[Regular Paper]

Hydrodesulfurization of Dibenzothiophene Catalyzed by Supported Metal Carbonyl Complexes (Part 8) Hydrodesulfurization of ^{35}S -Labeled Dibenzothiophene on Alumina-supported Ruthenium Sulfide–Cesium Catalysts

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In hydrodesulfurization (HDS) of ^{35}S -labeled dibenzothiophene (^{35}S DBT) catalyzed by alumina-supported ruthenium carbonyls–cesium hydroxide systems, the role of cesium was elucidated by tracing the behavior of ^{35}S on the working ruthenium catalysts. The HDS of ^{35}S DBT was performed in conditions: 280–320°C, 50 kg/cm², WHSV 14 h⁻¹, H₂ 18 l/h, DBT 1 wt%, precursor Ru₃(CO)₁₂-*n*CsOH/Al₂O₃ (*n*=0, 3, 6 or 9). During the reaction with sulfided catalysts, the changes in the radioactivities of unreacted ^{35}S DBT and product ^{35}S H₂S with reaction time were monitored. The rate constant (k_{release}) of release of ^{35}S H₂S was estimated from the first order plots of the increasing and decreasing radioactivities of product ^{35}S H₂S. The values of k_{release} decreased with increase in the amount of cesium added, indicating that the mobility of sulfur on the catalysts decreased by the addition of cesium. On the contrary, the amount of labile sulfur on the catalyst (S_0), which was calculated from the maximum amount of ^{35}S accommodated on the catalyst, increased with increase in the amount of cesium added and reached the maximum at Ru:Cs=1:2, which was kept with further addition of cesium (Ru:Cs=1:3). This shows that the active sites on the catalyst were not poisoned because S_0 did not decrease with the addition of excess amount of cesium. This maximum value of S_0 at Ru:Cs=1:2 corresponds to RuS_{1.52}. Assuming that ruthenium species are present as RuS₂, 76% of sulfur on the catalyst is labile. This indicates that the dispersion of ruthenium species could be significantly high. Further, it is suggested that cesium promoted the C–S bond scission of DBT and increased the activity by stabilizing Ru–S bonds for ruthenium sulfide.

1. Introduction

Recently, deep desulfurization of light gas oil has been one of urgent researches in the world and much attention has been focused on the development of new catalyst for deep desulfurization^{1),2)}. Among a number of attempts made to develop the new catalyst, nonsupported^{3)–5)} and supported^{6)–12)} ruthenium sulfides were found to be the most active for hydrodesulfurization (HDS) of thiophenes in transition metal sulfides. Pecoraro and Chianelli³⁾ initially reported that ruthenium sulfide is the most active for HDS of dibenzothiophene (DBT) among the transition metal sulfides. Supporting ruthenium sulfide appropriately is an attractive approach to increase catalytic activity. Harvey and Matheson⁶⁾, Mitchell *et al.*⁷⁾, Kuo *et al.*⁸⁾, De Los Reyes *et al.*⁹⁾ and Chary *et al.*¹⁰⁾ used supported ruthenium sulfide catalysts in HDS of thiophenes. With these catalysts, however, the HDS activity was rather low, probably because sulfidation of ruthenium species was incomplete and RuS₂ is unstable on a support in hydro-

gen atmosphere. Further, these HDS reactions were performed in atmospheric pressure, and so far the activities of supported ruthenium sulfide in a pressurized flow system have not yet been clarified in comparison with those of Co–Mo/Al₂O₃ and Ni–Mo/Al₂O₃. Recently, the authors reported that, in HDS of dibenzothiophene (DBT), the catalysts derived from supported metal carbonyls showed catalytic activity higher than those from conventional catalysts^{11),12)}. The cesium promoted ruthenium catalysts revealed that the activity is comparable with that of conventional Co–Mo/Al₂O₃^{13)–16)}.

On the other hand, it is essential, for the elucidation of the HDS mechanism, to know the behavior of sulfur on HDS catalysts. 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^{17)–23)}. In these reports, the use of ^{35}S tracer, such as ^{35}S -labeled H₂S, CS₂, or thiophene, was believed to enable to clarify the behavior of sulfur in catalysts. It has not been well-known, however, how sulfur in catalysts behaves in practical HDS reaction. The authors have already conducted hydrodesulfu-

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rization of ^{35}S -labeled dibenzothiophene (^{35}S]DBT) on sulfided Co-Mo/ Al_2O_3 , Ni-Mo/ Al_2O_3 , Mo/ Al_2O_3 , Co/ Al_2O_3 and Ni/ Al_2O_3 , and gained new insight of the mechanism of HDS by monitoring changes in radioactivities of unreacted ^{35}S]DBT and product ^{35}S]H $_2\text{S}$ ^{(24)~(28)}. It was found that the sulfur of 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 on the rate of ^{35}S]H $_2\text{S}$ formation from the catalyst, it was postulated that 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 $_2\text{S}$ and how sulfur in the sulfided catalyst participates in the actual HDS reaction.

