Hands-on 3. DFT adsorption

1. Why do we need adsorption energy?

What determines catalytic activity??

adsorption strength of adsorbates to the catalyst surface determines catalytic activity.

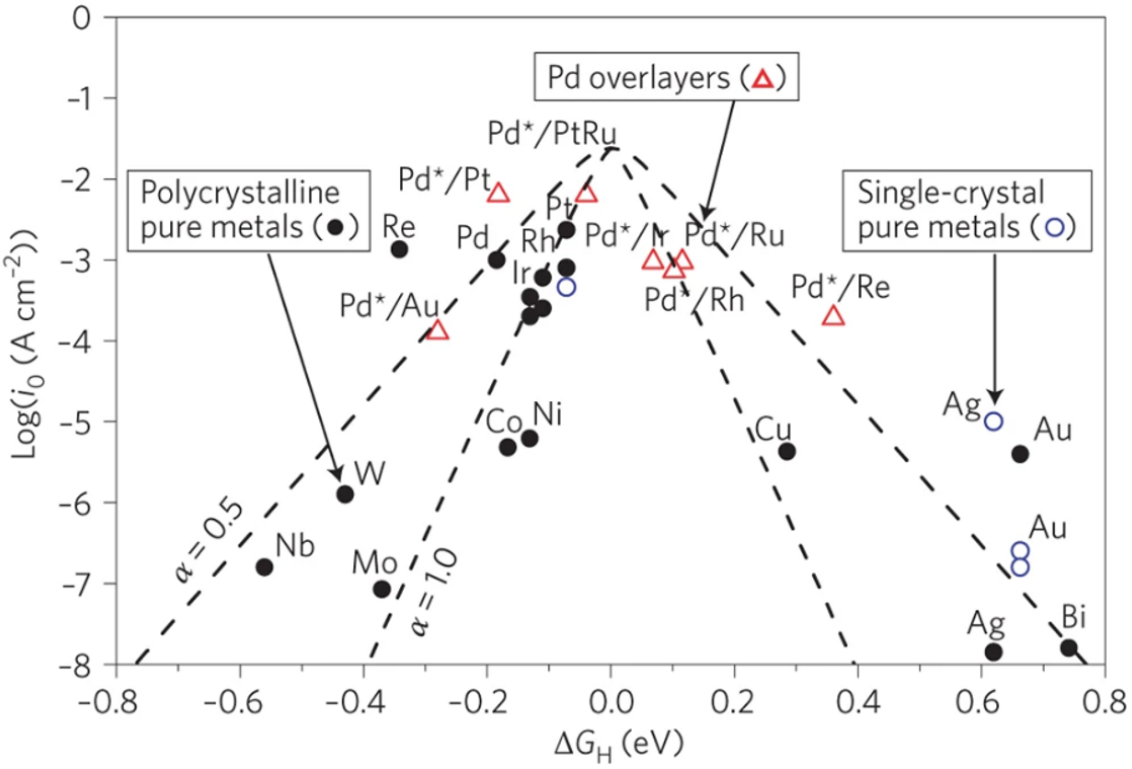
(Efficiency of energy, rate of synthesis, scalability etc.)

https://prod-files-secure.s3.us-west-2.amazonaws.com/b78ce7ef-d8d6-40c6-bc21-c6c847b5ab82/7cf0cadd-c5a1-4c2b-abf4-c385b9f6357c/singlerandom_system.mp4

https://opencatalystproject.org

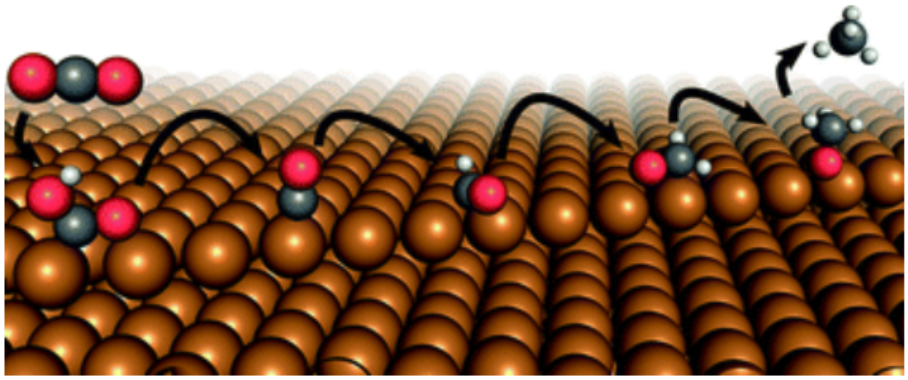
2. Success in chemical adsorption energy vs catalytic activity relations

