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Elucidation of hydrodesulfurization mechanism using ^{35}S radioisotope pulse tracer methods

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Abstract

Molybdenum-based catalysts as hydrodesulfurization (HDS) catalysts are among the most important industrial catalysts. One of the new approaches characterizing the structure of such catalysts and the behavior of sulfur over the "working" catalyst is a ^{35}S radioisotope pulse tracer method (RPTM). By tracing the behavior of sulfur in the HDS reaction and sulfur exchange reaction over the sulfided Mo/Al_2O_3 and $Co–Mo/Al_2O_3$ catalysts under practical reaction conditions, it becomes possible for us to observe the catalytic behavior of the catalyst in situ. The formation process of active sites, the important role that H_2S plays in this process, and the promotion by cobalt for Mo/Al_2O_3 catalyst have become better understood. © 1997 Elsevier Science B.V.

Keywords: Mo/Al_2O_3 catalyst; $Co–Mo/Al_2O_3$ catalyst; Hydrodesulfurization; Radioisotope pulse tracer method

1. Introduction

In recent years, much attention has been focused on the deep hydrodesulfurization (HDS) of light gas oil because the environment regulations become more and more strict. In order to achieve this purpose, it is necessary to develop a new catalyst with high activity and selectivity. In our recent work, a series of attempts using the kinetic analysis method have been made to explore the mechanism of the HDS reaction of light gas oil [1–4]. Further, we also reported that H_2S, which is a product, strongly inhibits the HDS reaction [5]. Thus, it is necessary to consider the effect of H_2S when a detailed kinetic analysis on the HDS reaction is conducted.

On the other hand, one of the methods to enhance the catalytic activity is to increase the content of active metals such as molybdenum and promoter cobalt or nickel. For this purpose, the dispersion state of molybdenum on the alumina support for the molybdena-alumina catalyst and the promotion effect of cobalt on the reactivity of molybdena-alumina catalyst must be clarified. Lot of efforts have been made to accomplish these objectives and we have understood now relatively well for both structural and catalytic aspects. However, the behaviors of sulfur species on working catalysts still remain to be solved. Since a ^{35}S radioisotope tracer method makes it possible to more directly estimate the inherent behavior of sulfur, this method has been developed to determine the behavior of sulfur compound, formed H_2S and the sulfur on the catalyst surface.

In this paper, a detailed kinetic analysis of the HDS reactions of dibenzothiophenes catalyzed by

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unpromoted Mo/Al_2O_3 and Co-promoted Mo/Al_2O_3 catalysts were performed and the inhibition effect of H_2S was initially discussed. Second, the behavior of sulfur in the HDS reaction was investigated using the ^{35}S labeled dibenzothiophene. Then the sulfur exchange of H_2S with a $Co–Mo/Al_2O_3$ catalyst was described using a ^{35}S radioisotope pulse tracer method. The attempt is focused on what is the relationship between the catalyst structure and the amount of labile sulfur, how H_2S is formed from the labile sulfur on the catalyst, and what is the promotion effect of cobalt for the molybdenum catalyst. Finally, the correlation between the amount of labile sulfur, the rate constant of sulfur exchange and the activity of the catalyst is discussed.

2. Inhibition effect of H_2S on HDS reaction

There are a lot of sulfur-containing compounds such as alkyldibenzothiophene in light gas oil [6,7]. In a practical HDS of light gas oil, hence, the concentration of formed H_2S will actually be very high. The effect of H_2S on the HDS reaction cannot be neglected in a practical HDS of light gas oil. Therefore, the detailed kinetic analysis of HDS of dibenzothiophenes (DBTs) is important to more accurately understand the mechanism of hydrodesulfurization. In order to estimate the effect of H_2S on the reaction, H_2S, one of products of the HDS reaction, was added to the reaction system [5]. The HDS reaction was carried out in a high pressure fixed bed flow reactor under the following conditions: total pressure 50 atm, WHSV $70\ h^{-1}$, Gas/Oil 1100 NL/L, initial concentrations of DBTs 0.1–0.4 wt%, partial pressure of H_2S 0–0.88 atm, and temperature range between 180°C and 360°C.

Taking into account that the HDS rate of DBT was approximately zero order to the hydrogen pressure above 20 atm [5], we used a simple Langmuir–Hinshelwood rate Eq. (1) for the hydrodesulfurization of DBT:

$$r_{\mathrm{HDS}} = k_{\mathrm{HDS}} K_{\mathrm{DBT}} P_{\mathrm{DBT}} / (1 + K_{\mathrm{DBT}} P_{\mathrm{DBT}} + K_{\mathrm{H_2S}} P_{\mathrm{H_2S}}), \tag{1}$$

where r_{HDS} is the HDS rate, k_{HDS} is the rate constant of HDS, K_{DBT} and $K_{\mathrm{H_2S}}$ are the adsorption equilibrium constants of DBT and hydrogen sulfide, P_{DBT} and $P_{\mathrm{H_2S}}$ are partial pressures of DBT and hydrogen sulfide, respectively. The equation was also available for the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT).

