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An amphiphilic catalyst based on sandwich-type polyoxometalate for deep desulfurization of fuels in ionic liquid

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Abstract:

A cobalt-based polyoxometalate, $(\text{STA})_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$ (SEP) (STA = stearyltrimethylammonium), was prepared by ionic exchange of $\text{K}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$ and STA•Cl. SEP was approved as an effective catalyst for desulfurization of fuels in [Bmim]PF₆ by using aqueous H₂O₂ as oxidant in extraction and catalytic oxidative desulfurization system (ECODS). The optimum desulfurization conditions were obtained: DBT could be completely removed with only O/S molar ratio of 4 in 40 min at 60°C in three-liquid-phase micro-emulsion system. The catalyst could be recycled conveniently and reused for at least six times without significantly reducing desulfurization efficiency. Therefore, this catalyst had an excellent regeneration and good prospect of industrial application. For different substrates, the efficiencies of sulfur removal decreased in the following orders: DBT > 4,6-DMDBT > BT under the same conditions. Furthermore, the catalytic oxidation desulfurization mechanism of SEP was studied.

Keywords: desulfurization, catalysis, ionic liquid, cobalt, sandwich-type polyoxometalate

1 Introduction

In recent years, a large number of fuel oils have been demanded in industries and daily life with the rapid development of society. At the same time, air pollution, caused by SO_x emissions, is one of the most serious environmental problems in the world, and automobile exhaust is the main source of SO_x emanated from the combustion of sulfur compounds in gasoline and diesel oil¹. The currently adopted main industrial method is hydrodesulfurization (HDS). But the hydrodesulfurization method has limitations, it is less effective for refractory sulfur containing compounds such as dibenzothiophene (DBT)

and its derivatives due to several catalyst surface interactions and stereo hindrance.²⁻⁵ Deep desulfurization of transportation fuels has become an important research subject owing to the increasingly stringent requirements and fuel specifications for environmental protection in many countries.⁶ In order to obtain the fuels with a ultra-low sulfur content, it is necessary to explore other alternative desulfurization technology to remove the sulfur-containing compounds. Recently, the extraction and catalytic oxidative desulfurization system (ECODS) with ionic liquid (IL) has been developed and considered as a simple, mild, and environmentally benign method for deep desulfurization.^{7,8} Various oxidants have been used in oxidation process, such as t-BuOOH,⁹ O₃,¹⁰ H₂O₂,¹¹ O₂¹² and solid oxidizing agents.¹³ Among these oxidants, H₂O₂ is attractive because only producing water as a byproduct, it provides a high content of active oxygen and is much cheaper and safer than organic peroxides or peracids.¹⁴ Reported IL in ECODS including metal-based IL,⁷ Brønsted acidic IL,¹⁵ Lewis acidic IL¹⁶ and IL/catalysts¹¹ presented good efficiencies in oxidative desulfurization.

Polyoxometalates (POMs) are attractive compounds and their molecular properties (composition, size, shape, charge density, thermal stability and redox potential) can be tuned in a wide range.¹⁷⁻²⁰ Such as Keggin-type polyoxometalates, have been utilized widely as catalysts for both homogeneous and heterogeneous reactions.^{21, 22} In recent years, several researchers have reported using sandwich-type polyoxometalates as catalysts for the oxidation of alcohols, diols, pyridine derivatives, amines, and aniline derivatives with hydrogen peroxide, and for the epoxidation of alkenes.²³⁻²⁶ Weakley et al. first reported the synthesis of [Co₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻ as a sandwich-type polyoxoanion.²⁷ Then, Hill and co-workers reported using this POM as catalyst for water oxidation for the first time in 2010 *Science*.²⁸ However, cobalt-based polyoxometalate K₁₀[Co₄(H₂O)₂(PW₉O₃₄)₂] (abbreviated Co₄(PW₉)₂) has not applied to for oxidative desulfurization under neutral conditions. Co₄(PW₉)₂ is of particular interest and the focus of the current investigation because it incorporates the moderately earth abundant element cobalt. Recent progress in POM surface chemistry has found that positively charged surfactants can replace the counterions of POMs, resulting in surfactant encapsulated clusters (SECs) with a core-shell structure and a well-defined composition.²⁹ POMs encapsulated by surfactants with various alkyl chain lengths have amphiphathy. The amphiphilic catalysts assemble at the interface of emulsion droplets, dramatically increasing the total interface area and thus the ECODS performance. Song et al. synthesise amphiphilic lanthanide-containing polyoxometalates by surfactant encapsulation.³⁰ Li and the cooperators reported the oxidation of dibenzothiophene (DBT) with molecular oxygen as the oxidant using an

