Synthesis of transition-metal phosphides from oxidic precursors by reduction in hydrogen plasma

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ABSTRACT

A series of transition metal phosphides, including MoP, WP, CoP, Co_2P, and Ni_2P, were synthesized from their oxidic precursors by means of hydrogen plasma reduction under mild conditions. The effects of reduction conditions, such as metal to phosphorus molar ratio, power input, and reduction time, on the synthesis of metal phosphides were investigated. The products were identified by means of XRD characterization. It is indicated that metal phosphides were readily synthesized stoichiometrically from their oxides in hydrogen plasma under mild conditions.

1. Introduction

Transition-metal phosphides possess unique physical and chemical properties which make them attractive and promising in the fields of catalysis, electronics, optoelectronics, and magnetic applications [1,2]. There are a variety of methods for synthesizing metal phosphides, including direct reaction of metals and phosphorus for prolonged periods at high temperature, reaction of phosphine with metals or metal oxides, thermal decomposition of single-source precursors, reduction of metal phosphates by hydrogen, electrolysis of molten metal phosphate salts, solid-state metathesis, and self-propagation high-temperature synthesis [3–5]. Nevertheless, these methods usually require extremely harsh conditions (high temperature), toxic reagents or very long synthesis time. In addition, most of these methods are not suitable for preparing the supported metal phosphides as catalysts.

Metal phosphides show high catalytic activities in hydrogenation [6], hydrodesulfurization (HDS) [3], and hydrodenitrogenation (HDN) [7]. The conventional synthesis procedure for metal phosphide catalysts is temperature-programmed reduction in hydrogen. However, it is neither thermodynamically nor kinetically favorable to transform oxide precursors to phosphides by hydrogen reduction. It is therefore essential to perform the reduction at high temperature and low water vapor pressure [8]. In the conventional temperature-programmed reduction proce-

dure, metal phosphides can only be obtained at a low heating rate and a high H_2 flow velocity so as to keep very low vapor pressure on the surface. Another disadvantage of the conventional method is that excess phosphorus is needed because phosphorus loss occurs due to the migration of volatile phosphorus species in the long time and high temperature reduction.

Recently, we reported a new approach to synthesizing metal phosphides, i.e. reduction from the oxidic precursors in H_2 plasma as a communication [9]. In this approach, metal phosphides can be obtained in H_2 plasma under mild conditions in short time. In the present work, crystalline WP, MoP, CoP, Co_2P, Ni_2P were synthesized in hydrogen plasma, and the effects of reduction conditions were investigated.

2. Experimental

All the reagents, including $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $(NH_4)_2HPO_4$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $(NH_4)_6W_{12}O_{39}$, were of AR grade. Hydrogen, with a purity of 99.99%, was supplied by Guangming Gas Co. (Dalian, China).

The oxidic precursors were prepared by co-precipitation from metal salts and $(NH_4)_2HPO_4$ by adjusting the pH of the aqueous solution, followed by drying at 120 °C for 12 h, and temperature-programmed calcination in air at 500 °C for 3 h (heating rate 10 °C min^{-1}). The oxidic precursors were pelleted, crushed, and sieved to 20–40 meshes.

The synthesis of metal phosphides by hydrogen plasma reduction was conducted in a dielectric barrier discharge (DBD) reactor

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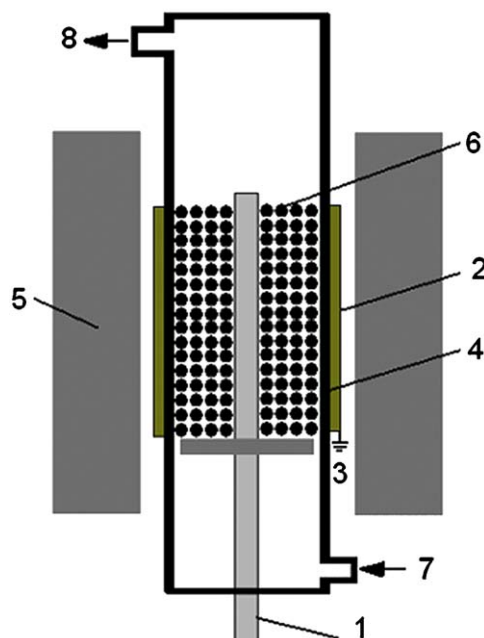E-mail address: ajwang@dlut.edu.cn (A. Wang).

