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Alkyl Ammonium Tungstate Bonded to Fe_3O_4@SiO_2 Nanoparticles; a highly efficient Catalyst for the Oxidation of Symmetrical Sulfides to Symmetrical Sulfoxides

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ABSTRACT

A magnetic organic-inorganic hybrid of Fe_3O_4@SiO_2-functionalized propylpiperazine-1,4-diium tungstate (**A**) nanoparticles with a spherical structure was prepared and completely characterized by XRD, SEM, TGA-DTA, and FT-IR spectral techniques. The magnetic hybrid was used in the oxidation of symmetrical sulfides to symmetrical sulfoxides under ambient conditions. The excellent yields of sulfoxides, easy operation, and recovery, magnetic properties of the catalyst, and environmentally friendly system are the key advantages of this method.

Keywords: *Magnetic nano catalysis; Organic-inorganic hybrids; Oxidation; Symmetrical sulfide; Symmetrical sulfoxide*

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1. Introduction

One of the important reasons for researchers' interest in sulfur-containing compounds is their abundance in nature and the fact that sulfur is considered one of the most widely used elements in biologically and medicinally active compounds. Sulfur-containing compounds can be used for various applications from starting materials to useful intermediates in organic reactions. In particular, symmetrical and unsymmetrical sulfides and their sulfoxide analogous, which have been widely used as solvents, glycosyl donors in oligosaccharide synthesis, and intermediates in total organic synthesis show useful antibacterial, antifungal, anti-atherosclerotic, and antihypertensive activities. Therefore, the preparation of sulfur-containing compounds through the development of new, efficient, and safe methods is of particular importance [1-6].

In general, the synthesis of symmetrical and unsymmetrical sulfoxides has been carried out by different methods such as reaction of sulfur dioxide with organolithium or Grignard reagents [7], palladium-catalyzed arylation of alkyl and aryl sulfonate anions [8], reaction of aryl benzyl sulfoxides with aryl bromides [9], reaction of benzyl halides with DMSO [10], addition of thiols to olefins and alkynes [11], Reinheckel protocol [12], Heck vinylations [13], etc. Many of these methods are limited to a narrow range of substrates and always involve complex and harsh reaction systems.

Sulfide oxidation is considered the simplest, cheapest, and most affordable method of preparing sulfoxides. This method is one of the most efficient methods due to the use of different symmetric and asymmetric derivatives of sulfides. So far, various oxidants including arylthiolated Au_{25}(F-Ph)18^- nanocluster [14], H_2O_2 [15], sodium hypochlorite [16], H_5IO_6 [17], urea-hydrogen peroxide complex [18], tert-butyl hydroperoxide [19], ionic liquids containing

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hypervalent iodine [20], $NaBrO_3$ [21], and *N*-fluorobenzenesulfonimide [22] have been used in the process of oxidizing sulfides to sulfoxides. Among these, H_2O_2 is regarded as a superior oxidant in various aspects including simplicity of use, economic efficiency, and compatibility with the environment. One of the main problems of using hydrogen peroxide as an oxidant is the lack of proper ability to oxidize organic compounds and the need to use a catalyst at the same time. So far, several catalytic systems for the oxidation of sulfides to sulfoxides in the presence of H_2O_2 have been reported. The use of metal oxides, Bronsted acids, and supported and complex systems such as SnO_2 nanoparticles [23], cobalt(III)–salen ion [24], dioxo molybdenum(vi) complex immobilized on ascorbic acid-coated TiO_2 nanoparticles [25], copper-Schiff base complex [26], poly(amidoamine) coupled phosphomolybdate hybrid [27], tin porphyrin-based porous aromatic frameworks [28], $ZnFe_2O_4$@l-Arginine-Ni [29], poly (ethylene oxide) composite (Fe_3O_4@PEO-SO_3H) [30], triperoxido derivatives of Nb(V) and Ta(V) immobilized on chitosan [31], and hollow Ag/Mn(btc) [32] are among these examples.

Although many of the reported catalysts have shown positive and appropriate performance, the development of an economical and environmentally friendly method using recyclable catalysts is still of interest to researchers. Therefore, in continuation of our ongoing research [33-48], in this work, a catalyst with a hybrid organic-inorganic structure has been developed and its performance in the oxidation of symmetric sulfides to symmetric sulfoxides has been investigated (**Scheme 1**).

