Deep desulfurization from fuel oil via selective oxidation using an amphiphilic peroxotungsten catalyst assembled in emulsion droplets

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Abstract

A recyclable amphiphilic catalyst, which composed of peroxotungsten anion and quaternary ammonium cation assembled in the interface of the emulsion droplets, shows high selectivity and activity in the oxidation of sulfur-containing molecules to sulfones with hydrogen peroxide in diesel under mild reaction conditions. All the sulfur-containing molecules present in diesel can be completely oxidized into sulfones with ∼100% selectivity of sulfones in W/O (H_2O_2-in-diesel) emulsion system. The sulfones can be readily separated from the diesel, and the sulfur level of the desulfurized diesel can be lowered from about 500 ppm to below 1 ppm with about 98% yield of oil. In addition, the S-containing molecules in straight-run gas oil are also readily oxidized to their corresponding products in the O/W emulsion reaction medium. The S-level of oil layer of the oxidized oil was reduced to below 1 ppm from 312 ppm in the original straight-run gas oil with above 99% yield of oil. The amphiphilic catalysts serve as not only a catalyst but also an emulsifying agent to stabilize the emulsion droplets. The emulsion droplets are not only in the highly dispersed form but also behave like homogenous catalyst with high activity. The limitations due to interphase mass transport are greatly reduced in emulsion reaction medium. Moreover, the emulsion catalysts can be easily separated and recycled by demulsifying.
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Keywords: Recoverable catalysts; Desulfurization; Emulsion catalysis; Oxidation; Sulfides; Diesel; Gasoline

1. Introduction

Emulsion consists of one liquid dispersed in the form of small, spherical droplets in another immiscible liquid. Emulsions are optically untransparent and thermodynamically unstable systems, with droplet diameters in the range of 0.1–10 μm [1]. The amphiphilic surfactants are usually added to emulsion systems, assembling in the interface of the emulsion droplets, thus providing a protective membrane that prevents the droplets from flocculating or coalescing and enhancing the droplets formation and stability. The properties of emulsion have been investigated extensively in last decades, and the emulsions have been widely utilized as media for food, cosmetics, pharmaceutical industries, nanoparticle synthesis and enhanced oil recovery [1–3], but the emulsion reaction medium has not been well introduced into organic synthesis in the biphasic catalytic system.

Phase-transfer catalysis (PTC) and micellar catalysis (MC) as the conventional reaction media have received widely attention in synthetic organic chemistry [4,5], they often result in dramatic increases in reaction rates through introducing the surfactant to the reaction systems. In recent years, the emulsion or microemulsion as the reaction media for organic synthesis has been studied [6–8]. The emulsion reaction system can overcome reagent incompatibility problems because high concentrations of both hydrophilic and hydrophobic compounds can be dissolved simultaneously and also provide a high interfacial area per unit volume therefore the reaction rates in the emulsion system can be greatly increased. In these systems, the catalysts usually dissolve in the continuous phase or inside the emulsion droplets, and the surfactant molecules adsorb on the surface of emulsion droplets, thus the catalysts are difficult to be separated and recycled from the emulsion system (Fig. 1A).

Recently, Kobayashi and Wakabayashi [9] developed a Lewis acid–surfactant-combined catalyst (LASC), which composed
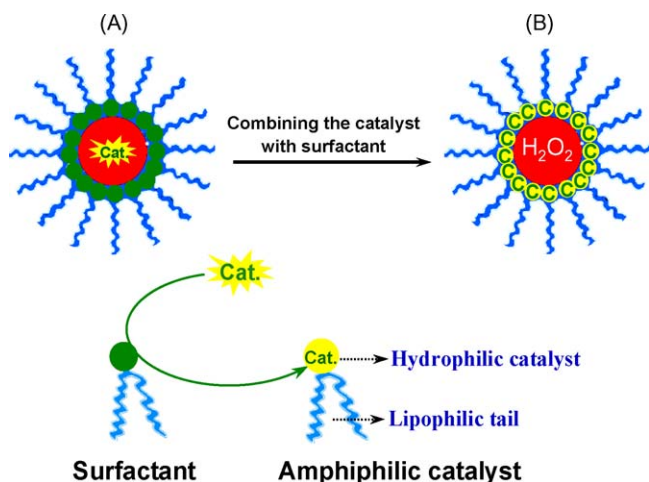
Fig. 1. Principle of recyclable amphiphilic catalyst assembled in emulsions. (A) The surfactant molecules adsorb on the surface of emulsion droplets, and the catalysts are in the emulsion droplets, the catalysts are difficult to be separated and recycled from the emulsion system. (B) Combining the catalyst with surfactant to form an amphiphilic catalyst, assembling in the interface of emulsion droplets instead of only simple surfactant.

