Surface reactivity and heterogeneous catalysis – a theoretical perspective

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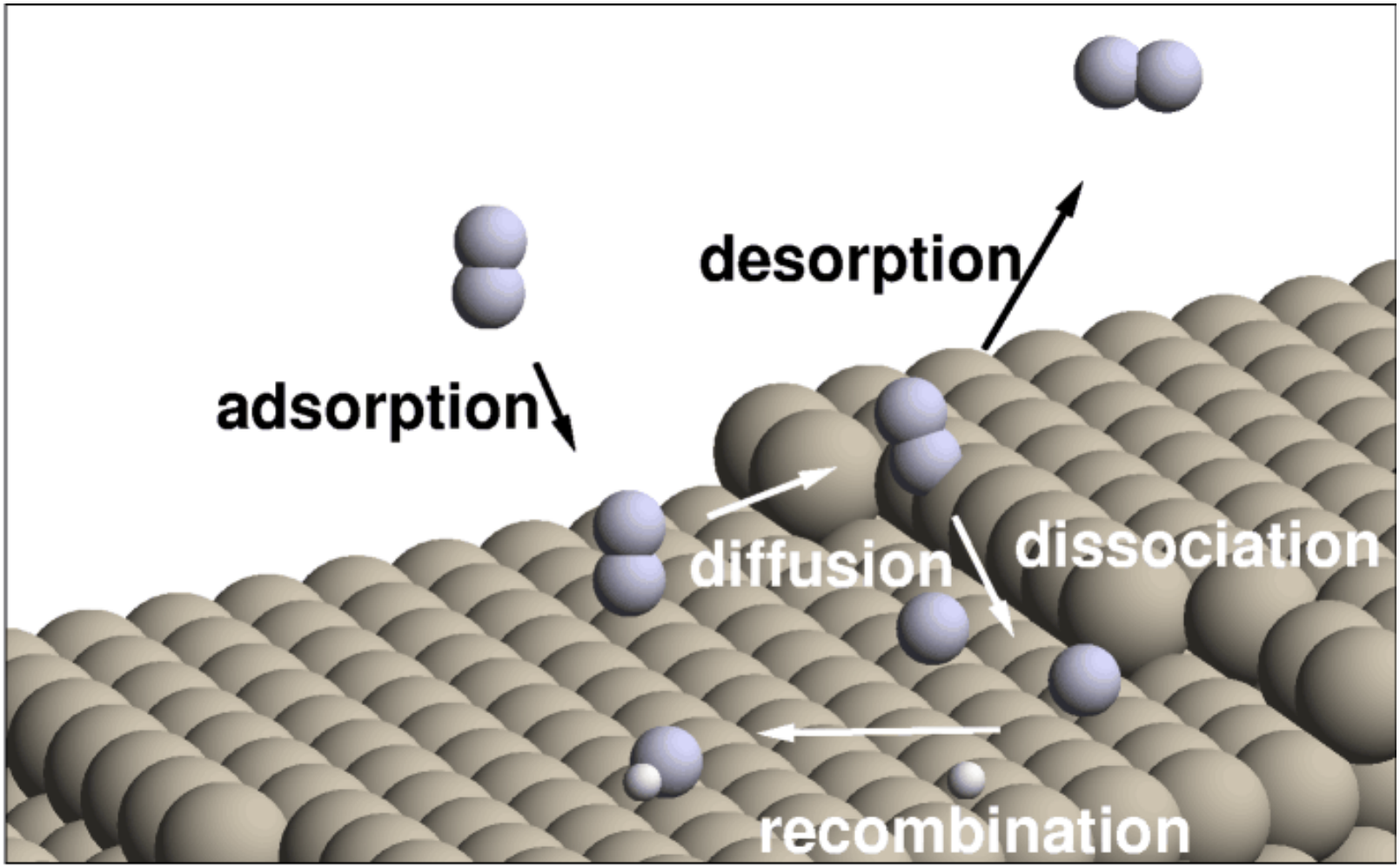
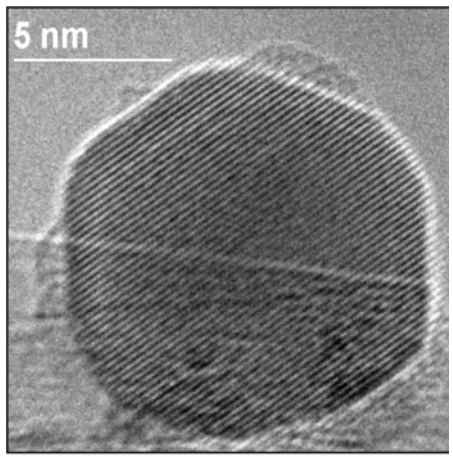
Heterogeneous Catalysis

– a solid surface helping a chemical reaction along



Heterogeneous catalysis



Energy

Chemical production

Environmental protection

Ressources

Enabeling technology

Possibilities for society

Heterogeneous Catalysis

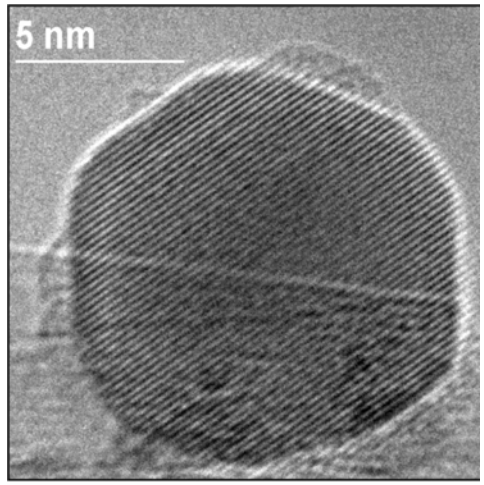
- Basis for 20-30 % of the GNP*
- Used everywhere:
  - fuel processing
  - fertilizers
  - polymers
  - pharmaceuticals
  - environmental protection
  - ….
- Need for new catalysts for energy conversion

* Maxwell, Stud. Surf. Sci. Catal. **101**, 1 (1996).

Heterogeneous catalysis

The challenge:

- To develop a molecular level picture of the way surfaces catalyze chemical transformations
- To use the insight in the design of new catalysts

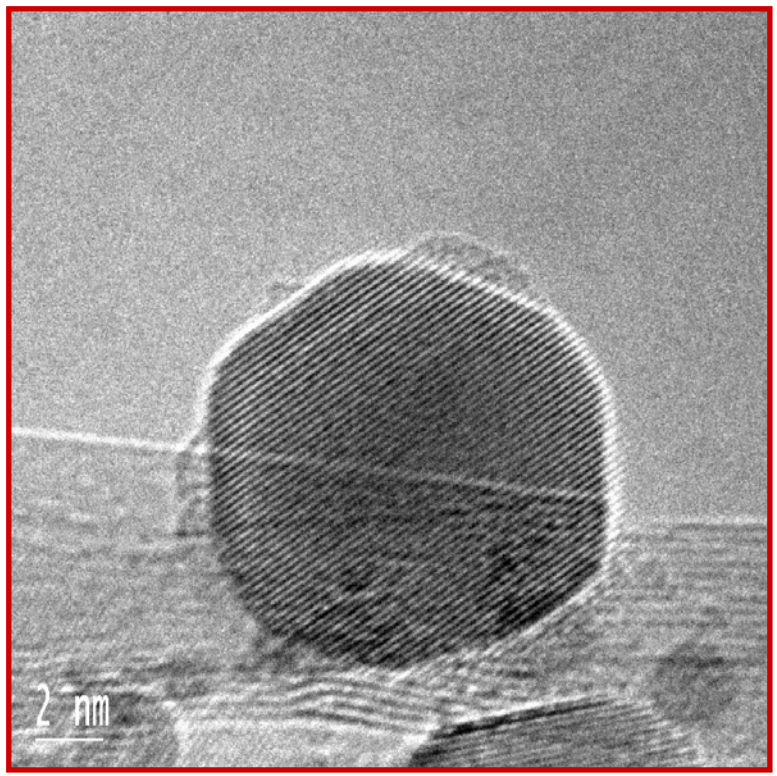


New possibilities:

- Better experimental methods
- Computational methods (density functional theory) can contribute

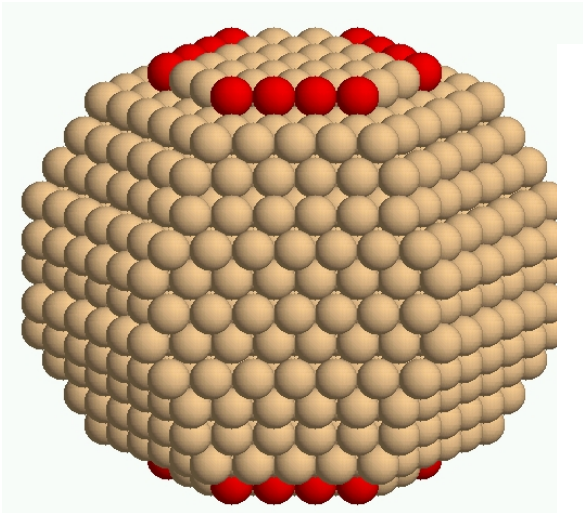
Heterogeneous Catalysis
– is nanotechnology

