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Oxidation of Aromatic Sulfur Compounds Catalyzed by Organic Hexacyanoferrates in Ionic Liquids with a Low Concentration of H₂O₂ as an Oxidant

Wei Jiang,[†] Wenshuai Zhu,^{*,†} Yonghui Chang,^{†,‡} Huaming Li,^{*,†} Yanhong Chao,[†] Jun Xiong,[†] Hui Liu,[†] and Sheng Yin[†]

[†]School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, People's Republic of China

[‡]Key Laboratory of Tropical Medicinal Plant Chemistry of Ministry of Education, College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou, Hainan 571158, People's Republic of China

S Supporting Information

ABSTRACT: A series of organic hexacyanoferrates were synthesized and employed as catalysts in ionic liquids (ILs) for catalytic oxidation of dibenzothiophene (DBT), benzothiophene (BT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT). High activity was achieved using 1-butyl-3-methylimidazolium hexacyanoferrate ([C₄mim]₃Fe(CN)₆) as a catalyst and 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim]BF₄) as an extractant in the presence of H₂O₂ under mild conditions. It was interesting to find that the concentration of H₂O₂ had a significant influence on desulfurization efficiency. The sulfur removal was 76.3% with 30 wt % H₂O₂ as an oxidant, while it could reach 97.9% with 7.5 wt % H₂O₂. Electron spin resonance (ESR) spectroscopy measurements gave the evidence that the active oxygen species O₂^{•−} was generated in the catalytic oxidative desulfurization process, and gas chromatography–mass spectrometry (GC–MS) analysis indicated that the sulfur compounds were oxidized to the corresponding sulfones. The influence factors, such as reaction temperature, time, concentration, and dosage of H₂O₂, amount of catalyst, catalytic system recycling, and different sulfur-containing compounds, were investigated. The kinetic investigations showed that oxidation of sulfur compounds presented a pseudo-first-order kinetic. Under the optimal conditions, the catalytic system could be recycled at least 4 times without a remarkable decrease in activity.

1. INTRODUCTION

The sulfur compounds in fuels are known to have a negative impact on the environment because of SO_x emissions from their combustion exhausts. Conventional hydrodesulfurization (HDS) is most widely used in refineries to remove aliphatic and acyclic sulfur compounds. However, it is less effective for treating some refractory sulfur compounds, such as benzothiophenes (BTs) and dibenzothiophenes (DBTs).^{1–4} To achieve deep desulfurization, severe operating conditions, such as high temperature, high pressure, and high hydrogen consumption, are required, leading to high capital and operating costs. Therefore, it is essential to develop alternative non-HDS methods to produce clean diesel containing a low sulfur concentration.^{5–9} Among them, oxidative desulfurization (ODS) is considered to be one of the most promising processes because of its high efficiency for removing refractory sulfur compounds under mild conditions.^{10–17}

Our previous work reported an ionic liquid (IL) extraction and catalytic oxidative desulfurization (ECODS) system, which could oxidize the sulfur compounds to their corresponding sulfones.^{18–26} To date, some catalysts or ILs, such as FeCl₃,¹⁹ tetramethylammonium tetrachloroferrate ([CH₃]₄N][FeCl₄],²² 1-butyl-3-methylimidazolium tetrachloroferrate ([C₄mim][FeCl₄]),¹⁸ trioctylmethyl ammonium tetrachloroferrate ([C₈H₁₇]₃CH₃N][FeCl₄],²¹ and triethylamine tetrachloroferrate ([Et₃NH][FeCl₄]),²⁰ were developed by our group, and they all showed good performance in oxidative desulfurization. Then, other Fe-based ILs, e.g., [C₄mim]FeCl₃²⁷ and [C₄MPy]-

FeCl₄,²⁸ were synthesized and used to investigate the oxidative removal of sulfur compounds from diesel fuels. The oxidant used in these desulfurization systems was hydrogen peroxide (H₂O₂). Moreover, H₂O₂ is the most common oxidant in other oxidative desulfurization fields,^{29–34} partly because it is a commercial product often used at the industrial level and gives only water as a byproduct.³⁵ Although H₂O₂ is one of the best candidates as an oxidant, a high concentration of H₂O₂ is a potentially explosive issue during transportation and may do harm to human health. However, it is hard to activate low-concentration H₂O₂ to oxidize DBTs in fuels, and few examples have been reported.³⁶ Therefore, the use of low-concentration H₂O₂ in oxidative desulfurization will be an environmentally friendly and safe process.

