Supporting Information

Electrochemically Tunable Proton-Coupled Electron Transfer in Pd-Catalyzed Benzaldehyde Hydrogenation

Katherine Koh*, Udishnu Sanyal*, Mal-Soon Lee, Guanhua Cheng, Miao Song, Vassiliki-Alexandra Glezakou, Yue Liu, Dongsheng Li, Roger Rousseau, Oliver Y. Gutiérrez,* Abhijeet Karkamkar,* Miroslaw Derewinski, and Johannes A. Lercher*

anie_201912241_sm_miscellaneous_information.pdf
Section S1. Experimental Section

Section S2. H₂ adsorption experiment (H₂/D₂ exchange)

Section S3. Density-functional-theory (DFT)-based ab initio molecular dynamics (AIMD) simulations
Section S1. Experimental Section

S1.1. Materials
Carbon felts (CF, 0.25 inch thick) were obtained from Alfa Aesar. Polyaniline, sucrose, Ludox ® HS-40 (40 wt.%), sodium hydroxide (NaOH, 97%), nitric acid (HNO₃, 70%), sodium acetate/acetic acid buffer solution (3 M, pH 5.2), benzaldehyde (99.5 %), benzyl alcohol (99.8%), palladium (II) nitrate hydrate, hydrochloric acid (HCl), cyclohexanone, 1-butanol, dichloromethane, 1 wt.% Pd/C, deuterium oxide (D₂O, 99.9%) and graphite rod (99%), phosphoric acid, disodium phosphate (NaH₂PO₄), sodium carbonate (Na₂CO₃), sodium bicarbonate (NaHCO₃) were purchased from Sigma-Aldrich and used as received.

S1.2. Characterization
X-ray photoelectron spectrometer (XPS) were operated by the physical electronics instruments (PHI) Quantum 2000 XPS equipped with Al K. The binding energies of all the XPS spectra were calibrated to C 1s binding energy to be 284.8 eV and deconvolutions of each peaks were done with CasaXPS software. A Technai F20 instrument was used for transmission electron microscopy (TEM). TEM particle sizes are measured by counting particles (> 150 particles) and calculated by equation 1.

\[
d_{\text{TEM}} = \frac{\sum n_i a_i^3}{\sum n_i a_i^2}
\]

(Equation 1)

A Shimadzu GC-2010 plus was used for the chromatographic measurements. Cyclohexanone was used as the external standard. Plasma treatment was operated by Harrick Plasma PDC-001. Electrochemical experiments were performed by using a BioLogic SP-150 potentiostat. Specific surface areas and pore size distributions of the catalysts were derived, according to Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models, from N₂ physisorption isotherms measured at 77 K on Micromeritics ASAP 2020. The samples were outgassed before measurements at 523 K for 2 h.
Preparation of modified carbon felts

**Scheme S1.** Schematic description of modified carbon felts (surface area vs. functionality).

**Preparation of O$_2$ Plasma treated carbon felt:** The parent carbon felts (2 x 3 x 0.6 cm) were placed into the radio frequency plasma chamber and evacuated until it reached 6.7 Pa or lower. O$_2$ gas was then introduced into the chamber with 20 ml·min$^{-1}$ of flow rate until it reached 133 Pa and evacuated again to 6.7 Pa or lower. Flowing O$_2$ gas (5-10 ml·min$^{-1}$) was used to keep the pressure of 73 Pa for 15 min and turned on the RF power as high (30 W) to generate plasma for 10 min.

**Preparation of HNO$_3$ treated carbon felt:** The pristine carbon felts were soaked into 16 M of nitric acid solution and boiled it for 3-36 h. The resulting nitric acid treated carbon felts were washed with copious DI water and dried in a vacuum oven.

**Carbonization of polyaniline (PANI) or sucrose in carbon felts with and without SiO$_2$:** The solutions of carbon source (PANI or sucrose) were prepared by stirring 0.625 g of PANI (or sucrose) with 5 mL of Millipore water and 5 mL of Ludox® HS-40 at room temperature overnight. A desired amount of 50 wt.% carbon source solution were drop casted on O$_2$ Plasma treated CF and evaporated the solution in 80 °C oven for overnight.

