



# Catalytic oxidative desulfurization of fuels in acidic deep eutectic solvents with $[(C_6H_{13})_3P(C_{14}H_{29})]_3PMo_{12}O_{40}$ as a catalyst

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## Abstract

Deep eutectic solvents (DESs) are a new class of green solvents analogous to ionic liquids due to their biodegradable capacity and low cost. However, the direct extractive desulfurization of diesel oil by DESs cannot meet the government's standard. In this work, amphiphilic polyoxometalates were synthesized and characterized by FT-IR and mass spectrometry. The oxidative desulfurization results showed that benzothiophene (BT) could be completely removed by employing a  $[(C_6H_{13})_3P(C_{14}H_{29})]_3PMo_{12}O_{40}$ , DES (ChCl/2Ac) and  $H_2O_2$  system. It was also found that the organic cation of catalysts played a positive role in oxidative desulfurization. The reaction conditions, such as reaction temperature and time, the amount of catalyst and DES and  $H_2O_2/S$  (O/S) molar ratio, were optimized. Different sulfides were tested to determine the desulfurization selectivity of the optimal reaction system, and it was found that 97.2% of dibenzothiophene (DBT) could be removed followed by 80.7% of 4-MDBT and 76.0% of 4,6-DMDBT. After reaction, the IR spectra showed that the catalyst  $[(C_6H_{13})_3P(C_{14}H_{29})]_3PMo_{12}O_{40}$  was stable during the reaction process and the oxidative product was dibenzothiophene sulfone (DBTO<sub>2</sub>). Furthermore, the catalyst can be regenerated and recycled for four runs with little loss of activity.

**Keywords** Diesel · Oxidative desulfurization · Deep eutectic solvents · Polyoxometalates ·  $H_2O_2$

## 1 Introduction

Deep desulfurization of fuels is a worldwide topical issue because of the air pollution caused by  $SO_x$ . Thus, increasingly strict regulations have been implemented to limit sulfur content in fuels to 10 ppm or even lower (Xiao

et al. 2014; Zhang et al. 2018; Li et al. 2018; Liu et al. 2013; Wu et al. 2017). For example, since 2017 the sulfur content in diesel fuel and gasoline must be not higher than 10 ppm according to the latest standard in China. Hydrodesulfurization (HDS) is a classic technology that can remove most of the sulfides in fuels but can barely remove aromatic sulfides or needs harsh conditions such as temperature  $>370$  °C and pressure  $>40$  atm (Zeng et al. 2017; Zhang et al. 2016; Wu et al. 2016; Rafiee et al. 2016; Kianpour and Azizian 2016). Therefore, exploiting alternative or supplementary desulfurization approaches is highly desirable for petroleum refineries (Rezvani et al. 2018; Ja'fari et al. 2018; Zhang et al. 2017; Li et al. 2017a, b; Jiang et al. 2014a, b).

Extractive desulfurization is a feasible approach because of its simple and mild conditions (Nejad and Beigi 2015). The common extractants are organic solvents, ionic liquids and deep eutectic solvents (DESs) (Jiang et al. 2015; Li et al. 2016a, b, c; Zhao et al. 2016; Jiang et al. 2016; Zhang et al. 2018). Among the three types of solvent, DESs, a eutectic mixture of two or more components, are the most promising extractants due to their low cost and

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biodegradability. However, the extraction efficiency is still not very high in a one-step extraction. Li et al. (2016a, b, c) reported several tetrabutyl ammonium chloride-based DESs for extractive desulfurization and tetrabutyl ammonium chloride/polyethylene glycol (TBAC/PEG) showed 82.8% of desulfurization efficiency in one cycle. Hence, it is essential to extract for five cycles to reach deep desulfurization (Li et al. 2016a, b, c). Another sample using carboxylic acid-based DESs for extractive desulfurization was also faced with the obstacle of low desulfurization efficiency (Li et al. 2016a, b, c). Some researchers tried to add an oxidant to acidic DESs to establish a new desulfurization system, that is, extraction and catalytic oxidative desulfurization (ECODS) (Yin et al. 2015; Lu et al. 2015; Liu et al. 2016; Hao et al. 2017). Two *p*-toluenesulfonic acid-based DESs were employed as extractants and catalysts and H<sub>2</sub>O<sub>2</sub> was used as oxidant for oxidation of benzothiophene (BT) and the desulfurization efficiency could reach up to 99.99% (Yin et al. 2015). Lu and his group (Lu et al. 2015) found that an oxalate-based DES showed good catalytic activity with H<sub>2</sub>O<sub>2</sub> as an oxidant and 91% of dibenzothiophene (DBT) could be removed. Therefore, compared with extractive desulfurization, the oxidative desulfurization with DESs may be more promising due to its high activity. However, the reported DESs in oxidative desulfurization are very few probably owing to the difficulty of exploiting efficient DESs.

