JOURNAL OF CATALYSIS **143**, 239–248 (1993)

Mechanism of Hydrodesulfurization of Dibenzothiophene on Co–Mo/Al_2O_3 and Co/Al_2O_3 Catalyst by the Use of Radioisotope ^{35}S Tracer

TOSHIAKI KABE,[1] WEIHUA QIAN, SHINJI OGAWA, AND ATSUSHI ISHIHARA

Department of Chemical Engineering, Tokyo University of Agriculture and Technology, Nakamachi, Koganei, Tokyo 184, Japan

Received January 13, 1993; revised April 22, 1993

In order to estimate the behavior of sulfur on hydrodesulfurization catalyst, the ^{35}S-labelled dibenzothiophene (^{35}S–DBT) was hydrodesulfurized on sulfided Co–Mo/Al_2O_3 and Co/Al_2O_3 in a fixed-bed pressurized flow reactor. During the reaction, the radioactivities of unreacted ^{35}S-DBT and formed ^{35}S–H_2S were monitored. The rate of the release of sulfur on the catalyst was estimated from the rates of an increase and a decrease of the radioactivity in formed ^{35}S–H_2S. The activation energies of the release of sulfur were 3.7 and 9.9 kcal/mol for sulfided Co–Mo/Al_2O_3 and Co/Al_2O_3, respectively. The amount of labile sulfur (S_0), which could be calculated from the maximum amount of ^{35}S accommodated on the catalyst, increased with increasing temperature. When it was assumed that sulfur in sulfided Co–Mo/Al_2O_3 existed in the form of Co_9S_8–MoS_2/Al_2O_3, the ratio of labile sulfur to total sulfur did not exceed 50%, even under conditions where the rate of DBT HDS is relatively high. On the contrary, the ratio of labile sulfur to total sulfur for Co/Al_2O_3 exceeded 80%.

INTRODUCTION

In recent years, much attention has been focused on deep hydrodesulfurization (HDS) of light oil. It has become more important to develop a new catalyst with high activity and selectivity. For this purpose, a series of attempts have been made to explore the reaction mechanism for HDS of light oil (*1, 2*). In regard to mechanism of HDS on sulfided catalyst, a number of studies have been performed and several models such as the monolayer model (*3–5*), the contact synergy model (*6*), the intercalation model (*7, 8*) and the edge decoration model (*9, 10*) have been proposed. Further, MES (*11–13*) and EXAFS (*14–16*), as well as conventional XPS, FTIR, TPD, TPR, and TPS methods (*17–21*), and a deuterium tracer method (*22*) have been used to characterize the surface structure of HDS catalyst *in situ*. Because most of these were performed under static experimental conditions or under atmospheric pressure, however, the structure of catalysts during practical performance of HDS could not be clarified.

On the other hand, in spite of a number of studies on HDS, problems concerning the behavior of sulfur species on the catalyst still remain to be solved. In order to explore the behavior of sulfur species on the catalyst, radioisotope tracer methods using radioactive ^{35}S have been developed by several researchers (*23–29*). Lukens *et al.* (*23*) have measured the accessible surface area of supported transition metal sulfides by isotope exchange with a labelled H_2S in liquid scintillation solution. Kalechits and coworkers (*24, 25*) have shown that in the hydrogenation of a mixture of benzene and $C^{35}S_2$ on WS_2 catalyst, the catalyst sulfur was exchanged with radioactive sulfur of the feedstock. This labile sulfur would be a part of the nonstoichiometric sulfur of the catalyst which would be responsible for the

---

[1] To whom correspondence should be addressed.

0021-9517/93 $5.00

acceleration of acid catalyzed reaction (isomerization and cracking). Gachet *et al.* (*26*), Isagulyants *et al.* (*27*), and Dobrovolszky *et al.* (*28*) have carried out the HDS of thiophens on a Co–Mo catalyst which was sulfided by ^{35}S-labelled H_2S or radioactive ^{35}S-labelled thiophene. By tracing change of the ^{35}S in produced ^{35}S–H_2S during the reaction of ^{32}S-thiophenes, it was suggested that two types of sulfur appeared during the hydrodesulfurization reaction: labile sulfur and fixed sulfur. The amount of the labile sulfur which was progressively replaced during the reaction was about 20 wt% of the sulfur of the catalyst in its stationary state. It was deduced that a fixed sulfur which did not directly participate in the catalytic action would be located on the molybdenum and cobalt sulfide lattices. It was also found that H_2S was not formed directly from the sulfur of DBT but from the sulfur on the catalyst. Gellman *et al.* used radiotracer (^{35}S) labelling techniques to measure rates of hydrogenation of sulfur adsorbed on the Mo(100) surface (*29*). This use of ^{35}S or ^{3}H was believed to enable to clarify the behavior of sulfur in catalysts. However, there are no reports where the behavior of ^{35}S on catalysts during practical performance of HDS have been determined exactly.

