Revised: 21 December 2020

### FULL PAPER

### Oxo-vanadium(IV) unsymmetrical Schiff base complex immobilized on $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles: A novel and magnetically recoverable nanocatalyst for selective oxidation of sulfides and oxidative coupling of thiols

Abolfazl Mahdian <sup>(1)</sup> | Mehdi Hatefi Ardakani <sup>(1)</sup> | Esmaeil Heydari-Bafrooei <sup>(1)</sup> | Samira Saeednia <sup>(2)</sup>

Department of Chemistry, Faculty of Science, Vali-e-Asr University of Rafsanjan, Rafsanjan, Iran

#### Correspondence

Mehdi Hatefi Ardakani, Department of Chemistry, Faculty of Science, Vali-e-Asr University of Rafsanjan, Rafsanjan 77188-97111, Iran. Email: m.hatefi@vru.ac.ir; m\_hatefi\_chem@yahoo.com

**Funding information** Vali-e-Asr University of Rafsanjan In this research, an unsymmetrical salen-type oxo-vanadium(IV) complex, [VO(salenac-OH)] (salenac-OH = [9-(2',4'-dihydroxyphenyl)-5,8-diaza-4-methylnona-2,4,8-trienato](-2)), was synthesized and covalently immobilized on the surface of magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The resulting  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO (salenac-OH)] nanoparticles were characterized by several techniques including Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning and transmission electron microscopies (SEM and TEM), energydispersive X-ray (EDX) spectroscopy, vibrating sample magnetometry (VSM), thermal gravimetric analysis (TGA), inductively coupled plasma (ICP), and elemental analysis. The prepared γ-Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanoparticle was utilized as an efficient catalyst for selective oxidation of sulfides to sulfoxides using 30% H<sub>2</sub>O<sub>2</sub> as oxidant and oxidative coupling of thiols into disulfides with urea/H<sub>2</sub>O<sub>2</sub> (UHP) as an oxidizing reagent. The products were achieved with good to excellent yields at room temperature with no over-oxidation of sulfoxides and disulfides to unexpected by-products. This catalyst can be magnetically recovered by applying an external magnet and reused for five continuous cycles in both oxidation reactions without a significant loss in its catalytic activity. Furthermore, the FT-IR spectrum and XRD pattern of the recovered catalyst showed no critical change to those of the fresh one.

#### **KEYWORDS**

magnetic nanocatalyst, oxo-vanadium(IV) complex, sulfide, thiol,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticle

### **1** | INTRODUCTION

The selective oxidation of sulfides into the corresponding sulfoxides has taken up a great part in modern synthetic organic chemistry.<sup>[1]</sup> Organic sulfoxides play an essential role in the synthesis of chemically useful and biologically active compounds including drugs, flavors, germicides, and catabolism regulators.<sup>[2]</sup> On the other hand, the

removal of sulfur compounds such as dibenzothiophene (DBT) from fuels is a necessary action in the petrochemical processes. The main reason for S removal is, however, that a few parts per million of sulfur are enough to poison the catalysts used for the purification of the exhaust gases of diesel cars. In this regard, for removing these compounds from fuels, the oxidation of sulfur compounds coupled with the extraction of the resulting sulfone by means of a solvent has been reported.<sup>[3]</sup> Likewise, the conversion of thiols to disulfides is essential in medical, biological, and industrial areas. Disulfides are used to stabilize peptides in proteins, design of rechargeable lithium batteries, sulfonylation of enolates, and as vulcanizing agent for rubber and elastomers.<sup>[4]</sup> Unfortunately, some methods based on the oxidation of sulfides and thiols require hazardous and toxic reagents or include overoxidation of sulfides and thiols to undesired by-products.<sup>[5]</sup> Hence, further progress in eco-friendly selective oxidation of sulfides to sulfoxides and thiols to disulfides using less poisonous catalysts, oxidants, and solvents is still needed. Recently, a series of Fe/Fe<sub>3</sub>C-containing nitrogen-doped porous carbon microspindles (Fe/Fe<sub>3</sub>C@NC-x, where x represents the pyrolysis temperature from 500°C to 800°C) have been constructed by the pyrolisis of a metal-organic framework precursor as highly selective catalysts for the oxidation of sulfides to sulfoxides under mild reaction conditions.<sup>[6]</sup> Also, Xu et al. developed a visible-light-induced strategy for the selective aerobic oxidation of thiols to disulfides and oxidative synthesis of asymmetric disulfides on anatase TiO<sub>2</sub> as a nontoxicity, low cost, and high availability photocatalyst.<sup>[7]</sup>

Azomethines or Schiff base ligands significantly contribute to the extension of transition metal coordination chemistry due to their facile synthesis, structural variety, biological and catalytic properties, and chemical and thermal stability.<sup>[8,9]</sup> Unsymmetrical Schiff base ligands are of great importance because of their optoelectronic, electrochemical, and magnetic properties.<sup>[10]</sup> Also, the existence of bonds between the central metal ions and unsymmetrical Schiff base ligands in natural systems has been reported.<sup>[11]</sup>

In recent years, special attention has been paid to oxovanadium(IV) Schiff base complexes due to their catalytic applications, biological roles in biochemical processes, and interesting structural features.<sup>[12]</sup> The vanadium's ability to quickly change its oxidation states between +IV and +V makes this element well-suited elements for catalytic oxidation reactions.<sup>[13]</sup> In the catalysts field, the immobilized oxo-vanadium complexes catalyze various reactions such as oxidation of alcohols, epoxidation of alkenes and allyl alcohols, conversion of sulfides to sulfoxides, and oxidative coupling of thiols to disulfides.<sup>[14-18]</sup> Recently, Oi and coworkers prepared a novel N-incorporated carbonsupported vanadium catalyst (V@CN-750) via in situ pyrolysis of chitin and the VO(acac)<sub>2</sub> complex. The V@CN-750 catalyst exhibited excellent activity, selectivity, and recyclability in the selective oxidation of sulfides to sulfoxides under mild conditions.<sup>[19]</sup> Moreover, the titanium dioxide doped with vanadium(V-TiO<sub>2</sub>) showed high activity in the photocatalytic oxidation of sulfide to sulfoxide under UV irradiation.<sup>[20]</sup>

Homogeneous metal-based Schiff base complexes (notably, the expensive metal ones) have limited catalytic applications because of complications in their separation and reusability. Moreover, deactivation of homogeneous catalysts occurs by the formation of  $\mu$ -oxo and dimeric peroxo-species.<sup>[21]</sup> These problems can be overcome by immobilization of metal Schiff base complexes on suitable solid supports.

