



## Research Note

Preparation of Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> by temperature-programmed reduction of a phosphate precursor with a low P/Ni ratioXiang Li<sup>a,b,c</sup>, Jianpeng Feng<sup>a</sup>, Jingyu Guo<sup>a</sup>, Anjie Wang<sup>a,b,c,\*</sup>, Roel Prins<sup>d</sup>, Xinping Duan<sup>e</sup>, Yongying Chen<sup>a,b</sup><sup>a</sup>State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, No. 2 Linggong Road, Dalian 116024, People's Republic of China<sup>b</sup>Liaoning Key Laboratory of Petrochemical Technology and Equipment, Dalian University of Technology, No. 2 Linggong Road, Dalian 116024, People's Republic of China<sup>c</sup>Penn State and Dalian University of Technology Joint Center for Energy Research (JCER), Dalian University of Technology, No. 2 Linggong Road, Dalian 116024, People's Republic of China<sup>d</sup>Institute of Chemical and Bioengineering, ETH Zurich, 8093 Zurich, Switzerland<sup>e</sup>Department of Chemistry, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, Xiamen University, Xiamen 361005, People's Republic of China

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## ABSTRACT

Ni<sub>2</sub>P that was highly active in the hydrodesulfurization of dibenzothiophene was obtained by reduction of a phosphate precursor with a P/Ni molar ratio as low as 1.2 over cerium oxide-modified Al<sub>2</sub>O<sub>3</sub> (Ce-Al<sub>2</sub>O<sub>3</sub>) and macroporous Al<sub>2</sub>O<sub>3</sub> (M-Al<sub>2</sub>O<sub>3</sub>). <sup>27</sup>Al MAS NMR revealed that this is likely due to the low reactivity of pentahedrally coordinated Al<sup>3+</sup> (Al(P)) with phosphorus oxide. Because the major Al species in Ce-Al<sub>2</sub>O<sub>3</sub> and M-Al<sub>2</sub>O<sub>3</sub> is Al(P), less phosphorus is consumed by the Al<sub>2</sub>O<sub>3</sub> support upon calcination and thus more phosphorus is available for the formation of Ni<sub>2</sub>P during the reduction stage.

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## 1. Introduction

Metal-rich transition-metal phosphides (e.g., Ni<sub>2</sub>P, MoP, WP, CoP, and Co<sub>2</sub>P) are promising catalysts for a variety of reactions such as hydrotreating, hydrogenation, hydrodeoxygenation, and hydrogen evolution [1–4]. Among the transition-metal phosphides, Ni<sub>2</sub>P has attracted particular attention due to its high catalytic performance and resistance to poisoning [5,6]. There are various methods for synthesizing transition-metal phosphides, the most commonly used being the temperature-programmed reduction of the corresponding metal phosphate precursors in flowing H<sub>2</sub> (TPR) [7].

Al<sub>2</sub>O<sub>3</sub> is one of the most widely used supports for industrial catalysts because of its unique properties, such as good mechanical properties and stability, high surface area and porosity, and low price. Unfortunately, phosphate interacts strongly with Al<sub>2</sub>O<sub>3</sub> to form AlPO<sub>4</sub> upon calcination of alumina-supported phosphate

[7]. Thus, a large proportion of the phosphate is unavailable for reduction to phosphide and excess phosphorus has to be added to form metal phosphide particles on Al<sub>2</sub>O<sub>3</sub> [7–9]. Sawhill et al. showed that phase-pure Ni<sub>2</sub>P on Al<sub>2</sub>O<sub>3</sub> could only be obtained from a phosphate precursor with a P/Ni molar ratio higher than 2.0 [9]. SiO<sub>2</sub> does not interact strongly with phosphate [7], and therefore phase-pure Ni<sub>2</sub>P was obtained on SiO<sub>2</sub> from a phosphate precursor with a P/Ni molar ratio as low as 0.8 [9]. The large excess of P and the presence of AlPO<sub>4</sub> in Al<sub>2</sub>O<sub>3</sub>-supported Ni<sub>2</sub>P catalysts had a strong negative influence on the dispersion of Ni<sub>2</sub>P and its hydrodesulfurization (HDS) performance [9]. Consequently, the thiophene HDS turnover frequency (TOF) of Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> was much lower than that of Ni<sub>2</sub>P/SiO<sub>2</sub> [9]. Hence, alternative approaches using phosphorus sources other than phosphate have been developed for the preparation of Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub>. For instance, Guan et al. prepared a Ni<sub>2</sub>P/γ-Al<sub>2</sub>O<sub>3</sub> catalyst by thermal decomposition of a mixture of nickel chloride and sodium hypophosphite [10] and of a mixture of nickel oxide and sodium hypophosphite [11]. The resulting Ni<sub>2</sub>P/γ-Al<sub>2</sub>O<sub>3</sub> catalyst possessed a P/Ni ratio of 0.59. The HDS activity of the Ni<sub>2</sub>P/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was about as high as that of Ni<sub>2</sub>P/MCM-41 [11]. Cecilia et al. synthesized Ni<sub>2</sub>P/γ-Al<sub>2</sub>O<sub>3</sub> by temperature-programmed reduction of Ni(H<sub>2</sub>PO<sub>3</sub>)<sub>2</sub> [12]. The

