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Study of Hydrodesulfurization of Dibenzothiophene on Ni–Mo/Al_2O_3, Mo/Al_2O_3, and Ni/Al_2O_3 Catalysts by the Use of Radioisotope ^{35}S Tracer

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The radioisotope tracer method has been used to quantify the behavior of sulfur on sulfided Ni–Mo/Al_2O_3, Mo/Al_2O_3, and Ni/Al_2O_3. The apparent activation energies of HDS reaction for DBT for the three catalysts were 20 ± 1 kcal/mol. The formation rate constants of ^{35}S–H_2S were determined and the amount of labile sulfur on the sulfided catalysts was estimated by tracing the changes in radioactivities of the unreacted ^{35}S–DBT and the formed ^{35}S–H_2S during the HDS reaction of ^{35}S-labeled dibenzothiophene (^{35}S–DBT). It was deduced that ca. 75% of sulfur in the sulfided Mo/Al_2O_3 was related to HDS reaction at infinite rate of HDS. Compared with the amounts of labile sulfur in the sulfided Ni–Mo/Al_2O_3, Mo/Al_2O_3, and Ni/Al_2O_3, it was determined that the amounts of labile sulfur were 1.6, 9.8, and 18.4 mg sulfur/g catalyst at 280°C for the three catalysts, respectively. And it was suggested that the sulfur in the form of NiS on the sulfided Ni–Mo/Al_2O_3 was not labile and that the sulfurs attached to both Mo and Ni atom were more labile and related to HDS. The promotion of Ni for Mo-based catalysts was attributed to the sulfur bonded to both Mo and Ni in the MoS_2 phase being more labile.

1. INTRODUCTION

Mo-based catalysts used in hydrodesulfurization (HDS) of petroleum feedstocks and recently in the deep HDS of light oil have been extensively studied (1–4). However, the catalysts' structures have been ambiguous. Recent studies showed that the sulfides in sulfided Mo-based catalysts were present in the form of MoS_2-like phases (5, 6) and that CoMoS and NiMoS-like phases existed in sulfided Co or Ni–Mo/Al_2O_3 (7, 8). Moreover extensive studies of sulfided Mo-based catalysts have indicated that the HDS activity is related to the presence of sulfur vacancies on the MoS_2 structure (9–11). The addition of Co or Ni leads to a large increase in the activity, which can be attributed to the promoter decorating the edges of MoS_2 with so-called CoMoS or NiMoS type structures (12, 13). However, there are other facts indicating that the formation of a special association between Mo and promoters is not the only reason for synergy. Delmon and co-workers (14–16) have shown that catalysts containing little or no CoMoS or NiMoS phase were quite active and sometimes had a more stable activity. In an attempt to reconcile different results concerning the surface structure of the catalysts based on Mo/Al_2O_3 and the mechanism of HDS, the use of radioisotope ^{35}S as a tracer provided a clue to this exploration because the sulfur played the most important role in the HDS reaction (17–19).

It was well known that dibenzothiophenes are sulfur-containing compounds very difficult to desulfurize even under deep HDS conditions (2, 3). Thus, we have already performed the hydrodesulfurization of ^{35}S-labeled dibenzothiophene on the sulfided Co–Mo/Al_2O_3 and Mo/Al_2O_3, and gained new insight into the mechanism of HDS by monitoring the changes in the radioactivities of the unreacted ^{35}S-DBT and the formed ^{35}S-H_2S (17–19). We found that the sulfur on dibenzothiophene (DBT) was not directly released as hydrogen sulfide but initially accommodated on the catalyst, and that ^{35}S accommodated on the catalyst could not be removed without the incorporation of sulfur from HDS of sulfur compounds. On the basis of quantitative analysis of the rate of ^{35}S-H_2S formation from the catalyst, it was postulated that the sulfur on the sulfided catalyst was labile and the amount of labile sulfur on the catalysts varied with the reaction conditions. This method made it possible to understand more exactly how sulfur in DBT is translated to H_2S, and how sulfur in the sulfided catalyst participates in the actual HDS reaction.

In order to elucidate the role of labile sulfur in the HDS reaction and the promotion effect of Ni on sulfided Ni–Mo/Al_2O_3, the HDS reactions of ^{35}S–DBT were carried out on sulfided Ni–Mo/Al_2O_3, Mo/Al_2O_3, and Ni/Al_2O_3. The generation mechanism of labile sulfur and the relation between the labile sulfur and active sites of HDS were further expounded on the basis of the role of labile

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sulfur in these catalysts. In addition, the results for Co-Mo/Al_2O_3 reported in Ref. (17) were also discussed because of its similarity with Ni-Mo/Al_2O_3.

2. EXPERIMENTAL

2.1. *Materials*

^{32}S-DBT and ^{35}S-labeled dibenzothiophene were synthesized according to the method reported in the previous paper (17). Decalin was a commercial GR grade. Commercial Ni-Mo/Al_2O_3 (MoO_3: 15.3 wt%, NiO: 2.9 wt%, surface area: 197 m^2/g) was used in this work. Mo/Al_2O_3 (MoO_3 16.0 wt%) and Ni/Al_2O_3 (NiO 3.0 wt%) were prepared by the conventional impregnation technique using aqueous solutions of ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) and nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), respectively. After the impregnation, the samples were dried in air at 120°C for 10 h and calcined at 450°C for 24 h.

2.2. *Apparatus and Procedure*

The detail of a used apparatus was described in the previous paper (17). HDS reaction was carried out with a pressurized flow reactor, and the typical reaction conditions were as follows: catalyst 1 g (20–35 mesh), total pressures 50 kg/cm^2, reaction temperature 210–400°C, flow rate of hydrogen 25 liters/h, WHSV 28 h^{-1}, and concentration of DBT in decalin 1.0 wt%. The catalysts were presulfided with a mixture of 5.0 vol% H_2S in H_2 at 400°C for 3 h prior to the reaction. The reactor was cooled in the H_2S/H_2 stream to reaction temperature and pressurized by hydrogen. Then the solution containing DBT was fed into the reactor by a liquid pump (Kyowa Seimitsu KHD-16). The H_2S produced during the reaction was absorbed by bubbling through a commercial basic scintillator solution (Carbosorb, Packard Co. Ltd.). The compositions of liquid product were analyzed by gas chromatography. Radioactivities of the unreacted ^{35}S-DBT in liquid product and the formed $^{35}S-H_2S$ in the absorbed solution were measured by a liquid scintillation counter (LSC-1000, Aloka Co. Ltd.).

Two typical operation procedures were as follows:

Operation procedure 1: (a) A decalin solution of 1 wt% ^{32}S-DBT was pumped into the reactor until the conversion of DBT became constant (about 3 h). (b) After that, decalin solution of 1 wt% ^{35}S-DBT was substituted for that of ^{32}S-DBT. The reaction with ^{35}S-DBT was performed until the formation amount of $^{35}S-H_2S$ became constant (about 4 h). (c) Then, the reactant solution was returned again to the decalin solution of 1 wt% ^{32}S-DBT and reacted for 4–5 h.

Operation procedure 2: Operation steps (a) and (b) in this procedure were the same as those in operation procedure 1. (c) the decalin solution of ^{35}S-DBT was replaced by decalin and reacted for 4 h. (d) After that, decalin solution of 1 wt% ^{35}S-DBT was substituted for decalin and reacted for 4–5 h.

