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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% H_2O_2 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 H_2O_2 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.

Keywords: Ionic liquid; Oxidative desulfurization; Thiophene

1. Introduction

Sulfur oxides (SOx) are derived from sulfur and oxygen molecules of which sulfur dioxide (SO_2) contributed more in the lower atmosphere [1]. Sulfur content in diesel fuel has been known as a main contributor to air pollution that emitted SO_2 along with particulate matter from vehicles. Besides other anthropogenic activities causing emissions of SOx, 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 oxidization 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-methyl-pyrrolidonium tetrafluoroborate ([Hnmp]BF_4) 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-methyl-pyrrolidonium tetrafluoroborate ([Hnmp]BF_4) 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][HSO_4]) and N-butyl-pyridinium hydrogen sulfate ([C_4Py][HSO_4]) 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][$FeCl_4$] 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][$FeCl_4$] was perceived at 40 °C. Furthermore, [BPy][$FeCl_4$] 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]Clx/($ZnCl_2$)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/$ZnCl_2$ has the highest S-removal efficiency. Subsequently, two functional acidic ILs ([$(CH_2)_4SO_3$HMIm][Tos]) and [$(CH_2)_4SO_3$ HMIm][$ZnCl_3$]) 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 O_2 in presence of aldehyde as the sacrificial agent at 60 °C for 8 h and Anderson type polyoxometalates under 80 °C for 10 h [41]. Wang, Huo and co-workers have reported peroxo-titanium complex $[C_{18}H_{37}N(CH_3)_3]_7[PW_{10}Ti_2O_{38}(O_2)_2]$ and projected that these complexes could deliver reactive peroxo species to the substrates. The molecular oxygen could be transferred from $Ti(O_2)$ species to the substrates, and lead to the oxidation of organic substrates with O_2 as oxidant as an alternative of H_2O_2. The catalyst could completely oxidize DBT to sulfone using O_2 as the oxidant under mild conditions such as 90 °C and atmospheric pressure. Moreover, the reverse-micellar polyoxometalate (POM) catalysts can be separated and recycled easily and the sulfones can be removed directly from diesel by extraction of MeCN. However, loss of the POM could not be explained during recycling process.

Another group has designed [42] a new reaction-controlled foam-type catalyst by pairing 1-hexadecyl-3-methylimidazolium cation with peroxomolybdate anion. This catalyst interchanged from the powder to the foam-type active species, demonstrating an efficient catalyst in the oxidative desulfurization process. Li et al. have synthesized [43] a tungsten-containing ionic liquid (IL) $[(C_6H_{13})_3PC_{14}H_{29}]_2W_6O_{19}$ and successfully applied in the desulfurization process of a model oil containing dibenzothiophene with aqueous hydrogen peroxide. The task-specific IL not only assisted in the extraction of organo-sulfur compounds but also was used as a catalyst for the hydrogen peroxide for the oxidation of organic sulfur compounds by forming IL emulsions. Recently, Hou et al. [44] have reported peroxotungsten anion-based ionic liquid-type catalysts used for the deep desulfurization of model oil containing dibenzothiophene (DBT) with H_2O_2 as an oxidant. It was specified that the H-bonding interaction between the proton in imidazolium and the basic S atom in the DBT molecule played a vital role in augmenting the catalytic activity.

The oxidation of thiophene and DBT by H_2O_2 under mild conditions would be of great importance in industry due to its lower costs and environmentally benign nature. In order to accomplish this, the main task is to seek an active and durable catalyst under mild temperature and atmospheric pressure. Tang et al. [45] reported a new solid acidic polymeric ionic liquid from polymerizable Brønsted acidic ionic liquid and divinylbenzene (DVB). This hydrophobic exhibited an efficient oxidative desulfurization with more than 95% under moderate condition. Prompted to this, the carboxyl acid functionalized CFPIL catalyst is prepared and characterized by various techniques like FT-NMR, Fourier transform infrared spectroscopy (FTIR). This prepared catalyst is then assessed for its ability to remove the sulphur from the model diesel (thiophene in isooctane). An oxidizing agent such as H_2O_2 is used in the sulphur removal. The experimental studies are carried out in a round bottom glass reactor equipped with a total reflux system. The reactor is immersed in an oil-bath with thermostatic controller to carry out the reactions at different temperatures to find out an optimal temperature. The reactor setup with oil bath is mounted on a magnetic stirrer. The reactive system is consist of model diesel, H_2O_2 and CFPIL catalyst. Finally, the effects of the hydrogen peroxide, amount of CFPIL, temperature-time and recyclability are examined with both model and real diesel sample.

