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Boehmite silica sulfuric acid: as a new acidic material and reusable heterogeneous nanocatalyst for the various organic oxidation reactions

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Abstract In this research, project boehmite silica sulfuric acid (Boehmite-SSA) has been applied as new acidic porous catalyst for the selective oxidation of sulfides to sulfoxides and oxidative coupling of thiols to corresponding disulfides using hydrogen peroxide as oxidizing agent. The products have been obtained in short reaction times and high yields. Boehmite nanoparticles was prepared, coated by silica and then reacted with chlorosulfuric acid to obtain Boehmite-SSA. This catalyst was characterized by FT-IR, TGA/DTA, XRD, TEM, SEM, EDS and BET techniques. BET curve of boehmite nanoparticles identified as a typical type IV isotherm (definition by IUPAC), which are the characteristics of mesoporous material. Nitrogen adsorption/desorption measurement indicated that boehmite nanoparticles had BET surface area of about 122.8 m²/g. The catalyst was easily separated and reused for the several runs without significant loss of its catalytic efficiency.

Keywords Boehmite nanoparticles · Sulfoxide · Disulfide · Silica sulfuric acid · Oxidation

Introduction

Boehmite nanoparticle is a cubic orthorhombic structure of aluminum oxide hydroxide which can prepared in water using commercial available materials [1]. The

Arash Ghorbani-Choghamarani arashghch58@yahoo.com structure of boehmite consists of double sheets of octahedral with aluminum ions, and the sheets themselves are composed of octahedral chains [2]. Recently, boehmite nanoparticles have been used as an optical material, absorbent, coatings, cosmetic products, composite reinforcement material in ceramics, vaccine adjuvants, pillared clays and sweep flocculation for fresh water treatment [1, 3, 4]. Also boehmite was used as the precursor material for the synthesis of alumoxanes [4]. Boehmite nanoparticles have several attractive features such as non-toxic, easily and readily available, high surface area (>120 m²/g), ease of surface modification, easy and inexpensive procedure of preparation, favorable biocompatibility and thermal, chemical and mechanical stability [5, 6]. Also the surface of boehmite nanoparticles covered with hydroxyl groups, which existence of many hydroxyl groups on the nanoboehmite surface provide valuable sites that can be grafted with various functional groups to produce expensive supported-catalysts [7, 8]. However, alumina has been used as catalyst support [9-12] but modification of boehmite nanoparticles has been rarely reported as heterogeneous support in the recovering and recycling of expensive homogeneous catalysts [13]. Therefore, owing to the context of reuse of catalyst and green chemistry, herein boehmite-SSA as a new nano heterogeneous catalyst has been reported for the selective oxidation of sulfides to sulfoxides and oxidative coupling of thiols to corresponding disulfides using hydrogen peroxide (with only H₂O as a by-product) as an inexpensive and environmental oxidant. The oxidation of sulfides to sulfoxides and oxidative coupling of thiols into corresponding disulfides are useful in the synthesis of new molecules, as well as for various medical, chemical, biological, materials and nanotechnological applications [14-23].

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Experimental

Materials

Chemicals and solvents used in this work were obtained from Sigma-Aldrich, Fluka or Merck chemical companies and used without further purification. Boehmite-SSA was characterized using a Holland Philips X'pert X-ray powder diffraction (XRD) diffractometer, at a scanning speed of 2° /min from 2° to 80° . The particle size and morphology were investigated by a FESEM-TESCAN MIRA3 scanning electron microscopy (SEM), on an accelerating voltage of 25.0 kV and also using Zeiss-EM10C transmission electron microscope (TEM). IR spectra were recorded as KBr pellets on a VRTEX 70 model BRUKER FT-IR spectrophotometer. Thermogravimetric analyses (TGA) of the samples were recorded using a Shimadzu PL-STA 1500 device in the temperature range 30-800 °C. Nitrogen adsorption/ desorption isotherms were recorded at 120 °C with a Brunauer-Emmett-Teller Analysis Adsorption BELSORP Mini II.

Preparation of catalyst

The solutions of NaOH (6.490 g) in 50 mL distilled water were added to the solutions of $Al(NO_3)_3 \cdot 9H_2O$ (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 was 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 (boehmitesilica) was filtered and washed with ethanol and distilled water; the obtained boehmite-silica was dried at room temperature.

Scheme 1 Synthesis of boehmite-SSA

The obtained boehmite-silica (0.5 g) was dispersed in dry n-hexane (5 mL) by ultrasonic bath for 30 min. Subsequently, chlorosulfuric acid (0.75 mL) was added drop wise over a period of 30 min and the mixture was stirred for 4 h at room temperature. Then, the final product was filtered and washed by dry ethanol and n-hexane, respectively, to remove the unattached substrates. The product (boehmite-SSA) dried at room temperature and stored in a refrigerator.

