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## Catalytic transfer hydrogenation of bio-based furfural by palladium supported on nitrogen-doped porous carbon

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# **Graphical Abstract**



# Highlights of the present work

- 1. Nitrogen-doped porous carbon (NPC) was produced via zeolite templating.
- 2. Pd NPs with 2-4 nm sizes are incorporated on the NPC by chemical reduction.
- 3. Pd/NPC showed good activity in the transfer hydrogenation of furfural using 2-butanol.

4. Heterogeneous Pd/NPC catalyst was reusable up to five runs without decreases in activity.

#### Abstract

Highly porous carbon was prepared via a zeolite hard templating route. Subsequent melamine treatment produced nitrogen-functionalized carbon (NPC), which was used as a support to anchor Pd nanoparticles (Pd/NPC) of sizes 2-4 nm using the chemical reduction method. Various analytical techniques were used to characterize the textural properties, structure, and chemical nature of the catalyst. Pd/NPC was then employed as a catalyst for the transfer hydrogenation of biomass-derived furfural (FF) to furfuryl alcohol (FFA) with alcohol as a hydrogen donor, and the effect of temperature, hydrogen donor species, reaction time, and catalysts loading were investigated. The Pd/NPC catalyst was reusable up to five times without any apparent loss of its activity and selectivity. A possible mechanistic pathway for the catalytic transfer hydrogenation of FF over Pd/NPC catalyst was proposed.

**Keywords:** Catalytic transfer hydrogenation; Porous carbon; Palladium nanoparticles; Biomass; Furfural; Meerwein–Ponndorf–Verley reduction.

#### **1. Introduction**

Biomass refining is important in the context of depleting fossil fuel reserves and environmental pollution resulting from the production of fuels, because it reduces the emission of greenhouse gases [1, 2]. It is a sustainable process and produces high value-added chemicals. Consequently, the high oxygen-containing hemicellulose biomass has been utilized worldwide as a preferred carbon source, which produces fuels, FF, 5-hydroxymethyl furfural, sorbitol, and levulinic acid [3]. Among these, FF is a major biomass-based platform chemical and enables the

synthesis of various other chemicals via hydrogenolysis, hydrogenation, oxidation, and aldol condensation [4, 5]. Particularly, the selective hydrogenation of FF to FFA is regarded as a pivotal industrial process. This is because FFA can be used to produce lysine, vitamin C, fibers, lubricants, adhesives, and resins. [1, 6, 7]. Conventionally, copper chromite catalyst with high pressure gaseous H<sub>2</sub> at a high temperature has been employed in the industry for the hydrogenation of FF to FFA. Improper disposal of the catalyst leads to severe environmental pollution owing to the high toxicity of Cr<sub>2</sub>O<sub>3</sub> [1]. Therefore, various Cr-free supported metal and alloy catalysts, including Pd/C [8, 9], Pd/CNT [10], Pd/Al<sub>2</sub>O<sub>3</sub> [11], Pt/Al<sub>2</sub>O<sub>3</sub> [12], Ru/C [13], Cu/SBA-15 [14], Mo<sub>2</sub>C [15], Cu/ZnO [16], Pt/CeO<sub>2</sub> [17], Pd-Cu/SiO<sub>2</sub> [18], Ni-Fe/SiO<sub>2</sub> [19], Pd-Cu/MgO [20], Ru/Zr-MOFs [21], and CuMgAl [6] have been developed for the gas/liquid phase hydrogenation reaction of FF in the pressure gas phase hydrogenation reaction requires considerable energy, which is a safety issue, and yields high amounts of by-product. These limitations have encouraged the exploration for alternative environment friendly and economically viable synthetic routes.

Catalytic transfer hydrogenation (CTH) with an alcohol and/or formic acid hydrogen source has recently emerged as a promising greener alternative route for the hydrogenation reactions of carbonyl compounds, which avoids the requirement of high-pressure H<sub>2</sub> gas. Furthermore, CTH utilizes an alcohol as the hydrogen source, which is advantageous because of the higher selectivity in the transformation of the carbonyl group to the hydroxyl group via the Meerwein-Ponndorf-Verley (MPV) reduction as compared to the use of corrosive formic acid [22]. Recently, several acid- and/or base-containing heterogeneous solid-supported metal complex and nanoparticles (NPs) catalysts have been reported for the highly efficient hydrogenation of biomassderived FF using alcohol as a hydrogen donor. For instance, Hermans et al. [23] reported the Cu/,

Ni/, and Pd/Fe<sub>2</sub>O<sub>3</sub>-catalyzed hydrogenation of FF with 2-propanol (2-PrOH) at 180 °C. These authors were able to achieve 35–45% conversion of FF and 75% selectivity to FFA using Cu and Ni/Fe<sub>2</sub>O<sub>3</sub> and 100% conversion of FF with 57% selectivity to FFA over Pd/Fe<sub>2</sub>O<sub>3</sub>. Yang et al. used Ni/Fe<sub>2</sub>O<sub>4</sub> catalyst and 2-PrOH at 180 °C for the hydrogenation of FF and obtained 94% yield of FFA [24]. Dieguez et al. used an NHC-based Ir complex with 2-PrOH under reflux for the hydrogenation of C=O, C=N, and C=C bonds and achieved >90% yield of the desired products [25]. Lu et al. reported the Cu/MgO-Al<sub>2</sub>O<sub>3</sub> catalyzed hydrogenation with 2-PrOH at 210 °C and obtained almost full conversion with 90% FFA [26].

