Deep oxidative desulfurization with task-specific ionic liquids: An experimental and computational study

Jianzhou Gui [a,*], Dan Liu [a,b], Zhaolin Sun [a], Daosheng Liu [a], Dayoung Min [b], Busub Song [b], Xilai Peng [a]

[a] College of Chemistry and Materials Science, Liaoning Shihua University, Fushun 113001, Liaoning, PR China
[b] Division of Green Chemistry, Korea Research Institute of Chemical Technology (KRICT), Sinseongno 19, Yuseong-gu, Daejeon 305-600, Republic of Korea

ARTICLE INFO

ABSTRACT

A series of task-specific acidic ionic liquids (TSILs), immiscible with oil, halogen-free and containing –COOH group in the cations, were used for oxidative desulfurization as both the catalyst and extractant. The removal of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) from model diesel at 298 K could reach 96.7% and 95.1%, respectively. The TSIL could be recycled 5 times without any apparent loss of the catalytic activity. Meanwhile, the structures, acidities and interactions between the cation and the anion of TSILs have been investigated by density functional theory (DFT) method, and found that catalytic properties of TSILs are close related to the structures, acidities and extraction capabilities. Furthermore, an oxidative desulfurization mechanism has been proposed.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Deep removal of sulfur from fuels, particularly from gasoline and diesel, has been an important and challenging issue in worldwide petroleum refining industry, which is not only due to increasingly stringent environmental regulations on sulfur concentration of transport fuel, but also because of the great importance for making ultra-low-sulfur fuels for fuel cell applications [1–3].

Nowadays hydrodesulfurization (HDS), a conventional hydrotreating method, can be effective to remove sulfides, disulfides, mercaptans and light thiophenic sulfur compounds, however, difficult in the removal of the most refractory sulfur molecules such as alkyl derivatives of DBT because of steric hindrance. To achieve low sulfur level by HDS, problems including high operating cost, shorter lifetime of catalyst, higher hydrogen consumption and lower lubricating properties of treated diesel would be brought. Alternative desulfurization processes that operate under mild conditions without H_2 consumption have been extensively investigated, among which oxidative desulfurization (ODS) has received wide attention. Organic S compounds can be selectively oxidized to sulfoxides or sulfones, and then removed by polar extractant for achieving ultra-low-sulfur fuel. However, the extractant is usually volatile organic compound, which is flammable and finally leads to further environmental and safety concerns.

Ionic liquids (ILs) have been regarded as "green solvent" in separations, chemical synthesis, electrochemistry, catalysis and so on. Recently, ODS method combined with H_2O_2 as the oxidant in IL was developed to be effective [4–11]. Wei and coworkers reported an one-pot desulfurization of light oils by chemical oxidation and solvent extraction in ILs, and found that [BMIm]PF_6 was more effective than [BMIm]BF_4 for increasing the rate of chemical oxidation [4]. Zhao et al. applied the coordinated IL in ODS process for the removal of thiophene using acetic acid as the catalyst [5]. Yen et al. reported ultrasound-assisted oxygenative desulfurization in halogen-free ILs together with trifluoroacetic acid, which turns to be a multiple phase-transfer catalysis process [6]. Li and his coworker carried out oxidative desulfurization of model diesel in ILs, combined with the catalysts decatungstates [7], phosphotungstic acid [8], V_2O_5 [9], peroxophosphomolybdate [10], and peroxotungsten or peroxomolybdenum complexes [11]. Generally, the ILs work as reaction media and extractant in the above reports, and additional catalyst was needed.

Recent advance in ILs research provided another route for achieving TSILs in which a functional group is covalently tethered to the cation or anion of the ILs, especially to the two N atoms of the imidazole ring. It was expected that these TSILs may further enlarge the application scope of ILs in chemistry [12]. Until now, only a few reports have been published on ODS with TSILs working as both a catalyst and extractant. Gao and his coworkers use [HMIm]BF_4 as a catalyst and solvent to removal 60–93% sulfur from DBT-containing model oil, however, the exact catalytic role of IL was not proposed, and the amount of IL is quite large ($V_{model\,oil\,(1000\,\mu g/mL\,S)}/V_{IL} = 3.2:5$) [13]. Zhao et al. reported effective

* Corresponding author. Tel.: +86 413 6865161.
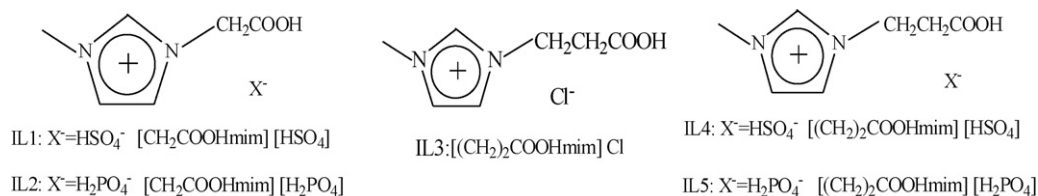 E-mail addresses: guijz@lnpu.edu.cn, jzgui@hotmail.com (J. Gui).

Fig. 1. Structures of five TSILs.

oxidative desulfurization of model diesel by Brönsted acid ionic liquid (N-methyl-pyrrolidonium tetrafluoroborate) both as extractant and catalyst in the presence of H_2O_2, and the catalytic role of IL is to decompose H_2O_2 to form hydroxyl radicals that were strong oxidizing agents for DBT. The drawback of this method is the large amount of IL ($V_{model\ oil}/V_{IL} = 1:1$) [14]. At the same time, the anions of these ILs are usually BF_4^- or PF_6^- which yields white fumes of HF or hydrate precipitates easily. So there is still much room for the development of more effective and halogen-free TSILs for ODS process.

