



# Ionic liquid extraction and catalytic oxidative desulfurization of fuels using dialkylpiperidinium tetrachloroferrates catalysts

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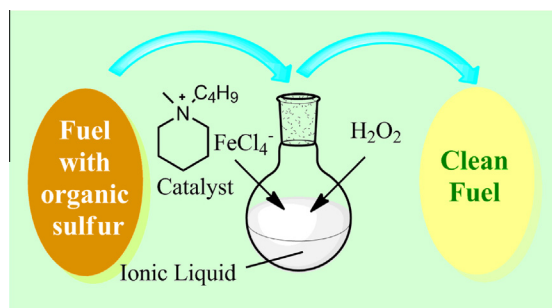
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## HIGHLIGHTS

- A family of dialkylpiperidinium tetrachloroferrate catalysts were synthesized and characterized systematically.
- Compared with the previous work, the utilization of H<sub>2</sub>O<sub>2</sub> was promoted.
- The interaction between DBT and ionic liquid has been identified by UV–Vis spectra.
- The oxidative product was determined by GC–MS analysis.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A new family of dialkylpiperidinium tetrachloroferrate catalysts, such as [C<sub>2</sub>OHmpip]FeCl<sub>4</sub>, [C<sub>4</sub>mpip]FeCl<sub>4</sub>, [C<sub>8</sub>mpip]FeCl<sub>4</sub>, and [C<sub>12</sub>mpip]FeCl<sub>4</sub>, were synthesized and characterized by FT-IR, Raman, and ESI-MS. Their catalytic activities for oxidation of dibenzothiophene (DBT) in extraction and catalytic oxidative desulfurization system (ECODS) were evaluated using different ionic liquids. Results indicated that the 97.1% removal of DBT was obtained with [C<sub>4</sub>mpip]FeCl<sub>4</sub> as catalyst in ionic liquid [C<sub>8</sub>mim]BF<sub>4</sub> at 30 °C in 60 min. The optimal H<sub>2</sub>O<sub>2</sub>/sulfur molar ratio was only 3.5:1, which suggested that the catalyst was one of the most efficient catalysts reported so far. UV–Vis spectra provided an evidence that the lower desulfurization reactivity in PF<sub>6</sub><sup>-</sup>-containing ionic liquids was attributed to the strong interaction between ionic liquid and DBT. Through the gas chromatography–mass spectrometer (GC–MS) analysis, dibenzothiophene sulfone was proved to be the only product of oxidation of DBT. Furthermore, the process of ECODS system was confirmed by GC–MS.

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## 1. Introduction

Air pollution, caused by the emission of SO<sub>x</sub>, is one of the most serious environmental problems in the world, and automobile exhaust is the major source of SO<sub>x</sub> emanated from the combustion of sulfur compounds in gasoline and diesel oil. Current Hydrodesulfurization (HDS) technique must be operated at high

temperature and pressure and consumes large amounts of hydrogen [1–4]. Also some refractory sulfur compounds, such as dibenzothiophene (DBT) and its derivatives, are more difficult to be removed. Thus, complementary desulfurization processes to HDS have been investigated to achieve the lowest level of sulfur (<10 ppm) [5–8]. Oxidative desulfurization (ODS) has stolen the limelight owing to mild operating conditions and no consumption of H<sub>2</sub> [9–17].

Generally, ODS processes usually are achieved through two steps. Firstly, sulfur compounds are selectively oxidized to sulfoxides and sulfones, which would then be removed by

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appropriate extractants or adsorbents [18–22]. Organic solvents are usually utilized as extractants, which would cause further environmental and security problems as these solvents are generally flammable and volatile organic compounds. Instead of the organic solvents, ionic liquids (ILs) viewed as “green solvents” can address this issue in ODS processes [4,23–28].

