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Palladium Nanoparticles Supported on Nitrogen-Functionalized Active Carbon: A Stable and Highly Efficient Catalyst for the Selective Hydrogenation of Nitroarenes

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Nitrogen-functionalized active carbon-supported ultrasmall Pd nanoparticles were conveniently prepared by using a postloading method. The Pd catalyst was highly active and selective for the hydrogenation of nitroarenes at room temperature under ambient pressure. Reducible groups such as ketone, carboxylic acid, and ester were not hydrogenated, and the corresponding anilines were obtained quantitatively. The Pd catalyst demonstrated high stability and could be reused 10 times without the loss of catalytic performance.

Introduction

The hydrogenation of organic compounds is synthetically important both in the laboratory and in industry,[1] and the reduction of nitroarenes to anilines is widely used in industrial processes because functionalized anilines are industrially important intermediates for fine chemicals such as agrochemicals, pharmaceuticals, and dyestuffs.[2] The classical methods for the hydrogenation of nitroarenes use various transition-metal catalysts, such as Pt,[3] Pd,[4] and Ru.[5] However, with these highly active supported metal catalysts, it is difficult to avoid side reactions, particularly if the nitro substrates with other reducible groups are used. To solve this problem, other metal catalysts (Au,[6] Ag,[7] and Cu[8]) were developed for the selective hydrogenation of nitroarenes; however, the activity of such metal catalysts was not always high and the reaction conditions were harsh. In addition, the use of other hydrogen sources as stoichiometric reducing agents could result in high selectivity but a large amount of wastes was produced.[9] From a sustainable point of view, the development of efficient and recyclable supported Pd nanoparticle (PdNP) catalysts with high activity and selectivity for the hydrogenation of nitro compounds with H_2 as a hydrogen source is highly desirable.

Pd/C catalysts with good chemical stability are widely used in many chemical processes, especially involving H_2, such as hydrogenation, dehydrogenation, and hydrogenolysis.[10] The catalytic activity of PdNPs supported on carbon materials is highly dependent on the nature of surface functional groups present on the support, which can affect the particle size dispersion and chemical state of PdNPs.[11] The particle size has a significant effect on hydrogenation reactions. Previous studies have revealed that the formation of weak hydrogen bonds on the surface is the key factor for the hydrogenation to occur, and the accessibility of these H atoms is found to be the origin of the high activity of particles due to their nanoscale dimensions.[12] In addition, the chemical state of PdNPs has a significant effect on the catalytic performance of Pd/C catalysts and the oxide state and even the near-surface composition of PdNPs can be altered, rendering the stabilization of Pd in the most suitable oxidation state difficult in hydrogenation reactions.[13]

N-doped carbon materials have recently attracted research interest because of their remarkable performance as catalytic supports.[14] Doping with the electron-rich N atoms could modify the surface structure of carbon materials, with increased *p*-binding ability and improved basicity.[15] The N doping of carbon materials could realize the high dispersion of PdNPs and stabilize the small-sized PdNPs on the carbon support, and small-sized PdNPs and the synergistic effect of the N species could accelerate the selective hydrogenation of phenol[11b] and quinoline.[16] It has also been reported that the Pd/N-functionalized carbon nanotube catalyst showed good stability because of the structural and electronic promoting effect of the N-functionalized carbon nanotube support.[12a] Our study has demonstrated that the N species as electron donors

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in the carbon support could increase the electron intensity of the support for stabilizing the small-sized PdNPs, affect the oxidation state of Pd, and promote the selective hydrogenation activities.[17]

Herein, the commercially available and cheap active carbon was initially functionalized with melamine at different temperatures to yield the corresponding N-hybrid carbon supports (NAC-*T*, in which NAC represents N-functionalized active carbon and *T* represents treatment temperature), which could be ideal supports for the postloading of PdNPs to prepare the NAC-supported PdNPs (Pd@NAC-*T*). The catalytic activity and stability of the resultant Pd@NAC-*T* were investigated in the hydrogenation of nitro compounds under ambient reaction conditions.

