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Recent Advances in the Science and Technology of Desulfurization of Diesel Fuel Using Ionic Liquids

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1. Introduction

Sulfur-containing compounds in transportation fuels are converted by combustion to SO_x , which is a major source of acid rain and air pollution [1]. For environmental protection purposes, many countries have mandated a reduction in fuels sulfur level down to 10 ppm by 2009 [2,3], and with more and more stringent regulatory constraints, it is a trend to achieve little-to-no sulfur fuels in the next several years.

In the petroleum industry, low-sulfur fuels are often obtained from hydrocracking processes or hydrotreating processes [4]. Although hydrotreating processes have been highly effective for the reduction of sulfur levels, further improvement of the hydrodesulfurization efficiency is limited to increasingly severe operational conditions at escalated cost. Moreover, when the deep hydrodesulfurization of motor fuels is needed, not only the energy and hydrogen consumption will be evidently increased, but undesired side reactions (such as the saturation of more olefins) also will be induced. Such side reactions result in a decrease in the octane number of the gasoline.

Ionic liquids, a new class of green solvents, have recently been undergoing intensive research on the removal of thiophenic sulfur species (e.g., dibenzothiophene) from fuels because of the limitation of the traditional hydrodesulfurization method in removing these species. Ionic liquids have the ability of extracting aromatic sulfur-containing compounds at ambient conditions without H_2 consumption. In addition Ionic liquids are immiscible with fuel, and the used Ionic liquids can be regenerated and recycled by solvent washing or distillation [5-9]. The desulfurization using ionic liquids has received growing attention [10-26].

In 2003, Lo et al. first reported chemical oxidation in conjunction with Ionic liquid extraction for oxidative desulfurization. Using the IL $[\text{BMIm}]\text{PF}_6$ as extractant, acetic acid as catalyst,

and H_2O_2 as oxidant, the sulfur removal of DBT in model oil was increased significantly to 85%. The oxidation of organosulfur compounds to their corresponding sulfones catalyzed by polyoxometallic acids and their salts in Ionic liquids was also reported [27, 28]. Furthermore, it is well-known that homogeneous catalysts are difficult to separate from their reaction products limiting their recyclability. Currently, more efficient ODS systems solely containing H_2O_2 as oxidant, acidic ionic liquid, [HMIm]BF₄ or [Hnmp]BF₄ as extractant and catalyst have been reported by Lu et al. [29] and Zhao et al. [30] respectively.

Different types of ionic liquids, Imidazolium, pyridinium, and ammonium based Ionic liquids with different anion were demonstrated to be potentially applicable for sulfur removal from transportation fuels. Holbrey et al. [31] investigated the DBT extraction power from dodecan. This study ranks ionic liquids desulfurization ability by cation following the sequence methyl pyridinium \geq pyridinium \approx imidazolium \approx pyrrolidinium with much less significant variation with anion type. Recently, several pyridinium ionic liquids have been investigated for desulfurization-oriented purposes [32, 33]. In this chapter, the removal of sulfur compounds (S-compounds) from diesel fuels with different Ionic liquids are systematically reviewed.

2. Current Desulfurization Technologies

2.1. General Overview

Diesel fuel is a multi-purpose petroleum fuel used in trucks, trains, boats, buses, planes, heavy machinery and off-road vehicles. It also remains one of the largest sources of fine particle air pollution, which has serious health impacts. Besides fine particles or soot, Diesel-fueled engines also emit nitrogen oxides that can form ground level ozone.

Beginning in 2001, the U.S. Environmental Protection Agency (EPA) passed rules requiring use of ultra-low sulfur diesel (ULSD) fuel in diesel engines like trucks and buses, construction equipment, and more recently, stationary sources. Ultra-low sulfur diesel (ULSD) has only 15 parts per million (ppm) of sulfur. Low sulfur fuel has 500 ppm sulfur and uncontrolled sulfur diesel may have levels much higher [34-37].

The use of ULSD fuel in conjunction with re-designed advanced emission-control devices lowers the levels of released hydrocarbons, sulfur and nitrogen compounds, along with harmful particulate matter, to almost zero. Nitrogen oxides chemically react to form a lower-atmosphere ozone layer and contribute to acid rain. Burning ULSD fuel greatly cuts the amount of sulfur dioxide, a major contributor to acid rain. The oxides rise high into the atmosphere, lowering the pH of rain drops.

2.2. Description of Hydrodesulfurization (HDS) Process

Hydrodesulfurization (HDS) also known as a hydrotreating process, is one of the most common desulfurization methods that have been used in refinery processes, since the

1950s. HDS is a catalytic chemical process widely used to remove sulfur (S) from natural gas and from refined petroleum products such as gasoline or petrol, jet fuel, kerosene, diesel fuel, and fuel oils. The purpose of removing the sulfur is to reduce the sulfur dioxide (SO₂) emissions that result from using those fuels in automotive vehicles, aircraft, railroad locomotives, ships, gas or oil burning power plants, residential and industrial furnaces, and other forms of fuel combustion.

The industrial hydrodesulfurization processes include facilities for the capture and removal of the resulting hydrogen sulfide (H₂S) gas. In petroleum refineries, the hydrogen sulfide gas is then subsequently converted into byproduct elemental sulfur or sulfuric acid (H₂SO₄). In fact, the vast majority of the 64,000,000 metric tons of sulfur produced worldwide in 2005 was byproduct sulfur from refineries and other hydrocarbon processing plants. Sulfur contents in crude oil may be categorized to the following groups [38]:

- 1- Free Elemental Sulfur
- 2- Mercaptans & Thiols (R-SH)
- 3- Hydrogen Sulfide
- 4- Sulfides
- 5- Disulfides (R-S-S-R')
- 6- Poly Sulfides (R-S_n-R')
- 7- Thiophenes and their derivatives such as BT and DBT

In a typical catalytic hydrodesulfurization unit, the feedstock is deaerated and mixed with hydrogen, preheated in a fired heater (600°-800° F) and then charged under pressure (up to 1,000 psi) through a fixed-bed catalytic reactor

Although HDS, a high-pressure, high-temperature catalytic process that converts organic sulfur to hydrogen sulfide gas, can remove various types of sulfur compounds, some types of heterocyclic sulfur compounds existing in petroleum cannot be removed [39].

2.3. Biodesulfurization (BDS)

Biodesulfurization (BDS), based on the application of microorganisms that selectively remove sulfur atoms from organosulfur compounds, appears as a viable technology to complement the traditional hydrodesulfurization of fuels.

