Formation of active sites and hydrodesulfurization activity of rhodium phosphide catalyst: Effect of reduction temperature and phosphorus loading

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Highlights

► The Rh-1.5P catalyst exhibited the highest activity among the investigated catalysts.

► Rh₂P was easily formed in catalysts with a higher P loading.

► Higher P loadings and higher reduction temperatures led to aggregation of Rh species.

► RhP₂ exhibits lower catalytic activity than Rh₂P.

► High HDS activity was caused by small Rh₂P formation at lower reduction temperature.
### Graphical abstract

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_P loading (P/Rh ratio)_

- Rh
- Rh\(_2\)P
- RhP\(_2\)
- SiO\(_2\)

*High HDS activity*
Formation of Active Sites and Hydrodesulfurization Activity of Rhodium Phosphide Catalyst: Effect of Reduction Temperature and Phosphorus Loading

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Abstract

Effects of reduction temperature and phosphorus loading on rhodium phosphide (Rh$_2$P) formation and on the catalytic activity of Rh-xP catalysts for hydrodesulfurization (HDS) were investigated to prepare highly active HDS catalysts. Analysis of the Rh-xP catalysts showed that a suitable P loading for HDS activity is 1.5 wt%—four times greater than that of an Rh catalyst. Temperature-programmed reduction and X-ray diffraction analyses of the Rh-xP catalysts showed that Rh$_2$P is readily formed in catalysts with higher P loading. In contrast, the results of transmission electron microscopy observation and CO adsorption experiments indicated that the Rh$_2$P particle size increased with increasing P content. Thus, the high HDS activity of the Rh-1.5P catalyst was explained by the formation of small Rh$_2$P at a relatively low reduction temperature (550 °C).

Keywords

Rhodium phosphide catalyst; Hydrodesulfurization; Phosphorus loading; Reduction temperature; Active site formation
1. Introduction

During the past decade, the development of technologies capable of solving environmental problems such as acid rain and global climate change have attracted substantial attention on a global scale. The combustion of organic sulfur compounds in fuels used for boilers and engines results in the formation of sulfur oxides (SO\textsubscript{X}). SO\textsubscript{X} causes acid rain and deactivates automotive exhaust catalysts. Regulation of SO\textsubscript{X} emissions from ships is expected to become more stringent because the fuels for ships contain greater quantities of sulfur compounds compared to gasoline and diesel fuel. Thus, the petroleum industry has been producing clean fuels via hydrodesulfurization (HDS) processes that use sulfided Co(Ni)Mo/Al\textsubscript{2}O\textsubscript{3} catalysts. Recently, the petroleum industry claimed that the development of highly active HDS catalysts that exhibit greater activity than commercial CoMo catalysts will prevent acid rain and the deactivation of automotive exhaust catalysts [1-3].

Methods of preparing highly active CoMo-based HDS catalysts, such as the Co chemical vapor deposition technique [4, 5] and the addition of citric acid [6] or phosphorus [5, 7, 8], have been widely investigated.
Furthermore, new active phases other than sulfided CoMo catalysts have been reported by numerous researchers. Noble metals [9-14] and transition-metal carbides [15-18], nitrides [15, 19], and phosphides [2, 3, 18, 20-40] have been used as new HDS catalysts, and new transition-metal phosphides such as Ni$_2$P [2, 3, 18, 20-31] and MoP [30-35] have received extensive attention [30]. In particular, Ni$_2$P catalysts have demonstrated high potential for use in the HDS reaction. Reports have described the effects of P loading on the formation of the nickel phosphide phase and on the catalyst’s HDS activity. The reduction of precursors that contain less P is known to proceed via the Ni$_{12}$P$_5$ phase, which is an intermediate in the formation of Ni$_2$P [35]. In addition, the reduction of precursors with higher P concentrations results in the formation of the Ni$_2$P phase [20, 21, 25, 29]. The optimal P/Ni ratio for HDS activity was found to be 0.8–2.2, which is greater than the stoichiometric P/Ni ratio in Ni$_2$P (0.5). However, we [37-39] and Bussell et al. [3, 40] have reported that rhodium phosphide (Rh$_2$P) supported on SiO$_2$ exhibits high and stable catalytic activity toward the HDS reaction. As with the Ni$_2$P catalysts, the P/Rh ratio should also strongly affect the
formation of Rh$_2$P and the HDS activity of Rh catalysts. Previously, we reported that the support strongly affects the formation of Rh$_2$P and its HDS activity and that SiO$_2$, TiO$_2$, and Al$_2$O$_3$ supports showed superior HDS activity compared to MgO and ZrO$_2$ supports [38]. However, the formation of Rh$_2$P on Al$_2$O$_3$ is difficult because of the formation of AlPO$_4$ [3], and the turnover frequency (TOF) of Rh$_2$P is remarkably enhanced by the interaction between the active phase and TiO$_2$ [38]. Thus, SiO$_2$, which does not exhibit a strong interaction with Rh$_2$P or P when used as a support, is a superior support for clarifying the effects of the P loading on Rh$_2$P formation and on its catalytic HDS activity. As previously noted, numerous reports have described the effects of P loadings on the formed phases and on their HDS activities. However, the effect of P loading on the reducibility of phosphates and on the formation temperature of phosphides, especially noble metal phosphides, has scarcely been reported. In addition, reduction temperature is one of the most important factors in evaluating the reducibility of phosphates and the formation of phosphides. Herein, the effects of reduction temperature and P loading on the formation of rhodium phosphides (Rh$_X$P$_Y$) and on the HDS activity of
Rh$_2$P/SiO$_2$ catalysts were examined to enable the preparation of highly active phosphided HDS catalysts.

