Appendix B

Adsorption Structures Involving The $(\sqrt{5} \times \sqrt{5})R27°$

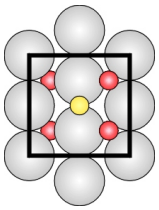
B.1 O And CO In A $(\sqrt{5} \times \sqrt{5})R27°$ Surface Unit Cell

To setup the phase diagram of the Pd(100) surface in a constrained equilibrium with an oxygen and CO gas phase (cf. Chapter 7) a large number of possible configurations of O and/or CO adsorbed in the different high symmetry sites on the Pd(100) surface and on the $(\sqrt{5} \times \sqrt{5})R27°$ surface oxide structure have been calculated. In the following all considered configurations involving the surface oxide structure are listed. As explained in Chapter 7 only the most stable structures, which minimize the Gibbs free energy of adsorption, ΔG^{ads}, for a given chemical potential of oxygen and CO, appear in the 2D-surface phase diagram as shown in Fig. 7.6 and Fig. 7.7. Since configurations having the same number of oxygen atoms (N_{O}) and CO molecules (N_{CO}) will have the same dependence on the oxygen and CO chemical potentials, only the one having the lowest binding energy, $\Delta\widetilde{E}^{\mathrm{bind}}_{\mathrm{O,CO@Pd}}$, as defined in Eq. 7.3 will appear as stable structure in the surface phase diagram. The presented configurations are thus grouped into structures having an equivalent oxygen and CO coverage and all energies, $\Delta E'_{N_{\mathrm{O}},N_{\mathrm{CO}}}$, are given with respect to the binding energy of the most favorable structure for each specific coverage, which is marked by a frame. All energies have been calculated using the PBE exchange-correlation functional and a computational setup as described on Page 66. The '$\gtrsim$' sign indicates that the structure has been calculated using a slab with only 3 palladium layers to separate the upper and lower surface oxide trilayer instead of the otherwise used 5 palladium layers. Unstable structures are marked by a '$-$' sign.

The different configurations are represented by schematic illustrations, where large grey spheres indicate palladium atoms in the reconstructed surface oxide layer, small red ones oxygen atoms and small yellow ones CO molecules. Additionally, in all figures the $(\sqrt{5} \times \sqrt{5})R27°$ surface unit cell is shown.

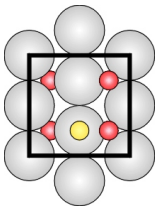
4 O and 1 CO

Structure 001



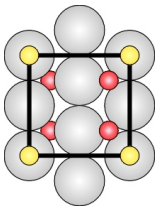
$\Delta E'_{4,1} = 0.00\,\mathrm{eV}$

Structure 002



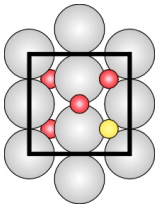
$\Delta E'_{4,1} = 0.31\,\mathrm{eV}$

Structure 003



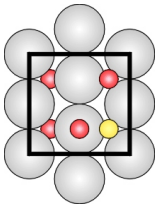
$\Delta E'_{4,1} = 0.81\,\mathrm{eV}$

Structure 004



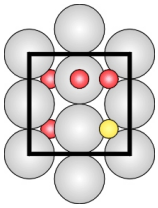
$\Delta E'_{4,1} = 1.13\,\mathrm{eV}$

Structure 005



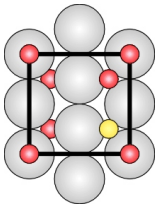
$\Delta E'_{4,1} = -$

Structure 006



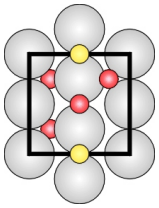
$\Delta E'_{4,1} = -$

Structure 007



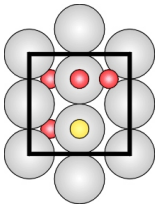
$\Delta E'_{4,1} = -$

Structure 008



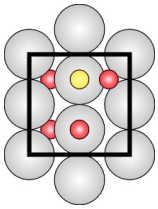
$\Delta E'_{4,1} = 1.36\,\mathrm{eV}$

Structure 009



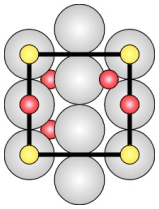
$\Delta E'_{4,1} \gtrsim 2.81\,\mathrm{eV}$

