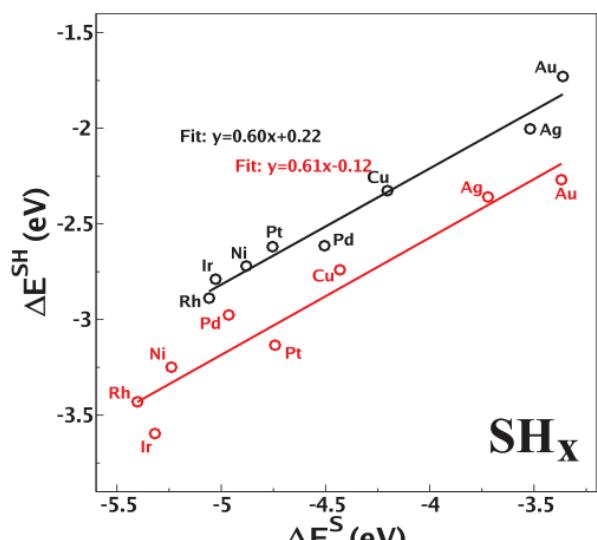
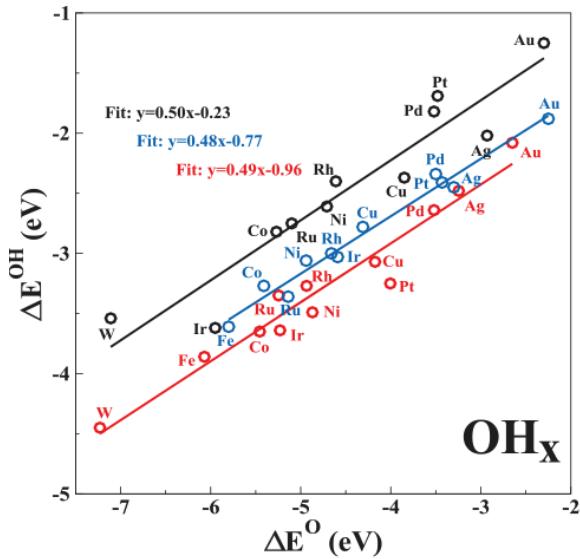
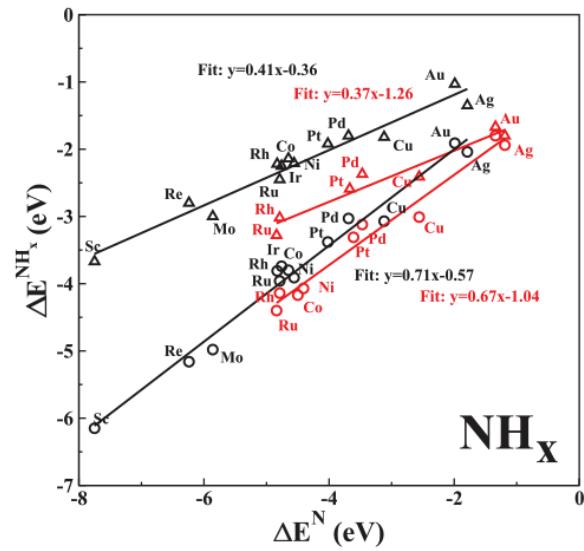
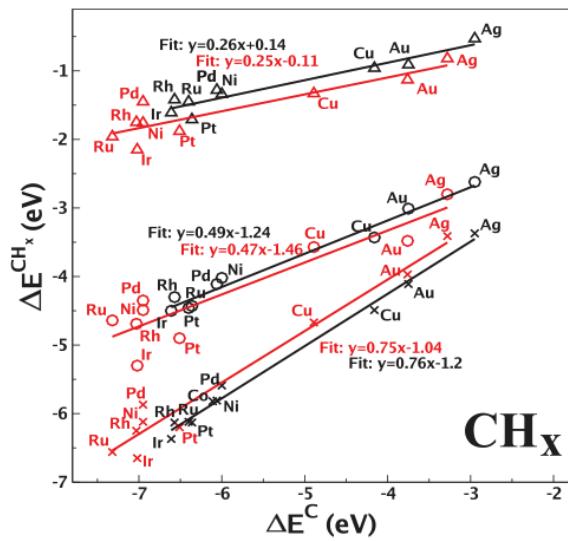


