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Ultra-deep desulfurization of diesel by selective oxidation with $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ catalyst assembled in emulsion droplets

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Abstract

The oxidation of sulfur-containing compounds (benzothiophene, dibenzothiophene, and their derivatives) in diesel was conducted in emulsion oxidative system (water in oil [W/O]) composed of diesel, 30 wt% hydrogen peroxide, and an amphiphilic catalyst $[C_{18}H_{37}N(CH_3)_3]_4$-$[H_2NaPW_{10}O_{36}]$ under mild conditions. The amphiphilic catalyst in the W/O emulsion system exhibits very high catalytic activity such that all sulfur-containing compounds in either model or actual diesel can be selectively oxidized into their corresponding sulfones using hydrogen peroxide ($O/S \leqslant 3$) as an oxidant. The catalytic oxidation reactivity of sulfur-containing compounds was found to be in the following order: benzothiophene < 5-methylbenzothiophene < dibenzothiophene < 4,6-dimethyldibenzothiophene. Although benzothiophene is relatively difficult to oxidize, it can be efficiently oxidized in the emulsion system. The sulfones can be readily separated from diesel by an extractant. The sulfur level of a prehydrotreated diesel can be lowered from 500 to 0.1 ppm after oxidation and then extraction, whereas the sulfur level of a straight-run diesel can be decreased from 6000 to 30 ppm after oxidation and extraction.

Keywords: Ultra-deep desulfurization; Catalytic oxidation; Emulsion catalysis; $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$; Diesel; Benzothiophene (BT); 4,6-Dimethyldibenzothiophene (4,6-DMDBT); Extraction

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1. Introduction

Currently, ultra-deep desulfurization of fuel oil is attracting wide interest because of more stringent U.S. environmental regulations limiting the sulfur level in diesel to <15 ppm by the year 2006 [1,2]. Hydrodesulfurization (HDS) is highly efficient in removing thiols, sulfides, and disufides; however, conventional HDS has difficulty reducing refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives, especially 4,6-dimethyldibenzothiophene (4,6-DMDBT), to an ultra low level [3–5]. Severe operating conditions (e.g., high temperature, high pressure, and high hydrogen consumption) are required for HDS to achieve ultra-deep desulfurization of diesel, and achieving these conditions requires significant capital expenditure. Therefore, the development of alternative ultra-deep desulfurization processes, such as adsorption [6,7], extraction [8], oxidation [9–11], and bio-processes [12], is desired. Oxidative desulfurization (ODS) combined with extraction is considered one of the most promising of these processes. In previous work [13] we reported that a $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ catalyst, assembled in an emulsion in diesel, could selectively oxidize DBT and its derivatives into their corresponding sulfones using H_2O_2 as an oxidant under mild conditions. The sulfones can be readily separated from the diesel using an extractant, and ultra-deep desulfurization of diesel can be achieved [13].

But the oxidative activity of this system is not high enough to efficiently oxidize benzothiophene (BT) and its derivatives, which are present largely in nonhydrotreated diesel, and achieving ultra-deep desulfurization of various actual diesels is difficult with this system. This emulsion system has been used only for the desulfurization of prehydrotreated diesel, which usually has a sulfur content <1000 ppm. Developing the emulsion catalyst so that it can treat various diesels with a wide range of sulfur content is a highly desired goal.

The aim of this work is to develop an efficient system for the oxidation of sulfur-containing compounds, especially BT and

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its derivatives, present in both prehydrotreated diesel and non-hydrotreated diesel with sulfur content >1000 ppm. We found that $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ assembled in emulsion exhibits high catalytic activity in the oxidization of BT and its derivatives under mild conditions. The oxidized sulfone products can be readily separated from diesel. The sulfur level of a prehydrotreated diesel can be lowered from 500 to 0.1 ppm after desulfurization, and that of a straight-run diesel can be lowered from 6000 to 30 ppm after desulfurization. These results meet the current emission control standard for diesel.

2. Experimental

2.1. Characterization of catalyst

^{31}P-NMR spectra were recorded at 9.4 T on a Bruker DRX 400 spectrometer. The ^{31}P MAS-NMR spectra of the catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ with high-power proton decoupling was performed at 161.9 MHz with a BBO MAS probe lead using 4-mm ZrO_2 rotors and 2.0 µs pulse, 2 s repetition time, and 2048 scans, with the sample spun at 8 kHz. The ^{31}P chemical shifts were referenced to 85% H_3PO_4 aqueous solution. X-ray fluorescence (XRF) was performed with a Panalytical Magix spectrometer to determine the Na/P/W molar ratios. The infrared spectrum of the catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$, diluted with KBr and pressed into a pellet, was recorded on a Nicolet 470 FTIR spectrometer.

