Deep oxidative desulfurization of fuels by Fenton-like reagent in ionic liquids

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The oxidation of dibenzothiophene (DBT), benzothiophene (BT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in model oil was studied in the extraction and catalytic oxidative desulfurization (ECODS) system at room temperature (30 °C). Various Fenton-like reagents, such as Co^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+} and H_2O_2, were screened for desulfurization in ionic liquids. The experimental results demonstrated that the desulfurization system containing anhydrous $FeCl_3$, H_2O_2, and $[bmim]BF_4$ exhibited high catalytic activity. The sulfur removal of DBT-containing model oil could reach 96.1%, which was obviously superior to mere solvent extraction with $[bmim]BF_4$ (28.5%) or catalytic oxidation without $[bmim]BF_4$ (7.3%). In a combination of extraction and oxidation, the sulfur content decreased from 500 ppm to 5 ppm, when the hydrogen peroxide was added into the desulfurization system in four batches. The catalytic oxidation reactivity of the sulfur-containing compounds was found to be in the following order: DBT > BT > 4,6-DMDBT. Moreover, the desulfurization system could be recycled five times without a significant decrease in activity.

Introduction

During the last few decades, environmental pollution caused by exhaust emissions is one of the most serious problems in the world and SO_x produced irreversibly poisons the noble metal catalysts in automobiles, which attracted much attention focused on the deep desulfurization of light oils.[1] The environmental regulations for transportation fuels are becoming more and more severe, and the S-limit of the gasoline and diesel oil will probably be reduced to about 10 ppm in many countries by 2010.[2]

In the petroleum refining industry, the sulfur-containing compounds like thiols, sulfides and disulfides, are carried out mostly *via* hydrodesulfurization (HDS).[3,4] However, it is difficult to remove some refractory sulfur compounds with stereo hindrance, such as dibenzothiophene (DBT) and its derivatives [methyldibenzothiophene (MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT)].[5] In order to achieve deep desulfurization, severe operating conditions [*e.g.*, high temperature (T > 623 K), high pressure (3–10 MPa) and high hydrogen consumption] and large capital cost are required for HDS.[2,6] Therefore, alternative desulfurization technologies for fuels have been investigated extensively. For instance, approaches based on oxidation,[1,4-18] extraction,[2,19-23] adsorption,[24,25] biodesulfurization[26] and others[27] have been developed recently. Among these methods, the oxidative desulfurization combined with extraction attracts wide interest, which is considered as one of the most promising processes. In this process, sulfur compounds present in the fuels are oxidized to their corresponding sulfoxides and sulfones, which can be removed by extraction with organic extractants, such as dimethyl sulfoxide (DMSO),[12] acetonitrile,[18] 1-methyl-2-pyrrolidinone (NMP) and dimethylformamide (DMF), *etc.*[28] However, the further environmental and safety concerns caused by the flammable and volatile organic compounds (VOCs), such as wastewater emission and fire hazards, become one of the prime concerns.[16]

Room temperature ionic liquids (RTILs) have been extensively employed in catalysis,[14] electrochemistry,[29] synthesis of nanomaterials,[30] *etc.*, because of their low melting point, high thermal stability, negligible vapor pressure and so on. Various desulfurization systems by extraction with different ILs have been reported, owing to their high affinity to sulfur-containing compounds, such as $[emim][EtSO_4]$,[2] $[bmim][OcSO_4]$,[2] $[bmim]FeCl_4$,[14] $[Me_3NCH_2C_6H_5Cl]Zn_2Cl_5$,[16] $[bmim]PF_6$,[19,23] $[bmim]BF_4$,[19,23] $[omim]BF_4$,[19] $[bmim][CF_3SO_3]$,[19] $[omim][OcSO_4]$,[19] $[bmim]AlCl_4$,[19] $[emim]FeCl_4$,[20] $[bmim]Cu_2Cl_3$,[21] [bmim][DBP],[22] [emim][DEP].[22] However, most of the efficiency of sulfur removal extracted merely with ILs is relative low due to the similarity between the sulfur-containing molecules and remaining diesel fuels. More recently, a new and effective approach that is chemical oxidation in conjunction with ILs extraction has been explored in order to improve the desulfurization efficiency.[5,13-17] For example, the oxidative desulfurization of fuels catalyzed by acidic ionic liquids $[hnmp]BF_4$ using H_2O_2 as oxidant has been researched by Zhao and coworkers,[15] who pointed out that ILs could decompose H_2O_2 to form hydroxyl radicals which could oxidize the sulfur compounds to their corresponding sulfones in the IL phase. Wei *et al.* found that the rate of chemical oxidation in the water-immiscible $[bmim]PF_6$ was higher than that in the water-miscible $[bmim]BF_4$.[17] An extraction and catalytic oxidative desulfurization system composed of IL, H_2O_2 and catalyst was reported by our groups,[13] and the sulfur removal of DBT-containing model oil could reach 99% in $[bmim]BF_4$. All the

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results of these experiments indicated that the desulfurization yield of sulfur compounds is superior to the simple extraction with ILs.

