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Deep desulfurization of fuels based on oxidation/extraction process with acidic deep eutectic solvents

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Abstract: Organic sulfide in fuels has become an important reason for the formation of haze weather. The desulfurization of fuels has become a frontier scientific topic demanding prompt solutions. Research shows that the emergence of acidic deep eutectic solvents (DESs) has provided a new route for the deep oxidation/extraction desulfurization of fuels because of its cheap and easily obtained raw materials, higher desulfurization efficiencies, environmental friendly property and simple synthetic process. Through the smart design, series of acidic DESs with different acidity were synthesized. These acidic DESs were applied for the deep oxidation/extraction desulfurization of modeling and real fuels successfully. Results show that the acidity of deep eutectic solvent is the main factor that determines the oxidation/extraction process. The desulfurization capability has positive correlation with DESs' acidity, that is, the stronger of DESs' acidity, the higher of desulfurization efficiencies were achieved. In optimal conditions, the desulfurization efficiencies of DESs choline chloride/*p*-toluenesulfonic acid (ChCl/*p*-TsOH) and tetrabutylammonium chloride/*p*-toluenesulfonic acid (TBAC/*p*-TsOH) can reach up to 99.99%. For the real fuel, the desulfurization efficiency can reach up to 97.25% and 95.90%, respectively. Finally, the final product was characterized and oxidation/extraction mechanism was also investigated and the possible desulfurization route was proposed. The above study will provide new technology for desulfurization process of fuels.

1. Introduction

In recent years, production of clean fuels has become an important research topic around the world. SO_X, which are generated by the burning of organic sulfide in fuels, have become one of the most important reasons for the serious environmental pollution and the formation of haze weather. Stringent requirements have been made on sulfur content in fuels by most countries. In order to prevent the pollution from vehicle emission, the decrease of sulfur content from the source has become the main trend. The new technologies were suggested to be adopted to reduce the sulfur content in fuels [1-3].

Presently, hydrodesulfurization process (HDS) is the "golden" desulfurization method, which is being applied in most refineries. However, for organic sulfide with larger steric, such as thiophene and their derivative, HDS is not so efficient. It is difficult to achieve deep desulfurization of fuels. Therefore, as a complementary approach, non-hydrodesulfurization (Non-HDS) methods were widely investigated, which has become a research focus[4]. Many Non-HDS methods are being probed, such as biological desulfurization process, membrane technology, alkylation, adsorption, extraction and oxidation/ extraction process[5]. Oxidation/extraction desulfurization technology can be divided into two processes. First, organic sulfide in fuels is oxidized to the corresponding sulfoxide and sulfone, then extracted by efficient polar solvents. This process can be carried out under normal temperature and pressure. Furthermore, its investment is lower than HDS. So, it is a very promising desulfurization technology. However, the commonly used extractants are most organic ones, which are volatile and toxic, serious environmental pollution will be caused. Therefore, the development of green solvents can be great significance to realize and simplify the desulfurization process. This green solvents should act as catalyst, solvent and extractant so that "one pot" deep desulfurization of fuels can be achieved, which will greatly promote the industrialization of oxidation/extraction desulfurization process. Deep eutectic solvents (DESs) are a new type of solvents. Its physical and chemical properties are similar to ionic liquids (ILs). So it is also known as the ionic liquids analogues. Its excellent physical and chemical properties have gained widespread attention. Deep eutectic solvents refers to the melting substance formed by two or three cheap, green components connecting with each other through hydrogen bonding[6,7]. It has good chemical stability and thermal stability. At the same time, the hydrogen bond donor (HBD) and acceptor (HBA) can be chosen according to demands. Compared with the ionic liquids, the raw materials of DESs are cheap and easily obtained. Notably, the synthetic process is simple, and the other organic solvents need not to be introduced, which can be very environmentally friendly. Therefore, DESs are considered to be an alternative to volatile organic solvents as 'green' solvent[8-10]. DESs has been widely concerned in preparation of materials[11], catalytic reaction[12], electrical chemistry[13], chemical separation process[14-19], and so on. DESs can receive or give electron or proton to form the hydrogen bonds; therefore, it has good capability to dissolve many compounds. However, compared with the widespread use of ILs in chemical separation process, application of DESs has been just at its beginning stage, mainly including extraction of glycerol[15] and phenol[16] from the biodiesel, uptake of saponins[17] and phenolic metabolites[18], separation of the cellulose component[19] and extraction of protein[20], desulfurization of fuels[21-23]. Until now, the application of DESs as "three agents in one" for the removal of organic sulfide with oxidation/extraction coupling process has not been reported. Nevertheless, as analogs of DESs, ionic liquids were widely probed in liquid-liquid extraction[24],organic sulfide extraction or oxidation/extraction desulfurization process, mainly about the extraction or oxidation/extraction desulfurization with imidazolium and pyridyl based ILs[25-30], desulfurization using Lewis and Bronsted acid ILs[31-33], extraction and catalytic oxidation desulfurization with ionic liquids[34-36] and catalytic oxidation/extraction desulfurization with functionalized ionic liquids [37-39].