The main objective of this work is to use the Brønsted acidic CFPIL as a catalyst for oxidative desulfurization (ODS) of model and real diesel in the presence of H_2O_2 by chemical oxidation. A coordination compound was formed between the cation of the ionic liquid and hydrogen peroxide which decomposed to hydroxyl radicals. The sulfur-containing compounds in model oil were removed from the ionic liquid phase and converted to their analogous oxidation products by the hydroxyl radicals. Thus, this protocol is giving practical solutions for environmental problems related with sulfur emission.

2. Experimental procedures

2.1. Reagent and instrument

All chemicals used were of reagent grade with highest purity available. 4-Vinylbenzyl chloride and 3-bromopropionic acid were purchased from Sigma Aldrich and VBC was used by washing with dil. NaOH, AIBN, H_2O_2, and thiophene were purchased from Avra Synthesis Private Limited. Isooctane and solvent were purchased from SDFCL, and THF benzimidazole was purchased from Spectrochem Pvt. Ltd. and used as received.

NMR spectra for all synthesized compounds were recorded in $CDCl_3$, DMSO-*d6* on Bruker Spectrophotometer operating at 400 MHz; GC spectrum from Shimadzu GC-2010 plus Gas chromatograph Column model Rtx-1 (crossbond 100% dimethylpolysiloxane) 30 meters, 0.32 mm 0.5 Micrometer Max Prog. Temp. 350 °C.

2.2. Synthesis of carboxyl functionalized poly(ionic liquid)

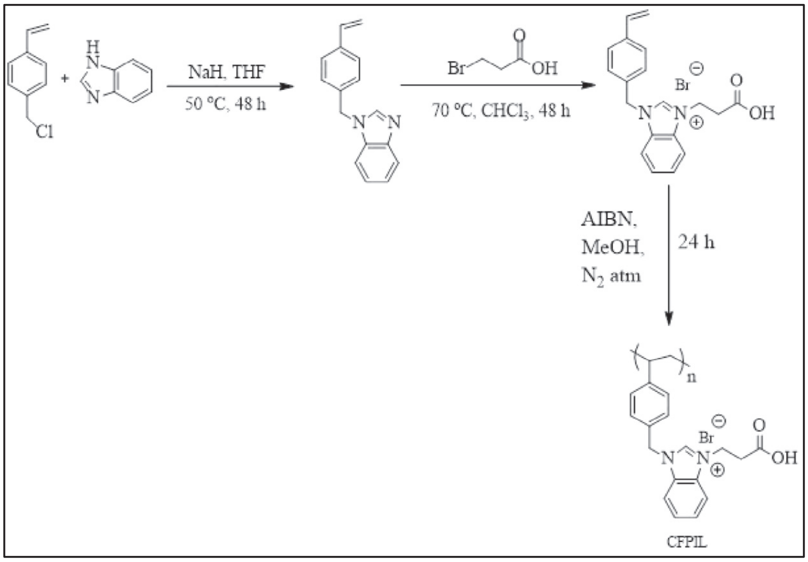
2.2.1. Synthesis of 1-(4-vinylbenyl)-1H-benzimidazole

1-(4-vinylbenyl)-1H-benzimidazole was synthesized according to the literature procedure [46]. In a typical method, THF solution of 4-vinylbenzyl chloride (8.44 g, 50 mmol) was added dropwise to a stirred solution of benzimidazole (5.9 g, 50 mmol) and sodium hydride (1.2 g, 50 mmol) at 50 °C in 150 mL THF and stirred for 48 h. After completion of reaction it was filtered and THF was removed by evaporation under vacuum. Dark brown oil was obtained, DCM was added and the organic layer was washed with deionized water (5 × 25 mL) and dried with Na_2SO_4, filtered and the DCM was removed by evaporation to get the yellowish solid of 1-(4-vinylbenzyl)-1H-benzimidazole (Yield 9.36 g, 80%).

