



Short Communication

Rhodium phosphide catalyst for hydrodesulfurization: Low temperature synthesis by sodium addition

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ABSTRACT

Effect of sodium (Na) addition on rhodium phosphide (Rh₂P) formation on MFI zeolite, SiO₂ and Al₂O₃ and hydrodesulfurization (HDS) activity were examined. The TPR results revealed that Na addition enhanced reducibility of phosphates. The XRD results indicated that Rh₂P phase was easily formed on NaMFI support as compared with on HMFI support. The maximum HDS activity of Rh–P/NaMFI catalyst was obtained at lower reduction temperature and this activity was higher than that of Rh–P/HMFI catalyst. We concluded that since Na would weaken interaction between Al and phosphate, high HDS activity of Rh–P/NaMFI catalyst was observed at lower reduction temperature.

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1. Introduction

One of the most important processes for prevention of the air pollution is hydrodesulfurization (HDS) to produce low sulfur fuels. In the recent year, the sulfur regulations of diesel fuel and gasoline have been strict. Therefore, it is necessary to develop new HDS catalysts. Transition metal phosphides, such as Ni₂P [1,2], MoP [3] and CoP [4], have been reported as new HDS catalysts. Our group [5] and Bussell's [6] group reported that Rh₂P/SiO₂ catalyst showed higher HDS activity than Ni₂P/SiO₂ catalyst.

Ammonium dihydrogen phosphate (NH₄H₂PO₄) is widely used as a phosphorus precursor for preparation of phosphide catalyst. Prins and Bussell reported that the P–O bond is strong, and its reduction requires high temperature (400–1000 °C), even with hydrogen [7]. It is well known that Al₂O₃ is a preferred support for commercial catalysts. Unfortunately, phosphate strongly interacts with Al₂O₃ to form AlPO₄ upon calcination of Al₂O₃-supported phosphate [7]. Thus, the transition metal phosphide catalysts supported on zeolites and SiO₂-Al₂O₃ have been scarcely reported suggesting that Al in these supports also strongly interact with phosphate. In fact, Robinson et al. concluded that low HDS activity of P-doped Ni/SiO₂-Al₂O₃ catalyst was due to lack of Ni₂P formation [8]. On the other hand, Oyama et al. reported that both H- and K-form USY zeolite-supported Ni₂P catalysts showed high HDS activities and the activity of Ni₂P/HUSY catalyst was stabilized by K ion exchange [9]. Moreover, NH₄H₂PO₄ condenses into polyphosphate at higher

temperature [10]. In contrast, Na addition inhibits formation of polyphosphate [11]. This indicates that the amount of condensed P–O–P bonds, which would have stronger bonding than P–O–H, in the precursor of phosphide catalyst can be decreased by Na addition. If Na, but not Al, preferentially interacts with phosphate, phosphide catalyst would be easily formed by a decreasing reduction temperature of phosphate on aluminosilicate support.

Many HDS catalysts supported on zeolites, which are crystalline aluminosilicate, have been studied [12–14]. Especially, the Pt/HMFI catalyst has superior HDS activity [13,15]. Besides, it can be expected that Na addition enhances stability of HDS activity as compared with H-form zeolite, as well as Ni₂P/K-USY catalyst [9]. In the present work, Rh₂P formation on NaMFI and HMFI and HDS activities of these catalysts were investigated to improve the reducibility of phosphates by Na addition. Furthermore, Rh₂P formation on Na-added SiO₂ and Al₂O₃ was also examined to clarify the effect of Na addition on reducibility of phosphates.

2. Experimental

2.1. Catalyst preparation

The Na- and H-form of MFI (Si/Al = 11, Tosoh) were used as zeolite supports. HMFI zeolite was obtained by ion exchange of NaMFI with 1 mol/L HCl aqueous solution. The Na contents of NaMFI and HMFI were analyzed by ICP-AES and the amount of Na was 1411 and 4 μmol/g, respectively. That is, Na content in NaMFI support was 3.2 wt.%. The Rh and P supported on MFI (Rh–P/MFI) catalysts were

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prepared with rhodium (III) chloride trihydrate ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) and $\text{NH}_4\text{H}_2\text{PO}_4$ aqueous solution described former literature [5,16,17]. The amount of Rh loading was 5 wt.% and P addition was 1.5 wt.%.

