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Article

Oxidative desulfurization of diesel fuel with caprolactam-based acidic deep eutectic solvents: Tailoring the reactivity of DESs by adjusting the composition

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ABSTRACT

Despite the significance of hydrogen bonding in deep eutectic solvents (DESs) for desulfurization processes, little is understood about the relationship between the DES composition, hydrogen-bonding strength, and oxidative desulfurization activity. In this study, a new family of caprolactam-based acidic DESs was prepared with different molar ratios of caprolactam and oxalic acid. The prepared DESs were characterized by differential scanning calorimetry, Fourier transform infrared spectroscopy, ^{1}H nuclear magnetic resonance, and thermogravimetric analyses. These DESs were employed for oxidative desulfurization reactions and the desulfurization efficiency was found to vary regularly with the DES composition. The factors influencing the removal of dibenzothiophene were systematically investigated and the desulfurization efficiency of the caprolactam-based acidic DESs reached as high as 98% under optimal conditions. The removal of different sulfur compounds followed the order: dibenzothiophene > 4,6-dimethyldibenzothiophene > benzothiophene. The combined experimental data and characterization results revealed that the oxidative desulfurization efficiency of the system was influenced by the hydrogen bonding interactions with the DES, which can be optimized by adjusting the DES composition. These findings regarding hydrogen bonding in DESs provide new insight for better understanding of the mechanism of diesel deep desulfurization processes.

1. Introduction

The sulfur oxides in automobile exhaust have become a key aspect of the problem of acid rain and particulate matter (PM) 2.5. As a result, governments around the world regulate the composition and quality of transportation fuels to reduce such automobile exhaust emissions. Since 2006, the U.S. environmental legislation has limited the sulfur content in diesel to 15 μg g^{-1} [1–3]. Hydrodesulfurization (HDS) processes have been commercially applied to produce diesel fuel as a mature technology carried out under high hydrogen pressures and temperatures. However, the reduction of thiophenic compounds and their derivatives is difficult [4]. In addition, the harsh reaction conditions and high costs hamper further developments in desulfurization systems. Therefore, alternative processes for the deep desulfurization of fuels have become a hot topic from the perspective of high energy-efficiency applications. Among them, oxidative desulfurization (ODS) has been recently attracting a lot of attention for its mild operating conditions in the absence of hydrogen [5–15]. Nevertheless, the main limitation in the industrial application of ODS is the use of large amounts of volatile and flammable organic extractants, which

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result in further environmental pollution and safety issues. To solve these problems, a system combining ionic liquid (IL) extraction with catalytic oxidative desulfurization was successfully introduced, which could avoid the above environmental safety issues [16–21]. The industrial scale application of IL technologies still possess some challenges in terms of purification difficulties, high cost, low biodegradability, and hazardous toxicity [22–24]. Therefore, the exploration of new green solvents for desulfurization processes at large scale is urgent.

Deep eutectic solvents (DESs), a new class of versatile alternatives to ILs, have shown tremendous promise [25–28]. DESs refer to eutectic mixtures constituted by two or three cheap environmental ingredients associated via hydrogen bonding. They not only display the advantages of traditional ILs, but also surmount some of their deficiencies [26]. DESs exhibit extraordinary physical and chemical properties, such as viscosity, polarity, surface tension, conductivity, thermal stability, negligible vapor pressure, and being non-flammable. Moreover, these eutectic mixtures are nontoxic, biodegradable, inexpensive, and easy to prepare from natural and ready-made raw materials. As a new type of green solvents, research on DESs has intensified in the last decade, ever since their potential in new chemical technologies was realized [29,30]. Among the existing literatures, the ODS of fuels using DESs has attracted wide attention [31–38]. Li's group synthesized a series of acidic DESs for deep oxidation/extraction desulfurization of model fuels and the desulfurization efficiency of such DESs reached up to 99.99% [31]. Zhu *et al.* [32] developed a liquid-liquid extraction and photochemical oxidative desulfurization system exhibiting a dibenzothiophene (DBT) removal of up to 98.6% under UV light irradiation. Li's group utilized the DES choline chloride/2 polyethylene glycol for desulfurization and the removal of DBT reached up to 99.1% [33]. Mao *et al.* [34] reported a class of propionic acid-based DESs ($C_3H_6O_2$/*X* $ZnCl_2$, *X* = 0.1–0.6) and the desulfurization of DBT reached 99.42%. In a previous work, we found that the aromaticity of sulfur compounds was weakened by strong hydrogen bonding interactions in DESs, leading to easier oxidation to the corresponding sulfones by peracids [35]. Despite the significance of hydrogen bonding in DESs in desulfurization reactions, little understanding exists on the relationship between the DES composition, hydrogen-bonding strength, and oxidative desulfurization activity. As is well known, compared to the prediction of hydrogen-bonding strength (*hydrogen bond puzzle*) [39], establishing its relationship with the oxidation desulfurization efficiency has proven to be more difficult. Therefore, the relevant works in the literature are just preliminary investigations and further insight is urgently required.