The interest in ILs has been growing rapidly due to the unique physical and chemical properties such as non-volatility, good thermal stability and recyclability [29–33]. Furthermore, the two steps of ODS can be reduced to one by using ILs extraction and catalytic oxidative desulfurization (ECODS) [34–36]. Recently, our group has reported several tetrachloroferrate ( $\text{FeCl}_4^-$ ) based ILs, such as  $[\text{C}_4\text{mim}]\text{FeCl}_4$  [37],  $[\text{Et}_3\text{NH}]\text{FeCl}_4$  [38],  $[\text{BPy}][\text{FeCl}_4]$  [39] and  $[(\text{C}_8\text{H}_{17})_3\text{CH}_3\text{N}]\text{FeCl}_4$  [40], in ECODS system. In these processes, ILs acted as reaction media and extractants and 30 wt%  $\text{H}_2\text{O}_2$  was oxidant. They all showed good extraction and catalytic activity, however, there were still some drawbacks that should be overcome. For example, the amount of ILs was quite large when the former two ILs were used as extractants ( $m(\text{model oil})/m([\text{C}_4\text{mim}]\text{FeCl}_4) = 3:1$ ,  $V(\text{model oil})/V([\text{Et}_3\text{NH}]\text{FeCl}_4) = 5:2$ ). For the latter two ILs, much more  $\text{H}_2\text{O}_2$  was required ( $n(\text{H}_2\text{O}_2)/n(\text{S}) > 8$ ). We also have been studied an ECODS system with  $[(\text{CH}_3)_4\text{N}]\text{FeCl}_4$  as catalyst in ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_4\text{mim}]\text{BF}_4$ ) [41], but large amount of  $\text{H}_2\text{O}_2$  was still mandatory to achieve deep desulfurization. This implied the insufficient catalytic activity of the previous catalysts. Therefore, more efficient catalysts should be developed from both industrial and green chemistry perspectives. Furthermore, it will be interesting to study the effect of different catalytic systems or various types of catalysts on oxidative desulfurization.

In this work, a new family of dialkylpiperidinium tetrachloroferrate catalysts, such as  $[\text{C}_2\text{OHmpip}]\text{FeCl}_4$ ,  $[\text{C}_4\text{mpip}]\text{FeCl}_4$ ,  $[\text{C}_8\text{mpip}]\text{FeCl}_4$ , and  $[\text{C}_{12}\text{mpip}]\text{FeCl}_4$  (Scheme 1), were synthesized and utilized as catalysts in the ECODS process with  $\text{H}_2\text{O}_2$  as oxidant. It was found that  $[\text{C}_4\text{mpip}]\text{FeCl}_4$  exhibited highest activity in the oxidation of DBT and the sulfur removal could reach 97.1% in 60 min at 30 °C, in which ionic liquid 1-n-octyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_8\text{mim}]\text{BF}_4$ ) was used as extractant. The amount of  $\text{H}_2\text{O}_2$  was only 0.273 mmol ( $\text{H}_2\text{O}_2/\text{sulfur molar} = 3.5$ ), which was much lower than that used in the previous work [40–42]. The difference of the desulfurization activities in various ILs, such as  $[\text{C}_4\text{mim}]\text{BF}_4$ ,  $[\text{C}_8\text{mim}]\text{BF}_4$ , 1-butyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_4\text{mim}]\text{PF}_6$ ) and 1-n-octyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_8\text{mim}]\text{PF}_6$ ), were testified through UV–Vis spectra. Besides, the recycling of catalytic system containing  $[\text{C}_8\text{mim}]\text{BF}_4$  and  $[\text{C}_4\text{mpip}]\text{FeCl}_4$  was also investigated. ECODS process was researched and validated by GC–MS.

## 2. Experimental

### 2.1. Materials

1-Methylpiperidine was commercially available from Aladdin Chemical Co., Ltd. Benzothiophene (BT), dibenzothiophene

(DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) were purchased from Sigma–Aldrich. The ILs 1-butyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_4\text{mim}]\text{BF}_4$ ), 1-n-octyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_8\text{mim}]\text{BF}_4$ ), 1-butyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_4\text{mim}]\text{PF}_6$ ) and 1-n-octyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_8\text{mim}]\text{PF}_6$ ) were purchased from Shanghai Chengjie Chemical Co., Ltd. Other materials were commercial reagent grade and were obtained from Shanghai Sinopharm Chemical Co., Ltd.

### 2.2. Preparation of the dialkylpiperidinium tetrachloroferrate catalysts ( $[\text{Rmpip}]\text{FeCl}_4$ )

The preparation of dialkylpiperidinium tetrachloroferrate catalysts are illustrated in Scheme 2. Firstly, an acetonitrile solution of 1-Methylpiperidine (mpip, 0.1 mol) and chloralkane (RCl, 0.1 mol) was stirred at 60 °C for 48 h. The solvent was removed under reduced pressure and remaining solid was washed with acetone and diethyl ether to give a white powder dialkylpiperidinium chloride ( $[\text{Rmpip}]\text{Cl}$ ) ( $[\text{C}_8\text{mpip}]\text{Cl}$ , a yellow powder). Secondly,  $[\text{Rmpip}]\text{FeCl}_4$  was synthesized by stirring  $[\text{Rmpip}]\text{Cl}$  with an equimolar amount of ferric chloride in ethyl alcohol at room temperature for 4 h. The solvents were removed under reduced pressure and the residue dried in vacuo at 80 °C for 24 h.