3. RESULTS

3.1. *Mo/Al_2O_3*

A solution of 1 wt% ^{35}S-DBT was reacted on sulfided Mo/Al_2O_3 (MoO_3: 16 wt%) according to operation procedure 1 at 340°C and 50 kg/cm^2. The changes in radioactivities of the unreacted ^{35}S-DBT and the produced $^{35}S-H_2S$ with the reaction time are shown in Fig. 1. After ^{35}S-DBT was substituted for ^{32}S-DBT, the radioactivities of the unreacted ^{35}S-DBT in the liquid product increased and approached a steady state immediately. In the case of the produced $^{35}S-H_2S$, however, about 130 min were needed to approach the steady state in released radioactivities, the same as the case of Mo/Al_2O_3 (MoO_3: 12.5%) described in the previous paper (18). When the solution of ^{35}S-DBT returned to that of ^{32}S-DBT at 380 min, the radioactivities of the unreacted ^{35}S-DBT also decreased immediately from steady state to normal state. But the time delay for the produced $^{35}S-H_2S$ from its steady state to normal state was ca. 130 min as shown in Fig. 1. As reported in the previous paper (18), these results indicate that the sulfur in DBT is not directly released as hydrogen sulfide but accommodates on the catalyst.

Instead of the replacement of the ^{35}S-DBT solution with the ^{32}S-DBT solution, the ^{35}S-DBT solution was replaced by decalin solvent following the operation procedure 2. The change in radioactivities of the produced $^{35}S-H_2S$ with the reaction time was also shown in Fig. 1. When decalin solvent was substituted for the reactant solution of ^{35}S-DBT, a portion of ^{35}S, which is represented

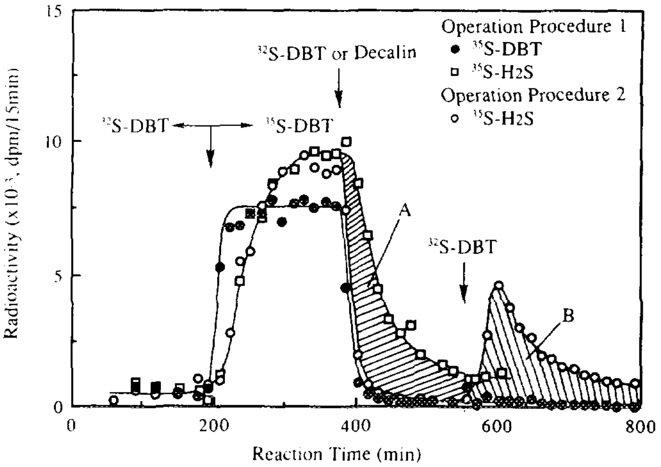

FIG. 1. Changes in radioactivities of unreacted ^{35}S-DBT and formed $^{35}S-H_2S$ with reaction time. (●) Unreacted ^{35}S-DBT; (□) formed $^{35}S-H_2S$ in operation procedure 1. (○) Formed $^{35}S-H_2S$ in operation procedure 2. Mo/Al_2O_3, 340°C, 50 kg/cm^2.

TABLE 1

Kinetic Parameters at Various Hydrodesulfurization Conditions on Ni–Mo/Al_2O_3, Mo/Al_2O_3, and Ni/Al_2O_3

Catalyst	Ni–Mo/Al_2O_3					Mo/Al_2O_3				Ni/Al_2O_3		
Reaction pressure (kg/cm^2)	50	50	50	50	50	50	50	50	50	50	50	50
Reaction temperature (°C)	210	230	240	260	280	300	320	340	360	360	380	400
Concentration of DBT (wt%)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Conversion from GC analysis	12.7	29.1	43.3	64.5	99.5	22.1	45.5	59.9	75.3	10.4	18.6	32.3
Conversion from radioactivity of ^{35}S	11.8	28.9	42.1	63.0	97.1	24.0	46.4	58.0	73.9	10.6	18.8	31.1
Labile sulfur, S_0 (mg/g of cat.)	6.6	11.2	14.7	16.2	18.4	13.1	21.1	25.9	29.8	7.2	9.9	12.8
S_0/S_{Total}[a] (%)	8.2	13.9	18.2	20.1	22.8	18.4	29.6	36.3	41.8	55.8	76.7	99.2
Rate constant of formed H_2S												
k ($\times 10^{-2}$ min^{-1})	1.57	2.13	2.40	3.26	4.40	1.38	1.76	1.83	1.94	1.17	1.54	2.06
$S_0 \times k$ (mg/min.g.cat.)	0.104	0.239	0.352	0.525	0.810	0.181	0.371	0.473	0.577	0.084	0.152	0.263
Reaction rate of DBT (mg/min.g.cat.)	0.104	0.238	0.353	0.526	0.812	0.180	0.371	0.489	0.616	0.085	0.152	0.264

[a] S_{Total} is defined as the amount of total sulfur when metal sulfides in the sulfided catalysts were present as MoS_2 or NiS.

with the shade area (A) in Fig. 1, remained on the catalyst. It shows that even though the catalyst was reduced in the high pressure atmosphere of hydrogen for ca. 4 h, ^{35}S was still retained on the catalyst and ^{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 ^{32}S–DBT at 550 min in Fig. 1, this portion of ^{35}S could be released again as ^{35}S–H_2S. Almost all ^{35}S on the catalyst could be replaced by ^{32}S derived from HDS of ^{32}S–DBT. This can be verified by the fact that the shade area (B) is approximately equal to the shade area (A). This is consistent with the results in the case of Mo/Al_2O_3 (MoO_3: 12.5%) containing lower Mo loading (18).

In order to investigate the effect of reaction temperature, same experiments were conducted at 300, 320, 340, and 360°C under 50 kg/cm^2. The steady radioactive state of ^{35}S–DBT was immediately achieved at every reaction temperature. At the replacement of ^{35}S–DBT to ^{32}S–DBT, the radioactivity of ^{35}S–DBT also decreased immediately at every temperature. The change in a value of the radioactivity observed at the steady state corresponded to the change of a conversion of DBT. Moreover, the conversions derived from gas chromatography analysis agreed with that determined from the radioactivities of the unreacted ^{35}S–DBT in the liquid product (Table 1). Figure 2 shows the changes in radioactivity of the produced ^{35}S–H_2S with reaction time at 300, 320, 340 and 360°C. Contrary to the case of ^{35}S–DBT, the time delays for ^{35}S–H_2S released to approach a steady state in radioactivities were significantly affected by the reaction temperature. The time delays observed for ^{35}S–H_2S became shorter with the increase in the reaction temperature. They were 160, 145, 130, and 115 min at 300, 320, 340, and 360°C, respectively.