Results and Discussion

NAC-600, NAC-700, and NAC-800 were initially prepared by heat treatment of the resultant mixture of commercially available active carbon and melamine through wet impregnation at the corresponding temperature. Element analysis characterizations reveal that the N content of NAC-600, NAC-700, and NAC-800 decrease significantly with the increase in heating temperature (Table 1). The melamine molecules can be self-condensed to carbon nitride after an appropriate thermal treatment, and the resultant carbon nitride can be further decomposed at a high temperature (>500 °C).[18] During our preparation, carbon nitride could be formed on the surface of active carbon and its further decomposition could be accelerated at a higher reaction temperature, which could reduce the N content of NAC-*T*. The N 1s X-ray photoelectron spectroscopy (XPS) spectra of NAC-600, NAC-700, and NAC-800 are shown in Figure 1. The N 1s spectra of these three samples can be well fitted to three components: the peak at 398.5 eV can be assigned to the pyridinic N, the peak at 400 eV is attributed to pyrrolic N,[19] and the peak at 401 eV is attributed to classical graphitic-type quaternary N. Although the N content decreases from 18.56 to 7.25 wt% with the increase in temperature, the relative content of graphitic-type quaternary N increases but the relative content of pyrrolic N decreases (Table 1). These variations indicated that the carbon nitride species reconstructed to form the proper ring system to fit the requirements of the locally graphitized structure.

Table 1. N content and N dopant state of NAC-600, NAC-700, and NAC-800.

Sample	N content[a] [%]	Content of different N species relative to total N[b]		
		Quaternary N	Pyrrolic N	Pyridinic N
NAC-600	18.56	0.27	0.24	0.49
NAC-700	11.02	0.30	0.18	0.52
NAC-800	7.25	0.33	0.14	0.53

[a] Determined from element analysis; [b] Determined from XPS analysis.

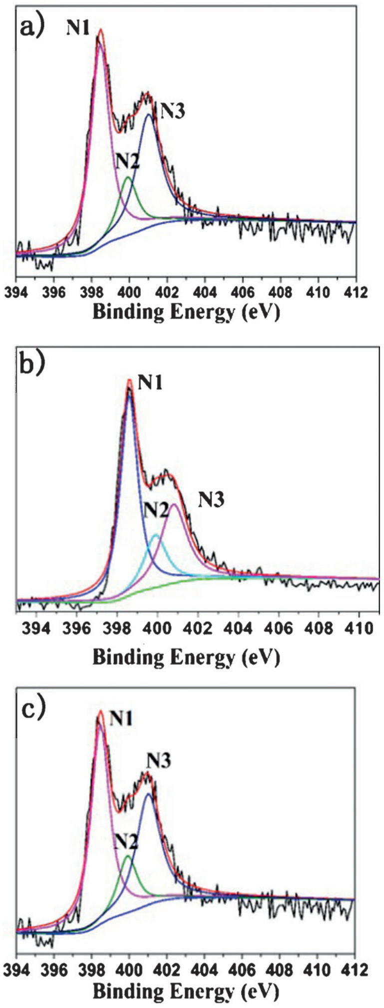


Figure 1. N 1s XPS spectra of a) NAC-600, b) NAC-700, and c) NAC-800.

On the basis of the above analysis, the NAC-*T* supports with high N content could be interesting supports for the immobilization of small-sized PdNPs; herein, 2 wt% PdNPs was loaded onto the NCA-*T* supports to produce Pd@NAC-600, Pd@NAC-700, and Pd@NAC-800. First, TEM and high-angle annular dark-field scanning TEM (HAADF-STEM) were used to test the morphology and distribution of the supported PdNPs (Figure 2, 1 a, 2 a, and 3 a). The TEM images of Pd@NAC-*T* reveal that PdNPs are finely and uniformly dispersed on the surface of NAC-*T* supports. However, the aggregation of PdNPs is not observed. The HAADF-STEM images of Pd@NAC-*T* show that PdNPs appear as white dots and are homogeneously dispersed on the surface of NAC-*T* supports and all PdNPs are uniform in size and shape (Figure 2, 1 b, 2 b, and 3 b). Furthermore, the particle size distributions of PdNPs for Pd@NAC-600, Pd@NAC-700, and Pd@NAC-800 are quite similar (Figure 2, 1 c, 2 c, and 3 c). The high-resolution TEM (HRTEM) observations suggested that PdNPs are highly crystalline and demonstrate well-resolved lattices of approximately 0.23 nm identified as the *d*-spacing of the (111) plane of face-centered cubic Pd (Figure 2, 3 d). Moreover, the elemental mapping images of the representative cat-

