A general approach to the synthesis of metal phosphide catalysts

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ABSTRACT

A simple and efficient approach to the preparation of hollow or porous metal phosphide nanoparticles was presented. Bulk and supported Ni$_2$P, CoP, FeP, and Cu$_3$P were successfully synthesized by reducing metal pyrophosphate precursors in flowing hydrogen. The structural properties of these samples are investigated using X-ray powder diffraction, transmission electron microscopy, inductively coupled plasma and X-ray photo-emission spectroscopy. The Ni$_2$P/SiO$_2$ catalysts were used for the gas phase catalytic hydrodesulfurization of dibenzothiophene. The hydrodesulfurization activity of the catalyst reached 99% when the reaction temperature was 340 °C. In the paper, a possible reaction mechanism was discussed to form Ni$_2$P, CoP, FeP, and Cu$_3$P. The route and mechanism could also be applied to the preparation of other metal phosphides.

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1. Introduction

Transition metal phosphides have attracted much attention due to their important properties and potential applications in many fields, such as electricity, mechanics, corrosion-resistance, catalysis, and so on [1–3]. Among these metal phosphides, Ni$_2$P has good catalytic activity in the hydrodesulfurization (HDS) of crude oil fractions [4–6]. Therefore, studying universal synthetic routes that prepare transition metal phosphides with control over both the composition and the morphology is very important. In the past years, many synthesis routes have been reported regarding the preparation of transition metal phosphide catalysts. These methods include temperature-programmed reduction (TPR) of metal phosphates or metal phosphites, the reduction of metal oxide nanoparticles by phosphine (PH$_3$), and the decomposition of metal hypophosphites, and so on [7–14]. In this aspect, we have reported the preparation of Ni$_2$P catalysts by treating an amorphous Ni–B alloy with PH$_3$ [15]. The as-prepared catalysts exhibited excellent catalytic activity in the hydrodesulfurization (HDS) of dibenzothiophene (DBT).

In this paper, we present a new method for preparing bulk and supported Ni$_2$P catalysts using hollow nanostructures. This method is also general for synthesizing other transition metal phosphides, such as CoP, Cu$_3$P, FeP, and so on. Unlike previous methods that involve heating them to programmed temperatures, this approach uses only metal pyrophosphates as precursors and directly heats them to prepare corresponding metal phosphides in flowing hydrogen. Through this new route, nanostructures such as hollow spheres of Ni$_2$P and FeP, as well

as porous CoP and Cu$_3$P can also be synthesized successfully, which can provide much larger surface areas and more active sites so that the Ni$_2$P catalyst can show better activity for dibenzothiophene HDS. In addition, supported metal phosphide catalysts can be prepared easily using this new process.

2. Experimental methods

2.1. Synthesis of bulk and supported Ni$_2$P, CoP, FeP, and Cu$_3$P

Commercially available solvents and reagents were used without further purification. In a typical reaction, metal pyrophosphates precursors (Ni$_2$P$_2$O$_7$, Fe$_2$P$_2$O$_7$, Co$_2$P$_2$O$_7$, and Cu$_2$P$_2$O$_7$) were firstly prepared by mixing the stoichiometric amounts of potassium pyrophosphates (K$_4$P$_2$O$_7$ · 3H$_2$O) and metal chlorides (NiCl$_2$ · 6H$_2$O, FeCl$_2$ · 4H$_2$O, CoCl$_2$ · 6H$_2$O, and CuCl$_2$ · 2H$_2$O) under intense stirring. The obtained precipitate was filtered and washed with water. The precursors were dried at 80 °C for 3 h in a vacuum oven. A small quantity of metal pyrophosphates was placed in a tubular reactor and was directly heated at 700 °C in flowing H$_2$ at a rate of 10 mL/min. The reaction was maintained for 7 h and then the corresponding products were cooled to room temperature. Finally, the samples were passivated in a flow of 1 vol.% O$_2$/N$_2$. For the SiO$_2$-supported (calcined at 773 K and sieved below 100 mesh) Ni$_2$P (Ni$_2$P/SiO$_2$), potassium pyrophosphates and Ni^{2+} at a mole ratio of 1:2 were introduced into SiO$_2$ supports by incipient wetness impregnation. The as-prepared supported precursors were dried at 80 °C for 3 h in a vacuum oven. Other steps are the same as the preparation of the bulk metal phosphides. The Ni$_2$P/SiO$_2$ catalyst, with theoretical loading of 10 wt.%, was prepared.