consisting of a quartz tube and two electrodes. Configuration of the DBD discharge reactor was shown in Fig. 1. The high-voltage electrode was a stainless-steel rod with a diameter of 2.5 mm, which was installed along the axis of the quartz tube and connected to an alternating current supply. The grounding electrode was an aluminum foil, which was wrapped around the quartz tube and linked to ground by a wire. For each run, 0.8 g precursor was charged into the quartz tube. Hydrogen from a gas cylinder was allowed to pass through the bed at 150 ml min^{-1} to flush air out of the reactor. At a constant H$_2$ flow, a high voltage of 9–11 kV, varying with the generator input voltage (40–90 V), was supplied by a plasma generator. The discharge frequency was tuned to be around 10 kHz. The total input was measured by the product of current and voltage of the generator input. Due to the high voltage, it is impossible to measure the bed temperature during plasma discharge. Our previous measurement by means of an infrared imager (ThermoVision A40M) [9] showed that the temperature rise in the bed was not significant. In a typical reduction, the input voltage of the generator was kept at a specific value (45–90 V) for desired time (15–240 min). After reduction, the plasma generator was turned off, and the reactor was allowed to cool down to room temperature in H$_2$ flow. Then, the obtained material was passivated in a 10 ml min^{-1} flow of 0.5 mol% O$_2$ in He for 2 h at room temperature [9].

The crystal phases of the synthesized materials were characterized by XRD patterns, which were measured on a Rigaku D/Max 2400 diffractometer with nickel-filtered Cu$K\alpha$ radiation at 40 kV and 100 mA. HRTEM images of Ni$_2$P were taken on a Philips CM200 FEG instrument. The atomic ratios of metal to phosphorus in the oxidic precursor and the synthesized metal phosphide were determined by means of ICP-OES system (Optima 2000DV, Perkin Elmer).

3. Results

3.1. Nickel phoshpide

Our previous study showed that Ni$_2$P and Ni$_3$P could be synthesized stoichiometrically from their oxide precursors by H$_2$ plasma reduction [9]. Because Ni$_2$P is more important in hydrotreating catalysis, the effects of reduction conditions on the formation of Ni$_2$P were investigated systematically. Fig. 2 shows the XRD patterns of the materials obtained from Ni and P oxides by H$_2$ plasma reduction at various power input. The power was tuned by adjusting the input voltage of the plasma generator. At 45 V for 60 min, only Ni$_{12}$P$_5$ was obtained. Increasing the voltage or power input led to the transformation of Ni$_{12}$P$_5$ to Ni$_2$P. At 60 V × 0.40 A, a pure Ni$_2$P phase was obtained. HRTEM images in Fig. 3 indicate that crystalline Ni$_2$P particles of 100–150 nm were synthesized from the oxidic precursor by H$_2$ plasma reduction.

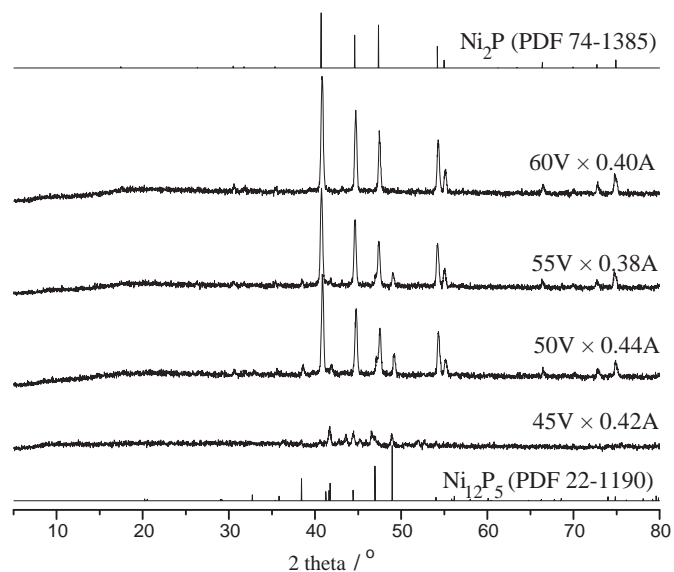Reduction time is another important factor determining the formation of crystal phases in the reduction. As seen in Fig. 2, a mixture of Ni$_2$P and Ni$_{12}$P$_5$ were obtained at 50 V for 120 min. When the reduction time increased to over 120 min, high crystalline Ni$_2$P particles were synthesized at 50 V (Fig. 4). It is interesting to note that Ni$_{12}$P$_5$ phase formed in 15 min.

