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Hydrogenation of Benzoic Acid and Derivatives over Pd Nanoparticles Supported on N-Doped Carbon Derived from Glucosamine Hydrochloride

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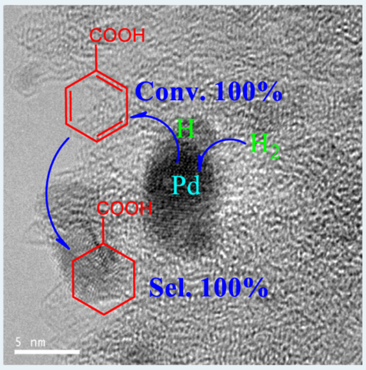
Supporting Information

ABSTRACT: A novel N-doped carbon (CN) was prepared by the hydrothermal method using glucosamine hydrochloride as both carbon and nitrogen precursor, followed by a postsynthesis heat treatment. Pd@CN exhibited 9 times higher activity compared to that of commercial Pd@AC on hydrogenation of benzoic acid to cyclohexanecarboxylic acid. The influence of solvent and substituent were also investigated. Besides, the hydrogenations of various benzoic acids have been carried out over Pd@CN.

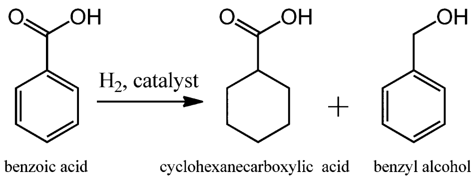


KEYWORDS: *N-doped hydrothermal carbon, benzoic acid, chemoselective hydrogenation, heterogeneous catalyst, mild condition*

The chemoselective hydrogenation of benzoic acids (BA) to cyclohexanecarboxylic acid (CCA) (Scheme 1) is the most important reaction in the synthesis of caprolactam from toluene in the SNIA process (developed by SNIA S.p.A., Italy), and CCA is also an important organic intermediate for the synthesis of pharmaceuticals for example praziquantel and ansatrienin.[1−3] Because of the great importance of CCA in both chemical and pharmaceutical industries and because almost all of the CCA is obtained by chemoselective hydrogenation of BA, chemoselective hydrogenation of BA to CCA has attracted great interest over the world.[4−7] However, it is one of the most challenging transformations in the synthesis of fine chemicals and intermediates because of the need to overcome the high resonance energy of aromatic ring.[8,9] On the other hand, aromatic ring hydrogenation generally requires more severe conditions than those required to hydrogenate other functional groups which would normally lead to preferential reaction of the latter relative to the former.[7−9]

Traditionally, hydrogenation of benzoic acid and derivatives have been carried out by using stoichiometric Na−K alloys.[10]

Scheme 1. Hydrogenation of Benzoic Acid



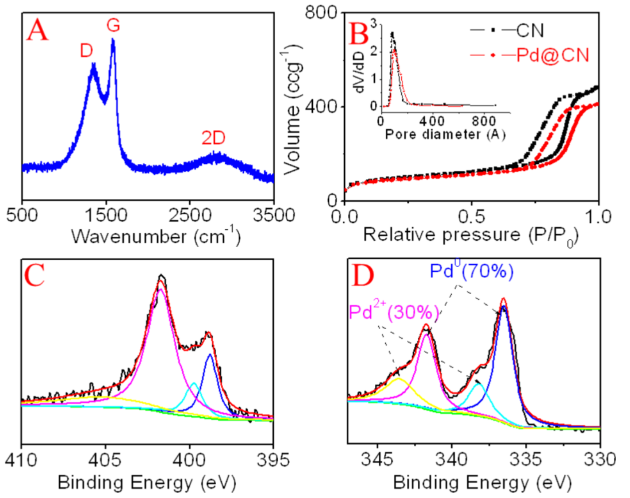


Figure 1. (A) Raman spectra of CN. (B) N_2 adsorption/desorption isotherms and pore size distribution of CN and Pd@CN. (C) XPS curve of CN (N 1s). (D) XPS curve of Pd@CN (Pd 3d).

