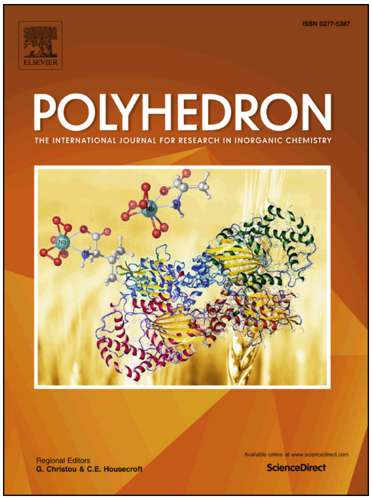

Chemo-selective oxidation of sulfide to sulfoxides with H_2O_2 catalyzed by oxo-vanadium/Schiff-base complex immobilized on modified magnetic Fe_3O_4 nanoparticles as a heterogeneous and recyclable nanocatalyst

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PII: S0277-5387(18)30586-2
DOI: https://doi.org/10.1016/j.poly.2018.09.034
Reference: POLY 13433

To appear in: *Polyhedron*

Received Date: 7 June 2018
Accepted Date: 15 September 2018

Please cite this article as: H. Veisi, A. Rashtiani, A. Rostami, M. Shirinbayan, S. Hemmati, Chemo-selective oxidation of sulfide to sulfoxides with H_2O_2 catalyzed by oxo-vanadium/Schiff-base complex immobilized on modified magnetic Fe_3O_4 nanoparticles as a heterogeneous and recyclable nanocatalyst, *Polyhedron* (2018), doi: https://doi.org/10.1016/j.poly.2018.09.034

Chemo-selective oxidation of sulfide to sulfoxides with H_2O_2 catalyzed by oxo-vanadium/Schiff-base complex immobilized on modified magnetic Fe_3O_4 nanoparticles as a heterogeneous and recyclable nanocatalyst

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Abstract. In this study, a schiff-base oxo-vanadium complex supported on magnetic Fe_3O_4 nanoparticles [VO(BINE)@Fe_3O_4] is prepared as a novel magnetically interphase nanocatalyst and its structural features are evaluated using different methods of TEM, SEM, EDX, ICP, VSM, TGA and FT-IR. Catalytic investigations demonstrate that this catalyst can catalyze chemoselective oxidation of sulfides to sulfoxides in high yields and short times at room temperature using hydrogen peroxide, as a green oxidant. The catalyst can be recovered up to 8 cycles without noticeable leaching and loss of catalytic activity.

Keywords: Sulfides, Sulfoxides, Hydrogen peroxide, Oxo-vanadium complex, Magnetically catalyst

Introduction

Though selective oxidation of sulfides and converting them to sulfoxides or sulfones is so invaluable in organic chemistry, it has remained an endeavor [1,2]. Consequently, scientists have attempted to propose and confirm an innovative method to oxidize sulfides. The first sulfoxide procurement approach refers to Maercker's work, in 1865. Since then, many procedures have been developed to conduct transformation of sulfides into sulfoxides [3]. For this purpose, several oxidants have been widely applied including concentrated HNO_3, high-valence metal salts [4], sodium metaperiodate, m-chloroperoxybenzoic acid [5], halogens and nitrogen pentoxide [6-10]. Unfortunaly, many of the developed procedures require hazardous and toxic reagents [11], are complicated methods [12] or involve overoxidation of sulfoxides, which results in unexpected sulfones or undesired by-products [13,14]. That is why many researchers have focused on developing innovative and effective catalytic systems that use an alternative oxidant, are able to surpass the outlined restrictions and satisfy eco-sustainability and green chemistry requirements, particularly atom economy. An appropriate oxidant candidate is aqueous 30% H_2O_2, which is known as an ecological oxidant, since it demonstrates several extraordinary advantages such as being low cost and eco-friendly, possessing an efficient-oxygen content and generatig water as an oxidation side product [15].

If the devised catalytic system employs a homogeneous catalyst, then it will be necessary to remove the expensive catalyst from the reaction vessel and use a chromatographic technique to retrieve the catalyst [16]. Therefore, manufactured catalytic arrangements should be considered to contain supported organic and metal based catalyst materials to activate hydrogen peroxide [17]. Such catalyst can be retrieved from the reaction vessel and reused, conveniently. Though this research area has advanced over years, most devised methods have failed in controlling the reaction process to gain selective and excellent yields of sulfoxide or sulfone products. A class of catalysts that has attracted much interest corresponds to vanadium (V)

Schiff base complexes due to their noticeable functional compatibilities and provision of high selectivity in oxidation reactions of sulfides [18].

To enhance reusability of the utilized catalyst, magnetic property can be included. Magnetic organic-inorganic nanocomposites have become popular among academic and industrial scholars as magnetic catalysts. Using such catalytic magnetic nanoparticles (NPs) can facilitate catalyst isolation and recycling, which is a common problem in many homogenous and heterogeneous catalytic processes [19-21]. Furthermore, magnetic catalysts can be recovered after several subsequent catalytic runs by application of an external magnetic field while conserving their catalytic efficiencies [22].

There are several reports on the immobilization of Schiff base oxo-vanadium complex on solid supports and use of the resultant materials in the liquid phase selective oxidation in the presence of peroxides as oxidants [23]. In continue of our attempts towards developing efficient and ecofriendly heterogeneous catalysts [23], herein, we synthesize a new oxo-vanadium Schiff base complex supported on magnetic nanoparticles, i.e. VO(BINE)@Fe_3O_4, characterize it and explore its catalytic features in chemoselective oxidation of sulfides to sulfoxides using green H_2O_2 oxidant (Figure 1).

2. Experimental

2.1. Preparation of Fe_3O_4/Pr-NH_2

Fe_3O_4/Pr-NH_2 was synthesized according to the synthesis method described in our previous report [23d].

