Electronic Supplementary Information for:

A dimer path for CO dissociation on PtSn

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Contents

Effect of Sn adatoms on direct CO dissociation for SnO_X/Pt(111)/Pt_3Sn.....2

Reactant, transition and product states for direct CO dissociation 4

Pathways for SnO_x formation on $Pt_{15}Sn$-skin systems with 3 Sn adatoms 6

CO dimer formation with Pt ad-atoms on Pt(111) 7

Alternative CO dissociation routes on Pt(100) and Pt(111).....8

References 10

Effect of Sn adatoms on direct CO dissociation for $SnO_X/Pt(111)/Pt_3Sn$

In the main text, direct CO dissociation is reported in the case of three adatoms in the $(4 \times 2\sqrt{3})_{rect}$ surface cell. Here we report how the dissociation barrier could be influenced by the number of Sn atoms, Table S1 and Figure S1. CO dissociation is studied on Pt-skin systems with 0, 1, 2 and 3 surface Sn ad-atoms at a coverage of 0.50 ML CO. The corresponding dissociation pathways are shown in Figure S1(a) and transition states are visualized in Figure S1(b). The CO-dissociation starts with the CO molecule adsorbed in a hollow site (hcp for bare Pt and fcc for Pt with Sn adatoms). We find that the differential CO adsorption energy is reduced when the number of Sn adatoms is increased. This effect is most probably related to the increased "effective CO coverage" as Sn blocks adsorption sites. The barrier for the CO dissociation is lowered with increased number of Sn ad-atoms. The lowering is correlated with a decreased C-O bond length at the transition state, signaling an earlier transition state.

Table S1: Calculated differential CO adsorption energy ($\Delta E_{ads,CO,diff}$), reaction barriers ($\Delta E^{\ddagger}$) and reaction energies (ΔE_r) for direct CO dissociation on $Sn_x/Pt(111)/Pt_3Sn(111)$ at 0.50 ML CO. $d(C\text{-}O)_{TS}$ is the calculated C-O bond distance in the transition state. Energies and distances are reported in eV and Å, respectively.

# Sn adatoms = x	$\Delta E_{ads,CO,diff}$	$\Delta E^{\ddagger}$	ΔE_r	$d(C\text{-}O)_{TS}$ (Å)
0	**-1.59**	**3.78**	**2.81**	**1.81**
1	**-1.21**	**2.93**	**2.89**	**2.20**
2	**-1.12**	**2.35**	**1.95**	**2.08**
3	**-0.89**	**2.16**	**1.64**	**1.98**

