

Aerobic oxidative desulfurization of benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene using an Anderson-type catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$

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Benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are oxidized to their corresponding sulfones by an Anderson-type catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ using molecular oxygen as the oxidant under mild reaction conditions. These refractory sulfur-containing compounds can be oxidized completely in the absence of any sacrificial agent. Solvents such as acetonitrile and water play a negative effect on the oxidative desulfurization system. The catalytic activities of the amphiphilic Anderson catalysts depend on the quaternary ammonium cations. The reactivity of the sulfur-containing compounds follows the order 4,6-DMDBT > DBT > BT.

Introduction

Sulfur in transportation fuels, particularly in gasoline and diesel, is a major source of air pollution. Hydrosulfurization (HDS) is highly efficient in removing thiols, sulfides and disulfides from fuels, however is less effective for refractory sulfur-containing compounds, such as dibenzothiophene (DBT) and its derivatives.¹ Developing non-HDS technologies for the production of clean diesel with extremely low concentrations of sulfur-containing compounds is still a challenge for both academia and industry.²

One of the most promising alternative processes is the oxidative desulfurization (ODS) process, which includes the oxidation of sulfur-containing compounds to corresponding sulfones and their removal from diesel by extraction or adsorption. The ODS process offers several advantages over the HDS process. For example, refractory compounds, predominantly 4,6-dibenzothiophenes (4,6-DMDBT), can be oxidized under mild conditions (ambient temperature and pressure) and are very difficult to remove through conventional HDS.^{3–6} Up to now, many types of oxidative systems have been attempted, such as H_2O_2 /inorganic acids,⁷ H_2O_2 /organic acids,^{8,9} H_2O_2 /heteropolyacid,¹⁰ H_2O_2 /Ti-containing zeolites,¹¹ H_2O_2 /ionic liquid^{12,13} and other non-hydrogen peroxide systems (e.g., *t*-butyl hydroperoxide, etc.).^{14,15}

Although catalytic ODS of these refractory sulfur-containing compounds can show high activity, most of these processes use hydrogen peroxide as the oxidant. The oxidation of these refractory sulfur-containing compounds using molecular oxygen

as the oxidizing agent under mild conditions has long been desired due to its low cost and green chemistry advantages.¹⁶ Nevertheless, it is difficult to oxidize these refractory sulfur-containing compounds present in diesel using molecular oxygen as the oxidant under mild conditions. The oxidation of these refractory compounds by molecular oxygen has been achieved at high temperatures or in the presence of a sacrificial agent in a few reports.^{17–19} On the other hand, molecular oxygen takes part in preferably non-selective radical reactions, which results in the autooxidation of a large quantity of hydrocarbons present in diesel at high temperatures.²⁰ Another disadvantage is that using a large amount of sacrificial agent increases the operating cost and leads to difficulties in separation.

Therefore, selective oxidation of refractory sulfur-containing compounds using molecular oxygen as the oxidant under mild conditions is still a highly challenging subject. Here, we report that an Anderson-type catalyst, $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$, can oxidize these refractory sulfur-containing compounds present in diesel to their corresponding sulfones without any sacrificial agent using molecular oxygen as the oxidant under mild conditions.

Results and discussion

Structure of the Anderson-type polyoxometalate catalyst

Polyoxoanions, such as Keggin-type polyoxometalates, have been utilized widely as catalysts for both homogeneous and heterogeneous reactions.^{21,22} However, Anderson-type compounds have not received much attention as catalysts.^{23–25} This is the first time that this kind catalyst has been utilized for the selective aerobic oxidation of sulfur-containing compounds present in diesel. As shown in Fig. 1, the Anderson structure contains an IO_6 octahedron that is surrounded by six MoO_6 groups. The six Mo atoms form hexagons around the heteroatom, resulting in a structure with an approximate D_{3d} symmetry structure. The Anderson structure may be described as an isopolyoxometalate

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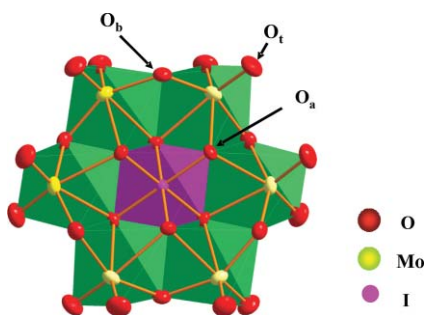


