

## Ionic Liquid Based Polyoxometalate as an Industrial Candidate for Extractive Desulfurization without Chemical Intermediates Production

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This work involves the extractive oxidation of mixed thiophenic compounds model oil over an oxidative polyoxometalate-based catalytic system. Phosphotungstic acid-pyridine compound combining of Keggin-structured polyoxometalate anion with sulfonate functionalized cation was applied as catalyst in sulfur removal. Model oil was simulated using a mixture of the sulfur compounds dibenzothiophene, benzothiophene and thiophene in *n*-heptane. At optimization strategy, different extractive solvents including isopropanol, ethanol, dimethylformamid and acetonitrile in desulfurization performance were used. Some important reaction parameters including catalyst loading, dose of the oxidizing agent, existence of nitrogen compounds and aromatic hydrocarbons (toluene, xylene and mesitylene) were considered on the oxidative desulfurization (ODS) *via* a one-step process under optimized conditions.

**Keywords:** Model oil, Desulfurization, Extraction, Ionic liquids, Polyoxometalate

### INTRODUCTION

A major source of environmental pollution is sulfur in transportation fuels from automobiles and industry which is converted into sulfur oxide (SO<sub>x</sub>) and discharges to the air. SO<sub>x</sub> causes air pollution and acid rain that can cause serious respiratory problems for human [1]. Sulfur containing compounds (S-compounds) such as thiophenes (T) contribute to corroding parts of internal combustion in engines and poison catalysts. As a response, stringent worldwide environmental regulations have been proposed to decrease the sulfur content in recent years. Therefore, it is expected to decrease the level of sulfur in gasoline and diesel globally under 50 μg g<sup>-1</sup> during the next years. Various processes of desulfurization as an important global subject have been considered to decrease the sulfur content of fuel to ultra-low levels [2]. Desulfurization makes the formation of SO<sub>x</sub> least, that is one of the factor pioneers to acidic rain.

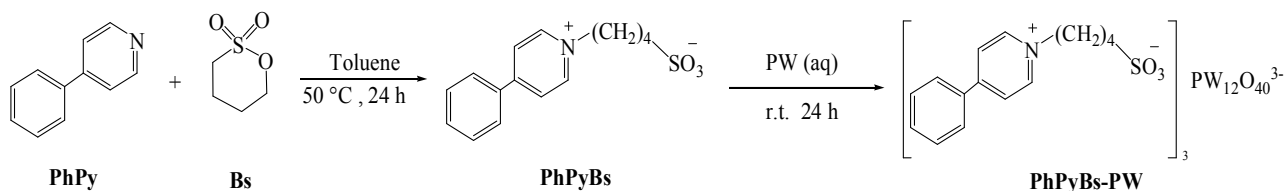
So far, numerous desulfurization methods have been

investigated such as hydrodesulfurization (HDS), extractive desulfurization, biodesulfurization and oxidative desulfurization (ODS) to lead low sulfur level in fuels [3-6]. The most widely used method to decrease the sulfur level of fuels is HDS. It is very difficult to removed aromatic S-compounds such as dibenzothiophene (DBT) and its derivatives by HDS methods due to the low reactivity of these S-compounds [7,8]. Also, conventional HDS method has many problems, such as high temperature (300-400 °C), high hydrogen pressure (30-70 atm), long residence time, and high operating-cost of equipment and hydrogen. As a result, it is necessary to develop new and suitable approaches for desulfurization and decrease the cost of treating fuels.

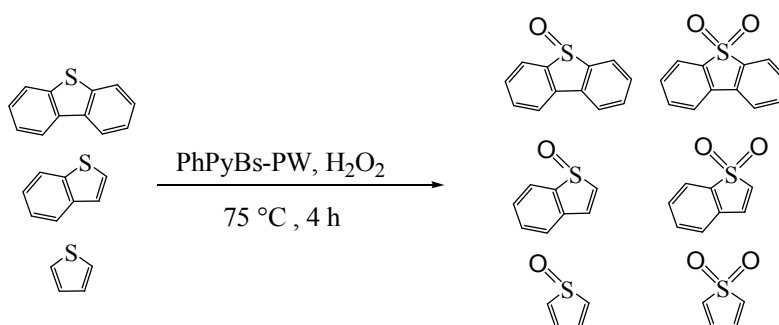
ODS methods are the hot research subject because of the advantages such as no need to hydrogen atmosphere, relatively low temperatures and mild reaction conditions [9-11].