2.2.2. Synthesis of carboxyl functionalized ionic liquid

1-(4-vinylbenyl)-1H-benzimidazole (7.02 g, 30 mmol) and 3-bromopropionic acid (4.56 g, 30 mmol) were mixed in 100 mL chloroform and heated at 70 °C for 48 h. The solid that appeared was filtered, and washed with chloroform (3 × 50 mL) to get the solid ionic liquid with polymerizable group (Yield: 5.8, 50.08%) [47,48].

^1H NMR (400 MHz, DMSO-d_6) δ: 12.67 (s, 1H), 9.99 (s, 1H), 8.15–8.13 (d, 2H), 7.94–7.92 (d, 2H), 7.67–7.65 (d, 2H), 7.49–7.47 (d, 2H), 6.75–6.68 (dd, 1H), 5.87 (d, 1H), 5.83–5.78 (s, 2H), 5.29–5.27 (d, 1H), 4.73–4.70 (t, 2H), 3.04–3.01 (t, 2H).



Scheme 1. Synthesis of carboxyl functionalized poly(ionic liquid)[CFPIL].

^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 171.79, 143.06, 137.47, 135.90, 133.41, 131.18, 130.65, 128.62, 126.64, 126.59, 115.23, 114.00, 113.89, 49.57, 42.80, 32.75.

2.2.3. Synthesis of carboxyl functionalized poly(ionic liquid)

For polymerization reaction, ionic liquid monomer (4.5 g, 11.65 mmol) and AIBN (0.466 mmol, 0.076 g) were mixed in a 100 mL methanol and refluxed at 70 °C for 24 h under nitrogen atmosphere. After 24 h, methanol was removed by Rotavapor to get the viscous polymer; diethyl ether was added and washed three times (3 × 30 mL) to get the white solid carboxyl functionalized poly(ionic liquid) as shown in Scheme 1 (Yield: 3.56 g, 79.11%).

^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 10.55 (s, 1H), 9.99 (s, 1H), 8.14 (s, 2H), 7.94 (s, 2H), 7.65 (s, 2H), 7.49 (s, 2H), 5.87 (s, 2H), 4.72 (s, 2H), 3.02 (s, 2H), 1.54 (s, 1H), 1.42 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 171.83, 143.04, 135.90, 133.37, 131.20, 130.68, 128.58, 126.61, 115.27, 113.98, 51.79, 49.59, 42.78, 32.70, 22.03 (Figs. 1–3).

2.3. Preparation of model oil and desulfurization

Model oil was prepared by dissolving thiophene in iso-octane (S-content 1500 ppm). In a typical desulfurization experiment, 10 mL model oil and 0.6 g CFPIL catalyst were added to 50 mL round bottom flask. Then the required amount

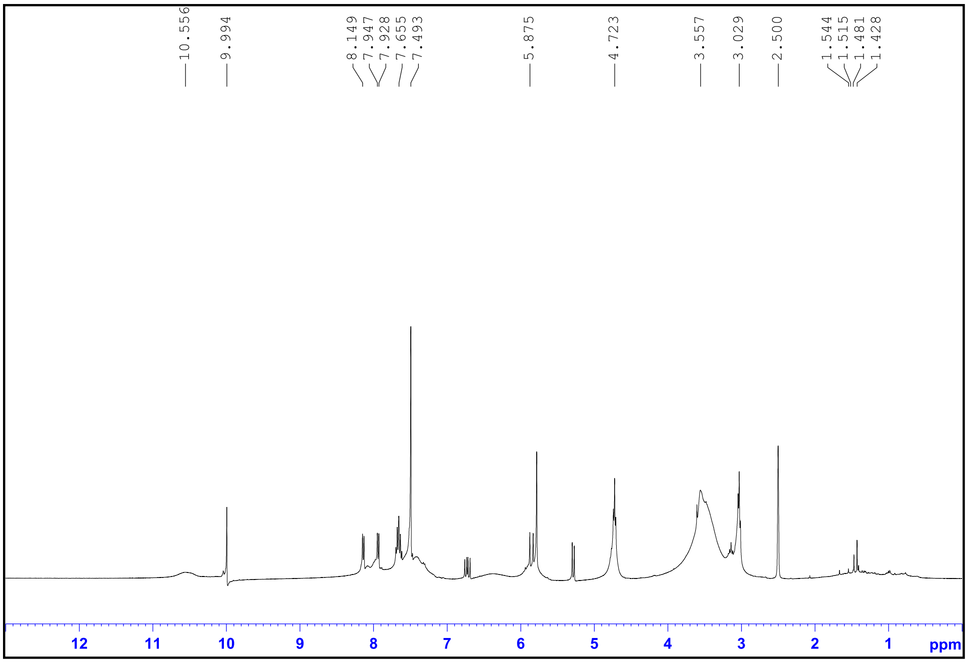


Fig. 1. ^{1}H NMR spectrum of carboxyl functionalized poly(ionic liquid).

