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Elucidation of Behavior of Sulfur on Sulfided Co–Mo/Al$_2$O$_3$ Catalyst Using a ^{35}S Radioisotope Pulse Tracer Method

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A ^{35}S radioisotope pulse tracer method was used to elucidate the behavior of sulfur on a sulfided Co–Mo/Al$_2$O$_3$ under the practical hydrodesulfurization (HDS) conditions. ^{35}S-labeled H$_2$S (^{35}S–H$_2$S) and dibenzothiophene (^{35}S-DBT) were synthesized. Then, the exchange reactions with ^{35}S–H$_2$S and the HDS reaction of ^{35}S-DBT were carried out at 200–400°C and 10–50 kg/cm^2. By tracing the change in radioactivity of released ^{35}S–H$_2$S, amounts of labile sulfur involved in the reactions and the rate constants of H$_2$S formation from the labile sulfur were determined. The amount of labile sulfur increased with increasing temperature, and the release rate of ^{35}S–H$_2$S increased with increasing the supply rate of sulfur. The sulfur exchange with H$_2$S was very rapid at each temperature. Comparison of the amounts of labile sulfur and the rate constants of sulfur exchange in HDS reactions with those in sulfur exchange with H$_2$S suggests that the transformation between the labile sulfur and the vacancies on the catalyst surface would predominantly proceed through the sulfur exchange with H$_2$S even in the HDS reactions. It was also found that the addition of H$_2$S inhibited the HDS reaction of DBT while it increased the sulfur exchange rate.

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1. INTRODUCTION

Alumina-supported, cobalt-promoted molybdenum sulfide hydrotreating catalysts have been widely used in many refineries and the mechanism of hydrodesulfurization (HDS) has been investigated in many industrial and academic laboratories. The introduction of various physical and chemical characterization techniques such as conventional XPS, HETM, FTIR, TPR, and TPS methods (1–6) resulted in significant progress in the understanding of the surface structures present in Mo-based catalysts supported on alumina. In recent years, Mössbauer emission spectroscopy (MES) (7–9) and extended X-ray fine structure (EXAFS) (10–12) have been used to estimate the fine structure of the catalyst. A CoMoS model proposed by Topsøe *et al.* showed the active phase which consists of small MoS$_2$ particles with Co promoter atoms decorating their edges. The amount of Co in CoMoS could be determined by *in situ* ^{57}Co MES (7, 8) and the hydrodesulfurization activity of thiophene was found to be proportional to the quantity of Co–Mo–S phase. EXAFS study (12) has also indicated that the Mo atom in Co–Mo–S has an MoS$_2$-like structure as suggested in MES studies. However, the precise local structure of Co-promoted sites has been under discussion (13).

In order to obtain a better understanding of these sulfided catalysts, the elucidation of the detailed behavior of sulfur is important. For this purpose, much attention has been focused on an isotope tracer method because it can directly estimate the behavior of sulfur in working catalysts. Recently, a number of sulfur exchange studies using ^{35}S–H$_2$S as a tracer have been reported (14–18). These studies usually showed that more than one type of sulfur bonding existed, as evidenced by different rates and extents of exchange with time and temperature. Dissociative adsorption of H$_2$S and the presence of SH groups on the catalyst surface were implied in these studies. However, these methods could not estimate the behavior of sulfur on working catalysts. Recently, we have directly performed HDS reaction of ^{35}S-labeled dibenzothiophene on sulfided Mo/Al$_2$O$_3$ (19, 20), Co–Mo/Al$_2$O$_3$ (21), and Ni–Mo/Al$_2$O$_3$ (22) catalysts under practical HDS conditions. It was found that a portion of sulfur on the sulfided catalysts was labile sulfur, the amount varying with the reaction conditions. It was also suggested that there was a transformation between labile sulfur and vacancies on the sulfided catalysts (22).

Moreover, when the hydrodesulfurization reactions of thiophene, etc., were performed on a ^{35}S-labeled sulfided Mo/Al$_2$O$_3$, the release rate of ^{35}S–H$_2$S from the catalyst was independent of the kinds of sulfur compounds but dependent upon the amount of ^{32}S incorporated into the catalyst (20). This implies that H$_2$S may play an important role in the transformation process between labile sulfur and the vacancy. In our study, we are interested in the relationship between the structure of catalysts and the amount of labile sulfur and in how H$_2$S is formed from labile sulfur on the catalyst. In this work, a pulse of ^{35}S–H$_2$S was used for the exchange reaction of H$_2$S with a commercial Co–Mo/Al$_2$O$_3$ catalyst. The behavior of labile sulfur was determined by evaluating the release of ^{35}S–H$_2$S from the ^{35}S-labeled catalyst. Furthermore, the catalyst was labeled in a

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hydrodesulfurization reaction of ^{35}S-labeled dibenzothiophene and then various sulfur-containing compounds were introduced to the catalyst. The behavior of sulfur in the hydrodesulfurization reaction was compared with that in sulfur exchange with H_2S to further investigate the formation of H_2S from the catalyst.

2. EXPERIMENTAL

2.1. *Materials*

The commercial dibenzothiophene (^{32}S-DBT), benzothiophene (BT), thiophene (T), and decalin were made available by Kishida Co. Ltd. Hydrogen (99.99%) was supplied by Tohei Chemicals. A series of hydrogen sulfide (^{32}S–H_2S) in hydrogen (^{32}S–H_2S, 0.1–5.0%) was supplied by Takachiho Chemicals. ^{35}S-labeled dibenzothiophene (^{35}S-DBT) was synthesized according to a method reported in a previous paper (21). ^{35}S-labeled hydrogen sulfide (^{35}S–H_2S) was prepared as follows: To obtain ^{35}S-labeled sulfur, a commercially available toluene solution of ^{35}S (total radioactivity: 0.9 mCi, Amersham, Co. Ltd.) was mixed sufficiently with 0.75 g sulfur (^{32}S) and then the toluene in the mixture was removed *in vacuo*. The ^{35}S-labeled sulfur (0.75 g) was charged to an autoclave (500 ml). After being purged with H_2, the autoclave was pressurized with H_2 into 15 kg/cm^2, and heated at 5°C/min and kept at 430°C for about 30 min. Then the autoclave was rapidly cooled to room temperature. The concentration of H_2S in the autoclave was measured with the precipitation of PbS using an aqueous solution of $Pb(CH_3COO)_2$. Then the concentration of ^{35}S–H_2S was diluted with H_2 to that needed for each reaction.