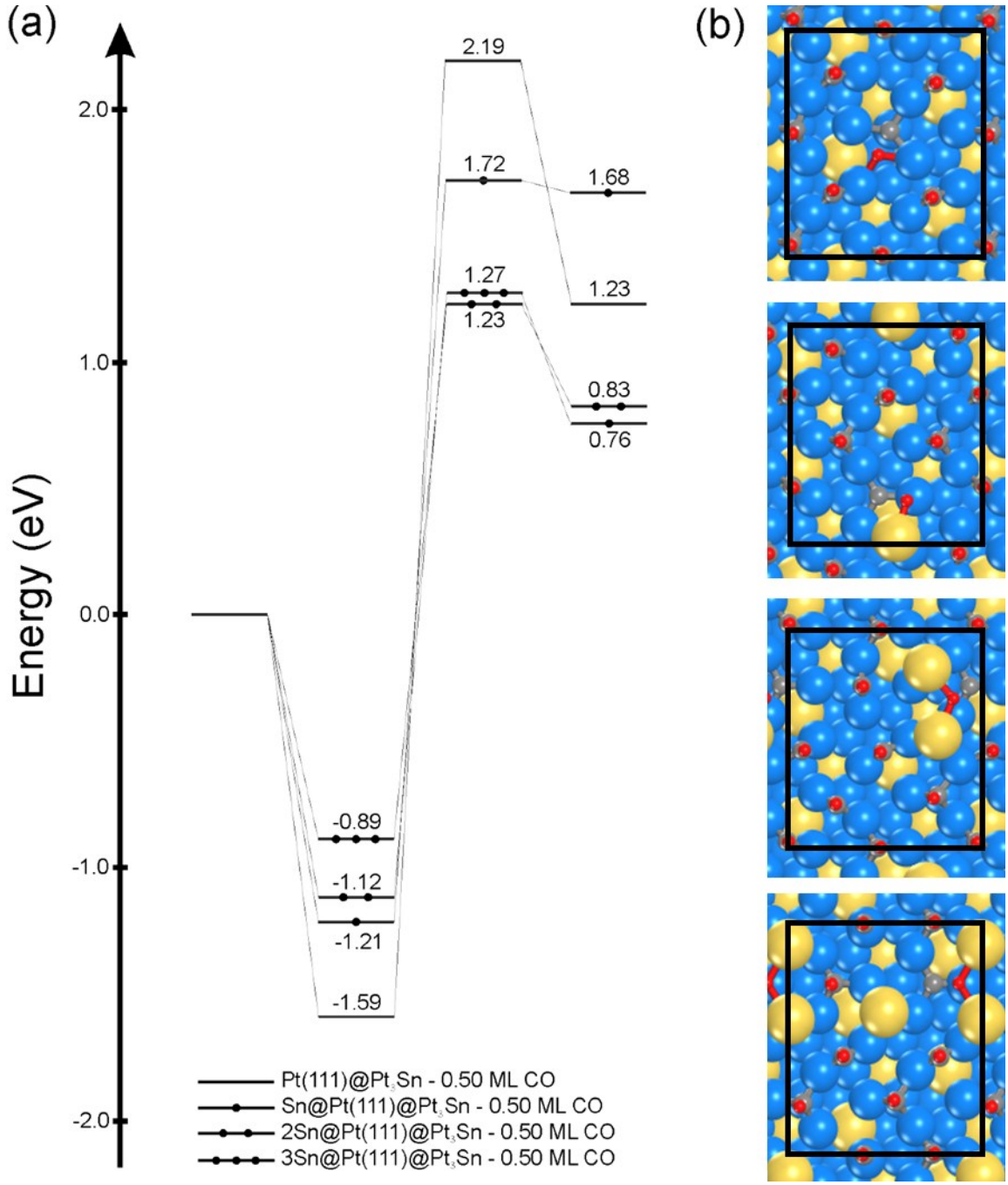

Figure S1: (a) Energy diagram of reactants, products and transition states of direct CO dissociation on Sn_x/Pt(111)/Pt_3Sn with 0, 1, 2 and 3 Sn-atoms (b) atomic models of the transition states. Atomic color codes: Pt (blue), Sn (yellow), O (red) and C (gray).