Hexacyanoferrates are usually used as a redox couple in the electrochemical field.³⁷ However, there are very few examples of the application of hexacyanoferrates in catalysis,³⁸ especially in activation of low-concentration H₂O₂. Here, we first report the oxidation of DBT, BT, and 4,6-dimethyldibenzothiophene (4,6-DMDBT) with low-concentration H₂O₂ using the ECODS system, with the organic hexacyanoferrates [C_nmim]₃Fe(CN)₆ (where *n* = 2, 4, and 8) as a catalyst and [C₄mim]BF₄ as an extractant. In this system, [C₄mim]₃Fe(CN)₆ exhibited the highest activity in the presence of 7.5 wt %

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Table 1. Sulfur Removal of Different Desulfurization Systems^a

entry	desulfurization system	sulfur removal (%)		
		30 wt % H ₂ O ₂	7.5 wt % H ₂ O ₂	without H ₂ O ₂
1	IL			23.2
2	IL/H ₂ O ₂	21.7	19.0	
3	IL/catalyst I/H ₂ O ₂	74.5	86.7	
4	IL/catalyst II/H ₂ O ₂	76.3	97.9	
5	IL/catalyst III/H ₂ O ₂	73.5	91.1	

^aExperimental conditions: catalyst I, [C₂mim]₃Fe(CN)₆; catalyst II, [C₄mim]₃Fe(CN)₆; catalyst III, [C₈mim]₃Fe(CN)₆; *n*(catalyst), 0.039 mmol; model oil, 5 mL; IL([C₄mim]BF₄), 1 mL; O/S, 4; *T*, 40 °C; and *t*, 5 h.

H₂O₂ and the catalytic system could be recycled 4 times with a slight decrease in activity. Furthermore, the reaction mechanism was investigated by ultraviolet–visible (UV–vis), electron spin resonance (ESR) spin-trap technique, and gas chromatography–mass spectrometry (GC–MS) analysis.

2. EXPERIMENTAL SECTION

2.1. Materials. BT, DBT, and 4,6-DMDBT were purchased from Sigma-Aldrich. The ILs 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim]BF₄), 1-*n*-octyl-3-methylimidazolium tetrafluoroborate ([C₈mim]BF₄), 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim]PF₆), and 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ([C₈mim]PF₆) was purchased from Shanghai Chengjie Chemical Co., Ltd. Other materials were commercial-reagent-grade and were obtained from Shanghai Sinopharm Chemical Co., Ltd. Model oils were prepared by dissolving DBT and BT in *n*-octane to give solutions with a sulfur content of 500 and 250 ppm, respectively. In addition, tetradecane was added to the model oil as an internal standard. The H₂O₂ concentration was measured by titration with potassium permanganate solution, which was determined by sodium oxalate.

2.2. Instruments. The Fourier transform infrared (FTIR) spectra of catalysts (KBr pellets) were tested with a Nicolet Nexus 470 FTIR instrument. Electrospray ionization–mass spectrometry (ESI–MS) spectra were collected on a LXQ linear ion trap mass spectrometer. UV–vis spectra were recorded on UV-2450 spectrophotometer (Shimadzu Corporation, Japan). Elementary analyses were carried out with CHN-O-Rapid (Heraeus Corporation). Sulfur compounds in IL phase were extracted by diethyl ether and determined by GC–MS (Agilent 7890A/5975C). X-band ESR spectra were recorded at room temperature on a JES FA200 spectrometer. The settings for the ESR spectrometer were as follows: center field, 336.496 mT; sweep width, 5 mT; microwave frequency, 9.5 GHz; modulation frequency, 100 kHz; and power, 0.998 mW.

2.3. Preparation of [C_{*n*}mim]₃Fe(CN)₆ (where *n* = 2, 4, and 8). A aqueous solution (50 mL) of K₃Fe(CN)₆ (3 mmol) and [C_{*n*}mim]BF₄ (9 mmol) were mixed and stirred for 24 h at room temperature. The precipitate (KBF₄) was filtered off, and the filtrate was concentrated by evaporating the solvent. Then, the resulting mixture was purified by methanol. After the solvent was removed under reduced pressure, the remaining solid was washed with diethyl ether and dried at 40 °C in a vacuum for 24 h to give the product as a yellow green powder.

Data for [C₂mim]₃Fe(CN)₆: IR (KBr, cm^{−1}): ν = 2115 (C≡N). ESI–MS: 111 [C₂mim]₄Fe(CN)₆⁺, 434 [C₂mim]₂Fe(CN)₆[−]. Elemental analysis calcd (%) for C₃₀FeH₁₅N₁₂: C, 52.85; H, 6.10; N, 30.82. Found: C, 52.58; H, 6.31; N, 30.90.

Data for [C₄mim]₃Fe(CN)₆: IR (KBr, cm^{−1}): ν = 2115, 2107 (C≡N). ESI–MS: 139 [C₄mim]₄Fe(CN)₆⁺, 490 [C₄mim]₂Fe(CN)₆[−]. Elemental analysis calcd (%) for C₃₀FeH₁₅N₁₂: C, 57.23; H, 7.20; N, 26.70. Found: C, 57.34; H, 7.35; N, 26.70.

Data for [C₈mim]₃Fe(CN)₆: IR (KBr, cm^{−1}): ν = 2115, 2106 (C≡N). ESI–MS: 195 [C₈mim]₄Fe(CN)₆⁺, 602 [C₈mim]₂Fe(CN)₆[−]. Elemental analysis calcd (%) for C₃₀FeH₁₅N₁₂: C, 63.22; H, 8.72; N, 21.06. Found: C, 63.35; H, 9.02; N, 20.94.