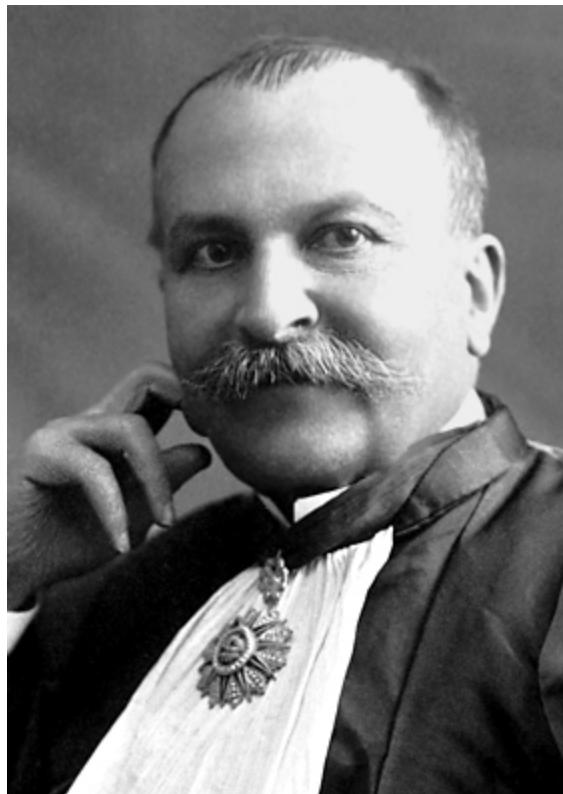


Hands-on 4. DFT adsorption 2

▼ Scaling relation

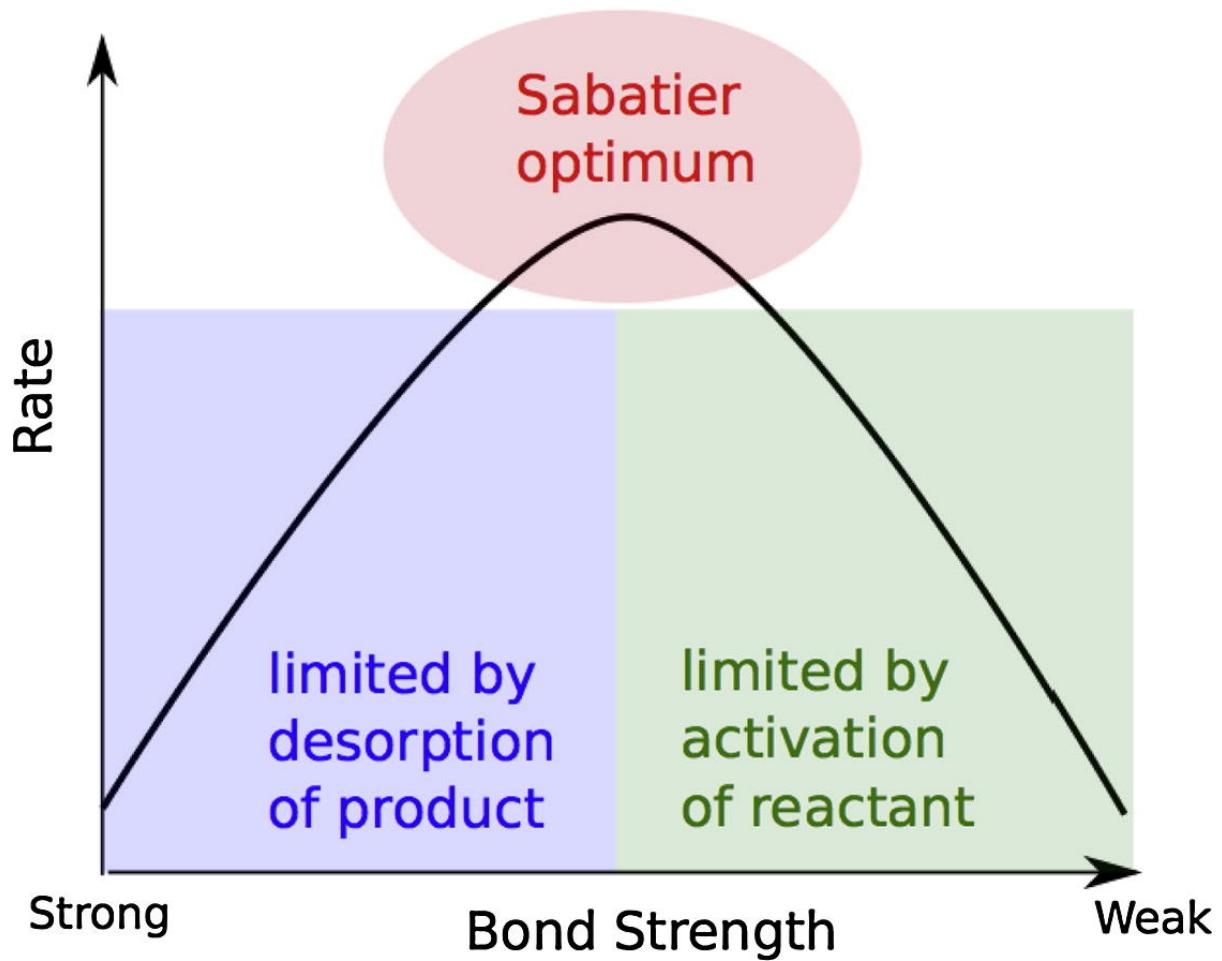


