Appendix C

Lattice Gas Hamiltonian

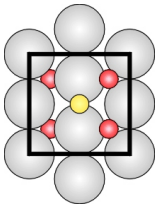
To evaluate the binding energies of the oxygen atoms and CO molecules during the kinetic Monte Carlo simulations (cf. Chapter 8) a lattice gas Hamiltonian (LGH) is used. Including only nearest neighbor pair interactions the LGH is given by

$$\begin{aligned} H = &\sum_i \left[n_{\mathrm{O},i} E^0_{\mathrm{O},i} + n_{\mathrm{CO},i} E^0_{\mathrm{CO},i} \right] \\ &+ \sum_{ij} \left[V_{\mathrm{O-O},ij}\, n_{\mathrm{O},i}\, n_{\mathrm{O},j} + V_{\mathrm{CO-CO},ij}\, n_{\mathrm{CO},i}\, n_{\mathrm{CO},j} + V_{\mathrm{O-CO},ij}\, n_{\mathrm{O},i}\, n_{\mathrm{CO},j} \right] \quad , \end{aligned} \tag{C.1}$$

where j only runs over the corresponding neighboring sites. Thus, the LGH contains 14 different parameters, including 4 on-site energies for O and CO in bridge or hollow sites on the $(\sqrt{5} \times \sqrt{5})R27^\circ$ surface oxide structure ($E^0_{\mathrm{O,br}}$, $E^0_{\mathrm{O,hol}}$, $E^0_{\mathrm{CO,br}}$ and $E^0_{\mathrm{CO,hol}}$), and 10 nearest neighbor pair interactions including 6 different interactions between like species ($V_{\mathrm{O-O,br-br}}$, $V_{\mathrm{O-O,hol-hol}}$, $V_{\mathrm{O-O,br-hol}}$, $V_{\mathrm{CO-CO,br-br}}$, $V_{\mathrm{CO-CO,hol-hol}}$, $V_{\mathrm{CO-CO,br-hol}}$) and 4 between unlike species ($V_{\mathrm{O-CO,br-br}}$, $V_{\mathrm{O-CO,hol-hol}}$, $V_{\mathrm{O-CO,br-hol}}$, $V_{\mathrm{O-CO,hol-br}}$). In this Appendix the 29 different configurations of O and/or CO on the surface oxide, which have been used for the fitting of the 14 LGH parameters, are presented with the corresponding lattice gas expansion and DFT binding energies. The DFT binding energies of each configuration have been calculated employing Eq. (8.3). The PBE exchange-correlation functional has been used and the computational setup is equivalent to the one discussed on Page 66. The numbering of the listed structures follows the one used in Appendix B. The 14 LGH parameters have then been obtained by solving the resulting set of 29 linear equations using a least square fit.

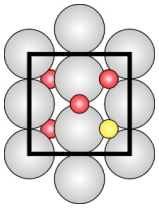
The different configurations are represented by schematic illustrations, where large grey spheres indicate palladium atoms in the reconstructed surface oxide layer, small red ones oxygen atoms and small yellow ones CO molecules. Additionally, in all figures the $(\sqrt{5} \times \sqrt{5})R27^\circ$ surface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

1. Structure 001



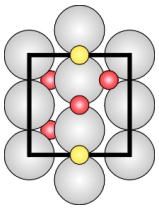
$$-4.643\,\mathrm{eV} = 2E^0_{\mathrm{O,hol}} + E^0_{\mathrm{CO,br}} + 4V_{\mathrm{O-O,hol-hol}} + 4V_{\mathrm{O-CO,hol-br}}$$

2. Structure 004



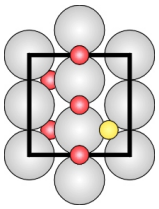
$$\begin{aligned}-3.519\,\mathrm{eV} = {} & E^0_{\mathrm{O,hol}} + E^0_{\mathrm{O,br}} + E^0_{\mathrm{CO,hol}} \\ & + 2V_{\mathrm{O-O,br-hol}} + 4V_{\mathrm{O-CO,hol-hol}} + 2V_{\mathrm{O-CO,br-hol}}\end{aligned}$$