General procedure for the oxidation of sulfides

A mixture of sulfide (1 mmol), H_2O_2 (0.4 mL) and boehmite-SSA (0.003 g) in ethyl acetate (2 mL) was stirred at room temperature (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 Na₂SO₄ (1.5 g). Finally, ethyl acetate was evaporated, and product obtained in good to high yield.

General procedure for the oxidative coupling of thiols

Boehmite-SSA (0.002 g) was added to a mixture of thiol (1 mmol) and H_2O_2 (0.4 mL) in ethyl acetate (2 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 Na₂SO₄ (1.5 g). The products were obtained in good to high yield.

Results and discussion

In continuation of our studies on the application of modified boehmite nanoparticles in organic reactions [3, 6], herein, we have prepare report the boehmite silica sulfuric acid (boehmite-SSA) as a high efficient, nanoparticles and





Fig. 1 SEM image of boehmite (a), boehmite-silica (b) and boehmite-SSA (c)

reusable heterogeneous catalyst for some organic oxidation reactions such as oxidation of sulfides into sulfoxides and oxidative coupling of thiols into their corresponding disulfides using H_2O_2 as oxidant at room temperature.

The Boehmite-SSA was prepared by the concise route that has been outlined in Scheme 1.

Boehmite nanoparticles and boehmite-SSA have been characterized by FT-IR spectroscopy, thermogravimetric

analysis (TGA), transmission electron microscope (TEM), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and N_2 adsorption–desorption isotherms.

The morphological and size of the catalyst was evaluated by scanning electron microscopy and transmission electron microscope. The unit cells of boehmite were generated in regular geometric shape (Fig. 1a). Also, the SEM



Fig. 2 TEM image of boehmite-SSA



Fig. 3 EDS spectrum of boehmite-SSA

image of the boehmite-silica showed that particles have a regular geometric shape in comparison with nanoboehmite (Fig. 1b). As shown in Fig. 1c, the catalyst was formed of nanometer-sized particles (20–50 nm). Also, the size and morphology of boehmite-SSA was studied by TEM technique. As shown in Fig. 2, the unit cells of boehmite-SSA were obtained in regular geometric shape with about 20–40 nm.

In order to extend the scope of characterization of this catalyst, a typical EDS spectrum prepared from boehmite-SSA that is shown in Fig. 3. As it can be seen from this figure, EDS spectrum shows the presence of O, Al, Si and S species in the catalyst (Fig. 3).

The TGA was used to determine the percentage of chemisorbed silica sulfuric acid onto boehmite nanoparticles. The TGA curve of boehmite nanoparticles (black curve), boehmite-silica (pink curve) and boehmite-SSA (green curve) is shown in Fig. 4a. In the TGA curves, physically adsorbed water mass loss occurred at temperatures below 250 °C as well as the endothermic weight loss at 300 °C is attributed to water loss from structural hydroxyl groups in the precursor [24]. In TGA/DTA curve of the boehmite-SSA, a weight loss of about 41 % from 200 to 800 °C is observed (Fig. 4b). Meanwhile, weight loss about 16 and 20 % from 200 to 800 °C is occurred for boehmite nanoparticles and boehmite-silica, respectively. These results were shown that silica sulfuric acid groups have been grafted on the surface of boehmite nanoparticles.

The XRD patterns of boehmite nanoparticles, boehmitesilica and boehmite-SSA are shown in Fig. 5. As it can be seen from Fig. 5, the boehmite phase was characterized 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) from the XRD patterns, which all the peaks can be confirmed the crystallization of boehmite with an orthorhombic unit cell [7, 13]. The results of XRD patterns of boehmite-silica and boehmite-SSA reveal that the surface modification of the boehmite nanoparticles does not lead to their phase change. Also, the broad peaks around $2\theta = 20-30$ in the XRD patterns of boehmite-silica and boehmite-SSA are typical for silica and can't be seen in boehmite itself [28].

