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Supported ionic liquid [Bmim]FeCl$_4$/Am TiO$_2$ as an efficient catalyst for catalytic oxidative desulfurization of fuels

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Abstract

High activity oxidation of sulfur compounds to sulfones in extractive coupled with catalytic oxidative desulfurization (ECODS) system catalyzed by supported ionic liquid [Bmim]FeCl$_4$/Am TiO$_2$ was reported. The catalysts were analyzed by thermogravimetric (TG), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). It was found that [Bmim]FeCl$_4$ and Am TiO$_2$ had a synergistic effect on the desulfurization system. Effects of calcination temperature of the catalyst and various reaction conditions on the catalytic activity of desulfurization were investigated. Meanwhile, GC-MS analysis were employed to prove the process of the desulfurization. As a solid catalyst, the supported ionic liquid could be separated from the reaction easily. The recycling tests showed that the desulfurization efficiency still remained 100% after 25 times reused. Therefore, the ECODS system has excellent reusability and is promising for industrial application on catalytic oxidative desulfurization.

Keywords: supported ionic liquid catalyst; desulfurization; Am TiO$_2$; dibenzothiophene; catalytic oxidation.

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1. Introduction

Sulfur compounds in fuel is converted to SO_x during combustion, which not only causes serious environmental pollution, but also irreversibly poisons the metal catalysts in automobiles. Consequently, many countries have legislated more stringent environmental regulations to restrict the sulfur content of fuels.[1-2] As sulfur compounds in fuels have greatly contribution to the air pollution of the environment, much attention has been given to the desulfurization of fuel in the past few decades.

In the petroleum refining industry, hydrodesulfurization (HDS) is a conventional method for the removal of sulfur compounds such as thiols, sulfides and disulfides. However, it is difficult to remove some aromatic sulfur containing compounds such as benzothiophene (BT), dibenzothiophene (DBT), 4,6-dimethyl dibenzothiophene (4,6-DMDBT) and their derivatives under mild conditions. To achieve the purpose of deep desulfurization, the conditions of high temperature and pressure as well as highly active catalysts are used in HDS, resulting in a significant increase in the expense. Therefore, various desulfurization technologies have attracted widely attention, such as adsorption[3-8], extraction[9-11], bioprocess[12] and oxidation[13-20]. Among these methods, oxidative desulfurization (ODS) is regarded as a promising strategy to achieve low sulfur content fuel under mild conditions. The oxidants used in ODS include molecular oxygen[21-23], ozone[24], organic peroxide[25] and hydrogen peroxide (H_2O_2)[13-16, 26, 27]. Among these oxidants, H_2O_2 has been extensively used because of its high activity and the only production water after reaction. Many approaches have been used in combination of ODS, such as photocatalytic oxidation[28], microwave catalytic oxidation[29], solvent extraction and oxidation[30, 31] and so on.

Room temperature ionic liquids (ILs) have been traditionally employed as good solvents and extractants in desulfurization of fuels.[11, 26, 32] Due to the unique physical and chemical properties such as non-volatility, good thermal stability, negligible vapor pressure and good solubility characteristics, the ILs received particular interests as novel catalysts in homogeneous system.[33-36] Recently, there has been an increasing attention on supported ILs to structure heterogeneous catalytic systems.[37-39] The supported ILs exhibit similar or enhanced chemical properties and have the advantage

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of being a solid catalyst, which make the catalysts separate from the reaction mixtures conveniently. Another advantage of supported ILs is that loading the ILs on a suitable carrier could increase the dispersion and number of active sites.[37] This process reduces not only the amount of ILs but also the costs. Consequently, various supports have been researched such as layered materials[40], porous glasses[41], mesoporous materials[42, 43], silica gel[44] and metallic oxide[45]. In addition, titanium dioxide (TiO_2) as a good carrier has versatile applications in photocatalysis[28] and photoelectrochemistry[46]. For example, Chen et. al reported a one-pot sol-gel method for the synthesis of Ag/TiO_2 catalyst with highly dispersed Ag on the surface of TiO_2 carrier.[47] The TiO_2-supported Ag catalyst displayed excellent catalytic activity in the reduction of methylene blue in the aqueous phase. Meanwhile, task-specific basic ionic liquid was prepared and successively immobilized on mesoporous silicas of MCM-41 and SBA-15 by Yin and the cooperators.[48] The supported ionic liquid catalyst showed high catalytic performance and good reusability for Knoevenagel condensation in aqueous media. In view of the characters of TiO_2 carrier and supported ionic liquid, this work focused on the supported ILs with the carrier of Am TiO_2 and applied in thermocatalytic oxidative desulfurization system.

The [Bmim]$FeCl_4$ IL has been used in the desulfurization system, however, a large amount of [Bmim]$FeCl_4$ was used and it was difficult to be separated and recycled after the reaction.[49, 50] In this work, [Bmim]$FeCl_4$ was loaded on Am TiO_2 first, and then the supported ionic liquid was employed as catalyst in the extractive coupled with catalytic oxidative desulfurization (ECODS) system. Compared to the previous literature, the as-prepared supported catalyst is superior to most of the traditional heterogeneous solid catalysts on the removal of DBT (Table S1 in Supporting Information). The amount of [Bmim]$FeCl_4$ used in the desulfurization system is very low and it could be separated from the extractant easily after the reaction. The defective sites on the surface of Am TiO_2 have a strong adsorption to atom with lone pair electrons[51, 52], which makes Am TiO_2 an ideal carrier in the supported ionic liquid. The desulfurization efficiency of the supported IL improved significantly compared with the simple mixing of the two substances, indicating that

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$[Bmim]FeCl_4$ and Am TiO_2 had a synergistic effect on the desulfurization system. In addition, the ECODS system had an excellent reused performance with an extremely low amount of catalyst. The desulfurization efficiency still remain 100% after recycling for 25 times, this result is far superior to the reported literature.[43, 53] It will be conducive to catalytic oxidative desulfurization research for industrial application.

2. Experimental section

2.1 materials

BT, DBT and 4,6-DMDBT were purchased from Sigma-Aldrich. Tetradecane was purchased from Aladdin. Tetrabutyl titanate, absolute ethyl alcohol, 30 wt.% H_2O_2, Iron (III) chloride anhydrous ($FeCl_3$) and *n*-octane were purchased from Sinopharm Chemical Reagent Co., Ltd. The conventional ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim]BF_4$), 1-n-octyl-3-methylimidazolium tetrafluoroborate ($[Omim]BF_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[Bmim]PF_6$), 1-n-octyl-3-methylimidazolium hexafluorophosphate ($[Omim]PF_6$) and the 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) were purchased from Shanghai Chengjie Chemical Co., Ltd. *N*-octane was of chemical pure, other chemicals used in the experiments were of analytical reagent grade without further purification.

2.2 **Preparation of $[Bmim]FeCl_4$/Am TiO_2 catalyst**

The $[Bmim]FeCl_4$ was prepared based on the previous work.[49] The supported ionic liquid catalyst was carried out via the following steps (scheme 1). First, 4.6 mmol tetrabutyl titanate was dissolved in 10 mL absolute ethyl alcohol under stirring, then 0.9 mL deionized water was added to form solution A. Next, 0.5 mmol $[Bmim]FeCl_4$ was dissolved in 10 mL absolute ethyl alcohol to form solution B. Solution A was magnetically stirred for 0.5 h at room temperature, and then solution B filled slowly and stirred for another 2 h to form a homogeneous mixed solution. The mixed solution was aged overnight, and then drying at 60^{o}C and 100^{o}C to obtain a powder. Finally, the powder was calcined in muffle furnace from room temperature to

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250^{o}C under air atmosphere with a heating rate of 5^{o}C/min and then kept at 250^{o}C for 180 min before cooling. Am TiO_2 and other samples with different metal-based ionic liquids and treated temperatures were prepared with the similar method above.

