

Online Resource 1

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First principles investigation of water adsorption, dopant segregation and surface thermodynamics of Mg and Sr substituted CaO(001) for Ca(OH)₂/CaO thermochemical energy storage

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This Online Resource contains Figures S1 to S8 and Tables S1 to S5 referred to in the main article. Every figure and table was produced from the output of the calculations described in the main article; no additional calculations were run for them. All quantities were computed with the settings described in Section 2 of the main article (PBE, 90/360 Ry, four layer slab, (2 × 2) surface cell, 1/4 ML).

Table S1. All optimised adsorption states (all split). E_{ads} : adsorption energy (PBE and PBE+D3 on the PBE geometry, eV); O_w to M: distances from the hydroxyl oxygen to its two nearest cations (Å); $O_w \cdots H_s$ and $O_s H_s$: hydrogen bond and new surface hydroxyl (Å); h : height of O_w above the mean height of the top layer cations (Å); last column: cations within 2.9 Å of the proton accepting oxygen O_s . “start” marks a starting bridge from which the hydroxyl moved.

Surface	State	PBE	PBE+D3	O_w to M	$O_w \cdots H_s$	$O_s H_s$	h	O_s bonded to
CaO	OH on top of Ca	−0.778	−0.967	2.27 (Ca), 3.37 (Ca)	1.452	1.047	1.98	Ca
CaO	OH bridging two Ca	−0.843	−1.048	2.46 (Ca), 2.50 (Ca)	1.478	1.033	1.83	Ca
CaO:Mg	OH on top of Mg (intact start)	−0.954	−1.156	1.98 (Mg), 3.31 (Ca)	1.478	1.028	1.63	Ca
CaO:Mg	OH on top of Mg (split start)	−0.952	−1.149	1.99 (Mg), 3.30 (Ca)	1.470	1.030	1.63	Ca
CaO:Mg	OH bridging two Ca, H on O next to Mg	−1.175	−1.361	2.37 (Ca), 2.53 (Ca)	1.537	1.018	1.68	Ca, Mg
CaO:Mg	started on a Ca and Mg bridge, OH moved away from Mg	−0.629	−0.813	2.37 (Ca), 2.88 (Mg)	1.405	1.069	1.82	Ca, Mg
CaO:Sr	OH on top of Sr	−0.822	−0.989	2.45 (Sr), 3.39 (Ca)	1.434	1.058	1.76	Ca, Sr
CaO:Sr	OH bridging two Ca, H on O next to Sr	−0.777	−0.958	2.44 (Ca), 2.69 (Ca)	1.458	1.043	1.87	Ca, Sr
CaO:Sr	OH bridging Ca and Sr	−0.982	−1.154	2.45 (Ca), 2.61 (Sr)	1.525	1.028	1.77	Ca, Sr
CaO:(Mg,Sr)	OH bridging Ca and Sr, H on O next to Mg	−1.176	−1.347	2.47 (Ca), 2.52 (Sr)	1.569	1.015	1.71	Ca, Mg, Sr
CaO:(Mg,Sr)	same state from a second start	−1.178	−1.353	2.43 (Ca), 2.52 (Sr)	1.574	1.014	1.69	Ca, Mg, Sr
CaO:Mg(sub)	OH bridging two Ca, H on O above Mg	−0.792	−0.985	2.46 (Ca), 2.47 (Ca)	1.474	1.033	1.77	Ca, Mg
CaO:Mg(sub)	OH bridging two Ca, away from Mg	−0.807	−1.003	2.51 (Ca), 2.54 (Ca)	1.457	1.045	1.86	Ca

Table S2. Convergence and consistency checks on the most stable state on pure CaO(001).