The need to produce more environmentally friendly chemical processes has led to increased interest in replacing stoichiometric reagents with reusable heterogeneous catalysts.

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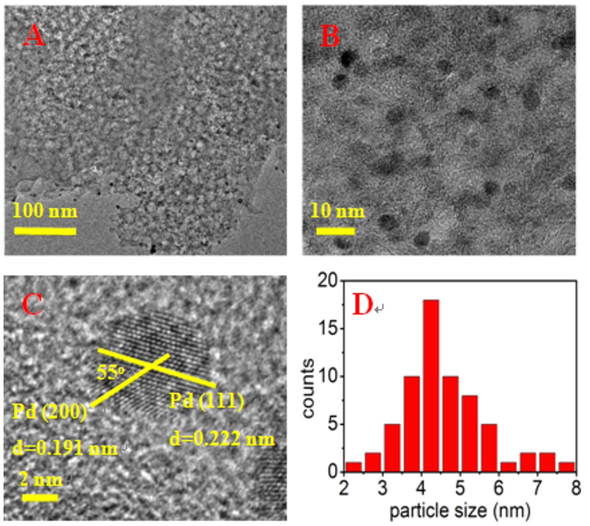


Figure 2. HRTEM images (A, B, and C) and particle size distribution (D) of Pd@CN.

Table 1. Catalytic Results of Pd@CN and Other Pd Catalysts[a]

entry	catalyst	yield (%)	TOF (h^{-1})
1	Pd@CN	100	0.883
2	Pd@TiO_2	10	0.088
3	Pd@CeO_2	13	0.115
4	Pd@MgO	0	0
5	Pd@γ-Al_2O_3	21	0.186
6	Pd@AC	11	0.097
7[b]	Pd@AC	34	0.300
8	Pd@$CN_{0.132}$	81	0.716
9	Pd@HC	14	0.124
10[c]	Pd@CN	50	106

[a]Reaction conditions: benzoic acid 61 mg (0.5 mmol), catalyst 50 mg, Pd (4.7 mol % to substrate), solvent water 25 mL, 85 °C, H_2 1 bar, 24 h. [b]Data from ref 11, reaction conditions: benzoic acid 61 mg (0.5 mmol), Pd@AC 100 mg, Pd (9.4 mol % to substrate), solvent water 50 mL, 85 °C, H_2 1 bar, 24 h. [c]Reaction conditions: benzoic acid 2.44 g (20 mmol), Pd@CN 50 mg, Pd (0.12 mol % to substrate), solvent water 50 mL, 120 °C, H_2 40 bar, 4 h.

Table 2. Hydrogenation of BA over Pd@CN in Various Solvents[a]

entry	solvents	conv. (%)	sel. (%)	p^b	δ^c
1	water	100	100	10.2	0.792
2[d]	ethanol	10	100	4.3	3.54
3	DMSO	0	0	7.2	1.07
4	DMF	0	0	6.4	
5	dioxane	0	0	4.8	1.95
6	acetic acid	9	100	6.2	2.61
7[e]	isopropyl alcohol	6	100	4.3	3.77
8	toluene	0	0	2.4	2.98

[a]Reaction conditions: BA 61 mg (0.5 mmol), Pd@CN 50 mg, Pd (4.7 mol % to substrate), solvent 25 mL, H_2 1 bar, 85 °C, 24 h. [b]Solvent polarity. [c]Solubility of H_2 (10^{-6} mol cm^{-3}, taken from ref 28. [d]Reaction conditions: BA 61 mg (0.5 mmol), Pd@CN 50 mg, ethanol 25 mL, H_2 1 bar, 75 °C, 24 h. [e]Reaction conditions: BA 61 mg (0.5 mmol), Pd@CN 50 mg, isopropyl alcohol 25 mL, H_2 1 bar, 80 °C, 24 h.