Polyoxometalates are commonly used in the field of catalysis because of their adjustable acid–base and redox properties over a wide range (Omwoma et al. 2015; Li et al. 2017a, b; Ma et al. 2017; Lu et al. 2017; Bertleff et al. 2017; Jiang et al. 2017; Chen et al. 2013). In our previous work, an oxidative desulfurization system with DESs as extractants was developed and commercial phosphotungstic acid (PTA) showed superior catalytic activity (Liu et al. 2016). However, it is difficult to separate and recycle the catalyst from the reaction system, and this may hinder the application of the PTA/DESs system. Thus, development of easily separable catalysts in the DESs system is necessary. In this work, amphiphilic polyoxometalates were introduced to acidic DESs to evaluate their catalytic performance. The main advantage is that these catalysts can be separated from the reaction system due to the fact that the DESs can be dissolved in water, but the catalysts amphiphilic polyoxometalates are insoluble. Then different DESs, catalysts with different cations and reaction conditions, with model oils with different aromatic sulfides, olefins and aromatics, were investigated.

## 2 Experimental

### 2.1 Preparation of catalysts and DESs

According to the method in the literature (Zhu et al. 2015a, b), a solution of trihexyltetradecyl phosphonium chloride ( $[(C_6H_{13})_3P(C_{14}H_{29})]Cl$ ; 1, 2, 3 mmol) in 20 mL of anhydrous ethanol was added dropwise into 50 mL of ethanol solution of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·26H<sub>2</sub>O (1 mmol) while stirring for 4 h at room temperature. A bright yellow precipitate was formed, filtered and washed several times with anhydrous ethanol. Then, the catalysts,  $[(C_6H_{13})_3P(C_{14}H_{29})]H_2PMo_{12}O_{40}$  (PH<sub>2</sub>Mo),  $[(C_6H_{13})_3P(C_{14}H_{29})]_2HPMo_{12}O_{40}$  (PHMo) and  $[(C_6H_{13})_3P(C_{14}H_{29})]_3PMo_{12}O_{40}$  (PMo), can be obtained by drying at 50 °C in vacuum for 24 h.

The DES ChCl/2Ac was simply prepared by mixing choline chloride (ChCl) with acetic acid (Ac) at a molar ratio of 1:2. The mixture was then warmed to 80 °C and stirred for 3 h. DES ChCl/2Fo and TBAC/2Ac were obtained according to the same process with formic acid (Fo) as a hydrogen bond donor and tetrabutylammonium chloride (TBAC) as a quaternary ammonium salt.

### 2.2 Desulfurization procedure

Preparation of model oils: The sulfur compounds including BT, DBT, 3-MBT, 4-MDBT and 4,6-DMDBT were dissolved in *n*-octane, respectively, with tetradecane as an internal standard. The sulfur contents of these model oils are 500 mg L<sup>-1</sup>.

The desulfurization tests were performed in a self-made two-necked flask, to which a certain amount of catalysts, DES, model oil and H<sub>2</sub>O<sub>2</sub> were added in turn. The reaction mixture was stirred in a water bath at a set temperature for 3 h. The model oil in the upper layer was periodically withdrawn and analyzed by gas chromatography–flame ionization detection (GC-FID) with the analytical conditions listed in our previous work (Zheng et al. 2015; Jiang et al. 2014a, b).