The atomic ratios of Ni$_2$P and Ni$_3$P as well as their oxidic precursors (Table 1) indicate that there was little difference between metal phosphides and their oxidic precursors, suggesting that no loss of phosphorus occurred in the plasma reduction procedure.

3.2. Cobalt phosphides

Recently, Autumn et al. reported cobalt phosphides also showed fairly high HDS activity [10]. In addition, CoP can be used as a potential contact material to InP for application in electronic devices, owing to its metallic nature [11]. It is also a potential candidate in thermoelectric applications [12].

Fig. 5 shows the XRD patterns of the synthesized materials from Co and P oxides with atomic ratio of 1 by H$_2$ plasma reduction at various power input for 60 min. A mixture of cobalt phosphate and CoP formed at low power input. With increasing power input, the portion of CoP phase was increased. Pure CoP crystals were obtained at 90 V for 60 min. Alternatively, increasing reduction time at lower power input, such as 80 V × 0.30 A, also led to the formation of pure CoP crystal phase (Fig. 6). Compared

Fig. 1. The configuration of the DBD reactor: (1) high-voltage discharge electrode; (2) grounding electrode; (3) ground; (4) quartz tube; (5) insulator; (6) solid precursor bed; (7) gas inlet; (8) gas outlet.

Fig. 2. XRD patterns of the synthesized materials by H$_2$ plasma reduction at various power input for 120 min from Ni and P oxides with Ni/P atomic ratio of 2.

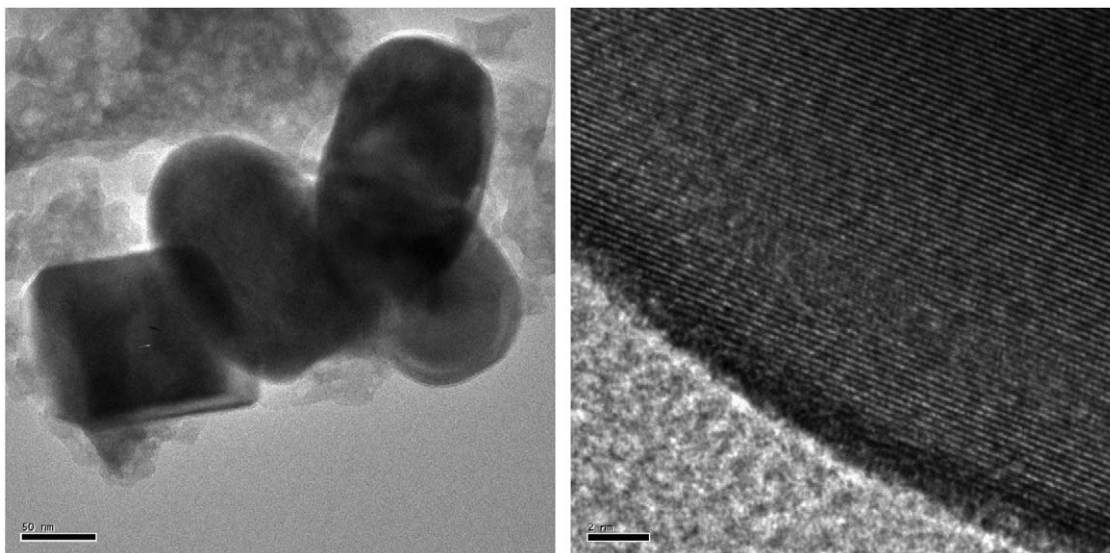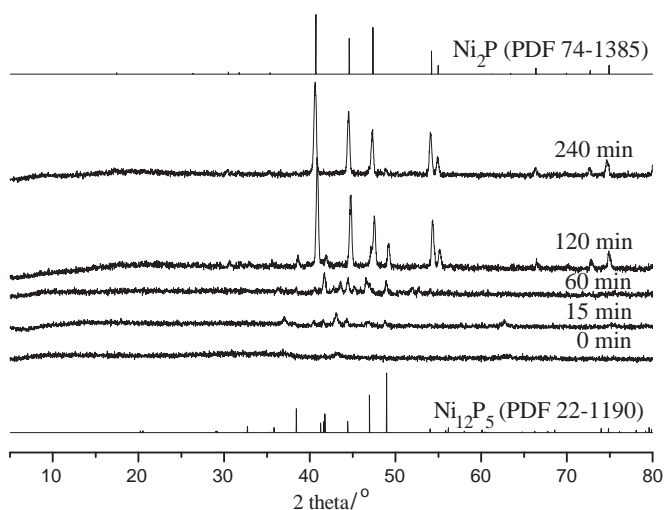**Fig. 3.** HRTEM images of Ni_2P particles synthesized by H_2 plasma reduction.

