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# Polymeric Ionic Liquid Nanogel Anchored Tungstate Anions: A Robust Catalyst for Oxidation of Sulfides to Sulfoxides

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## Abstract

A new heterogeneous catalytic system was prepared by immobilization of tungstate ions on cross-linked poly(ionic liquid) nanogel. The solid nanogel was easily synthesized by surfactant-less method. The resulting catalyst was highly active in selective oxidation of sulfides to sulfoxides by  $\text{H}_2\text{O}_2$ . The oxidation reaction was successfully performed in solvent free condition with high yield. The catalyst was recycled and reused for several cycles of reactions without any significant loss of catalytic activity.

**Keyword:** Nanogel, Poly(ionic liquid), Oxidation

## Introduction

Catalytic oxidation reactions by  $\text{H}_2\text{O}_2$  have attracted much attention in recent years.<sup>1-3</sup>  $\text{H}_2\text{O}_2$  is an inexpensive oxidant with high oxygen content and thus can be used as an appropriate reagent for oxidation reactions. Many different transition metal complexes such as manganese,<sup>4,5</sup> molybdenum,<sup>6,7</sup> rhenium<sup>8,9</sup> and tungsten<sup>10-11</sup> have been used as catalyst in these reactions. However, because of its high efficiency and selectivity in oxidation reactions, tungsten-based catalysts are more attractive than others. Noyori et al. have used tungsten-based catalyst for oxidation of cyclohexene to adipic acid in the presence of a phase transfer catalyst.<sup>12</sup> This organic solvent- and halide-free method was also used in other oxidation reactions, as well.<sup>13</sup> Other tungsten-based catalysts were also developed for oxidation reactions.<sup>14,15</sup> However most of these catalysts are homogenous and thus it is difficult to separate them from reaction medium.

An alternative method for improving catalyst separation and reuse is immobilization of catalyst on solid supports. Tungstate catalyst can be immobilized on a solid support and a heterogeneous system will result in. Different supports have been used for this purpose such as polymers,<sup>16,17</sup> silica particles,<sup>18,19</sup> mesoporous silica<sup>20,21</sup> and magnetic nanoparticles.<sup>22</sup>

Aside from the great advantages of heterogeneous catalysts, there are also some problems in using them. They usually have lower catalytic activity than homogenous catalysts. Low loading and high leaching of the catalyst and slow penetration of organic substrate into the catalyst are other disadvantages of heterogeneous catalytic systems. So it is important to design a catalyst with high efficiency and recyclability as well as good stability.

Recently ionic liquids (ILs) have attracted great attention due to their unique properties.<sup>23,24</sup> They have high thermal stability, low flammability and variable polarities. ILs have negligible vapor pressure and can be used as green solvent. Poly(ionic liquids) (PILs) are polymers composed of ILs as repeating units. Imparting ILs in polymeric structures can lead

to support materials for heterogeneous catalytic systems. They have been used as support for catalysts in many reactions.<sup>25,26</sup> As a new class of materials, PILs have found many applications.<sup>27-29</sup> They benefit from properties of both ILs and polymers. PILs contain many ionic groups in their structure and thus can carry many different counterions. As a consequence, using PILs as solid supports can lead to heterogeneous catalytic system with high catalyst loading and catalytic activity.

Herein, we report synthesis of a new heterogeneous catalytic system by immobilization tungstate ions on cross-linked PIL nanogel. The supports are synthesized by polymerization of ILs monomers in the presence of a cross-linker. Then, tungstate ions are immobilized on PIL nanogel via a counterion exchange reaction to form an active catalyst. This catalyst is used in oxidation reaction of sulfides by H<sub>2</sub>O<sub>2</sub>. The synthesized catalyst exhibits high catalytic activity in this reaction.

## Experimental

### Reagents and Analysis

1-Vinylimidazole was purchased from Aldrich and distilled under low pressure before use. 1-bromododecane (Merck), 1,4-dibromobutane (Aldrich) and 2'-Azobis(2-methylpropionamidine)dihydrochloride (V50, Kanto, 97%) were used without further purification.

