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Effects of Support on Formation of Active Sites and Hydrodesulfurization Activity of Rhodium Phosphide Catalyst

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The effects of the support on active site formation and hydrodesulfurization (HDS) activity of Rh₂P catalyst were examined, using metal oxides (MO_x), such as SiO₂, TiO₂, Al₂O₃, MgO and ZrO₂, as the support. Rh₂P was formed on MO_x support after reduction of supported rhodium and phosphorus (Rh–P) catalysts. However, differences in the formation temperatures of Rh₂P were observed by changing the MO_x support. Furthermore, the HDS activities of the supported Rh–P catalysts strongly changed with higher reduction temperature. The order of HDS activities of Rh–P/MO_x catalysts reduced at optimal temperatures was SiO₂ ~ TiO₂ ~ Al₂O₃ > MgO > ZrO₂. The TOF of Rh–P/MO_x catalysts was enhanced by increasing the reduction temperature to form Rh₂P. The order of TOF of supported Rh₂P catalysts was TiO₂ > ZrO₂ > Al₂O₃ > SiO₂ > MgO, and this order disagreed with that of thiophene conversion. The high TOF of Rh–P/TiO₂ catalyst may be explained by formation of partially sulfided TiO₂ in the HDS reaction. The low TOF of Rh–P/MgO catalyst was attributed to the basicity of the support with low sulfur tolerance.

Keywords

Rhodium phosphide catalyst, Metal oxide support, Hydrodesulfurization, Thiophene

1. Introduction

Hydrodesulfurization (HDS) is one of the most important processes used in the petroleum industry for the production of clean fuels which prevent acid rain and deactivation of automotive exhaust catalysts. CoMo/Al₂O₃ catalysts have been widely used in the HDS process. In the past decade, regulation of the sulfur contents of gasoline and diesel fuel in Japan has become significantly more severe. In the near future, regulation of sulfur oxides (SO_x) emission from ships will be stricter, because fuels for ships contain larger amounts of sulfur compounds compared with gasoline and diesel fuel. Therefore, the petroleum industry is depending on the development of highly active HDS catalysts to produce cleaner fuels.

The preparation of highly active CoMo-based HDS catalysts has been widely investigated, such as Ti-modification of Al₂O₃ support¹⁾, Co-CVD technique^{2),3)},

and addition of chelating agents^{4),5)}, citric acid⁶⁾ and phosphorus^{3),7),8)}. Furthermore, new active phases, not sulfided CoMo catalysts, have been reported by many researchers. Noble metals^{9)–14)}, transition metal carbides^{15)–17)}, nitrides^{15),18)} and phosphides^{19)–26)} have been employed as new HDS catalysts. Transition metal phosphides, such as Ni₂P^{19)–24)} and MoP^{25)–28)}, have received much attention as new HDS catalysts. In particular, Ni₂P catalyst has high potential for the HDS reaction. On the other hand, we have reported that noble metal phosphides, especially rhodium phosphide (Rh₂P), supported on SiO₂ have high and stable catalytic activity for the HDS of thiophene²⁹⁾. Furthermore, Bussell *et al.* reported that Rh₂P/SiO₂ catalyst has high activity for the HDS of dibenzothiophene³⁰⁾. However, the effect of the support on the HDS activity of Rh₂P catalyst remains unknown. The support affects the HDS activity of CoMo catalyst³¹⁾ and the acidity of the support enhances the sulfur tolerance of noble metal-based HDS catalyst^{32)–34)}. Since AlPO₄ inhibits formation of Ni₂P, Al₂O₃ is not suitable as a support for Ni₂P catalyst²²⁾. Therefore, the effects of the support

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on the formation and catalytic activity of Rh₂P for the HDS reaction require investigation.

The present study examined the effect of metal oxide (MO_x) support on phosphidation of Rh species to form active sites and the HDS activity of supported Rh₂P catalyst.

2. Experimental

2.1. Preparation of Catalysts

We used MO_x, such as silica (SiO₂), alumina (Al₂O₃), titania (TiO₂), magnesia (MgO) and zirconia (ZrO₂), as supports. The Rh/MO_x catalysts were prepared by an impregnation method using aqueous solution of rhodium (III) chloride trihydrate (RhCl₃·3H₂O). The amount of Rh loading was 5 mass%. Impregnated catalysts were dried at 110 °C for 24 h followed by heat treatment in a nitrogen stream at 450 °C for 1 h to decompose the salt. The supported Rh catalysts were then pressed into disks and crushed to obtain 30-42 mesh size granules. The sieved catalysts were calcined in air at 500 °C for 4 h. The increase rate of heat treatment and calcination was 10 °C·min⁻¹. P-added Rh (Rh-P) catalysts were prepared by the same procedure using RhCl₃·3H₂O and ammonium dihydrogen phosphate (NH₄H₂PO₄) aqueous solutions. The amount of P addition was 1.5 mass%.

