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#### Selective hydrogenation of quinoline into 1,2,3,4tetrahydroquinolines over nitrogen-doped carbon supported Pd catalyst

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In this study, we have developed a sustainable method for the hydrogenation of quinolines to 1,2,3,4-tetrahydroquinolines under mild conditions over a nitrogen-doped carbon supported Pd catalyst with abundant porous structure (abbreviated as Pd/CN). The mesoporous structure of the nitrogen-doped carbon support was prepared by the pyrolysis of glucose and melamine using eutectic salts of KCl and ZnCl<sub>2</sub> as the porogen. Due to the high nitrogen content in the support, Pd nanoparticles were homogeneously dispersed on the surface of nitrogen-doped carbon materials with an ultra-small size of 1.9 nm in a narrow size distribution. The as-prepared Pd/CN catalyst showed high catalytic activity towards the hydrogenation of quinolines at 50 °C and 20 bar H<sub>2</sub>, affording the corresponding 1,2,3,4-tetrahydroquinolines with yields in range from 86.6-97.8 %. More importantly, the Pd/CN catalyst was highly stable without the loss of its catalytic activity during the recycling experiments. The use of renewable resources to prepare the catalyst makes this method promising for the sustainable 1,2,3,4-tetrahydroguinolines from the hydrogenation of guinolines.

#### Introduction

Catalytic hydrogenation reactions are very useful for achieving many types of fine and bulk chemicals.<sup>1-2</sup> Among the various types of hydrogenation reactions, selective hydrogenation of Nheteroarenes is a challenge catalytic reaction, because of the high stability of the aromatic rings and also the potential poisoning of the catalysts by either substrates or their reduced products.<sup>3</sup> However, the selective hydrogenation of N-heteroarenes into saturated N-heterocyclic compounds is a very useful chemical reaction. The as-produced saturated N-heterocyclic compounds are widely present as the building blocks in many natural products as well as the pharmaceutical industry, because they often surpass their less soluble aromatic analogues in terms of key pharmacokinetic parameters such as bioavailability.<sup>4</sup> For instance, 1,2,3,4-tetrahydroguinoline (THQ) and 1.2.3.4tetrahydroisoguinoline (THIQ) are commonly present in alkaloids and are required in pharmaceutical and agrochemical synthesis. Saturated N-heterocyclic compounds have been generally synthesized by the hydrogenation of the corresponding unsaturated congeners.<sup>5-9</sup> Among these processes, catalytic reduction of Nheteroarenes with H<sub>2</sub> as the hydrogen source has been widely regarded as the most convenient and most promising one, as hydrogen represents an atom-economic and clean reducing agent.

The hydrogenation of quinoline with H<sub>2</sub> has been performed

#### either by homogeneous metal catalysts or heterogeneous catalysts. The first example on the use of homogeneous catalyst for the hydrogenation of quinoline was reported by Fish and co-workers in 1982.<sup>10</sup> After that, many kinds of homogeneous catalysts mainly including noble-metal catalysts have been used for the hydrogenation of quinoline.<sup>11-13</sup> Unfortunately, these homogeneous catalytic systems displayed low activity, and require high pressures, elevated temperatures, as well as the complex ligands. Very recently, Beller and co-workers reported a new homogeneous cobalt catalvst with tetradentate ligand tris(2-(diphenylphosphino)phenyl)phosphine), which catalvzed hydrogenation of quinolines under mild conditions (10 bar of H<sub>2</sub> and 60 °C).<sup>14</sup> Although this method is effective for the hydrogenation of quinoline, it is difficult to recycle and reuse of the homogeneous catalysts as well as the complex ligands. To address the drawbacks of homogeneous catalysts, great effort has been devoted to the design of heterogeneous catalysts for this transformation. $^{9,\ 15\text{-}20}$ Although great achievements have been attained over heterogeneous catalysts, some reported methods still demonstrate some drawbacks. For example, the nitrogen-doped Pd catalyst can promote the hydrogenation of quinoline under mild conditions (1 bar H<sub>2</sub> and 40 °C), but a high loading of Pd (4.7 mol% relative to quinoline) was required.9 Dyson and co-workers reported a Rhodium nanoparticle-Lewis acidic ionic liquid catalyst for the reduction of quinolines, affording the aim products with yield in the range from 60~85% after 15~48 h at 80~120 °C under 30 bar hydrogen pressure with Rh loading of 1%.<sup>19</sup> In addition, this catalytic system was not stable as the conversion of quinoline decreased from 90% in the first run to 84% after the sixth run. Therefore, there is still a large room to design new catalytic systems for the effective and sustainable hydrogenation of quinoline into

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1,2,3,4-tetrahydroquinoline with a low metal loading and high stability.