2.4. Oxidative Desulfurization Procedure. In a typical reaction run, [C₄mim]₃Fe(CN)₆ (24.6 mg, 0.039 mmol), IL [C₄mim]BF₄ (1 mL), model oil (5 mL), and H₂O₂ were added to a two-necked flask. Then, the mixture was stirred for 5 h at 40 °C under atmospheric pressure. After reaction, the model oil was separated by decantation for further analysis via gas chromatography–flame ionization detection (GC–FID, Agilent 7890A, HP-5 column, 30 m long × 0.32 mm inner diameter × 0.25 μ m film thickness; injector port temperature, 250 °C; detector temperature, 300 °C; and oven temperature, starting at 100 °C and rising to 200 °C at 15 °C/min for DBT and BT starting at 100 °C, rising to 160 °C at 20 °C/min, and then rising to 230 °C at 25 °C/min for 4,6-DMDBT). The sulfur removal was calculated as in eq 1, where C₀ (ppm) is the initial sulfur concentration in the model oil and C_{*t*} (ppm) is the terminal sulfur concentration at any time *t* (min).

$$\text{sulfur removal (\%)} = (1 - C_t/C_0) \times 100 \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. Investigation of Different Desulfurization Systems. DBT was selected as a representative sulfur compound in fuel because it was one of the main refractory sulfur compounds in the HDS treatment. The ionic liquid [C₄mim]BF₄ was chosen as an extractant because of its remarkable selectivity of extraction sulfur compounds from model oil.³⁹ The conversion of DBT in model oil was used to calculate the removal of sulfur. The sulfur removal in different systems was listed in Table 1. When [C₄mim]BF₄ was used as an extractant to remove DBT, the extractive desulfurization efficiency was only 23.2%. With the addition of 30 or 7.5 wt % H₂O₂, the sulfur removal decreased a little to 21.7 or 19.0%. The phenomena might be ascribed to the fact that the H₂O₂ solution into the IL phase made some extracted DBT return to the oil phase.⁴⁰ The sulfur removal increased sharply to 74.5% for IL/[C₂mim]₃Fe(CN)₆/30 wt % H₂O₂ (entry 3 in Table 1), 76.3% for IL/[C₄mim]₃Fe(CN)₆/30 wt % H₂O₂ (entry 4 in Table 1), and 73.5% for IL/[C₈mim]₃Fe(CN)₆/30 wt % H₂O₂ (entry 5 in Table 1). The results showed the advantage of ECODS with the organic hexacyanoferrates over desulfurization by mere extraction or oxidation without catalysts. In comparison to 30 wt % H₂O₂, 7.5 wt % H₂O₂ exhibited a higher oxidative performance. For example, the sulfur removal could reach 97.9% with [C₄mim]₃Fe(CN)₆ as a catalyst, 86.7% with [C₂mim]₃Fe(CN)₆ as a catalyst, and 91.1% with [C₈mim]₃Fe(CN)₆ as a catalyst. The reason will be given in the following section. We also found that the catalytic activity was in the following order: [C₄mim]₃Fe(CN)₆ > [C₈mim]₃Fe(CN)₆ > [C₂mim]₃Fe(CN)₆. Therefore, deep desulfurization could be obtained with [C₄mim]₃Fe(CN)₆ as a catalyst and 7.5 wt % H₂O₂ as an oxidant in [C₄mim]BF₄.

3.2. Reaction Mechanism of Oxidative Desulfurization. The ECODS reaction mechanism was investigated via UV–vis and ESR spin-trap technique. Figure 1 shows UV–vis

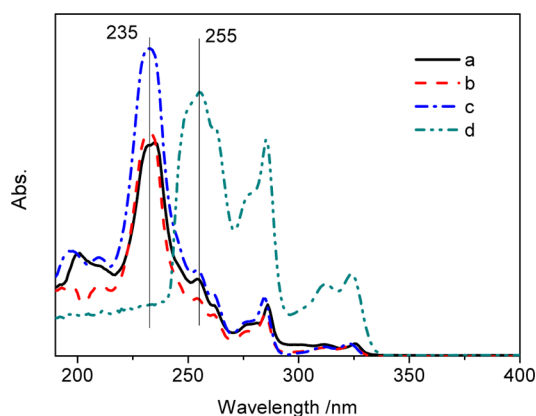


Figure 1. UV-vis spectra of (a) DBT in *n*-octane, (b) DBT extracted in CH_3OH , (c) DBT extracted in CH_3CN , and (d) DBT extracted in $[\text{C}_4\text{mim}]\text{BF}_4$.

spectra of DBT in *n*-octane and DBT extracted in solvents. An absorption band at 235 nm can be observed for DBT in *n*-octane.⁴¹ After DBT was extracted in CH_3OH and CH_3CN , the absorption bands of DBT remained at about 235 nm. When DBT was extracted into $[\text{C}_4\text{mim}]\text{BF}_4$, this band shifted to 255 nm, suggesting that the structure of DBT was distorted in $[\text{C}_4\text{mim}]\text{BF}_4$. This might be attributed to the polarization of DBT by the fluorine ion.⁴² In addition, the oxidation of DBT in CH_3OH and CH_3CN was only 78.2 and 62.5% (see Table S1 of the Supporting Information), respectively, which was greatly lower than that in $[\text{C}_4\text{mim}]\text{BF}_4$ (94.3%). Therefore, the nature of the extractant had an important effect in the ECODS system, and the aromaticity of DBT might decrease in $[\text{C}_4\text{mim}]\text{BF}_4$, which made DBT easier to be oxidized.

