Thermodynamic study of benzene and hydrogen coadsorption on Pd(111)

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Supporting information



Figure S 1: Surface Gibbs free energies as a function of temperature for the two consecutive systems with benzene and $\theta_{\rm H}$ = 0.67 or 0.78 hydrogen coverage (blue and red lines, respectively). The values are obtained by applying a frequency cutoff of 25 or 50 cm⁻¹ (full and dotted lines, respectively).

Geometry with spurious frequencies	Number of frequencies replaced
Benzene + $\theta_{\rm H} = 0.78$	2
Benzene + $\theta_{\rm H} = 0.89$	2
Benzene + $\theta_{\rm H} = 1$	3
Benzene + $\theta_{\rm H} = 1.11$	2
Benzene + $\theta_{\rm H} = 1.22$	3
Benzene + $\theta_{\rm H} = 1.33$	3
Benzene + $\theta_{\rm H} = 1.44$	4
Benzene + $\theta_{\rm H} = 1.56$	5
Benzene + $\theta_{\rm H} = 1.67$	4
Benzene + $\theta_{\rm H} = 1.78$	4
Benzene + $\theta_{\rm H} = 1.89$	5

Table S 1: Geometries in which spurious imaginary (or positive but $< 25 \text{ cm}^{-1}$) frequencies are replaced and number of these frequencies that are replaced.

Thermodynamic calculations:

The surface Gibbs free energy is calculated as shown in eq. (S1).

$$\Gamma(T, p_i) = \begin{pmatrix} G_{ads}(T) - n_{Pd} \cdot G_{bulk}(T) - \sum_i n_i \cdot G_{m, gas, i}(T, p_i) \\ \frac{1}{2 \cdot A} \end{pmatrix}$$
(S1)

With G_{ads} and G_{bulk} the Gibbs free energy of respectively the adsorbate complex and bulk Pd atom, and $G_{m,gas}$ the molar Gibbs free energy of the gas phase species. n_{Pd} and ni represent respectively the number of Pd atoms in the unit cell and the number of adsorbed molecules at the corresponding evaluated coverage. A is the surface area of the unit cell, which is multiplied by two because of the two surfaces that the slab has in the periodic DFT calculations.

The Gibbs free energy of the adsorbed complex and the bulk is calculated from the enthalpy and entropy values, as shown in eq. (S2) and eq. (S3).

$$G_{ads} = (H - T \cdot S) = (E_{el} + ZPVE + U^{vib}(T)) - T \cdot S_{vib}(T)$$
(S2)

$$G_{bulk} = (H - T \cdot S) = (E_{el} + ZPVE + U^{vib}(T)) - T \cdot S_{vib}(T)$$
(S3)

With E_{el} the electronic energy of the relaxed slab, ZPVE the zero point vibrational contributions, U_{vib} the thermal correction to the enthalpy, T the temperature, and S_{vib} the vibrational entropy. The molar gas phase Gibbs free energy, G_{gas} , accounts for the same terms as the ones in eq. (S2) and eq. (S3), and considers also the free energy contributions from the translational and rotational gas phase modes, $U^{trans+rot}$ and $S^{trans+rot}$, which are also calculated from statistical thermodynamics. Additionally, the molar gas phase Gibbs free energy includes the term that accounts for the gas phase pressure, in which k_B is the Boltzmann constant, T the temperature (K), p_i the pressure of the gas phase species i (bar), and p^o the standard pressure of 1 bar, as shown in eq. (S4).

$$G_{m,gas} = (H - T \cdot S) = \left[\left(E_{el} + ZPVE + U^{vib} + R \cdot T + U^{trans + rot} \right) \right] - T \cdot \left(S^{vib} + S^{trans + rot} \right) + R \cdot T \cdot \ln \frac{p}{p^o}$$
(S4)