During the past few years, we have been committed to the investigation of ILs and DESs applied in chemical separation process, especially extraction removal of organic sulfide from fuels[21,40-42]. In our previous work, acidic functionalized ionic liquids can be effectively applied to remove organic sulfide from fuels[41]. It was also found that acidity is also important factors affecting oxidation / extraction desulfurization process. To our regret, the acidity of functionalized ionic liquids is still difficult to achieve precise control. At the same time, the cost of raw materials for synthesizing functionalized ILs is still high. Moreover, the complex synthesis process and the introduction of the organic solvent will influence the greenness of ILs. The above reasons have become obstacles for application of functionalized ILs in desulfurization process. To be noted, for real diesel fuels, it is also not efficient. How to design and develop new solvents that can conquer with the above problem efficiently has become an urgent problem. Through our previous research, DESs was first used as extractants for desulfurization of fuels[21]. Research shows that the emergency of deep eutectic solvents (DESs) has provided a new route for the deep oxidation/extraction desulfurization of fuels because of its cheap and easily obtained raw materials, higher desulfurization efficiencies, environmental friendly property and simple synthetic process. As the follow-up work, acidic DESs were designed, synthesized and their oxidation/extraction desulfurization capability were also investigated. To optimize the oxidation/extraction desulfurization process, the main factors that affect the desulfurization of fuels were studied systematically. With the above study, the theoretical foundation of desulfurization process for the smart design of DESs and the adjustment of desulfurization process was built up. This will provide a new theoretical and technological support for deep desulfurization of fuels.

2. Experimental

2.1 Synthesis of acidic DESs

Quaternary ammonium salts were chosen as HBA and some typical acids with different acidity were chosen as HBD. Synthesis process was carried out in a round-bottomed flask. Raw materials were purified before use. Then HBA and HBD were mixed at a certain molar ratio (mostly 1:1 or 1:2 in this research). After two compositions become liquid with heating, the system was stirred vigorously with a magnetic stirrer at a certain temperature, ranging from 60 ℃ to 120 ℃. The reaction process would be about 3～5 hours. Synthesis process of ChCl/ *p*-TsOH was taken as an example to illustrate the synthesis of DESs. In a 100 ml round bottom flask, equipped with a magnetic stirrer, the molar ratio 1:2 of choline chloride and *p*-toluene sulfonic acid were mixed. After those two compositions become liquid with heating, the system was stirred at 80℃ for 4 hours. Then ChCl/*p*-TsOH can be got (*S*.Fig.1a). Finally, the purity of DESs was confirmed by using ^{1}H NMR listed in supporting information *S*.Fig.2. The characterization of the other DESs were listed as *S*.Fig.3~*S*.Fig.8).

2.2 Oxidation/extraction process

Benzothiophene (BT) was chosen as typical sulfur content and *n*-octane as typical fuels. The sulfur content of the model oil was adjusted to 1600 ppm. Desulufurization process was carried out in self-made equipment. DES, H_2O_2 and Oil were mixed by certain molar ratio and then added into pear-shaped bottle subsequently (*S*.Fig.1b and S.Fig.1e).The mixture was stirred for 60 min at 25 ℃ in a water bath except for otherwise defined. Finally, the oxidation/extraction equilibrium reached (*S*.Fig.1c and S.Fig.1f). The ratio of reactants was adjusted according to the different experimental conditions. All the experiments in this study were done in duplicates to determine reproducibility, and the experimental errors were within 3%. As for the desulfurization of real fuels, similar process was adopted.