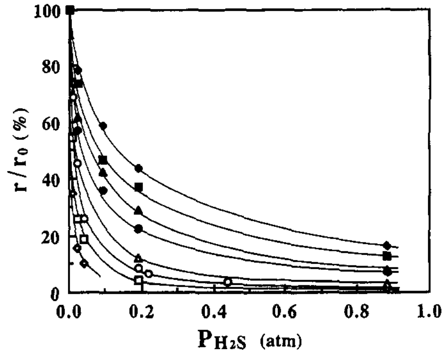


Fig. 1. Effect of partial pressure of H_2S on HDS reactivity of DBTs (50 atm, $Co–Mo/Al_2O_3$). r_0: HDS rate of DBTs without addition of H_2S; r: HDS rate of DBTs with addition of H_2S; open symbols for DBT: (◇) 200°C, (□) 220°C, (○) 240°C, (△) 260°C; solid symbols for 4,6-DMDBT: (●) 240°C, (▲) 260°C, (■) 280°C, (◆) 300°C.

Fig. 1 shows the effect of the partial pressure of H_2S on HDS rates of DBT and 4,6-DMDBT. Both the HDS rates of DBT and of 4,6-DMDBT decreased with increasing the partial pressure of H_2S. The HDS rate of DBT at the H_2S partial pressure of 0.19 atm decreased to about 9% and 12% of those without addition of H_2S at 240°C and 260°C, respectively. The HDS rate of 4,6-DMDBT at the H_2S partial pressure of 0.19 atm decreased to about 22% and 29% of those without addition of H_2S at 240°C and 260°C, respectively. This result indicated that the HDS rate of DBT was more strongly inhibited by H_2S as compared with 4,6-DMDBT. On the other hand, it can be observed that the retarding effects of H_2S on HDS of DBT and 4,6-DMDBT decrease with rising temperature. The inhibition of H_2S on the HDS rate of DBT over a Mo/Al_2O_3 (MoO_3: 12 wt%) catalyst at 240°C was compared with that over the $Co–Mo/Al_2O_3$ catalyst in Fig. 2. The inhibition of H_2S on Mo/Al_2O_3 was much stronger than that on $Co–Mo/Al_2O_3$. Similar results were also obtained in the HDS reaction of 4, 6-DMDBT.

The results obtained in the HDS reactions under several conditions were dealt with according to the Langmuir–Hinshelwood rate equation (1). The rate constants of HDS (k_{HDS}), the adsorption equilibrium

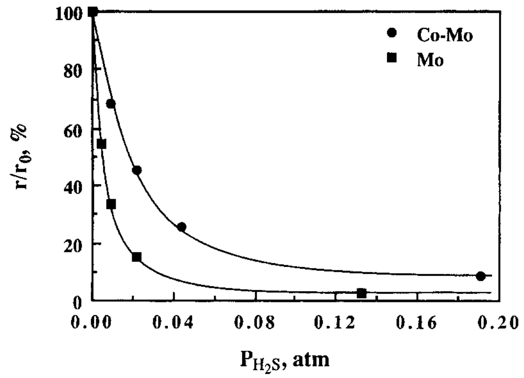


Fig. 2. Effect of partial pressure of H_2S on HDS reactivity of DBT (50 atm, 240°C).

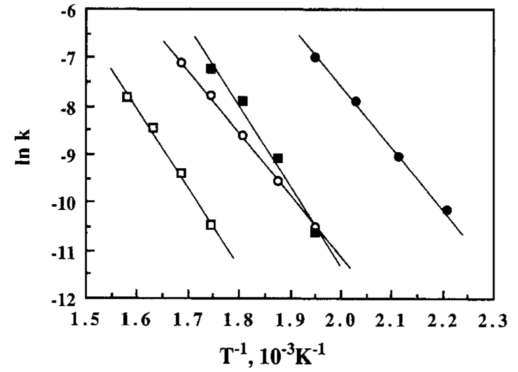


Fig. 3. Arrhenius plots of HDS reaction rate constants. Mo/Al_2O_3: (○) DBT; (□) 4,6-DMDBT; $Co–Mo/Al_2O_3$: (●) DBT, (■) 4,6-DMDBT.

