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Phosphorus and nitrogen-doped palladium nanomaterials support on coral-like carbon materials as the catalyst for semi-hydrogenation of phenylacetylene and mechanism study



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ABSTRACT

In this work, two types of polyporous and coral-like materials (CN) with high specific surface area are prepared using sodium glutamate as a carrier. At the same time, a CN-supported phosphorus-nitrogendoped palladium nanomaterial CN-P-Pd is synthesized and applied to the preparation of styrene by selective hydrogenation of phenylacetylene under mild conditions. As shown in the TEM images, Pd nanoparticles with a particle size of about 4.4 nm are uniformly dispersed on the surface of the carrier. The results of N₂ adsorption-desorption reveal that the surface area of the prepared catalyst (CN-P-Pd) is 1307 m²g⁻¹. In addition, the experimental exploration shows the intervention of P in carbon-nitrogen materials can contribute to improve the selectivity of the reaction, which can be attributed to the fact that P element can change the electron density of Pd. Meanwhile, it is found that the solvent not only affects the activity of catalyst, but also the selectivity of the reaction. Kinetic study shows the activation energy of the reaction is 4.5 kl/mol. With the increase of the reaction temperature, the dissolution rate of hydrogen in the solvent gradually slows down, which inhibits the progress of the reduction reaction. Mechanistic studies demonstrate that the carbon-nitrogen materials have strong adsorption capacity for substrates, and also provide more adsorption sites for phenylacetylene. Additionally, the optimal catalyst (CN-P-Pd) also has high reaction activity to other alkynes and the conversion can reach at 95%. Moreover, the optimal catalyst can be reused several times without significant reduction in reaction activity.

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1. Introduction

Reaction of selective reduced acetylene compounds plays an important role in industrial and chemical research. Production of sedatives, anesthetics, vitamins and fragrances require the selective reduction of acetylene compounds [1,2]. In particular, the selective hydrogenation of phenylacetylene to styrene has been widely used in the polymerization industry, and the catalyst for the industrial reaction is $Pd/CaCO_3$ treated with Pd [3,4]. However, the disadvantage of this type of catalyst is that the selectivity to alkene is low and the introduced Pb element is very harmful to the environment and human health. Researching other Pb-free and high

selectivity alkene catalysts to replace the industrial catalyst is attracting the research interest. There a number of metals such as Pd, Au, Pt, Rh, Ni and Ru [5], which can catalyze selective hydrogenation of phenylacetylene [6–9]. Nonetheless, the catalytic effects of these catalysts still need to be improved in terms of selectivity to alkene. Hence, it is still of great significance to develop a catalyst for improving the selectivity of alkene.

Many studies have reported the use of palladium modified by doping other metals or changing the support to improve the selectivity of the catalyst [10,11]. At present, the most researched is the modification of palladium with transition metals. Ni modified Pd nanoparticles catalyst (Pd/Ni-N/C) perform high selectivity of alkene with 96.8% [12]. And Cu modified Pd nanoparticles catalyst of PdCu/ Al₂O₃ produce 86.3% selectivity [13]. Ag also can modify Pd to prepare the catalyst Ag₇₅Pd₂₅, which selectivity is 87.5%. In general, there are many reports investigated transition metals modification the Pd and performed highly selective hydrogenation of the

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phenylacetylene to styrene [14–18]. Although these catalysts could perform well with regard to conversion and selectivity, the participation of noble metals and high reaction pressure also restrict the application in industry. At the same time, a good carrier is also one of the factors that affect the reaction conversion [5,19–21]. Carriers can not only increase the dispersion of palladium nanoparticles but also change the electronic state of palladium to increase selectivity of reaction [18,22,23]. Pd/CeO₂ catalyst produces 97.4% selectivity with conversion of 70.3% [24]. Pd/MCF-ss catalyst produces 88% yield of the styrene with conversion of 100% [25]. Nitrogen doped carbon material is believed a great carrier [26,27], which has high surface area, better stability and electrical conductivity [28–30]. The lone pairs of electrons of nitrogen or phosphorus atom can modify the palladium nanoparticles and fix the Pd nanoparticles to increase the recyclability of the catalyst [25,31]. Up to now, Pd catalyst doped with P has been extensively studied in oxidation reaction [32–34]. However, to our knowledge, there has been no report on the doping of P and N elements on Pd-supported carbon materials in the selective hydrogenation of phenylacetylene to styrene.

