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FULL PAPER

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Preparation and characterization of Cu (II) Schiff base complex functionalized boehmite nanoparticles and its application as an effective catalyst for oxidation of sulfides and thiols

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The synthesis, characterization, and evaluation of a Schiff base Cu (II) complex functionalized boehmite nanoparticles (Cu-complex-boehmite) as a new catalyst for oxidation of sulfides and thiols in the presence of hydrogen peroxide with complete selectivity and high conversion under solvent-free and mild reaction conditions were reported. Characterization of the catalyst was performed with various physicochemical methods. This effective catalyst was evaluated in terms of activity and reusability. It indicated high catalytic activity, good recoverability and reusability, and supplied the corresponding products in high yields and short reaction times. In addition, it shows notable advantages such as simplicity of operation, heterogeneous nature, easy work up, and it could be used at least eight times with no significant loss of its activity.

KEYWORDS
Boehmite nanoparticles, hydrogen peroxide, oxidation, sulfide, thiol

1 | INTRODUCTION

Boehmite nanoparticles contain a cubic orthorhombic structure of aluminium oxide hydroxide. These nanoparticles are synthesized in water by commercially available materials.[1] The structure of boehmite consists of double sheets of octahedral with aluminium ions, and the sheets themselves are composed of octahedral chains.[2]

Boehmite nanoparticles have several interesting features such as stable orthorhombic structure, high specific surface area, non-toxicity, easily and readily available material, thermal and mechanical stability, ease of surface modification, an easy and inexpensive procedure of preparation and favorable biocompatibility.[2,3] Bohemite nanoparticles are also covered with hydroxyl groups. These hydroxyl groups provide valuable sites that can react with various functional groups to produce expensive catalysts such as metal complexes.[3,4]

On the other hand, bohemite is widely used as absorbents,[5] catalysts,[2] filler in the membranes,[6] optical materials,[7] coating[8] and composite reinforcement material in ceramics.[9] Bohemite has also been used as a precursor to the synthesis of alumoxanes.[10]

Recently, metal complexes of Schiff-bases have been used for the synthesis of a variety of catalysts.[11] However, for the synthesis of the most efficient and recyclable catalysts, Schiff base compounds have been grafted on heterogeneous supports.[12] Because of their excellent performance in a wide range of organic transformations, the Schiff base transition metal complexes are considered to be one of the best catalytic compounds.[13,14] Herein, we report the new Schiff-base complexes of Cu (II) grafted on boehmite nanoparticles for the oxidation of sulfides to sulfoxides and also the oxidative coupling of thiols into the corresponding disulfides under mild reaction conditions. These reactions are useful in the synthesis of new medical, chemical, and biological compounds, and nanotechnological applications.[15–24] Hydrogen peroxide used as a green, cheap and environmentally benign oxidant has been applied for these oxidation reactions.[25]

2 | RESULTS AND DISCUSSION

After successful synthesis of Cu-complex-boehmite (Scheme 1), the catalyst was characterized by various methods such as Fourier transform infrared spectroscopy (FT-IR), energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray diffraction (XRD) techniques.

2.1 | Characterization of the catalyst

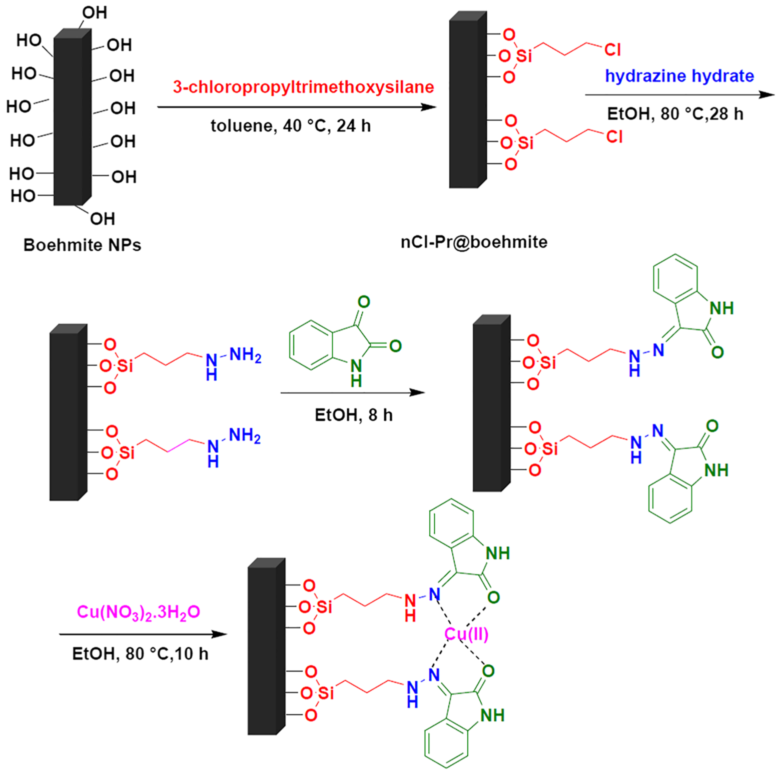
The XRD pattern of Cu-complex-boehmite is shown in Figure 1. In this pattern, the boehmite phases identified by the peak positions at 14.90, 28.75, 38.80, 46.60, 48.50, 51.98, 56.30, 58.90, 65.10, 65.68, 68.09, and 72.38 were corresponded respectively to crystal planes of boehmite nanoparticles in orthorhombic unit cell (Figure 1).[26,27]