A commercial Co–Mo/Al_2O_3 (MoO_3: 12.3 wt%, CoO: 3.8 wt%) was crushed and screened to 20–80 mesh granules.

2.2. *Apparatus and Procedure*

All reactions were conducted with a pressurized fixed bed flow reactor which was described in Ref. (19). The hydrodesulfurization reactions were carried out under the following conditions: 50 kg/cm^2, 200–280°C, and WHSV 28 h^{-1}. Concentrations of sulfur compounds in decalin were 0.46–1.0 wt%. The sulfur exchange reactions were conducted under the following conditions: 230–400°C, 10–50 kg/cm^2, concentrations of H_2S in H_2 0.05–0.3 vol%, and flow rate of H_2S 80–208 ml/min. After being calcined at 430°C for 20 h in air, the catalyst was presulfided with a 5 vol% H_2S/H_2 gas mixture by heating to 200°C at a rate of 5°C/min and to 400°C at a rate of 2°C/min, and then maintaining at 400°C for 3 h. After presulfidation, the reactor was cooled in the H_2S/H_2 stream to each reaction temperature and pressurized with hydrogen (or a gas of H_2S in H_2). Then the hydrodesulfurization reaction (or a sulfur exchange reaction) was performed. Liquid products in the hydrodesulfurization reaction were analyzed by a gas chromatography with a flame ionization detector (FID). The ^{35}S–H_2S was absorbed by bubbling through a basic scintillation solution. The radioactivities of ^{35}S–H_2S in gas products and ^{35}S-DBT in liquid products were measured by a liquid scintillation counter. The details of the analysis are described elsewhere (19).

Two typical operating procedures were as follows:

Operating procedure 1 (OP1: ^{35}S–H_2S pulse tracer method). (a) A mixed gas of ^{32}S–H_2S and H_2 was introduced to the sulfided catalyst for about 3.5 h. (b) Then the gas was switched to a mixed gas of ^{35}S–H_2S and H_2 for 4–6 h. (c) After the radioactivity of ^{35}S–H_2S collected in an exit of reactor approached a constant value, the catalyst bed was purged by nitrogen for 2 h to remove any adsorbed H_2S. (d) Finally, the gas was switched to the gas of ^{32}S–H_2S in H_2 again in order to measure accurately the amount of ^{35}S exchanged to the catalyst in step (b).

Operating procedure 2 (OP2: ^{35}S-DBT pulse tracer method). (a) A decalin solution of 1 wt% ^{32}S-DBT was fed into the reactor until the conversion of DBT became constant (about 3 h). (b) After this, a decalin solution of 1.0 wt% ^{35}S-DBT was substituted for that of 1.0 wt% ^{32}S-DBT. The reaction with ^{35}S-DBT was performed until the amount of ^{35}S–H_2S formed was constant (about 4 h). (c) The decalin solution of ^{35}S-DBT was replaced by decalin and reacted for about 3 h. (d) After this, a decalin solution of sulfur compound (or a mixed gas of ^{32}S–H_2S and H_2) was introduced and reacted for about 4 h.

For the two operating procedures, the amount of sulfur exchanged in the reaction was calculated from the total radioactivity of ^{35}S–H_2S releasing in the operating step (d) according to the calculation method described elsewhere (19). The recovered radioactivity was within a relative deviation of about 5% for all experiments.

3. RESULTS

3.1. *Labile Sulfur in Sulfur Exchange Reaction with ^{35}S–H_2S*

The sulfur exchange reaction with ^{35}S–H_2S according to operating procedure 1 (OP 1) was monitored by tracing the change in radioactivity of ^{35}S–H_2S. Figure 1 shows the change in radioactivity of ^{35}S–H_2S with reaction time at 260°C and 50 kg/cm^2. After the sulfur exchange with 0.1 vol% ^{32}S–H_2S in hydrogen was carried out for about 3 h, the gas was switched to a 0.1 vol% ^{35}S-labeled H_2S (^{35}S–H_2S) in hydrogen. The radioactivity of ^{35}S–H_2S detected slowly increased and approached a steady state at about 120 min after ^{35}S–H_2S was introduced. It was observed that a portion of ^{35}S, corresponding to the shaded area (A) in Fig. 1, accommodated onto the catalyst through the sulfur exchange. When ^{35}S–H_2S was subsequently

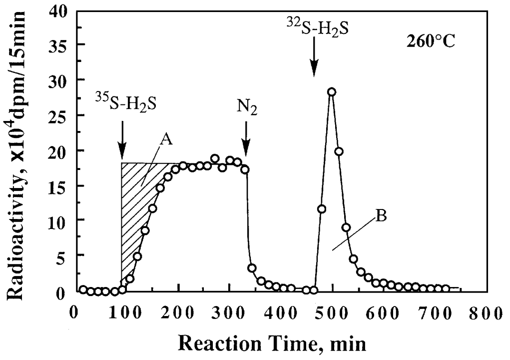


FIG. 1. Change in the radioactivity of released $^{35}S{-}H_2S$ with the reaction time. 50 kg/cm^2; 0.1 vol% H_2S; 80 ml/min.

