



Oxidative desulfurization of model diesel via dual activation by a protic ionic liquid



Hongying Lü*, Shunan Wang, Changliang Deng, Wanzhong Ren, Baocun Guo

Green Chemistry Centre, College of Chemistry and Chemical Engineering, Yantai University, Yantai, 264005, China

HIGHLIGHTS

- A protic ionic liquid, [Hnmp]HCOO, was used as in ODS.
- The mechanism of ODS was involved in dual activation by the PIL.
- The [Hnmp]HCOO exhibited high catalytic activity in ODS.
- The amounts of PILs and oxidant dosage play vital roles in desulfurization system.
- This system can be recycled five times with an unnoticeable decrease in activity.

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ABSTRACT

A novel and green carboxylate-anion-based protic ionic liquid (PIL), [Hnmp]HCOO, was prepared through a simple and atom economic neutralization reaction between N-methyl-2-pyrrolidonium (NMP) and formic acids. Both FT-IR spectra and ¹H NMR confirmed its simple salt structure. [Hnmp]HCOO exhibited so high catalytic activity that the dibenzothiophene (DBT) removal reached 99% at 50 °C in 3 h under conditions of $V_{\text{PIL}}/V_{\text{model oil}} = 1:10$ and $\text{H}_2\text{O}_2/\text{DBT}$ (O/S, molar ratio) = 5. The catalytic oxidation reactivity of S-compounds was found to be in the order of DBT > 4,6-dimethyldibenzothiophene (4,6-DMDBT) > benzothiophene (BT). The investigation on mechanism showed that oxidative desulfurization was realized through dual activation of PIL. Moreover, [Hnmp]HCOO can be recycled for five times with an unnoticeable decrease in desulfurization activity.

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1. Introduction

Deep desulfurization of diesel is an urgent research topic. U.S. government issued environmental regulations to limit the sulfur level in diesel to be less than 15 ppm in 2006 [1–4]. Hydrodesulfurization (HDS) is highly efficient in removing thiols, sulfides and disulfides. However, it is extremely difficult and costly to achieve this aim by using the technology because it requires operation of catalytic reactors at high pressure and temperature [5]. Therefore, developing non-HDS technologies for production of clean diesel with extremely low concentration of S-compounds is still a challenge for both academia and industry.

It is evident that the advantages of oxidative desulfurization (ODS) are its mild reaction conditions and no using of expensive hydrogen. Another feature of ODS is that the refractory S-compounds in HDS can be easily converted by oxidation. Therefore, ODS as one of the most promising alternative technologies has attracted much attention in past decades [6,7]. ODS processes are involved in the oxidation of S-compounds to corresponding sulfones and the removal of sulfones from diesel by extraction or adsorption [8,9]. In the first step, organic acid (formic acid, acetic acid etc.) as one of classic catalysts was utilized for the catalysis in ODS [10–13]. However, liquid organic acids have disadvantages such as unrenewable and high

regeneration cost, resulting in the low economical efficiency [14,15]. In the second step, a polar organic solvent, such as acetonitrile, dimethyl sulfoxide (DMSO), and N-methyl-2-pyrrolidonium (NMP), was usually utilized as extraction solvent. These solvents are flammable and volatile organic compounds, which can cause further environmental and security problems [16].

Ionic liquids (IL) are low melting salts with high thermal stability and very low vapor pressure. They also show good extraction ability for aromatic S-compounds, and immiscibility with aliphatic liquids such as fuel oil [17,18]. Therefore, it can effectively avoid environmental and security problems. Recently, combination of catalytic oxidation and ILs extraction (ECODS) has been proven to be a promising desulfurization method due to its significant promotion of desulfurization efficiency [19–22]. In most cases, ILs have an asymmetrically substituted cation (e.g., imidazolium, pyrrolidinium, pyridinium, ammonium, phosphonium) and an anion (especially halogen-based anions, e.g., [Cl⁻], [Br⁻], [I⁻], [BF₄⁻], [AlCl₄⁻], [PF₆⁻]). To avoid the toxicity of halogen anion-containing ILs, biomaterial-derived products such as organic acids or amino acids have been used to create a new and safe type of ILs known as “bio-ILs” or “green ILs” [23–26].

The aim of this work is to develop a novel and green PIL desulfurization system. We report the preparation of a carboxylate-anion-based PIL by neutralization of NMP and formic acid (Scheme 1). It was found that [Hnmp]HCOO exhibited the high activity in the oxidation/extraction of model diesel. The effect of important factors such as temperature, amount of [Hnmp]HCOO and oxidant dosage on desulfurization efficiency and recycling of PIL was studied. The investigation on desulfurization mechanism was also conducted.

* Corresponding author. Tel.: +86 5356902063.
E-mail address: hylv@ytu.edu.cn (H. Lü).