Enzymes in the bacteria selectively oxidize the sulfur, then cleave carbon-sulfur bonds. BDS will operate at ambient temperatures and atmospheric pressure and thus will require substantially less energy than conventional HDS methods to achieve sulfur levels below those required by current regulatory standards. BDS generates a fraction of the CO₂ that is generated in association with HDS, and it does not require hydrogen. Additionally, BDS can effectively remove some key sulfur-containing compounds that are among the most difficult for HDS to treat. BDS can be used instead of, or complementary with, HDS [40-52].

2.4. Oxidative Desulfurization (ODS)

Oxidative desulfurization is considered as the latest unconventional desulfurization process which involves chemical oxidation of divalent organic sulfur compounds to the corresponding hexavalent sulfur, also known as sulfone[53-61].

2.5. Adsorptive Desulfurization (ADS)

In adsorptive desulfurization process, OSCs are adsorbed into a specified solid adsorbent so as to produce none- or low-sulfur fuel. Depending on the interaction between OSCs and the adsorbent, adsorptive desulfurization can be classified into direct adsorption desulfurization and reactive adsorption desulfurization [62].

3. Desulfurization of diesel fuels by extraction with ionic liquids

3.1. Desulfurization of diesel fuels by extraction with N-alkyl-pyridinium-based ionic liquids

3-Methylpyridinium-based ionic liquids were demonstrated to be effective for the selective removal of aromatic heterocyclic sulfur compounds from diesel at room temperature by Gao and coworkers [32]. The results indicated that the extractive performance using 3-methylpyridinium-based ionic liquids followed the order of 1-octyl-3-methylpyridinium tetrafluoroborate ($[C_8^3MPy][BF_4]$) > 1-hexyl-3-methylpyridinium tetrafluoroborate ($[C_6^3MPy][BF_4]$) > 1-butyl-3-methylpyridinium tetrafluoroborate ($[C_4^3MPy][BF_4]$). For a given IL, the sulfur removal selectivity of sulfur compounds followed the order of dibenzothiophene (DBT) > benzothiophene (BT) > thiophene (TS) > 4,6-dibenzothiophene (4,6-DMDBT) under the same conditions, except for $[C_8^3MPy][BF_4]$ ionic liquid, which followed the order of DBT > BT > 4,6-DMDBT > TS. The 3-methylpyridinium-based ionic liquids are insoluble in diesel while diesel has a certain solubility in 3-methylpyridinium-based ionic liquids, with the content varying from 6.1 wt % for $[C_4^3MPy][BF_4]$ to 9.5 wt % for $[C_8^3MPy][BF_4]$. The spent ionic liquid saturated sulfur compounds could be regenerated by a water dilution process. Considering these results, ionic liquids studied in this work are more competitive and feasible for extractive desulfurization applications. Moreover, the extractive desulfurization using 3-methylpyridinium-based ionic liquids could be used at least as a complementary process to hydrodesulfurization (HDS).

The pyridinium-based ionic liquids are employed as phase-transfer catalysts (PTCs) for phase-transfer catalytic oxidation of dibenzothiophene (DBT) dissolved in n-octane by D. Zhao and coworkers [63]. The partition coefficients of DBT between ionic liquids and n-octane are investigated. Then H_2O_2 -formic acid is used as an oxidant and ionic liquids are used as PTCs. The reaction turns to be heterogeneous and desulfurization rate of DBT increased apparently. When IL ($[BPy]HSO_4$) is used as PTC, and the condition are: temperature is 60 °C, time is 60 min, H_2O_2 /sulfur molar ratio (O/S) is 4, the desulfurization rate reaches the maximum (93.3%), and the desulfurization of the real gasoline is also investigat-

ed, 87.7% of sulfur contents are removed under optima reaction conditions. The PTC [BPy]HSO₄ can be recycled for five times without significant decrease in activity. The ability of the ionic liquids to extract DBT from oil phase follows the order below: [BPy]HSO₄>[BPy]H₂PO₄>[BPy]SCN>[BPy]BF₄. The ionic liquid [BPy]HSO₄ has the highest KN value 1.42, followed by the ionic liquid [BPy]H₂PO₄, the KN value is 1.24. figure 1 is shown oxidation mechanism of DBT using ionic liquid as phase-transfer catalyst.

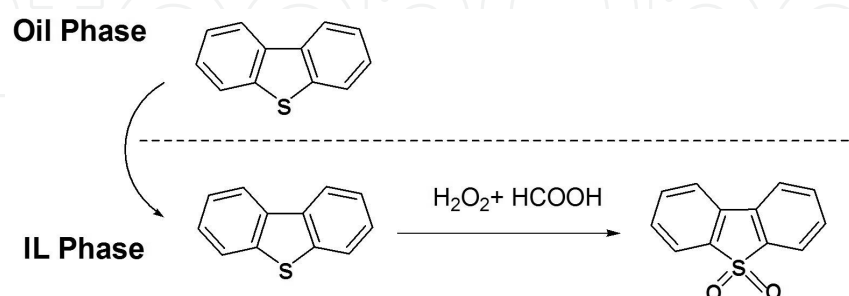


Figure 1. Oxidization mechanism of DBT using ionic liquid as phase-transfer scatalyst.

[Reproduced from Zhao D, Wang Y, Duan E, Zhang J. Oxidation Desulfurization of Fuel using Pyridinium-Based Ionic Liquids as Phase-Transfer Catalysts. *Fuel Proces Tech.* 2010; 91(12):1803–1806, Copyright (2010), with permeation from Elsevier]

Suitability of a pyridinium ionic liquid as a solvent in desulfurization has been analyzed by Arce and coworkers [64]. (Liquid + liquid) equilibria for ternary systems composed by 1-hexyl-3,5-dimethyl pyridinium {bis(trifluoromethylsulfonyl) imide, thiophene, and three hydrocarbons representative of fuel (n-heptane, 2,2,4 trimethylpentane, and toluene) have been determined at T = 298.15 K and atmospheric pressure. High solubility of thiophene in the ionic liquid and also of toluene have been found, being this solvent practically immiscible with 2,2,4 trimethylpentane and heptane. The chemical structure of [hmpy] [NTf₂] was shown in figure 2.