Reactant, transition and product states for direct CO dissociation

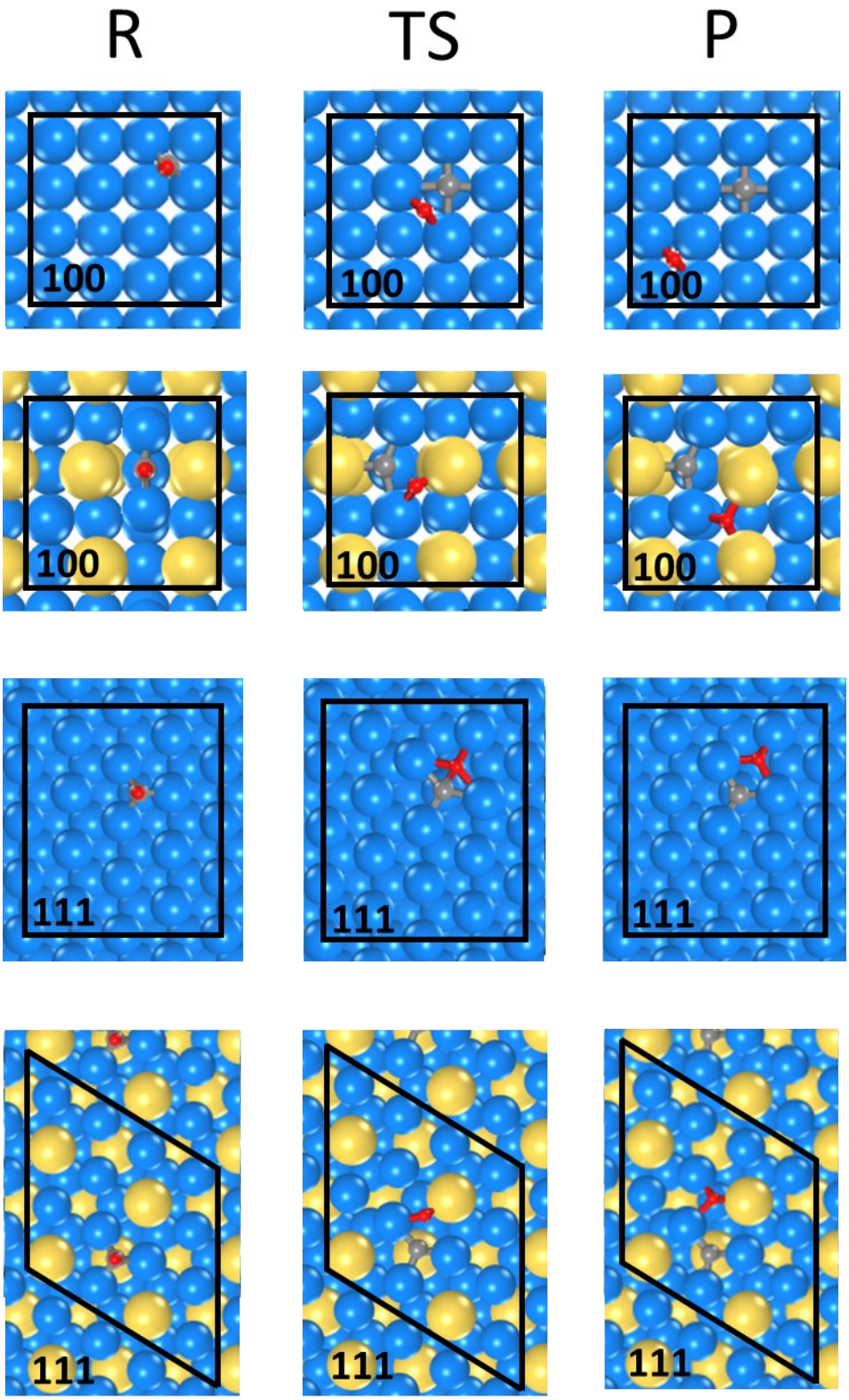

Figure S2: Atomic models of reactants, products and transition states of direct CO dissociation at 100 and 111 surfaces for Pt and Pt_3Sn. Atomic color codes: Pt (blue), Sn (yellow), O (red) and C (gray).