Generally, a heterogeneous catalyst is composed of an active phase (metal or metal oxides) and support. Besides the active sites, the supports also showed a great effect on the catalytic activities of heterogeneous catalysts,<sup>21,22</sup> as different supports have different properties such as acid-base properties, redox properties, and texture properties. Among various kinds of supports, carbon materials are fascinating supports for metal nanoparticles, due to their unique properties, such as extraordinary chemical, mechanical, and thermal stability, and wide abundance in nature.<sup>23,24</sup> However, metal nanoparticles that supported on the carbon materials are generally suffered from the loss of their catalytic activities due to the leach of active phase into the reaction solutions, owing to the weak interaction between the support and the metal nanoparticles. One of the most prominent methods to improve the stability of the metal nanoparticles is achieved by the modification of carbon materials by the introduction of nitrogen atoms into their structure.<sup>25, 26</sup> The lone pair electrons in nitrogen atoms have a strong interaction with metal nanoparticles and prevent the growth of metal nanoparticles. In addition, the lone pair electrons can interact with the carbon  $\pi$  system, which causes structural irregularity of the hexagonal carbon ring and greatly alters the physical and chemical properties of the carbon materials, such as basicity, catalytic activity, oxidative stability, and so on.<sup>27, 28</sup>

From the viewpoints of green and sustainable chemistry, it is highly attractive to explore inexpensive, abundant and renewable resources to produce nitrogen-doped carbon material with large specific surface area and high nitrogen content.<sup>29, 30</sup> In this context, biomass resource represents a nature abundant carbon source. Melamine is considered as a nitrogen-enriched, inexpensive and commercially available raw material, which has received a great interest as a nitrogen-precursor for the synthesis of nitrogen-doped carbon materials. As a support to immobilize metal nanoparticles, the abundant porous structure of the supports is also of great importance in the catalytic activities of the catalysts, especially for liquid phase chemical reactions.<sup>31</sup> Hence, the renewable glucose and melamine were respectively used as the carbon and nitrogen sources for the preparation of nitrogen doped carbon materials with high surface area based on a "Salt templating" strategy using the KCl/ZnCl<sub>2</sub> mixture (KCl: ZnCl<sub>2</sub> at 51 : 49, melting point at 230 °C) as the porogen and solvent.<sup>32</sup> The as-prepared nitrogen-doped carbon materials were used to immobilize Pd nanoparticles for the hydrogenation of quinoline, demonstrating high catalytic activity under very mild conditions.

#### **Experimental Section**

#### Materials

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All of the chemicals except glucose were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). All solvents and glucose were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and used directly without purification.

#### Synthesis of mesoporous N-doped carbon materials

Typically, melamine (1.5 g) and glucose (1.0 g) were mixed with the  $KCl/ZnCl_2$  mixture (12 g, KCl:  $ZnCl_2$  molar ratio at 51: 49) by grinding at room temperature. Subsequently, the mixture was subjected to

the carbonization with a gradient heating mode. Firstly, the sample was heated from room temperature to 240 °C at a heating rate of 3 °C/min and then kept at this temperature for 4 h. After that, the temperature was increased from 240 °C to 800 °C at a heating rate of 1 °C/min, and maintained at the final temperature for 6 h. After cooling to room temperature, the as-prepared black solid was ground to into powder in an agate mortar, and washed with deionized water to completely remove the salts until there was no Cl- detected in the supernatant. The as-made nitrogen doped carbon material was dried at 60 °C in a vacuum over overnight, and the product was abbreviated as CN.

The as-prepared CN (200 mg) was dispersed in distilled water (50 mL) with an assist of ultrasonication for 1 h at room temperature. Then Na<sub>2</sub>PdCl<sub>4</sub> (11.27 mg) in 2 mL of distilled water was added, and the mixture stirred at room temperature for 1 h. Then NaBH<sub>4</sub> (15.0 mg) in distilled water (3.0 mL) was added dropwise into the above suspension. After the addition of NaBH<sub>4</sub>, the mixture was stirred for 12 h at room temperature to fully load the Pd nanoparticles onto the support. Finally, the catalyst was collected via filtration, washed with distilled water for several times, and finally dried in a vacuum oven at 60 °C for 12 h. The asmade catalyst was abbreviated as Pd/CN.

#### **Catalyst characterization**

Transmission electron microscope (TEM) images of the samples were performed on an FEI Tecnai  $G^2$ -20 instrument. The sample was firstly dispersed in ethanol and dropped onto copper grids for observation. The morphologies of the catalysts were observed by an SU8000 field-emission scanning electron microscope (SEM, Hitachi, Japan) at an accelerating voltage of 15 kV. X-ray powder diffraction (XRD) patterns of the catalysts were conducted on a Bruker advanced D8 powder diffractometer (Cu Ka). All XRD patterns were collected in the 20 range of 10-80° with a scanning rate of 0.016 °/s. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo VG scientific ESCA MultiLab-2000 spectrometer with a monochromatized AI Ka source (1486.6 eV) at constant analyzer pass energy of 25 eV. The binding energy was estimated to be accurate within 0.2 eV. All binding energies were corrected referencing to the C1s (284.6 eV) peak of the contamination carbon as an internal standard. The palladium content in the catalysts was determined by inductively coupled atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). Raman spectra were measured on a confocal laser micro-Raman spectrometer (Thermo Fischer DXR) equipped with a diode laser of excitation of 532 nm (laser serial number: AJC1200566). Spectra were obtained at a laser output power of 1 mW (532 nm), and a 0.2 s acquisition time with 900 lines/mm grating (Grating serial number: AJG1200531) in the wavenumber range of 50–3500 cm<sup>-1</sup>. The textural properties of the Pd/CN were characterized by  $N_2$  adsorption-desorption measurements. Specific surface areas of the supports or the catalysts were measured by N2 physisorption by using a Micromeritics Tristar II 3020.