Six N-alkyl-pyridinium-based ILs, N-butyl-pyridinium nitrate ([BPy]NO₃), N-ethyl-pyridinium nitrate ([EPy]NO₃), N-butyl-pyridinium tetrafluoroborate ([BPy]BF₄), N-ethyl-pyridinium tetrafluoroborate ([EPy]BF₄), N-ethyl-pyridinium acetate ([EPy]Ac), and N-butyl-pyridinium acetate ([BPy]Ac), were prepared and tested in the extraction desulfurization of gasoline by wang and coworkers [65]. It is found that [BPy]BF₄ has the best effect on the selective removal of sulfur-containing compounds from gasoline at room temperature among these ionic liquids. The extraction rate of [BPy]BF₄ is 45.5%. The desulfurization effect of [EPy]BF₄ is the lowest. The used ILs can be regenerated by rotary evaporation or re-extraction using tetrachloromethane. Thermosolvatochromism has been studied in three series of ionic liquids, pyridinium-based 1-butylpyridinium, 1-hexylpyridinium, and 1-octylpyridinium with bis(trifluoromethylsulfonyl) imide [NTf₂] and tetrafluoroborate [BF₄] anions, pyrrolidinium-based ionic liquids 1-methyl-1-butylpyrrolidinium, 1-methyl-1-hexylpyrrolidinium, 1-methyl-1-octylpyrrolidinium with bis(trifluoromethylsulfonyl) imide anion and phosphonium-based ionic liquids tetrabutylphosphonium with alanate and valinate anions by Khupse and cowork-

ers [66]. The effect of increase in alkyl chain length and temperature on normalized polarity E_T^N , Kamlet-Taft parameters, hydrogen bond donor ability (R), hydrogen bond acceptor ability (S), and polarizability (π^*) was investigated in the temperature range of 298–353 K.

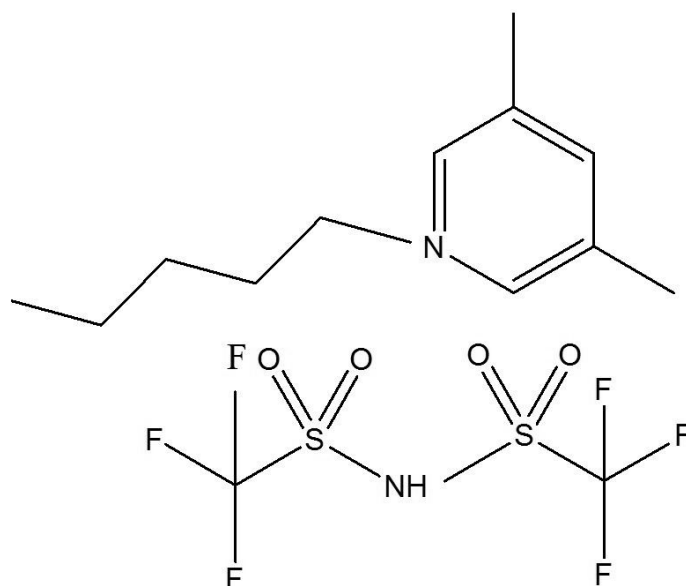


Figure 2. Chemical structure of ionic liquid [hmpy][NTf₂]. No permission.

[Reproduced from Arce A, Francisco M, Soto A, Evaluation of the Polysubstituted Pyridinium Ionic Liquid [hmpy][Ntf₂] as a Suitable Solvent for Desulfurization: Phase Equilibria. *J. Chem. Thermodynamics* 2010; 42(6): 712–718, Copyright (2010), with permission from Elsevier]

Interestingly, the polarity decreases with temperature in the case of pyridinium- and pyrrolidinium-based ionic liquids, and it increases with temperature in the case of phosphonium-based ionic liquids.

3.2. Desulfurization of fuel Using Imidazolium-based ILs

N-butylimidazole-derived dialkylphosphate ionic liquids are demonstrated to be effective for extractive removal of aromatic sulfur compounds (S-compounds) from fuel oils by Nie and coworkers [67], and show strong preferential extraction for aromatic S-compound versus toluene. Sulfur partition coefficients (K_N) between ionic liquid and fuel oil at 298.15 K are determined experimentally over a wide range of sulfur content. The results show that the sulfur removal selectivity for a specific ionic liquid is dependent on the molecular structure of the S-compounds and follows the order dibenzothiophene > benzothiophene > thiophene > 3-methylthiophene, and the efficiency of the ionic liquids for removal of aromatic S-compounds is dependent on the size and structure of both cations and anions of the ionic liquids. For the dialkylphosphate ionic liquids studied with the same anion, the longer the alkyl substitute to the imidazolium ring is the higher the K_N value for that ionic liquid, and a similar trend is found for the ionic liquids with same cation. The chemical structures of ionic liquids were shown in figure 3.

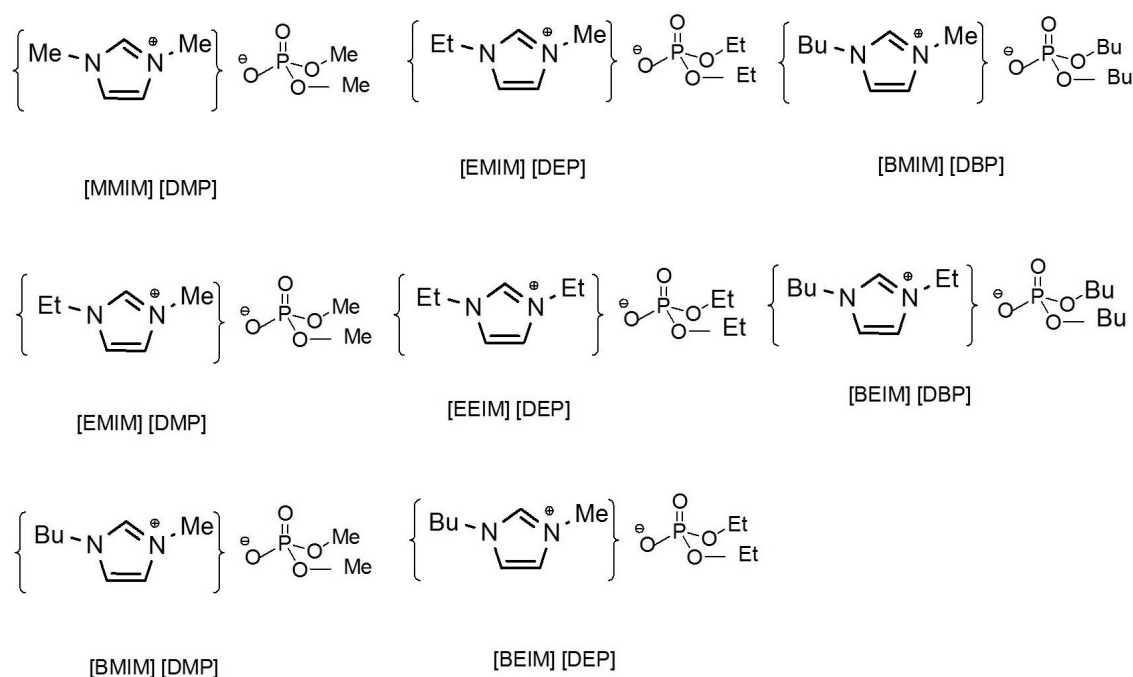


Figure 3. Structures of *N,N*-dialkylimidazolium dialkylphosphate ionic liquids.