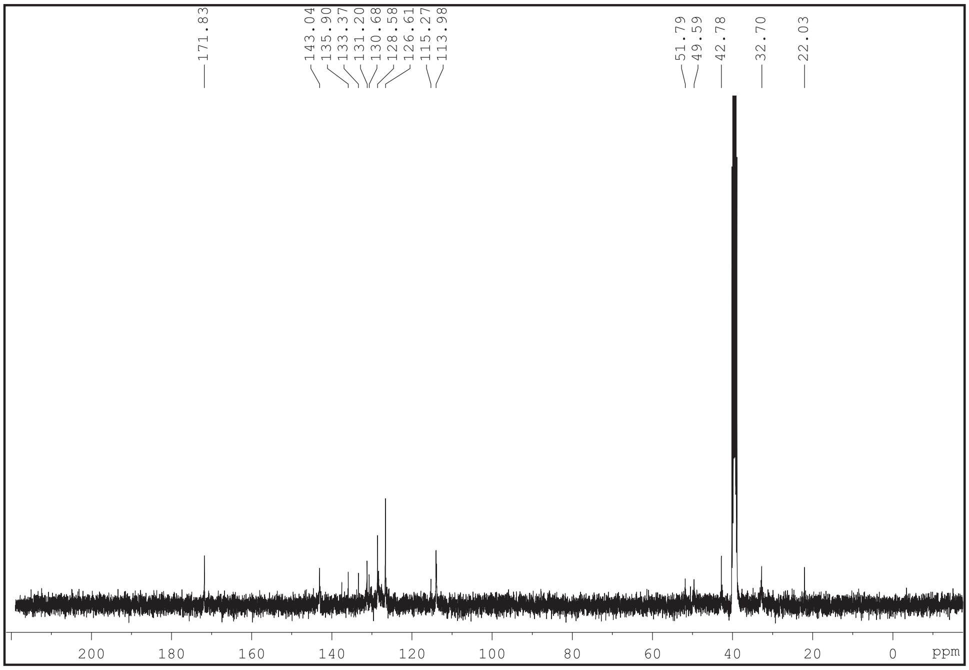


Fig. 2. ^{13}C NMR spectrum of carboxyl functionalized poly(ionic liquid).

of hydrogen peroxide (30 wt%) was charged and the resulting mixture was placed for a period of time at 70 °C with constant stirring. The mixture was settled for 5–10 min for phase-splitting and the upper oil phase was analyzed for the sulfur content. The lower aqueous phase containing catalyst was reused after regeneration.

2.4. *Sulfur content analysis*

The sulfur content of model oil was determined by gas chromatography (GC) using the internal standard method with n-hexane as the internal standard. After the oxidative desulfurization, the concentration of sulfur-containing compound in

