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Oxidative desulfurization of dibenzothiophene and diesel over $[Bmim]_3PMo_{12}O_{40}$

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ABSTRACT

A hybrid material ($[Bmim]_3PMo_{12}O_{40}$) was synthesized by reacting $H_3PMo_{12}O_{40}$ with the ionic liquid 1-butyl-3-methyl imidazolium bromide. SiO_2-supported $[Bmim]_3PMo_{12}O_{40}$ showed a high catalytic activity in the oxidation of dibenzothiophene (DBT) with 29% H_2O_2 aqueous solution as the oxidant. Maximum activity was observed at a loading of 20 wt.% $[Bmim]_3PMo_{12}O_{40}$ on SiO_2, and 100% DBT conversion was achieved at 60 °C, atmospheric pressure, and an oxygen to sulfur (O/S) molar ratio of 3.0 in 100 min. The high performance of $[Bmim]_3PMo_{12}O_{40}/SiO_2$ might be attributable to its amphiphilicity, which enhances adsorption of both H_2O_2 and sulfur-containing compounds. $[Bmim]_3PMo_{12}O_{40}/SiO_2$ could be easily separated by centrifugation and reused without deactivation after seven runs. Quinoline and carbazole had slightly positive effects on DBT oxidation, whereas indole had a negative effect. The high performance of $[Bmim]_3PMo_{12}O_{40}$ was verified in the sulfur removal from a real diesel by means of oxidation followed by dimethylformamide extraction.

1. Introduction

Sulfur in transportation fuels is a major source of air pollution from automobiles. The increasingly stringent fuel specifications worldwide require reducing the sulfur contents of the fuels to an ultra low level [1]. Conventionally, sulfur-containing compounds in fuels are removed via hydrodesulfurization (HDS) in a refinery. However, polyaromatic sulfur-containing compounds, such as DBT and its derivatives, show significantly lower HDS activity than thiophene and benzothiophenes (BT) [2]. As a consequence, it is necessary to operate the HDS process under elevated temperatures and pressures to achieve deep desulfurization, leading to increased operation costs.

Recently, oxidative desulfurization (ODS) has attracted attention as one of the most effective methods to remove the remaining polyaromatic compounds in hydrotreated engine fuels. The polyaromatic sulfur-containing compounds show higher reactivity in oxidation than thiophenes and BT, in the reverse reactivity order of HDS [3]. ODS takes place under mild conditions, converting sulfur-containing compounds to the corresponding polar sulfones which can be easily removed by solvent extraction [3] or by adsorption [4]. In ODS, the oxidant and the corresponding catalytic system determine the performance and feasibility of the reaction system. The oxidants used in ODS include hydrogen peroxide [5–9], organic peroxides [10,11], nitric acid/NO_2 [12], ozone [13], molecular oxygen [14], and potassium superoxide [15]. Of these oxidants, H_2O_2 has been extensively investigated because it is highly reactive and produces only water as the by-product after donating the active oxygen atom in ODS. The oxidation of sulfur-containing compounds takes place effectively in the presence of formic acid [3] and acetic acid [16], which, however, become more corrosive when they are oxidized by H_2O_2 to peracids (the intermediates). Moreover, a large excess of H_2O_2 is generally needed in the above reaction system. Recently, it has been reported that polyoxometalates show high activity in the oxidation of sulfur-containing compounds [9,17–19], whereas no corrosive species are involved in the reaction system.

In the oxidation of organic sulfur-containing compounds catalyzed by polyoxometalates, the mass transfer across the interface of aqueous phase and oil phase is the rate-limiting step. As a consequence, a phase transfer agent (PTA) is usually added to the reaction system in order to enhance the mass transfer. Collins et al. [18] investigated DBT oxidation with H_2O_2 using phosphotungstic acid as the catalyst and tetraoctylammonium bromide as the PTA. At optimal conditions, 100% conversion of DBT could be reached, and all the sulfur-containing compounds in a gas oil were oxidized by this catalyst system. Te et al. [9] compared the catalytic performances of phosphotungstic-, phosphomolybdic-, silicotungstic-, and silicomolybdic-H_2O_2 systems using tetraoctylammonium bromide as the PTA in the oxidation of DBT, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene (4,6-DMDBT). They found that the phosphotungstic-H_2O_2 system had the highest activity, whereas the silicotungstic-H_2O_2 and silicomolybdic-H_2O_2 systems showed the lowest activity. The presence of PTA enhances the mass transfer

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and thus the oxidation, but makes the separation of catalyst from the fuel more difficult [20]. Moreover, the nitrogen-containing PTA will lead to an increased nitrogen content of fuel if the PTA is not completely recovered.

More recently, the cation of PTA and the anion of heteropoly acids were combined to synthesize a variety of amphiphilic catalysts, such as $[C_{18}H_{37}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$ [14], $[(C_{18}H_{37})_2N^+(CH_3)_2]_3[PW_{12}O_{40}]$ [21], and $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ [22]. The amphiphilic catalysts assemble at the interface of emulsion droplets, dramatically increasing the total interface area and thus the ODS performance. However, the demulsification for catalyst recovery is often challenging in a large-scale unit.

It is well accepted that nitrogen-containing compounds have negative effects on the HDS process [23,24]. In ODS catalysis, only a few papers investigated the influence of nitrogen-containing compounds. Cedeño et al. [25] found that quinoline, indole, and carbazole poisoned the catalytic sites and thus decreased the ODS activity in the V_2O_5/Al_2O_3–H_2O_2 system. Jia et al. [26] reported that pyridine, pyrrole, quinoline, indole, and carbazole suppressed the oxidation of sulfur-containing compounds in both TS-1-H_2O_2 and Ti-HMS-H_2O_2 oxidation systems. They attributed the negative effects to the preferential strong adsorption of the nitrogen-containing compounds and their oxidized products on the active sites of the solid catalysts.