To further clarify the reaction mechanism, an ESR spin-trap technique was employed to probe the active oxygen species with DMPO as traps. As shown in Figure 2, no ESR signals

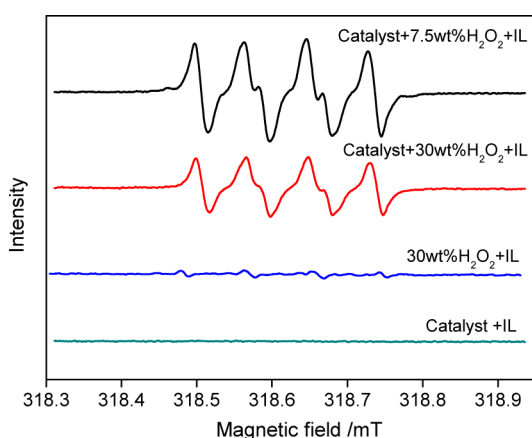


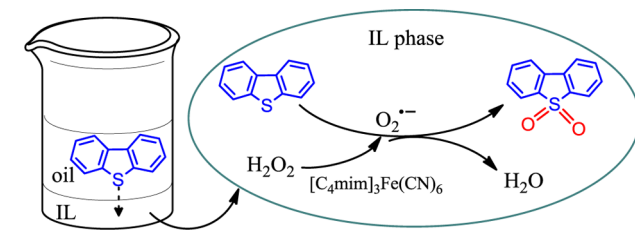
Figure 2. ESR spectra of the $\text{DMPO}-\text{O}_2^{\bullet-}$ adduct generated in the oxidative desulfurization process.

were observed when H_2O_2 was absent. Very weak characteristic peaks of $\text{DMPO}-\text{OH}^\bullet$ signals could be obtained as the reaction was performed without catalyst, which may have resulted from the thermal decomposition of H_2O_2 itself.⁴³ However, the characteristic sextet peaks of the $\text{DMPO}-\text{O}_2^{\bullet-}$ adduct were clearly observed in the presence of IL, catalyst, and 30 wt % H_2O_2 .^{44–46} According to the ESR signals, we could conclude that $\text{O}_2^{\bullet-}$ was generated by $[\text{C}_4\text{mim}]\text{Fe}(\text{CN})_6$ upon

interaction with H_2O_2 in IL. Interestingly, the ESR signal could be enhanced after the concentration of H_2O_2 decreased from 30 to 7.5 wt %, indicating that more $\text{O}_2^{\bullet-}$ was produced. This result was consistent with the fact that the sulfur removal increased from 76.3 to 97.9% (Table 1). Thus, an obvious conclusion could be drawn that $\text{O}_2^{\bullet-}$ was the main active oxygen species on oxidation of DBT in this desulfurization system.

It is well-known that $\text{O}_2^{\bullet-}$ is not stable in an aqueous environment. However, this stability issue could be addressed with $[\text{C}_4\text{mim}]\text{Fe}(\text{CN})_6$ as a catalyst, because when the concentration of H_2O_2 decreased while the O/S molar ratio remained constant, that is, more water was introduced to the reaction system, the amount of $\text{O}_2^{\bullet-}$ did not decrease but increased a lot (verified by Figure 2), which indicated that $\text{O}_2^{\bullet-}$ was stable in the $[\text{C}_4\text{mim}]\text{Fe}(\text{CN})_6$ – $[\text{C}_4\text{mim}]\text{BF}_4$ system containing a certain amount of water. On the other hand, the utilization efficiency of H_2O_2 increased remarkably. For instance, approximately 50% hydrogen peroxide was decomposed in our previous work²² using $[(\text{CH}_3)_4\text{N}]\text{FeCl}_4$ as a catalyst, while 10.3% hydrogen peroxide was decomposed with $[\text{C}_4\text{mim}]\text{Fe}(\text{CN})_6$ as a catalyst (see Table S2 of the Supporting Information). The contrast provided direct evidence that $[\text{C}_4\text{mim}]\text{Fe}(\text{CN})_6$ could stabilize $\text{O}_2^{\bullet-}$ in the desulfurization process. The oxidation products of the sulfur compounds were the corresponding sulfones and discussed at a later stage. Therefore, a plausible mechanism was proposed in Scheme 1. First, DBT in model oil was extracted into the IL

Scheme 1. Proposed Mechanism of the Oxidative Desulfurization Process



phase upon mixing model oil and IL. Then, $\text{O}_2^{\bullet-}$ generated by the interaction between $[\text{C}_4\text{mim}]\text{Fe}(\text{CN})_6$ and H_2O_2 in the IL phase can oxidize DBT to dibenzothiophene sulfones (DBTO_2), which preferred to remain in the IL phase because of its higher polar. Therefore, a continuous decrease of the DBT concentration in model diesel was observed.