Palladium is commonly the metal of choice in selective hydrogenation, and this is often partnered by active carbon as a support due to its high surface area and the relative low cost. However, palladium is generally regarded as a poor catalyst for the hydrogenation of most aromatic rings at low temperature,[11,12] and the reaction condition is usually harsh, for example, in supercritical CO_2 fluid under a high pressure.[6] The ring hydrogenations of benzoic acid and derivatives were also performed over other carbon-supported precious metals (i.e., Pt@C, Ru@C, and Rh@C),[6,13−18] metal alloy (Pd_xRu_y,[19] RuPt,[20] Ni−Zr−B,[5] NiPdB[21]), and platinum nanowire.[22] Raney Ni is an attractive catalyst in the hydrogenation of BA due to its much lower cost, but the activity remains poor.[23] Therefore, alternative heterogeneous catalysts for selective hydrogenation of BA under rather mild conditions are desirable.

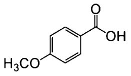
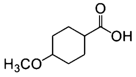
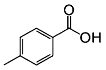
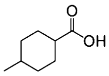
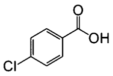
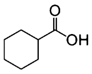
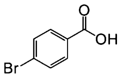
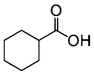
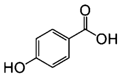
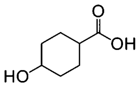
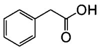
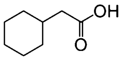
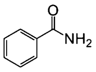
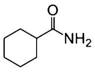
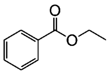
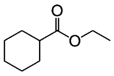
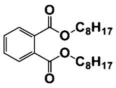
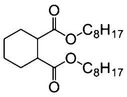
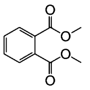
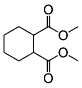
Recently, our group has demonstrated that N-doped carbon derived from N-containing ionic liquid is a highly active support for the biofuel upgrade; however, the ionic liquid precursor is expensive, and it is not good for the large scale production.[24] In this work, a novel N-doped carbon (CN) was prepared by a hydrothermal method using inexpensive, harmless, and naturally available glucosamine hydrochloride as both carbon and nitrogen precursor, followed by a postsynthesis heat treatment. Pd nanoparticles were then trapped in CN by a simple ultrasonic-assisted deposition method,[25,26] which served as highly active and recyclable catalyst for the chemoselective hydrogenation of BA to CCA under mild reaction conditions (85 °C, H_2 0.1 MPa).

The elemental analysis results of CN, as listed in Table S1, indicate that the N content of this carbon material is about 7.0 wt %, with atom ratio of C to N about 0.077. Raman spectrum of CN (Figure 1A) shows two sharp peaks which correspond to G band and D band of displacement of carbon atoms during vibration, respectively, with I_D/I_G = 0.80. The G band at ∼1590 cm^{-1} indicates the formation of graphitic order or the in-plane vibration of sp^2 carbon atoms, whereas the D band at ∼1350 cm^{-1} is a defect-induced feature representing the nonperfect crystalline structure of the material. The mesoporous structure of CN is identified by N_2 adsorption/desorption isotherms and pore size distribution, as shown in Figure 1B. A typical hysteresis loop of type IV, which is particular for mesoporous materials could be easily seen, and the average pore diameter is 11.6 nm, which agrees with the size of template silica sphere (12 nm) finely. Because of the mesoporous structure, the surface area of CN is as high as 324 m^2/g, and it decreases slightly to 302 m^2/g after loading of Pd nanoparticles. Besides, the average pore size of Pd@CN is measured to be 11.7 nm, meaning the loading of Pd nanoparticles has little influence on the mesoporousity of CN. The Pd status of Pd@CN is then determined by XPS, as shown in Figure 1D, and it is found that the ratio of Pd^0 is as high as 70% and the ratio of the oxidized Pd^{2+} is 30%.