Nowadays, nanoparticles, specially magnetic nanoparticles (MNPs), are employed as catalyst supports because of their unique properties, including ease of separation by a magnet, high surface area, high dispersion, low toxicity, appropriate recycling of catalyst, and remarkable stability.<sup>[22-26]</sup> Whereas most heterogeneous systems require filtration, centrifugation, or tiresome workup to recover the catalysts from the final reaction, the magnetic nanocatalysts can be magnetically separated from the reaction medium with no need for filtration or centrifugation steps. Furthermore, the MNPs can be prepared from inexpensive materials and can be simply modified through appropriate surface modifications.<sup>[27]</sup> Recently, the combination of MNPs and lavered double hydroxide (LDH) as magnetic-LDH has been provided to be applied in a wide range of synthetic methods because the achieved nanoparticles possess a high surface to volume ratio, which increases their activity and selectivity.<sup>[28]</sup> Among the many available MNPs, the maghemite  $(\gamma - Fe_2O_3)$  nanoparticles have been specially interesting due to their excellent properties. The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles are super paramagnetic materials used in catalysis, sensors, drug delivery systems, magnetic resonance imaging (MRI), and biology.<sup>[29]</sup> Moreover, the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposites with tin oxide, graphene oxide, silica, and starch find applications in catalysis, optical device, and selective removal of heavy metal ions from aqueous solution.<sup>[30]</sup> Recently, Abbasi et al. and Amini et al. synthesized Ag γ-Fe<sub>2</sub>O<sub>3</sub> supported on hydroxyapatite-core-shell nanoparticles (y-Fe<sub>2</sub>O<sub>3</sub>@Hpa-Ag NPs) as an efficient and magnetically recyclable catalyst for the synthesis of coumarin derivatives and regioselective ring opening of epoxides.<sup>[31,32]</sup> Also, preparation and application of Fe<sup>2+</sup> and Ni<sup>2+</sup> immobilized on hydroxyapatite-core-shell y-Fe<sub>2</sub>O<sub>3</sub> nanoparticles as efficient catalysts for the various organic reactions have been reported.[33-36]

In this work, an oxo-vanadium(IV) complex containing an unsymmetrical salen-type Schiff base was synthesized and immobilized covalently on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> MNPs. The prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanoparticles were fully characterized by various physicochemical methods and successfully used for selective oxidation of sulfides to sulfoxides and oxidative coupling of thiols to disulfides at room temperature.

### 2 | EXPERIMENTAL

### 2.1 | Materials and methods

All the materials used were of commercial reagent grade acquired from Merck or Fluka chemical companies. The Fourier transform infrared (FT-IR) spectra were recorded as KBr disks by a Thermo Scientific Nicolet iS10 FT-IR spectrophotometer. The UV-vis spectrum was recorded using a T80 UV-vis spectrophotometer. An ICP-SpectroCiros CCD spectrometer was used to evaluate the metal content of the catalyst. The X-ray diffraction (XRD) patterns of the powder samples were recorded at room temperature by a Panalytical X'pert Pro diffractometer with Cu-Kα radiation. The scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis were performed via a Zeiss Sigma VP-500 system. The transmission electron microscope (TEM) images were taken using a Zeiss-EM10C instrument. The magnetic measurements were carried out by an LBKFB Meghnatis Daghigh Kavir vibrating sample magnetometer (VSM). The thermal gravimetric analysis (TGA) was conducted on a Rheometric Scientific STA 1500 system. The elemental analysis was performed by a Vario EL III CHNS analyzer. The reaction progress was checked through the thin-layer chromatography (TLC) of silica-gel polygram SILG/UV 254 plates. The gas chromatography (GC) analyses were carried out by a Philips GC-PU 4600 instrument equipped with a flame ionization detector (FID).

### 2.2 | Synthesis of [VO(salenac-OH)] complex

Schiff Unsymmetrical tetradentate base ligand, salenac-OH = [9-(2',4'-dihydroxyphenyl)-5,8-diaza-4-methylnona-2,4,8-trienato](-2), was synthesized in good yield based on the procedure described in the literature.<sup>[37]</sup> To prepare oxo-vanadium(IV) Schiff base complex, [VO(salenac-OH)], 1 mmol of VO(acac)<sub>2</sub>, that is, 0.265 g, was dissolved in 25-ml warmed methanol, and the obtained solution was added dropwise to the stirred solution of 1 mmol (0.262 g) of Schiff base ligand in 25-ml methanol. After refluxing the reaction mixture for 4 h, it was allowed to be cooled to room temperature. The resultant green solid product was collected and washed several times with methanol and then purified from hot methanol (yield: 65%). Anal calc. for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>V (%): C, 51.36; H, 4.94; N, 8.56, found: C, 51.27; H, 5.12; N, 8.45. FT-IR (KBr pellet, cm<sup>-1</sup>): 3450 (OH), 1621 (C=N), 1595 (C=N), 1447 (C=C, aromatic), 988 (V=O). UV-vis (CH<sub>3</sub>CN, λ<sub>max</sub>/nm): 235, 273, 365.

### 2.3 | Synthesis of γ-Fe<sub>2</sub>O<sub>3</sub> MNPs

The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> MNPs were synthesized via a chemical coprecipitation method described in the literature.<sup>[38]</sup> Briefly, 1.99 g of FeCl<sub>2</sub>·4H<sub>2</sub>O and 3.25 g of FeCl<sub>3</sub>·6H<sub>2</sub>O were dissolved in 30 ml of deionized water under N<sub>2</sub> atmosphere at room temperature. Then 200 ml of a 0.6-M NH<sub>4</sub>OH solution was added drop by drop to the mixture under continuous stirring at room temperature to set the reaction pH of 11. The resultant black dispersion was stirred continuously for 1 h at room temperature and subsequently refluxed for 1 h to obtain a brownish dispersion. Afterward, the nanoparticles were magnetically collected and washed repeatedly with deionized water. Finally, the synthesized particles were heated at 250°C for 3 h to give a reddish-brown powder.