In this work, two types of high surface area polyporous and corallike carbon materials were synthesized from sodium glutamate [11]. Moreover, the P and N doped Pd nanoparticles supported on polyporous and coral-like carbon materials are also prepared and applied to selectively hydrogenate phenylacetylene under mild reaction conditions. Experimental exploration shows the prepared catalyst has high surface area (1307 m²g⁻¹) and the Pd nanoparticles are uniformly dispersed on the surface of the carrier from TEM images. Furthermore, the catalyst can reach high selectivity (98.1%) and high conversion rate (99.9%) under the conditions of 25 °C and H₂ (1 atm). In addition, recyclability was also implemented, and it was found that the conversion rate and selectivity did not significantly decrease after 5 cycles. Finally, the mechanism and kinetics of the reaction were also studied.

2. Experimental section

2.1. Materials

All the reagents and solvents used in the synthesis of catalyst were purchased from commercial sources without further purification unless otherwise stated. Palladium acetate and phenylacetylene were purchased from Sigma Aldrich.

2.2. Preparation of the precursor (CN)

Firstly, to a one-necked 50 mL round-bottomed flask equipped with a mechanical stirrer were added sodium glutamate (2 g), sodium salt (4 g) and deionized water (15 mL). The reaction was heated at 80 °C for 2 h with vigorous stirring until the water was completely evaporated. Subsequently, the mixture was cooled to room temperature and collected, followed by washing with ethanol (3 × 20 mL) and drying in a drying oven at 80 °C overnight. Lastly, the powder was fully ground and calcined at 800 °C for 2 h under N₂ atmosphere. The black powder was obtained and washed by deionized water for three times, followed by drying in a vacuum drying oven at 60 °C for 24 h. Finally, the synthesized powder was named by CN. Furthermore, different ratios of CN were produced separately. And named CN_x (x = m (sodium choride)/m (sodium glutamate)).

2.3. Preparation of the CN-Pd and CN-P-Pd

Firstly, a mixture of CN (50 mg) and palladium acetate solution in acetonitrile (2 mg/mL, 0.5 mL (0.25 or 1 mL)) was added to roundbottom flask and then 5 mL of absolute ethyl alcohol was also added. Next, the absolute ethyl alcohol was evaporated to dry at 80 °C under magnetic stirring, and then a mixed powder of Pd and CN was



Fig. 1. Preparation of the carbon materials and catalysts.

obtained. Finally, the mixture was calcined at 400 °C for 4 h under H_2 atmosphere. After cooled to room temperature, the CN-Pd catalyst was collected and thoroughly ground. In addition, the preparation of the CN-P-Pd was the same as the CN-Pd except adding 2 g phosphate source when calcined under H_2 atmosphere.(Fig. 1).

2.4. Catalysts test

The selective hydrogenations of the substrate reactions were conducted in round-bottom flask under H_2 (1 atm). The progress of the catalysts test was as follows: substrate (1.5 mmol), catalysts (5 mg) and solvent (15 mL) were mixed in the round-bottom flask and the reaction was continued for 0.5 h under vigorous stirring at temperature of 25 °C and hydrogen pressure of 1 atm. Subsequently, the product was collected, filtered, extracted and further analyzed by GC-MS (Agilent 6, 890 N/5, 937 N).

The activity of the catalysts were calculated as follows: conversion (%) = $100 \times ([C_0]-[C_1]/[C_0])$, selection (%) = $100 \times ([C']-[C''])/[C']$, TOF = $(C_0-C_1) \times V/(M_{Pd})$, The substrate concentration at the beginning and end of the reaction was represented by $[C_0]$ and $[C_1]$, respectively. Similarly, [C'] and [C''] were the concentrations of the product and target product at the end of the reaction, respectively. And M_{Pd} was mole number of Pd in catalyst.

