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Deep removal of sulfur from real diesel by catalytic oxidation with halogen-free ionic liquid

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Abstract−A halogen-free task-specific ionic liquid (TSIL) of 1-(2-carboxylic acid) ethyl-3-methylimidazolium bisulfate ([$(CH_2)_2$COOHmim] [HSO_4]) is applied for deep oxidative desulfurization of real diesel as a catalyst and reaction media. The sulfur level of real diesel can be reduced from 200 to 20.5 μg/g at room temperature with small amount of ionic liquid using H_2O_2 as an oxidant. The used ionic liquid can be easily recycled and no obvious decrease in catalytic activity can be found after recycling five times.

Key words: Desulfurization, Real Diesel, Catalytic Oxidation, Ionic Liquid, Task-specific

INTRODUCTION

Room temperature ionic liquids (RTIL), as a new kinds of designable materials, have aroused much interest not only as environmentally benign alternative solvents for separations, chemical synthesis, electrochemistry and catalysis, but also as functional materials, e.g. catalyst, template for inorganic synthesis. They possess favorable properties such as negligible vapor pressure, high polarity, non-flammability, easy handling, and good solvating capability to many substrates and catalysts. Therefore, RTILs are potential materials for wide applications, especially desulfurization of diesel fuel [1].

The extractive desulfurization (EDS) of fuels by ionic liquids (ILs) has been discussed for several years as an interesting alternative route to provide ultra clean diesel oils [2-8]. Clear advantages of EDS are that such a process would work at or around ambient temperature and pressure without the need for hydrogen. The efficiencies of sulfur removal, however, are rather low and in the range 10-30% [4]. Most recently, it has been reported that the efficiency of extraction increases if the S-species are previously oxidized to the corresponding sulfoxides or sulfones because the distribution coefficient of these species is much higher than that of non-oxidized derivatives. A halogen-free IL of 1-ethyl-3-methylimidazolium diethyl phosphate, [EMIM] [DEP] was used for multi-step extraction of oxidized sulfur compounds from model diesel (DBT) and real diesel [8].

Recently, oxidative desulfurization (ODS) has been suggested as one of the most promising processes [9-12], especially in ionic liquid media. In this process, the sulfur compounds are oxidized to the corresponding sulfones, which show larger polarity and are easy to remove in the subsequent extraction process by polar solvent. Many results for desulfurization of model diesel using the system (ionic liquid/H_2O_2/catalyst) have been reported [13-21]. Generally, the ionic liquids work as both reaction media and extracting solvent; catalysts such as polytungstates [13], V_2O_5 [14], heteropolyacid [15], Fe^{3+} [16], molybdic compounds [17], acetic acid [18-20], and formic acid [21] are added. All of those ionic liquids used are imidazolium tetrafluoroborate ([bmim] BF_4) or hexafluorophosphate ([bmim] PF_6) [13-21]. If the ionic liquids containing halogen atoms such as BF_4^- and PF_6^- anions are used, white fumes of HF or hydrate precipitates are formed easily, leading to environmental and safety problems. Also, the ODS of real diesel in ionic liquid is not well studied.

On account of their designable character of ionic liquid, the variation in properties as a consequence of small changes in molecular structure has greatly made it promising for wide applications. Recently, attempts have been made to design task-specific ionic liquid (TSIL) having the function of both catalyst and reaction media. According to Zhao et al., N-methyl-pyrrolidonium tetrafluoroborate ([Hnmp][BF_4]) is an effective ionic liquid catalyst for ODS of diesel [22]; however, relatively high quantity of ionic liquids corresponding $V_{IL}/V_{diesel}=1:1$ was used and the anion of TSIL contains halogen atoms.

Therefore, more task-specific and halogen-free ionic liquids need to be designed which can work as both catalyst and reaction media for ODS process especially for real diesel.