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resulting Ni<sub>2</sub>P/γ-Al<sub>2</sub>O<sub>3</sub> possessed high initial HDS activity, but suffered from deactivation with time on stream. Cho et al. obtained Ni<sub>2</sub>P/γ-Al<sub>2</sub>O<sub>3</sub> by phosphidation of Ni(acac)<sub>2</sub> with trioctylphosphine in the presence of trioctylphosphine oxide in the liquid phase [13]. Yang and Prins [14] prepared a Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalyst by treating a metallic Ni/Al<sub>2</sub>O<sub>3</sub> precursor with a 10% PH<sub>3</sub>/H<sub>2</sub> mixture at 250 °C. However, according to Da Silva et al. [15], these alternative routes have disadvantages that may limit their application. This means that currently the TPR method is still the most feasible way to prepare supported Ni<sub>2</sub>P catalysts. Thus, a lowering of the P/Ni ratio in the nickel phosphate precursor on Al<sub>2</sub>O<sub>3</sub> must be achieved for the preparation of high-performance Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts.

In the present work, we report the synthesis of Ni<sub>2</sub>P supported on cerium oxide-modified Al<sub>2</sub>O<sub>3</sub> (Ce–Al<sub>2</sub>O<sub>3</sub>) and on macromesoporous Al<sub>2</sub>O<sub>3</sub> (M–Al<sub>2</sub>O<sub>3</sub>) from a phosphate precursor with a P/Ni molar ratio of 1.2 by the TPR method. This value is about half of that (2.0) reported for the preparation of Ni<sub>2</sub>P/γ-Al<sub>2</sub>O<sub>3</sub> [9], and close to that (0.8) required for the formation of phase-pure Ni<sub>2</sub>P on SiO<sub>2</sub> [8]. Our results suggest that the coordination state of Al<sup>3+</sup> in Al<sub>2</sub>O<sub>3</sub> is a critical factor affecting the reduction of the nickel phosphate precursor to Ni<sub>2</sub>P.

## 2. Experimental methods

### 2.1. Preparation of Al<sub>2</sub>O<sub>3</sub> supports

Ce–Al<sub>2</sub>O<sub>3</sub> was prepared by a glycine–nitrate combustion method [16]. A solution of 12.00 g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 15 mL deionized water was added dropwise and under stirring to a solution of 4.00 g glycine in 15 mL deionized water. The pH was adjusted to 2–3 with diluted HNO<sub>3</sub> after 0.347 g Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 0.2 g polyethylene glycol 4000 were added. Polyethylene glycol 4000 must be added; otherwise the specific surface area of the Ce–Al<sub>2</sub>O<sub>3</sub> sample is too small. This mixture was aged at ambient temperature for 12 h and then heated at 120 °C until a viscous gel was obtained. The sample was heated to 750 °C at a heating rate of 5 °C/min and calcined at 750 °C for 4 h to produce the final Ce–Al<sub>2</sub>O<sub>3</sub> with a CeO<sub>2</sub> loading of 7.8 wt.%.

Macromesoporous γ-Al<sub>2</sub>O<sub>3</sub> (M–Al<sub>2</sub>O<sub>3</sub>) was synthesized according to the method of Liu and Yang [17]. 3.75 g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 0.84 g citric acid were dissolved in 20 mL of ethanol at ambient temperature, and then 1.0 g P123 was added under vigorous stirring. The formed mixture was covered with PE film, stirred for 12 h at 60 °C in a water bath, and put into an oven at 60 °C to undergo solvent evaporation. After 4 days of aging, a colorless and transparent solid was produced. Subsequent calcination at 400 °C for 4 h resulted in the formation of porous M–Al<sub>2</sub>O<sub>3</sub>.