Both Fenton reagent (Fe^{2+}/H_2O_2) and Fenton-like reagent (Fe^{3+}/H_2O_2) are advanced oxidation processes (AOPs) which have been mostly employed to treat various wastewaters.[31] Dai *et al.* have developed a oxidative desulfurization method using ultrasound in combination with Fenton reagent in the present of CH_3COOH to obtain low sulfur diesel fuel.[27] However, little research attention has been paid to the utilization of Fenton-like reagent in desulfurization systems. The aim of this work is to investigate the important role of a Fenton-like reagent in ILs in the process of desulfurization. In this paper, the low cost metal salts and H_2O_2 were employed in the extraction and catalytic oxidative desulfurization system. The deep removal of DBT could be achieved in the desulfurization system containing anhydrous $FeCl_3$, H_2O_2, and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) by contrast with other different systems.

Results and discussion

Influence of different desulfurization systems on removal of DBT in *n*-octane

The data in Table 1 shows three different desulfurization systems of extraction, extraction coupled with chemical oxidation and extraction coupled with catalytic oxidation. [bmim]BF_4, 1-*n*-octyl-3-methylimidazolium tetrafluoroborate ([omim]BF_4), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) and 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ([omim]PF_6) were immiscible with model oil. Anhydrous $FeCl_3$ could dissolve in IL, but it hardly dissolved in the model oil. Compared with [omim]BF_4, [bmim]PF_6 and [bmim]PF_6, aqueous hydrogen peroxide could only dissolve in [bmim]BF_4. Therefore, the reaction system including [bmim]BF_4 was a biphasic system (IL/oil), in which the IL phase, along with catalyst and H_2O_2, was the lower layer and the oil phase was the upper layer. However, the reaction system including [omim]BF_4, [bmim]PF_6 or [omim]PF_6 formed triphasic system (IL/H_2O_2/oil), in which the lowest layer was the IL phase and catalyst, aqueous hydrogen peroxide as oxidizing agent was in the middle and the oil phase was the upper layer. Thereby the model oil could be easily separated from the desulfurization systems.

Table 1 Comparison of different desulfurization systems of model oil[a]

		S-removal of different desulfurization systems (%)		
Entry	Type of ILs	IL[b]	IL + H_2O_2	IL+ anhydrous $FeCl_3$ + H_2O_2
1	[bmim]BF_4	28.5	32.4	96.1
2	[omim]BF_4	47.1	49.9	72.2
3	[bmim]PF_6	25.4	34.8	94.4
4	[omim]PF_6	48.8	49.8	54.1

[a] Model oil was prepared by dissolving DBT in *n*-octane to give solutions with an S-content of 500 ppm. *Experimental conditions*: T = 30 °C, t = 4 h, model oil = 5 mL, IL = 2 mL, [n(DBT)/n(catalyst) = 1], [$n(H_2O_2)/n$(DBT) = 6]. [b] The mixture was stirred at 30 °C for 15 min.

As shown in Table 1, when [bmim]BF_4 was used as an extractant to remove DBT from model oil, the desulfurization efficiency of [bmim]BF_4 was poor (sulfur removal only reached 28.5%). The sulfur removal increased to 32.4% with the addition of H_2O_2 in [bmim]BF_4. In the case of the extraction coupled with oxidative desulfurization system composed of [bmim]BF_4, H_2O_2 and anhydrous $FeCl_3$, the removal of DBT increased sharply and reached 96.1%. The same trends were found in other ILs, which the sulfur removal ranged from 54.1% to 94.4% (Table 1, entries 2 to 4). Therefore, the role of catalyst was very significant in the desulfurization system and the anhydrous $FeCl_3$ revealed high catalytic activity, especially in [bmim]PF_6 and [bmim]BF_4. It was found that the ability of [omim]BF_4 or [omim]PF_6 to extract DBT from *n*-octane is better than that of [bmim]BF_4 or [bmim]PF_6, respectively. However, the experimental results of extraction coupled with catalytic oxidation were just contrary. Compared with the same cation of [omim]$^+$, the sulfur removal in ILs with [bmim]$^+$ could achieve 96.1% ([bmim]BF_4) and 94.4% ([bmim]PF_6), respectively. The data also demonstrated that the efficiency of extraction coupled with oxidative desulfurization was better in a biphasic system than that in a triphasic system, in the case of ILs including the same cations. Before DBT was oxidized in the biphasic system, it was extracted into IL, in which the catalyst and H_2O_2 dissolved. However, there was only catalyst in the IL phase in the triphasic system. On this account, it is easier for DBT to be oxidized in biphasic system than that in triphasic system.

