO-NPs (1 g) was dispersed in 50 ml of toluene by bath sonication and, then, guanidine nitrate (2.5 mmol) and the three ethyl amine (4 ml) were combined to the reaction mixture. Subsequently, the obtained suspension was stirred under inert N₂ atmosphere for 72 hr at 100 °C and, then, the modified nanomaterials (Guanidine@Boehmite) were washed with EtOH. Finally, 1 g of Guanidine@Boehmite was dispersed in EtOH (25 ml) by bath sonication, and, then, Cu (NO₃)₂.9H₂O (2.5 mmol) was added to the resulting suspension. The reaction mixture was refluxed and stirred under inert N2 atmosphere for 20 hr. The final products (Cu-Guanidine@BO-NPs) were isolated by filtration and washed with EtOH and H₂O.

2.3 | Experimental procedure for the synthesis of tetrazoles

A mixture of benzonitrile compounds (1 mmol) and NaN₃ (1.6 mmol), in the presence of Cu-Guanidine@BO-NPs (40 mg, containing 0.44 mol% of copper), was magnetically stirred in PEG-400 as green solvent at 120 °C. In addition, the reaction process was controlled by TLC. Finally the nanocatalyst was removed by filtration after cooling the mixture. The recovered catalyst was washed by ethyl acetate and, in continuation, the products were extracted with ethyl acetate and aqueous solution of hydrochloric acid (4 N). The organic solvent was decanted and dried by anhydrous Na₂SO₄. Finally, pure products were isolated by evaporation of ethyl acetate.

2.4 | Experimental procedure for the sulfoxidation of sulfides

Cu-Guanidine@BO-NPs (10 mg, containing 0.11 mol% of copper) were mixed to 1 mmol of sulfide and 0.5 ml of H_2O_2 (33%). Subsequently, the resulting mixture was magnetically stirred at room temperature under solvent free conditions. The reaction process was controlled by TLC. Afterwards, the catalyst was removed by filtration and, then, the mixture was dilute with H_2O and ethyl acetate. The mixture of the products and ethyl acetate was dried by anhydrous Na₂SO₄. Finally, pure products were isolated by evaporation of ethyl acetate. The selected spectral data may be found online in the supporting information.

2.5 | Selected spectral data

2.5.1 | 1-(4-(1H-tetrazol-5-yl)phenyl) ethanone

¹H NMR (400 MHz, DMSO): $\delta_{\rm H} = 17.12$ (b, 1H), 8.22–8.20 (d, J = 8 Hz, 2H), 8.20–8.18 (d, J = 8 Hz, 2H), 2.67 (s, 3H) ppm. ¹³C NMR (100 MHz, DMSO): $\delta_{\rm C} = 197.9$, 155.7, 138.9, 129.6, 128.8, 127.7, 27.4 ppm.

2.5.2 | 2-(1H-tetrazol-5-yl)benzonitrile

¹H NMR (400 MHz, DMSO): $\delta_{\rm H}$ = 8.13–8.09 (t, J = 8 Hz, 2H), 7.99–7.94 (t, J = 8 Hz, 1H), 7.83–7.79 (t, J = 8 Hz, 1H) ppm. ¹³C NMR (100 MHz, DMSO): $\delta_{\rm C}$ = 156.0, 135.4, 134.3, 131.9, 130.2, 128.1, 117.7, 110.7 ppm.

2.5.3 | 5-(3-nitrophenyl)-1H-tetrazole

¹H NMR (400 MHz, DMSO): $\delta_{\rm H}$ = 8.83–8.81 (t, *J* = 4 Hz, 1H), 8.48–8.39 (m, 2H), 7.92–7.87 (t, *J* = 8 Hz, 1H) ppm. ¹³C NMR (100 MHz, DMSO): $\delta_{\rm C}$ = 155.0, 148.3, 133.1, 131.2, 126.2, 125.6, 121.5 ppm.