Example 1. Hydrogen evolution electrode

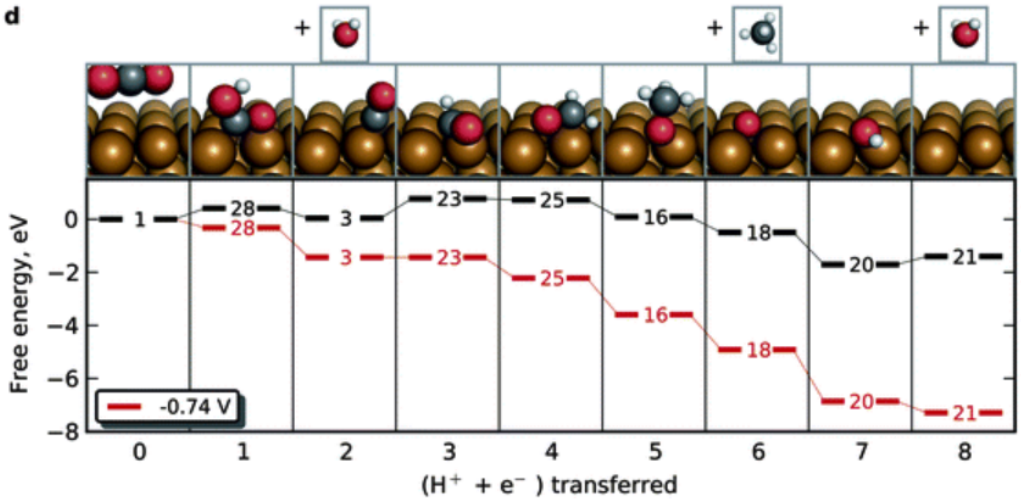


Nørskov *et al*. Nature Mater. **5**, 909–913 (2006)

