

Supporting Information for
**Hydrogen Chemisorption Isotherms on Pt Particles at Catalytic Temperatures:
Langmuir and Two-Dimensional Gas Models Revisited**

Mónica García-Diéguez,¹ David D. Hibbitts,^{1,2,*} and Enrique Iglesia^{1,3,*}

¹ Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA, 94720

² Department of Chemical Engineering, University of Florida, Gainesville, FL, 32601

³ Division of Chemical Sciences, E.O. Lawrence Berkeley National Laboratory, Berkeley, CA, 94720

* to whom correspondence should be addressed: hibbitts@che.ufl.edu, iglesia@berkeley.edu

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Section S1. Details of Standard Statistical Mechanics Treatments

The enthalpy of a given state can be written as the sum of the DFT-derived energy (E_0), zero-point vibrational enthalpy ($ZPVE$) and vibrational, translational and rotational enthalpy (H_{vib} , H_{trans} and H_{rot}):

$$H = E_0 + ZPVE + H_{vib} + H_{trans} + H_{rot} \quad (S1)$$

similarly, the free energy of a state can be written as:

$$G = E_0 + ZPVE + G_{vib} + G_{trans} + G_{rot} \quad (S2)$$

and entropy can be determined for a state with a known H and G at a given T :

$$S = \frac{H - G}{T} \quad (S3)$$

For calculations which include a periodic Ir(111) surface (including adsorbed species and transition states on that surface), there are no translational or rotational degrees of freedom and DFT-derived vibrational frequencies can be used to determine the $ZPVE$, H_{vib} and G_{vib} shown in Eqns. S4-6.

$$ZPVE = \sum_i (1/2 v_i h) \quad (S4)$$

$$H_{vib} = \sum_i \left(\frac{v_i h e^{-\frac{v_i h}{kT}}}{1 - e^{-\frac{v_i h}{kT}}} \right) \quad (S5)$$

$$G_{vib} = \sum_i \left(-kT \ln \frac{1}{1 - e^{-\frac{v_i h}{kT}}} \right) \quad (S6)$$

Gas-phase molecules have translational and rotational degrees of freedom; thus H_{trans} , H_{rot} , G_{trans} and G_{rot} must also be computed:

$$H_{trans} = 5/2 kT \quad (S7)$$

$$H_{rot,linear} = kT \quad (S8)$$

$$H_{rot,nonlinear} = 3/2 kT \quad (S9)$$

$$G_{trans} = -kT \ln \left[\left(\frac{2\pi M k T}{h^2} \right)^{3/2} V \right] \quad (\text{S10})$$

$$G_{rot} = -kT \ln \left[\frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\theta_x \theta_y \theta_z} \right)^{1/2} \right] \quad (\text{S11})$$

$$\theta_i = \frac{h^2}{8\pi^2 I_i k} \quad (\text{S12})$$

where I_i is the moment of inertia about axes x, y or z and σ is the symmetry number of the molecule, 2 for H_2 .

Section S2. Derivation of Thermodynamic Treatments

The surface area (A_{surf}) of the two-dimensional adsorbed phase is constant (analogous to a constant volume in a three-dimensional system), and therefore the enthalpy is identical to the internal energy ($H = U$) and the Gibb's free energy is identical to the Helmholtz free energy ($G = A$).

$$G = A = -k_B T \ln Q \quad (\text{S13})$$

Entropy can be obtained from the Helmholtz free energy via a Maxwell relation:

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N, A_{\text{surf}}} \quad (\text{S14})$$

For identical non-interacting classical particles, we can describe the single-particle partition function (q) in a two-dimensional potential energy surface as:

$$q = \frac{1}{\Lambda_{th}^2} \iint e^{\left(\frac{-E(x,y)}{k_B T}\right)} dx dy \quad (\text{S15})$$

The integral above is done over the entire metal surface (A_{surf}) and $E(x, y) \geq 0$, therefore the integral has a maximum value of A_{surf} . Let's define (to make things simpler), the area from the PES per surface metal atom as α_{PES} :

$$\alpha_{PES} = \frac{1}{N_{M_{\text{surf}}}} \iint e^{\left(\frac{-E(x,y)}{k_B T}\right)} dx dy = \iint_{1 \times 1} e^{\left(\frac{-E(x,y)}{kT}\right)} dx dy \quad (\text{S16})$$

Note: If the potential energy surface is flat, then α_{PES} is the area of a 1×1 Pt (111) surface. The total canonical partition function is:

$$Q = \frac{q^N}{N!} \quad (\text{S17})$$

and we can substitute Eq. S15 into that, and apply Stirling's approximation, to get:

$$Q = \frac{\alpha_{PES}^N N_{M_{\text{surf}}}^N e^N}{\Lambda_{th}^{2N} N^N} = \frac{\alpha_{PES}^N e^N}{\Lambda_{th}^{2N} \theta^N} \quad (\text{S18})$$

where N is the number of H^* adsorbates and θ is the ratio of H^* to surface-metal atoms. Substituting the expression for Q into Eq. S17.

$$G_{H^*, \text{avg}, \text{PES}}^{xy} = A_{H^*, \text{avg}, \text{PES}}^{xy} = -RT \left[\ln \left(\frac{\alpha_{PES}}{\Lambda_{th}^2 \theta} \right) + 1 \right] \quad (\text{S19})$$

Before defining the entropy, I will put the definition of α back in. The average (or integral) molar translational free energy of a species with a given potential energy surface, $E(x, y)$, is:

$$G_{H^*, \text{avg}, \text{PES}}^{xy} = A_{H^*, \text{avg}, \text{PES}}^{xy} = -RT \left[\ln \left(\frac{1}{\Lambda_{th}^2 \theta} \iint_{1 \times 1} e^{\left(\frac{-E(x,y)}{kT}\right)} dx dy \right) + 1 \right] \quad (\text{S20})$$

where we will bound the integral within a 1×1 surface. Differentiation gives:

$$S_{H^*, \text{avg}, \text{PES}}^{xy} = -\left(\frac{\partial A_{H^*, \text{avg}, \text{PES}}^{xy}}{\partial T}\right)_{A, N} \quad (\text{S21})$$

$$S_{H^*, \text{avg}, \text{PES}}^{xy} = R \left[\ln \left(\frac{1}{\Lambda_{th}^2 \theta} \iint_{1 \times 1} e^{\left(\frac{-E(x,y)}{kT}\right)} dx dy \right) + \frac{\iint_{1 \times 1} \frac{E(x, y)}{kT} e^{\left(\frac{-E(x,y)}{kT}\right)} dx dy}{\iint_{1 \times 1} e^{\left(\frac{-E(x,y)}{kT}\right)} dx dy} + 2 \right] \quad (\text{S22})$$

The other term we will define is a Boltzmann-averaged energy (β_{PES}):

$$\beta_{PES} = \iint_{1 \times 1} \frac{E(x, y)}{kT} e^{\left(\frac{-E(x, y)}{kT}\right)} dx dy \quad (S23)$$

Computing the differential free energy and entropies from these average properties gives (and substituting Eqs. S16 and 23 for α and β):

$$G_{H^*,PES}^{xy} = -RT \ln \left(\frac{\alpha_{PES}}{\Lambda_{th}^2 \theta} \right) \quad (S24)$$

$$S_{H^*,PES}^{xy} = R \left[\ln \left(\frac{\alpha_{PES}}{\Lambda_{th}^2 \theta} \right) + \frac{\beta_{PES}}{\alpha_{PES}} + 1 \right] \quad (S25)$$

These equations are used as the starting point for determining the two-dimensional translational free energy and entropy for adsorbed H* as further described in the main text. The free energy of a 2-D system described by a PES is given by Eq. S24. For a flat PES (ideal gas), the ‘area’ of the PES (α_{PES}) is the area of each metal atom (α_0):

$$G_{H^*,ideal}^{xy} = -RT \ln \left(\frac{\alpha_0}{\Lambda_{th}^2 \theta} \right) \quad (S26)$$

In an excluded area model, with an otherwise-flat PES, this area is decreased by the area of a H* atom, when such an atom is present. As such, α_0 is replaced by $(\alpha_0 - \theta b)$:

$$G_{H^*,co-area}^{xy} = -RT \ln \left(\frac{\alpha_0 - \theta b}{\Lambda_{th}^2 \theta} \right) \quad (S27)$$

Taking the derivative of this free energy term at constant T and N (number of H*) gives the entropy:

$$S_{H^*,co-area}^{xy} = - \left. \frac{\partial G_{H^*,co-area}^{xy}}{\partial T} \right)_{A,N} \quad (S28)$$

gives an expression for the two-dimensional translational entropy of an excluded-area gas model:

$$S_{H^*,co-area}^{xy} = R \left[\ln \left(\frac{1}{\Lambda_{th}^2} \cdot \frac{\alpha_0 - \theta b}{\theta} \right) + 1 - \frac{b}{\alpha_0 - \theta b} \right] \quad (S29)$$

