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Plasma Chemistry

The Synthesis of Metal Phosphides: Reduction of Oxide Precursors in a Hydrogen Plasma**

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Phosphorus can react with most elements of the periodic table to form different classes of phosphides, ranging from ionic for the alkali and alkaline-earth elements to metallic or covalent for the transition elements and covalent for the main-group elements. Among them, InP and GaP (III–V semiconductors) have various applications in telecommunications, optoelectronic devices and solar cells,[1,2] while transition-metal phosphides are attractive candidates for high-performance catalytic, electronic, and magnetic applications.[3]

A variety of methods for synthesizing bulk metal phosphides, including direct reaction of the appropriate elements for prolonged periods at high temperature, reaction of phosphine with metals or metal oxides, reduction of metal phosphates by hydrogen, electrolysis of molten metal phosphate salts, solid-state metathesis, thermal decomposition of single-source precursors, and self-propagation high-temperature synthesis, are known.[4–6] These methods typically require extremely high reaction temperatures (sometimes above 1000 °C) and/or long reaction times. 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, and in cases where yellow phosphorus and sodium are employed, care must be taken to ensure the rigorous absence of oxygen and water.[7]

Only two methods, namely the reduction of metal phosphates by H_2[4] and the phosphidation of metals or metal oxides with PH_3/H_2,[5] are generally feasible for the preparation of supported transition-metal phosphides for use as hydrotreating or hydrogenation catalysts. Supported metal phosphides are usually prepared by the reduction method due to the high toxicity of PH_3. Nevertheless, the conversion of oxide precursors to phosphides is neither thermodynamically nor kinetically favorable. Since the formation of Ni_2P from the oxides by means of the temperature-programmed reduction (TPR) method (Scheme 1) is thermodynamically unfavorable, the forward reaction has to be aided by high temperature and low water vapor pressure.[8] Thus, Ni_2P can only be obtained at a low heating rate (e.g. 1 °C min^{-1}) and a high H_2 flow velocity to purge the water (by-product) off the solid surface. The forward reaction is slow because the H_2 molecules must be split into hydrogen atoms, therefore the metal oxide must first be reduced and then spilt-over hydrogen atoms can reduce the phosphorus oxide, followed by a solid-state reaction to form the metal phosphide. As a consequence, Ni_2P can only be prepared by means of the TPR method above 550 °C.

$$4\ \mathrm{NiO\ (s)} + \mathrm{P_2O_5\ (s)} + 9\ \mathrm{H_2\ (g)} \xrightleftharpoons[\text{[very fast]}]{\text{[slow]}} 2\ \mathrm{Ni_2P\ (s)} + 9\ \mathrm{H_2O\ (g)}$$

Scheme 1. A simplified equation for the synthesis of Ni_2P from its oxide precursors by H_2 reduction.

Herein we describe 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. High-energy electrons collide inelastically with hydrogen molecules in the plasma and transfer their energy to the latter, which leads to the production of excited hydrogen species and ions with a significantly higher reduction ability than molecular hydrogen.[9] These reactive species can reduce both the metal oxide precursor and the phosphorus oxide, therefore oxide precursors can be converted into metal phosphides in the H_2 plasma under very mild conditions. Both bulk and supported metal phosphides are accessible in this approach.

The XRD patterns of the bulk products synthesized from nickel and phosphorus oxides at different reduction times (Figure 1) indicate that Ni_2P crystals begin to form in the H_2 plasma within 10 min. This reaction time is very much shorter than that used in the traditional TPR reduction method (over 10 h).[4]

No external heating was applied during the reduction. Because a thermocouple cannot be used in the presence of plasma, the temperature in the bed could not be measured directly during the reduction. A temperature rise due to the elastic collisions of high-energy electrons with the reactant molecules will take place, but this rise is not likely to be significant because the total power input is generally around 24–32 W in the steady state. A temperature-distribution

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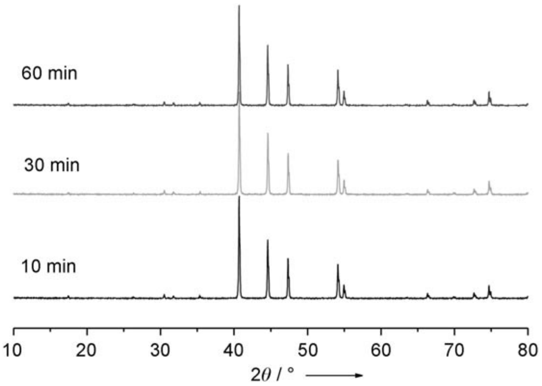

Figure 1. XRD patterns of the bulk Ni_2P samples synthesized by the H_2 plasma reduction method at various times. The atomic ratio of Ni/P in the precursors was 2.0. The total input of the AC power was 70 V × 0.35 A.

measurement across the reaction bed, using an IR imager, showed that the bed temperature was around 150 °C (Figure S2 in the Supporting Information). This indicates that the enhanced reduction can be ascribed to irradiation by the cold plasma.

