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Synthesis and oxidative desulfurization of novel lactam-based Brønsted-Lewis acidic ionic liquids

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HIGHLIGHTS

- A novel kind of Brønsted-Lewis acidic ILs was developed.
- The ILs were investigated in ODS process and exhibited highly efficient catalytic performance.
- S-content in diesel was reduced to less than 10 ppm through a one-step ODS.
- Multi-phase systems consisted of water, oil and ILs were investigated.

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ABSTRACT

Novel Brønsted-Lewis acidic ionic liquids having a protonated N-octylcaprolactam-based cation and $Cl/nZnCl_2$ anion ($n = 1$, 2 and 3) were synthesized and investigated as catalysts in the oxidative desulfurization (ODS) of both model oil and real diesel fuel, with hydrogen peroxide (H_2O_2, 30 wt%) as oxidant. It is observed that the ODS performance increases significantly with the increase of $ZnCl_2$ proportion. Then detailed experiments for the ODS of model oil were carried out with $[Hnoc]Cl/3ZnCl_2$ to investigate the influence of some important factors, including reaction temperature, molar ratio of H_2O_2/S, ILs dosage, initial S-content and sulfide species. It is worth noting that, with the mass ratio of ILs/oil of only 1:20, satisfactory conversion rate can also be achieved for the removal of dibenzothiophene (DBT), and the ILs were used for six cycles without a noticeable decrease in activity. What is more important, the ILs can reduce the S-content of a real diesel from 559.7 ppm to 8.2 ppm with 98.5% sulfur removal rate and 96.3% diesel recovery through a one-step ODS process. Deduced from the GC-PFPD spectra, almost all the original S-compounds and their oxidized products were completely converted and extracted, respectively. The outstanding desulfurization efficiency can be attributed to the good phase transfer property of the ILs.

1. Introduction

Sulfur compounds, which naturally exist in petroleum, are significantly enriched in diesel distillate in petroleum refining process. Diesel fuel is the most commonly used fuel in transportation and industrial, however the combustion of sulfur containing diesel causes significant environmental and health problems [1–3]. Thus, increasingly stringent regulations in the maximal S-content of diesel have been established in many countries, which put forth a critical challenge to the refinery industry. At present, the traditional hydrodesulfurization (HDS), a conventional commercial technology, is wildly employed for the purification of fuels. Though HDS can remove various S-compounds such as thiols, sulfides and disulfides, it is a high energy consumption process and inefficient for the removal of heterocyclic sulphenic compounds [4]. Therefore, it is desirable to develop alternative or supplementary technologies with the advantages of low energy consumption and high selectivity. Hundreds of papers have been published regarding the non-HDS technologies based on extraction [5,6], oxidation [7–10] and adsorption process [11,12]. Among them, oxidative desulfurization (ODS) is considered as one of the most promising methods to obtain ultra-low S-content fuels.

In a typical ODS process, S-compounds in fuel are oxidized to their corresponding sulfones first, which can be subsequently removed by extraction, adsorption, distillation or decomposition [1–3,13]. Hydrogen peroxide is the most extensively adopted

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oxidant, due to its high reactivity and low price [9]. Numerous catalysts based on organic acid [14,15], metallic oxide [7,8] and polyoxometalates [16–19] were reported to be effective in ODS and led to good results. In the recent years, ionic liquids (ILs) were designed to act as catalysts for oxidation of S-compounds [20,21]. Those refractory sulphenic compounds show good oxidative activities in ILs under mild conditions. In addition, the oxidative products such as sulfones or sulfoxides can be easily extracted by ILs.

It's well known that the physical and chemical properties of ILs could be adjusted by changing the structures and combination of cations and anions [22]. In this way, a lot of work about ODS based on functionalized IL has been reported [23–26]. Recently, metal halide-containing ILs, a kind of Lewis acidic ILs have been attracted more attentions due to the high ODS efficiency [27–32]. The ODS process in ILs is commonly regarded as a coupling of extraction and reaction processes. Both theoretical and experimental work has demonstrated that the metal halide-based Lewis acid anion could form π-complexation bonding with aromatic S-compounds and thus enhance the extraction of sulfur species [33–36]. Furthermore, the strong oxidant hydroxyl radicals are formed and take part in the oxidative reactions [37,38]. These factors of Lewis acidic ILs offer a high reaction rate to the conversion of S-compounds. On the other hand, various Brønsted acidic ILs have also been reported to be the ODS catalysts [39–41]. However, they are not always competitively effective, since it often took a long time to obtain deep sulfur removal. In spite of the low catalytic activity, several papers demonstrated the co-catalysis effect of Brønsted acidic groups for the oxidative reaction of S-compounds [17,42]. The hydrogen bonds formed between active H and S atoms enhance the oxidative reactivities of S-compounds and further promote the sulfur removal efficiency. In this way, the Brønsted-Lewis acidic ILs may lead to a qualitative leap in desulfurization efficiency. Recent papers have described their suitable catalytic reactions, such as dimerization [43], alkylation [44] and oxidation [45,46]. Compared with the traditional catalyst or ILs, the Brønsted-Lewis acidic ILs often exhibited better catalytic performances.

