Journal of the Iranian Chemical Society
https://doi.org/10.1007/s13738-018-1526-5

ORIGINAL PAPER

Nickel(II) immobilized on dithizone–boehmite nanoparticles: as a highly efficient and recyclable nanocatalyst for the synthesis of polyhydroquinolines and sulfoxidation reaction

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Received: 29 April 2018 / Accepted: 11 October 2018

Abstract

In this work, in the first stage, boehmite nanoparticles were easily fabricated via addition of NaOH solution to a solution of $Al(NO_3)_3.9H_2O$ at room temperature in water. Then, nickel–dithizone catalyst was supported on boehmite nanoparticles (Ni-dithizone@boehmite). Ni-dithizone@boehmite is a low-cost, nontoxic, and recoverable catalyst, which provides an environment friendly reaction conditions. In the second stage, catalytic activity of this catalyst was studied in the synthesis of polyhydroquinoline derivatives and selective oxidation of sulfides to sulfoxides. The reactions not require very high temperatures or inert atmosphere. The developed heterogeneous catalyst could be easily separated by centrifugation and recycled for several runs without leaching of Nickel from the surface of the catalyst or significant loss of its catalytic activity.

Keywords Boehmite nanoparticles · Nickel · Polyhydroquinolines · Sulfoxides · Heterogeneous catalyst

Introduction

The heterogeneous metal catalysts supported on solid nanoparticles have acquired much interest due to their environmentally friendly, recyclability and operational benefits in comparison with their homogeneous counterparts [1–5]. Boehmite (aluminum oxide hydroxide) is one of the useful nanomaterials for the preparation of metal-supported catalysts, due to presence of high density of hydroxyl groups on its surface [6, 7]. Moreover, boehmite nanoparticles with high surface area and high stability compared to most nanoparticles make it as very appropriate support, which is applicable in different organic reactions [8]. Boehmite has been used in catalysis, separation, ceramics, adsorption, abrasives, fibers, and biomedical applications [9–11]. Boehmite is also used as a starting material in the preparation of alumina [9, 12]. Several methods such as sol–gel, hydrothermal, precipitation, and hydrolysis of aluminum have been used for the preparation of boehmite nanoparticles that most of them have focused on preparation conditions, morphology, and chemical or physical properties of boehmite [13–17]. Nevertheless, only a few application of the boehmite nanoparticles have been reported as support for the preparation of heterogeneous catalysts [18–23]. Therefore, herein we have used boehmite nanoparticles as support to fabricate nickel-supported catalyst (Ni-dithizone@boehmite), then its catalytic application was studied for synthesis of polyhydroquinoline derivatives and selective oxidation of sulfides to sulfoxides.

The synthesis of sulfoxides is an important transformation in organic chemistry, because sulfoxides are useful in the synthesis of drugs, enzyme activation, natural products, germicides, and in medicinal chemistry [24–27]. For example, allicin, sulindac, modafinil, garlicnin B-2, garlicnin L-1 and omeprazole are several typical examples of the sulfoxide derivatives with pharmaceutical and biological activities [28, 29]. Among the various oxidants such as metal oxidants, organic oxidant, peroxides and halogens, H_2O_2 was commonly used for this transformation as an inexpensive and environmentally benign oxidant [30–35]. Likewise, polyhydroquinoline derivatives have important biological activities such as calcium channel blockers and have been utilized for the treatment of cardiovascular diseases such as nicardipine, nifedipine, and amlodipine [36–39]. Therefore, the synthesis of polyhydroquinolines and sulfoxides has remarkable attention in organic chemistry.