2. Experimental

2.1. Catalyst preparation

Silica (SiO$_2$, BET surface area 295 m$^2$ g$^{-1}$) was supplied by Nippon Aerosil Co. The Rh/SiO$_2$ catalyst was prepared by an impregnation method described previously [37-39]. Rhodium(III) chloride trihydrate (RhCl$_3$·3H$_2$O, Kanto Chemical Co.) was used as a precursor for the catalysts and was dissolved in water. The Rh loading amount was 5 wt%. After impregnation, the catalyst was dried at 110 °C for 24 h, followed by heat treatment under nitrogen (N$_2$) stream at 450 °C for 1 h in order to decompose the Rh salts. The sieved catalysts (30- to 42-mesh-size granules) were calcined in air at 500 °C for 4 h. The ramp rate for the heat treatment and calcination was 10 °C min$^{-1}$. P-added 5 wt% Rh (Rh-P)/SiO$_2$ catalysts were prepared using the same procedure, except with aqueous solutions of RhCl$_3$·3H$_2$O and ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$, Kanto Chemical Co.). The P concentration was
varied from 0.8 to 3.0 wt%. These catalysts were labeled as Rh-xP, where “x” denotes the P loading (wt%). The P/Rh molar ratio in the catalysts with 0.8, 1.5, 2.2, and 3.0 wt% P was 0.5, 1.0, 1.5, and 2.0, respectively.

2.2. Hydrodesulfurization of thiophene

The HDS of thiophene was performed at 350 °C under 0.1 MPa using a conventional fixed-bed flow reactor. The calcined catalyst (0.1 g) was charged into the quartz reactor and heated (10 °C min⁻¹) in a helium (He) stream (30 ml min⁻¹) at 500 °C for 1 h, following which it was reduced by H₂ (30 ml min⁻¹) at 350–700 °C for 1 h. A hydrogen–thiophene gas mixture (H₂/C₄H₄S = 30), obtained by passing a H₂ stream through a thiophene trap cooled at 0 °C, was then introduced into the reactor (W/F = 37.9 g h mol⁻¹). The reaction products were analyzed using a gas chromatograph equipped with a flame ionization detector (FID) and a silicone DC-550 (length: 2 m, temperature: 110 °C) and Al₂O₃/KCl plot (ID: 0.53 mm, length: 25 m, film thickness: 10 µm, temperature: 60–190 °C, rate: 7.5 °C min⁻¹) columns.

The rate constant was calculated from the following equation under the assumption of a pseudo-first-order reaction:
\[
    k_{HDS} = \frac{-\ln(1-x/100)}{W/F} \tag{1}
\]

where \(k_{HDS}\) is the reaction rate of thiophene HDS (mol h\(^{-1}\) g\(^{-1}\)) and \(x\) is the conversion rate at 3 h (%).

2. 3. Catalyst characterization

The Rh and Rh-xP catalysts were characterized using \(N_2\) adsorption, temperature-programmed reduction (TPR), X-ray diffraction (XRD), transmission electron microscopy (TEM), and carbon monoxide (CO) adsorption analyses. Measurements of \(N_2\) adsorption at −196°C were performed using a Micromeritics ASAP 2010. The catalysts were evacuated at 300 °C for 10 h prior to the \(N_2\) adsorption measurements. The surface area of the catalysts was calculated by the Brunauer–Emmett–Teller (BET) method. TPR measurements were performed using a Shimadzu GC-8A gas chromatograph. The supported Rh or Rh-xP catalysts (0.1 g) were heated in a He stream (30 ml min\(^{-1}\)) from room temperature to 500 °C at 10 °C min\(^{-1}\), followed by He treatment at 500 °C for 1 h. After this He treatment, the catalysts were cooled to 30°C in a He stream, and the He was switched to a hydrogen–nitrogen (5 vol%\(H_2\)-\(N_2\)) gas mixture at 30 °C for 0.5 h before
the measurement was performed. The TPR spectrum was recorded over the temperature range of 30 to 800 °C at 10 °C min⁻¹, using a thermal conductivity detector (TCD) to monitor H₂ consumption. Water was removed using a molecular sieve trap. The XRD patterns of the calcined and reduced catalysts in air were measured using a Rigaku MiniFlex equipped with a Cu Kα radiation source operated at 30 kV and 15 mA. The crystallite size of the metallic Rh and RhₓPy were calculated using Scherrer’s equation:

\[ d = \frac{K \lambda}{B \cos \theta} \]  

(2)

where \( d \) is the crystallite size (nm), \( B \) is the full-width at half maximum of the selected peak (FWHM, radians), \( K \) is shape factor (0.9), and \( \lambda \) is the wavelength of the X-ray radiation (15.4184 nm). The XRD peaks at 34.2° (Rh₂O₃, (114) plane), 40.9° (Rh, (111) plane), 46.7° (Rh₂P, (220) plane), and 23.9° (RhP₂, (11-1) plane) were used to calculate the \( B \) parameter.

TEM observations were performed using a JEOL JEM-2000FX. The conditions of TEM operation were an acceleration voltage of 200 kV and a magnification of 120,000×. The particle size distribution and average particle size were determined from the measurements of 1000 particles in
the TEM micrographs. The CO uptake of the supported Rh and Rh-P catalysts was measured using the pulse method. The supported Rh or Rh-xP catalysts (0.1 g) were treated in He at 500°C (10 °C min⁻¹) for 1 h, followed by reduction in H₂ at 350–750 °C for 1 h. CO was injected onto the catalyst layer at 25 °C using a sampling loop (1.0 ml). The amount of CO adsorbed was measured with a Shimadzu GC-8A gas chromatograph equipped with a TCD.