Chemical structure of particles was characterized by Fourier transform infrared (FTIR) spectroscopy using an ABB Bomem MB-100 spectrophotometer. Thermal gravimetric analysis (TGA) was performed by a TGA Q 50 thermogravimetric analyzer with heating rate of 10 °C/min under nitrogen atmosphere. Shape and morphology of particles were observed using a Philips CM30 transmission electron microscope (TEM).

### Synthesis of IL monomer and cross-linker

IL monomer was synthesized by reaction of 1-vinylimidazole and 1-bromododecane. In a typical run, 20 mL methanol was poured into a round-bottom flask and 2.82 g (30 mmol) 1-vinylimidazole and 7.44 g (30 mmol) 1-bromododecane were added to it. The resulting mixture was stirred at 60 °C for 20 h. Then, the flask was cooled to room temperature and its content was poured in 250 mL diethyl ether. In order to precipitate the product, the resulting solution was placed in refrigerator for 5 h. The solid product was filtered and washed with diethyl ether three times and dried in vacuum at 50 °C.

The cross-linker, 1,4-butanediyl-3,3'-bis-1-vinylimidazolium dibromide (BVD), was synthesized by reaction of 1-vinylimidazole and 1,4-dibromobutane with molar ratio of 2:1. The detail of procedure is similar to the synthesis of IL monomer.

### Synthesis of catalyst

A round-bottomed flask equipped with a condenser was charged with 50 mL water. 2 g IL monomer and 0.3 g BVD were added and argon gas was purged into the solution for 20 min. Then, V50 (0.03 g) was added to the solution and the flask was placed in an oil bath at 70 °C. After 24 h, the solid product was separated by centrifuge and washed three times with methanol. The resulting cross-linked PIL nanogel (NPILBr) was dried in vacuum at 50 °C.

An anion exchange reaction was used to immobilize tungstate on the synthesized PIL nanogel. 1.0 g powdered PIL nanogel was dispersed in 50 mL water and 1.5 g Na<sub>2</sub>WO<sub>4</sub>·H<sub>2</sub>O was added to it. The solid product was vigorously stirred (1200 rpm) for 3 days at room temperature. The solid product (NPILW) was separated by centrifuge and washed three times with water (5×100 mL) and twice with methanol (2×20 mL) and dried in vacuum at 50 °C.

### Oxidation reactions catalyzed by PILW

The synthesized PILW catalyst was used in oxidation reactions of sulfides by  $\text{H}_2\text{O}_2$ . In a round-bottomed flask, 3mmol  $\text{H}_2\text{O}_2$ , 1mmol sulfide and 10 mg PILW were loaded and the mixture was stirred at room temperature for a defined time. After the completion of the reaction, methanol was added and catalyst was separated by centrifuge. The solid catalyst was washed with methanol, dried at 50 °C and used for another run. The product mixture in the filtrate were extracted by ethyl acetate and analyzed by gas chromatography (GC).

## Results and discussion

### Synthesis of catalyst

IL monomer and cross-linker were synthesized by quaternization reaction of 1-vinylimidazole with 1-bromododecane and 1,4-dibromobutane, respectively.<sup>30</sup> Cross-linked PIL nanogel was synthesized by dispersion polymerization of 3-*n*-dodecyl-1-vinylimidazolium bromide in water (Fig. 1). Since ionic liquid monomer has long alkyl chain, it acts like surfactant. Therefore, aggregation of monomers in water produces nanosized micelle which after copolymerization PIL nanogel is obtained. These nanoparticles were used as supports for immobilization of tungstate anions. Tungstate anions were immobilized on the PIL nanoparticles by anion exchange reaction in which bromide was exchanged by tungstate. The long alkyl chains in catalyst structure provide a hydrophobic surface on PILW which improve the adsorption of hydrophobic substrates on the surface of catalyst.