Fig. 4. XRD patterns of the materials obtained at different time from Ni and P oxides with Ni/P atomic ratio of 2 by H_2 plasma reduction at $50\,V \times 0.44\,A$ input.

Fig. 5. XRD patterns of the materials synthesized from Co and P oxides with atomic Co/P ratio of 1 by H_2 plasma reduction for 60 min.

Table 1
Atomic ratio of metal to phosphorus in precursors and metal phosphides.

	Oxidic precursor	Metal phosphide
Ni_2P	2.06	2.07
Ni_3P	3.08	3.05
CoP	0.98	0.98
Co_2P	1.90	1.92

with the synthesis of Ni_2P, more severe reduction conditions are necessary to obtain pure CoP crystals.

Fig. 7 illustrates the XRD patterns of the synthesized materials from different atomic Co/P ratio. Similar to the synthesis of nickel phosphides [9], pure CoP and Co_2P crystals were obtained stoichiometrically from their oxidic precursors with Co/P ratio of 1 and 2, respectively. The atomic ratios of CoP and Co_2P as well as their oxidic precursors (Table 1) indicate that there was little difference between metal phosphides and their oxidic precursors.
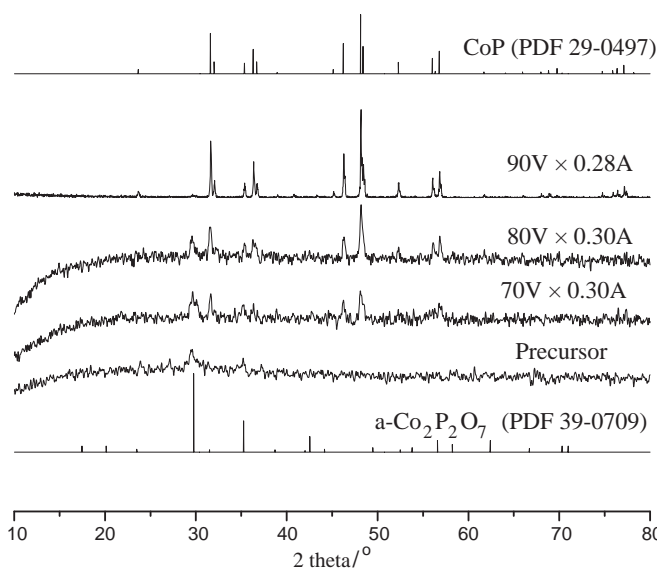
3.3. Molybdenum phosphide and tungsten phosphide

In our previous study, we found that the H_2 plasma reduction method was also applicable in the synthesis of MoP and WP. In the present work, the effects of the reduction conditions were investigated in more detail.

