Chapter 5 Computational design of catalytic materials

- **An introduction to catalysis and surface chemistry**
- d-Band theory of catalysis
- Photocatalysis and plasmon-enhanced catalysis

Why R& D in catalysis is important

➢ 27 % of GNP and 90 % of chemical industry involve products made using catalysts.

➢ To discover alternate sources of energy/fuels/raw material for society needs.

➢ Pollution control to prevent global warming.

Chemical Reaction

Thermodynamics says NOTHING about the rate of a reaction (recall: Metropolis Monte Carlo vs. Kinetic Monte Carlo) .

Thermodynamics: Consider the problem about "will a reaction occur ?"

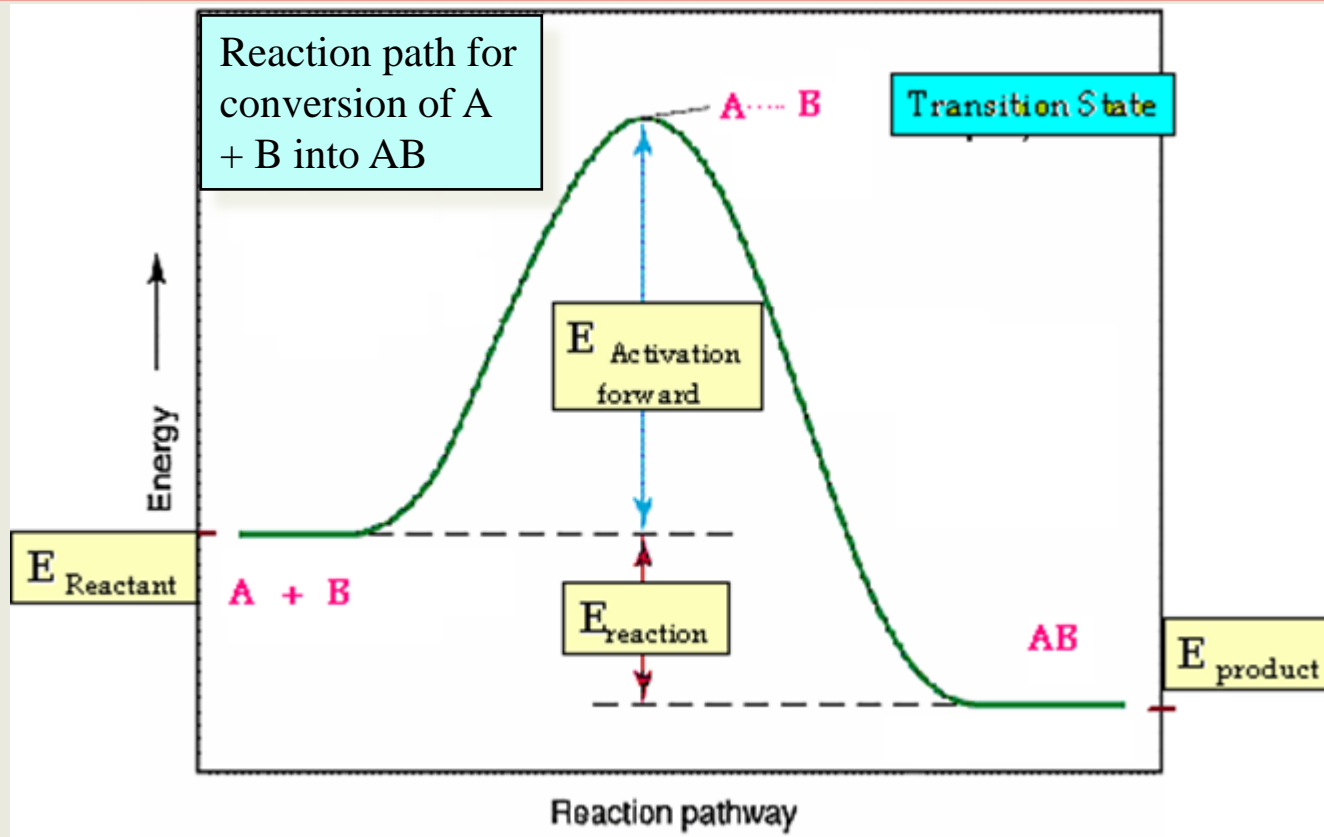**Kinetics:** If so, how fast ?

What is a Catalyst ?

➢ Catalyst is a substance that increases the rate of the reaction at which a chemical reaction approaches equilibrium, without being substantially consumed in the process. Catalyst affects only the rate of the reaction, i.e. **Kinetics**.

➢ It changes neither the thermodynamics of the reaction nor the equilibrium composition.

Conditions for a Good Solid Catalyst

- High activity per unit of volume in the eventual reactor
- High selectivity
- Sufficiently long life time with respect to deactivation
- Possibility to regenerate, particularly if it deactivates fast
- Reproducible preparation
- Sufficient thermal stability against sintering, structural changes or volatilization
- High mechanical strength with respect to crushing (e.g. under the weight of the catalyst bed or during the shaping processes)
- High attrition resistance (mechanical wear)
- ….

Kinetic vs. Thermodynamic

Reaction path for conversion of A + B into AB

A····B

Transition State

$E_{Activation\ forward}$

Energy

$E_{Reactant}$

A + B

$E_{reaction}$

AB

$E_{product}$

Reaction pathway

Activation Energy: The energy required to overcome the reaction barrier. Usually given a symbol E_a *or* $\Delta G^{\neq}$

The Activation Energy (E_a) determines how fast a reaction occurs, the *higher Activation barrier, the slower the reaction rate. The lower the activation barrier, the faster the reaction*

Kinetic vs. Thermodynamic

$$A + B \rightarrow A_{ad} + B \rightarrow A_{ad} + B_{ad} \rightarrow AB$$
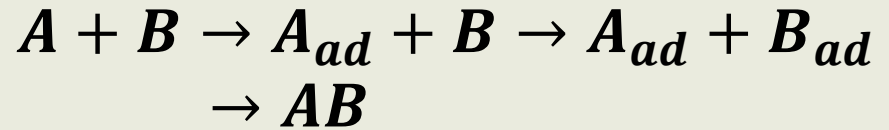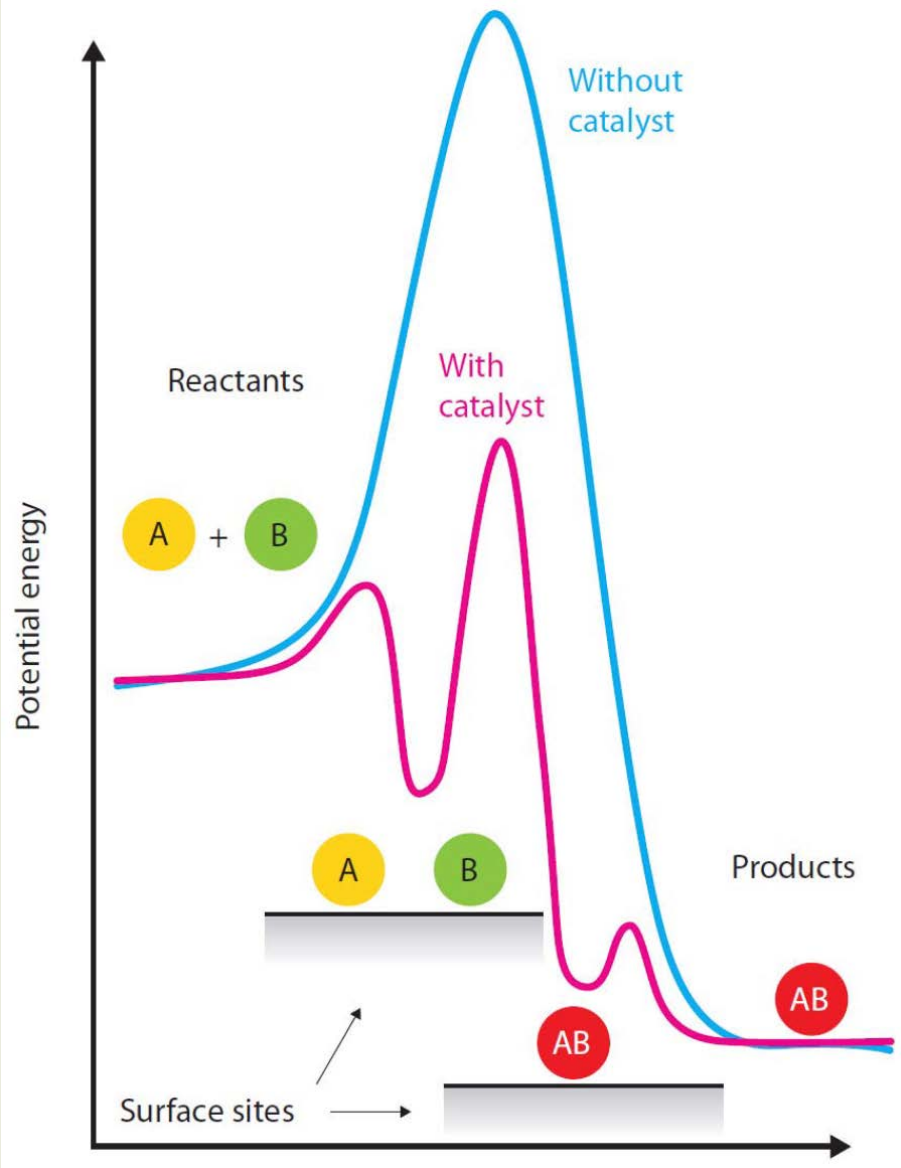
Catalyst lowers the activation energy for both forward and reverse reactions.

This means, the catalyst changes the reaction path by lowering its activation energy and consequently the *catalyst increases the rate of reaction*.

Adsorption and Catalysis

Adsorbent: surface onto which adsorption can occur.

      Examples: catalyst surface, activated carbon, alumina, etc.

Adsorbate*: molecules or atoms that adsorb onto the substrate.

      Examples: nitrogen, hydrogen, carbon monoxide, water, etc.

Adsorption: the process by which a molecule or atom adsorb onto a surface of substrate.

Coverage*: a measure of the extent of adsorption of a specie onto a surface

H H H H H H H H H adsorbate

adsorbent

coverage θ = **fraction of surface sites occupied**

H H H H H
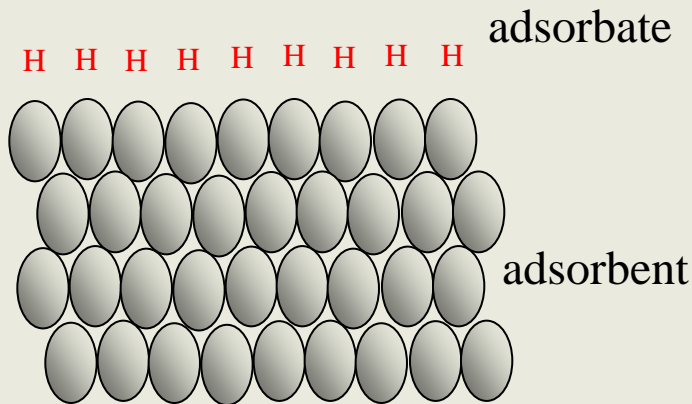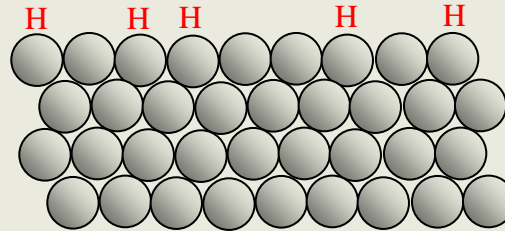
Adsorption

In physical adsorption

1. The bond is a van der Waals interaction

2. Adsorption energy is typically 5-10 kJ/mol. (much weaker than a typical chemical bond)

3. Many layers of adsorbed molecules may be formed.
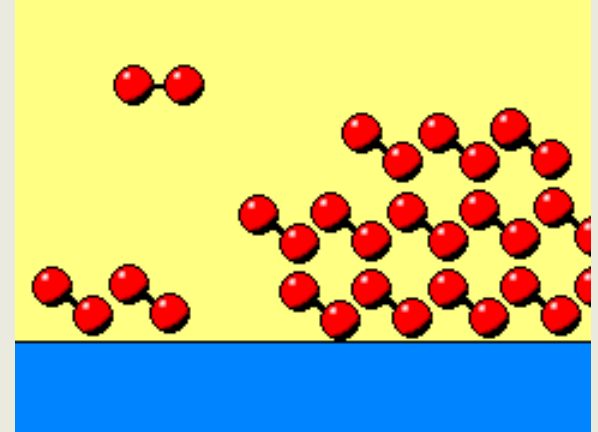
Adsorption

For chemical adsorption

1. The adsorption energy is comparable to the energy of a chemical bond.

2. The molecule may chemically adsorb intact (left) or it may adsorb dissociatively (right).

3. The chemisorption energy is 30-70 kJ/mol for molecules and 100-400 kJ/mol for atoms.
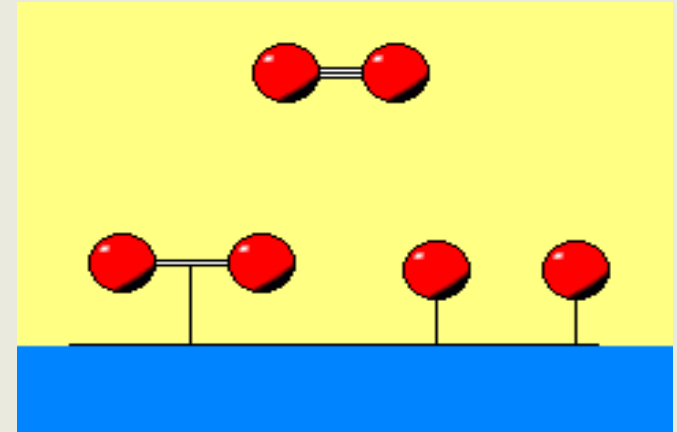
Characteristics of Chemi- and Physisorptions
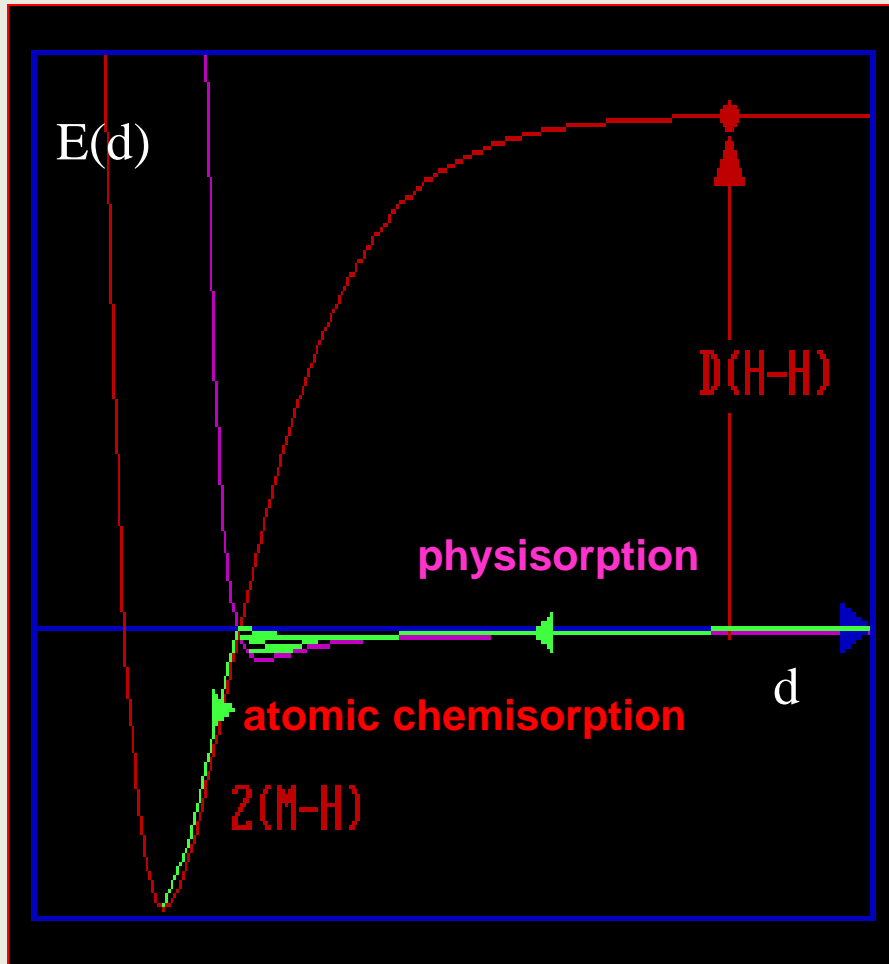
$\Delta E(ads)$ < $\Delta E(ads)$
Physisorption   Chemisorption

small minima   large minima
weak Van der Waal   formation of surface
attraction forces   chemical bonds

CO

physisorption/
desorption

chemisorption
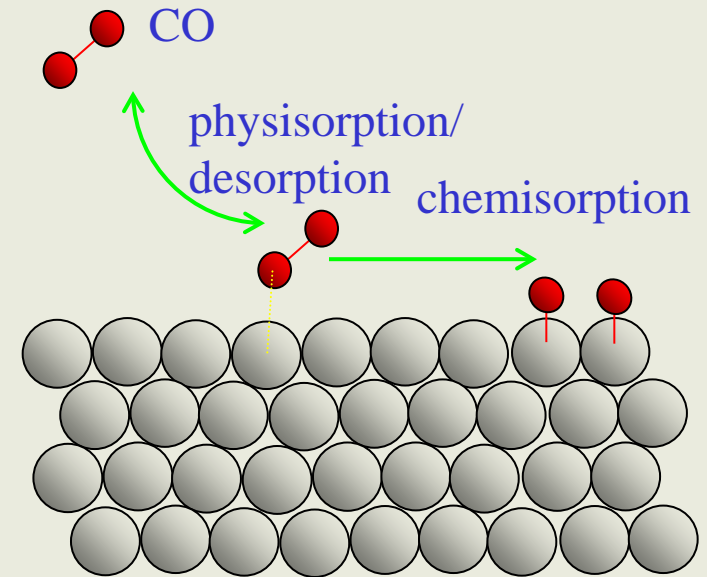
Adsorption Energy

coverage θ = fraction of surface sites occupied
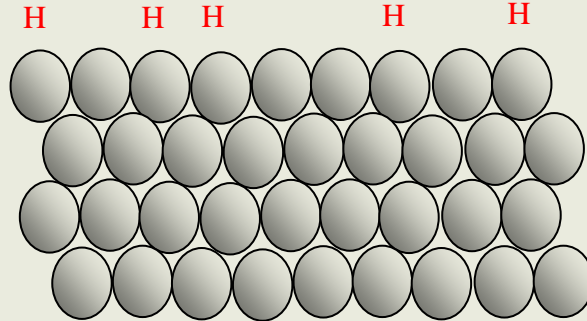
The average binding energy of adsorbate B can be evaluated with

$$B(\theta) = \frac{[E_{A\ on\ Pt[111]}(\theta) - N_A E_{atom\ A} - E_{Pt[111]}]}{N_A},$$

where N_A represents the number of adsorbate A, and
$E_{A\ on\ Pt[111]}(\theta)$ = Total energy of the A/Pt{111} system,
$E_{atom\ A}$ = Total energy of the atomic species **A**,
$E_{Pt[111]}$ = Total energy of the bare platinum surface, respectively.

Binding Energy of an Adsorbate

DFT calculated binding energies (B) in kJ ·mol−1 and bond lengths in Å for O/Pt{111} in a 2×2 unit-cell

2×2-3O
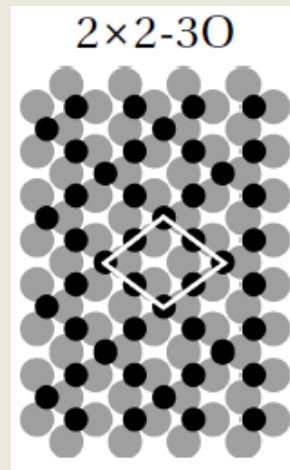
	hcp	fcc	bridge	top	
B	-355	-402	-333	-254	Your DFT calc
B	-366	-411	-350	-254	M. Lynch and P. Hu, Surf. Sci. 458, 1 (2000)
B	-355	-398	-342		A. Bogicevic, *et al.* Phys. Rev. B 57, R4289 (1998)
Pt–O bond	2.06	2.05	1.99	1.83	Your DFT calc
Pt–O bond	2.06	2.05	1.99	1.85	M. Lynch and P. Hu, Surf. Sci. 458, 1 (2000)

Where molecules/atoms can adsorb?
Overview on the adsorption sites on crystal surface

Crystal Structure

- A crystal has a periodic unit cell structure and a lattice constant which minimize the total energy
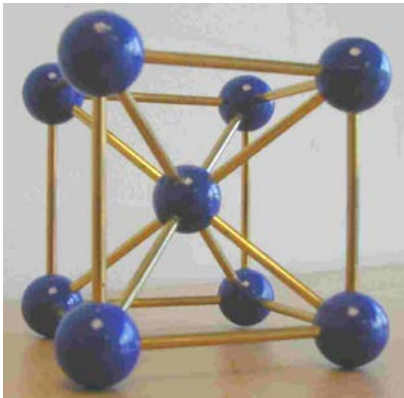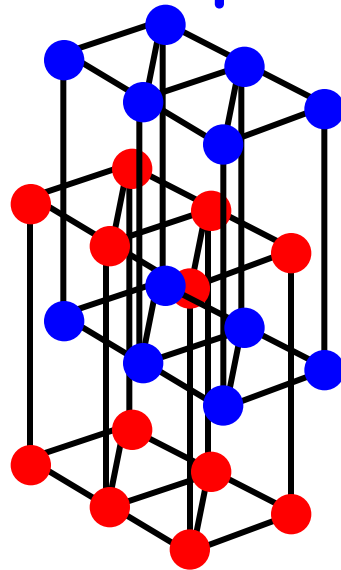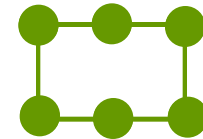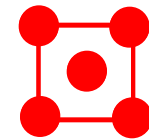
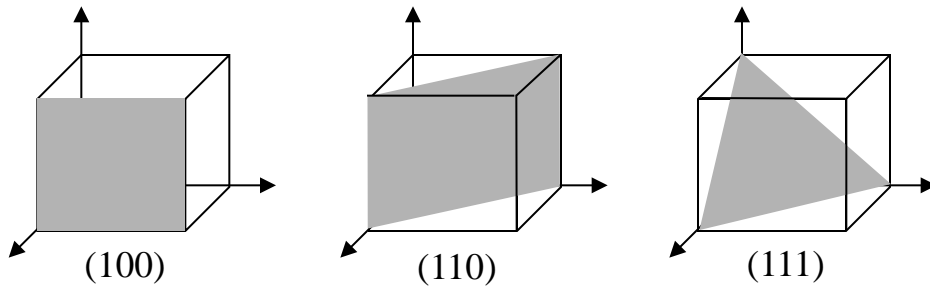## bcc hcp fcc
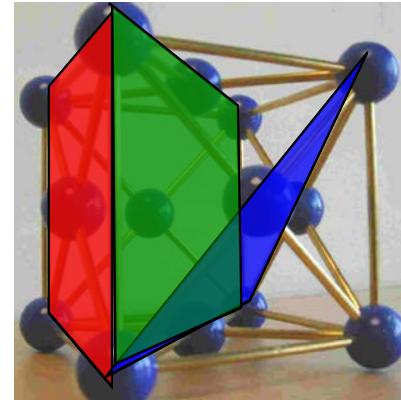
(100)
(110)
(111)
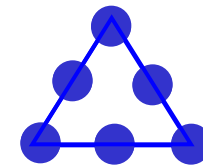
- Engineering materials consist usually of grains of single crystals (mm)
- Laboratory single crystals consist of one grain (cm) ~ 40 M atoms in the SAME array!
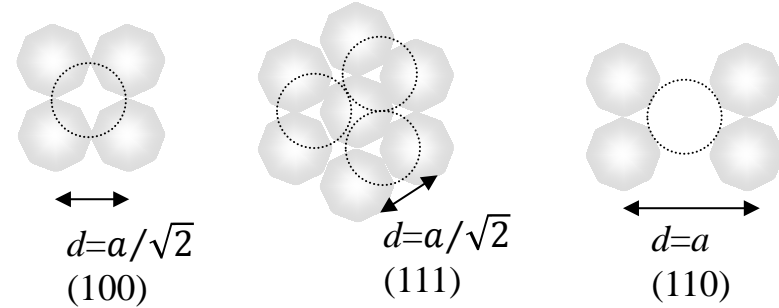
Surface Crystallography

$$\vec{H} = h\,\vec{x} + k\,\vec{y} + l\,\vec{z}$$

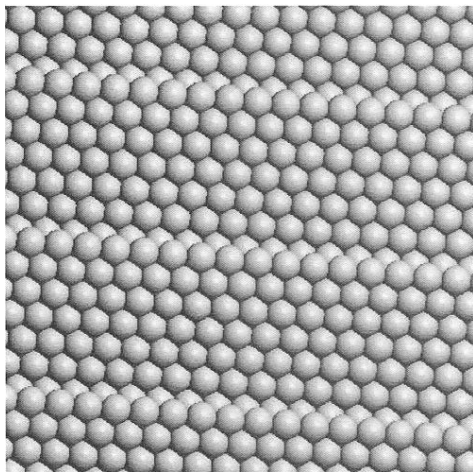(100)   (110)   (111)

Surface Density
fcc: (111)>(100)>(110)
bcc: (110)>(100)>(111)

fcc

$d=a/\sqrt{2}$
(100)

$d=a/\sqrt{2}$
(111)

$d=a$
(110)

Stepped surfaces

fcc (755)

bcc

$d=a$
(100)

