Review

Oxidative desulfurization of fuel oils using ionic liquids: A review

Abdul Waheed Bhutto [a,b,1], Rashid Abro [a,1], Shurong Gao [a], Tauqeer Abbas [c,d], Xiaochun Chen [a,*], Guangren Yu [a,*]

[a] Beijing Key Laboratory of Membrane Science and Technology & College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China
[b] Department of Chemical Engineering, Dawood University of Engineering and Technology, Karachi, Pakistan
[c] Petronas Ionic Liquid Center, Department of Chemical Engineering, Universiti Teknologi Petronas, Malaysia
[d] Department of Chemical Engineering, COMSATS Institute of Information Technology, Lahore, Pakistan

ARTICLE INFO

ABSTRACT

Due to sterically-hindered adsorption of some thiophenic sulfur compounds (S-compounds) such as thiophene, dibenzothiophene and their derivatives on catalyst surface, hydrodesulfurization (HDS) is not effective to remove such thiophenic S-compounds in fuel oils. To produce clean fuel oils with lower S-content (e.g., S < 10 ppm), severe conditions such as high temperature, high pressure, active catalyst and complex process are required in HDS, which, however, results into higher cost, more olefin loss, and lower oil yield. Although some alternative methods such as extraction (EDS), oxidation (ODS), adsorption (ADS) and bio desulfurization (BDS) have been studied, no one is widely used in commercial scale due to some respective problems. In the past few decades, ODS of fuel oils using ionic liquids (ILs) has drawn increasing attentions, and many works have been published. In this new method, instead of traditional organic solvents, ILs are employed as extractants or/and catalysts, where S-compounds are extracted into ILs phase and oxidized to their sulfone products, and these more polar sulfones are removed easily. ILs have some advantages such as non-volatility, wide liquid range, high thermal and chemical stability, regenerability and reusability, which make this new ILs-based method avoid the problems such as solvent loss/contamination and difficult separation and regeneration in tradition ODS with organic solvents. It is worth noting that the numerous species and the designability of ILs produce a very huge candidate pool for selecting one suitable IL for oxidative desulfurization. Recently, many scientific findings about ODS using ILs have shown its good future. Here, we give a review for these interesting results to illustrate the novelty, problem and perspective of such a new method.

© 2016 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Desulfurization of fuel oils such as diesel, fluidized catalytic cracking (FCC) gasoline, kerosene, jet fuel and heating oil is an important practice in oil refining. Sulfur compounds (S-compounds) in fuel oils are undesirable as they create problems during refining as well as during their commercial use. During refining, S-compounds tend to deactivate some catalysts used in oil processing and cause corrosion problems in, pumping, pipeline and refining equipment. During the commercial use of fuel oils, S-compounds are transferred to sulfur oxides in combustion, and then to sulfates, acid rain, or other particulates which are harmful to the environment. Moreover, the S-compounds in the exhaust gases can significantly harm the emission control technology designed to meet NO_x and suspended particulate matter (SPM) emission standards. With increasing environmental concerns, all developed and developing countries are implementing strict standards to limit the S-content in fuel oil, as shown in Figs. 1 and 2. Fulfilling the required lower S-compounds specifications, represents a major operational and economic challenge for the petroleum refining industry [1–4]. Therefore, intensive study may help to find more economical and viable deep desulfurization technologies.

Hydrodesulfurization (HDS) is a widely used commercial method to remove S-compounds in fuel oils. In HDS, S-compounds are converted into H_2S and matching hydrocarbons in the presence of catalyst (Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3) at high temperatures (300–340 °C) and pressures (20–100 atm of H_2), and H_2S is subsequently separated from fuel oils and oxidized into elemental sulfur in the Claus process. HDS process is efficient in eliminating sulfides thiols, disulfides and thiols but is less effective for heterocyclic

* Correspondence authors. Tel.: +86 10 6443 3570; fax: +86 10 6443 3570.
 E-mail addresses: chenxc@mail.buct.edu.cn (X. Chen), gryu@mail.buct.edu.cn (G. Yu).
 [1] These authors have contributed equally to this work.
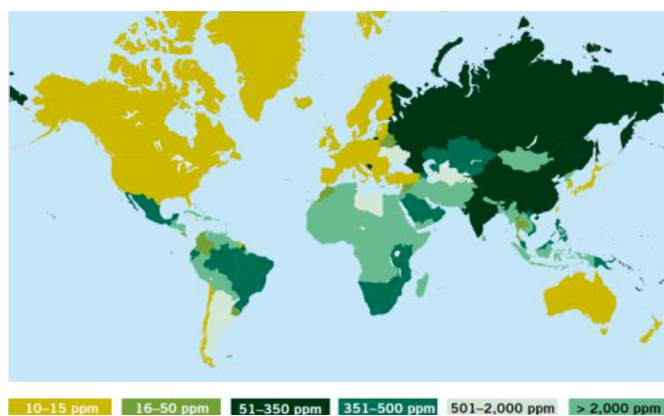
Fig. 1. Maximum diesel sulfur limits, January 2014 [4].

10–15 ppm 16–50 ppm 51–350 ppm 351–500 ppm 501–2,000 ppm > 2,000 ppm
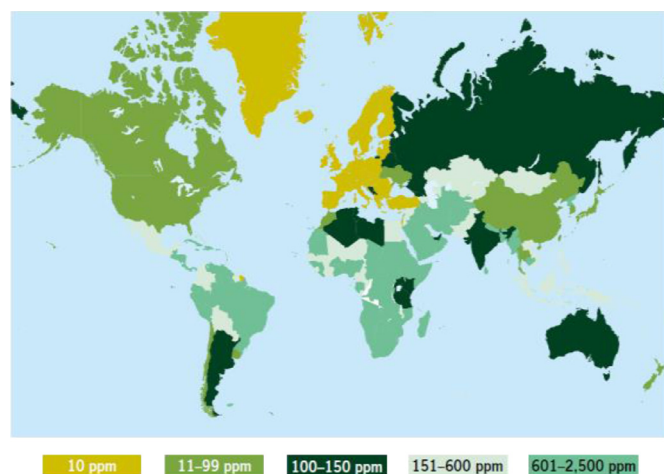
Fig. 2. Maximum gasoline sulfur limits, January 2014 [4].

10 ppm 11–99 ppm 100–150 ppm 151–600 ppm 601–2,500 ppm

Fig. 3. S-compounds in fuel oils.

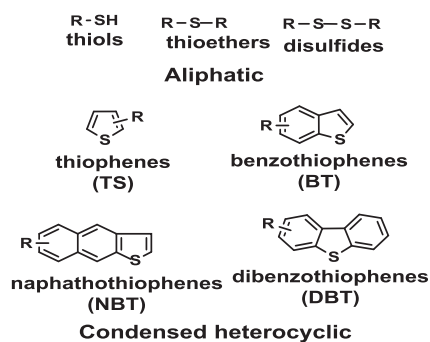S-compounds such as thiophene (TS), dibenzothiophene (DBT) and their derivatives, especially 4,6-dimethyldibenzothiophene (4,6-DMDBT) because of the ineffective adsorption of these heterocyclic S-compounds on catalyst surface. Some typical S-compounds in fuel oils are shown in Fig. 3. To remove these heterocyclic S-compounds in HSD, the reactor size unit needs to be increased by factors of 5–15 and the pressure and temperature have to be elevated further more with more active catalysts. These steps result into significantly increase in the operational and capital costs and also leads to undesired side reactions bringing saturation of olefins and loss of octane number [5–8]. To overcome drawbacks of HDS in deep desulfurization, some alternative approaches such as,

Table 1

Different adsorbents used in ADS at optimized conditions. Reprinted with permission from Ref. [2]. Copyright 2014 Royal Society of Chemistry.

Adsorbents	Model oil	S-comp.	Initial S: (ppm)	Temp. (K)	Pressure (atm)	S-removal
Activated carbon	Gas oil	DBT	178	198	1	95%
	Gas oil	TS	300	243	1.5	88%
Alumina	Gas oil	DBT	700	393	N/A	30%
Zeolites from coal	Hexane	TS, BT	500	303	1	63%
NiMoP/Al$_2$O$_3$	Hexane	DBT	450	600	40	56%
Gallium + Y-zeolite	Nonane	DBT	500	333	N/A	97%
Cu-zirconia	Octane	TS	2000	180	N/A	99%
Ruthenium complexes	Hexane	DBT	40	298	1	55%

Table 2

Bio-desulfurization by different microorganisms. Reprinted with permission from Ref. [2]. Copyright 2014 Royal Society of Chemistry.

Microorganism	Model oil	Initial S: (ppm)	Temp (K)	S-removal
Gordoniaalkanivorans RIPI90A	Hexadecane	320	303	90%
Mycobacterium sp. ZD-19	Hexadecane	92	303	100%
Mycobacterium goodii X7B	Tertradecane	200	313	99%
Rhodococcuserythropolis IGTS8	Hexadecane	100	303	80%
Gordoniaalkanivorans strain 1B	Heptane	100	308	63%
Bacillus subtilis WU-S2B	Tridecane	100	323	50%
Pseudomonas stutzeri UP-1	Hexadecane	500	304	74%
Sphingomonassubarctica T7b	Gas oil	280	300	94%
Bacterium, strain RIPI-22	Hexadecane	100	303	77%
Pseudomonas delafieldii R-8	Diesel oil	591	303	47%

oxidation (ODS), extraction (EDS) and adsorption (ADS) (Table 1 shows different adsorbents used in ADS at optimized conditions), and bio desulfurization (BDS) (Table 2 shows bio-desulfurization by different microorganisms) are under considerations.

Since refractory heterocyclic S-compounds such as TS, DBT and their derivatives are easily removed by the oxidative desulfurization (ODS) [9], therefore ODS is currently being explored as a promising method to accomplish an ultra-low S-level in fuel oil because it is simple in processing and high efficiency [10]. No use of expensive hydrogen is another advantage of ODS. In subsequent operation, oxidized compounds can be extracted from fuel oils through contacting oxidized fuel oils with non-miscible polar solvents. Many organic solvents have been used in ODS such as acetonitrile, *N*,*N*-dimethylformamide (DMF), methanol, furfural and dimethylsulfoxide (DMSO) *N*-methyl pyrrolidone (NMP), methanol [11]. However, these solvents are volatile which result in not only solvent volatile loss and contamination but also make the solvent recovery difficult.

Ionic liquids (ILs), just emerging in the past few decades, are a class of new solvents, which are promising alternatives to traditional volatile solvents used in ODS. ILs, composed entirely of organic cation and inorganic or organic anion, have been explored as green solvents, owing to their exclusive properties such as thermal and chemical stability, negligible volatility, good solubility characteristics and the variety of structures available [12–15].

ILs have been investigated as extractive reagents in extractive desulfurization, as has been reviewed in our recent publication [2]. Recently, researchers have been attempting to use ILs as solvents in ODS as well as both catalysts and extractive reagents in coupled extractive–oxidative desulfurization. Such ODS with ILs shows very positive results and also eliminates the loss of volatile solvent and contamination/pollution. ODS with ILs also ensures easy regeneration and good stability. In addition to this, it also ensures that those heterocyclic S-compounds unreactive to HDS are efficiently removed in only single stage to obtain clean fuel oils with S < 10 ppm.

Table 3
List of some common oxidants and their active oxygen content. Reprinted with permission from Ref. [108]. Copyright 2003 Royal Society of Chemistry.

Oxidant	Active oxygen (wt%)	By-product
H_2O_2	47.1	H_2O
t-BuOOH	17.8	*t*-BuOH
HNO_3	25.0	NO_x, N_2O, N_2
N_2O	36.4	N_2
NaClO	21.6	NaCl
$NaClO_2$	35.6	NaCl
NaBrO	13.4	NaBr
$C_5H_{11}NO_2$ [a]	13.7	$C_5H_{11}NO$
$KHSO_5$ [b]	10.5	$KHSO_4$
$NaIO_4$	29.9 [c]	NaI
PhIO	7.3	PhI
H_2O_2	47.1	H_2O

[a] *N*-Methylmorpholine *N*-oxide (NMO).
[b] Stabilized and commercialized as the "triple salt": $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$.
[c] Assuming all 4 oxygen atoms are used.

Besides homogeneous catalytic ODS, many research groups have committed to heterogeneous catalysis system of supported ILs, ILs emulsion, and ILs photo catalysis. This work reviews recent progress and developments to purify the fuel oil to S-free or S-ultralow fuels by ODS with ILs technology, also the issues of traditional ODS.

2. Oxidative desulfurization (ODS)

ODS has been considered as a promising method for deep desulfurization of fuel oils [9]. As shown in the following reactions, in ODS the S-compounds are oxidized to sulfones using an oxidant. The sulfone compounds are then easily separated from the fuel oil by a solvent taking advantage of due their higher polarity [2]. Thus, ODS process comprises of two stages: (i) oxidation; (ii) followed by separation operations.

$$R - S - R' \xrightarrow{[O]} R - SO_2 - R'$$
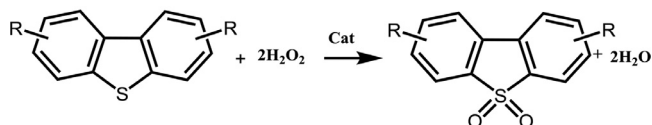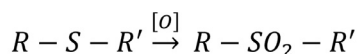
Oxidization brings dramatic changes in physical properties of S-compounds. Such as methyl sulfide (CH_3SCH_3) is a light S-compound with density 0.846 g/mL, water-insoluble, low boiling liquid (36 °C), whereas methyl sulfoxide ($CHSOCH_3$) is a heavy with density 1.481 g/mL, high boiler (189 °C) and water-miscible liquid [16].