In general, selective ODS has two original steps: firstly, oxidation of the S-compounds to the corresponding sulfoxides or sulfones in the presence of an oxidant [12]. Higher polarities of oxidized S-compounds than their parent

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*Scheme 1.* Schematic illustration for preparation of PhPyBs-PW



*Scheme 2.* Schematic illustration for ODS process

S-compounds and the other hydrocarbons, permit us to remove them by various separation processes such as solvent extraction and adsorption. Thus, the second step is using a non-miscible polar organic solvent as extractive solvent, such as acetonitrile (MeCN), dimethyl sulfoxide (DMSO), or N,N-dimethylformamide (DMF). Extractive solvents with higher polarity are more effective because of polarity of oxidized compounds. There are further environmental and security problems because of flammability and volatility of these organic solvents [13].

Numerous catalytic systems have been introduced for ODS methods. Among them, catalytic systems which used polyoxometalates (POMs) like POMs-based ionic liquid (POM-IL) have attracted more attention because of their special properties such as redox potentials, solubility, thermal and oxidative stability [14-17]. In recent years, many attentions have been paid to the properties of POM-ILs which can be achieved by changing their cations and anions. Many POM-ILs especially Keggin type POM-ILs have been investigated in ODS methods, and very satisfying results achieved [18-22].

According to our previous studies on application of POM-ILs in oxidation of sulfur-based compounds as

capable catalysts, we present our results on development of an efficient ODS system for the removal of S-compounds model oil.  $[4\text{-PhPyBs}]_3\text{PW}$  (Scheme 1) was synthesized by reacting  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (PW) (inorganic anion) with the sulfonate functionalized cation  $[4\text{-PhPyBs}]$ , and evaluated in the oxidation of model oil. For the experimental study T, benzothiophene (BT) and DBT (Scheme 2) were selected because they are the most widely used compounds in fuels.

## EXPERIMENTAL

### General Remarks

All organic materials and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (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 FT-IR Rayleigh. Electrochemical experiments were performed with a computer controlled  $\mu$ -Autolab modular electrochemical system (SAMA500 ElectroAnalyzer system). Various model oils with 1000 ppm concentration were prepared to investigate several factors as shown in Table 1.

**Table 1.** Different Mmodel Oils

Entry	Model feeds	Amounts of the compound	Notation
1	DBT	500 ppm S	F
	BT	250 ppm S	
	T	250 ppm S	
	<i>n</i> -Heptane	Balance	
2	Feed + MeCN	1000 ppm S	F <sub>1</sub>
3	Feed + isopropanol ( <sup>i</sup> PrOH)	1000 ppm S	F <sub>2</sub>
4	Feed + DMF	1000 ppm S	F <sub>3</sub>
5	Feed + EtOH	1000 ppm S	F <sub>4</sub>
6	Feed + EtOH + indole (I)	1000 ppm S + 20-100 ppm N	F <sub>5</sub>
7	Feed + EtOH + quinoline (Q)	1000 ppm S + 20-100 ppm N	F <sub>6</sub>
8	Feed + EtOH + I + Q	1000 ppm S + 20-100 ppm N	F <sub>7</sub>
9	Feed + EtOH + toluene + mesitilene + xylene	1000 ppm S + 40 vol.% of hydrocarbons	F <sub>8</sub>

### Synthesis of PW-based IL Catalyst

1,4-Butane sultone (Bs) (0.1 mol) and 4-Phenyl-pyridine (PhPy) (0.1 mol) were mixed and stirred at 50 °C for 48 h at nitrogen atmosphere (Scheme 1). Formed white precipitate (PhPyBs) was filtered, washed with diethylether and dried at room temperature under vacuum. An aqueous solution of PhPyBs (0.3 mol) was added drop-wise to aqueous solution containing of PW (0.1 mol). Mixture was stirred at room temperature for 24 h. Then water was removed in vacuum to find product as golden solid powder [23,24].

