Oxidative Desulfurization of Middle Distillate
— Oxidation of Dibenzothiophene Using t-Butyl Hypochlorite —

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The oxidation of dibenzothiophene (DBT) was conducted using t-butyl hypochlorite (t-BuOCl) in the presence of several catalysts. In a flow reactor under ambient pressure at 30-70°C, more than 90% of DBT could be oxidized in the decahydronaphthalene (decalin) solution. The catalyst was necessary to oxidize dibenzothiophene with t-BuOCl, and γ-alumina (Al2O3) supported catalysts have relatively high activities. At the same time, the activities of the metal-loaded Al2O3 catalysts had shown the same activities as those of the Al2O3 support, indicating that the Al2O3 support itself possessed such activity. Further, the effect of a variety of model compounds found in light gas oil (LGO) such as n-pentadecane, 2,4,4-trimethylpentene, xylene, and indole on the oxidation of DBTs were also investigated.

1. Introduction

A new method to reduce the sulfur content in fuel oil is needed today to meet the future environmental legislation on the sulfur content (lower than 50 ppm). The conventional method for reducing sulfur is catalytic hydrodesulfurization (HDS) under severe conditions. It was reported that methyl substitution at 4- and 6-position of dibenzothiophene (DBT) remarkably retarded the rate of HDS, and the reactivities of alkyl substituted DBTs decreased in the order: DBT > 4-MDBT > 4,6-DMDBT. Thus, 4-methylidibenzothiophene (4-MDBT) and 4,6-dimethylidibenzothiophene (4,6-DMDBT) are very difficult to desulfurize even under deep desulfurization conditions. The need to remove alkyl substituted DBTs will be “bottleneck” for super deep desulfurization.

The oxidative desulfurization (ODS) is considered to be one of the new promising methods for super deep desulfurization of light gas oil (LGO). Various studies on ODS of real feeds have been reported, and ODS has several advantages in contrast with HDS. For example, ODS can be carried out under very mild conditions, as room temperature and atmospheric pressure that can reduce the investment cost. In oxidation, the divalent sulfur of DBTs can be oxidized by the electrophilic addition reaction of oxygen atoms to the hexavalent sulfur of DBT sulfones. Hence, the higher is the electron density of a sulfur atom in a sulfur-containing compound, the higher is the reactivity of oxidation. By the electron donation of a methyl group, therefore, the reactivities of DBTs decrease in the order: 4,6-DMDBT > 4-MDBT > DBT, reversing the order of reactivities in HDS.

Many types of oxidants have been used, and various consequences of ODS methods have been reported. We had reported that LGO containing 150 ppm DBT and 145 ppm 4,6-DMDBT, was oxidized using ozone in a batch reactor. Since ozone is a highly reactive oxidant, DBTs in LGO were converted quantitatively to DBT sulfones. Aida et al. had reported that for selective oxidation of sulfur compounds in fuel oil, persulfuric acid, pertrifluoroacetic acid, a mixture of formic acid or trifluoroacetic acid and hydrogen peroxide etc., were some of the most positive oxidants. However, in these reactions the reactor is limited to a batch type because these oxidants are water soluble and because of the need for sufficient mixing. If the selective catalytic oxidation of sulfur compounds in the liquid fuel using a flow reactor could be possible, the amount treated would increase remarkably. In order to develop ODS by means of a flow reaction process, it is necessary to find an oil-soluble oxidant.

The DBT sulfone generated by oxidation possesses chemical and physical properties significantly different from the hydrocarbon in LGO; therefore, it can easily be removed by such procedures as distillation, solvent extraction, chromatographic adsorption, and decomposition. Wallace et al. reported that the selectivity of decomposition with alkaline was in the order: sulfone > sulfoxide >> sulfide. The advantages of the decomposition method lie in being able to use a flow reaction system and the need for catalyst regeneration is not required.

The aim of the present work is to establish a scientific basis for the development of a new deep desulfuriza-
tion technology by means of research the oxidation mechanism prior to the decompositions of organic sulfur compounds, e.g., DBT sulfones, that are included in light gas oil, for example.