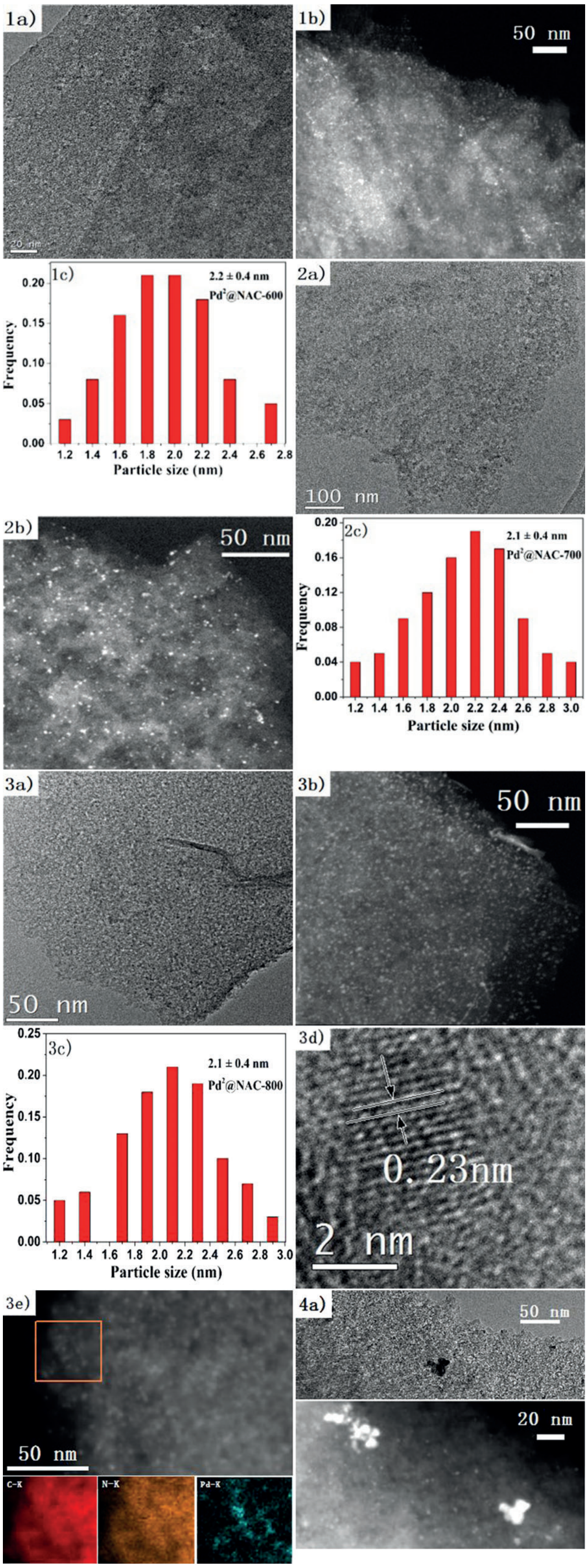


Figure 2. TEM, HAADF-STEM, and particle size distribution images of 1 a–c) Pd@NAC-600, 2 a–c) Pd@NAC-700, and 3 a–c) Pd@NAC-800; 3 d) HRTEM image of Pd@NAC-800; 3 e) elemental mapping analysis of Pd@NAC-800; 4 a) TEM and HAADF-STEM images of Pd@AC.

alyst Pd@NAC-800 also confirm that the N and Pd atoms are all homogeneously dispersed on the materials (Figure 2, 3 e).

To further clarify the stabilizing role of the N-doped functionalities, the original active carbon without N doping is used as a support to prepare the corresponding supported PdNP catalytic material (Pd@AC, 2 wt % Pd), as revealed in its TEM and HAADF-STEM images (Figure 2, 4 a), and most of the PdNPs are distributed on the surface of active carbon. The particle size distribution of Pd@AC is larger than that of Pd@NAC-*T*, and the PdNP aggregation in Pd@AC is observed. These differences reveal that the N species can be a key factor in preventing the aggregation of PdNPs and stabilizing the formed PdNPs mainly on the surface of N-doped active carbon.