In our previous studies, several types of task specific ILs have been synthesized and used in all kinds of applications such as Beckmann rearrangement [23], alkylation [24], esterification [25,26], Biginelli Reaction [27], oxidation [28,29], polymerization [30] and especially desulfurization [3,31,32]. Several different ILs were applied for extractive desulfurization of diesel to study the extraction capability of different cations and anions of ILs, and it was found that [$(CH_2)_4SO_3$Hmim] [Tos] revealed highest capacity for S-compounds extraction from diesel fuel [3]. When this IL was applied as a reaction media for ODS of S-compounds in real diesel using Na_2WO_4 as a catalyst and H_2O_2 as an oxidant, high desulfurization results were obtained [32]. Based on these previous results, a series of halogen-free task-specific ILs with two Brönsted acid sites were synthesized firstly in our group and showed good desulfurization performance for model diesel [31]. In this study, a halogen-free task-specific IL [$(CH_2)_2$COOHmim] [HSO_4] was applied as a catalyst

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Table 1. Pre-hydrotreated diesel properties

Density (293 K) (g/ml)	0.855
Viscosity (293 K) (mm^2/s)	4.069
Total Sulfur (ppm)	200
Total Nitrogen (ppm)	12
Aromatics (wt%)	41.2
Distillation temp. (°C)	
Initial boiling point (IBP)/10%	172/222
30%/50%	245/264
70%/90%	293/335
95%/Final boiling point (FBP)	356/358

and reaction media in the deep ODS of commercial diesel. Our interested diesel is pre-desulfurized by HDS and difficult for deep desulfurization. To the best of our knowledge, it is the first trial to use halogen-free TSIL in the ODS of real diesel without adding additional catalyst at room temperature. This provides a potential deep desulfurization candidate for industrial application.

EXPERIMENTAL

1. Materials and Reagents

All solvents and chemicals in the experiment were commercially available and used without further purification. Pre-hydrotreated commercial diesel containing 200 μg/g S from Fushun Research Institute of Petroleum and Petrochemicals in SINOPEC was used for deep oxidative desulfurization; its properties are listed in Table 1.

2. Preparation of Ionic Liquid

The ionic liquid, $[(CH_2)_2COOHmim] [HSO_4]$ was synthesized by a two-step method through 1-methylimidazole combined first with 3-chloropropionic acid to form zwitterions salts, followed by addition of concentrated sulphuric acid (97%). The detailed preparation procedure is in our previous work [26].

3. Oxidative Desulfurization of Real Diesel

The oxidative desulfurization was carried out in a 50-mL round-bottom flask. In a typical run, 3 ml of predesulfurized diesel (200 μg/g S), 0.3 ml of 30 wt% H_2O_2 and 6 mmol of IL were added to the flask and the mixture was stirred vigorously at room temperature (298 K) for 210 min. In static condition, the reaction mixture exists as two phases; the upper diesel phase can be separated easily from the lower ionic liquid phase by decantation or by a separating funnel. Then the separated diesel phase was extracted by N-methyl-2-pyrrolidone (NMP) to remove residual oxidized sulfur compounds. The sulfur content in diesel was measured by a microcoulometric detector. The sulfur compounds were identified by gas chromatography coupled with an atomic emission detector (GC-AED).

Analysis of peroxycarboxylic acids: The concentration of peroxycarboxylic acid was tested according to the methods in our previous study [31]. In a typical run, 120 mmol IL and 10 mL 30% H_2O_2 were added in 50 ml clean ground-glass flasks, and well mixed by stirring (500 rpm) for 210 min at different temperatures. Samples were obtained from the reactant mixture by a plastic syringe (to avoid contamination of the solution by trace of metals) and analyzed by the Greenspan and Mackellar method [33]. Each datum was the average result of at least double tests.

4. Recycling of Used Ionic Liquid

The used ionic liquid was dried under vacuum at 383 K for 4 h, then the fresh diesel and hydrogen peroxide were added the recycled IL for the next run.

RESULTS AND DISCUSSION

1. Effect of Reaction Time on Sulfur Removal

Fig. 1 shows the effect of reaction time on catalytic oxidative desulfurization catalyzed by TSIL $[(CH_2)_2COOHmim] [HSO_4]$ at 298 K. The desulfurization occurs quite fast and the sulfur content drops from 200 μg/g to 45.8 μg/g within 20 minutes. The sulfur content in diesel decreases continuously with increasing reaction time and reaches to 20.4 μg/g after 210 min. Further reaction does not result in lower sulfur content, which indicates that the oxidation reaction ends within 210 min.