A large number of active hydrogen species, such as H, H^+, H_2^+, and H_3^+, exist in the H_2 plasma, and these species possess much higher reduction abilities than molecular H_2.[9] It is therefore not necessary to heat the oxide precursors to elevated temperatures during the reduction. Moreover, plasmas can be used to clean the surface of solids,[10] therefore this surface cleaning ability may accelerate the desorption of the by-product water molecules, thereby facilitating the forward reaction in Scheme 1.

The synthesis of metal phosphides by the TPR method requires the use of excess phosphorus in the oxide precursors because phosphorus loss occurs due to migration of volatile phosphorus species in the high-temperature reduction.[11,12] Both Ni_2P and Ni_3P are formed stoichiometrically in the H_2 plasma reduction, as evidenced by the XRD patterns of the nickel phosphides synthesized from oxide precursors with different Ni/P atomic ratios (Figure 2).

The very low heating rate that must be used in the conventional TPR method implies that the reduction is the rate-limiting step. The surplus volatile phosphorus species generated in H_2 may also be purged off in the high-velocity H_2 flow, thus leading to a loss of phosphorus. The reduction is significantly enhanced in a H_2 plasma, however, therefore it is possible to synthesize the metal phosphides stoichiometrically without appreciable phosphorus loss. Indeed, when phosphorus is used in excess it might form volatile phosphorus species, which adsorb on the metal phosphide sites and block the catalytic reaction.

Supported transition-metal phosphides are used as novel hydrodesulfurization (HDS) catalysts.[4,5] We decided to use mesoporous MCM-41 to support Ni_2P and tested its performance in the removal of sulfur from dibenzothiophene (DBT) in the HDS reaction. The conventional TPR method was used to prepare a Ni_2P/MCM-41 sample for comparison. The Ni_2P/MCM-41 sample prepared by the plasma reduction (PR) method was found to exhibit a substantially higher HDS activity than that prepared by the TPR method (Table 1). Moreover, the PR-prepared catalyst remained active and stable over a period of at least two days (Figure S3 in the Supporting Information). In agreement with the difference in catalytic activity, the PR sample showed a significantly higher CO chemisorption uptake, which is a measure of the number of accessible active HDS sites of the Ni_2P catalysts, than the TPR sample (Table 1).[11] Similar results were obtained for bulk Ni_2P (Table S1 in the Supporting Information).

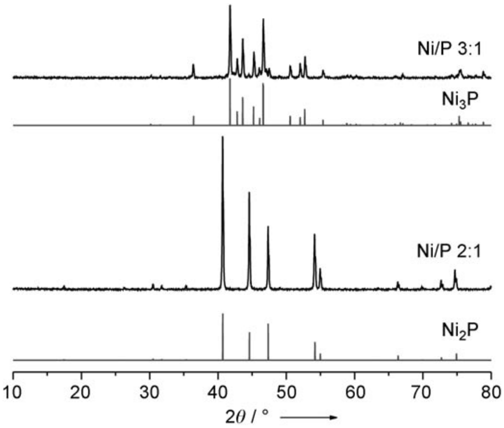

Figure 2. XRD patterns of the nickel phosphides synthesized from oxide precursors with different Ni/P atomic ratios in H_2 plasma for 60 min. The total input of the AC power was 60 V × 0.4 A. Gray: simulated patterns.

Table 1: CO chemisorption and HDS catalytic performance of Ni_2P/MCM-41 prepared by different reduction methods.

Method	CO uptake [μmol g^{-1}]	DBT conversion [%]		TOF [s^{-1}]	
		280 °C	300 °C	280 °C	300 °C
TPR	21	44	68	0.0066	0.01
PR	29	62	89	0.0068	0.01

No XRD peaks were observed for either TPR- or PR-prepared Ni_2P/MCM-41 with a low loading level (Figure S4 in the Supporting Information), thus indicating that the Ni_2P particles are small. The TEM images (Figure 3) confirmed this but did not indicate a difference in the particle size

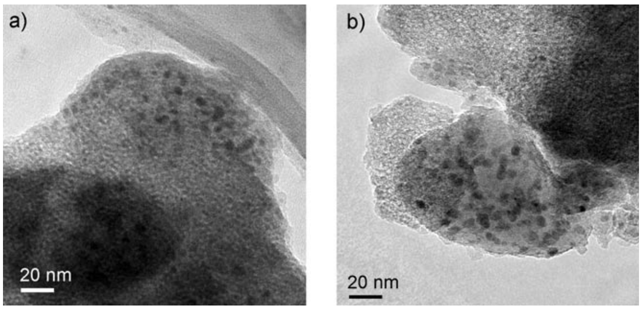

Figure 3. TEM images of Ni_2P/MCM-41 with a total loading of 20 wt% prepared by different reduction methods: a) PR, b) TPR.

