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# Oxo-vanadium complex immobilized on chitosan coated-magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>): A heterogeneous and recyclable nanocatalyst for the chemoselective oxidation of sulfides to sulfoxides with $H_2O_2$

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Abstract. This article presents the synthesis of Schiff base oxo-vanadium complex immobilized on chitosan coated-magnetic  $Fe_3O_4$  nanoparticles [VO(CS)@Fe\_3O\_4] as a new magnetic interphase nanocatalyst. This type of functionalizing the surface of magnetic particles is a graceful method for bridging the gap between two types of heterogeneous and homogeneous catalysis. The characterization of as-synthesized nanocatalyst was performed through fourier transformed infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (TGA), vibrating sample magnetometer (VSM), and X-ray photoelectron spectroscopy (XPS). The chemoselective oxidation of sulfides to sulfoxides using green oxidant of hydrogen peroxide at ambient temperature in high-yield was catalyzed with VO(CS)@Fe<sub>3</sub>O<sub>4</sub>. The synthesized catalyst can be used up to 8 times with no considerable leaching and change in its activity. Both improvement of catalytic performance and easy separation for the reaction procedure were obtained because of the presence of oxo-vanadium and the magnetic core.

#### Keywords: Vanadium, Magnetic, Chitosan, Sulfides, Sulfoxides, Hydrogen peroxide

#### **1. Introduction**

Organic chemists have interested in sulfoxides for a longtime because these compounds as a functional group can transfer into different type of organo-sulfur compounds through different reactions. This property is valuable for synthesizing drugs and sulfur-substituted natural products.<sup>1,2</sup> Even though there are variety types of oxidants with ability to convert sulfides to the corresponding sulfoxides, the cautious control of the reaction conditions such as the amount of oxidants is needed for most of reagents for minimizing the production of sulfones as side products.<sup>3</sup>

Nowadays, there are many types of traditional oxidants for oxidation of the sulfide,<sup>4f,i,5</sup> but aqueous hydrogen peroxide is mostly interested because it is clean, , cheap, readily accessible and environmentally friendly as its side products is only water.<sup>4d,e,6</sup> A suitable catalyst is usually required for activating hydrogen peroxide as it is a relatively weak oxidant and induces oxidations slowly.<sup>4c,h,7</sup> Therefore, an enormous number of effective catalysts based on transition metal have been offered for oxidizing sulfides using hydrogen peroxide.<sup>4c,d,f,h,i,5,6,7,8</sup> However, only a few of them can prevent production of sulfone at the sulfoxide step. Moreover, most of protocols have one or more restrictions such as the difficult recovery of the catalyst, expensive, requiring a promoter or a co-catalyst, <sup>4c,d,i</sup> high temperature, time-consuming reaction, using chloro-hydrocarbon solvents, using large amount of hydrogen peroxide and low TON. Consequently, the efforts continue to find a suitable alternative catalysts and protocols that obey green chemistry.

A recently kind of functional substance is surface functionalized magnetic iron oxide nanoparticles (NPs), which have been infinitely used in the fields of biotechnology and catalysis. Among different types of available magnetic nanoparticles (MNPs) utilized as the core magnetic support, Fe<sub>3</sub>O<sub>4</sub> nanoparticles are mostly interested because of their specific properties such as high surface areas, low toxicity and superparamagnetic behavior.<sup>9-14</sup> Moreover, all ferrites are metal oxides, which present a considerable amount of hydroxyl groups on the external surface of their particles.<sup>15</sup> Therefore, well-defined shells of different substances are formed for surrounding the ferrite core or, in those cases that the target is the functional materials, suitable functional groups are formed to support various types of actuators, ligands, and/or catalysts via covalent bonding.<sup>16</sup> Crucially, the magnetic-supported catalysts show excellent catalytic property and good chemical stability, and their swell is also resistance in organic solvents.<sup>17-19</sup>

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.<sup>20</sup> In the context of developing the effective and eco-friendly heterogeneous catalysts,<sup>21</sup> we conducted a study on the synthesis of oxo-vanadium Schiff base complex supported on chitosan coated-MNPs (VO(CS)@Fe<sub>3</sub>O<sub>4</sub>) as a new catalyst for oxidizing the sulfides to sulfoxides chemo-selectively using hydrogen peroxide as a green oxidant (Scheme 1).