#### General procedure of the hydrogenation of quinoline

The catalytic hydrogenation of quinoline was performed in a stainless steel autoclave. In a typical run, quinoline (1 mmol), the Pd/CN catalyst (20 mg) and toluene (15 mL) were charged into the reactor. After the removal of the air in the reactor by the exchange with  $H_2$  for 5 times, 20 bar  $H_2$  was charged at room temperature. Then the reaction was carried out at 50 °C with a magnetically stirring at 1000 rpm. Afterwards, the autoclave was cooled to room temperature with ice-cold water, and depressurized. The reaction

mixture was diluted to a certain volume and the reaction mixture was analyzed by gas chromatography.

### Analytic methods

A 7890F gas chromatography (GC) was used to analyze the products, which is equipped with a crosslinked capillary HP-5 column (30 m×0.32 mm×0.4 mm) and a flame ionization detector. The temperature of the column was initially kept at 80 °C for 3 min, and then increased at a rate of 20 °C·min<sup>-1</sup> to 220 °C. Products were identified by comparison of the retention time of the unknown compounds with those of standard compounds and quantified based on the internal standard method.

## **Results and Discussion**

Procedures of the preparation of the Pd/CN is shown in Scheme 1. The CN support was prepared by pyrolysis of the glucose and melamine mixture in the presence of  $ZnCl_2/KCl$ . Pd nanoparticles were deposited on the surface of NC by the reduction of  $Pd^{2+}$  with NaBH<sub>4</sub>, giving rise to the Pd/CN catalyst. The Pd weight percentage was determined to be 2.0 wt. % by ICP-AES, which was very close to the theoretical data.



Fig. 1  $N_2$  adsorption/desorption isotherms of the CN and Pd/CN catalyst and corresponding Barrett-Joyner-Halenda (BJH) pore-size distribution curve.

The isotherm and the Barrett–Joyner–Halenda (BJH) pore size distribution of the Pd/CN catalyst are shown in Fig. 1.  $N_{\rm 2}$  adsorption–desorption isotherm curves of these samples show a H4 hysteresis loop, typical of the existence of mesoporous structures. However, they also exhibit a typical I-type isotherm with

equilibrium in the P/P<sub>o</sub> range of 0–0.1, indicating that the Pd/CN catalyst also have microporous structure. Pore size distribution of the Pd/CN catalyst is shown in the insert of Fig. 1, and it demonstrates that Pd/CN catalyst has both micropores and mesopores (Fig. 1).

The total Brunauer–Emmett–Teller (BET) surface area, and pore volumes of the CN support were determined to be 412  $m^2/g$  and 0.42  $m^3/g$ , respectively. After the deposition of Pd nanoparticles, there was a slight decrease both in the surface area and pore volume, which were 398  $m^2/g$  and 0.40  $m^3/g$ . The large porosity of the catalyst permits fast diffusion of reactants to the Pd nanoparticles in the pores, facilitating the reaction.



Fig. 2 TEM image (a) and HRTEM image ( b) of the Pd/CN catalyst.

The morphology of the as-prepared Pd/CN catalyst was examined by TEM. TEM image of the Pd/CN catalyst (Fig. 2) indicated that Pd nanoparticles (the dark dots) with ultra-small size were homogeneously distributed on the surface of the nitrogendoped carbon material, which were clearly observed in the high resolution TEM image of the Pd/CN catalyst (Fig. 2). The average size of Pd nanoparticles was calculated to be 1.9 nm. The high dispersion and ultra-small size of Pd nanoparticles should be mainly caused by the presence of nitrogen atoms in the carbon support, as lone pair electrons in the nitrogen atoms have a strong interaction with Pd nanoparticles.<sup>33</sup>

The XRD patterns of the Pd/CN catalyst is shown in Fig. 3. A graphitic stacking peak was observed at  $2\theta = 26.0^{\circ}$ , which should be assigned to the (002) plane of graphite carbon. The presence of the peak at = 26.0° suggested that this material has been highly carbonized.<sup>34</sup> In addition, the other peak with a large width and a low intensity was observed at  $2\theta = 42.6^{\circ}$ , suggesting that the formation of intralayer condensation for the material. However, no characteristic peaks were observed for the metallic Pd nanoparticles in the XRD patterns of the Pd/CN catalyst. This may due to the homogenous distributed Pd nanoparticles with an ultrasmall size, which cannot be detected by XRD.