2.2. Preparation of VO(BINE)@Fe_3O_4

500 mg of the prepared Fe_3O_4/Pr-NH_2 NPs were dispersed in 70 mL ethanol through 20 mon sonication. Then, 1 mmol 1,2-bis(2-formyl naphthoxy)ethane was added to the obtained solution and the solution was stirred for 24 h under N_2 atmosphere, at 80 ºC. In the next step, the heated reaction mixture was permitted to cool down to room temperature. The resultant NPs, i.e. Fe_3O_4/Schiff base (BINE) particles, were washed several times with ethanol, removed from the solution via magnetic decantation and dried up at room temperature. After that, the resulted 500 mg BINE NPs were dispersed in 50 mL EtOH-H_2O (1:1) solution for 20 min, in an ultrasonic bath. Next, a 20 mL aqueous solution of vanadyl acetylacetonate (0.265 g; 0.001 mol) was mixed with the BINE mixture and refluxed for 24 h. In this way, VO(BINE)@Fe_3O_4 particles formed. The produced NPs were removed by magnetic decantation and washed using ethanol, water and acetone, subsequently, to eliminate any unattached substrate. According to atomic absorption spectroscopy measurements, the obtained catalyst had 0.29±0.001 mmol g^{-1} vanadyl content.

2.3. Typical experimental procedure for sulfoxide preparation

A 5-mL round bottom flask was used as the reactor. At each synthesis trial, 30 mg VO(BINE)@Fe_3O_4 nanocatalyst (0.9 mol%) and 30% (w/w) H_2O_2 oxidant (2.0 mmol) were added to 1 mmol sulfide, successively, and the prepared reaction mixture was stirred for the desired time on a magnetic stirrer, at room temperature. TLC (EtOAc/n-hexane, 1/10) and GC were employed to track progress of the reaction. After reaction completion, an external magnet was applied to separate the catalyst from the reaction products (within 5 s) and the reaction mixture was washed two times with diethyl ether (3 mL) and decanted. The mixture of organic compounds was dried over anhydrous Na_2SO_4. Then, Et_2O was evaporated under reduced pressure to achieve pure products in 80% to 96% yields.

3. Results and discussion

3.1. Preparation and characterization of VO(BINE)@Fe_3O_4

VO(BINE)@Fe_3O_4 nanocatalyst was prepared in several subsequent steps. First, Fe_3O_4 was synthesized based on our previous work [23e]. Then, the iron oxide particles were coated with 3-aminopropyltriethoxysilane (APTES) to give aminopropyl-functionalized magnetic NPs. Next, the functionalized amino groups reacted with 1,2-bis(2-formyl naphthoxy)ethane to form Fe_3O_4/Schiff base (BINE). At the end, the Fe_3O_4 immobilized Schiff base (BINE@Fe_3O_4) was coordinated with $VO(acac)_2$ to generate oxo-vanadium complex supported on magnetic NPs (VO(BINE)@Fe_3O_4). Finally, the VO(BINE)@Fe_3O_4 NPs were separated by an external magnet and vacuum dried. The synthesis steps carried out to produce the catalyst are depicted in Scheme 1. Elemental analysis determined that ~0.32 mmol of Schiff base has linked to 1 g of Fe_3O_4. Moreover, these values declared that all anchored BINE ligand have efficiently and approximately coordinated with V ions giving the required catalytic active sites. The catalyst was characterized by FTIR, CHN, XRD, FESEM, TEM, EDS, ICP and VSM analysis methods.

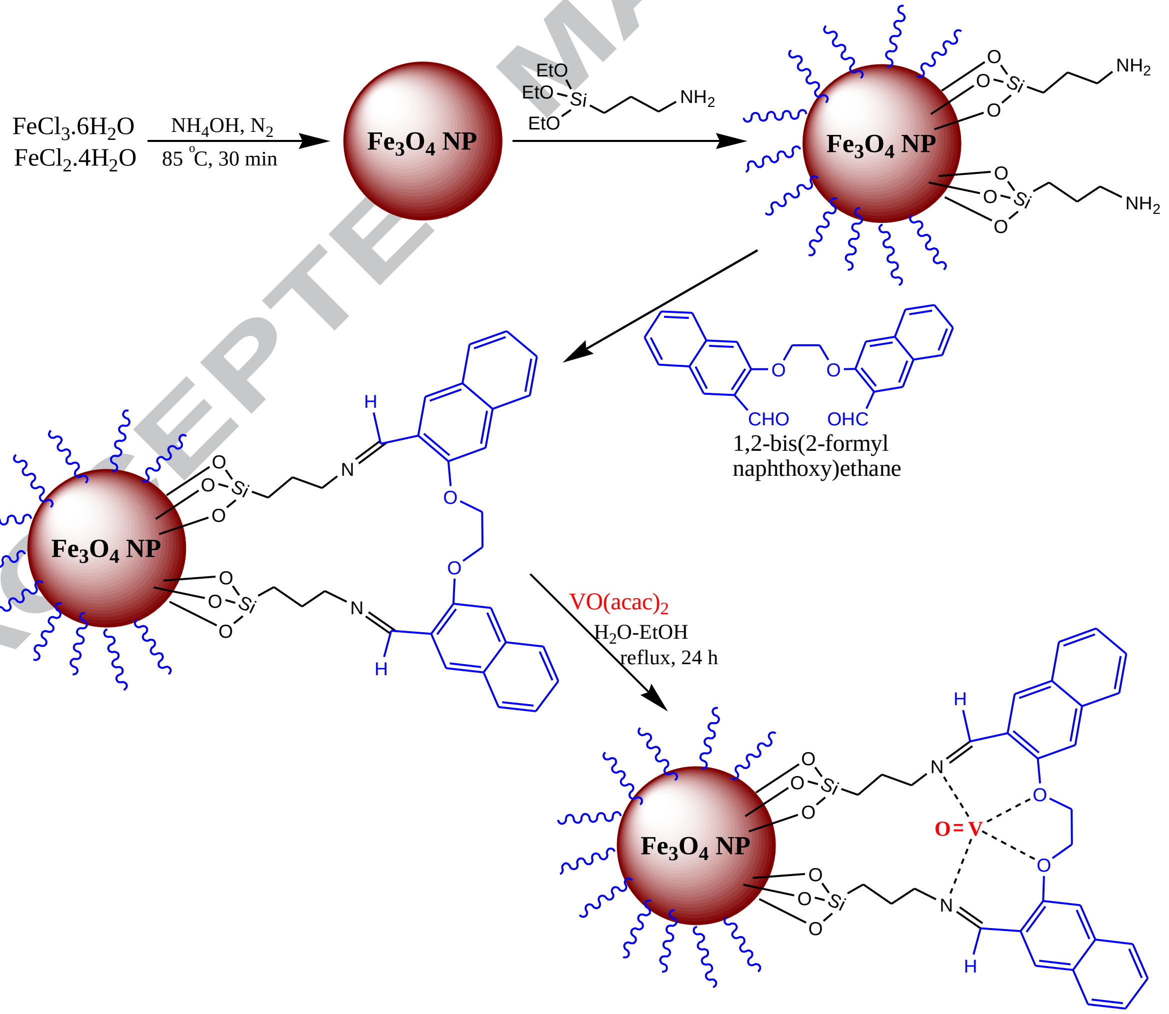


Fig. 1. Preparation of VO(BINE)@Fe_3O_4 nanocatalyst.

