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Deep Hydrodesulfurization of Light Gas Oil (Part 2) Effect of Hydrogen Sulfide on Hydrodesulfurization of Dibenzothiophenes Included in Hydrotreated Light Gas Oil

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Sulfided Co-Mo/Al₂O₃ catalyst was used to investigate the hydrodesulfurization (HDS) of dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) included in hydrotreated light gas oil (H-LGO) of less than 0.168 wt% of sulfur-content. The behavior of DBT, 4-MDBT, and 4,6-DMDBT in HDS was traced under the following conditions: temperature 290-370°C, LHSV 2-10 h⁻¹, and Gas/Oil 125 N/l. The HDS of these compounds was treated as a pseudo-first-order reaction with respect to their concentrations. The ratio between HDS rate constants of various DBTs in H-LGO was substantially larger than that between the comparable constants in straight-run LGO (SR-LGO). Activation energies of the HDS of DBTs increased in the order DBT < 4-MDBT < 4,6-DMDBT, while the differences between the activation energies were larger for H-LGO HDS than for SR-LGO HDS. It thus appeared that H-LGO HDS formed a lesser quantity of H₂S than did SR-LGO HDS. The retarding effect of H₂S on HDS was investigated by using polysulfide, which easily formed H₂S under HDS conditions. The retarding effect of H₂S on HDS decreased in the order DBT > 4-MDBT, while the HDS of 4,6-DMDBT was not retarded. These results could be explained by assuming a competitive adsorption between DBTs and H₂S.

1. Introduction

The call for deep hydrodesulfurization (HDS) of light gas oil (LGO) has presented a challenge of global scope. To achieve it, novel catalysts must be developed and the reaction mechanisms of deep HDS be further elucidated. For this purpose, many researchers have performed model reactions to investigate the HDS of sulfur compounds contained in LGO^{1)~9)}. However, the kinetics of dibenzothiophenes (DBTs), and in particular that of 4-methyldibenzothiophene (4-MDBT) and that of 4,6-dimethyldibenzothiophene (4,6-DMDBT) in HDS of LGO have received but little attention. Further, the effect of H₂S on HDS is important because H₂S directly retards the activities of DBTs in HDS. Previously, in our study to elucidate the mechanisms of DBTs in the HDS of LGO, we observed that LGO components such as phenanthrene and acridine retarded the HDS of DBTs¹⁰⁾. Moreover, a number of sulfur compounds were included in LGO. The sulfur content was about 1.5 wt%, and a large amount of H₂S was formed by HDS reactions¹¹⁾. It was therefore difficult to directly investigate the retarding effect of H₂S on the HDS of DBTs in LGO in detail. In this

study, we investigated the effect of H₂S on the HDS of DBT, 4-MDBT, and 4,6-DMDBT included in hydrotreated LGO (H-LGO) containing less than 0.168 wt% sulfur, and we traced the reaction behavior of DBTs under such low sulfur concentration. Reaction rate constants and activation energies were estimated by treating the HDS reaction of these compounds as pseudo-first-order reactions with respect to their concentrations.

2. Experimental

2.1. Materials

Hydrogen and hydrogen sulfide in hydrogen were obtained from the Tohei Chemical Co., Ltd. An original hydrotreated light gas oil (OH-LGO) and a straight-run light gas oil (SR-LGO) were obtained from the Nippon Ketjen Co., Ltd. DBT was obtained from the Tokyo Kasei Kogyo Co., Ltd. 4-MDBT and 4,6-DMDBT were synthesized according to the methods previously reported^{12)~14)}. Organic polysulfides R-S_n-R (CS-40) was obtained from Dainippon Ink and Chemicals, Inc., and it had ligand R=C₈ and whose average sulfur chain length was *n* = 4.7 (Table 1). The catalyst used was a commercially available Co-Mo/Al₂O₃ catalyst (MoO₃, 17.0 wt%; CoO₃, 4.5 wt%)

