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REVIEW ARTICLE

Oxidative desulfurization of fuels using ionic liquids: A review[#]

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Abstract Extractive oxidation, wherein aromatic sulfur-containing compounds are extracted and subsequently oxidized to their corresponding sulfones, has proven to be one of the most effective desulfurization methods for producing ultra-low sulfur content fuels. As non-volatile and highly designable solvents, ionic liquids (ILs) have attracted considerable attention for the oxidative desulfurization of fuels. In this review, we systematically discuss the utility of ILs in catalytic and extractive oxidation, including their role as extractant, catalyst, or both. We also discuss the challenges facing the use of ILs in this regard, including their relatively high cost and excessive viscosity, as well as their efficiency and stability as catalyst.

Keywords oxidative desulfurization, ionic liquids, extraction, fuels, petroleum, polyoxometalates

1 Introduction

Crude oils typically contain 0.1–3.0 wt-% sulfur in various compounds, depending on the origin and processing of the oil. The combustion of sulfur-containing fuels emits sulfur oxides (SO_x) which exert a detrimental impact on human health, the environment, and the economy. Sulfur oxides are precursors to the formation of sulfate aerosols which contribute to respiratory diseases. Perhaps most notoriously, sulfur oxides react with moisture in air to produce acid rain, which is harmful to soil and marine life. Moreover, sulfur in fuels is the leading cause of catalyst poisoning of emission control systems and malfunction within various automotive sensors [1,2].

To reduce the impact of SO_x emissions from fuel burning on human health and the environment, stringent regulations have been imposed on oil refineries to reduce the statutory sulfur contents of fuels by the U.S. Environmental Protection Agency (EPA; 15 ppm for diesel since 2006 and 30 ppm for gasoline since 2005) as well as by EU legislation (10 ppm for both diesel and gasoline since 2010) [3]. Petroleum-based oil with an extremely low sulfur content is known as ultra-low-sulfur fuel. It remains challenging, however, to efficiently achieve these low sulfur contents with current technologies involving conventional refining processes. Conventionally, hydrodesulfurization (HDS) has been employed by oil refineries to convert organic sulfur in fuel to H_2S using metal catalysts (such as Co-Mo/Al_2O_3, Ni-Mo/Al_2O_3, or Ni-W/Al_2O_3) [4,5]. However, this process suffers from several drawbacks such as the need for high temperatures (300−400 °C) and pressures (20−100 atm of H_2), and reduced octane/cetane number [6]. Additionally, the HDS process is normally primarily effective for removing paraffinic sulfur compounds such as thiols, sulfides, and disulfides. Indeed, aromatic sulfur-containing molecules including benzothiophene (BT), dibenzothiophene (DBT), and their alkylated derivatives are very difficult to remove through HDS catalysis [7,8]. Although some new catalysts (including the unsupported trimetallic Mo-W-Ni HDS catalyst known as NEBULA developed by ExxonMobil, Akzo Nobel, and Nippon Ketjen) have been shown to be effective in removing refractory sulfur compounds and producing diesel oil with a 10 ppm sulfur content, such deep HDS processes require large energy and hydrogen consumption [6,9]. Therefore, alternative deep desulfurization methods are urgently sought for the production of clean fuels. These methods include oxidative desulfurization, bio-desulfurization, reactive adsorption, non-destructive adsorption, *N*-adsorption, extractive desulfurization (EDS), and others; however, each of these methods still faces its own unique

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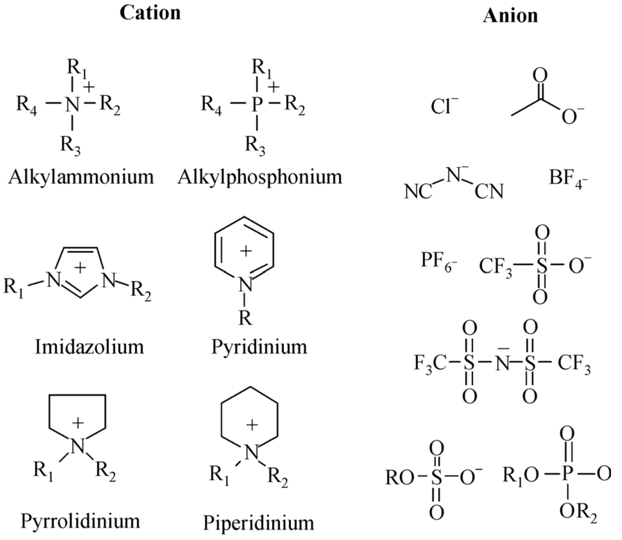
[#] Dedicated to the 120th Anniversary of Tianjin University challenges [3]. Among these alternative methods, oxidative and extractive processes show great promise for industrial-scale applications because of a number of advantages, including low cost of energy, the elimination of hydrogen usage, mild operating conditions, and retention of the chemical structure of the fuels, all without the requirement for special equipment. One drawback, however, is that both methods require the use of large quantities of volatile organic solvents as extractants, which in itself imposes important health and environmental concerns.

Ionic liquids (ILs) are made entirely of ions and remain liquid (i.e., molten) at temperatures below 100 °C. Typical IL cations contain nitrogen (for example, ammonium, imidazolium, pyridinium, pyrrolidinium, or piperidinium ions) or phosphorous (most notably, tetraalkylphosphonium). Among the most common anions for generating ILs are the halides, BF_4^-, PF_6^-, $CH_3CO_2^-$, $CF_3CO_2^-$, NO_3^-, Tf_2N^- [i.e., $(CF_3SO_2)_2N^-$, bis(trifluoromethylsulfonyl) imide], $(NC)_2N^-$, $[RSO_4]^-$, and $[R_2PO_4]^-$. Some representative cations and anions are illustrated in Scheme 1. As a new generation of non-aqueous solvents, ILs have many desirable properties including low vapor pressure, a wide liquid range, low flammability, high ionic conductivity, high thermal conductivity, strong dissolution capability towards many substrates, excellent thermal and chemical stability, and a wide electrochemical potential window [10]. Due to these unique and attractive properties, ILs have been widely evaluated as solvents or (co-)catalysts in a variety of applications including organic catalysis [10–12], inorganic synthesis [13], biocatalysis [14,15], polymerization [16], and engineering fluids [17,18]. Most notably, the physical properties of ILs (such as polarity, hydrophobicity, and hydrogen-bond basicity) can be finely adjusted through careful selection and combination of the constituent cations and anions. For example, ILs can be made to be miscible, partially miscible, or fully immiscible with water, or possess different polarities to match the individual applications [10]. The capacity to adjust physicochemical properties at will is a huge asset when considering the high performance extraction of sulfur compounds from fuel.

Owing to these beneficial properties and fundamental tunability, pilot investigations considering ILs as promising alternate solvents for the deep desulfurization of fuel have been conducted [3,19,20]. Now this research field can be broadly categorized into two types: extractive desulfurization and oxidative extractive desulfurization.

For extractive desulfurization, common ILs studied in extraction processes include imidazolium- and pyridinium-based ILs carrying anions consisting of BF_4^-, PF_6^-, alkylsulfates, or alkylphosphates, Lewis and Brønsted acidic ILs, and redox ILs (such as $[BMIM]Cl/AlCl_3$ and $FeCl_3/[BMIM]Cl$). Recent reviews [3,21] have systematically discussed the progress in this area, and thus we only examine a few typical examples here. Bosmann et al. [22] investigated various imidazolium- and chloroaluminate-based ILs and found multi-stage extraction to be very effective in removing sulfur. Several ILs (e.g., $[EMIM][BF_4]$, $[BMIM][PF_6]$) exhibited high selectivities in extracting aromatic sulfur and nitrogen compounds [23]. Ultra-low levels of sulfur (< 10 ppm) were obtained via a five-step cross-current extraction of *n*-dodecane using the halogen-free ILs $[BMIM][(Me(CH_2)_7SO_4]$ and $[EMIM][EtSO_4]$ [24]. In other work, CuCl-based imidazolium ILs were prepared and demonstrated a remarkable ability for removing sulfur from gasoline [25]. The removal of mercaptans (compounds containing the thiol group, viz., R-SH) from hydrocarbons streams (e.g., crude oil and natural gas) was achieved by reacting basic metal salts with mercaptans, followed by the sorption of the resulting mercaptides by ILs [26]. Alonso et al. [27] obtained ~80%



Scheme 1 Structures of typical cations and anions used in IL formulation

extraction of thiophene and dibenzothiophene in a three-stage process using [C_8MIM][BF_4]. Very recently, Hansmeier et al. [28] investigated pyridinium- and imidazolium-based ILs paired with various anions for the extractive removal of aromatic sulfur and nitrogen compounds from gasoline and diesel, and found that $(NC)_2N^-$ and $C(CN)_3^-$ based ILs are superior to sulfolane as solvents for this extraction. Asumana et al. [29] also suggested that $(NC)_2N^-$ based imidazolium and sulfonium ILs as extractants were more effective for carbazole-containing fuel oil (up to 97% extraction efficiency) than for pyridine-containing fuel oil (up to 73% efficiency). In summary, extractive desulfurization using ILs has many advantages, including the elimination of volatile organic solvents, low energy consumption, and low waste handling; however, its major drawback is the low efficiency and poor selectivity in achieving ultra-low-sulfur contents (< 10–15 ppm), even when employing muti-step extractions.

For oxidative extractive desulfurization using ILs, the extraction of sulfur-containing compounds/products and the chemical or catalytic oxidation of sulfur compounds are integrated into a single, concerted process [3,30]. Major advances in this field include the design and use of ILs as extractants, the preparation of new IL-type catalysts, and the combination of these two strategies. This review aims to provide a critical analysis of these advances and offer some insightful guidance for future developments in this area.

