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Priority Communication

Alternative synthesis of bulk and supported nickel phosphide from the thermal decomposition of hypophosphites

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ABSTRACT

This paper presents an alternative method for the preparation of bulk and supported nickel phosphide by the heat treatment of a mixed salt precursor (nickel chloride and sodium hypophosphite) in a static protecting gas atmosphere up to 300 °C. After reduction at 500 °C, a Ni_2P/MCM-41 catalyst exhibits good hydrodesulfurization activity for dibenzothiophene with a turnover frequency at 330 °C of 1.1×10^{-3} s^{-1}.

1. Introduction

Metal phosphides, a class of materials with unique physical and chemical properties, have attracted considerable attention for their wide applications in many fields. In particular, metal phosphides used as catalytic materials show excellent activity for certain reactions with activity similar to that of noble metal catalysts [1].

A variety of methods have been developed for the synthesis of phosphides, including solvothermal reactions [2], decomposition of single-source precursors [3], high temperature annealing of organometallic and solid-state precursors [4], the coreaction of organometallic reagents with phosphines [5], the reactions of trioctylphosphine (TOP) with metal salts [6], the conversion of preformed metal nanoparticles into metal phosphides by solution-mediated reaction with TOP [7], the decomposition of nickel thiophosphate ($NiPS_3$) [8]. These methods typically require extremely high reaction temperatures and/or long reaction times. The temperature-programmed reduction (TPR) [9,10] method was proved to be an effective and general way to prepare active catalysts. However, the synthesis also requires relatively high temperature for the reduction of the metal phosphate precursors. Metal phosphides can be obtained under milder conditions in a solvothermal approach, but this method is not feasible for the deposition of metal phosphides on supports [11]. Wang et al. developed a plasma method to create a low-temperature method [12]. It is a new strategy for synthesizing metal phosphides that uses nonthermal H_2 plasma as the reduction medium instead of the H_2 used in the TPR method. Our approach is different from the above methods.

In this paper, nickel phosphide was synthesized from the decomposition of hypophosphite precursors, and we call the method the "DH method". Compared with the above methods, the DH method only requires a heat treatment followed by a moderate temperature reduction.

2. Experimental methods

2.1. Synthesis of bulk and supported nickel phosphide

As an example, the preparation of Ni_2P is illustrated as follows. In a typical precursor synthesis, nickel chloride hexahydrate (9.70 g) and sodium hypophosphite (6.43 g) were dissolved in 40.0 mL deionized water. The solution was evaporated slowly to dehydrate and was dried at 80 °C for 8 h. A yellow solid was obtained as the precursor. At the beginning, the air in the reactor was removed by flowing Ar, after which the resulting solid was treated at 300 °C for 0.5 h in a static Ar atmosphere. The product was cooled to ambient temperature under Ar and was washed several times with deionized water to remove ion impurities, after which the wet material was dried at 120 °C for 3 h.

To make the supported phosphide by impregnation, a certain amount of support was added to the solution described above. The sample was dried at 80 °C for 8 h, and the remaining steps were similar to those described above. For comparison, nickel phosphide supported on mesoporous alumina and MCM-41 (supplementary

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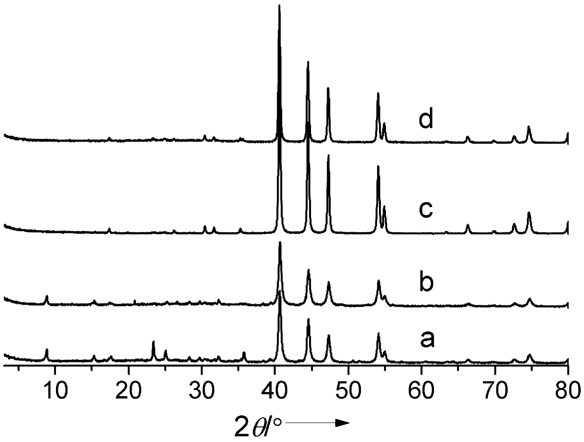

Fig. 1. The XRD patterns of the samples prepared from the precursors, which consist of NaH_2PO_2 and $NiCl_2$ with different molar ratios ($NaH_2PO_2/NiCl_2$): (a) 1.25, (b) 1.33, (c) 1.50, (d) 1.75.

material, 738 $m^2\,g^{-1}$) were also successfully prepared using the TPR method [13,14].

2.2. Characterization

Powder X-ray diffraction patterns (XRD) of the catalysts were obtained on a Rigaku D/max 2500 X-ray diffractometer (Cu$K\alpha$, $\lambda = 1.54178$ Å). 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 JEOL-2010 FEF high resolution transmission electron microscope. Nitrogen adsorption was measured with a BEL-MINI adsorption analyzer. The CO chemisorption of the supported Ni_2P sample was performed with Micromeritics AutoChem II 2920 gas-adsorption equipment. Chloride ion in the products was obtained on a DX-120 ion chromatograph (IC).