In the present work, a hybrid material $[Bmim]_3PMo_{12}O_{40}$, which was synthesized by reacting $H_3PMo_{12}O_{40}$ with the ionic liquid [Bmim]Br, was evaluated in the oxidation of BT, DBT, and 4,6-DMDBT. The effects of quinoline, indole, and carbazole on the performance of the hybrid material in the oxidation of DBT were investigated. In addition, the oxidation system was tested in the sulfur removal of a real diesel.

2. Experimental

Phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot 6H_2O$, AR grade), hydrogen peroxide (29% by titration, AR grade), quinoline (AR grade), indole (AR grade), carbazole (AR grade), indigo (AR grade), dimethylformamide (DMF) (AR grade), and toluene (AR grade) were purchased from Sinopharm Chemical Reagents Co., Ltd. (China) and used without purification. SiO_2 was the product of Shenyang Chemical Co., Ltd. (China). A diesel fraction was sampled from a hydrotreating unit of Dalian West Pacific Petrochemical Company Co., Ltd. (China). 1-Butyl-3-methyl imidazolium bromide ([Bmim]Br) ionic liquid (purity: >97%) was synthesized by means of a micro-channel reactor system [27].

$[Bmim]_3PMo_{12}O_{40}$ was synthesized according to the procedure in the literature [28]. One gram of [Bmim]Br was dissolved in 50 mL of deionized water, and 2.78 g of $H_3PMo_{12}O_{40}\cdot 6H_2O$ was dissolved in 30 mL of deionized water. The [Bmim]Br solution was added dropwise into the $H_3PMo_{12}O_{40}\cdot 6H_2O$ solution, yielding a yellowish green precipitate. The resulting suspension was stirred for 2 h at room temperature, and the solid product was separated by filtration, washed with deionized water, and then dried overnight at 100 °C. In order to verify the structure of the product ($[Bmim]_3PMo_{12}O_{40}$), Fourier transform infrared spectra (FT-IR) of both the reactants and the products were recorded on an Equinox 55 spectrometer. UV–vis spectra were obtained on a Jasco V-550 spectrophotometer, and the surface area of the hybrid material $[Bmim]_3PMo_{12}O_{40}$ was measured on a Micromeritics Tristar 3020 instrument.

Supported $[Bmim]_3PMo_{12}O_{40}$ was prepared by a co-precipitation method. One gram of carrier (SiO_2, Al_2O_3, or TiO_2) was dispersed in 50 mL of deionized water, and [Bmim]Br (0.029–0.175 g) was added dropwise to the slurry and stirred for 1 h. Then, 30 mL of the aqueous solution of $H_3PMo_{12}O_{40}\cdot 6H_2O$ (0.081–0.486 g) was added dropwise. The resulting slurry was stirred for 2 h at room temperature, and the solid product was separated by filtration, washed with deionized water, and then dried overnight at 100 °C. The SiO_2-supported $[Bmim]_3PMo_{12}O_{40}$ catalyst was denoted as $[Bmim]_3PMo_{12}O_{40}/SiO_2$. The surface areas and pore volumes of $[Bmim]_3PMo_{12}O_{40}$ supported on different carriers were measured on a Micromeritics Tristar 3020 instrument.

In a typical DBT oxidation, 20 mL of model fuel (DBT in toluene) was added to a three-neck flask, which was heated to the reaction temperature in an oil bath. And 0.2 wt.% DBT in toluene was used for the investigation of bulk and supported $[Bmim]_3PMo_{12}O_{40}$. The catalyst (0.025–0.1 g) was added into the flask to obtain a suspension, and then, 0.06 mL of 29% H_2O_2 aqueous solution, which is equivalent to the O/S molar ratio of 3.0, was added to start the reaction. To investigate the effect of nitrogen-containing compounds on the oxidation of DBT, 0.2 wt.% indole, quinoline, or carbazole was added to the DBT-containing toluene solution. Liquid samples were taken at an interval of 20 min to determine the concentration variation of the sulfur- and/or nitrogen-containing compounds with time. Both feed and products were analyzed on an Agilent-6890$^+$ gas chromatograph equipped with an FID using an HP-5 capillary column (5% phenyl methyl polysiloxane, 30.0 m × 320 μm × 0.25 μm). The oxidation products of nitrogen compounds were identified by means of LC–MS (HP1100LC/MSD). The conversions of sulfur- and nitrogen-containing compound in the feed were used as a measure of the catalytic performance.

In the ODS of a real diesel, 10 ml diesel (sulfur content: 530 ppm) was used. The solid catalyst was separated by centrifugation after oxidation, and then, 10 mL of DMF was used to extract the generated sulfones from 10 mL of the oxidized diesel (O/S molar ratio: 3.0–10.0, reaction temperature: 50–80 °C). The sulfur contents of the diesel fuels were measured on a ZWK-2001 microcoulometry instrument.

3. Results and discussion

3.1. Oxidation of sulfur-containing compounds

The FT-IR and UV–vis spectra of the synthesized material (Figs. S1 and S2 in Supporting information) are in agreement with those of $[Bmim]_3PMo_{12}O_{40}$ reported in the literature [28]. This hybrid material showed a fairly high activity in the oxidation of DBT (Fig. 1). It is indicated that the reaction temperature dramatically affected the oxidation rate in the presence of a large excess of H_2O_2. Fig. 2 shows that O/S molar ratio also had significant influence on the oxidation over bulk $[Bmim]_3PMo_{12}O_{40}$. In the