In this study, the authors report here the HDS of ^{35}S]DBT catalyzed by Al_2O_3 -supported ruthenium sulfide-cesium catalysts to elucidate the behavior of sulfur on the ruthenium catalysts and the role of cesium in HDS. Initially, the amount of labile sulfur and the release rate constant of H $_2\text{S}$ on presulfided ruthenium catalysts were estimated. Then, total amount of sulfur combined into the catalyst was estimated by direct HDS reaction of ^{35}S]DBT without presulfiding the ruthenium catalysts. The preliminary results appear in the literature⁽²⁹⁾.

2. Experimental Section

2.1. Materials

Commercially available $\text{Ru}_3(\text{CO})_{12}$, cesium hydroxide ($\text{CsOH}\cdot\text{H}_2\text{O}$), decalin and methanol (GR grade) (Kishida Chemicals) were used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Alumina, as gamma-alumina was supplied from Japan Ketjen Co., Ltd., 260 m^2/g of which was crushed and screened to provide 0.84- to 1.19-mm granules and used in this work. Alumina was dried in vacuum at 350°C for 4 h prior to use and stored in Ar atmosphere. ^{35}S]DBT was synthesized by the following method: Firstly, to obtain ^{35}S -labeled sulfur, commercial grade toluene solution of ^{35}S (total radioactivity: 1 mCi) (Amersham Co., Ltd.) was mixed sufficiently with 8.7 g sulfur (^{32}S), and the toluene in mixture was evaporated at room temperature, and sulfur mixture was dried for 24 h in vacuo until the toluene was entirely removed. Using this ^{35}S -labeled sulfur, DBT was synthesized according to a method developed by Gilman *et al.*⁽³⁰⁾. Crystallizing the crude DBT from ethanol, colorless needles (purity exceeding 99.9%) were obtained. ^{32}S]DBT was synthesized by a similar method. Hydrogen (99.99%) was obtained from Tohei Chemicals. Hydrogen sulfide in hydrogen

(H $_2\text{S}$ 3.0%) was obtained from Takachiho Chemicals.

2.2. Preparation of Catalyst

2.2.1. $\text{Ru}_3(\text{CO})_{12}$ - $n\text{CsOH}/\text{Al}_2\text{O}_3$ ($n=0, 3, 6$ or 9)

0.26 mmol of $\text{Ru}_3(\text{CO})_{12}$ and 0-2.4 mmol of cesium hydroxide were dissolved in methanol (10 ml) and stirred at 25°C for 30 min. After the reaction, 0.92 g of gamma- Al_2O_3 (> 20 mesh) was added into the reaction mixture and stirred for 2 h. Solvent was removed in vacuo.

2.2.2. $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$

0.168 g of $\text{Ru}_3(\text{CO})_{12}$ was dissolved in THF. 0.92 g of Al_2O_3 was added to the solution and stirred for 2 h. The solvent was removed in vacuo.

2.3. Apparatus and Procedures

A catalyst precursor was placed in a pressurized fixed-bed flow reactor (8 mm ID $\times$ 300 mm), heated at 5°C/min and presulfided at 300°C in a flow of H $_2$ in H $_2$ (H $_2\text{S}$ 3%) for 3 h. After presulfiding, the reactor was adjusted to expected temperature and was pressurized with hydrogen. The solution containing DBT was, then, supplied with a feed pump (Kyowa Seimitsu KHD-16). HDS of DBT was carried out under the following conditions: temperature, 280-320°C; 50 kg/cm^2 ; H $_2$ 18 l/h; WHSV 14 h^{-1} ; initial concentration of DBT in decalin, 1.0 wt%; catalyst, 1.0 g; Ru 8 wt%. The weight of the catalyst includes the weights of metal and support. The produced H $_2\text{S}$ 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 $_2\text{S}$ solution samples were collected every 15 min.