3.3. Influence of the Concentration and Dosage of H_2O_2 on the Removal of DBT. To elucidate the influence of the concentration of H_2O_2 on the desulfurization, different concentrations of H_2O_2 were applied under the experimental conditions of $T = 40^\circ\text{C}$, model oil (5 mL), $[\text{C}_4\text{mim}]\text{BF}_4$ (1 mL), H_2O_2 (0.312 mmol), and $[\text{C}_4\text{mim}]\text{Fe}(\text{CN})_6$ (0.039 mmol). As seen in Figure 3a, when the concentration of H_2O_2 decreased from 30 to 7.5 wt %, the sulfur removal increased from 76.3 to 97.9%. However, the sulfur removal dropped after the concentration of H_2O_2 decreased to 6 wt %. Therefore, the influence of dosage of H_2O_2 was investigated using 7.5 wt % H_2O_2 as an oxidant. $\text{H}_2\text{O}_2/\text{DBT}$ (O/S) molar ratios of 2:1, 3:1, and 4:1 were plotted in Figure 3b. The sulfur removal increased from 51.8% at O/S = 2:1 to 97.9% at O/S = 4:1. According to the stoichiometric reaction, 2 mol of hydrogen peroxide is consumed for oxidation of 1 mol of DBT to DBT sulfone

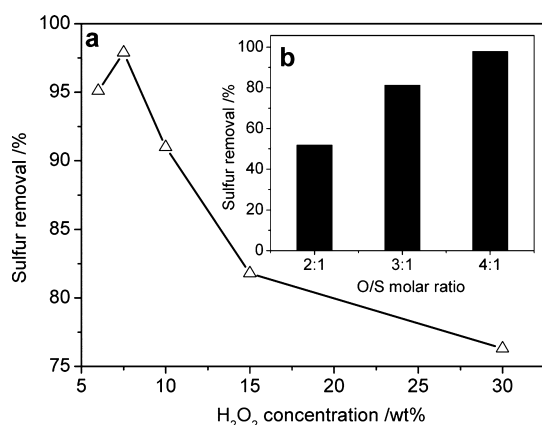


Figure 3. Influence of the concentration and dosage of H₂O₂ on the removal of DBT. Experimental conditions: [C₄mim]₃Fe(CN)₆, 0.039 mmol; model oil, 5 mL; [C₄mim]BF₄, 1 mL; T, 40 °C; t, 5 h; (a) O/S, 4; and (b) [H₂O₂], 7.5 wt %.

(DBTO₂). However, it is well-known that there is a competition between the decomposition of hydrogen peroxide and the DBT oxidation reaction.²² Therefore, O/S = 4 was the optimal dosage in the present study.

3.4. Influence of the Reaction Temperature and Time on the Removal of DBT. The sulfur removal with different reaction times at different temperatures is given in Figure 4. As

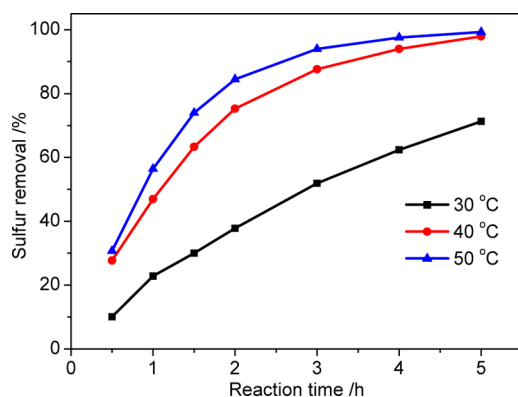


Figure 4. Influence of reaction temperature and time on sulfur removal. Experimental conditions: [C₄mim]₃Fe(CN)₆, 0.039 mmol; model oil, 5 mL; [C₄mim]BF₄, 1 mL; and O/S, 4.

expected, the conversion of DBT increased with the increasing reaction time. For example, 27.7% sulfur removal was obtained in 0.5 h at 40 °C, and the sulfur removal increased dramatically to 97.9% after 5 h. It can be found that the trend of sulfur removal was similar at 30 and 50 °C. However, the desulfurization efficiency at 30 °C was only 71.3% after 5 h. In combination of the 99.3% sulfur removal at 50 °C, it could be concluded that the reaction temperature profoundly enhanced the desulfurization rate. This trend was not in line with the result of our previous work^{18–22} with the Fe-based catalytic system, and the difference might be due to the different ligands to iron. From the practical point of view, 40 °C was chosen as an appropriate reaction temperature for the present ECODS process, because a higher temperature could result in higher operation cost and thermal decomposition of H₂O₂.