The desulfurization results of the model oil catalyzed by different catalysts are shown in Fig. 1. The sulfur removal only got to 32.4% without any catalyst. Among the different Fenton-like systems, such as Co^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+} or Fe^{3+} and H_2O_2, the Fe^{3+}/H_2O_2 system exhibited high catalytic activity and the sulfur removal of DBT-containing model oil could reach 96.1%. In our desulfurization systems, the sulfur removal catalyzed by the Fenton-like reagent containing Fe^{3+} and H_2O_2 was better than that catalyzed by Fenton reagent. Comparatively, the different catalysts containing various anions showed different desulfurization efficiencies, such as $Fe(NO_3)_3 \cdot 9H_2O$ (36.9%) and $Fe_2(SO_4)_3$ (33.5%). It is obvious that $FeCl_3$ had better catalytic ability than the others, and the anion played an important role

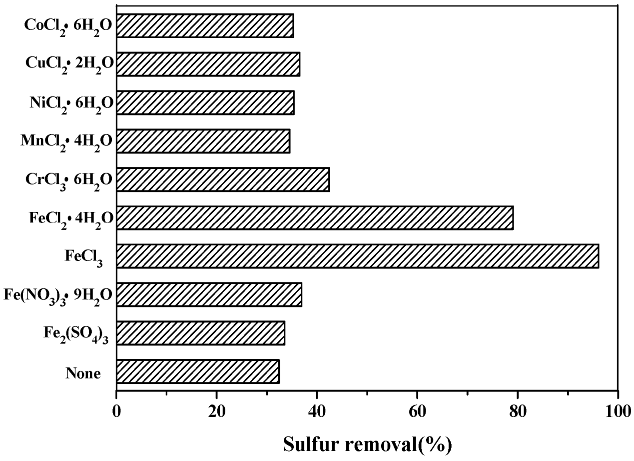


Fig. 1 Sulfur removal in [bmim]BF_4 treated with different catalysts. *Experimental conditions*: T = 30 °C, t = 4 h, model oil = 5 mL, IL = 2 mL, [n(DBT)/n(catalyst) = 1], [$n(H_2O_2)/n$(DBT) = 6].

in the catalytic desulfurization system. In a word, anhydrous $FeCl_3$ showed the highest catalytic activity among the different metal salts. As such, further research was focused on studying desulfurization system containing anhydrous $FeCl_3$, H_2O_2, and [bmim]BF_4.

Influence of the amount of IL

Fig. 2 shows that IL played a significant role in the desulfurization system. Without IL, the sulfur removal only got to 7.3% in the desulfurization system. As the amount of IL increased continuously, it was clear that the desulfurization efficiency was enhanced. When the amount of IL was 1 mL and 2 mL, the removal of DBT was 84.6% and 96.1%, respectively. However, the trend of sulfur removal was stable when the amount of IL increased to 3 mL. Although the ability of [bmim]BF_4 to extract DBT from *n*-octane increased with the increasing amount of IL, the consistency of the catalyst in [bmim]BF_4 reduced. This experimental phenomenon was caused by these two reasons simultaneously. Therefore, the desulfurization efficiency increased greatly with the addition of IL to the desulfurization system, compared with catalytic oxidation without IL.

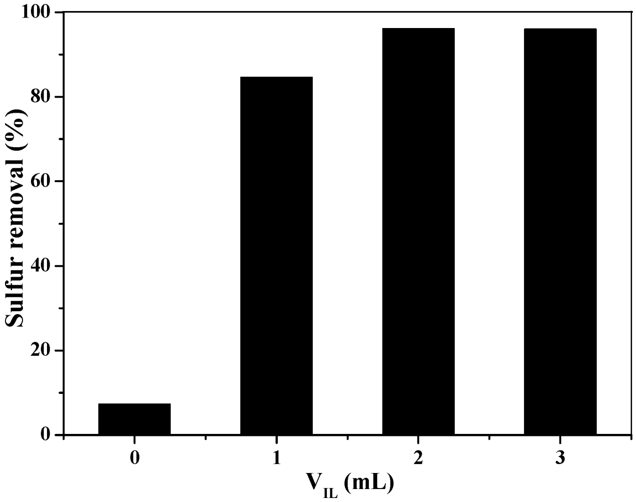


Fig. 2 Influence of the amount of IL on the removal of DBT. *Experimental conditions*: $t = 4$ h, $T = 30$ °C, model oil = 5 mL, [n(DBT)/n(catalyst) = 1], [$n(H_2O_2)/n$(DBT) = 6].

Influence of the molar ratios of H_2O_2 and DBT

To investigate the influence of the amount of oxidizing agent on the oxidative properties, various H_2O_2/sulfur (O/S) molar ratios on the removal of DBT are given in Fig. 3. Stoichiometrically, 2 mol of H_2O_2 are consumed for oxidation of the sulfur-containing compounds to their corresponding sulfones, for example, the oxidation of DBT to $DBTO_2$. However, the experimental results exhibited the molar ratio of H_2O_2 and sulfur had a strong effect on the reaction. As the O/S molar ratios increased from 2 : 1 to 10 : 1, the removal of DBT from the model oil increased from 71.3% to 96.1%. It is clear that the sulfur removal reached a plateau of 96.1% when the O/S molar ratio got to 6 : 1. There was no evident change of sulfur-removal to further increase the amount of H_2O_2, after O/S molar ratio of 6 : 1. Considering the practical situation in the reaction, using an O/S molar ratio of 6 : 1 was proper.

