Deep desulfurization of diesel by selective oxidation using amphiphilic paradodecatungstate catalyst

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ABSTRACT
An amphiphilic paradodecatungstate catalyst, [(C18H37)2N(CH3)2]9[NaH2W12O42] was prepared and characterized by Fourier transform infrared spectroscopy, UV–visible spectrum, differential thermal analysis, and thermogravimetric analysis. The amphiphilic catalyst exhibits very high catalytic activity that dibenzothiophene (DBT) in model diesel can be oxidized into dibenzothiophene sulfones using hydrogen peroxide as an oxidant. The reactivity of sulfur compounds decreased in the order of DBT > 4,6-DMDBT > BT > 5-MBT. The reaction rates of these sulfur compounds are sensitive to the electron density on sulfur atoms and the steric hindrance of the substituted groups of sulfur compounds. The sulfur level of a commercial diesel after desulfurization can drop from 200 ppm to about 12 ppm.

GRAPHICAL ABSTRACT

Introduction
Sulfur in transportation fuels remains a major source of air pollution. It not only poisons the catalysts used in automotive and portable fuel cells but also causes a series of environmental problems, such as acid rain and particulate matter (PM) 2.5. In the

United States, since 2006, very stringent environmental regulations have limited sulfur level in diesel to less than 15 ppm.1 Optimal hydrodesulfurization (HDS) is difficult and costly to reduce the level of dibenzothiophenes (DBTs), especially those with alkyl substituents, at 4 and 6 positions.2 Therefore, alternative desulfurization techniques have been extensively
investigated. Among them, oxidative desulfurization (ODS) combined with extraction is considered to be one of the most promising processes.\(^3\)

Recently, a series of amphiphilic catalysts for ODS in diesel had been reported.\(^4\) The amphiphilic catalysts showed remarkably high selectivity and activity in the ODS of diesel. It was suggested that the catalyst molecule, as an emulsifying agent, could be uniformly distributed in the water–oil interface and forms a film around the dispersed water droplets. The lipophilic quaternary ammonium cations lie on the oil side and the hydrophilic heteropolyanions lie on the aqueous side. Hydrogen peroxide (H\(_2\)O\(_2\)) can continuously supply active oxygen to heteropolyanions, and heteropolyanions oxidize sulfur compounds to corresponding sulfone in water–oil interface. Fortunately, the conjecture was directly confirmed by fluorescence microscopy.\(^5\) It encouraged us and led to further research into ODS with amphiphilic catalyst in this study.

In this paper, a novel amphiphilic catalyst [(C\(_{18}\)H\(_{37}\))\(_2\)N(CH\(_3\))\(_2\)]\(_9\)[NaH\(_2\)W\(_{12}\)O\(_{42}\)] was developed. The amphiphilic paradodecatungstate catalyst was synthesized by using a combination of hydrophilic paradodecatungstate anions and lipophilic surfactant. It exhibited very high activity that DBT can be completely oxidized to dibenzothiophene sulfones (DBTOS) at 60°C in 60 min (Scheme 1). Also, we have investigated the effect of reaction temperature, oxidant dosage, and the nature of sulfur compounds on desulfurization efficiency. The desulfurization performance of an actual commercial diesel was also examined.

**Results and discussion**

**Structure of the paradodecatungstate anion catalyst**

As shown in Figure 1, the paradodecatungstate anion is centrosymmetric and comprises four corner-sharing groups of two types of trimetallic units [W\(_3\)O\(_{13}\)] and [W\(_3\)O\(_{14}\)]. In one type, three W atoms define an equilateral triangle, which is analogous to the trimetallic groups constituting the Keggin isomer, while in the other type, three W atoms define an angular open trimer. Two regular and two open trimer units assemble around a central cavity, which contains two disordered protons.\(^6\) The W–O bonds in [H\(_2\)W\(_{12}\)O\(_{42}\)]\(^{10−}\) can be divided into three types: (i) tungsten-terminal oxygen bonds, in which the oxygen is linked to one W atom; (ii) tungsten-doubly bridging oxygen bonds, in which the oxygen connects two W atoms; and (iii) tungsten-triply bridging oxygen bonds, in which the oxygen joins three W atoms.\(^6b\)

**Characterization of catalyst**

The infrared (IR) spectrum of [(C\(_{18}\)H\(_{37}\))\(_2\)N(CH\(_3\))\(_2\)]\(_9\)[NaH\(_2\)W\(_{12}\)O\(_{42}\)] is shown in Figure S1 (available online in Supplemental Materials). The spectrum of paradodecatungstate anions is in agreement with previously reported analyses.\(^6b,7\) The bands at 976 and 950 cm\(^−1\) are assigned to the vibrations of W–O terminal groups. In the region of 900–800 cm\(^−1\), the bands are
attributed to the stretching of (W-O-W) groups corresponding to the edge-sharing octahedra. The next group of bands between 800 cm\(^{-1}\) and 600 cm\(^{-1}\) can be assigned to (W-O-W) remaining stretchings. In addition, the peaks at 2850 cm\(^{-1}\) and 2920 cm\(^{-1}\) belong to the vibrations of quaternary ammonium cations.

