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One-pot synthesis of Pd nanoparticle catalysts supported on N-doped carbon and the application in the domino carbonylation

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ABSTRACT: In this work, we report a novel and facile procedure to one pot prepare palladium nanoparticles catalysts supported on porous N-doped carbon (Pd@CN^T) by direct carbonization of palladium-N-heterocyclic carbene coordination polymer (P-Pd-NHC). This method could be conveniently extended to the synthesis of the Ni and alloy (Pd_xNi_y) nanoparticles catalysts (Ni@CN⁸⁰⁰, Pd_xNi_y@CN⁸⁰⁰). The treatment temperature played an important role on the growth and properties of the resultant M@CN^T, wherein M@CN⁸⁰⁰ carbonized at 800°C showed well monodispersed metal nanoparticles (MNPs), graphene-like layers of the N-doped carbon supports and strong interaction between MNPs and the support. Pd@CN⁸⁰⁰ displayed high efficiency and stable recyclability toward the domino carbonylative synthesis of pyrazole derivatives. Interestingly, its catalytic performance has been even higher than that of the representative PdCl₂(PPh₃)₂ within six runs.

1. INTRODUCTION

Recently, the synthesis of supported MNPs as heterogeneous catalyst for liquid phase reactions has attracted extensive research interests.¹⁻³ Impregnation and coprecipitation are commonly used methods to prepare these supported catalysts, however, either the aggregation of MNPs or the irreversible leaching of metal atoms from the supports during the reaction will inevitably reduce their catalytic activity and stability, which are also the limitations of the post-loading methodology to the practical applications. Additionally, the preparation of such kind of catalysts usually needs to use excess reducing reagents such as NaBH₄ and LiAlH₄ resulting inorganic wastes. Therefore, the development of methodology to expediently synthesize active and stable supported MNPs for liquid phase reactions is highly desirable.^{1,4}

Nanostructured porous carbon materials have been the popular catalytic supports due to their high surface area and good stability.⁵⁻¹⁵ It is known that traditional carbons (including carbon black, activated carbon, carbon nanofibers and carbon nanotubes) are poor in functional groups, and so their supported MNPs by ordinary impregnation often result in aggregation or leaching of the particles in the liquid solution because of the weak interaction between MNPs and the carbon supports. A possible solution to enhance the catalytic performance and the stability of such kind of catalysts is the introduction of functional groups (e.g. nitrogen groups) on the surface of the supports.¹⁶⁻¹⁹ Among the procedures used to

synthesize nitrogen-doped (N-doped) carbons, in situ doping by using nitrogen-containing precursors can realize a homogeneous incorporation of nitrogen into carbons. Following such direct carbonization method, Antonietti, Dai and their coauthors have prepared functional N-doped carbons.²⁰⁻²⁴ These N-doped carbon materials themselves have shown novel physicochemical properties and could be better supports to stabilize and disperse MNPs for the post-preparation.^{10,12,25,26} However, to the best of our knowledge, no one-pot synthesis of MNPs catalysts supported on N-doped carbon without using any reducing agents has ever been reported.

Transformations of rationally synthesized molecular compounds to materials constitute an important new direction in both structural inorganic chemistry and materials chemistry, which will enable possible pathways for the rational design of materials.²⁷ Based on this concept, in situ carbonization of structurally defined organometallic coordination polymers containing both nitrogen and metal atoms could possibly be an option for one-step preparation of metal-supported N-doped carbon catalytic materials. Additionally, high carbonization yields, certain amount of functional groups loading and homogeneous distributions of MNPs in the carbon matrix, are also the important key factors for the development of a procedure to synthesize such catalytic material.²³ In the last decade, N-heterocyclic carbene (NHC) metal complexes have found wide range of applications in catalysis and material.^{28,29} We herein report a facile one-pot synthesis of (hetero)metallic(Ni, Pd or Ni_xPd_y) nanoparticles supported N-

doped carbon catalytic materials from the corresponding (hetero)metal-NHC coordination polymers. Such kind of supported catalysts displayed narrow metal size distribution, good stability and efficient catalytic activity toward a four-component cascade carbonylation reaction to yield heterocyclic pyrazole.

Based on our and other reported knowledge³⁰⁻³³, transition metal acetate salts, such as Pd(OAc)₂ and Ni(OAc)₂, could easily react with imidazolium C2-H of the NHC precursor to form a M-C bond, which could be a bridge to intermolecularly link polydentate NHCs and generate a coordination polymer. Meanwhile, Dai and coworkers have found that the nitrile arm of an ionic liquid is a key to attain high carbon yields of the resultant metal-free carbon nitride materials.^{34,35} It is assumed that a metal-NHC coordination polymer with functional nitrile arms could be an ideal precursor for the one-pot preparation of metal-supported N-doped carbon catalysts via high temperature carbonization, by which the carbon, nitrogen atoms and MNPs would be homogeneously reassembled to form MNPs embedded N-doped carbon catalysts.