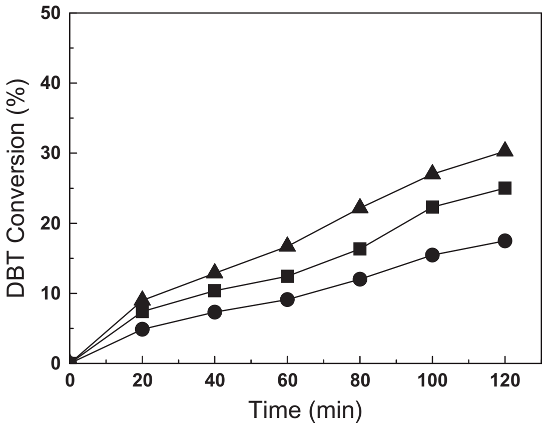

Fig. 1. Variation of DBT conversion with time in oxidation over bulk $[Bmim]_3PMo_{12}O_{40}$ using H_2O_2 at an O/S molar ratio of 3.0 and different temperatures. 40 °C (●), 60 °C (■), and 80 °C (▲).

oxidation, there exist two parallel reactions, in which H_2O_2 is involved. The undesirable thermal decomposition of H_2O_2, which is non-catalytic, takes place simultaneously with the catalytic oxidation. The competition of these two parallel reactions determines the utilization of H_2O_2 in the reaction and thus the conversion of DBT. The decomposition rate of H_2O_2 mainly depends on temperature, whereas the oxidation rate also depends on the availability of catalytically active sites. It is therefore preferable to support the hybrid material over a suitable carrier to increase its dispersion and number of active sites.

Table 1 shows the catalytic performance of $[Bmim]_3PMo_{12}O_{40}$ supported on various carriers at a loading of 20 wt.% in comparison with the same amount of bulk $[Bmim]_3PMo_{12}O_{40}$ in the oxidation of 0.2 wt.% DBT. All the supported $[Bmim]_3PMo_{12}O_{40}$ catalysts showed much higher activity than the bulk catalyst. The surface areas of bulk and supported $[Bmim]_3PMo_{12}O_{40}$ on TiO_2, Al_2O_3, and SiO_2 were 17, 36, 116, and 186 m^2/g. It appears that the enhancement in catalytic performance is due to the increased surface area. Among the supported catalysts, $[Bmim]_3PMo_{12}O_{40}/SiO_2$ showed the highest oxidation activity.

Fig. 3 illustrates the catalytic performance of $[Bmim]_3PMo_{12}O_{40}/SiO_2$ at different loadings. The support SiO_2 hardly showed any activity in the oxidation of DBT, and the supported $[Bmim]_3PMo_{12}O_{40}$ catalysts were more active than the bulk one. A maximum activity was observed at a loading of 20 wt.% $[Bmim]_3PMo_{12}O_{40}$. At lower loading, the surface of SiO_2 was not fully covered, although $[Bmim]_3PMo_{12}O_{40}$ was highly dispersed. On the other hand, at higher loading, the aggregation of $[Bmim]_3PMo_{12}O_{40}$ lowered the dispersion, leading to reduced surface area. Therefore, 20 wt.% $[Bmim]_3PMo_{12}O_{40}/SiO_2$ was used in the following investigation.

Fig. 4 shows the effect of catalyst amount on DBT oxidation. The oxidation rate increased with increasing catalyst amount, because of the increase in total amount of active sites. At a $[Bmim]_3PMo_{12}O_{40}$ to sulfur ([P]/S) molar ratio of 0.042, DBT could be completely oxidized in 60 min at 60 °C and O/S ratio of 3.0. When the [P]/S ratio was decreased to 0.021, it took longer time to achieve complete DBT conversion. If the [P]/S ratio was further decreased to 0.011, it was impossible to completely convert DBT to its sulfone in 120 min. Apparently, it is unfavorable to conduct the oxidation at low reaction rate for a long period of time. Therefore, a [P]/S molar ratio of 0.021 was chosen in the following investigation.

Table 1
Surface area and catalytic performances in DBT oxidation of bulk and supported $[Bmim]_3PMo_{12}O_{40}$.

Catalyst	Surface area (m^2/g)	DBT conversion[a] (%)
$[Bmim]_3PMo_{12}O_{40}$	17	12.4
$[Bmim]_3PMo_{12}O_{40}/SiO_2$	186	88.3
$[Bmim]_3PMo_{12}O_{40}/Al_2O_3$	116	64.6
$[Bmim]_3PMo_{12}O_{40}/TiO_2$	36	32.5

[a] Reaction conditions: 60 °C; O/S molar ratio, 3.0; 60 min.

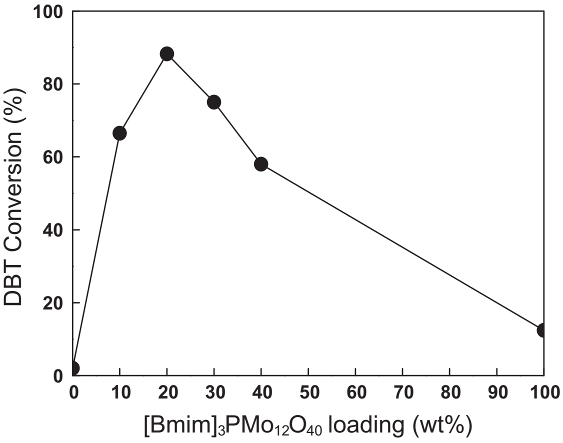

Fig. 3. Performance of bulk and SiO_2-supported $[Bmim]_3PMo_{12}O_{40}$ at different loadings in the oxidation of DBT at 60 °C and an O/S molar ratio 3.0 in 60 min.