2.2. Oxidation of model sulfur-containing compounds

In a typical run, a water bath was heated to 20–40 °C. The model sulfur-containing compound (BT, 5-MBT, DBT, or 4,6-DMDBT) was dissolved in a flask with 25 ml decalin and a sulfur concentration of 1000 ppm. The catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ (0.06 g) and oxidant H_2O_2 (0.22 ml, 30 wt%) were added to the solution simultaneously. The mixture was stirred at 1000 rpm, and a turbid W/O emulsion immediately formed. The emulsion was periodically sampled, and these samples were placed into an ice chamber to stop the reaction. The sulfur content of the upper clear solution was determined by microcoulometry after the catalyst and sulfones were precipitated by centrifugation.

2.3. Oxidation and desulfurization of the prehydrotreated diesel

Oxidation of the prehydrotreated diesel was carried out as follows. The prehydrotreated diesel (25 ml, 500 ppm S) was mixed with an aqueous solution of hydrogen peroxide (0.08 ml, 30 wt%) and the catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ (0.02 g) at room temperature (22 °C). The mixture was stirred at 1000 rpm, and a turbid W/O emulsion immediately formed. After 1 h, the catalyst was precipitated by centrifugation, and the oxidized diesel was analyzed by gas chromatography coupled with flame photometric detection (GC-FPD).

The sulfones in the prehydrotreated diesel after oxidation can be removed by a polar extractant, such as 1-methyl-2-pyrrolidone. The oxidized diesel was extracted three times by an aqueous solution of 1-methyl-2-pyrrolidone (80 wt%, with some water added to increase recovery). The solvent/diesel ratio was kept at 1/1 by volume, and the mixture was shaken for 2 min at room temperature before the diesel and solvent layers were separated from one another. The sulfur content in the original diesel and that in the desulfurized diesel were determined by microcoulometry (detection limit, 0.1 ng/µl).

2.4. Oxidation and desulfurization of the straight-run diesel

Oxidation of the straight-run diesel was carried out as follows. The straight-run diesel (25 ml, 6000 ppm S) was mixed with aqueous hydrogen peroxide (1.45 ml, 30 wt%) and the catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ (0.14 g) at 30 °C. The mixture was stirred at 1000 rpm, and a turbid W/O emulsion immediately formed. After 2 h, the catalyst was precipitated by centrifugation, and the oxidized diesel was analyzed by the GC-FPD. The sulfones in the straight-run diesel after oxidation were removed in the same manner as for the prehydrotreated diesel, except the extraction was performed five times.

2.5. Analysis of sulfur content

The total sulfur content of the samples was determined by microcoulometry (detection limit, 0.1 ng/µl). The original diesel and the diesel after oxidation and desulfurization were analyzed by GC-FPD (GC: Agilent 6890N equipped with a capillary column [PONA, 50 m × 0.2 mm i.d. × 0.5 µm]; FPD: Agilent H9261). Analysis conditions were as follows: injection port temperature, 280 °C; detector temperature, 250 °C; oven temperature program, 100 °C, hold for 1 min, 100–150 °C at a 10 °C/min gradient, hold for 1 min, 150–280 °C at a 5 °C/min gradient, hold for 12 min; split ratio, 1/100; carrier gas, ultra-purity nitrogen; column flow, 0.9 ml/min; reagent gases, air flow of 100 ml/min, hydrogen flow of 75 ml/min; injection volume of sample, 1 µl.

3. Results and discussion

3.1. Characterization of catalyst

The ^{31}P MAS-NMR spectrum of the catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$, shown in Fig. 1a, consisted of a signal at −10.5 ppm of $[PW_{10}O_{36}]^{7-}$ [14,15] and a weak peak at about 3.2 ppm, assigned to some species with lower P/W ratios [16]. The catalyst was also characterized by XRF. The Na/P/W molar ratio of the catalyst was found to be 1.26:1:9.85. These results indicate that the catalyst is composed mainly of $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ together with small amounts of heteropoly tungstophosphate species with lower P/W ratios.