### 2.4 | Synthesis of chloro-functionalized $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>

The prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles (1.8 g) were sonicated in 50 ml of dry toluene for 30 min. Then 2 ml of 3-chloropropyltrimethoxysilane was added to the dispersed  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles under mechanical stirring. The resultant mixture was refluxed under N<sub>2</sub> atmosphere for 48 h. Then the obtained chloro-functionalized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were magnetically collected, washed with toluene, deionized water, and ethanol in turn, and finally dried under vacuum.<sup>[38]</sup>

### 2.5 | Preparation of γ-Fe2O3@[VO (salenac-OH)] nanocatalyst

The synthesized chloro-functionalized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (2 g) was dispersed in 50 ml of dry acetone by sonication for 30 min. Afterward, 0.5 g of the synthesized [VO(salenac-OH)] complex was added to the above stirring mixture. The resultant suspension was refluxed for 24 h. The solid product was then collected with a permanent magnet and washed with acetone three times. Finally, the obtained solid was dried in an oven at 90°C for 4 h to furnish  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanocatalyst.

### 2.6 | General procedure for the oxidation of sulfides to sulfoxides with 30% $H_2O_2$ catalyzed by $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)]

In a typical procedure, 25 mg (0.70 mol%) of the prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanocatalyst, 1 mmol of sulfide, and 3 mmol 30% H<sub>2</sub>O<sub>2</sub> were mixed in 4 ml of

WILEY Organometallie 4 of 16

1,2-dichloroethane inside a test tube. This mixture was magnetically stirred at room temperature, and the reaction progress was checked by TLC or GC. After completion of the reaction, the catalyst was magnetically collected, washed with Et<sub>2</sub>O, and dried in an oven of 80°C. Lastly, to achieve the pure product, it was extracted with  $CH_2Cl_2$  (3 × 10 ml) and purified on a silica-gel column. Some of the products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC spectra (Supporting Information).

### 2.7 | General procedure for the oxidative coupling of thiols to disulfides with UHP catalyzed by $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)]

To a mixture of thiol (1 mmol) and  $urea/H_2O_2$  (UHP) (5 mmol) in ethanol (4 ml), 25 mg (0.70 mol%) of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] was added. Then the mixture was stirred at room temperature, and the progress of reaction was monitored using the TLC technique. At the end of the reaction, the catalyst was separated with a magnet, rinsed several times with Et<sub>2</sub>O, and dried in the oven at 80°C. Finally, the corresponding disulfide was extracted with  $CH_2Cl_2$  (3 × 10 ml) and refined by a silicagel column. The <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC spectra of some of the products are given in the Supporting Information.

#### 2.8 Selected spectral data (Figures S1-**S8)**

Dibenzyl sulfoxide (Table 2, entry 1), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.49–7.44 (m, 6H), 7.43–7.35 (m, 4H), 3.90 (m, 4H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 129.62, 128.83, 128.23, 127.18, 56.78.

Methylphenyl sulfoxide (Table 2, entry 4), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.45 (m, 5H), 2.63 (m, 3H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 145.83, 131.06, 129.32, 123.54, 43.72.

Bis(4-methylphenyl) disulfide (Table 4, entry 1), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.50 (d, 4H), 7.18 (d, 4H), 2.38 (s, 6H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 134.94, 134.06, 133.51, 132.16, 131.97, 127.67, 20.54.

Diphenyl disulfide (Table 4, entry 3), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.52-7.45 (m, 4H), 7.32-7.19 (m, 6H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 135.15, 132.45, 130.79, 130.19,

#### **RESULTS AND DISCUSSION** 3

### 3.1 | Characterization of [VO(salenac-

the V=O stretching vibration frequencies.

Figure 2 shows the UV-vis spectrum of the [VO (salenac-OH)] complex. Three bands were seen in the spectrum at 235, 273, and 365 nm. The two bands in the higher energy region (235 and 273 nm) were attributed to the  $\pi \to \pi^*$  transitions, and the band at 365 nm was assigned to the  $n \rightarrow \pi^*$  transitions. Also, a band with very low intensity appeared at 597 nm, which was attributed to the d-d transition.



FIGURE 1 Fourier transform infrared spectrum of [VO(salenac-OH)] complex

OH)] complex The synthesized [VO(salenac-OH)] complex was characterized by elemental analysis (CHN), FT-IR, and UV-vis spectra. In the FT-IR spectrum of [VO(salenac-OH)] complex (Figure 1), two bands appeared at 1621 and 1595 cm<sup>-1</sup> due to the two different C=N bonds in the unsymmetrical Schiff base ligand. The observed bands at 1447 and 3450 cm<sup>-1</sup> can be assigned to the aromatic C=C and O-H stretching vibrations, respectively. Similarly, the appeared band at 988 cm<sup>-1</sup> was attributed to





## 3.2 | Preparation and characterization of γ-Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanocatalyst

The preparation procedure of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] heterogeneous nanocatalyst is shown in Scheme 1. First, the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> MNPs were synthesized by chemical coprecipitation of ferric and ferrous ions in the alkali solution. Then the prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were allowed to react with 3-chloropropyltrimethoxysilane to give chloro-functionalized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Finally,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO (salenac-OH)] nanocatalyst was synthesized via covalent grafting of [VO(salenac-OH)] complex on the surface of the chloro-functionalized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles.

The prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanocatalyst was characterized by FT-IR and EDX spectra, XRD patterns, SEM and TEM images, VSM measurements, TGA,

inductively coupled plasma (ICP), and elemental analysis. The ICP analysis showed that 0.28 mmol of vanadium was anchored on 1.0 g of the supported catalyst.

FT-IR spectra of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, chlorofunctionalized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanocatalyst, and the recovered  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] are shown in Figure 3. In all the spectra, the band revealed around 550–640 cm<sup>-1</sup> is attributed to the stretching vibrations of the Fe—O bond in these compounds.<sup>[39]</sup> In Figure 3b,c, the band positioned at around 2920 cm<sup>-1</sup> may be related to the C—H bond's stretching vibrations in methylene groups.<sup>[40]</sup> In the FT-IR spectrum of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] (Figure 3c), two bands appeared at 1628 and 1591 cm<sup>-1</sup> are assigned to the vibrations of two different azomethine (C=N) groups of the unsymmetrical Schiff base ligand in the immobilized



**SCHEME 1** Preparation process of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO (salenac-OH)] nanocatalyst



**FIGURE 3** FT-IR spectrum of (a)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, (b) chloro-functionalized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, (c)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanocatalyst, and (d) recovered  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] after five uses

[VO(salenac-OH)] complex. Also, the band at 1450 cm<sup>-1</sup> can be assigned to the aromatic C=C stretching vibrations of the immobilized [VO(salenac-OH)] complex. Moreover, the band that appeared at 983 cm<sup>-1</sup> in the FT-IR spectrum of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] is attributed to the V=O stretching vibrations.<sup>[41]</sup> These results indicate that the [VO(salenac-OH)] complex has been successfully grafted onto the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> MNPs.

