1 Introduction

Ultra-desulfurization of gasoline and diesel oil is important because the sulfur compounds have brought many negative influences on the weather and health. Many countries have formulated strict environmental regulations to limit the sulfur content in the fuels (sulfur content < 10 ppm).12

In order to remove organic sulfur from petroleum products, the hydrodesulfurization (HDS) technology1 has been widely applied in the refining enterprises. However, HDS needs strict operating conditions,4 such as high temperature and high pressure, which result in the increase in the operational cost. Meanwhile, it is difficult to remove dibenzothiophene (DBT) and its derivatives due to space hindrance.3 In order to overcome the shortcomings of HDS, some non-HDS technologies such as adsorption desulfurization (ADS),6–7 oxidative desulfurization (ODS),8–11 biological desulfurization (BDS)12 and extractive desulfurization13 have been widely investigated. Among them, the oxidative desulfurization has become a hot topic because of its potential advantages such as mild reaction conditions and high desulfurization rate for dibenzothiophene (DBT) and its derivatives. In the oxidative desulfurization process, sulfur is oxidized into sulfone by oxidants such as molecular oxygen,14 H2O2,15 NO2 (ref. 15) and substitute solid.16 Among these, H2O2 is a widely used oxidant because of its economic and environmental benefits.

DES as an ionic liquid is composed of a cation and an anion, and has some desirable properties17–20 such as excellent solubility, non-volatility, and non-flammability. Moreover, DES containing hydrogen bonding networks is liquid at room temperature. DES as an environment-friendly solvent is applied in synthesis,21 catalysis,22 separation23 and electrochemistry.24 In last several years, DES has been applied to the desulfurization process due to its higher desulfurization rate.25–28 For instance, Li et al.29 synthesized 1.6Et3NHCl–FeCl3 extract, which facilitated the desulfurization rate up to 87%. Chen et al.30 reported that [Hnmp]Cl/ZnCl2 was applied in oxidative desulfurization and its desulfurization rate reached up to 99.9% for the model diesel oil. Li et al.31 reported that C8H15NO–0.3FeCl3 was used as an extractant as well as a catalyst in ODS and the removal rate of DBT was 97% in 3 h. Chen et al.32 synthesized [C5H9NO]+Cl/3ZnCl2 and 99.9% sulphur-removal rate could be obtained. Dong et al.33 found that the removal rate of DBT can reach up to 100% using [C6MPy]+Cl/FeCl3 as extractants and catalysts in ODS. In the process of desulfurization of oil, N,N-dimethylformamide (DMF) is often selected as an effective extractant.34–36 However, it is difficult to industrialize because the DMF dosage is too large. In this work, [HDMF]Cl-based DES is synthesized by a simple method. A small amount of DES used as an extractant and catalysts in ODS, and the removal rate of DBT still can reach more than 97%.

2 Experiment

2.1 Materials

2.1.1 Chemicals. DBT (98%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, 97%), benzothiophene (BT, 99%) and thiophene (TH, 99%) were purchased from Aladdin reagent. N-Octane, HCl, C3H7NO, FeCl3, ZnCl2, H2O2 (AR, 30 wt%) and CCl4 were purchased from Sinopharm Chemical Reagent Co., Ltd.
(99%) were purchased from Tianjin Damao Chemical Reagent Factory.

2.1.2 Instruments. Gas chromatography was performed on an Agilent 7890A GC with an FID detector using a 30 m packed HP5 column. Oxidation products of DBT, DBT, DES and the raw materials were characterized by Fourier-transform infrared spectroscopy (WQF-520; Beijing Bei-fen Ruili Analytical Instrument Co., Ltd, China) and ESI-MS using the Bruker Daltonics APEX-II (Bruker Daltonics Inc, USA).

2.2 Synthesis

2.2.1 Preparation of [HDMF]Cl. HCl (36%) was added to N,N-dimethylformamide at a molar ratio of 1 : 1 and stirred for 3 hours at 50 °C. Water in the solution was removed by rotary evaporation after stirring. Finally, the [HDMF]Cl solution was obtained.

2.2.2 Preparation of [HDMF]Cl/XMCln. [HDMF]Cl and MCln were added into a 100 mL cylindrical vessel. The mixture was heated in air with stirring using a glass rod until the complete dissolution of the compounds resulted in a transparent and viscous liquid. [HDMF]Cl/XMCln was obtained. The synthetic mechanism of DES is shown in Fig. 1.