of water-stable Lewis acidic cations such as scandium and anionic surfactants. The surfactant-type catalysts have been successfully used for various typical carbon–carbon-forming reaction such as aldol, allylation, and Mannich-type reactions in colloidal dispersion systems. And Kaur and Kozhevnikov [10] and Neumann and Khenkin [11] have reported a similar concept which using the amphiphilic quaternary ammonium tungstophosphate $Q_3\{PW_4[WO(O_2)_2]_4\}$ as catalyst for the epoxidation of olefins in emulsion/microemulsion systems, and the catalyst can be reused. In principle, through combining the catalyst with surfactant to form a surfactant-type catalyst, and tuning the hydrophile–lipophile balance (HLB) of surfactants, the amphiphilic catalyst may act as an emulsifying agent to stabilize the emulsion droplets instead of only simple surfactant, assembling in the interface of emulsion droplets (Fig. 1B), and the amphiphilic catalyst could deposit between the water and oil phases after demulsification, This can be provided a simple method for the catalyst and surfactant to separate and recycle.

Recently, we have developed an amphiphilic $Q_3PW_{12}O_{40}$ emulsion catalyst for the oxidation of sulfur-containing molecules to sulfones in diesel [12a] and the selective oxidation of alcohols to ketones [12b], using H_2O_2 as oxidant in emulsion. Furthermore, the emulsion droplets can be demulsified by centrifugation and the catalyst can be easily separated and recycled. However, the $Q_3PW_{12}O_{40}$ catalyst is not stable and easily depolymerizes into several smaller active species after it reacts with hydrogen peroxide [12c]. In this work, we report an emulsion catalyst $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ that is synthesized by using a combination of hydrophilic peroxotungsten anions and lipophilic surfactant (quaternary ammonium cations). Selective oxidation of sulfur-containing molecules in diesel was carried out with amphiphilic $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst in the W/O emulsion systems. It was found that the emulsion catalyst can be assembled in interface of the emulsion droplets and is very active and selective in the oxidation of DBT-like to

sulfone under mild conditions. The catalyst can be completely oxidized sulfur-containing molecules into sulfones diesel with stoichiometric amounts of H_2O_2 are consumed. The sulfones can be readily separated from the diesel, and the sulfur level of the desulfurized diesel can be lowered from about 500 ppm to below 1 ppm. The emulsion catalyst can be easily recovered and reused after demulsification. These provide a green, highly active and highly selective oxidation process to achieve the ultra-deep desulfurization of fuel oil.

2. Experimental

2.1. Preparation of amphiphilic catalysts based on quaternary ammonium peroxotungstens

Preparation of amphiphilic catalysts is described as follows [13,14]: a solution of pyridine-2-carboxylic acid (7.4 g, 60 mmol) in 10 ml water was added to a solution of 75 ml of 30% hydrogen peroxide containing tungstic acid (15 g, 60 mmol) at 0 °C. The resulting solution was stirred overnight at room temperature. Then a solution of quaternary ammonium cation (60 mmol, $Q = (C_4H_9)_4N^+$, $[(CH_3)_3N^+(C_{18}H_{37})]$, and $[(C_{18}H_{37})_2N^+(CH_3)_2]$) in 30 ml of alcohol (95%) was added dropwise into the above aqueous solution. A white precipitate was immediately formed. After continuously stirring for 24 h, the resulting mixture was filtered and dried at 40 °C in vacuum for 24 h to produce a family of the amphiphilic $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalysts with different chain lengths of the quaternary ammonium cations ($Q = (C_4H_9)_4N^+$, $[(CH_3)_3N^+(C_{18}H_{37})]$, and $[(C_{18}H_{37})_2N^+(CH_3)_2]$) catalysts (yield: 80–90%).