Section S3. Adsorption Isotherms

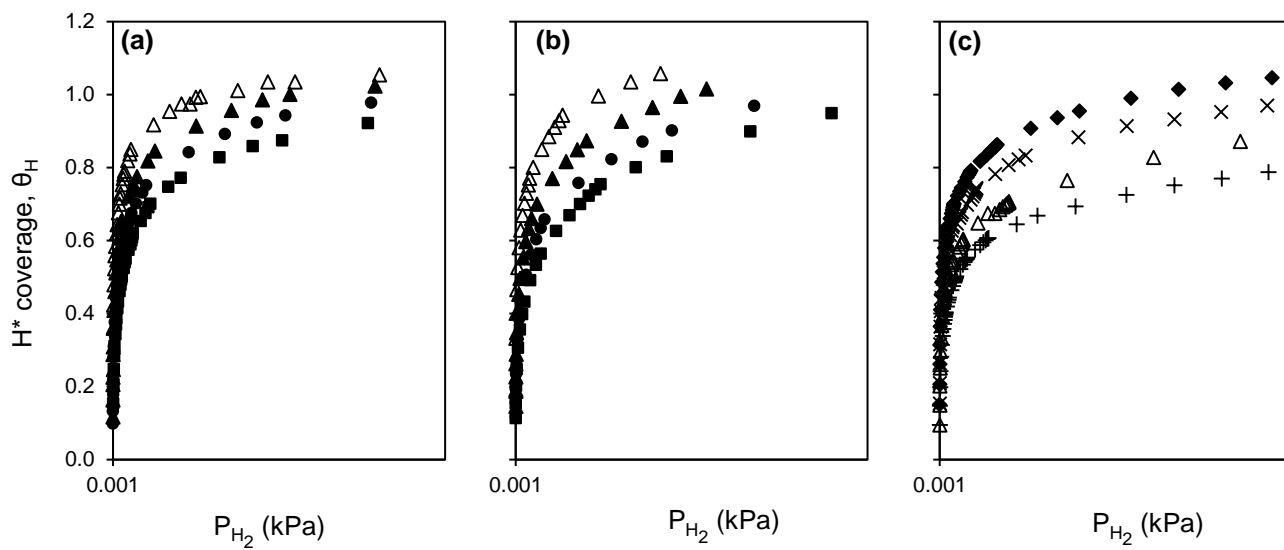


Figure S1. Adsorption isotherms for H₂ dissociative adsorption on Pt (1.6 % wt. Pt/Al₂O₃ 9.1 nm (a) and 3.0 nm (b) mean cluster size; 1 % wt. Pt/SiO₂ 1.6 nm mean cluster size (c)) at 673 K (■), 623 K (●), 573 K (▲), 548 K (+), 523 K (△), 498 K (×) and 473 K (◆).

Section S4. Temperature Dependence of the Heat of Adsorption and Entropy Loss

S2.1. Change in enthalpy:

The temperature dependence of the isosteric heat of adsorption as a consequence of the change in enthalpy upon H₂ dissociative adsorption is given by the difference in heat capacities ($-\Delta\bar{C}_p$) between the gas phase (C_g) and the adsorbate (\bar{C}_a):

$$\left(\frac{\partial Q_H}{\partial T}\right)_{\theta_H} = \left(\frac{\partial H_g}{\partial T}\right) - 2\left(\frac{\partial \bar{H}_a}{\partial T}\right) = (C_g - 2\bar{C}_a)_p = -\Delta\bar{C}_p \quad (S30)$$

where, H_g and \bar{H}_a are the molar gas-phase enthalpy and the differential adsorbed phase enthalpy, respectively. The isosteric heat of adsorption ($(Q_H)_{\theta_H}$) is related to the differential heat of adsorption (Q_H) by: $(Q_H)_{\theta_H} = Q_H + RT$.

Local (S31a) and mobile (S31b) dissociative H₂ adsorption can be described by the following expressions:

$$\theta_H = \frac{K_H^{1/2} P_{H_2}^{1/2}}{1 + K_H^{1/2} P_{H_2}^{1/2}} \quad K_H P_{H_2} = \left(\frac{\theta_H}{1 - \theta_H}\right)^2 \quad (S31a)$$

$$\theta_H = K_H^{1/2} P_{H_2}^{1/2} \quad \text{or} \quad K_H P_{H_2} = \left(\left(\frac{\theta_H}{1 - \theta_H}\right) \exp\left(\frac{\theta_H}{1 - \theta_H}\right)\right)^2 \quad (S31b)$$

where P_{H_2} is the hydrogen pressure at equilibrium and K_H is the equilibrium constant given in both cases by:

$$K_H = K_0 \exp\left(\frac{E}{RT}\right) \quad (S32)$$

in which E is the potential minimum energy of an adsorbed molecule and K_0 can be estimated by statistical mechanics as:

$$K_0(T) = \frac{(q_a(T))^2}{Q_{\text{gas}}(T)} \quad (S33)$$

q_a and Q_{gas} are the molecular partition functions of the adsorbed (H^*) and gas (H_2) phases, respectively. Substituting Equations (S31a-b), (S32) and (S33) into Equation (4) gives:

$$(Q_H)_{\theta_H} = E - RT^2 \left(\frac{\partial \ln K_0(T)}{\partial(T)}\right)_{\theta_H} \quad (S34)$$

The partition function for H₂ in the gas phase is given by the product of the partition functions for the different degrees of freedom (vibrational ($q_{g,v}$), translational ($q_{g,t}$) and rotational ($q_{g,r}$):

$$Q_{\text{gas}}(T) = q_{g,v} q_{g,t} q_{g,r} \quad (S35)$$

$$q_{g,v} = \frac{\exp\left(\frac{1}{2\tau_{g,v}}\right)}{\exp\left(\frac{1}{\tau_{g,v}}\right) - 1} \quad (\text{S36a})$$

$$\text{with } \tau_{g,v} = \frac{T}{\Phi_{g,v}} \text{ and } \Phi_{g,v} = \frac{h\nu_g}{\kappa}$$

$$q_{g,t} = \frac{(2\pi m\kappa T)^{3/2}}{h^3} V \quad (\text{S36b})$$

$$q_{g,r} = \frac{8\pi^2 I\kappa T}{\sigma h^2} = \tau_{g,r} \quad (\text{S36c})$$

$\tau_{g,v}$ is the vibrational temperature, ν_g is the vibrational frequency of H_2 in the gas phase, h and κ are the Planck's and Boltzmann's constants, respectively. m is the mass of H_2 , V is the volume, I is the moment of inertia, σ is the symmetry factor (2 for H_2) and $\tau_{g,v}$ is the rotational temperature.

The partition function of H^* (q_a) is given by the product of contributions of the molecular partition function vibrational ($q_{a,v}$) and translational ($q_{a,t}$):

$$q_a(T) = q_{a,v} q_{a,t} \quad (\text{S37})$$

For the adsorbate phase we have considered two different extreme cases for the state of H^* : localized immobile adsorption and mobile adsorption.

Localized Immobile Adsorption:

For localized immobile adsorption, we approximate translational DOF as two additional vibrations such that H^* has three vibrational degrees of freedom, one normal to the surface and two parallel:

$$q_a(T) = q_{a,v} = \prod_{i=1}^3 \frac{\exp\left(\frac{1}{2\tau_{a,vi}}\right)}{\exp\left(\frac{1}{\tau_{a,vi}}\right) - 1} \quad (\text{S38})$$

$$\text{with } \tau_{a,vi} = \frac{T}{\Phi_{a,vi}} \text{ and } \Phi_{a,vi} = \frac{h\nu_{ai}}{\kappa}$$

ν_{gi} is the vibrational frequency i for adsorbed hydrogen (H^*), $\tau_{a,vi}$ is the vibrational temperature for the ν_{gi} . Substituting Equations (S32) and (S35) in Equation (S33), the K_0 for immobile adsorption is:

$$K_0(T) = \frac{h^3}{\kappa T (2\pi m \kappa T)^{3/2}} \frac{\left(\Omega_{el} \prod_{i=1}^3 \frac{\exp\left(\frac{1}{2\tau_{a,vi}}\right)}{\exp\left(\frac{1}{\tau_{a,vi}}\right) - 1} \right)^2}{\tau_{g,r} \frac{\exp\left(\frac{1}{2\tau_{g,v}}\right)}{\exp\left(\frac{1}{\tau_{g,v}}\right) - 1}} \quad (S39)$$

