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Catalytic oxidation of thiophene and its derivatives via dual activation for ultra-deep desulfurization of fuels

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ABSTRACT

A catalyst system composed of tungstate and Brønsted acidic ionic liquids (BAILs) was found to be highly active for the oxidative desulfurization (ODS) removal of thiophene, benzothiophene (BT), and their derivatives from model oil using 30 wt.% H_2O_2 as the oxidant. Five BAILs, [Hnmp]BF_4, [Hmim]BF_4, [Hnmp]HSO_4, [Hmim]HSO_4, and [Hnmp][CH_3SO_3] (nmp = N-methyl-pyrrolidonium, mim = N-methylimidazolium), and various commercial tungstate compounds were investigated. High activity was obtained for the combination of ammonium tungstate and BAILs [Hnmp]BF_4. In this catalytic reaction, sulfur content of model oil containing BT could be decreased from 700 ng μL^{-1} to less than 1 ng μL^{-1}. Turnover frequency (TOF) for BT oxidation is higher than 194×10^{-3} s^{-1} and that of in non-BAILs [Bmim]BF_4 is less than 11×10^{-3} s^{-1}. Noteworthily, the ODS of thiophene, which has been regarded as difficult task, can be also achieved up to 99% conversion with a TOF of 7×10^{-3} s^{-1}. The FT-IR, ^1H NMR and electrochemical measurements evidences indicate that the strong hydrogen bonding between the sulfur-containing compounds and [Hnmp]BF_4 and the oxidative function of the tungstate synergistically activate the reactants and result in the excellent catalytic performance.

1. Introduction

The deep removal of sulfur-containing compounds from fuel oils has become an increasing challenge as growing environmental concern. The industrial desulfurization is traditionally carried out by catalytic hydrodesulfurization (HDS) technology. However, the HDS process requires both high temperatures and high pressures of H_2, which results in high operating-cost and octane-number loss particularly for FCC gasoline [1]. Therefore, the development of alternative ultra-deep desulfurization processes is highly desired.

A variety of alternative routes such as oxidative desulfurization (ODS), biodesulfurization, adsorptive desulfurization, extractive desulfurization of sulfur compounds using solvents and ionic liquids, have been investigated to remove sulfur from diesel streams or FCC gasoline to ultra low levels. Among them, selective catalytic oxidation combined with extraction has been extensively studied for ultra-deep desulfurization. Until 2010, five processes involving the ODS route for deep desulfurization of diesel were in commercialization stage. These include (i) Sulphco process, (ii) Lyondell chemicals process, (iii) Enichem/UOP process, (iv) Unipure process, and (v) PetroStar process, which utilize H_2O_2, t-butyl hydroperoxide (TBHP), and peroxyacid (peroxo acetic acid) as oxidizing agent. These processes require two steps, oxidation of sulfur-containing compounds to sulfone in the first step followed by extraction sulfone from the oxidized fuels in the second step [2]. In addition to ODS method, there are abundant studies about extraction with ionic liquids (ILs) for ultra-desulfurization. However, most of the efficiency of sulfur removal extracted merely with ILs is relatively low due to the similar polarity between the sulfur-containing molecules and remaining diesel fuels. More recently, a new and effective approach that is chemical oxidation in conjunction with ILs extraction (ECODS) has been explored in order to improve the efficiency of desulfurization [3]. However, to date, the efficiency of ECODS system for FCC gasoline is still low [4–14], because the major sulfur-containing compounds of FCC gasoline, thiophene, and its derivatives are difficult to be oxidized [15].

The inertness of the thiophene in the oxidation is mainly due to its aromaticity and low electron density on its sulfur atom. So highly reactive oxidants, such as dimethyldioxirane [16] and peracids [17,18], were used to oxidize thiophene in early years. As a clean oxidant, hydrogen peroxide has always been attractive. Oxidation of thiophene was once achieved with titanium silicates-1 (TS-1) for ODS using aqueous H_2O_2 as oxidant [19,20]. However, suffering from the small size of the micro pores, TS-1 is not suitable for the oxidation of bulky sulfur compounds, like BT and its derivatives. Therefore, the prerequisite pursuit in ultra-low sulfur gasoline is to explore an efficient catalytic system for broad reactant scopes in the oxidation of sulfur-containing compounds, particularly thiophene-like ones with electron-deficiency.

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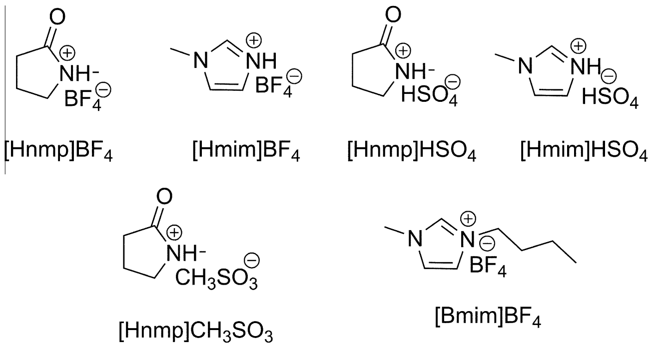
In this work, we found that a catalyst consisted of commercial ammonium tungstate and commonly used BAILs could achieve high activity in the oxidation of thiophene, BT, and their derivatives under mild conditions using aqueous hydrogen peroxide as oxidant. We also discussed the mechanism based on a concept of metal oxide-Brønsted acid dual activation where the interaction between sulfur-containing compound and BAILs was believed to be critical for the high oxidative activity.