The images of scanning electron microscopy (SEM) provide detailed information on the size and morphology of the boehmite nanoparticles and Cu-complex-boehmite nanoparticles. These images show that these nanoparticles are uniform in size, nano-sized, and well dispersed (Figure 2).

TEM image can reveal internal structure and measures more accurate of particle size and morphology. As shown in Figure 3, the unit cells of Cu-complex-boehmite nanoparticles were obtained in cubic orthorhombic structures with about 20–40 nm in size. In fact, nanocatalysts are characterised by the unique nanoscale properties that originate from their highly reduced dimensions. The size and shape of a catalyst particle strongly affect its reaction performance when it is on the nanometre scale. Especially, controlling the catalyst particle morphology allows a selective exposure of a larger fraction of the reactive facets on which the active sites can be enriched and tuned. This desirable surface coordination of catalytically active atoms or domains substantially improves catalytic activity, selectivity, and stability.

The EDX pattern of Cu-complex-boehmite shows the presence of Cu, Al, C, N, O and Si atoms, which it suggests that successful grafting and immobilizing of Schiff-base and Cu on the surface of boehmite support have occurred (Figure 4).

The FT-IR spectra for boehmite (a), complex-boehmite (b) and Cu-complex-boehmite nanoparticles (c) are shown in Figure 5. As shown in spectrum **a**, the strong band of hydroxyl groups on the surface of boehmite nanoparticles is observed at 3275 cm^{-1}.[15,28] In spectra **a-c**, several peaks at 605, 790 and 830 cm^{-1} are related to the Al-O bonds in boehmite structure.[6] Also, the nitrate impurity



SCHEME 1 Synthesis of Cu-complex-boehmite nanoparticles.

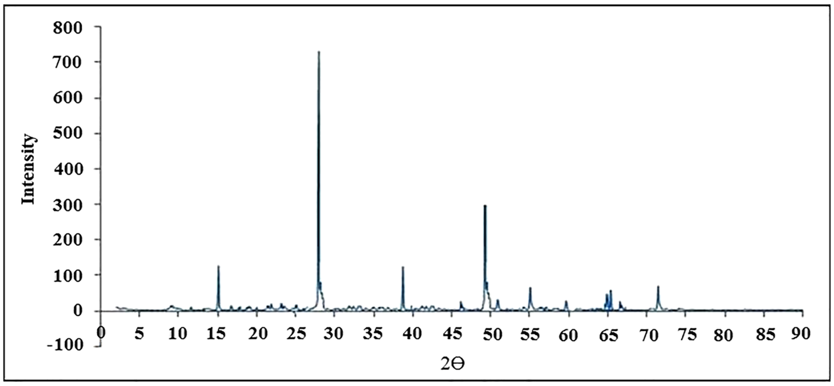


FIGURE 1 The XRD pattern of Cu-complex-boehmite nanoparticles

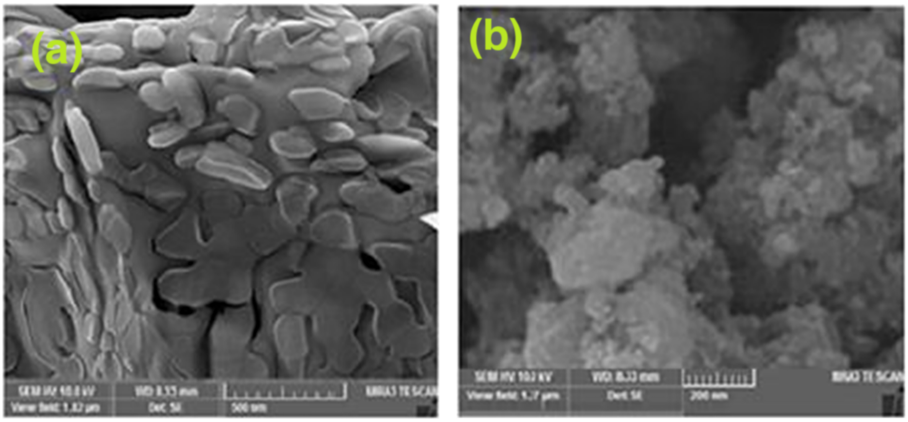


FIGURE 2 SEM images of boehmite (a) and Cu-complex-boehmite nanoparticles (b)