The XRD pattern of the prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO (salenac-OH)] catalyst is shown in Figure 4a. The diffraction peaks around  $2\theta = 30.4^{\circ}$ ,  $35.7^{\circ}$ ,  $43.4^{\circ}$ ,  $53.7^{\circ}$ ,  $57.4^{\circ}$ , and  $63.0^{\circ}$  correspond to Bragg reflections from (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) planes of face-centered cubic structure of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, respectively (JCPDS File No. 04-0755). The average crystallite size of the prepared catalyst determined using the Debye–Scherrer formula is about 34.8 nm.

SEM image of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] catalyst is shown in Figure 5. As seen, it presents a uniform and spherical morphology of the MNPs. Furthermore, its EDX spectrum (Figure 6) confirms the expected C, N, O, Fe, and V species in the prepared catalyst.

The particle size and structure of the prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanocatalyst were further determined through the TEM images (Figure 7). They show the approximately spherical shape of nanoparticles with an average diameter of 40 nm.

The magnetic properties of the synthesized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@ [VO(salenac-OH)] nanocatalyst were measured using a VSM at room temperature. The saturation magnetization of bare  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles has been reported<sup>[38]</sup> as



**FIGURE 4** X-ray diffraction pattern of (a) fresh and (b) recovered  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO (salenac-OH)] catalyst



**FIGURE 5** Scanning electron microscope image of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@ [VO(salenac-OH)]

68.5 emu g<sup>-1</sup>, and the saturation magnetization of the prepared catalyst is 54.5 emu g<sup>-1</sup> (Figure 8). The decrease observed in the magnetization of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] with respect to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is caused by the grafting of organic layers, including oxo-vanadium complex on the surface of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. However,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanocatalyst, despite its decreased magnetization compared with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, can be quickly separated from the reaction mixture by an external magnet.

The thermal stability of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanocatalyst was studied by TGA. The TGA curve of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] (Figure 9) shows two weight loss steps. The first one (about 2.5%) around 120°C is associated with the loss of water molecules adsorbed on





FIGURE 7 Transmission electron microscope images of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)]

the support.<sup>[42]</sup> In comparison, the second one (about 9.4%) in the  $250-800^{\circ}$ C range may be related to the decomposition of organic component attached to the



**FIGURE 6** Energy-dispersive X-ray spectrum of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)]



**FIGURE 8** Magnetization curve of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)]



**FIGURE 9** Thermal gravimetric analysis curve of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@ [VO(salenac-OH)]

support. According to the TGA profile, the amount of organic compounds supported on the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles is estimated to be 0.26 mmol g<sup>-1</sup>. These results are in good agreement with the elemental analysis (N = 0.76%) and ICP data.

### 3.3 | Catalytic performance

### 3.3.1 | Oxidation of sulfides to sulfoxides catalyzed by $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)]

Following the characterization of the synthesized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)], its catalytic activity was studied in the oxidation of various sulfides at room temperature.

To explore the optimum reaction conditions, different solvents and solvent-free conditions were applied in the oxidation of dibenzyl sulfide as a model substrate. Among the studied solvents, 1,2-dichloroethane  $(C_2H_4Cl_2)$  was found to be the best, and the highest sulfoxide yield was achieved in this solvent (Table 1, entries 1-8). Subsequently, different amounts of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] catalyst were used in the model reaction, and the superior sulfoxide yield was obtained with 0.70 mol% (25 mg) of the catalyst (Table 1, entries 8 and 12-16). It is notable that with no catalyst, the oxidation of dibenzyl sulfide was incomplete even after 24 h (Table 1, entry 12). Additionally, the ability of different oxidants including 30% H<sub>2</sub>O<sub>2</sub>, UHP, tert-BuOOH (TBHP, 70% aqueous solution), and NaIO<sub>4</sub> was examined in the oxidation of dibenzyl sulfide as a model substrate, and 30% H<sub>2</sub>O<sub>2</sub> gave the best sulfoxide yield (Table 1, entries 8 and 17-20). It is worth mentioning that  $H_2O_2$  is a cheap, easy-to-handle, and environmentally acceptable oxidant. The various molar ratios of H<sub>2</sub>O<sub>2</sub>/ sulfide were also examined for the model oxidation reaction, and the optimum molar ratio of H<sub>2</sub>O<sub>2</sub> to substrate of 3:1 mmol was found to be ideal for this system (Table 1, entries 8–11). In addition, when excess amount of  $H_2O_2$ (4 mmol) was employed, the sulfoxide yield was decreased due to the consecutive reaction of the transformation of sulfoxide to sulfone (Table 1, entry 9).

The catalytic ability of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanocatalyst was studied in the oxidation of various sulfides in the optimized conditions (Scheme 2). As summarized in Table 2, a wide variety of sulfides were successfully oxidized to their corresponding sulfoxides with good to excellent yields. In this protocol, the oxidation of diphenyl sulfide as sterically hindered and diethyl sulfide as linear sulfides completed with good yields (Table 2, entries 6 and 8). The chemo-selectivity of this method was also notable. The conversion of sulfides containing hydroxyl group (Table 2, entry 7) and C=C bonds (Table 2, entries 9 and 10) into their corresponding sulfoxides is accompanied by no carbonyl and epoxide by-products.

Based on the literature,<sup>[43]</sup> a possible mechanism for the oxidation of sulfides to sulfoxides with  $H_2O_2$  in the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] catalyst is proposed (Scheme 3). At first,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] reacts with  $H_2O_2$  to form intermediate **A**, which is converted to the active oxidant **B**. Next, nucleophilic attack of the sulfide on this intermediate gives cation **C**, which produces the corresponding sulfoxide and regenerates the catalyst for the subsequent catalytic cycle.