The XRD patterns of Pd@NAC-*T* show high-intensity (0 0 2) and (1 0 0) diffraction peaks corresponding to the graphitic carbon; however, the characteristic diffraction peaks of Pd are not observed, which indicates that the supported PdNPs have small particle sizes and are homogeneously dispersed on the surface of the carbon matrix (Figure 3, 3 a). The Pd XPS spectra of Pd@NAC-*T* show a doublet corresponding to Pd $3d_{5/2}$ and Pd $3d_{3/2}$. The Pd $3d_{5/2}$ peak at 335.8 eV is attributed to Pd^0 (metallic Pd), whereas the Pd $3d_{3/2}$ peak at 337.8 eV is attributed to Pd^{2+} (PdO).[10] According to the XPS data for Pd@NAC-*T*, Pd^0 is formed as the major phase on the surface of the support.

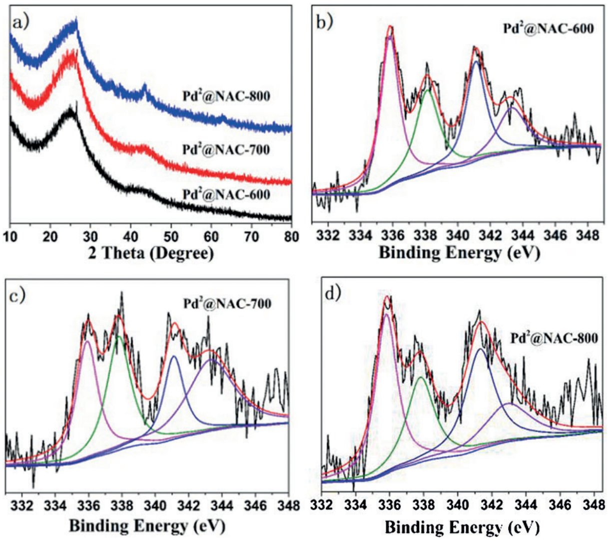
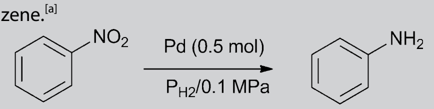


Figure 3. a) XRD patterns of Pd@NAC-*T*; Pd 3d XPS spectra of b) Pd@NAC-600, c) Pd@NAC-700, and d) Pd@NAC-800.

The hydrogenation of nitrobenzene is performed as the model reaction, and the results are listed in Table 2. The hydrogenation of a less polar substrate in more polar solvents is preferred.[20] However, in the heterogeneous catalytic system, the solvation of the reacting species and its effect on the overall reaction mechanism are not clearly understood.[21] The effect of solvents on the hydrogenation of nitrobenzene was initially investigated with the representative catalyst Pd@NAC-800 at room temperature under atmospheric pressure of H_2 gas. The solvent has a strong effect on the catalytic efficiency in the

Table 2. Evaluation of different solvents and catalysts for the reduction of nitrobenzene.[a]



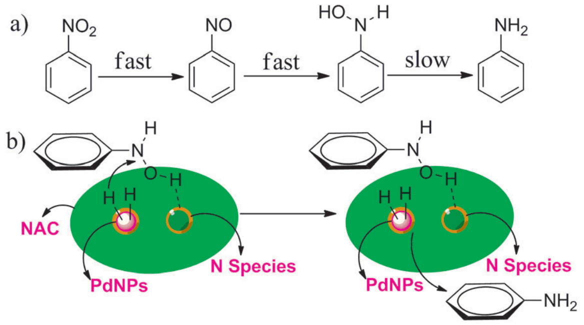
Entry	Catalyst	Solvent	Conv./select. [%]	Yield[b] [%]
1	Pd@NAC-800	ethanol	89/>99	89
2	Pd@NAC-800	methanol	82/>99	82
3	Pd@NAC-800	acetonitrile	28/>99	28
4	Pd@NAC-800	THF	42/>99	42
5	Pd@NAC-800	water	66/>99	66
6	Pd@NAC-800	xylene	<5/>99	<5
7	Pd@NAC-800	dichloromethane	73/>99	73
8	Pd@NAC-700	ethanol	68/>99	68
9	Pd@NAC-600	ethanol	55/>99	55
10	Pd/C[c]	ethanol	41/>99	41

[a] Reaction conditions: 1 mmol of nitrobenzene, 0.5 mol% Pd, 2 mL solvent, room temperature, $t=1$ h; [b] Determined from GC and GC–MS analyses with toluene as an internal standard; [c] 5 wt% Pd/C (1 mol% Pd was used in this reaction) was purchased from Alfa Aesar.

present catalytic system; methanol or ethanol can give, respectively, 82 and 89% yields within 1 h (Table 2). Other solvents regardless of their polarities, such as acetonitrile, THF, *n*-hexane, and water, are significantly less effective, and no hydrogenation occurs in xylene. Because of the toxicity of methanol, ethanol was herein selected as the optimal solvent.

