Supporting Information

First Principles Micro-Kinetic Modeling of Methane Oxidation over Pd(100) and Pd(111)

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First principles Calculations

Binding Geometries & Energies

The optimized geometries of the adsorbates are included as .xyz files as part of the supporting information.

Vibrational Wavenumbers

The vibrational wavenumbers are given as the comment line in the .xyz files that constitute the other part of the supporting information. They were all calculated using finite differences in the harmonic approximation. Some low frequency translational and rotational modes are presented too, which are to be considered inaccurate.

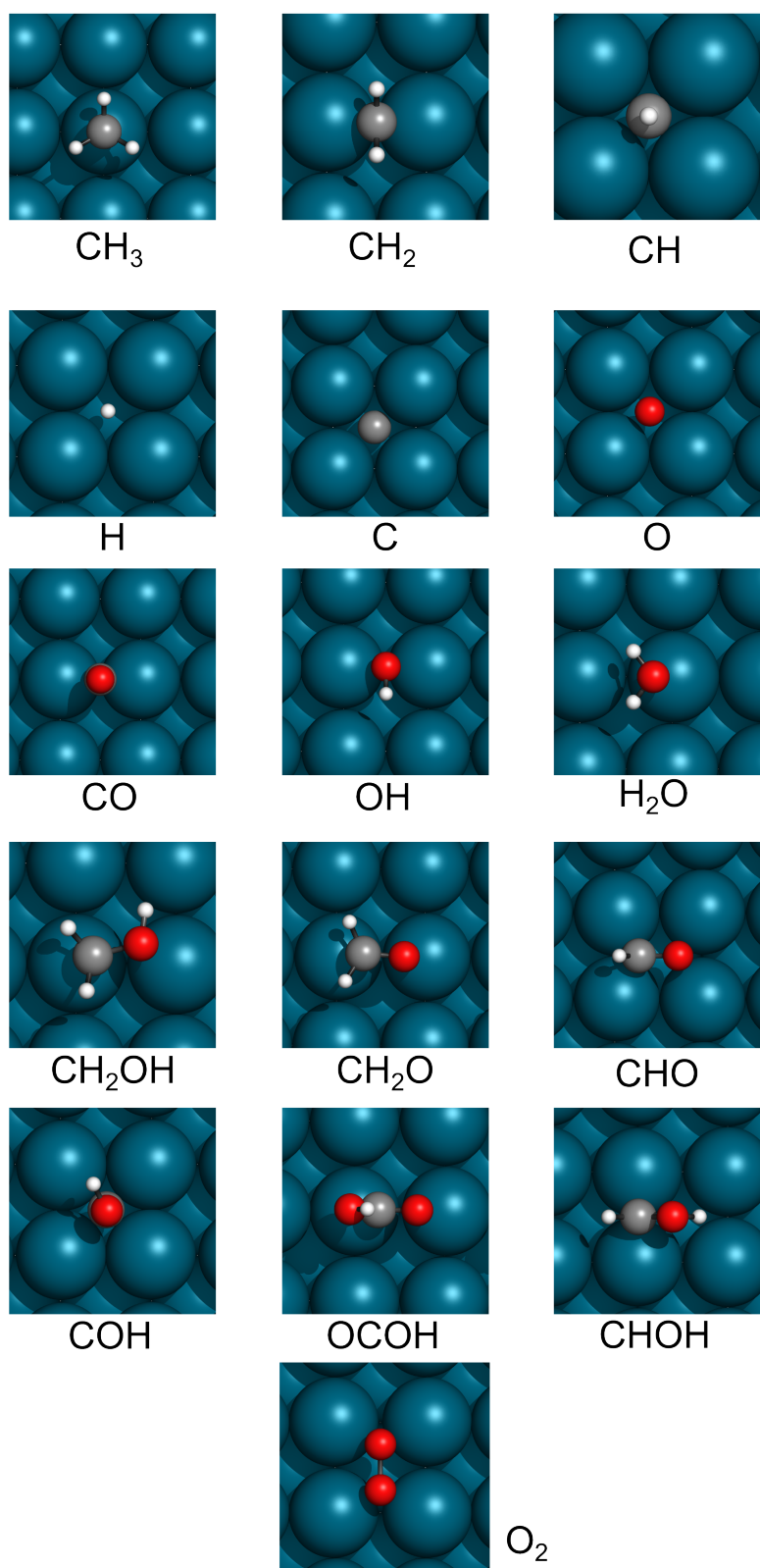*To whom correspondence should be addressed

