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Promoting Role of Iron Series Elements Modification on Palladium/Nitrogen Doped Carbon for the Semihydrogenation of Phenylacetylene

Wei Zhang,^[a] Wei Wu,^[a] Yu Long,^[a] Jiaheng Qin,^[a] Fushan Wang^[b] and Jiantai Ma*^[a]

Abstract: In this work, an effective and versatile modification approach of palladium (Pd)/nitrogen doped carbon by iron series element for the semihydrogenation of phenylacetylene is presented. Pd and iron series element M (M= Fe, Co or Ni) particles were co-reduced and supported on nitrogen-doped activated carbon (Pd-M/NC). Experimental results showed that the Pd-M/NC exhibited relatively good catalytic performance when the Pd/M content mass ratio was approximately 1:1. The selectivity of styrene could be maintained at relatively good levels even with the prolongation of reaction time. The good catalytic effect of the Pd-M/NC may be attributed to the incorporation of iron series element species. The catalysts had been characterized in detail and contrastive study was made to validate the modification effect. The catalyst could maintain its catalytic activity and selectivity in the recycle process. This work may show industrial application potentiality and developing directions in selective hydrogenation process.

Introduction

Styrene is an important monomer for producing polystyrene, acrylonitrile butadiene styrene (ABS) resin and styrene-butadiene rubber (SBR) in industry. However, phenylacetylene is a harmful substance in styrene raw materials, which is easy to cause the poisoning of polymerization catalyst and affect the polymerization degree. Therefore, removing phenylacetylene from crude styrene is an important step in producing high quality styrene monomer. In industry, selective hydrogenation is the most popular and efficient way of removing alkynes presented in alkenes or converting alkynes into alkenes.^[1] Because phenylacetylene hydrogenation is a cascade reaction, intermediate styrene will be over-hydrogenated to ethylbenzene,^[2] therefore, the maximum conversion of phenylacetylene and avoiding the loss of styrene in the

meantime are doubly important, which embody the concepts of atomic economy and green chemistry.

It is worth noting that in a wide range of hydrogenation catalysts, Palladium on carbon (Pd/C) is known as the first commercialized carbon-supported metal catalyst and is widely used in industry in the past several decades. Because Pd has the specific power for dissociating hydrogen gas (H₂) into active H atoms.^[3] And owing to that carbon-based support generally shows high specific surface area, pore volume, thermal stability, and most importantly, the low cost of mass production.^[4] However, for lack of anchor points for the active phase, Pd nanoparticles (NPs) with uneven dispersion (or aggregated ones) and leaching of Pd NPs from the carbon surface are often generated. The abundant microporous structure in common carbon also limits the mass transfer of reactive molecules.^[5] When used for the semihydrogenation of phenylacetylene, Pd/C always shows a low selectivity of styrene and poor reusability. Another prominent example is the commonly used Lindlar catalyst. Benefit from the interaction effects of Pd with lead, sulphur or quinolone, Lindlar catalyst exhibits relatively better selectivity than Pd/C. Unfortunately, Lindlar catalyst is denoted as "poisoned catalyst" due to the presence of toxic additives, which is environmentally unfriendly.^[3a, 6] Thus the research and development focused on practical and environmentally friendly Pd supported on carbon catalysts for the semihydrogenation of phenylacetylene is of great significance.

As compared with poisoning treatment on Pd, using more greener and effective way to modify Pd to improve the selectivity is very necessary. By adding another non-toxic metal, especially the non-noble metal (Fe, Co, Ni, Cu, Ga or Zn) to influence the Pd surface area or active sites is thought to provide new possibility and attempt. Because the geometric effect and/or electronic effect would affect the catalytic system, thus could increase the selectivity compared to the monometallic Pd system.^[2b, 7] What's more, using dopants or ligands (N, P or S) as a structural modifier to influence the interactions between Pd and heteroatoms is also a very convenient method to improve the selectivity of Pd. The modification of the Pd by heteroatoms may influence the exposed surface of Pd, and then affect the selectivity.^[8] Recently, as a new and emerging material, N-doped carbon (NC) has attracted increasing attention based on the reason that N doping can affect the interactions between metal and support.^[9]

From the perspective of green chemistry and sustainable development, and based on the above considerations, we would prefer to choose more greener, appropriate and efficient ways to modify Pd/C. Thus, in this work, (i) as a cheap catalyst carrier, activated carbon was functionalized with melamine firstly, and then followed the high temperature calcination, we acquired the