2.2. Oxidation of model sulfur-containing molecules in W/O emulsion system

In a typical reaction run, the sulfide was dissolved in an Erlenmeyer flask containing 25 ml of decahydronaphthalene (S: 600 ng/μl). Then the $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst (0.02 mmol) and hydrogen peroxide (0.16 g, 30 wt.%, $H_2O_2/S = 3:1$) were added into the solution. This mixture was heated to 50 °C under vigorous stirring, and the turbid W/O emulsion was formed. After reaction, the emulsion reaction system was separated by centrifugation, and the upper decahydronaphthalene solution was subjected to GC–FPD and microcoulometry analysis.

2.3. Selective oxidation of real diesel in W/O emulsion system

A 100-ml Erlenmeyer flask was charged with 50 ml of prehydrotreated diesel (500 ppm S), 0.05 g of $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$, and 30 wt.% of H_2O_2 ($H_2O_2/S = 3$, molar ratio). This mixture was heated to 35 °C and the turbid W/O emulsion was formed under vigorous stirring. After continuously stirring for 4 h, the emulsion system was separated by means of centrifugation. The sulfones in the diesel can be removed by extraction with a polar extractant, such as 1-methyl-

2-pyrrolidinone, and the desulfurized diesel is obtained. The sulfur content in original diesel and the desulfurized diesel was determined by GC–FPD and microcoulometry.

2.4. Selective oxidation of straight-run gas oil in W/O emulsion system

A 100-ml Erlenmeyer flask was charged with 50 ml of straight-run gas oil (312 ppm S), 0.05 g of $[(C_{18}H_{37})_2N^+(CH_3)_2]$ $[W(O)(O_2)_2(C_5H_4NCO_2)]^-$, and 30 wt.% of H_2O_2 ($H_2O_2/S = 3$, molar ratio). This mixture was heated to 35 °C and the turbid W/O emulsion was formed under vigorous stirring. After continuously stirring for 2 h, the emulsion system was separated by centrifugation. Then the gasoline was extracted with H_2O, and the desulfurized gasoline is obtained. The sulfur content in the original gasoline and the desulfurized gasoline was determined by GC–FPD and microcoulometry.

3. Results and discussion

3.1. Oxidation of model sulfur-containing molecules in W/O emulsion system

The amphiphilic catalysts as emulsifying agent have pronounced effect on the stabilization/breaking of emulsion droplet. Here, we synthesized a family of the amphiphilic $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalysts with different chain lengths of the quaternary ammonium cations ($Q = (C_4H_9)_4N^+$, $[(CH_3)_3N^+(C_{18}H_{37})]$, and $[(C_{18}H_{37})_2N^+(CH_3)_2]$). So the hydrophile–lipophile values and emulsifying ability of the amphiphilic catalysts can be adjusted according to the catalytic reactions by optimizing the type and structure of the quaternary ammonium cations. The structure of the catalyst was showed in Fig. 2.