2.5.4 | 2-(1H-tetrazol-5-yl)phenol

¹H NMR (400 MHz, DMSO): $\delta_{\rm H}$ = 12.04 (br, 1H), 8.00–7.96 (d, J = 8 Hz, 1H), 7.42–7.36 (t, J = 8 Hz, 1H), 7.08–7.04 (d, J = 8 Hz, 1H), 7.02–6.96 (t, J = 8 Hz, 1H), 3.49 (br, 1H) ppm. ¹³C NMR (100 MHz, DMSO): $\delta_{\rm C}$ = 155.3, 151.6, 132.6, 129.0, 119.7, 116.3, 110.5 ppm.

2.5.5 | 4-(1H-tetrazol-5-yl)benzonitrile

¹H NMR (400 MHz, DMSO): $\delta_{\rm H} = 8.22-8.19$ (d, J = 12 Hz, 2H), 8.09–8.06 (d, J = 12 Hz, 2H) ppm.

2.5.6 | 5-phenyl-1H-tetrazole

¹H NMR (400 MHz, DMSO): $\delta_{\rm H}$ = 8.05–8.01 (m, 2H), 7.62–7.57 (m, 3H) ppm.

2.5.7 | 5-(4-nitrophenyl)-1H-tetrazole

¹H NMR (400 MHz, DMSO): $\delta_{\rm H}$ = 8.45–8.42 (d, *J* = 12 Hz, 2H), 8.30–8.28 (d, *J* = 12 Hz, 2H) ppm. ¹³C NMR (100 MHz, DMSO): $\delta_{\rm C}$ = 148.7, 130.6, 128.2, 124.6 ppm.

2.5.8 | 5-(2-chlorophenyl)-1H-tetrazole

¹H NMR (400 MHz, DMSO): $δ_{\rm H}$ = 7.81–7.79 (d, *J* = 8 Hz, 1H), 7.72–7.69 (d, *J* = 12 Hz, 1H), 7.66–7.55 (m, 2H), ppm.

2.5.9 | 4-(1H-tetrazol-5-yl)phenol

¹H NMR (400 MHz, DMSO): $\delta_{\rm H}$ = 10.16 (br, 1H), 7.86–7.84 (d, *J* = 8 Hz, 2H), 6.95–6.93 (d, *J* = 8 Hz, 2H) ppm.

2.5.10 | 2-(phenylsulfinyl)ethanol

 $^1\mathrm{H}$ NMR (400 MHz, CDCl₃): δ_H = 7.70–7.65 (m, 2H), 7.62–7.49 (m, 3H), 5.35 (br, 1H), 4.21–4.14 (m, 1H), 4.03–3.96 (m, 1H), 3.18–3.12 (m, 1H), 2.96–2.90 (m, 1H) ppm.

2.5.11 | (methylsulfinyl)benzene

¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ = 7.68–7.65 (m, 2H), 7.61–7.56 (m, 1H), 7.55–7.52 (m, 2H), 2.74 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃, ppm) δ = 131.0, 129.4, 127.3, 123.5, 43.9 ppm.

2.5.12 | 1-(butylsulfinyl)butane

¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H} = 2.72-2.55$ (m, 2H), 1.77-1.67 (quint, J = 8 Hz, 2H), 1.55-1.36 (m, 2H), 0.96-0.91 (t, J = 8 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃, ppm) $\delta = 52.0$, 24.5, 22.0, 13.6 ppm. 4 of 14 WILEY Organometallic

2.5.13 | 1-(methylsulfinyl)dodecane

¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H} = 2.80-2.63$ (m, 2H), 2.57 (s, 3H), 1.81–1.70 (m, 2H), 1.39–1.26 (m, 18H), 0.90–0.86 (t, *J* = 8 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃, ppm) $\delta = 54.3$, 38.1, 31.4, 29.1, 29.0, 28.89, 28.86, 28.7, 28.3, 22.2, 22.1, 13.6 ppm.

