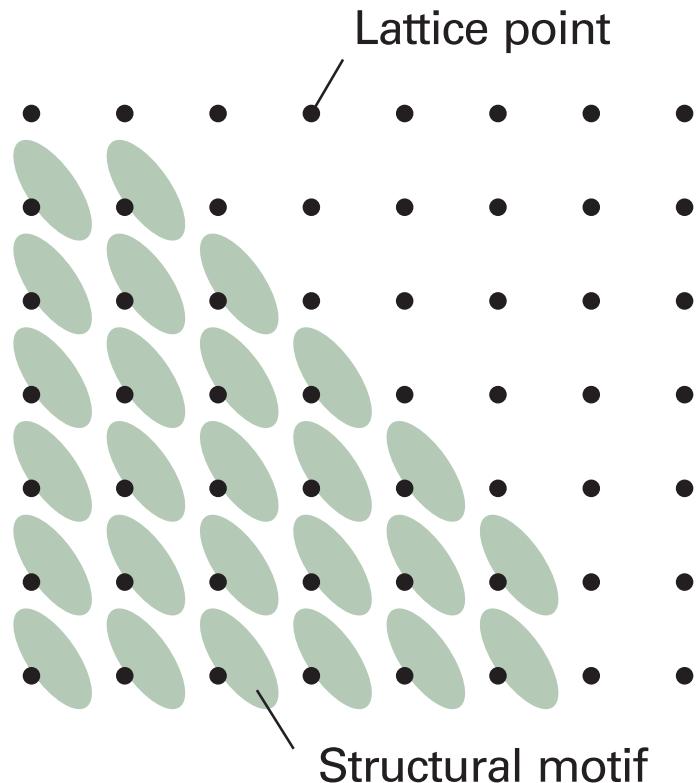


Surface structures and the *d*-band model of adsorbate binding

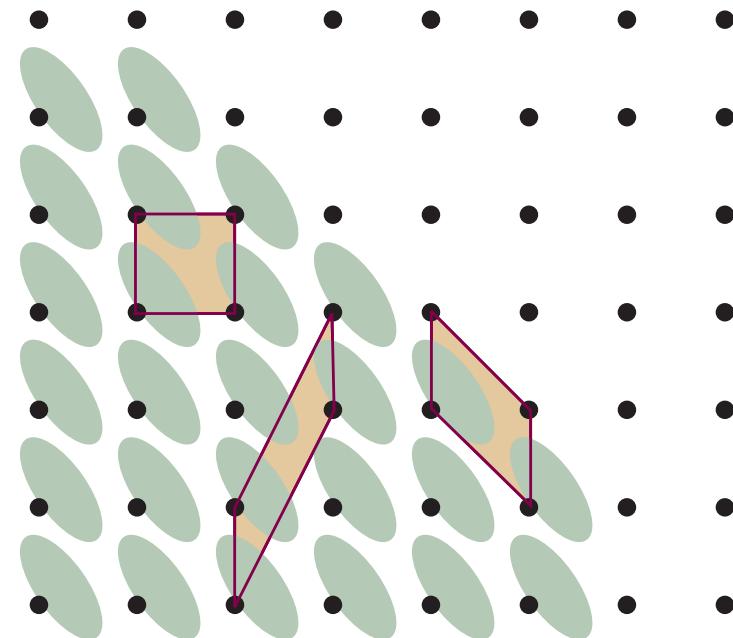
Crystal lattices

Crystals are composed of repeating structural motifs

Lattice: formed by points representing locations of repeating motifs



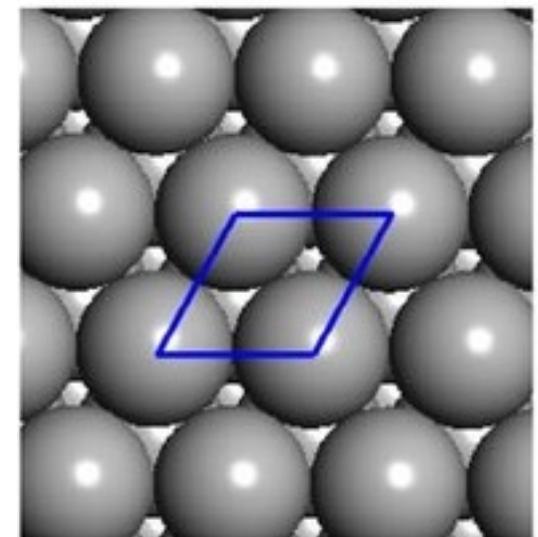
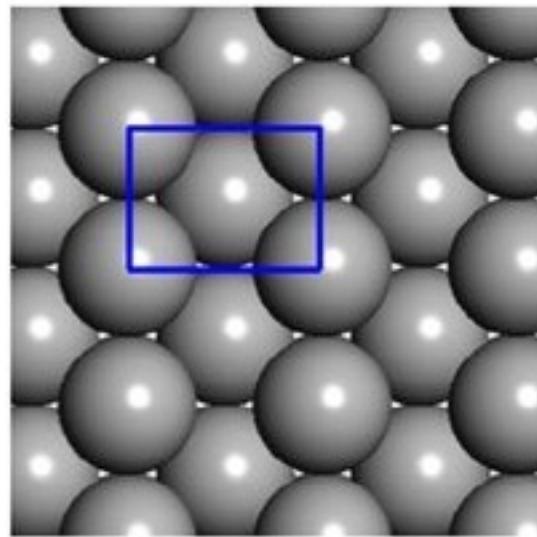
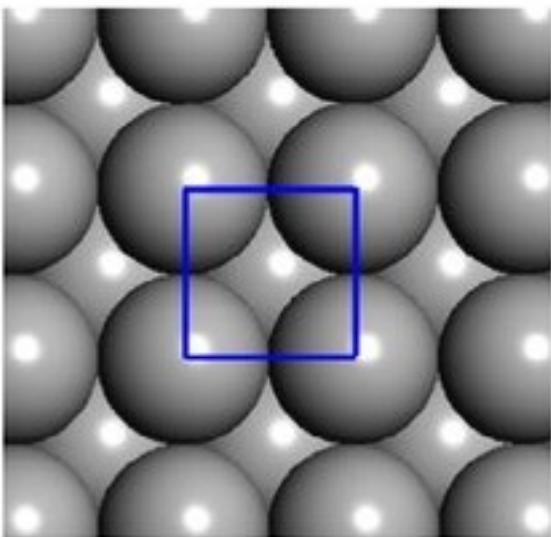
Unit cell: a parallel-sided unit from which the entire crystal structure can be constructed using *translations*



Unit cells are not unique

Solid Surfaces

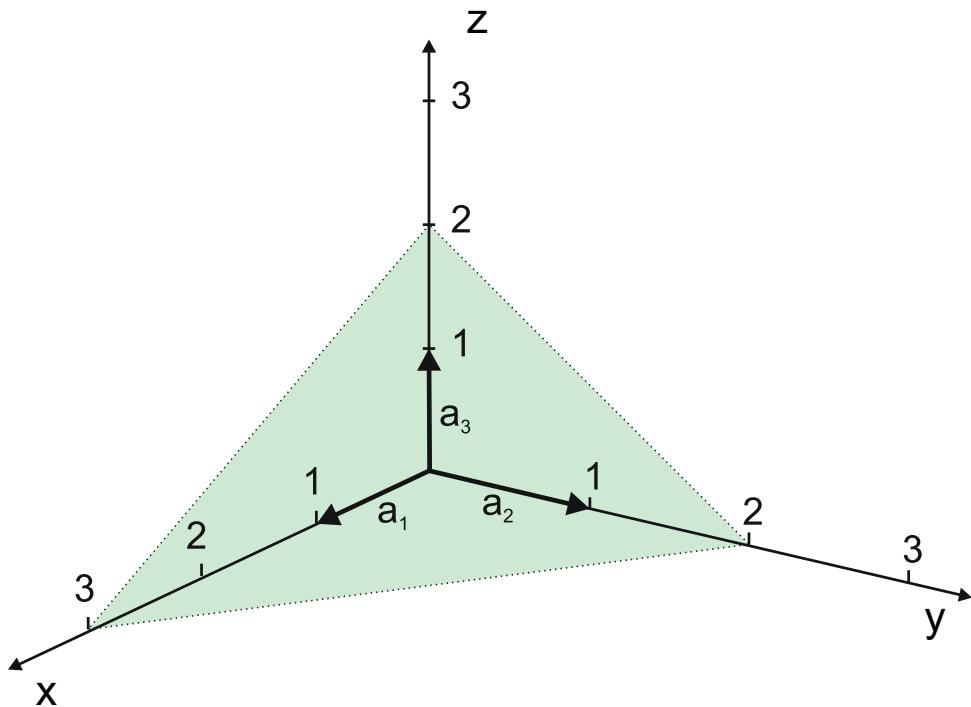
- Cuts in different directions of crystals give surfaces with different structures
- Cuts in a FCC structure:



How to classify/identify the various possible surfaces?

Miller indices

The **Miller index** of a plane (hkl), identifies the plane with axis intercepts of $1/h$, $1/k$, $1/l$. where h , k , and l are the smallest possible integers.



The plane intersects at
 $x = 3$, $y = 2$, $z = 2$

Inverse:
 $1/3, 1/2, 1/2$

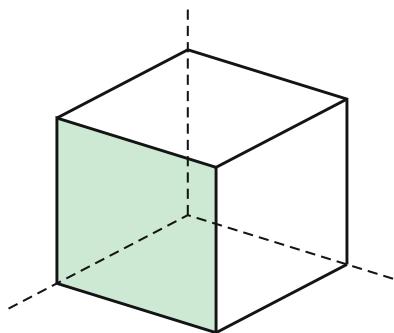
Smallest integers (multiply each
Inverse intercept by 6):
 $h = 2, k = 3, l = 3$

(233) surface

Miller indices

The **Miller index** of a plane (hkl), identifies the plane with axis intercepts of $1/h$, $1/k$, $1/l$. where h , k , and l are the smallest possible integers.

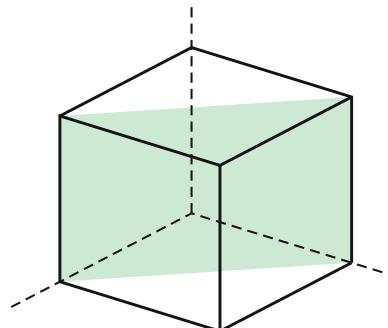
Consider a cubic lattice



The plane intersects at
 $x = 1, y = \infty, z = \infty$

Inverse:
1,0,0

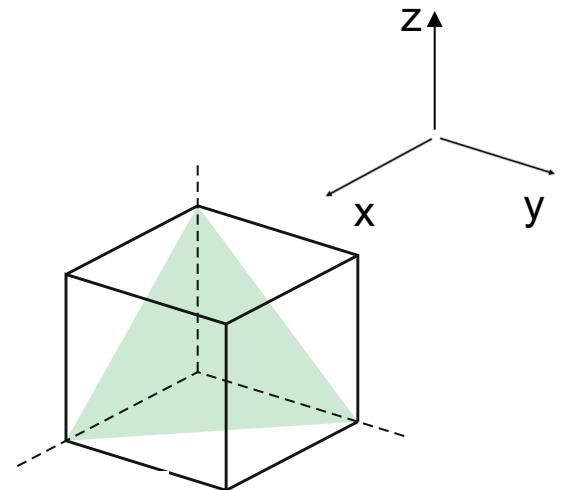
Smallest integers:
 $h = 1, k = 0, l = 0 \rightarrow (100)$



The plane intersects at
 $x = 1, y = 1, z = \infty$

Inverse:
1,1,0

Smallest integers:
 $h = 1, k = 1, l = 0 \rightarrow (110)$

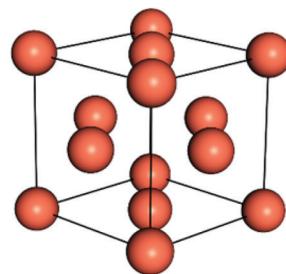
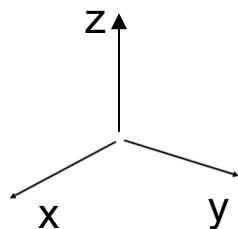


The plane intersects at
 $x = 1, y = 1, z = 1$

Inverse:
1,1,1

Smallest integers:
 $h = 1, k = 1, l = 1 \rightarrow (111)$

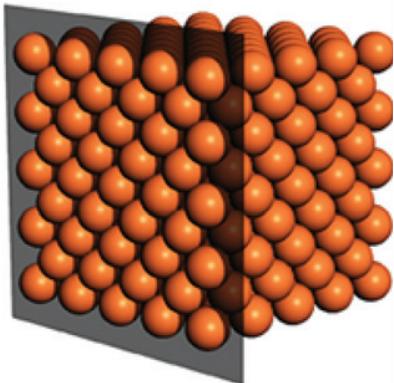
Surfaces in a FCC structure



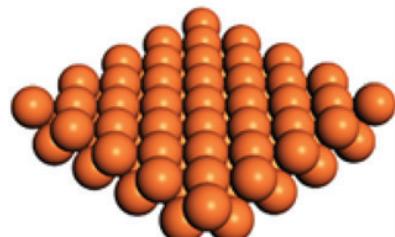
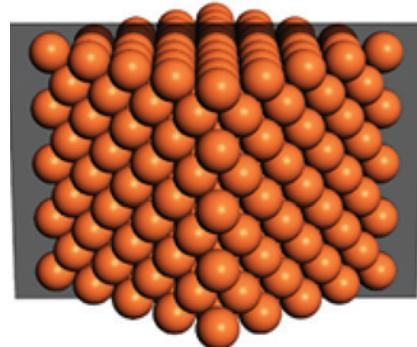
unit cell

studied in your
exercises

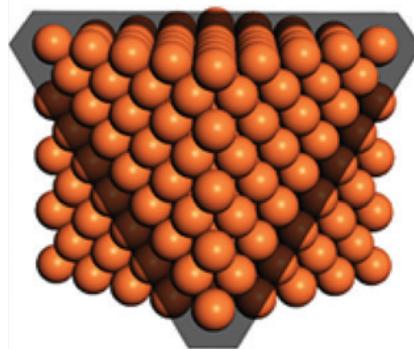
100



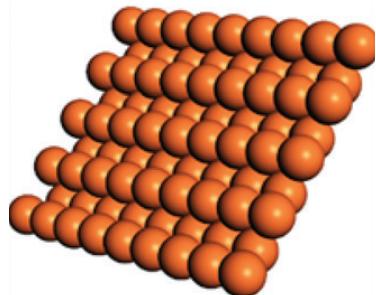
110



111



cubic



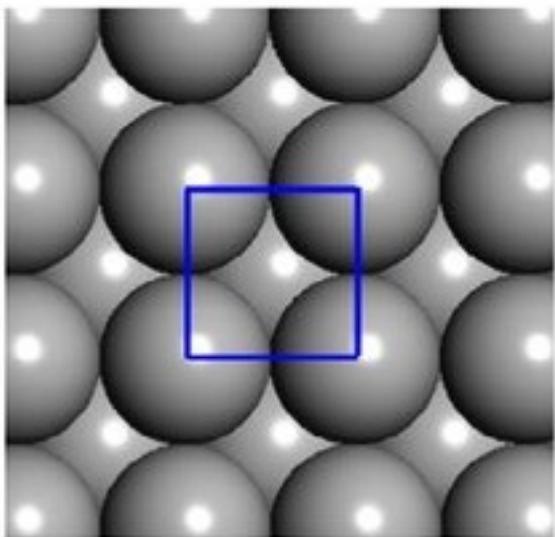
stepped

close-
packed

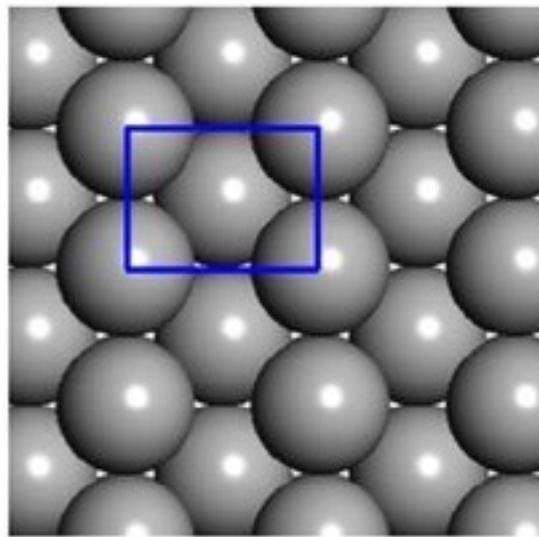
Surfaces in a FCC structure

- Top views with unit cells for the surfaces

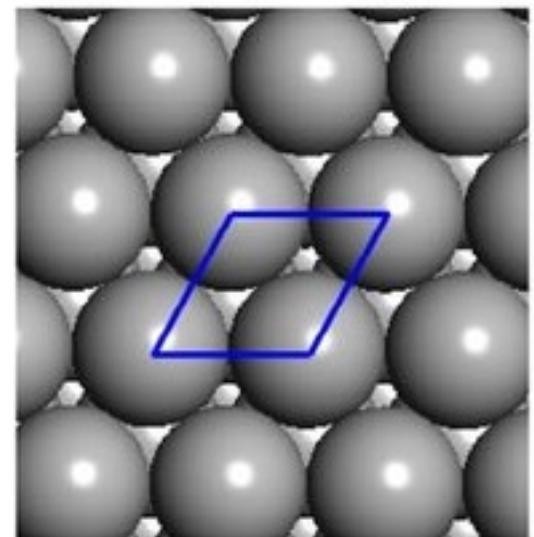
(100)



