Keggin-structured polyoxometalate-based ionic liquid salts: Thermoregulated catalysts for rapid oxidation of sulfur-based compounds using H_2O_2 and extractive oxidation desulfurization of sulfur-containing model oil

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ABSTRACT

A family of benign polyoxometalate-based ionic liquid salts (POM-ILs) was designed and prepared by combining Keggin-structured polyoxometalate inorganic anions with sulfonate functionalized organic cations. The resultant salts were characterized, and catalytically evaluated by oxidation of sulfur-based compounds. They exhibited good-to-high yields and selectivities for target sulfides in oxidation reaction. Cyclic voltammetry (CV) was used to investigate the redox behavior of these catalysts. Also, an extractive and catalytic oxidation desulfurization (ECOD) system composed of ionic liquid salt, hydrogen peroxide as the basic experiment was used for the removal of sulfur-containing compounds from the model oil at suitable temperature. The reaction system was homogeneous during the reaction and then became heterogeneous at lower temperature which could be easily recovered and reused.

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1. Introduction

In the past few decades, the use of polyoxometalates (POMs) and POM-based compounds as catalysts has become a significant area of research. In particular, POMs have received much interest in the area of acid and oxidation catalysis because of their acidic and redox properties, which can be controlled at the molecular or atomic level [1,2]. They have been of extreme interest as oxidation catalysts due to both their resistance toward oxidation and compatibility with various oxygen sources [3]. The combination of organic species with POMs can cause the formation of POM-based hybrid materials that are emerging to be very important in catalysis [4–7]. On the other hand, ionic liquids (ILs) are well-known reaction media/catalysts with structural versatility, [8,9] and a variety of novel ILs have been developed rapidly with functional groups tethered to their cations or anions [10]. In addition, the high valence POM anions have been also employed as the counter negative ions for ILs [11,12]. In recent years, the use of POM-based IL (POM-IL) to catalyze organic reactions is an ongoing research area [13]. Some POM-IL composites have been reported and employed as catalysts for acid-catalyzed reactions [14,15].

ILs are defined as pure compounds, consisting only of cations and anions (i.e., salts), which melt at or below 100 °C [16]. ILs have been widely vaunted as greener solvents, suitable for a range of organic reactions and providing possibilities such as control of product distribution, [17] enhanced rate [18] and/or reactivity, [19] ease of product recovery, [20] catalyst immobilization, [21] and recycling [22]. The interest in ILs is due to many possible combinations of cations and anions, allowing the fine-tuning of their density, viscosity, melting point, hydrophobicity and most importantly their solvent power. When an alkane sulfonic acid group is covalently tethered to the IL cation, the IL would be a strong Brönsted acid [23]. These SO_3H-functionalized ILs have exhibited great potential in replacement of conventional homogenous and heterogeneous acidic catalysts because they are flexible, nonvolatile, noncorrosive and immiscible with many organic solvents [24,25]. Brönsted acidic ILs consist of the useful characteristics of solid acids and mineral liquid acids are designed to replace traditional mineral liquid acids such as sulfuric acid and hydrochloric acid in chemical procedures [26].

Sulfoxides ($RR'SO$) and sulfones ($RR'SO_2$) are of immense interest because of their extensive applications as reagents in organic chemistry as well as synthetic intermediates for the construction of various chemically and biologically active molecules [27]. Additionally, oxidation of the sulfur center plays a significant role in pharmaceutical industry and petroleum industry [28,29]. Thus, selective oxidation of sulfides to sulfoxides or sulfones has been the subject of extensive studies, and a variety of procedures for their preparation are available [30–33]. H_2O_2 was widely employed as terminal, green and inorganic oxidant because

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of its natural advantage such as high atomic efficiency and H_2O as sole by product, so it is undoubtedly to be an ideal option in sulfide oxidation catalysis [34].

By 2010, petroleum industry is bound to produce ultra low sulfur diesel containing a maximum of 15 ppm sulfur. The removal of aromatic sulfur compounds from diesel oil is becoming increasingly difficult because of its resistance to hydrodesulfurization (HDS) [35]. Also HDS is only effective on aliphatic sulfur structures such as thiols, thioethers and disulfides, etc. Sulfur-containing aromatic compounds (including thiophene and its derivatives) are barely removed by this process. Due to this reason, alternative desulfurization technologies have been developed, including adsorption [36], extraction [37], and selective oxidation [38]. Extractive desulfurization is believed to be one of the best methods because the process operation is easy. Oxidative desulfurization has gained more attention in recent years owing to its advantages, such as mild reaction conditions [39,40]. ILs are attractive solvents for desulfurization and are competitive with respect to molecular solvents and provide an important green alternative in removing such compounds by liquid–liquid extraction [41].

