Supporting Information

Effects of Catalyst Model and High Adsorbate Coverages in ab initio Studies of Alkane Hydrogenolysis

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S1. Details of Density Functional Calculations of Thermochemical Properties

Frequency calculations were performed on gas phase molecules and all optimized adsorbed species to determine zero-point vibrational energies (ZPVE), and vibrational, translational and rotational enthalpy and free energy. These terms were then used, together with electronic energies (E_0 , provided by VASP), to estimate enthalpies:

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

and free energies:

$$G = G_0 + \text{ZPVE} + G_{\text{vib}} + G_{\text{trans}} + G_{\text{rot}}$$
(S2)

for all reactants, products, and transition states at 593 K. For calculations which include a periodic Ir(111) surface or Ir₁₁₉ particle, there are no translational or rotational degrees of freedom and DFT-derived vibrational frequencies can be used to determine the ZPVE, $H_{\rm vib}$, and $G_{\rm vib}$

$$ZPVE = \sum_{i} (\frac{1}{2}\nu_{i}h) \tag{S3}$$

$$H_{vib} = \sum_{i} \left(\frac{\nu_i h e^{\frac{-\nu_i h}{kT}}}{1 - e^{\frac{-\nu_i h}{kT}}} \right)$$
(S4)

$$G_{vib} = \sum_{i} \left(-kT \ln \frac{1}{1 - e^{\frac{-\nu_i \hbar}{kT}}} \right)$$
(S5)

For gaseous molecules, translational and rotational enthalpies and free energies were also computed from statistical mechanics:

$$H_{trans} = \frac{5}{2}kT \tag{S6}$$

$$H_{rot,linear} = kT \tag{S7}$$

$$H_{rot,nonlinear} = \frac{3}{2}kT \tag{S8}$$

$$G_{trans} = -kT \ln\left[\left(\frac{2\pi MkT}{h^2}\right)^{3/2} V\right]$$
(S9)

$$G_{rot} = -kT \ln\left[\frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\theta_x \theta_y \theta_z}\right)^{1/2}\right]$$
(S10)

$$\theta_i = \frac{h^2}{8\pi^2 I_i k} \tag{S11}$$

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 H₂ and 6 for C₂H₆). Equations S10–S12 obtained from: McQuarrie, D. A.; Statistical Mechanics; Sausolito, CA.



Figure S1. *CH–CH* bond cleavage transition state on the 3×3 Ir(111) surface at different number of vacancies ($\gamma = 0-9$ for a–g). Shown beneath each image are the effective free energy and enthalpy barriers (blue, bold) calculated using Equation 8, and the free energy and enthalpy to form the transition state once the vacancies have been formed (italic, red) calculated using Equation 11 (kJ mol⁻¹, 593 K, 1 bar H₂). Shadings in (a–f) represent vacant sites on a H*-covered surface and are omitted from the bare surface (g).



Figure S2. *CH–CH* bond cleavage transition state on the 4×4 Ir(111) surface at different number of vacancies ($\gamma = 0-16$ for a–g). Shown beneath each image are the effective free energy and enthalpy barriers (blue, bold) calculated using Equation 8, and the free energy and enthalpy to form the transition state once the vacancies have been formed (italic, red) calculated using Equation 11 (kJ mol⁻¹, 593 K, 1 bar H₂). Shadings in (a–f) represent vacant sites on a H*-covered surface and are omitted from the bare surface (g).



Figure S3. *CH–CH* bond cleavage transition state on the 6×6 Ir(111) surface at different number of vacancies ($\gamma = 0-36$ for a–g). Shown beneath each image are the effective free energy and enthalpy barriers (blue, bold) calculated using Equation 8, and the free energy and enthalpy to form the transition state once the vacancies have been formed (italic, red) calculated using Equation 11 (kJ mol⁻¹, 593 K, 1 bar H₂). Shadings in (a–f) represent vacant sites on a H*-covered surface and are omitted from the bare surface (g).

S3. Examined configurations for *CH–CH* activation on the Ir₁₁₉ particle



Figure S4. Examined configurations for *CH–CH* bond cleavage on the terrace sites of the Ir₁₁₉ particle at different number of vacancies ($\gamma = 0-19$). Shown beneath each image are the effective free energy and

enthalpy barriers (blue, bold) calculated using Equation 8, and the free energy and enthalpy to form the transition state once the vacancies have been formed (italic, red) calculated using Equation 11 (kJ mol⁻¹, 593 K, 1 bar H₂). Shadings in represent vacant sites.





Figure S5. Examined configurations for *CH–CH* bond cleavage on the corner/edge sites of the Ir₁₁₉ particle at different number of vacancies ($\gamma = 0$ –19). Shown beneath each image are the effective free energy and enthalpy barriers (blue, bold) calculated using Equation 8, and the free energy and enthalpy to form the transition state once the vacancies have been formed (italic, red) calculated using Equation 11 (kJ mol⁻¹, 593 K, 1 bar H₂). Shadings in represent vacant sites.

S4. Transition State Structures for C-C bond cleavage in ethane-derived intermediates

Figure S6. Transition state structures for C–C bond cleavage in ethane-derived intermediates (a) $*CH_3CH_2*$, (b) $*CH_2CH_2*$, (c) $*CH_3CH*$, (d) $*CH_3C*$, (e) $*CH_2CH*$, (f) $*CH_2C*$, (g) *CHC*, and (h) *CC* on the 4 × 4 Ir(111) surface at $\gamma = 2$. Shown beneath each image are the effective free energy and enthalpy barriers (blue, bold) calculated using Equation 8, and the free energy and enthalpy to form the transition state once the vacancies have been formed (italic, red) calculated using Equation 11 (kJ mol⁻¹, 593 K, 1 bar H₂).

Figure S7. Transition state structures for C–C bond cleavage in ethane-derived intermediates (a) $*CH_3CH_2*$, (b) $*CH_2CH_2*$, (c) $*CH_3CH*$, (d) $*CH_3C*$, (e) $*CH_2CH*$, (f) $*CH_2C*$, (g) *CHC*, and (h) *CC* on the 4 × 4 Ir(111) surface at $\gamma = 4$. Shown beneath each image are the effective free energy and enthalpy barriers (blue, bold) calculated using Equation 8, and the free energy and enthalpy to form the transition state once the vacancies have been formed (italic, red) calculated using Equation 11 (kJ mol⁻¹, 593 K, 1 bar H₂).

Figure S8. Transition state structures for C–C bond cleavage in ethane-derived intermediates $*CH_3CH_2^*$, $*CH_2CH_2^*$, $*CH_3CH^*$, and $*CH_3C^*$ on the Ir₁₁₉ particle at $\gamma = 2$ and 4. Shown beneath each image are the effective free energy and enthalpy barriers (blue, bold) calculated using Equation 8, and the free energy and enthalpy to form the transition state once the vacancies have been formed (italic, red) calculated using Equation 11 (kJ mol⁻¹, 593 K, 1 bar H₂).

Figure S9. Transition state structures for C–C bond cleavage in ethane-derived intermediates *CH₂CH*, *CH₂C*, *CHC*, and *CC* on the Ir₁₁₉ particle at $\gamma = 2$ and 4. Shown beneath each image are the effective free energy and enthalpy barriers (blue, bold) calculated using Equation 8, and the free energy and enthalpy to form the transition state once the vacancies have been formed (italic, red) calculated using Equation 11 (kJ mol⁻¹, 593 K, 1 bar H₂).