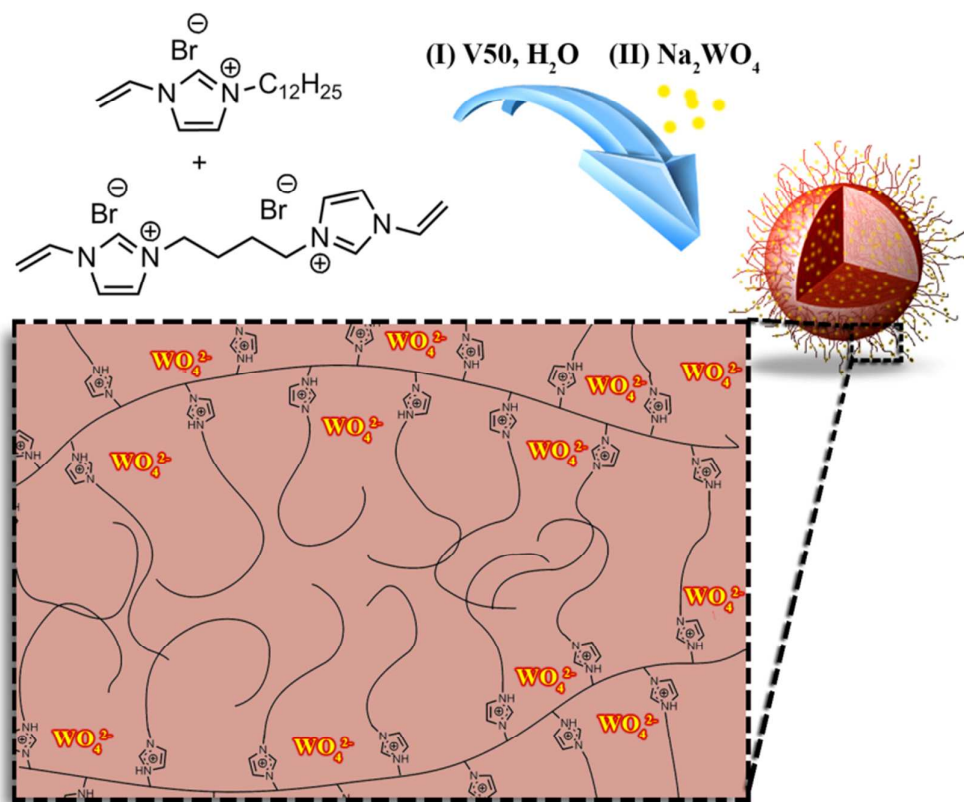
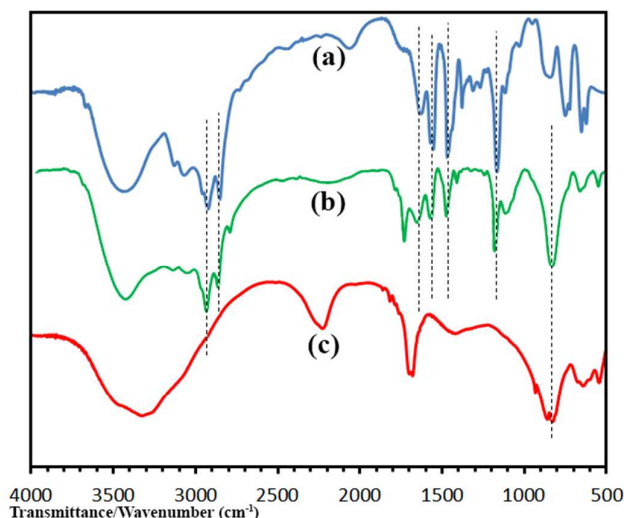