#### 2. Experimental Section

#### 2.2. Preparation of the magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (MNPs):

MNPs were synthesized through co-precipitation of Fe (III) and Fe (II) ions with a molar ratio of 2:1 in the presence of ammonium hydroxide .In general, 100 mL solution containing FeCl<sub>3</sub>.6H<sub>2</sub>O (5.838 g, 0.0216 mol) and FeCl<sub>2</sub>.4H<sub>2</sub>O (2.147 g, 0.0108 mol) was prepared and heated at 85 °C under N<sub>2</sub> atmosphere and strongly stirred (500 rpm). Then, 10 mL of 25% NH<sub>4</sub>OH was slowly injected into this mixture in one step. The black MNPs was instantly formed after addition the ammonia solution to the Fe<sup>2+/</sup>Fe<sup>3+</sup> salt solution. The stirring the mixture was continunied for 25 min and the mixture was cooled to ambient temperature. Then, dark MNPs were magnetically separated from the solution and washed three times with DI water.

#### 2.3. Preparation of the CS@Fe<sub>3</sub>O<sub>4</sub> (Chitosan@Fe<sub>3</sub>O<sub>4</sub>):

First, 100 mL of 2% (v/v) acetic acid solution containing 1.0 g of chitosan (98% NH<sub>2</sub>) was prepared and stirred sonically for 1 h. Then, magnetic chitosan nanoparticles (CS@Fe<sub>3</sub>O<sub>4</sub>) were synthesized as following. 400 mg of wet precipitated (frsh) magnetite was dispersed in 80 mL of prepared chitosan solution (weight ratio of chitosan to Fe<sub>3</sub>O<sub>4</sub>= 2:1). The obtained mixture was brought to 150 mL, stirred for 1 h, at ambient temperature and neutralized with 10% (w/v) solution of NaHCO<sub>3</sub>. After subsiding the foam, the mixture was centrifuged to collect the precipitates and the obtained precipitates were washed twice with deionized water and dried at room temperature by spreading on a glass plate.

#### 2.4. Preparation of the VO(CS)@Fe<sub>3</sub>O<sub>4</sub>:

500 mg of synthesized  $CS@Fe_3O_4$  was sonically dispersed in EtOH-H<sub>2</sub>O (1:1, 100 mL) for 20 min. Then, 0.265 g of vanadyl acetylacetonate (0.001 mol) was dissolved in 20 mL water and added to the obtained mixture. The resulted mixture was refluxed for 24 hours. In the next step, VO(CS)@Fe\_3O\_4 was magnetically separated and washed using ethanol, distilled

water and acetone, respectively for removing probable unattached substrates. Moreover, the vanadyl content of the catalyst was obtained  $0.34\pm0.001$  mmol.g<sup>-1</sup> using atomic absorption spectroscopy.

#### **2.5.** Typical experimental procedure for the preparation of sulfoxides:

1.5 mmol 30% (w/w)  $H_2O_2$  and 30 mg VO(CS)@Fe<sub>3</sub>O<sub>4</sub> nanocatalyst (1 mol%) were sequentially added, to sulfide (1 mmol) in a 5 ml round bottom flask and the resulted mixture was magnetically stirred at ambient temperature for desired time. The reaction progress was checked using TLC (EtOAc/n-hexane, 1/10). After completion of the reaction, the catalyst was magnetically isolated from the product through only 5 s and was washed twice using % mL Et<sub>2</sub>O, decanted and dried using anhydrous Na<sub>2</sub>SO<sub>4</sub> and diethyl ether evaporation under decreased pressure. The pure products were obtained in 80-96% yields.

#### 3. Results and discussion

#### 3.1. Preparation and Characterization of VO(CS)@Fe<sub>3</sub>O<sub>4</sub> nanocatalyst

The synthesis of Fe<sub>3</sub>O<sub>4</sub> particles was performed according to our previous report [21a], and the prepared MNPs were subsequently coated with chitosan (CS) for preparing chitosan coated-magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (CS@Fe<sub>3</sub>O<sub>4</sub>). Then, the coordination of CS@Fe<sub>3</sub>O<sub>4</sub> using VO(acac)<sub>2</sub> causes the corresponding oxo-vanadium complex supported on chitosan coated-magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (VO(CS)@Fe<sub>3</sub>O<sub>4</sub>). Lastly, an external magnet was used to collect the mixture and the separated mixture was dried in vacuum. The synthesis of the nanocatalyst is demonstrated in Scheme 1. The vanadium (IV) content of the nanocomposite was  $0.34\pm0.001$  mmol.g<sup>-1</sup> as predicted via atomic absorption spectroscopy. The catalyst was characterized through FTIR, XRD, XPS, FESEM, EDX, TEM, TGA, ICP and VSM.



