

Supporting Information

Dehydrogenation of Formic Acid at Room Temperature: Boosting Palladium Nanoparticle Efficiency by Coupling with Pyridinic-Nitrogen-Doped Carbon

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Supporting Information

1. Chemicals and materials

Formic acid (HCOOH, FA, 99 wt %), chitosan ((C₆H₁₁NO₄)_n), low viscosity <200 mPa·s), acetic acid (C₂H₄O₂, 99.5 wt %), urea (CO(NH₂)₂, 99.5 wt %), melamine (C₃N₆H₆, 99 wt %), polyethyleneimine (PEI, 99 wt %, M.W. 600), polyacrylamide ((C₃H₅NO)_x), peptone (C₂N₃H₃), polyacrylonitrile ((C₃NH₃)_n), pyridine (C₅H₅N, 99 wt %), piperidine (C₅NH₁₁, 99 wt %), triethylamine (NEt₃, 99.5 wt %), aniline (C₆NH₇, 99.5 wt %), acetonitrile (C₂NH₃, 99 wt %), pyrrole (C₄NH₅, 99 wt %), 3-aminopyridine (C₅N₂H₆, 99 wt %), 1,10-phenanthroline (C₁₂N₂H₈, 99 wt %), diethylamine (C₄NH₁₁, 99 wt %), *n*-butylamine (C₄NH₁₁, 99 wt %), N,N-dimethylethanolamine (C₄NH₁₁O, 99 wt %), triethanolamine (C₆NH₁₅O₃, 98 wt %), palladium chloride (PdCl₂, Pd ≥ 60.0 wt %), rhodium chloride hydrate (RhCl₃·xH₂O, Rh ≥ 38.5 wt %), chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, Pt ≥ 37.5 wt %), chloroauric acid tetrahydrate (HAuCl₄·4H₂O, Au ≥ 48.5 wt %), ruthenium chloride hydrate (RuCl₃·xH₂O, Ru ≥ 37.5 wt %), iridium chloride (H₂IrCl₆, Ir ≥ 35.0 wt %), silver nitrate (AgNO₃, 99.8 wt %), 5.0 wt % Pd/Al₂O₃, and 10.0 wt % Pd/C were supplied by Alfa Aesar and used without further purification.

TiO₂ (P25) and CeO₂ (Adnano 90) were supplied by Evonik. Graphite powder, H₂SO₄ (98 wt %), NaOH (99 wt %), NaBH₄ (99.5 wt %), NaNO₃ (99 wt %), KMnO₄ (98 wt %), H₂O₂ (30 wt %), HCl (38 wt %), NH₃·H₂O (28 wt %), and MgSO₄ were purchased from Aladdin.

2. Catalyst preparation

2.1 Preparation of CN_x materials: These materials were prepared with bio-chitosan-based pyrolysis strategy.^[S1] 1.0 g chitosan was firstly dissolved in 20 mL of a 5% acetic acid/water solution, and then calculated amount of melamine was added into them with vigorous stirring at 25 °C to achieve a homogeneous semitransparent paste. After drying at 65 °C for 10 h, a single block of white solid was obtained and then transferred into a crucible with a cover. Slow pyrolysis was carried out at 800 °C for 5 h under an Ar atmosphere, with a ramping rate of 3 °C min⁻¹. Moreover, different temperatures (700, 800, and 900 °C) and varying precursor weight ratios of chitosan/melamine were applied to obtain the CN_x (where x denotes the N/C molar ratio based on elemental analysis data). Other chemicals, such as urea, polyethyleneimine, peptone, etc. were also used to synthesize CN_x with chitosan.

2.2 Preparation of Pd/CN_x catalysts: A series of Pd/CN_x catalysts with the actual Pd loading of 1–12 wt % (based on ICP bulk chemical analysis) were prepared via a facile wet chemical reduction method.^[S2] Briefly, 0.25 g CN_x was introduced into 200 mL distilled H₂O at 25 °C under stirring. Then an appropriate amount of PdCl₂ solution (6 g L⁻¹) was added into the solution. After stirring at 25 °C for 0.5 h, 0.1 M NaOH was slowly added into the mixed solution for adjusting the pH at the constant value of 9.5. After stirring for 1 h, the calculated amount of NaBH₄ solution (freshly prepared, *n*_{NaBH₄}/*n*_{Pd} = 15/1) was rapidly injected into the CN_x-PdCl₂ solution. After stirring the resultant mixture for 5 h at 25 °C, the suspension was filtered and extensively washed with distilled water until it was chloride-free.

The sample was dried in air at 100 °C for 12 h to give a black Pd/CN_x sample.

2.3 Preparation of graphite oxide (GO): GO was prepared by a modified Hummers method.^[S3] Briefly, 2.0 g as-received graphite powders was stirred in concentrated H₂SO₄ (46 mL) at 25 °C, and NaNO₃ (1.0 g) was added. After over continuous stirring for over 2 h, the mixture was cooled to 0 °C and KMnO₄ (6.0 g) was slowly added to the suspension under vigorous stirring. The rate of addition was controlled to prevent the rapid rise in the temperature of the suspension (should be < 10 °C). After that, the mixture was stirred at 25 °C for 1 h, followed by further stirring at 35 °C for 3 h. Then distilled water (92 mL) was slowly added to the reaction vessel. The diluted suspension was stirred for an additional 15 min and further diluted with distilled H₂O (280 mL) and then H₂O₂ (20 mL, 30 wt %) was added. After filtered and washed with 5% HCl aqueous solution, the resulting gel-like material was dried in air at 65 °C to give a fine dark brown GO powder.

2.4 Preparation of 10 wt % Pd/r-GO: The Pd/r-GO catalyst with the actual Pd loading of 10 wt % (based on ICP bulk chemical analysis) was prepared by following the wet chemical reduction procedure.^[S2] Briefly, 0.5 g GO was introduced into 200 mL distilled H₂O at 25 °C under stirring. Then 0.1 M NaOH was slowly added into the GO solution for adjusting the pH at the constant value of 9.5. After stirring at 25 °C for 24 h, an appropriate amount of PdCl₂ solution (6 g L⁻¹) was added into the solution at a fixed pH (9.5). After stirring for 1 h, the calculated amount of NaBH₄ solution (freshly prepared, $n_{\text{NaBH}_4}/n_{\text{Pd}} = 15/1$) was rapidly injected into the GO-PdCl₂ solution. After stirring the resultant mixture for 2 h at 25 °C, the suspension was filtered and extensively washed with distilled water until it was chloride-free. The sample was dried in air at 100 °C for 12 h to give a black Pd/r-GO sample.

2.5 Preparation of mpg-C₃N₄ and Pd/mpg-C₃N₄ catalysts: The mpg-C₃N₄ material was synthesized by the method as introduced by Antonietti et al.^[S4] The 10 wt % Pd/mpg-C₃N₄ catalyst was prepared by following the wet chemical reduction procedure of Pd/CN_x catalysts as described above.

2.6 Preparation of 1 wt % Au/CN_{0.25} catalyst: The catalyst was prepared following a procedure as described elsewhere.^[S5] Typically, the PVA (Au/PVA = 1.5/1, wt/wt) was added to an aqueous solution containing 0.5 mM HAuCl₄ at 25 °C under vigorous stirring. The obtained solution was then left under stirring for 10 min. Following the rapid injection of an aqueous solution of 0.1 M NaBH₄ (Au/NaBH₄ = 1/5, mol/mol), the color of the solution turns orange/brown indicating the formation of Au NPs. The CN_{0.25} solution (prepared via the method mentioned above) was then added to the colloidal Au solution under stirring and kept in contact until total adsorption (1 wt % of gold on the support) occurred. After 2 h, the slurry was filtered and the resulting sample was dried at 25 °C in vacuum for 12 h.

2.7 Preparation of 5 wt % Pt/CN_{0.25}, 5 wt % Ru/CN_{0.25}, 5 wt % Rh/CN_{0.25}, and 5 wt % Ir/CN_{0.25} catalysts: In analogy to the case of Pd/CN_x, these catalysts were prepared by the procedure of wet chemical reduction.

2.8 Preparation of 10 wt % Pd/TiO₂, 10 wt % Pd/ZrO₂, and 10 wt % Pd/CeO₂ catalysts: These catalysts were prepared using the routine incipient wetness technique. Appropriate amount of TiO₂ (P25) ZrO₂ or CeO₂ was added to the aqueous solution of PdCl₂. After a perfect mixing of the corresponding

slurries and static standing for 12 h, the sample was dried at 100 °C for 12 h, followed by reduction in 5 vol% H₂/Ar at 400 °C for 2 h.

2.9 Preparation of PVA-stabilized 10 wt % Pd/CN_{0.25} catalyst: This catalyst was prepared following a procedure as described elsewhere.^[S6] Typically, the PVA ($n_{\text{PVA}}/n_{\text{Pd}} = 10/1$) was added to an aqueous solution containing 2 mM PdCl₂ at 25 °C under vigorous stirring. The obtained solution was then left under stirring for 10 min. A following rapid injection of an aqueous solution of 0.1 M NaBH₄ (freshly prepared, $n_{\text{NaBH}_4}/n_{\text{Pd}} = 15/1$), led to formation of a dark orange-brown solution, indicating the formation of the palladium sol. The CN_{0.25} solution (prepared via the method mentioned above) was then added to the colloidal palladium solution under stirring and kept in contact until total adsorption (10 wt % of palladium on the support) occurred. After 2 h stirring, the slurry was filtered and the resulting sample was dried at 100 °C in air for 12 h.

3. Catalyst characterization

3.1 Elemental analysis: The metal loading was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

3.2 Elemental analysis of non-metal: Elemental analysis (EA, CHN mode) was performed using a vario EL III (Analytensysteme GmbH) instrument to determine the carbon, nitrogen, hydrogen, and oxygen contents of the samples.

3.3 BET analysis: The BET specific surface areas of the prepared catalysts were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 °C prior to acquiring the adsorption isotherm.

3.4 X-ray diffraction (XRD) analysis: The crystal structures were characterized with XRD on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu K α radiation source at 40 kV and 40 mA.

3.5 X-ray photoelectron spectroscopy (XPS): XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg K α , $h\nu = 1253.6$ eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

3.6 Field emission scanning electron microscopy (FESEM): The field emission scanning electron microscopy (FESEM) measurements were carried out on a Nova NanoSEM 450 field-emission scanning electron microscope.