2.3 Analytical methods

The sulfur content of fuels was measured by Gas Chromatograph (GC). The chromatogram conditions are listed as follows: chromatogram column: HP-5; injection volume: 1 μL; carrier gas (N_2): 210 mL/min; H_2: 40 mL /min; air: 350 mL/min; flux: 1.6 mL/min, constant flow mode; inlet temperature: 300 ℃; detector temperature: 300 ℃; column temperature: heating from 120 ℃ to 150 ℃ with 15 ℃/min increase, 150 ℃ to 160 ℃ with 2 ℃/min increase, 160 ℃ to 250 ℃ with 25℃/min increase. The concentration of BT was measured with internal standard method, using hexadecane as the internal standard solvent. The concentration of hexadecane was 2000 ppm. The analysis of standard curve is shown in *S*.Fig.9. The correlation coefficient achieves 0.99997. The sulfur content of real fuels was determined by micro-coulometry. EPR signal of radicals trapped by DMPO were recorded at ambient temperature on a JES FA200 spectrometer. After bubbling O_2 for 10 min, the samples were introduced into the quartz cup inside the microwave cavity. The setting for the EPR spectrometer were listed as follows: center field, 336.50 mT; sweep width, 5 mT; microwave frequency, 9.5 GHz; modulation frequency, 100 kHz; power, 0.998 mW.

3. Results and discussions

3.1 Effect of different types of DESs

Our previous research showed that the acidity of functionalized ILs has a significant influence on the oxidation/extraction desulfurization process, while the acidity of functionalized ionic liquids is difficult to control precisely[42]. However, the acidity control of deep eutectic solvent is relatively simple, which can be realized through the proper choosing of hydrogen bond donor (HBD). This provides a good choice in solvent selection for oxidation/extraction desulfurization. Therefore, in accordance with the acidity of HBD, series of deep eutectic solvents were designed and synthesized. Based on the above principle, *p*-toluenesulfonic acid (*p*-TsOH), 5-sulfosalicylic acid (SSA), para aminosalicylic acid (PAS) were chosen as HBD, and choline chloride(ChCl), tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), tetraethylammonium chloride (TEAC) and tetraethylammonium bromide (TEAB) as a hydrogen bond acceptor (HBA). In addition, their oxidation/ extraction desulfurization capability is probed, which was shown in Fig.1. The results show that the hydrogen bond donor and acceptor affect the oxidation/extraction process greatly. HBD has greater influence on the desulfurization process than HBA. Furthermore, the acidity of deep eutectic solvent is the main factor that determines the oxidation/extraction process. Under the same conditions, the desulfurization capability has positive correlation with DESs' acidity, that is, the stronger of DESs' acidity, the higher of its desulfurization efficiencies. The molar ratio of HBA to HBD influences the desulfurization greatly. Higher amount of acids is beneficial the desulfurization process. With the same molar ratio, the sequence of desulfurization efficiency is listed as follows: *p*-toluenesulfonic acid (*p*-TsOH) > 5-sulfosalicylic acid (SSA) > 4-aminosalicylic acid (PAS). The desulfurization efficiencies of DESs ChCl/*p*-TsOH and TBAC/*p*-TsOH (molar ratio of HBA:HBD is 1:2) can reach up to 99.99%. Deep desulfurization of fuels was realized with 'one pot' process.

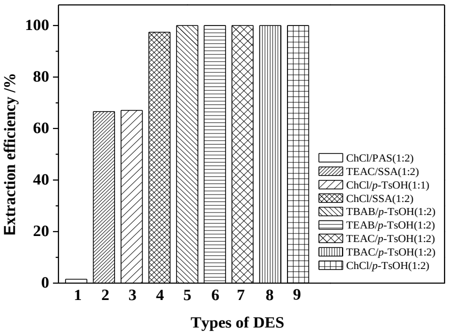

Fig.1 Effect of different types of DESs

3.2 Effect of the oxidant

As it is known that many DESs also have extraction desulfurization capability [21]. In optimal conditions, its extraction efficiency can reach 71.06%. So, the necessity of introducing oxidant should also be investigated for the acidic DESs based desulfurization process. From Fig.2, if oxidant is not introduced, the desulfurization efficiency can be only 25.17% and 37.79% for ChCl/*p*-TsOH and TBAC/*p*-TsOH, respectively**.** However, after the introduction of H_2O_2, the desulfurization efficiency can reach 99.99%. Therefore, oxidant can be very significance to achieve deep desulfurization process.