The polymer (PANI or sucrose) deposited CFs were then pyrolyzed at 800 °C in a temperature controlled tube furnace under flowing N$_2$ (100 ml·min$^{-1}$). The temperature was increased with the ramp of 1 °C·min$^{-1}$ up to 300 °C and maintained for 3 h. Then, the temperature was increased to 800 °C with the ramp of 10 °C·min$^{-1}$, kept for 2 h and cooled to room temperature. Etching of the silica was performed by soaking carbonized CFs in 1 M of NaOH in an autoclave at 100 °C for 24 h. Finally the obtained CFs were filtered and washed with DI water. The final products were denoted as PANI CF and Sucrose CF. For the modification of felts with PANI and Sucrose without SiO$_2$, the solutions of the carbon source (0.625 g of carbon source in 10 mL of water) were used undergoing the same steps as described above but without Ludox®.

**Synthesis of Pd/modified carbon felts:** 0.5 wt% Pd/CF catalyst were prepared by wet impregnation method. The required amount of palladium nitrate was first dissolved in 2 mL of
Millipore water. The solution was then drop-casted on the functionalized CFs and dried at 80 °C overnight. Pd (II)/functionalized CFs were then heated at 180 °C for 3 h under N₂ to decompose palladium nitrate followed by reduction at 250 °C under 5 % of H₂/N₂ for 3 h to obtain Pd(0). The temperature ramp rate of 2 °C·min⁻¹ was used in the stepwise procedure. The gas flow rate was 100 mL·min⁻¹ during thermal treatment.

Preparation of carbon felt electrode: Pd/modified carbon felts (2 x 3 x 0.6 cm) were connected to graphite rod by using epoxy glue.

S1.4. Boehm titration\[S1]\n0.25 g of carbon felt were first grinded and then dispersed in 25 mL of 0.025 M of NaOH. The NaOH solution was standardized with equimolar solutions of potassium hydrogen phthalate. The mixture of grinded carbon and NaOH were shaken at 140 rpm for 24 h and filtered. The aliquot (10 mL) of filtered NaOH solution were then titrated with 0.025 M of HCl solution (the HCl solution was standardized with standard NaOH solution). Total acidities (n_{CSF}) were determined by equation 2.

\[
n_{CSF} = [B]V_B - [HCl]V_{HCl}V_B/V_a \quad \text{(Equation 2)}
\]

Where [B] and V_B were concentration and volume of the reaction base mixed with carbon; [HCl] and V_{HCl} were concentration and volume of acid titrated; V_a the volume of the aliquot taken from the V_B.

S1.5. Electro catalytic hydrogenation (ECH) and open circuit voltage (OCV)
The two-compartment batch electrolysis cell described in Ref. \[S2\] was used to perform electrocatalytic hydrogenation (ECH) experiments. In general, cathodic and anodic compartments were separated by a Nafion 117 proton exchange membrane (Ion Power, Inc.). Pd/CFs were used as working electrodes in the cathode compartment. The size of Pd-modified CFs used as cathodes was 2 cm x 1.5 cm and 0.5 cm thickness. A platinum mesh (Alfa Aesar, 99.9 %) was used as counter electrode in the anodic compartment. An Ag/AgCl electrode (saturated KCl) (Ametek) with a double junction protection was used as reference electrode. Polarization of the catalyst was performed at -40 mA for 30 min to ensure the complete reduction of metal. 20 mM of benzaldehyde in sodium acetate-acetic acid buffer (60 mL) was added into the cathode compartment wherein the anode compartment contained acetate buffer (pH 5.2) as the electrolyte. ECH experiments were performed at constant potential while a flow of N₂ was kept through the reactant solution. All reactions were performed at atmospheric pressure and constant potential (-0.1 V vs RHE). All procedures were performed with an electrochemical workstation Bio Logic SP-150. By using potentiostatic electrochemical impedance spectroscopy (PEIS) the solution resistance was determined and then compensated 85% during the experiment. The remaining 15% of the resistance was corrected manually afterwards. Electrochemical experiments at varying pH (pH 2.5 and pH 10.5) were performed in solutions containing phosphoric acid (0.062 M of phosphoric acid with 0.14 M of disodium phosphate) and ii) sodium carbonate-sodium bicarbonate (0.08 M and 0.02 M). The ionic strengths were calculated and adjusted at 0.34 by adding NaCl. In ECH experiments, all experiments were operated as described in above.
Catalytic hydrogenation under open circuit voltage (OCV) was performed with grinded Pd/modified CFs and operated under 20 mM of benzaldehyde with 1 bar of H₂ gas instead of applied potential.

