1. Introduction

The sulfur content of heavy oil fuel for ships will be strictly regulated in the near future to prevent air pollution and acid rain, so methods to reduce the sulfur content, such as the hydrodesulfurization (HDS) process, are highly desirable. Heavy oil contains alkyl group-substituted dibenzothiophenes, in which the alkyl group close to the sulfur atom causes steric hindrance. Steric hindrance in refractory organic sulfur compounds can be decreased by hydrogenation of the aromatic rings. Therefore, the development of highly active HDS catalysts with greater hydrogenation activities than commercial sulfided Co(Ni)Mo/Al₂O₃ catalysts is essential. Noble metals with high hydrogenation activity are used as catalysts for many hydrogenation reactions. However, noble metal catalysts are easily deactivated by the H₂S produced in the HDS reaction. Therefore, high hydrogenation activity and high sulfur tolerance are very important factors to develop highly active HDS catalysts for heavy oils.

Metal phosphides are a recent development in highly active HDS catalysts. We reported that rhodium phosphide (Rh₂P) supported on silica showed higher activities for hydrogenation of biphenyl and HDS of 4,6-dimethyldibenzothiophene than sulfided NiMo/Al₂O₃ and other noble metal phosphide catalysts. High HDS activity of the Rh₂P catalyst will depend on the high hydrogenation activity for aromatic compounds and sulfur tolerance. The phosphorus component preferentially interacts with the SiO₂ support but excess phosphate interacts with Rh₂O₃ and/or forms rhodium phosphate. Since reduction of these phosphate species occurs at lower temperature than that of phosphate on SiO₂, Rh₂P is readily formed in the catalysts with higher P loading. The P/Rh ratio and reduction temperature strongly affect the formation of Rh₂P, but the sulfur tolerance remains unclear.

The sulfur tolerance properties of catalysts may be evaluated by many methods, such as catalytic activity tests under sulfur compounds, catalytic activity tests after sulfidation, crystalline structure analysis by X-ray diffraction (XRD) patterns of the catalysts, and temperature-programmed sulfidation (TPS) technique. The TPS profile of the Rh/SiO₂ catalyst demonstrated a peak attributed to Rh₂S₃ formation around 400 °C. The TPS profiles of P-added Rh (Rh₃P) catalysts showed this peak shifted to higher temperatures and lower intensity with higher P/Rh ratio or reduction temperature. Quantitative analysis of TPS profiles revealed that the amount of reacted H₂S was remarkably lower (about 80 %) with P/Rh ratio more than 1.5, compared with Rh catalyst. The amount of reacted H₂S decreased with greater intensity of the Rh₂P peak in the XRD pattern, indicating that Rh₂P has high sulfur tolerance. Furthermore, the relationship between P/Rh ratio and S/Rh ratio (calculated from TPS profile) of Rh₃P catalysts agreed with the reported S/Rh value, showing the TPS method has high validity for qualitative analysis. We conclude that the TPS technique is a superior method for evaluation of sulfur tolerance for phosphide catalysts, and Rh₂P has remarkably high sulfur tolerance compared with Rh catalyst.

Keywords
Temperature-programmed sulfidation, Sulfur tolerance, Rhodium phosphide, Hydrogen sulfide

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alysts after reaction under sulfur compounds\textsuperscript{6,9,11,13,18,22}, metal-sulfur bond strength determined by temperature-programmed reduction (TPR) profile of sulfided catalysts\textsuperscript{24,25}, CO uptake of the catalysts after HDS reaction\textsuperscript{9,11,13,14}, and sulfidation\textsuperscript{13,24}, sulfur content of the catalyst after HDS reaction\textsuperscript{9,11,13,14}, other reactions under sulfur compounds\textsuperscript{23,26} and sulfidation\textsuperscript{12,15,18}. However, only qualitative or quantitative information can be obtained by conventional methods.

