



Oxidative desulfurization of fuels catalyzed by ammonium oxidative-thermoregulated bifunctional ionic liquids



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HIGHLIGHTS

- A series of oxidative-thermoregulated bifunctional ionic liquids have been developed.
- IL/toluene/*n*-octane or *n*-dodecane system has the property of thermoregulation.
- The thermoregulated system is used for H₂O₂ oxidative desulfurization of model fuels.
- The reaction and the separation are well integrated.

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ABSTRACT

A series of developed ammonium oxidative-thermoregulated bifunctional ionic liquids (ILs) catalysts have been synthesized. The structures of these task-specific ionic liquids (TSILs) are characterized by FT-IR and ¹H NMR. The thermoregulated properties of ILs in aqueous and common organic solvent are investigated. The prepared ionic liquid has the cloud point (CP) in aqueous, and has the minimum solubility in toluene. The ionic liquid has the corresponding critical solution temperature (CST) in toluene/*n*-octane or *n*-dodecane mixed solvents, which makes the system with the thermoregulated feature of “homogeneous at high temperature, heterogeneous at low temperature”. The developed thermoregulated system has been used for catalytic H₂O₂ oxidative desulfurization of model fuels to achieve an integration of homogeneous catalysis and heterogeneous separation. The recycle of the ionic liquid catalyst is easily achieved. The desulfurization rate only keeps a gradually slight drop during the recycles of the catalyst.

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1. Introduction

With the increasing demand for liquid hydrocarbon fuels in global scope, the pollution resulting from sulfur in fuels becomes more and more serious every day. Deep desulfurization of fuels has become a very important research subject worldwide, due to environmental concern and the upcoming stricter sulfur legislative regulation. Conventional hydrodesulfurization (HDS) is highly efficient for the removal of thiols, sulfides, and disulfides. However, it is difficult to reduce refractory thiophenic compounds and their alkyl-substituted derivatives existing in current liquid hydrocarbon fuels [1,2]. Moreover, severe operation conditions, expensive equipments, high hydrogen consumption and other disadvantages hamper the application of HDS in deep desulfurization. Therefore, non-HDS techniques such as adsorption [3], extraction [4],

oxidation [5–7], and biodesulfurization [8] have gathered people's attention and become a hot topic of research. There have been some reviews related to desulfurization of fuels in the open literatures [9–11]. Among these non-HDS techniques, oxidative desulfurization (ODS) has been considered as one of the promising alternative methods for deep desulfurization, because it can be performed under moderate conditions to remove the refractory sulfur compounds. In ODS, the sulfur compounds are oxidized to the corresponding sulfoxides and/or sulfones, which can be more easily removed by extraction or adsorption. By the combination of oxidation and extraction or adsorption, the sulfur content of fuels can be greatly reduced.

From an environmental standpoint, room-temperature ionic liquids (RTILs) with many unique properties have become increasingly popular as green reaction media or extractants in research and development [12,13]. Some RTILs used as extractants in extraction desulfurization have been reported from 2001 [14–16]. Recently, the combination of oxidation and RTIL extraction in ODS has been

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explored [17–20]. Basis on the designability of ionic liquid structure, a lot of task-specific ionic liquids (TSILs) which endow the ionic liquid with a capacity to behave not only as a reaction or extraction medium but also as a reagent or catalyst in some reactions or processes have been designed and synthesized [21–23]. A new family of ionic liquids with heteropolyanion as acidic or oxidative catalysts recently has attracted intense interest [24–27]. Heteropolyanion-based ionic liquids as oxidative catalysts used for ODS of fuels have showed good sulfur removal [28,29].

In this paper, a series of novel heteropolyanion-based ionic liquids as oxidative-thermoregulated bifunctional catalysts have been designed and synthesized by introducing polyoxyethylene (POE) chain as the thermoregulated structure unit and using heteropolyanion as catalytic oxidation group. The developed TSILs have been applied for catalyzing ODS of fuels with H_2O_2 as oxidant. By using the thermoregulated property of the ionic liquid, the homogeneous catalysis and the heterogeneous separation in the new catalytic system can be well integrated. Here, we report the detail of the study.

2. Materials and methods

2.1. Materials and product analysis

All chemicals were used as purchased and of reagent grade. The solvents were dried by known procedures and used freshly distilled. The product was analyzed by a Nicolet-510P IR spectrometer. 1H NMR spectrum was recorded on a Bruker AV 500 MHz spectrometer with tetramethylsilane as the standard. The sulfur content of model oil was measured by a WK-2D microcoulometric detector.

