Novel synthesis of dispersed molybdenum and nickel phosphides from thermal carbonization of metal- and phosphorus-containing resins†

Zhiwei Yao,* Jin Tong, Xue Qiao, Jun Jiang, Yu Zhao, Dongmei Liu, Yichi Zhang and Haiyan Wang

Dispersed pure phases of MoP and Ni2P nanoparticles supported by carbon were synthesized by carbonization of metal- and phosphorus-containing resins under an inert atmosphere. The solid products and the evolution of gases during the carbonization process were investigated by various techniques, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), N2 adsorption–desorption analysis, and mass spectrometry (MS). The resins underwent two carbonization stages: the low-temperature carbonization stage (<650 °C) and the high-temperature carbonization stage (≥650 °C). There was an initial reduction of Mo and Ni precursors in the low-temperature region. However, the formation of phosphides was observed in the high-temperature carbonization stage, in which Mo(Ni) and POx species were further reacted with the carbonization products (C, H2 and CH4) to yield Mo(Ni) phosphide. Note that compared with the traditional H2-temperature-programmed reduction (H2-TPR) method, this novel synthesis route produced a large amount of CO besides H2O, leading to a lower water vapor pressure. In addition, the residual carbon produced from resin can play a role in bonding of nanoparticle aggregation. Therefore, the better dispersions and higher surface areas of the as-prepared phosphide nanoparticles were attributed to the mitigation of hydrothermal sintering and the intimate contact between phosphide nanoparticles and carbon species.

1. Introduction

Due to the fact that transition metal interstitial compounds (e.g. carbides, nitrides and phosphides) show unique performances similar to noble metals, they have attracted much attention in recent decades and have been regarded as substitutes for noble metal materials in various fields such as fuel cells, dye-sensitized solar cells and catalysis.1–5 Compared with metal carbides and nitrides, metal phosphides have been studied more extensively in recent years owing to their unprecedented properties and potential applications in many areas, including catalysis, magnetism, electronics, optoelectronics, lithium batteries, solar cells and so on.6,7 Particularly in the aspect of catalysis, MoP and Ni2P phosphides have been studied more extensively in recent years owing to their unprecedented properties and potential applications in many areas, including catalysis, magnetism, electronics, optoelectronics, lithium batteries, solar cells and so on.6,7 Particularly in the aspect of catalysis, MoP and Ni2P phosphides were reported to be excellent hydrotreating catalysts in terms of both activity and resistance to poisoning.6,8 Since the discovery of the size-dependent catalytic performance of materials with nanoscale sizes, more and more efforts have been focused on synthetic methods for preparing nanosized metal phosphides. During the last twenty years, a wide range of methods have been developed for the preparation of nanoscale MoP and Ni2P phosphides, such as direct reduction of phosphate in H2 or H2 plasma,6,9,10,12,13 decomposition of high-boiling point tri-n-octylphosphine (TOP),14–16 decomposition of single-source precursors in solution,17 chemical vapor deposition,18 and microwave or solvo-thermal synthesis.19,20 Nevertheless, most of these routes generally involve highly toxic phosphorus sources (e.g. P4, PH3 and TOP) or complicated steps that cannot afford the requirements of green synthesis of phosphate catalysts. Only one method mentioned above, the H2-temperature-programmed reduction (H2-TPR) method (Scheme 1),3 has been recognized as an effective and environmentally friendly approach to prepare bulk and supported MoP and Ni2P catalysts due to the use of a nontoxic phosphorus source [(NH4)2HPO4] and a green reducing agent (H2). Unfortunately, a large amount of water generated during the reaction process can result in
2. Experimental