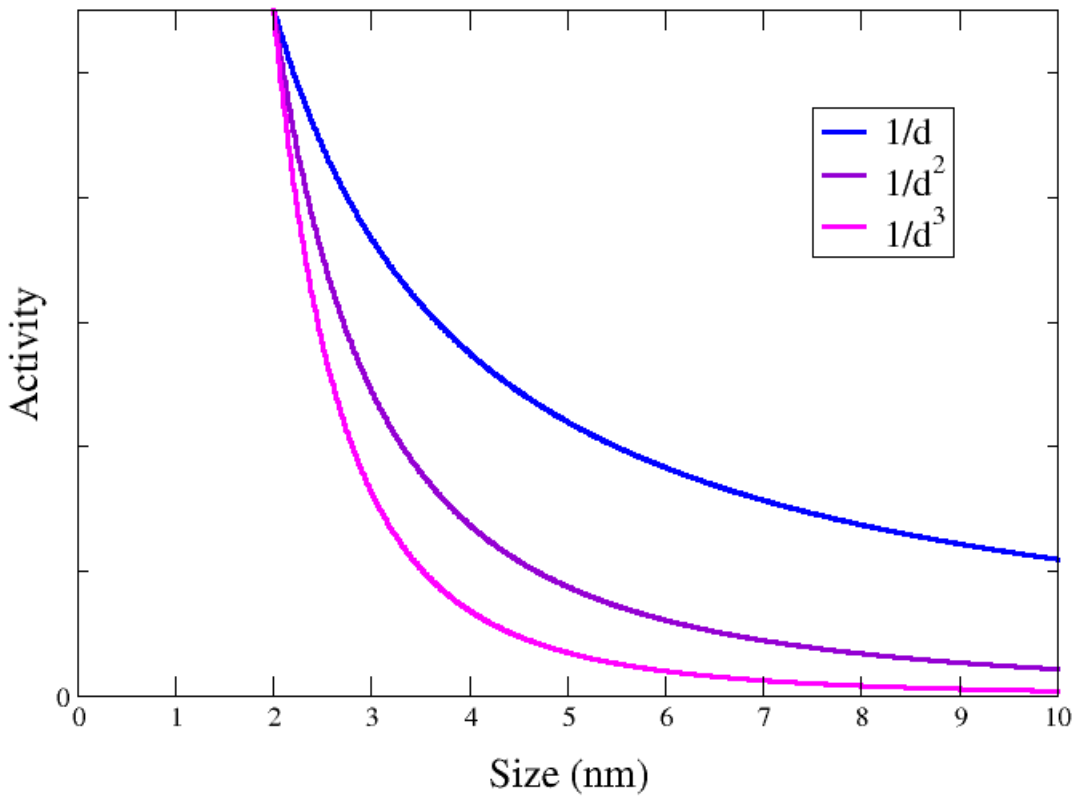
In situ TEM image of Ru/BN catalyst for ammonia synthesis



Hansen, Wagner, Hansen, Dahl, Topsøe, Jacobsen, Science **294**, 1508 (2001)

Why nano-particles





Particle with radius d

Volume ~ d^3

Activity ~ d^n

All surface contributes: n=2
Only steps/corners: n=1
Only corners: n=0

Activity per volume ~ $1/d^{3-n}$

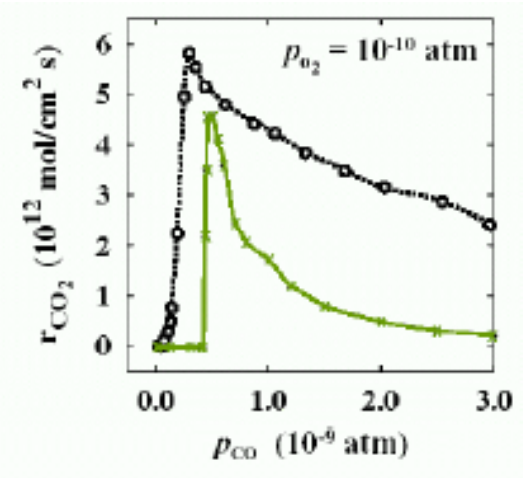
+ extra nano-effects?

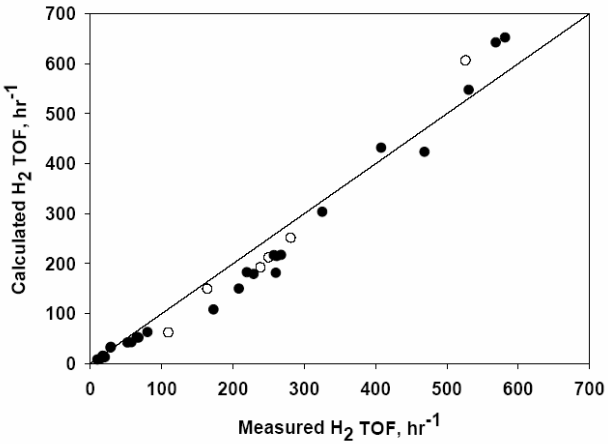
Theory of heterogeneous catalysis

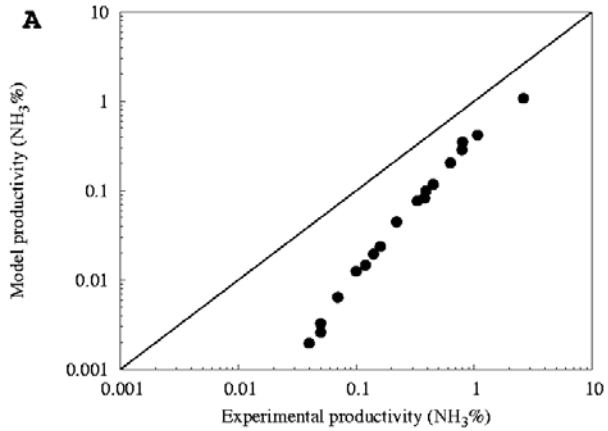
- Detailed treatment of specific reactions
  - Insight into the quality of theoretical methods (DFT)
  - Detailed comparison to experiments
  - Specific examples of the principles behind heterogeneous catalysis

- Understanding of trends
  - Insight into general parameters determining the catalytic activity (reactivity and selectivity) of a catalytic reaction).
  - Basis (eventually) for design?

Detailed treatment of specific reactions







CO oxidation on RuO_2(110)
Reuter, Frenkel, Scheffler,
PRL **93**, 116105 (2004).

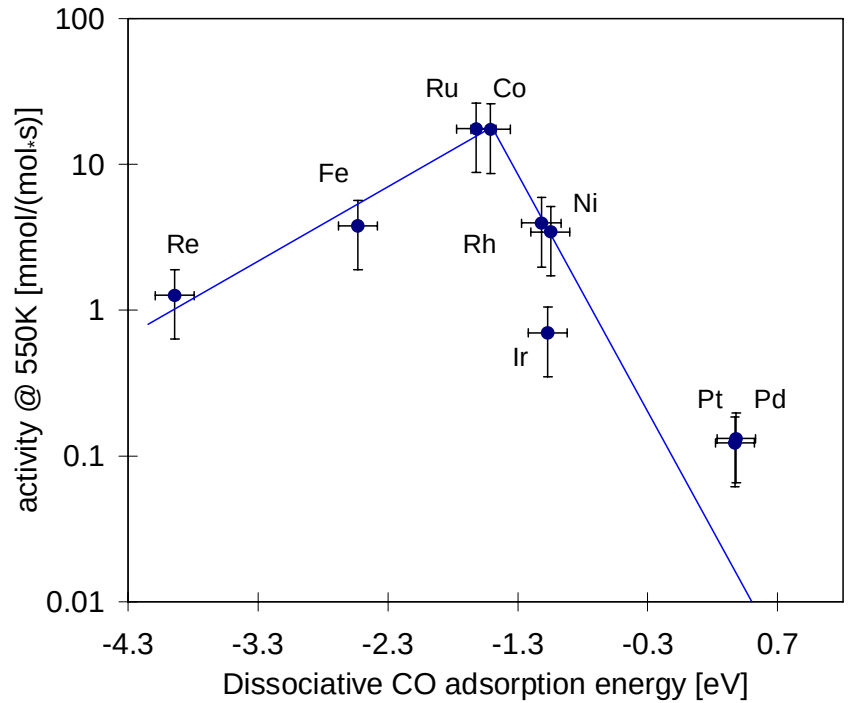
Methanol Decomposition on Pt
Kandoi, Greeley, Sanchez-Castillo, Evans, Gokhale, Dumesic, Mavrikakis
Top. Catal. **37** 17 (2006)

Ammonia synthesis on Ru
Honkala, Remediakis, Logadottir, Nørskov, Hellmann,
Dahl, Carlsson, Christensen,
Science **307**, 555 (2005)

Understanding of trends

Methanation

$CO+3H_2 \rightarrow CH_4 + H_2O$



- 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?

