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Hydrodesulfurization and Hydrogenation Reactions on Noble Metal Catalysts

I. Elucidation of the Behavior of Sulfur on Alumina-Supported Platinum and Palladium Using the ^{35}S Radioisotope Tracer Method

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Hydrodesulfurization (HDS) reactions of ^{35}S-radioisotope-labeled dibenzothiophene (DBT) were carried out over a series of γ-Al_2O_3-supported noble-metal-containing catalysts at 5.00 MPa and at 260 and 280°C. The amount of sulfur (S_{TOTAL}) accommodated on the catalyst and the amount of labile sulfur (S_0) participating in the reaction were determined using a direct method, the ^{35}S radioisotope pulse tracer method, which has recently been developed by the authors. It was observed that both S_{TOTAL} and S_0 increased linearly with an increase in active metal loading. At the same time, it was found that the sulfided test noble metal catalysts corresponded to a S/Pt (Pd) ratio of 0.25 and that almost all the labile sulfur on these catalysts was mobile in the HDS reaction. Further, the activities of both HDS and hydrogenation reactions over the bimetallic catalyst (Pt–Pd) were higher than those of the monometallic catalysts tested together, whereas the synergetic effects observed on the Pt–Pd catalyst were not as significant as in typical Co–Mo catalyst cases.

Key Words: **noble metal catalyst; hydrodesulfurization; hydrogenation; ^{35}S radioisotope tracer method; platinum; palladium.**

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1. INTRODUCTION

The growing knowledge about the aromatics contained in diesel fuels with respect to 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 stringent each year. 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. Cooper *et al.* reported that under moderate conditions, a γ-Al_2O_3-supported platinum catalyst can saturate 60–70% of the aromatics occurring in Kuwait heavy gas oil (HGO) (1). However, one of the major problems associated with the use of platinum and palladium is their high sensitivity to the sulfur compounds that are usually present in hydrogenation feedstocks (2–4), and it is often taken as a fact that the feedstocks normally need a severe hydrotreating pretreatment to attain sulfur concentration reductions below a few parts per million (5). Thus, noble metal catalysts will be of limited use because of such severe pretreatment unless they are proven to withstand the sulfur tolerance problems involved. Recent studies show that the addition of a second transition metal may effectively improve the activity of these catalysts and their tolerance to sulfur (6–11). It has also been reported that the sulfur tolerance of a noble metal catalyst can be increased with the use of zeolite as a support (6, 12–16). The sulfur poisoning was attributed to the fact that the adsorption of H_2S decreases the metal–support interaction, and thereby promotes the platinum migration which eventually leads to the increase in platinum particle size (9, 17). Meanwhile, recent studies show that some noble metal catalysts may not be as sensitive to sulfur as has generally been recognized (18–21). Therefore, we feel that it is worth while to investigate the fundamental catalytic features of the noble metal catalysts of our interest.

Before our present study, radioactive ^{35}S-labeled dibenzothiophene ([^{35}S]DBT) was synthesized, and its hydrodesulfurization (HDS) reaction was carried out according to the ^{35}S radioisotope pulse tracer method (RPTM) over sulfided Mo-based catalysts under practical HDS conditions (22–26). The hydrogenation (HYD) activity of phenanthrene (PHE) over monometallic and bimetallic catalysts—Pt/Al_2O_3, Pd/Al_2O_3, and $Pt–Pd/Al_2O_3$—was then investigated in the presence of dibenzothiophene (DBT). The bimetallic catalyst ($Pt–Pd/Al_2O_3$) showed some synergetic effects, but not as significant as in typical Co–Mo catalyst cases, whereas the former showed better

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performance in the HYD reaction of PHE in the presence of 1 wt% DBT than the latter. It was also found that only a small amount of labile sulfur was accommodated on the test noble metal catalysts in both the HDS reaction of DBT and the HYD reaction of PHE (27). These findings suggest that the test noble metal catalysts differed from those conventional Mo- or W-based hydrotreating catalysts.

The present study considered the HDS reactions of the ^{35}S-radioisotope-labeled DBT carried out over a series of Pt/Al_2O_3, Pd/Al_2O_3, and Pd–Pt/Al_2O_3 catalysts under practical HDS conditions, in which the ^{35}S RPTM was used to investigate the amount of sulfur accommodated and the behavior of sulfur on the sulfided noble metal catalysts in the HDS reaction.