2.2. Characterization of Catalysts

Supported Rh and Rh-P catalysts were characterized by temperature-programmed reduction (TPR), X-ray diffraction (XRD), and BET surface area and CO adsorption measurements. TPR spectra were measured using a Shimadzu GC-8A gas chromatograph. Supported Rh or Rh-P catalysts (0.1 g) were heated in a helium stream (30 mL·min⁻¹) from room temperature to 500 °C at 10 °C·min⁻¹, followed by heating at 500 °C for 1 h in helium. The calcined catalysts were then cooled to 30 °C in a helium stream, and the helium was switched to 5 vol% hydrogen-nitrogen (H₂-N₂) gas mixture at 30 °C for 30 min before measurement. Water was removed with a molecular sieve trap. The TPR spectra were recorded through the range from 30 to 850 °C at 10 °C·min⁻¹, using a thermal conductivity detector (TCD) to monitor hydrogen consumption. XRD patterns of calcined and reduced catalysts were measured by a Rigaku MiniFlex with Cu Kα radiation at 30 kV and 15 mA. Crystallite sizes of Rh and Rh₂P were calculated by Scherrer's equation. Measurement of BET surface area was carried out using a Micromeritics ASAP 2010. The catalysts were evacuated at 300 °C for 5 h before nitrogen adsorption at -196 °C. CO adsorption on supported Rh and Rh-P catalysts was measured using the pulse method. Supported Rh or Rh-P catalysts (0.1 g) were treated in helium at 500 °C (heating rate: 10 °C·min⁻¹) for 1 h, followed by reduction in hydrogen at 350-850 °C for

1 h. CO was injected onto the catalyst layer at 25 °C using the sampling loop. The amount of CO adsorbed was measured with a Shimadzu GC-8A gas chromatograph equipped with a TCD.

2.3. Hydrodesulfurization of Thiophene

HDS of thiophene was performed at 350 °C under 0.1 MPa using a conventional fixed bed flow reactor. The catalyst (0.1 g) was charged into the quartz reactor and was heated (10 °C·min⁻¹) in a helium stream (30 mL·min⁻¹) to 500 °C and heated for 1 h. After helium treatment, the catalyst was reduced under hydrogen (30 mL·min⁻¹) at 350-850 °C for 1 h. Hydrogen-thiophene gas mixture (H₂/C₄H₄S = 30), obtained by passing a hydrogen stream through a thiophene trap cooled at 0 °C, was introduced into the reactor. The reaction condition (*W/F*) was 37.9 g·h·mol⁻¹. The reaction products were analyzed with a gas chromatograph (FID) equipped with silicone DC-550 (2 m, 135 °C) and VZ-7 (4 m, 0 °C) columns. Commercial CoMoP/Al₂O₃ (Co: 2.5 mass%, Mo: 10.0 mass% and P: 2.1 mass%) catalyst was used to assess the supported Rh-P catalysts. Pre-sulfided CoMoP/Al₂O₃ catalyst was prepared using 5 vol% hydrogensulfide-hydrogen (H₂S-H₂) at 400 °C after hydrogen reduction at 450 °C.

3. Results and Discussion

3.1. Effect of Reduction Temperature on Formation of Rh₂P

3.1.1. XRD Patterns of Calcined Rh and Rh-P Catalysts

To analyze the Rh species after calcination, the XRD patterns of MO_x-supported Rh and Rh-P catalysts were observed. **Figures 1 and 2** show the XRD patterns of supported Rh and Rh-P catalysts after calcination at 500 °C, respectively. The peak of Rh₂O₃ (2θ = 34.2°) appeared on the XRD patterns of Rh/SiO₂ (**Fig. 1 (i)**, (b)), Rh-P/SiO₂ (**Fig. 2 (i)**, (b)) and Rh-P/TiO₂ (**Fig. 2 (iii)**, (b)). However, this peak was not observed in the XRD patterns of Rh and Rh-P supported on Al₂O₃ (**Figs. 1 and 2 (ii)**, (b)) and MgO (**Figs. 1 and 2 (iv)**, (b)) indicating that the Rh species were highly dispersed on MgO and Al₂O₃ supports. Since the XRD pattern of Rh/ZrO₂ catalyst (**Fig. 1 (v)**, (b)) showed no peaks of Rh or Rh₂O₃, Rh species were highly dispersed on ZrO₂ support. On the other hand, the XRD pattern of Rh-P/ZrO₂ included the peaks of metallic Rh (**Fig. 2 (v)**, (b)), indicating that most large Rh particles formed after salt decomposition were not oxidized by calcination at 500 °C.

