



# TiO<sub>2</sub> nanoparticles and Preyssler-type heteropoly acid modified nano-sized TiO<sub>2</sub>: A facile and efficient catalyst for the selective oxidation of sulfides to sulfones and sulfoxides

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## ABSTRACT

A new and efficient synthetic method has been developed for the selective conversion of sulfides into their corresponding sulfones and sulfoxides using H<sub>2</sub>O<sub>2</sub> in the presence of neat or Preyssler-type heteropoly acid modified nano-sized TiO<sub>2</sub> as catalyst, respectively. The reaction was performed at room temperature with quantitative yields. The catalyst is reusable without significant loss of activity for the next oxidation reaction.

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## 1. Introduction

Sulfones and sulfoxides are important intermediates in the synthesis of many interesting biologically active compounds [1–5]. Omeprazole and Figpronil pesticide are two typical examples of extensive application of these intermediates in pharmaceutical and fine chemical industries [6]. For this reason the oxidation of sulfides to sulfoxides or sulfones has been the subject of many studies and a large number of synthetic procedures are now available [7–10]. The advantages of application of hydrogen peroxide are due to its effective oxygen content, eco-friendly green oxidant, low cost, and also safety in storage and operation [11,12]. Various methods including gold(III)–hydrogen peroxide [13], silica-immobilized vanadyl alkyl phosphonate–sodium bromate [14], silica sulfuric acid–hydrogen peroxide [15] and titanium based catalysts are used for oxidation of sulfides.

Heteropoly acids (HPs) normally operate either as multi-electron oxidants or strong acids. Their acid strength are usually higher than classical acids [16,17]. They are also used as industrial catalysts for several liquid-phase reactions [18–21].

Recently, nanomaterials have been a topic of interest as heterogeneous catalysts since they have extraordinary properties relative to their corresponding bulk materials. Currently, nanometal oxides have drawn the researchers' attention due to their unusual physical and chemical catalytic properties [22–24] and are proved to be promising catalysts because of their high activity, non-toxicity, ease of availability, reusability, strong oxidizing power, and long-term stability [7,25–27].

The aim of this study is to investigate the enhancement of selectivity and efficiency of the nano-sized TiO<sub>2</sub> for oxidation of sulfides into their corresponding sulfoxides by supporting of Preyssler heteropoly acid on TiO<sub>2</sub> nanoparticles (Scheme 1).

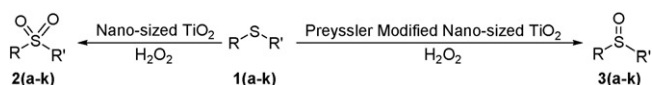
## 2. Experimental

### 2.1. Reagents

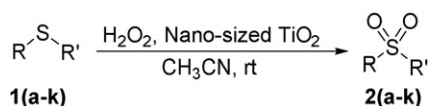
Methyl phenyl sulfide was purchased from Merck and used as such without further purification. The commercially available micro-TiO<sub>2</sub> was obtained from Merck. Titanium tetra-*n*-butoxide (TTB) obtained from Fluka and converted into the nano-sized TiO<sub>2</sub> according to literature [28].

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Scheme 1.



Scheme 2.

## 2.2. General procedure for oxidation of sulfides to sulfones

To a stirred mixture of sulfide (**1a–k**) (1 mmol) and nano-sized TiO<sub>2</sub> (0.31 mmol, 25 mg) in CH<sub>3</sub>CN (10 ml), 30% H<sub>2</sub>O<sub>2</sub> (2.5 equiv., 0.15 ml) was added at room temperature. After the completion of

**Table 1**  
Solvent effect on chemoselective oxidation of methyl phenyl sulfide to sulfone.

Solvent	Sulfide %	Sulfoxide %	Sulfone %
CH <sub>3</sub> CN	0	0	100
<i>t</i> -Butanol	0	6	94
MeOH	0	43	57
Acetone	0	26	74
THF	16	82	4
AcOH	0	90	10

All the reactions were carried out with 1 mmol of methylphenylsulfide, 25 mg of nano-sized TiO<sub>2</sub> (15 nm) in 10 ml of solvent and 2.5 equiv. of 30% aqueous hydrogen peroxide at room temperature after 1.5 h.