3.5. Influence of the Amount of Catalyst on the Removal of DBT. The influence of the amount of catalyst on the desulfurization process was studied by varying the amount of [C₄mim]₃Fe(CN)₆ from 0.0098 to 0.078 mmol. As shown in Figure 5, the DBT removal increased notably from 75.5 to

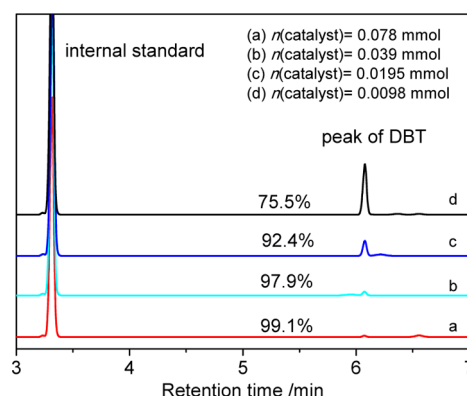


Figure 5. Influence of the amount of catalyst on the removal of DBT. Experimental conditions: T, 40 °C; model oil, 5 mL; [C₄mim]BF₄, 1 mL; O/S, 4; and t, 5 h.

97.9% as the amount of catalyst increased from 0.0098 to 0.039 mmol and then increased mildly when the mass of catalyst increased from 0.039 to 0.078 mmol. It was obvious that the excessive catalyst was not necessary and for an economical purpose. Thus, 0.039 mmol was chosen as the most suitable quantity in this experiment.

3.6. Influence of Different ILs on the Removal of DBT. In the present ECODS process, ILs were deemed as a reacting phase and, thus, different ILs had a significant influence on the sulfur removal performance. The tests with different ILs, such as [C₄mim]BF₄, 1-*n*-octyl-3-methylimidazolium tetrafluoroborate ([C₈mim]BF₄), 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim]PF₆), and 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ([C₈mim]PF₆), were carried out in the presence of 7.5 and 30 wt % H₂O₂, respectively. The results in Figure 6 showed that DBT removal with 7.5 wt % H₂O₂ was greater than that with 30 wt % H₂O₂ in all of the ILs above. Furthermore, it was found that the difference in activity depended upon the nature of the ILs. In comparison to the ILs with PF₆[−] anion, the ILs with BF₄[−] anion were more beneficial to the sulfur removal.

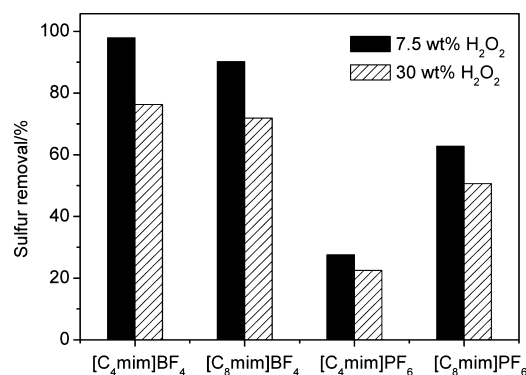


Figure 6. Influence of different extractants on removal of DBT. Experimental conditions: [C₄mim]₃Fe(CN)₆, 0.039 mmol; T, 40 °C; model oil, 5 mL; IL, 1 mL; O/S, 4; and t, 5 h.

3.7. Oxidation of Different Sulfur-Containing Compounds. The performance of catalyst $[\text{C}_4\text{mim}]_3\text{Fe}(\text{CN})_6$ for different sulfur-containing compounds, including DBT, BT, and 4,6-DMDBT, was evaluated in Figure 7. The sulfur removal was

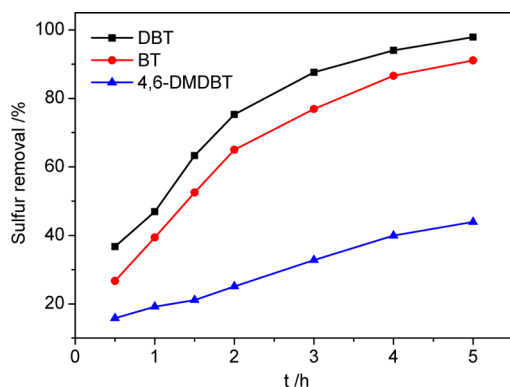


Figure 7. Removal of different sulfur-containing compounds. Experimental conditions: $[\text{C}_4\text{mim}]_3\text{Fe}(\text{CN})_6$, 0.039 mmol; T , 40 °C; model oil, 5 mL; $[\text{C}_4\text{mim}]\text{BF}_4$, 1 mL; O/S, 4; and t , 5 h.

increased with the increasing reaction time. Under the same conditions, the final desulfurization efficiency for DBT, BT, and 4,6-DMDBT was 97.1, 91.1, and 43.9%, respectively. The difference might be correlated with the electronic density of sulfur atoms and the steric hindrance effect. As calculated by Otsuki et al.,⁴⁷ the electron density on the S atom of BT (5.758) was lower than that of DBT (5.739), leading to a lower reactivity of BT. The lowest reactivity of 4,6-DMDBT may be attributed to the steric hindrance effect of the methyl groups, which was an obstacle for the approach of the sulfur atom to

the catalytic active species.^{19,48} The results indicated that the steric hindrance gave a greater effect on oxidative desulfurization. However, the removal of 4,6-DMDBT could increase to 90.2% after optimization of the reaction condition ($[\text{C}_4\text{mim}]_3\text{Fe}(\text{CN})_6$, 0.078 mmol; T , 40 °C; model oil, 5 mL; $[\text{C}_4\text{mim}]\text{BF}_4$, 1 mL; O/S, 12; and t , 5 h). Therefore, the organic hexacyanoferrates showed great potential for desulfurization of diesel fuel in the future.

