

Electronic Supplementary Information for: Number of Outer Electrons as Descriptor for Adsorption Processes on Transition Metals and Their Oxides

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1. Construction of the Adsorption Energy Grid

In order to create the adsorption energy grid one only has to know the slope of one of the lines and its offset, given that the rest of the lines are supposed to have the same slope and should be equidistant from one another. Thus, there are several possible ways to proceed; we chose to use the average slope of all linear fits in Figure S.1 (~ 0.365 V) and to use the offset of the linear regression for metals (~ -3.50 eV).

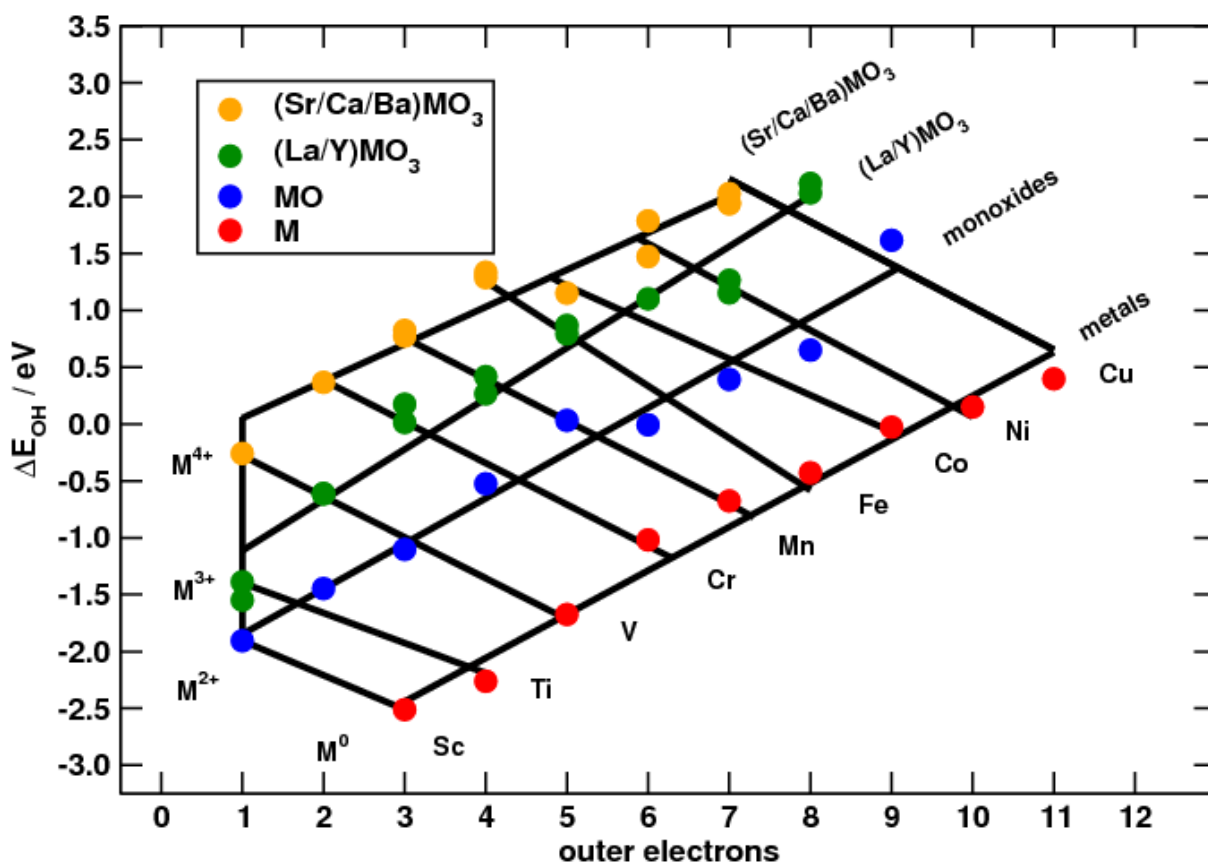


Figure S.1. Linear fits correlating outer electrons and *OH adsorption energies for metals, monoxides and perovskites. The average magnitude of the slopes in both directions is ~ 0.365 V. The offset of the line for metals is ~ -3.50 eV.

