Oxidative Desulfurization of Naphtha with Hydrogen Peroxide in Presence of Acid Catalyst in Naphtha/Acetic Acid Biphasic System

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Oxidative desulfurization of naphtha with H2O2 in the presence of H2SO4 in the naphtha/acetic acid (AcOH) biphasic system was investigated. All organosulfur compounds examined were smoothly oxidized in AcOH by peracetic acid effectively formed from AcOH and H2O2 in the presence of H2SO4. The order of the oxidation reactivities was sulfides, disulfides > benzothiophenes > thiophenes. The organosulfur compounds in octane were also oxidized with H2O2 in the presence of H2SO4 in the octane/AcOH biphasic system. The oxidation proceeded in the AcOH phase and most of the oxidized sulfur compounds resided in this phase, resulting in the successive removal of the sulfur compounds from the octane phase. This oxidative treatment effectively reduced the sulfur content of naphtha, and adsorption with silica gel further reduced the sulfur content to below 0.5 mass ppm. In addition, hydrodesulfurization is an effective pretreatment for this oxidative desulfurization of naphtha, resulting in further reduction of the sulfur content to below 0.1 mass ppm.

Keywords
Oxidative desulfurization, Naphtha, Hydrogen peroxide, Acetic acid, Thiophene, Hydrodesulfurization

1. Introduction

Organosulfur compounds in petroleum-derived fuels are usually removed by hydrodesulfurization (HDS), but the conventional HDS process cannot economically produce ultra-clean fuels with extremely low sulfur content, especially for fuel cell vehicles. Accordingly, alternative processes such as oxidative desulfurization (ODS), adsorptive desulfurization, biodesulfurization, and others have been investigated1). ODS processes have received considerable attention since they are achieved under mild reaction conditions without hydrogen.

Naphtha, a promising fuel candidate for fuel cell vehicles, contains significant amounts of organosulfur compounds such as thiols, sulfides, disulfides, thiophenes and benzothiophenes. Among the organosulfur compounds thiophenes are the most refractory compounds in the ODS process due to their low reactivities to oxidation3), so development of effective oxidation methods for thiophenes is important for producing ultra-clean naphtha. Several oxidation processes for thiophenes by using formic acid-H2O23), formic acid-H2O2-phase transfer catalyst-ultrasonication4), formic acid-H2O2-silica gel5), acetic acid (AcOH)-H2O2-quaternary ammonium coordinated ionic liquid6), H2O2-Ti-containing molecular sieves7), H2O2–titanium silicate8)–10), H2O2–Au/titanium silicate11), and H2O2–molybdophosphoric acid-phase transfer catalyst12) have been reported. We previously demonstrated that thiophenes can be oxidized with H2O2–tungstophosphoric acid (TPA) in both AcOH and octane/AcOH organic biphasic systems, and that the biphasic oxidative treatment is effective for the ODS of naphtha13). Furthermore, we have shown that dibenzothiophenes were smoothly oxidized with H2O2 in the presence of H2SO4 in a similar organic biphasic system using AcOH as a polar solvent, due to the formation of peracetic acid (AcOOH)14). Here we report application of the biphasic oxidative treatment with AcOH-H2O2 in the presence of H2SO4 to the ODS of naphtha, and examine the effect of HDS on ODS.

2. Experimental

2.1. Materials

All organosulfur compounds, diphenyl sulfide (DPS), 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. Straight-run naphtha (NAP; boiling range, 343-424 K;
S, 257 mass ppm) and hydrodesulfurized naphtha (NAPH; S, 11.3 mass ppm) were the same products as used in previous work\textsuperscript{13}). AcOH and octane were used as solvents. Hydrogen peroxide (aqueous solution, 35 wt\%) was used as an oxidant. Silica gel (silica gel No.923, Davison Chemical Corp.) purchased from Wako Pure Chemical Industries, Ltd. was used as an adsorbent.

2.2. Oxidation of Organosulfur Compounds in AcOH Solution

In a typical run, a glass reaction vessel charged with 50 ml of 2.5 mM (1 mM = 1 mmol・dm\(^{-3}\)) solution of organosulfur compound in AcOH containing 10 mM H\(_2\)SO\(_4\) was heated to 313 K with stirring, and then 0.5 ml of 35 wt\% H\(_2\)O\(_2\) aqueous solution was added to initiate the oxidation. The concentration of the organosulfur compound was measured by the same high performance liquid chromatography (HPLC) method as before\textsuperscript{13}).