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NC with rich mesopores to enhance the mass transfer. (ii) When the NC was applied as the support materials, the N-containing groups could enhance their wetting properties, which was effective for the metal NPs deposition in liquid phase by impregnation. What's more, the contained N species could act as the sufficient anchoring sites for the growth of metal NPs to increase the stability and dispersion, and the introduced various metal-support interactions from N doping may do good to the catalytic process. (iii) Different mass ratios of non-precious iron series element were used to modify Pd and were immobilized onto NC. The incorporation of another metal with Pd led to the formation of some Pd-M (Fe, Co or Ni) nano-alloys, and the interactions between the two metal NPs were proved to influence the selectivity compared with monometallic Pd catalysts. In this work, most significantly, the prepared Pd/NC with iron series element modification had all the above advantages, donated as Pd-M/NC. Fine tuning of the original metal content allowed us to adjust the optimum ratio, and hence to optimize the selectivity. When applied to the semihydrogenation of phenylacetylene, the catalysts exhibited good catalytic effect for the semihydrogenation of phenylacetylene as the Pd/M content mass ratio was approximately 1:1. Detailed characterization and catalytic experiment had been made to validate the iron series elements modification on influencing the catalytic performance of Pd/NC catalysts.

Results and Discussion

Catalyst characterization

The preparation procedure of Pd-M/NC is schematically illustrated in Figure 1. Firstly, commercial activated carbon treated with acids was surface functionalized with carboxylic acids and others acid groups. When the treated activated carbon and melamine were mixed and dispersed in solvent, the amino-groups in melamine could interact with the acid groups in treated activated carbon. After the removal of solvent, the solid products

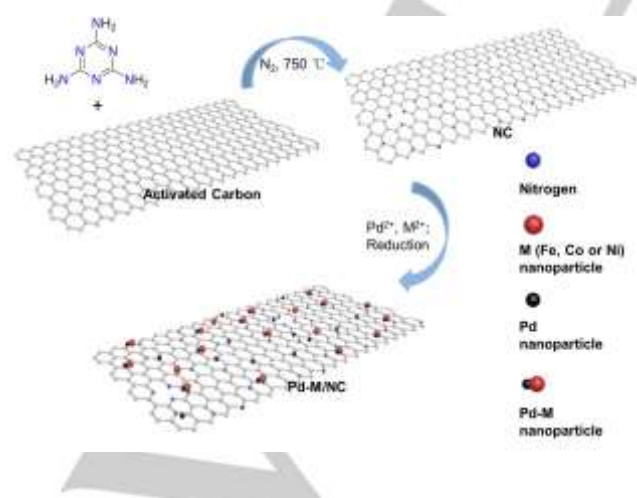


Figure 1. The synthetic procedures of Pd-M/NC.

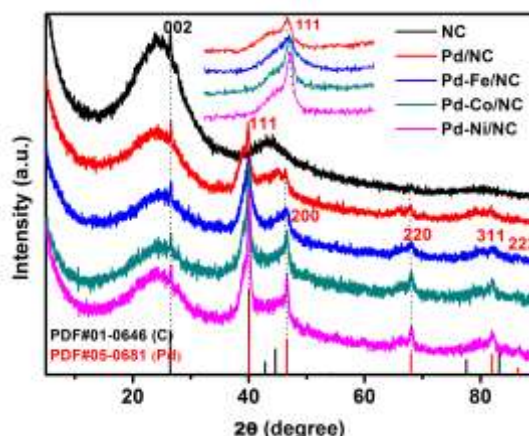


Figure 2. XRD patterns of NC, Pd/NC and Pd-M/NC.

were calcined at high temperature under a N_2 atmosphere, and the NC was produced. Subsequently, the NC was used as support to immobilize metal NPs or bimetallic alloys. The contained N species in NC could function as the sufficient anchoring to adsorb Pd^{2+} and M^{2+} , then the NC that adsorbed Pd^{2+} and M^{2+} was reduced by H_2 under high temperature firstly to formalize the metal NPs, and $NaBH_4$ aqueous solution was used to further reduce the metal NPs to zero valent. Finally, the Pd/NC with iron series element modification was obtained (Pd-M/NC).