In Table S.1 we present all the slopes used in the average. As can be noted in Figure S.1, the slopes for metals, monoxides and perovskites are positive, whereas those of pure elements are negative; therefore, when averaging we used the absolute values of the negative ones. The average of the data set (~ 0.365 V) and its standard deviation (~ 0.052 V) are also presented. Note that in this case the standard deviation of the data is quite small and thus it is appropriate to use the average to represent the whole distribution.

Table S.1. Slopes obtained through linear fitting of the data in Figure S.1. The average of the set and its standard deviation are also provided.

System	Slope / V
M	0.379
MO	0.398
(La/Y)MO ₃	0.446
(Sr/Ca/Ba)MO ₃	0.326
Sc	0.303
Ti	0.265
V	0.360
Cr	0.365
Mn	0.365
Fe	0.458
Co	0.320
Ni	0.381
Cu	0.375
Average	0.365
Std Deviation	0.052

It is known that each group of compounds (metals, monoxides and the two families of perovskites) has its own straight line of which we know already the slope:

$$\text{For metals: } \Delta E_{OH}^M = 0.365N - 3.50 \quad (1)$$

$$\text{For monoxides: } \Delta E_{OH}^{MO} = 0.365N + A \quad (2)$$

$$\text{For (La/Y)MO}_3: \Delta E_{OH}^{(La/Y)MO_3} = 0.365N + B \quad (3)$$

$$\text{For (Sr/Ca/Ba)MO}_3: \Delta E_{OH}^{(Sr/Ca/Ba)MO_3} = 0.365N + C \quad (4)$$

Where N represents the number of outer electrons. Moreover, it is known that each element, e.g. V, has its own straight line of which we know already the slope:

$$\Delta E_{OH}^M = -0.365N + D \quad (5)$$

Finally, the lines of elements (negative slopes) and compounds (positive slopes) must cross each other at integer number of outer electrons. In the case of V, its line must intercept that of metals at a number of outer electrons of 5 (i.e. the number of valence electrons of V); that of monoxides at 3 (i.e. the number of outer electrons of V in VO); that of (La/Y)MO₃ at 2 (i.e. the number of outer electrons of V in LaVO₃ or YVO₃); and that of (Sr/Ca/Ba)MO₃ at 1 (i.e. the number of outer electrons of V in SrVO₃).

Solving these simple equations, one finds $A = -1.99$, $B = -1.26$, $C = -0.53$, and $D = 0.20$. The offsets for the rest of the elements can be found similarly. The Mean Absolute Error (MAE) between the

predicted *OH adsorption energies of the grid and the actual values found with DFT is ~ 0.20 eV. Moreover, the MAEs for *OOH and *O adsorption energies are ~ 0.20 and 0.36 eV, respectively.

2. Adsorption Energy Grids for *OOH and *O

In Figures S.2 and S.3 we present the adsorption energy grids for *OOH and *O. They were calculated in the same way as that for *OH, described in the previous section of this Supplementary Information.