A Keggin-type POM-IL catalytic oxidation reaction has been developed, which achieves complete oxidation of a series of sulfides to their corresponding sulfoxides in a short time and mild conditions. In addition in this study, these POM-IL salts were used as catalyst for desulfurization of model oil, which have proven to be effective.

2. Experimental

2.1. General remarks

All organic materials and $H_3PW_{12}O_{40}$ (PW) were purchased commercially from Fluka Chemical Corp. and Merck & Co., Inc. and were used without further purification. FT-IR spectra were recorded with KBr pellets using a WQF-510 FTIR Rayleigh. Electrochemical experiments were performed with a computer controlled μ-Autolab modular electrochemical system (SAMA500 Electro Analyzer system). The products were analyzed by gas chromatography–mass spectroscopy (GC–MS) Agilent Technologies 6890N instrument, equipped with a capillary column 19019J-413 HP-5, and a flame ionization detector.

2.2. Preparation of PW-based ionic liquid salts

PW-based ILs were synthesized following the procedure in Scheme 1. As an example for the preparation of compound II, 4-phenyl-pyridine (PhPy) (1.55 g, 0.01 mol) and 1,4-butane sultone (Bs) (1.36 g, 0.01 mol) were dissolved in toluene (10 mL) and stirred at 50 °C for 48 h under nitrogen atmosphere. A white solid zwitterion PhPyBs was formed; it was filtered and washed with ether three times, then dried in a vacuum. The resulting PhPyBs (8.74 g, 0.03 mol) was added to the aqueous solution of $H_3PW_{12}O_{40}$ (PW) (28.8 g, 0.01 mol), followed by the stirring of the mixture at room temperature for 24 h. Water was removed in vacuum to give the final product as solid. QBs-PW (I) and PyBs-PW (III) were prepared based on the same method using the corresponding starting materials.

2.3. Catalytic activity test

#### 2.3.1. General procedure for oxidation of liquid sulfides to their corresponding sulfoxides

To a mixture of sulfide (1 mmol) and 30% aq. H_2O_2 (1 mmol) in 4 mL H_2O, catalyst (40 mg) was added and the mixture was stirred at room temperature for the time specified. Completion of the reaction was indicated by TLC (n-hexane/ethyl acetate 2:1 as eluent). After completion, the reaction mixture was cooled to 5 °C. The catalyst precipitated as solid at the bottom layer and could be easily separated by decantation (or filtration). The product was at the upper liquid layer. The resulting solution was concentrated under reduced pressure to afford the essentially crud products. Further purification was achieved by short column chromatography on silica gel with n-hexane/ethyl acetate as eluent (method a).

2.3.2. General procedure for oxidation of solid sulfides to their corresponding sulfoxides

To a mixture of sulfide (1 mmol) and 30% aq. H_2O_2 (2 mmol) in H_2O: EtOH (7:3 v/v, 4 mL), catalyst (80 mg) was added and the mixture was stirred at 70 °C for the time specified. Completion of the reaction was indicated by TLC (n-hexane/ethyl acetate 2:1). After completion, the reaction mixture was cooled to 5 °C. The catalyst precipitated as solid at the bottom layer and could be easily separated by decantation (or filtration). The product was at the upper liquid layer. The resulting solution was concentrated under reduced pressure to afford the essentially crud products. Further purification was achieved by short column chromatography on silica gel with n-hexane/ethyl acetate as eluent (method b).