3.7 Transmission electron microscopy (TEM): A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the TEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. The size distribution of the metal nanoparticles was determined by measuring about 200 random particles on the images.

3.8 High-resolution transmission electron microscopy (HRTEM): A JEM 2100F electron microscope

operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the HRTEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. The size distribution of the metal nanoparticles was determined by measuring about 200 random particles on the images.

3.9 High-angle annular dark-filed scanning transmission electron microscopy (HAADF-STEM): HAADF-STEM images were obtained on a JEM 2100F electron microscope equipped with a field-emission-gun (FEG) operated at 200 kV and using a HAADF detector. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids.

3.10 Attenuated total reflectance-infrared (ATR-IR) measurements: The infrared data was collected using a Nicolet 6700 ATR-IR spectrometer with a liquid-nitrogen-cooled MCT detector. The spectra were obtained by averaging 128 scans with a resolution of 4 cm^{-1} over wavenumbers ranging from 800 to 4000 cm^{-1} . For CO adsorption, the Pd catalysts were dissolved in approx. 2 mL water, first a spectrum of un-CO treated sample was collected, and then it was treated with CO for 1 h before a spectrum of this was collected. Each spectrum was obtained at room temperature by subtracting the background spectrum of the un-CO treated sample.

3.11 Quantitative analysis of trace CO in the H₂-containing stream: CO concentration with very low levels can be reliably measured by using a gas chromatograph (Agilent 6890 GC) analysis system equipped with a methanizer and a flame ionization detector (FID, detection limit ~ 1.0 ppmv). Prior to the analysis, the catalyst in methanizer was reduced *in situ* by 5 vol % H₂/Ar at 400 °C for 1 h. The evolved gas was first cleaned by concentrated NaOH solution for potential CO₂-trapping and MgSO₄ powder for moisture-trapping, then flowing the methanizer at 300 °C under atmospheric pressure. The effluent from methanizer was again cleaned by MgSO₄ powder and later analyzed by the FID. For calibration purpose, the methanation data of a series of premixed reference gases containing different concentrations CO in H₂ were also collected using the similar method.

3.12 CO chemisorption measurements: Pd surface area was measured by CO chemisorptions using AutoChem HP 2950 apparatus with quantitative loop from Micromeritics. The sample was first pretreated with 5 vol % H₂/Ar at 400 °C for 2 h, and then pure CO was pulsed over the sample at 25 °C for several times to saturated adsorption. The total amount of CO adsorbed was measured by assuming a chemisorption stoichiometry of CO/Pd=1 and a Pd surface atomic density of $1.27 \times 10^{19}\text{ m}^{-2}$.^[S7,S8] The dispersion (D) was calculated according to the formula of $D = (\text{surface number of Pd atoms})/(\text{total number of Pd atoms})$.

4. Catalytic activity measurement

4.1 Decomposition of FA in an open system: All catalytic experiments were carried out under ambient atmosphere of air. It should be noted that the use of oxygen atmosphere (O₂) gave essentially the same rate of H₂ evolution as air in this reaction. All reactions, unless otherwise stated, were performed in a

double-walled thermostatically controlled reaction vessel (10 mL) under steady magnetic stirring (800 rpm) at given temperature (10–35 °C) with a reflux condenser, which is connected to an automatic gas burette, where the gases are collected. In addition, evolved gas was qualitatively and quantitatively analyzed by GC (Agilent 6820 equipped with a TDX-01 column connected to a thermal conductivity detector). Typically a ratio of hydrogen and carbon dioxide of 1:1 (\pm 5%) is detected. The initial TOF was calculated based on the FA conversion level at 15%.

4.2 Large-scale durability of 10 wt % Pd/CN_{0.25} catalyst for dehydrogenation of FA: For the large-scale durability experiment, 100 mL scale of 1.0 M aqueous FA and 75.4 μ mol Pd catalyst were placed in a reaction vessel (150 mL) using water bath under steady magnetic stirring (800 rpm) at 25 °C with a reflux condenser, which is connected to an automatic gas burette, where the gases are collected. In addition, the evolved gas was qualitatively and quantitatively analyzed by GC (Agilent 6820 equipped with a TDX-01 column connected to a thermal conductivity detector). After reaction of 10 h, the centrifuged catalysts from parallel activity tests were collected and washed with distilled water, followed by drying in air at 100 °C for 12 h. All catalytic activity tests were repeatedly carried out by following the same procedure as described above.

4.3 Pressurized H₂ generation in a closed system: The catalytic experiment was carried out in a Hastelloy-C high-pressure Parr autoclave (50 mL). Typically, 10.0 mL scale of 1.0 M aqueous FA and 37.7 μ mol Pd (Pd/CN_{0.25}) were placed in the autoclave. Then the autoclave was sealed and the internal air was degassed quickly and completely using N₂ at room temperature. The stirrer was started (800 rpm) when the desired temperature of 25 °C was reached.

4.4 Hydrogenation of CO₂ by using 10 wt % Pd/CN_{0.25}: The catalytic hydrogenation experiments were carried out in a Hastelloy-C high-pressure Parr autoclave (50 mL). Typically, 5.0 mL scale of 1.0 M aqueous amine and 9.4 μ mol Pd catalyst were placed in the autoclave. Then the autoclave was sealed, and CO₂/H₂ mixture gas was charged into it after internal air being degassed completely using N₂ at 25 °C. The stirrer (800 rpm) was started until the desired temperature (80–130 °C) was reached. After a certain time, the autoclave was placed in cool water and the gas was carefully released. The gaseous mixture was analyzed using an Agilent 6820 GC equipped with a TDX-01 column connected to a TCD. The reaction mixture was transferred into a centrifuge tube and the solid catalyst was separated by centrifugation. Formate product concentrations were monitored by high-performance liquid chromatography (HPLC) on an anion-exclusion column (Tosoh TSKgel SCX(H⁺)) using aqueous H₂SO₄ solution (5 mM) as eluent and an ultraviolet detector (λ = 210 nm).

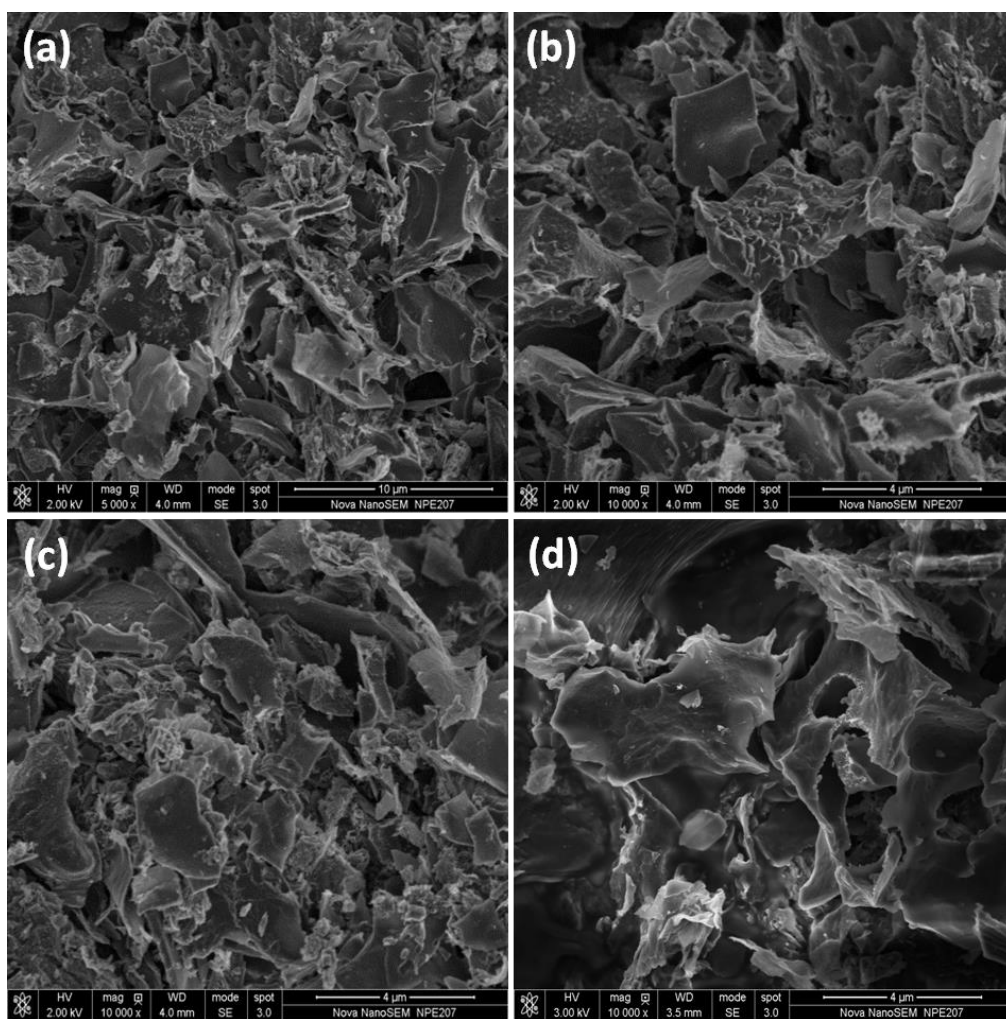


Figure S1. SEM images of (a) CN_{0.15}, (b) CN_{0.23}, (c) CN_{0.62}, and (d) CN_{0.95} samples.

Table S1: Textural properties of CN_x prepared from the combination of chitosan and melamine.