Several carbon-supported metal NPs have also been applied as hydrogenation catalysts. The hydrophobic nature of carbon supports was expected to be more advantageous than other supports as the former would adsorb the less hydrophilic organic compounds more easily and effectively promote the reaction [27, 28]. Vlachos et al. reported Ru/RuO<sub>2</sub>/C catalyzed hydrogenation with different alcohols to obtain 2-methylfuran as the main product [29, 30]. Fu et al. conducted the hydrogenation of FF with 2-butanol (2-BuOH) at 120 °C over a nitrogen-doped carbon (NPC)-supported iron catalyst, which yielded almost 80% FFA [31]. Xiao et al. used Cu-Co/C as a catalyst and reportedly achieved 99% conversion of FF with 2-BuOH at 150 °C, which resulted in complete conversion to FFA [33]. Recently, Singh et al. reported the hydrogenation of carbonyl compounds over a graphene oxide-supported Pd catalyst with 2-PrOH [34]. It is worth noting that these catalytic systems required a high reaction temperature and suffered the loss of their stability during the recycling runs.

Recently, Kim et al. have developed a facile route to form 3D graphene-like carbon structure selectively inside a  $Ca^{2+}$ -exchanged zeolite template by ethylene pyrolysis [35]. The

intrinsic properties of the zeolite-templated carbons such as the high specific surface area provided by the 3D graphene-like carbon layers with a uniform pore network (around 1 nm pore size) and high thermal stability can provide a useful support material for catalysis [36]. Hara et al. synthesized the SO<sub>3</sub>H-bearing zeolite-templated microporous carbons via post-synthetic sulfonation of carbon with chlorosulfuric acid, and the resulting acid-functionalized carbon showed high catalytic activity for the hydrolysis of cellobiose and the Beckmann rearrangement owing to the high surface area and uniform microporous structure [37]. Katz et al. reported the post-synthetically acid-functionalized zeolite-templated microporous carbons for the adsorption of long-chain glucan and their hydrolysis to glucose in up to 87% yield [38, 39]. Recently, Sazama et al. reported that the 3D graphene-like zeolite-templated microporous carbons were used as an efficient catalyst for the hydrogenation of alkenes, aromatic alkynes, and cycloalkenes [36]. Encouraged by these results of the zeolite-templated microporous carbon materials, herein we have prepared nitrogen-doped porous carbon (NPC). The material was doped with nitrogen postsynthetically by using melamine as the nitrogen source, and used as a solid support to immobilize Pd NPs. The resultant Pd/NPC was explored as a solid catalyst for the liquid phase CTH of FF using alcohol as a hydrogen source (Scheme 1). The catalyst showed high activity and selectivity to FFA. A possible mechanistic pathway for the CTH of FF over Pd/NPC catalyst was also proposed based on experimental results and previous literature reports.

#### 2. Experimental section

#### 2.1. Materials

Calcium chloride hexahydrate, melamine,  $Pd(OAc)_2$ , hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 98 %), acetone, FF, KOH, triethylamine (TEA), tripotassium phosphate (K<sub>3</sub>PO<sub>4</sub>), potassium *tert*-butoxide (K<sup>t</sup>OBu), and all alcohols used in this study were obtained from Sigma Aldrich (USA)

and used as received. Activated carbon (AC; Vulcan) was received from Cabot Corporation (USA).

#### 2.2. Preparation of PC

The carbon support was prepared via a hard-templating route using zeolite as the template. The protocol was based on a previously reported procedure [35].  $\beta$ -Zeolite (Si/Al = 14, Tosoh) and ethylene gas were used as a sacrificial template and a carbon source, respectively. Prior to carbon deposition within the  $\beta$ -zeolite, ion-exchange into the zeolite was performed with a 0.5 M aqueous solution of calcium chloride hexahydrate at room temperature. Next, 20 g of  $Ca^{2+}\beta$ -zeolite was placed in a quartz plug-flow reactor equipped with a 15-mm diameter fritted disk. The reactor was then heated to 650 °C at a heating rate of 5 °C min<sup>-1</sup> under dry N<sub>2</sub> flow. After stabilizing the temperature at 650 °C, a mixture of ethylene, N<sub>2</sub>, and water vapor (10/87/3) was passed through the zeolite bed. The flow rate of the gas mixture was 800 cm<sup>3</sup> min<sup>-1</sup>. The gas flow was continued until the carbon deposition process gave a carbon yield of *ca*. 320 mg  $g^{-1}$ , which indicated complete carbon deposition into the zeolite pores. After full deposition, the ethylene and water vapor feeds were stopped. The reactor was then heated to 900 °C under dry N<sub>2</sub> flow. The temperature was maintained for 2 h to rigidify the carbon frameworks formed in the  $\beta$ -zeolite. After cooling the reactor, the resultant sample was treated repeatedly with a 0.3 M HF/0.15 M HCl solution to remove the zeolite framework. The final carbon products were collected by filtration, washed with deionized water, and dried at 100 °C.