2.1 Sample preparation

The raw resin used was a D201 × 1 cinnamic strong alkali anion exchange resin (purchased from Shanghai Jinkai resin Co. Ltd.). Fig. 1 shows the chemical structure of this raw resin. Firstly, the raw resin was dried at 110 °C for 12 h, and then ground to fine powder. After that, the resin powder was incipient-wetness impregnated with an aqueous solution of metal salt ([NH₄]₆Mo₇O₂₄·4H₂O or Ni(NO₃)₂·6H₂O) and (NH₄)₂HPO₄ with 30 wt% metal loading and a given metal/P ratio (R). In the case of nickel, a few drops of HNO₃ were needed to give rise to a homogeneous solution. The slurries were evaporated at 110 °C for 12 h to obtain (Mo,Ni),P-containing resins (designated as Mo/P-R and Ni/P-R, R = 1, 1.3, 1.5, 1.8 or 2). Finally, the dried resin precursors were heated from room temperature (RT) to a given value at a rate of 10 °C min⁻¹ under Ar (50 ml min⁻¹) and maintained at this temperature for 1 h, followed by cooling to RT under an Ar flow, and then passivated in a 1% O₂/Ar flow for 2 h. A series of products were obtained from heating at 500, 600, 700, 800 and 900 °C, designated as Mo/P-R-T and Ni/P-R-T for Mo and Ni samples (R = 1, 1.3, 1.5, 1.8 or 2, T = 500, 600, 700, 800 and 900 °C).

2.2 Sample characterization

The microstructure of the samples was determined by using an X-ray diffractometer (XRD, X’Pert Pro MPD) equipped with a Cu Kα source and by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis ultra (DLD) equipped with an Al Kα X-ray source. The binding energies (±0.2 eV) were referenced to the C 1s peak at 284.6 eV due to adventitious carbon. The morphologies of the samples were characterized by using a scanning electron microscope (SEM, Hitachi S-4800) equipped with an energy dispersive X-ray (EDX) spectroscope and transmission electron microscope (TEM, Philips Tecnai 10). The BET surface area and pore structure of the samples were measured through nitrogen adsorption at liquid-nitrogen temperature (77 K) by using a surface area analyzer (NOVA4200). The chemical composition of the samples was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The processes of thermal carbonization were carried out under an Ar flow (30 ml min⁻¹). The sample (0.1 g) was heated from 100 to 800 °C at a heating rate of 10 °C min⁻¹, and then was held at 800 °C for 30 min. The Hiden HPR20 mass spectrometer (MS) was used for detection.

3. Results and discussion

3.1 Microstructural characterization

In order to gain insights into the formation mechanism of the final phosphide products, the (Mo,Ni),P-containing resin precursors and the products obtained from thermal carbonization of these precursors needed to be characterized. Fig. 2 shows

\[
z\text{MoO}_3(s) + \text{PO}_4(s) + (2x+y)\text{H}_2(\text{g}) \xrightarrow{\text{slow, very fast}} \text{M}_x\text{P}(s) + (2x+y)\text{H}_2\text{O}(\text{g})
\]

Scheme 1 A simplified equation for the preparation of metal phosphides by the H₂-TPR method.

Recently in our laboratory, highly dispersed phosphides have been prepared by dimethyl ether (DME) and hexamethylenetetramine (HMT) routes. However, it is still worthwhile to expand green preparation techniques for synthesizing dispersed nanosized MoP and Ni₂P catalysts.

Ion exchange resin is composed of a porous polymer network with tunable functional organic groups. Following a facile impregnation procedure, one or more ionic guests can be simultaneously and dispersively introduced into the resin framework or covered on the surface. After thermal carbonization at high temperatures, the resin is converted to carbon that can play a double role as a reducing agent and support for nanoparticles. Based on these unique properties of ion exchange resin, well dispersed Mo and W carbide particles (<10 nm) have been prepared from carbonization of metal-containing resin precursors. The two studies (ref. 31 and 32) reported that these dispersed carbides could act as highly efficient Pt catalyst supports for methanol electro-oxidation. Note that the electrocatalytic activity of Pt supporting on the above-mentioned Mo carbide was higher than that of commercial Pt/C catalysts. However, some details were still missing about the formation processes of carbides in the studies. Therefore, it is worthwhile to investigate the formation mechanism of interstitial compounds synthesized by this novel resin-based route for the design of improved catalytic materials.

In this work, it is the first time that dispersed metal phosphides (MoP and Ni₂P nanoparticles) were synthesized by a resin-based route. XRD, XPS, SEM, TEM, ICP-AES, N₂ adsorption–desorption analysis, and MS were adopted for the investigation of solid and gas products, and to gain insights into the formation mechanism of phosphides during thermal carbonization processes.