Two typical operation procedures were applied. Operational procedure 1 (OP1): (a) A decalin solution of 1 wt% ^{32}S]DBT was pumped into the reactor until the conversion of DBT became constant (about 3.5 h). (b) After that, the decalin solution of 1 wt% ^{35}S]DBT (6000 dpm/g) was substituted for that of ^{32}S]DBT. The reaction with ^{35}S]DBT was performed until the amount of $^{35}\text{H}_2\text{S}$ released into exit of the reactor became constant (about 7 h). (c) The reactant solution was, then, changed back to the decalin solution of 1 wt% ^{32}S]DBT. This reaction of ^{32}S]DBT was continued for about 8 h.

Operational procedure 2 (OP2): After a catalyst precursor was placed in a pressurized fixed-bed flow reactor, the reactor was pressurized with hydrogen and heated at 5°C/min to expected temperature, and then the solution containing ^{35}S]DBT was supplied with the feed pump, without presulfiding. The reaction with ^{35}S]DBT was carried out at the expected temperature until the amount of $^{35}\text{H}_2\text{S}$ released into exit of the reactor became constant. The reactant solution of ^{35}S]DBT was, then, replaced by ^{32}S]DBT solution. The reaction was continued for about 8 h.

○ $[^{35}\text{S}]\text{DBT}$; □ $[^{35}\text{S}]\text{H}_2\text{S}$; ■ Conversion of DBT.
 $\text{Ru}_3(\text{CO})_{12}-6\text{CsOH}/\text{Al}_2\text{O}_3$; 280°C , $50\text{ kg}/\text{cm}^2$, $\text{WHSV} = 14\text{ h}^{-1}$,
 Gas flow $18\text{ l}/\text{h}$.

Fig. 1 Change in Radioactivities with Reaction Time

2.4. Analytical

The components of liquid products were analyzed by gas chromatography with FID detector (Hitachi 163), using a commercial capillary G-column 250, supplied from Chemicals Inspection & Testing Institute. Radioactivities of unreacted $[^{35}\text{S}]\text{DBT}$ in liquid product and the product $[^{35}\text{S}]\text{H}_2\text{S}$ in scintillator solution were measured by a liquid scintillation counter (LSC-1000, Aloka Co., Ltd.)^{31)~33)}.

3. Results and Discussion

3.1. HDS of $[^{35}\text{S}]\text{DBT}$ on Presulfided Ruthenium Catalysts

Initially the HDS of $[^{35}\text{S}]\text{DBT}$ were conducted over ruthenium catalysts, such as presulfided $\text{Ru}_3(\text{CO})_{12}-n\text{CsOH}/\text{Al}_2\text{O}_3$ systems ($n=0, 3, 6$ or 9) according to OP 1. Shown in Fig. 1 are the changes in the radioactivities of unreacted $[^{35}\text{S}]\text{DBT}$ and produced $[^{35}\text{S}]\text{H}_2\text{S}$, and the conversion of DBT with reaction time at 280°C , using $\text{Ru}_3(\text{CO})_{12}-6\text{CsOH}/\text{Al}_2\text{O}_3$ system. After the conversion, in the HDS of $[^{32}\text{S}]\text{DBT}$, had reached constant value and solution of $[^{32}\text{S}]\text{DBT}$ was replaced by that of $[^{35}\text{S}]\text{DBT}$, the radioactivities of unreacted $[^{35}\text{S}]\text{DBT}$ in liquid products increased with the reaction time and reached a steady state, immediately. On the contrary, the time delay, in the case of $[^{35}\text{S}]\text{H}_2\text{S}$, was about 6 h. Then, the decalin solution of $[^{32}\text{S}]\text{DBT}$ was again substituted for $[^{35}\text{S}]\text{DBT}$, in a similar way. The time delay, attributed to decrease of radioactivities of unreacted $[^{35}\text{S}]\text{DBT}$, from steady state to normal state, was also 30 min; while that for the $[^{35}\text{S}]\text{H}_2\text{S}$ was about 6 h. The results indicate that the sulfur in DBT is not directly released as hydrogen sulfide, but accommodated on the catalyst, and is consistent with those from Al_2O_3 -supported molybdenum catalysts^{24)~28)}.

Data concerning the catalyst derived from

□ Decreasing period; ○ Increasing period.
 $\text{Ru}_3(\text{CO})_{12}-6\text{CsOH}/\text{Al}_2\text{O}_3$; 280°C , $50\text{ kg}/\text{cm}^2$, $\text{WHSV}=14\text{ h}^{-1}$,
 Gas flow $18\text{ l}/\text{h}$.