The UV-Vis spectrum of \([\text{C}_{18}\text{H}_{37}\text{N(CH}_3)_2\text{]}_9\text{NaH}_2\text{W}_{12}\text{O}_{42}\] was performed in the acetonitrile solution (Figure S2; available online in Supplemental Materials). The bands at 274 nm and 195 nm are attributed to \(p_\pi\text{(Od)}\rightarrow d_\pi^*(W)\) transitions in W=O bands and \(d_\pi-p_\pi-d_\pi^*\) transitions respectively between the energetic levels of W-O-W tricentric bonds.\(^8\)

The TG curve of \([\text{C}_{18}\text{H}_{37}\text{N(CH}_3)_2\text{]}_9\text{NaH}_2\text{W}_{12}\text{O}_{42}\] showed two weight loss steps (Figure S3; available online in Supplemental Materials). The first weight loss was 2.0% around 160°C, which corresponds with the loss of discrete water molecules, and suggests the molar ratio of water molecules to heteropolyanions as 9.0:1. The second weight loss of 61.4% between 160°C and 500°C is ascribed to the loss of quaternary ammonium cations. The total weight loss was 63.4%, which agreed with the calculated value of 63.8%.

**Effect of reaction temperature on conversion of DBT**

The oxidation reaction under different temperatures was investigated. As shown in Figure 2, the conversion of DBT reached 52, 66, and 97% in 15 min when the temperature was at 40, 50, and 60°C respectively. The conversion of DBT reached 100% at 60°C in 60 min. The result indicated that a lower reaction temperature was unfit for the oxidation of DBT, and the conversion of DBT increased gradually with increasing temperature. However, the conversion of DBT decreased to 93% when the temperature was increased to 70°C in 15 min. It is implied that there are two apparent competing reactions: oxidation of DBT and nonproductive decomposition of hydrogen peroxide.\(^9\) The high temperature is conducive to the nonproductive decomposition of hydrogen peroxide. Therefore, in the present study, the reaction temperature was set at 60°C in most cases.

**Effect of the H\(_2\)O\(_2\)/DBT (O/S) molar ratios on conversion of DBT**

To investigate the effect of dosage of oxidizing agent on oxidative properties, the oxidation of DBT under various O/S molar ratios was carried out at 60°C. It was found that O/S molar ratio has a strong influence on reaction rate (Figure 3). The removal of DBT increased from 62% at O/S = 2 to 91% at O/S = 3 in 1 h. When the O/S ratio reached 4, the time for 97% removal of DBT was 1 h. Further increasing the O/S ratio to 5, the removal of DBT reached 100% in 1 h. The curve of O/S ratio at 5 and 6 is substantially coincident, which may be caused by the increasing of nonproductive decomposition with the increasing of concentration of hydrogen peroxide.\(^4b, 9\) In the present study, after thorough consideration, O/S = 5 was chosen in most cases.

**Effect of nature of sulfur compounds**

The reactivity of four sulfur compounds, including BT, 5-MBT, DBT, and 4,6-DMDDBT (S = 500 ppm) in model diesel, was evaluated. The removal of sulfur compounds versus reaction time at 60°C is shown in Figure 4. The catalytic oxidation reactivity of...
sulfur compounds can be listed as follows: DBT > 4,6-DMDBT > BT > 5-MBT. These results suggest that the electron density on sulfur atoms and steric effect might play an important role in this oxidative desulfurization system. The lowest electron density on the sulfur atom of BT (5.696) lead to lower reactivity. The reactivity trend of DBTs > BTs indicated the intrinsic activities of sulfur compounds. The electron density differences of DBT and 4,6-DMDBT (5.758 and 5.760 for DBT and 4,6-DMDBT respectively) is so small that these can be ignored, so is the difference between BT and 5-MBT (5.739 and 5.741 for BT and 5-MBT respectively). Therefore, the reactivity trends of DBT > 4,6-DMDBT and BT > 5-MBT suggested that reactivity decreased with the increasing of steric hindrance of reactants. It can be concluded that the reaction rates of these sulfur compounds are sensitive to the electron density on sulfur atoms and the steric hindrance of the substituted groups of sulfur compounds.

