燃油氧化脱硫

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摘要: 综述了燃油的氧化脱硫, 包括一些具有吸引力的氧化脱硫方法, 如 H_2O_2 /有机酸, H_2O_2 /杂多酸, H_2O_2 /含钛分子筛和其它非过氧化氢体系 (如叔丁基过氧化物等). 对本课题组开发的新型乳液催化氧化脱硫体系进行了详细的介绍. 在乳液体系中, 界面间的传质限制被大大降低. 在温和条件下, 双亲性乳液催化剂可以将柴油中的含硫化合物选择氧化成其相应的砜类化合物. 氧化得到的砜可以使用极性萃取剂将其从油品中除去. 经过氧化和萃取之后, 加氢柴油中的硫含量可以从几百 $\mu\text{g/g}$ 降低至 0.1 $\mu\text{g/g}$, 而直馏柴油中的硫含量则可以从 6000 $\mu\text{g/g}$ 降低至 30 $\mu\text{g/g}$.

关键词: 氧化脱硫; 乳液催化; 萃取; 燃油

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Oxidative Desulfurization of Fuel Oils

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Abstract: Several attractive approaches toward oxidative desulfurization of fuel oils, such as using H_2O_2 /organic acids, H_2O_2 /heteropolyacid, H_2O_2 /Ti-containing zeolites, and other non-hydrogen peroxide systems (e.g., *t*-butyl hydroperoxide etc.) are reviewed. A new alternative oxidative desulfurization process using emulsion catalysts was developed mainly by our group, is introduced in detail. Limitations because of interphase mass transfer are greatly reduced in the emulsion reaction medium. The amphiphilic emulsion catalysts can selectively oxidize the sulfur-containing molecules present in diesel to their corresponding sulfones when using H_2O_2 as the oxidant under mild conditions. The sulfones in the oxidized fuel oils can be removed by a polar extractant. The sulfur level of a prehydrotreated diesel can be lowered from a few hundred $\mu\text{g/g}$ to 0.1 $\mu\text{g/g}$ after oxidation and subsequent extraction whereas the sulfur level of a straight-run diesel can be decreased from 6000 to 30 $\mu\text{g/g}$ after oxidation and extraction.

Key words: oxidative desulfurization; emulsion catalysis; extraction; fuel oil

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Much interest has been shown over the last decade for the application of oxidative desulfurization (ODS) to liquid fuels [1–5]. This has been because of the very stringent environmental regulations that have limited the level of sulfur

in diesel to less than 15 $\mu\text{g/g}$ since 2006 in the US, less than 10 $\mu\text{g/g}$ since 2005 in Europe, and less than 50 $\mu\text{g/g}$ since 2008 in Beijing and Shanghai in China [6,7]. In addition, trace amounts of sulfur can poison the noble metal catalysts

used in the reforming and transforming process of fuels and the electrode catalysts used in fuel cell stacks. Hydrodesulfurization (HDS) is highly efficient for the removal of thiols, sulfides, and disulfides. However, it is difficult to reduce refractory sulfur-containing compounds such as dibenzothiophene and its derivatives especially 4,6-dimethyldibenzothiophene (4,6-DMDBT) to an ultra low level using only conventional HDS [8–12]. Severe operating conditions such as high temperatures, high pressures, and high hydrogen consumption are required for HDS to achieve the ultra-deep desulfurization of diesel. High capital and operating costs are inevitable. Therefore, it is necessary to develop alternative ultra-deep desulfurization processes such as adsorption [1,13–16], extraction [17–20], oxidation [21–25] and bioprocesses [26–30]. Among these, ODS combined with extraction or adsorption is considered to be one of the most promising processes.

ODS offers several advantages compared with HDS. For example, the refractory-substituted dibenzothiophenes (DBTs) are easily oxidized under low temperature and pressure conditions so expensive hydrogen is not required and, therefore, the capital requirement for an ODS unit is significantly less than that for a deep HDS unit. As the use of expensive hydrogen is avoided, these processes are more suitable for small and medium size refineries; especially those that are isolated and not located close to a hydrogen pipeline [31].