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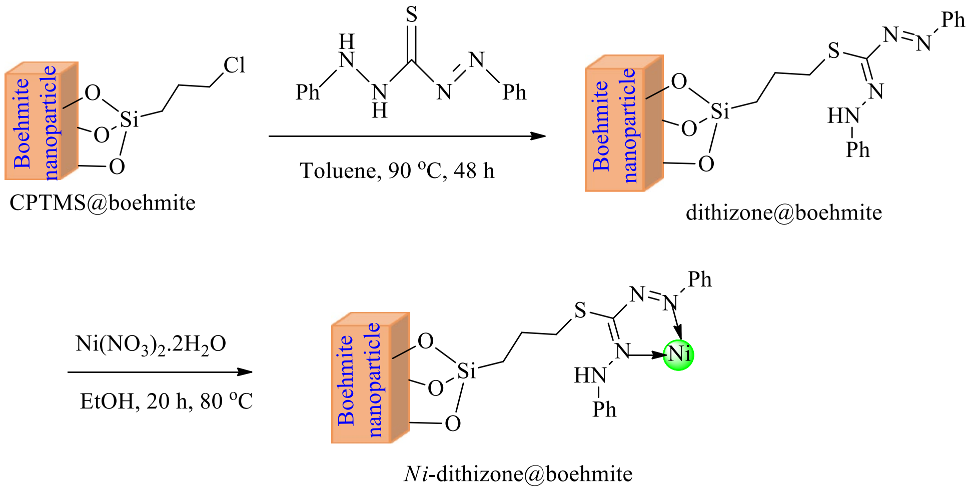


Scheme 1 Synthesis of Ni-dithizone@boehmite

Experimental

Preparation of catalyst

Modified boehmite nanoparticles with (3-chloropropyl)-trimethoxysilane (CPTMS@boehmite) was prepared according to recent reported method [10]. The above-mentioned solid (1.0 g) was mixed with dithizone (2.0 mmol) and stirred at 90 °C in toluene for 48 h. The resulting solid (dithizone@boehmite) was separated using simple filtration, washed with ethanol and dried at room temperature. Finally, for the preparation of catalyst, the dithizone@boehmite (1.0 g) was dispersed in ethanol and mixed with 2.0 mmol of Ni(NO$_3$)$_2$.2H$_2$O. Then, the obtained mixture was stirred at 80 °C for 20 h. The solid product (Ni-dithizone@boehmite) was obtained by simple filtration, washed with ethanol and dried at 50 °C.

General procedure for the synthesis of polyhydroquinoline derivatives

A mixture of aldehyde (1.0 mmol), dimedone (1.0 mmol), ethyl acetoacetate (1.0 mmol), ammonium acetate (1.3 mmol) and Ni-dithizone@boehmite (20.0 mg) was stirred in PEG at 80 °C and the progress of the reaction was monitored by TLC in *n*-hexane:acetone solution (volume ratio, 8:2). After completion of the reaction, catalyst was separated by simple filtration and washed with ethyl acetate. Products were extracted with water and ethyl acetate. Then, the organic layers were dried over anhydrous Na$_2$SO$_4$ (1.5 g) and then, solvent was evaporated to obtain pure products. All products were recrystallized in ethanol.

