Deep Desulfurization of Fuels by Heteropolyanion-Based Ionic Liquid

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A new heteropolyanion-based ionic ([Hmim]$_5$PMo$_{10}$V$_2$O$_{40}$) was synthesized by the reaction of molybdo-vanadophosphoric acid (H$_5$PMo$_{10}$O$_{40}$) with *N*-methylimidazole. [Hmim]$_5$PMo$_{10}$V$_2$O$_{40}$ showed a high catalytic activity in the oxidative desulfurization of sulfur-containing compounds in 1-methylimidazolium tetrafluoro-borate ([Hmim]BF$_4$) ionic liquid using 30% aqueous H$_2$O$_2$ as the oxidant. The catalytic system was of high activity, simplified workup and flexible recyclability. The catalytic oxidation reactivity of sulfur-containing compounds decreased in the order dibenzothiophene (DBT) > 4,6-dimethyldibenzothiophene (4,6-DMDBT) > benzothiophene (BT). The influences of various parameters including reaction time (t) and temperature (T), catalyst dosage, and oxidant to sulfur molar ratio n(O)/n(S) on the desulfurization of model oil were investigated in details. 99.1% of DBT conversion in the model oil was achieved at atmospheric pressure under the optimal conditions: n(O)/n(S) = 4:1, 60 ^{o}C, 100 min and molar ratio of catalyst to sulfur of 0.062. The ionic liquid can be recycled six times without significant decrease in activity.

Key Words : Oxidative desulfurization, Extraction, Dibenzothiophene, Molybdovanadophosphoric acid, Ionic liquid

Introduction

Deep desulfurization of transportation fuels has received more and more attention due to the increasing stringent regulations and fuel specifications in many countries for environmental protection.[1] In industry, removal of sulfur-containing compounds is mainly performed by the conventional hydrodesulfurization (HDS), which is efficient in the desulfurization of aliphatic and alicyclic sulfur-containing compounds. However, it exits limited efficiency on the desulfurization of dibenzothiophene (DBT) and its derivatives such as benzothiophene (BT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) exited in oils by HDS due to the steric hindrance of these compounds.[2-4] In order to achieve ultra low sulfur level of fuels, the conventional HDS has to be operated at high temperature and high pressure with hydrogen, leading to an increase in cost. Therefore, it is desirable to develop some alternative approaches, such as oxidative desulfurization (ODS),[5-9] adsorptive desulfurization,[10] extractive desulfurization[11,12] and bio-desulfurization,[13] to obtain ultra clean fuels and oil.

Among all these processes, the ODS process turns out to be one of the most promising processes due to short reaction time, moderate reaction conditions, high efficiency and selectivity. In the ODS process, DBT and its derivates can be selectively oxidized into the corresponding sulfoxides and sulfones, which can be removed by extraction. Therefore, highly efficient oxidant and extractant are crucial to the ODS process. Various oxidants including H$_2$O$_2$,[7-9,14] organic peroxide,[15] potassium superoxide,[16] molecular oxygen,[17] ozone,[18] and nitric acid/NO$_2$[19] were investigated in the ODS process. Among them, H$_2$O$_2$ has been widely used due to its

high reactivity, affordable cost and the only by-product of water. On the other hand, extractants such as *N,N*-dimethyl-formamide (DMF),[20] acetonitrile,[21] methanol[1] and dimethyl sulfoxide (DMSO)[22] also play a vital role in the ODS process. They are widely used for the removal of sulfoxides or sulfones from fuels in the ODS process, which are highly reactive. However, the use of flammable and volatile organic compounds as the extractant in ODS may cause environmental problems.

