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## ARTICLE

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## Nickel Schiff-base complexes immobilized on boehmite nanoparticles and their application in the oxidation of sulfides and oxidative coupling of thiols as novel and reusable nano organometal catalysts

Arash Ghorbani-Choghamarani,<sup>\*</sup> Bahman Tahmasbi, Fatemeh Arghand and Sara Faryadi

Boehmite nanoparticles were prepared by very simple and inexpensive procedure in water at room temperature using commercially available materials. Two Schiff-base complexes of nickel have been immobilized on the boehmite nanoparticles. These catalysts were characterized by FT-IR spectroscopy, TGA, XRD, BET, UV-DRS, TEM, SEM, EDS and ICP-OES techniques. These compounds were applied as catalyst for the oxidation of sulfides to sulfoxides and oxidative coupling of thiols to disulfides under mild reaction conditions at room temperature. These catalysts were recovered by simple filtration and reused for several times without significant loss of their catalytic efficiency.

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## **1** Introduction

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Solid catalysts have been widely employed as useful, recoverable and recyclable catalysts in organic synthesis [1, 2]. One way to reach this goal is immobilization of homogeneous catalysts on insoluble supports. The catalytic activity of these solid materials could also efficiently increases using nanomaterial support [3]. Because, when the size of the support is decreased to the nanometre scales, the surface area is substantially increased and the support can be evenly dispersed in solution, to form a homogenous emulsion [4]. Therefore, nanocatalysts can be used as bridge to improve the gap between homogeneous and heterogeneous catalysis, preserving the desirable attributes of both systems [5]. One of the novel supports is boehmite ( $\gamma$ -AlOOH) nanomaterial with orthorhombic unit cells, which it is rarely employed as heterogeneous support for the immobilization of homogeneous catalysts [6]. Nanoboehmite have several attractive 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, easy and inexpensive procedure of preparation and favourable biocompatibility [7, 8]. Additionally, the surface of nanoboehmite is covered with hydroxyl groups. These surface hydroxyl groups provide valuable sites that can be grafted with various functional groups in order to produce expensive supported-catalysts such as metal complexes [8, 9]. Boehmite has been used as an absorbent, optical material, composite reinforcement material in ceramics, cosmetic products, vaccine adjuvants, starting material in the synthesis of alumina pillared clays and sweep-flocculation for fresh water treatment [5, 10]. Recently, metal complexes of Schiff-bases have been emerged for the development of a variety of catalysts [11] however, for effective and easier recovered, Schiff base compounds have been grafted on heterogeneous supports [12]. Schiff base transition metal complexes are considered as promising candidates because of their excellent catalytic performances in a wide range of organic transformations [13]. Herein, we report new Schiff-base complexes of nickel grafted on boehmite nanoparticles for the oxidation of sulfides to sulfoxides and also oxidative coupling of thiols into corresponding disulfides under mild reaction conditions. Sulfoxides and disulfides are useful in the synthesis of new products and play an important role in various medical and biological applications [14, 15]. For example, omeprazole and the pesticide fipronil are two typical examples of the sulfoxide derivatives in pharmaceutical and fine chemical industries [16]. Likewise, disulfide bond formation is important in peptides, bioactive molecules as well as oil sweetening processes [17, 18]. Disulfides are used in sulfonylation of enolates and other anions and also useful as vulcanizing agents [17-19]. For this reason, many methods including various catalysts and different oxidants have been developed over the years to perform these transformations [14-19]. Concerning the green oxidant, hydrogen peroxide (with only H<sub>2</sub>O as a by-product) as an inexpensive and

environmentally benign oxidant has been applied for these oxidations [20].

## 2 Results and discussion

#### 2.1 Catalyst preparation

The catalysts were prepared by the concise route outlined in Scheme 1. Initially, boehmite nanoparticles have been prepared via addition of NaOH to the solution of Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O as source of aluminium at room temperature. Ultimately, boehmite nanoparticles coated with silica using tetraethylorthosilicate (TEOS). Subsequently, the facial silanol groups were functionalized with APTES, and Schiff-base ligands were formed using condensation of 5-bromosalicylaldehyde or salicylaldehyde with terminal amine groups, which grafted on boehmite nanoparticles. Finally, the Ni-Schiff base complexes supported on boehmite nanoparticles (Ni-complex-boehmite) were prepared via complexation of BS-Schiff base with Ni(NO<sub>3</sub>)<sub>2.6</sub>H<sub>2</sub>O. These nanomaterials have been characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), inductively coupled plasma atomic emission spectroscopy (ICP-OES), Brunauer-Emmett-Teller (BET), UV-vis diffuse reflectance spectra (UV-vis DRS), X-ray diffraction (XRD) thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR) techniques.



Scheme 1. Synthesis of Ni-complex-boehmite.