The unit cell used in the calculation has two surfaces because a vacuum layer is included between periodic images to avoid interactions in the direction perpendicular to the slab. The Pd atoms in the upper surface are relaxed during the geometry optimization ("top surface"), on which the corresponding coverage of species *i* is adsorbed. However, the Pd atoms that compose the lower ("bottom") surface are constrained to the bulk geometry, and on this surface no species are adsorbed (i.e. mixed slab in Fig. S1). The electronic energy obtained from the periodic DFT calculations corresponds to the whole slab, which includes these two surfaces. Therefore, the surface free energy that can be derived from this electronic energy corresponds to an average value of these two surfaces, while only the upper one is of interest. In order to calculate an approximate value for a completely optimized single surface $(\Gamma_{el,relaxed})$, the procedure proposed by Chizallet et al. [10] was followed. The average surface energy of the mixed-surface unit cell is counted twice (mixed slab), and the surface energy of a completely non-optimized unit cell (fixed slab) is subtracted, i.e. the energy of the unit cell with all atoms in the bulk structure and without adsorbate (see eq. (S2) and Fig. S2). The result is divided by two to obtain the value for one surface, since the frequency analysis to calculate entropies and enthalpies is performed only for the relaxed surface.





Four different approaches have been considered to calculate surface Gibbs free energies. The first approach, i.e. PW91- E_{el} , assumes that the vibrational frequencies have only a small

contribution to the surface Gibbs free energy. This is usually done because obtaining vibrational frequencies for adsorbed species is computationally very demanding and not always straightforward. Gibbs free energies for adsorbate and bulk are approximated by the electronic energy from the PW91 functional, neglecting all vibrational contributions and retaining only rotational and translational contributions for gas phase molecules, as shown in eq. (S6).

$$\Gamma^{PW91-E_{el}} = \Gamma_{el,relaxed} - n_i \left(\frac{\sum_{i} \left(U^{trans+rot} - T \cdot S^{rot+trans} + R \cdot T \cdot \ln\left(\frac{p_i}{p^o}\right) \right)_{gas,i}}{A} \right)$$
(S6)

The second approach, i.e. *PW91-G*, calculates the Gibbs free energy including vibrational contributions for the *ads*, *bulk* and *gas* terms, because entropy contributions to the surface Gibbs free energies may play an important role in the thermodynamic phase diagram, particularly for larger molecules such as benzene. Adsorbates are considered immobile⁷³ for the whole range of coverages and, therefore, Gibbs free energy contributions from translational and rotational modes are only included for gas phase species, see eq. (S7).

$$\Gamma^{PW91-G} = \Gamma_{el,relaxed} + \frac{\left(\left(ZPVE + U^{vib}\right) - T \cdot S^{vib}\right)_{ads}}{2 \cdot A} - \frac{n_{Pd} \cdot \left(\left(ZPVE + U^{vib}\right) - T \cdot S^{vib}\right)_{bulk}}{2 \cdot A} - n_{i}\left(\frac{\sum_{i} \left(\left(ZPVE + U^{vib} + R \cdot T + U^{trans+rot}\right) - T \cdot (S^{vib} + S^{trans+rot}) + R \cdot T \cdot \ln\left(\frac{p_{i}}{p^{o}}\right)\right)_{gas,i}}{2 \cdot A}\right)$$
(S7)

The third vdW-DF- E_{el} approach uses the electronic energies with the opt-PBE vdW-DF and neglects vibrational contributions, as shown in eq. (S8).

$$\Gamma^{vdW-DF-E_{el}} = \Gamma_{el,relaxed,vdW-DF} - n_i \left(\frac{\sum_{i} \left(U^{trans+rot} - T \cdot S^{rot+trans} + R \cdot T \cdot \ln\left(\frac{p_i}{p^o}\right) \right)_{gas,i}}{A} \right)$$
(S8)

The final approach gives a rough picture of the results that would be obtained if vdW-DF vibrational contributions are included and the vdW-DF method is used to calculate electronic energies. This is done by adding the PW91 vibrational contributions to the vdW-DF electronic energy term, since the vibrational contributions using the vdW-DF has not been calculated due to computational constrains. This approach is defined as vdW-DF- G_{PW91} , as is shown in eq. (S9).