3 | RESULTS AND DISCUSSION

In this research project, an environmentally friendly and economical route is reported for a copper catalyst on the modified boehmite NPs (Cu-Guanidine@BO-NPs). In this sense, boehmite NPs were prepared by dropwise addition of NaOH aqueous solution to Al (NO₃)₃.9H₂O aqueous solution.^[42] Afterwards, the hydroxyl groups on the surface of boehmite NPs were modified by 3-chloropropyltrimethoxysilane (CPTMS) by which nPr-Cl@BO-NPs were prepared. In the next step, the terminal Cl groups in nPr-Cl@BO-NPs were successfully replaced by guanidine through substation reaction in toluene at 100 °C under basic conditions of triethylamine (Et₃N). It is worth mentioning that guanidine has been supported on BO-NPs (Guanidine@BO-NPs) within 72 hr. The final catalyst (Cu-Guanidine@BO-NPs) was prepared by stabilization of copper on the surface of the modified boehmite NPs by guanidine (Scheme 1).

In the next step, Cu-Guanidine@BO-NPs were characterized by SEM, WDX, EDS, TGA, BET and AAS techniques.

3.1 | Catalyst characterizations

The diameter size and morphology of Cu-Guanidine-@BO-NPs were obtained by SEM technique whose images are illustrated in Figure 1. Homogeneous and nearly cubic orthorhombic structures of Cu-Guanidine-@BO-NPs are shown in SEM images. Moreover, SEM images indicate that the particles of this catalyst are between 40–60 nm in size.

In order to show the elements content, EDS analysis was performed for Cu-Guanidine@BO-NPs. As shown in Figure 2, this catalyst was formed from Al (9.07%A), O (57.11%A), Si (6.19%A), C (15.07%A), N (10.77%A) and Cu (1.78%A) species. In addition, as shown in Figure 3, WDX was used for the distributions of elements in the catalyst structure. In this regard, Figure 3 illustrates a good homogeneous distribution of the elements for this catalyst. Besides, the exact condensation of Cu in Cu-Guanidine@BO-NPs which was calculated by AAS was found to be $0.112 \times 10^{-3} \text{ mol g}^{-1}$.

In order to determine the amount of organic layers which were immobilized on boehmite NPs. TGA analysis was performed. TGA-DTG-DTA diagrams of Cu-Guanidine@BO-NPs are shown in Figure 4. These diagrams show three weight losses between 25 °C-800 °C. The Frist loss as displayed before 200 °C was related to the removal of the adsorbed solvents (about 5%) which were physically adsorbed in the catalyst.^[23] The second of one was observed between 200-500 °C because of the calcination of organic layers on boehmite NPs which was approximately 34% of the weight loss. The final weight loss in TGA diagram of Cu-Guanidine@BO-NPs was observed above 500 °C, which may be related to transformation of thermal phase of boehmite NPs, that it is 4% of weight loss.^[29] As shown, Cu-Guanidine@BO-NPs were stable up to 200 °C confirming the fact that guanidine complex of copper was covalently fabricated on the surface of boehmite nanoparticles. Therefore, this catalyst can be employed in various organic reactions under hard conditions.



SCHEME 1 Synthesis of Cu-Guanidine@BO-NPs



FIGURE 1 SEM images of Cu-Guanidine@BO-NPs



FIGURE 2 EDX spectrum of Cu-Guanidine@BO-NPs

Nitrogen adsorption-desorption isotherms of Cu-Guanidine@BO-NPs are shown in Figure 5. Based on the IUPAC classification, boehmite NPs display an isotherm of mesoporous material.^[51] The obtained surface area of Cu-Guanidine@BO-NPs is 63.39 m²/g which is lower than boehmite NPs (122.8 m²/g^[27]). The decrease in the surface area of the catalyst, greater than parent boehmite

NPs, is due to the immobilization of organic content and Cu-complex on boehmite NPs.^[27] Moreover, BET analysis of Cu-Guanidine@BO-NPs which indicated a lower pore volume (0.36 cm³ g⁻¹) than the free boehmite nanoparticles (0.589 cm³ g^{-1[52]}) confirmed the successful grafting of guanidine and copper complex on the surface of boehmite nanoparticles.