$d=\sqrt{2}\,a$
(111)

$d=a$
(110)
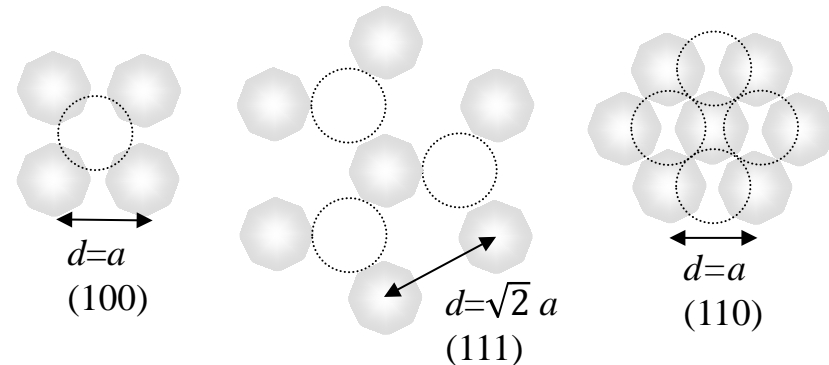
Adsorption Sites

(100)   (111)   (110)
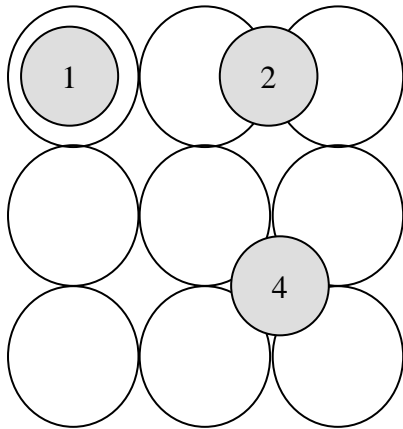
1	On top	

2	Bridge	

3	Long bridge	

4	Four fold hollow	
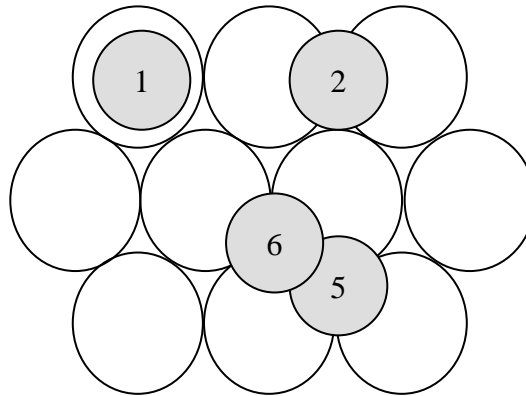
5	Three fold hollow FCC	
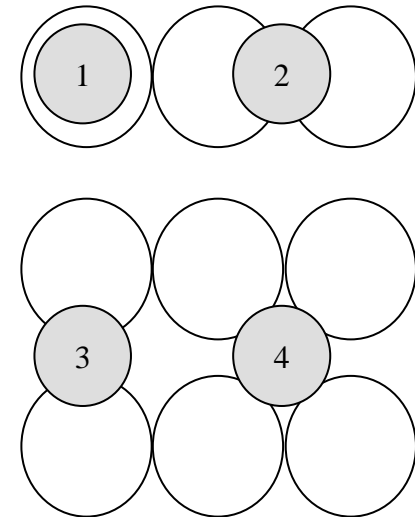
6	Three fold hollow BCC	

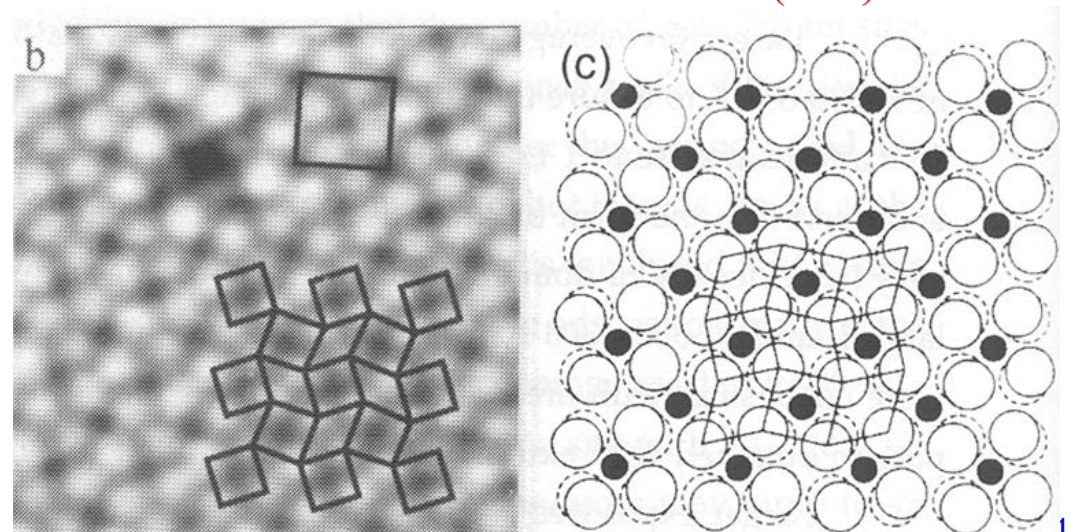# Adsorption Sites

Example: Binding energies [kJ $\cdot$ mol−1 per adsorbate] on Pt{111}

adsorbate	hcp	fcc	bridge	top
H	-261	-264	-261[a]	-261
N	-421	-449	-353[a]	-206[a]
NH	-343	-387	-281[a]	-123[a]
NH$_2$			-298	-247
NH$_3$				-68
NO	-170	-187		-146
O	-355	-390	-333[a]	-254[a]
OH			-214	-213
H$_2$O				-23

[a]geometry optimisation of adsorbates is restricted along the surface normal

The Two-dimensional Lattice

a_1 a_2
square

a_1 a_2
primitive rectangular

a_1 a_2
centered rectangular

a_1 60° a_2
hexagonal

a_1 a_2
oblique

p(2x2)

c(2x2)

(2x2)S–Ni(100)

$(\sqrt{2} \times \sqrt{2})R45°$ S–Ni(100)
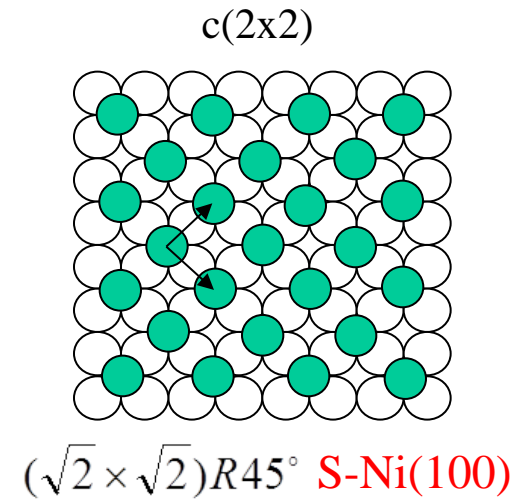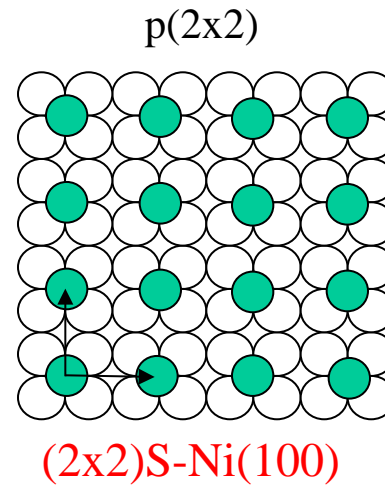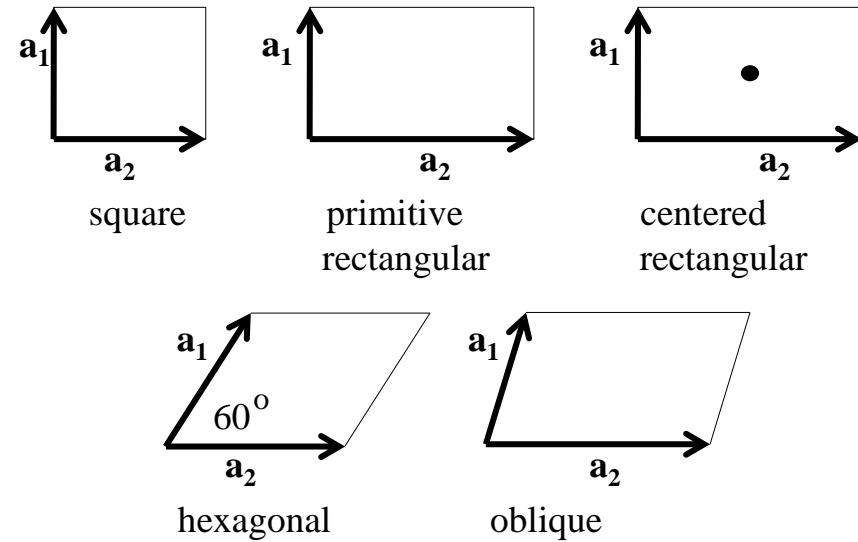
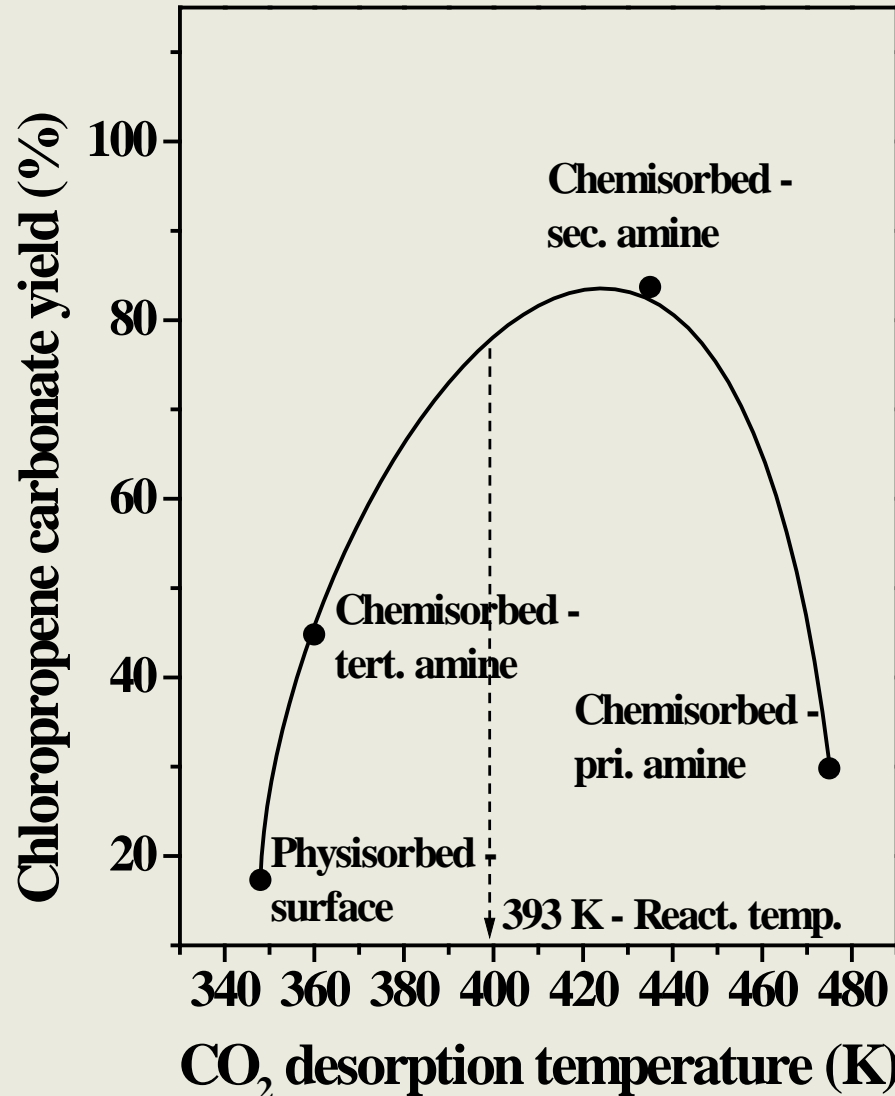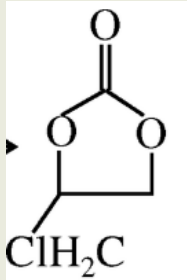Clock reconstruction C-Ni(100)

b

(c)

The Sabatier Principle

"There is an optimum of **the rate of a catalytic reaction** as a function of **the heat of adsorption**"---Sabatier,1905
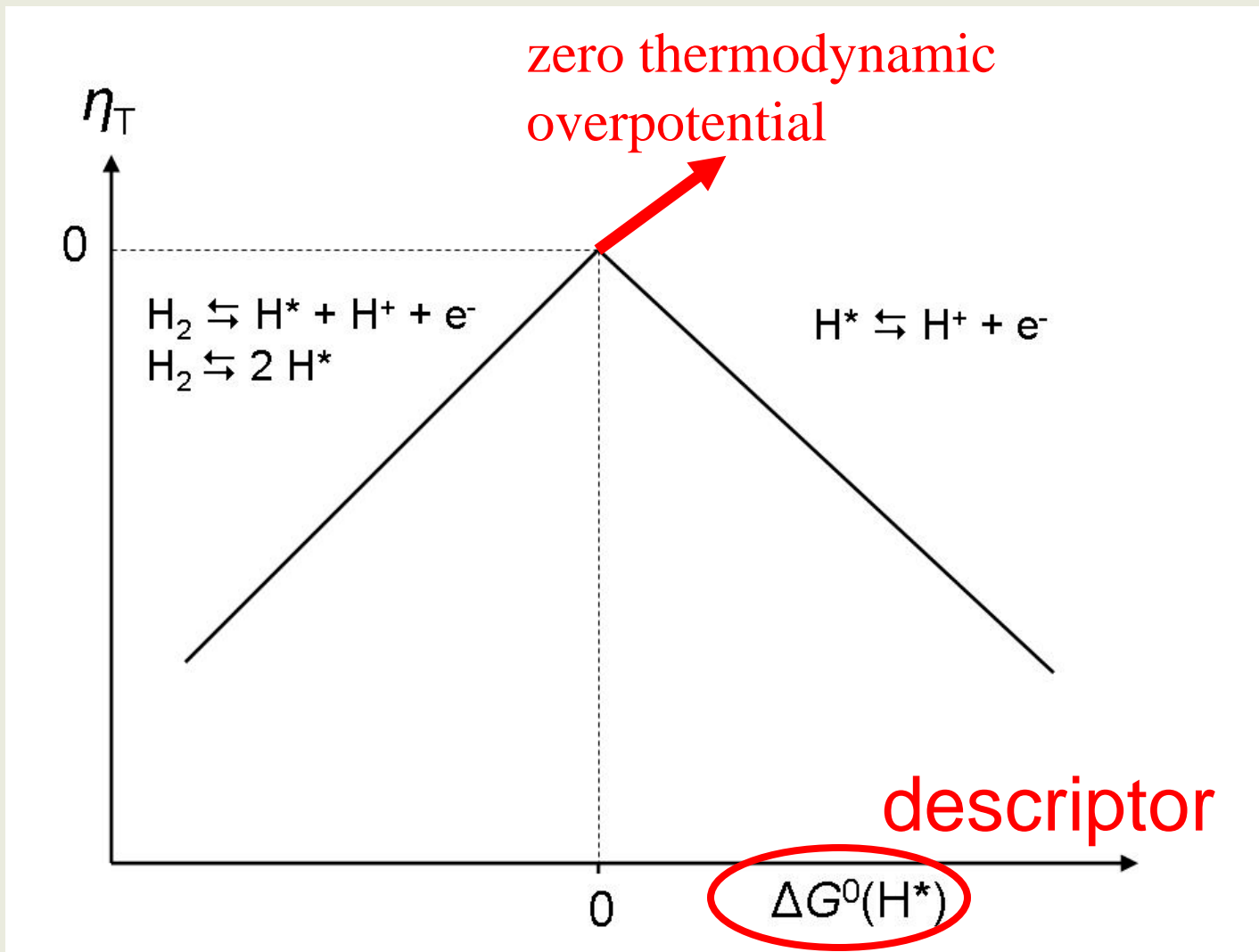
The reason is: If the adsorption is too weak, the catalyst has little effect; If too strong, the adsorbates will be unable to desorb from the surface. Hence, the interaction between reactants or products with surface should be neither too strong nor too weak.

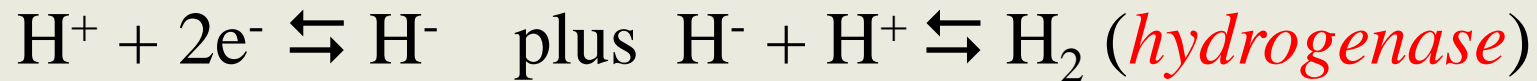# Sabatier Principle - Optimal basicity results in high carbonate yields (MMM 90, 314, 2006)

Efficient transformation of CO2 into useful chemicals

Thermodynamic Volcano Plot

R.Parsons,Trans.Faraday Soc. (1958); H.Gerischer (1958)   M.T.M.Koper, H.A.Heering, in press
J.K.Nørskov et al., J.Electrochem.Soc. (2004)   M.T.M.Koper, E.Bouwman, Angew.Chem.Int.Ed. (2010)

Generalization

$H^+ + e^- \leftrightarrows H_{ads}$ plus $2 H_{ads} \leftrightarrows H_2$ (*electrochemistry*)

$H^+ + 2e^- \leftrightarrows H^-$ plus $H^- + H^+ \leftrightarrows H_2$ (*hydrogenase*)

The optimal electrocatalyst is achieved if each step is thermodynamically neutral.

The H intermediate must bind to the catalyst with a bond strength equal to ½ E(H-H).

Experimental Volcano Plot for H₂ Evolution

J.Greeley, J.K.Nørskov, L.A.Kibler, A.M.El-Aziz, D.M.Kolb, ChemPhysChem 7 (2006) 1032
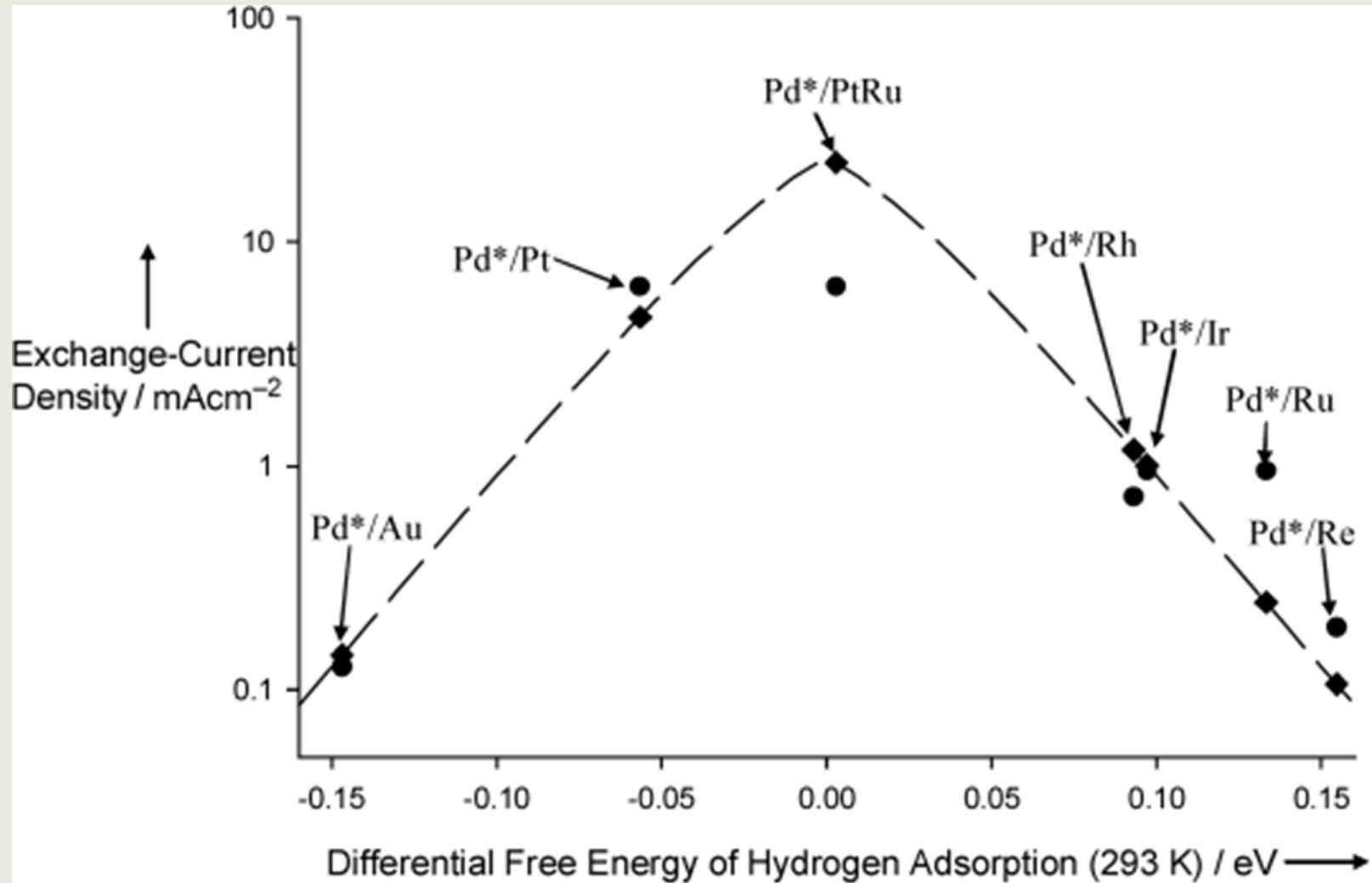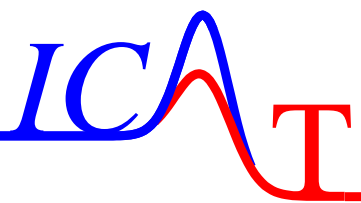
Surface Free Energy

- Surfaces are always covered by the component or structure that lowers surface free energy of the system.

- Clean, polycrystalline metals expose mostly their most densely packed surface.

- Open surfaces such as fcc (110) often reconstruct to a geometry in which the number of neighbors of a surface atom is maximized.

- In **alloys**, the component with the lower surface free energy segregates to the surface.

- Impurities in metals, such as C, O, or S, segregate to the surface.

- Small metal particles on an oxidic support sinter at elevated temperatures because loss of surface area means a lower total energy.

- In oxidic systems, the surface free energy provides a driving force for spreading over the surface if the active phase has a lower surface free energy than the support.

Alloys

minority element	bulk
Ru, Ir	Co
Fe, Ru, Rh, Ir, Pt	Ni
Ni, Pt	Cu
Fe, Co	Rh
Fe, Co, Ni, Cu	Pd
Co, Ni, Cu, Rh, Pd, Pt	Ag
Fe, Co, Ru	Ir
Fe, Co, Ni, Cu, Ru, Rh	Pt
Fe, Co, Ni, Cu, Rh, Pd, Pt	Au

minority element	bulk
Fe, Co	Cu
Ru, Rh, Ir	Pd
Fe, Ru, Ir	Ag
Ru, Ir	Au

alloy formation   **phase-separation**

minority atoms dissolve in bulk
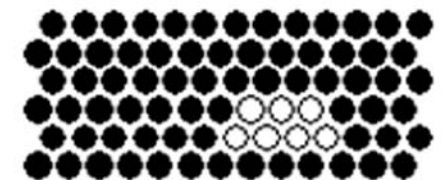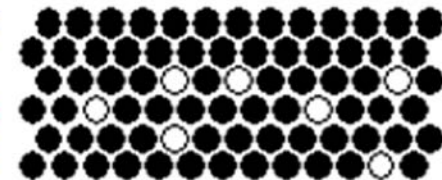
minority atoms segregate to surface
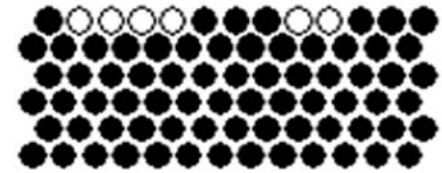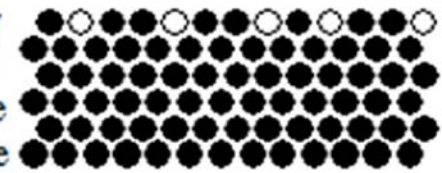
minority element	bulk
Co, Rh, Pd	Fe
Ag, Ir, Pt, Au	Fe
Rh, Pd, Ag, Pt, Au	Co
Cu, Pd, Ag, Au	Ni
Ag, Au	Cu
Fe, Co, Ni, Pt, Au	Ru
Ni, Pt	Rh
Au	Pd

minority element	bulk
Ni, Cu	Fe
C	Co
Cu, Pd, Ag	Ru
Cu, Pd, Ag	Rh
Ag	Pd
Cu, Pd, Ag, Pt, Au	Ir
Ag, Au	Pt
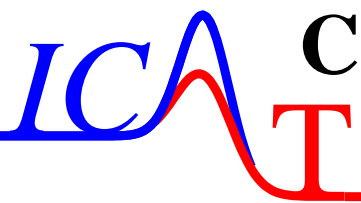
Characteristics of Small Particles and Porous Materials

1) The surface energy for each surface (h,k,l) is plotted in a polar plot so the length of the vector is proportional to the surface energy. $\gamma(hkl)$

2) At the end of the vector, a surface plane is defined orthogonal to the vector.