#### 2.3. Preparation of N-doped porous carbon (NPC)

In a typical synthesis, PC (1.0 g) and melamine (1.0 g) were suspended in ethanol (EtOH) and the mixture was stirred at room temperature (RT) for 30 min. Subsequently, the resultant mixture was heated to 100  $^{\circ}$ C with stirring to remove ethanol. The residual material was transferred

into an alumina boat for carbonization. The boat was placed in a horizontal quartz tube furnace under dry  $N_2$  flow for 30 min and then heated to 800 °C for 2 h with a ramp rate of 2 °C min<sup>-1</sup>. After carbonization, the system was cooled to RT naturally to obtain NPC. For comparison, nitrogen-doped AC (NAC) was also prepared by the same procedure.

#### 2.4. Preparation of Pd/NPC catalyst

Pd NPs were anchored on NPC via an impregnation method. NPC (1.0 g) was suspended in acetone (40 mL) and Pd(OAc)<sub>2</sub> (40 mg) was added at RT under stirring. After 4 h, the mixture was filtered and washed with acetone to remove the unbound Pd(OAc)<sub>2</sub> and dried at RT for 1 h. The resultant solid was immersed in methanol (40 mL) and then N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (2 mL) was added slowly under vigorous stirring. After 2 h, the final black solid was isolated by filtration, washed with methanol (20 mL), and dried at 80 °C for 3 h in vacuum to obtain the Pd/NPC solid catalyst. For comparison of the catalytic performance, Pd/PC (without N-doping), Pd/AC, and Pd/NAC were also prepared by the aforementioned procedure.

#### 2.5. Catalysts characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å) at a scan rate of 2° min<sup>-1</sup> over 2 $\theta = 5.90^\circ$ . Raman spectra were measured on a MonoRa 750i/ELT10000 spectrometer with  $\lambda_{ex} = 1064$  nm using a Nd:YAG laser source. X-ray photoelectron spectroscopy (XPS) was conducted using an X-ray photoelectron spectrometer (Thermo Scientific, USA) with AlK $\alpha$  radiation. The nitrogen adsorption measurements were performed with a BELsorp-max analyzer (BEL, Japan) at 77 K to obtain the adsorption-desorption isotherms. Specific surface area and pore size distribution were calculated from Brunauer–Emmett–Teller (BET) and non-local density functional theory with slit pore model. Elemental analysis (EA) for carbon, hydrogen, and nitrogen was performed using an

Elementar Vario EL-III analyzer. Inductively coupled plasma-optical emission spectroscopy (ICP-OES, PerkinElmer Optima 7300 DV, USA) was performed to determine the Pd loading. The morphologies, particle sizes, and dispersions of Pd particles deposited onto the PC and/or NPC support materials were determined by transmission electron microscopy (TEM, Philips, CM200 UT).

#### 2.6. Catalytic reactions

CTH of FF was performed in a 15 mL ACE pressure tube (Sigma Aldrich, USA) equipped with a magnetic stirrer. In a typical procedure, FF (1.0 mmol), base (0.5 mmol), Pd/NPC catalyst (60 mg; 1.05 mol%), and 2-BuOH (5 mL) were charged into the pressure tube, which was then sealed. The reaction tube was heated to a desired temperature in a temperature-controlled silicone oil bath during the reaction. After the reaction was complete, the tube was cooled to RT and the catalyst was separated using a 0.2 µm membrane filter. The products in the liquid phase were quantitatively determined by gas chromatography (GC). The gas chromatograph was equipped with a HP-5 capillary column (HP6890 model, Agilent Technologies, USA) and a flame ionization detector. The side product was identified by GC together with mass spectroscopy (GC-MS, Varian 1200 L single quadrupole with 3800GC model, Agilent Technologies, USA). The conversion of FF was estimated from the amount of FF consumed after the reaction divided by the initial amount of FF. Similarly, the selectivity to FFA was determined from the amount of FFA product divided by the amount of all products in the liquid mixture.