3. Results and Discussion

3.1. HDS of Thiophene over Rh-xP Catalysts

3.1.1. HDS Activities of the Rh-xP Catalysts

Previously, we reported that reduction temperature strongly affects the HDS activity of Rh-1.5P catalysts [37-39]. Thus, the HDS activity of Rh-xP catalysts reduced at various temperatures was examined in this work. Figure 1 shows the effect of reduction temperature on the HDS activity (rate constant) of the Rh-xP catalysts after reaction for 3 h. The HDS activity of the Rh catalyst barely changed with an increase in reduction temperature. In contrast, an optimal reduction temperature for
the maximum HDS activity of the P-added Rh catalysts was clearly observed. The optimal reduction temperature for achieving maximum HDS activity of the Rh-xP catalysts decreased with increasing P content. Moreover, the HDS activity of the catalysts with a 3.0 wt% P loading decreased remarkably with an increase in reduction temperature.

The HDS activity of the Rh-xP catalysts reduced at the optimal temperature is shown in Fig. 2 as a function of the P loading. The maximum HDS activity for the Rh-xP catalysts was obtained at a P loading of 1.5 wt%. This activity was four times greater than that of the Rh catalyst.

3.1.2. Selectivity of Products

The HDS reaction products were butanes, butenes, tetrahydrothiophene (THT), and trace amounts of cracking products. The selectivity for each reaction product in the HDS of thiophene over the Rh-xP catalysts is listed in Table 1. Because the selectivities of butanes, butenes, and THT depend on P loading, reduction temperature, and thiophene conversion rate, the effect of the P loading on the product selectivities should be evaluated at the same reduction temperature and
with a similar thiophene conversion rate. The Rh-0.8P and Rh-1.5P catalysts that were reduced at 650 °C exhibited similar conversion rates, where butanes were readily formed on the Rh-xP catalysts with lower P loadings. In contrast, the THT selectivity of the Rh-0.8P catalyst reduced at 650 °C was lower than that of the Rh-1.5P catalyst. The same THT selectivity trend was observed for the Rh-1.5P and Rh-2.2P catalysts reduced at 450 °C.

Furthermore, the effect of W/F on the product selectivities of Rh and Rh-1.5P catalysts reduced at 650 °C are listed in Table 2. At similar conversion rates, THT selectivity increased with increasing P loading, but butanes selectivity decreased. Thus, the P loading strongly affected the selectivities for butanes and THT.

3. 2. Characterization of the Rh-xP Catalysts

3. 2. 1. BET Surface Area of the Calcined Rh-xP Catalysts

The surface area of the calcined Rh-xP catalysts is shown in Table 3. The Rh catalysts exhibited the same surface area as the SiO\textsubscript{2} support (295 m\textsuperscript{2} g\textsuperscript{-1}). The surface area of the Rh-xP catalysts decreased with increasing P loading. However, the surface area was hardly changed when the P
loading was increased from 2.2 to 3.0 wt%. These results indicate that phosphates preferentially interact with the support, but not with Rh species, to aggregate SiO$_2$ particles.

3. 2. 2. XRD Patterns of the Calcined Rh-xP Catalysts

Figure 3 shows the XRD patterns of the Rh-xP catalysts after calcination at 500 °C. The main peak of Rh$_2$O$_3$ was observed in the XRD patterns of the Rh-xP catalysts, and this peak barely changed when the P loading was increased to 1.5 wt%. However, the XRD patterns of the Rh-2.2P and Rh-3.0P catalysts showed remarkably sharp peaks associated with metallic Rh.

The crystallite sizes of the metallic Rh and Rh$_2$O$_3$ in the catalysts, as calculated using Scherrer’s equation, are also listed in Table 3. The crystallite size of the Rh$_2$O$_3$ increased with an increase in the P loading. In particular, a large crystallite size was observed in the catalysts with higher P loadings (2.2 and 3.0 wt%). The large metallic Rh particles probably formed during decomposition of the Rh-based salt. Because oxygenation proceeds from the surface to the bulk, a large Rh particle, which has a high diffusion resistance, will remain in the metallic Rh state
after calcination.

3.2.3. TPR of the Rh-xP Catalysts

Reduction temperature and P loading strongly affected the HDS activity of the Rh-xP catalysts, as shown in Figs. 1 and 2. Therefore, the TPR traces of the Rh-xP catalysts were examined to clarify the effect of the P loading on the reducibility of the rhodium oxide and phosphate species. Figure 4 shows the TPR trace of the Rh-xP catalysts. The peak at 60°C, which was attributed to the reduction of Rh$_2$O$_3$, appeared in the TPR trace of the Rh catalyst (Fig. 4, (a)). The peak for Rh$_2$O$_3$ reduction was observed from 60 to 140 °C in the TPR trace of Rh-xP catalysts. When the P loading was increased, this peak shifted to a higher temperature. The same trend was observed in the TPR traces for the Ni-P catalysts [21, 24]. The phosphate would cover Rh$_2$O$_3$ particles, causing the peak temperature of the Rh$_2$O$_3$ reduction to shift. However, the reduction temperature of Rh$_2$O$_3$ in the Rh-0.8P catalyst hardly changed compared with that of Rh$_2$O$_3$ in the Rh catalyst. These results imply that phosphate preferentially interacts with SiO$_2$ but not with Rh$_2$O$_3$.

