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Research Note

A novel synthetic approach to synthesizing bulk and supported metal phosphides

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ABSTRACT

This paper presents a novel synthetic approach to synthesizing metal phosphides. Both bulk and supported Ni_2P, Cu_3P, MoP, and InP were synthesized by thermal decomposition of their metal oxide and hypophosphite precursors. Mechanistic studies of Ni_2P were carried out using a separated-bed tube reactor, and the result indicates that NiO is reduced by PH_3 (produced from decomposition of NaH_2PO_2) at 300 °C. Ni_2P hollow spheres were successfully synthesized by this method, which indicates that it is possible to synthesize metal phosphides with special morphology by using metal oxides with special morphology as precursors.

1. Introduction

Metal phosphides have attracted considerable attention because of their advanced catalytic, electronic, and magnetic applications. Among the metal phosphides, nickel phosphide (Ni_2P) shows excellent activity in the hydrotreating of crude oil fractions such as gasoil and naphtha [1]. The good cyclability and fair reversible capacity of copper phosphide (Cu_3P) can make it an alternative negative electrode in special battery designs [2]. In particular, the second-generation semiconductor material indium phosphide (InP) has various applications in telecommunications, optoelectronic devices, and solar cells [3].

It is well known that there are many ways to synthesize metal phosphides. These include temperature-programmed reduction (TPR) of metal phosphates [4] or metal phosphites [5,6], solvothermal reactions [7], decomposition of single-source precursors [8], high temperature annealing of preformed nanoparticle precursors [9], the reduction of metal oxide nanoparticles by PH_3/H_2 [10], the reaction of trioctylphosphine (TOP) with metal salts [11], the conversion of preformed metal nanoparticles into metal phosphides by solution-mediated reaction with TOP [12], the decomposition of nickel thiophosphate ($NiPS_3$) [13,14], the reduction of oxide precursors in a hydrogen plasma [15], and the decomposition of metal hypophosphites [16,17].

Herein, we describe a modified approach for synthesizing metal phosphides. In contrast to the previous methods, our approach uses bulk or supported metal oxide as precursor. Both bulk and supported Ni_2P, Cu_3P, MoP, and InP can be synthesized by this method under mild conditions, which is more universal than the decomposition of metal hypophosphites [16,17]. On the one hand, metal nitrates are easily purchased and have a better solubility than metal chlorides, which is advantageous to the synthesis of supported metal phosphides. On the other hand, some supported metal phosphides could not be synthesized from metal chlorides. For instance, $CuCl_2$ and NaH_2PO_2 will be rapidly precipitated in the solution; thus, it is difficult to synthesize supported Cu_3P from the decomposition of metal hypophosphites. Interestingly, the morphology of the metal phosphides can be successfully inherited from the metal oxide precursors, which indicates that it is possible to synthesize metal phosphides with special morphology by using metal oxides with special morphology as precursors. Therefore, both bulk metal phosphides with special morphology and supported metal phosphides that are used as catalysts can be synthesized by this new synthetic approach. Similar to our previous work [16], the synthesis is not affected by the heating rates. It only requires a simple calcination in a static Ar atmosphere.

2. Experimental methods

2.1. Synthesis of bulk and supported metal phosphide

Alumina (Tianjin Research Institute of Chemical Industry) was calcined at 600 °C for 3 h and had a specific surface area of 212 $m^2 g^{-1}$, a pore volume of 0.39 $cm^3 g^{-1}$, and a Barett–Joyner–Halenda (BJH) average pore size of 4.8 nm. Siliceous MCM-41 (Tianjin Chemist Scientific Ltd.) had a specific surface area of 889 $m^2 g^{-1}$, a pore volume of 1.01 $cm^3 g^{-1}$, and a BJH average pore

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size of 3.32 nm. All reagents were analytical pure grade and purchased from Tianjin Guangfu Fine Chemical Research Institute, China.

In a typical experiment, metal phosphide was obtained as follows. The stoichiometric amount of sodium hypophosphite was dissolved in deionized water with magnetic stirring to form a clear solution. Then metal oxide was added, which was obtained by the calcination of metal nitrate ($Ni(NO_3)_2$ for Ni, $Cu(NO_3)_2$ for Cu, $(NH_4)_6Mo_7O_{24}$ for Mo, and $In(NO_3)_3$ for In) at 500 °C for 2 h in a muffle furnace. Then, the slurry was evaporated slowly to dehydrate the product, and the product was dried at 80 °C for 8 h and subsequently heated at the required temperature (300 °C for Ni and Cu, and 400 °C for Mo and In, which was set according to the initial hydrogen reduction temperatures of their metal oxides) for 0.5 h in a static Ar atmosphere. The product was cooled to ambient temperature under Ar, washed three times with deionized water, and dried at 120 °C for 3 h. To make the supported metal phosphide by impregnation, a certain amount of support was added to the solution of the metal nitrate ($(NH_4)_6Mo_7O_{24}$ for Mo). The sample was dried at 120 °C for 3 h, and supported metal oxide was obtained by the calcination of sample at 500 °C for 2 h in a muffle furnace, and the remaining steps were similar as those described above. In our approach, a 10% excess of P was used when supported metal phosphide was synthesized.