2.3 Desulfurization experiment

Model oil (500 µg g⁻¹) was prepared by dissolving 1.437 g DBT in 500 mL n-octane. To implement the ODS process, the model oil, DES and 30 wt% H₂O₂ were added into a three-necked flask. The mixture was stirred at 50 rpm in a water bath at a particular temperature. The oil taken out from the upper layer in every 20 min was analyzed by gas chromatography on an Agilent 7890A GC with a 30 m packed HP5 column. The removal rate was calculated by the formula:

\[
\text{Sulfur removal rate} = \frac{S_{\text{tot}} - S_{\text{res}}}{S_{\text{tot}}} \times 100\%
\]

where \( S_{\text{tot}} \) (500 µg g⁻¹) is the total content of the sulfur compound in the model oil, \( S_{\text{res}} \) is the residual content of the sulfur compound after the ODS process.

3 Results and discussion

3.1 ESI-MS spectra of [HDMF]Cl-0.2FeCl₃

In order to determine the structures of [HDMF]Cl-0.2FeCl₃ and [HDMF]Cl/ZnCl₂, the ESI-MS spectra of [HDMF]Cl-0.2FeCl₃ and [HDMF]Cl/ZnCl₂ were obtained. The results are shown in Fig. 2. From the ESI-MS spectrum of [HDMF]Cl-0.2FeCl₃, the peaks observed at \( m/z = 163 \) and 198 correspond to FeCl₃ and FeCl₄⁻, respectively. The peak at \( m/z = 201 \) can be attributed to [HDMF] ClFeCl₂⁺. The peaks at \( m/z = 163 \) and 198 correspond to those in a previous report.²⁹,³⁰ The peak at \( m/z = 201 \) demonstrates that there is a reaction between [HDMF]Cl and FeCl₃. The lone pair electrons of N in [HDMF]Cl and an unoccupied orbital of Fe in FeCl₃ form a covalent bond. 4 mol of [HDMF]Cl supplies four electrons and 1 mol Fe supplies four half-unoccupied orbitals resulting in the molar ratio of 4 : 1 for [HDMF]Cl and FeCl₃.

3.2 FTIR characterization

Infrared spectrum peaks of ZnCl₂, FeCl₃, [HDMF]Cl, [HDMF]Cl-0.2FeCl₃ and [HDMF]Cl/ZnCl₂ have been displayed in Fig. 3. The peaks correlated to the bending of N–H at 665 cm⁻¹, bending of C–H at 887 and 1390 cm⁻¹, the stretching vibrations of C=N at 1021 and 1177 cm⁻¹, and that of C=O at 1654 and 1717 cm⁻¹, the stretching vibration of C=H at 2778 and 2995 cm⁻¹, and that of N–H at 3421 cm⁻¹ in [HDMF]Cl are shown in Fig. 3. It can be observed that some infrared spectrum peaks of [HDMF]Cl-0.2FeCl₃ and [HDMF]Cl/ZnCl₂ have been synthesized. [HDMF]Cl/ZnCl₂ only has anion spectrum show that all species of [HDMF]Cl-0.2FeCl₃ are anion.

![Fig. 1 Synthesis of [HDMF]Cl/XMCln.](image)
3.3 Hydrogen spectrum of [HDMF]Cl/ZnCl$_2$

The hydrogen spectrum of [HDMF]Cl-0.2FeCl$_3$ cannot be detected due to the magnetic properties of iron. The hydrogen spectrum of [HDMF]Cl/ZnCl$_2$ was recorded and the results are displayed in Fig. 4. This is because the zinc chloride and [HDMF]Cl formed a hydrogen bond. The formation of hydrogen bond leads to the disappearance and the shift of hydrogen bonds in [HDMF]Cl. The $\delta = 2.90$ and 8.02 are attributed to the hydrogen bonds of $-\text{CH}_3$ and $-\text{CH}=\text{O}$, respectively. The $\delta = 4.05$ is the hydrogen bond formed between N and HCl. As seen from Fig. 4, these peaks of hydrogen bonds broaden and are shifted. The new peak is attributed to the hydrogen bond between Cl in ZnCl$_2$ and H in [HDMF]Cl. These results are also seen in another ref. 36.