▼ Sabatier principle

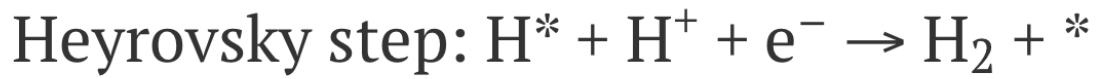
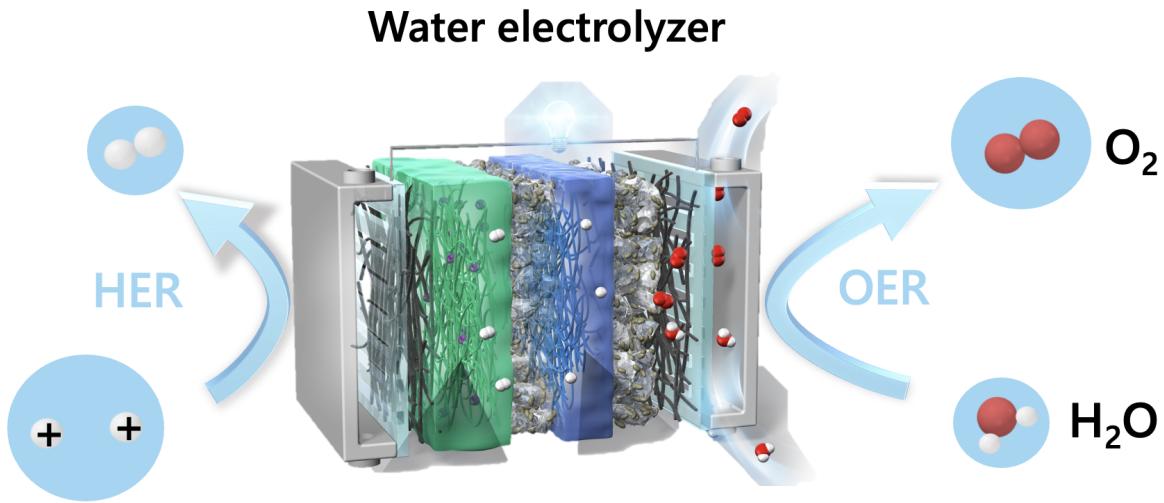