Fig. 1 Chemical structure of D201 × 1 cinnamic strong alkali anion exchange resin (Cl⁻ type).

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the XRD patterns of the (Mo,Ni),P-containing resin precursors (Mo/P-1 and Ni/P-2) as well as the raw resin for comparison. It can be seen from Fig. 2 that the raw resin was completely amorphous. After introducing the metal and P into the resin, the Ni species on the resin were amorphous, and most of the Mo species should also be amorphous because only the NH₄H₂PO₄ phase (2θ = 16.8, 23.8, 29.1 and 45.3°) and a very small amount of not-well-defined phase (marked with an asterisk) were observed on the Mo/P-1 sample. The unidentified species was probably due to unknown ammonium molybdenum oxide or ammonium (hydrogen) phosphate. In order to confirm whether ion exchange occurred during incipient-wetness impregnation of ion exchange resins with the solution containing Mo(Ni) and P, a portion of impregnated resin was treated sequentially by washing, drying and carbonization. The XRD patterns (Fig. S1†) of the washed precursors were similar to that of the raw resin except that the XRD pattern of the washed Mo/P-1 sample showed an amorphous species within the 5–13° 2θ range. However, the XRD patterns (Fig. S2†) of the carbonized samples indicated that no diffraction peaks were assigned to metals or metal-containing compounds. Therefore, it was reasonable to deduce that there was no obvious (or a little) exchange of ions between resin and metal-containing salt solutions. In other words, the Mo and Ni species should mainly be introduced into the pores of resin or covered on the surface during the incipient-wetness impregnation process.

Fig. 3 shows the XRD patterns of the thermal carbonization products of the Mo,P-containing resin precursor with a Mo/P ratio of 1 after heating at different temperatures. It can be seen that the Mo/P-1-500, Mo/P-1-600 and Mo/P-1-700 samples were almost amorphous, but the Mo/P-1-800 sample demonstrated diffraction peaks at 27.9, 32.0, 42.9, 57.0, 64.7, 67.4, 74.0 and 85.5°, corresponding to the (001), (100), (101), (111), (200), (201) and (112) reflections of MoP, respectively. There were no peaks that can be assigned to Mo oxides, Mo phosphates or other Mo phosphides, indicating that the as-prepared MoP material was phase-pure. The results suggested that the MoP cannot be formed until the carbonization temperature was increased up to 800 °C.

Fig. 4 shows the XRD patterns of the thermal carbonization products of Ni,P-containing resin with a Ni/P ratio of 2 after heating at different temperatures. After thermal carbonization at 500 and 600 °C, the Ni/P-2-500 and Ni/P-2-600 samples demonstrated the diffraction peaks of the Ni metallic phase (2θ = 44.3, 51.7 and 76.1°, indexing respectively to the (111), (200) and (220) planes). When the carbonization temperature was increased to 700 °C, Ni₃P (2θ = 41.8, 43.6, 45.2 and 46.6°, due respectively to the (231), (112), (240) and (141) planes) was obtained as the main phase with a small amount of Ni₁₂P₅. With a further increase in temperature, there was a clear phase transformation in the sample from a high Ni/P ratio to a low

![Fig. 2 XRD patterns of the (Mo,Ni),P-containing resin precursors as well as raw resin for comparison.](image1)

![Fig. 3 XRD patterns of the carbonization products of Mo,P-containing resin (Mo : P = 1) after heating in an Ar flow at different temperatures.](image2)

![Fig. 4 XRD patterns of the carbonization products of Ni,P-containing resin (Ni : P = 2) after heating in an Ar flow at different temperatures.](image3)
Ni/P ratio (Ni₂P → Ni₁₂P₅ → Ni₂P). Nevertheless, the phase composition of the phosphide product was still a mixture of Ni₂P (2θ = 40.7, 44.6, 47.4 and 54.2°), corresponding respectively to the (111), (201), (210) and (300) planes) and Ni₁₂P₅ (2θ = 38.4, 41.8, 47.0 and 49.0°), corresponding respectively to the (112), (400), (240) and (312) planes) up to a carbonization temperature as high as 900 °C. It was also found in a traditional H₂-TPR method that although the preparation was carried out with a stoichiometric ratio of 2 : 1 Ni : P, the as-prepared phosphide tended to be a mixed phase (Ni₂P and Ni₁₂P₅) probably due to the loss of phosphorus in the preparation process.³³,³⁴ It was suggested that the excess phosphorus might be necessary in the preparation of phase-pure Ni₃P.³³