2.3. Oxidation of Organosulfur Compounds in Organic Biphasic System

An octane solution of 2.5 mM BT or DMT was used as model naphtha. In a typical run, 50 ml of model naphtha was mixed with 25 ml of AcOH containing 20 mM H\(_2\)SO\(_4\). This mixture was heated to 343 K with stirring, and then 2 ml of 35 wt\% H\(_2\)O\(_2\) aqueous solution was added to initiate the oxidation. The concentration of BT or DMT in octane was determined by HPLC.

3. Results and Discussion

3.1. Oxidation of Organosulfur Compounds in AcOH Solution

Naphtha contains thiols, sulfides, disulfides, thiophenes and benzothiophenes as organosulfur components. The conventional HDS method can easily remove aliphatic thiols, sulfides, and disulfides from naphtha\textsuperscript{2)}, so the oxidation reactivities of the other organosulfur compounds present in naphtha were examined.

Figures 1(a) and 1(b) show the disappearance of organosulfur compounds during the oxidation process. The organosulfur compounds were oxidized by AcOOH effectively produced from AcOH and H\(_2\)O\(_2\) in the presence of a strong acid such as H\(_2\)SO\(_4\)\textsuperscript{14),15)). Thiophenes are refractory to oxidation due to the low electronic densities of sulfur\textsuperscript{3)}, but those were effectively oxidized under the conditions in Fig. 1(b). The oxidation rates decreased in the order DPS > DPDS > 3-MB > 2-MB >...
5-MB > BT > DMT > 2-MT, 3-MT > TH. Therefore, the oxidation reactivities of the organosulfur compounds decreased in the order sulfides, disulfides > benzo-thiophenes > thiophenes. Methyl substituents increased the oxidation reactivities of benzo-thiophenes and thiophenes, probably due to the increase of the electron density on sulfur atom. The difference in oxidation reactivities of MBs probably resulted from the promoting effect of the methyl substituent. A similar reactivity trend was observed in the tungstophosphoric acid-catalyzed oxidation with H$_2$O$_2$.

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

In order to evaluate the applicability of the proposed oxidation system to the ODS of naphtha, the oxidations of organosulfur compounds in model naphtha/AcOH biphasic system were investigated. An octane solution of BT or DMT was used as model naphtha. Figure 2 shows the disappearance of BT or DMT in the octane phase during the oxidation. Without oxidation, 26% of BT was extracted from the octane phase into the AcOH phase under the conditions used. BT was smoothly oxidized by AcOOH in the AcOH phase, and the oxidation product, benzothiophene-1,1-dioxide (BTDO), resided predominantly in the AcOH phase because of its high polarity, resulting in the successive removal of BT from the octane phase (Scheme 1). DMT was similarly oxidized and removed from the octane phase, although less DMT (15%) was transferred into the AcOH phase compared with BT. Accordingly, this organic biphasic oxidation system could achieve substantial desulfurization of the model naphtha only by phase separation, since the sulfur compounds in the model naphtha were effectively oxidized and most of the oxidized sulfur compounds was located mainly in the AcOH phase. The oxidation mechanism was the same as that of dibenzo-thiophenes.

3.3. Oxidative Desulfurization of Naphtha

The results of the ODS of NAP with H$_2$O$_2$ in the presence of H$_2$SO$_4$ in the naphtha/AcOH biphasic system are summarized in Table 1. A small reduction in

![Fig. 2](attachment:image.png) **Fig. 2** Disappearance of BT (○) or DMT (●) in Octane during the Oxidation with H$_2$O$_2$ in the Presence of H$_2$SO$_4$ at 343 K in the Octane/AcOH Biphasic System

![Scheme 1](attachment:diagram.png) **Scheme 1**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Naphtha</th>
<th>Temperature [K]</th>
<th>35 wt% H$_2$O$_2$ [mL]</th>
<th>Acid catalyst</th>
<th>Sulfur content [mass ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Initial</td>
</tr>
<tr>
<td>1</td>
<td>NAP</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>257 ± 3</td>
</tr>
<tr>
<td>2</td>
<td>NAP</td>
<td>313</td>
<td>1.0</td>
<td>H$_2$SO$_4$</td>
<td>257 ± 3</td>
</tr>
<tr>
<td>3</td>
<td>NAP</td>
<td>313</td>
<td>3.0</td>
<td>H$_2$SO$_4$</td>
<td>257 ± 3</td>
</tr>
<tr>
<td>4</td>
<td>NAP</td>
<td>333</td>
<td>1.0</td>
<td>H$_2$SO$_4$</td>
<td>257 ± 3</td>
</tr>
<tr>
<td>5</td>
<td>NAP</td>
<td>333</td>
<td>3.0</td>
<td>H$_2$SO$_4$</td>
<td>257 ± 3</td>
</tr>
<tr>
<td>6</td>
<td>NAP</td>
<td>343</td>
<td>1.0</td>
<td>H$_2$SO$_4$</td>
<td>257 ± 3</td>
</tr>
<tr>
<td>7</td>
<td>NAP</td>
<td>343</td>
<td>3.0</td>
<td>H$_2$SO$_4$</td>
<td>257 ± 3</td>
</tr>
<tr>
<td>8</td>
<td>NAPOD$^a$</td>
<td>343</td>
<td>1.0</td>
<td>H$_2$SO$_4$</td>
<td>12.3 ± 0.1</td>
</tr>
<tr>
<td>9</td>
<td>NAPH</td>
<td>343</td>
<td>1.0</td>
<td>H$_2$SO$_4$</td>
<td>11.3 ± 0.1</td>
</tr>
<tr>
<td>10</td>
<td>NAPH</td>
<td>343</td>
<td>3.0</td>
<td>H$_2$SO$_4$</td>
<td>11.3 ± 0.1</td>
</tr>
</tbody>
</table>