In this study, t-butyl hypochlorite (t-BuOCl) was used as an oil-soluble oxidant. The oxidation of DBT in decahydronaphthalene (decalin) solution was performed both in the presence and in the absence of catalysts using a flow reaction system and also a batch system. Further, the effects of various compounds such as n-pentadecane, 2,4,4-trimethylpentene (diisobutylene), xylene, indole and diisobutylene, decalin solution, and 0.05-0.20 g of catalyst were added. The mixture was stirred and heated in the range 30-70°C, then, 0.05 ml of t-BuOCl was added. The t-BuOCl/DBT ratios were 4-16 mol/mol. The reaction was continued for 120 min.

The oxidation in a flow reactor was conducted in a 100 ml two-neck Pyrex glass flask with a magnetic stirrer. 80 ml of decalin solution of DBT or that containing 5 model compounds, e.g., DBT, n-pentadecane, xylene, indole and diisobutylene, decalin solution, and 0.05-0.20 g of catalyst were added. The mixture was stirred and heated in the range 30-70°C, then, 0.05 ml of t-BuOCl was added. The t-BuOCl/DBT ratios were 4-16 mol/mol. The reaction was continued for 120 min.

The oxidation in a flow reactor was conducted in a 10 mm-i.d., 200 mm length Pyrex glass tube packed with 0.10 g of the catalyst diluted with quartz sand (30-50 mesh) to 1.0 cm³ bed volume and 12.7 mm bed height. A decalin solution of DBT or a solution containing 5 model compounds and t-BuOCl was pumped into the reactor. The reaction was carried out under the following conditions: LHSV, 60-600 h⁻¹; contact time, 0.1-1.0 min; reaction temperature, 30-70°C; pressure, atmospheric pressure; concentration of DBT, 152 ppm; the amount of addition of model compounds, 0-0.5 ml; and molar ratio of t-BuOCl/DBT = 8.

The identification and quantification analyses of the reaction products were made using a gas chromatography, i.e., GC/MS (Shimadzu GCMS-QP5050) and GC-FID, GC-FPD (Shimadzu GC-14A) equipped with a methylsilicone capillary column.

3. Results and Discussion

3.1. Oxidation of DBT with t-BuOCl in the Presence of Al₂O₃ Catalysts

In order to understand the role of t-BuOCl in the oxidation more precisely, the oxidation of DBT with t-BuOCl was initially carried out in a batch reaction system in the presence of 3%-Pt/Al₂O₃. Figure 1 shows the effect of 3%-Pt/Al₂O₃ on the conversion of DBT in decalin solution. The conversion of DBT increased with increasing amount of 3%-Pt/Al₂O₃, but almost no oxidation of DBT was observed in the absence of the catalyst. Moreover, the decrease in the DBT concentration caused by adsorption on the catalyst was not observed in the absence of t-BuOCl. These results indicated that the catalyst was necessary for oxidation of DBT to DBT sulfone with t-BuOCl.

<table>
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<tr>
<th>Table 1</th>
<th>Properties of Feed Hydrotreated Light Gas Oil HT-LGO</th>
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<td>Sulfur</td>
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<td>Nitrogen</td>
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<td>4,6-Dimethylbenzenothiophene</td>
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supplied by Catalysis Society of Japan. ZnO (10.4 m²/g) and MgO (130 m²/g) were prepared by calcinating ZnCO₃ and Mg(OH)₂ at 700°C for 10 h. SiO₂-gel (Wako Chemicals Co.; >600 m²/g) and Diaion SK 1B (Cation exchange resin, Mitsubishi Chemicals Co., Ltd.: <1 m²/g) were used without further treatment. The treatment of γ-Al₂O₃ with KOH (K/Al₂O₃) was carried out by mixing 15 ml of 0.5 N-KOH aqueous solution and 5 g of γ-Al₂O₃ and stirred for 15 min and dried at 120°C for 10 h.