Sample	BET surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]	Pore diameter [nm]
CN _{0.15}	201	0.2297	14.9
CN _{0.23}	226	0.2532	12.2
CN _{0.39}	244	0.2721	8.9
CN _{0.62}	271	0.2983	6.1
CN _{0.95}	285	0.3342	5.8

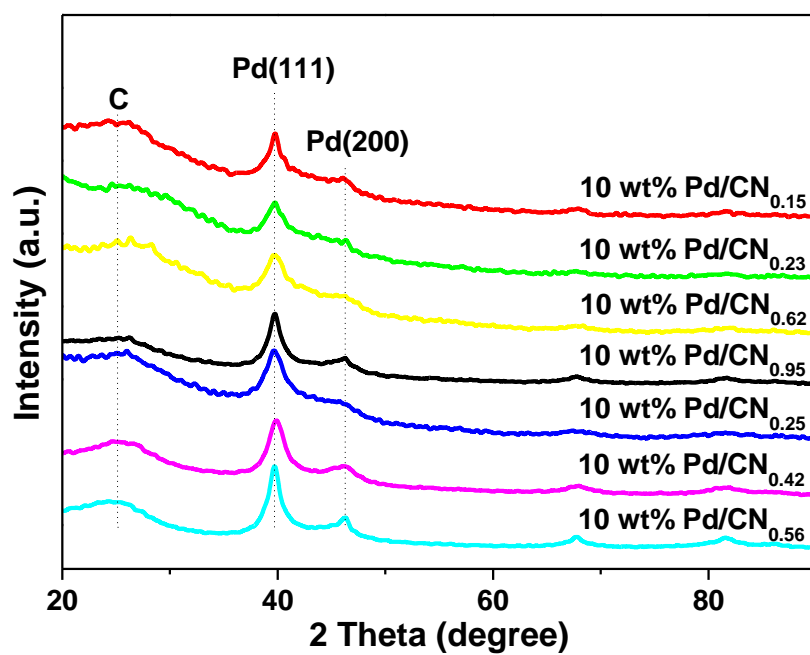


Figure S2. XRD patterns of Pd/CN_x catalysts.

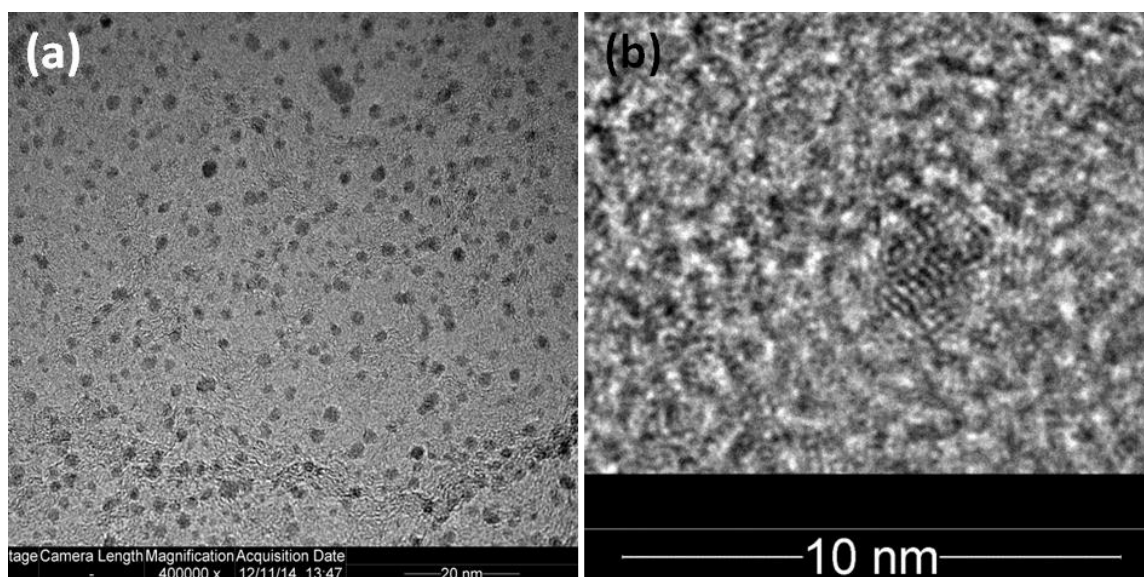


Figure S3. HRTEM images of 10 wt % Pd/CN_{0.23} catalyst.

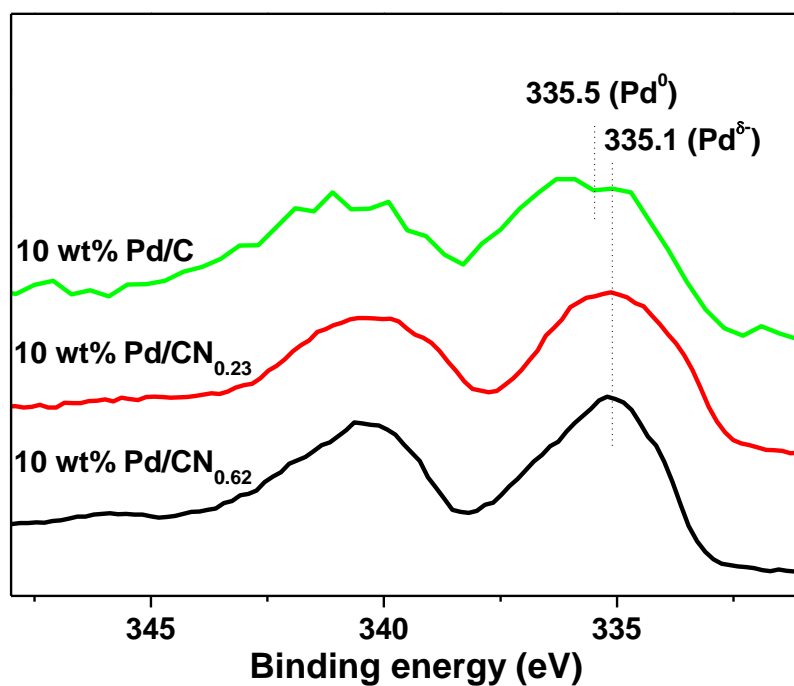


Figure S4. XPS data of Pd/C and Pd/CN_x catalysts.

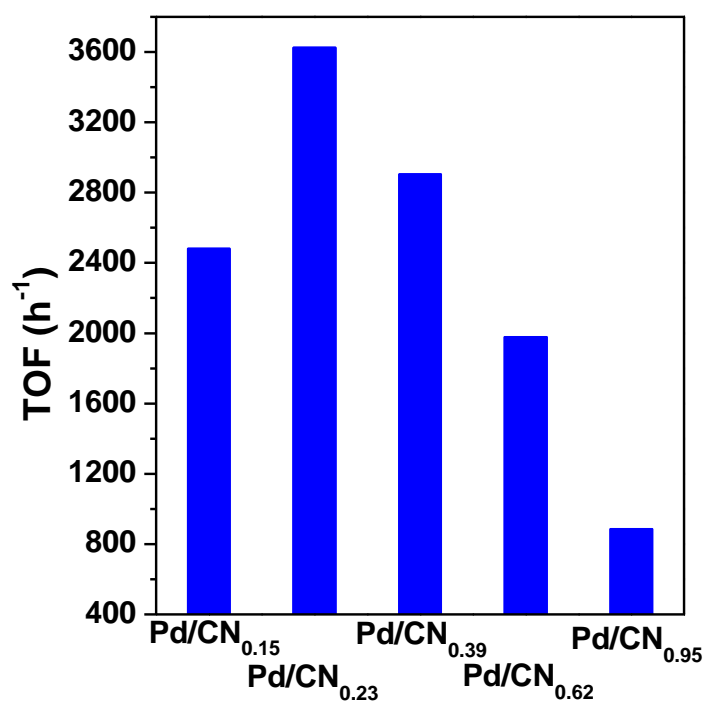


Figure S5. Activity of 10 wt % Pd/CN_x (the CN_x were prepared from the combination of chitosan and melamine) catalysts for FA dehydrogenation. Reaction conditions: 5.0 mL scale of 1 M aqueous FA, 37.7 μmol Pd, 25 °C.

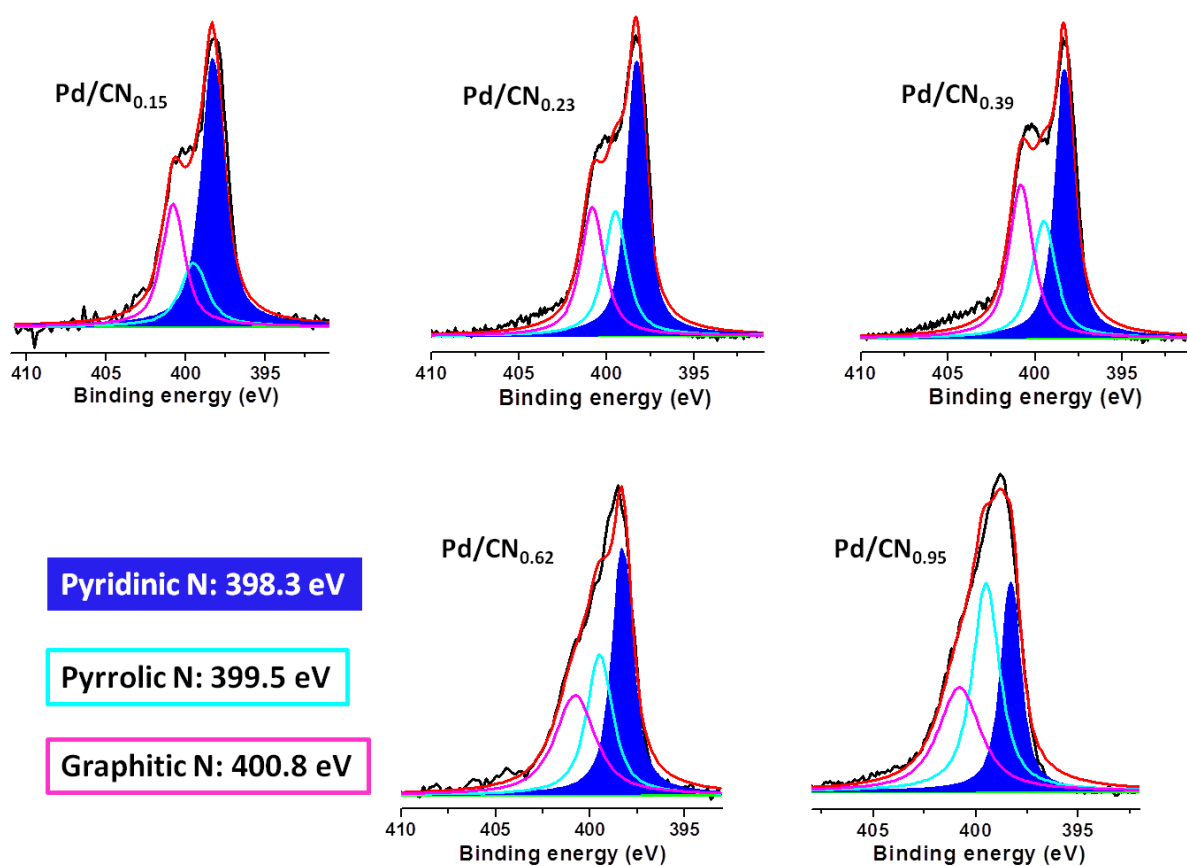


Figure S6. XPS of the N 1s for the 10 wt % Pd/CN_x (the CN_x were prepared from the combination of chitosan and melamine) catalysts.