Furthermore, Pd@NAC-600, Pd@NAC-700, and the commercially available Pd/C catalysts were compared. The catalytic performance of Pd@NAC-*T* was better than that of the commercial Pd/C; the conversion of nitrobenzene with different catalysts decreased in the following order: Pd@NAC-800 > Pd@NAC-700 > Pd@NAC-600 > Pd/C; and the turnover frequencies of Pd@NAC-800, Pd@NAC-700, Pd@NAC-600, and Pd/C for the hydrogenation of nitrobenzene are 178, 136, 110, and 82 h^{-1}, respectively. The catalytic differences could be attributed to the N dopant state in the support. The N content in our catalyst support decreased along with the increase in pyrolysis temperature; however, the relative content of pyridinic and graphitic-type quaternary N increased. Owing to its electron-donating properties, pyridinic N is considered to constitute the main transition-metal-binding site in the metal–CN (N-doped carbon) catalyst.[22] At the same time, the carbon nitride species formed from melamine could further reconstruct to form the proper ring system with the locally graphitized structure at a higher temperature. All these could change the physicochemical and electronic properties of the NAC support and PdNPs and thus improve the catalytic performance of Pd@NAC-800.

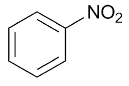
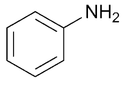
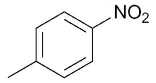
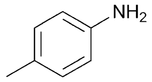
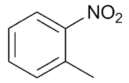
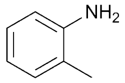
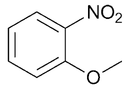
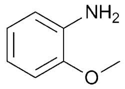
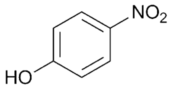
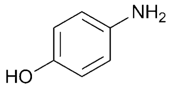
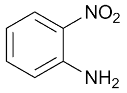
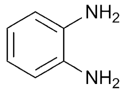
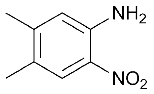
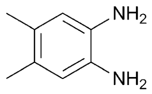
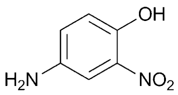
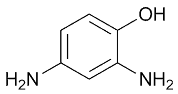
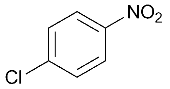
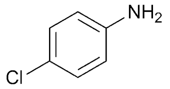
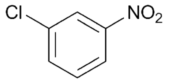
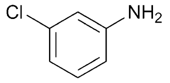
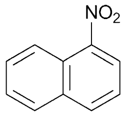
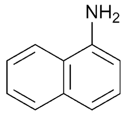
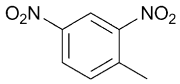
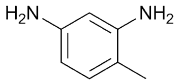
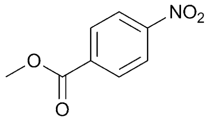
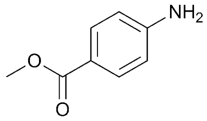
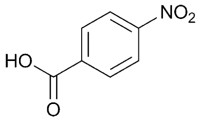
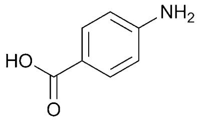
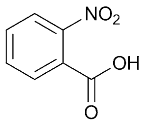
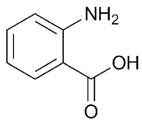
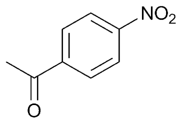
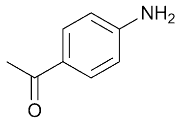
The widely accepted mechanism of the hydrogenation of nitrobenzene was proposed by Haber in 1898 (Scheme 1).[23] First, the nitro group is reduced to a nitroso group, and then a second equivalent of H atom can result in the formation of hydroxylamine. Finally, aniline is obtained with the addition of the third equivalent H atom. In these three steps, the major challenge is to avoid the accumulation of intermediates, such as hydroxylamine, because they can undergo strong exothermic disproportionation and other side reactions.[24] We and others have reported that the N species in the carbon support could improve the catalytic activity and selectivity of cyclohexanone in the hydrogenation of phenol because doping with the electron-rich N atoms modifies the surface structure of carbon materials owing to the increased interaction between phenol and the support via the hydrogen bond (–OH···N) and the electron-donating effect of N species in N-doped carbon materials could increase the electron density of the anchored Pd.[11b,17a] In addition, the liquid phase semihydrogenation of phenylacetylene and the selective hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline could achieve the high catalytic activity and selectivity because N doping of the carbon material could increase the electron density of PdNPs supported on the carbon material.[16,25] In such a hydrogenation system, the N species in the carbon support could play two roles: 1) It is possible that the hydroxylamine molecule can interact with the surface through the hydroxyl group to form –OH···N or –OH···π interactions. Therefore, the adsorption of the hydroxylamine molecule on the surface of the support could be facilitated because of the existence of N species. 2) The N species in the carbon support could act as electron donors and change the electron density of the carbon matrix and thus increase the electron density of PdNPs. The hydrogenation of the hydroxylamine molecule could be accelerated (Scheme 1 b).