### Preparation of Mixed Thiophenic Model Oil and ODS Procedure

The model oil was prepared as follows: DBT, BT and T (500, 250 and 250 ppm) were dissolved in 5 ml *n*-heptane to obtain a solution with sulfur concentration of 1000 ppm as model oil F (Table 1, entry 1). 4-PhPyBs-PW (0.02 g) as catalyst and H<sub>2</sub>O<sub>2</sub> (molar ratio of O/S = 6/1) were poured into the F model oil. Then, ODS process was carried out at 75 °C and the mixture was stirred mechanically about 4 h in

a round bottom flask (Scheme 2).

### ODS of Model Oil with Various Extractant Solvents

Oxidation reaction was carried out using 4-PhPyBs-PW (0.02 g) as catalyst, H<sub>2</sub>O<sub>2</sub> aqueous solution (molar ratio of O/S = 6/1), 5 ml of model oil F at 75 °C for 4 h. A typical ODS process was started by adding different extractant solvents (MeCN, EtOH, <sup>i</sup>PrOH or DMF) (1:1; v/v ratio) at 75 °C for 4 h (Table 1, entries 2-5).

### Effect of Nitrogen Compounds in ODS

A typical ODS process was started by adding nitrogen compounds (N-compounds) at 75 °C for 4 h. To study the influence of N-compounds on the oxidation of S-compounds, 100 ppm N-compound (I or/and Q 20-100 ppm) was added to model oil F<sub>4</sub> (Table 1, entries 6-8). The oxidation reaction was carried out using 0.02 g of 4-PhPyBs-PW as catalyst, H<sub>2</sub>O<sub>2</sub> aqueous solution (molar ratio of O/S = 6/1), and 5 ml of model oil F<sub>4</sub> at 75 °C.

### Effect of 1-Ring Aromatic Hydrocarbons in ODS

40 vol.% of aromatic hydrocarbon was added to model oil F<sub>4</sub> in order to study the influence of 1-ring aromatic hydrocarbons such as toluene, mesitylene and xylene (Table 1, entry 9). The oxidation reaction was carried out using 4-PhPyBs-PW (0.02 g) as catalyst, H<sub>2</sub>O<sub>2</sub> aqueous solution (molar ratio of O/S = 6/1), 5 ml of model oil F<sub>4</sub> and EtOH as extractant solvent (1:1; v/v ratio) at 75 °C for 4 h.

## RESULTS AND DISCUSSION

### Effect of Amount of the Catalyst on Sulfur Removal

Figure 1 reveals the effect of catalyst amount on the ODS reaction under various catalyst quantities. The amount of the catalyst, 4-PhPyBs-PW, had an obvious effect on the desulfurization efficiency [25]. The removal of S-compounds with augment of catalyst during the reaction, is related to increasing of total amount of active sites [26]. The removal of S-compounds was 85% over 0.01 g catalyst after 4 h. Removal of S-compounds was improved from 85% with 0.01 g catalyst to 95% with 0.02 g catalyst. Hence, a proper amount of the catalyst plays a role in booming thiophenic compounds to transform, and 0.02 g is chosen as the optimal amount.

### Effect of Molar Ratio of O/S in Sulfur Removal

The amount of oxidizing agent has a significant influence on ODS process [27]. As shown in Fig. 2, with the increasing of molar ratio of O/S, S-compounds removal increased and reached to 95% at molar ratio of O/S = 2/1, which is in accordance with the stoichiometry of the oxidative reactions. By increasing the dosage of oxidant to molar ratio of O/S = 4, nearly complete S-removal was found 85% after 4 h. Thus, the O/S = 4 was a suitable choice in this work.

### Effect of Various Solvents in Sulfur Removal

Type of solvent is an important factor on the ODS process. More polar solvents could extract the products efficiently due to higher polarity of the products than the corresponding sulfides. However, this process is intensely influenced by the type of the catalyst and nature of the substrate. Furthermore, the dependence of the solvent with

the catalyst is accounted as a factor that must be considered as an optimizing factor during the ODS process [28]. Hence ODS of model oil (F) containing various S-compounds was carried out at optimized reaction conditions with numerous extractant solvents. To search the effect of various solvents on the ODS, different solvents such as MeCN, DMF, *i*PrOH and EtOH, named F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub> and F<sub>4</sub>, respectively, were applied in the model oil (F) (Table 1).