2. Experimental

2.1. General

Thiophene, 2-methylthiophene (2-MT), 3-metylthiophene (3-MT), 2,5-dimethylthiophene (2,5-DMT), 2,3,5-trimethylthiophene (2,3,5-TMT), and BT were purchased from Alfa Aesar. Six model oils were prepared by dissolving thiophene, 2-MT, 3-MT, 2,5-DMT, 2,3,5-TMT, and BT in n-octane to give solutions with S-contents of 700 ng μL^{-1}. The BAILs [Hnmp]BF_4, [Hmim]BF_4, [Hnmp]HSO_4, [Hmim]HSO_4, and [Hnmp]CH_3SO_3 used in this work were synthesized according to the procedures described in the literatures [13,14,21–23]. The ionic liquid [Bmim]BF_4 was purchased from Shanghai Cheng Jie Chemical Co. Ltd. (Scheme 1). Other reagents were obtained from commercial sources and used without purification. Aqueous H_2O_2 was stored at 4 °C.

Infrared spectra (IR) were recorded on a Nicolet NEXUS 470 FT-IR Spectrometer in ambient air at room temperature. The IR spectra of the IL/thiophene mixture were taken by a KBr liquid cell from 400 to 4000 cm^{-1} with 4 cm^{-1} resolution and averaged 10 times. Other IR spectra were collected in KBr pellets. GC–MS was conducted on Agilent 6890N GC/5973 MS detector. ^1H NMR spectra were recorded on a Bruker DRX 400 MHz type spectrometer at room temperature (400 MHz) and internally referenced to tetramethylsilane signal. Coaxial NMR experiments were conducted as follows: the samples were loaded in a stem coaxial NMR capillary tube which inserted into 5 mm NMR tube with D_2O; the residual DOH in D_2O was used as the ^1H NMR external reference at 4.790 ppm. Electrochemical measurements were carried out in the three-electrode type cell. The volume of the electrolyte was 10 mL. A glassy carbon electrode and a platinum disk with a surface area of 0.068 cm^2 were used as working and counter electrodes, respectively. The working electrode was polished with a 10 mm alumina, rinsed with distilled water, and then electrochemically activated in 1 M H_2SO_4 solution. All potentials were estimated using a saturated calomel electrode (SCE) as the reference electrode and the scan rate of the potential was 4 mV s^{-1}. The remained sulfur-containing compounds in model oil after oxidation were analyzed by GC-SCD (sulfur chemiluminescence detection) (GC: Agilent 7890A equipped with a capillary column [PONA, 50 m × 0.2 mm i.d. × 0.5 μm]; SCD: Agilent G6600A-S355). The total sulfur contents of the samples were determined by Antek 9000S total sulfur analyzer. (Precision:±5 ppb or ±2% RSD).



Scheme 1. Structures of ILs used in this work.

2.2. General procedure for ODS of sulfur-containing compounds and recycling of catalyst

In a typical experiment, a mixture including 20 mL pre-prepared model oil with sulfur content 700 ng μL^{-1}, 0.5 mL 30 wt.% H_2O_2, 4 g of [Hnmp]BF_4, and 4 mol% catalyst in 50 mL vessel was stirred vigorously at 60 °C. After the reaction, the sulfur content of the model oil phase was analyzed directly by GC-SCD or Antek 9000S total sulfur analyzer. The recycling of catalyst was conducted as follows: after the reaction, ionic liquid phase was separated and extracted with diethyl ether (4 mL × 3). The water in ionic liquid phase was removed under reduced pressure by rotary evaporation equipment at 90 °C for 2 h. Then, fresh aqueous H_2O_2 (30 wt.%) and model oil were added to ionic liquid phase for the next reaction cycle.

2.3. Product identification and analysis

After the reaction, the ILs phase was separated and extracted with diethyl ether (4 mL × 3). The organic phase was collected, dried with anhydrous Na_2SO_4, and concentrated for product analysis.

3. Results and discussion

3.1. Effect of different ILs on ODS of thiophene

In our initial study, we selected liquid–liquid extraction and catalytic oxidative desulfurization to investigate the oxidative removal of thiophene from model oil (thiophene in n-octane) using 30 wt.% H_2O_2 as oxidant. ILs can partially extract sulfur-containing compounds from n-octane [6]. H_2O_2 is miscible with selected ILs. So thiophene is extracted by ILs firstly and then oxidized in ILs. The data in Table 1 show desulfurization systems of extraction, the extraction combined with a chemical oxidation, and the extraction combined with the catalytic oxidation reaction in six different ILs. In the extraction coupled with catalytic oxidation process, commercial ammonium tungstate was selected as catalyst. When [Bmim]BF_4 was used as an extractant to remove thiophene from model oil, the desulfurization efficiency is poor (the removal of thiophene is only 15.3%). Either extraction combined with chemical oxidation or extraction combined with catalytic oxidation does not show obvious removal of thiophene. However, when [Bmim]BF_4 was replaced with [Hnmp]BF_4, the conversion of thiophene is increased sharply and can reach as high as 99.4% in the case of the extraction coupled with catalytic oxidation. It indicates that [Hnmp]BF_4 not only serves as extractant and reaction media but also acts as co-catalyst.

To investigate the effect of different BAILs on the reaction, [Hmim]BF_4, [Hnmp]HSO_4, [Hmim]HSO_4 and [Hnmp]CH_3SO_3 were

Table 1
Desulfurization performances via extraction with different ILs, extraction coupled with chemical oxidation and ECODS with catalysts containing ammonium tungstate and different ILs.