2 ILs as extraction solvents

Table 1 summarizes known extraction capabilities of various ILs toward aromatic sulfur-containing compounds, such as DBT. Most of ILs have modest Nernst partition coefficients (K_N) of about 1–2, although values as high as 4 were observed, for some systems. When ILs are engaged as extractants, various catalysts have been evaluated for H_2O_2-oxidized desulfurization processes. A highly efficient catalyst for this process is the transition metal clusters known as the polyoxometalates (POMs). POMs belong to a group of metal oxide clusters of early transition metals (V, Mo, W, Nb, etc.) and lanthanides/actinides, and they exhibit strong Brønsted acidity, rapid reversible multi-electron redox transformations under mild conditions, and tunable acid-base and redox properties over a wide range [49]. Thus, POMs have been widely used as acidic and redox-bifunctional catalysts in homogeneous and heterogeneous reaction systems, including many oxidative desulfurization systems. Table 2 gives representative examples of the catalytic oxidative desulfurization of DBT using polyoxometalate/IL systems, and the following sections provide detailed elaborations.

2.1 Molybdenum-based catalysts

The Li group [50] pioneered the field of IL-based oxidative desulfurization of fuel, using peroxotungsten and peroxomolybdenum complexes (e.g., $WO(O_2)_2\cdot$Phen$\cdot H_2O$ and $MoO(O_2)_2\cdot$Phen, Phen = 1,10-phenanthroline) as catalysts, H_2O_2 as oxidant, and ILs as extractants for DBT removal from *n*-octane. This integrated oxidative extraction system greatly improved the desulfurization efficiency, resulting in 98.6% DBT removal at 70 °C in 3 h by using $WO(O_2)_2\cdot$Phen$\cdot H_2O$ and [BMIM][BF_4] (*vs.* 50.3% sulfur removal in the absence of IL). They [51] further designed an extractive oxidative desulfurization process using [BMIM][BF_4] as extractant, 30% H_2O_2 as oxidant, and Mo compounds (such as $Na_2MoO_4\cdot 2H_2O$) as catalyst, for the ultra-deep removal of BT, DBT, and 4,6-DMDBT from model fuel, resulting in 99.0% sulfur removal at 70 °C in 3 h (Scheme 2). It was suggested in this report that the molybdic compound could be oxidized by H_2O_2 to a peroxomolybdic compound, which was dissolved in the IL phase to catalyze the oxidation. The water-miscible IL [BMIM][BF_4] was found to be more effective for oxidative desulfurization than its water-immiscible analogs [OMIM][BF_4], [BMIM][PF_6], and [OMIM][PF_6] due to three-phase partitioning (i.e., IL/H_2O_2/oil) in the latter. In addition, the desulfurization efficiency was clearly influenced by the nature of the anion, showing a decreasing efficiency order of $BF_4^- > PF_6^- > CF_3COO^-$. The Li group [52] further demonstrated that the combined use of $[Bu_4N]_3PO_4[MoO(O_2)_2]_4$ (catalyst), H_2O_2 (oxidant) and [BMIM][BF_4] (extractant) led to 97.3% removal of DBT from a model fuel, with the reactivity for different sulfur compounds decreasing in the order DBT > 4,6-DMDBT > BT. More recently, to improve the low catalytic activity of simple molybdenum salts (such as $Na_2MoO_4\cdot 2H_2O$) toward oxidative desulfurization in water-immiscible ILs, the Li group [39] synthesized peroxo-molybdenum amino acid complexes [$MoO(O_2)_2\cdot$(amino acid), where amino acid = glycine, alanine, or glutamic acid] as catalysts for the extractive oxidation of DBT. They observed that the new catalysts were highly active in both water-miscible ([BMIM][BF_4]) and water-immiscible ([BMIM][PF_6], [OMIM][BF_4], and [OMIM][PF_6]) ILs, leading to the removal of 99.2% DBT, 93.2% BT, and 99.6% 4,6-DMDBT under optimal conditions. Zhu et al. [53] reported a new catalytic system consisting of H_2O_2, phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot 26H_2O$), and [BMIM][$BF_4$] which achieved 99.4% DBT removal under optimum conditions. Lü et al. [40] investigated the oxidative desulfurization of model fuels using 30 wt-% H_2O_2 as oxidant, an Anderson-type $[(C_4H_9)_4N]_6[Mo_7O_{24}]$ catalyst, and [BMIM][PF_6] as water-immiscible IL extractant, reporting a 99% DBT removal in 2 h at 50 °C, although the reactivity of other sulfur compounds appeared to be lower (DBT > 4-MDBT > 4,6-DMDBT > BT). Finally, the Meng group [54] prepared several ILs containing

Table 1 Nernst partition coefficients (K_N) of aromatic sulfur-containing compounds

#	Substrate	IL	Oil	Oil/IL /($v \cdot v^{-1}$)	T/°C	K_N in /($mg_s \cdot L_{IL}^{-1}$)/($mg_s \cdot L_{oil}^{-1}$)	Ref.
1	DBT	[BMIM]Cl/$AlCl_3$	*n*-Dodecane	1:1	r.t.	4.0	[20]
2	DBT	[BMIM][BF_4]	*n*-Dodecane	1:1	r.t.	0.7	[20]
3	DBT	[BMIM][PF_6]	*n*-Dodecane	1:1	60	0.9	[20]
4	DBT	[BMIM][dca]	*n*-Hexane	1:1	25	2.28	[31]
5	DBT	[BMIM][$OctSO_4$]	*n*-Dodecane	1:1	r.t.	1.9	[20]
6	Thiophene	[BMIM][$OctSO_4$]	*iso*-Octane	1:1	r.t.	0.7	[20]
7	BT	[BMIM][$OctSO_4$]	*n*-Dodecane	1:1	r.t.	1.6	[20]
8	4,6-DMDBT	[BMIM][$OctSO_4$]	*n*-Dodecane	1:1	r.t.	0.9	[20]
9	DBT	[EMIM][dca]	*n*-Hexane	1:1	25	1.3	[31]
10	DBT	[EMIM][$EtSO_4$]	*n*-Dodecane	1:1	r.t.	0.8	[20]
11	Thiophene	[EMIM][$EtSO_4$]	*iso*-Octane		r.t.	0.53	[32]
12	BT	[EMIM][$EtSO_4$]	*iso*-Octane		r.t.	0.70	[32]
13	DBT	[EMIM][$EtSO_4$]	*iso*-Octane		r.t.	0.99	[32]
14	DBT	[MMIM][Me_2PO_4]	*n*-Dodecane	1:1	r.t.	0.7	[20]
15	DBT	[OMIM][BF_4]	*n*-Octane	5:1		2.91	[33]
16	BT	[OMIM][BF_4]	*n*-Octane	5:1		2.33	[33]
17	4,6-DMDBT	[OMIM][BF_4]	*n*-Octane	5:1		1.70	[33]
18	DBT	[BuPy][BF_4]	*n*-Octane	1:1	40	0.83	[34]
19	DBT	[BuPy][BF_4]	*n*-Dodecane	1:1	r.t.	0.77	[35]
20	DBT	[BuPy][SCN]	*n*-Octane	1:1	40	1.14	[34]
21	DBT	[BuPy][HSO_4]	*n*-Octane	1:1	40	1.42	[34]
22	DBT	[BuPy][H_2PO_4]	*n*-Octane	1:1	40	1.24	[34]
23	DBT	[HexPy][BF_4]	*n*-Dodecane	1:1	r.t.	1.42	[35]
24	DBT	[OctPy][BF_4]	*n*-Dodecane	1:1	r.t.	1.79	[35]
25	DBT	[3-Me-BuPy][BF_4]	*n*-Dodecane	1:1	r.t.	2.08	[36]
26	DBT	[3-Me-HexPy][BF_4]	*n*-Dodecane	1:1	r.t.	2.89	[36]
27	DBT	[3-Me-OctPy][BF_4]	*n*-Dodecane	1:1	r.t.	3.11	[36]
28	DBT	[MePyo][BF_4]	*n*-Octane	1:1	60	0.64	[37]
29	DBT	[$EtMe_2S$][dca]	*n*-Hexane	1:1	25	0.84	[31]
30	DBT	[$Me_3NCH_2C_6H_5$]Cl·2$ZnCl_2$	*n*-Octane	5:1	30	2.03	[38]
31	DBT	[S2][dca]	*n*-Hexane	1:1	25	1.08	[31]

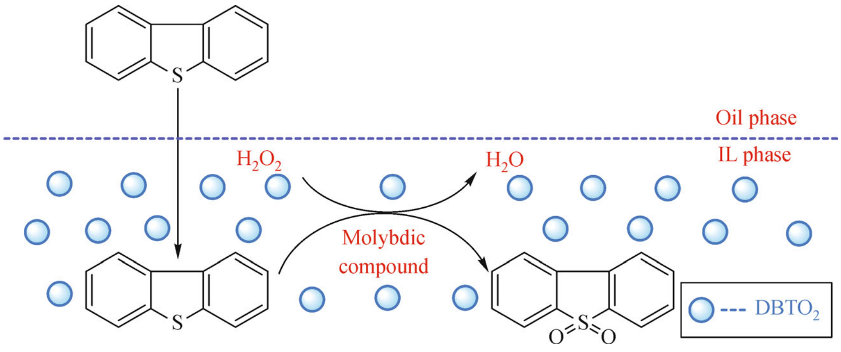
phosphate anions (i.e., [MMIM][Me_2PO_4], [EMIM][Et_2PO_4], [BMIM][Bu_2PO_4]), and evaluated them as extractants in the H_2O_2-oxidized desulfurization of 4,6-DMDBT from a model oil catalyzed by $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The sulfur removal was 89.2% at 50 °C in 3 h by using [BMIM][Bu_2PO_4] in the catalytic system, much higher than that by solvent extraction with IL alone (9.3%) or catalytic oxidation without use of IL (5.3%).

