Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Ab initio coverage-dependent microkinetic modeling of benzene hydrogenation on Pd(111)

Supporting information

Section S1. Calculation of rate and equilibrium coefficients

S1.1 Statistical thermodynamics

The vibrational partition function is calculated within the harmonic oscillator approximation (and is referred to the vibrational ground state level, not the bottom of the potential wells):

$$q_{\mathrm{vib}} = \prod_{i}^{3N} \frac{1}{1 - e^{-\frac{h\nu_i}{k_B T}}} \tag{1}$$

This yields for the thermal corrections to the enthalpy $\Delta H_{0\rightarrow T}$

$$\Delta H_{0\to T} = R\sum_{i=1}^{3N-6} \frac{h\nu_i}{k_B(1-e^{-\frac{h\nu_i}{k_B T}})} \tag{2}$$

Together with the Zero-Point vibrational Energy:

$$ZPE = \sum_{i}^{3N} \frac{h\nu_i}{2} \tag{3}$$

This allows to calculate the enthalpy allows to determine the enthalpy of a species, which, for a surface species, is equal to the internal energy:

$$H(T) = E_{\mathrm{el}} + ZPVE + \Delta H_{0\to T} \tag{4}$$

With E_{el} the electronic energy.

The vibrational contribution to the entropy amounts to:

$$S_{\mathrm{vib}} = R\sum_{i=1}^{3N} \left[\frac{h\nu_i}{k_B T\left(e^{\frac{h\nu_i}{k_B T}} - 1\right)} - \ln\left(1 - e^{-\frac{h\nu_i}{k_B T}}\right) \right] \tag{5}$$

Gas phase species

The partition functions are calculated assuming separability of the translational, rotational, vibrational and electronic contributions, and using the rigid external rotation and harmonic oscillator (HO).

The translational contribution to the total partition function is expressed as:

$$q_{\mathrm{translation}}(V,T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V_m \tag{6}$$

with V_m the molar volume equal to RT/p for an ideal gas.

The electronic contribution is approximated by the spin multiplicity ω_0, the degeneracy of the ground electronic state. Excited electronic states are ignored ($RT \ll \varepsilon_{\mathrm{elec},1}$ at T=1000 K):

$$q_{\mathrm{elec}} = \omega_0 \tag{7}$$

All the gas phase species considered in this work are closed-shell molecules, for which ω_0=1. The external rotation contribution is evaluated based on the rigid rotor formalism:

$$q_{\mathrm{rotation,ext}}(T) = \frac{\sqrt{\pi}}{\sigma_{ext}} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{\frac{3}{2}} \sqrt{I_{princ,x} I_{princ,y} I_{princ,z}} \tag{8}$$

where I_j are the principal moments of inertia and σ_{ext} is the external symmetry number.

Finally, all internal rovibrational modes are treated as coupled harmonic oscillators, leading to the contribution:

$$q_{\mathrm{rovib,HO,V=0}} = \prod_{i}^{3N-6} \frac{1}{1 - e^{-\frac{h\nu_i}{k_B T}}} \tag{9}$$

in which the harmonic frequencies ν_i are obtained from VASP using the PW91 or optBPE vdw-DF functional (no scale factor for the frequencies is used).

Entropies, heat capacities and contributions to the enthalpy have been calculated using ideal gas statistical thermodynamics:

$$S = k_B \left(\ln Q + T \frac{\partial \ln Q}{\partial T} \right) \tag{10}$$

$$C_P = k_B + k_B T \left(2 \frac{\partial \ln Q}{\partial T} + T \frac{\partial^2 \ln Q}{\partial T^2} \right) \tag{11}$$

$$U_{\mathrm{therm\,corr}} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \tag{12}$$

with Q the canonical partition functions.

S1.2 Reaction Thermodynamics

The adsorption enthalpy of benzene (and similarly other hydrocarbons) is expressed as:

$$\Delta_{ads} H(\mathrm{B}) = H(\mathrm{B}_{\mathrm{ads}}) - H_{\mathrm{B,gas}} - H_{\mathrm{cat}} \tag{13}$$

With $H(\mathrm{B}_{\mathrm{ads}})$ the enthalpy of the 3x3 unit cell with adsorbed benzene, $H_{\mathrm{B,gas}}$ the enthalpy of gas phase benzene, and H_{cat} the enthalpy of the vacant unit cell. For dissociative hydrogen adsorption, this equation becomes

$$\Delta_{ads}H(\mathrm{H_2}) = 2H(H_{\mathrm{ads}}) - H_{\mathrm{H2,gas}} - 2H_{\mathrm{cat}} \tag{14}$$

