



Synthesis of amphiphilic peroxophosphomolybdates for oxidative desulfurization of fuels in ionic liquids

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Abstract

Three amphiphilic peroxophosphomolybdates $[\text{C}_4\text{mim}]_3\text{PMo}_4\text{O}_{24}$, $[\text{C}_8\text{mim}]_3\text{PMo}_4\text{O}_{24}$ and $[\text{C}_{16}\text{mim}]_3\text{PMo}_4\text{O}_{24}$ were synthesized and characterized. These catalysts were used for extraction and catalytic oxidative desulfurization of fuel with H_2O_2 as an oxidant and ionic liquid $[\text{C}_4\text{mim}]\text{BF}_4$ as an extractant. It was found that $[\text{C}_{16}\text{mim}]_3\text{PMo}_4\text{O}_{24}$ showed the highest catalytic activity and the sulfur content could decrease to 7.5 ppm. In contrast, the desulfurization system shows very low performance without H_2O_2 or ionic liquid. The detailed reaction conditions were optimized including reaction time, temperature, the dosage of H_2O_2 and catalyst, and different sulfur compounds. After the reaction, the catalysts and the ionic liquid can be cycled 8 times with a little decrease in desulfurization efficiency.

Keywords Peroxophosphomolybdate · Oxidative desulfurization · Ionic liquid · H_2O_2

1 Introduction

The combustion of sulfur-containing compounds in fuel oils produces a large amount of sulfur oxides, which are major air pollutants (Zhang et al. 2018; Hou et al. 2018). In the recent years, deep desulfurization of fuel oils has attracted worldwide interests due to the growing environmental concerns. Although the traditional

hydrodesulfurization (HDS) can remove aliphatic sulfur compounds, it is less effective in removing alkyl-substituted aromatic sulfur compounds such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) (Jiang et al. 2017a, b; Li et al. 2018). At present, the possible tactics to improve desulfurization efficiency include adsorptive desulfurization (Yang et al. 2018; Nejad and Beigi 2015), extractive desulfurization (Raj et al. 2018; Jiang et al. 2015) and oxidative desulfurization (Jiang et al. 2014a, b; Yang et al. 2017).

Among these strategies, oxidative desulfurization combined with extraction shows a promising prospect owing to its high desulfurization efficiency (He et al. 2017; Lu et al. 2017; Hao et al. 2017; Xun et al. 2016; Zhang et al. 2014). In this approach, the sulfur compounds are firstly oxidized to the corresponding sulfones or sulfoxides, which can be removed by extraction with polar solvents. In the early stage, Li and his group reported emulsion systems with amphiphilic catalysts, showing high catalytic activity for oxidative desulfurization (Li et al. 2004; Zhang et al. 2012). However, the use of organic solvents after oxidation may do harm to the environment. Ionic liquids (ILs) are being explored as “green” substitutes for volatile organic solvents because of their low volatility (Dai et al. 2017; Sun and Zhao 2011). Recently, a one-step desulfurization system, ionic liquid extraction combined with oxidative

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desulfurization (EODS), has been widely studied (Zhang et al. 2017; Xu et al. 2017; Moghadam et al. 2017; Rafiee et al. 2016). In this process, the sulfur compounds are firstly extracted by ILs and oxidized by aqueous hydrogen peroxide in the IL phase. Compared with extractive desulfurization only by ILs, the system consisted of imidazolium-based ILs and H₂O₂–acetic acid and showed a great increase in desulfurization efficiency (Lo et al. 2003). However, a large amount of ILs and H₂O₂ are required, which increases the cost to the refinery.