Temperature-programmed sulfidation (TPS) is a technique to evaluate the optimum formation temperature for sulfide catalysts under gas containing H\textsubscript{2}S\textsuperscript{29,30}. In addition, the TPS profile of a catalyst that is difficult to form sulfides, such as noble metal phosphides, can demonstrate the detailed sulfidation behavior of the catalyst. The TPS profile provides qualitative and quantitative information derived from the temperature and area of the H\textsubscript{2}S consumption peaks. However, use of the TPS profile to evaluate the sulfur tolerance of the catalyst has never been reported.

This study examined the sulfur tolerance of rhodium phosphate catalysts using TPS measurement as a new method. The effect of P loading (P/Rh ratio) and reduction temperature on the sulfur tolerance properties of rhodium phosphate catalysts were also studied.

2. Experimental

2.1. Catalyst Preparation

SiO\textsubscript{2} (BET surface area 295 m\textsuperscript{2} g\textsuperscript{–1}) was supplied by Nippon Aerosil Co. SiO\textsubscript{2}-supported Rh and P-added Rh (Rh-P) catalysts were prepared by an impregnation method described previously\textsuperscript{17,20,22}, Rhodium chloride trihydrate (RhCl\textsubscript{3}-3H\textsubscript{2}O, Kanto Chemical Co.) and ammonium dihydrogen phosphate (NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}, Kanto Chemical Co.) were used as Rh and P precursors, respectively, and dissolved in distilled water. After impregnation, the catalysts were dried (110 °C, 24 h), followed by heat treatment in a nitrogen (N\textsubscript{2}) stream to decompose the salt (450 °C, 1 h), and calcination in air (500 °C, 4 h). The ramp rate for the heat treatment and calcination was 10 °C min\textsuperscript{–1}. The Rh loading amount was 5 wt\textsuperscript{%}. The amount of P loading was varied from 0.8 to 3.0 wt\textsuperscript{%}. The P/Rh molar ratios were 0.5, 1.0, 1.5, and 2.0 in the catalysts with 0.8, 1.5, 2.2, and 3.0 wt\textsuperscript{%} P loading, respectively. These catalysts were labeled as Rh-P (x), where “x” denoted the P/Rh molar ratio. P/SiO\textsubscript{2} (1.5 wt\textsuperscript{%} P loading) was also prepared by the same procedure as the Rh-P catalysts.

2.2. Characterization

TPS measurement was performed using a fixed bed flow reactor. The calcined catalyst (0.05 g) was charged into the quartz reactor, and heated (10 °C min\textsuperscript{–1}) in a helium (He) stream (30 mL min\textsuperscript{–1}) from room temperature to 500 °C and held for 1 h, followed by reduction in a hydrogen (H\textsubscript{2}) stream (30 mL min\textsuperscript{–1}) at 350-650 °C for 1 h. After the reduction process, the catalyst was cooled to 30 °C in an He stream, and the He was purged with hydrogen sulfide-nitrogen (3 vol\% H\textsubscript{2}S-N\textsubscript{2}) gas mixture for 0.5 h before the TPS measurement. The TPS profile was recorded from 30 to 600 °C at 10 °C min\textsuperscript{–1}. The concentration of H\textsubscript{2}S was measured using a Shimadzu UV-Vis spectrometer (UV-1800) at 230 nm. The TPS profile of CuO (0.0362 g) was used as a reference to calculate the S content in the Rh-P(x) catalyst from the TPS profile area. CuO reacts with H\textsubscript{2}S to form CuS (CuO + H\textsubscript{2}S → CuS + H\textsubscript{2}O). According to the stoichiometric S/Cu ratio (1/1) of this equation, S atoms per unit area was obtained from the TPS profile of CuO. To calculate H\textsubscript{2}S consumption from the TPS profile of Rh-P(x) catalysts, the area of positive peaks (without negative peaks) was calculated from 30 to 300 °C or 350 °C.

The XRD pattern of the reduced catalyst was obtained using a Rigaku Ultima IV equipped with a Cu Kα (λ = 0.15405 nm) radiation source operated at 40 kV, 40 mA, and 2° min\textsuperscript{–1}. Reduction of the catalyst was carried out under the same conditions as pretreatment for TPS measurements.