(110)

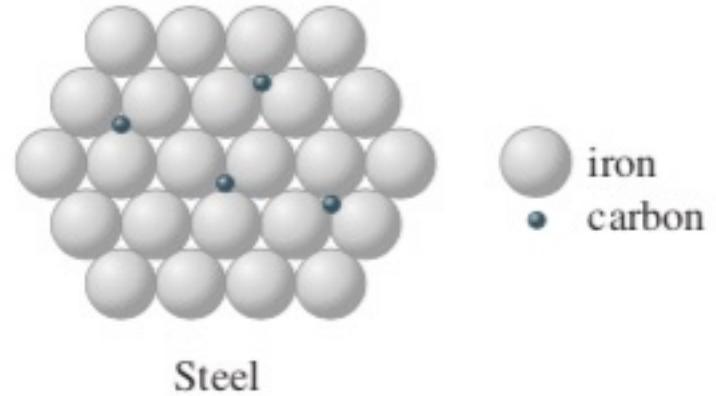
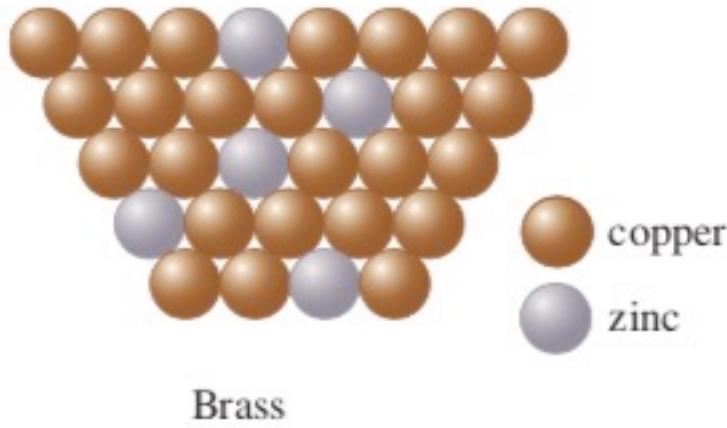


(111)



Metal alloys

Metal alloys: mixtures of elements



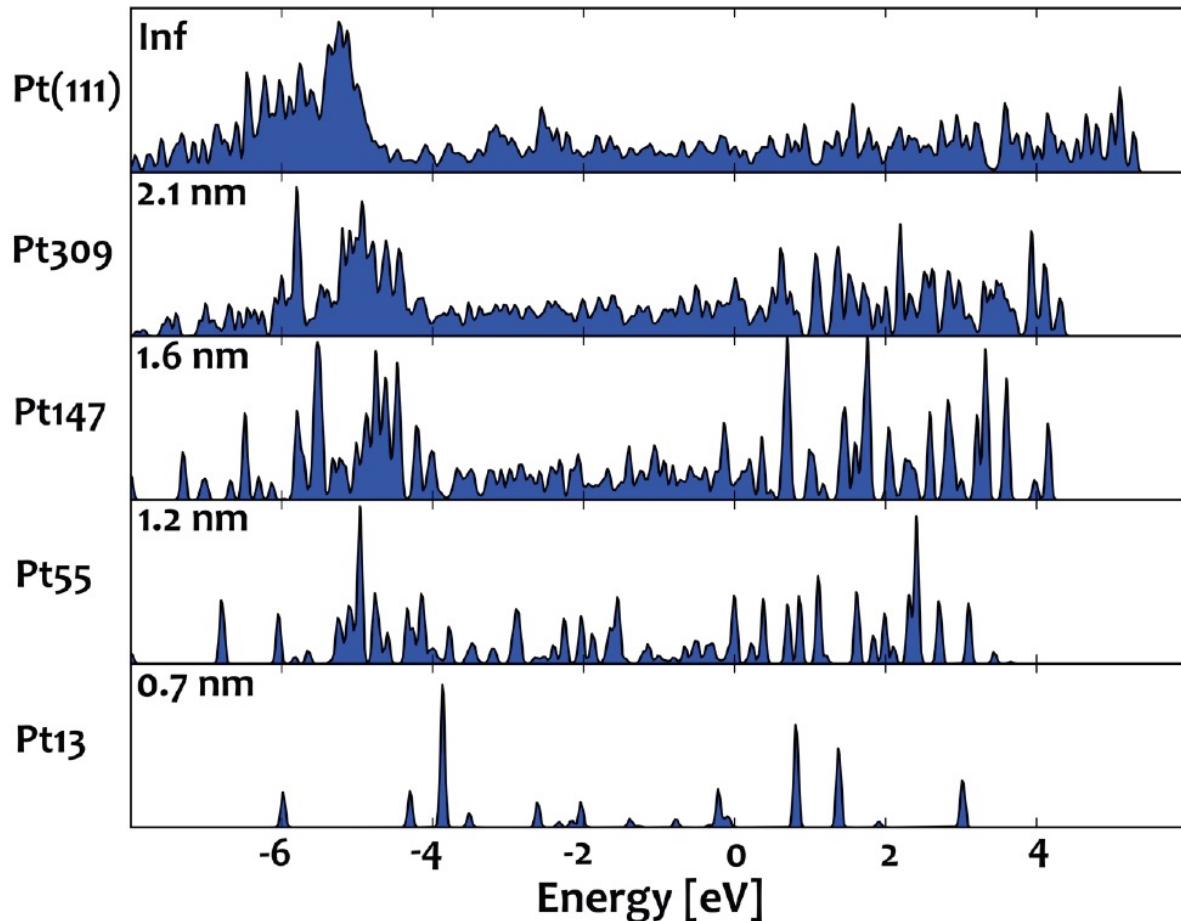
Substitutional alloy: host metal (e.g. Cu) atom replaced by atoms of similar size (Zn)

Interstitial alloy: interstices (holes) of metal occupied by small atoms

Introduction of other atoms changes properties – including *binding properties (and corresponding catalytic activity)*- of the host metal!

From clusters to extended surface

density of s-states on Pt:



Continuous, broad
"band" of states seen
around ~100 atoms

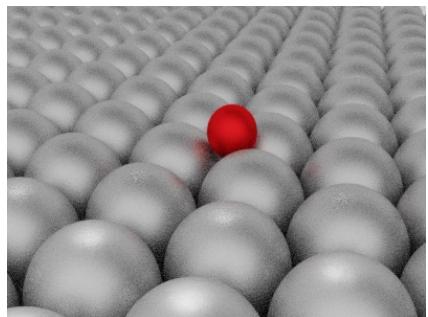
discrete states (like
molecules)

Adsorption energies

Adsorption and activation energies determine catalytic activity

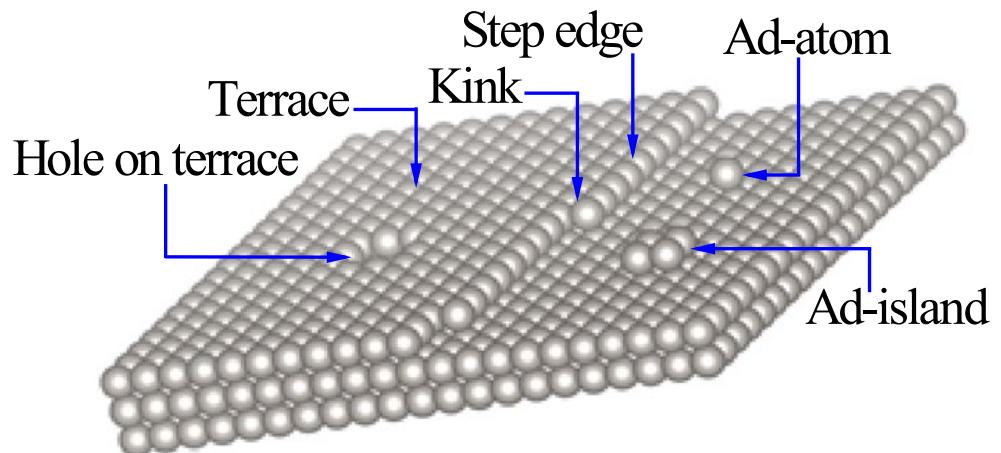
For adsorption of species A on a surface site *: $A + * \rightarrow A^*$, the adsorption energy is: $\Delta G_A = G(A^*) - G(*) - G(A)$

The more negative the ΔG_A , the stronger the binding



O* on Pt(111)

(explore trends in O* and OH* across metals in exercise)



- A heterogeneous, rough surface has a variety of sites
- Different sites bind differently to adsorbates and have different activities

Adsorption energies: examples

CO* adsorption:

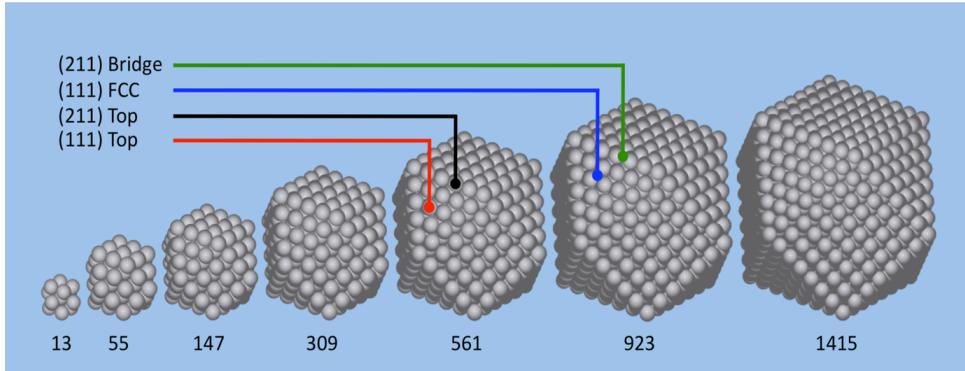
- $\Delta G_{\text{CO}^*} = G(\text{CO}^*) - G(^*) - G(\text{CO}_{(g)})$

O* adsorption:

- $\Delta G_{\text{O}^*} = G(\text{O}^*) - G(^*) - \frac{1}{2}G(\text{O}_2)_{(g)}$
- $\Delta G_{\text{O}^*} = G(\text{O}^*) - G(^*) - [G(\text{H}_2\text{O}_{(l)}) - G(\text{H}_2)_{(g)}]$

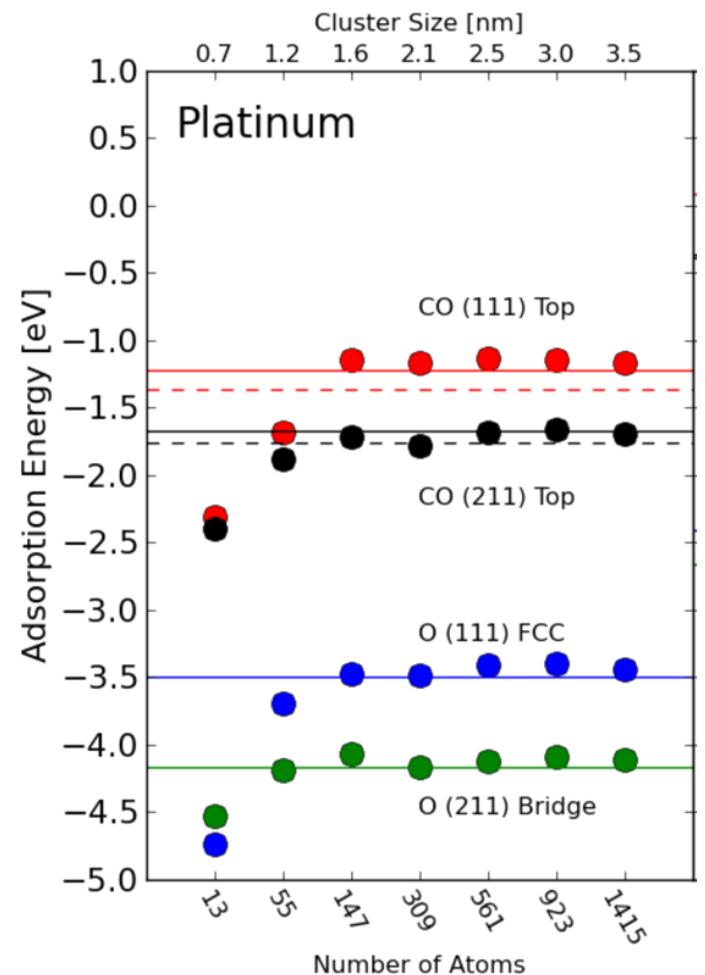
(can convert between 2 definitions of ΔG_{O^*} with known differences in G of reference molecules)

From clusters to extended surfaces

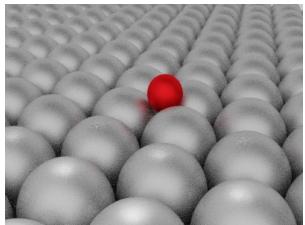


ΔG_{CO^*} and ΔG_{O^*} on various sites approach those of the corresponding extended "infinite" surface site around 100 atoms

→ periodic, infinitely extended surfaces are usually adequate models of nanoparticle facets

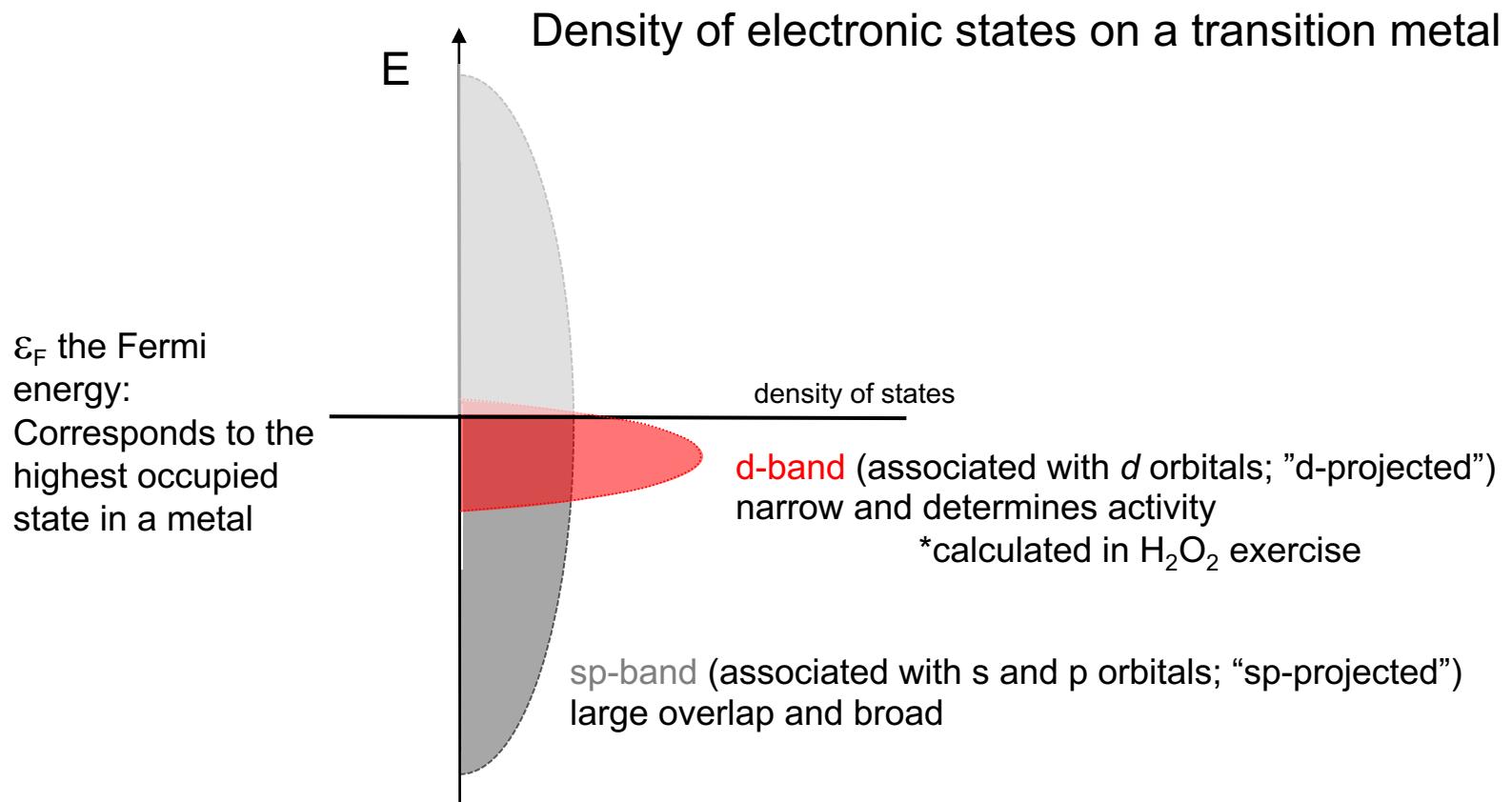


Electronic structure of transition metals



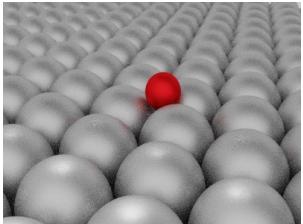
O* on Pt(111)

What determines the adsorption energy?



