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A Novel Route to the Preparation of Carbon Supported Nickel Phosphide Catalysts by a Microwave Heating Process

Lining Ding · Mingyuan Zheng · Aiqin Wang · Tao Zhang

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Abstract A simple and efficient approach based on microwave heating process was developed to prepare carbon supported nickel phosphide. In this approach, red phosphorus was used as a P source and carbon acted as both the support and the microwave absorbent. The red phosphorus was homogeneously mixed with Ni-impregnated carbon by milling, and then subjected to microwave heating. After several minutes by microwave heating in Ar or H_2 atmosphere, the nickel phosphide, Ni_2P, was produced on the carbon support, while the temperature of the sample bed was only 473 K or even lower during the reaction. It was also found that the preparation atmosphere had significant effects on the phosphide formation. Compared to the preparation in Ar, the nickel phosphides prepared in H_2 were more readily formed and more highly dispersed on the carbon support due to PH_3 formation during the reduction process. The as-prepared nickel phosphide catalysts exhibited much higher activities in selective hydrogenation of 1,3-butadiene compared to that prepared by the conventional heating method, which was attributed to the high dispersion of Ni_2P prepared by the microwave heating method.

Keywords Carbon · Nickel phosphide · Red phosphorus · Microwave · High dispersion · Hydrogenation · 1, 3-butadiene

L. Ding · M. Zheng · A. Wang · T. Zhang (✉)
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, CAS, 116023 Dalian, People's Republic of China
e-mail: taozhang@dicp.ac.cn

L. Ding
Graduate School of the Chinese Academy of Sciences, 100049 Beijing, China

1 Introduction

Over the past decade, many research communities have shown great interest in transition metal phosphides due to their promising catalytic performances in a variety of hydrotreating reactions [1–11]. For instance, nickel phosphide (Ni_2P) has been found to be highly active for hydrogenation [2, 3], hydrodenitrogenation (HDN) [4, 11], and hydrodesulfurization (HDS) [4–10]. Stimulated by these potential applications, innovations in synthesis methods have been greatly encouraged, such as reduction of phosphates [1–11], phosphine method, [12, 13] solvothermal synthesis using elemental P as the phosphorus source [14–16], thermal decomposition of hypophosphites [17], and thermal decomposition of metal-phosphine complexes [18, 19]. For the purpose of catalysis, the catalyst must have a large surface area so as to create active sites as many as possible. In this respect, the temperature programmed reduction (TPR) of phosphates which was first developed by Oyama et al. [11], seems to be the most effective method. However, the formation process of Ni_2P from the phosphates by TPR method is neither thermodynamically nor kinetically favorable, and thereby requires a high temperature and a slow heating rate [20]. Typically, the TPR process for preparing a Ni_2P catalyst takes 8 h or even longer. Clearly, such a low preparation efficiency needs to be improved greatly.

It has been established that microwave irradiation is a low energy cost and high efficiency heating mode. Compared with conventional heating mode, the microwave heating often results in higher yields and shorter reaction time in material synthesis [21–25]. Especially, it presents unique advantages in synthesis of carbon-based materials because carbon itself is a good microwave absorbent. For example, interconnected cable-like Ag/C [26], spherical

Se/C nanocomposites [27], superparamagnetic porous Fe_3O_4/C nanocomposites [28] and nearly monodispersed nanostructured tungsten carbide particles on carbon nanotubes [29], have been successfully prepared by microwave irradiation. However, there has been no any report so far, to the best of our knowledge, on the synthesis of carbon supported transition metal phosphides by microwave irradiation in spite of their excellent catalytic performances in HDS [30].

Herein we describe a new and facile method for synthesis of carbon-supported Ni_2P catalysts by microwave heating. In this synthesis, activated carbon (AC) acts both as the support to disperse Ni_2P nanoparticles and as the microwave absorbed heating medium, while red phosphorus is used as the P source because it can readily react with metal halide at a relatively low temperature to form metal phosphide [12–14]. With the aid of microwave irradiation, the whole reaction process took only less than 7 min, significantly more efficient than the conventional heating. More important, the Ni_2P/AC catalysts prepared by this method exhibited superior performance in the selective hydrogenation of 1,3-butadiene in contrast to that prepared via the conventional heating method.