2.1. Oxidant in ODS

ODS process was first studied using nitrogen dioxides (NO_2) as an oxidant and methanol as solvent. After that many oxidants have been investigated. Table 3 gives the list of some common oxidants and their active oxygen content. The oxidants donate oxygen atom to the S-compounds in sulfides, disulfides, thiols and their derivatives to form sulfones or sulfoxides. Among these all oxidants, H_2O_2 has been proven as the best oxidant. Table 3 indicates that H_2O_2 gives the highest percentage of active oxygen. The other advantages for the use of H_2O_2 are, low cost, non-polluting, non-strongly corrosive, and commercial availability [17]. The main challenge using H_2O_2 as an ODS oxidant is the slow rate of reaction due to mass-transfer restriction in the biphasic oxidation process with the consequent energy consuming biphasic separation.

According to Ma et al. [18] if a gas is used as an oxidizing agent in ODS, oil–water bi phasic problems would not exist.

2.2. Catalyst in ODS

Many catalysts such as acetic acid, vanadium pentoxide, decatungstates, peroxotungsten and peroxomolybdenum complexes, *etc.* have been investigated in ODS. Among these compounds most of studies focused on molybdenum (Mo) based heterogeneous catalyst. It was found that the Mo catalyst supported on Al_2O_3 showed strong catalytic activity compared with Mo catalyst supported on TiO_2 and SiO_2 compounds. Nevertheless, Mo tends to leach into the reaction medium, where the catalyst is not so much stable and the key portion of the catalytic activity is the solubilized molybdenum. The oxidation activity of each S-compound increased with the increasing molar ratio of O/S, *i.e.*, 3 and then leveled off beyond this value. The oxidative reaction of S-compound can be considered as a first-order reaction with superficial activation energies 28 ± 1 kJ/mol [19].

The polyaromatic S-compounds show higher reactivity in ODS than TSs and BTs, in the reverse reactivity order of HDS [20]. In polyoxometalates catalyzed oxidation of S-compounds mass transfer across the interface of aqueous phase and oil phase is the rate-limiting step. Under such situation phase transfer agent (PTA) is usually added to the reaction system in order to enhance rate of mass transfer. 100% oxidation of DBT in a gas oil was achieved with H_2O_2 as oxidation agent using phosphotungstic acid as the catalyst and tetraoctylammonium bromide as the phase transfer agent, at optimal conditions [21]. Zhang et al. [22] suggested that $[C_4mim]_3PMo_{12}O_{40}/SiO_2$ could effectively catalyze the oxidation of BT, DBT, and 4,6-DMDBT using H_2O_2 as the oxidant under mild conditions. Complete DBT conversion was obtained at 60 °C, an O/S molar ratio of 3.0, and thermal equilibrium in 100 min. The oxidation reactivity decreased in the order: DBT > 4,6-DMDBT > BT. H_2O and $[C_4mim]_3 PMo_{12}O_{40}/SiO_2$ phases were easily separated from the oil by centrifugation method. It was also reported that quinoline and carbazole have constructive effects on oxidation, as they help to slow down the H_2O_2 thermal decomposition. The $[C_4mim]_3 PMo_{12}O_{40}/SiO_2$-$H_2O_2$ oxidation system is effective in removing bulky S-compounds from diesel fuels.

2.3. Separation operations

The second step in ODS is the elimination of the oxidized compounds from fuel oil. The oxidized S-compounds from the fuel oils can be extracted by non-miscible polar solvents. In subsequent operation, the oxidized compounds and polar solvent are separated from the fuel oils by gravity separation or centrifugation. Sulfones are extracted by polar solvents such as acetonitrile, DMF, methanol, furfural, DMSO, NMP and methanol in a simple process under milder conditions with low equipment and operation costs. Nevertheless these solvents are volatile and harmful to environment and human health and less efficient [23,24].

Fig. 4 shows the flowchart of biphasic oxidation/extraction simultaneous ODS process. Oxidation is accomplished by reacting an oxidant with fuel oil under specific conditions. The reaction conditions should be selected in such a way that reaction is stopped before the oxidant agents reacts with other less reactive organic compounds of fuel oil. Down the reaction, oxidant agents can be regenerated for further usage. Different chemical and physical post-treatment methods can be used to remove any unused oxidant that remains in the fuel oil, such as washing, extraction. The fuel oil is water washed to recover any traces of dissolved extraction solvent and polished using other methods, such as by absorption using silica gel and alumina. The desulfurization efficiency for
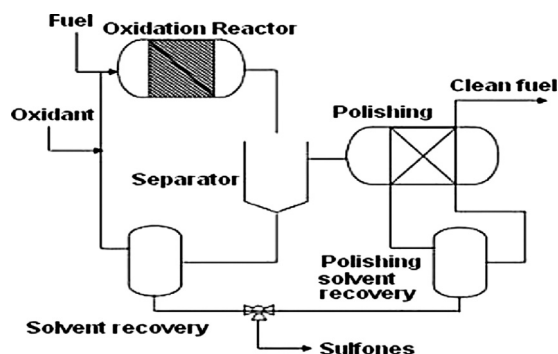
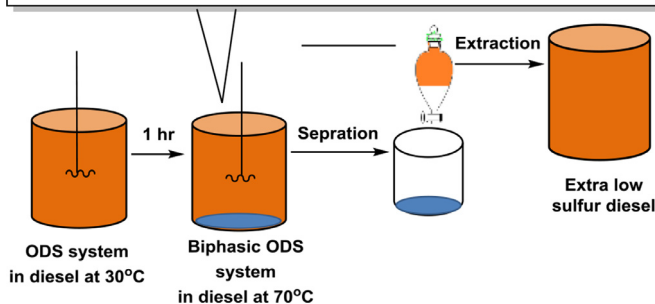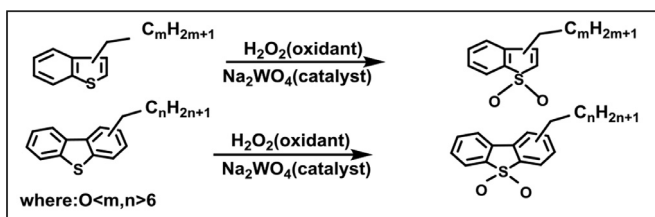**Fig. 4.** Flow chart of biphasic simultaneous oxidation/extraction ODS unit.

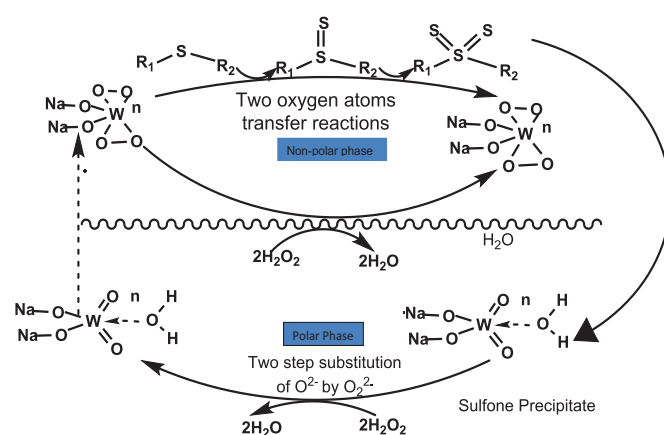
Fig. 5. ODS reaction, biphasic system.

Fig. 6. Homogeneous biphasic ODS system without PTA. Reprinted with permission from Ref. [30]. Copyright 2010 Elsevier.
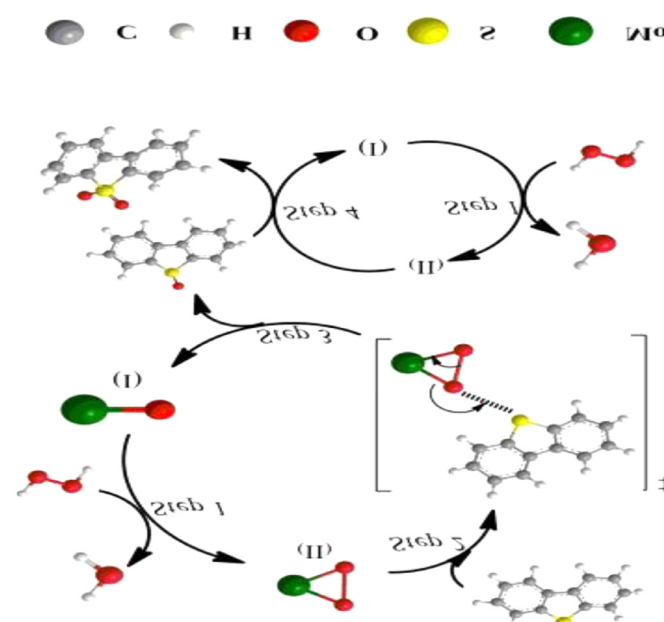

Fig. 7. Mechanism proposed for oxidation of S-compound to sulfone over the active species. Reprinted with permission from Ref. [31]. Copyright 2013 Elsevier.

fuel oils lies in the order straight-run light gas oil > commercial fuel oil > light cycle oil.

2.4. Oxidative reaction mechanism

Generally in the ODS reactions, the divalent sulfur atom are converted into sulfone by electrophilic addition of oxygen atoms from the H_2O [24–27]. Fig. 5 illustrates the overall and schematic diagram of ODS process. Many ODS mechanisms have been previously proposed. Jiang et al. [28] have reviewed different approaches toward ODS of fuel oils including H_2O_2/organic acids system, H_2O_2/heteropolyacid system, H_2O_2/MoO_x system, H_2O_2/Ti-containing zeolites system, and t-butyl hydroperoxide (TBHP) (non-hydrogen peroxide) systems. Unlike H_2O_2, TBHP is completely fuel soluble eliminating the need of biphasic systems [29]. Quaternary ammonium cations and heteropoly tungstophosphate ions also develop an efficient system for the ODS of diesel. Amphiphilic catalyst with a proper quaternary ammonium cation can form metastable emulsion droplets in diesel with an aqueous H_2O_2 solution. The size and type of quaternary ammonium cation play a vital role in the formation of metastable emulsion droplets [28]. Al-Shahrani et al. [30] explained the detailed mechanism of homogeneous biphasic ODS system that does not uses PTA in Fig. 6. Biphasic system formation starts once the catalyst mixes with the H_2O_2 and fuel oils in acetic acid.

Zhu et al. [31] investigated ODS using surfactant-type polyoxometalate-based ILs, such as $[(nC_8H_{17})_3NCH_3]_3\{PO_4[MoO(O_2)_2]_4\}$, $[(n\text{-}C_{12}H_{25})_3NCH_3]_3\{PO_4[MoO(O_2)_2]_4\}$, $[(n\text{-}C_8H_{17})_3NCH_3]_3\{PO_4[WO(O_2)_2]_4\}$ and $[(n\text{-}C_{12}H_{25})_3NCH_3]_3\{PO_4[WO(O_2)_2]_4\}$.

The study proposed overall mechanism of catalytic desulfurization in four steps as shown in Fig. 7, which are: (1) the active peroxo species $[Mo(O_2)]$ is regenerated from the reaction of $[Mo(O)]$, when surfactant-type polyoxometalate-based ILs (SPILs), reacting with excess H_2O_2. (2) An oxygen transfers from the active $[(Mo(O_2)]$ to the sulfide leads formation of the transition state. (3) A complete O-transfer to the sulfide takes place, which yields the sulfoxide and the $[Mo(O)]$. (4) The active species, i.e., $[(Mo(O_2)]$ takes part in the ODS, which leads to the resultant sulfone and the regeneration of the $[Mo(O)]$.

Chen et al. [32] proposed the desulfurization of DBT catalyzed by $[C_{16}mim][PyW]$ as shown in Fig. 8. The proposed mechanism suggested that hydrogen bonding interaction between the H_2 position of the imidazolium cation and S atom of the DBT molecules plays an important role in enhancing the desulfurization efficiency.