Scheme 1. a) Haber mechanism of the hydrogenation of nitrobenzene with transition-metal catalysts; b) possible mechanism of the hydrogenation of hydroxylamine.

Then, the substrate tolerance of present NAC supported with small-sized PdNPs was also investigated. The optimized Pd@NAC-800 demonstrated high catalytic activity for the hydrogenation of nitrobenzene with low catalyst loading and high aniline yield (Table 3, entry 1). Substrates with electron-donating groups also worked efficiently and gave excellent yields of the corresponding amine products within 2 h (Table 3, entries 2–5). The introduction of an *ortho* substituent onto the phenyl ring could slow the hydrogenation, and good yields could be readily obtained by increasing the reaction time to 4 h (Table 3, entries 6–8). The hydrogenation reactions of *p*- and *m*-chloronitrobenzene were also performed with the corresponding aniline, and 82 and 86% yields, respectively, were obtained (Table 3, entries 9 and 10); in addition, the hydrodechlorination of aryl chloride was observed as a side reaction.

Table 3. Reduction of nitroarenes to anilines.[a]

Entry	Reactant	t [h]	Product	Conv./ select. [%]	Yield[b] [%]
1		2		>99/>99	99
2		2		>99/>99	99(96)
3		2		>99/>99	99
4		2		>99/>99	99
5		2		>99/>99	99
6		4		>99/>99	99(95)
7		4		97/>99	97
8		4		98/>99	98
9		3		>99/82	82[c]
10		3		>99/86	86[c]
11		8		>99/>99	99(95)
12		12		96/>99	96
13		10		>99/>99	99(94)
14		5		>99/>99	99(93)
15		5		>99/>99	99
16		4		>99/>99	99(95)

[a] Reaction conditions: 1 mmol of substrate, 0.5 mol% Pd, 2 mL ethanol, room temperature unless otherwise indicated; [b] Yields were based on nitroarenes, which were determined from GC analysis with toluene as an internal standard; values in parentheses are the yields of the isolated products; [c] Aniline was generated as a byproduct.

In addition, Pd@NAC-800 demonstrated high catalytic activity for the hydrogenation of more steric 2-nitronaphthalene and 2,4-dinitrotoluene with two nitro substituents (Table 3, entries 11 and 12).

The selective hydrogenation of nitrobenzene derivatives that contained other reducible groups is a challenging task in organic synthesis. The reducible carbonyl groups, such as ester, carbonyl acid, and ketone, were inert in the present catalytic system, and quantitative amine products were obtained (Table 3, entries 13–16).

