Ultra-Deep Desulfurization of Diesel: Oxidation with a Recoverable Catalyst Assembled in Emulsion

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Abstract: A $[(C_{18}H_{37})_2N^+(CH_3)_2]_3$-$[PW_{12}O_{40}]$ catalyst, assembled in an emulsion in diesel, can selectively oxidize the sulfur-containing molecules present in diesel into their corresponding sulfones by using H_2O_2 as the oxidant under mild conditions. The sulfones can be readily separated from the diesel using an extractant, and the sulfur level of the desulfurized diesel can be lowered from about 500 ppm to 0.1 ppm without changing the properties of the diesel. The catalyst demonstrates high performance ($\geq 96\%$ efficiency of H_2O_2, is easily recycled, and

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$\sim 100\%$ selectivity to sulfones). Metastable emulsion droplets (water in oil) act like a homogeneous catalyst and are formed when the catalyst (as the surfactant) and H_2O_2 (30%) are mixed in the diesel. However, the catalyst can be separated from the diesel after demulsification.

Introduction

Ultra-deep desulfurization of fuel oils has become an environmentally urgent subject worldwide. Very stringent environmental regulations limit the sulfur levels in diesel fuels to less than 15 ppm by the year 2006.[1–3] However, it is very difficult to decrease the sulfur content from several hundred ppm to a few ppm with current technology. 4,6-dimethyldibenzothiophene (4,6-DMDBT) and its derivatives are the most refractory sulfur-containing molecules present in diesel and are extremely difficult to remove by means of conventional hydrodesulfurization (HDS).[4–7] Operation at high temperatures and pressures is inevitably required to remove these refractory sulfur molecules and obtain the ultra-deep desulfurization of diesel fuels. However, this brings about a number of problems including high investment, high operating cost, reduction of the catalyst cycle length, and increase

in the hydrogen consumption due to the hydrogenation of aromatics present in diesel fuels.[5,6]

The ultra-deep desulfurization of fuel oils is not only used for producing clean fuels to meet the new emission control standards, but also for producing sulfur-free hydrogen used in fuel-cell systems, in which the hydrogen can be produced potentially through the reforming of fuel oils.[8,9] Fuel-cell systems must be run with little-to-no sulfur content, because sulfur can irreversibly poison the precious metal catalysts and electrodes used.[9]

For these reasons, alternate desulfurization processes are absolutely necessary for producing clean fuels. Possible strategies to realize ultra-deep desulfurization currently include adsorption,[10,12] extraction,[17] oxidation,[13,14] and bioprocesses.[15,16] Selective catalytic oxidation combined with extraction is one of the most promising ultra-deep desulfurization methods. Liquid-liquid extraction has been effectively utilized to remove sulfur and/or nitrogen molecules from petroleum distillates and synfuels.[17] However, the efficiency of sulfur removal is low due to the similarity between the sulfur-containing molecules and the remaining diesel fuels. Since the polarity of sulfones is greater than that of the corresponding sulfides, the solubility of sulfones in a polar solution is much higher than that of sulfides. The efficiency of desulfurization, by using either extraction or adsorption, can be significantly increased after oxidizing sulfides into sulfones. At present, the main obstacles to the industrial application of the process are 1) the low-oxidation activity and low selectivity of the sulfides present in fuel oils, 2) the difficulties in separation and recovery of the catalysts after the

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reactions, 3) the low efficiency of H_2O_2 utilization, and 4) the introduction of other components in oxidation systems.[7]

The selective oxidation of sulfides present in fuel oils has been a challenge for a long time. Many types of oxidative systems have been attempted, such as H_2O_2/inorganic acids,[17] H_2O_2/organic acids,[18] H_2O_2/heteropolyacid,[5,7,18] H_2O_2/Ti-containing zeolites,[19] and other non-hydrogen peroxide systems (e.g., NO_2, O_3, etc.).[17,18] However, the selectivity in these systems is not high enough to oxidize the sulfides present in diesel fuels, and some unsaturated hydrocarbons of the fuel are also oxidized. Furthermore, a large quantity of oxidant is required[5] and the operating cost is increased.