In order to design TSILs for oxidative desulfurization, i.e. ILs can works both as a catalyst and extractant, several requirements for IL should be taken into consideration: (1) the ILs should be immiscible with fuels, then two phases will appear. In this case, water and the sulfones produced can be easily extracted into the IL phase, which will provide a convenient way for the separation of product fuel from the reaction mixture; (2) some functional group for catalytic oxidation should be introduced; (3) the ILs have good extraction capacity to S-compounds, which is a requirement for TSIL working as a phase transfer catalyst.

Our group had synthesized several TSILs and applied them in Beckmann rearrangement, alkylation, esterification, oxidation, polymerization reactions and so on [15–23]. Recently, the effect of different cations or anions on extractive desulfurization has been investigated in our group [22]. With our continuous research in TSILs and desulfurization, a series of ILs with two Brönsted acid sites have been designed and firstly synthesized in our group [23]. The carboxylic acid (−COOH) group with catalytic oxidative function was introduced into the cations of several acidic ILs, and their anions are $[HSO_4]^-$ and $[H_2PO_4]^-$ (see Fig. 1). In this study, those TSILs were used as both catalyst and extractant for oxidative desulfurization of model diesel, which have proven to be effective and combined the oxidation and extraction process in one step. Meanwhile, the structures, interactions between cation and anion, acidities of these ILs were studied by DFT method. To the best of our knowledge, it is the first report on oxidation desulfurization with halogen-free TSILs without adding additional catalyst.

2. Experimental

2.1. Preparation of TSILs

The TSILs were prepared by two-step synthesis through 1-methylimidazole combined first with chloroacetic acid or 3-chloropropionic acid to form zwitterions salts, followed by addition of concentrated sulphuric acid (97%) or o-phosphoric acid (85%). The detailed preparations are in our previous work [23]. The C, N and H elemental analyses were performed on an Elementar Vario EL element analyzer. IR spectra (FTIR) were recorded on a PE Spectrum™ GX FTIR spectrometer using liquid film. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were obtained on Varian Mercury-plus 300BB instruments as solutions in deuterium substituted reagent. Chemical shifts were reported in parts per million (ppm, d). The thermal decomposition point of ionic liquids was determined by TGA (Perkin-Elmer TGA Pyris1 instrument,

10 K min^{-1} heating rate under nitrogen). Densities were measured using a U-shape vibrating-tube densimeter (Model DA-500) operating in a static mode. The rheometer used (Brookfield, RVDV-III$^+$) allows measurements from 293 to 393 K at atmospheric pressure and in a wide viscosity range (from 100 to 3 M cP).

IL1: density: 1.377 g/mL (298 K); viscosity: 1000.6 MPa s (353 K). ^{1}H NMR (300 MHz, DMSO-d_6, TMS); 3.87 (s, 3H), 5.11 (s, 2H), 7.70 (s, 2H), 9.10 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, TMS); δ 36.52, 50.26, 123.89, 124.38, 138.35, 168.89. IR (cm^{-1}): 3158, 2509, 1741, 1572, 1364, 1168, 1176, 1050, 852, 639,588. $C_6H_{10}O_6N_2S$ (237.13) calcd: C, 34.96; H, 4.85; N, 13.58. Found: C, 34.03; H, 4.90; N, 13.62. The thermal decomposition point of IL1: 578.5 K.

IL2: density: 1.340 g/mL (298 K); viscosity: 9896.9 MPa s (353 K). ^{1}H NMR (300 MHz, D$_2$O, TMS); 3.22 (s, 3H), 4.44 (s, 2H), 6.81 (t, 2H), 8.10 (s, 1H). ^{13}C NMR (75 MHz, D$_2$O, TMS); δ 35.74, 49.55, 123.17, 124.11, 136.90, 169.54. IR (cm^{-1}): 3158, 2488, 1734, 1572, 1364,1212, 1191, 1168, 995, 639, 621. $C_6H_{11}O_6N_2P$ (237.04) calcd: C, 34.98; H, 5.34; N, 13.59. Found: C, 34.88; H, 5.39; N, 13.60. The thermal decomposition point of IL2: 572.5 K.

IL3: density: 1.115 g/mL (298 K); viscosity: 1175.4 MPa s (353 K). ^{1}H NMR (300 MHz, DMSO-d_6, TMS); 2.84 (t, 2H), 3.82 (s, 3H), 4.31 (s, 2H), 7.71 (s, 1H), 7.79 (s, 1H), 9.33 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, TMS); δ 34.92, 36.36, 45.53, 123.02, 124.05, 137.60, 172.45. IR (cm^{-1}): 3158, 2586, 1743, 1572, 1364, 1168, 639. $C_7H_{11}O_2N_2Cl$ (190.53) calcd: C, 44.13; H, 5.77; N, 14.70. Found: C, 44.23; H, 5.59; N, 14.88. The thermal decomposition point of IL3: 516.4 K.

IL4: density: 1.195 g/mL (298 K); viscosity: 9677.1 MPa s (353 K). ^{1}H NMR (300 MHz, D$_2$O, TMS); 2.28 (t, 2H), 3.16 (s, 3H), 3.74 (t, 2H), 6.70 (s, 1H), 6.79 (s, 1H), 8.01 (s, 1H). ^{13}C NMR (75 MHz, D$_2$O, TMS); δ 33.84, 35.65, 44.71, 122.21, 123.59, 136.29, 173.87. IR (cm^{-1}): 3158, 3098, 2602, 2486, 1749, 1572, 1364, 1287, 1168, 1069, 1006, 885, 850, 639, 614, 454. $C_7H_{12}O_6N_2S$ (252.14) calcd: C, 38.19; H, 5.45; N, 12.12. Found: C, 38.23; H, 5.49; N, 12.37. The thermal decomposition point of IL4: 524.3 K.