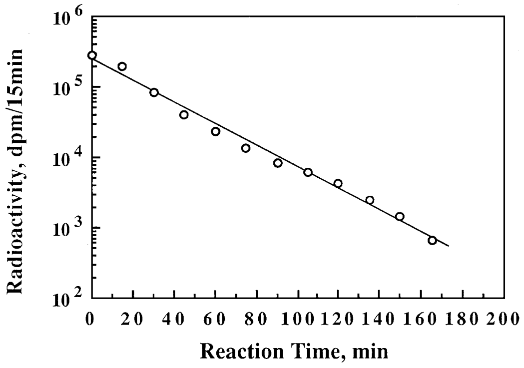


FIG. 2. First-order plot of $^{35}S{-}H_2S$ release rate.

replaced by $^{32}S{-}H_2S$ at 460 min, ^{35}S remaining on the catalyst was exchanged with $^{32}S{-}H_2S$ and released as $^{35}S{-}H_2S$ again in step (d) as shown in Fig. 1 (area B). This portion of ^{35}S represented the total amount of sulfur exchanged on the catalyst under this reaction condition. According to a method reported in Ref. (19), the amount of labile sulfur (S_0) can be calculated from the total radioactivity released in the step (d), i.e., area B. The amount of labile sulfur S_0 and the ratio of S_0 to total sulfur (S_0/S_{Total}), where total sulfur was assumed to be present in the form of MoS_2 and Co_9S_8, are 15.3 mg of sulfur/g of catalyst and 22.1%, respectively (Table 1).

In order to more accurately discuss the process of sulfur exchange, the exchange rate constant was determined according to the following method. A first-order plot of the release rate of $^{35}S{-}H_2S$ in step (d) is drawn in Fig. 2 and a good linear relationship was obtained. This can be revealed as an exponential function over time,

$$\ln y = \ln z - kt \quad \text{or} \quad y = ze^{-kt}, \qquad [1]$$

where y denotes the release rate of $^{35}S{-}H_2S$ at time t (dpm/min); z an initial exchange rate (dpm/min); k the release rate constant of $^{35}S{-}H_2S$, i.e., the rate constant of sulfur exchange (min^{-1}); t the reaction time (min). Thus, the exchange rate constant (k) was determined from the slope of linear relationship and is listed in Table 1. Furthermore, an initial sulfur exchange rate was obtained from a product of labile sulfur (S_0) and the exchange rate constant (k) and is listed in Table 1.

To investigate the effect of pressure, the experiments were performed at 10 and 30 kg/cm^2 with the gas of 0.1 vol% H_2S at 260°C, where partial pressures of H_2S were relevantly 0.01 and 0.03 kg/cm^2. Almost the same results were obtained, as shown in Fig. 3. According to the method mentioned above, the amounts of labile sulfur and exchange rate constants were obtained and they are presented in Table 1. It shows that no significant differences in the amounts of labile sulfur and the release rate constants of $^{35}S{-}H_2S$ were observed for the reactions at 10, 30, and 50 kg/cm^2.

In contrast to the effect of partial pressure of H_2S, when the concentration of H_2S was changed from 0.1 to 0.05 vol% at 260°C and 50 kg/cm^2, the release rate of $^{35}S{-}H_2S$ significantly decreased, as shown in Fig. 4. Similar to the case shown in Fig. 1, the release rate constant was determined and it is presented in Table 1. The release rate constant decreased from 4.02×10^{-2} to 2.43×10^{-2} min^{-1} while the amount of labile sulfur was approximately the same as that in the case of 0.1 vol% H_2S. Therefore, it could be suggested that the sulfur exchange rate depends on the concentration

TABLE 1

Results of the Sulfur Exchange Reactions on the Sulfided $Co{-}Mo/Al_2O_3$

Reaction pressure (kg/cm^2):	50	50	50	50	30	10	50	50	30	50	50	30
Reaction temperature (°C):	230	260	260	260	260	260	280	300	300	400	400	400
Flow rate of gas (ml/min):	80	80	80	208	80	80	80	80	80	80	208	80
Concentration of H_2S (vol%):	0.1	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Partial pressure of H_2S (kg/cm^2):	0.05	0.03	0.05	0.05	0.03	0.01	0.05	0.05	0.03	0.05	0.05	0.03
Labile sulfur, S_0 (mg/g.cat.)	10.7	14.6	15.3	14.5	15.5	14.5	19.4	19.7	20.8	30.5	29.4	27.8
S_0/S_{Total}^{a} (%):	15.4	21.1	22.1	20.9	22.4	20.9	28.0	28.4	30.0	44.0	42.4	40.1
Exchange rate constant, k (10^{-2}/min):	4.51	2.43	4.02	8.07	3.82	4.02	3.11	3.12	3.11	2.17	4.05	2.08
Initial exchange rate, $S_0 \times k$ (mg/min · g.cat.):	0.48	0.38	0.62	1.17	0.59	0.58	0.60	0.61	0.65	0.66	1.19	0.58

[a] S_{Total} is defined as the amount of total sulfur when metal sulfides were present as MoS_2 and Co_9S_8.

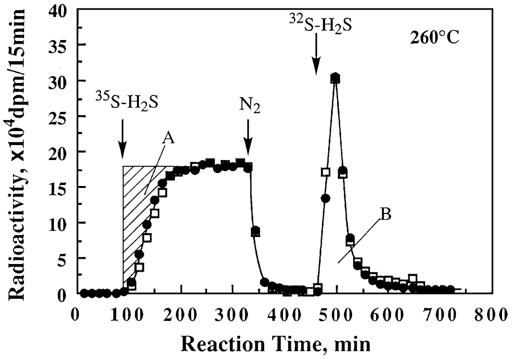


FIG. 3. Effect of the partial pressure of H$_2$S on the sulfur exchange. (□) 30 kg/cm^2 (P_{H_2S}: 0.03 kg/cm^2); 0.1 vol% H$_2$S; 80 ml/min. (●) 10 kg/cm^2 (P_{H_2S}: 0.01 kg/cm^2); 0.1 vol% H$_2$S; 80 ml/min.

of H$_2$S, i.e., the rate of sulfur incorporation to the catalyst, although the amount of labile sulfur remained constant at the same temperature.