Fig. 1 The Anderson-type $[\text{IMo}_6\text{O}_{24}]^{5-}$ polyoxometalate.

containing a crown of six octahedrons sharing an edge. In the Anderson structure, the oxygen atoms are classified into three groups, and the positions of these types are depicted in Fig. 1. O_a ($\text{I}-\text{O}_a-\text{Mo}_2$) is a bridge oxygen between the I octahedron and two Mo groups, O_b ($\text{Mo}-\text{O}_b-\text{Mo}$) is another bridge oxygen between two edge-sharing Mo groups and O_t is the terminal oxygen that is bonded to each group.

The aerobic oxidation of DBT using different Anderson species

The catalytic activities of Anderson catalysts for the desulfurization of DBT using molecular oxygen as the oxidant are listed in Table 1. DBT is not oxidized at all without the catalyst. Also, the DBT is hardly oxidized when using $\text{Na}_5[\text{IMo}_6\text{O}_{24}]$ as the catalyst without any surfactant because of the insolubility of the catalyst in the reaction system and the mass-diffusion limitations of the liquid–solid–gas three-phase system. It is worthwhile to note that the conversion of DBT can reach to 84% with the addition of the surfactant octadecyl trimethyl ammonium chloride (OTAC), suggesting that the surfactant plays an important role in this reaction. When the amphiphilic catalyst $[(\text{C}_{18}\text{H}_{37})\text{N}(\text{CH}_3)_3]_5[\text{IMo}_6\text{O}_{24}]$ was used, the conversion of DBT increased to 100% in 10 h, which is a little higher than the combination of $\text{Na}_5[\text{IMo}_6\text{O}_{24}]$ and surfactant. This result indicates that the amphiphilic catalyst is very active for the oxidation of DBT using O_2 as the oxidant. The oxidation of DBT was further confirmed by sulfur-specific gas chromatography (GC) analyses and the IR spectrum of the product after the aerobic oxidation of DBT (the infrared absorptions at 1165 and 1288 cm^{-1} are attributed to sulfones⁸), as shown in Fig. 2.

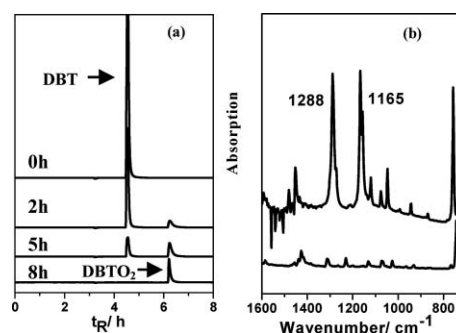


Fig. 2 (a) Sulfur-specific GC-FPD chromatograms of the oxidation of DBT in decalin and (b) spectroscopic characterization of production (DBTO_2) after the aerobic oxidation of DBT. Conditions: $[(\text{C}_{18}\text{H}_{37})_2\text{N}(\text{CH}_3)_2]_5[\text{IMo}_6\text{O}_{24}]$ (0.01 mmol), DBT (S: 500 ppm) in 50 mL decalin, reaction temperature 80°C , oxidant O_2 (1 atm).

Effect of solvents on the aerobic oxidation of DBT

The solvent effect was also investigated for the oxidation of DBT using O_2 as the oxidant. As shown in Table 1, DBT can be oxidized completely within 8 h using $[(\text{C}_{18}\text{H}_{37})_2\text{N}(\text{CH}_3)_2]_5[\text{IMo}_6\text{O}_{24}]$ as the catalyst. When acetonitrile was used, the activity of $[(\text{C}_{18}\text{H}_{37})_2\text{N}(\text{CH}_3)_2]_5[\text{IMo}_6\text{O}_{24}]$ decreased sharply, and only 23% conversion of DBT could be obtained after 10 h. A similar tendency was also observed for the combination of $\text{Na}_5[\text{IMo}_6\text{O}_{24}]$ and surfactant. If water was added to the reaction system, the conversion of DBT was less than 5% over $[(\text{C}_{18}\text{H}_{37})_2\text{N}(\text{CH}_3)_2]_5[\text{IMo}_6\text{O}_{24}]$ after 10 h. This does not agree with our previous work in the emulsion system,¹⁹ where acetonitrile was considered to be one of the most suitable solvents for ODS, probably owing to a different reaction mechanism. Intuitively, there is a strong interaction between the Anderson-type catalyst and acetonitrile or water, which occupies lots of the active sites of this polyoxometalate, leading to a decreased conversion of DBT.