Check	Value	Change
E_{ads} , four layers, 2 × 2 × 1 (production)	−0.843 eV	ref.
E_{ads} , 3 × 3 × 1	−0.845 eV	−0.001 eV
E_{ads} , 4 × 4 × 1	−0.845 eV	−0.002 eV
E_{ads} , five layers (three relaxed)	−0.845 eV	−0.002 eV
Geometry cutoff 70 Ry vs 90 Ry: shift of $E(\text{slab}+\text{H}_2\text{O}) - E(\text{slab})$, all surfaces	0.015 to 0.017 eV	< 2 meV in relative values
Average surface energy of the clean slab, four / five layers	0.645 / 0.644 J m ^{−2}	−0.001 J m ^{−2}
Bulk CaO energy from slab difference vs bulk calculation (companion study)		1.1 meV f.u. ^{−1}

Table S3. Löwdin charges of the most stable adsorption state (e ; charge = valence electrons of the neutral atoms minus Löwdin population), change of the Löwdin population of the slab and of the proton accepting oxygen O_s relative to the clean slab, and minimum of the cumulative charge $\Delta q(z)$ of the density difference on the full FFT grid (e). Löwdin values depend on the projection basis; only differences between surfaces carry meaning.

Surface	$q(O_wH)$	$q(H_s)$	$q(\text{adsorbate})$	$\Delta N(\text{slab})$	$\Delta N(O_s)$	min $\Delta q(z)$
CaO	-0.574	0.307	-0.267	-0.288	-0.230	-0.202
CaO:Sr	-0.589	0.306	-0.283	-0.297	-0.244	-0.222
CaO:Mg	-0.587	0.319	-0.267	-0.285	-0.232	-0.196
CaO:(Mg,Sr)	-0.603	0.319	-0.284	-0.298	-0.247	-0.220
CaO:Mg(sub)	-0.566	0.306	-0.260	-0.281	-0.223	-0.202

Table S4. Harmonic frequencies of the adsorbate (cm^{-1} ; three atoms, slab frozen, central differences of $\pm 0.015 \text{ \AA}$ at 70 Ry) and zero point energy (eV). The highest mode is the stretch of the bridging hydroxyl O_wH and the second highest the stretch of the new surface hydroxyl O_sH (identified from the eigenvectors). No imaginary modes were found. Free H_2O (companion study): 1600, 3701 and 3816 cm^{-1} , ZPE 0.565 eV.

Surface	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ZPE
CaO	120	181	333	385	464	1173	1217	2366	3787	0.622
CaO:Sr	135	177	342	378	450	1159	1207	2463	3777	0.625
CaO:Mg	145	221	309	351	474	1100	1176	2613	3796	0.631
CaO:(Mg,Sr)	162	196	331	365	471	1111	1126	2693	3785	0.635
CaO:Mg(sub)	102	179	352	400	468	1200	1242	2197	3773	0.615

Table S5. (a) Segregation energies $E_{\text{seg}} = E(\text{dopant in 2nd layer}) - E(\text{dopant in top layer})$ (eV; positive: top layer preferred), PBE and PBE+D3 (D3 on the PBE geometries). The last two rows give the temperature below which Mg prefers the top layer when each surface cell is either empty or holds one water molecule in equilibrium with the vapour (two state site, Eq. (7) and Section 2.5 of the main article); with the CS entropy these crossover temperatures are 789 and 633 K. (b) Desorption temperature (K) at 0.023 and 1 bar in the three thermochemical models. The soft mode floor of 50 cm^{-1} in the harmonic model has no effect, since the lowest adsorbate mode is 102 cm^{-1} .

