



Short communication

# Bulk and Al<sub>2</sub>O<sub>3</sub>-supported Ni<sub>2</sub>P HDS catalysts prepared by separating the nickel and hypophosphite sources

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## ARTICLE INFO

## Article history:

Received 23 November 2015

Received in revised form 6 January 2016

Accepted 7 January 2016

Available online 12 January 2016

## Keywords:

Nickel phosphide

Hypophosphite

Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts

Hydrodesulfurization

## ABSTRACT

Bulk Ni<sub>2</sub>P and Al<sub>2</sub>O<sub>3</sub>-supported Ni<sub>2</sub>P were prepared at low phosphidation temperature (300 °C) from Ni<sub>9</sub>S<sub>8</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub>, which were separated to avoid the formation of phosphate inside the support pores. The unsupported product phases were characterized by XRD and the Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts by XRD, BET and TEM. A 10 wt.% Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalyst, made by the Ni(NO<sub>3</sub>)<sub>2</sub>-NiO-Ni<sub>9</sub>S<sub>8</sub>-Ni<sub>2</sub>P path at a P/Ni ratio of 3, showed the highest activity in the hydrodesulfurization of dibenzothiophene. By separating the nickel and hypophosphite sources, Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts could be obtained at low phosphidation temperature and with low degree of blockage of pores by surplus phosphorus.

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## 1. Introduction

Metal phosphides have been proposed as alternative hydrotreating catalysts [1–3]. Since the first publication on the application of metal phosphides in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) [4], temperature-programmed reduction (TPR) of a metal salt and a phosphate precursor in hydrogen [5] became the method of choice for preparing metal phosphides. The metal phosphides were found to have the following activity sequence in hydrotreating: Ni<sub>2</sub>P > WP > MoP > CoP > Fe<sub>2</sub>P, with Ni<sub>2</sub>P as the most active catalyst [6]. While unsupported Ni<sub>2</sub>P has a low surface area, a support with high-surface area is needed to disperse Ni<sub>2</sub>P uniformly [7–12].

γ-Al<sub>2</sub>O<sub>3</sub> is the most commonly used support for HDS catalysts and has unique properties. However, the use of γ-Al<sub>2</sub>O<sub>3</sub> as support for metal phosphides is difficult because the reduction of phosphate requires elevated temperature in excess of 600 °C [13,14]. PO<sub>4</sub><sup>3-</sup> can strongly interact with γ-Al<sub>2</sub>O<sub>3</sub> to form AlPO<sub>4</sub> at the high temperature used in the TPR method. AlPO<sub>4</sub> cannot easily be reduced to phosphide, not even at very high temperature, and this restricts the formation and dispersion of the active metal phosphide phase. As a consequence, excess phosphate has to be added to form metal phosphide particles on γ-Al<sub>2</sub>O<sub>3</sub>, leading to blocking of the pores of the support [15].

Phosphites (P(III)) [16–18] and in particular hypophosphites (P(I)) [19–24] are easier to reduce than phosphates (P(V)) and make it possible to prepare Ni<sub>2</sub>P at lower temperature. Cecilia et al. used P(III) to prepare bulk Ni<sub>2</sub>P at 375 °C [16]. Bulk and supported Ni<sub>2</sub>P were synthesized using hypophosphites and nickel salts at 200–300 °C [20–24]. Song et al. prepared Ni<sub>2</sub>P catalysts by phosphiding NiS with NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub> at 350 °C [25].

Whereas phosphate and phosphite must be reduced with H<sub>2</sub> to make PH<sub>3</sub>, which can reduce the nickel cations and form nickel phosphide, hypophosphite disproportionates to PH<sub>3</sub> and phosphate or phosphite upon heating. The advantage of hypophosphite is that it disproportionates already at low temperature, and that the interaction between phosphorus and γ-Al<sub>2</sub>O<sub>3</sub> can, thus, be kept low. The disadvantage of hypophosphite is that the co-product phosphate (or phosphite) will cause pore blockage of the catalyst. The phosphate and other salts have to be removed from the catalyst by thorough washing in several steps [20,21], but this makes catalyst preparation more difficult.

To avoid this disadvantage of hypophosphite, we tried to avoid pore blockage by phosphate and washing by separating the nickel source and hypophosphite source, so that the gaseous PH<sub>3</sub>, but not the phosphate (or phosphite), will reach the nickel. We prepared Ni<sub>2</sub>P by phosphiding Ni<sub>9</sub>S<sub>8</sub> with NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub> at 300 °C not by mixing the Ni precursor and NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub>, but by positioning the P source upstream of the Ni source. The conditions for preparing Ni<sub>2</sub>P with separate P and Ni sources were studied with bulk samples. The optimum phosphiding conditions were then applied to the preparation of

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Ni<sub>2</sub>P supported on alumina and the resulting catalyst was tested in the HDS reaction of dibenzothiophene.

