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Environmentally Evaluation for Desulfurization of Gas Oil with [BMIM][$FeCl_4$] based on Catalytic Ionic Liquids at Room Temperature

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Environmental concerns have driven the need to remove sulfur-containing compounds from fuel. The removal of sulfur compounds from fuel (gas oil) with [BMIM][$FeCl_4$] based ionic liquids as catalyst were systematically investigated. The results show that the absorption capacity of an ionic liquid for the sulfur compounds in gas oil relies on its structure and its size. In the case of the examined gas oil, both the cation tail length and the time adsorbed ionic liquid with gas oil promote the desulfurization ability of the examined ionic liquids. The results also show that imidazolium-based ionic liquid have high extraction efficiencies, presumably owing to the fact that the rings of the sulfur compounds are similar to the imidazolium head ring. With the 1: 5 mass ratio of ionic liquid / gas oil, the rates of the desulfurization of gas oil reach 80.0, 88.5 % within the first 60 and 90 min respectively. It is found [BMIM][$FeCl_4$] based ionic liquids has the best effect on the selective removal of sulfur-containing compounds from gas oil at room temperature. Moreover the results show that the kinetics of desulfurization of gas oil can be described well with the first-order equation.

Key words: Absorption, Ionic liquid, Sulfur removal, Gas oil.

Emissions of sulfur oxides cause serious impact on human and environment, both directly and as a result of the way they react with other substances in the air. Sulfur oxides are main precursors of atmospheric acidification, aerosol generation, and acidic dry and wet deposition[1].

Sulfur in a gaseous state mixes with oxygen to form sulfur dioxide, which is hazardous. Inhalation of sulfur fumes causes irritation of the eyes, nose and respiratory track, which leads to headaches, dizziness and nausea. High levels of sulfur can burn the skin, and it can also cause pulmonary edema, a condition in which the lungs are filled up with fluids. Inhaling sulfur may also cause coughing, sneezing or labored breathing (El Kady, *et al*, 2010). When sulfur dust comes into contact with oxygen to become sulfur dioxide, it has serious environmental hazards. It affects the living organisms around the area. Sulfur causes vascular damage in veins of the brain, the heart and the kidney. Sulfur can also cause damage to the internal enzyme systems of animals.

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Diesel engines play a vital role in world economy, especially in transportation. Exhaust from traditional diesel engines using high-sulfur fuel contains high concentrations of respirable carbonaceous particles with absorbed organic compounds. Recognition that some of these compounds are mutagenic has raised concern for the cancer-causing potential of diesel exhaust exposure.

The International Agency for Research on Cancer (1989) classified whole diesel exhaust as - “probably carcinogenic to humans”. This classification stimulated even more stringent regulations for particulate matter that required further technological developments. These included improved engine control, improved fuel injection system, enhanced exhaust cooling, use of ultra low sulfur fuel, wall-flow high-efficiency exhaust particulate filters, exhaust catalysts, and crankcase ventilation filtration[2-4].

Deep removal of sulfur from fuels, particularly from gasoline and diesel, has been an important and challenging issue in worldwide petroleum refining industry, which is not only due to increasingly stringent environmental regulations on sulfur concentration of transport fuel, but also because of the great importance for making ultra-low-sulfur fuels for fuel cell applications[5-7].

Refinery industry utilizes catalytic processes for desulfurization of transportation fuels through hydroprocessing. While the performance of conventional hydroprocessing catalysts have been highly effective for the reduction of sulfur levels, further removal of residual sulfur from the processed fuels is seen to largely increase the cost of hydroprocessing. The processes are highly energy intensive and consume large amount of hydrogen[9-11].