Stability is the most important character for a good solid catalyst in the solid–liquid reaction, particularly if the reactant or the product has a strong coordination ability toward the supported metal catalyst, which could possibly accelerate the irreversible leaching of metal atoms from the supports. The N-doped carbon materials could be an excellent support for stabilizing PdNPs.[17a,26] As indicated in Figure 4d, Pd@NAC-800 demonstrated stable recyclability upon filtration from the reaction mixture and washing with ethanol. The catalyst could be used for 10 successive cycles in the hydrogenation of nitrobenzene, and a yield of 99% was well maintained. After removal of the Pd@NAC-800 catalyst, the Pd concentration in the reaction solution was obtained to be less than 0.1 ppm by using inductively coupled plasma atomic emission spectroscopy. Nitrobenzene (1 mmol) was again added to the filtrate, and the mixture was held at room temperature and 0.1 MPa H_2 pressure. In this case, no reaction proceeded. These results indicated that leaching of Pd into the liquid phase was negligible and the observed catalysis was intrinsically heterogeneous. The separated Pd@NAC-800 catalyst after the tenth reaction run was also examined by using TEM, HAADF-STEM, and XPS. Compared with the images of the fresh Pd@NAC-800 catalyst, TEM and HAADF-STEM images of the recycled catalyst Pd@NAC-800 do not show any obvious changes. The small-sized PdNPs are still homogeneously dispersed on the surface of the support, and the particle size distribution of the catalyst is 2.2 ± 0.5 nm, which is close to that of the fresh catalyst. Its Pd 3d XPS data reveal that Pd^0 is still the main metal species and the obvious change in the Pd^0 content is not detected. All these analyses further indicated that the N incorporation on the surface of the carbon support could efficiently stabilize PdNPs and prevent their aggregation.

Conclusions

A series of N-functionalized active carbon (NAC) were conveniently prepared from the cheap active carbon and used as supports of small-sized Pd nanoparticle catalysts. Of all the catalysts, Pd@NAC-800 demonstrated high catalytic performance and excellent chemoselectivity for the selective hydrogenation of nitro compounds to the corresponding aniline derivatives. The N species could stabilize Pd nanoparticles and prevent their aggregation; at the same time, the N species and their state could accelerate the hydrogenation reaction. Moreover, the Pd@NAC-800 catalyst

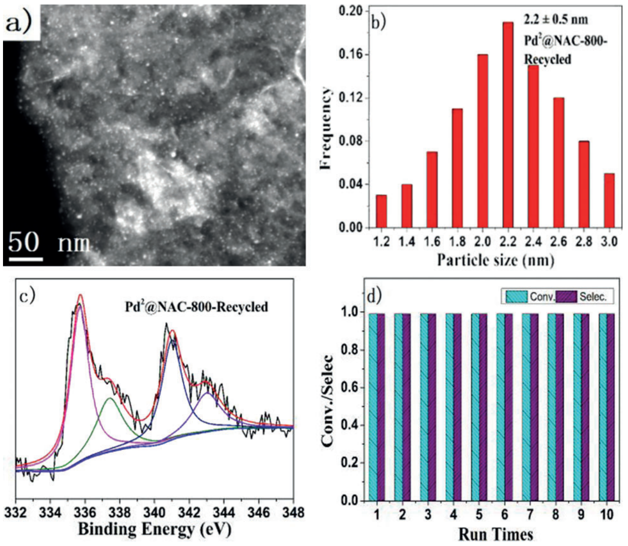


Figure 4. a) HAADF-STEM, b) distribution of particle size, and c) Pd 3d XPS spectra of Pd@NAC-800 after 10 runs; d) recycle experimental data for Pd@NAC-800. Reaction conditions: 5 mmol of nitrobenzene, 0.5 mol% Pd@NAC-800, 5 mL of ethanol, room temperature, $t = 3$ h, $P = 0.1$ MPa H_2.

could be used 10 times without the loss of product yield. Investigations on the preparation of other supported metallic or heterometallic nanoparticle catalysts and their catalysis are ongoing in our laboratory.

Experimental Section

N-Functionalization of active carbon with melamine through heat treatment

In general, active carbon (10 g) and melamine (10 g) were added into a 250 mL round bottom flask containing ethanol (160 mL), and the resultant mixture was heated to 80 °C to volatilize the solvent under stirring. The solid mixture was loaded into the high-temperature reactor, and the reactor was kept in the muffle furnace; then, it was heated up to the targeted temperature (600, 700, and 800 °C; ramp rate: 3 °C min^{-1}) and held for 2 h. Finally, the reactor was cooled to RT and the N-doped active carbon materials were obtained. Those carbon materials were labeled NAC-*T* (in which *T* represented the treatment temperature in the muffle furnace).