2.2 Tungsten-based catalysts

A second set of examples involves the use of tungsten (W) compounds as catalysts. The Li group [42] prepared three decatungstates (i.e., $[Bu_4N]_4W_{10}O_{32}$, $[Me_4N]_4W_{10}O_{32}$, and $[Et_3NC_7H_7]_4W_{10}O_{32}$) as catalysts for extractive and oxidative desulfurization using [BMIM][PF_6] as extractant and H_2O_2 as oxidant. Under optimum conditions, the sulfur content in the model oil (1000 ppm) was reduced to 8 ppm, with the reactivity of sulfur compounds decreasing in the order of DBT > 4,6-DMDBT > BT. The Li group [45] suggested that a catalytic system consisting of $H_3PW_{12}O_{40} \cdot 14H_2O$, 30% H_2O_2, and [BMIM][BF_4] could remove 98.2% of DBT at 30 °C in 1 h, and 100% of BT, DBT, and 4,6-DMDBT at 70 °C in 3 h. The Gui group [55] tested the oxidative desulfurization of DBT in

Table 2 Catalytic oxidative desulfurization of DBT by polyoxometalate/IL systems

#	Catalyst	Extractant	DBT/cat, molar ratio	H_2O_2/DBT, molar ratio	*T*/°C	*t*/min	*S*/ppm	Sremoval /%	Ref.
1	$MoO(O_2)_2\cdot$Glycine	$[BMIM][PF_6]$	10	4	70	180	–	99.2	[39]
2	$MoO(O_2)_2\cdot$Glycine	$[BMIM][BF_4]$	10	4	70	180	–	99	[39]
3	$MoO(O_2)_2\cdot$Glycine or $Na_2MoO_4\cdot 2H_2O$	$[BMIM][BF_4]$	10	4	70	180	–	99	[39]
4	$[(C_4H_9)_4N]_6[Mo_7O_{24}]$	$[BMIM][PF_6]$	100	5	50	120	500	99	[40]
5	$[(C_{12}H_{25})N^+Me_3]_4[Mo_8O_{26}]$	$[HO_3S(CH_2)_3\text{-MIM}][BF_4]$	10	8	70	180	1000	100	[41]
6	$[(C_4H_9)_4N]_4W_{10}O_{32}$	$[BMIM][PF_6]$	100	3	60	30	1000	98	[42]
7	$[(CH_3)_4N]_4W_{10}O_{32}$	$[BMIM][PF_6]$	100	3	60	30	1000	97	[42]
8	$[(C_2H_5)_3(C_7H_7)]_4W_{10}O_{32}$	$[BMIM][PF_6]$	100	3	60	30	1000	66	[42]
9	$Na_4W_{10}O_{32}$	$[BMIM][PF_6]$	100	3	60	30	1000	95	[42]
10	$[(C_8H_{17})_3NCH_3]_2W_6O_{19}$	$[OMIM][PF_6]$	50	3	60	60	500	98	[43]
11	$Na_7H_2EuW_{10}O_{36}\cdot 32H_2O$	$[BMIM][BF_4]$	20	3	60	10	1000	99	[44]
12	$Na_7H_2LaW_{10}O_{36}\cdot 32H_2O$	$[BMIM][BF_4]$	20	3	60	20	1000	99	[44]
13	$Na_7H_2LaW_{10}O_{36}\cdot 32H_2O$	$[BMIM][BF_4]$	100	3	60	25	1000	99	[44]
14	$Na_7H_2LaW_{10}O_{36}\cdot 32H_2O$	$[BMIM][BF_4]$	100	5	60	20	1000	99	[44]
15	$H_3PW_{12}O_{40}$	$[BMIM][BF_4]$	100	3	30	60	1000	98	[45]
16	$[PSPy]_3PW_{12}O_{40}$	$[BMIM][BF_4]$	120	4	30	60	500	81	[46]
17	$[PSPy]_3PW_{12}O_{40}$	$[BMIM][PF_6]$	120	4	30	60	500	96	[46]
18	$[PSPy]_3PW_{12}O_{40}$	$[OMIM][BF_4]$	120	4	30	60	500	77	[46]
19	$[PSPy]_3PW_{12}O_{40}$	$[BMIM][PF_6]$	120	4	30	60	500	99	[46]
20	$Na_7H_2EuW_{10}O_{36}\cdot 32H_2O$	$[BMIM][BF_4]$	20	5	30	20	1000	99	[44]
21	$Na_7H_2LaW_{10}O_{36}\cdot 32H_2O$	$[BMIM][BF_4]$	100	5	30	40	1000	99	[44]
22	$Na_7H_2LaW_{10}O_{36}\cdot 32H_2O$	$[BMIM][BF_4]$	50	5	30	30	1000	99	[44]
23	$Na_7H_2LaW_{10}O_{36}\cdot 32H_2O$	$[BMIM][BF_4]$	20	5	30	25	1000	100	[44]
24	V_2O_5	$[BMIM][BF_4]$	20	6	30	240	1000	98.7	[47]
25	$VO(acac)_2$	$[BMIM][BF_4]$	20	5	30	120	–	99.6	[48]



Scheme 2 The extractive and catalytic oxidation process of deep desulfurization, using dibenzothiophene (DBT) as the aromatic sulfur-containing compound for illustration. (Reprinted with permission from Ref. [51], Copyright © 2012 Royal Society of Chemistry)

n-tetradecane using H_2O_2 as oxidant, catalyzed by $Na_2WO_4\cdot 2H_2O$ in $[HSO_3(CH_2)_4\text{-MIM}][OTs]$, which achieved 99.4% sulfur removal at 50 °C after 3 h. Chao et al. [56] reported 99.7% DBT removal from model fuel at 60 °C in 3 h by using a catalytic system of $Na_2WO_4\cdot 2H_2O$, 30 wt-% H_2O_2, and $[BMIM][BF_4]$. Chuang et al. [57] investigated the extractive sulfur removal of DBT and 4,6-DMDBT oxidized by H_2O_2/tungstophosphoric acid using different ILs, and found that the efficiency decreased in the order [OMIM][PF_6] > [BMIM][PF_6] > [BMIM][BF_4]. It should be noted that first two ILs lead to triphasic systems (oil/H_2O_2/IL), whereas [BMIM][BF_4] should form a biphasic system (i.e., oil/(H_2O_2 + IL)). Under optimal conditions, a 95% desulfurization efficiency was achieved in a one-batch process for diesel light oil (i.e., the sulfur content was reduced from 897 to 42 ppm). Zhang et al. [58] suggested that the combined use of ammonium tungstate [$(NH_4)_2WO_4$] and a Brønsted acidic IL (*N*-methylpyrrolidonium tetrafluoroborate) showed high activities toward the oxidative desulfurization (ODS) of thiophene, BT, and their derivatives using 30 wt-% H_2O_2; in particular, up to 99% conversion of thiophene could be obtained at 60 °C. The Li group [59] loaded different amounts of phosphotungstic acid on ceria (CeO_2) supports, and found that the thus obtained new catalysts for DBT removal using [OMIM][BF_4] as extractant and H_2O_2 as oxidant had a 99.4% desulfurization efficiency. The oxidative reactivity of aromatic sulfur-containing compounds in this catalytic system decreased in the order of DBT > 4,6-DMDBT > BT. The Gui group [60] investigated the oxidative desulfurization of real diesel using H_2O_2 as oxidant and Na_2WO_4 as catalyst in [$HO_3S(CH_2)_4$-MIM][OTs], and found that 88.4% sulfur removal was achieved after extraction of the oil phase by *N*-methyl-2-pyrrolidone following the reaction at 50 °C for 3 h. The Zhou group [61] examined the oxidative removal of DBT from *n*-octane by using H_2O_2 as oxidant, Na_2WO_4 as catalyst, and acidic ILs such as [$HO_3S(CH_2)_3$-MIM][BF_4] as extractants, achieving almost complete removal of DBT at 60 °C for 3 h. The same group [41] further evaluated several surfactant-type quaternary ammonium salts of the octamolybdates as catalysts for the extractive oxidation of DBT from *n*-octane using acidic ILs as extractants, and observed complete removal of DBT at 70 °C within 3 h when using [$(C_{12}H_{25})N^+Me_3]_4[Mo_8O_{26}]$ as the catalyst and [$HO_3S(CH_2)_3$-MIM][BF_4] as the extracting phase. The effectiveness of acidic ILs in desulfurization was found to decrease in the orders of imidazolium > triethylammonium > pyridinium (for cations) and $BF_4^- > HSO_4^- > H_2PO_4^-$ (for anions). Xu et al. [62] demonstrated that the oxidative extraction of sulfur compounds could completely remove DBT and 4,6-DMDBT by using 30% H_2O_2 as oxidant, commercial tungsten carbide as catalyst, and [OMIM][PF_6] as extractant. The Song group [44] found that lanthanide-containing polyoxometalates $Na_7H_2LnW_{10}O_{36}\cdot 32H_2O$ (Ln = Eu, La) could also act as effective catalysts for extractive and oxidative desulfurization, yielding efficiencies of 100% (DBT), 92% (4,6-DMDBT), and 80% (BT) when using [BMIM][BF_4] as the extractant and H_2O_2 as the oxidant. Chen et al. [63] anchored the lanthanide-containing polyoxometalate $Na_7H_2LaW_{10}O_{36}\cdot 32H_2O$, in nanoparticle form, onto an amino-modified mesoporous silica support and found that the combination of this catalyst with [BMIM][BF_4] as the extraction solvent in the presence of H_2O_2 resulted in nearly quantitative conversion of DBT within 35 min. Even on a large scale (1000 mL) with an initial sulfur content of 1000 ppm, almost 100% sulfur removal was reached after 45 min, showing the promise of this approach.