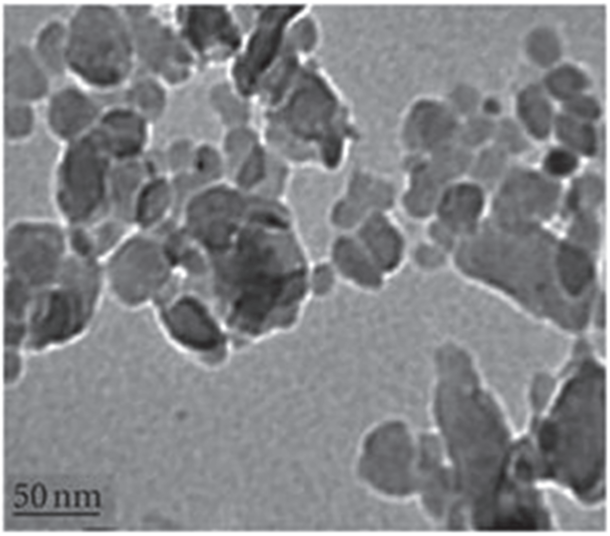


FIGURE 3 TEM image of Cu-complex-boehmite nanoparticles

and hydrogen bonds (OH ... OH) vibrations are appeared at 1636^{-1}.[29,30] In spectrum **b**, the modification of boehmite nanoparticles with 3-chloropropyltrimethoxysilane is authenticated by C–H stretching vibration (3155 cm^{-1}) and O-Si stretching vibration (1058 cm^{-1}). Also, a band is observed at 1642 cm^{-1} due to the C=N stretching of the azomethine group. These bands prove that isatin and hydrazine hydrate have been successfully grafted onto the nPr-Cl-boehmite nanoparticles. The C=O stretching vibration of the amide group occurs at 1705 cm^{-1}. The free ligand exhibits (C=N) stretching at 1642 cm^{-1} while in the complexes, this band shifts to the reduced frequency, appearing at 1606 cm^{-1} as a result of coordination of the nitrogen with the metal (spectrum **c**).

2.2 | Catalytic application of the catalyst

The catalytic activity of the catalyst was evaluated in the oxidation of diethyl sulfide and 4-methylthiophenol to form the corresponding sulfoxide and disulfide as the principal products (Scheme 2). The yields of the products are 95% and 97%, respectively with a turnover frequencies (TOF) of 207 and 159 min^{-1}. All the employed precursors in the synthesis exhibited high TON and TOF, indicating a great efficiency of the catalyst (Table 2).

To optimize the reaction conditions, we investigated the oxidation of diethyl sulfide and oxidative coupling of 4-methylthiophenol as the model compounds using