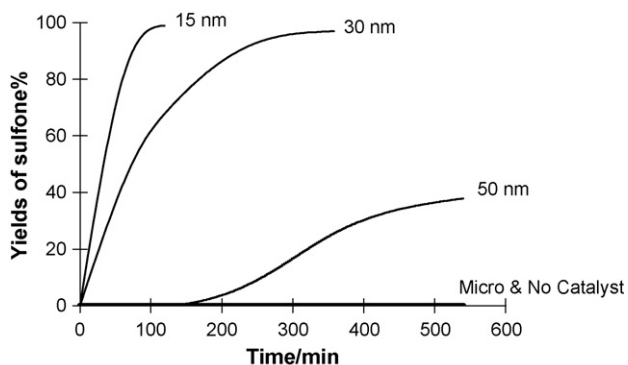
the reaction, which was monitored by TLC, the catalyst was centrifuged off. The organic phase was evaporated and then CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added to the resultant. It was washed with water (2 × 10 ml) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure to afford the crude product.

**Table 2**  
Substrates tested in oxidation of sulfides to sulfones with H<sub>2</sub>O<sub>2</sub> in the presence of nano-sized TiO<sub>2</sub> (15 nm)<sup>a</sup>.

Entry	Substrate	Time (h)	Conversion (%)	Yield (%) <sup>b</sup>	
				Sulfoxide	Sulfone
1		1.5	100	0	100
2		3	95	0	100
3		5.5	100	0	100
4		3	100	0	100
5		10	100	0	100
6		5.4	100	0	100
7		1.5	100	0	100
8		4.5	100	0	100
9		7	100	0	100
10		10	100	20	80
11		8.5	100	5	95

<sup>a</sup> All the reactions were carried out with 1 mmol of substrate, 25 mg of nano-sized TiO<sub>2</sub> (15 nm) in 10 ml of CH<sub>3</sub>CN and 2.5 equiv. of 30% aqueous hydrogen peroxide at room temperature.

<sup>b</sup> Determined by <sup>1</sup>H NMR and were compared with the authentic samples.

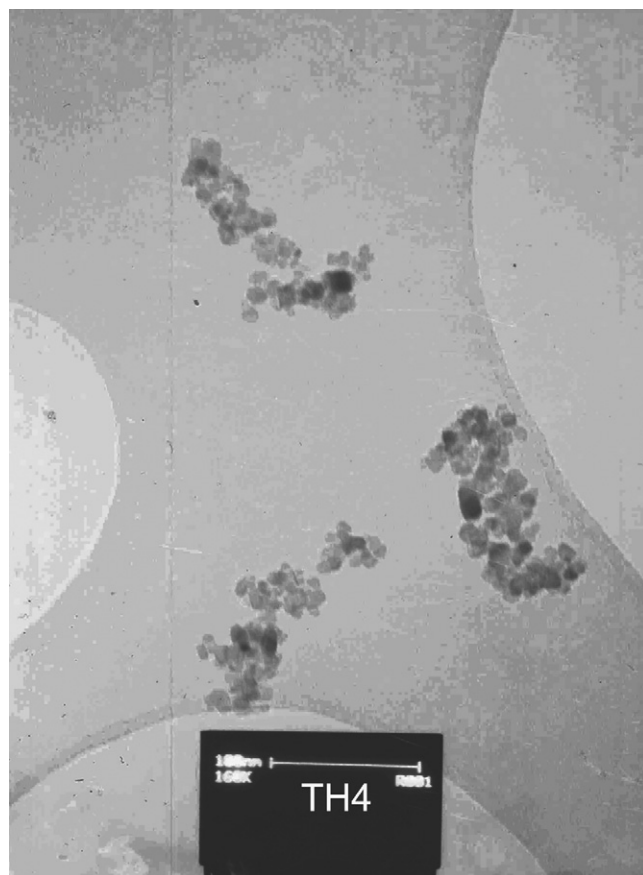


**Fig. 1.** The effect of  $\text{TiO}_2$  particle size on rate of oxidation of sulfides to sulfones. All the reactions were carried out with substrate (1 mmol), aqueous hydrogen peroxide (2.5 equiv.) and  $\text{TiO}_2$  (25 mmol, 20 mg) in  $\text{CH}_3\text{CN}$ .