Fig. 1b displays the FTIR spectrum of the catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$. The bands at 1083, 1052, 958,

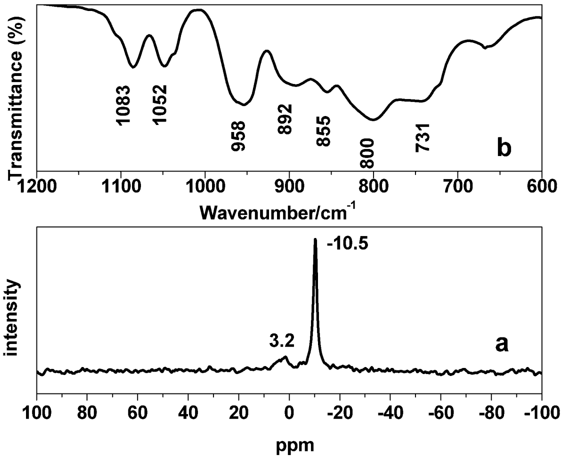


Fig. 1. Spectroscopic characterization of the $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ catalyst. (a) ^{31}P MAS NMR spectrum; (b) FTIR spectrum.

892, 855, 800, and 731 cm^{-1} indicate this catalyst consist of heteropoly tungstophosphate species [17–19]. A similar spectrum of $NaPW_{11}O_{39}$ was obtained by Pizzio et al. [19]. As a result, the structure of $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ is similar to that of $NaPW_{11}O_{39}$, which has a lacunar Keggin-type structure.

3.2. *Influence of quaternary ammonium on catalytic activity*

As determined in previous work [13,20], an amphiphilic catalyst with a proper quaternary ammonium cation can form metastable emulsion droplets in diesel with an aqueous H_2O_2 solution, demonstrating high oxidative activity, and can be separated after reaction through centrifugation and demulsification. For example, $(C_{18}H_{37})_2N^+(CH_3)_2$ is a proper quaternary ammonium cation, as we reported previously [13,20]. We tested other quaternary ammonium cations and found that $(C_{18}H_{37})N^+(CH_3)_3$ forms metastable emulsion droplets more readily than $(C_{18}H_{37})_2N^+(CH_3)_2$ in diesel. Moreover, the catalyst with $(C_{18}H_{37})N^+(CH_3)_3$ has higher catalytic activity than the catalyst with $(C_{18}H_{37})_2N^+(CH_3)_2$, as shown in Fig. 2. Consequently, $(C_{18}H_{37})N^+(CH_3)_3$ was chosen as the cation of the catalyst. The catalytic activity of $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ for the BT oxidative reaction is also shown in Fig. 2. Clearly, $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ (TOF > 50 h^{-1}) has much higher catalytic activity than $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ (TOF < 10 h^{-1}) for the oxidation of BT, which is present largely in nonhydrotreated diesel. Therefore, the new emulsion system may be applied to various actual diesels that contain a wide range of sulfur compounds. The emulsion droplets formed by $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ in the prehydrotreated diesel and hydrogen peroxide were confirmed by optical microscopy (Fig. 3).

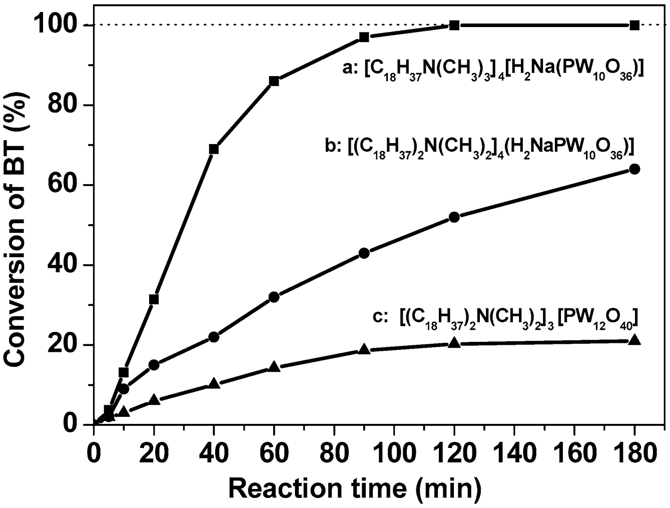


Fig. 2. Conversion of benzothiophene (S: 1000 ppm) versus the reaction time in emulsion. Conditions: temperature, 30 °C, $S/H_2O_2 = 1/3$ (molar ratio), benzothiophene (S: 1000 ppm) in decalin. (a) $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$; (b) $[(C_{18}H_{37})_2N(CH_3)_2]_4[H_2NaPW_{10}O_{36}]$; (c) $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$.