3.4 Different desulfurization system

In order to investigate the influence of H$_2$O$_2$, [HDMF], [HDMF]Cl, [HDMF]Cl/ZnCl$_2$ and [HDMF]Cl-0.2FeCl$_3$ on desulfurization activity, different desulfurization systems were selected as shown in Table 1. The removal rate of DBT in model oil increased with an increase in H$_2$O$_2$ and DES. [HDMF] is a good extractant for sulfide in oil. The desulfurization rate could reach up to 75% when the volume ratio of [HDMF] and model oil was 1 : 1. The high dose of [HDMF] is harmful for the environment. Hence, [HDMF]Cl/MCl$_n$ was synthesized and applied to desulfurization, and the volume ratio of [HDMF] and model oil was decreased to 0.2. As shown in Table 1, desulfurization systems of [HDMF]Cl-ZnCl$_2$ + H$_2$O$_2$ and [HDMF]Cl-0.2FeCl$_3$ + H$_2$O$_2$ showed excellent desulfurization activities. Lewis acids can accelerate H$_2$O$_2$ degradation to hydroxyl radicals$^{35}$ in the system of oxidative desulfurization and result in high desulfurization activity. However, very high molar ratio of [HDMF]Cl to MCl$_n$ decreased the desulfurization rate. The strong acidity accelerate decomposition of H$_2$O$_2$ (ref. 37) result in decrease of oxidant ability in the desulfurization system. Therefore, [HDMF]Cl-0.2FeCl$_3$ and [HDMF]Cl-1.0ZnCl$_2$ are the most suitable ones for the desulfurization system. The desulfurization rates of [HDMF]Cl-0.2FeCl$_3$ and [HDMF]Cl-1.0ZnCl$_2$ are 20.36% and 15.3%, respectively, without the addition of H$_2$O$_2$. However, the rates are only 9.2% and 9.6% in the system of [HDMF]Cl and [HDMF]Cl + H$_2$O$_2$, respectively. These experimental results demonstrate that H$_2$O$_2$ and Lewis acids are indispensable for the desulfurization system.

We investigated the influence of temperature, O/S, volume ratio of DES and model oil on desulfurization activity. The optimal desulfurization conditions are listed in Table 2. High temperature, O/S molar ratio and volume ratio of DES and the model oil can accelerate the reaction rate and improve the desulfurization activity. However, very high temperature leads to the decomposition of H$_2$O$_2$ into H$_2$O and O$_2$.$^{38}$ A very high O/S molar ratio results in the high production of H$_2$O.$^{39}$ Too high
volume ratio of DES and model oil results in more sulfide being extracted into the DES phase, resulting in the decrease of O/S molar ratio. This reduces the desulfurization activity of the system. Thus, the optimal conditions of desulfurization are listed in Table 2.

### 3.5 Influence of different sulfur compounds on the desulfurization system

To investigate the influence of [HDMF]Cl-0.2FeCl₃ + H₂O₂ and [HDMF]Cl/ZnCl₂ + H₂O₂ on the different sulfur compounds, four sulfur compounds, namely, as DBT, 4,6-DMDBT, BT and TH were selected and the reactions were carried out under optimal conditions. From the ref. 40, it was known that the order of electron cloud density is 4,6-DMDBT (5.760) > DBT (5.758) > BT (5.739) > TH (5.696). As shown in Table 3, the order of oxidative desulfurization is DBT > 4,6-DMDBT > BT > TH in the systems of [HDMF]Cl-0.2FeCl₃ + H₂O₂ and [HDMF]Cl/ZnCl₂ + H₂O₂. It can be concluded that the bigger electron cloud density can easily remove sulfur. The electron cloud densities of DBT and 4,6-DMDBT were 5.758 and 5.760, respectively. The desulfurization rate of DBT was higher than that of 4,6-DMDBT. This could be attributed to the steric hindrance of two methyls of 4,6-DMDBT, which inturn hinders the desulfurization reaction.

### 3.6 Recovery-regeneration of ILs

The upper oil phase was removed using a separating funnel after the oxidative desulfurization reaction. The water in the DES was removed by rotary evaporation. The DES was extracted three times using carbon tetrachloride (CCl₄) of equal volume. The recycling experiments were carried out by adding fresh H₂O₂, model oil, and the recovered DES at the optimal conditions. As shown in Table 4, the desulfurization activity of [HDMF]Cl-0.2FeCl₃ decreased from 98.08% to 96.01%, and the desulfurization rate of [HDMF]Cl/ZnCl₂ decreased from 99.2% to 97.6% after seven cycles. This can be attributed to a little loss of DES and the residual oxidation products of DBT in the DES during the recovery process.