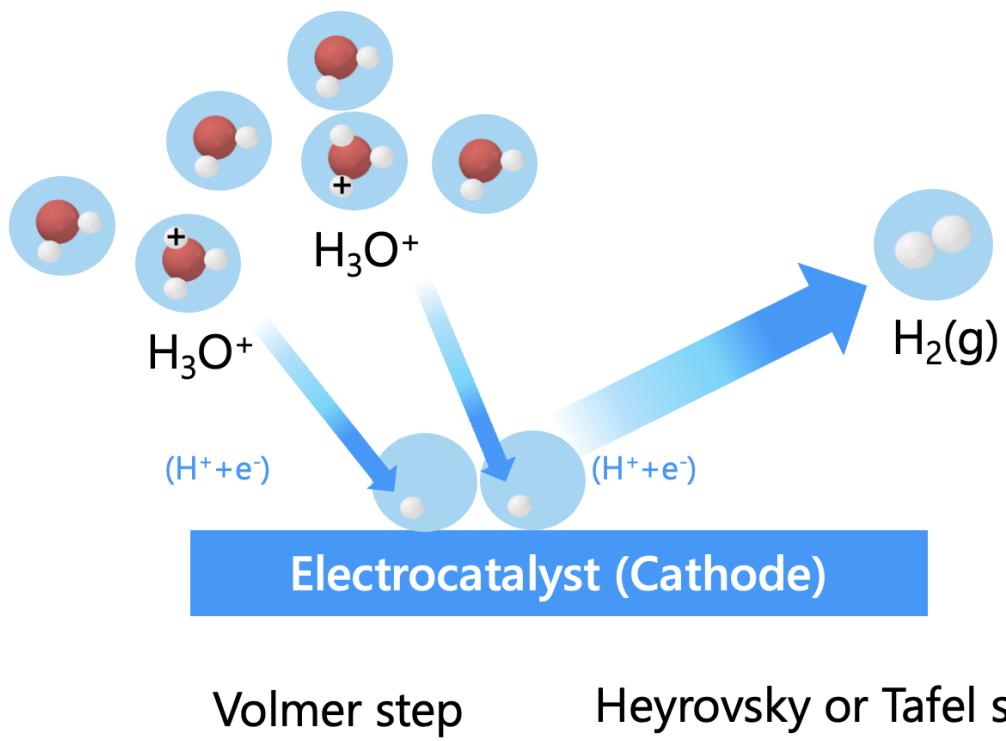
Paul Sabatier

"the interactions between the catalyst and the reactants should be "just right"; that is, neither too strong nor too weak. "



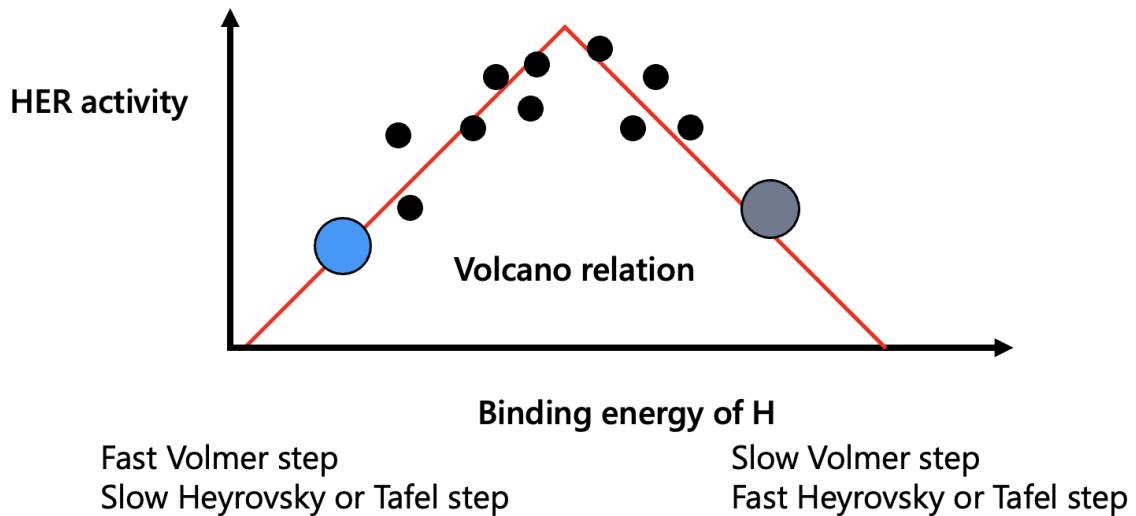
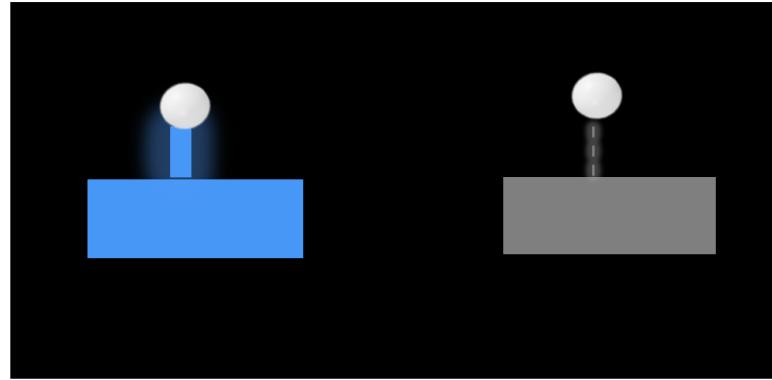
Example: Hydrogen evolution reaction

