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A combination desulfurization method for diesel fuel: Oxidation by ionic liquid with extraction by solvent

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ABSTRACT

Ionic liquids (ILs) are intensively studied in the oxidative desulfurization of diesel fuel, where ILs act as both extractants and catalysts with adding another oxidant such as H_2O_2 solution. Some thiophenic sulfur compounds can be effectively removed from some model diesel fuels with this method, while it is hard to reduce the sulfur content to a desirable level like less than 10 ppm with this method when people investigated the real diesel fuels. In this work, we developed a new combination desulfurization method, first oxidative desulfurization by ILs as both extractants and catalysts with 30 w% H_2O_2 as oxidant, then followed by desulfurization by solvent extraction. Four ILs and ten solvents were investigated for real diesel fuels. The effects of different factors on desulfurization performance were systematically studied, e.g., ILs species, solvents species, temperature, time, IL/oil mass ratio, extractant/oil mass ratio, multiple desulfurization, regeneration of ILs and solvents. The results show such a combination method is effective to reduce the sulfur content in real diesel fuels to a desirable level, e.g., the sulfur content in FCC diesel fuel was reduced to 8.1 ppm from original 150 ppm after one step oxidation by $[(CH_2)_4SO_3HMIm][Tos]$ (ILs/oil mass ratio of 1/2; 3 h, 348.15 K, O/S molar ratio of 40/1) and two-step extraction by DMF (extractant/oil mass ratio 1/2, 30 min, 298.15 K). ILs and solvents can be regenerated and recycled with negligible activity loss.

1. Introduction

Desulfurization of fuel oils is an important process in oil refining and the hydrodesulfurization (HDS) is widely employed in industry [1]. Increasing environmental concerns, more stringent statutory limits imposed on sulfur content (S-content) in fuel oils [2,3], and the ineffectiveness of HDS to remove aromatic and hindered structure of S-compounds have driven researchers to seek alternative desulfurization methods to HDS. Some alternative methods to HDS such as oxidation, adsorption, extraction, and bioprocesses have been studied, among which oxidative desulfurization (ODS) is more competitive, since ODS is efficient in removing the thiophenic S-compounds under mild conditions with low costs [4–10]. Studies on ODS using ILs [11] have been reported recently in literatures [12–15]. It has been observed that ODS using ILs which served as both extractants and catalysts can effectively remove those HDS-immune cyclic S-compounds and reduce the S-component in fuel oils [16–18], which presents a good industrial prospect.

Most works, however, were focused on the investigation of model diesel fuel. However, ODS of the real oil is rarely studied and the desulfurization efficiency is not ideal as shown in Table 1 [3,13,14,16]. In practice, multistage ODS of the real oil using ILs still cannot effectively desulfurization [16,18] and can't meet the requirement of stringent legislation [19–24]. For example, in our previous work, we observed the S-content of real FCC diesel fuel (the initial S-content is 224.6 ppm) can be reduced to 37.4 ppm with 83.3% S-removal efficiency after five stages by [Hnmp]Cl/$ZnCl_2$. The reason that may lead to low desulfurization performance of real diesel fuel was described [25–28], i.e., the more complex S-compounds in real diesel fuel and the sulfones formed from oxidation of S-compounds might remain in oil phase [28,29]. We also found that the S-content in real fuel can be reduced to 5.3 ppm with 97.6% S-removal efficiency when used furfural as extractive reagent to treat the fuel after six stage of ODS (mass ratio of furfural to oil, 1:3; 20 min; 30 °C) by [Hnmp][$ZnCl_3$] [18]. Therefore, coupled oxidation-extraction desulfurization is a kind of effective method of desulfurization and a more systematic investigation for this method for real diesel

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Table 1
Oxidative desulfurization of real oils by ILs.

ILs	Real oil (initial S-content)	S-removal efficiency	Reaction condition	Ref.
$[C_8^3MPy]FeCl_4$	gasoline (468 ppm)	44.2%	T, 298 K; t, 30 min; mass ratio of IL/Oil, 1/3; O/S, 6	[3]
$[C_4mim]Cl/3ZnCl_2$	FCC diesel fuel (460 ppm)	63.5%	T, 318.15 K; t, 3 h; mass ratio of IL/Oil, 1/2; O/S, 60	[13]
$[Hnmp][H_2PO_4]$	diesel fuel (750 ppm)	64.3%	T, 333.15 K; t, 5 h; volume ratio of IL/Oil, 1/1; O/S, 16.	[14]
[(CH2)4SO3HMIm][ZnCl3]	deisel fuel (225 ppm)	40.7%	T, 333 K; t, 3 h; mass ratio of IL/Oil, 1/2; O/S, 30	[16]
$[(CH_2)_4SO_3HMIm][Tos]$	deisel fuel (225 ppm)	43.7%	T, 348 K; t, 3 h; mass ratio of IL/Oil, 1/2; O/S, 40	[16]

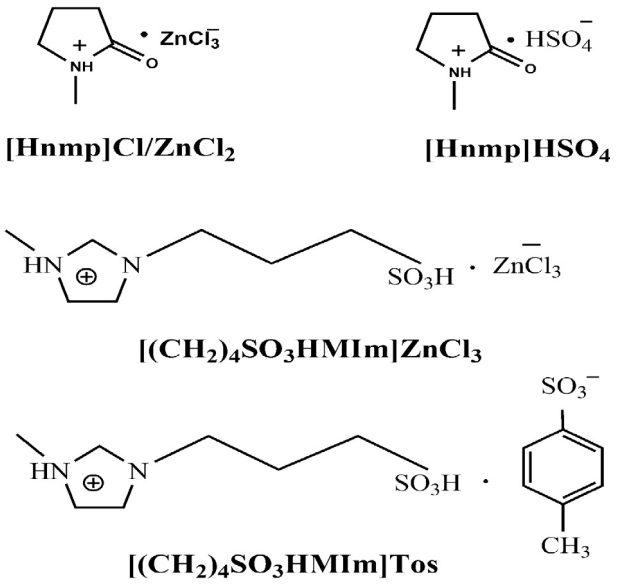

Fig. 1. Structures of the ILs used in this work.

fuel is desired.