# 3.3.2 | Oxidative coupling of thiols to disulfides catalyzed by $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO (salenac-OH)]

In the second part of our study, the prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@ [VO(salenac-OH)] nanoparticles were used as the catalyst

1	Solvent-free	0.70	$30\% \ H_2O_2$	23
2	CH <sub>3</sub> OH	0.70	$30\%~\mathrm{H_2O_2}$	15
3	EtOH	0.70	$30\% \ H_2O_2$	27
4	H <sub>2</sub> O	0.70	$30\% H_2O_2$	18
5	CH <sub>3</sub> CN	0.70	$30\% \ \mathrm{H_2O_2}$	35
6	$CH_3COCH_3$	0.70	$30\% H_2O_2$	43
7	CHCl <sub>3</sub>	0.70	$30\% \ H_2O_2$	67
8	$C_2H_4Cl_2$	0.70	$30\% \ H_2O_2$	95
9 <sup>a</sup>	$C_2\mathrm{H}_4\mathrm{Cl}_2$	0.70	$30\% \ H_2O_2$	85
$10^{b}$	$C_2\mathrm{H}_4\mathrm{Cl}_2$	0.70	$30\% \ H_2O_2$	57
11 <sup>c</sup>	$C_2 \mathrm{H}_4 \mathrm{Cl}_2$	0.70	$30\% \ H_2O_2$	25
12 <sup>d</sup>	$C_2\mathrm{H}_4\mathrm{Cl}_2$	0	$30\% \ \mathrm{H_2O_2}$	0
13	$C_2H_4Cl_2$	0.14	$30\% \ H_2O_2$	24
14	$C_2\mathrm{H}_4\mathrm{Cl}_2$	0.28	$30\% \ \mathrm{H_2O_2}$	45
15	$C_2\mathrm{H}_4\mathrm{Cl}_2$	0.42	$30\% \ \mathrm{H_2O_2}$	63
16	$C_2 \mathrm{H}_4 \mathrm{Cl}_2$	0.56	$30\% \ H_2O_2$	75
17	$C_2\mathrm{H}_4\mathrm{Cl}_2$	0.70	Urea/H <sub>2</sub> O <sub>2</sub> (UHP)	55
18	$C_2\mathrm{H}_4\mathrm{Cl}_2$	0.70	tert-BuOOH	23
19	$C_2\mathrm{H}_4\mathrm{Cl}_2$	0.70	NaIO <sub>4</sub>	12
20	$C_2H_4Cl_2$	0.70	No oxidant	0

Catalyst (mol%)

TABLE 1 Optimization of the reaction parameters in the oxidation of dibenzyl sulfide catalyzed by y-Fe2O3@ [VO(salenac-OH)] at room temperature

> Note: Reaction conditions: dibenzyl sulfide (1 mmol), solvent (4 ml), oxidant (3 mmol), catalyst, reaction time (1 h). Bold emphasis is used due to contrast and comparison with other data.

 $^{a}H_{2}O_{2} = 4 \text{ mmol.}$ 

Entrv

Solvent

 ${}^{b}H_{2}O_{2} = 2 \text{ mmol.}$ 

 $^{c}H_{2}O_{2} = 1 \text{ mmol.}$ <sup>d</sup>Reaction time = 24 h.

for the oxidative coupling of thiols into disulfides at room temperature. To find the best reaction conditions, 4-methyl thiophenol was selected as the model substrate, and the influence of the nature of solvent (Table 3, entries 1-7), amount of catalyst (Table 3, entries 2 and 8-12), and kind of oxidant (Table 3, entries 2 and 13-16) were investigated for this oxidation reaction. The results (Table 3) indicate that the optimum conditions for the completion of the reaction are catalyst (0.70 mol%, 25 mg), UHP (5 mmol) as oxidant, and EtOH as the solvent.

The generality of this protocol has been demonstrated by the successful conversion of different thiols to the corresponding disulfides with excellent yields (Scheme 4, Table 4). This oxidizing system allowed the chemoselective oxidation of 2-mercaptoethanol to the corresponding disulfide (Table 4, entry 8). Interestingly, the hydroxyl group in this substrate remained intact during the oxidation reaction.

Organometallic\_WILEY Chemistry

9 of 16

Isolated yield (%)

Applied

Oxidant

A possible mechanism for the oxidative coupling of thiols to the corresponding disulfides with UHP as the oxidant in the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] catalyst is outlined in Scheme 5.<sup>[44]</sup>

To show that the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] catalyst is truly heterogeneous, a hot filtration test was carried out in the oxidation of 4-methyl thiophenol under



SCHEME 2 Oxidation of sulfides with 30% H<sub>2</sub>O<sub>2</sub> catalyzed by γ-Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)]

MAHDIAN ET AL.





 $\label{eq:constraint} \textbf{TABLE 2} \quad \text{Oxidation of sulfides to sulfoxides with 30\% H}_2O_2 \text{ catalyzed by } \gamma \text{-} \text{Fe}_2O_3@[VO(\text{salenac-OH})] \text{ at room temperature}$ 

 $\label{eq:Note: Reaction conditions: sulfide (1 mmol), C_2H_4Cl_2 (4 ml), 30\% H_2O_2 (3 mmol), catalyst (0.70 mol\%). ^aIsolated yields.$ 

<sup>b</sup>Yields determined by gas chromatography.

 $\begin{array}{ll} \textbf{SCHEME 3} & \text{Proposed mechanism for} \\ \text{oxidation of sulfides with 30\% $H_2O_2$ catalyzed by} \\ \gamma\text{-Fe}_2O_3@[VO(salenac\text{-}OH)] \end{array}$ 



**TABLE 3**Optimization of thereaction conditions in the oxidativecoupling of 4-methyl thiophenolcatalyzed by  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] at room temperature

Entry	Solvent	Catalyst (mol%)	Oxidant	Isolated yield (%)
1	CH <sub>3</sub> OH	0.70	UHP	43
2	EtOH	0.70	UHP	95
3	H <sub>2</sub> O	0.70	UHP	27
4	CH <sub>3</sub> CN	0.70	UHP	35
5	$\rm CH_3 COCH_3$	0.70	UHP	47
6	$C_2 H_4 Cl_2$	0.70	UHP	25
7	CHCl <sub>3</sub>	0.70	UHP	18
8 <sup>a</sup>	EtOH	0	UHP	0
9	EtOH	0.14	UHP	23
10	EtOH	0.28	UHP	45
11	EtOH	0.42	UHP	62
12	EtOH	0.56	UHP	75
13	EtOH	0.70	$30\% \ \mathrm{H_2O_2}$	58
14	EtOH	0.70	tert-BuOOH	35
15	EtOH	0.70	NaIO <sub>4</sub>	15
16	EtOH	0.70	No oxidant	0

*Note*: Reaction conditions: 4-methyl thiophenol (1 mmol), solvent (4 ml), oxidant (5 mmol), catalyst, reaction time (45 min).