To confirm successful functionalization of the Fe_3O_4 NPs with BINE Schiff base groups, Fourier transform infrared (FT-IR) spectroscopy was performed. Figure 2 shows FTIR spectra of (a) magnetic Fe_3O_4 NPs, (b) amino-functionalized magnetic NPs, i.e. Fe_3O_4/Pr-NH_2, and (c) Fe_3O_4/Schiff base (BINE). FT-IR spectrum for Fe_3O_4 NPs (Figure 2a) contains a peak at 3437 cm^{-1}, which refers to symmetric and asymmetric stretching vibrational modes of O-H bonds attached to surface of the iron atoms [24]. Also, it outlines several bands with low wavenumbers ($\leq$700 cm^{-1}) corresponding to Fe-O bonds of Fe_3O_4. Fe-O vibrational bands related to bulk Fe_3O_4 should appear at 570 cm^{-1} and 375 cm^{-1}. However, as size of the particles is reduced and we have Fe_3O_4 NPs, the peaks are accompanied with a blue shift and have peaked at 634 cm^{-1} and 568 cm^{-1} [23e]. FT-IR spectra of Fe_3O_4/Pr-NH_2 and Fe_3O_4/ BINE (Figures 2b and 2c, respectively), outline almost similar peak positions for Fe-O bond vibrations. Meantime, observation of a vibrational band at 1000 cm^{-1} approves presence of APTMS on surface of the Fe_3O_4 NPs, which is associated with Fe-O-Si stretching vibrations [25, 26]. In Figures 1b and 1c, the peaks positioned at 2959 cm^{-1} and 3085 cm^{-1} are assigned to aliphatic and aromatic C-H bonds of Fe_3O_4/Pr-NH_2 and Fe_3O_4/Schiff base (BINE), respectively. The $\sim$1080 cm^{-1} peak is attributed to Si-O-Si stretching modes of Fe_3O_4/Pr-NH_2 and Fe_3O_4/BINE. These vibrational bands approve successful coating of the Fe_3O_4 NPs by silica and the Schiff base precursor. Furthermore, the 1624, 1581, 3028 and 1436 cm^{-1} peaks, which are ascribed to C=NH, C=C, aryl C-H stretches and C-N stretching of amine respectively, verify attachment of primer of Schiff base groups to surface of the Fe_3O_4/Pr-NH_2 NPs [23c]. All these peaks clarify that surface of the Fe_3O_4 NPs has been modified by BINE groups, successfully, and the NPs are ready for metal-ligand coordination.

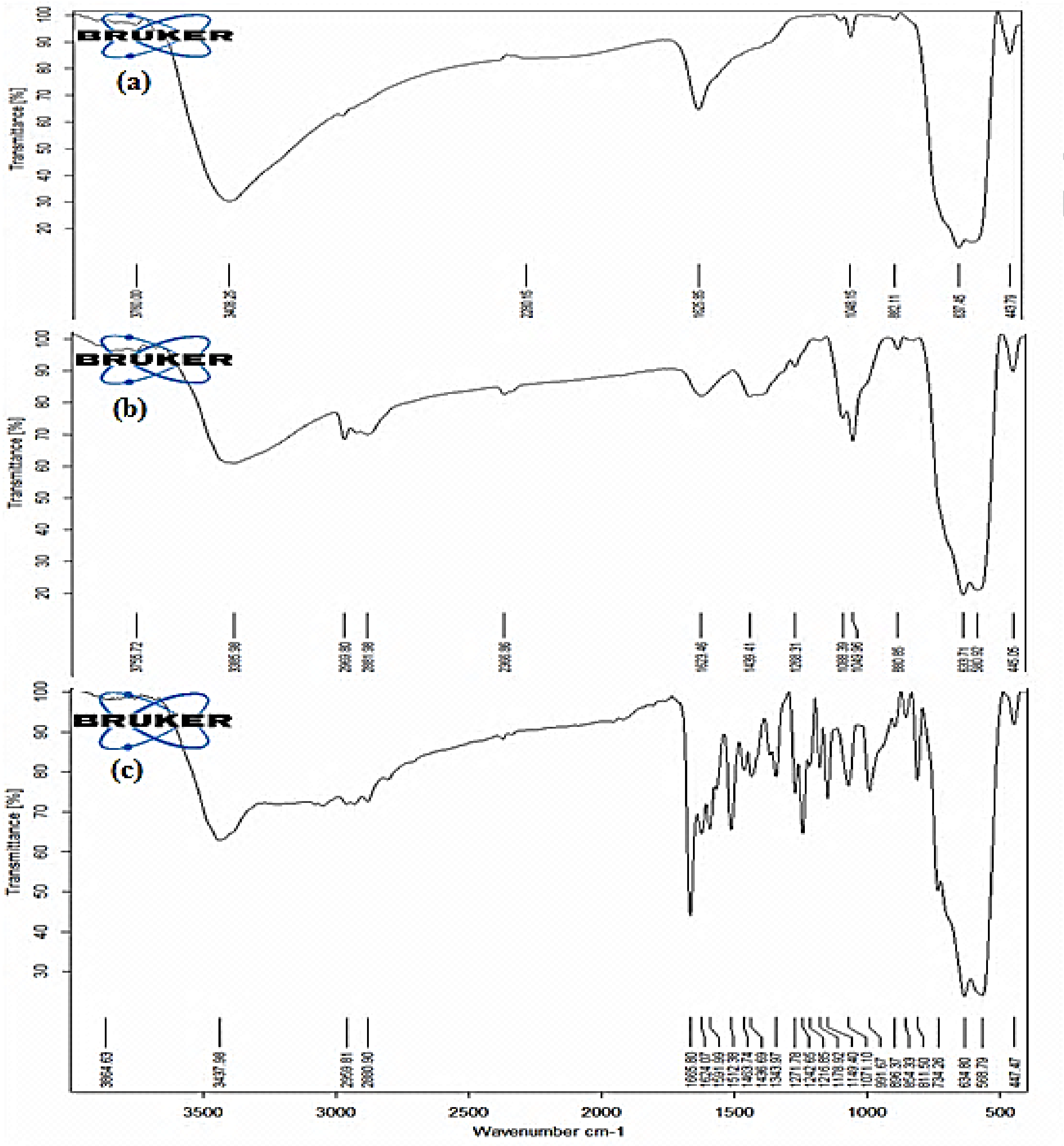


Fig. 2. FT-IR spectrum of (a) magnetic Fe_3O_4 nanoparticles, (b) amino-functionalized magnetic (Fe_3O_4/Pr-NH_2) nanoparticles, and (c) Fe_3O_4/Schiff base (BINE).

