



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 (Rh₂P) 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 Rh₂P 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 Rh₂P 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 Rh₂P at a relatively low reduction temperature (550 °C).

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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_x). SO_x causes acid rain and deactivates automotive exhaust catalysts. Regulation of SO_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/Al₂O₃ 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 [4,1] and the addition of citric acid [5] or phosphorus [1,6,7], have been widely investigated. Furthermore, new active phases other than sulfided CoMo catalysts have been reported by numerous researchers. Noble metals [8–13] and transition-metal carbides [14–17], nitrides [14,18], and phosphides [2,3,17,19–39] have been used as new HDS catalysts. Transition-metal phosphides such as Ni₂P [2,3,17,19–30] and MoP [29–34] have received extensive attention [29]. In particular, Ni₂P 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 Ni₁₂P₅ phase, which is an intermediate in the formation of Ni₂P [34]. In addition, the reduction of precursors with higher P concentrations results in the formation of the Ni₂P phase [19,20,24,28]. 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 Ni₂P (0.5). However, we [36–38]

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and Bussell et al. [3,39] have reported that rhodium phosphide (Rh_2P) supported on SiO_2 exhibits high and stable catalytic activity toward the HDS reaction. As with the Ni_2P catalysts, the P/Rh ratio should also strongly affect the formation of Rh_2P and the HDS activity of Rh catalysts. Previously, we reported that the support strongly affects the formation of Rh_2P and its HDS activity and that SiO_2 , TiO_2 , and Al_2O_3 supports showed superior HDS activity compared to MgO and ZrO_2 supports [37]. However, the formation of Rh_2P on Al_2O_3 is difficult because of the formation of AlPO_4 [3], and the turnover frequency (TOF) of Rh_2P is remarkably enhanced by the interaction between the active phase and TiO_2 [37]. Thus, SiO_2 , which does not exhibit a strong interaction with Rh_2P or P when used as a support, is a superior support for clarifying the effects of the P loading on Rh_2P 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_xP_y) and on the HDS activity of $\text{Rh}_2\text{P}/\text{SiO}_2$ 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 $295\text{ m}^2\text{ g}^{-1}$) was supplied by Nippon Aerosil Co. The Rh/SiO_2 catalyst was prepared by an impregnation method described previously [36–38]. Rhodium(III) chloride trihydrate ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 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 $10^\circ\text{C min}^{-1}$. P-added 5 wt% Rh (Rh-P)/ SiO_2 catalysts were prepared using the same procedure, except with aqueous solutions of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, 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 ($10^\circ\text{C min}^{-1}$) in a helium (He) stream (30 ml min^{-1}) at 500°C for 1 h, followed by reduction in H_2 (30 ml min^{-1}) at $350\text{--}700^\circ\text{C}$ for 1 h. A hydrogen–thiophene gas mixture ($\text{H}_2/\text{C}_4\text{H}_4\text{S}=30$), obtained by passing a H_2 stream through a thiophene trap cooled at 0°C , was then introduced into the reactor ($W/F=37.9\text{ g h mol}^{-1}$). 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 $\text{Al}_2\text{O}_3/\text{KCl}$ plot (ID: 0.53 mm, length: 25 m, film thickness: $10\ \mu\text{m}$, temperature: $60\text{--}190^\circ\text{C}$, rate: $7.5^\circ\text{C min}^{-1}$) columns.

The rate constant was calculated from the following equation under the assumption of a pseudo-first-order reaction:

$$k_{\text{HDS}} = \frac{-\ln(1-x/100)}{W/F} \quad (1)$$

where k_{HDS} is the reaction rate of thiophene HDS ($\text{mol h}^{-1}\text{ g}^{-1}$) 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 $10^\circ\text{C min}^{-1}$, 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% $\text{H}_2\text{--N}_2$) 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 $10^\circ\text{C min}^{-1}$, using a thermal conductivity detector (TCD) to monitor H_2 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 $K\alpha$ radiation source operated at 30 kV and 15 mA. The crystallite size of the metallic Rh and Rh_xP_y were calculated using Scherrer's equation:

$$d = \frac{K\lambda}{B \cos \theta} \quad (2)$$

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 λ is the wavelength of the X-ray radiation (0.154184 nm). The XRD peaks at 34.2° (Rh_2O_3 , (1 1 4) plane), 40.9° (Rh, (1 1 1) plane), 46.7° (Rh_2P , (2 2 0) plane), and 23.9° (RhP_2 , (1 1 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 $120,000\times$. 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 ($10^\circ\text{C min}^{-1}$) for 1 h, followed by reduction in H_2 at $350\text{--}700^\circ\text{C}$ 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 [36–38]. Thus, the HDS activity of Rh-xP catalysts reduced at various temperatures was examined in this work. Fig. 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

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