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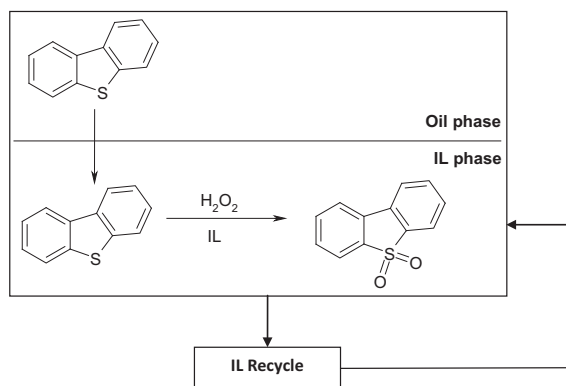
Design rules of ionic liquids tasked for highly efficient fuel desulfurization by mild oxidative extraction

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HIGHLIGHTS

- Ionic liquids comprise low basicity/nucleophilicity anions and hydrophilic cations.
- [Choline][Tf₂N]–V₂O₅ system afforded quantitative removal of sulfur compounds.
- [Choline][Tf₂N] is a low-cost solvent with potential for large-scale desulfurization.

GRAPHICAL ABSTRACT



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ABSTRACT

The deep desulfurization of petroleum-based fuels using oxidative extraction processes has been hampered by the lack of suitable solvent systems and by the poor availability of inexpensive and efficient catalysts. As a strategy to address this limitation, the present study evaluates a number of hydrophilic and hydrophobic ionic liquids (ILs) for the oxidative extraction of dibenzothiophene (DBT) and other aromatic sulfur compounds (e.g., thiophene, TS, benzothiophene, BT, and 4,6-dimethyldibenzothiophene, DMDBT) from *n*-octane using H₂O₂ as the oxidant and V₂O₅ as the catalyst. Our findings are significant for petroleum desulfurization and suggest that ILs for effective sulfur removal will typically comprise low basicity/nucleophilicity anions paired to cations possessing some hydrophilic character. Among a number of suitable ILs identified for this application, [Choline][Tf₂N] is particularly promising as a relatively low-cost solvent ideal for use in oxidative extraction to desulfurize fuel. The [Choline][Tf₂N]–V₂O₅ system afforded essentially quantitative removal of DBT, BT, and DMDBT at room temperature, even for initial sulfur levels as high as 3000 ppm. This advance enables a highly efficient and cost-effective desulfurization process that has a promising industrial application for producing ultra-low-sulfur fuel.

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1. Introduction

Petroleum-based fuel with an ultra-low-sulfur content is becoming necessary in order to minimize SO_x emissions from fuel combustion, as dictated both by stringent U.S. Environmental Protection Agency (EPA) regulations (15 ppm for diesel since 2006 and

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30 ppm for gasoline since 2005), and by EU legislation (10 ppm for both diesel and gasoline since 2010) [1]. However, it remains a challenge to efficiently remove sulfur compounds (especially aromatic ones) to meet these ultra-low-sulfur targets with current technologies built around conventional refining processes. For example, conventional hydrodesulfurization (HDS) processes present several disadvantages including the requirement for high temperatures (300–400 °C) and pressures (20–100 atm of H₂), a reduced octane/cetane number [2], and particular difficulty in removing aromatic sulfur molecules such as thiophene (TS), benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (DMDBT) [3,4]. A number of alternate deep desulfurization methods are being actively explored, such as oxidative desulfurization, bio-desulfurization, reactive adsorption, non-destructive adsorption, N-adsorption, and extractive desulfurization (EDS), and others. However, each of these methods still faces its own particular hurdles [1]. Among these methods, the oxidative extraction method uniquely combines an oxidation reaction with an extraction process, making it quite promising for practical, industrial-scale applications owing to its low energy cost, elimination of hydrogen usage, mild operating conditions, and retention of the chemical structure of the fuel, all without the requirement for specialized equipment. A disturbing drawback of oxidative extraction, however, is the requirement for large quantities of volatile organic solvents as extractants, which in itself imposes important health, environmental, and economic concerns.

The last few years have been witness to an explosion of interest in using ionic liquids (ILs) as non-volatile (and potentially recyclable) alternatives for extraction and oxidative extraction processes toward the desulfurization of liquid fuels. Recent efforts in extractive desulfurization using ILs in general [1,5], as well as oxidative extraction desulfurization with ILs in particular [6], have been reviewed recently. In the latter approach, the extraction of sulfur compounds/products and the chemical/catalytic oxidation of sulfur compounds are integrated into a single, concerted process (see Fig. 1) [1,7]. Major areas of focus of this line of research entail the design of polyoxometalate (POM)-type catalysts, the use of ILs-based extractants, the design of ionic liquid catalysts, and the combination of these approaches [6]. However, most of the approaches up till now have involved expensive catalysts, somewhat costly imidazolium-derived ILs, and reaction temperatures above ambient, typically in the 30–70 °C range or higher. This study addresses these limitations by developing a strategy for the efficient oxidative extraction of aromatic sulfur compounds from fuel that makes use of inexpensive non-imidazolium ILs used in concert with a

cheap V₂O₅ catalyst under very mild reaction conditions, including a room temperature reaction employing H₂O₂ as the oxidant.

