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Hydrodesulfurization and hydrogenation reactions on noble metal catalysts

Part II. Effect of partial pressure of hydrogen sulfide on sulfur behavior on alumina-supported platinum and palladium catalysts

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Abstract

Hydrodesulfurization (HDS) reactions of the ^{35}S radioisotope-labeled dibenzothiophene (DBT) were carried out over 10% Pd/Al_2O_3 and 2% Pt–10% Pd/Al_2O_3 catalysts. The total amount of the sulfur (S_{total}) accommodated on the catalysts and the amount of labile sulfur (S_0) participating in the HDS reaction were determined using a ^{35}S radioisotope tracer method. The sulfided state of noble metal sulfides on two catalysts changed depending on the partial pressure of H_2S in the reaction atmosphere. Taking into account the amount of the sulfur accommodated on the alumina support, the sulfided Pt or Pd species on the catalysts are presented in the form of PdS_x or PtS_x ($x = 0$–0.25) in lower partial pressures of H_2S under 5.2 kPa. At the same time, all the sulfur incorporated into the catalyst were almost the labile sulfur. On the other hand, the sulfur further incorporated into the Pd catalyst with further increasing the partial pressure of H_2S in a reaction system over 5.8 kPa, resulting in the formation of the phase of PdS. In contrast, there was no significant change in both S_{total} and S_0 even though the partial pressure of H_2S in the atmosphere increased into ca. 17 kPa in the case of Pt–Pd catalysts. The structures of $PdS_{0.25}$ and $PtS_{0.25}$ in the Pt–Pd catalyst remained.

Keywords: Platinum catalyst; Palladium catalyst; Dibenzothiophene; Hydrodesulfurization; Sulfur behavior; Hydrogen sulfide effect

1. Introduction

Growing knowledge about the aromatics contained in diesel fuels and their adverse effects causing undesired emissions in exhaust gases and resultant health hazards has led to limitations on the use of these aromatics around the world. Under such circumstances, refiners are required to develop new catalysts capable of higher hydrogenation activity in order to meet the emission standards that have been made more and more stringent each year [1–5]. Noble metal catalysts such as γ-Al_2O_3-supported platinum and palladium catalysts are known to be highly active in the hydrogenation of aromatics [6–11]. However, one of the major problems associated with the use of platinum and palladium is their high sensitivity to sulfur compounds that are usually present in hydrogenation feedstocks [12]; hence, a severe hydrotreating is necessary to attain sulfur concentration reductions below a few ppm. Recent studies show that utilizing an acidic support such as zeolite [13,14] and adding a transition metal may effectively improve the activity of these catalysts and their tolerance to sulfur [15–19]. However, despite the improvement, the catalyst for aromatic reduction still suffers from low sulfur tolerance. The retardation in improving the sulfur resistance of the supported Pt catalyst may be due to a poor understanding of the fundamental chemistry involved in the behavior of sulfur on the catalyst in the hydrotreating process. Recently, the behavior of noble metal catalysts in the HDS has been investigated using a ^{35}S radioisotope pulse tracer method (^{35}S RPTM), which has been recently developed [9–11,20]. The hydrogenation activity of phenanthrene (PHE) over the monometallic and bimetallic catalysts—Pt/Al_2O_3, Pd/Al_2O_3, and $Pt–Pd/Al_2O_3$—was investigated in the presence of dibenzothiophene (DBT). Although the bimetallic catalyst ($Pt–Pd/Al_2O_3$) did not show some synergetic effects in HDS reactions, this catalyst showed better

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performance in the hydrogenation reaction of PHE in the presence of 1 wt% DBT than the CoMo catalyst. Further, it was found that both the amount of the sulfur (S_{total}) accommodated on the catalyst and the amount of the labile sulfur (S_0) participating in the reaction increased linearly with increase in active metal loading [11].

It is well known that the stable sulfides of noble metal change depending on the ratio of H_2S/H_2 in the atmosphere, especially in the case of supported catalysts [21–25]. Since HDS reactions are normally carried out in hydrogen, the reduction of sulfur species might result in the generation of vacant sites. Thus, behavior of the sulfided active metals on the working catalysts is not yet clarified. Mangnus et al. proposed from the thermodynamic equilibrium point of view that the reduction of transition metal sulfides may occur depending on the H_2S/H_2 ratio in the reactor, for instance, the reduction of PtS to Pt may occur when the said ratio is less than 0.2 [24]. Because this ratio generally falls between 10^{-1} and 10^{-3} under typical HDS conditions, it is assumed that the sulfided Pt and Pd are present in the forms of PtS_{1-x} and PdS_{1-x} [11,22–24,26]. In our previous study, all noble metal catalysts were determined as nearing the state equivalent to the S/Pt (or Pd) ratio, 0.25, much lower than that of the stoichiometric state platinum or palladium sulfide [11]. This suggests that the Pt (Pd)–S bond strength is so weak to allow the lower sulfur accommodation on the catalysts, and that the sulfur accommodation may depend on the partial pressure of H_2S in the atmosphere.

In the present study, the HDS reactions of the ^{35}S radioisotope-labeled DBT were carried out over Pd/Al_2O_3 and $Pd–Pt/Al_2O_3$ catalysts under practical HDS conditions. The reaction conditions such as concentration of DBT, the pressure of hydrogen, and space velocity were changed to investigate the effect of the partial pressure of H_2S in the atmosphere on the amount of sulfur accommodated and the behavior of sulfur on the noble metal catalysts. Further, the effects of the sulfur additive present in the feedstocks on the catalytic performance were examined to clarify resultant differences in sulfur tolerance between the catalysts.

