



# Low-temperature synthesis of rhodium phosphide on alumina and investigation of its catalytic activity toward the hydrodesulfurization of thiophene

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## ABSTRACT

In this study, the low-temperature synthesis of rhodium phosphide (Rh<sub>2</sub>P) on alumina (Al<sub>2</sub>O<sub>3</sub>) using triphenylphosphine (TPP) as a phosphorus (P) source and its catalytic activity toward hydrodesulfurization (HDS) were investigated to prepare a highly active HDS catalyst. TPP was more easily reduced than phosphate, and Rh<sub>2</sub>P was formed in the P(T)/Rh/Al<sub>2</sub>O<sub>3</sub> catalyst prepared from TTP at lower temperature as compared with the temperature required by Rh-P(A)/Al<sub>2</sub>O<sub>3</sub> catalyst prepared from a phosphate precursor. However, after reduction at a low temperature (450 °C), excess P covered the surface of Rh<sub>2</sub>P. The optimal reduction temperature for HDS rate of the P(T)/Rh/Al<sub>2</sub>O<sub>3</sub> catalyst (650 °C) was lower than that of the Rh-P(A)/Al<sub>2</sub>O<sub>3</sub> catalyst (800 °C). Furthermore, this temperature was slightly higher than the optimal reduction temperature for CO uptake (600 °C). These results are explained as follows: HDS rate is increased by both elimination of excess P on the active sites at higher reduction temperatures and enhancement of the crystallinity of Rh<sub>2</sub>P. Furthermore, because the particle size of the P(T)/Rh/Al<sub>2</sub>O<sub>3</sub> catalyst (ca. 1.2 nm) was substantially smaller than that of the Rh-P(A)/Al<sub>2</sub>O<sub>3</sub> catalyst, the P(T)/Rh/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited greater HDS rate compared with the Rh-P(A)/Al<sub>2</sub>O<sub>3</sub> catalyst.

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## 1. Introduction

Recently, the petroleum industry has claimed that the development of highly active hydrodesulfurization (HDS) catalysts that exhibit greater activity than commercial CoMo catalysts will prevent air pollution, acid rain, and the deactivation of automotive exhaust catalysts [1–3]. New active phases, especially nickel phosphide (Ni<sub>2</sub>P), have received extensive attention [2–22]. Furthermore, our group [23–27] and Bussell's group [3,28] reported that rhodium phosphide (Rh<sub>2</sub>P) supported on SiO<sub>2</sub> exhibits high and stable catalytic activity toward the HDS reaction.

Phosphate reduction is a convenient and simple method to prepare phosphide catalysts [16]. Because phosphate has strong P–O

bonds, phosphate reduction requires high temperatures [3]. In general, SiO<sub>2</sub>, which does not strongly interact with phosphate, is a suitable support for phosphide catalysts [2,3,10,11]. For industrial usage, Al<sub>2</sub>O<sub>3</sub> is a suitable support because it exhibits greater mechanical strength and stability than SiO<sub>2</sub>. Unfortunately, Al<sub>2</sub>O<sub>3</sub> is not a suitable support for phosphide catalysts, because phosphate reacts with Al<sub>2</sub>O<sub>3</sub> to form AlPO<sub>4</sub> [3,6,10,11]. In fact, we have reported that the optimal reduction temperature (800 °C) for HDS activity of the Rh-P/Al<sub>2</sub>O<sub>3</sub> catalyst is remarkably higher than that for HDS activity of the Rh-P/SiO<sub>2</sub> catalyst (550 °C) and that this higher temperature induces aggregation of Rh<sub>2</sub>P [24,27]. Therefore, we expect that high HDS activity can be obtained via the low-temperature synthesis of highly dispersed Rh<sub>2</sub>P on an Al<sub>2</sub>O<sub>3</sub> support.