Effect of the quaternary ammonium cations on the aerobic oxidation of DBT

As is known, the catalytic activity of the amphiphilic catalysts depends on the quaternary ammonium cation and polyoxometalate anion. Three kinds of catalysts with different quaternary ammonium cations were synthesized in order to investigate the effect of the quaternary ammonium cations

Table 1 Oxidation of DBT by molecular oxygen with Anderson-type catalysts^a

Entry	Catalyst	OTAC/mmol	Solvent/mL	Time/h	Conversion of DBT (%)	TOF/h ⁻¹
1	—	0	0	10	0	—
2	$\text{Na}_5\text{IMo}_6\text{O}_{24}$	0	0	24	<5	—
3	$\text{Na}_5\text{IMo}_6\text{O}_{24}$	0.05	0	10	84	—
4	$\text{Q}^1_5\text{IMo}_6\text{O}_{24}$	0	0	10	74	1.8
5	$\text{Q}^2_5\text{IMo}_6\text{O}_{24}$	0	0	10	100	3.7
6	$\text{Q}^3_5\text{IMo}_6\text{O}_{24}$	0	0	8	100	12.8
7	$\text{Na}_5\text{IMo}_6\text{O}_{24}$	0.05	CH_3CN (50)	10	14	—
8	$\text{Q}^3_5\text{IMo}_6\text{O}_{24}$	0	CH_3CN (50)	10	23	—
9	$\text{Q}^3_5\text{IMo}_6\text{O}_{24}$	0	H_2O (5)	10	<5	—

^a The conversion of DBT was calculated as follows: Q^1 : dodecyl trimethyl ammonium chloride (DTAC), Q^2 : octadecyl trimethyl ammonium chloride (OTAC), Q^3 : dioctadecyl dimethyl ammonium chloride (DODMAC). Conditions: catalyst (0.01 mmol), DBT (147 mg, 0.8 mmol) in 50 mL decalin, reaction temperature 80°C and O_2 (1 atm).

on the performance of the amphiphilic catalysts (Fig. 3). From the TOF of the three catalysts, the reaction activity decreases in the order $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}] > [(C_{18}H_{37})N(CH_3)_3]_5[IMo_6O_{24}] > [(C_{12}H_{25})N(CH_3)_3]_5[IMo_6O_{24}]$, as shown in Table 1. $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$, with two C_{18} carbon chains, exhibits the highest activity among the three catalysts investigated. The catalyst $[(C_{12}H_{25})N(CH_3)_3]_5[IMo_6O_{24}]$, with the shortest carbon chain, exhibits the lowest DBT conversion. This may be ascribed to the effect of the nature of the quaternary ammonium cation, as surfactants were believed to activate oxygen in early literature.^{26–28} The charge of the central atom is increased by electrons in-flowing from electron donor substituents, which has a great effect on the catalytic activity of the amphiphilic catalysts.²⁶ Detailed investigations on this result are in progress.

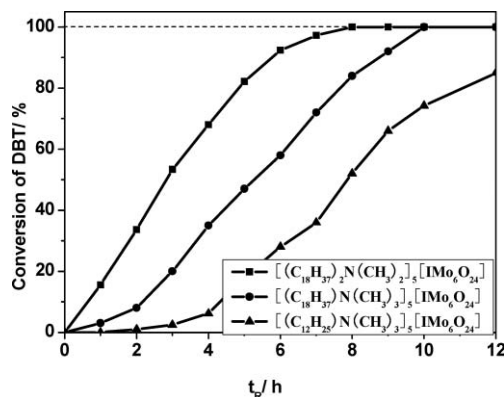


Fig. 3 The conversion of dibenzothiophene (S: 500 ppm) vs. reaction time. Conditions: $Q_5[IMo_6O_{24}]$ (0.01 mmol), DBT (S: 500 ppm) in 50 mL decalin, 80 °C, oxidant O_2 (1 atm).