2.4. Extractive catalytic oxidative desulfurization of model oil (ECOD)

The typical process is as the two following methods: 1) the model oil was prepared by dissolving the required amount of dibenzothiophene (DBT) with the different sulfur concentrations (100, 700 and 1000 ppm) in 5 mL of n-hexane in a round bottom flask equipped with a mechanical stirrer. 2) DBT (500 ppm), methyl phenyl sulfide (MPS) (250 ppm) and thiophene (250 ppm) were dissolved in 5 mL of n-hexane to get the model oil with a sulfur concentration of 1000 ppm (g/mL). The reactor was then heated to 70 °C with a catalyst loading of 0.02 g in H_2O:EtOH (7:3 v/v, 5 mL), and the mole ratio of H_2O_2 to sulfur containing compounds was 12:1. The mixture was then stirred up to a reaction time of 6 h. Upon the cooling of the mixture to room temperature, the catalyst appeared at the bottom of the reactor as a solid, and recovered by centrifuging while the product appeared as liquid at the upper layer. After that, 5 mL of diethyl ether as an extractant was added to the mixture and stirred for 10 min. The biphasic mixture was separated by decantation. The product was at the upper liquid layer and analyzed by GC–MS.
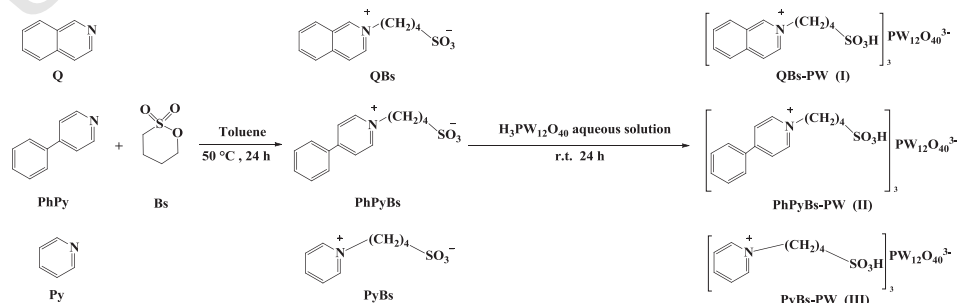
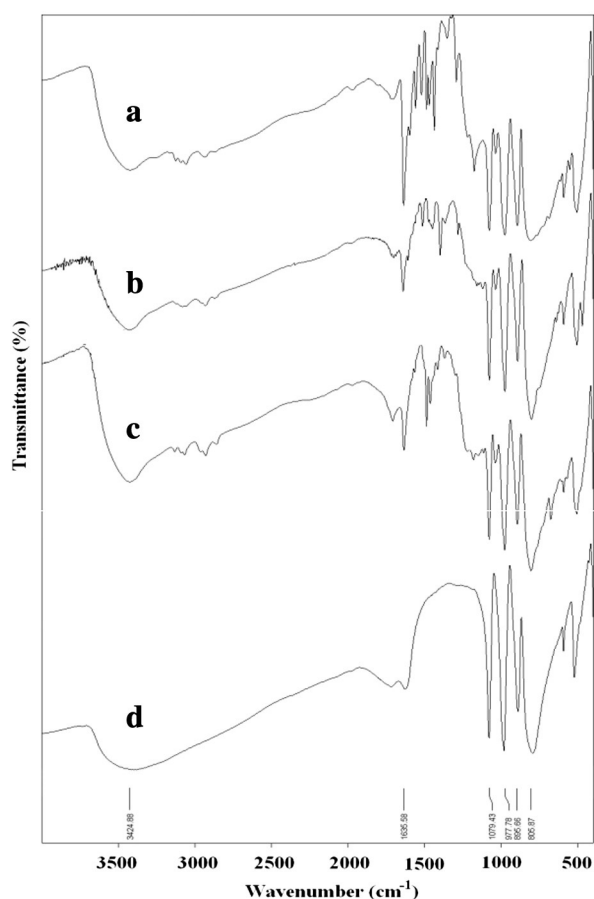**Scheme 1.** Schematic illustration for preparation of POM-ILs.

Fig. 1. FT-IR spectra for compounds (a) PhPyBs-PW, (b) QBs-PW, (c) PyBs-PW and (d) PW.

2.5. Cyclic voltammetry

The electrochemical reduction of POM-ILs (5×10^{-4} M) was studied in phosphate buffer (0.1 M), pH = 1. A glassy carbon electrode was used as the working electrode and Ag/AgCl as the reference electrode. Cyclic voltammograms (v, 0.1 V s^{-1}) were obtained at ambient temperature (20 ± 5 °C).