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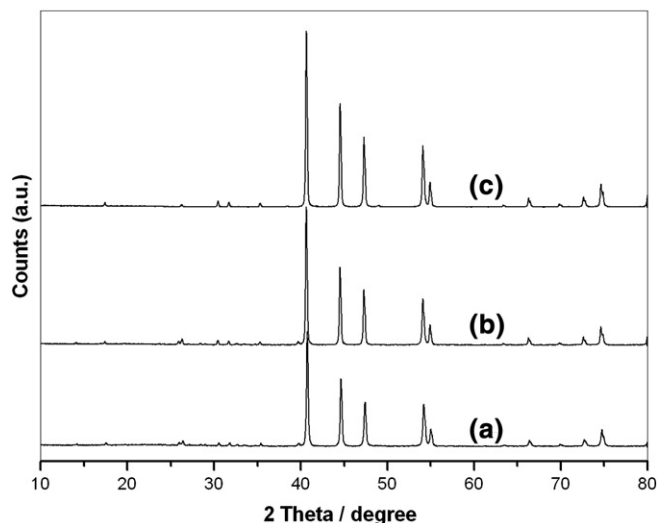
Fig. 1. The XRD patterns of the as-prepared Ni_2P at 700 °C for 3–7 h in H_2 flow. (a) 3 h, (b) 5 h, (c) 7 h.

2.2. Characterization

The products were characterized by using X-ray diffraction (XRD) recorded on a Rigaku D/max 2500 powder diffractometer equipped with monochromatic high-intensity CuKα radiation (λ = 1.5406 Å). The morphology and size of the as-prepared products were observed by a Hitachi H-7650 transmission electron microscopy (TEM). The elemental content of the samples was determined using the inductively coupled plasma (ICP-AES, 9000(N + M)) method. The binding energy (BE) was measured by an X-ray photoelectron spectrometer (XPS, Perkin-Elmer PHI5300). In the XPS analysis, the calibration of BE is the standard peak of adventitious carbon (C_{1s}). The BE has been calibrated according to the standard peak of carbon (C_{1s}) in the manuscript. C1s is set to 284.48 eV.

2.3. Catalytic activity test

The HDS of dibenzothiophene was carried out in a flowing fixed-bed reactor using a feed consisting of a decalin solution of DBT (0.5 wt.%). The conditions of the HDS reaction were 320–340 °C, 3.0 MPa, WHSV = 9 h^{-1}, and H_2 flow rate 90 ml min^{-1}. The DBT feeding rate in catalyst 13.5 g/g · h. 1.0 mL (0.6 g) of Ni_2P/SiO_2 catalyst diluted with quartz sands to 5.0 mL was reduced by heating from room temperature to a certain temperature in H_2 (200 mL min^{-1}), maintaining the sample at that temperature for 2 h, before changing the temperature to the desired reaction temperature. Liquid samples were collected every hour and analyzed by a gas chromatography with a flame ionization detector (FID) and a capillary column (OV101). The DBT conversion was used as a measure of the HDS activity [15].