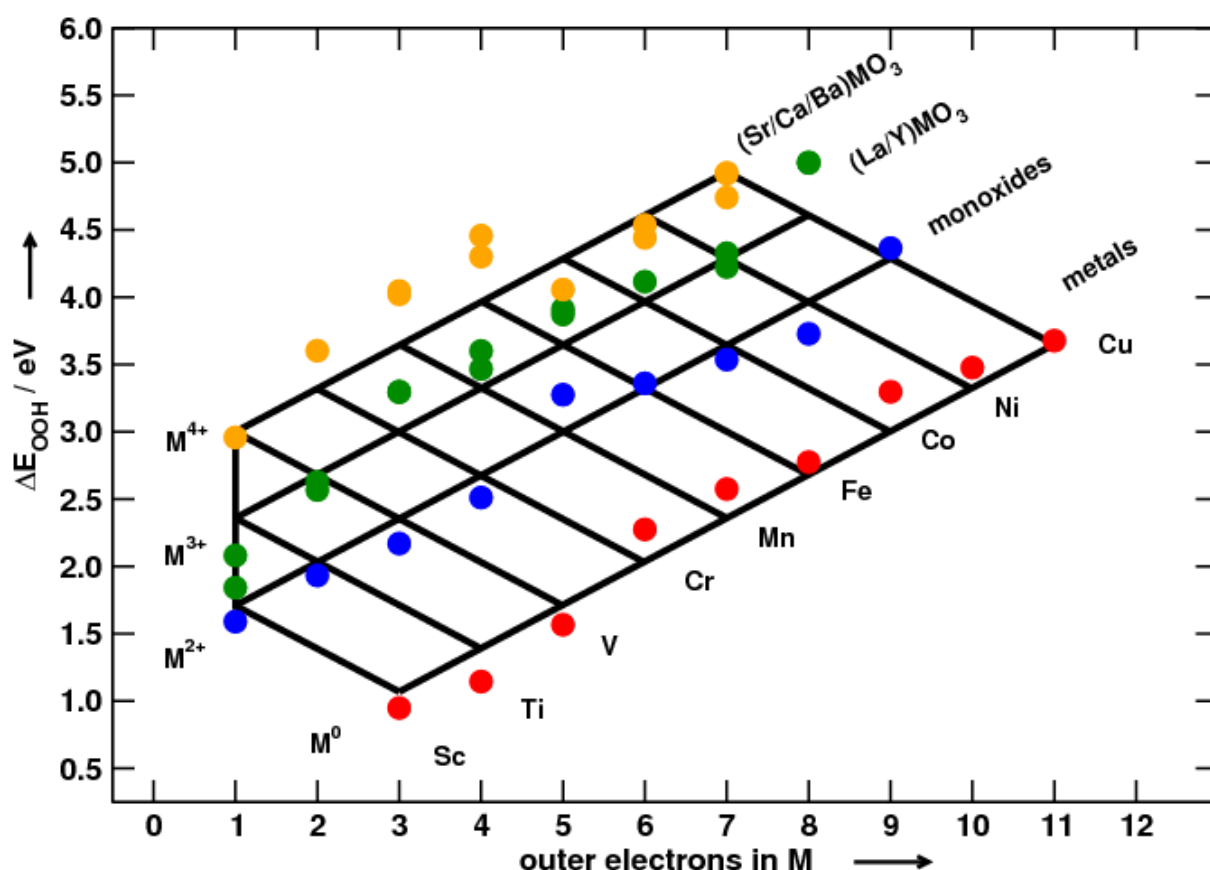


Figure S.2. Adsorption energy grid for *OOH adsorbed on various classes of compounds and different chemical elements.

In the case of *OOH, the average slope corresponds to 0.322 V with a standard deviation of 0.057 V. Moreover, the offset for the metals line is found to be 0.10 eV.

On the other hand, for the *O adsorption energies the average slope is 0.704 V with a standard deviation of 0.139 V. Moreover, the offset for the metals line is -5.89 eV.

Note that the errors tend to increase when describing the *O adsorption energies. Therefore, for the purpose of modeling catalytic reactions, descriptors based on the *OH or *OOH adsorption energies would be more recommendable, as they would provide higher accuracy.