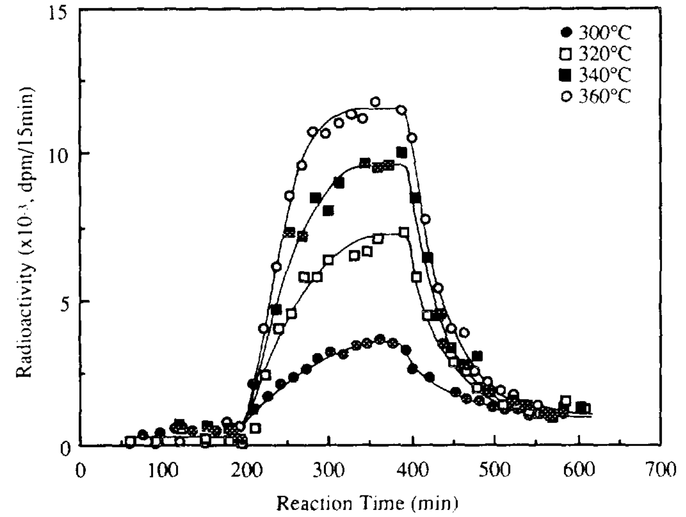

FIG. 2. Changes in radioactivities of formed ^{35}S–H_2S with reaction time for various temperatures. Mo/Al_2O_3, 300–360°C, 50 kg/cm^2.

3.2. *Ni/Al_2O_3*

Hydrodesulfurization of ^{35}S–DBT on the sulfided Ni/Al_2O_3 was also performed with the operation procedure 1. The conversions derived from GC analysis were also in good agreement with the determination from ^{35}S-radioactivities of the liquid products (Table 1). The reactivity at 360°C is only one-seventh of the reactivity in the case of Mo/Al_2O_3 under the same reaction conditions. Similarly to Mo/Al_2O_3, the steady state for the radioactivity of the unreacted ^{35}S–DBT was always immediately achieved at every temperature, while the time delay for the produced ^{35}S–H_2S to approach the steady state was about 150, 110, and 70 min at 360, 380, and 400°C, respectively. The time delay for Ni/Al_2O_3 at 360°C (Fig. 3) was longer than that (ca. 115 min) for Mo/Al_2O_3 at 360°C (Fig. 2). This result shows that the time delay for ^{35}S–H_2S elution is not due to the adsorption/desorption of H_2S on

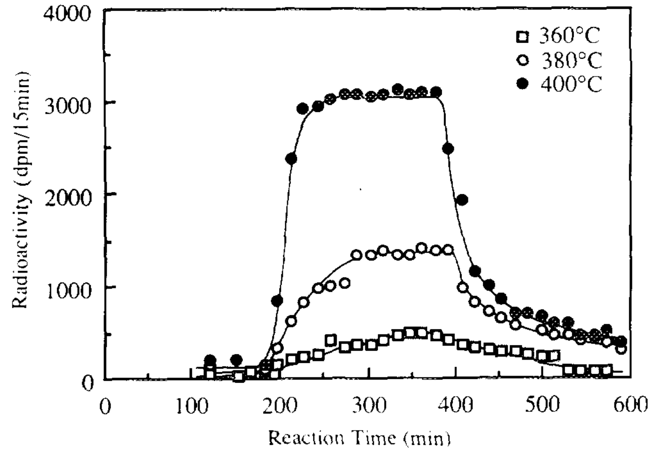

FIG. 3. Changes in radioactivities of formed $^{35}S-H_2S$ with reaction time for various temperatures. Ni/Al_2O_3, 360–400°C, 50 kg/cm^2.

the alumina support, but to the sulfur exchange between the sulfur in DBT and sulfur on the catalyst.

3.3. $Ni-Mo/Al_2O_3$

When the HDS reaction of ^{35}S-DBT was performed with the sulfided $Ni-Mo/Al_2O_3$ with operation procedure 1, the steady state for the radioactivity of ^{35}S-DBT was also immediately achieved at every reaction temperature as in the case of Mo/Al_2O_3. After the replacement ^{35}S-DBT by ^{32}S-DBT, the radioactivity of ^{35}S-DBT also decreased immediately at every temperature. The conversions obtained from the value of radioactivities at the steady state also agreed with the conversions of DBT derived from GC analysis as shown in Table 1. It can be observed that the reactivity at 240°C with $Ni-Mo/Al_2O_3$ is similar to that with Mo/Al_2O_3 at 320°C. The changes in radioactivities of the formed $^{35}S-H_2S$ with reaction time at 210, 230, 240, 260, and 280°C are shown in Fig. 4. Compared with the case of ^{35}S-DBT, the time delays observed for $^{35}S-H_2S$ were significantly affected by the reaction temperature. As in the case of Mo/Al_2O_3, the time delay for $^{35}S-H_2S$ became longer with decreased reaction temperature.

For the sulfided $Ni-Mo/Al_2O_3$, the HDS reaction following operation procedure 2 was also carried out. Figure 5 shows the changes in radioactivities of produced $^{35}S-H_2S$ with lapse of time at 260°C. When ^{35}S-DBT was replaced by ^{32}S-DBT (operation procedure 1), $^{35}S-H_2S$ was released and approached slowly a normal state of radioactivities. In contrast,when ^{35}S-DBT was replaced by decalin (operation procedure 2), the radioactivity of $^{35}S-H_2S$ decreased immediately and a portion of ^{35}S was held on the catalyst. The remaining ^{35}S was shown by the shade area (C) in Fig. 5. As described in Section 3.1, these differences also indicate that sulfur accommodated on the catalyst cannot be released without the supply of sulfur by HDS of DBT on the sulfided $Ni-Mo/Al_2O_3$. As in the case of Mo/Al_2O_3, when decalin solvent was replaced again by the solution of ^{32}S-DBT, however, ^{35}S was released as $^{35}S-H_2S$ and a peak of radioactivity was shown in the shade area (D), which was also approximately equal to the area (C).

3.4. The Formation Rate Constant of $^{35}S-H_2S$ and the Amount of Labile Sulfur

In the previous papers (17, 18), we reported that changes in the radioactivity of the $^{35}S-H_2S$ formed during the decreasing period could be expressed as an exponential function of reaction time. The formation rate of $^{35}S-H_2S$ from the catalysts could be treated as a first order reaction. In this work, the first order plots of the formation rate of $^{35}S-H_2S$ from the catalysts were also obtained for all reaction. As the examples, the first order plots of radioactivities of formed $^{35}S-H_2S$ at 260°C for $Ni-Mo/Al_2O_3$ and at 340°C for Mo/Al_2O_3 were shown in Fig. 6. These lines can be revealed as a function of time;

$$\ln y = \ln z - kt, \qquad [1]$$

where y represents the radioactivity of $^{35}S-H_2S$ (dpm/min), z the radioactivity of $^{35}S-H_2S$ at steady state (dpm/min), k the rate constant of the release of $^{35}S-H_2S$ (min^{-1}), and t reaction time (min). Furthermore, the first order plot of the values, where the radioactivity of each increasing period of produced $^{35}S-H_2S$ in Fig. 1 was subtracted from that at steady state, also showed the linear relationship (Fig. 6) and two slopes at this temperature were overlapped each other for Mo/Al_2O_3. The same result was also obtained for $Ni-Mo/Al_2O_3$ (Fig. 6). This indicates that the rate of release of $^{35}S-H_2S$ is equal to that of

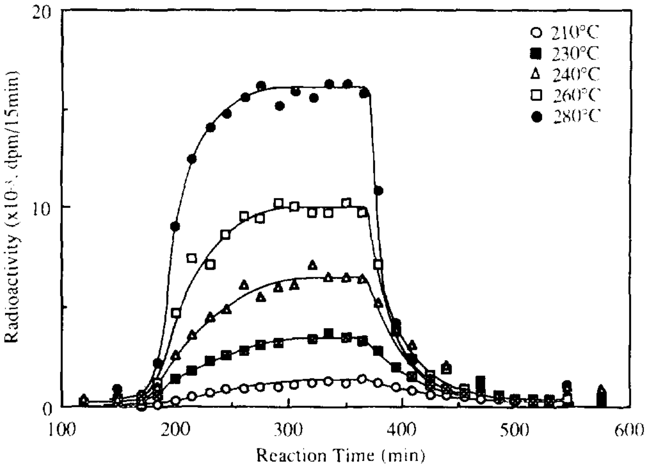

FIG. 4. Changes in radioactivities of formed $^{35}S-H_2S$ with reaction time for various temperatures. $Ni-Mo/Al_2O_3$, 210–280°C, 50 kg/cm^2.