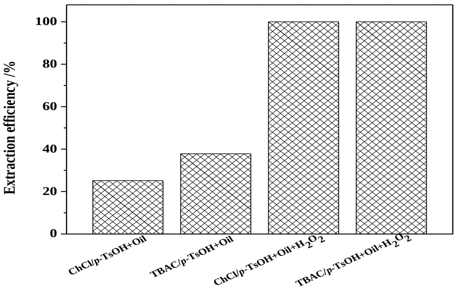

Fig.2 Necessity of introducing oxidant

The amount of oxidant is an important factor that influences the oxidation/extraction desulfurization process. And it is also an important standard that can measure the suitability of the solvent. The less of the amount of oxidant used and the higher desulfurization efficiency can be obtained is an important basis for the choice of the new solvents. With the above reason, effect of amount of oxidant is investigated. Results show that desulfurization efficiency increases gradually with the increase of oxidant dosage (Fig.3). If DES ChCl/*p*-TsOH was chosen, the desulfurization efficiency can reach 99.99% when m (H_2O_2): m (Oil) is 0.05:1. To be noted that this result is out of our expectation because so little oxidant is needed and so much higher desulfurization was got. When the TBAC/*p*-TsOH as extractant, the desulfurization efficiency achieves 99.99% when m (H_2O_2): m (Oil) is 0.3:1. Further increase of the amount of H_2O_2 will not lead to the increase of desulfurization efficiency. Compared with the above two DESs, ChCl/*p*-TsOH desulfurization system need less oxidant, so it will be more significant for its future industrial application. It can be easily seen that in ChCl/*p*-TsOH system, less amount of oxidant is needed compared with TBAC/*p*-TsOH and acidic functionalized ionic liquids [41]. The probable reason for this is that the structure of ChCl/*p*-TsOH is more suitable for the oxidation/extraction of sulfur content.

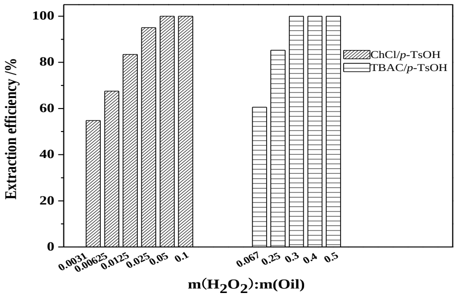

Fig.3 Effect of the amount of oxidant

3.3 Optimization of the oxidation/extraction process

Many factors affect the desulfurization process, such as the amount of DESs, extraction time, system temperature, stirring speed. So the above parameters were investigated to optimize the desulfurization process, which can be of great importance for its application in real fuels system.

As mentioned above, DESs are cheaper. However, less amounts of DESs needed and higher oxidation/extraction efficiencies achieved is always our goals. Effect of the amount of DESs and extraction time were investigated in detail shown in Fig.4. It can be seen that with the increase of the amount of DESs, the desulfurization efficiency also increase. When the amount of DESs to fuels comes to 0.5:1, the desulfurization efficiency can achieve 99.99% in 60 min. While for 0.4:1 or 0.2:1, the equilibrium time would be longer. The reason is that larger consumption of DESs will lead to its higher DESs concentration. The electron density of sulfur atoms on benzothiophene is easy to be polarized because of the interactions between DESs and BT. Furthermore, more proportion of DESs will also provide more active acidity spot, which enhances the oxidation ability of H_2O_2. Although larger amount of DESs is beneficial for desulfurization process including shorter equilibrium time and higher desulfurization efficiency, its cost must be considered so that applied in real fuels system. So the mass ratio of DESs to fuels 0.5:1 was chosen, with which the equilibrium time, desulfurization efficiency and the cost is more preferable. To be noted, until now the above results is one of the least amount of solvents used that can get so much higher desulfurization efficiency. Moreover, to guarantee a sufficient equilibrium, 60 min was chosen as reaction time in the following experiment.