2. Experimental

2.1. Materials

Decalin, used as a solvent, was of the commercial GR grade (Kishida Chemicals). Dibenzothiophene ([^{32}S]DBT) and ^{35}S-labeled dibenzothiophene ([^{35}S]DBT) were synthesized according to a method previously employed [27]. Hydrogen (99.99%) was supplied by Tohei Chemicals. Hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), and palladium chloride ($PdCl_2$) were of the commercial GR grade (Kishida Chemicals). All scintillation solvents used for the radioactivity measurement were available from Packard Japan Co., Ltd. The γ-Al_2O_3 used as a support was supplied by Nippon Ketjen Co., Ltd., as 1/32 inch extrudate.

Table 1
Active metal loadings and surface area of prepared catalysts

Catalyst	Pt (mmol/g_{cat})	Pd (mmol/g_{cat})	BET surface area (m^2/g_{cat})	Pore volume (cm^3/g_{cat})
Al_2O_3			256	0.650
10% Pd/Al_2O_3		0.938	232	0.553
2% Pt–10% Pd/Al_2O_3	0.103	0.938	230	0.536

2.2. Preparation of catalysts

The catalysts used in the present study were prepared by the usual impregnation method. For 10% Pd/Al_2O_3 catalyst, 20- to 80-mesh γ-Al_2O_3 was impregnated with an aqueous solution of $PdCl_2$ as required. This was followed by oven drying at 120 °C for 3 h and then calcined in the air at 400 °C for 15 h. A 10% Pd/Al_2O_3 catalyst was consecutively impregnated with an aqueous solution of H_2PtCl_6 to obtain a bimetallic catalyst, 2% Pt–10% Pd/Al_2O_3. The chemical composition and BET surface areas of these prepared catalysts are shown in Table 1.

2.3. ^{35}S radioisotope pulse tracer method

Experiments using the [^{35}S]DBT tracer were carried out with a fixed-bed reactor of conventional design; details of this reactor are described elsewhere in Ref. [27]. After being calcined overnight in the air at 400 °C, the test catalyst was pretreated at 400 °C for 3 h under atmospheric pressure with hydrogen at a flow rate of 1.8×10^{-3} m^3/h. The reactor was then cooled in the hydrogen stream to the reaction temperature and pressurized with hydrogen. A decalin solution of [^{35}S]DBT was then introduced into the reactor by high-pressure liquid pump (Kyowa Seimitsu KHD-16).

Typical reaction conditions involved were the amount of catalyst, 1 g; hydrogen flow rate, 2.5×10^{-2} m^3/h; WHSV, 14–28 h^{-1}; pressure, 1.0–5.0 MPa; concentration of DBT in decalin, 0.1–4.0 wt%; and temperature, 260 °C. The liquid products were collected from the gas–liquid separator and put under gas chromatographic component analysis using an FID detector (Shimadzu 17A, Shimadzu Co., Ltd.) and a commercially available column (DB-1, 0.25 mm × 60 m). The products were identified by their retention time examined relative to the standard chemicals provided (Tokyo Chemical Industry Co., Ltd.). The H_2S produced was absorbed by bubbling through a commercially available scintillation solution (Carbosorb, Packard Japan Co., Ltd.). For each run, the liquid products and absorbed H_2S solution samples were collected every 15 min. The radioactivities of both [^{35}S]DBT unreacted in the liquid product and [^{35}S]H_2S formed in the absorbed solution were measured with a liquid scintillation counter (Beckman LS-6500, Beckman Co., Ltd.) after adding a proper scintillation solvent (Permafluor or Instaflour, Packard Japan Co., Ltd.) to each of the fractions sampled. For the liquid scintillation counting, an explanatory literature is available [28].

Typical operating procedures followed were as follows: (a) The reaction system was pressurized by hydrogen to the pressure desired and heated at the reaction temperature, respectively. (b) A decalin solution of 1 wt% [^{35}S]DBT was pumped into the reactor until the amount of the formed [^{35}S]H_2S had become constant (ca. 6 h). (c) The decalin solution of [^{35}S]DBT was replaced by decalin, and the reactor system was purged with decalin and hydrogen for ca. 3 h. (d) The decalin solution of [^{32}S]DBT of various concentrations was substituted for decalin, and reacted for 4–5 h. For the analysis of sulfur effects on the catalytic performance, the decalin solution of DBT was also used containing 0.059 and 0.156 wt% sulfur adjusted with the addition of polysulfide (C_8H_{17}–S_n–C_8H_{17}, $n = 4.8$: 39.0 wt% of sulfur).