3. Structure 008



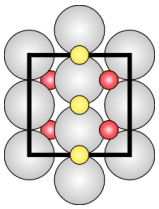
$$\begin{aligned}-3.293\,\mathrm{eV} = {} & E^0_{\mathrm{O,hol}} + E^0_{\mathrm{O,br}} + E^0_{\mathrm{CO,br}} \\ & + 2V_{\mathrm{O-O,br-hol}} + 2V_{\mathrm{O-CO,hol-br}} + 4V_{\mathrm{O-CO,br-br}}\end{aligned}$$

4. Structure 012



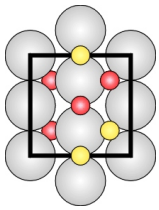
$$-2.016\,\mathrm{eV} = 2E^0_{\mathrm{O,br}} + E^0_{\mathrm{CO,hol}} + 4V_{\mathrm{O-O,br-br}} + 4V_{\mathrm{O-CO,br-hol}}$$

5. Structure 015



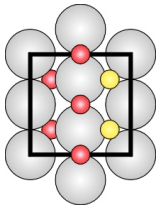
$$\begin{aligned}-5.214\,\mathrm{eV} = {} & 2E^0_{\mathrm{O,hol}} + 2E^0_{\mathrm{CO,br}} \\ & + 4V_{\mathrm{O-O,hol-hol}} + 4V_{\mathrm{CO-CO,br-br}} + 8V_{\mathrm{O-CO,hol-br}}\end{aligned}$$

6. Structure 021



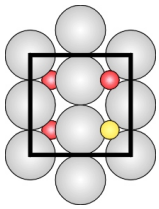
$$-4.285\,\mathrm{eV} = E^0_{\mathrm{O,hol}} + E^0_{\mathrm{O,br}} + E^0_{\mathrm{CO,hol}} + E^0_{\mathrm{CO,br}} + 2V_{\mathrm{O-O,br-hol}} + 2V_{\mathrm{CO-CO,br-hol}} + 4V_{\mathrm{O-CO,hol-hol}} + 4V_{\mathrm{O-CO,br-br}} + 2V_{\mathrm{O-CO,br-hol}} + 2V_{\mathrm{O-CO,hol-br}}$$

7. Structure 025



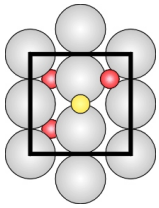
$$-2.947\,\mathrm{eV} = 2E^0_{\mathrm{O,br}} + 2E^0_{\mathrm{CO,hol}} + 4V_{\mathrm{O-O,br-br}} + 4V_{\mathrm{CO-CO,hol-hol}} + 8V_{\mathrm{O-CO,br-hol}}$$

8. Structure 028



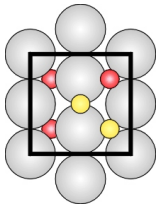
$$-3.277\,\mathrm{eV} = E^0_{\mathrm{O,hol}} + E^0_{\mathrm{CO,hol}} + 4V_{\mathrm{O-CO,hol-hol}}$$

9. Structure 029



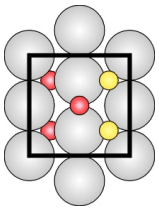
$$-3.080\,\mathrm{eV} = E^0_{\mathrm{O,hol}} + E^0_{\mathrm{CO,br}} + 2V_{\mathrm{O-CO,hol-br}}$$

10. Structure 040



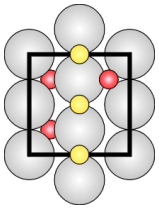
$$-4.210\,\mathrm{eV} = E^0_{\mathrm{O,hol}} + E^0_{\mathrm{CO,hol}} + E^0_{\mathrm{CO,br}} + 2V_{\mathrm{CO-CO,br-hol}} + 4V_{\mathrm{O-CO,hol-hol}} + 2V_{\mathrm{O-CO,hol-br}}$$