$a$) NAPOD was prepared under the conditions described in the entry 6.
the sulfur content of NAP was observed without oxidation (entry 1), suggesting that only solvent extraction is not sufficient. On the other hand, the oxidative treatments of NAP resulted in large reductions in the sulfur content of NAPO from 257 mass ppm to less than about 12 mass ppm, indicating that this oxidative treatment would be effective for the desulfurization of naphtha. Oxidation of the organosulfur compounds in NAP was confirmed by GC-FPD method as described previously [13].

The large sulfur reductions in NAPO demonstrated that most of the oxidized sulfur compounds were removed only by separation of the naphtha and AcOH phases since the oxidized sulfur compounds resided mainly in AcOH phase, possibly due to their high polarities. However, further sulfur reduction would require the removal of the remaining traces of the oxidized sulfur compounds in NAPO. In the ODS process, the oxidized sulfur compounds must be removed from the fuels after oxidation by extraction, adsorption, distillation, or decomposition. Adsorption with silica gel was carried out for further sulfur reduction in NAPO since silica gel is an effective adsorbent for removal of oxidized sulfur compounds from naphtha [16]. Further sulfur reductions in NAPOD were observed by adsorption with silica gel, suggesting that the remaining oxidized sulfur compounds could be efficiently removed. The reduction in sulfur content was further magnified by increasing the amounts of H$_2$O$_2$ and the temperature, so the sulfur contents were further reduced with increasing severity of oxidation conditions. The sulfur content was decreased to 0.34 mass ppm under the severest conditions (entry 7). However, the sulfur content of NAPOD could be reduced only to 0.61 mass ppm by reprocessing, although the initial sulfur content was 12.3 mass ppm (entry 8). In contrast, the sulfur contents of NAPH were effectively reduced to below 0.1 mass ppm, although the initial sulfur content of NAPH was similar to that of NAPOD. These results suggest that trace amounts of sulfur compounds refractory to oxidation will remain in NAPOD, but not in NAPH. The sulfur compounds in NAPOD and NAPH were impossible to identify by GC-FPD due to the very low levels. However, it was assumed that the refractory sulfur compounds would be thiophenes, especially TH, since they showed low reactivities in oxidation, and that NAPH would contain very little thiophenes since they would be thoroughly removed by HDS. The same effect of HDS on sulfur reduction in naphtha was observed in TPA-catalyzed ODS with H$_2$O$_2$ [13]. Therefore, HDS would provide an effective pretreatment for the ODS of naphtha, probably due to the removal of thiophenes.

4. Conclusion

The present study demonstrated that the organosulfur components were smoothly oxidized with H$_2$O$_2$ in the presence of H$_2$SO$_4$ in the octane/AcOH biphasic system as well as in AcOH, due to the formation of peracetic acid. The organic biphasic oxidation system effectively desulfurized real naphtha, and adsorption with silica gel was effective for further sulfur reduction in the oxidized naphtha. Therefore, oxidative treatment will be useful for the ODS of naphtha. Furthermore, HDS provides efficient pretreatment for ODS by the removal of thiophenes refractory to oxidation, so sequential HDS and ODS treatments should be effective for ultra-deep desulfurization of naphtha.

References

要　　旨

ナフサ／触媒二相系中での硫黄活化下における過酸化水素によるナフサの酸化脱硫

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ナフサ／触媒二相系中での硫黄活化下における H2O2 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、触媒中において硫黄活化下、酢酸と H2O2 から結果的に生成する過酢酸により酸化された。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。有機二相系中において、オクタン中の有機硫黄化合物は、硫黄活化下、酢酸・H2O2 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から排出され、オクタン相からの硫黄化合物の連続的除去が達成された。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
0.5 mass ppm 以下まで低減された。さらに、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。