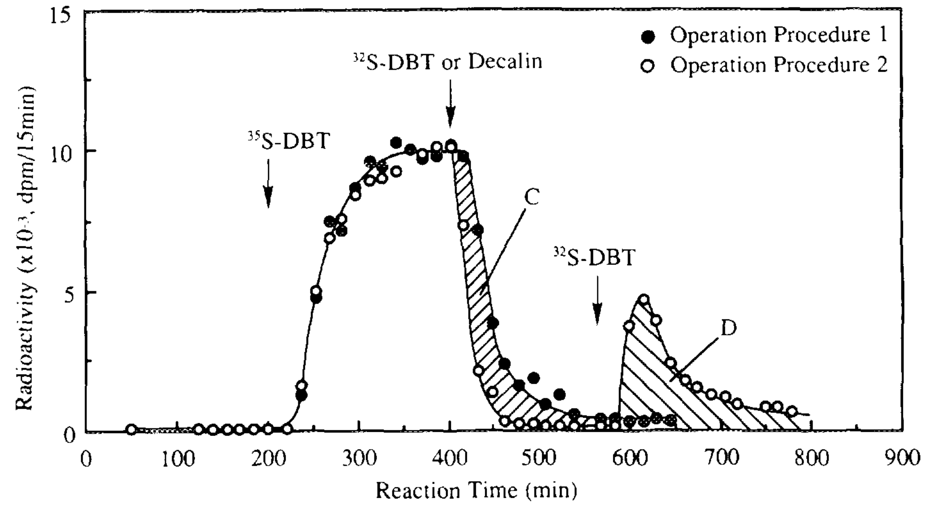

FIG. 5. Changes in radioactivities of formed $^{35}S-H_2S$ with reaction time: (●) Formed $^{35}S-H_2S$ in operation procedure 1. (○) Formed $^{35}S-H_2S$ in operation procedure 2. Ni-Mo/Al_2O_3, 260°C, 50 kg/cm^2.

$^{32}S-H_2S$, and that the isotopic effect between ^{35}S and ^{32}S would be negligible.

After the radioactivities of $^{35}S-H_2S$ reached the steady state, the difference of total radioactivities introduced from ^{35}S-DBT into the catalyst with those of the formed $^{35}S-H_2S$ is equivalent to the total radioactivities remaining on the catalyst. This corresponds to area (A) or (B) in Fig. 1. The area is z/k (dpm) which can be calculated from the integral (t: $0 - \infty$) of Eq. [1]. Since all ^{35}S on the catalyst was originated from the desulfurization of ^{35}S-DBT, the concentration of ^{35}S in sulfur introduced to the catalyst by the HDS of DBT at the steady state should be equal to the concentration of ^{35}S in sulfur of ^{35}S-DBT, because the isotope effect between ^{35}S and ^{32}S was thought to be negligible. The concentration of ^{35}S in sulfur of ^{35}S-DBT could be defined as $^{35}S_{DBT}/S_{DBT}$ (dpm/g), where $^{35}S_{DBT}$ is radioactivities in 1 mol of DBT (dpm/mol) and S_{DBT} is the amount of sulfur in 1 mol DBT (g/mol). According to this, the amount of labile sulfur on the catalyst (S0) can be presented by $(z/k)(^{35}S_{DBT}/S_{DBT})$. The reaction rate constants and the amounts of labile sulfur for all catalysts under various reaction conditions were obtained and were summarized in Table 1.

The apparent activation energies of HDS for DBT on all catalysts calculated from the Arrhenius plots of the rates of HDS (Fig. 7) were about 20 ± 1 kcal/mol for Mo/Al_2O_3, Ni/Al_2O_3, Ni-Mo/Al_2O_3, Co/Al_2O_3, and Co-Mo/Al_2O_3. This was consistent with the results reported in Ref. (3). It implies that the same reaction process occurs

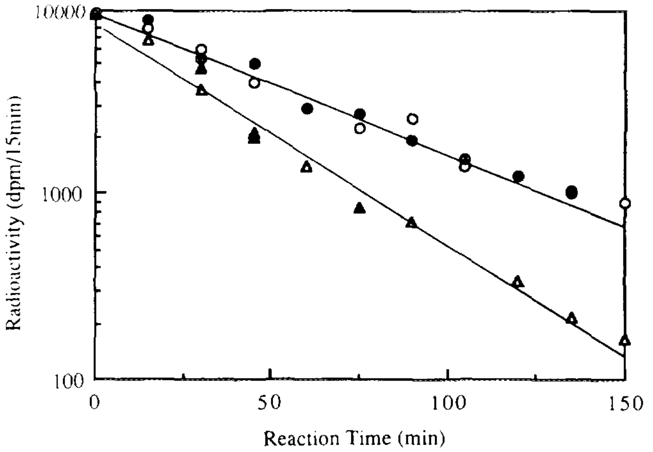

FIG. 6. First order plots of formed $^{35}S-H_2S$ with reaction time. Mo/Al_2O_3, 340°C, 50 kg/cm^2. (○) Decreasing period, and (●) increasing period. Ni-Mo/Al_2O_3, 260°C, 50 kg/cm^2. (△) Decreasing period, and (▲) increasing period.

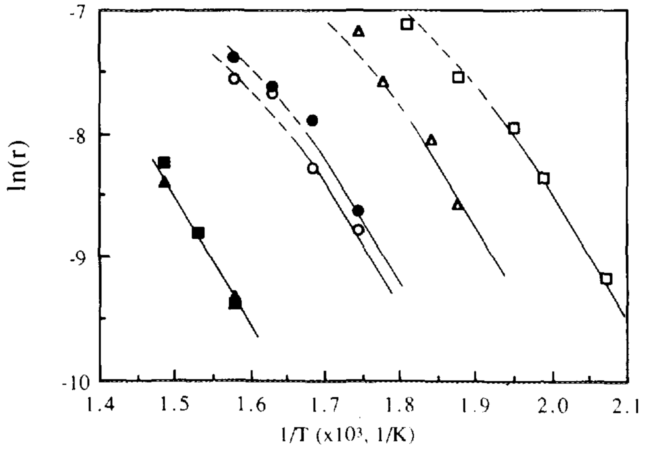

FIG. 7. Arrhenius plots of the rates of HDS: (○) Mo/Al_2O_3 (12.5%); (●) Mo/Al_2O_3 (16.0%); (□) Ni-Mo/Al_2O_3; (■) Ni/Al_2O_3; (△) Co-Mo/Al_2O_3; (▲) Co/Al_2O_3.

either on sulfided Mo/Al_2O_3 or on sulfided $Ni–Mo/Al_2O_3$ or $Co–Mo/Al_2O_3$.