The mesoporous structure of Pd@CN was also confirmed by high-resolution transmission electron microscopy (HRTEM), as shown in Figure 2A. The well-dispersed Pd nanoparticles can be clearly seen, and the average size of the Pd crystallite is measured to be 4.6 nm. Figure 2C presents two kinds of crystal planes of Pd nanoparticles, and the crystal plane spacings are measured as 0.222 and 0.191 nm, corresponding to the (111) and (200) planes, respectively, with a plane angle of 55°.

The hydrogenation of BA to CCA was carried out over Pd@CN at 85 °C under 1 bar of H_2 first. After 24 h, 100% yield of CCA was obtained over Pd@CN, with a TOF of 0.883 h^{-1}, as presented in Table 1, entry 1. Other frequently used heterogeneous Pd-based catalysts including Pd@metal oxide (Pd@TiO_2, Pd@γ-Al_2O_3, etc.) and Pd@AC showed much poorer hydrogenation activities at the same reaction conditions.

Table 3. Hydrogenation of Benzoic Acid Derivatives[a]

Entry	Substrate	Product	Pressure (bar)	Time (h)	Conv. (%)	Sel.[b] (%)
1			1(10)	24(6)	49 (100)	92 (trans: cis=14:86)
2			1 (10)	24 (4)	67 (100)	100 (trans: cis=34:66)
3			1	24	100	100
4			1	24	100	100
5			1	24	100	89 (trans: cis=21:79)
6			1	24	82	100
7			1	24	78	100
8			1 (10)	24 (6)	45 (100)	100
9[c]			10	24	80	100
10[c]			10	24	90	88 (trans: cis=3:97)

[a] Reaction conditions: substrate 0.5 mmol, Pd@CN 50 mg, Pd (4.7 mol % to substrate), water 25 mL, 85 °C, 24 h. [b] Selectivity of ring hydrogenation product. [c] Reaction in ethanol.

For instance, only 10% yield of CCA was obtained over Pd@TiO_2, and the TOF was 0.188 h^{-1} (Table 1, entry 2); the yields over the other Pd@metal oxide catalysts were also poor (Table 1, entries 3−5). The commercial Pd@AC showed a yield of 11% at this reaction condition, whereas a yield of 34% could be obtained with the double amount of catalyst Pd@AC according to the literature (Table 1, entries 6−7).[27] Pd nanoparticles supported on ionic liquid derived N-doped carbon, Pd@$CN_{0.132}$, which showed excellent activity for the hydrodeoxygenation of vanillin,[24] was tested for the hydrogenation of BA, and the yield of CCA was 81% at the same reaction condition (Table 1, entry 8). Pd nanoparticles supported on hydrothermal carbon (HC) derived from glucose resulted in a CCA yield of only 14%, with TOF = 0.124 h^{-1} (Table 1, entry 9), meaning the N atoms in Pd@CN are of crucial importance on the catalytic activity. When the hydrogenation of BA over Pd@CN was carried out under harsh conditions, for example, 120 °C and 4.0 MPa H_2, after 4 h, the CCA yield was 50%, and the TOF can reach to 106 h^{-1} (selectivity toward CCA is 100%, Table 1, entry 10). Besides, Pd@CN is of good reusability (Figure S1). The XPS analysis of the recovered catalyst showed a Pd^0 ratio of 68% (Figure S2), very close to the fresh catalyst. And the leaching of Pd in solution is negligible (<0.1 ppm).

Considering the important role solvent plays in determining the reaction rate or the distribution of products, various solvents have been investigated in the hydrogenation of BA to CCA. The corresponding conversion and selectivity are summarized in Table 2, along with the physical and chemical properties of solvents including polarity and solubility of H_2. Among the solvents tested, water, which has the least solubility of H_2, gave a full conversion and 100% selectivity toward CCA (Table 2, entry 1), whereas ethanol, acetic acid, and isopropyl alcohol with relative high solubility of H_2 were found to be much less effective; no more than 10% conversion were achieved for these three solvents (Table 2, entries 2, 6−7). It is interesting that in the other four solvents, DMSO, DMF, dioxane, and toluene, the hydrogenation occurs minimally, and the conversion were nearly 0 (Table 2, entries 3−5, 8).