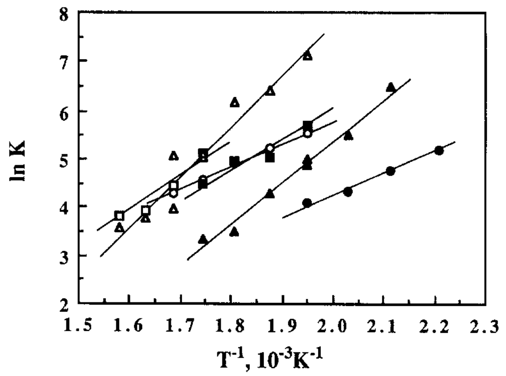


Fig. 4. Van't Hoff plots of adsorption equilibrium constants. Mo/Al_2O_3: (○) DBT, (□) 4,6-DMDBT, (△) H_2S; $Co–Mo/Al_2O_3$: (●) DBT, (■) 4,6-DMDBT, (▲) H_2S.

constants of DBTs (K_{DBTs}), and the adsorption equilibrium constants of hydrogen sulfide (K_{H_2S}) were calculated. Further, the activation energies of HDS reactions of DBTs, and the heats of adsorption of DBTs and H_2S on the catalyst were estimated from Arrhenius (Fig. 3) and van't Hoff plots (Fig. 4). The activation energies of HDS of DBT or 4,6-DMDBT on Mo/Al_2O_3 and $Co–Mo/Al_2O_3$ catalysts were almost the same, and these values were 24±2 and 33±2 kcal/mol, respectively (Fig. 3). Further, the heats of adsorption of DBT or 4,6-DMDBT on the two catalysts were approximately the same, and these values were 10±1 and 14±2 kcal/mol, respectively (Fig. 4). In contrast to this, the heats of adsorption of H_2S on Mo/Al_2O_3 and $Co–Mo/Al_2O_3$ were different from each other and were 21±1 and 17±1 kcal/mol, respectively. The heats of adsorption of DBT, 4,6-DMDBT and H_2S over each catalyst increased in the order DBT<4,6-DMDBT<H_2S. Moreover, the adsorption equilibrium constants over each catalyst also increased in the same order. This means that H_2S adsorbed more strongly than DBTs and thus inhibited the HDS of DBTs through competitive adsorption. This can be verified by fact that the inhibition of H_2S on the HDS of 4,6-DMDBT was less than that of DBT because 4,6-DMDBT more strongly adsorbs on the catalyst than DBT. Compared with the Mo/Al_2O_3 catalyst, all the adsorption equilibrium constants on the $Co–Mo/Al_2O_3$ catalyst decreased because of the addition of Co, as shown in Fig. 4. On the other hand, there were little change in the heats of adsorption of DBTs and only the heat of adsorption of H_2S on $Co–Mo/Al_2O_3$ catalyst was lowered from 21 to 17 kcal/mol. This means that the addition of Co relatively suppresses the competitive adsorption of H_2S with DBTs, and then decreases the inhibition of H_2S on the HDS reactions of DBTs, as shown in Fig. 2. Therefore, the promotion effect of Co for Mo/Al_2O_3 catalyst may be attributed to that Co enhances the mobility of sulfur on the catalyst and suppresses the inhibition of H_2S by weakening the adsorption of H_2S on the catalyst.

As mentioned above, H_2S may strongly influence the mobility of sulfur on the catalyst. In order to monitor the behavior of sulfur on working catalysts in situ the isotope tracer method may be very efficient. Therefore, the behavior of sulfur on the sulfided Mo/Al_2O_3 and $Co–Mo/Al_2O_3$ catalysts in the HDS of DBT and in the sulfur exchange with H_2S was investigated using the ^{35}S radioisotope pulse tracer method (RPTM).

3. Behavior of sulfur in HDS reaction

It was well known that DBTs are sulfur-containing compounds very difficult to desulfurize even under deep HDS conditions [2,7]. Therefore, DBT is a good model compound of sulfur-containing compounds present in light gas oil. We have synthesized the radioactive ^{35}S-labeled dibenzothiophene (^{35}S-DBT) and have directly performed the HDS reaction of ^{35}S-DBT on the sulfided Mo/Al_2O_3, $Co–Mo/Al_2O_3$ and $Ni–Mo/Al_2O_3$ catalysts under practical HDS conditions [8–11]. On the basis of quantitative analysis of the formation rate of ^{35}S-H_2S, it was found that the sulfur on the sulfided catalyst was labile, the amount of which varied with the reaction conditions. Here, a typical result of the HDS of ^{35}S-DBT over the sulfided $Co–Mo/Al_2O_3$ was initially used to simply present a ^{35}S RPTM.