2.3. Catalytic activity test

The HDS catalytic activities were evaluated using 0.3 wt% dibenzothiophene in decalin. The HDS reaction was carried out in a continuous-flow fixed-bed microreactor. The catalyst was pelleted, crushed and sieved with 20–40 mesh. 1.00 g of the catalyst was diluted with SiO_2 to a volume of 5.0 mL in the reactor. Prior to reaction, catalysts were pretreated in situ with flowing H_2 (60 $mL\,min^{-1}$) 3 h. 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} at atmospheric pressure. Liquid products were collected every hour after a stabilization period of 6 h. Both feed and products were analyzed with an FULI 9790 gas chromatograph equipped with an FID detector and an OV-101 column. The DBT conversion and turnover frequency (TOF) [15] were used to evaluate the HDS activity.

3. Results and discussion

3.1. Synthesis of bulk and supported nickel phosphide

As shown in Fig. 1, bulk Ni_2P was prepared from the mixed-salt precursor, with NaH_2PO_2 and $NiCl_2$ at molar ratios between 1.5 and 1.75. The typical diffraction peaks of Ni_2P are clearly shown. We have also studied the impact of different thermal decomposition temperatures, times and heating rates on the products (supplementary material, Fig. 1). The XRD patterns show that nickel phosphide can be synthesized at 250 °C in 10 min and synthesis is not affected by the heating rates.

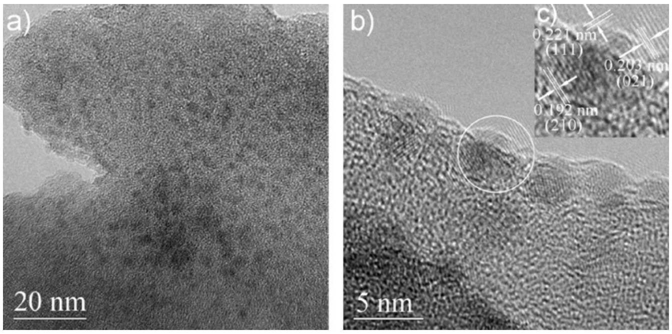

Fig. 2. The as-prepared Ni_2P/MCM-41 catalysts with loading of 32 wt% treated at 300 °C for 0.5 h in an Ar atmosphere: (a) HRTEM micrograph, (b) an enlarged image of the catalysts, (c) the magnified HRTEM image of the selected frame from image (b).

Table 1
Catalytic activity of the as-prepared Ni_2P/γ-Al_2O_3 (nickel loading 10 wt%) catalysts and Ni_2P/MCM-41 (nickel loading 10 wt%) catalysts at 330 °C.

Catalyst	Conversion of DBT (%)	CO uptake ($\mu mol\,g^{-1}$)	O_2 uptake ($\mu mol\,g^{-1}$)	TOF ($10^{-3}\,s^{-1}$)
Ni_2P/γ-Al_2O_3[a]	96	–	–	–
Ni_2P/γ-Al_2O_3[b]	42	–	–	–
Ni–Mo–S/Al_2O_3[c]	76	–	718	0.25
Ni_2P/MCM-41[a]	90	23	–	1.06
Ni_2P/MCM-41[b]	75	18	–	1.11

[a] Prepared by the DH method.
[b] Prepared by the TPR method.
[c] Ni–Mo–S/Al_2O_3 (Shell 324) reported by Oyama et al. [16].

A series of Ni_2P/MCM-41 catalysts has been successfully prepared by treating MCM-41-supported mixed salt precursors (supplementary material, Fig. 2). A high resolution TEM image of the as-prepared 32 wt% Ni_2P/MCM-41 (Fig. 2) shows fairly uniform nanoparticles with a size of 2–5 nm, which indicates good dispersion on the support. A magnified high resolution TEM image of the selected frame from Fig. 2b given in Fig. 2c, yields *d*-spacing values of 0.221, 0.203 and 0.192 nm, respectively, for the (111), (021) and (210) crystallographic planes of Ni_2P, which are in good agreement with the calculated values. It indicates the formation and good dispersion of nanocrystalline Ni_2P on the MCM-41 support.

The ICP results showed that the composition of the nickel phosphide nanoparticles was Ni/P = 1/0.59. The amount of chloride ion in the products was 0.019 wt%, which is particularly problematic for catalysis. The IC result indicates that washing the catalyst several times with deionized water can remove most of the chloride ions.