2. EXPERIMENTAL

2.1. *Materials*

Decalin, used as a solvent, was of commercial GR grade (Kishida Chemicals). Dibenzothiophene (DBT) and [^{35}S]DBT were synthesized according to the method previously employed (22). 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 commercial GR grade (Kishida Chemicals). All scintillation solvents used for radioactivity measurement were from Packard Japan Co., Ltd. The γ-Al_2O_3 used as a support was supplied by Nippon Ketjen Co., Ltd. as 1/32-in. extrudate, the physical properties of which are shown in Table 1.

2.2. *Preparation of Catalysts*

The catalysts used in the present study were prepared by the usual impregnation method: for monometallic catalysts, 20- to 80-mesh γ-Al_2O_3 was impregnated with an aqueous solution of H_2PtCl_6 or $PdCl_2$ as required. This was followed by oven drying at 120°C for 3 h, and then the catalyst was calcined in the air at 400°C for 15 h. The catalysts prepared were labeled x% Pt/Al_2O_3 or x% Pd/Al_2O_3, where the value of x indicates the weight percentage of either Pt or Pd in the catalyst; 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 RPTM*

Experiments using the [^{35}S]DBT tracer were carried out with a fixed-bed reactor of conventional design; details of this reactor are described in Ref. (24). 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^{-1}. The reactor was then cooled to the reaction temperature, in a hydrogen stream and pressurized with hydrogen. A feed mixed with 1 wt% [^{35}S]DBT was introduced into the reactor by use of a high-pressure liquid pump (Kyowa Seimitsu KHD-16).

Typical reaction conditions involved were the following: amount of catalyst, 1 g; hydrogen flow rate, 2.5×10^{-2} m^3 h^{-1}; WHSV, 28 h^{-1}; pressure, 5.00 MPa; concentration of DBT in decalin, 1.0 wt%; and temperatures, 260 and 280°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 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 a proper scintillation solvent (Permafluor or

TABLE 1

Active Metal Loadings and Surface Area of Prepared Catalysts

Catalyst	Pt (mmol g Cat.$^{-1}$)	Pd (mmol g Cat.$^{-1}$)	BET surface area (m^2 g Cat.$^{-1}$)	Pore volume (10^{-6} m^3 g Cat.$^{-1}$)
Al_2O_3			256	0.650
2% Pt/Al_2O_3	0.103		254	0.640
4% Pt/Al_2O_3	0.205		254	0.637
6% Pt/Al_2O_3	0.310		240	0.594
2% Pd/Al_2O_3		0.188	253	0.630
6% Pd/Al_2O_3		0.565	240	0.591
10% Pd/Al_2O_3		0.938	232	0.553
20% Pd/Al_2O_3		1.884	209	0.473
2% Pt–10% Pd/Al_2O_3	0.103	0.938	230	0.536

Instaflour, Packard Japan Co., Ltd.) was added to each of the fractions sampled. For the liquid scintillation counting, explanatory literature is available (22).

Typical operating procedures were followed. (a) After the test catalyst was calcined in the air at 400°C for 20 h, the reaction system was pressurized and heated to 5.00 MPa and 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 became 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 1 wt% [^{32}S]DBT was substituted for decalin and reacted for 4–5 h.

2.4. *Measurement of Catalytic Activity*

The ^{35}S radioisotope tracer method employed allows us to evaluate the HDS and HYD activities simultaneously by gas chromatographic analysis of the DBT conversion. The detectable products of the HDS reaction of DBT were biphenyl (BP), cyclohexylbenzene (CHB), and a trace of dicyclohexyl (DCH). The rate constants (k_{HDS}) of the pseudo-first-order HDS reactions of DBT [(mol DBT converted) h^{-1} (g Cat.)$^{-1}$] over a series of the catalysts prepared were determined using

$$k_{\mathrm{HDS}} = -\ln(1 - x/100)F/w, \qquad [1]$$

where x is the percentage of DBT conversion, F is the feed rate [(mol DBT) h^{-1}], and w is the weight of the catalyst (g). In the same manner, the rate constants (k_{HYD}) of the pseudo-first-order HYD reactions of DBT were determined from the CHB formation.