Entry	Type of ILs	Thiophene removal of different desulfurization systems (%)		
		Extraction with IL	IL + H_2O_2	IL + catalyst + H_2O_2
1	[Bmim]BF_4	15.3	18.5	19
2	[Hmim]HSO_4	4.3	13.3	23.8
3	[Hnmp]SO_3CH_3	9.4	15.9	44.8
4	[Hmim]BF_4	4.2	20.7	47.1
5	[Hnmp]HSO_4	10.0	30.2	63.5
6	[Hnmp]BF_4	10.4	19.6	99.4

Experimental conditions: T = 60 °C, t = 5 h, 20 mL model oil of thiophene in n-octane with S-contents 700 ng μL^{-1}, ILs = 4 g, H_2O_2/thiophene = 10 (molar ratio), S/C = n(S)/n (catalyst (based on W)) = 25, catalyst: ammonium tungstate.

used for ODS. The removal of thiophene is in the range of 4.2–10.4% for these four ionic liquids by a single extraction. With adding of H_2O_2, the removal of thiophene is still insufficient. The results are 13.3%, 15.9%, 20.7%, and 30.2% while using [Hmim]HSO_4, [Hnmp]SO_3CH_3, [Hmim]BF_4, and [Hnmp]HSO_4, respectively. When catalytic amount of ammonium tungstates were added to the reaction mixtures, the conversion of thiophene increases to 23.8% for [Hmim]HSO_4, 44.8% for [Hnmp]SO_3CH_3, 47.1% for [Hmim]BF_4, and 63.5% for [Hnmp]HSO_4. This indicates that these BAILs play an important role in catalytic oxidation of thiophene.

3.2. Effect of different catalysts on ODS of thiophene

The data in Table 2 show that the removal of thiophene was only 19.6% without catalyst. Among various commercial catalysts, tungstate-based catalysts exhibit the relatively high activity, especially ammonium tungstate, H_2WO_4 and $Na_2WO_4{\cdot}2H_2O$, which catalyzed the oxidation of thiophene with over 97% conversion. The high activities of tungstate-based catalysts might attribute to peroxo-species $[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$ which are formed in the mixture of tungsten-based precursors with H_2O_2 [24]. Under the same reaction conditions, WO_3 and $H_3PW_{12}O_{40}{\cdot}6H_2O$ (HPA) show very low activities which might be due to the poor solubility of WO_3 and HPA in BAILs.

3.3. Sulfur removal of different sulfur-containing compounds

The ODS of six model sulfur-containing compounds from model oil was carried out under the same conditions. As shown in Fig. 1a, when the ratio of substrate/catalyst (S/C) is equal to 100, the TOF in the oxidation of different sulfur-containing compounds decreases for ODS in the follow order: BT > 2,3,5-3MT > 2,5-2MT > 3-MT > 2-MT > thiophene. This order agrees well with the electron density on the sulfur atom [15]. When the ratio of S/C is 25 (Fig. 1b), all of sulfur-containing compounds we selected are removed completely in 5 h. Significantly, for ODS of BT, excellent catalytic activity is achieved with high TOF ($194 \times 10^{-3}\ s^{-1}$). Therefore, the catalytic system we developed has a broad substrate scope in aromatic sulfur-containing compounds.

3.4. Influence of temperature on ODS of BT and difference of activation energies for oxidation BT in presence of BAILs and non-BAILs

In the foregoing experiments, the catalyst consisted of ammonium tungstate and [Hnmp]BF_4 showed high catalytic activity for ODS of thiophene, BT, and its derivates. In order to obtain the apparent activation energy of the oxidation in BAILs [Hnmp]BF_4 and in non-BAILs [Bmim]BF_4, the oxidation of BT in the presence of [Hnmp]BF_4 or [Bmim]BF_4 was carried out under different temperatures. Fig. 2a displayed conversion of BT *vs.* reaction time under various temperatures using [Hnmp]BF_4 as extractant and reaction media with 1 mol% ammonium tungstate (based on tungsten content). The oxidation reaction was run efficiently under 60 °C, and the activity decreased with decreasing temperature. At the same reaction time, the conversion of BT increased from 53% at 20 °C to 96% at 60 °C in 1 h. When BAIL [Hnmp]BF_4 was replaced by non-BAIL [Bmim]BF_4, the conversion of BT is only 49% at 60 °C and less than 5% at 20 °C (Fig. 2b).

From the reaction rates determined at various temperatures, the apparent activation energies for the oxidation of BT were calculated derived from the Arrhenius equation (Fig. 3). In the ODS system in the presence of non-BAIL [Bmim]BF_4, 76.8 kJ mol^{-1} apparent activation energy was obtained. However, less than 40 kJ mol^{-1} apparent activation energy was calculated when the oxidation was carried out in the presence of BAIL [Hnmp]BF_4.

Table 2
Conversion of thiophene via ECODS with catalyst containing various commercially tungsten, molybdenum or vanadium containing compounds and [Hnmp]BF_4.

Entry	Catalyst	Thiophene removal of different desulfurization systems (%)		
		1 h	3 h	5 h
1	$(NH_4)_{10}H_2(W_2O_7)_6{\cdot}H_2O$	64	96.4	99.4
2	H_2WO_4	45.5	86.6	98.3
3	$Na_2WO_4{\cdot}H_2O$	33.9	82.5	97.7
4	WO_3	7.6	13.5	18.3
5	$H_3PW_{12}O_{40}{\cdot}xH_2O$	12.5	15.3	15.6
6	$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$	18.3	25.4	30.8
7	H_2MoO_4	17.9	21.5	31.2
8	$Na_2MoO_4{\cdot}2H_2O$	12.8	17.9	21.4
9	MoO_3	9.5	10.2	10.9
10	V_2O_5	15.2	16.3	17.3

Experimental conditions: $T = 60$ °C, $t = 5$ h, 20 mL model oil of thiophene in n-octane with S-contents 700 ng μL^{-1}, [Hnmp]BF_4 = 4 g, H_2O_2/thiophene = 10, thiophene/W, Mo or V = 25 (molar ratio).

