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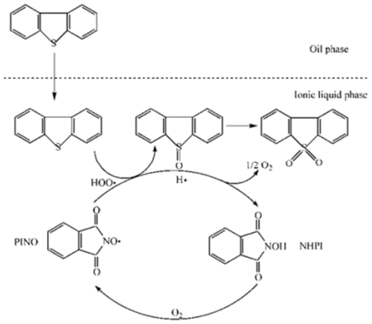
One-pot extractive and oxidative desulfurization of liquid fuel by NHPI with molecular oxygen in ionic liquids



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One-pot extractive and oxidative desulfurization of liquid fuel with molecular oxygen in ionic liquids

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Benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethlydibenzothiophene (4,6-DMDBT) were extracted from oil phase to ionic liquid phase, and then oxidized to the corresponding sulfone by the cheap catalyst, *N*-hydroxyphthalimide (NHPI), using molecular oxygen as the oxidant in one-pot. The system can be recycled 5 times without a significant decrease in desulfurization.

Sulfur compounds in fuels are converted to SOx during combustion, which results in acid rain and poisons catalytic converters in cars. Primarily for environmental concerns, governments worldwide have issued increasingly stringent regulations to limit sulfur levels in fuels. In the petroleum refining industry, the conventional method for reducing sulfur is catalytic hydrodesulfurization (HDS), which is highly effective for removing thiols, sulfides, and disulfides. However, it is difficult to remove thiophenes with steric hindrance on the sulfur, such as dibenzothiophene (DBT) and it derivatives.[1] Severe HDS conditions are required in order to remove such compounds. These operating conditions result in large hydrogen consumption and a significant increase in the operating expenses. Therefore, extensive research is carried out to propose alternative technologies to obtain low-sulfur fuels.[2] Ionic liquids (ILs) as a type of "green solvent" were widely used as extractant in lab for extractive desulfurization of fuel.[3] The efficiencies of sulfur removal, various kinds of ILs used as extractants, however, are rather low because of the similar polarity between the sulfur-containing molecules and the fuels. To obtain deep desulfurization, multistage extraction must be operated. In order to obtain deep desulfurization, oxidative desulfurization was combined with extraction using ILs as extractant or extractant/catalyst. Lo et al. combined oxidative desulfurization (ODS) and extraction with ILs, [BMIM]BF_4 or [BMIM]PF_6 as extractant and organic acid, AcOH, as a catalyst in the presence of H_2O_2.[4] The Li group used the peroxotungsten complex, polymolybdates as the catalyst, and ILs as the excractant to desulfurize organic sulfur of fuels in the presence of H_2O_2.[5] The different acid ILs and ILs based on metal were also employed as extractant and catalyst at the same time for desulfurization of fuel.[6] However, the oxidant, H_2O_2, in the above-mentioned ODS system is expensive.

The oxidation of the refractory sulfur-containing compounds using molecular oxygen instead of hydrogen peroxide as oxidizing agent under mild conditions has long been desired due to it's the economical and environmental points of view. However, the direct introduction of molecular oxygen to thiophenes is difficult, because the ground state of molecular oxygen is the inert triplet. In order to use molecular oxygen as oxidant for desulfurization, the aldehydes were used as co-oxidants.[7] The polyoxometalates, the metallophthalocyanines and the lactones were also examined as catalyst for desulfurization under different conditions.[8]

NHPI is a cheap, nontoxic catalyst easily prepared by the reaction of phthalic anhydride and hydroxylamine. It acts as a precursor of phthalimido-N-oxyl (PINO) radical, which is the effective abstracting species in all of the free radical processes mediated by this N-hydroxy derivative.[9] In this work, we firstly report the one-pot oxidative and extractive desulfurization of BT and DBTs in fuel oil by NHPI as catalyst with molecular oxygen as the oxidant, and using IL, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) as extractant of low volatility.

The desulfurization of DBT was investigated with the extraction combined with catalytic oxidation system using molecular oxygen as oxidant.† Extractive and oxidative desulfurization of model oil containing DBT was conducted in a 70 mL autoclave with 0.3 MPa molecular oxygen at 120°C. The oil phase was examined at different reaction time with the sulfur specific gas chromatography (GC-FPD). Figure.1 shows GC-FPD analyse before and after the extractive and catalytic oxidation of DBT. The peak area of DBT decreased with increasing reaction time. The DBT presented in n-octane was not detected after extraction and catalytic oxidation at 120 °C in 5h. The oil phase did not contain the corresponding oxides, which indicated that all of DBT had been removed from model oil to IL phase.