emulsion catalytic system where an amphiphilic catalyst $[C_{18}H_{37}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$ acts as the surfactant.¹²

In this work, $(STA)_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$ was prepared by ionic exchange of $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$ and $STA \cdot Cl$. The desulfurization performance of $(STA)_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$ was investigated in ECODS using H_2O_2 as oxidant and $[Bmim]PF_6$ as extractant for the model oil containing refractory sulfur compounds. It was found that DBT can be rapidly and completely oxidized to the corresponding sulfoxide and sulfone in this emulsion system under mild conditions, because the catalyst presented both hydrophilic and lipophilic properties. Moreover, the mechanism of ECODS and the performance of recycling for SEP were also studied.

2 Experimental

2.1 Materials and methods

All reagents and solvents used in this work are available commercially and were used as received, unless otherwise indicated. Model compounds and chemicals, including trimethylstearylammmonium chloride (CTAB, Energy Chemical), dibenzothiophene (DBT), benzothiophene (BT), 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) (ChinaPingmeiShenmaEnergy&ChemicalGroup Co., Ltd.), commercially available H_2O_2 (30% in water) were directly used as received without further purification. The compound $A-\beta-Na_8HPW_9O_{34} \cdot 27H_2O$ (A-PW₉) was prepared as previously described.³¹ FT-IR spectra were measured on a Mattson Alpha-Centauri spectrometer in the range of 4000-400 cm^{-1} , using KBr pellets. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D/Max 2000 X-ray diffractometer with graphite monochromatized Cu/K α radiation ($k = 1.5418 \text{ \AA}$) and 2θ ranging from 5 to 50° with an increment of 0.02 and a scanning rate of 5 min^{-1} . GC (Agilent 7820A, HP-5) analysis was operated with ultrapure nitrogen as carrier gas. The injection volume of sample was 1 μL . The investigating conditions were adjusted as following: injection port temperature 200°C, detector temperature 250°C and oven temperature 150°C. The removal efficiencies of DBT were calculated by internal standard method.

2.2 Preparation of catalyst

2.2.1 $Co_4(PW_9)_2$ Preparation

The synthesis of $Co_4(PW_9)_2$ has been performed according to a procedure established previously.³² Solid A-PW₉ (2.00 g, 0.7 mmol) was dissolved in 15 mL water. With stirring at ambient temperature,

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.41 g, 1.4 mmol) was added to this solution. The resulting purple suspension was heated to 60 °C for 20 min until a deep purple solution was resulted. To this hot reaction mixture solid KCl (4~6 g) was added and the solution was heated to 80 °C for 1 h. A purple to violet crystalline solid precipitated upon cooling to room temperature overnight. The solid was collected by filtration, washed three times with 1 mL of ice cold water, and recrystallized from a minimum amount of hot water (70 °C) with cooling to room temperature overnight. After filtration and drying in vacuo, $\text{Co}_4(\text{PW}_9)_2$ was isolated as purple violet crystals (Yield:54%). Its identity was confirmed by single crystal X-ray diffraction (Fig.S1).

2.2.2 SEP Preparation

Synthesis of surfactant-encapsulated POM (SEP): In a typical synthesis, an aqueous solution of $\text{Co}_4(\text{PW}_9)_2$ was dropped into a solution of STA•Cl in alcohol with continuous stirring. The molar ratio between STA•Cl and $\text{Co}_4(\text{PW}_9)_2$ was maintained at 10:1. The obtained product was filtered and washed with water and ethanol before drying for 24 h.

