



Using functional acidic ionic liquids as both extractant and catalyst in oxidative desulfurization of diesel fuel: An investigation of real feedstock



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HIGHLIGHTS

- Five functional Brønsted or Brønsted–Lewis acidic ILs are prepared.
- Such acidic ILs act as both extractive and catalytic solvents in desulfurization.
- S-content in diesel fuel is reduced to <10 ppm through coupled EDS–ODS.
- Desulfurization condition is mild with very low loss of desulfurization efficiency.
- Nature of S-compounds in diesel fuel is determined by GC–SCD.

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ABSTRACT

Desulfurization of diesel fuel with ionic liquids (ILs), as alternative to traditional hydrodesulfurization (HDS), has been studied intensively for the latest years. Most works, however, were focused on the investigation of model diesel fuel. In this work, two acidic ILs ($[(\text{CH}_2)_4\text{SO}_3\text{HMIm}][\text{Tos}]$ and $[(\text{CH}_2)_4\text{SO}_3\text{HMIm}][\text{ZnCl}_3]$) were synthesized and studied their desulfurization performance for real diesel fuel in a coupled oxidative–extractive way, where 30 wt% H_2O_2 acted as oxidant and ILs served as both extractants and catalysts with adding no acidic catalysts that were usually used in traditional oxidative desulfurization. The influences, on desulfurization, of temperature, time, mass ratio of ILs/oil, molar ratio of O/S, multiple desulfurization and ILs recycle were investigated. It was observed that sulfur content (S-content) in the real diesel fuel was reduced to <10 ppm from original 225 ppm in a coupled oxidative–extractive way ($[(\text{CH}_2)_4\text{SO}_3\text{HMIm}][\text{Tos}]$; mass ratio of ILs/oil 1/2; 3 h, 348.15 K and molar ratio of O/S 40/1 in oxidative step; 30 min and 333.15 K in extractive step). These results are more competitive than other previous results. After 5 cycles of oxidative desulfurization with used ILs, the loss of efficiency is less than 1% at a mild temperature. Distribution of S-compounds in diesel fuel before and after desulfurization were determined by gas chromatograph with sulfur chemiluminescence detector. This work shows that such acidic ILs are capable of removing S-compounds effectively from real diesel fuel with a coupled oxidative–extractive operation.

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1. Introduction

S-compounds are converted into SO_x that causes acid rain and air pollution when diesel fuel is combusted in automobile engine, also reduces combustion efficiency of diesel fuel and increases emission of other particulates [1–3]. Therefore, many countries

set stringent legislation to limit S-content in diesel fuel [4–7], i.e. S-content <10 ppm in European Unions, <15 ppm in USA, while for Japan and some countries in continental Europe taxes on fuel exceed the statutory limit [4,5]. Ultra-low or zero S-content in diesel fuel is desired.

HDS is the most widely used technology for desulfurization of diesel fuel [8,9]. In this process, S-compounds are removed through reacting with hydrogen to be converted into H_2S and other hydrocarbons. However, a large amount of hydrogen consumption,

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expensive catalysts, high temperature (>300 °C), and high pressure (3–10 MPa) are generally needed in HDS [3–6]; what's more, HDS is less effective for removing some heterocyclic S-compounds such as thiophene (TS), dibenzothiophene (DBT) and their derivatives because of the steric hindrance on catalyst.

Desulfurization of diesel fuel with ILs has been being studied intensively in extractive or oxidative way for years [10–14], especially the latter where S-compounds can be removed more effectively. In a typical oxidative desulfurization (ODS), ILs were used as extractants with H₂O₂ solution as oxidant and some acids such as acetic acid [15,16], V₂O₅ [17], decatungstates [18] as catalysts. Regeneration and contamination of such acidic catalysts have become problems of such catalysis process.