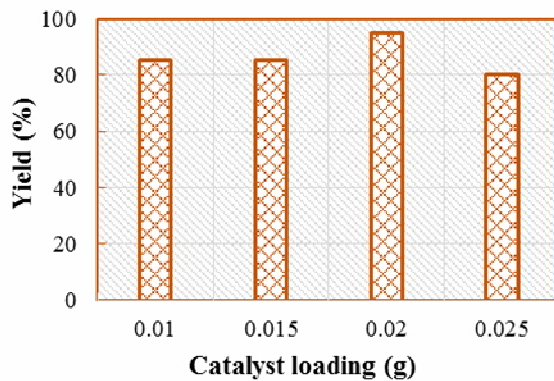
It should be noted that S-removal in the absence of the catalyst and in the presence of 0.02 g of the catalyst but in room temperature were negligible in the optimum reaction conditions. Also, S-removal was checked in F<sub>4</sub> as model oil in optimum reaction conditions in the presence of 0.005 g of organic (PhPyBs) and also 0.015 g of PW as inorganic parts (according to the stoichiometric molecular weights), after 2 h S-removal were negligible and 75% respectively. Also, it should be noted that using PW as catalyst in such reaction sometimes makes a limitation for recovery and reusing. Remaining of a little amount of PW in oil changes other specification of oil.

### Effect of N-compounds on the ODS

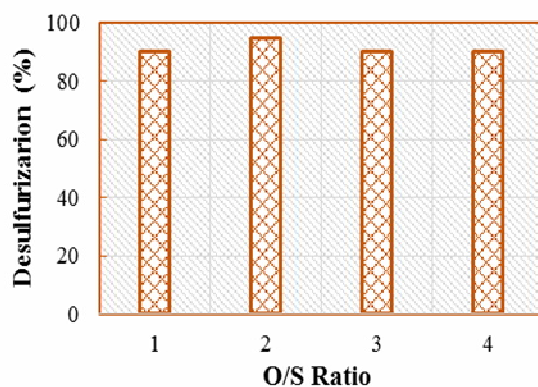
Since both of N- and S-compounds are in fossil fuels, investigation of oxidation of S-compounds in the presence of N-compounds is necessary. The effect of N-compounds on the ODS process of the catalyst was also explored. The ODS process of model oil containing thiophenic compounds was done under adjusted reaction conditions in the presence of I and (or) Q (Fig. 4). Concentration of added N-compounds varied from 20 to 100 ppm. N-compounds got oxidized to corresponding products in short time. In fact, in the presence of these N-compounds, the reaction rate of oxidation for S-compounds was reduced (Fig. 4). There is a competitive adsorption between S- and N-compounds of model oil for catalytic sites.

### Effect of Aromatic Hydrocarbons on the ODS

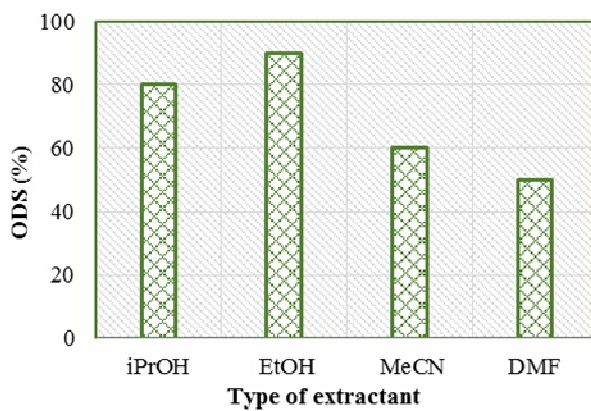
Since large quantities of aromatic hydrocarbons exist in actual oils, it is necessary to investigate the effect of these compounds on the ODS process. The S-compounds removal rate by adding of 1-ring aromatics such as toluene, xylene and mesitylene 40 vol.% is presented in Fig. 5. Result showed that the oxidation of S-compounds positively is affected by existence of these aromatic hydrocarbons. This



