SUPPORTING INFORMATION

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Supporting Methods

CO Pulse Chemisorption.

Micromeritics Autochem II 2920 Chemisorption Analyzer was used for the CO pulse chemisorption. A glass wool bed was prepared in a quartz U-tube, and 100 mg of Pd/TiO₂ was loaded. After that, the following sequence was applied: the catalyst was reduced under H₂ flow (10% in Ar) at a flow rate of 30 cm³/min for 60 min at 100 °C followed by He flow (flow rate: 50 cm³/min) for 30 min for removal of excess surface bonded H atoms. The temperature was then cooled to 40 °C under He flow and held for 30 min. The catalyst was then subjected to CO pulses (10% in He).

The percentage dispersion (%D) of Pd of the catalysts was calculated from chemisorption data based on the following equation:

$$D\% = \frac{S_f M V_{ad}}{m W V_m} \ 100 \tag{1}$$

where S_f = stoichiometry factor (Pd/CO molar ratio) = 1, M = atomic mass of Pd (106.42 g mol⁻¹), V_{ad} = volume of chemisorbed CO (mL) under standard temperature and pressure (STP) conditions, m = mass of the sample (g), W = weight fraction of Pd in the sample as determined by ICP-OES, and V_m = molar volume of CO (22,414 mL mol⁻¹) under STP conditions.

The cubic crystallite size of Pd was calculated based on the following equations:

Pd crystallite size (nm) =
$$\frac{6M}{m W d_{Pd} N_a SA_{Pd}}$$
 (2)

Pd surface area
$$(m^2 g^{-1} \text{ of Pd}) = \frac{S_f^* N_a^* S A_{cross}^* V_{ad}}{m^* W^* V_m}$$
 (3)

where M = atomic mass of Pd (106.42 g mol⁻¹), m = mass of the sample (g), W = weight fraction of Pd in the sample as determined by ICP-OES; d_{Pd} = density of palladium (1.202 × 10⁻²⁰ g nm⁻³), N_a= Avogadro's number (6.023 × 10²³ mol⁻¹); SA_{cross} = palladium cross-sectional area (7.87 × 10⁻²⁰ m²), SA_{Pd} = palladium surface area from the equation above (nm² g⁻¹ of Pd). The number 6 is derived from assuming a cubic geometry.

NMR Spectroscopy.

¹³C DEST, ¹³C RD, and ¹³C R_1 NMR data were collected at 25 °C on Bruker 400, 600, and 800 MHz spectrometers equipped with triple resonance z-gradient cryoprobes and using the pulse sequences shown in the literature (1). All experiments were acquired with 32 dummy scans and 128 scans with a recycle delay of 5 s between each scan. ¹³C DEST experiments were performed using two saturation field strengths, 500 and 1000 Hz, applied for 1 s, and using the pulse program described in the literature (1). A total of 32 different offsets between ±25 kHz were recorded, including saturation power controls where the field was set to 0 Hz. ¹³C CPMG experiments were performed using field strengths between 100 and 1000 Hz by varying the delay time between 180° pulses in the π -pulse train. Relaxation delays were in the range of 60 to 500 ms. ¹³C R_1 values were measured according to the pulse sequences from the literature (1). NMR spectra were processed and analyzed using Mnova NMR software (http://mestrelab.com/software/mnova/nmr/).

The experimental error was evaluated to be $\leq 5\%$ of the measured value for DEST and $\leq 10\%$ of the measured value for RD and R_1 experiments by running repeats of the above experiments.

Data Analysis and Fitting

The ¹³C RD, ¹³C R_1 , and ¹³C DEST data measured at two spectrometer fields (for the RD and R_1 experiments) and two saturation field strengths (for the DEST experiment) were fit globally using a two-site exchange model and mode-free analysis for motional dynamics of the bound state. Experimental data were compared with model-based simulated data using the following objective function.

$$\chi^{2} = (\chi^{2}_{C-RD} + \chi^{2}_{C-R1} + \chi^{2}_{C-DEST})/n_{df}$$
(6)

where χ^2_{C-RD} , χ^2_{C-R1} , and χ^2_{C-DEST} are the objective functions for the ¹³C RD, ¹³C R₁, and ¹³C DEST experiments, respectively, and n_{df} is the number of degrees of freedom. The χ^2 functions for each experiment are defined as following:

$$\chi_{C-RD}^{2} = \sum_{i} \sum_{j} \sum_{k} \left(R_{2}^{obs,i,j,k} - R_{2}^{calc,i,k,j} \right)^{2} / \sigma_{C-RD}^{i,j,k}$$
(7)

$$\chi_{C-R1}^{2} = \sum_{i} \sum_{j} \left(R_{1}^{obs,i,j} - R_{1}^{calc,i,k} \right)^{2} / \sigma_{C-R1}^{i,j}$$
(8)

$$\chi^{2}_{C-DEST} = \sum_{i} \sum_{l} \sum_{m} \left(I^{obs,i,l,m} - I^{calc,i,l,m} \right)^{2} / \sigma^{i,l,m}_{C-DEST}$$
(9)

where the summation indices *i*, *j*, *k*, *l*, and *m* refer to the peak index, spectrometer frequency, CPMG field, saturation field, and frequency offset, respectively, the *calc* and *obs* superscripts denote calculated and experimental data, respectively, *l* indicates the normalized peak intensity, and σ is the experimental error associated with each data point.