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#### 2.2 Catalyst characterizations

The size and morphology of boehmite nanoparticles was considered by SEM analysis. The SEM image of boehmite was shown that these nanoparticles were formed of nanometre-sized in quite homogeneous cubic orthorhombic structures (Figure 1a). Also the size and morphology of nickel Schiff base complex supported on boehmite (Ni-complex-boehmite II) were studied by TEM technique. As shown in Figure 1b, the unit cells of Ni-complex-boehmite II were obtained in cubic orthorhombic structures with dimensions of 45 and 120 nm. Also, the TEM image of the Ni-complex-boehmite II showed that particles have a regular geometric shape in comparison with nanoboehmite (Figure 1b). To investigate the characterization of these catalyst, a typical EDS spectrum taken from the Nicomplex-boehmite I that was shown in Figure 2. The EDS spectra at different points of the image confirm the presence of Ni in the prepared modified nanoparticles. The EDS spectrum shows the presence of C, O, N, Al, Si and Ni species in the catalyst (Figure 2). Also, to extend the scope of catalysts characterization, we have determined the loading of Ni on boehmite nanoparticles, by ICP-OES technique. The Ni amount of the immobilized catalyst on boehmite nanoparticles was found to be  $67.98 \times 10^{-5}$  and  $36.97 \times 10^{-5}$ <sup>5</sup> mol g<sup>-1</sup> based on inductively coupled plasma atomic emission spectroscopy (ICP-OES) for catalyst I and II respectively.



Figure 1. a) SEM image of boehmite nanoparticles and b) TEM image of Ni-complex-boehmite **II**.



Figure 2. EDS spectrum of Ni-complex-boehmite I.

The XRD patterns of boehmite nanoparticles were shown in Figure 3. As it can be seen from Figure 3, the boehmite phase was identified from the XRD patterns by the peak positions at 14.40 (0 2 0), 28.41 (1 2 0), 38.55 (0 3 1), 46.45 (1 3 1), 49.55 (0 5 1), 51.94 (2 0 0), 56.02 (1 5 1), 59.35 (0 8 0), 65.04 (2 3 1), 65.56 (0 0 2), 68.09 (1 7 1), and 72.38 (2 5 1), which all peaks have been confirmed the crystallization of boehmite with an orthorhombic unit cell [6, 21].



Figure 3. The XRD pattern of boehmite nanoparticles.

Immobilization of Schiff base complexes on functionalized nanoboehmite was inferred using TGA diagram. The TGA curve of nanoboehmite, boehmite coated by silica (boehmite-silica), Ni-complex-boehmite I and Ni-complex-boehmite II are shown in Figure 4. The weight loss at temperatures below 200 °C is due to the removal of physically adsorbed solvents [22]. The boehmite and boehmite-silica are found to show a mass percentage loss of about 15% and 20% respectively, while the Ni-complex-boehmite I and Ni-complex-boehmite II has the greatest mass loss, at 50% and 45% respectively. On the basis of this result, the well grafting of nickel complexes on the boehmite nanoparticles is verified.



Figure 4. TGA diagram of a) nanoboehmite, b) boehmite coated by silica (boehmite-silica), c) Ni-complex-boehmite II and d) Ni-complex-boehmite I.

Successful functionalization of boehmite nanoparticles can be inferred from FT-IR spectra. Figure 5 shows FT-IR spectra for boehmite nanoparticles (a), boehmite-silica (b), boehmite-silica nanoparticle functionalized with APTES (BS-APTES) (c), Schiff base grafted on boehmite-silica (BS-Schiff base) II (d), BS-Schiff base I (f), Ni-complex-boehmite II (e) and Ni-complex-boehmite I (g). The FT-IR spectrum for the nanoboehmite shows a stretching vibration at 3086 and 3308 cm<sup>-1</sup> from both symmetrical and asymmetrical modes of the O-H bonds, which are attached to the surface of boehmite nanoparticles. The structure of boehmite was confirmed via FT-IR by several peaks at 477, 613 and 735 cm<sup>-1</sup>, which corresponds to the characteristic absorption of Al-O bonds [8]. Also, the nitrate impurity vibration at 1650  $\text{cm}^{-1}$  and the vibrations of hydrogen bands OH...OH by two strong absorption bands at 1164 and 1069 cm<sup>-1</sup> were observed in FT-IR spectrum [8, 10]. As it can be seen in Figure 5b-5g, the Si-O-Si bond's asymmetric stretching vibration and symmetric stretching vibration appear at 1072 cm<sup>-1</sup> and 770 cm<sup>-1</sup>, respectively, which indicates that the silica organic group has successfully coated the surface of boehmite nanoparticles [23]. In the FT-IR spectra of BS-APTES (Figure 5c), the presence of the anchored APTES was confirmed by C-H and N-H stretching vibrations that appear at 2931 cm<sup>-1</sup> and 3097-3425 cm<sup>-1</sup> respectively.