2.3 Vanadium and rhenium catalysts

Vanadium and rhenium compounds have also been examined as catalysts for oxidative desulfurization. The Li group [47] evaluated V_2O_5 as a catalyst for oxidative sulfur removal using H_2O_2 and [BMIM][BF_4], and reported that 98.7% DBT removal was achieved under optimum conditions, compared to 16.5% by IL extraction alone and just 2.8% for oxidation without IL extraction. The sulfur removal efficiency decreased in the order of DBT > BT > 4,6-DMDBT. It was proposed in this study that V_2O_5 was oxidized by H_2O_2 into peroxovanadium compounds, which then oxidized the sulfur compounds to their corresponding sulfones. Mota et al. [64] recently prepared acetylacetonate complexes of oxovanadium (IV) (i.e., VO(X-acac)$_2$ where X = Cl, CH_3, or CH_3CH_2) and employed them as catalysts and H_2O_2 in the IL-based extractive and oxidative desulfurization of a model fuel containing BT, DBT, and 4,6-DMDBT. They observed > 95% conversions of BT and DBT with [BMIM][Tf_2N], however, the other two ILs ([BMIM][OTf] and [BMIM][BF_4]) gave only low-to-moderate activities for all catalysts, perhaps due to the higher coordinating ability of these two anions than Tf_2N^-. The Zhou group [65] prepared amphiphilic vanadium (V)-based catalysts, $[C_{18}H_{37}N(CH_3)_3]_{3+x}[PMo_{12-x}V_xO_{40}]$ (x = 1, 2, or 3), and dissolved them in [BMIM][PF_6] to form H_2O_2-in-[BMIM][PF_6] emulsion systems for the quantitative removal of DBT from model oil with 92% sulfur removal from gasoline. Zhu et al. [48] obtained 99.6% DBT removal at 30 °C in 2 h by using an oxidative extraction system consisting of VO(acac)$_2$, 30% H_2O_2, and [BMIM][BF_4]. Most recently, Zhou et al. [66] found that methyltrioxorhenium (MTO) could catalyze the extractive oxidation of sulfur compounds using H_2O_2 and ILs such as [BMIM][BF_4], to accomplish 99% removal of thiophene from *n*-octane and 91% sulfur removal from fluid catalytic cracking (FCC) gasoline at 60 °C within 3 h.

2.4 Other catalysts

Catalysts other than POMs have also been investigated and showed promise in oxidative desulfurization processes involving ILs. Early on, Lo et al. [67] proposed a “one-pot” operation wherein the sulfur compounds in light oils were extracted by ILs ([BMIM][BF_4] or [BMIM][PF_6] in this case) and then further oxidized by H_2O_2/acetic acid to form sulfones. In this study, the DBT content in the oil layer (tetradecane) was reduced from 758 ppm to 7.8 ppm after

6 h (99% removal). At a much higher sulfur content (8040 ppm DBT), this extractive and catalytic system removed 85% sulfur by using [BMIM][PF_6] but only 55% sulfur by using [BMIM][BF_4]. In line with results from other groups, this process was reported to have a higher efficiency by an order of magnitude over extraction by the corresponding IL alone. Taha et al. [68] indicated that the oxidative desulfurization of DBT with H_2O_2 as oxidant using an acetic acid/sulfuric acid mixture as catalyst could be improved by using the IL [BMIM][$OctSO_4$] (a 72% DBT removal compared to 34% removal without the IL). The Soto group [69] recently evaluated several ILs for the oxidative-extractive desulfurization of fuels, and found that the use of [HMMPy][Tf_2N] and [EMIM][Tf_2N] with H_2O_2/acetic acid eliminated 96.5% and 82.0% sulfur, respectively, from real diesel at 50 °C. Moreover, they found that the desulfurization ability decreased in the order [HMMPy][Tf_2N] > [EMIM][Tf_2N] > [EMIM][Et_2PO_4] > [EMIM][OAc]. The Zhao group [70] reported that the complex of [Bu_4N]Br with caprolactam as a phase-transfer catalyst (PTC) could promote oxidative desulfurization using H_2O_2/acetic acid to achieve a 98.8% removal of thiophene from *n*-octane and 95.3% sulfur removal rate for actual FCC gasoline. Zhao et al. [71] later applied the [Bu_4N]Br/caprolactam system for the oxidative extraction of DBT using H_2O_2/acetic acid, and reported a 98.6% DBT removal at 50 °C within 30 min. The same group [34] evaluated several *N*-butylpyridinium ($BuPy^+$) ILs as PTCs for the desulfurization of DBT using the H_2O_2/formic acid catalytic oxidation system. Here, the effectiveness of the IL anion on desulfurization rate was found to decrease in the order $HSO_4^- > H_2PO_4^- > SCN^- > BF_4^-$ with a 93.3% DBT removal obtained with [BuPy][HSO_4] at 60 °C for 1 h. Nejad et al. [72] reported 97.1% sulfur removal from real gasoline with an initial sulfur content of 1400 ppm at 50 °C in 1 h when using [BMIM][$AlCl_4$] as extractant, H_2O_2 as oxidant, and formic acid as catalyst. Cheng and Yen [73] found that [BMIM][$MeSO_4$] could act as PTC for the oxidative extraction of sulfur compounds using H_2O_2 and trifluoroacetic acid, yielding removal efficiencies of 98.9% (DBT), 99.4% (BT), and 97.6% (thiophene) at 50 °C for 3 h (i.e., 10 min under ultrasound followed by 170 min under stirring). The Liang group [74] recently prepared several benzimidazolium-based ILs and noted that *N*-octylbenzimidazolium acetate could act as PTC to catalyze oxidative removal of thiophene from *n*-heptane (up to 87.5% removal at 70 °C within 3 h) using H_2O_2. The Lü group [75] found that *N*-methyl-2-pyrrolidonium formate could catalyze the oxidative removal of DBT using H_2O_2, leading to 99% removal efficiency after 3 h at 50 °C. The reactivity of different substrates under this catalytic system decreased in the order DBT > 4,6-DMDBT > BT.

The Li group [76] examined a number of Fenton-like reagents including Co^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+} and H_2O_2 for the oxidative desulfurization of a model fuel using ILs as extractants. The effectiveness of ILs for sulfur removal decreased in the order of [BMIM][BF_4] > [BMIM][PF_6] > [OMIM][BF_4] > [OMIM][PF_6]. Under the best conditions using $FeCl_3$, H_2O_2, and [BMIM] [BF_4], 96.1% of DBT could be removed from the model fuel, a significant improvement over solvent extraction with [BMIM][BF_4] (28.5%) or catalytic oxidation without IL extraction (7.3%). In another example, the Li group [77] immobilized [C_3MIM]Cl onto MCM-41 (a mesoporous molecular sieve material) via covalent linkage, followed by mixing with $FeCl_3$ solution to produce immobilized Fenton-type catalysts for removing up to 92.7% of DBT from model fuel using a H_2O_2/[OMIM][BF_4] system at 30 °C for 1 h. The reactivity of sulfur compounds using this system decreased as DBT > *n*-dodecanethiol > BT > 4,6-DMDBT. Similar work by the same team [78] involved grafting of [C_3MIM]Cl onto mesoporous silica SBA-15 followed by mixing with $FeCl_3$ solution to yield a new catalyst for oxidative desulfurization using [OMIM][BF_4] as extractant and H_2O_2 as oxidant. Under optimum conditions, 94.3% removal of DBT from *n*-octane was observed. The effectiveness of ILs for desulfurization using this approach decreased in the order [OMIM] [BF_4] > [BMIM][BF_4] > [OMIM][PF_6], [BMIM][PF_6]; the corresponding reactivity of sulfur compounds decreased in the order DBT > *n*-dodecanethiol > BT. Jiang et al. [33] prepared Fenton-type catalysts by mixing choline chloride with metal salts (i.e., $FeCl_3$, $ZnCl_2$, or $SnCl_2$) and found that, when choline/$FeCl_4$ was employed as the catalyst, 94.9% and 97.2% DBT removal efficiencies were obtained with the use of [BMIM][BF_4] and [OMIM] [BF_4] respectively. The Wang group [79] reported that *N*-hydroxyphthalimide could be an effective catalyst for extractive and oxidative desulfurization using molecular O_2 as oxidant and [BMIM][BF_4] as extractant. Under optimized conditions, the authors report that DBT can be quantitatively removed (100%) from *n*-octane for an initial sulfur concentration of 500 mg·mL^{-1} at 120 °C for 5 h; the reactivity of sulfur compounds was found to decrease in the typical order of DBT > BT > 4,6-DMDBT. Jiang et al. [80] examined the use of [BMIM]$_3$[Fe(CN)$_6$] as a catalyst for the extractive oxidation of aromatic sulfur-containing compounds in the presence of 7.5 wt-% H_2O_2 using [BMIM][BF_4] as extractant, and reported removal efficiencies of 97.9% for DBT, 91.1% for BT, and 43.9% for 4,6-DMDBT at 40 °C for 5 h. Electron spin resonance (ESR) spectra suggest that the interaction of the catalyst with H_2O_2 in [BMIM][BF_4] produces $O_2^{\cdot -}$ species, which are responsible for oxidizing the sulfur compounds to the corresponding sulfones. Interestingly, the Zhang group [81] found that cobalt phthalocyanines [CoPc(Cl)$_n$, n = 4, 8, 12, or 16] could effectively catalyze the oxidative extraction of DBT using air as the oxidant and IL as extractant, achieving up to 90% DBT removal at room temperature within 2 h for 0.3 wt-% of CoPc(Cl)$_{16}$. The catalytic activity increased with n in the order CoPc (Cl)$_4$ < CoPc(Cl)$_8$ < CoPc(Cl)$_{12}$ < CoPc(Cl)$_{16}$. This new cobalt phthalocyanine catalytic system was capable of reducing the sulfur content in actual gasoline from 1000 ppm to 30 ppm. A recent contribution from the Sengupta group [32] examined oxidative desulfurization using [EMIM][EtSO$_4$] as extractant and H_2O_2 as oxidant for titanium-based catalysts, realizing the removal of 90.7% thiophene (titanium silicate-1 catalyst), 70.3% BT (titanium-beta catalyst), and 74.4% DBT (titanium-beta catalyst) after 2 h at 60 °C. In this instance, however, the performance using IL was inferior to that using DMSO as solvent.