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Fig. 3 XRD pattern of the Pd/CN catalyst.

The valence states of nitrogen and palladium were characterized by XPS. As far as the Pd 3d XPS spectrum (Fig. 4 a) concerned, it can be fitted into two peaks of metallic Pd 3d<sub>5/2</sub> and Pd  $3d_{3/2}$ , with the binding energies at 335.9 and 341.2 eV, respectively.<sup>35</sup> However, two peaks with the binding energy higher than the metallic Pd at 337.8 and 343.5 eV are assigned to Pd(II)  $3d_{5/2}$  and Pd(II)  $3d_{3/2}$ .<sup>35</sup> The high resolution N 1s XPS spectrum of the Pd/CN catalyst is shown in Fig. 4 b. Three types of nitrogen with different binding energies are observed after the fitting of the N 1s XPS spectrum. The three fitted peaks with the binding energies at about 398.5, 399.5 and 400.8 eV could be attributed to the corresponded to pyridinic N, pyrrolic N and graphitic N, respectively.<sup>36</sup> Similarly, the C 1s XPS spectrum of the Pd/CN catalyst can also be fitted to three kinds of carbon (Fig. 4 c), and their binding energies are 284.6 eV (C=C), 286.2 eV (C-O), and 288.4 eV (O-C=O). The surface composition of C, N, and Pd were determined to be 81.4 at.%, 9.8 at.% and 3.6 at.% by XPS method, respectively.





Fig. 4 The high resolution XPS spectra of the a) Pd 3d, b) N 1s and c) C 1s in the Pd/CN catalyst.

#### Catalytic hydrogenation of quinoline in different solvents

The catalytic activity of the as-prepared Pd/CN catalyst was evaluated by the hydrogenation of quinoline into 1,2,3,4-tetrahydroquinoline (py-THQ), which involves the regio-selective hydrogenation of the nitrogen-containing ring (Scheme 2). However, the complete hydrogenation product decahydroquinoline (DHQ) and the benzene ring hydrogenation product 5,6,7,8-tetrahydroquinoline (bz-THQ) may also form during the reaction process (Scheme 2). For example, it was reported that the commercial Pd/C catalyst only gave an 84% selectivity (60 °C, 2MPa H<sub>2</sub>) toward py-THQ.<sup>37</sup>



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Table 1. The results of the hydrogenation of quinoline into py-THQ in different solvents.

Entry	Catalyst	Solvent	Conversion (%)	Yield (%)	Selectivity (%)
1	Pd/CN	H <sub>2</sub> O	36.1	10.7	29.6
2	Pd/CN	Ethanol	35.8	24.1	67.3
3	Pd/CN	THF	97.1	93.8	96.6
4	Pd/CN	Acetonitrile	91.7	90.4	98.5
5	Pd/CN	Hexane	96.8	87.5	90.4
6	Pd/CN	Toluene	92.7	92.7	100
7	CN	Toluene	0	0	-

 $^a$  Reaction conditions: quinoline (1 mmol), Pd/CN (0.38 mol% Pd relative to quinoline), solvent (10 mL), 50  $^{\circ}$ C, 10 bar H\_2, 10 h.

Initially, the reaction was performed under mild conditions (50 °C and 10 bar H<sub>2</sub>) in different solvents, because the properties of the solvents can alter the mechanistic aspects of a reaction via a change in the free energy state of the reactants, which can alter the favourability of different reaction paths.<sup>38</sup> As demonstrated in Table 1, the catalytic activity of the Pd/CN catalyst and the selectivity of py-THQ were greatly affected by the reaction solvent. In general, the reactions in water and ethanol with strong polarity produced lower or mediate quinoline conversions as well as the lower selectivity of py-THQ (Table 1, Entries 1-2). Besides the aim product of pv-THQ. DHQ and bz-THQ were also observed. High quinoline conversions in the range from 91.7% to 97.1% were attained in the solvents with mediate polarity such as toluene, THF and acetonitrile as well as the non-polar solvent of hexane (Table 1, Entries 3-6). Of particular note is that the Pd/CN catalyst promoted these reactions in these solvents with the exclusive formation of py-THQ with no evidence of benzene ring reduction or complete hydrogenation, that is, exclusive nitrogen-containing ring hydrogenation. According to the results in Entries 3-6, the polarity of the solvents shows no significant effect on the catalytic performance of the Pd/CN catalyst towards the hydrogenation of quinoline. Thus, we presumed that the lower activity of the Pd/CN catalyst in water and alcohols was probably caused by the fact that water and alcohols could stabilize quinoline through hydrogen bonds between them. Under the mild conditions (50  $^{\circ}$ C and 10 bar H<sub>2</sub>), py-THQ was attained in a high yield of 92.7% in toluene after 10 h with 100% selectivity of py-THQ . Therefore, toluene was used as the reaction solvent in the following experiments. Our Pd/CN catalyst showed comparable activity as the ordered mesoporous carbon nitride supported Pd catalyst (Pd/ompg- $C_3N_4$ ) catalyst, which can also promote this transformation at low temperatures (40-60 °C).9 According to the literatures,<sup>39</sup> we speculated that the nitrogen atoms in the Pd/CN catalyst played two key roles in the high catalytic activities. On the one hand, the lone pair electron should have a strong interaction with Pd nanoparticles, resulting in an enhancement dispersion of the Pd nanoparticles as well as the enhancement of the electron density of Pd nanoparticles, which were believed to play great role in the improvement of the catalyst activity of the Pd nanoparticles. On the other hand, the nitrogen atoms should act as a Lewis base to promote the heterolytic cleavage of  $\rm H_2.$   $^{40}$ 