Table S2: Changes of surface pyridinic N/Pd molar ratio.^[a]

Sample	Bulk N/Pd molar ratio	Surface N/Pd molar ratio	Pyridinic N content [%]	Surface pyridinic N/Pd molar ratio
Pd/CN _{0.15}	10.15	3.12	55.77	1.74
Pd/CN _{0.23}	14.42	3.49	54.73	1.91
Pd/CN _{0.39}	21.31	4.01	45.64	1.83
Pd/CN _{0.62}	28.60	4.38	34.46	1.51
Pd/CN _{0.95}	35.82	4.91	26.27	1.29

[a] The CN_x were prepared from the combination of chitosan and melamine, and the Pd loadings were 10 wt %.

Table S3: Effect of modification by model organic molecules on catalytic behavior of Pd/C and Pd/Al₂O₃ catalysts for dehydrogenation of FA.^[a]

Entry	Catalyst	Metal loading [wt %]	D _{NP} [nm]	TOF [h ⁻¹] ^[b]	TOF [h ⁻¹] ^[c]
1	Pd/C	10	3.5	35, with 40 ppm CO	201
2 ^[d]	Pd/C	10	3.5	26	173
3 ^[e]	Pd/C	10	3.5	49	352
4 ^[f]	Pd/C	10	3.5	66	480
5 ^[g]	Pd/C	10	3.5	75	678
6	Pd/Al ₂ O ₃	5	3.2	31	124
7 ^[d]	Pd/Al ₂ O ₃	5	3.2	21	113
8 ^[e]	Pd/Al ₂ O ₃	5	3.2	39	178
9 ^[f]	Pd/Al ₂ O ₃	5	3.2	52	248
10 ^[g]	Pd/Al ₂ O ₃	5	3.2	62	315

[a] Reaction conditions: 5 mL scale of 1 M aqueous FA, 37.7 μmol Pd, 25 °C. [b] Based on total Pd atoms. [c] Based on surface Pd sites, the dispersion was calculated from CO chemisorption. The sample (0.1 g) was added into an aqueous solution (5 mL) containing model molecules (1 mmol, [d] pyrrole, [e] pyridine, [f] 3-aminopyridine, and [g] 1,10-phenanthroline), and the suspension was stirred for 12 h at 25 °C, followed by resting for another 12 h. After the adsorption, the catalyst was recovered by centrifugation and drying in air at 80 °C for 12 h, and then was used for catalytic reactions.

The bare Pd/C showed little activity with TOF of only 201 h⁻¹, and a high content of toxic CO was also produced. The modification by pyrrole decreased the performance. On the other hand, the modification of Pd/C with 1,10-phenanthroline significantly accelerated both activity and H₂ selectivity. The performance was also improved by pyridine and 3-aminopyridine. Similar results were also obtained for the Pd/Al₂O₃ catalysts containing different functional groups on surface.

Table S4: Dehydrogenation of FA: comparison of selected N-containing compounds with bio-chitosan-based pyrolysis strategy for preparation of CN_x for supporting Pd catalysts.^[a]

Compound	Pd/CN _x ^[b]	D _{NP} [nm]	Time [min] ^[c]	TOF [h ⁻¹] ^[d]	TOF [h ⁻¹] ^[e]
PEI	Pd/CN _{0.19}	3.5	2.8	425	3034
urea	Pd/CN _{0.25}	3.1	1.6	752	5530
polyacrylamide	Pd/CN _{0.22}	3.0	3.4	351	2700
peptone	Pd/CN _{0.35}	3.5	3.1	391	2604
polyacrylonitrile	Pd/CN _{0.28}	3.3	4.1	295	1845
pyridine	Pd/CN _{0.21}	3.1	2.5	482	3573
piperidine	Pd/CN _{0.18}	3.5	4.3	279	1744
triethylamine	Pd/CN _{0.27}	3.2	2.5	488	3754
aniline	Pd/CN _{0.31}	3.2	3.0	401	2509
acetonitrile	Pd/CN _{0.16}	3.4	3.3	369	2636

[a] Reaction conditions: 5 mL scale of 1 M aqueous FA, 37.7 μmol Pd, 25 °C. [b] The Pd loadings were 10 wt %. [c] Corresponding to the reaction time of FA conversion at 15%. [d] Based on total Pd atoms. [e] Based on surface Pd sites, the dispersion was calculated from CO chemisorption.

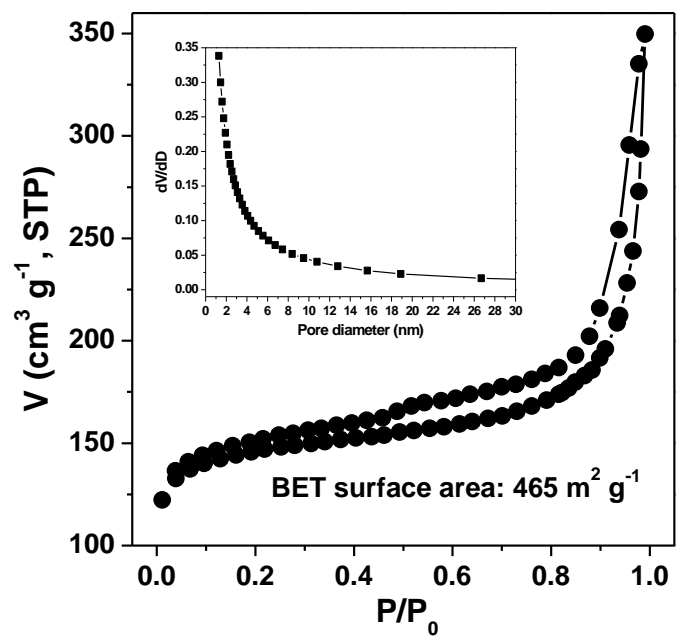


Figure S7. N₂ adsorption-desorption isotherms of CN_{0.25} prepared from the combination of chitosan and urea.

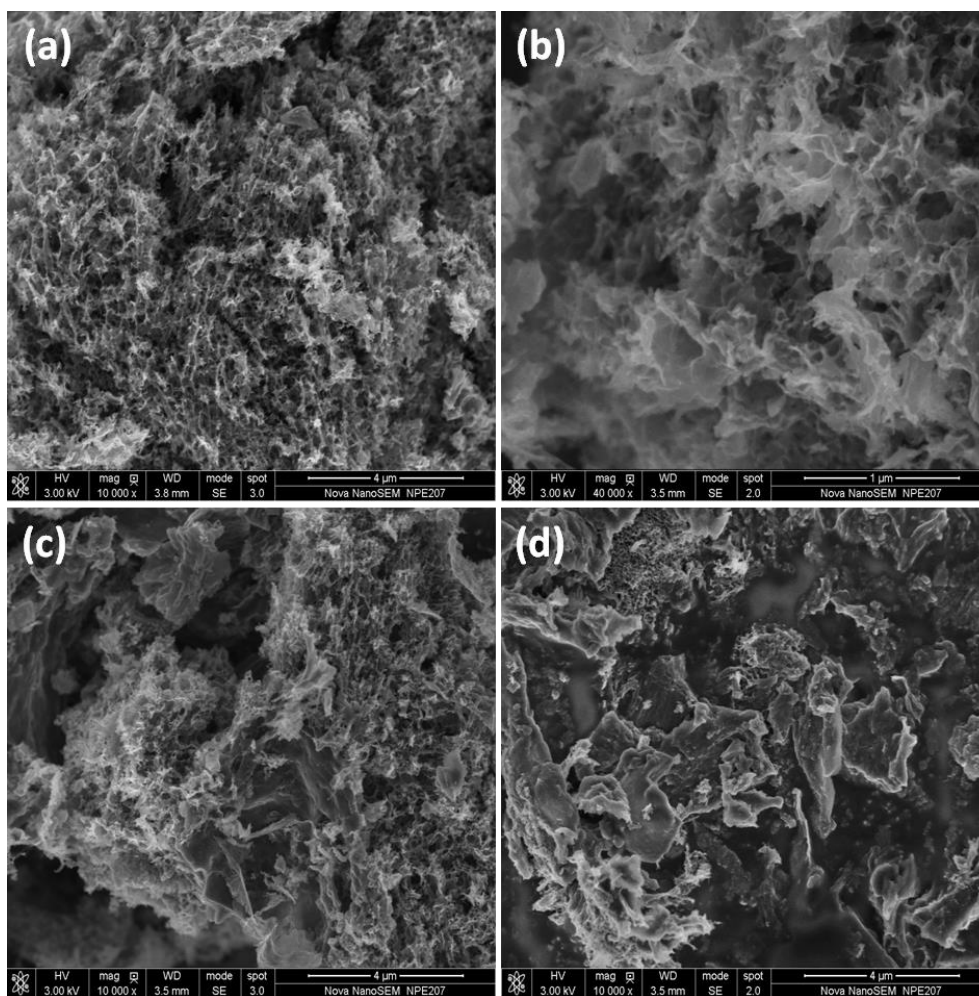


Figure S8. SEM images of (a) CN_{0.17}, (b) CN_{0.25}, (c) CN_{0.42}, and (d) CN_{0.56} samples.

