



Research paper

Deep-desulfurization of the petroleum diesel using the heterogeneous carboxyl functionalized poly-ionic liquid

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Abstract

Acidic carboxyl functionalized poly(ionic liquid) (CFPIL) has been synthesized and characterized by various techniques like FT-NMR, Fourier transform infrared spectroscopy (FTIR). In this work, deep oxidative desulfurization of model oil (thiophene dissolved in iso-octane) by CFPIL catalyst was carried out in presence of 30 wt% H₂O₂ solution as an oxidant. The effects of the hydrogen peroxide, amount of CFPIL, temperature-time and recyclability are scrutinized systematically. It was found that the effective molar proportion of H₂O₂ to sulfur was 4:1 at 70 °C in 180 min with 0.6 g catalyst, removing 100% thiophene from model oil. This method has shown high efficiency for the removal of thiophene, which is difficult to remove from the oil than benzothiophene and dibenzothiophene. Additionally, an oxidative desulfurization mechanism has been proposed according to the experimental results. This catalytic system by CFPIL offers advantages such as higher efficiency, low amount of ionic liquid, simple work up for separating oil from the catalyst and ease of recycling. This protocol inclines to show that diesel fuels in industry can be purified to sulfur-free or ultra-low sulfur fuels by further deep oxidative desulfurization with CFPILs after hydrodesulfurization.

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1. Introduction

Sulfur oxides (SO_x) are derived from sulfur and oxygen molecules of which sulfur dioxide (SO₂) contributed more in the lower atmosphere [1]. Sulfur content in diesel fuel has been known as a main contributor to air pollution that emitted SO₂ along with particulate matter from vehicles. Besides other

anthropogenic activities causing emissions of SO_x, transportation can also contribute to high local ambient concentrations of the pollutants. This environmental issue has caused an extensive worry and new regulation to lower the sulfur content (S-content) in fuel oils is constantly being presented by governments. Hence, environmental guidelines have been announced in many countries to radically diminish the influence of sulfur compounds. The permissible limit of sulfur compounds in diesel fuels is 10–15 ppm worldwide. This ultra-low sulfur contents can be attained by deep hydrodesulfurization (HDS) of middle distillate streams [2]. However, hydrodesulfurization requires hydrogen consumption, expensive catalysts, and drastic process parameters such as high temperature (>300 °C) and high pressure (3–10 MPa). Moreover, it is also not as much of effective for eradicating some condensed heterocyclic Sulfur compounds like dibenzothiophene (DBT), benzothiophene (BT) and thiophene or their derivatives due to sterically hindered adsorption of these compounds on the adsorbents [3]. Thus, some alternate deep desulfurization techniques are preferred. In recent times, studies on deep desulfurization of fuel

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oils are being attentive on ionic liquid (IL) trappings, where S-compounds are reduced by extractive desulfurization (EDS) using ILs [4–9] or oxidative desulfurization (ODS) by oxidation of S-compounds using oxidants [10].

ILs are a novel class of organic salts that are entirely consist of organic cations and organic or inorganic anions, and known as “green solvents” in the past few decades [11]. The most significant reason is that ionic liquids acquire negligible vapor pressure, so they do not vaporize to environment. Secondly, they are good solvents for a complete range of organic and inorganic materials. Thirdly, some of them are not miscible with organic solvents and hence they afford an alternative for non-aqueous nature for two-phase systems. Finally, ionic liquids have good thermal/chemical stability and nonflammability, and can be reused to offer similar performance in chemical transformations [1,12–17]. As a result, the extraction of sulfur using ILs to remove sulfur compounds such as thiophene has been extensively described.

However, the effectiveness of sulfur removal is relatively low in extraction desulfurization along with loss of fuels [18], whereas oxidative process using ILs with H_2O_2 oxidant not only enhances sulfur removal but also decreases the cost of desulfurization. Zhao et al. [19] have utilized N-methylpyrrolidonium tetrafluoroborate ([Hnmp]BF₄) as an extracting reagent and a catalyst for oxidative desulfurization (ODS) of model oil and diesel fuel in the presence of H_2O_2 as an oxidant. The same author [20] has successfully demonstrated N-methylpyrrolidonium tetrafluoroborate ([Hnmp]BF₄) as an extracting reagent and a catalyst to remove dibenzothiophene (DBT). The probable catalytic oxidative desulfurization mechanism of DBT by IL catalysts and the kinetics of extraction were proposed. A series of task-specific acidic ionic liquids (TSILs), containing –COOH group in the cations, were used for oxidative desulfurization as both the catalyst and extractant [21]. The TSILs were found very effective in desulfurization (96.7%) from the model oil at 298 K. The other group [22,23] has shown remarkable performance of the Brønsted acidic ionic liquids 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO₄]) and N-butyl-pyridinium hydrogen sulfate ([C₄Py][HSO₄]) as extractant and catalyst for the removal of sulphur from the diesel.