3. Results and discussion

3.1. Characterization of catalysts

The crystal structure and phase composition of the catalysts were systematically investigated by using X-ray powder diffraction (XRD) patterns and Raman. The XRD pattern is shown in Fig. 2a, which shows that the catalyst has two strong orthogonal peaks. The two strong peaks at 40° and 46° are corresponding to the (111) and (200) crystal planes, respectively. Which showing the typical crystallization mode of Pd particles (JCPDS-65-2867). Besides, the XRD pattern also showed that the Pd supported on the CN material is in the form of the elementary substance. Raman scattering spectroscopy is shown the detail defect information of the catalyst and CN (Fig. 2b). The two peaks at about 1350 cm⁻¹ and 1580 cm⁻¹ correspond to the characteristic D band and G band of graphitized carbon, respectively, indicating the formation of structural defects in the graphitic plane and the E_{2g} vibrational mode of the sp²⁻ bond graphitic carbons [35,36]. The intensity of the D band and G band (I_D/I_G) shows the degree of lattice defects and graphitization of the carbon materials. In addition, it is worth noting that the I_D/I_G ratios of the



Fig. 2. (a) XRD pattern of the catalyst, (b) Raman of the CN and CN-P-Pd.

CN and CN-P-Pd are both 0.92, indicating that the carbon materials have a strong degree of graphitization and doped P and loaded Pd do not affect its graphitization.

The scanning electron microscopy (SEM) images shown in Fig. 3. The morphology of CN and CN-P-Pd-1.4 is shown in Fig. 3a and b, which demonstrate the polyporous and coral-like structural characteristics. By carefully observing its structure, we can find that the porous structure has slightly changed after phosphating, which may be attributed to the temperature change and the loading of palladium particles for the second calcination. Similarly, Fig. 3c and d show the projection electron microscope images of CN and CN-P-Pd-1.4, respectively. It can be seen from Fig. 3c that CN exhibits a porous structure, which is consistent with the result of Fig. 3a. However,

Fig. 3d is the pattern of the CN-P-Pd-1.4, which clearly indicates that the structure of the carbon material is altered by doping of P and Pd, and part of the coral-like porous structure characteristics has changed significantly due to the collapse of the structure. Generally, it also indicates that the structure of carbon materials does not change significantly with the intervention of P and Pd. The AFM image in Fig. S2 demonstrates the diameter of Pd nanoparticles on the CN-P-Pd-1.4 is about 15 nm and highly dispersed on the CN materials.

The transmission electron microscopy (TEM) images showed in Fig. 4. The TEM image of the CN-P-Pd-1.4 is illustrated in Fig. 4a and b. In detail, according to the particle size statistics, the particle size of the Pd nanoparticles range from 2 to 8 nm. It is worth noting that



Fig. 3. (a) and (b) SEM image of the CN, (c) and (d) SEM image of the CN-P-Pd-1.4.



Fig. 4. (a) HRTEM of the CN-P-Pd-1.4, (b) TEM images of the CN-P-Pd-1.4, (c) HAADF-STEM image of the CN-P-Pd-1.4, (d-g) mapping of the C, N, P and Pd.

particles with the particle size of 3.5 nm are about 40% of all the particles. Moreover, the average size of the Pd nanoparticles is about 4.4 nm (the inset in Fig. 4b). HRTEM and Fourier transformation (FFT) images are shown in Fig. 4a which is the enlarged view of the Fig. 3d, the lattice fringes of the Pd can further explain that the particles are Pd nanoparticles. In Fig. 4a, the spacing of lattice fringes are 0.23 nm and 0.195 nm, which correspond the lattice plane of the Pd (111) and Pd (200), respectively. Additionally, the angle of the two lattice fringes is 54.7°, which is the characteristic angle of the Pd nanoparticles, corresponding to JCPDS 65-2867 and the result of the XRD (Fig. 2a) [37]. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and the Mapping results of different element in Fig. 4(c-g). The Mapping of the C and N element indicating that they are uniform distribution. Additionally, the P and Pd are successful doped on the carbon materials. Moreover, the mapping images also show that content of the Pd and P are lower than the content of the C and N.

The surface area and pore size are all have a large impact on the activity of the catalyst. The surface area and pore size of the prepared catalyst are analyzed by Nitrogen adsorption–desorption. Fig. 5 demonstrates that both CN and CN-P-Pd-1.4 have mesoporous properties. Minutely, Fig. 5a exhibits that the initial quantity adsorbed are not from zero, which due to the unique micropore character of the carbon materials and catalyst. In addition, the order of the initial quantity adsorbed of the materials sort from large to small are CN and CN-P-Pd-1.4, which indicates that the CN has a large micropore volume and the doped Pd can reduce the micropore volume. The microporous characters of CN were investigated by nitrogen adsorption-desorption as shown in Fig. 5c and d, which reveals that the CN have micropore characteristic. Pore width images shown in Fig. 5b, revealing that the pore width rages from 2 nm to 5 nm. The surface area and average of the pore width and pore volume are shown in Table 1. The surface area of the CN-P-Pd, which is 1307 m^2g^{-1} lower than the surface area of CN, reveals that doped Pd and P can decrease the surface area. Meanwhile, the surface area of the CN-P-Pd-1.4 is also pleasant. The volume of the CN and CN-P-Pd are 0.91 cm³g⁻¹ and 0.72 cm³g⁻¹, respectively. Which not only indicates that the introduction of Pd and P effectively reduces the volume of CN, but also explains that Pd nanoparticles are uniformly dispersed in the tunnel. The pore size analysis of CN and CN-P-Pd-1.4 indicate the loaded Pd and P doping have little effect on the pore size. In general, the prepared carbon materials and catalyst have characteristics of large surface area, large pore volume and small pore size. Meanwhile, the enhance in the reactivity of the optimum catalyst is closely related to the porous structure and these characteristics.