Fig. 8a shows the XRD patterns of the materials synthesized from Mo and P oxides with atomic Mo/P ratio of 1 at different power input for 60 min. It is indicated that the synthesis of MoP is easier than that of CoP, but more difficult than that of Ni_2P. In the synthesis of MoP, no intermediate phase appeared at lower power input. The transformation of W and P oxides to WP is similar to that of Mo–P oxides to MoP (Fig. 8b) in that no intermediate phase was observed.

From Fig. 9, it can be seen that pure crystalline MoP and WP were obtained when the reduction time was prolonged. Fig. 10 indicates that highly crystalline MoP or WP could be obtained only stoichiometrically from the oxidic precursor. An excess of
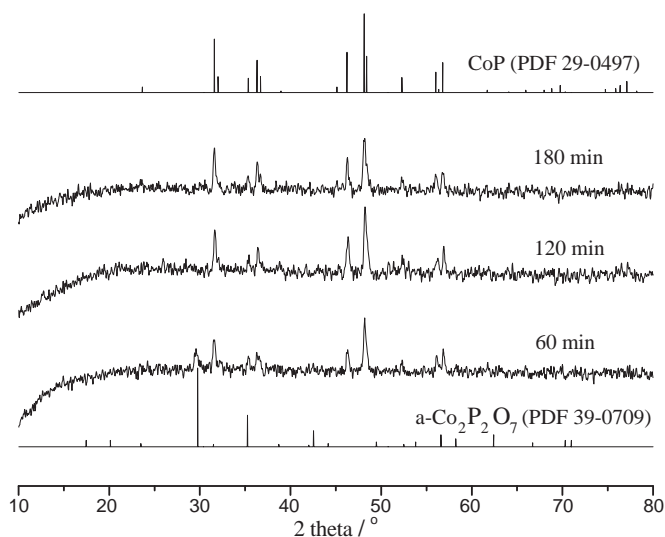
Fig. 6. XRD patterns of the synthesized materials from Co and P oxides with atomic Co/P ratio of 1 by H_2 plasma reduction at $80 V \times 0.30 A$ for different reduction time.
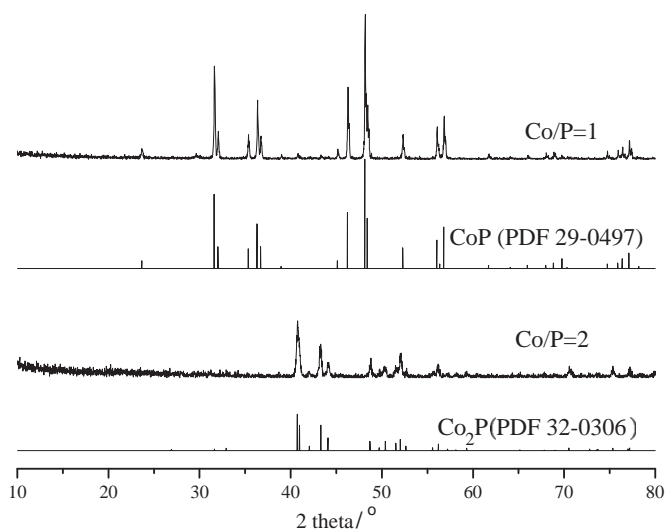
Fig. 7. XRD patterns of the synthesized materials from Co and P oxides with atomic Co/P ratio of 1 and 2 by H_2 plasma reduction $90 V \times 0.28 A$ for 60 min.
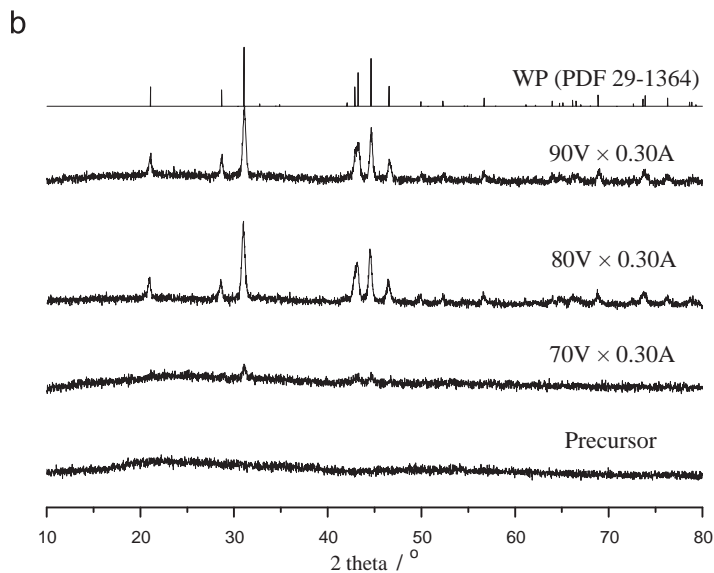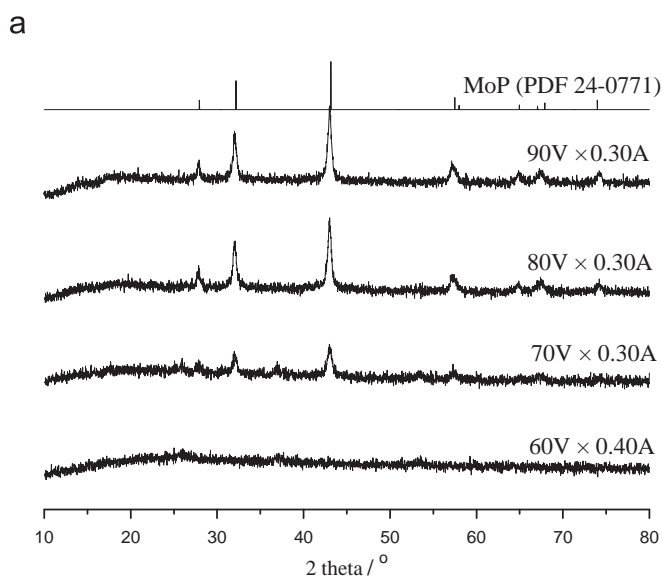
metal or phosphorus in the precursor led to lower crystallinity of MoP or WP.