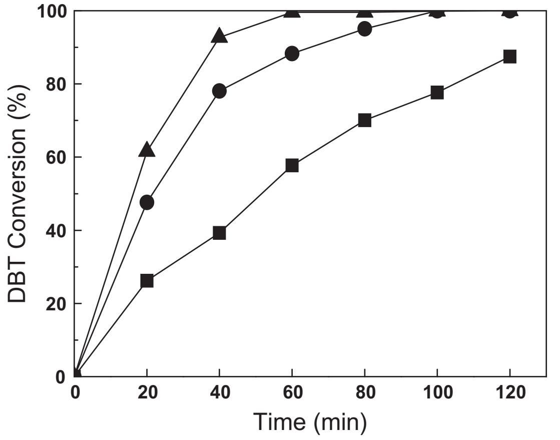

Fig. 4. Conversion as a function of time in the oxidation of DBT over $[Bmim]_3PMo_{12}O_{40}/SiO_2$ (20 wt.%) at 60 °C, O/S molar ratio of 3.0, and different [P]/S molar ratios. (▲) 0.042, (●) 0.021, and (■) 0.011.

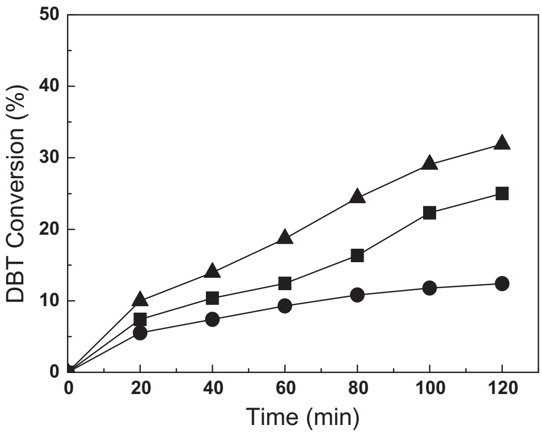

Fig. 2. Variation of DBT conversion with time in oxidation over bulk $[Bmim]_3PMo_{12}O_{40}$ using H_2O_2 at 60 °C and different O/S molar ratio. 2.0 (●), 3.0 (■), and 4.0 (▲).

The O/S molar ratio is an important factor that affects the efficiency and economy of the reaction system. In the early studies on ODS over polyoxometalates, very high O/S molar ratios were used to enhance the kinetics. For example, an O/S molar ratio of 148 was used for the phosphotungstic acid–H_2O_2 oxidation system [18] and 162 for the polyoxometalate acid–H_2O_2 system [9]. Apparently, such a high O/S molar ratio is unfavorable, because a large excess of expensive H_2O_2 is wasted and the unreacted H_2O_2 poses a safety risk.

At a stoichiometric O/S molar ratio (2.0), DBT conversion reached 75.1% in 120 min and did not change thereafter in the oxidation of DBT over $[Bmim]_3PMo_{12}O_{40}/SiO_2$ (Fig. 5). In other words, 75% of H_2O_2 was utilized in the oxidation whereas the other 25% was wasted due to thermal decomposition. When the O/S was increased to 2.5, a nearly complete DBT conversion (99.7%) was achieved in 140 min. When the ratio was increased to 3.0, complete DBT conversion was obtained in 120 min. Further increase

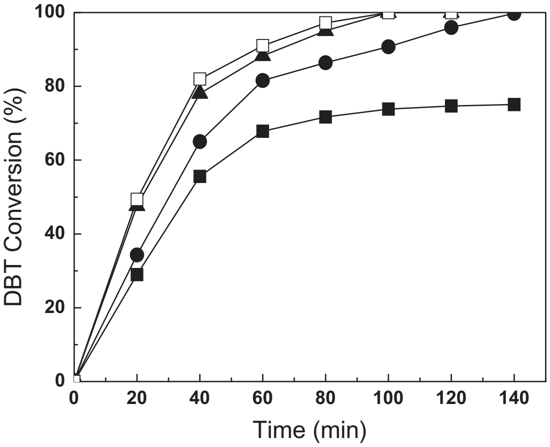

Fig. 5. Variation of DBT conversion with reaction time in oxidation over $[Bmim]_3PMo_{12}O_{40}/SiO_2$ (20 wt.%) at 60 °C and different O/S molar ratio. (■) 2.0, (●) 2.5, (▲) 3.0, and (□) 4.0.

in O/S molar ratio (4.0) shortened the reaction time needed for complete DBT conversion, suggesting that the reaction rate was strongly dependent on H_2O_2 concentration. The high utilization of H_2O_2 in the $[Bmim]_3PMo_{12}O_{40}/SiO_2$–$H_2O_2$ oxidation system may be attributed to the replacement of H^+ by $[Bmim]^+$. Lü et al. reported that, when H^+ was replaced by quaternary ammonium cations, a high utilization of H_2O_2 could be obtained [22].

In principle, increasing reaction temperature accelerates both DBT oxidation and H_2O_2 thermal decomposition, which take place in parallel. Fig. 6 indicates that DBT conversion increased slowly with time at low temperature (40 and 50 °C). It is likely that the oxidation reaction rate at low temperatures might be limited by kinetics. At higher temperature, DBT conversion was markedly enhanced, and complete conversion of DBT was achieved in 100 min at 60, 70, and 80 °C. The curves for 60, 70, and 80 °C had similar shapes, which differed from those for 40 and 50 °C, and the differences among them were small. It may suggest that the rate of oxidation is limited by diffusion at high temperatures. Nevertheless, DBT conversion showed a different trend when the temperature was increased to 90 °C. A high conversion (92.5%) could be obtained in 20 min, but thereafter, the conversion increased only slightly with reaction time, and it was impossible to achieve complete conversion at 90 °C. The reason may be that H_2O_2 decomposes dramatically at high temperature and that there was not much H_2O_2 available after 20 min. It is therefore favorable to conduct the oxidation of DBT over $[Bmim]_3PMo_{12}O_{40}/SiO_2$ at low temperatures, such as 60 °C.

