Supporting Information

Oxygen-Doped Carbon Supports Modulate the Hydrogenation Activity of Palladium Nanoparticles Through Electronic Metal-Support Interactions

Radhika G. Rao,^{1,2} Raoul Blume,³ Mark Greiner,³ Pei Liu,⁴ Thomas W. Hansen,⁴ Kathleen S. Dreyer,⁵ David D. Hibbitts,⁵ and Jean-Philippe Tessonnier^{1,2,*}

¹ Department of Chemical and Biological Engineering, Iowa State University,

Ames, Iowa 50011, United States

² Center for Biorenewable Chemicals (CBiRC), Ames, Iowa 50011, United States

³ Max Planck Institute for Chemical Energy Conversion, Heterogeneous Reactions Group,

45470 Mülheim an der Ruhr, Germany

⁴ National Centre for Nano Fabrication and Characterization, DTU Nanolab, Technical University of Denmark, Lyngby 2800, Denmark

⁵ Department of Chemical Engineering, University of Florida, Gainesville,

Florida 32611, United States

* Corresponding author. Email: tesso@iastate.edu

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Tables S1-S5

Table S1. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) results for the Pd/CNT catalysts synthesized in the present study. The annealing temperature corresponds to the temperature applied after (post-synthetically) metal deposition and reduction in hydrogen.

Pd/CNT catalyst annealing temperature (°C)	Pd metal loading (wt.%) ^[a]
Pristine	3.1 ± 0.1
400	3.0 ± 0.3
550	2.9 ± 0.1
700	2.9 ± 0.1
850	2.9 ± 0.1

[a] All samples were analysed in triplicates to obtain the standard deviation.

Table S2. Average palladium particle sizes as obtained from ac-STEM-HAADF, XRD and hydrogen chemisorption. The corresponding Pd surface area calculated from the 1st isotherm is also provided. The theoretical atomic cross section area for Pd used for the calculation was 0.0787 nm².

Pd/CNT catalyst	Doutiolo sizo fuom	Dantiala siza fuerra	Hydrogen chemisorption		
annealing temperature (°C)	ac-STEM (nm)	XRD (nm)	Particle size (nm)	Surface area (m ² /g)	
Pristine	4.14 ± 1.56	5.1 ± 0.3	4.57	5.1 ± 0.3	
400	5.70 ± 2.50	5.5 ± 0.3	5.49	5.5 ± 0.3	
550	6.60 ± 3.77	5.5 ± 0.3	7.89	5.5 ± 0.3	
700	10.11 ± 7.49	11.3 ± 0.5	10.48	11.3 ± 0.5	
850	/	10.6 ± 0.3	23.86	10.6 ± 0.3	

Support annealing temperature (°C)	Support O/C ratio	Support work function (eV)	Catalyst work function (eV)
Pristine	0.12	4.80	5.10
200	0.11	4.76	5.00
400	0.08	4.48	4.80
600	0.03	/	4.73

Table S3. Work functions measured by ultraviolet photoelectron spectroscopy (UPS) for the synthesized CNT supports and corresponding Pd/CNT catalysts. The ratios of surface oxygen to carbon were obtained from X-ray photoelectron spectroscopy analysis of the supports.

Table S4. Work functions and surface concentrations (carbon, oxygen, palladium) measured by ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) for the catalyst precursor $Pd(NO_3)_2/CNT$ annealed at various temperatures. The oxygen concentration and corresponding O/C and O/Pd are estimations as O1s and Pd $3p_{3/2}$ spectra overlap and cannot be reliably deconvoluted.