(a)

Dopant and surface	PBE	PBE+D3
Mg, clean surface	-0.287	-0.295
Mg, one H_2O per cell	0.081	0.063
Sr, clean surface	0.457	0.471
Mg with H_2O in equilibrium with the vapour: crossover temperature at 1 bar (K)	529	627
Mg with H_2O in equilibrium with the vapour: crossover temperature at 0.023 bar (K)	442	526

(b)

Surface	Harmonic, PBE		Harmonic, PBE+D3		CS entropy, PBE	
	0.023 bar	1 bar	0.023 bar	1 bar	0.023 bar	1 bar
CaO	433	524	543	658	624	788
CaO:Sr	503	609	595	723	711	894
CaO:Mg	599	727	700	851	829	1037
CaO:(Mg,Sr)	598	725	692	840	830	1038
CaO:Mg(sub)	420	507	524	636	606	766

Supplementary figures

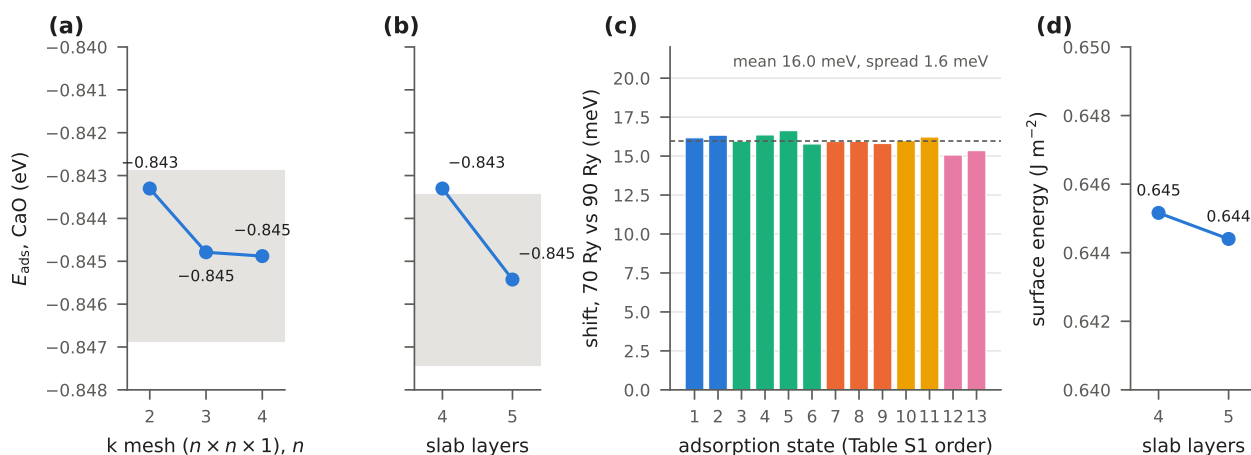


Figure S1. Convergence checks. (a) Adsorption energy of the most stable state on pure CaO against the k point mesh (four layers). (b) The same against slab thickness ($2 \times 2 \times 1$ mesh). Grey bands: ± 2 meV around the best converged value. (c) Shift of $E(\text{slab}+\text{H}_2\text{O}) - E(\text{slab})$ between geometries optimised at 70 Ry and energies at 90 Ry, for all 13 states in the order of Table S1; dashed line: mean. (d) Average surface energy of the clean slab against slab thickness.