The different desulfurizations systems with and without O_2 were empolyed to investigate whether the molecular oxygen is oxidant. The results are listed in Table 1. The sulfur removal of DBT was only 32.9%

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and 33.5% with [Bmin]BF_4 or [Bmin]BF_4/NHPI in the presence of N_2 (entry 1,2), respectively. The desulfurization depends on the extractive property of [Bmin]BF_4. But the sulfur removal of DBT increased sharply and reached 100% with O_2 at the same temperature and reaction time (entry 3). The desulfurization ratio can be reached 51.6% when air is used as oxidant at the same conditions. Compared with molecular oxygen, air contains less molecular oxygen (about 21%). The results clearly demonstrate that the molecular oxygen is the oxidant and join the oxidation of the sulfur compounds. The catalyst is active for the oxidation of DBT to corresponding oxides. Zhang et al reptorted that no ionic liquid was detected in the organic phase after absorption measurement.[3] The GC with nitrogen and phosphorus detector (NPD) showed no nitrogen peak in model oil. It indicated that model oil did not contain ionic liquid and catalyst. Few n-octane can be extracted into ionic liquid because of the n-octane inserting into the dynamic molecular structure of IL, but it can be recovered with distilling the used IL after desulfurization.[3]

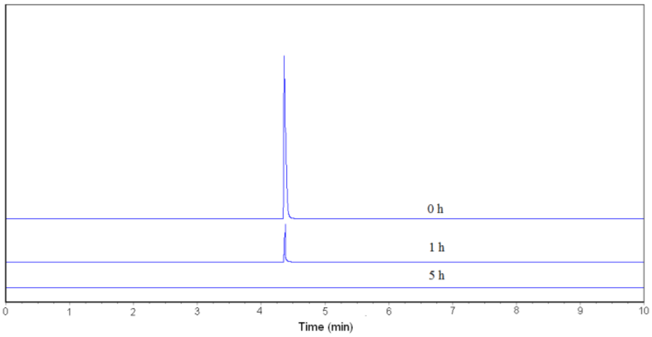

Figure 1. GC-FPD chromatograms for the extractive and oxidative desulfurization of DBT at different time. (Conditions: DBT model oil (500μg/mL), 10 mL; [Bmin]BF_4, 4 mL; catalyst NHPI, 10mmg; oxidant O_2, 0.3MPa; reaction temperature 120°C; reaction time 5h)

Table 1. Influence of different desulfurization systems

entry	desulfurization system	sulfur removal (%)
1	[Bmin]BF_4+O_2	32.9
2	[Bmin]BF_4+NHPI +N_2	33.5
3	[Bmin]BF_4+NHPI +O_2	100
4	[Bmin]BF_4+NHPI +Air	51.6

Conditions: DBT model oil (500μg/mL), 10 mL; [Bmin]BF_4, 4 mL; catalyst NHPI, 10mmg; N_2, O_2, Air, 0.3MPa; reaction temperature 120°C; reaction time 5h.

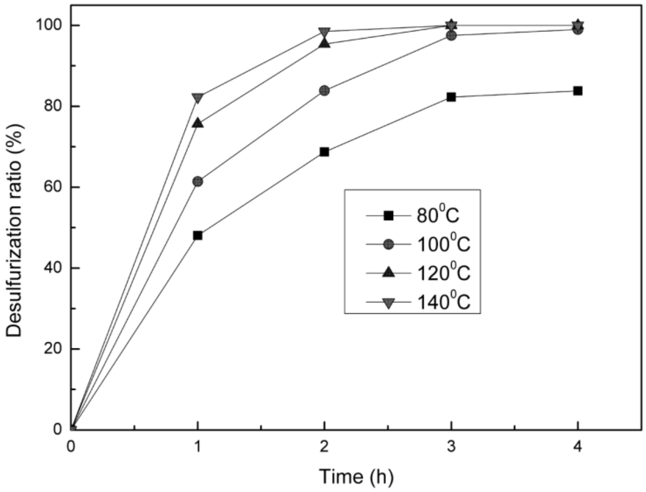

Figure 2. The effect of temperature on the DBT removal. (Conditions: DBT model oil (500μg/mL), 10 mL; [Bmin]BF_4, 4 mL; catalyst NHPI, 10mmg; oxidant O_2, 0.3MPa)