$$\Gamma^{PW91-G_{PW91}} = \Gamma_{el,relaxed,vdW-DF} + \frac{\left(\left(ZPVE + U^{vib}\right) - T \cdot S^{vib}\right)_{ads,PW91}}{2 \cdot A} - \frac{n_{Pd} \cdot \left(\left(ZPVE + U^{vib}\right) - T \cdot S^{vib}\right)_{bulk,PW91}}{2 \cdot A} - \frac{n_{Pd} \cdot \left(\left(ZPVE + U^{vib}\right) - T \cdot S^{vib}\right)_{bulk,PW91}}{2 \cdot A} - \frac{n_{i}}{\left(\frac{\sum_{i} \left(\left(ZPVE + U^{vib} + R \cdot T + U^{trans+rot}\right) - T \cdot (S^{vib} + S^{trans+rot}) + R \cdot T \cdot \ln\left(\frac{p_{i}}{p^{o}}\right)\right)_{gas,i,PW91}}{2 \cdot A}\right)}{2 \cdot A}$$
(S9)

To compare the results obtained between the two first $PW91-E_{el}$ and PW91-G approaches, surface Gibbs free energies are broken into it constituent terms, i.e. enthalpy, entropy and pressure terms, as shown in eq. (S10).

$$\Gamma = \Gamma_H + \Gamma_S - n_i \left(\frac{R \cdot T \cdot \ln\left(\frac{p_i}{p^o}\right)}{2 \cdot A} \right)$$
(S10)

The enthalpy and entropy terms used in *PW91-E_{el}* are respectively shown in eq. (S11) and eq. (S12), i.e. $\Gamma_H^{PW91-E_{el}}$ and $\Gamma_S^{PW91-E_{el}}$, and they are compared to the corresponding ones used in the *PW91-G* approach, see eq. (S13) and eq. (S14).

$$\Gamma_{H}^{PW91-E_{el}} = \Gamma_{el,relaxed}^{PW91-E_{el}} - \frac{n_i \cdot \sum_{i} U_{m,gas,i}^{trans+rot}}{2 \cdot A}$$
(S11)

$$\Gamma_{S}^{PW91-E_{el}} = \frac{-n_{i} \cdot \sum_{i} - T \cdot S_{m,gas,i}^{trans+rot}}{2 \cdot A}$$
(S12)

$$\Gamma_{H}^{PW91-G} = \Gamma_{el,relaxed}^{PW91-G} + \frac{\left(ZPVE + U^{vib}\right)_{ads} - n_{Pd} \cdot \left(ZPVE + U^{vib}\right)_{bulk} - n_{i} \cdot \sum_{i} \left(ZPVE + U^{vib}_{m} + U^{trans+rot}_{m} + RT\right)_{gas}}{2 \cdot A}$$
(S13)

$$\Gamma_{S}^{PW91-G} = \frac{\left(-T \cdot S^{vib}\right)_{ads} - n_{Pd} \cdot \left(-T \cdot S^{vib}\right)_{bulk} - n_{i} \cdot \sum_{i} \left(-T \cdot \left(S_{m}^{vib} - S_{m}^{trans+rot}\right)\right)_{gas,i}}{2 \cdot A}$$
(S14)

Calculations of benzene pressure as a function of hydrogen pressure for the coadsorption of a fixed benzene coverage with increasing hydrogen coverages:

For benzene and hydrogen coadsorption, the benzene coverage has been fixed in the periodic DFT calculations, however, each condition (T,p_{H2}) requires a different benzene pressure in order to fix the benzene coverage at $\theta_B = 0.11$.

The benzene pressure has been calculated from a Langmuir model for coadsorption, as shown in eq. (S15), given a hydrogen pressure and a fixed benzene coverage, and the equilibrium coefficients at a certain temperature from the periodic DFT calculation.

$$p_B = \frac{\theta_B \cdot \sqrt{p_{H_2} \cdot K_{H_2}} + \theta_B}{K_B - \theta_B \cdot K_B}$$
(S15)

The values of surface Gibbs free energies depend on both hydrogen and benzene gas-phase pressures. However, the transition line in the thermodynamic phase diagram between two consecutive coverages, which are obtained in the same unit cell and at the same benzene coverage, is not affected by benzene pressure, as it is shown in Fig. S2.



Fig. S 3: Surface Gibbs free energies as a function of temperature for the coadsorption systems with benzene and $\theta_{\rm H} = 0.44$ (blue) and benzene with $\theta_{\rm H} = 0.89$ (red) using a benzene pressure of 1 bar (full lines) or the one obtained from a Langmuir model for benzene and hydrogen coadsorption.