In our previous work, we synthesized a series of acidic ILs such as x[C₄mim]Cl/yMCl₂ (M = Zn, Fe, Cu, Mg, Sn, Co; x:y = 1:3, 1:2, 1:1, 2:1, 3:1), [(CH₂)₄SO₃Hmim][HSO₄], [Hmim][HSO₄], [Bmim][HSO₄] and [SO₃H-C₄mim]HSO₄ [19,20]. We investigated their oxidative desulfurization with H₂O₂ solution as oxidant, where such acidic ILs acted as both extractants and catalysts. It was interestingly observed that these acidic ILs can effectively remove S-compounds in diesel fuel, e.g., in the H₂O₂/[C₄mim]Cl/2ZnCl₂ system, 100% S-removal efficiency was obtained (90 °C; mass ratio of IL/oil, 1:2; molar ratio of O/S, 8:1; 1 h) [20]. Some other ILs such as [Hnmp]BF₄ [21], [Hmim]BF₄ [22], [(CH₂)₂COOHmim][HSO₄] [23] and [Hnmp]H₂PO₄ [24] were also reported. Most studies were focused on model diesel fuel while only a few researchers tested the real diesel fuel (Table 1). A more systematic investigation for real diesel fuel is desired.

In this work, we synthesized five functional acidic ILs, i.e., Brønsted acidic [(CH₂)₄SO₃Hmim][HSO₄], [(CH₂)₄SO₃Hmim][H₂PO₄] and [(CH₂)₄SO₃Hmim][Tos], Brønsted–Lewis acidic [(CH₂)₄SO₃Hmim][ZnCl₃] and [(CH₂)₄SO₃Hmim][FeCl₄], their structures are shown in Fig. 1. We studied their coupled oxidative–extractive desulfurization of real diesel fuel. The influences, on desulfurization, of temperature, time, mass ratio of ILs/oil, molar ratio of O/S, multiple desulfurization and ILs recycle were investigated for selected [(CH₂)₄SO₃Hmim][Tos] and [(CH₂)₄SO₃Hmim][ZnCl₃]. Distribution of S-compounds in diesel fuel before and after desulfurization were determined by GC-SCD. This work will show that such acidic ILs are capable of removing S-compounds effectively from real diesel fuel. To the best of our knowledge, it is the first time to reduce S-content in real diesel fuel to less than 10 ppm with ILs.

2. Experimental section

2.1. Chemicals

The chemicals and suppliers are as follows, N-methylimidazole (>99.0%), Shanghai SenHao Fine Chemical; 1,4-butane sultone (≥98%), J&K Chemical; zinc chloride, iron chloride, 30 wt% H₂O₂ aqueous solution, hydrochloric acid, phosphorous acid, concentrated sulphuric acid, toluene and anhydrous ether, Beijing Chemical Works. Coker diesel fuel (S, 224.6 ppm) was supplied by SINOPEC Beijing Yanshan Petrochemical Co., Ltd.

Table 1
Oxidative desulfurization of real oils by ILs.

ILs	Real oil (initial S-content)	S-removal efficiency (%)	Reaction condition	Refs.
[C ₃ mpy]FeCl ₄	Gasoline (468 ppm)	44.2	T, 298 K; t, 30 min; mass ratio of IL/Oil, 1/3; O/S, 6	[5]
[C ₄ mim]Cl/3ZnCl ₂	FCC diesel fuel (460 ppm)	63.5	T, 318.15 K; t, 3 h; mass ratio of IL/Oil, 1/2; O/S, 60	[19]
[Hnmp][H ₂ PO ₄]	Diesel fuel (750 ppm)	64.3	T, 333.15 K; t, 5 h; volume ratio of IL/Oil, 1/1; O/S, 16.	[24]
[BMIM][HSO ₄]	Diesel fuel (97 ppm)	85.8	RT; t, 2 h; volume ratio of IL/Oil, 1/1; O/S, 5	[29]
[(CH ₂) ₄ SO ₃ Hmim][ZnCl ₃]	Diesel fuel (225 ppm)	40.7	T, 333 K; t, 3 h; mass ratio of IL/Oil, 1/2; O/S, 30	This work
[(CH ₂) ₄ SO ₃ Hmim][Tos]	Diesel fuel (225 ppm)	43.7	T, 348 K; t, 3 h; mass ratio of IL/Oil, 1/2; O/S, 40	This work

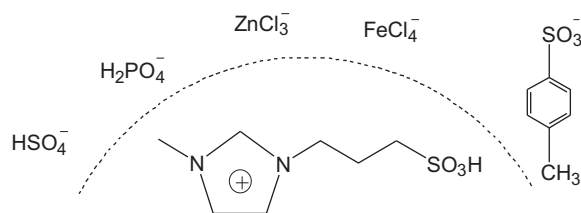


Fig. 1. Structures of the ILs used in this work.