Scheme 1: Synthesis of VO(CS)@Fe<sub>3</sub>O<sub>4</sub> and its application for oxidizing sulfides to sulfoxides chemo-selectively using H<sub>2</sub>O<sub>2</sub>

In order to prove the existence of the chitosan coating, FTIR spectra of Fe<sub>3</sub>O<sub>4</sub>, chitosan, and CS@Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared (Fig. 1) to study the possible functional groups contributing in binding procedure. As can be observed, the naked Fe<sub>3</sub>O<sub>4</sub> nanoparticles showed a strong stretching absorbance peak at 574.68 cm<sup>-1</sup> corresponding to Fe–O–Fe groups (Fig. 1a). In the spectrum of chitosan (Fig. 1b), the corresponded absorption bands of amide I and -NH<sub>2</sub> in amide group bending vibration was observed at 1641 cm<sup>-1</sup> and 1590 cm<sup>-1</sup>, respectively. The adsorption peaks of chitosan were appeared at 1376 cm<sup>-1</sup> (–C–O– stretching of primary alcoholic group), 1151 cm<sup>-1</sup> (asymmetric stretching of –C–O–C– bridge) and 1027 cm<sup>-1</sup> (C–N bond) [22,23]. The FTIR spectrum of CS@Fe<sub>3</sub>O<sub>4</sub> nanoparticles showed that the characteristic peak of Fe–O–Fe shifted to 580 cm<sup>-1</sup> (Fig. 1c) and all characteristic peaks of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and chitosan. These outcomes are in accordance with literatures [24,25].



Fig. 1 FTIR of a)  $Fe_3O_4$ ; b) CS; and c) CS@Fe\_3O\_4.

The scanning electron microscopy was used to study size and morphology of VO(CS)@Fe<sub>3</sub>O<sub>4</sub>. The FESEM image of a) Fe<sub>3</sub>O<sub>4</sub>; and c) VO(CS)@Fe<sub>3</sub>O<sub>4</sub> showed that the prepared catalyst is nanometer quasi-spherical with an average diameter of  $30\pm5$  nm (Fig. 2). Moreover, a continuous polymer layer can be seen on the VO(CS)@Fe<sub>3</sub>O<sub>4</sub> catalyst surface comparing to Fe<sub>3</sub>O<sub>4</sub>. In addition, the EDX detector coupled to the SEM was used to

prove the presence of chitosan (CS) shell on the  $Fe_3O_4$  NPs surface that the results confirmed the existence of Fe, C, N, and O in Figure 2b. The observing the V(IV) signal in the nanocatalyst's EDX (Fig. 2d) showed the effective coordination of  $VO(acac)_2$  salt on CS@Fe<sub>3</sub>O<sub>4</sub>.



**Fig. 2** FESEM images of a)  $Fe_3O_4$ ; c)  $VO(CS)@Fe_3O_4$ ; and EDX data for b)  $CS@Fe_3O_4$ ; d)  $VO(CS)@Fe_3O_4$ .

HRTEM image of VO(CS)@Fe<sub>3</sub>O<sub>4</sub> was presented in Fig. 3. It clearly shows well dispersion of the prepared catalyst and several larger structures, which can be attributed to the aggregation/coalescence of each nanoparticles. It can be observed that grey VO(CS) shells covered dark Fe<sub>3</sub>O<sub>4</sub> cores, confirming the effective coating procedure of VO(CS) materials.



