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Sulfur exchange on Co–Mo/Al_2O_3 hydrodesulfurization catalyst using ^{35}S radioisotope tracer

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Abstract

A commercial Co–Mo/Al_2O_3 catalyst was labeled with the radioisotope ^{35}S in hydrodesulfurization (HDS) of ^{35}S-labeled dibenzothiophene (^{35}S-DBT) in a high-pressure flow reactor at 50 kg/cm^2. Then, HDS of 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) or sulfur exchange of H_2S were carried out on the labeled catalyst at 50 kg/cm^2 and 260–360°C. The amounts of labile sulfur participating in the reaction were determined from the radioactivity of ^{35}S-H_2S released from the ^{35}S-labeled catalyst. In the HDS reactions, the amount of labile sulfur participating in the reaction decreased in the order: DBT > 4-MDBT > 4,6-DMDBT. In the sulfur exchange reaction with H_2S, the adsorption of H_2S on the catalyst reached saturation above a H_2S partial pressure of 0.36 kg/cm^2. It was suggested that the release of H_2S from the labile sulfur may be the rate determining step of the HDS reaction.

1. Introduction

Recently, much attention has been focused on deep hydrodesulfurization (HDS) of light oil. It was reported that methyl substitution at 4 and 6-position of dibenzothiophene remarkably retarded the rate of HDS and that 4-methyldibenzothiophene (4-MDBT) or 4,6-dimethyldibenzothiophene (4,6-DMDBT) was very difficult to remove even under deep desulfurization conditions [1–3]. Although the kinetic studies on HDS of dibenzothiophenes were carried out [2–4], the exact reason why the difference of HDS rate of DBTs was caused has not been clarified yet. In recent years, ^{35}S radioisotope tracer method has been developed [5–8]. We conducted directly the HDS reaction of ^{35}S-labeled dibenzothiophene to trace the behavior of ^{35}S on sulfided Mo-based catalysts during practical HDS [9–11]. By tracing the changes in radioactivities of unreacted ^{35}S-DBT and formed ^{35}S-H_2S, the behavior of sulfur on the catalyst was determined. It was found that the sulfur on the catalyst was mobile and that the reactivity of the catalyst changed depending on the amount of labile sulfur and the conversion rate between the labile sulfur and the active sites. Co or Ni made the sulfur in MoS_2 phase adjacent to the promoter atom more labile.

In this paper, we attempt to elucidate the retarding effect of methyl substituents on the HDS reaction of DBTs using ^{35}S radioisotope tracer. After a Co–Mo/Al_2O_3 catalyst was labeled with ^{35}S during HDS of ^{35}S-DBT, the HDS reactions of 4-MDBT and 4,6-DMDBT or the exchange reactions with H_2S were carried out on the catalyst. The extent of sulfur exchange was determined.

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2. Experimental

^{32}S-DBT, ^{35}S-DBT, 4-MDBT and 4,6-DMDBT were synthesized according to the methods reported in previous papers [4,10]. A commercial Co–Mo/Al_2O_3 (Ketjen Fine-124) was used and presulfided with 3 vol.-% H_2S/H_2 at 400°C for 3 h. The reactions were carried out with a high-pressure-flow reactor at 50 kg/cm^2, 260-360°C, WHSV 28–70 h^{-1}, amount of catalyst 0.2–1.0 g. The concentrations of sulfur compounds in decalin were 0.1–3.0 wt.-% and of H_2S in H_2 were 0.12–3.4 vol.-%. Products were analyzed by a gas chromatography. The produced ^{35}S-H_2S was absorbed by bubbling through a basic scintillation solution. The radioactivity was measured by a liquid scintillation counter.

Typical two operation procedures were as follows: Operation procedure 1: (i) A decalin solution of 1 wt.-% ^{32}S-DBT was fed into the reactor until the conversion of DBT became constant. (ii) After that, the reactant solution was switched on to a decalin solution of 1 wt.-% ^{35}S-DBT until the amount of ^{35}S-H_2S released from the exit of reactor became constant (about 2.5 h). (iii) 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 (i) and (ii) in this procedure were the same with them in Operation procedure 1. (iii) The reactant solution of ^{35}S-DBT was replaced by decalin and the catalyst was purged with H_2 for about 3 h. (iv) Then, a solution of sulfur compound or a mixed gas of H_2S and H_2 was introduced and reacted for about 3.5 h.