In order to solve this problem, an efficient extraction and catalytic oxidative desulfurization (ECODS) system has been raised by our group (Jiang et al. 2014a, b, 2017a, b; Zhu et al. 2015; Wang et al. 2017). The aim of this system is to explore efficient catalysts and select suitable ILs as solvents. To date, several kinds of catalyst have been reported, e.g., polyoxometalates (Hao et al. 2015), tetrachloroferrates (Jiang et al. 2014a, b), iron porphyrins (Zhao et al. 2017) and metal oxide (Chen et al. 2017). However, there are few reports that focus on exploring peroxopolyoxometalates as catalysts for oxidative desulfurization. In this work, three amphiphilic peroxophosphomolybdates were synthesized and characterized by elemental analysis, Fourier transformer infrared (FTIR), and thermogravimetric and differential scanning calorimetry (TG-DSC). It was found that [C₁₆mim]₃[PMo₄O₂₄] showed the best sulfur removal probably because of its long carbon chain. After optimizing the reaction conditions, the removal of DBT could get to 98.8% at 60 °C with [C₄mim]BF₄ IL as the extractant. In addition, the reaction system could be cycled at least for 8 times without a significant loss of desulfurization efficiency.

2 Experimental

2.1 Materials

All chemicals used were from commercial sources. Phosphomolybdic acid hydrate (H₃PMo₁₂O₄₀·13H₂O), 30 wt% H₂O₂, ether, ethanol, tetradecane and *n*-octane were supplied by Sinopharm Chemical Reagent. Dibenzothiophene (DBT), benzothiophene (BT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) were bought from Sigma-Aldrich. 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl), 1-octyl-3-methylimidazolium chloride ([C₈mim]Cl), 1-hexadecyl-3-methylimidazolium chloride ([C₁₆mim]Cl) and 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim]PF₄) were obtained from Shanghai Chenjie Chemical Co. Ltd., China.

2.2 Characterization

Fourier transformer infrared (FTIR) spectrum was performed on a Nicolet 7100 spectrophotometer at room temperature. Determination of element content was recorded on an elemental analyzer (CHN-O-Rapid, Germany Heraeus Co. Ltd.). Thermogravimetric analysis was undertaken on a simultaneous thermal analyzer (STA-449C Jupiter, Germany NETZSCH Co. Ltd.).

2.3 Synthesis of [C_{*n*}mim]₃PMo₄O₂₄ (*n* = 4, 8, 16)

Typically, 1 mmol H₃PMo₁₂O₄₀·13H₂O was dissolved in 10 mL H₂O₂ under continuous stirring. Then, a mixture of 40 mL H₂O₂ and 3.1 mmol [C_{*n*}mim]Cl (*n* = 4, 8, 16) was dropped into the above mixture solution, which was kept at 100 °C for 4 h. Subsequently, the sample was centrifuged and washed. The final products, [C_{*n*}mim]₃[PMo₄O₂₄], were kept in a vacuum.

2.4 Desulfurization tests

The DBT, BT and 4,6-DMDBT were dissolved in *n*-octane and tetradecane was used as the internal standard. The content of DBT, BT and 4,6-DMDBT was 500 ppm, 250 ppm and 250 ppm, respectively.

The extractive desulfurization experiments were conducted in a double-neck flask with 1 mL ionic liquid IL and 5 mL model oil for 5 min under continuous stirring. With the addition of a certain amount of H₂O₂, 5 mL model oil and catalyst, the oxidative desulfurization process was performed. After the reaction, 1 μL of the oil phase (upper layer) was collected and analyzed by gas chromatography until the two phases were separated. The sulfur removal was used to indicate the desulfurization rate of the model oil. A gas chromatograph with a flame ionization detector (GC-FID) (Agilent 7890A; HP-5, 30 m × 0.32 mm × 0.25 μm) was used to investigate the content of sulfur-containing compounds in the model oil.