X-ray photoelectron spectroscopy (XPS) is employed to determine the chemical composition and valence states on the surface of the catalyst. Generally, Fig. 6a shows the full scan spectra of the CN-Pd-1.4 and CN-P-Pd-1.4. The two strong peaks of 285 eV and 532 eV correspond to C 1s and O 1s respectively. In addition, two weak peaks are N 1s and Pd 3d, demonstrating the surface of catalyst is composed of C, N, O, P, and Pd elements. High resolution spectra of C 1s is shown in Fig. 6b, which can be deconvoluted two peaks of C-C and C-N correspond to 284.6 eV and 285.7 eV, respectively [38,39]. High resolution spectra of N 1s (Fig. 6c) is deconvoluted into two peaks of graphite nitrogen and pyridine nitrogen at 401.1 eV and 399.1 eV, respectively [40,41]. Fig. 6d shows the high resolution spectra of P, peak at 133.5 eV is assigned to oxidized phosphorus [42]. Similarly, Fig. 6e illustrates the high resolution spectra of Pd, two peaks observed at binding energies 335.6 eV and 341.2 eV corresponding to the $Pd^0 3d_{5/2}$ and $Pd^0 3d_{3/2}$, revealing that the valence state of Pd in catalyst is zero [43,44]. The high resolution spectra of Pd in CN-P-Pd-1.4 and CN-Pd-1.4 are shown in Fig. 6f and it can be



Fig. 5. (a, b) N2 adsorption-desorption isotherms and the corresponding pore size distribution of the catalyst, (c, d) mesoporous and micropore analysis of CN.

Table 1 N_2 adsorption-desorption analysis of the CN and CN-P-Pd-1.4.

Sample	Surface area	Average pore	Pore volume
	(m²/g)	width (nm)	(cm ³ /g)
CN	1632	2.25	0.91
CN-P-Pd-1.4	1307	2.22	0.72

found that the Pd^0 peak of CN-P-Pd-1.4 is shift by 0.8 eV compared to the Pd^0 peak of CN-Pd-1.4. Similarly, an offset occurred at 338 eV. The shift of the binding energy reveals that the electron density of Pd decrease in the 3d, and the center of the p-band in Pd have a slight down-shift, which is attributed to the P-Pd bond formed by P and Pd [45].

3.2. Performance of catalysts

The catalytic performances of all catalysts are shown in Table 2. Generally, entry 1–4 indicate that the CN material is not reactive toward the phenylacetylene hydrogenation reaction. Effect of Pd loading on catalytic activity is shown in entry 5–14, demonstrating that the Pd catalyst with mass fraction is 1.4 wt% has the best catalytic activity. Obviously, lower or higher mass fraction of Pd all not perform the well activity. In addition, the optimal ratio of catalysts such as entry 5 and entry 9 can have a significant effect on catalytic activity. This may be attributed to the better dispersion of Pd particles on the CN material. The reaction time of the entry 12 is 1 h,

reflecting that prolong reaction time did not achieve expected goal. Besides, the selectivity of the catalyst can be significantly improved when phosphorus is incorporated as illustrated entry 14, and it can be seen that when doped the P element, the electron density of Pd decrease in the 3d from Fig. 6f. Hence, we conclude that this catalyst perform highly selectivity is due to the fact that intervention of P can change the electron cloud density of Pd. Generally, we can draw a conclusion that catalyst of CN-P-Pd-1.4 perform the highest selectivity and conversion, which is demonstrated by the higher TOF value (4542 h⁻¹).