3. RESULTS

3.1. *Pt/Al_2O_3*

For the determination of sulfided working catalysts, the HDS reaction of 1 wt% ^{35}S-labeled DBT was carried out over the 4% Pt/Al_2O_3 catalyst at 5.00 MPa and at 260°C. Figure 1 shows the typical results obtained with the ^{35}S RPTM: initially, a 1.0 wt% solution of [^{35}S]DBT was introduced and reacted until the formation of [^{35}S]H_2S became 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 catalyst sulfidation. The radioactivities of both formed [^{35}S]H_2S and unreacted [^{35}S]DBT increased and approached a constant value while the [^{35}S]DBT solution was introduced for 45 min. The amount of the ^{35}S supplied to the catalyst from the hydrodesulfurization of [^{35}S]DBT was then determined to be as large as that of the ^{35}S released from the catalyst as [^{35}S]H_2S. The balance thus reached indicated the completion of the sulfur incorporation process, i.e., sulfidation.

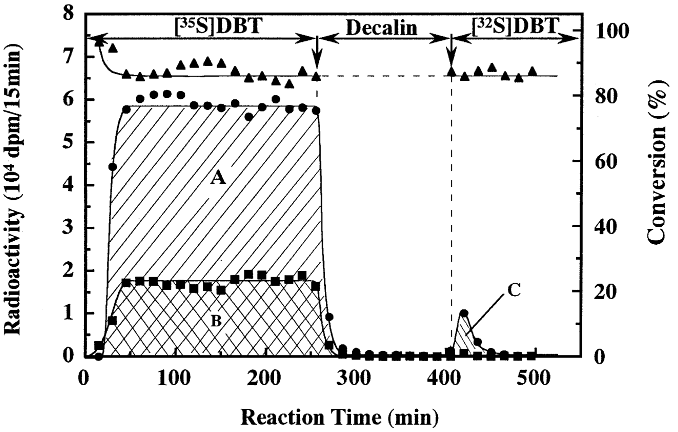

FIG. 1. Changes in radioactivities of unreacted [^{35}S]DBT and formed [^{35}S]H_2S and DBT conversion with reaction time. Conditions: 4% Pt/Al_2O_3, 260°C, 5.00 MPa. ■, [^{35}S]DBT; ●, [^{35}S]H_2S; ▲, conversion.

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 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. The total radioactivity remaining on the catalyst for the time interval (0–400 min), S_{R} (dpm), can be calculated from the balance of radioactivity,

$$S_{\mathrm{R}} = S_{\mathrm{T}} - S_{\mathrm{H}} - S_{\mathrm{D}}, \qquad [2]$$

where S_{T} (1.272×10^6 dpm) is the total radioactivity of the [^{35}S]DBT in the reactant solution, S_{H} (9.556×10^5 dpm) is the total radioactivity of the [^{35}S]H_2S released from the catalyst, i.e., area A in Fig. 1, and S_{D} (2.463×10^5 dpm) is the total radioactivity of the unreacted [^{35}S]DBT, i.e., area B in Fig. 1. The ^{35}S concentration in the sulfur of the [^{35}S]DBT can be defined as $^{35}S_{\mathrm{DBT}}/S_{\mathrm{DBT}}$ (dpm/g), where $^{35}S_{\mathrm{DBT}}$ is the radioactivity of 1 mol of DBT (dpm/mol) and S_{DBT} is the amount of sulfur in 1 mol of DBT (g/mol). From this relationship, the total amount of the sulfur accommodated on the catalyst (S_{TOTAL}) can be given by

$$\begin{aligned} S_{\mathrm{R}}/(^{35}S_{\mathrm{DBT}}/S_{\mathrm{DBT}}) &= (7.001 \times 10^4) \times (1.531 \times 10^{-7}) \\ &= 0.01071 \text{ (g/g of catalyst)} \\ &= 1.63 \text{ (mol of sulfur/mol of Pt)}. \end{aligned}$$

As in our previous papers (22, 23), it is proposed that some portion of the sulfur on the working catalyst participates in the HDS reaction, and this portion of sulfur is defined as labile sulfur. Further, the amount of labile sulfur (S_0) participating in the HDS reaction over the Pt catalyst was determined according to the following method: The catalyst was purged with decalin and hydrogen, and the [^{32}S]DBT solution was substituted for decalin solvent