3. Results and Discussion

3.1. Identification of Peaks Observed in the TPS Profiles

Figure 1(a) shows the TPS profiles of the SiO\textsubscript{2} support, and P/SiO\textsubscript{2} and Rh/SiO\textsubscript{2} catalysts after reduction at 450 °C. A negative peak was observed around 60 °C in all profiles. The peak for desorption of H\textsubscript{2}S appeared in the TPS profile of MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}\textsuperscript{30}. Therefore, this negative peak was attributed to H\textsubscript{2}S desorption. The order of H\textsubscript{2}S desorption amount was Rh (39.3 µmol g\textsuperscript{–1}) > SiO\textsubscript{2} (25.8 µmol g\textsuperscript{–1}) > P/SiO\textsubscript{2} (13.7 µmol g\textsuperscript{–1}). On the other hand, the specific surface area of Rh catalyst (289 m\textsuperscript{2} g\textsuperscript{–1}) was little changed with SiO\textsubscript{2} support (295 m\textsuperscript{2} g\textsuperscript{–1}), indicating that H\textsubscript{2}S was strongly adsorbed on Rh compared with the SiO\textsubscript{2} support. The specific surface area of P/SiO\textsubscript{2} catalyst (231 m\textsuperscript{2} g\textsuperscript{–1}) was slightly (1.3 times) lower than that of the SiO\textsubscript{2} support. However, the P/SiO\textsubscript{2} catalyst showed about 1.9 times lower H\textsubscript{2}S desorption amount than the SiO\textsubscript{2} support. These results imply that H\textsubscript{2}S was little adsorbed on P. Thus, H\textsubscript{2}S was selectively adsorbed on Rh.

Peaks attributed to H\textsubscript{2}S consumption were not observed in the TPS profiles of SiO\textsubscript{2} and P/SiO\textsubscript{2} above 100 °C. Thus, SiO\textsubscript{2} and P did not react with H\textsubscript{2}S. The H\textsubscript{2}S consumption peak appeared around 400 °C in the TPS profile of Rh catalyst. Elemental analysis of Rh/carbon catalyst treated with 15 % H\textsubscript{2}S-H\textsubscript{2} at 400 °C for 4 h revealed that S/Rh ratio was greater than 1.5, which is the stoichiometric ratio for Rh\textsubscript{2}S\textsubscript{3}. Furthermore, Rh\textsubscript{2}S\textsubscript{3} can be formed in the Rh/SiO\textsubscript{2} catalyst after
sulfidation with 5% H$_2$S-H$_2$ at 400 °C for 3 h. Therefore, this peak was attributed to the reaction of H$_2$S with Rh to form Rh$_2$S$_3$.

H$_2$S consumption increased with temperatures above 500 °C with the Rh catalyst. This H$_2$S consumption above 500 °C was attributed to the endothermic decomposition of H$_2$S (H$_2$S $\rightarrow$ H$_2$ + S). Metal sulfide catalysts, such as MoS$_2$ and WS$_2$, have high activities for H$_2$S decomposition$^{34}$. Rh$_2$S$_3$ in the Rh catalyst would also catalyze H$_2$S decomposition.

Figure 1(b) shows the TPS profile for the second run of the Rh catalyst. The catalyst was cooled from 600 to 30 °C in 3 vol% H$_2$S-N$_2$ after the first run. H$_2$S consumption was only observed above 500 °C in the TPS profile of the second run, indicating that the H$_2$S consumption occurred through decomposition.

Figure 2 shows the TPS profiles of Rh-P ($x = 0.0$-$2.0$) catalysts reduced at 450 °C. The intensity of the negative peak, which appeared around 60 °C, decreased with higher P loading. These results will be discussed in section 3.3. The intensity of the peak attributed to Rh$_2$S$_3$ formation (around 400 °C) decreased with higher P loading, indicating that high P loading inhibits the formation of sulfide species. H$_2$S decomposition was also observed in the TPS profiles of P-added Rh (Rh-P ($x = 0.5-2.0$)) catalysts, as discussed in section 3.2. Thus, H$_2$S consumption in the range from 30 to 500 °C was attributed to the reaction of H$_2$S with Rh to form sulfide species.