3 Results and discussion

3.1 Characterization

The results of the elemental analysis and the determination of the active oxygen content of the three catalysts are given in Table 1. The active oxygen content of the catalyst was determined by the following method: A certain amount of catalyst was added to 10 mL of DMF. Then, 5 mL of 0.5 mol L⁻¹ H₂SO₄ was used to adjust the pH to 2.5. After that, 0.5 g KI and 3 drops of 3% ammonium molybdate

Table 1 Elemental analysis of the catalysts

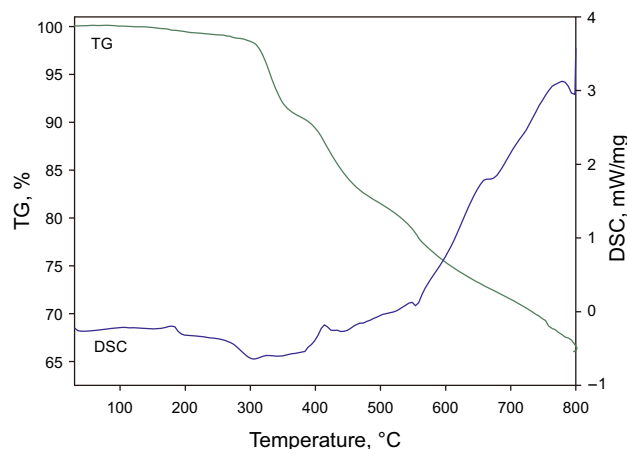
Entry	Catalysts	Data	H%	C%	N%	(O)%
1	[C ₄ mim] ₃ PMo ₄ O ₂₄	Experimental	2.98	23.26	6.09	5.01
		Calculated	3.73	23.70	6.91	5.26
2	[C ₈ mim] ₃ PMo ₄ O ₂₄	Experimental	4.62	30.86	5.50	4.35
		Calculated	5.02	31.23	6.07	4.62
3	[C ₁₆ mim] ₃ PMo ₄ O ₂₄	Experimental	6.86	42.1	4.53	3.63
		Calculated	6.85	41.87	4.88	3.72

solution were added to the above solution, which was kept in the shade for 5 min. Finally, the well-calibrated Na₂S₂O₃ solution was used to titrate the above solution until the color was light yellow, and then 3 mL of 0.5% starch indicator was added to the solution, continuing dropping to the blue exactly disappeared. The mass percentage of active oxygen can be calculated by Eq. (1):

$$(O)\% = \frac{c(\text{Na}_2\text{S}_2\text{O}_3) \times V(\text{Na}_2\text{S}_2\text{O}_3) \times 10^{-3} \times M(\text{O}_2^{2-})}{4 \times m_{\text{catal}}} \times 100\%, \quad (1)$$

where $c(\text{Na}_2\text{S}_2\text{O}_3)$ is the concentration of Na₂S₂O₃ solution, $V(\text{Na}_2\text{S}_2\text{O}_3)$ is the volume of consumed Na₂S₂O₃ solution, and $M(\text{O}_2^{2-})$ is the molecular weight of O₂²⁻. As given in Table 1, the experimental data of samples were similar to the theoretical calculation data.

The FTIR spectra of catalysts are given in Table 2. For [C₄mim]₃PMo₄O₂₄, the peaks at 956, 877, 589, 532, 1078 and 1062 cm⁻¹ were assigned to Mo=O vibration, O–O vibration, Mo(O)₂ asymmetrical stretching vibration, Mo(O)₂ symmetrical stretching vibration and PO₄ vibration, respectively. For [C₈mim]₃PMo₄O₂₄, the peaks at 957, 875, 592, 545 and 1062 cm⁻¹ were assigned to Mo=O vibration, O–O vibration, Mo(O)₂ asymmetrical stretching vibration, Mo(O)₂ symmetrical stretching vibration and PO₄ vibration, respectively. For [C₁₆mim]₃[PMo₄O₂₄], the peaks at 965, 873, 588, 543, 1071 and 1040 cm⁻¹ were assigned to Mo=O vibration, O–O vibration, Mo(O)₂ asymmetrical stretching vibration, Mo(O)₂ symmetrical stretching vibration and PO₄ vibration, respectively. The

**Fig. 1** TG/DSC curves of [C₄mim]₃PMo₄O₂₄

characteristic peaks of the catalysts were similar to the literature values (He et al. 2008).