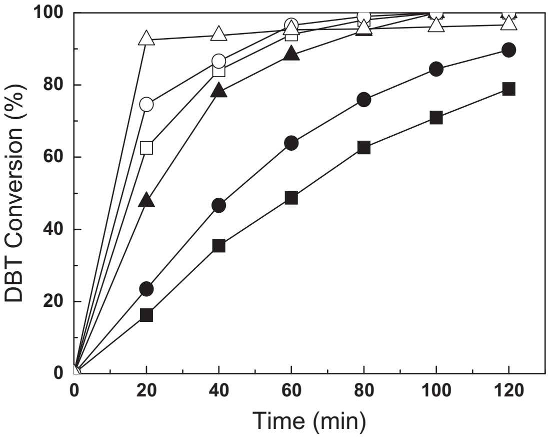

Fig. 6. Variation of DBT conversion with reaction time in oxidation over $[Bmim]_3PMo_{12}O_{40}/SiO_2$ (20 wt.%) at an O/S molar ratio of 3.0 and different temperatures. (■) 40 °C, (●) 50 °C, (▲) 60 °C, (□) 70 °C, (○) 80 °C, and (△) 90 °C.

Fig. 7 shows photographs taken of the phase behavior of the $[Bmim]_3PMo_{12}O_{40}/SiO_2$ catalyst. When $[Bmim]_3PMo_{12}O_{40}/SiO_2$ was added to water in a test tube, it precipitated immediately at the bottom (Fig. 7A). The subsequent addition of toluene led to three phases: toluene at the top, water in the middle, and the solid ($[Bmim]_3PMo_{12}O_{40}/SiO_2$) at the bottom (Fig. 7B). When the tube was shaken vigorously for a few minutes, the solid was lifted to the interface between toluene and water (Fig. 7C). This clearly shows that $[Bmim]_3PMo_{12}O_{40}/SiO_2$ is amphiphilic. The amphiphilicity makes it possible that both aqueous H_2O_2 and organic sulfur-containing compounds readily absorb on $[Bmim]_3PMo_{12}O_{40}/SiO_2$.

Fig. 8 shows the H_2O_2 concentration in the liquid phase, measured by titration, as a function of reaction time. It is illustrated that no H_2O_2 was detected immediately after the addition of H_2O_2 in the presence of $[Bmim]_3PMo_{12}O_{40}/SiO_2$. Meanwhile, the color of $[Bmim]_3PMo_{12}O_{40}/SiO_2$ changed from yellow-green to orange. The pore volume of the catalyst, which was calculated from its N_2 adsorption isotherm, was 1.43 mL/g, which was large enough to accommodate the aqueous H_2O_2 solution (0.06 mL). It is therefore proposed that H_2O_2 is immediately adsorbed on the catalyst and reacts with $[PMo_{12}O_{40}]^{3-}$ to form an active intermediate species $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ [29,30]. On the other hand, the sulfur-containing compound in the organic phase gradually diffuses and adsorbs on the suspended catalyst particles, where the active intermediate species $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ donates oxygen atoms to the sulfur-containing compounds, converting the sulfur-containing compound to its sulfone. Because only 0.06 mL of aqueous H_2O_2 solution, which adsorbs on the catalyst particles, is needed for 20 mL model fuel, both water and catalyst can be easily separated together from the oil phase simply by centrifugation and filtration. As a consequence, there is hardly any liquid loss after the oxidation.

The recovery and reusability of the catalyst were investigated in the oxidation of DBT. Because $[Bmim]_3PMo_{12}O_{40}$ does not dissolve either in water or in aromatics, no leaching was observed for $[Bmim]_3PMo_{12}O_{40}/SiO_2$ in the oxidation of DBT. The reusability of the catalyst was investigated at two conversion levels: (1) complete conversion at 60 °C in 120 min and (2) around 65% conversion at 50 °C in 60 min (Table 2). In the case of complete conversion, when the catalyst was reused without any treatment, its performance began to decline slightly after 4 runs (Table 2). Nevertheless, if the catalyst was heated at 100 °C for 5 h after each run, the catalytic performance did not change in 7 runs. Similarly, the catalyst did not show any deactivation if it was dried after each

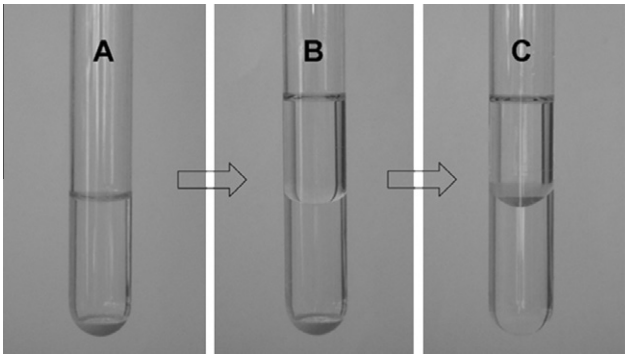

Fig. 7. Pictures recorded at different steps in mixing water (lower phase), $[Bmim]_3PMo_{12}O_{40}/SiO_2$, and toluene (upper phase). (A) After addition of $[Bmim]_3PMo_{12}O_{40}/SiO_2$ powder to water, (B) after subsequent addition of toluene; (C) after shaking of the mixture.

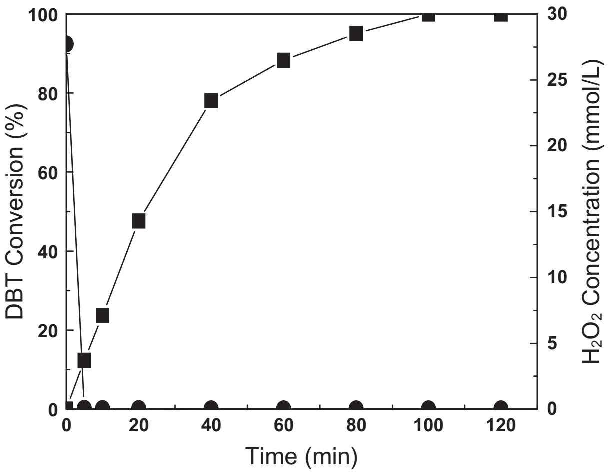

Fig. 8. Variation of H_2O_2 concentration (●) and DBT conversion (■) with reaction time in the oxidation over $[Bmim]_3PMo_{12}O_{40}/SiO_2$ (20 wt.%) at 60 °C and an O/S molar ratio of 3.0.