3.2. Relationship between Rh$_2$P Formation and Sulfur Tolerance

The negative peak appearing around 60 °C (Figs. 1 and 2) was attributed to H$_2$S desorption, indicating that this H$_2$S species cannot react with Rh to form sulfides. Since the HDS reaction occurs at 280-420 °C$^{35}$, the present HDS process was usually carried out around 350 °C. Therefore, the amount of H$_2$S consumption was evaluated as the area of the positive peaks in the TPS profile from 30 to 350 °C (excluding the negative peak). The effect of P loading on H$_2$S consumption of Rh-P ($x$) catalysts reduced at 450 °C is shown in Fig. 3. The amount of H$_2$S consumption linearly decreased with higher P/Rh ratio from 0 to 1.5, implying that the sulfur tolerance of Rh was enhanced by higher P load-
ing. H₂S consumption little changed as the P/Rh ratio was increased from 1.5 to 2.0.

The intensities of the Rh₂P peak (at 46.7°) in the XRD patterns of Rh-P (x) catalysts reduced at 450 °C are also shown in Fig. 3. Intensity of the Rh₂P peak was obtained by subtracting baseline intensity (183.3 cps) from observed intensity. The intensity of the Rh₂P peak was very low for the Rh catalyst, indicating that Rh₂P was not formed in the Rh catalyst. The intensity of the Rh₂P peak was the same for the Rh-P (0.5) catalyst as for the Rh catalyst. Therefore, the Rh₂P phase was little formed in the Rh-P (0.5) catalyst reduced at 450 °C. However, the amount of H₂S consumption decreased with higher P/Rh ratio from 0 to 0.5. We previously reported that formation of the Rh₂P phase was observed in the XRD patterns of Rh-P (x) catalysts with high P/Rh ratio (1.5 and 2.0) 20). Furthermore, the H₂ consumption peak appeared at 450 °C in the TPR profile of Rh-P (0.5) catalyst 20). Thus, a very thin and/or amorphous Rh₂P layer, undetectable by XRD, was probably formed on the Rh particle in the Rh-P (0.5) catalyst reduced at 450 °C. The intensity of the Rh₂P phase observed in the XRD pattern increased with higher P/Rh ratio. These results revealed that formation of the Rh₂P phase is important to enhance the sulfur tolerance of Rh-based catalyst. On the other hand, H₂S decomposition was observed above 500 °C in the TPS profiles of Rh-P (x) catalysts (Fig. 2) with P/Rh ratio above 1.0, in which Rh₂S₃ was little formed. This result implies that Rh₂P also acts as a catalyst for H₂S decomposition.

Table 1 shows the Rh species observed by XRD and the amount of H₂S consumption over the Rh-P (x) catalysts reduced at 450 °C. H₂S consumption for Rh catalyst was 375.0 µmol g⁻¹. Rh-P (0.5) catalyst, in which a very thin Rh₂P layer would be formed, showed approximately 30 % lower H₂S consumption (255.7 µmol g⁻¹) compared to Rh catalyst. Additionally, the Rh-P (x = 1.0, 1.5, and 2.0) catalysts, in which the peaks for Rh₂P were observed in the XRD pattern, showed remarkably higher sulfur tolerance compared to Rh catalyst. H₂S consumption was remarkably (about 80 %) suppressed, especially above P/Rh ratio of 1.5, compared with Rh catalyst. These results revealed that sulfur tolerance was enhanced by formation of the Rh₂P phase.