Temperature (°C)	Work function (eV)	O/C ratio	O/Pd ratio	C (at.%)	O (at.%)	Pd (at.%)	
25	5.10	0.21	2.7	65	14	5	
100	5.00	0.18	2.2	65	12	5	
125	4.90	0.19	2.4	66	12	5	
150	4.88	0.17	2.2	67	12	5	
200	5.00	0.12	1.6	70	8	5	
225	4.97	0.12	1.7	72	8	5	
250	4.91	0.10	1.5	73	7	5	
300	4.87	0.09	1.6	76	7	4	

Table S5. Metal loading determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES), average particle size from hydrogen chemisorption, and $Pd^{0}/Pd^{\delta+}$ ratio determined by XPS for pre-synthetically annealed Pd/CNTs catalysts. The annealing temperature corresponds to the temperature applied before metal deposition and reduction in hydrogen.

Support annealing temperature (°C)	Pd metal loading (wt.%) ^[a]	Particle size from chemisorption (nm)	$Pd^{0}/Pd^{\delta+}$ ratio
Pristine	3.1 ± 0.1	4.57	2.2
200	3.2 ± 0.3	4.94	2.0
400	3.3 ± 0.1	5.08	1.9
600	3.9 ± 0.2	4.98	1.6

[a] All samples were analysed in triplicates to obtain the standard deviation.

Figures S1-S12





Figure S1. Aberration-corrected scanning transmission electron micrographs acquired with a high-angle annular dark field detector of the Pd/CNT catalysts (a,b) pristine (no annealing) and post-synthetically annealed in nitrogen at (c,d) 400 °C, (e,f) 550 °C, and (g,h) 700 °C. The corresponding particle size distributions are presented in Fig. S2.



Figure S2. Particle size distributions calculated from ac-STEM-HAADF images of the Pd/CNT catalysts a) pristine (no annealing) and post-synthetically annealed in nitrogen at b) 400 °C, c) 550 °C, and d) 700 °C. The corresponding average particle sizes (μ) and standard deviations (σ) are provided as well.



Figure S3. X-ray diffractograms for the Pd/CNT catalysts post-synthetically annealed in nitrogen at 400, 550, 700, and 850 °C.







Figure S4. Aberration-corrected transmission electron micrographs of Pd/CNT catalysts a) pristine, and annealed post synthesis at b) 400 °C, c) 550 °C, d) 700 °C, and e) 850 °C. Micrographs reveal carbon overlayers on the Pd nanoparticles of the sample annealed at 850 °C.



Figure S5. *In situ* X-ray photoelectron spectra for Pd/CNT catalysts at room temperature, under vacuum and at increasing temperature under hydrogen, respectively. A) Original O 1s spectra (top) and the difference spectrum between RT in vacuum and at 30°C in H₂. B) Original Pd 3d spectra (top) and the difference spectrum between RT in vacuum and at 30°C in H₂.



Figure S6. Rates for CALD conversion normalized with Pd active metal surface area and the particle sizes obtained from hydrogen chemisorption for Pd/CNT catalysts annealed post-synthesis.



Figure S7. Representation of palladium nanoparticle of radius (R) with the Pd^{δ^+} phase affecting the metal atoms at the interface until a height (x).



Figure S8. CH* binding energy (kJ mol⁻¹) on a Pd (111) surface (c), as well as Pd₁₁₉ (**a** and **b**) and Pd₂₉₃ (**d** and **e**) clusters on pristine (**a** and **d**) and functionalized (**b** and **e**) graphene supports. Dots indicate three-fold hcp sites, other sites are three-fold fcc on the (111) surface or four-fold hollow on the (100) surface. Gray-green coloring indicates unexamined binding sites.



Figure S9. O* binding energy (kJ mol⁻¹) on a Pd (111) surface (c), as well as Pd₁₁₉ (**a** and **b**) and Pd₂₉₃ (**d** and **e**) clusters on pristine (**a** and **d**) and functionalized (**b** and **e**) graphene supports. Dots indicate three-fold hcp sites, other sites are three-fold fcc on the (111) surface or four-fold hollow on the (100) surface. Gray-green coloring indicates unexamined binding sites.