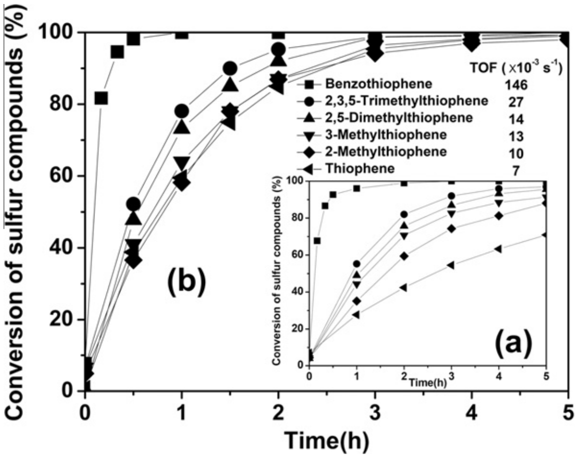


Fig. 1. Conversion of sulfur-containing compounds versus the reaction time at (a) S/C = 100 and (b) S/C = 25. Experimental conditions: $T = 60$ °C, 20 mL model oil of sulfur-containing compounds in n-octane with S-contents 700 ng μL^{-1}, [Hnmp]BF_4 = 4g, H_2O_2/S = 10 (molar ratio), S/C = $n(S)/n$ (catalyst(based on W)), catalyst: ammonium tungstate. TOF value was based on the <30% conversion, and given in mole of conversion of reactant per mole of W in the catalyst per hour.

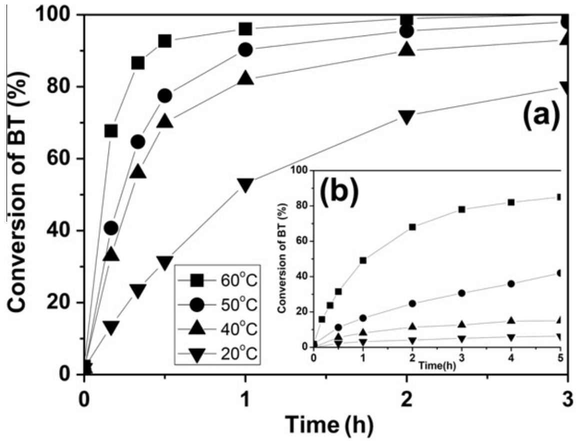


Fig. 2. Conversion of BT versus the reaction time on the reaction temperature via ECODS with catalysts containing ammonium tungstate and (a) [Hnmp]BF_4 (b) [Bmim]BF_4. Experimental conditions: 20 mL model oil of BT in n-octane with S-contents 700 ng μL^{-1}, ILs = 4g, H_2O_2/BT = 2.5(molar ratio), S/C = 100, catalyst: ammonium tungstate.

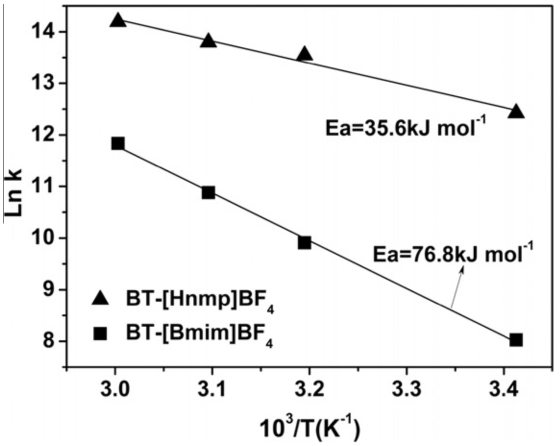


Fig. 3. Arrhenius activation energies for BT oxidation in BAIL [Hnmp]BF_4 and [Bmim]BF_4.

Therefore, the reaction rates in all the sulfur-containing compounds are enhanced in the presence of the BAILs. The function of BAILs will be discussed in section below.

3.5. Oxidation products

Qualitative measurements of oxidative products were done as follows. The sulfur species could not be detected in oil phase and all of products exist in the ILs phase due to the different chemical polarity between products and model oil. After the reaction, the ILs phase was separated and extracted with diethyl ether (4 mL × 3). The organic phase was collected, dried with anhydrous Na_2SO_4, and concentrated for GC–MS analysis. GC–MS analysis of the products from thiophene oxidation gives two main compounds for qualitative analysis (Fig. S1 in Supporting information). The spectra of products A and B match that of benzaldehyde (C_7H_6O, MW=106) and benzoic acid ($C_7H_6O_2$, MW=122), respectively. After a complete reaction, $Ba(NO_3)_2$ solution was added to the ILs phase. A white precipitate appeared immediately. After washed with an excess of H_2O and dried, the XRD pattern of the precipitate is attributed to $BaSO_4$ (Fig. 4a). It is clear that the oxidation reaction of thiophene takes place and yields the SO_4^{2-} and oxygenates.

The mass spectra of products B and C from oxidation of 2-MT match that of 2-methylbenzoic acid ($C_8H_8O_2$, MW = 136.1) and 3-methylbenzoic acid ($C_8H_8O_2$, MW = 136.0), respectively (Fig. S2 in Supporting information). The mass spectrum of product A shows the molecular ion peak at *m*/*z* 130.0 and the strongest peak at *m*/*z* 82.1 due to the furan radical cation (Fig. 4b). Based on the similar results from characterizing thiophene 1,1-dioxide using EI-MS in the literature [16], it implies that 2-MT 1,1-dioxide is the major product after the ODS.

One major product and some minor products were obtained from the oxidation of 2,5-DMT and 2,3,5-TMT (Figs. S3 and S4 in Supporting information). The MS of main product shows the molecular ion peak at *m*/*z* 144.0 for 2,5-DMT and at *m*/*z* 158.0 for 2,3,5-TMT, which are assigned to corresponding 1,1-dioxides. Thus, 2,5-DMT 1,1-dioxides and 2,3,5-TMT 1,1-dioxides are the main oxidative products from 2,5-DMT and 2,3,5-TMT. The oxidative product of BT is BT-sulfone which can be isolated by flash chromatography on silica gel and characterized by ^1H NMR and IR (Fig. S5 in Supporting information).