3. Results and discussion

3.1. Characterization of the catalyst

Elemental analyses for POM-ILs are as follows. Based on the elemental analysis data, it seems that trisubstituted heteropoly salts were formed.

Calc. for QBs-PW: C, 12.74; H, 1.32; N, 1.14; S, 2.62. Found: C, 12.77; H, 1.36; N, 1.15; S, 2.62. Calc. for PhPyBs-PW: C, 14.39; H, 1.45; N, 11.12; S, 2.56. Found: C, 14.43; H, 1.48; N, 1.12; S, 2.57. Calc. for PyBs-PW: C, 9.19; H, 1.20; N, 1.19; S, 2.73. Found: C, 9.21; H, 1.23; N, 1.20; S, 2.75.

The FT-IR spectra are quite useful to identify structural and bonding changes in the Keggin unit present in POM-ILs. FT-IR spectra of catalysts are illustrated in Fig. 1, comparing with that of the neat PW. It can be seen that in a wavenumber region of 800–1100 cm^{-1}, PW gave four featured peaks (1080 (P–O$_a$), 984 (W=O$_d$), 889 (W–O$_b$–W) (corner-sharing), and 806 cm^{-1} (W–O$_c$–W) (edge-sharing)) assigned to the Keggin structure. Two bands around 3500 and 1610 cm^{-1} were assigned to the modes of O–H and H$_2$O, respectively [42]. For all the samples, in spite of the decrease of peak intensities and slight shift of peak positions, the four peaks appeared distinctively, which indicates that the Keggin structure of PW was well reserved after the protons in the PW were substituted by the organic cations. On the other hand, S=O stretching vibrations at 1037 and 1170 cm^{-1} were detected to verify the presence of sulfonic groups in catalysts. These observations
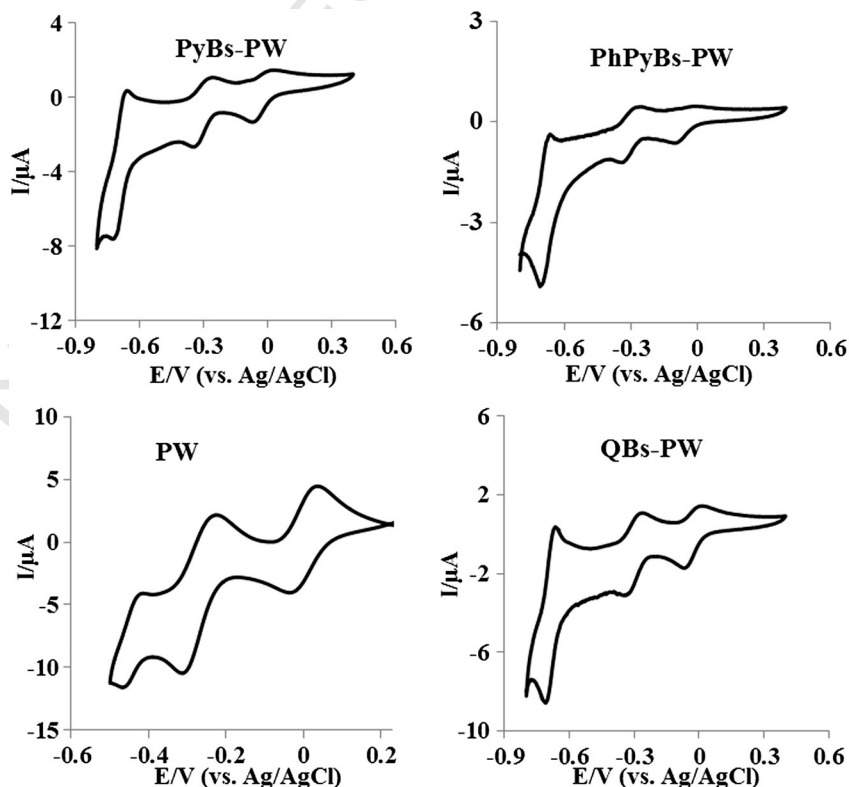

Fig. 2. Cyclic voltammograms of PW and POM-ILs (5×10^{-4} M) in phosphate buffer (0.1 M), pH = 1, scan rate: 0.1 V/s, ambient temperature (20 ± 5 °C).

again confirm that the combination of organic cations with PW via ionic linkage produces a family of organic POM salts.