## 3 Results and discussion

### 3.1 Characterization of catalysts

FT-IR spectra of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, PMo, PHMo and PH<sub>2</sub>Mo are shown in Fig. 1. The peaks at 1065, 965, 870 and 790 cm<sup>-1</sup> of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> are attributed to the Keggin units. The prepared catalysts also have Keggin units because of their four characteristic peaks at 1065, 960, 881 and 809 cm<sup>-1</sup>. However, the shift of the absorption bands

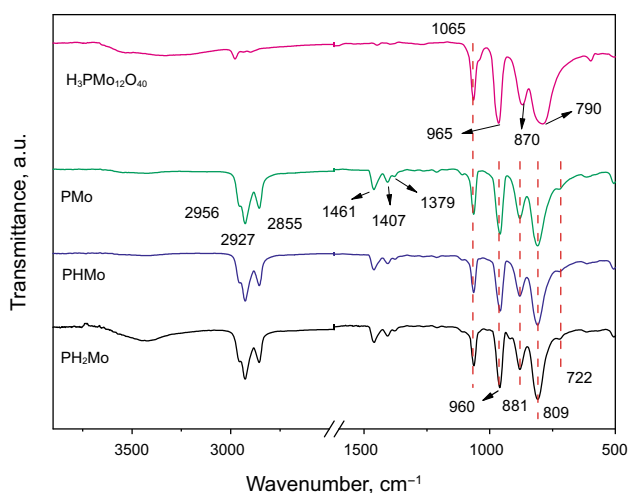


Fig. 1 FT-IR spectra of catalysts

indicates electrostatic interactions between  $[(C_6H_{13})_3P(C_{14}H_{29})]^+$  cations and  $[PMo_{12}O_{40}]^{3-}$  anions (Xu et al. 2013). Compared with the IR spectrum of  $H_3PMo_{12}O_{40}$ , the catalysts showed extra absorption peaks, such as the C–H stretching vibration at 2956, 2927 and 2855  $cm^{-1}$  and the bending vibration of  $CH_3$  and  $CH_2$  at 1461, 1407 and 1379  $cm^{-1}$ . The weak band at 722  $cm^{-1}$  indicates the bending vibration of  $-(CH_2)_n-$  ( $n > 4$ ). Based on above discussion, the catalysts are prepared successfully by metathetical reaction. The mass spectra of these catalysts also confirmed this conclusion because they all show the same cation  $[(C_6H_{13})_3P(C_{14}H_{29})]^+$  ( $m/z = 484$ ) and anion  $[(C_6H_{13})_3P(C_{14}H_{29})PMo_{12}O_{40}]^{2-}$  ( $m/z = 1153$ ).

### 3.2 Effect of the cation on sulfur removal

Organic cations may act as a phase transfer agent to adsorb the weakly polar sulfide molecules or as an emulsifying agent to stabilize emulsion droplets, which can enhance the catalytic ability of catalysts (Nisar et al. 2011; Xu, et al. 2013). Three Mo-based catalysts were prepared by changing the molar ratio of  $[(C_6H_{13})_3P(C_{14}H_{29})]Cl$  and  $H_3PMo_{12}O_{40}$ . As shown in Fig. 2,  $PH_2Mo$  with 1 mol of organic cation per mol of catalyst exhibited the lowest desulfurization efficiency of 68.1%. The desulfurization efficiency increased to 79.6% with  $PMo$  as a catalyst, which had 3 mol of organic cation per mol of catalyst. Therefore, the catalytic activity of the catalyst could be enhanced by the organic cation. Acidity may promote the catalytic activity of catalysts according to the literature (Hao et al. 2017; Zhu et al. 2015a, b; Zhang et al. 2018). In this work, although the  $PH_2Mo$  and  $PHMo$  are Brønsted acidic, their catalytic activities are still lower than the non-acidic  $PMo$ , suggesting that the organic cation plays a more important role than acidity.