The three sulfur-containing compounds mentioned above could be oxidized to their corresponding sulfones, which were determined by GC–MS analysis. After the reaction, the IL phase was separated and extracted with diethyl ether. The organic phase was collected and concentrated for GC–MS analysis. The sulfur oxidation products could not be detected in the oil phase, and all of the products existed in the IL phase because of the different chemical polarities between products and model oil. As shown in Figure 8a, the mass spectrum of the product showed the molecular ion peak at m/z 216.0 for DBT, which was assigned to DBTO_2 . Similar oxidation products of BT and 4,6-DMDBT were obtained, and the mass spectra in panels b and c of Figure 8 matched that of BTO_2 (166.0) and 4,6-DMDBT O_2 (246.0), respectively.

3.8. Recycling of the Catalytic System. The cycle property was an important factor and essential to be investigated. After the first reaction run, the upper layer was separated by decantation. The IL phase was distilled at 40 °C in vacuum for 12 h to evaporate the residual H_2O_2 , H_2O , and model oil. Then, fresh H_2O_2 and model oil were added for the next cycle under the same conditions. The results in Figure 9 showed that the system could be recycled at least 4 times without a significant decrease in activity. However, the sulfur removal decreased to 85.7% after 5 times. The decrease of

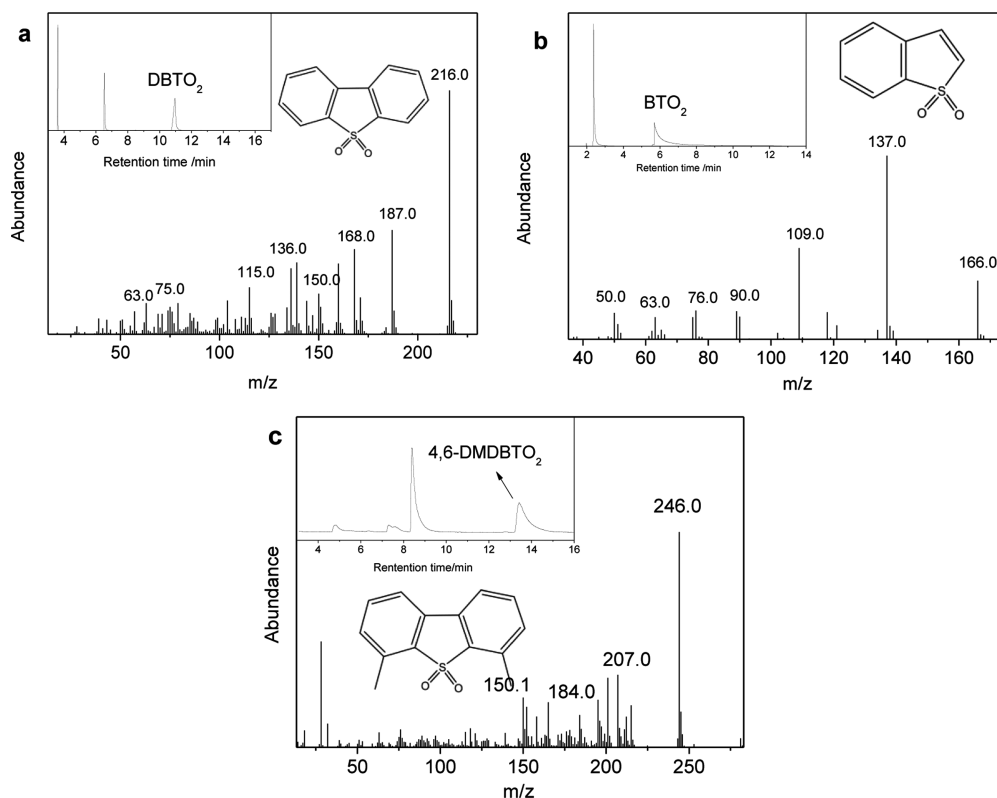


Figure 8. GC–MS of the oxidation products.

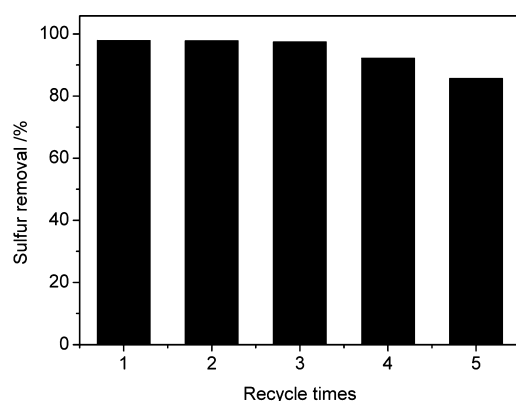


Figure 9. Recycling of the catalytic system containing $[\text{C}_4\text{mim}]\text{BF}_4$ and $[\text{C}_4\text{mim}]_3\text{Fe}(\text{CN})_6$ on the removal of DBT. Experimental conditions: $[\text{C}_4\text{mim}]_3\text{Fe}(\text{CN})_6$, 0.039 mmol; model oil, 5 mL; $[\text{C}_4\text{mim}]\text{BF}_4$, 1 mL; O/S, 4; and T , 40 °C.