[Reproduced from Nie Y, Li C, Meng H, Wang Z. *N,N*-Dialkylimidazolium Dialkylphosphate Ionic Liquids: Their Extractive Performance for Thiophene Series Compounds from Fuel Oils Versus the Length of Alkyl Group. *Fuel Proces Tech.* 2008; 89 (10): 978–983, Copyright (2008), with permeation from Elsevier]

Two types of ionic liquids, 1-alkyl-3-methylimidazolium [AMIM] tetrafluoroborate and hexafluorophosphate and trimethylamine hydrochloride (AlCl_3 -TMAC), were demonstrated to be potentially applicable for sulfur removal from transportation fuels by Zhang and Coworkers [68]. EMIMBF₄ (E = ethyl), BMIMPF₆ (B = butyl), BMIMBF₄, and heavier AMIMPF₆ showed high selectivity, particularly toward aromatic sulfur and nitrogen compounds, for extractive desulfurization and denitrogenation.

The used ionic liquids were readily regenerated either by distillation or by water displacement of absorbed molecules. The absorbed aromatic S-containing compounds were quantitatively recovered. Organic compounds with higher aromatic δ -electron density were favorably absorbed. Alkyl substitution on the aromatic rings was found to significantly reduce the absorption capacity, as a result of a steric effect. The cation and anion structure and size in the ionic liquids are important parameters affecting the absorption capacity for aromatic compounds. At low concentrations, the N- and S-containing compounds were extracted from fuels without mutual hindrance. AlCl_3 -TMAC ionic liquids were found to have remarkably high absorption capacities for aromatics.

To develop an advanced desulfurization process that can be carried out under mild conditions without pressurized hydrogen or catalysis that has been evaluated for the extraction of thiophenic sulfur from a model fuel using the ionic liquids, 1-alkyl-3-alkyl imidazolium alkyl sulfate at room temperature was investigated by Mochizuki [69].

Six types of halogen-free ionic liquids with different alkyl chain lengths were prepared. The extraction yield of dibenzothiophene was higher than that of diphenylsulfide and diphenyldisulfide. The extraction yield of dibenzothiophene increased linearly with an increase in the length of alkyl chains and the mass ratio of the ionic liquid to the model fuel. The effect because of the change in the type of solvent was not appreciable, and dibenzothiophene was efficiently removed regardless of whether tetralin, benzene, or n-dodecane was used as the solvent.

The extractive and oxidative deep desulfurizations of model fuel oils using a low-viscosity ionic liquids, i.e., 1-ethyl-3-methylimidazolium dicyanamide ($[\text{C}_2\text{mim}][\text{N}(\text{CN})_2]$), are investigated by Yu and coworkers [70]. $[\text{C}_2\text{mim}][\text{N}(\text{CN})_2]$ is capable of effectively extracting thiophene (TS) and dibenzothiophene (DBT) from oils. The sulfur content in the raffinate phases is only ~ 10 ppm after a few extraction steps. A short extraction equilibrium time of < 5 min is observed.

The extraction operation is insensitive to temperature, and it can be effectively performed at or around room temperature. Unexpectedly, the oxidative removal of DBT by such a dicyanamide-based ionic liquid is not effective and is not as good as the corresponding extraction operation. Such an undesirable oxidative desulfurization is understood at a molecular level from *ab initio* calculations, and it may be ascribed to the strong intermolecular interaction between CH_3COOH or CH_3COOOH and $[\text{C}_2\text{mim}][\text{N}(\text{CN})_2]$ phase. Therefore, such a dicyanamide-based ionic liquid is efficient for direct extractive desulfurization, while it is less efficient for oxidative desulfurization.

An extraction and catalytic oxidation desulfurization (ECODS) system composed of V_2O_5 , 30 wt% H_2O_2 and 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{Bmim}]\text{BF}_4$) as the basic experiment was used for the removal of DBT from the model oil at moderate temperature (30°C) by Xu and coworkers [71]. In the reaction process, V_2O_5 was oxidized by H_2O_2 into peroxovanadium compounds. Meanwhile, the sulfur-containing compounds, such as benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT), were extracted into ionic liquid from the model oil and oxidized into their corresponding sulfones by peroxovanadium compounds. The reactivity of sulfur-containing compounds in the ECODS followed this order: $\text{DBT} > \text{BT} > 4,6\text{-DMDBT}$. In the case of ECODS, the sulfur removal of DBT can reach 98.7%, which was superior to that of the simple extraction with IL (16.5%) or the catalytic oxidation (2.8%). This ECODS system could be recycled seven times without a significant decrease in activity. Supposed Mechanism of the Deep ECODS Using V_2O_5 Catalyst in ionic liquid shows in figure 4.

In order to obtain the ultra low-sulfur diesel, deep desulfurization of diesel oil has become a vital subject of environmental catalysis studies. Extraction and catalytic oxidation desulfurization (ECODS) system is one of the most promising desulfurization processes. A series of Keggin-type POM-based ionic liquids hybrid materials $[\text{MIMPS}]_3\text{PW}_{12}\text{O}_{40} \cdot 2\text{H}_2\text{O}$ (1-(3-sulfonic group) propyl-3-methyl imidazolium phosphotungstate), $[\text{Bmim}]_3\text{PW}_{12}\text{O}_{40}$ (1-butyl 3-methyl imidazolium phosphotungstate), $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}$ (1-butyl 3-methyl imidazolium phosphomolybdate) and $[\text{Bmim}]_4\text{SiW}_{12}\text{O}_{40}$ (1-butyl-3-methyl imidazolium silicotungstate) have been developed in this study, and the reaction has performed using the POM-ILs materials as catalysts, H_2O_2 as oxidant, and ionic liquid (IL) as solvent by Zhu and coworkers [72]. Through ex-

perimental evaluations, $[\text{MIMPS}]_3\text{PW}_{12}\text{O}_{40} \cdot 2\text{H}_2\text{O}$ was found to be the best catalyst, with an S-removal of 100% at 30 °C for 1 h. The main factors affecting the process including temperature, catalyst dosage, and O/S ($\text{H}_2\text{O}_2/\text{DBT}$) molar ratio were investigated in detail. Under the optimal conditions, DBT (dibenzothiophene) and 4,6-DMDBT (4,6-dimethyl-dibenzothiophene) could achieve high desulfurization efficiency. Moreover, the reaction system also exhibited high activity in actual diesel oil, which could be reduced from 1113 ppm to 198 ppm. The reaction system could recycle 8-times with a slight decrease in activity.