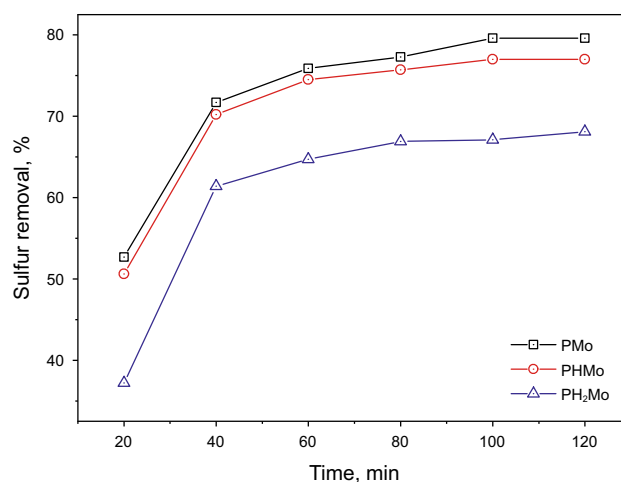


Fig. 2 Effect of the cation on sulfur removal. Experimental conditions:  $n(\text{catalyst}) = 0.0078$  mmol, molar ratio  $n(O)/n(S) = 2$ ,  $ChCl/2Ac = 2.5$  mL, model oil = 5 mL,  $T = 50$  °C,  $t = 120$  min

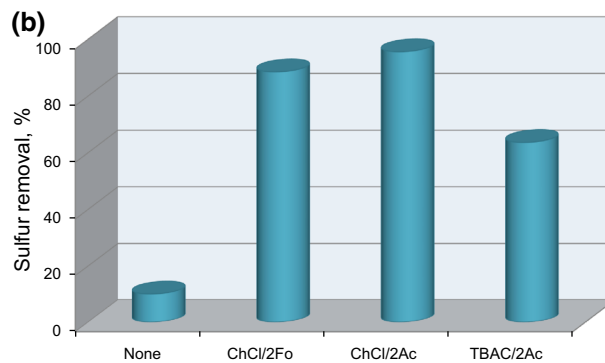
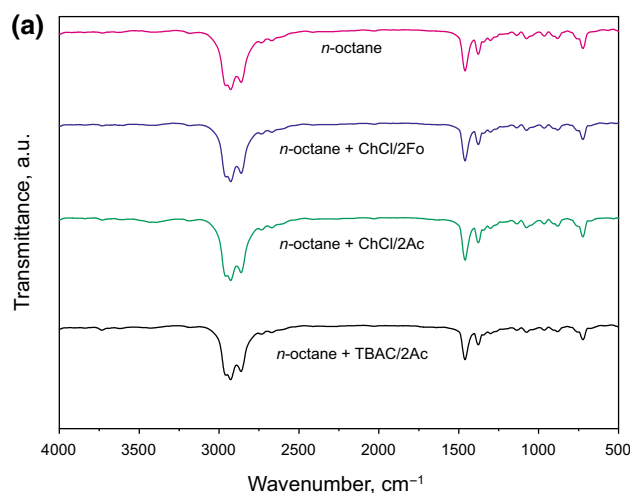


Fig. 3 a FT-IR spectra of *n*-octane after mixing with DESs and b desulfurization efficiency of different DESs. Experimental conditions:  $n(\text{catalyst}) = 0.0156$  mmol, molar ratio  $n(O)/n(S) = 3$ , DES = 2.5 mL, model oil = 5 mL,  $T = 50$  °C,  $t = 120$  min