11. Structure 044



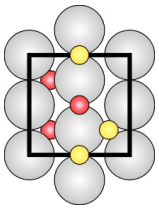
$$-3.263\,\mathrm{eV} = E^0_{\mathrm{O,br}} + 2E^0_{\mathrm{CO,hol}} + 4V_{\mathrm{CO-CO,hol-hol}} + 4V_{\mathrm{O-CO,br-hol}}$$

12. Structure 047



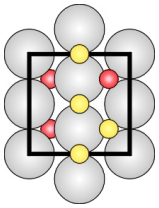
$$-3.888\,\mathrm{eV} = E^0_{\mathrm{O,hol}} + 2E^0_{\mathrm{CO,br}} + 4V_{\mathrm{CO-CO,br-br}} + 4V_{\mathrm{O-CO,hol-br}}$$

13. Structure 050



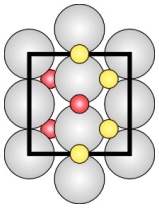
$$\begin{aligned}-2.958\,\mathrm{eV} = {} & E^0_{\mathrm{O,br}} + E^0_{\mathrm{CO,hol}} + E^0_{\mathrm{CO,br}} \\ & + 2V_{\mathrm{CO-CO,br-hol}} + 4V_{\mathrm{O-CO,br-br}} + 2V_{\mathrm{O-CO,br-hol}}\end{aligned}$$

14. Structure 054



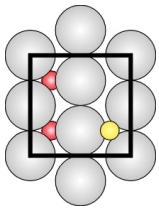
$$\begin{aligned}-4.861\,\mathrm{eV} = {} & E^0_{\mathrm{O,hol}} + E^0_{\mathrm{CO,hol}} + 2E^0_{\mathrm{CO,br}} \\ & + 4V_{\mathrm{CO-CO,br-br}} + 4V_{\mathrm{CO-CO,br-hol}} \\ & + 4V_{\mathrm{O-CO,hol-hol}} + 4V_{\mathrm{O-CO,hol-br}}\end{aligned}$$

15. Structure 057



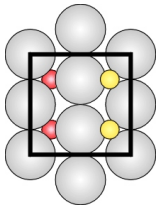
$$\begin{aligned}-3.927\,\mathrm{eV} = {} & E^0_{\mathrm{O,br}} + 2E^0_{\mathrm{CO,hol}} + E^0_{\mathrm{CO,br}} \\ & + 4V_{\mathrm{CO-CO,hol-hol}} + 4V_{\mathrm{CO-CO,br-hol}} \\ & + 4V_{\mathrm{O-CO,br-br}} + 4V_{\mathrm{O-CO,br-hol}}\end{aligned}$$

16. Structure 060



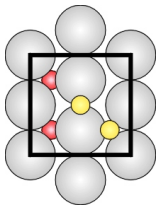
$$-1.922\,\mathrm{eV} = E^0_{\mathrm{CO,hol}}$$

17. Structure 064



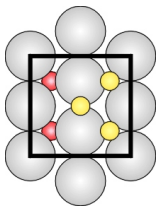
$$-3.397\,\mathrm{eV} = 2E^0_{\mathrm{CO,hol}} + 4V_{\mathrm{CO-CO,hol-hol}}$$

18. Structure 065



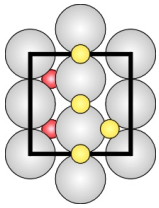
$$-3.206\,\mathrm{eV} = E^0_{\mathrm{CO,hol}} + E^0_{\mathrm{CO,br}} + 2V_{\mathrm{CO-CO,br-hol}}$$

19. Structure 072



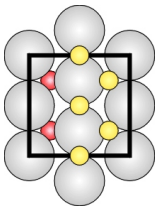
$$-4.126\,\mathrm{eV} = 2E^0_{\mathrm{CO,hol}} + E^0_{\mathrm{CO,br}} + 4V_{\mathrm{CO-CO,hol-hol}} + 4V_{\mathrm{CO-CO,br-hol}}$$