Fig. 1 Preparation of PILW catalyst

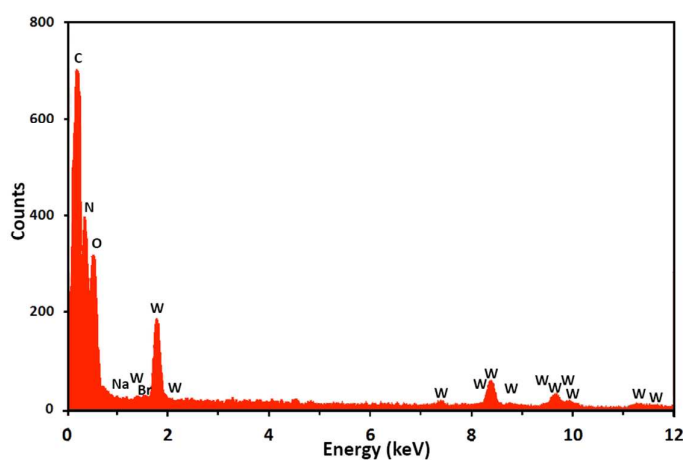
### Characterization of catalyst

FTIR spectrum of cross-linked PILs is shown in Fig. 2a. Peaks at  $2850\text{ cm}^{-1}$  and  $2950\text{ cm}^{-1}$  are related to C-H stretching vibration and peaks at  $1565\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  are attributed to stretching vibration of C=C and C=N bond of imidazolium ring, respectively. The results show that PIL nanoparticles were successfully synthesized. In the spectrum of tungstate-immobilized PILs (Fig. 2b), a new peak was appeared at  $822\text{ cm}^{-1}$ . This peak which is also present in the spectrum of  $\text{Na}_2\text{WO}_4$  (Fig. 2c), is attributed to W=O stretching vibration, indicating successful exchange of tungstate with bromide in PIL structure.



**Fig. 2** FTIR spectra of PILBr (a), PILW (b), and Na<sub>2</sub>WO<sub>4</sub>·H<sub>2</sub>O (c).

The presence of tungstate in the catalyst was also confirmed by energy dispersive x-ray (EDX) spectroscopy, as depicted in Fig. 3. Also, no Na atom was observed in EDX spectrum of PILW demonstrating that ratio of imidazolium cation to WO<sub>4</sub> anion is 2:1. Moreover, the EDX spectrum shows that all bromide anions were almost exchanged with WO<sub>4</sub>.



**Fig. 3** EDX spectrum of PILW

TGA spectra of PILBr and PILW (Fig. 4) show a weight loss in about 100 °C for both samples, which is related to the removal of adsorbed water molecules. The main weight loss,



however, occurred in the range of 200-300 °C, is attributed to complete thermal degradation of PIL network. The thermal degradation of catalyst structure occurs in lower temperature for PILW than PILBr due to the presence of active  $\text{WO}_4$  anions in PILW. However, the degradation of structure of PILW starts at 160 °C, but it is still enough for catalytic purpose.

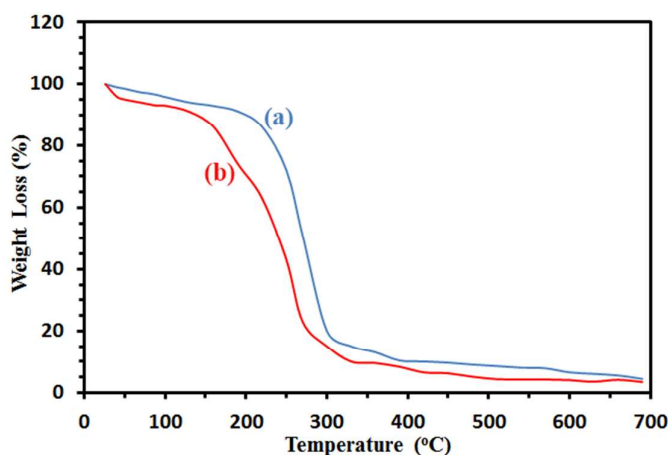


Fig. 4 TGA curves of PILBr(a), and PILW (b).

Fig. 5 shows TEM image and size distribution diagram of the synthesized PILW nanoparticles. It is observed that the synthesized particles are nearly spherical and their mean size is around 100 nm.