IL5: density: 1.233 g/mL (298 K); viscosity: 9539.6 MPa s (353 K). ^{1}H NMR (300 MHz, D$_2$O, TMS); 2.47 (t, 2H), 3.36 (s, 3H), 3.94 (t, 2H), 6.90 (s, 1H), 6.97 (s, 1H), 8.22 (s, 1H). ^{13}C NMR (75 MHz, D$_2$O, TMS); δ 33.89, 35.64, 44.60, 122.20, 123.52, 136.30, 174.05. IR (cm^{-1}): 3158, 1726, 1572, 1364, 1167, 1109, 997, 639, 621. $C_7H_{13}O_6N_2P$ (252.05) calcd: C, 38.21; H, 5.91; N, 12.72. Found: C, 38.43; H, 5.79; N, 12.58. The thermal decomposition point of IL5: 506.1 K.

2.2. Catalytic oxidative desulfurization

Model diesel was prepared by dissolving DBT or 4,6-DMDBT in n-tetradecane to form solutions with sulfur content of 500 μg/g. The oxidative desulfurization experiments were carried out in a 25-mL round-bottom flask. The mixture containing 10 mL model diesel, 2.5 mmol IL and 1 mL 30 wt% H_2O_2 was stirred vigorously at room temperature (298 K). Upon standing, the upper phase (model diesel) was separated easily from the IL phase by decantation at room temperature and analyzed the sulfur content of diesel phase by gas chromatography coupled with an atomic emission detector (GC-AED) and microcoulometry.
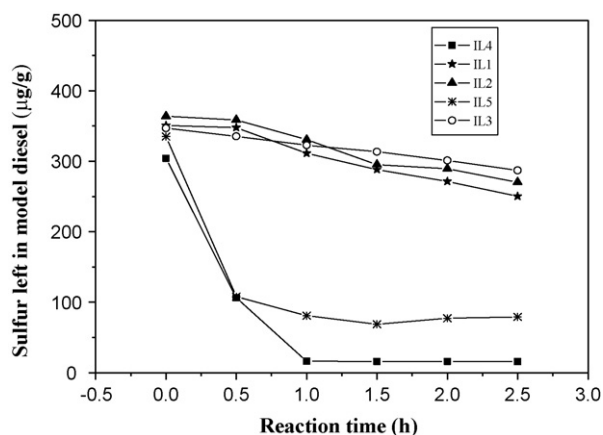
Fig. 2. ODS results of model diesel catalyzed by difference TSILs.

2.3. Analysis of peroxycarboxylic acids

In order to demonstrate the existence of peroxycarboxylic acid, the reaction of IL and oxidant were carried out in 50 mL clean ground-glass flasks. 75 mmol IL and 30 mL 30% H_2O_2 were added in the flask, and well mixed by stirring (500 rpm) at room temperature (298 K). Samples were withdrawn from the mixture by a plastic syringe (to avoid contamination of the solution by trace of metals) and analyzed by the Greenspan and Mackellar method [24]. Each datum was the average result of at least double tests.

2.4. Calculation methods

All calculations were performed by applying the generalized gradient-corrected density functional theory using the DMol³ module in Materials Studio package of Accelrys. BLYP exchange correlation function, double-numeric quality basis set with polarization functions were both employed and all electrons are included throughout the calculations. A thermal smearing of 0.005 Hartree was used to improve the computational performance. All SCF tolerances were set to fine, i.e., the tolerance of energy, gradient and displacement are converged to 1.0e−5 Ha., 0.002 Ha./Å and 0.005 Å, respectively.

The structures of the cations were optimized and related electric properties were also calculated, and finally equilibrium existing modes of the cation and anion in five TSILs were investigated.

3. Results and discussion

3.1. Effect of different TSILs

The effect of different TISLs on oxidative desulfurization capacity of model diesel is shown in Fig. 2. Before the oxidant H_2O_2 was added (reaction time $t = 0$), the model sulfur compound (DBT) had partially extracted by ILs. Their extraction desulfurization capability decreased in the following order: IL4 > IL5 > IL3 > IL1 > IL2. It shows that TSILs with cation [(CH₂)₂COOHmim] (including IL4, IL5 and IL3) has better extraction capability than those with [CH₂COOHmim] as cation. This may be caused by increasing the branch length of cations.

As for the TSILs with the same cation, the desulfurization capability of ILs decreased as follows: IL4 > IL5 > IL3; IL1 > IL2. This can be explained by the rate of forming peroxycarboxylic acid by the reaction of these TSILs with hydrogen peroxide. The peroxycarboxylic acid generated in situ is expected to be the active species for DBT oxidation. Thus, it was of interest to explore the influence of peroxycarboxylic acid formation in different TSILs on DBT conversion.
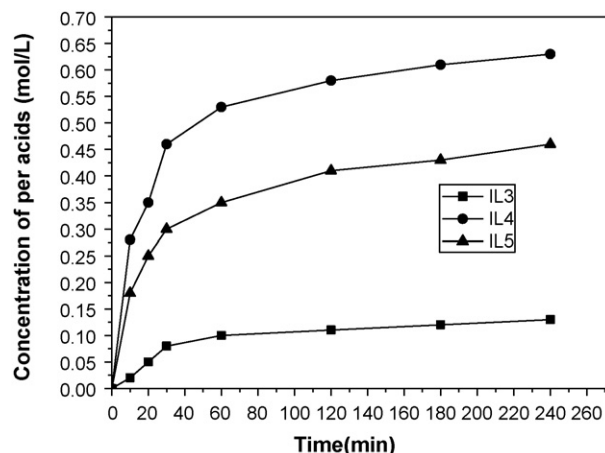

Fig. 3. Mole concentration of peroxycarboxylic acids versus time at 298 K in different TSILs.