The ODS of different sulfur-containing compounds

The performance of catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ for different sulfur-containing compounds, including benzothiophene (BT), DBT and 4,6-dimethyldibenzothiophene (4,6-DMDBT), was evaluated using molecular oxygen as the oxidant (Fig. 4). All the sulfur-containing compounds mentioned above can be oxidized to their corresponding sulfones. The catalytic activity for the oxidation of sulfur-containing compounds decreases in the order 4,6-DMDBT > DBT > BT. As calculated by Kabe *et al.*,^{8,9} the electron density on the sulfur atoms is 5.739 for BT, 5.758 for DBT and 5.760 for 4,6-DMDBT. The result indicates that the reaction rates of these sulfur-containing compounds increases with the electron density on the sulfur atom. Therefore, the reactivity trend reflects the intrinsic properties of the sulfur-containing compound. Gas chromatography (GC) analyses before and after the aerobic catalytic oxidation of sulfur-containing compounds in a model of diesel (decalin) was used to confirm that all the sulfur-containing compounds had been completely oxidized to sulfones (Fig. 5).

The conversion of different sulfur-containing compounds increased with increasing temperature, as shown in Fig. 6. 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. 7).

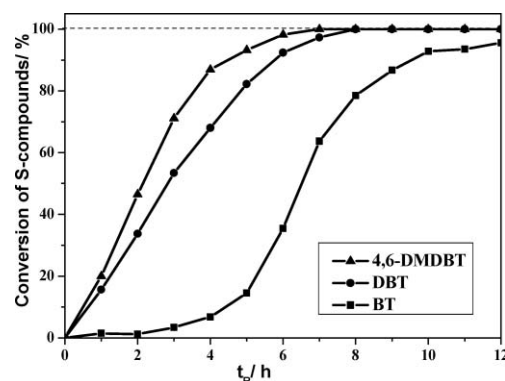


Fig. 4 The conversion of sulfur-containing compounds vs. reaction time at 80 °C. Conditions: $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ (0.01 mmol), sulfur-containing compound (S: 500 ppm) in 50 mL decalin, reaction temperature 80 °C, oxidant O_2 (1 atm).

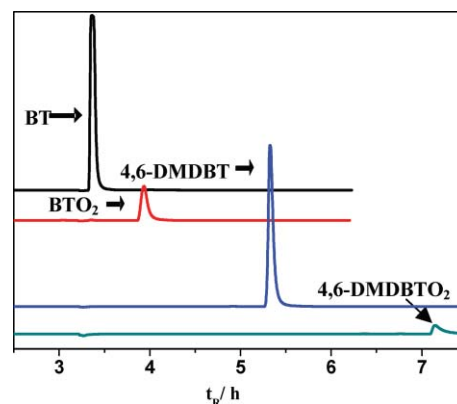


Fig. 5 Sulfur-specific GC-FPD chromatograms of the oxidation of sulfur-containing compounds in decalin. Conditions: $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ (0.01 mmol), sulfur-containing compound (S: 500 ppm) in 50 mL decalin, reaction temperature 80 °C, oxidant O_2 (1 atm).

The activation energy data again showed the following reactivity order: 4,6-DMDBT > DBT > BT.

Possible mechanism of the aerobic oxidation of sulfur-containing compounds

The ODS reaction mechanism was also investigated. Fig. 8 shows the UV-vis spectra of $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ in decalin with and without the introduction of molecular oxygen; similar absorption bands at 201 and 254 nm are observed. Upon the addition of DBT, the band at 254 nm disappears and a new band appears at 233 nm. These results suggest that the Anderson-type polyoxometalate is easily coordinated by sulfur-containing compounds such as DBT, but not with molecular oxygen. This suggests a proposed mechanism, as shown in Scheme 1. The active sites of the Anderson-type polyoxometalate react with DBT, a transfer state is formed, and then the activated DBT is oxidized to the corresponding sulfone and the catalyst reduced. Subsequently, the reduced catalyst is recycled in presence of dioxygen. During the process of the oxidation of sulfur-containing compounds, the Anderson-type polyoxometalates are reduced. However, the reduced polyoxometalates are often