Subsequently, the influence of the precursor molar ratio of Ni/P was investigated. Fig. 5 shows the XRD patterns of nickel phosphides prepared at 800 °C through varying the precursor Ni/P molar ratio (R) from 2 to 1. It is clear that when the R was decreased from 2 to 1.5, the diffraction peaks of Ni₁₂P₅ gradually weakened but those relating to Ni₂P became stronger. However, conversely, with a further decrease of the R to 1.3, the reflections corresponding to Ni₁₂P₅ (Ni₂P) began to strengthen (weaken), and there was an additional new set of peaks (2θ = 30.0, 35.5 and 43.1°) due to the Ni₃P₂O₇ phase. It is worth noting that this pyrophosphate was obtained as a nearly single phase when the R = 1.5 at 900 °C (see the XRD pattern in Fig. 5).

For the sake of comparison, Table 1 lists the phase structures of the products obtained in the study. It was obvious that pure MoP can be obtained by carbonizing its corresponding precursor with a stoichiometric ratio of 1 : 1 Mo : P at 800 °C. However, the preparation of phase-pure Ni₃P was not as easy as that of MoP because it depended not only on the carbonization temperature but also on the initial Ni/P molar ratio. Fortunately, pure Ni₃P can be obtained by carbonization of the resin precursor with a small excess of phosphorus (Ni/P = 1.5) at a high temperature of 900 °C. Table 2 lists the ICP-AES results for the precursors and carbonization products obtained in the study. In the case of Mo samples, the Mo/P atomic ratio of Mo/P-1-800 was similar to that of Mo/P-1 and the values were nearly identical to the corresponding stoichiometric ratio of 1/1 for MoP. The result indicated that there was no loss of

![Fig. 5 XRD patterns of the carbonization products of Ni₃P-containing resin with different Ni/P molar ratios after heating in an Ar flow at 800 °C.](image-url)
Mo and P during the carbonization process. In the case of Ni samples, it was obvious that some P was lost from the precursors except for Ni/P-1 during the carbonization process. Generally, using (NH₄)₂HPO₄ as the phosphorus source, there were possible processes (the volatilization of POₓ and the generation of PH₃) which contributed to the loss of P in these samples.³⁵ In the current preparation processes, no trace of PH₃ was detected in the MS signal, as proved later. Thus, the P lost during the carbonization of Ni,P-containing resins should be originated from the volatile POₓ. However, the fact that no loss of P was observed in the Ni/P-1-800 sample was reasonable because Ni₂P₂O₇ was not reduced even at a temperature as high as 800 °C (see Fig. 5). Finally, the bulk Ni/P atomic ratio of the Ni/P-1.5-900 sample was found to be 2.02, which provided supplementary evidence that the Ni-1.5-900 sample was indeed pure Ni₂P. Table 3 lists the textural properties of these pure phosphide samples. Note that the surface areas of Mo and Ni phosphides prepared by the resin route were significantly higher than those of the corresponding phosphides prepared by the traditional H₂-TPR method.³⁶ In particular, the MoP sample showed a high surface area of 201.2 m² g⁻¹, which was about forty times higher than that of the MoP sample (5.3 m² g⁻¹) reported by others.³⁶ Thereafter, XPS analysis was used to further determine the surface composition of the as-prepared pure phosphides (Mo/P-1-800 and Ni/P-1.5-900). Fig. 6 shows the XPS spectra in the Mo 3d, Ni 2p and P 2p regions for the two samples obtained in this study (see the full scan width XPS spectra in Fig. S3†). Based on the curve fitting analysis of the XPS spectra, the binding energies of Mo 3d⁵/₂, Ni 2p₃/₂ and P 2p₃/₂ and the distribution of the corresponding species is estimated (Table 4). Since the as-prepared MoP and Ni₂P samples were usually passivated prior to exposure to air, the surface regions of the phosphides should be dominated by the oxidized species and the underlying reduced species related to phosphide phases.³⁷ The binding energies of oxidized Mo (233.2 eV), Ni (856.1 eV) and P (133.0–133.7 eV) were in accordance with assignments by others to Mo⁶⁺ (Mo oxide), Ni²⁺ (Ni phosphate) and P⁵⁻ (phosphate) species,²⁴,³⁷ respectively. In the case of phosphided species, the binding energy peaks at 228.4, 853.4 and 129.7–129.9 eV were attributed to Mo⁵⁺ (MoP), Ni²⁺ (Ni₂P) and P⁵⁻ (phosphide)³⁶ respectively. Note that the XPS Ni 2p₃/₂ spectrum of the Ni/P-1.5-900 sample showed only one peak at 853.4 eV for Ni₂P species which was far away from the value (852.6 eV) for Ni₁₂P₃,²¹ indicating that the Ni/P-1.5-900 sample synthesized was indeed pure Ni₂P rather than the mixed phase (Ni₂P and Ni₁₂P₃). The result was in agreement with the observation of phase-pure Ni₂P in the XRD pattern of the Ni/P-1.5-900 sample (see Fig. 5).