The properties of sulfur and carbon are similar in some ways, e.g., the electronegativity of sulfur is very similar to that of carbon. Therefore, the sulfur-carbon bond is relatively non-polar and sulfur-containing compounds exhibit properties quite similar to their corresponding organic compounds [20]. This is the reason why the solubilities of sulfur-containing compounds and hydrocarbons in polar and non polar solvents are nearly identical.

However, if these sulfur-containing compounds that are present in fuels could be oxidized to their corresponding sulfoxides or sulfones their solubility in polar solvents would increase with an increase in their polarity. The electronic *d*-orbitals of sulfur are available for the oxidation of sulfur-containing compounds that will react with oxidants relatively easily [20]. The dipole moment of the oxidized sulfur-containing compounds increases and they are more soluble in polar solvents.

Generally, desulfurization by selective oxidation involves two main steps: First, the sulfur-containing compounds present in diesel are oxidized to the corresponding sulfoxides and sulfones by an oxidant, and then these sulfoxides and sulfones are removed from diesel by extraction, adsorption, or distillation [32,33].

Currently, the main obstacles to the industrial application of ODS are (1) their low-oxidation activity and their low

selectivity for the sulfides present in fuel oils, (2) the difficulties in separation and recovery of the catalysts after the reactions, (3) the low utilization efficiency of H_2O_2 , and (4) the introduction of other components to the oxidation systems [21,25].

Oxidative desulfurization was reported in the literature as early as 1954 [34,35]. However, it was not paid much attention before the current regulations requiring the production of ultra-low sulfur fuel oils. In the last decade many types of oxidative systems have been investigated such as H_2O_2 /organic acids [17,20,36], H_2O_2 /heteropolyacid [3,37], H_2O_2 /Ti-containing zeolites [38–41], and other non-hydrogen peroxide systems (e.g., *t*-butyl hydroperoxide (TBHP), O_2 etc.) [34,42–44]. Some promising systems are discussed below.

1 Oxidative desulfurization

1.1 H_2O_2 /organic acid system

The major organic acids used in ODS are acetic acid and formic acid. For example, conversion/extraction desulfurization (CED) technology began in 1996 when Petro Star Inc. combined conversion and extraction to remove sulfur from diesel fuel [20]. First, the fuel is mixed with H_2O_2 /acetic acid (peroxyacetic acid) and the oxidative reaction takes place below 100 °C under atmospheric pressure. This is followed by a liquid/liquid extraction to obtain a fuel with low sulfur and an extract with high sulfur. Finally, the low sulfur fuel may require additional treatment. The extraction solvent is then removed from the extract for re-use and the concentrated extract is made available for further processing to remove sulfur and to produce hydrocarbon (see Fig. 1).

Fig. 1. Simplified diagram of the CED technology [20].

In a laboratory-scale experiment the fuel did not change significantly and it remained within the quality guidelines. The sulfur levels were markedly reduced from 4720 $\mu\text{g/g}$ to 70 $\mu\text{g/g}$ after processing and the American Petroleum Insti-

tute (API) gravity as well as the cetane number improved.

The extraction solvent is also important for the success of this process. In the CED process the production of cost effective solvent cocktails is most important. High desulfurization efficiencies are required and only a slight influence on the non-polar fuel constituents is allowed.