To determinate the formation of the prepared samples, X-ray powder diffraction (XRD) was measured in the first step. The wide-angle powder XRD patterns of NC, fresh Pd/NC and Pd-M/NC were shown in Figure 2. The NC, Pd/NC and Pd-M/NC showed intense diffraction peaks centered at about 26° , which corresponded to the (002) planes of graphitic carbon.^[10] The peaks at 40.1° , 46.7° , 68.1° , 82.1° and 86.5° appeared in the Pd/NC and Pd-M/NC, corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of Pd, which showed a typical face centered cubic crystal structure of Pd (JCPDS-05-0681).^[11] The inset figure displayed the XRD result of the Pd (1 1 1) peak in the narrow range between 35° and 45° . In this range, the peak of Pd (1 1 1) plane for all Pd-M/NC samples shifted to higher value compared to Pd/NC. The peak shifting indicated that some Pd-M alloys were generated as the iron metal atoms M (Fe, Co or Ni) may embedded into the Pd lattice.^[12] The existence of some Pd-M alloys may lead a dilution of Pd, which may develop advantageous effects for the semihydrogenation of phenylacetylene.^{[7], [13]} No diffraction peaks due to M (Fe, Co or Ni) species were detected from the patterns, which indicated that the M species were amorphous.^{[12b], [14]} Therefore, when measured the morphology of the prepared three Pd-M/NC samples (Figure 3A-C) by transmission electron microscopy (TEM), the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Figure 3a-c) were taken and a good element distribution could be seen. The Pd NPs loaded on NC (Pd/NC) showed a better dispersity, while the Pd/C showed more agglomerated particles (Figure S1). The C, N,

M (Fe, Co or Ni) and Pd were observed clearly through the corresponding element mapping analysis, which were well dispersed in the catalysts. Determination of metal element contents was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES), the actual contents of Pd and M (Fe, Co or Ni) in the three Pd-Fe/NC, Pd-Co/NC and Pd-Ni/NC were list in Table 1, the Pd/M mass ratio was approximately 1:1, which was roughly the same with the initial addition amount of preparation process. What's more, the energy dispersive spectrometer (EDS) analysis (Figure S2) was also applied to characterize the chemical composition of the three Pd-M/NC samples. From the EDS spectra, the corresponding peaks of C, N, M (Fe, Co or Ni) and Pd were existed, which conformed the successful modification of Pd/NC by M (Fe, Co or Ni). The copper (Cu) peak was brought from Cu grid in TEM analysis.

The detailed electronic states and chemical compositions of the prepared samples surface were investigated by X-ray photoelectron spectroscopy (XPS) analysis (Figure 4). The wide-scan spectra of all the samples showed the existence of C, N, O, Pd. Three Pd-M/NC also showed the existence of M (Fe, Co or Ni), which was in concordance with the results of elements mapping and EDS (Figure S2). The high resolution C 1s XPS spectra of the samples were shown in Figure 4b, all the samples possessed three peaks centered at 284.5, 285.5 and 286.8 eV, which were corresponding to C=C, C-N or C-C and C-O groups.^[15] The N 1s spectra (Figure 4c) could be deconvoluted into two main peaks with binding energies at 398.2 and 400.4 eV that corresponded to pyridinic N and pyrrolic N, respectively. The different type N could function as sufficient anchoring sites to stabilize metal NPs and thus improve the catalytic selectivity.^[9a, 16] Pd states of the Pd/NC and Pd-M/NC samples

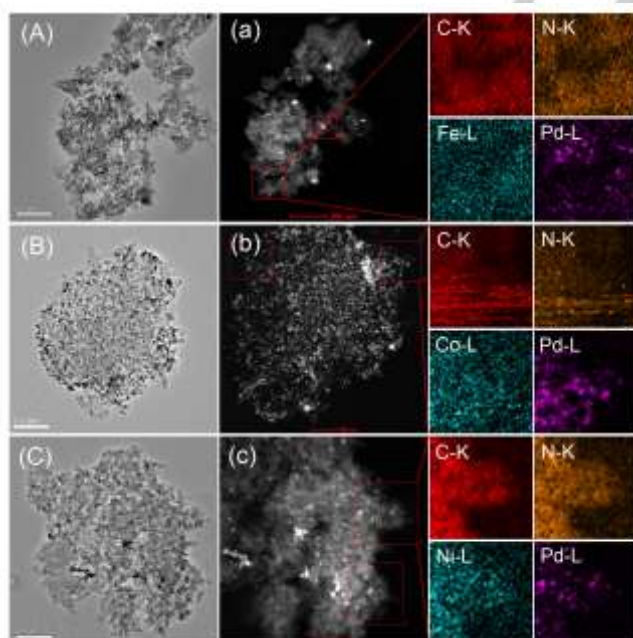


Figure 3. TEM images of Pd-Fe/NC (A), Pd-Co/NC (B) and Pd-Ni/NC (C); HAADF-STEM images of Pd-Fe/NC (a), Pd-Co/NC (b) and Pd-Ni/NC (c), and the images of corresponding element mapping analysis.