Figure S10. H* binding energy (kJ mol⁻¹) on a Pd (111) surface (c), as well as Pd₁₁₉ (**a** and **b**) and Pd₂₉₃ (**d** and **e**) clusters on pristine (**a** and **d**) and functionalized (**b** and **e**) graphene supports. Dots indicate three-fold hcp sites, other sites are three-fold fcc on the (111) surface or four-fold hollow on the (100) surface. Gray-green coloring indicates unexamined binding sites.



Figure S11. Models used for the four-layer, periodic Pd (111) surface (c), as well as Pd_{119} (**a** and **b**) and Pd_{293} (**d** and **e**) clusters on pristine (**a** and **d**) and functionalized (**b** and **e**) graphene supports.

Figure S12. Detailed view of the Pd_{119} cluster supported on graphene (a and b) and on a functionalized graphene support (c and d).

Internal and External Mass Transfer Analysis

The stacked cup carbon nanotube (CNT) catalyst support is represented by a cylindrical geometry as depicted in Figure A.

Figure A. Representation of the cylindrical carbon nanotube of length L and inner radius R.

Component A is hydrogen and B is cinnamaldehyde. The molar fluxes of the components A and B are represented by N_A and N_B respectively. The length of the CNT is represented by L and its inner radius is represented by R.

The following assumptions were made while conducting the internal mass transfer analysis: i) concentration of component A (C_A) and concentration of component B (C_B) are constant in the radial direction, ii) reaction only occurs on the catalyst surface, and iii) the system is under steady state.

Based on the kinetic trace of the reaction (Figure B), which depicts a straight-line plot for the change in cinnamaldehyde concentration with time, the reaction was assumed to be 0th order with respect to cinnamaldehyde. The reaction was considered to be 1st order with respect to hydrogen, based on the common assumption for this reaction as reported in the literature.¹

Figure B. Kinetic trace for palladium catalyst supported on CNTs conducted at 80 °C, stirring rate = 500 rpm, hydrogen flow rate = 20 ml min⁻¹, mass of catalyst = 100 mg, and mass of cinnamaldehyde = 5 g.

Mass balance analysis on component A is represented by equation S1:

$$(\pi R^2 N_A) \Big|_z - (\pi R^2 N_A) \Big|_{z+\Delta z} - k_a C_A 2\pi R \Delta z = 0$$
(S1)

Divide by $\pi R\Delta z$ and take limit of Δz tending to 0, to obtain equation S2:

$$-R\frac{dN_A}{dz} - 2k_a C_A = 0 \tag{S2}$$

Fick's law for molar flux of component A is defined in equation S3:

$$N_A = -D_A \frac{dC_A}{dz} \tag{S3}$$

where, D_A is the effective diffusion coefficient of the reactant A, which is hydrogen.

Substituting equation S3 in equation S2, we obtain equation S4:

$$RD_A \frac{d^2 C_A}{dz^2} - 2k_a C_A = 0 \tag{S4}$$

where, k_a is the reaction rate constant based on catalyst surface area.

In order to non-dimensionalize the equation, we define the following parameters:

$$y = \frac{C_A}{C_{AS}} \tag{S5}$$

where, C_{AS} is the concentration of the reactant A in the bulk of the solvent.

$$x = \frac{z}{L}$$
(S6)

Using the parameters defined in equation S5 and S6, equation S4 can be written as:

$$RD_A \frac{C_{AS}}{L^2} \frac{d^2 y}{dx^2} - 2k_a C_{AS} y = 0$$
 (S7)

Rearranging terms to obtain:

$$\frac{d^2y}{dx^2} - \frac{2k_a L^2}{RD_A}y = 0 \tag{S8}$$

We now define the Thiele modulus (φ^2), as follows:

$$\varphi^2 = \frac{2k_a L^2}{RD_A} \tag{S9}$$

Substituting equation S9 in equation S8, we obtain:

$$\frac{d^2y}{dx^2} - \varphi^2 y = 0 \tag{S10}$$

The solution to the differential equation described above is as follows:

$$y = c_2 \sinh(\varphi x) + c_1 \cosh(\varphi x)$$
(S11)

The boundary conditions for this system can be defined as follows:

At
$$x = 0$$
, $\frac{dy}{dx} = 0$ and at $x = \frac{1}{2}$, $y = 1$

Using these boundary conditions and the equation S11 can be written as follows:

$$y = \operatorname{sech}\left(\frac{\varphi}{2}\right) \cosh(\varphi x) \tag{S12}$$

Effectiveness factor (η) is defined as the ratio of the actual rate of the reaction to the rate of reaction with no diffusion limitations, as represented below:

$$\eta = \frac{D_A \pi R^2 \left(\frac{dC_A}{dz}\right) \Big|_{z=\frac{L}{2}}}{k_a C_{AS} 2\pi R \frac{L}{2}}$$
(S13)

Non-dimensionalizing equation S13 using the parameters defined in equation S5 and S6, and the Thiele modulus as defined in equation S9, we obtain:

$$\eta = \frac{2}{\varphi^2} \left(\frac{dy}{dx} \right) \Big|_{x = \frac{1}{2}}$$
(S14)

Differentiating equation S12 with respect to x, we obtain:

$$\left(\frac{dy}{dx}\right)\Big|_{x=\frac{1}{2}} = \operatorname{sech}\left(\frac{\varphi}{2}\right)\varphi\sinh\left(\frac{\varphi}{2}\right)$$
 (S15)

Substituting equation S15 in equation S14, we obtain the effectiveness factor to be as follows:

$$\eta = \frac{2}{\varphi} \tanh\left(\frac{\varphi}{2}\right) \tag{S16}$$

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To calculate the Thiele modulus using equation S9, the value of k_a was calculated by multiplying the k_v , the rate constant based on catalyst volume, which was obtained from the catalytic data, with the characteristic length, a, defined as follows:

$$a = \frac{Volume}{Surface area}$$
(S17)

For a tubular catalyst, volume of the inner pore is $\pi R^2 L$ and the inner surface area of the pore open on both ends is $2\pi RL$. This results in the characteristic length of R/2. The values for the inner radius of the tube and the length were obtained to be 17.5 nm and 10 µm, respectively, from the literature.² Therefore, the value of *a* was 8.75 nm.

 k_v was obtained to be 1.07 s⁻¹ from the kinetic data and multiplying the k_v with *a*, the value of k_a was obtained to be 9.3625 x 10⁻⁹ m s⁻¹.

The effective diffusion coefficient for hydrogen was taken to be 8.4 x 10^{-9} m² s⁻¹ based on the calculations reported by Toebes et al.³

Substituting these values in equation S9, the Thiele modulus (φ^2) was estimated to be 0.013. The effectiveness factor (η) was estimated to be 0.999 using equation 16 and the above obtained value of φ^2 . This combination of the Thiele modulus and effectiveness factor confirms that the reaction is not mass transfer limited in hydrogen under the conditions used in this study.

For studying the internal mass transfer limitations on component B, which is cinnamaldehyde, mass balance was conducted using equation S18:

$$(\pi R^2 N_B) \Big|_z - (\pi R^2 N_B) \Big|_{z+\Delta z} - k_a C_A 2\pi R \Delta z = 0$$
(S18)

Divide by $\pi R\Delta z$ and take limit of Δz tending to 0, to obtain equation S19:

$$-R\frac{dN_B}{dz} - 2k_a C_A = 0 \tag{S19}$$

Fick's law for molar flux of component B is defined in equation S20:

$$N_B = -D_B \frac{dC_B}{dz} \tag{S20}$$

where, D_B is the effective diffusion coefficient of the reactant B, which is cinnamaldehyde.