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Table 1 Properties of CS-40

Formula		R-S _n -R
Sulfur content	[mass%]	39.0
Density @ 15°C	[g/ml]	1.043
Pour point	[°C]	-35.0
Flash point	[°C]	144
Toxicity		low
Appearance and odor		odorless yellow oil

Table 2 Properties of Feedstock

		H-LGO	SR-LGO
Sulfur	[wt%]	0.168	1.50
Nitrogen	[ppm]	80	140
Carbon	[wt%]	86.3	85.2
Hydrogen	[wt%]	13.2	12.7
Density @ 15°C	[g/ml]	0.848	0.858
Saturated fraction	[wt%]	65.0	67.0
Aromatics	[wt%]		
1 ring		29.2	18.3
2 rings		5.5	13.6
3 rings		0.3	0.9
4 and more than 4 rings		0.1	0.2

supplied as 1/32-inch extrudates, which were crushed and screened to 20-35 mesh granules.

2.2. Arrangement of Concentration of DBTs in Hydrotreated LGO and the Properties of LGOs

The original hydrotreated light gas oil (OH-LGO) contained 4,6-DMDBT and C3-DBT. We have previously reported that dibenzothiophenes in straight-run LGO (SR-LGO) can be classified with respect to the HDS of DBT, 4-MDBT, and 4,6-DMDBT⁷⁾. This indicates that the HDS of these compounds is the key reaction in deep desulfurization of SR-LGO. Since DBT and 4-MDBT were absent in OH-LGO and the amount of 4,6-DMDBT was less than that of SR-LGO, the arrangement of DBT, 4-MDBT, and 4,6-DMDBT was accomplished by adding these compounds to OH-LGO. In this study, SR-LGO and LGO (H-LGO) prepared and hydrotreated were used, and the properties of these oils are shown in **Table 2**. Amounts of saturated fraction and aromatic fractions with several rings were determined by HPLC using silicagel column modified by cyano group (*n*-heptane/tetrahydrofuran (THF: 0.2 vol%)). Aromatics were monitored by a refractive index detector. The standard samples for aromatics with 1, 2, 3, and 4 rings were benzene, naphthalene, anthracene and 2,3-benzanthracene, respectively. **Figures 1 and 2** show the chromatogram of GC-FPD for sulfur compounds in H-LGO and SR-LGO, which included 0.168 wt% and 1.5 wt% of total sulfur, respectively. **Table 3** shows the sulfur contents of dibenzothiophenes in H-LGO and SR-LGO.

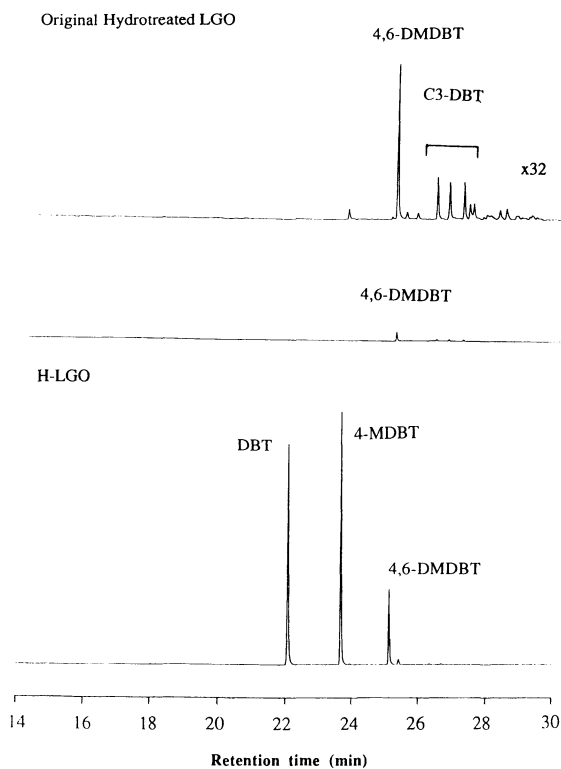


Fig. 1 GC-FPD Chromatogram of Polyaromatic Sulfur-containing Hydrocarbon (original hydrotreated LGO and H-LGO)