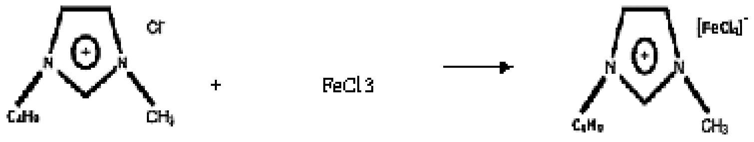
Ionic liquids have been studied for possible applications related to green chemical processes, such as liquid/liquid extractions, gas separations, electrochemistry and catalysis[12, 13]. These liquids are easy to handle because of no-volatility, non-flammability, and high thermal stability. Therefore they pose little environmental harm. Ionic liquids are widely used in extraction, desulfurization, and scale removal because of their excellent solubility and catalytic properties in a wide temperature range[14-16].

In this work, the absorption of gas oil was studied using the modified ionic liquid with different ratio.

EXPERMINTAL

Preparation of [BMIM][$FeCl_4$] Based Ionic Liquids

The synthesis of the modified ionic liquid is as follows. Under the protection of nitrogen, the modified ionic liquid (dual-functionalized ionic liquid) was prepared by simple addition of metal chloride to imidazolium cations (imidazolium chloride) (molar ratio 1:1) Eq. (1). Imidazolium cations were placed in the three-necked glass flask with a magnetic stirrer and metal chloride was then very slowly added under stirring. The reaction of metal chloride and imidazolium cations was highly exothermic and care had to be taken not to permit the temperature of the mixture to rise above 60°C; otherwise, thermal decomposition occurred. The resulting melt was used for testing in the reactions[16].



(1)

Catalyst Characterization

Fourier transform infrared (FTIR) spectroscopy

To obtain detailed information about the molecular structure of the supported catalysts, the IR transmission spectroscopic investigation was carried out at room temperature on Mattson 8100.spectrometer using KBr disc method. IR data were collected by averaging 32 scans with a spectral resolution of 4 cm^{-1} over the wave number range of 400-1200 cm^{-1}. Fourier transform infrared spectroscopic (FTIR) analysis was carried out by using an ATI Mattson Genessis Ser FTIR Tm infrared spectrophotometric.

Differential thermal analysis (DTA) and Thermal gravimetric analysis (TGA)

Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA), were performed to trace the structure changes accompanying the thermal treatment. This technique was recorded simultaneously on an apparatus manufactured by TGA-50 shimadzu instrument, in the range from 40 to 600°C.The heating rate was 10 K/min under nitrogen atmosphere.

The Desulfurization Procedure

The desulfurization experiments were conducted in a 100 ml glass flask. The gas oil and ionic liquids were added into the flask at room temperature. The mass ratio of ILs to the gas oil was 1:5. The biphasic mixture was then stirred for 15-75 min. The sulfur contents in gas oil before and after each extraction experiment were analyzed using the quantitative analyzed by ED-XRF Analyzer-Phoenix.

RESULTS AND DISCUSSION

Infrared Spectroscopy (FTIR)

Much broader band was observed for ionic liquid [BMIM][Cl] (sample a) which is assigned to N-H stretch at wave number 3600-3180, this peak is disappeared in modified ionic liquid [BMIM][FeCl$_4$] (sample b) but observed bands in the region 3750-3400 cm^{-1}, indicate the presence of Lewis and brönshated acid sites. This peak is the main character to indicate the activity of the catalyst.

Various bands Figure (1) in the spectrum were identified from which corresponding to alkenes asymmetric stretching bands of CH and C=C at wave number 3081 and 1629 cm^{-1} for sample (a), which were shifted to bands at wave number 3103 and 1721 (sample b) due to interaction with iron salt FeCl$_3$.