**Product analysis and turnover frequency (TOF)**

The reactions were followed by periodically withdrawing aliquots of 1 mL from the cathode compartment of the electrochemical cell (ECH reaction) or from the batch reactor (OCV reaction). The organic phase was separated from the aqueous phase by extraction with 3 mL of dichloromethane with cyclohexanone as an external standard. The GC was equipped with a plot Q capillary column (30 m x 250 μm) and a flame ionization detector.

Initial rates and turnover frequencies were calculated using equations 3 and 4.

\[
\text{Rate (mol·g}_{\text{Pd}}^{-1}·\text{s}^{-1}) = \frac{\text{moles of product}}{\text{total gram of Pd x time}} \\
\text{TOF (h}^{-1})= \frac{\text{moles of product}}{\text{moles of Pd x time x metal dispersion}}
\]

(Equation 3)

(Equation 4)

Where moles of Pd were obtained from ICP and metal dispersion was calculated by TEM.

Faradaic efficiency (FE) was calculated by equation 5.

\[
\text{FE (%)} = \frac{\text{Electron consumed by hydrogenation of organics}}{\text{Total electrons passed}} \times 100
\]

(Equation 5)

**S1.6. Chemical titration**

Chemical titration for Pd/modified CFs were carried out under OCV reaction (20 mM of benzaldehyde in 120 mL of acetate buffer). Four different molar ratio of 1-butanethiol to Pd (0, 0.03, 0.05, and 1) were added to the solution and OCV rates were measured in each concentrations. Prior to each additions of 1-butanethiols, 15 min of stirring were operated without H₂ gas and product analysis were operated by GC as described above.
**Figure S1.** N₂ adsorption/desorption profiles for Parent CF and modified CFs.

**Table S1.** Physical structure of modified CF.

|                | BET Surface area (m²·g⁻¹) | Total pore vol.ᵃ (cm³·g⁻¹) | Micropore vol.ᵇ (cm³·g⁻¹) | Mesopore vol. (cm³·g⁻¹) |
|----------------|-----------------------------|-----------------------------|-----------------------------|--------------------------|
| Parent CF      | 1                           | 0.000                       | N/A                         | 0.000                    |
| PANI CF (low)  | 28                          | 0.009                       | 0.009                       | 0.001                    |
| PANI CF        | 110                         | 0.125                       | 0.015                       | 0.110                    |
| Sucrose CF (low)| 35                          | 0.012                       | N/A                         | N/A                      |
| Sucrose CF     | 35                          | 0.104                       | 0.001                       | 0.103                    |
| HNO₃ CF        | 35                          | 0.010                       | 0.007                       | 0.003                    |
| O₂ Plasma CF   | 3                           | 0.001                       | N/A                         | N/A                      |

ᵃ Obtained from the BJH adsorption branch of the isotherm; ᵇ Calculated from t-plot.
Figure S2. High resolution X-ray photoemission spectroscopy (XPS) spectra of C\textsubscript{1}s region: (a) Parent CF, (b) PANI CF (c) Sucrose CF, (d) HNO\textsubscript{3} CF, (e) O\textsubscript{2}Plasma CF, (f) relative percentage of oxygen functional groups.
**Figure S3.** Deconvoluted N1s XPS spectra of PANI CF. Four different nitrogen species (Pyridinic N⁺-O⁻, pyrrolic, quarternary and pyridinic N) are determined.

**Table S2.** Acid properties of selected Pd/Modified CF materials.

|                | Total acidity after Pd supported[^a] [µmol·g⁻¹] | Relative area (%) of C1s XPS |
|----------------|-----------------------------------------------|-----------------------------|
|                |                                               | R=COOH | R=OH | >C=O |
| Pd/PANI CF[^b] | 52                                            | 5.2[^i] | 19.9[^i] | 9.4[^i] |
| Pd/Sucrose CF[^b] | 120                                           | 2.5 | 11.4 | 5.2 |
| Pd/HNO₃ CF     | 260                                           | 2.4 | 12.2 | 5.4 |
| Pd/O₂ Plasma CF| 240                                           | 3.3 | 13.2 | 6.5 |

[^a] Total acidity (carboxylic, phenolic, lactonic) from Boehm titration; [^b] Carbonization with hard template (®Ludox HS-40);[^c] Atomic percentage are overlapping with carbon-nitrogen and carbon-oxygen bond e.g., C-NH/C-OH, C=N/C=O.
Table S3. Chemical properties of Pd/Modified CFs.