2. EXPERIMENTAL SECTION

2.1 Synthesis of P-M-NHC. A novel and tridentate NHC precursor, [TPBAIm][NTf₂]₃, with functional nitrile arms was initially prepared in high yield from readily accessible starting materials [Scheme S1 in the Supporting Information (SI)]. Subsequently, as shown in Scheme 1, [TPBAIm][NTf₂]₃ and 1.5 equivalent of Pd(OAc)₂ or Ni(OAc)₂ or their mixture with certain mole ratio were dissolved in 10 mL of DMF with the presence of 3.6 equivalent of NaOAc and were stirred at 110 °C for 24 h. A pale yellow precipitate was formed, and the precipitate was isolated by filtration and rinsed with DMF (3 × 30 mL) and EtOH (3 × 30 mL) to remove unreacted salts. Solvent was removed by heating the material at 150 °C for 24 h under vacuum to yield the desired P-M-NHC. Taking P-Pd-NHC as an example, [TPBAIm][NTf₂]₃ (1.0 mmol) reacted with Pd(OAc)₂ (1.5 mmol) in the presence of NaOAc (3.6 mmol) in 10 mL of DMF at 110 °C. Finally, 970 mg of P-Pd-NHC was isolated.

2.2 Synthesis of M@CN^T. The carbonization was performed under N₂ atmosphere. A certain amount of specific P-M-NHC was introduced into a quartz tube and the temperature was controllably ramped at a rate of 10 °C min⁻¹ to a final temperature (300, 400 and 800 °C), and then the final temperature was maintained for 1 h to finish the one-pot synthesis of monometallic or bimetallic nanoparticle catalysts supported N-doped porous carbon, generally named as M@CN^T, wherein CN represents N-doped carbon support and M stands for Ni or Pd or Pd_xNi_y, and T is the carbonization temperature. Additionally, for the sake of comparison, the ligand precursor [TPBAIm][NTf₂]₃ was also similarly carbonized at 800 °C under N₂ for 1 h, and the product was named as LP⁸⁰⁰.

2.3 Material Characterization. NMR spectra were obtained on a BRUKER DRX spectrometer operating at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR. Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent

peak multiplications. High resolution mass spectra (HRMS) were recorded by Bruker microTOF-II (ESI). Elemental analyses were carried out on a Vario EL analyzer. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on a Shimadzu ICPS-8100 equipment by the chemical analysis team in RIKEN. The detection of palladium content was carried out on an Atomic absorption spectroscopy (AAS) and its model is 180-80. Powder X-ray diffraction (XRD) measurements were performed using an X'Pert Pro multipurpose diffractometer (PANalytical, Inc.) with Ni-filtered CuKα radiation (0.15046 nm) at room temperature from 10.0 ° to 80.0 ° (wide angle). Measurements were conducted using a voltage of 40 kV, current setting of 40 mA, step size of 0.02 °, and count time of 4 s. The nitrogen adsorption and desorption isotherms at -196 °C were recorded on an Autosorb-iQ analyzer (Quantachrome Instruments, Boynton Beach, FL). Prior to the tests, samples were degassed at 200 °C for 4 h. The specific surface areas were calculated via the BET method in the relative pressure range of 0.05–0.3, the single-point pore volume was calculated from the adsorption isotherm at a relative pressure of 0.990. Transmission electron microscopy and High resolution transmission electron microscope (TEM, HRTEM) experiments were conducted in a JEM-2010 TEM with an accelerating voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) analyses of the catalysts were performed on a Thermo Fisher Scientific K-Alpha spectrometer. Thermogravimetric-differential scanning calorimetry (TG-DSC) measurements were carried out on a NETZSCH STA 449F3 thermogravimetric analyzer from room temperature to 800 °C at a rate of 10 °C/min under nitrogen atmosphere.

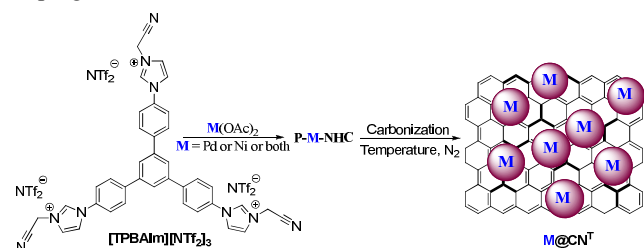
2.4 Catalytic application in the domino carbonylation. Representative Pd@CN⁸⁰⁰ (0.01 mmol), iodobenzene (0.5 mmol), phenylacetylene (0.60 mmol), phenylhydrazine (0.65 mmol), Et₃N (1.0 mmol) and 1.5 mL of MeOH were introduced into a 50 mL Schlenk tube with a magnetic bar, then the glass tube was vacuumed and purged with CO (99.99 % purity) three times before it was finally pressurized with 1.0 atm of CO gas. Subsequently, the reaction mixture was stirred at 70 °C for 6 h. After cooling to room temperature, excess CO was carefully released and the crude product was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as eluent to afford the pyrazole product.