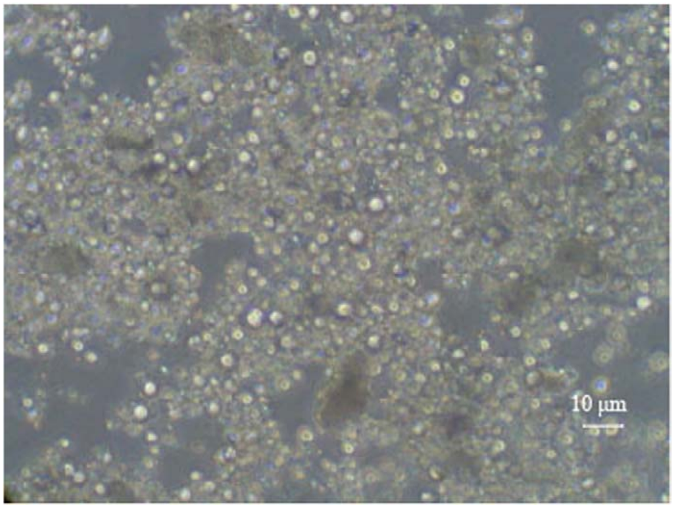


Fig. 3. Optical micrograph of the mixture of the prehydrotreated diesel (25 ml, sulfur: 500 ppm), $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ (0.020 g), and H_2O_2 (0.08 ml).

3.3. *Influence of reaction temperature on reactivity of the sulfur-containing compounds*

The reactivity of different sulfur-containing compounds, including BT, 5-methylbenzothiophene (5-MBT), DBT, and 4,6-DMDBT (S: 1000 ppm), was estimated for selective oxidation using the emulsion catalyst. The conversions of sulfur-containing compounds versus the reaction times at 20, 30, 35, and 40 °C in the emulsion system are shown in Figs. 4 and 5. At all temperatures studied, catalytic oxidation reactivity of the sulfur-containing compounds is in the following order: BT < 5-MBT < DBT < 4,6-DMDBT. As calculated by Shiraishi et al. [8] and Otsuki et al. [10], the electron densities on sulfur atoms are 5.739 for BT, 5.741 for 5-MBT, 5.758 for DBT, and 5.760 for 4,6-DMDBT. These results indicate that the reaction rates of these model sulfur-containing compounds increase with increasing electron density on the sulfur atoms. Consequently, the oxidation of BTs and DBT with $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ in emulsion is through an electrophilic addition reaction of oxygen atoms.

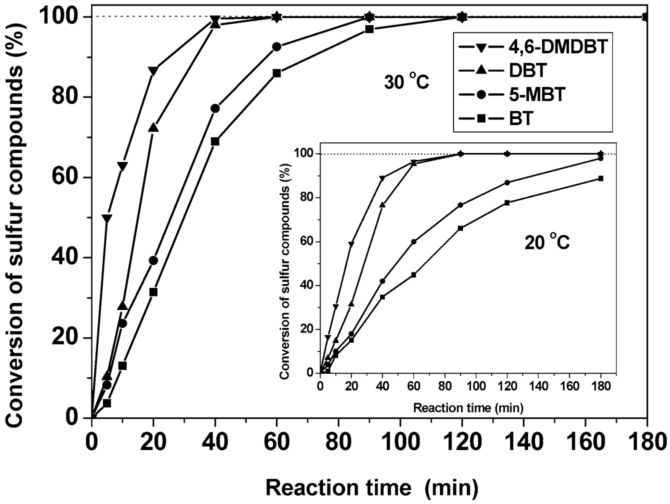


Fig. 4. Conversion of sulfur-containing compounds versus the reaction time in emulsion at 20 and 30 °C. Conditions: $S/H_2O_2 = 1/3$ (molar ratio), sulfur-containing compounds (S: 1000 ppm) in decalin.