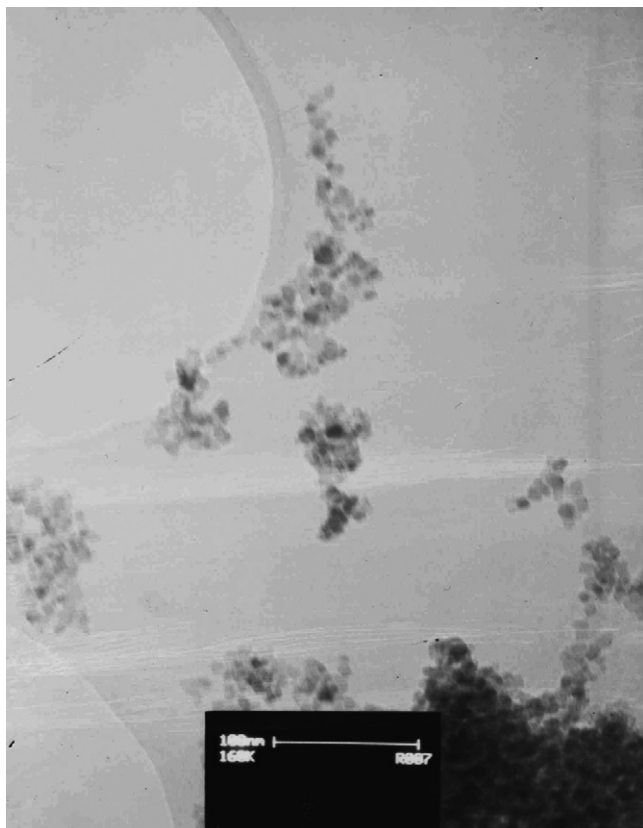
Further purification obtained by column chromatography using n-hexane:ethyl acetate (5:1) as eluent. The spectral data of the resulted products were in accordance with those of the authentic samples.

### 2.3. Preparation of the catalyst; Preyssler acid ( $\text{H}_{14}\text{NaP}_5\text{W}_{30}\text{O}_{110}$ ) supported on $\text{TiO}_2$ nanoparticles (Preyssler/nano-sized $\text{TiO}_2$ )

To a solution of Preyssler acid (0.500 g) in absolute ethanol (10 ml),  $\text{TiO}_2$  nanoparticles (1.000 g) was added and stirred for 12 h at  $20^\circ\text{C}$ . The solid was separated, and stirred again in another fresh absolute ethanol (10 ml) for 1 h. Finally, the catalyst was filtered and washed with ethanol and dried at  $100^\circ\text{C}$ . The mass increase measurement of the resulted Preyssler modified nano-sized  $\text{TiO}_2$  showed the Preyssler-type heteropoly acid content supported



**Fig. 3.** TEM image of Preyssler acid modified nano-sized  $\text{TiO}_2$ .

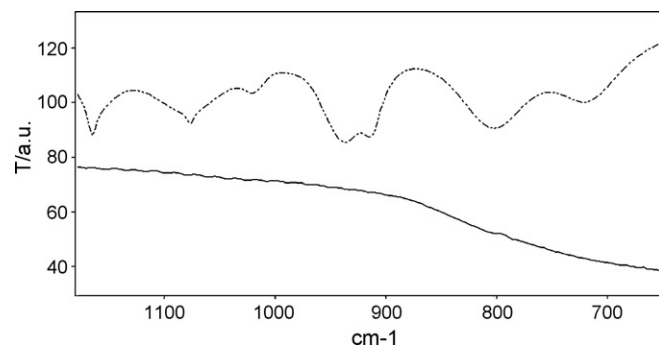


**Fig. 2.** TEM image of  $\text{TiO}_2$  nanoparticles.

on  $\text{TiO}_2$  nanoparticles is 0.043 mmol Preyssler acid per 1 g nano- $\text{TiO}_2$ .

### 2.4. General procedure for the oxidation of sulfides to sulfoxides

A mixture of various thioethers (1 mmol) and Preyssler acid/nano-sized  $\text{TiO}_2$  catalyst (25 mg) in *i*-propyl alcohol (10 ml) was stirred vigorously for 15 min at room temperature. Then, aqueous solution of 30%  $\text{H}_2\text{O}_2$  (2.5 equiv., 0.15 ml) was added to the mixture in three portions. After the completion of the reaction which was monitored by TLC, the catalyst was centrifuged and filtered off. Water (20 ml) was added and the mixture was extracted by  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20$  ml) and the combined organic phase dried over



**Fig. 4.** The IR spectra of nanoparticles of  $\text{TiO}_2$  (—) and Preyssler acid modified nano-sized  $\text{TiO}_2$  subtracted from nano-sized  $\text{TiO}_2$  (---).