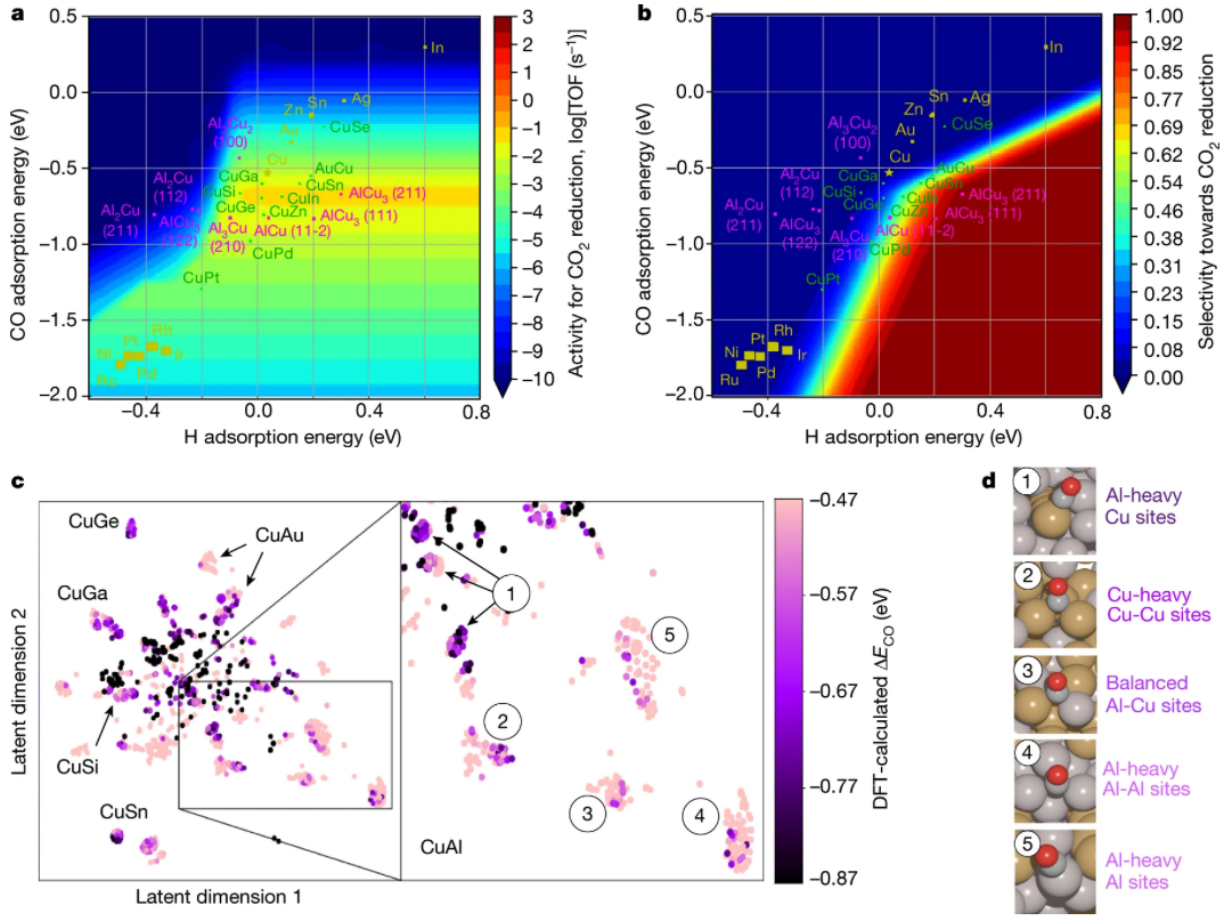
Example 2. CO2 reduction electrode

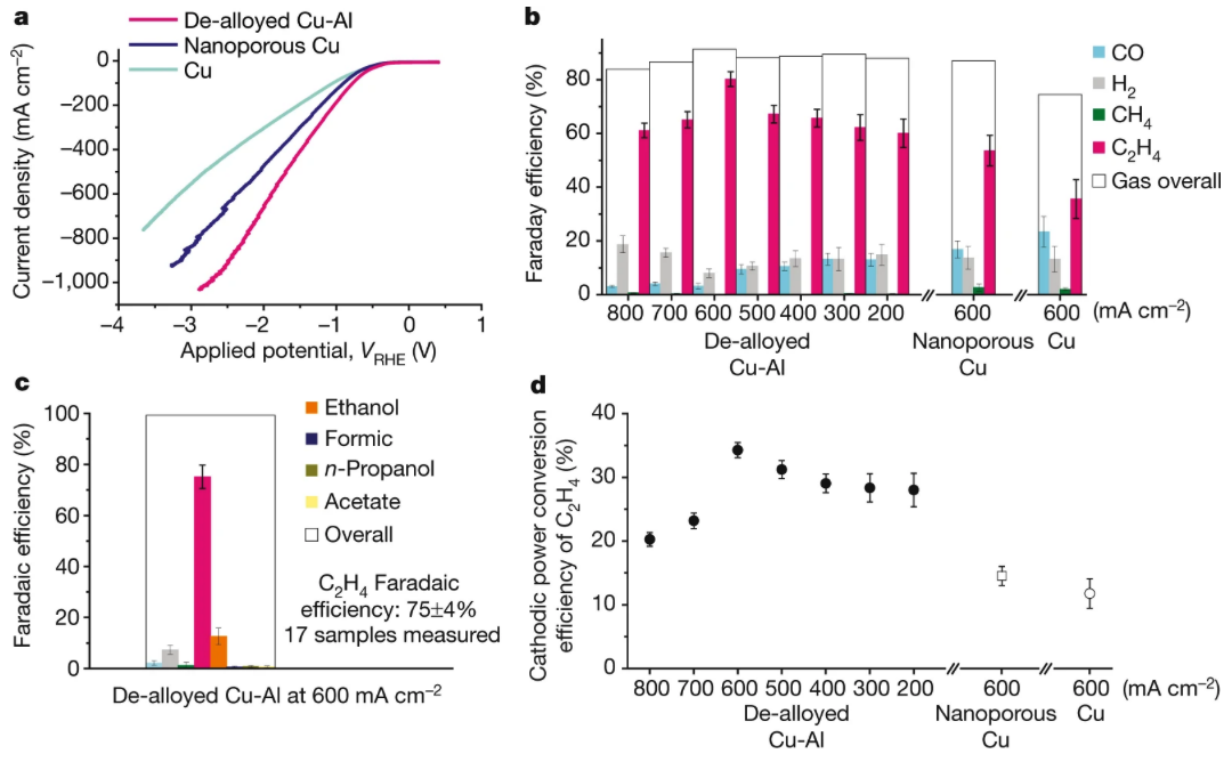


$$CO_2 + 8(H^+ + e^-) \rightarrow CH_4 + 2H_2O$$



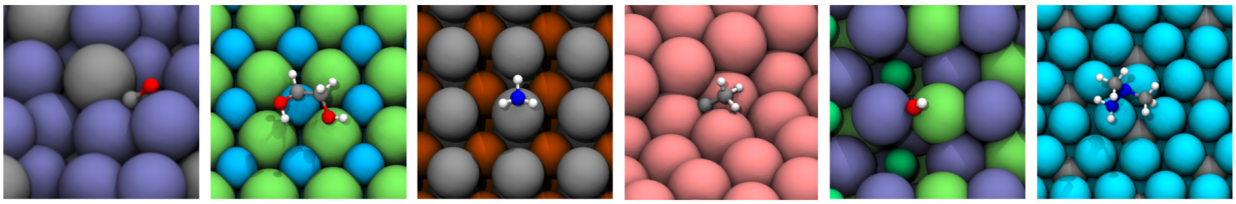
Energy Environ. Sci., 2010,**3**, 1311-1315





Nature **volume 581**, pages 178–183 (2020)