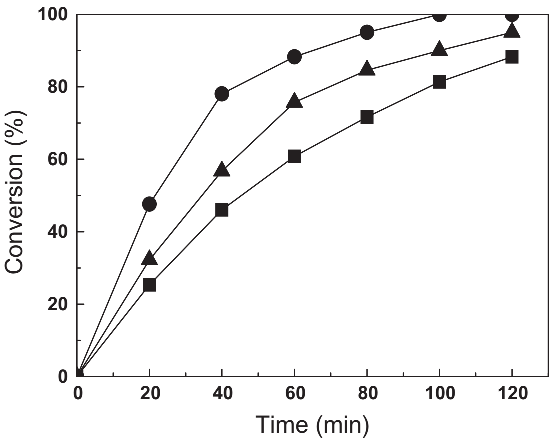

Fig. 9. Conversion variation with reaction time in the oxidation of BT (■), DBT (●), and 4,6-DMDBT (▲) over $[Bmim]_3PMo_{12}O_{40}/SiO_2$ (20 wt.%) at 60 °C and an O/S molar ratio of 3.0.

run. However, it is interesting to see that the conversion increased steadily after each run if the catalyst was not dried. Apparently, the increased conversion is related to the accumulated H_2O_2 on the catalyst surface from the previous run. On the other hand, the slight deactivation at complete conversion might be due to the dilution of H_2O_2 by the residual H_2O, which is retained on the surface of the catalyst after reaction. A comparison of the FT-IR spectrum of fresh catalyst with that of the spent one illustrates that the Keggin structure was well preserved (Fig. S3 in Supporting information).

Fig. 9 compares the reactivities of BT, DBT, and 4,6-DMDBT in the oxidation catalyzed by $[Bmim]_3PMo_{12}O_{40}/SiO_2$. The oxidation reactivity decreased in the order: DBT > 4,6-DMDBT > BT, the same order as observed in the polyoxometallates–H_2O_2 biphasic catalytic system [9]. The electron densities on the sulfur atoms in BT, DBT, and 4,6-DMDBT are 5.739, 5.758, and 5.760 [3]. The lowest reactivity of BT may be related to its lowest electron density, whereas the low reactivity of 4,6-DMDBT may be attributed to the steric hindrance by methyl groups in the 4,6-DMDBT molecule.

3.2. Role of nitrogen-containing compounds in the oxidation of DBT

It has been reported that nitrogen-containing compounds have a negative effect in the oxidation of sulfur-containing compounds in the V_2O_5/Al_2O_3–H_2O_2, TS-1-H_2O_2, and Ti-HMS-H_2O_2 oxidation systems [25,26]. The authors attributed the lower activities to the poisoning of the active sites by nitrogen-containing compounds. On the other hand, Ishihara et al. [10] reported that nitrogen-containing compounds could be oxidized in the ODS oxidation system and that the oxidation activity decreased in the order: indole > quinoline > acridine > carbazole. This may suggest that the lowered ODS activity be related to the competition of the parallel oxidation of nitrogen-containing compounds. To clarify the effects of nitrogen-containing compounds, we investigated the behavior of quinoline, indole, and carbazole in the oxidation system.

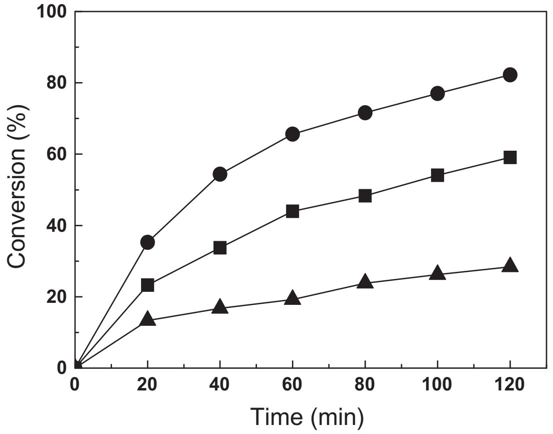

Fig. 10. Conversion variation with time in the oxidation of indole (●), quinoline (■), and carbazole (▲) over $[Bmim]_3PMo_{12}O_{40}/SiO_2$ (20 wt.%) at 60 °C and 0.06 mL H_2O_2 aqueous solution.

Fig. 10 shows that indole, quinoline, and carbazole all could be oxidized in the oxidation system. The oxidation activity decreased in the order: indole > quinoline > carbazole, which is agreement with the results reported by Ishihara et al. [10] and Shiraishi et al. [31]. The lower oxidation activity of carbazole is attributed to enhanced steric hindrance by the two aromatic rings although the electron density on the nitrogen atom is the highest. The higher activity of indole than quinoline is ascribed to the higher electron density on the nitrogen atom in indole.

Table 2
DBT conversion in oxidation over fresh and reused $[Bmim]_3PMo_{12}O_{40}/SiO_2$.

Reaction conditions	Treatment	Run						
		1	2	3	4	5	6	7
60 °C, 120 min O/S ratio: 3.0	No	100.0	100.0	100.0	99.4	99.2	96.3	92.2
	Drying	100.0	100.0	100.0	100.0	100.0	100.0	100.0
50 °C, 60 min O/S ratio: 3.0	No	64.8	67.8	69.1	72.9	75.3	80.9	87.3
	Drying	64.4	64.9	64.8	64.5	64.9	65.0	64.6

The oxidation products of nitrogen-containing compounds depend on the reaction conditions. Indole was reported to be oxidized to indigo under mild reaction condition [32]. The LC–MS analysis of the reaction product indicated the presence of indigo, isatin, and indirubin. For the oxidation of quinoline, many studies were focused at high temperature (>200 °C) [33]. In our [Bmim]$_3$PMo$_{12}$O$_{40}$/SiO$_2$—H$_2$O$_2$ oxidation system, the oxidation of quinoline occurred at mild conditions, and the main oxidation product was identified by LC–MS to be quinoline nitrogen oxide [34]. The main products of carbazole oxidation were found to be carbazole-1,4-dione [35], which can be converted into a polymer containing C=O and OH groups in the presence of H$_2$O$_2$ [31], and hydroxycarbazole.