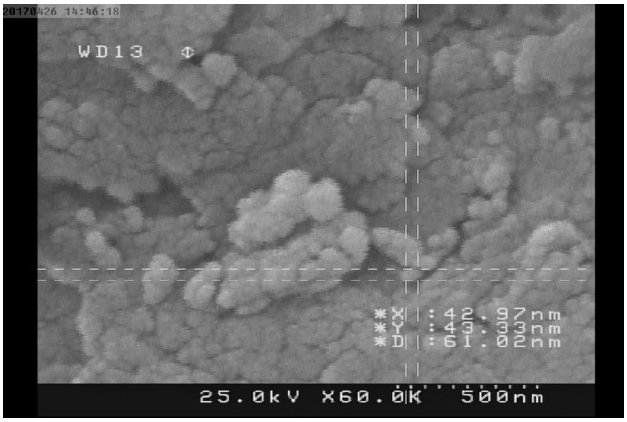


Fig. 1 SEM image of Ni-dithizone@boehmite

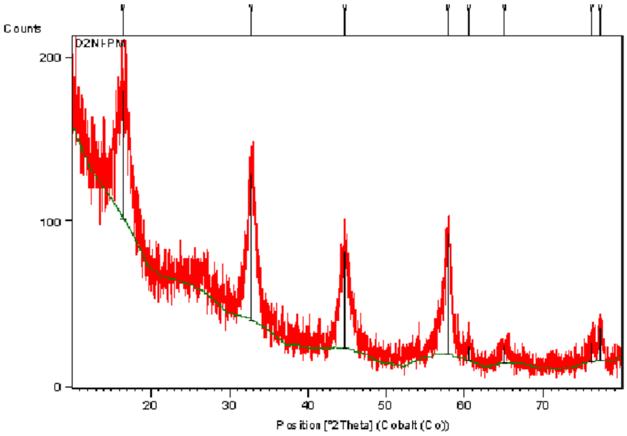


Fig. 2 XRD pattern of Ni-dithizone@boehmite

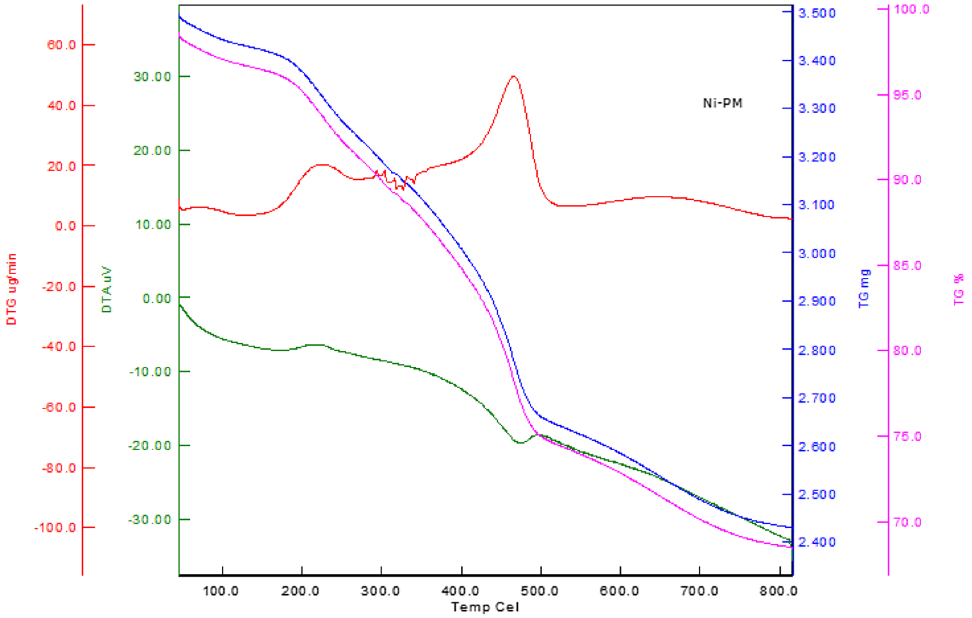
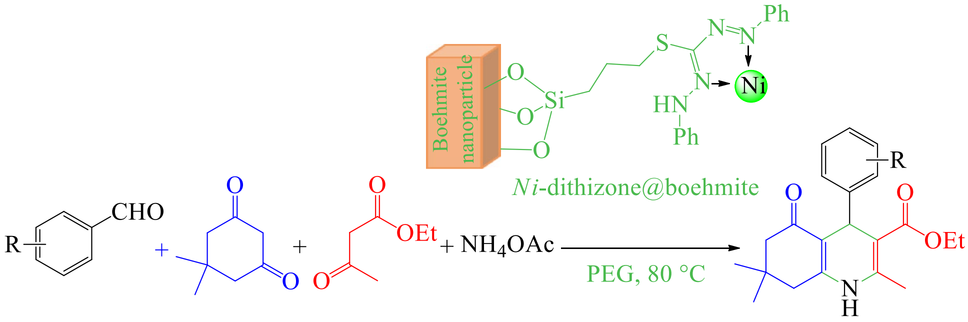