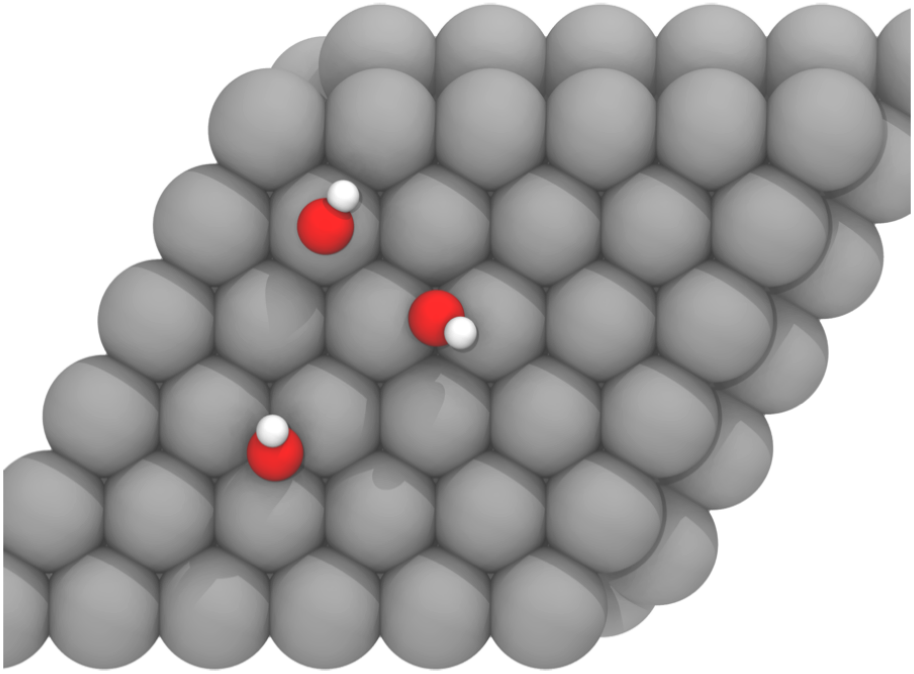
We can play with catalysts and adsorbates

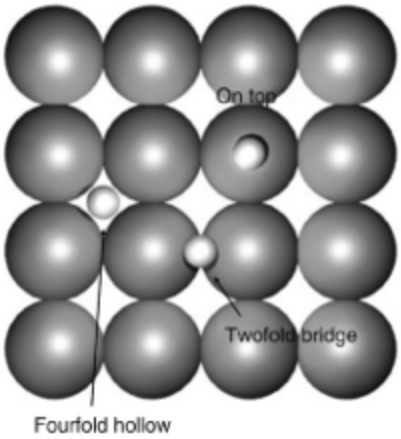


https://arxiv.org/pdf/2010.09435

3. How to calculate adsorption energy

3.1. Place your atom or molecule on surface at different sites



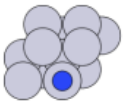
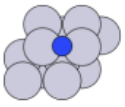
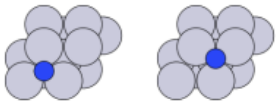
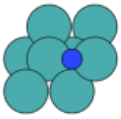
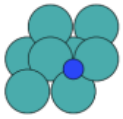


$$E_{\text{ads}} = E_{\text{H/surf}} - \frac{1}{2}E_{\text{H}_2\text{(g)}} - E_{\text{surf}}$$

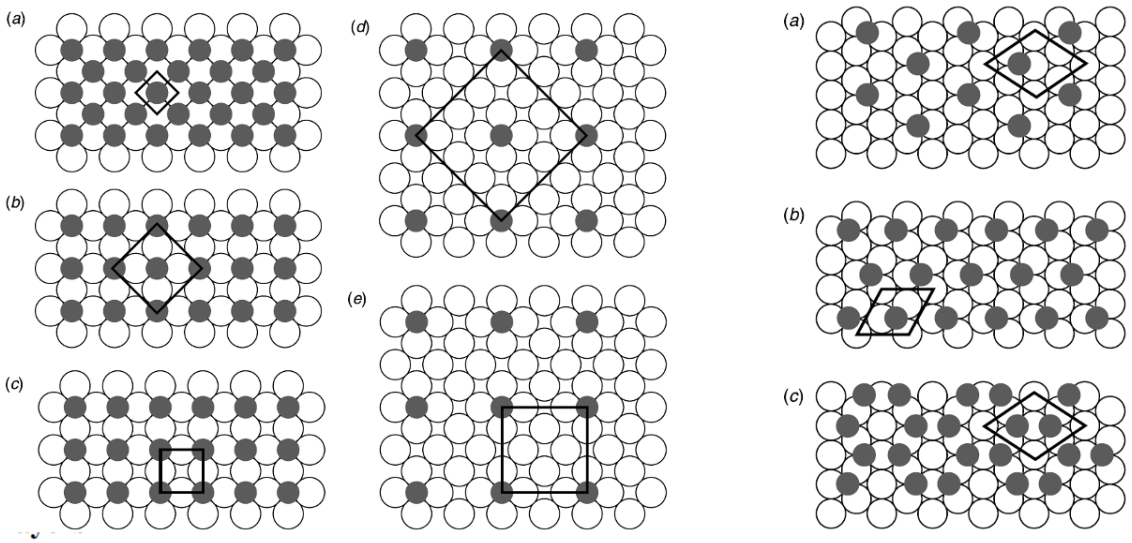
TABLE 4.3 Results of Calculations for H Adsorption on Cu(100) as Described in Text[a]