### 3.3 Selection of a suitable DES

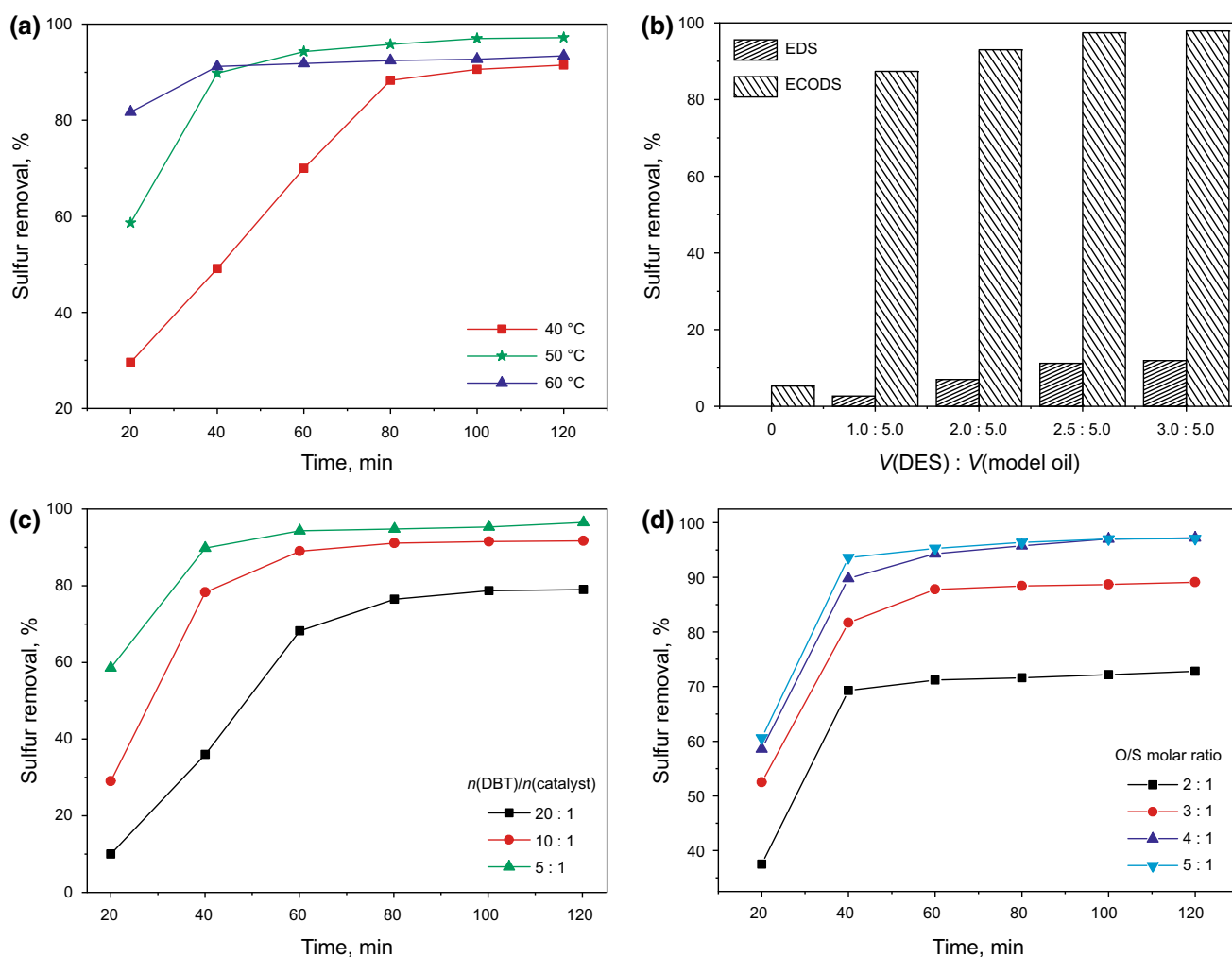
It is a challenge to select a suitable extractant because the extractant should be not dissolved in oil. IR spectra may be an effective analytical method to determine whether the acid DESs dissolve in oil owing to the characteristic absorption of the carbonyl group. Figure 3a plots the IR spectra of *n*-octane, *n*-octane saturated with ChCl/2Fo, *n*-octane saturated with ChCl/2Ac, and *n*-octane saturated with TBAC/2Ac. All samples presented the same absorption bands as *n*-octane, indicating the DESs cannot dissolve in the fuel. Figure 3b shows the desulfurization with the three DESs with PMo as a catalyst. The sulfur removal was only 10.0% without using an extractant. However, it increased to 88.5%, 95.6% and 63.6% with ChCl/2Fo, ChCl/2Ac and TBAC/2Ac as extractants, respectively. It can be concluded that DESs play an extremely positive role

in oxidative desulfurization. Furthermore, the carbon chain length of DESs also greatly affects the desulfurization efficiency.