2.3 Characterization of the catalysts

Thermogravimetric (TG) analysis was done on STA-449C Jupiter (NETZSCH Corporation, Germany). The sample was tested from room temperature to 600^{o}C under air atmosphere with a heating rate of 10^{o}C/min. The powder X-ray diffraction (XRD) analysis was carried out on a Bruker D8 diffractometer with high-intensity Cu-Kα radiation. Fourier Transform Infrared Spectroscopy (FT-IR) were performed on a Nicolet FT-IR spectrophotometer (Nexus 470, Thermo Electron Corporation) using KBr pellets at room temperature. X-ray photoelectron spectroscopy (XPS) was measured on a PHI5300 with a monochromatic Mg- Kα source to explore the elements on the surface. The GC-MS analysis was measured on Agilent 7890/5975C-GC/MSD (HP-5 MS column, 30 m × 250 μm i.d. × 0.25 μm; temperature program: 100ºC-temperature rising 15ºC/min - 200ºC for 10 min) to characterize the oxidized sulfur compounds after the desulfurization reaction.

2.4 Oxidative desulfurization procedure

In a typical reaction run, 5 mg $[Bmim]FeCl_4$/Am TiO_2, 1 mL conventional IL and 5 mL model oil with DBT were added into a flask. Then 32 μL H_2O_2 was added, and the mixture was stirred vigorously to complete the desulfurization reaction. After the reaction, the remained sulfur-containing compounds in model oil were analyzed by GC-FID (Agilent 7890A; HP-5, 30 m × 0.32 mm i.d. × 0.25 μm; FID: Agilent). The conversion of DBT in the model oil was used to calculate the removal of sulfur compounds. Model oils were prepared by dissolving DBT, BT and 4,6-DMDBT in n-octane with a corresponding S-content of 500 ppm, 250 ppm, and 250 ppm, respectively. The internal standard was tetradecane.

3. Results and discussion

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3.1 Characterization of the catalysts

In order to investigate the correlation between structure and properties of the catalysts, various of characteristics were taken. TG analysis of TiO_2 and $[Bmim]FeCl_4/TiO_2$ under air atmosphere were first taken to study the calcining process of the samples. Then Am TiO_2 and the catalysts calcined under different temperatures were characterized by wide-angle powder XRD, FT-IR and XPS. As shown in Fig. 1(A), when the catalyst and TiO_2 were calcined at 250^{o}C, the weight loss of TiO_2 was 3.8% more than $[Bmim]FeCl_4/TiO_2$. Since there was no obvious loss of $[Bmim]FeCl_4$ when the temperature was below 290^{o}C [Fig. 1(B)], this difference of loss was caused by the decomposition of $Ti(OH)_4$ and the desorption of water on the catalyst. As could be seen in Fig. 2, no typical diffraction was detected in the samples calcined at 250^{o}C [Fig. 2(a) and (b)], indicating that the synthesized TiO_2 might present in an amorphous structure. As for TiO_2, the FT-IR spectra characteristic peaks around 633 cm^{-1}, 1400 cm^{-1} and 1548 cm^{-1} were observed in Fig. 3(a). The peak at 1400 cm^{-1} were attributed to Ti-O bond, which came from $Ti(OH)_4$.[54] When the calcination temperatures up to 400^{o}C, since the $[Bmim]FeCl_4$ decompose violently, the difference of the loss between the two samples reached 6.9% [Fig. 1(A)]. Finally, calcination temperatures at 550^{o}C, the weight loss of $[Bmim]FeCl_4/TiO_2$ was 8.3% more than TiO_2 [Fig. 1(A)]. The decomposition of $[Bmim]FeCl_4$ would result in the decrease of catalytic activity in the ECODS system. As the catalysts calcined at 400 and 550^{o}C, the diffraction peaks were observed and became stronger with the increasing of calcination temperature [Fig. 2 (c) and (d)]. The peaks at 25.36^{o} (101), 38.02^{o} (111), 48.12^{o} (200) and 55.12^{o} (211) were clearly representative of the anatase phase TiO_2 (JSPDF NO.84-1285). As displayed in Fig. 3, The peaks at 1400 cm^{-1} turned weak when the calcination temperatures increased from 250^{o}C to 550^{o}C, meaning the $Ti(OH)_4$ had broken down into TiO_2 and H_2O. The absorption peak of C=N in the imidazole ring was around 1591 cm^{-1}, however, there was no obvious peaks found from the curves in Fig. 3(b)-(d), that's because the peak was covered by TiO_2 around 1548 cm^{-1}. Meantime, as shown in the Fig. 3(B) (the catalyst calcination temperatures at 250^{o}C), the ring stretching vibrations of the imidazole ring around

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1164 cm^{-1} and 1107 cm^{-1} could be detected[55]. The results proved that [Bmim]FeCl$_4$ has been loaded on Am TiO$_2$ and intact.

The XPS analysis provided further information for the evaluation of the purity and surface composition of the [Bmim]FeCl$_4$/Am TiO$_2$ catalyst calcined at 250^{o}C. The survey XPS spectrum in Fig. 4(A) demonstrated that the main elements on the surface of the catalyst are C, O, N, Cl, Ti and Fe. The C 1s peak shown in Fig. 4(B) with two peaks around 284.9 eV and 288.5 eV could be assigned to the sp^2 hybridization of carbon atoms [56]. As can be seen from Fig. 4(C), the N 1s peak is located at 399.8 eV, which could be ascribed to sp^2-hybridized nitrogen (C=N-C)[56]. The high-resolution spectrum [Fig. 4(D)] showed that the peak binding energies of 529.9 eV was assigned to O 1s [54]. The peak binding energy of 198.1 eV is ascribed to Cl 2p [Fig. 4(E)] [57]. The Ti 2p region displayed in Fig. 4(F) with the characteristic peaks at 458.4 and 464.0 eV was ascribed to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ respectively[54]. The result of XPS further confirmed the existence of [Bmim]FeCl$_4$ and Am TiO$_2$ in the [Bmim]FeCl$_4$/Am TiO$_2$ composites, which is consistent with the result of FT-IR analysis.

3.2 Effects of the calcination temperatures on sulfur removal

To investigate the effect of calcination temperatures of the catalysts on sulfur removal[58], three temperatures of 250^{o}C, 400^{o}C and 550^{o}C were taken on [Bmim]FeCl$_4$/TiO$_2$. The results of various calcination temperatures catalysts with different reaction times were shown in Fig. 5. The results indicated that sulfur removal decreased from 99.6% to 31.3% in 1 h with the increasing temperatures from 250^{o}C to 550^{o}C. There is no significant increase in sulfur removal when prolonging the reaction time for another 30 min. Based on the results of TG analysis (Fig. 1), [Bmim]FeCl$_4$ remained stable at 250^{o}C and began to decompose at 290^{o}C, meaning that the catalyst calcined at 250^{o}C presents the highest desulfurization efficiency among the three calcination temperatures. However, as the carrier Am TiO$_2$ transformed from amorphous to anatase phase at 400 and 550^{o}C, the defective sites on the surface reduced, and it weakened the performance of attracting DBT. Both of the two factors resulted in the higher calcination temperatures, the lower sulfur removal

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was obtained in the ECODS system. Thus, the catalyst calcined at 250°C and reaction for 1 h were chosen as the optimal conditions in the desulfurization system.