The effect of temperature on the conversion efficiency of DBT was investigated at 0.3MPa of initial pressure. The removal of sulfur-containing compound increased with enhancing reaction temperature, as shown in Figure 2. Increasing reaction temperature from 80°C to 140°C led to a noticeable increment of removing DBT from oil phase. The desulfurization ratio of DBT was up to 100% at 140°C in 3h compared with 82.3% at 80°C. The DBT can be also removed completely at 120°C in 3h. In addition, the influence of pressure on sulfur removal was examined. The results are shown in Figure 3. With increasing pressure of oxygen from 0.17MPa to 0.3 MPa, more DBT was removed from oil phase. But the desulfurization ratio did not change when the pressure exceeded 0.3 MPa in 3h. The results demonstrate that oxidation of DBT can be facilitated by dissolved oxygen in liquid phase, which is more concentrated at higher pressure.

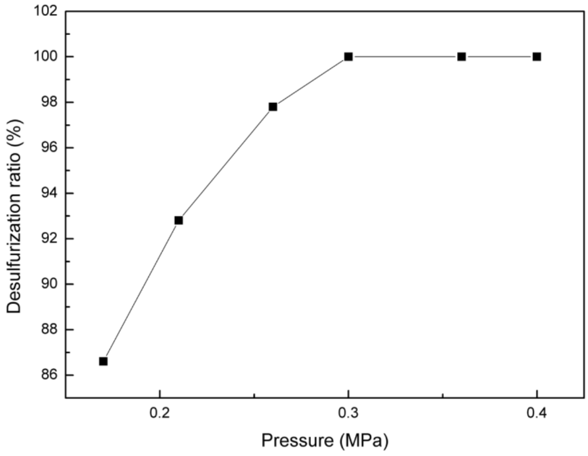

Figure 3. The effect of O_2 pressure on the DBT removal. (Conditions: DBT model oil (500μg/mL), 10 mL; [Bmin]BF_4, 4 mL; catalyst NHPI, 10mmg; reaction temperature 120°C; reaction time 3h)

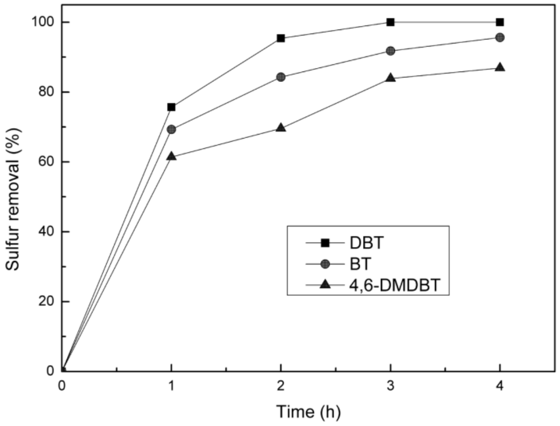

Figure 4. Effect of different sulfur species on sulfur removal. (Conditions: sulfur model oil (500μg/mL), 10 mL; [Bmin]BF_4, 4 mL; catalyst NHPI, 10mmg; oxidant O_2, 0.3MPa; reaction temperature 120°C)

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The reactivity of different sulfur-containing compounds, including BT, DBT and 4,6-DMDBT which the initial concentration of sulfur in model oil was 500 μg/mL respectively, was estimated for oxidation with this system at the same condition. The removal of sulfur-containing compounds versus the reaction times in the system is shown in Figure 4. The desulfurization ratio of sulfur-containing compounds decreases in the order DBT> BT >4,6-DMDBT. The sulfur removal order of four sulfur compounds by extraction and catalytic oxidation process was not consistent with the previous reports. As calculated by Shiraishi et al. and Otsuki et al., the electron densities on sulfur atoms are 5.739 for BT, 5.758 for DBT and 5.760 for 4,6-DMDBT.[10] These calculated results indicate that these model sulfur-containing compounds are oxidized easily with increasing electron density on the sulfur atoms. The difference of sulfur removal in this desulfurization system with previous reports may be due to the extractive desulfurization system. For sulfur compounds, DBT and BT, the extractive performance grows with the increase of the aromatic π-electron density. But for 4,6-DMDBT, the methyl substitution at the 4 and 6 positions of DBT remarkably retards the extractive performance of [Bmim]BF_4, which leads to the less 4,6-DMDBT removal than DBT and BT from oil phase.[6]

