Articles

Oxidative Desulfurization of Dibenzothiophene Catalyzed by Brønsted Acid Ionic Liquid

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Brønsted acid ionic liquid, N-methyl-pyrrolidonium tetrafluoroborate ([Hnmp]BF$_4$), was employed as an extractant and a catalyst to remove dibenzothiophene (DBT) from model oil in the presence of H$_2$O$_2$. The kinetics and mechanism of DBT oxidation by [Hnmp]BF$_4$ and H$_2$O$_2$ were proposed. DBT could be effectively removed from the oil phase by this process. Most of the oxidative products were in the ionic liquid phase for their higher polar property without additional extraction by solvent. The room-temperature ionic liquid [Hnmp]BF$_4$ could be recycled 7 times without a significant decrease in the desulfurization activity.

Introduction

In recent years, deep desulfurization of transportation fuels, such as gasoline and diesel fuel, has become an important research subject because exhaust gases containing SO$_x$ are a major cause of air pollution and poison noble metal catalysts irreversibly in automobiles. To protect the environment against SO$_x$ pollution, the demand for sulfur content in transportation fuels has become more and more stringent in the past 2 decades. The S content in both gasoline and diesel will probably have reached an average value of about 10 mg/L in many countries by 2010.[1]

Conventionally, hydrodesulfurization (HDS) has been employed by refineries to remove organic sulfur from fuels. Generally, this allows for the elimination of aliphatic and alicyclic sulfur compounds. However, alkylthiophenes, benzothiophene (BT), dibenzothiophene (DBT), and its derivatives, especially 4,6-dimethyldibenzothiophene (4,6-DMDBT), are difficult to be eliminated because of the sterically hindered adsorption of these compounds on the catalyst surface.[2,3] Moreover, during the deep HDS processes, the energy and hydrogen consumption will be evidently increased. Thus, alternative ways that are carried out at moderate conditions without requiring H$_2$, such as oxidative desulfurization (ODS), biodesulfurization, extractive desulfurization, and adsorptive desulfurization, are investigated.[4−14]

Ionic liquids (ILs) have the ability of extraction of aromatic sulfur-containing compounds at ambient conditions, for example, normal atmospheric temperature, normal atmosphere, and

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(1) Esser, J.; Wasserscheid, P.; Jess, A. *Green Chem.* **2004**, *6*, 314–312.
(2) Shafi, R.; Hutchings, G. J. *Catal. Today* **2000**, *59*, 423–442.
(3) Ma, X. L.; Sakanishi, K.; Mochida, I. *Ind. Eng. Chem. Res.* **1994**, *33*, 218–222.
(4) Otsuki, S.; Nonaka, T.; Takashima, N.; Qian, W.; Ishihara, A.; Imai, T.; Kabe, T. *Energy Fuels* **2000**, *14*, 1232–1239.
(5) Filippis, P. D.; Scarsella, M. *Ind. Eng. Chem. Res.* **2008**, *47*, 973–975.
(6) Xu, X.; Moulijn, J. A.; Ito, E.; Wagemans, R.; Makkee, M. *ChemSusChem* **2008**, *1*, 817–819.
(7) Kong, L. Y.; Li, G.; Wang, X. S.; Wu, B. *Energy Fuels* **2006**, *20*, 896–902.
(8) Yang, J.; Hu, Y.; Zhao, D.; Wang, S.; Lau, P. C. K.; Marison, I. W. *Biochem. Eng. J.* **2007**, *37*, 212–218.

especially without H$_2$.[10] To obtain deep desulfurization, multistage extraction must be operated because efficiencies of sulfur removal, various kinds of ILs used as extractants, however, are rather low. Lo et al.[15] combined ODS and extraction with ILs [BMIM]BF$_4$ or [BMIM]PF$_6$. In that process, organic acid, AcOH, as a catalyst was added to the extractive/oxidative system. Lu et al.[16] used acid ILs to extract and oxidize S compounds in the fuel. The Li group[17−19] used the peroxotungsten complex, polymolybdates as the catalyst, and ILs as the excractant to desulfurize organic sulfur of fuels in the presence of H$_2$O$_2$.