3.3 Effect of different desulfurization system on sulfur removal

The desulfurization systems had great effect on sulfur removal [59, 60], the results of various systems contained different catalysts are shown in Fig. 6. As can be seen, the sulfur removal was only 32.3% without catalyst. The sulfur removal reached 82.1% when the [Bmim]$FeCl_4$ and Am TiO_2 were employed only by simple mix together. If the [Bmim]$FeCl_4$ was loaded on Am TiO_2 first, and then used as catalyst in the ECODS system, the sulfur removal increased evidently and reached 99.6%. These results indicated that [Bmim]$FeCl_4$ and Am TiO_2 had a synergistic effect after loading, which could improve the desulfurization efficiency greatly. However, sulfur removal in desulfurization systems containing other supported ionic liquid, for example, [Bmim]$CuCl_3$/Am TiO_2, [Bmim]$ZnCl_3$/Am TiO_2 and [Bmim]$CoCl_3$/Am TiO_2, were below 65%. It's obvious that [Bmim]$FeCl_4$/Am TiO_2 had the best catalytic ability among different supported ionic liquid catalysts. Further research was focused on studying the desulfurization system catalyzed by [Bmim]$FeCl_4$/Am TiO_2.

3.4 Effect of the amount of catalyst on sulfur removal

Fig. 7 shows the effect of catalyst amount on sulfur removal, and sulfur removal increased with the increasing of catalyst amount. When the amount of the catalyst was increased from 1 mg to 5 mg, the sulfur removal increased from 86.2% to 99.6% in 1 h. Compared with the previous research, this work greatly reduced the amount of [Bmim]$FeCl_4$ to achieve ultra deep desulfurization.[49] However, when 7.5 mg catalyst was used, the sulfur removal was only reached 98.4%, which is due to [Bmim]$FeCl_4$ might increase the decomposition of H_2O_2, resulting in reduced efficiency of the oxidant.[37] Therefore, 5 mg catalyst was chosen as the most suitable amount in the following investigation.

3.5 The effect of different reaction temperature on sulfur removal

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The reaction temperature is an important parameters in the desulfurization system, the sulfur removal at different reaction temperatures and times were displayed in Fig. 8. With the increase of the temperature from 40 to 60^{o}C, a continuous increase in the removal of DBT was observed. When the desulfurization system was reacted for 1 h, the sulfur removal was 47.4%, 79.6% and 99.6% at 40, 50 and 60^{o}C, respectively. However, the sulfur removal appeared to be unsatisfactory at 30^{o}C, mainly owing to the catalyst and oxidant cannot work efficiently at a low reaction temperature.[61] Based on the above results, the reaction temperature of 60^{o}C was recommended.

3.6 The effect of different n(H_2O_2)/n(DBT) on sulfur removal

To investigate the amount of H_2O_2 on the removal of DBT, the desulfurization reaction was carried out under various molar ratios of H_2O_2 and DBT (O/S) at 60^{o}C. According to the stoichiometric reaction, 2 mol of H_2O_2 are consumed for oxidation of 1 mol DBT to $DBTO_2$. However, as shown in Fig. 9, the sulfur removal was only 62.3% when the O/S was 2 within 1 h. The reason for this was that there existed two parallel reactions in the oxidation, one was the oxidation of DBT and the other was the self-decomposition of H_2O_2. When the O/S rose to 4, sulfur removal reached 99.6% in 1 h. Thus, the O/S of 4 was chosen as the optimal ratio.

3.7 Effects of different extractants on sulfur removal

In the ECODS system, one of the main factors was the kind of extractants. To investigate the influence of different extractants on desulfurization, four conventional ILs [Bmim]BF_4, [Omim]BF_4, [Bmim]PF_6 and [Omim]PF_6 were used in ECODS system. [Bmim]$FeCl_4$/Am TiO_2 was insoluble in the ILs, which made the catalyst easy to be separated and recovered after reaction. In addition, neither the catalyst nor the ILs could dissolution in the model oil. The results in Table 1 showed the sulfur removal in ECODS system with the four ILs were 75.8%, 99.6%, 17.9% and 32.2%, respectively, while the sulfur removal in the extractive desulfurization (EDS) system were 17.2%, 29.3%, 15.1% and 26.5%, respectively.[61] Therefore, [Omim]BF_4 was

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chosen as the suitable extractant in the desulfurization experiments.

3.8 Effects of the nature of the substrates on sulfur removal

The nature of the substrates is a crucial factor to influence the sulfur removal in the desulfurization system. Besides DBT, two other representatives BT and 4,6-DMDBT were chosen to investigate the desulfurization efficiency. As shown in Fig. 10, the sulfur removal decreased in the order DBT > BT > 4,6-DMDBT under the corresponding reaction conditions. The sulfur removal of DBT and BT increased over time obviously, and the sulfur removal of DBT could reach deep desulfurization within 1 h, while the sulfur removal of BT increased from 56.2% in 1 h to 81.3% in 2 h. However, what's unexpected is that the removal of 4,6-DMDBT in the desulfurization system is poor, the sulfur removal was only 28.9% in 1 h and increased slightly in another hour (35%). For DBT and BT, the result could be attributed to the different electron density of the sulfur atoms[62], the electron density of BT (5.739) is lower than DBT (5.758), which led to the low desulfurization efficiency. Though 4,6-DMDBT had the highest electron density (5.760) of the three sulfur containing compounds, the two methyl groups on the benzene ring brought great steric hindrance, which became the main difficulties and caused the lowest sulfur removal in the ECODS system.[59, 60]

3.9 Recycling performance of the ECODS system

Recycling ability and multiphase reaction are two important factors in industrial application. The recycling performance of the ECODS system was investigated on the removal of DBT in model oil. Judging from the results reported in literatures[43, 50, 53], the stability and recycle ability of the ECODS system in this work was more outstanding than other desulfurization systems. Since the catalyst and IL were immiscible in the model oil, the model oil could be transferred from the system by decanting and drying easily, then new model oil containing DBT was added for next run. There was some white DBT sulfone residue in the system after oxidation. Though the amount of DBT sulfones increased over reaction times, it has no effect on the

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sulfur removal ability in the ECODS system. The results in Fig. 11 showed that the ECODS system had an excellent recycling performance, the sulfur removal could still reach 100% after recycling for 25 times. This result also showed that [Bmim]$FeCl_4$ did not leak from the carrier after the reaction, since the sulfur removal was only 82.1% when the [Bmim]$FeCl_4$ and Am TiO_2 were employed with simple mixed together (Fig. 6). Supported ionic liquid has unique advantages compared with other ionic liquid catalysts. The excellent cycling performance would promote the ECODS system applied to industrial application of catalytic oxidative desulfurization.