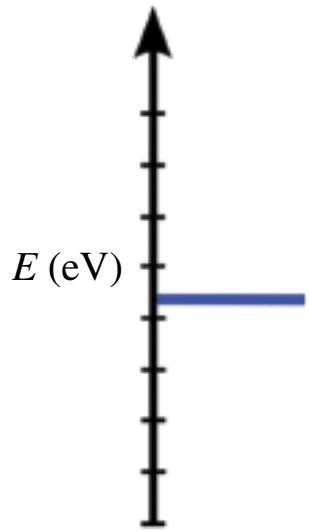
The position of the *d*-band ('center') relative to ϵ_F determines the adsorption strength

d-band model of adsorbate binding



O* on Pt(111)
What determines the adsorption energy?

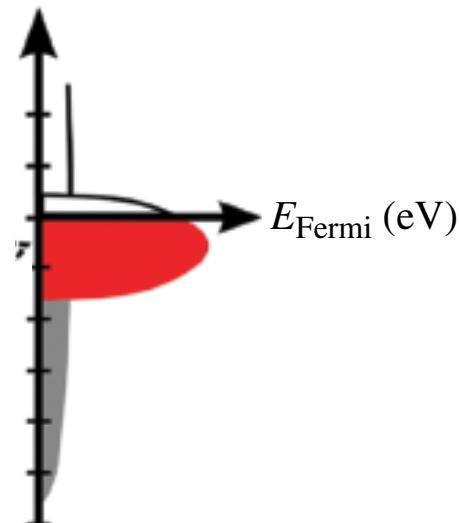
Atomic
energy state



e.g. a *p*-orbital on O

Interaction with broad
sp-band broadens the
adsorbate state

Transition metal
electronic states



Interaction with narrow d-band splits
adsorbate state into bonding and
antibonding states

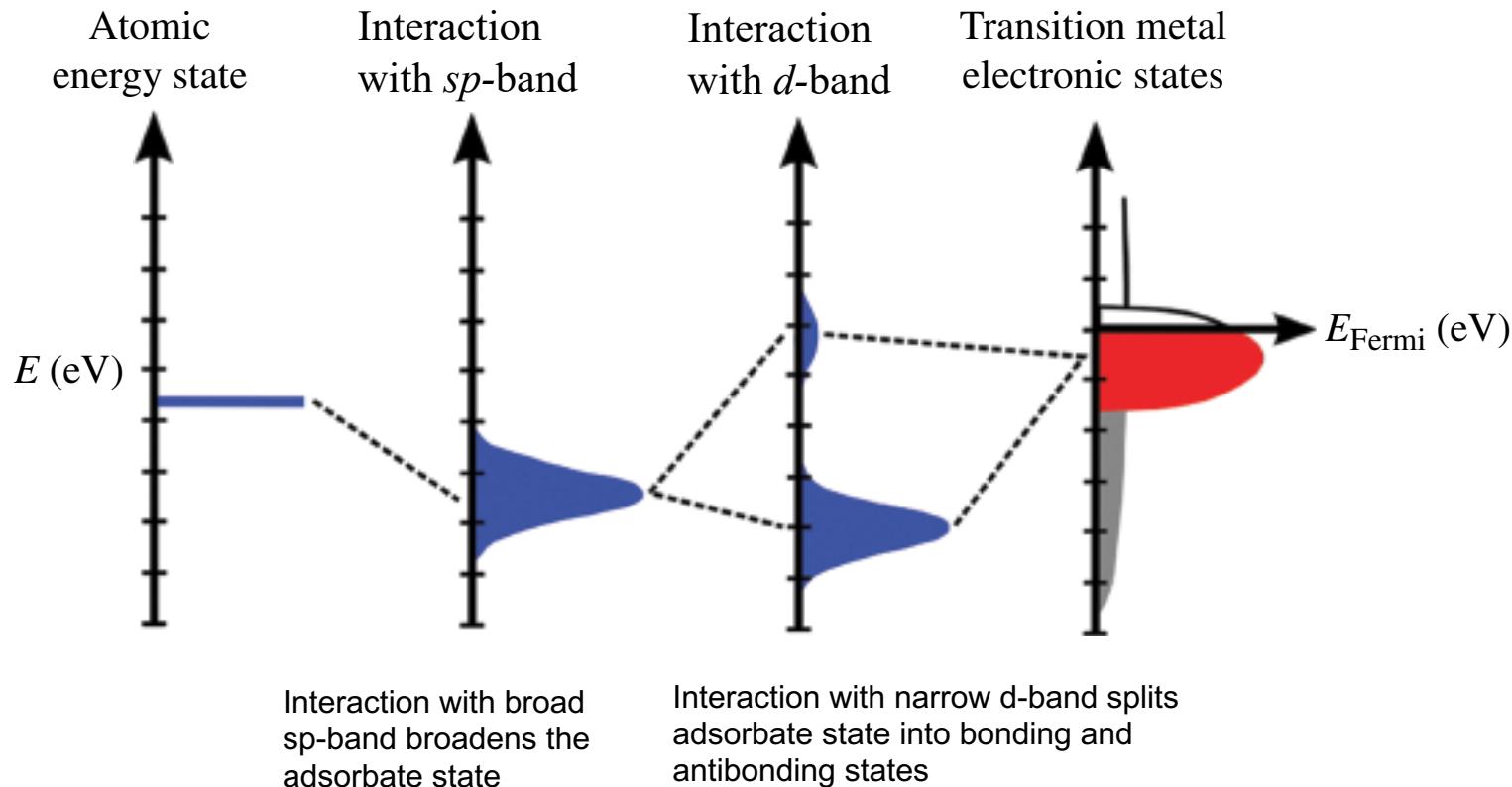
d-band model of adsorbate binding

Adsorption energy has 2 contributions:

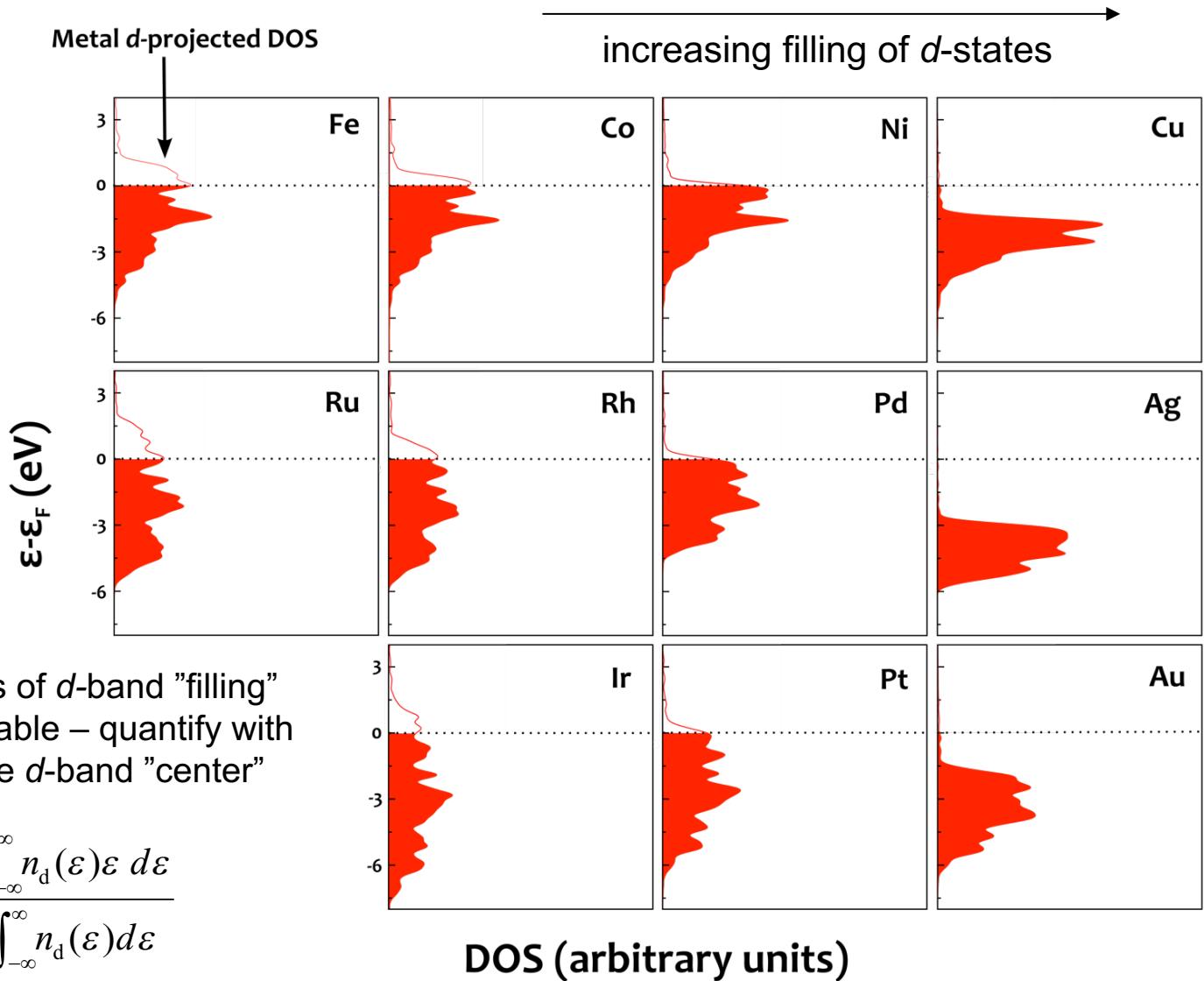
$$\Delta E = \Delta E_{\text{sp}} + \Delta E_{\text{d}}$$

large and independent of metal

varies amongst metals and determines trends in binding strength across them

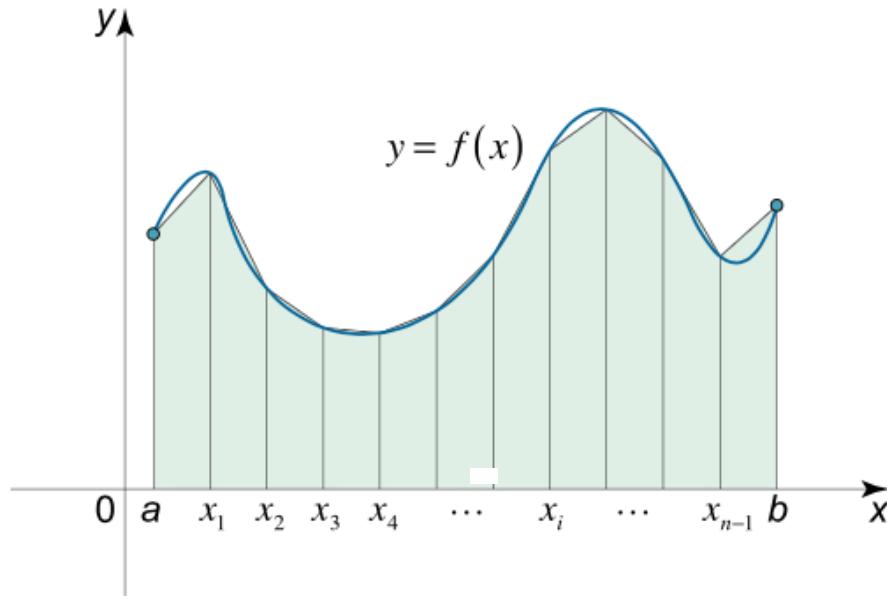


d-band model of adsorbate binding



Exercise: determine(d) the d-band centers of metals relative to the ϵ_F

Side note: recall numerical integration from calculus



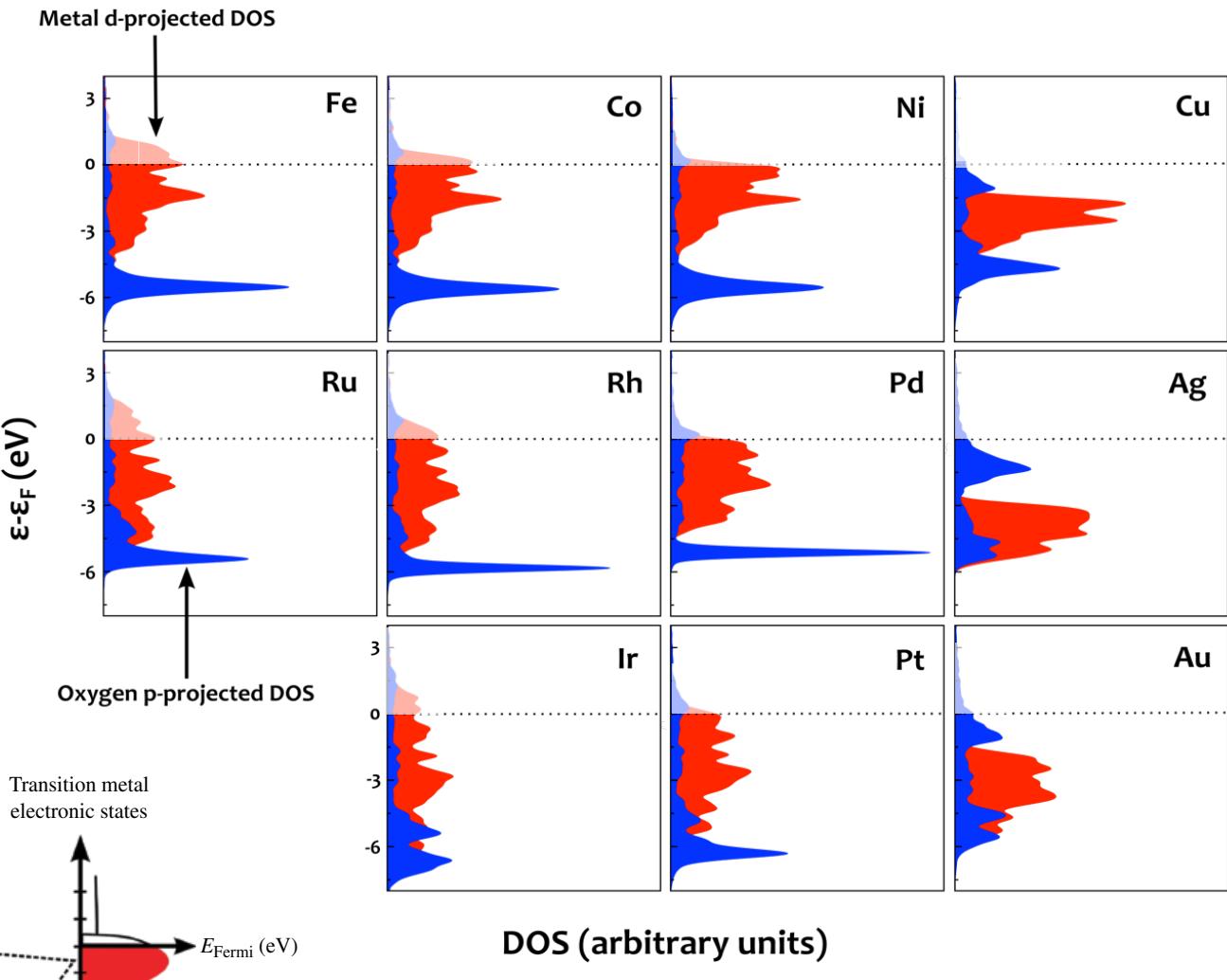
The Trapezoidal Rule for approximating $\int_a^b f(x) dx$ is given by

$$\int_a^b f(x) dx \approx T_n = \frac{\Delta x}{2} [f(x_0) + 2f(x_1) + 2f(x_2) + \cdots + 2f(x_{n-1}) + f(x_n)],$$

where $\Delta x = \frac{b-a}{n}$ and $x_i = a + i\Delta x$.

d -band model of adsorbate binding

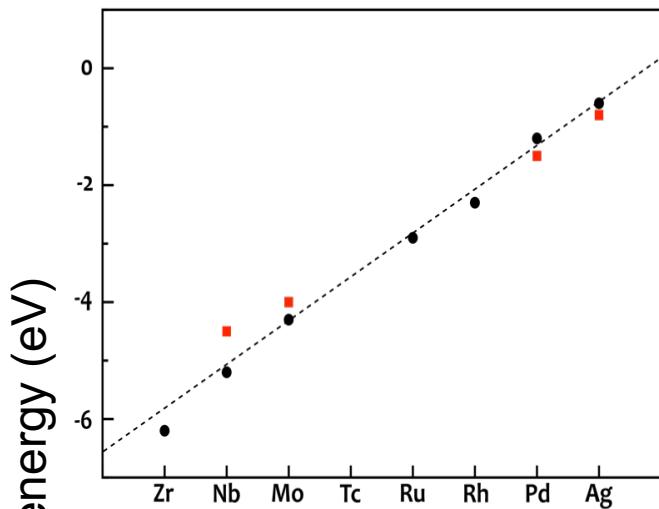
ε_d relative to ε_F
determines the degree of
filling of the *antibonding*
(AB) adsorbate states