System temperature is a useful criterion for evaluating the possibility of oxidation/extraction desulfurization process applied in real fuels. Effect of system temperature was investigated systematically listed Fig.5. It is indicated that the higher of the system temperature, the higher of desulfurization efficiency can be achieved at the beginning stage. However, after 60 min the desulfurization can reach 99.99% at all temperature, which mean that temperature will not influence the desulfurization process anymore. The result also shows that higher temperature will result in shorter equilibrium time. The probable reason for this is that higher temperature is more beneficial for the decomposing of H_2O_2 at beginning. However, with the increase of reaction time, adequate H_2O_2 decompose to achieve the same desulfurization efficiencies. In this specific case, 25 ℃ was chosen as system temperature throughout the investigation because 60 min is preferable in this work. The above results would be significant for its application in real fuels because this process can be operated just in normal temperature.

Stirring speed is another factor that influences the desulfurization process. Fig.6 shows the effect of stirring speed on desulfurization efficiency. As the speed increases, the desulfurization efficiencies are gradually increasing. To achieve deep desulfurization efficiency more than 99.99%, ChCl/*p*-TsOH and TBAC/*p*-TsOH can reach their equilibrium in 50 min and 60 min at 800 rpm, respectively. The reason would be the higher of the stirring speed will be beneficial for the mass transfer and promotion of collision area, and then the reaction time was shortened. In the following experiments, 800 rpm was chosen as stirring speed.

