



Efficient oxidative desulfurization of diesel fuel using amide-based ionic liquids



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HIGHLIGHTS

- ILs having a protonated amide-cation were investigated in ODS process.
- S-components can be completely converted in a short time.
- The mechanism was studied by experimental and theoretical methods.
- Both hydrogenated diesel and straight-run diesel were used for desulfurization.

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ABSTRACT

A series of Brønsted acidic ionic liquids having a protonated amide- or lactam-based cation were synthesized and investigated as extractants and catalysts in the extraction combined with oxidative desulfurization (ECODS) of both model oil and diesel fuel, with hydrogen peroxide (H₂O₂, 30 wt%) as oxidant. Each of them showed obvious removal of benzothiophene (BT) and dibenzothiophene (DBT) in model oil. Among them, [HCPL][TFA] exhibited the best performance by completely removing BT and DBT in a short time. The detailed structure and conformation of [HCPL][TFA] were investigated by ¹H NMR and FTIR as well as theoretical calculation. HCPL⁺ cation was verified to exist in an enol form, which was supposed to contribute to high desulfurization performance by improving the formation of peroxides. In the end, two kinds of diesel were used to evaluate its desulfurization performance. [HCPL][TFA] can reduce the S-content of real hydrogenated diesel from 659.7 ppm to 8.62 ppm with 98.69% S-removal efficiency after two ECODS processes. Furthermore, the total S-content of straight-run diesel fuel was reduced to 89.36 ppm from 11,034 ppm with a similar S-removal rate. The results of GC-PFPD before and after each ECODS process indicated that almost all the original S-compounds in diesel had been converted to their corresponding oxidation products. The desulfurization performance was actually restricted by extraction capability.

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1. Introduction

In the recent years, worldwide environmental regulations toward transportation fuels have been increasingly strict in order to reduce the air pollution and related public health impacts [1]. S-compounds in diesel fuel are converted into SO_x when combusted and further reduce combustion efficiency and increase emission of particulates [1–3]. Many countries mandated stringent

legislation to cut diesel fuel S-content down to 10 ppm, which put forth a critical challenge to the refinery industry [1]. The traditional hydrodesulfurization (HDS) is a high-pressure, high-temperature catalytic process which can remove various types of sulfur compounds by converting organic sulfur to hydrogen sulfide gas. However, when the deep desulfurization of diesel fuel is needed, HDS is less effective for removing heterocyclic S-compounds such as benzothiophene (BT), dibenzothiophene (DBT) and their derivatives [4]. Due to this reason, many groups have been engaged in the exploitation of non-HDS technologies, such as extraction [5,6], oxidation [7–10] and adsorption [11–14]. Among these non-HDS methods, extraction combined with oxidative desulfurization (ECODS) using ionic liquid is regarded as one of the most promising

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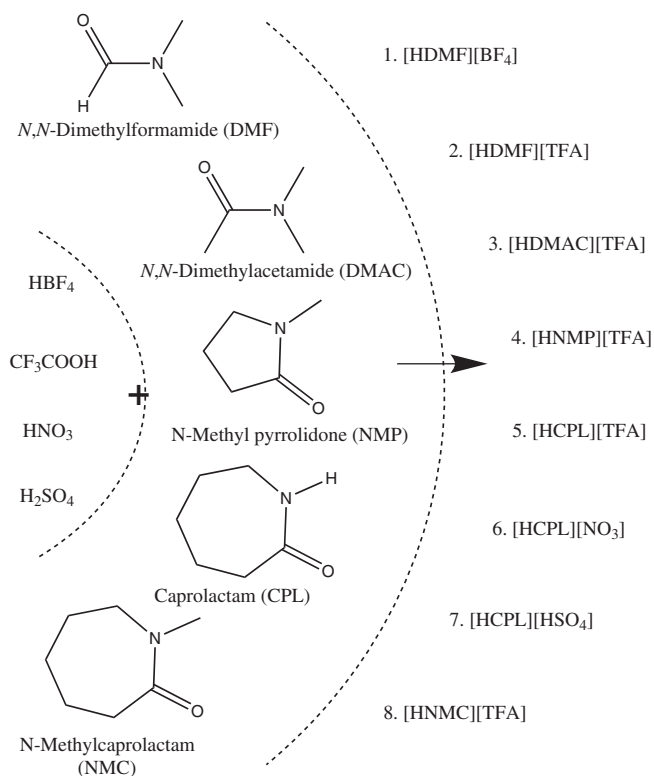


Fig. 1. Ionic liquids synthesized in this study.

methods for the deep desulfurization of diesel fuel [15–17]. Those S-compounds which are difficult to remove in HDS show good oxidation activity in ionic liquids under mild conditions. Moreover, as the oxidation products, sulfones and sulfoxides can be easily extracted by ionic liquids.