From above results, a summary of oxidative products of thiophene and its derivates is given in Scheme 2. It is clear that thiophene 1,1-dioxide is unstable and then the consequent reactions are followed, yielding benzaldehyde, benzoic acid, and sulfuric acid. As the number of substitute-group on thiophene increasing, the corresponding 1,1-dioxide becomes more stable. As a result, 1,1-dioxides of 2-MT, 2,5-DMT, and 2,3,5-TMT are detected by the GC–MS.

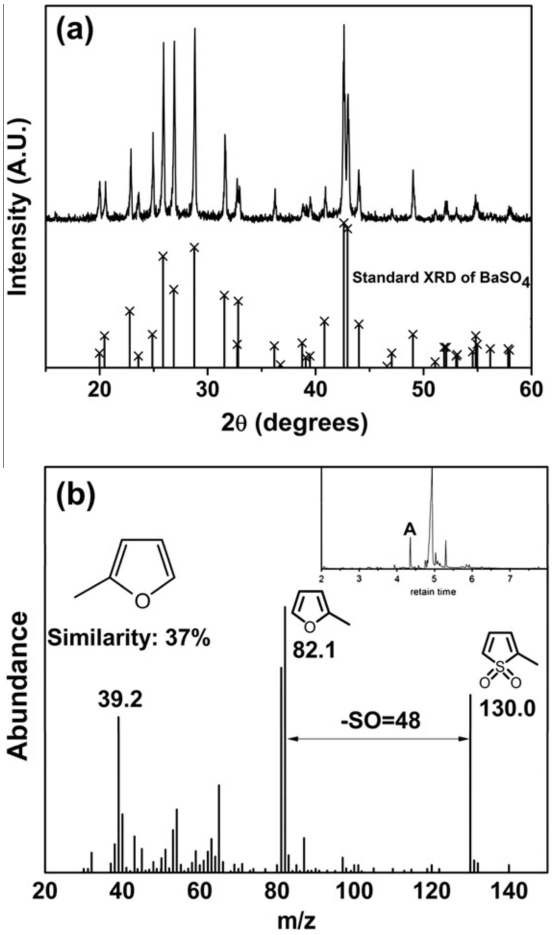


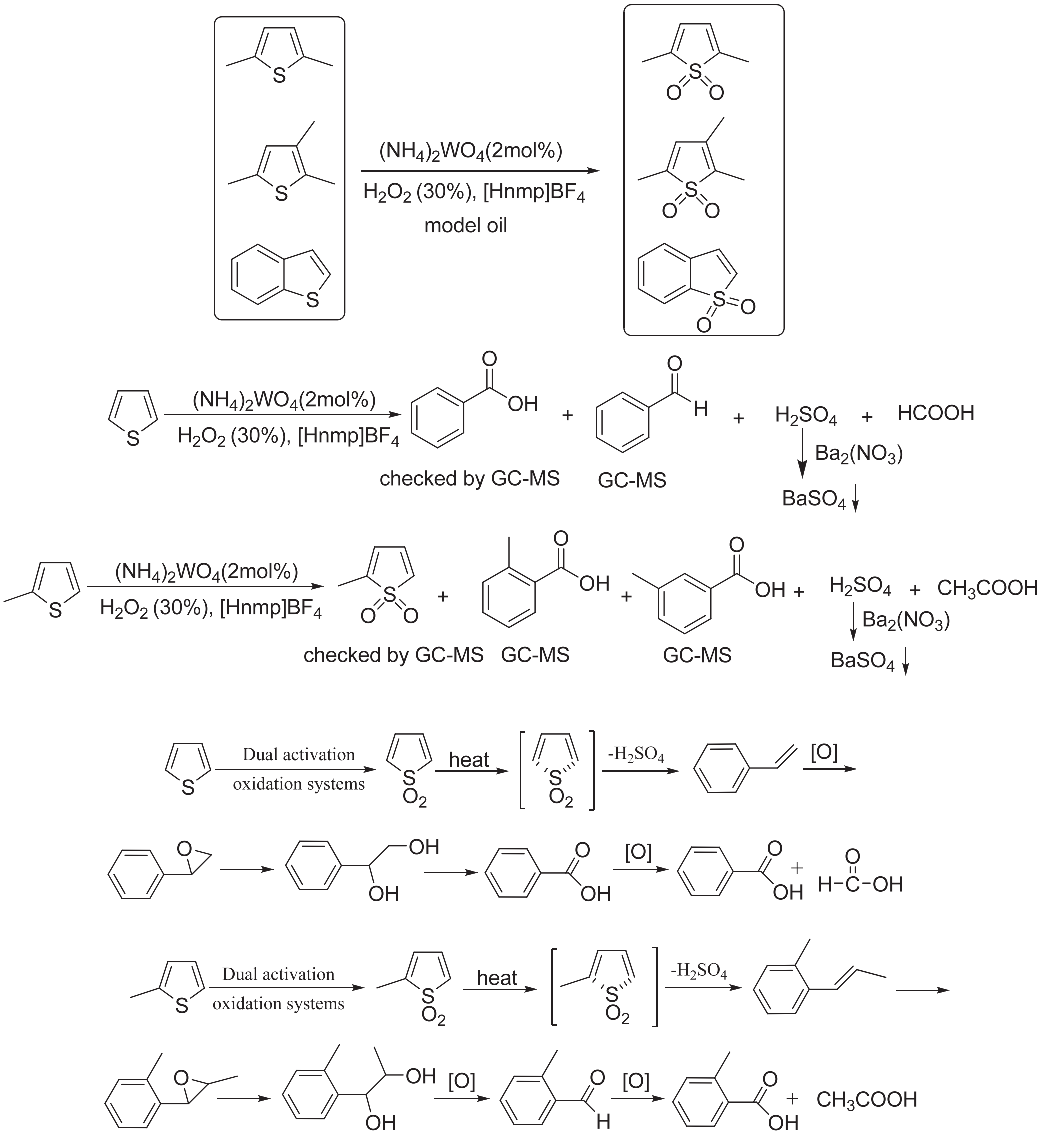
Fig. 4. (a) The powder-XRD patterns of $BaSO_4$ precipitation; (b) the mass spectrogram of one oxidized product of 2-MT.