2.3 Preparation of ionic liquid and oxidative desulfurization procedure

Ionic liquid [Bmim]PF₆ was synthesized as mentioned in the literature.³³ Model oils were prepared by dissolving DBT, BT and 4,6-DMDBT in n-octane with a corresponding S-content of 500 ppm, respectively. In a typical experiment, a mixture including catalyst, 30% H₂O₂, 1mL IL and 5 mL model oil containing DBT in a flask was stirred vigorously at 60 °C. After the reaction, the remained sulfur content of the model oil was analyzed directly by GC.

3 Results and discussion

3.1 Characterization of the SEP

The FT-IR spectra of $\text{Co}_4(\text{PW}_9)_2$, STA•Cl and SEP are shown in Fig. 1. The bands at 1040, 931, 880, and 734 cm⁻¹ indicated that the SEP still kept the polyoxoanions structure. The band at 1040 cm⁻¹ was attributed to the $\nu(\text{P-O})$ vibration, and the bands at 931, 880, and 734 cm⁻¹ were assigned to the $\nu(\text{W-O}_t)$, $\nu(\text{W-O}_b\text{-W})$, and $\nu(\text{W-O}_c\text{-W})$ vibrations (O_t = terminal oxygen, O_b = bridged oxygen between corner-sharing octahedra, O_c = bridged oxygen between edge-sharing octahedra), respectively. The band at 1470 cm⁻¹ was clearly rooted in STA⁺. It was visibly suggested that the STA⁺ and $\text{Co}_4(\text{PW}_9)_2$ constituted SEP precisely.

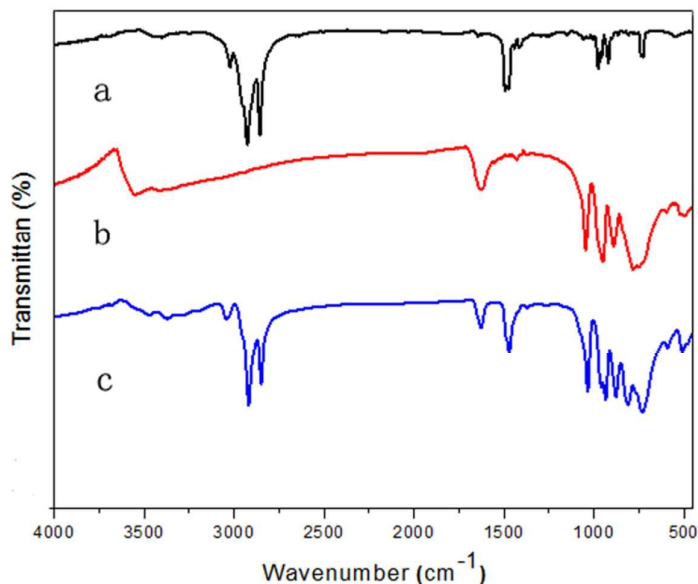


Fig. 1 FT-IR spectra of (a) STA•Cl, (b) Co₄(PW₉)₂ and (c) SEP.

3.2 Influence of different desulfurization systems on removal of DBT

Effect of different desulfurization systems on desulfurization efficiency is shown in Table 1. The results exhibit that efficiency of the proposed ECODS was greater than that of extraction, oxidation and catalytic oxidation, attributed to their dissimilarity in chemical properties. The persistence of catalyst with IL and oxidant in the same reaction stimulates ligand effect which stabilizes the oxidant and subsequently enhances activity. In addition, the IL-catalyst complexation exhibits hydrophobicity, which contributes to the recreation equilibrium of sulfur among oil and IL by not only trapping sulfur but also improving oil-model solubility in ionic liquid, thus, improving the sulfur removal.