3.10 The proposed reaction process of ECODS system

In order to research the mechanism of the ECODS system, sulfur compounds in model oil phase and IL phase were measured by GC-MS. During the reaction, DBT was first extracted into ionic liquid phase from oil phase under rigorous stirring, then it was oxidized by H_2O_2 with catalyst. After reaction, the model oil was in the upper layer while the others were in the lower layer. The model oil was withdrawn and analyzed by GC-MS directly after reaction for 30 min, 60 min and recycled for 25 times, the results were shown in Fig. 12(A). There was a strong peak belong to DBT (m/z = 184.0) [53, 63] in the oil phase with the sulfur removal of 74.2% after reaction for 30 min. The peak of DBT was not obvious after reaction for 60 min because the sulfur removal reached 99.6%. There was no peak of DBT to be found in the oil phase since the sulfur removal remained 100% after 25 times recycled. The results of IL phase was shown in Fig. 12(B), the ionic liquid phase was first re-extracted by tetrachloromethane, and then detected by GC-MS. The peak of $DBTO_2$ (m/z = 216.0) [53, 63] could be detected in ionic liquid phase, meaning $DBTO_2$ was the final oxidizing product of DBT. Based on the results above, apart from the ultra low content of DBT, there was no other sulfur containing compounds detected in the oil phase after reaction, meaning clean oil was obtained after catalytic oxidative desulfurization.

Conclusions

In conclusion, a supported ionic liquid catalyst [Bmim]$FeCl_4$/Am TiO_2 was

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synthesized and investigated in this work. The catalyst had high desulfurization efficiency in the removal of DBT in ECODS system. The most appropriate conditions, catalyst calcination temperature of 250^{o}C, amount of the catalyst of 5 mg, temperature of 60^{o}C, O/S of 4, extractant of 1 mL, reaction time of 1 h were obtained. GC-MS analysis was employed to detect the sulfur containing compounds after the reaction and to investigate the process of the ECODS system. The ECODS system presents an excellent recycling performance with extremely low amount of supported ionic liquid, the desulfurization efficiency still remain 100% after recycling for 25 times. Therefore, the supported ionic liquid catalyst is promising for catalytic oxidation desulfurization in industrial application.

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References

1 J. Zhang, D. S. Zhao, L. Y. Yang and Y. B. Li, *Chem. Eng. J.*, 2010, **156**, 528-531.
2 B. B. Shao, L. Shi and X. Meng, *Ind. Eng. Chem. Res.*, 2014, **53**, 6655-6663.
3 W. L. Li, Q. F. Liu, J. M. Xing, H. S. Gao, X. C. Xiong, Y. G. Li, X. Li and H. Z. Liu, *AIChE J.*, 2007, **53**, 3263-3268.
4 Y. L. Zhang, Y. X. Yang, H. X. Han, M. Yang, L. Wang, Y. N. Zhang, Z. X. Jiang and C. Li, *Appl. Catal., B*, 2012, **119**, 13-19.
5 J. M. Palomino, D. T. Tran, J. L. Hauser, H. Dong and S. R. J. Oliver, *J. Mater. Chem. A*, 2014, **2**, 14890-14895.
6 J. Xiao, X. X. Wang, Y. S. Chen, M. Fujii and C. S. Song, *Ind. Eng. Chem. Res.*, 2013, **52**, 15746-15755.
7 J. Xiao, X. X. Wang, M. Fujii, Q. J. Yang and C. S. Song, *AIChE J.*, 2013, **59**, 1441-1445.
8 J. Xiong, W. S. Zhu, H. P. Li, W. J. Ding, Y. H. Chao, P. W. Wu, S. H. Xun, M. Zhang and H. M. Li, *Green Chem.*, 2015, **17**, 1647-1656.
9 A. Bosmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz and P. Wasserscheid, *Chem. Commun.*, 2001, 2494-2495.

View Article Online
DOI: 10.1039/C5RA00999E

10 Y. Nie, C. X. Li, A. J. Sun, H. Meng and Z. H. Wang, *Energy Fuels*, 2006, **20**, 2083-2087.

11 C. P. Li, D. Li, S. S. Zou, Z. Li, J. M. Yin, A. L. Wang, Y. N. Cui, Z. L. Yao and Q. Zhao, *Green Chem.*, 2013, **15**, 2793-2799.

12 S. Guchhait, D. Biswas, P. Bhattacharya and R. Chowdhury, *Chem. Eng. J.*, 2005, **112**, 145-151.

13 D. Huang, Z. Zhai, Y. C. Lu, L. M. Yang and G. S. Luo, *Ind. Eng. Chem. Res.*, 2007, **46**, 1447-1451.

14 C. Komintarachat and W. Trakarnpruk, *Ind. Eng. Chem. Res.*, 2006, **45**, 1853-1856.

15 J. T. Sampanthar, H. Xiao, H. Dou, T. Y. Nah, X. Rong and W. P. Kwan, *Appl. Catal., B*, 2006, **63**, 85-93.

16 B. Y. Zhang, Z. X. Jiang, J. Li, Y. N. Zhang, F. Lin, Y. Liu and C. Li, *J. Catal.*, 2012, **287**, 5-12.

17 Y. Lu, Y. Wang, L. D. Gao, J. C. Chen, J. P. Mao, Q. S. Xue, Y. Liu, H. H. Wu, G. H. Gao and M. Y. He, *ChemSusChem*, 2008, **1**, 302-306.

18 J. H. Xu, S. Zhao, W. Chen, M. Wang and Y. F. Song, *Chem. Eur. J.*, 2012, **18**, 4775-4781.

19 C. Li, Z. X. Jiang, J. B. Gao, Y. X. Yang, S. J. Wang, F. P. Tian, F. X. Sun, X. P. Sun, P. L. Ying and C. R. Han, *Chem. Eur. J.*, 2004, **10**, 2277-2280.

20 Y. S. Chi, C. P. Li, Q. Z. Jiao, Q. S. Liu, P. F. Yan, X. M. Liu and U. Welz-Biermann, *Green Chem.*, 2011, **13**, 1224-1229.

21 H. Y. Lü, J. B. Gao, Z. X. Jiang, Y. X. Yang, B. Song and C. Li, *Chem. Commun.*, 2007, 150-152.

22 W. Zhang, H. Zhang, J. Xiao, Z. X. Zhao, M. X. Yu and Z. Li, *Green Chem.*, 2014, **16**, 211-220.

23 J. Wang, Q. Guo, C. Zhang and K. Li, *RSC Adv.*, 2014, **4**, 59885-59889.

24 C. H. Ma, B. Dai, P. Liu, N. Zhou, A. J. Shi, L. L. Ban and H. W. Chen, *J. Ind. Eng. Chem.*, 2014, **20**, 2769-2774.

25 A. Chica, A. Corma and M. E. Domine, *J. Catal.*, 2006, **242**, 299-308.

26 F. T. Li, C. G. Kou, Z. M. Sun, Y. J. Hao, R. H. Liu and D. S. Zhao, *J. Hazard. Mater.*, 2012, **205**, 164-170.

27 D. S. Zhao, J. L. Wang and E. Zhou, *Green Chem.*, 2007, **9**, 1219-1222.

28 W. S. Zhu, C. Wang, H. P. Li, P. W. Wu, S. H. Xun, W. Jiang, Z. G. Chen, Z. Zhao and H. M. Li, *Green Chem.*, 2015, **17**, 2464-2472.