The reaction enthalpy for the hydrogenation from the intermediate BH$_i$ to BH$_{i+1}$ is calculated using

$$\Delta_{ads}H(\mathrm{BH}_i \rightarrow \mathrm{BH}_{i+1}) = H(\mathrm{BH}_{i+1,\mathrm{ads}}) + H_{\mathrm{cat}} - H(\mathrm{BH}_{i,\mathrm{ads}}) - H(\mathrm{H_{ads}}) \tag{15}$$

And activation enthalpies similarly as

$$\Delta^{\neq}H(\mathrm{BH}_i \rightarrow \mathrm{BH}_{i+1}) = H(\mathrm{T}S_{i,\mathrm{ads}}) + H_{\mathrm{cat}} - H(\mathrm{BH}_{i,\mathrm{ads}}) - H(\mathrm{H_{ads}}) \tag{16}$$

Adsorption, reaction and activation entropies are calculated using the equivalent equations to those mentioned above.

S1.3 Rate equations

Molecular adsorption is considered to be non-activated, and the adsorption rate is expressed as

$$r_{ads,molec} = k_{ads,molec} p_i \theta^* \tag{17}$$

With p_i the pressure of the adsorbate in gas phase and θ^* the fraction of free sites.

For **molecular desorption** the rate coefficient is expressed as function of the adsorption equilibrium K_{ads} and rate coefficient for adsorption, to ensure thermodynamic consistency:

$$k_{des,molec} = \frac{k_{ads,molec}}{K_{ads}} \tag{18}$$

Dissociative adsorption ($H_{2(g)}$ + 2* → 2H*) is also considered non-activated. The expressions are analogous:

$$r_{ads,diss} = 2k_{ads,diss} p_i \theta^{*2} \tag{19}$$

With similar expressions for the rate coefficient, and reverse rate coefficient.

For the **surface reactions**, hydrogen addition and elimination, the rate equation is

$$r_{for} = k_{for}\theta_{BHi}\theta_H - k_{rev}\theta_{BHi+1}\theta^* \tag{20}$$

The derivation of the Arrhenius parameters from the thermodynamic formulation of transition state theory:

$$k_{\mathrm{surface}} = \frac{k_B T}{h} \exp\left(\frac{\Delta^{\ddagger} S}{R}\right) \exp\left(-\frac{\Delta^{\ddagger} H}{RT}\right) \tag{21}$$

Is done as follows, using the Arrhenius definition of the activation energy E_a :

$$\begin{aligned} E_a(T) &= RT^2 \frac{\partial}{\partial T} \ln k \\ &= \Delta^{\ddagger} H + RT \end{aligned} \tag{22}$$

Substituting this activation energy into the transition state theory expression yields the pre-exponential factor:

$$A = \frac{k_B T}{h} e \exp\left(\frac{\Delta^{\ddagger} S}{R}\right) \tag{23}$$

Section S2. Correction of gas phase reaction thermodynamics

$$\Delta \mathrm{H_r}(450\mathrm{K}) = \sum_{\mathrm{prod,j}} \mathrm{n_j} \cdot \Delta \mathrm{h}^0_{\mathrm{f,j}} + \sum_{\mathrm{prod,j}} \mathrm{n_j} \cdot \Delta \mathrm{H}_{(298 \rightarrow 450\mathrm{K}),\mathrm{j}} - \left(\sum_{\mathrm{react,i}} \mathrm{n_i} \cdot \Delta \mathrm{h}^0_{\mathrm{f,i}} + \sum_{\mathrm{react,i}} \mathrm{n_i} \cdot \Delta \mathrm{H}_{(298 \rightarrow 450\mathrm{K}),\mathrm{i}} \right) \tag{S7}$$

$$\Delta S_{\mathrm{r}}(450\mathrm{K}) = \sum_{\mathrm{prod,j}} \mathrm{n_j} \cdot \mathrm{S}^0_{\mathrm{j}} + \sum_{\mathrm{prod,j}} \mathrm{n_j} \cdot \Delta S_{(298 \rightarrow 450\mathrm{K}),\mathrm{j}} - \left(\sum_{\mathrm{react,i}} \mathrm{n_i} \cdot \mathrm{S}^0_{\mathrm{i}} + \sum_{\mathrm{react,i}} \mathrm{n_i} \cdot \Delta S_{(298 \rightarrow 450\mathrm{K}),\mathrm{i}} \right) \tag{S8}$$

Standard enthalpy of formation values (Δh^0_f) and standard entropy values (S^0) are tabulated by NIST or found in literature and are reported in Table S1 [3, 4].

Table S1. Standard enthalpy of formation (Δh^0_f, in kJ mol^{-1}) and standard entropy (S^0, in J mol^{-1} K^{-1}) values used in this work [3, 4] (298 K).