It is instructive to compare the catalytic oxidative desulfurization of DBT by POM catalyst systems reported in the literature.³⁴⁻³⁸ As shown in Table 2, the selected POMs are H₃PW₁₂O₄₀·14H₂O, [Bmim]₃PMo₁₂O₄₀/SiO₂, [(C₈H₁₇)₃NCH₃]₂W₆O₁₉, [C₁₈H₃₇N(CH₃)₃]₇[PW₁₁O₃₉], Na₁₂[WZn₃(H₂O)₂(ZnW₉O₃₄)₂]·46H₂O and SEP. Compared to the classical POM catalysts with Keggin structure (Table 2, entry 1 and 2), different amphiphilic POM catalysts (Table 2, entry 3 and 4) and

sandwich-type POM $\text{Na}_{12}[\text{WZn}_3(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2] \cdot 46\text{H}_2\text{O}$ (Table 2, entry 5), SEP/[Bmim]PF₆/H₂O₂ show excellent sulfur removal.

Table 1 Influence of different desulfurization systems on removal of DBT

Entry	Desulfurization system	Sulfur removal (%)
1	[Bmim]PF ₆	20.50
2	[Bmim]PF ₆ + H ₂ O ₂	24.72
3	SEP + H ₂ O ₂	77.34
4	SEP+ [Bmim]PF ₆ + H ₂ O ₂	100

Reaction conditions: Model oil (S in n-octane = 500 ppm) 5 ml, [Bmim]PF₆ = 1 mL, T = 60 °C, t = 60 min, O/S = 4, n(sulfur)/n(catalyst) = 20:1.

Table 2 Catalytic oxidative desulfurization of DBT by POM catalyst systems.

entry	Catalyst	Extractant	T (°C)	t (min)	S removal (%)
1	H ₃ PW ₁₂ O ₄₀ ·14H ₂ O	[bmim]BF ₄	30	60	98.2
2	[Bmim] ₃ PMo ₁₂ O ₄₀ /SiO ₂	-	60	60	100
3	[(C ₈ H ₁₇) ₃ NCH ₃] ₂ W ₆ O ₁₉	[bmim]PF ₆	60	20	74
4	[C ₁₈ H ₃₇ N(CH ₃) ₃] ₇ [PW ₁₁ O ₃₉]	[bmim]PF ₆	30	60	99.1
5	Na ₁₂ [WZn ₃ (H ₂ O) ₂ (ZnW ₉ O ₃₄) ₂]·46H ₂ O	-	60	240	70
6	SEP	[bmim]PF ₆	60	40	100

3.3 Performance of desulfurization investigations

As shown in Fig. 2, Co₄(PW₉)₂ was used in ECODS at 90 min, which sulfur removal was only 78.3%. But the ECODS activity increased sharply when SEP supported, DBT could be completely removed at 40 min. This is owing to the surfactant cation to increase the total interface area, which helps to attract the sulfide molecules closer. So we choose SEP as catalyst, investigating the influence factor for ECODS, including catalyst dosage, H₂O₂/DBT molar ratio (O/S), reaction temperature and time, different substrates. Additionally, the recycling of catalyst and the mechanism of ECODS were researched.