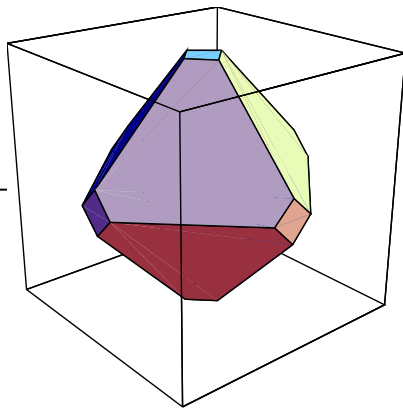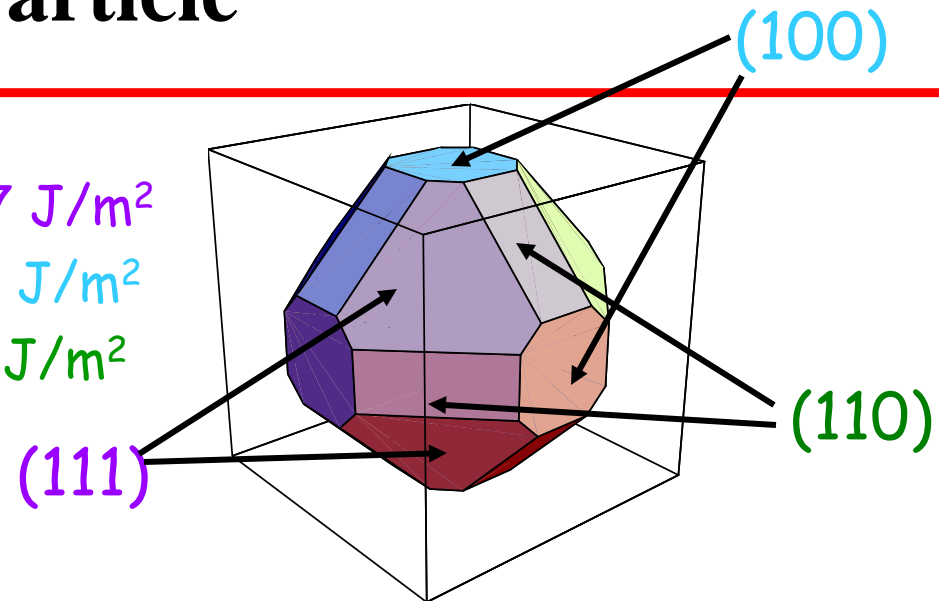3) **The inner envelope of these surfaces defines the equilibrium shape.**
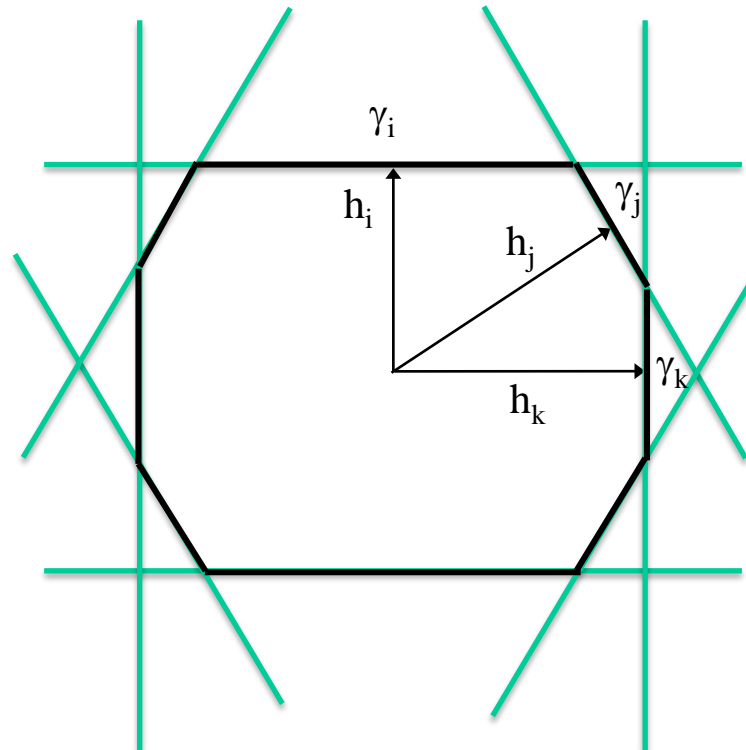
Free Particle

- Simulation for free fcc particle with (100) facet up:
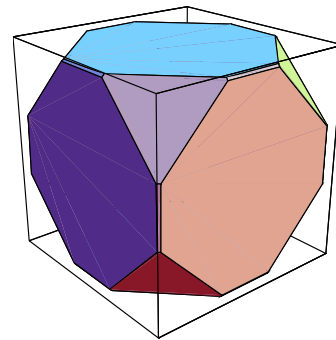
γ_{111}= 1.97 J/m^2
γ_{100}= 2.2 J/m^2
γ_{110}= 2.1 J/m^2

(100)

(110)

(111)

➡ γ_{111}= 1.5 J/m^2
γ_{100}= 2.2 J/m^2
γ_{110}= 2.1 J/m^2

➡ γ_{111}= 1.97 J/m^2
γ_{100}= 1.5 J/m^2
γ_{110}= 2.1 J/m^2
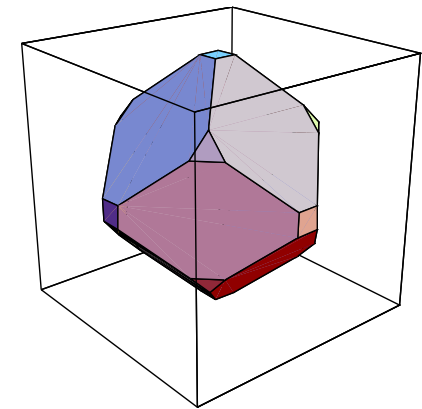
γ_{111}= 1.97 J/m^2
γ_{100}= 2.2 J/m^2
➡ γ_{110}= 1.7 J/m^2

The Wulff Construction
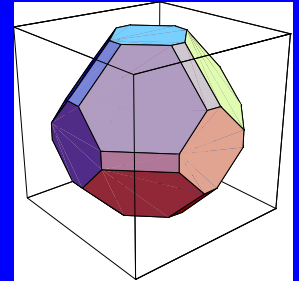
$$\Delta h_i = \frac{\beta h_i}{\gamma_i}$$

β is the adhesion energy at the surface

$\Delta h_j = 0$

No Wetting

Complete Wetting

$\Delta h_j > 2h_i$
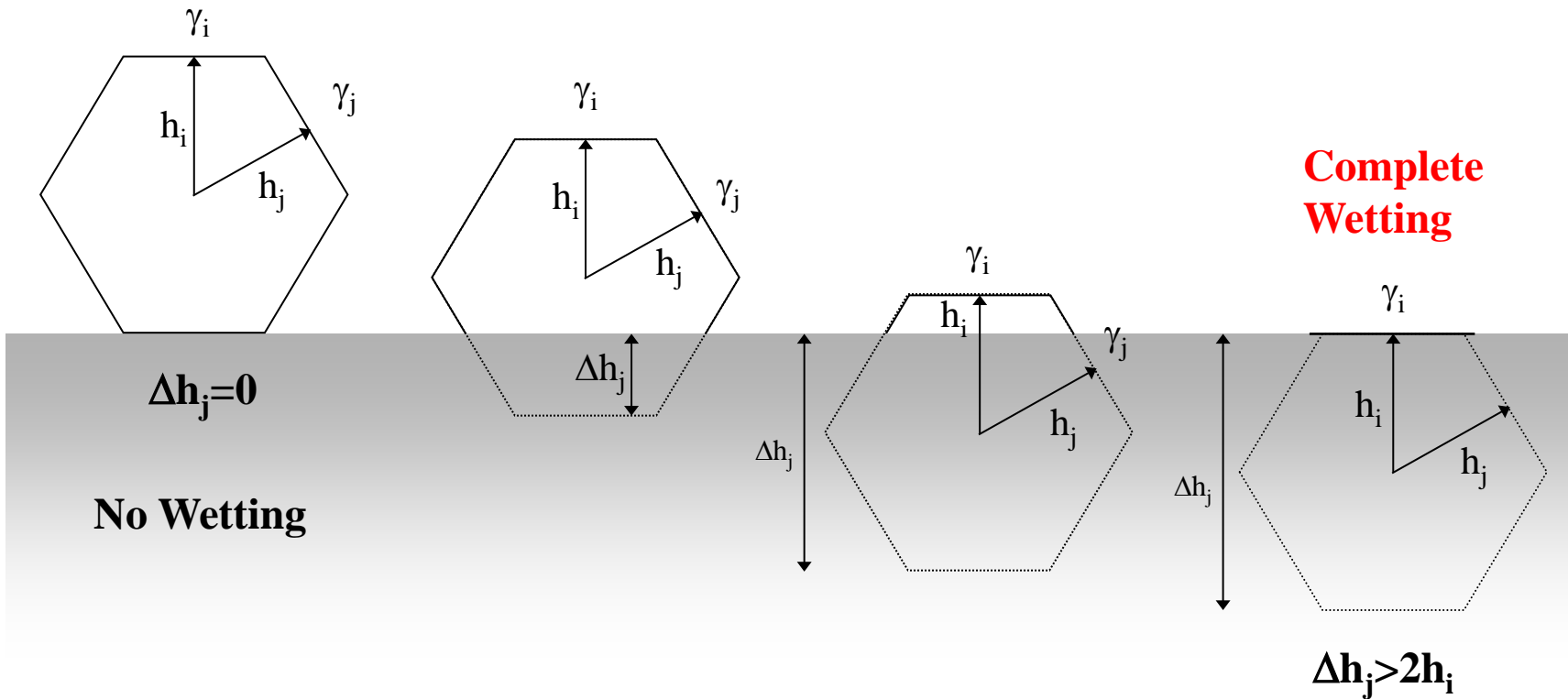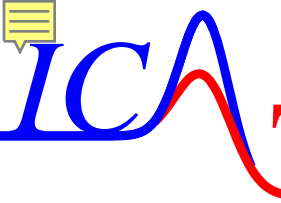
$$\gamma_s = \gamma_{interface} - \gamma_{substrate}$$

(100)

(100)

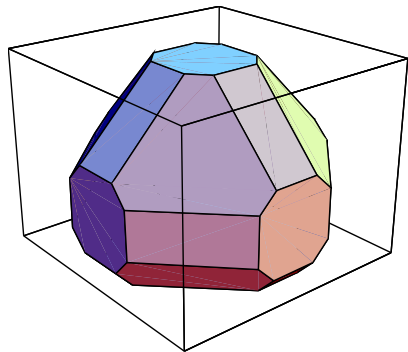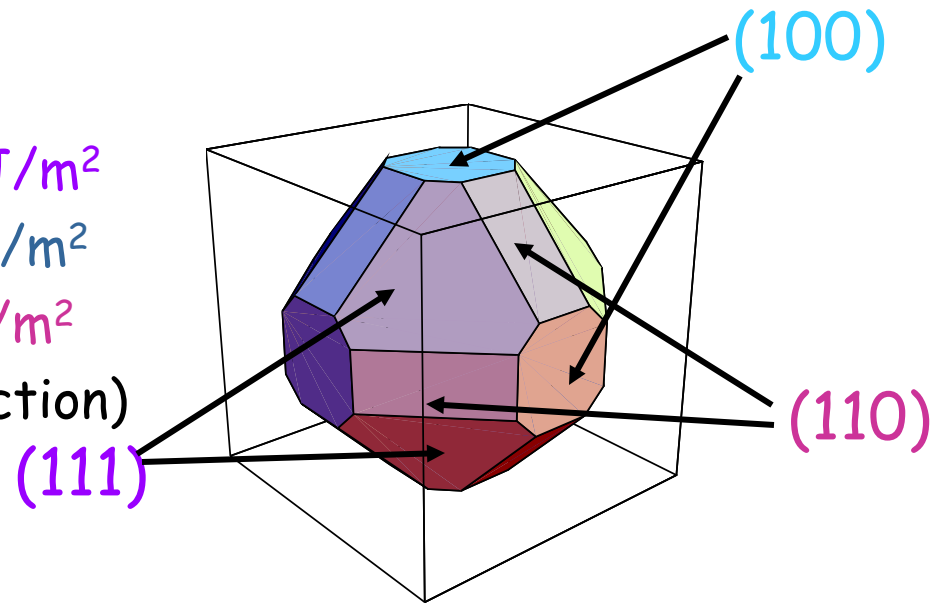(111) (110)

(100)

γ_s
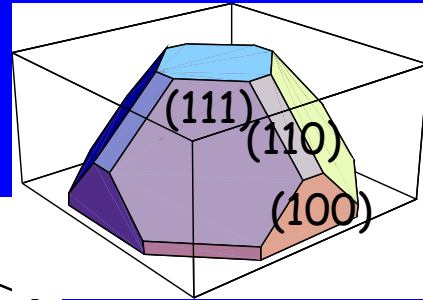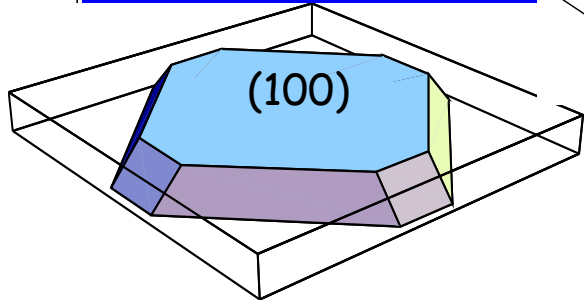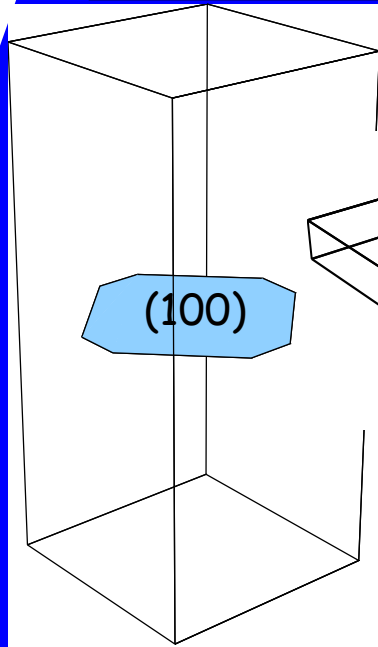
-1.0   -0.8   0.0   +1.0

Top and contact planes are (100), calculated Cu energies

Adsorbed Particle

- Simulation for adsorbed fcc particle with (100) facet up:

γ_{111}= 1.97 J/m^2
γ_{100}= 2.2 J/m^2
γ_{110}= 2.1 J/m^2
(no interaction)

(100)

(110)

(111)

A little interaction
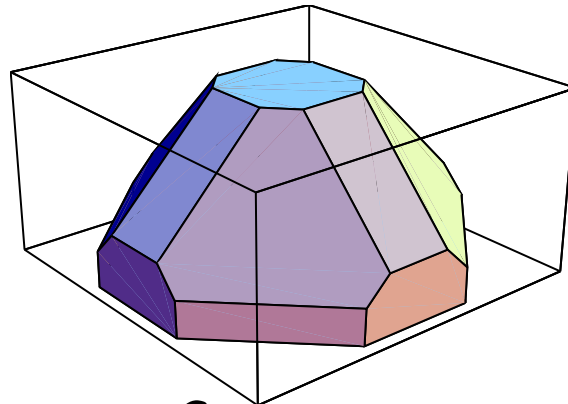
Some interaction
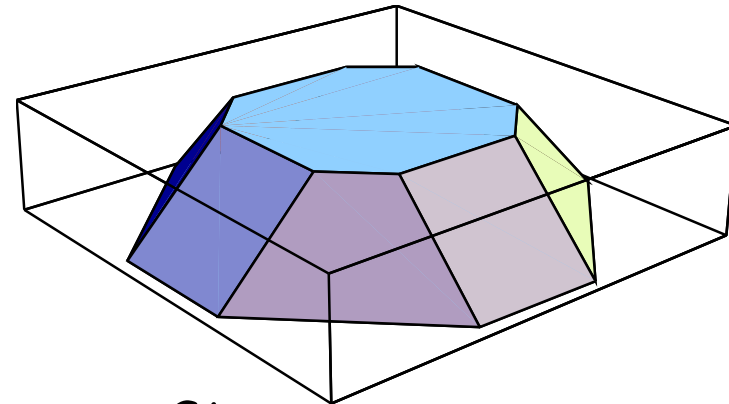
Strong interaction

Examples of Particles on Surfaces

Dependence upon h/w

(111) facet

(100) facet

h/w = 0.2
a/b = 0.4

h/w = 0.1

h/w = 0.5

a/b = 0.2

a/b = 0.8

Dependence upon a/b
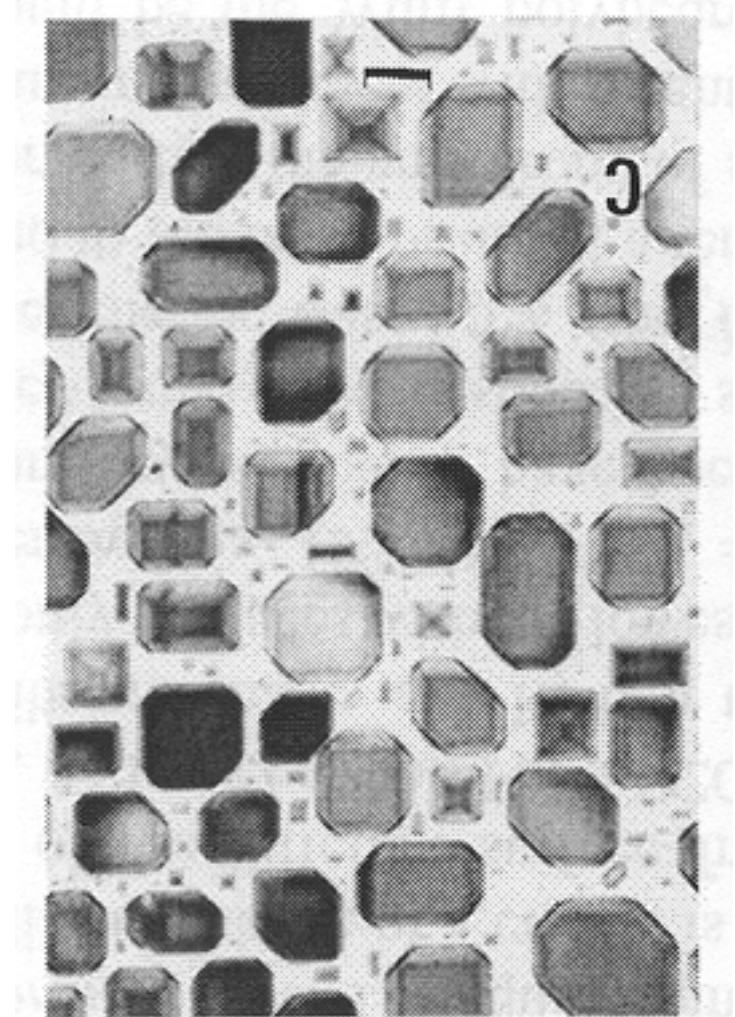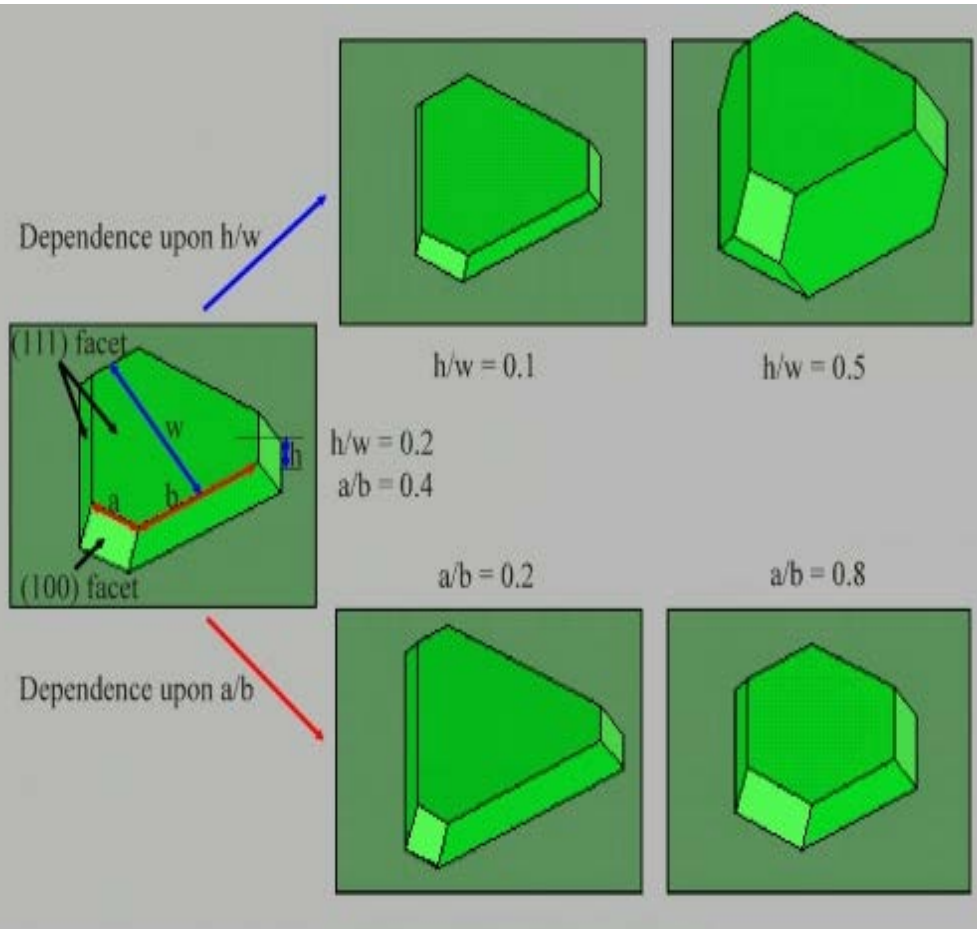
Adhesion Energy
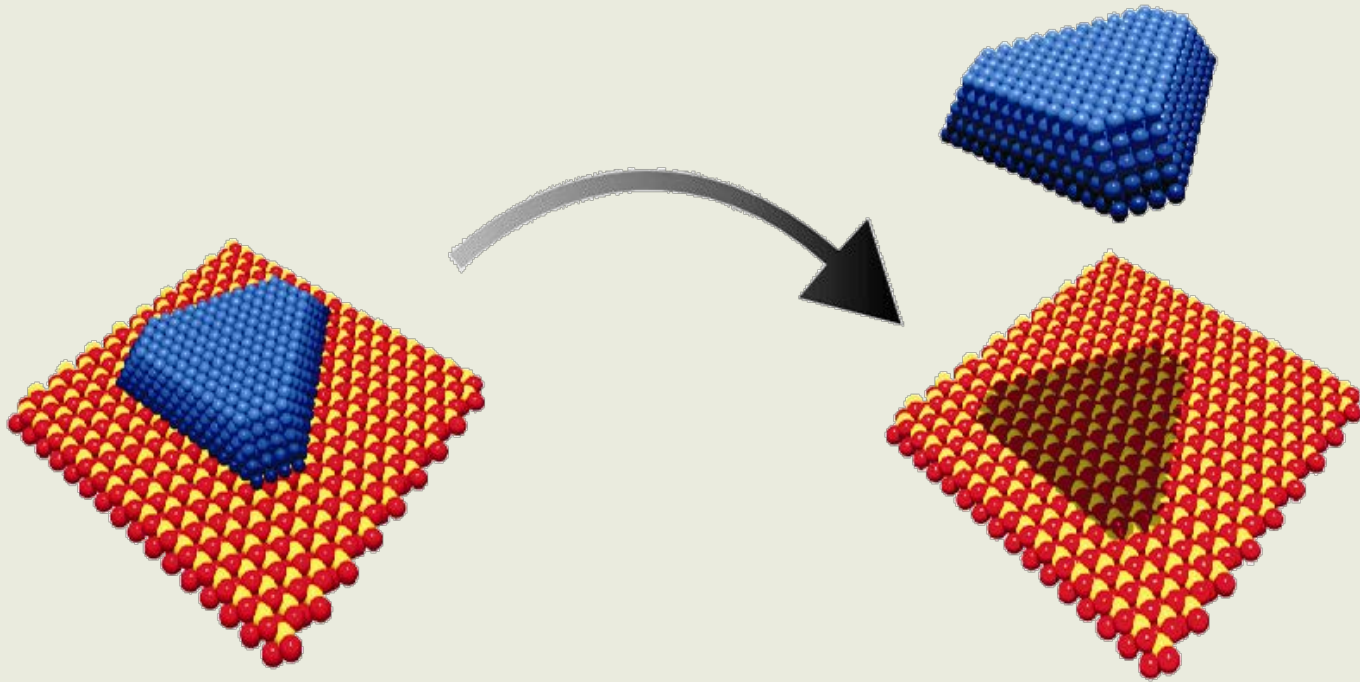
$$W_{adh} = \gamma_{100} + \gamma_{substrate} - \gamma_{interface}$$

The energy per unit area needed to pull the system into its constituents

Adsorption Mechanisms

Langmuir-Hinshelwood mechanisms:

1. Adsorption from the gas-phase

2. Desorption to the gas-phase

3. Dissociation of molecules at the surface

4. Reactions between adsorbed molecules

Two Questions:

• Does the reaction has a Langmuir-Hinshelwood mechanism?