2. 2. Apparatus and Procedure

The oxidation in a batch reactor was conducted in a 100 ml two-neck Pyrex glass flask with a magnetic stirrer. 80 ml of decalin solution of DBT or that containing 5 model compounds, e.g., DBT, n-pentadecane, xylene, indole and diisobutylene, decalin solution, and 0.05-0.20 g of catalyst were added. The mixture was stirred and heated in the range 30-70°C, then, 0.05 ml of t-BuOCl was added. The t-BuOCl/DBT ratios were 4-16 mol/mol. The reaction was continued for 120 min.

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0.2 g, the maximum conversion of DBT reached 76.4%; however, the increase in the conversion of DBT in each case leveled off with increasing reaction time. This result may be attributed to the decrease in the concentration of t-BuOCl because of its low thermostability at 70°C. Moreover, DBT sulfone generated over the catalyst may have covered the active sites and acted as a catalytic poison. If the reaction temperature could be kept lower, the recovery of t-BuOCl after oxidation could have been increased. A high recovery of the oxidant could be carried out by means of distillation in vacuo.

Figure 2 shows the effect of the amount of t-BuOCl on conversion of DBT. The conversion of DBT increased by increasing the amount of t-BuOCl. The conversions of DBT reached 96.6, 62.3 and 42.8% when the t-BuOCl/DBT ratios were 16, 8 and 4 mol/mol, respectively. 2 moles of t-BuOCl were required stoichiometrically for the oxidation of 1 mole of DBT into corresponding sulfone. In this study, the conversion of DBT could reach more than 60% with 8 mol/mol of ratio of t-BuOCl to DBT that was only 4 times greater than the stoichiometric amounts. Therefore, the selectivity of the oxidant in the present study can be considered as significantly high compared with the results reported previously.

The product from the oxidation of DBT was DBT sulfone, and t-BuOCl was transformed to t-butyl chloride (t-BuCl), which was determined by GC-MS and IR analyses. Johnson et al. and Skattebøl et al. reported the products found from the oxidation of thianes and sulfides with t-BuOCl at very low temperatures were sulfoxides. In the present study, the formation of corresponding sulfone can be explained as follows:

DBT reacts with t-BuOCl to produce DBT sulfoxide and t-BuCl; then DBT sulfoxide reacts with t-BuOCl to produce DBT sulfone. Sheldon reported that the mechanism involved a metal peroxides intermediate formed by reaction of an oxometal group with alkyl hydroperoxide. A hypothetical mechanism of DBT oxidation with t-BuOCl is shown in Scheme 1. The hydroxyl group on the surface of alumina reacts with t-BuOCl to produce intermediate-peroxides and t-BuCl. The peroxides then react with DBT to produce DBT sulfoxide, and further oxidation produces the corresponding sulfone. This mechanism is similar to the mechanism involved in oxidation using H2O2 and formic acid.

After oxidation with t-BuOCl, the contamination of reacted oil with chlorine compounds such as unreacted t-BuOCl, t-BuCl and other chlorinated compounds may occur, and the environmental pollution originated from the formation of these compounds may be brought out. Therefore, it is necessary to remove t-BuOCl and t-BuCl (Boiling point 79.6°C and 51°C, respectively) from the reacted oil by distillation and to reduce the amount of t-BuOCl used in the oxidation to avoid the formation of other chlorination compounds.

Figure 3 shows the changes in the conversion of DBT with contact times (1/LHSV) at 30, 50 and 70°C in the presence of 0.1 g of 3%-Pt/Al2O3 in a flow reactor system. There was no significant difference in the conversion of DBT at 30°C and at 50°C. The maximum conversion of DBT reached 80% at both temperatures. The conversion of DBT at 70°C, however, leveled off at ca. 60% in spite of the increase in contact time more than 0.4 min. This is attributed to the low thermostability of t-BuOCl. Therefore, the conversion of DBT at 70°C was lower than that at 30°C or at 50°C.
because of the decrease in the concentration of t-BuOCl.