Species	Δh^0_f (kJ mol^{-1})	S^0 (J mol^{-1} K^{-1})
H_2	0.0	130.68
benzene	82.9	268.6
1,3-cyclohexadiene	104.58	303.41
cyclohexene	-4.32	310.45
cyclohexane	-124.6	298.19

The enthalpy and entropy change between 298 K and 900 K ($\Delta H_{298\rightarrow900K}$ and $\Delta S_{298\rightarrow900K}$) have been calculated using the following equations [4]:

$$C_p^0 = A + BT + CT^2 + DT^3 + ET^4 \tag{S9}$$

$$H^0 - H^0_{298.15K} = \int C_p \, dT = A \cdot T + B \cdot T^2/2 + C \cdot T^3/3 \tag{S10}$$

$$S^0 = \int \frac{C_p}{T} dT = A \cdot \ln(T) + B \cdot T + C \cdot T^2/2 \tag{S11}$$

In these equations C^0_p is the heat capacity in J mol^{-1} K^{-1}, H^0 is the standard enthalpy in kJ mol^{-1}, S^0 is the standard entropy in J mol^{-1} K^{-1} and T is the temperature in K/1000. A to C are parameters that are tabulated or can be obtained fitting the heat capacity C_p of the gas phase species as function of the temperature, which are also tabulated values. The heat capacities from which parameters A to C have been determined are given in Table S2.

Table S2. Heat capacitiesto which the parameters A to C in the equations (S9)-(S11) have been fitted.

	Temperature (K)			
Species	300	400	500	600
H_2	28.85	29.18	29.26	29.32
benzene	83.02	113.52	139.35	160.09
1,3-cyclohexadiene	94.8	128.55	157.99	182.24
cyclohexene	102.16	139.7	173.27	201.44
cyclohexane	106.11	148.64	188.68	223.38

The resulting reaction enthalpies are given in Table S3.

Table S3. Reaction enthalpies and entropies of the overall gas phase reactions at 450 K derived from NIST data, and calculated using the PW91 and optPBE vdw-DF functional.

		ΔH_r (kJ mol^{-1})			ΔS_r (J mol^{-1}K^{-1})		
		NIST	PW91	optPBE	NIST	PW91	optPBE
(1)	$B + 3\,H_2 \rightleftharpoons CHA$	-220.4	-198.1	-179.3	-388.4	-388.2	-388.7
(2)	$B + 2\,H_2 \rightleftharpoons CHE$	-95.1	-79.6	-75.2	-234.6	-256.7	-241.5
(3)	$B + H_2 \rightleftharpoons 13CHD$	18.2	32.2	20.5	-102.7	-109.8	-110.4

Section S3. Low-coverage results (PW91)

Table S4: Kinetic and thermodynamic parameters for each hydrogenation step in the full reaction network with the PW91 functional at 450 K. Benzene adsorbs and reacts on a hollow-hcp(0) site, and the values are calculated θ_H=0.11 and θ_{BHi}=0.11 in different unit cells.

Reaction	label	E_a (kJ mol^{-1})		A (s^{-1})		k (s^{-1})		Δ_rH (kJ mol^{-1})	Δ_rS (J mol^{-1}K^{-1})	K_{eq}
		forward	reverse	forward	reverse	forward	reverse			
H_2 + 2* → 2H*	-	0	124.9	5.4E+09	5E+19	5.4E+09	1.6E+05	-124.9	-190.7	3.4E+04
B(g) + * → B*	a	0	96.1	8.6E+08	3E+18	8.6E+08	2.0E+07	-96.1	-182.5	4.2E+01
B*+H*→BH*	b	111	39	5.3E+14	5.46E+12	7.8E+01	1.7E+08	71.8	38.0	4.5E-07
BH*+H*→13CHD*	c-1	85	28	6.4E+13	2.20E+12	8.8E+03	1.3E+09	57.3	28.1	6.5E-06
BH*+H*→13DHB*	c-2	113	49	3.6E+14	1.30E+14	2.8E+01	2.5E+08	63.7	8.5	1.1E-07
BH*+H*→14CHD*	c-3	118	41	8.7E+13	1.54E+13	1.8E+00	2.5E+08	76.6	14.4	7.2E-09
13CHD*+H*→123THB*	d-1	94	67	3.6E+14	2.71E+12	4.4E+03	5.0E+04	27.3	40.7	8.9E-02
13CHD*+H*→124THB*	d-2	107	40	4.2E+14	2.06E+13	1.7E+02	4.4E+08	66.4	25.0	3.9E-07
13DHB*+H*→123THB*	d-3	90	69	1.6E+15	1.13E+12	5.9E+04	1.2E+04	21.0	60.2	5.1E+00
13DHB *+H*→124THB*	d-4	94	34	7.8E+14	3.69E+12	8.7E+03	3.8E+08	60.0	44.5	2.3E-05
13DHB *+H*→135THB	d-5	126	46	7.2E+14	3.60E+13	1.6E+00	1.8E+08	80.6	24.9	8.9E-09
14CHD *+H*→124THB	d-6	83	36	5.5E+14	5.28E+12	1.1E+05	3.2E+08	47.1	38.6	3.6E-04
123THB*+H*→CHE*	e-1	82	22	1.7E+14	6.24E+11	4.8E+04	1.6E+09	59.9	46.8	3.1E-05
123THB*+H*→1235THB *	e-2	132	45	1.1E+14	8.34E+12	6.0E-02	4.6E+07	86.2	21.6	1.3E-09
124THB*+H*→CHE*	e-3	86	65	7.9E+14	4.33E+11	7.6E+04	1.1E+04	20.8	62.5	7.0E+00
124THB*+H*→1235THB *	e-4	102	55	1.1E+15	1.29E+13	1.5E+03	4.9E+06	47.1	37.3	3.0E-04
123THB*+H*→1245THB*	e-5	100	40	1.2E+15	9.40E+12	3.1E+03	2.3E+08	60.2	40.5	1.3E-05
135THB*+H*→1235THB *	e-6	97	74	3.4E+14	3.57E+11	1.7E+03	1.0E+03	23.9	56.9	1.6E+00
CHE*+H*→C-hexyl*	f-1	78	47	1.8E+14	2.34E+13	1.8E+05	9.0E+07	31.0	17.1	2.0E-03
1235THB *+H*→C-hexyl*	f-2	83	79	6.4E+14	3.92E+12	1.4E+05	3.0E+03	4.6	42.3	4.7E+01
1245THB *+H*→C-hexyl*	f-3	96	102	1.0E+15	2.23E+13	7.9E+03	3.7E+01	-5.7	32.0	2.2E+02
C-hexyl*+H*→CHA*	g	70	61	2.2E+16	1.36E+12	1.7E+08	1.2E+05	9.1	80.6	1.4E+03
CHA* → CHA(g) + *	h	5.9	0	1.7E+14	8.3E+08	1.7E+14	8.3E+08	5.9	115.0	2.1E+05