Abbreviation: UHP, urea/ $H_2O_2$ . Bold emphasis is used due to contrast and comparison with other data. <sup>a</sup>Reaction time = 24 h.

Thiol

Entry



Time

Yield (%)<sup>a</sup>

Product



**TABLE 4** Oxidative coupling of thiols into disulfides using urea/ $H_2O_2$  catalyzed by  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] at room temperature



*Note*: Reaction conditions: thiol (1 mmol), EtOH (4 ml), urea/ $H_2O_2$  (5 mmol), catalyst (0.70 mol%). <sup>a</sup>Isolated yields.

<sup>b</sup>Yield determined by gas chromatography.

optimal reaction conditions. Typically, after 25 min, the catalyst was separated by an external magnet, and the filtrate was allowed to stir for an additional 45 min. The reaction yield was 55% after 25 min and 60% after an additional 45 min. This observation showed that the leaching of the immobilized Schiff base complex into the reaction mixture should be negligible, and the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@ [VO(salenac-OH)] catalyst acts heterogeneously.



**TABLE 5** Comparison of catalytic activity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] with the reported catalysts in the oxidation of methyl phenyl sulfide and oxidative coupling of 4-methyl thiophenol

Entry	Substrate	Catalyst	Conditions	Time (min)	Yield (%)	Ref.
1	Methyl phenyl sulfide	V(IV)O-MCM-41	EtOH/UHP, r.t.	480	95	Nikoorazm et al. <sup>[44]</sup>
2	Methyl phenyl sulfide	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @VO(salen)	CH <sub>3</sub> OH/CH <sub>2</sub> Cl <sub>2</sub> / UHP, r.t.	360	83	Bagherzadeh et al. <sup>[45]</sup>
3	Methyl phenyl sulfide	VO(acac)@Sb@SMNPs	$C_2H_4Cl_2/TBHP$ , $85^{\circ}C$	60	100	Bagherzadeh et al. <sup>[46]</sup>
4	Methyl phenyl sulfide	Co@SiO <sub>2</sub> [(EtO) <sub>3</sub> Si-L <sup>3</sup> ]/ Mn(III)	$\mathrm{CH_3CN/H_2O_2,65^{\circ}C}$	50	99	Ghahri-Saremi et al. <sup>[47]</sup>
5	Methyl phenyl sulfide	Fe <sub>3</sub> O <sub>4</sub> /salen of Cu(II)	EtOH/H <sub>2</sub> O <sub>2</sub> , $60^{\circ}$ C	180	83	Ghorbani-Choghamarani et al. <sup>[48]</sup>
6	Methyl phenyl sulfide	γ-Fe <sub>2</sub> O <sub>3</sub> @[VO(salenac- OH)]	$C_2H_4Cl_2/H_2O_2$ , r.t.	60	93	This work
7	4-Methyl thiophenol	Co(phcy)(SO <sub>3</sub> Na) <sub>4</sub>	$H_2O/air$ , 60°C	360	95	Dou et al. <sup>[49]</sup>
8	4-Methyl thiophenol	Co-Salophen	EtOH/air, 60°C	180	96	Chai et al. <sup>[50]</sup>
9	4-Methyl thiophenol	Ni-SMTU@boehmite	EtOH/H <sub>2</sub> O <sub>2</sub> , r.t.	80	94	Ghorbani-Choghamarani et al. <sup>[51]</sup>
10	4-Methyl thiophenol	Fe <sub>3</sub> O <sub>4</sub> -Adenine-Zn	EtOAc/H <sub>2</sub> O <sub>2</sub> , r.t.	90	99	Tamoradi et al. <sup>[52]</sup>
11	4-Methyl thiophenol	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub> @Mn (III)	CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> OH, UHP, r.t.	120	83	Bagherzadeh et al. <sup>[53]</sup>
12	4-Methyl thiophenol	γ-Fe <sub>2</sub> O <sub>3</sub> @[VO(salenac- OH)]	EtOH/UHP, r.t.	45	95	This work

Abbreviations: MNPs, magnetic nanoparticles; r.t., room temperature; UHP, urea/H<sub>2</sub>O<sub>2</sub>.

**TABLE 6** Reusability of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] catalyst in the oxidation of dibenzyl sulfide with 30% H<sub>2</sub>O<sub>2</sub> at room temperature

Run	Yield (%)	TON	TOF (h <sup>-1</sup> ) <sup>a</sup>
1	95	135.7	135.7
2	93	132.8	132.8
3	90	128.6	128.6
4	90	128.6	128.6
5	87	124.3	124.3

*Note*: Reaction conditions: dibenzyl sulfide (1 mmol),  $C_2H_4Cl_2$  (4 ml), 30%  $H_2O_2$  (3 mmol), catalyst (0.70 mol%), reaction time (1 h). <sup>a</sup>TOF = TON/time (h).

**TABLE 7** Reusability of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] catalyst in the oxidative coupling of 4-methyl thiophenol with urea/H<sub>2</sub>O<sub>2</sub> at room temperature

Run	Yield (%)	TON	TOF $(h^{-1})^a$
1	95	135.7	180.9
2	92	131.4	175.2
3	90	128.6	171.4
4	87	124.3	165.7
5	87	124.3	165.7

*Note*: Reaction conditions: 4-methyl thiophenol (1 mmol), EtOH (4 ml), urea/ $H_2O_2$  (5 mmol), catalyst (0.70 mol%), reaction time (45 min). <sup>a</sup>TOF = TON/time (h).

The activity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] nanocatalyst in the catalytic oxidation of methyl phenyl sulfide and oxidative coupling of 4-methyl thiophenol was compared with the performance of some other catalysts (Table 5). Accordingly, these protocols have several advantages, namely, high yields of products, short reaction times, and convenient catalyst recyclability by an applied magnetic field.

### 3.4 | Catalyst reusability

The recovery and reusability of catalysts are of great concern from economic, environmental, and industrial perspectives. In this regard, the reusability of the synthesized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] catalyst was investigated in the oxidation of dibenzyl sulfide and oxidative coupling of 4-methyl thiophenol under the optimum reaction conditions. Following each reaction, the catalyst was collected magnetically from the reaction mixture and used in the next run after washing with Et<sub>2</sub>O and drying in the oven at 80°C. The results in Tables 6 and 7 show that the catalyst can be reused five times in both oxidation reactions with no considerable loss in its initial activity.