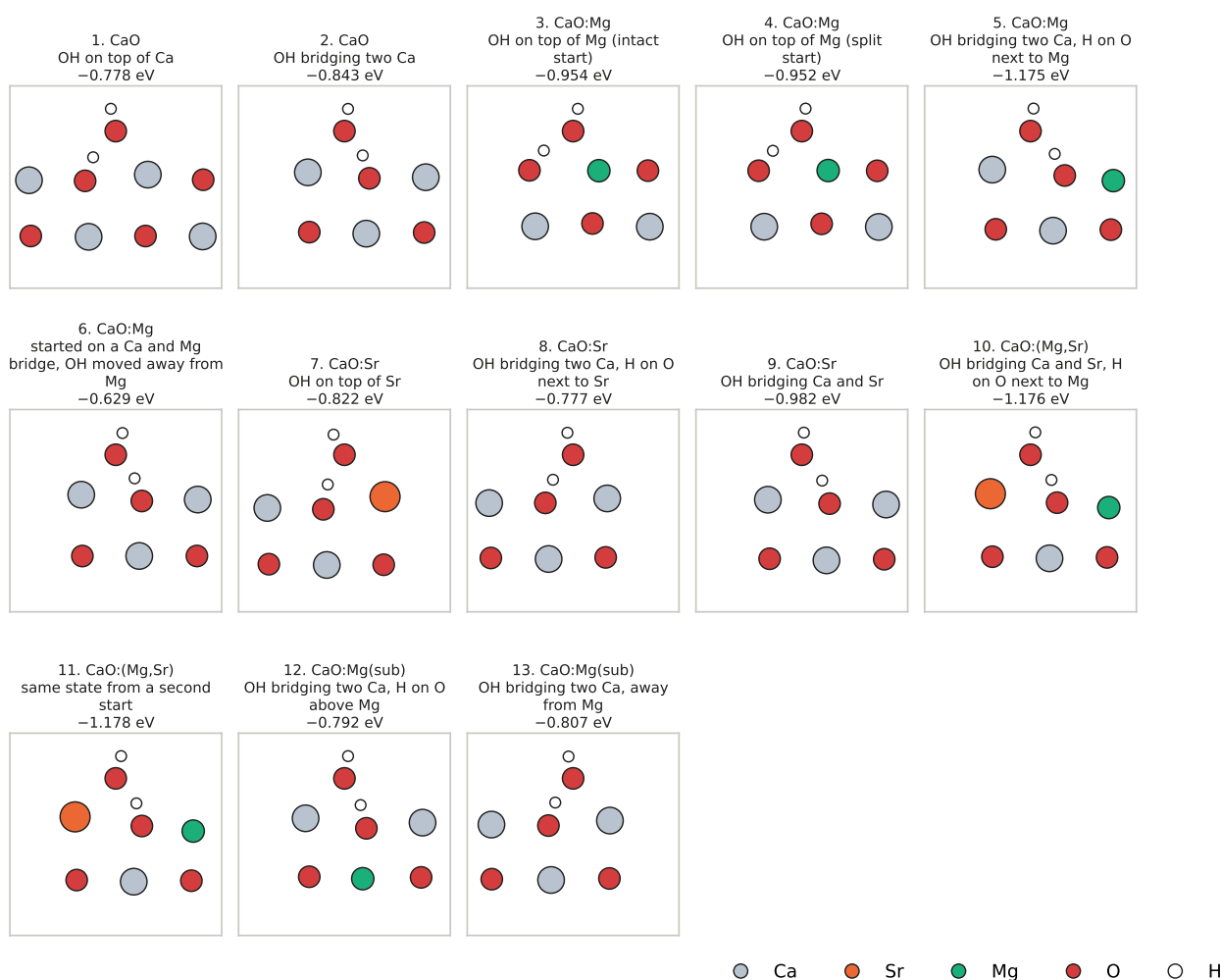


Figure S2. Side views of all 13 optimised adsorption states (atoms near the vertical plane through the hydroxyl oxygen), numbered as in Table S1, with their PBE adsorption energies. Every state is split.