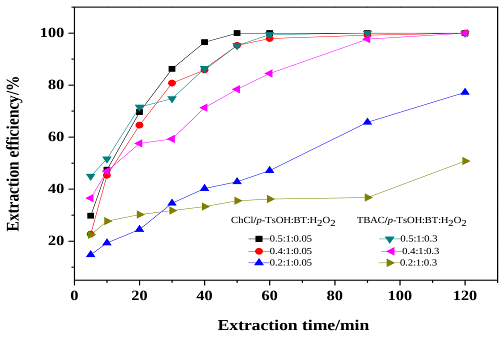

Fig.4 Effect of the amount of DESs on extraction efficiency

（25℃,800rpm）

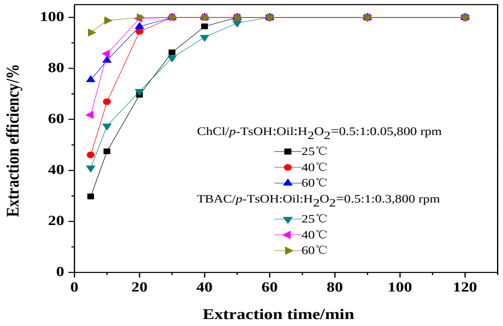

Fig.5 Effect of system temperature

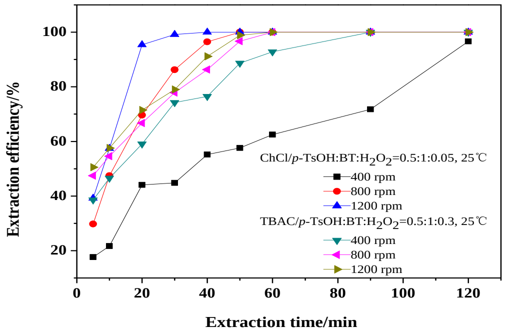

Fig.6 Effect of stirring speed

3.4 Recycling of used DESs

For industrialization of DESs, recycling and reuse can be importance not only from economic aspect but from environmental aspect. ChCl/*p*-TsOH is taken as an example to investigate the possibility of recycling and reusing of DESs. It is indicated that the recycling of the DES can be realized only washing by water. Since the sulfur oxides are insoluble and the ChCl/*p*-TsOH is soluble in water, the used ChCl/*p*-TsOH is extracted by washing with water. The sulfur oxides precipitated in the form of a white solid and was filtered. Finally, the aqueous ChCl/*p*-TsOH solution was dried using vacuum distillation. The desulfurization efficiencies are very stable after four times of recycling (Fig.7). The desulfurization can reach 98.87% after four times recycling, and the loss of DESs each cycle is not more than 2%. Furthermore, from ^{1}H NMR characterization, the structures of DESs do not change (Fig.8). Pure ChCl/*p*-TsOH: ^{1}HNMR (500 MHz, CD_3CN) δ7.69(d, *J*=8.2Hz, 4H),7.66 (s,3H), 7.27(d,*J*=8.1Hz,4H),3.93(m,2H),3.38(t,*J*=5.0Hz,2H),3.09(s,9H), 2.39(s,6H). Recycled ChCl/*p*-TsOH: ^{1}HNMR (500 MHz, CD_3CN) δ8.03 (s,3H), 7.69(d, *J*=8.0 Hz, 4H), 7.29(d, *J*=7.9Hz,4H), 3.93(m,2H), 3.38 (t, *J*=5.0 Hz, 2H), 3.09 (s,9H), 2.40 (s,6H). Based on the above investigation, DESs was recycled and reused successfully. TBAC/*p*-TsOH were also recycled with the same procedure. The result of its ^{1}H NMR characterization was listed in *S*.Fig.10.

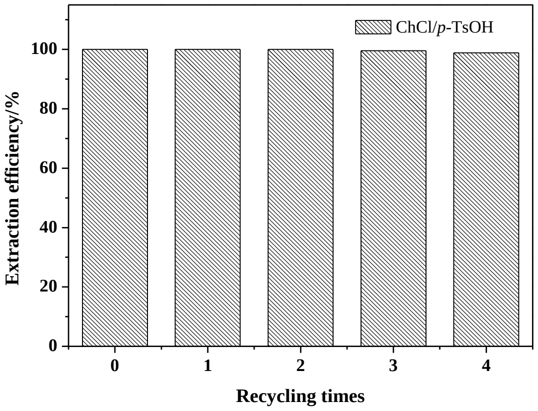

Fig.7 Extraction performance of the recycled DES

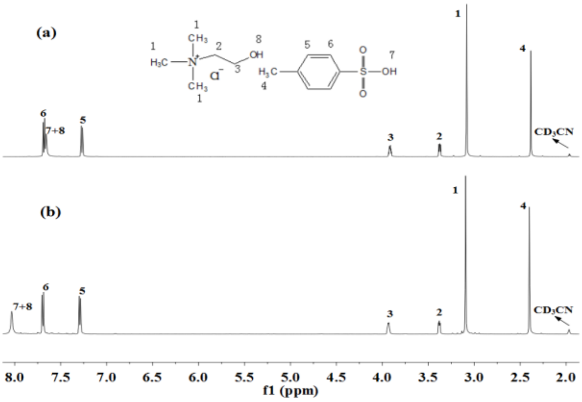

Fig.8 Structures of pure and recycled ChCl/*p*-TsOH

(a) Pure ChCl/*p*-TsOH (b) Recycled ChCl/*p*-TsOH

3.5 Characterization of final product

Form the recycling process, the white solid, namely sulfur oxide was obtained. The revealing of its structure would be valuable for the investigation of the oxidation/extraction mechanisms. To get the right composition and structure of the white solid, ^{1}H NMR and GC-MS were used for the characterization. The result of ^{1}H NMR was listed in *S*.Fig.11, and summarized as follows: ^{1}H NMR (500 MHz, CD_3CN) δ 7.75 (d, J = 7.5 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 6.9 Hz, 1H), 6.90 (d, J = 6.9 Hz, 1H). It can be seen that this solid is probably BTO_2. To confirm the structure of the oxidized products, the separated sulfur oxide was also characterized by GC-MS listed in *S*.Fig.12. GC-MS (EI, 70ev), m/z (%) 166 (43, M^+), 137 (100), 118 (16), 109 (43), 89(15). It is clearly shown that final oxidation products, benzothiophene sulfone (BTO_2) is obtained. Unfortunately, the intermediate cannot be observed. Perhaps the benzothiophene sulfoxide (BTO) also appeared as transition state during the oxidation/extraction process, but it was not found in the final product.