Structure 010



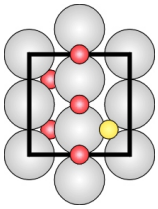
$\Delta E'_{4,1} = -$

Structure 011



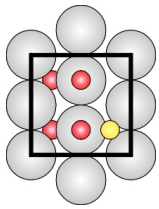
$\Delta E'_{4,1} = -$

Structure 012



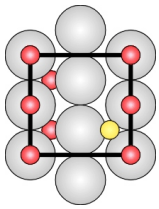
$\Delta E'_{4,1} = 2.65\,\mathrm{eV}$

Structure 013



$\Delta E'_{4,1} = -$

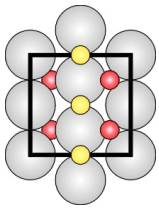
Structure 014



$\Delta E'_{4,1} = -$

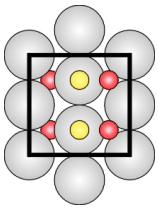
4 O and 2 CO

Structure 015



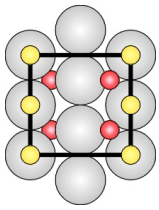
$\Delta E'_{4,2} = 0.00\,\mathrm{eV}$

Structure 016



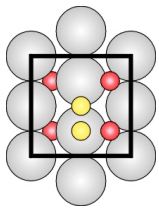
$\Delta E'_{4,2} = 0.48\,\mathrm{eV}$

Structure 017



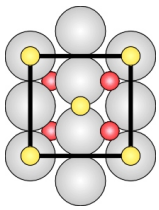
$\Delta E'_{4,2} = -$

Structure 018



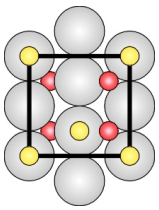
$\Delta E'_{4,2} = -$

Structure 019



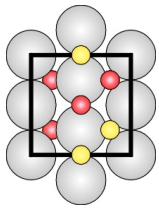
$\Delta E'_{4,2} \gtrsim 0.60\,\mathrm{eV}$

Structure 020



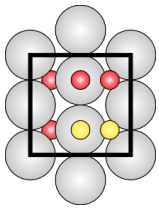
$\Delta E'_{4,2} \gtrsim 0.91\,\mathrm{eV}$

Structure 021



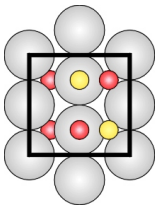
$\Delta E'_{4,2} = 0.93\,\mathrm{eV}$

Structure 022



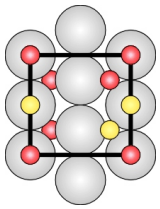
$\Delta E'_{4,2} \gtrsim 2.68\,\mathrm{eV}$

Structure 023



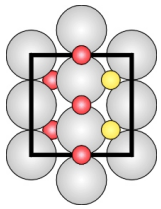
$\Delta E'_{4,2} = -$

Structure 024



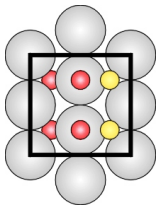
$\Delta E'_{4,2} = -$

Structure 025



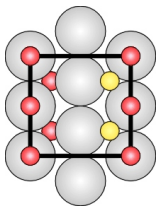
$\Delta E'_{4,2} = 2.27\,\mathrm{eV}$

Structure 026



$\Delta E'_{4,2} = -$

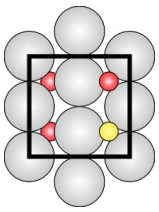
Structure 027



$\Delta E'_{4,2} = -$

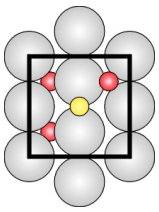
3 O and 1 CO

Structure 028



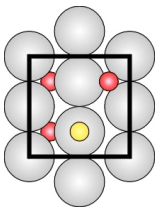
$\Delta E'_{3,1} = 0.00\,\mathrm{eV}$

Structure 029



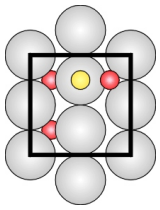
$\Delta E'_{3,1} = 0.20\,\mathrm{eV}$

Structure 030



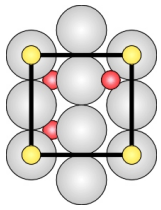
$\Delta E'_{3,1} \gtrsim 0.07\,\mathrm{eV}$