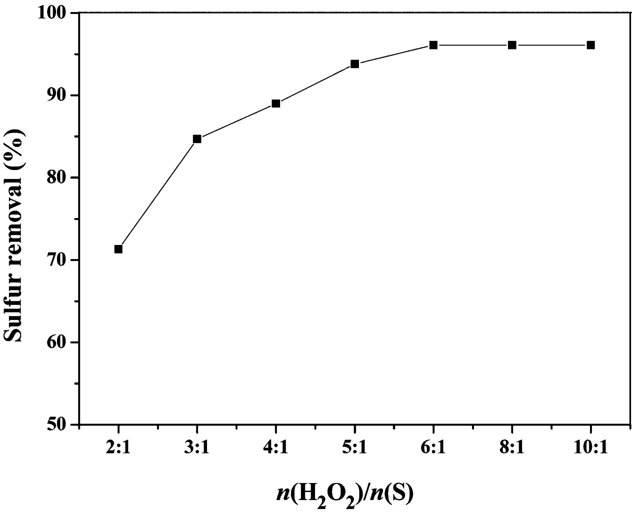


Fig. 3 Influence of the molar ratios of H_2O_2 and sulfur (DBT) on removal of DBT. *Experimental conditions*: $T = 30$ °C, $t = 4$ h, model oil = 5 mL, IL = 2 mL, [n(DBT)/n(catalyst) = 1].

Influence of molar ratios of catalyst and DBT

To study the influence of the amount of catalyst on the oxidative properties, experiments where the catalyst/sulfur (Fe^{3+}/S) molar ratios varied from 1 : 5 to 5 : 1 were carried out under the same reaction conditions (Fig. 4). The results show the sulfur removal was linearly increased in the range of the Fe^{3+}/S molar ratio from 1 : 5 to 1 : 1. When the Fe^{3+}/S molar ratio reached a critical value (1 : 1), the sulfur removal was up to 96.1%, compared with 28.8% at a molar ratio of 1 : 5 and 86.9% at a molar ratio of 1 : 2. However, the sulfur removal dropped as the molar ratio was changed from 1 : 1 to 5 : 1, with sulfur removals of 91.2% (2 : 1) and 76.2% (5 : 1), respectively. The reason was that an excess amount of the catalyst could promote the severe decomposition of H_2O_2, which resulted in the decrease in desulfurization

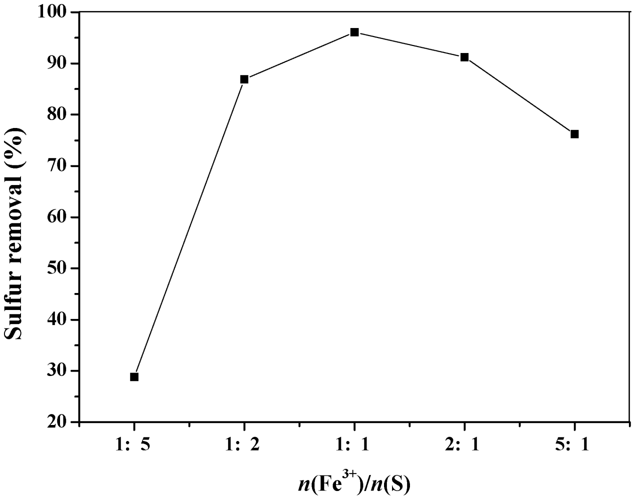


Fig. 4 Influence of the molar ratios of catalyst and sulfur on the removal of DBT. *Experimental conditions*: $T = 30$ °C, $t = 4$ h, model oil = 5 mL, IL = 2 mL, [$n(H_2O_2)/n$(DBT) = 6].

efficiency. In this case, the loaded molar weight of catalyst was just the molar weight of the DBT in catalytic oxidation system.

Influence of the time and temperature

The desulfurization system composed of anhydrous $FeCl_3$, H_2O_2 and $[bmim]BF_4$ was used to research the influence of various reaction time and temperatures. As can be seen from Fig. 5, sulfur removal of DBT-containing model oil increased at different temperatures with the increasing time. For instance, sulfur removal of DBT increased from 84.7% to 96.1% at 30 °C for 4 h. However, the sulfur removal increased slowly to 96.3% when the time reached 5 h. After a combination of extraction and catalytic oxidation, DBT was oxidized in the IL phase after it was extracted from *n*-octane. Therefore, the concentration of DBT in *n*-octane decreased continuously at various temperatures. However, the results displayed the reaction activity decreased as the temperature increased. Sulfur removal could reach 96.1% at 30 °C for 4 h, but only got to 87.6%, 79.2% at 40 °C and 50 °C, respectively. It was because that more H_2O_2 decomposed with the increasing temperature, leading to the worse utilization of H_2O_2 in the oxidative desulfurization.