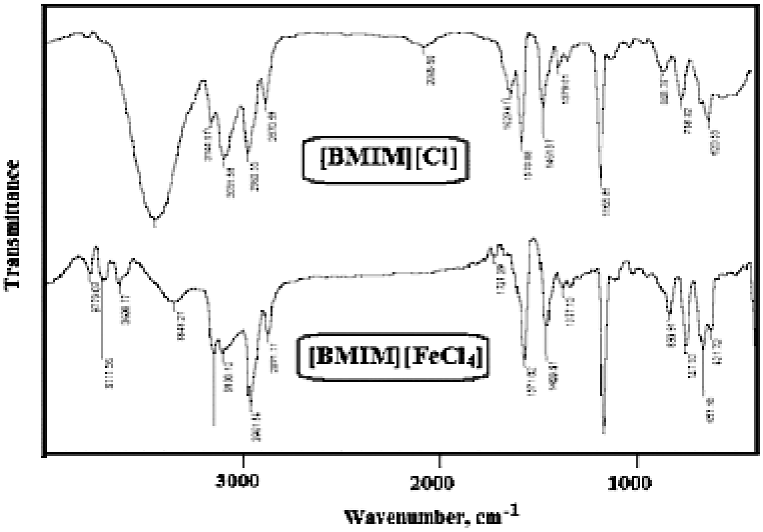


Fig. 1. FTIR Spectra for the as prepared samples; a) ionic liquids [BMIM][Cl] and b) modified ionic liquids [BMIM][FeCl$_4$] based ionic liquids

The very sharp bands in samples (a & b) at wave number 1186 cm^{-1} could be due to the presence of C-N stretch band related to imidazolium ring. The peak at 1570 cm^{-1} that corresponds to imidazole ring stretching in pure [BMIM]Cl, the occurrence of complexation between [FeCl$_3$]and pure [BMIM]Cl can be further proved by the formation of a shoulder at 1571 cm^{-1} in [BMIM][FeCl$_4$].

Thermal Decomposition Temperatures (DTA) and Thermal Gravimetric Analysis (TGA)

As illustrate in Figure (2), shows the DTA curves of the thermal decomposition of ILs. Several endothermic peaks were observed in the DTA curve. The 1st peak is a relatively located at about 70.61°C, indicating the loss of water of crystallization (H_2O) for [BMIM] FeCl$_4$ (MIL).

The increase of temperature was

accompanied by successive appearance of other endothermic peaks; their maxima are located at 380.26° for [BMIM] FeCl$_4$, based ionic liquid, respectively. These peak are related to the successive decomposition of the produced type of Imidazolium chloride based ionic liquids, which slightly affected by the alkyl chain on the ionic liquid and the variation of anions, i.e. the thermal stability is seen to vary with the cation-anion combination under study.

The result from TGA curves Figure (2) for [BMIM] FeCl$_4$ based ionic liquid. From this figure it can be seen that the sample standed to decompose gradually at 270.15^o, 380.26^{o}C with a total loss of 19.62 and 58.95 wt %. This showed that the stability of [BMIM] FeCl$_4$ based ionic liquid is attained up to 380^{o}C.

Determination of the equilibrium time for gas oil desulfurization

In the present study, gas oil was treated with [BMIM][FeCl$_4$] to establish the time required to reach the absorption equilibrium. The single extractions were conducted for 15, 30, 45, and 60 min at 298.15 K with fixed mass ratios of 1:1, 1:2 and 1:5 (the ratio of ionic liquid to gas oil). The sample in the upper phase was carefully separated with a pipette from the ionic liquid phase for analysis. The results, in Figure (3) show that 60 min of contact between the gas oil phase and the ionic liquid phase is more than sufficient to establish the equilibrium.

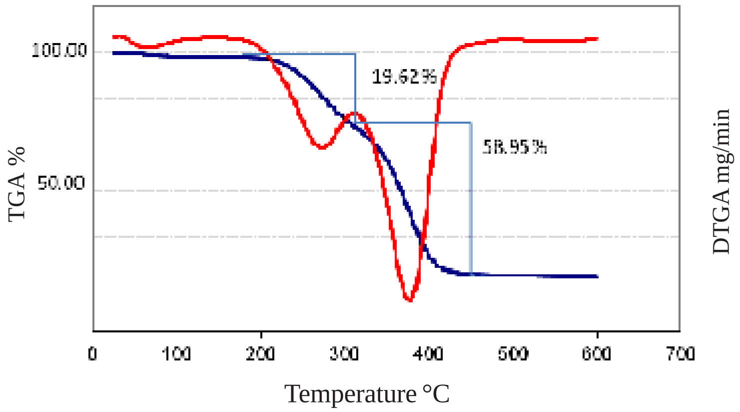


Fig. 2. DTGA & TGA for [BMIM] FeCl$_4$ based ionic liquid

The reason that ionic liquids can be used in desulfurization may be that molecules with highly polarizable π- electron density (such as thiophene) preferably insert into the dynamic molecular structure of the ionic liquids, and the driving force

