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Fe₃O₄/PEG-SO₃H as heterogeneous and magnetically recyclable nanocatalyst for oxidation of sulfides to sulfones or sulfoxides

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Abstract. We detail below of sulfonated-polyethylene glycol coated Fe_3O_4 nanocomposite ($Fe_3O_4/PEG-SO_3H$) as a greatly effective and ecological nanocatalyst for the selective oxidation of sulfides to sulfoxides or sulfones, in brilliant yields under solvent-free conditions, whilst employing 30% hydrogen peroxide as an oxidant. A number of sulfides containing alcohol, ester, and aldehyde functional groups are fruitfully and selectively oxidized without altering the desired characteristics. The magnetic nanocatalyst ($Fe_3O_4/PEG-SO_3H$) can be conveniently and swiftly retrieved through the utilization of an external magnetic tool and recycled for greater than 10 reaction runs without significantly decreasing its catalytic behavior.

Keywords: Magnetic, Nanocatalyst, Sulfide, Sulfone, Sulfoxide

1. Introduction

Immobilization of homogeneous catalysts on solid supports provides intriguing paths for the advancement of innovative and stimulating catalysts due to their simple separation from the reaction vessel, permitting the salvage of the solid and later its reapplication. The greatest band of evolution in the surface immobilization strategy is the covalent fastening of the organic compound or ligand to the solid surface [1]. The addition of organic moieties with pendant fastened chains, either to the external component or the interior surface, is a procedure applied to alter the physical and chemical traits of natural or synthesized substances. It can enhance the capabilities of the new multifunctional substances- considered as "inorganic-organic hybrids"- to work in various academic or technological applications [2]. An unambiguous benefit of this form of hybrids is the optimal blend of both organic and inorganic characteristics in a single nanomaterial [2].

The selective oxidation of sulfides to sulfoxides or sulfones has been an endeavor for a long time and is a valuable conversion used in organic chemistry [1,2]. The outcomes resulted in scientists attempting to validate the chance of formulating an innovative method for the oxidation of sulfides. After the earliest recorded procurement of sulfoxides by Maercker in 1865, a large portion of procedures have been advanced for this transformation of sulfides to sulfoxides [3], and a number of other oxidants, including high-valence metal salts, concentrated HNO₃ [4], m-chloroperoxybenzoic acid, sodium metaperiodate [5], halogens, and nitrogen pentoxide, have been vastly applied for the oxidation of sulfides [6-10]. Regrettably, a large portion of the procedures utilize hazardous, toxic reagents [11] or complex reaction methods [12] are convoyed by overoxidation of sulfoxides to the expected sulfones or other undesired by-products [13,14]. To deal with these restrictions and accounting the eco-sustainability, green chemistry, and especially atom economy, a great amount of research has been focused on enhancing innovative and effective catalytic systems, based on the employment of aqueous 30% H₂O₂ as a final ecological oxidant due to its extraordinary advantages such as its low cost, eco-friendliness, efficient-oxygen content, and the formation of water as a side product [15].

Using a homogeneous catalyst in such a process will require the expensive catalyst to be removed from the reaction vessel and a chromatographic method for this retrieval is unavoidable [16]. We are therefore reliant on manufacturing catalytic arrangements that are based on organic material and metal as well as supported catalysts for the activation of hydrogen peroxide in this procedure [17], which can simply be retrieved from the reaction vessel and reemployed. Despite the advancements made over the years, most of the methods mentioned in academic literature describe fruitless efforts at controlling the reaction for selective and excellent yielding procurement of sulfoxide or sulfone. All the while, a selection of vanadium (V) Schiff base complexes has received noticeable praise for their great functional compatibilities and selectivity in the oxidation of sulfides [18].

Quite recently, a magnetically solid acid composite was prepared with the assistance of PEG. Initially a PEG layer was coated on the Fe₃O₄ NP's surface and then sulfonated- polyethylene glycol coated Fe₃O₄ nanocomposite (Fe₃O₄/PEG) was produced as a significantly effective solid acid magnetic nanocatalyst by chlorosulfonic acid and utilized as a magnetic nanocatalyst (Fe₃O₄/PEG-SO₃H) in the Paal-Knorr reaction [19]. Following through with our investigation to produce selective, efficient and ecological methods and catalysts in organic synthesis [20], we disclose the study of the selective oxidation of sulfides to sulfoxides or sulfones under mild conditions, utilizing sulfonated-polyethylene glycol coated Fe₃O₄ nanocomposite (Fe₃O₄/PEG-SO₃H) (Scheme 1).