Metal oxide (MO_x) supports, SiO_2 and Al_2O_3 were used to evaluate effect of Na addition. Na-added MO_x (denoted as Na- MO_x) was prepared by an impregnation method using NaNO_3 aqueous solution. The Na loading was 0.7 wt.% (Supplementary data). The impregnated supports were dried at 110 °C for 24 h, followed by calcination at 400 °C for 1 h. The Na- MO_x - and MO_x -supported Rh-P catalysts were also prepared by the same preparation method of Rh-P/MFI catalysts. Furthermore, sodium dihydrogen phosphate (NaH_2PO_4) was used as a phosphorus source to prepare the Rh-P-Na catalyst. In this case, P/Rh molar ratio was kept constant ($\text{P/Rh} = 1$) and resulting Na content was 1.1 wt.%.

2.2. Catalyst characterization

The supported Rh-P catalysts were characterized by temperature-programmed reduction (TPR) and X-ray diffraction (XRD). TPR profiles were recorded using thermal conductivity detector (TCD) to monitor consumption of H_2 . The calcined Rh-P catalysts (0.1 g) were heated in helium (He) stream from room temperature to 500 °C at 10 °C/min, followed by treating at 500 °C for 1 h. After cooling to 30 °C, a He stream was switched to a 5 vol.% hydrogen–nitrogen ($\text{H}_2\text{-N}_2$) gas mixture for 30 min before measurement. Water was removed by a molecular sieve trap. The TPR profiles were measured from 30 to 850 °C at 10 °C/min in a 5 vol.% $\text{H}_2\text{-N}_2$ stream. XRD patterns of the catalysts after calcination and reduction were obtained by Rigaku MiniFlex with $\text{Cu K}\alpha$ radiation at 30 kV and 15 mA.

2.3. HDS activity measurement

Measurements of catalytic activity for thiophene HDS were carried out using conventional fixed bed flow reactor at 350 °C under 0.1 MPa and were described elsewhere [5,16,17]. Briefly, the calcined Rh-P catalyst (0.1 g) was pretreated in a He stream at 500 °C for 1 h, followed by in-situ reduction in a H_2 stream at 450–850 °C for 1 h. The reaction products were analyzed by gas chromatograph (flame ionization detector, FID and/or flame photometric detector, FPD). Thiophene conversion was calculated using FID equipped with Silicone DC-550 (2.5 m, 135 °C) column or FPD equipped with Silicone DC-550 (2.0 m, 40–90 °C) column. Composition of products was analyzed by FID equipped with $\text{Al}_2\text{O}_3/\text{KCl}$ PLOT (0.53 mm \times 25 m, 60–190 °C) column.

3. Results and discussion

3.1. Formation of Rh_2P

Effect of reduction temperature on Rh_2P formation in Rh-P/MFI catalysts was investigated. Fig. 1 shows the TPR profiles of the Rh-P/MFI catalysts. The peak temperature of H_2 consumption was divided into four parts: below 100 °C, 100–180 °C, 180–500 °C and above 500 °C. Two reduction peaks (below 120 °C and around 120–150 °C) were observed in the TPR profile of Rh/ Al_2O_3 catalyst [18]. The former was attributed to the bulk rhodium-oxide (RhO_x) crystallites and the latter was attributed to the RhO_x species interacting with the Al_2O_3 surface [18]. Both XRD patterns of calcined Rh-P/MFI catalysts showed broad peaks of Rh_2O_3 at around 34° (Fig. 2(i) and (ii), (b)). Therefore, in both TPR profiles of Rh-P/MFI catalysts, the peaks of H_2 consumption appeared below 180 °C were assigned to reduction of RhO_x including Rh_2O_3 . The peak for RhO_x reduction in the NaMFI-supported catalyst was observed at 81 °C, though that in the HMFI-supported catalyst was observed at 139 °C. The small amount of RhO_x interacted with NaMFI support can be explained as follows. It was reported that Rh complex $[\text{Rh}(\text{H}_2\text{O})_6 - n\text{Cl}_n]^{3-n}$ exchanged into zeolite at 90 °C by using RhCl_3 aqueous solution [19]. The catalyst prepared from impregnation