Simulation of ¹³C RD experiments

¹³C- R_2 rates for any specific value of *i*, *j*, and *k* were calculated as:

$$R_2^{calc,i,k,j} = \frac{\ln(M(t_1)/M(t_2))}{t_2 - t_1}$$
(10)

where t_2 is the constant relaxation delay during the RD experiment and t_1 is 0 seconds. M(t) is the transverse magnetization, which is given by:

$$M(t) = (AA^*A^*A)^n M(0)$$
(11)

$$M(0) = \begin{bmatrix} M^F \\ M^A \end{bmatrix}$$
(12)

M(0) is the initial magnetization for each site in the exchange model. For the two-site exchange model, M^{F} and M^{A} are the transverse magnetizations of free and adsorbed states, respectively. The parameter *n* is the number of CPMG cycles used, A^{*} is the complex conjugate of *A*, and *A* is given by:

$$A = e^{-R\tau_{CP}/2} \tag{13}$$

 τ_{CP} is the time delay between two π pulses during the CPMG pulse train. *R* is given by the summation:

$$R = iR^{CS} + R^{rel} + R^{ex} \tag{14}$$

$$R^{CS} = \begin{bmatrix} 0 & 0\\ 0 & -\Delta\omega^{FA} \end{bmatrix}$$
(15)

$$R^{rel} = \begin{bmatrix} R_2^F & 0\\ 0 & R_2^A \end{bmatrix}$$
(16)

$$R^{ex} = \begin{bmatrix} k_{FA}^{app} & -k_{AF} \\ -k_{FA}^{app} & k_{AF} \end{bmatrix}$$
(17)

for the two-site exchange model. Here, $\Delta \omega^{ij}$ is the difference in frequency between the states *i* and *j* (in rad s⁻¹), R_2^i is the intrinsic transverse relaxation rate of state *i*, and k_{ij} is the exchange rate between states *i* and *j*. The intrinsic relaxation rate of the free ligand (R_2^F) was measured experimentally and the rate for the bound state(R_2^A) was fit calculated based on motional models (see ¹³C R_1/R_2 Relaxation Modeling).

Simulation of ¹³C *R*¹ experiments

¹³C R_1 values from inversion recovery experiments are calculated in a very similar manner to the above procedure for R_2 :

$$R_1^{calc,i,j} = \frac{\ln(M(t_1)/M(t_2))}{t_2 - t_1}$$
(18)

Here t_2 is the relaxation delay and t_1 is 0 seconds. M(t) is the longitudinal magnetization which is given by:

$$M(t) = (AA^*A^*A)M(0)$$
(19)

$$M(0) = \begin{bmatrix} M^F \\ M^A \end{bmatrix}$$
(20)

M(0) is the initial magnetization for each site in the exchange model. Here, we use the example of a two-site exchange. A^* is the complex conjugate of A, and A is given by:

$$A = e^{-Rt} \tag{21}$$

t is the time delay during the relaxation evolution. R is given by the summation:

$$R = R^{rel} + R^{ex} \tag{22}$$

$$R^{rel} = \begin{bmatrix} R_1^F \\ & R_1^A \end{bmatrix}$$
(23)

$$R^{ex} = \begin{bmatrix} k_{FA}^{app} & -k_{AF} \\ -k_{FA}^{app} & k_{AF} \end{bmatrix}$$
(24)

for a two-site exchange model. The definitions of the variables are the same as for the R_2 simulation, with the addition of R_1^i , which represents the intrinsic longitudinal relaxation rate of state *i*. The relaxation rate of the free ligand (R_1^F) is measured experimentally, but the bound state ¹³C relaxation rate (R_1^A) is calculated from motional models (see ¹³C R_1/R_2 Relaxation Modeling).

