



Full Length Article

Deep desulfurization of fuels with cobalt chloride-choline chloride/polyethylene glycol metal deep eutectic solvents

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ABSTRACT

Deep eutectic solvents (DESs) are receiving increasing attention as ionic liquid analogues because of their environmentally friendly and very low-price characteristics. In this study, metal-based deep eutectic solvents (MDESs) were synthesized by combining cobalt chloride (CoCl_2), a hydrogen bond acceptor (HBA) such as choline chloride (ChCl), and hydrogen bond donors (HBDs) such as polyethylene glycol (PEG-200), ethylene glycol (EG), glycerol (GL), and propionic acid (Pr). The MDESs were used for the extractive catalytic oxidative desulfurization (ECODS) of fuels. Solid peroxymonosulfate (PMS) was selected as an oxidant over common ECODS oxidants such as liquid hydrogen peroxide because the former is cheaper, more stable, and less corrosive. The MDESs played dual roles (i.e., extractant and catalyst) during the ECODS process. One of the MDESs prepared ($\text{CoCl}_2\text{-ChCl}/2\text{PEG}$) showed fast reaction rates with nearly 100% dibenzothiophene removal under the optimal conditions (6 g of model oil with an initial sulfur content of 500 ppm, 0.9 g of PMS solution, 2 g of $\text{CoCl}_2\text{-ChCl}/2\text{PEG}$, 20 °C, and 60 min). The DESs prepared showed an outstanding recycling performance after 6 cycles without a significant decrease in activity. In the ECODS system, the reactivity of the three sulfur substrates studied followed the order: dibenzothiophene (DBT) > 4,6-dimethyldibenzothiophene (4,6-DMDBT) > benzothiophene (BT). In the case of the HBDs, the desulfurization efficiencies followed the sequence: PEG-200 > Pr > EG > GL. The oxidative product was dibenzothiophene sulfone (DBT_2O_2).

1. Introduction

China has been suffering from frequent haze pollution during the past 15 years. In case of heavy haze events, the contribution rate of sulfate to fine PM 2.5 particles in the atmosphere reaches values higher than 20%. According to a recent report [1], the formation of sulfate in the atmosphere involves alkaline aerosol components-trapped SO_2 , which is subsequently oxidized by NO_2 in aerosol water, which acts as a reactor. Therefore, sulfur oxides (SO_x) are one of the most important sources of air pollution. On the other hand, acid rain can be also formed by sulfur compounds generating numerous negative environmental impacts such as soil acidification, river pollution, forest destruction, buildings corrosion, and catalyst poisoning, among others [2]. Combustion of sulfur-containing fuels is one of the main SO_x emission sources to the atmosphere. In order to control the amount of SO_x in the atmosphere, many countries have enacted legislation for limiting the sulfur contents in fuel. For example, China enacted the Chinese national V standard on April 1st, 2016 in an attempt to reduce the sulfur content in oils below 10 ppm [3]. Thus, current desulfurization technology must be upgraded to meet this stringent limitation on sulfur content in oil.

The extractive catalytic oxidative desulfurization (ECODS) process showed excellent sulfur removal efficiency at nearly room temperature and atmospheric pressure, requiring only simple agitation [4]. On the ECODS process [5], ionic liquids (ILs) were first selected as extractants of sulfur compounds from the oil to the IL phase. In a subsequent step, a catalyst present in the IL along with an oxidant achieved the conversion of the sulfur compounds and their removal from the oil. Zhao et al. [6] employed [Bmim]PF₆-based ILs as extractant and Fe(III) porphyrins as catalyst. H_2O_2 was selected as an oxidant along with Fe(III) porphyrins to form a Fenton-like oxidation system that was able to keep a high desulfurization efficiency after 6 cycles. Li et al. [7] used the low cost $\text{FeCl}_3\text{-N-methyl-pyrrolidone}$ (NMP)-based ILs (Fe-ILs) along with an oxidant such as H_2O_2 to remove DBT. With six recycled tests, the activity performance did not show a significant decrease and the main oxidation product was DBT_2O_2 . Zhu et al. [8] selected a simple liquid-liquid extraction ECODS system composed of a molybdc compound, 30% H_2O_2 , and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄) to remove DBT. The sulfur removal was reached to nearly 99% at 60 °C after 3 h.