#### 3. Results and discussion

#### 3.1. Characterization of the catalyst

Highly porous nitrogen-doped carbon was successfully synthesized, and Pd NPs were immobilized via a chemical reduction method using Pd(OAc)<sub>2</sub> as the precursor. The structures of

the as-synthesized carbon materials and carbon-supported Pd NPs were characterized by powder XRD, Raman spectroscopy, EA, XPS, N<sub>2</sub>-adsorption isotherms, and TEM. The XRD patterns of the prepared PC, NPC, Pd/PC, and Pd/NPC materials are shown in Fig. 1(a). The highly ordered microporous structure of PC was confirmed by a characteristic peak at ~7.5° [35]. In addition, all samples showed two broad diffraction peaks at  $\sim 24$  and  $43^{\circ}$ , which corresponded to the (002) and (100) diffraction planes, respectively. The high intensity peak of the (002) plane could be ascribed to a long-range order of the stacking of the aromatic planes of carbon and the XRD peak of the (100) plane was attributed to the highly disordered graphitic structures [40, 41]. The diffraction peaks of Pd NPs were not observed in the XRD pattern of Pd/NPC as the Pd particles were highly dispersed on the nitrogen-doped porous carbon support and were of small sizes [42, 43]. The chemical and structural features, degree of hybridization, and disorder properties of the prepared carbon samples were examined using Raman spectroscopy. The Raman spectra of PC, NPC, and Pd/NPC materials in the range from 1000 to 2000 cm<sup>-1</sup> (Fig. 1(b)) showed two characteristic G and D bands: the G band at ~1590 cm<sup>-1</sup> was assigned to the primary in-plane vibrational mode  $sp^2$ hydridized carbon atoms in a hexagonal graphitic ring and the D band at ~1300 cm<sup>-1</sup> corresponded to the structural defects in the graphitic  $sp^2$  network [40]. These structural defects were caused by the impregnation of nitrogen, oxygen, metals, and other impurities that dissociated the  $sp^2$  bonds to produce sp<sup>3</sup> C–C bonds [44]. The degree of graphitization and the interaction between the nanometals and carbon support was determined by the ratio I<sub>D</sub>/I<sub>G</sub>. The I<sub>D</sub>/I<sub>G</sub> ratio of the prepared catalysts increased from 0.98 for PC to 1.04 for NPC and 1.38 for Pd/NPC. The I<sub>D</sub>/I<sub>G</sub> ratio of Pdincorporated NPC was higher than that of pure PC and N-doped PC, indicating that the introduction of Pd metal on the NPC reduced the degree of graphitization. This result was attributed to the interaction between the  $\pi$ -electrons of the carbon material and the metallic Pd particles. The C, H,

and N contents of the PC and NPC materials were determined by EA. The O content was calculated using EA results by subtracting the sum of C, N, and H contents from 100. The C, H, and O contents of PC were 91.41, 2.47, and 6.12%, respectively. Likewise, the C, H, N, and O contents of NPC were determined to be 79.68, 2.04, 11.30, and 6.98%, respectively. The Pd contents of Pd/PC, Pd/NPC, Pd/AC, and Pd/NAC, were measured by ICP-OES and found to be 1.73, 1.85, 1.52, and 1.68 wt%, respectively.

The nature of chemical bonding and presence of nitrogen and oxygen atoms in the chemical structure of the carbon samples were assessed by XPS. The C 1s high resolution XPS of PC (Fig. 2(a)) exhibited six deconvoluted binding energy peaks: the strong peak at 284.4 eV was ascribed to the graphitic C=C structure, the peak at 285.6 eV corresponded to the *sp*<sup>3</sup> hybridized C–C species (*sp*<sup>3</sup> hybridization was due to the presence of graphitic structural defects, which was consistent with the XRD and Raman spectroscopy results), the peak at 286.5 eV was ascribed to the presence of the C–O bond, and the peaks at 287.7, 289.2, and 291.1 eV were attributed to the presence of C=O, COO bonds (–COOH group), and  $\pi$ – $\pi$ \* transition [45, 46]. The O 1s deconvoluted spectrum of PC (Fig. 2(b)) showed three different environmental binding energy peaks at 531.4, 533.0, and 534.7 eV, which were assigned to the C–O, C=O, and COO groups, respectively. These results indicated that the prepared PC was distorted graphitic in character with C–C, C–O, C=O, and –COOH functional groups.

Figure 3 shows the C, O, and N 1s XPS of NPC, in which C and O 1s revealed almost a similar set of binding energy peaks as PC. This result implied that the same functional groups as PC were present in NPC. While untreated PC did not show any noticeable peak in the N 1s XPS region (Fig. 2(c)), the nitrogen-treated PC displayed a strong N 1s peak at ~400 eV (Fig. 3(c)) corresponding to the incorporation of nitrogen on the carbon surface. The N 1s XPS of NPC

exhibited four deconvoluted binding energy peaks at 398.8, 400.0, 401.1, and 402.6 eV for pyridinic-N, pyrrolic-N, graphitic-N, and oxygenated-N, respectively [47], These species were involved in the stabilization of the metal particles and improved the catalytic activity in the hydrogenation reaction.