The FT-IR spectrum of BS-Schiff base II and BS-Schiff base I exhibits a weak bands at 1636 and 1635 cm<sup>-1</sup> respectively, which attributed to the vibrations of C=N bands in the BS-Schiff bases that are absent in BS-APTES; while in the Ni-complex-boehmite II (Figure 5e) and Ni-complex-boehmite I (Figure 5g), these bands were shifted to lower frequency and appeared at 1628 and 1629 cm<sup>-1</sup> respectively, which indicates the formation of Ni Schiff base complexes. C-O stretching vibrations show a peak at 1250-1300 cm<sup>-1</sup> [24]. The stretching vibrations of phenolic C-O bonds of the BS-Schiff base spectrum, which was shifted to higher frequencies in the spectrum of the Ni-complex-boehmite, indicating that the electron density in the phenolic C-O bond was increased by the deprotonation and coordination of the phenolic oxygen [25].



Figure 5. FT-IR spectra of boehmite nanoparticles (a), boehmitesilica (b), BS-APTES (c), BS-Schiff base II (d), BS-Schiff base I (f), Ni-complex-boehmite II (e) and Ni-complex-boehmite I (g).

The nitrogen adsorption-desorption isotherms of boehmite nanoparticles, Ni-complex-boehmite I and Ni-complex-boehmite II are shown in Figure 6. The hysteresis loop can be identified as type IV (definition by IUPAC), which is characteristic of mesoporous materials. It can be seen that the BET surface area and pore volume decrease after deposition of Ni metal on the support. The decrease in pore volume and surface area of Ni-complex-boehmite I and Ni-complex-boehmite II was attributed to the immobilization of organic layers and Ni-complex on the boehmite pores. These results are strong evidences that Ni-complex was bonded on the boehmite nanoparticles.

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Figure 6. Nitrogen adsorption-desorption isotherms of samples: (a) boehmite nanoparticles, (b) Ni-complex-boehmite I and (c) Ni-complex-boehmite II.

The UV-DRS spectra of BS-Schiff base I, BS-Schiff base II, Nicomplex-boehmite I and Ni-complex-boehmite II are shown in Figure 7. The spectra for both ligands and both complexes show absorbance bands between 350-450 nm could be attributed to intraligand ( $\pi$ -  $\pi$ \* and n-  $\pi$ \*) charge transfer transition. In both Ni complexes two broad peaks between 500-650 nm assigned to d-d transition of Ni that are absent in BS-Schiff base I and II.



Figure 7. UV-DRS spectra for BS-Schiff base I (pink line), BS-Schiff base II (green line), Ni-complex-boehmite I (black line) and Ni-complex-boehmite II (blue line).

## 2.3 Catalytic study

In order to consider the catalytic activity of Ni-complex-boehmite (**I** and **II**), oxidation of sulfides to sulfoxides and also oxidative coupling of thiols into disulfides have been performed in the presence of these nanomaterials.



Scheme 2. Ni-complex-boehmite I or II catalyzed the oxidation of sulfides to sulfoxides and oxidative coupling of thiols into disulfides.

In order to optimize reaction conditions, we examined the oxidation of methylphenyl sulfide and oxidative coupling of naphthalene-2thiol as a model compounds using H<sub>2</sub>O<sub>2</sub> (0.4 mL) in various solvents and in the presence different amount of Ni-complex-boehmite I (Table 1). As shown in Table 1, in the oxidative coupling of naphthalene-2-thiol, the best results were obtained in ethanol using 0.004 gr (0.27  $\times$  10<sup>-3</sup> mol %) of Ni-complex-boehmite I at room temperature (Table 1, entry 5). Also the solvent-free condition in the presence of 0.003 gr ( $0.20 \times 10^{-3}$  mol %) of Ni-complex-boehmite I was found to be ideal reaction conditions for the conversion of methylphenyl sulfide to the methylphenyl sulfoxide (Table 1, entry 12). Also we examined the oxidation of methylphenyl sulfide and oxidative coupling of naphthalene-2-thiol as a model compounds in various solvent and in the presence of different amount of Nicomplex-boehmite II using H<sub>2</sub>O<sub>2</sub> (0.4 mL) (Table 2). The best results were obtained in the presence of 0.008 gr ( $0.29 \times 10^{-3} \text{ mol }\%$ ) of Ni-complex-boehmite II in the oxidation of methylphenyl sulfide and oxidative coupling of naphthalene-2-thiol respectively (Table 2, entries 3 and 13).

Table 1. Optimization of reaction conditions for the oxidation of methylphenyl sulfide and oxidative coupling of naphthalene-2-thiol in the presence of Ni-complex-boehmite I using  $H_2O_2$  (0.4 mL).