As proposed formation of benzoic acid from thiophene in Scheme 2, more H_2O_2 should be required in the oxidation of thiophene and 2-MT. As shown in Table 3, when 2.5 equivalents of H_2O_2 were used in the oxidation of 2-MT, only 45.3% conversion was obtained (Table 3, entry 3). As the equivalent of H_2O_2 was increased to 10, the oxidation of thiophene and 2-MT could get complete conversion (Table 3, entry 1 and 2). However, when 2.5 equivalents of H_2O_2 were used in the oxidation of BT, 2,3,5-3MT and 2,5-2MT, over 90% conversions were achieved. Corresponding efficiency of hydrogen peroxide utilization was around 60%.

3.6. Obtaining of ILs-free desulfurized oil and recycling of the catalyst containing [Hnmp]BF_4 and ammonium tungstate

During the course of desulfurization using BAILs [Hnmp]BF_4, the unwanted "contamination" of the desulfurized oil with [Hnmp]BF_4 was investigated. After the oxidation, ionic liquid phase was separated and the nitrogen content in oil phase is less than 50 ppm through elementary analysis. We could obtain the ILs-free model oil by washing once with H_2O.

The recycling test of the catalyst containing [Hnmp]BF_4 and ammonium tungstate was also investigated. When the reaction was finished, ionic liquid phase was separated and washed with ethyl ether. After removing H_2O from ionic liquid phase under



Scheme 2. The oxidized products of thiophene and its derivatives and proposed formation process of Benzoic acid.

reduced pressure, fresh H_2O_2 and model oil were added to ionic liquid phase for the next cycle of the reaction. Table 4 shows no significant deterioration of activity for the recovered catalyst even after seven times of use.

3.7. The selectivity in the oxidation of thiophene catalyzed by ammonium tungstate in the presence of [Hnmp]BF_4

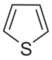
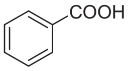
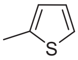
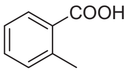
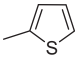
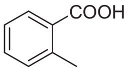
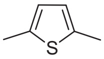
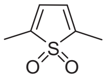
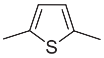
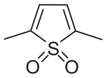
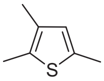
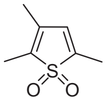
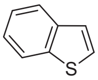
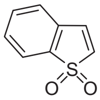
We developed a multi-component system to oxidize electron-poor aromatic compound including thiophene, BT, and its derivates. As the important constituents of gasoline, olefins and aromatics were introduced to the reaction mixture to clarify the effects for oxidation of thiophene. If 30 wt.% toluene was added to the reaction mixture, less influence to desulfurization was observed and 98% conversion of thiophene was obtained. However, when 30 wt.% cyclohexene was added to the reaction system, the removal of thiophene was sharply decreased and only 25% conversion was obtained. We thought that cyclohexene is easier to be oxidized than thiophene. Therefore, the selectivity in the oxidation of thiophene in the presence of olefin is more challenging and the effort on this aspect is under processing.

3.8. Mechanistic studies

3.8.1. IR studies on interaction between thiophene and BAILs [Hnmp]BF_4

Infrared spectroscopy has been used to determine the interaction between ILs and organic compound [25]. Fig. 5a shows the IR spectra in the range from 650 to 850 cm^{-1} of [Hnmp]BF_4, thiophene and the mixture of them at molar ratio of 2. The IR results indicate that the structure of thiophene is distorted according to the appearance of a new peak at 735 cm^{-1} and the weakening one at 713 cm^{-1} which is assigned to =C—H bending vibrations of thiophene [26], when BAILs are mixed with thiophene. The relative intensity of the new peak appeared at 735 cm^{-1} for different BAILs containing thiophene is found to be in accord with the activity in ODS of thiophene (Table 1, Fig. 5b). The thiophene shows the highest reactivity in the oxidation catalyzed by ammonium tungstate in [Hnmp]BF_4; accordingly, the new peak intensity of [Hnmp]BF_4 is the strongest one among various BAILs. This means that the structure of thiophene is distorted in [Hnmp]BF_4 stronger than in others. This might be attributed to the acidity of BAILs and the polarization of thiophene by fluorine ion [27].

Table 3
Catalytic oxidation of various sulfur-containing compounds with aqueous 30% H_2O_2 under dual activation conditions [a].

Entry	Substrate	Time (h)	Conv. (%)[b]	Main product[e]	Yield (%)	H_2O_2 eff. (%)[f]
1[c]		3	95.4		–	–
2[c]		3	98.0		–	–
3[d]		3	45.3		–	–
4[c]		3	98.7		88.3	17.6
5[d]		3	93.5		87.6	58.4
6[d]		3	92.5		90.3	60.2
7[d]		0.5	98.2		96.5	64.3

[a] Experimental conditions: T = 60 °C, 20 mL model oil of thiophene in n-octane with S-contents 700 ng μL^{-1}, $[Hnmp]BF_4$ = 4 g, S/C = 25 (molar ratio, based on W), catalyst: ammonium tungstates.
[b] Conversion was determined by GC-SCD with an external standard technique.
[c] 10 equivalent H_2O_2 was used.
[d] 2.5 equivalent H_2O_2 was used.
[e] Main product was determined by GC–MS.
[f] H_2O_2 efficiency was calculated as mole of main product produced per mole of H_2O_2 consumed.