Numerous reports have described the synthesis of phosphide catalysts at low temperatures. Teixeira da Silva et al. reported that the formation temperature of Ni<sub>2</sub>P, which was prepared from

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a phosphate precursor, can be decreased by the addition of Pd [29]. Previously, we reported that the reduction temperature of phosphates on  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  substrates and the formation temperatures of  $\text{Rh}_2\text{P}$  were decreased by the addition of Na [30]. However, noble metal addition is not an appropriate method for the synthesis of noble metal phosphides, and added Na would decrease the catalytic activity. Thus, phosphite, which is more reducible than phosphate, has been used as a P precursor to form noble metal phosphides [31]. However, phosphite on an  $\text{Al}_2\text{O}_3$  support is less reducible than that on other supports [32]. Some P precursors without oxygen, such as phosphine ( $\text{PH}_3$ ) and trioctylphosphine (TOP), have been reported [3,12,33,34].  $\text{PH}_3$  easily reacts with metals to form phosphides at low temperatures; however, this reagent is highly toxic. TOP also reacts with metal precursors such as acetylacetonate complexes to form phosphides at lower temperatures. But this method requires a large amount of a P precursor. Furthermore, the washed phosphides were impregnated into  $\text{Al}_2\text{O}_3$  to obtain the supported catalyst [35], which is a complicated method. On the other hand, some reports described synthesis of  $\text{Ni}_2\text{P}$  catalyst using triphenylphosphine ( $(\text{C}_6\text{H}_5)_3\text{P}$ , TPP) [36,37], but this method was also carried out in trioctylamine solution under  $\text{N}_2$  flow.

In our previous paper, we reported that rhodium and palladium phosphides were more easily formed using TPP compared with the corresponding phosphides prepared from phosphate, even in cases where the phosphides prepared from phosphate were calcined [25]. TPP is widely used as a ligand for homogeneous noble metal catalysts, indicating that TPP preferentially adsorbs onto noble metals rather than onto the supporting substrates. In addition, we observed that the phosphates that interacted with noble metals were more easily reduced than those on supports [26]. We expect that  $\text{Rh}_2\text{P}$  would easily form on  $\text{Al}_2\text{O}_3$  when TPP is used as a P precursor. In this study, the low-temperature synthesis of  $\text{Rh}_2\text{P}$  on  $\text{Al}_2\text{O}_3$  using TPP was examined to enhance the HDS activity of this phosphide-based catalyst.

## 2. Experimental

### 2.1. Catalyst preparation

Alumina ( $\text{Al}_2\text{O}_3$ , BET surface area  $101 \text{ m}^2 \text{ g}^{-1}$ ) was supplied by Nippon Aerosil Co. The  $\text{Rh}/\text{Al}_2\text{O}_3$  was prepared using an impregnation method. Rhodium(III) chloride trihydrate ( $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ , Kanto Chemical Co.) was used as an Rh precursor and was dissolved in water. The Rh loading was 5 or 10 wt%. After impregnation, the  $\text{Rh}/\text{Al}_2\text{O}_3$  was dried at  $110^\circ\text{C}$  for 24 h, followed by heat treatment under an  $\text{N}_2$  stream at  $450^\circ\text{C}$  for 1 h to decompose the Rh salt. The ramp rate for the  $\text{N}_2$  treatment was  $10^\circ\text{C min}^{-1}$ .

The TPP-added  $\text{Rh}/\text{Al}_2\text{O}_3$  ( $\text{P(T)}/\text{Rh}/\text{Al}_2\text{O}_3$ ) catalyst was also prepared by an impregnation method. A TPP hexane solution was impregnated into  $\text{Rh}/\text{Al}_2\text{O}_3$ . The P loading was 1.5 or 3 wt%, and the P/Rh molar ratio in the catalysts was 1.0. The  $\text{P(T)}/\text{Rh}/\text{Al}_2\text{O}_3$  catalyst was dried under an  $\text{N}_2$  stream at  $110^\circ\text{C}$  for 24 h to avoid oxidation of TPP. After drying, the catalyst was sieved into 30- to 42-mesh-size granules. The high-loading (Rh: 10 wt%, P: 3 wt%) catalyst was labeled as HL-P(T)/ $\text{Rh}/\text{Al}_2\text{O}_3$ .