3.2. Electrochemical studies

POM-ILs have been studied for their catalytic and electrocatalytic properties. Fig. 2 shows the cyclic voltammograms of POM-IL salts (5×10^{-4} M) in phosphate buffer at a scan rate of 0.1 V/s in room temperature. PW shows three couples of sharp and well-defined redox waves corresponding to reversible two-electron reduction/oxidation processes of the PW. As can be seen in Fig. 2, three reversible redox peaks can be observed clearly in voltammogram of every sample. The cathodic peak currents were almost the same as the corresponding anodic peak currents. The electrochemical studies reveal that the as-prepared POM-ILs show electrochemical responses, which prove the presence of POM in the prepared salts.

3.3. Oxidation of sulfides

The synthetic approach of POM-ILs is as follows (Scheme 1): in the first step, the neutral nucleophiles react with sultone to give zwitter-ions. Therefore, as a precursor, the physicochemical properties of zwitterions directly affect the nature of the final ILs. PyBs, QBs and PhPyBs are zwitterionic compounds, because the N atom in their heterocyclic ring has a positive charge, and the sulfonate group has a negative charge. In the second step, it is desired that the sulfonate group be converted into corresponding alkane sulfonic acid in the presence of strong acid. The nature of ILs depends on the three-dimensional network of anions and cations by weak interaction between them, such as hydrogen bonds, van der Waals and Columbic forces [43–45]. The coupling of Keggin anion with organic cation protection results in a molecularly defined hybrid structures with a strongly hydrophobic character.
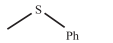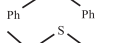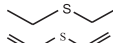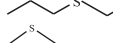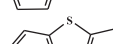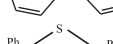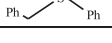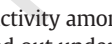
The effect of the kind of organic cations on the oxidative desulfurization has been investigated. Three cations (pyridine (Py), 4-phenylpyridine (PhPy), quiniline (Q)) were investigated. In order to optimize the reaction conditions, oxidation reaction of MPS as a model compound was examined using 30% aq. H_2O_2 under various reaction conditions (Table 1). In the oxidative system, one of the main factors was the amount of H_2O_2 and catalyst. Thus, it was of interest to explore the influence of the H_2O_2 dosages on removal of sulfide. With equal molar amounts of H_2O_2 and MPS, methyl phenyl sulfoxide (MPSO) was produced with 100% selectivity. According to the results in Table 1, optimal reaction conditions were achieved at H_2O_2 dosages to sulfide 1:1, amount of the catalyst was 40 mg at room temperature. To compare

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Table 2

Results of oxidation reaction of sulfides to their corresponding sulfoxides with 30% aq. H_2O_2 using PhPyBs-PW as catalyst.

Entry	Substrate	Time (min)	Yield (%)[a]
1		2 [b]	95
2		135 [b]	70
3		50 [b]	98
4		22 [b]	98
5		2 [b]	98
6		8 [b]	95
7		2 [b]	98
8		2 [c]	70
9		10 [c]	98
10		10 [c]	90

[a] Isolated yield.
[b] Sulfide (1 mmol), 30% aq. H_2O_2 (1 mmol), 4 mL H_2O, PhPyBs-PW as catalyst (40 mg), r.t.
[c] Sulfide (1 mmol), 30% aq. H_2O_2 (2 mmol), H_2O:EtOH (7:3 v/v, 4 mL), PhPyBs-PW as catalyst (80 mg), 70 °C.

the relative reactivity among three different catalysts, the oxidation of MPS was carried out under the same reaction conditions (Table 1, entries 4–7). The data indicate that QBs-PW (**I**) and PhPyBs-PW (**II**) are considerably more efficient than PyBs-PW (**III**) as catalyst. At the end of the reaction, the catalyst was recovered by cooling the reaction mixture to 5 °C, dried in vacuum and weighed. A loss of 15 wt.% of the PhPyBs-PW (compared with the amount of the catalyst in the first run) was found. At the end of the reaction, QBs-PW was soluble and did not appear at the bottom of the reactor as solid even at 5 °C. Also, PyBs-PW (**III**) is relatively soluble in the reaction mixture. So among the three catalysts, PhPyBs-PW was found to be the most promising in recycling (85 wt.% of the catalyst was precipitated at the end of the reaction) and gave the highest yield.