The reaction was carried out with a pressurized fixed bed flow reactor [8]. Fig. 5 shows the changes in radioactivities of unreacted ^{35}S-DBT and formed ^{35}S-H_2S with reaction time at 260°C and 50 kg/cm^2. Initially, a decalin solution of 1 wt% dibenzothiophene (^{32}S-DBT) was pumped into the reactor until the conversion of DBT became constant (about 3 h). After that, decalin solution of 1 wt% ^{35}S-DBT was substituted for that of ^{32}S-DBT at about 200 min. The reaction with ^{35}S-DBT was performed until the formation amount of ^{35}S-H_2S became constant (about 3.5 h). Then the reactant solution was returned again to the decalin solution of 1 wt% ^{32}S-DBT at about 390 min and reacted for 4–5 h [10]. After ^{35}S-DBT was substituted for ^{32}S-DBT, the radioactivity 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. When the solution of ^{35}S-DBT returned to that of ^{32}S-DBT at about 390 min, the radioactivities of the unreacted ^{35}S-DBT also decreased immediately from the steady state to normal state. However, the time delay for the produced ^{35}S-H_2S from its steady state to normal state was about 130 min as shown in Fig. 5. These results indicate that the sulfur in DBT is not directly released as hydrogen sulfide but accommodates on the catalyst.

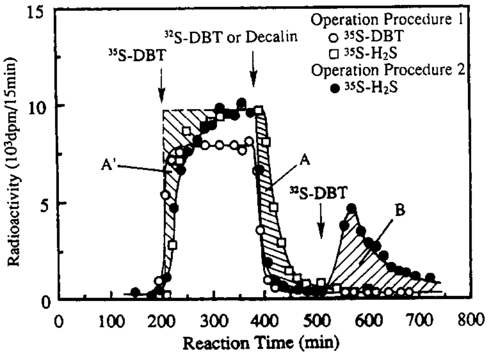


Fig. 5. Change in radioactivity of unreacted ^{35}S-DBT and formed ^{35}S-H_2S with reaction time. $Co–Mo/Al_2O_3$; 50 kg/cm^2; 260°C; DBT: 1 wt%.

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 at about 390 min. The change in radioactivity of the produced ^{35}S-H_2S [●] with the reaction time was also shown in Fig. 5. When decalin solvent was substituted for the solution of ^{35}S-DBT, the release of ^{35}S-H_2S rapidly decreased, indicating that a portion of ^{35}S, which is represented with the shade area A in Fig. 5, remained on the catalyst. When decalin solvent was replaced with ^{32}S-DBT at 505 min in Fig. 5, this portion of ^{35}S was released as ^{35}S-H_2S, again (shaded area B). This portion of ^{35}S was approximately equal to shaded area A, denoted as the total amount of labile sulfur on the catalyst under this reaction condition. According to the method reported in [8], the amount of labile sulfur can be calculated from the total radioactivity of released ^{35}S-H_2S after ^{32}S-DBT was introduced again, 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 15.6 mg of sulfur/g of catalyst and 22.5%, respectively (Table 1).

To more accurately discuss the release process of ^{35}S-H_2S, the release rate constant was determined. It was found that, after ^{32}S-DBT was substituted for decalin solvent, the release of ^{35}S-H_2S from the catalyst could be fit with a first-order reaction. Thus, the release rate constant of ^{35}S-H_2S (k), i.e., the rate constant of sulfur exchange was determined [12] and is listed in Table 1. The results at several temperatures

Table 1
Results of HDS reactions and exchange reactions on sulfided Co–Mo/Al_2O_3 (50 kg/cm^2)

Temperature (°C)	240	260	280	260	260
Reactant	DBT[b]	DBT[b]	DBT[b]	DBT+H_2S[c]	H_2S[d]
Conversion (%)	29.5	62.3	90.9	21.1	—
Concentration of H_2S[e] (vol%)	0.040	0.084	0.125	0.329	0.300
Rate constant, k (10^{-2} min^{-1})	1.90	3.20	3.72	8.21	8.14
Labile sulfur, S_0 (mg/g-cat.)	13.1	15.6	21.8	15.8	16.1
S_0/S_{Total}[f] (%)	18.9	22.5	31.4	22.8	23.2

[a] The catalyst was labeled by ^{35}S in the HDS reaction of ^{35}S-DBT.
[b] Dibenzothiophene.
[c] Dibenzothiophene+0.3 vol% H_2S.
[d] 0.3 vol% H_2S.
[e] The total concentration of H_2S formed and added.
[f] S_{Total} is defined as the amount of total sulfur when metal sulfides were present as MoS_2 and Co_9S_8.

are also listed in Table 1. The ratios of the amounts of labile sulfur to total sulfur increased from 18.9% to 31.4% with increasing temperature from 240°C to 280°C.