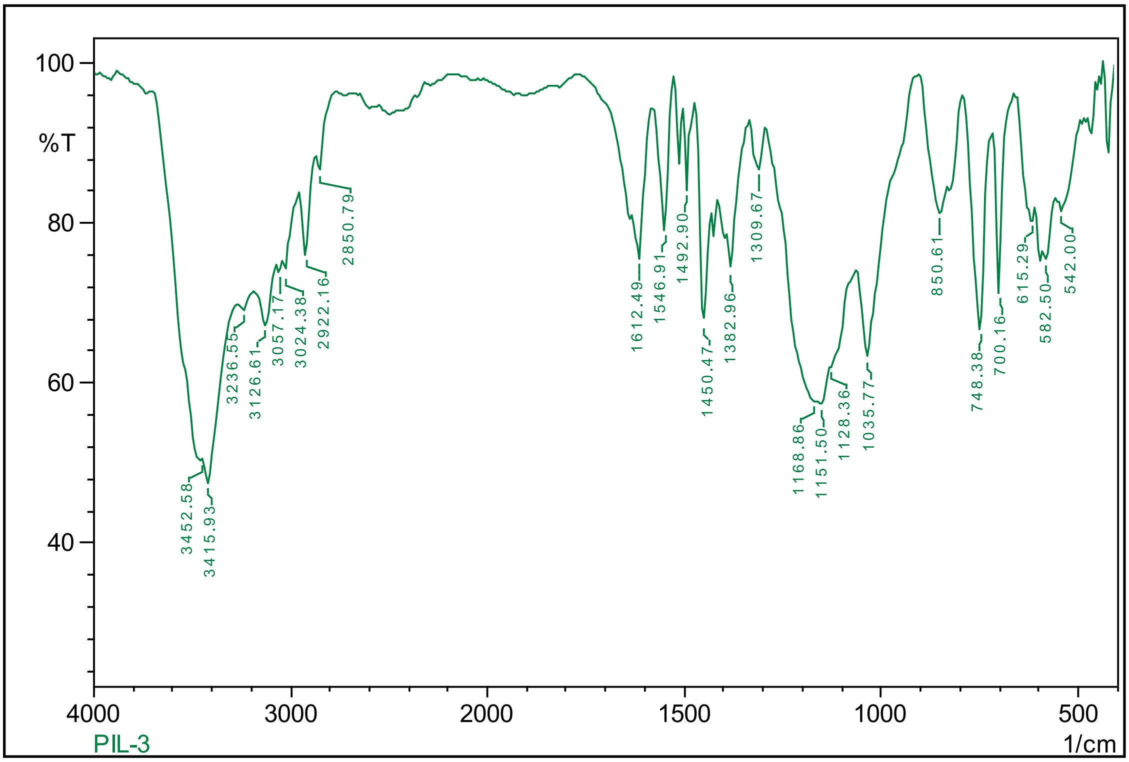


Fig. 3. FT-IR spectrum of carboxyl functionalized poly(ionic liquid).

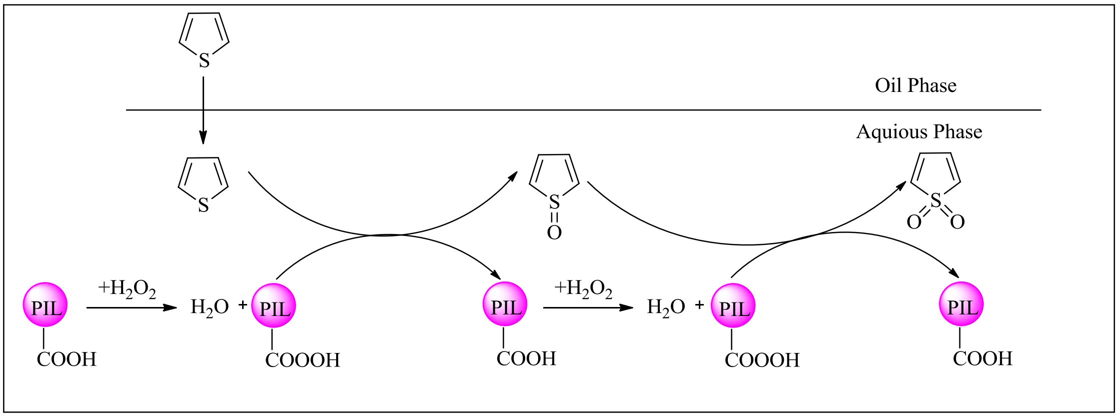


Fig. 4. Oxidative desulfurization of model oil by the CFPIL-H_2O_2.

the model oil was analyzed by a Gas Chromatography-Flame Ionization Detector (GC-FID) with n-hexane as the internal standard. The internal standard method for measuring the sulfur content of model oil has the advantages as compared to external standard method because it has high accuracy and reproducibility, and no error mixing with sample, and its retention time was similar to that of thiophene but their peaks could be completely separated.

The following are the gas chromatography conditions: Shimadzu GC-2010 plus, gas chromatograph (FID detector); injector temperature of 280 °C, a detector temperature of 300 °C. The column oven temperature was 70 °C for 1 min, and then it was heated to 150 °C at the rate 5 °C/min and kept for 2 min. Nitrogen was used as carrier gas.