2. Experimental

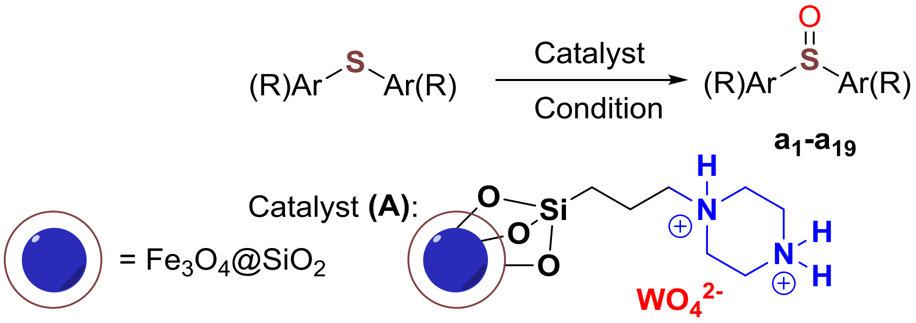
2.1. General procedure:

In a round-bottomed flask, 5 eq of H_2O_2 was added to 2 mmol of sulfide dissolved in 10 mL of ethanol and 0.025g of catalyst **A.** The reaction mixture was then stirred mechanically at 25°C and the progress of the reaction was monitored by TLC. Finally, an external magnet was used to remove the catalyst and the pure products were obtained through column chromatography (Silica gel, Hexane/EtOAc as eluent).

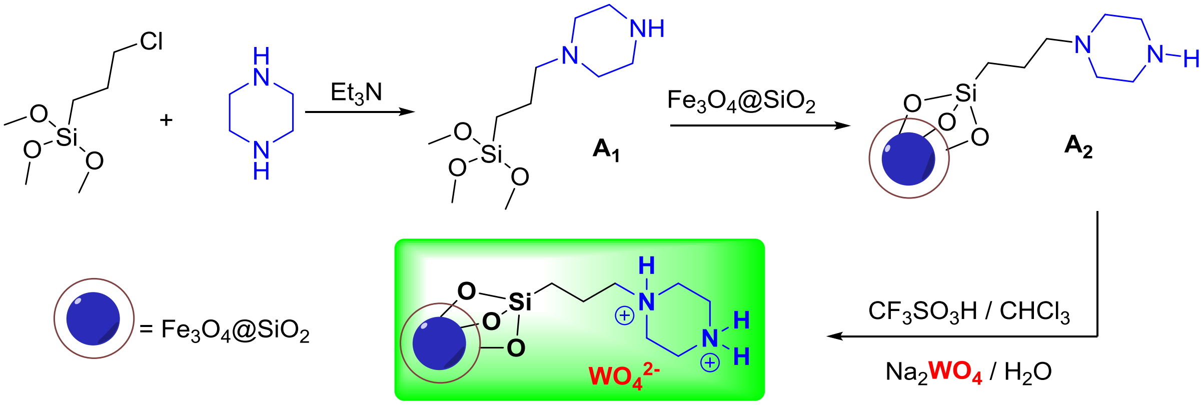
(Note: See Supporting Information for more details of preparation of catalyst and spectra)

3. Results and Discussion

The preparation of $Fe_3O_4@SiO_2$-functionalized propylpiperazine-1,4-diium tungstate (**A**) is shown in **Scheme 2**. First, product $\mathbf{A_1}$ was prepared from the reaction of piperazine with (3-chloropropyl) trimethoxysilane in the presence of Et_3N as the base and trapping agent for HCl gas, which subsequently reacted with $Fe_3O_4@SiO_2$ nanoparticles to form $\mathbf{A_2}$. (**A**) was then prepared by acidification using trifluoromethane sulfonic acid (triflic acid) and subsequent ion exchange of triflate ion by sodium tungstate.



Scheme 1. Catalytic oxidation of symmetrical diaryl(alkyl)sulfides to their sulfoxides analogous



Scheme 2. Preparation of A

The thermal behavior of A was investigated by TGA-DTA analysis (**Fig. 1**). The sample showed a major mass loss in the range of 100-550°C mainly due to the removal of the adsorbed water and the decomposition of the organic part of the compound. Accordingly, the ratio of inorganic to organic parts is nearly 2/1, which is close to the ratio of initial substrates. The WO_4^{2-} values of the catalyst were determined by titration using a barium chloride solution at 0.37 mmol/g. Accordingly, the H^+ capacity of the sample was found to be 0.72 mmol H^+/g.

Fig. 2 shows the XRD pattern of (**A**). The pattern showed a cubic structure of Fe_3O_4 with characteristic peaks at 30.16, 35.61, 43.29, 53.43, 57.43, 62.86, and 73.87 [°2Ө]. The pattern also showed a shoulder located in the 10-30 (°2Ө) range, which may be due to the amorphous phase of silica. The FE-SEM images of the catalyst (A) are depicted in **Fig. 3**. As observed in **Fig. 3**, the catalyst has a homogeneously spherical morphology with an average diameter of less than 100 nm. The EDS analysis indicated the presence of Fe (48.48%), Si (9.18%), W (6.47%), N (0.91%), C (2.92%), and O (31.33%), which confirmed the integration of WO_4^{2-} into the sample. The FT-IR spectrum of the catalyst is depicted in **Fig. 4**. The spectrum shows distinctive peaks centered at 3684 and 3657 cm^{-1}, which could be assigned to the stretching vibration of N-H bands. The WO_4^{2-} group is responsible for the distinctive peak at 1603 cm^{-1}. The sharp peaks located at 639 and 489 cm^{-1} correspond to the W-O and Fe-O bonds, respectively. The signals ascribed to the vibration of C-H, C-C, Si-O-Si, and C-N bonds could be observed at 2980, 1356, 1124, 1027, 971, and 889 cm^{-1}, respectively.