|                         | Pd<sup>a</sup> [wt.%] | Particle size<sup>b</sup> [nm] | Dispersion<sup>b</sup> [%] | TOF<sup>c</sup> (rates) [h<sup>-1</sup> (µmol·g<sub>Pd</sub>·s<sup>-1</sup>)] |
|-------------------------|------------------------|-------------------------------|-----------------------------|---------------------------------------------------------------------------------|
| Pd/PANI CF (low)        | 0.3                    | 5.8                           | 18                          | 337 (187)                                                                         |
| Pd/PANI CF<sup>d</sup>  | 0.4                    | 4.7                           | 21                          | 360 (200)                                                                         |
| Pd/Sucrose CF (low)     | 0.3                    | 6.0                           | 17                          | 675 (332)                                                                         |
| Pd/Sucrose CF<sup>d</sup>| 0.5                    | 5.0                           | 20                          | 797 (411)                                                                         |
| Pd/HNO<sub>3</sub> CF   | 0.4                    | 4.7                           | 21                          | 1004 (558)                                                                        |
| Pd/O<sub>2</sub> Plasma CF | 0.4               | 5.2                           | 19                          | 2762 (1441)                                                                       |

<sup>a</sup>Obtained from inductively coupled plasma optical emission spectrometry (ICP-OES); <sup>b</sup>Average particle sizes and dispersion are determined by TEM; <sup>c</sup>Turnover frequency (TOF) and rates are calculated based on initial conversion; <sup>d</sup>Carbonization with hard template (®Ludox HS-40, surface area of 110 m<sup>2</sup>·g<sup>-1</sup>).
Figure S4. XPS spectra of C1s region of Pd/modified CFs: (a) Pd/PANI CF, (b) Pd/Sucrose CF, (c) Pd/HNO₃ CF and (d) Pd/O₂ Plasma CF.
Figure S5. X-ray photoelectron spectroscopy of Pd 3d region: (a) Pd/PANI CF, (b) Pd/Sucrose CF, (c) Pd/HNO$_3$ CF, and (d) Pd/O$_2$ Plasma CF.
Figure S6. TEM images and their size distributions of (a) Pd/PANI CF, (b) Pd/PANI CF (low), (c) Pd/Sucrose CF, (d) Pd/Sucrose CF (low), (e) Pd/HNO$_3$CF, (f) Pd/O$_2$ Plasma CF.
Figure S7. Rates of benzaldehyde hydrogenation with different ratio of 1-butanol and Pd (0, 0.03, 0.05, and 0.1). (a) Pd/PANI CF, (b) Pd/PANI CF (low), (c) Pd/Sucrose CF, (d) Pd/Sucrose CF (low), (e) Pd/HNO₃ CF, (f) Pd/O₂ Plasma CF. Rates were calculated based on amount of Pd. In this titration, we assumed a stoichiometric 1:1 molar ratio of Pd to 1-butanol.
Figure S8. Concentration profiles of reactant (benzaldehyde) and product (benzyl alcohol) during the electrocatalytic hydrogenation reaction: (a) Pd/PANI CF, (b) Pd/Sucrose CF, (c) Pd/HNO$_3$ CF, (d) Pd/O$_2$ Plasma CF. The reactions were performed at ambient conditions, pH 5.2 (acetate buffer), and -0.1 V vs RHE.
Figure S9. Recyclability test for Pd/HNO$_3$ CF and their initial TOFs for each cycle (inserted graph). The reactions were performed at ambient conditions, pH 5.2 (acetate buffer), and -0.1 V vs RHE.

Figure S10. ECH rates of benzaldehyde profile along with surface area for different catalysts. Surface areas of the catalysts were measured by N$_2$ physisorption. The reactions were performed at ambient conditions, pH 5.2 (acetate buffer), and -0.1 V vs RHE.
Figure S11. Faradaic efficiency (a) and current densities observed during the electrocatalytic hydrogenation of benzaldehyde on Pd/modified CFs. The reactions were performed at ambient conditions, pH 5.2 (acetate buffer), and -0.1 V vs RHE.
**Figure S12.** Pd 3d of XPS for different Pd/modified.