Figure S1: Geometry of optimized adsorbates on Pd(100). Atom color code: H (white), C (black), O (red) and Pd (blue).
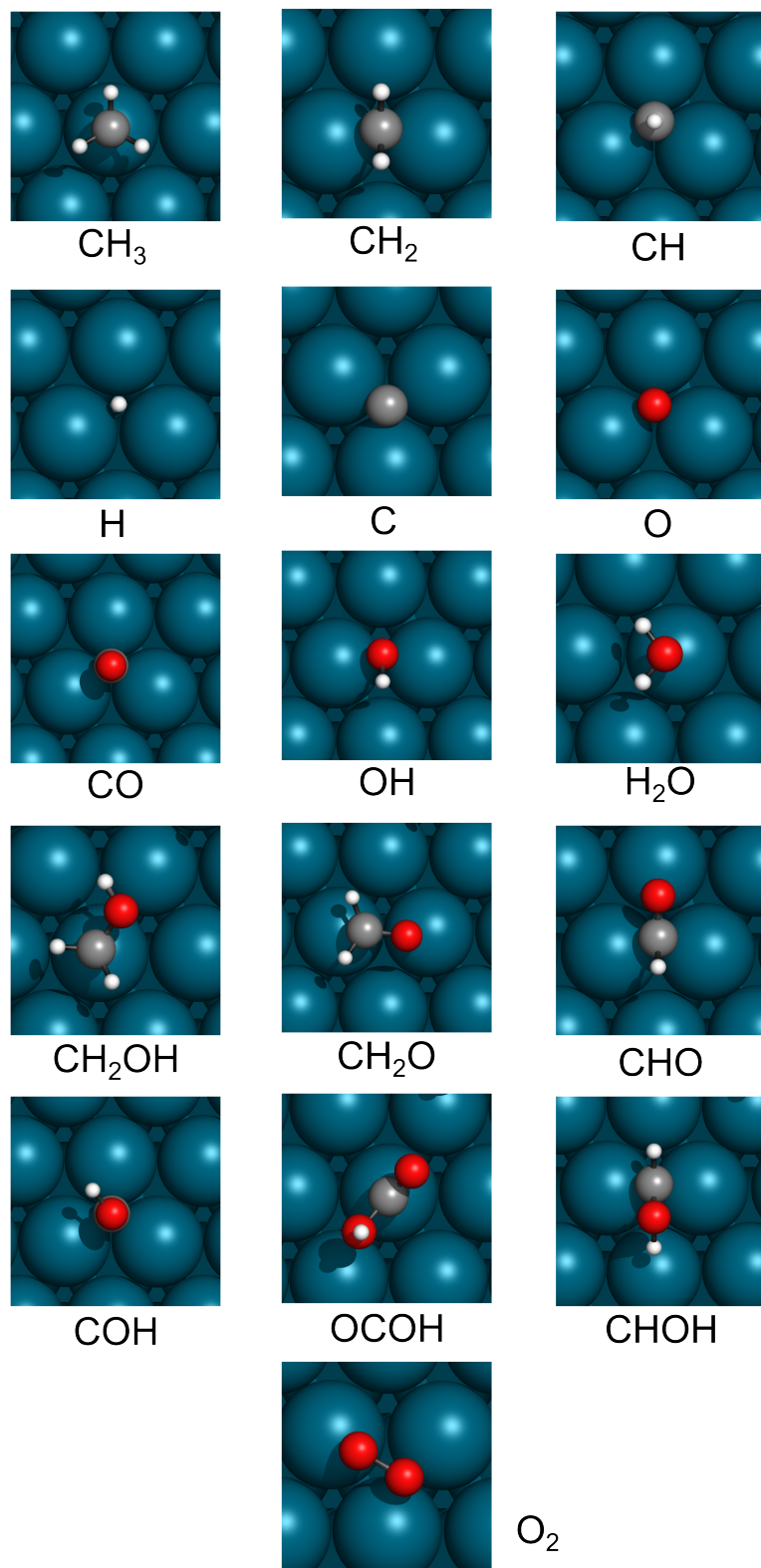
