Study of Hydrodesulfurization by the Use of ³⁵S-Labeled Dibenzothiophene. 2. Behavior of Sulfur in HDS, HDO, and HDN on Sulfided Mo/Al₂O₃ Catalyst

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To investigate the behavior of sulfur during the hydrodesulfurization (HDS), ${}^{35}S$ -labeled dibenzothiophene ([${}^{35}S$]DBT) was reacted on a sulfided Mo/Al₂O₃. It was found that ${}^{35}S$ in [${}^{35}S$]DBT was accommodated on the catalyst and the concentration of ${}^{35}S$ on the catalyst always reached a steady state under fixed reaction conditions. ${}^{35}S$ accommodated on the catalyst cannot be removed without the incorporation of sulfur from HDS of sulfur compounds such as DBT, benzothiophene, thiophene, and thiophenol. The removal rate of ${}^{35}S$ from the catalyst depended upon the rate of HDS of these compounds, that is, the amount of sulfur incorporated into the catalyst. It was suggested that H₂S is formed from some portion of sulfur on the surface of the catalyst other than from that in the sulfur compounds. When hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) reactions were carried out on the catalyst containing ${}^{35}S$, some portion of ${}^{35}S$ could be replaced by oxygen atoms and released as [${}^{35}S$]H₂S; in contrast to this, ${}^{35}S$ was hardly replaced by N atoms.

Introduction

Although a number of attempts have been made to elucidate the mechanism of hydrodesulfurization (HDS),1-8 there are few examples which enable us to determine the behavior of sulfur in desulfurization catalyst. Recently, some researchers used ³⁵S as a tracer of HDS to dissolve this problem.⁹⁻¹⁴ However, they could not determine the behavior of sulfur on sulfided catalyst under the operation condition of HDS reaction because ³⁵S was not used under the operation condition of HDS. In the preceding paper in this issue, we reported the first example of HDS of ³⁵S-labeled DBT on sulfide Mo/Al₂O₃ under the operating conditions of HDS, which has achieved the determination of labile sulfur on the catalyst.¹⁵ It was found that the amount of labile sulfur on sulfided Mo/Al₂O₃ increases with an increase in temperature and the initial concentration of DBT. Furthermore, we found that all the Mo atoms on the catalyst existed as $MoS_{1.92}$. However, it was not yet clear whether sulfur on the catalyst can be released by the adsorption of DBT or by the incorporation of sulfur of DBT.

Regarding the adsorption of molecules onto Mo/Al₂O₃ catalysts, aromatics and unsaturated hydrocarbons could be strongly adsorbed on the catalyst to inhibit the reaction. We have already reported that aromatics retarded HDS of DBT.¹⁶ It has been reported that sulfur, oxygen, and nitrogen compounds can adsorb more strongly on the catalyst than can hydrocarbons in hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO).^{17,18} In the course of our study, we are interested in the reactivities of sulfided catalysts with aromatic compounds containing nitrogen and oxygen as well as sulfur compounds. In this paper, we have investigated the hydrotreating of dibenzothiophene (DBT), benzothiophene (BT), thiophene (T), thiophenol (TP), dibenzofuran (DBF), carbazole (CBL), and quinoline (QNL) on ³⁵S-sulfided Mo/Al₂O₃ by tracing the changes in the radioactivity of 35S. We expected to have more information concerning the behavior of sulfur on a sulfided molybdenum catalyst. When these compounds containing heteroatoms are hydrogenolyzed on the sulfided catalyst, the heteroatoms will be incorporated into the catalyst, and as a result, 35S may be released as $[^{35}S]H_2S$. If ^{35}S on the catalyst cannot be released with the introduction of the compound containing heteroatoms, the effect

of their adsorption on the catalyst may be estimated based on the behavior of the sulfur remaining on the catalyst.

Experimental Section

Materials. Benzothiophene, thiophene, thiophenol, dibenzofuran, carbazole quinoline, and Decalin were obtained from Kishida Co. Ltd. [³²S]DBT was synthesized according to the method reported by Gilmon.¹⁹ ³⁵S-labeled dibenzothiophene was obtained from the process in previous paper.¹⁵

 Mo/Al_2O_3 catalyst containing 12.5 wt % MoO_3 was prepared by conventional impregnation technique with the use of ammonium heptamolybdate. Further details on the catalyst were given in the previous paper.¹⁵ Before the reaction, the catalyst was presulfided with 5% H_2S/H_2 gas mixture by heating to 200 °C at a rate of 5 °C/min and then to 400 °C at a rate of 2 °C/min, and maintained at 400 °C for 3 h.