The VSM analysis of **(A)** was performed at room temperature and the corresponding magnetization hysteresis curves are shown in **Fig. 5**. Fe_3O_4, $Fe_3O_4@SiO_2$, and sample A showed reasonable values of magnetic parameters such as saturation magnetization (M_s), remanence magnetization (M_r), and coercivity field (H_c) (**Table 1**).

The lower saturation magnetization of (**A)** compared to Fe_3O_4 and $Fe_3O_4@SiO_2$ is due to the diamagnetic effect of the organic chain. It seems that the saturation magnetization of the sample is sufficient for separation from a solution. Observations show that the sample could be recovered and easily separated by an external magnet.

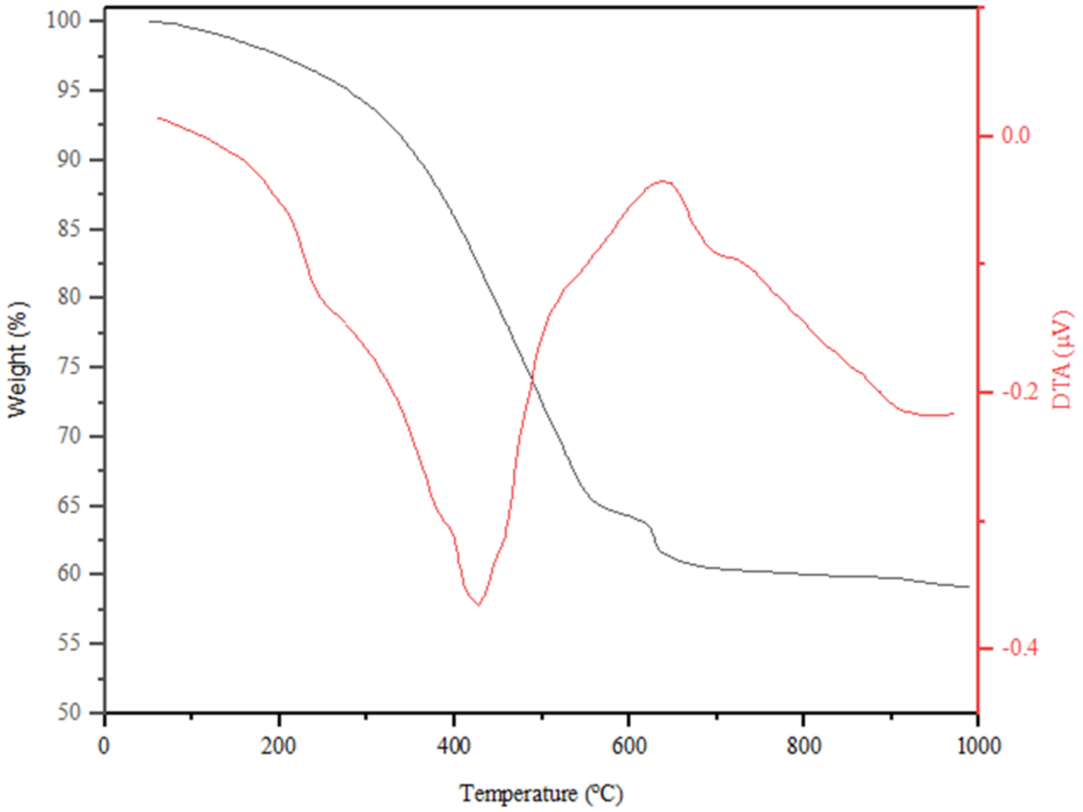


Fig. 1. TGA-DTA analysis of A

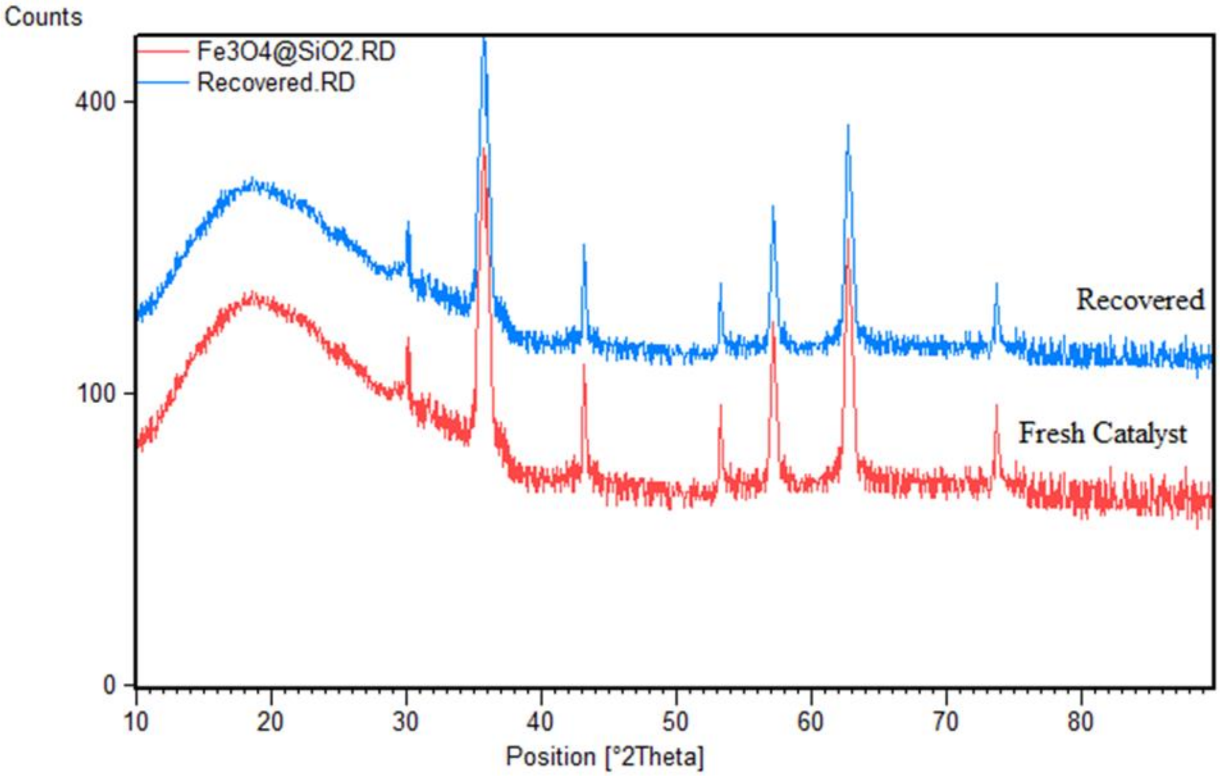


Fig. 2. XRD patterns of fresh and recovered catalyst **(A)**

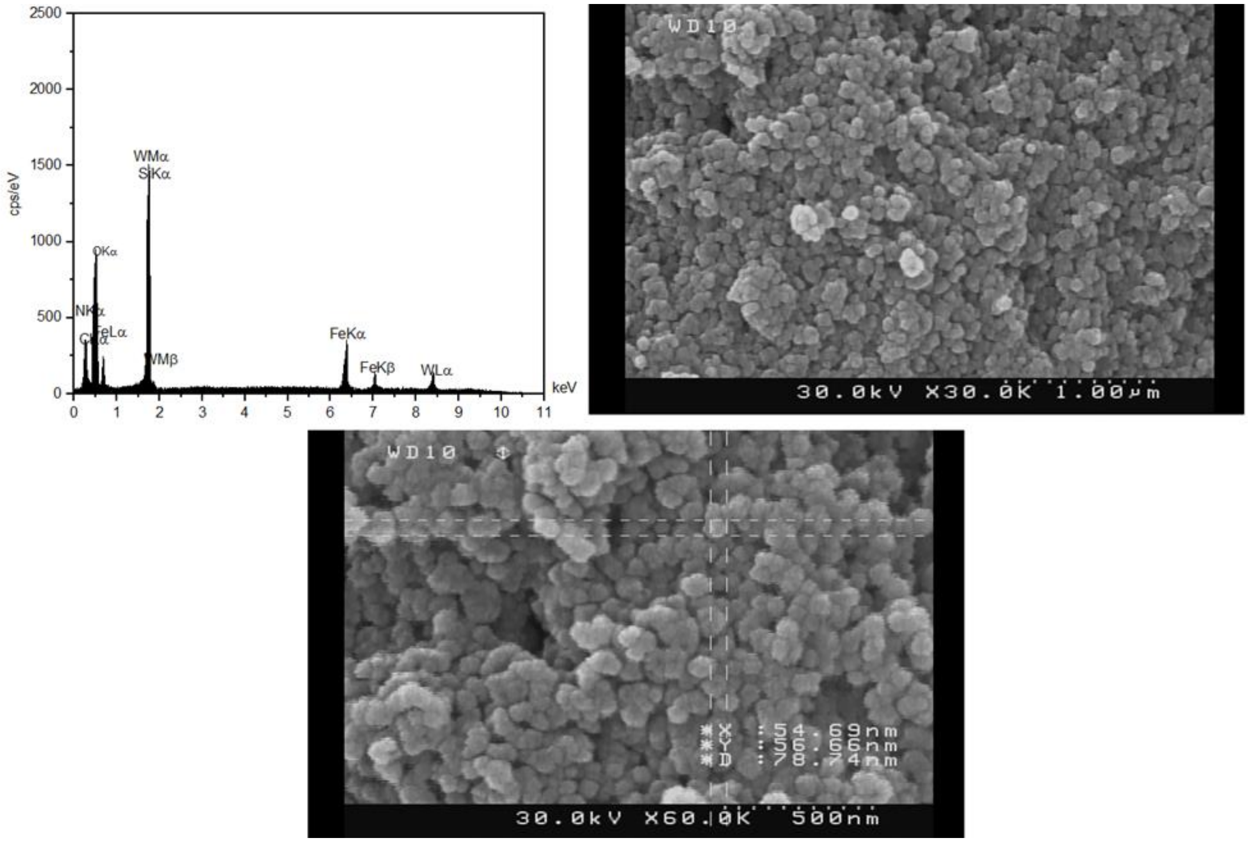


