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Organic-inorganic polyoxometalate based salts as thermoregulated phase-separable catalysts for selective oxidation of thioethers and thiophenes and deep desulfurization of model fuels

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Abstract

Synthesis of various organic-inorganic polyoxometalate based salts composed of sulfonated pyridinum cations and the Keggin tungstophosphate anion ($PW_{12}O_{40}^{3-}$) and their subsequent application in the oxidation of methyl phenyl sulfide with hydrogen peroxide in aqueous media was reported. Special attention was paid to the temperature-dependent solubility of the salts as a function of the organic cation in water. Cyclic voltammetry was further used for the investigation of the redox behavior of these catalysts. Based on these properties, a novel thermoregulated phase-separable catalyst was introduced and successfully used for the selective oxidation of the sulfur-containing model oil (methyl phenyl sulfide, dibenzothiophene and thiophene) was also studied under optimized conditions. In both cases, excellent conversion and selectivity were obtained in relatively short reaction times. This novel catalyst showed the characteristic of homogeneous reaction at ambient temperatures and phase-separation at lower temperatures. By simple decantation, the catalyst could be easily separated from the products upon cooling of the reaction mixture and could be reused several times with high recycling efficiency.

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Keyword: Polyoxometalates; Thermoregulated catalyst; Deep desulfurization; Sulfur; Oxidation

1. Introduction

The research and application of "Green Chemistry" principles have led to the development of cleaner processes. In this sense, polyoxometalates (POMs) are widely-used as green catalysts especially in H₂O₂-based oxidation reactions [1-6], whereas no corrosive species are involved in the reaction system. Much attention has currently been focused on the use of the POMs as catalysts in the selective oxidation of organic sulfur compounds [7-10], not only for the syntheses of sulfoxides and sulfones as synthetic intermediates in pharmaceutical field [11] but also in the oxidative desulfurization (ODS) process as an effective method to remove of sulfur compounds from fuels and industrial effluents, in order to satisfy the new environmental legislations [12-14].

The homogeneous POMs are remarkably efficient, but they share a common drawback: separation and reuse of the catalyst is extremely difficult. For this reason, future practical applications of POMs will also require methods for "catalyst engineering" to aid in catalyst recovery and recycling. Recently, many improvements were developed for the synthesis of new organic-inorganic salts through the different combinations of various organic cations with POM anions [15-17]. Obviously, these new hybrids have emerged as one of the most potentially significant fields of investigation in catalysis [18-21]. Until now, a few reports have been published on ODS catalyzed with organic-inorganic POM-based salts [22-29]. Recent examples can be classified into two groups. One of them includes amphiphilic catalysts that have been synthesized by combining quaternary ammonium cations and POMs anions [22-24]. These compounds have ability to form emulsion droplets, which perform as homogeneous catalysts in the interface of two immiscible liquids to achieve high activities during the oxidative process. However, the de-emulsification for catalyst recovery is often

challenging in a large-scale unit. Catalyst recovery in an active form suitable for recycling is generally not feasible and the products may be contaminated with catalyst residues. This situation often leads to the expensive purification procedures which disagree with the development of more sustainable processes.

Recent advances in ionic liquids (ILs) research provide another route for achieving organic-inorganic POM-based salts which have been constructed by creation of electrostatic interactions between the organic IL cation and the POM anion (POM-IL salts) [15-17]. To our knowledge there are few papers about the use of POM-based salts in the selective oxidation of organic sulfur compounds and applications in the elimination of sulfur content in diesel are quite limited. [MIMPS]PW/[Omim]PF₆ and [PyPS]PW/[Omim]PF₆ catalytic systems (Scheme 1) have been used to deep desulfurization of fuels [25, 26]. However, the disadvantages of these strategies are also obvious. While used as the reaction media, the [Omim]PF₆ is consumed in large amounts. Bearing in mind that [Omim]PF₆ is fairly expensive and easily yields white fumes of HF or hydrate precipitates. Furthermore, the selectivity for sulfoxides and sulfones present in diesel oil is imperfect and problems associated with catalyst recycling remains a major challenge. Therefore designing a POM-IL system, which can combine the advantages of homogeneous and heterogeneous catalysts, is an attractive field in the chemical research area.