Ionic liquids have been widely investigated as environmentally benign alternative solvents for desulfurization due to negligible vapor pressure, easy separation, and recyclability. The extraction of fuels using ILs such as [bmim]BF$_4$,[23] [bmim]PF$_6$,[23,24] [omim][OcSO$_4$],[23] [bmim]Cl/AlCl$_3$,[23] [bmim][DBP],[25] TMAC/AlCl$_3$,[11] and FeCl$_3$-[bmim]Cl[26] have been reported. However, the efficiency of sulfur removal is rather low in extraction desulfurization mere with ionic liquid. To increase the sulfur removal, chemical oxidation combined with extraction was investigated, and the results showed that the sulfur removal efficiency of fuels was increased remarkably.[7,20,27] Although the efficiency of sulfur removal increased after H$_2$O$_2$ was introduced into the reaction system by Lu group, high temperature (90 ^{o}C) caused quick H$_2$O$_2$ decomposition[7]. And in their extended work, they introduced the molybdophosphate-based ionic liquid[28] to the reaction system as the catalyst, which showed higher efficiency than their previous work. Catalytic oxidation combing with extraction using H$_2$O$_2$ as the oxidant has been reported by Li group,[8] and it proved to be of high efficiency. However, the complicated synthesis process of the catalyst is unfavorable to be commercialized. In their extended work, they used a commercially available catalyst, H$_3$PW$_{12}$O$_{40}$·14H$_2$O.[29] They

combined the catalyst with H_2O_2 and IL [bmim]BF_4 and achieved 98.2% removal efficiency of DBT from model oil at 30 °C in 1 h. Comparing with the desulfurization by mere solvent extraction with IL or catalytic oxidation, combination of catalytic oxidation and extraction in IL can deeply remove DBT from oil.

Recently, heteropolyanion-based ionic liquids have attracted considerable interest. They were composed of polyoxometalates and ionic liquids, which retained the heteropolyanion structure and showed hybrid properties of both polyoxometalates and organic segments. Up to now, many new ionic liquids reported were used as electrochemicals rather than catalysts.[30,31] Only a few ionic liquids were used as the catalysts in the esterification[32,33] and oxidation reactions.[14,34] Li *et al.* found that the heteropolyanion-based ionic liquid was quite efficient in deep desulfurization of fuels.[34] Zhang *et al.* used [Bmim]$_3$PMo$_{12}$O$_{40}$ as the catalyst for oxidative desulfurization of dibenzothiophene and 100% DBT conversion at was obtained at 60 °C.[9]

Molybdovanadophosphate heteropoly acid showed high reactivity for esterification[32,33] and oxidation reactions.[35-38] However, to the better of our knowledge, limited work has been reported on the study of molybdovanadophosphate-based ionic liquid for oxidative desulfurization. Herein, a new heteropolyanion-based ionic liquid [Hmim]$_5$PMo$_{10}$V$_2$O$_{40}$ was synthesized by the reaction of H_5PMo$_{10}$V$_2$O$_{40}$ with the ionic liquid *N*-methylimidazolium, and used as the catalyst in the ODS process. Moreover, the influences of reaction conditions, such as reaction time and temperature, catalyst amount, molar ratio of H_2O_2 to DBT (n(O)/n(S)) on the desulfurization were investigated in details.

Experimental

Dibenzothiophene (DBT, 99%), benzothiophene (BT, 97%) and 4,6-dimethyldibenzothiophene (4,6-DBT, 99%) were purchased from Acros Organics (USA). Disodium phosphate dodecahydrate (Na$_2$HPO$_4$·12H$_2$O), hydrogen peroxide (H$_2$O$_2$), sodium metavanadate (NaVO$_3$), Sodium molybdate dihydrate (Na$_2$MoO$_4$·2H$_2$O), sulfuric acid, *n*-octane, diethyl ether were purchased from Sinopharm Chemical Reagent Co., Ltd. *N*-Methylimidazole (purity > 99%) was purchased from Linhai Kaile Chemical Factory (Zhejiang, China). All chemicals were of analytical grade.