4. DISCUSSION

Results of EXAFS have indicated that molybdenum sulfide in sulfided Mo/Al_2O_3 is present as in the MoS_2-like phase (5, 6). In a previous paper (18), we tried to estimate quantitatively the amount of sulfur in the sulfided Mo/Al_2O_3 (MoO_3 12.5%) under the practical reaction condition and determined that molybdenum sulfide was present in the form of $MoS_{1.92}$. Thus, we could assume that the molybdenum sulfide is present as the MoS_2 for Mo/Al_2O_3 (MoO_3 16.0%).

For the sulfided Ni/Al_2O_3, the forms of nickel sulfide may be relatively complicated. The Ni–S phase diagram is very complex but there are two relatively stable sulfides, i.e., Ni_3S_2 and NiS (20). The free energies of formation of Ni_3S_2 and NiS are quite comparable (20). The stability of these sulfides will depend on the temperature and H_2/H_2S ratio in the gas phase (21). From Table 1, we could calculate the ratios of labile sulfur to total sulfur present as either Ni_3S_2 or NiS, as shown in Table 2. The ratios of labile sulfur to total sulfur at 380°C and 400°C would become more than 1, if the nickel sulfide was present as Ni_3S_2. Obviously, NiS is a more possible form of nickel sulfide in the sulfided Ni/Al_2O_3.

For the sulfided $Ni–Mo/Al_2O_3$, it is very difficult to determine the form of metal sulfide because of the complexity of bimetal system. Results of EXAFS have indicated that molybdenum sulfide is still present in the MoS_2-like phase (6, 7). Therefore, we could assume that nickel sulfide and molybdenum sulfide in the sulfided $Ni–Mo/Al_2O_3$ were still present in the form of NiS and MoS_2, respectively.

On the basis of this assumption, it was further assumed that only sulfur present in the NiS phase in the sulfided $Ni–Mo/Al_2O_3$ was labile and that sulfur present in the form of MoS_2 was not labile. The ratio of the amount of labile sulfur to total amount of sulfur present in the NiS phase for Ni/Al_2O_3 and $Ni–Mo/Al_2O_3$ was plotted against the rate of HDS in Fig. 8. Considering the similarity between $Co–Mo/Al_2O_3$ and $Ni–Mo/Al_2O_3$, the results for Co/Al_2O_3 and $Co–Mo/Al_2O_3$ in Ref. (17) were also shown in Fig. 8, where it was assumed that only sulfur present in the form of Co_9S_8 in $Co–Mo/Al_2O_3$ was labile and that sulfur in the form of MoS_2 was not labile. The ratio of labile sulfur to total sulfur present in the form of NiS or Co_9S_8 in the sulfided $Ni–Mo/Al_2O_3$ or $Co–Mo/Al_2O_3$ became more than one at rate of HDS over 0.29 mg of sulfur/min · g of catalyst. This indicates that sulfur in the form of MoS_2, other than in the form of NiS or Co_9O_8, was also labile in the sulfided $Ni–Mo/Al_2O_3$ or $Co–Mo/Al_2O_3$.

TABLE 2

The Ratios of Labile Sulfur to Total Sulfur on Sulfided Ni/Al_2O_3

Temperature, °C	360	380	400
Labile sulfur, mg of sulfur/g of catalyst	7.2	9.9	12.8
Ratio I[a] (%)	84.5	115.2	149.4
Ratio II[b] (%)	55.8	76.7	99.2

Note. It was assumed that all sulfur were present as [a] Ni_3S_2; [b] NiS.

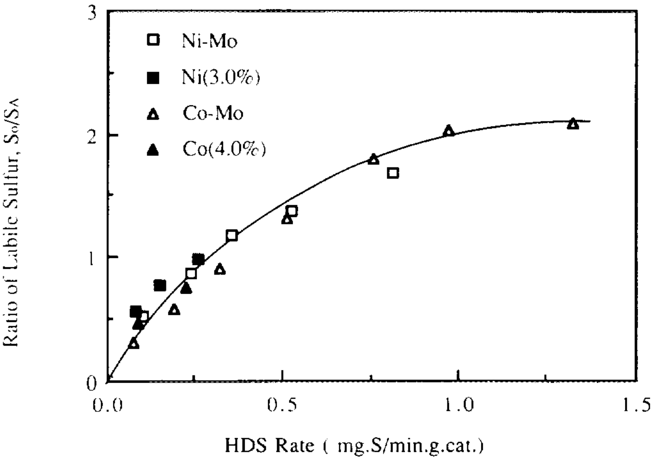

FIG. 8. Plots of ratio of labile sulfur vs rate of DBT HDS. For open symbols, which belong to $Ni–Mo/Al_2O_3$ (□) and $Co–Mo/Al_2O_3$ (△), it was assumed that the sulfur in MoS_2 phase was not labile but only the sulfur in NiS or Co_9S_8 phase was labile in the sulfided $Ni–Mo/Al_2O_3$ and $Co–Mo/Al_2O_3$. The solid symbols belong to Ni/Al_2O_3 (■) and Co/Al_2O_3 (▲). The ratios of labile sulfur on the sulfided catalysts were estimated from S_0/S_A (S_A: total amount of sulfur present in the form of NiS or Co_9S_8 in the sulfided Ni/Al_2O_3, $Ni–Mo/Al_2O_3$, Co/Al_2O_3, and $Co–Mo/Al_2O_3$).

To obtain more useful insight for labile sulfur, the amounts of labile sulfur at 280°C for Mo/Al_2O_3, Ni/Al_2O_3, and $Ni–Mo/Al_2O_3$ were compared. The amount of labile sulfur in sulfided Ni/Al_2O_3 at 280°C can be deduced to be 1.6 mg of sulfur/g of catalyst from the dependence of the amount of labile sulfur on the temperature. Similarly, the amount of labile sulfur in the sulfided Mo/Al_2O_3 (MoO_3 16.0%) at 280°C can also be deduced to be 9.8 mg of sulfur/g of catalyst. On the other hand, the amount of labile sulfur in the sulfided $Ni–Mo/Al_2O_3$ at 280°C was 18.4 mg of sulfur/g of catalyst, as shown in Table 1. Comparing the amounts of labile sulfur in the three catalysts, it can be assumed that sulfur in the form of NiS in $Ni–Mo/Al_2O_3$ is relatively nonlabile and that only sulfur in the form of MoS_2 in $Ni–Mo/Al_2O_3$ is labile. In addition, when the same treatment method was applied to the sulfided Mo/Al_2O_3 (MoO_3 12.5%), Co/Al_2O_3, and $Co–Mo/Al_2O_3$ as reported in the previous papers (17, 18), the amounts