Figure S2: Geometry of optimized adsorbates on Pd(111). Atom color code: H (white), C (black), O (red) and Pd (blue).
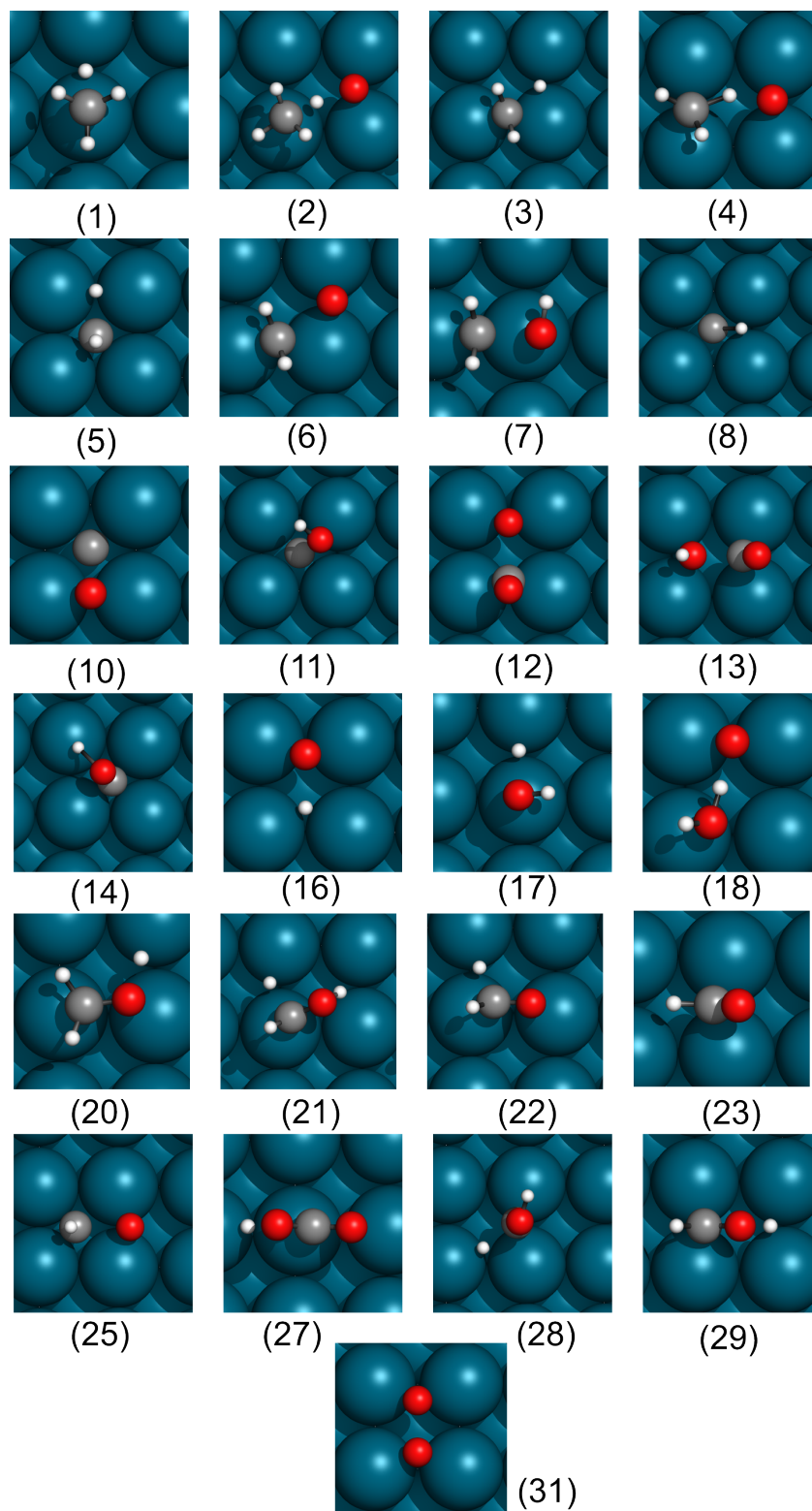
Figure S3: Transition states on Pd(100). Numbering