sulfur removal might be attributed to the increasing oxidation product DBTO_2 that accumulated in the IL phase.¹⁹

3.9. Kinetics of the Catalytic Desulfurization of Model Oil. Reaction kinetics was a greatly important parameter to explain the oxidation of sulfur compounds. Experiments were performed with $[\text{C}_4\text{mim}]_3\text{Fe}(\text{CN})_6/[\text{C}_4\text{mim}]\text{BF}_4/\text{H}_2\text{O}_2$ to obtain kinetic parameters of the oxidation of sulfur compounds. The rate constant for the apparent consumption of sulfur compound was obtained from the pseudo-first-order eqs 2 and 3 as follows:

$$-dC_t/dt = kC_t \quad (2)$$

$$\ln(C_0/C_t) = kt \quad (3)$$

where C_0 and C_t were the initial sulfur concentration and the sulfur concentration at time t , respectively. $\ln(C_0/C_t)$ against the reaction time was plotted in Figure 10. The linear fit of

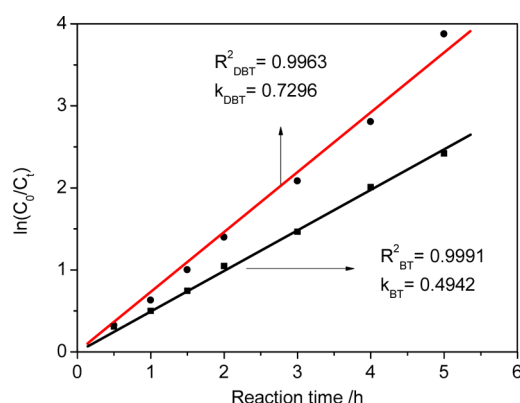


Figure 10. Pseudo-first-order kinetics for oxidation of DBT and BT. Experimental conditions: $[\text{C}_4\text{mim}]_3\text{Fe}(\text{CN})_6$, 0.039 mmol; model oil, 5 mL; $[\text{C}_4\text{mim}]\text{BF}_4$, 1 mL; O/S, 4; and T , 40 °C.

$\ln(C_t/C_0)$ against the the reaction time demonstrated the pseudo-first-order kinetics characteristics for oxidation of DBT and BT using catalyst $[\text{C}_4\text{mim}]_3\text{Fe}(\text{CN})_6$ ($R^2_{\text{DBT}} = 0.9963$, and $R^2_{\text{BT}} = 0.9991$). The apparent rate constants k of DBT and BT were 0.7296 and 0.4942 h^{-1} , respectively.

4. CONCLUSION

A deep desulfurization process based on extraction using $[\text{C}_4\text{mim}]\text{BF}_4$ and catalytic oxidation with a series of organic hexacyanoferrates catalyst $[\text{C}_n\text{mim}]_3\text{Fe}(\text{CN})_6$ (where $n = 2, 4$, and 8) was developed. The sulfur removal could increase to 97.9, 91.1, and 43.9% for DBT, BT, and 4,6-DMDBT, respectively, with $[\text{C}_4\text{mim}]_3\text{Fe}(\text{CN})_6$ as a catalyst and 7.5 wt % H_2O_2 as an oxidant. The catalyst could interact with H_2O_2 in $[\text{C}_4\text{mim}]\text{BF}_4$ to generate $\text{O}_2^{\bullet-}$, which could oxidize the sulfur compounds to the corresponding sulfones. Moreover, $\text{O}_2^{\bullet-}$ could remain stable in the reaction process, and only 10.3% H_2O_2 was decomposed. The sulfur conversion followed the pseudo-first-order kinetics, with the reaction rate constants of 0.7296 and 0.4942 h^{-1} for DBT and BT, respectively. Moreover, the catalytic system could be recycled at least 4 times without a vital decrease in activity. Therefore, deep desulfurization has been obtained with low concentration of H_2O_2 as oxidant. It provides a safer and more environmentally friendly way for the oxidative desulfurization of diesel oil.

■ ASSOCIATED CONTENT

Supporting Information

FTIR of (a) $[\text{C}_2\text{mim}]_3\text{Fe}(\text{CN})_6$, (b) $[\text{C}_4\text{mim}]_3\text{Fe}(\text{CN})_6$, and (c) $[\text{C}_8\text{mim}]_3\text{Fe}(\text{CN})_6$ (Figure S1), ESI-MS of catalysts in CH_3OH (Figure S2), oxidation of DBT in different extractants (Table S1), and decomposition of H_2O_2 in the reaction process (Table S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*Telephone: +86-511-88791800. Fax: +86-511-88791708. E-mail address: zhuws@ujs.edu.cn.

*Telephone: +86-511-88791800. Fax: +86-511-88791708. E-mail address: lihm@ujs.edu.cn.

Notes

The authors declare no competing financial interest.

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