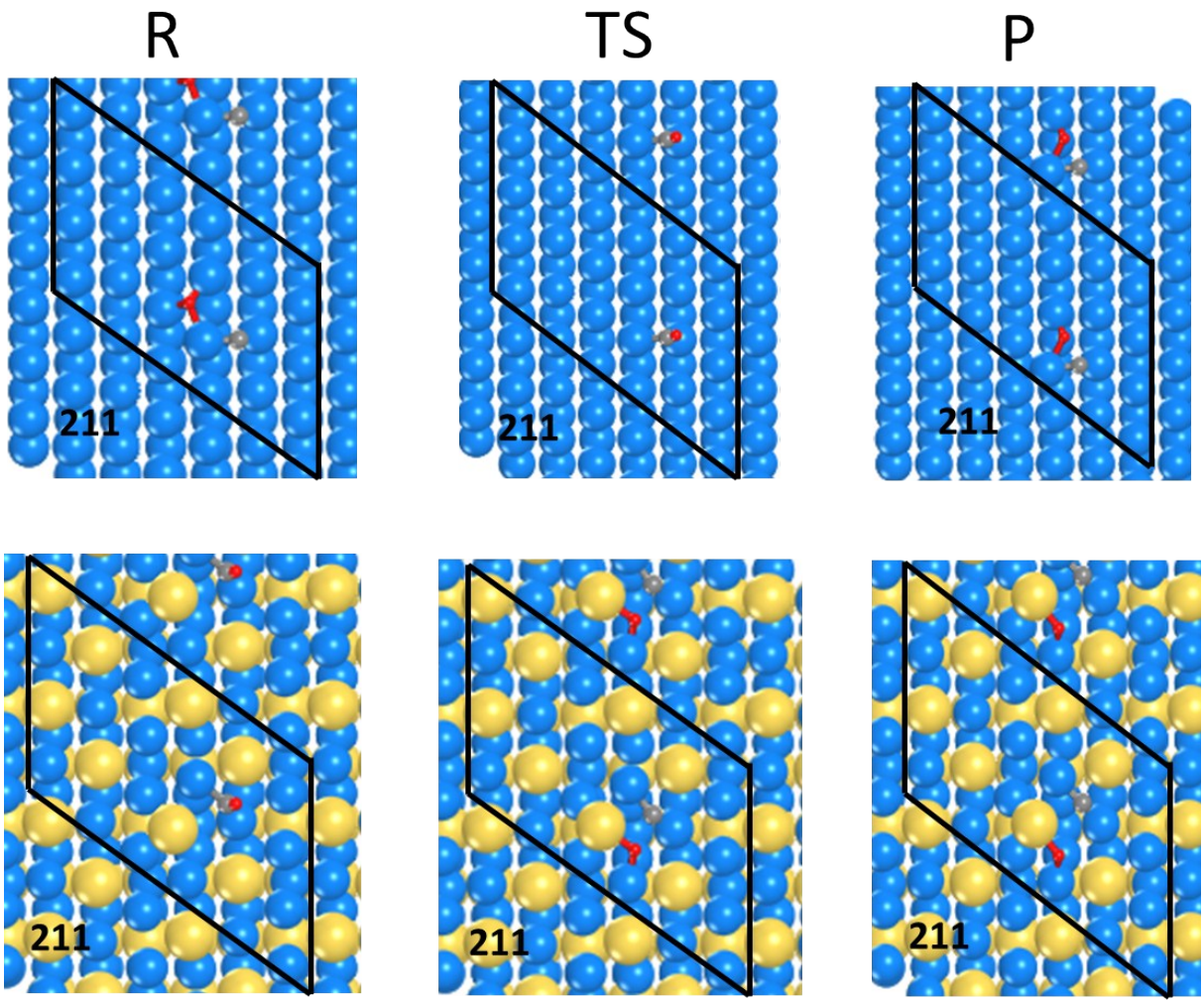

Figure S3: Atomic models of reactants, products and transition states of CO dissociation modeled at 211 surfaces for Pt and Pt_3Sn. Atomic color codes: Pt (blue), Sn (yellow), O (red) and C (gray).