Catalyst Preparation. H_5PMo$_{10}$V$_2$O$_{40}$ was prepared as the same procedure in the previous literature.[39] The aqueous solutions of Na$_2$HPO$_4$·12H$_2$O, NaVO$_3$ and Na$_2$MoO$_4$·2H$_2$O were prepared in appropriate molar ratio in boiling water. The heteropoly acid formed was extracted with diethyl ether and sulfuric acid. The product was separated by thoroughly drying the ether layer in the vacuum desiccator for 1 day. Then the orange powder was recrystallized for further use.

N-Methylimidazolium molybdovanadophosphate ([Hmim]$_5$-PMo$_{10}$V$_2$O$_{40}$) was synthesized according to the procedure in the literature.[40] In a typical preparation, *N*-methylimidazole (25 mmol) was added dropwise to a solution of H_5PMo$_{10}$-V$_2$O$_{40}$ (5 mmol) in deionized water (50 mL) and the mixture

was stirred at room temperature. The resulted yellow precipitate was immediately formed and the suspension continued stirring 2 h. The yellow precipitate was filtered, washed with deionized water, and then dried at 80 °C in vacuum for 24 h. Calcd for [Hmim]$_5$PMo$_{10}$V$_2$O$_{40}$: C, 11.27; H, 1.17; N, 6.65; O, 30.06; P, 1.45; Mo, 44.63; V, 4.77. Found: C, 11.31; H, 1.21; N, 6.63; O, 30.13; P, 1.42; Mo, 44.61; V, 4.69. The heteropolyanion-based ionic liquid hybrid can be dissolved in dimethylsulfoxide (DMSO), but not dissolve in water or other common organic solvents, which is different from its parent compounds. This is in agreement with the results in the previous literatures.[40]

Characterization. X-ray fluorescence spectra (XRF) for O, P, V and Mo elemental analysis was performed with a Panalytical Magix spectrometer. The C, H and N elemental analysis were performed on a PE2400 elemental analyzer. IR spectra of samples (KBr pellets) were recorded on a PerkinElmer infrared spectrometer in the range of 400-4000 cm^{-1}. X-ray diffraction (XRD) measurements were performed on a Philips Analytical X-ray Diffractometer using a Cu Kα radiation (1.5406 Å) source at 40 kV and 30 mA, from 5 to 40° with a scan rate of 0.5°/min. UV-vis spectra were performed on TU-901 spectrophotometer in the spectral range of 200-800 nm (in acetonitrile).

Oxidative Desulfurization Process. DBT was dissolved in n-octane to get the model oil with sulfur concentration of 1000 ppm (BT, 1000 ppm; 4,6-DMBT, 500 ppm). In a typical run: 5 mL model oil was introduced into a three-necked glass reactor equipped with a condenser and a thermometer and the reactor was placed in a constant temperature water bath to keep the reactor at the desired temperature. 3.5 mg of catalyst and a certain amount of aqueous H$_2$O$_2$ solution (30 wt %) were added to the reactor and then 5 mL [Hmim]BF$_4$ was added to the mixture and this time was recorded as the initial reaction time. The resulting mixture was stirred at the reaction temperature for a fixed time. After reaction, the upper clear liquid phase was withdrawn and analyzed on an Agilent-6890$^+$ gas chromatograph equipped with an FID using an HP-5 capillary column (30 m × 0.32 mm id × 0.25 μm).