2 Experiments

2.1 Catalyst Preparation

To prepare Ni_2P/AC precursor, 3.0 g of the AC powders (Norit, $S_{BET} = 709\ m^2/g$) were impregnated with an aqueous solution of 1.677 g of nickel chloride hydrate ($NiCl_2 \cdot 6H_2O$), and then dried at 298 K overnight and at 393 K for another 3 h in air. 0.2 g of this precursor was then milled with red phosphorus at a desired Ni/P ratio in an agate mortar to give the Ni_2P/AC precursor.

The as-prepared precursor was loaded in a quartz tube reactor which was aligned vertically at the center of the microwave cavity so that the region was seated in the microwave field at maximum intensity [31]. Ar or H_2 flow was allowed to pass through the reactor at a rate of 150 mL min^{-1}. The temperature of the reaction bed was measured using an IR imager. The reaction was initiated by microwave irradiation at the working power of 50 W, and stopped until no white fume released from the reactor. After the reaction, the sample was cooled down to ambient temperature and then passivated in 0.5% O_2/N_2 (20 mL min^{-1}) for 3 h.

For comparison, a conventional heating method was also employed to prepare Ni_2P/AC catalyst. The precursor was heated in a flow reactor system as described above, but with an electric oven at a rate of 2 K min^{-1} and held at the set temperature for 90 min.

2.2 Catalyst Characterization

The XRD patterns of the catalysts were recorded on a PW3040/60 X' Pert PRO (PANalytical) diffractometer equipped with a Cu Kα radiation source ($\lambda = 0.15432$ nm), operating at 40 kV and 40 mA. The morphologies of samples were observed with transmission electron microscopy (TEM) using a JEOL JEM-2000EX microscope operated at 120 kV. The gaseous products during the synthesis were analyzed with an in situ mass spectrometer (Omini-star, GSD-300). The chemisorption of CO was conducted on a Micromeritics autochem II 2910 automated catalyst characterization system. Usually, 0.1 g of a sample was loaded in a quartz reactor and pretreated in H_2 at 773 K for 2 h. After the sample was cooled in He stream, pulses of 5% CO/He were dosed in and the metal dispersions were auto-calculated accordingly. Both the metal and P contents were determined by inductively coupled plasma (ICP) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

2.3 Catalytic Activity Tests

The catalytic performances of the Ni_2P/AC samples were evaluated for selective hydrogenation of 1, 3-butadiene. The reaction was conducted in a fixed-bed continuous-flow reactor at ambient pressure. Prior to the reaction, 0.05 g of the catalyst was reduced in H_2 at a flow rate of 20 mL min^{-1} at 673 K for 2 h and cooled to room temperature in H_2. Then, the reacting gas containing 1 vol% 1,3-butadiene, 50% H_2 and balance N_2 was allowed to pass through the reactor at a flow rate of 30 mL min^{-1}. The reaction products were on line analyzed by gas chromatography (Agilent 6890N) equipped with a flame ionization detector and a DSP capillary column.

3 Results and Discussion

3.1 Characterization of the Catalysts

Before being subjected to the microwave irradiation, the red phosphorus was homogeneously mixed with $NiCl_2$-impregnated AC support by milling. XRD pattern of the precursor with Ni/P ratio of 1/3 shows diffraction lines of well-crystallized $NiCl_2 \cdot 2H_2O$ phase (Fig. 1). The absence of red phosphorus in the XRD pattern is due to its amorphous nature. This result indicates no reaction occurs between $NiCl_2$ and red phosphorus at this stage. Upon being microwave irradiation in the Ar atmosphere, however, a fast chemical reaction took place accompanied with release of a significant amount of white fume. During the reaction, some light sparkles occurred randomly