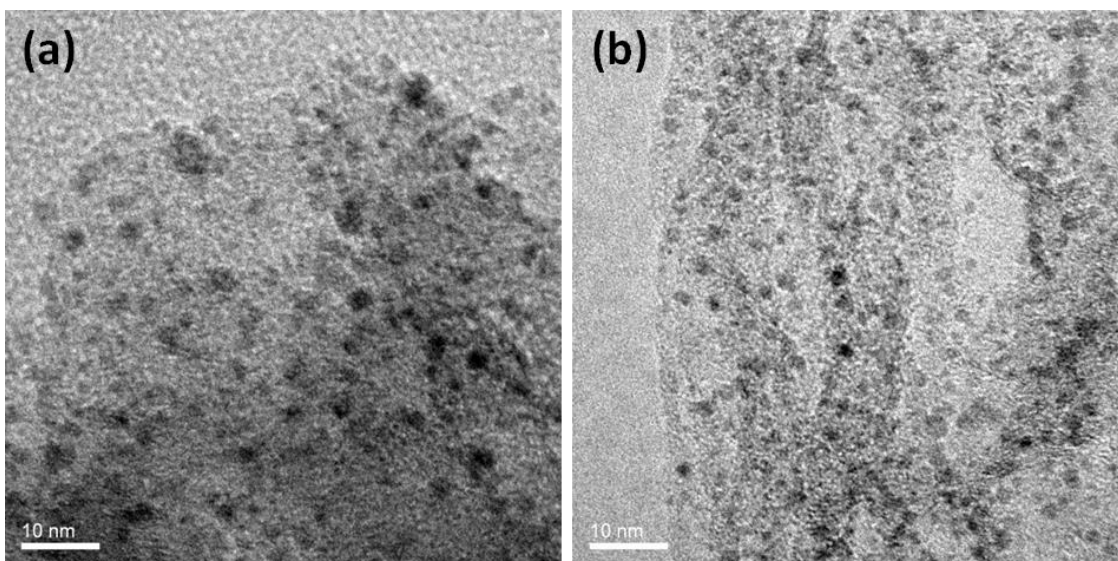


Figure S9. TEM images of (a) Pd/CN_{0.17} and (b) Pd/CN_{0.42} catalysts.

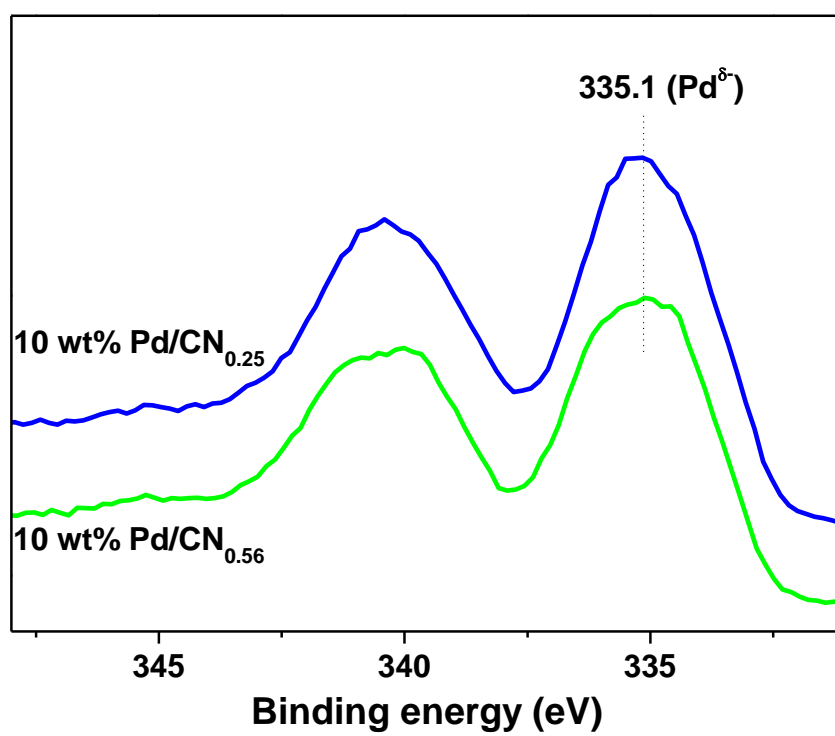


Figure S10. XPS data of Pd/CN_{0.25} and Pd/CN_{0.56} catalysts.

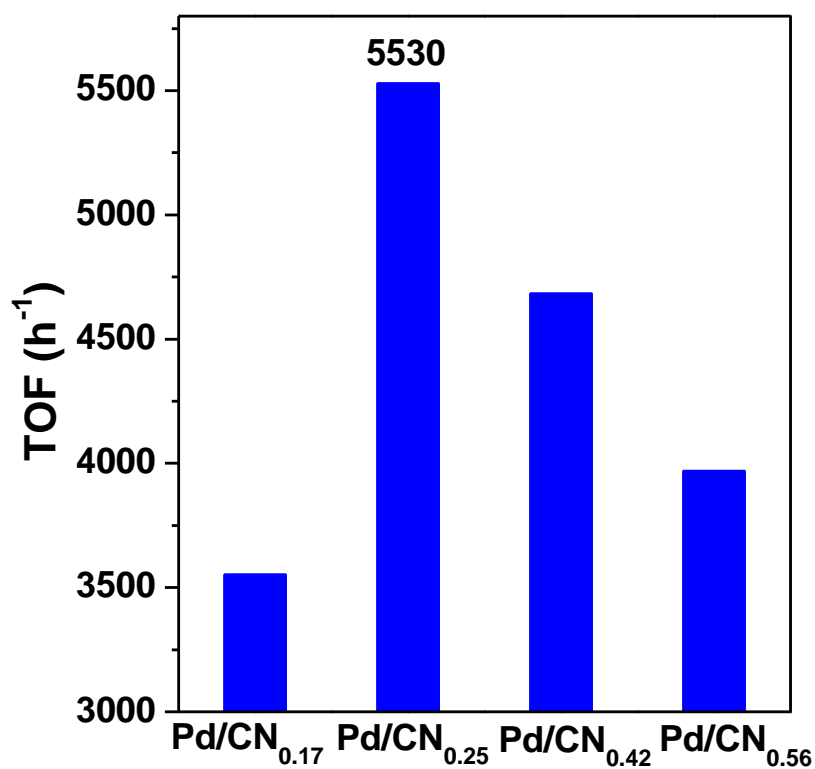


Figure S11. Activity of 10 wt % Pd/CN_x (the CN_x were prepared from the combination of chitosan and urea) catalysts for FA dehydrogenation. Reaction conditions: 5.0 mL scale of 1 M aqueous FA, 37.7 μmol Pd, 25 °C.

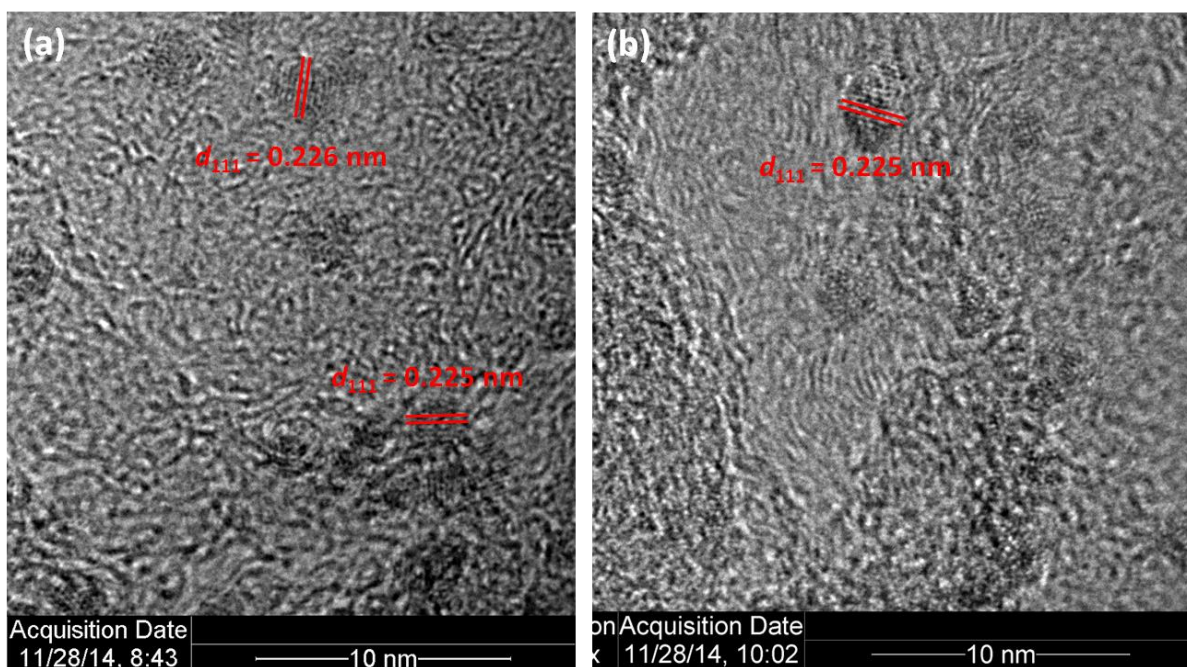


Figure S12. HRTEM images of (a) 10 wt % Pd/CN_{0.25} and (b) 10 wt % Pd/CN_{0.56} catalysts.

Table S5: Changes of surface pyridinic N/Pd molar ratio.^[a]

Sample	Bulk N/Pd molar ratio	Surface N/Pd molar ratio	Pyridinic N content [%]	Surface pyridinic N/Pd molar ratio
Pd/CN _{0.17}	11.28	3.59	51.17	1.84
Pd/CN _{0.25}	15.39	4.29	50.82	2.18
Pd/CN _{0.42}	22.41	4.31	47.81	2.06
Pd/CN _{0.56}	26.93	4.50	42.65	1.92

[a] The CN_x were prepared from the combination of chitosan and urea, and the Pd loadings were 10 wt %.

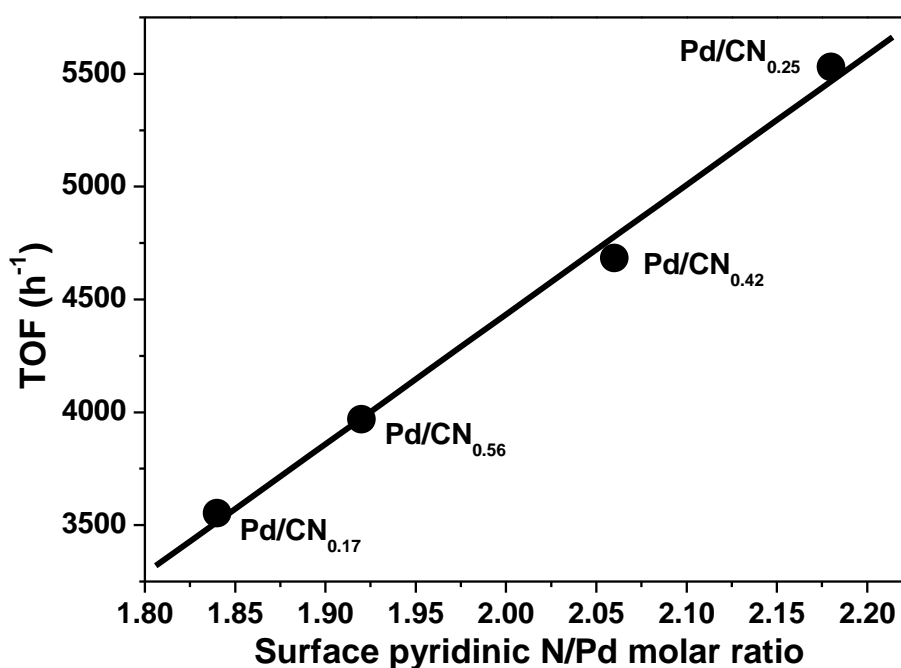


Figure S13. Correlation between the surface pyridinic N/Pd molar ratio and the initial TOF value using Pd/CN_x catalysts (the CN_x were prepared from the combination of chitosan and urea).