Calculation of the temperature for the transition between clean surface and adsorbed benzene, for the coadsorption of benzene and increasing hydrogen coverages:

The transition line from $\theta_B = 0.11 / \theta_H = 0$ to $\theta_B = \theta_H = 0$ is included in the thermodynamic phase diagrams for coadsorption, a transition that is clearly dependent on the pressure of benzene. This line is obtained as follows: first, for every point in the transition from benzene adsorbed (B_{ads}) to the first thermodynamic most stable coadsorbed system, T₁ temperatures in Table S2, the pressures of benzene required to obtain $\theta_B = 0.11$ at a given temperature and hydrogen pressure are calculated using a simple Langmuir model for coadsorption, as shown in eq. (S15) and the values listed in Table S2. The adsorption equilibrium coefficients are obtained from the DFT calculations with the corresponding functional. Assuming that for a given hydrogen pressure the obtained benzene pressures remains constant with increasing temperatures, the same Langmuir model is then used to find the temperatures at which the benzene coverage decreases to $\theta_B = 0.05$, T₂ in Table S2, which can be used to represent the transition from the clean surface to the benzene covered surface.

Geometries evaluated for hydrogen adsorption:

For the adsorption of hydrogen up to $\theta_{\rm H} = 1$, the following cases were evaluated:

- a) Adsorption up to $\theta_{\rm H} = 1$ on a single type of surface site (most stable case, on fcc sites)
- b) Adsorption up to $\theta_{\rm H} = 1$ on a single type of subsurface site
- c) Every combination of two types of surface sites up to $\theta_{\rm H} = 1$
- d) Every combination of two types of subsurface sites up to $\theta_{\rm H} = 1$
- e) Every combination of surface and subsurface sites up to $\theta_{\rm H} = 1$

For the adsorption of hydrogen from $\theta_H > 1$ to $\theta_H = 2$, the following cases were evaluated:

- a) Combination of $\theta_H = 1$ surface hydrogen with up to $\theta_H = 1$ subsurface hydrogen (most stable)
- b) Combination of $\theta_H = 1$ subsurface hydrogen with up to $\theta_H = 1$ surface hydrogen.
- c) Combination of $\theta_H = 1$ surface hydrogen with up to $\theta_H = 1$ surface hydrogen on a different site.
- d) Combination of $\theta_H = 1$ subsurface hydrogen with up to $\theta_H = 1$ subsurface hydrogen on a different site.

Geometries evaluated for hydrogen and benzene coadsorption:

A lesser amount of combinations were evaluated for the coadsorption with benzene due to the large number of possible cases. Conclusions from the adsorption of hydrogen alone, such as that the bridge sites are not stable at higher coverage and diffuse to hollow sites, were incorporated in the rationale what the most possible surface configuration of all the hydrogen atoms could be.

For the coadsorption up to the surface-layer saturation, i.e., $\theta_H = 0.89$, combinations of the two most stable sites (fcc and hcp) were evaluated. As an example, at $\theta_H = 0.44$ these following cases were studied:

- a) Benzene + all atoms in fcc sites
- b) Benzene + all atoms in hcp sites
- c) Benzene + $\theta_{\rm H}$ = 0.33 fcc + $\theta_{\rm H}$ = 0.11 hcp

- d) Benzene + $\theta_H = 0.11$ fcc + $\theta_H = 0.33$ hcp
- e) Benzene + $\theta_{\rm H}$ = 0.22 fcc + $\theta_{\rm H}$ = 0.22 hcp

A similar approach was used to evaluate absorption up to the subsurface-layer saturation, but now considering combination of the three, octasubsurface, tetrasub13, and tetrasub31, sites.

For coverages above $\theta_H > 0.89$, and up to 1.33, every combination of benzene + $\theta_H = 0.89$ fcc + subsurface hydrogen atoms was investigated.