Simulation of ¹³C DEST experiments

Signal intensities for the simulated DEST experiment are calculated with the following differential equation:

$$\begin{bmatrix} E/2\\ I_x^F\\ I_y^F\\ I_x^A\\ I_x^A\\ I_y^A\\ I_z^A \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & R_2^F + k_{FA}^{app} & \Omega^F & -\omega_y & -k_{AF} & 0 & 0\\ 0 & -\Omega^F & R_2^F + k_{FA}^{app} & \omega_x & 0 & -k_{AF} & 0\\ 0 & -\Omega^F & R_2^F + k_{FA}^{app} & \omega_x & 0 & -k_{AF} & 0\\ -2\Theta^F & \omega_y & -\omega_x & R_1^F + k_{FA}^{app} & 0 & 0 & -k_{AF}\\ 0 & -k_{FA}^{app} & 0 & 0 & R_{2,A}^0 + k_{AF} & \Omega_A & -\omega_y\\ 0 & 0 & -k_{FA}^{app} & 0 & -\Omega_A & R_{2,A}^0 + k_{AF} & \omega_x\\ -2\Theta^A & 0 & 0 & -k_{FA}^{app} & \omega_y & -\omega_x & R_{1,A}^1 + k_{FA} \end{bmatrix}$$
(25)

This formulation is for a two-site exchange model. Here, $\Theta^p = R_1^p I_z^p$ (where I_z^p is the equilibrium longitudinal magnetization of state *p*), *I* represents the magnetization of a ¹³C nucleus in the rotating frame, Ω^p is the difference between the resonance frequency of state *p* and the applied saturation field, $\omega_{y,x}$ is the continuous wave saturation field strength on the applied axis, and *E* is unity. The value of *I*^{cac/} is determined by the ratio of the solution to the above equation with and without saturation applied, respectively.

¹³**C** R_1/R_2 *Relaxation Modeling.* Relaxation rates (R_1 and R_2) for ¹³C spins bound to a nanoparticle surface are calculated based on rotational motion. This includes contributions from the tumbling of the nanoparticle as well as the local motion of phenol. The general equation to calculate R_1 and R_2 considering dipolar and CSA relaxation mechanisms are:

$$R_{1} = \frac{d^{2}}{4} (J(\omega_{H} - \omega_{C}) + 3J(\omega_{C}) + 6J(\omega_{C} + \omega_{H})) + c^{2}J(\omega_{C})$$
(25)

$$R_2 = \frac{d^2}{8} (4J(0) + J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H) + 6J(\omega_C + \omega_H)) + \frac{c^2}{6} (4J(0) + 3J(\omega_C))$$
(26)

Where:

$$d = \frac{\mu_0}{4\pi} \hbar \gamma_C \gamma_H r^{-3} \tag{27}$$

$$c = \frac{\gamma_C B_0 \Delta \sigma}{\sqrt{3}} \tag{28}$$

$$J(\omega) = \frac{2}{5}S^2 \left[\frac{\tau_{NP}}{1+\tau_{NP}^2 \omega^2}\right] + \frac{2}{5}(1-S^2) \left[\frac{\tau_e}{1+\tau_e^2 \omega^2}\right]$$
(29)

$$\frac{1}{\tau_e} = \frac{1}{\tau_{NP}} + \frac{1}{\tau_{loc}} \tag{30}$$

 μ_0 is the magnetic permittivity, \hbar is the reduced Planck's constant, γ_u is the gyromagnetic ratio of the specified nuclei, r is the internuclear bond distance (taken to be 1.09 Å here), $J(\omega)$ is the spectral density function, τ_{NP} and τ^{loc} are the rotational correlation time for the nanoparticle and the local motion of the ligand, respectively. $\Delta\sigma$ is the chemical shift anisotropy (for aromatic C-H is approximately 200 ppm) (2, 3). S^2 is the generalized order parameter for use in model-free analysis of motion. S^2 is a fittable parameter whose value is the same regardless of the C-H bond vector due to the rigid structure of phenol.

Global fitting parameters. The optimization was run using p_F , k_{AF} , τ_A^{loc} , and the order parameter of the adsorbate state, S^2 , as global parameters. The remaining values of populations and rate constants were calculated using the following equations:

$$p_A = 1 - p_F \tag{32}$$

$$k_{FA}^{\alpha\beta\rho} = k_{AF} \times p_A / p_F \tag{33}$$

 τ_{NP} was calculated to be 3.2 µs by using the average nanoparticle size and assuming spherical symmetry (33 nm, Supplementary Figure S3) and the Stoke-Einstein equation. This value was held constant during the data fitting procedure.

Error on the fitted parameters was computed by Monte Carlo simulation of synthetic datasets from the estimated experimental error (see NMR Spectroscopy section)

Scripts and Pulse Programs. All Matlab scripts and pulse programs used here can be found at <u>https://group.chem.iastate.edu/Venditti/downloads.html</u> for download.



Figure S1. ¹³C DEST profiles (saturation field = 1 kHz) measured for the ortho (red), meta (green), and para (blues) positions of PhOH in the absence (cross) and in the presence (circle) of (**a**) 1 wt% TiO₂ and (**c**) 1 wt% Pd/TiO₂. ¹³C RD profiles measured for the ortho (red), meta (green), and para (blues) positions of PhOH in the absence (cross) and in the presence (circle) of (**b**) 1 wt% TiO₂ and (**d**) 1 wt% Pd/TiO₂. All data were acquired on an 800 MHz spectrometer.