To investigate the effect of the quaternary ammonium cations on the emulsion properties of the catalytic system, the oxidation of dibenzothiophene (DBT) to sulfone was performed with the oil-in-water (O/W) emulsion system containing different amphiphilic quaternary ammonium catalysts in an emulsion system. The results are showed in Fig. 3. The $(C_4H_9)_4N^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst with a shorter alkyl chain is difficult to form emulsion droplets and cannot stabilize the dispersion system. The catalyst gives the conversion of 50% of dibenzothiophene (DBT) at reaction times of 5 h (Fig. 3B). If the $[(CH_3)_3N^+(C_{18}H_{37})]$ $[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst with longer chain is used, metastable emulsion droplet can be formed during the reaction, the dibenzothiophene (DBT) can be completely oxidized into sulfones at reaction times of 2 h (Fig. 3C). It was found that a milky metastable emulsion is readily formed when the $[(C_{18}H_{37})_2N(CH_3)_2]$ $[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst with two longer alkyl chains is used under the reaction conditions. The emulsion catalyst exhibits high reaction activity and the complete conversion of DBT was reached at reaction times of less than 120 min (Fig. 3D). The results indicate that the size and hydrophile–lipophile values of the amphiphilic catalyst have pronounced effect on the emulsion droplets stability and the
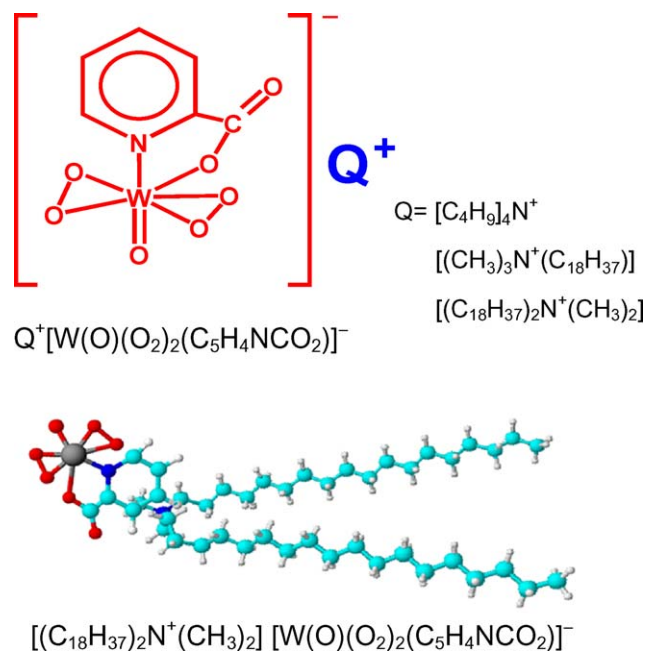

$Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$

$[(C_{18}H_{37})_2N^+(CH_3)_2] [W(O)(O_2)_2(C_5H_4NCO_2)]^-$

Fig. 2. The structure of the amphiphilic $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalysts based on quaternary ammonium peroxotungsten ($Q = (C_4H_9)_4N^+$, $[(CH_3)_3N^+(C_{18}H_{37})]$, and $[(C_{18}H_{37})_2N^+(CH_3)_2]$).

catalytic activity. The emulsion droplets can provide a high interfacial area and the reaction rate can be highly increased. The limitations due to interphase mass transport are greatly reduced in emulsion reaction medium.

The emulsion system also can be applied to the selective oxidation of benzothiophene (BT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). The water-in-oil (W/O) emulsion can be formed by mixing the $[(C_{18}H_{37})_2 N(CH_3)_2]$ $[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst, sulfide, and hydrogen peroxide in proper proportions under vigorous stirring. The BT and 4,6-DMDBT can be completely oxidized
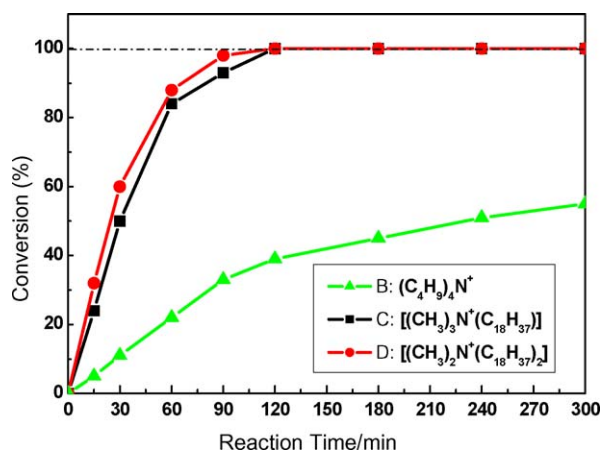