FESEM and TEM identified morphology and size of the hybrid organic-inorganic catalyst (VO(BINE)@Fe_3O_4). According to FESEM image of VO(BINE)@Fe_3O_4, its particles are uniform and nanometer-sized (Figure 3). Also, the TEM image indicates successful production of the modified Fe_3O_4 magnetic NPs with a homogenous distribution of particles (Figure 4). Magnification of the TEM image, unravels slight aggregation and a stacking texture, which is an outcome of attractive magnetic interaction between the catalyst NP structures. Mean diameter of the Fe_3O_4 core in the NPs is about 10 to 15 nm.

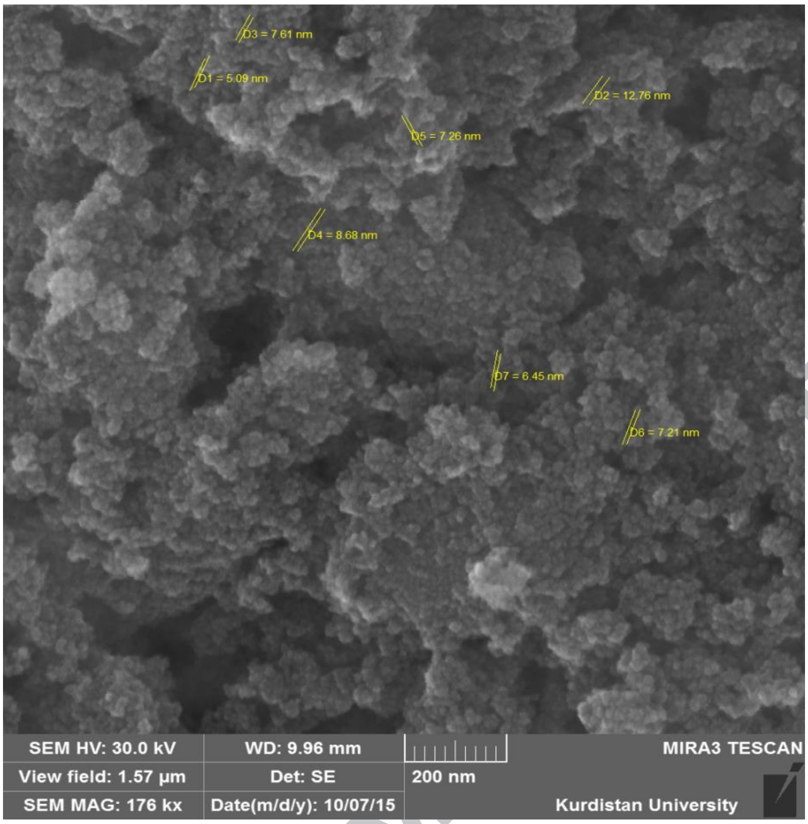


Fig. 3. FESEM image of VO(BINE)@Fe_3O_4 nanocatalyst.

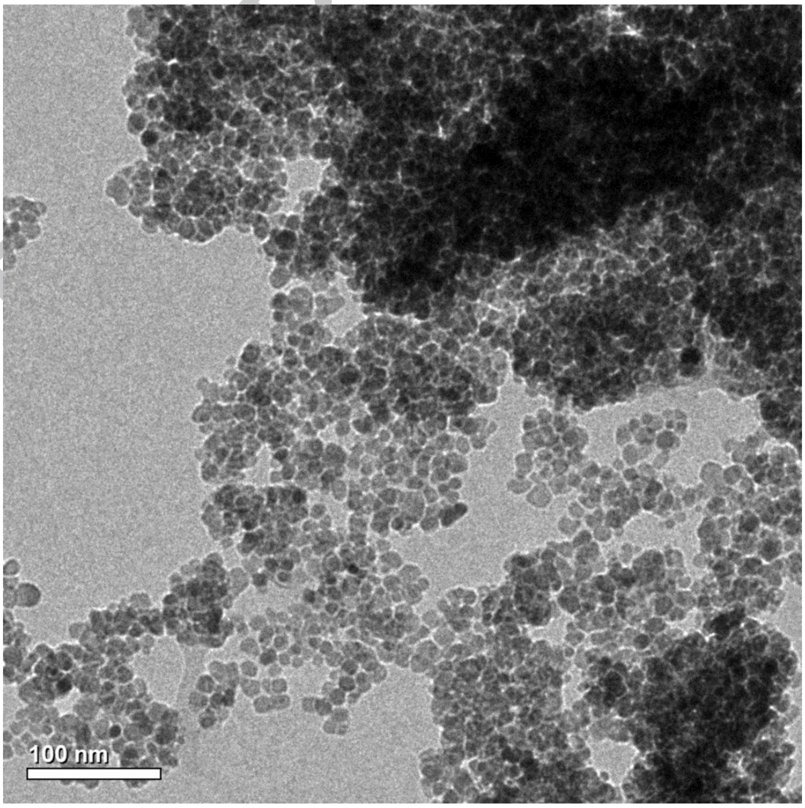


Fig. 4. a) TEM image of VO(BINE)@Fe_3O_4 nanocatalyst.

Successful immobilization of oxo-vanadium Schiff base complex on Fe_3O_4 surface was also approved using an EDX detector coupled with FESEM. In this way, Fe, V, C, N, O and Si were detected (Figure 5).