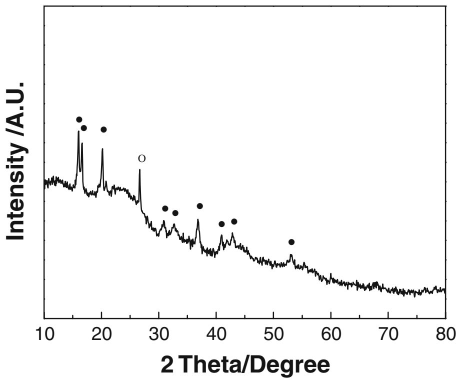

Fig. 1 XRD pattern of the precursor with Ni/P molar ratio of 1/3. (*filled circle*): $NiCl_2 \cdot 2H_2O$; (*open circle*): activated carbon

throughout the catalyst bed due to electronic discharge between the sharp points in the carbon support [32], but no obvious plasma was observed in the heating zone. Meanwhile, the temperature of the catalyst bed was rapidly increased up to 433 K within the beginning 2 min and then kept basically at this temperature in the following steady stage. The white fume produced from the heated catalyst bed was condensed at the outlet of the quartz reactor, forming some light yellow powders which are identified as white phosphorus because they will ignite upon exposed to air. After a period of less than 7 min, the white fume vanished and the reaction was stopped accordingly. Figure 2 presents the XRD patterns of the resultant samples from precursors with different Ni/P ratios. At the molar ratio of Ni to P being 1/2 (Fig. 2a), strong diffraction peaks corresponding to Ni_2P are observed, in addition to a small peak at $2\theta = 15.1°$ which is identified as $NiCl_2 \cdot 2H_2O$. This result indicates that most $NiCl_2$ reacted with red phosphorus under microwave irradiation, forming well-crystallized Ni_2P phase. Nevertheless, a small fraction of $NiCl_2$ was still intact. The reason for this is that the sublimation of red phosphorus took place simultaneously with the reaction with $NiCl_2$, as indicated by the release of white fume and formation of yellow powders at the outlet of the reactor. The sublimation of red phosphorus is inevitable, which leads to insufficient amount of P that can be used for reaction with $NiCl_2$. To promote the total conversion of $NiCl_2$ to nickel phosphide, the amount of P must further be increased.

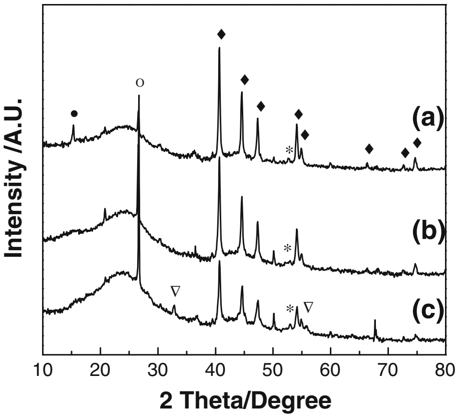

Fig. 2 XRD patterns of Ni_2P/AC catalysts prepared with different Ni/P ratios by microwave heating in Ar. **a** Ni/P = 1/2, **b** Ni/P = 1/3, **c** Ni/P = 1/5. (*filled diamond*): Ni_2P; (*asterisks*): Ni_5P_4; (*filled circle*): $NiCl_2$; (*inverse triangle*): NiP_2; (*open circle*): activated carbon

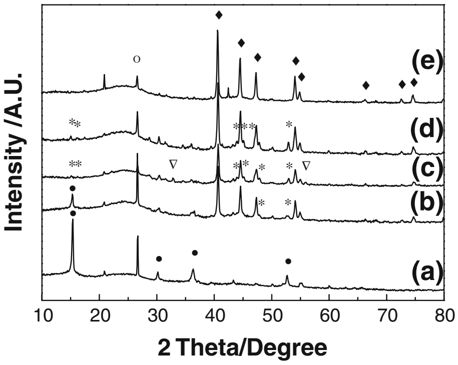

Fig. 3 XRD patterns of Ni_2P/AC catalysts prepared at different temperatures by conventional TPR method in Ar with Ni/P = 1/3: **a** 623 K, **b** 723 K, **c** 773 K, **d** 823 K, **e** 923 K. (*filled diamond*): Ni_2P; (*asterisks*): Ni_5P_4; (*filled circle*): $NiCl_2$; (*inverse triangle*): NiP_2; (*open circle*): activated carbon