Initial H Site	Adsorption Energy Relative to Hollow Site	Adsorption Energy Relative to H_2(g)	Local Minimum?
Fourfold hollow	0	−0.19	Yes
Twofold bridge	0.08	−0.11	No
On top	0.57	+0.38	No

[a]All energies are in electron volts (eV).

	Coordination			
Structure	**one-fold**	**two-fold**	**three-fold**	**four-fold**
M_{13}	 on-top	 two-fold	 three-fold	 four-fold
fcc (111)	 on-top	 bridge	 fcc, hcp	
bcc (110)	 on-top	 bridge	 hollow	

3.2. Concept of adsorbate coverage



	(1 × 1)	c(2 × 2)	c(4 × 4)
H coverage	1.00 ML	0.50 ML	0.125 ML
$E_{(ads)}$ relative to $\frac{1}{2}H_2$ (eV)	−0.08	−0.11	−0.19

Why it matters?

#Reaction of Ammonia Synthesis

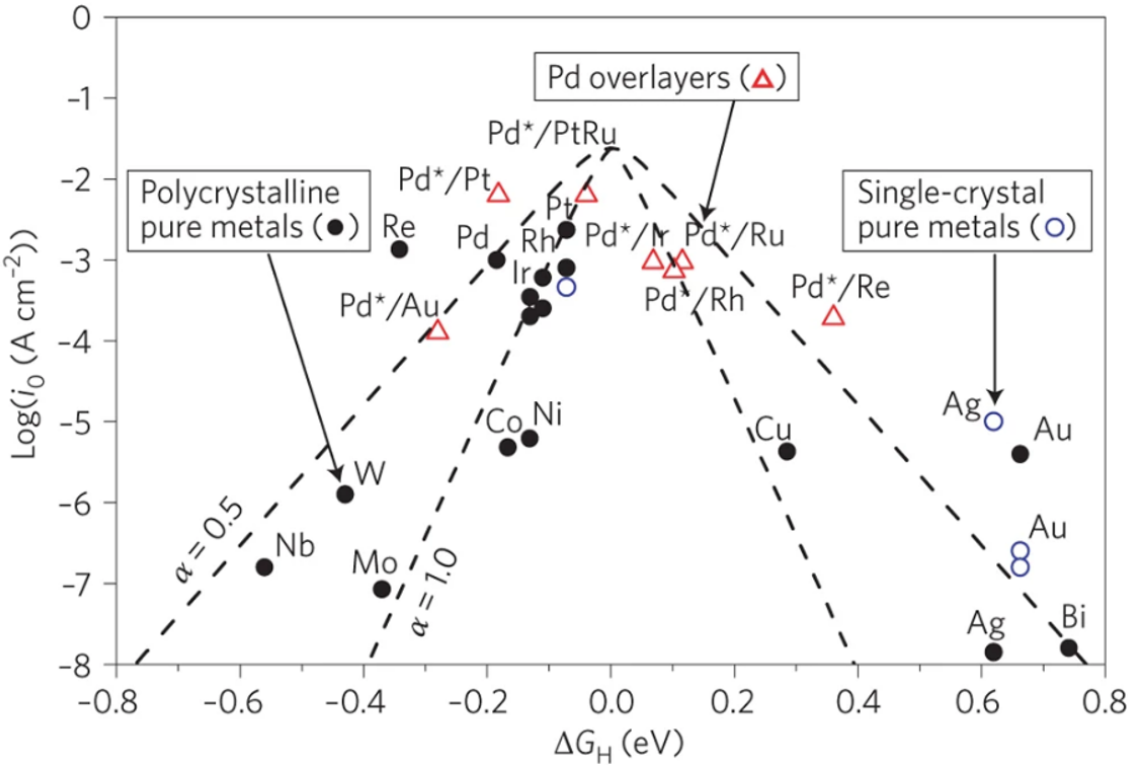
$$N_2 + 2* \rightarrow 2N^*$$
$$H_2 + 2* \rightarrow 2H^*$$
$$N^* + H^* \rightarrow NH^*$$
$$NH^* + H^* \rightarrow NH_2^* + *$$
$$NH_2^* + H^* \rightarrow NH_3^* + *$$
$$NH_3^* \rightarrow NH_3 + *$$

$$K_2 \cdot p_{H_2} \cdot \theta_*^2 = \theta_{H_2}$$
$$K_3\theta_N\theta_H = \theta_{NH}\theta_*$$
$$K_4\theta_{NH}\theta_H = \theta_{NH_2}\theta_*$$
$$K_5\theta_{NH_2}\theta_H = \theta_{NH_3}\theta_*$$
$$K_6\theta_{NH_3} = p_{NH_3}\theta_*$$