Finally, the morphologies of the pure phases of Ni₂P and MoP (hereafter denoted as R-Ni₂P and R-MoP, respectively) obtained by carbonization of resin precursors were characterized by SEM and TEM. For the sake of comparison, the

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Table 3 | Textural properties of the pure phosphide samples obtained in this study
<table>
<thead>
<tr>
<th>Sample</th>
<th>S_BET (m² g⁻¹)</th>
<th>D_p (nm)</th>
<th>V_p (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/P-1-800</td>
<td>201.2</td>
<td>5.89</td>
<td>0.30</td>
</tr>
<tr>
<td>Ni/P-1.5-900</td>
<td>69.3</td>
<td>1.25</td>
<td>0.22</td>
</tr>
</tbody>
</table>

S_BET = BET surface area; D_p = average pore diameter; V_p = total pore volume.
morphology of the carbonized raw resin (denoted as R) as well as those of Ni$_2$P and MoP (see their XRD patterns in Fig. S4,† hereafter denoted as H$_2$-Ni$_2$P and H$_2$-MoP, respectively) obtained by the traditional H$_2$-TPR method$^6$ were also characterized. Fig. 7 and S5† show the SEM images of the samples obtained by carbonization and H$_2$ reduction. In the case of the carbonized samples, the product R consisted of aggregates of irregularly shaped nanoplatelets (Fig. 7a), which was likely to be a carbon plate because the EDX result (see Table 5) revealed that only carbon and a trace amount of oxygen elements could be detected in this microregion. After introducing the metal and P into the resin, the SEM image of R-Ni$_2$P (Fig. 7b) showed that the Ni$_2$P particles in the size range from about 50 to 150 nm were well dispersed on these carbon platelets. As for the SEM image of the R-MoP sample (Fig. 7c), dispersed MoP nanoparticles (<50 nm) were also observed but these particles were wrapped with the carbon platelets rather than on their surfaces. In contrast, the H$_2$-Ni$_2$P and H$_2$-MoP showed aggregation morphologies (Fig. S5†), which was consistent with the SEM results reported by others.$^{24}$ These SEM results were in good agreement with the observation of TEM images (Fig. 8 and S6†). In order to gain insights into the homogeneity of the phosphides prepared by the resin route, the EDX measurement was undertaken three times for each material in terms of different microregions. It can be seen from Table 5 that the corresponding metal (Ni, Mo), P, C and O elements can be detected, and the compositions were variable in different microregions. The results indicated that some particle aggregation was not avoided on the surface of these phosphides because as regards the preparation of the precursors, the metal and P loadings were so high that the incipient wetness technique used cannot ensure these species to be very homogeneous in/on the resin.