Some papers have been published regarding the use of ILs for the deep oxidative desulfurization of real diesel [46–50]. In order that the S-content of real diesel can be reduced down to 10 ppm, the ODS were usually carried out with large dosage of ILs and sometimes using multi-stage processes. This large usage of ILs not only makes the process less economical but also increases the loss of hydrocarbon substances due to their dissolution in ILs. In our opinions, one of the effective methods to improve the desulfurization performance and reduce the dosage of ILs is enhancing the phase transfer capability of ILs.

Inspired by these reports, a novel kind of Brønsted-Lewis acidic ILs, i.e., $[Hnoc]Cl/nZnCl_2$ (n = 1, 2 or 3), with protonated N-octylcaprolactam-based cation and $ZnCl_2$ based anion were developed in this work. Their structures are shown in Fig. 1. The ILs were utilized as extractant and catalyst in the ODS process of model oil with H_2O_2 as oxidant. Many factors upon the ODS process were investigated in detail including composition of ILs, reaction temperature, molar ratio of H_2O_2/S, mass ratio of ILs/Oil, initial S-content, species of S-compounds and reusability. The ILs possessed an excellent desulfurization performance with relatively low ILs dosage. Following that, ODS were applied to a hydrogenated diesel, and the evolution of total S-content and speciation of S-compounds were measured.

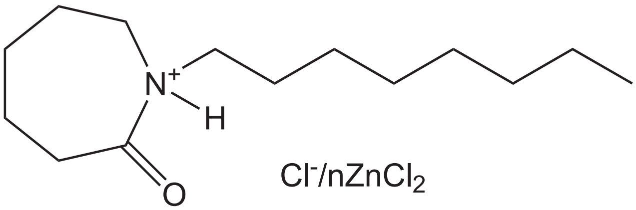

Fig. 1. Structure of ILs $[Hnoc]Cl/nZnCl_2$.

2. Experimental

2.1. Chemicals and materials

DBT (98%), thiophene (T, 99%), benzothiophene (BT, 98%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, 98%) hydrogen peroxide (30 wt%), zinc chloride (98%) and n-octyl bromide (98%) were purchased from Aladdin Reagent Co. Ltd. Ethanol (99%), caprolactam (99%), tetrahydrofuran (THF, 99%), n-octane (99%), hydrochloric acid (36.5 wt%), ethyl acetate (99%) and carbon tetrachloride (99%) were purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. Hydrogenated diesel was provided by SINOPEC Tianjin Petrochemical Co., Ltd.

2.2. ILs synthesis

The ILs were prepared via a three-step synthesis process (Scheme 1). N-octylcaprolactam was synthesized through the alkylation reaction of caprolactam, and then reacted with hydrochloric acid (HCl, 36.5 wt%) to form [Hnoc]Cl. Finally, $ZnCl_2$ was added to form the final ILs of $[Hnoc]Cl/nZnCl_2$. Detailed experimental procedures are provided in the Supplementary material. Densities and Viscosity of ILs synthesized in this work are listed in Table S1.

2.3. Desulfurization and analysis

Model oil was prepared by dissolving DBT in n-octane to reach 500 or 1000 ppm S-content. For oxidation of T, BT and 4,6-DMDBT, the model oil with initial S-content of 500 ppm was prepared.

The ODS process was conducted in a 50 mL jacketed reactor equipped with a magnetic stirrer and a reflux tube. Certain amounts of ILs and model oil were added into the reactor, and then vigorously stirred at 600 r/min. The needed temperature is realized by water circulation, and H_2O_2 was added to start the reaction. Each reaction totally lasted for 2 h. Samples were taken from the oil phase at set intervals and analyzed by gas chromatography (GC-FID; Agilent 7890A; HP-5, FID: Agilent) for the evolution of S-compounds concentration.

The removal of the sulfides was calculated as follows:

$$S\text{-}removal = \frac{C_0 - C_t}{C_0} \times 100\%$$

where C_0 is the initial concentration of sulfur in the model oil and C_t is the concentration of sulfur in the oil phase after the reaction began for a certain amount of time.

The ODS procedures of real diesel were similar to those of model oil. The total S-content was analyzed with an elemental analyzer (Analytical jena, multi EA 5000). Speciation of S-compounds before and after ODS process was identified using gas chromatography (GC-PFPD, Varian CP-3800, HP-5NS). More information about chromatography is given in Table S2.

3. Results and discussion

3.1. Characterization of the ILs

^{1}H nuclear magnetic resonance (NMR) spectra of the $[Hnoc]Cl/nZnCl_2$ systems were recorded on a VARIAN INOVA