Table S5: Kinetic and thermodynamic parameters for each hydrogenation step in the full reaction network with the PW91 functional at 450 K. Benzene adsorbs and react on a bridge(30) site, and the values are calculated considering θ_H=0.11 and θ_{BHi}=0.11 in different unit cells.

Reaction	label	E_a (kJ mol^{-1})		A (s^{-1})		k (s^{-1})		Δ_rH (kJ mol^{-1})	Δ_rS (J mol^{-1}K^{-1})	K_{eq}
		forward	reverse	forward	reverse	forward	reverse			
$H_2 + 2* \rightarrow 2H*$	-	0	124.9	5.4E+09	5E+19	5.4E+09	1.6E+05	-124.9	-190.7	3.4E+04
$B(g) + * \rightarrow B*$	a	0	113.0	8.6E+08	1E+19	8.6E+08	8.9E+05	-113.0	-194.0	9.6E+02
$B^*+H^*\rightarrow BH^*$	b	119	34	7.7E+14	3.7E+13	1.1E+01	4.2E+09	85.4	25.3	2.6E-09
$BH^*+H^*\rightarrow 13CHD^*$	c-1	100	48	2.0E+15	4.7E+12	4.6E+03	1.4E+07	52.6	50.4	3.4E-04
$BH^*+H^*\rightarrow 13DHB^*$	c-2	115	46	3.0E+15	1.2E+13	1.2E+02	5.8E+07	69.6	45.9	2.1E-06
$BH^*+H^*\rightarrow 14CHD^*$	c-3	123	41	1.7E+15	3.0E+13	9.9E+00	4.9E+08	81.3	33.4	2.0E-08
$13CHD^*+H^*\rightarrow 123THB^*$	d-1	117	82	1.3E+14	1.4E+12	3.1E+00	4.0E+02	35.4	38.2	7.6E-03
$13CHD^*+H^*\rightarrow 124THB^*$	d-2	146	33	4.0E+14	6.1E+12	5.0E-03	9.8E+08	113.0	34.8	5.1E-12
$13DHB^*+H^*\rightarrow 123THB^*$	d-3	87	69	5.3E+14	3.1E+12	4.0E+04	3.2E+04	18.4	42.7	1.2E+00
$13DHB\ ^*+H^*\rightarrow 124THB^*$	d-4	92	-4	2.3E+14	2.1E+12	5.2E+03	6.3E+12	95.9	39.3	8.3E-10
$13DHB\ ^*+H^*\rightarrow 135THB$	d-5	123	43	7.7E+13	5.6E+13	4.3E-01	6.1E+08	80.1	2.6	6.9E-10
$14CHD\ ^*+H^*\rightarrow 124THB$	d-6	101	17	1.8E+15	3.6E+12	3.1E+03	3.7E+10	84.2	51.8	8.5E-08
$123THB^*+H^*\rightarrow CHE^*$	e-1	82	32	1.4E+14	1.1E+12	4.0E+04	2.0E+08	50.1	40.4	2.0E-04
$123THB^*+H^*\rightarrow 1235THB\ ^*$	e-2	131	43	2.7E+14	1.5E+13	1.5E-01	1.3E+08	88.1	24.2	1.1E-09
$124THB^*+H^*\rightarrow CHE^*$	e-3	63	91	7.3E+14	3.8E+12	3.3E+07	1.1E+02	-27.4	43.7	2.9E+05
$124THB^*+H^*\rightarrow 1235THB\ ^*$	e-4	56	45	1.3E+15	4.6E+13	4.1E+08	2.5E+08	10.6	27.6	1.6E+00
$123THB^*+H^*\rightarrow 1245THB^*$	e-5	63	41	1.3E+15	2.5E+13	6.5E+07	4.2E+08	21.7	32.7	1.5E-01
$135THB^*+H^*\rightarrow 1235THB\ ^*$	e-6	90	53	6.7E+15	1.6E+12	2.3E+05	1.3E+06	37.6	69.4	1.8E-01
$CHE^*+H^*\rightarrow C\text{-}hexyl^*$	f-1	87	45	2.0E+15	3.1E+14	1.4E+05	2.0E+09	42.6	15.3	7.1E-05
$1235THB\ ^*+H^*\rightarrow C\text{-}hexyl^*$	f-2	79	74	5.8E+14	6.6E+12	3.7E+05	1.8E+04	5.4	37.1	2.0E+01
$1245THB\ ^*+H^*\rightarrow C\text{-}hexyl^*$	f-3	96	102	1.0E+15	2.2E+13	7.9E+03	3.7E+01	-5.7	32.0	2.2E+02
$C\text{-}hexyl^*+H^*\rightarrow CHA^*$	g	64	62	1.0E+15	1.8E+12	4.1E+07	1.3E+05	2.2	52.7	3.1E+02
$CHA* \rightarrow CHA(g) + *$	h	18.3	0	1.0E+17	8.3E+08	1.0E+15	8.3E+08	18.3	157.4	8.1E-07