• What is the precise nature of the reaction steps?
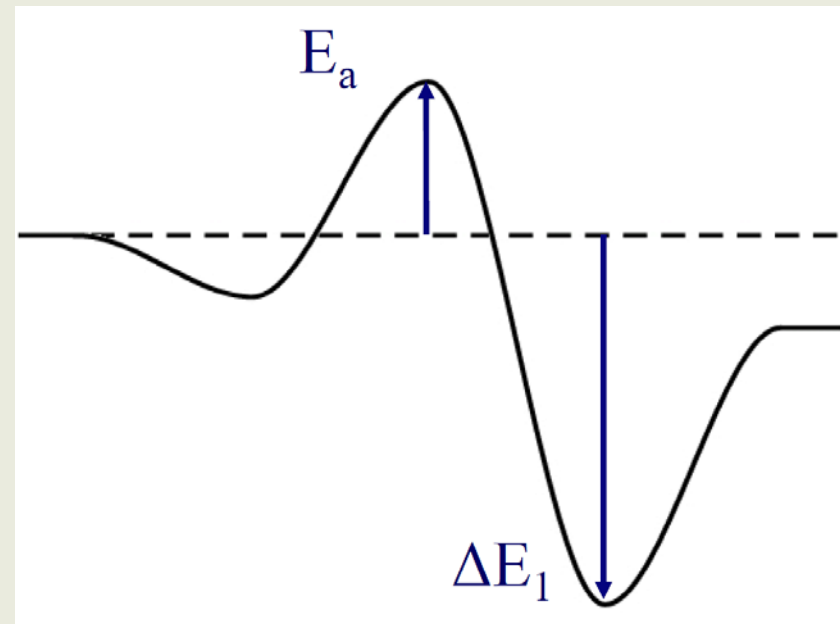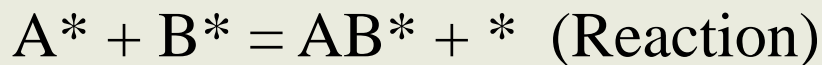
These questions **cannot be solved** without experimental or computational studies

Langmuir-Hinshelwood mechanism

Example: The Reaction $A_2 + 2B = 2AB$

which may have the following mechanism

(*: stands for a vacant site)

$A_2 + * = A_2*$ (A2 adsorption)

$A_2* + * = 2A*$ (Dissociation)

$B + * = B*$ (B adsorption)

$A* + B* = AB* + *$ (Reaction)
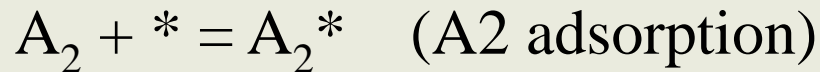
$AB* = AB + *$ (Desorption)

Eley-Rideal Mechanism

1. Adsorption from the gas-phase

2. Desorption to the gas-phase

3. Dissociation of molecules at the surface

4. Reactions between adsorbed molecules

5. Reactions between gas and adsorbed molecules

The last step is not included in a Langmuir-Hinshelwood mechanism.

Example with the reaction

$$A_2 + 2B = 2AB$$

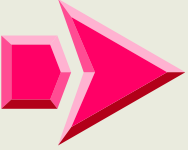which may have the following Eley-Rideal mechanism

$$A_2 + * = A_2*$$
$$A_2* + * = 2A*$$

$$A* + B = AB + *$$
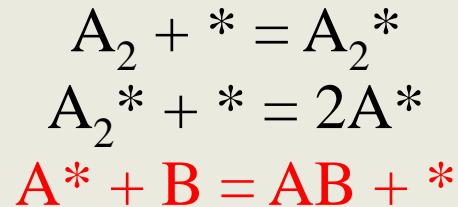
The last step is the direct reaction between the adsorbed molecule $A*$ and the gas-molecule B.

Eley-Rideal or Langmuir-Hinshelwood?

For the Eley-Rideal mechanism:

the rate will increase with increasing coverage until the surface is completely covered by A*.

For the Langmuir-Hinshelwood mechanism:

the rate will go through a maximum and end up at zero, when the surface is completely covered by A*.
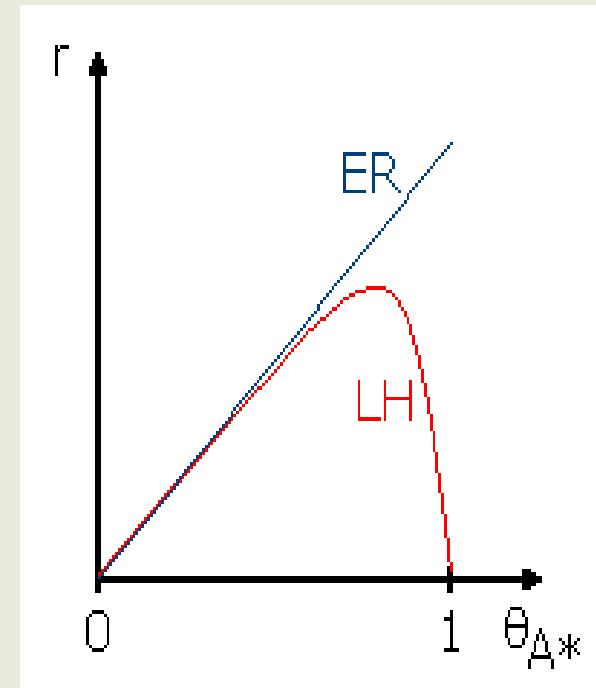
This happens because the step B + * = B* cannot proceed when A* blocks all sites.

The trick is that the step **B + * = B*** requires a free site.

Overview on Computational Catalyst Design

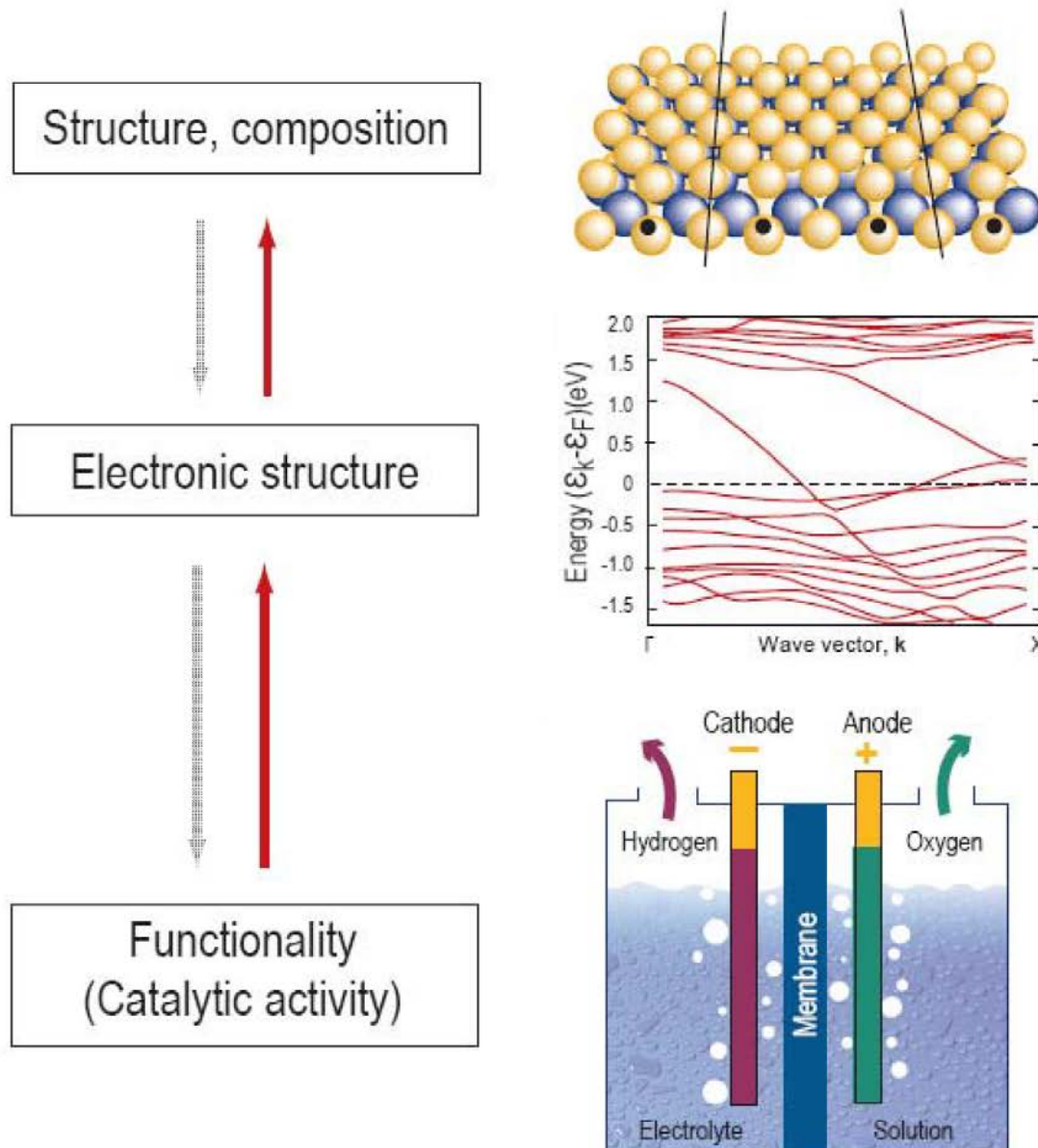# Computational Design at Atomic Scale

Nørskov, Bligaard
Rossmeisl, Christensen
Nature Chemistry
1, 37-46 (2009)

Heterogeneous Catalysis
Opportunities and challenges

J. K. Nørskov
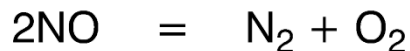
Center for Atomic-scale Materials Physics
Technical University of Denmark
norskov@fysik.dtu.dk now at Stanford)

- Challenges
    - Societal needs
    - Developing the basic understanding

- Opportunities
    - Designing at the nano-scale

Challenges I

Dream reactions waiting for a catalyst:

$$CH_4 + 1/2 O_2 = CH_3OH$$

$$CH_4 + 1/2 O_2 = CO + 2H_2$$

$$2CH_4 + O_2 = C_2H_4 + 2H_2O$$

$$n\,CH_4 = C_nH_{2n+2} + (2n-2)\,H_2$$

$$DME = C_2H_5OH$$

$$H_2 + O_2 = H_2O_2$$

$$2NO = N_2 + O_2$$

$$2N_2 + 2H_2O + 5O_2 = 4HNO_3$$
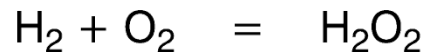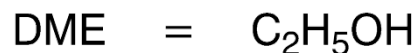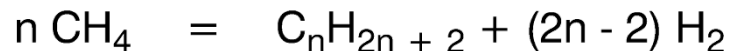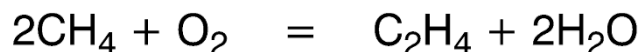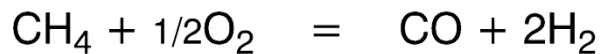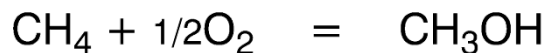
Challenges II

Dreaming on ….

- Heterogeneous catalysts for assymmetric synthesis
- Photolytic water splitting (hydrogen economy)
- Biomimetics, synthetic enzymes
- Non-thermal processes in general
  (e.g. electro- and photocatalysis)
- …

See: E. Derouane, CATTECH **5**, 226 (2001)

Challenges III

The science of heterogeneous catalysis:

- A comprehensive scientific basis
    - Much has been done
    - Much more is needed (oxides, size effects, photocatalysis, electrocatalysis, relation to homogeneous and enzyme catalysis …)
- Making the insight useful!
    - The ultimate test

Systematic "Computational Design"

- Direct computational search
- Data base screening
- Rational catalyst design: Discovery on the basis of insight via Descriptor-based search

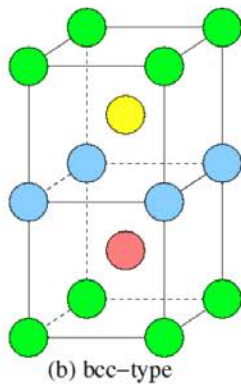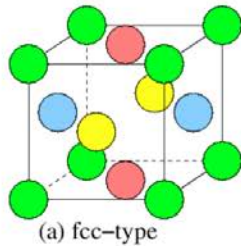# Direct Computational Search

Pick a set of structures/compositions

↓

Calculate their properties

Good enough ?

No ! → Choose better Structures/compositions

Yes!

Experimental testing
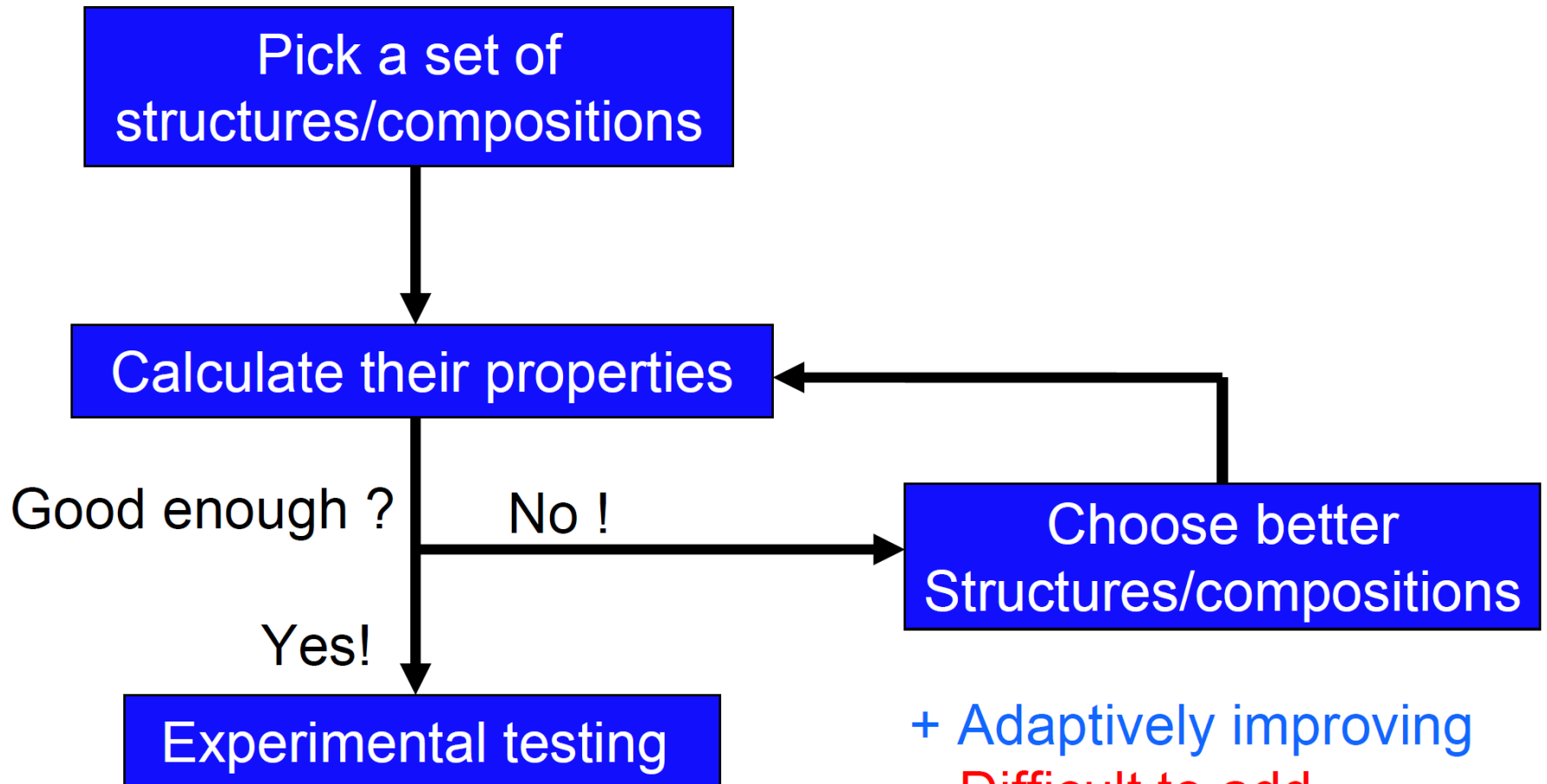
+ Adaptively improving

- Difficult to add constraints after a run

Direct Computational Search
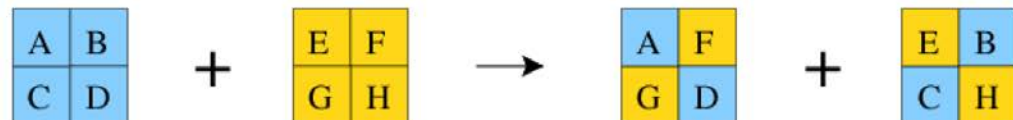
Evolutionary Algorithm

Four atom arrangements

(a) fcc–type

(b) bcc–type

(a) Gene pool

Al	Si								
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

(b) Individual

A	B
C	D

(c) Mating scheme

A	B		E	F	→	A	F		E	B
C	D	+	G	H		G	D	+	C	H

(d) Mutation scheme

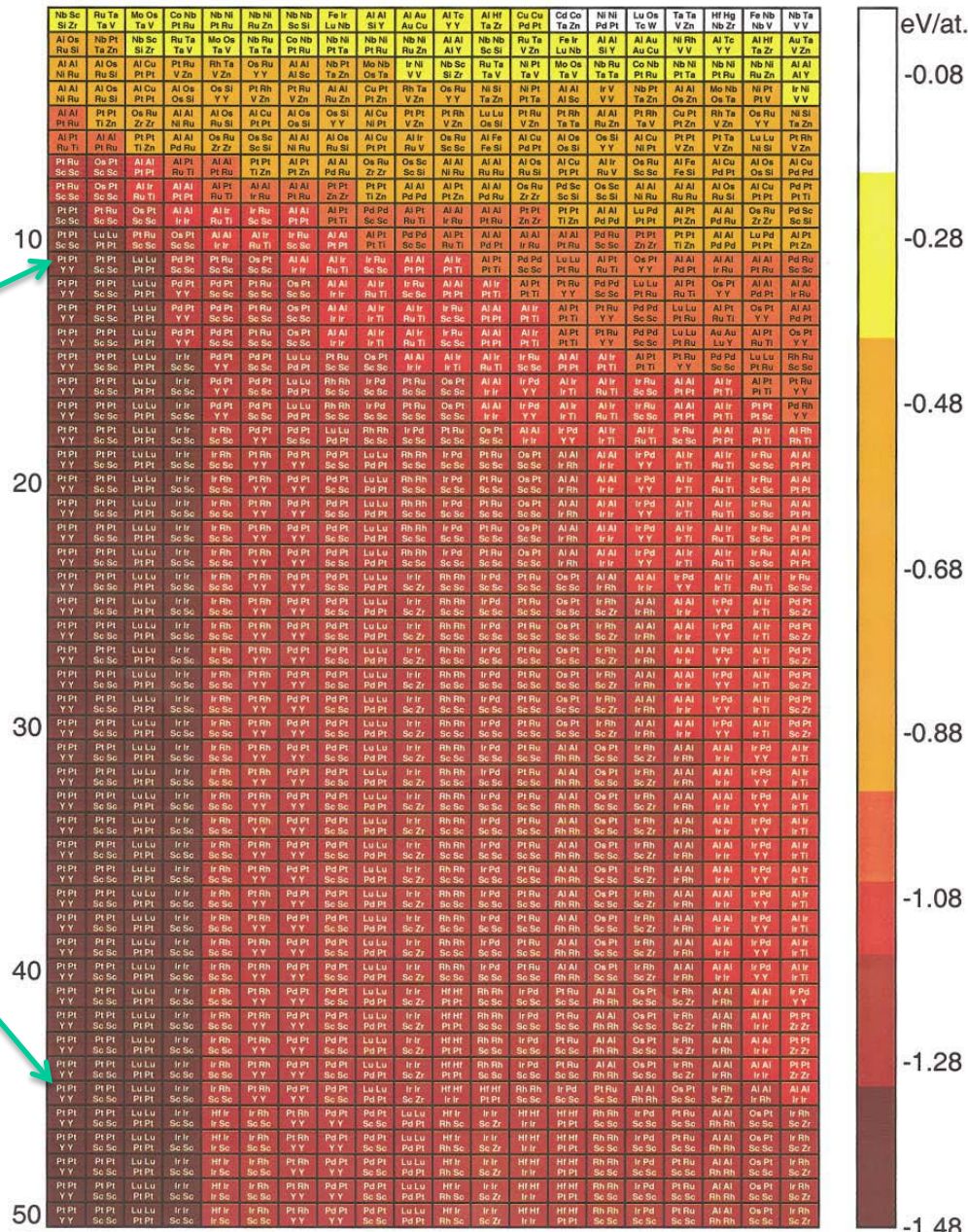| A	F	→	A	X
G	D		G	D

Johannessen, Bligaard, Ruban, Skriver, Jacobsen, Nørskov, *Phys. Rev. Lett.* **88,** 255506 (2002)

Direct Computational Search
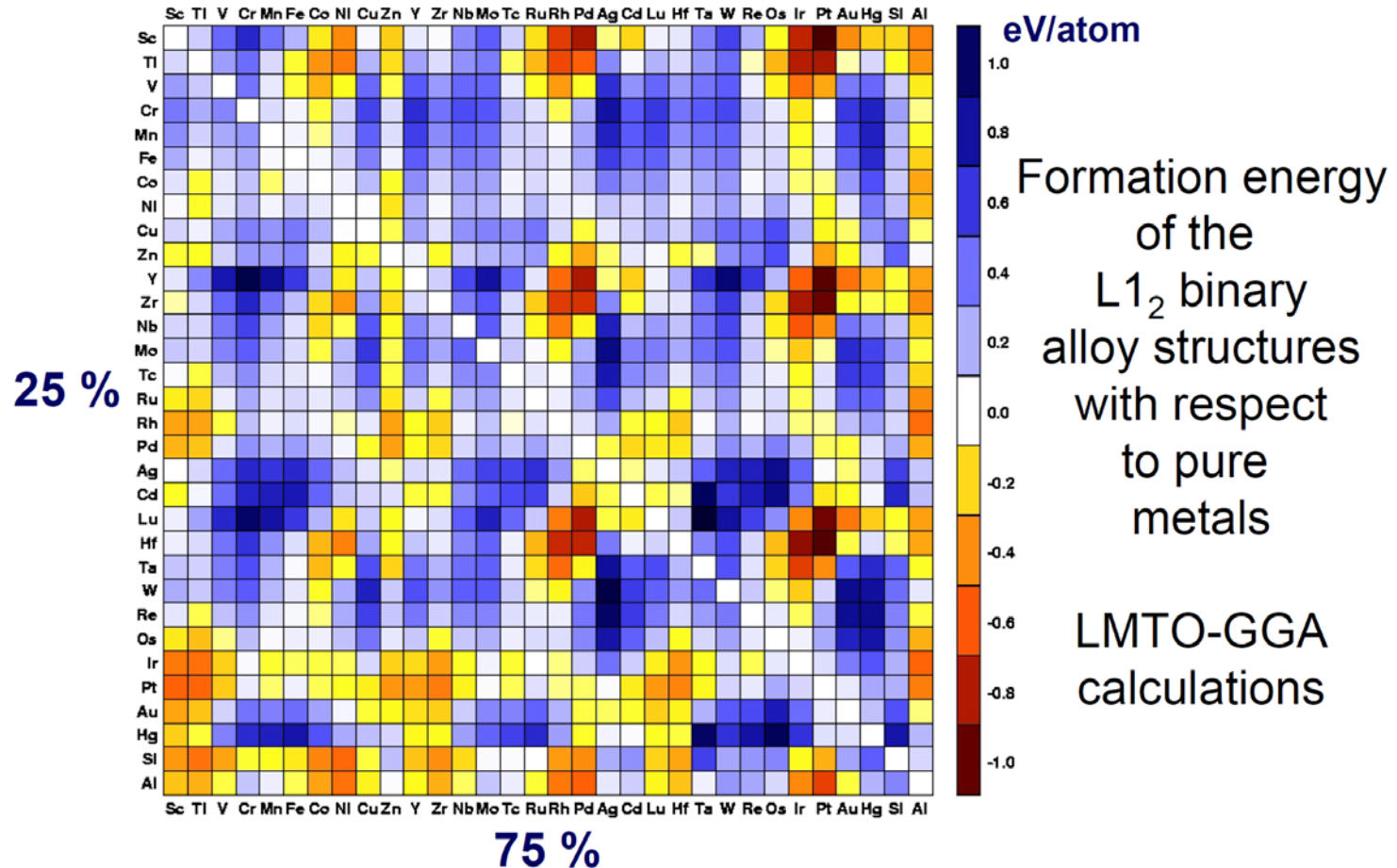
Evolutionary Algorithm

The most stable 4-component
ordered metal alloy ABCD is
found in the 11th
generation, and the 20 most
stable
have been determined in 45
generations.

Direct Computational Search

Structural stability of ordered alloys

Enthalpies of formation for the fcc-like $L1_2$ structure of binary alloys. Horizontally are the elements of 75% abundance in the binary alloy, vertically are the elements of 25% abundance.