Table 4
Recycling test of the catalyst containing $[Hnmp]BF_4$ and ammonium tungstate.

Cycle	1	2	3	4	5	6	7
Thiophene removal (%)	99.4	99.3	99.0	98.8	98.4	98.0	97.5

Experimental conditions: T = 60 °C, t = 5 h, 20 mL model oil of thiophene in n-octane with S-contents 700 ng μL^{-1}, $[Hnmp]BF_4$ = 4 g, thiophene/W = 25, H_2O_2/thiophene = 10 (molar ratio).

3.8.2. ^1H NMR studies on the interaction between thiophene and ionic liquids

The ^1H NMR spectra of ILs containing thiophene were recorded to further understand the interaction nature (Fig. 6). The ^1H NMR of the mixtures were examined in a stem coaxial NMR capillary tube inserted into 5 mm NMR tube loaded with D_2O. When thiophene is added into $[Bmim]BF_4$, the resonances for all protons of ILs significantly shift upfield because of the aromatic ring current effects [28,29]. However, in the BAILs $[Hnmp]BF_4$, the adding of thiophene makes resonance of the acidic proton shift a little bit downfield, and the resonances of other protons still shift upfield.

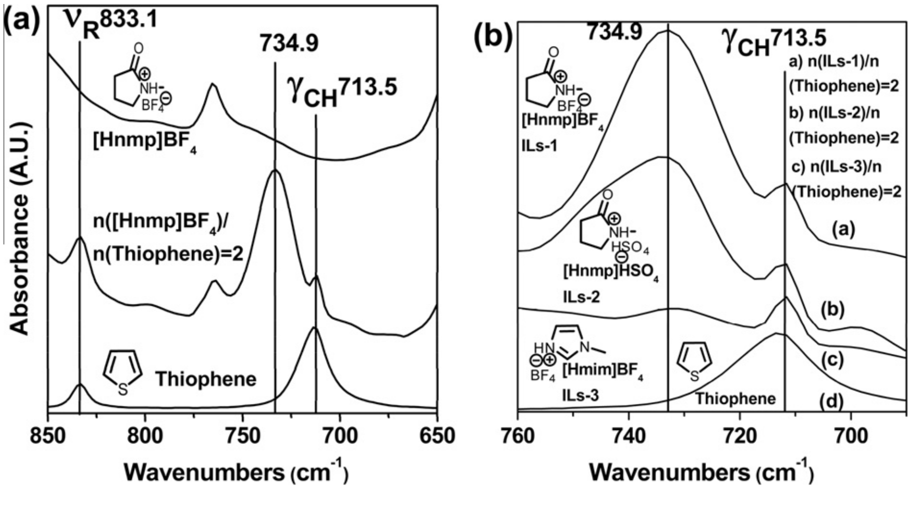


Fig. 5. FT-IR spectra of (a) thiophene, $[Hnmp]BF_4$ and the mixture of them; (b) thiophene mixed with $[Hnmp]BF_4$, $[Hnmp]HSO_4$ or $[Hmim]BF_4$.

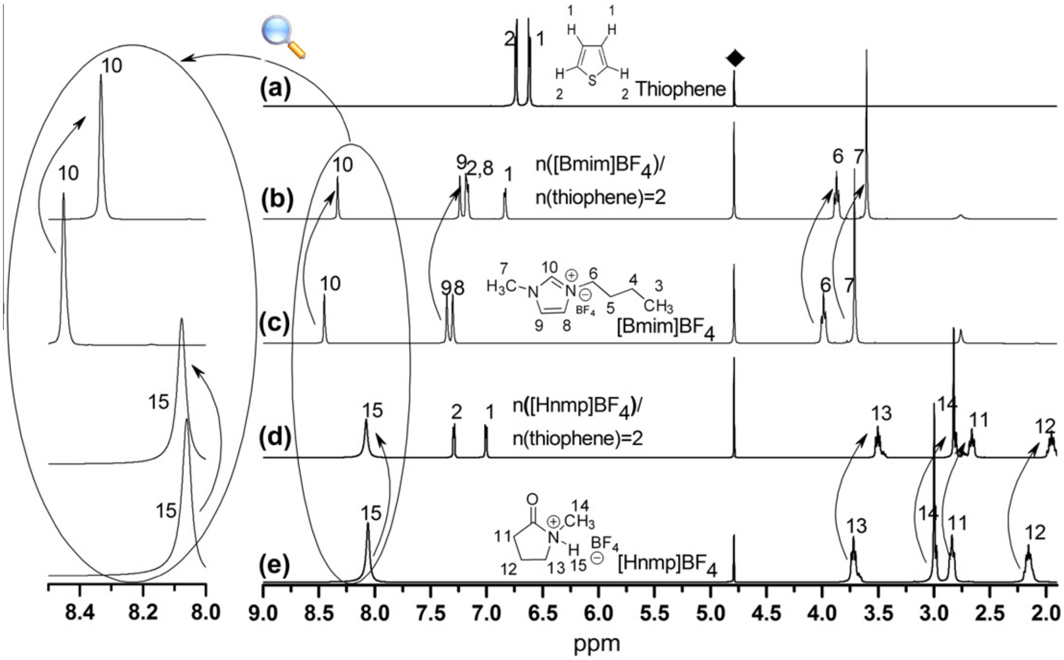


Fig. 6. ^{1}H NMR signals recorded for thiophene and the mixture of thiophene with [Bmim]BF_4 or [Hnmp]BF_4.

These results clearly show the existence of strong hydrogen bonding [30–32] between [Hnmp]BF_4 and thiophene.