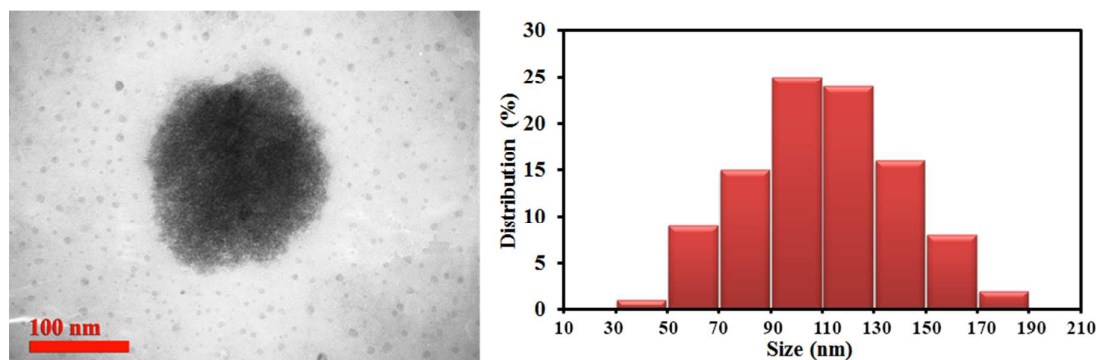


Fig. 5 TEM image and size distribution diagram of PILW particles

In order to measure the loading amount of Br<sup>-</sup> in PILBr, titration by AgNO<sub>3</sub> was used as a standard method (according to Mohr method) and it was found that the loading is 2.43 mmol.g<sup>-1</sup>. Elemental composition of PILBr and PILW is listed in Table 1. The loading amount of WO<sub>4</sub><sup>-</sup> catalyst on PIL supports was measured by inductively coupled plasma optical emission spectrometry (ICP-OES). The data obtained by ICP-OES showed that the loading amount of WO<sub>4</sub><sup>-</sup> ions on PILs is 1.2 mmol.g<sup>-1</sup>. XRF analysis also showed that there is no significant amount of Na<sup>+</sup>, confirming almost all characterized tungstate ions are exchanged with bromide in the PILW structure and no Na<sub>2</sub>WO<sub>4</sub> is physically adsorbed into the nanogel structure. The results show that ion exchange reaction was performed with a 2:1 ratio of imidazolium cations to WO<sub>4</sub><sup>-</sup> anions and yield of the ion exchange reaction is about 96%.

**Table 1** Results of CHN elemental analysis of catalyst

Entry	Catalyst	%C	%H	%N	% W <sup>a</sup>
1	PIL/Br	52.80	10.12	7.78	-
2	Fresh PIL/W	47.56	9.89	6.91	22.1
3	Recycled PIL/W	48.33	11.20	6.80	21.5

<sup>a</sup> Content of tungsten atom was measured by ICP-OES.

### Catalytic performance of PILW

The synthesized PILW nanogel was used as catalyst in oxidation reaction of sulfides to sulfoxides using H<sub>2</sub>O<sub>2</sub> as oxidant. The catalytic activity of PILW in oxidation of diphenylsulfide to diphenylsulfoxide in different conditions was investigated as control reaction and the results are listed in Table 2. As is shown in the Table, conversion and yield of the reaction in the absence of any catalyst are only 6 and 8 %, respectively. The reaction was performed with PILBr as catalyst in solvent free condition for 24 h at room temperature using 5 mmol H<sub>2</sub>O<sub>2</sub> as oxidant. The result showed that the presence of PILBr did not have any significant effect on conversion and yield of the reaction, indicating PILBr is inactive and does not have any catalytic activity in this reaction. Using 30 mg PILW significantly increased conversion and yield of the reaction to 95 and 99 %, respectively in just 3 h. By

decreasing catalyst loading to 20 and 10 mg, conversion and yield of the reaction was still high without significant changes. However, by further decreasing of catalyst loading to 5 %, conversion and yield of the reaction were decreased significantly and reached to 87 %. The results show that the optimized catalyst loading of PILW is 10 mg (1.2 mol%). The effect of the amount of H<sub>2</sub>O<sub>2</sub> on the reaction was also investigated and it was found that with using 3 mmol of H<sub>2</sub>O<sub>2</sub> the conversion and yield of the reaction is still high, but reducing the amount of H<sub>2</sub>O<sub>2</sub> to 1.5 mmol considerably reduces conversion and yield of the reaction. So the optimized amount of H<sub>2</sub>O<sub>2</sub> is 3 mmol. Since raising the temperature to 50 °C did not change conversion and yield of the reaction, room temperature was chosen as optimized temperature for further experiments. The reaction was also performed in different solvents such as water, acetonitrile, n-hexane and dichloromethane but the best catalytic performance was obtained in solvent free condition. The results indicated that PILW acts as an efficient catalyst in oxidation reaction of diphenyl sulfide to diphenylsulfoxide.