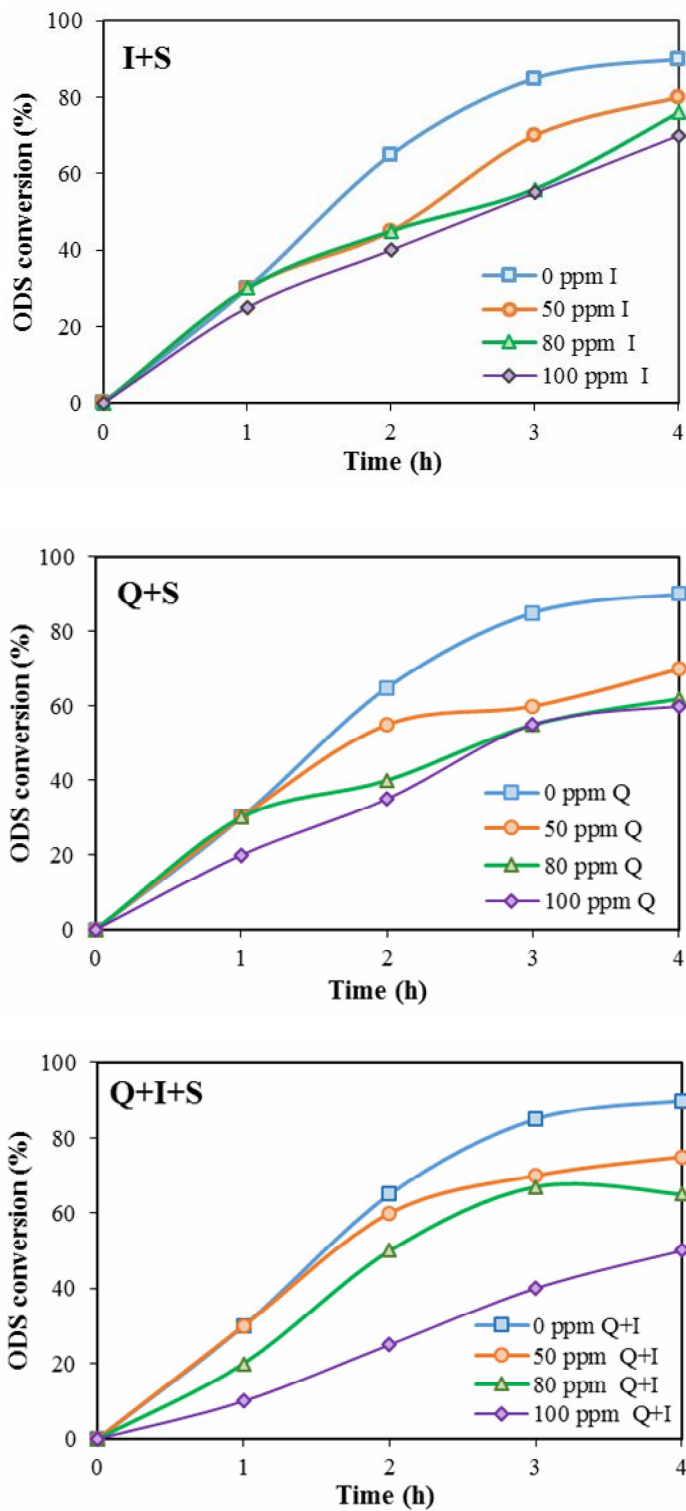
**Fig. 1.** Effect of catalyst loading on the ODS reaction of model oil ( $F_4$ ). Reaction conditions: molar ratio of O/S = 2/1 in *n*-heptane: EtOH (1:1 v/v) at 75 °C at 4 h.



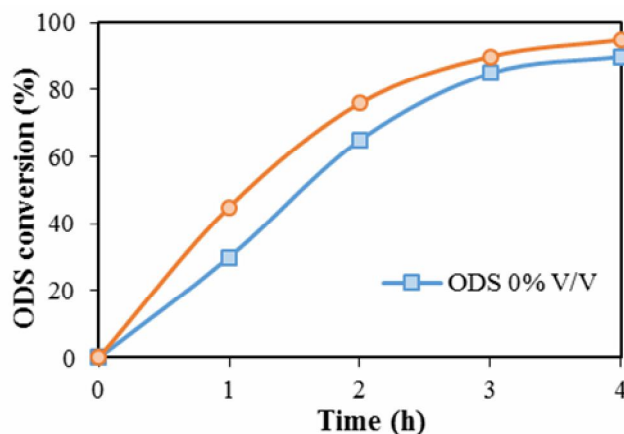
**Fig. 2.** Effect of molar ratio of O/S on the ODS reaction of model oil ( $F_4$ ). Reaction conditions: catalyst 0.02 g, in *n*-heptane: EtOH (1:1 v/v) at 75 °C at 4 h.