One has to take into consideration the fact that physical and chemical properties of the POM-ILs can be tuned by the change in the structure, functional group, or size of the ions [30]. With this fact in mind, we have designed and synthesized a series of novel POM-IL catalysts with the structure close to [PyPS]PW, including [BuPyPS]PW, [PhPyPS]PW, and [BzPyPS]PW (Scheme 1), and investigated the catalytic activities and temperature-dependent solubilities of these compounds in water. According to experimental findings, a novel thermoregulated phase-separable catalyst was introduced for selective oxidation of organic sulfur compounds in aqueous media. The desulfurization of model oil was also investigated

under optimized reaction conditions. This novel POM-IL catalyst can be easily separated from products upon cooling of the reaction solution. Thus, the problem associated with the separation and reuse of the catalyst can be well resolved. As to the knowledge of the authors, open literature does not show publications related with these new POM-ILs, therefore no information is available about their activities or temperature-dependent solubilities until now.



Scheme 1. POM-ILs structures.

2. Experimental

2.1. General

All reagents and solvents used in this work were obtained from Fluka, Aldrich or Merck and were used without further purification. $H_3PW_{12}O_{40}$ (PW) from Aldrich was used. UV-vis spectra were obtained with an Agilent (8453) UV-vis diode-array spectrometer using quartz cells of 1 cm optical path. NMR spectra were recorded on a Bruker Avance 200 MHz NMR spectrometer with D₂O as the solvent and TMS as the internal standard. IR spectra were recorded as KBr pellets using a Shimadzu 470 spectrophotometer. Elemental analyses were

performed using CHN Herause rapid model. Melting points were determined using a digital Gallenkamp apparatus and uncorrected. Electrochemical experiments were performed using a computer controlled μ -Autolab modular electrochemical system (Eco Chemie, Utrecht, the Netherlands) driven with GPES software (EcoChemie). The products were analyzed using gas chromatographic-mass spectroscopy (GC-MS) Agilent Technologies 6890N Instrument, equipped with a capillary column 19019J-413 HP-5, and a flame ionization detector.

2.2. Catalysts preparation

The POM-IL catalysts were synthesized following the procedure in Scheme 2. Typically, for the synthesis of $[PyPS]_3PW$ catalyst, pyridine (0.11 mol) and 1, 3-propanesultone (0.10 mol) were dissolved in toluene (30 mL) and stirred at 40 °C for 24 h under nitrogen atmosphere. A white precipitate (PyPS) was formed. It was filtered, washed with diethyl ether three times and dried in a vacuum. The resulting PyPS (0.06 mol) was added to an aqueous solution of PW (0.02 mol PW in 40 mL H₂O), and then the mixture was stirred at room temperature for 24 h. Water was removed in a vacuum to give the final product as a solid. Other catalysts were prepared accordingly.

Elemental analyses for the POM-ILs are as follows:

Calc. for [PyPS]PW: C, 8.27; H, 1.03; N, 1.20; S, 2.47. Found: C, 8.22; H, 1.05; N, 1.23; S, 2.70. Calc. for [BuPyPS]PW: C, 11.83; H, 1.65; N, 1.15; S, 2.63. Found: C, 11.85; H, 1.68; N, 1.16; S, 2.64. Calc. for [PhPyPS]PW: C, 13.57; H, 1.30; N, 1.13; S, 2.58. Found: C, 13.60; H, 1.32; N, 1.10; S, 2.59. Calc. for [BzPyPS]PW: C, 14.38; H, 1.45; N, 1.11; S, 2.56. Found: C, 14.41; H, 1.46; N, 1.12; S, 2.59.

Based on the elemental analyses data, it seems that the POM-IL salts basically consist of [PyPS]₃PW, [BuPyPS]₃PW, [PhPyPS]₃PW and [BzPyPS]₃PW respectively. Melting points, IR and ¹H NMR data of the organic cations and the POM-ILs are given in the supplementary information.