Substituting Equations (S39) in Equation (S34) gives the isosteric heat of adsorption as a function of vibrational and rotational temperatures:

$$(Q_H)_{\theta_H} = E - RT \left(-\frac{7}{2} + \frac{1}{\tau_{g,v}} \left(\frac{1}{2} - \frac{\exp\left(\frac{1}{\tau_{g,v}}\right)}{\exp\left(\frac{1}{\tau_{g,v}}\right) - 1} \right) + \sum_{i=1}^3 \frac{1}{\tau_{a,vi}} \left(\frac{2 \exp\left(\frac{1}{\tau_{a,vi}}\right)}{\exp\left(\frac{1}{\tau_{a,vi}}\right) - 1} \right) \right) \quad (S40)$$

Whose derivative with respect to the temperature at constant H^* coverage gives the difference in heat capacities between the adsorbate and the gas phase:

$$-\Delta \bar{C}_p = -R \left(-\frac{7}{2} + \frac{1}{\tau_{g,v}^2} \left(\frac{\exp\left(\frac{1}{\tau_{g,v}}\right)}{\exp\left(\frac{1}{\tau_{g,v}}\right) - 1} - \frac{\exp\left(\frac{2}{\tau_{g,v}}\right)}{\left(\exp\left(\frac{1}{\tau_{g,v}}\right) - 1\right)^2} \right) + \sum_{i=1}^3 \frac{2}{\tau_{a,vi}^2} \left(\frac{\exp\left(\frac{2}{\tau_{a,vi}}\right)}{\left(\exp\left(\frac{1}{\tau_{a,vi}}\right) - 1\right)^2} - \frac{\exp\left(\frac{1}{\tau_{a,vi}}\right)}{\exp\left(\frac{1}{\tau_{a,vi}}\right) - 1} \right) \right) \quad (S41)$$

Mobile Adsorption:

For the mobile adsorption, in which H^* vibrates normal to the surface and moves without constraints in the x and y directions parallel to the surface, the partition function of the adsorbate is given by:

$$q_a(T) = \Omega_{el} q_{a,v} q_{a,t}^{2D} = \Omega_{el} \frac{\exp\left(\frac{1}{2\tau_{a,v}}\right)}{\exp\left(\frac{1}{\tau_{a,v}}\right) - 1} \left(\frac{a^2 2\pi m \kappa T}{h^2} \right) \quad (S42)$$

where, a^2 is the unit area for the 2-dimensional adsorbed phase translational partition function.

K_0 for mobile adsorption is obtained by substituting Equations (S35) and (S42) in Equation (S33):

$$K_0(T) = \frac{(\Omega_{cl} a^2)^2 (2\pi m \kappa T)^{1/2}}{\kappa T h} \frac{\left(\frac{\exp\left(\frac{1}{2\tau_{a,v}}\right)}{\exp\left(\frac{1}{\tau_{a,v}}\right) - 1} \right)^2}{\tau_{g,r} \frac{\exp\left(\frac{1}{2\tau_{g,v}}\right)}{\exp\left(\frac{1}{\tau_{g,v}}\right) - 1}} \quad (S43)$$

The isosteric heat of hydrogen adsorption is then given by (substituting Equation (S43) into Equation (S34)):

$$(Q_H)_{\theta_H} = E - RT \left(-\frac{3}{2} + \frac{1}{\tau_{g,v}} \left(\frac{1}{2} - \frac{\exp\left(\frac{1}{\tau_{g,v}}\right)}{\exp\left(\frac{1}{\tau_{g,v}}\right) - 1} \right) + \frac{1}{\tau_{a,v}} \left(\frac{2 \exp\left(\frac{1}{\tau_{a,v}}\right)}{\exp\left(\frac{1}{\tau_{a,v}}\right) - 1} - 1 \right) \right) \quad (S44)$$

And the difference in heat capacities:

$$-\Delta \bar{C}_p = -R \left(-\frac{3}{2} + \frac{1}{\tau_{g,v}^2} \left(\frac{\exp\left(\frac{1}{\tau_{g,v}}\right)}{\exp\left(\frac{1}{\tau_{g,v}}\right) - 1} - \frac{\exp\left(\frac{2}{\tau_{g,v}}\right)}{\left(\exp\left(\frac{1}{\tau_{g,v}}\right) - 1\right)^2} \right) + \frac{2}{\tau_{a,v}^2} \left(\frac{\exp\left(\frac{2}{\tau_{a,v}}\right)}{\left(\exp\left(\frac{1}{\tau_{a,v}}\right) - 1\right)^2} - \frac{\exp\left(\frac{1}{\tau_{a,v}}\right)}{\exp\left(\frac{1}{\tau_{a,v}}\right) - 1} \right) \right) \quad (S45)$$

S2.2. Loss in entropy:

The temperature dependence of the loss in entropy as a result of the change in enthalpy with temperature can be estimated by applying a similar approach to that described above for changes in enthalpy.

The difference in heat capacities ($-\Delta \bar{C}_p$) between the gas phase (C_g) and the adsorbate (\bar{C}_a) can be also derived from the derivative of the molar and differential entropy of the gas and adsorbed phases at constant pressure:

$$-\Delta \bar{C}_p = T \left(\frac{\partial S_g}{\partial T} \right)_p - 2T \left(\frac{\partial \bar{S}_a}{\partial T} \right)_p = -T \left(\frac{\partial \Delta S_H}{\partial T} \right)_p \quad (S46)$$

which is equal to the change in heat of adsorption with the temperature. Thus the change in entropy with temperature is given by:

$$-\left(\frac{\partial \Delta S_H}{\partial T} \right)_p = \frac{-\Delta \bar{C}_p}{T} = \frac{1}{T} \left(\frac{\partial Q_H}{\partial T} \right)_\theta \quad (S47)$$

Section S5. Local Langmuir Isotherm for Non-Uniform Surfaces: Q_H Approach

The dissociative adsorption on a non-uniform surface can be described, regardless of the model, as a function of $(Q_H)_{\theta_H}$ or ΔG_H (change in Gibbs free energy), P_{H_2} and temperature (T) [1]. Next, we derive the adsorption isotherms that describe the experimental data for H_2 adsorption on Pt/ Al_2O_3 (9.1 nm and 3.0 nm Pt clusters) at 523-673 K for the whole range of H^* coverages registered ($\theta_H=0.2-0.8$) by applying site energy distribution treatments. Here, we illustrate the treatment for heterogeneous surfaces which have the probability of finding adsorption sites with a heat of adsorption between $(Q_H)_{\theta_H}$ and $(Q_H)_{\theta_H} + d(Q_H)_{\theta_H}$ that is described by the distribution function $f(Q_H)dQ_H$ (site Q_H distribution treatment). As (θ_H) represent the sum of all those different adsorptions (with different Q_H), the H^* coverages are then given by:

$$\theta_H = \int_0^{\infty} f(Q_H) \theta(Q_H) dQ_H \quad (S48)$$

where $\theta(Q_H)$ can be taken as the local Langmuir isotherm for H_2 dissociative adsorption on sites with heat of adsorption equal to $(Q_H)_{\theta_H}$:

$$\theta(Q_H) = \frac{(K_H P_{H_2})^{1/2}}{1 + (K_H P_{H_2})^{1/2}} \quad (S49)$$

which can be written in terms of Q_H and ΔS_H of adsorption:

$$\theta(Q_H) = \frac{\left(e^{\left(\frac{\Delta S_H(Q_H)}{R} \right)} e^{\left(\frac{Q_H}{RT} \right)} \left(\frac{P_{H_2}}{P_0} \right) \right)^{1/2}}{1 + \left(e^{\left(\frac{\Delta S_H(Q_H)}{R} \right)} e^{\left(\frac{Q_H}{RT} \right)} \left(\frac{P_{H_2}}{P_0} \right) \right)^{1/2}} \quad (S50)$$

P_0 is the standard state pressure, taken as 101.325 kPa (1 atm), and ΔS_H is a linear function of Q_H (Fig. S2 for Plot of ΔS_H vs. $(Q_H)_{\theta_H}$):

$$\Delta S_H(Q_H) = -a (Q_H)_{\theta_H} + b \quad (S51)$$

where a and b are constants that come from the linear fitting of the ΔS_H vs. $(Q_H)_{\theta_H}$ data (Table S1). ΔS_H in this case comes from the Langmuir analysis of the adsorption data and does not include the configurational part of the entropy; K_H is defined as in Equation (S49). Isothermic heats of adsorption ($(Q_H)_{\theta_H}$) were obtained by the van't Hoff equation.