Apparatus and Procedure. Details of the apparatus were also described in ref 15. In short, the reactions were carried out by a fixed-bed flow reactor under the conditions of 50 kg/cm², 360 °C and WHSV 28 h⁻¹. Products were analyzed by a gas chromatography with FID detector. The radioactivities of [³⁵S]-H₂S in gas and [³⁵S]DBT in liquid products were measured by a liquid scintillation counter.

Two typical operation procedures were as follows: Operation procedure 1: (a) A Decalin solution of 1 wt % [³²S]DBT was pumped into the reactor until the conversion of DBT became constant (about 3 h). (b) After that, a Decalin solution of 1 wt % [³⁵S]DBT was substituted for that of 1 wt % [³²S]DBT. The reaction with [³⁵S]DBT was performed until the amount of [³⁵S]H₂S released from the exit of the reactor became constant. (c) The reactant solution was then substituted again with a Decalin solution of 1 wt % [³²S]DBT and was reacted for 4–5 h. Operation procedure 2: Operation steps (a) and (b) in this procedure were same as in operation procedure 1. (c) The reactant solution of [³⁵S]DBT was replaced by Decalin. The reaction was continued for ca. 4 h. (d) After that, the Decalin solution of 1 wt % [³²S]-DBT or other heteroatom compound was substituted for Decalin and was reacted for about 4–5 h.

Results

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(a) HDS Reaction. When a solution of 1 wt % DBT was reacted according to the operation procedure 1 at 360 °C and 50 kg/cm²,

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Figure 1. Change in radioactivities of unreacted [³⁵S]DBT and formed [³⁵S]H₂S with reaction time. Reaction conditions: sulfided Mo/Al₂O₃, 360 °C, 50 kg/cm², DBT 1 wt %.

the changes in radioactivities of unreacted [35S]DBT and produced $[^{35}S]H_2S$ with the reaction time is shown in Figure 1. It is observed that the radioactivities of unreacted [35S]DBT in the liquid product increased and approached a steady state immediately. In the case of produced [35S]H₂S, however, about 120 min was needed to approach a steady state in the radioactivities of produced [35S]- H_2S . When the solution of [35S]DBT was replaced with that of [³²S]DBT at ca. 410 min, the radioactivities of unreacted [³⁵S]-DBT also decreased immediately from the steady state to the normal state. But the time delay for produced $[^{35}S]H_2S$ from its steady state to the normal state was about 120 min. Moreover, when the length of the catalytic bed was changed from 7 to 3 cm, the same HDS reactions were carried out at 360 °C and 50 kg/ cm², no effect on the time delay for [³⁵S]H₂S elution was found. It indicated that the time delay did not correspond to the adsorption/desorption of H₂S along the bed. As mentioned in the previous paper,¹⁵ these results indicate that the sulfur in DBT is not directly released as hydrogen sulfide but accommodates on the catalyst, and the changes in radioactivities of formed [³⁵S]- H_2S during the decreasing period can be also revealed as a exponential function for time.

Instead of the replacement of the $[^{35}S]DBT$ solution to the [³²S]DBT solution, the [³⁵S]DBT solution was replaced by Decalin solvent (operation procedure 2). The change in radioactivities of formed $[^{35}S]H_2S$ with the reaction time is also shown in Figure 1. It is observed that a portion of ³⁵S, which is represented by the shaded area A in Figure 1, remained on the catalyst when Decalin solvent was substituted for the reactant solution of [35S]-DBT. Even though when the catalyst was reduced in an atmosphere of hydrogen for ca. 3 h, $[^{35}S]H_2S$ was hardly produced. This indicates that the sulfur accommodated on the catalyst was not eluted without the supply of sulfur by HDS of DBT. However, when the reactant solution was replaced with [32S]DBT at ca. 590 min, this portion of ³⁵S can be released again as [³⁵S]H₂S as shown in Figure 1. Almost all ³⁵S on the catalyst could be replaced by ³²S derived from HDS of [³²S]DBT. This can be verified by a fact that the shaded area B is approximately equal to the shaded area A as shown in Table 2.