Recently, we reported the HDS reaction of ^{35}S-labelled DBT on sulfided Mo/Al_2O_3 where it was found that the amount of labile sulfur increased with increasing temperature and the initial concentration of DBT (*30*). In this paper, we have conducted HDS reaction of ^{35}S-labelled DBT to trace the behavior of ^{35}S on a sulfided Co–Mo/Al_2O_3 catalyst during practical performance of HDS. After hydrodesulfurization of ^{32}S–DBT reached the steady state, the reactant solution of ^{35}S–DBT was substituted for that of ^{35}S–DBT at the same concentration of DBT. The radioactivity of unreacted ^{35}S–DBT and formed ^{35}S–H_2S released from a pressurized flow reactor were monitored with time. After the radioactivity of formed ^{35}S–H_2S reached the steady state, the reactant solution of ^{32}S–DBT was substituted for that of ^{35}S–DBT at the same concentration of DBT again. The mobility of sulfur on the catalyst was estimated from the rates of an increase and a decrease of formed ^{35}S–H_2S. This method allowed us to understand more exactly how sulfur in DBT is translated to H_2S and how sulfur in the catalyst participates in the actual HDS reaction.

EXPERIMENTAL

Materials. Decalin (Kishida Chemicals) was the commercial GR grade and was further purified by passing column (i.d. 20 mm; 30 cm) containing activated alumina (0.063–0.200 mm). ^{35}S–DBT was synthesized by the following method: In order to obtain ^{35}S-labelled sulfur, the commercial toluene solution of ^{35}S (total radioactivity: 1 mCi) (Amersham, Co. Ltd.) was mixed sufficiently with 8.7 g sulfur (^{32}S), then the toluene in mixture was evaporated at room temperature, and the sulfur mixture was dried for 24 h *in vacuo* until the toluene was entirely removed. Using this ^{35}S-labelled sulfur, DBT was synthesized according to the method developed by Gilman and Jacoby (*31*). After the crude DBT was crystallized from ethanol, colorless needles (purity more than 99.9%) were obtained. ^{32}S–DBT was synthesized by the similar method. Hydrogen (99.99%) was obtained from Tohei Chemicals. Hydrogen sulfide in hydrogen (H_2S 3.0%) was obtained from Takachio Chemicals. The commercial Co–Mo/Al_2O_3 (Ketjen fine 124: MoO_3, 12.5 wt%; CoO, 3.8 wt%; surface area, 274 m^2/g) was supplied as a 1/32 extrudate which was crushed and screened to provide 20 to 34 mesh granules used in this work. Co/Al_2O_3 (CoO, 3.8 wt%) were prepared by the conventional impregnation method using cobalt nitrate, calcinated at 450°C over 24 h, crushed and screened to 20 to 34 mesh granules.

Apparatus and procedure. The reactor was a 8-mm-i.d. stainless-steel tube packed with 1.0 g of catalyst particles diluted with quartz (30–50 mesh) sand to 3.5 cm^3 bed volume and 7 cm bed height. The single charge was used throughout the entire series

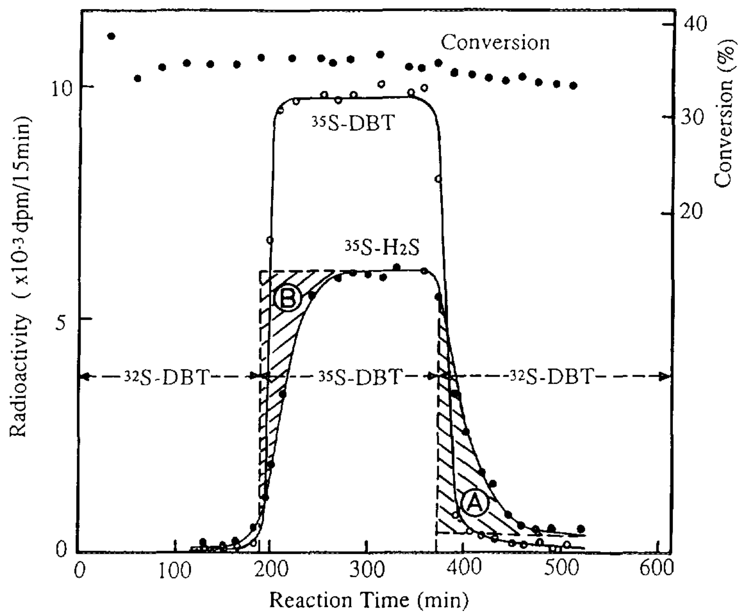

FIG. 1. Operation procedure in hydrodesulfurization of ^{35}S–DBT.

of experiments. After the catalyst bed was heated for more than 24 h at 450°C in air, it was presulfided with a mixture of 3% H_2S in H_2 flowing at 30 liter/h at atmospheric pressure and 400°C for 3 h. After these pretreatments, the reactor was cooled in a H_2S/H_2 stream to expected temperature and was pressurized by hydrogen. Then, the solution containing DBT was supplied to the feed pump (Kyowa Seimitsu KHD-16).