**Table 3**  
The data for the selective oxidation of methyl phenyl sulfide with H<sub>2</sub>O<sub>2</sub>.

Entry	Preyssler acid/TiO <sub>2</sub> (mmol/g)	Solvent	Time (h)	Temperature (°C)	Conversion (%) <sup>a</sup>	SO:SO <sub>2</sub> (%) <sup>b</sup>
1	None	CH <sub>3</sub> OH	3	25	30	71:29
2	Neat nano-sized TiO <sub>2</sub> (0.43 mmol)	CH <sub>3</sub> OH	1.5	25	100	43:57
3	Neat Preyssler (0.043 mmol)	CH <sub>3</sub> OH	1.5	25	80	62:38
4	0.012	CH <sub>3</sub> OH	1.5	25	100	70:30
5	0.025	CH <sub>3</sub> OH	1.5	25	100	80:20
6	0.043	CH <sub>3</sub> OH	1.5	25	100	95:5
7	0.050	CH <sub>3</sub> OH	1.5	25	100	80:20
8	0.065	CH <sub>3</sub> OH	1.5	25	100	70:30
9	0.073	CH <sub>3</sub> OH	1.5	25	100	65:35
10	0.043	<i>t</i> -BuOH	1	25	95	97:3
11	0.043	AcOH	1	25	91	83:17
12	0.043	THF	1	25	82	95:5
13	0.043	<i>i</i> -PrOH	1	25	100	98:2
14	0.043	CH <sub>3</sub> CN	1	25	78	70:30
15	0.043	CH <sub>3</sub> OH	1	25	88	100:0
16	0.043	Acetone	1	25	72	98:2
17	0.043	<i>i</i> -PrOH	1	5	61	100:0
18	0.043	<i>i</i> -PrOH	1	Reflux	96	79:21

<sup>a</sup> According to TLC monitoring.

<sup>b</sup> Selectivities are based on <sup>1</sup>H NMR spectroscopic integration.

anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then, the solvent was removed on a rotary evaporator under reduced pressure. The resulting products were determined by their <sup>1</sup>H NMR spectrums and compared with the authentic samples.

### 3. Results and discussion

In this work, nanoparticles of TiO<sub>2</sub> were prepared via sol–gel method by gradually adding titanium tetra-*n*-butoxide to a solution of deionized water in ethanol. The gel was prepared by aging the sol at room temperature for 24 h. The obtained gel was dried and calcinated at 350, 450 and 550 °C to give different particle sizes of nano-sized TiO<sub>2</sub>. The particle size distribution was estimated to be 15, 30 and 50 nm, respectively, determined by transmission electron microscopy (TEM) images. These particle sizes were in agreement with the calculated value of the crystalline sizes determined by XRD using Scherrer equation [29].

The first application of this catalyst was demonstrated by oxidation of various sulfides to the corresponding sulfones by H<sub>2</sub>O<sub>2</sub> in CH<sub>3</sub>CN (Scheme 2).

The effect of solvent on the rate and chemoselectivity of the reaction has been shown in Table 1. All the reactions were carried out with 1 mmol of substrate, 25 mg of nano-sized TiO<sub>2</sub> (15 nm) in 10 ml of solvent and 2.5 equiv. of 30% aqueous hydrogen peroxide at room temperature. All yields were measured after 1.5 h. It seems CH<sub>3</sub>CN is the best solvent for this purpose.

Generally, particle size is an important parameter for heterogeneous catalysis [30–32]. Therefore, the effect of particle size on the reaction rate and efficiency was studied by using various particle sizes of TiO<sub>2</sub>. An increase in reaction rate was observed as the particle size decreases (Fig. 1). When the reaction was performed without catalyst or with micro-TiO<sub>2</sub>, the conversion was not completed even after about 10 h.

**Table 4**  
The comparison of some other catalyst with Preyssler acid modified nano-sized TiO<sub>2</sub> (15 nm).

Entry	Catalyst	H <sub>2</sub> O <sub>2</sub> (mmol)	Temp. (°C)	Time (h)	Yield (%)		[Literature]
					Sulfoxide	Sulfone	
1	Na <sub>2</sub> WO <sub>4</sub> , C <sub>6</sub> H <sub>5</sub> PO <sub>3</sub> H <sub>2</sub> , [CH <sub>3</sub> ( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> N]HSO <sub>4</sub>	2.5	35	9	93	7	[34]
2	Methyltrioxorhenium (MTO)	2.2	60	3	97	2	[33]
3	Tungstate-exchanged Mg-Al-LDH	6		0.5	88	12	[35]
4	Sc(OTf) <sub>3</sub>	5		3	94	4	[36]
5	Preyssler acid modified nano-sized TiO <sub>2</sub>	2.5	25	1	98	2	– <sup>a</sup>

<sup>a</sup> Reaction conditions as exemplified in the experimental procedure.