4. Discussion

The synthesis of metal phosphides from their oxidic precursors by H_2 reduction could be expressed as the following equation:

$$z MO_x(s) + PO_y(s) + (nx + y)H_2(g) \underset{\text{very fast}}{\overset{\text{slow}}{\rightleftharpoons}} M_zP(s) + (nx + y)H_2O(g)$$

(1)
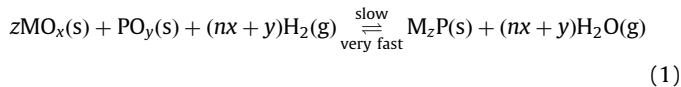
Transition-metal phosphides, such as MoP, WP, Ni_2P, CoP, and Co_2P, react with H_2O readily, leading to severe structure destruction of the formed phosphide crystal [13,14]. It is therefore essential to remove water, which is the by-product of the reduction, from the surface of the metal phosphide particles in the course of reduction. In conventional temperature-programmed reduction procedure, a very low heating rate (i.e. $1 °C min^{-1}$) and a high H_2 flow rate are used to keep low partial pressure of moisture.

In the conventional temperature-programmed reduction method, the reaction (1) usually takes place at elevated temperatures because there exist threshold temperatures for the synthesis of metal phosphides, such as Ni_2P, WP and MoP [15–17]. This is probably due to the low reduction ability of molecular hydrogen.

Because of the high temperature and low heating rate in the temperature-programmed reduction, the synthesis of metal phosphides generally takes more than 6 h. In H_2 plasma reduction, Ni_2P could be obtained in 60 min at power input of $60 V \times 0.40 A$ [9]. Although more harsh conditions were needed to synthesize CoP, Co_2P, MoP, and WP, the reduction times were dramatically shortened, compared with the conventional TPR method (Figs. 6 and 9).