The differential thermal analysis and thermogravimetric results of [C₄mim]₃[PMo₄O₂₄] are shown in Fig. 1. There was no mass loss of the catalyst below 100 °C, indicating that the catalyst did not contain crystal water. The sample exhibited weight loss between 158.0 and 202.4 °C, corresponding to the decomposition of peroxides groups. Above 305.8 °C, the main weight loss of catalyst was attributed to the decomposition of the cation [C₄mim]⁺ and anion without peroxides groups. The final product may be molybdenum oxides. For [C₈mim]₃[PMo₄O₂₄] and [C₁₆mim]₃[PMo₄O₂₄] in Figs. 2 and 3, the stability of these catalysts showed a similar trend with increasing temperature in air.

Table 2 IR characteristic bands of the catalysts

Entry	Catalyst	FTIR, cm ⁻¹					
		v(PO ₄)	v(M=O)	v(O–O)	v _{asym} [M(O) ₂]	v _{sym} [M(O) ₂]	
1	[C ₄ mim]PMo ₄ O ₂₄	1078	1062	956	877	589	532
2	[C ₈ mim]PMo ₄ O ₂₄	1076	1062	957	875	592	545
3	[C ₁₆ mim]PMo ₄ O ₂₄	1071	1040	965	873	588	543

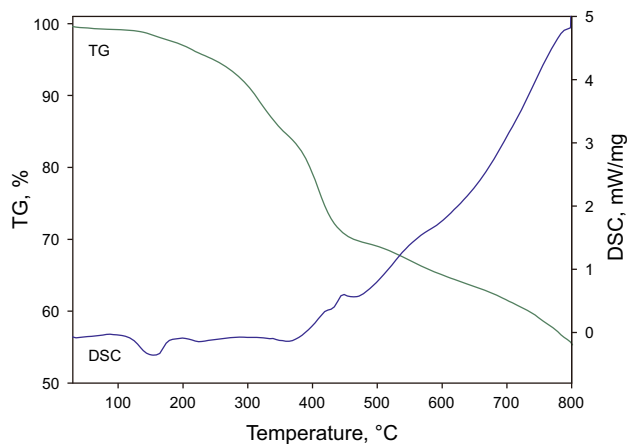


Fig. 2 TG/DSC curves of [C₈mim]₃PMo₄O₂₄

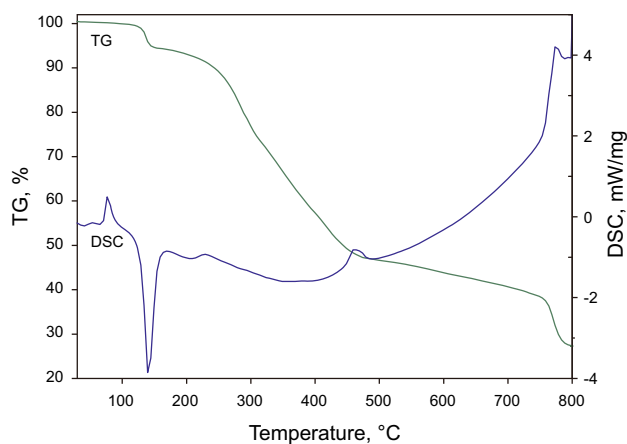


Fig. 3 TG/DSC curves of [C₁₆mim]₃PMo₄O₂₄

3.2 The performance comparison among different desulfurization systems

As given in Table 3, the extractive efficiency was 13.6% with [C₄mim]BF₄ as an extractant. With the addition of H₂O₂ as the oxidant, the oxidative desulfurization efficiency was increased to 27.0%. When [C₄mim]₃PMo₄O₂₄, [C₈mim]₃PMo₄O₂₄ and [C₁₆mim]₃PMo₄O₂₄ were used as