**Table 2** Control experiment of oxidation of diphenylsulfide<sup>a</sup>

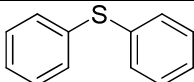
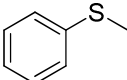
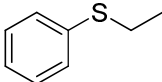
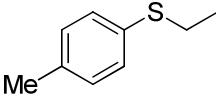
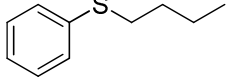
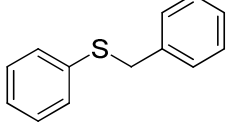
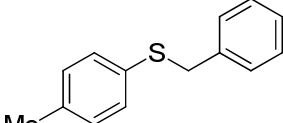
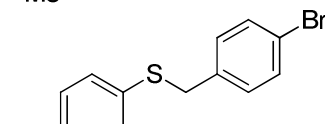
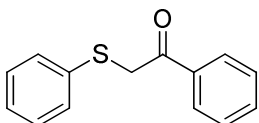
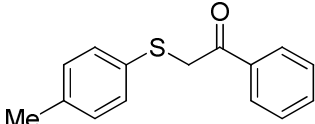
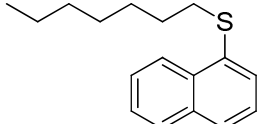
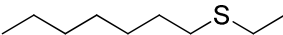
Entry	Catalyst	Cat. Loading (mg)	H <sub>2</sub> O <sub>2</sub> (mmol)	Solvent	T (°C)	Time (h)	Con. (%) <sup>b</sup>	Yield (%) <sup>c</sup>
1	-	-	5	Solvent free	r.t	24	6	6
2	PILBr	30	5	Solvent free	r.t	24	8	7
3	PILW	30	5	Solvent free	r.t	3	99	94
4	PILW	20	5	Solvent free	r.t	3	99	95
5	PILW	10	5	Solvent free	r.t	3	99	98
6	PILW	5	5	Solvent free	r.t	3	87	87
7	<b>PILW</b>	<b>10</b>	<b>3</b>	<b>Solvent free</b>	<b>r.t</b>	<b>3</b>	<b>99</b>	<b>98</b>
8	PILW	10	1.5	Solvent free	r.t	3	75	74
9	PILW	10	3	Solvent free	50	3	99	91
10	PILW	10	3	water	r.t	4	94	92
11	PILW	10	3	CH <sub>3</sub> CN	r.t	4	95	95
12	PILW	10	3	n-hexane	r.t	5	81	79
13	PILW	10	3	CH <sub>2</sub> Cl <sub>2</sub>	r.t	4	73	71

<sup>a</sup>Reaction condition: diphenyl sulfide (1 mmol), H<sub>2</sub>O<sub>2</sub> (30%), solvent (3 mL). <sup>b</sup>Conversions were calculated based on initial mmol of sulfide. <sup>c</sup>Yields were determined by GC.

The catalytic performance of PILW in oxidation reaction of other sulfide compounds was also studied. Different sulfide compounds were used as substrate in oxidation reaction based

on the optimized condition obtained in control reaction discussed previously. As is shown in Table 3, all reactions were performed with high conversion and yield; however aromatic sulfides produced higher yields.

**Table 3** Oxidation of sulfides to sulfoxides catalyzed by PIL/W

Entry	Sulfide	Time (h)	Con. (%)	Yield (%)
1		3	99	98
2		2	99	95
3		2.5	98	95
4		2.5	97	93
5		3.5	95	91
6		4	99	95
7		4	99	96
8		4	97	93
9		5	91	91
10		5	94	93
11		5	95	94
12		5	85	83

<sup>a</sup> Reaction condition: sulfide (1mmol), H<sub>2</sub>O<sub>2</sub> 30% (3 mmol), catalyst (10 mg), room temperature, solvent free. <sup>b</sup> GC yield.

### Recycling and leaching experiments

The recyclability of PILW was investigated in several runs of oxidation reaction of diphenyl sulfide to diphenylsulfoxide. At the end of the reaction, PILW was separated by centrifuge and its catalytic activity in next runs was investigated. As is shown in Fig. 6, the catalytic activity of PILW is preserved even after 8 runs and yield of the reaction does not change significantly.