2.3. Solubility measurement of the POM-ILs in water

Solubilities of the POM-ILs in water were measured by means of UV-vis spectroscopy according to the procedures previously reported in literature [31]. The quantitative determination of the amount of dissolved catalysts in water is based on the fact that the POM-ILs have charge transfer bands at 256 ([PyPS]PW), 251 ([BuPyPS]PW), 285 ([PhPyPS]PW) and 250 nm ([BzPyPS]PW) (see Fig. 1 in supplementary information). The calibration curve for each POM-ILs was prepared based on standards provided by our laboratory for absorbance values varying from 0.0 to 2.0. In this region the calibration curves were almost linear (see supplementary information). To measure the solubility of catalysts, excess amounts of the POM-ILs were added in water (5 mL) and vigorously stirred for 6 h at different temperatures. An aliquot was separated (from insoluble POM-ILs) by centrifugation and diluted by a factor of 5-20 times. Then the absorption value of these dilution solutions were measured, and the amount of dissolved POM-IL can be calculated using calibration curves, considering the diluted factor.

2.4. Voltammetry experiments

The electrochemical reduction of the 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 Vs⁻¹) were obtained at ambient temperature (20±5 °C).

2.5. Catalytic reactions

2.5.1. Reaction progress monitoring

Progress of model reactions was monitored by UV-vis spectroscopy which measured the decrease in the absorbance of methyl phenyl sulfide (MPS) or dibenzothiophene (DBT) during the reaction. Samples (100 μ L) were taken out from the reaction mixture at different reaction times and immediately treated with 1 mL of distilled water and shaken for few minutes. Later, 1 mL of n-hexane was added, and this mixture was again shaken and agitated to develop two phases: the non-polar phase containing MPS or DBT and the polar phase containing catalyst,

 H_2O_2 and corresponding sulfoxide and/or sulfone. The organic phase was separated and analyzed by UV-vis spectroscopy and the product was extracted using Et₂O from aqueous phase and analyzed after catalyst separation. The solution absorbance was measured at 250 nm for MPS and 230 nm for DBT. All the measurements were repeated at least three times and the reported values are averages of the individual runs.

2.5.2. Oxidation of liquid sulfides (Table 1, entries 1-7)

To a stirred mixture of the sulfide (5 mmol), and catalyst (0.05 g, 0.25 mol%) in water (10 mL), 30% aq. H_2O_2 (0.56 mL, 5mmol) was added in one portion. The slurry was stirred at room temperature for 20 min. The reaction mixture was cooled to 10 °C, and the catalyst was separated by filtration. The corresponding sulfoxide product was extracted with Et_2O from the reaction mixture. Evaporation of the solvent afforded the crude product. The crude product was purified by column chromatography on silica gel using EtOAc/hexane as eluent (method **a**).

Similar method was utilized to produce sulfones. In this case 2.2 mL of 30% aq. H_2O_2 (20 mmol) and 0.15 g of catalyst (0.75 mol%) were utilized (method **b**).

2.5.3. Oxidation of solid sulfur compounds (Table 1, entries 7-10)

To a stirred suspension of the substrate (5 mmol), catalyst (0.2 g, 1.0 mol%) in H₂O: EtOH (7:3 v/v, 10 mL), 30% aq. H₂O₂ (1.1 mL, 10 mmol) was added in one portion. The slurry was stirred at 60 °C for 45 min. The reaction mixture was cooled to 10 °C, and the catalyst was separated by filtration. The corresponding sulfoxide product was extracted with Et₂O from the reaction mixture. Evaporation of the solvent afforded the crude product. The crude product was purified by column chromatography on silica gel using EtOAc/hexane as eluent (method **c**). Similar method was utilized to produce sulfones. In this case 3.4 mL of 30% aq. H₂O₂ (30 mmol) was used for 60 min (method **d**).

2.5.4. Oxidative desulfurization of model oil

Two model oils were used: (1) Model fuel containing DBT (500 ppm means 500 mg of DBT per 1 L of n-decane), MPS (250 ppm) and thiophene (250 ppm) in 5 mL of n-decane with the corresponding total sulfur concentration 1000 ppm and (2) Model fuel containing DBT in 5 mL of n-decane with the sulfur concentration 100 ppm. The oxidation reaction was carried out using 4.0 μ mol catalyst (1.0 mol%), 2.5 mmol H₂O₂, 5 mL model oil in H₂O: EtOH (7:3 v/v, 5 mL) at 60 °C for 2 h. The oil phase was withdrawn and analyzed by gas chromatography (GC) for concentration of sulfur compounds. After the reaction, the reaction mixture was cooled to 10 °C, and the catalyst was recovered by centrifugation. The products were extracted using Et₂O from the solvent phase and analyzed by GC-MS.