Here we report that a catalyst, $[(C_{18}H_{37})_2N^+(CH_3)_2]_3$-$[PW_{12}O_{40}]$, assembled in emulsion in diesel, can selectively oxidize the 4,6-dimethyldibenzothiophene-like (4,6-DMDBT-like) compounds to sulfone with stoichiometric amounts of H_2O_2 under mild conditions. The sulfones can then be readily separated from the diesel using an extractant, and the catalyst can be recycled. The sulfur level of the desulfurized diesel can be lowered from about 500 ppm to 0.1 ppm without changing the properties of the diesel.

Results and Discussion

Catalysts with different quaternary ammonium cations were synthesized. Only catalysts with proper cations can form metastable emulsion droplets with H_2O_2 (30%) in diesel (water in oil) and be easily separated from the diesel. The catalyst with the proper quaternary ammonium cations essentially serves as a surfactant that keeps the emulsion droplets relatively stable. For example, $[\pi-C_5H_5N^+(C_{16}H_{33})]_3$-$[PW_{12}O_{40}]$ can form the 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.[20,21] $[(C_8H_{17})_4N^+]_3[PW_{12}O_{40}]$ is another possible active catalyst, but it cannot form a metastable emulsion droplet. Thus, this catalyst has a very low catalytic activity for the oxidation of sulfides present in diesel. These results indicate that the size and type of quaternary ammonium cations play a vital role in the formation of the metastable emulsion droplet. We found that the metastable emulsion droplets are readily formed when $[(C_{18}H_{37})_2N^+(CH_3)_2]_3[PW_{12}O_{40}]$ is mixed with H_2O_2 (30%) in diesel and stirred. The metastable emulsion droplets can be easily demulsified by centrifugation and the catalyst can then be recycled. Formation of the metastable emulsion droplets was confirmed by optical microscopy (Figure 1).

At first, 4,6-DMDBT was used as a model molecule for the oxidation test because it can represent the most refractory sulfur-containing molecules in oil. 4,6-DMDBT and its derivatives have the lowest reactivity in hydrodesulfurization (HDS) reactions and constitute the majority of the sulfur-containing molecules remaining in diesels after HDS treatment. Figure 2 shows the conversion of 4,6-DMDBT with reaction time at different temperatures. The results
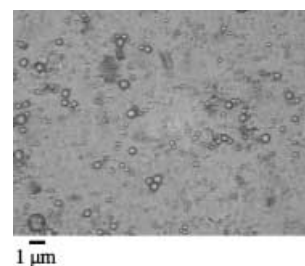

Figure 1. Optical micrograph of the reaction mixture of prehydrotreated diesel (50 mL, 0.053 wt% S), $[(C_{18}H_{37})_2N^+(CH_3)_2]_3[PW_{12}O_{40}]$ (0.010 g, 2.21 µmol), and H_2O_2 (0.19 mL, 1.84 mmol, 30 wt%).
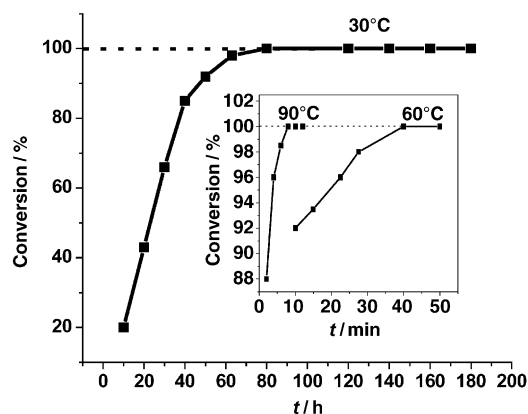

Figure 2. Conversion of 4,6-DMDBT after the oxidation with H_2O_2 as a function of reaction time at different reaction temperatures under the following conditions: catalyst/4,6-DMDBT/H_2O_2 = 1:319:833 (molar ratio).

demonstrate that 4,6-DMDBT can be completely oxidized into 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 $[(C_{18}H_{37})_2N^+(CH_3)_2]_3[PW_{12}O_{40}]$ catalyst assembled in emulsion is very active and selective in the oxidation of 4,6-DMDBT into sulfones even near to room temperature. The reaction time for a complete conversion can be shortened to 30 min and 8 min as the reaction temperature is elevated to 60°C and 90°C, respectively.