Fig. 2 First Order Plots of Release Rate of $[^{35}\text{S}]\text{H}_2\text{S}$

$\text{Ru}_3(\text{CO})_{12}-6\text{CsOH}/\text{Al}_2\text{O}_3$ system were treated as follows: The first order plot (Fig. 2) of the radioactivity of the decreasing period of $[^{35}\text{S}]\text{H}_2\text{S}$ in Fig. 1, indicates the linear relationship expressed as

$$\ln y = \ln z - k_{\text{release}} t \quad (1)$$

where, y represents the radioactivity of $[^{35}\text{S}]\text{H}_2\text{S}$ (dpm/min); z the radioactivity of $[^{35}\text{S}]\text{H}_2\text{S}$ at steady state (dpm/min); k_{release} the rate constant of the release of $[^{35}\text{S}]\text{H}_2\text{S}$ (min^{-1}); t the reaction time (min). The first order plot of the values, where each radioactivity of the increasing period of $[^{35}\text{S}]\text{H}_2\text{S}$ in Fig. 1 is subtracted from that at steady state, also shows the linear relationship (○) in Fig. 2 and two slopes at this temperature overlap each other. This indicates that the rate of release of $[^{35}\text{S}]\text{H}_2\text{S}$ is equal to that of $[^{32}\text{S}]\text{H}_2\text{S}$. The value of k_{release} represents the relative ease of migration of sulfur on the catalyst^{24)~28)}. The increasing period of $[^{35}\text{S}]\text{H}_2\text{S}$ indicates the process where ^{32}S on the catalyst is replaced by ^{35}S . In contrast, the decreasing period of $[^{35}\text{S}]\text{H}_2\text{S}$ indicates the process where ^{35}S on the catalyst is replaced by ^{32}S . The area A, which represents the amount of ^{35}S incorporated to the catalyst, therefore, is equivalent to the area B, which represents the amount of ^{35}S released from the catalyst. Further, when $[^{32}\text{S}]\text{DBT}$ was substituted for $[^{35}\text{S}]\text{DBT}$ after radioactivities of $[^{35}\text{S}]\text{H}_2\text{S}$ had reached the steady state, all ^{35}S accommodated on the catalyst was released as $[^{35}\text{S}]\text{H}_2\text{S}$. From the total amount of radioactivities of this released $[^{35}\text{S}]\text{H}_2\text{S}$ (Area B, x dpm), the amount of labile sulfur on the catalyst (S_0), which may represent the amount of the active sites, could be calculated^{24)~28)}. Since all ^{35}S on the catalyst had originated from the desulfurization of $[^{35}\text{S}]\text{DBT}$, the concentration of ^{35}S , in sulfur introduced to the catalyst by HDS of DBT at steady state should be equal to the concentration of ^{35}S

in sulfur of [^{35}S]DBT, because the isotope effect between ^{32}S and ^{35}S can be assumed to be very small. The concentration of ^{35}S in sulfur of [^{35}S]DBT could be defined as $^{35}\text{S}_{\text{DBT}}/S_{\text{DBT}}$ (dpm/g), where $^{35}\text{S}_{\text{DBT}}$ is radioactivities in 1 mol of DBT (dpm/mol) and S_{DBT} is the amount of sulfur in 1 mol DBT (g/mol). Accordingly, the amount of labile sulfur on the catalyst (S_0) can be presented by expression $(x)/(^{35}\text{S}_{\text{DBT}}/S_{\text{DBT}})$.

Shown in Fig. 3 are the changes in the radioactivities of produced [^{35}S]H $_2$ S with the reaction time, at 320°C using $\text{Ru}_3(\text{CO})_{12}-n\text{CsOH}/\text{Al}_2\text{O}_3$ systems ($n=0, 3, 6$ or 9). The first order plots of these catalysts, in the decreasing period of [^{35}S]H $_2$ S, are also shown in Fig. 4. The values of k_{release} and S_0 for these catalysts were estimated by similar methods described above, using these data, and are shown in Table 1. As described in the previous paper^{13)~16)}, the conversion of DBT increased with increase in the amount of cesium added, reaching the maximum at Ru:Cs = 1:2, while further addition of cesium decreased the conversion. Products were biphenyl (BP) and cyclohexylbenzene. The selectivity for BP was extremely high, even in the absence of cesium (Table 1). The values of S_0 for the catalysts increased with increase in the amount of cesium added and reached maximum at Ru:Cs = 1:2, which was maintained with further addition of cesium (Ru:Cs = 1:3). This shows that the active sites on the catalyst was not poisoned because S_0 did not decrease with the addition of excess amount of cesium. This maximum value of S_0 , at Ru:Cs = 1:2, corresponds to $\text{RuS}_{1.52}$. If it is assumed that ruthenium species would be present as RuS_2 , 76% of sulfur on the catalyst would be labile. The result shows that the dispersion of ruthenium species could be significantly high. The rate constant of [^{35}S]H $_2$ S release decreased with increase in cesium, indicating that the mobility of sulfur on the catalysts decreased by the addition of cesium. These results suggested that cesium strengthened Ru–S bonds of ruthenium sulfide. As a result, the C–S bond scission of DBT was promoted and the activity increased. Ru–S bonds, however, became too strong