Experimental

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Typical experimental procedure for the preparation of sulfoxides

In a 25 ml round bottom flask, 30% (w/w) H_2O_2 (1.2 equiv, 0.5 g) and the Fe₃O₄/PEG-SO₃H catalyst (10 mg) were successively added to sulfide (1 mmol) and the mixture was stirred magnetically at room temperature for desired time. The progress of the reaction was monitored by TLC (EtOAc/n-hexane, 1/10). After completion of the reaction, the catalyst was separated from the product by an external magnet (within 5 s) and the mixture was washed with Et₂O (2 × 5 mL) and decanted. The combined organics were dried over anhydrous Na₂SO₄ and then evaporation of diethyl ether under reduced pressure gave the pure products in 80-98% yields. Further purification was achieved by chromatography on silica gel with n-hexane/ethylacetate. All reaction products were identified by GC chromatogram, ¹H NMR, IR spectra and melting point as compared with authentic samples.

Typical experimental procedure for the preparation of sulfones

In a 25 ml round bottom flask, 30% (w/w) H_2O_2 (3 equiv, 1.2 g) and the Fe₃O₄/PEG-SO₃H catalyst (20 mg) were successively added to sulfide (1 mmol) and the mixture was stirred magnetically at room temperature for desired time. The progress of the reaction was monitored by TLC (EtOAc/n-hexane, 1/10). After completion of the reaction, the catalyst was separated from the product by an external magnet (within 5 s) and the mixture was washed with Et₂O (2 × 5 mL) and decanted. The combined organics were dried over anhydrous Na₂SO₄ and then evaporation of diethyl ether under reduced pressure gave the pure products in 80-98% yields. Further purification was achieved by chromatography on silica gel with 1:1 n-hexane/ethylacetate. All reaction products were identified by GC chromatogram, ¹H NMR, IR spectra and melting point as compared with authentic samples.

Procedure for reusing the catalyst

After the reaction time, the catalyst $Fe_3O_4/PEG-SO_3H$ was separated by an external magnet and washed several times with EtOH, water and acetone. Then, the recovered dried catalyst under vacuum was used for another run.

3. Results and Discussion

Polyethylene glycol (PEG) is used to alter Fe₃O₄ NPs and the newly synthesized Fe₃O₄/PEG is sulfonated by chlorosulfonic acid to make polyethylene glycol sulfonic acid-functionalized magnetic Fe₃O₄ nanoparticles (Fe₃O₄/PEG-SO₃H) as solid acid magnetic nanocatalyst. The content of acid sites of Fe₃O₄@PEG400-SO₃H nanocomposite was estimated by back titration using HCl (0.337 N). 10 mL of NaOH (0.130 N) was added to 0.1 g of this composite and stirred for 30 min. The catalyst was separated and washed with deionized water. The excess amount of NaOH was titrated with HCl (0.337 N) in the presence of phenolphthalein as indicator. The acid site content was 1.35 mmol g⁻¹. Also, the ion-exchange pH-analysis demonstrated a loading of 1.42 mmol SO₃H g⁻¹. The BET surface area, pore size and pore volume of this composite are 32.89 m²·g⁻¹, 22.1 nm and 0.09 m³·g⁻¹, respectively. Using 30% H₂O₂ as a green oxidant, the selective oxidation of sulfides to sulfoxides or sulfones was used to investigate the catalytic activity of the heterogeneous and magnetically recyclable solid acid nanocatalyst, Fe₃O₄/PEG-SO₃H (Scheme 1).



R₁, R₂ = alkyl and aryl

Scheme 1. $Fe_3O_4/PEG-SO_3H$ catalyzed the oxidation of using H_2O_2 .