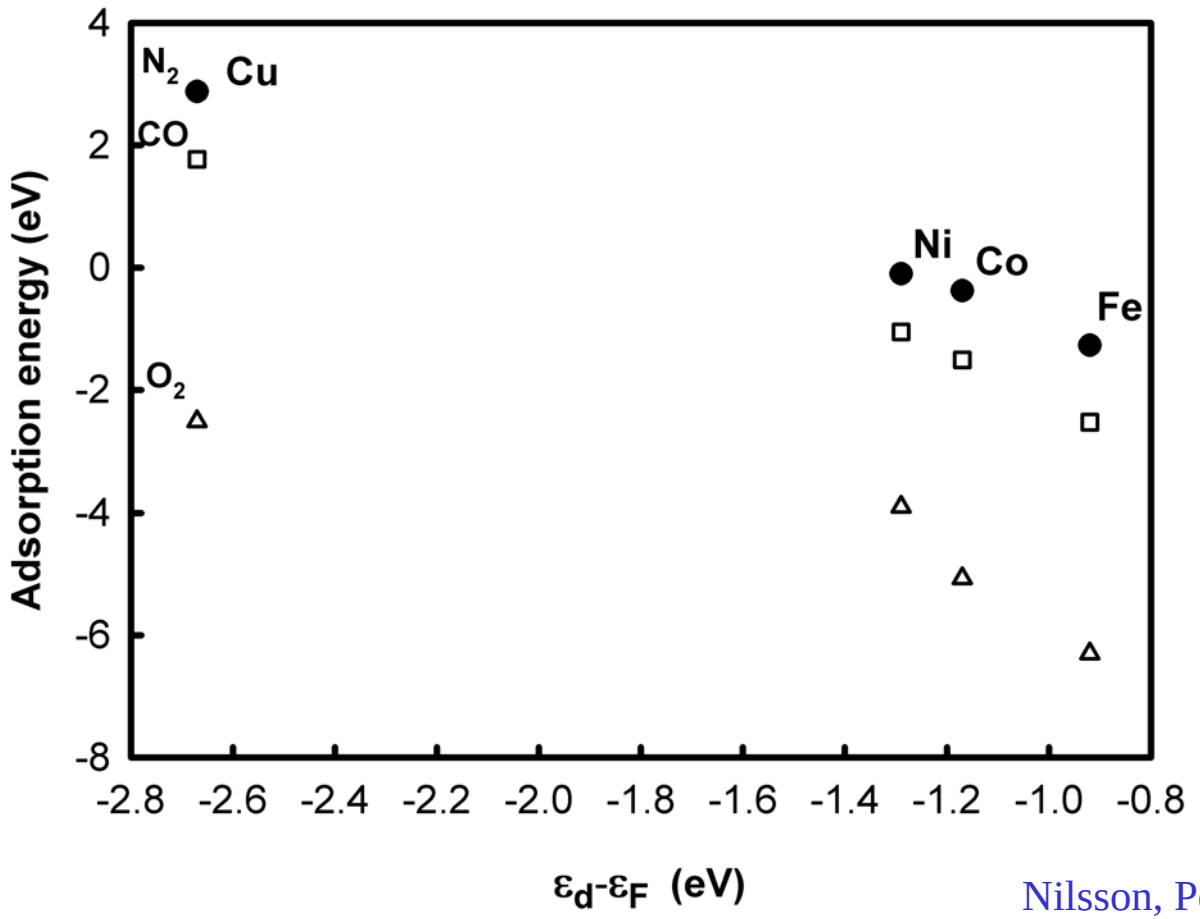
Bligaard, Nørskov, Dahl, Matthiesen, Christensen, Sehested, J. Catal. **224**, 206 (2004)

Understanding of trends

- The chemisorption bond
  - The d band model
  - The interpolation principle
- Activation barriers for surface reactions
  - Electronic and geometrical effects
- Correlations – BEP relations
- Linking trends in energetics to trends in reactivity
  - Volcano plots
  - The Sabatier analysis
- Attempts at design

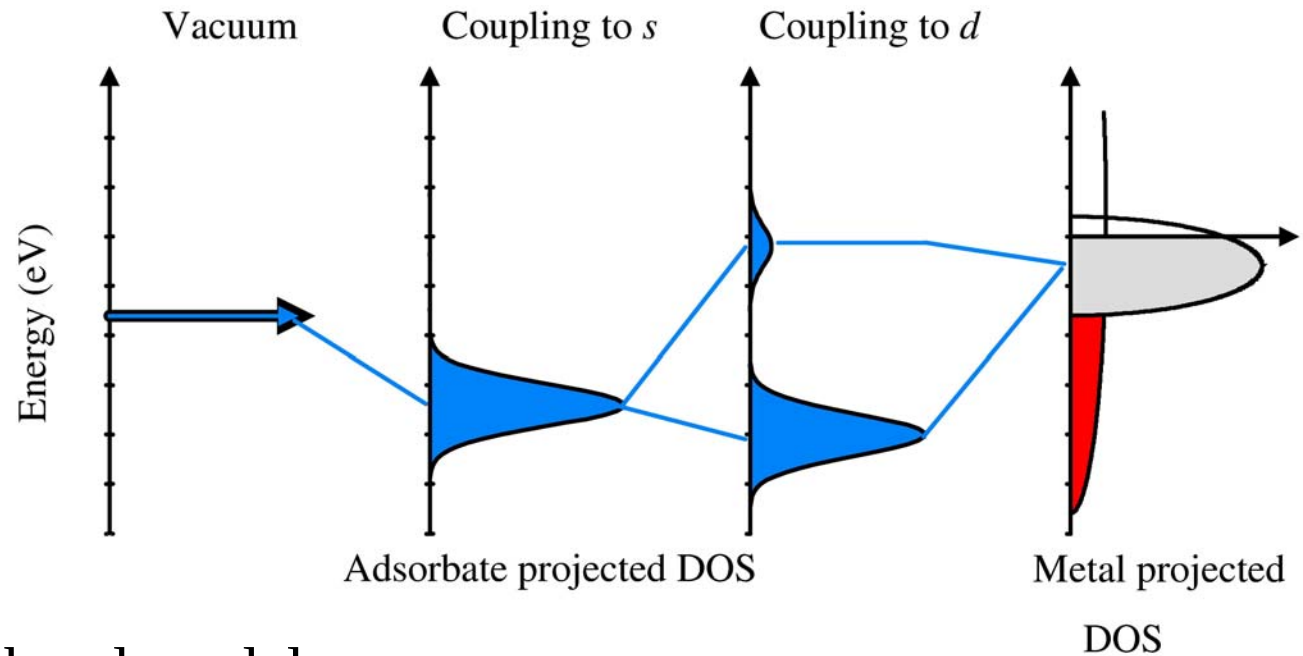
In the following we consider only processes taking place on metal surfaces, but many concepts may be more general …….

Trends in chemisorption energies



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

The adsorbate-surface interaction

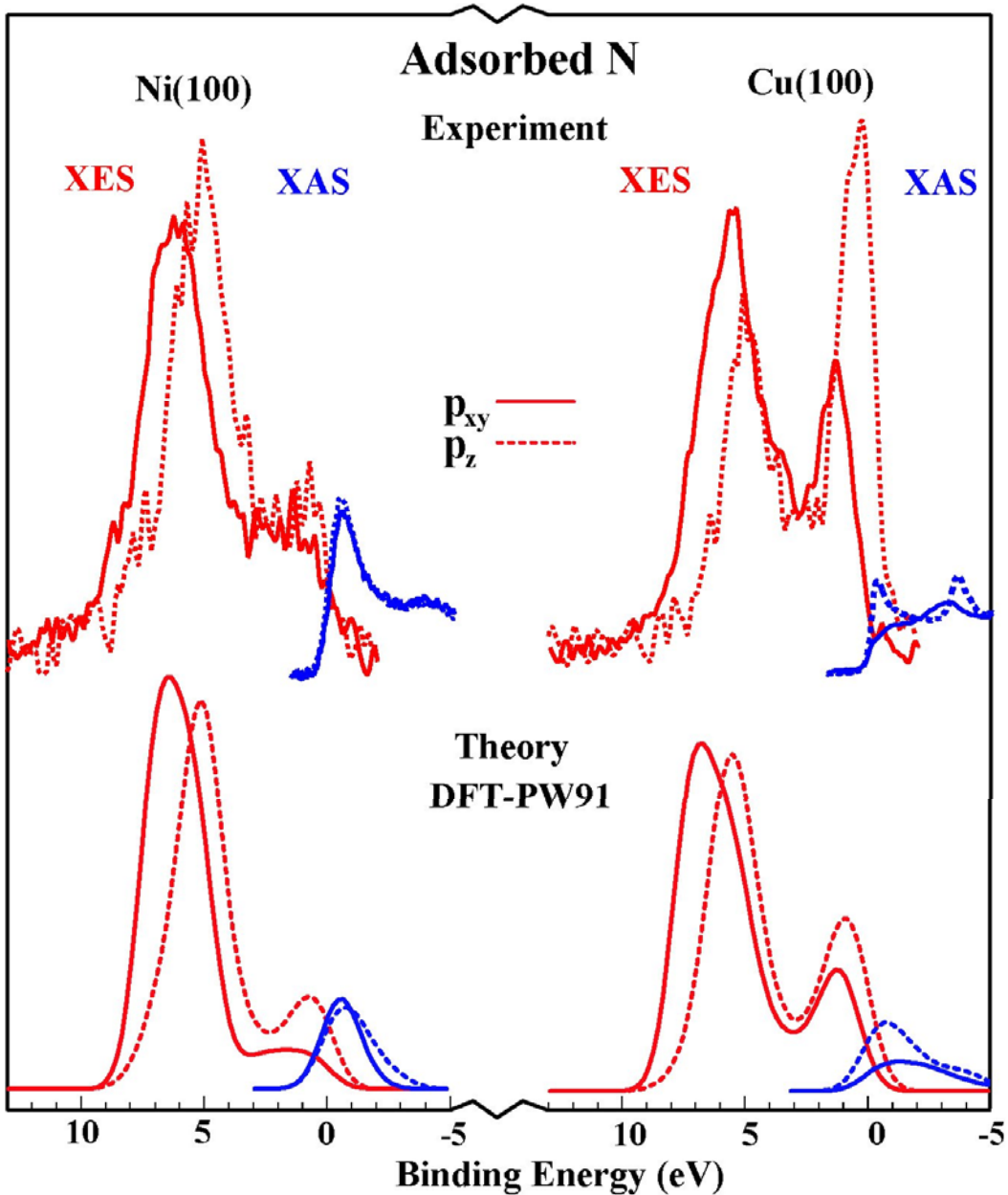


The d band model:

$$\Delta E = \Delta E_{sp} + \Delta E_{hyb-d} = \Delta E_{sp} + \sum_{a} \Delta E_{a-d}$$