Table 1. Textural parameters and metal element contents of the prepared samples

Entry	Catalysts	Pd (wt%)	M (Fe, Co or Ni) (wt%)	S _{BET} (m ² g ⁻¹)	V _{pore} (cm ³ g ⁻¹)	D _{pore} (nm)
1	NC	-	-	738	0.73	6.67
2	Pd-Fe/NC	2.57	2.91	665	0.68	6.83
3	Pd-Co/NC	2.45	2.95	694	0.69	6.68
4	Pd-Ni/NC	2.39	2.72	690	0.69	6.62

were also confirmed by XPS (Figure 4d). Pd 3d core level of the Pd/NC and three Pd-M/NC samples presented two main peaks located at about 335.5 and 341.0 eV, which were ascribed to Pd 3d 3/2 and Pd 3d 5/2, respectively.^[17] The results showed that the Pd (II) species were completely converted into Pd (0) through the two step reduction process. Interestingly, the Pd 3d peaks of Pd-M/NC positively shifted as compared to Pd/NC, which may due to the formation of some Pd-M alloys.^[18] The Pd peaks shifting provided further evidence of the iron series element modification on Pd. The modification may suppress the formation of β -Pd hydride and affect the selectivity.^[6a, 6b, 13, 19] And the high resolution XPS spectra of Fe 2p, Co 2p and Ni 2p were also obtained, shown in Figure S3.^[14, 20] The iron elements had oxidation states, which may be the possible surface oxidation when the catalysts exposed to air. These further confirmed the existence of Fe, Co and Ni in respective Pd-M/NC samples, which may have modification effect on Pd/NC and improve the selectivity.

The N₂ adsorption-desorption isotherms and the pore size distribution of the samples NC and Pd-M/NC were shown in Figure 5. A hysteresis loop was observed, showing a typical type-IV curve and revealing the existence of the uniform mesopores.^[10, 21] The parameters were displayed in Table 1. The

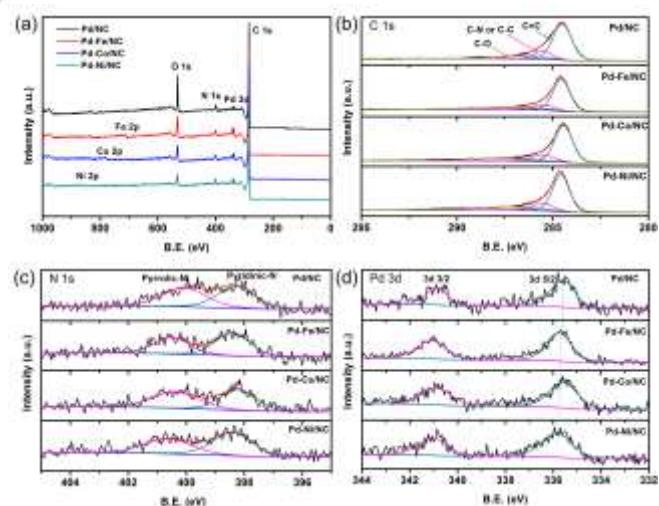


Figure 4. Wide-scan XPS spectra of Pd/NC and three Pd-M/NC samples (a); and high-resolution XPS spectra of C 1s (b), N 1s (c) and Pd 3d (d).

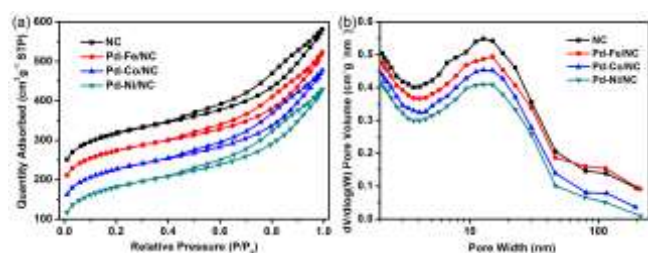


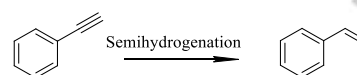
Figure 5. N_2 adsorption-desorption isotherms (a) and pore size distribution curves (b) of NC and Pd-M/NC.

Brunauer-Emmett-Teller (BET) specific surface area and pore volume of Pd-M/NC decreased compared to NC, which confirmed the successful loading of metal NPs. Nevertheless, the BET specific surface area and pore volume remained at high level. The existence of large specific surface and plentiful pore might play a crucial role on the mass transfer and substrate selectivity in the reaction. The pore size distribution of the tested materials was measured from the adsorption branches using the Barrett-Joyner-Halenda method. The appearance of the macropores might owe to the interspaces of the stack or accumulation between the carbon layers.

