Full Length Article

Phenylpropanoic acid-based DESs as efficient extractants and catalysts for the removal of sulfur compounds from oil

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HIGHLIGHTS

- The $C_9H_{10}O_2 \cdot 0.5ZnCl_2$ DESs is synthesized by simple mixture.
- The hight efficient desulpfurization system use little H_2O_2 at low temperature.
- The $C_9H_{10}O_2 \cdot 0.5ZnCl_2$ as extractant and catalyst apply to the ODS.
- The removal rate of 99.23%, 96.12% and 98.4% for DBT, BT and 4,6-DMDBT are attached.
- The desulpfurization system exhibits high desulfurization activity and stability.

GRAPHICAL ABSTRACT

$C_9H_{10}O_2 \cdot 0.5ZnCl_2$ DESs are synthesized by simple mixing of raw materials at 110 °C. The highly efficient desulphurization system developed uses a $C_9H_{10}O_2 \cdot 0.5ZnCl_2$ DESs as the extraction agent and catalyst, and H_2O_2 as the oxidant. In the oxidation desulfurization system, the H_2O_2 dose is very small and the temperature is low. The DESs were characterized through FT-IR, ESI-MS, and TGA. The characterization results show that formation of the DESs involves hydrogen bonding. Kinetic analysis demonstrates that the reaction velocity of extractant-oxidation desulfurization system is very fast. The desulfurization rates are 99.23% in 60 min and 96.12% in 120 min for DBT and BT, respectively. Recycling of the DESs is investigated, and the results show that the rate of desulfurization drops slightly after five recycles. This result demonstrates that the highly efficient desulfurization system exhibits excellent stability for sulfur compounds.
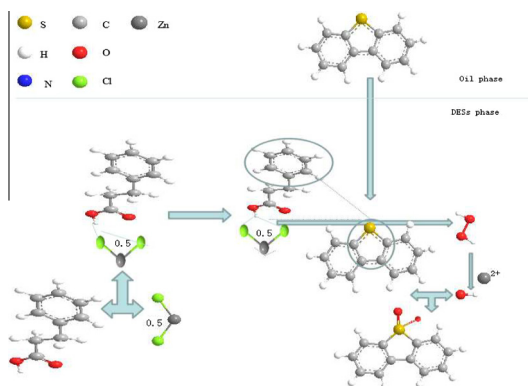
ABSTRACT

A series of Brønsted-Lewis acidic deep eutectic solvents (DESs) of $C_9H_{10}O_2 \cdot XZnCl_2$ (X from 0.5 to 3) were synthesized by simple mixing. The DESs were characterized by infrared spectroscopy, electrospray ionization mass spectrometry, and thermogravimetric analysis. The desulfurization of a model oil was investigated using $C_9H_{10}O_2 \cdot XZnCl_2$ as the extraction agent and catalyst, and H_2O_2 as the oxidant. The effects of the molar ratio of phenylpropanoic acid to zinc chloride, reaction temperature, oxygen to sulfur (O/S) molar ratio, and volume ratio of DESs to oil on the desulfurization rate were investigated. The optimal conditions for desulfurization were determined to be a phenylpropanoic acid to zinc chloride ratio of 2:1, a reaction temperature of 50 °C, an O/S ratio of 6, a DESs to oil volume ratio of 0.25:1, and a model oil dosage of 5 mL. Under the optimal conditions, a desulfurization rate of 99.23% in 80 min was achieved. The recyclability of the DESs was also investigated, and the results showed that the desulfurization rate

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decreased slightly after five runs. These results demonstrate that $C_9H_{10}O_2 \cdot 0.5ZnCl_2$ DESs exhibit high desulfurization activity and stability in extraction and oxidation desulfurization systems.

1. Introduction

SOx produced during gasoline and diesel combustion processes is the main cause of air pollution. Consequently, many countries have formulated strict environmental regulations that limit the sulfur content of emissions [1,2]. Hydrodesulfurization (HDS) is a widely employed industrial desulfurization process; however, it requires high temperature and pressure conditions [3], and has a low efficiency for aromatic sulfur compounds such as dibenzothiophene (DBT), benzothiophene (BT), and their derivatives. In recent years, several non-HDS technologies, such as extraction desulfurization (EDS), oxidative desulfurization (ODS), absorption desulfurization, and biological desulfurization, have been more widely researched [4–6]. In the ODS technique, aromatic sulfur compounds are oxidized to sulfones under mild conditions. Various oxidants are used in ODS, including NO_2, H_2O_2 [7], $KMnO_4$, and substitute solid. Of these, H_2O_2 is considered optimal because its by-product is water, which is harmless for environment.