As expected, at the molar ratio of Ni/P = 1/3 (Fig. 2b), the peak corresponding to $NiCl_2 \cdot 2H_2O$ disappears and diffraction peaks of Ni_2P are very strong, indicating the Ni species is completely transformed into nickel phosphides at this Ni/P ratio. With a further increase of the P amount to Ni/P = 1/5 (Fig. 2c), the intensities of the Ni_2P have some decrease while two new peaks at 32.7° and 55.7° corresponding to NiP_2 phase appear, suggesting too much excess phosphorus in the precursor favors the formation of phosphorus-rich nickel phosphides. It is also observed that the intensities of XRD peaks decrease with increasing the P content, suggesting that the excess P may lead to a decrease of the crystallinity of nickel phosphides. Evidently, Ni/P = 1/3 is the optimum ratio for the synthesis of phase-pure Ni_2P. It should be pointed out that in the three investigated samples, the formation of Ni_5P_4 seems to be inevitable although its amount is very tiny.

For comparison, conventional TPR method was also employed to prepare nickel phosphide catalyst in Ar atmosphere. The molar ratio of Ni to P was fixed at 1/3. As shown in Fig. 3a, even being treated at 623 K for 90 min, the sample still presented $NiCl_2$ diffraction peaks and no any nickel phosphides were detected by XRD. Further increasing the temperature to 723 K (Fig. 3b) led to the formation of mixed phases of Ni_2P and Ni_5P_4, and the unreacted $NiCl_2$ could still be detected at this temperature. Until up to 773 K, the diffraction peaks of $NiCl_2$ is no longer observed in the XRD patterns, indicating the Ni species in the precursor was completely transformed into Ni_2P, as well as a small amount of Ni_5P_4 and NiP_2. When the precursor was treated at the temperature as high as 923 K, phase-pure Ni_2P was obtained probably due to decomposition of Ni_5P_4 and NiP_2 into Ni_2P.

In comparison with the above conventional TPR method, the microwave irradiation manifests remarkable advantages. The reaction conditions are rather mild. The nickel phosphide can be formed at 433 K, which is around 300 K lower than that needed in the conventional heating method. The low temperature can effectively prevent the Ni_2P particles from sintering. Moreover, the reaction process under microwave irradiation is highly efficient since it takes only several minutes to finish the reaction in contrast to more than 5 h in the TPR method. According to literature [21], the excellent microwave absorbing characteristics of carbon would promote the formation of some local "hot spots" under the microwave irradiation. The reaction takes place around the hot spots whereas the average temperature of the whole catalyst bed is much lower. On the other hand, microwave heating provides a uniform reaction environment, which would facilitate the mass transfer and then speed up the synthesis process. These unique features of microwave irradiation can not be achieved by conventional heating.

Since the nickel phosphide is usually used as a hydrotreating catalyst, preparing it in a reducing atmosphere would most likely produce a catalyst with highly reduced surface and would be greatly beneficial to the catalytic reactions. Subsequently, we investigated the synthesis of nickel phoshpides under microwave irradiation in H_2 atmosphere. Similar to the phenomena observed during the preparation in the Ar atmosphere, some sparkles were generated randomly in the catalyst bed upon the microwave irradiation. The white fume of phosphorous was formed and then carried away with H_2 stream. No evident plasma was produced during the reaction. A noticeable difference from the case in Ar atmosphere is the bed temperature. The temperature of the catalyst bed was 473 K, which was 40 K higher than that in the case of Ar atmosphere. The difference in the catalyst bed temperature may be caused by the different physical properties of H_2 and Ar.

Figure 4 presents the XRD patterns of samples prepared with different Ni/P molar ratios in H_2. In contrast to the case in Ar where the molar ratio of Ni/P must be smaller than 1/2 for the complete transformation of $NiCl_2$ to nickel phosphide, the total transformation of $NiCl_2$ occurred even at Ni/P = 1/2 in H_2 atmosphere. Clearly, the presence of H_2 facilitates the formation of nickel phosphides. Further increasing the amount of phosphorus to the molar ratio of Ni/P = 1/3 and 1/5 led to the appearance of NiP_2 in addition to the predominant phase of Ni_2P. This is consistent with the results obtained in Ar atmosphere that much excess phosphorous in the precursor favored the formation of phosphorus-rich phosphides. For comparison, conventional TPR method in H_2 atmosphere was also employed to prepare nickel phosphide catalyst. Phase-pure Ni_2P phase could form only at or above 923 K (the XRD patterns are not shown here).