3. Results

3.1. *Determination of sulfur behavior using a ^{35}S radioisotope tracer method*

For the determination of sulfided working catalysts, the HDS reaction of 0.5 wt% ^{35}S-labeled DBT was carried out over the 10% Pd/Al_2O_3 catalyst at 5.00 MPa and at 260 °C. Fig. 1 shows the typical results obtained by the ^{35}S RPTM: initially, 0.5 wt% solution of [^{35}S]DBT was introduced and the HDS reaction continued about 4 h until the release of [^{35}S]H_2S had become constant. Despite the high DBT conversion determined, the [^{35}S]H_2S was not released immediately, which suggests the incorporation of some ^{35}S into the catalyst and progress in the sulfidation of the catalyst. The radioactivities of the unreacted [^{35}S]DBT and formed [^{35}S]H_2S increased and approached the steady state when the [^{35}S]DBT was introduced for 45 and 120 min, respectively. Then, to determine the amount of the sulfur accommodated on the catalyst in the HDS reaction of DBT, decalin solvent and hydrogen were introduced to purge the catalyst and reaction system at ca. 255 min for ca. 2.5 h. The radioactivities of both formed [^{35}S]H_2S and unreacted [^{35}S]DBT decreased rapidly and approached the background level. As proposed in Ref. [11], the total radioactivity incorporating onto the catalyst for the time interval (0–400 min) can be calculated from the balance of radioactivity between the total radioactivity of the [^{35}S]DBT introduced and that eluted involving the total radioactivity of the [^{35}S]H_2S released from the catalyst, i.e., area A in Fig. 1, and the total radioactivity of the unreacted [^{35}S]DBT, i.e., area B in Fig. 1. Then, the total radioactivity can be converted into the amount of sulfur accommodated on the catalyst (S_{total}) according to a method reported in Ref. [11]. The amount of total sulfur incorporated into the catalyst was 14.5 mg/g_{cat}.

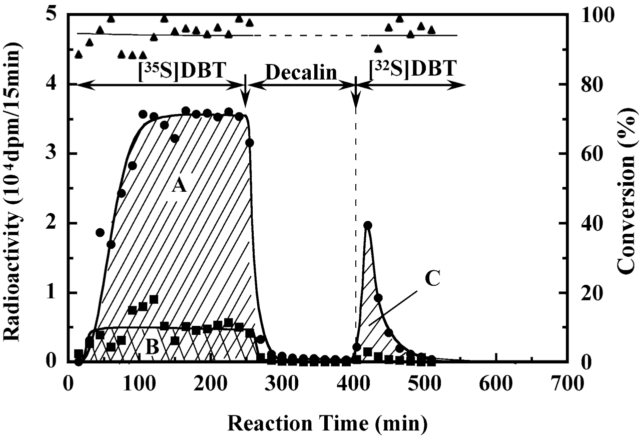

Fig. 1. Changes in radioactivities of unreacted [^{35}S]DBT and formed [^{35}S]H_2S and DBT conversion with reaction time. 10% Pt/Al_2O_3, 260 °C, 5.0 MPa, 0.5 wt% DBT. ■, [^{35}S]DBT; ●, [^{35}S]H_2S; ▲ conversion.

In order to determine the amount of the sulfur participating in the HDS reaction of DBT, i.e., labile sulfur, the decalin solvent was substituted for the [^{35}S]DBT to purge the catalyst at 255 min and continued for 2.5 h. After that, a decalin solution of [^{32}S]DBT was introduced and the HDS of DBT was carried out on the ^{35}S-labeled catalyst. A portion of the ^{35}S, which is indicated as the shaded area C in Fig. 1, was released from the catalyst as [^{35}S]H_2S when the [^{32}S]DBT was introduced. As reported in our previous papers [28,29], it is proposed that the portion of the sulfur on the working catalyst participates in the HDS reaction and that the said portion of sulfur is defined as labile sulfur. Similarly, the amount of this labile sulfur (S_0) participating in the HDS reaction over the Pd catalyst was determined from the total radioactivity of the [^{35}S]H_2S released by the introduction of the [^{32}S]DBT in the same manner as above [11]. The amount of labile sulfur was 5.47 mg/g_{cat}.

3.2. *Behavior of sulfur on Pd/Al_2O_3 catalysts*

To investigate the effects of H_2S partial pressure on the behavior of sulfur on the catalyst, i.e., S_{total} and S_0, similar experiments using the [^{35}S]DBT tracer were carried out over the 10% Pd/Al_2O_3 catalyst at 5.0 MPa and at 260 °C, where the DBT concentrations in decalin solution were varied between 0.1 to 3.0 wt% so that the partial pressure of H_2S in reaction atmosphere was changed by changing the HDS rate of DBT. Fig. 2 shows changes in the radioactivities of both formed [^{35}S]H_2S and unreacted [^{35}S]DBT in several reaction with different DBT concentrations. In all cases, the radioactivity of [^{35}S]H_2S increased and approached the steady state when the [^{35}S]DBT was introduced for 300, 180, 105, and 90 min, respectively. The time delay when the radioactivity of [^{35}S]H_2S reached the steady state was considered to be caused by the change in the concentrations of DBT, i.e., amount of H_2S formed from HDS of DBT. In the same manner as above, the amount of the sulfur accommodated on the catalyst was determined from the balance between the introduced radioactivity and eluted one. Similarly, the amount of the labile sulfur involved was determined from the total radioactivity of [^{35}S]H_2S released during the introduction of [^{32}S]DBT. The results are summarized in Table 2. As seen in Table 2, both values of S_{total} and values of S_0 increased

