[Regular Paper]

Tungstophosphoric Acid-catalyzed Oxidative Desulfurization of Naphtha with Hydrogen Peroxide in Naphtha/Acetic Acid Biphasic System

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The 12-tungstophosphoric acid (TPA)-catalyzed oxidative desulfurization of naphtha with H_2O_2 was investigated. All organosulfur compounds examined were efficiently oxidized with H_2O_2 and TPA catalyst in acetic acid (AcOH). The order of the oxidation reactivities was sulfides, disulfides > benzothiophenes > thiophenes. Methyl substituents on benzothiophenes and thiophenes increased the reactivity of the sulfur atom. The major oxidation products from the organosulfur compounds, except a few thiophenes, were the corresponding sulfones. The organosulfur compounds in octane were also oxidized with H_2O_2 and TPA catalyst in an octane/AcOH biphasic system. The oxidation proceeded in the AcOH phase and most oxidation products remained in this phase, resulting in the successive removal of the sulfur compounds from the octane phase. Using this oxidative treatment effectively reduced the sulfur content of naphtha, as the sulfur content was reduced to about 0.5 mass ppm after adsorption with silica gel. Hydrodesulfurization is an effective pretreatment for oxidative desulfurization of naphtha, by which the sulfur content can be reduced to below 0.1 mass ppm.

Keywords

Oxidative desulfurization, Naphtha, Tungstophosphoric acid, Hydrogen peroxide, Thiophene, Benzothiophene

1. Introduction

Naphtha is a promising fuel candidate for fuel cell vehicles. However, naphtha contains significant amounts of organosulfur compounds such as thiols, sulfides, disulfides, thiophenes and benzothiophenes, and these sulfur compounds poison the catalysts in fuel processors and fuel cells. Ultra-deep removal of sulfur from naphtha is very important for fuel cell applications and the sulfur content should be reduced to below 0.1 mass ppm¹⁾. Organosulfur compounds in petroleum-derived fuels are usually removed by hydrodesulfurization (HDS), but the HDS process cannot economically produce fuel with this low sulfur level. Accordingly, alternative methods such as oxidative desulfurization (ODS), adsorptive desulfurization, biodesulfurization, etc. have been developed^{2),3)}. ODS has several advantages compared to HDS: operation at near ambient temperatures and pressures, no use of hydrogen, and superior treatment of sterically hindered thiophenic compounds. Various oxidants such as formic acid- H_2O_2 ^{4),5)}, H_2O_2 -Ti-containing molecular sieves⁶⁾, H_2O_2 -titanium silicate⁷⁾, *t*-BuOOH-Mo/ Al_2O_3 ⁸⁾, H_2O_2 -phosphotungstic acid-phase transfer catalyst-ultrasonication⁹⁾, and O_2 -Co

catalyst-aldehyde¹⁰⁾ were recently used in oxidative processes.

Thiophenes are the major organosulfur compounds in naphtha, but little is known about the oxidation of thiophenes in the ODS process. The reactivities of thiophenes are lower than those of benzothiophenes and dibenzothiophenes⁶⁾. Moreover, thiophenes are not oxidized with formic acid and H_2O_2 at 323 K⁴⁾. Consequently, a method needs to be developed for the effective oxidation of thiophenes in naphtha. We previously demonstrated that dibenzothiophenes were smoothly oxidized with H_2O_2 in the presence of 12-tungstophosphoric acid (TPA) in an organic biphasic system, and that the sulfur content of a diesel oil was efficiently reduced^{11),12)}. This oxidative treatment can effectively oxidize thiophenes as well.

Here we report the TPA-catalyzed oxidation of organosulfur compounds with H_2O_2 in both acetic acid (AcOH) and organic biphasic systems. This oxidative process efficiently reduced the sulfur content of naphtha. The effect of HDS of naphtha on the outcome of ODS was also examined.

2. Experimental**2.1. Materials**

All organosulfur compounds, diphenyl sulfide (DPS),

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diphenyl disulfide (DPDS), thiophene (TH), 2-methylthiophene (2-MT), 3-methylthiophene (3-MT), 2,5-dimethylthiophene (DMT), benzothiophene (BT), 2-methylbenzothiophene (2-MB), 3-methylbenzothiophene (3-MB), and 5-methylbenzothiophene (5-MB), were commercial products, used as received. Hydrogen peroxide (aqueous solution, 35 wt%) and TPA were used as oxidant and catalyst, respectively. AcOH and octane were used as solvents. Silica gel (silica gel No.923, Davison Chemical Corp.) purchased from Wako Pure Chemical Industries, Ltd. was used as an adsorbent.