Table S1. Parameters for H₂ dissociative adsorption isotherm on Pt (1.6 % wt. Pt/Al₂O₃; 9.1 nm and 3.0 nm mean Pt cluster size) given by site $(Q_H)_{\theta_H}$ distribution treatment (Eq. S43).

Parameter	9.1 nm		3.0 nm	
	Initial ^a	Final ^b	Initial ^a	Final ^b
a (K ⁻¹) Eq. S5	0.0015	0.0017	0.0014	0.0014
b (J mol ⁻¹ K ⁻¹) Eq. S5	48.1	48.1	36.2	35.6
c (J mol ⁻¹) Eq. S7	86316	86316	94553	94553
d (J mol ⁻¹) Eq. S7	118350	118350	147830	147830
e (J mol ⁻¹) Eq. S7	73744	73744	91454	92596

^a Initial estimates for a and b from linear fitting of ΔS_H vs. $(Q_H)_{\theta_H}$ data (Eq. S51) and for c,d and e from quadratic fitting of $(Q_H)_{\theta_H}$ vs. θ_H data (Eq. S53)

^b Adjusted values after fitting of adsorption data with Equation (S55)

The site energy distribution $f(Q_H)$ is defined as:

$$f(Q_H) = \frac{d\theta_H}{dQ_H} \quad (S52)$$

which can be derived from the changes in $(Q_H)_{\theta_H}$ with H* coverage (Fig. 4a). We have interpolated between data points by considering that $(Q_H)_{\theta_H}$ changes with the square of θ_H as:

$$(Q_H)_{\theta_H} = c.\theta_H^2 - d.\theta_H + e \quad (S53)$$

where c, d and e are constants, that as first approximation are estimated from the quadratic fitting for the $(Q_H)_{\theta_H}$ vs. θ_H data (Table S1 for first estimates of these parameters). The distribution of energy site is then given by:

$$f(Q_H) = \frac{1}{\sqrt{d^2 - 4c.e + 4c.Q_H}} \quad (S54)$$

Substituting Equations (S31) and (S27) into Equation (S25) gives the H* coverages as a function of Q_H , P_{H_2} and T:

$$\theta_H(Q_H, P_{H_2}, T) = \int_{Q_{HMIN}}^{Q_{HMAX}} \left(\frac{1}{\sqrt{d^2 - 4c.e + 4c.Q_H}} \right) \frac{\left(e^{\left(\frac{b}{R}\right) \left(\frac{1-aT}{RT} Q_H\right)} \left(\frac{P_{H_2}}{P_0}\right) \right)^{1/2}}{1 + \left(e^{\left(\frac{b}{R}\right) \left(\frac{1-aT}{RT} Q_H\right)} \left(\frac{P_{H_2}}{P_0}\right) \right)^{1/2}} dQ_H \quad (S55)$$

in which, Q_{HMAX} and Q_{HMIN} are the maximum (at $\theta_H=0$) and minimum values of Q_H as indicated by the site energy distribution. The experimental values for θ_H as a function of P_{H_2} at each temperature are fitted using Equation (S55), and the parameters d, c and e are obtained (first estimates were taken from the

quadratic fitting of $(Q_H)_{\theta_H}$ vs. θ_H data, Eq. S53). Equation (S55) accurately describes the data for H₂ adsorption on Pt at 523-673 K, as shown by the fitting to the H₂ adsorption data (dotted lines Fig. S3; 9.1 nm Pt clusters; Fig. S4 for 3.0 nm Pt clusters), the parity plot of the θ_H experimental vs. θ_H calculated by Equation (S32) (Fig. S5 (a) 9.1 nm Pt clusters and (b) 3.0 nm Pt clusters) and the $(Q_H)_{\theta_H}$ vs. θ_H plot given by Equation (S53) with c, d and e parameters from fitting with Equation (S55) (Fig. S6 for Pt with 9.1 and 3.0 Pt cluster size).

The analogous treatment considering the distribution function $f(\Delta G_H)d\Delta G_H$ that describes the probability of finding adsorption sites with change in Gibbs free energy between ΔG_H and $\Delta G_H + d\Delta G_H$ was also considered and illustrated in the section S5. This treatment allows the determination of the H₂ isotherm without separating the entropy and enthalpy components of the equilibrium constant, which can be then obtained from the variation of ΔG_H with temperature. Site enthalpy and entropy distributions obtained after the site ΔG_H distribution treatment are consistent with those obtained by the Van't Hoff equation and the site $(Q_H)_{\theta_H}$ distribution treatment described above (Section S5, Fig. S12).

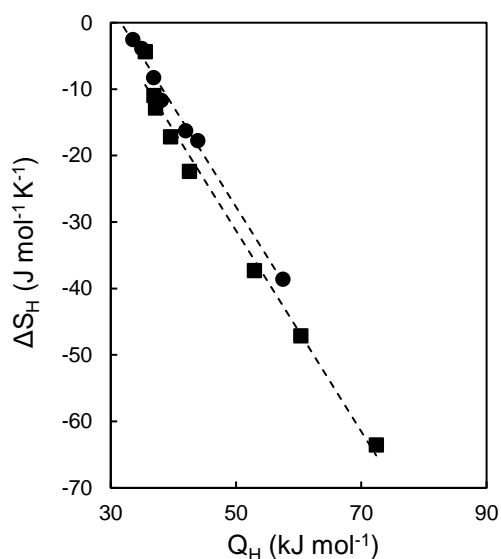


Figure S2. Loss in entropy (ΔS_H) upon H₂ dissociative adsorption on Pt (1.6 % wt. Pt/Al₂O₃; 3.0 nm (■) and 9.1 nm (●) mean cluster size) as a function of the isosteric heat of adsorption (Q_H). Dotted lines from linear fitting.

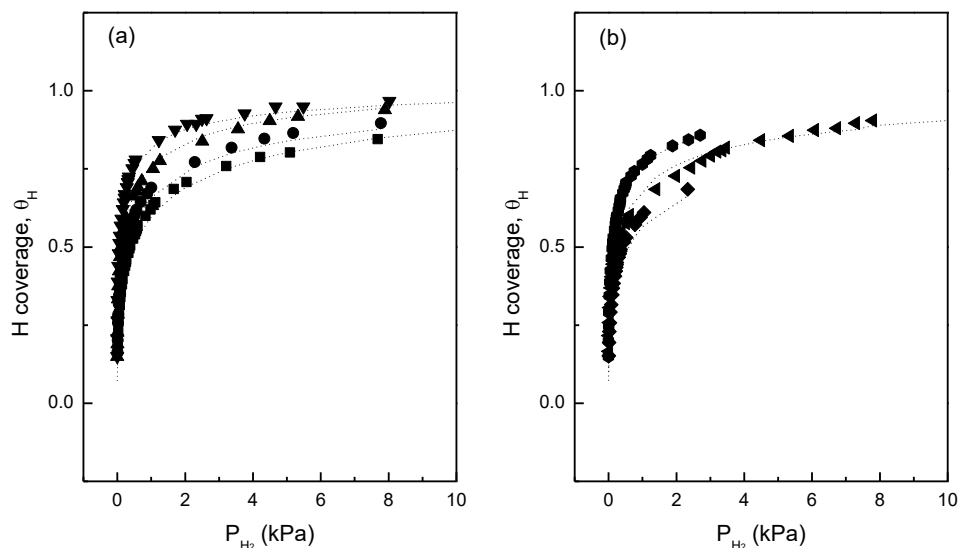


Figure S3. Adsorption isotherms for H_2 dissociative adsorption on 1.6 % wt. $\text{Pt}/\text{Al}_2\text{O}_3$ (9.1 nm mean cluster size) at (a) 673 K (■), 623 K (●), 573 K (▲) and 523 K (▼), and (b) 648 K (◆), 598 K (◄) and 548 K (⬤). Dotted lines fitting from site Q_{H} distribution treatment (Eq. S55).

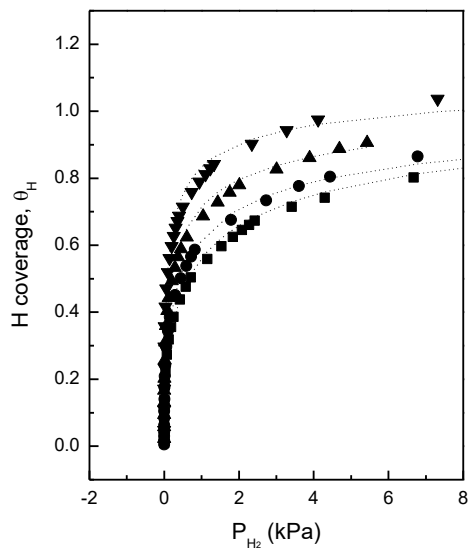


Figure S4. Adsorption isotherms for H_2 dissociative adsorption on 1.6 % wt. $\text{Pt}/\text{Al}_2\text{O}_3$ (3.0 nm mean cluster size) at 673 K (■), 623 K (●), 573 K (▲) and 523 K (▼). Dotted lines fitting from site energy distribution treatment (Eq. S55).