2.5 Catalyst-free processes

A few desulfurization processes have been carried out using IL extracting phases which involve no formal catalyst *per se*. For example, the Gao group [82] carried out the oxidative desulfurization of DBT in *iso*-octane using 30 wt-% H_2O_2 and [HMIM][BF$_4$], resulting in up to 93% sulfur removal after 6 h at 90 °C. Zhao et al. [83] studied the use of [BuPy][BF$_4$] as extractant for the oxidative removal of thiophene and DBT from *n*-octane, achieving 78.5% and 84.3% removal efficiencies, respectively, after 30 min at 55 °C; under optimized extraction conditions, 56.3% sulfur removal was obtained for gasoline with an initial sulfur content of 780 µg/mL. In a very recent example, Fang et al. [84] evaluated a number of hydrophilic ILs as extractants for the oxidative desulfurization of thiophene from model oil using H_2O_2 as the oxidant and determined that the efficiency followed the IL anions trend of $CF_3COO^- > HSO_4^- > HCOO^- > AlCl_4^- > OAc^-$. The use of the most effective phase ([BMIM][CF$_3$COO]) reduced the content of thiophene from 203 µg·mL^{-1} to as low as 7.3 µg·mL^{-1}.

2.6 Other advances

A more interesting trend in this area is the design of task-specific ILs for oxidative desulfurization. In one of the earlier contributions to the field, the Dupont group [85] synthesized task-specific ILs by grafting carboxylic acid and alkoxy groups to the imidazolium cation, followed by conversion to the hydrophobic Tf_2N^- form. These authors identified 1-carboxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide as an excellent extractant in a catalytic system comprising 30 wt-% H_2O_2 and acetic acid to reduce the contents of DBT, BT, and 2,5-dimethylthiophene to below 10 ppm after 4 h at 75 °C. This IL/H_2O_2/acetic acid system was applied to a real diesel sample resulting in an 80% reduction in sulfur content. Li et al. [86] later prepared a so-called "coordinated IL" by mixing *N*-methyl-pyrrolidone with anhydrous $SnCl_2$ at 80 °C. This novel IL showed a Nernst partition coefficient as high as 5.76 for DBT in *n*-octane, considerably higher than values for conventional ILs which typically fall in the 0.7–3.1 range (refer to Table 1). Given this promising result, this "coordinated IL" was tested as the extractant for the desulfurization of aromatic sulfur-containing compounds oxidized by H_2O_2/acetic acid, yielding a 94.8% sulfur removal for DBT in *n*-octane and 87.6% removal for actual diesel oil, both after 30 min at 30 °C. In addition, this new IL could be recycled and reused with little loss in activity.

Instead of a "one-pot" process, oxidation and extraction has also been used in two consecutive steps. Along these lines, Seeberger and Jess [87] suggested that the extraction efficiency is higher for sulfoxides and sulfones in [EMIM][Et$_2$PO$_4$] than for the initial (non-oxidized) sulfur compounds, indicating that one-pot processes may be inherently inefficient. They reported that four extraction steps could lower the total sulfur content from 100 ppm to 10 ppm. They also discussed the efficiency of the process and the required energy for regeneration of the sulfur-loaded IL. More recently, Wilfred et al. [88] oxided the sulfur compounds in diesel fuel by H_2O_2 using phosphotungstic acid as catalyst and trioctylmethylammonium chloride as the phase transfer agent. Following the oxidation step, various ILs were examined for the extraction of sulfones. The highest sulfur removal efficiency (91%) was obtained in 1-butyl-6-methylquinolinium dicyanamide, [BMQuin][(NC)$_2$N]. The IL extraction efficiency was observed to decrease in the following order: [BMQuin][(NC)$_2$N] > [BMIM][dca], [HMIM][OTf] > [TOMA]Cl, [BMIM][SCN] > [BMIM][OTf] > [BMIM][PF$_6$] > [C$_2$CN-BIM][SCN] > [C$_2$CN-BIM][dca], [EMIM][BF$_4$].

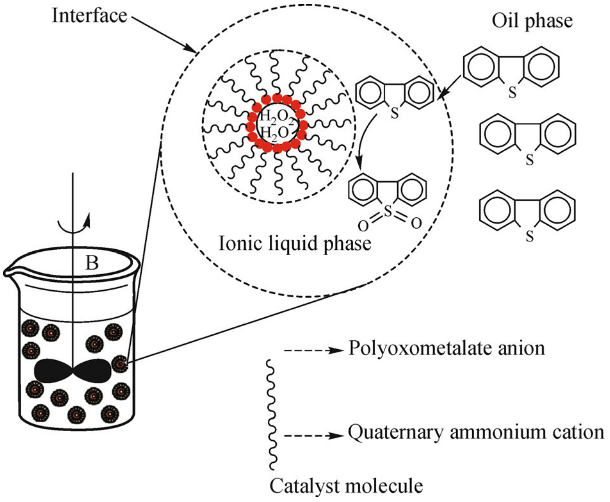
3 IL-derived catalysts

Recently, a number of IL-derived catalysts containing POM anions have been developed to improve the efficiency of oxidative desulfurization. In addition to the catalytic role of POM anions interacting with H_2O_2 [89], it is thought that the hydrophobic nature of the organic cations might endow these designed ILs with PTC-like behavior, augmenting the multi-phase oxidative desulfurization process. The Wang group [90] found that SiO_2-supported [BMIM]$_3$PMo$_{12}$O$_{40}$ exhibited a high catalytic activity in the oxidation of DBT by 29% H_2O_2 aqueous solution, leading to quantitative oxidation of DBT in toluene within 2 h at 60 °C and 97.9% sulfur removal from real diesel at 80 °C for 3 h. Interestingly, the addition of 0.2 wt-% of quinoline or carbazole showed a positive impact on the DBT oxidation, whereas the use of indole had a negative impact. Furthermore, the Li group [46] developed an IL-type catalyst, [(3-sulfonic acid)propylpyridine]$_3$PW$_{12}$O$_{40}$·2H$_2$O, for efficient sulfur removal (99.4% DBT, 98.8% 4,6-DMDBT, and 69.9% BT at 30 °C for 1 h) using [OMIM][PF$_6$] as the extractant and aqueous H_2O_2 as oxidant. This catalytic system enabled the reduction in sulfur content of FCC gasoline from 360 ppm to 70 ppm. The Li group [91] also synthesized new Keggin-type POM-based IL hybrid materials (such as

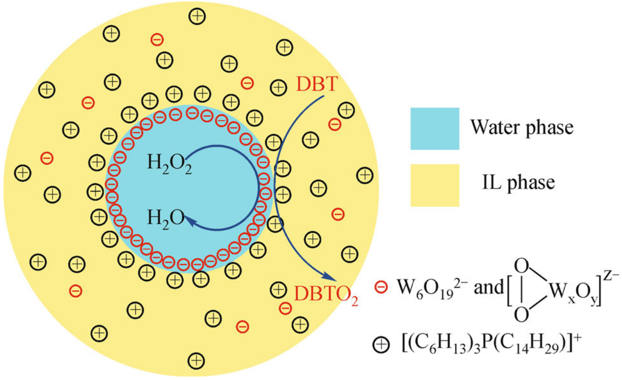
$[MIMPS]_3[PW_{12}O_{40}]\cdot 2H_2O$ {MIMPS = 1-(3-sulfo)propyl-3-methylimidazolium}, $[BMIM]_3[PW_{12}O_{40}]$, $[BMIM]_3[PMo_{12}O_{40}]$, and $[BMIM]_4[SiW_{12}O_{40}]$) and evaluated them as catalysts and imidazolium-based ILs ($BMIM^+$ and $OMIM^+$ paired with BF_4^- or PF_6^-) as solvents for the extractive, catalytic and oxidative desulfurization of a model fuel (DBT, BT, and 4,6-DMDBT in *n*-octane) as well as authentic diesel oil, both in the presence of H_2O_2. $[MIMPS]_3[PW_{12}O_{40}]\cdot 2H_2O$ was found to be the best catalyst, leading to high desulfurization efficiency toward DBT and 4,6-DMDBT, and reduction in the sulfur content of diesel oil from 1113 ppm to 198 ppm. To further improve the recyclability of such catalysts, Tang et al. [92] immobolized $[BMIM][PW_{12}O_{40}]$ onto hexagonal mesoporous silicas (HMS) for the oxidative desulfurization of a model fuel in the presence of H_2O_2, achieving 79%, 98%, and 88% conversions for DBT, BT, and 4,6-DMDBT, respectively. Zhang et al. [93] synthesized three Keggin-type phosphotungstates (i.e., $[pyridinium]_3PW_{12}O_{40}$, $[MIM]_3PW_{12}O_{40}\cdot 3Me$-imidazole, and $[Bu_4N]_3PW_{12}O_{40}$) to catalyze the oxidative desulfurization of 99.8% DBT at 40 °C in 1.5 h using H_2O_2 as oxidant and $[BMIM][PF_6]$ as extractant. Interestingly, these catalysts were soluble only in the IL phase, but not in the oil or aqueous phases. The Balula group [94] encapsulated the Keggin-type phosphotungstate $[Bu_4N]_3[PW_{12}O_{40}]$ in the chromium terephthalate metal-organic framework (MOF) MIL-101 and employed this catalyst in the one-pot extractive and oxidative desulfurization of a model fuel using $[BMIM][PF_6]$ as extractant and reaction medium and 30% H_2O_2 as oxidant, leading to exceptionally high conversions of sulfur compounds (500 ppm for each BT derivative) of 100% in 1 h for DBT, 100% in 3 h for 1-BT, and 99% in 4 h for 4,6-DMDBT. The MOF-immobilized catalyst could be recycled and reused at least three times with no appreciable reduction in catalytic efficiency. The Ma group [95] immobilized phosphotungstic acid containing 1-methyl-3-(triethoxysilyl)propylimidazolium chloride onto magnetic mesoporous silica rods, and employed this catalyst for oxidizing 99% of the DBT in acetonitrile using H_2O_2 at 40 °C within 6 h. Rafiee and Eavani [96] prepared a POM-based catalyst consisting of sulfonated pyridinum cations and a Keggin tungstophosphate anion ($PW_{12}O_{40}^{3-}$) and measured high activities in the oxidation of various sulfides including DBT and thiophene using H_2O_2, achieving up to 99% DBT removal. The Li group [97] constructed tungsten-containing meso-materials by using $[C_{16}MIM]Br$ as a template and $[C_{16}MIM]_3PW_{12}O_{40}$ as tungsten source. The resulting catalysts led to quantitative conversations of aromatic sulfur compounds in oxidative desulfurization using H_2O_2, with substrate reactivity decreasing in the order 4,6-DMDBT > DBT > BT > 1-dodecanethiol. Around the same time, Wang et al. [98] obtained 99.9% DBT removal under mild conditions by using 1-(4-sulfonic acid) methylimidazolium phosphotungstate as catalyst, H_2O_2 as oxidant, and CH_3CN/H_2O as the extractant phase. The Li group [99] linked $[C_3MIM][H_2PW_{12}O_{40}]$ onto mesoporous silica SBA-15 via silylation to design a new catalyst for oxidative desulfurization using H_2O_2. This system allowed for the quantitative removal of DBT and 4,6-DMDBT within 40 min at 60 °C and 81.3% removal of BT within 1 h. The Song group [100] covalently grafted imidazolium-based ILs onto calix [4] arene followed by anion exchange with $EuW_{10}O_{36}^{9-}$. These novel superhydrophobic inorganic – organic hybrid catalysts gave a rapid and quantitative oxidation of DBT at 70 °C within 5–7 min using H_2O_2 as oxidant. The substrate reactivity decreased in the order DBT > 4,6-DMDBT > BT, which is consistent with the electronic density of sulfur atoms and the steric hindrance of substituents on the substrates. The Zhu and Li groups [101] prepared W-containing mesoporous silicas at different calcination temperatures by using $[(n\text{-}C_8H_{17})_3NCH_3]_2W_2O_{11}$ as both the template and the W source. The resulting W-silicas showed a high catalytic activity for oxidative desulfurization of sulfur substrates using H_2O_2, yielding 99.6% DBT removal in just 1 h at 60 °C. They [102] further immobilized a W-based IL $[(C_6H_{13})_3PC_{14}H_{29}]_2W_6O_{19}$ onto the inorganic graphene analog hexagonal boron nitride (*h*-BN) as a catalyst for the efficient removal of 99.3% DBT from model fuel at 30 °C. Li et al. [103] performed the oxidative desulfurization of a model fuel catalyzed by $[HMIM]_5PMo_{10}V_2O_{40}$ using $[HMIM][BF_4]$ as the extractant and H_2O_2 as the oxidant, and found that the reactivity of aromatic sulfur compounds decreased in the order DBT > 4,6-DMDBT > BT. At the optimum condition, these researchers obtained 99.1% DBT conversion at 60 °C in 100 min. The Hu group [89] constructed three hydrophobic Keggin-type heteropolyacid catalysts (namely $[EMIM]PMo_{10}V_2O_{40}$, $[BMIM]PMo_{10}V_2O_{40}$, and $[HMIM]PMo_{10}V_2O_{40}$) and deployed them for the catalytic removal of DBT using H_2O_2 and acetonitrile. The activity of these catalysts decreased in the order corresponding to the alkyl chain length on the imidazolium cation; i.e., $HMIM^+ > BMIM^+ > EMIM^+$. Significantly, quantitive sulfur removal could be achieved under optimal conditions and the catalyst could be recycled at least six times with little loss in activity. Wu et al. [104] immobilized 1-methylimidazolium-3-propylsulfonate hydrosulfate on a Zr MOF prepared from zirconium tetrachloride and terephthalic acid. The new catalyst led to 94% sulfur (BT) removal at 40 °C and could be reused for at least six times with minimal loss in activity.