## 2. Experimental

### 2.1. Preparation of Ni<sub>2</sub>P and Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub>

NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub> (Aladdin) was used to prepare bulk Ni<sub>2</sub>P samples. The Ni source Ni<sub>9</sub>S<sub>8</sub> was made by treating NiO in a flow of a 10 vol% H<sub>2</sub>S/H<sub>2</sub> at 400 °C for 4 h and NiO was made by calcination of Ni(NO<sub>3</sub>)<sub>2</sub> (obtained by drying Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sinopharm Chemical Reagent Co.) at 120 °C for 12 h) at 400 °C for 3 h. The P and Ni sources were put in separate porcelain containers in a furnace, with the container containing the P source upstream of the container containing the Ni source. The containers were heated in a 10 mL min<sup>-1</sup> N<sub>2</sub> flow from room temperature to 120 °C at 2 °C min<sup>-1</sup>, holding at 120 °C for 1 h, further heating to 300 °C at 2 °C min<sup>-1</sup>, and holding at 300 °C for 1 h. After cooling below 35 °C, the N<sub>2</sub> flow was terminated and the nickel phosphide was passivated in flowing 10 vol% H<sub>2</sub>S in H<sub>2</sub> for 1 h. H<sub>2</sub>S passivation was found superior to O<sub>2</sub> passivation and to give a higher HDS activity [26]. A nickel phosphosulfide phase is formed during H<sub>2</sub>S passivation, which is considered responsible for the high HDS activity [27].

Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> was prepared by incipient wetness impregnation of Al<sub>2</sub>O<sub>3</sub> (Shandong Alumina Plant, surface area 147 m<sup>2</sup>/g, pore volume 0.38 cm<sup>3</sup>/g) with an aqueous Ni(NO<sub>3</sub>)<sub>2</sub> solution. After impregnation, the sample was left overnight in air, dried at 120 °C for 12 h, and then calcined in air at 400 °C for 3 h. After cooling, the resulting NiO/Al<sub>2</sub>O<sub>3</sub> was pelletized, crushed and sieved to 20–40 mesh size, and subsequently sulfidated in a flow of 10 vol% H<sub>2</sub>S/H<sub>2</sub> at 400 °C for 4 h. The resulting Ni<sub>9</sub>S<sub>8</sub>/Al<sub>2</sub>O<sub>3</sub> was put in a porcelain container and NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub> in another porcelain container, and both containers were placed in a furnace as described above.

For comparison, a catalyst was prepared by co-impregnation of Al<sub>2</sub>O<sub>3</sub> with a mixed solution of Ni(NO<sub>3</sub>)<sub>2</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub>, P/Ni = 3, and heating to 300 °C in N<sub>2</sub> for 1 h, followed by passivation as described above. One portion of this catalyst was used as such, the other portion was washed several times with water to remove phosphate [20,21]. The HDS activity of both catalysts was measured under the same conditions as the catalyst made by separating the Ni and P sources.

### 2.2. Characterization of Ni<sub>2</sub>P and Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub>

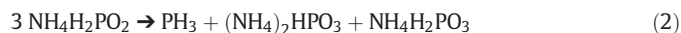
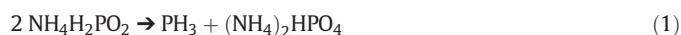
The bulk Ni<sub>2</sub>P and supported Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> samples were characterized by X-ray diffraction (XRD), N<sub>2</sub> adsorption–desorption, thermogravimetry and differential scanning calorimetry (TG-DSC), transmission electron microscopy (TEM) and temperature-programmed reduction in H<sub>2</sub> (H<sub>2</sub>-TPR). Powder XRD patterns of the samples were measured on a PANalytical X'Pert PRO diffractometer with Cu Kα monochromatized radiation (λ = 1.54 Å) operated at 45 kV and 40 mA, with a scan rate of 8° per min and a 2θ scan range from 5° to 75°. N<sub>2</sub> adsorption–desorption measurements were carried out on a Micromeritics Tristar II 3020 analyzer at –196 °C. Before measurement, the samples were outgassed overnight at 300 °C and 0.5 mbar. The surface area was calculated by the BET method and the average pore size and total pore volume were determined by the BJH method from the desorption branches of the isotherms. TEM was performed on a JEM-2100 UHR microscope (JEOL) at an accelerating voltage of 200 kV. The samples were first ground, then dispersed in ethanol in an ultrasonic bath, and finally placed on a cellulose-coated Cu grid. H<sub>2</sub>-TPR was conducted with a chemisorption analyzer (AutoChem HP, Micromeritics). A sample of 0.2 g was heated at 150 °C for 1 h and cooled to room temperature under a He flow to remove adsorbed materials. A mixture of 10 vol% H<sub>2</sub>/Ar (100 ml/min) was then introduced into the sample loop and the sample was heated to 900 °C at a rate of 10 °C/min. The H<sub>2</sub> consumption was detected by a thermal conduction detector.