It is worthy of note that all the four solvents (water, ethanol, acetic acid, and isopropyl alcohol) in which BA can be hydrogenated to CCA are protic solvents, whereas the other four solvents, in which the conversion of BA is close to 0, are aprotic and polar. A possible explanation is that the hydrogenation rate is related to H-bond donor capability of the solvents for protic solvents because the strong interaction between protic solvents and substrate by hydrogen bonding lowers the activation energy barrier and leads to high hydrogenation rate, although for aprotic polar solvents, solvents could strongly adsorb onto the catalyst surface and block the active sites, thereby inhibiting the hydrogenation rate, which was also observed in the hydrogenation of phenol and 2-butanone.[29,30]

To illustrate the general applicability of Pd@CN, the method was extended to ring hydrogenation of as many as 10 benzoic acid derivatives, and the results are presented in Table 3. First, the hydrogenations of *para*-substituted benzoic acids (−OCH_3,

$-CH_3$, $-Cl$, $-Br$, $-OH$) were investigated. The hydrogenations of *para*-chlorobenzoic acid and *para*-bromobenzoic acid both exhibited conversion of 100%; however, we noticed that the hydrogenations of *para*-halo benzoic acids did not give the corresponding *para*-halo cyclohexanecarboxylic acids as the final products, but rather, nonsubstituted cyclohexanoneboxylic acid was the product. It is known that the halo moiety of the aromatics is usually easy to be reduced under hydrogen pressure,[31] and this is applicable to the above-mentioned case. For the hydrogenations of *para*-methoxybenzoic acid and *para*-methylbenzoic acid, the conversions were 49% and 67%, which were much lower than that of nonsubstituted benzoic acid, suggesting that the electron-withdrawing group may restrain the hydrogenation. Hydrogenation of *para*-hydroxybenzoic acid gave a conversion of 100%, possibly owing to the H-bond between $-OH$ and solvent water, which is believed to be positive for the hydrogenation reaction.

Pd@CN also showed nice activity on the hydrogenations of phenylacetic acid and other benzoic acid derivatives, including benzamide, ethyl benzoate, and so on. Furthermore, 82% conversion of phenylacetic acid, 78% conversion of benzamide, and 45% conversion of ethyl benzoate were obtained over Pd@CN (Table 3, entries 6−8). For dimethyl phthalate (DMP) and dioctyl phthalate (DOP), which are two common plasticizers, under 10 bar H_2 pressure in ethanol at 85 °C, the conversions were 90% and 80%, respectively (Table 3, entries 9−10), which are very efficient at present.[32]

In summary, N-doped carbon (CN) was synthesized by using the hydrothermal method with glucosamine hydrochloride as both carbon and nitrogen source, and the Pd nanoparticles supported on CN were used as heterogeneous catalyst for the chemoselective hydrogenation of benzoic acid to cyclohexanecarboxylic acid. Pd@CN exhibited much higher activity than other Pd supported catalysts, including Pd@AC, Pd@metal oxide, among others, at low H_2 pressure and low temperature in water. For example, a 100% yield of CCA was achieved after 24 h at 85 °C under 1 bar H_2 in water, whereas at the same reaction conditions, only 11% yield of CCA was obtained over Pd@AC. Moreover, the reaction solvent has been proved to have significant influence on the reaction rate. The hydrogenations of benzoic acid derivatives were also investigated to illustrate the general applicability of Pd@CN, and substituent is believed to be of great influence on the reaction rate.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The experimental details, the elemental results of CN, and the recycle of Pd@CN, the XPS of the recovered catalyst Pd@CN in Supporting Information. 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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