Table 3 Sulfur removal of different desulfurization systems in model oil

Entry	Catalyst	Sulfur removal, %			
		Catalyst + H ₂ O ₂	IL + catalyst + H ₂ O ₂	IL + H ₂ O ₂	IL ^a
1	[C ₄ mim] ₃ PMo ₄ O ₂₄	29.1	41.6		
2	[C ₈ mim] ₃ PMo ₄ O ₂₄	44.3	88.9		
3	[C ₁₆ mim] ₃ PMo ₄ O ₂₄	87.5	98.3		
4				27.0	
5					13.6

Reaction conditions: V(C₄mimBF₄) = 1 mL, V(model oil (with 500 ppm DBT)) = 5 mL, T = 60 °C, O/S = 3 (molar ratio), t = 1 h, n(DBT)/n(Catalyst) = 10

^aThe mixture was stirred at 30 °C for 15 min

catalysts, the sulfur removal reached 87.5%, 44.3% and 29.1%, respectively, in the absence of extractant. The result indicated that the long carbon chain could improve the desulfurization efficiency probably due to the formation of an emulsion system (Zhang et al. 2010). When [C₄-mim]BF₄ was used, a bi-phase system was produced in the ECODS process due to the incompatibility between the IL and model oil, and the catalysts and oxidant were dissolved into the IL phase. The sulfur removal achieved 98.3% for [C₁₆mim]₃PMo₄O₂₄, 88.9% for [C₈mim]₃PMo₄O₂₄ and 41.6% for [C₄mim]₃PMo₄O₂₄, respectively. It could be concluded that the IL played a vital role in the desulfurization system not just as an extractant but also improving the usage of oxidant. The DBT dissolved in model oil could be removed quickly through the ECODS process, which showed much better performance than just single extraction or catalytic oxidation without IL.

3.3 The effects of reaction time and temperature for desulfurization performance

The experiment was performed at 40, 50 and 60 °C, respectively, to study the effect of reaction temperature on sulfur removal. The results in Fig. 4 showed that the sulfur removal increased when reaction time increased. When the temperature rose from 40 to 60 °C, the catalytic performance on desulfurization was 34.1%, 41.0% and 56.2% after 10 min and increased to 82.7%, 93.3% and 98.3% after 60 min, respectively. It could be concluded that reaction time and temperature are important for desulfurization.

3.4 The effect of oxidant usage on desulfurization performance of catalysts

The effect of oxidant usage on desulfurization performance was investigated, and the result is shown in Fig. 5. Using [C₁₆mim]₃[PMo₄O₂₄] as the catalyst, the sulfur removal increased when the molar ratio of H₂O₂ to sulfur (O/S) increased from 2:1 to 4:1. Despite the O/S molar ratio

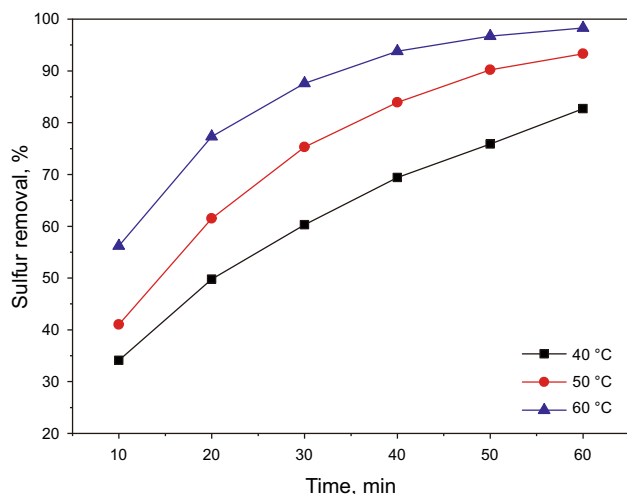


Fig. 4 Influence of the reaction time and temperature on sulfur removal. Reaction conditions: $V([\text{C}_4\text{mim}]\text{BF}_4) = 1 \text{ mL}$, $V(\text{model oil}) = 5 \text{ mL}$, $\text{O/S} = 4$ (molar ratio), $n(\text{DBT})/n(\text{catalyst}) = 10$