3.2. HDS activity

Table 1 shows a comparison of HDS activities of the catalysts prepared using different methods. The highly HDS activity of Ni_2P/Al_2O_3 catalysts prepared using the DH method indicates that alumina is a very good carrier for supported phosphide. From the comparison of HDS activities of Ni_2P/MCM-41 catalysts prepared using different methods. It is seen that the catalyst prepared using the DH method at 500 °C gave much better results than that prepared using the TPR method at 600 °C. The HDS activity of Ni_2P/Al_2O_3 and Ni_2P/MCM-41 prepared by DH method is much higher than that of a commercial catalyst, Ni–Mo–S/Al_2O_3 (Shell 324), with 76% HDS conversion [16]. The TOF of the Ni_2P/MCM-41 prepared by the DH method (1.06×10^{-3} s^{-1}) is quite similar to that prepared by the TPR method (1.11×10^{-3} s^{-1}). The high TOFs are due to low CO uptakes and the low CO uptakes may be due to lack of optimization of the catalysts. Nonetheless, the DH method is a promising method for further investigation.

3.3. *Investigation of the formation process*

Gopalakrishnan et al. [17] suggested that formation of phosphide occurs by direct reduction of the metal phosphate in hydrogen. Our research describes catalysts prepared using the DH method in a static Ar atmosphere at 300 °C. Thus, the formation process of nickel phosphide may be different from that reported by Gopalakrishnan et al. We propose that several possible reactions occur.

$$2NaH_2PO_2 + NiCl_2 = 2NaCl + Ni(H_2PO_2)_2, \tag{1}$$

$$Ni(H_2PO_2)_2 = PH_3\uparrow + NiHPO_4, \tag{2}$$

$$4PH_3 + 4NiHPO_4 + 2NiCl_2 = 3Ni_2P + P + 4H_3PO_4 + 4HCl, \tag{3}$$

$$(1)\times 4 + (2)\times 4 + (3) = (4),$$

$$\begin{aligned}&6NiCl_2 + 8NaH_2PO_2\\&\quad = 3Ni_2P + P + 4H_3PO_4 + 8NaCl + 4HCl\uparrow,\end{aligned} \tag{4}$$

$$(2)\times 4 + (3) = (5),$$

$$4Ni(H_2PO_2)_2 + 2NiCl_2 = 3Ni_2P + P + 12HCl\uparrow. \tag{5}$$

The XRD patterns of the precursor show that reaction (1) can occur in solution (supplementary material, Fig. 3). We designed a separated-bed experiment to prove that PH_3 can be produced from reaction (2) and $NiCl_2$ can be reduced by PH_3 at 300 °C (supplementary material, Fig. 4). $Ni(H_2PO_2)_2$ and $NiCl_2$ were separated by 5 mm SiO_2 and treated at 300 °C for 0.5 h in flowing Ar. The typical diffraction peaks of Ni_2P indicated that $NiCl_2$ can be reduced by PH_3 at 300 °C. At the same time, this also means that PH_3 could be obtained from decomposition of $Ni(H_2PO_2)_2$ at 300 °C. Because only nickel chloride exists, it will not be reduced at 300 °C in an Ar atmosphere, so Ni_2P was synthesized from $NiCl_2$ that was reduced by PH_3 at 300 °C. Reaction (4) shows that we can obtain Ni_2P by treating the precursor with NaH_2PO_2 and $NiCl_2$ in a molar ratio of 8:6 (1.33) at 300 °C. However, in our experiments, nickel salt could not be reduced completely at this molar ratio, because the end of the reactor was open. As shown in Fig. 1b, a weak peak at 8.83° attributed to the typical diffraction peak of nickel phosphate. Thus, we chose a molar ratio of 1.5 to ensure that nickel salt was fully reduced.

From the reaction equations, we can see that Ni^{2+} and $H_2PO_2^-$ are the key components in these reactions. As long as the above molar ratio is maintained, we could also synthesize Ni_2P from other nickel salts and other hypophosphites. In order to prove that reaction (5) was correct, we have used $NiCl_2{\cdot}6H_2O$ and $Ni(H_2PO_2)_2{\cdot}6H_2O$ as precursors to synthesize Ni_2P (supplementary material, Fig. 5). The XRD results indicate that our conjecture was correct.

4. Conclusions

In summary, Ni_2P can be prepared by a decomposition of hypophosphite (DH) method. This method is simple and the aqueous solution-based process can also be used for preparing supported nickel phosphides on MCM-41 and alumina supports with good dispersion. Evaluation of the catalytic activity of the materials reduced at 500 °C shows that the resultant catalyst exhibits good HDS activity with a TOF for dibenzothiophene HDS at 330 °C of $1.1 \times 10^{-3}\ s^{-1}$. The results suggest that these syntheses provide a potential new and general route for the preparation of bulk and supported nickel phosphide catalysts.

Supplementary material

Supplementary material for this article may be found on ScienceDirect, in the online version.

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