### 2.2. Preparation of the precursors of the supported phosphide catalysts

The precursor of the supported nickel phosphide catalyst was prepared by consecutive impregnation of the support (γ-Al<sub>2</sub>O<sub>3</sub> (Fushun Research Institute of Petroleum and Petrochemicals, SINOPEC, specific surface area 230 m<sup>2</sup>/g), fumed SiO<sub>2</sub> (specific surface area 282 m<sup>2</sup>/g), Ce–Al<sub>2</sub>O<sub>3</sub> or M–Al<sub>2</sub>O<sub>3</sub>) with an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, followed by an aqueous solution of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>. After each impregnation step the catalysts were dried in air at ambient temperature for 8 h and then in an oven at 120 °C for 10 h, and finally calcined at 500 °C for 4 h. The total loading of NiO and P<sub>2</sub>O<sub>5</sub> was 30 wt.% for all the supported Ni<sub>2</sub>P precursors. The Ni/P molar ratios of the precursors were 1.0 and 1.2. For comparison, a Ce–Al<sub>2</sub>O<sub>3</sub>-supported phosphorus oxide (P/Ce–Al<sub>2</sub>O<sub>3</sub>) with a P<sub>2</sub>O<sub>5</sub> loading of 17 wt.% was prepared following the above method without the addition of the Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution. The precursors of the molybdenum phosphide and tungsten phosphide

catalysts supported on Ce–Al<sub>2</sub>O<sub>3</sub>, M–Al<sub>2</sub>O<sub>3</sub>, or γ-Al<sub>2</sub>O<sub>3</sub> were prepared by a co-impregnation method. The support was impregnated with an aqueous solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (or (NH<sub>4</sub>)<sub>6</sub>W<sub>12</sub>O<sub>39</sub>·xH<sub>2</sub>O) and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>. The mixture was dried at 120 °C for 12 h and then calcined at 500 °C for 3 h to obtain the final oxidic precursor. The total loading of MoO<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> and that of WO<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> were 30 and 26 wt.%, respectively. The Mo(W)/P molar ratios of the precursors were 1.0 and 1.2. The phosphide catalyst was denoted as M–P(x)/support, where M represents the metal of the corresponding transition-metal phosphide and x is the P/metal molar ratio.

### 2.3. Hydrodesulfurization activity measurement

The HDS reaction was carried out in a fixed-bed stainless-steel tubular reactor. Prior to the reaction, an in situ H<sub>2</sub> TPR method was used to transform the precursor of nickel phosphide into the active phase [18]. The precursor was pelleted, crushed, and sieved to 20–40 mesh. A total of 0.20 g precursor was used for each run. The precursor was reduced in a 200 mL/min H<sub>2</sub> flow by heating from ambient temperature to 400 °C at 2 °C/min, then to 500 °C at 1 °C/min, and held at 500 °C for 2 h. Because the P–O bond in phosphate is strong, its reduction requires a high temperature [7]. According to our previous work [18], the optimal reduction temperature for the preparation of Ni<sub>2</sub>P/MCM-41 was 500 °C. Thus, we chose 500 °C as the final reduction temperature in the present study. After the precursor had been converted into a nickel phosphide, the reactor was cooled to the HDS reaction temperature. The HDS activities of the catalysts were evaluated with 0.8 wt.% dibenzothiophene (DBT) in decalin as the model feed. The reaction conditions were 280 °C, 4.0 MPa, and a WHSV of 32 h<sup>−1</sup>. The liquid products were analyzed by an Agilent-6890N gas chromatograph equipped with an FID detector using a commercial HP-5 column.

### 2.4. Characterization

Before characterization, all catalyst samples were prepared under the same conditions as used in the in situ reduction followed by passivation with 0.5% (volume) O<sub>2</sub> in Ar at ambient temperature, except that the precursors of molybdenum phosphide and tungsten phosphide were finally reduced at 850 °C. It is essential to passivate the obtained metal phosphides prior to exposure to air because they react vigorously with oxygen and water, leading to the formation of metal oxides. The XRD patterns of the catalysts were measured on a Rigaku D/Max 2400 diffractometer with nickel-filtered Cu Kα radiation at 40 kV and 100 mA. Nitrogen physisorption was performed on a Quantachrome Autosorb-1-MP analyzer. CO adsorption was measured using pulsed chemisorption as described elsewhere [19]. <sup>27</sup>Al MAS NMR spectra of the Al<sub>2</sub>O<sub>3</sub> supports were taken on an Agilent DD2 500 MHz NMR spectrometer. The Ni and P contents of the catalysts and their precursors were determined by an inductively coupled plasma optical emission spectrometer (ICP, Optima 2000DV). Transmission electron microscopy (TEM) images were obtained using a Tecnai G220 S-Twin microscope.

## 3. Results and discussion

The prepared Ce–Al<sub>2</sub>O<sub>3</sub> had a specific surface area of 79.5 m<sup>2</sup>/g. Its XRD pattern (Fig. S1 in the Supplementary Material) showed only two peaks with very low intensities at 2θ around 43° and 67°, indicating that Ce–Al<sub>2</sub>O<sub>3</sub> is mainly composed of amorphous Al<sub>2</sub>O<sub>3</sub>. The peak at 43° might be associated with a cerium oxide (CeO<sub>2–x</sub>, PDF 49-1415), while that at 67° is probably related to γ-Al<sub>2</sub>O<sub>3</sub> (PDF 10-0425). The XRD patterns of the Ni–P(x)/Ce–Al<sub>2</sub>O<sub>3</sub>

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