Structure 031



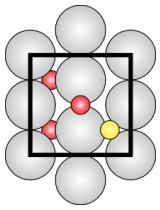
$\Delta E'_{3,1} \gtrsim 0.83\,\mathrm{eV}$

Structure 032



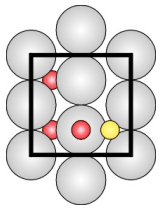
$\Delta E'_{3,1} \gtrsim 0.86\,\mathrm{eV}$

Structure 033



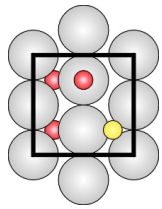
$\Delta E'_{3,1} = -$

Structure 034



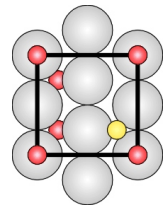
$\Delta E'_{3,1} \gtrsim 2.64\,\mathrm{eV}$

Structure 035



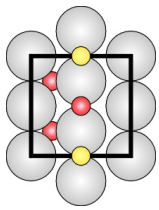
$\Delta E'_{3,1} = -$

Structure 036



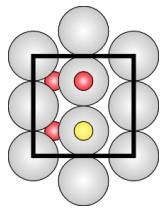
$\Delta E'_{3,1} = -$

Structure 037



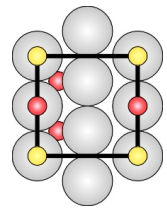
$\Delta E'_{3,1} = -$

Structure 038



$\Delta E'_{3,1} = -$

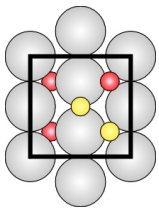
Structure 039



$\Delta E'_{3,1} = -$

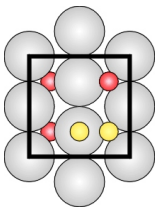
3 O and 2 CO

Structure 040



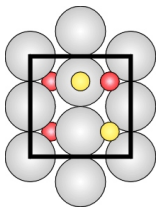
$\Delta E'_{3,2} = 0.00\,\mathrm{eV}$

Structure 041



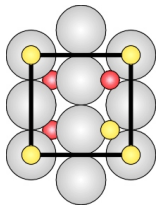
$\Delta E'_{3,2} \gtrsim 0.35\,\mathrm{eV}$

Structure 042



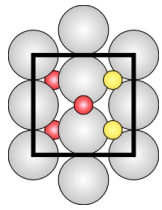
$\Delta E'_{3,2} \gtrsim 0.21\,\mathrm{eV}$

Structure 043



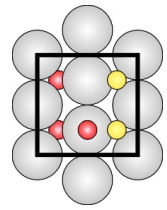
$\Delta E'_{3,2} \gtrsim 0.98\,\mathrm{eV}$

Structure 044



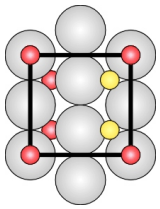
$\Delta E'_{3,2} = 0.95\,\mathrm{eV}$

Structure 045



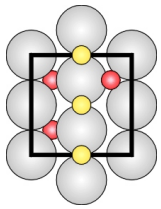
$\Delta E'_{3,2} \gtrsim 2.24\,\mathrm{eV}$

Structure 046



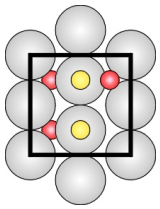
$\Delta E'_{3,2} = -$

Structure 047



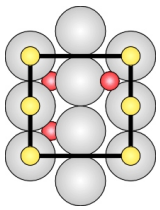
$\Delta E'_{3,2} = 0.32\,\mathrm{eV}$

Structure 048



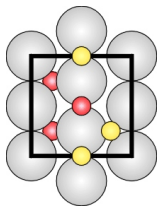
$\Delta E'_{3,2} \gtrsim 0.43\,\mathrm{eV}$