3.1.2. TPR Spectra of Rh and Rh-P Catalysts

The TPR spectra of MO_x-supported Rh and Rh-P catalysts were examined to obtain information about Rh₂P formation. The TPR spectra of supported Rh catalysts are shown in **Fig. 3**. The TPR spectra of MO_x support (a) included a small hydrogen consumption peak at

Fig. 1 XRD Patterns of Calcined and Reduced Rh Catalysts

550 °C for TiO₂ (iii) and 600 °C for ZrO₂ (v). However, no such peaks appeared in spectra of other MO_x supports. These results show that TiO₂ and ZrO₂ are reducible in contrast to the other supports. The peaks attributed to the reduction of Rh₂O₃ were observed around 50 to 150 °C in the spectra of Rh/MO_x catalysts (b). On the other hand, a peak around 450 °C was also observed in the spectra of Rh/MgO (iv), (b), which was attributed to the reduction of MgRh₂O₄³⁵⁾. However, the diffraction peaks of MgRh₂O₄ ($2\theta = 29.7, 35.0$ and 52.7°) were not observed in the XRD pattern of calcined Rh/MgO, as shown in Fig. 1 (iv), (b). These results indicate that highly dispersed MgRh₂O₄ was present in the Rh/MgO catalyst. Furthermore, the

spectrum of Rh/TiO₂ catalyst (iii), (b)) contained a broad peak around 650 °C, which was attributed to reduction of the support. The TPR spectra of Rh-P/MO_x catalysts are shown in Fig. 3. The peak of Rh₂O₃ reduction at 50 to 150 °C was also observed in all Rh-P catalysts, except for the MgO support. Moreover, the reduction peaks of phosphates were observed in the spectra of Rh-P catalysts.

However, the peak temperature attributed to phosphate reduction was remarkably changed by the type of MO_x support. In the spectrum of Rh-P/SiO₂ (i), (c)), broad peaks appeared at 270, 360 and 650 °C. Formation of Rh₂P from rhodium phosphate by hydrogen reduction is reported to occur at 350 °C³⁶⁾. Thus,

Fig. 2 XRD Patterns of Calcined and Reduced Rh-P Catalysts

the peak at 360 °C was attributed to the reduction of phosphates to form Rh₂P. The spectrum of Rh-P/TiO₂ ((iii), (c)), contained peaks at 280, 540 and 730 °C, and a shoulder peak appeared at 400 °C. This trend was the same as that observed for Rh-P/SiO₂. TiO₂ is well known to be more reducible than other metal oxides^{37,38}. Thus, the large peak observed at 540 °C would be attributed to the reduction of phosphate and TiO₂ support. The spectrum of Rh-P/Al₂O₃ catalyst ((ii), (c)), contained no peaks from 200 to 600 °C, but hydrogen consumption increased above 700 °C. This observation indicates that Rh₂P is difficult to form on Al₂O₃ compared with SiO₂ and TiO₂. The peak temperature in the TPR spectra of MoP/Al₂O₃ occurred at

about 800 to 900 °C²⁷, higher than that observed for MoP/SiO₂ (550 °C)²⁵. Furthermore, phosphorus reacts with the surface of Al₂O₃ to form AlPO₄ in Ni₂P/Al₂O₃ catalyst²². Thus, the peak observed at higher temperature in the TPR spectrum of Rh-P/Al₂O₃ was attributed to the reduction of AlPO₄ to form Rh₂P. The same trend was also observed in the TPR spectrum of Rh-P/ZrO₂ ((v), (c)) indicating that formation of Rh₂P is difficult on Al₂O₃ and ZrO₂ supports. On the other hand, the reduction peak of MgRh₂O₄ also appeared at 550 °C in the spectrum of Rh-P/MgO catalyst ((iv), (c)). Furthermore, no peaks of Rh species were found in the XRD pattern of Rh-P/MgO catalyst after calcination, as shown in Fig. 2 (iv), (b). This result shows that highly

Support: (i) SiO₂, (ii) Al₂O₃, (iii) TiO₂, (iv) MgO, (v) ZrO₂.
(a) Support, (b) Rh catalyst, (c) Rh-P catalysts.

Fig. 3 TPR Spectra of Rh and Rh-P Catalysts

dispersed MgRh₂O₄ is present in the Rh-P/MgO catalyst.