Above $\theta_{\rm H} > 1.33$, there are combinations that were not studied because the experience at lower coverage, the experience with hydrogen adsorption and the logic indicated that were, most possible, not the most stable. Additionally, this was evaluated in some cases to verify it, e.g. for the coadsorption of benzene + $\theta_{\rm H} = 1.55$, a case was studied in which one of the subsurface atoms was absorbed on other subsurface sites rather than the tetrasub13 site, however, the absorption of all atoms on the tetrasub13 site led always (above $\theta_{\rm H} \ge 1.22$) to the most stable case. From those studied, over 100 possible geometries, the most stable ones are shown in the manuscript.

Table S2: For each hydrogen pressure, p_{H2} in bar, temperature at which the first coadsorbed system is observed, T_1 in K, and corresponding pressure of benzene at a fixed 0.11 benzene coverage that is calculated from a Langmuir model for coadsorption using the values in the PW91-G approach. T_2 represents the temperature at which a lower benzene coverage of 0.05 is expected assuming the same benzene and hydrogen pressure.

p _{H2} (bar)	p_{H2} (bar) T_1		p _B	p _B (bar)		T_2	
	PW91-G	vdW-DF-E _{el}	PW91-G	vdW-DF-E _{el}	PW91-G	vdW-DF-E _{el}	
10 ²	979	832	1.37	1.19 10 ⁻³	1069	870	
10	857	724	2.73 10 ⁻¹	4.65 10 ⁻⁵	951	754	
1	759	639	5.24 10 ⁻²	1.74 10 ⁻⁶	850	664	
10 ⁻¹	680	571	9.72 10 ⁻³	6.21 10 ⁻⁸	763	592	
10 ⁻²	615	515	1.75 10 ⁻³	2.12 10 ⁻⁹	689	533	
10 ⁻³	560	468	3.05 10 ⁻⁴	6.98 10 ⁻¹¹	626	484	
10 ⁻⁴	514	428	5.21 10 ⁻⁵	2.22 10 ⁻¹²	571	442	
10 ⁻⁵	475	395	8.72 10 ⁻⁶	6.93 10 ⁻¹⁴	524	407	
10 ⁻⁶	441	366	1.43 10 ⁻⁶	2.12 10 ⁻¹⁵	483	377	
10 ⁻⁷	411	340	2.29 10 ⁻⁷	6.40 10 ⁻¹⁷	447	351	
10 ⁻⁸	384	318	3.61 10 ⁻⁸	1.89 10 ⁻¹⁸	416	328	
10 ⁻⁹	361	299	5.59 10 ⁻⁹	5.48 10 ⁻²⁰	387	307	
10 ⁻¹⁰	341	281	8.55 10 ⁻¹⁰	1.55 10 ⁻²¹	363	289	

Results

Table S3: Adsorption energies in kJ mol⁻¹ of hydrogen adsorbed at different coverages and sites up to saturation coverage. The values obtained with the vdW-DF functional for the hollow fcc site are shown between brackets.

Site	ΔE_{ads} (kJ mol _H ⁻¹)						
5110	0.25 ML	0.5 ML	0.75 ML	1 ML			
fcc	-54.2 (-43.4)	-51.5 (-40.6)	-49.5 (-38.3)	-47.9 (-36.6)			
hcp	-49.3	-46.6	-44.5	-42.9			
bridge	-39.2	-35.9	-32.6	-29.1			
top	-1.6	1.1	3.5	7.0			
octasub	-17.0	-15.6	-15.2	-14.5			
tetrasub31	-17.6	-17.6	-18.4	-19.6			
tetrasub13	-13.5	-13.6	-13.8	-14.4			

Table S4: Adsorption energy (kJ mol⁻¹) per mol of hydrogen for the adsorption of $0.25 \le \Theta_{\rm H} \le 1$ hydrogen coverage on a H-covered surface with $\Theta_{\rm H,initial} = 1$, for different combinations. The values obtained with the vdW-DF functional for the combination of $\Theta_{\rm H} = 1$ hydrogen fcc and addition of $0.25 \le \Theta_{\rm H} \le 1$ tetrasub13 hydrogen is shown between brackets.