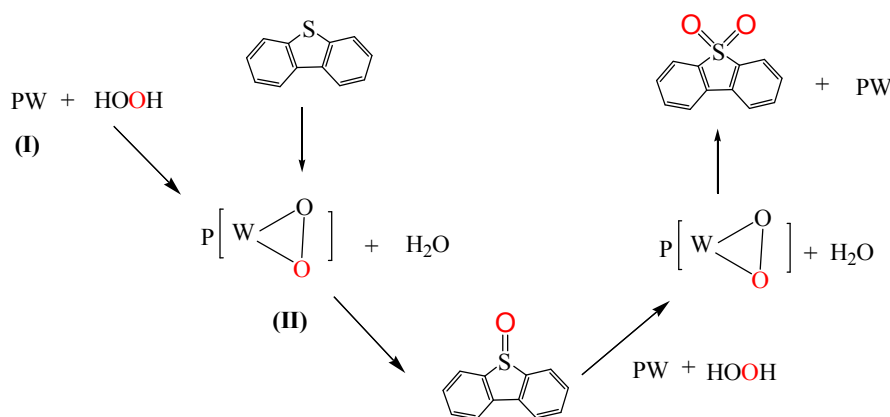
**Fig. 3.** Effect of various extractive solvents on the ODS of model oil ( $F$ ). Reaction conditions: catalyst 0.02 g, molar ratio of O/S = 6/1 in *n*-heptane: extractant (1:1 v/v) at 75 °C at 4 h.



**Fig. 4.** Effect of N-compounds 20-100 ppm on the ODS of model oil ( $F_4$ ). Reaction conditions: catalyst 0.02 g, molar ratio of O/S = 6/1 in *n*-heptane: EtOH (1:1 v/v) at 75 °C at 4 h.



**Fig. 5.** Effect of 1-ring aromatic compounds (toluene (To), xylene (X), mesitylene (M)) (the same vol.% of each one) at 40 vol.% in the ODS reaction of model oil ( $F_4$ ). Reaction conditions: catalyst 0.02 g, molar ratio of O/S = 6/1 in *n*-heptane: EtOH (1:1 v/v) at 75 °C.



*Scheme 3.* Possible mechanism for oxidation of DBT in the model oil

proposes that the ODS process has been enhanced by adding of 1-ring aromatic hydrocarbons. Based on literature, acceleration of the ODS in the presence of aromatics is caused by R-oxyhydroperoxide, that is formed *via* the reaction of the oxidation products of aromatics with the oxidizing agent [29]. It was found that the oxidation reactivity of S-compounds to R-oxyhydroperoxide depends on the net electron density on the S atom [30]. It is deduced that acceleration of the desulfurization of high electron density S-compounds in the presence of aromatics is due to the oxidation by R-oxyhydroperoxide. However, deceleration of desulfurization of S-compounds with low

electron density in the presence of aromatics is owing to competitive oxidation of the aromatics with that of S-compounds by the oxidizing agent.

### Suggested oxidation mechanism of S-compounds

The suggested mechanism of catalytic desulfurization is shown in Scheme 3. This schematic drawing shows the oxidation of DBT to relative sulfoxide and/or sulfone by the active species originated from the POM-IL. According to the literature [31-33] and our results, a possible mechanism for the catalytic oxidation of DBT might proceed the following path: At first, PW(O) part in POM gets oxygen

and forms catalytically active peroxo species (II) (PW(O<sub>2</sub>)) from the reaction of (I) with excess H<sub>2</sub>O<sub>2</sub>. After that an oxygen is transferred from the active PW-peroxo species (II) to the DBT which forms the transition state. Then, a complete oxygen transition to the DBT occurs, which produces the relative sulfoxide and the PW species (I). The formation of active species (II) takes part in the ODS similar to the first step, leading to oxide sulfoxide to the corresponding sulfone and the regeneration of the PW species (I).

## CONCLUSIONS

In this work, pyridine-based IL coupled with PW, [4-PhPyBs]<sub>3</sub>PW, was synthesized and its oxidative capability was investigated in ODS of mixed thiophenic model oil. This catalytic system brought a notable approach to the oxidation of S-containing compounds and showed excellent activity to remove sulfur contents of model oil. The effect of presence of N-compounds on the ODS was also considered. The results suggest that these compounds can inhibit the ODS process. The desulfurization of the S-compounds was accelerated when aromatic hydrocarbons were added.

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