In this paper, a series of caprolactam-based acidic DESs derived from common starting materials was prepared and employed as extractants and catalysts for the ODS of diesel. When employed in ODS reactions, the desulfurization efficiency was found to vary regularly with the DES composition. Under optimal conditions, the desulfurization efficiency of the caprolactam-based acidic DES reached 98%. The effect of the DES composition, reaction temperature, oxidant dosage, and different sulfur compounds on the desulfurization reaction was investigated. Since hydrogen bonding in caprolactam-based acidic DESs plays a vital role in ODS reactions, this work focused on the relationship between the ODS efficiency and hydrogen-bonding strength. Our findings on the effect of hydrogen bonding in DESs provide new insight into the mechanism of diesel deep desulfurization. The mechanism of this ODS system is also discussed based on a dual activation concept.

2. Experimental

2.1. Materials

Caprolactam (CPL), DBT, and benzothiophene (BT) were purchased from Macklin Reagent (Shanghai, China). Oxalic acid dihydrate and 4,6-dimethyldibenzothiophene (4,6-DMDBT) were purchased from Sinopharm Chemical Reagent (Shanghai, China). All the chemicals were analytical reagents dried under vacuum before use.

2.2. DES preparation

CPL was chosen as the HBA and oxalic acid (OXA) was chosen as the HBD. The synthesis process was performed in a round-bottomed flask. The DESs were prepared by stirring the two ingredients at given molar ratios at 80 °C until a homogeneous liquid was obtained [28]. This approach provided DESs with 100% atom economy and no by-product generation.

2.3. Characterization of DESs

The melting points (T_m) and glass transition temperatures (T_g) of the DESs were determined by differential scanning calorimetry (DSC 204 HP) from the second heating cycle, after initially heating the sample up to 100 °C and then cooling it to –70 °C. The T_m values were obtained by heating at a rate of 10 °C min^{-1} under nitrogen atmosphere. Fourier transform infrared (FT-IR) spectroscopy measurements were carried out on a Nicolet 470 FT-IR spectrometer using the KBr pellet technique. ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker DRX 400 MHz spectrometer at room temperature (400 MHz) and internally referenced to the tetramethylsilane signal in $CDCl_3$. Thermo-gravimetric analyses (TGA) were performed on a NETZSCH STA409PC thermal analyzer at a heating rate of 10 °C min^{-1} from 25 to 300 °C under nitrogen atmosphere.

2.4. Oxidation and desulfurization of model diesel

An oil bath was heated to the chosen temperature. The concentration of sulfur was 500 μg g^{-1} by dissolving the corresponding sulfur compound in *n*-octane. Tetradecane was chosen as the internal standard in such model diesel. The ODS system consisted of 2 mL DESs, 10 mL model diesel, and 0.09 mL of 30 wt% H_2O_2. The mixture was then stirred constantly for 3 h. Model diesel aliquots (top phase) were periodically withdrawn for analysis.