Figure 3 shows the sulfur-specific gas chromatography (GC) analyses of real diesel before and after the catalytic oxidation. The sulfides present in the diesel are mainly composed of a wide range of alkyl-substituted dibenzothiophenes. It is worthwhile to note that all the sulfur-containing molecules can be completely oxidized into sulfones, and consequently the sulfones can be completely extracted by a polar extractant. This indicates that the catalyst shows high activity, not only for the model compound 4,6-DMDBT, but also for the oxidation of all different types of sulfides present in real diesel. The used catalyst can be easily separated from the reaction system by demulsification and sedimentation. The recovered catalyst (after 3 cycles) shows almost the same catalytic performance as the fresh one, indicating that the catalyst can be recycled and reused for this reaction. The sulfur-specific GC and microcoulometry for the desulfurized real diesel show that the sulfur present in the diesel
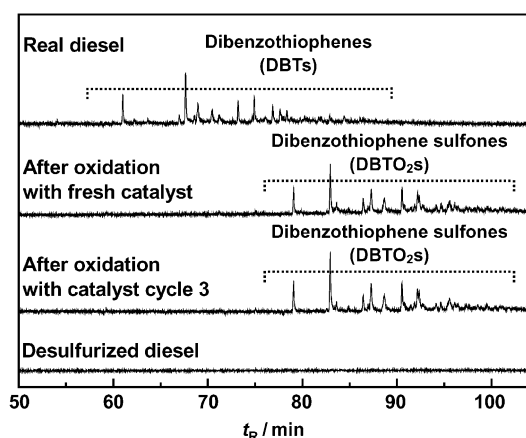
Figure 3. Sulfur-specific GC-AED chromatograms of real diesel, real diesel after oxidation, and desulfurized diesel. Gas chromatography (GC): Hewllet-Packard 6890 equipped with a capillary column (PONA, 50 m × 0.2 mm, id × 0.5 μm); atomic emission detector (AED): Hewlett-Packard G2350A. Analysis conditions were as follows: injection port temperature, 280 °C; AED transfer line/cavity temperature, 280 °C; oven temperature program, 120–280 °C at a 1.5 °C gradient, hold for 10 min; column pressure, 12 psi; carrier gas, helium; reagent gases, oxygen of 50 psi, hydrogen of 30 psi; wavelength for sulfur, 181 nm.

can be completely removed by the combined process of selective catalytic oxidation and extraction, and the sulfur content in the diesel after the process is below our detection limit, 0.1 ppm.

The remaining H_2O_2 was determined by $Ce^{IV}(SO_4)_2$ (0.1 M) titration.[22] The conversion was based on sulfides in the diesel, and the efficiency of H_2O_2 utilization was calculated according to the following formula: (no. mol sulfides)/(no. mol consumed H_2O_2) × 100. The efficiency of hydrogen peroxide utilization for the oxidation of sulfides present in diesel is more than 96 %, and the conversion of sulfides in diesel is 100 %, for both the fresh and the recovered catalysts. This indicates that any side reactions, such as the oxidation of compounds other than sulfides, are negligible. This is actually a green process as only stoichiometric amounts of H_2O_2 are consumed, and the only byproduct is water. This greatly reduces the H_2O_2 consumption and the operating cost, and makes the process promising for future applications.