Across periodic table: lower ε_d relative to ε_F ,
more AB states filled, weaker binding

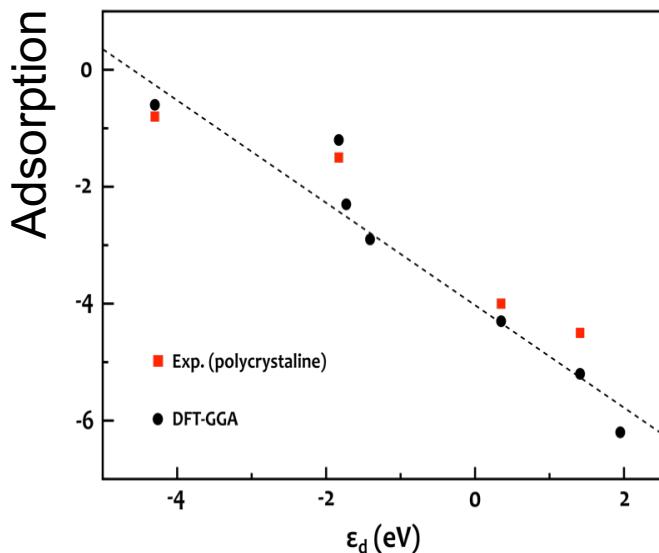
Trends in 4d series

Trends in 4d metals



The more *negative* the adsorption energy, the *stronger* the binding

Weakening binding as we go across periodic table (and ϵ_d decreases/ filling of anti-bonding states increases)

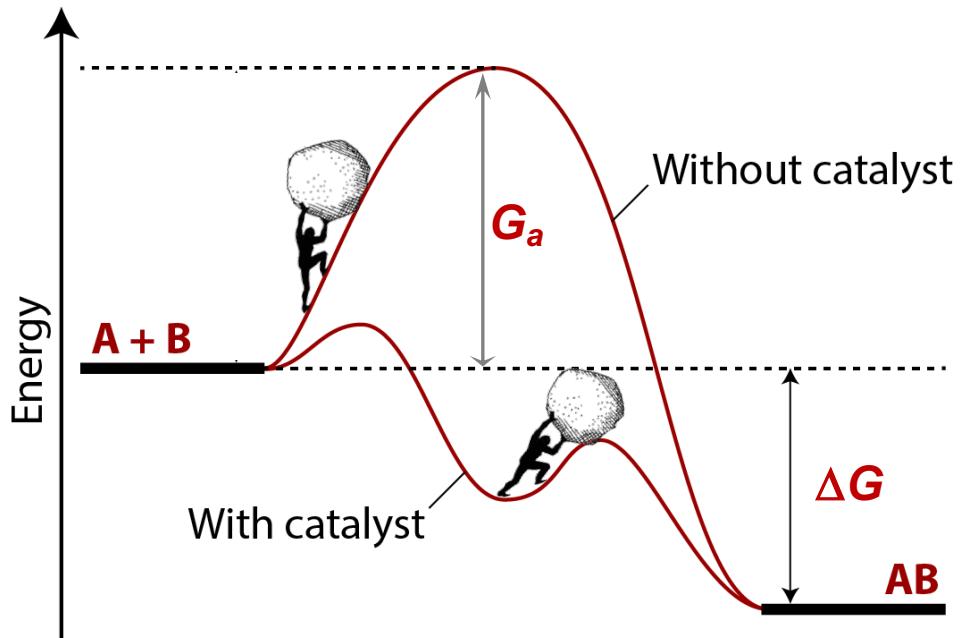


Binding strength increases (more negative adsorption energy) with increasing ϵ_d and less filling of antibonding states.

Exercise: examine trends in $\Delta G(\text{OH})$ vs ϵ_d

Chemical equilibria and kinetics

What is a catalyst?



Arrhenius law:

$$k = Ae^{-\frac{G_a}{k_b T}}$$

Kinetics determine reaction rates!

How do we relate the ΔG , G_a and corresponding K and k 's to an overall reaction rate?

Equilibrium constants

For a generic reaction with aqueous and gas reactants and products, e.g. $aA_{(aq)} + bB_{(g)} \rightleftharpoons cC_{(aq)} + dD_{(g)}$, what is the equilibrium constant K ?

- The equilibrium constant is related to the free energy of the reaction at standard conditions ΔG° and is given by:

$$K = \frac{[C]^c p_D^d}{[A]^a p_B^b} = \exp\left(-\frac{\Delta G^\circ}{k_B T}\right)$$

- Liquid and solid phases have fixed densities and activities of 1, and therefore do not need to be included explicitly in K .

Reaction kinetics

Consider the forward rates of elementary steps*:

*steps that don't have intermediate steps in their mechanism

Elementary Step	Rate Law
$A \rightarrow \text{products}$	
$A + A \rightarrow \text{products}$	
$(2A \rightarrow \text{products})$	
$A + B \rightarrow \text{products}$	

Reaction kinetics

Consider the forward rates of elementary steps*:

*steps that don't have intermediate steps in their mechanism

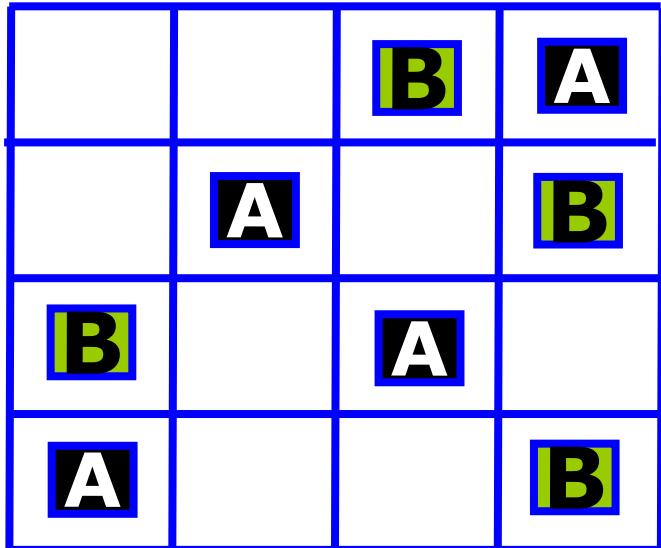
Elementary Step	Rate Law
$A \rightarrow \text{products}$	$\text{Rate} = k[A]$
$A + A \rightarrow \text{products}$ $(2A \rightarrow \text{products})$	$\text{Rate} = k[A]^2$
$A + B \rightarrow \text{products}$	$\text{Rate} = k[A][B]$

gas phase: write in terms of pressures

The activities of liquids and solids are again constant and = 1

What is new in surface reactions: coverage

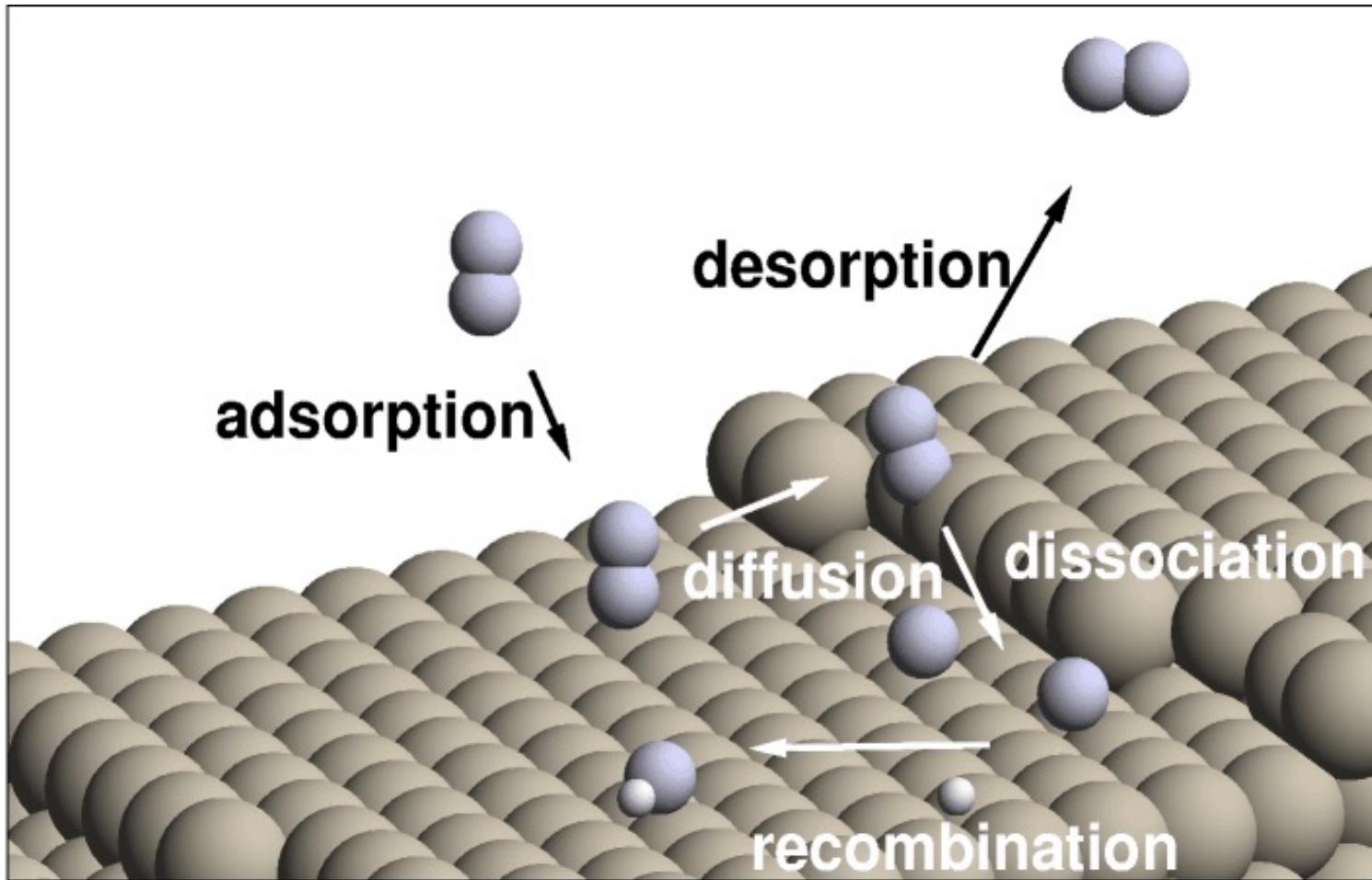
The “concentration” of an adsorbate A on a surface is given by its coverage: $\theta_A = \frac{\text{# species A on surface}}{\text{total number of surface sites}}$



What is the θ_A , θ_B , and θ_* ?
(* denotes an empty site)

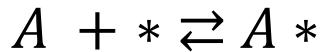
Use θ as a “concentration” of **adsorbates and empty sites** in the rates of elementary steps and equilibrium constants in your kinetic models. (Note: θ 's sum to 1)

Elementary surface reaction steps



Rates of elementary surface processes

Adsorption/desorption kinetics



What are the forward and backward rates?

$$r_{adsorption} = k_+ p_A \cdot \theta_*$$

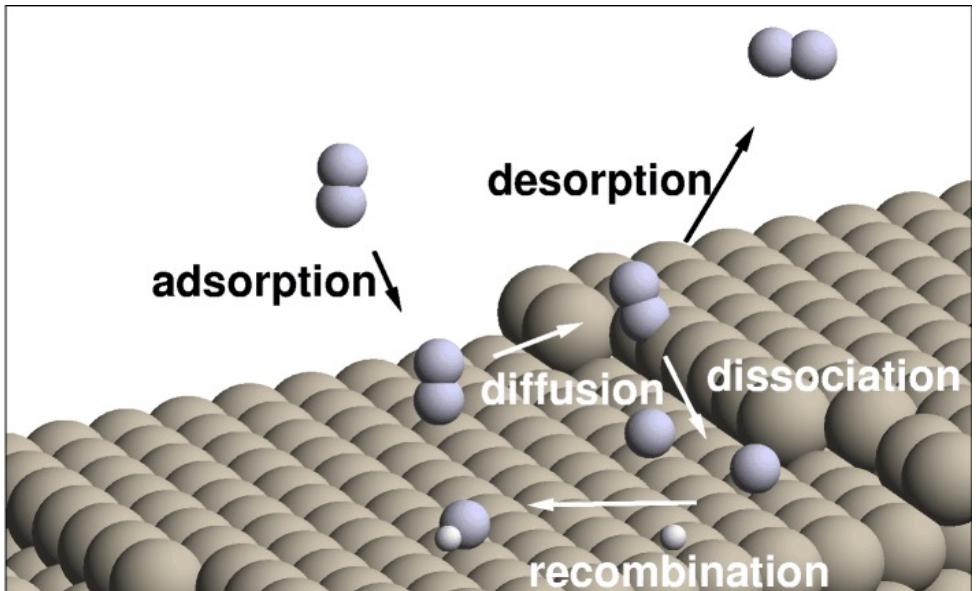
$$r_{desorption} = k_- \cdot \theta_A$$

At equilibrium:

$$r_{adsorption} = r_{desorption}$$

$$k_+ p_A \cdot \theta_* = k_- \theta_A$$

$$K_{ads} = \frac{\theta_A}{p_A \cdot \theta_*} = \frac{k_+}{k_-} = \exp \left[-\frac{\Delta G_{ads}^o}{kT} \right]$$



Rates of elementary surface processes



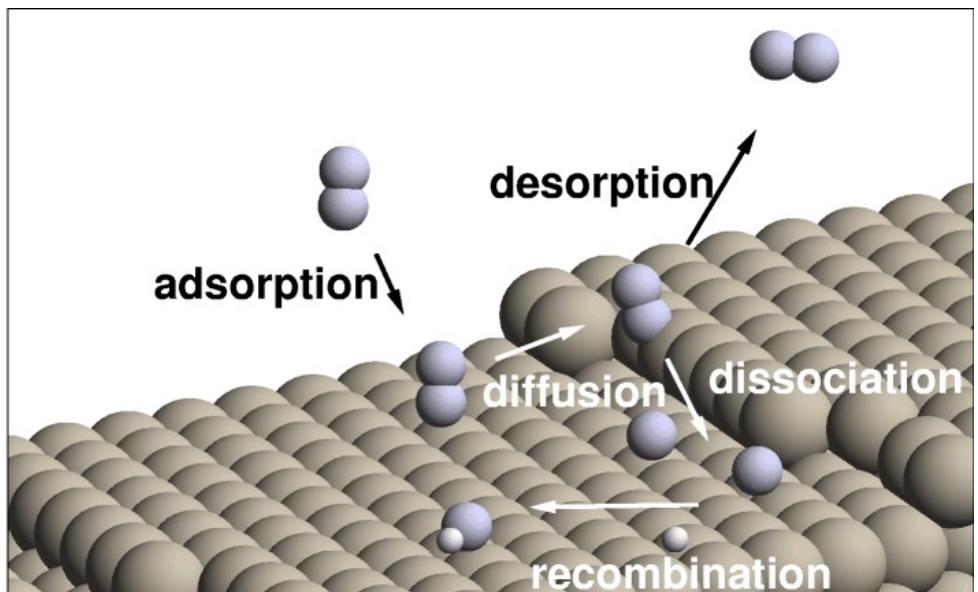
Dissociative adsorption:

$$r_{diss} = k_{diss} \cdot p_{A_2} \cdot \theta_*^2$$

This class: you examine the barriers for H_2O_2 dissociation

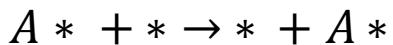
Associative desorption

$$r_{ass} = k_{ass} \cdot \theta_A^2$$



Rates of elementary surface processes

Diffusion (usually fast and negligible):



$$r_{dif} = k_{dif} \cdot \theta_A \cdot \theta_*$$

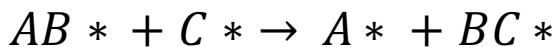
Coupling/scission reactions:



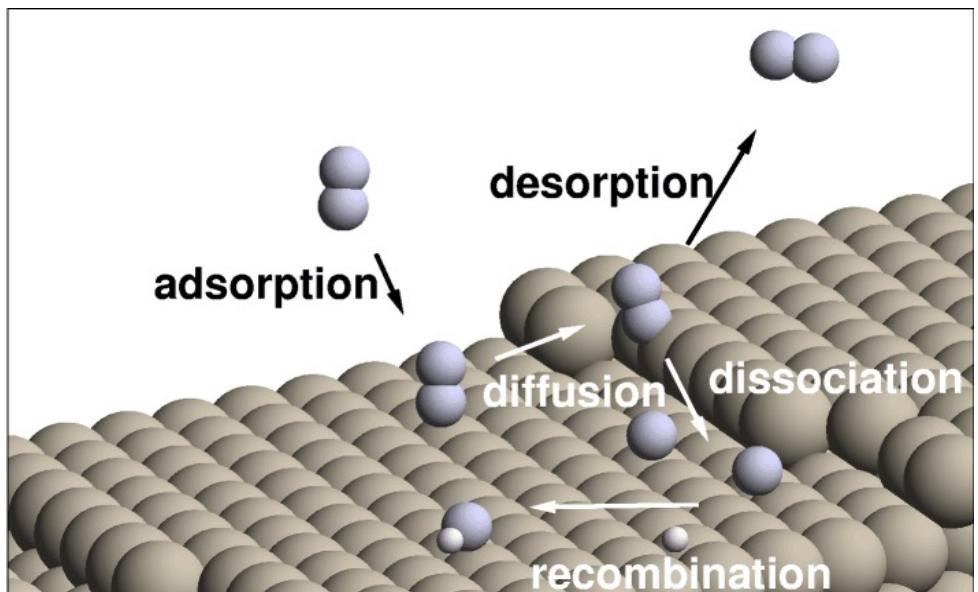
$$r_{coupling} = k_{coupling} \cdot \theta_A \cdot \theta_B$$

$$r_{scission} = k_{scission} \cdot \theta_{AB} \cdot \theta_*$$

Disproportionation reaction:



$$r_{disprop} = k_{disprop} \cdot \theta_{AB} \cdot \theta_C$$



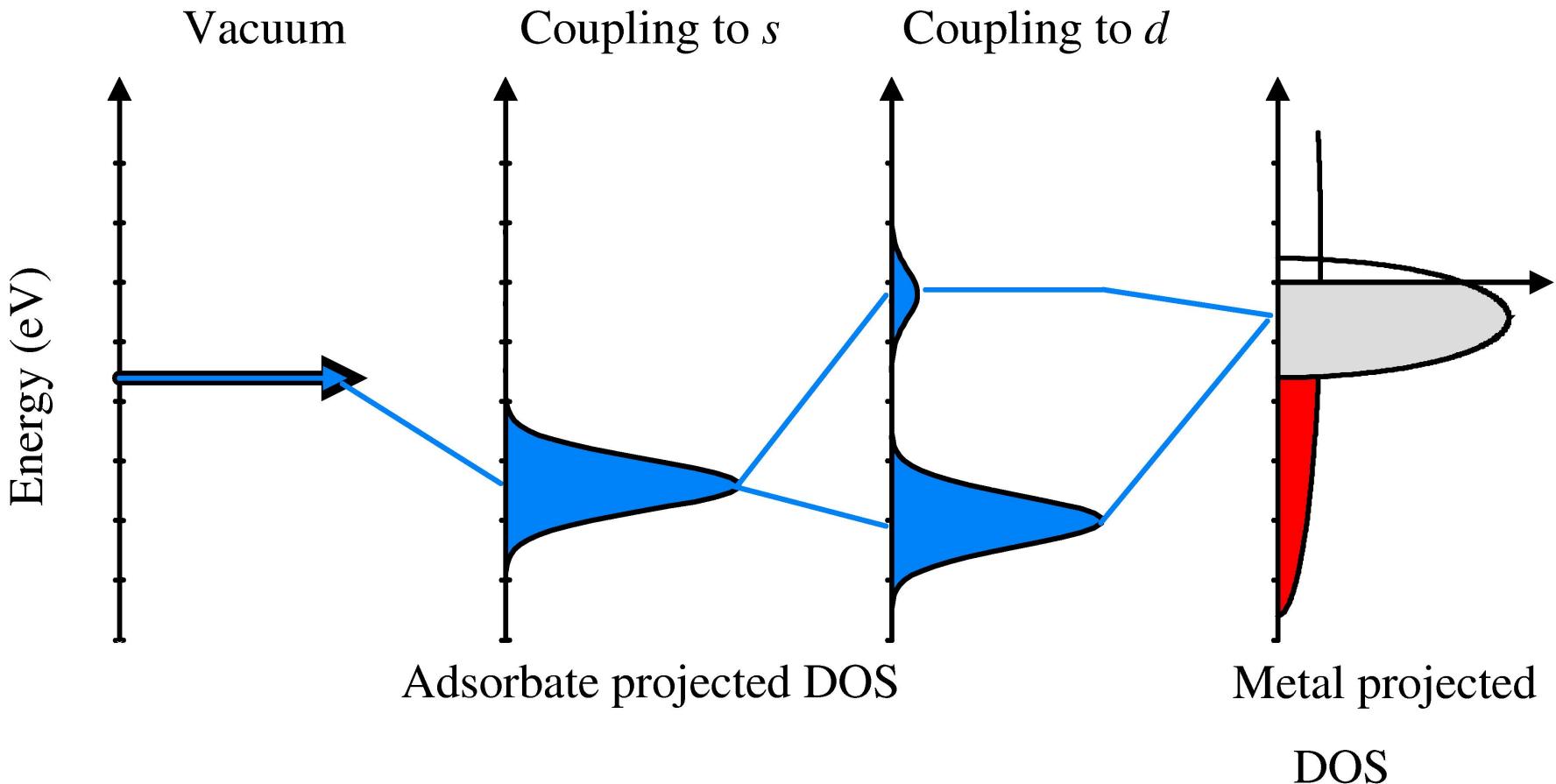
Descriptor-based catalyst design



Scaling relations, activity descriptors,
and activity volcanoes

The origin of catalytic trends

→ the *d*-band model



Hammer, Nørskov, *Nature* **376**, 238 (1995)

Hammer, Nørskov, *Adv. Catal.* **45**, 71 (2000)

Bligaard, Nørskov in *Chemical bonding at surfaces*, Elsevier (2008)

Corollary to the *d*-band model:

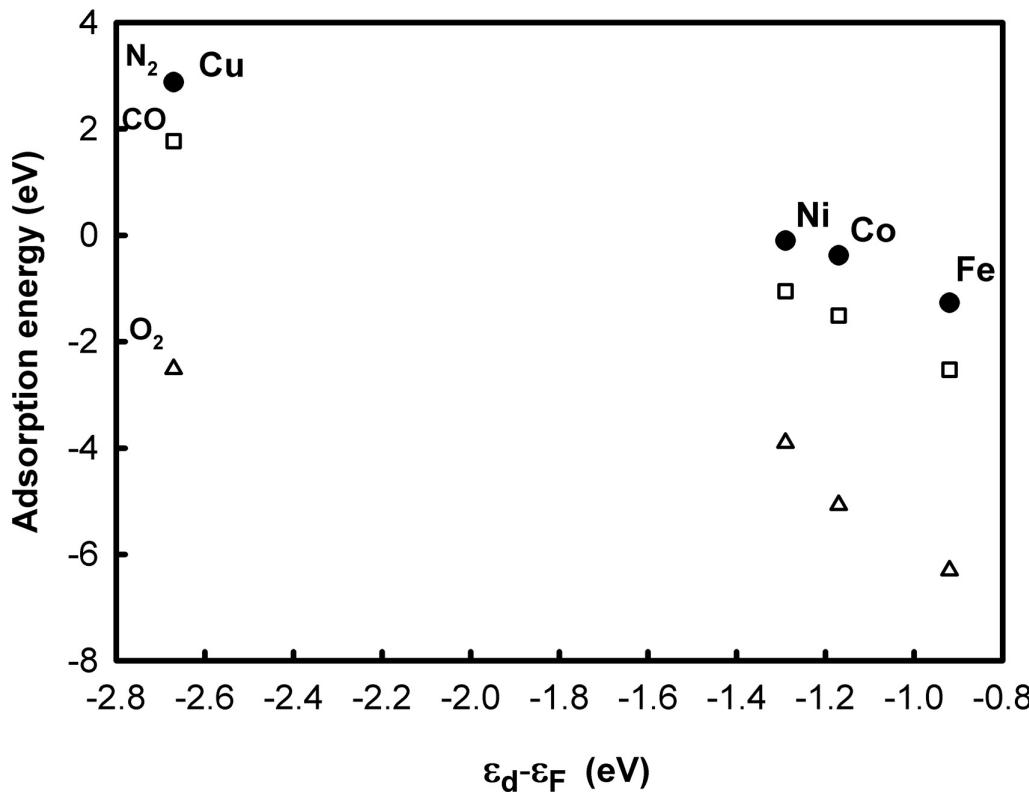
→ adsorbate energies scale

The 0th order *d*-band model:

Adsorption energies on 3d, 4d, and 5d metals is linear in the *d*-band center location

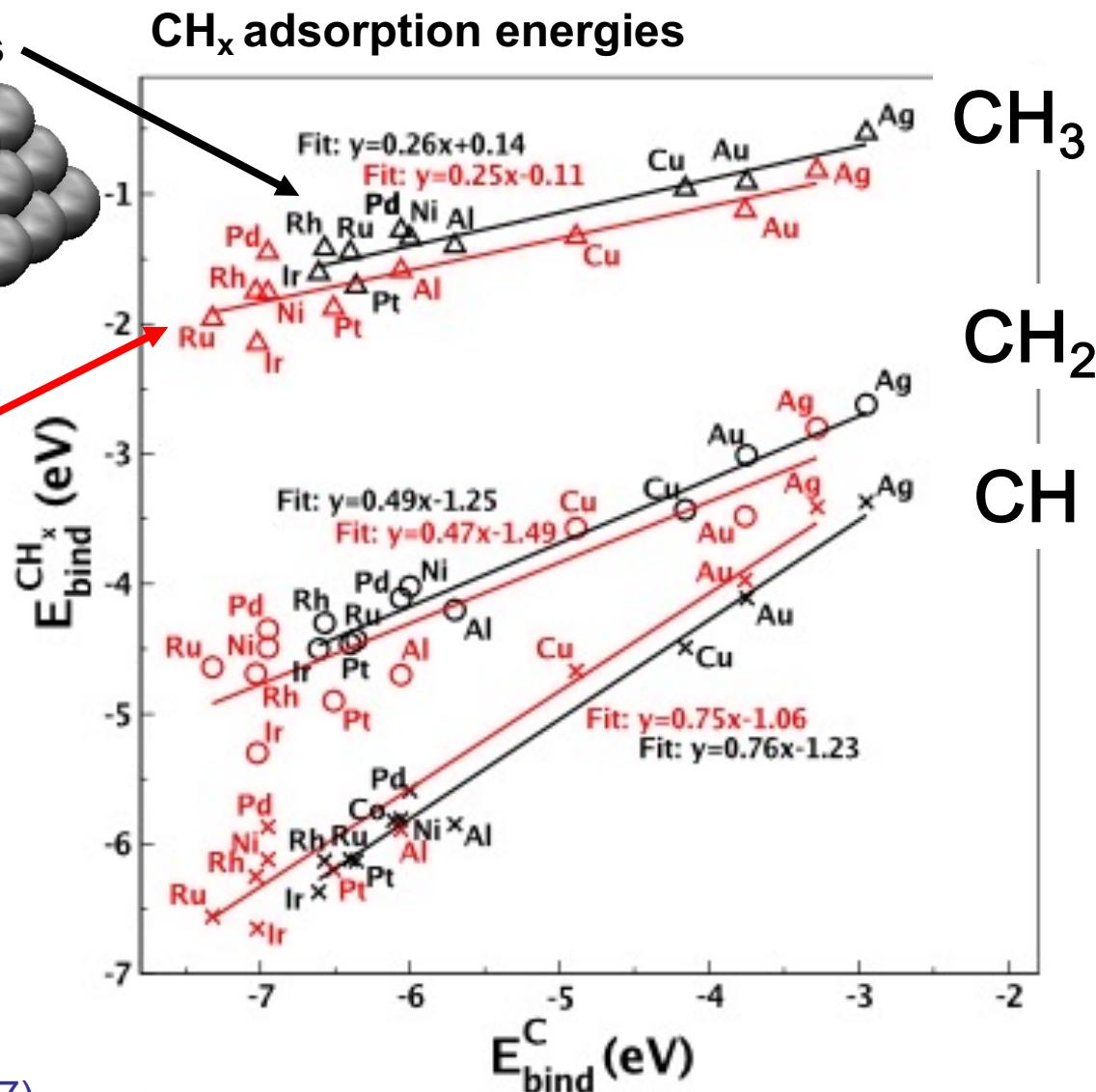
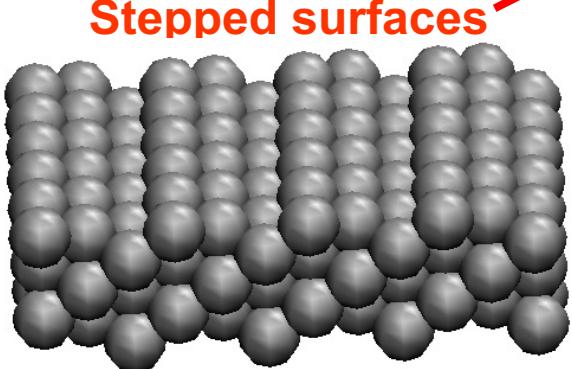
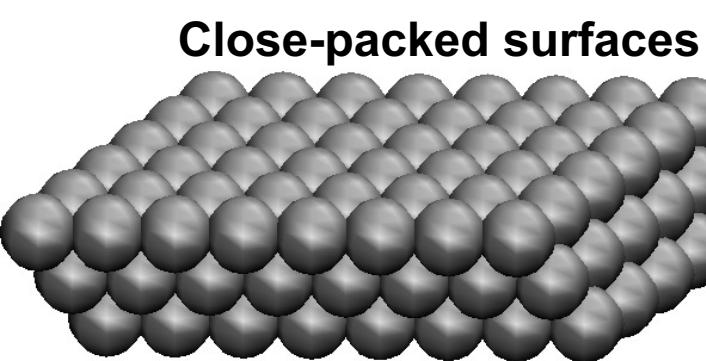
Corollary to *d*-band model:

The adsorption energy of any adsorbate scales with the adsorption energy of any other adsorbate on the d-metals



Nilsson, Pettersson, Hammer,
Bligaard, Christensen, Nørskov
Catal. Lett. **100**, 111 (2005)

Scaling relations: CH_x vs. C adsorption



Abild-Pedersen, Greeley, Studt
Rossmeisl, Munter, Moses
Skulason, Bligaard, Nørskov
Phys. Rev. Lett. **99**, 016105 (2007)

Rationalization of scaling relations

d-band model

Hammer and Nørskov, *Nature* **376** (1995) 238

+

Effective Medium Theory (EMT)

Nørskov and Lang, *Phys. Rev. B* **21**, 2131 (1980)

Nørskov, *Rep. Prog. Phys.* **53**, 1253 (1990)

→ Scaling slope
rationalization:

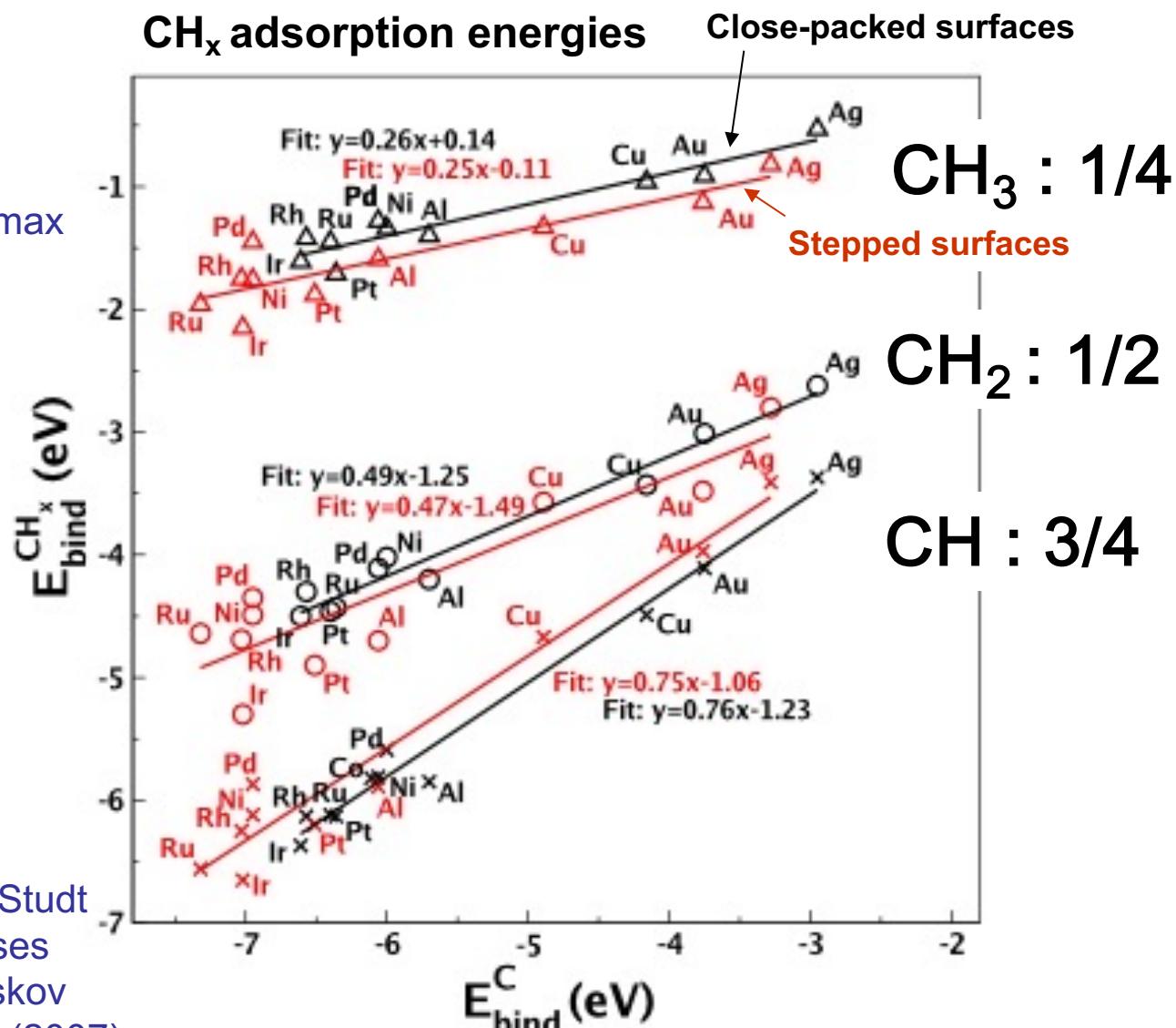
$$\Delta E^{AH_x} = \gamma(x) \Delta E^A + \xi$$

$$\gamma(x) = (x_{\max} - x) / x_{\max}$$

Abild-Pedersen, Greeley, Studt, Rossmeisl, Munter, Moses, Skulason
Bligaard, Nørskov, *Phys. Rev. Lett.* **99**, 016105 (2007)