A typical reaction was carried out under the following conditions: H_2 25 liter/h, WHSV 28-56 h^{-1}, reaction pressure 50 kg/cm^2, concentration of DBT in decalin 1–3 wt%, and reaction temperature 260–300°C. The produced H_2S was absorbed with a commercial basic scintillator solution (Carbsorb, Packard Co. Ltd.). The liquid product was collected from a gas–liquid separator. For each run, a liquid product and an absorbed H_2S solution samples were collected every 15 min. The components of liquid products were analyzed by gas chromatography with FID detector (Hitachi 163) using a commercial capillary column (G-column 250). Radioactivities of unreacted ^{35}S–DBT in liquid product and the formed ^{35}S–H_2S in scintillator solution were measured by a liquid scintillation counter (LSC-1000, Aloka, Co. Ltd.) (*32*).

Typical two operation procedures were applied. 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, the 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 amount of $^{35}H_2S$ released into exit of the reactor became constant. (c) Then, the reactant solution was returned again to the decalin solution of 1 wt% ^{32}S–DBT. This reaction of ^{32}S–DBT was continued for 4–5 h.

Operation Procedure 2: (a) and (b) in this procedure are the same as those in Operation Procedure 1. (c) The reactant solution of ^{35}S–DBT was replaced by decalin. The reaction was continued for about 4 h; (d) after that, ^{32}S–DBT solution was substituted for decalin and the reaction was continued for about 4–5 h.

TABLE 1

Conversion of DBT and Kinetic Parameters at Various Hydrodesulfurization Conditions on Co–Mo/Al_2O_3 and Co/Al_2O_3

	Catalyst							
	Co–Mo/Al_2O_3						Co/Al_2O_3	
Reaction pressure (kg/cm^2)	50	50	50	50	50	10	50	50
Reaction temperature (°C)	260	270	290	300	300	300	360	400
Concentration of DBT (wt%)	1.0	1.0	1.0	1.0	3.0	1.0	1.0	1.0
WHSV (h^{-1})	28	28	28	28	28	56	28	28
Conversion from GC analysis	23.4	39.4	62.6	92.4	53.9	59.8	11.0	28.0
Conversion from radioactivity of ^{35}S	23.7	37.8	59.7	90.1	53.0	57.2	11.5	28.8
Labile sulfur, S_0 (mg/g-cat)	5.8	12.6	19.9	26.1	30.3	29.5	7.15	11.4
Ratio of S_0/S_{total} (%)[a]	8.27	18.0	28.4	37.2	43.2	42.0	36.2	60.5
Rate constant of the release of ^{35}S–H_2S, k ($\times$ 10^{-2}/min)	2.26	2.45	2.71	2.92	4.65	3.34	1.26	2.00
Rate of the release of H_2S, $S_0 \times k$ (mg/min/g-cat)	0.13	0.31	0.54	0.76	1.41	0.99	0.09	0.23
Rate of DBT HDS, r (mg/min/g-cat)	0.19	0.32	0.51	0.76	1.32	0.98	0.09	0.23

[a] The ratio of the labile sulfur to total sulfur on Co_9S_8–MoS_2/Al_2O_3 or Co_9S_8/Al_2O_3 is given.

RESULTS AND DISCUSSION

Co–Mo/Al_2O_3

(a) Reaction following operation procedure 1. The changes in radioactivities of unreacted ^{35}S–DBT and produced ^{35}S–H_2S with the reaction time during the hydrodesulfurization (HDS) reaction at 270°C is shown in Fig. 1. After replacing the decalin solution of ^{32}S–DBT by that of ^{35}S–DBT, the radioactivities of unreacted ^{35}S–DBT in liquid products increased with the reaction time and reached a steady state immediately. In the case of produced ^{35}S–H_2S, however, the time delay to reach the steady state was about 100 min. When the solution of ^{35}S–DBT returned to that of ^{32}S–DBT, the radioactivities of unreacted ^{35}S–DBT also decreased immediately from the steady state to normal state. The time delay for produced ^{35}S–H_2S from its steady state to normal state was about 100 min. The result indicates that the sulfur in DBT is not directly released as hydrogen sulfide, but accommodated on the catalyst.

The conversion can be calculated from the radioactivity of ^{35}S–DBT at steady state as well as GC analysis of DBT and products. The conversions at various reaction conditions are listed in Table 1. The conversions derived from GC analysis were in good agreement with the determination from ^{35}S-radioactivities of the liquid products.