Results and Discussion

Characterization. The FT-IR spectra are useful to study the skeletal modes appearing between 700 and 1100 cm^{-1} of Keggin anions present in the heteropolyanion-based ionic hybrid material. As can be seen from Figure 1, the prominent FT-IR features of [PMo$_{10}$V$_2$O$_{40}$]$^{5-}$ anion cluster in the heteropolyanion-based ionic liquid are clearly marked in the stretching region of 700-1100 cm^{-1}, 1050-1100 cm^{-1} (P-O stretching), 900-1000 cm^{-1} (Mo/V=O stretching vibration), 850-900 cm^{-1} (stretching of Mo-O-Mo inter bridges between corner-sharing MoO$_6$ octahedron), 750-800 cm^{-1} (stretching of Mo-O-Mo intra bridges between edge-sharing MoO$_6$ octahedron), which indicates that the Keggin structures are retained in the hybrid material. On the other hand, the [Hmim]$^+$ can be identified by spectral features in the regions
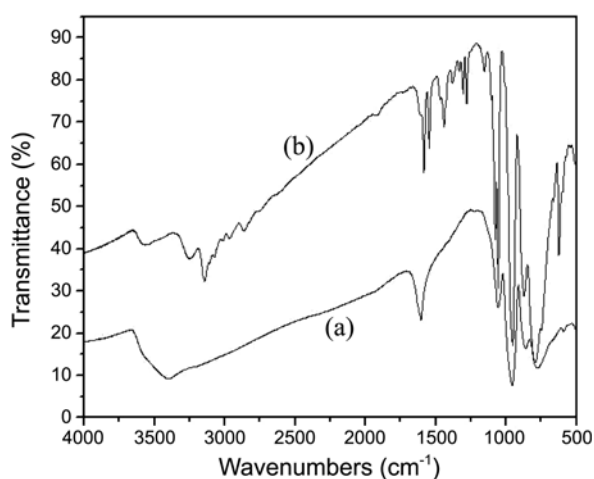
Figure 1. FTIR spectra of (a) $H_5PMo_{10}V_2O_{40}$ and (b) $[Hmim]_5$-$PMo_{10}V_2O_{40}$.

of 700-550 cm^{-1}, 1800-1130 cm^{-1} and 3200-2800 cm^{-1}. Analysis of the FT-IR spectra shows that the basic structure and geometry of the Keggin anion entrapped in the $[Hmim]^+$ cation was preserved.

The UV-vis spectra of $[Hmim]_5PMo_{10}V_2O_{40}$ is shown in Figure 2. Two absorption bands at 223 and 309 nm, was ascribed to the structure of $[PMo_{10}V_2O_{40}]^{5-}$.[41] The absorption band at 223 nm is due to O → Mo transition while the absorption band at 309 nm may be attributed to the charge transfer transition (O^{2-} → Mo^{6+}) in the Keggin units where Mo atoms are bonded to oxygen atoms located in bridge, corner and terminal positions.

The XRD analysis of the $[Hmim]_5PMo_{10}V_2O_{40}$ is shown in Figure S1. The peaks located at 2θ = 9.2, 9.8, 24.0, 28.5 and 34.0°, were ascribed to the Keggin structure. It is similar to the structure of $[PMo_{10}V_2O_{40}]^{5-}$ reported in the previous literature.[42] It was further confirmed that the synthesized heteropolyanion-based ionic liquid hybrid material retained the Keggin structure.

Influence of Different Desulfurization System on Sulfur Removal. Table 1 showed the sulfur removal efficiency in
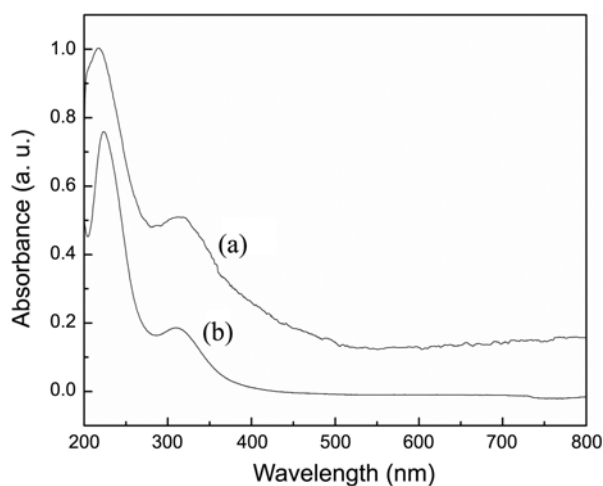

Figure 2. The UV-vis spectrum of (a) $H_5PMo_{10}V_2O_{40}$ and (b) $[Hmim]_5PMo_{10}V_2O_{40}$.