As shown in Fig. 3, the formations of peroxycarboxylic acids in different TSILs (IL3–5) were investigated without adding model diesel in the system. The efficiencies of forming peroxycarboxylic acid in these three TSILs decreased as follows: IL4 > IL5 > IL3, and the same trend can be found on their desulfurization capacity (see Fig. 2). Therefore, the formation rate of peroxycarboxylic acid was close related to the oxidation rate of DBT. Meanwhile, the acidity of their anions has the order of $[HSO_4]^- > [H_2PO_4]^- > Cl^-$, suggesting that the formation rate depends on the acidity of the ILs. It can be concluded that the stronger the acidity of IL is, the larger the rate of producing the peroxy acid groups (–COOOH) is, and the better the desulfurization performance is. This result agrees well with the previous studies that the existence of stronger acid will accelerate the formation of the peroxycarboxylic acid [25,26]. As for IL3, the anion has no acidity, while some conversion was noticeable. The reason is that the carboxylic acid itself can also dissociate H^+, which is able to act as a catalyst to accelerate the forming rate of peroxycarboxylic acid [26].

The preferred TSIL is IL4 (i.e. [(CH₂)₂COOHmim][HSO₄]), which has good extraction capability and stronger acidity. It could be concluded that the ODS results depends upon both the extraction ability and the acidity of TSILs.

3.2. ODS of model diesel (containing DBT or 4,6-DMDBT) by IL4

Figs. 4 and 5 show the sulfur-specific GC-AED chromatograph of model diesel (containing DBT and 4,6-DMDBT, respectively) before and after oxidation. All the DBT in model diesel were oxidized into its corresponding sulfone (DBTO₂) within 1.5 h, and almost all the sulfones produced were extracted into the ionic liquid phase (see Fig. 4). Because the TISLs were immiscible with model diesel, the model diesel can be easily separated by decantation after reaction. Dual functions of both oxidation and extraction were combined in one step for the desulfurization of model diesel. Therefore, this IL is quite efficient and effective for deep removal of DBT.

As for the removal of 4,6-DMDBT, the oxidation reaction would almost complete in 7 h and the oxidation product (see Fig. 5), i.e. the corresponding sulfone, remains little in the model diesel phase. This demonstrates that this ODS method is also suitable for the 4,6-DMDBT containing system. Fig. 6 indicates that the removal rate of DBT is much quicker than that of 4,6-DMDBT, while the relative order of oxidation desulfurization rate is 4,6-DMDBT > DBT when using acetic acid as the catalyst in earlier literature [27]. Our interesting result is found to be consistent with that of oxidative desulfurization in the catalytic system (peroxophosphomolybdate/H_2O_2/ILs), which has been owing to
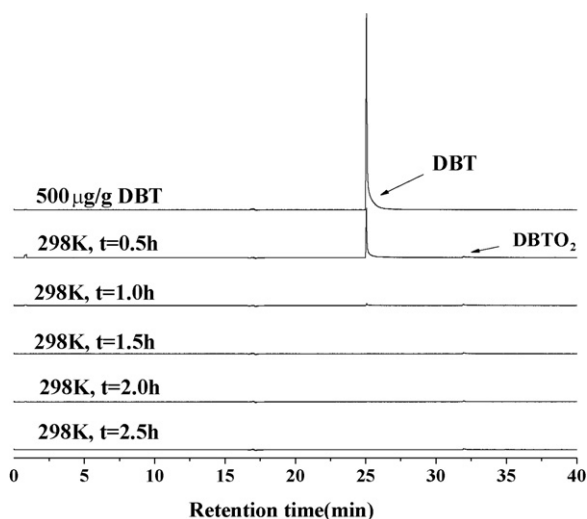
Table 1
Deprotonation energies of different Brönsted acid sites in cation A, B and C.

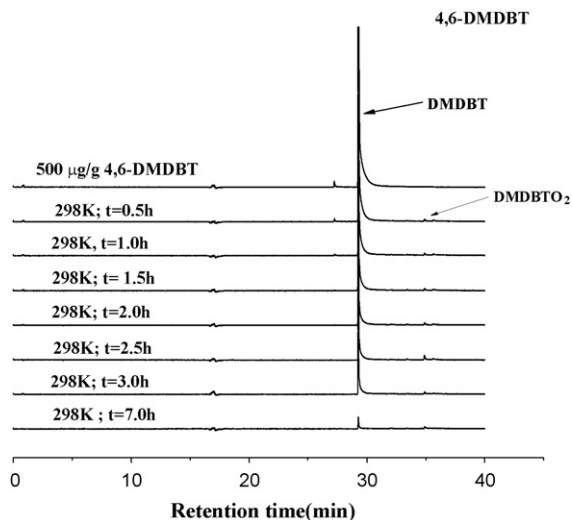| Deprotonation energies (kcal/mol)	H1	H2	H3	H atom in COOH group
A	291.1	287.5	270.7	253.8
B	292.1	287.7	271.4	278.1
C	293.7	293.1	273.6	287.4

Fig. 4. Sulfur-specific GC-AED chromatographs of model diesel (500 μg/g S of DBT in *n*-tetradecane) before and after oxidation.
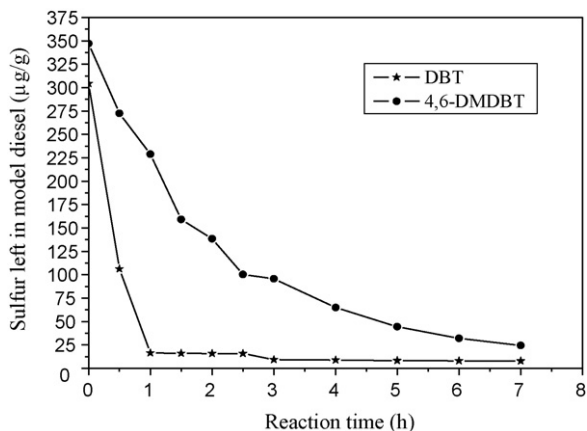

Fig. 5. Sulfur-specific GC-AED chromatograms of model diesel (500 μg/g S of 4,6-DMDBT in *n*-tetradecane) before and after oxidation.