Pathways for SnO_x formation on $Pt_{15}Sn$-skin systems with 3 Sn adatoms

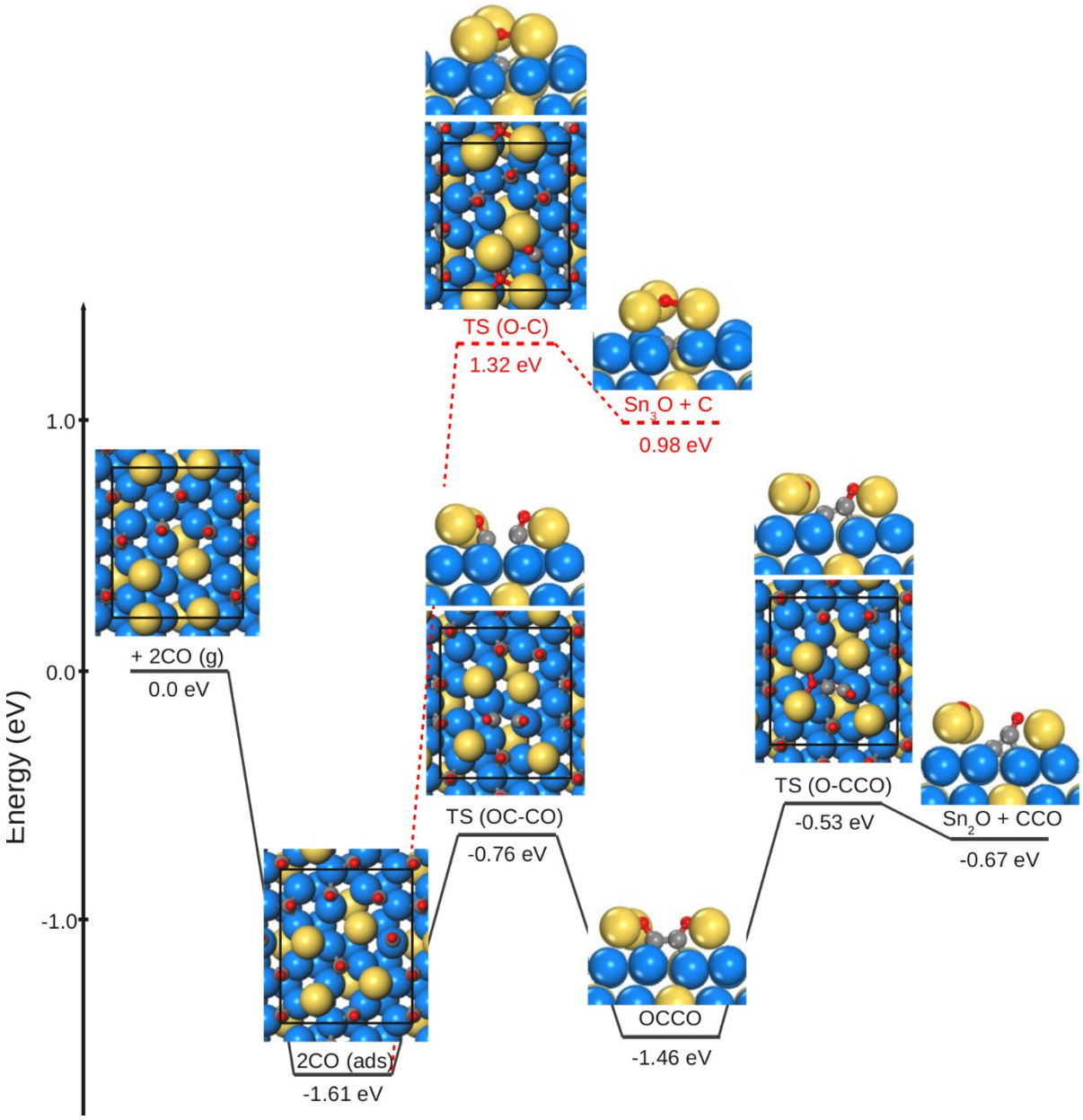

Figure S4. Pathway for SnO_x formation on a model of CO loaded $Sn_3/Pt_{15}Sn(111)/Pt_3Sn$ following the dimer route for CO dissociation. The C-C distance of the CO dimerization transition state is 2.02 Å, and the O-C distance in the subsequent oxygen split-off is 2.12 Å. Furthermore, the C-O distance during direct CO dissociation is 2.07 Å. Atomic color codes: Pt (blue), Sn (yellow), O (red) and C (gray).