Substituting equation S20 in equation S19, we obtain equation S21:

$$RD_B \frac{d^2 C_B}{dz^2} - 2k_a C_A = 0 \tag{S21}$$

Using equation S5 and S12 and using the value of φ^2 of 0.013 as obtained earlier, C_A was obtained to be:

$$C_A = C_{AS} \cosh\left(\frac{0.114z}{L}\right) \tag{S22}$$

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Substituting equation S22 in S21, we obtain:

$$RD_B \frac{d^2 C_B}{dz^2} - 2k_a C_{AS} \cosh\left(\frac{0.114z}{L}\right) = 0$$
(S23)

In order to non-dimensionalize the equation, we define the following parameter:

$$\alpha = \frac{C_B}{C_{BS}} \tag{S24}$$

where, C_{BS} is the concentration of the reactant B in the bulk of the solvent.

Using the parameters defined in equations S6 and S24, equation S23 can be written as:

$$RD_B \frac{C_{BS}}{L^2} \frac{d^2 \alpha}{dx^2} - 2k_a C_{AS} \cosh(0.114x) = 0$$
 (S25)

Rearranging terms to obtain:

$$\frac{d^2\alpha}{dx^2} - \frac{2k_a L^2 C_{AS}}{R D_B C_{BS}} \cosh(0.114x) = 0$$
 (S26)

We now define the Thiele modulus (φ'^2), as follows:

$$\varphi'^2 = \frac{2k_a L^2 C_{AS}}{R D_B C_{BS}} \tag{S27}$$

Substituting equation S27 in equation S26, we obtain:

$$\frac{d^2\alpha}{dx^2} - {\varphi'}^2 \cosh(0.114x) = 0$$
 (S28)

The solution to the differential equation described above is as follows:

$$\alpha = \frac{{\varphi'}^2 \cosh(0.114x)}{(0.114)^2} + c_2 x + c_1$$
(S29)

The boundary conditions for this system can be defined as follows:

At
$$x = 0$$
, $\frac{d\alpha}{dx} = 0$ and at $x = \frac{1}{2}$, $\alpha = 1$

Using these boundary conditions and the equation S29 can be written as follows:

$$\alpha = 1 - 77.0718{\varphi'}^2 + \frac{{\varphi'}^2 \cosh(0.114x)}{(0.114)^2}$$
(S30)

To calculate the value of φ'^2 , C_{AS} was estimated using the following equation obtained from the literature (Equation S31):⁴

$$\ln x_1 = -5.7347 - \frac{8.6743}{\frac{T}{100 \text{ K}}}$$
(S31)

Where,

 x_1 = mole fraction of hydrogen in dioxane

T = temperature of the solubility test in K

Using equation (S31), the mole fraction of hydrogen in dioxane at 80 °C was estimated to be 2.77 x 10^{-4} .⁴ This mole fraction represents a concentration of 6.47 x 10^{-6} g ml⁻¹ of hydrogen in dioxane. The concentration of cinnamaldehyde at 0% conversion was known based on the amount of reactant added and confirmed using the GC-FID analysis to be 90 mg ml⁻¹. At 10% conversion, the concentration of cinnamaldehyde was 81 mg ml⁻¹. The effective diffusion coefficient for cinnmaldehyde was taken to be 2 x 10^{-9} m² s⁻¹ based on the calculations reported by Toebes et al.³ With the help of these values and equation S27, the Thiele modulus was estimated to be 3.846 x 10^{-6} and 4.273 x 10^{-6} at 0 and 10% conversion, respectively.

The effectiveness factor (η') is defined as the ratio of the actual rate of the reaction to the rate of reaction with no diffusion limitations, as represented below:

$$\eta' = \frac{D_B \pi R^2 \left(\frac{dC_B}{dz}\right) \big|_{z=\frac{L}{2}}}{k_a C_{AS} 2\pi R \frac{L}{2}}$$
(S32)

Non-dimensionalizing equation S32 using the parameters defined in equations S6 and S24, and the Thiele modulus as defined in equation S27, we obtain:

$$\eta' = \frac{2}{\varphi'^2} \left(\frac{d\alpha}{dx}\right) \Big|_{x=\frac{1}{2}}$$
(S33)

Differentiating equation S30 with respect to x, we obtain:

$$\left(\frac{d\alpha}{dx}\right)\Big|_{x=\frac{1}{2}} = \frac{{\varphi'}^2 \ 0.114 \ \sinh(0.057)}{(0.114)^2} \tag{S34}$$