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25µm

Ο Κα1



FIGURE 3 Elemental mapping of (a) Al, (b) O, (c) Si, (d) C, (e) N, and (f) Cu for Cu-Guanidine@BO-NPs



(f)

Catalytic study of cu-guanidine@BO-3.2 NPs

(e)

The catalytic activity of Cu-Guanidine@BO-NPs was applied in the synthesis of 5-substituted tetrazoles and chemoselective sulfoxidation of sulfides.

Firstly, the catalytic synthesis of tetrazoles was studied in the presence of Cu-Guanidine@BO-NPs. The synthesis of 5-substituted tetrazoles from [3 + 2] cycloaddition of NaN₃ to the benzonitriles which is shown in Scheme 2 was catalyzed by Cu-Guanidine@BO-NPs. In order to find the best conditions for the preparation of tetrazoles, the [3 + 2] cycloaddition of NaN₃ to the benzonitrile was studied in various conditions (Table 1). In this regard, different amounts of the catalyst were

examined in the selected reaction (Table 1, entries 1-4). When this reaction was tested without Cu-Guanidine-@BO-NPs, the reaction did not take place (Table 1, entry 1). Meanwhile, the progress of the reaction was improved upon increasing in the amount of Cu-Guanidine@BO-NPs catalyst. As displayed in Table 1, 40 mg (containing 0.44 mol% of copper) of Cu-Guanidine@BO-NPs (Table 1, entry 4) was obtained as the optimum amount of the catalyst. Moreover, the progress of the reaction shows a significant dependence to nature and the amount of NaN₃. Therefore, the effect of solvents (Table 1, entries 6-10) and sodium azide concentration (Table 1, entries 4-8) were studied in the selected reaction. As shown in Table 1, 1.6 mmol of sodium azide in PEG-400 as solvent showed a better conversion of



FIGURE 4 TGA-DTG-DTA diagrams of Cu-Guanidine@BO-NPs





SCHEME 2 Synthesis of 5-substituted tetrazole derivatives in the presence of Cu-Guanidine@BO-NPs

^aIsolated yield.

benzonitrile to 5-phenyl-1H-tetrazole (Table 1, entry 5). Finally, the effect of temperature was examined by which 120 $^{\circ}$ C was selected.

In order to confirm the extend capability of this procedure, the reaction of NaN₃ with various electron-poor and electron-rich substituted nitriles was investigated in the presence of Cu-Guanidine@BO-NPs (Table 2). In addition, different aliphatic (Table 2, entries 11) and aromatic (Table 2, entries 1–10) nitriles were studied for the synthesis of tetrazoles whose corresponding products were isolated in exellent yields and high TON and TOF values. Moreover, several benzonitriles bearning ortho, meta and para functional groups were investigated for senthesis of the corresponding tetrazoles whose products were obtaied in good yields. The effect of electronic nature of aromatic ring in benzonitriles was compared to the reaction speed and the calculated TOF number for 4-hydroxybenzonitrile, 4-nitrobenzonitrile, and 4-acetylbenzonitrile. As shown, the calculated TOF numbers for these derivatives are 45.8, 8.7 and 6.2 h⁻¹, respectively. Therefore, their reactivity can be sorted as: 4-OH > 4-NO₂ > 4-COCH₃ which means that the functionalized benzonitriles with an electron-donating groups are reactive than the functionalized benzonitriles with an electron-withdrawing group.

Homoselectivity which is a great and imprtant property in the synthesis of various organic compounds is also observed in the same functional groups with similar electronic nature and steric hindrance.^[54,55] Homoselectivity of Cu-Guanidine@BO-NPs was investigated in the [3 + 2] cycloaddition of NaN₃ with terephthalonitrile (Table 2, entry 7) and phthalonitrile (Table 2, entry 8). Terephthalonitrile has two quite similar cyano functional groups on para position and phthalonitrile has two quite