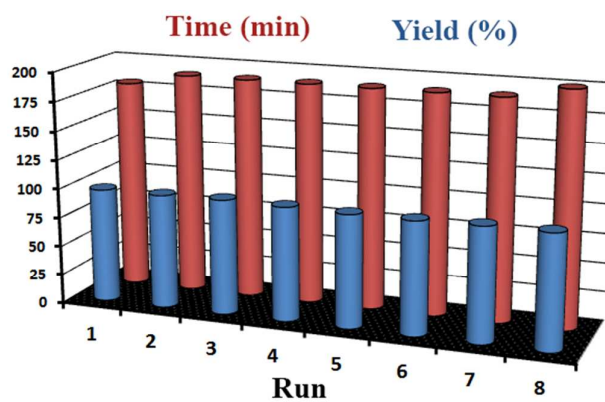
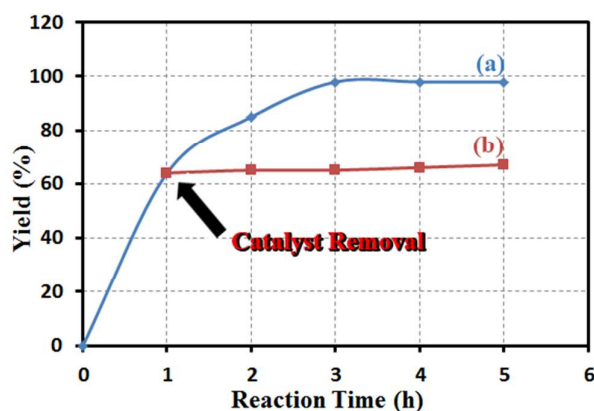


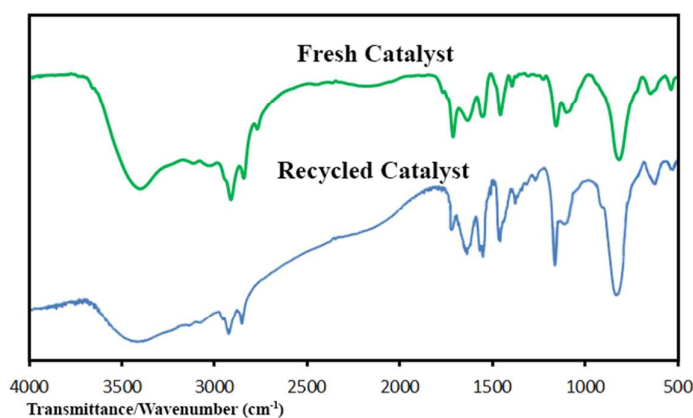
Fig. 6 Recycling experiment

The leaching of the catalyst in oxidation reaction of diphenyl sulfide was then studied. The reaction was stopped at half of the reaction time and the catalyst was separated from the solution. The remaining mixture was stirred for another period of half the reaction time. The leaching results are shown in Fig. 7. After removing the catalyst no more products were produced which indicates that catalyst leaching is negligible. Atomic adsorption spectroscopy of reaction mixture after catalyst separation also confirmed that no free tungstate ions are present in the solution. The results showed almost all tungstate ions are successfully immobilized on the PIL supports and do not exist as free ions in the solution.

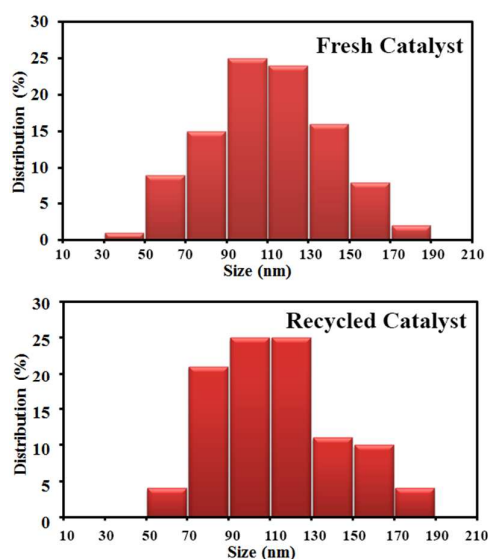


**Fig. 7** Leaching experiment. Blue line: reaction with PILW and red line: reaction without a catalyst.

The elemental analysis of fresh and recycled catalysts revealed that tungsten content of the catalyst does not significantly change after recycling, as represented in Table 1. Moreover, there is no significant change in the FTIR spectrum (Fig. 8) and size distribution diagram (Fig. 9) of the recycled catalyst compared with fresh catalyst, demonstrating the catalyst is stable even after 8 times use. The resulting particles represent an effective heterogeneous catalytic system for oxidation of sulfides.