3. Results and discussion

The POM-IL catalysts were synthesized by two-step atom economic reaction (Scheme 2). The zwitterionic-type precursors were prepared through a one-step direct sulfonation reaction of pyridine derivatives and 1, 3-propanesultone. The supernatant liquid was analyzed by GC-MS. Based on GC-MS results no by-product was produced in the zwitterions synthesis procedure. The zwitterions acidification was accomplished by mixing of zwitterions with PW, which led to the formation of organic-inorganic salt.



Scheme 2. Synthesis of POM-IL catalysts.

The IR spectra are quite useful to find structural and bonding changes in the Keggin unit present in the POM-ILs. The PW Keggin ion structure is well known and consists of a PO₄ tetrahedron surrounded by four W_3O_{13} groups formed by edge-sharing octahedra. These groups are connected to each other by corner-sharing oxygens [32]. Accordingly, PW shows typical bands for absorptions at 1080 (P-O), 984 (W=O), 896 and 814 (W-O-W) cm⁻¹. The IR spectra of the POM-ILs showed that the basic structure and geometry of the Keggin anion are preserved (Fig. 1).



Fig. 1. IR spectra of (a) PW, (b) [PyPS]PW, (c) [BuPyPS]PW, (d) [PhPyPS]PW, (e) [BzPyPS]PW and (f) reused [PhPyPS]PW.

Catalytic activities of the POM-ILs were investigated in the oxidation of MPS as a model substrate using aqueous H_2O_2 at ambient temperature in water. The oxidation progress with [PyPS]PW/H₂O₂ was monitored by UV-vis spectroscopy (more details were described in experimental section). It can be seen that the absorption band at 250 nm for MPS (in n-hexane) decreases significantly with increasing the reaction time (Fig. 2(a)). The decrease in the absorption maximum at 250 nm (ln(A₀/A₁)) as a function of reaction time for the organic cations, PW and the POM-ILs are shown in Fig. 2(b). A blank experiment performed in the absence of catalyst showed very low conversion. The counterpart cations showed remarkably poor activities while the conversion is better for the POM-ILs. The course of the oxidation reaction was strongly influenced by the nature of the organic cation in the POM-ILs and decreased in the following order: [PyPS]PW > [PhPyPS]PW > PW > [BuPyPS]PW > [BzPyPS]PW.

Solubility of the POM-ILs is the major factor that should be considered in their catalytic applications in view of catalyst recycling. The most used term to describe solvent–solute behavior is "polarity". The commonly held molecular view of polarity clearly is not appropriate to the POM-ILs. Until recently there was no systematic examination of the complicated nature of POM-ILs/solvent interactions. It seems that the polarity and subsequently solubility or hydrophobic/hydrophilic properties of these compounds as an organic-inorganic POM-based salts is affected by factors including intermolecular interactions such as van der Waals bonds, hydrogen-bonds and electrostatic interactions, the interaction of solvent with pi- and non-bonding electrons, hydrogen bond acidity and basicity and the dispersion force interactions. Each of above factors could be varied by changing the temperature and features which have a significant, temperature-dependent impact on the solubility of these POM-ILs. Solubility-temperature curves of the catalysts in water are shown in Fig. 3. [PyPS]PW shows high solubility in water even at low temperatures, so it is not suitable choice in the view of catalyst recycling. [BuPyPS]PW, [PhPyPS]PW and

[BzPyPS]PW catalysts show relatively good thermoregulated solubility in water. But, [BuPyPS]PW and [BzPyPS]PW exhibit low catalytic activities (Fig. 2 (b)). As a result, [PhPyPS]PW was selected as the best catalyst in terms of catalytic activity and solubility. It was insoluble below 15 °C and the solubility increases markedly when the temperature rises over 25 °C. In addition, the reversibility of solubility is also observed. When the temperature decreases below 15 °C, the catalyst dissolved in water precipitates again. Therefore, it may be separated from the reaction mixture, with high recycling efficiency.