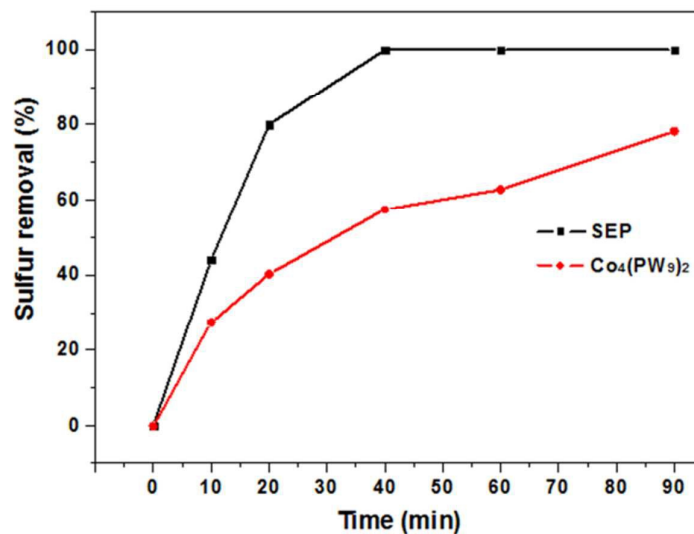


Fig. 2 The DBT conversion of using $\text{Co}_4(\text{PW}_9)_2$ (red) and SEP (black) as catalysts. Reaction conditions: Model oil (S in n-octane = 500 ppm) 5 ml, $[\text{Bmim}]\text{PF}_6 = 1$ mL, $t = 90$ min, O/S = 4, $T = 60^\circ\text{C}$, $n(\text{sulfur})/n(\text{catalyst}) = 20:1$.

3.3.1 Influence of different reaction temperature on desulfurization of model oil

The reaction temperature had a great effect on the catalytic activity of the catalysts. As shown in Fig. 3, the catalytic activities of the SEP in the oxidation of DBT at different temperatures, 30°C , 40°C and 60°C were compared. The results showed that the conversion of DBT was around 89% at 30°C after 60 min. By warming up the reaction temperature to 40°C , DBT conversion was increased to 96% in 60 min. Moreover, when the temperature was increased to 60°C , the 100% conversion of DBT was finished in 40 min. It was indicated that higher reaction temperatures, higher desulfurization efficiencies were obtained when the temperatures increased from 30°C to 60°C . That is to say temperature had a significant influence, affecting the desulfurization activity of the catalyst. By increasing the reaction temperature, more significant promotion on DBT oxidation rather than H_2O_2 thermal decomposition was observed. Therefore, the temperature was fixed at 60°C without increasing for investigation the influence of O/S molar ratio on DBT oxidation.

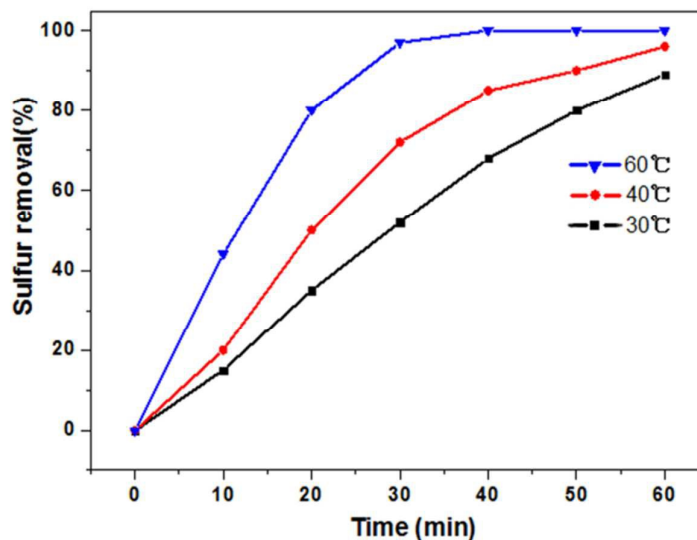


Fig. 3 Influence of reaction temperature on the removal of DBT. Reaction conditions: Model oil (S in n-octane = 500 pm) 5 ml, [Bmim]PF₆ = 1 mL, t = 60 min, O/S = 4, n(sulfur)/n(catalyst) = 20:1.

3.3.2 Influence of the H₂O₂/DBT molar ratio (O/S) on desulfurization of model oil

To elucidate the influence of the amount of H₂O₂ on the desulfurization, the oxidation of DBT in the model oil under different O/S molar ratios were carried out at 60°C. As shown in Fig. 4, the sulfur removal increased from 89.3% to 100% with O/S from 2 to 4 at 40 min. When the molar ratio of O/S was from 4 to 6, the desulfurization rate decreased. It is known that O/S should be 2 stoichiometrically, when DBT is oxidized completely. However, a stoichiometrical amount of H₂O₂ cannot give the complete oxidation of DBT in the system due to its self-decomposition.³⁹ Finally, O/S= 4 is the best O/S molar ratio for the catalytic oxidation system.