with the addition of excess amount of cesium. The formation of H $_2$ S and the regeneration of the coordinatively unsaturated sites were prevented, which resulted in decreasing the activity. It is also suggested that there is an optimum strength in Ru–S bond to obtain significantly high catalytic activity³⁴⁾.

The amount of labile sulfur represents the amount of

$\text{Ru}_3(\text{CO})_{12}-n\text{CsOH}/\text{Al}_2\text{O}_3$ ($n=0, 1, 2$ or 3).
320°C, 50 kg/cm 2 , WHSV=14 h $^{-1}$, Gas flow 18 l/h.

Fig. 3 Change in Radioactivities of [^{35}S]H $_2$ S with Reaction Time

$\text{Ru}_3(\text{CO})_{12}-n\text{CsOH}/\text{Al}_2\text{O}_3$ ($n=0, 1, 2$ or 3) with presulfiding;
320°C, 50 kg/cm 2 , WHSV=14 h $^{-1}$, Gas flow 18 l/h.

Fig. 4 First Order Plots of Release Rate of [^{35}S]H $_2$ S

Table 1 Hydrodesulfurization of ^{35}S -Labeled Dibenzothiophene over $\text{Ru}_3(\text{CO})_{12}-n\text{CsOH}/\text{Al}_2\text{O}_3$ Catalysts^{a)}

Run	Catalyst (Ru:Cs)	Conversion [%]	Selectivity for BP [%]	S_0^b [mg/g-cat]	S_0/S_{total}^c [%]	k_{release} [$\times 10^{-2}/\text{min}$]	HDS Rate ^{d)} [$\times 10^{-1}\text{mg/g-cat/min}$]	$S_0 \times k_{\text{release}}$ [$\times 10^{-1}\text{mg/g-cat/min}$]
1	1 : 0	50.1	95.1	9.2(RuS $_{0.36}$)	18	2.34	2.03	2.15
2	1 : 1	87.7	99.7	17.2(RuS $_{0.68}$)	34	1.92	3.56	3.30
3 ^{e)}	1 : 2	60.0	100	30.4(RuS $_{1.20}$)	60	0.79	2.43	2.40
4 ^{f)}	1 : 2	70.0	100	34.3(RuS $_{1.35}$)	68	0.86	2.84	2.95
5	1 : 2	94.0	99.0	38.5(RuS $_{1.52}$)	76	1.01	3.81	3.89
6	1 : 3	52.5	100	39.3(RuS $_{1.55}$)	78	0.60	2.13	2.36

a) OP 1. Catalyst: $\text{Ru}_3(\text{CO})_{12}-n\text{CsOH}/\text{Al}_2\text{O}_3$, 0.5 g, Ru 8 wt%, 320°C, 50 kg/cm 2 , WHSV 14 h $^{-1}$, H $_2$ 18 l/h, DBT 1 wt% in decalin.

b) The value given in a parenthesis represents the ratio of labile sulfur to ruthenium. c) For the value of S_{total} , it was assumed that ruthenium species would be present as RuS_2 . d) Calculated from the conversions. e) 280°C. f) 300°C.

active sites which can give the coordinatively unsaturated sites, while the rate constant of the release of $[^{35}\text{S}]\text{H}_2\text{S}$ represents the mobility of such active sites. As shown in **Table 1**, the HDS rate, calculated from the conversion, is in good agreement with the product ($S_0 \times k_{\text{release}}$) of the amount of labile sulfur on the catalyst and the rate constant of the release of $[^{35}\text{S}]\text{H}_2\text{S}$. The result indicates that the amount of labile sulfur and the rate constant of the release of $[^{35}\text{S}]\text{H}_2\text{S}$, which control the HDS rate, can be determined separately by using a ^{35}S tracer method shown here.