The N 1s high resolution XPS of Pd/NPC is shown in Fig. 4(a). The deconvolution of the N 1s spectrum of Pd/NPC exhibited four different binding energy peaks associated with the different nitrogen states of pyridinic-N (397.8 eV), pyrrolic-N (399.7 eV), graphitic-N (400.8 eV), and oxygenated-N (402.7 eV), in which the pyridinic-N binding energy was strongly shifted from the original value of 398.8 eV (without Pd). This result clearly demonstrated that most of the Pd particles were strongly bound to pyridinic-N in Pd/NPC. The level of reduction and electronic states of Pd particles were also examined using XPS and these results are shown in Fig. 4(b). The two strong Pd 3d binding energy peaks located at 340.7 and 335.4 eV were attributed to metallic Pd 3d<sub>3/2</sub> and 3d<sub>5/2</sub> states, whereas the other very weak doublet located at about 335.7 and 341.4 eV was assignable to Pd<sup>2+</sup>. These results indicated that the most of the Pd<sup>2+</sup> has been reduced to Pd<sup>0</sup> and only a small portion of Pd<sup>2+</sup> has been bound on the Lewis-base sites of pyridinic nitrogen species [48, 49].

The N<sub>2</sub> adsorption-desorption isotherms were measured at 77 K to determine the porous properties of the prepared carbon and Pd-incorporated samples (Fig. 5). It can be seen that all the samples exhibited type I isotherms with steep uptakes at low pressure (Fig. 5(a)), corresponding to the presence of micropores. The specific surface areas calculated from the BET model for PC, NPC, Pd/PC, and Pd/NPC were 3004, 1492, 2198, and 1010 m<sup>2</sup> g<sup>-1</sup>, respectively. A substantial reduction in the surface area was evident after melamine treatment and introduction of Pd NPs. The Pd NPs were bigger in size (see later) than the average pore diameter of PC (1.04 nm) and

NPC (0.96 nm) as shown in Fig. 5(b), and were likely formed primarily on the external surface of NPC via electrostatic interactions with the nitrogen [50]. Similar types of metal nanoparticles formed on external surface of the microporous solid materials for various liquid phase organic transformations in heterogeneous catalysis have been reported frequently [50-54]. Figure 6 shows the TEM images of Pd/PC and Pd/NPC catalysts. The Pd particles supported on NPC (Fig. 6(a, b)) were highly dispersed with uniform particle sizes of 2-4 nm, whereas the Pd particles supported on PC (Fig. 6(c)) were agglomerated and had an average size of ~7 nm. Uniformly dispersed Pd particles of small sizes were formed on NPC stabilized by nitrogen atoms [55]. On the other hand, the average Pd particle sizes are *ca*. 9 and 6 nm for Pd/AC (Fig. 6(d)) and Pd/NAC (Fig. 6(e)), respectively.

#### 3.2. Catalytic transfer hydrogenation of FF over Pd/NPC

The catalytic performance of the synthesized Pd catalysts was investigated for the transfer hydrogenation of FF to FFA using an alcohol as a hydrogen donor and solvents. The results of these experiments are summarized in Table 1. The reaction was conducted for 10 h with 2-PrOH and the conversion of FF and the selectivity to FFA was determined by GC analysis. Almost no FF conversion was observed when the reaction was conducted without a catalyst (Table 1, entry 1). The reaction performed either with PC and/or NPC alone led to ~10% conversion of FF (Table 1, entries 2 and 3), and only acetal product was formed (acetalization reaction between FF and 2-PrOH), as confirmed by GC-MS analysis, which may be due to the presence of the small portion of acid sites (-COOH group) in the catalysts [31, 56]. The Pd/PC catalyst achieved 42% conversion of FF with 71% selectivity to FFA, and acetal and tetrahydrofurfuryl alcohol (THFFA; over hydrogenation of FFA) were formed as by-products at 120 °C after 10 h (Table 1, entry 4), indicating that the Pd catalyst promoted the CTH reaction. On the other hand, when the reaction

was carried out over Pd/NPC under identical conditions, FF conversion increased to 68% with 82% selectivity to FFA (Table 1, entry 5), and a small amount of acetal and THFFA was formed as by-products, in which the high nitrogen contents on the support as well as the microporosity inhibited the acid-catalyzed bulky acetal by-product. These results clearly indicated that Pd/NPC possessed higher catalytic activity than Pd/PC, which suggested that specific Pd and nitrogen sites in the catalyst likely had a synergistic effect in the transfer hydrogenation of FF to FFA via the Meerwein–Ponndorf–Verley reduction. We also studied the importance and nature of a base in the CTH of FF. It was found that a base was essential when an alcohol was used as a hydrogen donor for extracting the proton from the alcohol, as the conversion of FF decreased in the absence of the base (Table 1, entry 6). Among the various inorganic (KOH, activated K<sub>3</sub>PO<sub>4</sub> (at 200 °C), and K<sup>t</sup>OBu) and organic (TEA) bases (Table 1, entries 5, 7–9), K<sup>t</sup>OBu gave the highest conversion of FF (92%) with 84% selectivity to FFA. When we reduced the concentration of the base from 0.5 mmol to 0.3 mmol, the conversion of FF was also reduced to 74% (Table 1, entry 10), indicating that 0.5 mmol of K<sup>t</sup>OBu was the optimum concentration for this reaction. The influence of temperature on the CTH of FF with 2-PrOH was examined in the range of 90-120 °C over the Pd/NPC catalyst. After 10 h, FF conversion improved from 32 to 92% when the reaction temperature was increased from 90 to 120 °C (Table 1, entries 9 and 11). At the same time, the FFA selectivity was also slightly affected by the reaction temperature.