CO dimer formation with Pt ad-atoms on Pt(111)

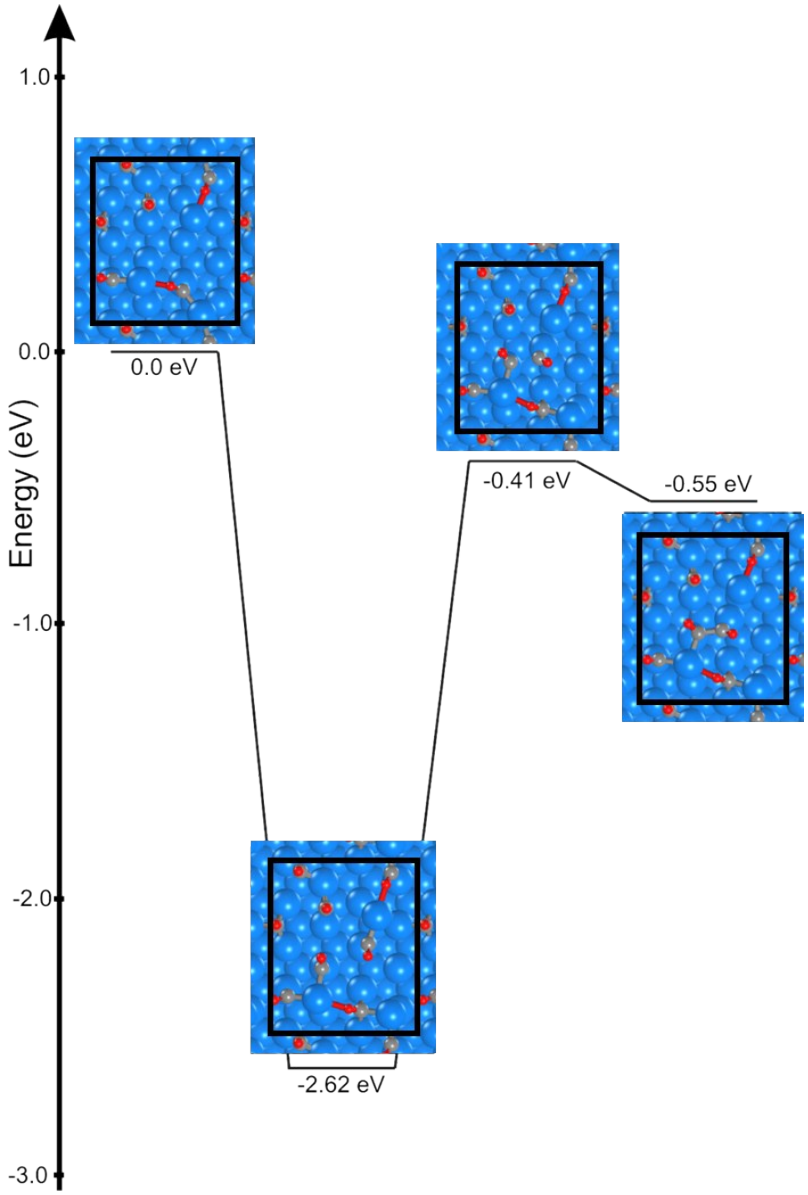

Figure S5: CO-dimer formation on Pt(111) with three Pt ad-atoms. Atomic color codes: Pt (blue), O (red) and C (grey).

Alternative CO dissociation routes on Pt(100) and Pt(111)

In addition to direct and dimer routes for CO dissociation, CO has been proposed to dissociate via the, so called, Boudouard reaction [1, 2] producing CO_2 and carbon.

$$CO + CO \rightarrow CO_2 + C$$

Here we investigate such possibilities on the bare Pt(100) and Pt(111) surface at a realistic CO coverage of 0.5 ML, Figure S7 and S8. The starting point for Pt(100) is two adsorbed CO in the surface cell. The dissociation of CO produces directly CO_2 and a C-C bond. The barrier for CO dissociation is 3.15 eV from the adsorbed state.