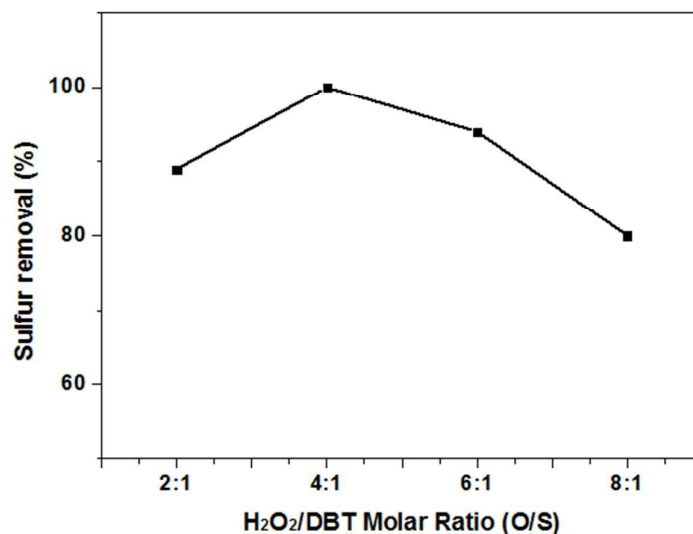


Fig. 4 Influence of O/S molar ratio on the removal of DBT. Reaction conditions: Model oil (S in n-octane = 500 ppm) 5 ml, [Bmim]PF₆ = 1 mL, $t = 60$ min, $T = 60^{\circ}\text{C}$, $n(\text{sulfur})/n(\text{catalyst}) = 20:1$.

3.3.3 Influence of the DBT/SEP molar ratio on desulfurization of model oil

Table 3 shows the sulfur removal of DBT in the model oil after the extraction and catalytic oxidation. The mixture of DBT and catalyst with 100:1, 80:1, 60:1, 40:1 and 20:1 molar ratios have been plotted. As can be seen, when the molar ratio of DBT and catalyst decreased from 100:1 to 20:1, the sulfur removal of model oil increased from 68.2% to 100%. In the ECODS system, the sulfur removal increased with increasing catalyst dosage. This experiment clearly demonstrated that the catalyst dosage was a main factor of influencing reaction activity.

Table 3 Influence of DBT/SEP molar ratio on the removal of DBT

entry	1	2	3	4	5
n(sulfur)/n(catalyst)	100:1	80:1	60:1	40:1	20:1
sulfur removal(%)	68.2	79.1	93.6	97.3	100

Reaction conditions: Model oil (S in n-octane = 500 ppm) 5 ml, [Bmim]PF₆ = 1 mL, $t = 40$ min, $T = 60^{\circ}\text{C}$, O/S = 4

3.3.4 Oxidation of different s-compounds on desulfurization of model oil

To investigate the desulfurization efficiency of different sulfur compounds, besides DBT, two

other sulfur containing compounds BT and 4,6-DMDBT were taken under the same conditions. The desulfurization system had excellent sulfur removal efficiency on all of the three kinds of substrates. As shown in Fig.5, the oxidation reactivity decreased in the order: DBT > 4,6-DMDBT > BT, the same order as observed in the polyoxometallates-H₂O₂ biphasic catalytic system.⁴⁰ In general, the oxidation reactivity of the sulfur compound increases with the increment in the electron density on its sulfur atom. The electron densities on the sulfur atoms in BT, DBT and 4,6-DMDBT are 5.739, 5.758, 5.760, respectively.⁴¹ The lowest reactivity of BT may be related to its lowest electron density. However, the electron density on the sulfur atom of 4,6-DMDBT is higher than that of DBT, but the oxidation reactivity of 4,6-DMDBT is still lower than that of DBT. This result is ascribed to the effect of the steric hindrance of the methyl groups, which causes the difficulty of the active species to approach the sulfur atom.⁴²