2.2. Characterization and activity test

Powder X-ray diffraction was performed on a Rigaku D/Max-2500 diffractometer, with Cu Kα at 40 kV and 100 mA. The compositions of the sample were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Transmission electron microscopy (TEM) images were acquired using a Philips Tecnai G^2 F-20 field emission gun transmission electron microscope. Nitrogen adsorption was measured with a BEL-MINI adsorption analyzer. The H_2-TPR and CO chemisorption were performed with Micromeritics chemisorb 2750 gas-adsorption equipment. The sample was loaded into a quartz reactor and pretreated in 10% H_2/Ar at 450 °C for 3 h. After cooling in He, pulses of 10% CO/He in a He carrier (25 cm^3 (NTP) min^{-1}) were injected at 30 °C through a loop tube. The electrochemical response of the samples was tested on a Land CT2001C instrument. The bulk copper phosphide was used in a two-electrode cell using metallic lithium as the negative electrode. The discharge and charge capacities were measured at 0.01–3.5 V and at a C/10 rate (37.7 mA g^{-1}). The HDS catalytic activities were evaluated using 3000 ppm dibenzothiophene (DBT) in decalin. The testing conditions for the HDS reaction were 330 °C, 3 MPa, WHSV = 6 h^{-1}, with a H_2 flow rate of 160 mL min^{-1}. Liquid products were collected every hour after a stabilization period of 6 h. Both feed and products were analyzed with a FULI 9790 gas chromatograph equipped with an FID detector and an OV-101 column. The DBT conversion and turnover frequency (TOF) [18] were used to evaluate the HDS activity.

3. Results and discussion

3.1. Synthesis of bulk and supported metal phosphide and activity

As shown in Fig. 1, the typical diffraction peaks of the samples are clearly shown, which indicate that bulk Ni_2P, Cu_3P, MoP, and InP were prepared from thermal decomposition of their metal oxide and sodium hypophosphite precursors. We chose mesoporous MCM-41 as the support to synthesize supported metal phosphides. The XRD patterns of the samples show that supported Ni_2P, Cu_3P, MoP, and InP were successfully prepared by treating the MCM-41-supported mixed salt precursors (Fig. S1). The ICP results showed that the composition of Ni_2P/MCM-41 (nickel loading 5 wt%) was Ni/P = 1/0.59, and no sodium ion was detected, which were almost the same with the results of bulk nickel phosphide. It is notable that both bulk and supported Cu_3P can be synthesized by this method. It provided a way to use supported Cu_3P as a catalyst for some reactions, because other methods to synthesize supported Cu_3P are very difficult. Hollow NiO microspheres were prepared according to the method of Wang et al. [19]; the microspheres are built from two-dimensional 100–500 nm nanosheets. Interestingly, hollow Ni_2P spheres were successfully synthesized by thermal decomposition of the as-synthesized hollow NiO spheres and sodium hypophosphite at 300 °C for 0.5 h. The XRD patterns of the as-prepared hollow Ni_2P spheres are exactly the same as that of pure Ni_2P. The structure of as-prepared Ni_2P microspheres was confirmed by TEM. Fig. S2a and S2b show typical TEM images of as-prepared Ni_2P microspheres. We can see that the diameter of the sphere is about 3.2 μm. As shown in Fig. S2c, the magnified HRTEM image of the frame selected from image (b) yields a *d*-spacing of 0.503 nm for the (1 0 0) crystallographic planes of Ni_2P, which is in good agreement with the calculated value. The formation of hollow Ni_2P microspheres indicates that it is possible to synthesize metal phosphides with special morphology by using metal oxides with special morphology as precursors.

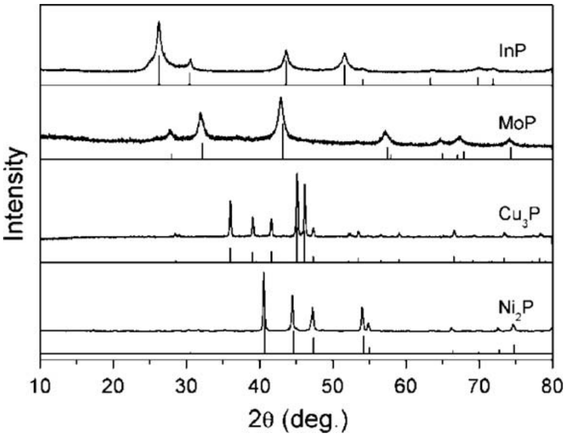

Fig. 1. Powder XRD patterns of bulk Ni_2P, Cu_3P, MoP, and InP synthesized from their metal oxide and hypophosphite precursors.