Entry	nitrile	Time (min)	Yield (%) ^a	TON	TOF (h^{-1})	Melting point (°C)	Reported M.P.
1	Benzonitrile	70	95	216	185.1	211 –213	210-212 [19]
2	4-hydroxybenzonitrile	285	96	218	45.8	230-232	231-233 [19]
3	3-Nitrobenzonitrile	270	96	218	48.4	149–151	149–152 ^[42]
4	2-Hydroxybenzonitrile	7	98	223	1911	223-225	224-226 [42]
5	2-phenylacetonitrile	260	94	214	49.4	121–122	120-123 [19]
6	4-Nitrobenzonitrile	24 h	92	209	8.7	221-223	219-221 [53]
7	Terephthalonitrile	340	96	218	38.5	253-255	254-257 [42]
8	Phthalonitrile	580	97	220	22.7	210-211	209-210 ^[19]
9	2-Chlorobenzonitrile	350	91	207	35.5	181–183	180–183 ^[42]
10	4-Acetylbenzonitrile	34 h	93	211	6.2	173–175	173–176 ^[42]
11	Pentanenitrile	780	85	193	14.8	41-43	41-43 [53]

TABLE 1 Optimization of the Synthesis of 5-phenyl-1H-tetrazole in the presence of Cu-Guanidine@BO-NPs

^aIsolated yield.

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Entry	Catalyst (mg)	Solvent	NaN ₃ (mmol)	Temperature (°C)	Time (min)	Yield (%) ^[a]
1	-	PEG	1.5	120	720	-
2	30	PEG	1.5	120	360	92
3	35	PEG	1.5	120	315	90
4	40	PEG	1.5	120	180	93
5	40	PEG	1.6	120	70	95
6	40	PEG	1.4	120	245	88
7	40	DMSO	1.6	120	150	85
8	40	DMF	1.6	120	190	91
9	40	H_2O	1.6	Reflux	210	87
10	40	EtOH	1.6	Reflux	260	83
11	40	PEG	1.6	100	420	90

similar cyano functional groups on ortho position of aromatic ring. Interestingly, this procedure afforded the mono-addition in the presence of Cu-Guanidine@BO-NPs (Scheme 3) which showed a good homoselectivity of this catalyst in the synthesis of tetrazole deraiivatives.

A cyclic mechanism for the synthesis of tetrazoles in the presence of Cu-Guanidine@BO-NPs is outlined in Scheme 4.^[54,56] The first step is the interaction of catalyst to the nitrile which provides the conditions for the nucleophilic addition of azide. This step is screened as intermediate I in Scheme 4. Subsequently, the [3 + 2]cycloaddition of NaN₃ to the benzonitrile gives intermediate II. Finally, intermediate II which is protonated by HCl produced the stable product IV and regenerated the catalyst, which can continue the catalytic cycle.

In the next study, the catalytic application of Cu-Guanidine@BO-NPs was performed in the chemoselective sulfoxidation of sulfides using hydrogen peroxide as green oxidant because it is very inexpensive and gives only water as the by-product (Scheme 5). In order to define the ideal conditions, the sulfoxidation of methyl phenyl sulfide by H2O2 as oxidant and Cu-Guanidine@BO-NPs as the catalyst was selected as the model reaction. Different amounts of this catalyst and several solvents were studied in the selected reaction at room temperature. The obtained results were displayed in Table 3. The selected reaction did not proceed in the absence of Cu-Guanidine@BO-NPs even after 600 min. Meanwhile, the speed of the reaction was increased upon increasing the catalyst concentration. Finally, 10 mg (containing 0.11 mol% of copper) of Cu-Guanidine@BO-NPs was selected as the best amount of the catalyst as the increasing amount of the catalyst to 12 mg (Table 3, entry 5) had no significant effect on the reaction speed or product yield. Moreover, the nature of the solvent was examined by which it was revealed that solvent free condition showed better results. The summarized results in Table 3



SCHEME 3 Homoselectivity of Cu-Guanidine@BO-NPs in the synthesis of tetrazole derivatives





SCHEME 4 A cyclic mechanism for the synthesis of tetrazoles in the presence of Cu-Guanidine@BO-NPs

illustrated that the best conditions for sulfoxidation of sulfides is 10 mg (containing 0.11 mol% of copper) of Cu-Guanidine@BO-NPs under solvent free conditions.