Fig. 2. (a) Monitoring of the decrease in MPS absorbance with increasing the reaction time; (b) Comparison of the oxidation rates of the catalysts, monitored by UV–vis spectroscopy at 250 nm (MPS: 5 mmol, H₂O₂: 10 mmol, and catalyst: 0.5mol%, in H₂O at room temperature).



Fig. 3. Solubility-temperature diagrams of the POM-ILs in water.

It has been reported that various peroxo complexes are formed during the reaction, in aqueous solutions of H_2O_2 with Keggin-type PW and they constitute the basis of what is called the Venturello–Ishii catalytic system [33-36]. These peroxo species actually catalyze the oxidation of organic compounds. The generation of active species was qualitatively studied using UV–vis spectroscopy of the [PhPyPS]PW catalyst under different conditions (Fig. 4). The UV–vis spectrum of the catalyst on addition of hydrogen peroxide showed appearance of a new broad band at about 370-400 nm and the shoulder peak at 275 nm disappeared. Further, with addition of MPS to a solution of the catalyst and H_2O_2 , the intensity of peak in region 370–400 nm was significantly decreased and the shoulder peak at 275 nm was observed. Based on these results, it is concluded that the reaction of [PhPyPS]PW with hydrogen peroxide leads to the reversible formation of the active species that catalyzes the oxidation of sulfides. However, there is still not a unanimous viewpoint for

the mechanisms of oxidations by POM-IL catalysts and, hence, the nature of active species remains unclear and it is under investigation in our laboratory.



Fig. 4.UV–vis spectra of [PhPyPS]PW catalyst in water before and during the oxidation reaction with H_2O_2 (Catalyst: 10^{-5} M; H_2O_2 : 5×10^{-2} M; MPS: 10^{-2} M).

Several studies showed that the presence of a large counter cation, structure and position of the counter cation around the Keggin cage and interaction between the counter cation and the POM anion influence the surface acid–basic properties of POM, kinds of active species, reaction pathway, and subsequently mechanism of oxidation [37-42]. Cavaleiro and co-workers [42] reported a radical mechanism for the oxidation of cyclooctane. They explained three step mechanisms:

1. Coordination of H_2O_2 to the W atoms of the tetrahexylammonium (THA) salt to form peroxo complex $[W_2O_3(O_2)_4]^{2-}$.

2. Formation of one-electron reduced tungsten.

3. Activation of H_2O_2 at the tungsten atoms, by means of the generation of HO[•] and HOO[•] radicals.

In order to test for an electron-transfer mechanism, the model reaction was carried out in the presence of acrylonitrile (2 mmol) as a well-known radical scavenger. The product yield was decreased from 90% to 68% under these conditions which showed that radical mechanism is at least one of the pathways in this oxidation reaction.

The redox properties of the catalyst play an important role in the occurrence of the radical process. The cyclic voltammograms of the POM-ILs are shown in Fig. 5. As a comparison, the cyclic voltammogram of the pure PW is also presented. PW shows three couples of sharp and well-defined redox waves correspond to reversible two-electron reduction/oxidation processes of the POMs [43]. The peak potentials of [PyPS]PW and [PhPyPS]PW catalysts lie almost at the same values as the parent PW and the redox activity of the anion is indeed preserved in these salts. But, as displayed in Fig. 5, the cyclic voltammograms of [BuPyPS]PW and [BzPyPS]PW catalysts show obvious differences. The initial reduction process (I/I') is irreversible and shifted to negative potentials. The other two reduction peaks (II/II' and III/III') are reversible but the reduction peak potentials shift towards negative values and the shift is more pronounced for [BzPyPS]PW compared with [BuPyPS]PW. Because of the poor catalytic activities of these catalysts (Fig. 2(b)), it can be suggested that the initial reduction process of PW plays an important role in model reaction.