### 2.3. HDS activity measurement of Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts

The catalytic reactions were carried out in a stainless-steel tubular reactor (10.0 mm i.d.) heated by three furnaces. A sample containing 0.20 g catalyst diluted with silicon carbide to 2.0 mL was used for each run. Prior to HDS reaction, the catalyst was reduced at a pressure of 1.0 MPa in a flow of 60 mL min<sup>-1</sup> H<sub>2</sub> by heating from room temperature to 120 °C at 2 °C min<sup>-1</sup>, holding at 120 °C for 2 h, further heating to 550 °C at 2 °C min<sup>-1</sup>, and finally holding at 550 °C for 1.5 h. Then the temperature was lowered to the reaction temperature of 330 °C. After increasing the pressure to 3.0 MPa, a feed of 0.5 wt% dibenzothiophene (DBT) dissolved in toluene was fed to the reactor at a rate of 6 mL h<sup>-1</sup>. Product samples were collected between 7 and 12 h after reaction and analyzed off-line by an Agilent-4500 gas chromatograph equipped with an HP-5 column and a flame ionization detector.

## 3. Results and discussion

To determine whether the co-product of phosphine (PH<sub>3</sub>) in the disproportionation of hypophosphite (Eqs. (1) or (2)) is phosphate or phosphite, we studied the TG-DSC of NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub>.



The formation of phosphate or phosphite determines the efficiency with which PH<sub>3</sub> is formed: 50% when phosphate forms (Eq. (1)) and only 33% when phosphite forms (Eq. (2)). The relative weight loss of about 20% between 250 and 350 °C agrees with Eq. (1) but not with Eq. (2). This proves that P(V) species were formed in the disproportionation of hypophosphite.

### 3.1. Preparation of Ni<sub>2</sub>P from Ni<sub>9</sub>S<sub>8</sub>

Because the amount of PH<sub>3</sub> that is taken up by the nickel salt for phosphidation depends on the amount of the hypophosphite, temperature and gas flow rate, we kept the flow rate of the N<sub>2</sub> carrier gas constant during all preparations. To study how efficient the PH<sub>3</sub> is used for phosphidation, we varied the P/Ni molar ratio in the containers to optimize the ratio needed to get pure Ni<sub>2</sub>P. The PH<sub>3</sub> in the exit gas was led through absorption bottles (MnO<sub>2</sub> first and then a NaOH solution), in which it reacts to a solution of sodium phosphate and phosphite. To study Ni<sub>9</sub>S<sub>8</sub> as Ni source for the formation of Ni<sub>2</sub>P, the XRD patterns of the products of the Ni(NO<sub>3</sub>)<sub>2</sub>-NiO-Ni<sub>9</sub>S<sub>8</sub>-Ni<sub>2</sub>P route were investigated. After calcination of Ni(NO<sub>3</sub>)<sub>2</sub> at 400 °C, the product showed the XRD peaks of NiO (Fig. 1). After sulfidation, the NiO peaks disappeared and the main product was Ni<sub>9</sub>S<sub>8</sub> (Fig. 1), indicating that the sulfidation was complete. The Ni<sub>9</sub>S<sub>8</sub> was then phosphided by positioning different amounts of NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub> in the first container. Besides peaks of Ni<sub>2</sub>P, peaks of Ni<sub>7</sub>S<sub>6</sub>, NiS and S were present at the low P/Ni ratio of 1. Because of these many peaks, we could not determine if the intermediate Ni<sub>12</sub>P<sub>5</sub> was formed as well. At the P/Ni ratio of 2, the main product of the phosphiding was Ni<sub>2</sub>P, but also some NiS was formed. At P/Ni = 3, the product was Ni<sub>2</sub>P and a small amount of (NH<sub>4</sub>)<sub>4</sub>P<sub>4</sub>O<sub>12</sub> (PDF 00-042-0221) and (NH<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (PDF 00-044-0800). At P/Ni = 4, the product was mainly Ni<sub>2</sub>P and some Ni<sub>5</sub>P<sub>4</sub>, (NH<sub>4</sub>)<sub>4</sub>P<sub>4</sub>O<sub>12</sub> and (NH<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub>. When NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub> is heated, NH<sub>3</sub> and PH<sub>3</sub> are released and PH<sub>3</sub> phosphides nickel sulfide to form Ni<sub>2</sub>P. When more PH<sub>3</sub> is available, Ni<sub>5</sub>P<sub>4</sub> can form. When PH<sub>3</sub> reacts with NiS, phosphorus is formed (Eq. (3)), but it is not stable at 300 °C in H<sub>2</sub>O vapor (Eq. (4)). The formed H<sub>3</sub>PO<sub>4</sub> then reacts with NH<sub>3</sub> to form (NH<sub>4</sub>)<sub>4</sub>P<sub>4</sub>O<sub>12</sub> and (NH<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, with phosphorus in the P(V) state.

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