ш <i>)</i> .				
Substrate	strate Solvent		Time	Yield
Substitute	Borrein	boehmite I (mg)	(min)	(%) <sup>a</sup>
Naphthalene-2-thiol	Ethanol	-	15	0
Naphthalene-2-thiol	Ethanol	1	15	40
Naphthalene-2-thiol	Ethanol	2	15	70
Naphthalene-2-thiol	Ethanol	3	15	75
Naphthalene-2-thiol	Ethanol	4	15	90
4-Methylthiophenol	Acetonitrile	4	20	30
4-Methylthiophenol	$CH_2Cl_2$	4	20	40
4-Methylthiophenol	Ethyl acetate	4	20	50
4-Methylthiophenol	Water	4	20	40
Methylphenyl sulfide	Solvent-Free	0	15	0
Methylphenyl sulfide	Solvent-Free	1	15	30
Methylphenyl sulfide	Solvent-Free	3	15	97
Methylphenyl sulfide	Solvent-Free	5	15	50
Methylphenyl sulfide	Solvent-Free	7	15	60
Methylphenyl sulfide	Ethanol	3	15	55
Methylphenyl sulfide	Acetone	3	15	50
Methylphenyl sulfide	$CH_2Cl_2$	3	15	20
Methylphenyl sulfide	Ethyl acetate	3	15	70
Methylphenyl sulfide	n-Hexane	3	15	10
	Substrate Naphthalene-2-thiol Naphthalene-2-thiol Naphthalene-2-thiol Naphthalene-2-thiol Naphthalene-2-thiol 4-Methylthiophenol 4-Methylthiophenol 4-Methylthiophenol 4-Methylthiophenol Methylphenyl sulfide Methylphenyl sulfide	SubstrateSolventNaphthalene-2-thiolEthanolNaphthalene-2-thiolEthanolNaphthalene-2-thiolEthanolNaphthalene-2-thiolEthanolNaphthalene-2-thiolEthanolNaphthalene-2-thiolEthanolA-MethylthiophenolAcetonitrile4-MethylthiophenolCH2Cl24-MethylthiophenolWater4-MethylthiophenolWater4-MethylthiophenolSolvent-FreeMethylphenyl sulfideSolvent-FreeMethylphenyl sulfideSolvent-FreeMethylphenyl sulfideSolvent-FreeMethylphenyl sulfideSolvent-FreeMethylphenyl sulfideCH2Cl2Methylphenyl sulfideCH2Cl2Me	SubstrateSolventNi-complex- boehmite I (mg)Naphthalene-2-thiolEthanol-Naphthalene-2-thiolEthanol1Naphthalene-2-thiolEthanol2Naphthalene-2-thiolEthanol3Naphthalene-2-thiolEthanol44-MethylthiophenolAcetonitrile44-MethylthiophenolCH2Cl244-MethylthiophenolEthyl acetate44-MethylthiophenolWater44-MethylthiophenolWater4Methylphenyl sulfideSolvent-Free0Methylphenyl sulfideSolvent-Free1Methylphenyl sulfideSolvent-Free3Methylphenyl sulfideSolvent-Free5Methylphenyl sulfideSolvent-Free3Methylphenyl sulfideSolvent-Free3Methylphenyl sulfideEthanol3Methylphenyl sulfideEthanol3Methylphenyl sulfideEthanol3Methylphenyl sulfideEthanol3Methylphenyl sulfideCH2Cl23Methylphenyl sulfideEthyl acetate3Methylphenyl sulfideEthyl acetate3Methylphenyl sulfideEthyl acetate3Methylphenyl sulfideCH2Cl23Methylphenyl sulfideTH2Cl23Methylphenyl sulfideTH2Cl23Methylphenyl sulfideTH2Cl23Methylphenyl sulfideTH2Cl23Methylphenyl sulfideTH2Cl23 <t< td=""><td>SubstrateSolventNi-complex- boehmite I (mg) (min)Naphthalene-2-thiolEthanol-15Naphthalene-2-thiolEthanol115Naphthalene-2-thiolEthanol215Naphthalene-2-thiolEthanol315Naphthalene-2-thiolEthanol4154-MethylthiophenolAcetonitrile4204-MethylthiophenolCH2Cl24204-MethylthiophenolCH2Cl24204-MethylthiophenolWater4204-MethylthiophenolWater4204-MethylthiophenolWater4204-MethylthiophenolSolvent-Free015Methylphenyl sulfideSolvent-Free115Methylphenyl sulfideSolvent-Free315Methylphenyl sulfideSolvent-Free715Methylphenyl sulfideSolvent-Free715Methylphenyl sulfideSolvent-Free315Methylphenyl sulfideCH2Cl2315Methylphenyl sulfideCH2Cl2315Methylphenyl sulfideEthyl acetate315Methylphenyl sulfideCH2Cl2315Methylphenyl sulfideEthyl acetate315Methylphenyl sulfideEthyl acetate315Methylphenyl sulfideEthyl acetate315Methylphenyl sulfideEthyl acetate315Methylphenyl sulfideT</td></t<>	SubstrateSolventNi-complex- boehmite I (mg) (min)Naphthalene-2-thiolEthanol-15Naphthalene-2-thiolEthanol115Naphthalene-2-thiolEthanol215Naphthalene-2-thiolEthanol315Naphthalene-2-thiolEthanol4154-MethylthiophenolAcetonitrile4204-MethylthiophenolCH2Cl24204-MethylthiophenolCH2Cl24204-MethylthiophenolWater4204-MethylthiophenolWater4204-MethylthiophenolWater4204-MethylthiophenolSolvent-Free015Methylphenyl sulfideSolvent-Free115Methylphenyl sulfideSolvent-Free315Methylphenyl sulfideSolvent-Free715Methylphenyl sulfideSolvent-Free715Methylphenyl sulfideSolvent-Free315Methylphenyl sulfideCH2Cl2315Methylphenyl sulfideCH2Cl2315Methylphenyl sulfideEthyl acetate315Methylphenyl sulfideCH2Cl2315Methylphenyl sulfideEthyl acetate315Methylphenyl sulfideEthyl acetate315Methylphenyl sulfideEthyl acetate315Methylphenyl sulfideEthyl acetate315Methylphenyl sulfideT