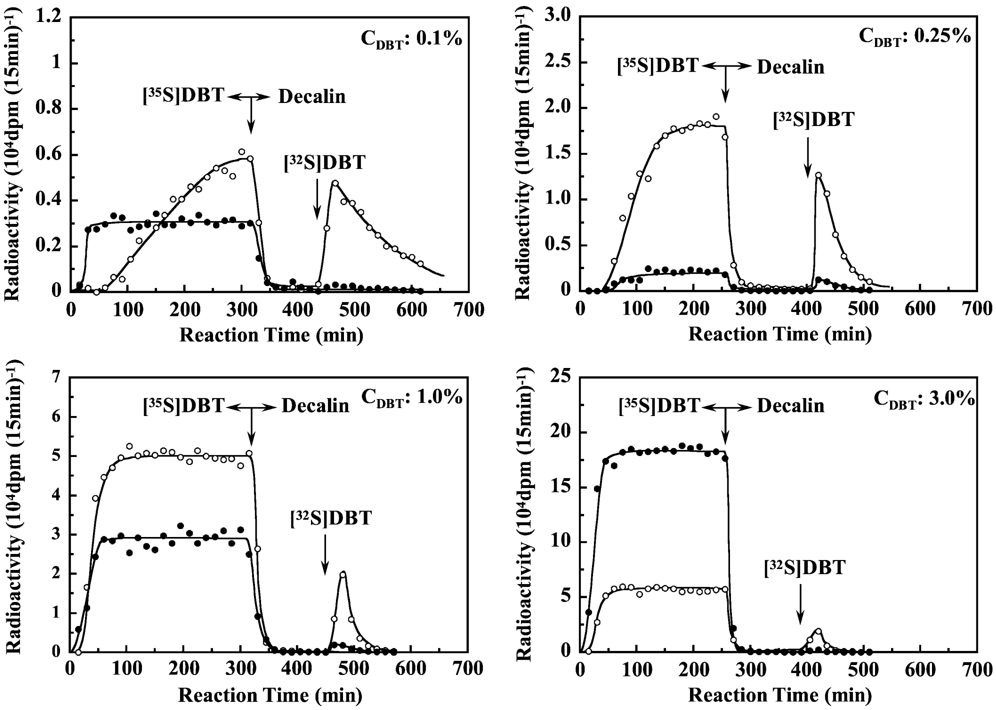

Fig. 2. Changes in radioactivities of unreacted [^{35}S]DBT and formed [^{35}S]H_2S with reaction time. 10% Pd/Al_2O_3, 260 °C, 5.0 MPa; concentration of DBT (C_{DBT}): 0.1–3.0 wt%. ●, [^{35}S]DBT; ○, [^{35}S]H_2S.

Table 2
Results of ^{35}S tracer experiments over a 10% Pd/Al_2O_3 catalyst at 260 °C

Concentration of DBT (wt%)	r_{HDS} (10^{-4} mol/(h g_{cat}))	S_{CHB} (%)	S_{total} (mg/g_{cat})	S_0 (mg/g_{cat})	H_2S/H_2 (10^{-3} mol/mol)	p_{H_2S} (kPa)
0.1	1.52	100	4.27	3.02	0.15	0.73
0.25	3.78	91.0	9.96	4.82	0.37	1.81
0.5	7.29	87.9	14.5	5.47	0.72	3.50
1.0	10.9	88.8	16.1	6.75	1.05	5.25
3.0	12.0	73.2	16.0	6.69	1.15	5.75
4.0	12.3	60.5	17.3	5.76	1.18	5.90

with an increase in the concentration of DBT, i.e., the partial pressure of H_2S, when the concentration of DBT was less than 1.0 wt%, and then approached respective constant values with a further increase in the concentration of DBT above 1.0 wt%. At the same time, the HDS rate of DBT shows the same tendency.

In order to further increase the partial pressure of H_2S in the atmosphere, the same ^{35}S tracer experiment was carried out using the decalin solution of 4.0 wt% DBT. The results are listed in Table 2. There is no significant increase in the HDS rate of DBT although the concentration of DBT increased from 3 to 4 wt%. Further, different from the case using lower concentrations of DBT, an increased in S_{total} and a decrease in S_0 were observed. This indicates that some variance in structure of the Pd catalyst occurred when the concentration of DBT increased up over 3.0 wt%. This is due to a sulfur poisoning effect occurring on the catalyst at higher partial pressures of H_2S in the reaction system as discussed later.

3.3. *Behavior of sulfur on Pt–Pd/Al_2O_3 catalysts*

Similarly, the HDS reaction of [^{35}S]DBT was performed over the 2% Pt–10% Pd/Al_2O_3 catalyst and the effect of concentration of DBT was investigated. Fig. 3 shows the changes in the radioactivities of both formed [^{35}S]H_2S and unreacted [^{35}S]DBT in several reactions with different DBT concentrations at 260 °C and 5.0 MPa. Results similar to those using the Pd/Al_2O_3 catalyst were obtained: the radioactivity of [^{35}S]H_2S increased with the reaction time and approached the steady state; the time when the steady state of radioactivity of [^{35}S]H_2S was obtained became longer if the concentration of DBT was lower. Further, the HDS reactions of [^{35}S]DBT of 1 wt% were carried out at 260 °C when total pressure was varied from 5.0 to 1.0 MPa, and weight-hour-space-velocity (WHSV) was varied from 28 to 14 h^{-1}. The changes in the radioactivities of both formed [^{35}S]H_2S and unreacted [^{35}S]DBT are shown in Fig. 4. According to the method described above, the values of the total amount of the sulfur accommodated on the catalyst and the amount of the labile sulfur involved were calculated from the radioactivity balance and the results are shown in Tables 3 and 4. It was observed that the HDS rate of DBT varied depending on the reaction conditions, resulting in the different H_2S/H_2 ratios in the reaction atmosphere. Further, the concentration of DBT did not significantly affect the selectivity for cyclohexylbenzene (CHB) while the selectivity remarkably changes with the total pressure and space velocity.