In H_2 plasma, high-energy electrons generated by plasma collide inelastically with hydrogen molecules, which lead to the production of excited hydrogen species and ions with a dramatically enhanced reduction ability [18]. These active species can promptly reduce the oxidic precursors whereas the plasma helps to remove the by-product water from the surface of metal phosphides. Consequently, the forward reaction in Eq. (1) will be significantly accelerated under plasma irradiation, leading to a quick formation of metal phosphides under mild conditions.
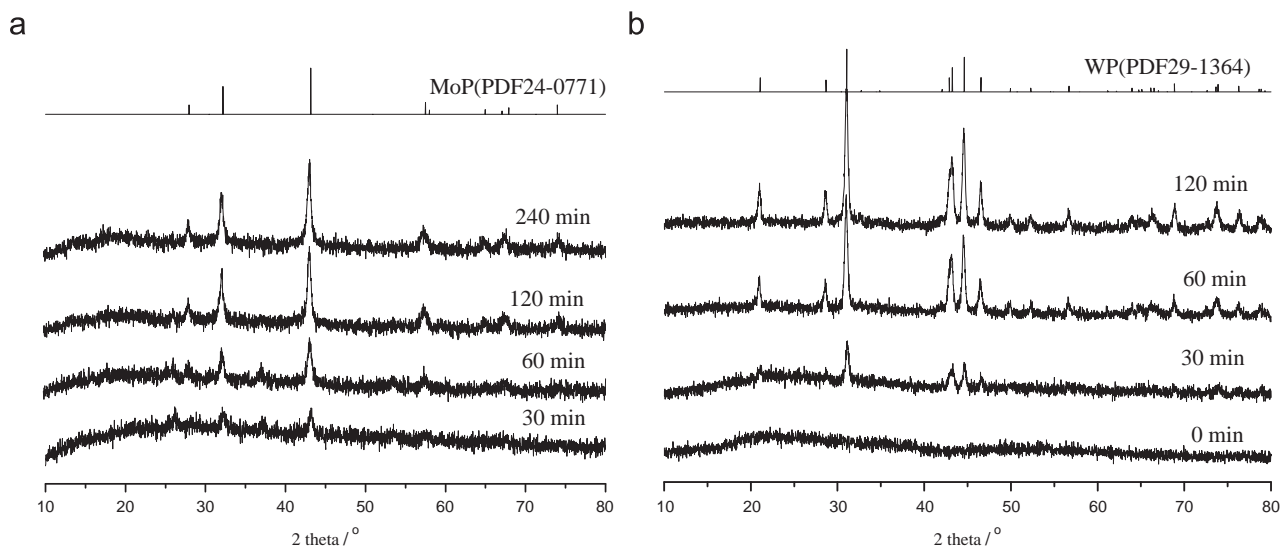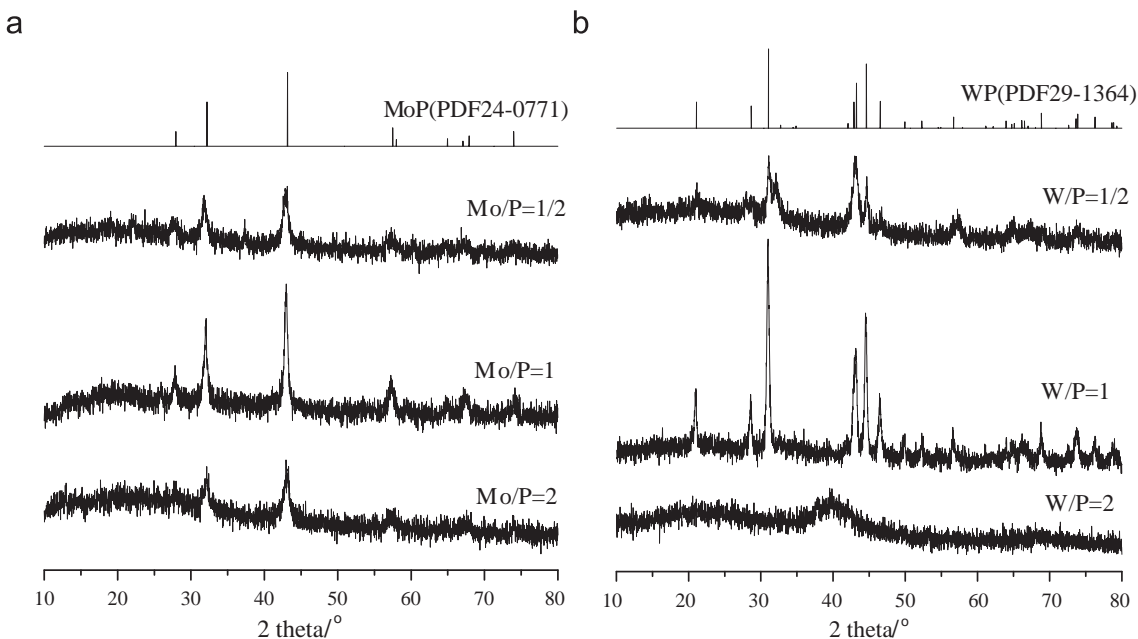
a