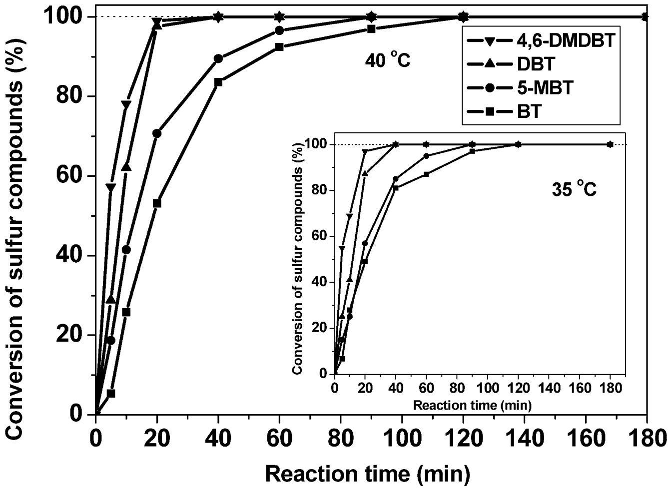


Fig. 5. Conversion of sulfur-containing compounds versus the reaction time in emulsion at 35 and 40 °C. Conditions: $S/H_2O_2 = 1/3$ (molar ratio), sulfur-containing compounds (S: 1000 ppm) in decalin.

The oxidation reactivity of the sulfur-containing compounds in the emulsion system is in agreement with that of the formic acid/H_2O_2 system [10] but not with that of the polyoxometallates/H_2O_2 in biphase catalytic system [21]. The formic acid/H_2O_2 and polyoxometallates/H_2O_2 in biphase catalytic systems demonstrated completely different reactivity orders for the oxidation of DBTs, due to the important role of the molecular size of the catalyst [21]. For the formic acid-catalyzed reaction, the formic acid (small size) can interact with sulfur without any steric hindrance from alkyl groups. Therefore, the reactivity trend obtained in formic acid-catalyzed reactions reflects the intrinsic oxidation reactivities of DBTs. Phosphotungstic compounds will convert to polyoxoperoxo complexes, such as $PO_4[WO(O_2)_2]_4^{3-}$, in the presence of hydrogen peroxide [22]. The tungsten atom in this polyoxoperoxo species is in a highly crowded, rigid structure. If DBT interacts with the structure via the sulfur atom to form a transition state, then the alkyl groups of dialkyl DBT likely are imposing steric hindrance. Thus, the oxidation reactivity trend in the polyoxometallates/H_2O_2 in a biphase catalytic system implies the existence of steric hindrance due to the alkyl groups. Our results suggest that there is little steric hindrance in the $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]/H_2O_2$ catalytic system, probably due to the effect of the emulsion. Intuitively, there is a high interfacial surface area of the metastable emulsion droplets in the emulsion system by which the steric hindrance is largely reduced.

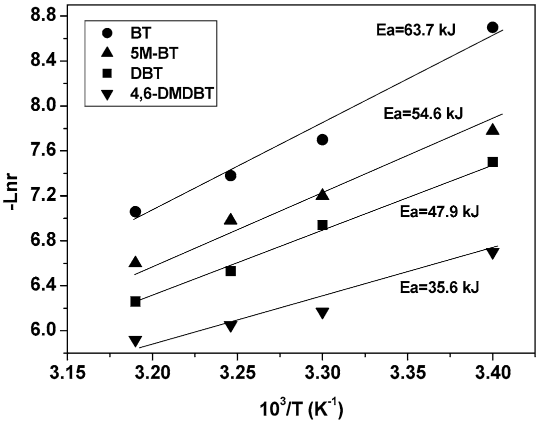


Fig. 6. Arrhenius activation energies for sulfur-containing compounds oxidation in emulsion system.

From the reaction rates determined at various temperatures, the apparent activation energies for the oxidation of the sulfur-containing compounds were derived from the Arrhenius equation (Fig. 6). The activation energy data again showed the following reactivity order: BT < 5-MBT < DBT < 4,6-DMDBT.

In the foregoing experiments, $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ showed high catalytic activity. The oxidation reaction was run under mild conditions, and the activity increased with increasing temperature. The reaction time for 100% conversion of 4,6-DMDBT at 20 °C was 90 min, reduced to 40 min at 30 °C. At 30 and 35 °C, the reaction time for 100% conversion of 5-MBT was <90 min. At the same time, the conversion of BT also increased from 75% at 20 °C to 100% at 30 °C for 120 min. The reaction time for 100% conversion of DBT and 4,6-DMDBT was decreased to close to 20 min, whereas the conversion of BT exceeded 85% within 40 min when the reaction temperature was increased from 30 to 40 °C. Although oxidation of BT is relatively difficult due to BT's low oxidative reactivity, it can be efficiently accomplished in the emulsion system. These results suggest that the sulfur-containing compounds (including DBT and its derivatives) present in the prehydrotreated diesel can be oxidized completely at room temperature, whereas the sulfur-containing compounds (including BT, DBT, and their derivatives) present in the nonhydrotreated diesel can be oxidized at 30 °C.