3.1.3. XRD Patterns of Reduced Rh/MO_x and Rh-P/MO_x Catalysts

The XRD patterns of reduced catalysts were examined to evaluate the formed Rh species. The XRD patterns of reduced Rh and Rh-P catalysts are shown in **Figs. 1** and **2**. In Rh catalysts (**Fig. 1**), except Rh/Al₂O₃, the peaks of Rh ($2\theta = 41.1, 47.9, 70.0$ and 84.5°) were observed and the intensity of peaks increased with higher reduction temperature. On the other hand, the

peaks of Rh₂P ($2\theta = 41.1, 47.9, 70.0$ and 84.5°) appeared in the XRD patterns of reduced Rh-P/MO_x catalysts, as shown in **Fig. 2**. However, the reduction temperature required for the appearance of Rh₂P peaks was remarkably changed by the type of support. This tendency was the same as that found by TPR spectra, as shown in **Fig. 3**. The relationships between reduction temperature and Rh species detected by XRD of Rh-P catalysts are listed in **Table 1**. Rh₂P was formed in Rh-P/SiO₂ and Rh-P/TiO₂ catalysts reduced at 450°C . Metallic Rh was only observed in Rh-P/Al₂O₃ and Rh-

Table 1 Observed Rh Species by XRD in Rh and Rh-P Catalysts Reduced at Various Temperatures

Support	Rh species				
	450 °C	550 °C	650 °C	750 °C	850 °C
SiO ₂	Rh, Rh ₂ P	Rh ₂ P	Rh ₂ P	—	—
Al ₂ O ₃	Rh	Rh	Rh	Rh, Rh ₂ P	Rh ₂ P
TiO ₂	Rh ₂ P	Rh ₂ P	Rh ₂ P	—	—
MgO	— ^{a)}	Rh ₂ P	Rh ₂ P	—	—
ZrO ₂	Rh	Rh, Rh ₂ P	Rh, Rh ₂ P	Rh ₂ P	—

a) No peaks of Rh species were observed.

● SiO₂, ▲ Al₂O₃, ■ TiO₂, ◆ MgO, × ZrO₂.

Fig. 4 HDS Conversion of Thiophene over Rh-P/MO_x Catalysts Reduced at 550 °C

P/ZrO₂ catalysts reduced at the same temperature. On the other hand, no peaks of Rh species were observed in the Rh-P/MgO catalyst reduced at 450 °C. Since the reduction peak attributed to MgRh₂O₄ was observed at 550 °C in the TPR spectrum of Rh-P/MgO (**Fig. 3** (iv), (c)), formation of Rh₂P did not occur in the Rh-P/MgO reduced at 450 °C. Rh₂P was formed in all Rh-P catalysts with higher reduction temperature. However, metallic Rh species were observed in Rh-P/Al₂O₃ and Rh-P/ZrO₂ catalysts reduced at 750 °C and 650 °C, respectively. This observation indicates that formation of Rh₂P is more difficult on Al₂O₃ and ZrO₂ than on other supports. The trend of these results agrees with that of TPR spectra, as shown in **Fig. 3**.

3.2. HDS Activities of Rh/MO_x and Rh-P/MO_x Catalysts

Figure 4 shows the HDS conversion of thiophene over Rh-P/MO_x catalysts reduced at 550 °C. The Rh-P catalysts showed stable activities with time-on-stream. However, the HDS activity of Rh-P/MgO catalyst remarkably decreased. It is well known that sulfur tolerance is increased by the acidity of the support^{(12),(13),(32)~(34)}. In contrast, MgO has basic properties indicating that the sulfur tolerance of Rh-P/MgO catalyst would be lower than that of other Rh-P/MO_x catalysts, thus accounting for the remarkable decrease of HDS activity

● SiO₂, ▲ Al₂O₃, ■ TiO₂, ◆ MgO, × ZrO₂.

Fig. 5 Effect of Reduction Temperature on HDS Activities of (i) Rh and (ii) Rh-P Catalysts

with time-on-stream observed with the Rh-P/MgO catalyst.

We previously reported that the HDS activity of Rh-P/SiO₂ catalyst was remarkably changed by the reduction temperature. Therefore, the effect of reduction temperature was examined on the HDS activities of Rh and Rh-P catalysts after 3 h reaction. Reduction temperature hardly affected the HDS activities of Rh catalyst with SiO₂, Al₂O₃ and MgO supports, as shown in **Fig. 5** (i). However, increasing reduction temperature reduced the HDS activities of TiO₂ and ZrO₂-supported Rh catalysts. In contrast, reduction temperature strongly affected the HDS activities of all Rh-P/MO_x catalysts, as shown in **Fig. 5** (ii). The HDS activities of Rh-P catalysts changed with increasing reduction temperature. The highest activity appeared at lower reduction temperature (550 °C) using SiO₂ support, whereas the highest HDS activities occurred on other supports reduced at higher temperature (above 650 °C). In particular, the reduction temperature for optimal HDS activity of Rh-P/Al₂O₃ catalyst was 800 °C. The optimal reduction temperature for the highest activity remarkably changed with the type of MO_x support. The explanation for these findings is that the formation temperature of Rh₂P significantly depends on the type of MO_x support, as shown in **Fig. 2** and **Table 1**.