Fig. 3. Reaction profiles for oxidation of dibenzothiophene (DBT) using amphphlic $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalysts with different quaternary ammonium cations in oil-in-water (O/W) emulsion ($B = (C_4H_9)_4N^+$, $C = [(CH_3)_3N^+(C_{18}H_{37})]$, and $D = [(C_{18}H_{37})_2N^+(CH_3)_2]$). Reaction conditions: dibenzothiophene (DBT) in 25 ml of decahydronaphthalene (S: 600 ng/μl), 0.02 mmol of the $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst and 0.16 g of hydrogen peroxide (30 wt.%, O/S = 3.0:1).

Table 1
Catalytic oxidation of sulfides present in real diesel (S: 500 ppm) using the W/O emulsion systems with different amphiphilic quaternary ammonium peroxotungsten as catalysts ($Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$, Q = quaternary ammonium cations) at 35 °C

Catalyst $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$	Sulfide conversion (%)	H_2O_2 efficiency (%)	Emulsion stability	Recovery yield of catalyst (%)
$(C_4H_9)_4N^+$	0	–	Unstable	0
$[(CH_3)_3N^+(C_{18}H_{37})]$	100	93	Metastable	∼68
$[(CH_3)_2N^+(C_{18}H_{37})_2]$ (fresh)	100	96	Metastable	∼90
Cycle 1	100	92	Metastable	∼88
Cycle 2	100	94	Metastable	∼92

Reaction conditions: 50 ml of prehydrotreated diesel (S: 500 ppm), 0.05 mmol of the $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst, sulfides:H_2O_2 = 1:3 (molar ratio) at 35 °C for 4 h. The catalyst was recovered by centrifugation and reused. The unreacted H_2O_2 was determined by $Ce(IV)(SO_4)_2$ (0.1 M) titration. The conversion was based on sulfides in the diesel, and the efficiency of H_2O_2 utilization was calculated according to the following formula: sulfides (mol)/consumed H_2O_2 (mol) × 100.

to corresponding sulfones under mild reaction conditions. It is worthwhile to point out that these organic sulfides such as BT, DBT and 4,6-DMDBT and their derivatives are the most refractory sulfur-containing molecules present in fuel oils and are extremely difficult to be removed using conventional hydrodesulfurization (HDS) [15–18]. Operation at higher temperatures, higher pressure, and more active catalysts with the hydrodesulfurization (HDS) technology is indispensable, but brings higher investment and higher operating cost. Oxidative desulfurization (ODS) turns out to be a promising method as the sulfur-containing compounds can be readily oxidized to sulfones under mild reaction conditions. The chemical and physical properties of sulfones are very different from those of the compounds of fuel oil. Therefore, they can easily be removed by conventional separation operations (e.g., distillation, solvent extraction, adsorption, etc.).

3.2. Selective oxidation of sulfides present in real diesel in W/O emulsion

Many types of oxidative systems of sulfides present in fuel oils have been reported, such as H_2O_2/organic acids, H_2O_2/inorganic acids, H_2O_2/Ti-containing zeolites and other non-hydrogen peroxide systems (e.g., N_2O, O_3, etc.) [19–25]. However, some components of the fuel are also oxidized along with the oxidation of S-containing molecules. Therefore, a large quantity of oxidant of hydrogen peroxide is consumed, thus increasing the operating cost. Here, we carried out the oxidation of sulfides present in real diesel (about 500 ppm S) by using the amphiphilic catalysts with different quaternary ammonium cations with O/S (H_2O_2/sulfides) molar ratio at 3.0 under mild conditions and the catalytic performance of the catalysts is listed in Table 1. It can be seen the catalysts with longer chain such as $[(CH_3)_3N^+(C_{18}H_{37})]$ $[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ and $[(C_{18}H_{37})_2N^+(CH_3)_2]$ $[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ can form metastable emulsion and oxidize the sulfur-containing molecules into sulfones with high utilization efficiency of hydrogen peroxide (>90%) and high recovery yield of the catalysts (∼90%). Small portion of catalyst lost in the emulsion reaction systems due to its amphiphilic property. But the lost catalyst can be removed and recovered by the extraction without affecting on the quality of the fuel oil. The formed metastable emulsion droplets during the reaction can be observed with the optical microscope (Fig. 4). Dynamic light scattering revealed that