Figure S2. Agreement between modelled and experimental ¹³C R_1 data measured for 10 mM PhOH in the presence of (**a**) 1 wt% TiO₂, (**b**) 1 wt% TiO₂ and 20 mM phosphate, (**c**) 1 wt% Pd/TiO₂, and (**d**) 1 wt% Pd/TiO₂ and 20 mM phosphate. The R_1 experiments were acquired on both 800 (orange) and 600 (blue) MHz spectrometers.



Figure S3. (a) XPS spectra of Pd/TiO₂-H (top) and Pd/TiO₂ before reduction (Pd/TiO₂-I) (bottom) showing the Ti 2p signals. (b) XPS spectra of Pd/TiO₂-H (top) and Pd/TiO₂-I (bottom) showing the Pd 3d signals. (c) XPS spectra of Pd/SiO₂-H (top) and Pd/SiO₂ before reduction (Pd/SiO₂-I) (bottom) showing the Pd 3d signals. The experimental data are shown as crosses, the fitted curves are shown as colored lines (blue for Pd/TiO₂ and orange for Pd/SiO₂). The base line is shown as a solid black curve. The XPS spectra for Pd/SiO₂-H and Pd/TiO₂-H show Pd 3d signals at the same position, indicating that the Pd site has the same oxidation state in the two materials.

Supporting Tables

Table S1. Kinetic, population, chemical shift, rotational correlation time, and order parameters for PhOH binding to TiO₂ derived from the global fitting of ¹³C DEST, ¹³C RD, and ¹³C R_1 data using a two-site exchange model. Definitions for each parameter are given in Figure 5 and in Supporting Methods. ¹³C $\Delta \omega^{FA}$ values are the absolute values of the ¹³C chemical shift difference in ppm between free and bound states.

Global Parameters	0 mM phosphate (2-site)	20 mM phosphate (2-site)
p_{F} (%)	98.98 ± 0.15	99.57 ± 0.03
$p_{A}(\%)$	1.02 ± 0.15	0.43 ± 0.03
$\tau_{c}^{loc,A}(ps)$	< 100	< 100
S_A^2	< 0.01	< 0.01
$k_{AF}(s^{-1})$	7660 ± 1598	2088 ± 202
$k_{FA}^{app}(s^{-1})$	79 ± 20	9 ± 1
Peak-specific parameter		
$^{13}C \Delta \omega^{FA} (ppm) o/m/p$	1.35 ± 0.25 / 1.57 ± 0.27 / 1.38 ± 0.26	1.18 ± 0.08 / 1.38 ± 0.08 / 1.02 ± 0.08

Table S2. Kinetic, population, chemical shift, rotational correlation time, and order parameters for PhOH binding to Pd/TiO₂ derived from the global fitting of ¹³C DEST, ¹³C RD, and ¹³C R_1 data using a two-site exchange model. Definitions for each parameter are given in Figure 5 and in Supporting Methods. ¹³C $\Delta \omega^{FA}$ values are the absolute values of the ¹³C chemical shift difference in ppm between free and bound states.

Global Parameters	0 mM phosphate (2-site)	20 mM phosphate (2-site)
$p_{F}(\%)$	98.79 ± 0.04	99.42 ± 0.03
$p_{A}(\%)$	1.21 ± 0.04	0.58 ± 0.03
$\tau_{C}^{loc,A}(ps)$	< 100	< 100
S_A^2	< 0.01	< 0.01
$k_{AF}(s^{-1})$	7435 ± 812	3329 ± 310
$k_{FA}^{app}(s^{-1})$	91 ± 10	19.4 ± 2.1
Peak-specific parameter		
¹³ $C \Delta \omega^{FA} (ppm) o/m/p$	0.69 ± 0.04 / 0.77 ± 0.05 / 0.68 ± 0.05	1.05 ± 0.06 / 1.06 ± 0.06 / 0.90 ± 0.05

References

- 1. T. K. Egner *et al.*, 'Surface Contrast' NMR Reveals Non-innocent Role of Support in Pd/CeO2 Catalyzed Phenol Hydrogenation. *ChemCatChem* **12**, 4160-4166 (2020).
- K. Pervushin, R. Riek, G. Wider, K. Wüthrich, Transverse Relaxation-Optimized Spectroscopy (TROSY) for NMR Studies of Aromatic Spin Systems in 13C-Labeled Proteins. *Journal of the American Chemical Society* **120**, 6394-6400 (1998).
- 3. W. S. Veeman, Carbon-13 chemical shift anisotropy. *Progress in Nuclear Magnetic Resonance Spectroscopy* **16**, 193-235 (1984).