In order to investigate the effect of the incorporation rate of sulfur on the release rate of ^{35}S–H$_2$S, the exchange was also performed with different flow rates (80 and 208 ml/min) of gas at 260 and 400°C, respectively. Figure 5 shows the change in radioactivity of ^{35}S–H$_2$S at 400°C and 50 kg/cm^2. Similar to the effect of the concentration of H$_2$S, the release rate of ^{35}S–H$_2$S significantly increased with increasing the flow rate of gas, that is, the incorporation rate of sulfur to the catalyst. Although the amounts of labile sulfur were approximately the same for two cases, the exchange rate constant increased from 2.17×10^{-2} to 4.05×10^{-2} min^{-1} with increasing the incorporation rate of H$_2$S from 80 to 208 ml/min. This further indicates that the rate of sulfur exchange depends only on the rate of sulfur incorporation.

The results in the sulfur exchange reactions at several temperatures are summarized in Table 1. The ratios of the amounts of labile sulfur to total sulfur increased from 15.4 to 44.0% with increasing temperature from 230 to 400°C. Further, the sulfur exchange reactions were very rapid at each temperature and the exchange rate constant depended on the incorporation rate of sulfur at a given temperature.

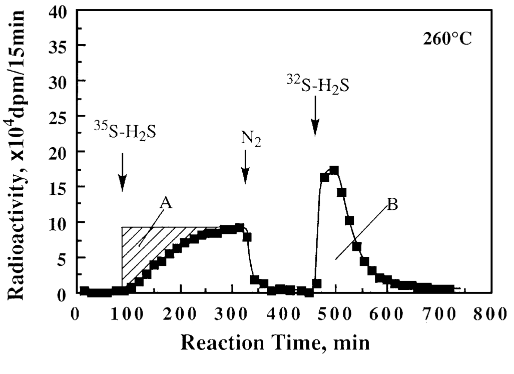


FIG. 4. Effect of the concentration of H$_2$S on the sulfur exchange. 50 kg/cm^2, 0.05 vol% H$_2$S; 80 ml/min.

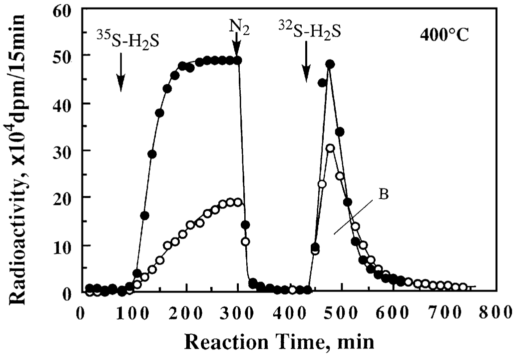


FIG. 5. Effect of the rate of sulfur incorporation on the release rate of ^{35}S–H$_2$S. (○) 50 kg/cm^2; 0.1 vol% H$_2$S; 80 ml/min. (●) 50 kg/cm^2; 0.1 vol% H$_2$S; 208 ml/min.

3.2. *Labile Sulfur in HDS Reactions of Dibenzothiophene, Benzothiophene, and Thiophene*

The hydrodesulfurization reaction of ^{35}S-labeled dibenzothiophene (^{35}S-DBT) was performed according to OP 2. Figure 6 shows the change in radioactivity with reaction time at 260°C, 50 kg/cm^2, and WHSV 28 h^{-1}. Similar to the case in the sulfur exchange reaction with ^{35}S–H$_2$S, the radioactivity of ^{35}S–H$_2$S formed increased and slowly approached a steady state after ^{35}S-DBT was substituted for ^{32}S-DBT. Then, when the ^{35}S-DBT solution was replaced by decalin, the radioactivity of formed ^{35}S–H$_2$S decreased immediately. Even though the catalyst was reduced in an atmosphere of hydrogen over ca. 2.5 h, ^{35}S–H$_2$S was scarcely produced. This indicated that the sulfur accommodated on the catalyst could not be eluted without a supply of sulfur derived from hydrodesulfurization of DBT. However, when ^{32}S-DBT solution was introduced at 510 min, this portion of ^{35}S was released as ^{35}S–H$_2$S again (Fig. 6, Area C). This portion of ^{35}S was approximately equal to Area (A-B), denoted total amount of labile sulfur on the catalyst under this reaction condition. According to the method reported in Ref. (19), the amount of labile sulfur can be calculated from the total radioactivity released in step (d), i.e., Area C.

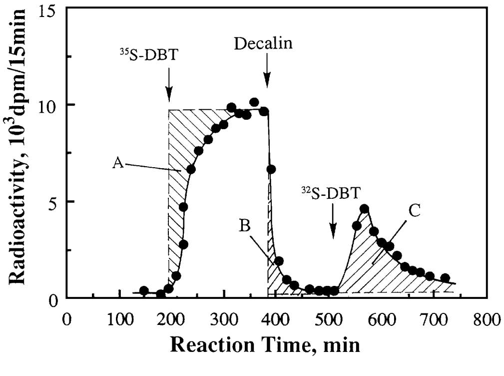


FIG. 6. Changes in the radioactivity of formed ^{35}S–H$_2$S with reaction time. DBT (1.0 wt%, 260°C).