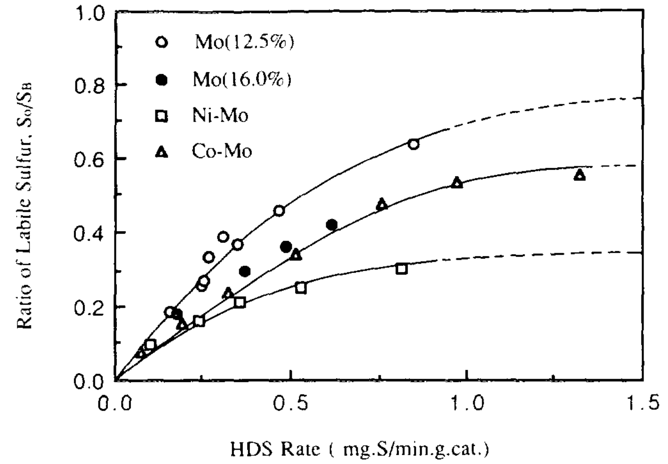

FIG. 9. Plots of ratio of labile sulfur vs rate of DBT HDS. (○) Mo/Al_2O_3 (12.5%), (●) Mo/Al_2O_3 (16%), (□) Ni–Mo/Al_2O_3, and (△) Co–Mo/Al_2O_3. It was assumed that the sulfur in NiS and Co_9S_8 phase was not labile but only the sulfur in MoS_2 phase was labile in the sulfided Ni–Mo/Al_2O_3 and Co–Mo/Al_2O_3. The ratios of labile sulfur on the sulfided catalysts were estimated from S_0/S_B (S_B: total amount of sulfur present in the form of MoS_2 in the sulfided Mo/Al_2O_3, Ni–Mo/Al_2O_3, and Co–Mo/Al_2O_3).

of labile sulfur for the three catalysts were 9.1, 2.0, and 19.9 mg of sulfur/g of catalyst at 290°C, respectively. It can also be assumed that sulfur in the form of Co_9S_8 in Co–Mo/Al_2O_3 is relatively nonlabile and that only sulfur in the form of MoS_2 in Co–Mo/Al_2O_3 is labile. On the basis of these assumptions, the ratios of the amount of labile sulfur to total sulfur present in the form of MoS_2 were plotted against the HDS rate as shown in Fig. 9. The ratios in sulfided Mo/Al_2O_3 (12.5%), Ni–Mo/Al_2O_3, or Co–Mo/Al_2O_3 increased with increased rate of HDS and approached the steady values for the three catalysts. These values at the infinite rate of HDS would be deduced to be ca. 0.75, 0.37, and 0.59 for Mo/Al_2O_3 (12.5%), Ni–Mo/Al_2O_3, and Co–Mo/Al_2O_3, respectively. At this time, the amounts of labile sulfur would be about 41.8, 25.2, and 32.3 mg of sulfur/g of catalyst; i.e., 1.30, 0.79, and 1.01 mmol of sulfur/g of catalyst for the three catalysts, respectively. In contrast, the content of Ni or Co in Ni–Mo/Al_2O_3 or Co–Mo/Al_2O_3 was 0.39 and 0.51 mmol/g of catalyst, respectively. This means that the numbers of labile sulfur were approximately twice those of Ni or Co atoms on sulfided Ni–Mo/Al_2O_3 or Co–Mo/Al_2O_3.

It should be noted that the data points for Mo/Al_2O_3 with 16% MoO_3 did not fall on the curve for Mo/Al_2O_3 with 12.5% MoO_3, as shown in Fig. 9. This may be due to lower dispersion of Mo species in Mo/Al_2O_3 with 16% MoO_3, because it is very difficult to maintain uniform dispersion of Mo species on the alumina support during the preparation of the catalysts with higher Mo loading by the impregnation method. Some portion of the Mo species may be present in the form of small MoS_2 crystallites in Mo/Al_2O_3 with 16% MoO_3 after the presulfurization. The HDS activity and the ratio of labile sulfur to total sulfur were very low for the unsupported MoS_2 (22). For instance, the HDS activity and the ratio of labile sulfur to total sulfur were 1.29×10^{-3} mol of DBT/min · mol of Mo and 3.5% at 400°C and 50 kg/cm^2. In contrast, the HDS activity and the ratio of labile sulfur to total sulfur on the 12.5% sulfided Mo/Al_2O_3 were 1.87×10^{-2} mol of DBT/min · mol of Mo and 45.5% at 360°C and 50 kg/cm^2. Thus, the actual content of well-dispersed Mo in Mo/Al_2O_3 with 16% MoO_3 may be less than in the case of Mo/Al_2O_3 with 12.5% MoO_3. This may cause the deviation between the two sulfided Mo/Al_2O_3 catalysts in Fig. 9. The specific reason is being investigated.

Molybdenum disulfide belongs to a group of the layered structures shown in Fig. 10(a) (23), and each layer is composed of sheets of Mo sandwiched between sheets of sulfur atoms. The bonding within a given layer is mainly covalent, whereas the bonding between layers is the van der Waals type. Recently, Topsøe and Topsøe have reported that the monolayer dispersion is maintained and the MoS_2 phase appears to be predominantly present as a two-dimensional single-slab structure oriented flat-wise on the alumina support (*c*-axis perpendicular to alumina surface) for Mo/Al_2O_3 up to 12% Mo (9, 24). Thus, it is an acceptable hypothesis that the MoS_2 phase is present as a single-slab structure flat on the surface of the alumina as shown in Fig. 10(b). However, since the locations of sulfurs on the surface of alumina were different from each other, the labile capacities of sulfurs would also be different. The sulfur between the molybdenum layer and the alumina surface (S_b) may be the most difficult to move, and the sulfur over the molybdenum layer (S_a) may be

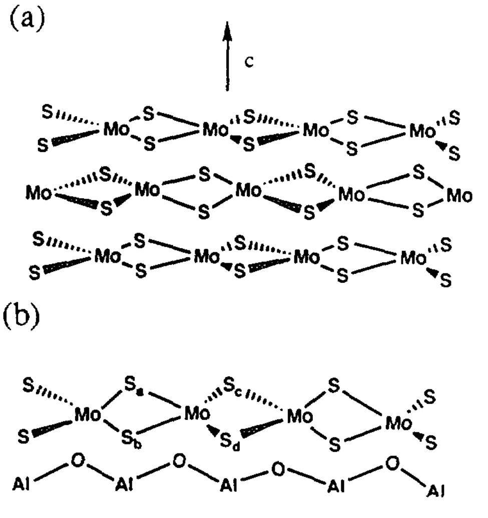

FIG. 10. The structure of MoS_2: (a) Crystal structure of molybdenum disulfide, and (b) structure of MoS_2 on sulfided Mo/Al_2O_3.

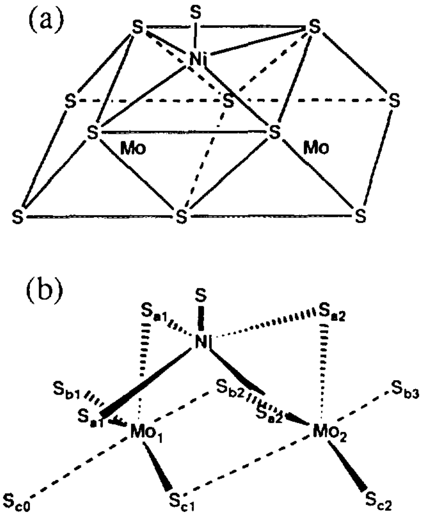

FIG. 11. The structure of sulfided Ni-Mo/Al_2O_3: (a) Square pyramidal structure, and (b) deformed tetrahedral structure of MoS_2 and structure of Mo-S-Ni.

the most labile. The sulfur in other sites (S_c or S_d), which forms a triangle with Mo parallel to alumina surface, may have intermediate labile capacity. This explains why the amount of labile sulfur changes depend on the reaction conditions (see Figs. 2, 3, 4, and Table 1). If the sulfur between the molybdenum and the alumina surface, S_b, was not labile, the amount of labile sulfur in the sulfided Mo/Al_2O_3 would be 75% of the total sulfur. This is in good agreement with the result that the labile sulfur is 75% of the total sulfur at an infinite rate of HDS, as shown in Fig. 9.