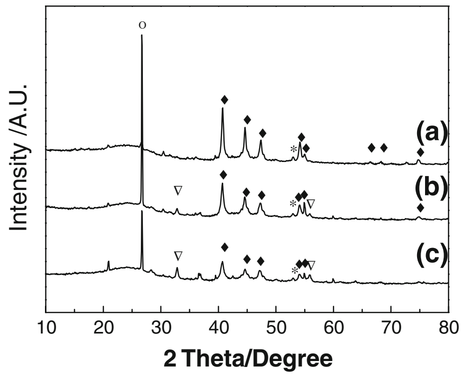

Fig. 4 XRD patterns of Ni_2P/C catalysts prepared with different Ni/P ratios by microwave heating in H_2. **a** Ni/P = 1/2, **b** Ni/P = 1/3, **c** Ni/P = 1/5. (*filled diamond*): Ni_2P; (*asterisks*): Ni_5P_4; (*inverse triangle*): NiP_2; (*open circle*): activated carbon

The gaseous products during the preparation were on line analyzed with mass spectroscopy to probe the reaction mechanism. As shown in Fig. 5a, the signals with $m/z = 31$ (P), 18 (H_2O), and 37 (HCl) were detected with the reaction time in the Ar atmosphere. In the first 2 min, only H_2O was detected, which originates from the crystalline water associated with nickel chloride. After 2 min of reaction, both HCl and P began to be detected. The reaction proceeded only about 2 min since no any other compound could be detected except H_2O. It is well known that white phosphorous is more reactive than the red one, and we did observe the formation of white phosphorus (white fume) during the reaction. Therefore, we propose that upon microwave irradiation, some local hot spots are produced on the carbon support due to the excellent microwave absorbing properties of the carbon. On or around these hot spots, red phosphorus transformed into more reactive white phosphorus, which then reacted with $NiCl_2$ according to the following pathway:

$$3NiCl_2 + 2P = 3Ni + 2PCl_3 \tag{1}$$

$$2Ni + P = Ni_2P \tag{2}$$

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl \tag{3}$$

In this reaction pathway, the white phosphorus reduces first Ni^{2+} to Ni^0, and then reacts with the Ni^0 to produce nickel phosphides. At the same time, the PCl_3 formed in the first step reacts with H_2O to form gaseous HCl. It should be pointed out that in the whole reaction process no any carbon-containing gases, such as CH_4, CO, or CO_2

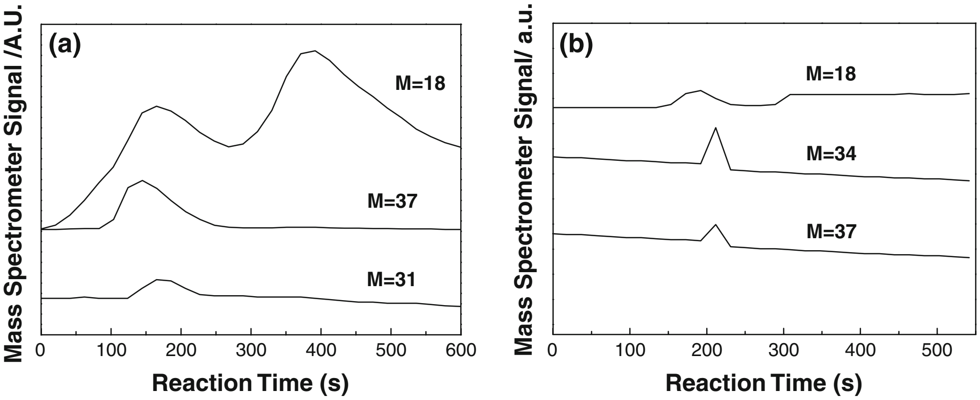

Fig. 5 Profiles of compounds with m/z of 18 (H_2O), 31(P), 34 (PH_3), and 37(HCl) in the outlet gas during the synthesis **a** in the Ar atmosphere; **b** in the H_2 atmosphere

were detected, indicating that the carbon support is inert at this temperature (the maximum bed temperature was only 433 K in the case of microwave). This is quite different from our previously reported Ni_2P where the support carbon acted also as the reducing agent for the phosphide formation at 1,073 K [33].