The same experiments were also carried out over the sulfided Mo/Al_2O_3 catalyst with 12 wt% MoO_3 [13], and the results are listed in Table 2. The amount of labile sulfur on the Mo/Al_2O_3 at 360°C (11.4 mg/g-cat.) is less than that on the Co–Mo/Al_2O_3 at 240°C (13.1 mg/g-cat.). That is, the difference in temperature of over 120°C is necessary to make the same amount of labile sulfur on the Mo/Al_2O_3 mobile as compared with the Co–Mo/Al_2O_3. This indicates that the addition of Co makes the sulfur on Mo/Al_2O_3 more labile.

In order to investigate the role that H_2S plays in the HDS reaction in detail, a gas of 0.3 vol% ^{32}S-H_2S in H_2 was introduced into the Co–Mo/Al_2O_3, which was labeled with ^{35}S in HDS of ^{35}S-DBT at 50 kg/cm^2 and 260°C. The change in radioactivity of formed ^{35}S-H_2S with the reaction time is shown in Fig. 6. Although ^{35}S remaining on the catalyst was also exchanged by ^{32}S in ^{32}S-H_2S and released as ^{35}S-H_2S, the release rate of ^{35}S-H_2S from the catalyst was much faster than that in the case of DBT. As shown in Table 1, the total amount of released ^{35}S was approximately equal to the amount of ^{35}S accommodated on the catalyst in the reaction of ^{35}S-DBT. This shows that all the 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.

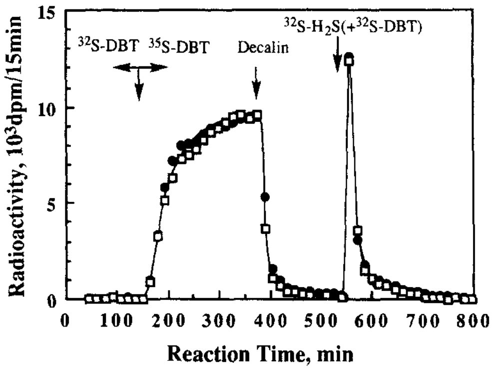


Fig. 6. Release of ^{35}S-H_2S in sulfur exchange reaction. (□) 0.3 vol% H_2S; (●) 0.3 vol% H_2S+1.0 wt% DBT.

Table 2
Results of HDS reaction on sulfided Mo/Al_2O_3 (MoO_3: 12.0 wt%) (50 kg/cm^2)

Temperature (°C)	320	340	360
Conversion (%)	26.2	46.1	66.9
Rate constant, k (10^{-2} min^{-1})	2.63	3.53	4.62
Labile sulfur, S_0 (mg/g-cat.)	8.04	10.1	11.4
S_0/S_{Total}[a] (%)	15.1	18.9	21.4

[a] For notation, see Table 1.

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 to the catalyst, which was labeled with ^{35}S in HDS of ^{35}S-DBT at 50 kg/cm^2 and 260°C. The result is also shown in Fig. 6. As described in Section 2, the HDS of DBT was inhibited by H_2S. Moreover, the release rate constant of ^{35}S-H_2S significantly increased from 3.20×10^{-2} to 8.21×10^{-2} min^{-1} but the amount of labile sulfur did not change with the addition of H_2S. As shown in Table 1, the release rate constant of ^{35}S-H_2S at 260°C decreased in the order: H_2S+DBT>H_2S>DBT. This is consistent with the decreasing order of total concentrations of H_2S, which is the sum of concentration of H_2S formed in HDS of DBT and added H_2S, as shown in Table 1. The rate of sulfur exchange may depend on the supply rate of sulfur to the catalyst. Thus the increase in H_2S concentration will increase the rate of sulfur exchange. In addition, the sulfur on the catalyst may preferably be exchanged with H_2S because H_2S more strongly adsorbed on the catalyst than DBT, as mentioned in Section 2.