Fig. 3. FE-SEM images and EDX analysis of A

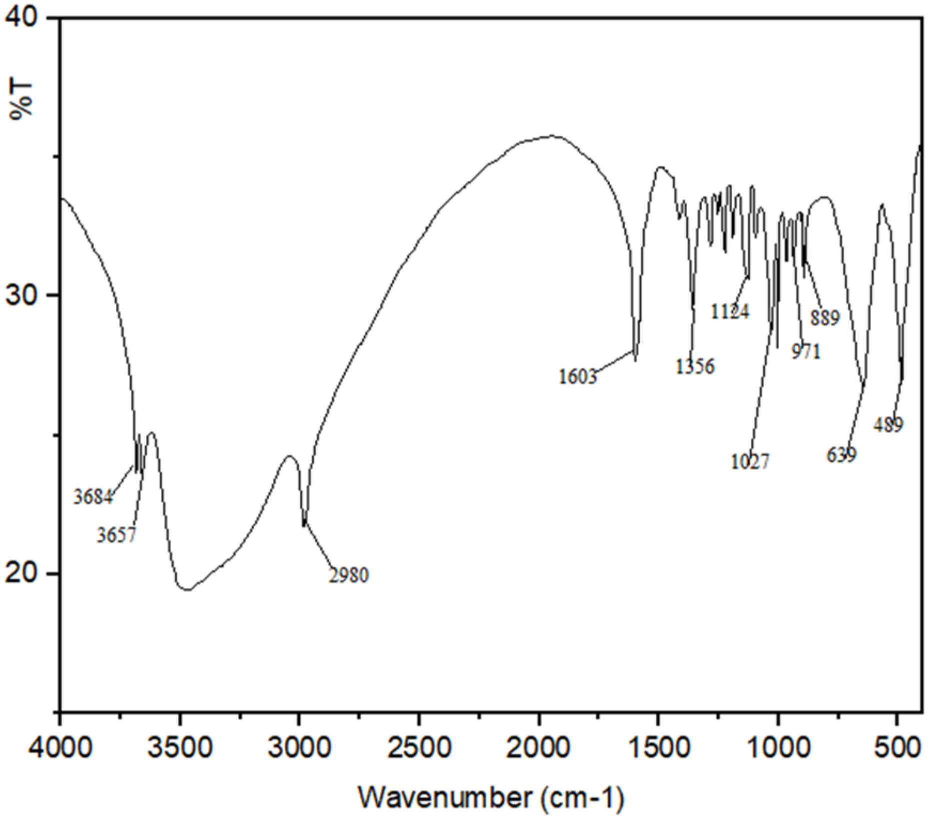


Fig. 4. FT-IR analysis of A

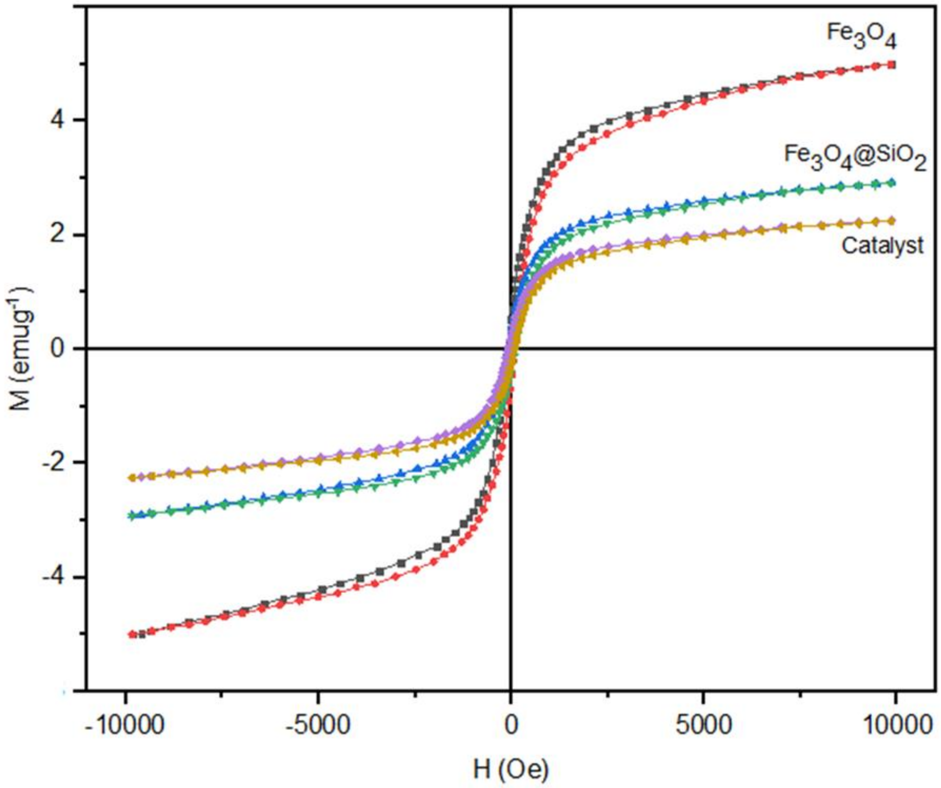


Fig. 5. VSM analysis of A

Table 1. Magnetic parameters of Fe_3O_4, Fe_3O_4@SiO_2, and A

Sample	M_s (memu/g)	M_r (memu/g)	H_c (Oe)
Fe_3O_4	4.87	0.7133	-157.31
Fe_3O_4@SiO_2	2.84	0.3134	-133.54
A	2.21	0.2418	-124.52

The prepared sample was then used as a catalyst in the oxidation of symmetrical sulfides in the presence of H_2O_2 as an oxidant. Initially, to find a suitable media for the process, the reaction was carried out in the catalyst bed and in different solvents. In addition, the effects of other parameters, which could affect the process, including catalyst dosage and oxidant concentration need to be investigated. Thus, diphenyl sulfide was selected as the substrate for oxidation to the corresponding sulfoxide analogous **(1a)**. The results of the