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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 (Al_2O_3) supported catalysts have relatively high activities. At the same time, the activities of the metal-loaded Al_2O_3 catalysts had shown the same activities as those of the Al_2O_3 support, indicating that the Al_2O_3 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-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are very difficult to desulfurize even under deep desulfurization conditions^{1),2)}. 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^{3)~7)}. 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 HDS³⁾.

Many types of oxidants have been used, and various consequences of ODS methods have been reported^{3)~11)}. 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 sulfones¹²⁾. Aida *et al.* had reported that for selective oxidation of sulfur compounds in fuel oil, peroxyacid, such as performic acid, pertrifluoroacetic acid, a mixture of formic acid or trifluoroacetic acid and hydrogen peroxide etc., were some of the most positive oxidants⁴⁾. 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 reactivity of decomposition with alkaline was in the order: sulfone > sulfoxide >> sulfide¹³⁾. 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-

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Table 1 Properties of Feed Hydrotreated Light Gas Oil

		HT-LGO
Sulfur	[ppm]	480
Nitrogen	[ppm]	40
Carbon	[wt%]	86.4
Hydrogen	[wt%]	13.1
Density	[g/ml at 15°C]	0.846
4,6-Dimethyldibenzothiophene	[wt%]	0.0145
Distillation data	[°C]	
IBP		158
10 vol%		247
20 vol%		272
30 vol%		289
50 vol%		320
70 vol%		353
80 vol%		373
90 vol%		396
EP		445

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, and indole found in LGO on the oxidation of DBTs were also investigated.

2. Experimental Section

2.1. Materials

DBT, *n*-pentadecane, diisobutylene, xylene, indole, *t*-BuOCl, and decalin were purchased from Kishida Chemicals Co. Dibenzothiophene-1,1-dioxide (DBT sulfone) used to identification was synthesized according to the methods reported^{14),15)}. LGO used in this study was a hydrotreated light gas oil, and its properties are shown in Table 1.

A commercial γ -alumina (Al_2O_3 , BET surface area: 256 m^2/g) and a commercial 20% Mo/ Al_2O_3 (217 m^2/g) supplied by Nippon Ketjen Co., Ltd. were both crushed and screened to provide 20 to 80 mesh granules and dried at 350°C for 4 h prior to use. 3% Pt/ Al_2O_3 was prepared by impregnation method using platinum chloride (PtCl_2) and Al_2O_3 . Mn/ Al_2O_3 and Co/ Al_2O_3 were prepared by the following procedure using metal acetylacetonates (Nihon Kagaku Sangyou Co.). Al_2O_3 was suspended in toluene solution of metal acetylacetonate and stirred under reflux for 4 h. After removing the toluene, calcination was carried out at 450°C over 24 h. TiO_2 (JRC-TIO-1: 70.8 m^2/g)

supplied by Catalysis Society of Japan. ZnO (10.4 m^2/g)¹⁶⁾ and MgO (130 m^2/g)^{17),18)} were prepared by calcinating ZnCO_3 and $\text{Mg}(\text{OH})_2$ at 700°C for 10 h. SiO_2 gel (Wako Chemicals Co.: > 600 m^2/g) and Diaion SK 1B (Cation exchange resin, Mitsubishi Chemicals Co., Ltd.: < 1 m^2/g) were used without further treatment. The treatment of $\gamma\text{-Al}_2\text{O}_3$ with KOH ($\text{K}/\text{Al}_2\text{O}_3$) was carried out by mixing 15 ml of 0.5 N-KOH aqueous solution and 5 g of $\gamma\text{-Al}_2\text{O}_3$ 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.

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 cm^3 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 mole 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 Al_2O_3 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/ Al_2O_3 . Figure 1 shows the effect of 3%-Pt/ Al_2O_3 on the conversion of DBT in decalin solution. The conversion of DBT increased with increasing amount of 3%-Pt/ Al_2O_3 , 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. In the case of

Reaction temperature 70°C, Catalyst 3%-Pt/Al₂O₃. Amount of catalyst: ○ 0.0 g, ● 0.05 g, ▲ 0.10 g, ■ 0.20 g.

Fig. 1 Effect of Amount of 3%-Pt/Al₂O₃ on Conversion of DBT

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 previously³⁾.

The product from the oxidation of DBT was DBT sulfone, and *t*-BuOCl was transformed to *t*-butyl chlorite (*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^{19),20)}. In the present study, the formation of corresponding sulfone can be explained as follows:

Reaction temperature 70°C, Catalyst 3%-Pt/Al₂O₃ 0.1 g. Ratio of *t*-BuOCl/DBT: ● 4, ▲ 8, ■ 16.