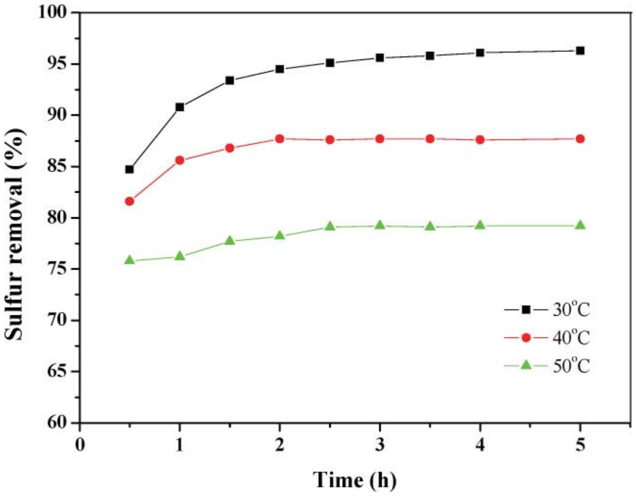


Fig. 5 Sulfur-removal after oxidation with anhydrous $FeCl_3$ as catalyst in $[bmim]BF_4$ *vs.* reaction time at various temperatures. *Experimental conditions*: model oil = 5 mL, IL = 2 mL, $[n(DBT)/n(catalyst) = 1]$, $[n(H_2O_2)/n(DBT) = 6]$.

Influence of adding H_2O_2 in different ways

The experiments of adding H_2O_2 in different ways were carried out in order to testify the influence of the self-decomposition of H_2O_2 in the process of oxidation of DBT. As shown in Table 2, the total amounts of H_2O_2 were the same in each of the three experiments. Compared with the S-removal of 96.1% when adding 6.0 equivalent H_2O_2 with DBT together at the starting time, the sulfur removal could get to 97.8% when 3.0 equivalents of H_2O_2 with DBT were added into the desulfurization system at the time of 0 h and 2 h in turn, respectively. However, it was found that the sulfur content decreased from 500 ppm to 5 ppm and reached 99.0% S-removal under the reaction condition that H_2O_2 was inserted into the oxidative system in four equal batches. Therefore, the deep desulfurization could be achieved in this way. This was mainly because that H_2O_2 could be sufficiently utilized in the experiments with the addition of H_2O_2 in batches, avoiding the concentration of H_2O_2 being too high and causing its severer self-decomposition at the starting time.

Table 2 Results of adding H_2O_2 in different ways on removal of DBT[a]

	$n(H_2O_2)/n(DBT)$				
Entry	0 h	1 h	2 h	3 h	Sulfur removal (%)
1	6.0	—	—	—	96.1
2	3.0	—	3.0	—	97.8
3	1.5	1.5	1.5	1.5	99.0

[a] *Experimental conditions*: T = 30 °C, t = 4 h, model oil = 5 mL, IL = 2 mL, $[n(DBT)/n(catalyst) = 1]$.

Influence of the different kinds of the substrate

The reactivity of different sulfur-containing compounds, including DBT, BT and 4,6-DMDBT, was estimated in the desulfurization system using anhydrous $FeCl_3$ as catalyst. As can be seen from Fig. 6, the sulfur removal decreased in the order DBT > BT > 4,6-DMDBT at 30 °C for 4 h after extraction combined with catalytic oxidation. The results also indicated that the removal of three sulfur compounds increased with the increasing time, reaching 96.1%, 76.6% and 32.6%, respectively.

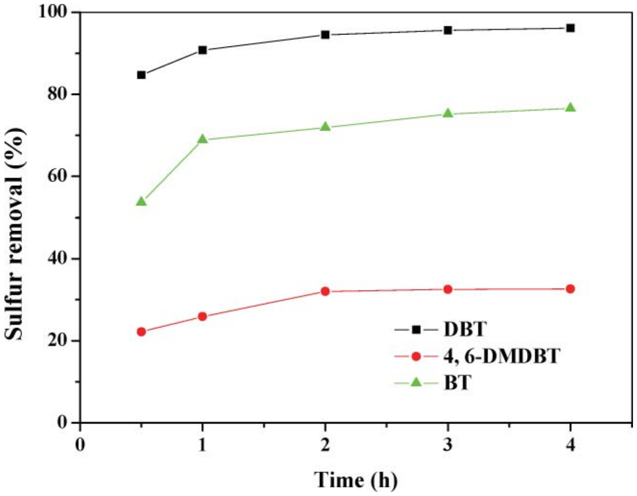


Fig. 6 Influence of different substrates in $[bmim]BF_4$ with anhydrous $FeCl_3$ as catalyst. *Experimental conditions*: T = 30 °C, t = 4 h, model oil = 5 mL, IL = 2 mL, $[n(DBT)/n(catalyst) = 1]$, $[n(H_2O_2)/n(DBT) = 6]$.