Chen et al. [24] have demonstrated an efficiency of Brønsted and Lewis acidic ILs for removing dibenzothiophene from model diesel fuels. This work inclines to show that diesel fuels can be refined to sulfur-free or ultra-low sulfur fuels by additional deep oxidative desulfurization by using ILs after hydrodesulfurization. Li and his research group [25] have emphasized the prospective potential use of a temperature-responsive magnetic IL [BPy][FeCl₄] in the field of petrochemical technology. The authors have indicated that, during oxidative desulfurization process, the thermo-regulated formation of liquid–liquid extractive and catalytic oxidation desulfurization system (ECODS) containing model oil, hydrogen peroxide and [BPy][FeCl₄] was perceived at 40 °C. Furthermore, [BPy][FeCl₄] displays good recyclability due to a strong response to a magnet and can be easily separated from model oil by applying an external magnetic field. The carboxylate-

anion-based protic ionic liquid (PIL), [Hnmp]HCOO, was synthesized from N-methyl-2-pyrrolidonium (NMP) and formic acid [26]. The [Hnmp]HCOO showed very high catalytic activity with 99% removal of dibenzothiophene (DBT) at 50 °C in 3 h under conditions of VPIL/Vmodel oil = 1:10 and H_2O_2 /DBT (O/S, molar ratio) = 5. Recently, Yu et al. [27] have synthesized several Brønsted–Lewis acidic N-methylpyrrolidonium zinc chloride ILs with different quantity of zinc chloride. The authors have examined the ODS of model diesel fuel and real FCC diesel fuel using [Hnmp]Cl_x/(ZnCl₂)_y as both extractant and oxidant with the usual conditions. It was observed that the S-removal efficiency is dependent on IL composition, and [Hnmp]Cl/ZnCl₂ has the highest S-removal efficiency. Subsequently, two functional acidic ILs ([(CH₂)₄SO₃HMIIm][Tos]) and [(CH₂)₄SO₃HMIIm][ZnCl₂]) were synthesized and investigated the performance for both extractant and catalyst in oxidative desulfurization of diesel fuel [28]. More recently, Zhang et al. [29] have reported various Brønsted acidic ionic liquids with a protonated amide- or lactam-based cation and scrutinized as extractants and catalysts in the removal of sulphur from the model oil. Among them, [HCPL][TFA] presented the best suitability by completely removing BT and DBT in a short time. Moreover, the S-content of hydrogenated diesel was reduced down to 10 ppm, which verified the feasibility of ODS as a supplementary of HDS for ultra-deep sulfur removal.

Although homogenous catalysts have excellent activity and selectivity, a major problem is the difficulty of their retrieval from the reaction medium. Precipitation with subsequent recovery, e.g. elimination of the precipitating counter-ion, or removal of the reaction products via distillation, which is an energy intensive process, is usually required in order to re-cycle homogeneous catalysts. Such methodology may often inactivate the catalyst. However, heterogeneous catalysts take over homogeneous ones and show good thermal stability, recovery, easy and cheap recyclability with multiple active sites except relatively low activities [30–33].

There have been many heterogeneous oxidative systems adopted for the removal of the sulfur compounds in fuels such as H_2O_2 /organic acid [34], H_2O_2 /Ti-zeolite [35], H_2O_2 /IL [36], H_2O_2 /heteropolyacid [37] and other non-hydrogen peroxide protocols [38]. Of these, the most acceptable green oxidant is H_2O_2 , as water is the only by-product for H_2O_2 oxidation. But, it can be observed that excess H_2O_2 is necessary in almost all of these oxidative desulfurization schemes. This was mostly due to two reasons: some catalysts would accelerate decomposition of H_2O_2 considerably, leading the low consumption of H_2O_2 for oxidative desulfurization; and the excess amount of oxidant could uphold the equilibrium reaction. Thus, the excess H_2O_2 could enhance the efficient desulfurization. As a result, in view of cost-effective reasons, exploring competent catalysts to minimize the amount of H_2O_2 used for ODS is required [39].

Few studies have been carried out to minimize consumption of H_2O_2 or molecular oxygen for oxidative desulfurization of organic sulphur. Li et al. [40] have testified amphiphilic POM emulsion catalysts for the oxidative desulfurization of dibenzothiophene with O₂ in presence of aldehyde as the

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