Fig. 3 TGA/DTA diagrams of Ni-dithizone@boehmite



Scheme 2 Synthesis of polyhydroquinoline derivatives in the presence of Ni-dithizone@boehmite

Table 1 Optimization conditions in condensation of benzaldehyde with dimedon, ethyl acetoacetate, and ammonium acetate for synthesis of polyhydroquinolines

Entry	Catalyst (mg)	Solvent	Temperature (°C)	Time (min)	Yield (%)[a]
1	10	PEG	80	40	53
2	15	PEG	80	40	69
3	20	PEG	80	30	95
4	25	PEG	80	25	96
5	20	H_2O	80	30	20
6	20	EtOH	Reflux	30	73
7	20	Ethyl acetate	Reflux	30	48
8	20	CH_3CN	Reflux	30	62
9	20	PEG	60	60	31

[a] Isolated yield

General procedure for the oxidation of sulfides to sulfoxides

0.008 g of Ni-dithizone@boehmite was added to a solution of sulfide (1.0 mmol) and 0.4 mL of H_2O_2 (33%). The obtained mixture was stirred under solvent-free conditions at room temperature for the specified times (Table 4) and the progress of the reactions was monitored by TLC in *n*-hexane:acetone solution (volume ratio, 8:2). After completion of the reaction, the catalyst was separated by simple filtration. The products were extracted with water and ethyl acetate, and dried over anhydrous Na_2SO_4. Then, the solvent

Table 2 Synthesis of polyhydroquinoline derivatives in the presence of *Ni*-dithizone@boehmite in PEG at 80°C

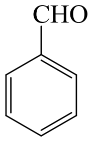
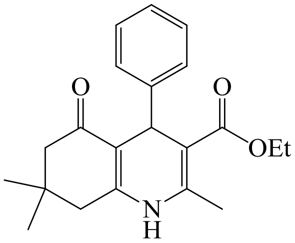
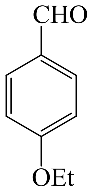
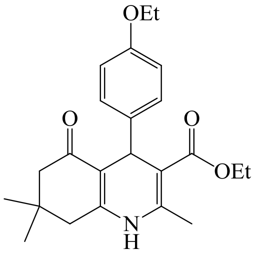
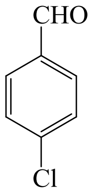
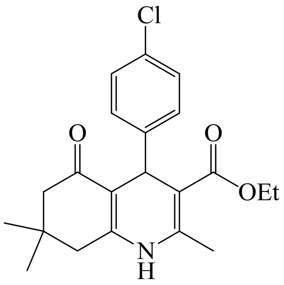
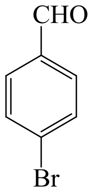
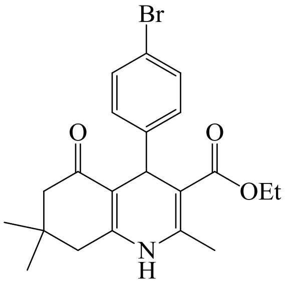
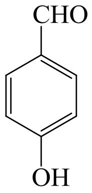
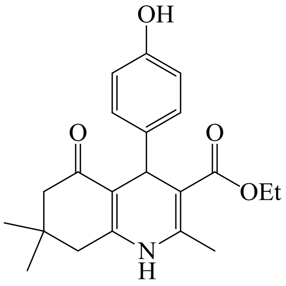
Entry	Aryl halide	Phenylating reagent	Time (min)	Yield (%)[a]	TOF (h^{-1})	Melting point (°C)	Reported M.P. [References]
1			30	95	231	217–219	216–218 [41]
2			130	96	54	175–178	176–178 [41]
3			280	96	25	234–237	235–238 [42]
4			240	94	28	251–253	252–253 [43]
5			45	93	151	230–233	230–232 [41]

Table 2 (continued)