### 3.4 Optimization of reaction conditions for sulfur removal

In the above experiments, PMo combined with ChCl/2Ac showed the best desulfurization performance, and thus these were selected to evaluate a series of parallel experiments to systematically study the effects of different reaction conditions on sulfur removal.

Different temperatures, such as 40, 50, and 60 °C, were tested for oxidative removal of DBT. Figure 4a shows that the sulfur removal was only 29.6% at 40 °C and 58.6% at 50 °C in 20 min, and it significantly improved to 81.7% as the temperature increased to 60 °C. However, the final



**Fig. 4** Effects of **a** temperature and time; **b** the amount of DES; **c**  $n(\text{DBT})/n(\text{catalyst})$  and **d** O/S molar ratio on desulfurization efficiency. Experimental conditions: model oil = 5 mL, **a**  $n(\text{catalyst}) = 0.0156$  mmol, O/S = 4 (molar ratio), ChCl/2Ac = 2.5 mL;

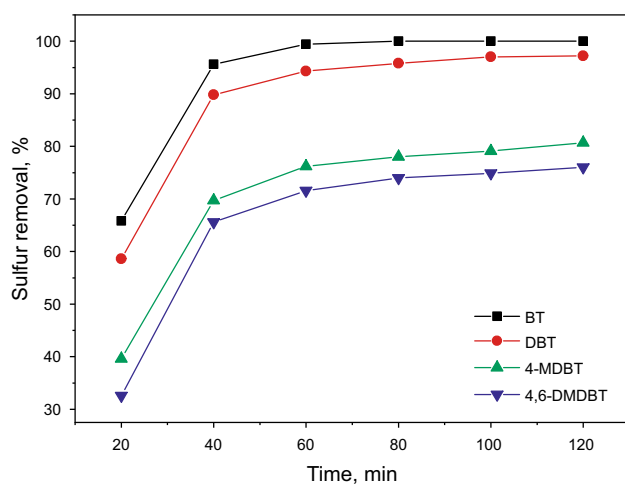
**b** O/S = 4, ChCl/2Ac = 2.5 mL,  $T = 50$  °C; **c** EDS time = 10 min,  $n(\text{catalyst}) = 0.0156$  mmol, O/S = 4,  $T = 50$  °C,  $t = 120$  min and **d**  $n(\text{catalyst}) = 0.0156$  mmol, ChCl/2Ac = 2.5 mL,  $T = 50$  °C

sulfur removal at 60 °C was lower than that at 50 °C probably due to the kinetic competition of the unproductive decomposition of H<sub>2</sub>O<sub>2</sub> (Yang et al. 2017). 50 °C might be the optimal reaction temperature, and the sulfur removal reached 97.2% at 120 min.

As shown in Fig. 4b, c, the amount of catalyst and extractant greatly affected the removal of DBT. The extractive desulfurization (EDS) rate was only 2.7% at  $V(\text{DES})/V(\text{model oil}) = 1:5$  and increased to 11.5% at  $V(\text{DES})/V(\text{model oil}) = 3:5$  (Fig. 4b). And the catalytic desulfurization rate was only 5.3% in the absence of DES (Fig. 4b). In order to obtain low-sulfur fuel, the amounts of catalyst and extractant were evaluated. The results showed that the 97.2% of DBT could be removed at  $V(\text{DES})/V(\text{model oil}) = 2.5:5$  and  $n(\text{DBT})/n(\text{catalyst}) = 5:1$ . Thus, both the catalyst and extractant played important roles in sulfur removal. Figure 4c shows that the H<sub>2</sub>O<sub>2</sub>/S (O/S) molar ratio has a crucial influence on the sulfur removal. According to a previous report (Jiang et al. 2017), the decomposition of H<sub>2</sub>O<sub>2</sub> is the competitive reaction to its oxidative reaction, resulting in an increase of H<sub>2</sub>O<sub>2</sub> dosage. The sulfur removal increased from 72.8% at O/S = 2 to 97.2% at O/S = 4, and excessive H<sub>2</sub>O<sub>2</sub> cannot promote the oxidation of DBT.