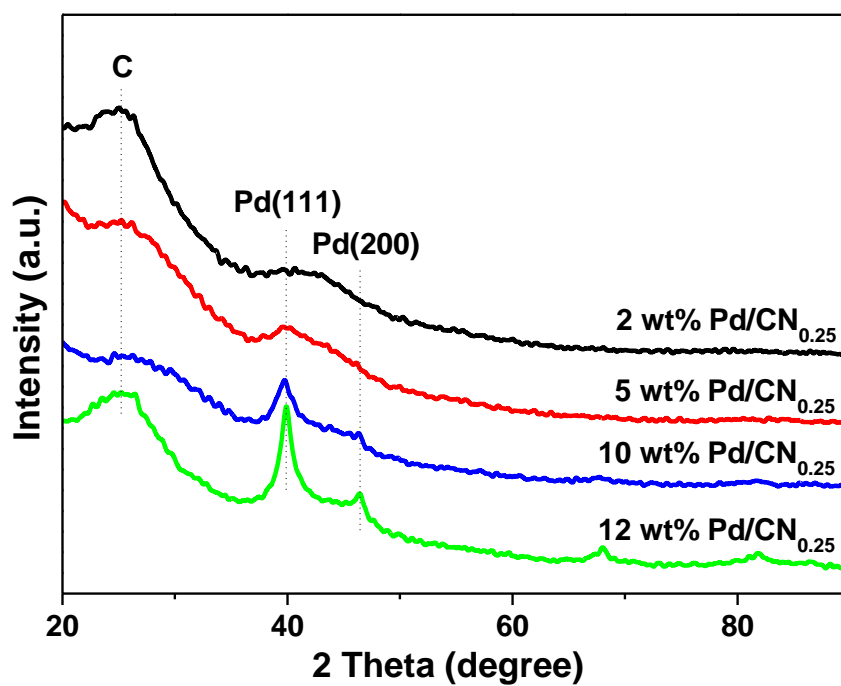


Figure S14. XRD patterns of Pd/CN_{0.25} with different Pd loadings.

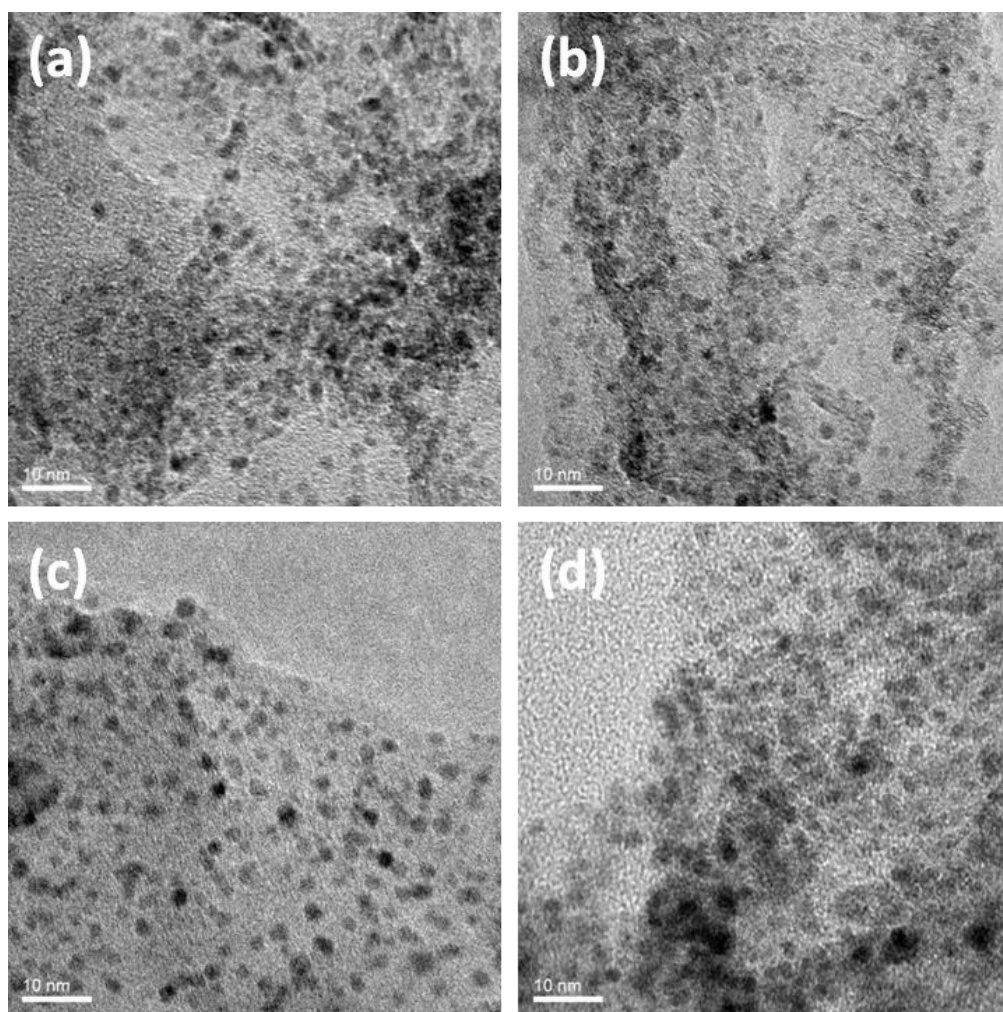


Figure S15. TEM images of Pd/CN_{0.25} with Pd loadings of (a) 5, (b) 8, (c) 10, and (d) 12 wt %.

Table S6: Modification of surface pyridinic N/Pd molar ratio with Pd loadings for Pd/CN_{0.25} catalyst.

Loading [wt%]	Bulk N/Pd molar ratio	Surface N/Pd molar ratio	Pyridinic N content [%]	Surface pyridinic N/Pd molar ratio
1	154.52	28.64	50.82	14.55
2	77.18	23.18	50.82	11.78
5	31.22	12.73	50.82	6.47
8	19.33	7.31	50.82	3.71
10	15.39	4.29	50.82	2.18
12	12.85	3.78	50.82	1.92

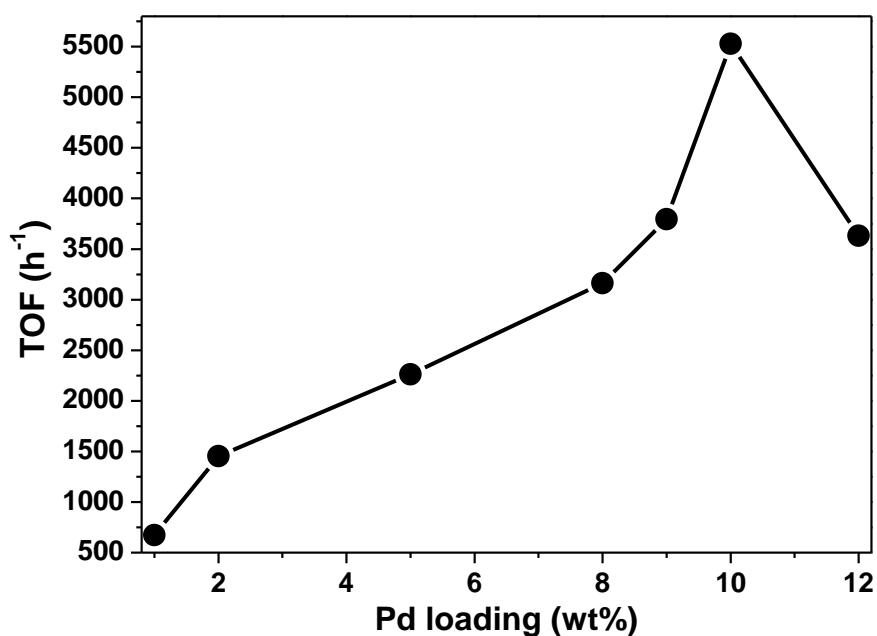


Figure S16. TOF as a function of the Pd loading on Pd/CN_{0.25} catalyst for the dehydrogenation of FA. Reaction conditions: 5 mL scale of 1 M aqueous FA, 37.7 μ mol Pd, 25 °C.

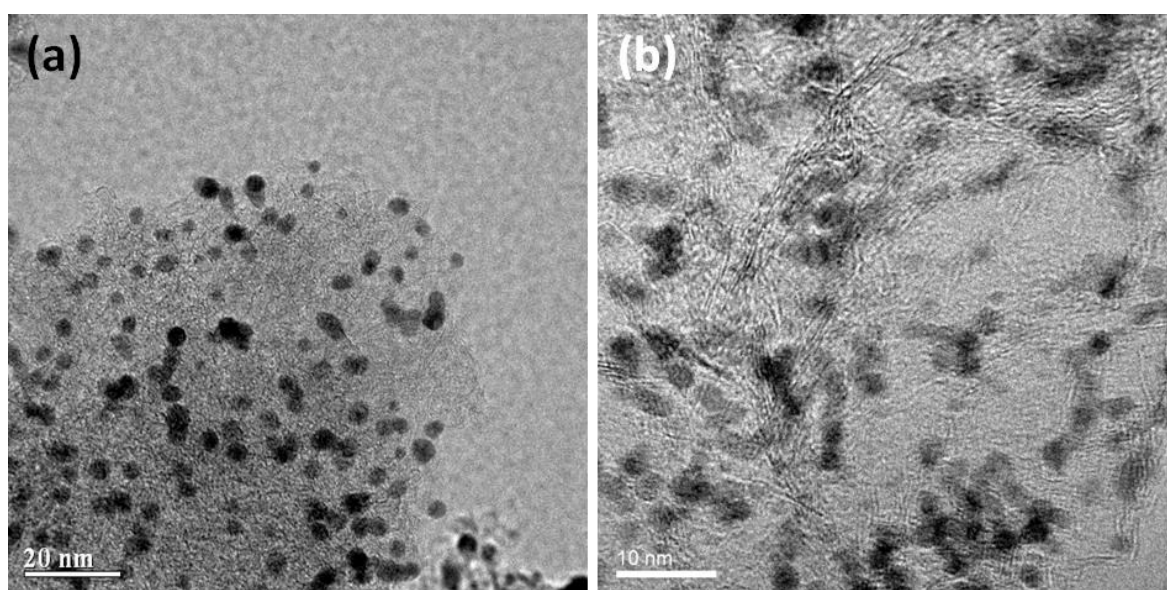


Figure S17. TEM images of (a) 1 wt % Au/CN_{0.25} and (b) 10 wt % PVA-stabilized Pd/CN_{0.25}.