For the sulfided Ni-Mo/Al_2O_3, the structure of the MoS_2-like phase located at the edge may be rearranged by the presence of Ni atoms, and the square pyramidal model may be an acceptable model. This idea was originally proposed by Ratnasamy and Sivasanker (25) and later by Topsøe's group in a more detailed model (26, 27). In recent works, Louwers and Prins have given further evidence about this model by the use of EXAFS (7). The square pyramidal coordination of the Ni atoms resembles that of the millerite structure. Ni atoms are connected to the MoS_2 crystallite by four sulfur atoms. An additional sulfur atom is attached in front of the Ni atom as shown in Fig. 11(a). Even in this model, one could still consider that the structure of MoS_2 is deformed tetrahedral and only the location of two other weak Mo–S bonds within the layers is changed as shown in Fig. 11(b). The Mo_1–S_{c0} or Mo_2–S_{c1}, and Mo_1–S_{b2} or Mo_2–S_{b3} bonds were considered as two other weak bonds assigned to the van der Walls type in this structure. As mentioned above, the sulfur in the Ni-Mo/Al_2O_3 or Co-Mo/Al_2O_3 is the most labile among sulfided Ni/Al_2O_3 or Co/Al_2O_3, and Ni-Mo/Al_2O_3 or Co-Mo/Al_2O_3. This is consistent with the bond energies of metal sulfide calculated by Nørskov *et al.* (28) and Topsøe *et al.* (29). They proposed that the bond energies of metal sulfide varied as follows: nickel or cobalt sulfide > molybdenum sulfide > NiMoS or CoMoS. Taking into account that the bond energy of Ni–S or Co–S is higher than that of NiMoS or CoMoS, it is reasonable that the sulfur attached to only Ni or Co atoms is more difficult to move. On the other hand, the atomic ratios of Ni/Mo and Co/Mo were 0.37 and 0.59 for Ni–Mo/Al_2O_3 and Co–Mo/Al_2O_3, respectively. These values are in very good agreement with ratios of labile sulfur to total sulfur obtained at the infinite HDS rate in Fig. 9. It indicates that an atom of Ni or Co promotes an atom of Mo or two atoms of sulfur in the adjacent MoS_2 phase. Furthermore, it was assumed that only sulfurs in the MoS_2 phase adjacent to Ni or Co atoms, i.e., S_{a1} or S_{a2} as shown in Fig. 11(b), were labile; the number of labile sulfurs in the Mo–S–Ni phase can be deduced to be twice that of Ni atoms. This is in very good agreement with the results obtained from Fig. 9.

The HDS activity of sulfided Mo-based catalysts would be relative to the existence of sulfur vacancies (uncoordinated sites). SH groups also played an important role in the HDS reaction (30, 31). Regarding the evidence for the presence of SH groups, studies of deuterium exchange (32), chemical titration by silver ions (33), and Raman spectroscopy (34) have provided such evidence. More recently, Topsøe and Topsøe postulated that SH groups existed at the edges of MoS_2, and found by FT-IR study on sulfided Mo-based catalysts (24) that SH groups and vacancies could interconvert and coexisted in close proximity. As mentioned above, H_2S was not formed directly from the sulfur in DBT, but from the sulfur on the catalyst. The absence of DBT did not generate H_2S, while the incorporation of sulfur in DBT onto catalyst generated H_2S (see Figs. 1 and 5). If the vacancies were the sites for the coordination with the heteroatoms of reactants, the mechanism of DBT HDS would be illustrated more simply, as shown in Fig. 12. It has also been assumed that only sulfur bonded to both Ni and Mo in the form of MoS_2 is labile in the scheme. When ^{35}S in DBT occupied the vacancy and the carbon–sulfur bonds were cleaved, ^{35}S would remain on the catalyst as a Mo–S species. The generation of H_2S will form a new vacancy on the catalyst. Thus, a shift of vacancy on the catalyst surface would occur. The possibility that the vacancy position may be easily shifted has been proposed by Ruette and Ludena in the molecular orbital calculations of the desulfurization reaction of thiophene over a Mo-Co catalyst (35). For this mechanism of HDS, it should be noted that only after the sulfur in DBT was incorporated into the catalyst, the sulfur on the catalyst surface was released as H_2S. This means that after an anion vacancy is occupied by a sulfur

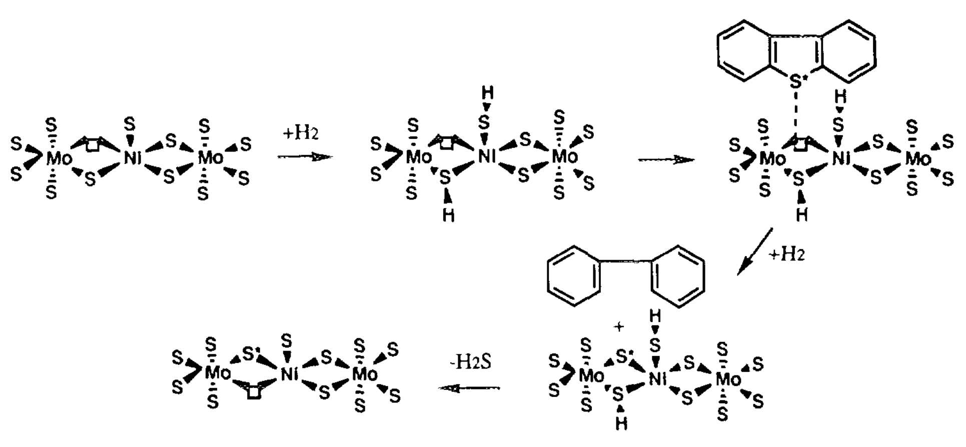

FIG. 12. The scheme of hydrodesulfurization of DBT on sulfided Ni–Mo/Al_2O_3.

atom removed from DBT, a new anion vacancy will appear on the catalyst surface.

It has been suggested that the amount of labile sulfur equals the total sulfur which can be converted to vacancies under a certain reaction condition for a catalyst. Although this amount corresponds closely to the reactivity of the catalyst, it was definitely not equal to the number of active sites. HDS reactivity of a catalyst will also depend upon the conversion rate between the labile sulfur and the vacancy-regeneration rate of active sites, as well as the amount of labile sulfur. Thus, the regeneration rate of active sites, as well as the amount of labile sulfur, varied with reaction conditions. Furthermore, the variation in the regeneration rate of active sites was more than that in the amount of labile sulfur. This could explain the correspondence between the amount of labile sulfur and the HDS rates shown in Fig. 9, where the reactivity of a catalyst could vary significantly although the amount of labile sulfur for the catalyst was approximately constant.