Fig. 6. Different desulfurization results of model diesel containing 4,6-DMDBT and DBT during oxidation catalyzed by IL4 at 298 K.

the steric hindrance of the methyl group of 4,6-DMDBT, i.e. the obstacle for the approach of the sulfur atom to the catalytic active species in IL [10]. In our experiments, it is proposed that the result is mainly caused by better extraction capability of [(CH$_2$)$_2$COOHmim] [HSO$_4$] for DBT than 4,6-DMDBT. As shown in Fig. 6, when the oxidant H$_2$O$_2$ was not added in the system, the model sulfur compounds (DBT and 4,6-DMDBT) had partially extracted by IL4. The extraction of DBT in IL4 is better than that of 4,6-DMDBT, and their sulfur content in model diesel changes from the initial 500 μg/g to 304.3 μg/g and 347 μg/g, respectively.

In this desulfurization process, as for the model diesels containing DBT and 4,6-DMDBT, the sulfur content can be decreased from the initial 500 μg/g to 16.35 and 24.43 μg/g after reacting for 7 h, respectively (see Fig. 6).

Because water and sulfones produced in the ODS process exists in the ionic liquid phase, the product diesel can be separated from the IL phase by simple decantation after reaction, which provided a simple way for separation. The ionic liquid phase separated was extracted three times with equal volume of 1,4-butyrolactone to remove the sulfones produced, and then dried under vacuum at 373 K for 2 h in order to remove the oxidant and water. Fresh H$_2$O$_2$ and model diesel then were added to the ionic liquid for the next run. The ionic liquid could be recycled for 5 times without any obvious change on the desulfurization capability.

3.3. Molecular modeling of TSILs

In this study, DFT method is also included to study the structures of TSILs, in order to find the relationships among the structures, interactions between the anion and cation, acidity and catalytic oxidation properties.

3.3.1. Effect of different cations

In order to study the effect of branch length on acidity, the imidazole-based cations with (–(CH$_2$)$_x$COOH) (*x* = 1, 2, 3) as a branch were optimized, and their structures were listed in Fig. 7.

Each of the three different cations, i.e. [CH$_2$COOHmim], [(CH$_2$)$_2$COOHmim] and [(CH$_2$)$_3$COOHmim], has four different active H atoms as the possible acidic sites, namely, H1, H2, H3, and H in –COOH group. The deprotonation energy for each site was calculated using the following equation:

$$E_{DP} = E_{cation} - E_{cation-H}$$

E_{DP} is the deprotonation energy; E_{cation} is the total energy of cation with the charge of +1; $E_{cation-H}$ is the total energy of cation when removing one active H atom. Bigger deprotonation energy will lead to weaker acidity of the Brönsted acid site.

The deprotonation energies of different Brönsted acid sites in cation A, B and C were combined in Table 1. It shows that the deprotonation energy of each protonic acid site in the imidazole ring would not change obviously when increasing chain length and H3 site is strongest in acidity. As for the –COOH group, the deprotonation energy increases and the acidity decrease with the increase of the chain length. This could be explained by the inductive effect of electron-withdrawing group (methyl imidazole-1-yl) on acidity of carboxylic acids (–COOH). Inductive effects operate through bonds by successive bond polarizations. As such, they diminish rapidly

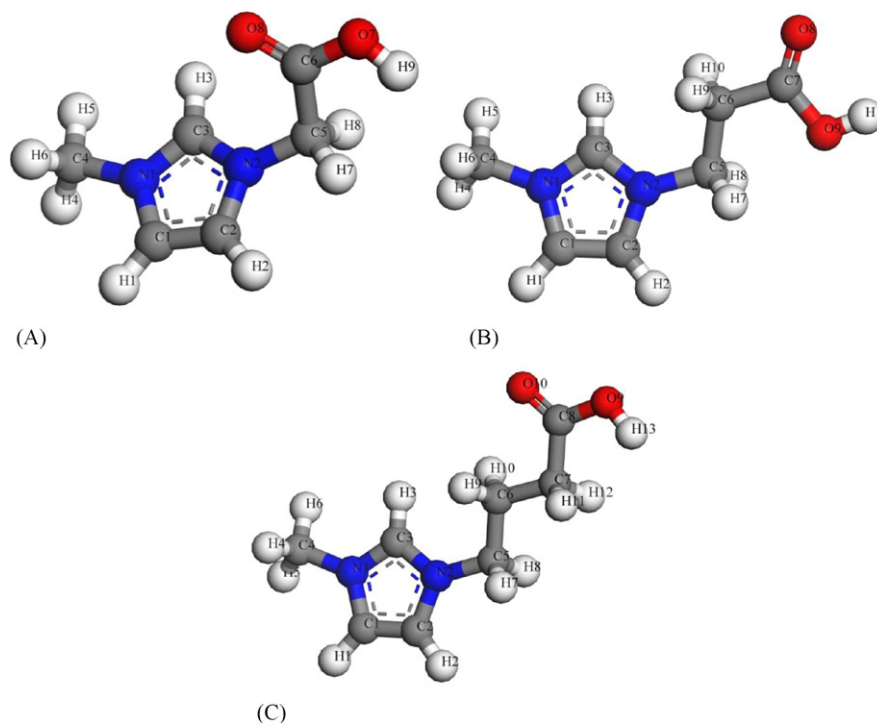**Fig. 7.** Optimized structures of cations in TSILs and their atom labeling. (A) Cation with branch chain –CH$_2$COOH. (B) Cation with branch chain –(CH$_2$)$_2$COOH. (C) Cation with branch chain –(CH$_2$)$_3$COOH.