<sup>a</sup> Isolated yield.

Table 2. Optimization of reaction conditions for the oxidation of methylphenyl sulfide and oxidative coupling of naphthalene-

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2-thiol in the presence of Ni-complex-boehmite II using  $H_2O_2$  (0.4 mL).

Entry	Substrate	Solvent	Ni-complex- boehmite II (mg)	Time (min)	Yield (%) <sup>a</sup>
1	Naphthalene-2-thiol	Ethanol	4	60	89
2	Naphthalene-2-thiol	Ethanol	6	60	92
3	Naphthalene-2-thiol	Ethanol	8	60	97
4	Naphthalene-2-thiol	Ethanol	10	50	94
5	4-Methylthiophenol	Acetonitrile	8	15	83
6	4-Methylthiophenol	$CH_2Cl_2$	8	15	65
7	4-Methylthiophenol	Ethyl acetate	8	15	81
8	4-Methylthiophenol	Water	8	15	20
9	4-Methylthiophenol	n-Hexane	8	15	62
10	Methylphenyl sulfide	Solvent-Free	2	95	93
11	Methylphenyl sulfide	Solvent-Free	4	95	95
12	Methylphenyl sulfide	Solvent-Free	6	95	94
13	Methylphenyl sulfide	Solvent-Free	8	95	98
14	Methylphenyl sulfide	Solvent-Free	10	95	92
15	Methylphenyl sulfide	$CH_2Cl_2$	8	95	53
16	Methylphenyl sulfide	Ethyl acetate	8	95	45
17	Methylphenyl sulfide	Ethanol	8	95	70
18	Methylphenyl sulfide	Acetonitrile	8	95	63
19	Methylphenyl sulfide	Water	8	95	42
<sup>a</sup> Icolo	tod mold				

<sup>a</sup> Isolated yield

In order to show the role of boehmite and Ni during the reactions, oxidation of methylphenyl sulfide was examined in the presence of Ni-complex-boehmite I and II compared to alone boehmite and boehmite-silica. The results of this comparison are shown in Table 3. As shown in Table 3, the methylphenyl sulfoxide was obtained in 47 and 18% of yield in the presence of boehmite and boehmite-silica, respectively. Also to investigate the efficient catalytic activity of heterogeneous catalysts I and II, catalytic activity of corresponding homogeneous catalysts have been compared with these heterogeneous catalysts. As shown in Table 3, catalytic activity of heterogeneous and reusable catalysts are comparable with their homogeneous catalysts, because: 1) the boehmite was formed of nanometre-sized particles (Figure 1), which; when the size of the support is decreased to the nanometre scale, the surface area is substantially increased and the support can be completely dispersed in the reaction mixture (forming a homogenous emulsion). 2) High-surface-area of boehmite-silica nanoparticles including many hydroxyl groups

leads to high catalyst loading capacity. Therefore, as shown in Table 3, these heterogeneous catalysts showed the advantages of both homogeneous (high catalytic activity) and heterogeneous (easy and rapid recoverability and recyclability) catalysts.

Table 3. The effect of boehmite or boehmite-silica and homogeneous catalyst I and II in comparison with Ni-complex-boehmite I and II in the oxidation of methylphenyl sulfide under optimized reaction conditions.

Entry	Substrata	Catalyst	Time	Yield
Entry	Substrate	Catalyst	(min)	$(\%)^{a}$
1	Methylphenyl sulfide	Boehmite nanoparticles	95	47 <sup>b</sup>
2	Methylphenyl sulfide	Boehmite-silica	95	18 <sup>b</sup>
3	Methylphenyl sulfide	Homogeneous catalyst I	80	98
4	Methylphenyl sulfide	Ni-complex-boehmite I	90	97
5	Methylphenyl sulfide	Homogeneous catalyst II	75	98
6	Methylphenyl sulfide	Ni-complex-boehmite II	95	98
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<sup>a</sup> Isolated yield. <sup>b</sup> Yield was obtained by plate chromatography.