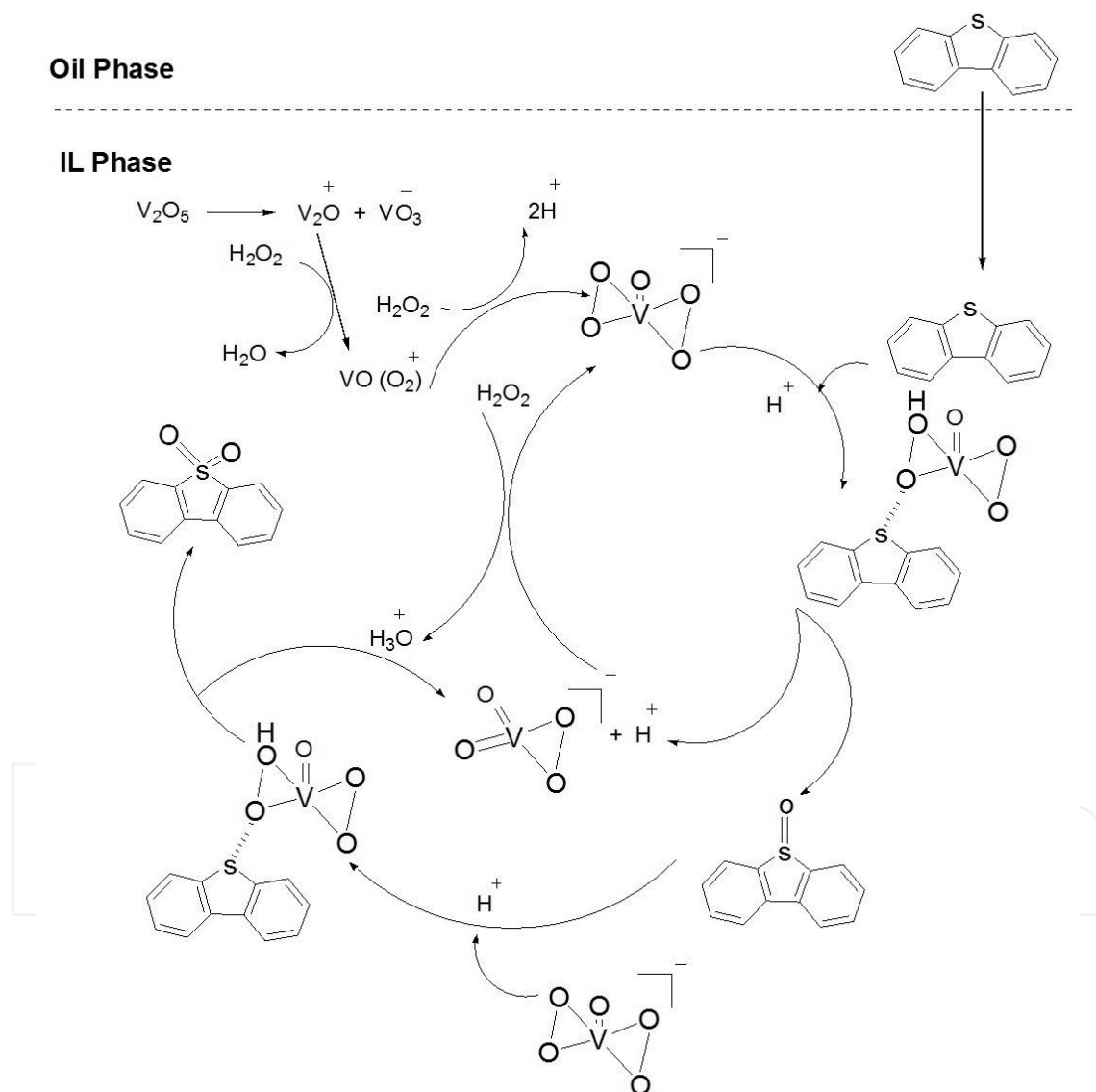


Figure 4. Supposed Mechanism of the Deep ECODS Using V_2O_5 Catalyst in ionic liquid.

[Reproduced from Xu D, Zhu W, Li H, Zhang J, Zou F, Shi H, Yan Y. Oxidative Desulfurization of Fuels Catalyzed by V_2O_5 in Ionic Liquids at Room Temperature. *Energy Fuels* 2009; 23(12): 5929–5933, Copyright (2009), with permeation from American Chemical Society]

Ozone associated with hydrogen peroxide as an advanced oxidation process had been employed to remove dibenzothiophene (DBT) in model oil in an ionic liquid system by Wang and coworkers [73]. DBT was oxidized available by ozone and hydroxyl radicals that were generated by ozone and hydrogen peroxide. The oxidative productions of DBT were extracted to the IL phase because of their high polarity. The IL can be recycled 5 times without a significant decrease in desulfurization activity.

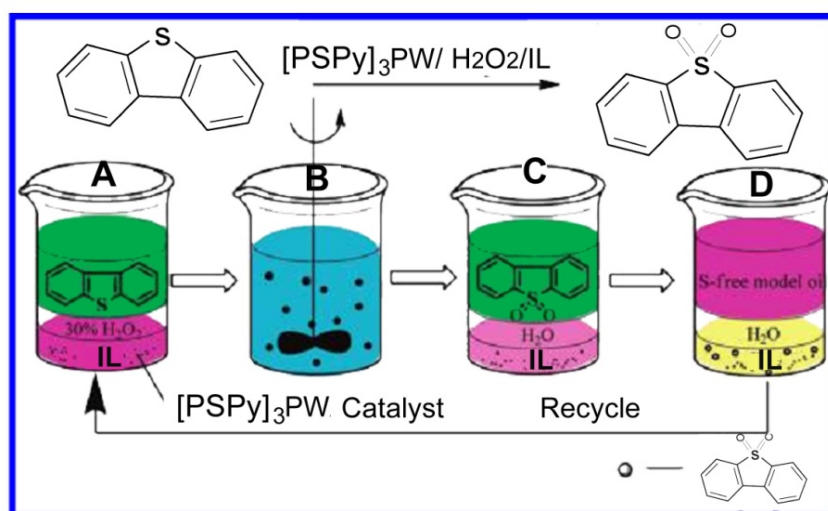


Figure 5. Catalytic Oxidation and Extraction of Sulfur Content Present in Model Oil: (A) before Oxidation; (B) during Oxidation; (C) after Oxidation; (D) with Extraction of Oxidative.