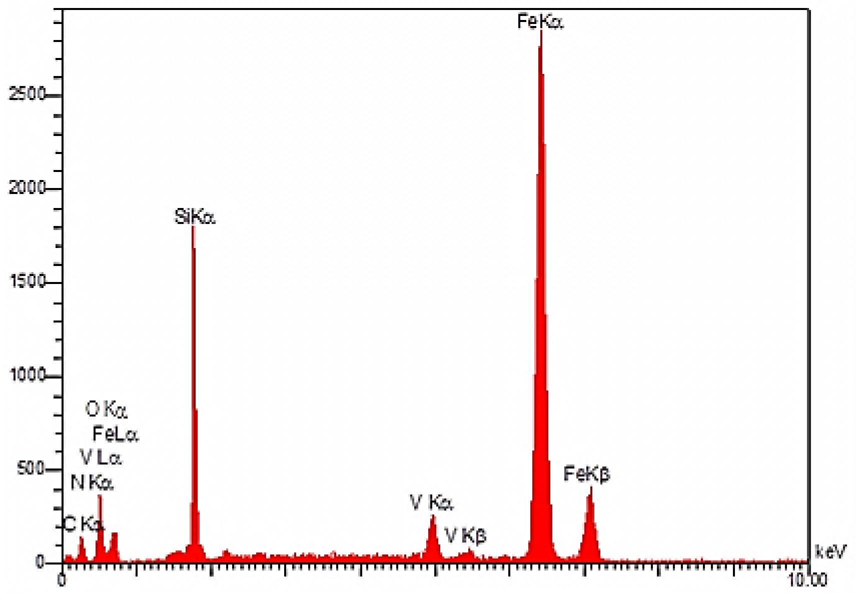


Fig. 5. EDX data for VO(BINE)@Fe_3O_4 nanocatalyst.

Figure 6a displays XRD pattern of VO(BINE)@Fe_3O_4 nanocatalyst. In this pattern, several diffraction peaks can be distinguished at 2θ of 30.2°, 35.8°, 43.4°, 53.6°, 57.2° and 62.8°. These peaks can be ascribed to (220), (311), (400), (422), (511) and (440) planes of cubic Fe_3O_4 structure (JCPDS 65-3107). Consequently, it can be inferred that presence of oxo-vanadium complex has not altered crystalline phase of Fe_3O_4. VSM was applied to measure magnetization of VO(BINE)@Fe_3O_4 NPs, at room temperature. According to the measured VSM curve, no hysteresis can be observed and remanence and coercivity are negligible. These evidences indicate super-paramagnetism of these NPs (Figure 6b). Saturation magnetization of VO(BINE)@Fe_3O_4 (29.2 emu g^{-1}) is less significant than saturation magnetization of Fe_3O_4 (62.3 emu g^{-1}) [23e] since the coated Schiff base oxo-vanadium complex layer is non-magnetic. Nevertheless, the obtained catalyst is sufficiently magnetic sensitive to enable its efficient and convenient separation from reaction mediums

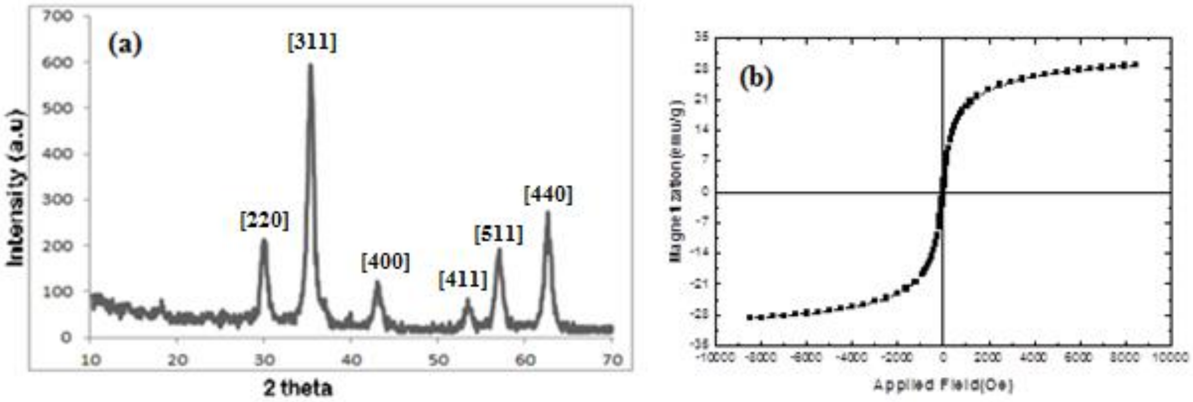


Fig. 6. a) XRD pattern and; b) VSM spectra of VO(BINE)@Fe_3O_4.

TGA analysis helped to evaluate stability of the synthesized VO(BINE)@Fe_3O_4 catalyst and percentage of organic functional groups bound to surface of the magnetic NPs. TGA curve of the catalyst (Figure 7) demonstrates 3.2% initial weight loss at temperatures lower than 200 °C. This weight loss is related to evaporation of physisorbed solvent molecules and loss of surficial hydroxyl groups of the support. Degradation of the organic groups is observed in the range of 250 to 520 °C, based on the identified second and third weight losses that sum up to 19%. Therefore, no catalyst weight loss, except solvent loss, is observed by elevating the temperature up to 200 ºC and only at temperatures above 250 °C the catalyst degrades thermally, which implies its high thermal stability. Such high thermal stability is advantageous since many organic compounds should be synthesized at high temperatures.