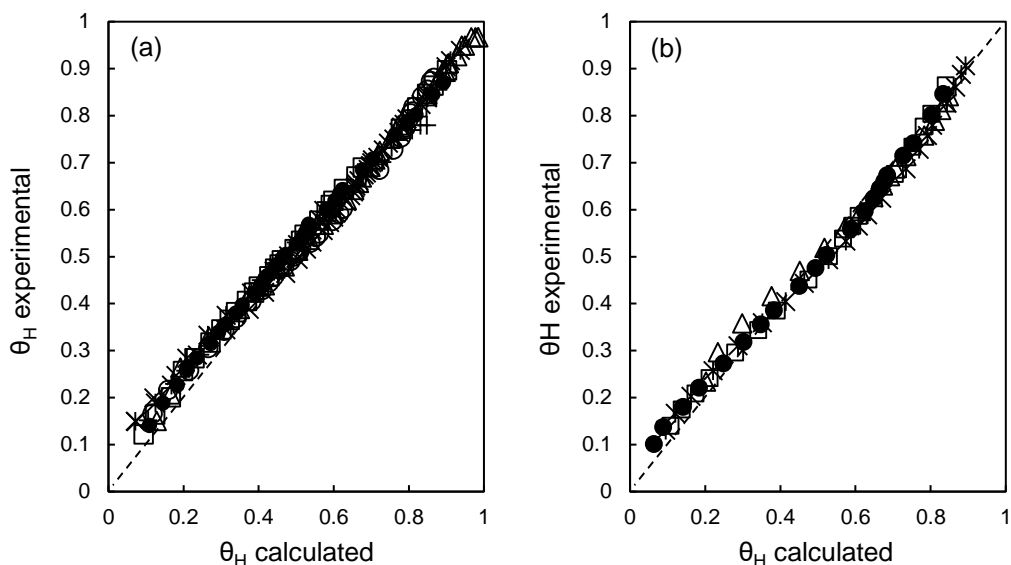


Figure S5. Parity plot of the θ_H experimental vs. θ_H calculated by site Q_H distribution treatment (Eq. (S55)) for H_2 dissociative adsorption on 1.6 % wt. Pt/ Al_2O_3 ((a) 9.1 nm and (b) 3.0 mean cluster size) at 673 K (●), 648 K (+), 623 K (□), 598 K (○), 573 K (*), 548 K (x) and 523 K (△).

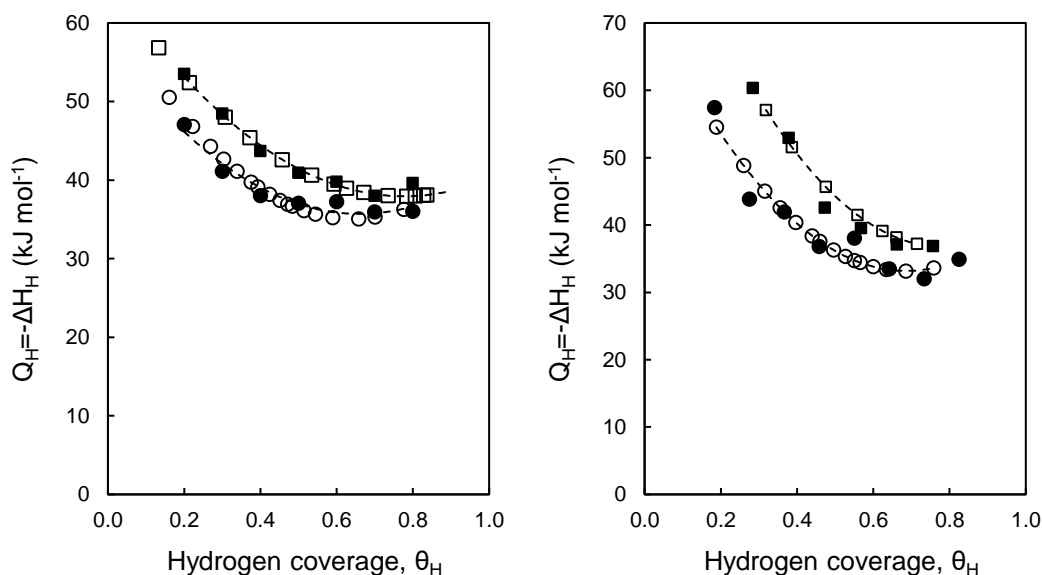


Figure S6. Isosteric heat of adsorption ($(Q_H)_{\theta_H}$; Eq. (S53)) as a function of H^* coverage (θ_H) during H_2 dissociative adsorption on 1.6 % wt. Pt/ Al_2O_3 (3.0 nm (□) and 9.1 nm (○) mean cluster size) after fitting of adsorption data with isotherm derived by the site Q_H distribution treatment (Eq. (S55); 523-673 K); Q_H for Pt samples with 3.0 nm (■) and 9.1 nm (●) mean cluster size obtained by the van't Hoff equation are plotted here for comparison.

Section S5. Local Langmuir Isotherm for Non-Uniform Surfaces: ΔG Approach

The isotherm for H₂ adsorption on a heterogeneous surface with a probability of finding adsorption sites with ΔG_H between ΔG_H and $\Delta G_H + d \Delta G_H$, described by the distribution function $f(\Delta G_H)d\Delta G_H$, and with hydrogen coverages (θ_H), is given by:

$$\theta_H(\Delta G_H, P_{H_2}, T) = \int_0^\infty f(\Delta G_H) \theta(\Delta G_H) d\Delta G_H \quad (S56)$$

where $\theta(\Delta G_H)$ is the local Langmuir isotherm

$$\theta(\Delta G_H) = \frac{\left(e^{\left(\frac{-\Delta G_H}{RT} \right) \left(\frac{P_{H_2}}{P_0} \right)} \right)^{1/2}}{1 + \left(e^{\left(\frac{-\Delta G_H}{RT} \right) \left(\frac{P_{H_2}}{P_0} \right)} \right)^{1/2}} \quad (S57)$$

in which, P_0 is the standard state pressure, taken as 1 atm (101.325 kPa).

The site energy distribution $f(\Delta G_H)$ at each temperature is defined as:

$$f(\Delta G_H) = \frac{d\theta_H}{d\Delta G_H} \quad (S58)$$

which can be derived from the changes in $(\Delta G_H)_{\theta_H, T}$ with H* coverage and temperature (Fig. S7).

$(\Delta G_H)_{\theta_H, T}$ as a function of H* coverage and temperature was calculated from the following equation:

$$(\Delta G_H)_{\theta_H, T} = -RT \ln \left[\frac{P_0}{P_{H_2}} \left(\frac{\theta_H}{1 - \theta_H} \right)^2 \right] \quad (S59)$$

$(\Delta G_H)_{\theta_H, T}$ changes with the square of θ_H as:

$$(\Delta G_H)_{\theta_H, T} = -c.\theta_H^2 + d.\theta_H - e \quad (S60)$$

where c, d and e are constants that are estimated from the quadratic fitting for the $(\Delta G_H)_{\theta_H, T}$ vs. θ_H data (Tables S2-S3).