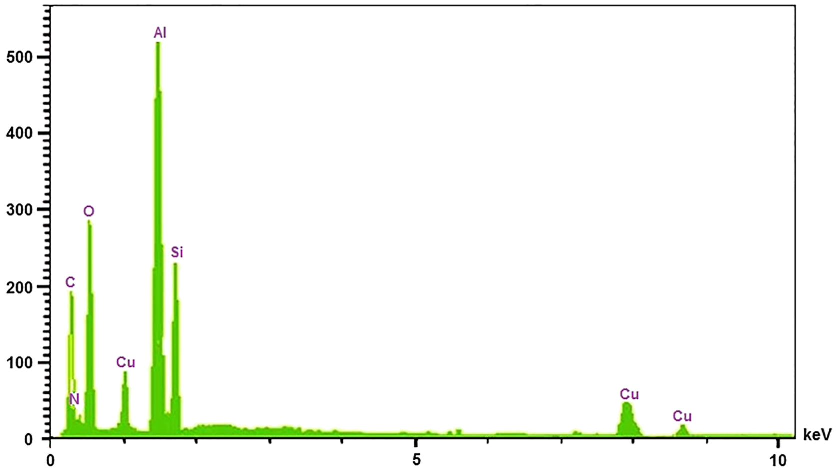


FIGURE 4 EDX pattern of Cu-complex-boehmite nanoparticles

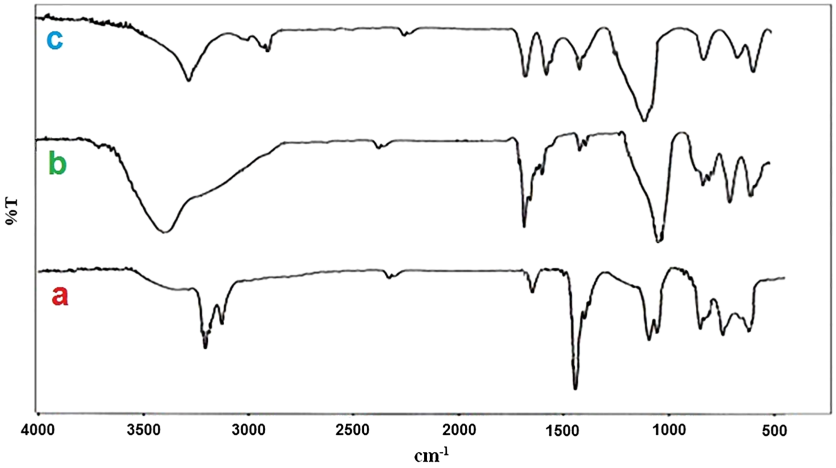
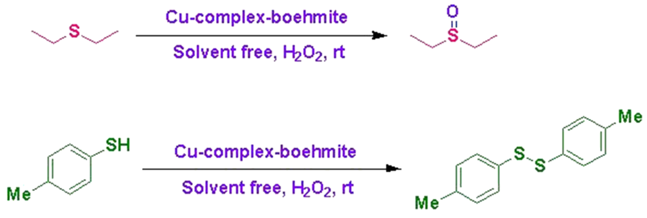


FIGURE 5 FT-IR spectra of boehmite (a), complex-boehmite (b) and Cu-complex-boehmite nanoparticles (c)



SCHEME 2 Cu-complex-boehmite catalyzed the selective oxidation of sulfides into sulfoxides and the oxidative coupling.

H_2O_2 (4 mmol, 0.4 mL) in various solvents and in the presence of different amount of Cu-complex-boehmite (Table 1). As shown in Table 1, the best result for the oxidative coupling of 4-methylthiophenol was obtained using 0.01 g of Cu-complex-boehmite at room temperature under solvent-free condition (Table 1, entry 11). Also, the solvent-free condition in the presence of 0.01 g of Cu-complex-boehmite was found to be the ideal reaction condition for the conversion of diethyl sulfide to the diethyl sulfoxide (Table 1, entry 2). The oxidation reactions of sulfides and thiols under solvent-free conditions afforded the corresponding products in good to excellent yields, while the oxidation reaction of diethyl sulfide in a solvent such as ethanol, water, ethyl acetate and dichloromethane was not complete after 30 min and led to 60, 55, 65 and 30% yields of the corresponding product, respectively. The oxidation reaction of 4-methylthiophenol in a solvent including ethyl acetate, acetone, ethanol and dichloromethane afforded *p*-tolyl disulfide after 45 min in 70, 75, 65 and 45% yields. The polar solvent solves the substrate and oxidizing agent and bring them close to interact better at the surface of the catalyst. But in this case, the presence of the solvent decreases the collision and interaction of sulfide with H_2O_2 and plays the role of deterrent. The polar solvents such as water and ethanol reduce the rate of the oxidation reaction of diethyl sulfide due to dilution of the oxidizing agent.

In order to show the role of boehmite and Cu during the reaction, the oxidation of diethyl sulfide was examined in the presence of Cu-complex-boehmite compared to alone boehmite. The diethyl sulfoxide was obtained in 53 and 95% yields in the presence of boehmite and Cu-complex-boehmite, respectively (Table 1).

With optimal conditions in hand, the oxidation reactions of various sulfides to their corresponding sulfoxides

TABLE 1 Optimization of the reaction conditions for both oxidation reactions[a]