29 M. Ibe, S. Gomez, K. A. Malinger, P. Fanson and S. L. Suib, *Appl. Catal., B*, 2007, **69**, 235-239.

30 H. S. Gao, C. Guo, J. M. Xing, J. M. Zhao and H. Z. Liu, *Green Chem.*, 2010, **12**, 1220-1224.

31 H. Y. Lü, S. N. Wang, C. L. Deng, W. Z. Ren and B. C. Guo, *J. Hazard. Mater.*, 2014, **279**, 220-225.

32 J. H. Xu, S. Zhao, Y. C. Ji and Y. F. Song, *Chem. Eur. J.*, 2013, **19**, 708-714.

33 P. S. Kulkarni and C. A. M. Afonso, *Green Chem.*, 2010, **12**, 1139-1149.

34 D. A. Vicic and W. D. Jones, *J. Am. Chem. Soc.*, 1997, **119**, 10855-10856.

35 E. Lissner, W. F. de Souza, B. Ferrera and J. Dupont, *ChemSusChem*, 2009, **2**, 962-964.

36 F. L. Yu, Y. Y. Wang, C. Y. Liu, C. X. Xie and S. T. Yu, *Chem. Eng. J.*, 2014, **255**, 372-376.

37 J. Zhang, A. J. Wang, X. Li and X. H. Ma, *J. Catal.*, 2011, **279**, 269-275.

38 Y. Chen, S. Zhao and Y. F. Song, *Appl. Catal., A*, 2013, **466**, 307-314.

39 H. Li, P. S. Bhadury, B. Song and S. Yang, *RSC Adv.*, 2012, **2**, 12525-12551.

View Article Online
DOI: 10.1039/C5RA00999E

40 W. S. Zhu, B. L. Dai, P. W. Wu, Y. H. Chao, J. Xiong, S. H. Xun, H. P. Li and H. M. Li, *ACS Sustainable Chem. Eng.*, 2015, **3**, 186-194.

41 M. Haumann, K. Dentler, J. Joni, A. Riisager and P. Wasserscheid, *Adv. Synth. Catal.*, 2007, **349**, 425-431.

42 X. Wang, X. Zhang, H. Liu, K. L. Yeung and J. Wang, *Chem. Eng. J.*, 2010, **156**, 562-570.

43 L. Zhang, Y. D. Cui, C. P. Zhang, L. Wang, H. Wan and G. F. Guan, *Ind. Eng. Chem. Res.*, 2012, **51**, 16590-16596.

44 M. Y. Zhu, G. Q. Luo, L. H. Kang and B. Dai, *RSC Adv.*, 2014, **4**, 16769-16776.

45 T. Selvam, A. Machoke and W. Schwieger, *Appl. Catal., A*, 2012, **445**, 92-101.

46 K. C. Goddeti, S. M. Kim, Y. K. Lee, S. H. Kim and J. Y. Park, *Catal. Lett.*, 2014, **144**, 1411-1417.

47 H. J. Zhang, X. Y. Li and G. H. Chen, *J. Mater. Chem.*, 2009, **19**, 8223-8231.

48 H. H. Zhao, N. Y. Yu, Y. Ding, R. Tan, C. Liu, D. H. Yin, H. Y. Qiu and D. L. Yin, *Micropor. Mesopor. Mat.*, 2010, **136**, 10-17.

49 H. M. Li, W. S. Zhu, Y. Wang, J. T. Zhang, J. D. Lu and Y. S. Yan, *Green Chem.*, 2009, **11**, 810-815.

50 S. H. Xun, W. S. Zhu, D. Zheng, L. Zhang, H. Liu, S. Yin, M. Zhang and H. M. Li, *Fuel*, 2014, **136**, 358-365.

51 U. Terranova and D. R. Bowler, *J. Phys. Chem. C*, 2010, **114**, 6491-6495.

52 G. Liu, J. A. Rodriguez, Z. Chang, J. Hrbek and L. Gonzalez, *J. Phys. Chem. B*, 2002, **106**, 9883-9891.

53 W. S. Zhu, P. W. Wu, L. Yang, Y. H. Chang, Y. H. Chao, H. M. Li, Y. Q. Jiang, W. Jiang and S. H. Xun, *Chem. Eng. J.*, 2013, **229**, 250-256.

54 C. Wang, W. S. Zhu, Y. H. Xu, H. Xu, M. Zhang, Y. H. Chao, S. Yin, H. M. Li and J. G. Wang, *Ceram. Int.*, 2014, **40**, 11627-11635.

55 F. Wang, Z. Q. Zhang, J. Yang, L. P. Wang, Y. Lin and Y. Wei, *Fuel*, 2013, **107**, 394-399.

56 Q. J. Xiang, J. G. Yu and M. Jaroniec, *Chem. Soc. Rev.*, 2012, **41**, 782-796.

57 J. Di, J. Xia, S. Yin, H. Xu, L. Xu, Y. Xu, M. He and H. Li, *RSC Adv.*, 2014, **4**, 14281-14290.

58 Z. Hasan, J. Jeon and S. H. Jhung, *J. Hazard. Mater.*, 2012, **205**, 216-221.

59 Y. Q. Jiang, W. S. Zhu, H. M. Li, S. Yin, H. Liu and Q. J. Xie, *ChemSusChem*, 2011, **4**, 399-403.

60 J. T. Zhang, W. S. Zhu, H. M. Li, W. Jiang, Y. Q. Jiang, W. L. Huang and Y. S. Yan, *Green Chem.*, 2009, **11**, 1801-1807.

61 Y. X. Ding, W. S. Zhu, H. M. Li, W. Jiang, M. Zhang, Y. Q. Duan and Y. H. Chang, *Green Chem.*, 2011, **13**, 1210-1216.

62 S. Otsuki, T. Nonaka, N. Takashima, W. H. Qian, A. Ishihara, T. Imai and T. Kabe, *Energy Fuels*, 2000, **14**, 1232-1239.

63 W. Jiang, W. S. Zhu, Y. H. Chang, Y. H. Chao, S. Yin, H. Liu, F. X. Zhu and H. M. Li, *Chem. Eng. J.*, 2014, **250**, 48-54.

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DOI: 10.1039/C5RA00999E

Figures captions

Fig. 1. TG analysis of (A): (a) Am TiO_2, (b) [Bmim]$FeCl_4$/Am TiO_2 and (B): [Bmim]$FeCl_4$.

Fig. 2. Wide angle XRD patterns at different calcination temperatures of (a) 250 ^oC TiO_2, (b) 250 ^oC [Bmim]$FeCl_4$/TiO_2, (c) 400 ^oC [Bmim]$FeCl_4$/TiO_2 and (d) 550 ^oC [Bmim]$FeCl_4$/TiO_2.

Fig. 3. FT-IR spectra of (a) 250 ^oC TiO_2, (b) 250 ^oC [Bmim]$FeCl_4$/TiO_2, (c) 400 ^oC [Bmim]$FeCl_4$/TiO_2 and (d) 550 ^oC [Bmim]$FeCl_4$/TiO_2.

Fig. 4. XPS spectra of [Bmim]$FeCl_4$/Am TiO_2. (A) survey of the catalyst; (B) C 1s; (C) N 1s; (D) O 1s; (E) Cl 2p and (F) Ti 2p3.

Fig. 5. The effects of different calcination temperatures on removal of DBT.

Fig. 6. The effect of different desulfurization systems on removal of DBT.

Fig. 7. The effect of the amount of catalyst on removal of DBT.

Fig. 8. The effects of different reaction temperatures on removal of DBT.

Fig. 9. The effect of H_2O_2/DBT (molar ratio) on removal of DBT.

Fig. 10. Removal of different substrates in the desulfurization system.

Fig. 11. The recycle performance of the desulfurization system.