The steady state for the radioactivity 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 conversion obtained from the value of radioactivities at the steady state agreed with the conversion of DBT as shown in Table 1. Figure 2 shows the change in radioactivities of formed ^{35}S–H_2S with reaction time at 260, 270, 290 and 300°C. Compared with the case of ^{35}S–DBT, the time delays observed for ^{35}S–H_2S were drastically affected by the reaction temperature. As the reaction temperature was lower, the time delays for ^{35}S–H_2S became longer.

(b) Reaction following operation procedure 2. Instead of the replacement of the ^{35}S–DBT solution to the ^{32}S–DBT solution, the ^{35}S–DBT solution was replaced by de-

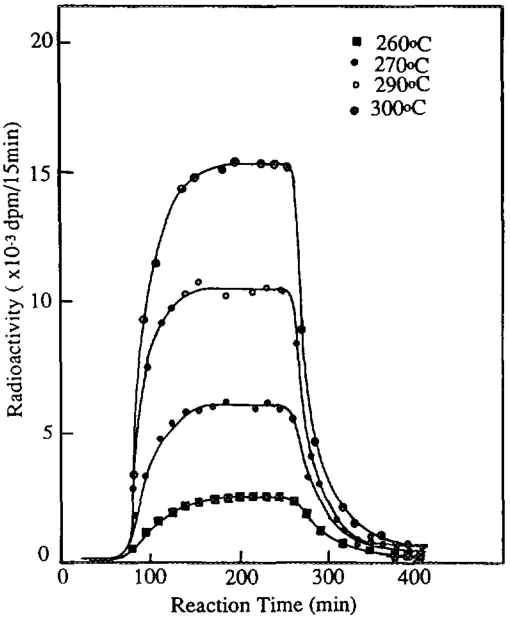

FIG. 2. Change in radioactivities of formed ^{35}S–H_2S with reaction time. Co–Mo/Al_2O_3, 50 kg/cm^2.

calin solvent (operation procedure 2). Figure 3 shows the change in radioactivities of the unreacted ^{35}S–DBT in liquid product and the produced ^{35}S–H_2S with the elapse of time at 300°C. When ^{35}S–DBT was replaced by ^{32}S–DBT (operation procedure 1), ^{35}S–H_2S was released (●). On the contrary, when ^{35}S–DBT was replaced by decalin (operation procedure 2), the radioactivity of ^{35}S–H_2S decreased immediately (○). This indicates that sulfur accommodated on the catalyst can not be released without supply of sulfur in DBT to the catalyst. Even though decalin was provided in hydrogen stream for about 4 h, ^{35}S was retained on the catalyst and ^{35}S–H_2S could be hardly detected. When decalin solvent was replaced again by solution of ^{32}S–DBT, ^{35}S was released as ^{35}S–H_2S and a peak of radioactivity was made as shown in Fig. 3. This peak area (D) was equal to the area (C).

Co/Al_2O_3

Hydrodesulfurization of ^{35}S–DBT catalyzed by Co/Al_2O_3 was performed with the operation procedure 1. The conversions de-

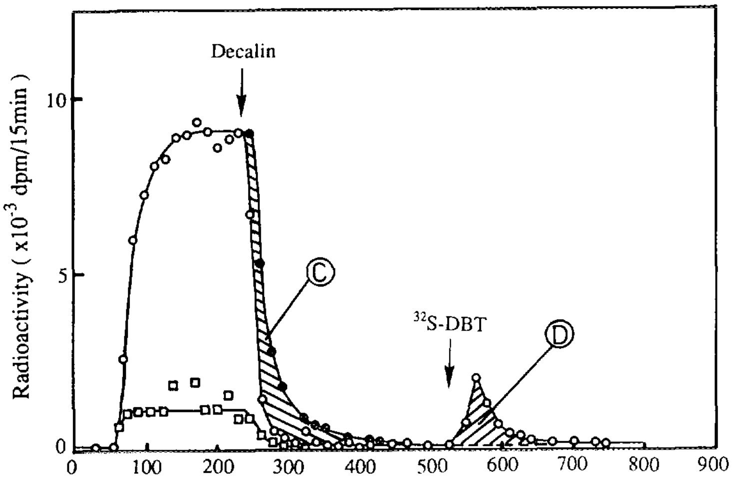

FIG. 3. Changes in radioactivities of unreacted ^{35}S–DBT and formed ^{35}S–H_2S with reaction time. Co–Mo/Al_2O_3, temperature 300°C and pressure 50 kg/cm^2. (□) Unreacted ^{35}S–DBT; (●) formed ^{35}S–H_2S in operation procedure 1, and (○) formed ^{35}S–H_2S in operation procedure 2.

rived from GC analysis were also in good agreement with the determination from ^{35}S-radioactivities of the liquid products (Table 1). In the case of Co/Al_2O_3 as well as $Co\text{-}Mo/Al_2O_3$, the steady state for the radioactivity of ^{35}S-DBT was immediately achieved at every reaction temperature, while the time delay of produced $^{35}S\text{-}H_2S$ to reach the steady state was about 150 min. This time delay for Co/Al_2O_3 at 400°C (Fig. 4) was longer than that with $Co\text{-}Mo/Al_2O_3$ at 270°C (Fig. 1). This result clearly shows that the time delay of $^{35}S\text{-}H_2S$ is not due to the adsorption of H_2S on Al_2O_3 but to the sulfur exchange within the sulfide.