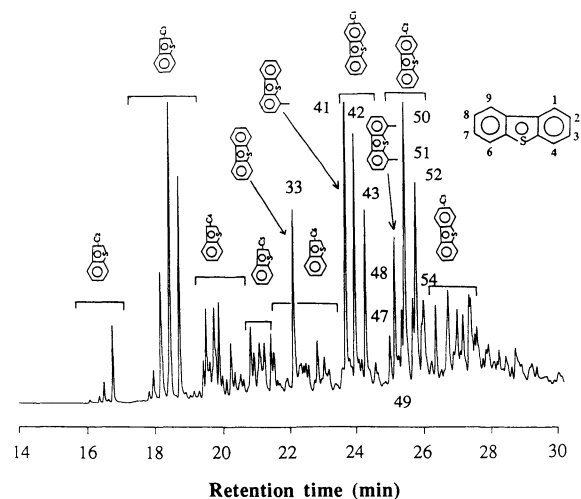


Fig. 2 GC-FPD Chromatogram of Polyaromatic Sulfur-containing Hydrocarbon (LGO)

2.3. Apparatus and Procedure

The reactor was a 20 mm-i.d. stainless steel tube packed with 2.54 g of catalyst particles diluted with 12 cc of quartz sand. The catalyst was presulfided with a mixture of 4.95 vol% H₂S in a stream of H₂ under atmospheric pressure at 30 l/h and 400°C for 3 h.

Table 3 Sulfur Contents of Dibenzothiophenes in Light Gas Oil

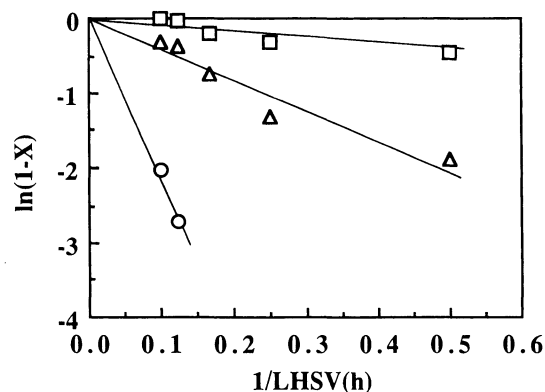
Sulfur-containing compounds	Sulfur content [wt%]	
	H-LGO	SR-LGO
Total sulfur [wt%]	0.168	1.50
Dibenzothiophenes		
Dibenzothiophene (Peak No.33)	0.0344	0.0186
C1-Dibenzothiophenes		
Peak No.41	0.0357	0.0230
Peak No.42	—	0.0211
Peak No.43	—	0.0152
C2-Dibenzothiophenes		
Peak No.47	—	0.0058
Peak No.48	0.0176	0.0126
Peak No.49	—	0.0071
Peak No.50	—	0.0242
Peak No.51	—	0.0079
Peak No.52	—	0.0182
Peak No.54	—	0.0075

After these pretreatments, the reactor was pressurized with hydrogen. The light gas oil was then supplied by a feed pump (Kyowa Seimitsu KHD-52). The HDS reactions were conducted under the following conditions: temperature 290-370°C, total pressure of 30 kg/cm², LHSV of 2-10 h⁻¹, and Gas/Oil ratio of 125 N/l. Samples were collected in a gas-liquid separator; then, after a change of reaction temperature and a wait of 4-5 h, the above procedure was repeated for a second time. The sulfur-containing products were analyzed by a gas chromatography with an FPD detector (Shimadzu GC-14A).