As described previously, the process of ODS system involved extraction and oxidation in two steps, and substrates were oxidized in the IL phase after they were extracted from *n*-octane. Therefore, the ability of IL to extract different substrates is an important factor influencing desulfurization efficiency. From the data in Table 3, 4,6-DMDBT shows a much lower Nernst partition coefficient (K_N) in comparison with DBT and BT. At the same time, the steric hindrance of the methyl groups of 4,6-DMDBT is an obstacle for the approach of the sulfur atom to the catalytic active species in IL. Owing to these two factors, the desulfurization efficiency of 4,6-DMDBT was the lowest. For DBT and BT, both the K_N and the electron density on sulfur

Table 3 Nernst partition coefficients (K_N) for extraction of substrates with [bmim]BF_4 and electron densities on sulfur atom

Entry	Substrate	K_N in (mg L^{-1})/(mg L^{-1})[a]	Electron density[b]
1	DBT	1.00	5.758
2	BT	0.57	5.739
3	4,6-DMDBT	0.17	5.760

[a] *Note*: units involve mass of substrate and volume of ionic liquid. *Experimental conditions*: $T = 30$ °C, $t = 15$ min, model oil = 5 mL, IL = 2 mL. [b] Results from Otsuki and coworkers.[7]

atom of DBT are higher than those of BT, which led to DBT having the highest oxidative reactivity. The results indicated that the reactivity order was affected by electron density, steric hindrance and Nernst partition coefficient simultaneously. Therefore, the catalytic oxidation reactivity of the different substrates was in the following order: DBT > BT > 4,6-DMDBT.

Regeneration/recycling of ionic liquid

The possibility of recycling the [bmim]BF_4 containing $FeCl_3$ was examined on the removal of DBT in ECODS system. After the reaction, the reaction system was still a biphasic system in which the IL phase, along with the catalyst and H_2O_2, was still the lower layer, so the oil phase could be separated from the biphasic system easily. Then, the ionic liquid phase was distilled in oil bath at 110 °C for 3 h in order to evaporate the residual oxidizing agents from the IL. Afterwards, the fresh H_2O_2 and model oil were added for the next run. From the results shown in Fig. 7, it was found that the desulfurization system could be recycled five times without an obvious decrease in the catalytic activity. The sulfur removal maintained 95.5% after four times in comparison with the first times (96.1%), and then decreased slightly to 92.8% in the fifth times. According to our observation, as the recycle times increased, more and more precipitation was produced in the IL in the process of the experiment (Fig. 8a, b and c). After the fifth cycle, the IL phase was removed from the desulfurization system and reextracted by tetrachloromethane at room temperature. Afterwards, the tetrachloromethane phase was separated and dried at 80 °C until a white crystal solid was produced (Fig. 8d). The white crystal solid was collected and characterized by FT-IR. The IR spectrum demonstrated two absorption bands at 1289 cm^{-1} and 1130 cm^{-1}, which were determined to probably be sulfone groups.[33] Therefore, the lower of sulfur removal might be due to the $DBTO_2$ produced, which led to the decrease in the extraction performance of IL.

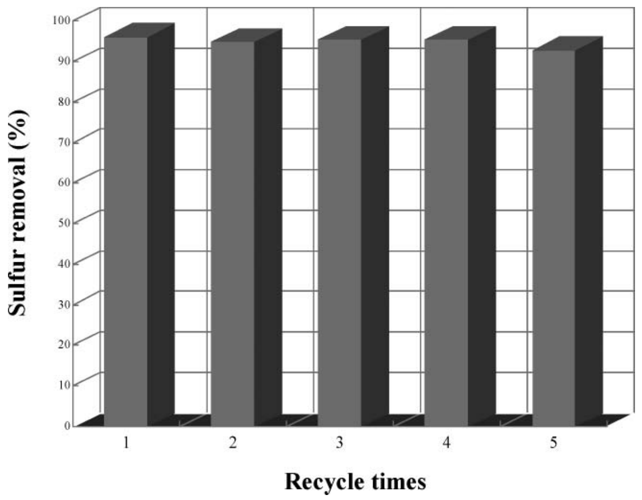


Fig. 7 Recycle of [bmim]BF_4 containing anhydrous $FeCl_3$ in desulfurization system. *Experimental conditions*: $T = 30$ °C, $t = 4$ h, model oil = 5 mL, IL = 2 mL, [n(DBT)/n(catalyst) = 1], [$n(H_2O_2)/n$(DBT) = 6].

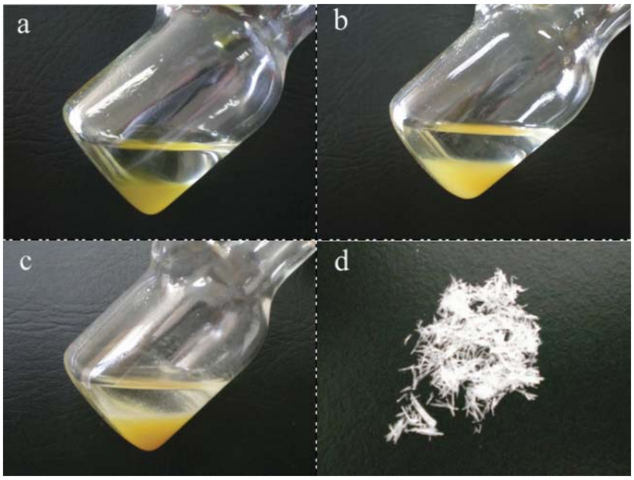


Fig. 8 The photos of ECODS systems and the reclaimed $DBTO_2$. (a) ECODS system containing anhydrous $FeCl_3$, H_2O_2, [bmim]BF_4 and DBT-containing model oil (before reaction). (b) ECODS system containing anhydrous $FeCl_3$, H_2O_2, [bmim]BF_4 and DBT-containing model oil (after reaction for 3 cycles). (c) ECODS system containing anhydrous $FeCl_3$, H_2O_2, [bmim]BF_4 and DBT-containing model oil (after reaction for 5 cycles). (d) Reclaimed $DBTO_2$ with CCl_4 from ECODS system after 5 cycles.