The TPR trace of a physically mixed Rh/SiO$_2$ and 1.5% P/SiO$_2$ catalyst
(0.05 + 0.05 = 0.1 g) was measured to define the reduction peak of the phosphates (Fig. 4, (b)). Two peaks were observed at approximately 50 °C and above 650 °C. In the mixed catalyst, the Rh₂O₃ barely interacted with the phosphate. Thus, these peaks were attributed to the reduction of the Rh₂O₃ and to the phosphates supported on the SiO₂, respectively. However, a reduction peak in the temperature range of 200–350°C was not observed in the trace of the mixed catalyst, indicating that this peak was attributed to the reduction of the phosphate that interacted with the Rh₂O₃.

In the temperature range above 250 °C in the TPR spectrum of the Rh-0.8P catalyst, two peaks were observed at 340 and 800 °C in (Fig. 4, (b)). For the Rh-1.5P catalyst, these peaks shifted to lower temperatures (270 and 680 °C, respectively) compared to those of the Rh-0.8P catalyst. However, a remarkable reduction peak appeared at 350–400 °C in the TPR trace of the catalysts with higher P loadings (2.2–3.0 wt%). Brock et al. have reported that Rh₂P is formed by the reduction of rhodium phosphate at 375 °C [41]. Furthermore, Oyama et al. reported that one reduction peak in the TPR trace of a Ni₂P/SiO₂ catalyst with a higher P/Ni ratio
(P/Ni > 1) was observed to appear at the same temperature as that of a peak in the TPR trace of bulk nickel phosphate during reduction [21]. These results suggest that the large peak at 350–400 °C in the TPR traces of catalysts with higher P loadings (2.2–3.0 wt%) can be attributed to the reduction of rhodium phosphate.

The peaks for $\text{P}_2\text{O}_5$ and $\text{P}_4\text{O}_7$ appeared in the XRD pattern of a 20 wt% Ni$_2$P/SiO$_2$ catalyst with a higher P loading (P/Ni = 2) [25]. This result indicates that the particle size of the phosphate increases with increasing P loading. Thus, enlarged phosphate particles that weakly interact with SiO$_2$ would cause a peak shift to lower temperatures.

3.2.4. XRD Patterns of the Reduced Rh-xP Catalysts

The XRD patterns of the reduced Rh-xP catalysts were examined to evaluate the formed Rh$_x$P$_y$. Figure 5 shows the XRD patterns of the Rh-xP catalysts reduced at 450–650 °C. The peaks for metallic Rh were only observed in the patterns of Rh catalysts reduced at any temperature. The same tendency was observed in the Rh-0.8P catalyst, but small peaks for Rh$_2$P appeared in the sample subjected to the highest reduction temperature (650 °C). The peaks for metallic Rh were observed in the
XRD patterns of the Rh-1.5 P catalyst reduced at 450 °C. However, these peaks disappeared when reduction temperature was increased, and Rh$_2$P peaks subsequently appeared. In addition, no metallic Rh peaks were observed in the Rh-xP catalysts with higher P loadings (greater than 2.2 wt%) reduced at any temperature. Thus, the TPR and XRD results indicated that Rh$_2$P is easily formed at higher P loadings and higher reduction temperatures. This phenomenon is can be explained as follows: the phosphate preferentially interacts with SiO$_2$, but excess phosphate interacts with Rh$_2$O$_3$ and/or forms rhodium phosphate. Because these phosphate species are reduced at lower temperatures than phosphates on SiO$_2$, Rh$_2$P is readily formed in the catalysts with higher P loadings. In contrast, the intensity of the Rh$_2$P peaks increased as the P loadings and reduction temperatures were increased. This result implies that excess P loading and a high reduction temperature cause sintering of Rh species. Furthermore, RhP$_2$ was formed in the catalyst with a higher P loading (3.0%) that that reduced at high temperature (650 °C).

Table 4 shows the effect of reduction temperature and P loading on the crystallite size of the metallic Rh and Rh$_X$P$_Y$, as calculated using
Scherrer’s equation. The crystallite size of the Rh in the Rh catalyst increased with increasing reduction temperature. However, irrespective of the increase in reduction temperature from 550 to 650 °C, the crystallite size of the metallic Rh in the Rh-0.8P catalyst decreased. The same tendency was also observed in the other Rh-xP catalysts. Furthermore, the crystallite size of the RhP₂ was smaller than that in the Rh-3.0P catalyst reduced at 650 °C. At the same reduction temperature, the crystallite size of the Rh species increased with increasing P loading and increasing reduction temperature.

Bussell et al. have reported that the average crystallite size of Rh₂P in a 5 wt% Rh₂P/SiO₂ catalyst (P/Rh = 0.75) is 10 nm, as determined from its XRD pattern [40]. This value is higher than our results. Furthermore, the particle sizes of the Rh-xP catalysts were examined in detail using TEM.

3. 2. 5. Particle Size of the Reduced Rh-xP Catalysts

Figure 6 shows the TEM images of the Rh-xP catalysts after reduction at 550 °C. For the Rh catalyst, highly dispersed particles were observed. However, an increase in the P content tended to result in larger particle
sizes. The particle size distribution of the Rh-xP catalysts after reduction at 450–650 °C, as determined from TEM images, is shown in Figure 7. For the Rh catalyst, the particle size distribution shifted toward larger particle diameters as reduction temperature was increased. In particular, all of the Rh-xP catalysts reduced at 650 °C showed a low frequency of the peak center and a broad distribution compared to those reduced at 450 and 550 °C.