optimization conditions are depicted in **Table 2**. First, the process was performed using different ratios of oxidant to the substrate (1:1; 1.2:1; and 2.5:1). The results revealed that the 2.5:1 ratio gave the highest yield of the product (**1a).** Similarly, ethanol was selected as the best solvent for the oxidation process while the suitable catalyst dosage was determined as 0.025g as it provided the highest yields at reasonable reaction times (**Table 2**).

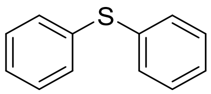
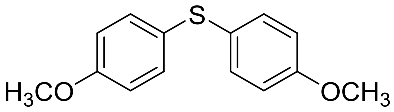
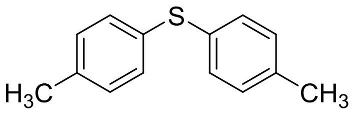
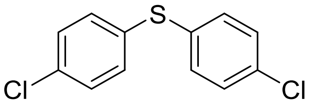
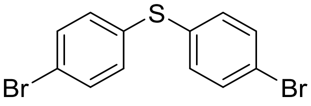
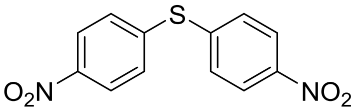
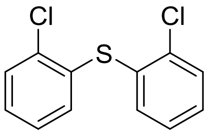
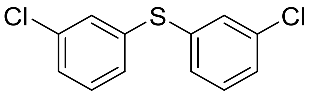
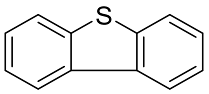
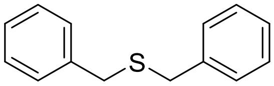
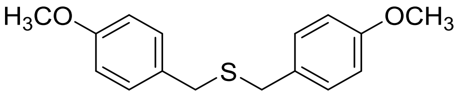
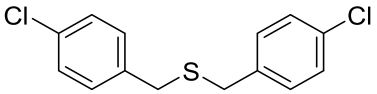
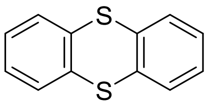
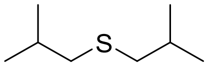
Afterward, the reaction was carried out using various symmetric aromatic and aliphatic sulfides under optimal conditions. It is expected that the electronic effects of the substituted groups on the aromatic ring in diaryl sulfides affect the reaction rate. According to the obtained results, electron-donating substituents increased the reaction rate while electron-withdrawing groups have an adverse effect on the reaction rate (**Table 3**). According to the published works [39-40], the oxidation of sulfides proceeded through the nucleophilic addition of sulfur atom to the protonated H_2O_2 leading to the formation of a sulfonium intermediate (**Scheme 3**). The electron-donating groups could stabilize the positive charge on the sulfur atom and thus the reaction rate increased.