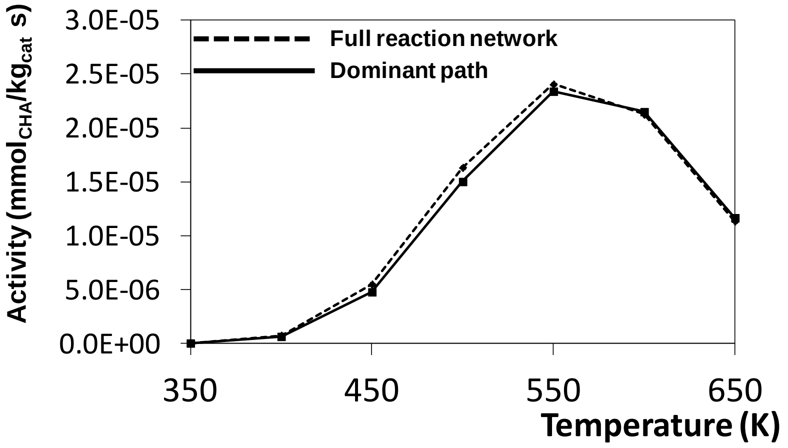

Figure S1: Catalytic activity (mmol$_{CHA}$ kg$_{cat}^{-1}$ s^{-1}) as a function of the temperature for the full reaction network, which considers all reactions, and for the dominant path, which considers the reactions with the highest rate coefficient of each hydrogenation step.

Table S6: Sensitivity analysis coefficient for the reactions in the dominant path at different temperatures, and considering θ_H=0.11 and θ_{BH}=0.11 adsorbed on different unit cells.

Reaction	X_{SA}		
	350 K	**450 K**	**550 K**
b	0.0	0.0	0.0
c1	0.0	0.0	0.0
d1	0.99	0.77	0.19
e1	0.0	0.0	0.0
f1	0.01	0.23	0.79
g	0.0	0.0	0.02