### Table 1: Observed Rh Species and H₂S Consumption of Rh-P (x) Catalysts Reduced at 450 °C

| Catalyst     | Observed species in XRD pattern | H₂S consumption [µmol g⁻¹] |
|--------------|---------------------------------|-----------------------------|
| Rh           | Rh                              | 375.0                       |
| Rh-P (0.5)   | Rh, Rh₂P                        | 255.7                       |
| Rh-P (1.0)   | Rh, Rh₂P                        | 154.8                       |
| Rh-P (1.5)   | Rh₂P                            | 68.1                        |
| Rh-P (2.0)   | Rh₂P                            | 55.8                        |

a) Temperature range: 30-350 °C.

3.3. Effect of Reduction Temperature on Sulfur Tolerance of Rh-P (x) Catalysts

Figure 4 shows the effect of reduction temperature on the intensity of the Rh₂P peak (46.7°) in the XRD patterns of the Rh-P (x) catalysts. Peak intensity hardly changed with higher reduction temperature in the Rh catalyst. On the other hand, the peak intensity of Rh₂P slightly increased with higher reduction temperature in the Rh-P (0.5) catalyst. The peak intensity for the Rh-P (0.5) catalyst reduced at 650 °C was marginally higher than that for Rh catalyst reduced at the same temperature. X-ray absorption near edge structure (XANES) spectroscopy revealed that the fractions of Rh and Rh₂P in the Rh-P (0.5) catalyst after reduction at 650 °C were 0.523 and 0.477, respectively 35). Thus, phosphidation of Rh proceeded at this reduction temperature, even though the difference in the XRD peak intensities between Rh and Rh-P (0.5) catalysts was very small. Furthermore, the intensity of Rh₂P remarkably increased with higher reduction temperature in the 1.0 and 1.5 P/Rh ratio catalysts. However, the maximum intensity of Rh₂P for the Rh-P (2.0) catalyst was observed at 450 °C. XRD analysis found that Rh₂P phase was formed in the Rh-P (2.0) catalyst after reduction at 650 °C 20). Thus, the decrease in Rh₂P peak intensity at higher reduction temperature (above 450 °C)
can be explained by the reaction of Rh₂P with excess P (P/Rh = 2.0) to form RhP₂. Since Rh₂P formation was influenced by the reduction temperature of the Rh-P(x) catalyst, reduction temperature strongly affected peak temperature and peak area in the TPS profile.

TPS profiles of Rh-P(x) catalysts reduced at 350-650 °C are shown in Fig. 5. The intensity of the negative peak around 60 °C decreased with higher reduction temperature in all catalysts. The same trend between P/Rh ratio and intensity of the peak around 60 °C was observed, as shown in Fig. 2. We previously reported that the particle size of Rh species increased with higher P/Rh ratio and reduction temperature²⁰. As described in section 3.1, H₂S was selectively adsorbed on the Rh sites. Thus, the decrease in the negative peak can be explained by decrease in the Rh sites with higher reduction temperature and P/Rh ratio. In spite of the changes in reduction temperature, the peak appeared around 400 °C in the TPS profiles of Rh catalyst (a), indicating that sulfidation behavior hardly changed since high reduction temperature did not affect Rh species. The peak also appeared around 400 °C in the TPS profiles of the P-added Rh catalysts (b)-(e) reduced at 350 °C, which can be attributed to the formation of Rh₂S₃. The intensities of the Rh₂P peaks for the 0.5 and 1.0 P/Rh ratio catalysts were the same as that of Rh catalyst as shown in Fig. 4. Since the phosphidation degree of Rh is low in these catalysts after reduction at 350 °C, the remaining metallic Rh species would react with H₂S to form Rh₂S₃. On the other hand, the intensity of the Rh₂P peak was relatively high in the Rh-P(x) catalysts with high P/Rh ratio (above 1.5), meaning that the phosphidation degree of Rh is very high. Previously, we reported that
phosphidation proceeds from the surface of the metallic Rh particles, so that structures consisting of metallic Rh cores covered with Rh$_2$P shells would be formed$^{20}$. A small amount of metallic Rh core would react with H$_2$S to form Rh$_2$S$_3$, resulting in the small peak around 400 °C in the TPS profiles of Rh-P (x) catalysts with high P/Rh ratio (above 1.5). The peak around 400 °C shifted to higher temperatures with higher reduction temperature in all Rh-P catalysts. Higher reduction temperature facilitated the formation of Rh$_2$P, as shown in Fig. 4. Therefore, the reactivity of Rh species for H$_2$S decreased with higher phosphidation degree.