Hammer and Nørskov, Nature **376**, 238 (1995) ; Adv. Catal. **45**, 71 (2000)

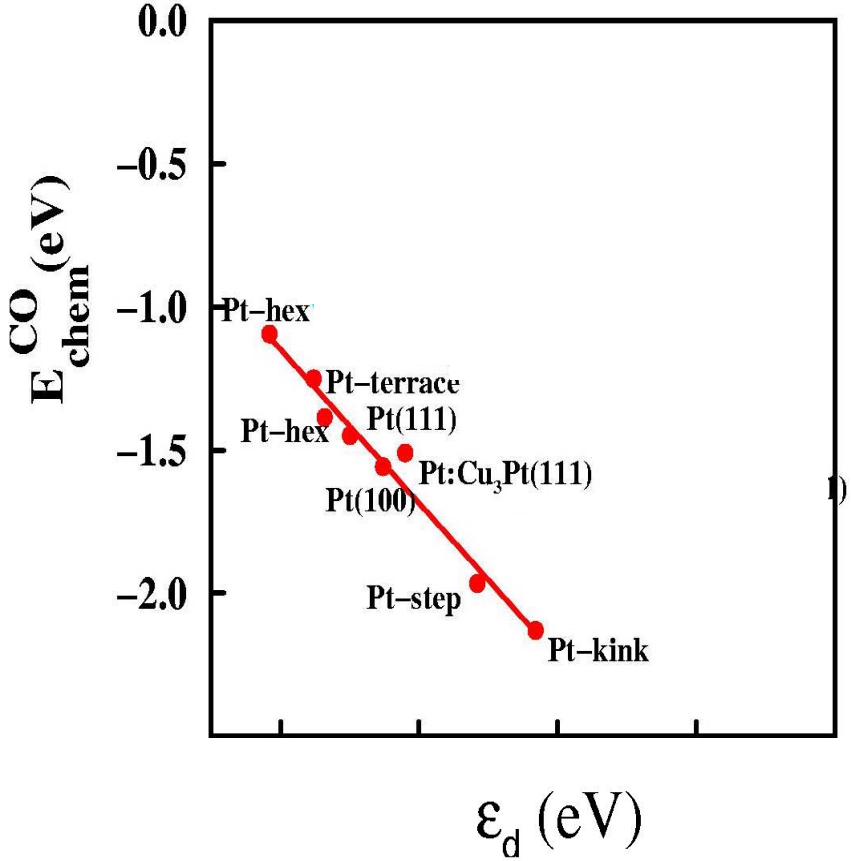
Nitrogen adsorption on Cu and Ni



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

Varying the surface structure

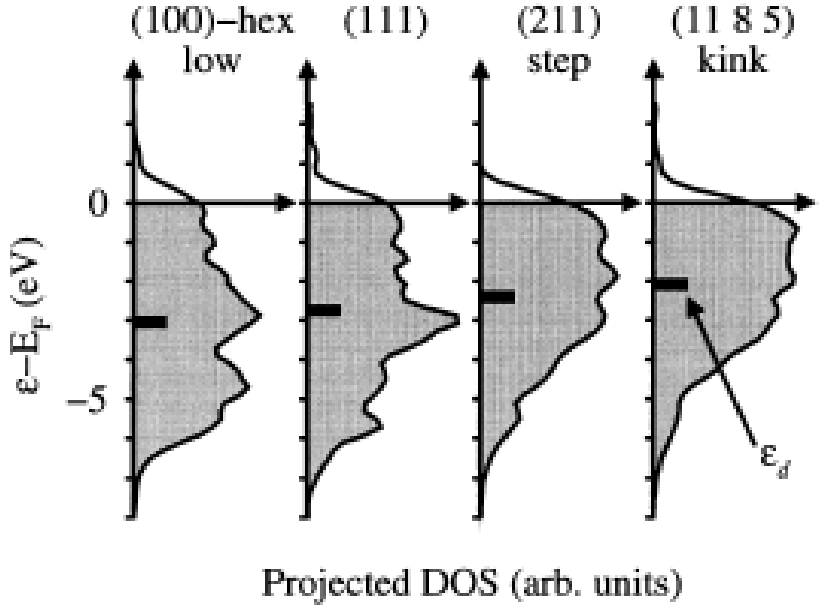
CO chemisorption



Mavrikakis , Hammer, Nørskov
Phys. Rev. Lett. **81**, 2819 (1998)

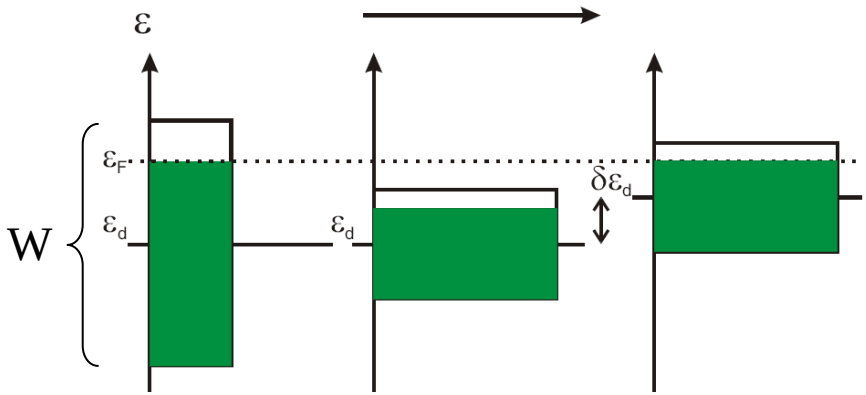
Varying the surface structure

DFT calculations:



Simple model:

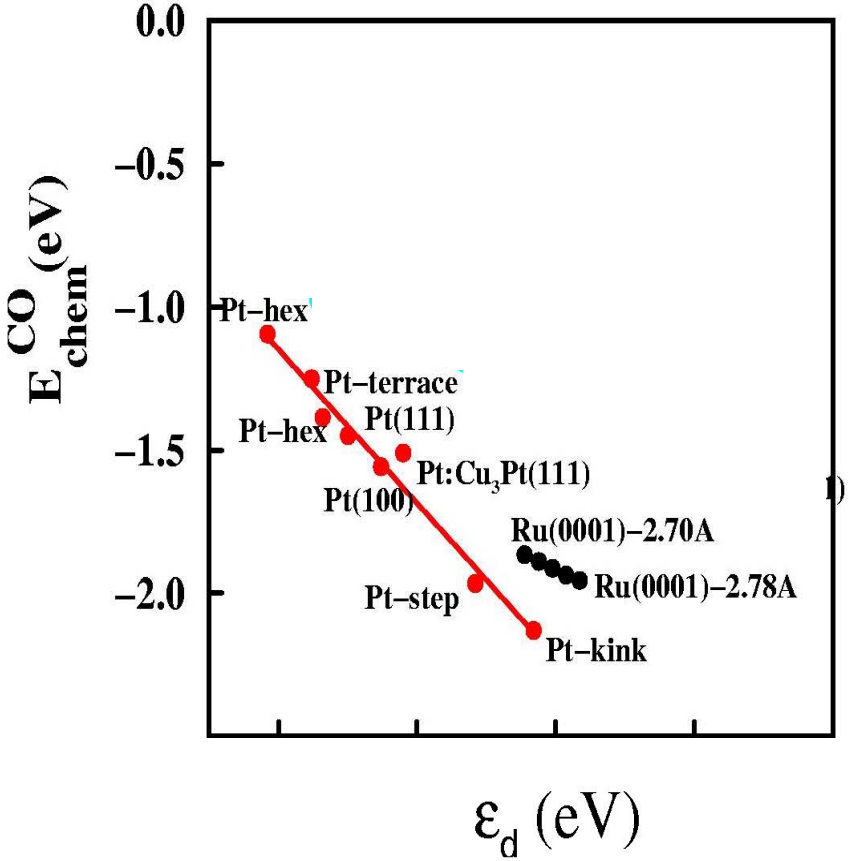
W smaller AND N_d const.
=> Up-shift in ϵ_d



$W \sim N_{nn}^{1/2}$
$W \sim V_{dd}$

Varying the surface strain

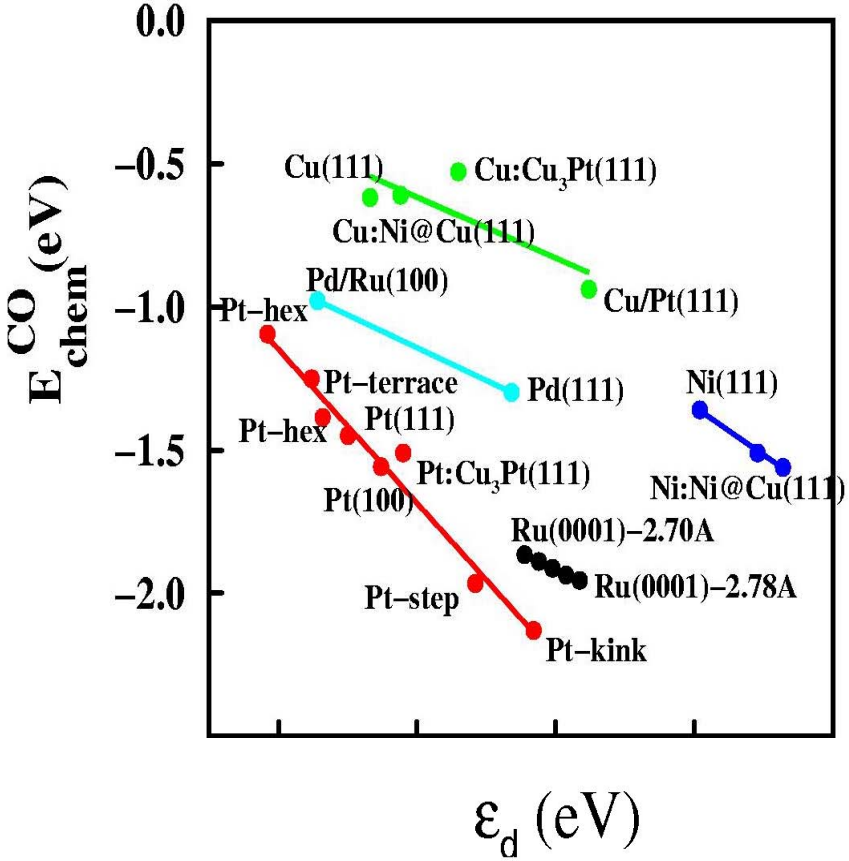
CO chemisorption



Mavrikakis , Hammer, Nørskov
Phys. Rev. Lett. **81**, 2819 (1998)