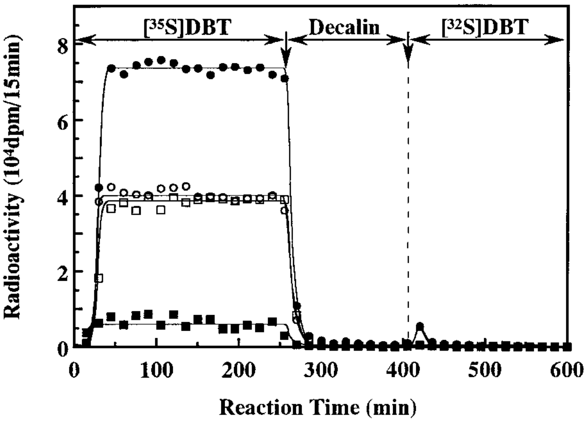

FIG. 2. Changes in radioactivities of unreacted [^{35}S]DBT and formed [^{35}S]H_2S with reaction time. Solid symbols for 280°C and open symbols for 260°C. Conditions: 2% Pt/Al_2O_3, 5.00 MPa. ●,○, [^{35}S]H_2S; ■,□, [^{35}S]DBT.

at ca. 400 min. A portion of the ^{35}S, which is indicated as the shaded area C in Fig. 1, was then determined to be released from the catalyst as [^{35}S]H_2S. In the same manner as above, the amount of the labile sulfur can be calculated from the total radioactivity of the [^{35}S]H_2S released by the introduction of [^{32}S]DBT: the calculated amount is only 2.61 mg of sulfur/g of catalyst, i.e., the shaded area C in Fig. 1.

To investigate temperature effects on the reaction, experiments using the [^{35}S]DBT tracer were carried out over the 2% Pt/Al_2O_3 catalyst with the solution of 1.0 wt% [^{35}S]DBT at 5.00 MPa and at 260 and 280°C. Figure 2 shows changes in the radioactivities with temperature of both formed [^{35}S]H_2S and unreacted [^{35}S]DBT: the radioactivities of these two components at the steady state differed at both 260 and 280°C because of different DBT conversions, whereas the shapes of the radioactivity curves were quite similar. Notably, the radioactivity of the [^{35}S]H_2S released by the introduction of the [^{32}S]DBT was nearly the same at the two temperatures. In the same manner as above, the amount of the sulfur accommodated on the catalyst and the amount of the labile sulfur involved were determined; the results are summarized in Table 2. As can be seen in Table 2, as the temperature rose from 260 to 280°C, both S_{TOTAL} and S_0 changed only slightly, whereas the HDS rate of DBT increased ca. 4.5 times.

TABLE 3

Activity of HDS and HYD and Amounts of Sulfur Accommodated and of Labile Sulfur on Platinum Catalysts at 260°C

Catalyst	DBT conversion (%)	Selectivity of CHB (%)	S_{TOTAL}[a] (mg g Cat.$^{-1}$)	S_0[b] (mg g Cat.$^{-1}$)
2% Pt/Al_2O_3	54.8	11.2	9.98	1.57
4% Pt/Al_2O_3	86.9	14.0	10.7	2.61
6% Pt/Al_2O_3	97.1	30.1	12.4	2.73

Note. [a,b] See Table 2.

Experiments using the same tracer method were also carried out over the 6% Pt/Al_2O_3 catalyst to investigate the effects of the Pt content on the behavior of sulfur on the catalyst. Table 3 shows the investigated effects of Pt loading on the DBT conversion and selectivity for cyclohexylbenzene (CHB) together with the calculated values of S_{TOTAL} and S_0 : all parameters involved increased with an increase in Pt content.

3.2. Pd/Al_2O_3

Figure 3 shows changes with time in the radioactivities of both unreacted [^{35}S]DBT and formed [^{35}S]H_2S as well as in the DBT conversion when the HDS reaction of [^{35}S]DBT was carried out over the 10% Pd/Al_2O_3 catalyst at 5.00 MPa and at 260°C. The radioactivities of these two components increased and approached the steady state when the [^{35}S]DBT was introduced for 60 and 90 min, respectively. It was also observed that the time delay caused by the 10% Pd/Al_2O_3 was longer than that caused by the 4% Pt/Al_2O_3 because of the higher active metal loading of the former, suggesting the concurrent sulfur accommodation on the 10% Pd/Al_2O_3 in larger amount. The total amount of sulfur accommodated was calculated from the balance of radioactivity in the same manner as that followed in Section 3.1. Area C in Fig. 3 indicates the amount

TABLE 2

Amounts of Sulfur Accommodated and of Labile Sulfur and Activity of HYD and HDS on 2% Pt/Al_2O_3 Catalyst

Temperature (°C)	Conversion (%)	S_{TOTAL}[a] (mg/g Cat.)	S_0[b] (mg/g Cat.)	k_{HDS}[c] (10^{-3} mol h^{-1} g Cat.$^{-1}$)	k_{HYD}[d] (10^{-4} mol h^{-1} g Cat.$^{-1}$)
260	54.8	9.98	1.57	1.21	0.97
280	97.1	11.8	1.68	5.41	2.06

[a] Amount of sulfur accomodated.