It should be pointed out that the relative molar ratio Pd to the quinoline is 0.38% In our catalytic methods, which was much lower than those previous work.<sup>9, 16</sup> For example, a high metal loading up to 4.7% was reported for the graphitic carbon nitrides supported Pd

catalyst.<sup>9</sup> In addition, the renewable glucose and commercially available melamine was used for the preparation of the nitrogen-doped carbon material in our study. Therefore, the nitrogen-doped carbon support prepared by our method is more sustainable than the previous work.<sup>9, 16</sup>

## The effect of hydrogen pressure on the hydrogenation of quinoline

The effect of hydrogen pressure on the hydrogenation of quinoline was also studied at the reaction temperature of 50 °C. As shown in Fig. 5, the hydrogen pressure showed a great effect on the catalytic activity of the Pd/CN catalyst at a low-pressure range. For example, the conversion of quinoline was only 16.6% at atmospheric hydrogen pressure after 10 h at 50 °C, and then it greatly increased to 50.5% under 2.5 bar hydrogen pressure. Further increasing the hydrogen pressure to 5 bar, quinoline conversion again greatly enhanced to 87.8% after 10 h. Then guinoline conversion slowly increased by increasing the hydrogen pressure from 5 bar to 20 bar, and then almost remained constant at 30 bar H<sub>2</sub> pressure. Under 20 bar hydrogen pressure, py-THQ was produced in a high yield of 97.8% without the formation of byproducts. The increase of hydrogen pressure results in an increase of hydrogen concentration in the reaction solution, thus accelerating the reaction rate. This phenomenon was much more obvious at a low hydrogen pressure range.



Fig. 5 The effect of hydrogen pressure on the hydrogenation of quinoline. Reaction conditions: quinoline (1 mmol), Pd/CN (0.38 mol% Pd relative to quinoline), toluene (10 mL), 50  $^{\circ}$ C, 10 h.

## The effect of the reaction temperature on the hydrogenation of quinoline

Secondly, reactions were also performed at different temperatures to investigate the effect of reaction temperature on the hydrogenation of quinoline. As shown in Fig. 6, the hydrogenation of quinoline was sensitive to the reaction temperature, but the selectivity of py-THQ remained 100% independent of the reaction temperature. The reaction was accelerated at an increase of the reaction temperature, and this phenomenon was much more distinct at low temperature range. For example, quinoline conversions were attained in 11.5% and 27.7% at the reaction temperatures of 30 °C and 40 °C after 10 h under 5 bar hydrogen pressure, respectively. Then the conversion of quinoline greatly increased from 27.7% at 40 °C to 87.8% at 50 °C after 10 h and 5 bar hydrogen pressure. The conversion of quinoline further increased to 97.3% after 10 h at 60 °C and 5 bar H<sub>2</sub>. The success of quinoline hydrogenation under mild conditions (low temperature and low

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hydrogen pressure) shows a great promising potential in the practical application, as these processes are environmentallyfriendly and energy-saving.



Fig. 6 The effect of reaction temperature on the hydrogenation of quinoline. Reaction conditions: guinoline (1 mmol), Pd/CN (0.38 mol% Pd relative to guinoline), toluene (10 mL), 5 bar H<sub>2</sub>, 10 h.

Time course of the products distribution the hydrogenation of auinoline



Fig. 7 Time course of the products distribution during the hydrogenation of quinoline.

To give more insight into the process of the hydrogenation of quinoline, time course of the product concentration changes was recorded in Fig. 7. The hydrogenation of quinoline was performed at 50 °C and 5 bar hydrogen pressure. During the reaction process, the molar percentage of quinoline gradually decreased, while the molar percentage of py-THQ gradually increased. During the reaction process, no other product was observed, suggesting that the hydrogenation of two carbon-carbon and carbon-nitrogen double bonds in the quinoline proceeded in a single step. It is worth noted that the hydrogenation rate was faster in an early reaction stage than the latter stage, which was due to the higher concentration in an early reaction stage. This Pd/CN catalyst is far more reactive than previously reported ones, for example, Yong Wang's group reported Co catalyst for quinoline hydrogenation in a higher temperature and hydrogen pressure (130 °C and 30 bar  $H_2)^{15}$ .