Numerous oxidants were suggested for oxidative desulfurization, such as hydrogen peroxide, organic peroxide, and dioxygen [18–20]. Among them, hydrogen peroxide is the most common oxidant, because of its easy preparation and no unwanted by-product except water. Various catalysts including organic acids, polyoxometalates and metal complexes have been explored in the presence of ionic liquids with BF₄⁻ or PF₆⁻ anions and led to good results [21–24]. In the recent years, various acidic ionic liquids were designed to act as both catalysts and solvents in ECODS process, without the need of external catalysts. Brønsted acidic ionic liquids such as [(CH₂)₂COOHmim][HSO₄], [CH₂COOHpy][HSO₄], and [Bmim][HSO₄] have been reported for sulfur removal [25–28]. However, the conversion efficiency of S-compounds in these ionic liquids is not very satisfying, since it often took hours to obtain deep S-removal. Different Lewis acidic ionic liquids with the basic structure of [C_nA]Cl/xMCl_y (where, A refers to the main structure of the cation, such as pyridinium and imidazolium; n is length of alkyl chains; M = Zn, Fe, Cu, Sn, etc.; x is commonly ranging from 1/3 to 3) have been investigated for oxidative desulfurization purposes by many researchers [29–32]. Hydroxyl radicals were formed and participated in the oxidation of S-compounds. As a result, in the Lewis acidic ionic liquid, the oxidation reaction is much more efficient. But Lewis acidic ionic liquids can also catalyze the decomposition of hydrogen peroxide [33], especially at high temperature, which will bring difficulty to operation and process intensification.

In this paper, we propose a class of amide-based ionic liquids to be both solvents and catalysts in the ECODS process. The synthesis and properties of amide-based ionic liquids were reported in some references [34,35]. However, they have not been widely studied

after that, compared with imidazolium- or pyridinium-based ionic liquids. In this work, eight amide-based ionic liquids were synthesized and listed in Fig. 1. The desulfurization performance of these low-cost ionic liquids was first evaluated under the same conditions for the oxidation of BT and DBT in model oil for a preliminary screening. The influence of cation structure and anion types were discussed. Among the ionic liquids, [HCPL][TFA] performed the best by completely converting BT and DBT. Thus, a more detailed assessment of its performance was conducted. Some important factors of desulfurization processes were investigated, such as reaction temperature, the ratio of O/S, the amount of IL and reusability. In order to explain the mechanism, the structure and conformation of [HCPL][TFA] was studied. Amide-based ionic liquids were reported to exist in two forms, namely, the keto form and the enol form [36]. So the structure of [HCPL][TFA] was characterized by means of DFT methods with the Gaussian 09 program package. A supposed mechanism was then put forward to explain the outstanding desulfurization performance of [HCPL][TFA]. Finally, ECODS was applied to both hydrogenated diesel and straight-run diesel, and the evolution of total S-content and speciation of S-compounds after each step were measured.

2. Experimental

2.1. Chemicals and materials

BT (>97%), DBT (>98%) and trifluoroacetic acid (>99%) were purchased from Aladdin Reagent Co. Ltd. N,N-Dimethylformamide (>99%), N,N-dimethylacetamide (>99%), N-methyl-2-pyrrolidinone (>99%), n-octane (>99%), caprolactam (>99%), N-methylcaprolactam (>98%), carbon tetrachloride (>99%), dichloromethane (>99%), tetrafluoroboric acid (40 wt%), sulfuric acid (98 wt%), nitric acid (65 wt%), sodium hydroxide (NaOH), hydrochloric acid (35 wt%) and hydrogen peroxide (≥30 wt%) were purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. All the chemicals were used without further purification. Hydrogenated diesel and straight-run diesel were provided by SINOPEC Tianjin Petrochemical Co., Ltd. The straight-run diesel was pre-treated by alkaline and acid washing successively with NaOH (8.0 wt%) and HCl (5.0 wt%) aqueous solution to remove elemental sulfur.

2.2. ILS synthesis and characterization

The amide-based ionic liquids in this work were prepared according to the literature procedure with little modification [34,37]. In a typical synthesis, 0.2 mol amide and 40 mL CH₂Cl₂ were charged into a 100 mL jacketed reactor and vigorously stirred at 0 °C. A dropping funnel attached to the reactor was charged with equimolar amount of acid. The neutralization reaction was done by slowly dropping the acid under 0–3 °C. The mixture was stirred at 0 °C for 30 min after dropping and further heated at 60 °C for 2 h. The solvent was removed using rotary evaporation and ionic liquid was obtained.

Densities and viscosities of ionic liquids synthesized in this work were listed in Table S1. The structures have been identified by ¹H NMR (VARIAN INOVA 500 MHz). The results were shown as follows:

N,N-dimethylformamidium tetrafluoroborate [HDMF][BF₄]: ¹H NMR (500 MHz, DMSO) δ 8.34 (s, 1H), 7.91 (s, 1H), 2.85 (s, 3H), 2.70 (s, 3H).

N,N-dimethylformamidium trifluoroacetate [HDMF][TFA]: ¹H NMR (500 MHz, DMSO) δ 15.12 (s, 1H), 7.93 (s, 1H), 2.87 (s, 3H), 2.72 (s, 3H).

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