Figure 6 shows the effect of reduction temperature on H$_2$S consumption of Rh-P (x) catalysts. H$_2$S consumption for the Rh catalyst was hardly changed with higher reduction temperature. However, H$_2$S consumption for the Rh-P (x) catalysts decreased with higher reduction temperature. This trend was predominantly observed in the high P/Rh ratio catalysts. H$_2$S consumption for the Rh-P (0.5) catalyst slightly decreased with higher reduction temperature from 550 to 650 °C. However, H$_2$S consumption for the Rh-P (1.0) catalyst remarkably decreased with the same range. We found that phosphate preferentially interacts with the SiO$_2$ support, but not with Rh species$^{20}$. Since phosphate interacting with SiO$_2$ is difficult to reduce compared with that interacting with Rh species, the formation of Rh$_2$P was also difficult in the lower ratio P/Rh catalyst$^{20}$. The fraction of Rh$_2$P was only 0.477 in the Rh-P (0.5) catalyst reduced at 650 °C$^{35}$. In contrast, metallic Rh species were not detected in the XRD pattern of Rh-P (1.0) catalyst after reduction at 650 °C$^{20}$. Thus, the different trends for H$_2$S consumption reduction in the Rh-P (0.5) and Rh-P (1.0) catalysts can be explained by the phosphidation degree of Rh. Rh-P (x) catalysts with P/Rh ratio above 1.0 reduced at optimal temperature showed low H$_2$S consumption (ca. 50 µmol g$^{-1}$). Since the amount of phosphate species interacting with Rh species increases with higher P/Rh ratio, Rh$_2$P is easily formed$^{20}$. Since phosphidation of Rh proceeds with higher P/Rh ratio, high P/Rh ratio (above 1.0) catalysts showed higher sulfur tolerance than Rh-P (0.5) catalyst. Furthermore, the peak intensity of Rh$_2$P decreased with higher reduction temperature from 450 to 650 °C in the Rh-P (2.0) catalyst, as shown in Fig. 4. This result can be explained by formation of RhP$_2$$^{20}$. However, the amount of H$_2$S consumption was hardly changed with higher reduction temperature from 550 to 650 °C. These results imply that sulfur tolerance was little changed by the type of phosphide species.

Figure 7 shows the relationship between peak intensities of Rh$_2$P and H$_2$S consumption from 30 to 350 °C in the Rh-P (x) catalysts. H$_2$S consumption decreased with higher Rh$_2$P intensity. These results revealed that the sulfur tolerance of Rh can be enhanced by Rh$_2$P formation.

3.4 Validation of Sulfur Tolerance by TPS Method

Sulfur tolerance of phosphide-based hydrodesulfurization catalysts was evaluated by a new TPS method. Therefore, the validation of sulfur tolerance of Rh-P (x) catalysts analyzed from TPS profiles must be discussed. Rh$_2$P/SiO$_2$ (P/Rh = 0.75) catalyst reduced at 650 °C, followed by sulfidation with 3 % H$_2$S-H$_2$ at 300 °C for 2 h, contained a small amount of sulfur (S/Rh = 0.19, elemental analysis)$^{18}$. According to this result, the sulfur tolerance of Rh-P (x) catalysts reduced at 650 °C were evaluated by analysis of TPS profiles from 30 to 300 °C. H$_2$S consumption and S/Rh ratio of Rh-P (x) catalysts reduced at 650 °C are listed in Table 2. The trend for H$_2$S consumption (30-300 °C) was the same as that in Table 1. The S/Rh ratios for Rh-P (0.5) and Rh-P (1.0) catalysts were 0.30 and 0.11, respectively.