The onset reduction potential for H₂O₂ was measured in the presence of PW, [PyPS]PW and [PhPyPS]PW. The direct reduction of H₂O₂ required a large over potential at most electrode surfaces and no obvious response was observed at the glassy carbon electrode under our experimental conditions. On the basis of the voltammetric results, the reduction of H₂O₂ in the presence of the PW anion occurred at a potential about -137 mV. It is more negative than the reduction potential in the presence of [PyPS]PW ($E_{\text{Red}}^{\text{Onset}} = 197 \text{ mV}$) and [PhPyPS]PW ($E_{\text{Red}}^{\text{Onset}} = 185 \text{ mV}$). Therefore, these POM-ILs can effectively activate the

 H_2O_2 molecule and showed higher catalytic activity compared with PW (Fig. 2(b)). However, the present results do not allow more detailed description of the reaction mechanism. More investigations are inprogress in our laboratory, and will be reported in due course.



Fig. 5. Cyclic voltammograms for PW (5 \times 10⁻⁴ M) and the POM-ILs (5 \times 10⁻⁴ M) in phosphate buffer (0.1 M), pH = 1, scan rate: 0.1 V/s, ambient temperature (20±5 °C).

The influence of different reaction parameters on the selectivity and efficiency of oxidation process was evaluated in the model reaction using [PhPyPS]PW as the best catalyst (Fig. 6). At different MPS/H₂O₂ ratios, we observed different relative amounts of methyl phenyl sulfoxide (MPSO) and methyl phenyl sulfone (MPSO₂) (Fig. (6a)). The optimized conditions for selective production of each of the two compounds were determined. With equal molar amounts of H₂O₂ and MPS, MPSO was produced with 94% selectivity. Using 0.25 mol% of the catalyst to MPS in the same conditions produced MPSO as the sole reaction product (Fig. 6(b)). On the other hand, with excess amounts of H₂O₂ (1:4) (Fig. 6(a)) and catalyst (0.75 mol% to MPS) (Fig. 6(c)), MPSO₂ appeared as the sole oxidation product at room temperature. With these optimized results in hand, a series of sulfides was subjected to oxidation under the specific conditions required for sulfoxide or sulfone production (Table 1). Various types of sulfides were oxidized to the corresponding sulfoxide or sulfone with excellent selectivity (Table 1, entries 1-7).



(a)



Fig. 6. Effect of (a) MPS: H_2O_2 molar ratio (catalyst loading: 0.5 mol%; MPS: 5 mmol), (b) catalyst loading (MPS: 5 mmol; H_2O_2 : 5 mmol) and (c) catalyst loading (MPS: 5 mmol; H_2O_2 : 20 mmol) in the selective oxidation of MPS in the presence of [PhPyPS]PW catalyst in H_2O at room temperature.

Table 1.	Selective	oxidation	of sulfides	to sulfoxides	and to	sulfones	with	30% aq.	H_2O_2
using [P	hPyPS]PW	as cataly	st.						

Б (Substrate	Yield ^a (selectivity) (%)				
Ениу		Sulfoxide ^b	Sulfone ^c			
1	Ph ^S	98 (100)	98 (100)			
2	Ph ^{-S}	98 (100)	98 (100)			
3	Ph ^{´S} `Ph	85 (100)	90 (94)			
4	≫S.,//	98 (100)	98 (100)			
5	∽ ^s ∽	90 (100)	95 (100)			
6	∕~ ^S √∕	90 (100)	95 (100)			
7	s J	75 (100)	80 (94)			
8	S S	95 (95) ^d	95 (100) ^e			
9	Ph ^S Ph	98 (100) ^d	98 (100) ^e			
10	Ph~S ^{Ph}	95 (95) ^d	90 (100) ^e			
^a Isolated yield.						
^b Metho	od (a).					
^c Metho	od (b).					
^d Method (c).						
^e Method (d).						

Because solid sulfur compounds (Table 1, entries 8-10) are insoluble in aqueous medium, it was necessary to use a co-solvent that solubilizes these compounds in water. Based on literature survey, in polar organic solvents such as acetonitrile, methanol, ethyl acetate and acetone, the oxidation reaction proceeded rather fast, and gave mixture of sulfoxides and