the size of the forming spherical emulsion droplets is about 600 nm in diameter that is within a range of typical emulsion size. While the $(C_4H_9)_4N^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst with a shorter alkyl chain cannot form the emulsion droplets and almost cannot catalyze the oxidation of the sulfides present in diesel fuels because the catalyst is water-soluble with poor emulsifying ability during the reaction. Fig. 5 shows the sulfur-specific gas chromatography (GC) analysis of real diesel before and after the catalytic oxidation. The sulfides present in the diesel are mainly composed of wide range of alkyl-substituted dibenzothiophenes (DBTs) (Fig. 5A). After the real diesel was oxidized with the $[(C_{18}H_{37})_2N(CH_3)_2]$ $[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst, the peaks of the DBTs completely disappear, while the peaks of the corresponding DBT sulfones appear at higher retention times (Fig. 5C), confirming that all the sulfur-containing molecules present in real diesel can be completely oxidized into sulfones in the W/O emulsion system under mild reaction conditions. The used catalyst can be easily separated from the reaction system by demulsification and sedimentation. The recovered catalyst (after two cycles) shows almost the same catalytic performance as the fresh one, indicating that the catalyst can be recycled and reused for this reaction (Table 1 and Fig. 5D). The sulfones can be
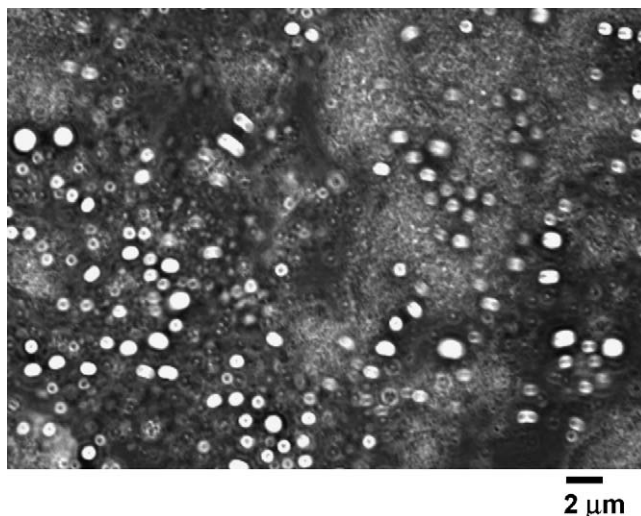

2 μm

Fig. 4. The optical micrograph of the reaction mixture of 50 ml of prehydrotreated diesel (500 ppm S), 0.05 g of $[(C_{18}H_{37})_2N^+(CH_3)_2]$ $[W(O)(O_2)_2(C_5H_4NCO_2)]^-$, and 30 wt.% of H_2O_2 (H_2O_2/S = 3, molar ratio).
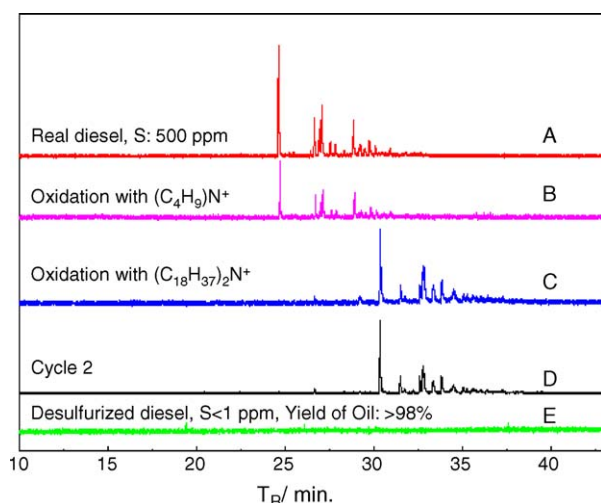
Fig. 5. Sulfur-specific GC–FPD chromatograms of real diesel, real diesel after oxidation and desulfurized diesel. Gas chromatography (GC): Agillent 6890 equipped with a capillary column (PONA, 50 m × 0.2-mm i.d. × 0.5 μm); reaction condition: 50 ml of prehydrotreated diesel (500 ppm S), 0.05 g of the catalyst, and 30 wt.% of H_2O_2 ($H_2O_2/S = 3$, molar ratio), 35 °C for 4 h.