3. Results and discussion

3.1. Oxidative desulfurization of model oil by the CFPIL

During oxidative desulfurization, thiophene in the model oil and the cation in the CFPIL with high polarity come into contact with thiophene to induce polarization of π-bond. The reaction mechanism of oxidative desulfurization, catalyzed by CFPIL, can be proposed in two steps (Fig. 4): firstly, the carboxylic acid group (−COOH) existing in the cation reacts with H_2O_2 in acidic environments, and a peroxycarboxylic acids group (−COOOH) with oxidation functions will be generated in situ. The thiophene in the reaction mixture is oxidized to its corresponding sulfoxide or sulfone by the peroxycarboxyl group, and the peroxycarboxyl ionic liquid is reduced to the original CFPIL. The oxidation product thiophene sulfoxide or sulfone, due to their high polarity, drives in aqueous phase (Fig. 5). GC-FID chromatograms of model oil in oxidative desulfurization showed that the concentration of thiophene in the model oil disappears completely during the process.

3.2. Effect of oxidative desulfurization conditions on the sulfur removal

3.2.1. Effect of oxidant dosage on the sulfur removal

In order to study the effect of the amount of H_2O_2 on catalytic oxidative desulfurization of thiophene, different H_2O_2/S (O/S) molar ratios were examined (Fig. 6). The removal of sulfur has improved with H_2O_2/S molar ratio up to H_2O_2:S 4:1 and then slightly reduced beyond this value. From the stoichiometry of the reaction, 1 mol of thiophene would require 2 mol of H_2O_2. On the other hand, the optimal value of O/S 4 was higher than the stoichiometric value of O/S 2. Once the O/S molar ratio raised from 1:1 to 4:1, the removal of thiophene

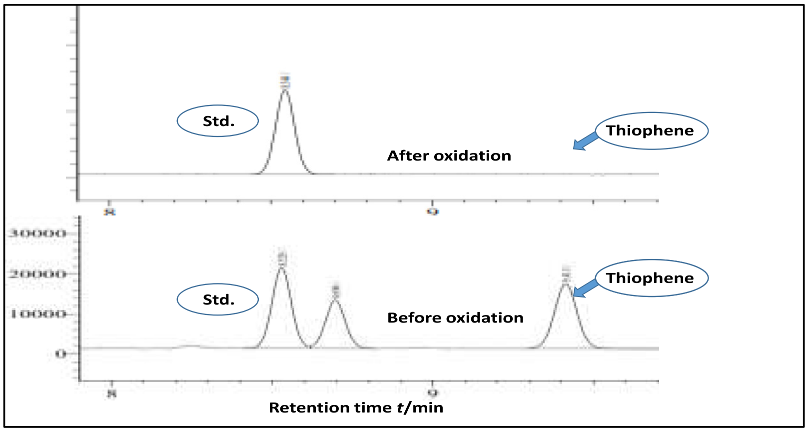


Fig. 5. GC-FID profiles of model oil before and after oxidation in oxidative desulfurization.

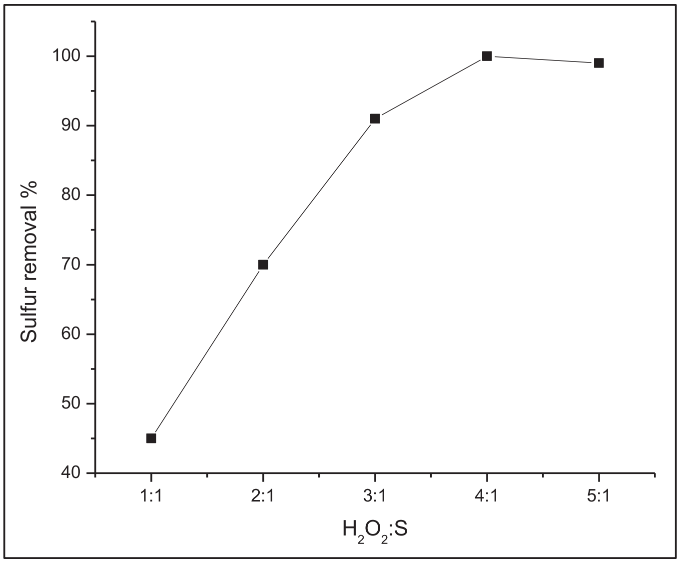


Fig. 6. Effect of oxidant dosage on the sulfur removal, reaction condition: 10 mL model oil, 0.6 g CFPIL, 70 °C, 3 h.

from the model oil improved from 45% to 100%. Thus, the O/S molar proportion 4:1 was the best ratio to attain deep desulfurization.