Immobilization of PdNPs

An aqueous solution of H_2PdCl_4 was initially prepared by mixing $PdCl_2$ (0.34 g) and the HCl aqueous solution (20 mL, 10% v/v) with stirring at RT until the salt dissolved homogeneously. Then, a certain amount of the prepared NAC powder was impregnated with the H_2PdCl_4 solution and the mixture was stirred for 5 h at RT. Subsequently, an excess of $NaBH_4$ aqueous solution was added slowly to the suspension mixture under ice bath conditions. Finally, the corresponding supported PdNPs were separated through filtration, washed sequentially with distilled water and absolute ethanol several times, and dried at 80 °C overnight in a vacuum oven to obtain the corresponding PdNP catalysts (labeled as Pd@NAC-*T*). The typical method for preparing Pd@NAC-800 was as follows: NAC-800 (1 g) was mixed with deionized water (20 mL) containing the H_2PdCl_4 solution (2 mL). The mixture was stirred for 5 h at RT. Then, an excess of $NaBH_4$ aqueous solution (144 mg dissolved in 10 mL of deionized water) was added slowly to the suspension mixture under ice bath conditions. The mixture was stirred for 1 h, and then the corresponding supported PdNPs were separated through filtration, washed sequentially with distilled water and absolute ethanol several times, and dried at 80 °C overnight in a vacuum oven to obtain Pd@NAC-800.

Pd@NAC-*T*-catalyzed hydrogenation of nitro compounds

Hydrogenation reactions were performed in a 50 mL Schlenk glass tube equipped with a magnetic bar. The heterogeneous Pd catalyst, substrate, and solvent were introduced into the tube, and then it was vacuumed and purged with H_2 thrice before it was finally pressurized with 0.1 MPa of H_2 gas. Subsequently, the reaction mixture was stirred at RT. After the completion of the reaction, excess H_2 was carefully released and the internal standard toluene was added. The resultant product mixtures were analyzed with an Agilent gas chromatograph. The recycle experiments were performed with use of a 350 mL Schlenk glass tube, and the catalyst was separated from the reaction mixture through filtration in the fresh run.

Instruments

Pd content and immobilization yield were obtained by using inductively coupled plasma atomic emission spectroscopy. The powder XRD measurements were performed with a PANalytical's X'Pert PRO multipurpose diffractometer with Ni-filtered CuK$_\alpha$ radiation ($\lambda = 0.15046$ nm) at RT and $2\theta = 10.0$–$80.0°$. TEM and HRTEM experiments were performed with a JEM-2010 transmission electron microscope operating at an accelerating voltage of 200 kV. XPS analyses of the catalysts were performed on a Thermo Fisher Scientific's K-Alpha X-ray photoelectron spectrometer.

NMR data for some of the products

***p*-Toluidine**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.04$–6.85 (m, 2H), 6.59 (dd, $J = 14.1$, 7.6 Hz, 2H), 3.66–3.45 (m, 2H), 2.23 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 143.8$, 129.8, 127.8, 115.4, 20.5 ppm.

Benzene-1,2-diamine: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.79$–6.65 (m, 4H), 3.36 ppm (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 134.8$, 120.3, 116.8 ppm.

Naphthalen-1-amine: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.52$–7.39 (m, 4H), 7.36–7.30 (m, 1H), 7.19–7.06 (m, 2H), 6.94–6.63 (m, 2H), 3.70 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 143.6$, 139.6, 130.5, 129.1, 128.9, 128.5, 127.7, 127.2, 118.7, 115.6 ppm.

Methyl 4-aminobenzoate: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.04$–7.75 (m, 2H), 6.80–6.57 (m, 2H), 4.10 (s, 2H), 3.85 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 167.2$, 150.9, 131.6, 119.6, 113.8, 51.6 ppm.

1-(4-Aminophenyl)ethanone: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.86$–7.76 (m, 2H), 6.65–6.61 (m, 2H), 4.12 (s, 2H), 2.50 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.5$, 151.3, 130.8, 126.8, 113.7, 26.1 ppm.

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Keywords: active carbon · hydrogenation · N-doped · nitroarenes · Pd nanoparticles

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