[b] Amount of labile sulfur.

[c] HDS rate constant.

[d] HYD rate constant.

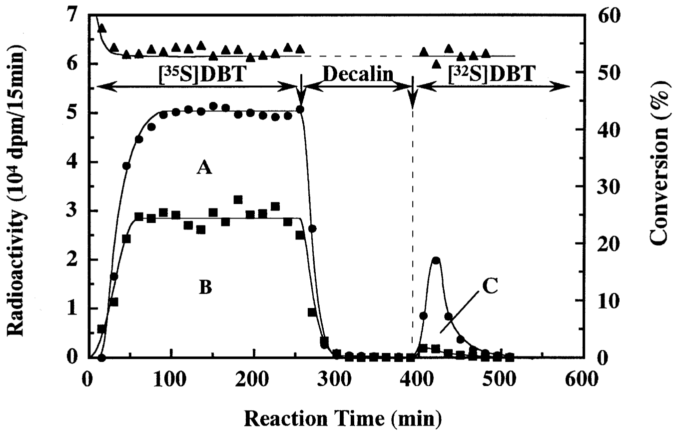

FIG. 3. Changes in radioactivities of unreacted [^{35}S]DBT and formed [^{35}S]H_2S and DBT conversion with reaction time. Conditions: 10% Pd/Al_2O_3, 260°C, 5.00 MPa. ■, [^{35}S]DBT; ●, [^{35}S]H_2S; ▲, conversion.

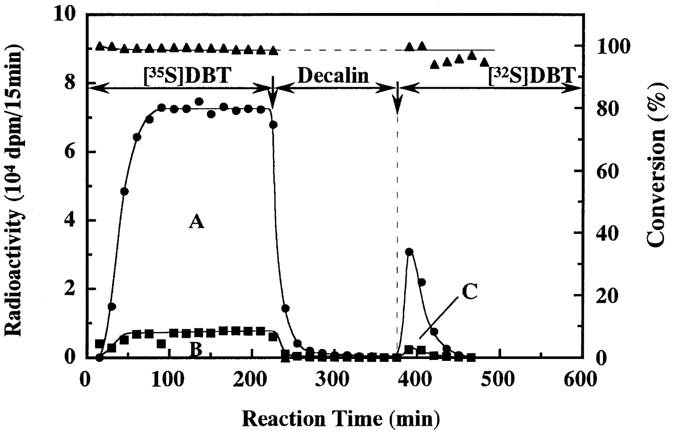

FIG. 4. Changes in radioactivities of unreacted [^{35}S]DBT and formed [^{35}S]H_2S and DBT conversion with reaction time. Conditions: 2% Pt–10% Pd/Al_2O_3, 260°C, 5.00 MPa. ■, [^{35}S]DBT; ●, [^{35}S]H_2S; ▲, conversion.

of labile sulfur participating in the HDS reaction over the ^{35}S-labeled 10% Pd/Al_2O_3 that was determined by measuring the total radioactivity of the [^{35}S]H_2S released by the HDS reaction of the [^{32}S]DBT.

Experiments using the ^{35}S radioisotope tracer were carried out over several Pd/Al_2O_3 test catalysts with Pd content adjusted to about 2, 6, and 20% to investigate the effects of the Pd loading on the conversion of DBT and selectivity for CHB. The results are shown in Table 4 together with the relevant S_{TOTAL} and S_0 values calculated. Similar to the cases of the Pt catalysts tested, all parameters involved increased with an increase in Pd loading, whereas all test Pd catalysts showed a higher hydrogenation selectivity than the Pt test samples.

3.3. *Pt–Pd/Al_2O_3*

The HDS reaction of the [^{35}S]DBT was performed over the 2% Pt–10% Pd/Al_2O_3 catalyst. Figure 4 shows results similar to those of the foregoing cases of the Pt/Al_2O_3 and Pd/Al_2O_3 catalysts. The radioactivities of both formed [^{35}S]H_2S and unreacted [^{35}S]DBT increased and approached the steady state when the [^{35}S]DBT was introduced for 60 and 90 min, respectively. The test catalyst showed a higher conversion of [^{35}S]DBT than all monometallic samples tested together. Table 4 shows the calculated values of the total amount of sulfur accommodated on the catalyst and the amount of labile sulfur involved. It was observed that this Pt–Pd sample showed the highest activity, suggesting that both Pt and Pd metal active sites worked effectively on the alumina support.