#### Substrate scope

Furthermore, the applicability of Pd/CN catalyst to different heterocyclic compounds was investigated with the aim of studying the generality of the protocol. All the reactions were performed under mild conditions (50 °C and 20 bar) over the Pd/CN catalyst and the results are summarized in Table 2. Different substituted quinoline derivatives reacted smoothly, leading to the production of the corresponding 1,2,3,4-tetrahydroquinolines with high yields. However, the substrates with different structures demonstrate different reactivities. For example, the reactions were retarded when methyl group was introduced. Therefore, a longer reaction time is needed for the hydrogenation of methyl substituted quinolines to corresponding 1,2,3,4-tetrahydroquinolines smoothly (Table 2, Entries 1 vs 2, 3). Quinolines with both electron-donating and -withdrawing substituents on the aromatic ring also smoothly underwent the hydrogenation, and only reduction of the heteroarene ring was observed (Table 2, Entries 4-6). Encouraged by the good results from the hydrogenation of quinolines, we applied this attractive protocol to the hydrogenation of heterocyclic ring of a series of other biologically important heteroaromatic nitrogen compounds. For example, this method is effective for the hydrogenation of quinoxaline with two nitrogen atoms in its structure (Table 2, Entry 7). More complex fused ring compounds including acridine and 7,8-benzoquinoline was hydrogenated to their corresponding tetrahydroderivatives (Table 2, Entries 8 & 9). Herein, the developed method demonstrates great promising for the mild and selective hydrogenation of N-heteroarenes.

Table 2. The results of the transfer hydrogenation of guinoline

Entry	Substrate	Product	Time (h)	Conversion (%)	Yield (%)
1			10	97.8	97.8
2 <sup>b</sup>			16	97.5	94.9
3 <sup>b</sup>	$\bigcirc \bigcirc$	ÇÇ	14	96.3	95.0
4 <sup>b</sup>	, L	₽ ₽	16	91.4	90.6
5 <sup>b</sup>	HO	HO	14	89.5	88.2
6 <sup>b</sup>	Meo	Meo	10	96.8	96.8
7 <sup>b</sup>			10	98.0	97.2
8 <sup>b</sup>			10	89.6	86.6
9 <sup>b</sup>			10	97.3	95.0

<sup>a</sup> Reaction condition: Substrate (1 mmol), toluene (10 mL), Pd/CN (0.38 mol% Pd relative to guinoline), temperature (50 °C) and H<sub>2</sub> pressure (20 bar)

#### Possible mechanism

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As far as the mechanism of the hydrogenation of quinoline, there have no evident mechanisms. According to our results, the structure of the Pd/CN catalyst as well as previous reports on the mechanism of the hydrogenation of quinoline, we would also like to shed some insight into the hydrogenation of quinoline over the Pd/CN catalyst. The first step of the hydrogenation of quinoline should be the activation of hydrogen molecules to produce the active hydrogen species. As far as the activation of hydrogen molecules is concerned, homolytic and heterolytic cleavage of H<sub>2</sub> have been generally accepted. The heterolytic cleavage of H<sub>2</sub> produces proton  $(H^{\dagger})$  and the hydride  $(H^{-})$ , which are often recognized for the reduction of polar bonds such as C=O and C=N bonds.<sup>41</sup> As known to us, nitrogen atoms with lone electron pair can serve as Lewis base,<sup>40</sup> we believe that nitrogen atoms as base sites can promote the heterolytic cleavage of  $H_2$ .<sup>42</sup> Therefore, a reaction mechanism was proposed for the hydrogenation of quinoline (Scheme. 3), a hydrogen molecule firstly absorbs on the surface of Pd nanoparticles, which then undergoes the heterolytic cleavage with an assist of nitrogen to give Pd-H ( $\delta^{-}$ ) and N-H ( $\delta^{+}$ ) species. Meanwhile, quinoline is chemisorbed on the surface of Pd nanoparticles, followed by the 1,2,3,4-tetrahydroquinoline with hydrogen transfer from Pd-H ( $\delta^{-}$ ) and N-H ( $\delta^{+}$ ) species.



#### Stability of the Pd/CN catalyst

Finally, the stability of the Pd/CN catalyst was studied. The hydrogenation of quinoline into py-THQ was used as the model reaction, which was performed at 50  $^{\circ}$ C and 5 bar H<sub>2</sub> pressure for 10 h. After reaction, the Pd/CN catalyst can be easily separated from the reaction solution by simple filtration, and it was successively washed with ethanol and water. The spent catalyst was dried in a vacuum oven overnight. The second run by the use of the spent catalyst was performed under the identical reaction conditions as the first run. Other cycles were repeated as described above. The catalyst is highly stable and can be reused for several cycles without losing its activity, which is of great importance in the practical applications (Fig. 8).