A combined oxidation and extraction desulfurization process is described in Scheme 1. A mixture of the $[(C_{18}H_{37})_2N^+(CH_3)_2]_3[PW_{12}O_{40}]$ catalyst and an H_2O_2 aqueous solution (30 %) is added to the diesel (Scheme 1A). An emulsion droplet (30 % H_2O_2 water in oil, w/o) is immediately formed with stirring (Scheme 1B). The catalyst in the emulsion droplets acts as a surfactant, and the H_2O_2 (30 %) in the emulsion can continuously supply active oxygen to the catalyst. The catalyst at the interface between the diesel and the H_2O_2 (30 %) then oxidizes the sulfides into sulfones in the diesel. This emulsion system behaves like a homogeneous catalyst and as a consequence, shows high activity even at relatively low temperatures (Scheme 1C). After the sulfides in diesel are completely oxidized, the catalyst can be separated from the diesel through demulsification and centrifugation (Scheme 1D). The sulfones in the diesel can
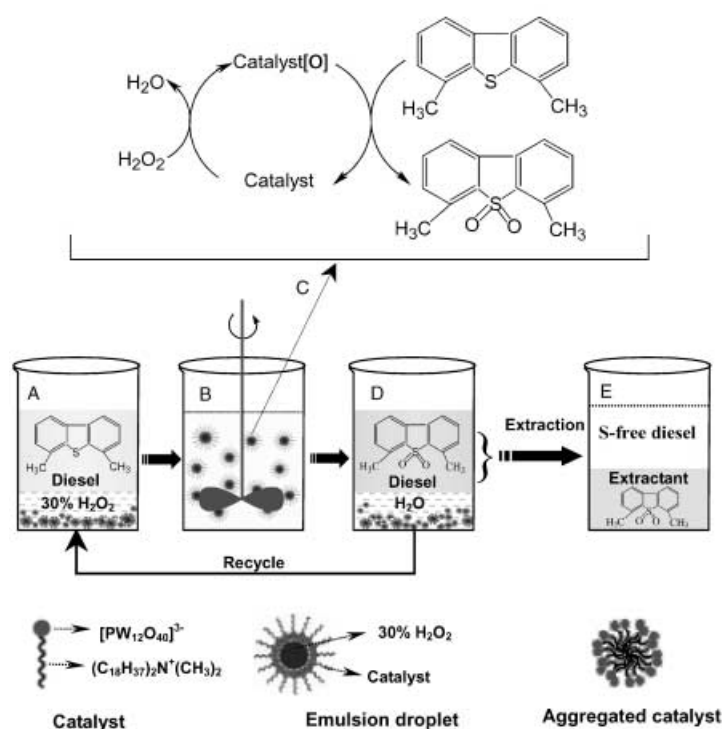
Scheme 1. Catalytic oxidation and extraction of sulfur-containing molecules present in real diesel: A) before oxidation; B) during oxidation; C) catalytic oxidation of sulfur-containing molecules in emulsion droplets; D) after oxidation; E) extraction with a polar extractant.

be removed by a polar extractant, and the sulfur-free diesel is obtained (Scheme 1E).

In summary, the catalyst $[(C_{18}H_{37})_2N^+(CH_3)_2]_3[PW_{12}O_{40}]$ assembled in emulsion droplets can selectively oxidize the sulfur-containing molecules present in diesel using H_2O_2 as an oxidant under mild conditions. The catalyst in the emulsion demonstrates high performance (≥ 96 % efficiency of H_2O_2, is easily recycled, and ~100 % selectivity to sulfones) that makes it possible to achieve the ultra-deep desulfurization (< 0.1 ppm sulfur).

Experimental Section

For a model reaction run, 4,6-DMDBT (0.1571 g, 0.704 mmol, 95 %) was dissolved in an Erlenmeyer flask (100 mL) with a solvent mixture of decahydronaphthalene (20 mL), tetrahydronaphthalene (15 mL), and *n*-dodecane (15 mL). Then, $[(C_{18}H_{37})_2N^+(CH_3)_2]_3[PW_{12}O_{40}]$ (0.010 g, 2.21 μmol) and hydrogen peroxide (0.19 mL, 1.84 mmol, 30 wt %) were added to the solution. This triphasic mixture was heated to 30 °C in 10 minutes and stirred at 1000 rpm. When the desired reaction time was reached, the Erlenmeyer flask was immersed in an ice-water bath. The catalyst was precipitated and the 4,6-DMDBT-sulfone was also precipitated as a white solid, as the 4,6-DMDBT-sulfone is not dissolved in the solvent, and was separated from the solution. The upper clear solution was removed after separation by means of centrifugation and subjected to GC-atomic emission detector (GC-AED) analysis.

For real diesel, an Erlenmeyer flask (100 mL) was charged with prehydrotreated diesel (50 mL, 0.053 wt % S), $[(C_{18}H_{37})_2N^+(CH_3)_2]_3[PW_{12}O_{40}]$ (0.010 g, 2.21 μmol), and H_2O_2 (0.19 mL, 1.84 mmol, 30 wt %). This triphasic mixture was heated to 30 °C and the temperature maintained while stirring at 1000 rpm for 20 min. The stirring was stopped, and the solution was cooled to room temperature and kept at this temperature

overnight. After finishing the selective oxidation of sulfides present in diesel, the catalyst was precipitated and separated by means of centrifugation. The sulfones in the diesel can be removed by 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 microcoulometry (detection limit: $0.1\ ng\,\mu L^{-1}$).

Acknowledgment

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