Deep eutectic solvents (DESs), a new type of ionic liquid [8,9], are of great interest in academic research owing to their excellent physical and chemical properties. DESs are usually composed of two components that interact via intermolecular hydrogen bonds. They have several desirable properties of conventional ionic liquids, such as chemical stability, low vapor pressure, and the fact that they can be designed for specific purposes. In addition, they have the advantages of diversity, low cost, and environmental friendliness. Furthermore, the raw materials for their synthesis are readily available, and they can be produced using simple synthetic processes without the assistance of other organic solvents. DESs have been applied in a wide variety of fields, including catalysis [10], organic synthesis [11], material preparation [12], electrochemistry [13], and separation processes [14]. DESs are also used in the extraction desulfurization of fuels [15–17]. However, desulfurization rates are low when using DESs as the extraction agents. A feasible strategy to improve desulfurization in these cases is to apply acid DESs as catalysts in the ODS of fuels. Zhu et al. [18] reported the synthesis of $ChCl \cdot 2CH_3COOH$ and its application to ODS, and found that the as-prepared $ChCl \cdot 2CH_3COOH$ exhibits excellent desulfurization activity for DBT in a model oil under UV irradiation. Lü et al. [19] synthesized oxalic acid-based DESs for application to DBT removal, and achieved a removal rate of 98% in 180 min. Dai et al. [20] synthesized DESs using methyl benzene sulfonic acid and choline chloride as raw materials, and used them to oxidize sulfides to sulfoxides. Furthermore, the desulfurization performances of choline chloride/p-toluenesulfonic acid (ChCl/p-TsOH) and tetrabutylammonium chloride/p-toluenesulfonic acid (TBAC/p-TsOH) systems were investigated by Yin et al. [21], and they reported desulfurization rates of more than 97% for a model oil and diesel oil.

In this study, novel acid DESs $C_9H_{10}O_2 \cdot X(ZnCl_2)$ were synthesized. Electrospray ionization mass spectrometry (ESI-MS), Fourier transform infrared (FT-IR) spectroscopy, and thermogravimetric analysis (TGA) were performed to characterize the as-prepared $C_9H_{10}O_2 \cdot X(ZnCl_2)$ DESs. The ODS performance of the system was studied using $C_9H_{10}O_2 \cdot X(ZnCl_2)$ as the extraction agent and catalyst, and H_2O_2 as the oxidant. The effects of the molar ratio of phenylpropanoic acid to zinc chloride, reaction temperature, oxygen to sulfur (O/S) molar ratio, amount of DESs, and the type of sulfur on the desulfurization rate were investigated. The kinetics and mechanism of the desulfurization reaction are discussed in detail.

2. Experimental

2.1. Materials

H_2O_2 (AR, 30 wt%; Fuchen chemical reagent factory in Tianjin); n-octane (Tianjin damao chemical reagent factory); DBT (98%, Aladdin reagent); BT (97%, Aladdin reagent); TH (99.8%, Aladdin reagent); 4,6-DMDBT (98%, Aladdin reagent); zinc chloride (AR grade, Its group chemical reagent co., LTD); phenylpropanoic acid (CP grade, Its group chemical reagent co., LTD); CCl_4 (99.5%, Tianjin Fuyu Fine Chemical Co., Ltd.); WK-2D comprehensive micro coulomb analyzer (Jiangsu Jiang electric analysis instrument co., LTD). Oxidation product of DBT, DBT, DESs and raw materials were determined on Fourier-transform infrared spectrometer (WQF-520; Beijing Beifen Ruili Instrument Company, China); Thermo gravimetric and differential thermal analysis for DESs and phenylpropanoic acid were observed on (TG-DTA; Model SDT 2960TA; TA Instruments, New Castle, DE, USA). Electrospray ionization mass spectrometry (ESIMS) (Waters Acquity UPLC Premier XE).

2.2. Synthesis

The DESs were prepared via a single-step synthesis process. The appropriate amounts of zinc chloride and phenylpropanoic acid were placed in a 100 mL cylindrical vessel and heated to 110 °C in air with continuous stirring using a glass rod until complete dissolution of the compounds to form a grass-green transparent solution. DESs of $C_9H_{10}O_2 \cdot XZnCl_2$ (X from 0.5 to 3) were obtained. The morphologies and reaction equation of the DESs are shown in Fig. S1.

2.3. Mutual solubility of the DESs and the model oil

The mutual solubilities of the DESs and the model oil were measured according to a previously published method [22]. Firstly, $C_9H_{10}O_2 \cdot XZnCl_2$ was added drop-wise into n-octane until the solution became turbid. The difference in the mass of the solution before and after addition was calculated. Secondly, the solubility of the model oil in the DESs were measured using gravimetric methods. The model oil was added drop-wise into the DESs until the solution became turbid. The difference in the mass of the DESs saturated with the model oil and the DES dried under vacuum at 55 °C was calculated.

2.4. Desulfurization experiments

A 500 μg/g (ppm) model oil was prepared by dissolving 1.437 g DBT in 500 mL n-octane. The model oil, DESs, and 30 wt% H_2O_2 were added to a three-necked flask, and stirred in a water bath at 50 °C. The upper oil phase was sampled every 20 min and its sulfur concentration was determined with a WK-2D micro coulomb analyzer. The desulfurization rate was calculated using the following formula [23]:

$$\text{ODS rate} = \frac{S_{tot} - S_{res}}{S_{tot}} * 100\%$$