When the Ni_2P/AC catalyst was prepared in the H_2 atmoshpere, besides the mass of 18 (H_2O) and 37 (HCl), the mass of 34 (PH_3) was also detected (Fig. 5b). However, no PH_3 was formed when the red phosphorus was solely loaded on the carbon support without nickel chloride. This result strongly suggests that the formation of PH_3 is facilitated by the presence of Ni. Based on this, the possible reaction pathway for the formation of nickel phosphides in the H_2 atmosphere can be depicted as following:

$$NiCl_2 + H_2 = Ni + 2HCl \tag{4}$$

$$2P + 3H_2 = 2PH_3 \tag{5}$$

$$4Ni + 2PH_3 = 2Ni_2P + 3H_2 \tag{6}$$

According to this proposed mechanism, $NiCl_2$ was first reduced by hydrogen to zero-valence nickel, and then the metallic nickel catalyzed the reaction betwen H_2 and P to form PH_3. As reported in literature [12, 13], phosphine was a good P source for the nickel phosphide preparation.

The nickel phosphide catalysts prepared under four typical conditions, i.e., Ni_2P/AC (microw-H_2), Ni_2P/AC (microw-Ar), Ni_2P/AC (oven-H_2), and Ni_2P/AC (oven-Ar), were characterized with various techniques. The Ni/P molar ratios in the precursors are all 1/3. As shown in Table 1, the actual Ni/P ratio in the catalysts strongly depends on the preparation method. ICP analyses show that the samples prepared under microwave irradiation have the Ni/P molar ratio of 1:0.96 (in H_2) and 1:1.32 (in Ar), while the samples prepared under conventional heating have the Ni/P molar ratio of 1: 0.88 (in H_2) and 1:1.13 (in Ar). In each case, more than half amount of phosphorus in the precursor was lost via volatilization during the preparation, and the loss of phosphorus was even more pronounced in the conventional TPR process.

On the other hand, the Ni/P molar ratios in the four samples are all apparently lower than 2, the stochiometric ratio of Ni to P in the Ni_2P product, suggesting that some surplus phosphorus remains on the carbon support. Moreover, the Ni_2P/AC (microw-H_2) has the P content one-third less than that of the Ni_2P/AC (microw-Ar). This might be related to the phosphine formation during the preparation in the hydrogen atmosphere, which can readily remove the P from the catalyst precursor. Ni_2P/AC (oven-Ar) and Ni_2P/AC (oven-H_2), on the other hand, have similarly low P content to that of the Ni_2P/AC (microw-H_2) probably due to the long heating process allowing more phosphorus being removed.

The CO adsorption measurements reveal the remarkable difference in the number of active sites over these catalysts. The CO uptake on the Ni_2P/AC (microw-Ar) is 9.0 μmol g^{-1}, approximately three times larger than that on the Ni_2P/AC (oven-Ar) catalyst. More intriguing, the CO uptake on the Ni_2P/AC (microw-H_2) attains up to 24.8 μmol g^{-1}, which doubles that on the Ni_2P/AC (oven-H_2) catalyst. Evidently, the microwave irradiation provides the catalysts with higher dispersion due to the low bed temperature and uniform heating mode. The H_2 atmosphere results in a much higher dispersion than the Ar thanks probably to the formation of PH_3. It was previously reported that silica-supported Ni_2P catalyst with high dispersion could be obtained by reducing Ni/SiO_2 in PH_3 and H_2 [12, 13].