The effect of solvent on selective reduction of phenylacetylene are shown in Table 3. From entry 1, it is known that high conversion and selectivity can be achieved when methanol is used as a solvent. However, the ethyl acetate as the solvent could not promote the reaction, we can infer that H_2 is insoluble in ethyl acetate, which makes it difficult for H_2 to contact with phenylacetylene and thus cannot promote the reduction of phenylacetylene. Compared the results of entry 1–5 and entry 6–11, we can conclude that catalyst exhibits a higher catalytic activity when alcohol compounds as the solvent than other compounds are more suitable as the solvent for selective hydrogenation of phenylacetylene. Hence, we choose the methanol as the optimal solvent for semi-hydrogenation of phenylacetylene to styrene.

Furthermore, the progress of the reaction is also affected by the concentration of phenylacetylene. Fig. 7 shows the relationship between reaction rate and concentration of phenylacetylene. As can be



Fig. 6. (a) Full scan XPS spectra of the catalyst, high resolution spectra of (b) C, (c) N, (d) P, (e) Pd, (f) Pd.

Table 2Catalytic performances of all the catalysts^a.



Entry	Catalyst	Conversion (%)	Selectivity for 2 (%)	$TOF(h^{-1})$
1	CN	0	0	0
2	CN ₁	0	0	0
3	CN _{1.5}	0	0	0
4	CN _{2.5}	0	0	0
5	CN-Pd-1.4	99.9	91.3	4544
6	CN1-Pd-1.4	84.4	65	2263
7	CN _{1.5} -Pd-1.4	95.6	71	2979
8	CN _{2.5} -Pd-1.4	90.1	84.2	3654
9	CN-Pd-0.8	41.1	99.5	3267
10	CN _{1.5} -Pd-0.8	35.2	91.1	2551
11	CN _{2.5} -Pd-0.8	37.4	94.3	2875
12 ^b	CN-Pd-0.8	75.2	96.1	2989
13	CN-Pd-3.0	99.9	78.2	1060
14 ^c	CN-P-Pd-1.4	99.9	98.1	4542

Reaction condition:

 $^a\,$ Phenylacetylene (1.5 mmol), catalyst (5 mg), solvent (15 mL), H_2 (1 atm), reaction time (0.5 h), temperature (25 °C).

^b Reaction time (1 h).

 $^{\rm c}~$ ICP shows the mass fraction of the P is 0.8 wt%.

seen in Fig. 7, we can conclude that when 5 mL of methanol is added, the reaction rate is significantly lower than other volumes of solvent. Therefore, it can be inferred that the dissolution rate of hydrogen is lower than its hydrogenation rate when the solvent is less, thus resulting in a decrease in the rate of reaction. Inversely, the reaction rate also demonstrated downward trend when the amount of the solvent was too large, which is attributed to the fact that the phenylacetylene cannot not adsorbed well to the catalyst, thus making the reaction did not proceed smoothly. Based on the above experimental exploration and analysis, 15 mL methanol as the optimum solvent volume.

Table 3Effect of solvent on selective reduction of phenylacetylene^a.

Entry	Solvent	Conversion (%)	Selectivity (%)	TOF h^{-1}
1	Methanol	99.9	98.1	4542
2	Ethanol	95.2	93.7	4323
3	Isopropanol	92.3	95.2	4192
4	Tertiary butanol	50.1	28	2290
5	n-butyl alcohol	78.4	61.5	3560
6	Ethyl acetate	0	0	0
7	Cyclohexane	71.3	78.2	3238
8	Acetonitrile	40.8	21.6	1853
9	Methylbenzene	52.1	40.5	2366
10	1,4 dioxane	61.3	98.5	2784
11	o-xylene	50.6	59.2	2298

 a Reaction condition: Phenylacetylene (1.5 mmol), catalyst (5 mg), solvent (15 mL), H₂ (1 atm) reaction time (0.5 h), reaction temperature (25 °C).



Fig. 7. Relationship between reaction rate and concentration of phenylacetylene. Reaction condition: phenylacetylene (1.5 mmol), catalyst (5 mg), solvent (methanol), H_2 (1 atm), temperature (25 °C).

Table 4

CN-P-Pd-1.4 selective	hydrogenation	of other	acetylene	compounds. ^a .
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⁽a) Reaction condition: acetylene compounds (1.5 mmol), catalyst (5 mg), methanol (15 mL), H2 (1 atm), reaction time (30 min), reaction temperature (25 °C). (b) Reaction time (50 min) other reaction condition are the same as the (a).