TABLE 2

Results in the HDS Reactions and the Exchange Reactions on the Sulfided Co–Mo/Al_2O_3[a]

Temperature (°C):	240	260	280	200	260	260	260	260
Reactant:		DBT[b]			T[c]	BT[d]	DBT + H_2S[e]	H_2S[f]
Conversion (%):	29.5	62.3	90.9	30.9	100	100	21.1	—
Concentration of formed H_2S (vol%):	0.040	0.084	0.125	0.042	0.137	0.137	0.029	0.300
Rate constant, k (10^{-2}/min):	1.90	3.20	3.72	2.31	5.02	4.95	8.21	8.14
Labile sulfur, S_0 (mg/g.cat.):	13.1	15.6	21.8	10.4	16.1	16.5	15.8	16.1
S_0/S_{Total}[g] (%):	18.9	22.5	31.4	15.0	23.2	23.8	22.8	23.2
$S_0 \times k$ (mg/min · g.cat.):	0.249	0.499	0.811	0.240	0.808	0.817	1.30	—
r_{HDS} (mg/min · g.cat.):	0.240	0.508	0.741	0.252	0.815	0.815	0.391	—

[a] The catalyst was labeled by ^{35}S in the HDS reaction of ^{35}S-DBT.

[b] Dibenzothiophene.

[c] Thiophene.

[d] Benzothiophene.

[e] Dibenzothiophene + 0.3 vol% H_2S.

[f] 0.3 vol% H_2S.

[g] For notation see Table 1.

Similar to the case of the sulfur exchange reaction, a first-order plot of the release rate of ^{35}S–H_2S could be drawn and a good linear relationship was obtained. The exchange rate constant (k) was also determined from the slope and it is presented in Table 2. When ^{35}S-DBT tracer experiments were carried out at 240 and 280°C, similar results were obtained (Table 2).

To survey the effect of sulfur compounds on the release rate of ^{35}S–H_2S, a decalin solution of 0.73 wt% BT containing the same molar concentration of sulfur as that of DBT was used in step (d). The change in radioactivity of formed ^{35}S–H_2S with the reaction time is shown in Fig. 7. When the reactant solution was changed from decalin to the decalin solution of BT, the formation rate of ^{35}S–H_2S was more rapid than that in the case of ^{32}S-DBT. Similarly, when a 0.46 wt% T solution having the same sulfur molar concentration as the DBT solution was used, the same formation curve of ^{35}S–H_2S as the case of benzothiophene was observed (Fig. 7).

To further investigate the effect of the rate of sulfur incorporation on the removal rate of sulfur from the catalyst, the HDS reaction of thiophene was carried out on the ^{35}S-labeled catalyst at 200°C. The change in radioactivity of ^{35}S–H_2S formed from the catalyst is also shown in Fig. 7. The conversion of thiophene and the amount of total radioactivity of released ^{35}S–H_2S decreased.

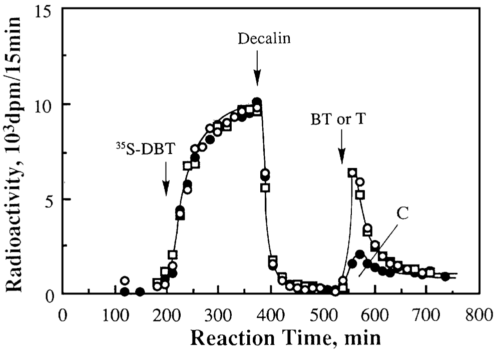


FIG. 7. Effects of sulfur compounds on the release rate of ^{35}S–H_2S in step (d). (○) Thiophene (0.46 wt%, 260°C). (●) Thiophene (0.46 wt%, 200°C). (□) Benzothiophene (0.73 wt%, 260°C).

In a similar manner as the case of DBT, the amounts of labile sulfur and the release rate constants of H_2S in the HDS reactions of T and BT were calculated and are listed in Table 2. All the amounts of labile sulfur were approximately the same in HDS of T, BT, and DBT at 260°C, while the release rate constant in the case of BT (or T) was more than that in the case of DBT. This could be attributed to an increase in the rate of ^{32}S incorporation derived from HDS of benzothiophene (or thiophene) because the HDS rate of benzothiophene or thiophene (conversions = 100%) was much faster than that of DBT (conversion = 62.3%). This indicates that the release rate of H_2S from the catalyst is only dependent upon the rate of sulfur incorporated into the catalyst. Moreover, the release rate of ^{35}S–H_2S in the HDS reaction of thiophene at 200°C was lower than that in the case of DBT at 260°C. This could be also attributed to the lower rate of sulfur incorporation at 200°C because the conversion of thiophene at 200°C (30.9%) is lower than that of DBT at 260°C (62.3%). It is noteworthy that the amount of labile sulfur at 200°C (10.4 mg of sulfur/g of catalyst) is also lower than that at 260°C (16.1 mg of sulfur/g of catalyst). These results indicate that the amounts of labile sulfur mainly depend on temperature while the release rate constants of H_2S increase with increasing the incorporation rate of sulfur.

3.3. Labile Sulfur in Sulfur Exchange Reaction with H_2S and HDS of DBT in the Presence of Added H_2S

After the catalyst was labeled with ^{35}S in the HDS reaction of ^{35}S-DBT at 50 kg/cm^2 and 260°C, a gas of 0.3 vol% ^{32}S–H_2S in H_2 was introduced in step (d). The change in

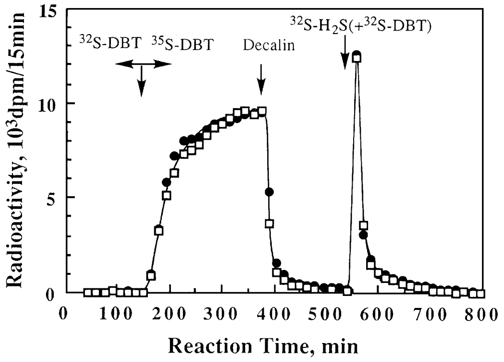


FIG. 8. Release of $^{35}S–H_2S$ in the sulfur exchange reaction with $^{32}S–H_2S$ in step (d) with or without DBT. (●) 0.3 vol% H_2S + 1.0 wt% DBT. (□): 0.3 vol% H_2S.

