Supporting Information

Effect of doping β-NiOOH with Co on the catalytic oxidation of water: DFT+U Calculations†

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1 Reaction paths: kinetic barriers

We take into account the activation barriers related to reactions 1.2 and 1.4 for path I and to the reaction 2.4 for path II.

The suggested path I mechanism is the following:

$$2\ H_2O^* + 2\ H_2O(l) \rightarrow H_2O^* + OH^* + H^+ + e^- + 2\ H_2O(l) \quad (1.1)$$
$$H_2O^* + OH^* + 2\ H_2O(l) \rightarrow 2\ H_2O^* + O^* + H^+ + e^- + H_2O(l) \quad (1.2)$$
$$2\ H_2O^* + O^* + H_2O(l) \rightarrow H_2O^* + OH^* + O^* + H^+ + e^- + H_2O(l) \quad (1.3)$$
$$H_2O^* + OH^* + O^* + H_2O(l) \rightarrow 2\ H_2O^* + O_2(g) + H^+ + e^-. \quad (1.4)$$

and the suggested path II mechanism is the following:

$$2\ H_2O^* + 2\ H_2O(l) \rightarrow H_2O^* + OH^* + H^+ + e^- + 2\ H_2O(l) \quad (2.1)$$
$$H_2O^* + OH^* + 2\ H_2O(l) \rightarrow 2\ OH^* + H^+ + e^- + 2\ H_2O(l) \quad (2.2)$$
$$2\ OH^* + 2\ H_2O(l) \rightarrow H_2O^* + OH^* + O^* + H^+ + e^- + H_2O(l) \quad (2.3)$$
$$H_2O^* + OH^* + O^* + H_2O(l) \rightarrow 2\ H_2O^* + O_2(g) + H^+ + e^-. \quad (2.4)$$

We computed the minimum energy pathways and activation barriers using the nudged elastic band (NEB) method[1]. During the NEB simulations, we used the quasi-Newton optimization scheme from Broyden[2]. We chose five images to describe the profile of reaction paths. The elastic constants related to the springs used to mimic the elastic band were 29.15 and 19.44 $eV/Å^2$ for k_{max} and k_{min}, respectively.

Figure S1 shows the energy profile path which describes the insertion of the oxygen in the surface lattice during reaction 1.2. The starting point configuration of the NEB simulation has a H_2O molecule and an oxygen atom adsorbed on two different Nickel atoms exposed by the β-NiOOH surface, respectively. This starting configuration is similar to Conf.2 of path I on the β-NiOOH surface. During the NEB simulation, the oxygen adsorbed on the surface moves into the lattice forming the last configuration, which is similar to Conf.3 of path I on the β-NiOOH surface. Interestingly, the reaction path is downhill with an activation energy of only 0.017 eV for this process, which confirms the possibility of the OER on the β-NiOOH surface according to the mechanisms I, as described in the paper.

Figure S2 shows the energy profile path which describes the release of the oxygen molecule occurring during both reactions 1.4 and 2.4. The starting point configuration of the NEB simulation is characterized by one oxygen atom adsorbed on one of the nickel atoms exposed by the β-NiOOH surface and another oxygen adatom inserted in the lattice. This configuration is similar to Conf.4 of the β-NiOOH surface for both path I and II. During the NEB simulation, the oxygen adatom inserted in the lattice and the oxygen adsorbed on the surface release, reaching the last configuration and restoring the initial catalyst. This final configuration of the path is similar to the Conf.1 for both path I and path II on the β-NiOOH surface. Also in this case, the reaction path is downhill with *zero* activation energy, which confirms the possibility of the OER on the β-NiOOH surface according to the mechanisms I and II, as described in the paper.

References

1 G. Henkelman and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9978.
2 C. Broyden, *Math. Comput.*, 1967, **21**, 368.