Figure 6 shows the HDS activities of Rh and Rh-P catalysts reduced at the optimal temperatures. Rh-P/MO_x catalyst showed higher activity than Rh/MO_x catalyst, indicating that formation of Rh₂P by P addition and reduction with hydrogen leads to enhanced activity. The order of HDS activities was as follows; SiO₂ ~ TiO₂ ~ Al₂O₃ > MgO > ZrO₂.

Table 2 shows the product distribution of thiophene HDS for various Rh/MO_x and Rh-P/MO_x catalysts reduced at the optimal temperature. Reduced and sulfided Rh/SiO₂ catalyst, as well as NiMo/Al₂O₃ catalyst, favored the direct desulfurization route with high biphenyl (BP) selectivity for the HDS of dibenzothiophene³⁰. On the other hand, Rh₂P/SiO₂ catalyst favored the hydrodesulfurization route with low BP selectivity³⁰. In our study, the selectivities of butanes and tetrahydrothiophene (THT) for Rh catalysts were increased by P addition, indicating that Rh-P/MO_x catalysts would favor the hydrogenation route compared

Rh catalyst: 400 °C; TiO₂, ZrO₂, 450 °C; Al₂O₃, 500 °C; SiO₂, MgO.
Rh-P catalyst: 550 °C; SiO₂, 650 °C; TiO₂, MgO, 700 °C; ZrO₂, 800 °C; Al₂O₃.

Fig. 6 HDS Activities of Rh and Rh-P Catalysts Reduced at Optimal Temperature

with Rh/MO_x catalysts. The SiO₂, Al₂O₃ and TiO₂-supported Rh-P catalysts showed the same conversion and selectivities of products. These results show that the reaction mechanism for HDS of thiophene is little changed by the type of support. The Rh-P/MgO and Rh-P/ZrO₂ catalysts showed higher THT selectivity than other Rh-P catalysts, which can be explained by the low conversion of thiophene. However, since Rh-P/ZrO₂ catalyst showed slightly lower HDS activity than Rh-P/MgO catalyst, the remarkably high THT selectivity of Rh-P/ZrO₂ cannot be explained by such low conversion. This result will be discussed in section 3.3.2.

3.3. Characterization of Rh and Rh-P Catalysts

3.3.1. BET Surface Area of Calcined Rh and Rh-P Catalysts

Table 3 shows the BET surface area of MO_x supports, and calcined Rh/MO_x and Rh-P/MO_x catalysts. The order of surface area of MO_x was as follows; SiO₂ > Al₂O₃ > TiO₂ > MgO > ZrO₂. The surface area of SiO₂, Al₂O₃ and TiO₂ hardly decreased after Rh loading, showing that Rh species were highly dispersed on these MO_x supports. On the other hand, the surface area of Rh/MgO catalyst was increased by Rh loading. The XRD patterns showed the intensity of the main peak attributed to MgO ($2\theta = 42.9^\circ$, 10174 cps) was remarkably smaller for calcined Rh/MgO than for MgO support (Rh unloaded, 25385 cps). Furthermore, the crystalline size of MgO (37.3 nm) calculated by Scherrer's equation decreased after Rh loading (21.0 nm), indicating that the surface of MgO had partially dissolved in the acidic RhCl₃·3H₂O aqueous solution. Therefore, the increase of surface area by Rh loading can be explained by the reaction of leached Mg species with Rh species to form MgRh₂O₄ as observed in **Fig. 3 (iv)**, (b). Increased surface area was also observed for Rh/ZrO₂ catalyst. The HCl impregnated ZrO₂, which contained the same amount of Cl as RhCl₃·3H₂O aqueous

Table 2 Distribution of Reaction Products in the HDS of Thiophene over Rh and Rh-P Catalysts Reduced at Optimal Temperature

Catalyst	Reduction temperature [°C]	Conversion [%]	Composition of HDS products [%]				
			C ₁ -C ₃ ^{a)}	Butanes	Butenes	1,3-Butadiene	THT ^{b)}
Rh							
SiO ₂	500	17.01	0.25	10.36	85.93	0.00	3.45
Al ₂ O ₃	450	8.75	1.86	14.71	82.17	0.00	1.26
TiO ₂	400	17.94	0.80	13.64	82.60	0.00	2.96
MgO	500	6.61	0.27	10.53	85.52	0.00	3.68
ZrO ₂	400	20.03	0.09	12.29	82.28	0.10	5.24
Rh-P							
SiO ₂	550	54.95	0.11	20.82	75.54	0.00	3.53
Al ₂ O ₃	800	54.55	0.16	20.86	75.15	0.01	3.83
TiO ₂	650	54.64	0.06	21.46	74.77	0.00	3.70
MgO	650	25.67	0.00	11.45	82.87	0.00	5.66
ZrO ₂	750	22.53	0.15	7.74	78.46	0.00	13.64

a) C₁-C₃ hydrocarbons.

b) Tetrahydrothiophene.