In order to show the generality of the oxidation method, various substituted sulfides containing aromatic and aliphatic moieties were subjected to oxidation using H<sub>2</sub>O<sub>2</sub> as the oxidant in the presence of nano-sized TiO<sub>2</sub> (15 nm). Table 2 shows the results of these oxidations.

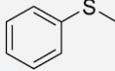
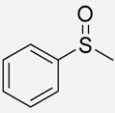
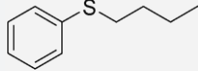
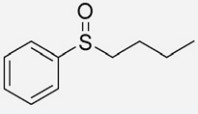
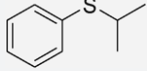
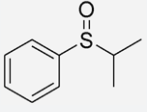
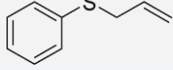
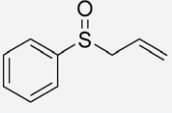
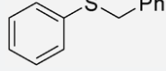
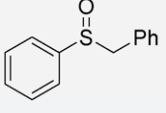
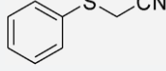
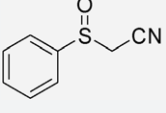
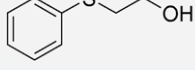
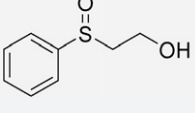
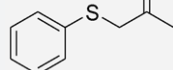
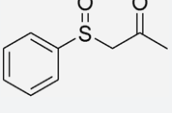
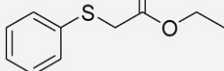
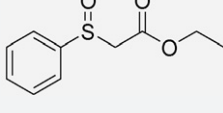
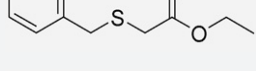
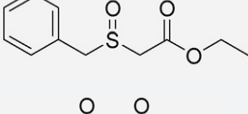
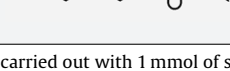
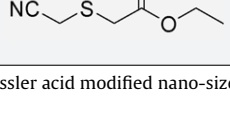
Both aliphatic and aromatic sulfides undergo the oxidation reaction, the latter being more reactive. The results of Table 2 demonstrate the reaction is chemoselective and the other functional groups like double bond, nitrile group, and hydroxyl group do not oxidize under these reaction conditions.

To demonstrate the reusability of the catalyst, it was also recovered from the oxidation reaction by centrifuge and washed with ethyl acetate (4 × 10 ml). It was used without further purification for the next oxidation reaction. There were no significant decreases in efficiency of the recovered catalyst compared to the fresh one. The catalyst was reusable at least up to four times.

The selectivity and catalytic activity of the synthesized TiO<sub>2</sub> nanoparticles were modified by Preyssler-type heteropoly acid, H<sub>14</sub>NaP<sub>5</sub>W<sub>30</sub>O<sub>110</sub>. To prepare the modified catalyst, a suspension of nano-sized TiO<sub>2</sub> and Preyssler-type heteropoly acid in absolute ethanol were stirred for 12 h. The mass increase measurement of the resulted modified catalyst showed 0.043 mmol Preyssler acid content per 1 g TiO<sub>2</sub> nanoparticles. The TEM images and the IR spectrum of the TiO<sub>2</sub> nanoparticles and Preyssler acid modified nano-sized TiO<sub>2</sub> are shown in Figs. 2 and 3. Although there are no significant differences in the TEM images, the IR spectrum of Preyssler acid modified nano-sized TiO<sub>2</sub> clearly shows the characteristic bands of Preyssler-type heteropoly acid bands in 1164, 1076, 1021, 937, 915 and 802 cm<sup>-1</sup> (Fig. 4).

In order to find the optimum reaction conditions for selective oxidation of sulfides to sulfoxides, the oxidation of methylphenylsulfide by hydrogen peroxide as a model experiment was studied

**Table 5**  
Oxidation of sulfides with H<sub>2</sub>O<sub>2</sub> in the presence of Preyssler acid modified nano-sized TiO<sub>2</sub><sup>a</sup>.