Some ionic salts are capable of functioning both as the catalyst and a surfactant (a PTC, in effect) in the oxidative desulfurization process. Along these lines, the Li group [43] synthesized three hexatungstate-based catalysts carrying long-chain quaternary ammonium cations (including $[(C_4H_9)_3NCH_3]_2W_6O_{19}$, $[(C_8H_{17})_3NCH_3]_2W_6O_{19}$, and $[(C_{12}H_{25})_3NCH_3]_2W_6O_{19}$) which could be dissolved in

[OMIM][PF$_6$] to form a water-in-IL emulsion system with aqueous H_2O_2. Such a catalytic system led to > 95% sulfur removal for a model oil (one comprising 500 ppm DBT, 250 ppm BT, and 250 ppm 4,6-DMDBT) and 94% sulfur removal for real gasoline after four consecutive runs. Similarly, Zhu et al. [105] examined metal-based, surfactant-derived methyltri-*n*-octylammonium peroxomolybdate and peroxotungstate ($[(CH_3)N(n\text{-}C_8H_{17})_3]_2Mo_2O_{11}$ and $[(CH_3)N(n\text{-}C_8H_{17})_3]_2W_2O_{11}$, respectively) as amphiphilic catalysts for the oxidative desulfurization of aromatic sulfur-containing compounds in *n*-octane. They observed 94.9%–99.7% DBT removal at 30 °C within 1 h using H_2O_2 as the oxidant and $[(CH_3)N(n\text{-}C_8H_{17})_3]_2Mo_2O_{11}$ as the catalyst, with an IL ($BMIM^+$ or $OMIM^+$ cations, BF_4^- or PF_6^- anions) extracting phase. The Zhou group [106] prepared an amphiphilic catalyst consisting of a quaternary ammonium cation $[C_{18}H_{37}(CH_3)_3]N^+$ and lacunary anion $[PW_{11}O_{39}]^{7-}$, forming an emulsion in [BMIM][PF$_6$] (Scheme 3). This amphiphilic system acts as both an emulsifying agent and a catalyst for the oxidative desulfurization of DBT oxidized by H_2O_2. This catalytic system followed pseudo-first-order reaction kinetics and was able to reduce the total sulfur content of real gasoline from 1236 to 65 ppm. The Li group [107] synthesized a tungsten-containing task-specific ionic salt $[(C_6H_{13})_3PC_{14}H_{29}]_2W_6O_{19}$ and then evaluated it for the oxidative desulfurization processing of a DBT-containing model oil. The aqueous H_2O_2 solution mixed with the ionic salt formed an emulsion catalytic system, acting as both the catalyst and the extraction medium (Scheme 4). The same group [108] also prepared several other surfactant-type POM-based ionic salts— including $[(n\text{-}C_8H_{17})_3NCH_3]_3PO_4[MoO(O_2)_2]_4$, $[(n\text{-}C_{12}H_{25})_3NCH_3]_3PO_4[MoO(O_2)_2]_4$, $[(n\text{-}C_8H_{17})_3NCH_3]_3PO_4[WO(O_2)_2]_4$, and $[(n\text{-}C_{12}H_{25})_3NCH_3]_3PO_4[WO(O_2)_2]_4$—for efficient (nearly quantitative) oxidative desulfurization following pseudo-first-order kinetics. The Song group [109] constructed a surfactant analog of a lanthanide-containing POM, $[(C_{12}H_{25})N(CH_3)_3]_9LaW_{10}O_{36}$, to form an emulsion system with ILs (such as [OMIM][PF$_6$]) and aqueous H_2O_2. This catalytic system showed a remarkable efficiency, even at the 1 L scale, achieving 99% surfur removal in 40 min from a model oil containing 1000 ppm sulfur (BT, DBT, and 4,6-DMDBT). The Lü group [110] developed a series of Anderson-type $[R_4N]_4[NiMo_{6-x}W_xO_{24}H_6]$ ($x = 0, 2, 4, 6$) catalysts and identified $[(C_4H_9)_4N]_4NiMo_6O_{24}H_6$ as the best catalyst for DBT removal using ILs as extractants and H_2O_2 as oxidant. The effectiveness of ILs for oxidative desulfurization was observed to decrease according to [BMIM][PF$_6$] > [OMIM][PF$_6$] > [BMIM][BF$_4$], all of which were far better than the performance in the absence of IL. The oxidation reactivity of aromatic sulfur-containing compounds in the new catalytic system decreased in the order DBT > 4-MDBT > 4,6-DMDBT > BT > 5-MBT (5-methylbenzothiophene). Favorably, the new catalytic reaction system could reduce the sulfur content of a commercial diesel fom 700 ppm to about 30 ppm.



Scheme 3 Catalytic oxidation of DBT in a water-in-IL emulsion system designed around an amphiphilic ionic catalyst consisting of a quaternary ammonium cation and a POM anion. (Reprinted with permission from Ref. [106], Copyright © 2011 American Chemical Society)



Scheme 4 Extractive and oxidative desulfurization using a catalytic water-in-IL emulsion system based on a tungsten-containing amphiphilic catalyst (Reprinted with permission from Ref. [107], Copyright © 2013 Royal Society of Chemistry)