Table 3 BET Surface Area of MO_x Supports and Rh and Rh-P Catalysts Measured by N₂ Adsorption at -196 °C

Support	Surface area [m ² ·g ⁻¹]		
	Support	Supported Rh catalyst	Supported Rh-P catalyst
SiO ₂	295	289	249
Al ₂ O ₃	101	101	88
TiO ₂	56	54	52
MgO	26	64	71
ZrO ₂	5	11	2

Table 4 Crystallite Size of Rh Calculated from XRD Patterns in Rh Catalysts Reduced at Various Temperatures

Support	Crystalline size [nm]		
	450 °C	550 °C	650 °C
SiO ₂	2.4	2.4	2.9
Al ₂ O ₃	0.8	1.1	1.0
TiO ₂	— ^{a)}	2.3	4.1
MgO	2.0	2.5	3.6
ZrO ₂	25.7	28.3	35.4

a) No peaks of Rh were observed.

solution and was prepared by the same procedure for preparing supported Rh catalyst, showed the same surface area as the original ZrO₂ (5 m²·g⁻¹), indicating that treatment with acidic solution did not enhance the surface area of ZrO₂. The XRD pattern of calcined Rh/ZrO₂ catalyst contained no peaks of Rh₂O₃ and Rh as shown in **Fig. 1 (v)**, (b). Thus, calcined Rh/ZrO₂ catalyst has high Rh₂O₃ dispersion. Assuming that the particle shape of Rh₂O₃ is spherical and the particle size is 5 nm, the surface area of Rh₂O₃ particles calculated from $S = 6/pd$ (S : surface area, p : density of Rh₂O₃, d : diameter) is approximately 145 m²·g⁻¹. Even if Rh loading is very low (5 mass%) compared with the ZrO₂ support, the surface area of Rh₂O₃ was remarkably higher than that of the ZrO₂ support. Therefore, high dispersion of Rh species leads to increased surface area. Furthermore, Rh-P/MO_x catalysts, except for Rh-P/MgO, had lower surface area than MO_x supports and Rh/MO_x catalysts, indicating that phosphate addition causes aggregation of Rh species. The high surface area of Rh-P catalyst using MgO support was attributed to the formation of MgRh₂O₄ as shown in **Fig. 3 (iv)**, (c).

3.3.2. Crystalline Sizes of Rh and Rh₂P Calculated from XRD

Crystalline sizes of Rh and Rh₂P were calculated from XRD patterns using Scherrer's equation to evaluate the effect of reduction temperature on particle size. **Table 4** shows the crystalline size of Rh in Rh/MO_x catalysts reduced at various temperatures. The smallest crystalline sizes (<5 nm) for Rh were observed in Rh/MO_x catalysts, except for Rh/ZrO₂ catalyst, reduced at various temperatures, indicating that the Rh particles

are highly dispersed on MO_x supports. However, the crystalline size of Rh on ZrO₂ was remarkable larger compared to that on other MO_x supports. On the other hand, Rh species were highly dispersed on ZrO₂ support after calcination (**Fig. 1 (v)**, (b) and **Table 3**). These results indicate that the particle size of Rh grows considerably after reduction.

The crystalline sizes of Rh and Rh₂P in Rh-P/MO_x catalysts are listed in **Table 5**. The crystalline sizes of Rh in Rh-P catalysts were larger than in Rh catalysts, in accordance with the trend in BET surface area, as shown in **Table 3**. The crystalline size of Rh₂P was smaller than that of Rh in all Rh-P catalysts, showing that small Rh particles may preferentially react with reduced P to form Rh₂P. The Rh-P/ZrO₂ catalyst had remarkable larger crystalline size of Rh₂P compared with other Rh-P/MO_x catalysts. Small noble metal particles are reported to show greater sulfur tolerance³⁷. Consequently, the Rh-P/ZrO₂ catalyst had low sulfur tolerance. H₂S formed by the HDS reaction of thiophene would poison the active sites for C-S bond cleavage on low sulfur tolerant Rh₂P catalyst. Therefore, the remarkably high THT selectivity of Rh-P/ZrO₂ catalyst (**Table 2**) can be explained by the low conversion and low sulfur tolerance due to the large Rh₂P particles.