Nitrogen-containing compounds coexist with sulfur-containing compounds in fossil fuels. It is therefore essential to investigate the oxidation of sulfur-containing compounds in the presence of nitrogen-containing compounds. Fig. 11a shows the DBT conversion in the presence of nitrogen-containing compounds, and Fig. 11b illustrates the simultaneous conversions of the nitrogen-containing compounds. The addition of carbazole improved rather than suppressed the performance of the [Bmim]$_3$PMo$_{12}$O$_{40}$/SiO$_2$—H$_2$O$_2$ oxidation system in the oxidation of DBT (cf. Fig. 6). The reaction time for complete conversion of DBT decreased from 100 min in the absence of carbazole to 80 min in the presence of carbazole at 60 °C. On the other hand, oxidation of carbazole took place simultaneously in a similar way as in the absence of DBT. The presence of quinoline increased the DBT conversion in the early stage, but DBT conversion leveled off after it reached 94%, indicating the depletion of H$_2$O$_2$ at the later stage. It is apparent that the oxidation of DBT takes place in parallel to that of nitrogen-containing compounds in the [Bmim]$_3$PMo$_{12}$O$_{40}$/SiO$_2$—H$_2$O$_2$ oxidation system. Carbazole and quinoline are competitors of DBT rather than poisoning the active sites on [Bmim]$_3$PMo$_{12}$O$_{40}$/SiO$_2$. The positive effects of carbazole and quinoline on the conversion of DBT may be related to their basicity, which slows down the thermal decomposition of H$_2$O$_2$. Because of the low reaction rate of carbazole, DBT conversion could achieve 100% in the competition. However, it is impossible to completely convert DBT into its sulfones in the presence of quinoline due to the comparable reaction rate at an O/(S + N) molar ratio of 1.25 in the oxidation of quinoline. When the O/(S + N) molar ratio was increased to 1.50, a complete DBT conversion was achieved in 80 min in the presence of quinoline at 60 °C (Fig. S4 in Supporting information).

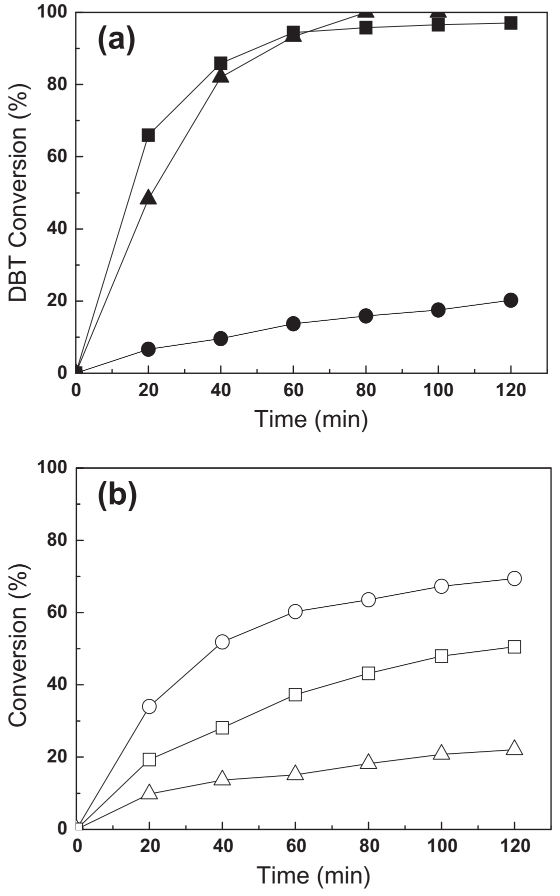

Fig. 11. (a) DBT conversion with reaction time in the oxidation over [Bmim]$_3$PMo$_{12}$O$_{40}$/SiO$_2$ (20 wt.%) at 60 °C and an O/S molar ratio of 3.0 in the presence of indole (●), quinoline (■), and carbazole (▲); (b) Conversion of indole (●), quinoline (□), and carbazole (△) with time.

Fig. 11a indicates that indole dramatically suppresses the oxidation of DBT on [Bmim]$_3$PMo$_{12}$O$_{40}$/SiO$_2$. On the other hand, the oxidation of indole was not remarkably affected by the presence of DBT. A comparison of the conversion of DBT with that of indole (Figs. 6 and 10) suggests that the oxidation rate of DBT was higher than that of indole. Therefore, it is unlikely that the dramatic decrease in DBT oxidation is due to the competitive utilization of H$_2$O$_2$ by DBT and indole. In other words, the lowered reaction rate of DBT oxidation must result from the poisoning or strong adsorption of the active sites by indole and its oxidized products. In the oxidation of indole in the absence and presence of DBT, we observed that the color of the reaction system changed to dark blue soon after the addition of H$_2$O$_2$. The dark blue is indicative of the formation of indigo, a dark blue dyestuff. The spent catalyst was heated at 100 °C for 4 h and then characterized by means of FT-IR measurements (Fig. 12). A comparison with the spectrum of fresh catalyst indicates that a new absorption band appeared at 1738 cm^{-1}, which is assigned to the vibration of a C=O group. It is therefore suggested that the product of indole oxidation, indigo [34], might strongly adsorb on the catalytic active sites, leading to a dramatically decreased reaction rate of DBT oxidation. To verify this hypothesis, indigo was added to the reaction mixture in the oxidation of DBT. Fig. 13 shows that indigo indeed had a marked negative effect on the oxidation of DBT over [Bmim]$_3$PMo$_{12}$O$_{40}$/SiO$_2$. Because indigo is not likely to be oxidized by H$_2$O$_2$ under the investigated reaction conditions, the negative effect of indigo may be related to its strong adsorption on the active sites.