Catalytic ability test

Based on our group's previous work, initially, Ni was chosen to modify Pd as its potential optimal modification effect.^[7] Thus, the semihydrogenation of phenylacetylene was firstly performed on Pd-Ni/NC to study the modifying effects of iron element on influencing the selectivity of Pd. Three different Pd/Ni mass ratio Pd-Ni/NC catalysts were prepared, denoted as Pd-Ni(2:1)/NC, Pd-Ni(1:1)/NC and Pd-Ni(1:2)/NC, respectively. The catalytic performance of different catalysts was listed in Table 2. As a blank test, Ni/NC showed no catalytic activity (entry 1). However, the conversion and selectivity of the three Pd-Ni/NC catalysts for the semihydrogenation of phenylacetylene were quite different (entries 2, 3 and 4). Pd-Ni(1:1)/NC showed suitable catalytic activity and good selectivity, and 100% phenylacetylene conversion with 94.8% styrene selectivity were achieved within 2 h. The selectivity could still maintain at relatively good level over 24 h. As for Pd-Ni(2:1)/NC, the "dilution" of Pd active sites by Ni was lower than Pd-Ni(1:1)/NC, which gave the more contiguous Pd sites. The selectivity decreased rapidly as more styrene converted to ethylbenzene in a short reaction time. Because the opportunity of styrene exposed to Pd active sites was high.^[13] In contrast, for Pd-Ni(1:2)/NC with more "dilution" of Pd active sites, although the selectivity of styrene could be sustained for a long time, the conversion of phenylacetylene was not very high. These results revealed that Pd was the dominant active species, and Ni was only a modifier. The catalytic performance of the three catalysts with different Pd/Ni ratio indicated that the modification of Ni to Pd had a big impact on the selectivity. What's more, a proper ratio of Pd/Ni would significantly affect

Table 2. The semihydrogenation of phenylacetylene catalyzed by Pd-Ni/NC^a



Entry	Catalyst	Time (h)	Conversion (%)	Styrene yield (%)	Selectivity (%)
1	Ni/NC ^b	1	trace	-	-
2	Pd-Ni(2:1)/NC	0.5	71.2	70.2	98.6
		1	98.8	80.8	81.8
		2	100	56.9	56.9
3	Pd-Ni(1:1)/NC	0.5	24.9	24.9	100
		1	51.0	49.7	97.4
		2	100	94.8	94.8
		2.5	100	81.6	81.6
		24	100	68.9	68.9
4	Pd-Ni(1:2)/NC	0.5	17.3	17.3	100
		1	25.3	25.3	100
		2	61.5	59.9	97.4
		2.5	83.7	81.3	97.1
		24	91.2	84.2	92.3

^a Reaction conditions: phenylacetylene 0.5 mmol, catalyst (Pd 0.25 wt% relative to phenylacetylene), ethanol 10 mL, 298 K, H_2 (1 atm).

^b The dosage of Ni/NC (Ni 2.89 wt%) was 5 mg.

the catalytic properties of the final catalyst. In our catalytic system, when the Pd/Ni ratio was about 1:1, Pd-Ni/NC exhibited relatively good reaction results.

The optimized Pd/M ratio was about 1:1, then Pd-Fe/NC and Pd-Co/NC with the 1:1 ratio were also prepared, and their catalytic performance for the semihydrogenation of phenylacetylene was studied. The reaction results of Pd-Fe/NC and Pd-Co/NC were shown in Table 3. Similarly to Pd-Ni/NC, the two catalysts also exhibited relatively good activity and selectivity, which may be ascribed to the modification of Pd by Fe or Co. A dilution of Pd with modifying metal would decrease the exposure of Pd active sites. Based on above test results, it demonstrated that modification of the Pd-based carbon catalysts with the iron series element (Fe, Co or Ni) could alter the selectivity of the catalysts. Relatively, Pd-Ni/NC showed a better catalytic result than Pd-Fe/NC and Pd-Co/NC within 2.5 h though the catalytic effect difference among them was not significant.

To show the catalytic performance more intuitively, the conversion of phenylacetylene and selectivity for styrene versus time (based on Table 2-3) by different Pd-M/NC samples were made in Figure 6. From Figure 6a-b, it clearly displayed that the

modification of Ni to Pd had a big impact on the selectivity. When the Pd:Ni ratio was about 1:1, it showed a moderate reaction effect with good conversion and selectivity. As for the modification effect of Pd by Fe or Co (Pd:M=1:1), from Figure 6c-d, they also showed a relatively good reaction results. High selectivity for styrene (about 90%) could be achieved at full phenylacetylene conversion, and the selectivity of styrene was maintained (>65%) even after a long reaction time. The results demonstrated that the successful modification effect of iron series element (Fe, Co or Ni) to Pd, leading to the improving catalytic performance with good conversion and selectivity.