We detail the chemoselective oxidation of sulfides to sulfoxides or sulfones with H_2O_2 in the presence of a catalytic proportion of $Fe_3O_4/PEG-SO_3H$ by monitoring the amount of H_2O_2 and catalyst and controlling these quantities (Scheme 1). Initially, to ensure optimal reaction conditions we determined the effect of various quantities of hydrogen peroxide and catalyst on the oxidation of diphenyl sulfide, a relatively inert substrate, as a model compound with respect to duration and resulting product yield (Table 1). Table 1 shows that even after 12 h, the reaction had not completed due to there being no catalyst (entries 4 and 10). When $Fe_3O_4/PEG-SO_3H$ was included, the times were reduced substantially and the yield had increased to 98%. H_2O_2 (1.2 equiv) in the presence of the nanocatalyst (10 mg) was discovered to be optimal for the entire transformation of sulfides to sulfoxides. The

application of excess H_2O_2 (3.0 equiv) in the presence of $Fe_3O_4/PEG-SO_3H$ (20 mg) resulted to the respective sulfone in a clean reaction.

Table 1

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Optimization of the amounts of H_2O_2 and $Fe_3O_4/PEG-SO_3H$ for the selective oxidation of diphenyl sulfide to diphenyl sulfoxide or diphenyl sulfone.^a

Entry	H_2O_2	Catalyst	Time	Yield (%) ^b	
	(equiv)	(mg)	(min.)	Sulfoxide ^b	Sulfone ^c
1	0.5	10	30	30	-
2	1.0	10	10	70	-
3	1.2	10	3	96	-
4	1.2	0	24 h	70	-
5	1.2	5	30	75	-
6	2.4	10	30	-	65
7	3.0	10	30	-	70
8	3.0	20	10	-	96
9	3.0	10	60	-	75
10	3.0	0.0	12 h	-	45

^aReaction conditions: sulfide (1 mmol), 30% H_2O_2 , Fe₃O₄/PEG-SO₃H, rt. ^bIsolated yield

The simplicity of this method has been highlighted by an easy oxidant of a vast number of alkyl, aryl and aromatic sulphides as shown in Tables 2. The reaction demonstrates appropriate general utilization for the synthesis of both sulfoxides and sulfones. The intended products were attained in minimal times and in excellent yields. It is important to understand that the sulphides were oxidized chemoselectively in the presence of functional groups impervious to oxidation, such as OH, C=C, C=NH, C=NOH, CHO (Table 2, entries 8, 15, 9, 11, 12, 16). The effect of steric hindrance to the oxidation by an *ortho* substituted system (Table 2, entry 5) was studied and the related products was obtained in good yields. The likely mechanism for the oxidation of sulphide to the respective sulfoxide or sulfone employing H_2O_2 in the presence of Fe₃O₄/PEG-SO₃H is outlined in Scheme 2.

Table 2

Selective oxidation of sulfides to sulfoxides or sulfones under solvent-free condition.

Entry	Substrate	Sulfoxide ^a		Sulfone ^b		
		Time (min) Yield		Time (min) Yield		Ref.
		(%)		(%)		
1	S S	3	96	10	96	25b
2	S_	3	92	15	92	25b
3	s,	2	92	10	90	25b

4	S_S_S	5	96	20	94	25b
5	NO ₂ S	15	90	30	90	21
6		10	90	30	85	25b
7	O ₂ N S	5	90	20	90	25b
8	Br	5	90	20	88	25b
9	ССССОН	10	90	30	85	25b
10	S S S S S S S S S S S S S S S S S S S	12	92	20	90	21
11	HON	10	92	30	88	25b
12	N S	12	90	30	85	25b
13	S S	10	96	25	90	25b
14	× _ S _ /	10	95	30	90	25b
15	, S, ОН	8	90	20	85	22
16	S H	10	85	20	82	22

^aReaction conditions: sulfide (1 mmol), 30% H_2O_2 (1.2 equiv), Fe₃O₄/PEG-SO₃H (10 mg), rt. ^bReaction conditions: sulfide (1 mmol), 30% H_2O_2 (3.0 equiv), Fe₃O₄/PEG-SO₃H (20 mg), rt.