In this paper, we employed Brønsted acid IL *N*-methyl-pyrrolidonium tetrafluoroborate ([Hnmp]BF$_4$) as an extractant and a catalyst for the ODS of model oil in the presence of H$_2$O$_2$. The possible oxidative desulfurization mechanism of DBT was proposed. Kinetics parameters of the extraction and catalytic oxidation of DBT by [Hnmp]BF$_4$ were measured and calculated.

Experimental Section

Extractive and Oxidative Desulfurization of Model Oil. The IL [Hnmp]BF$_4$ was prepared by the published procedure.[20] Desulfurization experiments were conducted in a 50 mL flask. In a typical run, the model sulfur-containing compound (DBT) was dissolved in 10 mL of *n*-octane and the sulfur concentration was 1550 μg/mL. Then, 10 mL of [Hnmp]BF$_4$ was added to the flask. The mixture was stirred and heated to 60 °C in a water bath. The sulfur concentration in *n*-octane was detected using a microcoulometric detector with the process of extraction. After 15 min, the sulfur concentration in model oil changed slightly. Oxidant H$_2$O$_2$ (30 wt %, 0.026 mL, H$_2$O$_2$/S = 3) was added to the mixture, which was stirred vigorously. The upper oil phase was periodically withdrawn and analyzed for sulfur content using the microcoulometric detector. Sulfur-containing compounds in the oil phase were analyzed by GC−FPD periodically.

Recovery/Regeneration of Used IL. The IL phase was separated using a separating funnel, and an equal volume of water was added to the solution of the IL. Then, the solution was cooled at 5 °C for 30 min. Some precipitate was removed by filtration. The precipitate was analyzed by a mass spectrometer (MS-2010EV, Shimazu, Japan). Oxidant and water were evaporated from the IL phase at 100 °C for 3 h by rotary evaporation. The residue was then extracted 3 times with an equal volume of diethyl ether to recover the IL for reuse.

Results and Discussion

Extractive Desulfurization of DBT from Model Oil by IL. The extraction of DBT in *n*-octane by IL, under different

Table 1. Effect of the Temperature on Sulfur Removal[a]

temperature (°C)	25	40	60	70
sulfur content (μg/mL)	754.9	733.2	716.1	753.3

[a] Conditions: extraction time, 60 min; sulfur concentration, 1550 μg/mL; $V_{model\ oil}/V_{IL}$, 1:1.

temperatures, was carried out at the volume ratio of 1:1 between IL and model oil. Sulfur content in model oil changed slightly after 15 min, and the *n*-octane−DBT−IL extraction equilibrium had been reached after 30 min. The effect of the temperature on the sulfur removal from the model oil using [Hnmp]BF$_4$ is shown in Table 1. With an increase of the temperature, the viscosity of IL was reduced, so that IL and DBT in model oil had more chance to contact each other, which resulted in more sulfur removal. However, IL has an extraction limit under some ratio between IL and model oil. The sulfur content did not decrease when ILs reached extraction saturation, although viscosity reduced with an increasing temperature. At the same time, oil volatilization resulted in a low desulfurization ratio.

ILs extracting aromatic S compounds from fuel oil is a physical process. Chemical bonds are not broken or formed, and only an intermolecular force is changed in the extractive process. The aromatic sulfur-containing molecules with highly delocalized electron density can be readily polarized through their interaction with the high polar IL. Molecules with highly polarizable π-electron density preferably insert into the dynamic molecular structure of the IL. The favorable electronic interaction of polarized aromatic molecules with the charged ion pairs of IL is the driving force for molecular insertion. On the other hand, the formation of liquid clathrate compounds of IL also extract the S compounds.[11,22] It can be seen that aliphatic and alicyclic sulfur compounds that do not have the aromatic property and polarity cannot polarize with IL; thus, these compounds are extracted little by IL-forming liquid clathrate compounds. Therefore, ILs extract more aromatic S compounds (thiophene, BT, and DBT) than aliphatic S compounds (sulfide and mercaptan).[10−12]