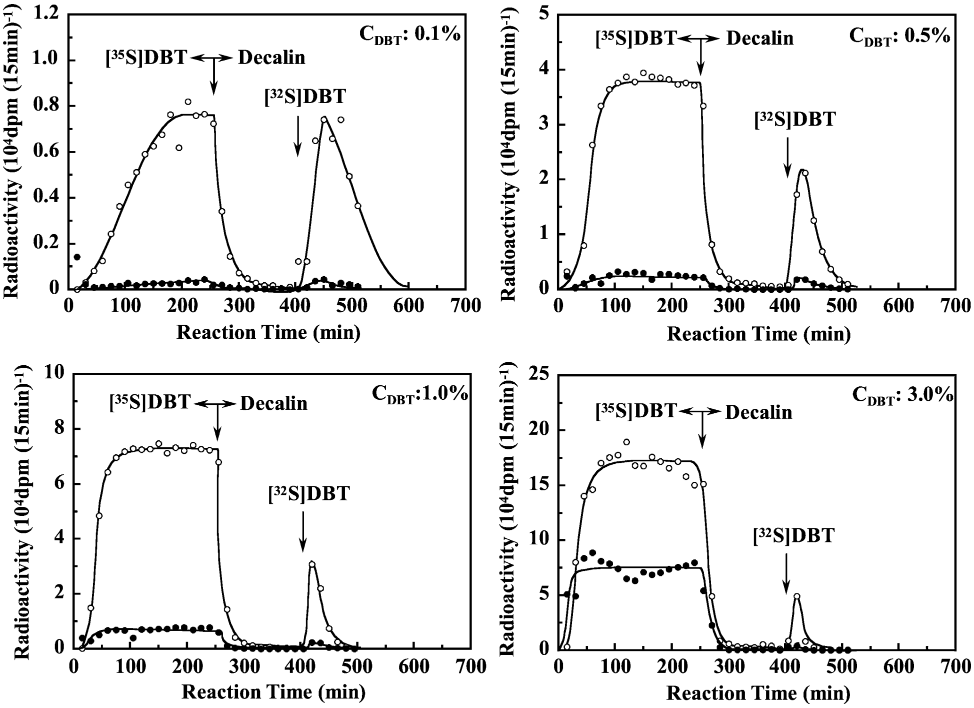

Fig. 3. Changes in radioactivities of unreacted [^{35}S]DBT and formed [^{35}S]H_2S with reaction time. 2% Pt–10% Pd/Al_2O_3; 260 °C; 5.0 MPa; concentration of DBT (C_{DBT}): 0.1–3.0 wt%. ●, [^{35}S]DBT; ○, [^{35}S]H_2S.

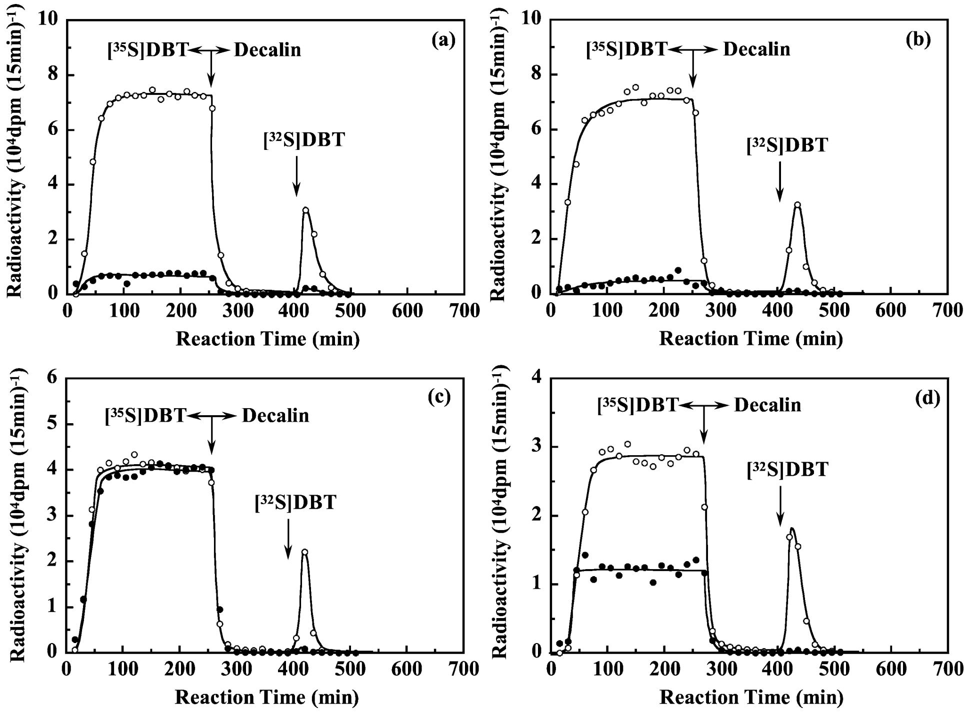

Fig. 4. Changes in radioactivities of unreacted [^{35}S]DBT and formed [^{35}S]H_2S with reaction time. 2% Pt–10% Pd/Al_2O_3; 260 °C; concentration of DBT: 1.0 wt%. (a) 5.0 MPa, WHSV 28 h^{-1}; (b) 2.5 MPa, WHSV 28 h^{-1}; (c) 1.0 MPa, WHSV 28 h^{-1}; (d) 1.0 MPa, WHSV 14 h^{-1}. ●, [^{35}S]DBT; ○, [^{35}S]H_2S.