Table 3. The semihydrogenation of phenylacetylene catalyzed by Pd-Fe/NC and Pd-Co/NC^a

Entry	Catalyst	Time (h)	Conversion (%)	Styrene yield (%)	Selectivity (%)
1	Pd-Fe/NC	0.5	54.7	53.2	97.3
		1	83.1	78.5	94.5
		2	100	87.0	87.0
		2.5	100	72.3	72.3
		24	100	67.4	67.4
2	Pd-Co/NC	0.5	26.3	26.3	100
		1	62.3	60.7	97.4
		2	100	92.1	92.1
		2.5	100	74.7	74.7
		24	100	66.3	66.3

^a Reaction conditions: phenylacetylene 0.5 mmol, catalyst (Pd 0.25 wt% relative to phenylacetylene), ethanol 10 mL, 298 K, H₂ (1 atm).

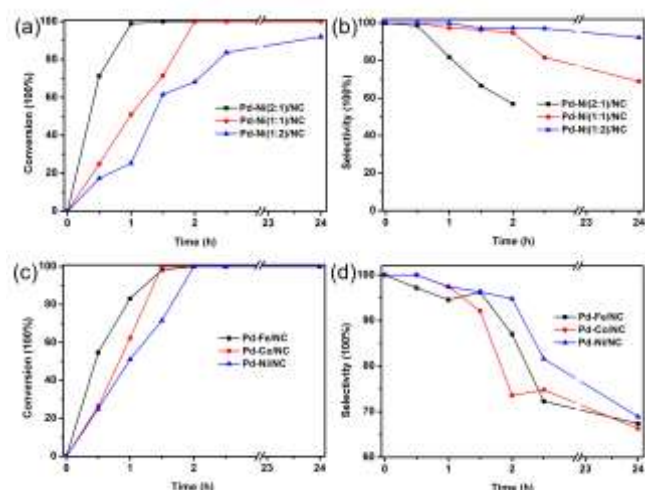


Figure 6. The conversion of phenylacetylene (a) and selectivity for styrene (b) versus time used Pd-Ni/NC with different Pd:Ni ratio; the conversion of phenylacetylene (c) and selectivity for styrene (d) versus time over different Pd-M/NC (Pd:M=1:1).

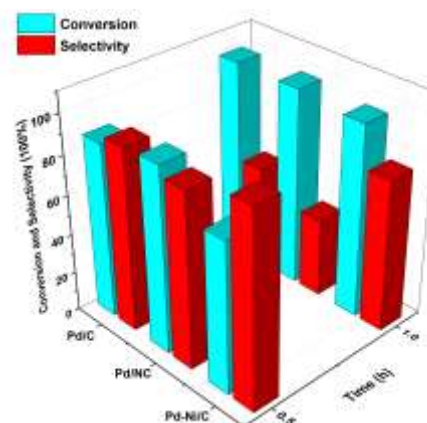


Figure 7. The comparison for the semihydrogenation of phenylacetylene catalyzed by commercial Pd/C, Pd/NC and Pd-Ni/C.

In order to further prove the modifying effects of iron series element, contrast test was made on commercial Pd/C (Pd 5.06 wt%), Pd/NC (Pd 2.62 wt%) and Pd-Ni/C (Pd 2.76 wt%, Ni 2.73 wt%) under the same Pd content relative to phenylacetylene (Pd 0.25 wt% relative to phenylacetylene). The comparison results were shown in Figure 7. Pd/C and Pd/NC supported only Pd NPs, which were not modified with a second metal. These two catalysts showed rather high catalytic activity but low selectivity. The selectivity for styrene of Pd/C and Pd/NC decreased rapidly in a short reaction time from 92.1 to 50.7 and 88.2 to 39.6, respectively, and some previous work had reported about the same phenomenon when the conversion of phenylacetylene was high.^[2b] Nevertheless, Pd modified with Ni supported on activated carbon (Pd-Ni/C), it showed better selectivity than Pd/C and Pd/NC, which implied that the modification of Pd with a second metal was an effective approach to increase the selectivity of Pd-based catalysts. And the comparison with other different Pd catalysts previous reported for the semihydrogenation of phenylacetylene was listed in Table S1, the Pd-M/NC showed a relatively good catalytic performance which may exhibit potential applications on the selective hydrogenation reactions.

To understand the promoting role of iron series element modification on Pd more intuitively, we made an intuitionistic description of different Pd catalysts in Figure 8. When supported Pd on activated carbon without N doping, the metal particles were inclined to be aggregated and large-size Pd NPs were prone to be formed, which could be reflect from the TEM images in Figure S1a-b. In the catalytic process, it might be the main cause for the degradation in activity of the catalyst. Compared with activated carbon, the incorporated N in NC materials could serve as anchoring sites for the growth of metal NPs, and then could disperse and stabilize the metal NPs to obtain NPs with a relatively good distribution (Figure S1c-d), thus the recycling capacity of the catalyst could also be increased. In order to further reduce the number of Pd active sites, iron series element (Fe, Co or Ni) was used to modify Pd. Iron series element combined with Pd would take part of the position of Pd surface.