The average particle sizes of the Rh-xP catalysts reduced at 450–650 °C, as calculated from TEM images, are listed in Table 5. The average particle size of all of the Rh-xP catalysts reduced at 550 °C was slightly larger (+0.1-0.2 nm) than that of the catalysts reduced at 450 °C. For catalysts with P loadings less than 1.5 wt%, the average particle size of the catalysts reduced at 650 °C was 0.5-0.6 nm larger than that of the catalysts reduced at 550 °C. For catalysts with a P loading greater than 2.2 wt%, the average particle size of the catalysts reduced at 650 °C was 0.1-0.4 nm larger than that of the catalysts reduced at 550 °C, thereby indicating that excess P inhibits sintering of Rh₂P at 650 °C. However, at the same reduction temperature, the average particle size increased with
increasing P content. These results reveal that an excess P loading (greater than 2.2 wt%) leads to the formation of large particles. The BET surface area (Table 2) and TPR (Fig. 4 (a)) results imply that phosphate preferentially interacts with the SiO₂ support, but not with Rh₂O₃. Therefore, this phenomenon is can be explained as follows: The phosphate preferentially interacts with SiO₂, but excess phosphate interacts with Rh₂O₃ and forms rhodium phosphate. Since reduction of these phosphate species occur at lower temperature than that of phosphate on SiO₂, Rh₂P is readily formed in the catalysts with higher P loading.

Bussell et al. reported an average particle size of Rh₂P of 3.3 ± 1.7 nm, as determined from TEM images [40]. This particle size is smaller than the particle size indicated by our results, as shown in Table 5. In this work, the Rh loading was 5 wt%, and this loading was higher than that used by Bussell’s group (Rh: 4.08 wt% and P: 0.92 wt%). Thus, our larger particle size can be explained by our higher Rh loading.

3. 2. 6. CO Uptake of Rh-xP Catalysts

Figure 8 shows the relationship between the reduction temperature and CO uptake of the Rh-xP catalysts. The CO uptake of the Rh-xP
catalysts decreased with an increase in reduction temperature. In particular, the CO uptake of the Rh-0.8P catalyst remarkably decreased as reduction temperature was increased from 600 to 650 °C. At higher reduction temperatures (greater than 600 °C), PO₄³⁻, which interacts with SiO₂, can be reduced to form P and/or PH₃, as shown in Fig. 4. Thus, a remarkable decrease in the CO uptake of the Rh-0.8P catalyst can be explained by the metallic Rh surface being covered by P and/or the formation of Rh₂P.

At the same reduction temperature, the CO uptake decreased with increased P loading. These trends are consistent with the average particle sizes measured from TEM images (Table 5), but not with the crystallite sizes calculated from the XRD patterns (Table 4). The trend of the particle sizes calculated from the XRD results can be explained as follows: If phosphidation proceeds from the surface of the metallic Rh particles, then structures that consist of metallic Rh cores covered with Rh₂P shells would be formed. The size of the Rh cores would decrease as the degree of phosphidation increased. Thus, the crystallite size of metallic Rh decreased with increasing reduction temperature, as shown in
Oyama et al. have reported that the Ni$_2$P active phase is blocked by excess P in Ni$_2$P/SiO$_2$ catalysts with higher P contents [22]. In addition, we confirmed that RhP$_2$ is formed in the Rh-3.0P catalyst reduced at 650 °C (Fig. 5). These results imply that reduced excess P species cover the surface of the Rh$_2$P and/or react with Rh$_2$P to form RhP$_2$.

### 3.2.7. Turnover Frequency of the Rh-xP Catalysts

The turnover frequency of the Rh-xP catalysts was calculated from the amount of exposed Rh (Rh$_{ex}$) and from the CO uptake. The Rh$_{ex}$ (mol g-cat$^{-1}$) values of the Rh-xP catalysts were calculated from their average particle size. Assuming that particles have a spherical or cubic shape, Rh$_{ex}$ can be estimated from following equation:

$$Rh_{ex} = \frac{6nf}{\rho D N_A} \times 10^7 \ (3)$$

where $n$ is the surface atom density (atoms cm$^{-2}$), $f$ is the fractional weight loading of the sample, $\rho$ is the theoretical bulk density (g m$^{-3}$), $D$ is the particle size calculated from TEM observations (nm), and $N_A$ is Avogadro’s number ($6.02 \times 10^{23}$). The values of $n$ were $1.60 \times 10^{19}$ and $7.63 \times 10^{19}$ atoms m$^{-2}$ for Rh ((111) plane) and Rh$_2$P ((111) plane),
respectively. Furthermore, the values of $\rho$ were 12.41 and 9.44 g cm$^{-3}$ for Rh and Rh$_2$P, respectively. The calculated Rh$_{ex}$ and chemisorbed CO/Rh$_{ex}$ values are listed in Table 6. The CO/Rh$_{ex}$ of the Rh catalyst reduced at any temperature was constant (ca. 1.7), indicating that CO species chemisorbed onto this catalyst would be dicarbonyl and linear types. However, the CO/Rh$_{ex}$ of the Rh-0.8P catalyst decreased with increasing reduction temperature, especially from 550 to 650 °C. In other Rh-xP catalysts, CO/Rh$_{ex}$ also decreased with increasing reduction temperature. Some CO species chemisorbed onto Rh$_2$P/Al$_2$O$_3$ catalysts, such as linear, bridge, and dicarbonyl types, have been identified by IR [42]. However, the CO/Rh$_{ex}$ ratios for the Rh-xP catalysts with higher P loadings (greater than 2.2 wt%) were less than 1. These results can be explained by the exposed Rh sites of Rh$_2$P being covered by reduced P and/or by CO linearly adsorbing onto the Rh-xP catalysts because of steric hindrance caused by excess P.