according to the reaction scheme in the kinetic model (Table 1 in main text). Atom color code: H (white), C (black), O (red) and Pd (blue).
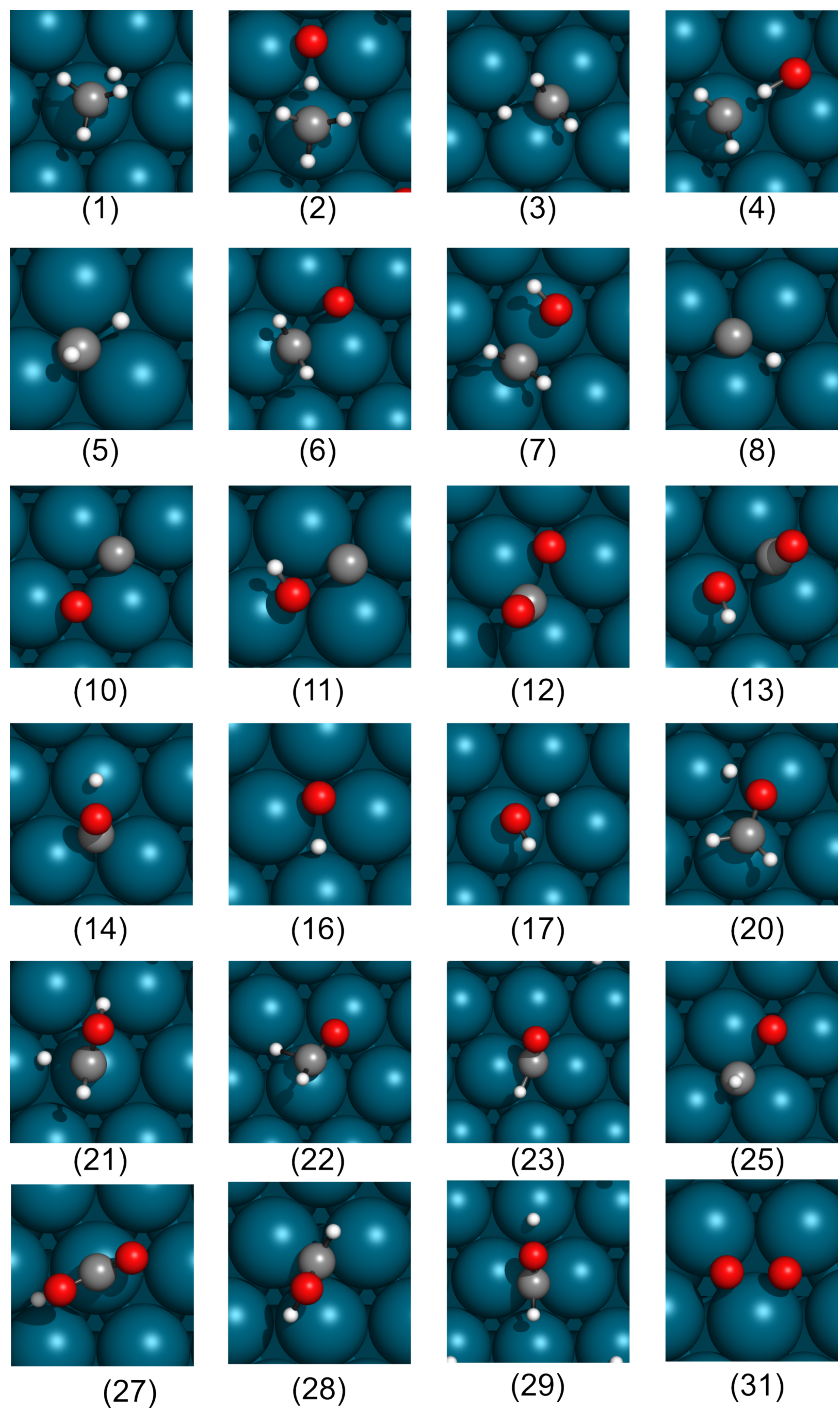
S4