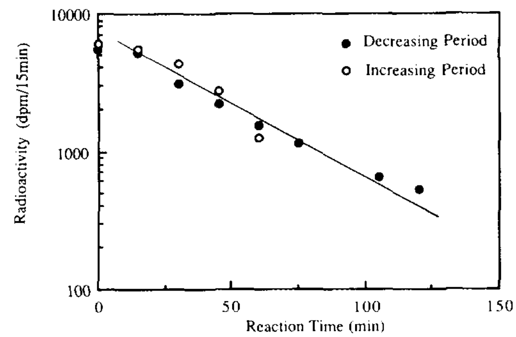

FIG. 5. First-order plots of $^{35}S\text{-}H_2S$ with reaction time. $Co\text{-}Mo/Al_2O_3$, temperature 270°C and pressure 50 kg/cm^2.

Calculation of the Rate Constant of $^{35}S\text{-}H_2S$ Release and the Amount of Labile Sulfur

Data for $Co\text{-}Mo/Al_2O_3$ and Co/Al_2O_3 were treated as follows: The first-order plot (Fig. 5) of the radioactivity of the decreasing period $^{35}S\text{-}H_2S$ in Fig. 1 indicates the linear relationship revealed as

$$\ln y = \ln z - kt, \qquad (1)$$

where y represents the radioactivity of $^{35}S\text{-}H_2S$ (dpm/min), z the radioactivity of $^{35}S\text{-}H_2S$ at steady state (dpm/min), k the rate constant of the release of $^{35}S\text{-}H_2S$ (min^{-1}), and t reaction time (min) (*30*). The slopes represent the rate constant of the release of $^{35}S\text{-}H_2S$. The rate constants at each temperature are also listed in Table 1. The activation energy of the release of $^{35}S\text{-}H_2S$ calculated from Arrhenius plot of the rate constants (Fig. 6) was 3.7 kcal/mol. The first order plot of the values, where each radioactivity of the increasing period of $^{35}S\text{-}H_2S$ in Fig. 1 is subtracted from that at steady state, also shows the linear relationship (○) in Fig. 5 and two slopes at this temperature are overlapped each other. This indicates that the rate of release of $^{35}S\text{-}H_2S$ is equal to that of $^{32}S\text{-}H_2S$.

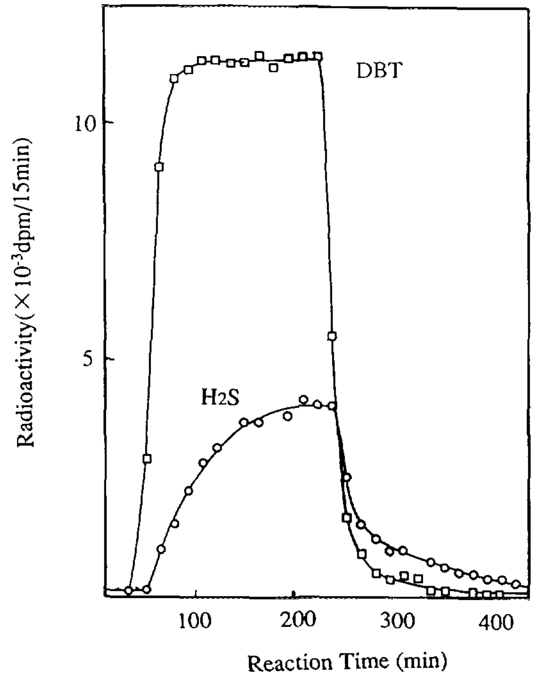

FIG. 4. Operation procedure in hydrodesulfurization of ^{35}S-DBT. Co/Al_2O_3, temperature 400°C and pressure 50 kg/cm^2.

After radioactivities of $^{35}S\text{-}H_2S$ reached the steady state, the difference of total radioactivities introduced from ^{35}S-DBT into the catalyst with those of the formed $^{35}S\text{-}H_2S$ is equivalent to total radioactivities remaining on the catalyst. This corresponds to an area (A) or (B) in Fig. 1. The area is z/k (dpm) which can be calculated from the integral (t: 0–∞) of Eq. (1). Since all ^{35}S on the catalyst was originated from the desul-