**Figure S13.** Rates of ECH of benzaldehyde correlated with the concentrations of acid sites of the modified carbon felts (blue squares) and with the concentration of acid sites in the corresponding Pd catalysts (red squares). Electrochemical tests were performed with solutions containing 20 mM benzaldehyde in acetate buffer (pH 5.2) at -0.1 V vs RHE. OCV experiments were performed with 1 bar H$_2$ instead of an external potential.
Figure S14. Turnover frequency (TOF) vs. density of acid sites (a) (obtained by dividing each concentration of acid sites per gram by the corresponding BET surface area); and rates per gram of catalyst along concentration of acid sites (b). TOFs were calculated from initial rates. The reactions were performed at ambient conditions, pH 5.2 (acetate buffer), and -0.1 V vs RHE.

Figure S15. Tafel plots for HER on Pd/HNO$_3$ CF and Pd/O$_2$ Plasma CF in absence of benzaldehyde. The reactions were performed at ambient conditions, pH 5 (acetate buffer), and Tafel slope were calculated from liner sweep voltammetry (scan rates 5 mV/s).
Figure S16. Absolute current densities measured for benzaldehyde hydrogenation and H₂ evolution (“Benzaldehyde hydrogenation” and “HER in the presence of benzaldehyde”, respectively) during ECH (electrocatalytic hydrogenation) experiments and for H₂ evolution in the absence of benzaldehyde (“HER in the absence of benzaldehyde”). The reactions were performed at ambient conditions, pH 5 (acetate buffer), and -0.1 V vs RHE.
Figure S17. TOF of electrocatalytic hydrogenation of benzaldehyde observed on two different catalysts (Pd/HNO$_3$CF-12 h and Pd/HNO$_3$CF-6 h with acid site concentrations of 0.2 µmol·g$^{-1}$, and 0.09 µmol·g$^{-1}$, respectively) at varying pH values (phosphate buffer pH 2.5, acetate buffer pH 5.2, and bicarbonate buffer pH 10.5 were used) and -0.1 V vs RHE.

Section S2. H$_2$ adsorption experiment (H$_2$/D$_2$ exchange)

The isotopic H$_2$/D$_2$ exchange experiments were carried out by reacting gaseous H$_2$ with liquid D$_2$O on Pd/C at 298 K in a 120 mL Hastelloy PARR autoclave. In a typical reaction, 30 mL D$_2$O, 2 bar H$_2$ and 2.5 mg Pd/C were loaded in the reactor. For the reaction in presence of benzaldehyde, 90 µL benzaldehyde was also loaded into the autoclave. Before the reaction, air was removed from the reactor by purging with 20 bar H$_2$ for three times. During the reaction, the gas phase products (HD and D$_2$) were sampled and analyzed by mass spectrometer (MS, Omni Star GSD 320). For the reaction in presence of benzaldehyde, products (benzyl alcohol) in aqueous phase were quantified using a gas chromatograph (GC) equipped with a wax capillary column (30 m × 250 µm) and a flame ionization detector (FID).

Table S4. Elementary steps and equations in the reaction of H$_2$ with D$_2$O without benzaldehyde.[S3]

