



Deep catalytic oxidative desulfurization of fuels by novel Lewis acidic ionic liquids



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ABSTRACT

In this work, novel Lewis acidic ionic liquids [ODBU]Cl/*n*ZnCl₂ (*n* = 1, 2, 3, 4 and 5) with alkylated 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) cation and ZnCl₂-based complex anion have been developed and utilized in extraction combined with oxidative desulfurization (ECODS) of both model oil and diesel fuel with hydrogen peroxide (H₂O₂, 30 wt%) as an oxidant. It was observed that the ECODS performance could be effectively optimized by the change of ZnCl₂ proportion. Some important reaction parameters such as reaction temperature, molar ratio of O/S, mass ratio of IL/oil and sulfide species were systematically investigated. Furthermore, the ILs could be reused for at least six cycles without noticeable changes in desulfurization performance as well as its chemical structure, thus revealing its good reusability. Finally, [ODBU]Cl/3ZnCl₂ was employed in the ECODS of a hydrogenated diesel, the S-content could be reduced from 559.7 ppm to 4.8 ppm with 99.2% sulfur removal via a one-step process under mild conditions.

1. Introduction

Nowadays, SO_x produced by combustion of sulfur-contained fuels in transportation and industry is the main cause of air pollution. As a response, worldwide environmental regulations towards transportation fuels have been increasingly strict, and many countries adopted standards to cut the S-content down to 10 ppm, which put forth a critical challenge to the refinery industry [1]. At present, the traditional hydrodesulfurization (HDS) is widely used for the deep desulfurization of fuels in petroleum processing industry. HDS is efficient for the removal of thiols, disulfides and thiols but less effective for that of heterocyclic S-compounds, such as benzothiophene (BT), dibenzothiophene (DBT) and their derivatives. Meanwhile, the energy consumption of HDS (350–400 °C, 30–100 bar hydrogen pressure) is ultra-high [2–4].

So far, alternative desulfurization methods have been widely investigated, and the corresponding technologies such as extractive desulfurization (EDS) [5–8], oxidative desulfurization (ODS) [9–15] and adsorptive desulfurization (ADS) [16–21] are developed to approach deep desulfurization. Among these studies, ODS is regarded as one of the most promising processes due to its high desulfurization efficiency for refractory sulfides under mild conditions. In a typical ODS process, aromatic sulfides can be firstly oxidized to their corresponding sulfones, and then removed by the extraction [22,23]. H₂O₂ is the commonly

employed oxidant due to its high reactivity, environmental compatibility and low price [24,25]. However, volatile and flammable organic solvents are usually utilized as the extractant, which may cause further environmental and security problems.

Ionic liquids (ILs), a class of new emerging green solvents, own exclusive properties, such as low melting point, negligible vapor pressure, excellent thermal stability and especially adjustable structure by changing components of cations and anions [26,27]. In recent research, some studies have reported that the extractive combined with catalytic oxidative desulfurization (ECODS) strategy, which could achieve ultra-deep desulfurization of model fuels with ILs as both the catalysts and extractants [28–32]. Various polyoxometalate-based ILs [11,13,28,29,33], Brønsted acidic ILs [34–36] and Lewis acidic ILs [27,37–41] have been explored, and led to good results. For instance, Li et al. prepared Lewis acidic IL C₅H₉NO·0.3FeCl₃ by reacting N-methylpyrrolidone with anhydrous FeCl₃ and employed it in ODS. (2015) [42]. Mokhtarani et al. (2016) synthesized Brønsted acidic ILs 1-octyl-3-methylimidazolium hydrogen sulfate ([Omim][HSO₄]) for oxidative desulfurization [30]. Jiang and co-workers (2017) proposed a polyoxometalate-based ionic liquid (POM-IL) [N-(3-sulfonatepropyl)-pyridinium]₃PMo₁₂O₄₀ for ODS process in the solvent-free system [28].