completely extracted by a polar extractant, such as 1-methyl-2-pyrrolidinone, and the desulfurized diesel is obtained. The sulfur-specific GC and microcoulometry for the desulfurized real diesel show that the sulfones present in the diesel can be easily removed, and the sulfur content in the diesel after the process is below 1 ppm with above 98% yield of diesel oil (Fig. 5E). The $(C_4H_9)_4N^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst with a shorter alkyl chain almost cannot catalyze the oxidation of the sulfides present in diesel fuels to sulfones (Table 1 and Fig. 5B). These results indicate only the amphiphilic catalyst with proper hydrophile–lipophile values can uniformly distribute in the water/oil interface and form a film around the dispersed water droplets. The state of the amphiphilic catalyst not only maintains the emulsion droplets stable but also provides higher interfacial surface area where the reaction takes place, resulting in more reaction encounter probability and high reaction rates. During the reaction, the highly dispersed droplets of 30% H_2O_2 in the emulsion system can continuously supply active oxygen to the catalyst. Then the sulfide was oxidized into sulfone by the amphiphlic catalyst in the water/oil interface. The oxidation of sulfur-containing molecules to sulfones in the W/O emulsion droplets can be described as in Scheme 1.

3.3. Selective oxidation of straight-run gas oil in W/O emulsion system

Ultra-deep desulfurization of straight-run gas oil (SR-LGO) via the oxidation mehtod has received much attention in recent years [20]. Here, selective oxidation of straight-run gas oil was studied in the W/O emulsion systems. Fig. 6 shows the GC–FPD chromatograms of straight-run gasoline before and after the catalytic oxidation. The sulfides present in SR-LGO are mainly composed of thioether and mercaptan compounds (Fig. 6A). The GC peaks of the sulfur compounds in SR-LGO of oxidized oil were completely disappear (Fig. 6B). The result indicates
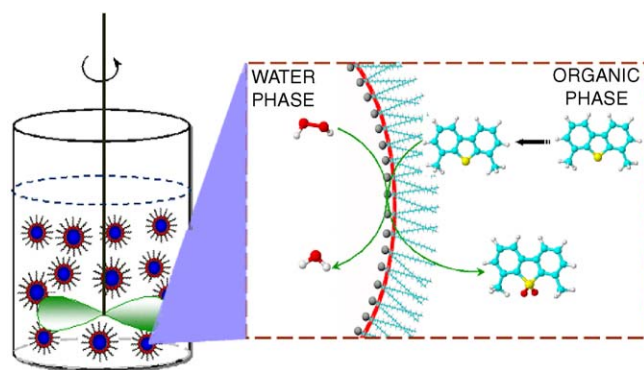
Scheme 1. The oxidation of sulfur-containing molecules to sulfones in diesel, using H_2O_2 as oxidant in the W/O emulsion droplets. The emulsion catalytic reaction medium is in the highly dispersed form and behaves like homogeneous catalysis. During the reaction, the hydrogen peroxide as oxidant in the emulsion droplets can continuously supply active oxygen to the catalyst then the substrate was oxidized into corresponding product by the amphiphilic catalyst in the water/diesel oil interface.

that the sulfides in straight-run gas oil are also readily oxidized to their corresponding products in the O/W emulsion under the mild reaction condition. The oxidative products are water-soluble and can be easily transferred to the water phase. The sulfur content of oil layer of the oxidized oil was reduced to below 1 ppm from 312 ppm in the original SR-LGO with above 99% yield of oil. So a combined oxidation and extraction can be completed using in the emulsion system. This provides a catalytic oxidation process that can selectively oxidize the sulfur-containing molecules present in SR-LGO using H_2O_2 as an oxidant under mild conditions.