Figure 9 shows the TOF values calculated from the Rh$_{ex}$ (TOF (Rh$_{ex}$)) and CO uptake (TOF (CO)) values. These TOFs varied in similar manners with increasing reduction temperature. The TOFs of the Rh catalyst
barely changed as reduction temperature was increased. Because the Rh
catalyst exhibited a high CO/Rh\textsubscript{ex} ratio (ca. 1.7), as shown in Table 6, the
TOF (Rh\textsubscript{ex}) would be more accurate than the TOF (CO). However, both
TOFs calculated from both the Rh\textsubscript{ex} (a) and CO uptake (b) of the Rh-0.8P
catalyst increased as reduction temperature was increased from 550 to
650 °C. For the Rh-1.5P catalyst, the TOF (CO) also increased with
increasing reduction temperature; however, the TOF (Rh\textsubscript{ex}) slightly
decreased with when reduction temperature was increased from 550 to
650 °C. Because the peak intensities of Rh\textsubscript{2}P increased with increasing
reduction temperature (Fig. 5), the enhancement of TOF was caused by
Rh\textsubscript{2}P formation. However, the TOFs of the Rh-2.2P catalyst decreased at
reduction temperatures greater than 550 °C. The same trend was observed
for the Rh-3.0P catalyst reduced at temperatures greater than 450 °C.

**Figure 10** shows the TOFs of the Rh-xP catalysts as a function of
their P loading. The TOFs were calculated from the maximum HDS
activity (Fig. 1). In the P-loading range from 0 to 1.5, the TOF (Rh\textsubscript{ex}) was
the same as the TOF (CO). In contrast, a remarkable difference between
these TOFs was observed in catalysts with higher P loadings (greater than
2.2 wt%). Furthermore, the CO/Rh\textsubscript{ex} ratios of these catalysts were significantly lower than those of catalysts with low P contents (0-0.8 wt%) (Table 6). Thus, the TOFs of the Rh-xP catalysts with higher P loadings include an error caused by the Rh sites being covered by excess P.

The TOF of the Rh-1.5P catalyst reduced at 550 °C, which exhibited the highest HDS activity (Fig. 2), was approximately 200 h\textsuperscript{−1}. In the HDS of thiophene at 370 °C, the TOF of the Ni\textsubscript{2}P/SiO\textsubscript{2} (P/Ni = 0.8) catalyst was ca. 76 h\textsuperscript{−1} (0.021 s\textsuperscript{−1}) [25]. The TOF of the Rh-1.5P catalyst was 2.6 times greater than that of the Ni\textsubscript{2}P/SiO\textsubscript{2} catalyst.

3.3 Effect of Reduction Temperature and P Loading on the HDS Activities of Rh-xP Catalysts

The TPR and XRD results revealed that an increase in the P content causes the reduction of phosphates at lower temperatures and decreases the formation temperature of Rh\textsubscript{2}P. Thus, the reduction temperature for the maximum HDS activity decreased with increasing P loading, as shown in Fig. 1.

For the Rh-0.8P catalyst, the maximum HDS activity and a high TOF
were obtained at a high reduction temperature (650 °C). Bussell et al. have reported that the Rh$_2$P/SiO$_2$ catalyst, which exhibits metallic properties and excellent hydrogenation activity, showed higher sulfur tolerance than the Rh/SiO$_2$ catalyst [40]. In fact, we observed peaks associated with metallic Rh and small peaks associated with Rh$_2$P in the XRD pattern of the Rh-0.8P catalyst reduced at 650 °C (Fig. 5). Thus, the enhanced activity of the Rh-0.8P catalyst can be explained by the formation of a Rh$_2$P shell structure containing a metallic Rh core. When reduction temperature was increased to 700 °C, the HDS activity of the Rh-0.8P catalyst decreased. In addition, the HDS activities of other Rh-xP catalysts reduced at temperatures greater than 650 °C were lower than that of catalysts reduced at temperatures less than 550 °C. The TEM observations and CO adsorption results revealed that the average metallic Rh and Rh$_2$P particle sizes increased as reduction temperature was increased from 550 to 650 °C. Therefore, the low HDS activities of the Rh-xP catalysts reduced at higher temperatures were due to sintering of the metallic Rh and Rh$_2$P particles. In addition, the HDS activity of the Rh-3.0P catalyst reduced at temperatures greater than 600 °C was lower
than that of the Rh catalyst reduced at the same temperature (Fig. 1). The XRD analysis showed that excess P reacts with Rh₂P to form RhP₂ in the Rh-3.0P catalyst reduced at 650 °C (Fig. 5). Metal-rich phosphides exhibit excellent hydrogenation activity [3], and Ni-rich phosphides exhibit much higher HDS activity than P-rich phosphides [24]. Korányi have reported that Ni₂P catalysts exhibit greater activity than NiP₂ catalysts [23]. For Ni₂P catalysts, the Ni(1) sites with tetrahedral coordination and four nearest-neighbor P atoms are responsible for direct desulfurization, whereas the Ni(2) sites with square pyramidal coordination and five nearest-neighbor P atoms are highly active sites for the hydrogenation route [28]. Furthermore, DFT calculation results have shown that P sites play an important role in the bonding of intermediates, such as H adatoms [18]. Because the coordination number of Rh-P in RhP₂ is greater than that in Rh₂P, Rh₂P favors the hydrogenation route to form THT. The Rh-3.0P catalyst exhibited remarkably lower CO/Rhₑₓ ratios compared to those of the Rh-xP catalysts with low P loadings (less than 1.5 wt%), indicating that the Rh sites were covered by excess P.