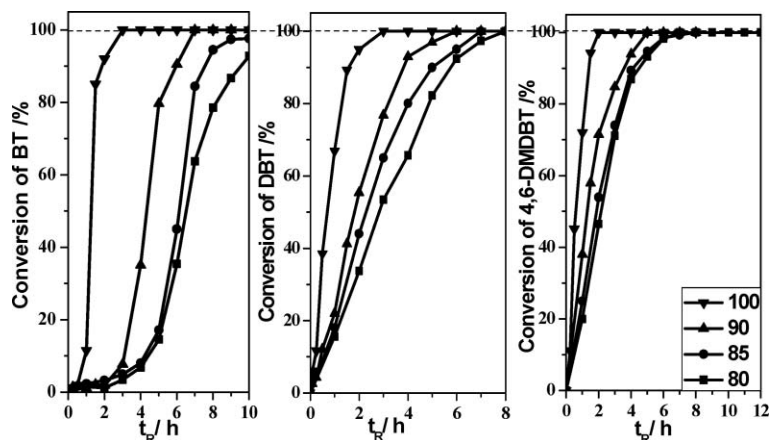


Fig. 6 The conversion of sulfur-containing compounds vs. reaction time at different temperature. Conditions: $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ (0.01 mmol); sulfur-containing compound (S: 500 ppm) in 50 mL decalin; oxidant, O_2 (1 atm).

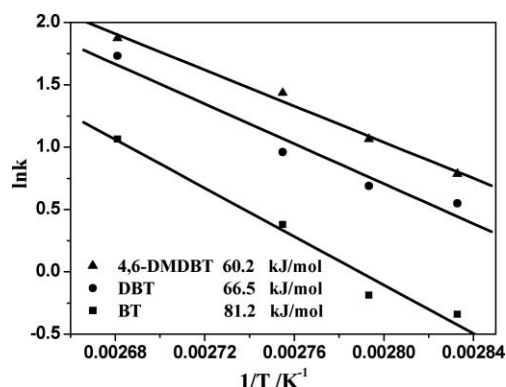


Fig. 7 Arrhenius activation energies for sulfur-containing compound oxidation with Anderson catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ using dioxygen as the oxidant. Conditions: $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ (0.01 mmol), sulfur-containing compound (S: 500 ppm) in 50 mL decalin, reaction temperature 80, 85, 90 and 100 °C, oxidant O_2 (1 atm).

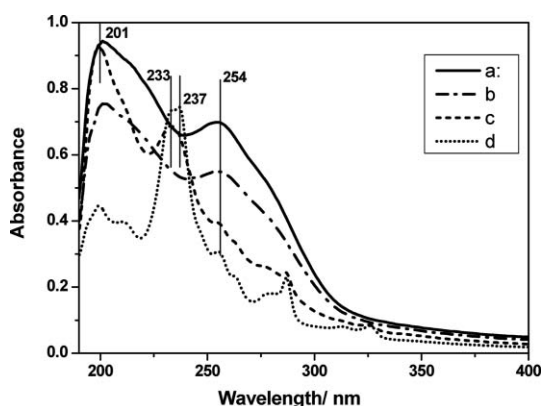
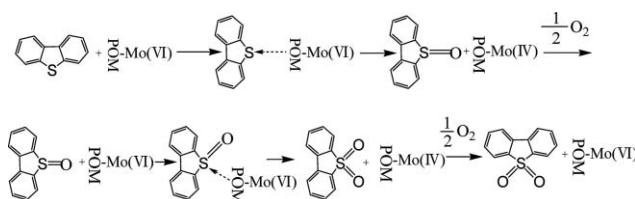


Fig. 8 UV-vis spectra of $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$. All spectra were collected from 0.02 mmol L^{-1} solutions (including $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ and DBT). (a) $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ dissolved in decalin at 80 °C for 0.5 h, (b) $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ in decalin after treatment with 1 atm of O_2 at 80 °C for 4 h, (c) $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$ in decalin after the addition of DBT at 80 °C for 4 h under highly pure nitrogen and (d) DBT dissolved in decalin at 80 °C for 0.5 h.