Straight-run naphtha (NAP) containing 257 mass ppm sulfur was used as a practical example of naphtha. The hydrocarbon composition of NAP measured by JIS K 2536-2 was as follows: paraffin, 67.0; olefin, 1.5; naphtene, 18.6; aromatic compound, 12.9 wt%. Hydrodesulfurized naphtha, NAPH, was prepared by HDS of NAP over Co-Mo/Al₂O₃ catalyst. The HDS reaction conditions were as follows: reaction pressure, 3 MPa; reaction temperature, 483 K; LHSV, 6 h⁻¹; H₂/oil, 150 N//l. The sulfur content of NAPH was 11.3 mass ppm.

2.2. Oxidation of Organosulfur Compounds in AcOH

In a typical run, a glass reaction vessel charged with 50 ml of 2.5 mM (1 M = 1 mol·dm⁻³) solution of organosulfur compound in AcOH was heated to 313 K with stirring, and then 0.5 ml of 35 wt% H₂O₂ aqueous solution dissolving 0.25 μmol of TPA was added to initiate the oxidation. Concentrations of the organosulfur compounds were measured by HPLC (high performance liquid chromatography) using a Shimadzu LC-10A system under the following conditions: column, Wakosil-II 5C18RS column (4.6 mm × 150 mm); eluent, MeCN-H₂O; flow rate, 1.0 ml/min; detection, absorbance at 250 nm for DPS, 240 nm for DPDS, 230 nm for TH, 2- and 3-MT, 235 nm for DMT, and 290 nm for BT, 2-, 3- and 5-MB. Oxidation products were characterized by GC-MS (gas chromatography-mass spectrometer) using a J&W Scientific DB-5MS capillary column (30 m×0.25 mm×0.25 μm) on a Thermo Fisher Scientific Trace MS system.

2.3. Oxidation of Organosulfur Compounds in Organic Biphasic System

An octane solution of 2.5 mM BT or DMT was used as the model naphtha. In a typical run, 50 ml of model naphtha was mixed with 25 ml of AcOH. This mixture was heated to 333 K with stirring, and then 2 ml of 35 wt% H₂O₂ aqueous solution dissolving 10 μmol of TPA was added to initiate the oxidation. Concentration of BT or DMT in octane was determined by HPLC as described above. Concentration of the oxidation product in each phase was determined by GC-FID (flame ionization detector) using a J&W Scientific DB-5MS capillary column (30 m×0.53 mm×

1.5 μm) on a Shimadzu GC-18A.

2.4. Oxidative Desulfurization of Naphtha

In a typical run, 50 ml of NAP was mixed with 25 ml of AcOH. This mixture was heated to 333 K with stirring, and then 1 ml of 35 wt% H₂O₂ aqueous solution dissolving 5 μmol of TPA was added to initiate the oxidation. After 2-h oxidation, 25 ml of H₂O was added and the oil phase was separated. The oil phase was washed with water and dehydrated with CaCl₂ to yield oxidized naphtha (NAPO). Three ml of NAPO was treated by adsorption with 100 mg of silica gel to produce desulfurized naphtha (NAPOD). The sulfur content was measured using a Horiba SLFA-UV21 analyzer. Sulfur-specific GC analysis was carried out using a J&W Scientific DB-5MS capillary column (30 m × 0.53 mm × 1.5 μm) on a Shimadzu GC-2010 with a flame photometric detector (FPD).

3. Results and Discussion

3.1. Oxidation of Organosulfur Compounds in AcOH Solution

The organosulfur compounds present in naphtha are thiols, sulfides, disulfides, thiophenes and benzothiophenes. The aliphatic thiols, sulfides, and disulfides can easily be completely removed by conventional HDS³⁾, so the oxidations of some other organosulfur compounds with H₂O₂ and TPA catalyst in AcOH were carried out to evaluate the oxidation reactivities.

TPA-catalyzed oxidations of the organosulfur compounds with H₂O₂ proceeded smoothly in AcOH (Figs. 1 (a) and 1 (b)). In the absence of TPA, the organosulfur compounds were oxidized by peracetic acid formed from H₂O₂ and AcOH, but the oxidations were slower than the TPA-catalyzed reactions: under similar conditions described in Fig. 1 (b) BT was completely oxidized within 15 min in the presence of TPA, but only 8% oxidized at 15 min in the absence of TPA. These results indicate that TPA is an efficient catalyst of the oxidation. Figure 1 (a) shows that the order of the oxidation rates was DPS > DPDS > 3-MB > 2-MB > 5-MB > BT > DMT > 2-MT, 3-MT > TH; that is, the order of the reactivities of the organosulfur compounds was sulfides, disulfides > benzothiophenes > thiophenes.