The influence of various hydrogen donors such as primary and secondary alcohols on the catalytic performance in the hydrogenation of FF with K<sup>t</sup>OBu was also studied at 120 °C and the results are shown in Fig. 7. When primary alcohols were used as hydrogen donors, ~30% conversion of FF with mainly acetal products was observed. On the other hand, linear secondary alcohols, especially 2-BuOH, led to 97% conversion of FF with 92% selectivity to FFA. In

contrast, with 2-PrOH as the hydrogen donor, a slightly lower conversion (92%) and selectivity (84%) was achieved, which may be due to the differences in alcohol dehydrogenation. However, in the case of cyclic secondary alcohols such as cyclohexanol, a very poor conversion of FF was detected. This was likely due to the poor interaction between the catalyst and cyclohexanol because of the steric hindrance, high viscosity, and high boiling point of cyclohexanol. The above results clearly showed that the FF conversion and selectivity were strongly dependent on the nature of the alcohol, and an increased FF conversion and high selectivity to FFA with different alcohols was achieved in the following order: cyclohexanol  $\leq$  EtOH  $\leq$  1-PrOH < 2-PrOH < 2-BuOH. We also compared the catalytic performance of Pd/NPC with that by Pd/AC and Pd/NAC catalysts in the CTH of FF. The Pd/AC catalyst showed only moderate catalytic activity (59% conversion of FF) with 51% yield of FFA (Table 1, entry 12) and acetal as a by-product. When the reaction was carried out with Pd/NAC, 81% conversion of FF with 77% yield of FFA (Table 1, entry 13) and 13% yield of THFFA was achieved. These results indicated that the Pd/NPC catalyst has better catalytic activity than Pd/AC and Pd/NAC, owing to the small particle size, high nitrogen contents, and 3D graphene-like porous structure with connectivity to form a porous network [36].

The effect of Pd/NPC catalyst loading on the conversion of FF was also investigated using 2-BuOH and K<sup>t</sup>OBu at 120 °C for 10 h. As shown in Fig. 8(a), 28% conversion of FF was detected using 30 mg of Pd/NPC, and it increased to 97% when the catalyst loading was increased to 60 mg. Interestingly, while the selectivity to FFA was unaffected by the increase in catalyst loading up to 60 mg, a further increase in the catalyst amount to 70 mg led to decrease in the selectivity to FFA and was accompanied by the formation of THFFA by-product because of the reaction of FFA with 2-BuOH.

To obtain a better understanding of the hydrogenation of FF, a time course plot was made for the reaction conducted over Pd/NPC catalyst (60 mg; 1.05 mol%) using FF (1 mmol), 2-BuOH (5 mL), and K'OBu (0.5 mmol) at 120 °C (Fig. 8(b)). The conversion of FF reached up to 30% with 90% FFA selectivity after 2 h and then increased gradually with increasing reaction time. The maximum conversion of FF (97%) was detected after 10 h reaction with 92% selectivity to FFA. After 10 h, the selectivity of FFA dropped to 85% because of the formation of THFFA by-product.

#### 3.3. Hot-filtration and recycling runs

A hot filtration experiment was performed to confirm the heterogeneous nature of the Pd/NPC catalyst in the CTH of FF in the presence of 2-BuOH and K<sup>t</sup>OBu at 120 °C (Fig. 8(b)). The Pd/NPC catalyst was separated from the reaction mixture by centrifugation after 4 h of reaction and the reaction was continued with the filtrate at 120 °C for another 6 h. Conversion of FF stopped completely after the catalyst was removed at 4 h of reaction time, which proved the heterogeneity of the catalyst during the reaction.