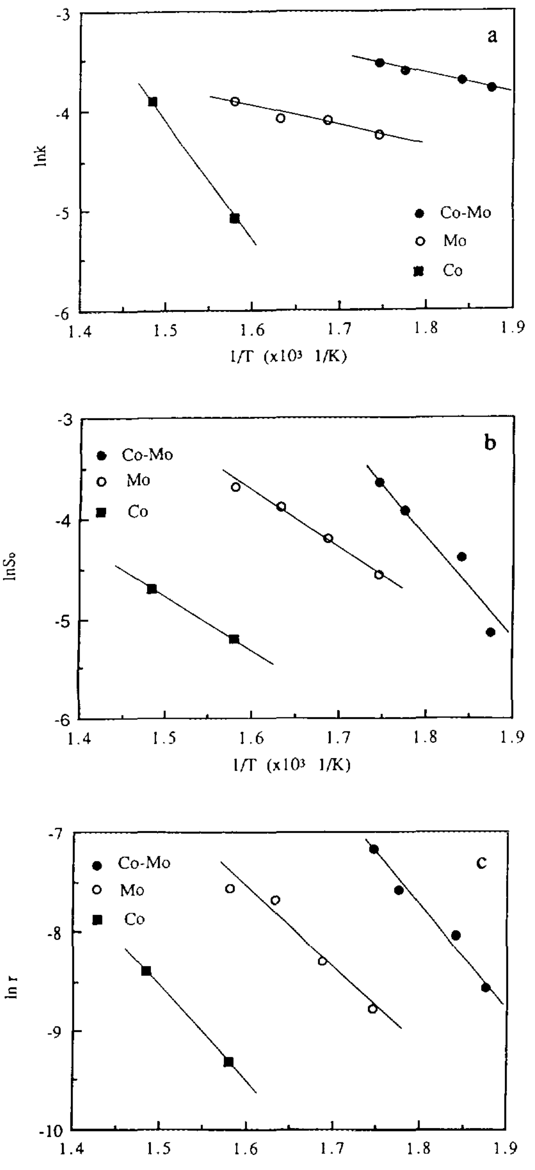

FIG. 6. Dependence of the rate constant of $^{35}S-H_2S$ release (k), the amount of labile sulfur (S_0), and the rate of DBT HDS (r) on temperature.

furization 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 can be assumed to be very small. The concentration of ^{35}S in sulfur of ^{35}S–DBT could be defined as $^{35}SDBT/SDBT$ (dpm/g), where $^{35}SDBT$ is radioactivities in 1 mol of DBT (dpm/mol) and SDBT is the amount of sulfur in 1 mol DBT (g/mol). According to this, the amount of labile sulfur on the catalyst (S_0) can be presented by $(z/k)/(^{35}SDBT/SDBT)$. These are also listed in Table 1.

If the sulfur on the catalyst was assumed to exist in Co_9S_8 and MoS_2 under the reaction condition (*33*), the total amount of sulfur on the catalyst is 70.1 mg/g.cat. At 50 kg/cm^2 and 300°C, the amount of labile sulfur was 26.1 mg/g.cat which corresponded to 37.2% of total sulfur in the catalyst (Table 1). Thus, we could conclude that the amount of labile sulfur on the catalyst increased with increasing temperature, and that only some portion of the total sulfur on the catalyst acts as active sites for HDS.

Dependence of the Rate Constant of ^{35}S–H_2S Release and the Amount of Labile Sulfur on Temperature

Dependence of S_0 on temperature is also shown in Fig. 6b, where the plot of ln So against 1/T indicate the linear relationship. This line can be revealed as follows:

$$\ln S_0 = \ln A + E/RT \qquad (2)$$

where S_0 is the amount of labile sulfur, A is the frequency factor, R is the gas constant, T is the temperature, and E is a constant. Dependence of S_0 on temperature can be determined by the value of E. E was 16.0 kcal/mol.

The product between the rate constant of the release of ^{35}S-H_2S and the amount of labile sulfur at each temperature ($S_0 \times k$) represents the rate of the release of H_2S which was nearly equal to the rate of DBT HDS (r) as shown in Table 1. Although the former was determined from the kinetic calculation of ^{35}S transfer and the latter was calculated from the conversion of DBT, both values should be same because the conversion of 1 mol of DBT forms 1 mol of H_2S in HDS. The agreement confirms the

TABLE 2

Dependence of the Rate Constants of Release of ^{35}S–H_2S, the Amount of Labile Sulfur, and the Rate of DBT HDS on Temperature

	Catalyst		
	Co–Mo/Al_2O_3	Co/Al_2O_3	Mo/Al_2O_3
Activation energy of release of ^{35}S–H_2S (kcal/mol)	3.7	9.9	4.2
Dependence of S_0 on temperature (kcal/mol)	16.0	9.9	10.7
Apparent activation energy of DBT HDS (kcal/mol)	19.7	19.8	14.9

validity of our remarks. Thus, the apparent activation energy (19.7 kcal/mol) calculated from plots of r vs $1/T$ shown in Fig. 6c is equal to the sum of the value of E (16.0 kcal/mol) and the activation energy of the release of ^{35}S–H_2S (3.7 kcal/mol).