Figure 8 shows the relationship between the P/Rh
Table 2  \( \text{H}_2\text{S} \) Consumption and S/Rh Ratio Calculated from TPS Profiles of Rh-P (x) Catalysts Reduced at 650 °C

| Catalyst     | \( \text{H}_2\text{S} \) consumption [µmol g\(^{-1}\)] | S/Rh ratio [-] |
|--------------|------------------------------------------------|----------------|
| Rh           | 259.4                                          | 0.53           |
| Rh-P (0.5)   | 146.7                                          | 0.30           |
| Rh-P (1.0)   | 55.7                                           | 0.11           |
| Rh-P (1.5)   | 35.8                                           | 0.07           |
| Rh-P (2.0)   | 34.1                                           | 0.07           |

a) Temperature range: 30-300 °C.

![Fig. 8](image_url) Relationship between P/Rh Ratio and S/Rh Ratio of Rh_P (x) Catalysts Reduced at 650 °C (temperature range of S/Rh: 30-300 °C)

ratio and the S/Rh ratio for Rh-P (x) catalysts. S/Rh ratio exponentially decreased with higher P/Rh ratio. The S/Rh ratio (0.19) for Rh_P/SiO\(_2\) (P/Rh = 0.75) catalyst can be plotted on the curve obtained from the results of Rh_P (x) catalysts. Therefore, the TPS method is a superior quantitative method to evaluate the sulfur tolerance of phosphide-based catalysts.

4. Conclusions

Rhodium phosphide (Rh\(_3\)P) has high hydrogenation activity, so has been extensively investigated as a highly active HDS catalyst for heavy oil. However, the sulfur tolerance of this catalyst, which is a very important property for the HDS catalyst, is unknown. In this study, the sulfur tolerances of Rh\(_3\)P-based HDS catalysts were evaluated by a new TPS technique. Higher P loading and reduction temperature of Rh-P (x) catalysts decreased the intensity of the peak for Rh\(_3\)S\(_2\) formation (around 400 °C), and shifted the peak to higher temperature in the TPS profile of Rh catalyst. XRD analysis revealed that the intensity of the Rh\(_3\)P peak increased with higher P/Rh ratio and reduction temperature. Thus, the sulfur tolerance of Rh-P (x) catalyst was enhanced by Rh\(_3\)P formation. Furthermore, \( \text{H}_2\text{S} \) consumption of Rh catalyst decreased with higher P/Rh ratio and reduction temperature. The S/Rh ratio previously reported can be plotted on the curve as a function of P/Rh and S/Rh obtained from the results of Rh-P (x) catalysts. We conclude that the sulfur tolerance of phosphide-based catalysts can be qualitatively and quantitatively evaluated by the TPS method.

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昇温硫化法によるリン化ロジウム触媒の耐硫黄性評価

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本研究では、リン化ロジウム（Rh3P）系脱硫触媒の昇温硫化（TPS）プロファイルを測定し、耐硫黄性を定性的かつ定量的な観点から評価した。Rh/SiO2触媒のTPSプロファイルでは、400℃付近にRh2S3の生成に起因するH2Sの消費ピークが見られた。これに対し、このピークはP/Rh比の増加および鈍元温度の上昇により、高温側へシフトし、小さくなることが分かった。さらに、TPSプロファイルを30～350℃までの範囲で定量した結果から、P/Rh比が1.5以上の触媒では、Rh種と反応するH2Sの量をRh触媒と比較しておよそ80%抑制できた。また、XRDにおけるRh3Pの回折ピーク強度が増加すると、Rh種と反応するH2Sの量は減少するため、Rh3Pが高い耐硫黄性を有していることを明らかにした。定量値から得られた触媒中のS含有量とP/Rh比との関係は、先に報告された硫化処理後のRh3P触媒に含まれるS量とよく一致しており、本法の妥当性が確認された。以上のことから、TPS法はリン化物触媒の耐硫黄性評価法として優れており、Rh3Pが高い耐硫黄性を有していることを定性的かつ定量的な観点から明らかにした。