To survey the effects of sulfur compounds on the substitution rate of sulfur on the catalyst, a Decalin solution of 0.73 wt % benzothiophene containing the same molar concentration of sulfur as that of DBT was used in step d of operation procedure 2. The change in radioactivities of formed $[^{35}S]H_2S$ with reaction time is shown in Figure 2. It can be observed that the formation curve of $[^{35}S]H_2S$ is the same as the case of $[^{32}S]DBT$, until operation step c. But during operation step d, namely, when the reactant solution changed from Decalin to the Decalin solution of benzothiophene, the $[^{35}S]H_2S$ formation rate, i.e., the rate for which ^{35}S on the catalyst was replaced by ^{32}S in benzothiophene, was more rapid than that in the case of $[^{32}S]DBT$. This could be attributed as the increase of ^{32}S incorporated from benzothiophene into the catalyst since HDS rate of benzothiophene was more rapid (conversion = 100%) than that of DBT (conversion = 59.3%; see Table 1).

When a Decalin solution of 0.46 wt % thiophene containing same sulfur molar concentration as the solution of DBT was used to conduct the same reaction, the same formation curve of $[^{35}S]$ - H_2S as the case of benzothiophene was observed (see Figure 3). This could be attributed as that the amount of sulfur converted from thiophene was same as that from benzothiophene under the present reaction conditions (see Table 1). This is also consistent with the conclusion postulated in the previous paper,¹⁵ where the replacement rate between sulfur on the catalyst and one in sulfurcontaining compounds depended upon the amount of sulfur incorporated into the catalyst. At the same time, these results also indicate that the replacement rate of sulfur is independent of kinds of sulfur compounds.

To further investigate the effects of the rate of sulfur incorporation on the removal rate of sulfur, a Decalin solution of 1 wt % thiophene containing about twice as much sulfur as that of 1 wt % DBT was used in operation step d. As expecting, the removal rate of sulfur was much more rapid as shown in Figure 3. Since the conversion of thiophene was yet 100% (see Table 1), the amount of sulfur incorporated into the catalyst is about three times as much as that in the case of 1 wt % DBT. In addition, when a Decalin solution of 1 wt % thiophenol, containing twice as much sulfur as that of 1 wt % DBT, was used, a formation curve of [35S]H₂S similar to the case of 1 wt % thiophene was obtained, because the conversion of thiophenol was also 100% and the rate of ³²S incorporation was similar as that of 1 wt % thiophene (see Table 1). This further indicates that the removal rate of sulfur is independent of the kinds of sulfur compounds and depends only upon the rate of sulfur incorporated into the catalyst.

Values of the areas representing the amount of sulfur released during the various operation steps shown in Figures 1–3 are listed in Table 2. Since these areas were all approximately similar, most of the 35 S on the catalyst which was incorporated into the catalyst during operation step b was replaced by 32 S during operation step d, although the replacement rates of sulfur were different from each other.

(b) Effect of Oxygen Compound. Figure 4 shows the changes in radioactivities of formed [35S]H2S when a solution of dibenzofuran (DBF) was used in the operation step d in the operation procedure 2. As reported by Lavopa et al.,²⁶ the major products were BP and CHB. It can be observed that the formation curve of $[^{35}S]H_2S$ is very different from those curves in the case of sulfur compounds. During operation step d, only a small portion of ³⁵S on the catalyst was eluted and released as [³⁵S]H₂S during the HDO reaction of DBF. This may be due to a low conversion of DBF (7.8%). To certify whether ³⁵S, which was not eluted during the HDO reaction of DBF, was still present on the catalyst, another operation step (e) was added. After HDO reaction of DBF was conducted for ca. 4 h, the solution of ³²S-DBT was substituted for that of DBF and then reacted for ca. 4 h. As shown in Figure 4, [35S]H₂S was produced again, and a sum of area F and area G, which represented respectively the radioactivities of [35S]H₂S released during operation steps d and e, is approximately equal to the area A (see Table 2). These indicate that the portion of ³⁵S remaining on the catalyst could be eluted and released as [35S]H₂S if ³²S was supplied.