In this work, we synthesized four ILs, i.e., N-methylpyrrolidonium sulfuric acid ([Hnmp][HSO_4]), 1-methyl-3-(4-sulfonic acid butyl) imidazole zinc chloride ([$(CH_2)_4SO_3HMIm$][$ZnCl_3$]), 1-methyl-3-(4-sulfonic acid butyl) imidazole p-toluenesulfonic acid ([$(CH_2)_4SO_3HMIm$][Tos]) and N-methylpyrrolidonium zinc chloride ([Hnmp][$ZnCl_3$]) (the structures are shown in Fig. 1) and studied their multiple oxidative desulfurization under the optimal conditions. On the basis of oxidative desulfurization by [$(CH_2)_4SO_3HMIm$][Tos], the coupled oxidation-extraction desulfurization of real diesel fuel were investigated by selected extraction agents. The influences, on extractive desulfurization, of temperature, time, mass ratio of extractants/oil, extractive stage, multiple desulfurization and extractants recyclability and multi-stage desulfurization were investigated for selected 1, 4-butyrolactone and DMF. This work will show that such coupled oxidation-extraction desulfurization method are capable of removing S-compounds effectively from real diesel fuel. To the best of our knowledge, it is the first time to research the coupled oxidation-extraction desulfurization with the organic solvent as extraction agent in detail.

2. Experimental

2.1. Materials

The materials and suppliers are as follows: N-methylimidazole (> 99%), Shanghai Senhao Fine Chemical; 1-methyl-2-pyrrolidone (≥99.0%), Tianjin Fu Chen Chemical Reagents Factory; 1,4-butane sultone (≥98%), J&K Chemical; zinc chloride, H_2O_2 (aqueous solution, 30 w%), hydrochloric acid, concentrated sulphuric acid, toluene, anhydrous ether, ethyl acetate, ethylene glycol, furfural, acetic acid, ethanol, glycol ether, furfuryl alcohol, 1, 4-butyrolactone, N,N-Dimethylformamide (DMF) and acetonitrile, Beijing Chemical Plant. Coker diesel fuel (S, 150, 225, 270, 2000 ppm) was supplied by SINOPEC Beijing Yanshan Petrochemical Co., Ltd. N-methylimidazole was further purified by distillation and the other chemicals were used as received.

2.2. Procedure

2.2.1. Preparation of ILs and real fuel oil

Synthesis of [Hnmp][HSO_4], [$(CH_2)_4SO_3HMIm$][$ZnCl_3$], [$(CH_2)_4SO_3HMIm$][Tos] and [Hnmp][$ZnCl_3$] are offered in other previous papers [16,18,27–29]. The different S-content of FCC diesel fuels obtained from Sinopec.

2.2.2. Desulfurization and analysis

In a typical ODS experiment, IL, H_2O_2, and diesel fuel were added into a 100 ml round-bottom flask and reacted with magnetic stirring at a certain temperature in a certain time. Then the mixture was settled for 5 min for phase-splitting and the upper oil phase was analyzed. In a coupled oxidation-extraction desulfurization, the separated diesel phase after oxidation were placed in a round-bottom flask with extractant and magnetically stirred at a specified temperature. After a certain time of extraction, the mixture was laid aside for 5 min for phase separation and settling. The upper oil phase was then analyzed. In this work, where first, ODS is carried out under the optimal experimental conditions with ILs; second, after oxidation, the diesel phase was extracted with organic solvents separately to remove residual sulfones in oil phase. S-content in diesel fuel was analyzed by WK-2D integrated micro-coulomb analyzer (Jiangfen Electroanalysis Co., Ltd.).

3. Results and discussion

3.1. Oxidative desulfurization

3.1.1. Multiple oxidative desulfurization

The optimal experimental conditions of oxidative desulfurization of real diesel by ILs, i.e., [Hnmp][HSO_4], [$(CH_2)_4SO_3HMIm$][$ZnCl_3$], [$(CH_2)_4SO_3HMIm$][Tos] and [Hnmp][$ZnCl_3$] are investigated. Because the detailed results of investigating the desulfurization conditions were given in our previous works [13,16,18], only the major results used in the present work are summarized briefly in Table 2. Eight-step oxidative desulfurization under the optimal conditions by these four ILs are shown in Fig. 2. The results show that [$(CH_2)_4SO_3HMIm$][Tos] has the highest one-step oxidative desulfurization efficiency following the order [$(CH_2)_4SO_3HMIm$][Tos] > [$(CH_2)_4SO_3HMIm$][$ZnCl_3$] > [Hnmp][HSO_4] > [Hnmp][$ZnCl_3$] with the efficiency of 43.7%, 40.7%, 38.6%

Table 2
Optimal conditions of oxidative desulfurization by ILs.

ILs	temperature	time	mass ratio of IL/Oil	mole ratio of O/S
[Hnmp][HSO_4]	60 °C	3 h	1/2	12
[$(CH_2)_4SO_3HMIm$][$ZnCl_3$]	60 °C	3 h	1/2	30
[$(CH_2)_4SO_3HMIm$][Tos]	75 °C	3 h	1/2	40
[Hnmp][$ZnCl_3$]	75 °C	3 h	1/2	50