Comparison between Co–Mo/Al_2O_3, Co/Al_2O_3, and Mo/Al_2O_3

The dependence of the rate constant of release of ^{35}S–H_2S (k), the amount of labile sulfur (S_0) and the rate of DBT HDS (r) on temperature was estimated in the cases of Co/Al_2O_3 and Mo/Al_2O_3 and the results are also shown in Figs. 6a–6c and Table 2, respectively. The dependence of the amount of labile sulfur on temperature in the case of Co–Mo/Al_2O_3 was largest among three. The ratios of the amount of labile sulfur to total sulfur were plotted against the rate of DBT HDS in Fig. 7 where the sulfurs on Co–Mo/Al_2O_3, Co/Al_2O_3, and Mo/Al_2O_3 were assumed to exist in Co_9S_8 and MoS_2, Co_9S_8, and MoS_2 under the reaction condition. The ratio decreased in the order Co/Al_2O_3 > Mo/Al_2O_3 > Co-Mo/Al_2O_3. If sulfur in Co_9S_8 of Co-Mo/Al_2O_3 was assumed to move prior to the movement of sulfur in MoS_2 of Co–Mo/Al_2O_3, the ratio of the labile sulfur in Co_9S_8 of Co–Mo/Al_2O_3 (○) was very close to that in Co_9S_8 of Co/Al_2O_3 in the range less than $r = 0.5 \times 10^{-3}$. Although the ratio was almost same at the rate of HDS, reaction temperature was quite different from each other and that of Co–Mo/Al_2O_3 was much lower than that of Co/Al_2O_3. In sulfided Co–Mo/Al_2O_3, it has been shown that cobalt sulfide is deposited on molybdenum sulfide (*17*). Sulfur in cobalt sulfide deposited on molybdenum sulfide

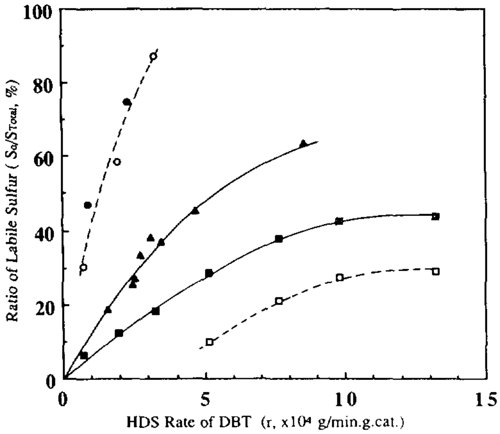

FIG. 7. Plots of ratio of labile sulfur vs rate of DBT HDS. For closed symbols, it was assumed that total sulfur in Mo/Al_2O_3 (▲) was present in the form MoS_2; total sulfur in Co–Mo/Al_2O_3 (■) was present in the form Co_9S_8 and MoS_2; total sulfur in Co/Al_2O_3 (●) was present in the form Co_9S_8. For open symbols which belong to Co–Mo/Al_2O_3, it was assumed that sulfur in MoS_2 cannot be labile until whole sulfur in Co_9S_8 becomes labile. In the range of r less than 5×10^{-4} g/(*min* g-*cat*), *ratio of labile sulfur in* Co–Mo/Al_2O_3 catalyst was estimated from $S_0/S_{Co_9S_8}$ (○); in the range of r more than 5×10^{-4} g/(min g-cat), ratio of labile sulfur in Co–Mo/Al_2O_3 catalyst was estimated from $(S_0-S_{Co_9S_8})/S_{MoS_2}$ (□). ($S_{Co_9S_8}$: total amount of sulfur present in the form of Co_9S_8 in Co–Mo/Al_2O_3 catalyst; S_{MoS_2}: total amount of sulfur present in the form of MoS_2 in Co–Mo/Al_2O_3 catalyst.)

may be more labile than that on alumina. In this case, the ratio of the labile sulfur in MoS_2 of Co–Mo/Al_2O_3 (☐) became lower in the range more than $r = 0.5 \times 10^{-3}$.

CONCLUDING REMARKS

HDS reactions of ^{35}S-labelled DBT on Co–Mo/Al_2O_3 and Co/Al_2O_3 were conducted to trace the behavior of ^{35}S on catalysts during practical performance of HDS. By the quantitative estimation of labile sulfur on the catalyst, it was found that the amount of labile sulfur increased with increasing temperature. This result suggests that the amount of the active catalytic site would increase with increasing temperature and the initial concentration of DBT. As described in previous report of HDS on Mo/Al_2O_3, this result indicates that active sites is not uniform. This is not consistent with the known kinetic description, such as Langmuir–Hinshelwood (L–H) rate equations, either (*34*). Because it is assumed in L–H mechanisms that the number of active sites for catalysis is constant and uniform, the values such as activation energy and heat of adsorption obtained there would be apparent.