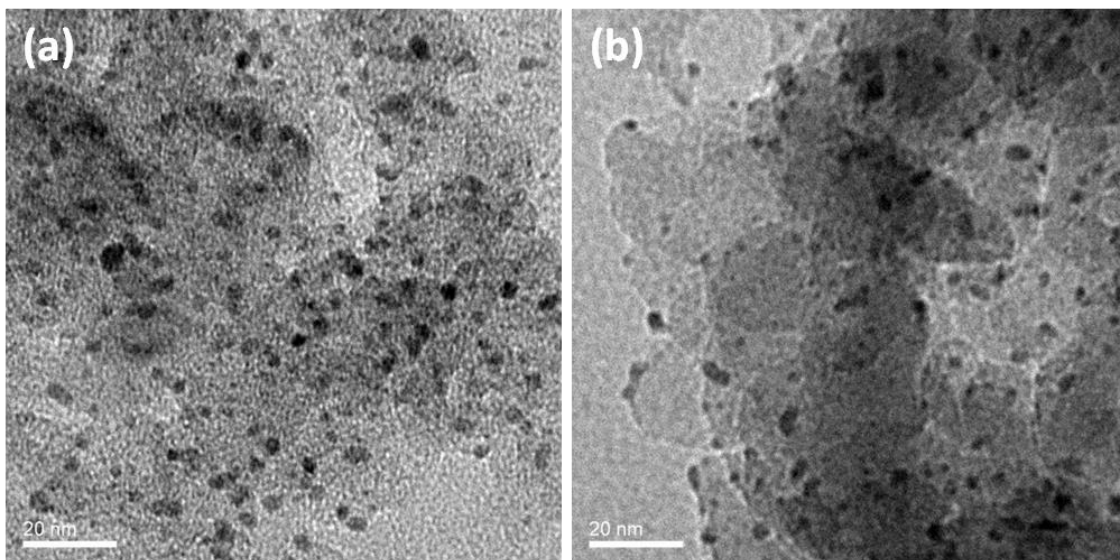


Figure S18. TEM images of (a) 10 wt % Pd/C, and (b) 10 wt % Pd/mpg-C₃N₄ catalysts.

Table S7: Activity of various catalysts for dehydrogenation of FA.^[a]

Entry	Catalyst	Metal loading [wt %]	D _{NP} [nm]	Time [min] ^[b]	TOF [h ⁻¹] ^[c]	TOF [h ⁻¹] ^[d]
1 ^[e]	CN _{0.25}	0	–	inactive	0	–
2	Au/CN _{0.25}	1	4.3	inactive	0	–
3	Pt/CN _{0.25}	5	3.2	inactive	0	–
4	Ru/CN _{0.25}	5	2.9	inactive	0	–
5	Rh/CN _{0.25}	5	3.5	inactive	0	–
6	Ir/CN _{0.25}	5	3.1	inactive	0	–
7	Pd/TiO ₂	10	3.9	92.6	13	–
8	Pd/ZrO ₂	10	4.3	54.7	22	–
9	Pd/CeO ₂	10	4.5	inactive	0	–
10	Pd/r-GO	10	3.2	20.4	59	393
11	Pd/mpg-C ₃ N ₄	10	3.0	6.6	182	1247
12	PVA-stabilized Pd/CN _{0.25}	10	4.6	8.3	145	1115

[a] Reaction conditions: 5 mL scale of 1 M aqueous FA, 37.7 μmol metal, 25 °C. [b] Corresponding to the reaction time of FA conversion at 15%. [c] Based on total metal atoms. [d] Based on surface Pd sites, the dispersion was calculated from CO chemisorption. [e] 100 mg CN_{0.25}.

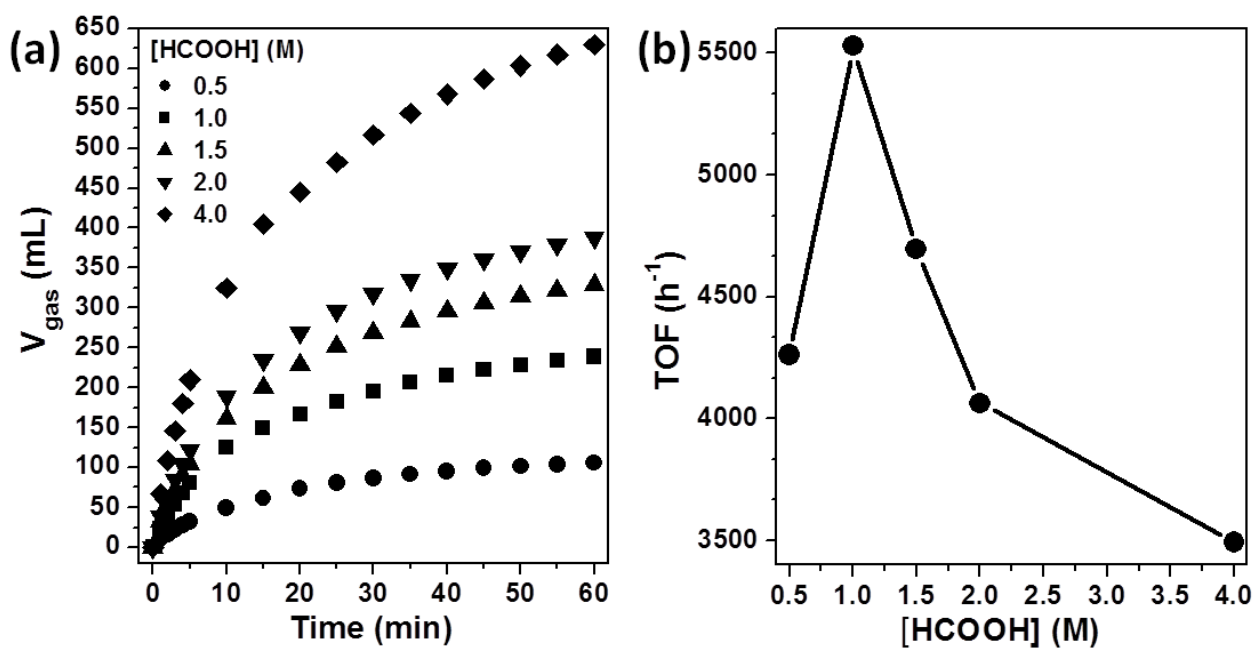


Figure S19. (a) The volume of the generated gas versus time for the dehydrogenation of FA catalyzed by 10 wt % Pd/CN_{0.25} catalyst at different initial FA concentrations and (b) Plot of TOF versus the initial FA concentration. Reaction conditions: 5 mL scale of aqueous FA, $n(\text{FA})/n(\text{Pd}) = 133$, 25 °C.

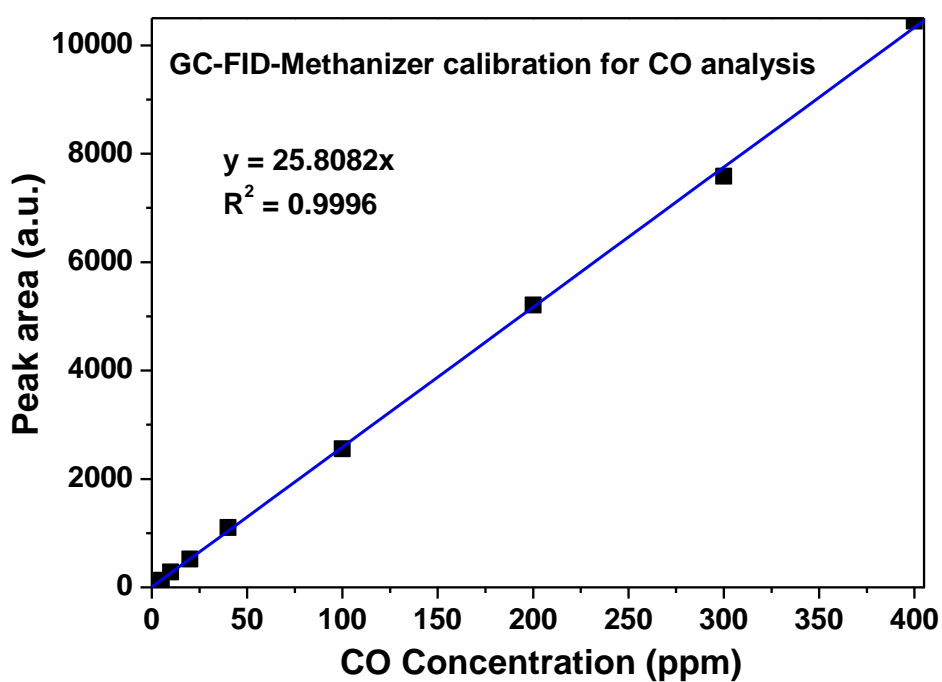


Figure S20. Calibration curve for CO quantitative analysis using the GC-FID-Methanizer.