After the completion of the fresh reaction performed as above typical procedure, the liquid reaction mixture was separated from Pd@CN⁸⁰⁰ catalyst through centrifugation, and the residual solid catalyst could be reused for the next run after addition of fresh reactants.

3. RESULTS AND DISCUSSION

The MNPs catalysts supported on N-doped carbon, M@CN⁸⁰⁰ (M = Pd, Ni), carbonized at 800 °C were initially prepared and their structure and morphology were characterized by transmission electron microscopy (TEM), as shown in Figure 1a, 1e and Figure S1, S2, the PdNPs in Pd@CN⁸⁰⁰ and NiNPs in Ni@CN⁸⁰⁰ are well monodispersed in different graphene-like layers of the N-doped carbon

supports and possess a uniform size distribution, which are quite narrow with 12.3 ± 1.1 nm for PdNPs (300 nanoparticles, Figure 1b) and 3.0 ± 0.5 nm for NiNPs (Figure 1f), respectively. Interestingly, this facile method could not only apply to the synthesis of monometallic MNPs-supported N-doped carbons, but also to the preparation of bimetallic nanostructured catalytic materials by carbonization corresponding P-Pd_xNi_y-NHC with certain metal ratio. It is revealed in Figure 1g, 1h and Figure S3 that the Pd₈₀Ni₂₀NPs of Pd₈₀Ni₂₀@CN⁸⁰⁰ are also homogeneously dispersed in the N-doped carbon matrix and its diameter is finely controlled at around 9.0 ± 1.0 nm, which is between the diameter of monometallic NiNPs and PdNPs. Subsequently, representative Pd_xNi_y@CN⁸⁰⁰ with different Pd and Ni ratio could be easily prepared in high yields. TEM analysis of Pd₅₀Ni₅₀@CN⁸⁰⁰ and Pd₂₀Ni₈₀@CN⁸⁰⁰ in Figure S4 and S5 showed that the alloy nanoparticles could also be well monodispersed in the resultant N-doped carbon supports. Additionally, as presented in Figure 2, the X-ray diffraction (XRD) patterns of Ni@CN⁸⁰⁰, Pd@CN⁸⁰⁰ and Pd_xNi_y@CN⁸⁰⁰ further proved that the monometallic PdNPs, NiNPs and bimetallic Pd_xNi_y alloy nanoparticles have been successfully obtained. All these characterizations indicate that the direct carbonization of structure-defined and readily synthesized metal-NHC coordination polymers is a facile and general methodology to prepare monometallic- and heterometallic-MNPs supported N-doping carbon materials.



Scheme 1. Synthesis of P-M-NHC and M@CN^T.

To gain more information about the formation of the nanoparticles, monometallic Pd@CN^T were taken as model samples to investigate further. Though the PdNPs loading for Pd@CN⁸⁰⁰ was as high as 24 % estimated by atomic absorption spectroscopy (AAS), it was observed that the PdNPs were homogeneously embedded on the nanostructured N-doped carbon supports from the TEM results. Furthermore, the well dispersed small metal nanoparticles could also be clearly seen from the STEM-HAADF image (Figure S1c) of Pd@CN⁸⁰⁰. It could be calculated from the high-resolution TEM (HRTEM, figure S1d) image of the Pd@CN⁸⁰⁰ that the interplanar spacing of the PdNPs particle lattices is 0.23 nm, which matched well with the (111) lattice spacing of face-centered cubic (fcc) Pd. A good indication of the growth mechanism of such kind of MNPs supported carbon catalysts came from the differences of PdNPs size distribution and N-doped carbon matrix morphology of Pd@CN⁴⁰⁰ and Pd@CN⁸⁰⁰, smaller and narrower PdNPs size distribution with 8.2 ± 0.8 nm could be obtained in Pd@CN⁴⁰⁰ (figure 1d), however, its supports displayed an amorphous morphology while the supporting matrix of Pd@CN⁸⁰⁰ exhibited layered graphene-like structure (Figure 1c), which suggested that the carbonization temperature played an crucial role in the syntheses of these catalytic materials. Additionally, it could be

speculated that the formation of PdNPs was initiated by the cleavage of Pd-C bond and then Pd, C and N atoms were assembling to grow to the optimal structured PdNPs supported N-functional carbon with the increasing temperature.