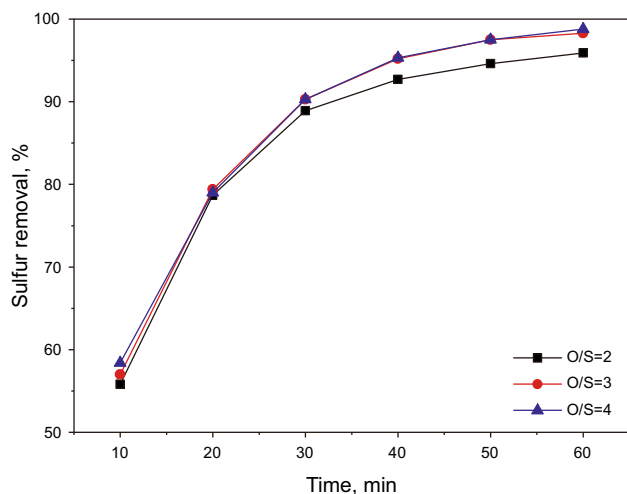


Fig. 5 Influence of different molar ratios of H_2O_2 to sulfur (O/S) on removal of DBT. Reaction conditions: $V([\text{C}_4\text{mim}]\text{BF}_4) = 1 \text{ mL}$, $V(\text{model oil}) = 5 \text{ mL}$, $t = 60 \text{ min}$, $n(\text{DBT})/n(\text{catalyst}) = 10$, $T = 60 \text{ }^\circ\text{C}$

being 2:1, the sulfur removal of DBT model oil could achieve 55.8% in 10 min and 95.9% in 60 min. However, when the O/S molar ratio was increased to 4:1, the sulfur removal of DBT model oil only improved to 58.4% in 10 min and 98.8% in 60 min. This feature indicated the high utilization of oxidant in the ECODS system due to the high sulfur removal at a low O/S molar ratio.

3.5 Investigation of the different sulfur-containing compounds

As shown in Fig. 6, another two sulfur-containing compounds benzothiophene (BT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) were evaluated with

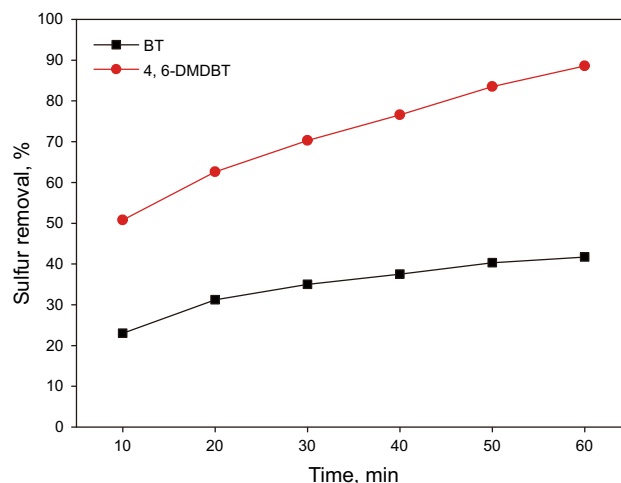


Fig. 6 Influence of the nature of the substrate on the desulfurization of $[\text{C}_{16}\text{mim}]_3[\text{PMo}_4\text{O}_{24}]$ as catalyst. Reaction conditions: $V([\text{C}_4\text{mim}]\text{BF}_4) = 1 \text{ mL}$, $V(\text{model oil with S} = 250 \text{ ppm}) = 5 \text{ mL}$, $t = 1 \text{ h}$, $n(\text{DBT})/n(\text{catalyst}) = 5$, $T = 60 \text{ }^\circ\text{C}$, $\text{O/S} = 3$ (molar ratio)