(c) Effect of Nitrogen Compounds. When a Decalin solution of a nonbasic nitrogen-containing compound (carbazole) was used in the operation step d in the operation procedure 2, it can be observed that $[^{35}S]H_2S$ was scarcely detected during operation step d (see Figure 5). This is because the conversion of carbazole is nearly zero. As reported by Behinde, ¹⁸ when a Decalin solution of quinoline was used in the operation step d in operation procedure 2, quinoline was hydrogenated rapidly to produce 1,2,3,4-tetrahydroquinoline and 5,6,7,8-tetrahydroquinoline but HDN of quinoline to give hydrocarbons occurred hardly (see Table 2).

	concenti	ration in decalin		rate constant, ×10 ⁶ L/ s g of catalyst		
compounds	wt%	×10 ² , mol/L	conversion, %			
dibenzothiophene (DBT)	0.998	4.77	59.3	7.98		
benzothiophene (BP)	0.728	4.77	100.0			
thiophene (T)	0.457	4.77	100.0			
• · · ·	1.00	10.35	100.0			
thiophenol (TP)	1.20	9.54	100.0			
dibenzofuran (DBF)	0.913	4.77	7.34	0.674		
carbazole (CRL)	0.908	4.77	0.0	0.0		
quinoline (QNL)	0.701	4.78	90.0 ^b	20.5		

^a Products were cyclohexylbenzene and biphenyl. ^b Products were mainly 1,2,3,4-tetrahydroquinoline and 3,4,5,6-tetrahydroquinoline.

TABLE 2: Radioactivities of [³⁵S]H₂S Produced from ³⁵S Remaining on the Catalyst during the Operation Step d in Various Hydrotreating Reactions Carried out Following the Operation Procedure 2

	reaction										
-			HDS			HDO					
-	DBT	BT	Т	Т	TP	DI	BF	CBL	C		
total radioactivities of formed [³⁵ S]H ₂ S, × 10 ⁻³ dpm	1.92	2.11	2.07	1.95	1.92	0.500	1.50ª	0	0	1.09ª	•

reference area B (Figure 1) C (Figure 2) D (Figure 3) E (Figure 3) F (Figure 4) G (Figure 4) (Figure 5) (Figure 5) H (Figure 5) ^a Radioactivities of formed [³⁵S]H₂S during another added operation steps e (see text). ^b Area A in Figue 1 is 1.92 × 10³ dpm.



Figure 2. Change in radioactivities of formed $[^{35}S]H_2S$ with reaction time. Reaction conditions: sulfided Mo/Al₂O₃, 360 °C, 50 kg/cm², BT 0.73 wt %.



Figure 3. Change in radioactivities of formed $[^{35}S]H_2S$ with reaction time. Reaction conditions: sulfided Mo/Al₂O₃, 360 °C, 50 kg/cm², T 0.46 wt % and 1 wt %.

At the same time, radioactivities of $[^{35}S]H_2S$ could hardly be detected (see Figure 5). After HDN reaction of quinoline was conducted for ca. 4 h, the operation step e was also added, namely, the solution of $[^{32}S]DBT$ was substituted for that of quinoline



Figure 4. Change in radioactivities of formed $[^{35}S]H_2S$ with reaction time. Reaction conditions: sulfided Mo/Al₂O₃, 360 °C, 50 kg/cm², DBF 0.91 wt %.



Figure 5. change in radioactivities of formed $[^{35}S]H_2S$ with reaction time. Reaction conditions: sulfided Mo/Al₂O₃, 360 °C, 50 kg/cm², CBL 0.91 wt %, QNL 0.70 wt %.

and reacted for ca. 4 h. Although $[^{35}S]H_2S$ was produced again as shown in Figure 5, the total radioactivities of released $[^{35}S]$ - H_2S (area H in Figure 5) were smaller than total radioactivities of ^{35}S remained on the catalyst (area A). This may be due to the fact that the catalyst was poisoned by quinoline since the reactivity of DBT HDS decreased from 59.3% to 33.3%. This makes it possible for a portion of ^{35}S to be still held on the catalyst. Because the HDS rate decreased, the amount of labile sulfur on the catalyst decreased.¹⁵