3. Results and discussion

3.1. *Label of labile sulfur on the catalyst during HDS of ^{35}S-DBT*

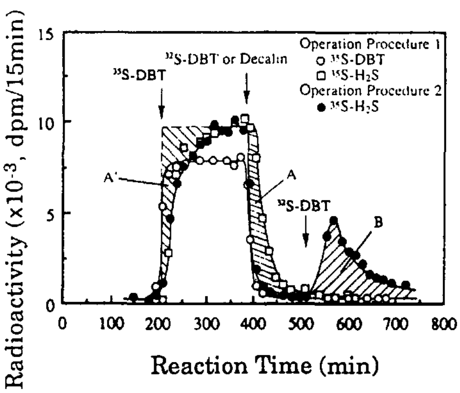

Fig. 1. Change in radioactivity of formed ^{35}S-H_2S with reaction time.

Fig. 1 displays the change in radioactivity with reaction time at 260°C, 50 kg/cm^2 and WHSV 28 h^{-1} (Amount of Catalyst: 1.0 g) according to the operation procedure 1. After ^{35}S-DBT was substituted for ^{32}S-DBT, the radioactivities of the unreacted ^{35}S-DBT increased and attained a steady state immediately. In the case of the produced ^{35}S-H_2S, however, about 130 min was needed to attain the steady state. 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, but the time delay for the produced ^{35}S-H_2S from its steady state to normal state was about 130 min. This indicates that the sulfur in DBT did not directly release as hydrogen sulfide but was retained on the catalyst. On the other hand, when ^{35}S-DBT solution was replaced by a decalin solvent according to the operation procedure 2, the radioactivity of formed ^{35}S-H_2S decreased immediately (Fig. 1). This indicates that a portion of ^{35}S (Area A or A') remained on the catalyst when only decalin flowed throughout the catalyst. ^{35}S-H_2S was hardly released even in the reduction atmosphere of high pressure of hydrogen. However, when ^{32}S-DBT solution at 510 min was introduced, this portion of ^{35}S was released as ^{35}S-H_2S again (Area B). This portion of ^{35}S was approximately equal to Area A that represented the total amount of labile sulfur on the catalyst under this reaction condition. Thus, one can consider that the labile sulfur on the catalyst

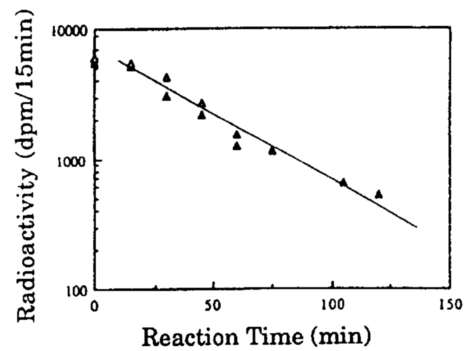

Fig. 2. First order plot of release $^{35}S\text{-}H_2S$.

was labeled completely by ^{35}S in the reaction process from the step (i) to (ii).

3.2. *Release rate of $^{35}S\text{-}H_2S$ from the catalyst and the amount of labile sulfur*

After ^{32}S-DBT was substituted for ^{35}S-DBT again, the first order plot of the radioactivity of produced $^{35}S\text{-}H_2S$ showed a linear relationship as shown in Fig. 2. This line can be expressed as:

$$\ln y = \ln z - kt \quad (1)$$

where y denotes the release rate of $^{35}S\text{-}H_2S$ (dpm/min), z the maximum release rate (dpm/min), k the release rate constant (min^{-1}), t the reaction time (min). The release rate constant of $^{35}S\text{-}H_2S$ was determined from the slope of linear relationship and listed in Table 1.

Since all ^{35}S on the catalyst originated from the desulfurization of ^{35}S-DBT and the isotope effect between ^{35}S and ^{32}S was negligible [10], the concentration of ^{35}S in sulfur introduced to the catalyst by HDS of ^{35}S-DBT should be equal to the concentration of ^{35}S in sulfur of ^{35}S-DBT. The concentration of ^{35}S in sulfur of ^{35}S-DBT could be defined as $^{35}S_{\text{DBT}}/S_{\text{DBT}}$ (dpm/g), where $^{35}S_{\text{DBT}}$ is radioactivity 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 exchange sulfur, i.e., labile sulfur, can be calculated from $S_a/(^{35}S_{\text{DBT}}/S_{\text{DBT}})$, where S_a is the total radioactivity released in step (iv) of operation procedure 2 and was presented in Table 1.

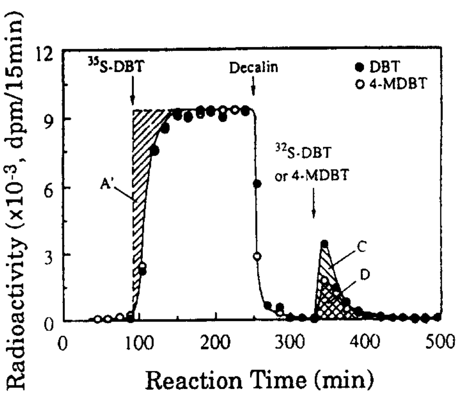

Fig. 3. Change in radioactivity of formed $^{35}S\text{-}H_2S$ with reaction time.