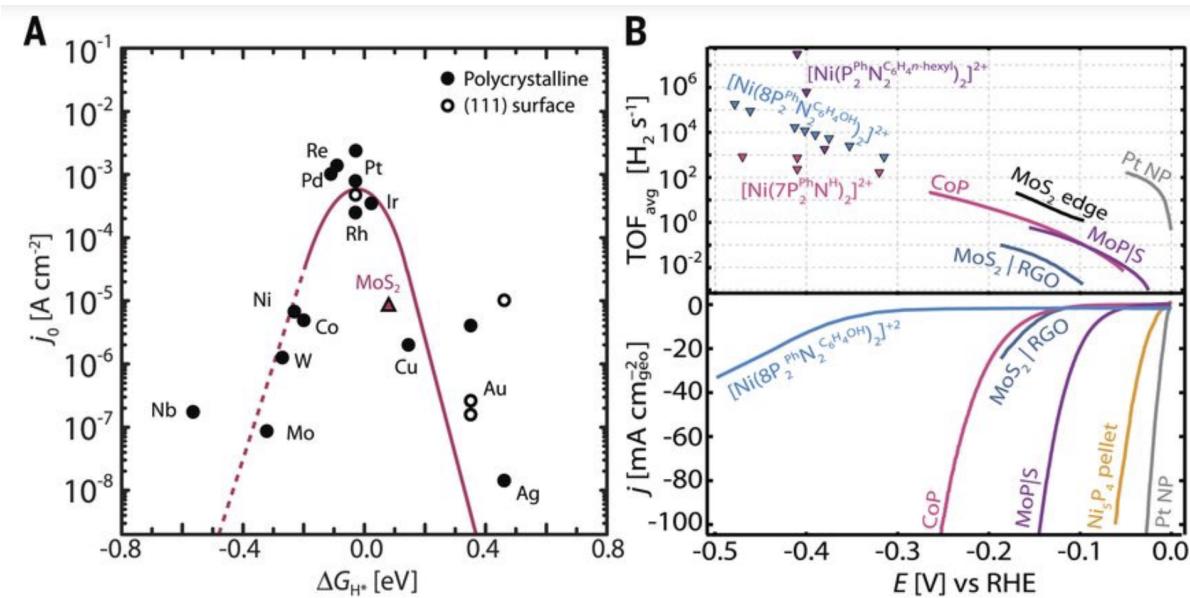




Strong binding catalyst

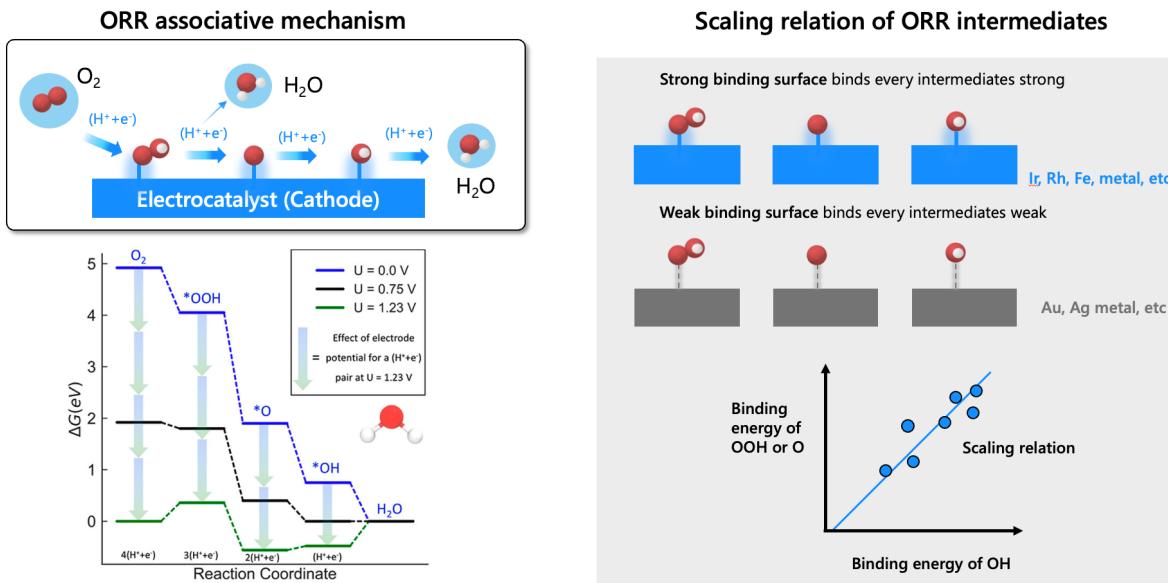
Weak binding catalyst





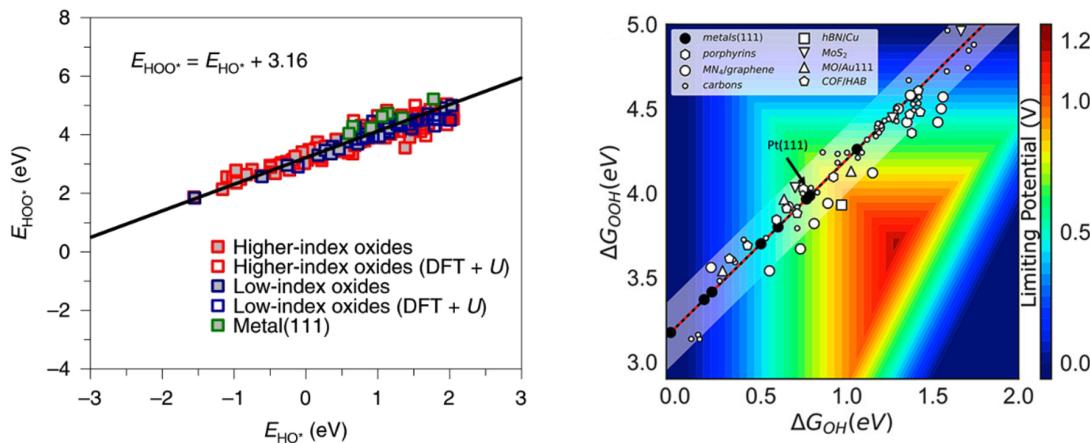
<https://www.science.org/doi/full/10.1126/science.aad4998>

Example: Oxygen reduction reaction



Kulkarni et al. Chem. Rev. **118**, 5, 2302 (2018).

Li, et al. Nat. Catal. **4**, 463 (2021).



Theoretical studies reveal that scaling relationships among ORR intermediates influence ORR catalytic activity. These relationships, give rise to a "volcano relation," explain the performance of Pt, Pd, and their alloys. However, the challenge of designing new catalysts that break these scaling rules has hampered progress.

Li, et al. Nat. Catal. 4, 463 (2021). Kulkarni et al. Chem. Rev. 118, 5, 2302 (2018)

▼ Electrode simulation: beyond adsorption energy



$$\mu(H^+) + \mu(e^-) = \frac{1}{2}\mu(H_2) - eU$$

the OER follows a four-electron mechanism.^{3,36} The free energy of a pair of proton and electron ($\text{H}^+ + \text{e}^-$) is calculated as a function of applied potential relative to reversible hydrogen electrode (U vs. RHE), *i.e.*, $\mu(\text{H}^+ + \text{e}^-) = 0.5\mu(\text{H}_2) - eU$, according to the computational hydrogen electrode (CHE) model proposed by Nørskov *et al.*³⁶ The potential determining step (pds) is defined as the last step to become downhill in free energy along the OER pathway with the increase of potential.³ The approach of introducing excess electrons and the additional computational details are given in the Methods section and Tables S1–S3 in the ESI.[†]

ACS Energy Lett. 2020, 5, 12, 3778–3787

▼ From adsorption energy to adsorption free energy

μ_{X*} is the chemical potential of the adsorbate bound on a surface, μ_* is the chemical potential of the surface, and μ_X is the chemical potential of the adsorbate in gas phase.