Data driven methods

- **High throughput screening**
  - Direct testing of many catalysts, fast, efficiently
- **Data mining**
  - Correlating catalytic activity/ selectivity/durability to descriptors that can be tabulated

Screening of Computed Data

Calculate properties for a large number of systems
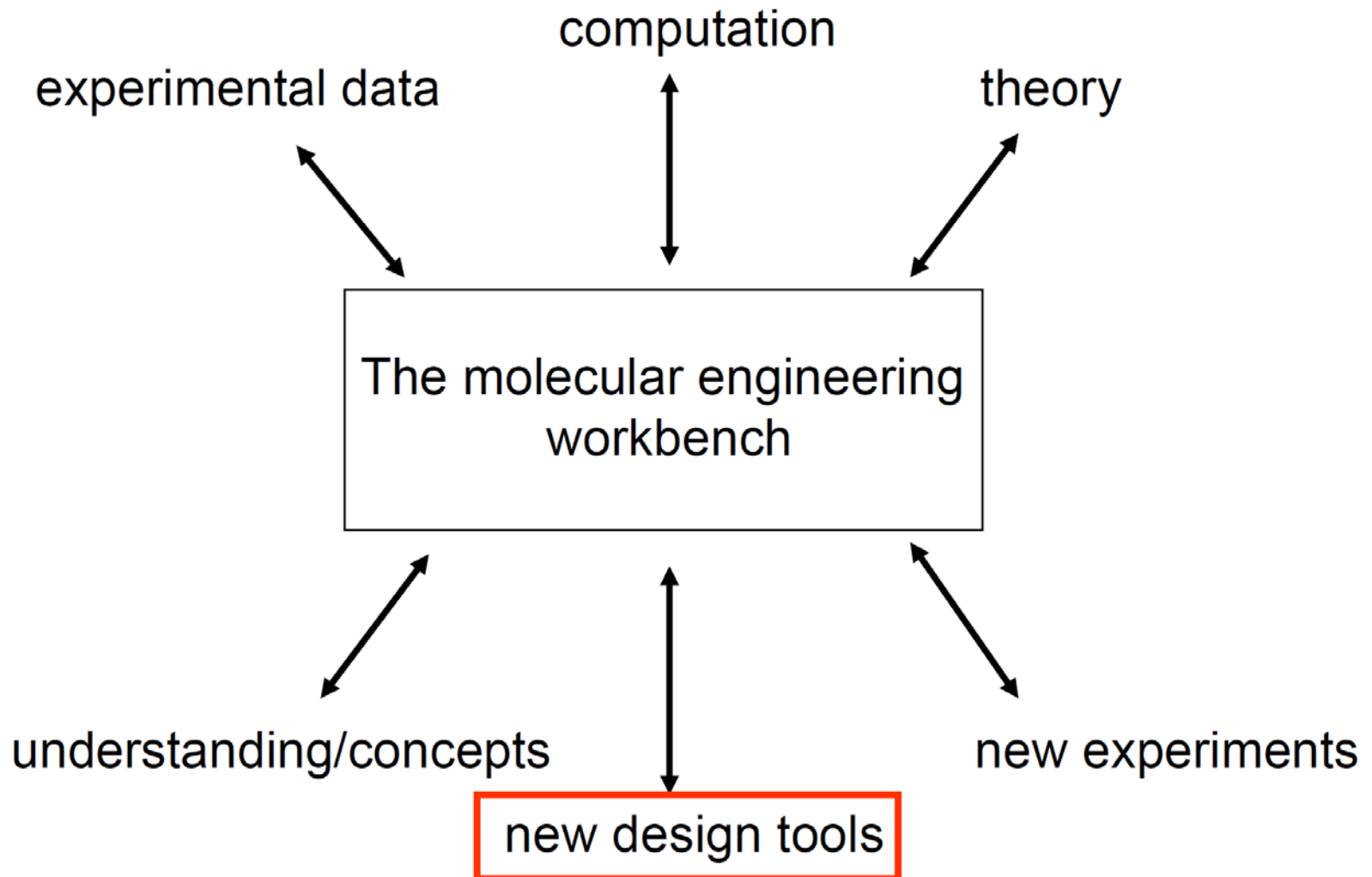
↓

Look for systems having good qualities

↓

Experimental testing
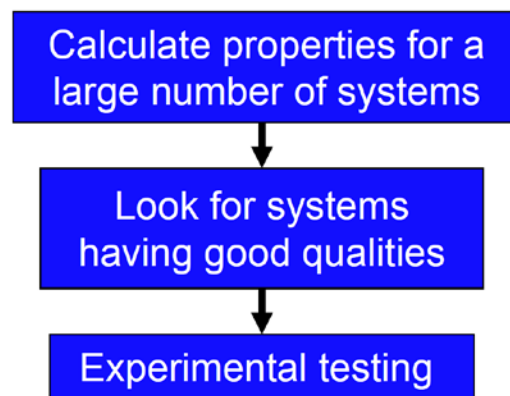
+ Ease of reusing data
- Difficult to include enough interesting systems

Data driven methods
The vision

The Computational Materials Data Repository

Alloy Formation Energies (LMTO)
- quaternary (43081)
- ternary (17563)
- binary (3473)

Alloy Formation Energies (EMTO)
- binary (8278)
- pure (333)

Segregation energies (1203)

Adsorption energies (7641)
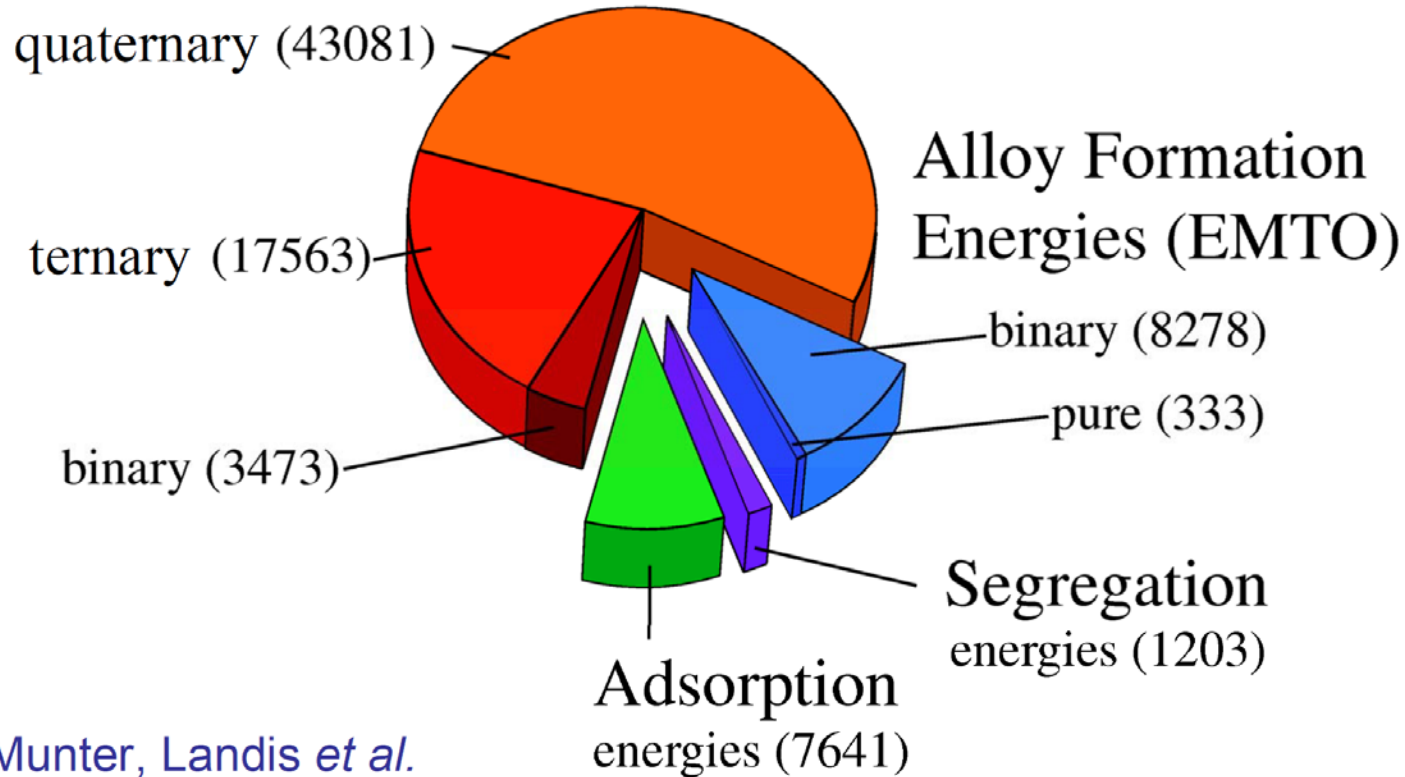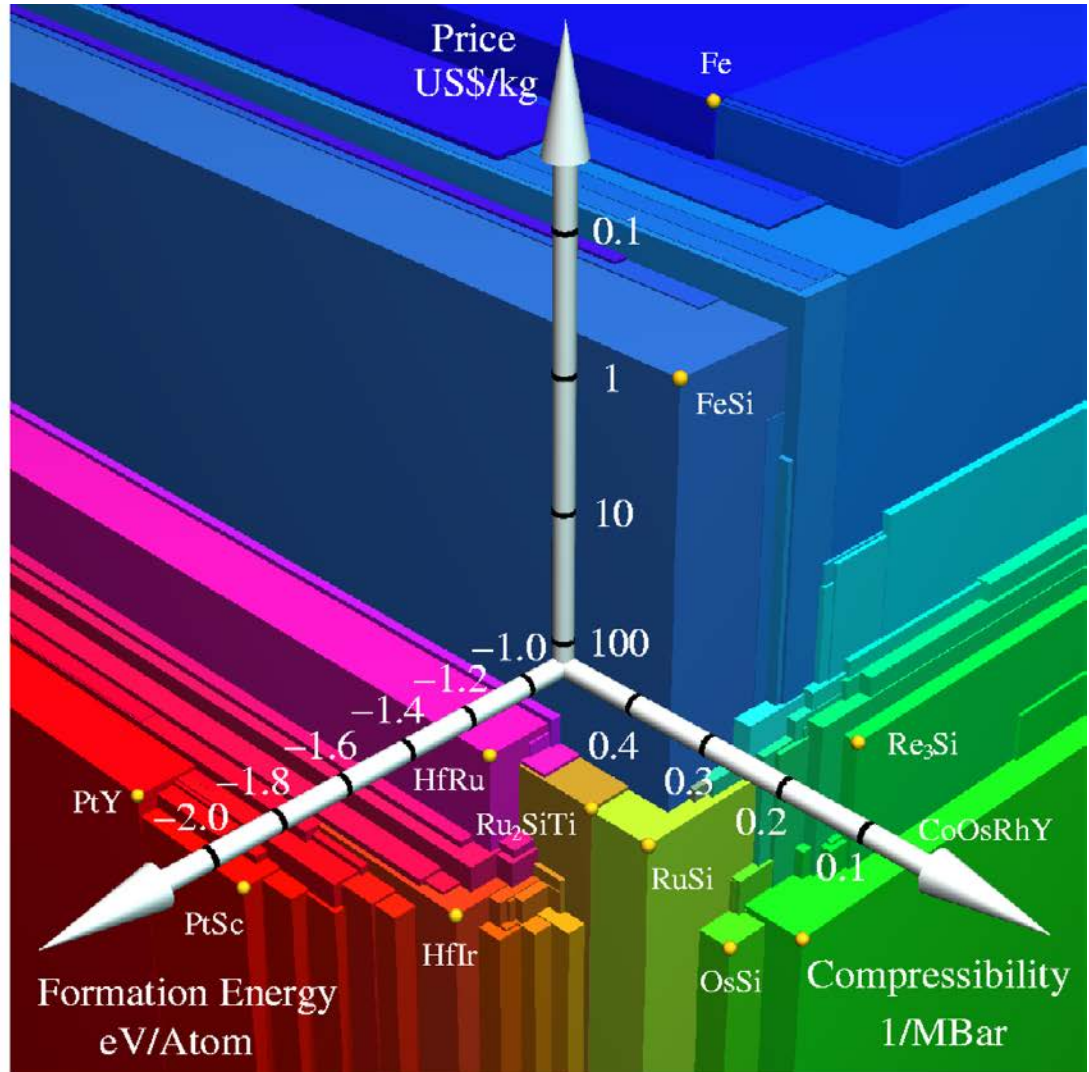
Munter, Landis *et al.*

→ International collaboration needed to reach relevant data base sizes

Data driven methods

Pareto optimality

(as a method for searching databases)

The 82 alloys with the most relevant properties are easily obtained from the full database of > 64,000 alloys.

Bligaard, Johannessen, Ruban, Skriver, Jacobsen, Nørskov, *App. Phys. Lett.* **83,** 4527 (2003)

Rational catalyst design

1. What determines the catalytic activity/selectivity/lifetime ?

2. How can we affect it?

- We have tremendous new possibilities

Understanding of trends

➢ The chemisorption bond
 –The d band model
 –The interpolation principle

➢ Activation barriers for surface reactions
 –Electronic and geometrical effects

➢ Correlations –Brønsted-Evans-Polanyi (BEP) relations
➢ Linking trends in energetics to trends in reactivity
 –Volcano plots
 –The Sabatier analysis

➢ Attempts at design

Descriptor-based search

The object of the game…

- Find sets of descriptors $\{D_{ik, \; k=1,2,..}\}$ of solid materials M_i , and a mathematical model F such that A_{ij} being the Turn Over Frequency of M_i as catalyst for the reaction j at operationg conditions C_j one has:

$$A_{ij}\left\{M_i, C_j\right\} = F\left(\left\{D_{ik}\right\}, C_j\right)$$

- Identify ranges of D_{ik} that maximize F

- Screen Databases of Materials Properties before screening real materials

- Better if one descriptor is sufficient, but do not take it for granted

- Much better if F has a sound physical basis

- Adsorbate/substrate bond strengths should provide good descriptors according to the **Sabatier principle**

The origin of catalytic trends: the *d*-band model
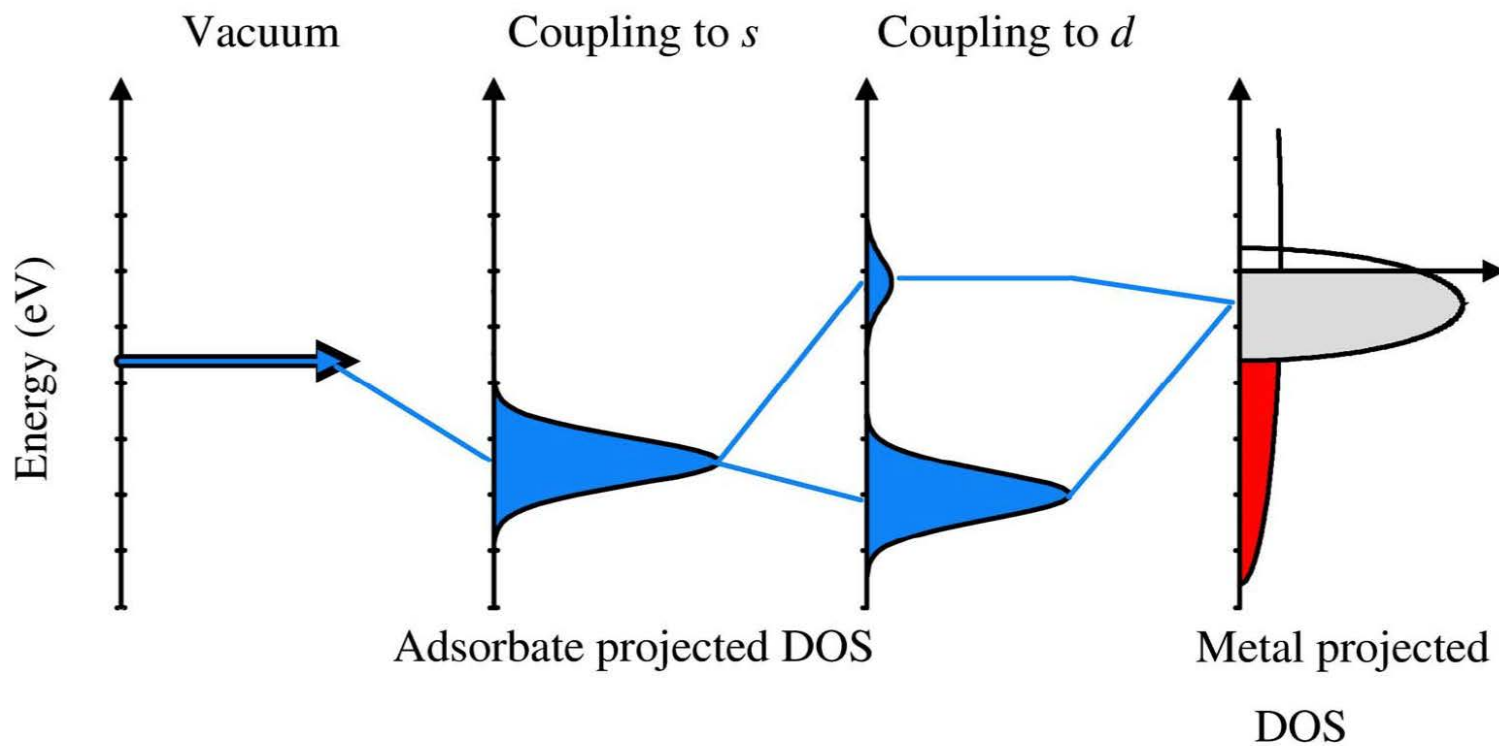
Hammer, Nørskov, Nature 376, 238 (1995)
Hammer, Nørskov, Adv. Catal. 45, 71 (2000)
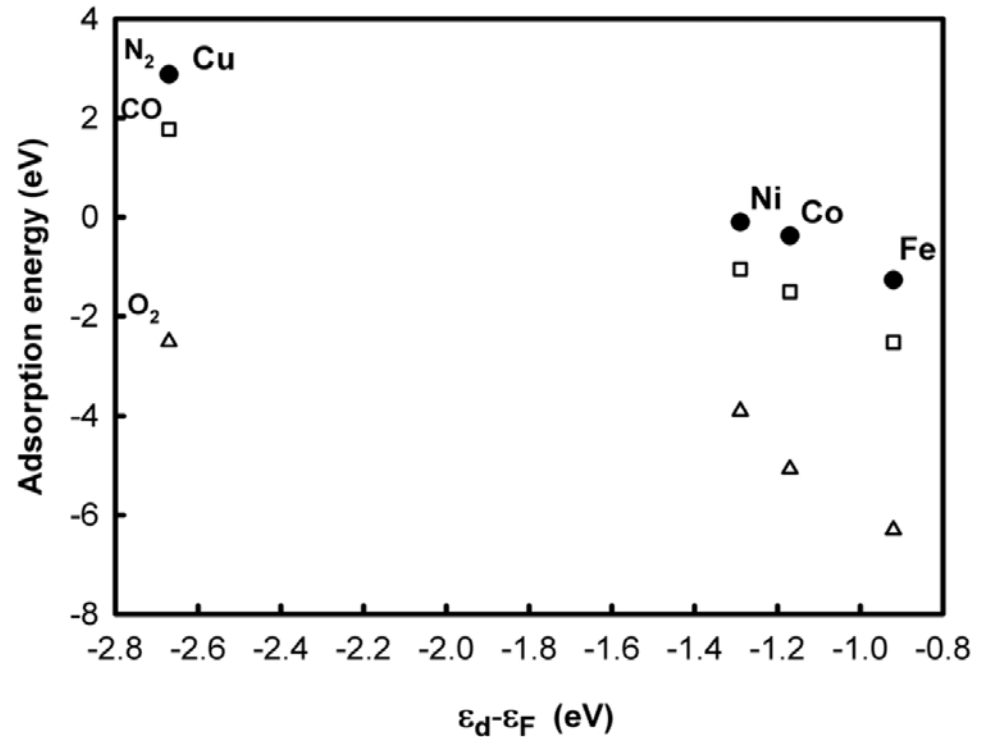Bligaard, Nørskov in Chemical bonding at surfaces, Elsevier (2008)

The 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
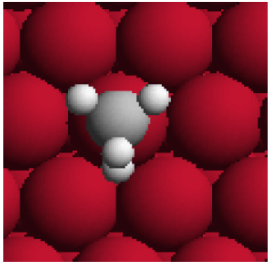

Nilsson, Pettersson, Hammer, Bligaard, Christensen, Nørskov
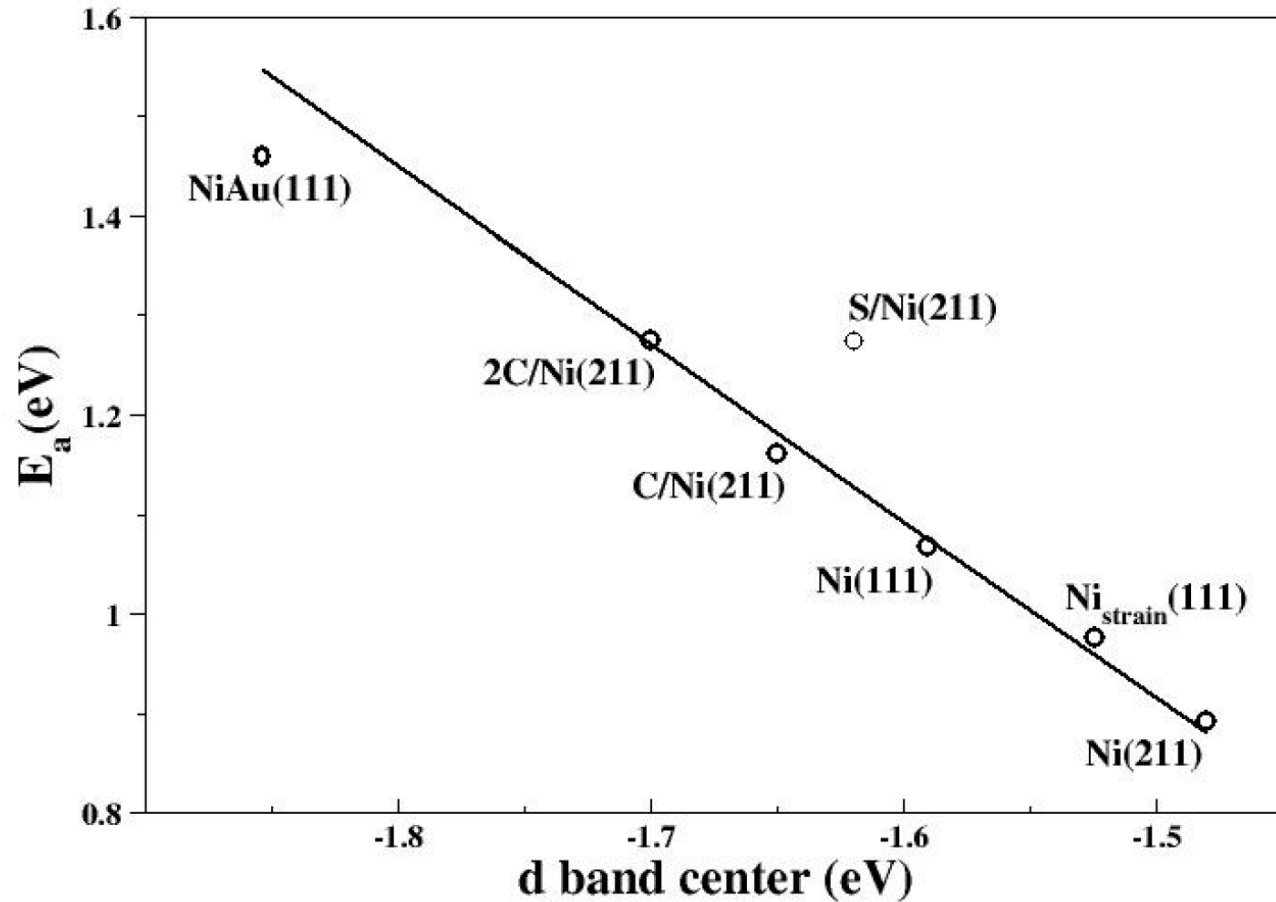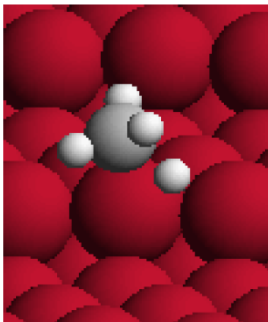*Catal. Lett.* **100**, 111 (2005)

Similar trends for activation energies

Methane dissociation on Ni surfaces
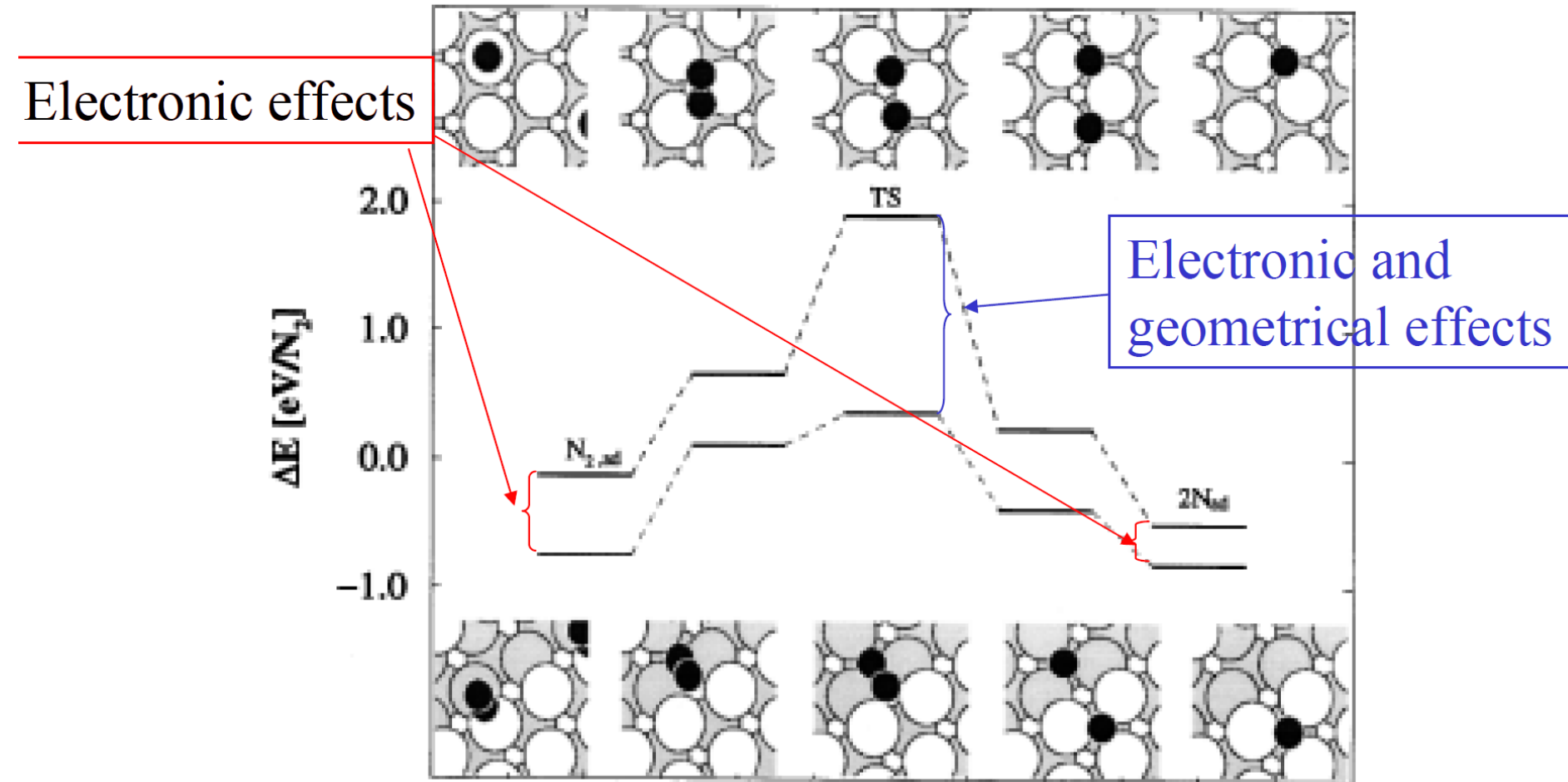
Abild-Pedersen, Greeley, Nørskov, Catal. Lett. 105, 9 (2005)