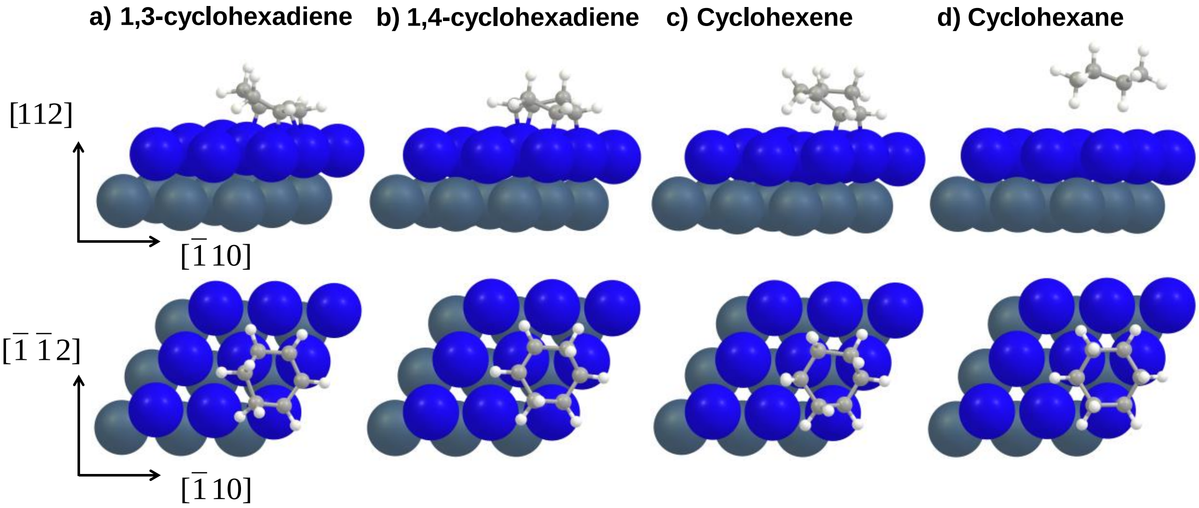
a) 1,3-cyclohexadiene **b) 1,4-cyclohexadiene** **c) Cyclohexene** **d) Cyclohexane**

Figure S2: Side and top view of the adsorption geometry of (a) 1,3-cyclohexadiene, (b) 1,4-cyclohexadiene, (c) cyclohexene and (d) cyclohexane on a clean surface. Pd atoms in the second layer are colored in grey for easier visualization

Table S7: Electronic barriers (kJ mol^{-1}) for the reactions in the dominant path (c1,d1, and e1) and for the reactions that deviate from the dominant path (left), and the difference relative to the corresponding reaction of the dominant path (right) (optPBE-vdW, $\theta_H = 0$) .

Reaction	$E_{el,a}$	$E_{el,a} - E_{el,a,\ dominant}$
	kJ mol^{-1}	
c1 (dominant)	97	0
c2	115	18
c3	120	23
d1 (dominant)	95	0
d2	110	15
e1 (dominant)	82	0
e2	131	49

Section S4. Coverage dependent results (optPBE vdw-DF)

Table S8: Benzene, 1,3-cyclohexadiene, cyclohexene and cyclohexane adsorption enthalpies and entropies for the adsorption on a clean Pd(111) surface, and pre-covered with 0.11, 0.44 and 0.67 hydrogen (optPBE-vdW, direct DFT values).

	ΔH_{ads} (kJ mol^{-1})				ΔS_{ads}(J mol^{-1} K^{-1})			
	Hydrogen coverage covering the surface				Hydrogen coverage pre-covering the surface			
	θ_H=0	θ_H=0.11	θ_H=0.44	θ_H=0.67	θ_H=0	θ_H=0.11	θ_H=0.44	θ_H=0.67
Benzene	-162.8	-155.2	-135.9	-77.5	-179.8	-179.0	-179.5	-145.4
1,3-cyclohexadiene	-173.4	-169.2	-151.7	-100.4	-192.3	-197.7	-203.2	-190.7
Cyclohexene	-108.6	-104.3	-96.9	-66.4	-170.4	-173.7	-175.1	-175.4
Cyclohexane	-81.2	-81.4	-84.4	-77.9	-126.2	-113.6	-111.9	-122.1

Table S9: Hydrogen adsorption enthalpies and entropies (kJ mol and J mol K, respectively) for θ_H=0.11 hydrogen adsorption on a covered surface with the product of each elementary reaction step in the dominant path ($BH_i + \theta_{H,final} \leftrightarrow BH_i + \theta_{H,initial}$)

	$\Delta H_{ads,H}$ (kJ mol^{-1})			$\Delta S_{ads,H}$ (J mol^{-1}K^{-1})		
	$\theta_{H,initial}$ = 0.11	$\theta_{H,initial}$ = 0.44	$\theta_{H,initial}$ = 0.67	$\theta_{H,initial}$ = 0.11	$\theta_{H,initial}$ = 0.44	$\theta_{H,initial}$ = 0.67
$BH_1 + \theta_{H,final} \leftrightarrow BH_1 + \theta_{H,initial}$	-53.6	-23.3	-19.3	-67.6	-61.4	-73.3
$BH_2 + \theta_{H,final} \leftrightarrow BH_2 + \theta_{H,initial}$	-55.8	-44.4	-25.8	-74.0	-70.9	-70.3
$BH_3 + \theta_{H,final} \leftrightarrow BH_3 + \theta_{H,initial}$	-53.4	-48.3	-23.5	-58.4	-76.2	-71.3
$BH_4 + \theta_{H,final} \leftrightarrow BH_4 + \theta_{H,initial}$	-55.6	-46.8	-34.0	-71.8	-67.5	-61.6
$BH_5 + \theta_{H,final} \leftrightarrow BH_5 + \theta_{H,initial}$	-57.4	-53.7	-22.0	-66.2	-72.5	-65.4
$BH_6 + \theta_{H,final} \leftrightarrow BH_6 + \theta_{H,initial}$	-60.2	-52.6	-45.3	-56.0	-58.2	-67.8
average H_2 adsorption	-113.0	-89.7	-56.6	-131.3	-135.6	-136.6