Scheme 1 The proposed mechanism for dioxygen activation and aerobic ODS.

known to undergo re-oxidation in the presence of molecular oxygen to complete the catalytic cycle.

Conclusion

Benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene can be oxidized to their corresponding sulfones with an Anderson-type polyoxometalate, $[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$, as a catalyst under mild conditions. The catalytic activities of the amphiphilic Anderson catalysts depends on the nature of the quaternary ammonium cation. It provides a new possible method for the ODS of diesel with molecular oxygen as the oxidant.

Experimental

Synthesis of catalysts

All chemicals were used as received. $Na_5IMo_6O_{24}$ was prepared according to procedures described elsewhere.^{23,29} An aqueous solution was prepared by dissolving 13.5 g of $Na_2MoO_4 \cdot 2H_2O$ in 50 mL water and then heating it to 95 °C. 6.2 mL of HCl was added slowly to the solution, followed by the dropwise addition of a hot solution of periodic acid (1.759 g in 10 mL water). Half of the reaction solution was evaporated. Upon cooling, white platelet type crystals precipitated from the solution.

$Q_3IMo_6O_{24}$ was prepared as follows: a 20 mL ethanolic solution with 5 mmol of quaternary ammonium was added dropwise into 40 mL of an aqueous solution of $Na_5IMo_6O_{24}$ (1 mmol) under stirring at room temperature. A snow-white precipitate was immediately formed. After continuously stirring for 4 h, the resulting mixture was filtered and dried at 60 °C in a

vacuum for 24 h to obtain the catalyst. There were three kinds of quaternary ammonium, including $[(C_{12}H_{25})N(CH_3)_3]Cl$, $[(C_{18}H_{37})_2N(CH_3)_2]Cl$ and $[(C_{18}H_{37})N(CH_3)_3]Cl$.

The ^{127}I chemical shifts were referenced to solid NaI. $\delta = 3092$, 3116 ppm, IR: $\nu = 942, 910, 720, 691, 629\text{ cm}^{-1}$

Characterization of the product after the aerobic oxidation of DBT

After the oxidation of DBT, the water bath was cooled to room temperature and kept at this temperature for 24 h. Then, white needle-type crystals (dibenzothiophene sulfone) were formed. The crystals were filtered and washed with n-heptane three times and dried at 50 °C in a vacuum for 24 h. The infrared spectrum of the product, diluted with KBr and pressed into a pellet, was recorded on a Nicolet 470 FT-IR spectrometer.

Oxidation of model sulfur-containing compounds

In a typical experiment, a water bath was heated to 80 °C. The model sulfur-containing compound (BT, DBT or 4,6-DMDBT) was dissolved in 50 mL of decalin in a flask, the sulfur concentration being 500 ppm. The catalyst $Q_5IMo_6O_{24}$ (0.01 mmol) was added to the solution and the obtained mixture stirred at 1000 rpm for 5 min. Molecular oxygen was then bubbled through the reaction solution. The solution was periodically sampled, and the sulfur content of the upper clear solution was determined by microcoulometry after the catalyst and sulfones had been precipitated by centrifugation.

Analysis of sulfur content

The total sulfur content of the samples was determined by microcoulometry (detection limit: 0.1 ng μL^{-1}). The sulfur-containing compounds present in diesel were analyzed by a gas chromatograph coupled to a flame photometric detector (GC-FPD). Gas chromatography: Agilent 6890 N equipped with a capillary column (PONA, 50 m \times 0.2 mm, id \times 0.5 μm), flame photometric detector (FPD): Agilent H9261. The 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^{-1} gradient, hold for 1 min, 150–280 °C at a 5 °C min^{-1} gradient, hold for 12 min, split ratio: 1/100, carrier gas: ultra-pure nitrogen, column flow: 0.9 mL min^{-1} , reagent gases air flow: 100 mL min^{-1} , hydrogen flow: 75 mL min^{-1} , the injection volume of the sample was 1 μL .

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