radioactivity of formed $^{35}S–H_2S$ with the reaction time is shown in Fig. 8. ^{35}S remaining on the catalyst was also exchanged by ^{32}S in $^{32}S–H_2S$ and released as $^{35}S–H_2S$. Although the release rate of $^{35}S–H_2S$ from the catalyst was much faster than that in the case of DBT, the total amount of ^{35}S released was approximately equal to the amount of ^{35}S accommodated on the catalyst in the reaction of ^{35}S-DBT as shown in Table 2. This shows that the whole labile sulfur labeled in the HDS reaction of ^{35}S-DBT can completely be released as $^{35}S–H_2S$ through sulfur exchange with H_2S. In order to investigate HDS of DBT in the presence of added H_2S, the gas of 0.3 vol% H_2S in H_2 and a decalin solution of 1.0 wt% DBT were simultaneously introduced in step (d), and the results are shown in Fig. 8 and Table 2. The hydrodesulfurization of DBT was inhibited by H_2S and the conversion of DBT decreased from 62.3 to 21.1%. Moreover, the release rate constant of $^{35}S–H_2S$ significantly increased from 3.20×10^{-2} to 8.21×10^{-2} min^{-1} although the amount of labile sulfur did not change with the addition of H_2S. The release rate constant of $^{35}S–H_2S$ at 260°C decreased in the order $H_2S + DBT > H_2S > DBT$ (Table 2). This result further indicates that the release rate of $^{35}S–H_2S$ is independent of the kinds of sulfur compounds and only depends on the incorporation rate of sulfur.

4. DISCUSSION

4.1. Amount of Labile Sulfur

Figure 9 shows the relationship between the amount of labile sulfur and temperature in the sulfur exchange reactions with $^{35}S–H_2S$ (□). The ratio of labile sulfur to total sulfur increased with temperature and approached about 44.0% at 400°C. This implies that the labile sulfur on the catalyst is not uniform, i.e., the strengths of sulfur bonds are different from each other. In a temperature-programmed reduction study on a sulfided $Co–Mo/Al_2O_3$ catalyst, Moulijn's group reported that sulfur was mainly reduced in two regions, 27–227°C and 527–1000°C (5, 6). Diez and Jubert also reported a very similar result from the molecular orbital calculation for a sulfided Mo/Al_2O_3 (23). They postulated that first sulfur atoms were removed from corner sites at relatively mild conditions (25–225°C), then edge sulfur atoms were removed (225–325°C), and finally basal plane sulfur atoms were removed (>525°C). Massoth and Zeuthen proposed that there was a difference in the strength of sulfur bonds on a sulfided Mo/Al_2O_3 (24). These results are in good agreement with our results. Thus, it can be considered that the sulfur exchange reaction would be limited to the weakest bonded sulfur atoms at lower temperature (below 400°C). This portion of sulfur might be attributed to that bonded with both Mo and Co atoms because the bond strength of sulfur in Co–S–Mo phase was considered to be the weakest (22). Nørskov *et al.* (25) and Topsøe *et al.* (26) reported that the bond energies of metal sulfide varied as follows: cobalt sulfide > molybdenum sulfide > CoMoS. Taking into account the bond energy, it seems that sulfur in MoS_2 phase adjacent to Co atoms are more labile and are preferably exchanged below 400°C.

4.2. Sulfur Exchange Reaction

Although there are many possible exchange mechanisms on the labile sulfur on the catalyst with H_2S, it is likely that the reaction proceeds through the transformation of SH groups and vacancies; evidence for the presence of SH groups has been provided by a number of studies (27–30). More recently, in an FT-IR study on sulfided Mo-based catalysts, it was postulated that SH groups existed at the edges of MoS_2 and that SH groups and vacancies could interconvert and coexist in close proximity (31, 32). Therefore, a hypothetical release route of $^{35}S–H_2S$ was postulated and is shown in Scheme 1. As mentioned above, it was considered that a portion of sulfur bonded with Co and Mo atoms was more labile and was present as SH groups in H_2 atmosphere below 400°C. When H_2S was formed and subsequently desorbed from the catalyst, an anion vacancy

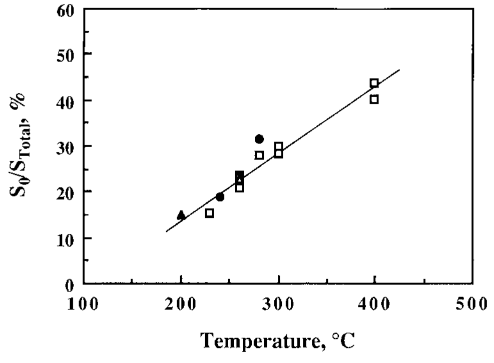
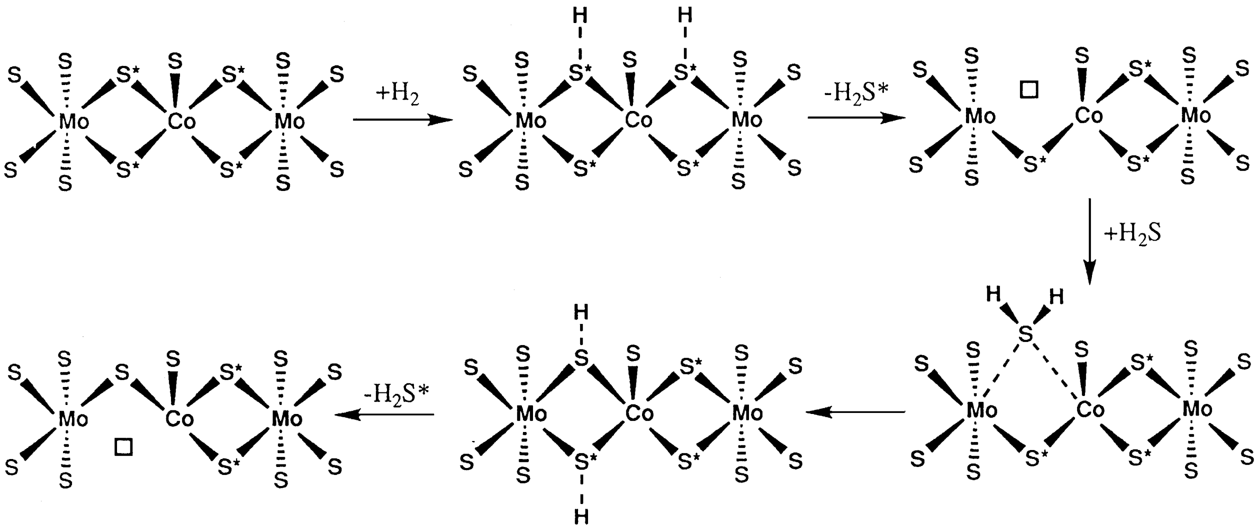