3.2. Effect of Catalyst on the Oxidation of DBT with t-BuOCl

Figure 4 shows the changes in the conversions of DBT with contact times at 30, 50 and 70°C in the presence of Al2O3. At 50°C, the maximum conversion of DBT reached 93.3% for contact time of 1.0 min. The conversion was 87.5% even at 30°C. However, the conversion of DBT at 70°C approached a steady value of ca. 62% for contact time more than 0.6 min, probably because of the probable occurrence of thermolysis of t-BuOCl. This result indicates that Al2O3 is one of the promising catalysts for oxidation of DBT with t-BuOCl. Moreover, oxidation of DBT using Al2O3 and t-BuOCl systems in a flow reactor is a convenient method because this system does not need to recover the aqueous fraction nor need to mix the oil and aqueous fraction as compared with the carboxylic acid and hydrogen peroxide system.

In order to search for the optimum catalyst for oxidation with t-BuOCl, oxidation of DBT in the presence of other supported catalysts and several metal oxides was conducted with the same method, and the results obtained are summarized in Table 2. Conversions of DBT with Al2O3-supported catalysts were in the range of 80-95% at 50°C, higher than those of the other metal oxides used. The conversion with the Al2O3-support without loading metals was 94%. The conversion of the metal-loaded Al2O3 catalysts was almost the same as that of the Al2O3-supported. Mn/sea sand and Mo/sea sand were also prepared by impregnation method and used for oxidation of DBT. The conversion of DBT using these catalysts was less than 5%. These results indicated that the metal loaded on Al2O3 did not affect the oxidation directly and that the oxidation occurred on the surface of Al2O3. When Al2O3 was treated with KOH, the conversion of DBT decreased because the number of acid sites on Al2O3 probably decreased as shown in Table 2. Moreover, conversions of DBT with base metal oxides were low and the conversion of DBT decreased in the order: γ-Al2O3 > TiO2, Diaion > SiO2 > ZnO >> MgO. It was reported that surface acidity of metal oxides was measured by
titration of n-butylamine using several indicators, and it was found in the order: Al$_2$O$_3$ > TiO$_2$, SiO$_2$ > ZnO >> MgO. Diaion (cation exchange resin) is considered to be a solid acid. The order of acidity of these catalysts/oxides seems to be the same to their order of activity, as was mentioned above. These results suggested that the acidic site of the catalyst acted as the active oxidation site of DBT with t-BuOCl. Although, a remarkable relationship between the surface area and conversion of DBT was not observed, a higher activity seemed to be obtainable when the acidic sites were stronger, and the surface area was larger.

### 3.3. Oxidation of DBT in the Presence of Other Compounds

Similarly, the oxidation of DBTs in LGO under the same conditions (Al$_2$O$_3$, 0.10 g; temperature, 50°C; mole ratio of t-BuOCl/DBT, 8) was carried out. No oxidation of DBTs in LGO was observed. This result indicated that the oxidation of DBTs with t-BuOCl was inhibited by other compounds found in LGO. In order to investigate the inhibiting effect of LGO addition on DBT oxidation, it was carried out in a batch reactor in decalin solution with the addition of a small amount of LGO. The concentrations of added LGO were 0, 120, 300 and 600 ppm, and the reaction was continued for 120 min. The results obtained are shown in Fig. 5. Conversions of DBT were not influenced by the addition of LGO up to 120 ppm. On the other hand, the addition of LGO to 300 ppm retarded the oxidation of DBT ca. 90%. Moreover, DBT conversion with increasing LGO to 600 ppm decreased to ca. 15% of that without addition of LGO. These results indicate that the retarding effect of addition of LGO on conversion of DBT is attributed to the presence of more reactive compounds than that of DBT in LGO.