2.5. Kinetics study of catalytic oxidation on S-compounds

The sequence of reaction involved in catalytic desulfurization as proposed by Zhu et al. [31] is shown in Fig. 9. According to the proposed mechanism, the first step of the reversible reaction is
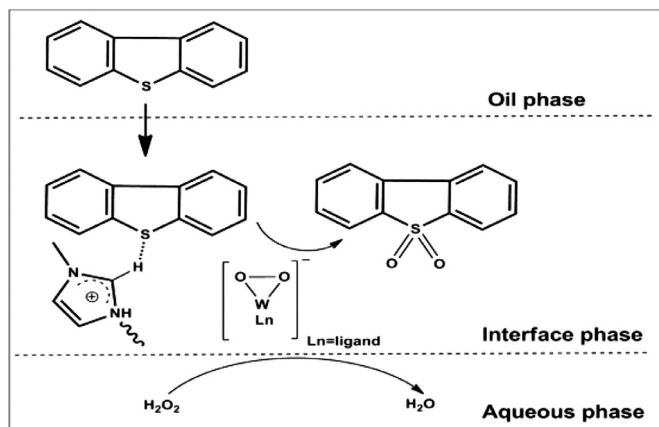
Fig. 8. Mechanism for the desulfurization of DBT proposed by Chen et al. Reprinted with permission from Ref. [32]. Copyright 2015 Royal Society of Chemistry.
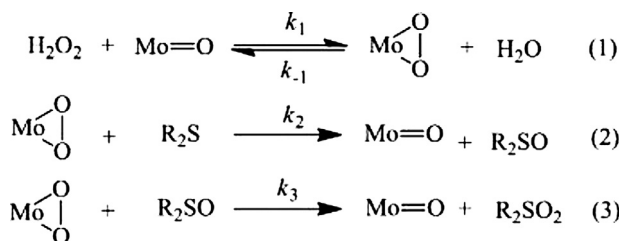

Fig. 9. Sequence involved in the oxidation reaction. Reprinted with permission from Ref. [31] Copyright 2013 Elsevier.

followed by oxidation phase reaction which leads to formation of R_2-SO and R_2-SO$_2$. The rate of the formation of SO$_2$ can be shown in Eq. (1):

$$r = -\frac{d[R_2S]}{dt} = -k_2[MoO_2][R_2S] \qquad (1)$$

$$\frac{d[MoO_2]}{dt} = k_1[H_2O_2][MoO] - k_{-1}[MoO_2]$$
$$- k_2[MoO_2][R_2S] - k_3[MoO_2][R_2SO] = 0 \qquad (2)$$

$$[Mo]T = [MoO] + [MnO_2] \qquad (3)$$

$$r = -\frac{d[R_2S]}{dt} = \frac{k_1k_2[Mo]_T[[H_2O_2][R_2S])}{k_{-1} + k_1[H_2O_2] + k_2[R_2S] + k_3[R_2SO]} \qquad (4)$$

The initial rate can be obtained as the following (Eq. (5)):

$$r_i = -\frac{\Delta[R_2S]_i}{\Delta t} = \frac{k_1k_2[Mo]_T[[H_2O_2][R_2S]_i]}{k_{-1} + k_1[H_2O_2]_i + k_2[R_2S]_i} \qquad (5)$$

As per operating conditions, $k_{-1} + k_1$ [H$_2$O$_2$] $\gg k_2$[R$_2$-S] is reasonable for the stability of (MoO$_2$). In this case, the oxidation rate is the first-order, solving Eq. (5) gives following two equations,

$$r = -\frac{d[R_2S]}{dt} = K[R_2S] \qquad (6)$$

$$K = \frac{k_1k_2[Mo]_T[H_2O_2]}{k_{-1} + k_1[H_2O_2]} \qquad (7)$$

Eq. (6) shows a linear relation between the t and [R$_2$-S] which drives through the origin point. Therefore, the catalytic ODS can be treated as the pseudo-first-order rate.

The rate constant for the apparent consumption of S-compound was obtained from the pseudo-first-order Eq. (6) as follows [33].
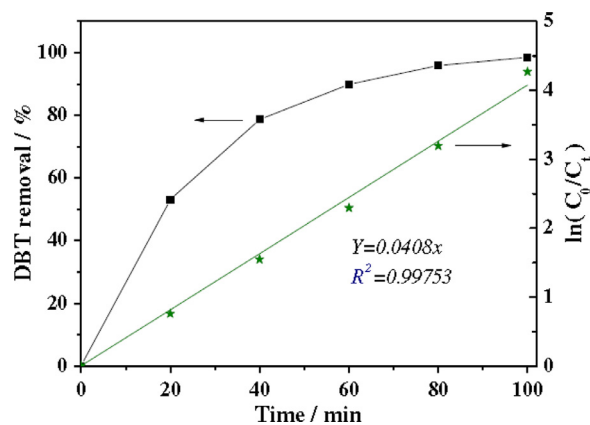
$$-\frac{dC}{dt} = kC_t \qquad (8)$$

Fig. 10. Time-course variation of DBT removal and ln(C_o/C_t). Reprinted with permission from Ref. [31]. Copyright 2013 Elsevier.
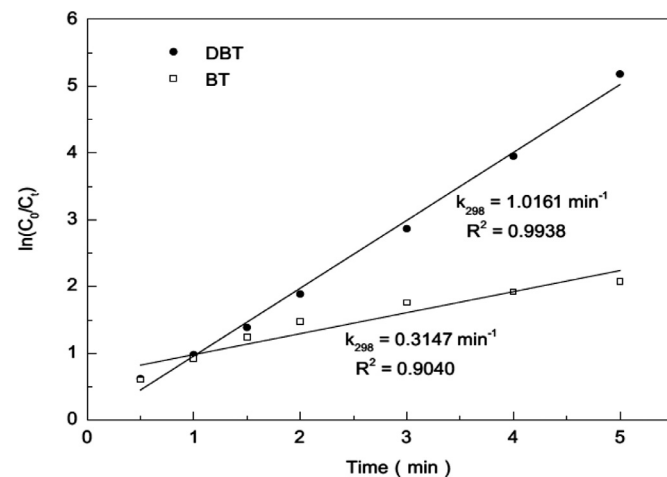
Fig. 11. Kinetics for oxidative desulfurization of DBT and BT by [C$_6$^{3}MPy]Cl/FeCl$_3$. Conditions: moil = 9 g, mIL = 3 g, O/S molar ratio = 4, T = 298 K. Reprinted with permission from Ref. [34]. Copyright 2013 John Wiley and Sons.

$$\ln\frac{C_o}{C_t} = kt \qquad (9)$$

$$t_{1/2} = 0.693/k \qquad (10)$$

The plot of ln(C_o/C_t) against t, a straight line with slope k was obtained (Fig. 10.). Half-life was calculated by Eq. (9), which was derived from Eq. (8) by replacing C_t with $C_o/2$. Based upon the kinetic data of the DBT oxidation, Zhu et al. [31] calculated the half-life of 17.00 min and the apparent rate constant (k) 0.0408 min^{-1} in accordance with an apparent first-order kinetic rate.

The kinetics for ODS of BT and DBT by [C$_6$^{3}MPy]Cl/FeCl$_3$ is shown in Fig. 11. which tells that the rate constant was 0.3147 and 1.0161 min^{-1} for BT and DBT at 298 K, respectively [34]. The rate constant values of bulkier S-compounds are higher in ODS when compared to the rate constant for the same compounds in HDS process [35].

3. ODS using ionic liquids

3.1. Ionic liquids (ILs)

ILs, termed as green solvents, can be used for desulfurization of liquid fuel due to their very low vapor pressure and wide range of applications with unique physical and chemical properties as mentioned above [36]. Their ability to be recycled without any impact

Fig. 12. Different structures for IL cations.

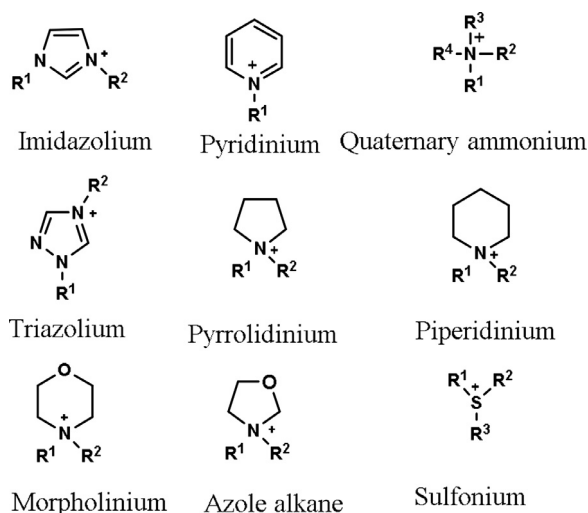on the environment provides impressive advantage in the present era of environmental concern [33]. In the past few years, significant literatures have become available in the area of preparation, characterization and application of ILs for synthesis, catalysis and separation.

ILs consist of organic cations and inorganic anions with side chains of alkyl or different functional group and aromatic moieties [37]. The main cations are imidazolium, ammonium, pyridiniuim, isoquinolonium, phosphonium and sulfonium as shown in Fig. 12.

3.2. Developments of IL

Introducing ILs into various processes has resulted in process improvements in terms of yield and productivity. The economic efficiency of ILs can be improved by recycling and reuse. Mai et al. [38] have recently summarized review of the methods for separation and recovery of ionic liquids.

ILs can be synthesized having an extensive variety of chemical and physical characteristics that can be fine-tuned by using altered anions and cations to meet the requirement of specific applications. ILs are noble solvents for an extensive range of both organic and inorganic species, and uncommon combinations of reagents can be brought into the identical phase. ILs possess structural features reminiscent of molten salts, ionic surfactants, ionic crystals and molecular liquids [39]. They are often linked of poorly coordinating ions, so they are highly polar yet non-coordinating solvents. ILs have solvent properties which are similar to polar protic liquids, molten salts, or bicontinuous microemulsions [39]. ILs are immiscible with many organic compounds such as hexane, toluene, octane and dodacane. Hydrophobic ILs work as immiscible polar phases with water. ILs are nonvolatile, hence they can be used in high-vacuum systems as well [40]. First Zhao et al. [41] and later Pârvulescu and Hardacre [42] have presented fairly complete commentary on catalysis using ILS. Jain et al. [43] have been reviewed synthesis of ILs and their applications in various chemical and biochemical transformations in eco-friendly milder conditions. Through selected examples Zhang et al. [44] have shown the advantages and potential of ionic liquids in exploring cleaner catalytic technologies, as compared to traditional catalytic processes. Zhang et al. [45] emphasized on the role of ILs as catalysts, solvents, or electrolytes in three areas: (i) CO_2 conversion to fuels and fuel additives, (ii) biomass pre-treatment and conversion to biofuels and (iii) solar energy and energy storage. Pollet et al. [46] has compared physicochemical properties and some key applications for:

(1) supercritical fluids, (2) gas-expanded liquids, (3) water at elevated temperature, (4) switchable solvents, specifically sulfolenes and reversible ILs. Doherty [47] has provided details about IL effects on selectivity, activity and different strategies in ILs based catalysis.

3.3. ODS using ILs

Lo et al. [48] were first to combine oxidation and extraction using ILs in a one-pot operation for deep desulfurization of fuel oils. Simultaneous extraction and oxidation of S-compounds from fuel oils in ILs rise the yield of desulfurization by about an order of magnitude relative to that of simply extracting with ILs. The ILs act as both extraction media for the S-compounds and deliver the oxidation conditions for the transformation of S-compounds to sulfones or sulfur oxides. An organic acid or a transition metal is required as a catalyst in the ODS process. Table 4 summarizes removal efficiency of ILs and organic solvents during the ODS under different reaction conditions.

Xu et al. have carried out a detailed theoretical study to better understand the mechanism of oxidative–extractive desulfurization of DBT from fuels by [C$_6$mim]BF$_4$ IL in the presence of H$_2$O$_2$ [68]. Lo et al. [48] found water-immiscible IL [C$_4$mim]PF$_6$ more-effective solvent than the water-soluble [C$_4$mim]BF$_4$ for providing an environment that results in a higher rate of chemical oxidation. However, ILs containing halogen atoms such as the anion BF$_4^-$ and PF$_6^-$ easily yield white fumes of hydrogen fluoride or hydrate precipitates, which will lead to potential environmental and safety problems.

Nie et al. [69] used Fe-containing ILs as solvent in ODS process to remove 100% S-content and reached reaction equilibrium fast with a constant apparent rate of 0.9951 min^{-1} at 298 K. Cooper et al. [70] observed that when a coordination compound is generated between H$_2$O$_2$ and an amide, such as urea; then the H$_2$O$_2$ on the coordination compound decomposes to yield hydroxyl radicals that are strong oxidizing agents. The study reported more than 95% desulfurization efficiency with [C$_4$mquin]N(CN)$_2$ at 30 °C at 500 rpm with 1:5 IL: oil mass ratio and 20 min time [71]. Zhao et al. [72] suggested that the S-contents of DBT dissolved in n-octane could be affectedly reduced using H$_2$O$_2$ as an oxidant and formic acid and pyridinium-based ILs as phase-transfer catalysts (PTCs). Jiang et al. [65] achieved high desulfurization efficiency of DBT both in hydrophilic IL [C$_4$mim]BF$_4$ (94.9%) as well as in hydrophobic IL [C$_8$mim]BF$_4$ (97.2%) by using ChFeCl$_4$ as a catalyst under mild conditions. Electron spin resonance measurements suggested that the active oxygen species generated by ChFeCl$_4$ and H$_2$O$_2$ in IL were involved in the catalytic oxidation of DBT. Jiang et al. [65] reported that [C$_8$bim]CH$_3$COO containing eight-carbon side chain has ideal catalytic activity for ODS. 87% of S-contents in the model oil was eliminated under the optimal conditions of ODS at 70 °C, 180 min oxidization time, 10 mL fuel oil dosage, and ILs/H$_2$O$_2$ volume ratio of 1:1.1. When acetic acid-based ILs were used as both catalysts and extractants, they displayed decent oxidative ability [73]. Devi Wilfred et al. [71] achieved desulfurization efficiency up to 99.9% through catalytic oxidation using [C$_4$mquin]N(CN)$_2$. Kulkarni and Afonso [74] applied [C$_4$mim]PF$_6$ oxidation–extraction system to actual fuel oil containing a S-content. After 10 h S-content decreased from 8040 to 1300 ppm. According to Zhao et al. [56] 99.4% S-content in the actual diesel fuel can be removed by Brønsted acid IL [C$_6$nmp]BF$_4$.