Fig. 12. The GC-MS of main compounds of the oil phase (A) and ionic liquid phase (B).

Scheme 1. Preparation of the supported ionic liquid catalyst [Bmim]$FeCl_4$/Am TiO_2

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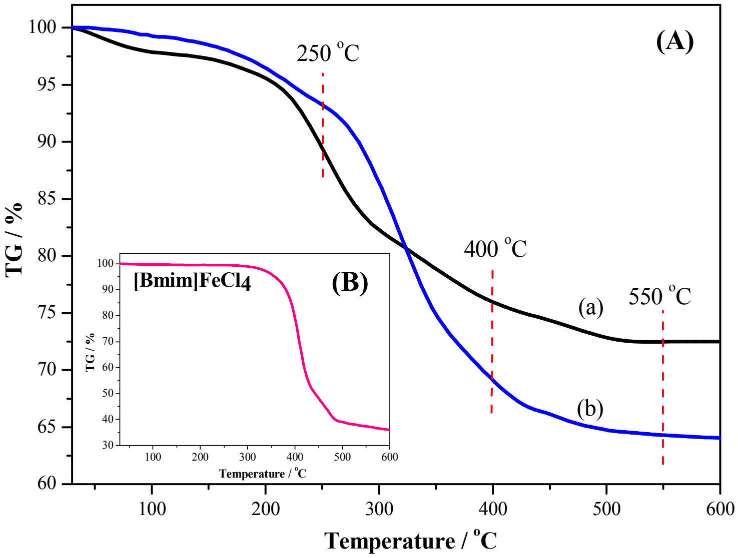
Figures



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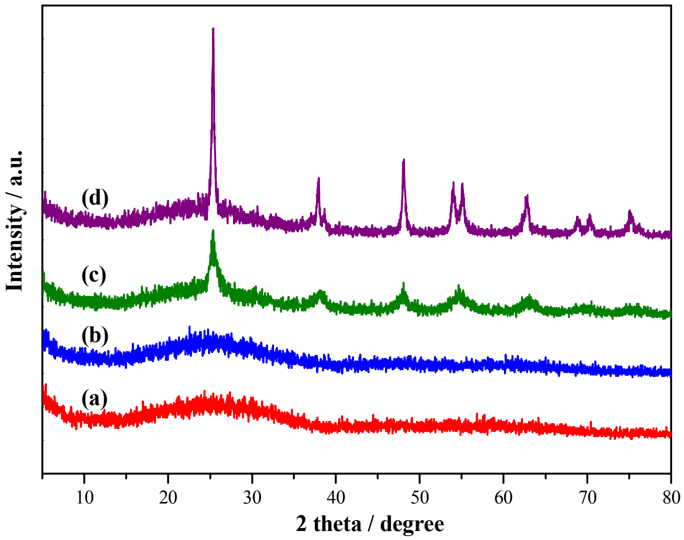

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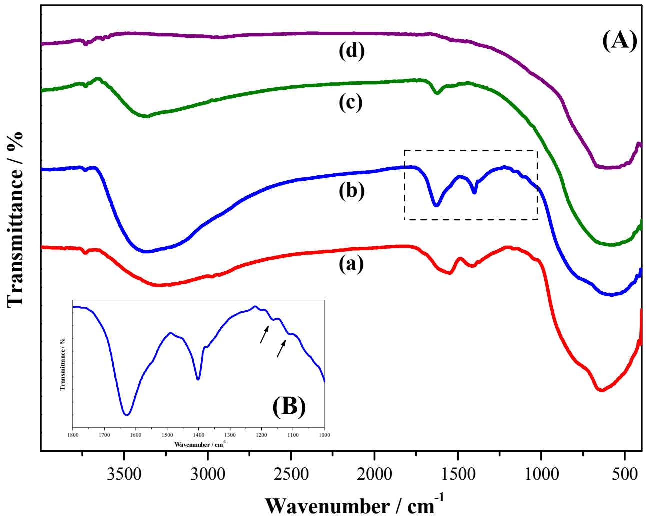

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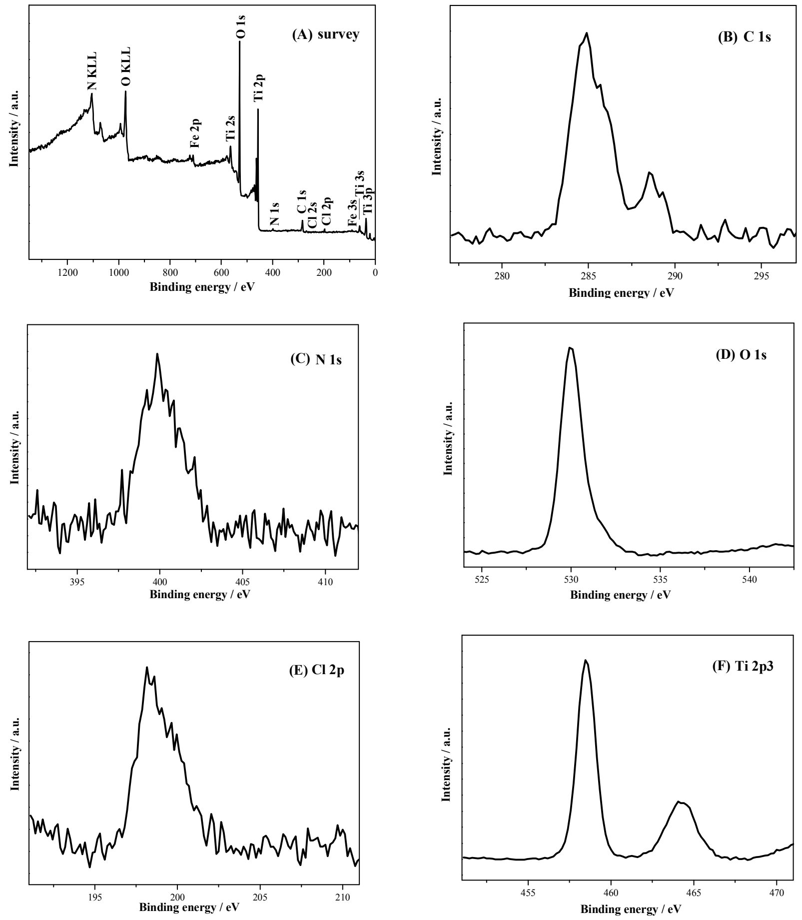

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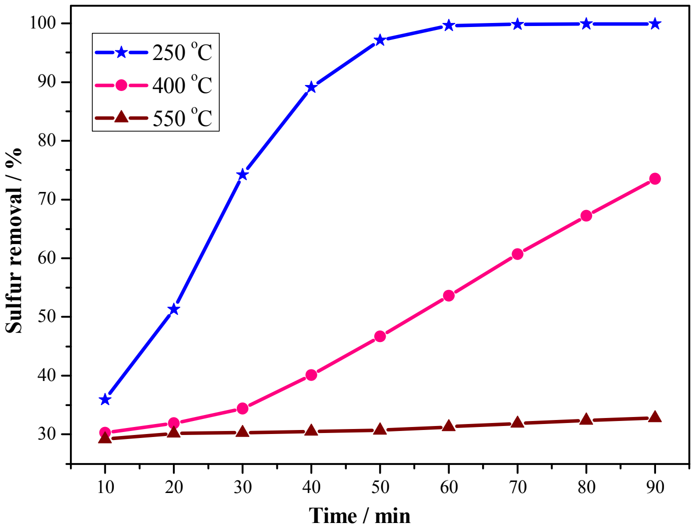

Fig. 5. The effects of different calcination temperatures on removal of DBT. Experiment conditions: *m*(catalyst) = 5 mg, *T* = 60 °C, $n(H_2O_2)/n(DBT)$ = 4:1, $V([Omim]BF_4)$ = 1 mL, *V*(model oil) = 5 mL.