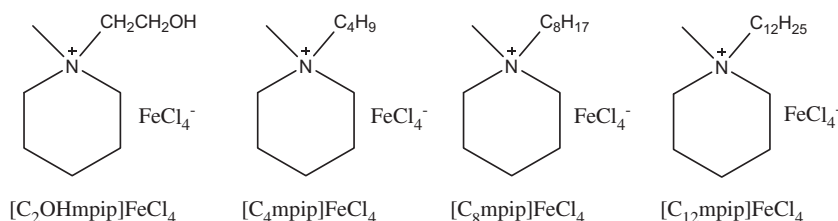
The FT-IR spectra of all the catalysts (KBr pellets) were recorded with a Nicolet Nexus 470 FT-IR instrument. Ultraviolet–visible (UV–Vis) spectra were performed on UV-2450 spectrophotometer (Shimadzu Corporation, Japan). Electrospray ionization mass (ESI–MS) spectra were collected on a LXQ Linear Ion Trap Mass Spectrometer. Raman tests were carried out by using Thermo Scientific DXR Smart Raman spectrometer equipped with a 532 nm excitation. NMR spectra were recorded on Bruker AV-400 spectrometer (Germany) using dimethyl sulfoxide (DMSO) and  $(\text{CH}_3)_4\text{Si}$  as the solvent and the reference, respectively.

Data for  $[\text{C}_2\text{OHmpip}]\text{Cl}$ :  $^1\text{H}$  NMR (400 MHz, DMSO),  $\delta$ : 5.78 (t,  $^3J_{\text{HH}} = 5.32$  Hz, 1H), 3.81 (m, 2H), 3.48 (m, 6H), 3.14 (s, 3H), 1.78 (m, 4H), 1.53 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz, DMSO),  $\delta$ : 19.86, 21.03, 48.81, 54.88, 61.17, 63.92. ESI–MS:  $[\text{C}_2\text{OHmpip}]^+$  144.2.

Data for  $[\text{C}_4\text{mpip}]\text{Cl}$ :  $^1\text{H}$  NMR (400 MHz, DMSO),  $\delta$ : 3.37 (m, 6H), 3.04 (s, 3H), 1.76 (m, 4H), 1.63 (m, 2H), 1.52 (m, 2H), 1.30 (m, 2H), 0.93 (t,  $^3J_{\text{HH}} = 7.40$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO),  $\delta$ : 14.01, 19.75, 19.79, 21.15, 24.46, 47.37, 60.21, 62.45. ESI–MS:  $[\text{C}_4\text{mpip}]^+$  156.2.

Data for  $[\text{C}_8\text{mpip}]\text{Cl}$ :  $^1\text{H}$  NMR (400 MHz, DMSO),  $\delta$ : 3.42 (m, 6H), 3.07 (s, 3H), 1.74 (m, 4H), 1.63 (m, 2H), 1.52 (m, 2H), 1.24 (m, 2H), 0.83 (t,  $^3J_{\text{HH}} = 7.04$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO),  $\delta$ : 14.33, 19.83, 21.07, 21.51, 22.50, 26.40, 29.00, 31.64, 47.21, 59.99, 62.53. ESI–MS:  $[\text{C}_8\text{mpip}]^+$  212.4.

Data for  $[\text{C}_{12}\text{mpip}]\text{Cl}$ :  $^1\text{H}$  NMR (400 MHz, DMSO),  $\delta$ : 3.2 (m, 6H), 3.01 (s, 3H), 1.77 (m, 4H), 1.64 (m, 2H), 1.53 (m, 2H), 1.25 (m, 18H), 0.86 (t,  $^3J_{\text{HH}} = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO),  $\delta$ : 14.40, 19.77, 21.18, 21.43, 22.55, 26.37, 29.01, 29.17, 29.30, 29.40, 31.75, 47.40, 60.30, 62.81. ESI–MS:  $[\text{C}_{12}\text{mpip}]^+$  268.4.



Scheme 1. Structure of the dialkylpiperidinium tetrachloroferrate catalysts.

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