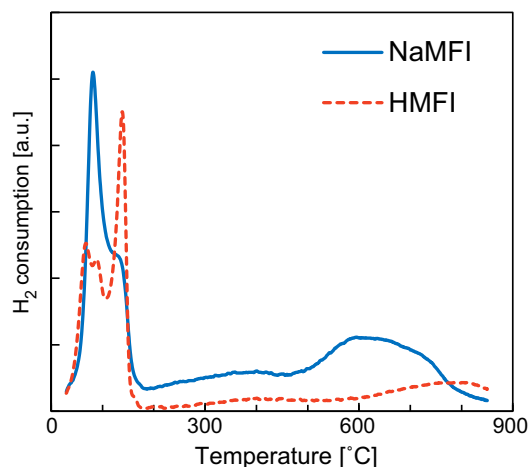


Fig. 1. TPR profiles of NaMFI- and HMFI-supported Rh-P catalysts.

method would also contain Rh complex interacted with cation exchange site because of increasing temperature to evaporate water. Since Na^+ remains in the Rh-P/NaMFI catalyst after evaporation, both cationic Rh complex and Na^+ interact with cation exchange site. In the calcination step, the Rh complex interacted with cation exchange site react with oxygen to form RhO_x interacted with support.

The TPR profile of Rh-P/ SiO_2 catalyst showed the peak above 150 °C, which was attributed to reduction of phosphates [5,17]. Therefore, the peaks above 180 °C were assigned to reduction of phosphates. The maximum peak temperature of NaMFI-supported catalyst was observed at 595 °C, but that of HMFI-supported catalyst was 784 °C. The peaks of phosphate reduction in the TPR profile of NaMFI-supported catalyst have higher H_2 consumption than that of HMFI-supported catalyst. Therefore, reduction of phosphates on NaMFI support would be more easily than on H-form.

Reducibility of phosphates in the Rh-P catalyst was remarkably changed by the kind of cation in the MFI support. Therefore, it is expected that formation temperature of Rh_2P would be also changed by cation species in the MFI. Relationship between reduction temperature and Rh_2P formation was examined by the XRD patterns of reduced Rh-P/MFI catalysts (Fig. 2). The Rh peaks were observed in the HMFI-supported catalyst reduced below 650 °C (Fig. 2(ii)). The XRD patterns of the catalyst reduced above 750 °C showed not only strong Rh peaks but also slight Rh_2P peaks. In the NaMFI-supported catalyst reduced at 450 °C, the Rh peaks were also observed (Fig. 2(i), (c)). On the other hand, intensity of the Rh peaks decreased and the Rh_2P peaks appeared with increasing reduction temperature. Finally, Rh_2P was formed completely in the NaMFI-supported catalyst reduced at 600–650 °C. These results indicate that Rh_2P was formed more easily on NaMFI support than on HMFI support. Furthermore, these results are in accordance with those of TPR profiles, as shown in Fig. 1.

3.2. Effect of Na addition on Rh_2P formation

The TPR profiles and XRD measurement of Rh-P/MFI catalysts are suggesting that Na would enhance reducibility of phosphates. Thus, effect of Na addition on reducibility of phosphates was investigated in detail by using MO_x and Na- MO_x supports. Na species on Na- SiO_2 was mostly NaNO_3 and that on Na- Al_2O_3 was mixed NaNO_3 and interacting with Al_2O_3 species (shown in Supplementary data). Fig. 3 shows the TPR profiles of Na- MO_x - and MO_x -supported Rh-P catalysts. Previously, we have reported that the reduction peak at 150–400 °C was attributed to the reduction of phosphates interacting with Rh in the Rh-P/ SiO_2 catalyst [17]. In the case of Rh-P/Na- SiO_2 catalyst, the significantly large peak appeared at 180–500 °C as compared with SiO_2 -supported catalyst (Fig. 3(a)). $\text{NH}_4\text{H}_2\text{PO}_4$,

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