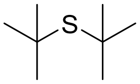
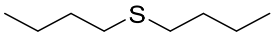
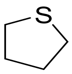
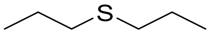
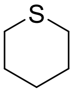
Table 2. Optimization of the reaction conditions

Entry	Catalyst	Condition	Time (h)	Yield (%)*
1	0.025g, 0.018 mmol H^+	EtOH, r.t.; H_2O_2 (30%, 5 eq.)	2.2	98
2	0.025g, 0.018 mmol H^+	EtOH, r.t.; H_2O_2 (30%, 4 eq.)	2.5	71
3	0.025g, 0.018 mmol H^+	EtOH, r.t.; H_2O_2 (30%, 2 eq.)	3	20
4	0.025g, 0.018 mmol H^+	Hexane, r.t.; H_2O_2 (30%, 5 eq.)	3	-
5	0.025g, 0.018 mmol H^+	CH_2Cl_2, r.t.; H_2O_2 (30%, 5 eq.)	3	-
6	0.025g, 0.018 mmol H^+	$CHCl_3$, r.t.; H_2O_2 (30%, 5 eq.)	3	-
7	0.025g, 0.018 mmol H^+	Toluene, r.t.; H_2O_2 (30%, 5 eq.)	4	20
8	0.025g, 0.018 mmol H^+	DMF, r.t.; H_2O_2 (30%, 5 eq.)	2	35
9	0.025g, 0.018 mmol H^+	H_2O, r.t.; H_2O_2 (30%, 5 eq.)	4	65
10	0.025g, 0.018 mmol H^+	EtOAc, r.t.; H_2O_2 (30%, 5 eq.)	5	30
11	0.01g, 0.0072 mmol H^+	EtOH, r.t.; H_2O_2 (30%, 5 eq.)	3	21
12	0.05g, 0.036 mmol H^+	EtOH, r.t.; H_2O_2 (30%, 5 eq.)	2	96
13	0.075g, 0.054 mmol H^+	EtOH, r.t.; H_2O_2 (30%, 5 eq.)	2	95
14	0.1g, 0.072 mmol H^+	EtOH, r.t.; H_2O_2 (30%, 5 eq.)	2	96
15	-	EtOH, r.t.; H_2O_2 (30%, 5 eq.)	5	-

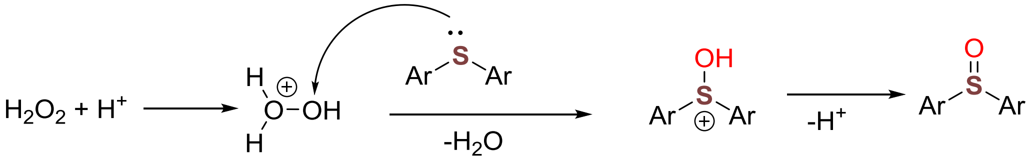
*Isolated Yield; Sulfide (2mmol), based on the preparation of **1a**

Table 3. Preparation of **(a_1-a_{19})**

Sulfide	Product	Time (h)	Yield (%)*	M.p. (°C)
	**a_1**	2.2	98	70-72
	**a_2**	1.5	99	105-107
	**a_3**	1.5	97	95-97
	**a_4**	4	96	115-117
	**a_5**	4	90	131-133
	**a_6**	5	75	151-153
	**a_7**	5	90	121-123
	**a_8**	4	95	114-116
	**a_9**	2.5	97	111-113
	**a_{10}**	2	98	130-132
	**a_{11}**	2	97	141-143
	**a_{12}**	4	90	155-157
	**a_{13}**	2.5	97	96-98
	**a_{14}**	3	89	Oil

	**a$_{15}$**	3	91	Oil
	**a$_{16}$**	3	90	Oil
	**a$_{17}$**	2.5	91	Oil
	**a$_{18}$**	3	92	Oil
	**a$_{19}$**	2.5	98	Oil

*Isolated Yields



Scheme 3. Reaction mechanism for the oxidation of sulfides to sulfoxides

The comparison of the catalytic potential of A with those of different Lewis and Bronsted acid catalysts indicated the good catalytic activity of A in terms of reaction time and yield (**Table 4**).

Finally, an external magnet could be used to recover the catalyst, which was then washed with ethanol, dried, and used again. The oxidation of diphenyl sulfide to diphenyl sulfoxide (**1a**) was chosen for the recovery test. The recovery experiments showed acceptable results after 11 catalytic runs (**Fig. 6**). The XRD pattern of the recovered catalyst confirmed the stability of the catalyst during the reaction (**Fig. 2**). In addition, after each run, the recovered catalyst was tested using titration by barium chloride solution. The results indicated good catalyst stability and no obvious leaching was detected.

Table 4: Comparison of the results of **A** with those of different catalysts

Entry	Catalyst	Time (h)	Yield (%)*
1	A	2.2	98
2	Na_2WO_4	5	18
4	ZnO	5	45
5	$ZnCl_2.6H_2O$	5	49
6	$FeCl_3.6H_2O$	5	64
7	SiO_2-$FeCl_3$	5	85
12	MgO	5	45
13	NiO	5	71
14	$MgCl_2.6H_2O$	5	40
15	$NiCl_2$	5	53
16	$NiSO_4$	5	31
17	$FeSO_4.6H_2O$	5	15

*Isolated Yield; Sulfide (2mmol), based on the preparation of **1a** (Condition: EtOH, r.t.; H_2O_2 (30%, 5eq), catalyst: 0.018 mmol)