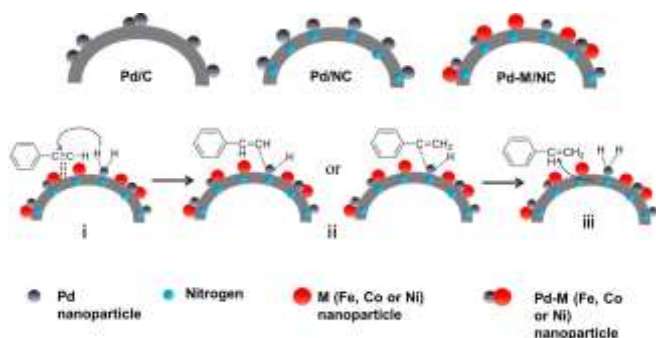


Figure 8. The intuitionistic description of different Pd catalysts, and the proposed reaction pathway for the semihydrogenation of phenylacetylene.

Therefore, the numbers of Pd active sites per unit area were decreased, or the dilution of the Pd active sites, which could achieve the goal of increasing the selectivity. The high selectivity of Pd-M/NC could be explained in terms of three possible sequential steps, which were schematically illustrated in Figure 8: (i) a phenylacetylene molecule were adsorbed onto the catalyst surface; (ii) the triple bond was converted to a double bond by the insertion of H atom generated from the dissociation of H_2 by Pd; (iii) the styrene molecule rapid detached from the catalyst surface.^[22] The iron elements metal occupied some portion of the Pd active sites, thus suppressed the contact opportunity of styrene with Pd active sites, which could increase the selectivity of the catalysts.

The stability of catalyst is an important evaluation factor. To measure the stability of these series of Pd-M/NC catalysts under mild conditions, Pd-Ni/NC was selected as the representative to investigate the recyclability for the semihydrogenation of phenylacetylene. The catalyst was recycled by centrifugation, washed with ethanol, and dried in a vacuum oven at ambient temperature for the next catalytic test. The recycling data in Figure 9a showed that the catalytic activity and selectivity still maintained at high levels even after four successive catalytic cycles. Through the XRD pattern (Figure 9b) of the recycled catalyst, only a small amount of Pd^0 was oxidized to PdO. It further revealed that the catalyst showed considerable stability and reusability.

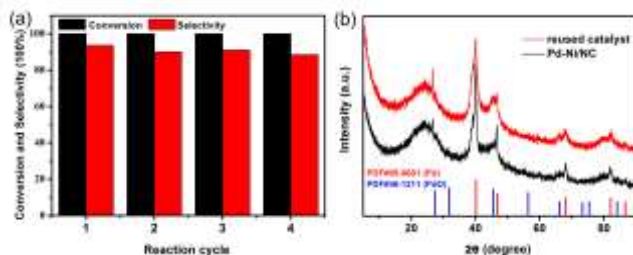


Figure 9. The recyclability results of Pd-Ni/NC (a) and XRD patterns of the fresh Pd-Ni/NC and the reused catalyst (b).

Conclusions

In conclusion, Pd-M/NC exhibited good catalytic performance for the semihydrogenation of phenylacetylene. The modification of Pd with iron series elements had been shown to promote the selectivity of the catalyst. And the Pd/M mass ratio also affected the selectivity of the target catalysts, the appropriate Pd/M ratio was 1:1. The doped N in carbon materials could disperse and stabilize the metal NPs, and the catalysts displayed good stability and recyclability. Thus, the modification of Pd/NC with iron series element demonstrated exciting potential as catalysts for the semihydrogenation of phenylacetylene. These results provide a reference for the modification of Pd-based catalysts in selective hydrogenation reactions.

Experimental Section

Materials

Iron dichloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) were provided by Tianjin Guangfu fine chemical research institute. $PdCl_2$ was supplied by Sigma-Aldrich. Melamine, urea and $NaBH_4$ were supplied by Chengdu Kelong chemical Co., Ltd. Commercially available activated carbon (Wood, $BET > 1000 \text{ m}^2 \text{ g}^{-1}$, HG/T 3491-1999) was provided by Lanzhou Aihua Chemical Company. Phenylacetylene (99%) and other chemicals were purchased from Tianjin Rionlon reagent Co., Ltd. All reagents were used as received.