3.6 Oxidation/extraction mechanisms

Oxidation/extraction mechanism is valuable for the understanding of the desulfurization process. It is also significant for the smart design of DESs extractants. As a new type of solvent, acidic DESs were first applied in oxidation/extraction desulfurization process acting as ‘three agents in one’. So its mechanism is also especially valuable. Combined with the spectrum characterization and factor study, the proposed extraction mechanisms for the given two processes were sketched in Fig.11. To confirm the proposed oxidatioin/extraction desulfurization process, EPR spin-trap technique (with DMPO) was used to probe the active oxygen species generated by the desulfurization process. EPR signals was listed in Fig.9~Fig.10. The process was described in detail as follows. Interestingly, with the same oxidant H_2O_2, different DESs used in this process can produce different active oxygen species, which means that the reactions obey different oxidation/extraction routes. Through EPR characterization, for TBAC/*p*-TsOH, the characteristic peak can be observed can be assigned to DMPO-.OH, that is to say, H_2O_2 decomposes to hydroxyl radicals (·OH) in the desulfurization process listed in Fig.9 [43-45]. However, for the ChCl/*p*-TsOH, the EPR signal can be assigned to DMPO-$O_2^{\cdot -}$. In this process, H_2O_2 is converted into $O_2^{\cdot -}$ radical species shown in Fig.10, which shows that the typical signals of $O_2^{\cdot -}$ trapped by DMPO (DMPO-$O_2^{\cdot -}$), and characteristic peaks of the DMPO-$O_2^{\cdot -}$ adducts are observed on ChCl/*p*-TsOH systems[43-46]. This difference probably results from the functional group of the hydrogen bond acceptor (HBA), namely alcoholic hydroxyl group in ChCl is the main reason for the production of $O_2^{\cdot -}$ for ChCl/*p*-TsOH. This phenomenon can be of great importance for the revelation of the desulfurization mechanisms. To be noted, the active oxygen species provided by discomposed H_2O_2 could not oxidize BT at the interface of model oil and DESs, which can be proved by the longer equilibrium time. So BT was extracted by DESs phase at the first stage. Then it was oxidized by the active species. Due to the polarity of BTO_2 is larger than BT, it has more tendency to dissolve in DESs. To be saturated, DESs will extract another part of BT, which was then oxidized too. The above specific process repeated continuously until reaching the reaction equilibrium. Because the dissolution process of BT in DESs takes longer time, the extraction equilibrium would be 60 min. It is much different from traditional extraction desulfurization process with shorter equilibrium time. From microstructure aspects, the S heteroatom in BT occurs sp^2 hybrid, which will result in the existence of two single pair electrons, one in 3p$_z$ hybrids orbital and the other in 3p$_{z.}$ At the same time, 3d space orbit on the sulfur atom makes the sulfur compounds more acceptable for the oxygen atoms to be oxidized into the corresponding sulfoxide. The formation of sulfone will increase the polarity of sulfide significantly and easy to dissolve in polar DESs. Notably, DESs has three functions in this desulfurization process: catalyst, solvent and extractant.

3.7 Desulfurization of real fuels

Through the above investigation, deep desulfurization of modeling fuels can be achieved by using this specific oxidation/extraction process. Its desulfurization efficiency can be more than 99.99%. However, the composition of the real fuels can be more complex than the modeling ones. Anyway, whether the process can be applied in the real fuel system is the key that determine the possibility of its future industrialization. Therefore, oxidation/extraction desulfurization of real fuel was carried out. In optimal conditions, the desulfurization efficiency of ChCl/*p*-TsOH and TBAC/*p*-TsOH can reach up to 97.25% and 95.90% with the initial sulfur content 1600 ppm, which mean that the deep desulfurization process can also be realized. However, the oxidation/extraction desulfurization process based on acidic functionalized ionic liquid is only efficient for modeling fuels, for real fuel system, it is not workable[38]. This would probably open a new route for the deep desulfurization of real fuels.