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Fig. 8 Reusability of the Pd/CN catalyst in the catalytic hydrogenation of quinoline. Reaction conditions: quinoline (1 mmol), toluene (10 mL), Pd/CN (0.38 mol% Pd relative to quinoline), temperature (50  $^{\circ}$ C), 10 h and H<sub>2</sub> pressure (5 bar).

We have provided two additional experiments to support our statements on the stability of the Pd/CN catalyst. On the one hand, the concentration of Pd in the reaction solution determined by ICP-AES was below the detection limit, suggesting that there was no leach of Pd from the Pd/CN catalyst. On the other hand, the spent Pd/CN catalyst was also characterized by TEM image (Fig. 9). It reveals that palladium nanoparticles still homogenous dispersed on the surface of the nitrogen-doped carbon support, albeit the average size of the Pd nanoparticles slightly increased from 1.9 to 2.2 nm after 6 runs. The high stability of the Pd/CN catalysts should be due to the presence of abundant nitrogen atoms in the support. The lone pair electrons in the electronegative nitrogen are expected to be more effective in retaining Pd nanoparticles.



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 $\ensuremath{\textit{Fig. 9}}$  TEMF image of the spent Pd/CN catalyst, and the size distribution of the palladium nanoparticles.

#### Conclusions

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In conclusion, a nitrogen-doped carbon material with a high surface area was successfully prepared from renewable biomass, and the as-prepared nitrogen-doped carbon shows a strong ability to anchor Pd nanoparticles with an ultra-small size of 1.9 nm. The Pd/CN catalyst demonstrated a high activity for the hydrogenation of quinolines to 1,2,3,4-tetrahydroquinolines under mild reaction conditions. This method can promote the hydrogenation of quinolines to afford the corresponding 1,2,3,4-tetrahydroquinolines with high to excellent yields (86.6-98.0 %) under mild conditions (50 °C, and 20 bar H<sub>2</sub>) without the reduction of other functional groups. More importantly, the Pd/CN catalyst was highly stable and can be reused without the loss of its catalytic activity. The Pd/CN catalyst shows a promising potential for the hydrogenation N-heteroarenes into saturated *N*-heterocyclic compounds.

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#### Notes and references

- 1 A. M. Robinson, J. E. Hensley and J. W. Medlin, ACS Catal., 2016, 6, 5026-5043.
- 2 K. Sivaranjan, O. Padmaraj, J. Santhanalakshmi, *New J. Chem.*, 2018, **42**, 1725-1735.
- 3 V. Baliah, R. Jeyaraman and L. Chandrasekaran, *Chem. Rev.*, 1983, **83**, 379–423.
- 4 A. R. Katritzky, S. Rachwal and B. Rachwal, *Tetrahedron*, 1996, **52**, 15031-15070.
- 5 H. Konnerth and M. H. G. Prechtl, *Green Chem.*, 2017, **19**, 2762-2767.
- 6 B. Vilhanova, J. A. van Bokhoven and M. Ranocchiari, *Adv. Synth. Catal.*, 2017, **359**, 677-686.