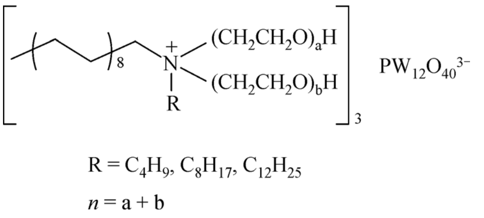
4 ILs as dual extractants and catalysts

Acidic ILs have been examined as catalysts and extractants for oxidative desulfurization. These studies primarily involve protic (Brønsted) ILs but Lewis acid ILs have been studied in desulfurization reactions as well. A few years back, the Zhao group [37] reported that *N*-methylpyrrolidonium tetrafluoroborate could perform dual roles as both extractant and catalyst in the extractive oxidation of DBT (100% removal) using H_2O_2, and it could be applied in the sulfur removal of actual diesel (99.4% removal). These scientists postulated that a coordination compound might be formed between H_2O_2 and the amide group of the IL cation, generating hydroxyl radicals as strong oxidizing agents. Later, the Gui group [111] prepared task-specific acidic ILs containing carboxylic acid ($-$COOH) groups tethered to imidazolium cations (for example, [$HOOCCH_2CH_2$-MIM][HSO_4]) as dual catalyst and extractant, obtaining 96.7% and 95.1% removal efficiencies for DBT and 4,6-DMDBT, respectively. They proposed that, in the presence of H_2O_2 in an acidic environment, the $-$COOH group pendant to the IL cation can be converted *in situ* to a peroxycarboxylic acid group ($-$COOOH) which then oxidizes the sulfur compounds to the corresponding sulfones. A testament to the viability of such an approach, use of a similar acidic IL led to the reduction in sulfur content of real diesel fuel from 200 ppm to 20.5 ppm at room temperature [112]. Gao et al. [113] have also evaluated [BMIM][HSO_4] and [BuPy][HSO_4] as dual extractant/catalyst ILs toward the desulfurization of diesel and found that, in particular, the use of [BMIM][HSO_4] led to very efficient (99.6%) removal of DBT from *n*-octane in 1.5 h at room temperature. They also indicated that the removal efficiency of sulfur compounds decreased in the order DBT > BT > thiophene > 4,6-DMDBT. Chi et al. [114] later incorporated the acidic species into the IL cation, showing that 1-ethyl-3-(4-sulfobutyl)imidazolium bis(trifluoromethylsulfonyl)imide ([C_4SO_3H-EIM][Tf_2N]) could act as both the catalyst and extractant for reducing DBT levels in *n*-octane from 1600 ppm to < 20 ppm. The extraction capability of ILs decreased in the order of [C_4SO_3H-EIM][Tf_2N] > [C_4SO_3H-EIM][HSO_4] > [BuPy][Tf_2N] > [BMIM][Tf_2N] > [BMIM][PF_6]. Li et al. [38] mixed benzyltrimethylammonium chloride and $ZnCl_2$ in a 1 : 2 molar ratio to generate a Lewis acidic IL ($Me_3NCH_2C_6H_5Cl \cdot 2ZnCl_2$), which was used as the extractant for oxidative desulfurization of DBT (up to 94% after 30 min) in *n*-octane by using H_2O_2 and an equal volume of acetic acid. Indeed, the Chen group [115] found that both Brønsted ([SO_3H-BMIM][HSO_4]) and Lewis acidic ([BMIM]Cl/2$ZnCl_2$) ILs performed commendably as dual extractants and catalysts to oxidatively remove 100% of the DBT from model diesel fuels. The Brønsted acidic IL was capable of reducing the sulfur content in commercial diesel fuel from 64 to 7.9 ppm, but proved to be less effective with coke diesel fuel with a higher sulfur content of 5380 ppm. This group [116] further assessed a series of Lewis acidic ILs [BMIM]Cl/MCl_2 (M = Zn, Fe, Cu, Mg, Sn, Co) as both extractants and catalysts for oxidative sulfur removal and ranked the efficiency of the metal chlorides for this purpose in the decreasing order Zn > Fe > Co > Mg > Cu > Sn. The sulfur content in real diesel could be reduced from 460 ppm to 168 ppm by using [BMIM]Cl/3$ZnCl_2$/H_2O_2 for a single run and to 43 ppm after five runs. Zhang et al. [117] prepared two Brønsted acidic ILs (*N*-carboxymethylpyridinium hydrogen sulfate, [$HOOCCH_2$Py][HSO_4], and *N*-carboxyethylpyridinium hydrogen sulfate, [$HOOC(CH_2)_2$Py][HSO_4]) and investigated their effectiveness as extractants/catalysts for oxidative desulfurization with H_2O_2. The use of [$HOOCCH_2$Py][HSO_4] led to the removal of 99.9% of DBT, 82.5% of BT, and 89.1% of 4,6-DMDBT at 30 °C. Recently, the Yu group [118] examined two acidic ILs ([$HO_3S(CH_2)_4$-MIM][OTs] and [$HO_3S(CH_2)_4$-MIM][$ZnCl_3$]) for the oxidative removal of sulfur compounds from real diesel fuel using 30 wt-% H_2O_2, followed by extraction of the residual sulfones in oil using conventional ILs ([MMIM][Me_2PO_4], [EMIM][Et_2PO_4], or [BMIM][Bu_2PO_4]). The surfur content could be reduced from 225 ppm to 4.6 ppm in the diesel fuel, representing a 98% removal efficiency by combination the ILs [$HO_3S(CH_2)_4$-MIM][OTs] and [EMIM][Et_2PO_4].

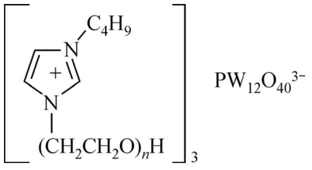
A number of Fenton-type redox systems of ILs have also been developed to act as both extractant and catalyst in oxidative desulfurization. The Li group [119] found that the redox system of [BMIM]Cl/$FeCl_3$ could simultaneously act as the extractant and catalyst for an efficient removal of 99.2% DBT from a model fuel at 30 °C in only 10 min using H_2O_2 as the oxidant. This group constructed Fenton-type ILs — including $Et_3NHCl/FeCl_3$, $Et_3NHCl/CuCl_2$, $Et_3NHCl/ZnCl_2$, $Et_3NHCl/CoCl_2$, $Et_3NHCl/SnCl_2$, and $Et_3NHCl/CrCl_3$ — and indicated that an effective desulfurization could be obtained for $Et_3NHCl/FeCl_3$ in only 5 min at 30 °C (i.e., sulfur removal of 97.1%, 86.9%, and 82.5% for DBT, BT, and 4,6-DMDBT, respectively). The optimized system led to a sulfur reduction in prehydrotreated gasoline from 150 to 15 $mg \cdot L^{-1}$ after two cycles of reaction. The Li group [120] further evaluated several Fenton-type ILs formed by mixing quaternary ammonium chlorides and metal chlorides (e.g., $FeCl_3$, $CuCl_2$, $ZnCl_2$, and $SnCl_2$) as catalysts for oxidative desulfurization of model fuels using H_2O_2 as oxidant. They observed 97.9% DBT removal by using [$(C_8H_{17})_3CH_3N$]Cl/$FeCl_3$ at 25 °C for 1 h, the reactivity of substrates decreasing in the order: DBT > BT > 4,6-DMDBT. This reaction system reduced the sulfur level of FCC gasoline from 360 ppm to 110 ppm. The Li group [121] also prepared three paramagnetic Fenton-like hybrid materials Q[$FeCl_4$] [Q = $(CH_3)_4N$, $C_{14}H_{29}N(CH_3)_3$, or $C_{18}H_{37}N(CH_3)_3$] and studied them as catalysts along with H_2O_2 as oxidant and ILs as extractants to achieve as much as 97% DBT removal from model fuel at 30 °C in 1 h. The catalytic activity of the tested catalysts decreased as [$(CH_3)_4N$][$FeCl_4$] > [$(C_{14}H_{29})N(CH_3)_3$][$FeCl_4$] > [$(C_{18}H_{37})N(CH_3)_3$][$FeCl_4$], whereas the effectiveness of the IL extractant decreased in this order: [BMIM][BF_4] > [OMIM][BF_4] > [OMIM][PF_6] > [BMIM][PF_6]. The Zhang group [122] synthesized three Lewis acidic *N*-alkyl-3-methylpyridinium tetrachloroferrates ([C_4^3MPy][$FeCl_4$], [C_6^3MPy][$FeCl_4$], and [C_8^3MPy][$FeCl_4$]) and evaluated them as both extractants and catalysts for the quantitative removal of DBT from model fuel using H_2O_2;

the reaction was reportedly complete within 10 min at room temperature. In addition, use of $[C_8^3MPy][FeCl_4]$ in the catalytic system could remove 44% of the sulfur from actual gasoline. The Li group [123] also investigated the temperature-responsive paramagnetic IL $[BuPy][FeCl_4]$ as catalyst and extractant for oxidative sulfur removal using H_2O_2 at 40 °C, observing desulfurization efficiencies of 95.3%, 75.0%, and 54.8% for DBT, BT, and 4,6-DMDBT, respectively, in only 10 min. The paramagnetic IL responded strongly to a permanent magnet and could be simply removed from the oil by applying an external magnetic field. Results from Dong et al. [124] further confirmed that the $[C_6^3MPy][FeCl_4]/H_2O_2$ system could remove 100% of the DBT from model fuel at 25 °C in 20 min; these authors also reported that this system removed 37.7% of the sulfur from real gasoline after one run and 99.7% after seven runs. The Li group [125] prepared a number of other paramagnetic ILs comprising the 1-butyric acid-3-methylimidazolium chloride/xFeCl$_3$ (i.e., $[C_3H_6COOH\text{-}MIM]Cl/xFeCl_3$; $x = 0.5$, 1, 1.5, 2) system and suggested that $[C_3H_6COOH\text{-}MIM]Cl/2FeCl_3$ proved quite effective for the extraction and catalyzed oxidative desulfurization of model oil (sulfur removal at 30 °C for 10 min: 100%, 100%, and 93.7% for BT, DBT, and 4,6-DMDBT, respectively). The Zhang group [126] recently evaluated the use of $[HOOC(CH_2)_2\text{-}MIM]Cl/nFeCl_3$, $[HOOC(CH_2)_2\text{-}MIM]Cl/nZnCl_2$, and $[AMIM]Cl/nFeCl_3$ as extractants/catalysts in extractive and oxidative desulfurization with 30 wt-% H_2O_2. They found that high sulfur removal efficiencies of up to 99.2% DBT removal could be achieved in 10 min at 25–30 °C for $FeCl_3$-based Ils, whereas 4–6 h at 60 °C was required for $ZnCl_2$-based ILs. Interestingly, the catalytic system could simultaneously remove nitrogen-containing compounds (e.g., pyridine, pyrrole, quinoline) from model fuel in 2 min at 25 °C.