Entry	Substrate	Solvent	Catalyst (g)	Time (min)	Yield (%)[b]
1	diethyl sulfide	Solvent-free	Cu-complex-boehmite (0.005)	30	60
2	diethyl sulfide	Solvent-free	Cu-complex-boehmite (0.01)	15	95
3	diethyl sulfide	Solvent-free	Cu-complex-boehmite (0.02)	15	95
4	diethyl sulfide	EtOH	Cu-complex-boehmite (0.01)	30	60
5	diethyl sulfide	H_2O	Cu-complex-boehmite (0.01)	30	55
6	diethyl sulfide	Ethyl acetate	Cu-complex-boehmite (0.01)	30	65
7	diethyl sulfide	CH_2Cl_2	Cu-complex-boehmite (0.01)	30	30
8	diethyl sulfide	Solvent-free	Boehmite (0.01)	65	53
9	diethyl sulfide	Solvent-free	-	90	10
10	4-methylthiophenol	Solvent-free	Cu-complex-boehmite (0.005)	50	75
11	4-methylthiophenol	Solvent-free	Cu-complex-boehmite (0.01)	20	97
12	4-methylthiophenol	Solvent-free	Cu-complex-boehmite (0.02)	20	97
13	4-methylthiophenol	Ethyl acetate	Cu-complex-boehmite (0.01)	45	70
14	4-methylthiophenol	Acetone	Cu-complex-boehmite (0.01)	45	75
15	4-methylthiophenol	EtOH	Cu-complex-boehmite (0.01)	45	65
16	4-methylthiophenol	CH_2Cl_2	Cu-complex-boehmite (0.01)	45	45
17	4-methylthiophenol	Solvent-free	-	90	18

[a] Reaction conditions: Diethyl sulfide or 4-methylthiophenol (1 mmol), H_2O_2 (4 mmol, 0.4 ml), the catalyst (0.01 g), solvent-free at room temperature.

[b] Isolated yield.

have been carried out (Table 2, entries 1–9). These oxidation reactions were performed under mild and completely heterogeneous conditions at room temperature using H_2O_2 as an oxidant, and the corresponding sulfoxides were obtained in high yields. Therefore, the results show that this method is efficient and effective for oxidation of a wide range of sulfides.

The role of Cu catalyst for the activation of hydrogen peroxide was identified. Although hydrogen peroxide (H_2O_2) is a powerful oxidizing agent but, it is not usually effective to oxidize the organic compounds by itself. Therefore, it has to be usually combined with catalysts or additional reagents in order to be activated.[33,34] The corresponding reactions in the absence of the catalyst under the same reaction conditions gave only 10% and 18% conversion to 1c and 2b (Table 2), while in the presence of the catalyst, the corresponding products (1c and 2b) were obtained in high yields (Table 1). The role of copper in the modified bohemite catalyst is to form the active oxidant-sulfide complex and then, by transfer of oxygen to sulfur, sulfoxide as a product was obtained and the rate of the reaction improved.

The generality of this approach has been demonstrated by a facile oxidative coupling of various thiols as shown in Table 2. It was shown a variety of thiols including aromatic and aliphatic thiols with different functional groups were successfully converted to the corresponding disulfides in excellent yields (Table 2, entries 10–16).

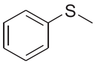
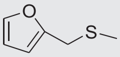
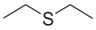
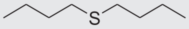
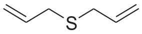
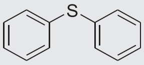
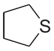
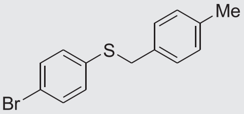
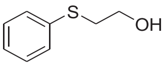
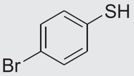
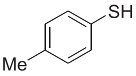
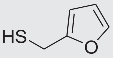
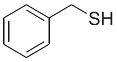
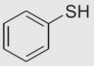
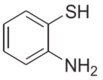
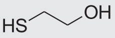
Because of the mildness of the reaction conditions, no overoxidation to sulfone (for oxidation of sulfides) and thiosulfinates, disulfoxides, sulfinyl sulfones or disulfones (for the oxidative coupling of thiols) was observed (Scheme 3).

Interestingly, hydroxyl groups in these substrates remained intact during the oxidation reactions (Scheme 4). These results indicate that this method can be used in the chemoselective oxidative coupling of thiols and oxidation of sulfides in the presence of other functional groups. It was revealed that this methodology is also effective for a wide range of thiols.

2.3 | Reusability of cu-complex-boehmite green catalyst in the oxidation of sulfides and thiols

The most effectual aspect of the catalyst is that a small amount of material can dramatically influence the results of a chemical reaction with no change by the reaction itself and it has the ability to recover and reuse without any significant loss of activity. This catalyst property is important with respect to environmental aspect. The stability and