Figure S4: Transition states on Pd(111). Numbering according to the reaction scheme in the kinetic model (Table 1 in main text). Atom color code: H (white), C (black), O (red) and Pd (blue).

Micro-Kinetic Modelling

Calculation of gas phase partition functions

The partition functions of gaseous molecules were calculated assuming that the vibrational, rotational and translational degrees of freedom are uncoupled. This results in a total partition function related to the entropy (Z) that is the product of the partition functions for each degree of freedom:

$$Z = Z_{\text{vib}} Z_{\text{rot}} Z_{\text{trans}} \tag{1}$$

The vibrational partition function is

$$Z_{\text{vib}} = \exp\left(\frac{-E_0}{k_{\text{B}}T}\right) \prod_i \frac{1}{1 - \exp\left(-\frac{\hbar\omega_i}{k_{\text{B}}T}\right)} \tag{2}$$

Where E_0 is the zero point energy, $\hbar$ is Planck's constant, k_{B} is Boltzmann's constant, T is the temperature and ω_i is the vibration frequency of mode i.

The rotational part of the partition function for the non-linear molecules was calculated by the following expression[S1]

$$Z_{\text{rot}} = \frac{1}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2}\right)^{3/2} \sqrt{\pi I_A I_B I_C} \tag{3}$$

where σ is the symmetry factor of the given molecule, I_A, I_B and I_C are the moments of inertia along three principal axes. Linear molecules have only two degrees of rotational freedom which for this case gives:

$$Z_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \frac{8\pi^2 k_B T I}{h^2} \tag{4}$$

Finally the translational partition function in 3 dimensions is given by[S1]

$$Z_{\text{trans}} = V \frac{(2\pi M k_B T)^{3/2}}{h^3} \tag{5}$$

where M is the molecule's mass, V is the volume that the molecule is confined to and T the temperature. V is calculated from the ideal gas law, thereby introducing a gas pressure.

Coverage dependence on barriers

We included a coverage dependent activation energy for the methane dissociation and lateral repulsions for O and C. We also include OH-OH interactions as was done in Ref.,[S2] but these do not affect the results significantly. The methane dissociation barriers E_a over Pd (step 1) and oxygen (step 2) were treated as follows:

$$E_a \quad \rightarrow \quad E_a \left(1 + \alpha_{\text{CH}_4} \theta_{\text{O}}\right) \tag{6}$$

Where θ_O is the oxygen coverage and α_{CH_4} a factor determining the coverage dependence. We calculated α_{CH_4} for 0, 1/9, 2/9 ML coverage and fitted a line to these points. Above 1/4 ML the metal becomes unstable, which makes it only possible to get values below that coverage. On Pd(111) we found $\alpha_{\text{CH}_4} = 0.2$ and on Pd(100) we found an oscillating behaviour on the barrier and set $\alpha_{\text{CH}_4} = 0.0$.

The O-O repulsions are important to include as they can be substantial.[S2] Also in this case we used a linear dependence on the barrier for oxygen desorption, E_a:

$$E_a \quad \rightarrow \quad E_a \left(1 - \alpha_{\text{O}} \theta_{\text{O}}\right) \tag{7}$$

For Pd(100) we used the values of the previous study[S2] $\alpha_{\text{O}} = 0.85$, and for Pd(111) $\alpha_{\text{O}} = 1.1$.

The C-C interactions we computed by computing the adsorption energy at C coverages

1/9,1/6,1/4 and 1/2 ML for Pd(100), whereas the Pd(111) surface reaches maximally 1/4 ML coverage. We did not include any higher coverages for Pd(111) to ensure self-consistent values for the interactions. The barriers involving carbon $E_C^{(i)}$ were scaled as follows:

$$E_C^{(i)} \quad \rightarrow \quad E_C^{(i)} \left(1 - \beta_C \theta_C / E_C^{(i)}\right) = E_C^{(i)} \left(1 - \alpha_C^{(i)} \theta_C\right) \tag{8}$$

Where on Pd(100) we found $\beta_C = 0.68\,\text{eV}$ and for Pd(111) we computed $\beta_C = 0.11\,\text{eV}$.

The OH-OH interactions are dependent on the specific surface geometry, and we scale the OH splitting to O+H according to:

$$E_a \quad \rightarrow \quad E_a \left(1 - \alpha_{OH} \theta_{OH}\right) \tag{9}$$

We used values of α_{OH} again from the previous study.[S2] On Pd(111) we set $\alpha_{OH} = 0.0$ and on Pd(100) we set $\alpha_{OH} = -0.16$, i.e. slightly net attractive.

Figure S5 shows our calculations of the scaling of the adsorption energies with surface coverages for C and O.
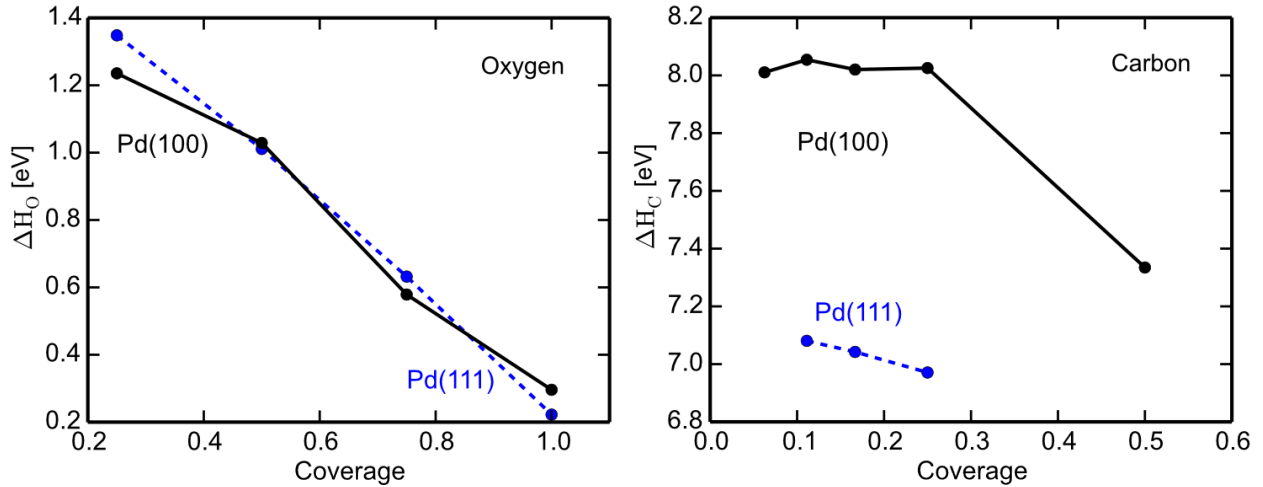