The electronic and geometrical factors in surface reactivity

N$_2$ dissociation on Ru surfaces:

Electronic effects

Electronic and geometrical effects

ΔE [eV/N$_2$]

2.0

1.0

0.0

−1.0

TS

N$_{2,ad}$

2N$_{ad}$
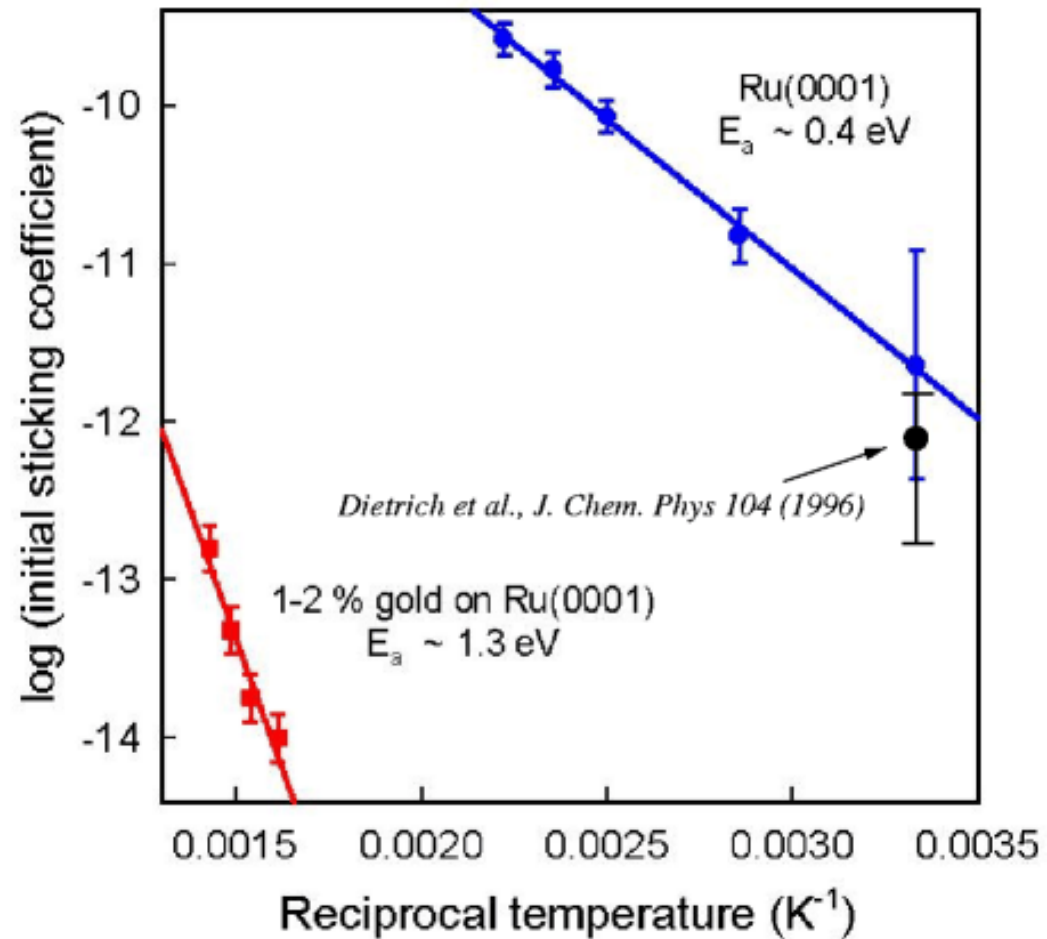
Experimental evidence for step-effect

Au decorates steps:

Hwang, Schroder, Gunther, Behm, Phys. Rev. Lett. 67, 3279 (1991)

Figure labels: Ru(0001) $E_a \sim 0.4$ eV; 1-2 % gold on Ru(0001) $E_a \sim 1.3$ eV; Dietrich et al., J. Chem. Phys 104 (1996). Axes: log (initial sticking coefficient) vs Reciprocal temperature (K^{-1}).
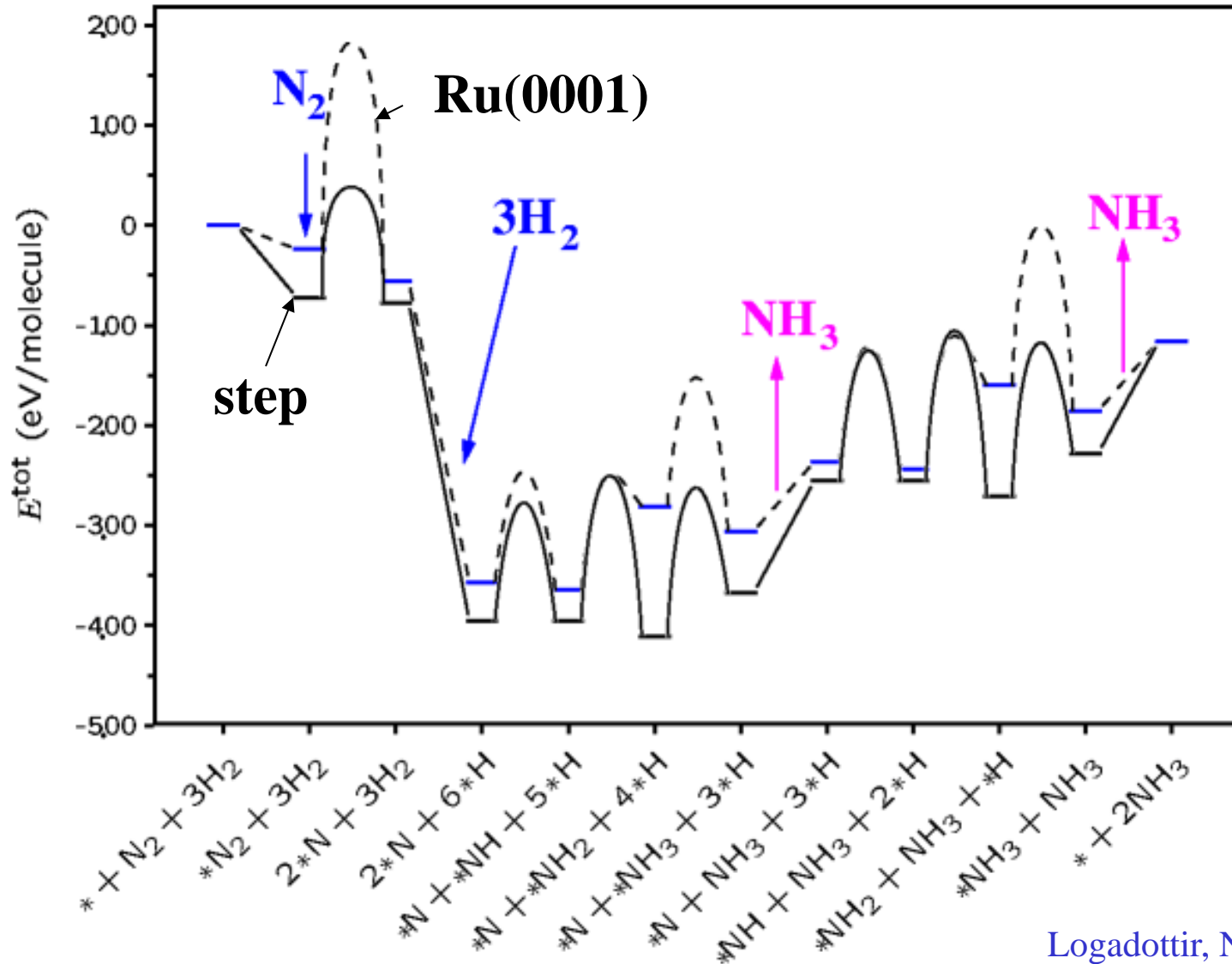
Dahl, Logadottir, Egeberg, Larsen, Chorkendorff, Törnqvist, Nørskov, Phys.Rev.Lett. **83**, 1814 (1999)
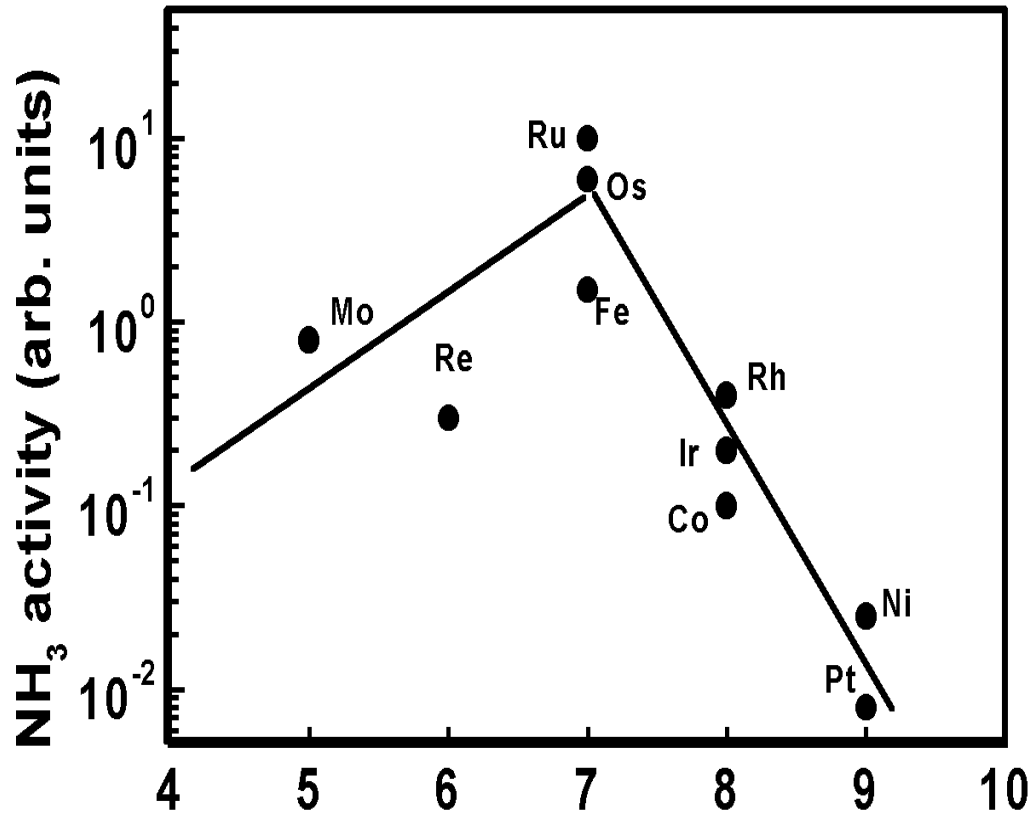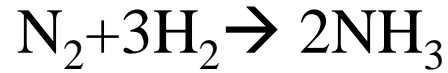
The Brønsted-Evans-Polanyi (BEP) Relation

ΔE [eV/N$_2$] : **Dissociative Adsorption Energy per N2**
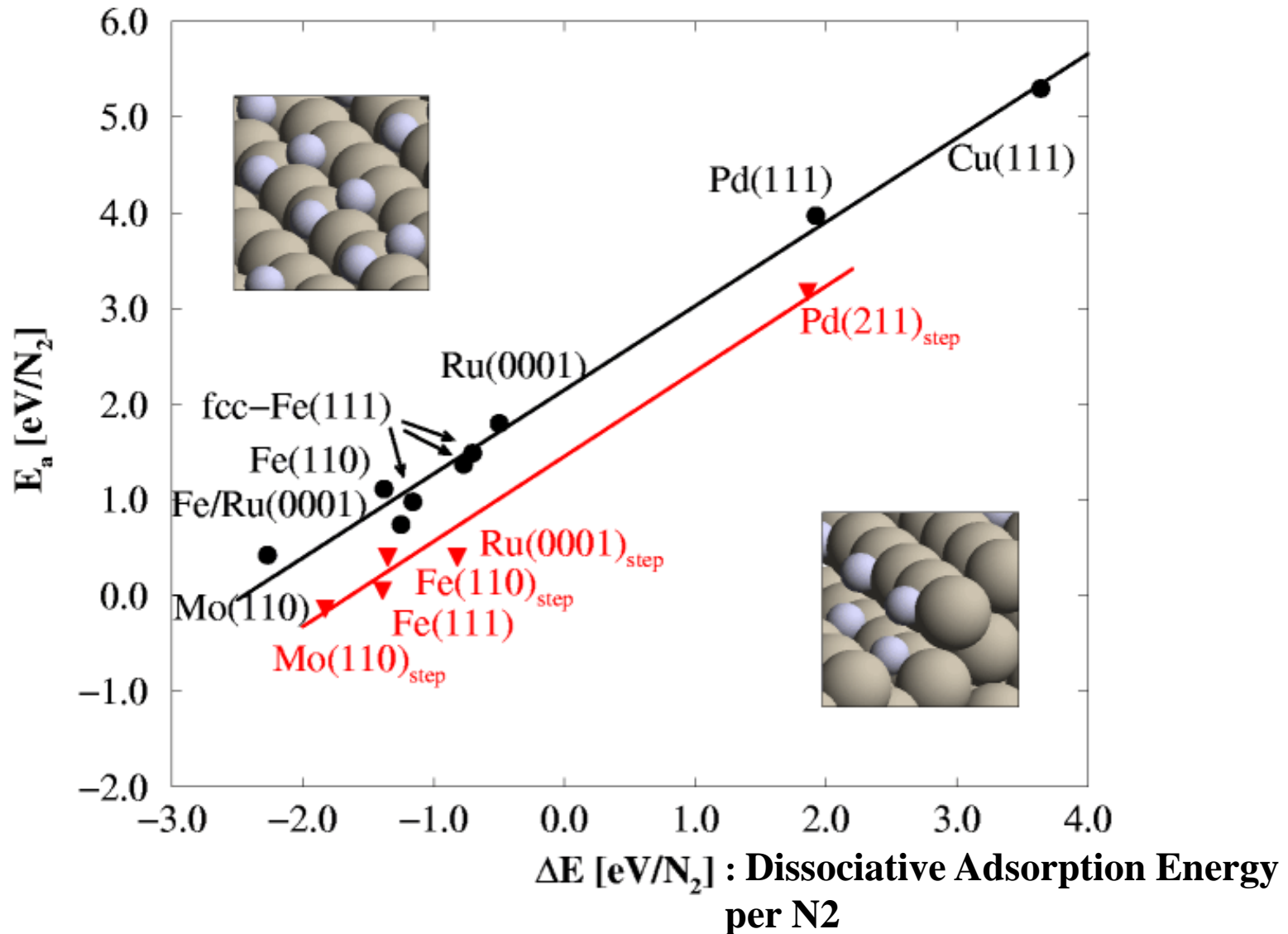
Logatottir, Rod, Nørskov, Hammer, Dahl, Jacobsen, J. Catal. **197**, 229 (2001)

Ammonia synthesis over Ru

Logadottir, Nørskov

Ammonia synthesis

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Number of d electrons, which Determine the Adsorption Energy of N2

Ozaki and Aika, *Catalysis* **1** (Anderson and Boudart, Ed.)

Another Example of the Volcano Plot

Methanation: CO+3H2→CH4 +H2O
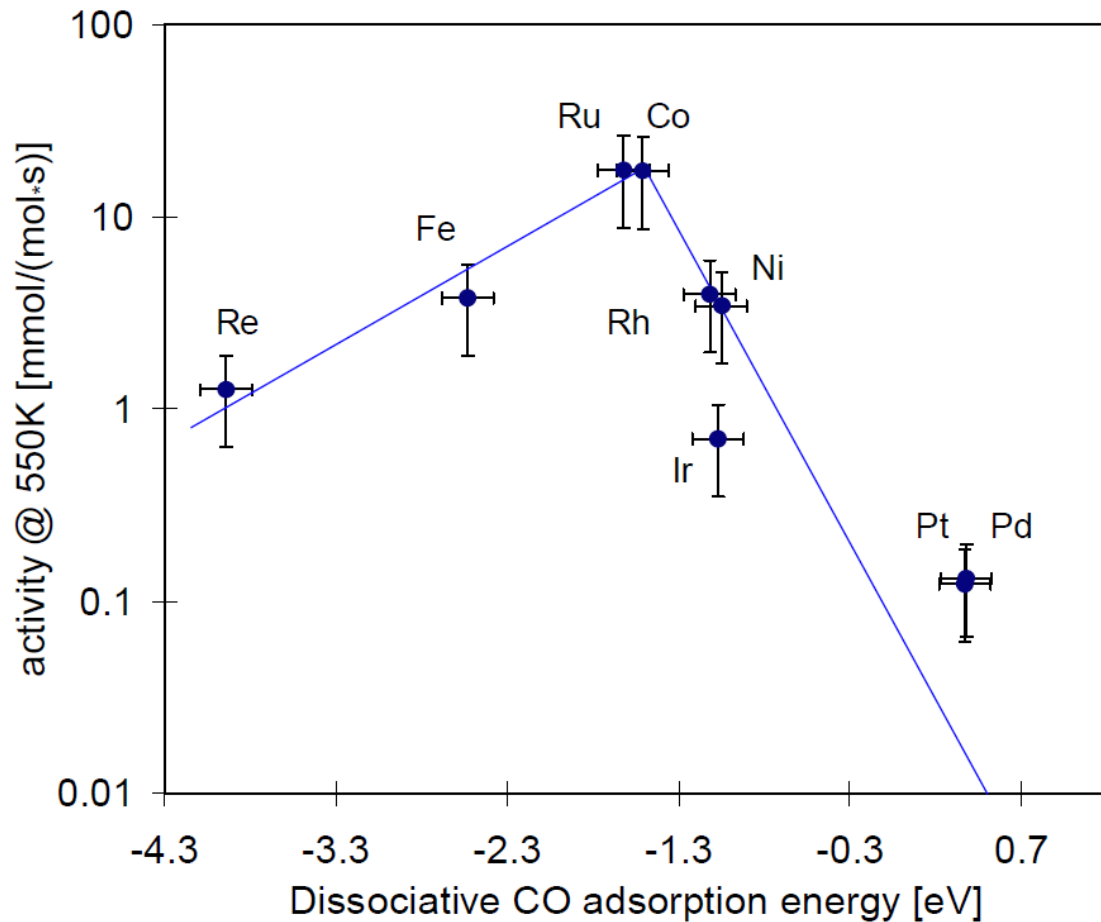
Why are Ru and Co the best catalysts?

• Why is the dissociative CO chemisorption energy a good descriptor?

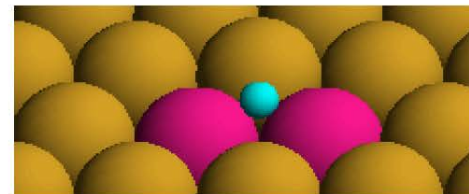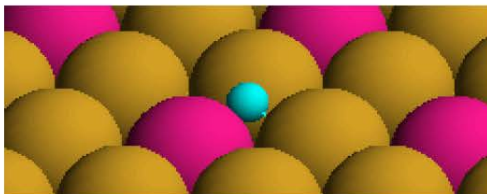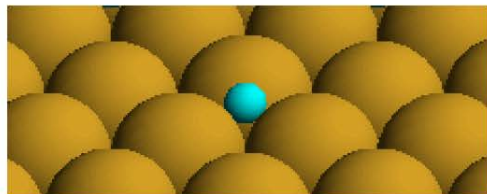• Could we find better or cheaper alternatives?