3. Results and Discussion

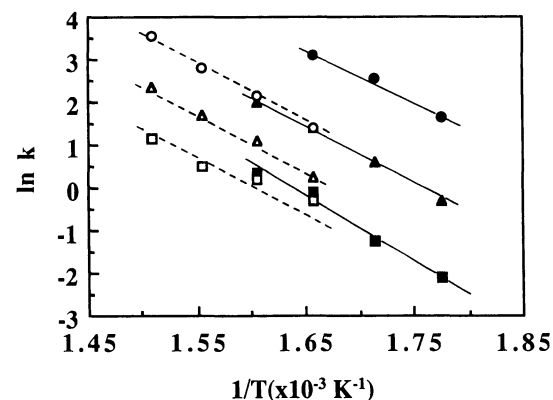
3.1. Kinetics on HDS of Dibenzothiophenes

The HDS of H-LGO was performed under the following conditions: Temperature 290-350°C, Gas/Oil ratio 125 N/l, and LHSV 2-10 h⁻¹. Pseudo-first-order plots of DBT, 4-MDBT, and 4,6-DMDBT are shown in Fig. 3. The approximate linear relationship was observed for each compound, and the HDS of each compound was treated as a pseudo-first-order reaction. Figure 4 shows the Arrhenius plots of pseudo-first-order rate constants of DBT, 4-MDBT, and 4,6-DMDBT, along with the results from the HDS of SR-LGO. Activation energies for DBT, 4-MDBT, and 4,6-DMDBT were calculated from the slopes of the straight lines, and these results are listed in Table 4. The values of activation energies increased in the order DBT (22 ± 3 kcal/mol) < 4-MDBT (27 ± 1 kcal/mol) < 4,6-DMDBT (31 ± 2 kcal/mol), and the differences between these values were large in comparison with those resulting from the HDS of SR-LGO. The results from the HDS of H-LGO approached those from the model HDS reactions using DBT (22 ± 2 kcal/mol), 4-



Reaction temperature: 330°C, Gas/Oil: 125 N/l, Oil: H-LGO.
○: DBT, △: 4-MDBT, □: 4,6-DMDBT.

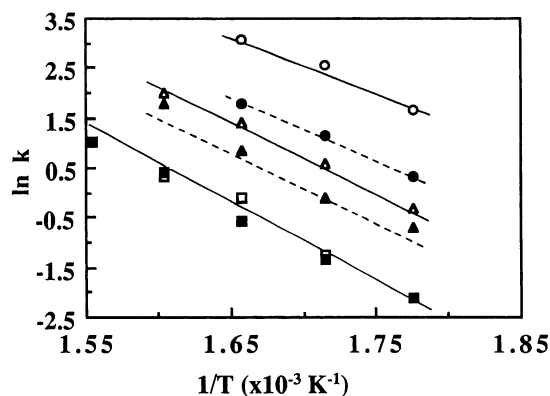
Fig. 3 Pseudo-first-order Plots of DBT, 4-MDBT, and 4,6-DMDBT



Gas/Oil: 125 N/l.
H-LGO; ●: DBT, ▲: 4-MDBT, ■: 4,6-DMDBT (—).
SR-LGO; ○: DBT, △: 4-MDBT, □: 4,6-DMDBT (---).

Fig. 4 Arrhenius Plots of DBT, 4-MDBT, and 4,6-DMDBT

MDBT (29 ± 1 kcal/mol), and 4,6-DMDBT (33 ± 2 kcal/mol)⁹. The SR-LGO included 1.5 wt% of sulfur while H-LGO included 0.168 wt% of sulfur. The HDS of SR-LGO formed H₂S in a greater quantity than did HDS of H-LGO. This may be related to the fact that the quantities of various components, including H₂S and solvents, are smaller in H-LGO than in SR-LGO. The rate constants of DBT, 4-MDBT, and 4,6-DMDBT in the HDS of H-LGO were 22, 4.1, and 0.91 h⁻¹ at 330°C, respectively. The ratio of rate constants was 24 : 4.5 : 1. In the HDS of SR-LGO, the ratio was 5.6 : 1.8 : 1 at 330°C. As mentioned above, the HDS of SR-LGO formed a greater quantity of H₂S than did HDS of H-LGO. In the model reaction, H₂S retarded the formation of biphenyls (BPs), rather than the formation of cyclohexylbenzenes (CHBs)¹⁵. The selectivity for biphenyl (BP) in the HDS of DBT is



Gas/Oil: 125 N//l, Oil: H-LGO.
 H-LGO; ○: DBT, △: 4-MDBT, □: 4,6-DMDBT (—).
 CS-40 + H-LGO; ●: DBT, ▲: 4-MDBT, ■: 4,6-DMDBT (---).