3. 2. HDS of $[^{35}\text{S}]\text{DBT}$ over Ruthenium Catalysts without Presulfiding Treatment

In HDS of $[^{35}\text{S}]\text{DBT}$ over presulfided ruthenium catalysts, the amount of labile sulfur could be determined. Total amounts of sulfur accumulated on catalysts, however, could not be estimated. To determine the total amount of sulfur on the catalysts, HDS of $[^{35}\text{S}]\text{DBT}$ over ruthenium catalysts was directly performed, without presulfiding treatment. Shown in **Fig. 5** are the changes in radioactivities of unreacted $[^{35}\text{S}]\text{DBT}$ and produced $[^{35}\text{S}]\text{H}_2\text{S}$ with reaction time, at 320°C , using $\text{Ru}_3(\text{CO})_{12}-6\text{CsOH}/\text{Al}_2\text{O}_3$. The radioactivity of $[^{35}\text{S}]\text{DBT}$ gradually increased and reached steady state at about 200 min. In contrast, the radioactivity of $[^{35}\text{S}]\text{H}_2\text{S}$ was not detected for about the initial 100 min, but then it picked and reached steady state. The amount of total sulfur incorporated in the catalysts (S_{total}) corresponds to the sum of the radioactivities of areas A and B and could be calculated. Further, after the radioactivity of $[^{35}\text{S}]\text{H}_2\text{S}$ reached steady state, the solution of $[^{35}\text{S}]\text{DBT}$ was replaced by that of $[^{32}\text{S}]\text{DBT}$. Similar to OP 1, the radioactivity of $[^{35}\text{S}]\text{DBT}$ decreased immediately and time delay in decrease of radioactivities of $[^{35}\text{S}]\text{H}_2\text{S}$, from the steady state to normal state, was observed. From the data on this decreasing period of $[^{35}\text{S}]\text{H}_2\text{S}$, the release rate constant of $[^{35}\text{S}]\text{H}_2\text{S}$ and the amount of labile sulfur could be calculated, and the results for cesium-promoted ruthenium catalysts are found in **Table 2**. Compared with presulfided catalysts, the catalysts without presulfiding treatment showed lower activities and the maximum of the conversion was observed at $\text{Ru}:\text{Cs} = 1:1$. Further, all the values for the labile sulfur and the rate constant

of H_2S release decreased, in comparison with those of sulfided catalysts. When the catalysts were not presulfided, activation of the catalysts was not enough to attain maximum activity. In presulfiding of the catalysts, it may be easier for the smaller hydrogen sulfide to be adsorbed on the catalysts and be able to expel carbon monoxide ligands. In contrast, it may be more difficult for larger DBT to gain access to the surface and expel carbon monoxide ligands. It seems that the phenomenon occurs especially for catalysts $\text{Ru}:\text{Cs} = 1:2$ or $1:3$, which have greater amount of alkali metals. The activity, therefore, may decrease at over $\text{Ru}:\text{Cs} = 1:2$. The amount of S_{total} increased with increasing added cesium. S_{total} at $\text{Ru}:\text{Cs} = 1:3$ corresponds to $\text{RuS}_{2.66}$, which exceeds usual RuS_2 , indicating that a part of cesium may be sulfided. In these catalysts, the tendency of the changes in the amount of labile sulfur and the rate constant of H_2S release were significantly similar to those of the presulfided catalysts. That is, with the addition of cesium, the amount of labile sulfur increased, giving the maximum value, and rate constant of H_2S release decreased monotonously. Further, most of the product was also BP (**Table 2**). These results suggested that the addition of cesium also served to strengthen the $\text{Ru}-\text{S}$ bond to promote $\text{C}-\text{S}$ bond scission of DBT and to increase the activity, and that

Fig. 5 Change in Radioactivities with Reaction Time

Table 2 Hydrodesulfurization of ^{35}S -Labeled Dibenzothiophene Catalyzed by Alumina-supported $\text{Ru}_3(\text{CO})_{12}-n\text{CsOH}$ Systems^{a)}