4. Sulfur exchange reaction with ^{35}S-H_2S

In order to more accurately comprehend the role of H_2S in the sulfur exchange, the sulfur exchange of ^{35}S-labeled hydrogen sulfide (^{35}S-H_2S) with the Co–Mo/Al_2O_3 was carried out [12]. Fig. 7 shows the change in radioactivity of released ^{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-H_2S in hydrogen. The ^{35}S-labeled catalyst, then, was purged with N_2 and 0.1 vol% ^{32}S-H_2S in hydrogen was introduced at about 460 min again. Similar to the case of the HDS of ^{35}S-DBT, the radioactivity of released ^{35}S-H_2S slowly increased and approached a steady state after ^{35}S-H_2S was introduced for about 120 min. When N_2 was introduced, the release of ^{35}S-H_2S decreased immediately, indicating that a portion of ^{35}S, corresponding to the shaded area A, was accommodated to the catalyst. This portion of ^{35}S remained on the catalyst released as ^{35}S-H_2S after N_2 was subsequently replaced by ^{32}S-H_2S at about 460 min, as shown in Fig. 7 (area B). This portion of ^{35}S represented the total amount of sulfur exchanged on the catalyst under this reaction condition. The amount of labile sulfur (S_0) can be calculated from the total radioactivity corresponding to area B and is listed in Table 3. Similar to the case of the HDS reaction, a first-order plot of the release rate of ^{35}S-H_2S could be drawn and a good linear relationship was also obtained [12]. The exchange rate constant (k) was also determined and is presented in Table 3.

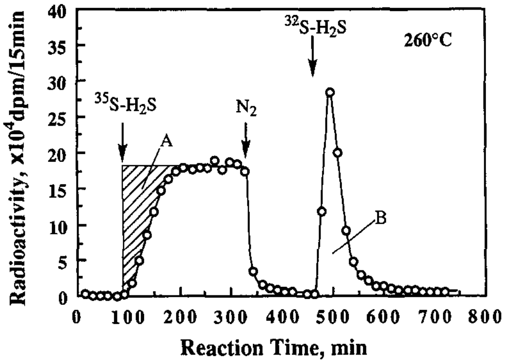


Fig. 7. Change in radioactivity of released ^{35}S-H_2S with reaction time. 50 kg/cm^2; 0.1 vol% H_2S; 80 ml/min.

To investigate the effect of pressure, the experiments were performed at 10, 30 and 50 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, 0.03 and 0.05 kg/cm^2. The amounts of labile sulfur and the exchange rate constants were obtained according to the same method and are presented in Table 3. 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. 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 (Table 3). The concentration of H_2S represented the supply rate of sulfur to the catalyst because other reaction conditions were maintained as constant. Actually, the rate of sulfur exchange decreased with decreasing the supply rate of sulfur to the catalyst. This indicates that the supply rate of sulfur may be the rate-determining step of sulfur exchange reaction and that the rate of sulfur exchange with H_2S is much more rapid than that predicted.

The amounts of labile sulfur in sulfur exchange at several temperatures are summarized in Table 3. The ratios of the amounts of labile sulfur to total sulfur increased from 21.1% to 44.0% with increasing temperature from 260°C to 400°C. Further, it is observed that the sulfur exchange reactions were very rapid at each temperature.

The amounts of labile sulfur (S_0, ●) listed in Table 3 are plotted against temperatures in Fig. 8.

Table 3
Results of sulfur exchange reactions on sulfided Co–Mo/Al_2O_3

Reaction pressure (kg/cm^2)	50	50	50	30	10	50	50	50
Reaction temperature (°C)	260	260	260	260	260	300	400	400
Flow rate of gas (ml/min)	80	80	208	80	80	80	80	208
Concentration of H_2S (vol%)	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Partial pressure of H_2S (kg/cm^2)	0.03	0.05	0.05	0.03	0.01	0.05	0.05	0.05
Exchange rate constant, k (10^{-2} min^{-1})	2.43	4.02	8.07	3.82	4.02	3.12	2.17	4.05
Labile sulfur, S_0 (mg/g.cat.)	14.6	15.3	14.5	15.5	14.5	19.7	30.5	29.4
S_0/S_{Total}[a] (%)	21.1	22.1	20.9	22.4	20.9	28.4	44.0	42.4

[a] For notation, see Table 1.

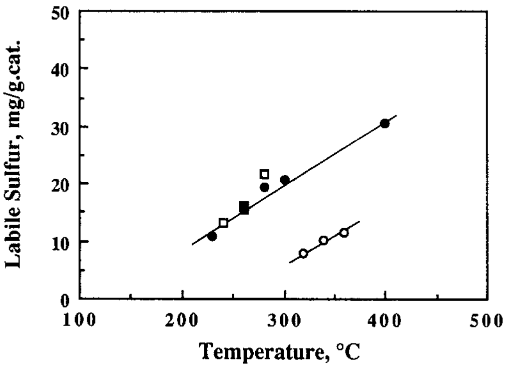
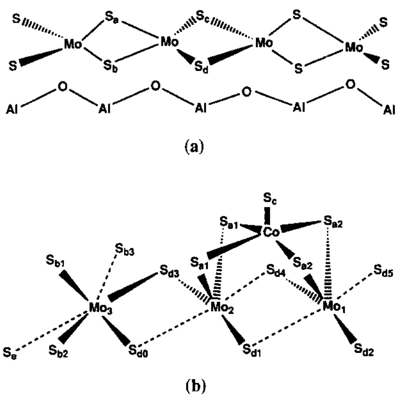


Fig. 8. Effect of temperature on amount of labile sulfur. Co–Mo/Al_2O_3: (□) from Table 1, (●) from Table 3; Mo/Al_2O_3: (○) from Table 2.