Θ	0.25 < Pm < 1	$\Delta E_{ads} (\text{kJ mol}_{\text{H}}^{-1})$					
•H,IIIIIai 1	0.25 <u>-</u> 0 _H <u>-</u> 1	$\Theta_{\rm H,total} = 1.25$	$\Theta_{\rm H,total} = 1.5$	$\Theta_{\rm H,total} = 1.75$	$\Theta_{\rm H,total} = 2$		
	tetrasub31	-38.6	-32.5	-27.6	-24.2		
faa	octasub	-38.9	-32.7	-28.0	-23.3		
100	tetrasub13	-39.8 (-28.3)	-34.3 (-22.6)	-30.1 (-18.4)	-26.8 (-15.1)		
	hcp	-33.1	-20.0	-0.3	19.1		
	octasub	-36.3	-31.7	-28.0	-24.2		
hen	tetrasub31	-30.5	-23.2	-18.0	-14.9		
пер	tetrasub13	-36.1	-31.5	-27.9	-25.2		
	fcc	-30.3	-20.0	0.0	19.1		
top	octasub	5.0	3.2	1.6	0.4		
	tetrasub31	7.3	6.4	4.7	2.5		
	tetrasub13	5.9	4.5	2.7	1.1		
	fcc	-18.3	-20.8	-22.8	-23.3		
	hcp	-18.4	-21.6	-23.7	-24.2		
octasub	top	-8.4	-4.4	-1.0	0.4		
	tetrasub31	-5.0	-2.1	0.9	1.3		
	tetrasub13	-6.7	-3.2	-1.8	-0.6		
	fcc	-23.2	-25.3	-25.7	-24.2		
	hcp	-18.9	-18.5	-17.1	-14.9		
tetrasub31	top	-12.8	-7.6	-2.4	2.7		
	octasub	-12.7	-7.3	-1.7	1.3		
	tetrasub13	-14.5	-10.4	-6.8	-2.5		
	fcc	-20.1	-23.6	-25.8	-26.8		
tetrasub13	hcp	-19.6	-22.6	-24.4	-25.2		
	top	-10.1	-5.9	-2.2	1.1		



Fig. S4: Surface Gibbs free energies and electronic energy term as a function of the temperature calculated for hydrogen adsorption on Pd(111) with the (a) *PW91-E_{el}* and (b) $vdW-DF-E_{el}$ approaches. The enthalpy and entropy terms in the surface Gibbs free energy are the same in both approaches, because they involve only translational and rotational modes for gas phase molecules, therefore, these are not shown.

	d _{C-C}	d _{C-Pd} d _{C-H}		d _{Benzene-1stPd}	C-C-C	C-C-H
	pm	pm	pm	pm	(°)	(°)
bridge(0)	143	245, 217	109	220	120	118
bridge(30)	144	224, 221	109	214	117, 121	118
hollow-hcp(0)	144	225	109	220	120	118
hollow-fcc(0)	144	230	109	227	120	118
hollow-hcp(30)	143	219	109	218	120	118
hollow-fcc(30)	143	220	109	228	120	118
top(0)	147	226	110	191	120	116
top(30)	140	280	109	274	120	120

Table S5: Geometrical features of benzene adsorbed on different sites at θ_B =0.11. Bond distances are shown in picometer while bond angles in °.

Table S6: Geometrical features of benzene adsorbed on hollow-hcp(0) sites at increasing coverage. Bond distances are shown in picometer while bond angles in °.

	d _{C-C}	d _{C-Pd}	d _{C-H}	d _{Benzene-1stPd}	C-C-C	С-С-Н
θ	pm	pm	pm	pm	(°)	(°)
6.25 10-2	144	224	109	212	120	118
0.11	144	225	109	220	120	118
0.17	142	227	109	216	120	120
0.25 (tilted)	140	330	109	431	120	120



Fig. S5: Thermodynamic phase diagram of benzene adsorption at the bridge(30) site on Pd(111) as a function of temperature (K) and benzene pressure (bar) for standard pressure of $p^o = 1$ bar using the *PW91-E_{el}* approach.



Fig. S6: Surface Gibbs free energies and electronic term for benzene adsorption on Pd(111) with the (a) $PW91-E_{el}$ and (b) $vdW-DF-E_{el}$ approaches. The enthalpy and entropy terms in the surface Gibbs free energy are the same in both approaches, because they involve only translational and rotational modes for gas phase molecules, therefore, these are not shown.