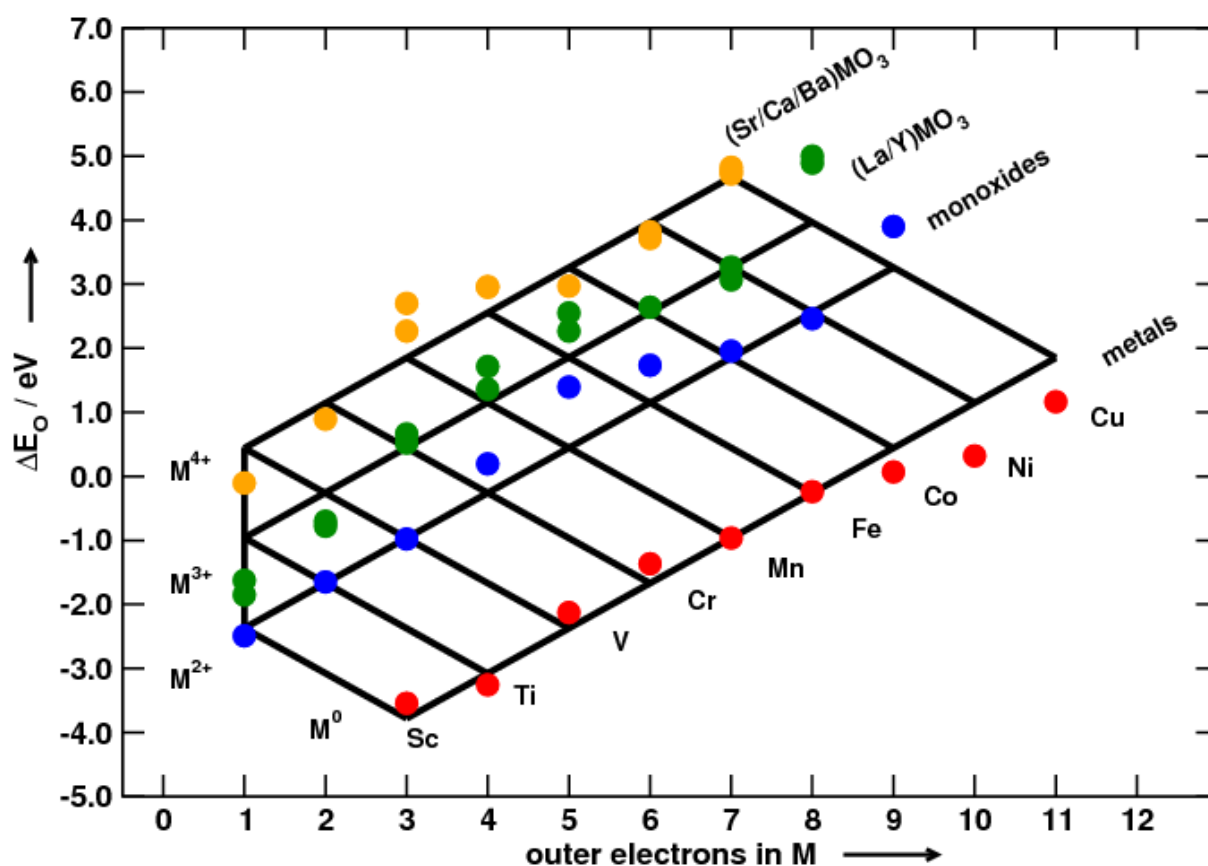


Figure S.3. Adsorption energy grid for $*O$ adsorbed on various classes of compounds and different chemical elements.

3. Additional Calculation Details

The crystallographic details of the oxide surfaces simulated in this study are the following: (100) surfaces of perovskites were constructed from their cubic bulk phase (space group $Pm\bar{3}m$), and (100) surfaces of monoxides (MO) from their bulk rock salt phase (space group $Fm\bar{3}m$); in both cases, relaxation was allowed to enable distortions in the octahedral framework due to Jahn-Teller and pseudo Jahn-Teller effects where appropriate. Metals were modeled in their closest-packed surfaces ((111) for Ni and Cu; (0001) for Sc, Ti and Co; and (110) for V, Cr, Mn, and Fe), and (110) surfaces of Mn_2O_3 in the bixbyite phase (space group $Ia\bar{3}$). The oxide surfaces used in the calculations are shown in Figure S.4, except for the (110) of Mn_2O_3 , shown as an inset in Figure S.4.