3. Results and discussion

3.1. Synthesis and formation mechanism of bulk and supported Ni_2P, CoP, FeP, and Cu_3P

Fig. 1 shows the XRD patterns of the as-prepared Ni_2P at 700 °C for 3–7 h in the H_2 flow. Fig. 1a shows that the typical diffraction peaks of Ni_2P [40.72°, 44.60°, 47.38°, 54.16°; Joint Committee on Powder Diffraction Standards (JCPDS) 89-4864] were found when the nickel pyrophosphates were heated at 700 °C for 3 h. However, a small amount of $(KPO_3)_n$ (14.18°, 26.00°, 26.24°, and 39.76°; JCPDS 47-0169) peaks can also be seen. The impurities of $(KPO_3)_n$ were produced by heating the remaining potassium phosphate in the nickel pyrophosphate precursors. When the nickel pyrophosphates were treated at 700 °C for
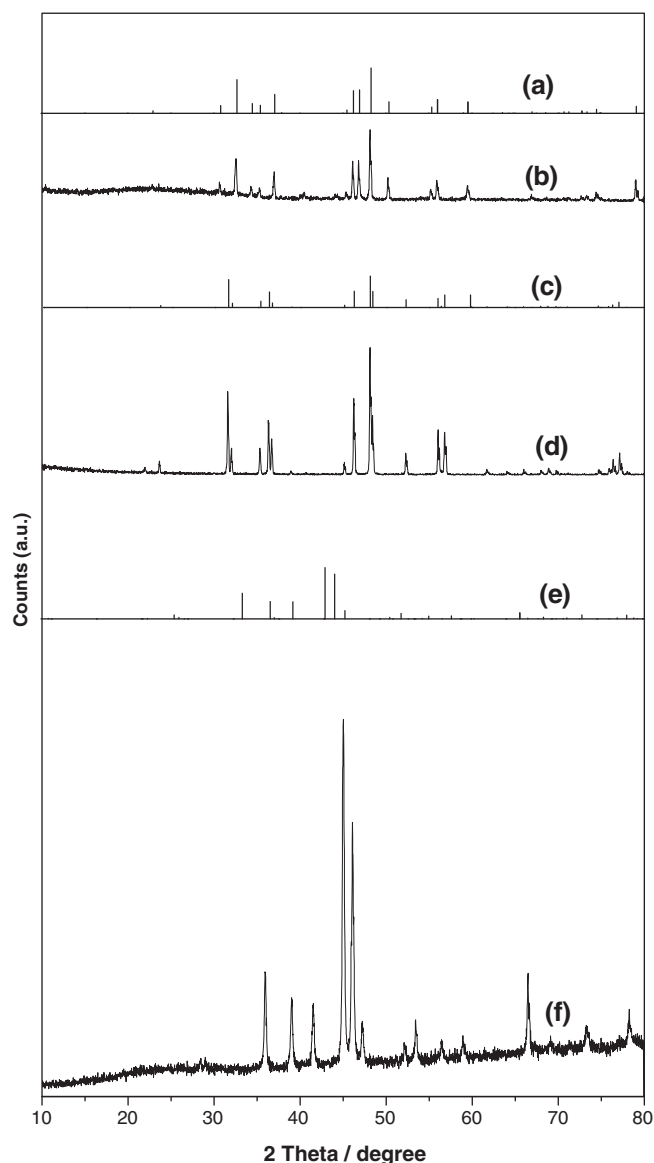

Fig. 2. The standard XRD diffraction patterns: (a) FeP, (c) CoP, and (e) Cu_3P. The XRD patterns of the as-prepared CoP, FeP, and Cu_3P at 700 °C for 7 h in H_2 flow. (b) FeP, (d) CoP, and (f) Cu_3P.

5 h, the three main diffraction peaks at 2θ = 40.58°, 44.48°, and 47.22° can be attributed to the hexagonal phase of Ni_2P (Fig. 1b). The peaks of $(KPO_3)_n$ disappeared in Fig. 1b. After thermal treatment for 7 h, no other impurities aside from Ni_2P (Fig. 1c) were present. In comparison with the three XRD patterns of the as-prepared Ni_2P, the peak intensity increased with increasing time, which shows that longer reaction times can promote better Ni_2P crystallization.

As shown in Fig. 1, unlike the traditional TPR method, no other byproducts such as Ni_3P, Ni_5P_4, and $Ni_{12}P_5$ and so on aside from Ni_2P were clearly in the decomposition process of nickel pyrophosphates at different reaction times. Therefore, the formation mechanism of Ni_2P-based on nickel pyrophosphates is as follows:

$$Ni_2P_2O_7 + 7H_2 = Ni_2P + 7H_2O\uparrow + P\uparrow. \tag{1}$$
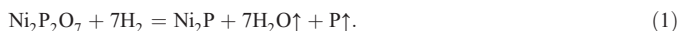
We found a small amount of cooling white phosphorus and water on the two ends of the tubular reactor in the thermal decomposition of nickel pyrophosphate, which shows that white phosphorus and water have been formed during the decomposition process. If we substituted the nickel pyrophosphates in the formula (1) for other metal pyrophosphates, the