2. Effect of Reaction Temperature

To see the effect of reaction temperature, catalytic oxidation was

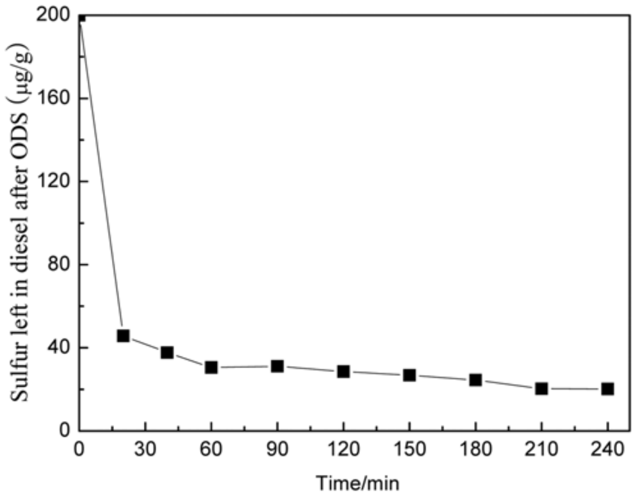

Fig. 1. Effect of reaction time on ODS (*Conditions*: 3 ml real diesel, 0.5 ml 30 wt% H_2O_2, 6 mmol IL, 298 K, V_{NMP}/V_{diesel}=1 : 1).

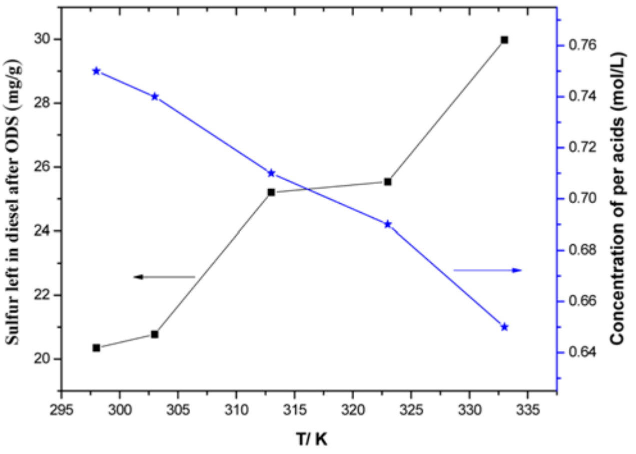

Fig. 2. Oxidative desulfurization results and mole concentrations of peroxycarboxylic acid vs. reaction temperatures (Conditions: 3 ml real diesel, 0.5 ml 30 wt% H_2O_2, 6 mmol ionic liquid, 210 min, V_{NMP}/V_{diesel}=1 : 1).

carried out at five different temperatures (Fig. 2). Interestingly, with the increase of reaction temperature, the desulfurization capability decreased. This can be explained by the concentration of peroxycarboxylic acid formed by the reaction of these TSILs with hydrogen peroxide. The peroxycarboxylic acid generated in-situ is expected to be the active species for oxidation reaction. Thus, it was of interest to explore the formation of peroxycarboxylic acid under different temperatures.

As shown in Fig. 2, increasing temperature would result in gradual decrease of the concentration of peroxycarboxylic acid on account of its unstable character, i.e., the peroxy acid -COOOH concentration will decrease due to its self decomposition under higher temperature. This finally leads to the decrease of the ODS performance with the increase of temperature. To check that the oxidation of aromatics present in diesel occurs competitively with sulfur compounds, oxidation of toluene, as a model aromatic compound, was carried out at the same oxidation condition. However, it was found that toluene could not be oxidized under 323 K (data not given here). Therefore, it is thought that lower temperature is more favorable to obtain high ODS performance, and the optimum reaction temperature is 298 K (room temperature), providing an energy-saving ODS process. The sulfur level of diesel could be reduced from 200 to 20.3 μg/g at 298 K, which can reach the requirement of deep desulfurization.