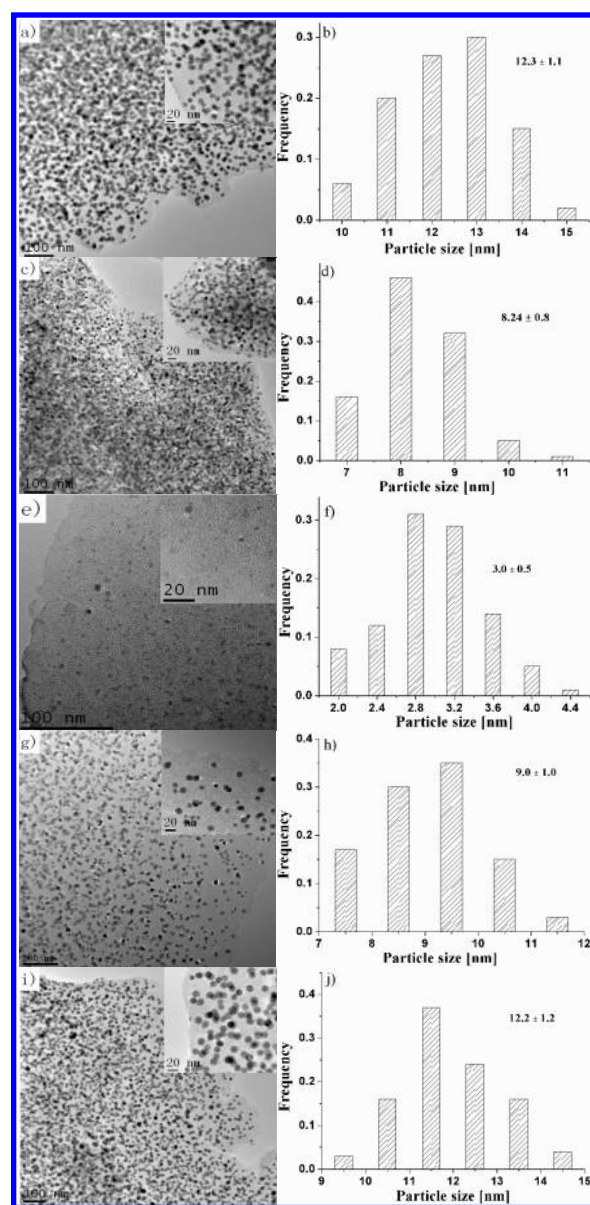


Figure 1. TEM pictures and metal nanoparticle size distribution of: a) and b) Pd@CN⁸⁰⁰. c) and d) Pd@CN⁴⁰⁰. e) and f) Ni@CN⁸⁰⁰. g) and h) Pd₈₀Ni₂₀@CN⁸⁰⁰. i) and j) recycled catalyst (Pd@CN⁸⁰⁰) after six runs.

The carbonization yield is also an important factor for the material synthetic method, as shown in Table 1, the yield of LP⁸⁰⁰ through carbonization of [TPBAIm][NTf₂]₃ at 800 °C is 37 wt %, and the formation of organometallic coordination polymer (P-Pd-NHC) could effectively enhance the carbonization yield to 58 wt %, affording structurally optimized Pd@CN⁸⁰⁰. Due to the similar manipulation procedure, thermogravimetric analysis (TGA) could be a good tool to detect the carbonization process of [TPBAIm][NTf₂]₃.

and P-Pd-NHC. It is revealed in Figure 3A that their decomposition occurred in two distinct steps, the first stage of [TPBAIm][NTf₂]₃ started at 337 °C, and P-Pd-NHC proceeded to decompose at a lower temperature (225 °C) possibly due to the initial disconnection of coordinative Pd-OAc bonds in the P-Pd-NHC, and both of their first decomposition stage completed until 500 °C. Their second decomposition phase were similar, ranging from 500 °C to 800 °C. The C, N and H content variations of P-Pd-NHC, Pd@CN⁴⁰⁰ and Pd@CN⁸⁰⁰ detected by EA are shown in Figure 3B, when temperature increased from 400 °C to 800 °C, N content decreased from 7.15 to 4.45 wt% and H content decreased to 0.85 wt%. These variations possibly indicated that the carbon nitride matrix reconstructed to form the proper ring system to fit the requirements of the locally graphitized structure, which is also in accordance with the TEM results showing the carbon nitride matrix changing from amorphous morphology for Pd@CN⁴⁰⁰ to the layered graphene-like structure of Pd@CN⁸⁰⁰. N₂ adsorption-desorption isotherms for LP⁸⁰⁰, Pd@CN⁴⁰⁰ and Pd@CN⁸⁰⁰ are given in Figure 4. Compared with Pd@CN⁴⁰⁰, the nitrogen sorption isotherms of Pd@CN⁸⁰⁰ and LP⁸⁰⁰ exhibit a type-H2 hysteresis loop, indicating the presence of mesoporosity. However, when the Pd nanoparticles are introduced into Pd@CN⁸⁰⁰, its specific surface area and the pore volume fell dramatically (Table 1).