The preparation of NC support

Firstly, commercial activated carbon was surface functionalized with carboxylic acids and others acid groups by concentrated nitric acid with refluxing.^[23] Then, 250 mg commercial activated carbon treated with acids, 140 mg melamine were mixed and dispersed in 50 mL ethanol by ultrasound for 1 h. After stirring the mixture for 24 h at ambient temperature, the solid products were collected by removing the solvent using reduced pressure distillation and dried in a vacuum oven at ambient temperature overnight. Finally, the above solid products were placed in a tubular furnace under the N_2 atmosphere with a ramp rate of $3 \text{ }^\circ\text{C min}^{-1}$ and held the temperature at $750 \text{ }^\circ\text{C}$ for 3 h, then cooled them to ambient temperature and finally the NC was obtained.

The preparation of target catalysts

The target catalysts Pd-M/NC were synthesized in accordance to the following experimental steps. Based on our previous work, we firstly prepared Pd-Ni(n)/NC with different Pd:M mass ratio to verify the best ratio ("n" indicates the mass ratio of Pd:M). 100 mg NC, 1.5 mL Pd^{2+} solution (2.0 mg mL^{-1}) and 1.5 mL Ni^{2+} solution (2.0 mg mL^{-1}) were added in 10 mL H_2O and 30 mL ethanol mixed solvent, dispersed by ultrasound for 1h and then stirred another 24 h at ambient temperature. Then, the solid products were collected by removing the solvent using reduced pressure distillation and dried in a vacuum oven at ambient temperature overnight. The above solid products were placed in a tubular furnace and reduced in H_2/N_2 flow at $450 \text{ }^\circ\text{C}$ for 2 h. To the complete reduction of the metal NPs, the products were further reduced by an excess amount of $NaBH_4$ aqueous solution (20 mL , 0.2 mol L^{-1}). Finally, the Pd-Ni(1:1)/NC was acquired. When the added volume of Ni^{2+} solution

was changed to 0.75 mL or 3.0 mL, Pd-Ni(2:1)/NC or Pd-Ni(1:2)/NC was also prepared, respectively.

The preparation process of Pd-Fe/NC or Pd-Co/NC was the same as the synthetic procedures of Pd-Ni/NC, just by replacing Ni²⁺ solution (2.0 mg mL⁻¹) with Fe²⁺ solution (2.0 mg mL⁻¹) or Co²⁺ solution (2.0 mg mL⁻¹).

For comparison, Ni supported on NC (Ni/NC) was also prepared, just with the addition of 1.5 mL Ni²⁺ solution. The preparation of Pd/NC was without the addition of M²⁺ (Fe, Co or Ni) solution, only 1.5 mL Pd²⁺ solution (2.0 mg mL⁻¹) to the system. The preparation of Pd-Ni/C was replaced NC with acids treated activated carbon, and other experimental procedures were the same.

Catalyst test

0.5 mmol phenylacetylene, a certain amount of catalyst was dispersed in 10 mL ethanol under sonication in a round-bottomed flask. Then, a balloon filled with H₂ was connected to the flask, and the air in the flask was quickly replaced by H₂ three times. The reaction was maintained at 25 °C under vigorous stirring. The reaction mixture was collected using a syringe at a certain time interval, and filtered through the membrane filter, the filtrate was diluted by absolute ethanol, and the reaction results were evaluated by an Agilent 5977E gas chromatography–mass spectrometry (GC–MS).

Characterization

The morphology and surface characteristics of the prepared samples were characterized by TEM using an accelerating voltage of 200 kV (Tecnai G2 F30) equipped with EDX (Tecnai G2, USA). A Rigaku D/max-2400 diffractometer equipped with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) was used to measure the XRD patterns of the samples in the 2θ range of 10–90°. XPS with X-ray source Al K α (Perkin-Elmer PHI-5702) was used to analyze the electronic states of the surface composition, and C 1s peak was used as the energy reference (284.6 eV). The BET specific surface areas, pore volume and pore-size distribution of the samples were analyzed by N₂ adsorption–desorption techniques at 77 K using a TriStar3020 (Micromeritics). PerkinElmer EA2400 II instrument was used to determine the C, N content of the samples (Elemental analysis results for the supports were listed in Table S2). The metal contents of the prepared catalysts were tested by ICP-AES. GC–MS (Agilent 5977E) was applied to estimate the results of the reactions.

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Keywords: Palladium • Iron series elements • Nitrogen-doped carbon • Simehydrogenation • Phenylacetylene

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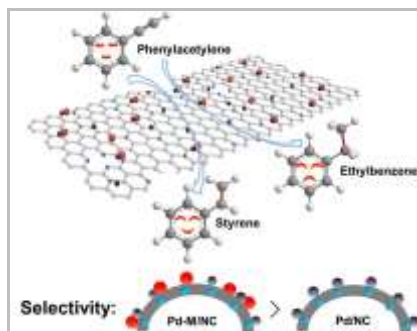
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Wei Zhang, Wei Wu, Yu Long, Jiaheng Qin, Fushan Wang and Jiantai Ma*

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