Because solid sulfur compounds (Table 2, entries 8–10) are insoluble in aqueous medium, it was necessary to use a co-solvent that solubilizes these compounds in water. In this study, EtOH was used as the co-solvent since it is derived from agricultural products and is renewable, biologically less objectionable in the environment and less toxic
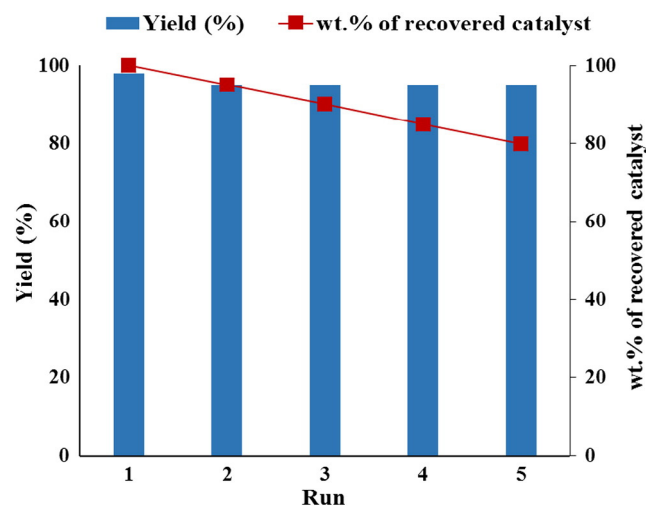
Table 1

Optimization of reaction conditions for oxidation of sulfides.

Entry	Catalyst	Catalyst (mg)	H_2O_2:sulfide	Time (min)	Yield (%)[a] Sulfoxide	Yield (%)[a] Sulfone
1	PhPyBs-PW	20	1:1	26[b]	90	5
2	PhPyBs-PW	40	1:1	2[b]	95	5
3	PhPyBs-PW	60	1:1	4[b]	95	5
4	PhPyBs-PW	40	2:1	2[b]	95	5
5	PyBs-PW	40	1:1	10[b]	95	5
6	QBs-PW	40	1:1	2[b]	95	0
7	Without catalyst	–	12:1	240[c]	30	0
8	PhPyBs-PW	40	2:1	10[c]	85	5
9	PhPyBs-PW	60	2:1	10[c]	85	5
10	PhPyBs-PW	80	2:1	10[c]	95	5
11	PhPyBs-PW	90	2:1	10[c]	80	5
12	PhPyBs-PW	80	1:1	15[c]	95	5

[a] Isolated yield.
[b] MPS (1 mmol), 4 mL H_2O and at r.t.
[c] Dibenzyl sulfide (1 mmol), H_2O: EtOH (7: 3 v/v, 4 mL) and at 70 °C.

Fig. 3. Reusability of PhPyBs-PW as catalyst in oxidation of dibenzyl sulfide (dibenzyl sulfide: 1 mmol, 30% aq. H_2O_2: 2 mmol and catalyst: 80 mg in H_2O: EtOH (7: 3 v/v, 4 mL) at 70 °C).
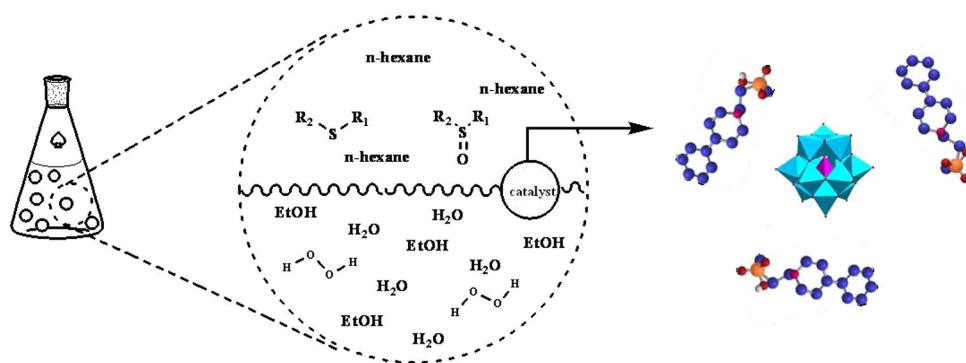
Scheme 2. PhPyBs-PW-catalyzed ECOD of model oil in the presence of H_2O_2.

compared with the other solvents. In order to optimize the reaction conditions, dibenzyl sulfide (as a solid sulfide) was selected as model substrate. The corresponding sulfoxide could be obtained in excellent yield in the presence of 80 mg of PhPyBs-PW as catalyst and 2:1 H_2O_2: sulfide ratio with trace over-oxidation product (Table 1, entries 8–11).