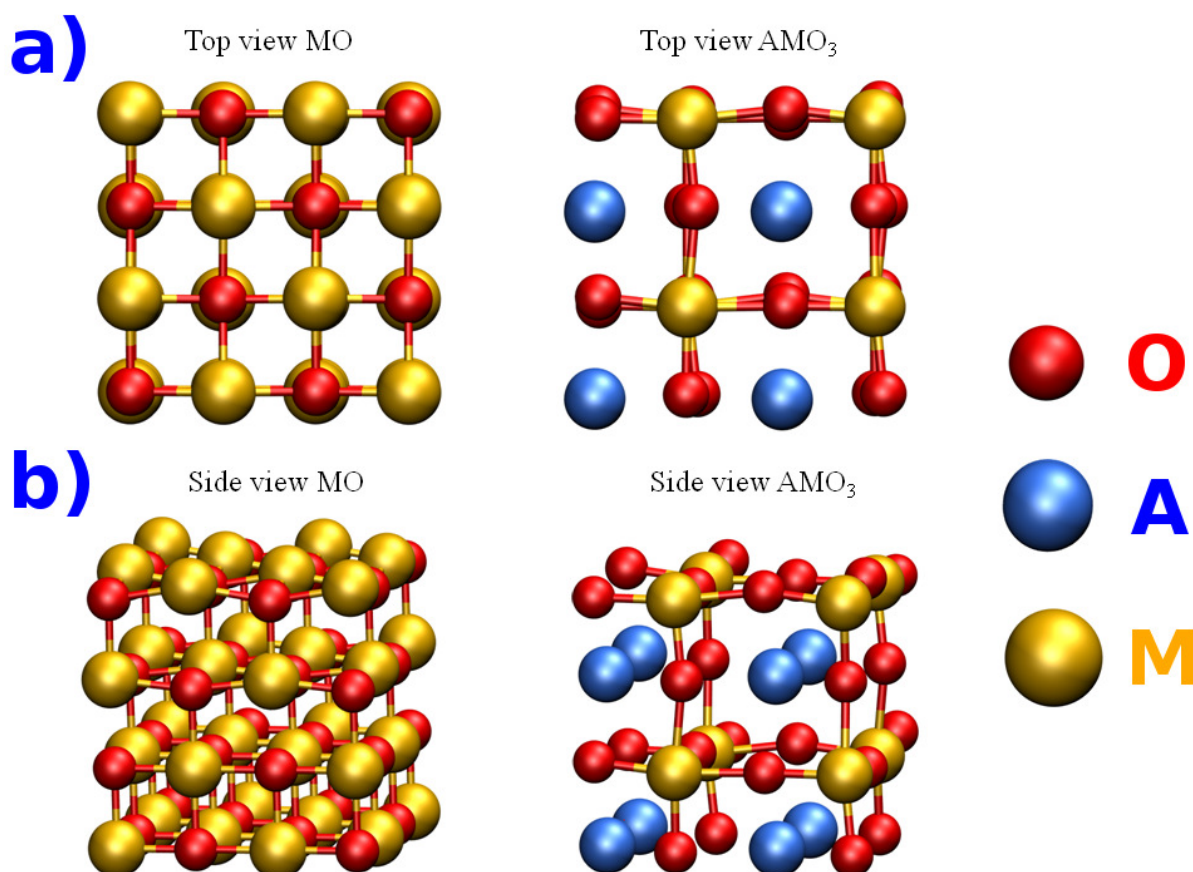


Figure S.4. Top and side views of a) monoxide, MO, (100) surfaces, and b) perovskite, AMO₃, (100) surfaces. Adsorption is considered only on top of surface transition metal atoms. A and M atoms in AMO₃ appear in blue and yellow, respectively, and oxygen atoms appear in red.

4. Trends in Adsorption Energies among Different Coordination Numbers within a Given Oxide Surface

Finally, we discuss the activity trends in the adsorption properties of inequivalent active sites with different coordination numbers within a given oxide surface. In this case we consider the (110) surface of Mn₂O₃. We studied again the *O, *OH, and *OOH adsorption on top of different surface Mn atoms which are surrounded by different number of O atoms (inset of Figure S.4). Roughly linear correlations were observed between the adsorption behavior at the specific Mn sites (A, B, C and D in Figure S.4) and the number of O atoms coordinated to it. The x-axis in Figure 3.b is the weighted average of inequivalent oxygen atoms coordinated to the Mn atom, defined as:

$$N_{total} = (N_{1C} + N_{2C} + N_{3C})/3 \quad (6)$$

Where N_{1C} , N_{2C} , N_{3C} , are the number of oxygen atoms coordinated to the Mn atom at distances 1C, 2C and 3C, respectively. Figure S.4 shows that the number of O atoms per transition metal is able to describe

the trends in the adsorption characteristics for a given surface, when all atoms are supposed to have the same formal oxidation state (+3 in this case). An increase in coordination of the transition metal atom reduces its possibility to create new bonds, resulting in a weakening of the interaction strength between the surface and the adsorbate similar to the cases analyzed in the main text.