ILs have become popular for ultra-deep desulfurization in the field

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of ECODS system [9–11] because of their green solvent characteristics and stable physico-chemical properties including non-emission, non-volatility, non-explosiveness, and easy-handling [12]. Furthermore, ILs have a strong polarity [13] which is advantageous for extraction separation processes. ILs were first published as desulfurization agents in 2001 [14]. However, the industrial application of ILs is hindered because of their very high price and high viscosity at nearly room temperature, especially in the desulfurization field.

H₂O₂ has been widely selected as an oxidant in ECODS systems [15–17], very few other substances such as oxygen was employed as an oxidant [18]. In our previous study [19], oxone, a solid salt, was first used as an oxidant coupled with [C₆mimCl]CoCl₂ ionic liquids to form the ECODS system, which exhibited a high desulfurization efficiency. However, H₂O₂ may become unstable and corrosive and therefore requires high equipment investment, although it is superior as an oxidant and is preferred in ECODS processes. Also, the high oxidation nature of the costly H₂O₂ can cause a high cost in transportation, storage, and subsequent application. By contrast, oxone also known as peroxymonosulfate (PMS), is a white solid powder and a classical oxidant used in the field of organic wastewater treatment [20–22]. PMS is stable below 65 °C and easily dissolves in water. Its solid nature is positive for storage, transportation, and handling.

Deep eutectic solvents (DESs) were firstly reported by Abbott [23] in 2001. DESs were acknowledged as a new class of IL analogues because these compounds share numerous physico-chemical properties with ILs (e.g., special solubility, structural stability, undetectable vapor pressure, non-flammability and wide liquid temperature range, among others) [24]. With regard to ILs, DESs have a number of advantages such as low price, simple synthetic conditions, accessible raw material, easy biodegradation, non-toxicity, and wide application area. In the past few years, the replacement of IL with DESs has attracted attention to researchers in the desulfurization area. Lue et al. reported on a combined (oxalate-based DES and H₂O₂) ECODS system showing nearly 100% DBT removal after 2 h at 60 °C [25]. Hao et al. [26] reported on a L-proline-based DES extractant coupled with H₂O₂ for desulfurization. This system allowed nearly complete (99%) removal of DBT at 60 °C in 2 h. Liu et al. [27] prepared choline chloride(ChCl)-based DESs as green solvents for ECODS processes. These systems contained phosphotungstic acid (HPW) as a catalyst and 30 wt% H₂O₂ solution as oxidant. It was found that nearly 99.1% of the initial DBT was removed from a model oil at 50 °C within 3 h.

In this work, a series of cobalt ion-based DESs (Co-DESs) were synthesized by mixing cobalt chloride (CoCl₂), a hydrogen bond acceptor (HBA) such as choline chloride (ChCl), and hydrogen bond donors (HBDs, e.g., polyethylene glycol (PEG-200), ethylene glycol (EG), glycerol (GL), and propionic acid (Pr)). The metal ion-based DESs served as catalyst, extractant, and green solvent in a ECODS system with PMS as an oxidant. The simulated sulfur-containing oil was prepared by adding DBT, BT, and 4,6-DMDBT to octane. Important parameters such as the Co-DESs and PMS dosage, the initial DBT concentration, the temperature, the different S-containing substances and metal ions, the different HBDs, and the number of recycling times were investigated. The oxidized products were collected via CHCl₃ extraction and identified by gas chromatography coupled with mass spectrometry (GC-MS). The oxidation mechanism was also discussed based on the experimental results.