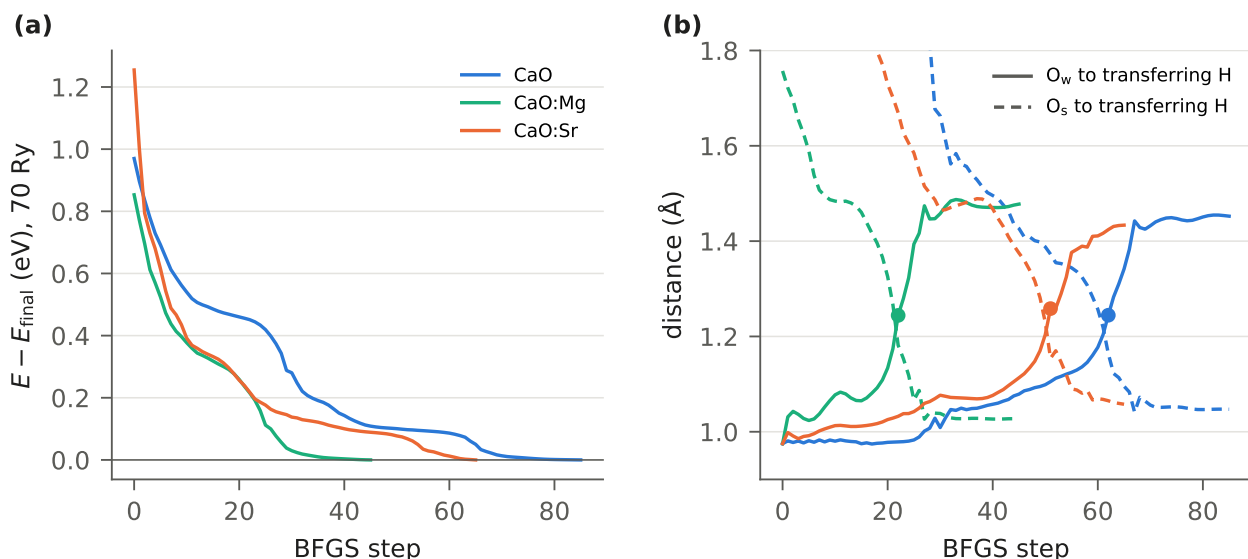


Figure S3. Geometry optimisation from an intact water molecule on top of a surface cation on CaO, CaO:Mg and CaO:Sr (70 Ry). (a) Energy relative to the final split state at each BFGS step. (b) Distance of the transferring hydrogen from the water oxygen O_w (solid) and from the accepting surface oxygen O_s (dashed); dots mark the step at which the hydrogen crosses the midpoint. A geometry optimisation is not a minimum energy path, so these curves show only that the intact molecule is not stable from these starts; they do not give a reaction barrier.

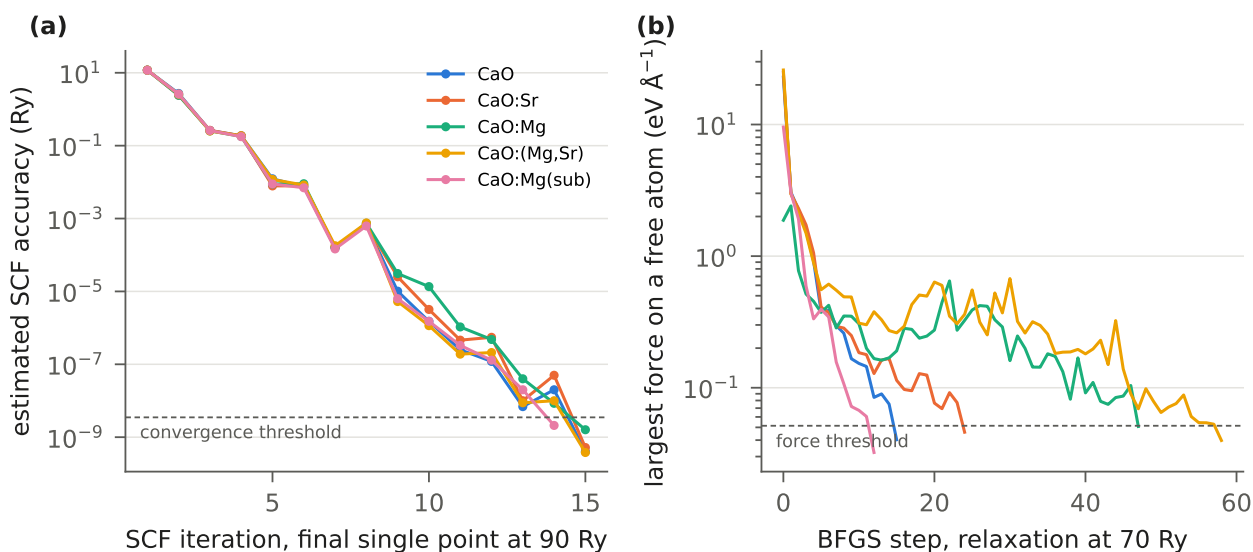


Figure S4. Calculation histories of the most stable state on each surface, taken from the Quantum ESPRESSO output. (a) Estimated SCF accuracy at each iteration of the final single point at 90 Ry; dashed line: convergence threshold. (b) Largest force on a free atom at each BFGS step of the last relaxation run at 70 Ry; dashed line: 2×10^{-3} Ry bohr⁻¹ (0.0514 eV Å⁻¹), the threshold used for these structures.