3. Effect of Ionic Liquid Amount

The effect of ionic liquid amount on oxidative desulfurization was also investigated. On account of the immiscibility of H_2O_2 solution with diesel oil, little possibility of direct oxidation of sulfur compounds using H_2O_2 in the absence of ionic liquids could be found (See Fig. 3). High conversion could be obtained even with small amount of ionic liquid. Only with 0.4 mmol of IL for 3 ml diesel could the sulfur level be reduced from 200 μg/g to 35.02 μg/g, which corresponds to the removal of 82.4% sulfur. This indicates that the used TSIL is quite effective catalyst for deep ODS. There was no improvement in sulfur removal with more than 6 mmol of TSIL.

4. Effect of the Oxidant Amount

To see the efficiency of hydrogen peroxide as an oxidant, ODS was carried out while changing hydrogen peroxide amount (Fig. 4). In the absence of the oxidant H_2O_2, partial sulfur compounds are extracted to the ionic liquid phase, so the ionic liquid here works as a phase-transfer catalyst, i.e., sulfur compounds are extracted and then oxidized in ionic liquid phase. The increase of the oxidant amount led to better desulfurization result. The sulfur level of diesel (3 ml) could be reduced to 36 μg/g with 0.08 ml of 30 wt% H_2O_2. To further reduce sulfur level to 20 μg/g requires 0.3 ml of H_2O_2.

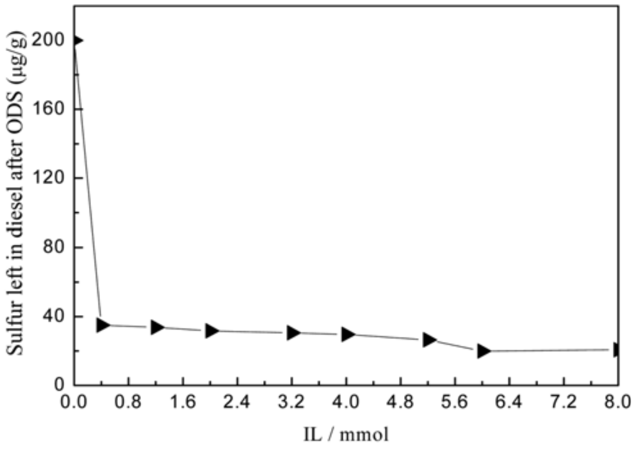

Fig. 3. Effect of ionic liquid amount on ODS (Conditions: 3 ml real diesel, 0.5 ml 30 wt% H_2O_2, 210 min, 298 K, V_{NMP}/V_{diesel}=1 : 1).

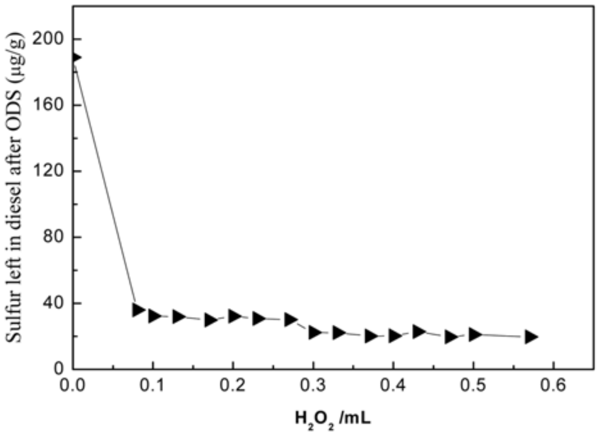

Fig. 4. Effect of oxidant amount on ODS (Conditions: 3 ml real diesel, 6 mmol IL, 210 min, 298 K, V_{NMP}/V_{diesel}=1 : 1).

5. Catalytic Oxidation Activity and Effect of Extractant Amount

The optimum oxidation reaction conditions are listed as follows: 3 ml pre-desulfurized diesel, 6mmol ionic liquid, 0.3 ml 30 wt% H_2O_2, 298 K, and 210 min. After oxidation, the system separated into two phases: the upper diesel phase and the lower ionic liquid phase. The ionic liquid and diesel phases can be separated easily by decantation, and the sulfur content of diesel drops from 200 to 114 μg/g and the DBT alkyl derivatives are transformed completely into oxidized S species (Fig. 5(a)→(b)). This indicates that the acidic TSIL has high catalytic oxidation activity for the refractory sulfur compounds existing in real diesel.