3.3. *Release of $^{35}S\text{-}H_2S$ during HDS of 4-MDBT and 4,6-DMDBT*

After labeled by ^{35}S at 340°C, 50 kg/cm^2 and WHSV 70 h^{-1} (Amount of Catalyst: 0.2 g) the catalyst was purged with H_2. A decalin solution of 1.0 wt.-% 4-MDBT was then introduced in step (iv) of operation procedure 2. ^{35}S remaining on the catalyst was also exchanged and released as $^{35}S\text{-}H_2S$ (Fig. 3). However, the

Table 1
Results of HDS reaction

Sulfur compounds	DBT			4-MDBT				4,6-DMDBT		
Temperature (°C)	260	340	340	260	320	340	340	320	340	360
Concentration (wt.-%)	1.0	1.0	3.0	1.0	0.4	0.4	1.0	0.4	1.0	0.4
Amount exchanged ($\times 10^3$ dpm)	4.9	12.0	11.4	1.5	5.69	6.49	10.7	2.80	5.57	4.87
Release rate constant, k ($\times 10^{-2}$/min)	2.73	8.86	13.0	0.41	1.92	1.33	3.71	0.73	2.77	2.83
Labile sulfur (mg/g cat.)	13.7	32.4	32.1	4.3	16.0	17.6	29.2	7.6	15.1	13.8
HDS rate, (mg/min/g cat.)	0.38	1.89	4.27	0.10	0.32	0.61	1.15	0.13	0.45	0.34

Reaction conditions: 50 kg/cm^2, WHSV 70 h^{-1}, catalyst: 0.2 g.

release rate was slower and total amount of released ^{35}S-H_2S (Area D) was less than that in the case of DBT (Area C) as shown in Fig. 3 and Table 1.

When the decalin solution of 0.4 wt.-% 4-MDBT was used, similar result was obtained (see Table 1). Either the release rate of ^{35}S-H_2S or total amounts of released ^{35}S-H_2S decreased with the concentrations of 4-MDBT. It is worthy to note that ^{35}S-labeled labile sulfur during HDS of ^{35}S-DBT could not completely release as ^{35}S-H_2S during HDS of 4-MDBT.

Similar results were also obtained when 4,6-DMDBT was introduced in step (iv). ^{35}S remaining on the catalyst was exchanged by ^{32}S in 4,6-DMDBT and was released as ^{35}S-H_2S. The release rate of ^{35}S-H_2S and the exchange amount of sulfur were much less than that in the case of DBT as presented in Table 1.

The effect of temperature was also investigated. The extent of sulfur exchange increased with the temperatures for both 4-MDBT and 4,6-DMDBT. Nevertheless, the extents were less than total labile sulfur labeled with ^{35}S under studied temperatures. These indicate that not all the labile sulfur participating in HDS of DBT take part in HDS of 4-MDBT or 4,6-DMDBT.

Similarly, the release rate constant and amount of labile sulfur were calculated and presented in Table 1 after introducing 4-MDBT and 4,6-DMDBT. The amount of labile sulfur in HDS of DBT was about 3.2 times of that in the case of 4-MDBT at 260°C and 50 kg/cm². This is approximately equal to the ratio of HDS rates between DBT and 4-MDBT, 3.7. This indicates that the HDS rate is proportional to the amount of labile sulfur. For 4-MDBT and 4,6-DMDBT, the same result was obtained. For example, two ratios of the amounts of labile sulfur and of the HDS rates were 2.1 and 2.5 at 320°C and 50 kg/cm², respectively. Therefore, it was suggested that the difference in the HDS rates for various sulfur compounds originated from the difference in the amounts of labile sulfur participating in reactions. Considering that the active site generated from the labile sulfur, number of active sites participating in HDS of 4-MDBT and 4,6-DMDBT would eventually decrease.

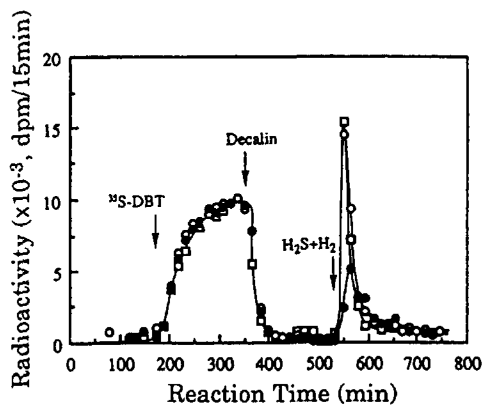

Fig. 4. Effect of concentration of H_2S on the release rate of ^{35}S-H_2S. □: 3.4%, ○: 0.72%, ●: 0.12%.