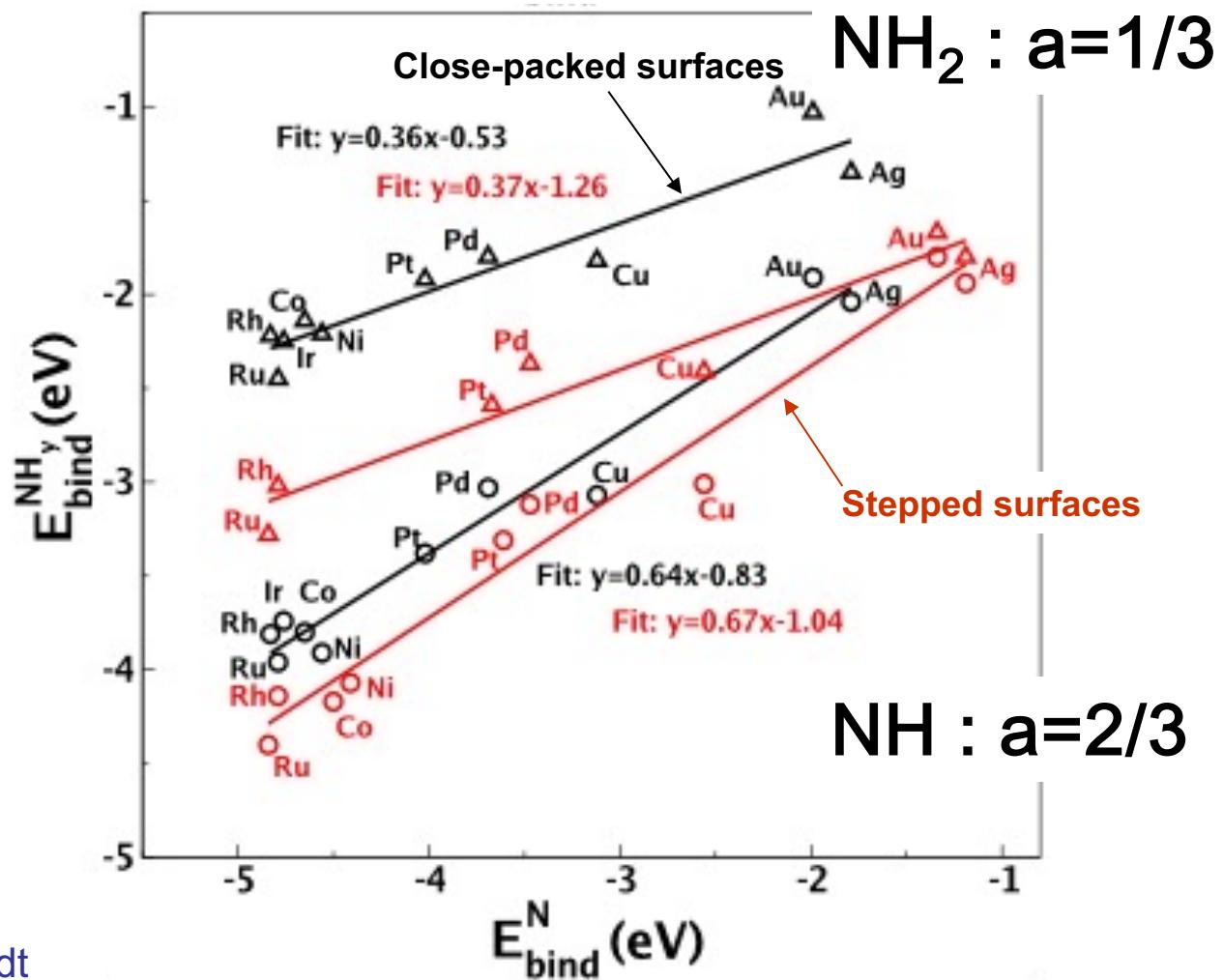
Scaling relations: CH_x vs. C

For AH_x :
 slope = $(x_{\max} - x)/x_{\max}$



Abild-Pedersen, Greeley, Studt
 Rossmeisl, Munter, Moses
 Skulason, Bligaard, Nørskov
 Phys. Rev. Lett. 99, 016105 (2007)

Scaling relations: NH_x vs. N



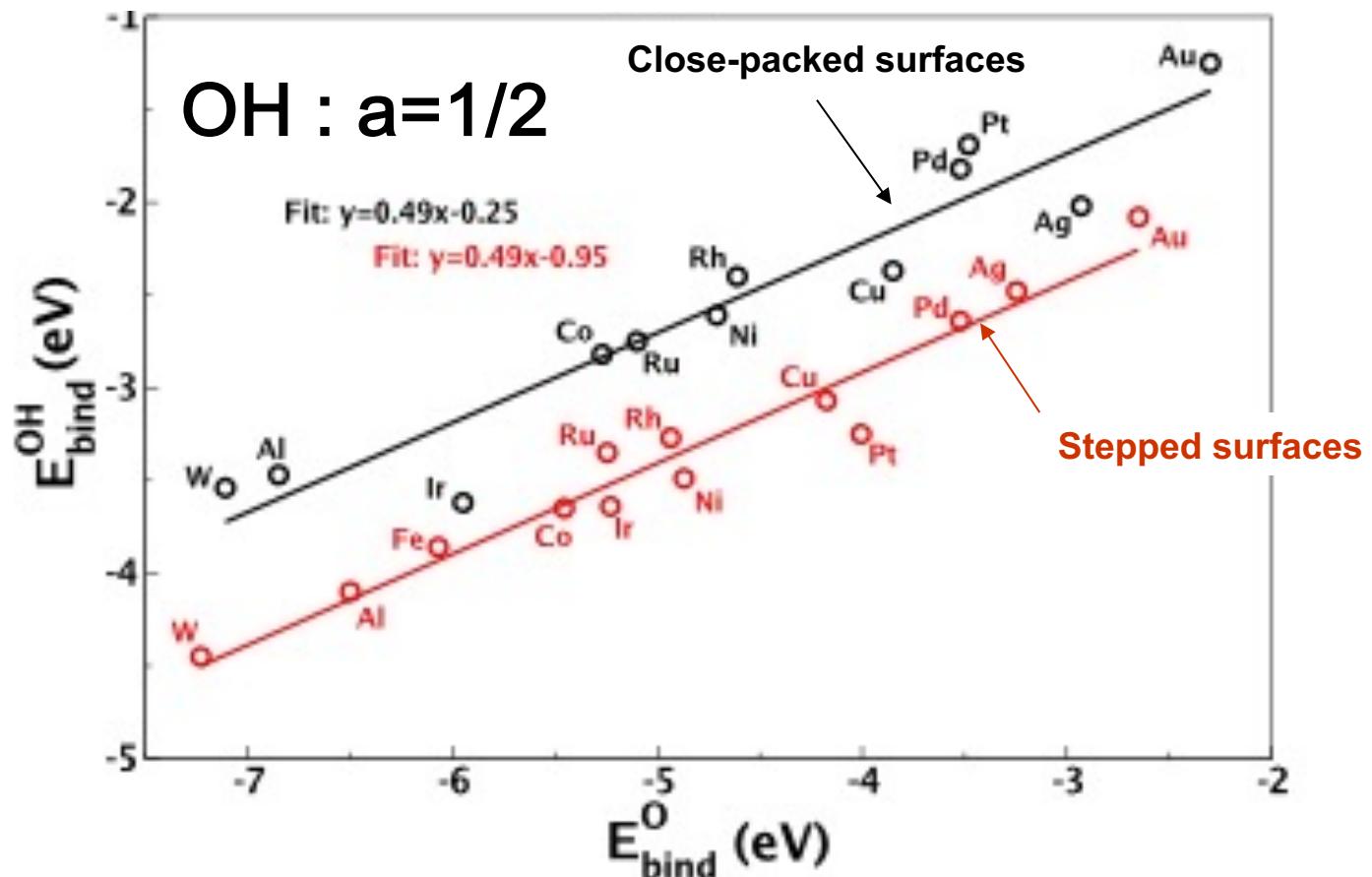
Abild-Pedersen, Greeley, Studt

Rossmisl, Munter, Moses

Skulason, Bligaard, Nørskov

Phys. Rev. Lett. 99, 016105 (2007)

Scaling relations: OH vs. O



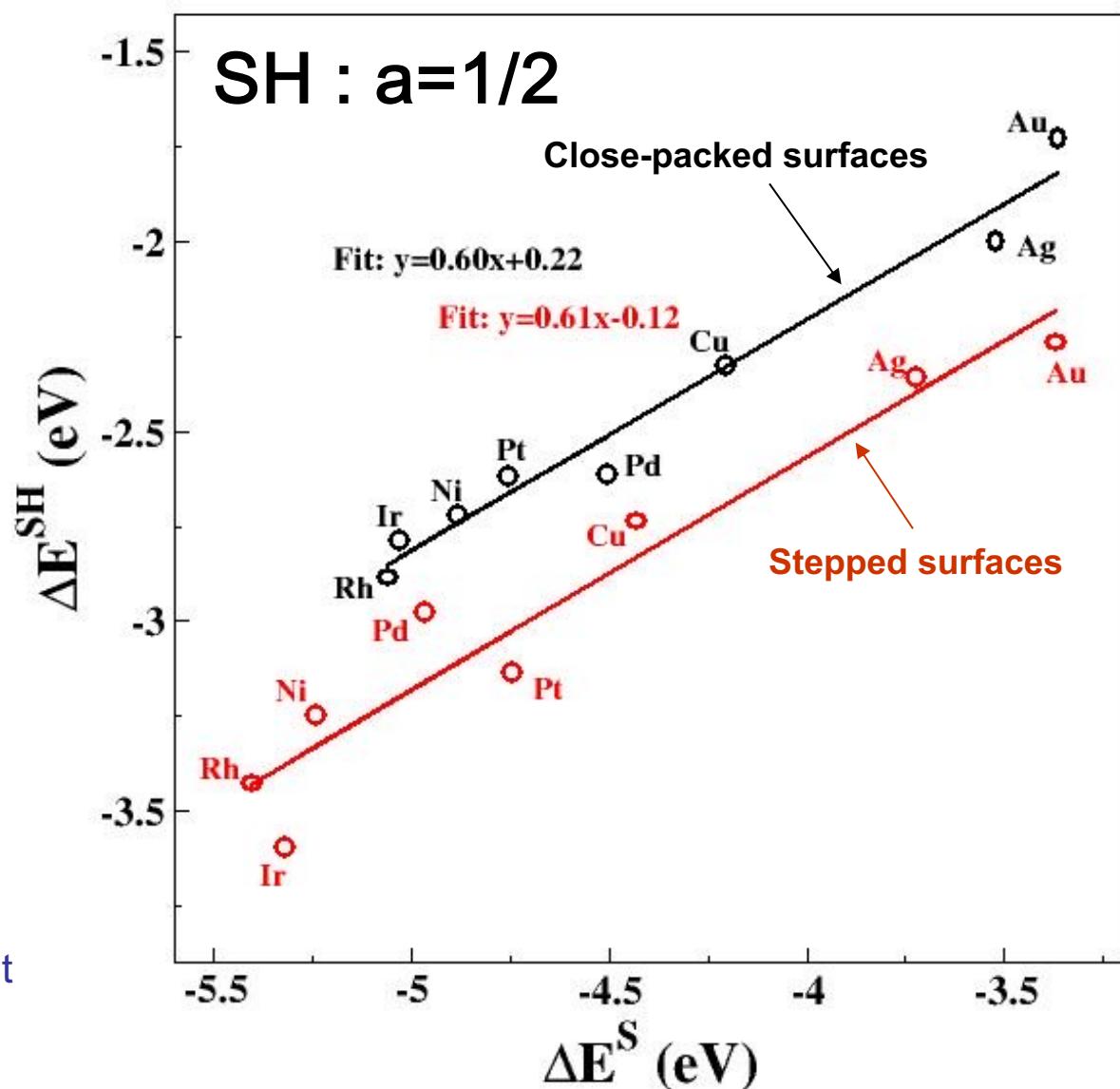
Abild-Pedersen, Greeley, Studt

Rossmeisl, Munter, Moses

Skulason, Bligaard, Nørskov

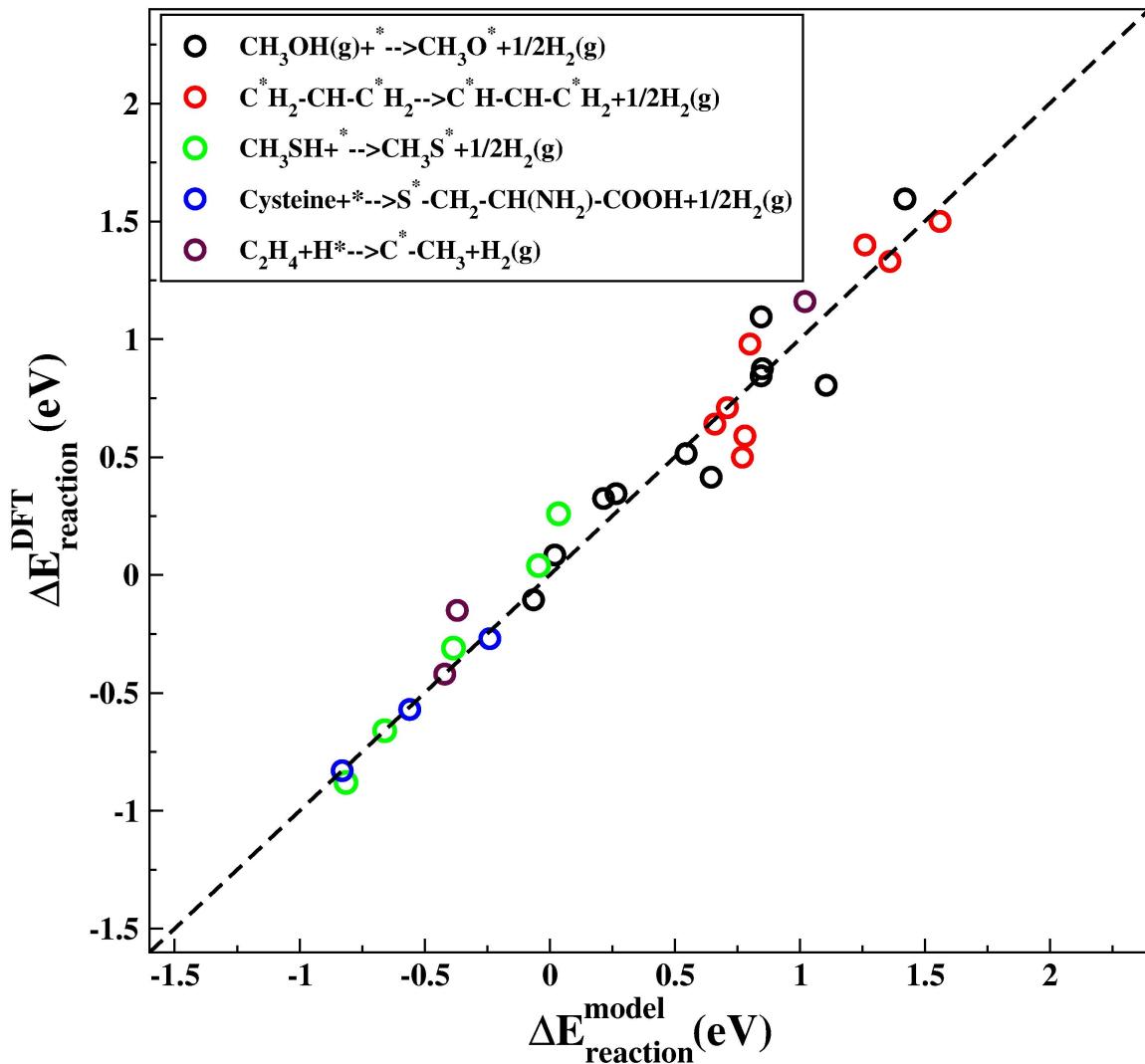
Phys. Rev. Lett. 99, 016105 (2007)