Use of acidic ILs has led to very good results in ODS of fuels without the need of addition of an external catalyst to the medium [75]. The intrinsic acidic character of the ILs allows them to act as both catalysts and solvents. It also eliminates the requirement of additional catalyst. The acidity of protons is mainly determined by their solvation. The acetic acid-based ILs act as both

Table 4
ODS results of Ionic liquids and organic solvents studies.

| ILs	Oxidant and catalyst	Oils/S-compounds	S-removal (%)	Reaction conditions	Ref.
$[C_4mim]BF_4$	H_2O_2 and $[(C_4H_9)_4N]_3\{PO_4[MoO(O_2)_2]_4\}$	n-Octane/DBT	97.3	T: 70 °C, t: 3 h, model oil: 5 mL, $[n(H_2O_2)/n$ (DBT)/n (catalyst) 200:100:1], IL: 1 mL	[49]
$[C_8mim]BF_4$	H_2O_2 and $[(C_4H_9)_4N]_3\{PO_4[MoO(O_2)_2]_4\}$	n-Octane /DBT	83.2	T: 70 °C, t: 3 h, model oil: 5 mL, $[n (H_2O_2)/n$ (DBT)/n (catalyst) 200:100:1], IL: 1 mL	[49]
$[C_4mim]PF_6$	H_2O_2 and $[(C_4H_9)_4N]_3\{PO_4[MoO(O_2)_2]_4\}$	n-Octane/DBT	90.7	T: 70 °C, t: 3 h, model oil: 5 mL, $[n (H_2O_2)/n$ (DBT)/n (catalyst) 200:100:1], IL: 1 mL	[49]
$[C_8mim]PF_6$	H_2O_2 and $[(C_4H_9)_4N]_3\{PO_4[MoO(O_2)_2]_4\}$	n-Octane/DBT	94.5	T: 70 °C, t: 3 h, model oil: 5 mL, $[n (H_2O_2)/n$ (DBT)/n (catalyst) 200:100:1], IL: 1 mL	[49]
$[C_8mim]TA$	H_2O_2 and $[(C_4H_9)_4N]_3\{PO_4[MoO(O_2)_2]_4\}$	n-Octane/DBT	67.6	T: 70 °C, t: 3 h, model oil: 5 mL, $[n (H_2O_2)/n$ (DBT)/n (catalyst) 200:100:1], IL: 1 mL	[49]
$[C_4mim]HSO4$	H_2O_2 and IL	Diesel fuel/DBT	85.5	IL/oil: 2:1, O/S: 5, T: rt, t: 1.5 h	[50]
$[C_4mim]HSO_4$	H_2O_2 and IL	n-Octane/DBT	99.6	IL/oil: 2:1, O/S: 5, T: rt, t: 1.5 h	[50]
$[C_6nmp]H_2PO_4$	H_2O_2 and IL	Real diesel	64.3	IL/oil: 2:1, O/S: 5, T: rt, t: 1.5 h	[51]
$[C_6nmp]H_2PO_4$	H_2O_2 and IL	n-Octane	99.8	IL/oil: 2:1, O/S: 5, T: rt, t: 1.5 h	[51]
$[C_6mim]BF4$	H_2O_2 and IL	Diesel	73.0	T: 90 °C, t: 6 h, Oil: 3.2 mL, IL: 5 mL, O/S: 10	[52]
$[C_6mim]BF4$	H_2O_2 and IL	iso-Octane/DBT	93.0	T: 90 °C, t: 6 h, Oil: 3.2 mL, IL: 5 mL, O/S: 10	[52]
$[C_6nmp]Cl/ZnCl_2$	H_2O_2 and IL	Diesel	83.9	T: 50 °C, t: 3 h, IL/oil: 1, ODS cycles: 6, O/S: 50	[53]
$[C_6nmp]Cl/ZnCl_2$	H_2O_2 and IL	Diesel	97	T: 50 °C, t: 3 h, IL/oil: 1, ODS cycles: 6, O/S: 50 and with one step EDS with furfural at T: 40 °C; t: 1 h, sol/oil ratio: 1	[53]
$[C_4mim]CL/2ZnCl_2$	H_2O_2 and IL	Diesel	87.7	T: 80 °C, t: 1 h, IL/oil: 1 or ½, ODS cycles: 7, O/S:50	[54]
DMF	$Fe/MoO_3-PO_4/(10:90)Al_2O_3$	Diesel	96	T: 30 °C, t: 1/2 h, sol/oil: 1, ODS cycles: 1, O/S(molar):3	[55]
$[C_6nmp]BF_4$	AcOH and ILs	Diesel	95.5	T: 60 °C; O/S :6; sulfur content of actual diesel fuel (3240 mg mL21); Vmodel oil/VIL = 1 : 1; reaction time 2 h	[56]
$[C_4Py]BF_4$	H_2O_2 and ILs	Gasoline	56.3	T: 55 °C, t: 30 min, $V(IL)/V(oil)/V(H_2O_2)$: 1:1:0.4	[57]
$[C_4mim]BF_4$	H_2O_2 and Na_2MoO_4	n-Octane	99.0	T: 70 °C, t: 3 h, model oil : 5 mL, IL: 1 mL, $[n(DBT)/n(catalyst)$: 20], $[n(H_2O_2)/n(DBT)]$: 4. a: The mixture was stirred at 30 °C for 15 min. b: The mixture was stirred at 70 °C for 3 h	[58]
$[C_8mim]BF_4$	H_2O_2 and Na_2MoO_4	n-Octane	67.6	T: 70 °C, t: 3 h, model oil: 5 mL, IL: 1 mL, $[n(DBT)/n(catalyst)$: 20], $[n(H_2O_2)/n(DBT)]$: 4. a: The mixture was stirred at 30 °C for 15 min. b: The mixture was stirred at 70 °C for 3 h	[58]
$[C_8mim]PF6$	H_2O_2 and Na_2MoO_4	n-Octane	69.8	T: 70 °C, t: 3 h, model oil: 5 mL, IL: 1 mL, $[n(DBT)/n(catalyst)$: 20], $[n(H_2O_2)/n(DBT)]$: 4. a: The mixture was stirred at 30 °C for 15 min. b: The mixture was stirred at 70 ◦C for 3 h.	[58]
$[C_8mim]PF6$	H_2O_2 and Na_2MoO_4	n-Octane	77.8	T: 70 °C, t: 3 h, model oil: 5 mL, IL: 1 mL, $[n(DBT)/n(catalyst)$: 20], $[n(H_2O_2)/n(DBT)]$: 4. a: The mixture was stirred at 30 °C for 15 min. b: The mixture was stirred at 70 °C for 3 h	[58]
$[C_8mim]TA$	H_2O_2 and Na_2MoO_4	n-Octane	49.0	T: 70 °C, t: 3 h, model oil: 5 mL, IL: 1 mL, $[n(DBT)/n(catalyst)$: 20], $[n(H_2O_2)/n(DBT)]$: 4. a: The mixture was stirred at 30 °C for 15 min. b: The mixture was stirred at 70 °C for 3 h	[58]
$[C_8mim]TA$	H_2O_2 and Na_2MoO_4	n-Octane	37.4	T: 70 °C, t: 3 h, model oil: 5 mL, IL: 1 mL, $[n(DBT)/n(Catalyst)$: 20], $[n(H_2O_2)/n(DBT)]$: 4. a: The mixture was stirred at 30 °C for 15 min. b: The mixture was stirred at 70 °C for 3 h	[58]
$[C_8{}^3MPy]FeCl_4$	H_2O_2 and ILs	n-Octane	73.4	T: 298 K, t: 15 min, IL/oil ratio: 1:1	[59]
$[C_6{}^3MPy]FeCl_4$	H_2O_2 and ILs	n-Octane	70.6	T: 298 K, t: 15 min, IL/oil ratio: 1:1	[59]
$[C_4{}^3MPy]FeCl_4$	H_2O_2 and ILs	n-Octane	68.2	T: 298 K, t: 15 min, IL/oil ratio: 1:1	[59]
$[C_4Py]BF_4$	H_2O_2 and ILs	n-Octane	56.3%	T: 55 °C; V (model oil)/V (IL): 1:1; t: 30 min	[57]
$[C_6nmp][HSO_4]$	H_2O_2 and ILs	Gasoline	94	T: 60 °C; V (oil)/V (IL): 1:1; t: 30 min. O/S = 16 with 5 EDS steps with furfural alcohol at T = 313 K, t = 1 h, sol/oil ratio = 1	[60]
$[C_6nmp][H_2PO_4]$	H_2O_2 and ILs	Gasoline	93	T: 60 °C; V (oil)/V (IL): 1:1; t: 30 min. O/S = 16 with 5 EDS steps with furfural alcohol at T = 313 K, t = 1 h, sol/oil ratio = 1	[60]
$[CH_2COOHPy]HSO_4$	H_2O_2 and ILs	n-Octane	99.7%	T: 50 °C, t: 40 min, 10 mL model oil, 0.6 mL IL, $n(H_2O_2)$: n(S):6	[61]
$[C_4mim] PF_6$	H_2O_2 and $[(C_4H_9)_4N]_6Mo_7O_{24}]$	Diesel/DBT and TS	99.0%	T: 50 °C, t: 3 h, S $H_2O_2{}^{-1}$: 1/5 (molar ratio), DBT (S: 500 ppm) in n-octane	[62]
$[C_4mim]BF_4$	H_2O_2 and TiO_2	Diesel/DBT	99.1	T :40 °C, m(catalyst): 10 mg, $V([Bmim]BF_4)$: 1 mL, V(model oil): 5 mL,$n(H_2O_2)/n(DBT)$:3, t : 90 min	[63]
$[C_4Py]BF_4$	H_2O_2 and $(CoPc(Cl)_n)$	Model gasoline	90	T: rt, ionic liquid to model oil 1.8:1; 0.3 wt% $CoPc(Cl)_{16}$ per 10 mL model oil; 100 mL/min air flow rate	[64]
$[C_4Py]BF_4$	H_2O_2 and $(CoPc(Cl)_n)$	Real gasoline	80	T: rt, ionic liquid to model oil 1.8:1; 0.3 wt% $CoPc(Cl)_{16}$ per 10 mL model oil; 100 mL/min air flow rate	[65]
$[C_4mim]BF4$	H_2O_2 and $ChFeCl_4$	Gasoline	90	T: 30 °C, t: 30 min, model oil: 5 mL, IL: 1 mL, m(catalyst): 0.030 g·$n(H_2O_2)/n(DBT)$: 6	[65]
$[C_4mim]BF4$	H_2O_2 and $ChFeCl_4$	Gasoline	97	T: 30 °C, t: 30 min, model oil: 5 mL, IL: 1 mL, m(catalyst): 0.030 g·$n(H_2O_2)/n(DBT)$: 6	[65]
$[(C_6H_{13})_3PC_{14}H_{29}]_2W_6O_{19}$	H_2O_2 and G-h-BN	n-Octane	99	T: 60 °C, t: 60 min, 5 mL model oil, $V(H_2O_2)$: 48 µL, m(IL): 0.3705 g	[66]
$[(C_6H_{13})_3PC_{14}H_{29}]_2W_6O_{19}$	H_2O_2 and ILs	n-Octane	97.8	T: 60 °C, t: 60 min, 5 mL model oil, $V(H_2O_2)$: 48 µL, m(IL): 0.3705 g	[67]
DMF	Acetic acid/H_2O_2	Model oil/DBT	50.8	T: 60 °C, t: 60 min, 5 mL model oil, $V(H_2O_2)$: 48 µL, m(IL): 0.3705 g	[23]
ACN	Acetic acid/H_2O_2	Model oil/DBT	59.7	T: 60 °C, t: 60 min, 5 mL model oil, $V(H_2O_2)$: 48 µL, m(IL): 0.3705 g	[23]
NMP	Acetic acid/H_2O_2	Model oil/DBT	55.3	T: 60 °C, t: 60 min, 5 mL model oil, $V(H_2O_2)$: 48 µL, m(IL) : 0.3705 g	[23]
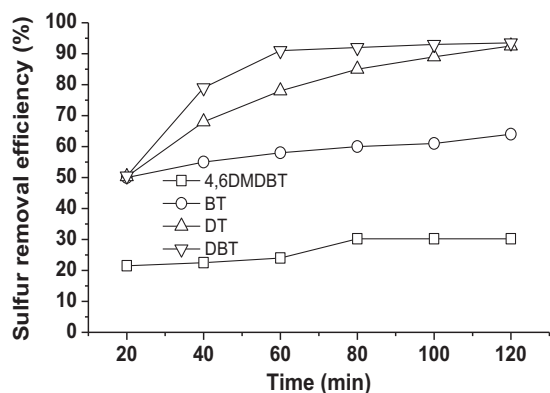
Fig. 13. The effect of different S-compounds on S-removal efficiency. Experimental conditions: 5-mL model oil, $n(H_2O_2)$ 0.39 mmol, $m([pmim]FeCl_4\text{-MCM-41})50.06$ g, $V([Omim]BF_4)51$ mL, $T = 30\,°C$, time = 1 h. Reprinted with permission from Ref. [79]. Copyright 2013 John Wiley and Sons.
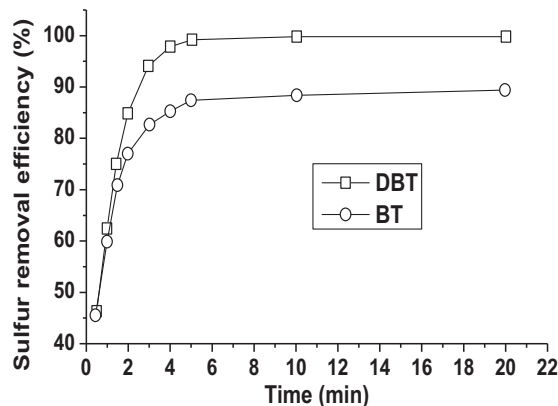

Fig. 14. Effect of different S-compounds on S-removal by $[C_6{}^3MPy]Cl/FeCl_3$. Conditions: initial S-content 1000 ppm, $m_{oil} = 9$ g, $m_{IL} = 3$ g, O/S molar ratio = 4, $T = 298$ K. Reprinted with permission from Ref. [34]. Copyright 2013 John Wiley and Sons.

phase-transfer catalysts and extractants with good oxidative ability. In this regard, study by Thomazeau et al. [76] has proposed an acidity scale that correlations the catalytic activities measured in various acidic reactions. Fang et al. [77] suggest that with imidazolium as the cation, the desulfurization capability of ILs decreases in the following order, $TFA^- > HSO_4^- > COO^- > AlCl_4^- > AcO^-$. The study also shows that when the acidity of IL is much stronger, the catalytic and extractive capability is better. When the anion is $HSO_4{}^-$, the order of the desulfurization capacity of different cation types is $[C_5mim]^+ > [C_3Py]^+ > [C_4mim]^+ > [C_3mim]^+ > [HSO_3-C_3\,mim]^+ > [HSO_4-C_3EA]^+ > [HSO_3-C_5Py]^+$. It shows that ILs with cation $[C_nmim]^+$ (including $[C_2mim]$, $[C_3mim]$, $[C_4mim]$, and $[C_5mim]$) have better extraction capability than those with $[HSO_3-C_3mim]^+$, $[HSO_4-C_3EA]^+$, and $[HSO_3-C_5Py]$ [77].