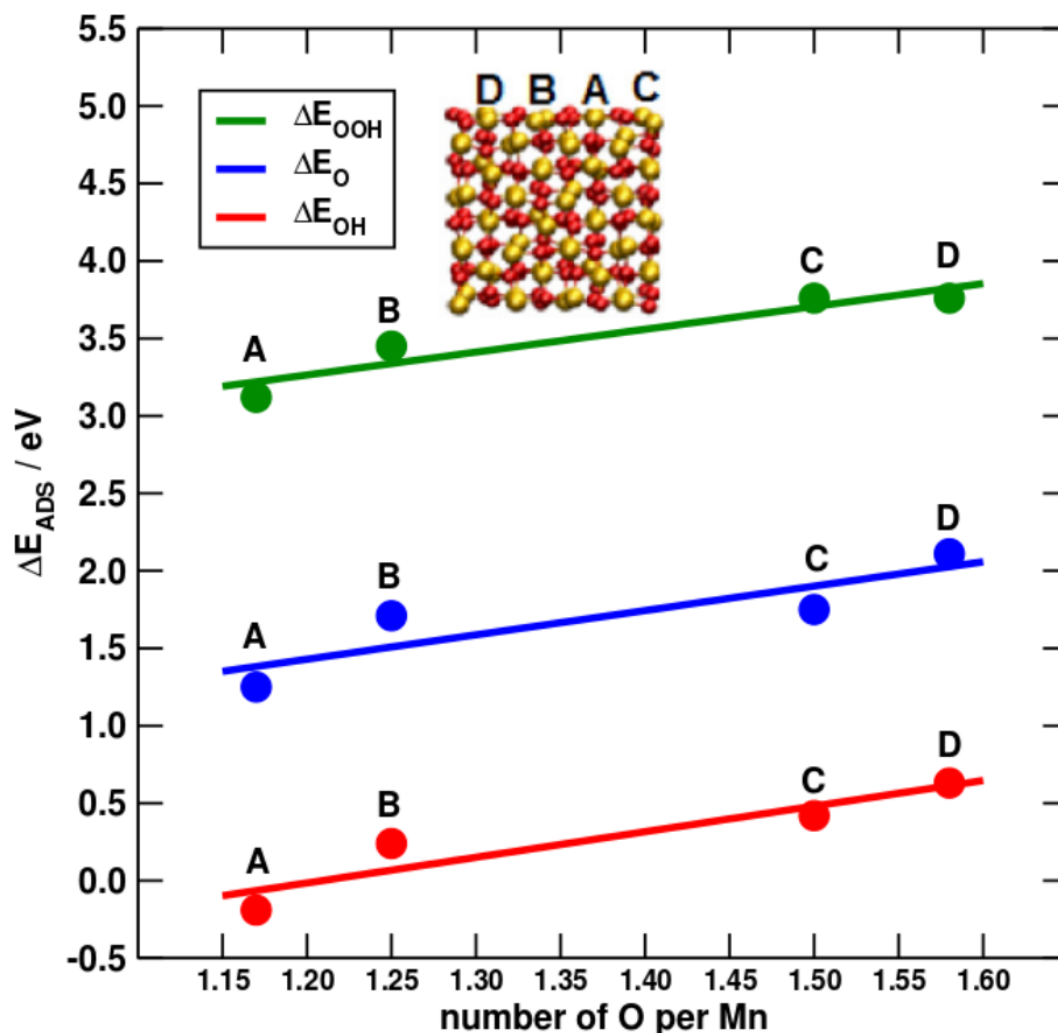


Figure S.4. Relations between adsorption energies of *O (blue), *OH (red) and *OOH (green) with respect to the oxygen number per transition metal over the Mn_2O_3 (110) surface. The inset in shows a side view of the surface with the inequivalent adsorption sites as A, B, C and D. The plot shows that the adsorption energies are systematically influenced by the number of oxygen ligands that each inequivalent site at the surface has. Thus, within a given facet, when the oxidation states are all the same, the trends can be captured by the coordination numbers.

5. Counting the Number of Outer Electrons

Here we present further details of the way we count the number of outer electrons of the metal ions throughout the manuscript for the particular case of Cr. The electronic configuration of pure Cr is: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$. Thus, it has $5 + 1 = 6$ valence electrons. Cr^{2+} has lost 2 electrons, so it has $6 - 2 = 4$ outer electrons. Since Cr^{3+} has lost 3 electrons, it has $6 - 3 = 3$ outer electrons. Cr^{4+} has lost 4 electrons,

so it has $6 - 4 = 2$ outer electrons. The case of Ni is analogous, so pure Ni has 10 outer electrons, Ni^{2+} has 8, Ni^{3+} has 7, and Ni^{4+} has 6. In Figure S.5.a we present the orbital splitting and the allocation of the outer electrons of Ni^{2+} , Ni^{3+} and Ni^{4+} , which correspond to the Ni ions present in NiO, LaNiO_3 and SrNiO_3 . Note that the orbital splitting shown in Figure S.5 is typical of octahedral complexes, with 3 orbitals of low energy and two orbitals of high energy. Moreover, in Figure S.5.b we present a summary of the orbital splitting and the distribution of outer electrons in the transition metal ions in LaMO_3 .