(a)

(b)

Fig. 9. (a) Structure of MoS_2 on sulfided Mo/Al_2O_3; (b) deformed tetrahedral structure of MoS_2 and structure of Co–S–Mo on sulfided Co–Mo/Al_2O_3.

For the Co–Mo/Al_2O_3 catalyst, the amount of labile sulfur increased with raising temperature from 200°C to 400°C. This indicates that labile sulfur on the catalyst may be not uniform, i.e., the strengths of sulfur bonds may be different from each other.

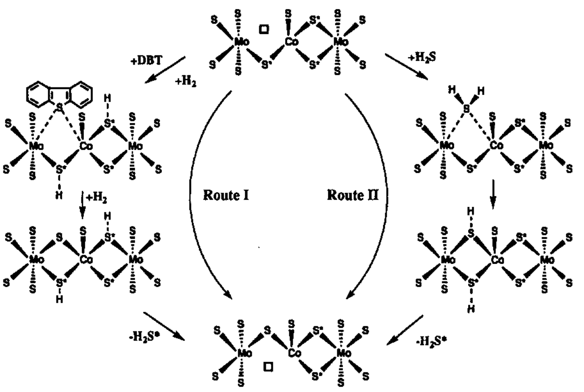
5. Structures of sulfided catalysts

It is commonly accepted that molybdenum interacts with hydroxyl group on the alumina carrier surface, resulting in the formation of a monolayer structure [13–16]. In a previous paper [13], the HDS of radioactive ^{35}S-DBT was carried out over a series of sulfided molybdena-alumina catalysts containing 6–20 wt% molybdena at several temperatures between 280°C and 380°C and under 50 kg/cm^2. The apparent activation energies were 20±2 kcal/mol for all catalysts, indicating that the mechanism of HDS and the nature of active sites did not vary with molybdenum content. Moreover, the amount of labile sulfur increased linearly with the molybdena content up to 16 wt%, indicating that monolayer dispersion of molybdenum sulfide on alumina was maintained up to 16 wt%. This agrees with our early work [17], where the monolayer dispersion of molybdenum on alumina was maintained up to 8–12 wt% molybdenum, i.e., 12–18 wt% molybdena. 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. 9(a) [11].

For a sulfided Co–Mo/Al_2O_3, the structure of MoS_2-like phase located in the edge may be rearranged because of the presence of Co atoms, and a square pyramidal model may be an acceptable model [18–20]. In recent works, Louwers and Prins have given further evidence about this model with EXAFS [21,22]. The square pyramidal coordination of the Co or Ni atom resembles that of the millerite structures. A Co atom is connected to MoS_2 by four sulfur atoms. An additional sulfur atom is attached to a Co atom. As proposed in [11], even in this model, one could still consider that the structure of MoS_2 was a deformed tetrahedral structure and only the locations of other two weak Mo–S bonds within the layers are changed, as shown in Fig. 9 (Structure b). The Mo_1–S_{d1} or Mo_2–S_{d0}, and Mo_1–S_{d5} or Mo_2–S_{d4} bonds were considered as the two weak bonds assigned to the van der Waals type in this structure. This is consistent with the bond energies of metal sulfide calculated by Nørskov et al. [23] and Topsøe et al. [24], where the bond energies of metal sulfide varied as follows: cobalt sulfide>molybdenum sulfide>CoMoS. Therefore, it is reasonable that the sulfurs in MoS_2 phase adjacent to Co or Ni atoms, i.e., S_{a1} or S_{a2} as shown in Fig. 9 (Structure b), were more labile and were preferably exchanged below 400°C. On the other hand, as temperature is raised over 400°C, moderately or strongly bonded sulfur, i.e., S_b, S_c, S_d and S_e in Fig. 9 (Structure b), will become mobile and will also be exchanged. Since the HDS reaction is usually carried out below 400°C, the portion of labile sulfur exchangeable below 400°C will more closely relate to the HDS reaction.