Scaling relations: SH vs. S



Abild-Pedersen, Greeley, Studt
Rossmeisl, Munter, Moses
Skulason, Bligaard, Nørskov
Phys. Rev. Lett. 99, 016105 (2007)

Predicting heats of reaction from scaling relations

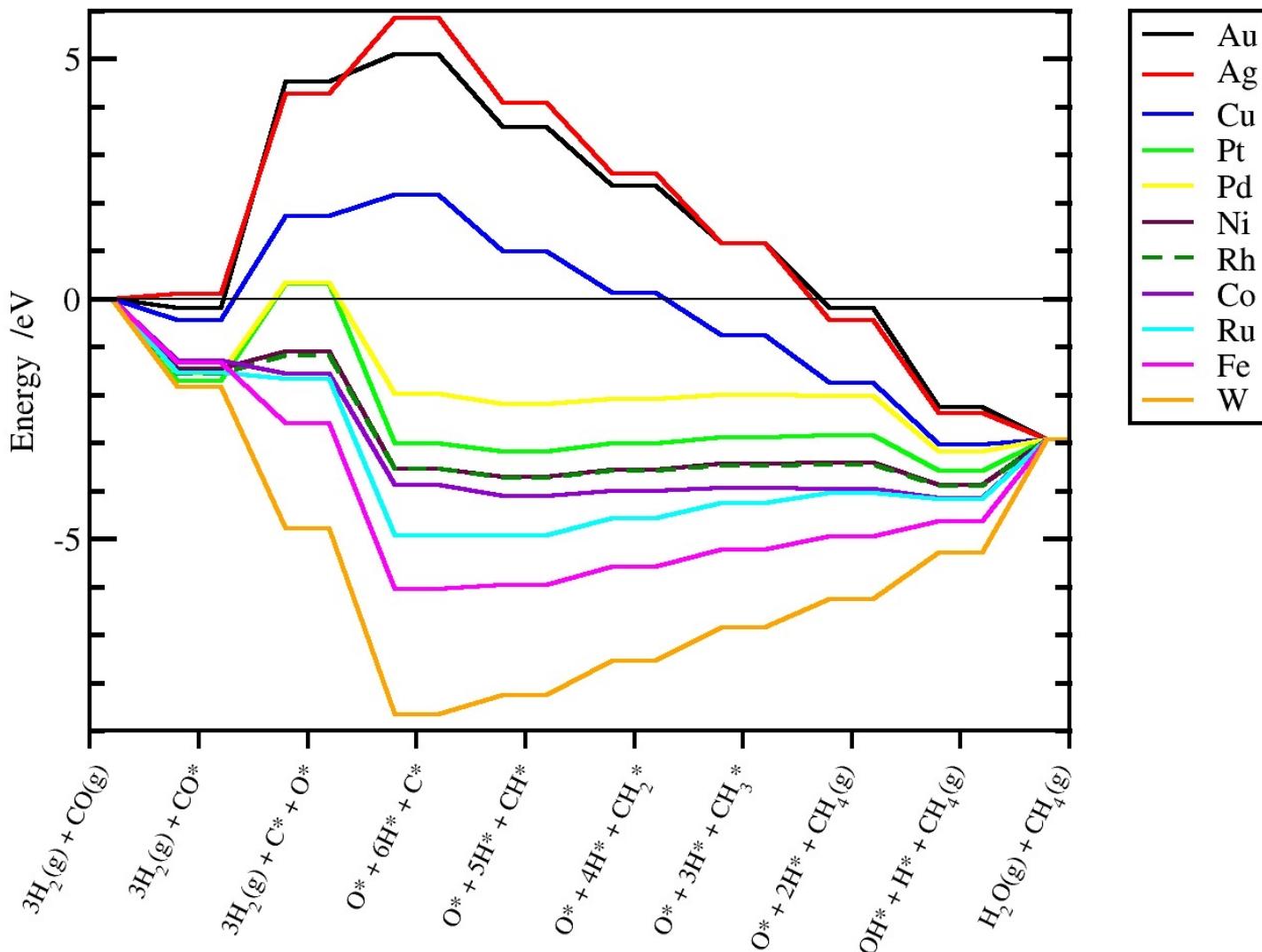


Requires :

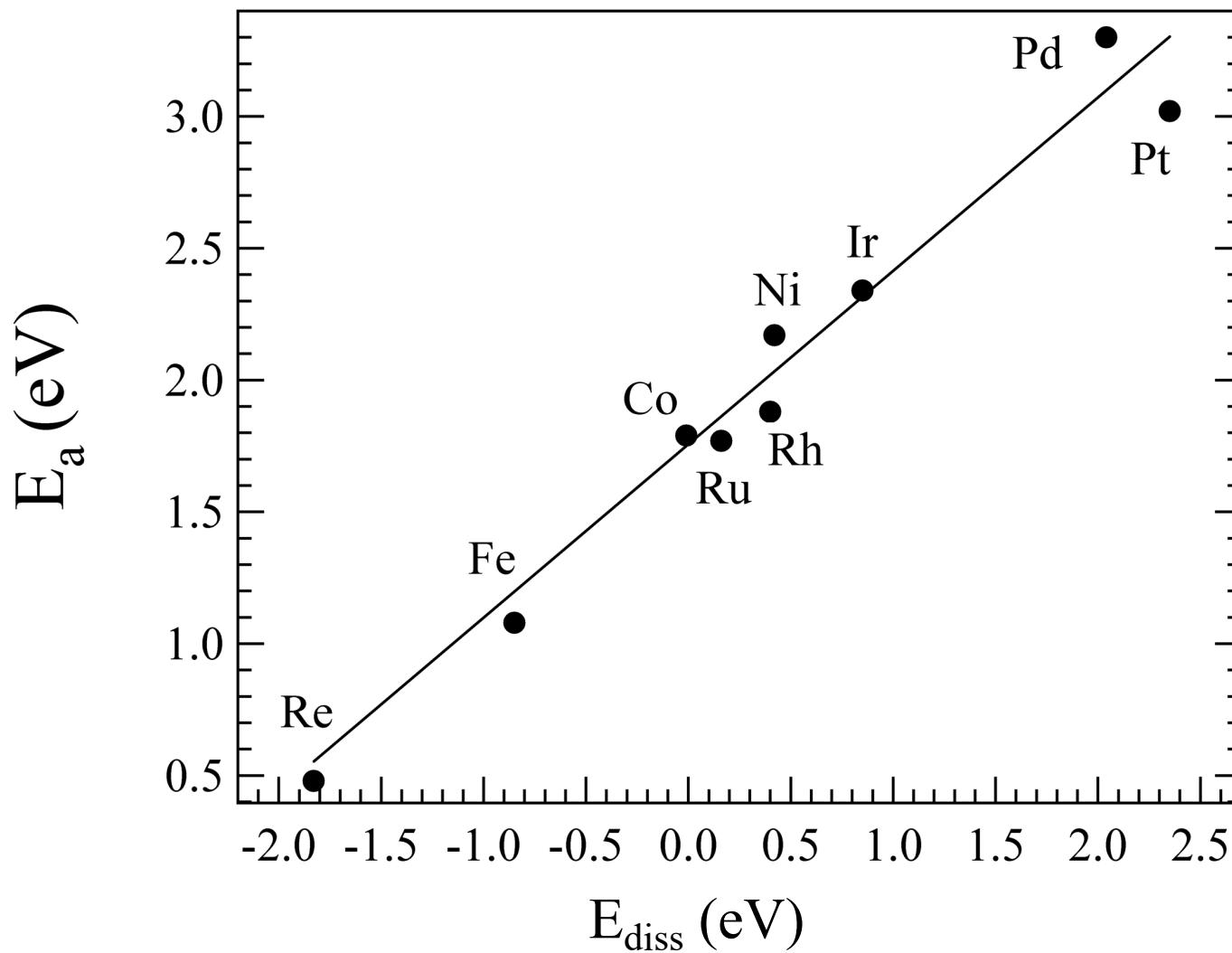
1. Atomic C, O, and S adsorption energies on all d-metals
2. Reaction intermediates on one metal (Pt)

Abild-Pedersen, Greeley, Studt
Rossmeisl, Munter, Moses
Skulason, Bligaard, Nørskov
Phys. Rev. Lett. **99**, 016105 (2007)

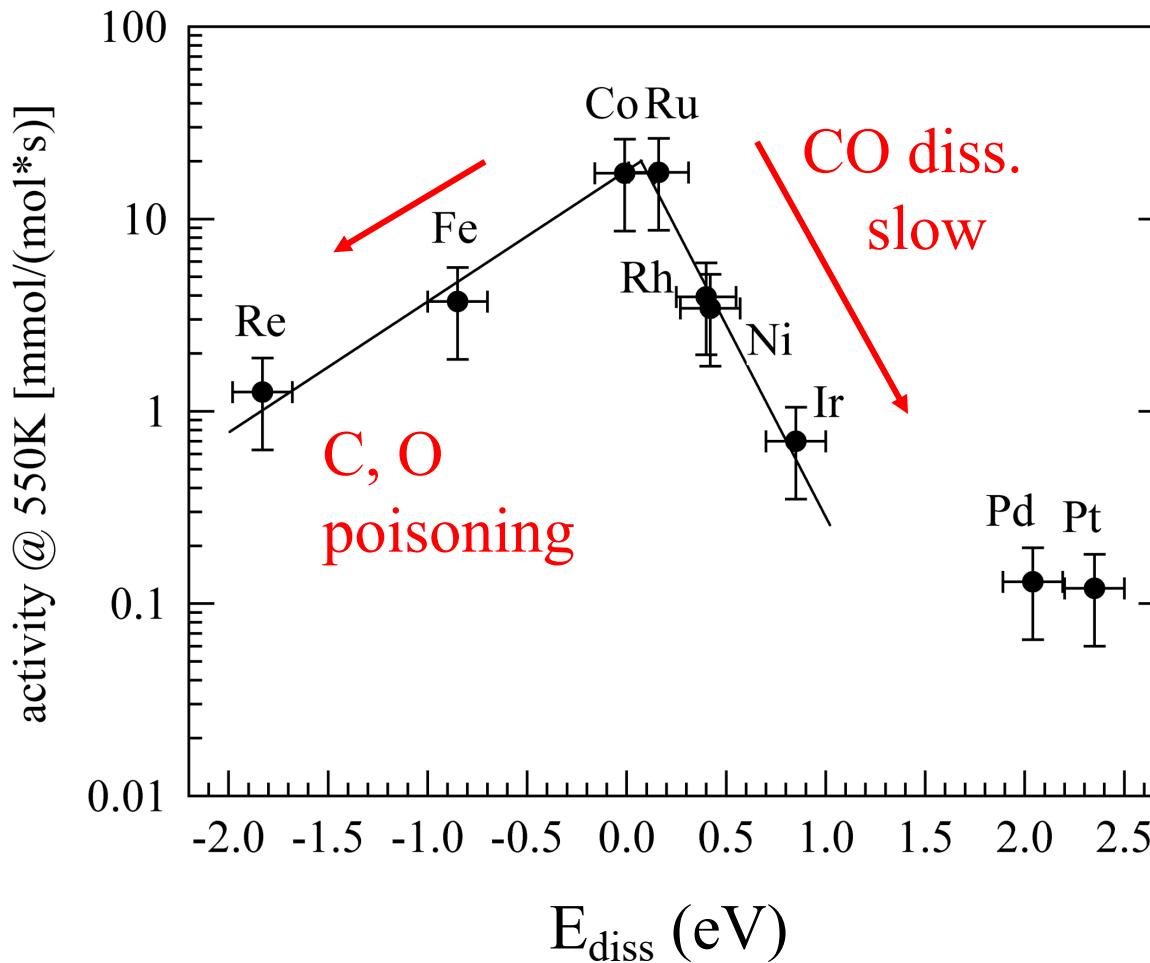
Scaling: Methanation



Brønsted-Evans-Polanyi (BEP) relations: → e.g. CO dissociation



Volcano: The methanation reaction:

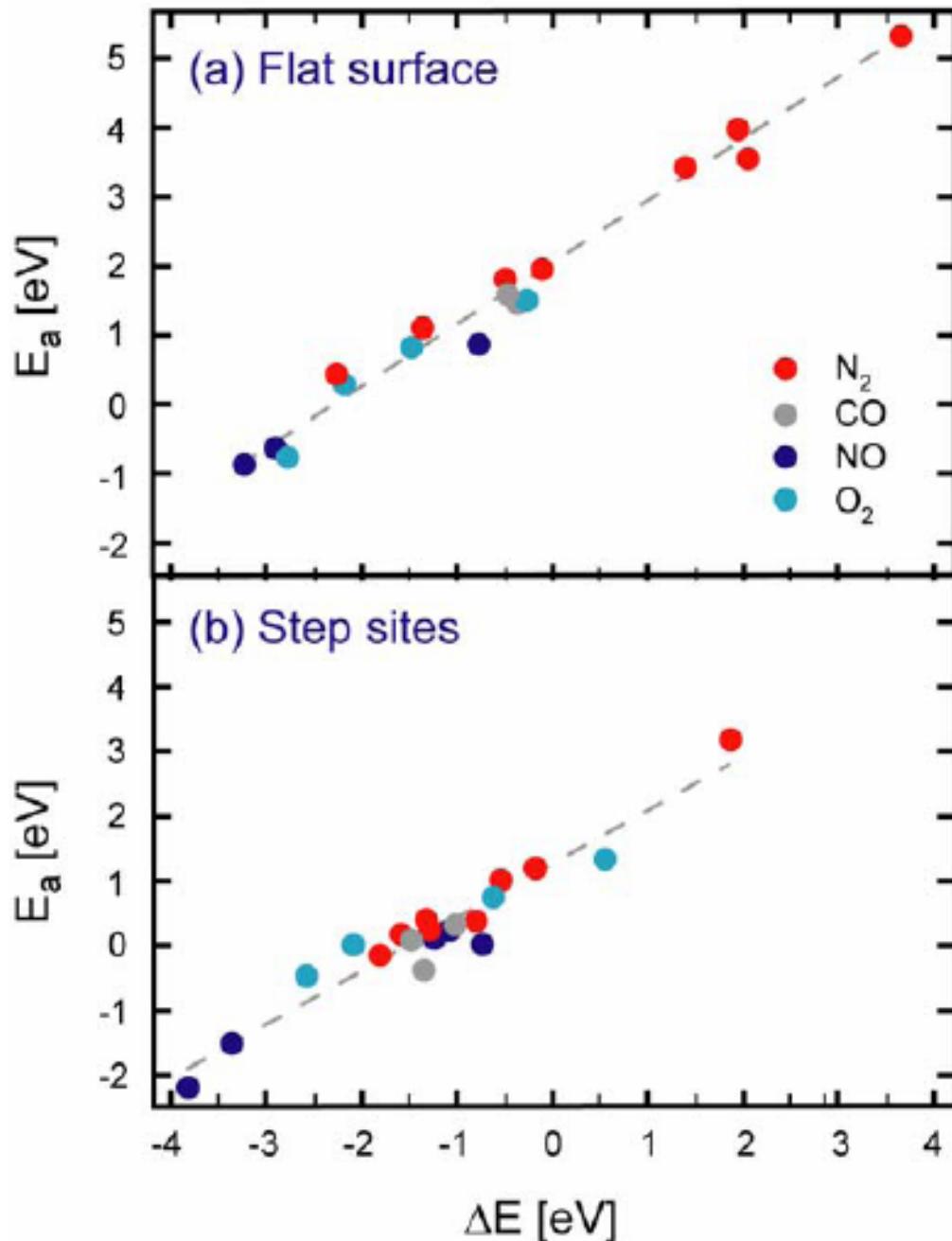


Sabatier, *Ber. Deutsch. Chem. Gesell.* **44**, 1984 (1911)

Bligaard, Nørskov, Dahl, Matthiesen, Christensen, Sehested, *J. Catal.* **224**, 206 (2004)

Bligaard, Nørskov in “*Chemical Bonding at Surfaces*”, Elsevier (2008)