Zhao et al. [56] optimized ODS of DBT in the model oil with Brønsted acidic ILs N-methyl-pyrrolidonium phosphate $[C_6nmp]H_2PO_4$ as catalytic solvent and H_2O_2 as oxidant. 99.8% DBT in the model oil was removed under the optimal conditions of molar ratio of H_2O_2 to sulfur of 16:1, reaction temperature of 60 °C, reaction time of 5 h, and volume ratio of model oil to ILs of 1:1. The desulfurization efficiency of actual diesel was 64.3% under the optimized conditions. The Brønsted acidic IL $[C_6nmp]H_2PO_4$ can be recycled six times without a significant decrease in activity.

Fenton-like reagents have also been studied for ODS. Fenton-like ILs $[(C_8H_{17})_3CH_3N]Cl/FeCl_3–H_2O_2$ system showed 97.9% S-removal as DBT in model oil reached. Likewise S-level of FCC gasoline could be reduced from 360 ppm to 110 ppm [78]. Dong et al. [34] studied the activity of $[C_6{}^3mpy]Cl/FeCl_3$ on BT and DBT. The results suggest S-removal followed the order of DBT > BT. Xiong et al. [79] investigated the catalytic performance of Fenton-like IL supported on meso-porous material MCM-4,1 with BT, DT, DBT, and 4,6-DMDBT.The results shown in Fig. 13 suggest that the S-removal decreased in following order: DBT > DT > BT > 4,6-DMDBT.

The difference in removal efficiency mainly came from aromatic π-electron density of S-compounds. The electron density on the sulfur atom of DBT, BT, and 4,6 DMDBT is 5.758, 5.739, and 5.760, respectively [80]. The relatively lower electron density of TS made ILs extraction after ODS process ineffective when attempting to desulfurized gasoline. Other aspects that need consideration include co-extraction of (un)desired compounds, integration of the process in the refinery, and life cycle analyses.

3.3.1. Effect of reaction temperature on S-removal

The influence of reaction temperature on removal of DBT by $[C_6{}^3mpy]Cl/FeCl_3$ in the presence of H_2O_2 is shown in Figs. 13

and 14. It can be seen that when the reaction temperature for $[C_6{}^3mpy]Cl/FeCl_3$ increases S-removal increases. However, when the temperature increases above 308 K, the S-removal decreases sharply. DBT is easier to remove than BT at 298 K by $[C_6{}^3mpy]Cl/FeCl_3$ [34]. For $[C_4mim]Cl/3ZnCl_2$, the highest S-removal efficiency of 99.9% is obtained at 45 °C after 7 h, but only 65.7% at 30 °C and 89% at 60 °C; what is more, the S-removal is 99.9% after 3 h at 45 °C, 47.4% at 30 °C and 62.1% at 60 °C [80]. According to Sachdeva and Pant [81] the formation of peroxide becomes quick at high temperature and increased conversion to sulfones.

Zhao et al. [51] found out the optimal temperature at 60 °C, for ODS of DBT in model oil (n-octane) with Brønsted acidic IL $[C_6nmp]H_2PO_4$ as catalyst and solvent and H_2O_2 as oxidant. Zhang et al. [82] used $[C_4mim]HSO_4$ in ODS of DBT in model oil. In their work complete conversion was realized at 60 °C in 30 min time. When temperature was increased to 80 °C, the desulfurization efficiency decreased to 96%. These studies suggest a high temperature is not favorable for the DBT removal. This might be because the decomposition of H_2O_2 was accelerated at high temperatures [83]. Therefore, ODS using ILs could be easily carried out at moderate (40–60 °C) temperature. The optimal temperatures depends upon nature of ILs [54]. Mostly, low viscous ILs track a minor decreasing or no effecting trend for S-removal efficiency with raising temperature from 40 to 50 °C. On the other side, for high viscosity ILs such as $[C_4mim]Cl/3ZnCl_2$, $[C_6nmp]H_2PO_4$ and $[C_4min][PF_6]$, trend becomes opposite, where an increase in temperature from ~40 °C corresponds to a slight or high increase in the desulfurization efficiency. The dissimilarities between the performance of low and high viscosities of ILs at different temperatures can be understood from the variation in the viscosity of ILs with increasing temperature. For high viscosity ILs, the increase in temperature result in significant decrease in viscosity of ILs as a result ILS and S-content of the oil have more opportunities to interact with each other, leading to the high S-content removal.

3.3.2. Mass ratio of IL to oil

The mass ratio of IL to oil is one of the significant factor for ILs selectivity for ODS or EDS using ILs. As mostly ILs are bit expensive, it is desired that a least quantity of them should be utilized in fuel oil desulfurization, but it is observed from the literature that the S-removal efficiency decreases with a decreasing mass ratio of IL to oil. For instance, the mass ratios of $[C_4mim]Cl/3ZnCl_2$ to oil were tested at 60 min and the order of S-content extraction in ODS efficiency follows the order $1:5 < 1:4 < 1:3 < 1:2 < 1:1 < 2:1$ (w/w) IL–oil. Table 5 [2] indicates that, with the increase

Table 5

S-removal efficiency vs mass ratio of IL/oil for [C$_4$mim]Cl/2ZnCl$_2$ and [SO$_3$H-C$_4$mim] HSO$_4$ [2].

ILs	Oil	O/S ratio	Time (h)	Temp. (K)	ODS efficiency for IL-oil mass ratio				
					1:5	1:3	1:2	1:1	2:1
[C$_4$mim]Cl/2ZnCl$_2$	Model diesel	8:1	1	363	92.2	97	98.5	100	N/A
[SO$_3$H_C4mim]HSO$_4$		8:1	6	333	93.9	95	96	98.1	N/A

of mass ratio of IL to oil, the S-removal efficiency increases both for [C$_4$mim]Cl/2ZnCl$_2$ and [SO$_3$H-C$_4$mim]HSO$_4$. Compared with the molar ratio of O/S, the effect of mass ratio of IL to oil is limited; for example, when the mass ratio of IL to oil is increased from 1:5 to 1:1, the S-removal is increased from 92.2% to 100% for [C$_4$mim]Cl/$_2$ZnCl$_2$ and from 93.9% to 98.1% for [SO$_3$H-C$_4$mim]HSO$_4$. Similar effects of mass ratio of IL to oil were obtained with a series of [BF$_4$] and [MeSO$_4$]-based ILs [2]. The study by Mochizuki and Sugawara [84] suggested that the extraction yield of DBT increased linearly with an increase in the length of alkyl chains and the mass ratio of the IL to oil. However it was also found that effect of mass ratio of IL to oil are not universal rate. This typically depends on how the individual chemical natures of ILs are related to their extraction abilities. The mass ratio of IL to oil has to be cautiously selected based on a compromise nature between S removal and oil recovery. The regeneration of ILs may also be considered for the process as this highly affects the overall process cost.

3.3.3. Regeneration of used ILs

After each ODS process finished, the IL is recovered and reused without significant loss of activity. Regeneration of ILs is an important feature for selection of ILs. It can compensate for the high cost of ILs. The methods of regeneration of S-loaded ILs may vary on the basis of the nature of the ILs and S-compounds. The regeneration of used hydrophilic ILs is carried out by dilution with water followed by simple distillation [80]. According to the study by Zhang et al. [82] [C$_4$mim]HSO$_4$ can be recycled five times with a slight loss in activity, *e.g.*, DBT removal dropped from 100% to 95% under the same experimental conditions. The study by Zhao et al. [72] suggests that IL [C$_6$nmp]BF$_4$ can be recycled seven times without a significant decrease in activity. [CH$_2$COOHPy]HSO$_4$ can be recycled nine times without a significant decrease in the sulfur removal [61]. Peroxotungsten anion-based ionic liquid-type catalysts could be recycled at least 10 times without any decrease in activity [32]. Wang et al. [85] suggested that during the recycling some IL was wasted when IL was separated and regenerated which result in little drop in DBT removal from the oil phase with the increase of the cycle. Zhang et al. [86] attribute the decrease of S-removal to the increase of oxidation product DBTO$_2$ that accumulates in the IL phase.

The desulfurization activity of [C$_6$^{3}mpy]Cl/FeCl$_3$ decreased from 100% to 94.5% after five cycles. Dong et al. [34] investigated the recycling of the used IL phase with and without distillation. Results are shown in Table 6 which suggest that the used IL [C$_6$^{3}mpy]Cl/FeCl$_3$ with distillation has a better recycling performance than [C$_6$^{3}mpy]Cl/FeCl$_3$ without distillation in the ODS process. Presence of white solid DBTO$_2$ also affects the performance of recycled ILs [34].

3.3.4. Concentration of H$_2$O$_2$ as oxidant

The concentration of H$_2$O$_2$ has a significant influence on desulfurization efficiency. Mostly, the S-removal efficiency increases with oxidant to S-compound (O/S) molar ratio. According to the stoichiometry of the ODS reaction, 2 mol of H$_2$O$_2$ are required for every 1 mol of DBT to give the corresponding sulfone, *i.e.*, DBT-sulfone (DBTO$_2$). Thus theoretical molar ratio of O/S is 2. Chen et al. [80] experimentally determined the effect of O/S molar ratio

Table 6

Recycling of [C$_6$^{3}MPy]Cl/FeCl$_3$ in desulfurization of model oil. Reprinted with permission from Ref. [34]. Copyright 2013 John Wiley and Sons.

Cycle	Cycle S-removal (%) (by ILs with distillation)	S-removal (%) (by ILs without distillation)
1	100	100.0
2	100	99.8
3	100	97.4
4	97.8	92.9
5	94.5	85.4

Conditions: initial sulfur (as DBT) content 1000 ppm, moil = 9 g, mIL = 3 g, O/S molar ratio = 4, t = 20 min, T = 298 K.
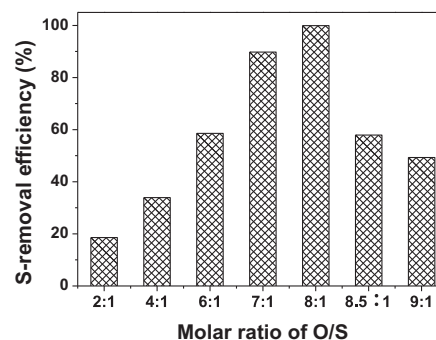

Fig. 15. Influence of the molar ratio of O/S on S-removal efficiency by [C$_4$mim]Cl/3ZnCl$_2$-H$_2$O$_2$(temperature,45 °C; time, 3 h; initial S-content, 505 ppm; mass ratio of IL/oil, 1/2). Reprinted with permission from Ref. [80]. Copyright 2012 Elsevier.

on S-removal by [C$_4$mim]Cl/3ZnCl$_2$. S-removal efficiency increased from 18.6% when the molar ratio of O/S was 2, to the maximum value of 99.9% when the molar ratio of O/S was 8. However with further increase in molar ratio of O/S, the S-removal efficiency decreased as shown in Fig. 15. The value was reduced to 49.3% when the molar ratio of O/S is 9. The stoichiometric H$_2$O$_2$ is not enough to oxidize all the DBT extracted into the IL phase because of decomposition of some H$_2$O$_2$ during ODS process. As a result excess H$_2$O$_2$ is required to ensure complete oxidation of DBT [87]. However too much excessive H$_2$O$_2$ solution dilutes the IL and negatively influence the extraction of DBT from fuel oil [75]. According to Jiang et al. [87] the S-removal was 76.3% with 30 wt% H$_2$O$_2$ which increased to 97.9% with 7.5 wt% H$_2$O$_2$. In the above study [C$_4$mim]$_3$ Fe(CN)$_6$ was used as a catalyst and [C$_4$mim]BF$_4$ as an extractant. The results of the ODS of model oil catalyzed by Fenton-like ILs at room temperature by Jiang et al. [78] are shown in Table 7.

3.3.5. Influence of molar ratio of ILs on S-removal

Chen et al. [80] investigated the effect of IL/oil mass ratio on S-removal. Their results are given in Fig. 16 which indicates that the quantity of IL has significant effect on the removal of DBT. The S-removal efficiency was increased from 49.1% to 99.9% when the mass ratio of IL/oil was increased from 1:5 to 1:2. However, the S-removal efficiency came down to 87.8% when mass ratio of IL/oil was further increased to 1:1. The reason being that when O/S molar ratio was reduced with the increase in IL/oil mass ratio, the IL

Table 7
Variation of types of ILs in the desulfurization system. "Reprinted with permission from Ref. [78]. Copyright 2011 John Wiley and Sons".