Varying the surface composition

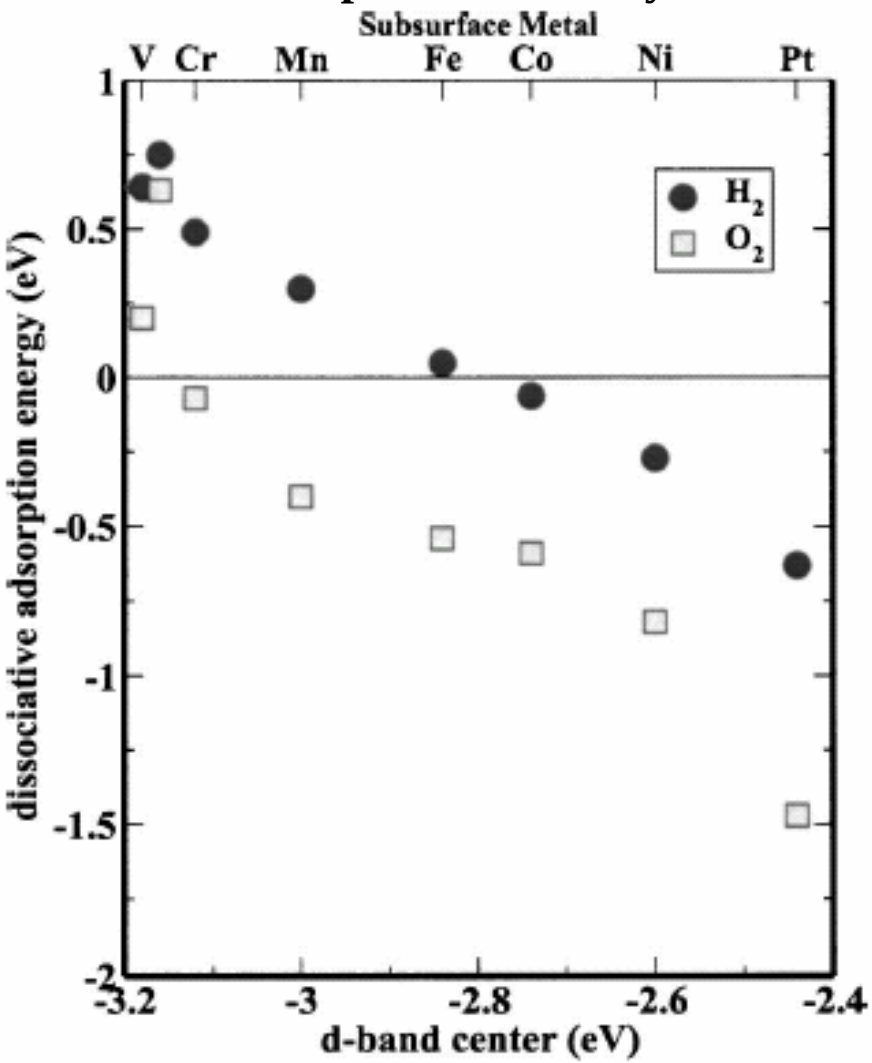
CO chemisorption

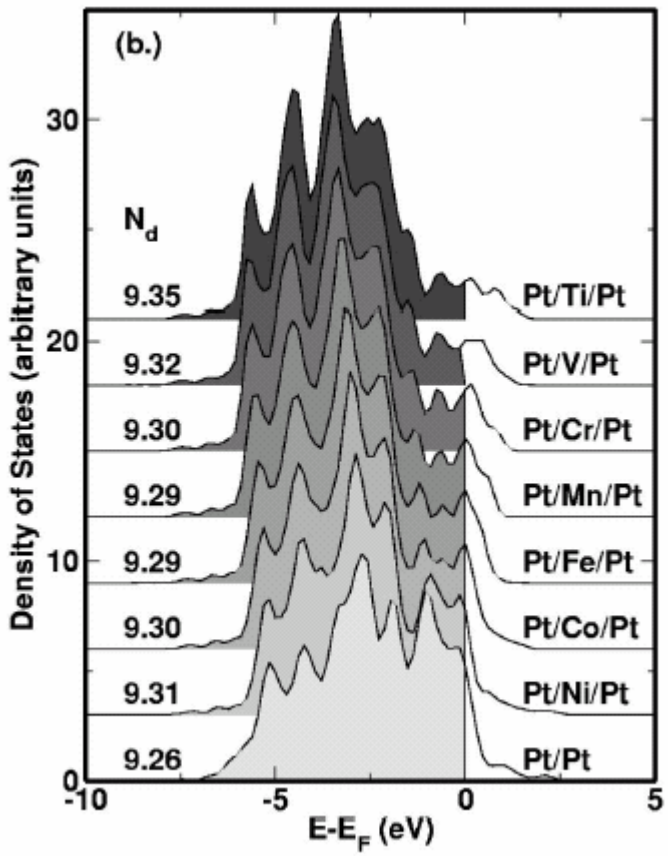


Mavrikakis , Hammer, Nørskov
Phys. Rev. Lett. **81**, 2819 (1998)