| Description | Reaction steps | Rate constant | Rate equation | Eq. No. |
|-------------|----------------|---------------|---------------|---------|
| H$_2$ adsorption | $H_2 + 2* \xrightarrow{k_a} 2H* $ | $k_a$ | $r_{ads} = k_ap_\text{H}_2(\theta)^2$ | (6) |
| D * formation | $D_2O + H* \xrightarrow{k_o} HD O +D* $ | $k_o$ | $r_{exc} = k_o(\theta)^2D_2O$ | (7) |
| H$_2$ desorption | $2H* \xrightarrow{k_a} H_2 + 2* $ | $k_a$ | $r_{des} = k_a(\theta)^2$ | (8) |

```
The reaction of gas H$_2$ with liquid D$_2$O generally involves the following elementary steps: dissociative adsorption of H$_2$ (Eq. 6), surface D formation (Eq. 7) and desorption of D$_2$, HD and H$_2$ (Eqs. 8-10) as shown in Table S4. According to the rate equations 8-10, $r_{H_2}$ can be expressed as a function of $r_{HD}$ and $r_{D_2}$:

$$r_{H_2} = \frac{[KIE]_{HD}^2 r_{HD}^{2}}{4 [KIE]_{D_2} r_{D_2}} \quad (Equation \ 11)$$

Considering a steady state reaction, in which the adsorption rate of H$_2$ equals to the desorption rate of H$_2$, HD and D$_2$ (without benzaldehyde),

$$r_{ads} = r_{H_2} + r_{HD} + r_{D_2} \quad (Equation \ 12)$$

The desorption rate of HD and D$_2$ can be obtained through analyzing gas products of H$_2$ reacting with D$_2$O, and the desorption rate of H$_2$ can be calculated based on Eq. 11.

In presence of benzaldehyde, the adsorption rate of H$_2$ should involve the H consumed by benzaldehyde hydrogenation, thus the equation should be expressed by follows,

$$r_{ads} = r_{H_2} + r_{HD} + r_{D_2} + r_{BA} \quad (Equation \ 13)$$

in which $r_{BA}$ denotes as the formation rate of benzyl alcohol.

The kinetic isotope effect [KIE]$_{HD}$ and [KIE]$_{D_2}$ are defined as their rate constant ratios,

$$[KIE]_{HD} = \frac{k_{H_2}}{k_{HD}}; \ [KIE]_{D_2} = \frac{k_{H_2}}{k_{D_2}}$$

The expression for the determination of kinetic isotope effects proposed by Bigeleisen and Goeppert-Mayer is shown in the following equation [S3],

$$EIE = \frac{k_{H_2}}{k_{D_2}} = S \ast M \ast I \ast EXC \ast ZPE \quad (Equation \ 14)$$

in which, $S$ factor (the ratio of the symmetry numbers for the various species) does not lead to isotopic fractionation, and $EXC$ factor (from the contributions of vibrationally excited molecules) is ignorable at room temperature. $M$ factor (molecular mass ratio, translational degrees of freedom related), $I$ factor (the moment of inertia ratio, rotational degrees of freedom related) and $ZPE$ (zero point energy) need to be figured out to calculate $KIE$. Thus, the $KIE$ in above equation is converted as follows,

| Reaction | Rate Expression | Rate Constant | Equation |
|----------|----------------|---------------|----------|
| HD desorption | $H + D \xrightarrow{k_{HD}} HD + 2$ | $k_{HD} = k_a / [KIE]_{HD}$ | (9) |
| D$_2$ desorption | $2D \xrightarrow{k_{D_2}} D_2 + 2$ | $k_{D_2} = k_a / [KIE]_{D_2}$ | (10) |
\[
[KIE]_{D_2} = \frac{k_{H_2}^{KIE}}{k_{D_2}^{KIE}} = \left(\frac{M_{H_2}^{\dagger}}{M_{D_2}^{\dagger}}\right)^{\frac{3}{2}} \left(\frac{(I_{H_2}^{\dagger})^2}{(I_{D_2}^{\dagger})^2}\right)^{\frac{1}{2}} \exp \left(-\frac{(ZPE_{H_2} - 2ZPE_{PdH}) - (ZPE_{D_2} - 2ZPE_{PdD})}{RT}\right)
\]

(Equation 15)

\[
[KIE]_{D_2} = \frac{k_{D_2}^{KIE}}{k_{D_2}^{KIE}} = \left(\frac{M_{H_2}^{\dagger}}{M_{D_2}^{\dagger}}\right)^{\frac{3}{2}} \left(\frac{(I_{H_2}^{\dagger})^2}{(I_{D_2}^{\dagger})^2}\right)^{\frac{1}{2}} \exp \left(-\frac{(ZPE_{H_2} - 2ZPE_{PdH}) - (ZPE_{D_2} - 2ZPE_{PdD})}{RT}\right)
\]

(Equation 16)

We assumed that the changes in mass and moments of inertia between Pd-H and Pd-D are negligible and calculated the M and I factor from the appropriate mass and moment of inertia ratios of H\(_2\), HD and D\(_2\) alone. The zero point energy \((ZPE, ZPE = 0.5\hbar\nu)\) for Pd-H, H\(_2\) and D\(_2\) can be checked from references [S5,6]. The ZPE\(_{PdH}\) can be calculated based on the vibrational frequency, which was estimated from that of Pd\(\cdots\)H bond, based on \(\nu_{\text{Pd-H}} = \sqrt{\frac{\mu_{\text{Pd-H}}}{\mu_{\text{Pd-D}}}}\) (\(\mu\) is the reduced mass).

The values of corresponding \(M\), \(I\) and \(ZPE\) factors involved in the calculation of kinetic isotope effects are listed in Table S5 and the calculated \([KIE]_{D_2}\) and \([KIE]_{D_2}\) at 298 K is 0.67 and 0.38, respectively.