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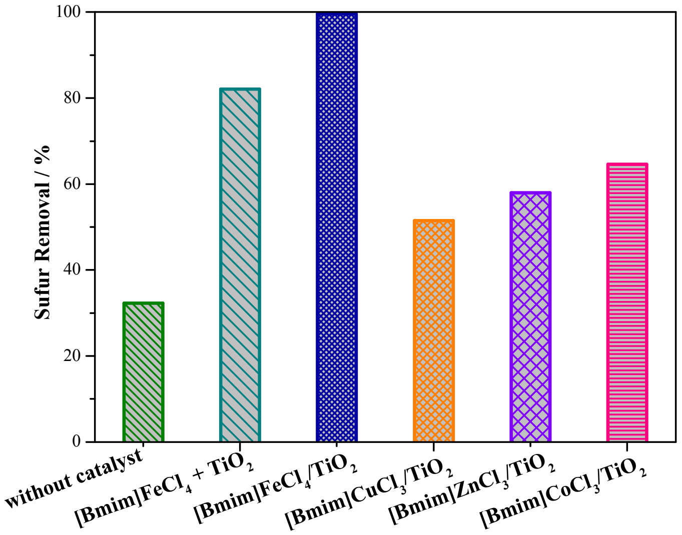

Fig. 6. The effect of different desulfurization systems on removal of DBT.

Experiment conditions: m(catalyst) = 5 mg, T = 60 ^{o}C, t = 1 h, $n(H_2O_2)/n$(DBT) = 4:1, V([Omim]BF$_4$) = 1 mL, V(model oil) = 5 mL;

Conditions of [Bmim]FeCl$_4$ + Am TiO$_2$: m([Bmim]FeCl$_4$) = 1.6 mg, m(Am TiO$_2$) = 3.4 mg.

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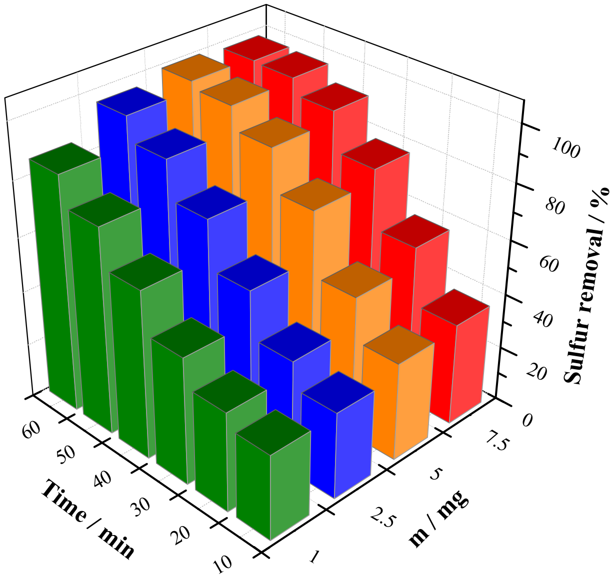

Fig. 7. The effect of the amount of catalyst on removal of DBT.

Experiment conditions: $T = 60\ ^{o}C$, $n(H_2O_2)/n(DBT) = 4{:}1$, $V([Omim]BF_4) = 1$ mL, V(model oil) = 5 mL.

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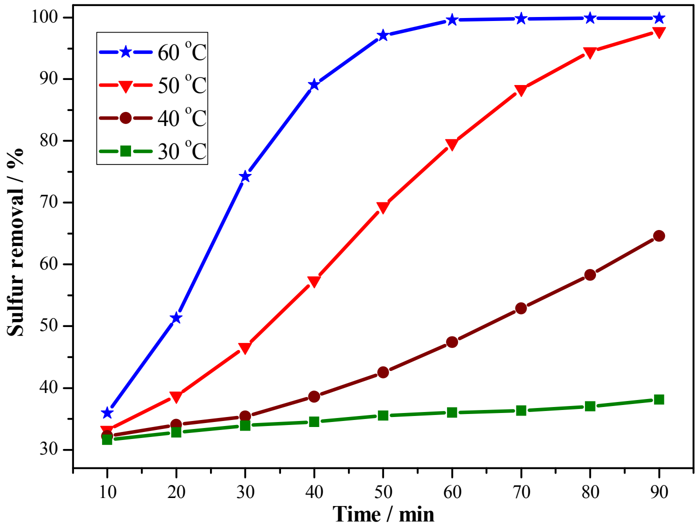

Fig. 8. The effects of different reaction temperatures on removal of DBT. Experiment conditions: *m*(catalyst) = 5 mg, *n*(H_2O_2)/*n*(DBT) = 4:1, *V*([Omim]BF_4) = 1 mL, *V*(model oil) = 5 mL.

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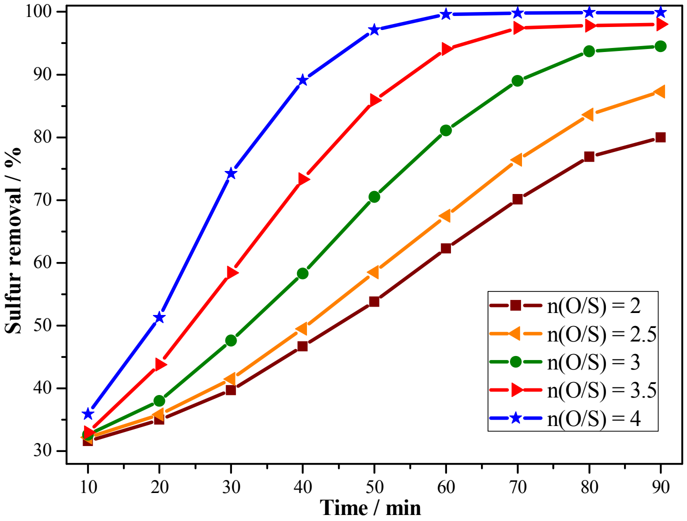

Fig. 9. The effect of H_2O_2/DBT (molar ratio) on removal of DBT.

Experiment conditions: m(catalyst) = 5 mg, T = 60 °C, V([Omim]BF_4) = 1 mL, V(model oil) = 5 mL.

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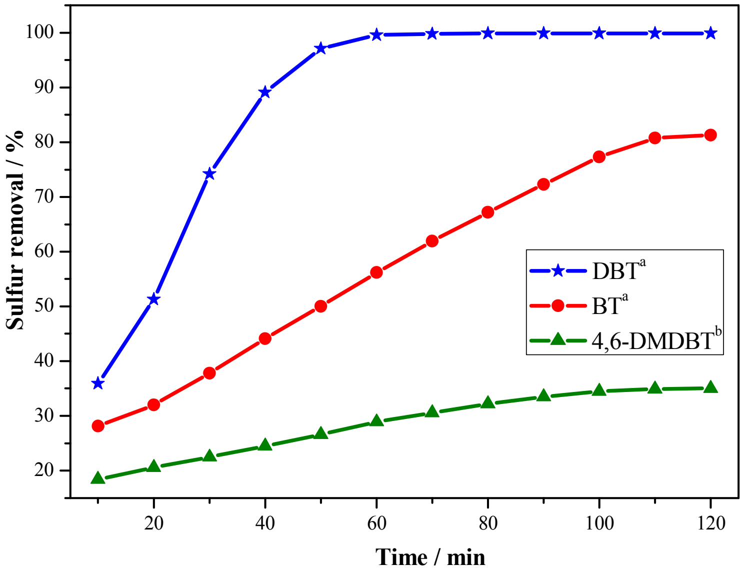

Fig. 10. Removal of different substrates in the desulfurization system.