### 3.5 Oxidative removal of different sulfur compounds from model oil

It is well known that many kinds of aromatic sulfur compounds in diesel fuel are difficult to remove by HDS technology (Yun and Lee 2013; Li et al. 2016a, b, c). Consequently, it is important to investigate the desulfurization selectivity of different sulfur compounds. As shown in Fig. 5, BT can be removed completely. The removal of



**Fig. 5** Oxidative removal of different sulfur compounds from model oil. Experimental conditions:  $n(\text{catalyst}) = 0.0156$  mmol, molar ratio  $n(\text{O})/n(\text{S}) = 4$ ,  $\text{ChCl}/2\text{Ac} = 2.5$  mL, model oil = 5 mL,  $T = 50$  °C

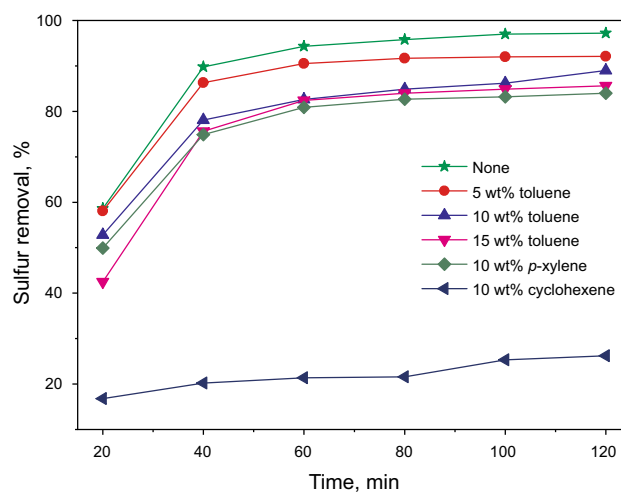
DBT can reach 97.2% followed by 4-MDBT (80.7%) and 4,6-DMDBT (76%). According to our previous work (Li, et al. 2016), the desulfurization efficiency was closely related to  $f^+(r)$  Fukui function on the S site. The  $f^+(r)$  values decrease in the order of  $\text{BT} > \text{DBT} > 4\text{-MDBT} > 4,6\text{-DMDBT}$ . It was found that the desulfurization selectivity of different sulfur compounds in this work was in accordance with the order of  $f^+(r)$  Fukui function value.

### 3.6 Effects of fuel composition on sulfur removal

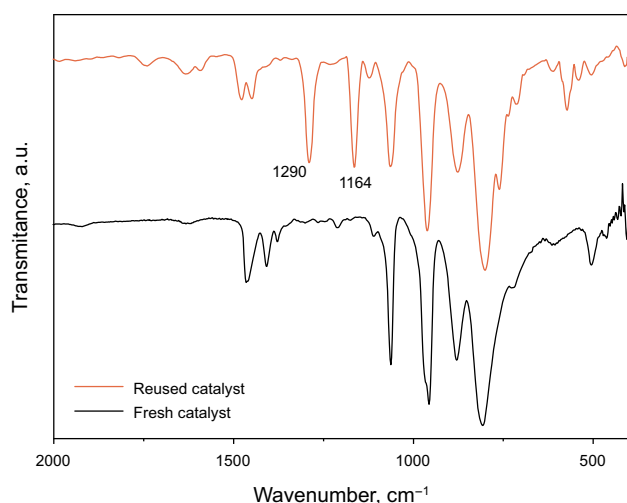
The actual fuel is complicated because of its components including olefins, aromatics and many other compounds (Xun et al. 2015; Wu et al. 2017; Xiao et al. 2014). In order to examine the effect of olefins and aromatics on sulfur removal, toluene, *p*-xylene and cyclohexene were added to the model oil with DBT as the modeled sulfur compound. Figure 6 shows that the sulfur removal decreased from 97.2% to 92.1%, 89.0% and 85.6% with the addition of 5 wt%, 10 wt% and 15 wt% toluene, respectively. The effect of *p*-xylene on sulfur removal was similar to that of toluene. However, the sulfur removal dropped sharply to 26.2% with addition of 10 wt% cyclohexene. Therefore, it could be concluded that cyclohexene was oxidized more easily than toluene, *p*-xylene and even DBT. It will be suggested that this desulfurization system should be used to treat actual fuels with a low concentration of olefins.