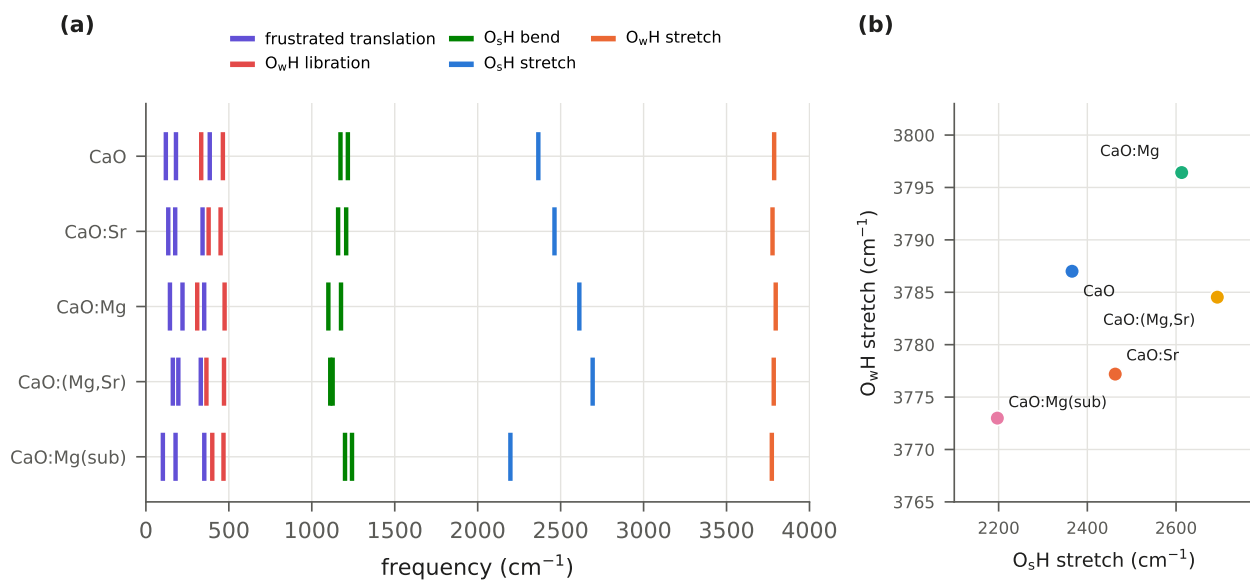


Figure S5. Vibrational fingerprint of the most stable state on each surface. (a) The nine adsorbate modes, coloured by their character as assigned from the eigenvectors. (b) Stretching frequency of the bridging hydroxyl O_wH against that of the new surface hydroxyl O_sH. Frequencies are listed in Table S4.