### 3.7 FT-IR characterization of oxidation products

According to the above experiment, DES was extracted by CCl₄. Then, CCl₄ was removed by rotary evaporation. Thereafter, a white powder was obtained. The infrared analysis of the white powder is shown in Fig. 5. The three infrared absorption peaks at 1166, 1047 and 1288 cm⁻¹ correspond to the three characterization peaks of dibenzothiophene sulfone (DBTO₂). It can be concluded that the oxidation product was DBTO₂ in the oxidative desulfurization system. DES was analyzed by FT-IR.

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### Table 1 Influence of different Lewis acid ILs on removal rate (5 mL model oil; 6 of O/S molar ratio; 1 mL of DESs; 40 °C; 20 min)

| ILs                          | Sulfur removal/% | Sulfur removal/% |
|------------------------------|------------------|------------------|
| [HDMF]Cl-0.1FeCl₃ + H₂O₂     | 83.46            | [HDMF]Cl-0.5ZnCl₂ + H₂O₂ | 63.8 |
| [HDMF]Cl-0.2FeCl₃ + H₂O₂     | 98.08            | [HDMF]Cl-1.0ZnCl₂ + H₂O₂ | 98.6 |
| [HDMF]Cl-0.3FeCl₃ + H₂O₂     | 95.96            | [HDMF]Cl-1.5ZnCl₂ + H₂O₂ | 98   |
| [HDMF]Cl-0.4FeCl₃ + H₂O₂     | 62.12            | [HDMF]Cl-2ZnCl₂ + H₂O₂    | 87   |
| [HDMF]Cl-0.5FeCl₃ + H₂O₂     | 29.18            | [HDMF]Cl 1.0ZnCl₂        | 15.3 |
| [HDMF]Cl-0.2FeCl₃            | 20.36            | [HDMF]Cl 1.0ZnCl₂        | 9.2  |
| [HDMF]Cl                     |                  | [HDMF]Cl + H₂O₂          | 9.6  |

v[HDMF] : v model oil = 1 : 1, extractive desulfurization rate = 75%

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### Table 2 Optimal condition of desulfurization reaction

| Condition | [HDMF]Cl-0.2FeCl₃ | Removal rate of DBT% | [HDMF]Cl/ZnCl₂ | Removal rate of DBT% |
|-----------|-------------------|---------------------|----------------|---------------------|
| T (°C)    | 40                | 98.08               | 60             | 99.21               |
| O/S       | 6                 | 98.12               | 6              | 99.12               |
| Volume ratio of DES/model oil | 0.2       | 98.0               | 0.15–0.2       | 99.08               |
| t (min)   | 30                | 98.10               | 60             | 99.16               |

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### Table 3 Desulfurization rate of different sulfides

| Sulfide      | [HDMF]Cl-0.2FeCl₃ t (min) | [HDMF]Cl/ZnCl₂ t (time) | Removal rate% |
|--------------|---------------------------|-------------------------|---------------|
| DBT          | 30                        | 98.08                   | 60            |
| 4,6 DMDBT    | 30                        | 95.4                    | 120           |
| BT           | 60                        | 42.99                   | 140           |
| HT           | 30                        | 13.91                   | 140           |

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spectroscopy in order to study its stability. From Fig. 6, the FT-IR spectrum of used DES shows peaks at 665, 887, 1390, 1021, 1177, 1654, 1717, 2778, 2995 and 3424 cm$^{-1}$. The new peak at 3424 cm$^{-1}$ is the stretching vibration of OH. This shows that the used DES absorbs a little bit of water in air. Water also can decrease the activity of DES, resulting in the decrease of desulfurization rate.

3.8 Mechanism of catalyzed oxidative desulfurization

DBT in model oil was chosen as a representative of sulfur compounds in the oxidative desulfurization system. DBT in model oil was partially extracted by the DMF of DES. FeCl$_3$ and ZnCl$_2$ can catalyze H$_2$O$_2$ to produce hydroxyl radicals (OH). Hydroxyl radicals as a strong oxidant can oxidize DBT into dibenzothiophene sulfone (DBTO$_2$). DBT continued to be extracted and oxidized in the subsequent cycles until DBT was completely transformed to DBTO$_2$. The mechanism of the catalytic oxidative desulfurization is shown in Fig. 7.

4 Conclusion

In this work, [HDMF]Cl$\cdot$0.2FeCl$_3$ and [HDMF]Cl/ZnCl$_2$ can be achieved up to 98.08% and 99.2%, respectively. Two systems of desulfurization saved lots of N,N-dimethylformamide and improved the desulfurization activities. Moreover, [HDMF]Cl$\cdot$0.2FeCl$_3$ can attain high desulfurization rate within a short time at low temperature.

Conflicts of interest

There are no conflicts to declare.

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