Mutual solubility of ionic liquid and *n*-octane

It is important to investigate the mutual solubility between the extractant and the fuel in the desulfurization system. In this paper, imidazole-based ILs were chosen as an extractant and the noticeable solubility of ILs in the model oil may not only contaminate the fuel but also lead to possible NO_x pollution during the process of removing the SO_x pollution. Therefore, the samples of IL-saturated *n*-octane, [bmim]BF_4 and *n*-octane were analyzed with high performance liquid chromatography (HPLC). As shown in Fig. 9, the retention times (t_R) of [bmim]BF_4 and *n*-octane were 1.635 min and 3.233 min, respectively. No IL peak was found in the sample of IL-saturated *n*-octane, which was a proof that [bmim]BF_4 has negligible solubility in model oil. Hence, the problem of the mutual solubility between the extractant and model oil could be avoided.

The suggested process and mechanism of ECODS

Although the Fenton-like reagent (Fe^{3+}/H_2O_2) has been widely applied to oxidize organic substrates,[34,35] the mechanism of this system was still far from being fully understood. Herein, the catalytic oxidation mechanism of DBT with Fenton-like reagent is explained.

For the Fenton-like reagent, the Fe^{3+} hydroperoxo intermediate ($[Fe^{III}OOH]^{2+}$) was firstly formed as in eqn (1) *via* hydrolysis instead of the break of the O–O bond of hydrogen peroxide.[34]

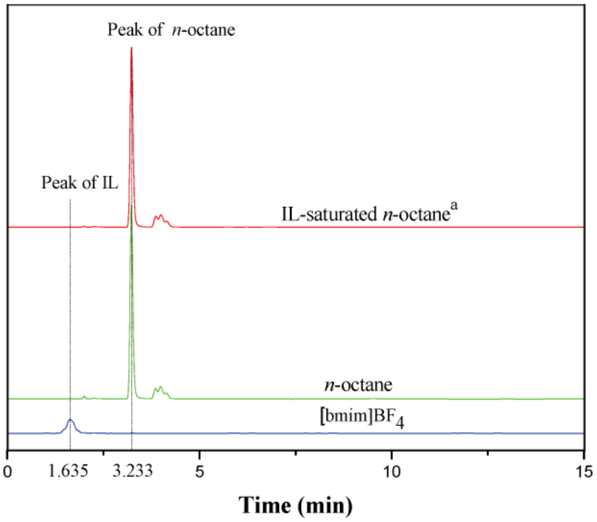


Fig. 9 HPLC chromatograms of [bmim]BF_4, *n*-octane and IL-saturated *n*-octane. ^a*Experimental conditions*: $T = 30$ °C, $t = 15$ min, *n*-octane = 5 mL, IL = 2 mL. *Note*: The peaks (retention time t_R, at about 4 min) were due to the impurities in *n*-octane.

$$Fe^{3+} + H_2O_2 \rightarrow [Fe^{III}OOH]^{2+} + H^+ \qquad (1)$$

The $[Fe^{III}OOH]^{2+}$ intermediate itself could be involved in substrate oxidation or decompose in three distinct pathways and generate different oxidants.[35,36]

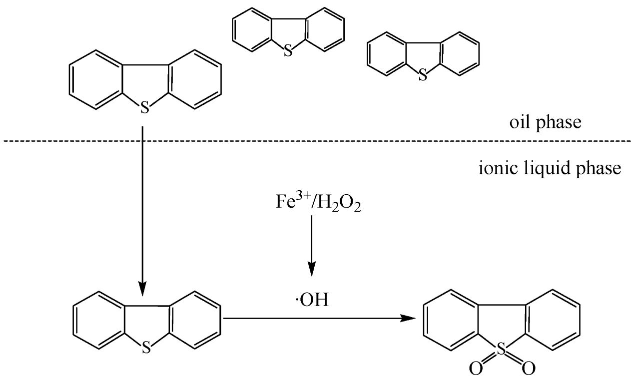
$$[Fe^{III}OOH]^{2+} \rightarrow [Fe^{V}O]^{3+} + OH^- \qquad (2)$$