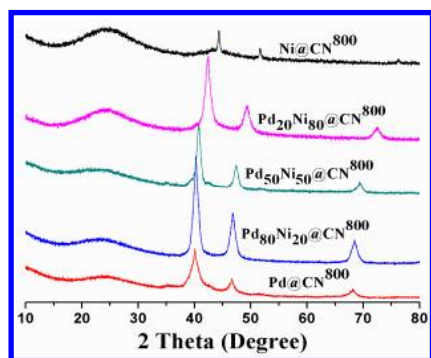


Figure 2. Wide-angle XRD patterns of Pd_xNi_y@CN⁸⁰⁰.

Table 1. Characteristics of LP⁸⁰⁰ and Pd@CN^T

Sample	Carbonization	S _{BET} (m ² g ⁻¹)	V _{BJH} (cm ³ g ⁻¹)
	Yield (%)		
LP ⁸⁰⁰	37	667	0.50
Pd@CN ⁴⁰⁰	90	344	0.17
Pd@CN ⁸⁰⁰	58	395	0.19

Figure 5a showed the XRD patterns of P-Pd-NHC and its carbonized Pd@CN^T at different temperatures. P-Pd-NHC precursor only displayed a broad band at ca. 25 °, indicating its amorphous nature and Pd²⁺ oxidation state of the coordination polymer. After P-Pd-NHC was carbonized to Pd@CN^T, three well-resolved peaks were observed in Pd@CN³⁰⁰, Pd@CN⁴⁰⁰, and Pd@CN⁸⁰⁰, respectively. The sharper peaks of the XRD patterns for Pd@CN⁸⁰⁰ proved that the highly crystalline face-centered cubic (fcc) Pd nanoparticles were obtained. The slightly broad peaks for Pd@CN³⁰⁰ and

Pd@CN⁴⁰⁰ shifted to lower values, which indicated PdC_x phase was formed during carbonization at 300 °C and 400 °C. These phenomena were consistent with the previous reports that the lattice parameter of bulk Pd with carbon occupying interstitial octahedral sites has increased.³⁶⁻³⁸ And when enhancing the treatment temperature to 800 °C under inert atmosphere, the interstitial carbon atoms would be expelled from the palladium lattice to form pure PdNPs.³⁶⁻³⁸

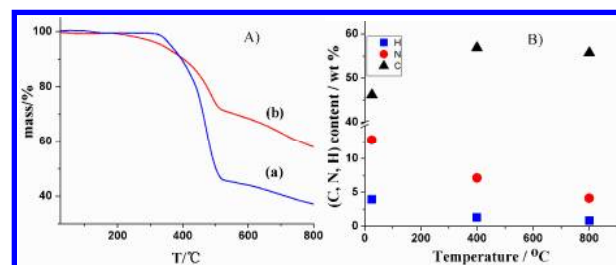


Figure 3. A): TG curves of a): [TPBAIm][NTf₂]₃; b): P-Pd-NHC under N₂ with a heating rate of 2 °C min⁻¹. B): C, N and H content of P-Pd-NHC, Pd@CN⁴⁰⁰, Pd@CN⁸⁰⁰ determined by elemental analysis (EA).

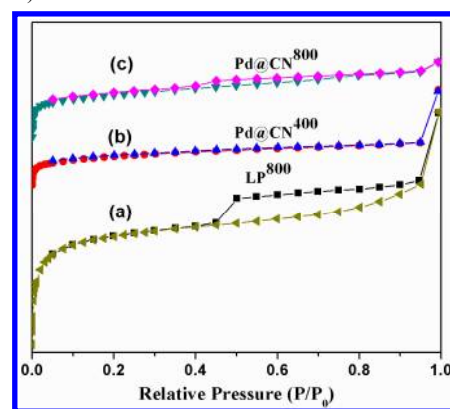


Figure 4. Nitrogen sorption of (a) LP⁸⁰⁰, (b) Pd@CN⁴⁰⁰ and (c) Pd@CN⁸⁰⁰.