### 3.7 Reusability of the catalyst

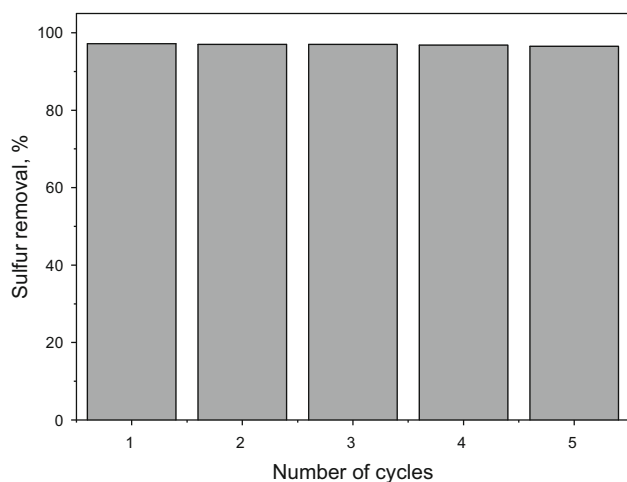
The reusability and stability of the catalyst are undoubtedly important factors for industrial application. The oil was removed by decantation after reaction, and then the catalyst



**Fig. 6** Effects of fuel composition on sulfur removal. Experimental conditions:  $n(\text{catalyst}) = 0.0156$  mmol, O/S = 4 (molar ratio),  $\text{ChCl}/2\text{Ac} = 2.5$  mL, model oil = 5 mL,  $T = 50$  °C



**Fig. 7** IR spectra of the fresh and reused catalysts



**Fig. 8** Reusability of the catalyst. Experimental conditions:  $n(\text{catalyst}) = 0.0156 \text{ mmol}$ ,  $\text{O/S} = 4$  (molar ratio),  $\text{ChCl}/2\text{Ac} = 2.5 \text{ mL}$ , model oil = 5 mL,  $T = 50 \text{ }^\circ\text{C}$

and oxidative product could be precipitated by adding deionized water into the DES phase. IR spectra of the fresh and used catalyst are plotted in Fig. 7, and the characteristic bands at 1065, 960, 881 and 809  $\text{cm}^{-1}$  showed no destruction of the Keggin structure. Also, the peaks at 1290 and 1164  $\text{cm}^{-1}$  were attributed to the stretching vibration of S=O in dibenzothiophene sulfone (DBTO<sub>2</sub>). The catalyst could be purified by washing the precipitate with ethyl ether several times. Then, the regenerated catalyst was evaluated with the addition of fresh model oil, DES and H<sub>2</sub>O<sub>2</sub> under the optimal conditions. The results in Fig. 8 showed that the PMo could be recycled four times without a significant decline in activity.

## 4 Conclusion

A deep desulfurization system with DES as extractant was explored. BT could be removed completely with ChCl/2Ac as extractant and [(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P(C<sub>14</sub>H<sub>29</sub>)]<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> as catalyst, followed by DBT, 4-MDBT and 4,6-DMDBT. Two other catalysts [(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P(C<sub>14</sub>H<sub>29</sub>)]<sub>2</sub>HPMo<sub>12</sub>O<sub>40</sub> and [(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P(C<sub>14</sub>H<sub>29</sub>)]<sub>2</sub>H<sub>2</sub>PMo<sub>12</sub>O<sub>40</sub> showed the lower activity than [(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P(C<sub>14</sub>H<sub>29</sub>)]<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, indicating the positive role of the long carbon chain cation of the catalysts. However, the long carbon chain of DESs exhibited a contrary role for oxidative desulfurization because the sulfur removal was 88.5% and 63.6% with ChCl/2Fo and TBAC/2Ac, respectively, while 95.6% with ChCl/2Ac. After reaction, the catalyst can be regenerated by water and recycled for at least four times. The reaction product was determined by IR spectra as DBTO<sub>2</sub>.

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