Because some of the produced sulfones have low solubility in IL, they exist in diesel phase. So an additional extraction step by NMP as a solvent is required. The amount of NMP required is decided by the content of sulfones in the diesel phase. To extract the produced sulfones from real diesel phase, NMP corresponding equal

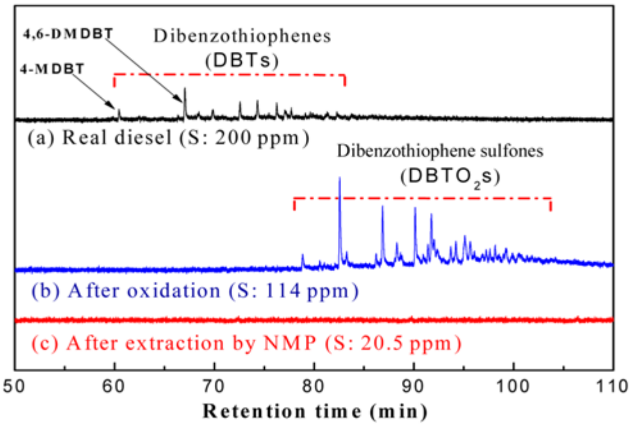

Fig. 5. Sulfur-specific GC-AED chromatograph of real diesel (a) before oxidation, (b) after oxidation and (c) after extraction by NMP.

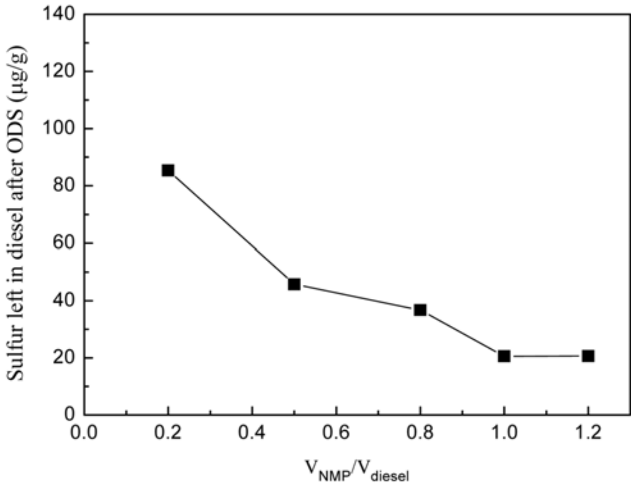

Fig. 6. Effect of extractant amount on ODS (Conditions: 3 ml real diesel, 0.3 ml 30 wt% H_2O_2, 6 mmol IL, 210 min, 298 K).

volume of diesel is required (See Fig. 6). That is, at V_{NMP}/V_{diesel} ratio of 1, the desulfurization reached a maximum value of 89.75% and only 20.5 μg/g of sulfur remained in diesel phase (Fig 5(c)). Future work on sulfones extraction in this process with different ILs is being carried out in our group.

6. Recycling of TSIL

For the technical application of the TSIL, the subsequent recycling of the TSIL is of vital importance. Water and part of sulfones produced in oxidation reaction was in ionic liquid phase. To examine the reusability of the TSIL, the ionic liquid phase was dried under vacuum at 383 K for 4 h to remove water, and then fresh real diesel and H_2O_2 were added to this recycled TSIL for the next run. All the S-species in real diesel was oxidized completely even after recycling 5 times. As shown in Fig. 7, it could be seen that the TSIL was recycled five times without any apparent loss on desulfurization capability. Therefore, this TSIL turns out to be a potential ODS catalyst for industrial use.