4. CONCLUSIONS

The hydrodesulfurization of ^{35}S-labeled dibenzothiophene (^{35}S-DBT) was carried out on sulfided Ni–Mo/Al_2O_3, Mo/Al_2O_3, and Ni/Al_2O_3, and the following conclusions were drawn. The similar apparent activation energies (20 ± 1 kcal/mol) of HDS reaction for DBT on all sulfided catalysts were estimated from the rate of HDS reaction. This implies that the same reaction process may occur on the sulfided Mo/Al_2O_3 and Ni–Mo/Al_2O_3 or Co–Mo/Al_2O_3. When the amounts of labile sulfur in sulfided Mo/Al_2O_3 and in Ni–Mo/Al_2O_3 or Co–Mo/Al_2O_3 are plotted against the rate of HDS, they increase with increased rate of HDS and reach 41.8, 25.2, and 32.3 mg of sulfur/g of catalyst at the infinite HDS rate for the three catalysts, respectively. When it was assumed that all sulfur in Mo/Al_2O_3 was present in the form of MoS_2, it was deduced that ca. 75% of sulfur in Mo/Al_2O_3 was involved in the HDS reaction. By comparing the amounts of labile sulfur in the sulfided Mo/Al_2O_3, Ni/Al_2O_3, or Co/Al_2O_3, and Ni–Mo/Al_2O_3 or Co–Mo/Al_2O_3, it was suggested that the sulfurs in NiS or the Co_9S_8 phase on the Ni–Mo/Al_2O_3 or Co–Mo/Al_2O_3 were not labile, and only sulfur bonded to both Ni and Mo in the form of MoS_2 was involved in the HDS reaction. The amount of labile sulfur in Ni–Mo/Al_2O_3 or Co–Mo/Al_2O_3 at infinite rate of HDS, 25.2, or 32.2 mg of sulfur/g of catalyst, corresponds to about 37 or 59% of sulfur present in the form of MoS_2. The atomic ratios of Ni/Mo or Co/Mo in used Ni–Mo/Al_2O_3 or Co–Mo/Al_2O_3 are 0.37 or 0.59. The results suggest that the addition of Ni or Co promotes the same amount of Mo species as of Ni or Co species in the sulfided Ni–Mo/Al_2O_3 or Co–Mo/Al_2O_3, and makes sulfur in this portion of Mo species more labile.

REFERENCES

1. Kabe, T., Ishihara, A., and Tajima, H., *Ind. Eng. Chem. Res.* **31**, 1577 (1992).
2. Ishihara, A., Itoh, T., Hino, T., Nomura, M., Qi, P., and Kabe, T., *J. Catal.* **140**, 184 (1993).
3. Kabe, T., Ishihara, A., and Zhang, Q., *Appl. Catal. A* **97**, L1 (1993).
4. Ishihara, A., and Kabe, T., *Ind. Eng. Chem. Res.* **32**, 753 (1993).
5. Bouwens, S. M. A. M., Prins, R., de Beer, V. H. J., and Koningsberger, D. C., *J. Phys. Chem.* **94**, 3711 (1990).
6. Bouwens, S. M. A. M., van Veen, J. A. R., Koningsberger, D. C., de Beer, V. H. J., and Prins, R., *J. Phys. Chem.* **95**, 123 (1991).
7. Louwers, S. P. A., and Prins, R., *J. Catal.* **133**, 94 (1992).
8. Topsøe, H., Clausen, B. S., Topsøe, N-Y., and Pedersen, E., *Ind. Eng. Chem. Fundam.* **25**, 25 (1986).
9. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **139**, 631 (1993).
10. Chianelli, R. R., *Catal. Rev. Sci. Eng.* **26**, 361 (1984).
11. Topsøe, H., Candia, R., Topsøe, N.-Y., and Clausen, B. S., *Bull. Soc. Chim. Belg.* **93**, 783 (1984).
12. Topsøe, H., Clausen, B. S., Topsøe, N.-Y. and Pedersen, E., *Ind. Eng. Chem. Fundam.* **25**, 725 (1984).

13. Wivel, C., Candia, R., Clausen, B. S., Mørup, S., and Topsøe, H., *J. Catal.* **68,** 453 (1981).
14. Karroua, M., Matralis, H., Grange, P., and Delmon, B., *J. Catal.* **139,** 371 (1993).
15. Delmon, B., *in* "Catalysis in Petroleum Refining 1989," (D. L. Trimm, S. Akaha, M. Absi-Halabi, and A. Bishara, Eds.), p. 1. Elsevier, Amsterdam, 1990.
16. Karroua, M., Grange, P., and Delmon, B., *Appl. Catal.* **50,** L5 (1993).
17. Kabe, T., Qian, W., Ogawa, S., and Ishihara, A., *J. Catal.* **143,** 239 (1993).
18. Qian, W., Ishihara, A., Shinji, O., and Kabe, T., *J. Phys. Chem.* **98,** 907 (1994).
19. Kabe, T., Qian, W., and Ishihara, A., *J. Phys. Chem.* **98,** 912 (1994).
20. Alcock, C. B., "Principles of Pyrometallurgy." Academic Press, London/New York, 1976.
21. Burch, R., and Collins, A., *J. Catal.* **97,** 385, (1986).
22. Qian, W., Ishihara, A., and Kabe, T., to appear.
23. Williams, R. H., and Mcevoy, A. J., *J. Phys., D: Appl. Phys.* **4,** 456 (1971).
24. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **139,** 641 (1993).
25. Ratnasamy, P., and Sivasanker, S., *Catal. Rev. Sci. Eng.* **22,** 401 (1980).
26. Clausen, B. S., Lengeler, B., Candia, R., Als-Nielsen, J., and Topsøe, H., *Bull. Soc. Chim. Belg.* **90,** 1249 (1981).
27. Topsøe, H., Clausen, B. S., Topsøe, N.-Y., Pedersen, E., Niemann, W., Müller, A., Bögge, H., and Lengeler, B., *J. Chem. Soc. Faraday Trans. 1* **83,** 2157 (1987).
28. Nørskov, J. K., Clausen, B. S., and Topsøe, H., *Catal. Lett.* **13,** 1 (1992).
29. Topsøe, H., Clausen, B. S., Topsøe, N.-Y., Hyldtoft, J., and Nørskov, J. K., *Prepr. Am. Chem. Soc. Div. Pet. Chem.* **38**(3), 638 (1993).
30. Topsøe, H., *in* "Proceedings of the NATO Advanced Study Institute on Surface Properties and Catalysis by Non-Metals: Oxides, Sulfides and Other Transition Metal Compounds, 1982," (J. P. Bonnelle, B. Delmon, and E. Derouane, Eds.), p. 329. Reidel, Dordrecht, 1983.
31. Muralidhar, G., Massoth, F. E., and Shabtai, J., *J. Catal.* **85,** 44 (1984).
32. Massoth, F. E., *J. Catal.* **36,** 164 (1975).
33. Maternova, J., *Appl. Catal.* **3,** 3 (1982).
34. Payen, E., Kasztelan, S., and Grimblot, J., *J. Mol. Struct.* **174,** 71 (1988).
35. Ruette, F., and Ludena, E. V., *J. Catal.* **67,** 266 (1981).