E _{ads,benzene} (kJ/mol)								
	Benzene + Surface	e hydrogen	Benzene + Subsurface hydrogen					
Hydrogen coverage	Bridge(30)	Hollow-hcp(0)	Hydrogen coverage	Bridge(30)	Hollow-hcp(0)			
0	-114.9	-100.0		-114.9	-100.0			
0.11 fcc	-106.0	-89.9	0.11 octasub	-105.7	-91.8			
0.11 fcc + 0.11 hcp	-91.9	-78.8	0.22 tetrasub	-100.1	-83.7			
0.22 fcc + 0.11 hcp	-77.0	-70.8	0.22 octasub + 0.11 tetrasub31	-88.9	-76.6			
0.33 fcc + 0.11 hcp	-62.8	-64.4	0.44 tetrasub31	-87.1	-71.1			
0.56 fcc	-42.5	-58.1	0.56 tetrasub31	-71.0	-59.3			
0.67 fcc	-11.5	-27.5	0.67 tetrasub31	-70.7	-56.9			
0.78 fcc	29.9	-15.1	0.78 tetrasub31	-62.1	-54.4			
0.89 fcc	36.4	-13.3	0.89 tetrasub31	-62.0	-51.0			
0.89 fcc+ 0.11 tetrasub	31 35.0	-12.5	1 tetrasub31	-61.2	-60.8			

Table S 7: Benzene adsorption energies in kJ mol⁻¹ on a pre-covered surface with hydrogen at surface and/or subsurface sites, and benzene adsorbing on bridge(30) or hollow-hcp(0) sites.

Benzene + Surface ($\theta_{surface}$ =	(0.89) + Subsurface	$(0.22 \le \theta_{\text{subsurface}} \le 1)$
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Hydrogen coverage ($\theta_{surface} + \theta_{subsurface}$)	Bridge(30)	Hollow-hcp(0)
0.89 fcc + 0.22 tetrasub13	33.7	-14.0
0.89 fcc + 0.33 tetrasub13	34.5	-15.7
0.89 fcc + 0.44 tetrasub13	27.6	-13.4
0.89 fcc + 0.56 tetrasub13	30.5	-13.3
0.89 fcc + 0.67 tetrasub13	32.8	-11.3
0.89 fcc + 0.78 tetrasub13	22.7	-10.3
0.89 fcc + 0.89 tetrasub13	24.6	-10.0
0.89 fcc + 1 tetrasub13	23.8	-11.5

Table S 8: Geometrical parameters of benzene hollow-hcp(0) and hydrogen coadsorbed on Pd(111) for hydrogen coverages between 0 (clean surface) and $\theta_{\rm H} = 1.89$. Average C-C bond length (pm), angle of C-H bond relative to the C atom at the opposite side of the ring (°), distance between the benzene centre of mass and the Pd top layer (pm), between the two first Pd layers (pm), and finally average bond distance (pm) between all hydrogen atoms, considering that fcc sites form three bonds with the Pd atoms

	a a	a a	D D I	D 14 D 15	
θ ₁₁	C-C	C-C-H*	B-Pd	Pd1-Pd2	H-Pd
υH	(pm)	(°)	(pm)	(pm)	(pm)
0	143.5	164.8	209	230	
0.11	143.4	165.1	221	231	180.7
0.22	143.2	165.5	220	232	180.9
0.33	143.1	165.7	220	232	180.4
0.44	143.0	165.8	221	233	180.2
0.56	142.7	166.8	226	234	178.0
0.67	142.2	168.8	239	235	179.2
0.78	139.8	179.5	346	233	180.5
0.89	139.7	179.8	386	233	
1	139.7	179.8	387	235	
1.11	139.7	179.8	398	238	
1.22	139.7	179.8	389	243	
1.33	139.7	179.8	385	247	
1.44	139.7	179.8	382	251	
1.56	139.7	179.8	379	255	
1.67	139.7	179.8	380	259	
1.78	139.7	179.8	383	263	
1.89	139.7	179.8	383	268	
Benzene gas phase	140.0	180.0			

* Corresponding to the carbon atoms at the opposite side of the aromatic ring.