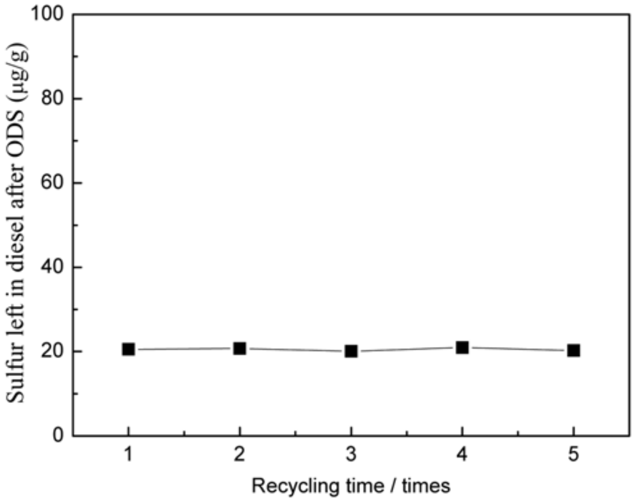

Fig. 7. Recycling of IL on ODS (Conditions: 3 ml real diesel, 0.3 ml 30 wt% H_2O_2, 6 mmol IL, 210 min, 298 K, V_{NMP}/V_{diesel}= 1 : 1).

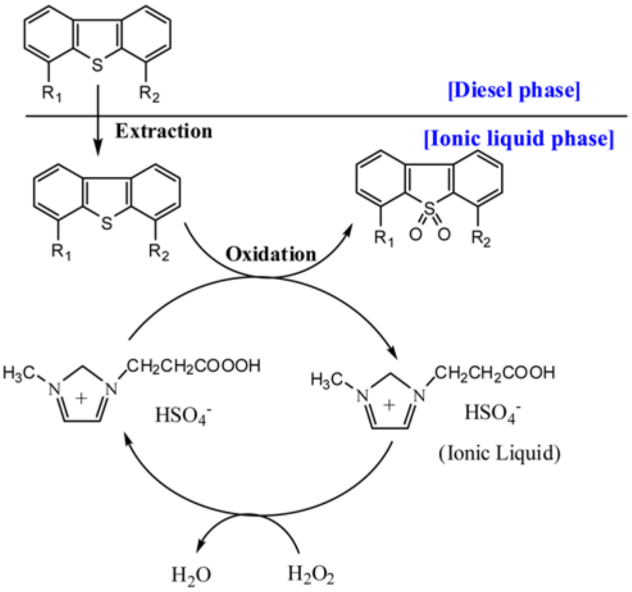

Fig. 8. Catalytic oxidative desulfurization mechanism in the task-specific ionic liquid ($[(CH_2)_2COOHmim]\ [HSO_4]$).

7. ODS Mechanism Catalyzed by this TSIL

According to previous publication and the above results on ODS of real diesel in this study, the TSIL works as both the catalyst and reaction media in the process and reaction mechanism can be suggested as in Fig. 8.

Alkyl dibenzothiophene is the major refractory sulfur compound remaining in the diesel and is extracted into the ionic liquid phase; meanwhile, the -COOH group in ionic liquid reacts with hydrogen peroxide and accepts the active oxygen atom to form peroxycarboxylic group (-COOOH) which is active species for the oxidation of sulfur compounds and transforms to the original form of TSIL by itself. Due to the presence of H_2O_2, the reaction of TSIL with H_2O_2 continues and then a new cycle begins.

CONCLUSIONS

A halogen-free TSIL of $[(CH_2)_2COOHmim][HSO_4]$, as a catalyst and reaction media, was applied firstly for deep ODS of real diesel. The refractory S compounds in real diesel predesulfurized by HDS can be completely oxidized to sulfones with small amount of ionic liquid at room temperature. Also, the diesel phase after ODS can be easily separated by decantation and then remove oxidized S species by extraction with NMP. After the ODS process, the sulfur content of diesel can be decreased from 200 μg/g to 20.5 μg/g, corresponding to the sulfur removal efficiency of 89.8%. The used TSIL can be recycled just by vacuum drying and revealed almost same ODS activity as that of fresh one even after five times of recycling. Good oxidation activity and reusability of TSIL, the convenience in separation of diesel from TSIL and room temperature conditions make it a potential deep ODS process for industrial use.

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