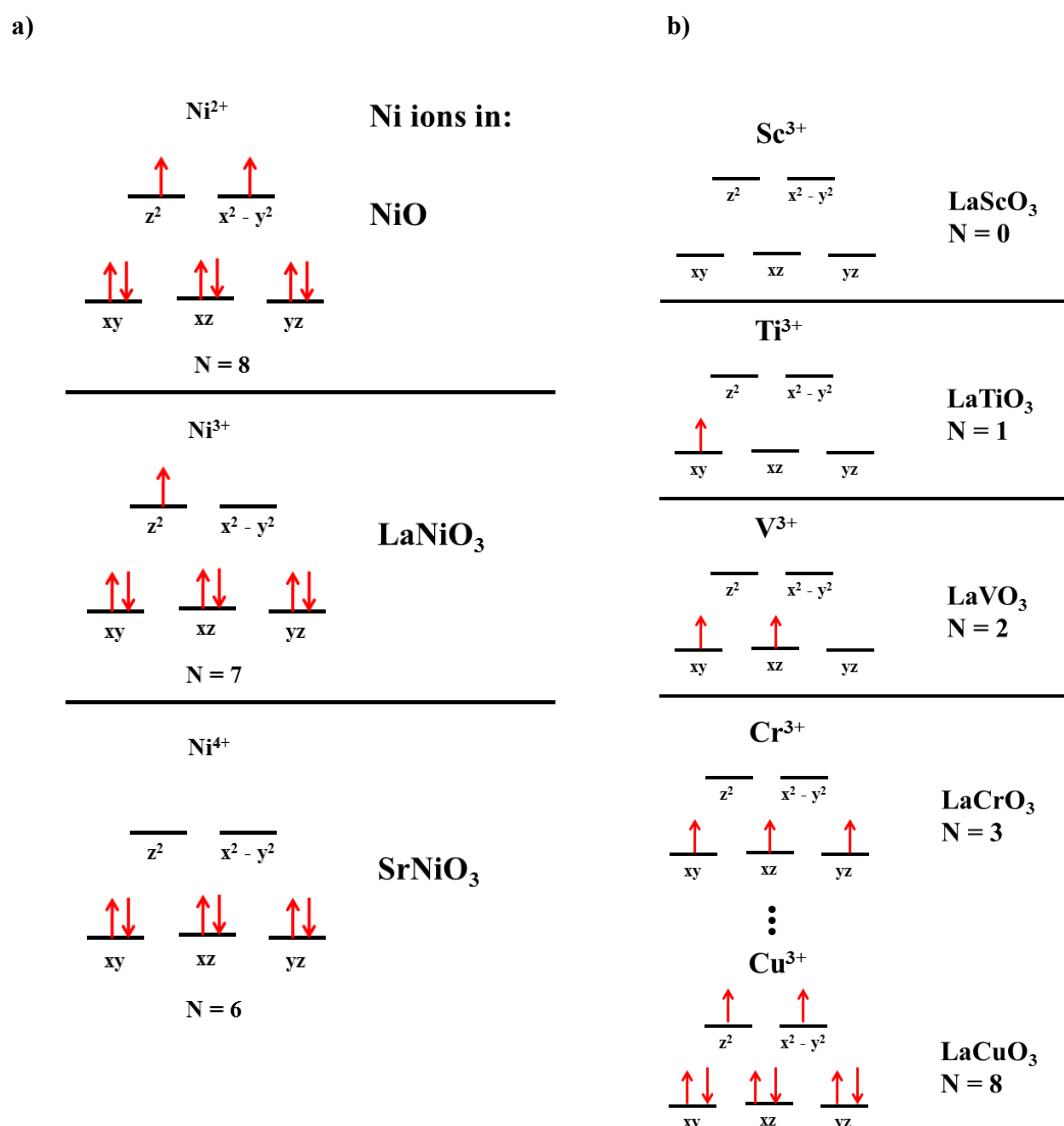


Figure S.5. Orbital Splitting and ground state electronic distribution of the outer electrons of a) the Ni ions in the oxides considered in this study. b) The M^{3+} transition metal ions present LaMO_3 .

From Figs 1 and 2 in the main text and S.5 here, we conclude that the decrease of the number of outer electrons for a given metal ion results in a weakening of the adsorption energies, while the opposite is true for different metal ions of the same oxidation state. This is because a decrease in the number of outer electrons of a given metal implies its further oxidation, which in turn decreases the reactivity (see Fig.

S.5.a). On the other hand, for a given oxidation state and different metal ions, increasing the number of outer electrons implies the filling of antibonding states (see Fig. S.5.a), which also decreases the reactivity. Interestingly, the effects have the same magnitude, as evidenced by the existence of the grids shown in Figs 3, S.2, and S.3.