0 nm

#### Fig. 3 HRTEM images of VO(CS)@Fe<sub>3</sub>O<sub>4</sub>

X-ray photoelectron spectroscopy (XPS) is an influential instrument for investigating the electronic characteristics of the species created on the surface, including the environment of electron, state of oxidation, and the binding energy of the core electron of the metal. XPS elemental survey scans of the surface of the VO(CS)@Fe<sub>3</sub>O<sub>4</sub> catalyst was shown in Fig. 4. The peaks related to oxygen, carbon, nitrogen, vanadium and iron are obviously observed in this spectrum. XPS analysis was also performed to determine the oxidation state of the V. In Fig. 5, the V binding energy of VO(CS)@Fe<sub>3</sub>O<sub>4</sub> shows two peaks centered at 524.3 and 517.2 eV contributing to V  $2p_{1/2}$  and V  $2p_{3/2}$ , respectively. Based on the previous studies [27], the Vanadium Oxides will have symmetric peak shapes and for V2p the V2p<sub>1/2</sub> component is much broader than the V2p<sub>3/2</sub> peak. Accordingly, V2p<sub>1/2</sub> peak is much shorter than estimated. These outcomes show that the V is in the (IV) form. The position of N 1s peak is frequently affected by the local chemical/physical environment around it, and its area showed two type of nitrogen, C-NH<sub>2</sub> (402 ev) and N-V(IV) (399.5 ev), that confirmed the effective bending of vanadium ions to the surface [28].



Fig. 4 XPS spectrum related to the elemental survey scan of VO(CS)@Fe<sub>3</sub>O<sub>4</sub>.



Fig. 5 XPS spectrum of VO(CS)@Fe<sub>3</sub>O<sub>4</sub> in the Fe2p, C1s, V2p, O1s, and N1s regions.

X-ray diffraction (XRD) analysis was used to study the structure and phase purity of structures. XRD patterns of Fe<sub>3</sub>O<sub>4</sub> NPs, pure chitosan, and as-prepared VO(CS)@Fe<sub>3</sub>O<sub>4</sub> NPs catalyst were shown in Fig. 6. The presence of six peaks at 20 about 30.2°, 35.7°, 43.4°, 53.7°, 57.4° and 62.8° corresponding to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) is in a good agreement with standard patterns of inverse cubic spinel magnetite (Fe<sub>3</sub>O<sub>4</sub>) crystal structure. The whole diffraction peaks are related to the magnetic cubic structure of Fe<sub>3</sub>O<sub>4</sub> (JCPDS 65-3107). The XRD pattern (Fig. 6c) of as-prepared VO(CS)@Fe<sub>3</sub>O<sub>4</sub> catalyst reveals the same diffraction peaks to that of Fe<sub>3</sub>O<sub>4</sub> NPs (Fig. 6a). By contrast with the XRD pattern of chitosan (Fig. 6b), it was found that an envelope peak centered at 20.2° in the XRD pattern of VO(CS)@Fe<sub>3</sub>O<sub>4</sub> (Fig. 6c) is the peculiar diffraction peak of the amorphous chitosan [29]. According to the obtained results, the crystalline phase of Fe<sub>3</sub>O<sub>4</sub> is not affected by the amorphous VO(CS) coating.



Fig. 6. XRD patterns of a) Fe<sub>3</sub>O<sub>4</sub>, b) CS, and c) VO(CS)@Fe<sub>3</sub>O<sub>4</sub>.

TGA analysis was used to determine the stability of the synthesized VO(CS)@Fe<sub>3</sub>O<sub>4</sub> catalyst as well as the percentage of organic functional groups on the surface of MNPs. The TGA results (Fig. 7) show an initial weight loss of 4.3% up to 100 °C that can be assigned to the physical adsorption of hydroxyl groups of the surface and solvent on the support. The catalyst

was thermally degraded above 200 °C that indicates the excellent thermo-stability of catalyst. The second and third weight loss of 23% in the range of 200-540 °C was because of the CS groups degradation. The man mass content of (CS)@Fe3O4 was expected 23% using the results of TGA.



Fig. 7 TGA curve of VO(CS)@Fe<sub>3</sub>O<sub>4</sub>

It was observing that that both prepared particles have minor coercivities, which show that they have a superparamagnetic nature. As can be observed in Fig. 8, saturation magnetizations are 62.3 and 32.3 emu g<sup>-1</sup> for Fe<sub>3</sub>O<sub>4</sub> and VO(CS)@Fe<sub>3</sub>O<sub>4</sub>, respectively. The order is because of an increase in the level of non-magnetic materials on the particle surface that results more percentage of the non-magnetic CS coating and the grafted catalyst layer. A direct outcome of this impact is that it VO(CS)@Fe<sub>3</sub>O<sub>4</sub> needs more time comparing to bare Fe<sub>3</sub>O<sub>4</sub> for separating from the solution.