3.4. Behavior of sulfur on Pd/Al_2O_3 catalysts in the presence of sulfur additive

In order to investigate the behavior of sulfur on the noble metal catalysts in an atmosphere of higher partial pressure of H_2S, and the effect of sulfur additive in reactant solution on the catalytic activity, the polysulfide of concentrations of 0.15 and 0.4 wt%, corresponding to sulfur contents of 0.059 and 0.156 wt%, was added into the decalin solutions of 1 wt% [^{35}S]DBT or [^{32}S]DBT; then similar ^{35}S tracer exper-

Table 3
Results of ^{35}S tracer experiments over a 2% Pt–10% Pd/Al_2O_3 catalyst at 260 °C

Concentration of DBT (wt%)	r_{HDS} (10^{-4} mol/(h g_{cat}))	S_{CHB} (%)	S_{total} (mg/g_{cat})	S_0 (mg/g_{cat})	H_2S/H_2 (10^{-3} mol/mol)	p_{H_2S} (kPa)
0.1	1.52	100	6.84	6.04	0.15	0.73
0.5	7.62	98.5	16.0	7.79	0.75	3.66
1.0	15.1	89.6	16.0	9.84	1.46	7.28
3.0	36.2	87.7	17.9	8.85	3.50	17.4

Table 4
Results of ^{35}S tracer experiments over a 2% Pt–10% Pd/Al_2O_3 catalyst at 260 °C

Pressure (MPa)	*SV* (h^{-1})	r_{HDS} (10^{-4} mol/(h g_{cat}))	S_{CHB} (%)	S_{total} (mg/g_{cat})	S_0 (mg/g_{cat})	H_2S/H_2 (10^{-3} mol/mol)	p_{H_2S} (kPa)
5.0	28	15.1	89.6	16.0	9.84	1.46	7.28
2.5	28	14.3	72.6	18.0	9.06	1.37	3.42
1.0	28	7.53	14.5	11.5	4.71	0.73	0.726
1.0	14	5.31	42.2	13.9	6.47	1.04	1.04

iments were carried out at 260 °C and 5.0 MPa. In the same manner as above, the amount of the sulfur accommodated on the Pd catalyst was determined from the balance between the introduced radioactivity and the eluted one. Similarly, the amount of the labile sulfur involved was determined from the total radioactivity of [^{35}S]H_2S released during the introduction of [^{32}S]DBT. The results are summarized in Table 5. Compared to the results in the absence of polysulfide, the addition of polysulfide remarkably hindered the HDS rate of DBT. The HDS rates in the presence of 0.059 and 0.156 wt% of sulfur decreased respectively to 82.3 and 53.1% of that without the addition of sulfur with no significant variance in the selectivity for CHB. Further, the value of S_{total} increased with increasing concentrations of added sulfur while the values of S_0 decreased. These results indicate that the sulfur accommodated into the catalyst and poisoned active sites on the catalyst, resulting in a decrease in the catalytic activity.

4. Discussion

4.1. Sulfur behavior on Pd/Al_2O_3 and Pt–Pd/Al_2O_3 catalysts in an atmosphere of lower partial pressure of H_2S

Fig. 5 shows the changes in total amounts of sulfur incorporated to the Pd catalyst (S_{total}) and the amount of labile sulfur (S_0) with the partial pressure of H_2S in the reaction atmosphere. Since the hydrogenolysis of polysulfide to form H_2S can easily occur, it was assumed that all the added sulfur transfers to hydrogen sulfide [9,30]. The data obtained in the case adding polysulfide (■, □) are also plotted in Fig. 5. The values of both S_{total} and S_0 monotonically increased with an increase in the partial pressure of H_2S in an atmosphere up to ca. 5.2 kPa, and approached respectively the constants 0.516 and 0.235 mmol/g_{cat}.

Table 5
Effect of sulfur additive on results of ^{35}S tracer experiments over a 10% Pd/Al_2O_3 catalyst at 260 °C

Concentration of added sulfur (%)	r_{HDS} (10^{-4} mol/(h g_{cat}))	S_{CHB} (%)	S_{total} (mg/g_{cat})	S_0 (mg/g_{cat})	H_2S/H_2 (10^{-3} mol/mol)	p_{H_2S} (kPa)
0	10.9	88.8	16.1	6.75	1.05	5.25
0.059	8.98	86.5	18.7	5.49	1.36	6.78
0.156	5.79	89.6	29.9	4.91	1.88	9.37