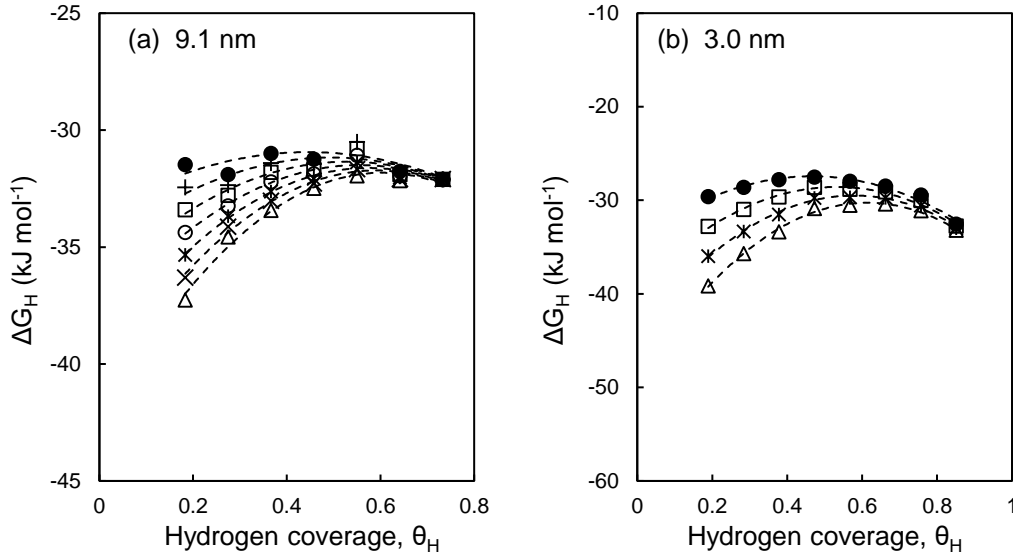


Figure S7. Change in Gibbs free energy (ΔG_H) as a function of the H^* coverage (θ_H) during H_2 dissociative adsorption on Pt (1.6 % wt. Pt/ Al_2O_3), (a) 9.1 nm and (b) 3.0 nm mean cluster diameter) at 673 K (●), 648 K (+), 623 K (□), 598 K (○), 573 K (*), 548 K (×) and 523 K (Δ).

The distribution of $(\Delta G_H)_{\theta_H, T}$ is then given by:

$$f(\Delta G_H) = \frac{1}{\sqrt{d^2 - 4c.e - 4c.\Delta G_H}} \quad (S61)$$

Substituting Equation (S57) and (S61) into Equation (S56) gives the H^* coverages as a function of ΔG_H , P_{H_2} and T:

$$\theta_H(\Delta G_H, P_{H_2}, T) = \int_{\Delta G_{HMIN}}^{\Delta G_{HMAX}} \left(\frac{1}{\sqrt{d^2 - 4c.e - 4c.\Delta G_H}} \right) \left(\frac{\left(e^{\left(\frac{-\Delta G}{RT} \right) \left(\frac{P_{H_2}}{P_0} \right)^{1/2}} \right)}{1 + \left(e^{\left(\frac{-\Delta G}{RT} \right) \left(\frac{P_{H_2}}{P_0} \right)^{1/2}} \right)} \right) d\Delta G_H \quad (S62)$$

in which, ΔG_{HMAX} and ΔG_{HMIN} are the maximum (at $\theta_H=0$) and minimum values of ΔG_H as indicated by the site energy distribution at each temperature. The experimental values for θ_H as a function of P_{H_2} at each temperature are fitted using Equation (S62), and the parameters d , c and e are optimized. Equation (S62) accurately describes the data for H_2 adsorption on Pt at 523-673 K, as shown by the fitting of the data for H_2 adsorption on Pt (dotted lines Fig. S8-9) and by the parity plot of the θ_H experimental vs. θ_H calculated (Eq. (S62), Fig. S10).

The enthalpy (Q_H) and entropy components (ΔS_H) of the change in Gibbs free energy were then obtained from linear fitting of ΔG_H vs. T data at each H^* coverage ($(\Delta G_H)_{\theta_H, T} = Q_H - \Delta S_H T$; Fig. S11), where the slope gives the loss in entropy upon adsorption and the intercept gives the isosteric heat of adsorption.

Figure S12 shows the isosteric heat of adsorption and the loss in entropy as a function of the H* coverage, which are consistent with those found by the Van't Hoff equation and the site $(Q_H)_{\theta_H}$ distribution treatment.

Table S2. Parameters for H₂ dissociative adsorption isotherm on Pt (1.6 % wt. Pt/Al₂O₃; 9.1 nm mean cluster size) given by site ΔG_H distribution treatment (Eq. S62).

T(K)	Parameter	c (J mol ⁻¹)		d (J mol ⁻¹)		e (J mol ⁻¹)	
		Initial ^a	Final ^b	Initial ^a	Final ^b	Initial ^a	Final ^b
	673	13263	13263	11827	11827	33577	33577
	648	15936	15936	15750	15750	35063	35063
	623	18609	18609	19674	19674	36549	36549
	598	21282	21282	23597	23597	38036	38036
	573	23956	23956	27521	27521	39522	39522
	548	26629	26629	31444	31444	41008	41008
	523	29302	29302	35368	35368	42494	42494

^a Initial estimates for c, d and e from quadratic fitting of (ΔG_H) vs. θ_H data (Fig. S7; Eq. S60)
^b Adjusted values after fitting of adsorption data with Equation (S62)

Table S3. Parameters for H₂ dissociative adsorption isotherm on Pt (1.6 % wt. Pt/Al₂O₃; 3.0 nm mean cluster size) given by site ΔG_H distribution treatment (Eq. S62).

T(K)	Parameter	c (J mol ⁻¹)		d (J mol ⁻¹)		e (J mol ⁻¹)	
		Initial ^a	Final ^b	Initial ^a	Final ^b	Initial ^a	Final ^b
	673	31365	31365	29223	29223	34236	34236
	623	37527	37527	39873	39873	39168	39168
	573	43689	43689	50522	50522	44100	44100
	523	49851	49851	61171	61171	49032	49032

^a Initial estimates for c, d and e from quadratic fitting of (ΔG_H) vs. θ_H data (Fig. S7; Eq. S60)
^b Adjusted values after fitting of adsorption data with Equation (S62)

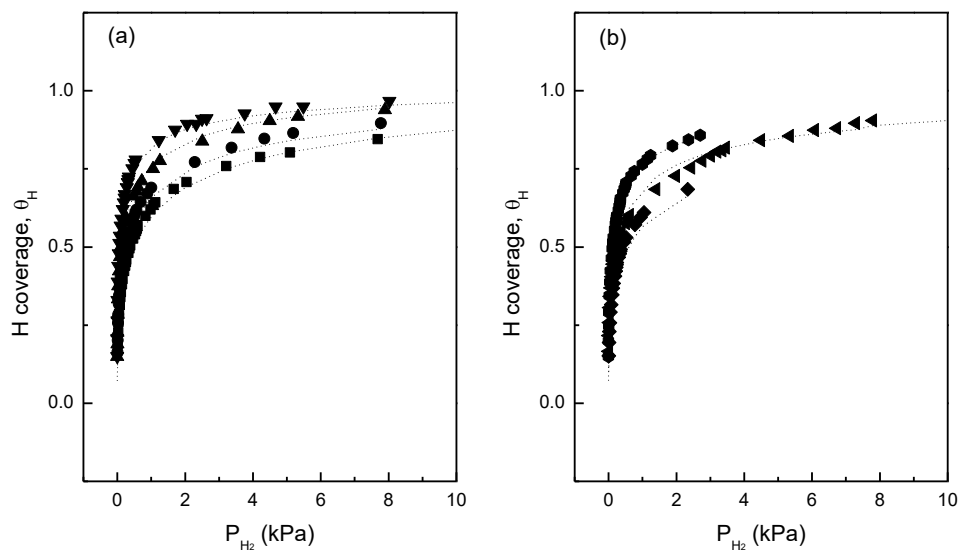


Figure S8. Adsorption isotherms for H₂ dissociative adsorption on 1.6 % wt. Pt/Al₂O₃ (9.1 nm mean cluster size) at (a) 673 K (■), 623 K (●), 573 K (▲) and 523 K (▼), and (b) 648 K (◆), 598 K (◄) and 548 K (●). Dotted lines fitting from site ΔG_H distribution treatment.

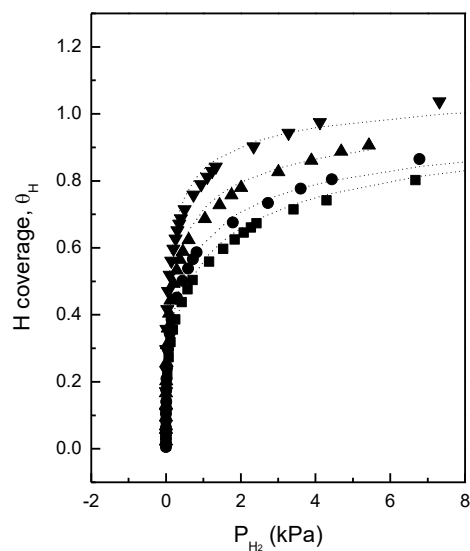


Figure S9. Adsorption isotherms for H₂ dissociative adsorption on 1.6 % wt. Pt/Al₂O₃ (9.1 nm mean cluster diameter) at (a) 673 K (■), 623 K (●), 573 K (▲) and 523 K (▼). Dotted lines fitting from site ΔG_H distribution treatment.