with distance so that very little effect results if an inductive effect must be transferred through more than four bonds. So the longer the distances between them, the weaker the inductive effect is and the weaker the acidity of carboxylic acids is. The strongest acid site is –COOH group in cation A, while H3 turns to be the major contribution to the acidity in cation B and C. As for the acidity of ILs, there are other factors on acidity exists, such as the acidity of anion, interaction between cation and anion.

3.3.2. Equilibrium existing mode of TSILs

The interaction modes between the cation and anion of each TSIL were investigated. The structures of their cation and anion were optimized, and then the configurations of every TSIL with various modes of interaction were geometrically optimized to find the most stable existing mode. The interaction energy between the cation and anion was calculated using this expression:

$$E_{int} = E_{anion} + E_{cation} - E_{anion+cation}$$

Among the five TSILs, it is easy to study the existing modes of IL3 on account of its simple anion Cl$^-$. Three types of interactions were investigated and shown as A, B and C in Fig. 8. The results show that: (A) When H11 forms one hydrogen bond with the anion Cl$^-$ (see Fig. 8A), only one hydrogen bond (O–)H11···Cl (1.598 Å) exists; and O–H11 bond length is 1.209 Å, which is much longer than normal O–H single bond. It indicates that forming hydrogen bond leads to weaker chemical bond between H and its adjacent O atom. (B) When H3 forms hydrogen bond with Cl as shown in Fig. 8B, two hydrogen bonds, (C–)H3···Cl (2.081 Å) and (C–)H10···Cl (2.601 Å), formed. This was contributed to the strong inductive effect of their adjacent electron withdrawing group, which makes H3 and H10 have more positive charges. Bond strength of C–H3 (1.108 Å) and C–H10 (1.110 Å) are weaker than normal C–H single bond. (C) The H3 and H11 interacted simultaneously with Cl (See Fig. 8C) and the structure parameters were combined in Table 2. Three hydrogen bonds, i.e. (C–)H3···Cl (2.115 Å) and (O–)H11···Cl (2.561 Å),

(C–)H10···Cl (2.246 Å), formed, and the bond lengths of C – H3, O–H11 and C–H10 are 1.120 Å, 0.997 Å and 1.100 Å, respectively. The interaction energy of cation and anion in A, B and C is −93.2, −111.3 and −113.4 kcal/mol as shown in Fig. 8. It can be seen that more hydrogen bonds forming will lead to more stable existing modes of IL. For IL3, the existing mode C is the most energetically stable one.

When the anion is oxy-acid group (including HSO$_4^-$ and H$_2$PO$_4^-$), the interaction between the cation and anion of IL is more complex. The hydrogen bonding is also the major contribution to the interactions between cation and anion. Various different hydrogen bonding modes are calculated, Results show that the terminal oxygen atom of anion should be more easily to form strong hydrogen bond, and more hydrogen bonds formed will lead to stronger interaction. As for anion HSO$_4^-$ and H$_2$PO$_4^-$, when the two terminating oxygen atom forms hydrogen bonds with H3 and H atom in –COOH group, respectively, the interaction energy tends to be more negative, and the existing mode of IL is more energetically stable. The optimized structures of most stable existing modes for four different ILs are shown in Fig. 9. Geometry parameters of most stable configurations of ILs are listed in Table 2.