Thus, the low HDS activity and remarkable THT selectivity of the
Rh-3.0P catalysts reduced at higher temperatures (Table 1 and 2) resulted from the formation of RhP2 and from a decrease in the number of active sites for C-S bond cleavage due to the coverage by excess P.

The optimal P loading for HDS activity of the Rh-xP catalysts was 1.5 wt%, as shown in Fig. 2. This result is explained as follows: At a lower P loading (0.8 wt %), a small amount of Rh2P formed at high reduction temperatures; however, a metallic Rh phase was also observed (Fig. 5), indicating that the degree of phosphidation was low compared with that of catalysts with high P loadings. Furthermore, the high reduction temperature simultaneously causes sintering of the active phase, as shown in Table 5 and in Fig. 8. In contrast, Rh2P was easily formed at low reduction temperatures in the catalysts with higher P loadings (greater than 2.2 wt %). However, the results of TEM observations and CO adsorption experiments showed that excess P causes aggregation and/or covering of Rh2P. Because moderate P loadings lead to the formation of well-dispersed Rh2P at a relatively low temperature (550 °C), the Rh-1.5P catalyst exhibited the highest HDS activity.
4. Conclusions

The effect of reduction temperature and P loading on the formation of active sites and on the HDS activity of Rh-xP/SiO$_2$ catalysts was investigated. Reduction temperature strongly affects the HDS activities of Rh-xP catalysts, and the optimal reduction temperature for maximum HDS activity decreased with increasing P content. The Rh-1.5P catalyst exhibited the highest HDS activity—four times higher than that of the Rh catalyst. Analysis of the TPR and XRD patterns of the Rh-xP catalysts revealed that the formation temperature of Rh$_2$P decreases with increased P loading. Furthermore, the formation of RhP$_2$ was observed in the Rh-3.0P catalyst after it was reduced at higher temperatures. Average particle size calculated from TEM images increased and CO uptake decreased with increased P loading. Thus, we concluded that a moderate P loading, which resulted in good reducibility of the phosphates and a small Rh$_2$P particle size, caused the high HDS activity of the Rh-1.5P catalyst.

Acknowledgment

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References


Figure captions

Figure 1  Relationship between the reduction temperature and HDS activity of Rh-xP catalysts.

Figure 2  Effect of P loading on the HDS activity of Rh-xP catalysts reduced at an optimal temperature.

Figure 3  XRD patterns of Rh-xP catalysts calcined at 500 °C.

Figure 4  TPR of Rh-xP catalysts: (a) TPRs of Rh-xP and Rh/SiO₂ + P/SiO₂ mixed catalysts (0.05 + 0.05 g) from 30 to 800 °C and (b) a magnified version of the 200 to 800 °C region of the TPR trace.

Figure 5  XRD patterns of Rh-xP catalysts reduced at 450–650 °C.

Figure 6  TEM images of Rh-xP catalysts reduced at 550 °C.

Figure 7  Particle size distribution of Rh-xP catalysts reduced at 450–650 °C.

Figure 8  Relationship between the reduction temperature and CO uptake of Rh-xP catalysts.

Figure 9  Relationship between the reduction temperature and TOF of Rh-xP catalysts calculated from (a) the theoretical number of exposed Rh atoms and (b) the CO uptake.
Figure 10  Effect of P loading on the TOF of Rh-xP catalysts calculated from the theoretical number of exposed Rh atoms and CO uptake.
Table 1  Selectivities of reaction products in the HDS of thiophene over Rh-xP catalysts. Reaction conditions: W/F = 37.9 g h mol$^{-1}$, H$_2$/C$_4$H$_4$S = 30, total pressure = 0.1 MPa.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reduction temperature (°C)</th>
<th>Conversion (%)</th>
<th>C$_1$-C$_3^a$</th>
<th>Butanes</th>
<th>Butenes</th>
<th>THT$^b$</th>
<th>Rx$^c$</th>
<th>CO$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>450</td>
<td>16.6</td>
<td>0.3</td>
<td>10.3</td>
<td>86.2</td>
<td>3.2</td>
<td>35.5</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>16.8</td>
<td>0.3</td>
<td>9.9</td>
<td>86.4</td>
<td>3.3</td>
<td>36.5</td>
<td>20.9</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>16.3</td>
<td>0.2</td>
<td>10.2</td>
<td>86.1</td>
<td>3.6</td>
<td>39.5</td>
<td>23.4</td>
</tr>
<tr>
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<td>64.1</td>
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<td>81.2</td>
<td>3.0</td>
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<td>3.4</td>
<td>119</td>
<td>113</td>
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<td>0.3</td>
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<td>74.5</td>
<td>3.4</td>
<td>152</td>
<td>137</td>
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<td>202</td>
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<td>650</td>
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<td>0.1</td>
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<td>81.0</td>
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<td>230</td>
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<td>204</td>
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<td>Rh-3.0P</td>
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<td>81.4</td>
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<td>138</td>
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<td>70.4</td>
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<td>5.0</td>
<td>75.4</td>
<td>19.0</td>
<td>38.7</td>
<td>118</td>
</tr>
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</table>