Fig. 5 Arrhenius Plots of DBT, 4-MDBT, and 4,6-DMDBT

higher than the selectivities for BPs in the HDS of 4-MDBT or 4,6-DMDBT⁹). Therefore, the HDS rate of DBT is more severely retarded by H₂S than that of 4-MDBT or 4,6-DMDBT. We proposed that the retarding effect of H₂S on the HDS of DBT in H-LGO was less than that in SR-LGO and that the ratio of rate constants between DBTs in H-LGO became larger than those in SR-LGO. The ratio of the rate constant for DBT in SR-LGO to that in H-LGO was 0.19. In contrast, the ratios of the rate constants for 4-MDBT and 4,6-DMDBT were approximately 0.31 and 0.8 at 330°C, respectively.

3.2. Effect of H₂S on HDS of Dibenzothiophenes

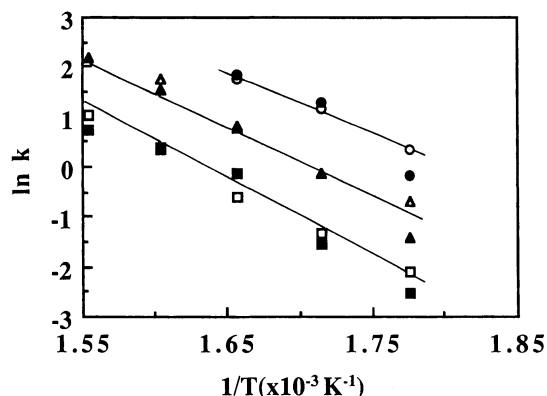
As mentioned above, it is presumed that light gas oil components, particularly H₂S, retard the HDS of DBTs. In the following experiment, we investigated the effect of H₂S on the HDS of DBTs in detail. The experiment was performed under the following conditions: Temperature 290-370°C, Gas/Oil ratio 125 N//l, and LHSV 2-4 h⁻¹. The light gas oil used was H-LGO. To the feed CS-40 was added. At the point when all of the CS-40 was presumed to be converted to H₂S, the concentration of H₂S formed by CS-40 conversion was approximately 4.5%, a value similar to that of the H₂S concentration evolved during HDS of SR-LGO (4.0% to 6.9% depending on the conversion of sulfur compounds). CS-40 completely decomposed at 290°C, a temperature lower than that used for HDS. The HDS of each sulfur compound can also be treated as a pseudo-first-order reaction. Figure 5 shows the Arrhenius plots of pseudo-first-order rate constants of DBT, 4-MDBT, and 4,6-DMDBT. Table 4 shows the activation energies for DBT, 4-MDBT, and 4,6-DMDBT, calculated from the slopes of the straight lines. The activation energy of DBT increased slightly, while that of 4-MDBT and that of 4,6-DMDBT did

Table 4 Activation Energies of Desulfurization of DBTs

Sulfur compounds	Activation energy [kcal/mol]		
	H-LGO	SR-LGO	CS-40 in H-LGO
DBT	22 ± 3	27 ± 2	25 ± 3
4-MDBT	27 ± 1	28 ± 2	27 ± 3
4,6-DMDBT	31 ± 2	27 ± 2	31 ± 2