Fig. 2 Effect of Amount of Oxidant on Conversion of DBT

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 hydroperoxide²¹⁾. 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 acid³⁾.

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

Scheme 1 Hypothetical Oxidation Mechanism of DBT with *t*-BuOCl Catalyst: 3%-Pt/Al₂O₃. Reaction temperature: ● 30°C, ▲ 50°C, ■ 70°C.

Fig. 3 Changes in Conversion of DBT with Contact Time

Catalyst: Al₂O₃. Reaction temperature: ● 30°C, ▲ 50°C, ■ 70°C.

Fig. 4 Changes in Conversion of DBT with Contact Time

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

Table 2 The Maximum Conversion and Surface Area of DBT Oxidation Using Flow Reactor (temperature 50°C, LHSV 60 h⁻¹)

Catalysts	Conversion [%]	Surface area [m ² /g]
6% Mn/ γ -Al ₂ O ₃	95	—
6% Co/ γ -Al ₂ O ₃	95	—
20% Mo/ γ -Al ₂ O ₃	85	217
3% Pt/ γ -Al ₂ O ₃	80	255
γ -Al ₂ O ₃	94	256
7% K/ γ -Al ₂ O ₃ ^{a)}	88	213
6% Mn/sea sand	5	< 1
6% Co/sea sand	3	< 1
TiO ₂	62	70.8
Diaion (cation exchange resin)	55	< 1
SiO ₂	50	> 600
ZnO	40	10.4
MgO	10	130

a) γ -Al₂O₃ treated with KOH.

titration of *n*-butylamine using several indicators, and it was found in the order: Al₂O₃ > TiO₂, SiO₂ > ZnO >> MgO^{22),23)}. Diaion (cation exchange resin) is considered to be a solid acid²⁴⁾. 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 (Al₂O₃, 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

Catalyst: Al₂O₃. Amount of catalyst: 0.10 g.
Reaction temperature: 50°C. Symbol: ◇ No addition, ● 120 ppm, ▲ 300 ppm, ■ 600 ppm.

Fig. 5 Effect of Addition of LGO on Conversion of DBT

Symbol: ◇ No addition, ● *n*-Pentadecane, ▲ Xylene, ■ LGO, ○ Diisobutylene, △ Indole.

Fig. 6 Effect of Addition of Model Compounds on Conversion of DBT

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 diisobutylene 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 diisobutylene and indole under present

Catalyst: Al_2O_3 . Amount of catalyst: 0.10 g.
Diisobutylene/DBT mole ratio: $\diamond$ 0.0, $\bullet$ 2.0, $\blacktriangle$ 4.0, $\blacksquare$ 8.0.

Fig. 7 Effect of Addition of Diisobutylene on Conversion of DBT

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. And 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 Al_2O_3 catalyst was applied

Catalyst: Al_2O_3 . Amount of catalyst: 0.10 g.
Indole/DBT mole ratio: $\diamond$ 0.0, $\bullet$ 1.0, $\blacktriangle$ 1.7, $\blacksquare$ 3.5.

Fig. 8 Effect of Addition of Indole on Conversion of DBT

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 sulfone reached 90% under ambient pressure at 50°C.
- (2) The conversion of DBT decreased in the order: $\gamma\text{-Al}_2\text{O}_3 > \text{TiO}_2$, Diaion $> \text{SiO}_2 > \text{ZnO} \gg \text{MgO}$. Moreover, the activities of the metal-loaded Al_2O_3 catalysts were approximately the same as the activity of Al_2O_3 support. These results suggested that the acidic sites of the catalysts acted as the active sites for the oxidation of DBT, and the Al_2O_3 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 $\gg$ aromatics and paraffins.

Nomenclatures

DBT	: dibenzothiophene
DBTs	: alkyl substituted dibenzothiophene
4-MDBT	: 4-methyldibenzothiophene
4,6-DMDBT	: 4,6-dimethyldibenzothiophene
HDS	: hydrodesulfurization
LGO	: light gas oil
ODS	: oxidative desulfurization

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要 旨

軽 油 の 酸 化 脱 硫

一次亜塩素酸-*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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次亜塩素酸-*t*-ブチルを酸化剤に用いて, 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 DBT デカヒドロナフタレン溶液を用いた流通式反応装置中での DBT の酸化反応の場合, 反応温度 30~70℃, 大気圧下で 90% の DBT 転化率が得られた。次亜塩素酸-*t*-ブチルを用いた DBT の酸化反応では触媒が必要であり, γ アルミナ触媒を用い

た場合, 高い DBT 転化率が得られた。金属担持アルミナ触媒の反応性はアルミナ担体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 よりも反応性の高いオレフィン類や窒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