Supporting information for Computational investigation of CO_2 electroreduction on tin oxide and predictions of Ti, V, Nb and Zr dopants for improved catalysis

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1 Details of benchmark calculations

We used both Γ-point and k-point sampling in CP2K to benchmark bulk and surface properties. All Γ-point calculations on bulk structures required sufficiently large unit cells in order to get converged properties. The cohesive energy of α-Sn and SnO_2 reported in Table 1 calculated with Γ-point sampling consisted of 64 Sn atoms and 128 SnO_2 formula units, respectively. For bulk data with k-points, we used 8 Sn atoms and 2 SnO_2 formula units per unit cell of Sn and SnO_2 and $8 \times 8 \times 8$ k-points for the calculations, respectively. Surface properties of Sn and SnO_2 calculated withΓ-point involved a Sn (100) surface (repeated 4×2 along x×y direction) and SnO_2 (110) surface (repeated 2×2 along x×y direction). For surface data with k-points, we use the same surface unit cells and $4 \times 4 \times 1$ k-points. For bulk properties calculated by VASP, we used a 8 atom Sn unit cell and a 2 formula unit cell SnO_2. Surface unit cells, repeated 1×1 along x×y direction, of Sn and SnO_2 were used to calculate all the surface properties. A energy cutoff of 700 eV (Sn) and 500 eV (SnO_2) and 5×5×5 Monkhorst-pack k-points was required to obtain converged properties in VASP.

Table 1: Surface lattice constants of slabs with and without oxygen defects

Surface	a / Å	b / Å	c / Å
Clean slab	13.61	6.46	40.00
Clean slab + 1 def	13.62	6.63	40.00
Clean slab + 2 def	13.57	6.69	40.00

2 Relative binding energy on all dopant elements

Table 2: Relative binding energy of H between 3H/1CO2 and 4H/1CO2 states for all the dopant elements

Dopant	ΔG(H*)	Overpotential (V)
Sn	0.69	-0.60
Ti	0.15	-0.06
V	-0.02	-0.11
Zr	0.49	-0.40
Co	0.99	-0.90
Pb	-0.48	-0.57
Zn	0.62	-0.52
Cd	0.17	-0.08
Nb	-0.42	-0.51
Sb	1.40	-1.30
Ta	0.84	-0.74

3 Role of solvation

We investigated the role of solvation using a different continuum solvation model, VASPSol, which is implemented in VASP. Single point energy calculations using PAW potential, PBE functional on optimized structures from CP2K were performed. The table below shows that the binding energy of the most relevant intermediates, the 3H/1CO_2 and 4H/1CO_2 states. The data below shows that solvation does not significantly affect the relative energetics of these two key intermediates.

Table 3: Relative energetics calculated with and without solvation

Energy	without solvation / eV	with solvation / eV
Binding energy of CO_2 to clean slab + 3H + 1def	0.33	0.41
Binding energy of CO_2 to clean slab + 4H + 1def	0.25	0.39
Relative stability between Fig 4.a and 4.b	0.09	0.08

4 Energetics

Table 4: Table of energies of SnO_2 surface with 0% defects and different concentration of adsorbates. (I) Energy of structures relaxed with k-point sampling , (II) Energy from a single energy calculation on a structure relaxed with no k-point sampling. x denotes geometries that did not converge with k-point sampling

Surface composition	E_{elec} (I) / eV	E_{elec} (II) / eV	ZPE	-TS
Clean slab	-30975.32			
+ 1H	-30992.59	-30992.51	0.30	-0.01
+ 2H	-31009.38	-31009.33	0.60	-0.02
+ $1CO_2$	-32003.14	-32003.09	0.41	-0.08
+ $2CO_2$	-33031.05	-33030.88	0.84	-0.11
+ 1H + $1CO_2$	-32019.79	-32019.74	0.77	-0.06
+ 2H + $1CO_2$	-32037.72	-32037.54	1.04	-0.08
+ 1H + $2CO_2$	-33048.30	-33048.20	1.14	-0.13
+ 2H + $2CO_2$	-33065.29	-33065.23	1.44	-0.14
+ 3H	x	-31026.38	0.91	-0.03
+ 3H + $1CO_2$	x	-32054.34	1.34	-0.08
+ 3H + $2CO_2$	x	-33081.24	1.83	-0.14
+ 4H	-31043.18	-31043.14	1.23	-0.03
+ 4H + $1CO_2$	x	-32070.54	1.69	-0.09
+ 4H + $2CO_2$	x	-33097.86	2.16	-0.13
+ 5H	x	-31058.41	1.54	-0.04
+ 5H + $1CO_2$	x	-32086.13	1.97	-0.09
+ 5H + $2CO_2$	-33113.48	-33113.49	2.45	-0.14

Table 5: Table of energies of SnO_2 surface with 25% defects and different concentration of adsorbates. (I) Energy of structures relaxed with k-point sampling , (II) Energy from a single energy calculation on a structure relaxed with no k-point sampling.

Surface composition	E_{elec} (I) / eV	E_{elec} (II) / eV	ZPE	-TS
Clean slab + 1def	-30538.93	-30538.78		
+ 1H	-30556.21	-30556.07	0.29	-0.02
+ 2H	-30574.41	-30574.19	0.61	-0.02
+ $1CO_2$	-31566.90	-31566.76	0.43	-0.05
+ $2CO_2$	-32594.51	-32594.32	0.86	-0.11
+ 1H + $1CO_2$	-31584.05	-31583.88	0.75	-0.06
+ 2H + $1CO_2$	-31601.77	-31601.70	1.03	-0.08
+ 1H + $2CO_2$	-32611.55	-32611.42	1.12	-0.16
+ 2H + $2CO_2$	-32628.86	-32628.66	1.49	-0.13
+ 3H	-30590.92	-30590.85	0.91	-0.03
+ 3H + $1CO_2$	-31618.39	-31618.31	1.32	-0.09
+ 3H + $2CO_2$	-32645.74	-32645.66	1.78	-0.15
+ 4H	-30607.55	-30606.21	1.21	-0.04
+ 4H + $1CO_2$	-31633.80	-31633.68	1.65	-0.09
+ 4H + $2CO_2$	-32661.27	-32661.16	2.07	-0.13

Table 6: Table of energies of SnO_2 surface with 50% defects and different concentration of adsorbates. (I) Energy of structures relaxed with k-point sampling , (II) Energy from a single energy calculation on a structure relaxed with no k-point sampling. x denotes geometries that did not converge with k-point sampling

Surface composition	E_{elec} (I) / eV	E_{elec} (II) / eV	ZPE	-TS
Clean slab + 2def	-30102.37	-30102.22		
+ 1H	x	-30119.08	0.30	-0.01
+ 2H	x	-30135.63	0.61	-0.02
+ 1CO2	-31129.88	-31129.66	0.42	-0.06
+ 2CO2	-32157.61	-32157.52	0.87	-0.10
+ 1H + 1CO2	-31146.20	-31146.12	0.71	-0.08
+ 2H + 1CO2	-31162.98	-31162.85	1.04	-0.07
+ 1H + 2CO2	-32173.27	-32173.09	1.19	-0.11
+ 2H + 2CO2	-32191.10	-32190.53	1.48	-0.13
+ 3H	-30152.50	-30150.86	0.92	-0.03
+ 3H + 1CO2	x	-31178.60	1.33	-0.09
+ 3H + 2CO2	x	-32206.70	1.77	-0.15