Table 1. Sulfur removal of different desulfurization systems

Entry	Catalyst system	Sulfur removal (%)
1	Ionic liquid	9.4
2	Ionic liquid + H_2O_2	48.6
3	Catalyst + H_2O_2	62.0
4	Catalyst + H_2O_2 + Ionic liquid	99.1

Experimental conditions: T = 60 °C, t = 100 min, 5 mL model oil of DBT in *n*-octane with S-contents 1000 μg/mL, ionic liquid ($[Hmim]BF_4$) = 5 mL, n(O)/n(S) = 4, n(catalyst)/n(S) = 0.062, catalyst: $[Hmim]_5$-$PMo_{10}V_2O_{40}$

Table 2. Comparison of the catalytic efficiency of $[Hmim]_5PMo_{10}$-V_2O_{40} with other reported catalysts for oxidative desulfurization using H_2O_2 as the oxidant

No.	Catalyst	Solvent	T/°C	t	Conv (%)
1	$[Hmim]_5 PMo_{10}V_2O_{40}$	$[Hmim]BF_4$	60	100 min	99.1
2	$[Hmim]_3 PMo_{12}O_{40}$	$[Hmim]BF_4$	50	4 h	90[28]
3		$[Hmim]BF_4$	90	6 h	93[7]
4	$[PSPy]_3PW$	$[Bmim]BF_4$	30	1 h	81.5[34]
5		$[Bmim]BF_4$	30	1 h	19.9[34]

desulfurization systems of extraction, extraction combined with chemical oxidation, catalytic oxidation, and catalytic oxidation combined with extraction. As shown in Table 1, the sulfur removal efficiency was only 9.4% when $[Hmim]BF_4$ was used to extract DBT from the model oil. The sulfur removal increased to 48.6% with the addition of H_2O_2, which was in agreement with the results in the previous literature.[7] The sulfur removal efficiency was 62.0% in catalytic oxidation system. However, 99.1% of sulfur removal efficiency was obtained when $[Hmim]_5PMo_{10}V_2O_{40}$, $[Hmim]BF_4$ and H_2O_2 were employed together for the desulfurization of model oil at 60 °C. Similar results were found in the previous literatures.[28,29,34,43]

Table 2 showed the comparison of the catalytic efficiency of $[Hmim]_5 PMo_{10}V_2O_{40}$ with other reported catalysts for oxidative desulfurization. It can be obviously found that heteropolyanion ionic liquid catalyst showed higher reactivity for oxidative desulfurization.

The experiment results demonstrated that the ionic liquid $[Hmim]BF_4$ and the catalyst $[Hmim]_5PMo_{10}V_2O_{40}$ played a significant role in the desulfurization system and a combination of catalytic oxidation and extraction in ionic liquid could be used for deep desulfurization of model oil, which was superior to mere extraction or mere catalytic oxidation.

Reaction Mechanism. $[Hmim]BF_4$ was immiscible with model oil. $[Hmim]_5PMo_{10}V_2O_{40}$ can be dissolved in H_2O_2 and H_2O_2 was miscible with $[Hmim]BF_4$. As a result, a biphasic system was formed when the model oil was added to the catalyst system containing $[Hmim]_5PMo_{10}V_2O_{40}$, H_2O_2, and $[Hmim]BF_4$. We have proposed the mechanism of oxidative desulfurization catalytic by $[Hmim]_5PMo_{10}V_2O_{40}$ ionic liquid. As shown in Scheme 1, $[PMo_{10}V_2O_{40}]^{5-}$ first reacted with H_2O_2 forming a peroxo species 1.[44-46] Then DBT was oxidized into sulfone (DBTOO) in ionic liquid phase by the reaction with species 1 as it was extracted from