Oxidation and desulfurization of actual commercial diesel

The desulfurization system was applied to the oxidation and desulfurization of actual commercial diesel (S = 200 ppm). Figure 5 shows the sulfur-specific gas chromatography (GC) analyses of both diesel before and after oxidation and desulfurized diesel. The commercial diesel contains a wide range of alkyl-substituted BTs and alkyl-substituted DBTs. Sulfur compounds present in diesel can be oxidized to sulfones at 60°C. The sulfones in oxidized diesel can be removed by a polar extractant, such as 1-methyl-2-pyrrolidone. The sulfur concentration in commercial diesel after desulfurization decreased to about 12 ppm. These results suggest that deep desulfurization of diesel could be achieved with this system.

Conclusions

Deep desulfurization of diesel based on catalytic oxidation with a paradocecataungstate catalyst [(C₁₈H₃₇)₂N(CH₃)₂][NaH₂W₁₂O₄₂] has been investigated. It is found that an amphiphilic catalyst can selectively oxidize the sulfur compounds present in diesel using hydrogen peroxide as an oxidant under mild conditions. The temperature and O/S play vital roles in the oxidation of sulfur compounds. The reactivity of sulfur compounds decreased in the following order: DBT > 4,6-DMDBT > 5MBT > BT. The reaction rates of these sulfur compounds are sensitive to the electron density on sulfur atoms and the steric hindrance of substituted groups of sulfur compounds. The sulfur level of commercial diesel after desulfurization can be dropped from 200 ppm to about 12 ppm.

Experimental

Chemicals and material

The model sulfur compounds (BT, 5-MBT, DBT, or 4,6-DMDBT) (AR) were the product of J&K Chemical Ltd.; decalin (AR), sodium tungstate dihydrate (AR), and acetic acid (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. All the chemicals were of analytical grade and used as received.

Synthesis of catalysts

Na₁₀H₂W₁₂O₄₂ was prepared according to the procedure described elsewhere with minor modification. Na₂WO₄ (20 g) was dissolved in water (40 mL). The pH of this solution was adjusted to 6.4 by addition of glacial acetic acid as required. The solution was set aside overnight for crystallization. A summary of crystallographic data and structural determination for the obtained colorless crystals are provided in Table S1 (available online in Supplemental Materials). The crystals were filtered, washed, and dried at 60°C in vacuum for 24 h.

[(C₁₈H₃₇)₂N(CH₃)₂][NaH₂W₁₂O₄₂] was prepared as follows: An ethanol solution of stoichiometric amount of quaternary ammonium salt was added to an aqueous solution of Na₁₀H₂W₁₂O₄₂, whereupon a snow white product precipitated. After continuously stirring for 4 h, the resulting mixture was filtered, washed, and dried at 60°C in vacuum for 24 h to obtain the required catalyst.

Oxidation and desulfurization of model diesel

In a typical run, a water bath was heated to a desired temperature. The model sulfur compounds (BT, 5-MBT, DBT, and 4,6-DMDBT) was dissolved in a flask respectively with decalin (25 mL), forming four different model diesels with a sulfur concentration of 500 ppm. The mixture containing model diesel (25 mL), 30% hydrogen peroxide, and an amphiphilic paradocecataungstate anion [(C₁₈H₃₇)₂N(CH₃)₂][NaH₂W₁₂O₄₂] was stirred vigorously using a stir bar. The ratio of reactants was adjusted according to different experimental conditions. The mixture was periodically sampled and analyzed. The total sulfur content of the samples was determined by an RPP-200A microcoulometry (Zhonghuan Analytical Instruments Co. Ltd., China); high purity nitrogen gas is used as a carrier gas, while high purity oxygen gas is used as a reaction gas; vaporization
zone temperature was 650°C, and combustion zone temperature was 800°C.

**Oxidation and desulfurization of actual diesel**

The diesel (25 mL, S = 200 ppm) was mixed with quantitative catalyst \((\text{C}_{18}\text{H}_{37})_2\text{N}(_3\text{H})_2\text{NaH}_2\text{W}_{12}\text{O}_{42}\). An aqueous hydrogen peroxide (30 wt%) was added to the reaction mixture at 60°C (catalyst:S:H_2O_2 = 1:100:500, molar ratio). The mixture was vigorously stirred for 2 h and the oxidized diesel was analyzed by GC coupled with flame photometric detection (GC-FPD).

The sulfones in the oxidized diesel were removed using N-methyl-2-pyrrolidone (NMP) as an extractant. The oxidized diesel was extracted thrice by an aqueous solution of NMP (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 10 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.

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