2. Experimental

2.1. Preparation of the metal ions-based DESs

ChCl was selected as a HBA. Polyethylene glycol (PEG-200), ethylene glycol (EG), glycerol (GL) and propionic acid (Pr) were chosen as HBDs. Cobalt chloride (CoCl₂) was chosen as catalysts. DBT, BT, and 4,6-DMDBT were dissolved in n-octane to prepare a series of model fuels with an initial sulfur content of 500 ppm (other concentrations

were prepared). All chemicals involved in this study were purchased from Aladdin Chemical reagent company. The Co-DES CoCl₂-ChCl/PEG-200 (CoCl₂-ChCl/2PEG) was synthesized by mixing under stirring (500 rpm) 0.1 mol of CoCl₂·6H₂O, 0.1 mol of ChCl, and 0.2 mol of PEG-200 at 105 °C in a thermostatic oil bath for 2 h. This synthetic method was applied to prepare other Co-DESs such as CoCl₂-ChCl/2EG, CoCl₂-ChCl/2GL, and CoCl₂-ChCl/2Pr.

2.2. ECODS process

The ECODS tests were carried out in a 40-mL two-necked flask equipped with a stirrer and a condenser. The reaction was carried out as follows. First, the Co-DES (e.g. CoCl₂-ChCl/2PEG) and a model fuel (e.g., DBT in octane) were added to the flask and the mixture was vigorously stirred for 30 min until the extraction equilibrium was reached at a certain temperature. A noticeable liquid-liquid interface between the simulated fuel (upper phase) and the Co-DES (lower phase) was formed during the extraction process. Second, a 20 wt% PMS solution (near saturation) was added to the flask and quickly diffused into the Co-DES phase. Subsequently, the mixture was vigorously stirred to complete the desulfurization reaction. In order to test the recycling performance of CoCl₂-ChCl/2PEG. The CoCl₂-ChCl/2PEG was recovered and reused for six times. The recycling experiment is that the CoCl₂-ChCl/2PEG was easily separated from the oil owing to their low mutual miscibility after the ECODS process. The recycled CoCl₂-ChCl/2PEG was heated at 150 °C for 6 h in order to decompose oxone and remove H₂O. The decomposition products, potassium sulfate and potassium bisulfate, can be separated out from Co-EDS. This ionic liquid recovery was carried out at 90 °C. The recycled Co-EDS was reused in a subsequent ECODS cycle of model oil at similar conditions.

2.3. Analytical methods

Aliquots of the upper phase (model fuel) were obtained at different reaction times and analyzed by ultraviolet-visible (UV-Vis) spectrophotometry. DBT in octane showed a characteristic absorption peak at 312 nm, and the standard curve for the absorbance (A) versus sulfur concentration (S) was $A = 0.04708S$ with a correlation coefficient (r) of 0.9992. All the samples were detected based this standard curve. The concentrations of BT and 4,6-DMDBT in octane were also detected following this approach. The characteristic absorption peaks of BT and 4,6-DMDBT were 297 and 312 nm, respectively. The standard curve of BT was $A = 0.07418 + 0.05366S$ with $r = 0.9998$, while the standard curve of 4,6-DMDBT was $A = 0.02337 + 0.0725S$ with $r = 0.9998$. The desulfurization efficiency was calculated using the following formula:

$$\text{Sulfur removal (\%)} = \frac{S_0 - S_t}{S_0} \times 100\% \quad (1)$$

where S_0 is the initial concentration of sulfur in oil and S_t is the concentration of sulfur at a time t .

GC-MS tests were carried out in an Agilent 7890A-5975C (USA) device. Chromatographic separation was carried out using a HP-5 capillary column (30 m × 0.32 mm i.d., 0.25 μm phase thickness).

3. Results and discussion

3.1. Effect of the CoCl₂-ChCl/2PEG dosage on the sulfur removal

Fig. 1 displays the effect of the CoCl₂-ChCl/2PEG dosage on the sulfur removal under fixed experimental conditions. The results indicated that the desulfurization process could be divided into two regions. The first region represents only the extraction process over the –30–0 min range. When the CoCl₂-ChCl/2PEG dosage varied from 1 to 3 g, the corresponding extraction desulfurization efficiency increased from 4 to 10%. These results reveal a single extraction process, however, the sulfur removal efficiency was lower than those previously

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