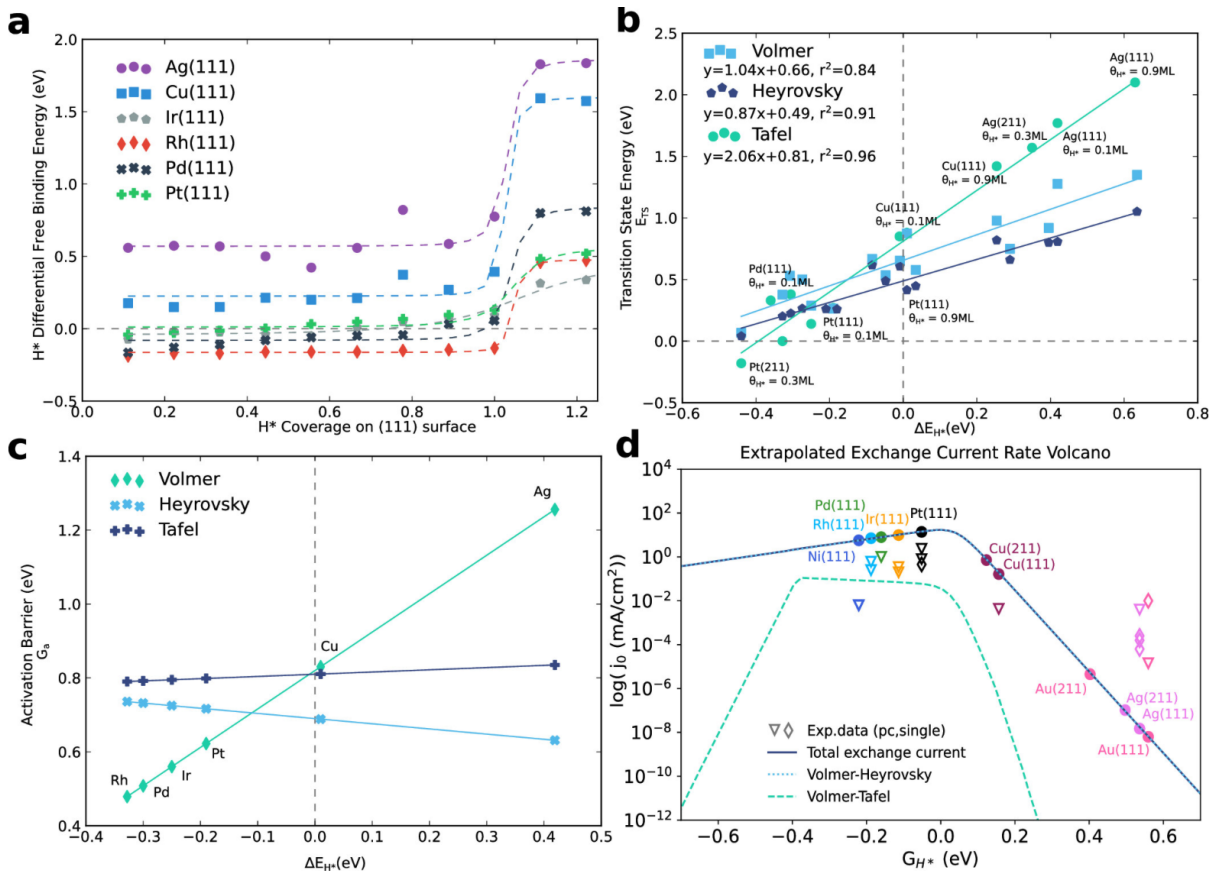
$$\theta_H = \sqrt{K_2 p_{H_2}}\theta_*$$
$$\theta_{NH_3} = \frac{p_{NH_3}}{K_6}\theta_*$$
$$\theta_{NH_2} = \frac{p_{NH_3}}{\sqrt{K_2 p_{H_2}}K_5K_6}\theta_*$$
$$\theta_{NH} = \frac{p_{NH_3}}{K_2 p_{H_2}K_4K_5K_6}\theta_*$$
$$\theta_N = \frac{p_{NH_3}}{K_2^{3/2}p_{H_2}^{3/2}K_3K_4K_5K_6}\theta_*$$

$$\theta_* = \frac{1}{1 + \sqrt{K_2 p_{H_2}} + \frac{p_{NH_3}}{\sqrt{K_2 p_{H_2}}K_5K_6} + \frac{p_{NH_3}}{K_2 p_{H_2}K_4K_5K_6} + \frac{p_{NH_3}}{K_2^{3/2}p_{H_2}^{3/2}K_3K_4K_5K_6} + \frac{p_{NH_3}}{K_6}}$$
$$R = R_1 = k_1 p_{N_2}\theta_*^2(1-\gamma)$$
$$\gamma = \frac{p_{NH_3}^2}{K_{\text{eq}}p_{H_2}^3 p_{N_2}}$$
$$K_{\text{eq}} = K_1K_2^3K_3^2K_4^2K_5^2K_6^2$$