The reactivity of the different sulfur-containing compounds including methyl phenyl sulfide, thiophenol, diphenyl sulfide, 4-methyldibenzothiophene (4-MDBT), DBT, benzothiophene (BT), 2-methylthiophene (2-MT), 2,5-dimethylthiophene (2,5-DMT), and thiophene was investigated for selective oxidation using hydrogen-peroxide and formic acid by Otsuki and colleagues [45]. The relationship between the electron densities of the sulfur atoms, which was estimated by molecular orbital (MO) calculations, and the oxidative reactivities of the sulfur-containing compounds was also investigated. The electron densities on the sulfur atom of the sulfur compounds are shown in Table 1. The electron densities of the thiophene derivatives varied between 5.696 (thiophene) and 5.760 (4,6-DMDBT). 2,5-DMT, 2-MT, and thiophene usually oxidize with difficulty because of their lower electron densities. BT (electron density 5.739) and other model compounds with higher electron densities were oxidized to form their corresponding sulfones. These apparent rate constants (k) decrease as follows: 4,6-DMDBT > 4-MDBT > DBT > BT. This result indicates that the rate constant increases with an increase in electron density (see Fig. 2).

A hydrogen peroxide and formic acid oxidizing system was also used to study the influence of the solvent on the oxidation rate of the sulfur-containing compounds in the organic phase [46]. The results indicate that heterocyclic sulfur-containing compounds such as benzo- and dibenzothiophene have different kinetic processes compared with thiols and sulfides. The aromaticity of organic solvents has a considerable influence on oxidation rates.

1.2 H₂O₂/heteropolyacid system

A new alternative oxidative desulfurization process has been introduced by British Petroleum to avoid the use of organic or inorganic acids [3]. In this process, the oxidation of dibenzothiophene was studied with hydrogen peroxide using phosphotungstic acid as the catalyst and tetraoctylammonium bromide as the phase transfer agent in a mixture of water and toluene. The catalyzed decomposition of hydrogen peroxide competes with dibenzothiophene oxidation and, therefore, the major cost involved in treating gas oils by oxidative desulfurization is the huge amount of hydrogen peroxide consumption; the sulfur-containing compounds that remain after HDS are particularly reactive toward oxidation and the consumption of hydrogen peroxide

Table 1 Electron densities on sulfur atoms and the rate constants [45]

Sulfur compound	Structure	Electron density	k (L/(mol·min))
Methyl phenyl sulfide		5.915	0.2950
Thiophenol		5.902	0.2700
Diphenyl sulfide		5.860	0.1560
4,6-DMDBT		5.760	0.0767
4-MDBT		5.759	0.0627
DBT		5.758	0.0460
BT		5.739	0.0574
2,5-DMT		5.716	—
2-MT		5.706	—
Thiophene		5.696	—

Fig. 2. Relationship between the rate constants k of the model compounds and their electron densities [45].

during this oxidation is proportional to the amount of sulfur to be oxidized. As a result, the combination of HDS and ODS treatments should be very effective and the oxidative desulfurization process complements conventional desulfurization. Figure 3 shows a scheme to combine the two processes on one site. The oxidized sulfur compounds can be separated from the oil by adsorption on silica gel.

To better understand the oxidation reactivities of the typical refractory sulfur compounds used in diesel fuels, Te

Fig. 3. Integrated HDS-ODS process [3].

et al. [37] studied the reactivity of DBT, 4-MDBT, and 4,6-DMDBT using toluene solutions as the model diesel in a polyoxometalate/ H_2O_2 system. The oxidation reactivities decreased according to $\text{DBT} > 4\text{-MDBT} > 4,6\text{-DMDBT}$, and the same reactivity trend was found for HDS. The apparent activation energies of DBT, 4-MDBT, and 4,6-DMDBT oxidation were 53.8, 56.0, and 58.7 kJ/mol, respectively. These results indicate that DBT oxidation was achieved under mild reaction conditions and it was easy to increase the reaction temperature or reaction time to achieve high conversions, even for the least reactive 4,6-DMDBT, which showed a decrease in reactivity compared with DBT as more methyl substituents were present at the 4 and 6 positions on the DBT rings.