Catalytic application of Cu-Guanidine@BO-NPs for sulfoxidation of sulfides was extend for a wide range of sulfides (Table 4). Various sulfoxides; including, aromatic and aliphatic sulfoxides were successfully synthesized in the presence of Cu-Guanidine@BO-NPs. Over-oxidation of sulfides to sulfone was not observed and pure sulfoxides were synthesized as the main products (Scheme 6). Chemoselectivity has been regarded as very significant in the synthesis of organic compounds such as druges, natural products and biological molecules. In this regard, among the few reactions that compete with each other, only one reaction is performed. The chemoselectivity of Cu-Guanidine@BO-NPs was investigated in the oxidation of 2-Phenylthioethanol (Table 4, entry 2) in which hydroxyl group can compete in the oxidation reaction with sulfide. As shown in Scheme 6, hydroxyl groups were remained intact under optimized conditions which confirms the chemoselectivity of this catalyst. Moreover, synthesis of sulfones by over oxidation can compete with the synthesis of sulfoxides. Meanwhile, sulfoxidation of sulfides was observed without over-oxidation to generate any byproduct such as sulfone.

A plausible reaction mechanism for the sulfoxidation of sulfides to sulfoxides in the presence of Cu-Guanidine-@BO-NPs is outlined in Scheme 7.^[57,58] At first, hydrogen peroxide is active by Cu-Guanidine@BO-NPs which gives intermediate **A** and further is converted to intermediate **B** as active oxidant. Next, nucleophilic attack of the sulfur of sulfide on this intermediate gives cation **C** which, in turn, produces the sulfoxide products and regenerates the catalyst. 10 of 14 **ILEY**

H₂O₂, Solvent-Free, r.t.

Cu-Guanidine@BO-NPs



SCHEME 5 Sulfoxidation of sulfides in the presence of Cu-Guanidine@BO-NPs

Entry	Catalyst (mg)	Amount of H ₂ O ₂ (ml)	Solvent	Time (min)	Yield (%) ^[a]
1	-	0.4	Solvent Free	600	-
2	5	0.4	Solvent Free	395	55
3	8	0.4	Solvent Free	395	80
4	10	0.4	Solvent Free	395	94
5	12	0.4	Solvent Free	385	96
6	10	0.4	EtOH	395	75
7	10	0.4	CH_2Cl_2	395	45
8	10	0.4	DMSO	395	63
9	10	0.4	EtOAC	395	12
10	10	0.5	Solvent Free	375	98
11	10	0.6	Solvent Free	370	95

TABLE 3 Optimization conditions for the sulfoxidation of sulfides in the presence of Cu-Guanidine@BO-NPs

^aIsolated yield.

TABLE 4 Sulfoxidation of sulfides in the presence of Cu-Guanidine@BO-NPs

Entry	Sulfide	Time (min)	Yield (%) ^a	TON	TOF (h^{-1})	Melting point (°C)	Reported M.P.
1	Methyl phenyl sulfide	375	98	891	142.5	30-32	30-32 [31]
2	2-Phenylthioethanol	85	94	854	602.8	Oil	Oil ^[29]
3	Methyl (undecyl)sulfane	420	92	836	119.4	59-62	61-64 [23]
4	Diallylsulfane	85	95	864	609.8	Oil	Oil ^[51]
5	Dibutylsulfane	330	91	827	150.3	Oil	Oil ^[29]

^aIsolated yields.



Chemoselective sulfoxidation of sulfides in the presence of Cu-Guanidine@BO-NPs

3.3 | Reusability of the catalyst

The separating and reusing the remaining catalysts are important steps in catalytic processes. Therefore, as screened in Table 1 (entry 4), the recyclability of Cu-Guanidine@BO-NPs was studied in the synthesis of 5-phenyl-1H-tetrazole with the [3 + 2] cycloaddition of NaN₃ to the benzonitrile under the optimized conditions (Figure 6). As the experiment reveals, it is at the end of the each reaction that the remained catalyst was recovered by centrifugation and being washed with ethyl acetate. The products were isolated using the extraction with H₂O and ethyl acetate and, then, the remained catalyst was reused in same reaction up to 6 times. The average isolated yields of products for 6 runs is 92.33%, which shows the good reusability of Cu-Guanidine@BO-NPs.