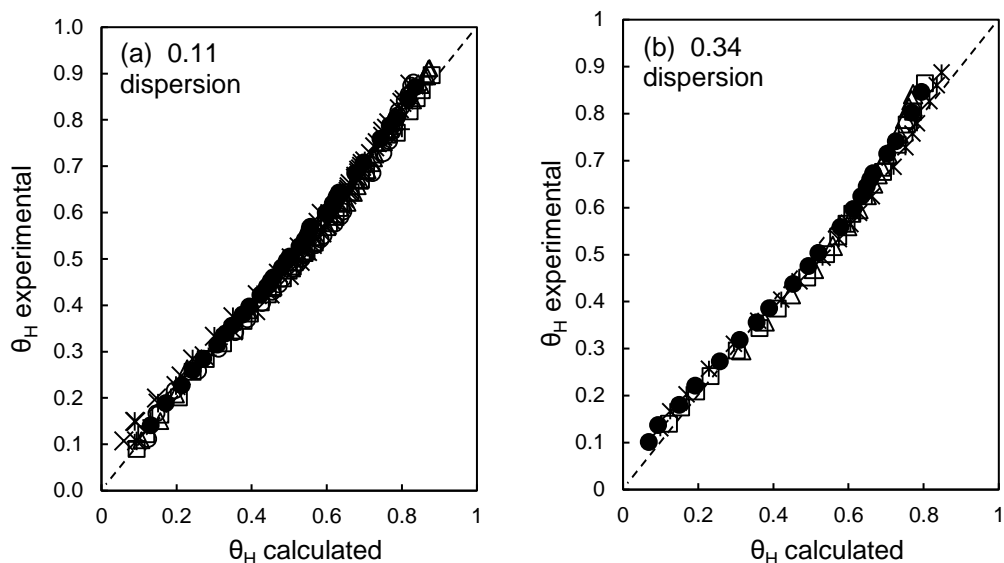


Figure S10. Parity plot of the θ_H experimental vs. θ_H calculated by site ΔG_H distribution treatment (Eq. S39) for H_2 dissociative adsorption on 1.6 % wt. Pt/ Al_2O_3 ((a) 9.1 nm and (b) 3.0 nm Pt cluster size) at 673 K (●), 648 K (+), 623 K (□), 598 K (○), 573 K (*), 548 K (×) and 523 K (△).

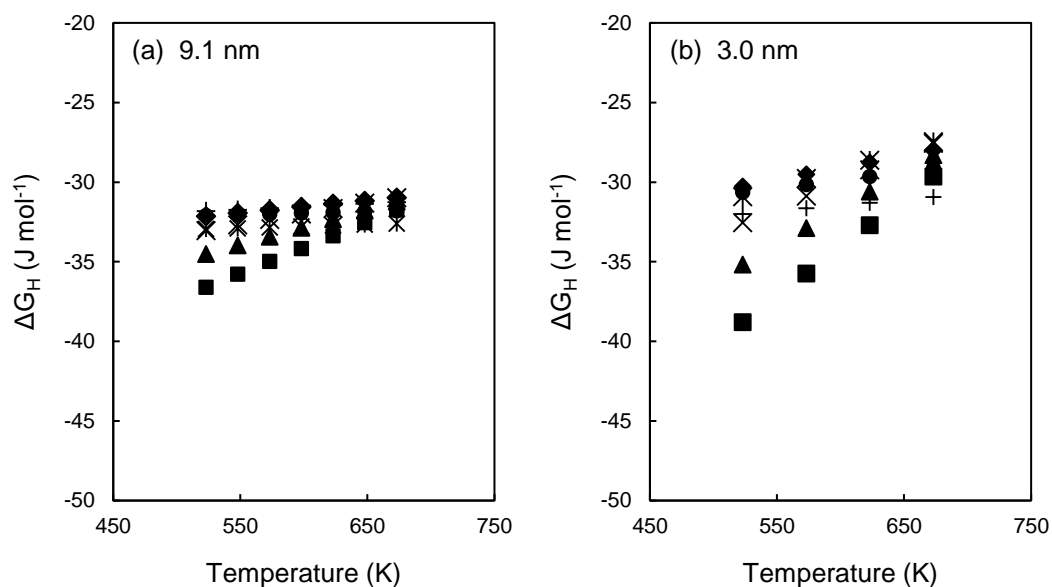


Figure S11. Change in Gibbs free energy (ΔG_H) upon H_2 dissociative adsorption on 1.6 % wt Pt/ Al_2O_3 ((a) 9.1 nm and (b) 3.0 nm mean Pt cluster size) as a function of the temperature at 0.2 (■), 0.3 (▲), 0.4 (×), 0.5 (*), 0.6 (◆), 0.7 (●) and 0.8 (+) H^* coverage (θ_H); obtained from the site ΔG_H distribution treatment.

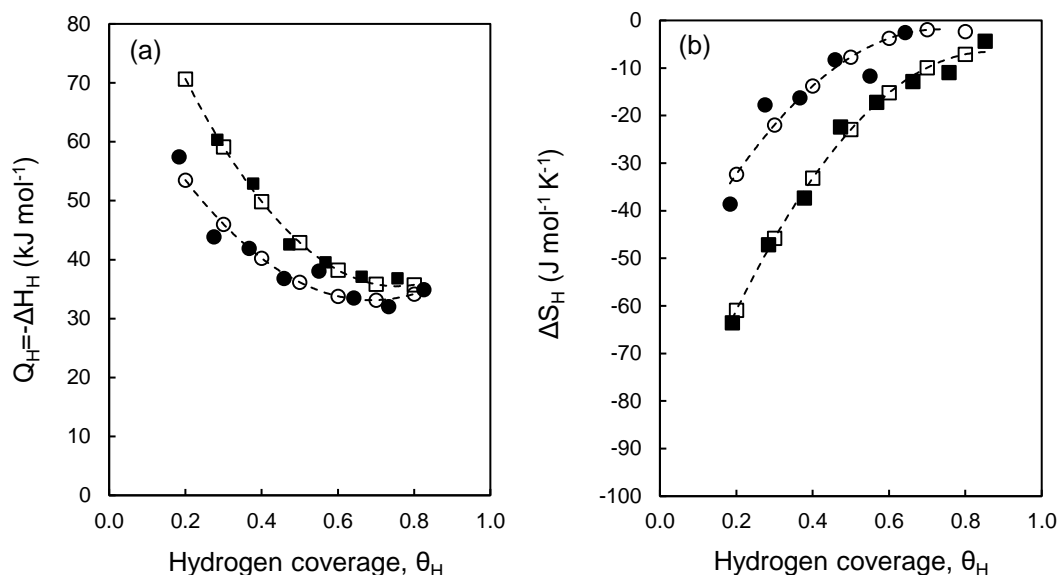


Figure S12. Isosteric heat of adsorption ((a); Q_H ; from intercept Fig. S11) and loss in entropy ((b); ΔS_H ; from slope Fig. S11) as a function of H^* coverage (θ_H) during H_2 dissociative adsorption on 1.6 % wt. Pt/ Al_2O_3 (3.0 nm (■) and 9.1 nm (●) mean Pt cluster size) after fitting of adsorption data with isotherm derived by the site ΔG_H distribution treatment (Eq (S62); 523-673 K); Q_H and ΔS_H for Pt samples with 3.0 nm (□) and 9.1 nm (○) mean cluster size obtained by the Van't Hoff equation are plotted here for comparison.

Section S6. Diffusion Barrier—Frustrated Translations

Figure S13 shows the translational entropy calculated as frustrated translations, where the 2-D translation is treated as two identical vibrations parallel to the surface (v_{ft}). These vibrations can be estimated as harmonic vibrations [2]:

$$v_{ft} = \sqrt{\frac{E_d}{2\lambda_d^2 m_H}} \quad (\text{S63})$$

where E_d is the diffusion barrier, λ_d is the nearest-neighbor Pt-Pt distance (0.277 nm), and m_H is the H^* mass.

The entropy for the frustrated translations ($S_{a,frustrated}$) for H^* is then calculated from the vibrational component given by Equation (S60).

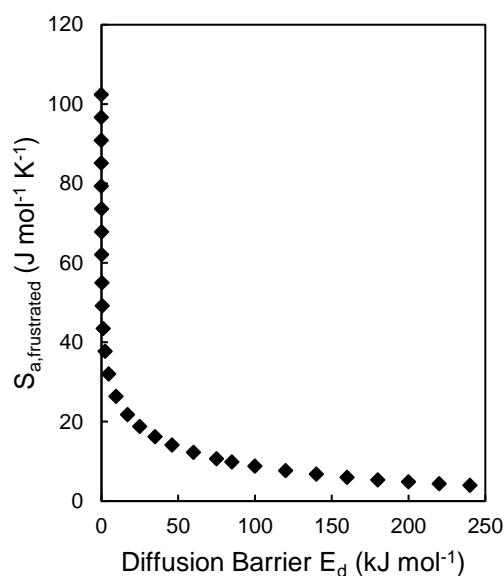


Figure S13. Frustrated translational entropy ($S_{a,frustrated}$) for H^* as a function of the diffusion barrier for lateral movement across the Pt surface (598 K).