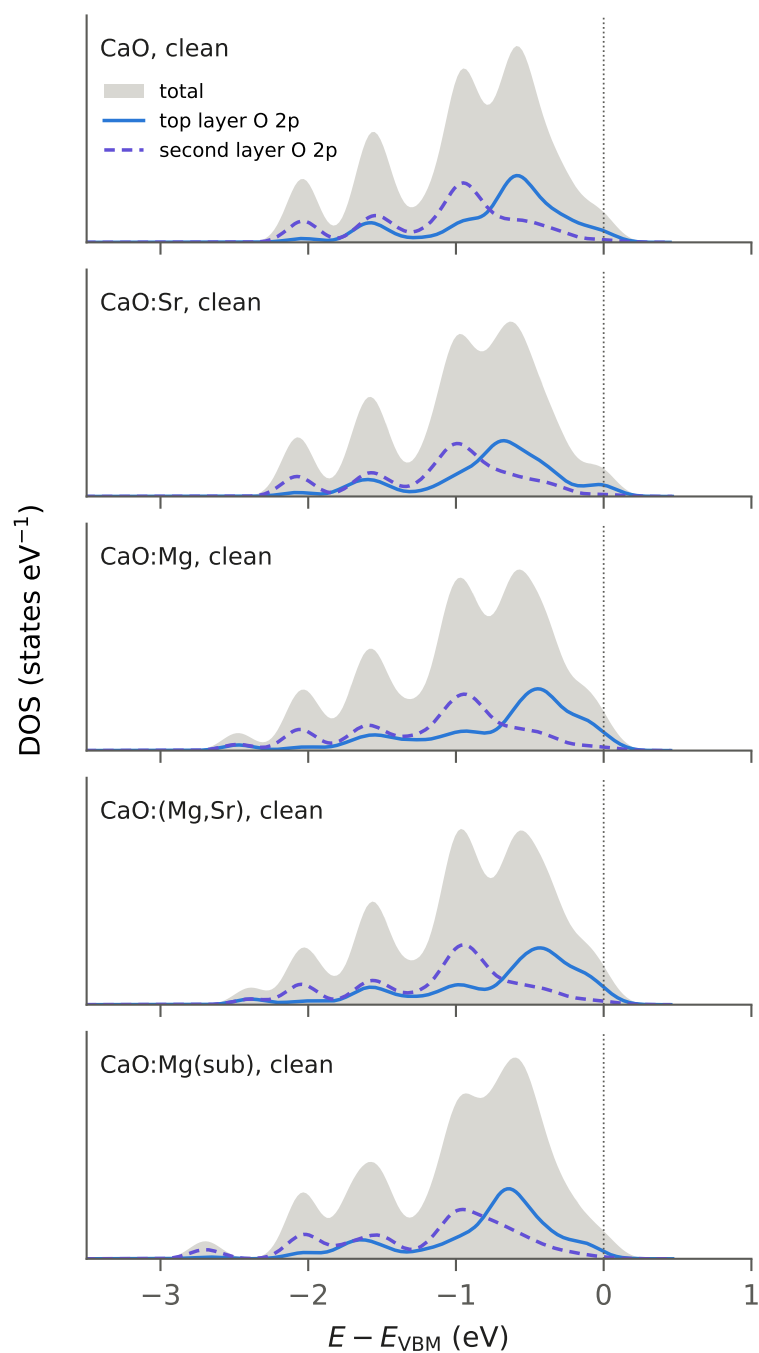


Figure S6. Projected densities of states of the clean surfaces, aligned at the VBM: total density of states (grey fill), 2p states of the top layer oxygens (solid) and of the second layer oxygens (dashed).