b

Fig. 8. XRD patterns of the synthesized materials from Mo and P oxides (Mo/P = 1) (a) and W and P oxides (W/P = 1) (b) by H_2 plasma reduction at different power input.

Fig. 9. XRD patterns of the synthesized materials from Mo and P oxides (Mo/P = 1) at 70 V × 0.30 A (a) and from W and P oxides (W/P = 1) at 80 V × 0.30 A (b) by H_2 plasma reduction for different reduction time.

Fig. 10. XRD patterns of the synthesized materials from Mo–P oxides and W-P oxides with various Mo/P and W/P atomic ratios by H_2 plasma reduction at 70 V × 0.30 A for 120 min.

Two solid reactants and a gaseous hydrogen molecule are involved in the forward reaction in Eq. (1). One of the reactant or its derivatives must migrate to meet the other reactant before the reaction can proceed. It is generally believed that the metal oxide is reduced to metal and then phosphorus species are reduced to volatile P or PH_3 [3]. Carenco et al recently reported the synthesis of Ni_2P nanoparticles from Ni(0) complexes and P [19]. Yang et al. synthesized Ni_2P from phosphidation of Ni by PH_3 [4]. The volatile species migrate to meet metal particles so as to form metal phosphide. At elevated temperature and high velocity of hydrogen flow, part of the volatile species may be flushed off the solid surface, leading to phosphorus loss in the course of high temperature reduction. It is therefore essential that excess phosphorus is present in the precursors to compensate the loss in the conventional TPR synthesis.

Our previous study showed that Ni_2P and Ni_3P could be synthesized stoichiometrically from their oxidic precursors [9]. In the present study, crystalline CoP and Co_2P were obtained stoichiometrically from their oxidic precursors (Fig. 6). Fig. 10 illustrates that highly crystalline MoP and WP were synthesized only at stoichiometric atomic Mo/P and W/P ratios. In the excess of metal or phosphorus, poor yield of MoP or WP was obtained. All these results indicate that excess phosphorus is not necessary in H_2 plasma reduction. This is probably due to the low temperature, which decreases the volatility of phosphorus species, suppressing the loss of phosphorus species.

According to the TPR profiles in the literatures [16,20], the main H_2 consumption peak temperatures of the phosphide precursors increased in the following order: $Ni_2P<MoP< CoP<WP$, in accordance with the threshold conditions in the

synthesis of the metal phosphides. It is therefore suggested that hydrogen plasma reduction does not change the transformation mechanism but enhance the forward reaction in Eq. (1), due to the generation of highly reactive hydrogen species and to the surface cleaning effects of plasma irradiation.

5. Conclusions

Our results demonstrated that H_2 plasma reduction is a more efficient approach to synthesizing metal phosphides than the conventional TPR method. The high efficiency is probably related with the highly reactive hydrogen species and the surface cleaning effects of plasma irradiation. Moreover, all the metal phosphides, including MoP, WP, CoP, Co_2P, and Ni_2P, were synthesized stoichiometrically from their oxidic precursors.

Acknowledgments

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