sulfones with good conversion [44-46]. Among them, methanol was consequently the solvent of choice. In this study, EtOH was used as the co-solvent since it is derived agricultural products and is renewable, biologically less objectionable in the environment and less toxic compared with methanol. In order to optimize the reaction conditions, DBT, one of the major sulfur-containing compounds present in fuels, was selected as model substrate. It showed absorption band at $\lambda_{max} = 230$ nm (Fig. 7(a)). We selected 7:3 v/v H₂O: EtOH ratio as the solvent composition, since higher amount of water resulted in precipitation of the DBT. The H₂O₂-oxidation of DBT was not performed at room temperature. Whereas by increasing the temperature up to 60 °C, the catalytic activity was significantly improved and DBT absorption band decreased significantly (Fig. 7(a)). Therefore, the oxidation reaction was performed using different concentrations of H₂O₂ and different amounts of the catalyst in 60 °C (Fig. 7(b)-7(d)). The corresponding sulfoxide could be obtained in excellent yield in the presence of 1 mol% of catalyst to DBT and 1:2 DBT/H₂O₂ ratio with trace over-oxidation product (Fig. 7c). With increasing the amounts of oxidant to 1:6 DBT/H₂O₂ ratio, the corresponding sulfone was obtained with 100% selectivity (Fig. 7(d)). The obtained results showed that the solid substrates were completely oxidized to the corresponding sulfoxide and sulfone under these optimized conditions (Table 1, entries 8-10).

Based on the above results, the catalytic system was used to ODS of model oil containing DBT (500 ppm), MPS (250 ppm) and thiophene (250 ppm) in 5 mL of n-decane with the total sulfur concentration 1000 ppm. At the end of the reaction, the upper phase was withdrawn and analyzed by GC. The sulfur in diesel fuel was reduced from 1000 ppm to 64 ppm (93.6%). In order to investigate the deep desulfurization efficiency of the catalyst, the catalytic system was used to ODS of model oil with low concentration of DBT (100 ppm level) in n-decane. The sulfur level was lowered from 100 to 0.8 ppm after ODS process. The remaining hydrogen peroxide was determined by $Ce^{VI}(SO_4)_2$ (0.1 M) titration [47] and the efficiency of H₂O₂ utilization was calculated according to the following formula: $[(2 \times mol (DBT))/(mol (H_2O_2))]$

consumed)]×100. The direct decomposition of hydrogen peroxide was observed during the oxidation process, but the efficiency of H_2O_2 was higher than 90% for desulfurization of this model oil (DBT = 100 ppm).



(b)



Fig. 7.^(a) Monitoring of the decrease in DBT absorbance with increasing the reaction time (DBT: 5 mmol, H_2O_2 : 20 mmol, and catalyst: 0.5 mol%, in H_2O : EtOH (7:3 v/v, 10 mL) at 60 °C); Effect of (b) DBT: H_2O_2 molar ratio (catalyst loading: 0.5 mol%, DBT: 5 mmol), (c) catalyst loading (DBT: 5 mmol, H_2O_2 : 10 mmol), and (d) catalyst loading (DBT: 5 mmol, H_2O_2 : 30 mmol) in the selective oxidation of DBT in the presence of [PhPyPS]PW catalyst in H_2O : EtOH (7:3 v/v, 10 mL) at 60 °C.

Easy recyclability and the prolonged retention of catalytic activity are very important features for practical applications of catalytic processes. [PhPyPS]PW catalyst has combined the advantages of a one-phase homogeneous catalysis with an easy way of catalyst separation. It was used in four 20 min catalytic cycles of MPS oxidation with H₂O₂ (Fig 8 (a)). After the reaction, the mixture was cooled to 15 °C and the catalyst was separated by filtration after each cycle, washed with ether and dried at 50 °C. Five consecutive preparation of MPSO showed no significant loss in yield. After five cycles, the catalyst was recovered and weighed. The loss of 12.5% was found, which is agree with the calculated amount according to Fig. 3 (the solubility of ionic liquids, 0.113 mg/mL at 15 °C) and the used solvents amount (2 mL) in each cycle. If the temperature is reduced to 10 °C after the each reaction cycle, the loss of the catalyst can reduced to 9.3% accordingly. When the equivalent amount of lost catalyst is added, the yield can be restored to 98%.