Figure 6 presents the TEM images of the four samples. It can be clearly seen that the particles on the Ni_2P/AC prepared by conventional heating are not uniform (Fig. 6a, d). Especially in Ar (Fig. 6a), both spherical and one-dimensional nanorods are observed, and particle sizes vary in the range of 20–200 nm. In contrast, the samples

Table 1 Characterization results of various catalysts

Catalyst[a]	Ni/P molar ratio	Particle sizes[c] (nm)	CO uptake (μmol g^{-1})
Ni_2P/AC (microw-H_2)	1:0.96	10–20	24.8
Ni_2P/AC (microw-Ar)	1:1.32	20–40	9.0
Ni_2P/AC (oven-Ar)[b]	1:1.13	20–200	2.9
Ni_2P/AC (oven-H_2)[b]	1:0.88	10–80	12.0

[a] Molar ratio of Ni to P in the precursors is always fixed at 1/3

[b] Ni_2P/AC (oven-Ar) and Ni_2P/AC (oven-H_2) were prepared at 923 K by the conventional heating method

[c] Particles sizes were estimated by the TEM images

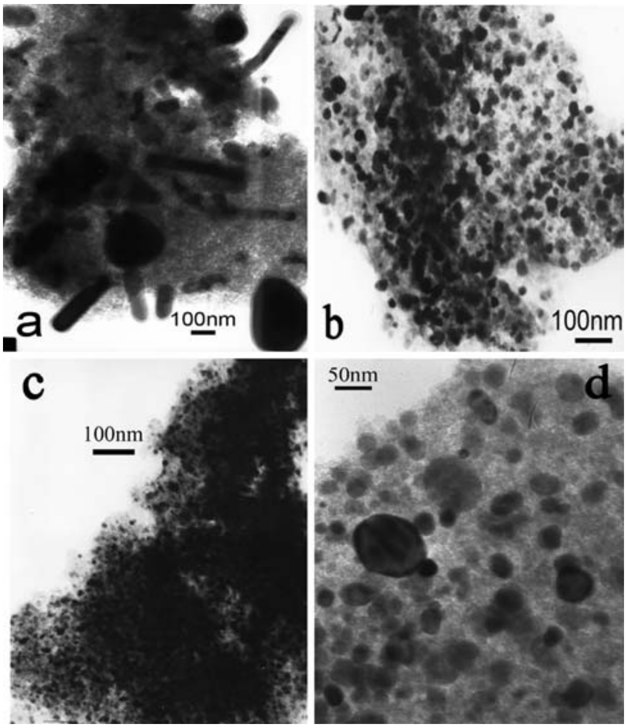

Fig. 6 TEM images of **a** Ni_2P/AC (oven-Ar), **b** Ni_2P/AC (microw-Ar), **c** Ni_2P/AC (microw-H_2), and **d** Ni_2P/AC (oven-H_2)

prepared by microwave irradiation have uniform and small particle sizes, 10–20 nm for Ni_2P/AC (microw-H_2), and 20–40 nm for Ni_2P/AC (microw-Ar). The TEM results are well consistent with the CO chemisorption data.