The catalytic activities of Ni_2P/Al_2O_3 and Ni_2P/MCM-41 prepared by thermal decomposition of supported NiO and NaH_2PO_2 were tested by the removal of sulfur from DBT in the HDS reaction. Table 1 shows a comparison of HDS activities of the catalysts prepared using different methods. The results indicated that both Ni_2P/Al_2O_3 and Ni_2P/MCM-41 catalysts prepared using two methods show similar high HDS activity. The results of electrochemical tests of the bulk Cu_3P electrode are given in Fig. S3, which are sim-

Table 1
CO chemisorption and HDS catalytic activity of the as-prepared $Ni_2P/\gamma\text{-}Al_2O_3$ (nickel loading 5 wt%) and Ni_2P/MCM-41 (nickel loading 5 wt%) catalysts prepared by different methods.

Catalysts	CO uptake (μmol g^{-1})	DBT conversion (%)	TOF (10^{-3} s^{-1})
$Ni_2P/\gamma\text{-}Al_2O_3$[a]	9	84	2.5
$Ni_2P/\gamma\text{-}Al_2O_3$[b]	9	85	2.5
Ni_2P/MCM-41[a]	13	100	2.1
Ni_2P/MCM-41[b]	13	100	2.1

[a] Prepared by our approach.
[b] Prepared by the decomposition of metal hypophosphites.

ilar to those reported by Pfeiffer et al. [2]. However, far from being a competitor material for graphite, the good cyclability and fair reversible capacity of Cu_3P can make it an alternative negative electrode in special battery designs.

3.2. Investigation of the formation process

We decided to use Ni_2P/MCM-41 as a typical phosphide to investigate the formation process of the metal phosphide. We propose that the following possible reactions occurred at 300 °C.

$$2NaH_2PO_2 = PH_3 \uparrow + Na_2HPO_4 \quad (1)$$

$$4PH_3 + 6NiO = 3Ni_2P + P + 6H_2O \quad (2)$$

A separated-bed experiment was designed to prove that PH_3 can be produced from reaction (1) and that NiO can be reduced by PH_3 at 300 °C in reaction (2). As shown in Fig. S4, 30 wt% NiO/MCM-41 and NaH_2PO_2 were separated by 5-mm quartz fiber and treated at 300 °C for 0.5 h in flowing Ar. The amount of NaH_2PO_2 was insufficient to completely reduce the nickel oxide. The existence of the typical diffraction peaks of Ni_2P indicate that NiO can be reduced by PH_3 at 300 °C, which is similar to those reported by Yang et al. [10]. At the same time, this also means that PH_3 could be obtained from decomposition of NaH_2PO_2 at 300 °C. No diffraction peaks of Ni were found in the XRD patterns, so PH_3 might be directly reduced NiO to Ni_2P without generating intermediate Ni. Compared with the TPR of the metal phosphate, Ni_2P could be obtained at a low temperature from thermal decomposition of nickel oxide and sodium hypophosphite. The main reason is that the Ni–O bond is weaker than the P–O bond, and nickel oxide could be easily reduced by PH_3 at a low temperature. From the H_2-TPR results of metal oxides, we found that the initial hydrogen reduction temperatures of NiO, CuO, MoO_3, and In_2O_3 were 275, 210, 373, and 355 °C, respectively (Fig. S5). We perhaps could estimate the synthesis temperature of metal phosphides from the initial hydrogen reduction temperature. In our experiments, Ni_2P, Cu_3P, MoP, and InP were synthesized at 300, 300, 400, and 400 °C, respectively.

4. Conclusions

In summary, both bulk and supported Ni_2P, Cu_3P, MoP, and InP were synthesized by thermal decomposition of their metal oxide and hypophosphite precursors. It is notable that the temperature of thermal decomposition is lower than for the TPR method, and this reaction does not require temperature programming. Mechanistic studies of Ni_2P were carried out using a separated-bed tube reactor, and the result indicates that NiO can be reduced by PH_3 (produced from decomposition of NaH_2PO_2) at 300 °C. At the same time, we found that PH_3 might be directly reduced NiO to Ni_2P without generating intermediate Ni. Ni_2P hollow spheres were successfully synthesized by this method, which indicates that it is possible to synthesize metal phosphides with special morphology by using metal oxides with special morphology as precursors.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2010.02.031.

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