[Reproduced from Huang W, Zhu W, Li H., Shi H, Zhu G, Liu H, Chen G. Heteropolyanion-Based Ionic Liquid for Deep Desulfurization of Fuels in Ionic Liquids, *Ind. Eng. Chem. Res.* 2010, 49(19):8998–9003. Copyright (2010), with permission from American Chemical society]

Peroxtungsten and peroxomolybdenum complexes such as $[\text{WO}(\text{O}_2)_2 \cdot \text{Phen} \cdot \text{H}_2\text{O}]$ and $[\text{MoO}(\text{O}_2)_2 \cdot \text{Phen}]$ (Phen: 1,10-phenanthroline) have been synthesized and characterized and were immobilized in 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{Bmim}]\text{BF}_4$), 1-n-octyl-3-methylimidazolium tetrafluoroborate ($[\text{Omim}]\text{-BF}_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{Bmim}]\text{PF}_6$), and 1-n-octyl-3-methylimidazolium hexafluorophosphate ($[\text{Omim}]\text{PF}_6$) for extraction and catalytic oxidation of dibenzothiophene (DBT) remaining in n-octane by Zhu and coworkers [27]. The results demonstrated that ionic liquid was only used as an extractant for DBT-containing model oil and the removal of sulfur was only about 12.2–22.0%. After addition of 30 wt % H_2O_2 in IL, model oil with 30.0–63.0% sulfur removal was given via chemical oxidation. While H_2O_2 and catalyst were introduced together, the removal of sulfur increased sharply. In the case of the system containing H_2O_2 , $\text{WO}(\text{O}_2)_2 \cdot \text{Phen} \cdot \text{H}_2\text{O}$ and $[\text{Bmim}]\text{BF}_4$, extraction and catalytic oxidation increased the sulfur removal to 98.6%. However, the oxidative desulfurization systems containing $\text{WO}(\text{O}_2)_2 \cdot \text{Phen} \cdot \text{H}_2\text{O}$ and H_2O_2 only led to 50.3% sulfur removal in the absence of ionic liquid. This experiment demonstrated that a combination of catalytic oxidation and extraction in ionic liquid can deeply remove DBT from model oil. This result

also indicated the remarkable advantage of this process over the desulfurization by mere solvent extraction with ionic liquid or catalytic oxidation without ionic liquid.

A heteropolyanion-based ionic liquid, [(3-sulfonic acid) propylpyridine]₃PW₁₂O₄₀ · 2H₂O, [PSPy]₃PW₁₂O₄₀ · 2H₂O, abbreviated [PSPy]₃PW, was synthesized and approved as an effective catalyst for desulfurization of fuels in [omim]PF₆ by using aqueous H₂O₂ as oxidant by Huang and coworkers [74]. The catalysis was fulfilled with advantages of high activity, simplified workup, and flexible recyclability. The catalytic oxidation reactivity of sulfur-containing compounds was in the order dibenzothiophene (DBT) > 4,6-dimethyldibenzothiophene (4,6-DMDBT) > benzothiophene (BT). The effects of the amount of [PSPy]₃PW, H₂O₂, and reaction time and temperature were investigated in detail. Under the optimal conditions, the removal of DBT achieved 99.4%. Especially, we found that the removal of 4,6-DMDBT could be up to 98.8%, and the system could be recycled at least 9 times without significant decrease in activity. The sulfur level of FCC gasoline could be reduced from 360 to 70 ppm in the extraction and catalytic oxidation system. Catalytic Oxidation and Extraction of Sulfur Content Present in Model Oil shows in figure 5.

3.3. Desulfurization of fuel using quaternary ammonium -based ionic liquids

With the aim of deep desulfurization of the gasoline, an amphiphilic catalyst, which is composed of lacunary anion [PW₁₁O₃₉]⁷⁻ and quaternary ammonium cation [C₁₈H₃₇(CH₃)₃N]⁺, assembled in hydrophobic ionic liquid emulsions, can oxidize the sulfur compounds present in oil into their corresponding sulfones under ambient reaction conditions by Ge and coworkers [75].

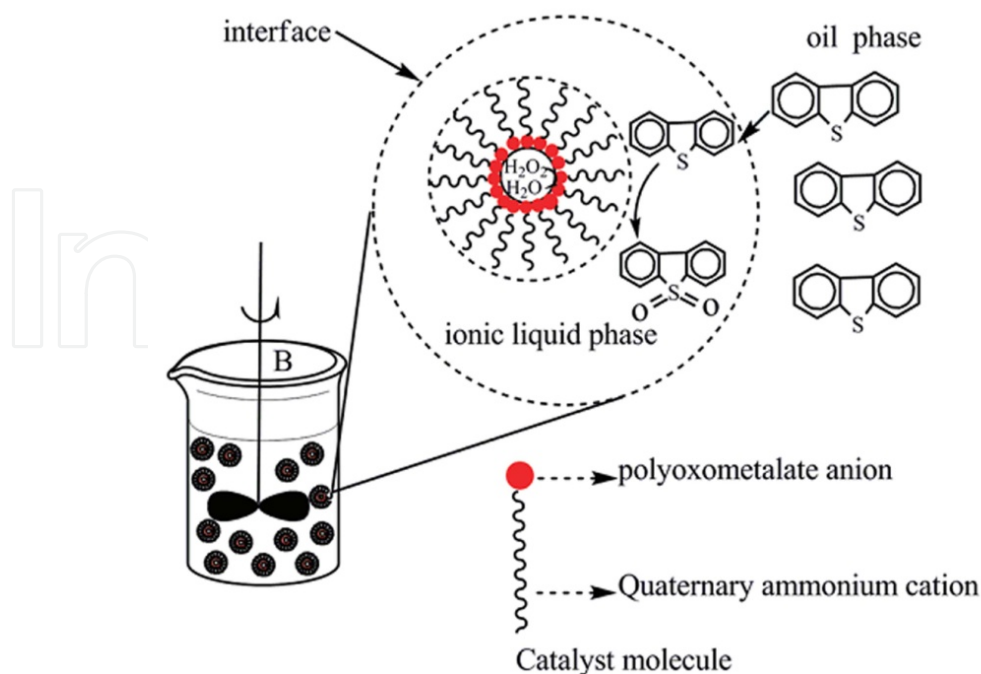


Figure 6. Catalytic Oxidation of DBT in Ionic Liquid Emulsion System.