Structure 049



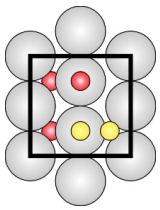
$\Delta E'_{3,2} \gtrsim 1.73\,\mathrm{eV}$

Structure 050



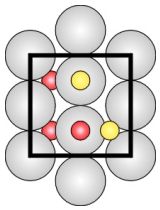
$\Delta E'_{3,2} = 1.27\,\mathrm{eV}$

Structure 051



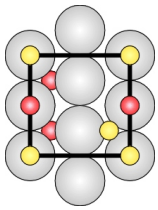
$\Delta E'_{3,2} = -$

Structure 052



$\Delta E'_{3,2} \gtrsim 2.41\,\mathrm{eV}$

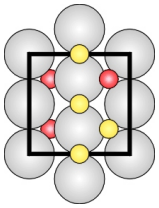
Structure 053



$\Delta E'_{3,2} = -$

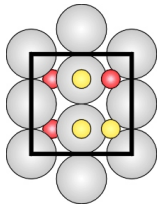
3 O and 3 CO

Structure 054



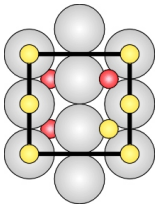
$\Delta E'_{3,3} = 0.00\,\mathrm{eV}$

Structure 055



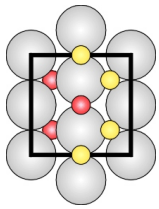
$\Delta E'_{3,3} \gtrsim 0.46\,\mathrm{eV}$

Structure 056



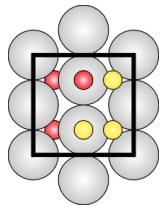
$\Delta E'_{3,3} = -$

Structure 057



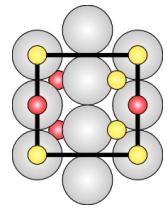
$\Delta E'_{3,3} \gtrsim 0.93\,\mathrm{eV}$

Structure 058



$\Delta E'_{3,3} = -$

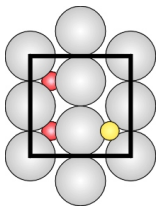
Structure 059



$\Delta E'_{3,3} = -$

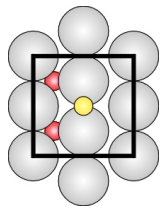
2 O and 1 CO

Structure 060



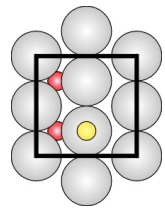
$\Delta E'_{2,1} = 0.00\,\mathrm{eV}$

Structure 061



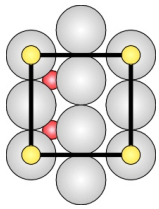
$\Delta E'_{2,1} = 0.03\,\mathrm{eV}$

Structure 062



$\Delta E'_{2,1} \gtrsim 0.52\,\mathrm{eV}$

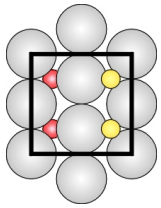
Structure 063



$\Delta E'_{2,1} = -$

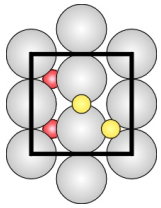
2 O and 2 CO

Structure 064



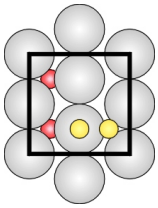
$\Delta E'_{2,2} = 0.00\,\text{eV}$

Structure 065



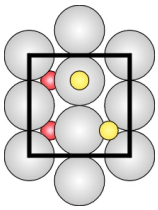
$\Delta E'_{2,2} = 0.21\,\text{eV}$

Structure 066



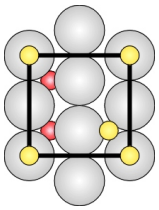
$\Delta E'_{2,2} \gtrsim 0.77\,\text{eV}$

Structure 067



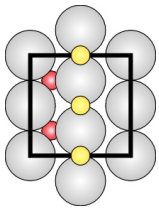
$\Delta E'_{2,2} \gtrsim 0.31\,\text{eV}$