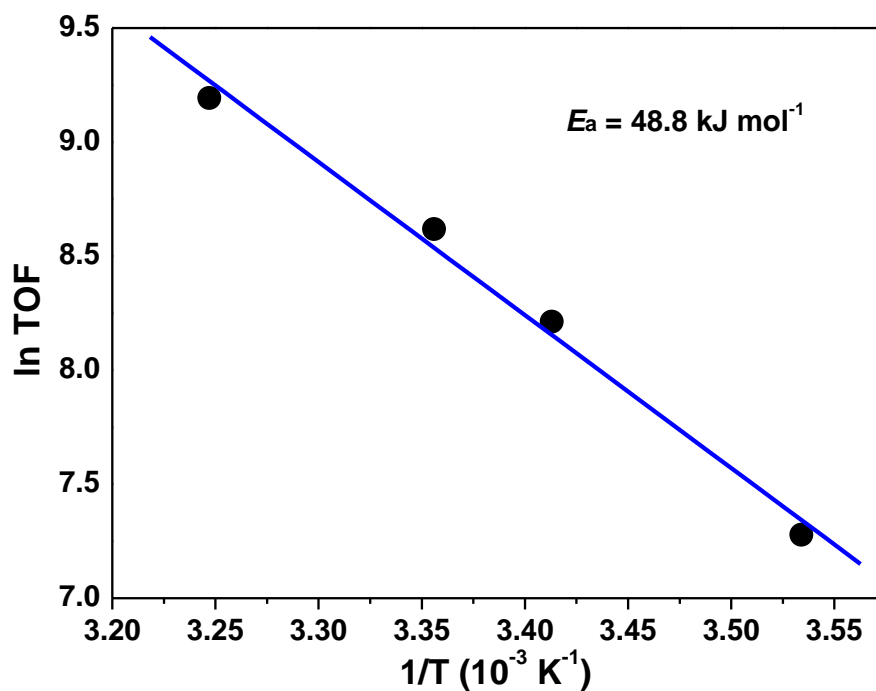


Figure S21. Arrhenius plot for 10 wt % Pd/CN_{0.25} catalyzed dehydrogenation of FA. Reaction conditions: 5 mL scale of 1 M aqueous FA, 37.7 μmol Pd.

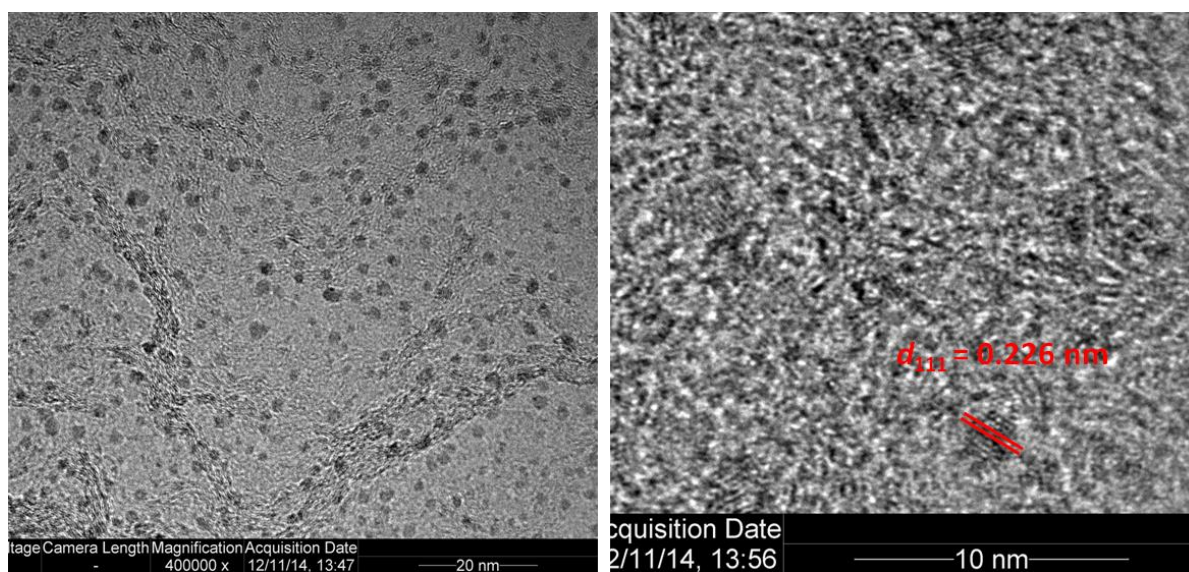


Figure S22. HRTEM images of the reused 10 wt % Pd/CN_{0.25} after six times.

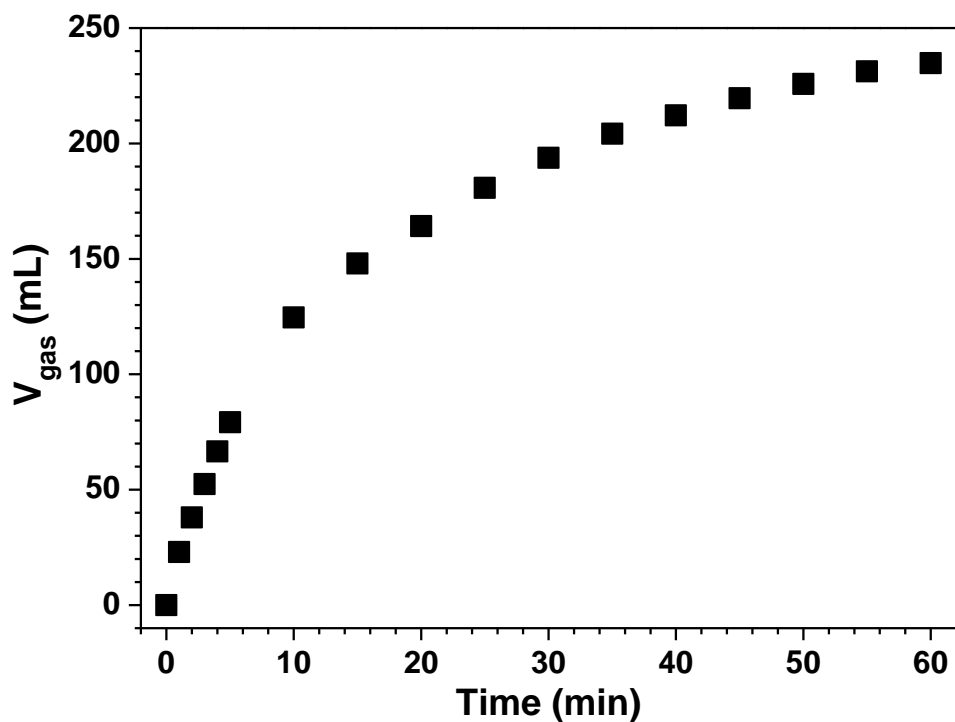


Figure S23. Air-stability of Pd/CN_{0.25} catalyst. Reaction conditions: 5.0 mL scale of 1 M aqueous FA, 37.7 μ mol Pd, 25 °C. Compared to the fresh one, Pd/CN_{0.25} stored for half a year at ambient conditions can still give ca. 235 mL of mixed gas for FA dehydrogenation.

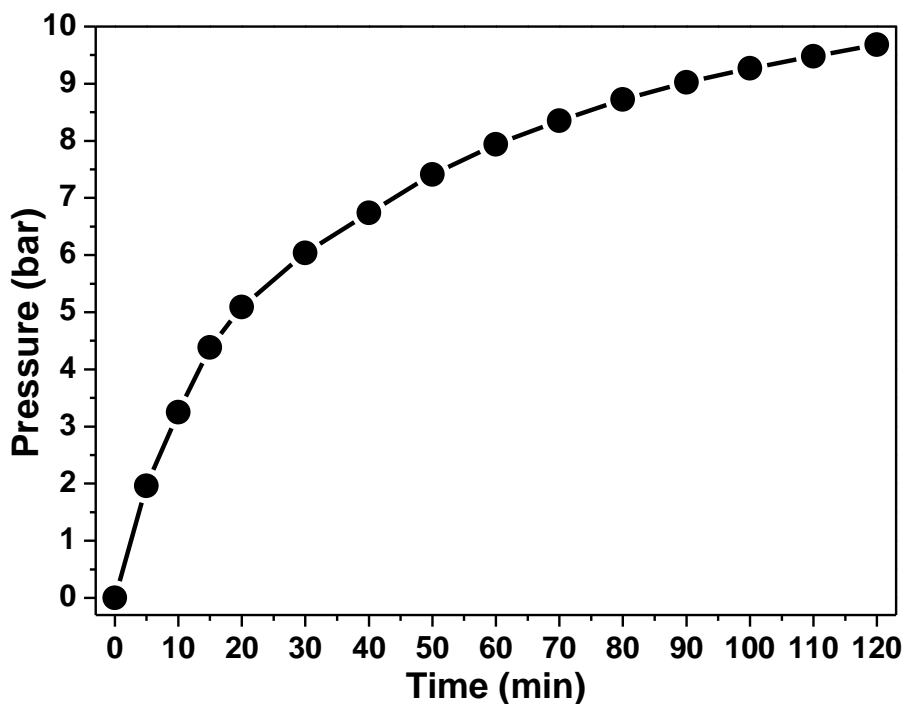
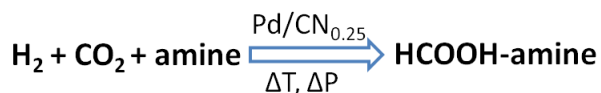


Figure S24. Pressure-time profile for FA dehydrogenation using 10 wt % Pd/CN_{0.25} in a closed system. Reaction conditions: 10 mL scale of 1 M aqueous FA and 37.7 μ mol Pd in 50 mL Parr autoclave, 25 °C.

Table S8: Hydrogenation of CO₂ using Pd/CN_{0.25}.^[a]

Entry	Amine	T [°C]	P _{H₂/CO₂} [bar] ^[b]	FA yield [%]	TON ^[c]	TON ^[d]
1	diethylamine	100	30/30	55.7	296	2176
2	<i>n</i> -butylamine	100	30/30	36.8	196	1441
3	dimethylethanolamine	100	30/30	81.3	432	3176
4	triethanolamine	100	30/30	47.5	252	1893
5	triethylamine	100	30/30	89.6	476	3500
6	triethylamine	130	30/30	97.2	517	3801
7	triethylamine	80	30/30	60.4	321	2360
8	triethylamine	100	40/20	68.1	362	2662
9	triethylamine	100	20/40	59.5	316	2324
10 ^[e]	triethylamine	100	30/30	82.8	1762	12956
11 ^[f]	triethylamine	100	30/30	96.6	18370	135074

[a] 5 mL scale of 1.0 M aqueous amine, 9.4 μmol Pd, 50 mL Parr autoclave, 10 h. [b] Pressure at 25 °C. [c] Based on total Pd atoms. [d] Based on surface Pd sites. [e] 5 mL scale of 4.0 M aqueous triethylamine. [f] 25 mL scale of 5.72 M aqueous triethylamine, 7.52 μmol Pd, 100 h.

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