20. Structure 075



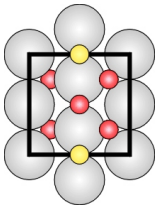
$$-3.962\,\mathrm{eV} = E^0_{\mathrm{CO,hol}} + 2E^0_{\mathrm{CO,br}} + 4V_{\mathrm{CO-CO,br-br}} + 4V_{\mathrm{CO-CO,br-hol}}$$

21. Structure 078



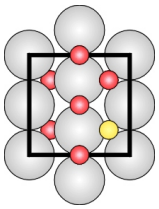
$$-4.637\,\mathrm{eV} = 2E^0_{\mathrm{CO,hol}} + 2E^0_{\mathrm{CO,br}} + 4V_{\mathrm{CO-CO,hol-hol}} + 4V_{\mathrm{CO-CO,br-br}} + 8V_{\mathrm{CO-CO,br-hol}}$$

22. Structure 081



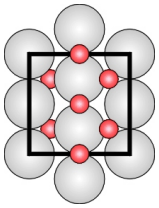
$$-4.474\,\mathrm{eV} = 2E^0_{\mathrm{O,hol}} + E^0_{\mathrm{O,br}} + E^0_{\mathrm{CO,br}} + 4V_{\mathrm{O-O,hol-hol}} + 4V_{\mathrm{O-O,br-hol}} + 4V_{\mathrm{O-CO,br-br}} + 4V_{\mathrm{O-CO,hol-br}}$$

23. Structure 090



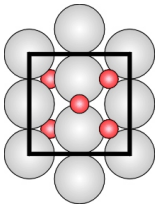
$$-3.394\,\mathrm{eV} = E^0_{\mathrm{O,hol}} + 2E^0_{\mathrm{O,br}} + E^0_{\mathrm{CO,hol}} + 4V_{\mathrm{O-O,br-br}} + 4V_{\mathrm{O-O,br-hol}} + 4V_{\mathrm{O-CO,hol-hol}} + 4V_{\mathrm{O-CO,br-hol}}$$

24. Structure 093



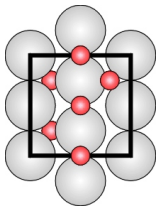
$$-3.561\,\mathrm{eV} = 2E^0_{\mathrm{O,hol}} + 2E^0_{\mathrm{O,br}} + 4V_{\mathrm{O-O,hol-hol}} + 4V_{\mathrm{O-O,br-br}} + 8V_{\mathrm{O-O,br-hol}}$$

25. Structure 099



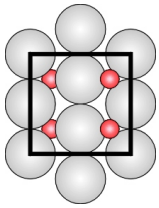
$$-3.845\,\mathrm{eV} = 2E^0_{\mathrm{O,hol}} + E^0_{\mathrm{O,br}} + 4V_{\mathrm{O-O,hol-hol}} + 4V_{\mathrm{O-O,br-hol}}$$

26. Structure 102



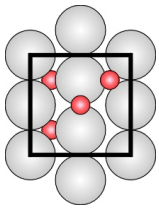
$$-2.428\,\mathrm{eV} = E^0_{\mathrm{O,hol}} + 2E^0_{\mathrm{O,br}} + 4V_{\mathrm{O-O,br-br}} + 4V_{\mathrm{O-O,br-hol}}$$

27. Structure 105



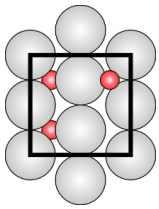
$$-3.714\,\mathrm{eV} = 2E^0_{\mathrm{O,hol}} + 4V_{\mathrm{O-O,hol-hol}}$$

28. Structure 106



$$-2.445\,\mathrm{eV} = E^0_{\mathrm{O,hol}} + E^0_{\mathrm{O,br}} + 2V_{\mathrm{O-O,br-hol}}$$

29. Structure 113



$$-1.825\,\mathrm{eV} = E^0_{\mathrm{O,hol}}$$