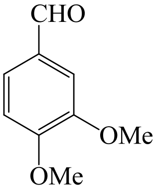
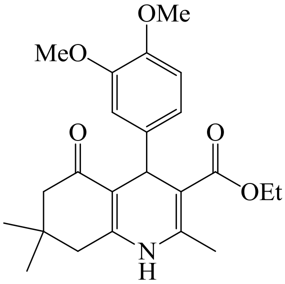
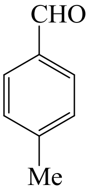
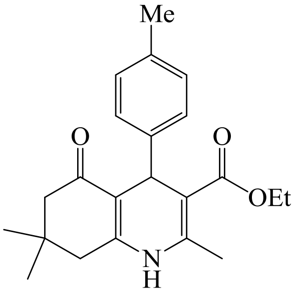
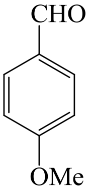
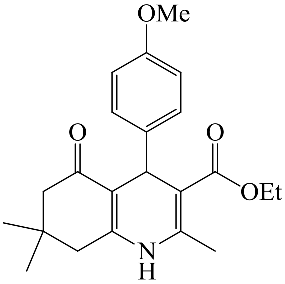
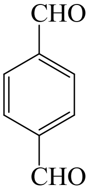
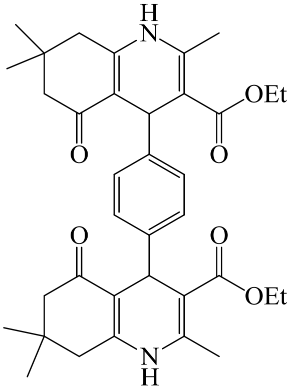
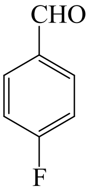
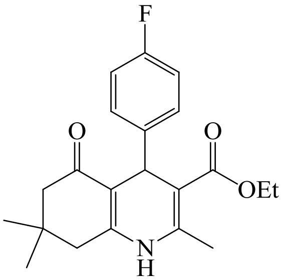
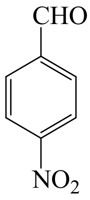
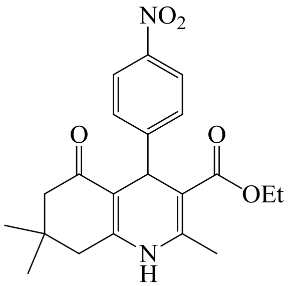
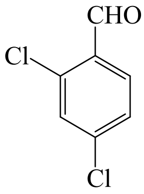
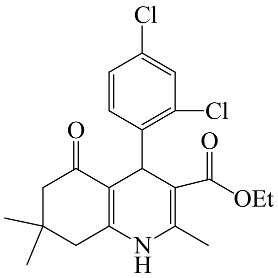
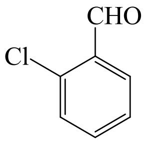
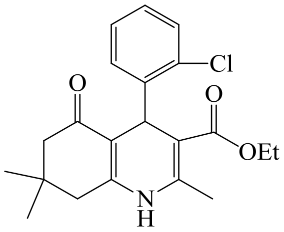
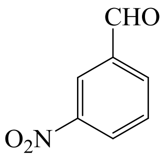
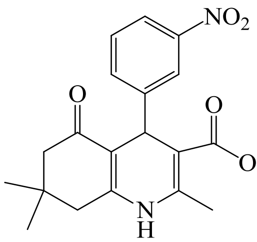
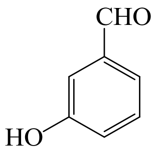
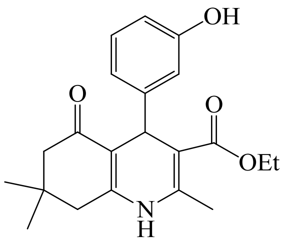
Entry	Aryl halide	Phenylating reagent	Time (min)	Yield (%)[a]	TOF (h^{-1})	Melting point (ºC)	Reported M.P. [References]
6			50	97	142	203–204	200–202 [41]
7			250	90	26	255–257	254–256 [41]
8			190	95	37	245–247	248–250 [44]
9			60	97	118	303–305	305–307 [44]
10			65	90	101	184–187	185–186 [43]