X-ray photoelectron spectroscopy (XPS) analysis was also used to study the variation of the Pd oxidation state in the precursor and resultant Pd@CN^T catalysts. As shown in Figure 5b, the Pd 3d photoelectron spectrum of P-Pd-NHC showed two peaks around 342.8 and 337.6 eV in the 3d_{3/2} and 3d_{5/2} levels, indicating the Pd species in the polymer precursor are Pd²⁺ state, which was also proved by previous XRD analysis. Although the XPS patterns of Pd@CN³⁰⁰ was still dominated by Pd²⁺ oxidation state, characteristic Pd⁰ species with 3d_{5/2} spin-orbit components at 335.0 and 335.5 eV assignable to metallic Pd and carbon-diffused PdC_x surface phase, respectively, started to be generated after heat treatment for P-Pd-NHC at 300 °C (Figure S6a). XPS measurement of Pd@CN⁴⁰⁰ showed most of the Pd species presented as Pd⁰ nanoparticles with small amount of oxidized Pd atoms in the N-doped carbon matrix (Figure S6b). Upon enhancing the carbonization temperature to 800 °C, the characteristic Pd photoelectron peaks indicated that the majority (roughly 81% based on XPS) of the Pd species are well-crystallized Pd⁰ nanoparticles (Figure S6c). It was reported that the introduction

of amine groups possessing electron-donor properties in the carbon carrier can stabilize high-dispersed Pd⁰ and prevented its re-oxidation.³⁹ In our case, the status of N in Pd@CN³⁰⁰, Pd@CN⁴⁰⁰ and Pd@CN⁸⁰⁰ can also be explored by XPS analysis of N1s, as shown in Figure 6a and Figure S7, the N1s spectra could be divided into two peaks, one peak at 398.4 eV ascribed to pyridine-like sp² nitrogen and another 400.9 eV peak attributed to the quaternary nitrogen.^{40,41} Therefore, the pyridinic nitrogen atoms along with the quaternary nitrogen in planar C-N-C-layers in our system can stabilize high-dispersed Pd⁰ prevent efficiently the re-oxidation of the Pd atoms.^{26,39} When a nitrogen atom is doped into carbon materials, the charge distribution of the carbon atoms will be influenced by the neighbor nitrogen dopants.⁴² Hence, the C1s spectrum for Pd@CN⁸⁰⁰ could also be deconvoluted into two peaks centered at 284.6 and 285.8 eV, corresponding to pure graphitic sites in the CN matrix and sp² carbon atoms bonded to the nitrogen inside the aromatic structure, respectively (Figure 6b).^{43,44}

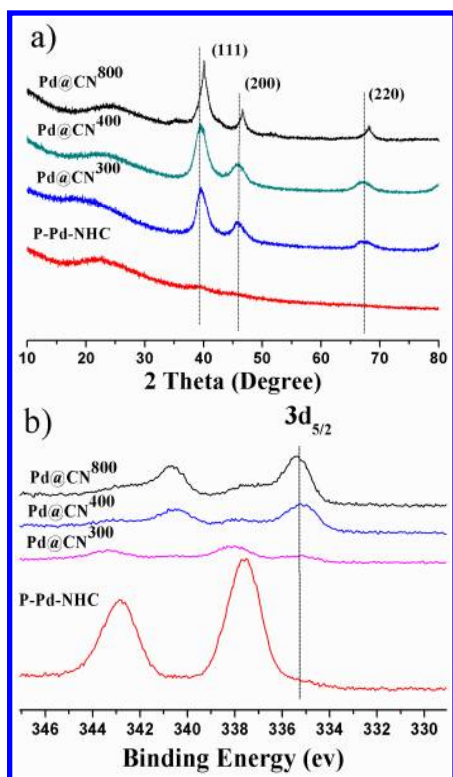


Figure 5. a) Wide-angle XRD pattern of Pd@CN^T; b) The Pd 3d XPS spectra of Pd@CN^T.

In present series of Pd@CN^T catalysts, strong metal-support interaction between Pd nanoparticle and the carbon nitride support can be speculated by the characteristic XPS peak at 335.5 eV, which could be attributed to the PdC_x phase formation^{45,46} and the interactions⁴⁷ between Pd nanoparticles and the carbon nitride matrix in Pd@CN³⁰⁰ and Pd@CN⁴⁰⁰. Pd 3d_{5/2} XPS peak at 335.5 eV of Pd@CN⁸⁰⁰ was exclusively induced by the strong interaction between Pd nanoparticles and N-doped carbon support since PdC_x phase formed in lower temperature has been transferred into metallic Pd

nanoparticles. Therefore, treatment of the organometallic coordination polymers homogeneously containing nitrogen and metal atoms could possibly be an alternative to realize the high dispersion of the nitrogen and MNPs in the carbon materials through their chemically assembling growth and thus increase the interaction between MNPs and supports. It is important to note that, comparing with PdC_x species, the pure Pd nanoparticles possibly show higher reactivity toward the oxidative addition of Pd⁰ onto C-X bond during the catalytic transformation of aryl halide.