Entry	ILs	S-removal (%)	
		Without H_2O_2[a]	With H_2O_2[b]
1	$[(C_8H_{17})_3CH_3N]Cl/FeCl_3$	30.6	97.9
2	$[(C_8H_{17})_3CH_3N]Cl/CuCl_2$	18.6	26.2
3	$[(C_8H_{17})_3CH_3N]Cl/SnCl_2$	22.1	25.8
4	$[(C_8H_{17})_3CH_3N]Cl/ZnCl_2$	20.5	19.8
5	$[(C_4H_9)_3CH_3N]Cl/FeCl_3$	15.3	95.8
6	$[C_{10}H21(CH_3)3N]Cl/FeCl_3$	17.2	93.4
7	$[(C_{10}H21)2(CH_3)2N]Cl/FeCl_3$	29.0	98.7

[a] Experimental conditions: model oil (5 mL), IL (0.702 mmol), $T = 25$ °C, $t = 1$ h.
[b] Experimental conditions: model oil (5 mL), IL (0.702 mmol), $T = 25$ °C, $t = 1$ h, $n(H_2O_2)/n(S) = 14{:}1$.
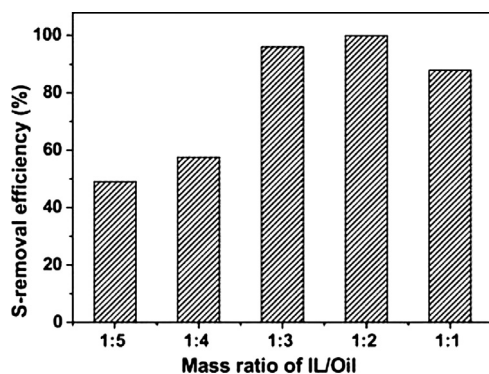

Fig. 16. Influence of the mass ratio of IL/oil on S-removal efficiency by $[C_4mim]Cl/3ZnCl_2$-H_2O_2 (temperature, 45°°C; time, 3 h; initial S-content, 505 ppm; molar ratio of O/S, 8). Reprinted with permission from Ref. [80]. Copyright 2012 Elsevier.

get capacity to extract more DBT [88], but the amount of H_2O_2 was kept constant so the O/S molar ratio is reduced, less S-compounds were oxidized. Similar results were obtained by both Zhang et al. [82] and Chen et al. [53].

3.3.6. Influence of viscosity of ILs on S-removal

ILs are prepared from two solid materials, which would lead to the high dynamic viscosity of the obtained ILs which limits their extraction ability [89]. Due to the much higher viscosity of ILs [90], the overall S-removal rate is limited by the mass transfer between phases with very active catalysts. With viscous IL, the overall S-removal rate is limited by the mass transfer between two phases which led to reduction in reaction rates and may also causes competitive unimolecular side reactions. Viscous IL also causes handling difficulties during filtration, decantation, and dissolution. ODS process can be more effective if the shortcomings of ILs on high cost and viscosity are overcome. Ionic liquids incorporating the bis(trifluoromethanesulfonyl) imide, $[NTf_2]^-$, anion are favoured for their low viscosities [90]. According to Li et al. $C_5H_9NO\cdot0.3$ $FeCl_3$ shows remarkable extraction ability for dibenzothiophene (DBT) with Nernst partition coefficients (k_N) above 7.5 [91]. Low viscosity IL allows extraction of oxidized sulfur compound in relatively short time at room temperature [89]. Increasing temperature reduces the viscosity of IL which increases the catalytic performance of IL. However, the decomposition of H_2O_2 accelerates at higher temperatures, leading to reduced desulfurization efficiency [92].

3.4. Other pattern of ODS with ILs

3.4.1. Supported ILs as catalytic solvent

Homogeneous catalytic processes need large amount of ILs that are costly and may affect the economic viability of a potential pro-

cess. The recovery of the ILs is another problem. This encouraged many groups to study heterogeneous supported ILs. A supported ILs catalyst is easily produced by immobilizing a certain amount of ILs on solid carrier. Solid supported ILs catalysts combined the advantages of ILs with the easy separation and recovery performance. Xun et al. [93] in their study of the synthesis of metal-based IL supported catalyst and its application in catalytic oxidative desulfurization of fuels prepared the heterogeneous catalyst by embedding $[C_4mim]FeCl_4$ IL in silica gel. The scheme given in Fig. 17 was followed to synthesize the $[C_4mim]FeCl_4$/silica gel catalysts. The amount of $[C_4mim]FeCl_4$ decreased sharply to reach deep desulfurization and solved the problems of recycle. The catalytic oxidation reaction of different S-containing compounds decreased in the order of DBT > BT > 4,6-DMDBT [93]. 1,2-dimethylimidazolium IL was found effective for removal of 77.7% DBT from model fuel at under the room temperature in 3 h only with 1/1 molar ration of 1,2-dimethylimidazolium IL to DBT. Moreover, the adsorbent 1,2-dimethylimidazolium IL can be recycled three times without a significant decrease in activity [94]. The desulfurization efficiency of $[Bmim]FeCl_4$ supported on Am TiO_2 remained 100% after reusing it for 25 times [95].

The drawback of heterogeneous catalysts is the lower exposure of reactants to catalytic sites which reduces their activities as compare to homogeneous catalysts. Additionally, heterogeneous catalyst also requires relative long reaction time and easily leaches active species into the reaction medium [96].

3.4.2. Catalytic ODS using IL emulsion system

Ge et al. [97] developed a catalytic oxidation IL emulsion desulfurization system composed of water-immiscible IL $[C_4mim]$ PF_6, 30 wt% H_2O_2, and an amphiphilic catalyst $[C_{18}H_{37}N(CH_3)_3]_7[PW_{11}O_{39}]$. Here $[C_{18}H_{37}N(CH_3)_3]_7[PW_{11}O_{39}]$ behaves both an emulsifying agent as well as a catalyst. $[C_{18}H_{37}N(CH_3)_3]_7[PW_{11}O_{39}]$ not only maintains the emulsion droplets stable but also provides higher interfacial surface area where the oxidation of S-compounds takes place. During the reaction, the IL emulsion functions as highly dispersed micro-reactors. The S-compounds in the model oil were first extracted into the IL emulsion phase and then oxidized to their corresponding sulfones by $[C_{18}H_{37}N(CH_3)_3]_7[PW_{11}O_{39}]$ in the $H_2O_2/[C_4mim]PF_6$ interface. The sulfones accumulated in the $[C_4mim]PF_6$ phase. After reaction, the desulfurization system quickly divided into two layers. The oil is separated from the biphasic system of the IL easily by simple decantation. For example $[C_4mim]PF_6$ emulsion desulfurization system could be recycled five times with an unnoticeable decrease in catalytic activity [98].

The milky-white IL emulsions are formed when H_2O_2 and $[C_{18}H_{37}N(CH_3)_3]_7[PW_{11}O_{39}]$ were added into $[C_4mim]PF_6$. The catalyst is distributed in the interface of H_2O_2 and water-immiscible ILs. In this emulsion reaction system, the catalyst molecule acts as an emulsifying agent, could be uniformly distributed in the interface of H_2O_2–IL, and forms a film around the dispersed IL droplets (Fig 18). Consequently, the lipophilic quaternary ammonium cations of the amphiphilic catalyst would lie on the oil side and the hydrophilic hetero poly anions would lie on the H_2O_2 side. Since hetero poly anions ($[PW_{11}O_{39}]_7-$) depolymerized into several smaller active species including $[(PO_4)(WO(O_2)_2)_4]_3-(PW_4)$, $[(PO_4)(WO(O_2)_2)_2(WO(O_2)_2-(H_2O))]_3-(PW_3)$, and $[(PO_3(OH))(WO(O_2)_2)_2]_2-(PW_2)$ in the presence of H_2O_2, because the IL emulsion was immiscible with n-octane and formed a biphasic system.

3.4.3. Photo-catalytic ODS using ILs

In the photo-catalytic ODS (PODS) S-compounds are extracted from non-polar oil phase to polar ILs. In polar $[C_4mim]BF_4$ IL S-compounds are photo-oxidized to the corresponding sulfones in
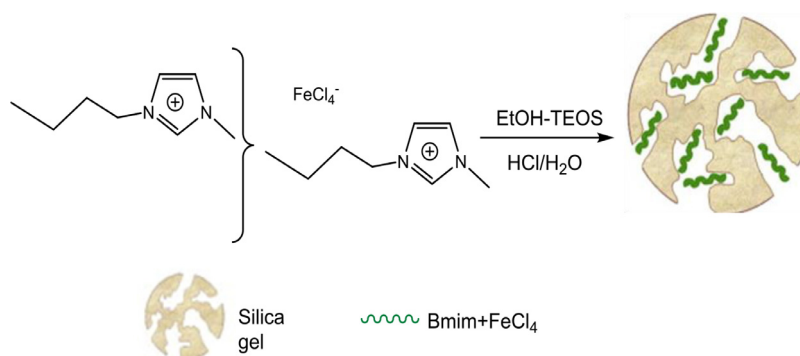
Fig. 17. The synthesis process of [C$_4$mim]FeCl$_4$/silica gel catalyst. Reprinted with permission from Ref. [93]. Copyright 2014 Elsevier.
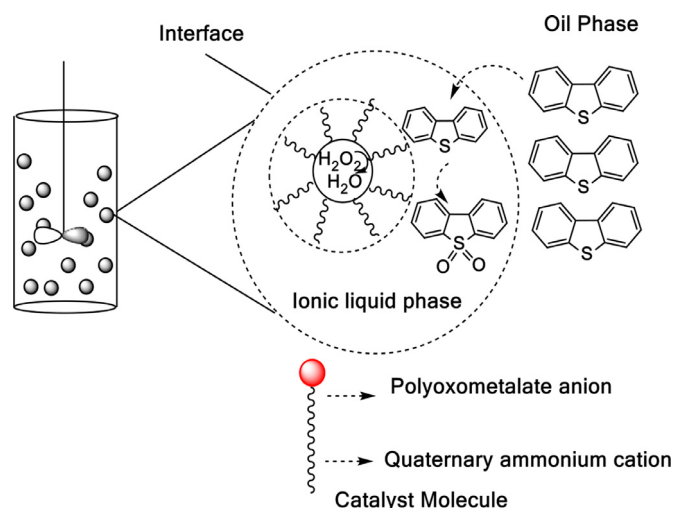

Fig. 18. Catalytic oxidation of DBT in IL emulsion system. Reprinted with permission from Ref. [97]. Copyright 2011 American Chemical Society.
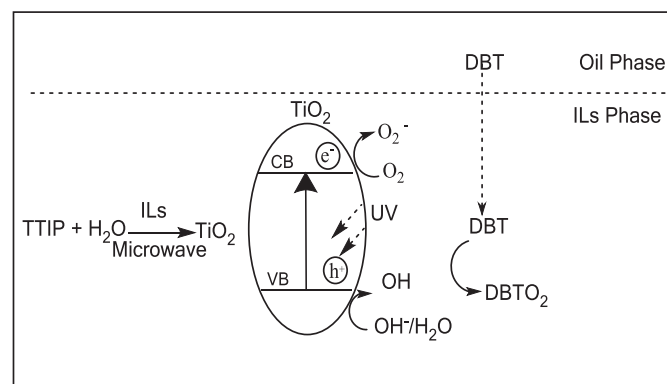

Fig. 19. *In situ* photo-catalytic oxidative desulfurization process of DBT. Reprinted with permission from Ref. [104]. Copyright 2012 American Chemical Society.

the presence of O$_2$, H$_2$O$_2$, or photosensitizers [99–101]. TiO$_2$ is most studied photo-catalyst in PODS due to its nontoxicity, chemical stability, low cost, and high photo-catalytic ability [102,103]. The *in situ* photo-catalytic oxidation process for DBT proposed by Xiao et al. [104] is shown in Fig. 19. Wang et al. [104] investigated the effect of microwave time on the photo-catalytic desulfurization ability of TiO$_2$ in the presence of O$_2$ and found that 98.2% and 94.3% sulfur could be removed from model oil and actual diesel oil, respectively, in 10 h UV irradiation under the conditions that V(IL)/V(oil) = 1:5, air flow = 200 mL/min. According to Wang et al. [104] when the TiO$_2$ in the IL was irradiated by UV light, the pho-

togenerated holes reacted with water or hydroxyl groups on the surface of TiO$_2$ to form $^\bullet$OH radicals, which oxidized DBT to DBTO$_2$ which subsequently transferred from oil to IL and was degraded continuously. The [C$_4$mim]BF$_4$ IL was recycled five times with a slight decrease in desulfurization efficiency.

Zaid et al. [105] studied the photo-oxidative–extractive deep desulfurization of diesel using Cu–Fe/TiO$_2$ and eutectic ionic liquid. First they synthesized series of bimetallic Cu–Fe/TiO$_2$ photo-catalysts using sol–gel hydrothermal method and then photo-catalysts were evaluated for photo-oxidative–extractive deep desulfurization of model oil. The study identified that 2.0 wt% Cu–Fe/TiO$_2$ photo-catalyst can efficiently oxidize sulfur species under mild conditions in the presence of hydrogen peroxide (H$_2$O$_2$: S molar ratio of 4) as oxidant and eutectic based ionic liquid as extractant.

3.4.4. Alkylation ODS using ILs

Use of alkylation desulfurization helps to avoid the side reaction of ODS and difficulties in separate the oxidative products from fuel oil. Weixia et al. [106] have reported desulfurization efficiency of exceeding 80% while studying the alkylation desulfurization of FCC gasoline catalyzed by IL AlCl$_3$-alkylammonium; the RON loss less than 2 units and the MON loss less than 1 unit. Tang et al. [107] prepared Brønsted acidic IL [BPY]HSO$_4$, which is stable in air and water, as the catalyst in the alkylation desulfurization. They reported desulfurization efficiency of 98.90% after reaction for 90 min at 65 °C with an IL/oil mass ratio of 0.09. After reaction, the MON and RON of FCC gasoline are decreased by 0.15 and 1.00.