Sub-surface alloys

H and O adsorption Pt overlayers

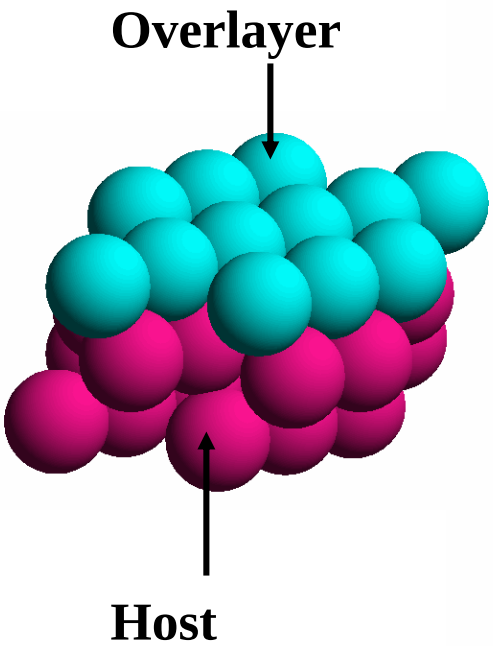


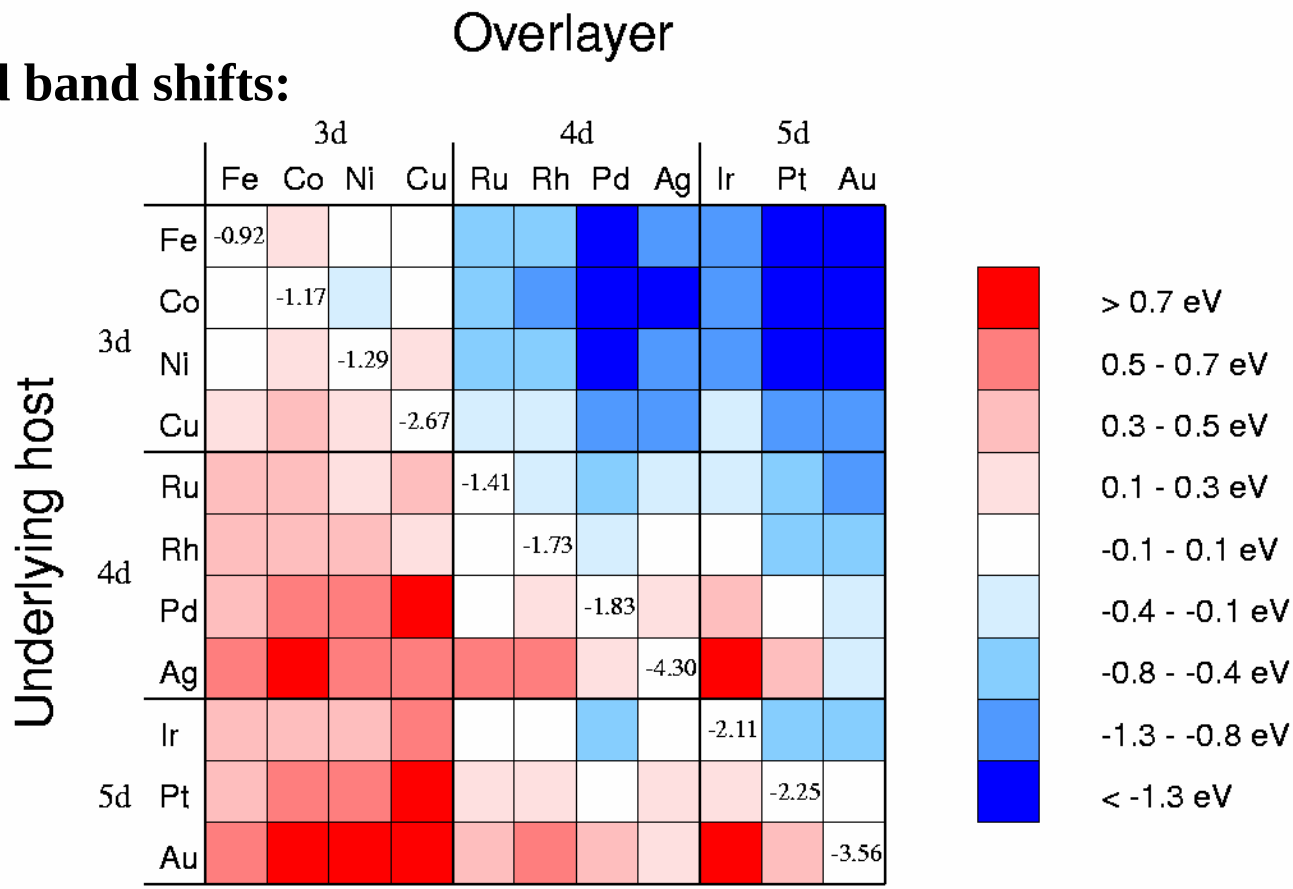


Kitchin, Nørskov, Barteau, Chen
J. Chem Phys. **120** 10240 (2004)

Strained overlayers

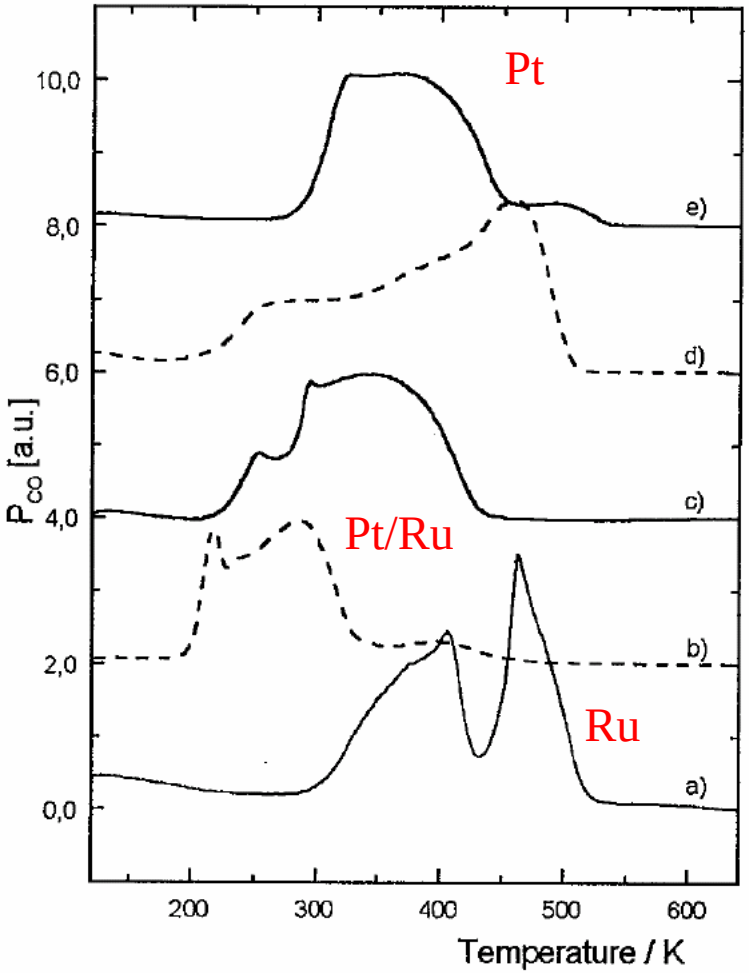
Calculated d band shifts:

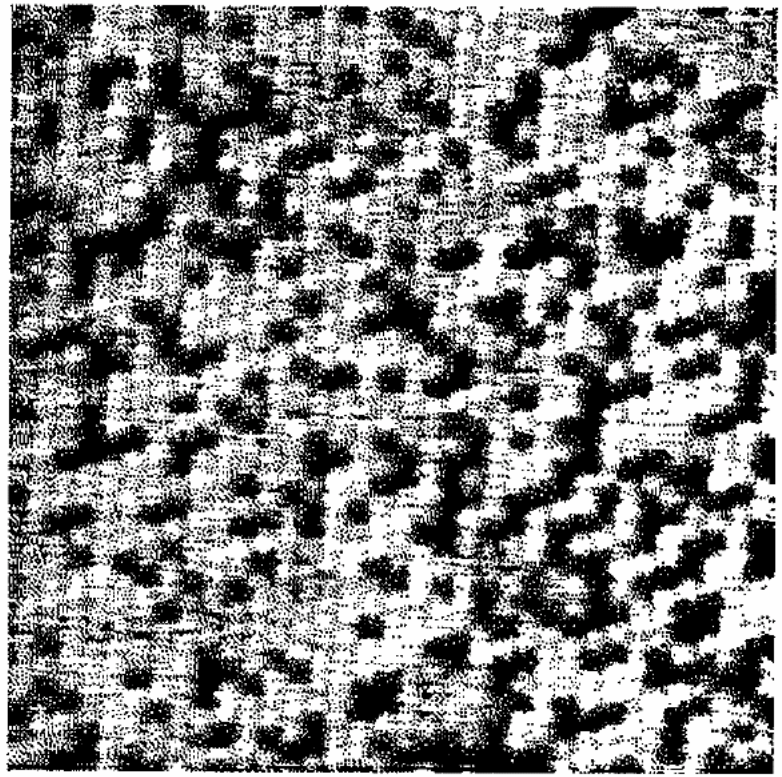




Ruban, Hammer, Stoltze, Skriver, Nørskov, J.Mol.Catal. A **115**, 421 (1997)

CO adsorption on Pt/Ru

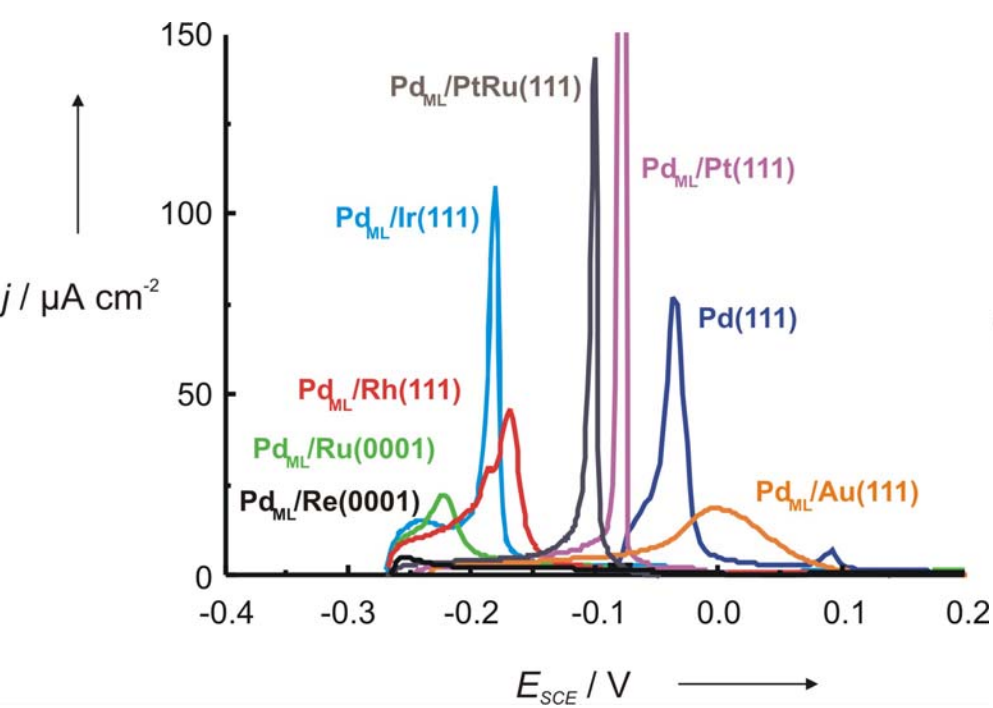


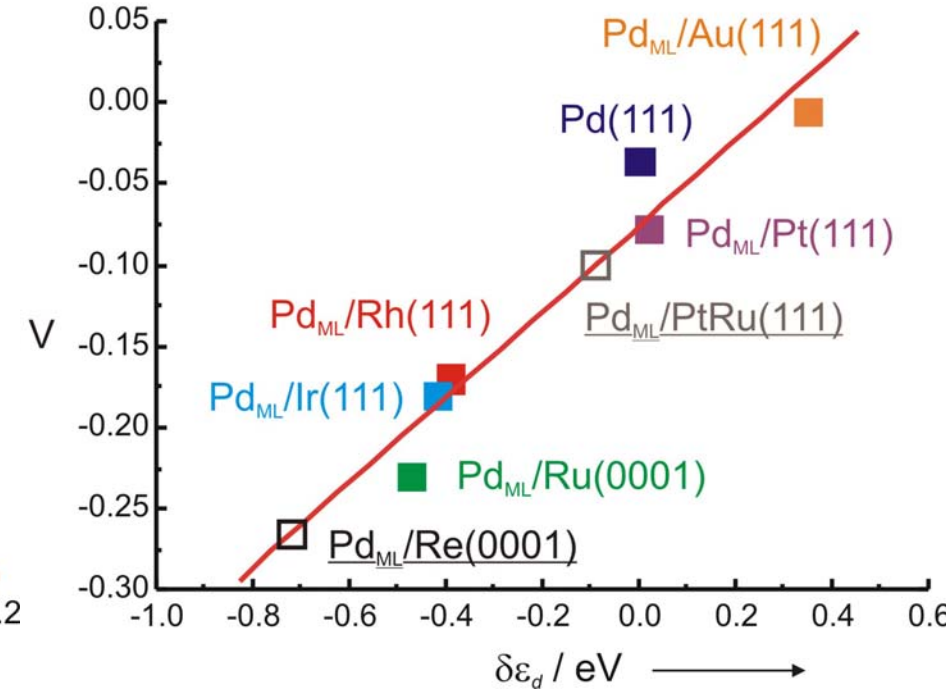


Behm, Acta Physica Polonica **93**, 259 (1998)

H adsorption on Pd overlayers

0.1 M H2SO4, 10 mVs-1





Kibler, El-Aziz, Hoyer, Kolb,
Angew. Chem. Int. Ed. **44** (2005) 2080.