1.3 $\text{H}_2\text{O}_2/\text{MoO}_x$ system

$\text{H}_2\text{O}_2/\text{MoO}_x$ is another major oxidative desulfurization system [47–52]. Garcia-Gutierrez et al. [49] investigated the reactivity of $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts in the oxidative desulfurization process of diesel fuel using hydrogen peroxide as the oxidizing reagent. The catalysts were prepared by equilibrium adsorption using several molybdenum precursors and alumina with different acidity values. They were characterized by Raman spectroscopy. The effect of reaction time, reaction temperature, nature of solvent, concentration of solvent and hydrogen peroxide, and content of molybdenum and phosphate in the catalysts was investigated. The results showed that the activity toward sulfur elimination depends mainly on the presence of hepta- and octamolybdates species on the supported catalyst and the use of a polar aprotic solvent. Likewise, the presence of phosphate markedly increases sulfur elimination. In this way, it is possible to reduce the sulfur level in diesel fuel from about 320 to less than 10 $\mu\text{g/g}$ at 60 $^\circ\text{C}$ under atmospheric pressure.

1.4 $\text{H}_2\text{O}_2/\text{Ti}$ -zeolite system

A series of novel Ti-containing zeolite materials have

been prepared for oxidative desulfurization [38,40,53–61]. For example, Kong et al. [41] synthesized an effective $\text{Ag}/\text{TS-1}$ (0.06 wt%) catalyst for the oxidative desulfurization of organic sulfur in gasoline by equal-volume impregnation. The Ag species was highly dispersed and the preferred deposition was around the Ti species of the TS-1 catalyst. A large amount of Ag loading adversely influences the performance of TS-1 because it may sterically hinder the oxidation of organic sulfur. The oxidative desulfurization of FCC gasoline was carried out over the $\text{Ag}/\text{TS-1}$ catalyst with H_2O_2 as the oxidant and water as the solvent. The results showed that the sulfur content in FCC gasoline decreased from 136.5 to 18.8 $\mu\text{g/g}$ after 4 h.

Park et al. [53] prepared mesoporous TS-1 catalysts by a nanocasting route using two different carbon template sources of CMK-3 and commercial carbon black. The catalytic performance of these samples for allylchloride epoxidation and oxidative desulfurization of the representative refractory sulfur compounds, DBT, and 4,6-DMDBT were compared with those of conventional TS-1. While the allylchloride epoxidation activity for the mesoporous TS-1 samples was similar, mesoporous TS-1 exhibited significantly higher catalytic activities than conventional TS-1 during oxidative desulfurization.

1.5 Non-hydrogen peroxide systems

The Lyondell Chemical Company has demonstrated another cost effective oxidative desulfurization process based on the use of TBHP as an oxidant [34]. Unlike hydrogen peroxide, TBHP is completely fuel soluble making it suitable for oxidative desulfurization. The fuel and TBHP was co-fed over a fixed-bed catalyst under mild temperatures and pressures. Oxidation takes place in less than 10 min with a near quantitative conversion of thiophenes to sulfones. *t*-Butyl alcohol, which is easily removed from the fuel during post processing is produced as a co-product during oxidation. This process was in continuous operation for over 5 months producing diesel with less than 10 $\mu\text{g/g}$ sulfur.

We believed that the ODS can be applied to industrial applications using a fixed-bed reactor with a one phase feed and without any additional solvent. Therefore, more attention has been given to $\text{MoO}_x/\text{Al}_2\text{O}_3$ [62–64] and a silica catalyst [65] etc., and these were also studied for the oxidative desulfurization using TBHP as the oxidant.

1.6 Emulsion catalysis system

The most widely used oxidants for the oxidation of organic sulfur compounds are hydrogen peroxide and organic peroxides such as TBHP. Hydrogen peroxide is a very at-

tractive oxidant for oxidative desulfurization because it is inexpensive and 'green'. A distinct advantage of hydrogen peroxide is the absence of liquid degradation products other than water. In addition it is relatively cheap at < 0.7 US dollar/kg (100% H_2O_2) and about 2.4 million metric tons are produced mainly for use as bleach [66]. Improvements and the development of hydrogen peroxide manufacturing have made this chemical a promising industrial-scale oxidizing agent [67].