In order to investigate which type of compounds in LGO can be a retardant, the oxidation of DBT in decalin solution containing 600 ppm of several model compounds was carried out at 50°C. The results obtained are shown in Fig. 6. The conversion of DBT was not influenced by the addition of n-pentadecane nor by addition of xylene indicating that aliphatic and aromatic hydrocarbons did not affect the oxidation of DBT. In contrast, the addition of disisobutylene and indole retarded the oxidation of DBT more significantly than that of LGO. Especially, no oxidation of DBT was observed by addition of indole. This result shows that olefin and nitrogen compounds similarly retard the oxidation of DBT because these compounds are more reactive than DBT under the conditions used in the present study. From the GC/MS analyses, the main oxidation products of disisobutylene and indole under present
conditions were 2-neopentylacrolein and 6-chloroindole, respectively.

In order to investigate the effects of the amount of diisobutylene and indole added on oxidation of DBT, it was carried out in decalin solution with different amounts of diisobutylene and indole, and the results obtained are shown in Figs. 7 and 8. Diisobutylene/DBT ratios were 0, 2.0, 4.0 and 8.0 mol/mol, while those of indole/DBT ratios were 0, 1.0, 1.7 and 3.5 mol/mol, respectively. Conversions of DBT decreased with increasing diisobutylene/DBT mole ratios. With the addition of 2.0 mol/mol diisobutylene, the DBT conversion decreased to 40% from 60% of that without the addition. Moreover, with the addition of 8.0 mol/mol, the DBT conversion decreased about 10%. Similarly, conversions of DBT decreased with increasing indole/DBT mole ratios. The similarity between the results with addition and without addition was approximately the same. With addition of 1.7 mol/mol indole, DBT conversion decreased to less than ca. 5% from 60% without addition. Moreover, with the addition of 3.5 mol/mol indole, no oxidation of DBT was observed. These results show that diisobutylene and indole retard the oxidation of DBT.

Other olefins, nitrogen compounds present in LGO such as acridine or carbazole, are also expected to have the same retarding effects because of their high reactivities.

4. Conclusions

The oxidation of DBT in decalin solution using t-BuOCl in the presence of an Al₂O₃ catalyst was applied both to the flow reaction system and to the batch system, and the following results were obtained:

1. The conversion of DBT (150 ppm) into DBT sulfoxide reached 90% under ambient pressure at 50°C.
2. The conversion of DBT decreased in the order: γ-Al₂O₃ > TiO₂, Diaion > SiO₂ > ZnO > MgO. Moreover, the activities of the metal-loaded Al₂O₃ catalysts were approximately the same as the activity of Al₂O₃ support. These results suggested that the acidic sites of the catalysts acted as the active sites for the oxidation of DBT, and the Al₂O₃ had its own active sites.
3. The oxidation of DBT was inhibited by other compounds found in LGO, and the extent of retardation decreased in the order: nitrogen compounds > olefins >> aromatics and paraffins.

Nomenclatures

DBT: dibenzothiophene
DBTs: alkyl substituted dibenzothiophene
4-MDBT: 4-methyl dibenzothiophene
4,6-DMDDBT: 4,6-dimethyl dibenzothiophene
HDS: hydrodesulfurization
LGO: light gas oil
ODS: oxidative desulfurization

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要旨

軽油の酸化脱硫

一次亜塩酸-t-ブチルを用いたジベンゾチオフェンの酸化反応

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次亜塩酸-t-ブチルを触媒に用いて，様々な触媒存在下でジベンゾチオフェン (DBT) の酸化反応を行った。152 ppm の DBT を使用した反応装置中での DBT の酸化反応の速度は 30 〜 70℃，大気圧下で 90% の DBT 転化率が得られた。次亜塩酸-t-ブチルを用いた DBT の酸化反応は低温で触媒が必要であり，γ-Alumina 転化を用いた場合，高い DBT 転化率が得られた。金属粉末アルミナ触媒の反応性はアルミナ粒子の反応性と同様の値であり，アルミナ自身が活性点として機能していることがわかった。軽油中で同様の条件下で DBT の酸化反応を行ったところ，DBT よりも反応性が高いオレフィン類や塩素化合物の存在により DBT の酸化反応は進行しなかった。

Keywords

Oxidative desulfurization, Light gas oil, t-Butyl hypochlorite, γ-Alumina, Dibenzothiophene, Flow reactor system