Through exploring experimental conditions, the best reaction condition of semi-hydrogenation of phenylacetylene to styrene is CN-P-Pd-1.4, methanol (15 mL), H_2 (1 atm) at 25 °C for 0.5 h.

In order to more comprehensively and extensively evaluate the excellent universality of the CN-P-Pd-1.4, experiments with different alkyne substrates are carried out and the results are illustrated in Table 4. Obviously, the CN-P-Pd-1.4 also has excellent catalytic activity for other acetylene compounds. Aromatic alkyne such as 4-methylphenylacetylene and 4-aminophenylacetylene as the substrate, the catalyst performs well conversion and selectivity than other acetylene compounds. In addition, entry 1, 4 and 7 prove that when the substrate contains an electron withdrawing group, the catalyst performs higher selectivity. Moreover, we also prolong the reaction time of entry 4 and 7 for other 20 min, and find that the selectivity of the two compounds slightly decreased. In general, the prepared catalyst of CN-P-Pd-1.4 have well performance for selective hydrogenation other acetylene compounds.

In addition to favorable catalytic activity, an outstanding heterogeneous catalyst should also have reliable recyclability and stable reusability.[46] Thus the recyclability and reusability of the CN-P-Pd-1.4 were investigated for selectivity hydrogenation of the phenylacetylene to styrene and illustrated in Fig. 8. The conversion and selectivity are also reliable after three times recycle of the catalyst. While the conversion rate drops to 90% after four or five recycle times, the selectivity remains reliable. We also collected the reaction solution for filtering out the catalyst after one recycle and continue react under the hydrogen atmosphere and 25 °C for other 30 min. The conversion and selectivity are also the same as the conversion and selectivity of one cycle, indicating that only a small amount of



Fig. 8. The recyclability and reusability of the CN-P-Pd-1.4. Reaction condition: phenylacetylene (1.5 mmol), catalyst (5 mg), methanol (15 mL), H_2 (1 atm), reaction time (30 min), reaction temperature (25 °C).



Fig. 9. Kinetic study of the selective hydrogenation of phenylacetylene (a and b) and styrene (c and d) with the CN-P-Pd-1.4 as the catalyst. Reaction condition: phenylacetylene (3 mmol), catalyst (5 mg), methanol (15 mL), H₂ (1 atm).

palladium is detached from the catalyst. In general, the prepared catalyst (CN-P-Pd-1.4) performs well recyclability and reusability.

To further understand the reaction mechanism, the kinetic study was investigated the reaction of selectivity hydrogenation phenylacetylene to styrene. The reaction conditions are phenylacetylene (3 mmol), methanol (15 mL), H₂ (1 atm). The relationship between reaction rate and reactants is expressed by formula (1). Additionally, the pressure of H₂ can be considered with a constant due to the H₂ pressure is always maintained at 1 atm as the reaction progresses. The formula (2) can be changed from the formula (1), and the reaction is pseudo *b* order reaction for substrate. Hence, the reaction rate is derived from the concentration of phenylacetylene varies with reaction time and the order of reaction can be obtained from formula (2). The activation energy can be calculated by Arrhenius formula (6).

$$r = k' P^{a}_{(H_2)} [c]^{b}$$
(1)

$$r = k[c]^b \tag{2}$$

$$\ln K = \ln A - E_a/RT \tag{3}$$

Where [*c*] is the concentration of phenylacetylene, *P* is the pressure of the H₂, *k* and *k'* represents the rate constant, and the *a* and *b* are the reaction order of the H₂ and [*c*], respectively. The activation energy is represented by Ea. The ideal gas constant (8.314 J mol⁻¹ K⁻¹) and the reaction temperature are represented *R* and T,

respectively. The relation between concentration of the phenylacetylene and reaction time was shown in Fig. 9a and the reaction rate can be obtained by analyzed. In addition, the relation between reaction rate and concentration of the phenylacetylene is shown in Fig. 9b. From Fig. 9b, we can know that $lnk_{25\,°C}$ and $lnk_{35\,°C}$ are 0.72 and 0.78, respectively. The activation energy Ea of the reaction was found to be 4.5 kJ/mol by the calculation of the Allenbius formula for the selective hydrogenation of phenylacetylene with a CN-P-Pd-1.4 catalyst. Fig. 9c and d illustrate the kinetic study of the hydrogenation of the styrene with Ea is 17.5 kJ/mol. Kinetic study of selective hydrogenation of phenylacetylene and styrene demonstrates that the CN-P-Pd-1.4 performs distinguished selectivity for selective reduction of phenylacetylene.