Run	Catalyst ($\text{Ru}:\text{Cs}$)	Conversion [%]	Selectivity for BP[%]	$S_{\text{total}}^{\text{b)}$ [mg/g-cat]	$S_0^{\text{c)}$ [mg/g-cat]	$S_0/S_{\text{total}}^{\text{d)}$ [%]	k_{release} [$\times 10^{-3}/\text{min}$]
7	1 : 0	38.5	96.0	21.5($\text{RuS}_{0.85}$)	8.33($\text{RuS}_{0.33}$)	39	1.87
8	1 : 1	63.5	99.1	28.1($\text{RuS}_{1.11}$)	13.7($\text{RuS}_{0.54}$)	49	1.86
9	1 : 2	50.8	99.0	46.1($\text{RuS}_{1.82}$)	26.7($\text{RuS}_{1.05}$)	58	0.86
10	1 : 3	18.9	100	67.5($\text{RuS}_{2.66}$)	22.6($\text{RuS}_{0.89}$)	33	0.41

a) OP 2. Catalyst: $\text{Ru}_3(\text{CO})_{12}-n\text{CsOH}/\text{Al}_2\text{O}_3$. 320°C , $50 \text{ kg}/\text{cm}^2$, WHSV 14 h^{-1} , H_2 $18 \text{ l}/\text{h}$, DBT $1 \text{ wt}\%$ in decalin. b) The value given in a parenthesis represents the ratio of total sulfur to ruthenium. c) The value given in a parenthesis represents the ratio of labile sulfur to ruthenium. d) The value of S_{total} in this calculation was estimated in this OP 2.

excess of cesium prevented the desorption of hydrogen sulfide, to thereby decreasing the activity.

3.3. The Structure of Cesium-promoted Ruthenium Catalysts and the Reaction Mechanisms

It was reported that RuS_2 lacked sufficient stability to keep the original structure in HDS reaction conditions³⁾. In the present study, however, it was suggested that the Ru–S bond in ruthenium sulfide could be stabilized by the addition of cesium, even in HDS reaction conditions. Especially, in the catalysts with higher amount of cesium, it can be assumed that RuS_2 is present on alumina. Structure of RuS_2 belongs to a group of pyrite structure³⁾. When an alumina-supported ruthenium catalyst was presulfided, the pyrite structure of RuS_2 was also observed on the alumina support³⁵⁾. On the other hand, it was reported that MoS_2 phase appeared to be predominantly present as two-dimension single slab structure, oriented flat-wise on the alumina support for $\text{Mo}/\text{Al}_2\text{O}_3$ up to 12% Mo ³⁶⁾. In the present study, when RuS_2 is assumed to be present on alumina in presulfided catalysts (Table 1), the ratios of S_0/S_{total} for the catalysts at $\text{Ru}:\text{Cs}=1:2$ and $1:3$ exceeded 75%. The result indicates that more than 75% of sulfur in RuS_2 is labile and that RuS_2 in these catalysts is successfully dispersed on alumina. For better understanding of the structure of the catalyst and the mechanism, it was assumed that the monolayer dispersion would be maintained and that RuS_2 phase would be present as two-dimension structure, oriented flat-wise

on the alumina support in Scheme 1. Since the location of sulfur on the surface of alumina were different from each other, the labile capacity of sulfur would be different, accordingly. The sulfur existing between ruthenium layer and alumina surface (S^b) might be the most difficult to move and accordingly the sulfur over ruthenium layer (S^a) might be the most labile. Sulfur in two other sites, (S^c and S^d), which forms a triangle with Ru parallel to the alumina surface, may have the middle state of labile capacity. This explains why the amount of labile sulfur changes depending on the reaction temperature (see Table 1). If the sulfur between ruthenium and alumina surfaces, S^b , would not be labile, the amount of labile sulfur in the sulfided $\text{Ru}-\text{Cs}/\text{Al}_2\text{O}_3$ would be 75% of total sulfur. This is in good agreement with the result that the amount of labile sulfur is 76% of the total sulfur assumed for the sulfided $\text{RuS}_2/\text{Al}_2\text{O}_3$ derived from $\text{Ru}_3(\text{CO})_{12}-6\text{CsOH}/\text{Al}_2\text{O}_3$.

The situation of cesium is ambiguous in the catalysts derived from $\text{Ru}_3(\text{CO})_{12}-n\text{CsOH}/\text{Al}_2\text{O}_3$. XPS analysis for these catalysts did not show the clear peak of cesium¹⁴⁾. It seems, therefore, that cesium is located between RuS_2 and alumina to stabilize Ru–S bonds or in the inside of alumina to neutralize the acid sites of alumina, as shown in Scheme 1. In RuS_2 sulfur is anionic and ruthenium is cationic. Such anionic sulfur may interact with cesium cation to stabilize Ru–S bonds. Scheme 2 shows the mechanism of hydro-

Scheme 1 Structure of RuS_2 on Cs-Promoted $\text{RuS}_2/\text{Al}_2\text{O}_3$ Catalyst