Table S10: Activation energy and pre-exponential factor (kJ mol^{-1} and s^{-1}, respectively) for the forward reactions of the dominant path as a function of the hydrogen coverage coadsorbed with the hydrocarbon reactant, calculated with the optPBE-vdW functional.

	E_a (kJ mol^{-1})				A (s^{-1})			
	θ_H=0	θ_H=0.11	θ_H=0.44	θ_H=0.67	θ_H=0	θ_H=0.11	θ_H=0.44	θ_H=0.67
B* + H* ↔ BH* + *	110	103	98	70	7.6 10^{13}	6.9 10^{13}	3.4 10^{13}	1.0 10^{13}
BH* + H* ↔ 1,3CHD* + *	97	91	60	54	1.4 10^{13}	1.3 10^{13}	1.2 10^{13}	2.1 10^{13}
1,3CHD * + H* ↔ 1,2,3-THB* + *	95	91	84	54	2.5 10^{13}	4.8 10^{13}	1.3 10^{14}	1.7 10^{14}
1,2,3-THB* + H* ↔ CHE* + *	81	75	67	47	2.1 10^{13}	6.4 10^{12}	1.5 10^{13}	1.1 10^{13}
CHE* + H* ↔ C-hexyl* + *	81	77	70	51	2.4 10^{13}	3.6 10^{13}	3.5 10^{13}	7.8 10^{13}
C-hexyl* + H* ↔CHA* + *	71	69	57	25	4.8 10^{13}	3.7 10^{13}	3.8 10^{13}	1.5 10^{13}

Table S11: Reaction enthalpy, reaction entropy (kJ mol^{-1} , kJ mol^{-1}K^{-1}) and equilibrium coefficient for the forward reactions of the dominant path as a function of the hydrogen coverage coadsorbed with the hydrocarbon reactant, calculated with the optPBE-vdW functional.

	ΔH_r (kJ mol^{-1})				ΔS_r (J mol^{-1} K^{-1})				K_{eq}			
	θ_H=0	θ_H=0.11	θ_H=0.44	θ_H=0.67	θ_H=0	θ_H=0.11	θ_H=0.44	θ_H=0.67	θ_H=0	θ_H=0.11	θ_H=0.44	θ_H=0.67
B* + H* ↔ BH* + *	62	55	45	27	0	–1	–2	–26	9.0 10^{-7}	6.3 10^{-6}	4.8 10^{-6}	3.5 10^{-5}
BH* + H* ↔ 1,3CHD* + *	49	43	9	–2	14	14	0	14	6.8 10^{-7}	5.8 10^{-5}	9.0 10^{-2}	10.0
1,3CHD * + H* ↔ 1,2,3-THB* + *	21	17	4	–19	6	12	22	13	7.4 10^{-3}	4.3 10^{-2}	4.6	786
1,2,3-THB* + H* ↔ CHE* + *	50	43	32	–3	22	12	19	4	2.2 10^{-5}	3.9 10^{-5}	1.9 10^{-3}	4.0
CHE* + H* ↔ C-hexyl* + *	23	19	16	–8	0	4	–1	10	2.3 10^{-3}	1.1 10^{-2}	1.2 10^{-2}	29.5
C-hexyl* + H* ↔CHA* + *	2	0	–20	–58	34	32	48	29	33	51	6.2 10^{4}	2.1 10^{8}

Table S12: Estimated parameters to model the adsorption and desorption ($E_{a,f}$ and $E_{a,r}$) ($\Delta^{\ddagger}S_f$ and $\Delta^{\ddagger}S_r$) as a function of total coverage θ_{total} (based on optPBE vdw-DF data, without experimental correction).

	$\Delta E_{ads} = a\theta_{total} + b$ (kJ mol^{-1})		$\Delta S_{ads} = a\theta_{total} + b$ (J mol^{-1} K^{-1})	
	a	*b*	*a*	*b*
Hydrogen	90.93	-132.31	-2.60	-134.03
Benzene	117.83	-181.77	44.07	-189.20
1,3-cyclohexadiene [a]				
Cyclohexene [a]				
Cyclohexane	2.88	-96.08	3.49	-119.89

[a] The equilibrium coefficient and desorption kinetics for this reaction is directly calculated from the experimental gas phase equilibrium and the other rate coefficients

Table S13: Estimated parameters to model the forward and reverse activation energies ($E_{a,f}$ and $E_{a,r}$) and activation entropies ($\Delta^{\ddagger}S_f$ and $\Delta^{\ddagger}S_r$) as a function of total coverage θ_{total}.