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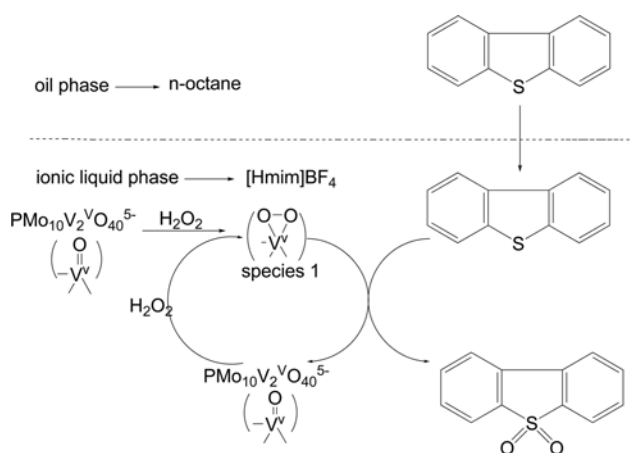
Scheme 1. Proposed mechanism of oxidative desulfurization catalytic by [Hmim]$_5$PMo$_{10}$V$_2$O$_{40}$ ionic liquid.

Figure 4. Influence of n(catalyst)/n(s) on the sulfur removal using [Hmim]$_5$PMo$_{10}$V$_2$O$_{40}$ as catalyst with n(O)/n(S) of 4:1 at 60 °C.

oil phase. The reaction was initiated by electron transfer between a generic substrate DBT and active peroxo species 1, yielding an oxidized product DBTOO and [PMo$_{10}$V$_2$O$_{40}$]$^{5-}$. As the reaction proceeded, peroxo species was continually formed in the excess H$_2$O$_2$, which kept the reaction activity and the mass transferring smoothly. After reaction, the heteropolyanion ionic liquid [Hmim]$_5$PMo$_{10}$V$_2$O$_{40}$ was recovered to its original state. (Characterizations showed in the supporting information).

Oxidation Reactivity of Different Sulfur Compounds. To investigate the influence of the catalytic system on the relative reactivity of different sulfur compounds, the oxidation of the representative sulfur compounds such as BT, DBT and 4,6-DMDBT was carried out at 60 °C. As shown in Figure 3, the oxidative reactivity of the sulfur-containing compounds decreased in the order DBT > 4,6-DMDBT > BT, which is in agreement with the results of the polyoxometalates/H$_2$O$_2$ in biphase catalytic system.[34] This may be related to electron densities of sulfur atoms. The electron densities on sulfur atoms are 5.739 for BT, 5.758 for DBT and 5.760 for 4,6-DMDBT.[5] Compared with DBT and 4,6-
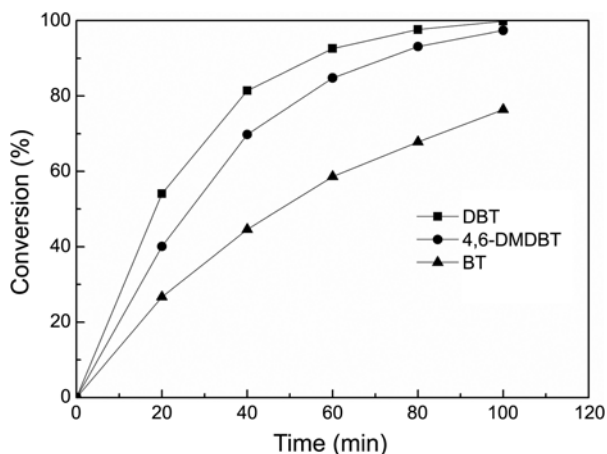
DMDBT, BT exhibited the lowest reactivity due to the lowest electron density on its sulfur atom. However, for 4,6-DMDBT and DBT, the difference in the electron density on the sulfur is very small, and it is the steric hindrance of the methyl groups that governs the reactivity. 4,6-DMDBT has two methyl groups, which become an obstacle for the sulfur atom to approach the catalytic active sites in a biphase system. As a result, the reactivity of the DBT was higher than that of 4,6-DMDBT.