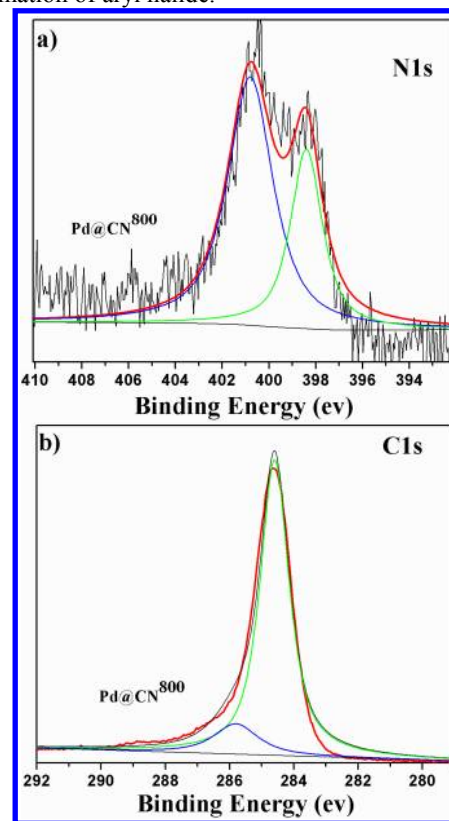
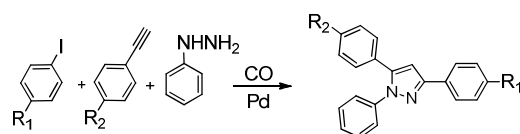


Figure 6. XPS analysis of Pd@CN⁸⁰⁰: a) N1s and b) C1s.

Multicomponent domino reactions are among the most powerful synthetic tools available because they allow rapid access to structural variation and complexity in a single reaction vessel without intermediary purification steps.⁴⁸⁻⁵⁰ However, those transformations are mainly achieved by the homogeneous catalysis of a noble metal catalyst and thus a recyclable catalyst system will promote it to be a more competitive and economical tool, especially in the preparation of heterocyclic compounds. Pyrazole, a five-membered heterocycle with two adjacent nitrogen atoms, has attracted considerable interests in medicinal and coordination chemistry.⁵¹⁻⁵⁴ Mori and coauthors⁵⁵ developed a homogeneous Pd-catalyzed four-component coupling carbonylation of aryl iodide, terminal alkyne and hydrazine to yield substituted pyrazole (see Table 2), but such method failed in the reaction with arylhydrazine. Later, Stonehouse et al.⁵⁶ disclosed another similar catalytic procedure replacing CO gas with solid Mo(CO)₆ as carbonyl resource, however, phenylhydrazine only giving 47% yield of the corresponding triaryl substituted pyrazole. One of the key factor of this tandem catalytic synthesis is to develop an active Pd⁰ catalyst to

initiate its oxidative addition onto the aryl C-X bond, this catalyst requirement matches well with the property of present Pd@CN⁸⁰⁰, which has very high and widely dispersed Pd⁰ metallic nanoparticle proportion as well as the stability support through the interaction with the N-doped porous carbon materials. To verify this assumption and proceed our ongoing interest on the Pd-catalyzed carbonylation reactions,⁵⁷⁻⁶¹ four-component carbonylation of iodobenzene, phenylacetylene, phenylhydrazine and CO gas was selected as a model reaction to test the catalytic performance of the heterogeneous Pd@CN^T catalysts. Such cascade reaction would be an initial carbonylative Sonogashira coupling between benzene iodide and aryl alkyne to yield α , β -alkynyl ketone^{55,62}, followed by the addition and cyclic condensation with phenylhydrazine to give the desired pyrazole product.⁶³⁻⁶⁶

Table 2. One-pot four-component synthesis of pyrazoles^[a].



Entry	catalyst	R ₁	R ₂	Yields ^[b] (%)
1	Pd@CN ⁸⁰⁰	H	H	92
2	Pd@CN ³⁰⁰	H	H	36
3	Pd@CN ⁴⁰⁰	H	H	62
4	PdCl ₂ (PPh ₃) ₂	H	H	83
5	Pd@CN ⁸⁰⁰	H	F	88
6	Pd@CN ⁸⁰⁰	H	<i>t</i> -Bu	81
7	Pd@CN ⁸⁰⁰	Cl	H	83
8	Pd@CN ⁸⁰⁰	Cl	F	93
9	Pd@CN ⁸⁰⁰	Cl	<i>t</i> -Bu	86
10	Pd@CN ⁸⁰⁰	Me	H	92
11	Pd@CN ⁸⁰⁰	Me	F	93
12	Pd@CN ⁸⁰⁰	Me	<i>t</i> -Bu	88
13 ^[c]	Pd@CN ⁸⁰⁰	H	H	84

[a] Reaction conditions: iodobenzene (0.5 mmol), arylacetylene (0.60 mmol), phenylhydrazine (0.65 mmol), catalyst (2.0 mol %), Et₃N (1.0 mmol), MeOH (1.5 mL), CO (1.0 atm), temperature (110 °C) and reaction duration (6 h). [b] Isolated yield. [c] Hydrazine hydrate.