1

2

3

3.4 | Comparison of the catalyst

The efficiency of Cu-Guanidine@BO-NPs was compared to old literatures. The obtained results for the reaction of benzonitrile with sodium azide in the presence of Cu-Guanidine@BO-NPs were compared to previous catalysts. This comparison is summarized in Table 5. In order to show the practically of Cu-Guanidine@BO-NPs, the reaction condition, isolated yields, reaction time and TON and TOF values were compared. As shown, the

best results were reached in the presence of Cu-Guanidine@BO-NPs as the catalyst in comparison to other catalysts. In this regard, the isolated yield, and TOF and TON values in the presence of Cu-Guanidine@BO-NPs are higher than other catalysts. Moreover, several reported procedures utilized the organic solvent (Table 5, entries 2-10) or employed the high temperature (Table 5, entries 6 and 11) which are expensive and not environment friendly; meanwhile, PEG was used as green solvent in the present work. In some other procedures,

4

Run number

5

6

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JAFA	RI	EТ	AL.

Entry	Catalyst	Reaction conditions	Time (min)	TOF (h ⁻¹)	Yield ^a (%) [Reference]
1	Pd-Arg@boehmite	PEG-400, 120 °C	420	7.7	97 ^[42]
2	(NH ₄)Ce (NO ₃) ₆	DMF, 110 °C	360	1.61	97 ^[59]
3	Fe ₃ O ₄ @SiO ₂ /Salen Cu (II)	DMF, 120 °C	420	-	90 ^[60]
4	AgNO ₃	DMF, 120 °C	300	1.66	83 [61]
5	Cu (OAc) ₂	DMF, 120 °C	720	0.32	98 [62]
6	Nano ZnO/Co ₃ O ₄	DMF, 120–130 °C	720	-	90 [63]
7	CuFe ₂ O ₄	DMF, 120 °C	720	-	82 ^[64]
8	CAN supported HY-zeolite	DMF, 110 °C	240	0.77	93 ^[65]
9	FeCl ₃ -SiO ₂	DMF, 120 °C	720	-	79 ^[66]
10	Md-Pt NPs@AC	DMF, 90 °C, microwave irradiation (140 W)	15	23.76	98 [67]
11	P ₂ O ₅ -SiO ₂	Solvent-Free, 130 °C or ultrasonic sonication, 45 °C	150	1.86	93 ^[68]
12	Cu-Guanidine@BO-NPs	PEG-400, 120 °C	70	185.1	95 [this work]

TABLE 5 Comparison of Cu-Guanidine@BO-NPs in the preparation of 5-phenyl-1H-tetrazole with previously reported catalysts

microwave irradiation (Table 5, entry 10) or ultrasonic sonication (Table 5, entry 11) were used in order to prepare the tetrazole derivatives.

4 | CONCLUSIONS

In conclusion, we have successfully stabilized a guanidine complex of copper on the surface of the modified boehmite NPs (Cu-Guanidine@BO-NPs) which was then characterized by TGA, AAS, BET, SEM, WDX and EDS. After NPs characterization, its catalytic application was studied in the synthesis of sulfoxides (using oxidation of sulfides) and 5-substituted tetrazole (using [3 + 2] cycloaddition of NaN₃ to the nitriles). The catalyst showed high catalytic activity in the descripted organic reactions. Besides, the products (tetrazoles and sulfoxides) were obtained in remarkable yields, high purity, and excellent TON and TOF values. Cu-Guanidine@BO-NPs catalyst illustrated a good selectivity in the sulfoxidation of sulfides without generating the sulfone as by-product. Similarly, this catalyst showed homoselectivity in the synthesis of tetrazole when disyano-functionalized benzonitriles were investigated. Moreover, this catalyst was recovered and recycled for 6 runs with 92.33% of average yields confirming the good reusability of this catalyst.

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