3.2 Catalytic Performances in Selective Hydrogenation of 1, 3-Butadiene Reaction

The catalytic performances of the Ni_2P/AC samples were evaluated for selective hydrogenation of 1, 3-butadiene, which is a subject of industrial importance for highly pure butenes production for the polymer industry [34]. The results are shown in Table 2. The four Ni_2P/AC catalysts with nominal Ni/P molar ratio of 1/3 exhibited a high selectivity towards partial hydrogenation, the selectivities to 1-butene and 2-butene were 31–38% and 60–65%, respectively, totally up to more than 96% towards the formation of butenes. Compared to the predominant occurence of 1,2-addition giving rise to 1-butene as the major product over transition metals such as Ni, Co, Pt, and Pd, [35] a distinctive feature of the Ni_2P lies in that the selectivity to 2-butene is much higher than that to 1-butene, indicating 1,4-addition governs the hydrogenation process over Ni_2P catalysts. This is consistent with the previous report [35, 36] that the presence of electronegative element such as S or P could modify the electronic property of transition metals and thereby reduce the ratio of 1-butene to 2-butene in the hydrogenation products of 1,3-butadiene. It is also noted that the ratios of *trans*-/*cis*-2-butene vary in the range of 2–3, which is in agreement with that reported on transition metals including Ni, suggesting the isomerization from *trans*-butadiene to *cis*-butadiene takes place facilely on either Ni or Ni_2P [35]. On the other hand, the amount of P imposed a great effect on the catalytic performance of Ni_2P/AC catalysts. For example, the Ni_2P (1/2)/AC catalyst prepared with microwave heating in Ar converted only 7.9% of 1, 3-butadiene at 573 K. The poor activity of this catalyst is due to the incomplete transformation of $NiCl_2$ which may cover the active sites of the Ni_2P. In contrast, the Ni_2P (1/3)/AC catalyst exhibited pretty good activity for the hydrogenation of 1,3-butadiene. However, comparing Ni_2P (1/3)/AC and Ni_2P (1/5)/AC catalysts, one can see that the excess P in the catalyst lowered the activity but meanwhile increased the selectivity to 2-butene and the *trans*-/*cis*-2-butene ratio in the product. Furthermore, the activities of the Ni_2P/AC catalysts prepared at the fixed Ni/P ratio of 1/3 depend strongly on the preparation methods. For example, at a reaction temperature of 433 K, the conversion of 1, 3-butadiene reached 93.6% over the Ni_2P/AC (microw-H_2) catalyst, while it was only 65.3% over the Ni_2P/AC (oven-H_2). Only at an elevated reaction temperature (e.g., 463 K) was the conversion of 1, 3-butadiene over the Ni_2P/AC (oven-H_2) more than 90%. Similarly, the Ni_2P/AC (microw-Ar) behaved more actively than the Ni_2P/AC (oven-Ar), but less than the Ni_2P/AC (microw-H_2). At the same Ni/P ratio

Table 2 Results of selective hydrogenation of 1,3-butadiene over different Ni_2P/AC catalysts

Catalyst[a]	Reaction temp. (K)	Conv. (%)	Sel. of butene (%)	Selectivity (%)			
				n-Butane	1-Butene	*trans*-2-Butene	*cis*-2-Butene
Ni_2P (1/3)/AC (microw-H_2)	433	93.6	97.2	2.8	34.0	46.8	16.4
Ni_2P(1/3)/AC (microw-Ar)	433	51.1	97.7	2.3	33.8	48.1	15.8
Ni_2P(1/3)/AC (microw-Ar)	473	91.1	97.5	2.5	37.6	41.5	18.4
Ni_2P(1/2)/AC (microw-Ar)	573	7.9	100	0.0	3.1	3.0	1.8
Ni_2P(1/5)/AC (microw-Ar)	573	48.9	100	0.0	13.9	25.6	9.4
Ni_2P(1/3)/AC (oven-H_2)	433	65.3	97.4	2.6	34.6	45.8	17.0
Ni_2P(1/3)/AC (oven-H_2)	463	92.6	96.3	3.7	36.8	40.1	19.4
Ni_2P(1/3)/AC (oven-Ar)	433	36.5	95.9	4.1	31.3	49.6	15.0
Ni_2P(1/3)/AC (oven-Ar)	523	94.6	97.7	2.3	35.3	45.6	16.8

[a] The figures in parenthesis after the Ni_2P indicate the molar ratios of Ni to P in the preparation precursors

of 1/3 (in the precursor), the activities follow the order of Ni_2P/AC (microw-H_2) > Ni_2P/AC (oven-H_2) > Ni_2P/AC (microw-Ar) > Ni_2P/AC (oven-Ar), totally in line with the dispersion of the active sites as measured by CO adsorption. Therefore, we can conclude that microwave irradiation in the H_2 atmosphere is a facile and effective way to prepare carbon supported phosphide catalysts with high dispersion and excellent catalytic performance.

4 Conclusion

A novel method based on microwave heating has been developed for synthesis of activated carbon supported nickel phosphide from precursors containing $NiCl_2$ and red phosphorus. In contrast to the high temperature and long reaction time needed in the conventional TPR method, our present microwave approach has the advantages of short reaction time and low bed temperature. The Ni_2P phase was formed even in several minutes at a low temperature of 433–473 K. The atmosphere also imposed an important effect on the dispersion of Ni_2P particles. H_2 leads to higher dispersion of active sites than Ar due to the formation of PH_3 in the former case, and then results in a higher activity for 1,3-butadiene hydrogenation. This method can also be extended to synthesis of other transition metal phosphides.

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