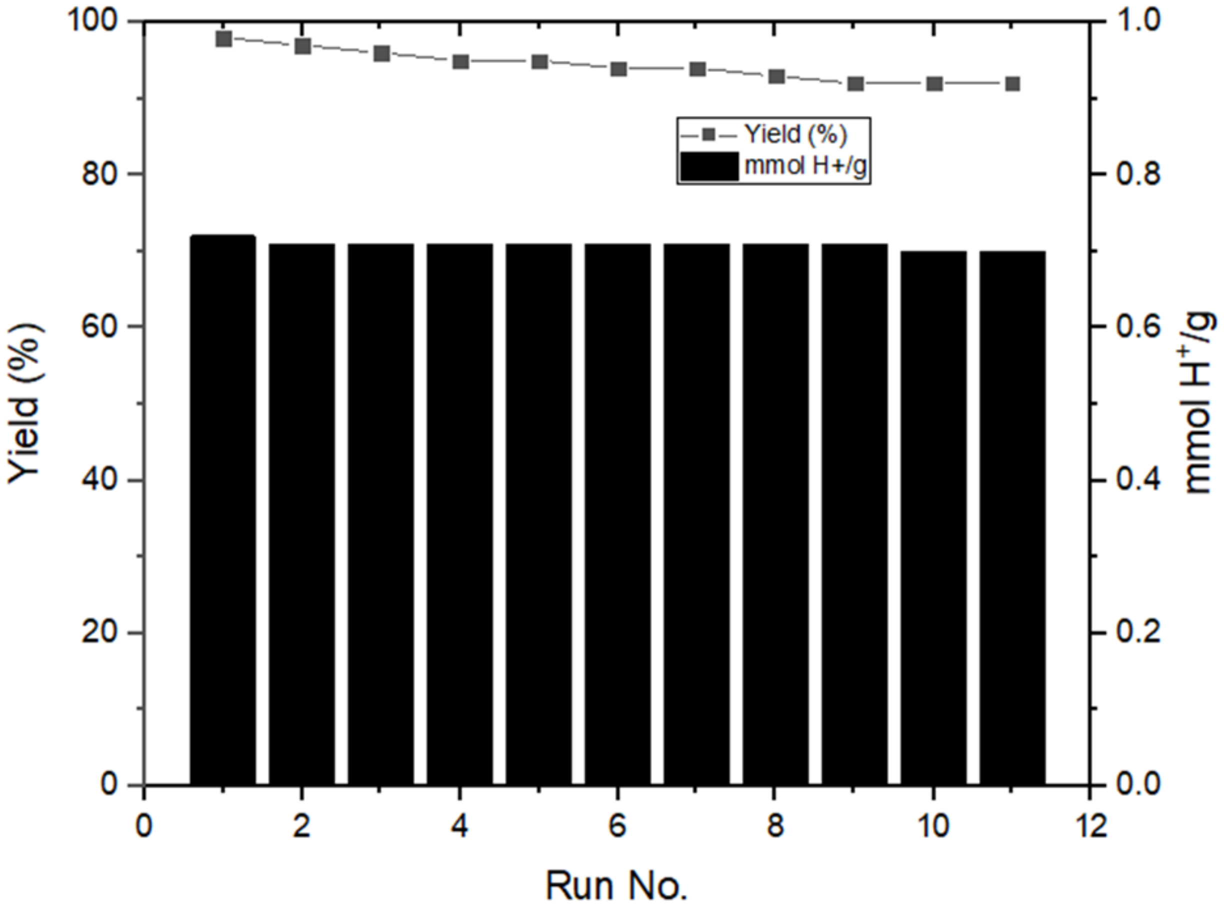


Fig. 6. Recovery of **A** and leaching test results in the oxidation of diphenyl sulfide to (**1a**)

4. Conclusions

$Fe_3O_4@SiO_2$ functionalized propylpiperazine-1,4-diium tungstate (**A**) was applied in the oxidation of symmetrical sulfide to sulfoxide analogous. The TGA-DTA analysis indicated the stability of this organic-inorganic hybrid up to 300 °C. In addition, the ratio of inorganic to organic parts was 2/1, which was close to that of the initial substrates. Using the barium chloride titration test, the H^+ capacity of the sample was determined to be 0.72 mmol H^+/g. The XRD pattern of the fresh and recovered samples of (**A**) confirmed the stability of the catalyst. The chemical composition of the catalyst determined by EDS analysis confirmed the integration of WO_4^{2-} into the sample. The VSM analysis of **(A)** showed reasonable magnetic behavior, indicating the recoverability and facile removal of the catalyst sample using an external magnet. The results of sulfide oxidation showed promising potential and easy recovery of magnetic nano-catalysts. In addition, the oxidation reactions were performed under mild conditions and the magnetic nano-catalyst showed excellent stability, activity, and reusability.

Declaration of Interest

The authors declare that they have no interest to influence the work reported in this paper.

Data Availability Statement

The spectral data, which could support our findings, are available as a supplementary material attached to this article.

Supplementary Materials

Supplementary data to this article is attached as a separate file.

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