3.4. Influence of the H_2O_2/sulfur molar ratio (O/S) on the reaction rate

To investigate the effect of the amount of oxidation agent on the oxidative properties, the oxidation of BT in emulsion un-

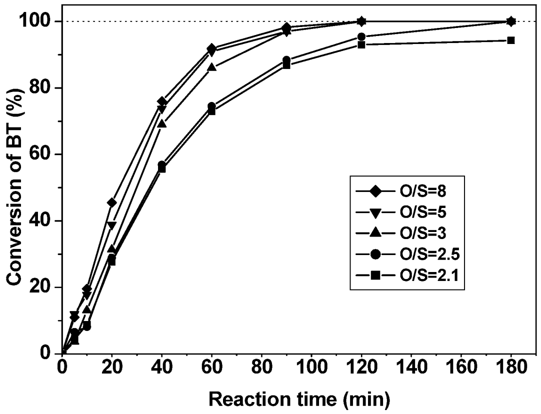
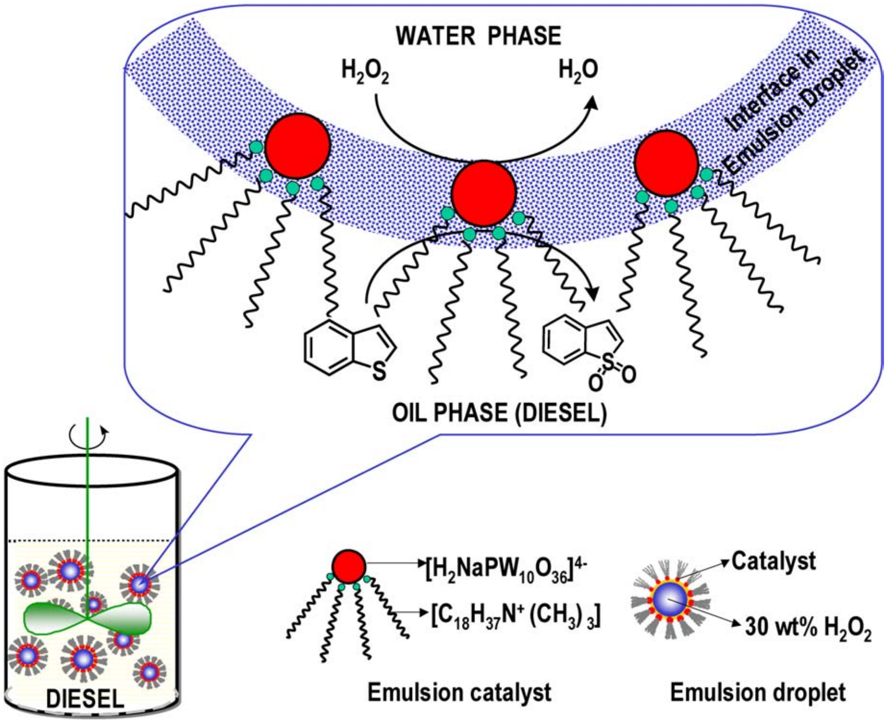


Fig. 7. The influence of the H_2O_2/sulfur molar ratio (O/S) on reaction rate. Conditions: $T = 30\,^\circ C$, benzothiophene (S: 1000 ppm) in decalin.