To investigate the extractive kinetics of [Hnmp]BF$_4$, extraction of DBT in *n*-octane by IL was carried out under the volume ratio of 1:1 between IL and model oil at 60 °C. C_A and C_B are the sulfur concentration in model oil and IL, respectively. The initial and equilibrium sulfur concentrations in model oil were C_{A0} (1550 μg/mL) and C_{Ae} (716.1 μg/mL), respectively. When the extraction process reached equilibrium, DBT was extracted from the oil phase to the IL phase and returned to the oil phase from the IL phase at the same time, which is a dynamic and reversible equilibrium. The extractive rate was assumed by pseudo-first-order and kinetics equations as follows:

$$-dC_A/dt = k_1 C_A - k_{-1} C_B \tag{1}$$

$$C_B = (C_{A0} - C_A)V_A/V_B = C_{A0} - C_A$$

$$-dC_A/dt = k_1 C_A - k_{-1} C_B = k_1 C_A - k_{-1}(C_{A0} - C_A) \tag{2}$$

When the extraction process reached equilibrium, the extractive rate was zero.

$$-dC_{Ae}/dt = k_1 C_{Ae} - k_{-1}(C_{A0} - C_{Ae}) = 0 \tag{3}$$

(9) Bösmann, A.; Datsevich, L.; Jess, A.; Lauter, A.; Schmitz, C.; Wasserscheid, P. *Chem. Commun.* **2001**, 2494−2495.

(10) Zhang, S.; Zhang, Z. C. *Green Chem.* **2002**, *4*, 376−379.

(11) Zhang, S.; Zhang, Q.; Zhang, Z. C. *Ind. Eng. Chem. Res.* **2004**, *43*, 614−622.

(12) Wang, J. L.; Zhao, D. S.; Zhou, E. P.; Dong, Z. *J. Fuel Chem. Technol.* **2007**, *35*, 293−296.

(13) Nie, Y.; Li, C. X.; Sun, A. J.; Meng, H.; Wang, Z. H. *Energy Fuels* **2006**, *20*, 2083−2087.

(14) Takahashi, A.; Yang, F. H.; Yang, R. T. *Ind. Eng. Chem. Res.* **2002**, *41*, 2487−2496.

(15) Lo, W. H.; Yang, H. Y.; Wei, G. T. *Green Chem.* **2003**, *5*, 639−642.

(16) Lu, L.; Cheng, S.; Gao, J.; Gao, G.; He, M. Y. *Energy Fuels* **2007**, *21*, 383−384.

(17) Zhu, W.; Li, H.; Jiang, X.; Yan, Y.; Lu, J.; Xia, J. *Energy Fuels* **2007**, *21*, 2514−2516.

(18) He, L.; Li, H.; Zhu, W.; Guo, J.; Jiang, X.; Lu, J.; Yan, Y. *Ind. Eng. Chem. Res.* **2008**, *47*, 6890−6895.

(19) Zhu, W.; Li, H.; Jiang, X.; Yan, Y.; Lu, J.; He, L.; Xia, J. *Green Chem.* **2008**, *10*, 641−646.

(20) Zhu, H. P.; Yang, F.; Tang, J.; He, M. Y. *Green Chem.* **2003**, *5*, 38−39.

(21) Cooper, M. S.; Heaney, H.; Newbold, A. J.; Sanderson, W. R. *Synlett* **1990**, 533−535.