Structure 068



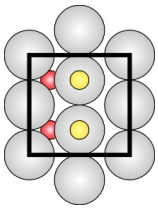
$\Delta E'_{2,2} = -$

Structure 069



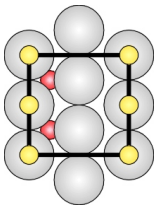
$\Delta E'_{2,2} = 0.05\,\text{eV}$

Structure 070



$\Delta E'_{2,2} \gtrsim 0.74\,\text{eV}$

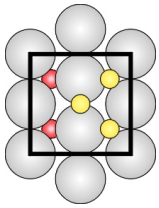
Structure 071



$\Delta E'_{2,2} \gtrsim 1.28$

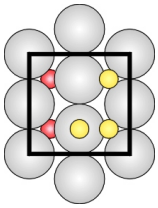
2 O and 3 CO

Structure 072



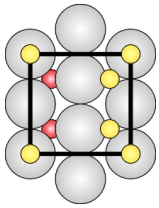
$\Delta E'_{2,3} = 0.00\,\text{eV}$

Structure 073



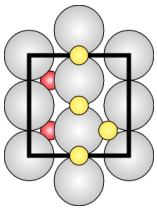
$\Delta E'_{2,3} \gtrsim 0.03\,\text{eV}$

Structure 074



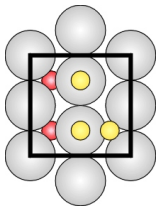
$\Delta E'_{2,3} = -$

Structure 075



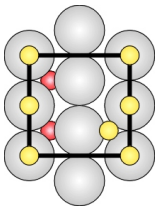
$\Delta E'_{2,3} = 0.18\,\text{eV}$

Structure 076



$\Delta E'_{2,3} \gtrsim 0.45\,\text{eV}$

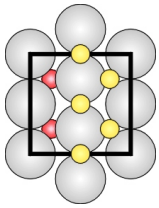
Structure 077



$\Delta E'_{2,3} \gtrsim 1.57\,\text{eV}$

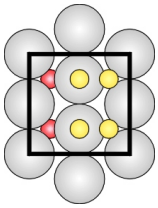
2 O and 4 CO

Structure 078



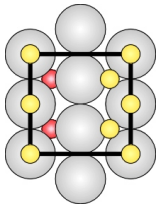
$\Delta E'_{2,4} = 0.00\,\text{eV}$

Structure 079



$\Delta E'_{2,4} \gtrsim 0.29\,\text{eV}$

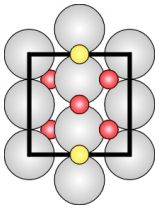
Structure 080



$\Delta E'_{2,4} \gtrsim 0.31\,\text{eV}$

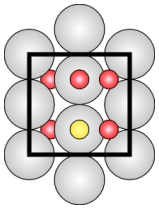
5 O and 1 CO

Structure 081



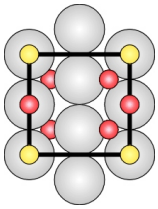
$\Delta E'_{5,1} = 0.00\,\text{eV}$

Structure 082



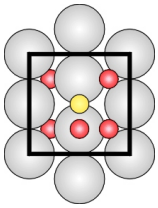
$\Delta E'_{5,1} \gtrsim 1.37\,\text{eV}$

Structure 083



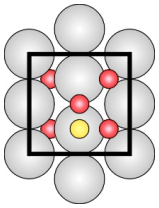
$\Delta E'_{5,1} = -$

Structure 084



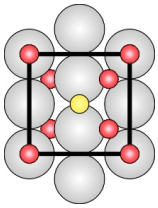
$\Delta E'_{5,1} = -$

Structure 085



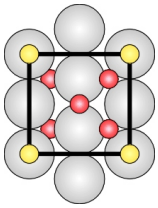
$\Delta E'_{5,1} = -$

Structure 086



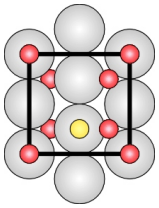
$\Delta E'_{5,1} = -$

Structure 087



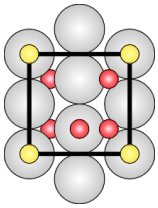
$\Delta E'_{5,1} \gtrsim 0.65\,\text{eV}$