-4 -3 -2 -1 0 1 2 3 4



Universality of BEPs

BEPs exist for a number of small molecules

- and happen to be identical



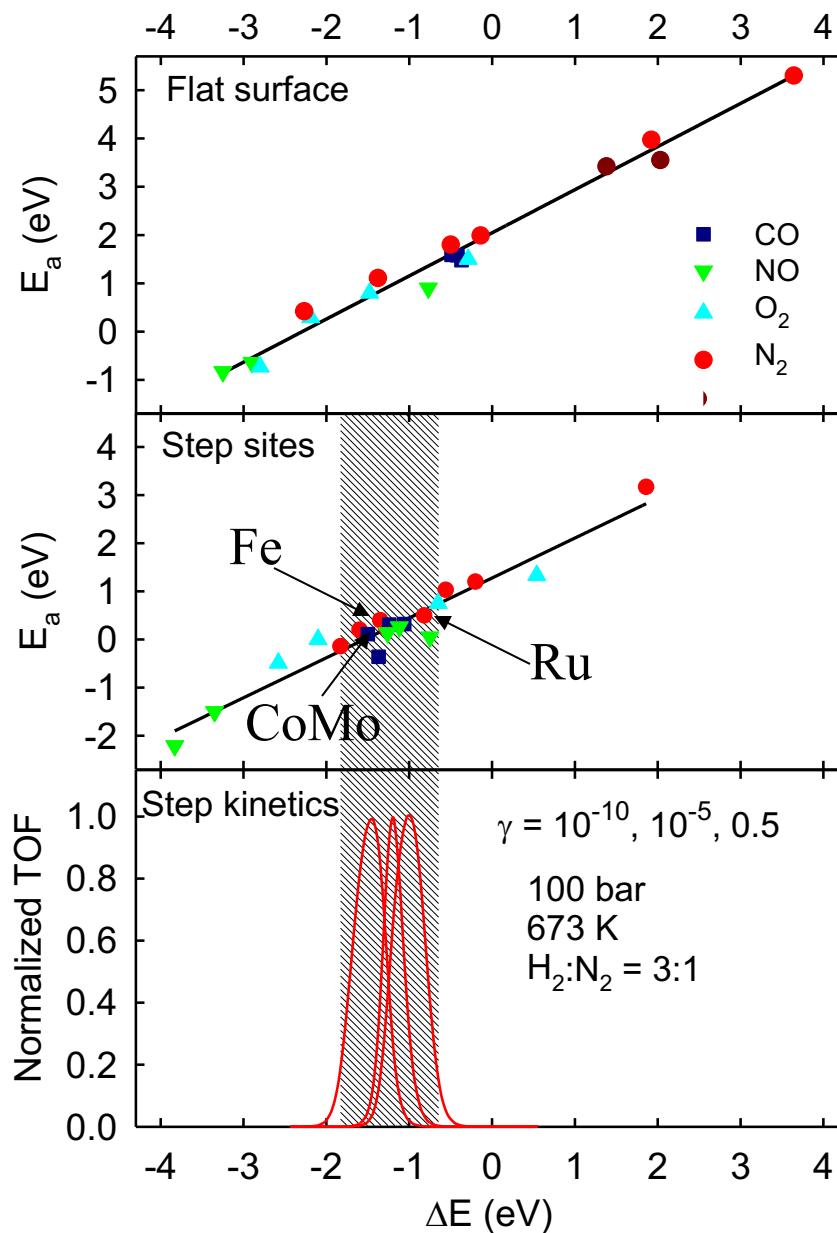
Omnipresence of volcanoes

- and very similar kinetics

Nørskov, Bligaard,
Logadottir, Bahn, Hansen,
Bollinger, Bengaard, Hammer,
Sljivancanin, Mavrikakis, Xu,
Dahl, Jacobsen
J. Catal. **209**, 275 (2002)

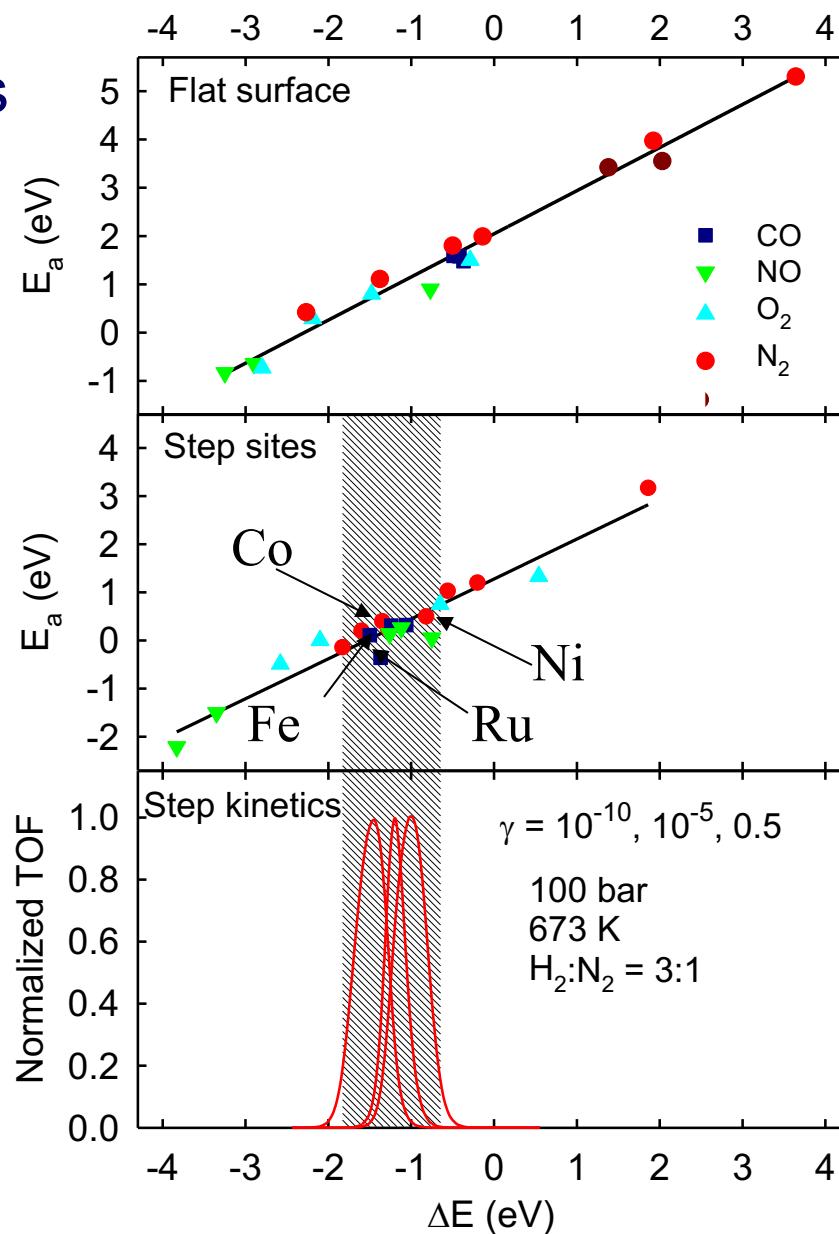
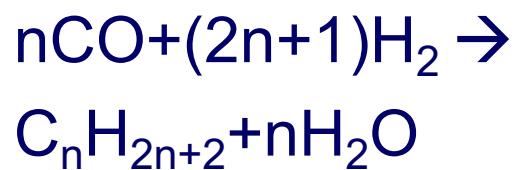
Understanding trends in catalytic activity

Ammonia synthesis :



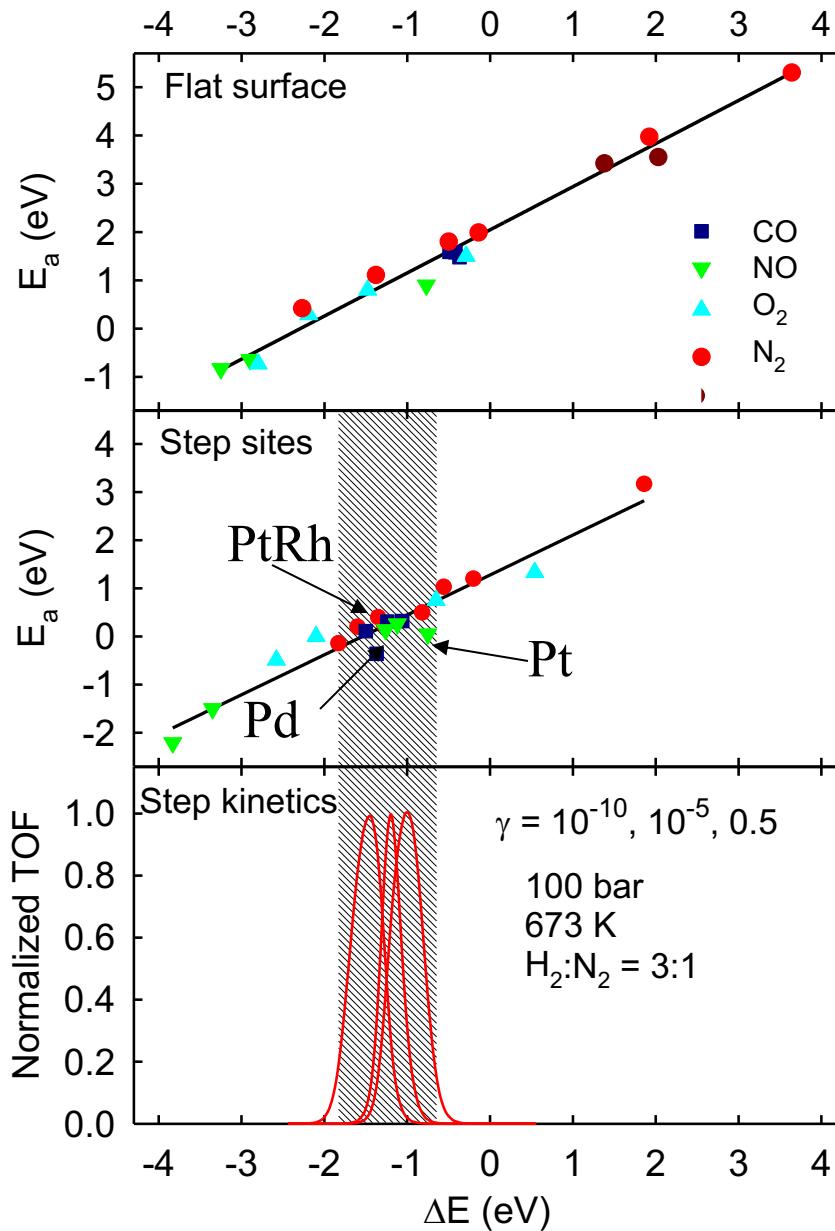
Understanding trends in catalytic activity

Fischer Tropsch synthesis
and methanation:



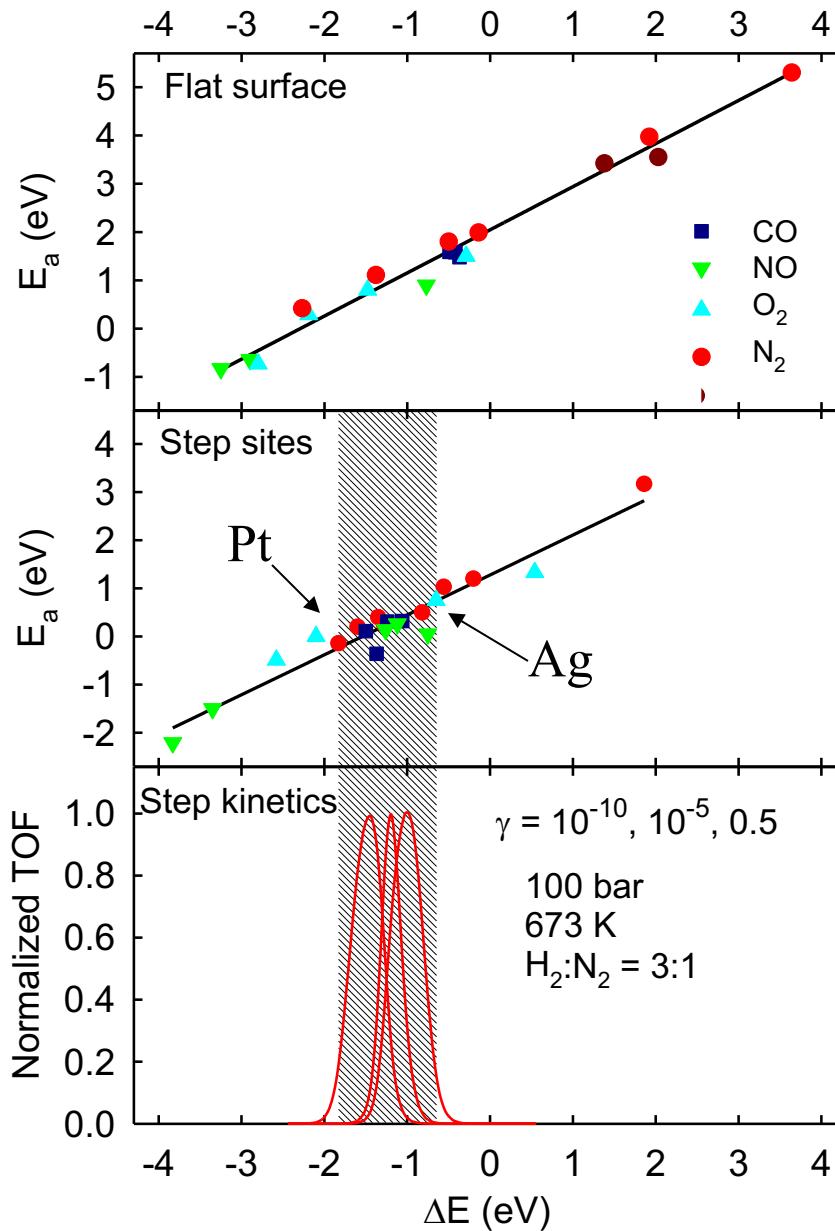
Understanding trends in catalytic activity

NO reduction:

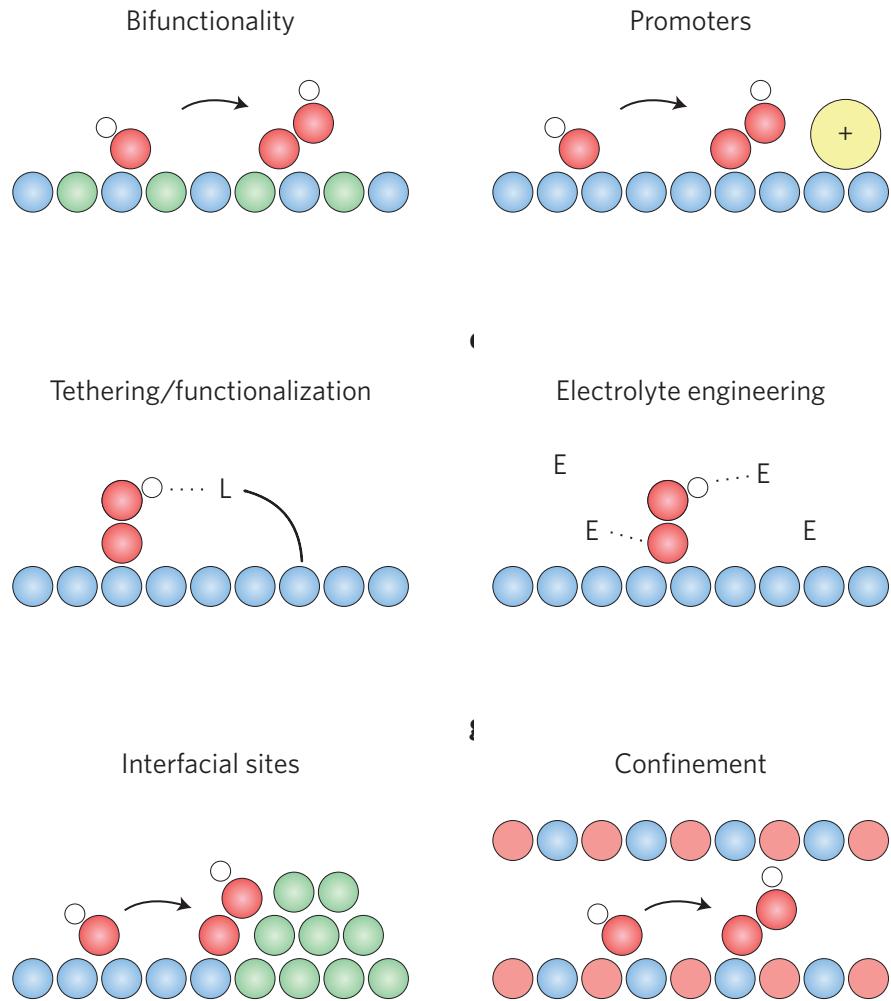


Understanding trends in catalytic activity

Oxidation:



Design rule II: Circumvent scaling!



Your imagination sets the limit

Montoya, Seitz, Chakthranont, Vojvodic, Jaramillo, Nørskov, *Nature Materials* **16**, 70 (2017)
Peterson, Nørskov, *J. Phys. Chem. Lett.* **3**, 251 (2012)