(22) Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C.; Rogers, R. D. *Chem. Commun.* **2003**, 476−477.
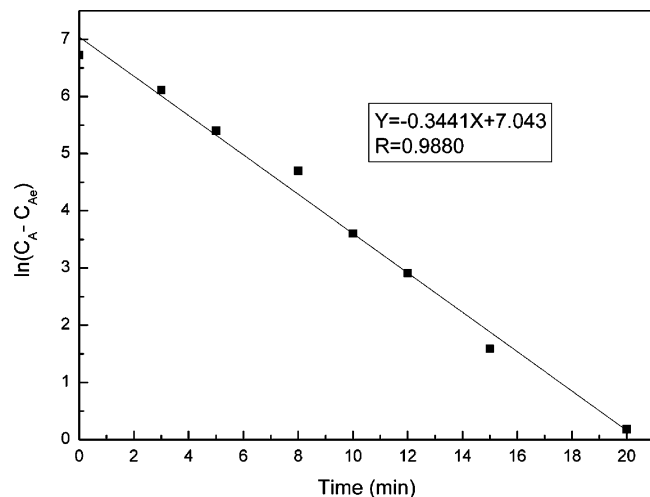
Figure 1. Pseudo-first-order kinetics for the extraction of DBT.

$$\frac{k_1}{k_{-1}} = \frac{C_{A0} - C_{Ae}}{C_{Ae}} \quad (4)$$

Equation 2 minus equation 3 is the following:

$$-d(C_A - C_{Ae})/dt = (k_1 + k_{-1})(C_A - C_{Ae}) \quad (5)$$

Then

$$-\int_{C_0}^{C_A} \frac{d(C_A - C_{Ae})}{(C_A - C_{Ae})} = \int_0^t (k_1 + k_{-1})dt \quad (6)$$

$$\ln\frac{C_{A0} - C_{Ae}}{C_A - C_{Ae}} = (k_1 + k_{-1})t$$

Figure 1 is the fitted linear regression of $\ln(C_A - C_{Ae})$ and t. k_1 and k_{-1} can be obtained from eq 4 and Figure 1. It can be seen that the extractive order is pseudo-first-order and experimental results are consistent with the simulation results in the dynamic model. The extractive apparent kinetics is

$$-dC_A/dt = 0.3441C_A - 246.3 \quad (7)$$

The half-live was 2.01 min calculated by $t_{1/2} = \ln 2/k$.

Role of Brønsted IL [Hnmp]BF4 in the ODS/Extraction of DBT. In a combination of extraction and oxidation, DBT was oxidized in the IL phase as it was extracted from the oil phase; therefore, a continuous decrease of the sulfur concentration in *n*-octane was observed for each solvent during the oxidation process. In this process, [Hnmp]BF4 is not only the extractant but also the catalyst. One of its possible catalytic roles is to decompose hydrogen peroxide to form hydroxyl radicals. Cooper et al.[21] found that a coordination compound could be generated between hydrogen peroxide and an amide, and then the hydrogen peroxide on the coordination compound decomposed to produce hydroxyl radicals that are strong oxidizing agents. DBT in the IL phase was oxidized to its corresponding sulfone by the hydroxyl radicals. The *n*-octane and IL ($V_{n\text{-octane}}/V_{IL}$ is 1:1) were mixed and stirred 1 h at 60 °C. Then, DBT sulfone[4] was added to the mixture, which were stirred for 1 h at 60 °C continuously. The oil phase was analyzed by a gas chromatography−flame photometric detector (GC−FPD) and microcoulometric detector, respectively. Sulfur compounds were not found in the respective oil phase. The facts indicate that the polar oxidative sulfur-containing products do not exist in the oil phase. The

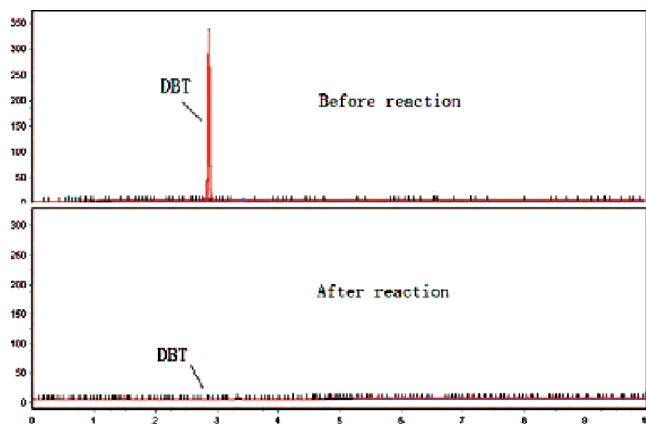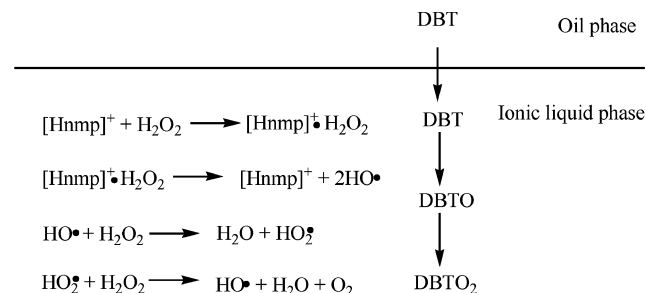**Scheme 1. Possible Oxidation Mechanism of DBT Catalyzed by IL**