### 3.2 Formation mechanism

To investigate the formation mechanism of phosphides, the carbonization processes of (Mo,Ni)$_x$P-containing resin precursors were followed by mass spectrometry (MS). As suggested by previous studies,$^{38,39}$ when the resins were carbonized under an inert atmosphere or vacuum, the volatile products should consist mainly of water, methane, hydrogen and ethene, with a comparatively low level of benzene and toluene. In the current study, only the results for masses ($m/z$) of 2, 16, 18, 28 and 44 were shown for understanding the formation mechanism, as the masses of 78 (C$_6$H$_6$), 91 (C$_7$H$_8$), 62 (C$_2$H$_3$Cl) and 34 (PH$_3$) were almost featureless or provided little additional information. Fig. 9 shows the thermal carbonization-MS profiles of the raw resin and (Mo,Ni)$_x$P-containing resin precursors. It was believed that the carbonization process of resin involved a series of dehydration and curing reactions in two stages: low-temperature carbonization (<650 °C) and high-temperature carbonization (≥650 °C).$^{30}$ In the case of raw resin, a large
quantity of multi-component gases was released in the low-temperature carbonization stage (see Fig. 9a) and the simultaneous signals of \( m/z = 2, 16, 18, 28 \) and 44 corresponded to \( \text{H}_2, \text{CH}_4, \text{H}_2\text{O}, \text{C}_2\text{H}_4 \) and \( \text{CO}_2 \), respectively. The \( \text{CO}_2 \) species can be detected might be due to the decomposition of porogenic agents trapped inside the pores during the synthesis process of ion exchange resin.\(^{40}\) In the high-temperature stage, there was only an intense peak of \( \text{H}_2 \) observed together with a weak \( \text{H}_2\text{O} \) emission, which might be attributed to the deep carbonization of resin. However, the delay of the \( \text{H}_2\text{O} \) response in reaching the maximum was possible due to the slow desorption of them on the surface, as suggested before.\(^{41}\)

In comparison with the raw resin, the MS profiles of (Mo, Ni),P-containing resin precursors showed several different features in both the low- and the high-temperature carbonization stages. On the one hand, in the low-temperature regions (see the details in Fig. S7†), there was an obvious consumption of \( \text{CH}_4 \) and \( \text{C}_2\text{H}_2 \), accompanied by first increasing and then decreasing the concentration of \( \text{H}_2 \). The results suggested that the decrease in the concentrations of \( \text{CH}_4, \text{C}_2\text{H}_2 \) and \( \text{H}_2 \) was probably due to the occurrence of reduction of the precursors by these reducing gases. The XRD investigation (Fig. 4) coincided with this suggestion, in which the formation of the metallic Ni phase was observed after heating the Ni,P-containing resin precursor at 500 or 600 °C. Although XRD
characterization cannot provide proof of the reduction of the Mo,P-containing resin precursor due to the fact that Mo/P-1-500 and Mo/P-1-600 were almost amorphous (Fig. 3), the amorphous high-valence Mo species in the precursor might be reduced to noncrystalline or very poorly crystalline low-valence Mo species under a CH$_4$ and H$_2$-containing atmosphere at 500–600 °C, as suggested before. Therefore, the MoP and Ni$_3$P nanoparticles obtained by carbonization of the corresponding resin precursors showed better dispersions and higher surface areas than those synthesized by the traditional H$_2$-TPR route. The advantages of the resulting dispersed MoP and Ni$_3$P nanoparticles are worth further exploration.

### 4. Conclusions

In summary, dispersed pure phases of MoP and Ni$_3$P supported by carbon were successfully synthesized for the first time by thermal carbonization of metal- and phosphorus-containing resins. Carbon itself, as well as H$_2$ and CH$_4$ produced in carbonization processes, was found to act as the redundant for the formation of phosphides. Unlike the traditional H$_2$-TPR method which produced H$_2$O as the only gas product, this novel synthesis route produced a large amount of CO$_2$ besides H$_2$O. The hydrothermal sintering of phosphate particles might be mitigated due to the lowering of the water vapor pressure. The carbon generated from resin can also play a role in bonding of nanoparticle aggregation. Hence, the dispersions and surface areas of the as-prepared MoP and Ni$_3$P were superior to those of the corresponding phosphides prepared by the H$_2$-TPR method. Herein, in this study we have developed a simple and effective route for preparing dispersed MoP and Ni$_3$P nanoparticles.

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### Notes and references