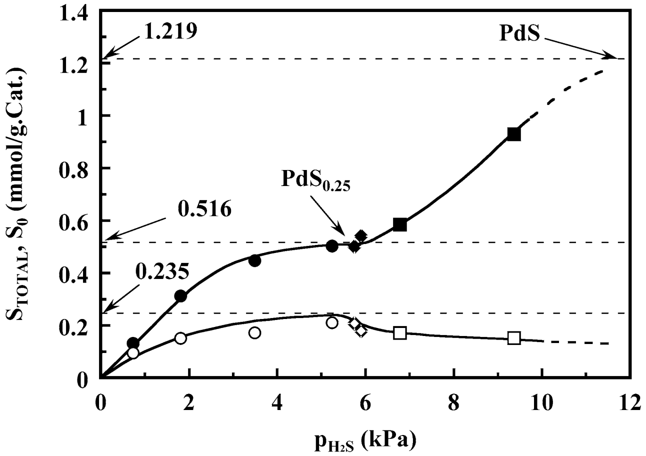

Fig. 5. Effect of partial pressure of H_2S on S_{total} and S_0 on a 10% Pd/Al_2O_3 catalyst at 260 °C. Solid symbol, S_{total}; open symbol, S_0.

Table 6
H_2S/H_2 equilibrium ratios for the reduction of bulk palladium and platinum sulfides at 260 °C

Equilibrium	H_2S/H_2 equilibrium ratios
$Pd + H_2S \leftrightarrow Pd_4S + H_2$	3.8×10^{-3}
$Pd + H_2S \leftrightarrow PdS + H_2$	8.5×10^{-3}
$Pt + H_2S \leftrightarrow PtS + H_2$	9.7×10^{-4}

The stable state sulfides of Pt and Pd are in the forms of PtS and PdS [21,31], whereas supported catalysts are more complicated to handle. The H_2S/H_2 equilibrium ratios for the reduction of the bulk Pd sulfides at 260 °C calculated from thermodynamic data using an Outokumpu HSC Chemistry software [9,32] are given in Table 6. This indicates that the form of Pd and Pt sulfides depends on the H_2S/H_2 ratio in the reaction atmosphere. It was suggested that the Pt/Al_2O_3 catalyst can be sulfided in a mixed gas of 15% H_2S + 85% H_2 to be present in the form of $PtS_{0.95}$ [22] and that the Pt/Al_2O_3 and Pd/Al_2O_3 catalysts can be sulfided in the forms of $PtS_{0.8}$ and $PdS_{1.3}$ [24] in a stream of 10% H_2S + 90% H_2 at 480 °C. It was proposed that Pd sulfide can be present in different sulfide phases in the range of the H_2S/H_2 ratios: Pd metal (at a H_2S/H_2 ratio below 0.008), Pd_4S (at H_2S/H_2 ratios between 0.008 and 0.025), and PdS at higher ratios [22]. Further, it was found that the sulfided noble metal catalysts corresponded to the S/Pt (or

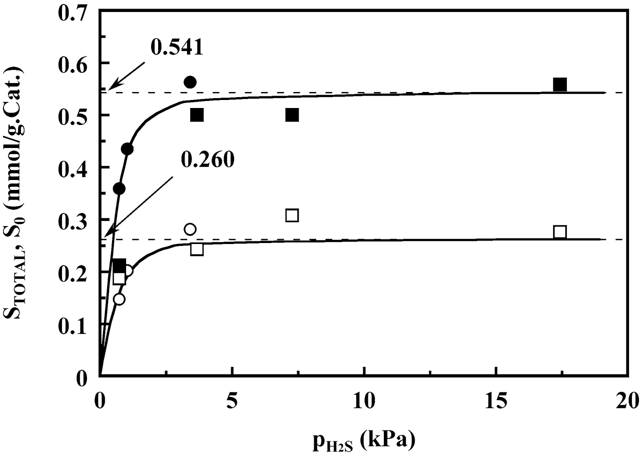

Fig. 6. Effect of partial pressure of H_2S on S_{total} and S_0 on a 2% Pt–10% Pd/Al_2O_3 catalyst at 260 °C. Solid symbol, S_{total}; open symbol, S_0.

Pd) ratio, 0.25, in the HDS reactions [11]. Therefore, taking into account the amount of sulfur accommodated into alumina support, which was 0.281 $mmol/g_{cat}$ [11], it is suggested that the sulfided species of Pd on Pd/Al_2O_3 catalysts is present in the form of PdS_x ($x = 0$–0.25) with the variance in the partial pressure of H_2S, and that the phase of $PdS_{0.25}$ is stable in an atmosphere of lower partial pressure of H_2S. Moreover, in the atmosphere where the partial pressure of H_2S is higher than ca. 3.5 kPa, the ratio of labile sulfur, i.e., S_0, to the remainder between total sulfur incorporated in to the catalyst and that originated from the alumina support, i.e., $S_{total} - 0.281$, is approximately one, indicating that all sulfurs on the catalyst are labile. This is consistent with the results proposed in previous papers [10,11].