3.4. *Comparison of Catalysts*

As mentioned under Experimental, the ^{35}S RPTM allows us to evaluate the HDS and HYD activities simultaneously. The pseudo-first-order reaction constants applied to HDS and HYD for all test catalysts were determined and plotted against the active metal loading (Figs. 5 and 6). Both k_{HDS} and k_{HYD} values increased linearly with increases in Pt and Pd loading at the lower range of content. The Pt

TABLE 4

Activity of HDS and HYD and Amounts of Sulfur Accommodated and of Labile Sulfur on Various Catalysts at 260°C

Catalyst	DBT conversion (%)	Selectivity of CHB (%)	$S_{\mathrm{TOTAL}}{}^a$ (mg g Cat.$^{-1}$)	$S_0{}^b$ (mg g Cat.$^{-1}$)
2% Pd/Al_2O_3	42.9	65.0	9.99	2.03
6% Pd/Al_2O_3	46.8	72.9	11.5	5.84
10% Pd/Al_2O_3	53.8	88.8	16.1	6.67
20% Pd/Al_2O_3	71.2	91.7	22.7	12.2
2% Pt–10% Pd/Al_2O_3	99.3	90.9	16.0	9.84

Note. ^{a,b} See Table 2.

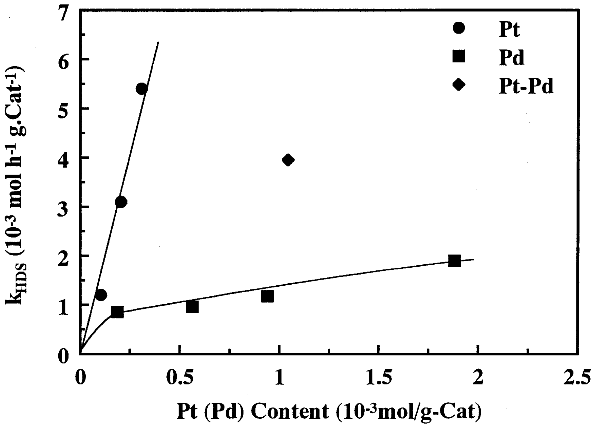

FIG. 5. Effect of active metal content on HDS rate constants. Conditions: 260°C, 5.00 MPa.

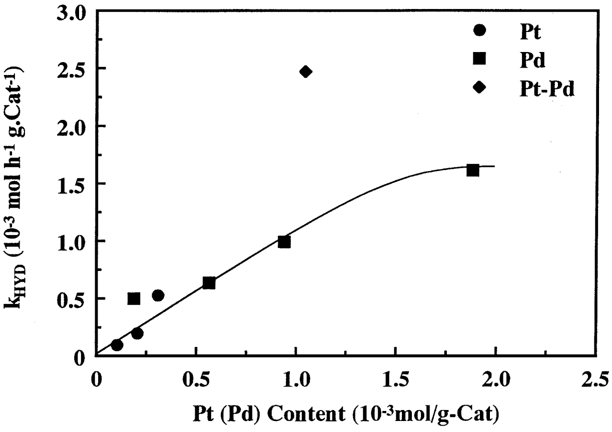

FIG. 6. Effect of active metal content on HYD rate constants. Conditions: 260°C, 5.00 MPa.

TABLE 5

Activity of HDS and HYD and Amounts of Sulfur Accommodated and of Labile Sulfur on Platinum Catalysts at 260°C

Catalyst	DBT conversion (%)	Selectivity of CHB (%)	S_{TOTAL}[a] (mg g Cat.$^{-1}$)	S_0[b] (mg g Cat.$^{-1}$)
2% Pt/Al_2O_3	54.8	11.2	9.98	1.57
2% Pt/Al_2O_3 + Al_2O_3[c]	66.9	10.6	19.0	1.45
Al_2O_3[d]	12.1	—	9.02	—

Note. [a,b] See Table 2.

[c] One gram of 2% Pt/Al_2O_3 catalyst was diluted with 1 g of alumina.