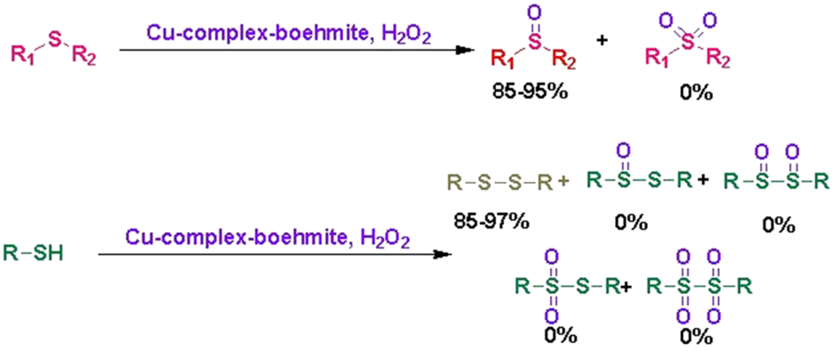
TABLE 2 The selective oxidation of sulfides into sulfoxides[a] and oxidative coupling of thiols into disulfides[b]

Entry	Substrate	Product	Time (min)	Yield[c] (%)	TON/TOF (min^{-1})	Ref
1		1a	15	95	3114/207	[17]
2		1b	25	90	2950/118	[31]
3		1c	15	95	3114/207	[17]
4		1d	20	93	3049/152	[15]
5		1e	30	85	2786/92	[32]
6		1f	15	95	3114/207	[17]
7		1 g	20	90	2950/147	[31]
8		1 h	25	93	3049/122	[32]
9		1i	30	90	2950/98	[28]
10		2a	30	90	2950/98	[17]
11		2b	20	97	3180/159	[17]
12		2c	25	95	3114/124	[31]
13		2d	20	90	2950/147	[31]
14		2e	20	85	2786/139	[15]
15		2f	20	95	3114/155	[28]
16		2 g	35	90	2950/84	[28]

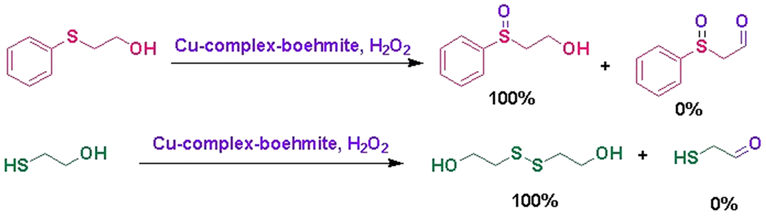
[a] The reaction conditions for the oxidation of sulfides: Sulfide (1 mmol), H_2O_2 (4 mmol, 0.4 ml), the catalyst (0.01 g), solvent-free at room temperature.

[b] The reaction conditions for the oxidative coupling of thiols: Thiol (1 mmol), H_2O_2 (4 mmol, 0.4 ml), the catalyst (0.01 g), solvent-free at room temperature.

[c] Isolated yield.



SCHEME 3 Oxidation of sulfides and oxidative coupling of thiols in the presence of the catalyst with no overoxidation product.



SCHEME 4 The chemoselective oxidation of sulfide and oxidative coupling of thiol in the presence of a hydroxyl functional group.

recyclability of this catalyst in the oxidation reactions of diethyl sulfide and 4-methylthiophenol are represented by the finding that the 8th consecutive productions of diethyl sulfoxide and di-4-methylphenyl disulfide were 94% and 90% complete after a reaction time of only 45 min and 50 min. The corresponding reactions in the absence of the catalyst under the same reaction conditions gave only 10% and 18% conversion to 1c and 2b (Table 1). The catalyst was recovered after the oxidation reaction by centrifuge and washed exhaustively with ethanol, and dried in vacuum. The results in Figure 6 indicate that this catalyst is recyclable for 8 runs without any significant loss of its catalytic activity. The main reason that the performance of the catalyst was slightly decreased is related to leaching, because the active center of the catalyst was reduced. Moreover, the possibility of aggregation is increased due to the leaching and this process also reduces the active site of the catalyst. Trivial loss of the catalyst occurred in the process of washing and separation after every recycling. The water generated during each oxidation reaction may lead to the Cu (II) Schiff base complex leaching from the surface of the catalyst. In addition, the morphology of the catalyst may be changed under the reaction conditions. Due to this matter, it could be supposed that the Cu^{2+} ions interact with more ligand sites and made the new complex form on the surface of the catalyst. Thus, Cu^{2+} could not use its active site in the reaction. It can be supposed that the catalyst has poisoned by itself under the repeated reaction conditions (auto poisoning). The process used is green in the sense that it is single step, done at room temperature under solvent-free conditions with recoverable and reusable catalyst.