**Fig. 8** FTIR spectra of fresh and recycled catalyst



**Fig. 9** Size distribution diagram of fresh and recycled catalyst

### Comparison with other catalysts

In order to have a better image of catalytic activity of the prepared catalyst, we compared the data obtained here by some other catalysts that recently have been used for oxidation of sulfides to sufoxides. For this purpose we chose catalytic oxidation of methyl phenyl sulfide by  $\text{H}_2\text{O}_2$ . Catalyst, yield of the reaction and other parameters related to the reaction condition are listed in Table 4. It is observed that the catalyst used in this study shows equal or even higher yield than the other catalysts. Considering the other parameters such as solvent, time and temperature reveals that the catalyst studied here is more advantageous than the others, since it benefits from a solvent-free condition, low temperature and relatively short reaction time. The loading of the catalyst is also higher than the other listed catalysts. Oxidation reaction of different sulfides with high yields is possible by using just a small amount of the catalyst. The results show that the prepared catalyst is comparable and in most cases is even advantageous over other catalysts that are already reported in the literature.

**Table 4** Comparison of activity of PILW with other reported catalysts in oxidation of sulfides to sulfoxides

Entry	Catalyst	Catalyst Loading (mmol/g)	Amount of used catalyst (mol%)	T (°C)	Time (h)	Solvent	Yield (%)
1	Fe <sub>3</sub> O <sub>4</sub> /CS/HWO <sup>a,31</sup>	2.05	0.33	25	4	CH <sub>3</sub> CN	83
2	BisILs-C <sub>8</sub> H <sub>17</sub> -W <sub>2</sub> <sup>b,32</sup>	0.332	1.5	25	1.5	CH <sub>2</sub> Cl <sub>2</sub> :CH <sub>3</sub> OH	95.5
3	PANW <sup>c,33</sup>	0.38	0.1	25	0.5	CH <sub>3</sub> OH	72
4	polymer-anchored Cu(II) <sup>34</sup>	0.75	0.75	25	3	CH <sub>3</sub> CN	84
5	Mo(VI)O <sub>2</sub> @SBA-15 <sup>35</sup>	0.18	0.45	26	3	CH <sub>3</sub> CN	89
6	Cr-MPTA-1 <sup>d,36</sup>	1.15	1.15	40	3	CH <sub>3</sub> CN	95
7	[C <sub>6</sub> mim] <sub>3</sub> PM <sup>e,37</sup>	0.4	2	30	0.5	CH <sub>3</sub> OH	96
8	MNP@PILWO <sub>4</sub> <sup>f,22</sup>	0.62	0.93	25	1	Solvent free	99
9	This study	1.2	1.2	25	2	Solvent free	95

<sup>a</sup> Protonated peroxotungstate immobilized on magnetic crosslinked chitosan

<sup>b</sup> Peroxotungstate immobilized on ionic liquid brushes

<sup>c</sup> Peroxotungstate(VI) immobilized on poly(acrylonitrile)

<sup>d</sup> Cr-grafted mesoporous polytriallylamine

<sup>e</sup> Ionic liquid-based polyoxometalate salt

<sup>f</sup> Tungstate immobilized on magnetic poly(ionic liquid)

**Conclusion**

In summary we prepared a poly(ionic liquid) nanogel with tungstate anions as a heterogeneous catalytic system for oxidation of sulfides to sulfoxides. The loading of tungstate on polymeric support was about 1.2mmol.g<sup>-1</sup> and the leaching of the catalyst was negligible. The prepared system represents an efficient highly stable catalyst for oxidation reaction of sulfides by H<sub>2</sub>O<sub>2</sub>. Many different sulfide compounds were used as substrate and in all cases oxidation was performed with high yield. The recyclability of the catalyst was also



investigated and it was found that the catalyst can be recovered and reused for several cycles of reaction and there is no reduction in catalytic activity even after 8 runs.

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