not change significantly. The extent of retardation decreased in the order DBT > 4-MDBT, and the ratio of the rate constant of DBT with H₂S to that of DBT without H₂S was 0.27. In contrast, the ratios for 4-MDBT and 4,6-DMDBT were 0.56 and 1.0 at 330°C, respectively, and the latter was not retarded by addition of H₂S. In the model reactions, heats of adsorption of DBT, 4-MDBT, and 4,6-DMDBT were about 11, 19, and 21 kcal/mol, respectively, indicating that DBT adsorbed on the catalyst more weakly than did 4-MDBT and 4,6-DMDBT^{6,7}). Further, the adsorption equilibrium constants for 4,6-DMDBT were higher than those for H₂S, while the adsorption equilibrium constants for DBT were lower than those for H₂S¹⁵). Therefore, the HDS of DBT was strongly retarded by H₂S, while that of 4,6-DMDBT was hardly retarded. These results suggest that the HDS of DBTs was retarded by competitive adsorption with H₂S. Further, as mentioned above, H₂S retards the formation of BPs, rather than that of CHBs¹⁵). In the HDS of DBT or 4-MDBT, the selectivity for BPs was higher than that in the case of 4,6-DMDBT. Therefore, the HDS of DBT or 4-MDBT was retarded more severely than that of 4,6-DMDBT. The ratio of the rate constants of DBT, 4-MDBT, and 4,6-DMDBT at 330°C was 11 : 4.1 : 1, smaller than that (24 : 4.5 : 1) of H-LGO. In the presence of H₂S, the formation of CHBs has advantages because the formation of BPs is more severely retarded. Further, in the formation of CHBs where an aromatic ring in DBTs is hydrogenated, it was reported that the retarding effects of the substituents were weakened and that conversions of DBTs became very similar^{6,9}). Therefore, the rate-constants ratio for the three compounds may become lower with H₂S addition to H-LGO.

In order to investigate the effect of H₂S in more detail, a 4.9% H₂S /H₂ gas mixture was used in place of CS-40. Reaction conditions of HDS were the same as of CS-40. The reactions of DBTs were treated as pseudo-first-order. The Arrhenius plots of DBT, 4-MDBT, and 4,6-DMDBT with CS-40 are shown in Fig. 6. These plots indicate that the retarding effects of H₂S by the H₂S/H₂ gas mixture were the same as those by CS-40. These results confirmed that the retarding effect of CS-40 on HDS was in fact that of H₂S evolved by the conversion of CS-40. The effect of CS-40 also suggests the possibility that this reagent can be used for presulfiding process without the use of gaseous hydro-



Gas/Oil: 125 N///, Oil: H-LGO.
 CS-40; ○: DBT, △: 4-MDBT, □: 4,6-DMDBT.
 H₂S/H₂; ●: DBT, ▲: 4-MDBT, ■: 4,6-DMDBT.

Fig. 6 Arrhenius Plots of DBT, 4-MDBT, and 4,6-DMDBT

gen sulfide.

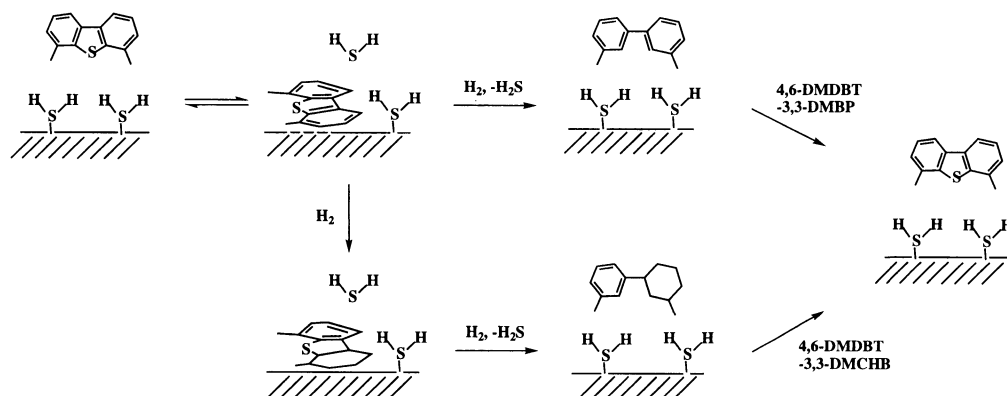
3.3. Reaction Mechanisms in HDS of Dibenzothiophenes in LGO