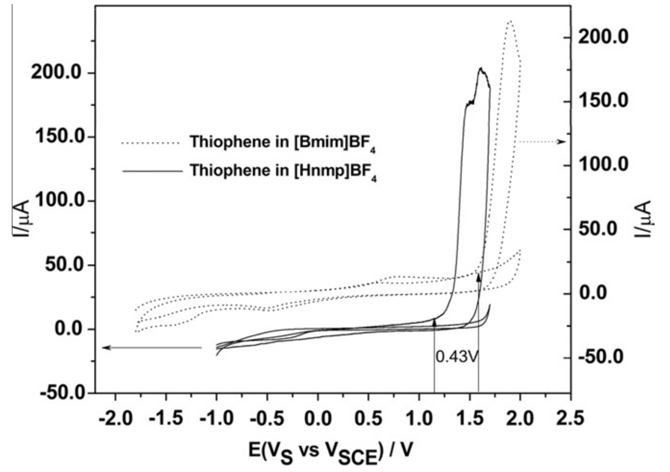
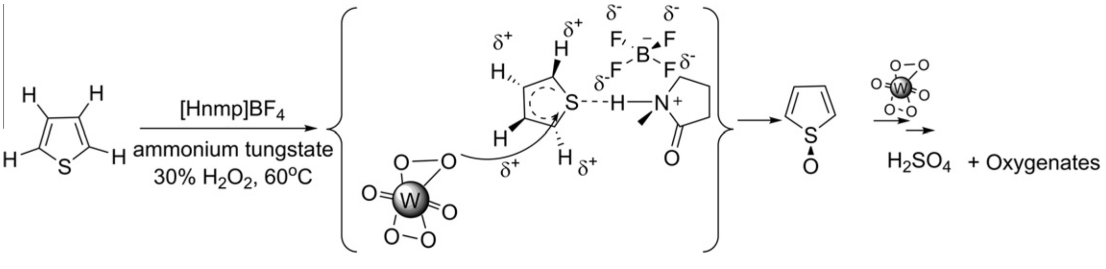


Fig. 7. Cyclic voltammograms curves of thiophene in [Bmim]BF_4 and [Hnmp]BF_4 (Thiophene in ILs with S-contents 700 ng μL^{-1}).

3.8.3. Cyclic voltammetry measurement on the interaction between thiophene and BAILs [Hnmp]BF_4

To obtain the experimental evidences for the existence of hydrogen bonding that may activate thiophene and promote the oxidation, the cyclic voltammograms (CVA) of [Bmim]BF_4, [Hnmp]BF_4, thiophene in ILs [Bmim]BF_4 and in BAILs [Hnmp]BF_4 were performed according to the literature [33]. The electrochemical windows of [Bmim]BF_4 and [Hnmp]BF_4 are found to be 3.8 V (from −1.8 to 2.0 V vs SCE) and 2.7 V (from −1.0 to 1.7 V vs SCE), respectively. The first electrochemical oxidation peak of thiophene occurs within the electrochemical window for thiophene in both ionic liquids. The first oxidation peak is assigned to an electron loss from the two highest occupied π-orbitals of six π electrons in aromatic system of thiophene [34,35]. Thus, it is considered as a measurement of the conjugation extent of thiophene. Fig. 7 shows the CVA curves of thiophene in [Bmim]BF_4 and [Hnmp]BF_4. The first oxidation peak of thiophene in [Hnmp]BF_4 occurs at 1.15 V ahead of that in [Bmim]BF_4. This indicates that thiophene is activated by forming hydrogen bonding with [Hnmp]BF_4. The aromaticity of thiophene is partially destroyed by the hydrogen bonding, and thus the oxidation takes place easily in the presence of [Hnmp]BF_4.

Based on the above mechanistic study, a plausible dual active model [36,37] was proposed (Scheme 3). [Hnmp]BF_4 activates thiophene through hydrogen bonding and polarization to destroy the aromaticity of thiophene. Both of activations work synergistically to make the oxidation of thiophene possible.



Scheme 3. Dual-activation model for the oxidation of thiophene on catalyst containing [Hnmp]BF_4 and ammonium tungstate.

4. Summaries

The main results of this work can be summarized as follows:

1. ODS catalyst composed of tungstate compounds and BAILs can effectively catalyze the oxidation of BT, 2,3,5-TMT, 2,5-DMT, 3-MT, 2-MT, and thiophene using H_2O_2 as the oxidant under mild condition. The catalytic oxidation reactivity of the sulfur-containing compounds is in the following order: thiophene < 2-MT < 3-MT < 2,5-DMT < 2,3,5-TMT < BT.
2. The TOF more than $194 \times 10^{-3}\ s^{-1}$ was observed for ODS of BT using catalyst containing tungstate compounds and BAIL $[Hnmp]BF_4$ in comparison with less than $11 \times 10^{-3}\ s^{-1}$ using catalyst containing tungstate compounds and non-BAIL $[Bmim]BF_4$.
3. The sulfur atom of thiophene is oxidized to SO_4^{2-} and the hydrocarbon part of thiophene is to oxygenates.
4. The ODS catalyst composed of $[Hnmp]BF_4$ and ammonium tungstate can be recycled seven times without significant loss in activity.
5. Based on FT-IR, ^1H NMR and electrochemical measurements, the hydrogen bonding between thiophene and $[Hnmp]BF_4$ and the polaraztion induced by ILs distorte the planar structure of thiophene, and decrease the aromaticity extent. This distortion together with the catalytic oxidation function of tungstate synergistically activates the thiophene and makes the ODS of thiophene efficiently.
6. The oxidation of thiophene, usually difficult, can be efficiently realized by using the catalyst containing tungstate compound and BAILs which play a triple role in ODS as extractant, reaction media and more importantly, as a catalyst. For $[Hnmp]BF_4$ and ammonium tungstate, up to 99% conversion can be achieved at 60 °C.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.11.003.

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