To investigate the reusability of Fe₃O₄/PEG-SO₃H, the catalyst was removed from the reaction mixture by a magnetic device as noted earlier and reapplied for the proceeding run after being rinsed with acetone. As expected, the catalyst was capable of being employed in 12 or more cycles for the oxidation of diphenyl sulfide to the respective sulfone. There was no evidence after 10 minutes of reaction that there was any decrease in conversions. (Fig. 1). A hot filtration test was also executed to check the leaching of sulfonic acid from the surface; but after 10 mins of reaction there was an insignificant quantity of reaction progress. The TEM image from the recycled catalyst after 12 cycles revealed that its nanostructure had been kept during the reactions and after the multiple runs (Fig. 2). Elemental analysis (CHNS) of

recovered catalyst following the 12 runs demonstrated that the leaching of active catalytic locations was less than 5 wt% from the total quantity of catalytic sites. Also, the ion-exchange pH-analysis for recovered catalyst demonstrated a loading of 1.34 mmol SO₃H g⁻¹. Additionally, this result confirmed by back-titration analysis of the catalyst.



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Fig. 1 Reusability of the nanocatalyst



Fig. 2. TEM images of fresh a); and reused catalyst Fe3O4/PEG-SO3H after the 12th run b).

The degree of crystallinity and phase investigation of $Fe_3O_4/PEG-SO_3H$ (a), and reused $Fe_3O_4/PEG-SO_3H$ (b) after the 12th run were performed by powder X-ray diffraction (XRD), which presented in Figure 3. It can be seen that the fresh catalyst has highly crystalline and cubic spinel structure which agrees with the standard Fe_3O_4 XRD pattern (cubic phase). This pattern is indicative of a crystallized structure at 20: 31.3°, 35.9°, 43.4°, 53.8°, 57.1° and 62.5°, which can be assigned to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) crystallographic faces of magnetite (reference JCPDS card no. 19-629). The position of peaks in reused $Fe_3O_4/PEG-SO_3H$ catalyst was consistent and do not show any change during the reaction process, which is indicative that the trystalline structure of the magnetite was essentially maintained.



Fig. 3. XRD patterns of fresh a); and reused catalyst Fe₃O₄/PEG-SO₃H after the 12th run b).

The DLS measurements were applied to verify the nanostructure of $Fe_3O_4/PEG-SO_3H$ that reused after 12 runs with fresh catalyst. Its demonstrated that the catalyst remained in same nanometer-sized particles as quasi-spherical without change with a mean diameter of 18-25 nm (Fig. 4).



Fig. 4. DLS images of fresh a); and reused catalyst Fe₃O₄/PEG-SO₃H after the 12th run b).

We compared the oxidation of diphenyl sulfide with data from the other academic sources with the results of the $Fe_3O_4/PEG-SO_3H$ to determine its catalytic power. Table 3 demonstrates that the procedures that were previously reported were prone to having at least one of the following disadvantages: elevated reaction temperatures [17,20-24], longer reaction times [17,21-24], use of a transition metal [16,21-24], and the necessity of volatile and/or toxic organic solvents [16-24].

Table 3: Comparison present methodology with literature in the synthesis of diphenyl sulfone.

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Entry	Reaction conditions	Time (min)	Yield%	Ref.
1	Fe ₃ O ₄ /PEG-SO ₃ H, solvent-free, r.t.	10	96	This work
2	MoO_2Cl_2 , acetone, r.t.	33	91	[16]
3	$H_5PMo_{11}Al_{0.5}V_{0.5}O_{40}$, CH ₃ CN, reflux	240	95	[17]
4	Silica sulfuric acid, CH ₃ CN,r.t.	45	95	[18]
5	TaCl ₅ , CH ₃ OH, reflux	210	90	[21]
6	Carbon-based solid acid, $C_2H_4C_{12}$, reflux	10	95	[22]
7	Pd Schiff base complex, CH ₃ CN, 50 °C	330	72	[23]
8	Au/CTN-silica, CH ₃ OH, 60 °C	180	96	[24]

4. Conclusions

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To conclude, the report has highlighted $Fe_3O_4/PEG-SO_3H$ as a heterogeneous magnetic nanocatalyst can encourage the selective oxidation of a number of sulfides into their respective sulfoxides and sulfones in the presence of H_2O_2 as the terminal oxidant. This acidic magnetic catalyst can effectively replace soluble acids as a result of their benefits, including high catalytic behavior under mild reaction conditions, good to excellent yields, control over the degree of oxidation (which offers access to sulfoxides or sulfones), high chemo-selectivity, convenient removal of the catalyst via and external magnetic device an recyclability of the catalyst for multiple runs without noticeable decreases in the reaction's yields.

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Graphical Abstract

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