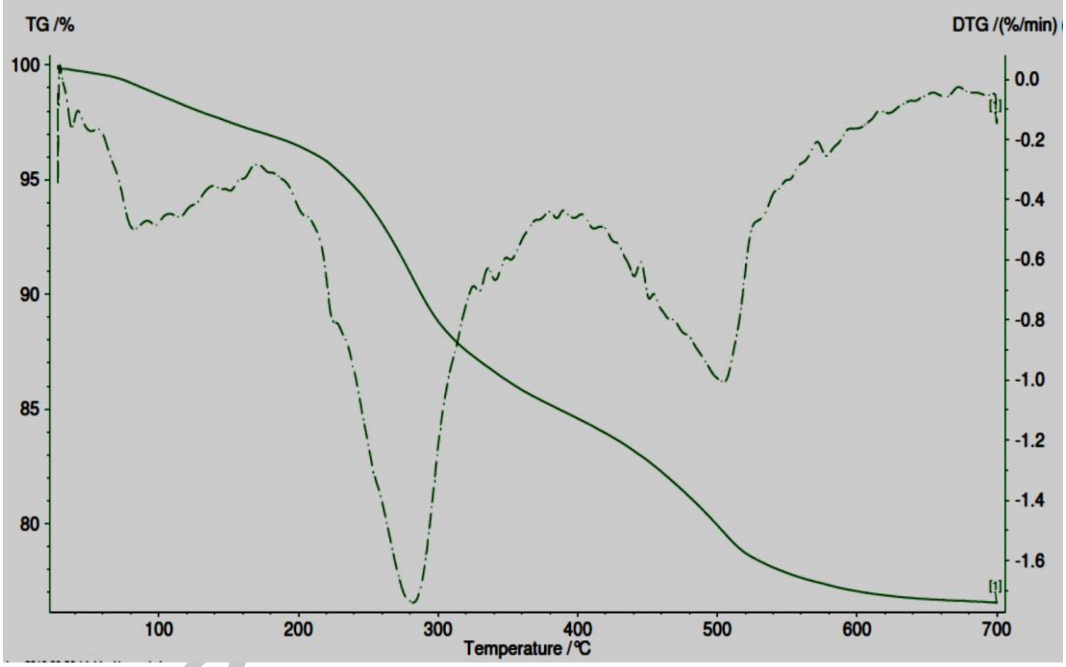


Fig. 7. TGA diagram for VO(BINE)@Fe_3O_4.

Nitrogen adsorption desorption isotherm was used for deter-mining the surface properties (Fig. 8). VO(BINE)@Fe_3O_4 shows type IV isotherm which exhibits the mesoporous structure and presence of nano-voids in this system. BET analysis of VO(BINE)@Fe_3O_4 demonstrates the specific surface area is estimated at about 55.2 m^2g^{-1}. Moreover, BJH pore size distribution of the catalyst shows a narrow mesopore size distribution centered at 25.8 nm. Its pore volume was estimated as 0.404 cm^3g^{-1} by BJH analysis. VO(BINE)@Fe_3O_4 represents the good BET surface area with the great pore volume, which makes it as a suitable option for catalytic system.

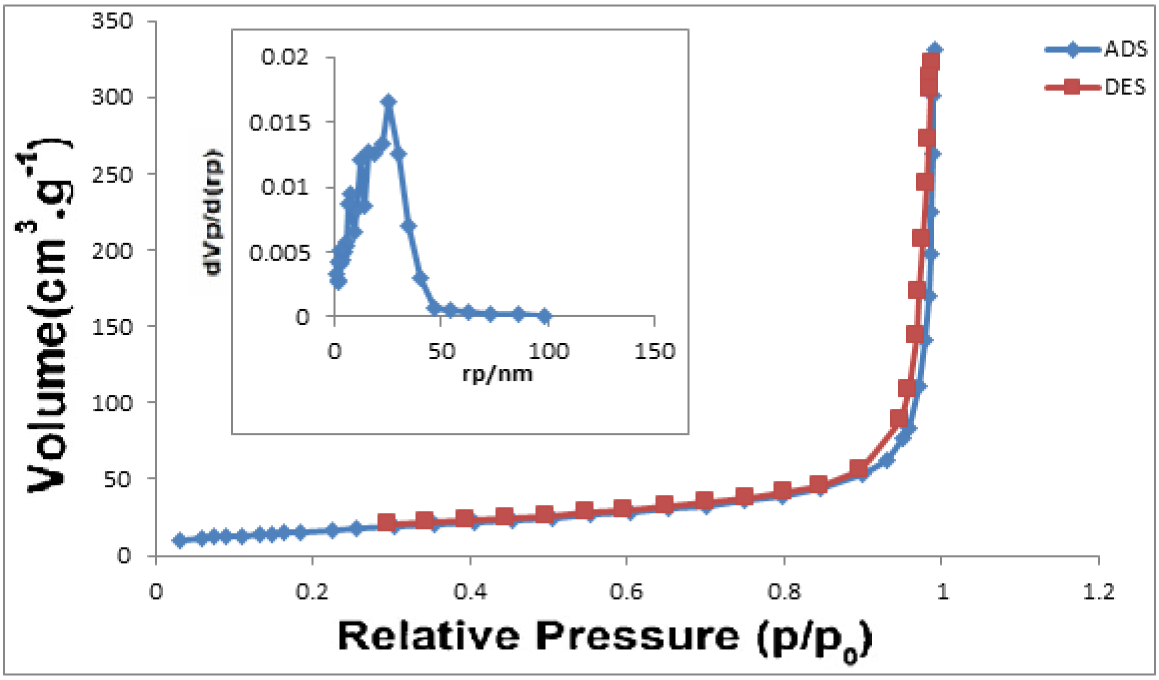


Fig. 8. BET Ads Des isotherm and pore size distribution of VO(BINE)@Fe_3O_4.

3.2. Catalytic application of VO(BINE)@Fe_3O_4 *in oxidation of sulfides to sulfoxides*

Solvent free catalytic activation of 30% H_2O_2 by VO(BINE)@Fe_3O_4, as a reusable organic-inorganic hybrid catalyst, and performance of the catalyst in chemo-selective oxidation of sulfides to sulfoxides was investigated at room temperature (Figure 9).

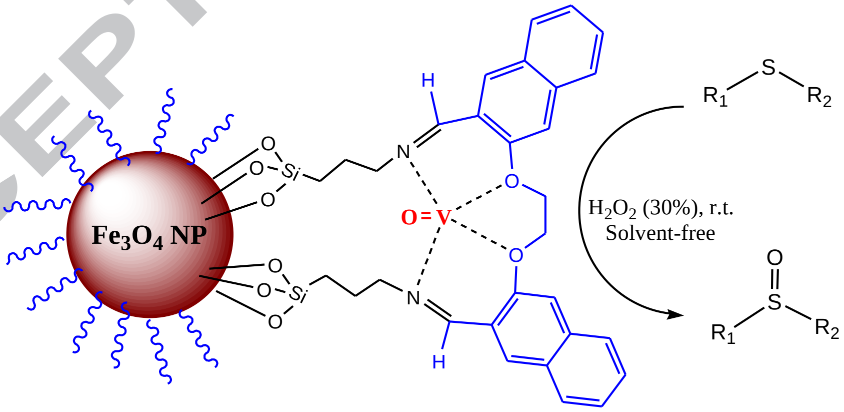


Fig. 9. VO(BINE)@Fe_3O_4 catalyzed the oxidation of sulfides to sulfoxides using H_2O_2.