2.2. Synthesis of oxidative-thermoregulated ionic liquids

n-Octadecylamine (0.01 mol) and 10 mL absolute ethyl alcohol were mixed in a 100 mL high-pressure reaction kettle. A certain volume of ethylene oxide (99%) was added. Under N_2 and stirring, the reaction was kept for 2 h at room temperature, then for another 5 h at 60 °C. After the reaction, the solvent and redundant ethylene oxide were removed by vacuum distillation to constant weight. Then the intermediate **1** was afforded as a sticky liquid. The intermediate **1** (0.01 mol) and different *n*-chloroalkane (*n*-chlorobutane 0.03 mol, *n*-chlorooctane 0.015 mol, or *n*-chlorododecane 0.015 mol) were added to a high-pressure reaction kettle. The 3 MPa N_2 was filled. Under stirring, the reaction was kept for 10–16 h at 90–120 °C. After the reaction, the mixture was washed with anhydrous diethyl ether, followed by drying in high vacuum to afford the corresponding intermediate **2**. The intermediate **2**

(0.024 mol) and 10 mL distilled water were added to a three-neck round-bottomed flask equipped with a thermometer, a reflux condenser and a constant pressure drop funnel. Under stirring, the solution was heated to 80 °C. Then, 10 mL aqueous of 12-tungstophosphoric heteropoly acid (0.008 mol) was dropped slowly. After completion of the dropping, the reaction was kept 80 °C for 6 h. After that, the reaction mixture was distilled in vacuum to remove the water and the produced hydrogen chloride. The corresponding product **3** was afforded.

2.3. Procedure of oxidative desulfurization

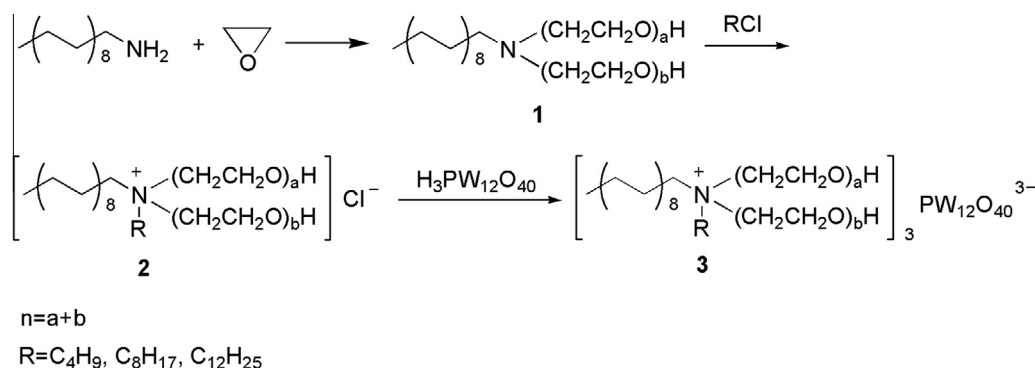
Model gasoline and diesel were prepared by dissolving the model sulfur-containing compound thiophene in *n*-octane or *n*-dodecane with a corresponding S-content of 697 ppm and 793 ppm, respectively. A certain amount of toluene, model oil, the ionic liquid and H_2O_2 (30 wt%) were added into a three-neck round-bottomed flask equipped with a thermometer and a reflux condenser. The reaction was carried out at the determined temperature for the given time in a water bath. After the reaction, the mixture was cooled to room temperature. The upper oil phase was withdrawn and then extracted with *N,N*-dimethylformamide (DMF). The sulfur content in model oil was analyzed using a microcoulometric detector. The lower ionic liquid catalyst was dried and directly reused by the addition of fresh model oil and toluene.

3. Results and discussion

3.1. Synthesis of ionic liquids

A series of eighteen ammonium oxidative-thermoregulated bifunctional ionic liquids have been synthesized by introducing the thermoregulated structure unit into ammonium cation and using heteropolyanion as the anion of ILs. The total synthesis route is outlined in Scheme 1. In brief, ethylene oxide is first converted into eighteen amine forming POE chain. Then, the corresponding intermediate **1** reacts with different *n*-chloroalkane to get intermediate **2** with chloride ion. The following anion exchange of intermediate **2** with phosphotungstic acid affords the oxidative-thermoregulated ionic liquid **3** with phosphotungstic anion.

In synthesis, the dosage of ethylene oxide determines the polymerization degree of ionic liquids (the average number of oxyethylene units per molecule). The value of polymerization degree (*n*) should equal the sum of *a* and *b* as shown in Scheme 1. Usually, the polymerization degree increases with the increasing ethylene oxide dosage. However, in consideration of the volume of autoclave and saturation of addition reaction, the maximum polymerization degree of the synthesized ionic liquids in the experiment is $n = 133$.



Scheme 1. The synthesis route of ammonium oxidative-thermoregulated ionic liquids.

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