**Table S5.** \(M\), \(I\) and \(ZPE\) values of H and D-containing species involved in the calculation for the KIE.

| Species | \(M\) (g·mol\(^{-1}\)) | \(I\) (×10\(^{-14}\) g·cm\(^{-2}\)) | \(ZPE\) (kJ·mol\(^{-1}\)) |
|---------|----------------|----------------|------------------|
| Pd-H    |                |                | 16.32            |
| Pd-D    |                |                | 11.59            |
| H\(_2\) | 2              | 4.67           | 26.1             |
| HD      | 3              | 6.21           | 22.6             |
| D\(_2\) | 4              | 9.31           | 18.5             |
Figure S18. H\textsubscript{2} adsorption rates (left) in absence of benzaldehyde and (right) in presence of benzaldehyde. \( R_{\text{ads}} \) is the rate of H\textsubscript{2} adsorption on Pd; \( R(\text{HD}) \), \( R(D_2) \) and \( R(H_2) \) are the desorption rate of HD, D\textsubscript{2} and H\textsubscript{2} from Pd; \( R(\text{BZH}) \) is the hydrogenation rate of benzaldehyde.

Section S3. Density-functional-theory (DFT)-based ab initio molecular dynamics (AIMD) simulations

We performed density-functional-theory (DFT)-based ab initio molecular dynamics (AIMD) simulations within the generalized gradient approximation with the exchange correlation functional of Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{57} as implemented in the CP2K package.\textsuperscript{58} For dispersion corrections to describe energies more precisely, Grimme’s third-generation corrections were used.\textsuperscript{59} For core electrons the norm-conserving pseudopotentials were used,\textsuperscript{60} while the valence wave functions were expanded in terms of double-\( \zeta \)-quality Gaussian basis sets optimized for condensed systems to minimize linear dependences and superposition errors.\textsuperscript{61} Electrostatic terms were calculated using an additional auxiliary plane-wave basis set with a 400 Ry cutoff.\textsuperscript{62} The \( \Gamma \)-point approximation was employed for the Brillouin zone integration.

To investigate benzaldehyde hydrogenation on Pd nanoparticle (NP) supported on functionalized graphene, we generated model systems consisting of functionalized graphene with hydroxyl or carboxyl group, benzaldehyde, Pd\textsubscript{50} NP, in the presence of water as shown in Figure S1. Starting from a structure with functional group in the proximity of the Pd NP, we obtained the lowest energy structure for each system having different functional groups, we performed NVT canonical ensemble simulations at 100 °C followed by annealing process. We also optimized structures where the proton of the functional group is solvated into the water to investigate possible acid-base catalysis in the system.
**Figure S19.** A model system with carboxyl functional group on graphene in the presence of water. Color code: cyan for C, red for O, white for H, olive for Pd.

**References**

[S1] H. P. Boehm Carbon 1994, 32, 759.

[S2] Y. Song, U. Sanyal, D. Pangotra, J. D. Holladay, D. M. Camaioni, O. Y. Gutiérrez, J. A. Lercher J. Catal. 2018, 359, 68.

[S3] G. Yang, S. A. Akhade, X. Chen, Y. Liu, M.-S. Lee, V.-A. Glezakou, R. Rousseau, J. A. Lercher Angew. Chem. Int. Ed. 2019, 58, 3527.

[S4] E. Buncel, C. C. Lee, in Isotopes in organic chemistry, Vol. 5, Elsevier, Amsterdam, 1977

[S5] J. Greeley, M. Mavrikakis, J. Phys. Chem. B 2005, 109, 3460.

[S6] K. K. Irkura, J. Phys. Chem. Ref. Data 2007, 36, 389.

[S7] Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. Phy. Rev. Lett. 1996, 77, 3865.

[S8] VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J., Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. Comput. Phys. Commun. 2005, 167, 103.

[S9] Grimme, S., Semiempirical GGA- type density functional constructed with a long- range dispersion correction. J. Comput. Chem. 2006, 27, 1787.
[S10] Goedecker, S.; Teter, M.; Hutter, J., Separable dual-space Gaussian pseudopotentials. Phys. Rev. B 1996, 54, 1703.

[S11] VandeVondele, J.; Hutter, J., Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. J. Chem. Phys. 2007, 127, 114105.

[S12] Lippert, B. G.; Parrinello, J. H.; Michele, A hybrid Gaussian and plane wave density functional scheme. Mol. Phys. 1997, 92, 477.