N-methylimidazole was further purified by distillation and the other chemicals were used as received.

2.2. ILs synthesis and characterization

Synthesis of [(CH₂)₄SO₃Hmim][HSO₄], [(CH₂)₄SO₃Hmim][H₂PO₄], [(CH₂)₄SO₃Hmim][Tos], [(CH₂)₄SO₃Hmim][ZnCl₃] and [(CH₂)₄SO₃Hmim][FeCl₄] are based on previous procedures [26–28].

[(CH₂)₄SO₃Hmim][Tos]. 0.1 mol 1,4-butane sultone and 0.1 mol 1-methylimidazole were charged into a 100 ml round-bottom flask and vigorously stirred at 40 °C for 10–12 h under protection of nitrogen. The obtained white solid was washed with toluene and anhydrous ether for three times and dried at 80 °C to get (CH₂)₄SO₃MIm as white powder. (CH₂)₄SO₃MIm was dissolved in 15 ml water and a stoichiometric amount of *p*-toluenesulfonic acid was dropped slowly at room temperature. After dropping, the mixture was stirred at 80 °C for 2 h. The water was removed under vacuum to get [(CH₂)₄SO₃Hmim][Tos] as viscous liquid at room temperature. The synthesis processes of [(CH₂)₄SO₃Hmim][HSO₄] and [(CH₂)₄SO₃Hmim][H₂PO₄] are similar to that of [(CH₂)₄SO₃Hmim][Tos].

[(CH₂)₄SO₃Hmim][ZnCl₃]. After dissolving (CH₂)₄SO₃MIm in 15 ml water, stoichiometric hydrochloric acid was dropped slowly at room temperature; the mixture was stirred at room temperature for 30 min after dropping and further heated in an oil bath at 90 °C for 2 h. The water was removed using rotary evaporation and viscous liquid of [(CH₂)₄SO₃Hmim]Cl was obtained at room temperature. [(CH₂)₄SO₃Hmim]Cl reacted with ZnCl₂ at 80 °C for 2 h to get [(CH₂)₄SO₃Hmim][ZnCl₃] as light yellow viscous liquid. The synthesis of [(CH₂)₄SO₃Hmim][FeCl₄] is similar to that of [(CH₂)₄SO₃Hmim][ZnCl₃].

The structures of [(CH₂)₄SO₃Hmim][Tos] and [(CH₂)₄SO₃Hmim][ZnCl₃] have been identified by ¹H NMR (AV300, Bruker, Germany). The results were shown as follow. [(CH₂)₄SO₃Hmim][ZnCl₃]: ¹H NMR (400 MHz, Acetone-d₆), δ: 8.70 (s, 1H), 7.40 (s, 1H), 7.29 (s, 1H), 4.72 (s, 1H), 4.16 (t, 2H), 3.79 (s, 3H), 2.85 (t, 2H), 1.92 (m, 2H), 1.64 (m, 2H). [(CH₂)₄SO₃Hmim][Tos]: ¹H NMR (400 MHz, Acetone-d₆), δ: 8.50 (s, 1H), 7.53 (s, 1H), 7.24 (s, 1H), 7.18 (s, 1H), 4.75 (s, 1H), 3.99 (t, 2H), 3.67 (s, 3H), 2.76 (t, 2H), 2.20 (s, 1H), 1.80 (m, 2H), 1.56 (m, 2H).

2.3. Desulfurization and analysis

In a typical ODS experiment, IL, H₂O₂, and diesel fuel were added into a 100 ml round-bottom flask and reacted with magnetic

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