Scheme 1 shows the reaction pathways for HDS of 4,6-DMDBT and the retarding effect of H₂S. As shown in **Scheme 1**, there is a competitive adsorption between H₂S and 4,6-DMDBT. Hydrodesulfurization of adsorbed 4,6-DMDBT to give 3,3-DMBP is the rate determining step and is affected by the concentration of adsorbed 4,6-DMDBT on the catalyst surface. In contrast, hydrogenation of adsorbed 4,6-DMDBT to give hydrogenated derivatives does not seem to be affected by the concentration of adsorbed 4,6-DMDBT on the catalyst surface. If it is affected, the retarding effects of H₂S are not different between the formations of BPs and CHBs; moreover, a more severe retarding effect on CHBs formation would be observed because HDS of hydrogenated derivatives of DBTs is also retarded by H₂S. As described above, the retarding effect of H₂S on CHBs formation is less than that on BPs formation

probably because hydrogenated derivatives of DBTs are more strongly adsorbed on the surface in competition with H₂S than DBTs themselves.

We have reported that the heats of adsorption increase in the order DBT < 4-MDBT < 4,6-DMDBT and that the difference in the heats of adsorption appears in the formation of BPs^(6,9). This shows that in the formation of BPs, DBTs are more strongly adsorbed on the surface in the order DBT < 4-MDBT < 4,6-DMDBT. However, even if methyl-substituted DBTs are adsorbed more strongly than DBT, the formation rate and selectivity of BPs are lower because the C-S bond scission for methyl-substituted DBTs is slower without the preceding hydrogenation of an aromatic ring. Although H₂S retards HDS of all DBTs, nonsubstituted DBT which has a smaller heat of adsorption is relatively more strongly retarded. At higher temperatures where HDS of gas oil is generally performed, the heat of adsorption for every compound decreases and large amounts of vacancies appear on the catalyst surface. Thus, under such conditions the retarding effect on HDS of 4,6-DMDBT, which is more strongly adsorbed, seems to be difficult to appear.

We have already reported that the addition of 5 wt% of aromatic compounds with 2 or 3 rings to the same SR-LGO used in the present study did not affect the HDS rate⁽¹⁰⁾. However, when another SR-LGO with a lower sulfur content was used, the addition of 3 rings phenanthrene retarded HDS while the addition of 2 rings methylnaphthalene did not. In HDS of DBT catalyzed by Co-Mo/Al₂O₃, biphenyl or naphthalene showed very little or no retarding effect^(2,16)~18), suggesting that HDS of DBT is only slightly or not at all inhibited by aromatic hydrocarbons under the condition where several % of H₂S is included in the system⁽²⁾. However, under low sulfur concentration conditions as in deep desulfurization, it was shown that HDS was retarded by the solvent and that the use of an aromatic solvent more severely retarded HDS. **Table 2** also



Scheme 1 Reaction Pathways for HDS of 4,6-DMDBT and Retarding Effect of H₂S

shows the contents of aromatics for H-LGO and SR-LGO. As in the present study, when the HDS rates for SR-LGO in Fig. 4 are compared with HDS rates for CS-40 + H-LGO in Fig. 5, the former values were found to be lower. As shown in Table 2, SR-LGO includes more 2 rings aromatics than H-LGO, indicating that the difference between the HDS rates of SR-LGO and CS-40 + H-LGO may be attributed to the presence of more 2 rings aromatics. However, under high contents of sulfur the retarding effect of the aromatic may be low. Another possibility for affecting the retarding effects was the nitrogen content. We reported that the retarding effect of nitrogen increased in the order $DBT < 4\text{-MDBT} < 4,6\text{-DMDBT}^{(10)}$. This order was, however, not consistent with the result of the present study. Both SR-LGO and H-LGO include nitrogen compounds while there is a difference in nitrogen contents between SR-LGO and H-LGO. Therefore, this cannot be concluded.