Influence of Catalyst Dose. The catalyst dose is a critical factor to influence reaction activity. To investigate the influence of catalyst amount on the catalytic properties, the oxidation of DBT were carried out at 60 °C under various molar ratios (n(catalyst)/n(s)). As shown in Figure 4, the DBT conversion increased with the increase of catalyst dosage. The sulfur removal efficiency increased remarkably from 68.7% to 99.1% when the molar ratio was increased from 0.041 to 0.062. When the molar ratio was changed to 0.083, DBT could be completely converted to sulfone (DBTOO) in 100 min. Therefore, a [catalyst]/s molar ratio of 0.062 was chosen in the present study.

Figure 3. Conversion variation with the reaction time in the oxidation of DBT (■), 4,6-DMDBT (●), BT (▲) using [Hmim]$_5$-PMo$_{10}$V$_2$O$_{40}$ as catalyst with n(O)/n(S) of 4:1 at 60 °C.

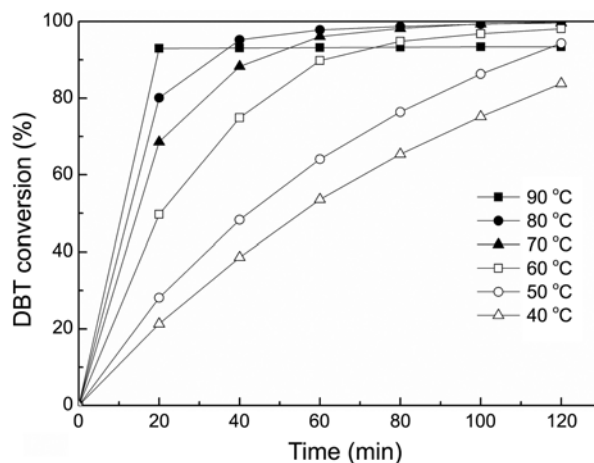**Figure 5.** Influence of reaction temperature on the DBT conversion using [Hmim]$_5$PMo$_{10}$V$_2$O$_{40}$ as catalyst with n(O)/n(S) of 4:1.
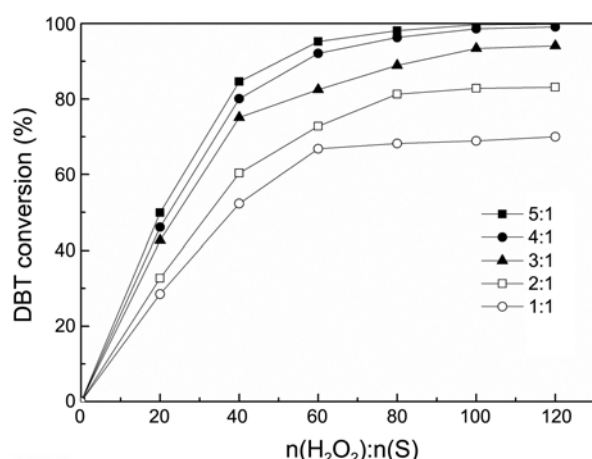
Figure 6. Influence of $n(O)/n(S)$ on the DBT conversion using $[Hmim]_5PMo_{10}V_2O_{40}$ as catalyst at 60 °C.

Influence of Reaction Temperature. To investigate the effect of reaction temperature on the removal of DBT, a series experiments were carried out under different temperatures. As shown in Figure 5, at low temperature (40 and 50 °C), DBT conversion was only 80% in 100 min. However, 99.1% sulfur removal efficiency was achieved in 100 min at 60 °C. When the temperature was increased to 90 °C, a high DBT conversion (94%) was obtained in 20 min. However, the DBT conversion increased slightly by adding the reaction time. This may be due to the decomposition of H_2O_2 at high temperature. Therefore, it is favorable to choose a low temperature for the oxidation of DBT such as 60 °C.