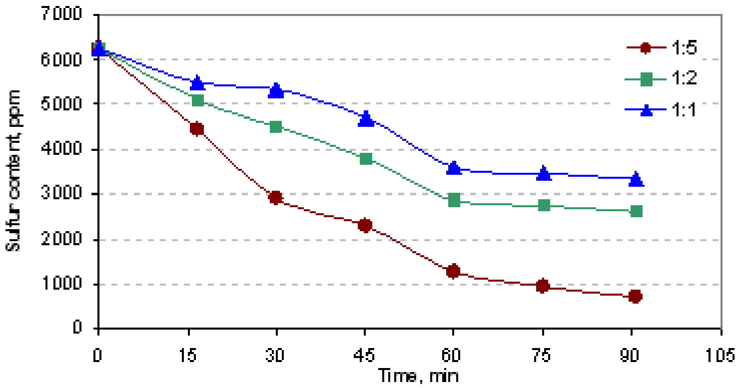


Fig. 3. Sulfur content in gas oil treated with [BMIM][FeCl$_4$] for different time.

for the molecular insertion is the favorable electronic interaction of polarized aromatic molecules with the charged ion pairs of ionic liquids[17]. Therefore, the sulfide compounds were retained in the ionic liquids, and then the gas oil will become lower-sulfur i.e. the strong affinity of the ILs for the sulfur compounds is related to the high polarity of the ionic liquid[18]. The mechanisms for the extraction of sulfur-containing compounds with Lewis-acidic ionic liquid are because the formation of liquid-clathrate compounds and π-π interactions between aromatic structures of the extraction target and the imidazolium ring system[19, 20].

The structural features of ionic liquids play an important role in the absorption of sulfide compounds, as shown in Figure 3. It is also found that the desulfurization ability in presence of ionic liquid is relation to the agitation. When the mixture is stirred vigorously, the desulfurization of gas oil is high, this because the viscosity of ionic liquid is higher than that of oil, and vigorously stirring can mix them together[17].

Desulfurization kinetics of Gas Oil with IL

The most of gas oil was desulfurized within the first 60 min. As illustrate in Figure (3) shows the progress of HDS conversion with reaction time. The loss of sulfur from the major sulfur-containing compounds with reaction time was found to follow pseudo-first-order kinetics Figure (4), which can be expressed in integral form as follows:

The experimental rate of gas oil desulfurization with ionic liquids may be expressed as Eq. (2)

$$\upsilon = -\mathrm{d}c / \mathrm{d}t = k\, c^{n} \qquad ...(2)$$

The integral formulae of Eq. (2) are Eq. (3).

$$\ln \upsilon = n \ln c + \ln k \qquad ...(3)$$

where υ is the reaction rate at time t (h), C the concentrations of substrate at time t (h), k the first-order rate constant (h-1), and n the order of the reaction.

$$\upsilon = -\mathrm{d}c / \mathrm{d}t = kc \qquad ...(4)$$

The integral formulae of Eq. (4) are Eq. (5), which indicate the rate constants for the apparent removed of sulfur compound.

$$\ln(C_0/C_t) = kt \qquad ...(5)$$

Where C_0 and C_t are the sulfur content of gas oil at time zero and time t(s), respectively, and k is the first-order rate constant (h^{-1}).

And Half-lives ($t_{1/2}$ (s)) are calculated using Eq. (6), which is derived from Eq. (5) by replacing C_t with $C_{0/2}$

$$t_{1/2} = \ln_2/k \qquad ...(6)$$

Fig. (4) shows the time-course variation of ln (C_0/C_t), the data of which were obtained from data shown in Fig. (3).

