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Supplementary information

SnO_2-supported single metal atoms: A Bifunctional Catalyst for the Electrochemical Synthesis of H_2O_2

Santiago Jimenez-Villegas, [a] Sara R. Kelly, [b] and Samira Siahrostami * [a]

Computational details

Calculation of absorption free energy

Catalytic activity of the SnO_2- supported single metal atoms was assessed via binding energies of reaction intermediates involved in the 2e- WOR and ORR. Namely, adsorption free energies, ΔG, of OH* and OOH* over two different surface-active sites (atop the single metal atom and on an adjacent Sn site) was explored. ΔG was calculated at zero potential and pH=0, using the following equation:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

Where ΔE, ΔZPE, and ΔS are adsorption energies with respect to water, zero-point energy difference and change in entropy, respectively. [1]
Additionally, the computational hydrogen electrode model (CHE) was implemented to calculate the free energy of all adsorbates. This approach assumes the chemical potential of a proton-electron pair to be equal to that of gas phase H_2 at U_{elec}=0.0 V vs. the reversible hydrogen electrode (RHE). By shifting the electron energy by $-eU_{elec}$ when e and U_{elec} are the elementary charge and electrode potential, respectively, the effect of the electrode potential is taken into account.[1]

Stability calculations

Satability of SnO_2- supported single metal atoms was investigated via formation energy calculations and resistance to dissolution. Formation energies were calculated through the following equation:[2]

$$\Delta E_{form} = E_{M-Supp} - E_M - E_{Supp}$$

Where E_{M-Supp}, E_M, E_{M-Supp} are electronic energies of metal-support complex, bulk metal atom and support materials, respectively. Dissoltion potential were calculated using the folowing:

$$U_{diss(Metal,SAC)} = U_{diss(\overset{\circ}{Metal,\ Bulk})} - \frac{\mu_{Metal,SAC} - \mu_{\overset{\circ}{Metal,\ Bulk}}}{ne}$$

where $U_{diss(\overset{\circ}{Metal,\ Bulk})}$, $\mu_{Metal,SAC}$, $\mu_{\overset{\circ}{Metal,\ Bulk}}$, and n are the dissolution potential of bulk metals, the chemical potential of metal atom in SAC system, that of bulk metal, and the number of electrons involved in the dissolution, respectively. $\mu_{Metal,SAC}$ were calculated as E_{M-Supp}.[2,3]

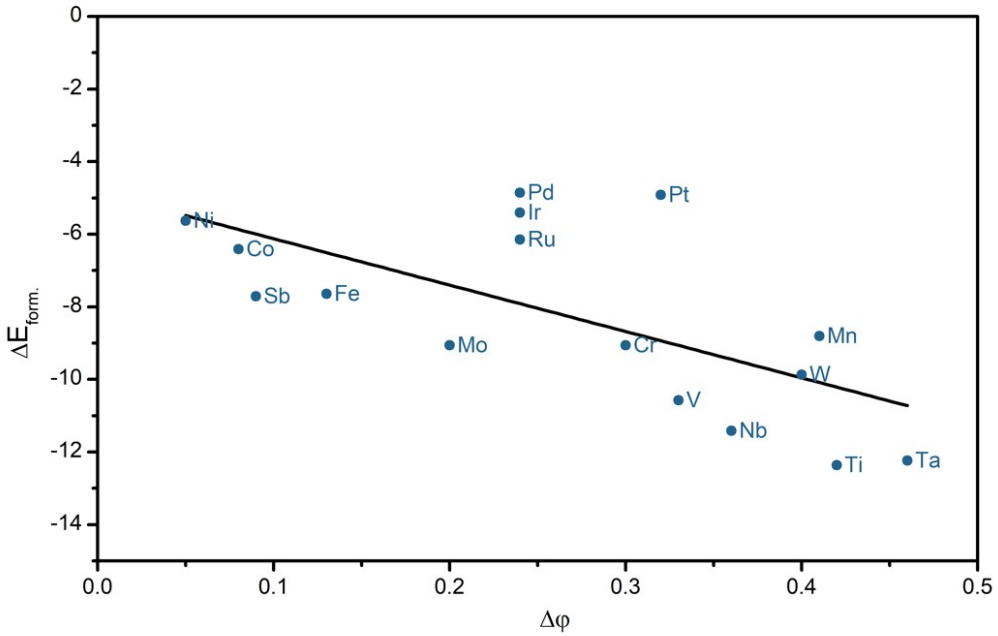

Figure 1. ΔE_{form} of SnO_2-supported single metal atoms as a function of the electronegativity difference ($\Delta\varphi$) between Sn and single metal atom. Black line represents linear fit.