[d] Calculation from results obtained in the case of 2% Pt/Al_2O_3 catalyst and in the case of 2% Pt/Al_2O_3 catalyst diluted with Al_2O_3.

test piece series showed a higher HDS activity than the Pd test piece series, whereas the HYD activities of both series were similar. In the case of the Pt–Pd catalyst, the catalytic performance was improved for both HDS and HYD reactions although the synergetic effect was not as significant as in typical Co–Mo catalyst cases. These results agree with those of our previous study (27). In Fig. 7, the total amount of sulfur accommodated on the catalyst and the amount of labile sulfur involved were plotted against the active metal content: regardless of the kind of active metal, the values of S_{TOTAL} and S_0 were observed to increase linearly with an increase in active metal content. In addition, the S_{TOTAL} line was extrapolated to an intercept of 0.281, which indicates that the amount of the sulfur accommodated on the catalyst at metal loading = 0; that is, the amount of the sulfur accommodated on the alumina support is ca. 0.281 mmol/g of catalyst. Due to the difficulty of directly determining the amount of the sulfur accommodated on the alumina support itself because of its lower catalytic activity, an experiment was designed to measure the total amount of sulfur accommodated: using the ^{35}S tracer, the experiment was conducted over 1 g of the 2% Pt/Al_2O_3 catalyst diluted with 1 g of the alumina support. As summarized in Table 5, the value of S_0 for the alumina-diluted 2% Pt/Al_2O_3 is very close to that for the intact 2% Pt/Al_2O_3; the DBT conversion is slightly enhanced for the treated test piece. This is assumed to be due to the alumina dilution effect and alumina's lower catalytic activity. On the other hand, the value of S_{TOTAL} for the alumina-diluted 2% Pt/Al_2O_3 is larger than that for the intact 2% Pt/Al_2O_3. The difference in S_{TOTAL} between these two test samples is attributed to the amount of the sulfur (S_a) accommodated on the alumina support: as shown in Table 5, the value S_a is 9.02 mg of sulfur/g of catalyst or 0.281 mol/g of catalyst, which is consistent with the value obtained from Fig. 7. The ratio of the sulfur accommodated on the active metal to the active metal content, S/Pt (or Pd) where $S = S_{\mathrm{TOTAL}} - S_a$, approaches 0.25 for all test catalyst cases when the value S_a is subtracted from the total accommodated sulfur amount; that is, Pt (or Pd) exists as Pt_4S (or Pd_4S) on the catalyst. Further, the S_0/S ratio approaches 100% for all test catalyst cases, suggesting that all sulfur in the noble metal sulfides is exchangeable and mobile in the HDS reactions.

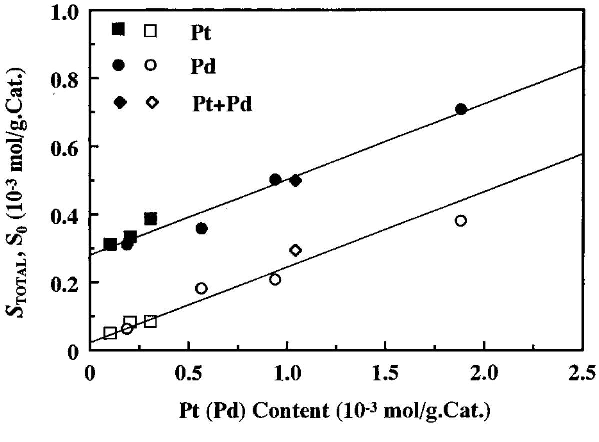

FIG. 7. Sulfidation of platinum and palladium species in Pt (Pd)/Al_2O_3 catalysts at 260°C. Solid symbols for S_{TOTAL} and open symbols for S_0. The straight line corresponds to S/Pt (Pd) = 0.25.