Substituting equation S34 in equation S33, we obtain the effectiveness factor to be as follows:

$$\eta' = 2 \frac{\sinh(0.057)}{0.114} \tag{S35}$$

The effectiveness factor was obtained to be 1 for the values of φ'^2 of 3.846 x 10⁻⁶ and 4.273 x 10⁻⁶ at 0 and 10% conversion, respectively. This combination of the Thiele modulus and effectiveness factor confirms that the reaction is not mass transfer limited in cinnamaldehyde under the conditions used in this study.

The effects of external mass transfer in the batch reactor were estimated using the mass transfer Biot number (Bi_m) , which allows us to compare the pore diffusion and film diffusion effects. The Bi_m was estimated with the following equation:⁵

$$Bi_{m} = \frac{k_{m}a}{D_{A}}$$
(S36)

Where,

 $k_m = Mass transfer coefficient$

 $D_A = Effective diffusion coefficient of reactant$

The value of a was obtained from equation S17 but this time using the external surface area and volume of the SCCNTs. The value of the outer radius of the tube was obtained to be 40 nm resulting in the characteristic length of 20 nm.

As the value of a and D_A are already known, k_m is the only unknown in the equation for calculating the Bi_m. The value of k_m was estimated using the Sherwood number (Sh) based on the Churchill Bernstein equation, as described below:

Sh = 0.3 +
$$\frac{0.62 \text{Re}^{\frac{1}{2}} \text{Sc}^{\frac{1}{3}}}{\left[1 + \left(\frac{0.4}{\text{Sc}}\right)^{\frac{2}{3}}\right]^{\frac{1}{4}}} \left[1 + \left(\frac{\text{Re}}{282000}\right)^{\frac{5}{8}}\right]^{\frac{4}{5}} = \frac{k_{\text{m}}a}{D}$$
 (S37)

Where,

Re = Reynolds number

Sc = Schmidt number

D = Mass diffusivity

This equation is applicable to a large range of Reynolds (Re) and Schmidt (Sc) numbers (Re.Sc > 0.4), as reported in previous studies.⁶ The Re was estimated using the following equation:

$$Re = \frac{\rho v L_c}{\mu}$$
(S38)

Where,

 ρ = Density of dioxane

v = Linear velocity of the agitator tip = angular velocity of the agitator (ω) x radius of the agitator (r')

 $L_c = Agitator diameter$

 μ = Dynamic viscosity of dioxane

The value of ρ and μ for dioxane at 298.15 K was taken to be 1028 kg m⁻³ and 1.177 kg m⁻¹ s⁻¹, as reported in the literature.⁷ The stir bar used in the experiment was cylindrical in shape with a diameter of 0.75 cm and a length of 2.5 cm. Using these dimensions, the Lc was estimated to be 0.1875 x 10⁻² m and the v was obtained to be 0.049 rad m s⁻¹ for a stirring speed of 500 rpm. Substituting these values in equation S38, the Re was estimated to be 53.46.

Based on literature data, Sc for liquid-phase is expected to be in the range of 10^2 to 10^4 and the mass diffusivities are expected to be in the range of $10^{-9.7,8}$ With the help of these values and the estimates for D_A and D_B as obtained earlier from the literature, the Bi_m was calculated. The Bi_m > 1 and of $\varphi'^2 < 1$ for all values of Re > 53.46. This confirmed that the reaction was not externally mass transfer limited in hydrogen or cinnamaldehyde.

Distribution of the Pd^{δ^+} phase on the surface vs perimeter of Pd nanaoparticles

Experimental values

The perimeter and surface area for each particle were calculated using equation (S39) and (S40), respectively.

Perimeter of one particle =
$$2\pi R'$$
 (S39)

Surface area of one particle =
$$2\pi R'^2$$
 (S40)

where, R' is the radius of the particle as obtained from hydrogen chemisorption and particles were assumed to be hemispherical in shape.