In contrast to the results of other solid catalysts and organic acids [25,26], [Bmim]$_3$PMo$_{12}$O$_{40}$/SiO$_2$ is not negatively affected or poisoned by nitrogen-containing compounds, except for indole, in the oxidation of sulfur-containing compounds. Possible reasons are as follows: (1) [Bmim]$_3$PMo$_{12}$O$_{40}$/SiO$_2$ is also an active catalyst

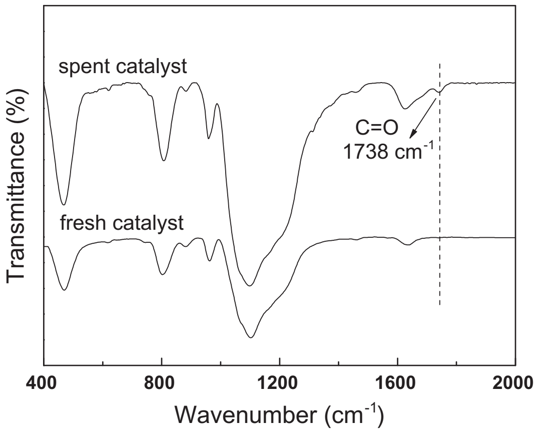

Fig. 12. FT-IR spectra of fresh and spent [Bmim]$_3$PMo$_{12}$O$_{40}$/SiO$_2$ (20 wt.%) after indole oxidation.

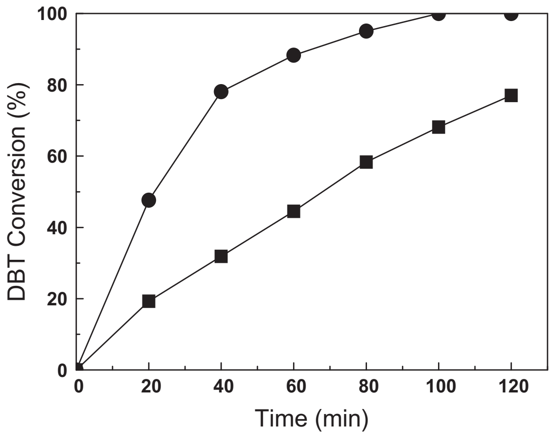

Fig. 13. Variation of DBT conversion with reaction time over $[Bmim]_3PMo_{12}O_{40}/SiO_2$ (20 wt.%) at 60 °C in the absence (●) and presence (■) of indigo.

Table 3
Performance of $[Bmim]_3PMo_{12}O_{40}/SiO_2$ in the ODS of a diesel fuel [a].

Run	Reaction temperature (°C)	O/S molar ratio	Sulfur removal (%)
1	50	5.0	84.1
2	60	5.0	91.3
3	70	5.0	95.1
4	80	5.0	97.9
5	50	3.0	80.2
6	50	10.0	86.5

[a] Reaction time: 180 min; sulfur content in the feed: 530 ppm; the obtained sulfones were removed by extraction using DMF with an oil/DMF volume ratio of 1.0.

for the oxidation of nitrogen-containing compounds and the absorbed nitrogen-containing compounds are subsequently oxidized; (2) the cation of the catalyst is $[Bmim]^+$, which does not react with nitrogen-containing compounds like H^+. The effects of carbazole and quinoline on the oxidation of sulfur-containing compounds depend on the balance between the suppressed thermal decomposition of H_2O_2 and their competitive oxidation. However, indole showed a significantly negative effect on the oxidation of DBT due to the strong adsorption of indigo formed in the oxidation of indole.

3.3. ODS of a real diesel

The $[Bmim]_3PMo_{12}O_{40}/SiO_2—H_2O_2$ oxidation system was evaluated in the ODS of a real diesel fuel with a sulfur content of 530 ppm. The generated sulfones in the oxidized fuel were removed through an extraction by DMF at an oil/DMF volume ratio of 1.0. Table 3 indicates that 97.9% of the sulfur in the diesel was removed in this oxidation system at O/S of 5.0 and 80 °C, followed by one time extraction with DMF. The sulfur content of the diesel fuel after oxidation and extraction decreased to 12 ppm. The results confirm that the $[Bmim]_3PMo_{12}O_{40}/SiO_2—H_2O_2$ oxidation system is effective in removing bulky sulfur compounds from diesel fractions.

4. Conclusions

1. $[Bmim]_3PMo_{12}O_{40}/SiO_2$, which is amphiphilic, could effectively catalyze the oxidation of BT, DBT, and 4,6-DMDBT using H_2O_2 as the oxidant under mild conditions. Complete DBT conversion was obtained at 60 °C, an O/S molar ratio of 3.0, and atmospheric pressure in 100 min. The oxidation reactivity decreased in the order: DBT > 4,6-DMDBT > BT.
2. $[Bmim]_3PMo_{12}O_{40}/SiO_2$ and water phase were easily separated together from the oil phase by centrifugation, and no deactivation was observed after seven runs if the spent catalyst was dried to remove the H_2O retained on the catalyst surface.
3. Carbazole and quinoline had positive effects on DBT oxidation, probably because they help to slow down the thermal decomposition of H_2O_2. The presence of indole inhibited DBT oxidation due to the strong adsorption of indigo generated by indole oxidation.
4. The $[Bmim]_3PMo_{12}O_{40}/SiO_2—H_2O_2$ oxidation system is effective in removing bulky sulfur-containing compounds from hydrotreated diesel fuels.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.01.016.

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