The emulsion catalysis is different from the phase-transfer catalysis (PTC) and micellar catalysis (MC) [4,5]. The micellar reaction media is usually encapsulated the catalysts in micelles, and the reactions are normally carried out in a homogenous or pseudohomogeneous phase. The phase-transfer catalysis is to
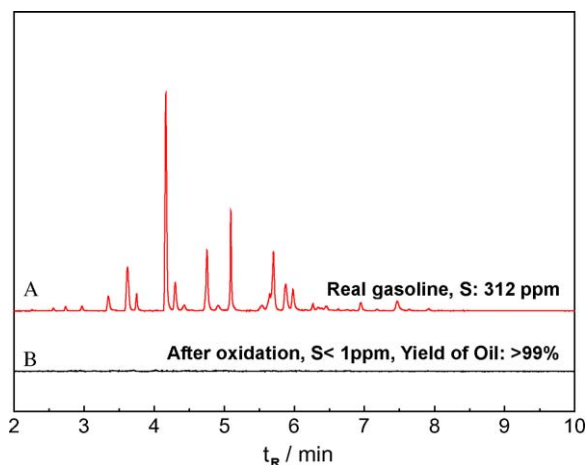

Fig. 6. Sulfur-specific GC–FPD chromatograms of straight-run gasoline before and after the catalytic oxidation. Gas chromatography (GC): Agillent 6890 equipped with a capillary column (PONA, 50 m × 0.2-mm (i.d.) × 0.5 μm); reaction condition: 50 ml of straight-run gasoline (312 ppm S), 0.05 g of $[(C_{18}H_{37})_2N^+(CH_3)_2]$ $[W(O)(O_2)_2(C_5H_4NCO_2)]^-$, and 30 wt.% of H_2O_2 ($H_2O_2/S = 3$, molar ratio), 35 °C for 4 h.

transfer a molecule or ion from one reaction phase to another, and the reaction occurs primarily within the bulk of oil phase. While the emulsion reaction system is that amphiphilic catalyst is assembled in the interface of emulsion droplets, not in the continuous phase or inside the emulsion droplet. The reactions take place in the interface of the emulsion droplets, which may provide unique microenvironment for substrates and catalyst. In addition, the emulsion catalysis provides a method of designing and organizing the amphiphilic catalyst in the molecular scale to enhance the reaction rate and to recycle the catalyst. Several quaternary ammonium peroxotungstens have been demonstrated in this work, but the idea of the amphiphilic catalysts is not limited to these catalysts, and the reaction could be extended to wide range of organic synthesis reactions when the catalysts are accommodated in the interface of the emulsion droplet.

4. Conclusions

In summary, we report an amphiphilic $Q^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$ catalyst for the selective oxidation of S-containing molecules present in diesel to sulfones in W/O emulsion systems. The emulsion catalyst possesses both hydrophilic and hydrophobic structure, and self-assembles in the interface of emulsion droplets where the chemical reaction takes place. The catalyst $[(C_{18}H_{37})_2N(CH_3)_2][W(O)(O_2)_2(C_5H_4NCO_2)]^-$ with longer chain shows high selectivity and activity in the oxidation of sulfur-containing molecules to sulfones in diesel with hydrogen peroxide under mild reaction conditions. For examples, BT, DBT, 4,6-DMDBT and their derivatives can be completely oxidized to corresponding sulfones with stoichiometric hydrogen peroxide. The sulfones can be readily separated from the diesel using an extraction and the sulfur level of the desulfurized diesel can be lowered from about 500 ppm to below 1 ppm. Moreover, the amphiphilic catalyst can be separated and recycled.

Acknowledgements

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