DPS and DPDS were oxidized much more rapidly than the thiophenic compounds, indicating that aromatic sulfides and disulfides were readily converted into the oxidation products. Methylated benzothiophenes were oxidized more readily than BT, and 2- and 3-MB were more reactive than 5-MB. Therefore, the methyl substituent on BT increased the oxidation reactivity of the sulfur atom and the promoting effect of the substituent on the thiophene ring was larger than that of the substituent on the benzene ring. The methyl substituents also promoted the oxidation of thiophenes, and the

Fig. 1 Disappearance of Organosulfur Compounds during the Oxidation with Hydrogen Peroxide and TPA Catalyst in AcOH

effect was dependent on the number of the methyl substituents. Similar effects have been noted in the oxidation of dibenzothiophenes^{4),13)~15)}, and the effect has been attributed to the increase of the electron density on sulfur atom with methyl substituents⁴⁾. Under the conditions described in **Fig. 1 (b)**, thiophenes were also oxidized sufficiently, demonstrating that all organosulfur compounds examined could be efficiently oxidized with H₂O₂ and TPA catalyst in AcOH, so this oxidation treatment was effective for ODS of naphtha.

The major oxidation products from most of the organosulfur compounds were identified as the corresponding sulfones by GC-MS. However, the oxidation products from TH, 2-MT, and 3-MT were not identified by GC-MS. The sulfoxides and sulfones formed by oxidation of thiophenes without substituents at both 2 and 5 positions would readily undergo Diels-Alder cycloaddition to produce dimer compounds (**Scheme 1**)⁶⁾.

3. 2. Oxidation of Organosulfur Compounds in Model Naphtha/AcOH Biphasic System

An octane solution of BT or DMT was used as the model naphtha. **Figure 2** shows the disappearance of BT or DMT in octane during the oxidation. Under the

Fig. 2 Disappearance of BT (○) or DMT (◆) in Octane during the Oxidation with Hydrogen Peroxide and TPA Catalyst at 333 K in an Octane/AcOH Biphasic System

experimental conditions employed, 26% of BT was transferred into the AcOH phase from the octane phase, and BT was smoothly oxidized with H₂O₂ and TPA catalyst in AcOH, resulting in the successive removal of BT from the octane phase (**Scheme 2**). This oxidation mechanism was similar to that of dibenzothiophenes¹²⁾. A lesser amount (15%) of DMT was transferred into the AcOH phase from the octane phase compared with that of BT, but DMT was similarly oxidized and removed from the octane phase. The main oxidation products of BT and DMT were benzo[*a*]thiophene-1,1-dioxide

(BTDO) and 2,5-dimethylthiophene-1,1-dioxide (DMTDO), respectively, and these polar molecules were predominantly dissolved in the AcOH phase: 98% of BTDO or 96% of DMTDO partitioned into the AcOH phase. The results demonstrated that the organosulfur compounds in model naphtha were essentially transferred into the AcOH phase by conversion to the oxidation products, and most of the oxidation products could be removed from this biphasic system simply by separation of the AcOH phase.

3.3. Oxidative Desulfurization of Naphtha

The results of TPA-catalyzed ODS of NAP with H_2O_2 are summarized in **Table 1**. Small reductions in the sulfur content of NAP were observed without H_2O_2 and TPA catalyst (entries 1, 6), suggesting that only solvent extraction would be inefficient. In contrast, the oxidative treatments of NAP with H_2O_2 and TPA catalyst resulted in substantial reductions in the sulfur content of NAP from 257 mass ppm to less than about 30 mass ppm, indicating that this oxidative treatment is effective for the desulfurization of naphtha. An increase in the amounts of H_2O_2 and TPA enhanced the reduction in sulfur content, probably due to the increasing degrees of oxidation of the organosulfur compounds. An increase of AcOH volume did not significantly

affect the reduction in sulfur content.

The oxidation of the organosulfur compounds in NAP by this oxidative treatment was confirmed with sulfur-specific GC (**Fig. 3**). The peaks of the sulfur compounds in NAP disappeared after the oxidation, and peaks of new sulfur-containing products, the corresponding oxidation products, appeared at higher boiling points in the AcOH phase. The results showed that the sulfur compounds were efficiently transferred from the NAP phase into the AcOH phase by conversion to the corresponding oxidation products. Consequently, most of the oxidized sulfur compounds could be removed from the NAP phase simply by separation of the two phases; this is consistent with the considerable reduc-

Scheme 2 Mechanism of TPA-catalyzed Oxidation of BT with Hydrogen Peroxide in an Octane/AcOH Biphasic System

Fig. 3 Sulfur-specific GC of (a) NAP, (b) NAPOD, and (c) AcOH Phases: the NAPOD and the AcOH phase were prepared under the conditions described in the entry 3 of Table 1

Table 1 Oxidative Desulfurization of NAP and NAPH with 35 wt% H_2O_2 for 2 h at 333 K