4. Challenge and perspective of ODS using ILs

Aiming at the replacement or supplement of the present inefficient and expensive HDS, to remove those heterocyclic S-compounds to produce clean ultra-low S or S-free fuel oils, ODS using ILs have been intensively studied recently. The research results presented and discussed above indicate a good perspective for such a new method, though some problems accompanied, the advantages and possible limitations are listed in Table 8.

Temperature, reaction/extraction time, mass ratio of IL-oil, molar ratio of O/S, *etc.*, have been thoroughly investigated, showing exciting results. Those heterocyclic S-compounds in fuel oils, which are unreactive to traditional HDS, can be expected to be removed completely at mild conditions such as lower temperature (*e.g.*, room temperature) and atmospheric pressure after few minutes of contacting. Using ILs instead of organic solvents in ODS excludes the loss and contamination of solvents and possible safety issue, makes the regeneration and separation of solvents or ILs easier, and the regenerated ILs can be recycled without any noticeable activity loss. It is worthy of noting that the properties of ILs vary enormously as a function of their molecular structure, that is

Table 8

Advantages and limitations of ODS using ILs.

Advantages	Limitations
• Mild conditions such as room temperature and atmospheric pressure with conventional reaction and separation refinery equipment	• Waste treatment of S-compound oxidized product of sulfones
• No consumption of expensive hydrogen or noble catalyst (in some cases, functional ILs can act as solvent and catalyst)	• Cost of ILs
• High efficiency to remove heterocyclic S-compounds immune to HDS	• Possible side reaction in ODS
• Easy regeneration, recycling, separation of solvent or ILs excluding of solvent loss and contamination	• Quantity and yield of fuel oil
• Enormous room left to design and prepare functional ILs with better desulfurization performances	
• Other advantages such as low-cost and high selectivity	

to say that the property of ILs can be tailored through elaborately selecting the paring of cation and anion or modifying the structure of cation or anion. Therefore, there is still a very enormous room left to optimize the ILs in their specific application in ODS.

Compared with the ODS using ILs as solvent and extractive reagent where one acidic catalyst is required generally, the ODS using some functional acidic ILs as both extractive reagent and catalyst where no additional catalyst is required is a better option, because there does not exist some problems such as difficult regeneration and recycling of catalyst in homogeneous catalysis and possible contamination of oils by catalyst. Some other options such as supported ILs as catalytic solvent, ILs emulsion and ILs photocatalysis are also worthy of being investigated.

There are some issues to be considered such as treatment of waste sulfones as oxidation product of S-compounds, cost of ILs and selectivity of ODS. In addition, most studies performed currently are focused on the investigation of model fuel oils, and researchers are encouraged to investigate the desulfurization of real feedstock such as gasoline and diesel fuels. Compared with many studies on desulfurization experiments, the desulfurization mechanism are rather scarce, and some computer simulations coupled with spectrum characterization studies will favor uncovering the mechanism. In near future, to promote the final pilot test or industrial application of such a new technology, some studies are desired, e.g., development of cheaper and more active ILs; set-up of kilogram/ton-scale of desulfurization process; optimization of operation conditions; investigations of loss, lifetime/stability, regeneration and reusability of ILs; evaluations on oil yield and oil quality.

5. Concluding remarks

S-compounds are the major harmful impurity in fuel oils, which result into the severe environmental issues in the combustion of fuel oils. Desulfurization of fuel oils is a key process in oil refining. Traditional HDS, due to its ineffectiveness to remove some heterocyclic S-compounds in fuel oils, is facing some challenges in producing clean ultra-low S or S-free fuel oils. Alternative methods are desired, among which ODS using ILs has been intensively studied recently. In this work, we reviewed these research results of ODS using ILs since 2003 when Lo et al. reported the first results, also the traditional ODS. This review clearly indicates that ODS using ILs can effectively remove those heterocyclic S-compounds in fuel oils and reduce the S-content to <10 ppm under mild conditions with a very good perspective for the application in future, although some issues have to be also addressed in future such as treatment

of waste sulfones, cost of ILs, selectivity of ODS and economic-technological evaluations at large scale of process.

The development of functional ILs and the ODS using such functional ILs as both extractive reagent and catalyst, also supported ILs as catalytic solvent, ILs emulsion and ILs photocatalysis, are expected to be studied further in future.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtice.2016.01.014.

References

[1] Mei H, Mei BW, Yen TF. A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization. Fuel 2003;82:405–14.

[2] Abro R, Abdeltawab AA, Al-Deyab SS, Yu G, Qazi AB, Gao S, et al. A review of extractive desulfurization of fuel oils using ionic liquids. RSC Adv 2014;67:35302–17.

[3] Hsu CS, Robinson P. Practical advances in petroleum processing. Springer Science & Business Media; 2007.

[4] OPEC. World oil outlook. Vienna, Austria: Organization of the Petroleum Exporting Countries (OPEC); 2014.

[5] Zhang H, Shan G, Liu H, Xing J. Preparation of (Ni/W)-γ-Al2O3 microspheres and their application in adsorption desulfurization for model gasoline. Chem Eng Commun 2007;194:938–45.

[6] Gao S, Chen X, Abro R, Abdeltawab AA, Al-Deyab SS, Yu G. Desulfurization of fuel oil: conductor-like screening model for real solvents study on capacity of ionic liquids for thiophene and dibenzothiophene. Ind Eng Chem Res 2015;54:9421–30.

[7] Nie Y, Li CX, Wang ZH. Extractive desulfurization of fuel oil using alkylimidazole and its mixture with dialkylphosphate ionic liquids. Ind Eng Chem Res 2007;46:5108–12.

[8] Zhu W, Wu P, Chao Y, Li H, Zou F, Xun S, et al. A novel reaction-controlled foam-type polyoxometalate catalyst for deep oxidative desulfurization of fuels. Ind Eng Chem Res 2013;52:17399–406.

[9] Campos-Martin JM, Capel-Sanchez MC, Perez-Presas P, Fierro JL. Oxidative processes of desulfurization of liquid fuels. J Chem Technol Biotechnol 2010;85:879–90.

[10] Shakirullah M, Ahmad W, Ahmad I, Ishaq M. Oxidative desulphurization study of gasoline and kerosene: role of some organic and inorganic oxidants. Fuel Process Technol 2010;91:1736–41.

[11] Gates BC, Topsøe H. Reactivities in deep catalytic hydrodesulfurization: challenges, opportunities, and the importance of 4-methyldibenzothiophene and 4, 6-dimethyldibenzothiophene. Polyhedron 1997;16:3213–17.

[12] Wu TY, Sun IW, Gung ST, Lin MW, Chen BK, Wang HP, et al. Effects of cations and anions on transport properties in tetrafluoroborate-based ionic liquids. J Taiwan Inst Chem Eng 2011;42:513–22.

[13] Du H, Zhang X, Kuang Y, Tan Z, Song L, Han X. Catalytic activity and process variables optimization during microwave synthesis of methyl caprylate over various multi-SO$_3$H functionalized ionic liquids. J Taiwan Inst Chem Eng 2014;49:51–7.

[14] Aghabarari B, Ghiaci M, Amini SG, Rahimi E, Martinez-Huerta MV. Esterification of fatty acids by new ionic liquids as acid catalysts. J Taiwan Inst Chem Eng 2014;45:431–5.

[15] Kurnia KA, Quental MV, Santos LM, Freire MG, Coutinho JA. Mutual solubilities between water and non-aromatic sulfonium-, ammonium- and phosphonium-hydrophobic ionic liquids. Phys Chem Chem Phys 2015;17:4569–77.

[16] Green JB, Yu SK, Pearson CD, Reynolds JW. Analysis of sulfur compound types in asphalt. Energy Fuels 1993;7:119–26.

[17] Dehkordi AM, Kiaei Z, Sobati MA. Oxidative desulfurization of simulated light fuel oil and untreated kerosene. Fuel Process Technol 2009;90:435–45.

[18] Ma C, Chen D, Liu F, Sun X, Xiao F, Dai B. Oxidative desulfurization of a model fuel using ozone oxidation generated by dielectric barrier discharge plasma combined with Co$_3$O$_4$/γ-Al$_2$O$_3$ catalysis. RSC Adv 2015;5:96945–52.

[19] Wang D, Qian EW, Amano H, Okata K, Ishihara A, Kabe T. Oxidative desulfurization of fuel oil: part I. Oxidation of dibenzothiophenes using tert-butyl hydroperoxide. Appl Catal A 2003;253:91–9.

[20] Jiang X, Li H, Zhu W, He L, Shu H, Lu J. Deep desulfurization of fuels catalyzed by surfactant-type decatungstates using H$_2$O$_2$ as oxidant. Fuel 2009;88:431–6.

[21] Collins FM, Lucy AR, Sharp C. Oxidative desulphurisation of oils via hydrogen peroxide and heteropolyanion catalysis. J Mol Catal A: Chem 1997;117:397–403.

[22] Zhang J, Wang A, Li X, Ma X. Oxidative desulfurization of dibenzothiophene and diesel over [Bmim]$_3$PMo$_{12}$O$_{40}$. J Catal 2011;279:269–75.

[23] Ali SH, Hamad DM, Albusairi BH, Fahim MA. Removal of dibenzothiophenes from fuels by oxy-desulfurization. Energy Fuels 2009;23:5986–94.

[24] Zhang M, Zhu W, Xun S, Li H, Gu Q, Zhao Z, et al. Deep oxidative desulfurization of dibenzothiophene with POM-based hybrid materials in ionic liquids. Chem Eng J 2013;220:328–36.

[25] García-Gutiérrez JL, Fuentes GA, Hernández-Terán ME, Murrieta F, Navarrete J, Jiménez-Cruz F. Ultra-deep oxidative desulfurization of diesel fuel with H$_2$O$_2$ catalyzed under mild conditions by polymolybdates supported on Al$_2$O$_3$. Appl Catal A 2006;305:15–20.

[26] Yu B, Xu P, Shi Q, Ma C. Deep desulfurization of diesel oil and crude oils by a newly isolated Rhodococcus erythropolis strain. Appl Environ Microbiol 2006;72:54–8.

[27] Song C, Ma X. New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. Appl Catal B 2003;41:207–238.

[28] Jiang Z, Lü Hongying, Zhang Y, Li Can. Oxidative desulfurization of fuel oils. Chin J Catal 2011;32:707–15.

[29] Tang Q, Lin S, Cheng Y, Liu S, Xiong JR. Ultrasound-assisted oxidative desulfurization of bunker-C oil using tert-butyl hydroperoxide. Ultrason Sonochem 2013;20:1168–71.

[30] Al-Shahrani F, Tiancun X, Green ML. Oxidative desulfurization offers route to ultralow-sulfur diesel. Oil Gas J 2010;108:41–7.

[31] Zhu W, Zhu G, Li H, Chao Y, Zhang M, Du D, et al. Catalytic kinetics of oxidative desulfurization with surfactant-type polyoxometalate-based ionic liquids. Fuel Process Technol 2013;106:70–6.

[32] Chen J, Chen C, Zhang R, Guo L, Hua L, Chen A, et al. Deep oxidative desulfurization catalyzed by an ionic liquid-type peroxotungsten catalyst. RSC Adv 2015;5:25904–10.

[33] Zhu W, Li H, Gu Q, Wu P, Zhu G, Yan Y, et al. Kinetics and mechanism for oxidative desulfurization of fuels catalyzed by peroxo-molybdenum amino acid complexes in water-immiscible ionic liquids. J Mol Catal A: Chem 2011;336:16–22.

[34] Dong Y, Nie Y, Zhou Q. Highly efficient oxidative desulfurization of fuels by Lewis acidic ionic liquids based on iron chloride. Chem Eng Technol 2013;36:435–42.

[35] Selvavathi V, Meenakshisundaram A, Sairam B, Sivasankar B. Kinetics of oxidative desulfurization of sulfur compounds in diesel fuel. Pet. Sci. Technol 2008;26:208–16.

[36] Blanchard LA, Hancu D, Beckman EJ, Brennecke JF. Green processing using ionic liquids and CO$_2$. Nature 1999 May 6;399:28–9.

[37] Zahn S, Kirchner B. Chemical modelling: applications and theory, 9. The Royal Society of Chemistry; 2012. p. 1–24.

[38] Mai NL, Ahn K, Koo YM. Methods for recovery of ionic liquids—a review. Process Biochem 2014;49:872–81.

[39] Hayes R, Warr GG, Atkin R. Structure and nanostructure in ionic liquids. Chem Rev 2015;115:6357–426.

[40] Welton T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chem Rev 1999;99:2071–84.

[41] Zhao D, Wu M, Kou Y, Min E. Ionic liquids: applications in catalysis. Catal Today 2002;74:157–89.

[42] Pârvulescu VI, Hardacre C. Catalysis in ionic liquids. Chem Rev 2007;107:2615–65.

[43] Jain N, Kumar A, Chauhan S, Chauhan SM. Chemical and biochemical transformations in ionic liquids. Tetrahedron 2005;61:1015–60.

[44] Zhang Q, Zhang S, Deng Y. Recent advances in ionic liquid catalysis. Green Chem 2011;13:2619–37.

[45] Zhang S, Sun J, Zhang X, Xin J, Miao Q, Wang J. Ionic liquid-based green processes for energy production. Chem Soc Rev 2014;43:7838–69.

[46] Pollet P, Davey EA, Ureña-Benavides EE, Eckert CA, Liotta CL. Solvents for sustainable chemical processes. Green Chem 2014;16:1034–55.

[47] Doherty S. Catalysis in ionic liquids: from catalyst synthesis to application. The Royal Society of Chemistry; 2014. p. 44–308. doi:10.1039/9781849737210-00044.

[48] Lo WH, Yang HY, Wei GT. One-pot desulfurization of light oils by chemical oxidation and solvent extraction with room temperature ionic liquids. Green Chem 2003;5:639–42.