Similar to the case using 10% Pd/Al_2O_3 catalyst, the values of both S_{total} and S_0 were also plotted against the partial pressure of H_2S in the atmosphere in Fig. 6. Regardless of the reaction conditions resulting in the change in the partial pressure of H_2S, the values of both S_{total} and S_0 increased monotonically with an increase in the partial pressure of H_2S in the atmosphere and then approached respectively the constants 0.541 and 0.260 $mmol/g_{cat}$. These values for the $Pt–Pd/Al_2O_3$ catalysts are greater than those for the Pd/Al_2O_3 catalysts. This indicates that the platinum sulfide species as well as palladium sulfides was formed and presented in the form of PtS_x ($x = 0$–0.25) on the Pt–Pd catalyst if taking into account the amount of sulfur accommodated into alumina support, 0.281 $mmol/g_{cat}$. Further, similar to the case of Pd/Al_2O_3 catalysts, when the partial pressure of H_2S in the atmosphere is higher than ca. 3.5 kPa, the ratio of labile sulfur, i.e., S_0, to the remainder between total sulfur incorporated into the catalyst and that originated from the alumina support, i.e., $S_{total} - 0.281$, is also approximately one, indicating that all sulfur on the catalyst is labile. This is consistent with the results proposed in previous papers [10,11].

4.2. *Sulfur behavior on Pd/Al_2O_3 and $Pt–Pd/Al_2O_3$ catalysts in an atmosphere of higher partial pressure of H_2S*

When the sulfur additive, polysulfide, was added in the reaction system, i.e., in an atmosphere of higher partial pressure of H_2S, it was observed that the value of S_{total} (■) further increased with increasing p_{H_2S}, and approached a constant value of 1.219 $mmol/g_{cat}$, which represents the total amount of sulfur present in the form of PdS on the Pd catalyst, as shown in Fig. 5. This means that the sulfur further incorporated into the Pd catalyst with further increases in p_{H_2S}. In contrast to this, the value of S_0 (☐) inversely decreased with further increases in p_{H_2S}, as shown in Fig. 5. It was proposed that S_0 represents the number of active sites present on the catalyst [1,10]. Thus, these results mean that the number of active sites decrease with the further incorporation of sulfur into the Pd catalyst and the formation of PdS phase. That is, the sulfur present in the form of PdS phase is almost not mobile. As shown in Table 2, the HDS rate of DBT only slightly increased with increasing concentrations of DBT from 1 to 3 wt%, especially from 3 to 4 wt%, although it is well known that the HDS rate increases with the concentration of DBT. At the same time, the selectivity for CHB also decreased significantly in the case using 3 or 4 wt% DBT. The phenomenon can be explained by the fact that the sulfur accommodation on the catalyst in an atmosphere of higher H_2S partial pressure brings about the formation of the PdS phase in which the sulfur is not mobile, i.e., unrelated to the HDS reaction.

On the other hand, the situation is different in the case of the Pt–Pd catalyst. As shown in Fig. 6, the behavior of sulfur on the Pt–Pd catalyst in an atmosphere of lower partial pressure of H_2S is similar to that in the Pd catalyst while the behavior of sulfur is remarkably different from each other in higher partial pressures of H_2S. Although no polysulfide was added in the case of the Pt–Pd catalyst, the upper limit value of p_{H_2S} tested is much higher than that in the case of the Pd catalyst due to the higher catalytic activity of the former. Even though the partial pressure of H_2S in the atmosphere increased into ca. 17 kPa, there is no significant change in both S_{total} and S_0. This suggests that the structures of $PdS_{0.25}$ and $PtS_{0.25}$ in the Pt–Pd catalyst remain, and that no significant sulfur poisoning occurs in the HDS on the Pt–Pd catalyst. That is, the sulfur tolerance of the Pt–Pd catalysts is improved, maybe due to the formation of a Pt–Pd alloy. This is consistent with the results reported by Cooper and Donnis [33] and Lin et al. [34].

5. Conclusions

The total amount of the sulfur (S_{total}) accommodated on the noble metal catalysts and the amount of the labile sulfur (S_0) participating in the HDS reaction were determined using the ^{35}S radioisotope tracer method. The sulfided state of noble metal sulfides on two catalysts changed depending on the partial pressure of H_2S in the reaction atmosphere and approached their stable states with increasing the partial pressure of H_2S to ca. 5.2 kPa. Taking into account the amount of the sulfur accommodated on the alumina support ($0.281\ \mathrm{mmol/g_{cat}}$), it was concluded that the sulfided noble metal species on the catalysts are presented in the form of PdS_x (or PtS_x) ($x = 0$–0.25) in the HDS reactions. At the same time, the fact that the amount of labile sulfur, i.e., the amount of sulfur participating in the HDS reactions (S_0), was close to that of $S_{\mathrm{total}} - 0.281$ in the case of lower partial pressure of H_2S indicates that all the sulfur in the phase of noble metal sulfide species were almost the labile sulfur.

When the partial pressure of H_2S in reaction system is above 5.8 kPa either by adding other sulfur compounds or by changing the concentration of sulfur-containing reactant, the behavior of sulfur on the Pd catalyst differs from that on the Pt–Pd catalysts. In the case of the Pd catalyst, the sulfur further incorporated into the Pd catalyst with further increases in p_{H_2S}, resulting in the formation of the PdS phase. At the same time, the amount of labile sulfur decreased with a further increase in p_{H_2S}, indicating that the sulfur in the phase of PdS is almost not mobile. On the other hand, in the case of the Pt–Pd catalysts, there was no significant change in both S_{total} and S_0 even though the partial pressure of H_2S in the atmosphere increased into ca. 17 kPa. This suggests that the structures of $PdS_{0.25}$ and $PtS_{0.25}$ in the Pt–Pd catalyst remain, and that no significant sulfur poisoning occurs in the HDS on the Pt–Pd catalysts.

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