between the two supported catalysts. Distinct XRD peaks were observed, however, for both TPR- or PR-prepared Ni_2P/MCM-41 when the loading was increased to 40 wt% (Figure S4). All these peaks seem to consist of a narrow peak superposed on a broader peak and the peaks of the PR sample are much broader. The TEM images (Figure S5 in the Supporting Information) indicate that the narrower, more intense peaks in the XRD patterns of the TPR-prepared Ni_2P/MCM-41 are due to the presence of a larger number of bulk Ni_2P particles in the matrix. The relatively low CO chemisorption data (10 $\mu mol\,g^{-1}$ for TPR-prepared Ni_2P/MCM-41 and 11 $\mu mol\,g^{-1}$ for PR-prepared Ni_2P/MCM-41) show that blockage of the pore channels of MCM-41 may occur when the larger bulk Ni_2P particles are present at a high loading level.

To further prove the feasibility of the H_2 plasma method in synthesizing metal phosphides, we used this approach to synthesize other metal phosphides. Figure 4 shows that pure WP, MoP, GaP, and InP crystals were obtained stoichiometrically from their oxide precursors by nonthermal H_2 plasma reduction. No excess of phosphorus is needed in the precursors in the synthesis of the above metal phosphides. These results prove that the hydrogen plasma reduction method is a facile and flexible approach for the synthesis of metal phosphides.

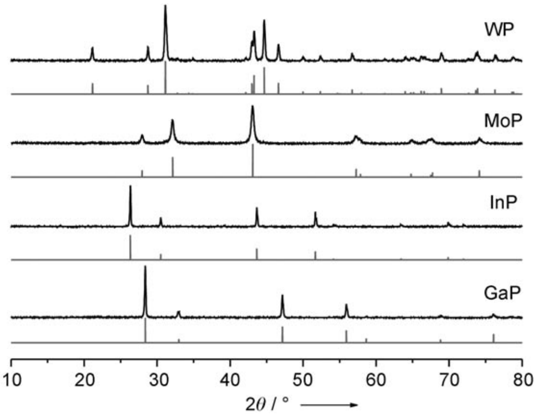

Figure 4. XRD patterns of WP, MoP, InP, and GaP synthesized from their oxide precursors in nonthermal H_2 plasma. Gray: simulated patterns.

Taking into consideration that metal oxides are easily homogeneously mixed, it should even be possible to synthesize ternary and quaternary metal phosphides such as GaInP and GaInAlP, which are important semiconductor materials in optoelectronic devices and solar cells. When H_2 is replaced by NH_3 and CH_4, it may also be possible to synthesize metal nitrides and carbides by the plasma approach.

Experimental Section

The bulk oxide precursors were prepared by co-precipitation from $Ni(NO_3)_2$ and $(NH_4)_2HPO_4$ by adjusting the pH of the aqueous solution, followed by calcination in air at 500 °C for 2 h. The supported oxide precursors were prepared by an incipient co-impregnation and calcination method, using a mesoporous molecular sieve MCM-41 (specific surface area: 1046 $m^2\,g^{-1}$; pore volume: 0.95 $m^3\,g^{-1}$; average pore diameter: 3.8 nm) as the support.[13] The oxide precursors were pelletized and sieved to 20–35 mesh. The synthesis of Ni_2P was carried out in a dielectric barrier discharge (DBD) reactor[14] consisting of a quartz tube and two electrodes (Figure S1 in the Supporting Information). The high-voltage electrode was a stainless-steel rod with a diameter of 2 mm, which was installed in 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. One gram of the precursor was charged into the quartz tube and pure hydrogen from a gas cylinder was passed through the bed at 150 $mL\,min^{-1}$ during the synthesis. The voltage of the high-voltage electrode was kept at around 12.8 kV and the discharge frequency at 12 kHz. For comparison, an MCM-41-supported Ni_2P sample was prepared by the H_2 TPR method. The obtained Ni_2P samples were passivated with 0.5% O_2 in He prior to exposure to air. The obtained Ni_2P samples, bulk or supported, were characterized by XRD (Rigaku D/Max 2400). The TEM images were recorded with a Philips Tecnai G220 instrument operating at 200 kV. The CO adsorption was measured with a chemisorption apparatus (Quantachrome Chembet-3000) at 30 °C, according to the method described in the literature.[15] The supported Ni_2P was tested in the HDS of DBT in a trickle-bed reactor.[13]

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