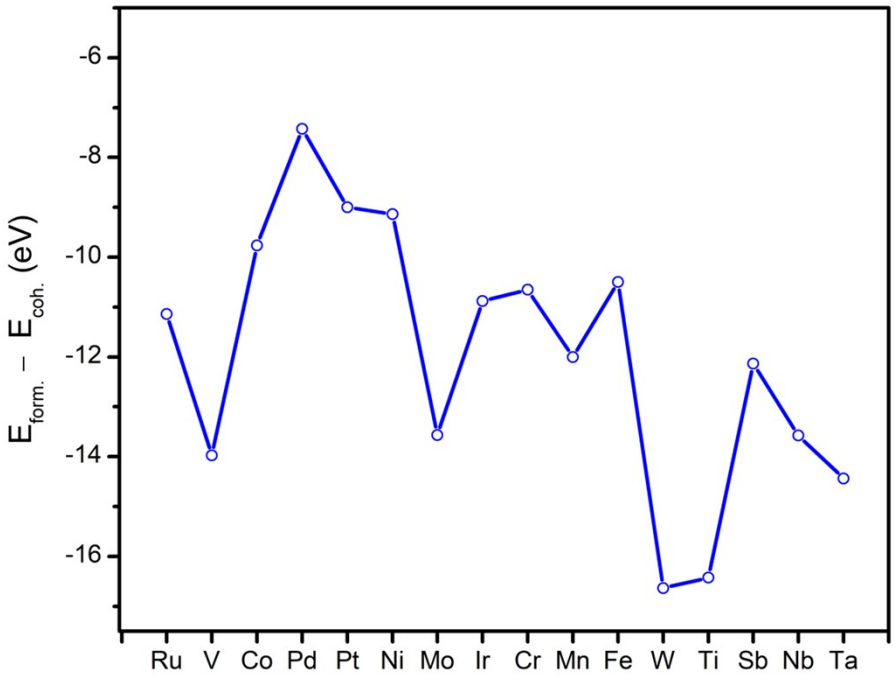

Figure 2. Difference between formation energy of the single metal with the SnO_2 support ($E_{form.}$) and cohesive energy ($E_{coh.}$) of the metal bulk. $E_{coh.}$ values were obtained from ref. [4,5]

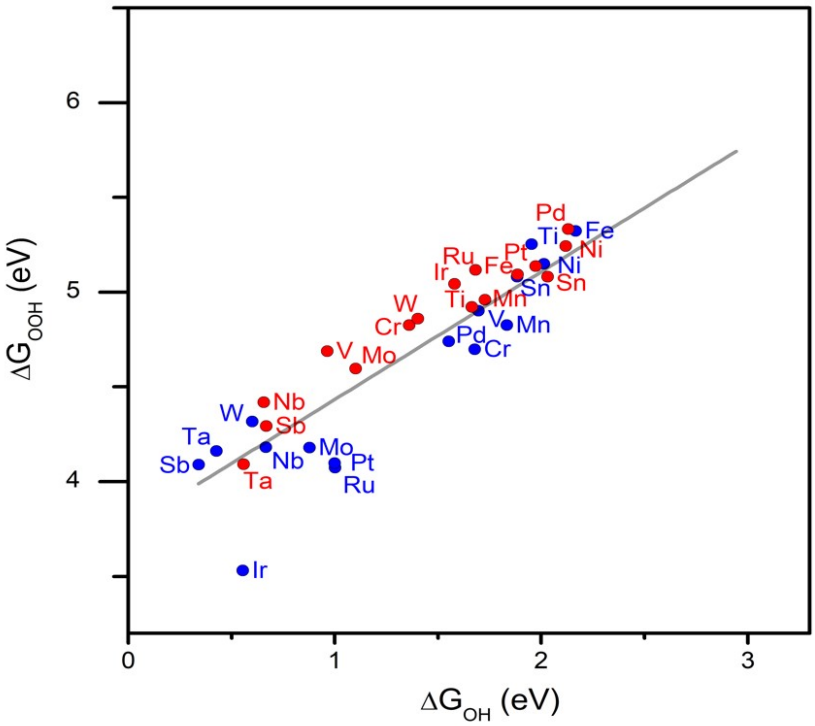

Figure 3. linear scaling relation between the Gibbs, ΔG, free binding energies of OOH* and OH* intermediates. Blue data points show ΔG when *OH, and *OOH intermediates are adsorbed on the surface of the single metal site, whereas red data points show DG of those adsorbed on the Sn site. Grey line represents linear fit.

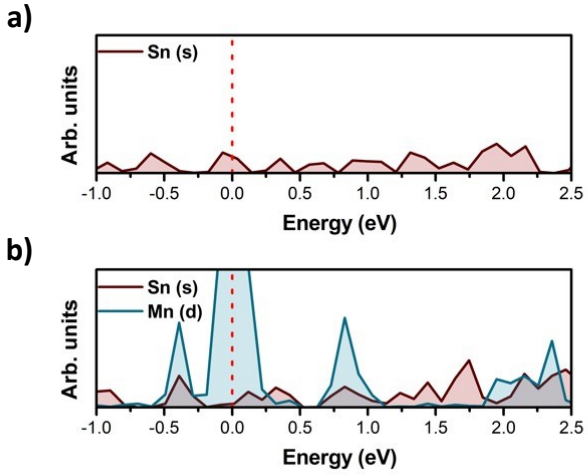

Figure 4. Density of states for a) pure SnO_2 and b) Mn:SnO_2. The SAC increases the density of states at the fermi level and results in activating the SnO_2 substrate and optimum interaction with the reaction intermediates.

References

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