$[\text{C}_{16}\text{mim}]_3[\text{PMo}_4\text{O}_{24}]$ as the catalyst. The removals of BT and 4,6-DMDBT are 41.7% and 88.6%, respectively, after 1 h under optimized conditions. The removal rates are lower than the removal of DBT. According to the previous study (Li et al. 2016), it is found that the catalytic activity of desulfurization was affected commonly by two factors, which are the electron density and the steric hindrance around the sulfur atoms. For one thing, it is the low electron density around the sulfur atoms of BT that leads to the lowest catalytic activity. For DBT and 4,6-DMDBT, the difference of the electron density is very small. The steric hindrance of the methyl groups around the sulfur atoms will be the main role affecting the reactivity. Thus, the desulfurization activity of different substrates decreased in the following order of $\text{DBT} > 4,6\text{-DMDBT} > \text{BT}$.

3.6 Influence of the usage of the catalyst

Table 4 reveals effects of the usage of the catalyst on sulfur removals. It is seen that the removal of DBT increased from 38.7% to 98.3%, when the molar ratios of catalyst/sulfur increased from 1:100 to 1:10. However, the

Table 4 Influence of the different catalyst/sulfur molar ratios on the removal of DBT

Entry	1	2	3	4	5
$n(\text{catalyst})/n(\text{sulfur})$	1:100	1:40	1:20	1:10	1:5
Sulfur removal, %	38.7	70.0	87.1	98.3	99.6

Reaction conditions: $V([\text{C}_4\text{mim}]\text{BF}_4) = 1 \text{ mL}$, $V(\text{model oil}) = 5 \text{ mL}$, $t = 1 \text{ h}$, $T = 60 \text{ }^\circ\text{C}$, $\text{O/S} = 3$ (molar ratio)

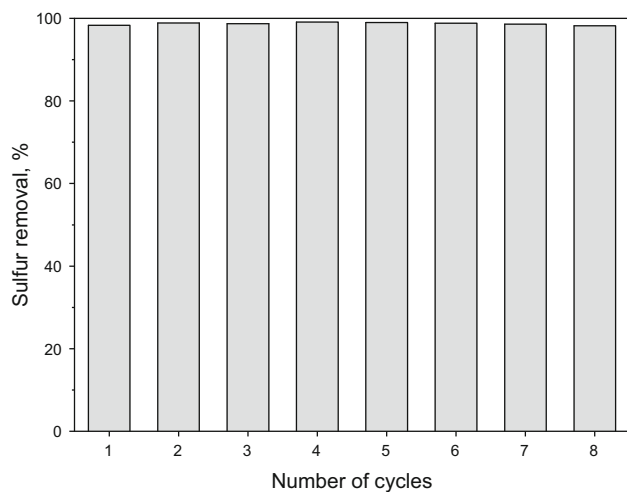


Fig. 7 Influence of the number of cycles on the sulfur removal. Reaction conditions: $V(\text{C}_4\text{mimBF}_4) = 1 \text{ mL}$, $V(\text{model oil with } S = 500 \text{ ppm}) = 5 \text{ mL}$, $t = 1 \text{ h}$, $T = 60 \text{ }^\circ\text{C}$, $n(\text{DBT})/n(\text{Catalyst}) = 5$, $O/S = 3$ (molar ratio)

sulfur removal rose by only 1.3% when the molar ratio of catalyst/sulfur was 1:5. Hence, it was proved that the amount of catalyst had an important influence on the removal of DBT and the appropriate catalyst/sulfur molar ratio might be 1:10.