From plots of ln(C_0/C_t) vs. time, we confirmed that the decrease in sulfur concentration was quite moderate up to 40 min, however, after 60, 90 min. of experiment, ln(C_0/C_t) was 0.55, 0.77 and 1.60 which means Ct /C0 was about 1.73, 2.17 and 4.95. for ratio (GO: IL) 1:1, 1:2 and 1:5 respectively. Thus, after 60 min. of experiment, the decrease in sulfur concentration was about 88.47 % for GO: IL ratio 1:5 was some what more reactive than other ratios. Treatment of the concentration vs. time in a simple first order form resulted in straight line plots of Ln C_0/C_t vs. time Figure (4) and the rate constants (k) and half-lives ($t_{1/2}$) accordingly calculated for

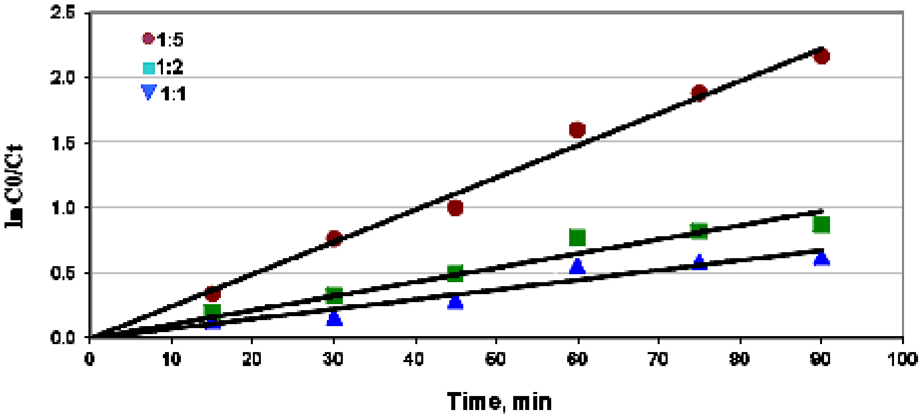


Fig. 4. Relationship between ln(C_0/C_t) and reaction time of gas oil desulfurized

each concentration are listed in Table 1. This table shows that the increase of ionic liquide concentration, increases the desulfurization of gas oil to reach a maximum of 88.47 % for 1:5 mole ratio (gas oil:IL). This phenomenon has been attributed to the favorable role of ionic liquid to continue absorption sulfur compound from gas oil. at higher concentration of ionic liquid, the reduction process takes place by absorption process of the gas oil on the surface of ionic liquid which causes the desulferizatiion of gas oil. Therefore, the sulfide compounds were retained in the ionic liquids, and then the gas oil will become lower-sulfur,[19] i.e. the strong affinity of the ILs for the sulfur compounds is related to the high polarity of the ionic liquid.

Table 1. Rate constants and half-lives for gas oil desulfurized

Gas oil : IL	R^2	rate const, k min^{-1}	$t_{1/2}$, h
1 : 1	0.9176	0.0074	92.40
1 : 2	0.9277	0.0108	64.17
1 : 5	0.9870	0.246	28.06

The desulfurization process of gas oil is fitted by different time. The results are shown in Fig. (3), in which R is the correlation coefficient. It can be seen from Figure (4) that the order of the reaction is approximately equal to 1 and the correlation coefficient is above 0.98. The results show that the kinetics of desulfurization of gas oil can be described well with the first-order equation[21].

CONCLUSIONS

Ionic liquids can be used as novel extractive solvents for deep desulfurization of gas oil, especially for the removal of the sulfur compounds intractable with common hydrodesulfurization techniques. The sulfur-removal ability of an ionic liquid depends on its structure and size. For the examined gas oil, the cation chain length exhibits a pronounced influence on the absorption of S-compounds, with promoted absorption capacity at elongated chain length. The desulfurization ability of the examined ionic liquids also increases with increasing the time of absorption capacity of ionic liquid with gas oil. Moreover, with the mass ratio of IL/ gas oil as 1 : 5, the rates of the desulfurization of gas oil can reach up to 80 % within the first 60 min. implying that these ionic liquids are indeed promising extractants for desulfurization.

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