$$[Fe^{III}OOH]^{2+} \rightarrow [Fe^{IV}O]^{2+} + {}^{\bullet}OH \qquad (3)$$

$$[Fe^{III}OOH]^{2+} \rightarrow Fe^{2+} + {}^{\bullet}OOH \qquad (4)$$

Both heterolysis and homolysis of this intermediate occurred simultaneously. Firstly, $[Fe^{III}OOH]^{2+}$ might undergo O–O bond heterolysis to produce the high-valency iron-oxo species $[Fe^{V}O]^{3+}$ [eqn (2)].[35,36] The second pathway was the homolysis of the O–O bond of the produced intermediate to form the ferryl ion and $^{\bullet}OH$ radicals [eqn (3)].[35,36] Both the ferryl ion and the $^{\bullet}OH$ radicals generated could attack the substrate,[36] and the $^{\bullet}OH$ radicals that were strong oxidants played the leading role.[37] Thirdly, the Fe–O bond could homolyze to give an $^{\bullet}OOH$ radicals [eqn (4)], and bimolecular self-reaction of the $^{\bullet}OOH$ radicals could also form the strong oxidant ($^{\bullet}OH$) with releasing oxygen.[36] The barrier for the O–O homolysis of $Fe^{III}OOH$ intermediate was even lower, by a significant amount.[34] Therefore, the $^{\bullet}OH$ radicals could be generated easier to oxidize the DBT in our desulfurization system.

[bmim]BF_4 was immiscible with model oil, as had been proved by the analysis with HPLC, so the extraction coupled with catalytic oxidative desulfurization system containing anhydrous $FeCl_3$, H_2O_2 and [bmim]BF_4 was a biphasic system. The processes of oxidation of sulfur compounds involved two steps in ECODS, which were the extractive process and the oxidative reaction.[15] The sulfur-containing compounds, such as DBT, were first extracted into the IL phase. Then, DBT was oxidized to $DBTO_2$ (Fig. 8d) in the IL phase by the $^{\bullet}OH$ radicals generated from the Fenton-like reagent, which was the second step. The oxidative reaction of DBT resulted in the decrease of the concentration of DBT in the ionic liquid, which continuously promotes the extraction process. In a combination of extraction and oxidation, the aim of the deep desulfurization can be achieved. The suggested process of extraction and catalytic oxidative mechanism of DBT is shown in Scheme 1.



Scheme 1 The suggested process of extraction and catalytic oxidation mechanism of DBT with Fenton-like reagent in the biphasic system.

Conclusion

The low cost metal salts were dissolved in [bmim]BF_4, [omim]BF_4, [bmim]PF_6, [omim]PF_6 to oxidize BT, DBT and 4,6-DMDBT with H_2O_2 for desulfurization at room temperature and all the experiments were conducted easily. Among the different desulfurization systems, the ECODS system containing anhydrous $FeCl_3$, H_2O_2 and [bmim]BF_4 showed the highest catalytic activity. The sulfur removal of DBT-containing model oil could reach 99.0% on condition that H_2O_2 was added into the desulfurization system in four batches. The catalytic oxidation reactivity of sulfur-containing compounds decreased in the order of DBT > BT > 4,6-DMDBT. On analyzing the sample of IL-saturated *n*-octane with HPLC, no IL peak was found, which is the proof that [bmim]BF_4 has negligible solubility in model oil. Moreover, this ECODS system could be recycled five times without a significant decrease in activity. With the efficient production of ionic liquids in the chemical industry, the method of extraction/oxidation desulfurization may be a simple, promising and environmentally-friendly process.

Experimental

Preparation of different model oils

DBT (2.932 g) was dissolved in *n*-octane (1000 mL). The sulfur content of model oil containing DBT was 500 ppm. With the same method, other kinds of model oil were prepared by dissolving BT and 4,6-DMDBT in *n*-octane to give corresponding sulfur contents of 250 ppm and 250 ppm.

Extraction coupled with catalytic oxidative desulfurization of model oil

The ionic liquids [bmim]BF_4, [omim]BF_4, [bmim]PF_6 and [omim]PF_6 were synthesized as mentioned in the literature procedure.[32] The extraction coupled with catalytic oxidative desulfurization experiments of the model oil were carried out in a home-made 40 mL two-necked flask. The required amounts of IL and catalyst were added to the flask in turn, which was stirred for about 10 min in order to make the catalyst dissolve in the IL sufficiently, and then 5 mL model oil and 30 wt% H_2O_2 were added. The mixture was stirred vigorously at 30 °C for 4 h in a water bath. With the same experimental method, the desulfurizaton experiments were carried out under other conditions.

Analysis of sulfur content

After the reaction, the upper phase (model oil) was withdrawn at room temperature and analyzed by gas chromatography (Agilent 7890A) with tetradecane as internal standard, coupled with a flame ionization detector (GC-FID). A 30 m × 0.32 mm inner diameter × 0.25 μm film thickness HP-5 capillary column was used for separation. The conversion of DBT in the model oil was used to calculate the removal of sulfur compounds.

Analysis of mutual solubility of ionic liquid and *n*-octane

The sample of IL-saturated *n*-octane was prepared by stirring the mixture of $[\text{bmim}]\text{BF}_4$ and *n*-octane at 30 °C for 15 min. The sample of IL-saturated *n*-octane, $[\text{bmim}]\text{BF}_4$ and *n*-octane were analyzed with HPLC (Agilent Technologies 1200 series equipped with a UV-Vis detector under 248 nm wavelength; column, Eclipse XDB-C18 (5 μm, 4.6 × 150 mm); temperature, 25 °C; mobile phase, methanol/water = 85/15; flowrate, 1.0 mL min^{-1}).

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