3.3.3. CO Adsorption on Rh/MO_x and Rh-P/MO_x Catalysts

The CO uptakes of Rh and Rh-P catalysts were examined to evaluate the HDS activities by turnover frequency (TOF). **Figure 7** shows the CO uptake of Rh and Rh-P catalysts as a function of reduction temperature. Rh/Al₂O₃ catalyst showed remarkably higher CO uptake compared to other Rh/MO_x catalysts. Assuming that CO molecules are linearly adsorbed onto Rh atom, Rh dispersion in Rh/Al₂O₃ catalyst reduced at 400 °C was about 1.3. After CO was adsorbed on Rh/Al₂O₃ catalyst with high dispersion, the Rh(CO)₂ species was identified by infrared spectroscopy³⁸. Thus, the remarkable CO uptake of Rh/Al₂O₃ could be explained by the formation of Rh(CO)₂ species. On the other hand, remarkable decrease of CO uptake was observed in Rh/TiO₂ catalyst with increasing reduction temperature. TiO₂ is a well-known reducible support and supported metals on reducible supports are covered by suboxide species such as TiO_x ($x < 2$), a phenomenon

Table 5 Crystallite Size of Rh and Rh₂P Calculated from XRD Patterns in Rh-P Catalysts Reduced at Various Temperatures

Support	Crystalline size [nm]				
	450 °C	550 °C	650 °C	750 °C	850 °C
Rh					
SiO ₂	6.2	— ^{a)}	— ^{a)}	—	—
Al ₂ O ₃	4.8	5.1	5.6	9.6	— ^{a)}
TiO ₂	— ^{a)}	— ^{a)}	— ^{a)}	—	—
MgO	— ^{a)}	— ^{a)}	— ^{a)}	—	—
ZrO ₂	29.3	32.6	34.0	— ^{a)}	—
Rh₂P					
SiO ₂	4.0	5.6	7.0	—	—
Al ₂ O ₃	— ^{b)}	— ^{b)}	— ^{b)}	5.3	8.5
TiO ₂	9.1	10.7	11.7	—	—
MgO	— ^{b)}	4.7	11.3	—	—
ZrO ₂	— ^{b)}	6.3	18.4	33.3	—

a) No peaks of Rh were observed.

b) No peaks of Rh₂P were observed.

Fig. 7 Relationship between Reduction Temperature and CO Uptake of (i) Rh and (ii) Rh-P Catalysts

called strong metal support interaction (SMSI)^{39,40)}. The peak of TiO₂ reduction appeared in the TPR spectrum of Rh/TiO₂, as shown in **Fig. 3 (iii)**, (b). Thus, the SMSI effect would result in remarkable decrease of CO uptake of Rh/TiO₂ with increasing reduction temperature. The CO uptake of Rh-P catalysts decreased compared with Rh catalysts, indicating aggregation of

Rh species and Rh₂P species formation on MO_x supports. Furthermore, CO uptake of Rh-P/TiO₂ catalyst decreased with increasing reduction temperature, but was similar to that of Al₂O₃ and SiO₂-supported Rh-P catalysts. Phosphorus addition presumably inhibited covering of the Rh₂P surface by TiO_x species.

Figure 8 shows the TOF of Rh and Rh-P catalysts for HDS of thiophene. The TOF was calculated using the CO uptake (assumed CO/Rh = 1). The TOF of Rh catalysts, except Rh/ZrO₂, increased with higher reduction temperature. The TOF of Pt/Al₂O₃ catalyst for thiophene HDS decreases with lower dispersion of Pt⁴¹⁾. Therefore, increased TOF of Rh catalysts would be caused by enlargement of the Rh crystalline size, as shown in **Table 4**. However, the TOF of Rh/ZrO₂ catalyst decreased with higher reduction temperature. ZrO₂ is well known to have acidic and basic properties. The acidity and basicity changed with calcination temperature. High calcination temperature leads to increased number of acidic sites without change in acid strength^{42,43)}. On the other hand, elevation of calcination temperature increases the number of basic sites and enhances the base strength of these sites^{42,43)}. Therefore, high reduction temperature would lead to changes in the acidity and basicity of the ZrO₂ support. The acidity of the support enhanced sulfur tolerance of the supported noble metal catalysts^{12),13),32)~34)}. The opposite trend in TOF is explained by the formation of strong basic sites on the ZrO₂ support which weakens the sulfur tolerance of the Rh particles.

On the other hand, the TOF of Rh-P catalysts significantly increased with higher reduction temperature. CO adsorbed on the two-fold Ni bridge site and formation of Ni(CO)₄, which are observed on supported Ni catalyst, are suppressed for the supported nickel phosphide (Ni₂P and Ni₁₂P₅) catalysts, and linearly bounded CO is observed by FT-IR²²⁾. Therefore, CO will lin-