4. DISCUSSION

4.1. *Sulfided Noble Metal Catalysts*

It has been reported that active metals on the conventional Mo- and W-based catalysts are nearly sulfided under moderate conditions, and even more so during the HDS reaction of DBT. On the contrary, the sulfide chemistry of Group VIII metals is complicated and each of the metal–sulfur systems dealt with has its own chemistry: structures and S/M ratios vary so widely. The stable-state sulfides of Pt and Pd are in the forms of PtS and PdS (28–31), whereas supported catalysts are more complicated to handle. Mangnus *et al.* proposed in a temperature-programmed reduction/sulfidation study on the alumina-supported transition metal catalysts 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 $PtS_{0.95}$ (31). Shabtai *et al.* determined the sulfur content of the Pt/Al_2O_3 and Pd/Al_2O_3 catalysts sulfided in a stream of 10% $H_2S + 90\%$ H_2 at 480°C, and concluded that the sulfided test samples are present in the forms of $PtS_{0.8}$ and $PdS_{1.3}$ (32). Since HDS reactions are normally carried out in hydrogen, the reduction of sulfur species might result in the generation of vacant sites. Thus, the 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 depend 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 (31). Because this ratio generally falls between 10^{-1} and 10^{-3} under the 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} (30, 33). In a recent EXAFS study on the Pt/BaK-LTL catalyst, Vaarkamp *et al.* proposed that each platinum atom is likely to be coordinated, on the average, with about one sulfur atom in its first coordination shell (17). Since sulfur tends to be adsorbed on the platinum surfaces in the hollow sites, the surface S/Pt atomic ratio is about 0.4, which is similar to our result. In our present study, all test noble metal catalysts were determined to approach the state equivalent to the S/Pt (or Pd) ratio of 0.25, much lower than that of the stoichiometric-state platinum or palladium sulfide. This suggests that the Pt (Pd)–S bond is so weak to allow lower sulfur accommodation on the test catalysts and that the sulfur accommodation may depend on the partial pressure of H_2S in the atmosphere. For this pressure-related aspect of sulfur accommodation, our more thorough studies are under way.

4.2. *Mobility of Sulfur on Noble Metal Catalysts*

As found in our preceding studies, a part of the total sulfur participated as labile sulfur in the HDS reactions over conventional Mo- or W-based catalysts (22–26). On the contrary, it was found in our present study that almost all sulfur accommodated on the noble metal catalyst was labile sulfur participating in the reaction, although the amount of this labile sulfur (S_0) was much smaller than that experienced with conventional Mo- or W-based catalysts. This difference in the value of S_0 suggests that the sulfur associated with the noble metal catalyst was eventually situated in the environment differently from that in conventional Mo-based catalysts. The sulfur mobility on the catalyst being dependent on the bond strength of the metal sulfide, the of platinum– or palladium–sulfur bond was assumed to be very weak. This assumption is consistent with the formation enthalpies of bulk sulfides listed in Table 6 (28, 29, 34): the enthalpies of PtS and PdS are much lower than those of MoS_2 and WS_2, suggesting that the Pt (Pd)–S bond is weaker. Topsøe and co-workers proposed that the bond energy of Pt–S is lower than that of Mo–S, and even lower than that of Co–Mo–S in *ab initio* calculations (35, 36). This is consistent with the results of our present study in which the labile sulfur on the noble metal catalyst showed high mobility in the HDS reaction. Generally, the catalytic activity was well correlated to the amount of labile sulfur that increased with a rise in reaction temperature (23–26); however, in our present study, no significant effects of temperature on the amount of labile sulfur were observed, as shown in Table 2, whereas the catalytic activity increased with a rise in temperature. These results imply that the HDS reaction mechanism on the noble metal catalyst apparently differs from that on the Mo-based catalyst.

TABLE 6

Enthalpy of Formation of Bulk Sulfides at 298.2 K

Catalyst	Sulfide	ΔH_f (kJ/mol)	Ref.
Mo/Al_2O_3	MoS_2	276.1, 276.0	28, 29
W/Al_2O_3	WS_2	259.4	28, 29, 34
Pt/Al_2O_3	PtS	83.1, 81.6	28, 29
Pd/Al_2O_3	PdS	70.7	28, 29, 34

5. CONCLUSIONS

The total amount of the sulfur (S_{TOTAL}) accommodated on the noble metal catalysts and the amount of labile sulfur (S_0) participating in the HDS reaction were determined using the ^{35}S radioisotope tracer method. Regardless of the kind of active metal used, both values S_{TOTAL} and S_0 increased linearly with an increase in active metal content. At the same time it was found that both S_{TOTAL} and S_0 were much smaller than those of conventional Mo-based catalysts and that almost all sulfur on the noble metal catalysts was exchangeable and mobile in the HDS reactions. It was concluded, taking into account the amount of sulfur accommodated on the alumina support, that the sulfided noble metal catalysts corresponded to a S/Pt (or Pd) ratio of 0.25 in the HDS reactions. These results suggest that the Pt (or Pd)–S bond is very weak. It was further found that both HDS and HYD activities of the bimetallic catalyst (Pt–Pd) were higher than those of the monometallic catalysts tested together, whereas the synergetic effects observed on this Pt–Pd catalyst were not as significant as those achieved with typical Co–Mo catalysts.

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