Fig. 8 VSM spectra of a) Fe<sub>3</sub>O<sub>4</sub> and b) VO(CS)@Fe<sub>3</sub>O<sub>4</sub>

#### 3.2. The catalytic application of VO(CS)@Fe<sub>3</sub>O<sub>4</sub> in the oxidation of sulfides to sulfoxides

In the continuing of our previous studies,<sup>21</sup> the catalytic activity of VO(CS)@Fe<sub>3</sub>O<sub>4</sub> was studied as a reusable organic-inorganic hybrid catalyst for the chemo-selective oxidation of sulfides to sulfoxides with 30%  $H_2O_2$  under solvent-free conditions at ambient temperature (Scheme 1).

For optimization of the reaction conditions, the oxidation of methyl phenyl sulfide with 30%  $H_2O_2$  as a model was studied under different reaction conditions in terms of time and product efficiency (Table 1). As can be observed in Table 1, the reaction could not be performed completely without VO(CS)@Fe<sub>3</sub>O<sub>4</sub> even after 24 h (entries 1 and 2).  $H_2O_2$  (2 equiv.) The optimal conditions for the converting methyl phenyl sulfide to methyl phenylsulfoxide effectively was found with catalytic amount of VO(CS)@Fe<sub>3</sub>O<sub>4</sub> (30 mg, 0.9 mol%) under solvent free condition at ambient temperature (Table 1, entry 5).

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

Addition of methyl phenyl sunde to methyl phenyl sunoxide.						
Entry	Catalyst (mol%)	$H_2O_2$ (mmol)	Solvent	Time (min)	Yield $(\%)^{a}$	
1	Catalyst-free	2.0	Solvent-free	24 h	35	
2	$Fe_{3}O_{4}(20)$	2.0	Solvent-free	24 h	45	
3	$VO(CS)@Fe_{3}O_{4}(0.3)$	2.0	Solvent-free	2 h	90	
4	$VO(CS)@Fe_{3}O_{4}(0.6)$	2.0	Solvent-free	45	90	
5	$VO(CS)@Fe_{3}O_{4}(0.9)$	2.0	Solvent-free	5	90	
6	$VO(CS)@Fe_{3}O_{4}(1.2)$	2.0	Solvent-free	5	90	
7	$VO(CS)@Fe_{3}O_{4}(0.9)$	1.0	Solvent-free	30	90	
8	$VO(CS)@Fe_{3}O_{4}(0.9)$	3.0	Solvent-free	5	90	
9	$VO(CS)@Fe_{3}O_{4}(0.9)$	2.0	EtOH	45	90	
10	$VO(CS)@Fe_{3}O_{4}(0.9)$	2.0	CH <sub>3</sub> CN	45	90	
11	VO(CS)@Fe <sub>3</sub> O <sub>4</sub> (0.9)	2.0	$CH_2Cl_2$	2 h	85	

<sup>a</sup>Determined by <sup>1</sup>H NMR.

As summarized in Tables 2, the generality of this technique has been highlighted by a simple oxidant of several aliphatic and aromatic sulfides. The reaction shows the proper general use for synthesising sulfoxides. The intended products were achieved quickly in good yields and with good turn over numbers (TON). It is important to understand that the chemoselectively oxidation of the sulfides occurred in the presence of functional groups resistant to oxidation, including OH, CHO, and COOMe (Table 2, entries 6-8).

**Table 2.** VO(CS)@Fe<sub>3</sub>O<sub>4</sub> catalyzed selective oxidation of sulfides to sulfoxides under solvent-free condition.<sup>a</sup>

Entry	Sulfide	Sulfoxide	Time (min)	Yield $(\%)^{b}$	TON $(h^{-1})^{c}$
1	S_	O=S S	5	90	100

2	s~	O=S	12	88	97.8
3	S Ph	O S Ph	10	90	100
4	s	O = S	15	85	94.5
5	O <sub>2</sub> N	O <sub>2</sub> N O <sub>2</sub> N	15	85	94.5
6	∕ <sup>s</sup> ∕∕oh	O S OH	5	84	93.3
7	сно	о "сно	12	80	88.9
8	SCOOMe	O II S COOMe	20	70	77.8
8	∕ <sup>S</sup> ∖	O S S	20	80	88.9
10	∕s∕_		20	75	83.3

<sup>a</sup>Reaction conditions: sulfide (1 mmol), 30%  $H_2O_2$  (2.0 mmol), VO(CS)@Fe<sub>3</sub>O<sub>4</sub> (30 mg, 0.9 mol%), rt. <sup>b</sup>Determined by <sup>1</sup>H NMR.