	$E_{a,f} = a\theta_{total} + b$ (kJ mol^{-1})		$E_{a,r} = a\theta_{total} + b$ (kJ mol^{-1})		$\Delta^{\ddagger}S_f = a\theta_{total} + b$ (J mol^{-1} K^{-1})		$\Delta^{\ddagger}S_r = a\theta_{total} + b$ (J mol^{-1} K^{-1})	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
B* + H* ↔ BH* + *	-53.54	117.34	-4.07	49.45	-24.00	13.15	9.23	6.55
BH* + H* ↔ 1,3CHD* + *	-69.71	104.27	11.43	45.99	3.50	-5.91	10.73	-19.50
1,3CHD * + H* ↔ 1,2,3-THB* + *	-54.50	103.74	2.72	74.25	23.17	-1.08	10.59	-8.93
1,2,3-THB* + H* ↔ CHE* + *	-47.05	87.03	25.59	26.46	-1.40	-5.46	15.62	-26.51
CHE* + H* ↔ C-hexyl* + *	-41.78	86.99	-1.17	57.78	11.64	-1.21	2.49	-0.58
C-hexyl* + H* ↔CHA* + *	-64.34	82.21	22.35	65.36	-12.06	6.81	-15.03	-27.73

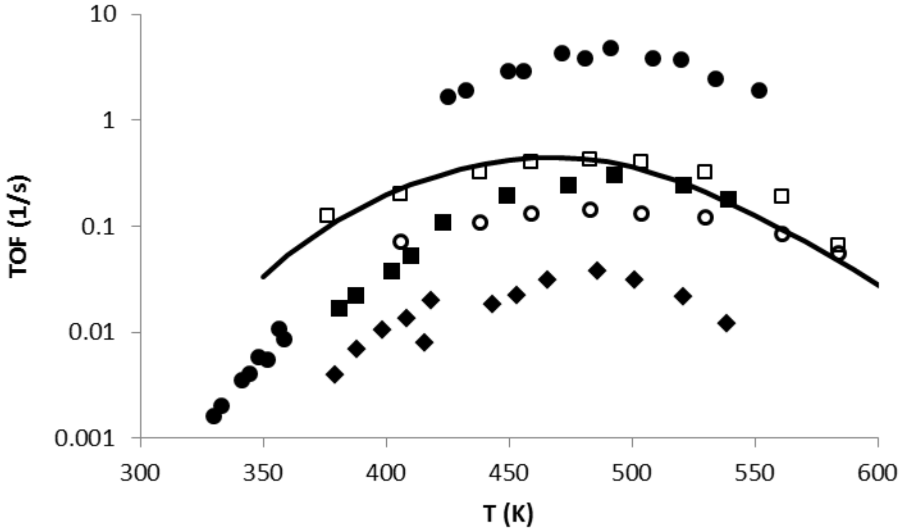

Figure S3: Turnover frequency as a function of the temperature for the coverage-dependent reactor simulations (full line), compared to experimental data (circles: Pd/SiO$_2$-Al$_2$O$_3$, squares: Pd/SiO$_2$, diamonds: Pd powder. Closed signs: Chou & Vannice 1987, Open signs: Orozco & Webb 1983) ($W/F_{B,in}$ = 13.5 kg$_{cat}$ s mol^{-1}; $p_{B,in}$ = 6.7 10^{-2} bar; $p_{H2,in}$ = 0.91 bar, i.e. the conditions of Chou and Vannice).

Table S14: Sensitivity analysis coefficient for the reactions along the dominant path at different temperatures for the coverage-dependent model. Sensitivity of the rate of production of cyclohexane, cyclohexene, and 1,3-cyclohexadiene.

Reaction	X_{SA} CHA			X_{SA} CHE			X_{SA} 13CHD		
	413 K	450 K	475 K	413 K	450 K	475 K	413 K	450 K	475 K
b	0.005	0.001	0.001	0.005	0.001	0.001	0.005	0.002	0.001
c1	0.523	0.305	0.179	0.510	0.294	0.172	0.506	0.292	0.172
d1	0.394	0.530	0.507	0.385	0.510	0.488	-0.521	-0.311	-0.170
e1	0.003	0.012	0.022	0.003	0.011	0.021	-0.002	-0.007	-0.007
f1	0.105	0.112	0.210	-0.788	-0.769	-0.663	-0.008	-0.036	-0.059
g	0.001	0.003	0.010	-0.005	-0.017	-0.032	0.002	0.000	-0.003