However, the oxidative desulfurization of diesel fuel using hydrogen peroxide as an oxidant involves an aqueous/organic biphasic catalytic system, in which the sulfur-containing compounds are present in the diesel phase while the hydrogen peroxide and the catalyst are present in the aqueous phase. Oxidation reaction rates in biphasic systems are low because of mass transfer limitations across the interface. The reaction may take place at the interface or in the bulk of one of the phases. The rate of the process will be determined either by the rate of the chemical reaction or by the rate of diffusion.

This disadvantage has been overcome by using surfactants [68,69], increasing the mixing speed [70], and using ultrasound [71–77]. Some fuel soluble oxidants such as TBHP have also been used as oxidants for oxidative desulfurization [62,63]. However, the cost of TBHP is higher than that of hydrogen peroxide and it is not the most suitable oxidative desulfurization method for industrial applications. Nevertheless, the utilization efficiency of hydrogen peroxide for the oxidation of sulfur-containing compounds is far lower. For example, the O/S ratio was found to be 160:1 in the formic acid/ H_2O_2 system [45] and 162:1 in the polyoxometalate/ H_2O_2 system [3] when using an aqueous solution of hydrogen peroxide (30 wt%). Most of the cost involved in treating gas oils by oxidative desulfurization is due to the over consumption of hydrogen peroxide, and the low utilization efficiency of hydrogen peroxide is not suitable for industrial scale application.

The selective oxidation of the sulfides present in fuel oils has been a challenge for a long time. Recently, a promising alternative oxidative desulfurization process, oxidative desulfurization using emulsion catalysis was developed by our group [21,23].

Two or more immiscible liquids mixed together can form emulsions by the introduction of surfactants. Emulsions consist of one liquid dispersed in the form of small spherical droplets in an immiscible liquid. Emulsions are optically non-transparent and thermodynamically unstable systems with droplet diameters of 0.1–10 μm [78]. High concentrations of hydrophilic and hydrophobic compounds can be dissolved simultaneously in an emulsion.

These emulsions can be considered to contain three regions: the interior of a droplet, the continuous phase, and

the interfacial membrane [78–81]. The interfacial membrane consists of a narrow region surrounding each emulsion droplet. This region is potentially very important in sulfur-containing compounds oxidation since it represents the region where sulfur-containing compounds, hydrogen peroxide, and catalysts interact with each other. For the emulsion reactions the colloidal particles form with surfactant molecules provide a high interfacial surface area and improve the reaction because the interphase mass transport limitations are greatly reduced or eliminated in the emulsion system.

In these emulsion systems, the catalysts usually dissolve in the continuous phase or inside the emulsion droplets and the surfactant molecules adsorb onto the surface of the emulsion droplets and, therefore, the catalysts are separated and recycled with difficulty from the emulsion system. The amphiphilic catalyst combines with the active catalyst and the surfactant and its hydrophile-lipophile balance (HLB) can be tuned. Therefore, the amphiphilic catalyst may act as an emulsifying agent to stabilize the emulsion droplets instead of a common surfactant, and it assembles at the interface of the emulsion droplets. This catalyst is deposited between the water and oil phases after demulsification. This provides a simple method to separate and recycle the catalyst and the surfactant (see Fig. 4) [82]. The formation of metastable emulsion droplets has been observed by optical microscopy (Fig. 5) [83].

Fig. 4. Principle of recyclable amphiphilic catalysts assembled in emulsions [82].

Fig. 5. Fluorescence optical micrograph of the emulsion system [83].