In order to obtain the total perimeter and the total surface area of all the nanoparticles in the catalyst, the values calculated for each particle were multiplied by the total number of particles (n). The number of particles in each catalyst were estimated using equation (S41).

$$n = \frac{Total \ volume \ of \ Pd}{Volume \ of \ each \ particle}$$
(S41)

As the total volume of Pd metal on each catalyst is constant due to the uniform loading of Pd, the numerator of the equation (S41) can be assumed to be constant. Therefore, n will only be dependent on the denominator of equation (S41). This correlation has been better explained in equation (S42).

$$n \propto \frac{1}{\left(\frac{2\pi R'^3}{3}\right)} \tag{S42}$$

Therefore, the total perimeter of all the particles can be estimated by multiplying equation (S39) and (S42) to obtain equation (S43).

Total perimeter
$$\propto \frac{1}{(R'^2)}$$
 (S43)

Similarly, the total surface area of all the particles can be estimated by multiplying equation (S40) and (S42) to obtain equation (S44).

Total surface area
$$\propto \frac{1}{(R')}$$
 (S44)

The total perimeter and total surface area were normalized using the highest value for estimated for them in each catalyst series.

Model values

Theoretical models were designed to estimate the activity of the nanoparticles with different sizes. Using the ratio of Pd⁰ and Pd^{δ +} as obtained from X-ray photoelectron spectroscopy studies and a depth of penetration for XPS of 2 nm, the average height (x), as shown in Figure S7, at the metal-support interface, which will be affected by the Pd^{δ +} phase, was calculated using equations S45 and S46. The height x was found to be approximately 0.45 – 0.57 nm.

Volume of particle analyzed by XPS =
$$\frac{\left[2\pi R'^3 - 2\pi (R'-2)^3\right]}{3}$$
 (S45)

Volume of Pd⁰ phase analyzed by XPS =
$$\frac{[2\pi(R'-x)^3]}{3}$$
 (S46)

Subtracting equation S46 from S45, equation S47 was obtained.

Volume of
$$Pd^{\delta+}$$
 phase analyzed by $XPS = \frac{[2\pi R'^3 - 2\pi (R'-2)^3]}{3} - \frac{[2\pi (R'-x)^3]}{3}$ (S47)

Dividing equation S46 by S47 and using R' from chemisorption and $Pd^{0}/Pd^{\delta^{+}}$ ratio from XPS, the height x was calculated and found to be 0.45 - 0.57 nm.

Using this height x, where the Pd^{δ^+} phase will predominantly be present, the area at the surface of the particle that will be affected by this phase was calculated using equation (S48). Similarly, the surface area that will be affected by the Pd^0 phase was calculated using equation (S49).

Surface area affected by
$$Pd^{\delta+}phase = 2\pi R'^2 - 2\pi (R' - x)^2$$
 (S48)

Surface area affected by
$$Pd^{0}phase = 2\pi (R' - x)^{2}$$
 (S49)

Theoretical total activity

$$= (Surface area affected by Pd^{\delta+}phase$$

$$* Intrinsic rate for the Pd^{\delta+}phase)$$

$$+ (Surface area affected by Pd^{0}phase$$

$$* Intrinsic rate for the Pd^{0}phase) (S50)$$

In Model 1, it was assumed that the intrinsic reaction rate was the same on Pd^0 and $Pd^{\delta+}$ sites. Therefore, the surface areas obtained from equation (S44) and (S45) were multiplied by the same intrinsic reaction rate of 70 mg ml⁻¹ h⁻¹ to obtain the total theoretical activity.

In Model 2, it was assumed that the intrinsic reaction rate was the different for the Pd^0 and $Pd^{\delta+}$ sites. Therefore, the surface areas obtained from equation (S44) and (S45) were multiplied by intrinsic reaction rates of 218 and 1 mg ml⁻¹ h⁻¹, respectively, to obtain the total theoretical activity.

Supplementary References

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