In this respect, first the reaction conditions were optimized by concentrating on oxidation of methyl phenyl sulfide, as a model sulfide, using 30% H_2O_2 under different reaction conditions. The obtained reaction times and product yields are listed in Table 1. As Table 1 implies, the oxidation reaction cannot complete without VO(BINE)@Fe_3O_4 catalyst even after 24 h (entries 1 and 2). On the other hand, complete oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide can be achieved using 2 eq. H_2O_2 and 30 mg VO(BINE)@Fe_3O_4 (0.9 mol%) at room temperature and under solvent free condition (Table 1, entry 5).

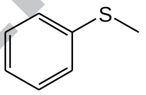
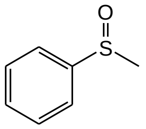
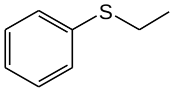
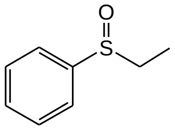
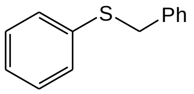
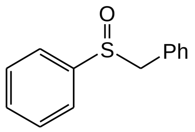
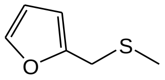
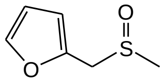
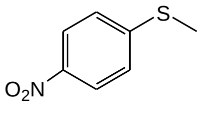
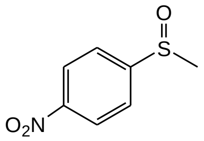
Table 1. Optimization of the amounts of H_2O_2 and VO(BINE)@Fe_3O_4 for the selective oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide.

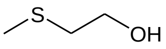
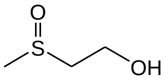
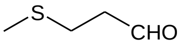
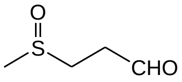
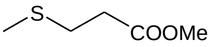
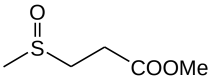
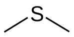
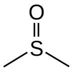
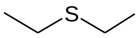
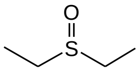
Entry	Catalyst (mol%)	H_2O_2 (mmol)	Solvent	Time (min)	Yield (%)[a]
1	Catalyst-free	2.0	Solvent-free	24 h	35
2	Fe_3O_4 (20)	2.0	Solvent-free	24 h	45
3	VO(BINE)@Fe_3O_4 (0.3)	2.0	Solvent-free	2 h	96
4	VO(BINE)@Fe_3O_4 (0.6)	2.0	Solvent-free	45	96
5	VO(BINE)@Fe_3O_4 (0.9)	2.0	Solvent-free	5	96
6	VO(BINE)@Fe_3O_4 (1.2)	2.0	Solvent-free	5	96
7	VO(BINE)@Fe_3O_4 (0.9)	1.0	Solvent-free	30	75
8	VO(BINE)@Fe_3O_4 (0.9)	3.0	Solvent-free	5	80
9	VO(BINE)@Fe_3O_4 (0.9)	2.0	EtOH	30	96
10	VO(BINE)@Fe_3O_4 (0.9)	2.0	CH_3CN	30	96
11	VO(BINE)@Fe_3O_4 (0.9)	2.0	CH_2Cl_2	2 h	90

[a]Determined by GC and no sulfone was observed..

Table 2 highlights generality of the proposed synthesis approach as an easy but efficient method to oxidize aliphatic and aromatic sulfides. So that, this catalyzed reaction is an appropriate method that can be utilized for general synthesis of sulfoxides. As Table 2 demonstrates, the intended products can be acquired in excellent yields, at minimal reaction times and with good turnover numbers (TON) and turnover frequencies (TOF). It should be noted that the sulfides oxidize chemoselectively regardless of the nature of sulfide functional groups, such as OH, CHO and COOMe (Table 2, entries 6-8).

Table 2. VO(BINE)@Fe_3O_4 catalyzed selective oxidation of sulfides to sulfoxides under solvent-free condition.[a]

Entry	Sulfide	Sulfoxide	Time (min)	Yield (%)[b]	TOF (h^{-1})[c]	TON (h^{-1})[d]
1			5	96	1280	106.7
2			10	95	633.3	105.5
3			6	96	1066.7	106.7
4			10	88	586.7	97.8
5			10	92	613.3	102.2

6			5	90	1200	100
7			10	85	566.7	94.4
8			15	78	346.7	86.7
8			15	85	377.8	94.4
10			15	80	355.5	88.9

[a] Reaction conditions: sulfide (1 mmol), 30% H_2O_2 (2.0 mmol), VO(BINE)@Fe_3O_4 (30 mg, 0.9 mol%), rt.

[b] Determined by GC and all products are known and were characterized by IR and NMR spectra as compared with those reported in the literature [27-30].

[c] TOF, turnover frequencies (TOF) = (Yield/Time)/Amount of catalyst (mol).

[d] TON, turnover number (TON) = Yield/Amount of catalyst (mol).

Figure 10 illustrates a proposed mechanism for oxidative conversion of sulfides to sulfoxides by the title catalyst. This conversion is the first stage of sulfide oxidation process. At the first step, hydrogen peroxide binds to the vanadium ion and peroxo-vanadyl species form. Then, the generated peroxo-vanadyl species undergoes a nucleophilic attack by sulfur atom of the sulfide. As it is known, the metal atom plays a role in formation of peroxo-metal species and activates H_2O_2 molecules [31-33].