The FT-IR spectrum of boehmite-SSA shows several peaks that are characteristic of a functionalized silica sulfuric acid, which clearly differs from that bare boehmite nanoparticles and boehmite-silica (Fig. 6). The FT-IR spectrum of the boehmite nanoparticles (Spectrum a) shows two strong bands at 3086 and 3308 cm⁻¹, which are due to the both symmetrical and asymmetrical modes of the O–H bonds on the surface of boehmite nanoparticles [25, 26]. In the FT-IR spectrum of boehmite nanoparticles (Spectrum a–c), several peaks that appear at 480, 605 and



Fig. 4 a TGA diagram of boehmite (*black line*), boehmite-silica (*pink line*) and boehmite-SSA (*green line*). b TGA/DTA analysis of boehmite-SSA



Fig. 5 XRD patterns of boehmite nanoparticles (*black line*), boehmite-silica (*red line*) and boehmite-SSA (*green line*)

735 cm⁻¹ can be related to the absorption of Al–O bonds [2, 6]. Also, the nitrate impurity vibration at 1650 cm⁻¹ and the vibrations of hydrogen bands OH…OH by two strong absorption bands at 1164 and 1069 cm⁻¹ were observed in FT-IR spectrum [2, 4, 6]. In the 1072 and 770 cm⁻¹ spectral region of the FT-IR spectra (Figure b and c), an overlap of the stretching vibration of the Si–O–Si bonds with Al–O and OH…OH stretching vibration leads to band broading [27–29]. In the FT-IR spectra of boehmite-SSA (Spectrum



Fig. 6 FT-IR spectra of \mathbf{a} boehmite, \mathbf{b} boehmite-silica and \mathbf{c} boehmite-SSA



Fig. 7 Nitrogen adsorption-desorption isotherms of boehmite nanoparticles

$$R_1 \stackrel{S}{\sim} R_2 \xrightarrow{Boehmite-SSA} R_1 \stackrel{O}{\longrightarrow} R_1 \stackrel{S}{\longrightarrow} R_2$$

Scheme 2 Boehmite-SSA catalyzed the oxidation of sulfides into sulfoxides

c), the existence of the grafted silica sulfuric acid groups is confirmed by SO₃–H groups vibrations that appear at 938–1220 and $3000-3400 \text{ cm}^{-1}$ [30].

The nitrogen adsorption–desorption isotherms of boehmite nanoparticles are shown in Fig. 7. Based on the IUPAC classification, these materials display a typical type IV isotherm, which is characteristic of mesoporous materials. Based on Brunauer–Emmett–Teller (BET), surface area for boehmite nanoparticles is 122.8 m²/g.

As a first part of our organic program, herein we described the oxidation of sulfides into sulfoxides in the present of boehmite-SSA using hydrogen peroxide (Scheme 2).

In obtained optimum condition, the various sulfides were converted to their corresponding sulfoxides in the presence of boehmite-SSA as catalyst at room temperature. All of

Table 1 Optimization of the reaction conditions for the oxidation ofsulfides (1 mmol) in the presence of different amounts of boehmite-SSA in various solvents using H_2O_2 (0.4 mL)

Entry	Sulfide	Solvent	Cat. (gr)	Time (min)	Yield (%) ^a
1	Methyl phenyl sulfide	Ethyl acetate	_	90	Trace ^b
2	Methyl phenyl sulfide	Ethyl acetate	0.002	90	90
3	Methyl phenyl sulfide	Ethyl acetate	0.003	60	98
4	Methyl phenyl sulfide	Ethyl acetate	0.005	50	98
5	Methyl phenyl sulfide	Acetone	0.003	60	97
6	Methyl phenyl sulfide	Ethanol	0.003	60	60
7	Methyl phenyl sulfide	Solvent free	0.003	60	40

^a Isolated yields

^b The reaction in the absence of catalyst

the products were obtained in high to excellent yields. The result of this study is summarized in Tables 1 and 2.

The possible mechanistic path for the oxidation of sulfides is shown in Scheme 3 [31]; one explanation for this transformation is the in situ formation of peroxy acid using the reaction of boehmite-SSA with H_2O_2 , followed by the oxygen transfer to the organic substrate (Scheme 3a). Another explanation is that boehmite-SSA acts as protic acid, which polarizes the O–O bond in hydrogen peroxide to produce the reactive oxygen transfer agent (Scheme 3b).

As a second part of our organic program toward the development of new methods for the coupling of thiols, herein we described the oxidative coupling of thiols into corresponding disulfides in the presence of boehmite-SSA using hydrogen peroxide (Scheme 4). In order to optimize reaction conditions, we examined the oxidative coupling of 2-mercaptobenzoxazole as a model compound using H_2O_2 (0.4 mL) in various solvents and in the presence of different amount of boehmite-SSA (Table 3). As shown in