Structure 088



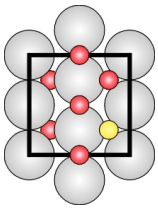
$\Delta E'_{5,1} = -$

Structure 089



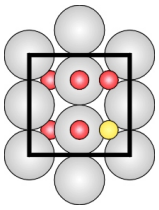
$\Delta E'_{5,1} = -$

Structure 090



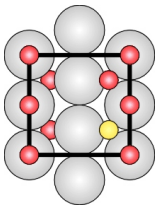
$\Delta E'_{5,1} = 1.12\,\text{eV}$

Structure 091



$\Delta E'_{5,1} = -$

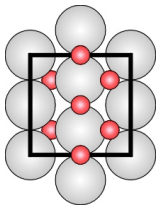
Structure 092



$\Delta E'_{5,1} = -$

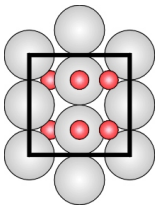
6 O and 0 CO

Structure 093



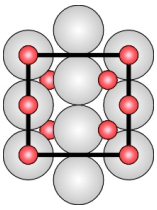
$\Delta E'_{6,0} = 0.00\,\mathrm{eV}$

Structure 094



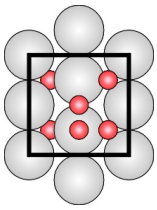
$\Delta E'_{6,0} = -$

Structure 095



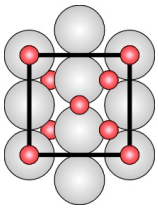
$\Delta E'_{6,0} = -$

Structure 096



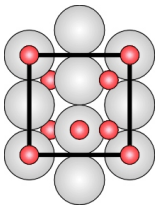
$\Delta E'_{6,0} = -$

Structure 097



$\Delta E'_{6,0} = -$

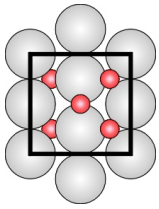
Structure 098



$\Delta E'_{6,0} = -$

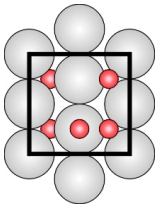
5 O and 0 CO

Structure 099



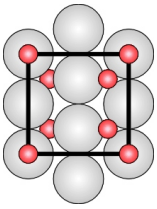
$\Delta E'_{5,0} = 0.00\,\mathrm{eV}$

Structure 100



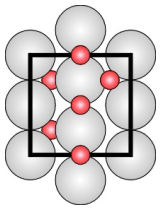
$\Delta E'_{5,0} = -$

Structure 101



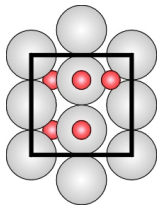
$\Delta E'_{5,0} = -$

Structure 102



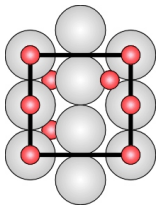
$\Delta E'_{5,0} \gtrsim 1.42\,\mathrm{eV}$

Structure 103



$\Delta E'_{5,0} = -$

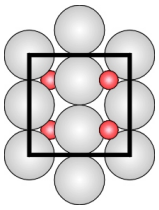
Structure 104



$\Delta E'_{5,0} = -$

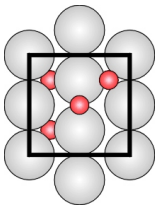
4 O and 0 CO

Structure 105



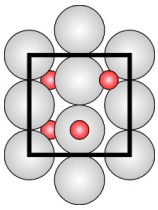
$\Delta E'_{4,0} = 0.00\,\mathrm{eV}$

Structure 106



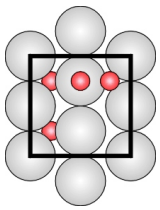
$\Delta E'_{4,0} = 1.27\,\mathrm{eV}$

Structure 107



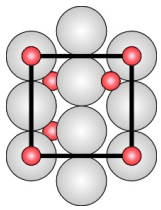
$\Delta E'_{4,0} = -$

Structure 108



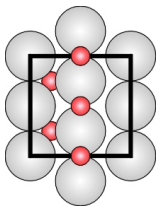
$\Delta E'_{4,0} \gtrsim 3.30\,\mathrm{eV}$