Reusability of [PhPyPS]PW catalyst was also investigated in model oil. After the reaction, model oil was transferred from the reaction vessel by separator funnel and the aqueous phase was cooled to 10 °C. The catalyst was separated by filtration, washed, dried and used in the next ODS reaction. The oil phase was analyzed by GC for concentration of sulfur compounds. The products were extracted by Et_2O from the solvent phase and analyzed by GC-MS. Corresponding sulfones have been obtained with excellent selectivities in all runs. The results indicate that the catalyst can be recycled five times with a slight decrease in desulfurization (Fig. 8 (b)). The IR spectrum of reused catalyst confirmed the existence of Keggin structure after five cycles (Fig. 1 (f)).

Table 2 shows the comparison of catalytic activity of [PhPyPS]PW catalyst with some reported POMs catalyzed H₂O₂-based sulfoxidation reactions. As can be seen, [PhPyPS]PW catalyst shows considerable activity with unique thermoregulated phase-separable behavior in comparison with the others.



Fig. 8. Reusability of [PhPyPS]PW catalyst in (a) oxidation of MPS (MPS: 5 mmol, H_2O_2 : 5 mmol, and catalyst: 0.25 mol% in H_2O at room temperature) and (b) oxidative desulfurization of model oil (DBT: 100 ppm in n-decane, H_2O_2 : 2.5 mmol, and catalyst: 1.0 mol% in H_2O : EtOH (7:3 v/v, 5 mL) at 60 °C for 2 h).

Table 2. Comparison of the reaction data with other reported methods.

Substrate	Catalyst	Reaction conditions	Yield (%)
MPS	[PhPyPS]PW	H ₂ O ₂ , H ₂ O, r.t., 20 min	98
MPS [48]	$CinH_3PMo_{12}O_{40}$, (Cin =	H ₂ O ₂ /urea, EtOH, r.t., 2 h	95
	cinchonine)	, , , ,	
MPS [7]	$PyH_3PMo_{11}VO_{40}$	H ₂ O ₂ , CH ₃ CN, r.t., 3 h	100
MPS [49]	$[\gamma - PW_{10}O_{38}V_2(\mu - OH)_2]^{3-1}$	H ₂ O ₂ /HClO ₄ , CH ₃ CN/tert-	99
		BuOH, r.t., 2h	
DBT(1000 ppm)	[PhPyPS]PW	H ₂ O ₂ , H ₂ O/EtOH, 60 °C, 2h	93.6
DBT(1000 ppm)	[PhPyPS]PW	H ₂ O ₂ , H ₂ O/EtOH, 60 °C, 2h	99.2

DBT (500 ppm) [50]	H ₃ PW ₁₂ O ₄₀ /TiO ₂	H ₂ O ₂ , CH ₃ CN, 60 °C, 2h	95.2
DBT (500 ppm) [26]	[Bmim] ₃ PMo ₁₂ O ₄₀ /SiO ₂	H ₂ O ₂ , 60 °C, 2h	100
DBT (500 ppm) [25]	[MIMPS] ₃ PW ₁₂ O ₄₀ 2H ₂ O	H ₂ O ₂ , [Omim]PF ₆ , r.t., 1 h	99.5

4. Conclusions

In agreement with the ever increasing environmental awareness, we developed a new reusable catalytic system for sulfoxidation reaction based on temperature-dependent solubility of the POM-ILs. This catalyst has been successfully applied for selective oxidation of thioethers and thiophenes to the corresponding sulfoxides and sulfones with dilute H_2O_2 , in water or EtOH: water biphasic system. The results showed that the catalyst has exhibited not only excellent redox property of POMs but also good recycling efficiency. Catalyst/product separation was very simple and the catalyst was recovered upon cooling of the reaction mixture and reused several times without obvious loss of catalytic activity. This catalyst also showed excellent activity for the removal of sulfur contents in model oil. So, it has a high potential as an effective catalyst for deep desulfurization of real diesel. We hope that the knowledge gained in this work will lead to the use of thermoregulated phase-separable POM-IL catalysts in a wide variety of organic reactions in aqueous media.

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Highlights

- Novel polyoxometalate salts were synthesized and characterized.
- They were used as thermoregulated phase-separable catalyst for ODS process.
- They showed characteristic of homogeneous catalysis and heterogeneous separation.
- The process was successfully used for deep desulfurization of model oil.
- There was no considerable loss in catalytic activity after several reaction cycles.

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