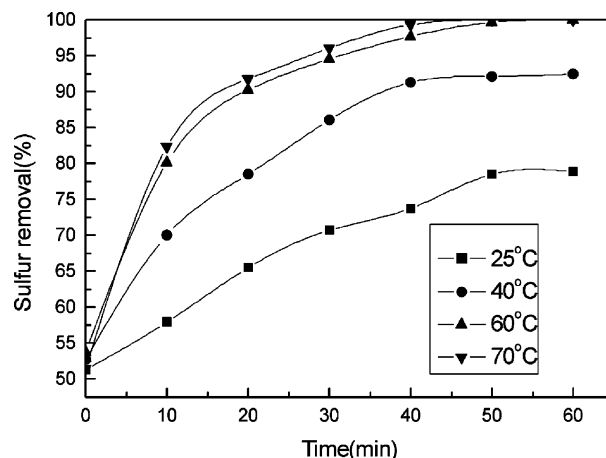**Figure 2.** GC−FPD chromatograms of DBT in model oil before and after oxidation.

Figure 3. Effect of the reaction temperature on sulfur removal. Conditions: H_2O_2/S, 3; sulfur concentration, 1550 μg/mL; $V_{\text{model oil}}/V_{IL}$, 1:1.

process whereby DBT was extracted from the model oil and oxidized in the IL system has been shown in Scheme 1. Figure 2 shows that sulfone does not exist in the oil phase because of the high polarity of the IL. DBT sulfone can be detected in the IL phase.

Kinetics of Oxidative DBT. Reaction kinetics is of great importance in explaining the reaction mechanism. The temperature affects kinetics of the reaction greatly. The effect of the reaction temperatures on the conversion of DBT was shown in Figure 3. The reaction activity increased with an increasing temperature. An increase in the reaction temperature from 25 to 40 °C led to a remarkable sulfur removal from 78.9 to 92.4% in 60 min. The reaction time for complete conversion could be shortened to 60 min as the reaction temperature was elevated to 60 °C. When the temperature was at 70 °C, the time for 100%

Table 2. Effect of the H₂O₂/S (O/S) Mole Ratio on Sulfur Removal^a

entry	H_2O_2/S (mol/mol)	sulfur removal
1	0	53.8
2	2	91.3
3	3	100
4	4	100
5	6	100

^{a} Conditions: reaction time, 60 min; *T*, 60 °C; sulfur concentration, 1550 μg/mL; $V_{model\ oil}/V_{IL}$, 1:1.

Table 3. Recycle of IL in the Desulfurization of Model Oil^a

cycle	sulfur removal (%)	cycle	sulfur removal (%)
1	100	6	99.5
2	99.8	7	99.6
3	99.3	8	98.1
4	98.9	9	95.2
5	99.7	10	97.3

^{a} Conditions: *T*, 60°C; H₂O₂/S, 3; sulfur concentration, 1550 μg/mL; $V_{model\ oil}/V_{IL}$, 1:1.

conversion of DBT decreased to 50 min. The sulfur-containing compounds in the final *n*-octane solution was not detected.