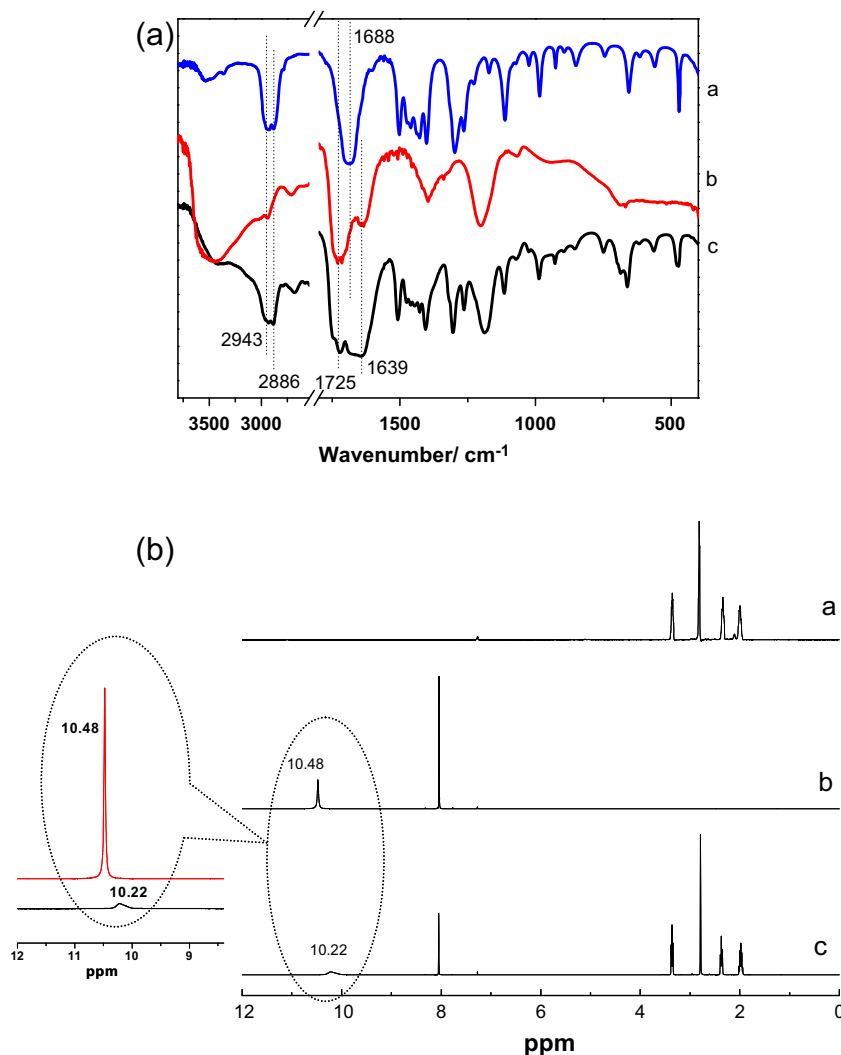
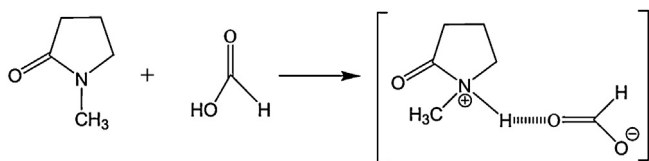


Fig. 1. Spectroscopic characterization of the NMP (a), HCOOH (b), and [Hnmp]HCOO (c). (a) FTIR spectrum; (b) ¹H NMR spectrum.



Scheme 1. Formation of the ionic liquid.

2. Experimental methods

2.1. Synthesis and characterization of PILs

All chemicals were used as received. [Hnmp]HCOO was prepared according to the procedure described elsewhere with minor modification [27,28]. The NMP was neutralized by dropwise addition of equal molar quantity of formic acid at room temperature. After vigorous stirring for 30 min, the mixture was heated to 80 °C and kept at this temperature under stirring for 3 h. Then, the impurities in mixture were evaporated under reduced pressure to obtain the required PIL.

The FT-IR spectra of liquid samples were recorded on a Nicolet 470 FT-IR Spectrometer using KBr pellet technique. ¹H NMR spectra were recorded on a Bruker DRX 400 MHz type spectrometer at room temperature (400 MHz) and internally referenced to tetramethylsilane signal in CDCl₃. Electrochemical measurements

were carried out in a three electrode electrochemical cell with scan rate of 100 mV s⁻¹. A glassy carbon electrode, a platinum wire electrode and an Ag/AgCl were used as working, counter and reference electrodes respectively. The working electrode was polished with 50 nm alumina slurry on the polishing cloth and rinsed copiously with water and ethanol, and then electrochemically activated in 1 M H₂SO₄ solution.

2.2. Oxidation and desulfurization of the model diesel

In a typical run, a water bath was heated to a desired temperature. The sulfur concentration was kept at 500 ppm by dissolving one of the model S-compound (BT, DBT or 4,6-DMDBT) in 500 mL n-octane. The mixture, containing 10 mL model diesel, 1 mL PIL and 0.09 mL of 30 wt% H₂O₂, was stirred vigorously at a certain reaction temperature for 3 h. The ratio of reactants was adjusted according to the different experimental conditions. The upper phase (model diesel) was periodically sampled and analyzed. The total sulfur contents of the samples were determined by microcoulometry.

3. Results and discussion

3.1. Characterization of the PIL

The structure of PIL was confirmed by their FT-IR spectra and ¹H NMR. The FT-IR spectra of NMP, formic acids, and [Hnmp]HCOO

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