3.2.2. Effect of carboxyl functionalized poly(ionic liquid) dosage on the sulfur removal

To know the catalytic effect of CFPIL on oxidative desulfurization of thiophene, the desulfurization system containing optimized H_2O_2 and the catalyst was used in varying amounts. As shown in Fig. 7, when the quantity of CFPIL was increased from 0.1 g to 0.6 g, the sulfur removal increased noticeably from 19% to 100%, but there was no change in the desulfurization with increase in catalyst to 0.7 g. The result indicated that the amount of catalyst had a major consequence on removal of thiophene in the desulfurization reaction.

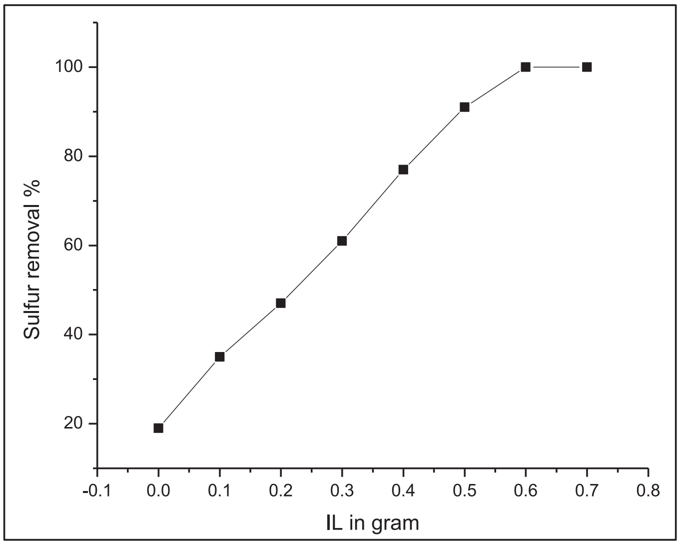


Fig. 7. Effect of CFPIL dosage on the sulfur removal reaction condition: 10 mL model oil, H_2O_2:S = 4:1, 70 °C, 3 h.

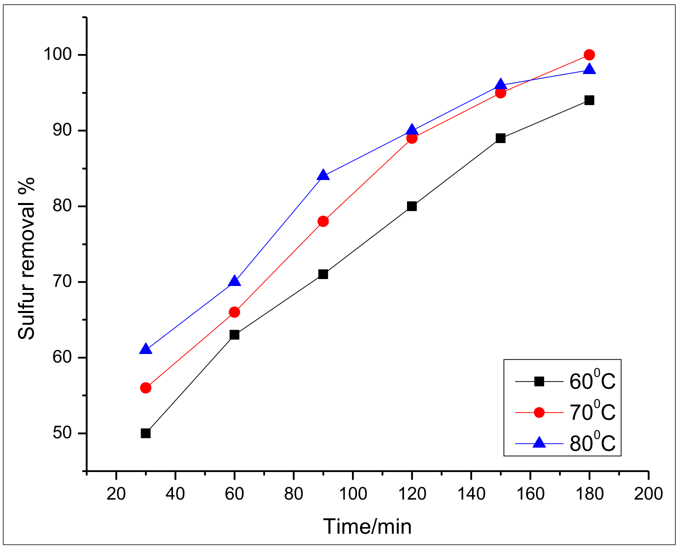


Fig. 8. Effect of reaction temperature and time on the sulfur removal reaction conditions: 10 mL model oil, H_2O_2:S = 4:1, 0.6 g (CFPIL).

3.2.3. Effect of reaction temperature and reaction time on the sulfur removal

In order to assess the role of the temperature and time on the oxidative desulfurization, the oxidation of thiophene was carried out in presence of CFPIL from 60 °C to 80 °C. Fig. 8 demonstrates oxidative desulfurization of thiophene on CFPIL at various temperatures and times. The catalytic oxidative desulfurization of thiophene at 60 °C, 70 °C and 80 °C was 50%, 56% and 61% for 30 min respectively and increases to 100% at 70 °C in 180 min. However, decomposition of H_2O_2 increases with higher temperature, which led to slightly lower sulfur removal (Fig. 8). Thus the rate of sulfur removal will no longer increase and even slightly decline at higher temperature. Hence, 70 °C was taken as the optimum reaction temperature in 180 min (3 h) for the best oxidative desulfurization.