Section S7. Detailed DFT Calculation Results

Table S4. Adsorption energies for H* on a Pt (111) surface at 593 K using the RPBE exchange-correlation functional. Table SXX in the SI shows the same data using the PW-91 functional.

<i>Unit</i> <i>Cell</i>	<i>H*</i> <i>Covg.</i>	<i>Mode</i>	$\Delta E_{0,H}$ kJ mol ⁻¹	$\Delta ZPVE_H$ kJ mol ⁻¹	$\Delta H_{vib,H}$ kJ mol ⁻¹	$\Delta S_{vib,H}$ J mol ⁻¹ K ⁻¹	$\Delta G_{vib,H}$ kJ mol ⁻¹	ΔH_H kJ mol ⁻¹	$Q_{H_2}^a$ kJ mol ⁻¹	ΔS_H^b J mol ⁻¹ K ⁻¹	$S_{H^*}^c$ J mol ⁻¹ K ⁻¹	ΔG_H kJ mol ⁻¹	<i>Frequencies</i> ^d cm ⁻¹		
1 × 1	1	atop	-20	5	6	18	-5	-17	35	-57	18	17	2249	401	400
1 × 1	1	fcc	-19	1	5	14	-3	-21	42	-62	14	15	1189	601	599
1 × 1	1	hcp	-14	1	6	15	-3	-17	33	-60	15	19	1197	543	538
1 × 2	1/2	atop	-26	5	6	19	-5	-23	46	-57	19	10	2258	381	379
1 × 2	1/2	fcc	-24	1	5	14	-3	-27	53	-61	14	10	1144	612	581
1 × 2	1/2	hcp	-20	0	6	15	-3	-23	46	-60	15	13	1151	560	532
1 × 3	1/3	atop	-26	5	6	19	-5	-24	47	-56	19	10	2260	376	374
1 × 3	1/3	fcc	-26	1	5	14	-3	-29	57	-61	14	8	1131	621	585
1 × 3	1/3	hcp	-22	0	6	15	-3	-24	49	-60	15	11	1142	559	528
2 × 2	1/4	atop	-29	5	6	19	-5	-27	53	-56	19	7	2259	369	369
2 × 2	1/4	fcc	-27	1	5	14	-3	-30	59	-61	14	7	1100	607	604
2 × 2	1/4	hcp	-23	0	6	15	-3	-26	52	-60	15	10	1115	548	547
2 × 3	1/6	atop	-29	5	6	19	-5	-27	53	-56	19	7	2258	366	363
2 × 3	1/6	fcc	-28	1	5	14	-3	-30	61	-61	14	6	1093	601	596
2 × 3	1/6	hcp	-23	0	6	16	-3	-26	53	-60	16	9	1111	538	533
3 × 3	1/9	atop	-29	5	6	20	-5	-26	52	-56	20	7	2258	360	358
3 × 3	1/9	fcc	-28	1	5	14	-3	-31	61	-61	14	6	1086	601	600
3 × 3	1/9	hcp	-23	0	6	16	-3	-26	52	-60	16	9	1103	537	536
3 × 4	1/12	atop	-30	5	6	19	-5	-27	54	-56	19	6	2263	366	364
3 × 4	1/12	fcc	-29	1	5	14	-3	-31	62	-61	14	5	1084	603	598
3 × 4	1/12	hcp	-24	0	6	16	-3	-27	54	-60	16	9	1102	540	530
4 × 4	1/16	atop	-31	5	6	19	-5	-28	56	-56	19	5	2262	369	368
4 × 4	1/16	fcc	-29	1	5	14	-3	-32	63	-61	14	5	1086	593	588
4 × 4	1/16	hcp	-24	0	6	16	-4	-27	54	-59	16	8	1102	524	523
4 × 4	1	atop	-10	6	6	16	-4	-7	15	-59	16	28	2241	451	450
4 × 4	1	fcc	-9	2	5	13	-3	-11	22	-63	13	26	1164	651	649
4 × 4	1	hcp	-2	1	5	14	-3	-5	9	-62	14	32	1162	610	607

^a $Q_{H_2} = -2(\Delta H_H)$ ^b Gas-phase H₂ has S_{trans} of 132 J mol⁻¹ K⁻¹ and S_{rot} of 19 J mol⁻¹ K⁻¹. ^c No configurational entropy is included here. ^d Vibrational frequency of H_{2(g)} is 4331 cm⁻¹.

Table S5. Adsorption energies for H* on a Pt (111) surface at 593 K using the PW-91 exchange-correlation functional.

<i>Unit</i>	<i>H*</i>	<i>Mode</i>	$\Delta E_{0,H}$	$\Delta ZPVE_H$	$\Delta H_{vib,H}$	$\Delta S_{vib,H}$	$\Delta G_{vib,H}$	ΔH_H	$Q_{H_2}^a$	ΔS_H^b	$S_{H^*}^c$	ΔG_H	<i>Frequencies</i> ^d		
<i>Cell</i>	<i>Covg.</i>		kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	$\text{J mol}^{-1} \text{K}^{-1}$	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	$\text{J mol}^{-1} \text{K}^{-1}$	$\text{J mol}^{-1} \text{K}^{-1}$	kJ mol^{-1}	cm^{-1}		
1 × 1	1	atop	-33	5	6	19	-5	-30	60	-57	19	4	2249	401	400
1 × 1	1	fcc	-35	2	5	13	-3	-37	73	-62	13	0	1189	601	599
1 × 1	1	hcp	-30	1	5	15	-3	-32	65	-60	15	4	1197	543	538
1 × 2	1/2	atop	-38	5	6	19	-5	-35	70	-56	19	-2	2258	381	379
1 × 2	1/2	fcc	-40	1	5	13	-3	-42	84	-62	13	-6	1144	612	581
1 × 2	1/2	hcp	-36	1	6	15	-3	-38	77	-60	15	-3	1151	560	532
1 × 3	1/3	atop	-38	5	6	19	-5	-36	71	-56	19	-2	2260	376	374
1 × 3	1/3	fcc	-42	1	5	14	-3	-44	88	-62	14	-8	1131	621	585
1 × 3	1/3	hcp	-37	1	5	15	-3	-40	80	-61	15	-4	1142	559	528
2 × 2	1/4	atop	-41	5	6	19	-5	-39	77	-56	19	-5	2259	369	369
2 × 2	1/4	fcc	-43	1	5	13	-3	-45	90	-62	13	-8	1100	607	604
2 × 2	1/4	hcp	-39	0	6	16	-3	-42	83	-60	16	-6	1115	548	547
2 × 3	1/6	atop	-41	5	6	20	-5	-38	77	-55	20	-6	2258	366	363
2 × 3	1/6	fcc	-44	1	5	13	-3	-46	92	-62	13	-9	1093	601	596
2 × 3	1/6	hcp	-39	0	6	15	-3	-42	83	-60	15	-6	1111	538	533
3 × 3	1/9	atop	-41	5	6	20	-5	-38	76	-55	20	-5	2258	360	358
3 × 3	1/9	fcc	-44	1	5	14	-3	-46	92	-62	14	-9	1086	601	600
3 × 3	1/9	hcp	-39	0	6	15	-3	-42	83	-60	15	-6	1103	537	536
3 × 4	1/12	atop	-42	5	6	20	-5	-39	78	-55	20	-6	2263	366	364
3 × 4	1/12	fcc	-44	1	5	13	-3	-47	93	-62	13	-10	1084	603	598
3 × 4	1/12	hcp	-40	0	6	15	-3	-42	85	-60	15	-7	1102	540	530
4 × 4	1/16	atop	-43	5	6	20	-5	-40	80	-56	20	-7	2262	369	368
4 × 4	1/16	fcc	-45	1	5	14	-3	-47	94	-61	14	-11	1086	593	588
4 × 4	1/16	hcp	-40	0	6	15	-3	-43	85	-60	15	-7	1102	524	523

^a $Q_{H_2} = -2(\Delta H_H)$ ^b Gas-phase H₂ has S_{trans} of 132 J mol⁻¹ K⁻¹ and S_{rot} of 19 J mol⁻¹ K⁻¹. ^c No configurational entropy is included here. ^d Vibrational frequency of H_{2(g)} is 4331 cm⁻¹.

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