<sup>°</sup>TON, turn over numbers (TON = Yield/Amount of catalyst (mol)).

Scheme 3 shows a reasonable catalytic mechanism for oxidizing sulfides to sulfoxides, which is the first step of the oxidation procedure. A can be observed, the formation of peroxovanadyl species is first occurred and subsequently, the sulfur atoms in the sulfide nucleophilically attack on the peroxo species. As known, the metal atom plays a role to create peroxo-metal species, which can activate the  $H_2O_2$  molecule [30, 31].



Scheme 3. Suggested mechanism for the sulfide oxidation using  $H_2O_2$  in the presence of  $VO(CS)@Fe_3O_4$ .

In order to study the reusability of VO(CS)@Fe<sub>3</sub>O<sub>4</sub>, it was magnetically isolated from the reaction mixture and reused for the offered procedure after rinsing with acetone. As estimated, the catalyst can be used 8 or more cycles for oxidizing methyl phenyl sulfide to the corresponding sulfoxide (Fig. 9). Moreover, a hot filtration test was performed for checking the leaching of V (IV) ions from the surface; however, the reaction progress was not quantitative significantly after 2 mins of reaction, the leaching of V(IV) into the reaction solution after 8 cycles was studied using ICP that was obtained 1.35% demonstrating the stability of the catalyst during the reaction.



Fig. 9. Reusability of nanocatalyst.

The comparison between the obtained results for oxidizing methyl phenyl sulfide in current study and other related academic report was performed to determine the catalytic power of

 $VO(CS)@Fe_3O_4$ . According to Table 3, the previous reported processes have at least one of the subsequent limitations: time-consuming reaction, using a transition metal and applying volatile and/or toxic organic solvents. The results of current study show that  $VO(CS)@Fe_3O_4$  is an appropriate catalyst for oxidizing of sulfides to sulfoxides selectively.

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

Entry	Reaction conditions	Time (min)	Yield%	Ref.
1	VO(CS)@Fe <sub>3</sub> O <sub>4</sub> , solvent-free, r.t.	6	90	This work
2	MNPs-based N-propylsulfamic acid, solvent-free, r.t.	80	87	[20d]
3	MCM-Mo, CH <sub>3</sub> CN,r.t., 40 °C	60	99	[32]
4	Silica-based tungstate interphase, CH <sub>3</sub> OH/CH <sub>2</sub> Cl <sub>2</sub> , r.t.	90	82	[33]
5	Peroxotungstate supported on silica, CH <sub>3</sub> OH/CH <sub>2</sub> Cl <sub>2</sub> , 8 °C	150	92	[34]
6	Tungstate-exchanged Mg–Al-LDH catalyst, H <sub>2</sub> O, r.t.	30	88	[35]
7	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /Mo, CH <sub>3</sub> CN, 50 ℃	90	92	[36]
8	VO(IV)–MCM-41, EtOH, r.t.	480	95	[20e]

#### 4. Conclusion

In conclusion, the new magnetic interphase nanocatalyst of oxo-vanadium Schiff base complex immobilized on magnetic  $Fe_3O_4$  nanoparticles [VO(CS)@MNPs] was successfully synthesized and characterized through different methods. It was also showed that VO(CS)@Fe<sub>3</sub>O<sub>4</sub> can be applied as a green, effective and reusable heterogeneous magnetic nanocatalyst for oxidizing a variety of sulfides to sulfoxides selectively using hydrogen peroxide under solvent-free conditions at ambient temperature. The advantages of this protocol are the utilize of a commercially accessible, green, inexpensive and chemically stabile oxidant, the mild conditions of reaction, easy operation, feasibility, short time of reaction, good to excellent efficiency, appropriate and easy recovery of the catalyst trough a suitable external magnetic field, reusability and excellent chemo-selectivity.

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### **Graphical Abstract**

Oxo-vanadium complex immobilized on chitosan coated-magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>): A heterogeneous and recyclable nanocatalyst for the chemoselective oxidation of sulfides to sulfoxides with  $H_2O_2$ 

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