3.7 Recycling of the IL and catalyst

The recycling performance of the IL and catalyst plays a key role in the practical application. The recycling experiment was carried out as follows. After the first reaction, the IL phase containing the catalyst was separated and heated at $110 \text{ }^\circ\text{C}$ for 3 h to remove the remaining hydrogen peroxide. Then, the regenerated IL and catalyst, fresh hydrogen peroxide and model oil were added to the flask for the next reuse. The sulfur removal only decreased from 98.3% to 95.9% after the 8th cycle (Fig. 7), which

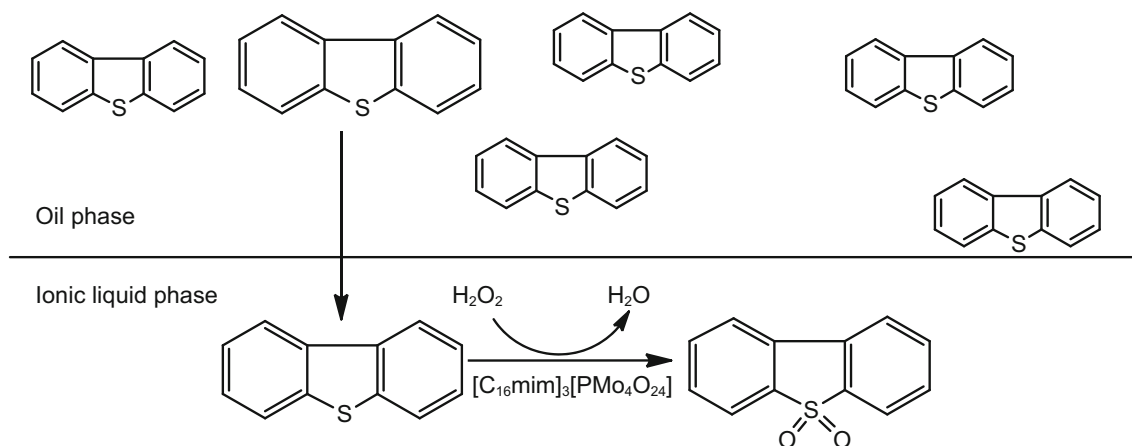
indicated that the IL and catalyst had good recycling performance. Along with the recycling, more and more reaction products could be deposited in the IL phase including $[\text{C}_{16}\text{mim}]_3[\text{PMo}_4\text{O}_{24}]$ with more recycling, causing IL curing and the accompanying decrease in sulfur removal.

3.8 The possible reaction process

DBT, a typical representative of an aromatic sulfur compound, can be removed completely by the desulfurization system containing $[\text{C}_{16}\text{mim}]_3[\text{PMo}_4\text{O}_{24}]$, H_2O_2 and $[\text{C}_4\text{mim}]\text{BF}_4$. The $[\text{C}_4\text{mim}]\text{BF}_4$ acts as both extractant and reaction medium to create a favorable environment in the reaction. The catalyst is easily dissolved in the IL. First, DBT is extracted into the IL phase and then oxidized to a more polar sulfone (Scheme 1) (Zhu et al. 2015; Lu et al. 2013). The sulfone is in the lower ionic liquid phase, which will promote the desulfurization reaction process. When the ionic liquid extraction is saturated, the sulfone is precipitated as a white solid from the ionic liquid and the sulfone can be removed from the desulfurization system by centrifugation.

4 Conclusion

Three peroxophosphomolybdates were successfully synthesized and characterized. Compared with the short carbon chains in cations of catalysts, a long carbon chain showed a positive effect on catalytic oxidation of DBT. The sulfur removal could reach 98.3% with $[\text{C}_{16}\text{mim}]_3[\text{PMo}_4\text{O}_{24}]$ as catalyst at $60 \text{ }^\circ\text{C}$ with $n(\text{DBT})/n(\text{Catalyst})/n(\text{H}_2\text{O}_2) = 10:1:30$. The desulfurization activity of different substrates decreased in the following order $\text{DBT} > 4,6\text{-DMDBT} > \text{BT}$. Apart from its high catalytic efficiency, the catalyst also showed outstanding recycling properties



Scheme 1 Extraction and catalytic oxidation reaction of DBT in an oil–ionic liquid system

and it could be cycled 8 times with very little loss of activity.

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