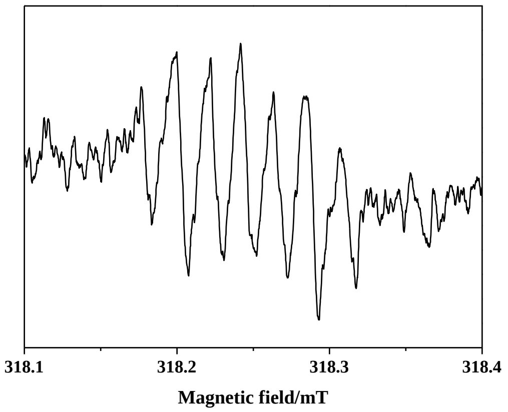

Fig.9 EPR spectra of DMPO-·OH adducts in TBAC/*p*-TsOH/H_2O_2 system

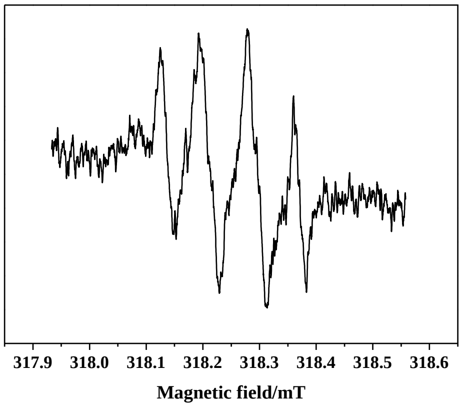

Fig.10 EPR spectra of DMPO-O2$^{\cdot -}$ adducts in ChCl/*p*-TsOH /H_2O_2 system

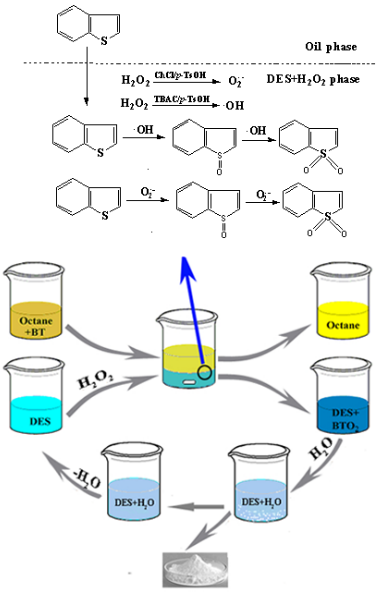

Fig.11 Proposed desulfurization mechanism

4. Conclusions

Through the smart design, series of acidic DESs with different acidity for the desulfurization process were synthesized. These DESs were applied for the deep oxidation/extraction desulfurization of modelling and real fuels successfully. After the selection of proper DESs, the desulfurization process was optimized through the study of the main parameters. It is indicated that the acidity of deep eutectic solvent is the main factor that determines the oxidation/extraction process. The desulfurization capability has positive correlation with DESs' acidity, that is, the stronger of DESs' acidity; the higher desulfurization efficiencies can be obtained. In optimal conditions, the desulfurization efficiencies of DESs can reach up to 99.99%. For the real fuels, the desulfurization efficiencies of ChCl/*p*-TsOH and TBAC/p-TsOH can reach up to 97.25% and 95.90% respectively, which is much higher than the traditional and functionalized ionic liquids. Deep desulfurization can be realized. Finally, the final product was characterized and oxidation/extraction mechanisms were also investigated systematically. Different DESs used in this process can produce different active oxygen species, which means that the reactions obey different oxidation/extraction routes. The above study will provide a new route for the deep desulfurization process of fuels.

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Notes and references

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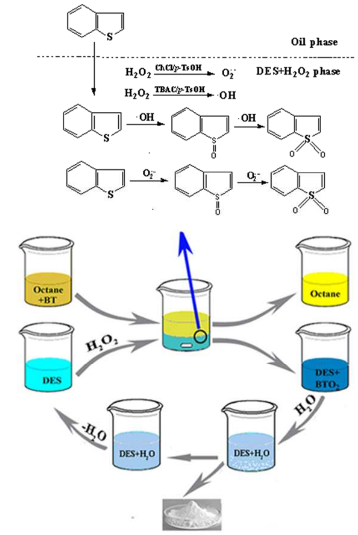

Series of acidic deep eutectic solvents were designed and synthesized， which could be used for the oxidation/extraction desulfurization of fuels successfully.