The generality of this approach has been demonstrated by a facile oxidation of various sulfides as shown in Table 4 (entries 1-10). As shown in Table 4, a variety of sulfides were successfully employed to prepare the corresponding sulfoxides. The sulfoxides were obtained in high yields. The experimental procedure is very simple. Therefore, the results revealed that this methodology is effective for the oxidation of a wide range of sulfides.

In order to explore the activity of these catalysts, various thiols including aromatic and aliphatic thiols with various functional groups were coupled in the presence of Ni-complex-boehmite under optimized conditions and the corresponding disulfide compounds obtained with good to excellent yields (Table 4, entries 11-20).

To show the chemoselectivity of the presented protocol, sulfides and thiols containing other functional groups were subjected to the oxidation reaction. These functional groups remained intact during the conversion of thiols to disulfides or sulfides into sulfoxides (Table 4, entries 5, 7 and 20). Because of mild conditions of described heterogeneous systems, there is no overoxidation to sulfone (for oxidation of sulfides) or thiosulfinates, disulfoxides, sulfinyl sulfones or disulfones (for the oxidative coupling of thiols) was observed.

Table 4.	Oxidation	of sulfides	and oxidative	coupling of thi	ols catalyzed b	y Ni-com	plex-boehmite I	or II
				1 0				

Entry Substrate		Droduat	Ni-co	Ni-complex-boehmite I		Ni-complex-boehmite II			Melting point ( °C)
Entry	Substrate	rrouuci	Time (min)	Yield (%) <sup>a</sup>	TOF (h <sup>-1</sup> )	Time (min)	Yield (%) <sup>a</sup>	TOF (h <sup>-1</sup> )	[Ref.]
1	CH <sub>3</sub>	2a	90	97	323.33	95	98	213.43	Oil [17]
2	S Et	2b	270	80	88.89	330	95	59.56	Oil [26]
3	S	2c	5	95	5700	5	97	4013.79	Oil [15]
4	s /	2d	25	97	1164	25	94	777.93	Oil [27]
5	∽ <sub>s</sub> ∽∽ <sup>OH</sup>	2e	10	80	2400	10	93	1924.14	Oil [15]

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6	$\mathcal{M}_2$ s $\mathcal{M}_2$	2f	195	95	146.15	150	97	133.79	Oil [16]
7	С С С С С С С С С С С С С С С С С С С	2g	10	90	2700	20	96	993.10	Oil [16]
8	Me	2h	160	85	159.37	130	98	155.97	Oil [27]
9	Me <sup>S</sup> C <sub>11</sub> H <sub>23</sub>	2i	180	80	133.33	150	99	136.55	62-65 [16]
10	∕S	2ј	60	85	424.99	70	99	292.61	Oil [16]
11	SH	4a	15	90	133.33	60	97	334.48	134-136 [15]
12	Me	4b	20	95	1055.55	15	96	1324.14	35-37 [28]
13	SH NH2	4c	50	85	377.77	60	91	313.79	82-84 [16]
14	SH SH	4d	80	97	269.44	120	92	158.62	174-176 [16]
15	SH N	4e	60	85	314.81	60	98	337.93	55-57 [28]
16	Br	4f	150	80	118.52	120	96	165.52	88-90 [16]
17	SH COOH	4g	120	90	166.67	120	97	167.24	275-279 [15]
18	Me N SH N Me	4h	60	95	351.85	25	98	811.03	159-161 [28]
19	HOOC	4i	60	80	296.30	70	94	277.83	Oil [15]
20	HO	4j	30	95	703.703	25	96	794.48	Oil [16]

<sup>a</sup>Isolated yield.

We have found that these catalysts were rapidly recovered and demonstrated remarkably excellent recyclability. In order to investigate this issue, the recyclability of these catalysts was examined in the oxidation of methyl phenyl sulfide and 4methylthiophenol. After the completion of the reaction, the catalyst was separated by centrifuge technique. The remaining catalyst was washed with ethylacetate to remove residual product. Then, fresh substrates was added to the remaining catalyst without any activation and subjected to the next run. As shown in Figure 6, described catalysts can be recycled up to 5 runs without any significant loss of their catalytic activities. In order to find the leaching of the catalysts, the amount of Ni in catalyst **II** were determined by ICP-OES after recycling. The amount of Ni in catalyst **II** was found to be  $33.4 \times 10^{-5}$  mol g<sup>-1</sup> based on ICP-OES for catalyst **II** (9 %) after recycling. Therefore the catalyst can be recovered and reused without any significant leaching of Ni. Based on ICP-OES results, amount of Ni in the catalysts after recycle are comparable with the fresh catalyst.



Fig 8. The recycling experiment of a) Ni-complex-boehmite I and b) Ni-complex-boehmite II in oxidation of methylphenyl sulfide and c) Ni-complex-boehmite I and d) Ni-complex-boehmite II in coupling of 4-methylthiophenol.