Scheme 2 Mechanism of Hydrodesulfurization of Dibenzothiophene on Cs-Promoted $\text{RuS}_2/\text{Al}_2\text{O}_3$ Catalyst

desulfurization of dibenzothiophene on Cs-promoted $\text{RuS}_2/\text{Al}_2\text{O}_3$ using the structure of RuS_2 in **Scheme 1**. Initially, RuS_2 reacts with hydrogen to produce an anion vacancy and hydrogen sulfide. ^{35}S]DBT adsorbs on the anion vacancy and reacts with hydrogen to produce biphenyl and ^{35}S -labeled RuS_2 . It can be considered that S^c and S^d also react similarly. In the absence of cesium, labile sulfurs such as S^a , S^c and S^d would be removed by reaction with hydrogen before one vacancy is occupied by sulfur of DBT.

4. Conclusions

In HDS of ^{35}S]DBT catalyzed by alumina-supported ruthenium carbonyls–cesium hydroxide systems, the role of cesium was elucidated by tracing the behavior of ^{35}S on the working ruthenium catalysts. The release rate constant (k_{release}) decreased with increase in the amount of cesium added, indicating that mobility of sulfur on the catalysts decreased by the addition of cesium. On the contrary, the amount of labile sulfur on the catalyst (S_0) increased with increase in the amount of cesium added and reached maximum at $\text{Ru}:\text{Cs}=1:2$, which was kept with further addition of cesium ($\text{Ru}:\text{Cs}=1:3$). Further, most of the product was BP. These results suggested that cesium promoted the C–S bond scission of DBT and increased the activity by stabilizing Ru–S bonds for ruthenium sulfide. Ru–S bonds, however, became too strong with the addition of excess of cesium. The formation of H_2S and the regeneration of the coordinatively unsaturated sites were prevented, which resulted in decreasing the activity.

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要 旨

担持金属カルボニル錯体を用いたジベンゾチオフェンの水素化脱硫反応（第 8 報）
アルミナ担持硫化ルテニウム-セシウム触媒による³⁵Sで標識したジベンゾチオフェンの水素化脱硫反応

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アルミナ担持ルテニウムカルボニル-セシウム水酸化物系触媒を用いて, ³⁵S で標識したジベンゾチオフェン (³⁵S]DBT) の水素化脱硫反応を行い, ルテニウム触媒上での硫黄の挙動を追跡することによりセシウムの役割を解明した。³⁵S]DBT の水素化脱硫反応を $\text{Ru}_3(\text{CO})_{12-n}\text{CsOH}/\text{Al}_2\text{O}_3$ ($n=0, 1, 2$ または 3), $280\sim 320^\circ\text{C}$, 50 kg/cm^2 , $\text{WHSV}=14\text{ h}^{-1}$, ガス流速 18 l/h の条件下で行った。硫化された触媒の反応において, 未反応の³⁵S]DBT および生成した ³⁵S]H₂S の放射エネルギーの経時変化を追跡した。³⁵S]H₂S 放出の速度定数 k_{release} は, 生成する ³⁵S]H₂S の放射能の増加と減少の速度の 1 次プロットより評価できた。 k_{release} の値はセシウムの添加量の増加に従い減少した。このことは, 触媒上の硫黄の移動性が減少したことを示している。これに対して, 触媒上に蓄積される ³⁵S の最大量よ

り計算される触媒上の移動可能な硫黄の量 (S_0) は, セシウムの添加量の増加に従い増加し, $\text{Ru}:\text{Cs}=1:2$ で最大値に達し, さらにセシウムを添加しても ($\text{Ru}:\text{Cs}=1:3$) 変化しなかった。 S_0 がセシウムの過剰の添加で減少しなかったことで, 触媒上の活性サイトはセシウムによって被毒されなかったことを示している。 $\text{Ru}:\text{Cs}=1:2$ における S_0 の最大値は $\text{RuS}_{1.52}$ に相当し, ルテニウム種が RuS_2 として存在すると仮定すれば, 触媒上の硫黄の 76% が移動可能であることを意味する。この結果は, ルテニウム種の分散度はかなり高いことを示している。さらにこれらの結果は, セシウムはルテニウム硫化物の Ru-S 結合を安定化することによって, C-S 結合の切断を促進し, 活性を向上させていることを示唆した。

Keywords

Hydrodesulfurization, Dibenzothiophene, Isotope, Ruthenium carbonyl, Cesium, Alumina support