Entry	sulfide	Product	Time (min)	Isolated yield (%)
1	SS		50	98
2	S	S=0	10	97
3	S → OH	S II O	20	96
4	С S ОН	О В ОН	25	97
5	S S		35	98
6	S S	S O O	75	95
7	S		180	95
8	Cl	Cl S	130	96
9	C ₁₂ H ₂₅ S C ₁₂ H ₂₅	$\begin{array}{c} O\\ \parallel\\ C_{12}H_{25} \\ \end{array} \\ \begin{array}{c} C\\ C_{12}H_{25} \\ \end{array} \\ \end{array} \\ \begin{array}{c} C\\ C_{12}H_{25} \\ \end{array} \\ \begin{array}{c} C\\ C_{12}H_{25} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} C\\ C_{12}H_{25} \\ \end{array} \\ \end{array} \\ \begin{array}{c} C\\ C_{12}H_{25} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} C\\ C\\ C_{12}H_{25} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} C\\ C\\ C_{12}H_{25} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} $ \\ \begin{array}{c} C\\ C\\ C_{12}H_{25} \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ C \\	120	94

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Table 3, in the oxidative coupling of 2-mercaptobenzoxazole, the best results were obtained in ethyl acetate in the presence 0.002 g of boehmite-SSA at room temperature (Table 3, entry 2). On the basis of the literatures, a plausible reaction mechanism for oxidative coupling of thiols in the presence of boehmite-SSA is shown in Scheme 5 [32]. Reaction of H_2O_2 with boehmite-SSA leads to the intermediate



Scheme 4 Boehmite-SSA catalyzed the oxidative coupling of thiols into disulfides

Table 3 Optimization of the reaction conditions for the oxidative coupling of thiols (1 mmol) in the presence of different amounts of boehmite-SSA in various solvents using H_2O_2 (0.4 mL)

Entry	Sulfide	Solvent	Cat. (gr)	Time (min)	Yield (%) ^a
1	2-Mer- captoben- zoxazole	Ethyl acetate	_	90	Trace ^t
2	2-Mer- captoben- zoxazole	Ethyl acetate	0.002	60	97
3	2-Mer- captoben- zoxazole	Ethyl acetate	0.003	55	97
4	2-Mer- captoben- zoxazole	Ethyl acetate	0.005	40	98
5	2-Mer- captoben- zoxazole	Acetonitrile	0.002	120	96
6	2-Mer- captoben- zoxazole	Ethanol	0.002	105	95
7	2-Mer- captoben- zoxazole	Solvent free	0.002	360	96

^a Isolated yields

^b The reaction in the absence of catalyst



R-SH

R - SOH

B

R - SH

H₂O

A which is active oxidant. Next, nucleophilic attack of the thiol on this intermediate gives intermediate \mathbf{B} which, in turn, produces the corresponding products using reaction with thiol (Table 4).

Because these heterogeneous oxidation systems were performed in mild condition, overoxidation for oxidation of sulfides or oxidative coupling of thiols was not observed (Scheme 6).

The recyclability of boehmite-SSA was examined for the oxidation of methyl phenyl sulfide and 4-methyl thiophenol in the presence of boehmite-SSA under described conditions. The catalyst has been reused up to 5 runs without any significant loss of its catalytic activity, and the average isolated yield was obtained in 96 % and 95, for the sulfoxide and disulfide products, respectively (Fig. 8).

In conclusion, boehmite silica sulfuric acid as new porous material has been introduced and an efficient and

Entry	Thiol	Product	Time (min)	Isolated yield (%)
1	SH	S-S C	50	98
2	H ₃ C SH	H ₃ C S-S CH ₃	10	96
3	Br	Br S-S Br	160	96
4	SH N	S-S-S-V	25	98
5	SH	S-S	75	97
6	H ₃ C N H ₃ C SH	H_3C N H_3C N N N CH_3 N CH_3 C	45	94
7	HO	HO	20	95
8	NH ₂ SH	NH ₂ H ₂ N S-S-S	90	96
9	COOH SH	COOH COOH	40	97

Table 4 Oxidative coupling of thiols into disulfides using hydrogen peroxide in the presence of boehmite-SSA at room temperature in ethyl acetate

environmentally friendly procedure has been developed for the oxidation of sulfides to sulfoxides and oxidative coupling of thiols into their corresponding disulfides in the presence of this heterogeneous catalyst. This catalyst was characterized by FT-IR, XRD, BET, TEM, SEM, EDS and TGA. Furthermore, the catalyst could be isolated with

Scheme 6 Oxidation of sulfides and oxidative coupling of thiols in the presence of boehmite-SSA using H₂O₂ without overoxidation



R-SH





Fig. 8 Reuse of the boehmite-SSA for the oxidation of methyl phenyl sulfide (pink column) and 4-methyl thiophenol (green column)

simple filtration and the average yields achieved above 95 % after reused at 5 cycles.

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