The efficiency of these nanocatalysts are demonstrated by comparison our result on the oxidation of methyl phenyl sulfide and oxidative coupling of 4-methylbenzenethiol with the previously reported procedures in the literature (Table 5). As it can be seen from this Table the good reaction time and higher yield than the other reported catalysts has been achieved. Also these new catalysts are comparable or may be better in terms of price, non-toxicity, stability and easy separation. In addition, these catalysts can be recycled at least 5 runs without any significant loss of their catalytic activity or metal leaching. Moreover, the mesoporous silica such as MCM-41, SBA-15 or some nanoparticles such as TiO<sub>2</sub> NPs, which have been used as catalyst support in the organic reactions, requires high temperature for calcination and a lot of time and tedious conditions to prepare. Also some of previously reported catalysts such as heteropolyacids, ionic liquids or some polymers are more expensive. Also preparation of boehmite nanoparticles was not air, or moisture sensitive, therefore this nanomaterial was prepared in water at room temperature without inert atmosphere.

Table 5. Comparison of Ni-complex-boehmite I and II for the oxidation of methyl phenyl sulfide and oxidative coupling of 4-methylbenzenethiol with previously reported procedure.

Entry	Substrata	Catalyst	Time	Yield <sup>a</sup> (%)
Entry Substrate		Catalyst	(min)	[Reference]
1	Ph-SCH <sub>3</sub>	NBS	270	93 [29]
2	Ph-SCH <sub>3</sub>	Ni-salen-MCM-41	156	95 [30]
3	Ph-SCH <sub>3</sub>	Cd-salen-MCM-41	150	98 [30]
4	Ph-SCH <sub>3</sub>	TsOH	240	88 [31]
5	Ph-SCH <sub>3</sub>	VO <sub>2</sub> F(dmpz) <sub>2</sub>	300	95[32]
6	Ph-SCH <sub>3</sub>	Heterocyclic amine salts of Keggin heteropolyacids	120	95 [33]
7	Ph-SCH <sub>3</sub>	polymer-anchored Cu(II)	180	90 [34]
8	Ph-SCH <sub>3</sub>	SiO <sub>2</sub> –W <sub>2</sub> –Im	150	91.9 [37]
9	Ph-SCH <sub>3</sub>	Ni-complex-boehmite I	90	97 [This work]
10	Ph-SCH <sub>3</sub>	Ni-complex-boehmite II	95	98 [This work]
11	p-MePh-SH	CuI/Cs <sub>2</sub> CO <sub>3</sub> /1,10-phen	720	97 [19]
12	p-MePh-SH	Ni-salen-MCM-41	25	95 [30]
13	p-MePh-SH	Cd-salen-MCM-41	20	97 [30]
14	p-MePh-SH	Fe NPs@SBA-15	45	94 [36]
15	p-MePh-SH	[bmim][SeO <sub>2</sub> (OCH <sub>3</sub> )]	120	99 [37]
16	p-MePh-SH	STA-RGO	25	85 [38]
17	p-MePh-SH	Mn–ZSM-5	360	83.2 [39]
18	p-MePh-SH	Ni-complex-boehmite I	20	95 [This work]
19	p-MePh-SH	Ni-complex-boehmite II	15	96 [This work]

<sup>a</sup> Isolated yield.

## **3** Conclusions

In summary, we have demonstrated that Ni-complex-boehmite (I and II) can be used as a green, efficient and reusable nanocatalysts for the oxidation of sulfides to sulfoxides and oxidative coupling of a wide range of thiols into disulfides using  $H_2O_2$  at room temperature. The advantages of this protocol are the use of commercially available materials, eco-friendly conditions, cheap oxidant, the mild reaction conditions, operational simplicity, practicability and good to high yields of reactions. Also the catalyst can be reused for 5 times without any significant loss of its activity. More importance, nanoboehmite is new support for the heterogenization of homogeneous catalysts, which has several advantages such as high surface area, easily and readily available material to prepare, thermal and mechanical stability, ease of surface modification, easy and inexpensive procedure of preparation.

#### 4 Experimental

#### 4.1. Preparation of the Ni-complex-boehmite

The solutions of 6.490 g NaOH in 50 mL of distilled water was added to the solutions of  $Al(NO_{3)3}.9H_2O$  (20 g) in 30 mL distilled water drop wise under vigorous stirring. The resulting milky mixture was subjected to mixing in the ultrasonic bath for 3 h at 25 °C. The resulted nanoboehmite was filtered and washed by distilled water and were kept in the oven at 220 °C for 4 h.

The obtained boehmite nanoparticles (1 g) were dispersed in water (10 mL) and ethanol (50 mL) by sonication for 30 min. Under continuous stirring, PEG (5.36 g), ammonia solution (10 mL) and TEOS (2 mL) were respectively added into the suspension, and continuously reacted for 38 h at room temperature. Then, the product (boehmite-silica) was filtered and washed with ethanol and distilled water, the obtained boehmite-silica was dried at room temperature.