Figure S5: The scaling of the adsorption energy with surface coverage for O(left) and C(right). The energy for C is with reference to the gas phase radical and O is with respect to O_2.

Sensitivity to Interactions

A sensitivity analysis for the TOFs dependence on the lateral interaction strengths are presented in Figure S6. The α values were varied and the TOFs were noted at each value of α. The results are affected only at lower temperatures, and are most pronounced for oxygen, where lowering the interaction strength by 20% yield a change in the TOF of ca. 2 orders of magnitude. Increasing the O-O repulsions by 20% yield a lower change of ca. 1 order of mangitude in the low temperature region.

The C-C interactions affect the TOFs at most by ca. 1 order of magnitude when lowering the repulsions by 20%. Here one can see that even though the C-C repulsions are modeled as linear, and thereby overestimated at some coverages between 0.1 and 0.5(see Figure S5), the results are not sensitive to this linear approximation.
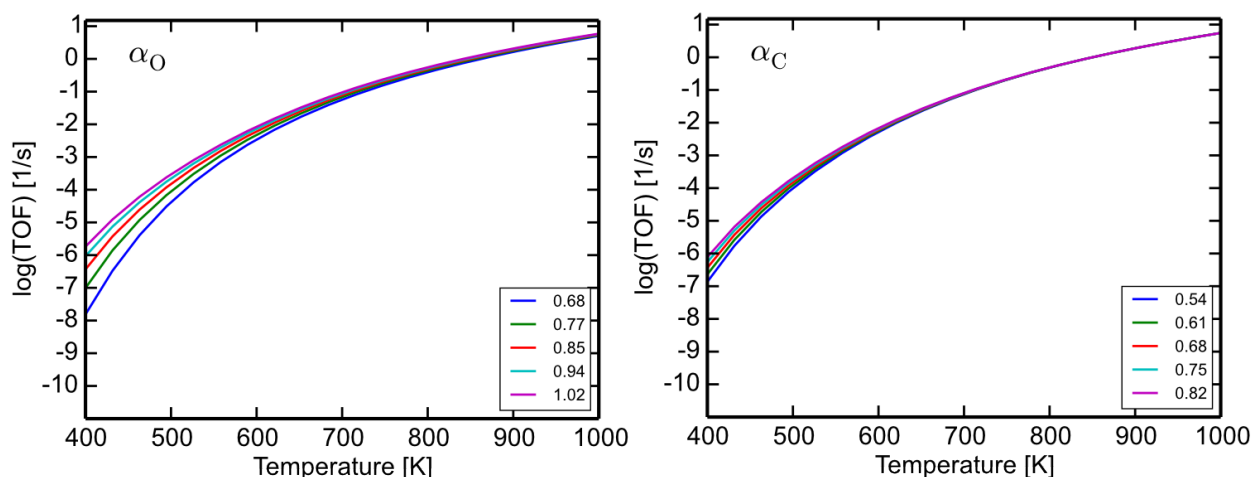

Figure S6: A sensitivity analysis of the TOF to the lateral interactions on the Pd(100) surface. The natural logarithm to the TOFs are on the 2nd axis and temperature on the 1st.

References

(S1) Chorkendorff, I.; Niemantsverdriet, J. W. *Concepts of Modern Catalysis and Kinetics*, second, revised and enlarged ed.; WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007; pp. 87-92.

(S2) Trinchero, A.; Hellman, A.; Grönbeck, H. *Surf. Sci.* **2013**, 616, 206–213.