Structure 109



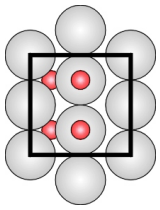
$\Delta E'_{4,0} = -$

Structure 110



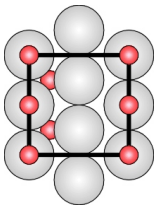
$\Delta E'_{4,0} = -$

Structure 111



$\Delta E'_{4,0} = -$

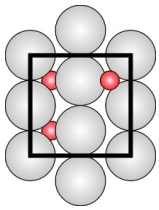
Structure 112



$\Delta E'_{4,0} = -$

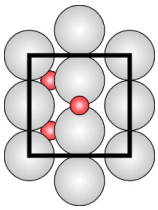
3 O and 0 CO

Structure 113



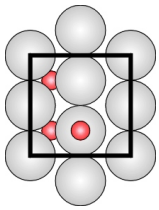
$\Delta E'_{3,0} = 0.00\,\mathrm{eV}$

Structure 114



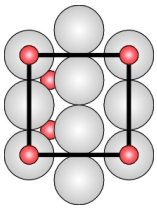
$\Delta E'_{3,0} \gtrsim 0.69\,\mathrm{eV}$

Structure 115



$\Delta E'_{3,0} \gtrsim 2.38\,\mathrm{eV}$

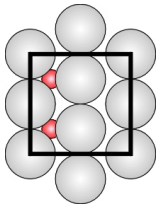
Structure 116



$\Delta E'_{3,0} = -$

2 O and 0 CO

Structure 117



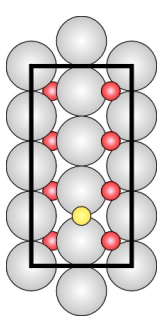
$\Delta E'_{2,0} = 0.00\,\mathrm{eV}$

B.2 O And CO In Larger $(\sqrt{5} \times \sqrt{5})R27°$ Surface Unit Cells

The interactions between adsorbates in neighboring $(\sqrt{5} \times \sqrt{5})R27°$ surface unit cells is investigated by calculations performed in larger surface unit cells. This is done for the adsorption of O and/or CO in bridge site in $(2 \times 1)-$ and $(1 \times 2)-(\sqrt{5} \times \sqrt{5})R27°$ surface unit cells. The interactions between adsorbates in hollow sites beyond the "(1×1)" surface unit cell has not been considered at this point. Also the interactions between adsorbates on the different top sites has not been investigated in more detail, since the resulting structures appear to be rather unstable and will thus not contribute to the resulting surface phase diagram (cf. Chapter 7).

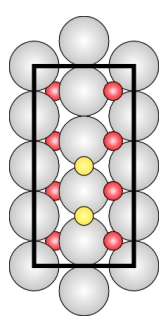
In structures 118–122 one or two CO molecules are adsorbed in bridge sites on the surface oxide structure. The binding energies are calculated with respect to the complete surface oxide, as given in Eq. (7.2), using the PBE exchange-correlation functional. Here, only the relative binding energies per CO molecule with respect to the lowest value are given. The structures exhibiting the lowest average binding energy per CO molecule is marked by a frame. Since structures 118, 120 and 121 are almost degenerate in the average binding energy, the interactions between CO molecules adsorbed in bridge sites at a distance ≥ 6.2Å, corresponding to the $(\sqrt{5} \times \sqrt{5})R27°$ surface unit cell vector, seem to be negligible. CO molecules adsorbed in directly neighboring bridge sites, though, show repulsive, lateral interactions (structure 119, 122).

Structure 118



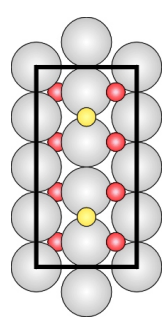
$\Delta E^{\text{bind}} = 0.00\,\text{eV}$

Structure 119



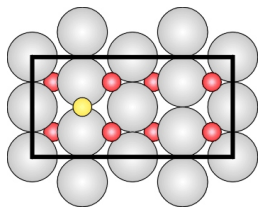
$\Delta E^{\text{bind}} \approx 0.10\,\text{eV}$

Structure 120



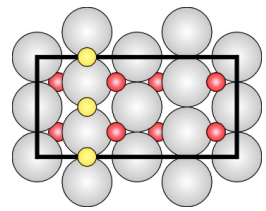
$\Delta E^{\text{bind}} \lesssim 0.05\,\text{eV}$