[49] He L, Li H, Zhu W, Guo J, Jiang X, Lu J, et al. Deep oxidative desulfurization of fuels using peroxophosphomolybdate catalysts in ionic liquids. Ind Eng Chem Res 2008;47:6890–5.

[50] Gao H, Guo C, Xing J, Zhao J, Liu H. Extraction and oxidative desulfurization of diesel fuel catalyzed by a Brønsted acidic ionic liquid at room temperature. Green Chem 2010;12:1220–4.

[51] Zhao DS, Sun ZM, Li FT, Shan HD. Optimization of oxidative desulfurization of dibenzothiophene using acidic ionic liquid as catalytic solvent. J Fuel Chem Technol 2009;37:194–8.

[52] Lu L, Cheng S, Gao J, Gao G, He MY. Deep oxidative desulfurization of fuels catalyzed by ionic liquid in the presence of H$_2$O$_2$. Energy Fuels 2007;21:383–4.

[53] Chen X, Guo H, Abdeltawab AA, Guan Y, Al-Deyab SS, Yu G, et al. Brønsted-Lewis acidic ionic liquids and application in oxidative desulfurization of diesel fuel. Energy Fuels 2015;29:2998–3003.

[54] 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;50:11690–7.

[55] Abdullah WN, Ali R, Bakar WA. In depth investigation of Fe/MoO$_3$–PO$_4$/Al$_2$O$_3$ catalyst in oxidative desulfurization of Malaysian diesel with TBHP-DMF system. J Taiwan Inst Chem Eng 2016;58:344–50.

[56] Zhao D, Wang J, Zhou E. Oxidative desulfurization of diesel fuel using a Brønsted acid room temperature ionic liquid in the presence of H$_2$O$_2$. Green Chem 2007;9:1219–22.

[57] Zhao D, Wang Y, Duan E. Oxidative desulfurization of fuel oil by pyridinium-based ionic liquids. Molecules 2009;14:4351–7.

[58] Zhu W, Li H, Jiang X, Yan Y, Lu J, He L, et al. Commercially available molybdic compound-catalyzed ultra-deep desulfurization of fuels in ionic liquids. Green Chem 2008;10:641–6.

[59] Nie Y, Dong Y, Bai L, Dong H, Zhang X. Fast oxidative desulfurization of fuel oil using dialkylpyridinium tetrachloroferrates ionic liquids. Fuel 2013;103:997–1002.

[60] Abro R, Gao S, Chen X, Yu G, Abdeltawab AA, Al-Deyab SS. Oxidative desulfurization of gasoline by ionic liquids coupled with extraction by organic solvents. J Braz Chem Soc 2015 http://dx.doi.org/10.5935/0103-5053.20150355.

[61] Zhang C, Feng WA, Pan XY, Liu XQ. Study of extraction-oxidation desulfurization of model oil by acidic ionic liquid. J Fuel Chem Technol 2011;39:689–93.

[62] Lü H, Deng C, Ren W, Yang X. Oxidative desulfurization of model diesel using [(C$_4$H$_9$)$_4$N]$_6$Mo$_7$O$_{24}$ as a catalyst in ionic liquids. Fuel Process Technol 2014;119:87–91.

[63] Zheng D, Zhu W, Xun S, Zhou M, Zhang M, Jiang W, et al. Deep oxidative desulfurization of dibenzothiophene using low-temperature-mediated titanium dioxide catalyst in ionic liquids. Fuel 2015;159:446–53.

[64] Zhang J, Li J, Ren T, Hu Y, Ge J, Zhao D. Oxidative desulfurization of dibenzothiophene based on air and cobalt phthalocyanine in an ionic liquid. RSC Adv 2014;4:3206–10.

[65] Jiang W, Zhu W, Li H, Chao Y, Xun S, Chang Y, et al. Mechanism and optimization for oxidative desulfurization of fuels catalyzed by Fenton-like catalysts in hydrophobic ionic liquid. J Mol Catal A: Chem 2014;382:8–14.

[66] Zhu W, Dai B, Wu P, Chao Y, Xiong J, Xun S, et al. Graphene-analogue hexagonal BN supported with tungsten-based ionic liquid for oxidative desulfurization of fuels. ACS Sustainable Chem Eng 2014;3:186–94.

[67] Zhu W, Ding Y, Li H, Qin J, Chao Y, Xiong J, et al. Application of a self-emulsifiable task-specific ionic liquid in oxidative desulfurization of fuels. RSC Adv 2013;3:3893–8.

[68] Xu H, Han Z, Zhang D, Liu C. Theoretical elucidation of the dual role of [HMIm] BF$_4$ ionic liquid as catalyst and extractant in the oxidative desulfurization of dibenzothiophene. J Mol Catal A: Chem 2015;398:297–303.

[69] Nie Y, Dong Y, Bai L, Dong H, Zhang X. Fast oxidative desulfurization of fuel oil using dialkylpyridinium tetrachloroferrates ionic liquids. Fuel 2013;103:997–1002.

[70] Cooper MS, Heaney H, Newbold AJ, Sanderson WR. Oxidation reactions using urea-hydrogen peroxide. A safe alternative to anhydrous hydrogen peroxide. ChemInform 1991;22. doi:10.1002/chin.199105124.

[71] Devi Wilfred C, Salleh MZ, Mutalib MI. Oxidative desulfurization of fuels using 1-butyl-6-methyl-quinolinium dicyanamide. Sep Sci Technol 2015;50:159–63.

[72] Zhao D, Wang Y, Duan E, Zhang J. Oxidation desulfurization of fuel using pyridinium-based ionic liquids as phase-transfer catalysts. Fuel Process Technol 2010;91:1803–6.

[73] Liang W, Zhang S, Li H, Zhang G. Oxidative desulfurization of simulated gasoline catalyzed by acetic acid-based ionic liquids at room temperature. Fuel Process Technol 2013;109:27–31.

[74] Kulkarni PS, Afonso CA. Deep desulfurization of diesel fuel using ionic liquids: current status and future challenges. Green Chem 2010;12:1139–49.

[75] Chen X, Guan Y, Abdeltawab AA, Al-Deyab SS, Yuan X, Wang C, et al. Using functional acidic ionic liquids as both extractant and catalyst in oxidative desulfurization of diesel fuel: an investigation of real feedstock. Fuel 2015;146:6–12.

[76] Thomazeau C, Olivier-Bourbigou H, Magna L, Luts S, Gilbert B. Determination of an acidic scale in room temperature ionic liquids. J Am Chem Soc 2003;125:5264–5.

[77] Fang D, Wang Q, Liu Y, Xia L, Zang S. High-efficient oxidation–extraction desulfurization process by ionic liquid 1-butyl-3-methyl-imidazolium trifluoroacetic acid. Energy Fuels 2014;28:6677–82.

[78] Jiang Y, Zhu W, Li H, Yin S, Liu H, Xie Q. Oxidative Desulfurization of fuels catalyzed by fenton-like ionic liquids at room temperature. ChemSusChem 2011;4:399–403.

[79] Xiong J, Zhu W, Li H, Xu Y, Jiang W, Xun S, et al. Immobilized fenton-like ionic liquid: catalytic performance for oxidative desulfurization. AIChE J 2013;59:4696–704.

[80] Chen X, Song D, Asumana C, Yu G. Deep oxidative desulfurization of diesel fuels by Lewis acidic ionic liquids based on 1-n-butyl-3-methylimidazolium metal chloride. J Mol Catal A: Chem 2012;359:8–13.

[81] Sachdeva TO, Pant KK. Deep desulfurization of diesel via peroxide oxidation using phosphotungstic acid as phase transfer catalyst. Fuel Process Technol 2010;91:1133–8.

[82] Zhang W, Xu K, Zhang Q, Liu D, Wu S, Verpoort F, et al. Oxidative desulfurization of dibenzothiophene catalyzed by ionic liquid [BMIm] HSO4. Ind Eng Chem Res 2010;49:11760–3.

[83] Lu L, Cheng S, Gao J, Gao G, He MY. Deep oxidative desulfurization of fuels catalyzed by ionic liquid in the presence of H_2O_2. Energy Fuels 2007;21:383–4.

[84] Mochizuki Y, Sugawara K. Removal of organic sulfur from hydrocarbon resources using ionic liquids. Energy Fuels 2008;22:3303–7.

[85] Wang J, Zhao D, Li K. Oxidative desulfurization of dibenzothiophene catalyzed by Brönsted acid ionic liquid. Energy Fuels 2009;23:3831–4.

[86] Zhang J, Zhu W, Li H, Jiang W, Jiang Y, Huang W, et al. Deep oxidative desulfurization of fuels by Fenton-like reagent in ionic liquids. Green Chem 2009;11:1801–7.

[87] Jiang W, Zhu W, Chang Y, Li H, Chao Y, Xiong J, et al. Oxidation of aromatic sulfur compounds catalyzed by organic hexacyanoferrates in ionic liquids with a low concentration of H_2O_2 as an oxidant. Energy Fuels 2014;28:2754–60.

[88] Liu D, Gui J, Song L, Zhang X, Sun Z. Deep desulfurization of diesel fuel by extraction with task-specific liquids. Pet Sci Technol 2008;26:973–82.

[89] Asumana C, Yu G, Li X, Zhao J, Liu G, Chen X. Extractive desulfurization of fuel oils with low-viscosity dicyanamide-based ionic liquids. Green Chem 2010;12:2030–7.

[90] Cousens NE, Kearney LJ, Clough MT, Lovelock KR, Palgrave RG, Perkin S. Preparation and characterisation of high-density ionic liquids incorporating halobismuthate anions. Dalton Trans 2014;43:10910–19.

[91] Li FT, Wu B, Liu RH, Wang XJ, Chen LJ, Zhao DS. An inexpensive N-methyl-2-pyrrolidone-based ionic liquid as efficient extractant and catalyst for desulfurization of dibenzothiophene. Chem Eng J 2015;274:192–9.

[92] Yansheng C, Changping L, Qingzhu J, Qingshan L, Peifang Y, Xiumei L, et al. Desulfurization by oxidation combined with extraction using acidic room-temperature ionic liquids. Green Chem 2011;13:1224–9.

[93] Xun S, Zhu W, Zheng D, Zhang L, Liu H, Yin S, et al. Synthesis of metal-based ionic liquid supported catalyst and its application in catalytic oxidative desulfurization of fuels. Fuel 2014;136:358–65.

[94] Cai YQ, Song GH, Liang DN. Desulfurization using the 1,2-dimethylimidazolium ionic liquid as an adsorbent. Chin Chem Lett 2015;26:317–19.

[95] Xun S, Zhu W, Zheng D, Li H, Jiang W, Zhang M, et al. Supported ionic liquid [Bmim] $FeCl_4$/Am TiO_2 as an efficient catalyst for the catalytic oxidative desulfurization of fuels. RSC Adv 2015;43:528–36.

[96] Xiong J, Zhu W, Ding W, Yang L, Chao Y, Li H, et al. Phosphotungstic acid immobilized on ionic liquid-modified SBA-15: efficient hydrophobic heterogeneous catalyst for oxidative desulfurization in fuel. Ind Eng Chem Res 2014;53:19895–904.

[97] Ge J, Zhou Y, Yang Y, Xue M. Catalytic oxidative desulfurization of gasoline using ionic liquid emulsion system. Ind Eng Chem. Res 2011;50:13686–92.

[98] Ito E, Van Veen JR. On novel processes for removing sulphur from refinery streams. Catal Today 2006;116:446–60.

[99] Shiraishi Y, Tachibana K, Hirai T, Komasawa I. Desulfurization and denitrogenation process for light oils based on chemical oxidation followed by liquid-liquid extraction. Ind Eng Chem Res 2002;41:4362–75.

[100] Lin F, Wang D, Jiang Z, Ma Y, Li J, Li R, et al. Photocatalytic oxidation of thiophene on $BiVO_4$ with dual co-catalysts Pt and RuO_2 under visible light irradiation using molecular oxygen as oxidant. Energy Env Sci 2012;5:6400–6406.

[101] Zhao D, Liu R, Wang J, Liu B. Photochemical oxidation–ionic liquid extraction coupling technique in deep desulphurization of light oil. Energy Fuels 2008;22:1100–3.

[102] Vargas R, Núñez O. The photocatalytic oxidation of dibenzothiophene (DBT). J Mol Catal A: Chem 2008;294:74–81.

[103] Shiraishi Y, Hirai T, Komasawa I. TiO_2-mediated photocatalytic desulfurization process for light oils using an organic two-phase system. J Chem Eng Jpn 2002;35:489–92.

[104] Wang XJ, Li FT, Liu JX, Kou CG, Zhao Y, Hao YJ, et al. Preparation of TiO_2 in ionic liquid via microwave radiation and in situ photocatalytic oxidative desulfurization of diesel oil. Energy Fuels 2012;26:6777–82.

[105] Zaid HF, Chong FK, Mutalib MI. Photooxidative–extractive deep desulfurization of diesel using Cu–Fe/TiO_2 and eutectic ionic liquid. Fuel 2015;156:54–62.

[106] Weixia H, Yunlong L, Xieqing W. Reducing sulfur content in FCC naphtha by using ionic liquid. Chem Ind Eng Prog 2004;23:297–9.

[107] Tang XD, Yuan JY, Li JJ, Zhang YF, Tao HU. Alkylation desulfurization of FCC gasoline catalyzed by pyridine ionic liquid. J Fuel Chem Technol 2015;43:442–8.

[108] Brégeault JM. Transition-metal complexes for liquid-phase catalytic oxidation: some aspects of industrial reactions and of emerging technologies. Dalton Trans 2003;17:3289–302.