In order to generalize the scope of the reaction, a series of structurally diverse sulfides (aryl, benzylic, linear and heterocyclic sulfides) was subjected to oxidation under the optimized reaction conditions in the presence of PhPyBs-PW as the best catalyst (Table 2). The sulfoxides were obtained in short reaction times and in excellent yields. Since, this oxidation reaction was generally considered to proceed via an electrophilic addition reaction of oxygen atoms, the sulfides with higher electron density on the sulfur atom should react easily [46].

The regenerability and reusability of a catalyst system are very important for a catalytic reaction. Activity of the reused catalyst was investigated through the oxidation reaction of dibenzyl sulfide in the presence of PhPySu-PW as catalyst (Fig. 3). Recovery of the catalyst was very convenient. After each run, the reaction mixture was cooled; catalyst appeared at the bottom of the reactor as solid and could be recovered by decantation (or filtration). There was no significant decrease in yield after five subsequent reactions. After five cycles, the catalyst was weighed, a loss of 20 wt.% of the catalyst (compared with the amount of the catalyst at the first run) was found. These results indicate that the catalyst shows no significant change in its activity and only a trace declining in the yield.

Based on the above results, the catalytic system was used to ECOD of model oil containing DBT (500 ppm), MPS (250 ppm) and thiophene (250 ppm) in 5 mL of n-hexane with the total sulfur concentration of 1000 ppm (Scheme 2). The sulfur in model oil was reduced from 1000 ppm to 10 ppm (90%). In order to investigate the desulfurization efficiency of the catalyst, the catalytic system was used to ECOD of model oil with low concentration of DBT (100 ppm level) in n-hexane. The sulfur level was lowered from 100 ppm to 25 ppm after ECOD process.

Table 3 shows the comparison of catalytic activity of PhPyBs-PW catalyst with some reported hybrid POM catalyzed H_2O_2-based sulfoxidation reactions. As can be seen, PhPyBs-PW catalyst shows considerable activity with unique thermoregulated phase-separable behavior in comparison with the others.

4. Conclusion

We report successful preparations of POM-IL salts by combining sulfonate functionalized cations with Keggin-structured POM. A new approach to the oxidation of sulfur-containing compounds was developed using the prepared POM-IL salts as catalyst. Various kinds of sulfides were successfully oxidized to their corresponding sulfoxides in a relatively good time. Also, the extractive and catalytic oxidation desulfurization of a synthetic mixture of model oil composed of sulfur-containing compounds and n-hexane was carried out with H_2O_2 as an oxidizing agent using these POM-IL salts as catalyst. It was found that PhPyBs-PW acted as homogeneous catalyst at the reaction temperature, and upon the cooling down of the reacted mixture, it resumed the solid state that can be easily recovered and reused. This procedure offers several major advantages: (1) the use of a chemically stabile catalyst; (2) highly efficient for the selective oxidation of structurally diverse sulfides in good to high yields; and (3) the avoidance of the usage of any addictive.

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Table 3
Comparison of the reaction data with other reported methods.

Substrate	Catalyst	Reaction conditions	Yield (%)
S—Ph	PhPyBs-PW	H_2O_2, H_2O, r.t., 2 min	95
S—Ph [47]	CinH$_3$PMo$_{12}$O$_{40}$	H_2O_2/urea, EtOH, r.t., 2 h	95
S—Ph [48]	PyH$_3$PMo$_{11}$VO$_{40}$	H_2O_2, CH$_3$CN, r.t., 3 h	100
Ph—S—Ph	PhPyBs-PW	H_2O_2, H_2O/EtOH, 60 °C, 10 min	98
Ph—S—Ph [47]	CinH$_3$PMo$_{12}$O$_{40}$	H_2O_2/urea, EtOH, r.t., 2 h	97
Ph—S—Ph [48]	PyH$_3$PMo$_{11}$VO$_{40}$	H_2O_2, CH$_3$CN, r.t., 30 min	94

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