The recovered catalyst has also been characterized via FT-IR and XRD techniques. The FT-IR spectrum of the recovered catalyst after five runs is shown in Figure 3d. The band around  $550-640 \text{ cm}^{-1}$  corresponds to Fe–O vibrations, and the ones at 2919 and 1447 cm<sup>-1</sup> are associated with aliphatic CH<sub>2</sub> groups and aromatic C=C stretching vibrations, respectively. Furthermore, the two bands at 1625 and 1593 cm<sup>-1</sup> are assigned to two different C=N stretching vibrations of the Schiff base ligand. Also, the recovered catalyst exhibits a band at 985 cm<sup>-1</sup> corresponding to the V=O stretching vibrations. All these IR bands emerge for the fresh catalyst (Figure 3c) as well. The XRD pattern of the recovered catalyst is shown in Figure 4b. As seen, it is in good agreement with that of the fresh catalyst (Figure 4a). Consequently, the



**FIGURE 10** Leaching test of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO (salenac-OH)] catalyst in the oxidation of dibenzyl sulfide

synthesized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO(salenac-OH)] catalyst has been stable during the present oxidation reactions.

### 3.5 | Leaching test

To verify that the vanadium leaching did not occur during the reaction, oxidation of dibenzyl sulfide was carried out in the optimized conditions. The catalyst was separated from the catalytic system when the yield was about 57% after 0.5 h. Subsequently, the filtrate was stirred at room temperature for an additional 1 h. No further yield of the reaction was observed after the removal of the catalyst (Figure 10). Also, the vanadium content in the filtrate solution was analyzed by atomic absorption spectroscopy (AAS), and it was found that only 1.5% of initial vanadium dissolved in the filtrate solution. These results show that leaching of the [VO(salenac-OH)] complex from the catalyst sample during the oxidation reaction was negligible, and the catalyst was stable.

### 4 | CONCLUSIONS

In summary, the heterogeneous magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@[VO (salenac-OH)] nanocatalyst was synthesized for the first time by covalent grafting of [VO(salenac-OH)] complex on the magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The synthesized catalyst was characterized through FT-IR and EDX spectra, XRD patterns, SEM and TEM images, VSM measurements, TGA, ICP, and elemental analysis. The results showed that this novel catalyst has high catalytic activity in the selective oxidation of sulfides to sulfoxides and oxidative coupling of thiols to disulfides under mild reaction conditions. Moreover, the involved catalyst can be magnetically separated from the reaction mixture and reused five times with no considerable change in its activity.

### ACKNOWLEDGMENTS

The support for this work by the Vali-e-Asr University of Rafsanjan is gratefully acknowledged. The corresponding author also thanks Professor Majid Moghadam from the University of Isfahan and Dr. Zahra Pakdin-Parizi from Razavi Hospital of Mashhad for their useful help.

### AUTHOR CONTRIBUTIONS

Abolfazl Mahdian: Conceptualization; formal analysis; investigation; methodology. Mehdi Hatefi Ardakani: Conceptualization; data curation; formal analysis; investigation; methodology; project administration; resources; software; supervision; validation; visualization. Esmaeil Heydari-Bafrooei: Conceptualization; formal analysis; investigation; visualization. **Samira Saeednia:** Conceptualization; formal analysis; investigation; visualization.

### DATA AVAILABILITY STATEMENT

The data that support the finding of this study are openly available in references.

### ORCID

Abolfazl Mahdian b https://orcid.org/0000-0001-6445-0930

Mehdi Hatefi Ardakani <sup>(b)</sup> https://orcid.org/0000-0002-2216-6840

Esmaeil Heydari-Bafrooei D https://orcid.org/0000-0001-9652-4041

Samira Saeednia D https://orcid.org/0000-0003-1058-2246

#### REFERENCES

- M. Hajjami, F. Ghorbani, S. Rahimipanah, S. Roshani, *Chin. J. Catal.* **2015**, *36*, 1852.
- [2] M. Nikoorazm, F. Ghorbani, A. Ghorbani-Choghamarani, Z. Erfani, J. Iran. Chem. Soc. 2019, 16, 553.
- [3] E. Doustkhah, H. Mohtasham, M. Hasani, Y. Ide, S. Rostamnia, N. Tsunoji, M. H. N. Assadi, *Mol. Catal.* 2020, 482, 110676.
- [4] A. Ghorbani-Choghamarani, Z. Darvishnejad, M. Norouzi, *Appl. Organomet. Chem.* 2015, 29, 170.
- [5] H. Veisi, A. Rashtiani, A. Rostami, M. Shirinbayan, S. Hemmati, *Polyhedron* 2019, 157, 358.
- [6] L. Fang, Q. Xu, Y. Qi, X. Wu, Y. Fu, Q. Xiao, F. Zhang, W. Zhu, Mol. Catal. 2020, 486, 110863.
- [7] H. Xu, J. L. Shi, S. Lyu, X. Lang, Chin. J. Catal. 2020, 41, 1468.
- [8] M. Nikoorazm, A. Jabbari, J. Porous Mater. 2017, 24, 477.
- [9] S. Biswas, A. Ghosh, Polyhedron 2013, 65, 322.
- [10] J. Gradinaru, A. Forni, V. Druta, F. Tessore, S. Zecchin, S. Quici, N. Garbalau, *Inorg. Chem.* 2007, 46, 884.
- [11] G. Grivani, S. Husseinzadeh-Baghan, M. Vakili, A. Dehno-Khalaji, V. Tahmasebi, V. Eigner, M. Dušek, J. Mol. Struct. 2015, 1082, 91.
- [12] G. Grivani, A. Ghavami, M. Kučeráková, M. Dušek, A. Dehno-Khalaji, J. Mol. Struct. 2014, 1076, 326.
- [13] M. Nikoorazm, A. Ghorbani-Choghamarani, M. Khanmoradi, *Appl. Organomet. Chem.* 2016, 30, 236.
- [14] H. Veisi, P. Safarimehr, S. Hemmati, J. Taiwan, Inst. Chem. Eng. 2018, 88, 8.
- [15] H. Veisi, S. Sajjadifar, P. Mohammadi-Biabri, S. Hemmati, Polyhedron 2018, 153, 240.
- [16] T. Ben Zid, I. Khedher, Z. Ksibi, J. M. Fraile, J. Porous, Mater. 2016, 23, 507.
- [17] A. Zabardasti, S. A. Shangaie, J. Iran. Chem. Soc. 2019, 16, 57.
- [18] F. Farzaneh, Y. Sadeghi, J. Mol. Catal. A: Chem. 2015, 398, 275.
- [19] Y. Qi, Q. Xu, G. Tu, Y. Fu, F. Zhang, W. Zhu, *Catal. Commun.* 2020, 145, 106101.
- [20] M. Radko, A. Kowalczyk, P. Mikrut, S. Witkowski, W. Mozgawa, W. Macyk, L. Chmielarz, *RSC Adv.* 2020, *10*, 4023.