REFERENCES

1. Kabe, T., Ishihara, A., and Tajima, H., *Ind. Eng. Chem. Res.* **31,** 1577 (1992).

2. Ishihara, A., Tajima, H., and Kabe, T., *Chem. Lett.*, 669 (1992).

3. Lipsch, J. G., and Schuit, G. C. A., *J. Catal.* **15,** 179 (1969).

4. Schuit, G. C. A., and Gates, B. C., *AIChE J* **19,** 3, 417 (1973).

5. Massoth, F. E., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 27, p. 265. Academic Press, New York, 1978.

6. Delmon, B., *in* "Proceedings, Climax 3rd International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 73. Climax Molybdenum Co., Ann Arbor, Michigan, 1979.

7. Voorhoeve, R. J. H., and Stuiver, J. C. M., *J. Catal.* **23,** 228 (1971).

8. Farragher, A. L. and Cossee, P., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), p. 1301. North-Holland, Amsterdam, 1973.

9. Ratnasamy, P., and Sivasanker, S., *Catal. Rev.-Sci. Eng.* **22,** 401 (1980).

10. Topsøe, H., Clausen, B. S., Candia, R., Wivel, C., and Morup, S., *J. Catal.* **68,** 433 (1981).

11. Wivel, C., Candia, R., Clausen, B. S., Mørup, S., and Topsøe, H., *J. Catal.* **68,** 453 (1981).

12. Topsøe, H., Clausen, B. S., Topsøe, N.-Y., and Pederson, E., *Ind. Eng. Chem. Fundam.* **25,** 2526 (1986).

13. Gage, M. W. J., de Beer, V. H. J., and van der Kraan, A. M., *Hyperfine Interact.* **69** (1–4), 795 (1991).

14. Clausen, B. S., Topsøe, H., Candia, R., Villadsen, J., Lengeler, B., Als-Nielsen, J., and Christensen, F., *J. Phys. Chem.* **85,** 3868 (1981).

15. Kulkarni, G. V., and Rao, C. N. R., *Catal. Lett.* **9**(5–6), 427 (1991).

16. Louwere, S. P. A., and Prins, R., *J. Catal.* **133,** 1 (1992).

17. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **84,** 386 (1983).

18. Okamoto, Y., Nakano, H., Shimokawa, T., Imanaka, T. and Teranishi, S., *J. Catal.* **50,** 447 (1977).

19. Salmeron, M., Somorjai, G. A., Wold, A., Chianelli, R. R., and Liang, K. S., *Chem. Phys. Lett.* **50,** 447 (1977).

20. Li, X. S., Xin, Q., Guo, X. X., Grange, P., and Delmon, B., *J. Catal.* **137,** 385 (1992).

21. Scheffer, B., Dekker, N. J. J., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121,** 31 (1990).

22. McCarthy, K. F., and Schrader, G. L., *J. Catal.* **103,** 261 (1987).

23. Lukens, H. R., Meisenheimer, J. R. G., and Wilson, J. N., *J. Phys. Chem.* **66,** 469 (1962).

24. Pavlova, K. A., Panteleea, B. D., Deryagina, E. N., and Kalechits, I. V., *Kinet. Katal.* **6**(3), 493 (1965).

25. Kalechits, I. V., and Deryagina, E. N., *Kinet. Katal.* **8**(3), 604 (1969).

26. Gachet, C. G., Dhainaut, E., de Mourgues, L., Candy, J. P., and Fouilloux, P., *Bull. Soc. Chim. Belg.* **90**(12), 1279 (1981).

27. Isagulyants, G. V., Greish, A. A., and Kogan, V. M., "Symposium of International Catalyst Annual Conference in Canada," p. 35, 1988.

28. Dobrovolszky, M., Tetenyi, D. M., and Zolton, P. P., *Chem. Eng. Commun.* **83,** 1 (1989).

29. Gellman, A. J., Bussell, M. E., and Somorjai, G. A., *J. Catal.* **107,** 103 (1987).

30. Kabe, T., Qian, W., Ogawa, S., and Ishihara, A., unpublished results.

31. Gilman, H., and Jacoby, A. L., *J. Org. Chem.* **4,** 108 (1939).

32. (a) Kobayashi, Y., Maudsley, D. V., "Biological Applications of Liquid Scintillation Counting." Academic Press, New York, 1974; (b) Horrocks, D. L., "Applications of Liquid Scintillation Counting." Academic Press, New York, 1974; (c) Crook, M., and Johnson, P. (Eds.), "Liquid Scintillation Counting," Vol. 4. Heyden, London, 1977.

33. de Beer, V. H. J., van Sint Fiet, T. H. M., van der Steen, G. H. A. M., Zwaga, A. C., and Schuit, G. C. A., *J. Catal.* **35,** 297 (1974).

34. Girgis, M. J., and Gates, B. C., *Ind. Eng. Chem. Res.* **30,** 2021 (1991).