Experiments to obtain kinetics parameters of oxidation of DBT were performed under 60 °C. To oxidize the sulfur-containing compounds to their corresponding sulfones using hydrogen peroxide as the oxidant, 2 mol of hydrogen peroxide are consumed for every 1 mol of sulfur-containing compound, according to the stoichiometric reaction. Sulfur removal in Table 2 at time zero reflects the ability of [Hnmp]BF₄ to extract DBT from *n*-octane. As shown in Table 2, the H₂O₂/S mole ratio has an influence on the reaction rate. The conversion of DBT increased from 91.3% at H₂O₂/S = 2 to 100% at H₂O₂/S = 3 in 60 min. When the H₂O₂/S ratio reached 4 or 6, the DBT can also be removed completely in 60 min. With a H₂O₂/S mole ratio > 3, more hydrogen peroxide decomposed to H₂O and O₂. The H₂O₂ cannot be used well. Therefore, H₂O₂/S = 3 was chosen in most cases in the present study. The rate constant for the apparent consumption of DBT was obtained from the pseudo-first-order equation

$$-dC_A/dt = kC_A \tag{8}$$

$$\ln\frac{C_{A0}}{C_A} = kt \tag{9}$$

where C_{A0} and C_A are the sulfur concentrations at time zero and time *t* (min) and *k* is the first-order rate constant (min⁻¹). When the DBT in the IL phase was oxidized, DBT in the model oil phase was extracted to the IL phase quickly to keep the extractive equilibrium. The limiting step of this reaction is the chemical reaction because of the fast extractive rate. When
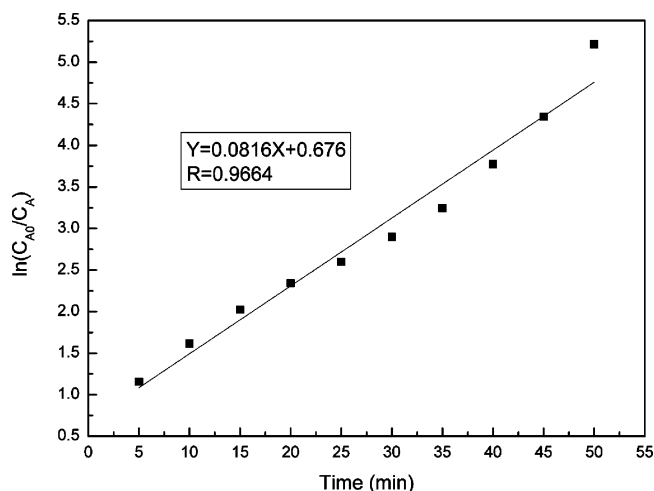
Figure 4. Pseudo-first-order kinetics for the oxidation of DBT.

ln(C_{A0}/C_A) was plotted against *t*, a straight line with slope *k* was obtained (Figure 4), indicating that oxidation of DBT catalyzed by IL follows pseudo-first-order kinetics with an apparent rate constant of 0.0816 min⁻¹. The half-live was 8.49 min calculated by $t_{1/2} = \ln 2/k$.

Regeneration/Recycling of the IL. We also investigated the possibility of recycling the [Hnmp]BF₄ ODS of DBT-containing model oil. After the reaction, the IL phase was separated and recycled as the catalyst and extractant for the next reaction. After 5 times, used IL was regenerated. The data shown in Table 3 indicate that the IL [Hnmp]BF₄ can be recycled 7 times without a significant decrease in activity. The reason less DBT was removed from the oil phase with the increase of the cycle may be that some IL was wasted when IL was separated and regenerated.

Conclusion

In conclusion, DBT can be effectively eliminated from model oil by Brønsted acid IL [Hnmp]BF₄ in the presence of H₂O₂. The role of IL in this system is not only as the extractant but also the catalyst. The possible oxidative desulfurization mechanism of DBT by IL catalysts was proposed. Kinetics of extraction and catalytic oxidation of DBT are pseudo-first-order, with apparent rate constants of 0.3441 and 0.0816 min⁻¹, respectively. In addition, the IL can be recycled 7 times without a significant decrease in the desulfurization activity.