6. Relation between HDS rate, labile sulfur and sulfur exchange rate

In order to understand the behavior of sulfur in the HDS reaction, the amounts of labile sulfur on the sulfided Co–Mo/Al_2O_3 [□] listed in Table 1 are plotted against temperature and added to Fig. 8. Essentially, there is less 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 may be 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 as shown in Fig. 10, where it was illustrated that some of the labile sulfur present in the form of Co–Mo–S phases desorb as H_2S from the catalyst and formed the vacancy. In the sulfur exchange with H_2S (Route II), 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 [12]. In HDS (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 both routes, the migration of vacancies on the catalyst always occurs due to the transformation between labile sulfur and vacancies on the catalyst surface. Massoth and Zeuthen [25] also postulated the migration of vacancies on the catalyst due to high mobility of labile sulfur. Table 3 shows that the exchange rate of sulfur in the sulfur exchange reactions is very rapid at every temperature. 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.



S*: ^{35}S; □ : Anion vacancy

Route I: Hydrodesulfurization; Route II: Sulfur Exchange

Fig. 10. Transformation between labile sulfur and vacancies on sulfided Co–Mo/Al_2O_3 in HDS.

Because a product of labile sulfur and the rate constant of sulfur exchange could be correlated with the HDS rate well, it was proposed that, under a given reaction condition, the amount of labile sulfur is correlated with the total amount of 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 (Table 4) [12]. Therefore, the

Table 4
Results of sulfur exchange reactions on sulfided Mo/Al_2O_3 (MoO_3: 12.0 wt%) (50 kg/cm^2; flow rate of gas: 208 ml/min; concentration of H_2S: 1.0 vol%)

Temperature (°C)	300	400	450
Exchange rate constant, k (10^{-2} min^{-1})	6.15	4.65	4.30
Labile sulfur, S_0 (mg/g-cat.)	6.91	12.0	15.7
S_0/S_{Total}[a] (%)	13.0	22.5	29.4

[a] For notation, see Table 1.

inhibiting effect of H_2S as described in Section 2 may be explained as follows. As mentioned in Section 4, the sulfur exchange rate with H_2S depended on the supply rate of sulfur to the catalyst, indicating that the rate of sulfur exchange was very rapid. Thus, a rapid adsorption/desorption of H_2S will always take place in the presence of H_2S formed in the HDS reaction, leading to an equilibrium of sulfur exchange with H_2S through route II, as shown in Fig. 10. When H_2S is added in the HDS of DBT, the rate of sulfur exchange with H_2S through route II will increase and a new equilibrium of sulfur exchange with H_2S will be established again. As a result, the number of vacancies will decrease although the amount of labile sulfur is constant under a given reaction condition. Thus, the HDS rate of DBT through the route I will be lowered with the addition of H_2S.

The amounts of labile sulfur on the Mo/Al_2O_3 (Table 2) are also plotted against temperature in Fig. 8 [○] to compare with Co–Mo/Al_2O_3 catalyst. The amount of labile sulfur in the case of the former was much less than that in the case of the latter. The sulfur on the Co–Mo/Al_2O_3 catalyst was more mobile than that on the Mo/Al_2O_3 catalyst. Co makes the sulfur bonded with both Mo and Co atoms, which might be the sulfur in the so-called 'CoMoS' phase, more mobile [11]. Therefore, the addition of cobalt will enhance the formation and desorption of H_2S from the labile sulfur, which may be the rate-determining step of HDS reactions. This agreed with the results of kinetic analysis in Section 2, where the addition of cobalt lowered the heat of adsorption of H_2S. Therefore, the promotion effect of cobalt for the Mo/Al_2O_3 catalyst is that cobalt lowers the strength of sulfur–molybdenum bond, and then the formation of H_2S from labile sulfur and subsequent desorption becomes more easy.

7. Conclusions

Many insights into the structure and catalytic properties of the sulfided Mo-based catalysts have been obtained using ^{35}S radioisotope pulse tracer methods (RPTM). These methods are important not only to elucidate the structure of actually working catalysts but also to design a completely new type of catalyst. It was found that the amount of labile sulfur increased with increasing temperature, and the release rate of ^{35}S-H_2S increased with increasing a supply rate of sulfur. The sulfur exchange with H_2S 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_2S suggests 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.

It was also suggested that the addition of H_2S inhibited the HDS reaction of DBTs through decreasing the amount of active sites participating in the HDS reaction of DBTs. Further, the promotion effect of cobalt for Mo/Al_2O_3 catalyst may be because the addition of Co resulted in decrease in the strength of sulfur–molybdenum bond. Thus the formation of H_2S from labile sulfur and subsequent desorption on Co–Mo/Al_2O_3 catalyst becomes more easy as compared with Mo/Al_2O_3 catalyst.

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