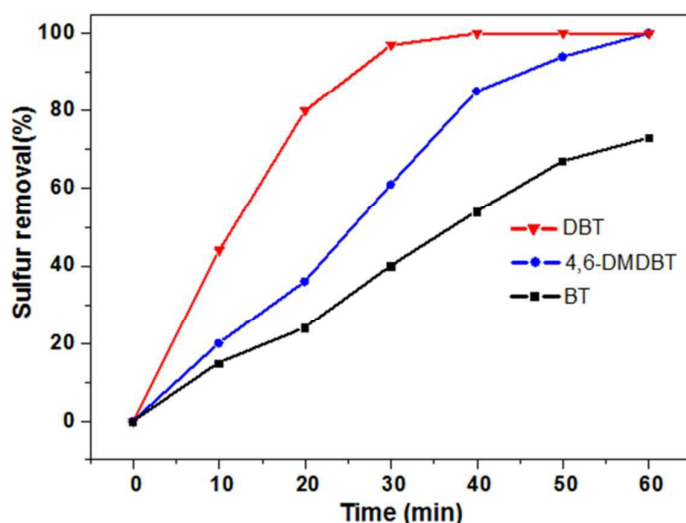


Fig. 5 Sulfur removal of different s-compounds in the desulfurization system. Reaction conditions: Model oil (S in n-octane = 500 ppm) 5 ml, [Bmim]PF₆ = 1 mL, t = 60 min, T = 60°C, O/S = 4, n(sulfur)/n(catalyst) = 20:1.

3.3.5 IL/SEP Recycling

In order to know whether the ionic liquid-type catalyst system would succumb to poisoning and lose its catalytic activity during the reaction. Use of recycled SEP/[Bmim]PF₆ for further oxidation of DBT was investigated. After the first run, the upper layer was separated by decantation. To speed up remove the water (reduced H₂O₂) in the system, the IL phase was distilled in a vacuum at 80°C for 2 h, and then fresh model oil and H₂O₂ were introduced for the next recycle. Fig. 6 shows the system could be recycled at least six times still achieve 97% without significant decrease in catalytic sulfur removal. At

the end of the oxidation desulphurization of the model sulfur compounds, the catalyst was filtered, washed with dichloromethane. Hill and co-workers have addressed a water oxidation mechanism consistent in the case of catalysis beginning with $\text{Co}_4(\text{PW}_9)_2$.⁴³⁻⁴⁶ The different catalyst both the sample SEP and Co^{2+} (CoO_x) cases were investigated in the oxidant system. As shown in Fig. S2, finding that Co^{2+} cations or CoO_x derived from aqueous Co^{2+} is not the dominant catalyst in the current.

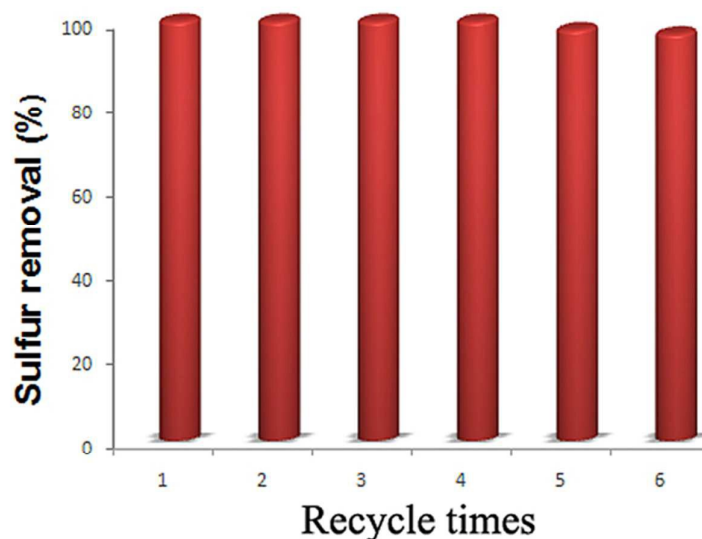
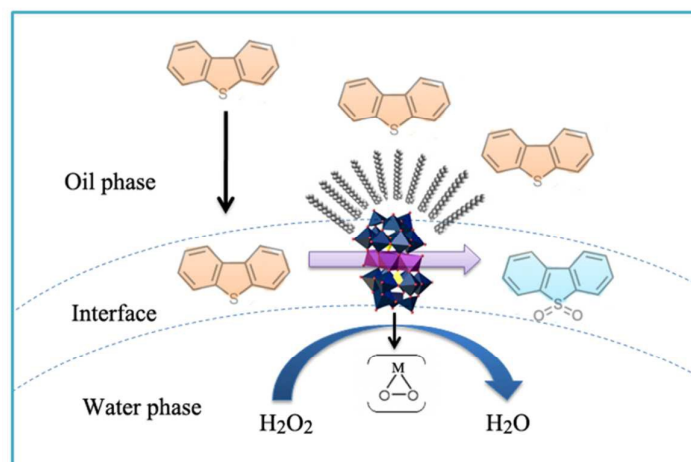