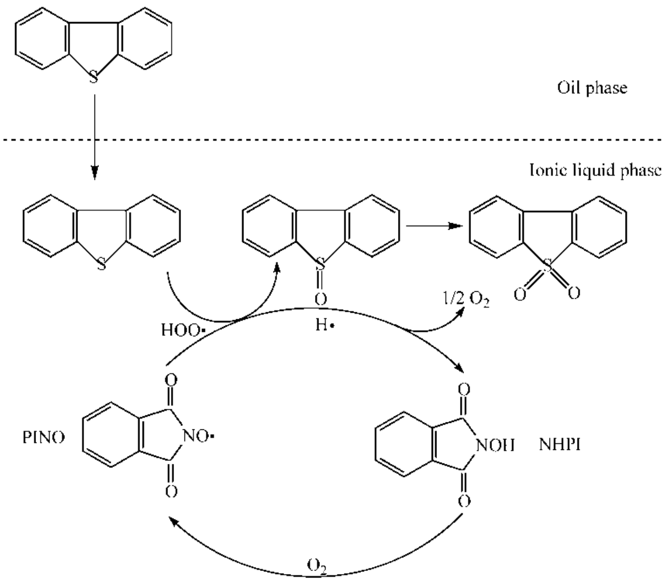

Figure 5. The proposed process and mechanism of extraction and catalytic oxidation of DBT in IL-NHPI-O_2 system

The proposed process and mechanism whereby DBT is extracted from oil phase and oxidized in the IL phase is as shown in Figure 5. In a combination of extraction and oxidation, DBT was oxidized in the IL phase as it was extracted from the oil phase, so a continuous decrease in the concentration of DBT in n-octane was observed for each solvent during the oxidation process. In this reaction system, the possible catalytic mechanism was due to free radical oxidation. The generation of PINO from NHPI under aerobic conditions wan confirmed by Einhorn et al.[11] This observation suggested that the hydrogen atom anchored to the N-hydroxy moiety in NHPI is easily abstracted by molecular oxygen to form PINO and hydroperoxyl radical, which is strong oxidizing agents. The DBT was firstly oxidized to DBTO, and then $DBTO_2$ by the hydroperoxyl radical. The sulfur-containing compound in the ionic liquids was oxidized to its corresponding sulfone by the hydroperoxyl radical. Because of the high polarity of IL, sulfone does not exist in the oil phase (figure 1). After reextraction, the DBT sulfone in ionic liquid can be detected with GC-MS (Agilent 7890A-5975C) as shown in figure 6.

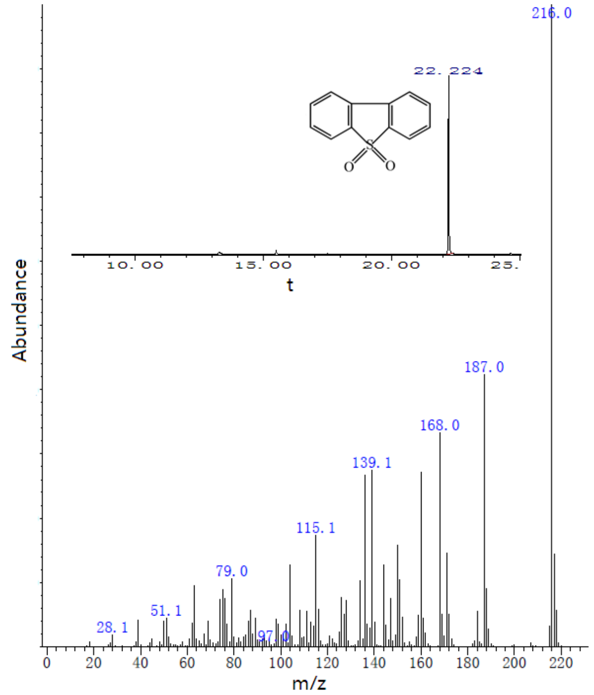

Figure 6. The GC-MS spectrogram of the oxidized productions of DBT.