FIG. 9. Effect of temperature on the ratio of labile sulfur to total sulfur. (□) From Table 1. (●) HDS of DBT. (■) HDS of BT. (▲) HDS of T. (○) 0.3% H_2S. (△) HDS of DBT with 0.3% H_2S.



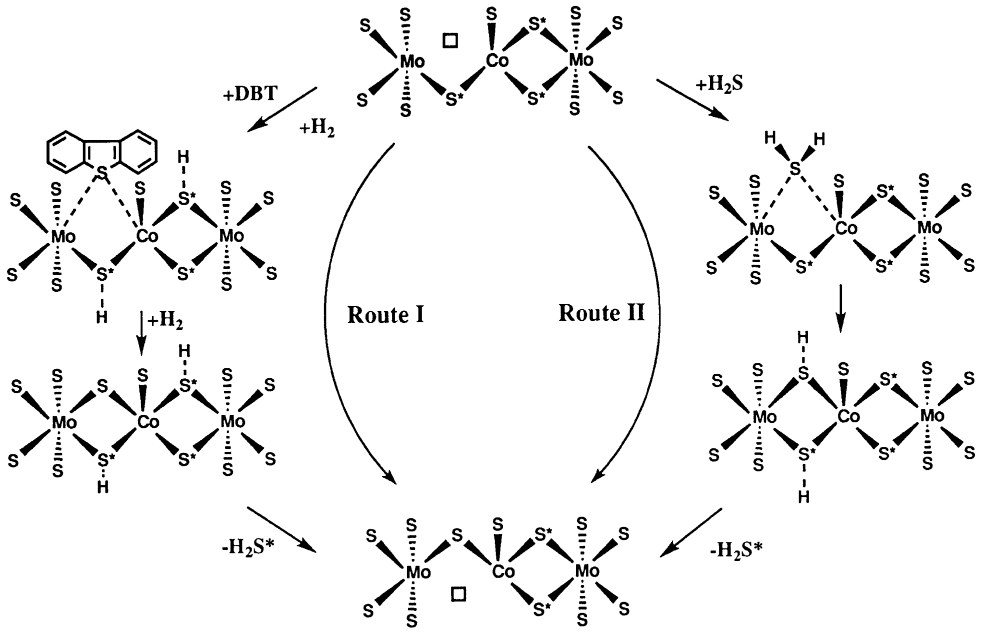
SCHEME 1. Exchange of the labile sulfur on the sulfided Co–Mo/Al_2O_3 with H_2S. S*: ^{35}S; (□) Anion vacancy.

occurred and the adjacent Mo^{4+} would be partially reduced to Mo^{3+} at the same time. On the other hand, if it is considered that reduction of Mo^{4+} to Mo^{3+} is difficult as reported by McGarvey and Kasztelan (33), the amount of active sites generated on the catalyst will actually be finite and this process perhaps may not continue only in H_2 under the present reaction conditions. This was supported indirectly by the fact that ^{35}S–H_2S was hardly detected even though the catalyst was reduced in H_2 in step (c) as shown in Figs. 6 and 7. When H_2S was introduced, the adsorbed H_2S dissociated and formed new SH groups with an adjacent labile sulfur due to high mobility of hydrogen atom. The old anion vacancy disappears and a new anion vacancy will occur after the desorption of H_2S formed from the labile sulfur. It is noteworthy that the extent of sulfur exchange was only about 44.0% of total sulfur at 400°C. It is well known that HDS reactions are generally carried out below 400°C. Therefore, this portion of labile sulfur is considered to be more closely related to the HDS reaction.

It was observed in the present work that under similar reaction conditions, the sulfur exchange rate even in lower rate of sulfur incorporation was higher than that in the HDS rate of DBT; i.e., the initial sulfur exchange rate was 1.17 mg of sulfur/min/g of catalyst at 260°C (Table 1) while the HDS rate of DBT was only 0.499 mg of sulfur/min/g of catalyst (Table 2). Startsev *et al.* reported a similar result where the sulfur exchange rates with H_2S on a series of Ni–Mo (W)/SiO_2 catalysts were one to two orders of magnitude greater than the rates of hydrogenation of butadiene in the HDS reaction of thiophene (34). Massoth and Zeuthen also postulated qualitatively a similar result in the sulfur exchange reaction with H_2S on a sulfided Mo/Al_2O_3 (24). Therefore, it is reasonable to consider that the sulfur exchange rate is very rapid under typical hydrodesulfurization reaction conditions.