Appropriately-engineered ILs have been shown to act both as the desulfurization catalyst and the reaction medium itself. For instance, the Xie group [127] developed a number of thermoregulated ammonium phosphotungstate ILs containing PEG-functionalized cations (Scheme 5). These novel ILs possess a cloud point in aqueous media and a minimum solubility in toluene. More particularly, these ILs display a critical solution temperature (CST) for mixtures of toluene and n-octane (or toluene and n-dodecane), allowing the system to be thermally regulated, becoming homogeneous (monophasic) at high temperature and heterogeneous (phase segregated) at low temperature. This thermoregulation behavior has been demonstrated to be advantageous in the catalyzed oxidative desulfurization of model fuels using H_2O_2 as oxidant, enabling homogeneous catalysis followed by heterogeneous separation. Removal of 92.3% of the thiophene from n-octane (a model for gasoline) was achieved by a reaction system summarized by: V(toluene) : V(model oil) = 1 : 1.5, IL (n = 96, R = C_4H_9), m(IL) : m(toluene) = 1.9, H_2O_2:S = 10 : 1, 50 °C and 90 min. In addition, a 93.2% desulfurization efficiency was obtained for thiophene in n-dodecane (a model of diesel) by using a system of V(toluene) : V(model oil) = 1 : 1.1, IL (n = 67, R = C_4H_9), m(IL) : m(toluene) = 2.2, H_2O_2 : S = 10 : 1, 60 °C and 120 min. The same group [128] further prepared thermoregulated imidazolium phosphotungstate ILs containing PEG-functionalized cations (Scheme 6) and applied the IL (n = 19)/DMF/n-octane thermoregulated system for the 85.3% removal of thiophene at $P(O_2)$ = 2.0 MPa and 100 °C in 90 min.



Scheme 5 Bifunctional ammonium phosphotungstate ILs for thermoregulated oxidative desulfurization



Scheme 6 Bifunctional 1-butyl-3-(poly(ethylene glycol))imidazolium phosphotungstate ILs for thermoregulated oxidative desulfurization

5 Other oxidative desulfurization techniques

The Zhao group [129] noted that use of ozone along with H_2O_2 in $[BMIM][BF_4]$ led to 98.6% DBT removal at 50 °C in 150 min, a result that likely stems from the generation of hydroxyl radicals as strong oxidants produced by the reaction of ozone and H_2O_2. Instead of using H_2O_2 as the oxidant, the Dai group [130] advanced the oxidation of sulfur compounds with ozone generated *in situ* by dielectric barrier discharge plasma using MnO_2 catalysts, followed by the extraction with an IL (e.g., [BMIM][OAc]). Under optimal conditions, the desulfurization efficiencies of thiophene, BT, DBT, and 4,6-DMDBT for a model fuel were 99.9%, 99.9%, 97.9%, and 90.7%, respectively. This group [131] also used the same plasma-generated ozone method, along with $[BMIM][FeCl_4]$ as extractant and diperiodatocuprate (III) as catalyst, for the removal of 97.5% of the DBT from model oil. They also demonstrated that the desulfurization efficiency for different ILs decreased in the order: $[BMIM][FeCl_4] > [BMIM][PF_6] > [BMIM][BF_4] > [BMIM]Cl >$

[HMIM]Cl ≈ DMF. The same group [132] further used the TiO_2/MCM-41 catalyst for oxidative desulfurization using the same technique and calculated removal efficiencies for thiophene, BT, DBT, and 4,6-DMDBT to be 99.9%, 99.9%, 98.6%, and 95.2%, respectively. The reactivity of sulfur compounds decreased in the order: thiophene > BT > > DBT > 4,6-DMDBT. Notably, this technique allows for the efficient removal of thiophene and BT which are generally difficult to remove by alternate oxidative desulfurization methods. Li et al. [133] examined the use of a 500-W high-pressure mercury lamp as the light source for the photocatalytic and oxidative desulfurization of gasoline using nanoscale TiO_2 photocatalyst, air as oxidant, and [BMIM][Cu_2Cl_3] as extractant, ultimately achieving 98.2% sulfur removal in 2 h under optimum conditions. Later on, Zhao et al. [134] synthesized TiO_2 by the sol-gel method and employed it as a photocatalyst for the oxidation desulfurization of fuel oil using air as oxidant and $Et_3NHCl\cdot FeCl_3$ as extractant, yielding a similar 98.5% sulfur removal after 3 h. Wang et al. [135] prepared TiO_2 nanopowders as catalyst for photocatalytic and oxidative desulfurization under UV irradiation using H_2O as a source of $\cdot OH$ radicals and [BMIM][BF_4] as the extractant phase, reaching 98.2% DBT removal from *n*-octane and 94.3% sulfur removal from diesel fuel in 10 h at room temperature. Wang et al. [136] studied cyclohexanone peroxide as the oxidant for DBT removal from fuels using IL extraction. This work established the effectiveness of ILs for desulfurization using cyclohexanone peroxide with decreasing effectiveness following the order [OMIM][BF_4] > [HMIM][BF_4] > [BMIM][BF_4]. Under optimum conditions in this study, the use of [OMIM][BF_4] led to 93.5% DBT removal from model fuel and 70.8% sulfur removal from gasoline at 40 °C.

Several years ago, the Zhao group [137] performed the photochemical oxidation and extraction of sulfur compounds by using H_2O_2 and UV irradation without catalyst at room temperature and obtained 99.5% DBT removal from *n*-octane and 90.6% sulfur removal from actual light oil when using [BMIM][PF_6] as extractant. The Li group [138] found that amorphous TiO_2 was a superb catalyst under UV irradiation for photocatalytic and oxidative sulfur removal using H_2O_2 as oxidant and [BMIM][BF_4] as extractant, resulting in 96.6% DBT removal from *n*-octane at 30 °C in 2 h while the reactivity of substrates decreased in the order of DBT > BT > dodecanethiol > 4,6-DMDBT. It was proposed that the TiO_2/UV system could increase the $\cdot OH$ concentration generated from H_2O_2. Zaid et al. [139] prepared TiO_2 doped with Cu, Fe, and Cu-Fe as photocatalysts which are active under visible light and evaluated the new catalysts in the photooxidative desulfurization of DBT in *n*-dodecane using H_2O_2 as oxidant followed by the extraction of the oxidized sulfur compounds by a deep eutectic solvent (DES) consisting of 1 : 2 choline chloride:glycerol; a 97% sulfur removal was accomplished using Cu-Fe/TiO_2.

Ferreira et al. [140] recently carried out the oxidation of DBT by H_2O_2 catalyzed by *p*-toluenesulfonic acid with [$(C_6H_{13})_3PC_{14}H_{29}$]Cl or Aliquat as the PTC, achieving up to 99% total conversion. The oxidation products, dibenzothiophene sulfoxide (DBTSO) and dibenzothiophene sulfone ($DBTSO_2$), were removed from diesel fuel by selective absorption using molecularly-imprinted polymer (MIP) created using $DBTSO_2$ as the template.

6 Theoretical studies

The Zhang group [141] probed the role of 1-methylimidazolium tetrafluoroborate in the oxidative desulfurization of DBT using H_2O_2 as oxidant through density functional theory (DFT) calculations. The IL was found to play dual roles as a catalyst and an extractant. As a catalyst, the cation acts as the donor of intermolecular hydrogen bonds and the anion acts as the acceptor of other intermolecular H-bonds to foster O–O and O–H cleavage of H_2O_2, to improve the stability of the transition state. As an extractant, both the IL cation and anion exhibit stronger interactions with dibenzothiophene sulfone ($DBTO_2$) than with DBT due to the higher dipolarity of $DBTO_2$, although the calculations reveal that the cation plays a more important role in the extraction of aromatic sulfur-containing compound from fuels for this particular IL.

7 Summary and future prospects

The oxidative desulfurization of fuels using ILs has a number of advantages: high energy-efficiency, effectiveness in achieving ultra-low levels of sulfur, and process simplification by combination of extraction and reaction into a “one-pot” procedure. However, challenges associated with this process certainly still remain, including: (i) the high cost associated with ILs based on relatively expensive cations (e.g., imidazoliums, pyridiniums) or anions (in particular, fluorinated species like Tf_2N^-), (ii) the relatively high viscosities of ILs, especially amphiphilic (surfactant-inspired) ones capable of performing phase transfer catalysis, and (iii) the poor biodegradability and high eco(cyto)toxicity of some ILs, causing serious consequences if they are released into the environment or come into contact with personnel. Therefore, there is a strong demand to develop new, inexpensive, and environmentally benign ILs as extractants and reaction media for oxidative desulfurization. Although deep eutectic solvents appear promising for addressing criteria (i) and (iii), they are likely to be far worse on point (ii), not to mention the conspicuous lack of hydrophobic DES availability. In any case, (iv) there is still plenty of room for improving the efficiency, stability, and reusability, and reducing cost of new catalysts exploited within (or, particularly, as an integral part of) ILs and DESs.

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Nomenclature

4,6-DMDBT = 4,6-dimethyldibenzothiophene

4-MDBT = 4-methyldibenzothiophene

BMIM$^+$ = 1-butyl-3-methylimidazolium

EMIM$^+$ = 1-ethyl-3-methylimidazolium

OMIM$^+$ = 1-octyl-3-methylimidazolium

C$_2$CN-BIM$^+$ = 1-propionitrile-3-butylimidazolium

MIMPS$^+$ = 1-(3-sulfo)propyl-3-methylimidazolium

BuPy$^+$ = *N*-butylpyridinium

HexPy$^+$ = *N*-hexylpyridinium

OctPy$^+$ = *N*-octylpyridinium

HMMPy$^+$ = 1-hexyl-2,4-dimethylpyridinium

3-Me-BuPy$^+$ = 1-butyl-3-methylpyridinium

3-Me-HexPy$^+$ = 1-hexyl-3-methyl pyridinium

3-Me-OctPy$^+$ = 1-octyl-3-methylpyridinium

PSPy = 1-(3-sulfopropyl)pyridinium

TOMA$^+$ = trioctylmethylammonium

MePyo$^+$ = *N*-methyl-pyrrolidonium

S2$^+$ = ethyltetrahydrothiophenium

Dca$^-$ = dicyanamide

OTs$^-$ = tosylate

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