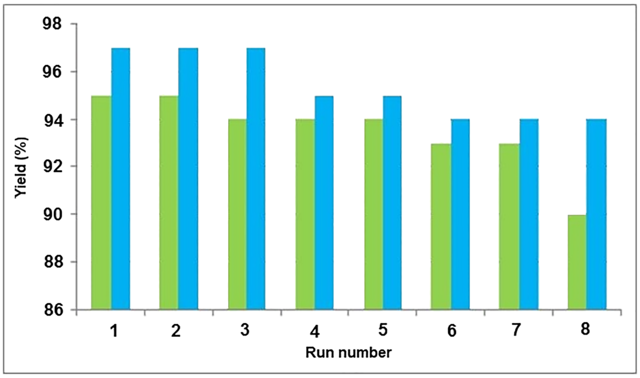


FIGURE 6 Recycling of Cu-complex-boehmite for the oxidation of methyl phenyl sulfide (green column) and 4-methyl thiophenol (blue column)

In continuation of this research work, the heterogeneity, efficiency and activity of the catalyst in the oxidation reaction of methyl phenyl sulfide was studied by performance of hot filtration experiment. Under optimized conditions, oxidation of diethyl sulfide was performed in the presence of Cu-complex@bohemite in which the yield of product in the half time of the reaction was 67%. Then, the reaction was repeated and the catalyst was separated in half time of the reaction. Afterward, continuous reaction was performed without Cu-complex@bohemite for a further 8 min, in which the yield of reaction was 71%. This observation confirmed that leaching of copper has not been occurred. To be more precise about the amount of copper leaching in the synthesis of diethyl sulfoxide, ICP-OES technique was used for checking the Cu loading amount before and after recycling of the catalyst. It was found that the amount of copper in fresh catalyst and the recycled catalyst after 8 times recycling is 3.05 and 2.87 $mmolg^{-1}$, respectively. Thus, ICP-OES analysis indicated that copper leaching of this catalyst is not significant.

TABLE 3 Comparison of this catalyst with the reported catalysts in the oxidation of methyl phenyl sulfide and 4-methylthiophenol

Entry	Substrate	Catalyst	Condition	Time	Yield[a] (%)	Ref
1	Methyl phenyl sulfide	Chiral (salen) Mn (III) complexes	CH_3CN,0 °C	3 hr	54	[35]
2	Methyl phenyl sulfide	Cu (II)-complex@Fe_3O_4	Solvent-free, rt	1 hr	98	[36]
3	Methyl phenyl sulfide	Ni-salen-MCM-41	EtOH, rt	2.6 hr	95	[37]
4	Methyl phenyl sulfide	LDH supported OsO_4	t-BuOH/H_2O, rt	3 hr	80	[38]
5	Methyl phenyl sulfide	Br_3-TEDETA@Bohemite	Ethyl actate, H_2O_2, rt	20 min	93	[39]
6	Methyl phenyl sulfide	VO-AMPD@SBA-15	S-F, H_2O_2, rt	60 min	98	[40]
7	Methyl phenyl sulfide	MCM-41-Adenine-Zr	S-F, H_2O_2, rt	55 min	96	[41]
8	Methyl phenyl sulfide	SBA-15@Serine@Pd	S-F, H_2O_2, rt	22 min	98	[42]
9	Methyl phenyl sulfide	Cu-complex-boehmite	Solvent-free, rt	15 min	95	This work
10	4-methylthiophenol	Ni-salen-MCM-41	EtOH, rt	25 min	95	[37]
11	4-methylthiophenol	Cobalt–iron magnetic composites	DMF, 50 °C	30 min	100	[43]
12	4-methylthiophenol	Monochloropoly (styrenehydantoin)	H_2O, rt	24 hr	50	[44]
13	4-methylthiophenol	VO-AMPD@SBA-15	EtOH, H_2O_2, rt	50 min	98	[40]
14	4-methylthiophenol	Fe_3O_4@MCM-41@Ni-P2C	EtOH, H_2O_2, rt	25 min	96	[45]
15	4-methylthiophenol	FeNPs@SBA-15	EtOH, H_2O_2, rt	45 min	94	[46]
16	4-methylthiophenol	MCM-41@Creatinine@Pr	EtOH, H_2O_2, rt	40 min	98	[47]
17	4-methylthiophenol	Cu-complex@boehmite	Solvent-free, rt	20 min	97	This work

[a]Isolated yield.

The efficiency of Cu-complex-boehmite is investigated by comparison of our results on the oxidation of methyl phenyl sulfide and oxidative coupling of 4-methylbenzenethiol with the previously reported procedures in the literature (Table 3). The results show that the catalyst has good performance with short reaction times and high yields of the products. Moreover, the new catalyst is comparable in terms of price, stability and non-toxicity. Additionally, the mesoporous silica such as MCM-41and SBA-15 used as catalyst support in the organic reactions, requires high temperature for calcination and a lot of time and tedious conditions to prepare. Also preparation of boehmite nanoparticles was not air, or moisture sensitive, therefore this nanomaterial was prepared in ethanol without inert atmosphere. This catalyst can be recycled at least 8 runs without any significant loss of their catalytic activity or metal leaching.