4.3. Transformation between Labile Sulfur and Vacancies

In order to compare the behavior of sulfur in the HDS reaction and in sulfur exchange reaction, the amounts of labile sulfur shown in Table 2 are also plotted against temperature in Fig. 9. Essentially, there is no significant difference in the amounts of labile sulfur in the HDS reaction and those in the sulfur exchange reactions at every temperature. These results indicate that labile sulfur in the HDS reaction is equivalent to that in the sulfur exchange with H_2S. Because H_2S is a product of HDS reaction, it is reasonable to assume that there are two routes of sulfur exchange in the HDS reaction. Scheme 2 shows the two routes where labile sulfur present in the form of Co–Mo–S phases desorbs as H_2S from the catalyst and formed a vacancy. In the sulfur exchange with H_2S (Route II in Scheme 2 or in Scheme 1), when one vacancy (active site) is occupied by sulfur in H_2S formed in the HDS reaction, a labile sulfur in another site is released as H_2S to form another new vacancy. In hydrodesulfurization (Route I), when a sulfur compound adsorbs on a vacancy, the C–S bond is subsequently cleaved, and the sulfur remains on the catalyst. Simultaneously, another labile sulfur is released as H_2S and a new active site is formed. In two routes, the migration of vacancies on the catalyst always occurs due to the transformation between labile sulfur and vacancies on the catalyst surface. In the sulfur exchange with ^{34}S–H_2S on a sulfided Mo/Al_2O_3 (24) Massoth and Zeuthen also postulated such the migration of vacancies on the catalyst due to high mobility of labile sulfur. Table 2 shows that the release rate constant becomes greater with an increase in the concentration of H_2S formed in the HDS reaction of sulfur compounds such as dibenzothiophene, benzothiophene, and thiophene at 260°C although the amount of labile sulfur scarcely changes. Moreover, these release rate constants



SCHEME 2. Transformation between labile sulfur and vacancies on the sulfided Co–Mo/Al_2O_3 in HDS. Route I, hydrodesulfurization; route II, sulfur exchange. S*: ^{35}S; (□) Anion vacancy.

are almost the same as those in the sulfur exchange reactions where the concentrations of H_2S used are the same as those in the HDS reaction. Therefore, it can be assumed that a rapid adsorption/desorption of H_2S will always take place in the presence of H_2S under typical hydroprocessing conditions, leading to a rapid interconversion of the active site and labile sulfur. Thus, the vacancies under reaction conditions will not be fixed, but will be mobile.

4.4. Relationship between HDS Rate, Labile Sulfur, and Sulfur Exchange Rate

In order to investigate the relationship between the amount of labile sulfur and the activity of the catalyst, a product of the amount of labile sulfur (S_0) and the rate constant (k) of sulfur exchange in the HDS reaction is plotted against the HDS reaction rate (r_{HDS}) in Fig. 10. A good linear relationship is obtained. This can be explained as follows: Under a given reaction condition, the amount of labile sulfur is correlated with the whole sulfur which can be transformed to the vacancies (active sites), and the rate constant of sulfur exchange is correlated with an average frequency of the transformation of a labile sulfur to an active site. Therefore, a product of labile sulfur and the rate constant of sulfur exchange will be correlated with the HDS rate. When H_2S is added, however, this relationship will become untenable. For instance, the point (●) obtained in HDS of DBT in the presence of 0.3 vol% H_2S deviated from the straight line as shown in Fig. 10. This may be attributed to the fact that the migration rate of vacancies through route II in Scheme 2 will be enhanced due to the addition of H_2S. That is, the amount of active sites related to the HDS reaction will decrease because of the addition of H_2S. Thus, the HDS rate through the route I will be inhibited by adding H_2S. As a result, the product of S_0 and k in this case (●) was greater than the HDS rate of DBT as shown in Fig. 10. This may explain the inhibiting effect of H_2S on the hydrodesulfurization of DBT reported by Zhang *et al.* and Ledoux *et al.* (35, 36).

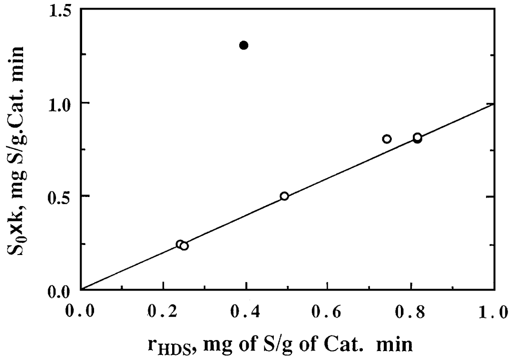


FIG. 10. Relationship within the amount of labile sulfur, the exchange rate constant, and the HDS rate.

5. CONCLUSIONS

The ^{35}S radioisotope tracer method provided a more accurate and efficient approach determining the behavior of sulfur under practical HDS reaction conditions. Both in the sulfur exchange reaction and in the hydrodesulfurization reaction, the amount of labile sulfur on the sulfided catalyst increased with temperature. This indicated that the strength of sulfur bonds was not uniform. Comparing the behavior of sulfur in HDS with that in sulfur exchange with H_2S, it was found that the amounts of labile sulfur were very similar to each other at a given temperature. Moreover, the sulfur exchange rate with H_2S depended on the rate of sulfur incorporation at a given temperature and the exchange rate was very rapid in the sulfur exchange reaction with H_2S at every temperature. Therefore, it was suggested that the sulfur exchange with H_2S was also very rapid in the hydrodesulfurization reactions. Based on these results, it was suggested that the transformation between labile sulfur and vacancies on the catalyst surface would predominantly proceed through the sulfur exchange with H_2S even in the HDS reactions.

On the other hand, the addition of H_2S significantly inhibited the HDS reaction of DBT but increased the sulfur exchange rate. Because the existence of H_2S could cause a decrease in the amount of active sites related to the HDS reaction, the HDS reaction of sulfur compounds was inhibited. In contrast, because the addition of H_2S remarkably increased the average frequency of the transformation of a labile sulfur to an active site, the sulfur exchange rate was enhanced.

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