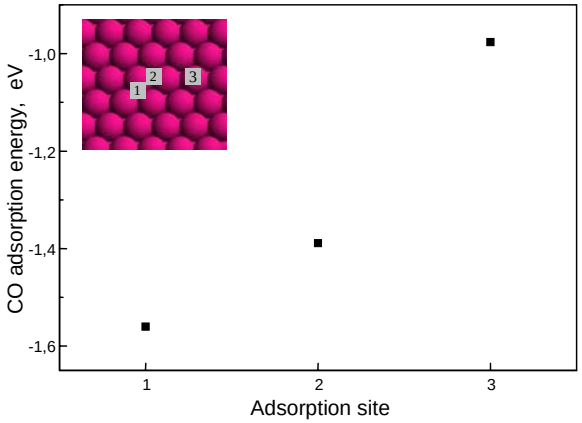
Ligand and ensemble effects

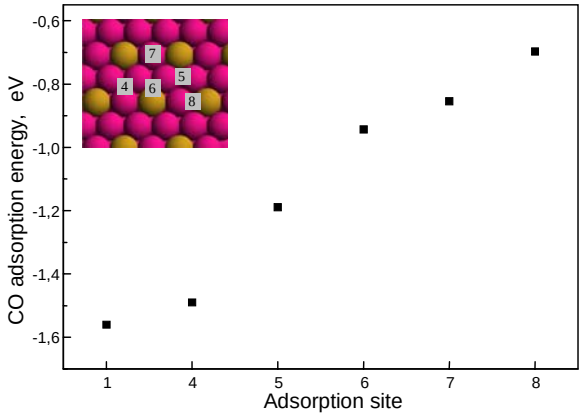
- **Ligand effect:** changes in the chemical properties of the atoms in the surface due to e.g. alloying

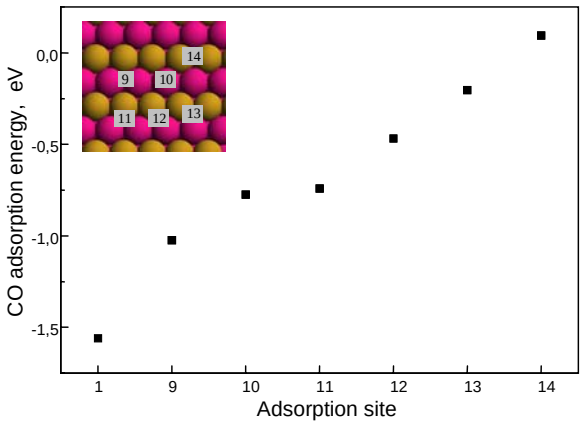
- **Ensemble effect:** changes in the catalytic properties of an ensemble of atoms in the surface when the chemical composition of the ensemble changes

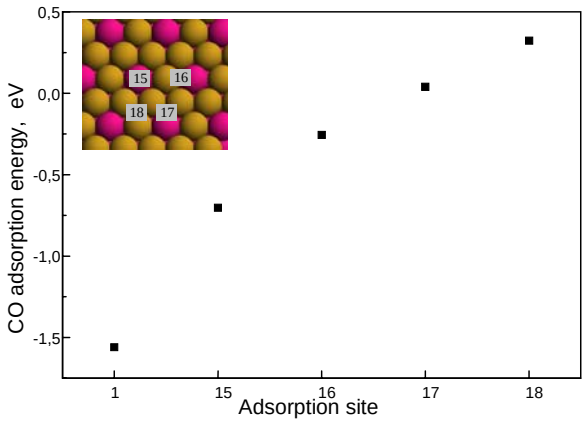
Sachtler, Somorjai, J. Catal. **81**, 7 (1983)

CO adsorption on Au/Pd(111)



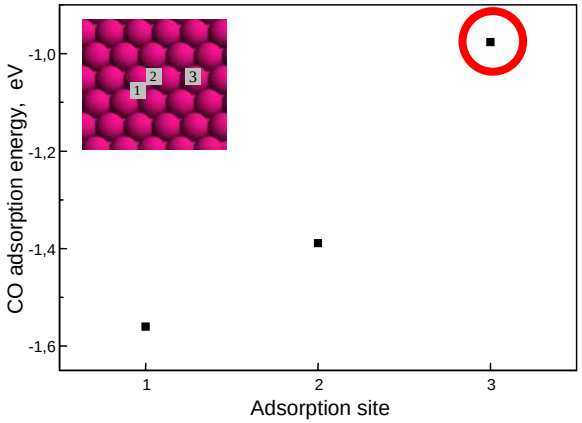


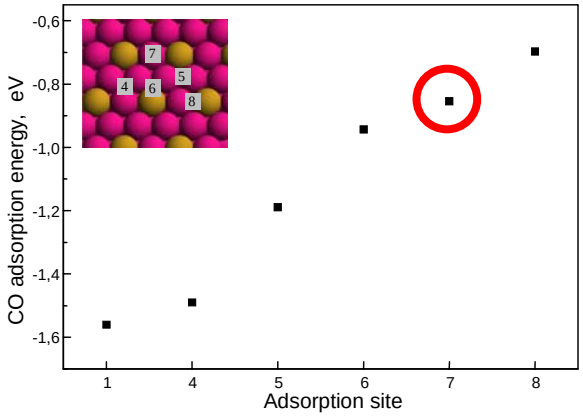


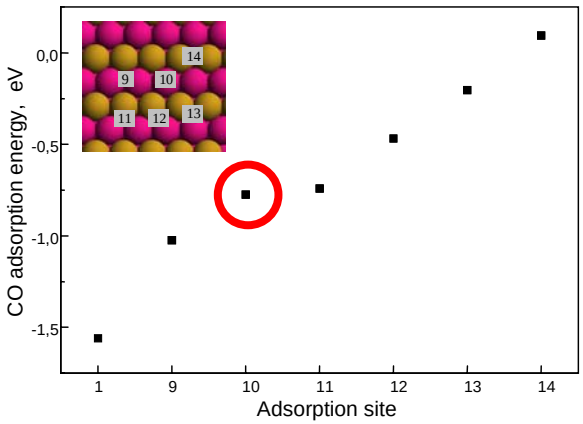


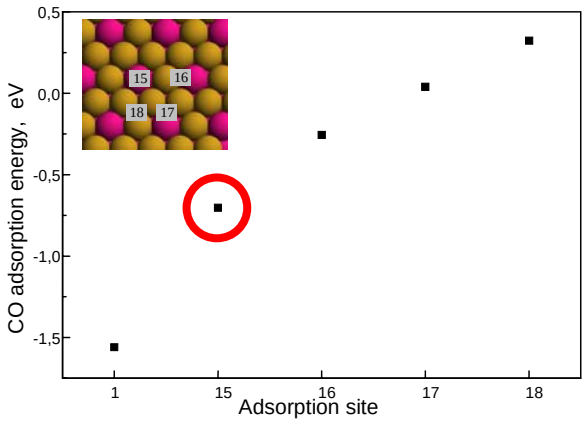
Liu, Nørskov, Phys.Chem.Chem.Phys. **3**, 3814 (2001)