Different quaternary ammonium cations and heteropolytungstophosphate ions were screened to develop an efficient system for the oxidative desulfurization of diesel. The results show that an amphiphilic catalyst with a proper quaternary ammonium cation can form metastable emulsion droplets in diesel with an aqueous H_2O_2 solution. It has high oxidative activity and can be separated after the reaction by centrifugation and demulsification. For example, $[p\text{-C}_5\text{H}_5\text{N}(\text{C}_{16}\text{H}_{33})]_3[\text{PW}_{12}\text{O}_{40}]$ can be used for the formation of water-in-oil microemulsion droplets with H_2O . However, these microemulsion droplets are too stable to be easily demulsified and it is difficult to separate the microemulsion catalyst from the diesel after the reaction. $[(\text{C}_8\text{H}_{17})_4\text{N}][\text{PW}_{12}\text{O}_{40}]$ is another possible active catalyst but it does not improve the formation of metastable emulsion droplets. Therefore, this catalyst has very low catalytic activity for the oxidation of sulfides in diesel. These results indicate that the size and type of quaternary ammonium cation plays a vital role in the formation of metastable emulsion droplets. $(\text{C}_{18}\text{H}_{37})_2\text{N}^+(\text{CH}_3)_2$ and $(\text{C}_{18}\text{H}_{37})\text{N}^+(\text{CH}_3)_3$ were found to be proper quaternary ammonium cations as reported previously [21,22,44,82,84,85]. A series of amphiphilic catalysts in the water/oil (W/O) emulsion system gave very high catalytic activity in that all the sulfur-containing compounds in the model or actual diesel were selectively oxidized to their corresponding sulfones using hydrogen peroxide ($\text{O/S} \leq 3$) as an oxidant under mild reaction conditions.

The oxidation of sulfur-containing compounds (BT, DBT, and their derivatives) in diesel was carried out (see Scheme 1). 4,6-DMDBT was initially used as a model molecule for the oxidation test because it represents the most refractory sulfur-containing molecules in fuels. 4,6-DMDBT and its derivatives have the lowest reactivity in HDS reactions and they are the major sulfur-containing molecules found in diesels after HDS treatment. Figure 6 shows the conversion of 4,6-DMDBT over different reaction times at different temperatures. The results demonstrate that 4,6-DMDBT can be completely oxidized to 4,6-DMDBT-sulfone at 30 °C in about 80 min. Only stoichiometric H_2O_2 is consumed and the turnover number (TON) is estimated to be higher than 300. These results indicate that the amphiphilic catalyst, $[(\text{C}_{18}\text{H}_{37})_2\text{N}(\text{CH}_3)_2]_3\text{-}[\text{PW}_{12}\text{O}_{40}]$, which assembled in the emulsion is very active and selective toward the oxidation of 4,6-DMDBT into sulfones, even near room temperature [21].

The reactivity of different sulfur-containing compounds including BT, 5-MBT, DBT, and 4,6-DMDBT (S: 1000 $\mu\text{g/g}$) was estimated for selective oxidation using another emulsion catalyst $[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3]_4[\text{H}_2\text{NaPW}_{10}\text{O}_{36}]$. The conversion of sulfur-containing compounds versus the reaction times at 35 and 40 °C in the emulsion system are shown

Scheme 1. Oxidation of BT, DBT, and 4,6-DMDBT to their corresponding sulfones in the W/O emulsion [84].

Fig. 6. Conversion of 4,6-DMDBT after oxidation with H_2O_2 as a function of reaction time at different reaction temperatures under mild conditions [21].

in Fig. 7. The catalytic oxidation reactivity of the sulfur-containing compounds increases according to the following: $\text{BT} < 5\text{-MBT} < \text{DBT} < 4,6\text{-DMDBT}$. The oxidation activity order of the sulfur-containing compounds in the emulsion system agrees with those in the formic acid/ H_2O_2 system [45] but not with that of the polyoxometalates/ H_2O_2 in the biphasic catalytic system [3,37].