As for ionic liquids (IL3–IL5) containing the same cation, the interaction energies between cation and anion are −113 kcal/mol, −94.0 kcal/mol and −110.0 kcal/mol, respectively. It means that the strength of the interaction between anion and cation increases in the following order: [(CH$_2$)$_2$COOHmim] [HSO$_4$] (IL4) < [(CH$_2$)$_2$COOHmim] [H$_2$PO$_4$] (IL5) < [(CH$_2$)$_2$COOHmim] Cl (IL3). When the interaction between cation and anion is stronger, that's to say, the hydrogen in cation is more difficult to remove because of hydrogen bonding, indicating that the acidity of TSIL will depends on the anion to a larger extent. According to above discussions, it is evident that the acidity of TSILs should decrease in the order of IL4 > IL5 > IL3, whose trend is the same to that of their desulfurization capability (see Fig. 2). Therefore, the desulfurization capability is close related to their acidity.
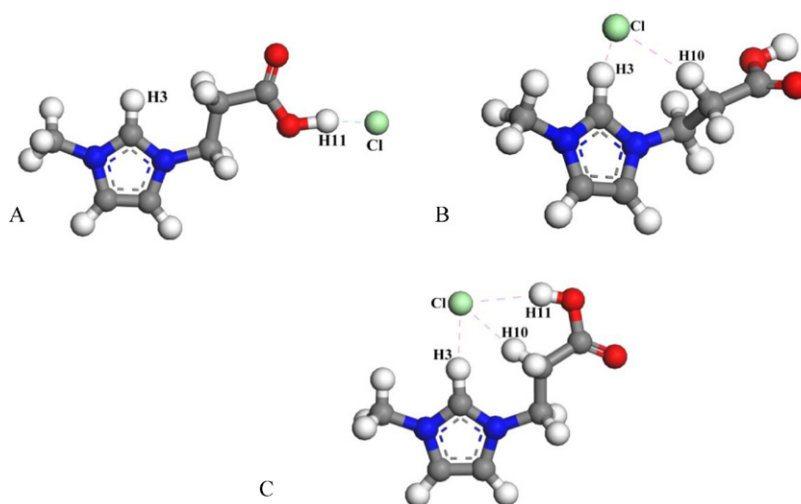
Fig. 8. Three different existing modes of [(CH$_2$)$_2$COOHmim] Cl (IL3). (A) One hydrogen bond formed (Cl$^-$···H11). (B) Two hydrogen bonds formed (Cl···H3; Cl···H10). (C) Three hydrogen bonds formed (Cl$^-$···H3; Cl···H11; Cl···H10).
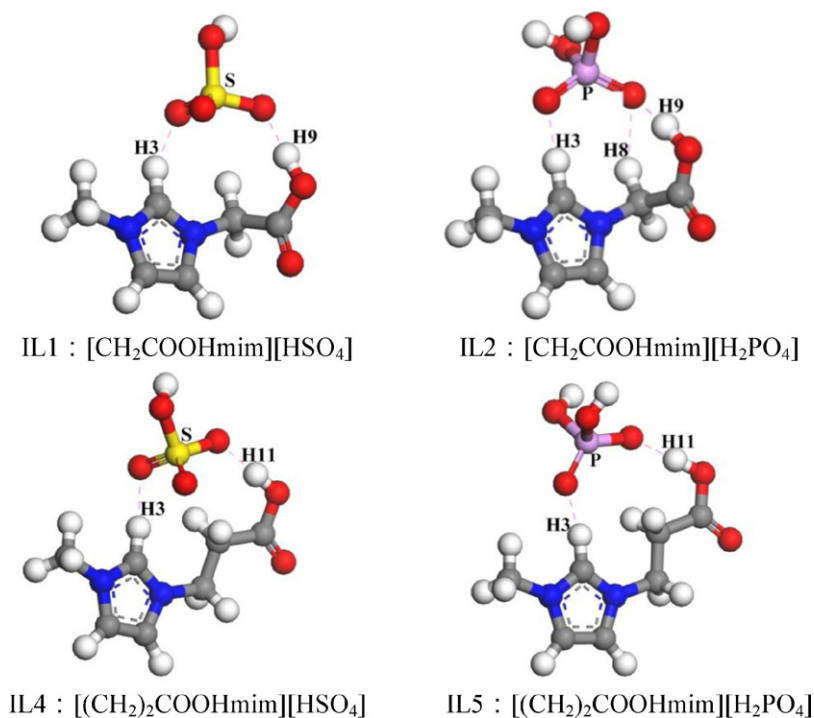

Fig. 9. Optimized structures of most stable hydrogen-bond modes for four different TSILs.

As for the IL1 and IL4 with the same anion [HSO$_4$]$^-$, the active H atoms in their cations will form hydrogen bonds with the terminal O atom of the anion and are difficult to remove, suggesting that the acidity of IL is largely determined by that of anion. So it can be concluded that IL1 and IL4 have similar acidity strength, and it is the same with the acidity of IL2 and IL5. However, catalytic oxidative desulfurization capability is in the order of IL5 >> IL2, IL6 >> IL3 (see Fig. 2), which indicated acidity is not the only factor for the desulfurization, and the extraction capability to sulfur compounds caused by different chain length is also the important factor.

Table 2
Geometry parameters of most stable existing modes of five TSILs.

| Ionic liquids	IL1	IL2	IL3	IL4	IL5
Interaction energy between cation and anion	−100.1	−116.2	−113.4	−94.0	−110.0
O–H bond lengths in –COOH group	1.023	1.048	0.997	1.003	1.021
Bond length between H3 and adjected C	1.091	1.112	1.120	1.097	1.114
H bond between (COO)H and anion (Å)	1.608	1.506	2.561	1.780	1.614
H bond between H3 and anion (Å)	1.992	1.766	2.115	1.912	1.703
Other H bond interaction	–	H8···O	H10···Cl	–	–
Bond length (Å)		2.248	2.246		
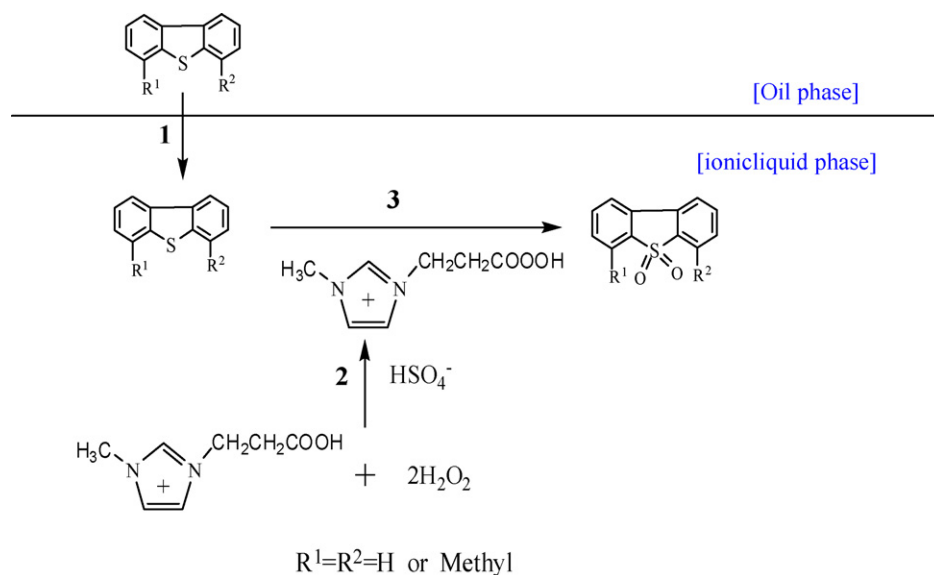
Fig. 10. Oxidation mechanism of sulfur compounds catalyzed by TSILs.