Table 2 (continued)

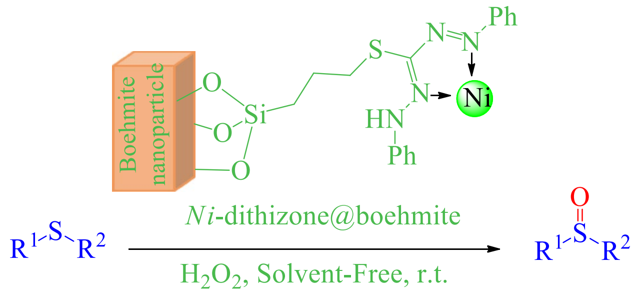
Entry	Aryl halide	Phenylating reagent	Time (min)	Yield (%)[a]	TOF (h^{-1})	Melting point (ºC)	Reported M.P. [References]
11			180	89	36	237–239	238–240 [44]
12			240	87	26	239–242	241–244 [45]
13			260	89	25	201–204	203–205 [42]
14			200	95	34	176–178	173–175 [41]
15			160	94	43	226–228	228–230 [41]

[a] Isolated yield

was evaporated and pure products were obtained in high to excellent yields.

Results and discussion

Boehmite nanoparticles were prepared and its surface was modified by CPTMS according to the reported procedure [10]. To synthesis of dithizone@boehmite, dithizone was immobilized on boehmite nanoparticles. Then, dithizone@



Scheme 3 Oxidation of sulfides to sulfoxides in the presence of Ni-dithizone@boehmite

Table 3 Optimization of reaction conditions for the oxidation of methyl phenyl sulfides in the presence of Ni-dithizone@boehmite at room temperature

Entry	Catalyst (mg)	Solvent	Time (min)	Yield (%)[a]
1	3	Solvent free	100	61
2	5	Solvent free	100	73
3	8	Solvent free	80	96
4	10	Solvent free	70	96
5	8	CH_3CN	80	33
6	8	Ethyl acetate	80	46
7	8	Ethanol	80	28
8	8	H_2O	80	52

[a] Isolated yield

boehmite was used as efficient and insoluble support for nickel(II) (Scheme 1). Further this catalyst (Ni-dithizone@boehmite) was characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic absorption spectroscopy (AAS), and inductively coupled plasma (ICP-OES) techniques.

Catalyst characterizations

SEM image of Ni-dithizone@boehmite is shown in Fig. 1. The particles size of this catalyst was studied by SEM technique that it was found to be between 40 and 60 nm. Also, the amount of Nickel on boehmite nanoparticles was measured using inductively coupled plasma (ICP) that was 0.41×10^{-3} mol g^{-1}, which this result has good agreement with atomic absorption spectroscopy (AAS) (0.39×10^{-3} mol g^{-1}).

The XRD pattern of Ni-dithizone@boehmite is shown in Fig. 2. As shown in Fig. 2, the boehmite phase was confirmed from the XRD pattern by the peak positions, which are in close agreement with standard XRD pattern of boehmite nanoparticles [12, 40] and all the peaks can be confirmed the crystallization of boehmite in orthorhombic unit cells [3, 40].

TGA/DTA diagrams of Ni-dithizone@boehmite are shown in Fig. 3. The mass loss about 10% before 250 °C is related to the evaporation of water and adsorbed solvents [41]. Also, the high decreasing of weight is related to immobilize organic layers that are decomposed upon heating from 250 °C to 500 °C (about 15%). Final weight loss (about 5%) which appeared above 500 °C may be related to transformation of thermal crystal phase of boehmite nanoparticles.