The formic acid/ H_2O_2 and polyoxometalates/ H_2O_2 in the biphasic catalytic systems have completely different reactivity orders for the oxidation of DBTs because of the important role of the molecular size of the catalyst [37]. For the formic acid catalyzed reaction the formic acid can interact with sulfur without any steric hindrance from alkyl groups. Therefore, the reactivity trend obtained in the formic acid catalyzed reactions reflects the intrinsic oxidation reactivi-

Fig. 7. Conversion of sulfur-containing compounds versus the reaction time in the emulsion at 35 (a) and 40 °C (b) [23].

ties of the DBTs. Phosphotungstic compounds convert to polyoxoperoxo complexes such as $\text{PO}_4[\text{WO}(\text{O}_2)_2]_4^{3-}$ in the presence of hydrogen peroxide [78,79,83]. The tungsten atom in this polyoxoperoxo species is in a highly crowded rigid structure. The alkyl groups of dialkyl DBT likely sterically hinder the polyoxoperoxo species from interacting with DBT via the sulfur atom to form a transition state. Therefore, the oxidation reactivity trend in polyoxometalates/ H_2O_2 in a biphasic catalytic system implies the presence of steric hindrance because of the alkyl groups. These results suggest that there is little steric hindrance in the amphiphilic catalysts/ H_2O_2 catalytic system probably because of the effect of the emulsion. A high interfacial surface area is evident for the metastable emulsion droplets in the emulsion system by which steric hindrance is largely reduced. Figure 8 shows a probable pathway for the oxidation reaction of BT to benzothiophene sulfone in the emulsion system. The 30 wt% H_2O_2 as the oxidant can continuously supply active oxygen to the heteropolyanions and the heteropolyanions at the water-oil interface of the emulsion droplets oxidize BT to benzothiophene sulfone.

To oxidize the sulfur-containing compounds to their corresponding sulfones using hydrogen peroxide as the oxi-

Fig. 8. Oxidation of BT in water/oil emulsion droplets [23].

dant, 2 mol of hydrogen peroxide is consumed for every mol of the sulfur-containing compound according to the stoichiometric reaction. The O/S molar ratio has a visible influence on the reaction rate. In previous oxidative desulfurization systems the O/S ratio was very high as we described above. However, the catalyst $[(\text{C}_{18}\text{H}_{37})_2\text{N}(\text{CH}_3)_2][\text{PW}_{12}\text{O}_{40}]$ [21] and $[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3]_4[\text{H}_2\text{NaPW}_{10}\text{O}_{36}]$ [23] give excellent performance with only hydrogen peroxide ($\text{O/S} \leq 3$) being consumed.

The sulfones in oxidized diesel can be removed by a polar extractant such as 1-methyl-2-pyrrolidone. The results of sulfur removal from diesel are listed in Table 2. The sulfur level of a pre-hydrotreated diesel was lowered from a few hundred $\mu\text{g/g}$ to 0.1 $\mu\text{g/g}$ after oxidation and then extraction (see Fig. 9). The sulfur level of a straight-run diesel decreased from 6000 to 30 $\mu\text{g/g}$ after oxidation and extraction (see Fig. 10). This process provides a green, low-cost, and effective way to remove sulfur from diesel.

2 Perspectives

Heightened environmental concerns and stringent regulations regarding the sulfur content of fuel have resulted in ultra-deep desulfurization becoming important. Selective oxidative desulfurization of diesel fuel is a promising desulfurization process. We highly recommended oxidative desulfurization using emulsion catalysis as a promising approach to address the issue of sulfur in fuel.

Table 2 Oxidation of the sulfur-containing compounds present in actual diesel and sulfur removal of actual diesel after extraction [23]

Diesel	Sulfur-containing compounds		Sulfur content ($\mu\text{g/g}$)		Sulfur removal (%)
	Original diesel	Oxidized diesel	Original diesel	Desulfurized diesel	
Pre-hydrotreated diesel	DBTs	DBTO ₂ s	500	0.1	> 99.9
Straight-run diesel	BTs and DBTs	BTO ₂ s and DBTO ₂ s	6000	30	99.6

Fig. 9. Sulfur-specific GC-FPD chromatograms of the pre-hydrotreated diesel, the pre-hydrotreated diesel after oxidation, and the desulfurized diesel [23].

Fig. 10. Sulfur-specific GC-FPD chromatograms of the straight-run diesel, the straight-run diesel after oxidation, and the desulfurized diesel [23].

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