SCHEME 1: Mechanism of Hydrodesulfurization for DBT on Sulfided Mo/Al₂O₃



Discussion

As shown in Figure 1, H₂S was not formed in the absence of DBT while the incorporation of sulfur in DBT onto the catalyst generated H_2S . The release of H_2S could form anion vacancies on the catalyst. It seems that the catalyst tends to keep a constant amount of anion vacancies under each reaction condition. Although we cannot estimate the amount of anion vacancies, this may be related to the amount of labile sulfur. To interpret why there is the time delay for $[^{35}S]H_2S$ to achieve a steady state of radioactivities, why the sulfur in the DBT is not directly released as H_2S , and why H_2S is formed from the sulfur on the catalyst, the tentative reaction Scheme 1 was considered to account for these phenomena. According to this scheme, the reaction would proceed with the following steps: (a) The sulfur compound adsorbs on an anion vacancy on the catalyst. (b) After the hydrogenolysis of C-S bonds, the hydrocarbon species are released into the gaseous phase, whereas the sulfur atom remained on the catalyst. Most of hydrogen may originate from the S-H groups. (c) The sulfur remaining on the catalyst is hydrogenated and forms a new S-H group. (d) At the same time, the release of hydrogen sulfide generates a new anion vacancy. Therefore, a shift of active sites on the catalyst surface would occur.

For this mechanism of HDS, only after the sulfur in DBT was incorporated into the catalyst was the sulfur on the catalyst surface released as H_2S . When an anion vacancy was occupied by sulfur removed from DBT, a new anion vacancy appeared on the catalyst surface. At that time, the probability of sulfur being released as H_2S for all labile sulfur may be same. Therefore, after [^{32}S]-DBT was substituted for [^{35}S]DBT in operation procedure 1 (see Figure 1), the decreasing curve of formed [^{35}S]H₂S can be revealed as an exponential function for time. In contrast to this, after [^{35}S]DBT was substituted for [^{32}S]DBT, the increasing curve of formed [^{35}S]H₂S can also be revealed as a logarithmic function for time. According to this mechanism, the product of HDS, biphenyl, was not delayed but eluted immediately as the same manner as DBT. It was consistent with the results in previous paper.¹⁵

When the HDO reaction of DBF was carried out on the catalyst labeled by ${}^{35}S$, only a small portion of ${}^{35}S$ was replaced with oxygen atoms and released as $[{}^{35}S]H_2S$ (see Figure 4) because of the low conversion of HDO of DBF. In addition, for the case of HDN of quinoline, although the hydrogenation rate of quinoline was very quick, the HDN reaction of quinoline hardly occurred (see Table 2). Thus, ${}^{35}S$ was scarcely replaced by nitrogen atoms (see Figure 5). On the contrary, for the HDS reaction of sulfur compounds such as thiophene which can be desulfurized more easily than DBT, ${}^{35}S$ remaining on the catalyst was replaced at a more rapid rate than that in the case of DBT. These results indicated that ${}^{35}S$ remaining on the catalyst could not be removed and released as $[{}^{35}S]H_2S$ until HDN, HDO, or HDS reactions have occurred. The hydrogenation reaction could not cause the

SCHEME 2: Structure of MoS₂ on Alumina



formation of H_2S . And the rate of $[{}^{35}S]H_2S$ formation will increase with the increase of rate of heteroatoms incorporated into the catalyst. The formation reaction of H_2S from the catalyst may not be a rate-determining step for HDS reaction but a fast reaction. This is consistent with the result that the formation rate of H_2S from the catalyst depended only upon the rate of sulfur incorporation into the catalyst and the kind of sulfur compound was irrelevant.

Concluding Remarks

In the previous paper,¹⁵ we concluded that the amount of labile sulfur on the sulfided catalyst changes depending on the reaction conditions. In the present paper, the structure of the active species shown in Scheme 1 was used in order to explain the mechanism of HDS simply. If the structure of molybdenum sulfide on alumina is be that shown in Scheme 1, all sulfur may be accessible. However, all sulfurs are not accessible practically. This represents that the structure of molybdenum sulfide on alumina is not uniform. Some researchers reported that MoS₂ is present as single-slab structures on alumina (structure A in Scheme 2).²⁹⁻³¹ Then, there would be some interactions between Mo and alumina. This would cause the difference among the environment of each sulfur as shown in structure A. Thus, the reactivity of each sulfur would be different from each other. In the present time, we can deny neither the structure A nor the structure B. Both structures may be present in the actual catalyst. This will be consistent with the fact that the structure of molybdenum species is not uniform.

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