2. Experimental method

2.1. Materials

Thiophene (TS) (>98.0%) was purchased from TCI America. Benzothiophene (BT) (97%) was obtained from Acros Organics. Dibenzothiophene (DBT) (98%), 4,6-dimethyldibenzothiophene (DMDBT) (97%), *n*-octane (98+%), and *n*-dodecane (99+%) were sourced from Alfa Aesar. Vanadium(V) oxide (V₂O₅, –22 mesh powder, 99.99% trace metals basis) produced by BeanTown Chemical (Hudson, New Hampshire) was ordered through VWR. The commercial sources or preparation routes for the various ILs were reported earlier [8].

2.2. Oxidative extraction desulfurization of model fuels by ILs

In this study, *n*-octane was used as a model fuel for gasoline, whereas *n*-dodecane was employed as a surrogate for diesel. The typical oxidative extraction procedure we follow is described in this fashion: 1.0 mL of surrogate fuel (*n*-octane or *n*-dodecane) containing 500 ppm sulfur from DBT (ppm is on a weight basis, i. e. 500 µg sulfur per 1 g of liquid fuel) was placed in a pre-cleaned and dried glass vial with a 5 mL capacity, followed by the addition of 1.0 mL of the IL, 40 µL of 30% (v/v) H₂O₂ (aq.), and 1.0 mg of V₂O₅. After closing the screw cap, the biphasic mixture was stirred at room temperature (~22 °C). At periodic intervals of 30 min or 1 h, the reaction mixture was transferred to a microcentrifuge tube and centrifuged for 2 min to achieve complete layer separation. A 50 µL aliquot of each layer was carefully withdrawn and immediately diluted with 450 µL of methanol (i. e., 10-fold dilution). The clear methanol solution (*n*-octane is soluble at this dilution; *n*-dodecane is only partially soluble in methanol, however, the sulfur compounds are extracted into methanol) was injected into an LC-20AT Shimadzu HPLC equipped with a SPD-20A UV–Visible dual-wavelength detector. The injection-loop volume was 20 µL and we used a Phenomenex® Kinetex C18 column (100 mm × 4.6 mm, particle size 2.6 µm). The isocratic eluent consisted of 80/20 (v/v) methanol/water for TS and DBT, 70/30 (v/v) methanol/water for BT, and 85/15 (v/v) methanol/water for DMDBT, all at a flow rate of 1.0 mL min⁻¹. The sulfur compounds were determined by UV–vis detection at 280 nm (DBT, BT, and DMDBT) or 210 nm (TS). The peak areas for the initial sulfur compounds present in the model fuel prior to the reaction were determined in a similar fashion by the same HPLC method. The peak areas at periodic reaction times were compared with the initial peak area to calculate the % removal of the sulfur compounds from the surrogate fuel and the sulfur content remaining within the IL layer.

3. Results and discussion

Initially, we carried out the room-temperature oxidative extraction reaction of DBT using H₂O₂ as the oxidant and V₂O₅ as the catalyst in equal volumes of IL and *n*-octane, the latter initially containing 500 ppm of sulfur (i. e. 500 µg sulfur per 1 g of liquid fuel) from DBT (Fig. 1). The catalyst primarily dispersed (thus offering facile catalyst recovery) or dissolved within the IL phase, thus the oxidation reaction mainly occurs in the IL phase or at the liquid-liquid interface. Periodically (every 30 min or 1 h), both the oil phase (*n*-octane) and the IL phase were withdrawn and analyzed for DBT content using HPLC, as described above.

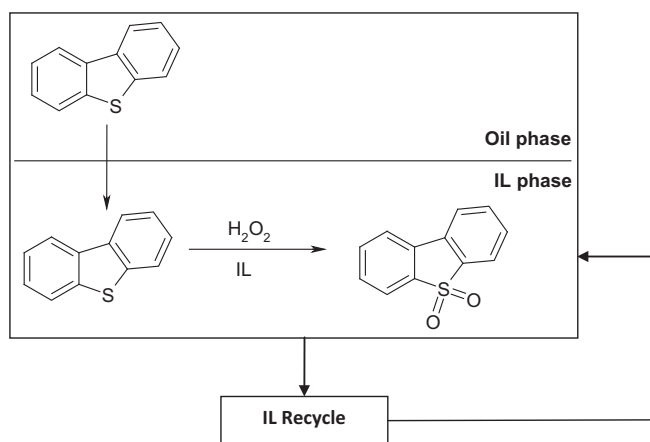


Fig. 1. Scheme depicting the desulfurization of DBT from a liquid fuel (oil) via oxidative extraction which involves an oil/ionic liquid (liquid/liquid) extraction coupled with a catalyzed oxidation process.

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