Application of Ni-dithizone@boehmite for the synthesis of polyhydroquinolines

The catalytic activity of Ni-dithizone@boehmite was studied in synthesis of polyhydroquinoline derivatives. Polyhydroquinolines were synthesized in the presence of Ni-dithizone@boehmite based on concise route outlined in Scheme 2.

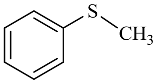
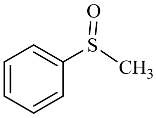
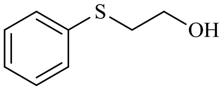
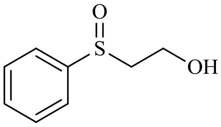
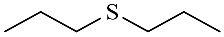
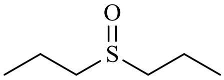
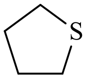
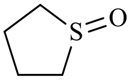
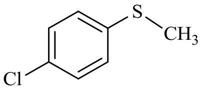
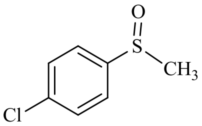
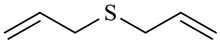
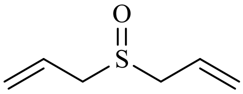
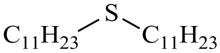
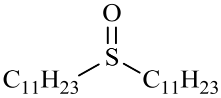
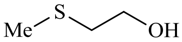
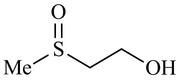
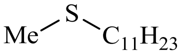
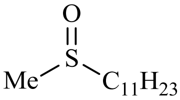
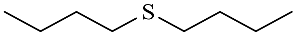
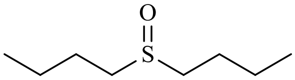
To optimize the reaction conditions for the synthesis of polyhydroquinolines, condensation of benzaldehyde with dimedone, ethyl acetoacetate, and ammonium acetate was selected as model reaction. Several parameters such as amount of Ni-dithizone@boehmite, effect of solvent and temperature were examined in the selected model reaction. Results of these studies are summarized in Table 1. As shown in Table 1, the best result was obtained in the presence of 20 mg (0.82 mol %) of Ni-dithizone@boehmite in PEG at 80 °C (Table 1, entry 3).

After optimizing of reaction conditions, the condensation of different aldehydes with ethyl acetoacetate, dimedone, and ammonium acetate was then tested to confirm the generality of this method and obtained results are summarized in Table 2. Polyhydroquinoline derivatives were obtained in high yields in the presence of Ni-dithizone@boehmite with high TOF numbers. As shown in Table 2, a variety of benzaldehydes bearing electron-donating and electron-withdrawing substituents (Such as OH, CH_3, OCH_3, OEt, halides, and NO_2) was successfully employed for the synthesis of polyhydroquinolines. Also, terephthalaldehyde was investigated and it was afforded the desired product in good yield (Table 2, entry 9).

Application of Ni-dithizone@boehmite for the oxidation of sulfides

Also, catalytic activity of Ni-dithizone@boehmite was studied in the selective oxidation of sulfides to sulfoxides. Sulfoxides were synthesized through oxidation of sulfides in the presence of Ni-dithizone@boehmite based on concise route outlined in Scheme 3. Oxidation of methyl phenyl sulfide using hydrogen peroxide was selected as model reaction for optimize reaction conditions. Obtained results of

Table 4 Selective oxidation of sulfides to sulfoxides in the presence of Ni-dithizone@boehmite

Entry	Sulfide	Product	Time (min)	Yield (%)a	TOF (h^{-1})	Melting point (ºC)	Reported M.P. [References]
1			80	96	218	30–32	30–32 [26]
2			15	97	1175	Oil	Oil [46]
3			15	95	1151	Oil	Oil [34]
4			5	97	3527	Oil	Oil [34]
5			360	80	40	Oil	Oil [46]
6			40	88	400	Oil	Oil [47]
7			120	90	136	84–87	85–89 [34]
8			20	93	845	Oil	Oil [46]
9			75	90	218	60–64	61–64 [26]
10			20	95	863	Oil	Oil [46]