Entry	Naphtha	TPA/ H_2O_2	Naphtha : AcOH [ml/ml]	Sulfur content [mass ppm]		
				Initial	NAPO	NAPOD
1	NAP	0 μmol /0 ml	50/25	257 ± 3	245 ± 1	—
2		0.25 μmol /0.5 ml			30.8 ± 0.1	3.62 ± 0.01
3		0.50 μmol /1.0 ml			27.6 ± 0.2	2.64 ± 0.01
4		5.0 μmol /1.0 ml			21.9 ± 0.1	1.49 ± 0.02
5		15 μmol /3.0 ml			6.21 ± 0.03	0.45 ± 0.02
6		0 μmol /0 ml			240 ± 2	—
7	NAPOD1 ^{a)}	0.50 μmol /1.0 ml	50/50	3.62 ± 0.01	20.7 ± 0.3	2.35 ± 0.01
8		5.0 μmol /1.0 ml			16.7 ± 0.1	1.27 ± 0.01
9		0.25 μmol /0.5 ml			2.43 ± 0.01	2.22 ± 0.02
10		5.0 μmol /1.0 ml			0.64 ± 0.01	0.60 ± 0.03
11		0.25 μmol /0.5 ml			11.3 ± 0.1	1.03 ± 0.08
12		5.0 μmol /1.0 ml			0.63 ± 0.01	0.07 ± 0.03

a) NAPOD1 and NAPOD2 were prepared under the conditions described in the entries 2 and 4, respectively.

tions in sulfur content of NAPO (**Table 1**). However, small amounts of the oxidized sulfur compounds remained in the NAPO after phase separation.

Accordingly, adsorption with silica gel was carried out since silica gel is an effective adsorbent for removal of oxidized sulfur compounds from naphtha¹⁶⁾. The sulfur contents of NAPO were further reduced (**Table 1**), suggesting that most of the sulfur compounds in NAPO were oxidized derivatives. Nevertheless, the sulfur content was decreased to only about 0.5 mass ppm even with a large excess of TPA and H₂O₂ (entry 5 in **Table 1**). In addition, the sulfur contents of NAPOD were little reduced by reprocessing (entries 9 and 10). These results suggest that trace amounts of sulfur compounds, which are resistant to oxidation, remain in NAPOD. Thiophenes, especially TH, are likely to be the main components of the sulfur compounds remaining in NAPOD since these molecules are the most resistant to oxidation. On the other hand, the sulfur contents of NAPH were effectively reduced to below 0.1 mass ppm, although the sulfur content of NAPH was higher than that of NAPOD, suggesting that most sulfur compounds remaining in NAPH are susceptible to oxidation. Therefore, HDS is an effective pretreatment for ODS of naphtha, probably due to the removal of thiophenes.

4. Conclusion

Investigation of the TPA-catalyzed oxidative desulfurization of naphtha with H₂O₂ showed that the organosulfur compounds present in naphtha readily underwent oxidation in AcOH. The organosulfur compounds efficiently underwent oxidation in an octane/AcOH biphasic system as well. The organic biphasic oxidation system effectively oxidized the organosulfur compounds in a practical example of naphtha, and most of the oxidized sulfur compounds were

removed from the naphtha simply by phase separation, resulting in substantial desulfurization. In addition, small amounts of the oxidation products remaining in the naphtha were efficiently removed by adsorption with silica gel. These results indicate that TPA-catalyzed oxidative treatment is effective for the ODS of naphtha. The removal of thiophenes by HDS is an efficient pretreatment for ODS since the thiophenes are the most resistant to oxidation. Therefore, the combination of HDS and ODS may be effective for producing sulfur-free naphtha for fuel cell vehicles.

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要 旨

ナフサ／酢酸二相系中でのナフサの過酸化水素によるタングストリン酸触媒酸化脱硫

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12-タングストリン酸 (TPA) 触媒存在下における H_2O_2 によるナフサの酸化脱硫について検討した。用いたすべての有機硫黄化合物は、酢酸中において H_2O_2 -TPA 触媒により効率的に酸化された。酸化反応性の順序は、スルフィド類, ジスルフィド類>ベンゾチオフェン類>チオフェン類であった。ベンゾチオフェン類およびチオフェン類のメチル置換基は硫黄原子の反応性を増大した。有機硫黄化合物類の主酸化生成物は、若干のチオフェン類を除いて、相当するスルホン類であった。オクタン／

酢酸二相系中において、オクタン中の有機硫黄化合物は H_2O_2 -TPA 触媒により同様に酸化された。酸化反応は酢酸相中で進行し、酸化生成物のほとんどがそこに留まることにより、オクタン相からの硫黄化合物の連続的な除去が達成された。ナフサ中の硫黄分はこの酸化的処理により効果的に削減され、シリカゲル吸着処理後の硫黄分は約 0.5 mass ppm まで低減された。水素化脱硫はナフサの酸化脱硫の前処理として効果的であり、硫黄分は 0.1 mass ppm 以下まで低減された。

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