In addition, in order to evaluate the ILs performances for practical industrial application, many researchers have applied the ECODS

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process to real fuel. Gao et al. (2007) reported that the Brønsted ionic liquids [Hmim]BF₄ could perform well in ODS of a commercial diesel. The S-content of the real diesel could be reduced from 1000 to 270 ppm (reducing 73.0%) under the condition of T = 90 °C, ILs/oil = 1.6/1 and H₂O₂/S = 40/1 [43]. Gao et al. (2010) also utilized [Bmim][HSO₄] to the desulfurization of a diesel with initial S-content of 97 ppm. The sulfur removal was obtained as 85.8% in 2 h at room temperature with ILs/oil = 1/1 and H₂O₂/S = 5/1 [44]. Zhang and co-workers (2014) used Lewis acid IL [C₆mim]Cl/2FeCl₃ for the desulfurization with a gasoline. The S-content of the gasoline reduced from 440.3 ppmw to 62.4 ppmw under the conditions of ILs/oil = 1/1 at 25 °C [12]. Yu et al. (2015) synthesized 1-methyl-2-pyrrolidonium zinc chloride ([Hnmp]Cl/ZnCl₂), a kind of Brønsted-Lewis acidic ILs, which was utilized in oxidative desulfurization of a FCC diesel fuel with the S-content of 224.6 ppm. The sulfur removal could reach 83.3% after a five-stage process at 75 °C [38]. A kind of Brønsted acid IL, caprolactamium trifluoroacetate, was synthesized by Sun et al. (2016) and used in ODS of a hydrogenated diesel with 659.7 ppm. The sulfur removal was 98.7% after two-stage ECODS process under the conditions of T = 40 °C, ILs/oil = 1/1, H₂O₂/S = 6/1 [45].

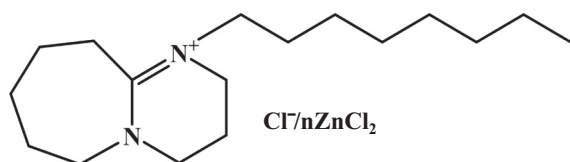
However, among the above studies, some shortcomings still exist and restrict the application of functionalized ILs in a large scale. Some expensive raw materials were used, which significantly increased the cost of the process. Some ILs did not possess good desulfurization performances, thus resulting in large usage of oxidant and multi-step ODS procedure. Poor stability of some protic or Brønsted acid ILs further led to the poor reusability [46]. Therefore, the development of stable, low-cost and high-efficient ILs to overcome such shortcomings is of great importance for further industrial application.

In this work, novel Lewis acidic ionic liquids [ODBU]Cl/nZnCl₂ (n = 1, 2, 3, 4 and 5) (Scheme 1) with alkylated 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) cation and ZnCl₂-based complex anion were developed via a simple two-step synthesis. The structures were confirmed by using various characterization techniques, including ¹H nuclear magnetic resonance (¹H NMR), fourier transform infrared spectroscopy (FT-IR) and mass spectrometry (MS). Then, the ILs were employed as catalysts in ODS of model oil with H₂O₂ as the oxidant, and the optimum composition of ILs was determined. Some important reaction parameters such as reaction temperature, molar ratio of O/S, mass ratio of IL/oil, sulfide species were systematically investigated. The stability as well as recyclability of the ILs were evaluated by repeating experiment as well as characterizations. Finally, a hydrogenated diesel was employed to actually investigate its sulfur removal performance.

2. Experimental

2.1. Chemicals and materials

Dibenzothiophene (DBT, 98%), benzothiophene (BT, 98%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, 98%), hydrogen peroxide (30 wt%) and zinc chloride (98%) were purchased from Aladdin Reagent Co., Ltd. n-Octane (99%), ethyl acetate (99%) and 1-chlorooctane (99%) were purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Heowns Biochemical Technology Co., Ltd. Hydrogenated diesel was provided by SINOPEC Tianjin. Petrochemical Co., Ltd.



Scheme 1. The structure of [ODBU]Cl/nZnCl₂.

2.2. Synthesis of ILs systems

The ILs [ODBU]Cl/nZnCl₂ (n = 1, 2, 3, 4 and 5) were prepared via a two-step approach, which is shown in Scheme 2. Firstly, 0.1 mol DBU and 1-chlorooctane (1.05 equiv.) were charged into a 100 mL hydrothermal kettle, and reacted at 50 °C for 24 h, based on the published similar reactions [47]. The solid product was washed with ethyl acetate to remove any unreacted starting materials and dried under vacuum at 120 °C for 24 h. Then, [ODBU]Cl and ZnCl₂ with different proportions were mixed in a flask and heated at 100 °C for 10 h in N₂ atmosphere. The final ILs products [ODBU]Cl/nZnCl₂ (n = 1, 2, 3, 4 and 5) were obtained and dried under vacuum for 12 h.