In addition, the stability of the Pd/NPC catalyst was examined by conducting recycling experiments under optimized conditions (i.e., K'OBu, 120 °C, 10 h). After each hydrogenation run, the Pd/NPC catalyst was recovered by centrifugation, washed with water (2×10 mL, to remove the base) and acetone (2×5 mL), dried at 50 °C for 1 h, and then directly reused for the next run. Figure 9 shows that the FF conversion and FFA selectivity remained nearly constant after five consecutive runs, demonstrating the high stability of the Pd/NPC catalyst. Subsequently, the spent catalyst (after fifth use) was further characterized by XRD, ICP-OES, XPS, TEM, and N<sub>2</sub>-adsorption isotherm analyses. The XRD pattern of the spent Pd/NPC catalyst (Fig. 1) exhibited the same pattern as the fresh catalyst, indicating that the structure of the catalyst was maintained after the reaction at 120 °C. The Pd content in the spent Pd/NPC catalyst was found to be 1.81 wt% by ICP-

OES, which was almost close to that of the fresh catalyst (1.85 wt%). This indicated a negligible loss of Pd particles. The Pd XPS analysis of the spent catalyst also showed almost the same pattern of binding energy peaks, (Fig. 4(b)), indicating that the most of the Pd particles maintained the Pd<sup>0</sup> state on the NPC support. The N<sub>2</sub>-adsorption isotherm of the spent Pd/NPC catalyst (Fig. 5) also almost exactly matched with that of the fresh catalyst and the BET surface area was found to be 1007 m<sup>2</sup> g<sup>-1</sup>. In addition, the TEM image of the spent catalyst (Fig. 6(f)) also showed an identical morphology of metallic Pd and no agglomeration with a slightly increased size of ~4 nm. These characterized results reflect that the Pd/NPC catalyst showed excellent stability and reusability without loss of its activity.

#### *3.4. Reaction pathway*

Recently, Zhao et al. reported the catalytic FF hydrogenation using Ni supported on Lewisbase nitrogen (from pyridinic nitrogen)-containing carbon. In this catalytic system, the nitrogen on the catalyst increased the adsorption of hydrogen molecules and metallic Ni, and also assisted in improving the interaction between the reactant and the catalytic sites of metallic Ni [57]. Similarly, NPC materials can reportedly improve the catalytic activity in many hydrogenation and oxidation reactions [58-60]. Based on the previous reports [57-60] and our experimental results, a possible reaction pathway for the CTH of FF was proposed and is shown in Scheme 2. The N species in the NPC support played two important roles in the hydrogenation reaction; the lone pair of electrons on nitrogen could abstract the proton from the alcohol and it could also increase the electron density of Pd NPs. In the first step, the base promoted the deprotonation of 2-BuOH, which led to the anchoring of the generated butanoxide ion on the metallic Pd surface and the proton was adsorbed on the pyridinic-N present in the catalyst. Next, the carbonyl group of FF was weakly adsorbed on Pd surface and formed intermediate (I), followed by the elimination of 2-butanone

yielded intermediate (III) via an attack of hydride ion to the carbonyl group of FF. Finally, furfuryl alkoxide abstracted a proton from the adjacent pyridinium ion and formed FFA. Thus, the catalytic results and mechanism proved that the presence of both nitrogen and Pd species in a single catalyst was synergistic for the hydrogenation of FF to FFA.

Finally, the catalytic efficiency of the present Pd/NPC system in the CTH of FF to FFA was compared with the efficiencies achieved with previously reported heterogeneous catalytic systems (Table 2). The reported catalytic systems often required high-pressure H<sub>2</sub> gas, expensive Ir and Ru precursors, relatively higher metal loading, longer reaction time, and higher reaction temperature. In contrast, the CTH system described in this work has shown a higher turnover frequency compared to others except for the high-cost Ir-carbene-complex.

#### 4. Conclusions

Pd NPs supported on N-doped porous carbon were prepared by the chemical reduction of the Pd<sup>2+</sup> ions immobilized on the support. The Pd/NPC catalyst was comprised of highly dispersed uniform particles with sizes of 2–4 nm, which were anchored on the pyridinic nitrogen atom in the carbon support. The Pd/NPC catalyst exhibited high activity and selectivity toward FFA in the catalytic transfer hydrogenation of biomass-derived FF using 2-BuOH as a hydrogen donor. The promising catalytic performance of Pd/NPC in comparison with other systems was likely a result of the synergistic effect offered by the nitrogen species and the Pd particles on the carbon network. The Pd/NPC catalyst could be recycled for up to five successive runs without any noticeable decrease in its activity and selectivity, and the hot-filtration experiments confirmed the heterogeneity of the catalyst. The high stability of the recovered catalyst was confirmed by various characterization tools.

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Scheme 1. Reaction scheme for the CTH of FF.



Scheme 2. Possible mechanistic pathway for the CTH of FF over Pd/NPC catalyst.



**Fig. 1.** (a) Powder XRD patterns of PC, NPC, Pd/PC, Pd/NPC, and reused Pd/NPC and (b) Raman spectra of PC, NPC, and Pd/NPC.



Fig. 2. (a) C 1s and (b) O 1s high resolution XPS of PC.



Fig. 3. (a) C 1s, (b) O 1s, and (c) N 1s high resolution XPS of NPC.



Fig. 4. (a) N 1s and (b) Pd 3d high resolution XPS of Pd/NPC.