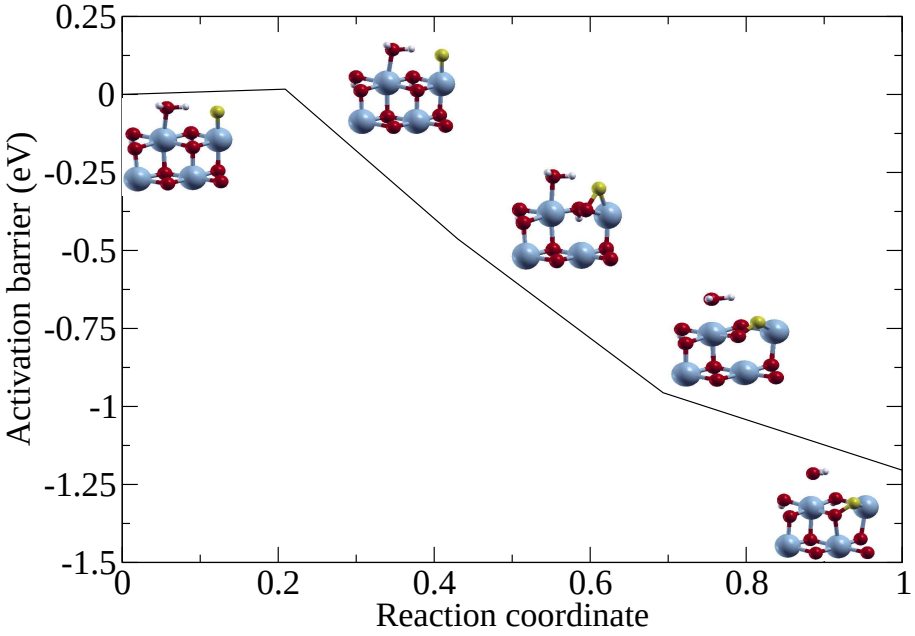

Fig. S1 Reaction path describing the insertion of the oxygen adatom in the lattice during reaction 1.2, according to path I. The oxygen inserted into the lattice is drawn in yellow. From left to right the energies (eV) of the configurations with respect to the first one, involved in the reaction path, are 0, 0.017, −0.46, −0.96 and −1.20, respectively

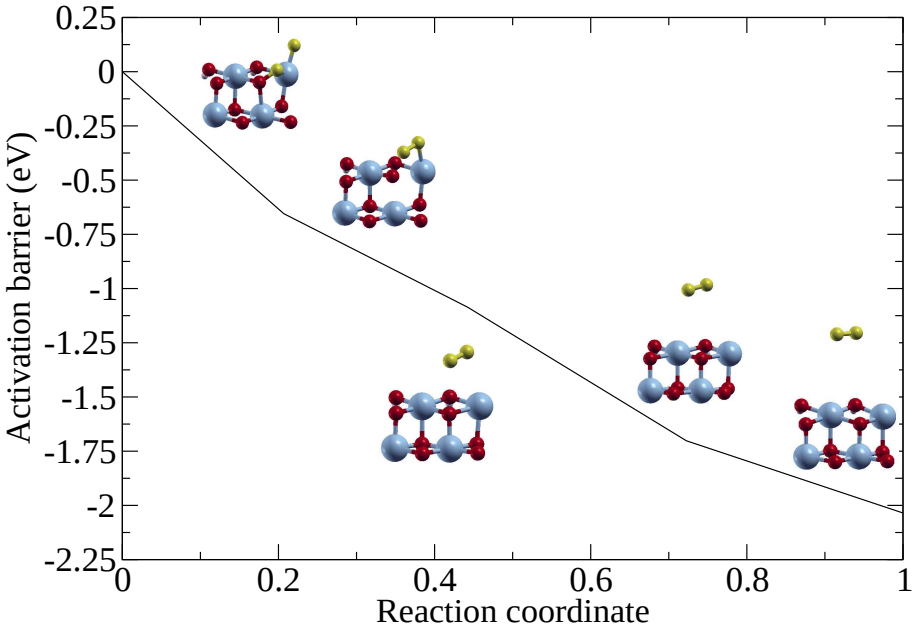

Fig. S2 Reaction path describing the release of the oxygen molecule during reactions 1.4 and 2.4, according to path I and path II, respectively. The oxygen atoms involved in the path are drawn in yellow. From left to right the energies (eV) of the configurations with respect to the first one, involved in the reaction path, are 0, −0.65, −1.09, −1.70 and −2.03, respectively