### 2.2. Catalyst characterization

The  $\text{P(T)}/\text{Rh}/\text{Al}_2\text{O}_3$  catalyst was characterized using temperature-programmed reduction (TPR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and carbon monoxide (CO) adsorption analyses. TPR measurements were performed using a Shimadzu GC-8A gas chromatograph. The catalyst (0.1 g) was heated in a

He stream ( $30 \text{ ml min}^{-1}$ ) from room temperature to  $110^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$ , followed by He treatment at  $110^\circ\text{C}$  for 1 h. After this He treatment, the catalyst was cooled to  $30^\circ\text{C}$  in a He stream, and the He was switched to a hydrogen–nitrogen (5 vol%  $\text{H}_2$  in  $\text{N}_2$ ) gas mixture at  $30^\circ\text{C}$  for 0.5 h before the measurement. The TPR profile was recorded as the temperature was increased from  $30^\circ\text{C}$  to  $850^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$ ; a thermal conductivity detector (TCD) and a flame ionization detector (FID) were used to monitor the  $\text{H}_2$  consumption and the formation of hydrocarbons, respectively. When a TPR profile was recorded by TCD, water was removed using a molecular sieve trap. XPS spectra of the catalysts after reduction were measured using a JEOL JPS-9010MX with Mg  $\text{K}\alpha$  radiation (10 kV, 5 mA). Binding energy of measured spectra were corrected using C 1s peak at 285.0 eV. The XRD patterns of the catalysts were collected using a Rigaku MiniFlex equipped with a Cu  $\text{K}\alpha$  radiation source operated at 30 kV and 15 mA. TEM observations were carried out using a JEOL JEM-2100F. The conditions of TEM operation were an acceleration voltage of 200 kV and a magnification of 600000x. 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  $\text{P(T)}/\text{Rh}/\text{Al}_2\text{O}_3$  catalysts was measured using the pulse method. The  $\text{P(T)}/\text{Rh}/\text{Al}_2\text{O}_3$  catalyst (0.1 g) was reduced under  $\text{H}_2$  at  $450^\circ\text{C}$ – $750^\circ\text{C}$  for 1 h. CO was injected into the catalyst layer at  $25^\circ\text{C}$  using a sampling loop (1.0 ml). The CO uptake was measured with a Shimadzu GC-8A gas chromatograph equipped with a TCD.

### 2.3. Hydrodesulfurization of thiophene

The HDS of thiophene was performed at  $350^\circ\text{C}$  under 0.1 MPa using a conventional fixed-bed flow reactor. The  $\text{P(T)}/\text{Rh}/\text{Al}_2\text{O}_3$  catalyst (0.1 g) was charged into the quartz reactor and heated ( $10^\circ\text{C min}^{-1}$ ) under an  $\text{H}_2$  stream ( $30 \text{ ml min}^{-1}$ ) at  $450^\circ\text{C}$ – $700^\circ\text{C}$  for 1 h. A hydrogen–thiophene gas mixture ( $\text{H}_2/\text{C}_4\text{H}_4\text{S}$  molar ratio=30), obtained by passing an  $\text{H}_2$  stream through a thiophene trap cooled at  $0^\circ\text{C}$ , 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 FID and silicone DC-550 (length: 2 m, temperature:  $110^\circ\text{C}$ ) and  $\text{Al}_2\text{O}_3/\text{KCl}$  plot (ID: 0.53 mm, length: 25 m, film thickness:  $10 \mu\text{m}$ , temperature:  $60^\circ\text{C}$ – $190^\circ\text{C}$ , rate:  $7.5^\circ\text{C min}^{-1}$ ) columns.

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

The turnover frequency (TOF,  $\text{h}^{-1}$ ) was calculated from the following equation:

$$\text{TOF} = \frac{F \cdot x / 100}{W \cdot A} \quad (2)$$

where  $F$  is the flow rate of thiophene ( $\text{mol h}^{-1}$ ),  $W$  is the weight of catalyst loading (g), and  $A$  is the CO uptake ( $\text{mol g}^{-1}$ ).

## 3. Results and discussion

### 3.1. Low-temperature synthesis of $\text{Rh}_2\text{P}$ on $\text{Al}_2\text{O}_3$ supports

We have reported that the reduction temperature strongly affects the formation of  $\text{Rh}_2\text{P}$  catalysts [23–27]. Therefore, the TPR profiles of the  $\text{P(T)}/\text{Rh}/\text{Al}_2\text{O}_3$  catalyst were examined to clarify the reducibility of the rhodium oxide and TPP. Fig. 1 shows the TPR profile of the  $\text{P(T)}/\text{Rh}/\text{Al}_2\text{O}_3$  catalyst recorded by TCD and FID. Some

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