The obtained boehmite-silica (1.5 g) was dispersed in 100 mL dry nhexane solution by sonication for 30 min, then (3-aminopropyl)trimethoxysilane (APTES) (2.5 mL) was added to the reaction mixture. The reaction mixture was stirred at 40 °C for 8 h. Subsequently, nanoparticles have been isolated by simple filtration and washed with ethanol. The nanoparticles (BS-APTES) were dried at room temperature. In order to prepare BS-Schiff base, the above mentioned solid (1 g) was refluxed with salicylaldehyde (1 mmol) or 5-bromosalicylaldehyde (1 mmol) in ethanol for 8h. The resulting solid (BS-Schiff base) was separated using filtration, washed with ethanol and dried at room temperature. Finally, for the preparation of Ni-complex-boehmite, the BS-Schiff base (1.0 g) was dispersed in ethanol and was mixed with 1.0 mmol of Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O. The mixture was stirred at 80 °C for 15 h. The solid product (Nicomplex-boehmite) was obtained after washing with ethanol and drying at 50 °C.

#### 4.2 General procedure for the oxidation of sulfides to sulfoxides

A mixture of sulfide (1 mmol),  $H_2O_2$  (0.4 mL) and Ni-complexboehmite I (0.003 g,  $0.20 \times 10^{-3}$  mol%) or Ni-complex-boehmite II (0.008 g,  $0.29 \times 10^{-3}$  mol%) was stirred at room temperature under solvent-free condition and the progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated using filtration and washed with ethyl acetate, and the product was extracted with ethyl acetate. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> (1.5 g). Finally, the organic solvents were evaporated, and products were obtained in good to high yield.

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# 4.3 General procedure for the oxidative coupling of thiols into disulfides

Ni-complex-boehmite I (0.004 g,  $0.27 \times 10^{-3}$  mol%) or Ni-complexboehmite II (0.008 g,  $0.29 \times 10^{-3}$  mol%) was added to a mixture of thiol (1 mmol) and H<sub>2</sub>O<sub>2</sub> (0.4 mL) in ethanol (3 mL). Then the mixture was stirred for the appropriate time at room temperature. The progress of reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by filtration and the mixture was washed with ethyl acetate. The product was extracted with ethyl acetate. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> (1.5 g). The products were obtained in good to high yield.

#### 4.4 Selected spectral data

Tetrahydrothiophene 1-oxide (Table 4, entry 3): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.27 (t, *J*= 7.5 Hz, 2H), 3.07 (t, *J*= 7.6 Hz, 2H) ppm.

Methyl(p-tolyl)sulfane (Table 4, entry 8): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 2.22$  (s, 3H), 2.57 (s, 3H), 7.19 (d, J= 3.2 Hz, 2H), 7.39 (d, J= 3.2 Hz, 2H) ppm.

**1-(Propylsulfinyl)propane (Table 4, entry 10):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.11$  (t, J= 6 Hz, 6H), 1.84-1.93 (m, 4H), 2.65-2.97 (m, 4H) ppm.

**1,2-di(naphthalen-2-yl)disulfane (Table 4, entry 11):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.49 (m, 4H), 7.63 (m, 2H), 7.74 (m, 2H), 7.80 (m, 4H), 8.11 (s, 2H) ppm.

**1,2-di-p-tolyldisulfane (Table 4, entry 12):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.35 (s, 6H), 7.12 (d, *J*= 7.9 Hz, 4H), 7.43 (d, *J*= 7.89 Hz, 4H) ppm.

**1,2-bis(benzo[d]thiazol-2-yl)disulfane (Table 4, entry 14):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.36 (t, *J*= 3.2 Hz, 2H), 7.48 (t, *J*= 3.2 Hz, 2H), 7.80 (d, *J*= 3.2 Hz, 2H), 7.94 (d, *J*= 3.2 Hz, 2H) ppm.

**1,2-bis(4-bromophenyl)disulfane (Table 4, entry 16):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.35 (d, *J*= 8.2 Hz, 4H), 7.42 (t, *J*= 8.2 Hz, 4H) ppm.

**1,2-bis(4,6-dimethylpyrimidin-2-yl)disulfane (Table 4, entry 18):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 2.40$  (s, 12H), 6.74 (s, 2H) ppm. **2,2'-Disulfanediyldiethanol (Table 4, entry 20):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 2.60$  (br, 2H), 2.89 (t, *J*= 5.6 Hz, 4H), 3.93 (t, *J*= 5.6 Hz, 4H) ppm.

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## **Graphical Abstract**

Nickel Schiff-base complexes immobilized on boehmite nanoparticles and their application in the oxidation of sulfides and oxidative coupling of thiols as novel and reusable catalysts

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Ni-complex-boehmite was prepared in water at room temperature using commercially available materials and applied as efficient nanocatalyst in the oxidation of sulfides and thiols.