- 7 T. He, L. Liu, G. T. Wu and P. Chen, *J. Mater. Chem. A*, 2015, **3**, 16235-16241.
- 8 Y. Duan, L. Li, M. W. Chen, C. B. Yu, H. J. Fan and Y. G. Zhou, J. Am. Chem. Soc., 2014, **136**, 7688-7700.
- 9 Y. T. Gong, P. F. Zhang, X. Xu, Y. Li, H. R. Li and Y. Wang, J. Catal., 2013, 297, 272-280.
- 10 R. H. Fish, A. D. Thormodsen and G. A. Cremer, J. Am. Chem. Soc., 1982, 104, 5234.
- 11 X. C. Zhang, Y. H. Hu, C. F. Chen, Q. Fang, L. Y. Yang, Y. B. Lu, L. J. Xie, J. Wu, S. J. Li and W. J. Fang, *Chem. Sci.*, 2016, 7, 4594-4599.
- 12 G. E. Dobereiner, A. Nova, N. D. Schley, N. Hazari, S. J. Miller, O. Eisenstein and R. H. Crabtree, J. Am. Chem. Soc., 2011, 133, 7547-7562.
- 13 Z. J. Wang, H. F. Zhou, T. L. Wang, Y. M. He and Q. H. Fan, Green Chem., 2009, **11**, 767-769.
- 14 R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell and M. Beller, *Angew. Chem., Int. Ed.*, 2017, 56, 3216-3220.
- 15 Z. Z. Wei, Y. Q. Chen, J. Wang, D. F. Su, M. H. Tang, S. J. Mao and Y. Wang, ACS Catal., 2016, 6, 5816–5822.
- 16 F. W. Zhang, C. L. Ma, S. Chen, J. F. Zhang, Z. H. Li, X. M. Zhang, *Mol. Catal.*, 2018, **452**, 145-153.
- L. C. Bai, X. Wang, Q. Chen, Y. F. Ye, H. Q. Zheng, J. H. Guo, Y. D. Yin and C. B. Gao, *Angew. Chem. Int. Ed.*, 2016, **55**, 15656-15661.
- 18 M. H. Tang, J. Deng, M. M. Li, X. F. Li, H. R. Li, Z. R. Chen and Y. Wang, Green Chem., 2016, 18, 6082-6090.
- 19 A. Karakulina, A. Gopakumar, I. Akcok, B. L. Roulier, T. LaGrange, S. A. Katsyuba, S. Das and P. J. Dyson, *Angew. Chem. Int. Ed.*, 2016, **55**, 292-296.
- 20 D. Ren, L. He, L. Yu, R. S. Ding, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, J. Am. Chem. Soc., 2012, **134**, 17592–17598.
- 21 N. Rui, Z. Y. Wang, K. H. Sun, J. Y. Ye, Q. F. Ge and C. J. Liu, *Appl. Catal.*, B, 2017, **218**, 488-497.
- 22 Y. Wang, J. Yao, H. Li, D. Su and M. Antonietti, J. Am. Chem. Soc., 2011, **133**, 2362-2365.
- 23 S. Navalon, A. Dhakshinamoorthy, M. Alvaro, M. Antonietti and H. Garcia, *Chem. Soc. Rev.*, 2017, 46, 4501-4529.
- 24 D. S. Su, G. D. Wen, S. C. Wu, F. Peng and R. Schlogl, Angew. Chem. Int. Ed., 2017, 56, 936-964.
- 25 D. A. F Goncalves, R. P. R. Alvim, H. A. Bicalho, A. M. Peres, I. Binatti, P. F. R. Batista, L. S. Teixeira, R. R. Resende, E. Lorencon, New. J. Chem., 2018, 42, 5720-5727.
- 26 Z. P. Li, X. C. Yang, N. Tsumori, Z. Liu, Y. Himeda, T. Autrey and Q. Xua, ACS Catal., 2017, 7, 2720-2724.
- 27 W. Yang, T. P. Fellinger and M. Antonietti, J. Am. Chem. Soc., 2011, **133**, 206-209.
- 28 P. F. Fulvio, J. S. Lee, R. T. Mayes, X. Q. Wang, S. M. Mahurin and S. Dai, Phys. Chem. Chem. Phys., 2011, 13, 13486-13491.
- 29 L. Zhao, L. Z. Fan, M. Q. Zhou, H. Guan, S. Y. Qiao, M. Antonietti and M. Titirici, *Adv. Mater.*, 2010, **22**, 5202-5206.
- M. Borghei, N. Laocharoen, E. Kibena-Poldsepp, L. S. Johansson, J. Campbell, E. Kauppinen, K. Tammeveski and O. J. Rojas, *Appl. Catal.*, B, 2017, 204, 394-402.
- 31 Y. F. Zhi, K. Li, H. Xia, M. Xue, Y. Mu and X. M. Liu, J. Am. Chem. Soc., 2017, **139**, 8697-8704.
- 32 N. Fechler, T. P. Fellinger and M. Antonietti, *Adv. Mater.*, 2013, **25**, 75–79.
- 33 Q. Y. Bi, J. D. Lin, Y. M. Liu, H. Y. He, F. Q. Huang and Y. Cao, Angew. Chem., Int. Ed., 2016, 55, 11849-11853.
- 34 M. Zhou, C. Yang and K. Y. Chan, Adv. Energy Mater., 2014, 4, 1400840.
- 35 R. W. J. Scott, A. K. Datye and R. M. Crooks, J. Am. Chem. Soc., 2003, 125, 3708–3709.
- 36 Y. Hou, Z. H. Wen, S. M. Cui, S. Q. Ci, S. Mao and J. H. Chen, Adv. Funct. Mater., 2015, 25, 872-882.

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- 37 H. Mao, C. Chen, X. P. Liao and B. Shi, J. Mol. Catal. A: Chem., 2011, 341, 51-56.
- 38 M. H. Abraham, P. L. Grellier, J. L. M. Abboud, R. M. Doherty and R. W. Taft, *Can. J. Chem. –Rev. Can. Chim.*, 1988, 66, 2673-2686.
- 39 X. K. Kong, Q. W. Chen and Z. Y. Lun, *ChemPhysChem*, 2014, **15**, 344–350.
- 40 D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, and J. Nakamura, *Science*, 2016, **351**, 361-365.
- 41 G. Lu, P. Zhang, D. Q. Sun, L. Wang, K. B. Zhou, Z. X. Wang and G. C. Guo, *Chem. Sci.*, 2014, **5**, 1082–1090.
- 42 P. Liu, Y. Zhao, R. Qin, S. Mo, G. Chen, L. Gu, D. M. Chevrier, P. Zhang, Q. Guo, D. Zang, B. Wu, G. Fu and N. Zheng, *Science*, 2016, **352**, 797–800.

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