3.4. The reaction mechanism of oxidative desulfurization predicted

According to the discussions above, the reaction mechanism of catalytic oxidation by TSILs can be predicted to experience three steps (see Fig. 10): firstly, the TSILs can extract the sulfur-compounds from the diesel; Secondly, the carboxylic acid group (−COOH) existing in the cation reacts with H_2O_2 in acidic environments, and a peroxycarboxylic acids group (−COOOH) with oxidation functions will be generated in situ; Thirdly, the sulfur compounds extracted into the TSILs were oxidized by the group (−COOOH) to the corresponding sulfones. Whether the rate determining step is the extraction (first step) or oxidation (second step) should be determined by the acid strength and the extraction capability of TSILs.

4. Conclusions

A series of TSILs, working as both catalyst and extractant for ODS process, has been investigated with both experimental and computational methods. The sulfur content of model diesel containing DBT and 4,6-DMDBT can be reduced from the initial 500 to 16.35 μg/g and 24.43 μg/g, and sulfur removal rate could reach 96.7% and 95.1%, respectively. The IL can be recycled 5 times without significant change on activity. DFT method has been applied to study the relationship among the structures, acidities and catalytic oxidation properties of these TSILs. At the same time, an oxidative desulfurization mechanism has been predicted according to the experimental and modeling results. This catalytic system by TSIL offers advantages such as higher efficiency, low amount of ionic liquid, low reaction temperature (298 K), easily separating oil from the catalyst and ease of recycling.

Acknowledgments

References

[1] O. Robert, S. Scott, NPRA Annual Meeting Technical Papers, 2007, AM-07-14.
[2] I.V. Babich, J.A. Moulijn, Fuel 82 (2003) 607.
[3] C. Song, X. Ma, Appl. Catal. B: Environ. 41 (2003) 207.
[4] W. Lo, H. Yang, G. Wei, Green Chem. 5 (2003) 639.
[5] D. Zhao, Z. Sun, F. Li, R. Liu, H. Shan, Energy Fuels 22 (2008) 3065.
[6] S. Cheng, T. Yen, Energy Fuels 22 (2008) 1400.
[7] H. Li, X. Jiang, W. Zhu, J. Lu, H. Shu, Y. Yan, Ind. Eng. Chem. Res. 48 (2009) 9034.
[8] H. Li, L. He, J. Lu, W. Zhu, X. Jiang, Y. Wang, Y. Yan, Energy Fuels 23 (2009) 1354.
[9] D. Xu, W. Zhu, H. Li, J. Zhang, F. Zou, H. Shi, Y. Yan, Energy Fuels 23 (2009) 5929.
[10] L. He, H. Li, W. Zhu, J. Guo, X. Jiang, J. Lu, Y. Yan, Ind. Eng. Chem. Res. 47 (2008) 6890.
[11] W. Zhu, H. Li, X. Jiang, Y. Yan, J. Lu, J. Xia, Energy Fuels 21 (2007) 2514.
[12] M. Vaultier, A. Kirschning, V. Singh, Task-Specific Ionic Liquids as New Phases for Supported Organic Synthesis, Wiley-VCH, Weinheim, 2007, pp. 1–20.
[13] L. Lu, S. Cheng, J. Gao, G. Gao, M. He, Energy Fuels 21 (2007) 383.
[14] J. Wang, D. Zhao, K. Li, Energy Fuels 23 (2009) 3831–3834.
[15] J. Gui, Y. Deng, Z. Hu, Z. Sun, Tetrahedron Lett. 45 (2004) 2681.
[16] J. Gui, H. Ban, X. Cong, X. Zhang, Z. Hu, Z. Sun, J. Mol. Catal. A: Chem. 225 (2004) 27.
[17] J. Gui, X. Cong, D. Liu, X. Zhang, Z. Hu, Z. Sun, Catal. Commun. 5 (2004) 473.
[18] J. Gui, D. Liu, X. Cong, X. Zhang, H. Jiang, Z. Hu, Z. Sun, J. Chem. Res. 8 (2005) 520.
[19] J. Gui, D. Liu, React. Kinet. Catal. Lett. 90 (2007) 35.
[20] J. Gui, D. Liu, C. Wang, F. Lu, J. Lian, H. Jiang, Z. Sun, Synth. Commun. 39 (2009) 3436.
[21] D. Liu, J. Gui, C. Wang, F. Lu, Y. Yang, Z. Sun, Synth. Commun. 40 (2010) 1004.
[22] D. Liu, J. Gui, L. Song, X. Zhang, Z. Sun, Petrol. Sci. Technol. 26 (2008) 973.
[23] D. Liu, J. Gui, X. Zhu, L. Song, Z. Sun, Synth. Commun. 37 (2007) 759.
[24] F.P. Greenspan, D.G. MacKellar, Anal. Chem. 20 (1948) 1061.
[25] X. Zhao, T. Zhang, Y. Zhou, D. Liu, J. Mol. Catal. A: Chem. 271 (2007) 246.
[26] S. Leveneur, T. Salmi, D.Y. Murzin, L. Estel, J. Warna, N. Musakka, Ind. Eng. Chem. Res. 47 (2008) 656.
[27] K. Yazu, M. Makino, K. Ukegawa, Chem. Lett. 33 (2004) 1306.