^{a}Isolated yield

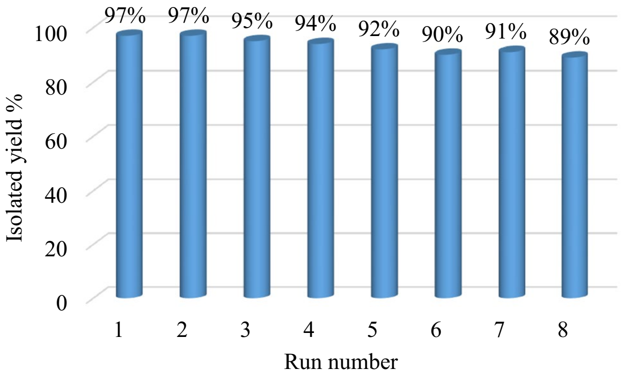


Fig. 4 Recycling of Ni-dithizone@boehmite in oxidation of tetahydrothiophen

Table 5 Comparison of Ni-dithizone@boehmite in the oxidation of methyl phenyl sulfide with previously reported catalysts

Entry	Catalyst	Time (min)	Yield^a (%) [References]
1	DSA@MNPs	360	98 [34]
2	Polymer-anchored Cu(II)	180	90 [48]
3	Cu-SPATB/Fe_3O_4	95	98 [49]
4	Cd-salen-MCM-41	150	98 [50]
5	TsOH	240	88 [51]
6	Ni-salen-MCM-41	156	95 [50]
7	VO_2F $(dmpz)_2$	300	95 [52]
8	Ni-dithizone@boehmite	80	96 [this work]

optimization conditions in model reaction are summarized in Table 3. As shown in Table 3, the best results were obtained in the presence of 0.008 g (0.33 mol%) of catalyst at room temperature under solvent-free conditions using 0.4 mL of H_2O_2.

In obtained optimum conditions, the various aliphatic and aromatic sulfides were successfully converted to their corresponding sulfoxides in the presence of *Ni*-dithizone@boehmite and all products were obtained in good yields without any byproduct from over oxidation such as sulfone. The result of these studies is shown in Table 4. To show the chemoselectivity of present methodology, sulfides including other functional groups such as olefin or hydroxyl groups were subjected to sulfoxidation reaction, that these functional groups remained intact during the oxidation conditions (Table 4, entries 2, 6 and 8).

Reusability of the catalyst

Recovering and recycling are major advantages of heterogeneous catalysts compared to homogeneous catalysts. Therefore, the reusability of Ni-dithizone@boehmite was confirmed in the oxidation of tetrahydrothiophen (Fig. 4). After completion of each reaction, the catalyst was recovered by centrifugation, washed with ethyl acetate and reused up to eight times without any significant loss of its catalytic activity. The average isolated yield for eight runs was 93.5%, which clearly indicate the practical reusability of Ni-dithizone@boehmite.

Comparison of the catalyst with previously reported catalysts

To show the activity and accessibility of Ni-dithizone@boehmite in comparison with previously reported catalysts, the results for the oxidation of methyl phenyl sulfide in the presence of Ni-dithizone@boehmite have been compared with previous catalysts and the results are summarized in Table 5. As shown in Table 5, Ni-dithizone@boehmite is more effective catalyst in selected reaction, which product was obtained in higher yields at shorter reaction time.

Conclusion

Ni-dithizone@boehmite was synthesized by a simple procedure as an efficient and reusable heterogeneous catalyst and characterized by SEM, XRD, TGA, AAS and ICP techniques. This catalyst was successfully applied for the synthesis of polyhydroquinoline derivatives and selective oxidation of sulfides to sulfoxides. Also Ni-dithizone@boehmite can be recovered and recycled over than eight times without any significant loss of its catalytic activity.

Acknowledgements Authors thank Ilam University and Iran National Science Foundation (INSF) for financial support of this research project.

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