[Reproduced from Ge J, Zhou Y, Yang Y, Xue M. Catalytic Oxidative Desulfurization of Gasoline Using Ionic Liquid Emulsion System. *Ind. Eng. Chem. Res.* 2011; 50(24): 13686–13692, Copyright (2011), with permeation from American Chemical Society]

In this process, catalytic oxidation of sulfur-containing molecules in model oil was investigated in detail under different reaction conditions (including different desulfurization systems, $\text{H}_2\text{O}_2/\text{DBT}$ molar ratio, temperature, and various sulfur compounds). Moreover; this ionic liquid emulsion system could be recycled five times with an unnoticeable decrease in catalytic activity, and, from the kinetics study, it can be shown that the catalytic oxidative reaction is a pseudofirst-order reaction and the half-life is 30.4 min. Furthermore, the mechanism of catalytic oxidation desulfurization was elaborated, and the total sulfur level of real gasoline can be decreased from 1236 to 65 ppm after catalytic oxidation using an ionic liquid emulsion system.

In this emulsion reaction system, the catalyst molecule acts as an emulsifying agent, could be uniformly distributed in the interface of H_2O_2 ionic liquid, and forms a film around the dispersed ionic liquid droplets (Scheme 1)

3.4. Extractive Desulfurization Using Fe-Containing Ionic Liquids

Fe^{III} -containing ionic liquids, prepared from the reaction of anhydrous FeCl_3 and imidazolium chloride ([imidazolium]Cl), were used as effective extractants for the desulfurization of a model oil containing dibenzothiophene (DBT) by Ko and coworkers [76]. The amount of DBT extracted increased with an increasing molar ratio of FeCl_3 /[imidazolium]Cl. The ability of the ionic liquids to extract DBT seems to be attributed to the combined effects of Lewis acidity and fluidity of ionic liquids.

$x\text{Et}_3\text{NHCl}_3 \text{FeCl}_3$ ($x=1.4-1.8$) ionic liquids were synthesized by mixing Et_3NHCl and anhydrous FeCl_3 at 80°C by Li and coworkers [77]. These were liquid at room temperature, with low viscosities, and exhibited remarkable abilities in effective desulfurization of thiophene in *n*-octane and fluid catalytic cracking (FCC) gasoline. Among them, $1.6\text{Et}_3\text{NHCl}_3 \text{FeCl}_3$ showed the highest sulfur removal. The anionic species FeCl_4^- existed in $1.6\text{Et}_3\text{NHCl}_3 \text{FeCl}_3$ ionic liquid, as detected by electrospray ionization-mass spectrometry (ESI-MS), and the ionic liquid was stable in air and moisture. Sulfur-free ($<10\text{mg/L}$) gasoline could be obtained after extraction twice using an ionic liquid/oil volume ratio of 1. The ionic liquid could be recycled 10 times by distillation with a slight decrease in activity. The influence of the $\text{Et}_3\text{NHCl}/\text{FeCl}_3$ molar ratio on the sulfur removal of thiophene is shown in Table 1.

Sulfur Removal (%)	ionic liquids	Sulfur Removal (%)	ionic liquids
41.2	[BMIm][O ₂ CSO ₄] ^b	80.2	1.4 Et ₃ NHCl. Fe Cl ₃
40.0	[C ₈ MIm]BF ₄ ^c	84.3	1.5 Et ₃ NHCl. Fe Cl ₃
51.7	[C ₈ MPy]BF ₄ ^d	87.6	1.6 Et ₃ NHCl. Fe Cl ₃

44.1	[OPy]BF ₄ ^e	86.5	1.7 Et ₃ NHCl. Fe Cl ₃
		85.2	1.8 Et ₃ NHCl. Fe Cl ₃

Table 1. Sulfur Removal of Thiophene Using ILs.

^aExtraction conditions: model oil, 10mL; IL, 10mL; the mixture was stirred at 20 °C for 10 min. ^b Results from Esser et al. ^cResults from Alonso et al. ^dResults from Liu et al., in which the extraction conditions were mass ratio oil/IL, 1:1; extraction time, 15 min; room temperature. ^e Results from Liu et al.

[Reproduced from Li FT, Liu Y, Sun ZM, Chen LJ, Zhao DS, Liu RH, Kou CG, Deep Extractive Desulfurization of Gasoline with xEt₃NHCl₃ FeCl₃ Ionic Liquids. *Energy Fuels*, 2010; 24(8): 4285–4289, Copyright (2010), with permission from American Chemical Society]

A series of polymer-supported metal chlorides imidazolium ionic liquid moieties, M/CMPS-Im(Cl) (M =CuCl, ZnCl₂ and FeCl₃), were synthesized by grafted method using chloromethylated polystyrene (CMPS) resin as support by Wang and coworkers [78].

The results showed that the surface of CMPS resin was covered with a thin layer of extraction activity components. Then, the synthesized CMPS-supported imidazolium-based ionic liquids were investigated to extract thiophene and its derivatives from model gasoline (n-octane/thiophene) under certain conditions. For a given imidazolium-based ionic liquid: first, the order of extraction capacity of extractant was CuCl/CMPS-Im(Cl) > ZnCl₂/CMPS-Im(Cl) > FeCl₃/CMPS-Im(Cl); the reason for this was that the π-complexation capability between Cu⁺ and thiophene was stronger than those of Fe³⁺ and Zn²⁺. Second, the sulfur removal selectivity of sulfur compound followed the order of TS < BT < DBT under the same conditions; it indicated that the extraction was favored for those aromatic heterocyclic sulfur compounds with higher density aromatic π-electrons density. Meanwhile, the effect of mass ratio of model gasoline to M/CMPS-Im(Cl) ionic liquids, different initial sulfur concentrations, and extraction time on desulfurization rates of M/CMPS-Im (Cl) ionic liquids was performed, respectively.