**Fig. 5.** (a)  $N_2$  adsorption-desorption isotherms of PC, NPC, Pd/PC, Pd/NPC, and reused Pd/NPC and (b) Pore size distribution plot of PC and NPC.



**Fig. 6.** TEM images of (a, b) Pd/NPC, (c) Pd/PC, (d) Pd/AC, (e) Pd/NAC, and (f) reused Pd/NPC catalyst.



Fig. 7. Influence of hydrogen donors in the CTH of FF over the Pd/NPC catalyst.



Fig. 8. Effect of (a) Pd/NPC catalyst loading and (b) reaction time on the CTH of FF to FFA.



**Fig. 9.** Recycling experiments of Pd/NPC catalyst in CTH of FF to FFA. Reaction conditions: FF (1.0 mmol), Pd/NPC (1.05 mol%), K<sup>t</sup>OBu (0.5 mmol), 2-BuOH (5 mL), 120 °C, 10 h.

Entre	Catalyst	Base	Conversion	Selectivity (%)				
Entry			(%)	FFA	Acetal	THFFA		
1	-	KOH	nr	nd	nd	nd		
2	PC	KOH	10	nd	100	nd		
3	NPC	KOH	8	nd	100	nd		
4	Pd/PC	KOH	42	71	25	4		
5	Pd/NPC	KOH	68	82	11	7		
6	Pd/NPC	-	17	5	95	nd		
7	Pd/NPC	TEA	19	13	85	2		
8	Pd/NPC	K <sub>3</sub> PO <sub>4</sub>	34	79	16	5		
9	Pd/NPC	K <sup>t</sup> OBu	92	84	10	6		
10 <sup>b</sup>	Pd/NPC	<b>K</b> <sup>t</sup> OBu	74	85	12	3		
11	Pd/NPC	K <sup>t</sup> OBu	61, <sup>c</sup> 32 <sup>d</sup>	80, 76	16, 22	4, 2		
12	Pd/AC	K <sup>t</sup> OBu	59	51	46	3		
13	Pd/NAC	<b>K</b> <sup>t</sup> <b>O</b> Bu	81	77	14	9		

Table 1. Screening of catalyst and reaction conditions for the transfer hydrogenation of FF.

<sup>a</sup>Reaction conditions: FF (1 mmol), catalyst (1.05 mol%), 2-PrOH (5 mL), base (0.5 mmol), temp (120 °C), time (10 h); <sup>b</sup>base (0.3 mmol); <sup>c</sup>temp (100 °C); <sup>d</sup>temp (90 °C); nr = no reaction; and nd = not detected.

**Table 2.** Comparison of catalytic efficiency of Pd/NPC with previously reported catalytic systems

 for the hydrogenation of FF.

S.No.	Catalyst	H2	Solvent/	Temp.	Time	FFA	TOF	Ref.	
		source	base	(°C)	(h)	Yield (%)	( <b>h</b> -1) <sup>a</sup>		
1.	Pd/Al <sub>2</sub> O <sub>3</sub>	45 bar H <sub>2</sub>	-	150	-	85	172 <sup>b</sup>	[11]	
2.	Rh/ED-KIT-6	НСООН	2-PrOH	100	5	99	204	[22]	
3.	Pd/Fe <sub>2</sub> O <sub>3</sub>	15 bar H <sub>2</sub>	2-PrOH	180	7.5	34	720	[23]	
4.	NHC-based Ir complex	2-PrOH	NaO <sup>i</sup> Pr	reflux	0.5	91	1400	[25]	
5.	Cu/AC-SO <sub>3</sub> H	4 bar H <sub>2</sub>	2-PrOH	120	1.5	100	262	[56]	
6.	Ni/NAC-1-1073	4 bar H <sub>2</sub>	2-PrOH	140	5	100	74	[57]	
7.	Al-Zr@Fe <sub>3</sub> O <sub>4</sub>	2-PrOH	-	180	4	85	57	[61]	
8.	Co-Ru/C	Benzyl alcohol	-	150	4	100	150	[62]	
9.	Ni–Cu/Al <sub>2</sub> O <sub>3</sub>	45 bar H <sub>2</sub>	2-PrOH	320	6	95	386	[63]	
10.	Ru-bis(diamine) complex	51 bar H <sub>2</sub>	EtOH	125	23	99	518	[64]	
11.	Cu–Mg–Al	2-PrOH	-	150	6	100	185	[65]	
12.	ME-ZrO <sub>2</sub>	2-PrOH	-	100	120	50	11	[66]	
13.	Pd/Al <sub>2</sub> (SiO <sub>3</sub> ) <sub>3</sub>	20 bar H <sub>2</sub>	Toluene	150	8	30	658	[67]	
14.	Pd/NPC	2-BuOH	KO <sup>t</sup> Bu	120	10	92	876	This work	
$HAP - Hydroxyapatite; ME-ZrO_2 - Microemulsion zirconia; aTOF = turnover frequency.$									