3 | EXPERIMENTAL

3.1 | General information

The materials were purchased from Merck and used without any purification. All reactions were monitored by TLC. X-ray powder diffraction (XRD) patterns were recorded with a Philips PW 1830 X-ray diffractometer using CuKα source ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) analysis was taken using a VEGA// TESCAN KYKY-EM 3200 microscope. Transmission electron microscopy (TEM) experiments were conducted on a Philips EM 208 electron microscope. NMR spectra were recorded with a Bruker DRX-400 AVANCE instrument (400 MHz for ^1H NMR). The spectra were obtained in $CDCl_3$ and DMSO-d_6 as solvent. FT-IR spectra were obtained with a Bruker vector 22 spectrophotometer. Energy-dispersive X-ray (EDX) spectroscopy patterns were obtained using a Seron model AIS2300C. The Cu loading was detected by inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian Vista MPX).

3.2 | Preparation of the catalyst

The solution of 13.0 g NaOH in 100 ml of distilled water was added to the solution of Al $(NO_3)_3.9H_2O$ (40.0 g) in 60 ml of distilled water dropwise under vigorous stirring. The milky mixture prepared in an ultrasonic bath was placed at 25 °C for 3 hr. The synthesized nanoparticles were filtered, washed by distilled water and dried in the oven at 100 °C for 4 h. The obtained boehmite nanoparticles (1.5 g) was dispersed in 50 ml of toluene by sonication for 30 min, and then 2.5 ml of (3-choloropropyl)triethoxysilane (CPTES) was added to the mixture. The reaction mixture was stirred at 40 °C for 24 hr. The prepared nanoparticles (nCl-propyl boehmite) were filtered, washed with ethanol and dried at room temperature. The nanoparticles (1 g) was dispersed in 50 ml of ethanol for 20 min, and then hydrazine hydrate (1 mmol) was added to the reaction mixture and stirred at 80 °C for 28 hr. The resulting nanoparticles were filtered, washed with ethanol and dried at room temperature. In order to prepare complex functionalized boehmite, the above mentioned solid (1 g) was refluxed with isatin (1 mmol) in ethanol for 8 hr. The resulting solid (complex-boehmite) was separated using filtration, washed with ethanol and dried at room temperature. Finally, for the preparation of Cu immobilized on complex functionalized boehmite, the complex-boehmite (1 g) was dispersed in ethanol and mixed with 1.0 mmol of Cu $(NO_3)_2.3H_2O$. The mixture was stirred at 80 °C for 10 hr and the solid catalyst (Cu-complex-boehmite) was obtained after washing with ethanol and drying at 50 °C.

3.3 | General procedure for oxidation of sulfides

In a 25 ml round button flask, sulfide (1 mmol), Cu-complex-boehmite (0.01 g), H_2O_2 (0.4 ml) were added and the mixture stirred at room temperature for appropriate period of time as indicated in Table 2. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by simple filtration and the product was extracted with CH_2Cl_2 (3 × 15 ml) and dried over anhydrous $MgSO_4$. Finally, sulfoxide was obtained as the only product in a very high isolated yield.

3.4 | General procedure for oxidation of thiols

In a 25 ml round button flask, H_2O_2 (0.4 ml) was added to thiol (1 mmol) and Cu-complex@boehmite catalyst (0.01 g). The mixture was stirred thoroughly for the required time under solvent free conditions at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by simple filtration and the corresponding product was extracted with CH_2Cl_2 (3 × 15 ml) and dried over anhydrous $MgSO_4$. Finally, disulfide was obtained in a very high isolated yield. The typical procedures for oxidation of diethyl sulphide and 4-methylthiophenol, FT-IR and 1H NMR spectrum of sulfoxides and 1H NMR spectrum of disulfides may be found online in the supporting information section at the end of the article (Figures S1–S14).

4 | CONCLUSION

Cu (II)–Schiff base complex functionalized boehmite nanoparticles are successfully synthesized and confirmed by XRD, FT-IR, TEM, SEM, and EDX techniques. This catalyst was shown environmentally safe heterogeneous solid catalyst used for the oxidation of sulfides and thiols under solvent-free conditions at room temperature. This method offers several advantages including short reaction times, good to excellent product yields, simple work-up as well as the ability to tolerate a wide variety of substituents in the substrates. Cu-complex-boehmite catalyst is recoverable and reusable catalyst.

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Additional supporting information may be found online in the Supporting Information section at the end of the article.

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