20 years of computational studies of hydrogen evolution electrode

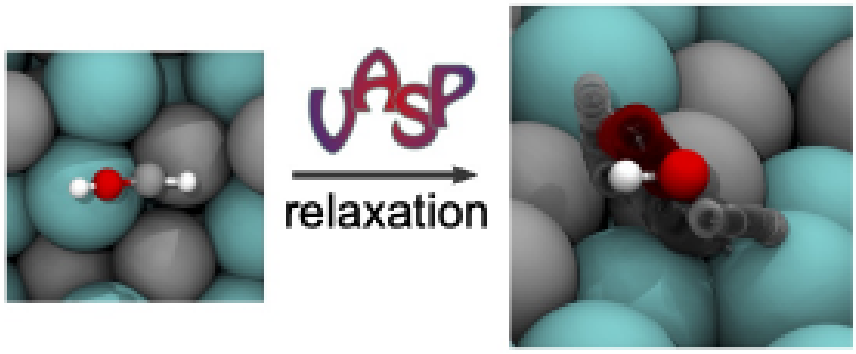


Nørskov *et al*. Nature Mater. **5**, 909–913 (2006)



Nørskov *et al*. J. Phys. Chem. C 2020, 124, 51, 28083–28092

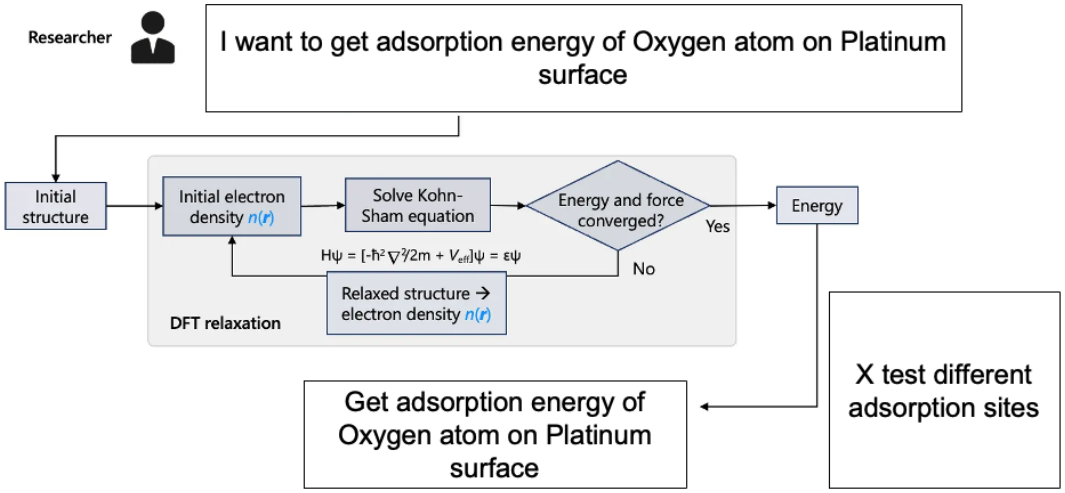
3.3 Computational time



Ulissi *et al.* ACS Catal., **11**, 10, 6059 (2021).

The DFT computation scales O(n3) with the number of electrons in the system. The DFT computations of 100 atoms approximately take ~1 hour per relaxation on