Structure 121



$\Delta E^{\text{bind}} \approx 0.00\,\text{eV}$

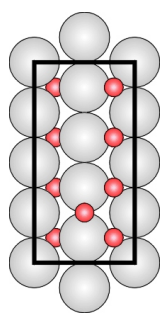
Structure 122



$\Delta E^{\text{bind}} \approx 0.20\,\text{eV}$

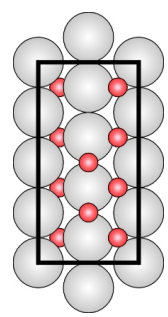
For the adsorption of oxygen in bridge sites a similar result is obtained (structures 123–126). Again the average binding energies per oxygen atom are given with respect to the lowest value. Also for the adsorption of oxygen in bridge sites a noticeable interaction is only observed for oxygen atoms adsorbed in directly neighboring bridge sites (structures 124, 126), whereas the interactions beyond the $(\sqrt{5}\times\sqrt{5})R27°$ surface unit cell appear to be negligible (structures 123, 125) .

Structure 123



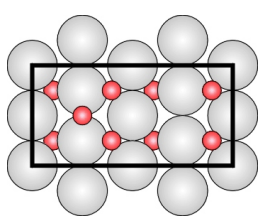
$\Delta E^{\text{bind}} = 0.00\,\text{eV}$

Structure 124



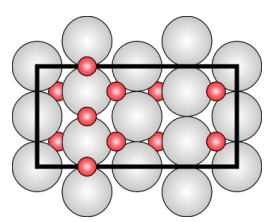
$\Delta E^{\text{bind}} \approx 0.17\,\text{eV}$

Structure 125



$\Delta E^{\text{bind}} \lesssim 0.03\,\text{eV}$

Structure 126

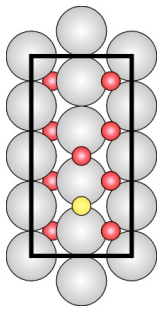


$\Delta E^{\text{bind}} \approx 0.30\,\text{eV}$

In structures 127–130 four different configurations are shown for the simultaneous adsorption of one oxygen atom and one CO molecule in bridge sites. The average binding energy of O and CO is calculated with respect to the complete surface oxide structure. Here, only relative values with respect to the lowest energy configuration

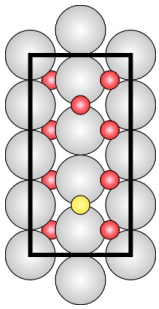
(marked by a frame) are given. Also here, repulsive, lateral interactions are observed for the adsorption in neighboring bridge sites (structures 127,129), whereas almost no interactions between adsorbates in neighboring cells are observed.

Structure 127



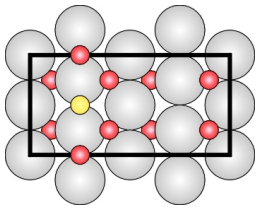
$\Delta E^{\text{bind}} \approx 0.10\,\text{eV}$

Structure 128



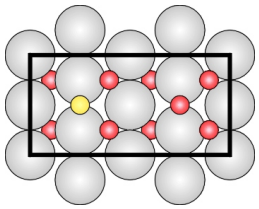
$\Delta E^{\text{bind}} \lesssim 0.01\,\text{eV}$

Structure 129



$\Delta E^{\text{bind}} \approx 0.32\,\text{eV}$

Structure 130



$\Delta E^{\text{bind}} = 0.00\,\text{eV}$

For the adsorption of oxygen and/or CO in bridge sites it is thus concluded, that within the $(\sqrt{5} \times \sqrt{5})R27°$ surface unit cell the lateral interactions lead to a reduction of the average binding energy, i.e. the adsorbate species show repulsive interactions. But these interactions do not appear to extend significantly beyond the $(\sqrt{5} \times \sqrt{5})R27°$ surface unit cell for the here aspired level of accuracy.

The setup of the lattice gas Hamiltonian (cf. Appendix C) can thus be restricted to first nearest neighbor interactions and the corresponding calculations can be performed within the $(\sqrt{5} \times \sqrt{5})R27°$ surface unit cell only.