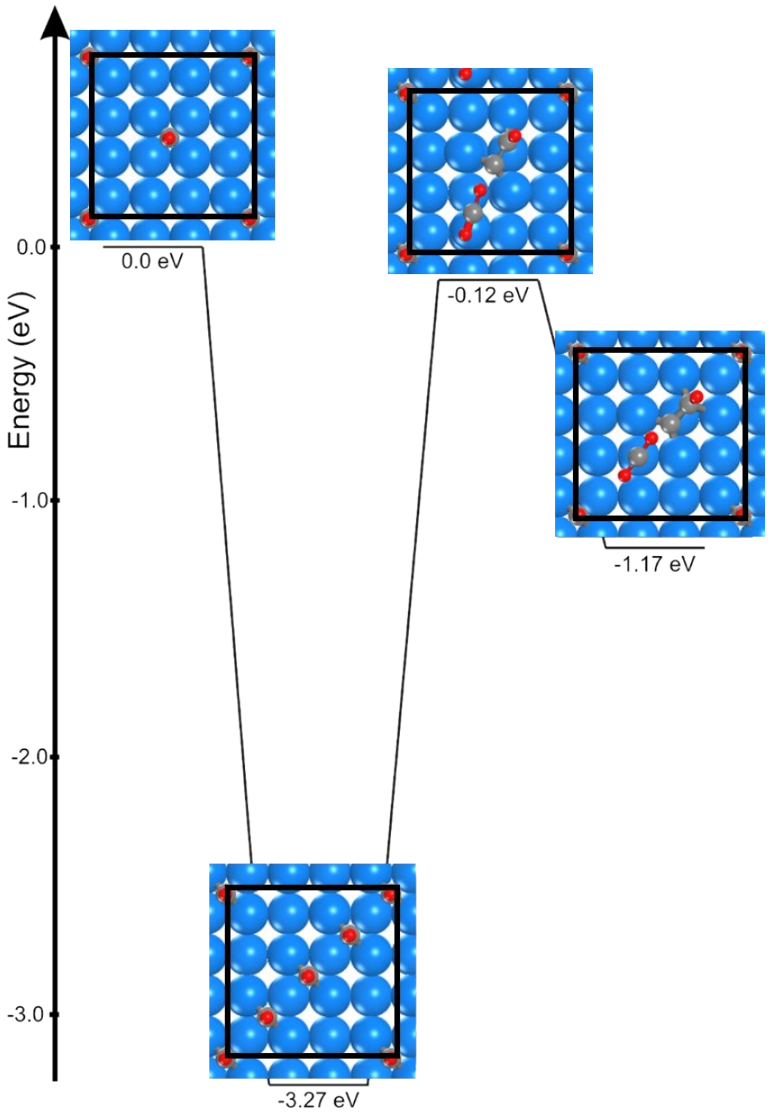

Figure S6: Boudouard pathway for CO dissociation on CO loaded Pt(100). Atomic color codes: Pt (blue), O (red) and C (grey).

Three paths for CO dissociation are investigated on Pt(111); i) direct CO dissociation, ii) direct Boudouard reaction and iii) Boudouard from the CO dimer, see Figure S8. The barrier for direct dissociation is 4.07 eV and for the direct Boudouard reaction it is 3.05 eV. Thus, these paths are unfeasible on flat (111) surfaces. Also the dimer path have a high effective barrier as the dimer is not stable in the absence of ad-atoms.