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

Calculated ammonia synthesis rates

$400 \ C, \ 50 \ bar, \ H_2:N_2=3:1, \ 5\% \ NH_3$

Logatottir, Rod, Nørskov, Hammer, Dahl, Jacobsen, J. Catal. **197**, 229 (2001)
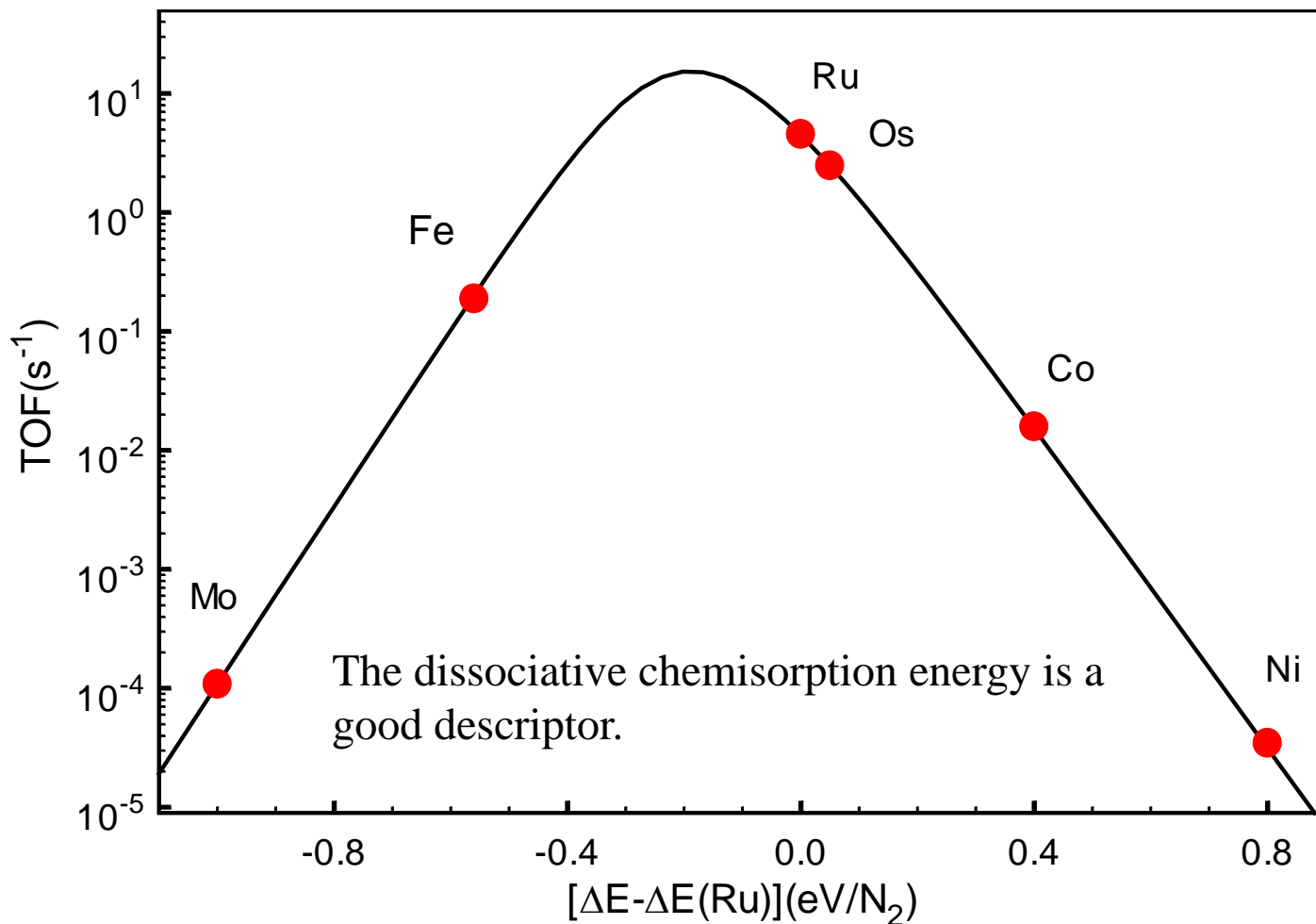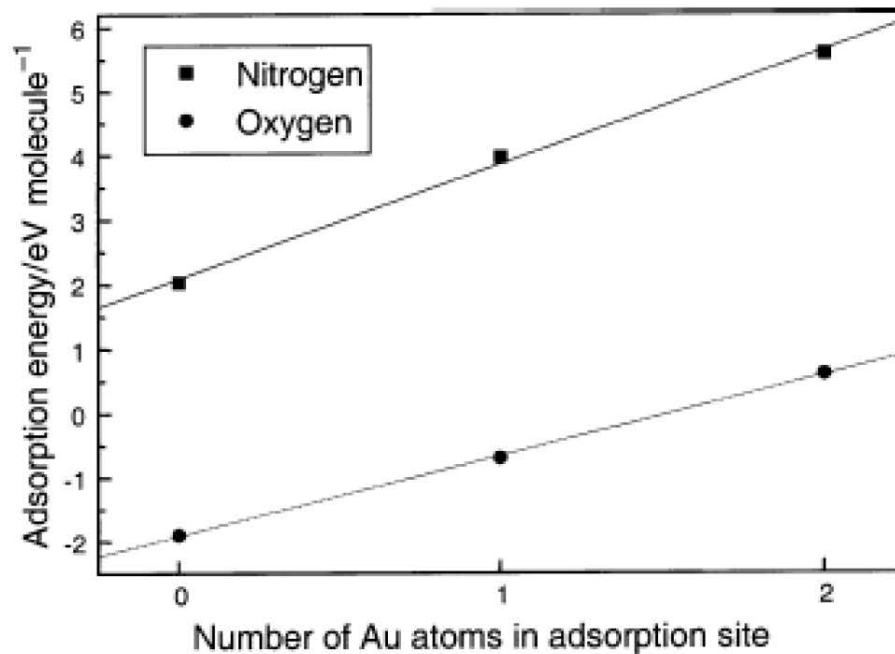
The interpolation principle
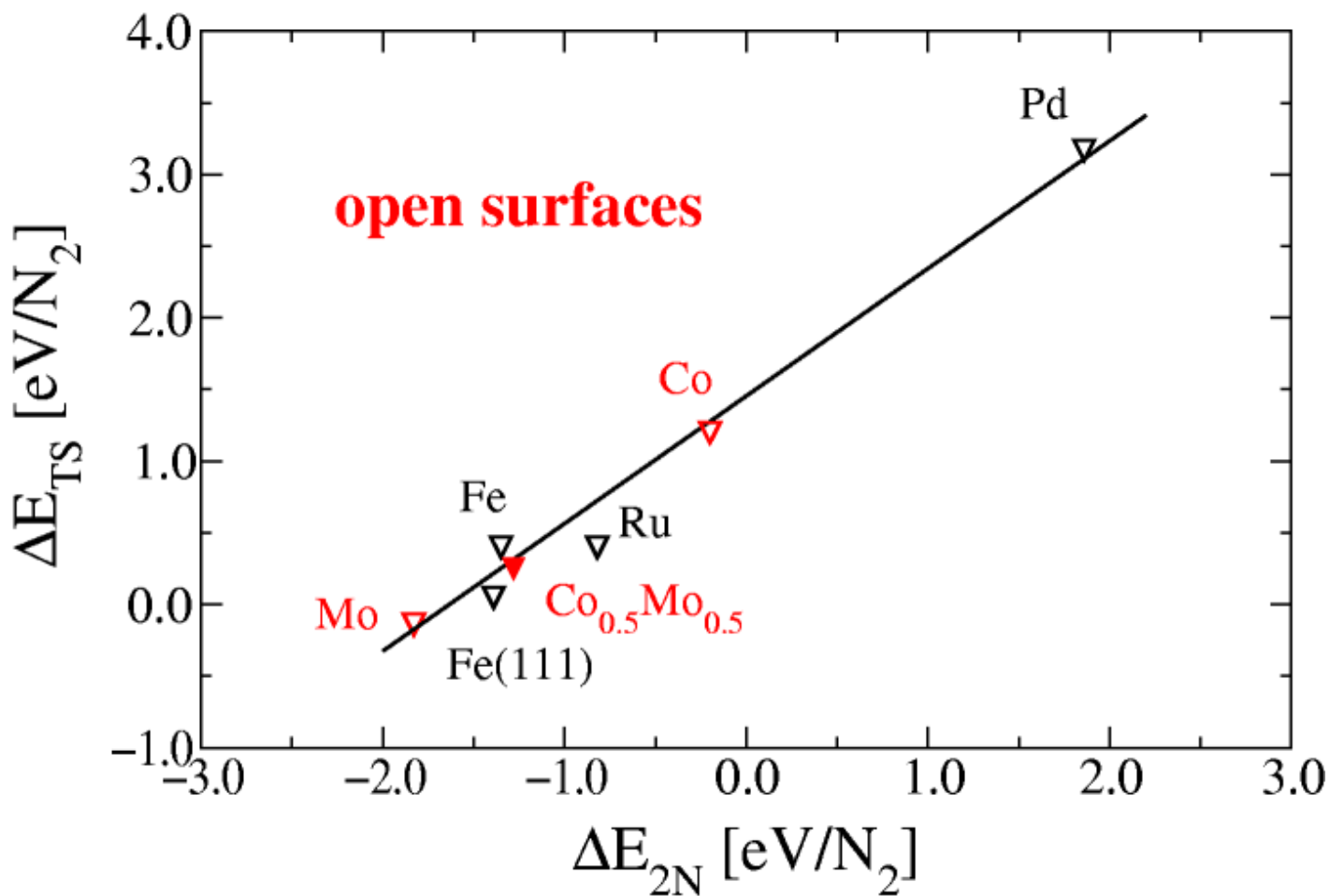
N and O adsorption on Au/Pd(111)

$$\Delta E(A_x B_{1-x}) \sim$$
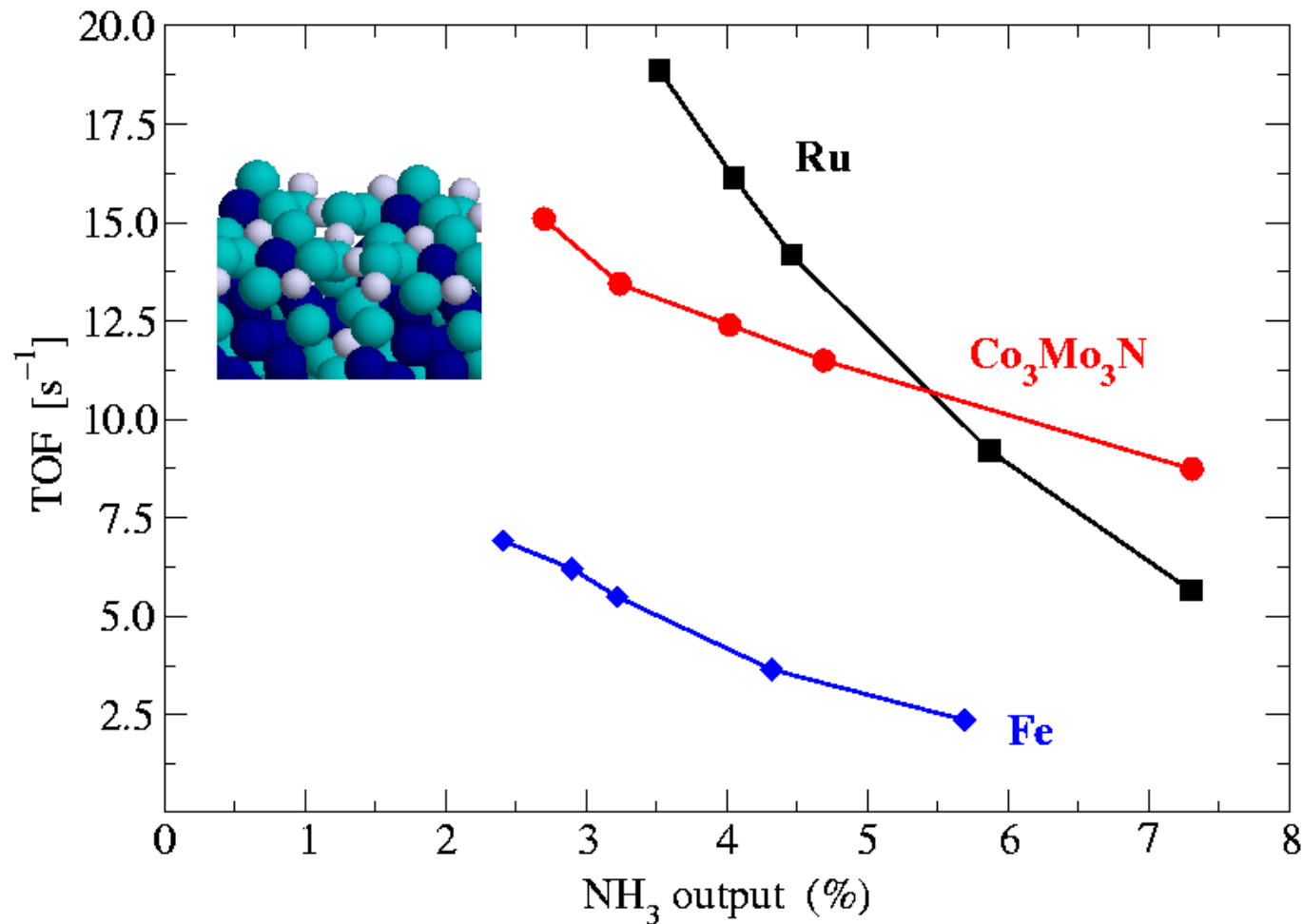$$x\, \Delta E(A) + (1-x)\, \Delta E(B)$$

Liu, Nørskov, Phys.Chem.Chem.Phys. 3, 3814 (2001) Jacobsen (Christensen), Dahl, Clausen, Bahn, Logadottir, Nørskov, JACS 123, 404(2001)

Interpolation in the periodic table

Jacobsen, Dahl, Clausen, Bahn, Logadottir, Nørskov, JACS **123** (2001) 8404.

Measured ammonia synthesis rates
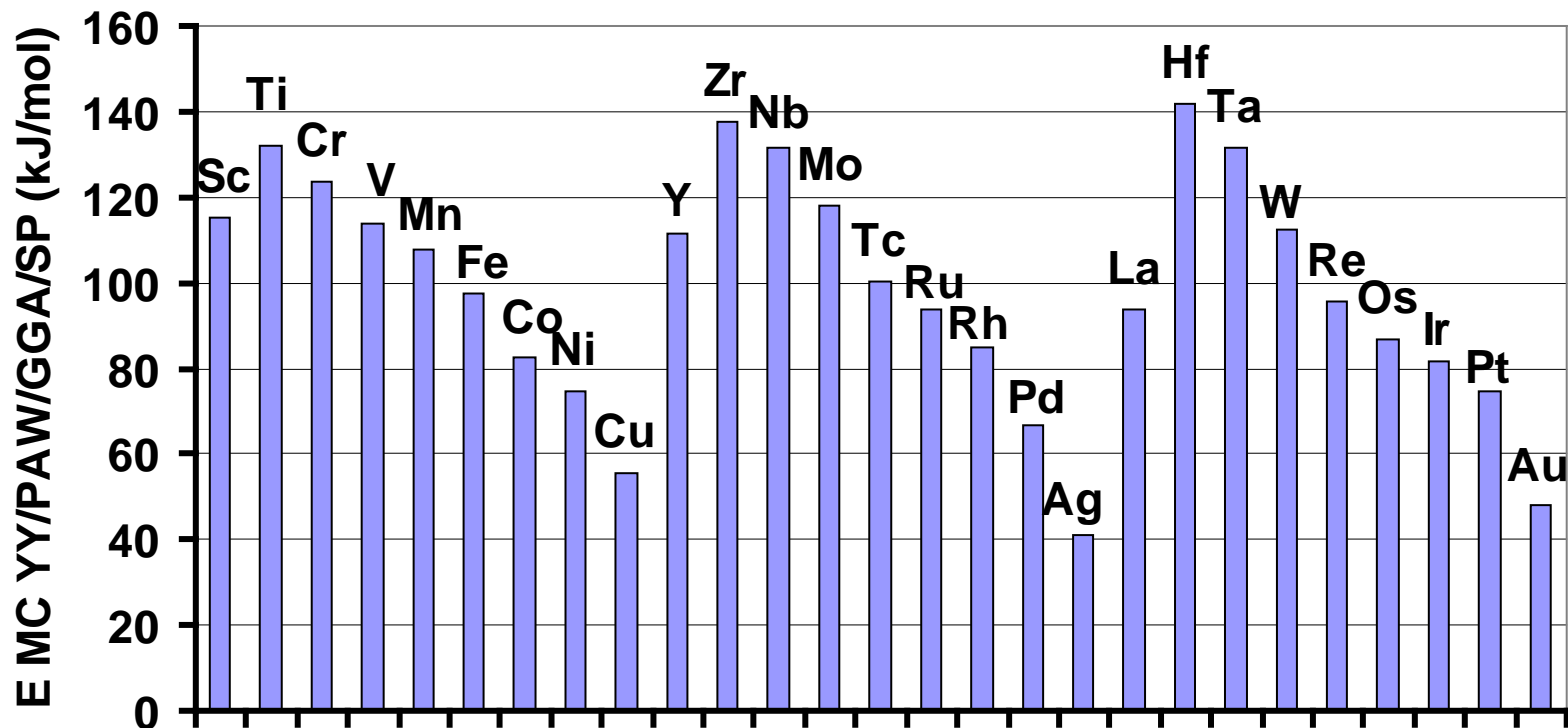
400 C, 50 bar, $H_2:N_2=3:1$

Jacobsen, Dahl, Clausen, Bahn, Logadottir, Nørskov, JACS **123** (2001) 8404.

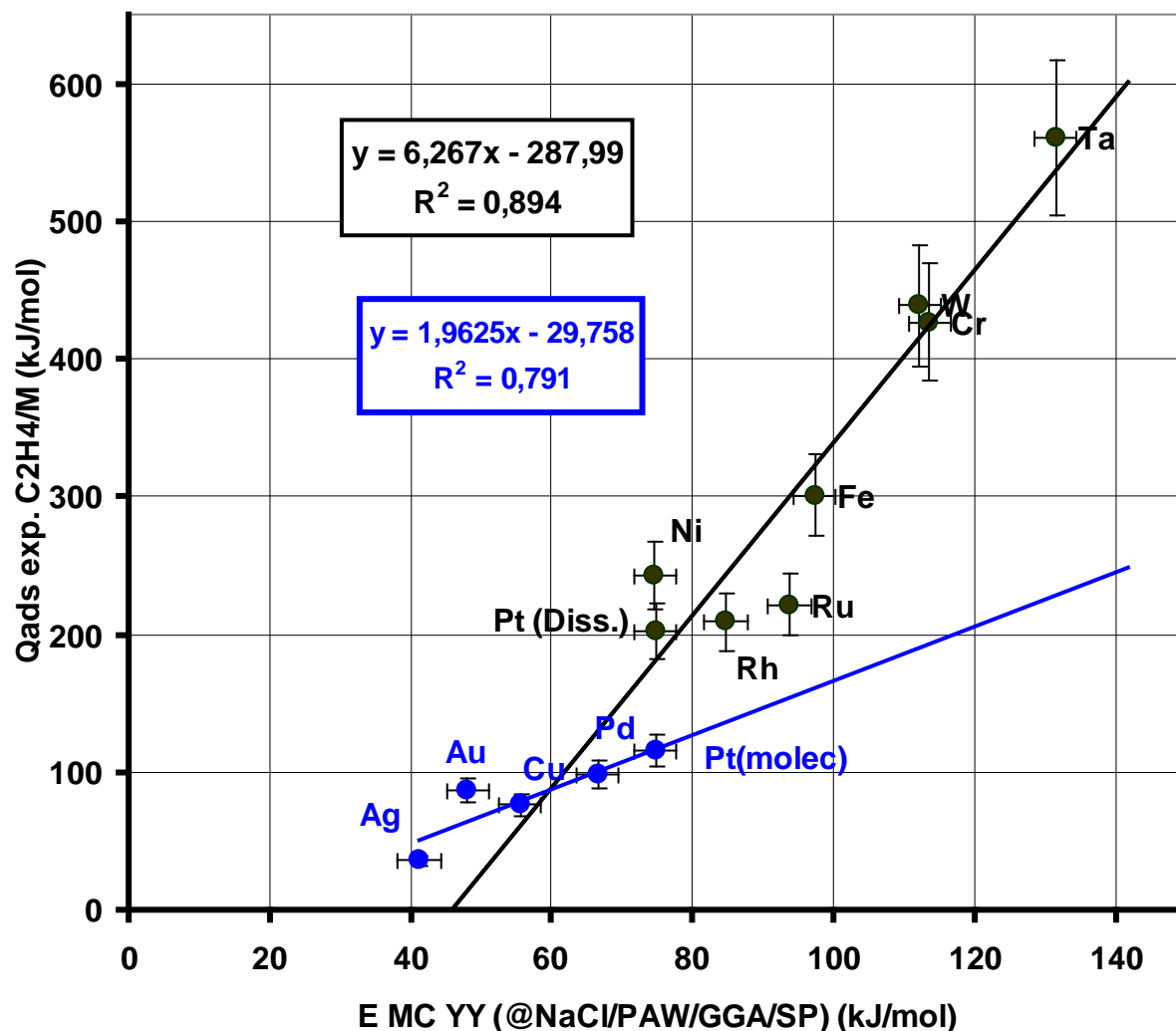# *Using DFT calculations in the search of prospective catalysts*

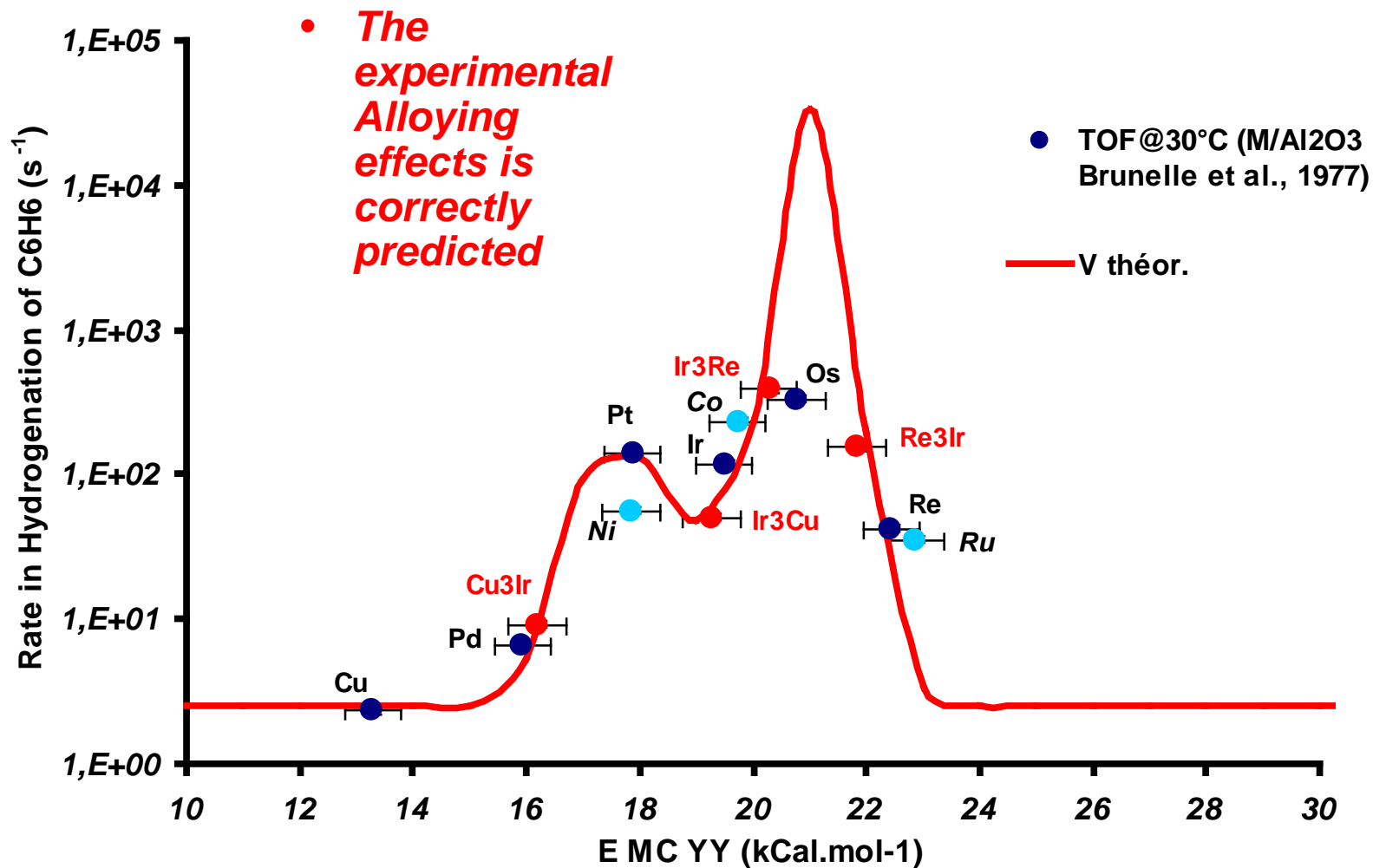
Periodic Trends for E MC in Fm-3m (NaCl) carbides

Using DFT calculations
in the search of prospective catalysts

- **E MC @ Fm-3m carbides is rather consistent with simple chemisorption models**

- **Onset of dissociative chemisorption as MC bond strength increases**

Adsorption of C$_2$H$_4$ 100K

		: di-σ bound					: π bound
		: No ads.					
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt

Qads exp. C2H4/M (kJ/mol) vs **E MC YY (@NaCl/PAW/GGA/SP) (kJ/mol)**

$$y = 6{,}267x - 287{,}99$$
$$R^2 = 0{,}894$$

$$y = 1{,}9625x - 29{,}758$$
$$R^2 = 0{,}791$$

Using DFT calculations
in the search of prospective catalysts

- *The experimental Alloying effects is correctly predicted*

Rate in Hydrogenation of C6H6 (s⁻¹)

- TOF@30°C (M/Al2O3 Brunelle et al., 1977)
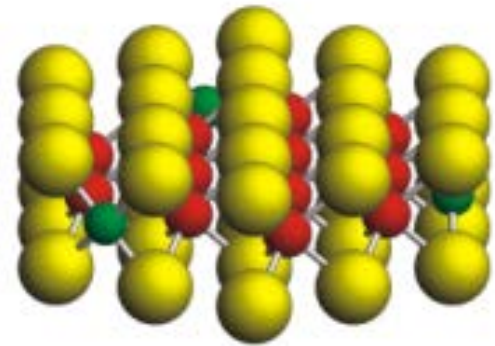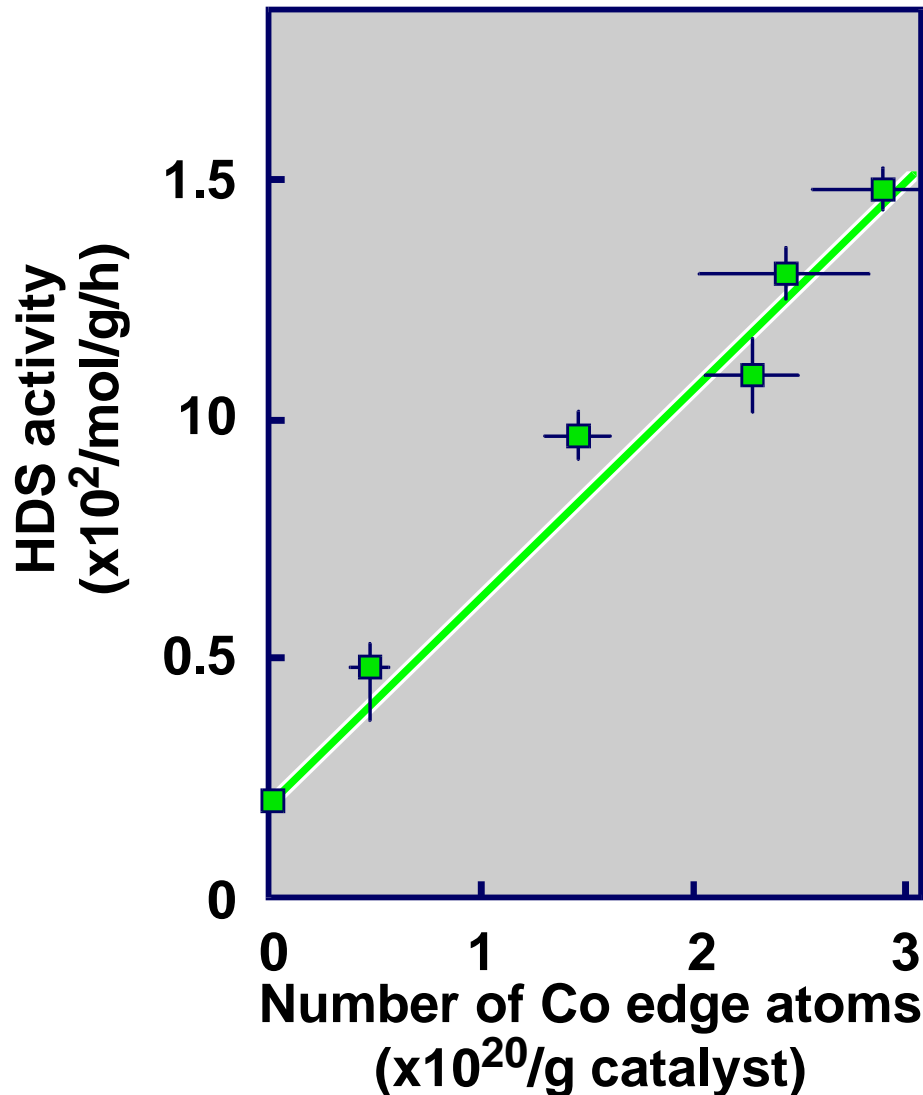— V théor.