Fig. 8 Relationship between Reduction Temperature and TOF of (i) Rh and (ii) Rh-P Catalysts

early adsorb on Rh₂P catalyst as well as Ni₂P catalyst. Furthermore, remarkable increase in TOF of Al₂O₃ and ZrO₂-supported Rh-P catalysts was observed at higher reduction temperatures compared with other catalysts. This trend was the same as the formation of Rh₂P observed in XRD patterns and TPR spectra, as shown in Figs. 2 and 3 ((ii) and (v)). These results indicate that the TOF of Rh-P catalysts was remarkably enhanced by the Rh₂P formation. The order of TOF for Rh-P catalysts was as follows; TiO₂ > ZrO₂ > Al₂O₃ > SiO₂ > MgO. TiO₂ is sulfided with 10 % H₂S-H₂ and sulfided TiO₂ acts as promoter for Mo-based HDS catalyst⁴⁴. Furthermore, sulfided TiO₂ is involved in the active phase of the HDS reaction⁴⁵. In the HDS reaction, the reduced TiO_x species may react with H₂S to form partially sulfided TiO₂ species (TiO_xS_y), and TiO_xS_y also acts as promoter to enhance the TOF of Rh-P catalyst. Thus, the remarkably high TOF of Rh-P/TiO₂ catalyst can be explained by the promotion effect of TiO_xS_y. Furthermore, the high TOF of Rh-P/ZrO₂ catalyst is explained by the remarkably larger crystalline size of Rh₂P compared with other Rh-P catalysts (Table 5) as well as Rh/ZrO₂ catalyst. However, the TOF of Rh-P/ZrO₂ catalyst did not decrease with higher reduction temperature. The basic properties of PO₄³⁻/ZrO₂ are decreased by reaction of the basic sites on ZrO₂ with

PO₄³⁻ to form acidic sites⁴⁶. Furthermore, the TPR spectra of Rh-P/ZrO₂ (Fig. 3 (v), (c)) showed that reduction of PO₄³⁻ occurred at higher temperatures (above 600 °C). Thus, since the remaining PO₄³⁻ prevented the formation of strong basic sites, the TOF of Rh-P/ZrO₂ catalyst was not decreased by higher reduction temperature. On the other hand, formation of Rh₂P enhances the TOF of Rh-P/ZrO₂ catalyst reduced at high reduction temperature (above 600 °C), as shown in Fig. 8 (ii). Regardless of the similar crystalline size of Rh₂P, the TOFs of Rh-P catalyst supported on Al₂O₃ and SiO₂ were higher than that supported on MgO, because the basic properties of MgO would lead to low sulfur tolerance of the Rh₂P catalyst.

4. Conclusions

Rh₂P was formed on MO_x support after reduction but differences in the formation temperatures of Rh₂P were observed by changing the MO_x support. Furthermore, the HDS activities of the supported Rh-P catalysts strongly changed with higher reduction temperature. Rh-P catalysts showed higher HDS activity than Rh catalysts and the order of HDS activities of Rh-P/MO_x catalysts reduced at optimal temperatures was SiO₂ ~ TiO₂ ~ Al₂O₃ > MgO > ZrO₂. On the other hand, the order of TOF of supported Rh-P catalysts calculated from CO uptake was TiO₂ > ZrO₂ > Al₂O₃ > SiO₂ > MgO, and this order disagreed with that of thiophene conversion. The high TOF of Rh-P/TiO₂ catalyst may be explained by formation of partially sulfided TiO₂. The low TOF of Rh-P/MgO catalyst was attributed to the basicity of the support with low sulfur tolerance.

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要 旨

リン化ロジウム触媒の活性点形成と水素化脱硫活性に与える担体の影響

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リン化ロジウム (Rh_2P) 触媒の活性点形成とその水素化脱硫 (HDS) 活性に対する担体の影響について検討した。担体には金属酸化物 (MO_x : SiO_2 , Al_2O_3 , TiO_2 , MgO および ZrO_2) を用いた。いずれの担体の場合でも担持ロジウム-リン (Rh-P) 触媒を水素還元すると Rh_2P が生成した。一方, Rh_2P の生成温度は担体により異なった。この Rh-P 触媒の HDS 活性は還元温度によって大きく変化した。最適な温度で還元した Rh-P/MO_x 触媒の HDS 活性の序列は $\text{SiO}_2 \sim \text{TiO}_2 \sim \text{Al}_2\text{O}_3 > \text{MgO} >$

ZrO_2 となった。また, 還元温度を上昇させると Rh-P/MO_x 触媒の TOF は増加し, これは Rh_2P が生成したためであることが分かった。 Rh-P/MO_x 触媒の TOF の序列は $\text{TiO}_2 > \text{ZrO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2 > \text{MgO}$ となり, これはチオフェン転化率の序列とは一致しなかった。 Rh-P/TiO_2 触媒が高い TOF を示した原因としては, 部分的に硫化された TiO_2 の生成が挙げられる。一方, Rh-P/MgO 触媒の TOF が低かったのは, MgO は塩基性担体であり耐硫黄性が低かったためと考えられる。

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