When CS-40 was added to H-LGO, CS-40 was completely decomposed to give H_2S and showed almost the same retarding effect as H_2S . However, in the case of SR-LGO, all the sulfur is not converted to H_2S and the remaining sulfur compounds, which were difficult to remove might have still been adsorbed on the surface. In HDS of SR-LGO, the concentration of H_2S formed changes in the range from 4.0% to 6.9% depending on the conversion of sulfur compounds. Therefore since such strongly adsorbed sulfur compounds, which was difficult to remove and which gradually produced H_2S directly retarded HDS of other sulfur compounds, and the retarding effect on HDS of SR-LGO seemed to be larger.

From the point of view of H_2S partial pressure needed to maintain appropriate sulfidation state and activity, it was shown that such state and activity could be maintained even in HDS of gas oil with low sulfur concentrations like H-LGO since the reactivities of DBTs in HDS of H-LGO are highest among the three oils, SR-LGO, H-LGO, and CS-40 + H-LGO. Therefore, the excess amount of H_2S formed still retards HDS under the condition presented here rather than by maintaining the appropriate sulfidation state and activity. We have already reported in our studies using ^{35}S that the catalyst sufficiently sulfided is not subject immediately to reduction even under H_2 pressure, and that after H_2 treatment for several hours, deactivation in HDS is not observed^(19),20). From these facts, it is likely that the activity of HDS is maintained when gas oil with sulfur content higher than 0.05 wt% is used. However, when gas oil with sulfur contents lower than 0.05 wt% is used, further investigation is needed.

4. Conclusions

HDS of DBT, 4-MDBT, and 4,6-DMDBT included

in hydrotreated light gas oil (H-LGO) was carried out using sulfided Co-Mo/ Al_2O_3 . The ratio between the HDS rate constants of DBTs in H-LGO was substantially larger than that between the comparable constants in straight-run LGO (SR-LGO). Activation energies of HDS of DBTs increased in the order $DBT < 4\text{-MDBT} < 4,6\text{-DMDBT}$, while the differences between the values of activation energy were larger for H-LGO HDS than for SR-LGO HDS. These results were attributed to the amount of H_2S formed in HDS of gas oils. In HDS of H-LGO, the retarding effect of H_2S on HDS decreased in the order $DBT > 4\text{-MDBT}$, while the HDS of 4,6-DMDBT was hardly retarded. These results could be explained by assuming a competitive adsorption between DBTs and H_2S .

Acknowledgments

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要 旨

軽油の深度水素化脱硫反応（第2報）水素化処理軽油に含まれるジベンゾチオフェン類の水素化脱硫反応に及ぼす硫化水素の影響

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硫化した Co-Mo/Al₂O₃ 触媒を用いて, 硫黄含有量が 0.168 wt% 以下の水素化処理軽油に含まれるジベンゾチオフェン (DBT), 4-メチルジベンゾチオフェン (4-MDBT) および 4,6-ジメチルジベンゾチオフェン (4,6-DMDBT) の水素化脱硫反応を検討した。反応は固定床流通式高圧反応装置を用いて, 反応温度 290~370℃, LHSV 2~10 h⁻¹, Gas/Oil 比 125 N/l の条件で行った。これらの化合物の反応は擬一次反応として整理した。水素化処理軽油中の DBT 類の脱硫反応速度比は直留軽油中の DBT 類の反応速度比よりもかなり大きな値となった。DBT 類の水素化脱硫反応の活性化エネルギーは 4,6-DMDBT >

4-MDBT > DBT の順に低下したが, 活性化エネルギーの値の差は直留軽油よりも処理軽油に対して大きかった。これは, 処理軽油の HDS で生成する H₂S の量が直留軽油の HDS から生成する H₂S に比べて少ないことによると考えられる。そこで, H₂S の発生源としてポリスルフィドを軽油に加えて, H₂S の阻害効果を検討した。H₂S による阻害効果は DBT > 4-MDBT の順に減少し, 4,6-DMDBT については阻害効果は認められなかった。これらの結果は, DBT 類と H₂S との競争吸着を仮定することで説明できた。

Keywords

Hydrodesulfurization, Gas oil, Alkyldibenzothiophenes, Hydrogen sulfide, Cobalt molybdenum catalyst, Alumina