E MC YY (kCal.mol-1)

Searching for appropriate descriptors

- Structure (in situ)

- Spectroscopy (in situ)

- Surface thermochemistry

- Calculations

- …

There is a large need for systematic data

- and for good descriptors
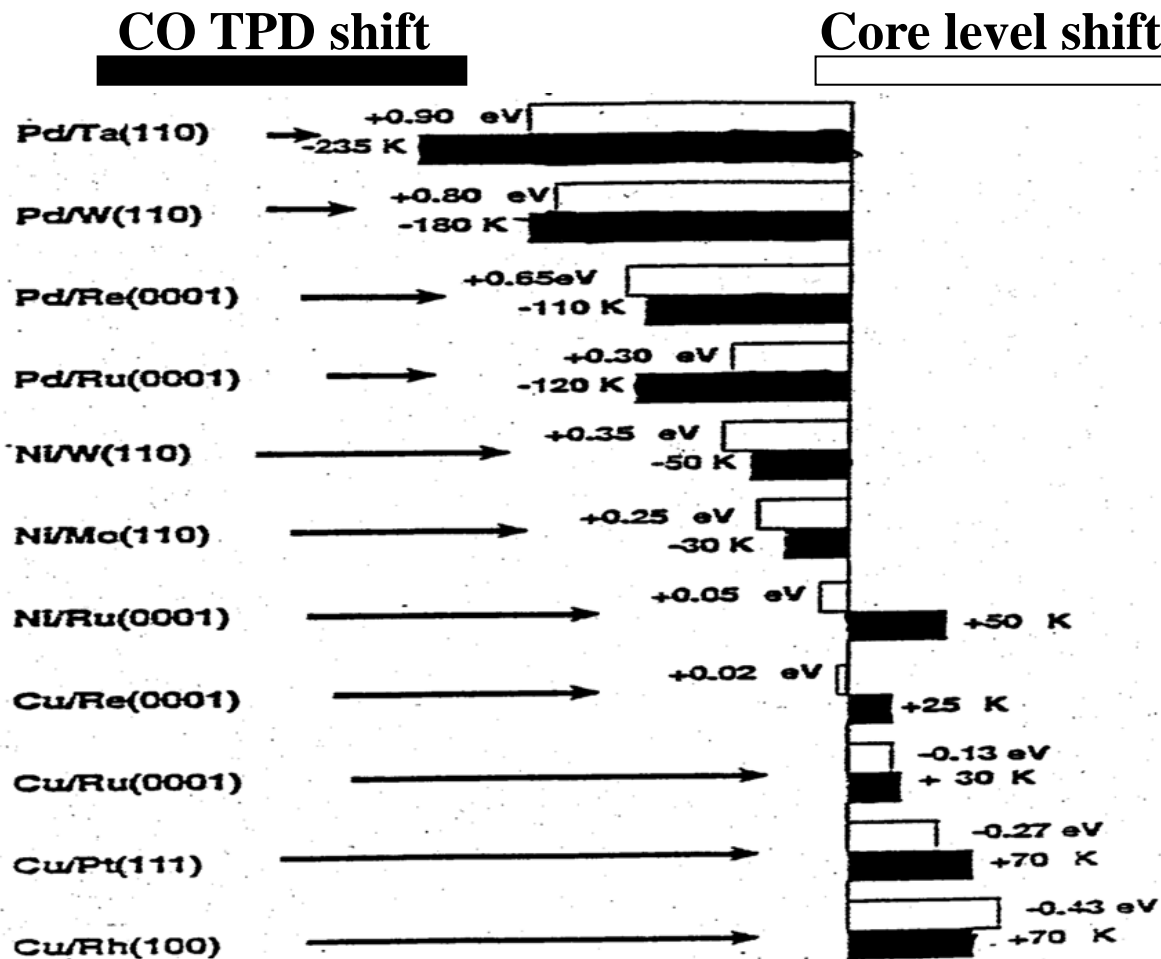
Structure-activity Correlation
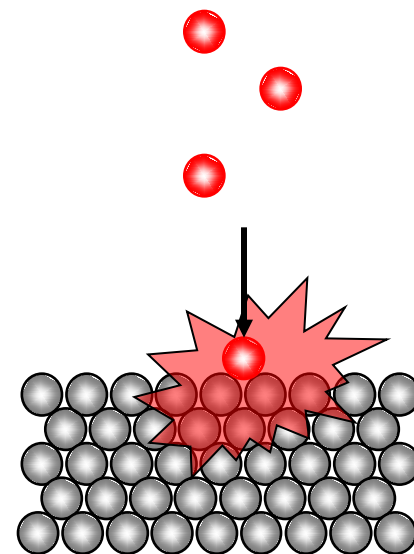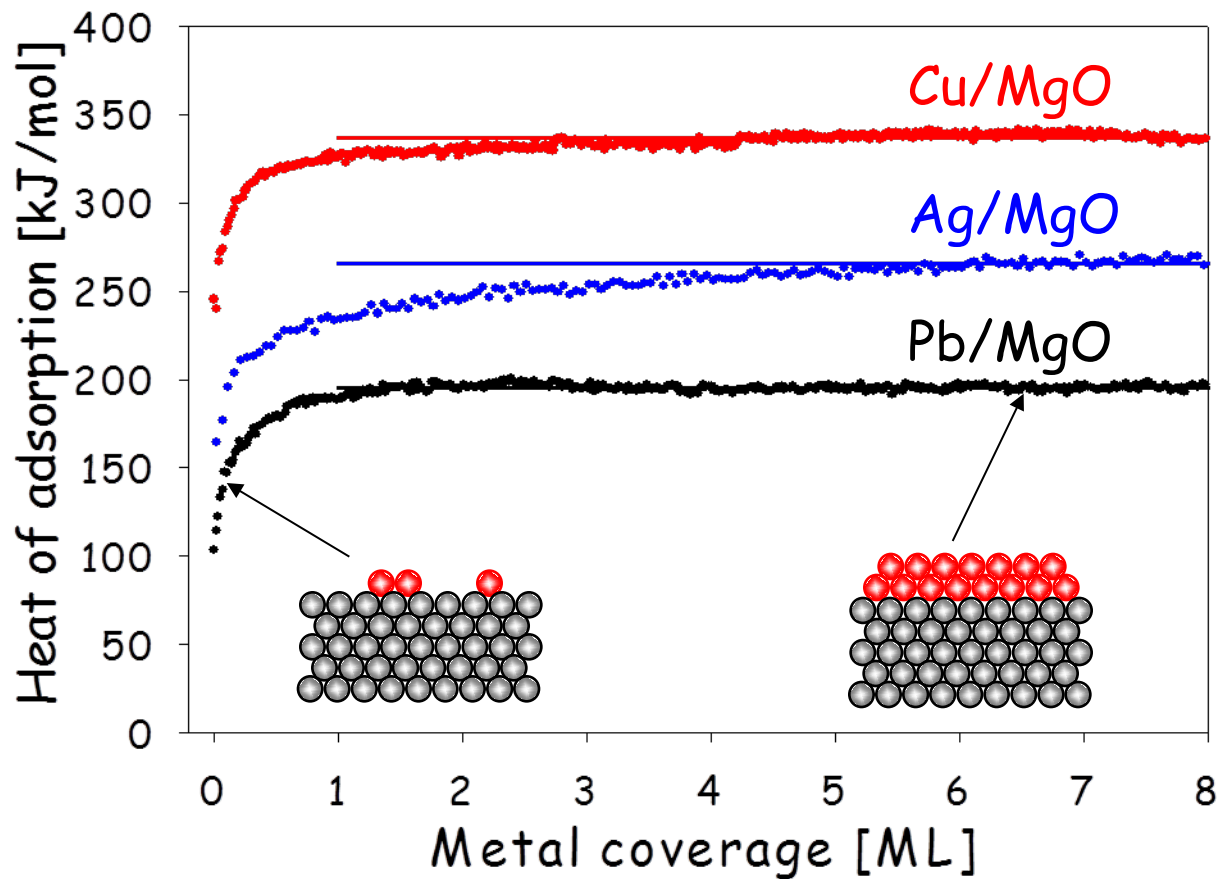## Hydrodesulfurization of thiophene

Topsøe, Clausen, Massoth
Hydrotreating Catalysis, Science and Technology
(Anderson and Boudart (Eds.), Springer (1996).

Descriptors from spectroscopy

Goodman and Rodriguez, Science **279** (1992) 897
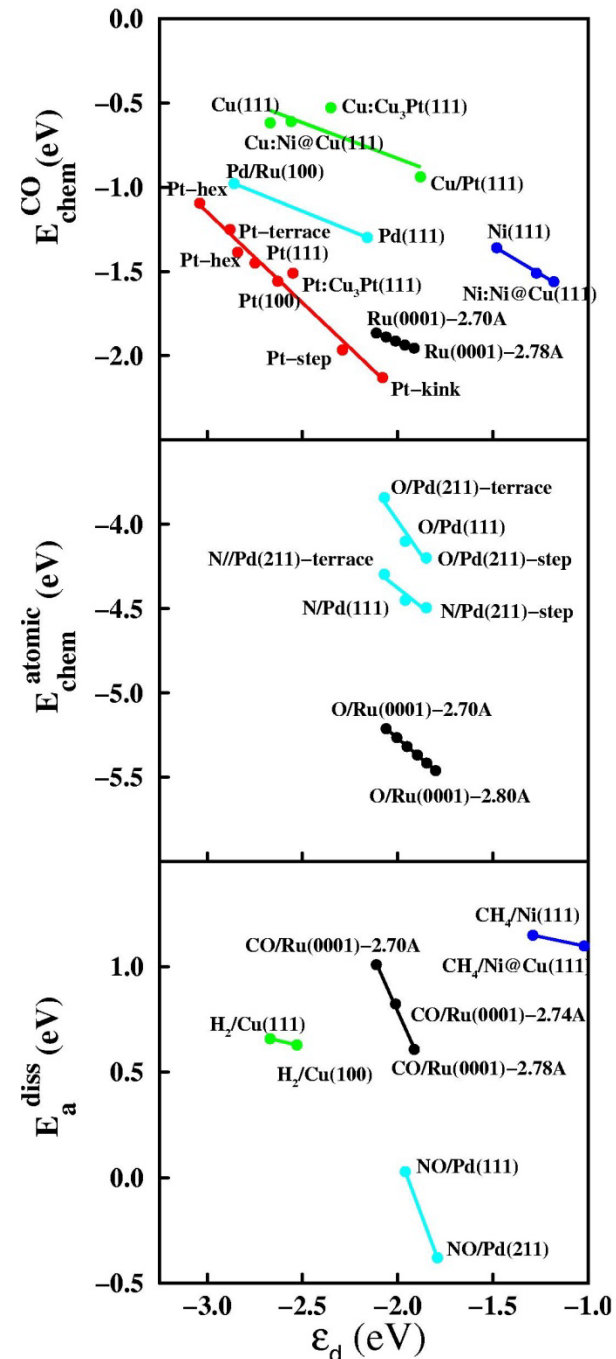
Single crystal microcalorimerty

Larsen, Starr, Campbell, Chem.Thermodyn. **33**, 333 (2001)
Brown, Kose, King, Chem. Rev. **98**, 797 (1998).

Descriptors from DFT

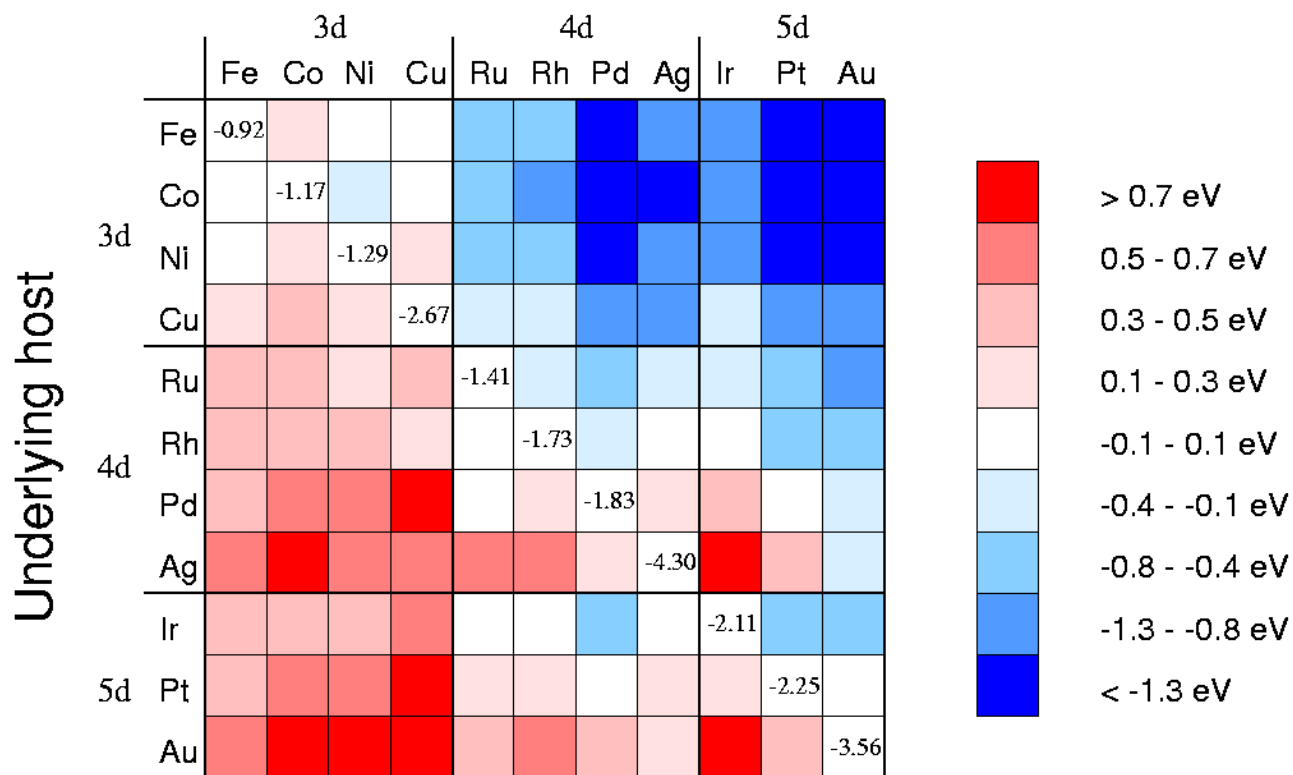Correlation between adsorption energies and activation barriers and the d-band center
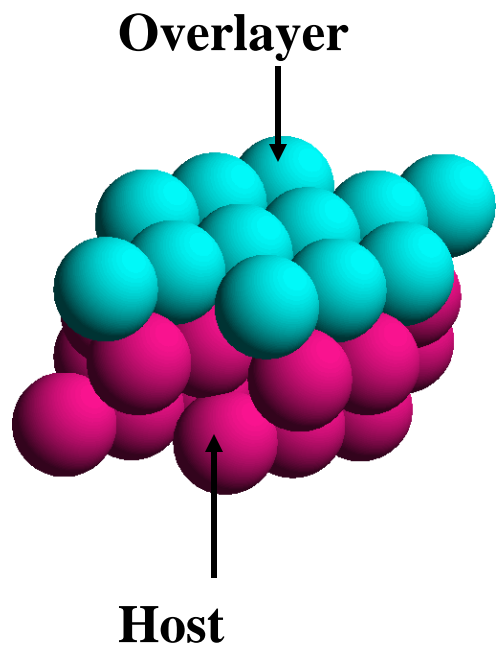
Mavrikakis , Hammer, Nørskov
Phys. Rev. Lett. **81**, 2819 (1998)

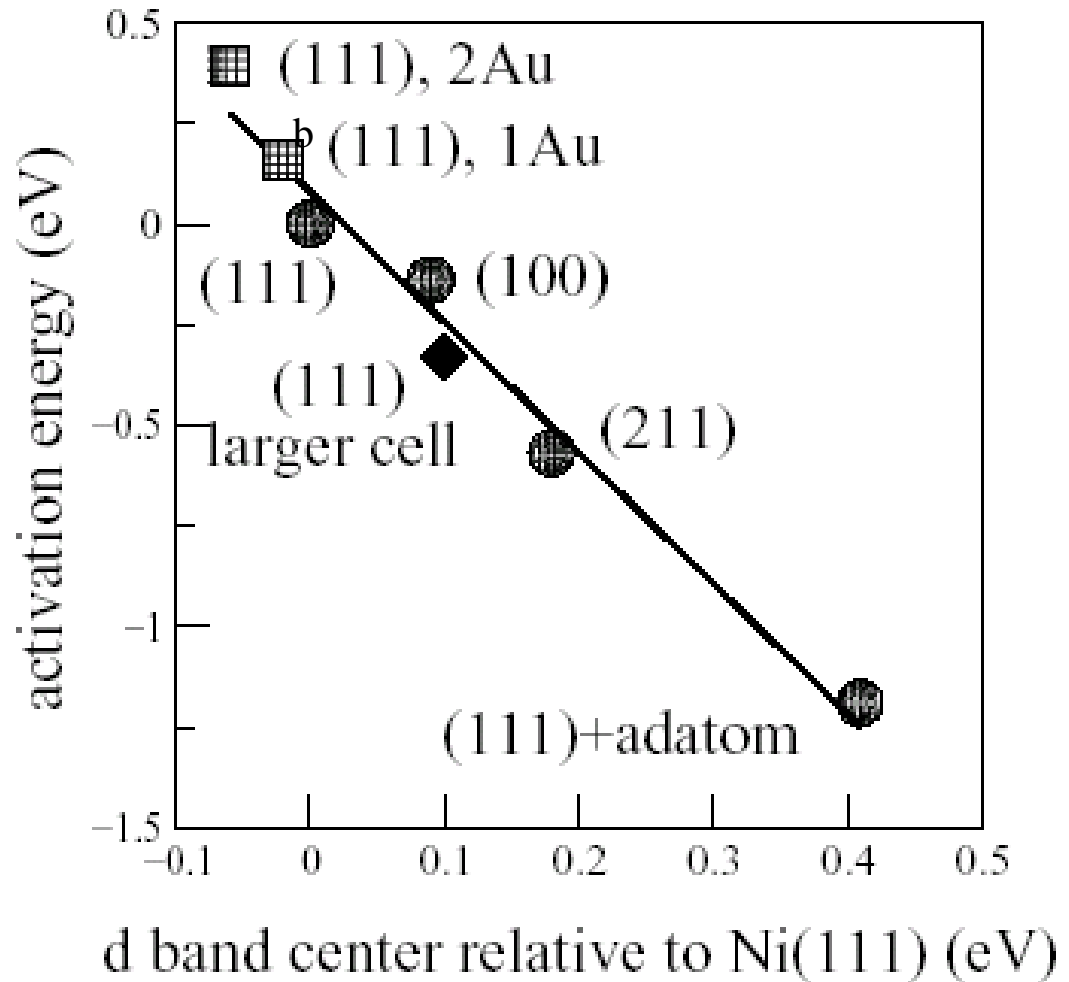# How can the *d*-band center be changed?

Calculated d band shifts:

Ruban, Hammer, Stoltze, Skriver, Nørskov, J.Mol.Catal. A **115**, 421 (1997)

Methane Activation

Transition state for CH_4
dissociation on Ni(211)

Bengaard, Rostrup-Nielsen, Nørskov
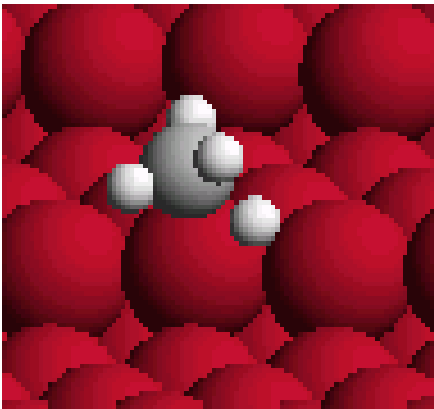
Status

- Well developed basic understanding – theory-experiment
- Beginning to be able to use it directly in catalyst design
- Some activity-descriptor correlations
- Host of new in situ methods for catalyst characterization
- New very powerful screening methods
- We have a starting point which is radically different from the situation 5 or 10 years ago!
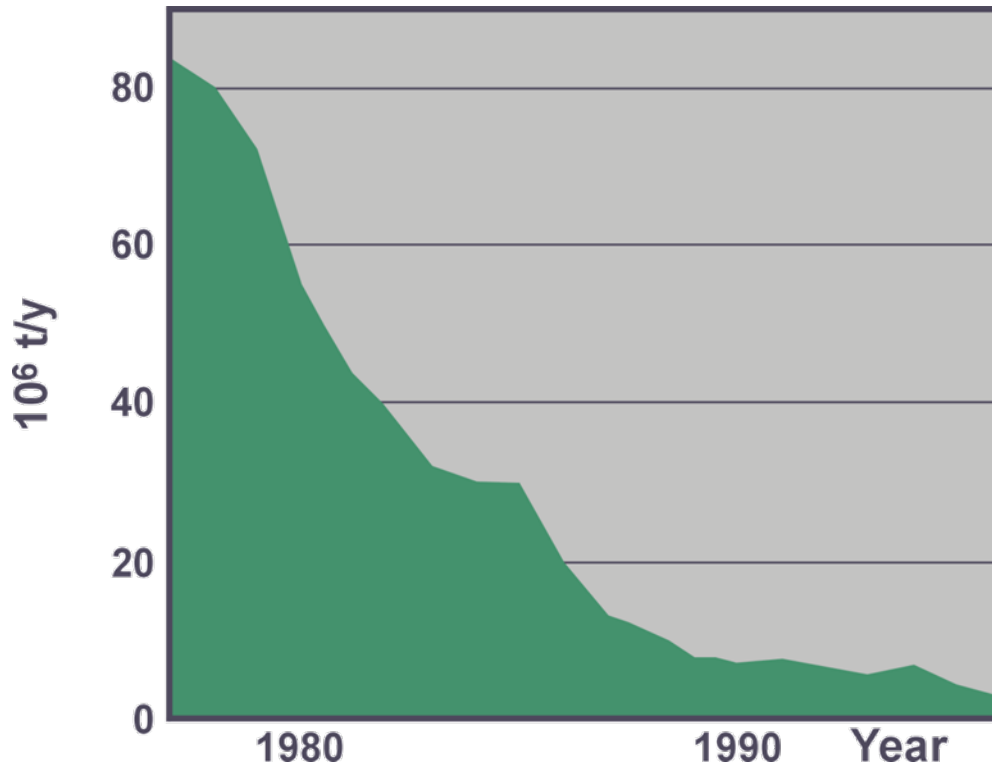
Moving forward

- More basic understanding –theory-experiment
- Integration of the conceptual framework for heterogeneous, homogeneous and enzyme catalysis
- More systematic data (descriptors)
- Better synthesis methods
- Better coupling of catalyst design and process engineering
- INTEGRATION

Case Study: Motivation

Hydrodesulfurization Catalysis

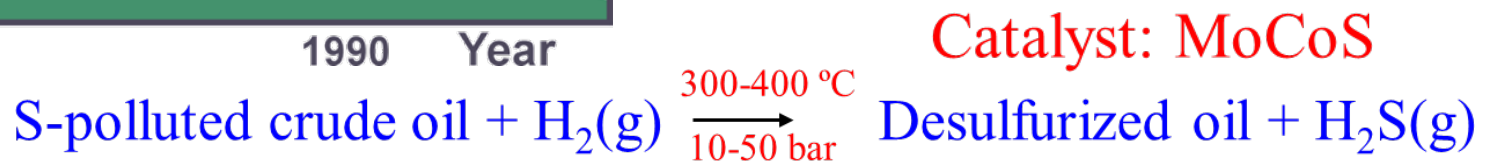- Large Environmental Impact
- New Technological Challenges

SO_2 emissions from fuels

New S regulations world wide

EU :

Year	ppm S in diesel
2000	350
2005	50
2010	10(?)

Catalyst: MoCoS

S-polluted crude oil + H_2(g) $\xrightarrow[\text{10-50 bar}]{\text{300-400 °C}}$ Desulfurized oil + H_2S(g)

Case Study

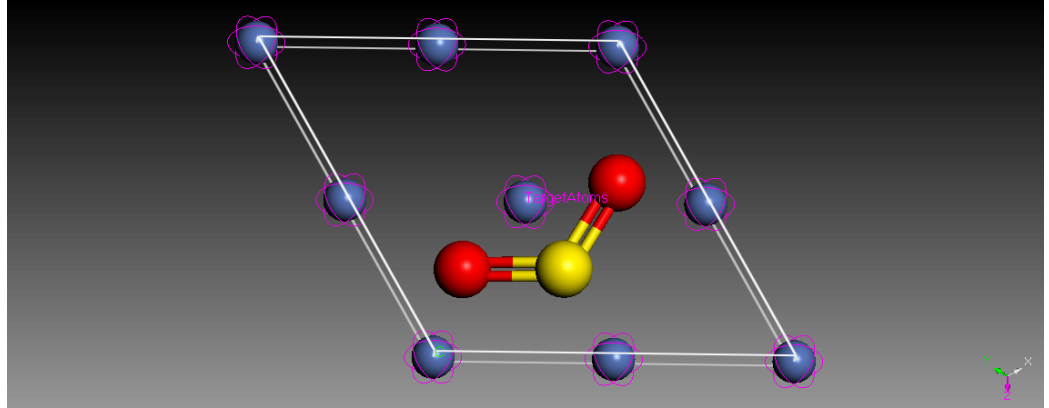What is the adsorption geometry of SO2 on Ni(111) surface?
---Use Adsorption Locator to search the adsorption geometries.

What is the adsorption energy?
--- Use the discovered geometry to simulate the adsorption energy via

$$B(\theta) = \frac{[E_{SO2\ on\ Ni[111]}(\theta) - N_{SO2}E_{tot}(SO2) - E_{Ni[111]}]}{N_{SO2}}$$

The most stable adsorption geometry found by Adsorption Locator is
(look into the Ni(111) surface)

$Form\ Forcite$: $B = -215.687294\frac{kcal}{mol} - [0 - 195.767273 \text{ kcal/mol}] = -20 \text{ kcal/mol}$