Fig. 6 The recycle times on the sulfur removal. Reaction conditions: Model oil (S in n-octane = 500 ppm) 5 ml, $[\text{Bmim}]\text{PF}_6 = 1 \text{ mL}$, $t = 60 \text{ min}$, $T = 60^\circ\text{C}$, $\text{O/S} = 4$, $n(\text{sulfur})/n(\text{catalyst}) = 20:1$.

3.3.6 The proposed reaction mechanism

The proposed possible mechanism of the catalytic oxidative desulfurization with SEP/ $[\text{Bmim}]\text{PF}_6/\text{H}_2\text{O}_2$ in three-liquid-phase micro-emulsion system in Scheme 1. The mechanism could be possibly postulated is based on some literatures.^{47,48} DBT as a representative sulfur compound in model oil was chosen in ECODS. Catalyst, $[\text{Bmim}]\text{PF}_6$, H_2O_2 and model oil were added into the reactor in turn and formed three phases (oil, aqueous and IL phases). After stirring, all the materials above were mixed together. Then, three phases could fully contact with each other and form three-liquid-phase micro-emulsion system. The SEP at the water/oil interface of the emulsion droplets are continuously oxidized by H_2O_2 to active peroxy species. These peroxy species function as intermediate oxidants, which oxidized DBT to DBTO_2 . Subsequently, the reduced catalyst continually combined with H_2O_2 . In this way, the reaction activity was kept and the mass transfer ran smoothly. DBTO_2 with higher polar was increased after oxidation, which was extracted into the IL phase continuously. Finally achieve the purpose of deep desulfurization. Based on this mechanism, the hydrophobic alkyl chain of surfactant which increase the

catalytic efficiency of surfactant-encapsulated POMs plays a key role. These long alkyl chains on the surface of POM cluster help to attract the weakly polar sulfide molecules closer to the surfactant via hydrophobic–hydrophobic interactions, where they are oxidized to sulfones by peroxy species.¹² As a result, amphiphilic POM shows superior catalytic efficiency compared to bare POM.



Scheme 1 Proposed mechanism of the catalytic oxidative desulfurization with SEP/[Bmim]PF₆/H₂O₂ in three-liquid-phase system.

4 Conclusions

In conclusion, an amphiphilic SEP was used to catalyze the oxidation of sulfur-containing compounds with ionic liquid in model oil using H₂O₂ as the oxidant under mild conditions. The DBT removal could reach 100% over the SEP in 40 min at 60°C. Oxidative reactivity of different sulfur compounds decreased according to the following order: DBT > 4,6-DMDBT > BT. Besides, the oxidation system could be recycled for six times without a significant decrease in activity. Moreover, a mechanism was proposed to investigate the oxidation process between POM-based catalyst and sulfur-containing compounds. This ionic liquid-type catalyst system is a simple, mild, and environmentally friendly approach for deep desulfurization.

Acknowledgements

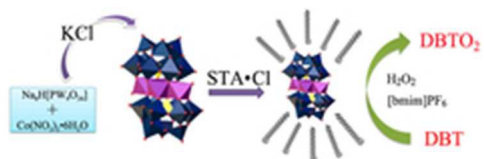
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