To our delight, as shown in Table 2, Pd@CN⁸⁰⁰ demonstrated efficient activity toward the one-pot synthesis of biaryl substituted pyrazole, giving a 92 % yield under 1.0 atm pressure of CO gas (Entry 1). However, its analogues carbonized at lower temperature, Pd@CN³⁰⁰ and Pd@CN⁴⁰⁰, only showed low to moderate activities (Entry 2 and 3). These catalytic activity differences are consistent with their properties of the corresponding Pd@CN^T based on TEM, XRD and XPS analysis, which revealed that Pd@CN⁸⁰⁰ has

higher proportion of well dispersed metallic Pd nanoparticles and stronger support stabilization effect. Surprisingly, the current heterogeneous catalytic system even presented higher reactivity than that of the representative homogeneous carbonylation catalyst, PdCl₂(PPh₃)₂, which yielded 85 % of the triphenyl-substituted pyrazole (Entry 4). This is possibly because the current cascade reaction is initiated by a Pd⁰ species and the homogeneous Pd²⁺ complex need to be reduced to Pd⁰ before it can undergo the oxidative addition onto the C-X bond of aryl halide. Furthermore, the present Pd nanoparticles catalysts supported N-doped carbon displayed good substrate tolerance, iodobenzenes and phenylacetylenes with different electronic donating or withdrawing substituents all worked perfectly with high isolated yields of the desirable pyrazoles (Entries 5-12, 81-93 %). Besides phenylhydrazine, the cascade carbonylative coupling reaction with the simple hydrazine could also proceed efficiently, giving an 84 % yield of the expected biaryl-substituted pyrazole (Entry 13).

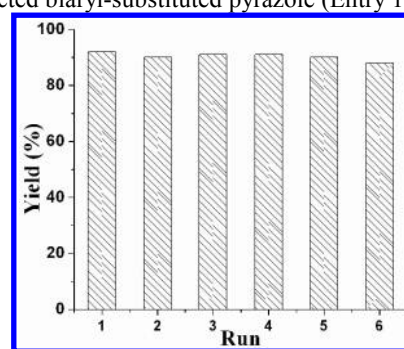


Figure 7. Recycle of the catalyst Pd@CN⁸⁰⁰. Reaction conditions: iodobenzene (0.5 mmol), phenylacetylene (0.60 mmol), phenylhydrazine (0.65 mmol), Pd@CN⁸⁰⁰ (2.0 mol%), Et₃N (1.0 mmol), MeOH (1.5 mL), CO (0.1 MPa), temperature (110 °C) and reaction duration (6 h).

Besides efficient catalytic activity, stable recyclability is also crucial for an outstanding heterogeneous catalyst from the viewpoint of both academic research and industrial applications. As shown in figure 7, Pd@CN⁸⁰⁰ demonstrated high stability and could be used at least six times by simple centrifugation without a significant loss of its catalytic performance. To further verify its stability, Pd concentration in the reaction solution was determined by ICP-AES to be less than 0.1 ppm, indicating that leaching of Pd into the liquid phase is negligible. Moreover, TEM analysis of the reused catalyst revealed that the dispersion and size distribution of PdNPs did not show any obvious change after six runs (Figure 1g and 1f) comparing with the fresh catalysts (Figure 1a and 1b). As expected, the nitrogen functionalities on the carbon matrix might act as a coordination donor ligand to tune the electronic property of PdNPs and thus enhance its stability as well as the catalytic activity.

4. CONCLUSION

In summary, a facile one pot methodology to prepare metallic and heterometallic nanoparticles catalysts supported on porous N-doped carbon by direct carbonization of a metal-NHC coordination polymer has been successfully developed. Deep investigations revealed that treatment temperature played an important role on the growth and properties of the resultant

M@CN^T. The novel Pd catalyst, Pd@CN⁸⁰⁰, displayed high activity and selectivity toward the domino carbonylative synthesis of pyrazole derivatives from three simple substrates and an atmosphere pressure of CO gas. Its outstanding catalytic performance has been even higher than that of the representative Pd²⁺ homogeneous catalyst within six runs. These promising characters of M@CN^T and their facile preparative method will prompt us to prepare more (hetero) metallic nanoparticles supported catalysts and investigate their sustainable catalysis in the further research.

ASSOCIATED CONTENT

SUPPORTING INFORMATION

The details of the preparation of materials and their characterizations, catalytic procedures and NMR spectra for the pyrazole products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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One-pot synthesis of Pd nanoparticle catalysts supported on N-doped carbon and the application in the domino carbonylation

A facile one pot procedure to prepare metallic and heterometallic nanoparticles catalysts supported on porous N-doped carbon by direct carbonization of novel metal-NHC coordination polymers has been developed. The representative Pd@CN⁸⁰⁰ exhibited high activity and stability toward the carbonylative domino syntheses of pyrazole derivatives under mild reaction conditions.