2.3. Desulfurization of the model oils and real diesel

Model oils were prepared by dissolving different S-compounds such as BT, 4,6-DMDBT and DBT in n-octane with a corresponding sulfur content of 500 and 1000 ppm, respectively.

The ECODS experiments of both the model oils and the real diesel (with the initial S-content of 559.7 ppm) were similar and repeated triplicate. The ODS reaction was performed in a 100 mL jacketed reactor with a magnetic stirrer and a reflux tube. The procedure was executed as follows: certain amount of ILs, model oil or real diesel and hydrogen peroxide aqueous solution were charged into the reactor and stirred vigorously. Each reaction or cycle lasted for 2 h totally. Samples were taken from the upper layer oil phase and analyzed the concentration of S-compounds by GC-FID (Agilent 7890A; HP-5, FID: Agilent) for model oil. Besides, speciation of S-compounds for real diesel was identified by GC-FPD (GC-7820, Lunan Analytical Instrument CO.,LTD; HP-5), and the total S-content was analyzed with an elemental analyzer (Analytical jena, multi EA 5000).

In addition, the sulfur removal was calculated as follows:

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

where C₀ (ppm) is the initial sulfur concentration at the beginning and C_t (ppm) is the sulfur concentration at certain time.

2.4. Characterization

The structures of the ILs were identified by ¹H NMR spectra (Fig. 1) recorded on a VARIAN INOVA 500 MHz spectrometer at room temperature, and their initial purities were also determined by the ¹H NMR spectra and summarized in Table S2.

[ODBU]Cl/ZnCl₂ (500 MHz, DMSO, ppm): δ 3.66–3.56 (m, 2H), 3.52–3.38 (m, 6H), 2.85 (d, J = 10.3 Hz, 2H), 2.05–1.85 (m, 2H), 1.77–1.45 (m, 6H), 1.26 (d, J = 5.7 Hz, 12H), 0.86 (t, J = 6.9 Hz, 3H).

[ODBU]Cl/3ZnCl₂ (500 MHz, DMSO, ppm): δ 3.58 (t, J = 13.9 Hz, 2H), 3.50–3.35 (m, 6H), 2.84 (t, J = 15.4 Hz, 2H), 2.02–1.81 (m, 2H), 1.74–1.42 (m, 6H), 1.25 (s, 12H), 0.84 (t, J = 6.5 Hz, 3H).

[ODBU]Cl/5ZnCl₂ (500 MHz, DMSO, ppm): δ 3.60 (dd, J = 16.0, 11.7 Hz, 2H), 3.55–3.37 (m, 6H), 2.84 (d, J = 10.3 Hz, 2H), 2.02–1.82 (m, 2H), 1.77–1.45 (m, 6H), 1.26 (d, J = 5.6 Hz, 12H), 0.86 (t, J = 6.9 Hz, 3H).

FT-IR spectra of the ILs were recorded on a Bio-Rad FTS 6000 FT-IR spectrometer using a KBr pellet technique. As is shown in Fig. 2, the three ILs have the similar structures. The IR peaks are observed at 2929 and 2856 (C–H str), 1621 (C=N bend), 1527 (C=N str), 1467 and 1447 (C–H bend), 1196 (C–C str) and 1045 (C–N str).

The nature of ZnCl₂-based complex anion in [ODBU]Cl/nZnCl₂ (n = 1, 3 and 5) was also determined by mass spectrometry. As shown in Fig. 3 and Fig. S1, the peaks are observed at m/z 170.83 and 305.96, which are corresponding to the [ZnCl₃][−] anion and [Zn₂Cl₅][−] anion. The results can be confirmed by published papers and our previous works [48,49]. Moreover, except for the two anions mentioned above, there was no signal of other anions detected, such as oxygen-containing anionic species, which clearly evidenced that the novel ILs were stable

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