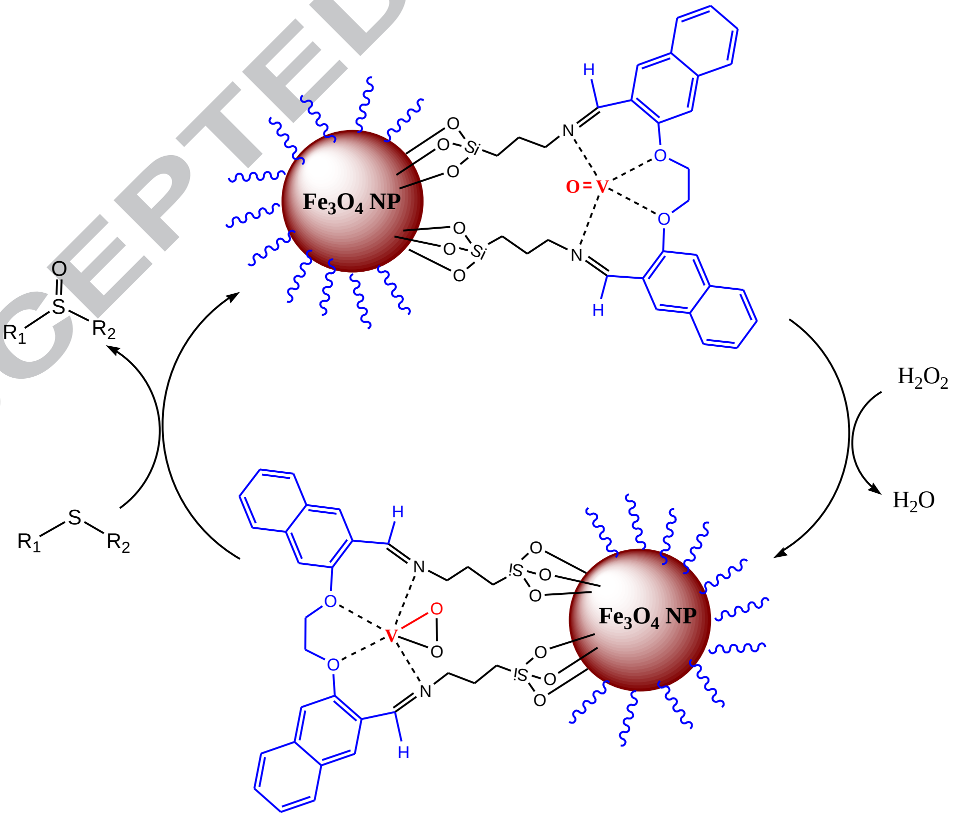


Fig. 10. Proposed mechanism for the sulfide oxidation with H_2O_2 in the presence of VO(BINE)@Fe_3O_4.

To test reusability of the catalyst, VO(BINE)@Fe_3O_4 was collected from the reaction mixture by applying a magnetic device, rinsed in acetone and reused in further catalytic runs. As it was expected, VO(BINE)@Fe_3O_4 can be employed for 8 or more subsequent catalytic cycles of methyl phenyl sulfide oxidation to its associated sulfoxide (Fig. 11). Also, a hot filtration test was conducted to explore leaching of V(IV) ions from surface of the catalyst. A negligible quantity of reaction progress was observed, even after 2 min reaction time. ICP analysis determined 1.35% V(IV) leaching into the reaction solution, after 6 catalytic runs. This insignificant leaching value verifies stability of the catalyst, under the reaction conditions.

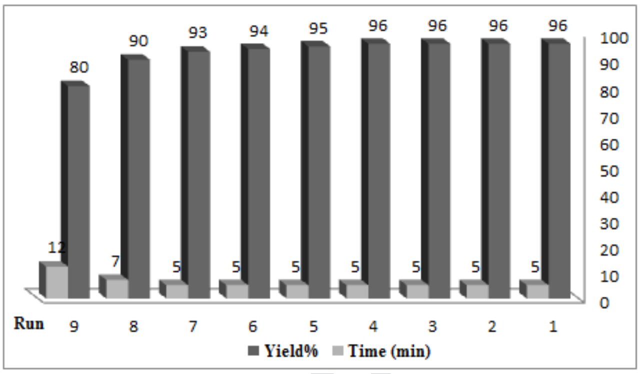


Fig. 11. Reusability of nanocatalyst.

Finally, activity of VO(BINE)@Fe_3O_4 in catalytic oxidation of methyl phenyl sulfide is compared with performance of other reported catalysts in Table 3. Accordingly, the previously reported catalytic procedures have exhibited one of the following disadvantages, at least: using transition metal, longer reaction times and requiring volatile and/or toxic organic solvents. Based on Table 3, it can be stated that VO(BINE)@Fe_3O_4 is a proper catalyst for chemoselective oxidation of sulfides to sulfoxides.

Table 3. Comparison present methodology with literature in the oxidation of methyl phenyl sulfide to methyl phenyl sulfuxide.

Entry	Reaction conditions	Time (min)	Yield %	TOF (h^{-1})^c	Ref.
1	VO(BINE)@Fe_3O_4, solvent-free, r.t.	5	96	1280	This work
2	MNPs-based *N*-propylsulfamic acid, solvent-free, r.t.	80	100	78.9	[23e]
3	MCM-Mo, CH_3CN,r.t., 40 ºC	60	99	839	[35]
4	Silica-based tungstate interphase, CH_3OH/CH_2Cl_2, r.t.	90	82	27.3	[36]
5	Peroxotungstate supported on silica, CH_3OH/CH_2Cl_2, 8 ºC	150	92	24.5	[37]
6	VO(acac)$_2$-exchanged polymer resin catalyst, H_2O, r.t.	10	98	98	[38]
7	Fe_3O_4@SiO_2/Mo, CH_3CN, 50 ºC	90	92	20.4	[39]
8	VO(IV)–MCM-41, EtOH, r.t.	480	95	-^{d}	[23f]
9	VO(IV) Schiff base complexes, EtOH, r.t.	10	100^a	-^{d}	[40]
10	oxovanadium(IV) Schiff base complex, solvent-free,45 °C	50	-^{b}	-^{d}	[18c]

^{a}Conversion (%).

^{b}The major product is sulfone.

^{c}TOF, turnover frequencies (TOF) = (Yield/Time)/Amount of catalyst (mol).

^{d}The catalyst's mol% is not reported in the paper.

4. Conclusion

This paper introduces an oxo-vanadium Schiff base complex supported on Fe_3O_4 nanoparticles [VO(BINE)@Fe_3O_4] as a novel magnetically interphase nanocatalyst and evaluates its properties by different techniques. It has also been demonstrated that VO(BINE)@Fe_3O_4 can be employed as a green, reusable and efficient heterogeneous nanocatalyst to oxidize a wide range of sulfides to sulfoxides, selectively, using H_2O_2 at room temperature and solvent free conditions. This protocol has several advantages including mild reaction conditions, using an eco-friendly, commercially available, cheap and chemically stable oxidant, simplicity of operation, short reaction times, practicability, good to high yields, convenient catalyst recyclability through applying an external magnetic field and excellent chemoselectivity.

Acknowledgement

We are thankful to Payame Noor University (PNU) and Kurdistan University of Iran for financial supports.

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Graphical Abstract

Chemo-selective oxidation of sulfide to sulfoxides with H_2O_2 catalyzed by oxo-vanadium/Schiff-base complex immobilized on modified magnetic Fe_3O_4 nanoparticles as a heterogeneous and recyclable nanocatalyst

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