3.4. Release of ^{35}S-H_2S in mixed gases of H_2S and H_2

To elucidate the formation mechanism of H_2S from the labile sulfur, the sulfur exchange with H_2S was carried out. After labeled with ^{35}S at 260°C, 50 kg/cm² and WHSV 28 h^{-1} (Amount of Catalyst: 1.0 g), the catalyst was purged with

Table 2
Results of sulfur exchange with H_2S

Temperature (°C)	200	200	200	230	260
Concentration of H_2S (vol.-%)	3.42	0.72		0.12	
Partial pressure of H_2S (kg/cm²)	1.71	0.36	0.06	0.06	0.06
Total radioactivities ($\times 10^4$ dpm)	2.75	2.81	2.54	2.65	2.76
Labile sulfur (mg/g cat.)	21.0	21.5	19.4	20.3	21.1
Release rate constant, k ($\times 10^{-2}$/min)	7.49	6.14	3.01	3.11	3.22

Reaction conditions: 50 kg/cm², WHSV 28 h^{-1}, catalyst: 1.0 g.
Note: The radioactivities of total labile sulfur was 2.76×10^4 dpm.

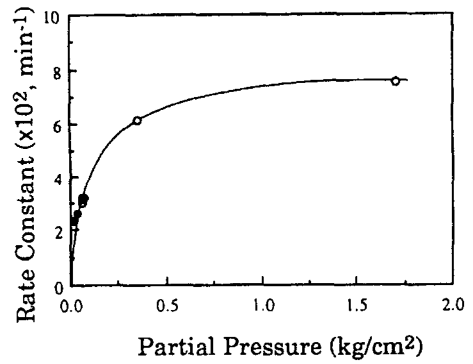

Fig. 5. Effect of partial pressure of H_2S on release rate of ^{35}S-H_2S.

H_2 and the temperature was regulated to 200°C. After introducing 3.4 vol.-% H_2S, ^{35}S-H_2S was released as shown in Fig. 4. The release rate of ^{35}S-H_2S was more rapid than that in the case of DBT (Fig. 1). Moreover, the total amount of the released ^{35}S was approximately equal to one remaining on the catalyst. As shown in Fig. 4, the release rate of ^{35}S-H_2S decreased with a decrease in the concentration of H_2S in H_2. Nevertheless, the total amounts of ^{35}S released as ^{35}S-H_2S were approximately equal to the total amount of ^{35}S remaining on the catalyst as shown in Table 2.

The effect of temperature was also investigated. The release rate of ^{35}S-H_2S varied with temperature only to a small extent.

The release rate constant of ^{35}S-H_2S in the exchange reaction with H_2S was plotted versus the partial pressure of H_2S in Fig. 5. The release rate constants almost trend toward the constant value above 0.36 kg/cm^2 of partial pressure of H_2S. It means that the adsorption of H_2S on the catalyst was on saturation under the present reaction condition. The release of ^{35}S-H_2S from the catalyst could be considered to be the determining-rate step for the exchange reaction with H_2S.

3.5. Inhibition of methyl substituents

Because of the interaction between the sulfur and support, the mobility of labile sulfur is not uniform. After the labile sulfur is removed as H_2S the active site is formed. Therefore, the amount of labile sulfur represented the number of active sites [11]. As motioned above, the amount of labile sulfur participating in HDS decreased in the order: DBT > 4-MDBT > 4,6-DMDBT. This indicates that the number of active sites participating in HDS of methyl-substituted DBTs decreased because of the existence of methyl substituents. On the other hand, because the methyl-substituted dibenzothiophene are more easy to adsorb on the catalyst than DBT, it was considered that the C–S bond scission of methyl-substituted DBTs adsorbed on the catalyst is blocked by the methyl substituents [4]. This may be because the electron distribution of sulfur atom in substituted DBTs will be different from that in DBT and a portion of active sites for methyl-substituted DBTs may be of higher acidity than that for HDS of DBT. This caused that a portion of ^{35}S-labeled labile sulfur in the HDS reaction of ^{35}S-DBT were was not exchanged and released as ^{35}S-H_2S during HDS of 4-MDBT and 4,6-DMDBT.

4. Conclusions

Under the same reaction condition, a portion of labile sulfur participating in the HDS reaction of DBT did not take part in the HDS reaction of 4-MDBT and 4,6-DMDBT. Moreover, the reaction rate was approximately proportional to the amount of labile sulfur. This means that number of active sites was proportional to the amount of labile sulfur. Compared with DBT, the number of active site participating in the HDS reaction of methyl-substituted DBTs decreased because of the existence of methyl groups. In the sulfur exchange reaction with H_2S, the adsorption of H_2S on the catalyst was at saturation above 0.36 kg/cm^2 of partial pressure of H_2S. The release of H_2S from the labile sulfur could be considered to be the determining-rate step of HDS reaction under this condition.

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