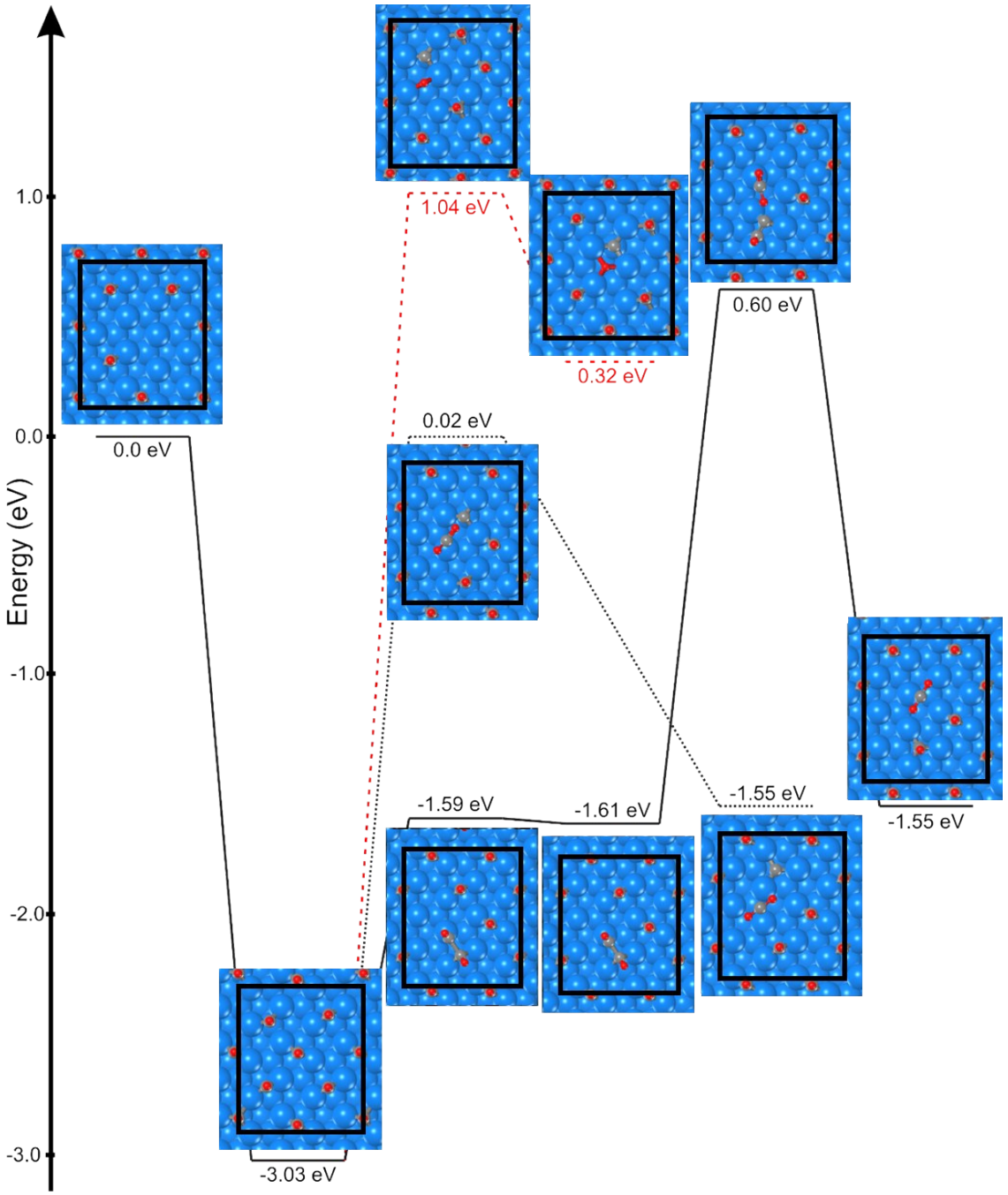

Figure S7: Three paths for CO dissociation on Pt(111); direct CO dissociation (red dotted line), direct Boudouard reaction (black dotted line), Boudouard from the CO dimer (black solid line). The calculations are performed with a 0.50 ML CO coverage. Atomic color codes: Pt (blue), O (red) and C (grey).

References

[1] K. McCrea, J. Parker, G. Somorjai, High-Pressure CO Dissociation and CO Oxidation Studies on Platinum Single Crystal Surfaces Using Sum Frequency Generation Surface Vibrational Spectroscopy, in: A.F. Carley, P.R. Davies, G.J. Hutchings, M.S. Spencer (Eds.) Surface Chemistry and Catalysis, Springer US, Boston, MA, 2002, pp. 55-78.
[2] K.R. McCrea, J.S. Parker, G.A. Somorjai, The Role of Carbon Deposition from CO Dissociation on Platinum Crystal Surfaces during Catalytic CO Oxidation: Effects on Turnover Rate, Ignition Temperature, and Vibrational Spectra, The Journal of Physical Chemistry B, 106 (2002) 10854-10863.