Experiment conditions: $T = 60\ ^{o}C$, V([Omim]BF_4) = 1 mL, V(model oil) = 5 mL;

a: m(catalyst) = 5 mg, $n(H_2O_2)/n$(DBT) = 4:1; b: m(catalyst) = 10 mg, $n(H_2O_2)/n$(DBT) = 8:1.

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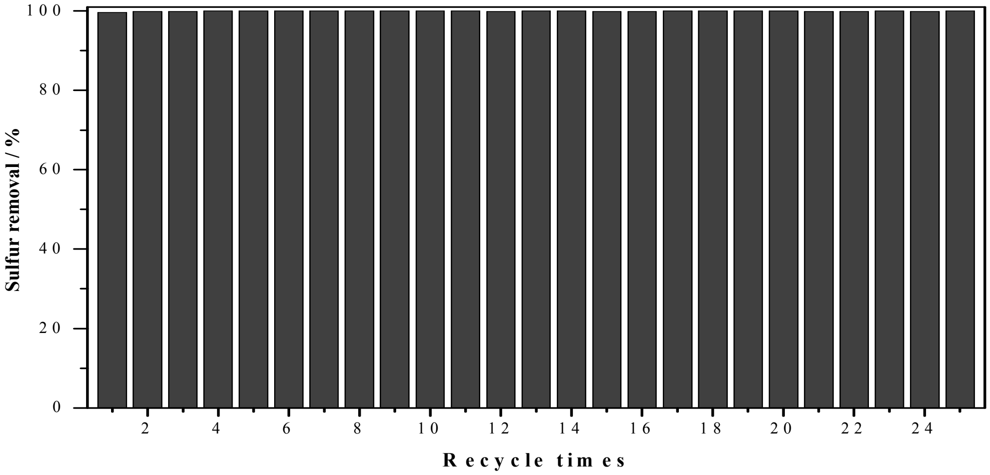

Fig. 11. The recycle performance of the desulfurization system.

Experiment conditions: m(catalyst) = 5 mg, T = 60 ^{o}C, t = 1 h, $n(H_2O_2)/n$(DBT) = 4:1, V([Omim]BF_4) = 1 mL, V(model oil) = 5 mL.

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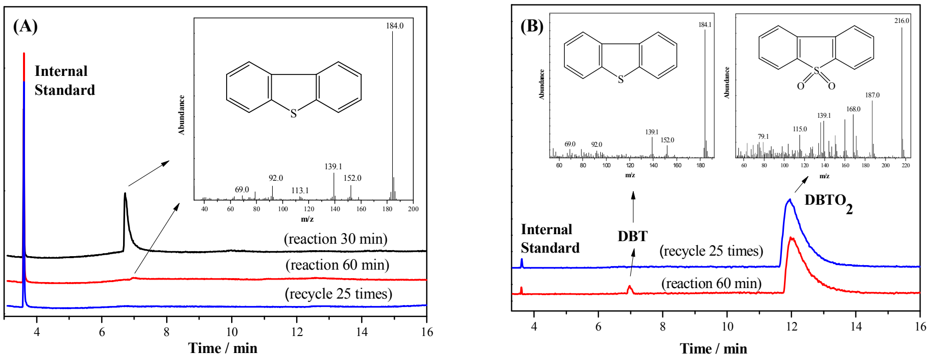

Fig. 12. The GC-MS of main compounds of the oil phase (A) and ionic liquid phase (B).

Experiment conditions: *m*(catalyst) = 5 mg, *T* = 60 ^{o}C, *n*(H_2O_2)/*n*(DBT) = 4:1, *V*([Omim]BF_4) = 1 mL, *V*(model oil) = 5 mL.

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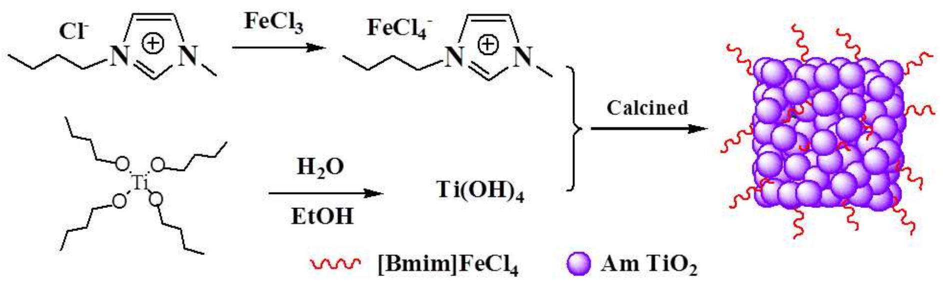

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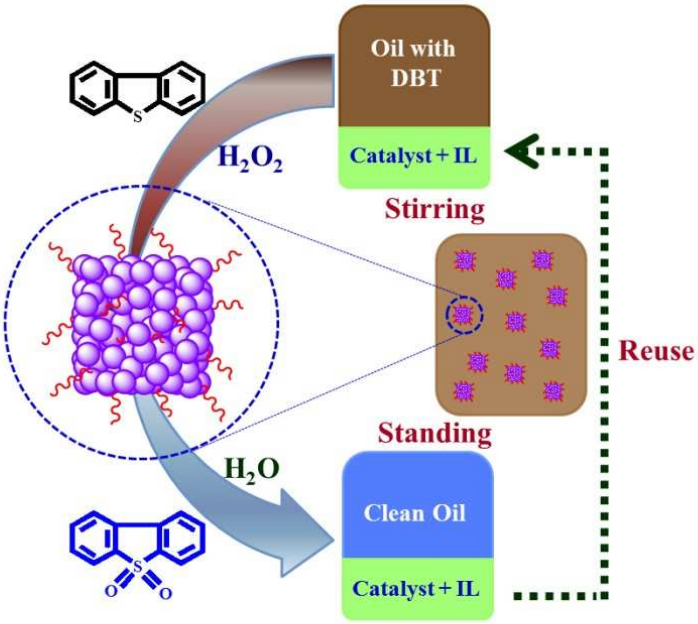

Scheme 2. The suggested process of the ECODS system.

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Table

Table 1. The effect of different extractants on removal of DBT

Entry	Different ILs	Sulfur removal / %	
		EDS[a]	ECODS[b]
1	$[Bmim]BF_4$	17.2	75.8
2	$[Omim]BF_4$	29.3	99.6
3	$[Bmim]PF_6$	15.1	17.9
4	$[Omim]PF_6$	26.5	32.2

Experiment conditions: a: T = 60 °C, t = 1 h, V_{IL} = 1 mL, V(model oil) = 5 mL. b: *m*(catalyst) = 5 mg, *T* = 60 °C, *t* = 1 h, $n(H_2O_2)/n(DBT)$ = 4:1, V_{IL} = 1 mL, *V*(model oil) = 5 mL.