3.3. Regeneration and recycling of the carboxyl functionalized poly(ionic liquid)

The recyclability of the CFPIL catalyst was studied on the removal of thiophene in catalytic oxidative desulfurization of thiophene system, as shown Fig. 9. After the oxidative desulfurization, the ionic liquid separated from the model oil phase is regenerated for recycling. Initially, the water in the ionic liquid was completely removed by rotary evaporation to get solid CFPIL. The recovered CFPIL solid was treated with acetonitrile (3 × 10 mL) to remove thiophene sulfone or sulfoxide. Finally, the regenerated CFPIL can be used to the next run for oxidative desulfurization reaction. The sulfur removal was 83% after the fifth cycle. So it may lead to the slight decline of catalytic activity in the recycles.

3.4. Oxidative desulfurization of real diesel fuel

In the preceding section, it was presented that thiophene in iso-octane can be successfully removed with CFPIL catalyst in

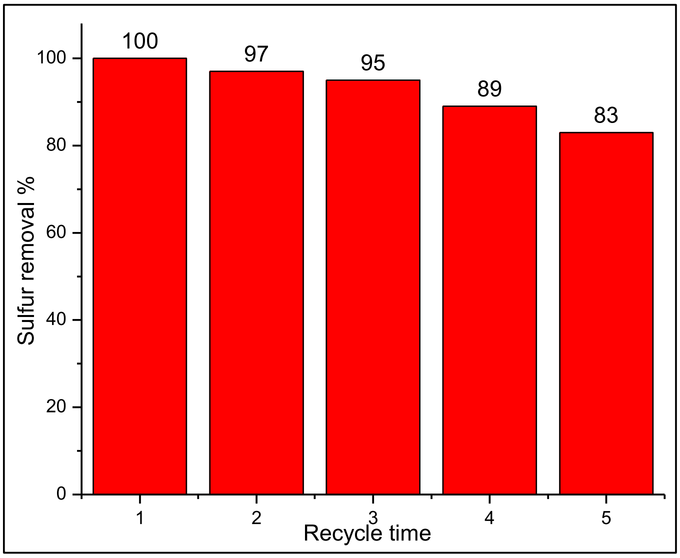


Fig. 9. Effect of ionic liquid recycling times on the sulfur removal reaction conditions: 10 mL model oil, 0.6 mL CFPIL, H_2O_2:S = 4:1, 70 °C, 3 h.

presence of H_2O_2. This protocol with optimized conditions was also verified for desulfurization of actual diesel fuel. It is well known that the real diesel fuel contains a combination of various sulfur-containing compounds, including thiophene, dibenzothiophene (DBT), benzothiophene (BT) and their alkyl-substituted derivatives. Zhao et al. [19] have described that BT and thiophene are very difficult to oxidize to form respective sulfones. It was observed that the oxidative desulfurization with CFPIL from actual diesel fuel is lower than that from model oil and the concentration of thiophene is reduced to 25% by using optimized conditions. This may be due to easier oxidation of other sulfur compounds compared to thiophene. These results propose that desulfurization of diesel fuel can be attained with this CFPIL–H_2O_2 system.

4. Conclusions

In this work, we have developed a new solid acidic CFPIL through the polymerization of acidic ionic liquid and characterized by various techniques. CFPIL showed high activity of oxidative desulfurization of thiophene at 70 °C in 180 min with 100% oxidation capacity. This protocol has shown high efficiency for the removal of thiophene, which is difficult to remove from the oil than benzothiophene and dibenzothiophene. The influences of hydrogen peroxide, amount of CFPIL, temperature, time and recyclability were investigated. 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. It was also observed that the loss of CFPIL, desulfurization activity, is negligible after 5 times of regeneration. This protocol was also verified with the real diesel fuel for the oxidative desulfurization and was found successful to remove sulfur compounds by using optimized conditions. This process may be an option to produce clean diesel fuels in industry for the removal of thiophene.

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