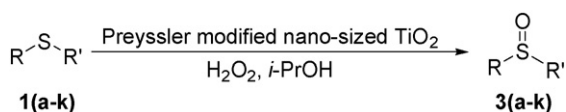
Entry	Substrate	Product	Time (min)	Yield (%) <sup>b</sup>
1			60	96
2			100	95
3			75	100
4			100	94
5			160	80
6			60	96
7			60	88
8			90	100
9			60	96
10			90	100
11			90	96

<sup>a</sup> All the reactions were carried out with 1 mmol of substrate, 25 mg of Preyssler acid modified nano-sized TiO<sub>2</sub> (15 nm) in 10 ml of *i*-PrOH and 2.5 equiv. of 30% aqueous H<sub>2</sub>O<sub>2</sub> at room temperature.

<sup>b</sup> Isolated yield.

at different Preyssler-type heteropoly acid/nano-sized TiO<sub>2</sub> ratios, solvents, and reaction times and temperatures (Scheme 3, Table 3).

The data in Table 3 demonstrates that the yield of the oxidation is very low in the absence of catalyst (entry 1). Although the con-



**Scheme 3.**

version occurs in high yield in the presence of neat nano-TiO<sub>2</sub>, but the molar ratio of sulfoxide to sulfone is almost the same (entry 2). In contrast to the results obtained by neat TiO<sub>2</sub>, chemoselectivity increases by using Preyssler acid/nano-sized TiO<sub>2</sub> as catalyst. A study on the Preyssler acid/nano-sized TiO<sub>2</sub> ratio reveals that the sulfoxide content of product reaches to a maximum value at the ratio of 0.043. The chemoselectivity is lost at lower and upper amounts of the Preyssler acid/nano-sized TiO<sub>2</sub> ratio (entries 6–9). While the SO content is 95% in the presence of Preyssler acid/nano-sized TiO<sub>2</sub> of 0.043, it decreases to 65% at the amount of 0.073, whereas nano-sized TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> and Preyssler acid/H<sub>2</sub>O<sub>2</sub> oxidizing

agents gave over oxidation sulfone product, but Preyssler acid modified nano-sized TiO<sub>2</sub> is a chemoselective system for preparation of sulfoxides in high yield with a trace amount of sulfone contamination.

The solvent effects on the ratio of the sulfoxide to sulfone are shown in entries 10–16 (Table 3). Whereas the highest chemoselectivity is observed in methanol, but the amount of conversion reaches to a value of 88% in this solvent after 1 h. Performing the reaction in *i*-PrOH as solvent has much higher yield with excellent chemoselectivity.

Table 3 also represents the chemoselectivity of the reaction as a function of temperature. As can be observed, the selectivity is higher at low temperatures (entries 13, 17 and 18). By increasing the temperature up to the reflux condition, the selectivity of the reaction decreases to the value of 79% (entry 18).

Moreover, the comparison of this method with the other similar methods including H<sub>2</sub>O<sub>2</sub> oxidation of methylphenylsulfide with a catalyst demonstrates nano-sized TiO<sub>2</sub> catalyst has appropriate effects on the efficiency of the oxidation (Table 4).

The reaction was extended to other starting substrates with different functional group after the reaction conditions for the selective oxidation of sulfides to sulfoxides was optimized. Table 5 shows the results for the selective oxidation of various sulfides into the corresponding sulfoxides.

Both aliphatic and aromatic sulfides undergo chemoselective oxidation reaction and the other functional groups like double bond, nitrile, hydroxyl, carbonyl and ester groups did not oxidize or react under the reaction conditions (entries 4, 6–10).

Due to the need to obtain catalysts for green processes, the use of recycled catalysts is required for reducing the catalytic cost. When the reaction was completed, the insoluble catalyst was filtered, dried under vacuum (20 °C), and reused. The catalyst was reused for four cycles without any significant loss of activity.

In summary, the present study represents the application of neat and Preyssler acid modified nano-sized TiO<sub>2</sub> as catalyst for the oxidation of sulfides to sulfones and sulfoxides, respectively, using aqueous hydrogen peroxide. The decreasing of the TiO<sub>2</sub> nanoparticle led to larger surface area and hence an acceleration of the reaction rate. On the other hand, modification of its surface with Preyssler-type heteropoly acid decreased the activity and enhanced the selectivity of the catalyst, so provided a chemoselective system for the oxidation of sulfides to sulfoxides. Therefore, the simplicity of the procedure, the mildness of the reaction conditions, high yields and chemoselectivities, the ease of catalyst separation from

the reaction mixture, and its reusability demonstrates the ability of this method.

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