To investigate the mechanism of the semi-hydrogenation of phenylacetylene to styrene, FT-IR and XPS conducted in-depth exploration of the reaction process. The FT-IR of the adsorption of phenylacetylene by CN-P-Pd-1.4 and CN-P-Pd-1.4 is illustrated in Fig. 10a. It can be distinctly observed that two new peaks appear at 694 and 756.3 cm⁻¹ after the adsorption of phenylacetylene, which indicates that the phenylacetylene has been adsorbed on the surface of the catalyst before the reaction occurs. To explore the adsorption site for adsorption of phenylacetylene, XPS characterization of catalysts adsorbing phenylacetylene was performed (Fig. 10b). In detail, Fig. 10b is the fine spectrum C 1s of CN-P-Pd-1.4 and CN-P-Pd-1.4 after adsorbing phenylacetylene. It can be found that one new peak occurred at 288.8 eV, which reveals that the phenylacetylene is



Fig. 10. (a) FT-IR and (b) XPS of CN-P-Pd-1.4 and CN-P-Pd-1.4 adsorption of phenylacetylene.



Fig. 11. Proposed reaction mechanism.

successfully adsorbed on the C atom. As a result, we infer the emergence of the new peak is attributed to the interaction between the C atom in phenylacetylene and the π electron of the benzene ring.

Based on the above experimental results, a possible reaction pathway of the chemo-selective hydrogenation process catalyzed by CN-P-Pd-1.4 catalyst is proposed in Fig. 11. The semi-reduction of phenylacetylene to styrene would proceed in several consecutive steps. Firstly, the phenylacetylene was adsorbed on the surface of carbon materials and the C atoms in the phenylacetylene interact with the π electrons of the benzene ring. Meanwhile, the H₂ was adsorbed on the surface of Pd nanoparticles and decomposed into hydrogen atoms on electronically Pd surface. [47] Secondly, -C=CH is combined with hydrogen and converted into-CH=CH₂, and then the product of styrene is desorbed from the surface of the C atom, which can effectively prevent further hydrogenation reactions and improve the selectivity of the catalyst. Moreover, CN-P-Pd-1.4 also has a larger specific surface area, which can provide more adsorption sites and promote the distribution of palladium nanoparticles with a smaller particle size. Besides, the intervention of phosphorus can change the electron density of Pd, thereby increasing the selectivity of the catalyst to styrene. These properties together promote the significant improvement of the catalytic activity and selectivity of CN-P-Pd-1.4. These properties all co-contributed to the significant improvement of catalytic activity and selectivity of the CN-P-Pd-1.4.

4. Conclusions

The results of the study present an efficient Pd supported on a large surface area carbon materials catalyst for selective hydrogenation of phenylacetylene to styrene. Through experimental exploration and screening, the optimal loading of palladium nanoparticles is 1.4 wt%, and we also find that doping with P element can significantly improve the selectivity of the catalyst. In addition, we acknowledge that the solvent affects the reaction rate and has a great influence on the selectivity of the catalyst. The optimum catalyst of the CN-P-Pd-1.4 have remarkable conversion and selectivity to hydrogenation of phenylacetylene to styrene and have highly reaction activity to other acetylene compounds. After kinetic study, the activation energy of the selectivity hydrogenation of phenylacetylene to styrene is 5.4 kJ/mol. Furthermore, mechanism study shows the carbon atoms is the adsorption site. Moreover, the catalyst still maintains excellent catalytic activity after recycling many times. Generally, the prepared CN-P-Pd-1.4 catalyst is outstanding heterogeneous catalysts for semi-hydrogenation of phenylacetylene to styrene.

CRediT authorship contribution statement

Lei Ma, Pengbo Jiang and Kaizhi Wang are responsible for the selection of manuscripts. Lei Ma, Li Gong and Xiao Mu are responsible for the design and implementation of the experiment. Lei Ma, Kai Lan, Xiaokang Huang, Ming Yang, Qi Jia, Xiao Mu, Yucong Xiong are responsible for the analysis and processing of experimental data. Lei Ma wrote the manuscript and Rong Li has revised the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at 10.1016/j.jallcom.2021.159047.

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