Influence of Molar Ratio of H_2O_2/DBT. Figure 6 shows the influence of the O/S molar ratio on the desulfurization of model oil. In the oxidative desulfurization system, the amount of H_2O_2 plays an important role on DBT conversion. According to the stoichiometric reaction, to oxidize the sulfur-containing compounds to the corresponding sulfones using H_2O_2 as the oxidant, 2 mol of H_2O_2 are consumed for 1 mol of sulfur-containing compounds. Therefore, in the

oxidative desulfurization system, a series of O/S molar ratios, such as 1:1, 2:1, 3:1, 4:1 and 5:1, were selected. When the O/S molar ratio was 1:1, the DBT conversion was 63.4% in 3 h. And DBT conversion increased from 63.4% to 99.1% at $n(O)/n(S)$ of 4:1 in 100 min. Further increasing the O/S molar ratio to 5:1 did not change the time needed for 99.1% DBT conversion; it remained at 100 min, which could be illuminated that there exited two apparent competing reactions: oxidation of DBT and decomposition of H_2O_2.[5,6,33] Therefore, the optimal $n(O)/n(S)$ of 4:1 was chosen in most cases in the present study.

Recycling of the Ionic Liquid The regenerability and recyclability of a catalyst is very important to catalytic reaction. After the reaction, the catalytic system still stayed the lower layer and the oil phase still the upper layer, as the model oil was immiscible with the ionic liquid. So the oil phase could be easily separated by decantation after the first run. Then the residual model oil and the IL phase were distilled under vacuum (0.01 Torr) at 70 °C for 1 h and the fresh H_2O_2 and model oil were added into the above ionic liquid for the second cycle under the same conditions. It was found that the catalytic system could be recycled at least six times with slight decrease in activity (Fig. 7).

Conclusion

In conclusion, the heteropolyanion-based ionic liquid showed high catalytic activity for oxdative desulfurization. And the reaction activity of different sulfur-containing compounds decreased in the order DBT > 4,6-DMDBT > BT. DBT conversion increased with O/S molar ratio, reaction temperature and catalyst amount. 99.1% DBT conversion was obtained under the optimal conditions: 60 °C, 100 min, $n(O)/n(S)$ of 4:1 and $n(catalyst)/n(s)$ of 0.062. The catalytic system is very effective under mild conditions, and moreover, it can recycle 6 times without significant decrease in activity and moreover, it is also environmentally friendly.
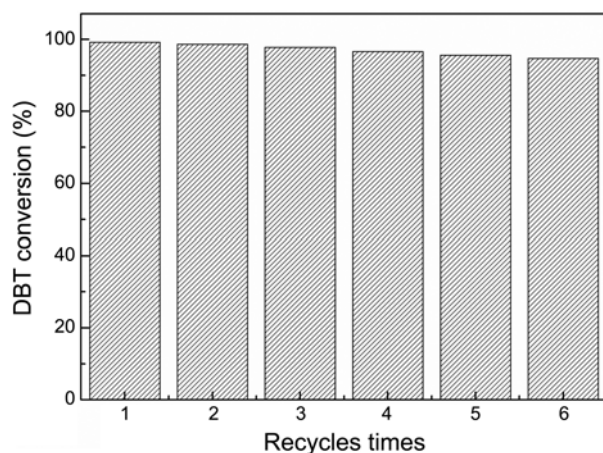
Figure 7. The recycles times on the DBT conversion with the hybrid materials as the catalyst at T = 60 °C, $n(O)/n(S)$ = 4:1, $n(catalyst)/n(s)$ = 0.062, t = 100 min, $[Hmim]BF_4$ 5 mL.

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