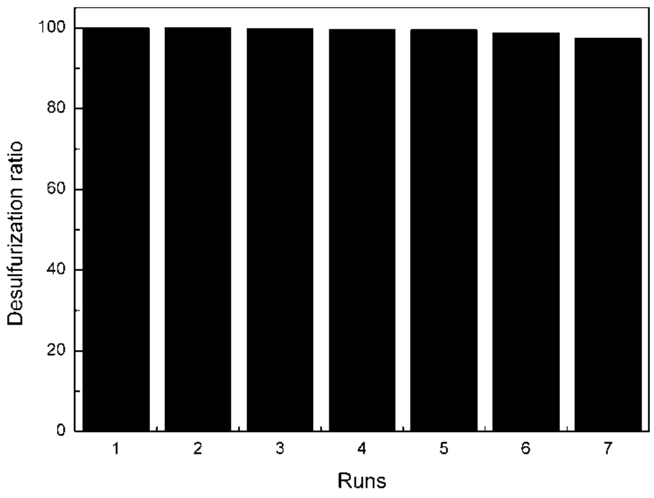

Figure 7. The recycling of ionic liquids-NHPI in extraction and oxidation desulfurization of model oil.

Some research had been reported that the different catalyst, such as heteropoly acid $H_5PV_2Mo_{10}O_{40}/SiO_2$, polyoxomolybdates $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18} \cdot 3H_2O$, $[C_8H_{17}N(CH_3)_3]_3H_3V_{10}O_{28}$, $[C_{18}H_{37}N(CH_3)_3]_7[PW_{10}Ti_2O_{38}(O_2)_2]$, $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$, and iron phthalocyanines or iron porphyrin were used to desulfurize fuel oil with O_2 as oxidant at normal pressure or compression.[8, 12] The DBT can be removed at normal pressure when heteropoly acid or polyoxomolybdates were used as catalyst under 120°C or lower temperature.[8] In order to remove DBT from model oil, O_2 was compressed to 0.3-0.5 MPa at 100°C-140°C, when iron phthalocyanines or iron porphyrin were employed as catalyst.[12] O_2 was also compressed in this work. However, NHPI is cheap and easily prepared compared with the mentioned catalysts.

The recycle of this desulfurization system has been investigated. After reaction, the oil phase and ionic liquid phase can be separated by separatory funnel. Then the used ionic liquids phase and fresh model oil was put into the autoclave for the next reaction. The system can be recycled 5 times without a significant decrease in desulfurization as shown in figure 7. After recycling 5 times, the desulfurization ratio can maintain 99.5%. With increasing runs, the ratio decreased because of the decomposition of PINO.[11]

Conclusions

In summary, the desulfurization system with $[Bmim]BF_4$ and catalyst, NHPI can oxidize BT and DBTs present in n-octane to the corresponding sulfones using molecular oxygen as the oxidant. The IL can be used as extractant. The corresponding sulfone exist in IL phase. The oxidation and extraction can proceed simultaneously. These results demonstrate that the molecular oxygen can be employed as oxidant for oxidative desulfurization instead of H_2O_2.

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Notes and references

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† Model oil was prepared by dissolving DBT or other sulphur-containing compounds (BT, 4,6-DMDBT) in n-octane giving a corresponding sulfur content 500 μg/mL. All the oxidative and extractive desulfurization experiments were conducted in 70 mL autoclave equipped with a magnetic stirrer, a pressure control valve and two thermocouples inside and outside of reactor. In a typical run, the model oil (DBT, 10mL, 500 μg /mL), the ionic liquid (4 mL) and catalyst (NHPI, 10mg) were added to the atuoclave. The reactor was closed and pressurized to 0.3MPa by a flow rate of O_2 (1 L/min) and then released the gas to substitute the O_2 for N_2 in air. After 3 times, the autoclave was heated to 120°C with stirring and kept 3h. The autoclave was cooled to room temperature in a water bath after the reaction. The O_2 was deprssurized slowly to atmospheric pressure and the reactor was opened. The upper oil phase was withdrawn and analyzed for sulfur content using the microcoulometric detector. The sulfurcontaining compounds were analyzed by gas chromatography coupled with flame photometric detection.

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