3.5. Optimization of oxidative desulfurization of dibenzothiophene using acidic ionic liquid

The oxidative desulfurization of dibenzothiophene (DBT) in n-octane as model oil with Brönsted acidic ionic liquids *N*-methyl-pyrrolidonium phosphate ([Hnmp]H₂PO₄) as catalytic solvent and H₂O₂ as oxidant was optimized by orthogonal experiments. 99.8% of DBT in the model oil was removed under the optimal conditions of molar ratio of H₂O₂ to sulfur of 16:1, reaction temperature of 60°C, reaction time of 5 h, and volume ratio of model oil to ionic liquids of 1:1 by ZHAO and coworkers [79]. The desulfurization efficiency of actual diesel was 64.3% under the optimized conditions. The influences of the desulfurization efficiency of DBT decreased in the following order: oxidation temperature > oxidation time > molar ratio of H₂O₂/sulfur (O/S) > volume ratio of [Hnmp]H₂PO₄ to model oil (VIL/Vmodel oil), according to extreme analysis of orthogonal test. The ionic liquid [Hnmp]H₂PO₄ can be recycled six times without a significant decrease in activity.

An acidic ionic liquid N-butyl-N-methylimidazolium hydrogen sulfate ([BMIm]HSO₄) was applied as extractant and catalyst for the oxidative desulfurization of dibenzothiophenes (DBT) in the presence of H₂O₂ in model oil by Zhang and coworkers [80]. Several parameters, e.g., catalyst amount, hydrogen peroxide quantity, reaction time, and temperature, were investigated in detail. The catalytic oxidative desulfurization rate can reach 100% for DBT in model oil. The ionic liquid [BMIm]HSO₄ can be recycled 5 times with only a slight reduction in activity.

Ionic liquids, a new class of green solvents, have recently been undergoing intensive research on the removal of thiophenic sulfur species (e.g., dibenzothiophene) from fuels because of the limitation of the traditional hydrodesulfurization method in removing these species. In this work, deep oxidative desulfurization of diesel fuels by six functional acidic ionic liquids are studied, in which ionic liquids are used as both extractant and catalyst, and 30 wt % H₂O₂ solution as oxidant by Yu and coworkers [81]. These ionic liquids include both Lewis acidic species such as 1-butyl-3-methylimidazolium chloride/2ZnCl₂ ([C₄mim]Cl/2ZnCl₂ and [C₄mim]Cl/ZnCl₂) and Brønsted acidic species such as 1-methyl-3-ethylcarboxylic acid imidazolium hydrogen sulfate ([CH₂COOHmim]HSO₄), 1-methyl-3-(butyl-4-sulfinate) imidazolium hydrogen sulfate ([SO₃HC₄mim]HSO₄), [Hmim]HSO₄, and [C₄mim]HSO₄ where different acidic groups such as H, COOH, and SO₃H are appended to the cations. Except for [CH₂COOHmim]HSO₄, both Brønsted and Lewis acidic ILs are capable of effectively removing dibenzothiophene from model diesel fuels, where 100% sulfur removal is obtained for [C₄mim]Cl/2ZnCl₂ and [SO₃HC₄mim]HSO₄. The effects of temperature, molar ratio of O/S, mass ratio of ionic liquid /oil, and ionic liquid regeneration on desulfurization are investigated systematically for [C₄mim]Cl/2ZnCl₂ and [SO₃HC₄mim]HSO₄. The desulfurization ability is not sensitive to the mass ratio of IL/oil, which is desired for reducing ionic liquid dosage in industrial application; the ionic liquids can be recycled six times with merely a negligible loss in activity. [C₄mim]Cl/2ZnCl₂ can reduce the sulfur content in real commercial diesel fuel from 64 to 7.9 ppm with a sulfur removal of 87.7%; however, it is not too effective for coke diesel fuel with high initial sulfur content of 5380 ppm. This work tends to show that diesel fuels can be purified to sulfur-free or ultralow sulfur fuels by further deep oxidative desulfurization by using ionic liquids after hydrodesulfurization. Lewis and Brønsted acidic ionic liquids used in this work show in figure 7.

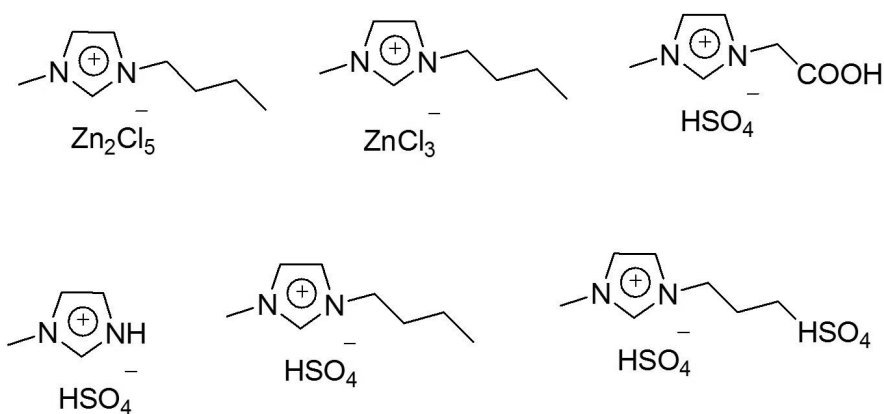


Figure 7. Lewis and Brønsted acidic ionic liquids used in this work.

[Reproduced from Yu G, Zhao J, Song D, Asumana C, Zhang X, Chen X. Deep Oxidative Desulfurization of Diesel Fuels by Acidic Ionic Liquids. *Ind Eng Chem Res* 2011; 50(20): 11690–11697, Copyright (2011), with permeation from American Chemical Society]

4. Conclusion

In view of stringent environmental regulations, utilization of sulfur-containing fuel oils has severe limitations regarding emission of sulfur dioxide. Technology for reduction of sulfur in diesel fuel to 15 ppm is currently available and new technologies are under development that could reduce the cost of desulfurization. Chemical oxidation in conjunction with ionic liquid extraction can increase the removal of sulfur sharply. Ionic liquids have the ability of extracting aromatic sulfur-containing compounds at ambient conditions without H_2 consumption. The cations, anions structure, and size of ionic liquids are important parameters affecting the extracting ability. In addition ionic liquids are immiscible with fuel, and the used ionic liquids can be regenerated and recycled by solvent washing or distillation.

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