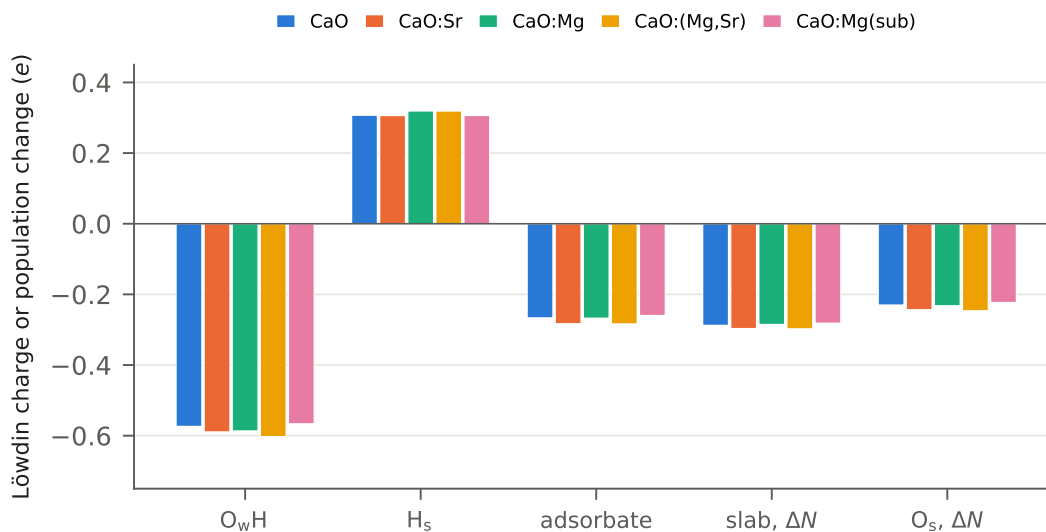


Figure S7. Löwdin charges of the hydroxyl O_wH , of the transferred proton H_s and of the whole adsorbate, and changes of the Löwdin population of the slab and of the proton accepting oxygen O_s relative to the clean slab (values in Table S3).

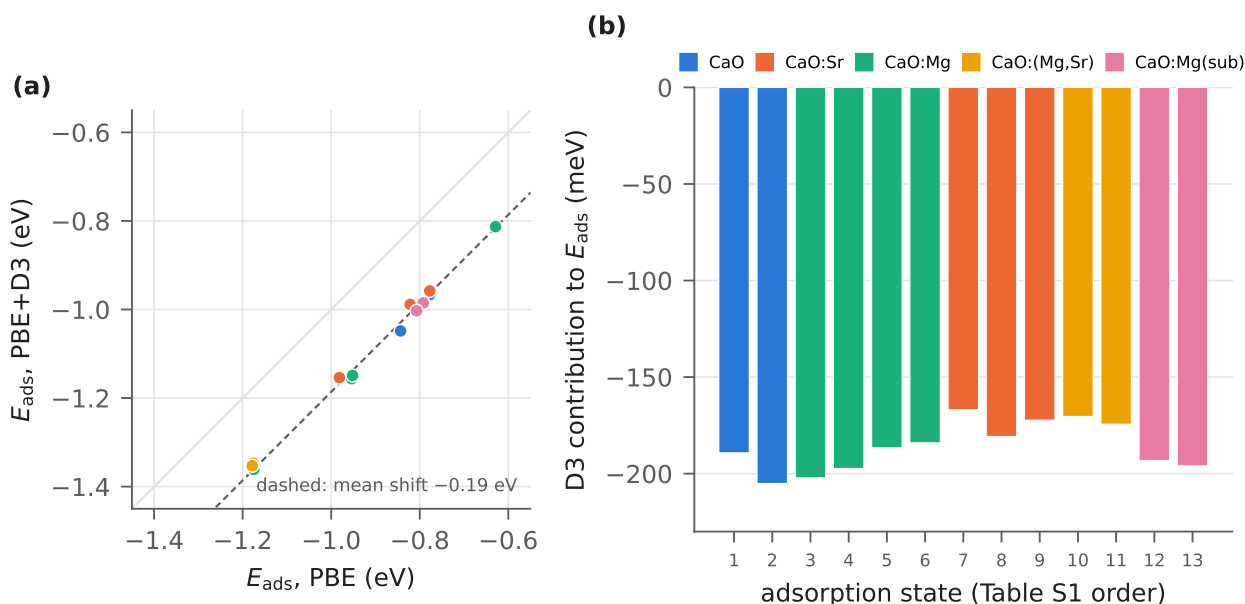


Figure S8. Effect of the D3 dispersion correction (Becke and Johnson damping) evaluated on the PBE geometries. (a) PBE+D3 against PBE adsorption energies of all 13 states; solid line: parity; dashed line: parity shifted by the mean D3 contribution. (b) D3 contribution to the adsorption energy of each state, numbered as in Table S1.