12 core CPUs. few hours~ day for get energy of one DFT structure

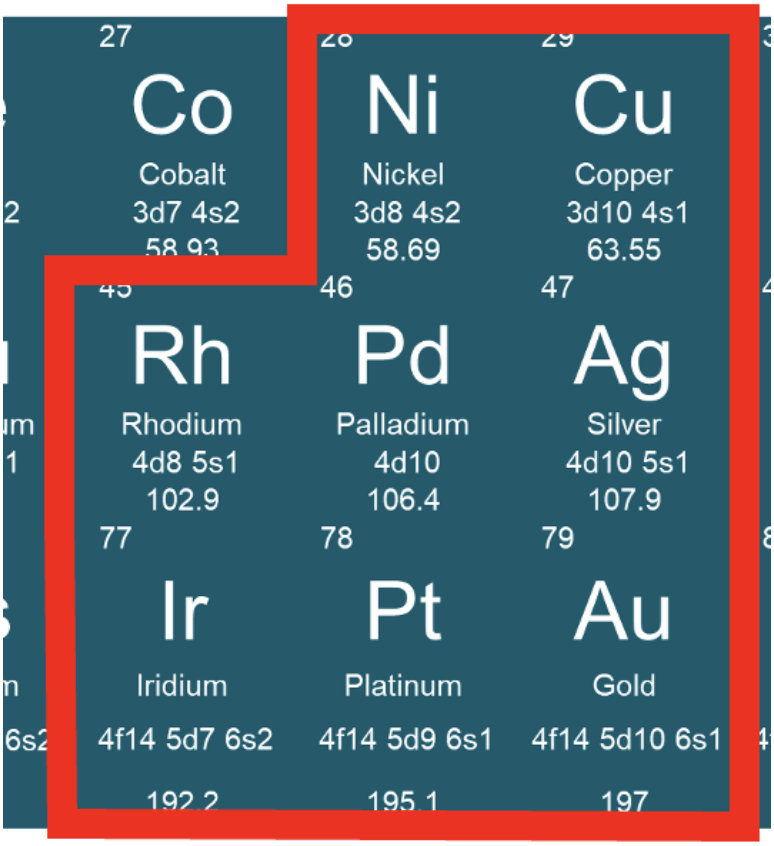


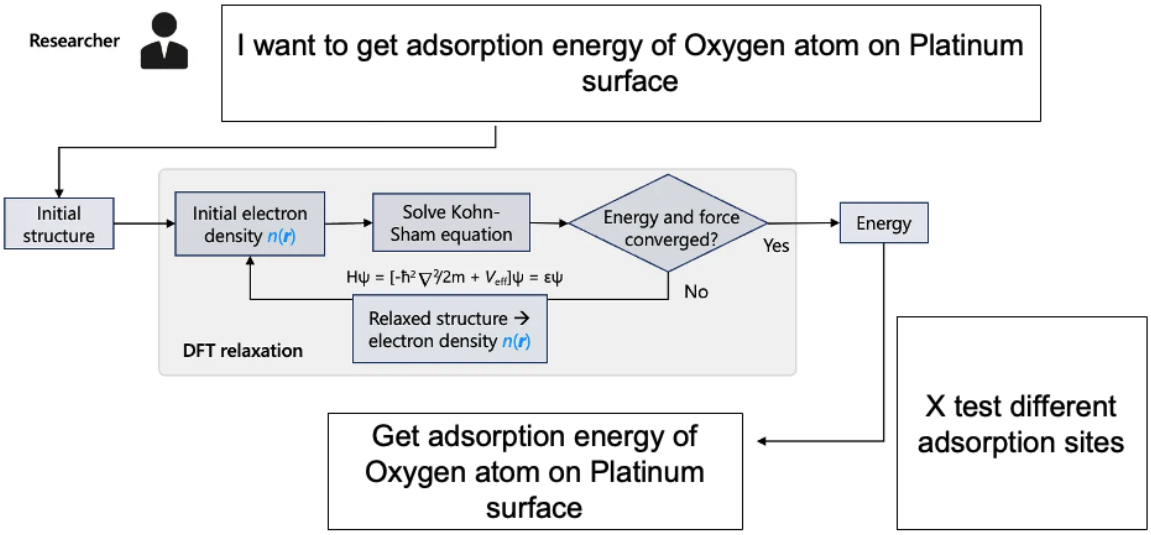
Assignment

Please **select one metal element (from the red box)** and complete the following tasks:

1. **Run a catalyst surface simulation** for the chosen metal. Calculate the adsorption energy of CO molecule and O atom. for oxygen atom, use half of O2(gas) energy for reference when calculating adsorption energy(as in tutorial notebook).
2. Compare the adsorption energies of CO on four sites of (111) facets
3. **Compare the adsorption energies** for two coverage (1ML and 1/4ML)

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)**


27
Co
Cobalt
3d7 4s2
58.93
28
Ni
Nickel
3d8 4s2
58.69
29
Cu
Copper
3d10 4s1
63.55
45
46
Rh
Rhodium
4d8 5s1
102.9
Pd
Palladium
4d10
106.4
47
Ag
Silver
4d10 5s1
107.9
77
Ir
Iridium
4f14 5d7 6s2
192.2
78
Pt
Platinum
4f14 5d9 6s1
195.1
79
Au
Gold
4f14 5d10 6s1
197


Researcher
I want to get adsorption energy of Oxygen atom on Platinum surface
Initial structure
Initial electron density n(r)
Solve Kohn-Sham equation
Energy and force converged?
Yes
No
Energy
Hψ = [-ħ²∇²/2m + V_eff]ψ = εψ
Relaxed structure → electron density n(r)
DFT relaxation
X test different adsorption sites
Get adsorption energy of Oxygen atom on Platinum surface