$$\Delta G_X = \mu_{X*} - \mu_* - \mu_X \quad (1)$$

Chemical potentials can be calculated^{5,8} using Supplementary Equation 2, where E is the electronic energy as calculated by density functional theory (DFT), ZPE is the zero-point energy, C_p is the heat capacity, T is temperature, S is entropy, $\Delta\mu_{solv}$ is the change in chemical potential from solvent [de]stabilization, and $\Delta\mu_{corr}$ is any experimental correction required to account for differences between experimental chemical potentials and DFT-based chemical potentials.

$$\mu = E + ZPE + \int C_p dT - TS + \Delta\mu_{solv} + \Delta\mu_{corr} \quad (2)$$

Literature⁹ reports that ZPE_{CO} is 0.130 eV, $\int C_p, CO dT$ is 0.091 eV at 298 K, S_{CO} is 0.002092 eV K⁻¹, and that $\Delta\mu_{exp, CO}$ is 0.02 eV for gas phase CO. Thus the chemical potential of CO in the gas phase is:

$$\begin{aligned}\mu_{CO, g} &= E_{CO, g} + ZPE_{CO, g} + \int C_p, CO dT - TS_{CO, g} + \Delta\mu_{solv, g} + \Delta\mu_{corr, g} \\ \mu_{CO, g} &= E_{CO, g} + 0.130 \text{ eV} + 0.091 \text{ eV} - (298 \cdot 0.002092) \text{ eV} + 0 \text{ eV} + 0.02 \text{ eV} \\ \mu_{CO, g} &= E_{CO, g} - 0.362 \text{ eV}\end{aligned}\quad (3)$$

The same method can be used to calculate the chemical potential of CO in the adsorbed-state (μ_{CO*}) given literature values⁹ for ZPE , C_p , and S as well as a solvation correction term⁵ (μ_{solv}) and an empirical correction term⁶ (μ_{corr})—see Supplementary Equation 4. Note that we assumed a CO stretch frequency of 2,000 cm⁻¹, and deviations from this frequency may cause errors.

$$\begin{aligned}\mu_{CO*} &= E_{CO*} + ZPE_{CO*} + \int C_p dT - TS_{CO*} + \Delta\mu_{solv} + \Delta\mu_{corr} \\ \mu_{CO*} &= E_{CO*} + 0.192 \text{ eV} + 0.085 \text{ eV} - (298 \cdot 0.000452) \text{ eV} - 0.2 \text{ eV} + 0.2 \text{ eV} \\ \mu_{CO*} &= E_{CO*} + 0.142 \text{ eV}\end{aligned}\quad (4)$$

Assuming that μ_* is equal to E_* and by combining Supplementary Equations 1, 3, and 4, we can calculate the change in chemical potential of adsorbing CO:

$$\begin{aligned}\Delta G_{CO} &= \mu_{CO*} - \mu_* - \mu_{CO} \\ \Delta G_{CO} &= [E_{CO*} + 0.142 \text{ eV}] - E_* - [E_{CO, g} - 0.362 \text{ eV}] \\ \Delta G_{CO} &= E_{CO*} - E_* - E_{CO, g} + 0.50 \text{ eV} \\ \Delta G_{CO} &= \Delta E_{CO} + 0.50 \text{ eV}\end{aligned}\quad (5)$$

In contrast to the methods we used to find the optimal ΔE_{CO} for CO₂ reduction, the literature sources^{4, 12} we used for the HER already performed the chemical potential calculations, allowing us to use their energy calculation methods directly:

$$\Delta G_H = \Delta E_H + 0.24 \text{ eV} \quad (7)$$

where the optimal ΔG_H value is -0.03 eV, yielding an optimal ΔE_H value of -0.27 eV.

<https://www.nature.com/articles/s41929-018-0142-1#MOESM1>

In short, For simplicity +0.24eV to hydrogen adsorption energy and +0.50eV for carbon monoxide adsorption energy

Assignment

Reproduce volcano plot of hydrogen evolution reaction. Please complete the following tasks:

1. Get H adsorption energy for Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au using 1×1 4 layers slab model with adsorption site 'fcc' site.
2. Plot H adsorption energy vs applied potential
3. **Compare the surface energies** of the (100), (110), and (111) facets.

Please submit your results along with a **concise explanation of your findings, limited to one page.** (format: studentnumber_name.doc (.pdf or whatever), ex)12345_seokhyunchoung.doc)