der various H_2O_2/sulfur (O/S) molar ratios was carried out at 30 °C. To oxidize the sulfur-containing compounds to their corresponding sulfones using hydrogen peroxide as the oxidant, 2 mol of hydrogen peroxide are consumed for 1 mol of sulfur-containing compound, according to the stoichiometric reaction. As shown in Fig. 7, the O/S molar ratio has a strong influence on the reaction rate. The conversion of BT increased from 95% at O/S = 2.1 to 100% at O/S = 2.5 in 3 h. When the O/S ratio reached 3, the time for 100% conversion of BT decreased to 2 h. Further increasing the O/S ratio to 5 and 8 did not change the time for 100% conversion of BT; it remained at 2 h. These findings demonstrate two apparent competing reactions: oxidation of BT and nonproductive decomposition of hydrogen peroxide [9,23,24]. With an O/S molar ratio >3, the concentration of hydrogen peroxide decreases due to decomposition. With an O/S molar ratio <3, the oxidation reaction rate is relatively slow. Therefore, O/S = 3 was chosen in most cases in the present study. Moreover, on the basis of our previous work [13,20], the catalyst molecule as an emulsifying agent could be uniformly distributed in the water–oil interface and form a film around the dispersed water droplets. Consequently, the lipophilic quaternary ammonium cations of the emulsifier would lie on the oil side and the hydrophilic heteropolyanions would lie on the aqueous side. Scheme 1 illustrates a probable pathway for the oxidation reaction of BT to benzothiophene sulfone in the emulsion system. First, the 30 wt% H_2O_2 as the oxidant can continuously supply active oxygen to the heteropolyanions. Second, the heteropolyanions in the water–oil interface of the emulsion droplets oxidize the BT to benzothiophene sulfone.

3.5. *Influence of sulfur-containing compound concentration on reaction rate*

The influence of the BT concentration on the reaction rate was also investigated. The sulfur concentration was varied from 500 to 2000 ppm while the O/S molar ratio was kept constant at 3. The conversions of BT with different concentrations versus reaction time are shown in Fig. 8. The reaction rate increased with increasing BT concentration. Similar results were reported by Fierro et al. [25] in the oxidation of sulfur-containing compounds with a biphasic oxidative catalytic system; this was explained by the influence of the hydrogen peroxide concentration.



Scheme 1. The oxidation of benzothiophene in water/oil emulsion droplets.

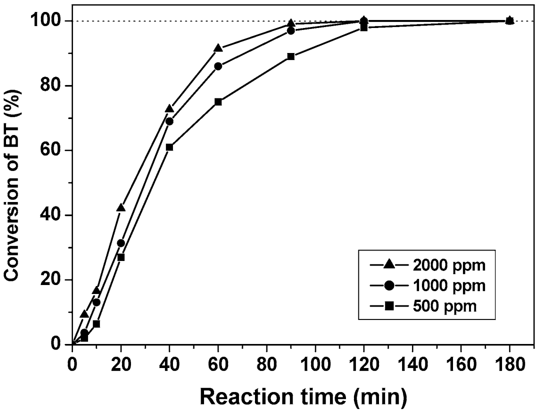


Fig. 8. The influence of the benzothiophene concentration on reaction rate. Conditions: $T = 30\,^{\circ}\mathrm{C}$, $S/H_2O_2 = 1/3$ (molar ratio), solvent: decalin.

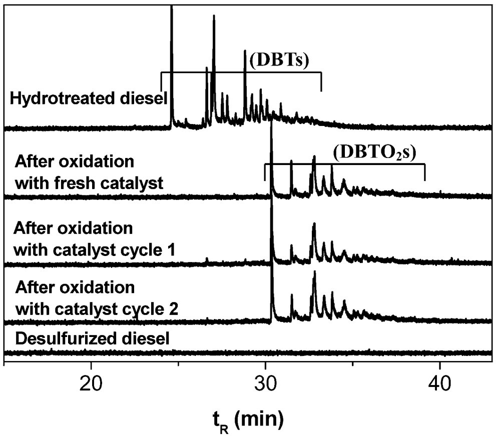


Fig. 9. Sulfur-specific GC-FPD chromatograms of the prehydrotreated diesel, the prehydrotreated diesel after oxidation, and the desulfurized diesel.

3.6. Oxidation and desulfurization of actual diesel

The oxidative desulfurization process was applied to the oxidation and desulfurization of actual diesel, such as a prehydrotreated diesel and a straight-run diesel. Figs. 9 and 10 show the sulfur-specific GC analyses of the original diesel before and after the catalytic oxidation. The prehydrotreated diesel contains a wide range of alkyl-substituted DBTs, whereas the straight-run diesel is composed mainly of various alkyl-substituted BTs and alkyl-substituted DBTs. All sulfur-containing compounds present in the prehydrotreated diesel can be completely oxidized to sulfones at room temperature (22 °C) in 1 h, whereas all sulfur-containing compounds present in the straight-run diesel can be oxidized at 30 °C in 2 h. These findings are also consistent with the order of oxidation reactivity of the model sulfur-containing compounds in decalin: DBTs > BTs. This suggests that $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ has high catalytic activity for all kinds of sulfur-containing compounds present in the actual diesel.