a C$_1$-C$_3$ hydrocarbons
b Tetrahydrothiophene
c Calculated from the theoretical number of exposed Rh atoms
d Calculated from the CO uptake
**Table 2** Effect of W/F on selectivities of reaction products in the HDS of thiophene over Rh-xP catalyst reduced at 650°C. Reaction conditions: W = 0.003-0.1 g, H₂/C₄H₄S = 30, total pressure = 0.1 MPa.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>W/F (g h mol⁻¹)</th>
<th>Conversion (%)</th>
<th>Selectivity of HDS products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C₁-C₃ᵃ Butanes Butenes THTᵇ</td>
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<tr>
<td>Rh</td>
<td>15.2</td>
<td>7.81</td>
<td>4.4  5.8  86.1  3.3</td>
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<td>37.9</td>
<td>16.3</td>
<td>0.2  10.2  86.1  3.6</td>
</tr>
<tr>
<td>Rh-1.5P</td>
<td>1.1</td>
<td>10.4</td>
<td>1.6  4.7  78.2  15.5</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>20.8</td>
<td>0.2  7.5  80.6  11.8</td>
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<td></td>
<td>7.6</td>
<td>30.8</td>
<td>0.4  11.0  80.7  8.0</td>
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<td></td>
<td>37.9</td>
<td>43.1</td>
<td>0.1  14.4  81.0  4.3</td>
</tr>
<tr>
<td>Rh-3.0P</td>
<td>37.9</td>
<td>7.49</td>
<td>0.5  5.0  75.4  19.0</td>
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</table>

ᵃ C₁-C₃ hydrocarbons  
ᵇ Tetrahydrothiophene
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Crystallite size (nm)</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Rh</td>
<td>289</td>
<td>1.2</td>
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<tr>
<td>Rh-0.8P</td>
<td>258</td>
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<td>-</td>
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<td>Rh-1.5P</td>
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<td>-</td>
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<td>Rh-3.0P</td>
<td>215</td>
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<td>15.7</td>
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</table>
Table 4  Crystalline size of Rh species calculated by Scherrer’s equation in XRD patterns of Rh-xP catalysts after reduction.

<table>
<thead>
<tr>
<th>Reduction temperature</th>
<th>350 °C</th>
<th>450 °C</th>
<th>550 °C</th>
<th>650 °C</th>
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<tbody>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>- / - / -</td>
<td>2.6 / - / -</td>
<td>2.6 / - / -</td>
<td>3.2 / - / -</td>
</tr>
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<td>- / - / -</td>
<td>3.1 / - / -</td>
<td>3.8 / - / -</td>
<td>3.5 / 2.2 / -</td>
</tr>
<tr>
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<td>6.7 / 3.3 / -</td>
<td>6.4 / 6.1 / -</td>
<td>- / 7.7 / -</td>
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<td>Rh-2.2P</td>
<td>- / - / -</td>
<td>- / 8.9 / -</td>
<td>- / 9.9 / -</td>
<td>- / 9.3 / -</td>
</tr>
<tr>
<td>Rh-3.0P</td>
<td>- / 12.2 / -</td>
<td>- / 9.4 / -</td>
<td>- / 13.2 / -</td>
<td>- / 12.7 / 10.9</td>
</tr>
</tbody>
</table>
### Table 5  Average particle diameter of Rh-xP catalysts after reduction measured from TEM images.

<table>
<thead>
<tr>
<th>Reduction temperature</th>
<th>350 °C</th>
<th>450 °C</th>
<th>550 °C</th>
<th>650 °C</th>
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</tr>
<tr>
<td>Rh</td>
<td>-</td>
<td>5.2</td>
<td>5.3</td>
<td>5.9</td>
</tr>
<tr>
<td>Rh-0.8P</td>
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<td>5.9</td>
<td>6.0</td>
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</tr>
<tr>
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<td>6.4</td>
<td>7.0</td>
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<tr>
<td>Rh-2.2P</td>
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<td>8.3</td>
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<td>Rh-3.0P</td>
<td>7.1</td>
<td>8.7</td>
<td>8.8</td>
<td>8.9</td>
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**Table 6** The theoretical number of exposed Rh atoms (Rh<sub>ex</sub>) and CO/Rh<sub>ex</sub> of reduced Rh-xP catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reduction temperature (°C)</th>
<th>Rh species for Rh&lt;sub&gt;ex&lt;/sub&gt; calculation (The most intense peak of XRD)</th>
<th>Rh&lt;sub&gt;ex&lt;/sub&gt; (μmol g-cat&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>CO/Rh&lt;sub&gt;ex&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
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<tbody>
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<td>Rh</td>
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<td>0.33</td>
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</table>

<sup>a</sup> CO uptake/the theoretical number of exposed Rh atoms ratio
Fig. 1
Fig. 2

$K_{\text{HDS}}$ (mmol h$^{-1}$ g-cat$^{-1}$) vs. P loading (wt%)
Fig. 3
Fig. 4

(a) TCD signal (a.u.) vs. Temperature (°C) for different samples:
- Rh/SiO₂ + 1.5P/SiO₂ (mixed, ×2)
- SiO₂
- Rh-3.0P
- Rh-2.2P
- Rh-1.5P
- Rh-0.8P
- Rh

(b) TCD signal (a.u.) vs. Temperature (°C) for different samples:
- Rh/SiO₂ + 1.5P/SiO₂ (mixed, ×2)
- SiO₂
- Rh-3.0P
- Rh-2.2P
- Rh-1.5P
- Rh-0.8P
- Rh
Fig. 5
Fig. 7
Fig. 8
Fig. 9

(a) TOF (h⁻¹) vs. Reduction temperature (°C)

Rh-3.0P
Rh
Rh-0.8P
Rh-1.5P
Rh-2.2P

(b) TOF (h⁻¹) vs. Reduction temperature (°C)

Rh-3.0P
Rh-2.2P
Rh-1.5P
Rh-0.8P
Rh
Fig. 10