16 of 16 WILEY Organometallic

- [21] S. Sobhani, Z. Mesbah-Falatooni, S. Asadi, M. Honarmand, Catal. Lett. 2016, 146, 255.
- [22] F. Hakimi, F. Mirjalili, M. Fallah-Mehrjardi, Asian J. Green Chem. 2019, 4, 183.
- [23] S. Shylesh, V. Schunemann, W. R. Thiel, Angew. Chem., Int. Ed. 2010, 49, 3428.
- [24] M. Hajjami, A. Ghorbani-Choghamarani, R. Ghafouri-Nejad, B. Tahmasbi, *New J. Chem.* 2016, 40, 3066.
- [25] S. Rezaei, A. Ghorbani-Choghamarani, R. Badri, Appl. Organomet. Chem. 2016, 30, 985.
- [26] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J. M. Basset, *Chem. Rev.* 2011, 111, 3036.
- [27] P. H. Li, B. L. Li, H. C. Hu, X. N. Zhao, Z. H. Zhang, Catal. Commun. 2014, 46, 118.
- [28] F. Majidi Arlan, R. Javahershenas, J. Khalafy, Asian J. Nanosci. Mater. 2020, 3, 238.
- [29] K. Sudhakar, A. P. Kumar, B. P. Kumar, A. Raghavender, S. Ravi, D. N. Kenie, Y. Lee, Asian J. Nanosci. Mater. 2018, 1, 172.
- [30] A. Subramaniyan, V. Veeraganesh, Asian J. Nanosci. Mater. 2018, 2, 92.
- [31] Z. Abbasi, S. Rezayati, M. Bagheri, R. Hajinasiri, *Chin. Chem. Lett.* 2017, 28, 75.
- [32] I. Amini, V. Azizkhani, E. Ezzatzadeh, K. Pal, S. Rezayati, M. H. Fekri, P. Shirkhani, Asian J. Green Chem. 2020, 4, 51.
- [33] S. Sajjadifar, S. Rezayati, Z. Arzehgar, S. Abbaspour, M. Torabi Jafroudi, J. Chin. Chem. Soc. 2018, 65, 960.
- [34] H. S. Haeri, S. Rezayati, E. Rezaee Nezhad, H. Darvishi, Res. Chem. Intermed. 2016, 42, 4773.
- [35] E. Rezaee Nezhad, S. Sajjadifar, Z. Abbasi, S. Rezayati, J. Sci. I. R. I. 2014, 25, 125.
- [36] S. Rezayati, Z. Abbasi, E. Rezaee Nezhad, R. Hajinasiri, A. Farrokhnia, *Res. Chem. Intermed.* 2016, 42, 7597.
- [37] N. T. S. Phan, D. H. Brown, H. Adams, S. E. Spey, P. Styring, *Dalton Trans.* 2004, 1348.
- [38] S. Sobhani, Z. Pakdin-Parizi, Appl. Catal. A: Gen. 2014, 479, 112.
- [39] N. Anand, K. H. P. Reddy, T. Satyanarayana, K. S. R. Rao, D. R. Burri, *Catal. Sci. Technol.* **2012**, *2*, 570.
- [40] A. Hasaninejad, M. Shekouhy, N. Golzar, A. Zare, M. M. Doroodmand, *Appl. Catal. A: Gen.* 2011, 402, 11.
- [41] A. Ghorbani-Choghamarani, L. Shiri, G. Azadi, Res. Chem. Intermed. 2016, 42, 6049.

- [42] S. Sobhani, F. Zarifi, Chin. J. Catal. 2015, 36, 555.
- [43] T. Tamoradi, M. Ghadermarzi, A. Ghorbani-Choghamarani, S. Molaei, *Res. Chem. Intermed.* 2018, 44, 4259.
- [44] M. Nikoorazm, A. Ghorbani-Choghamarani, N. Noori, Appl. Organomet. Chem. 2015, 29, 328.
- [45] M. Bagherzadeh, M. M. Haghdoost, A. Shahbazirad, J. Coord. Chem. 2012, 65, 591.
- [46] M. Bagherzadeh, M. Bahjati, A. Mortazavi-Manesh, J. Organomet. Chem. 2019, 897, 200.
- [47] S. Ghahri-Saremi, H. Keypour, M. Noroozi, H. Veisi, *RSC Adv.* 2018, *8*, 3889.
- [48] A. Ghorbani-Choghamarani, B. Ghasemi, Z. Safari, G. Azadi, *Catal. Commun.* 2015, 60, 70.
- [49] Y. Dou, X. Huang, H. Wang, L. Yang, H. Li, B. Yuan, G. Yang, Green Chem. 2017, 19, 2491.
- [50] P. J. Chai, Y. Shu Li, C. Xia Tan, Chin. Chem. Lett. 2011, 22, 1403.
- [51] A. Ghorbani-Choghamarani, P. Moradi, B. Tahmasebi, *RSC Adv.* 2016, 6, 56458.
- [52] T. Tamoradi, A. Ghorbani-Choghamarani, M. Ghadermarzi, N. J. Chem. 2017, 41, 11714.
- [53] M. Bagherzadeh, M. M. Haghdoost, F. Matloubi-Moghaddam, B. Koushki-Foroushani, S. Saryazdi, E. Payab, J. Coord. Chem. 2013, 66, 3025.

#### SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Mahdian A, Ardakani MH, Heydari-Bafrooei E, Saeednia S. Oxo-vanadium(IV) unsymmetrical Schiff base complex immobilized on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles: A novel and magnetically recoverable nanocatalyst for selective oxidation of sulfides and oxidative coupling of thiols. *Appl Organomet Chem*. 2021;35: e6170. https://doi.org/10.1002/aoc.6170