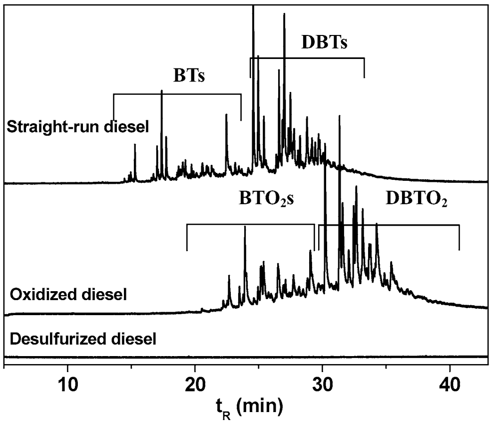


Fig. 10. Sulfur-specific GC-FPD chromatograms of the straight-run diesel, the straight-run diesel after oxidation, and the desulfurized diesel.

The sulfones in oxidized diesel can be removed by a polar extractant, such as 1-methyl-2-pyrrolidone. The efficiencies of oxidative desulfurization of diesel are listed in Table 1. The sulfur concentration of the prehydrotreated diesel after desulfurization can decrease to below the detection limit of 0.1 ppm, whereas the sulfur level of the straight-run diesel after desulfurization can drop to 30 ppm. These results suggest that ultra-deep desulfurization of diesel can be achieved with this emulsion system.

3.7. Efficiency of hydrogen peroxide utilization

As in our previous work [13], here the remaining hydrogen peroxide was determined by $Ce^{VI}(SO_4)_2$ (0.1 M) titration [26]. The conversion was based on sulfides in the diesel, and the efficiency of H_2O_2 utilization was calculated according to the following formula: $(2 \times \text{mol (sulfide)}/\text{mol } (H_2O_2) \text{ consumed}) \times 100\%$. Selective oxidation of the prehydrotreated diesel was obtained, and the efficiency of hydrogen peroxide utilization for oxidation of sulfide was found to be >98%. At the same time, the conversion of sulfides in diesel was 100% for both the fresh and recovered catalyst, as shown in Fig. 9.

In previous oxidative desulfurization systems, the O/S ratio was very high, for example, 160:1 in the formic acid/H_2O_2 system [10] and 162:1 in the polyoxometallate/H_2O_2 system [21] with an aqueous solution of hydrogen peroxide (30 wt%). Therefore, the catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ demonstrates high performance, with only hydrogen peroxide ($O/S \leqslant 3$) consumed.

Table 1
The oxidation of sulfur-containing compounds present in actual diesel and desulfurization efficiencies of actual diesel after extraction

Diesel	Sulfur-containing compounds		Sulfur content (ppm)		Sulfur removal (%)
	Original diesel	Oxidized diesel	Original diesel	Desulfurized diesel	
Prehydrotreated diesel	DBTs	$DBTO_2$s	500	0.1	>99.9
Straight-run diesel	BTs and DBTs	BTO_2s and $DBTO_2$s	6000	30	99.6

4. Conclusion

An ultra-deep desulfurization process for diesel, based on catalytic oxidation with the catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ assembled in emulsion droplets followed by extraction, was developed in this work. Our main findings can be summarized as follows:

1. Sulfur-containing compounds in model and actual diesel can be selectively oxidized using hydrogen peroxide (O/S $\leqslant 3$) in an emulsion catalytic system. The catalytic oxidation reactivity of the sulfur-containing compounds occurs in the following order: BT < 5-MBT < DBT < 4,6-DMDBT. The reactivity of these model sulfur-containing compounds increases with increasing electron density on the sulfur atom, and the oxidation of BTs and DBTs with $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]/H_2O_2$ in emulsion is an electrophilic addition of oxygen atoms.
2. The reaction rates of the oxidation of sulfur-containing compounds increase with temperature and with the molar ratio of hydrogen peroxide and the sulfur-containing compounds.
3. The catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ assembled in emulsion droplets shows a very high intrinsic catalytic activity; it can selectively oxidize not only BTs, but also all kinds of sulfur-containing compounds present in model and actual diesel using an approximately stoichiometric amount of H_2O_2 as an oxidant under mild conditions.
4. The sulfones in the diesel can be removed by a polar extractant, and this process provides a green, low-cost, and effective way to remove sulfur from diesel.

Acknowledgments

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