CO atop Pd with varying ligands



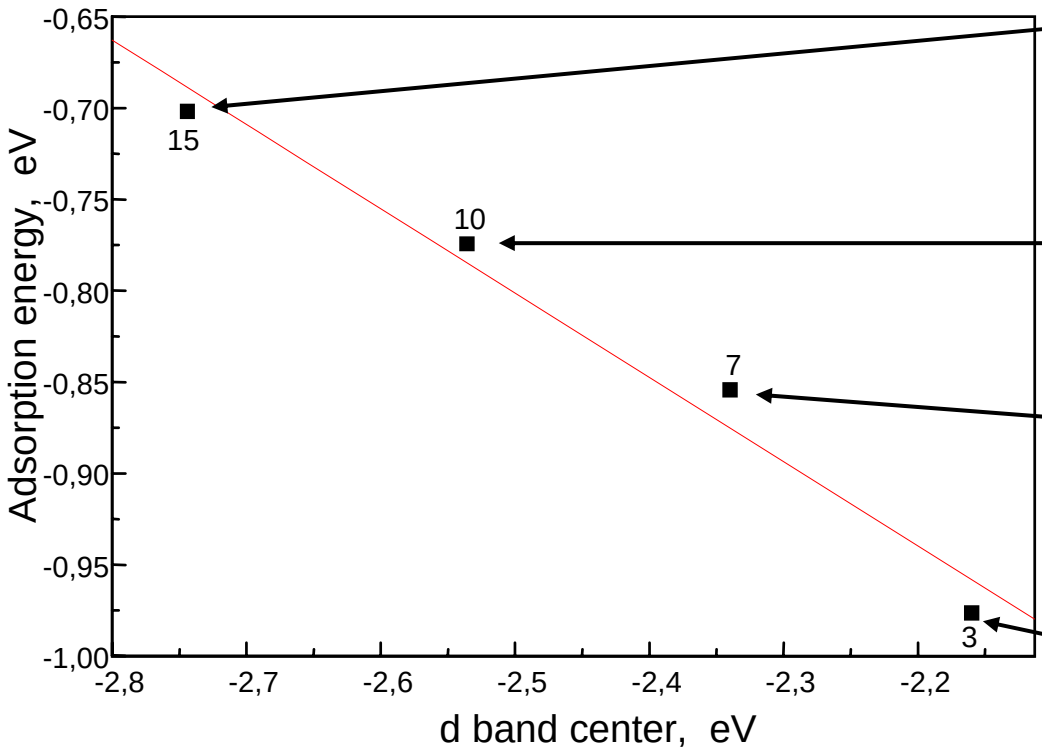


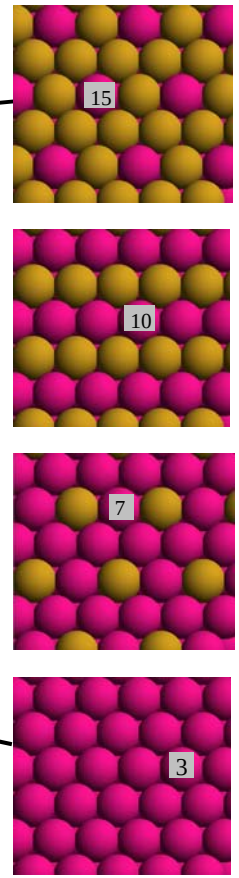




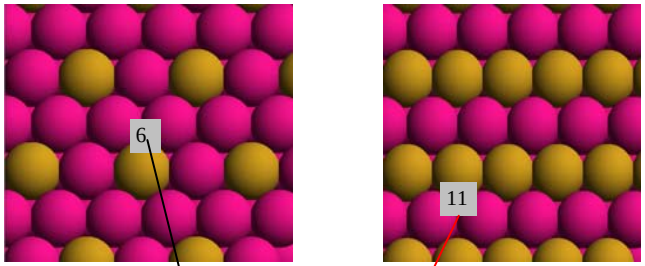
Ligand effects

Adsorption ontop a Pd atom
with varying number of Au ligands

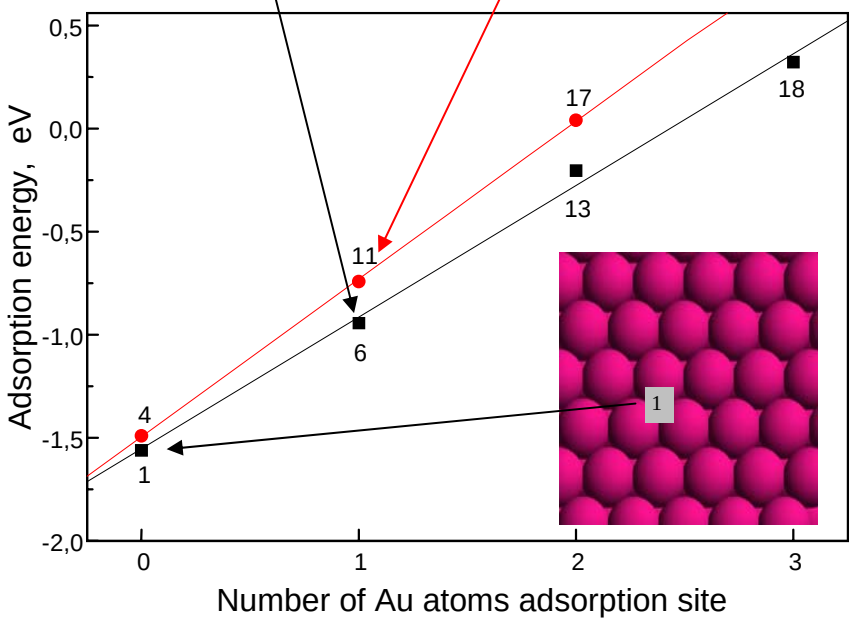


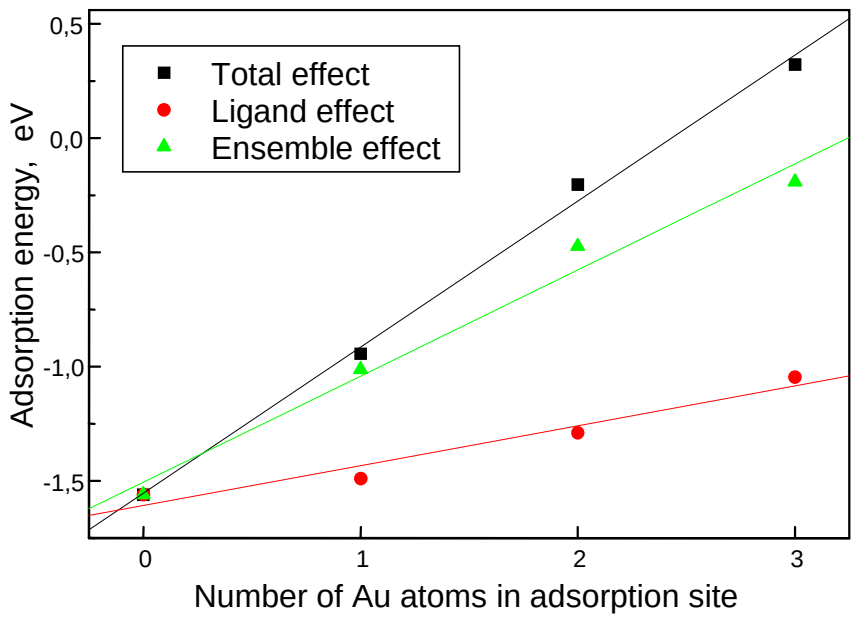


Ensemble effects



Three-fold adsorption – vary the composition of the surface ensemble

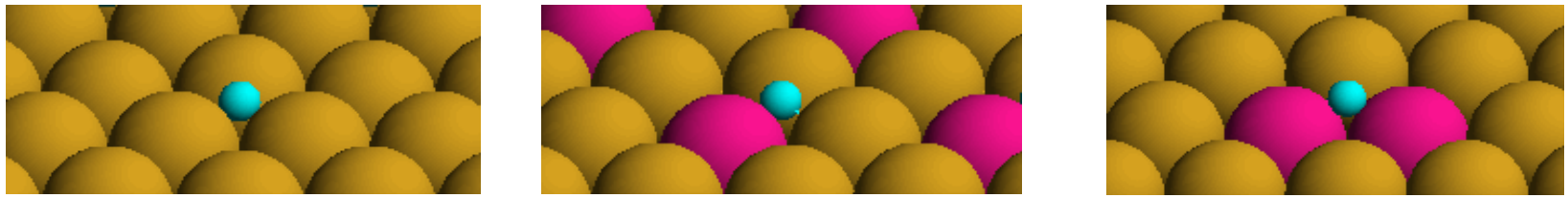




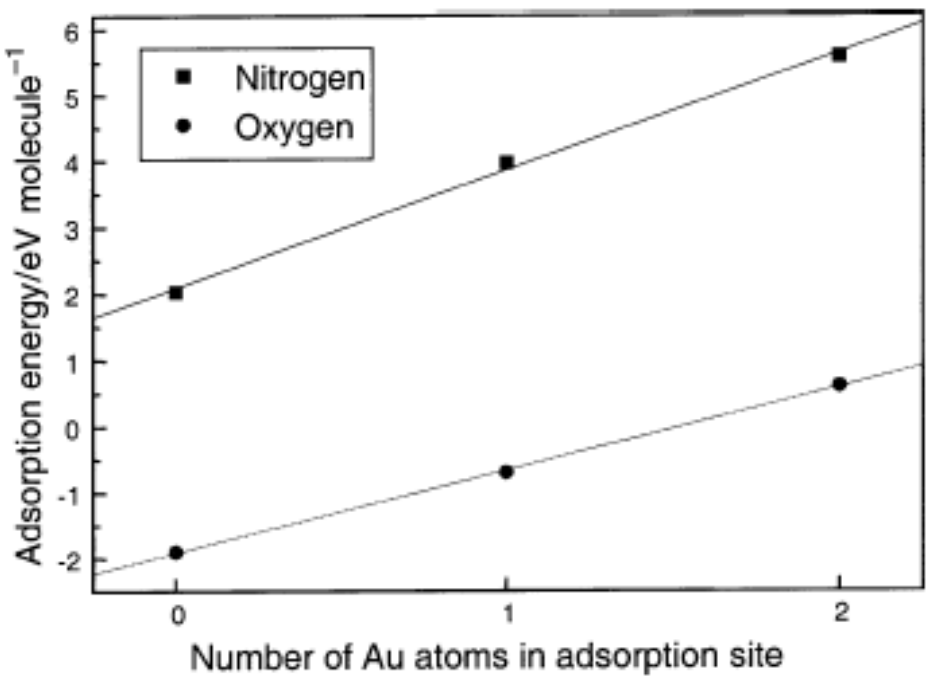
Liu, Nørskov, Phys.Chem.Chem.Phys. **3**, 3814 (2001)

The interpolation principle

N and O adsorption on Au/Pd(111)



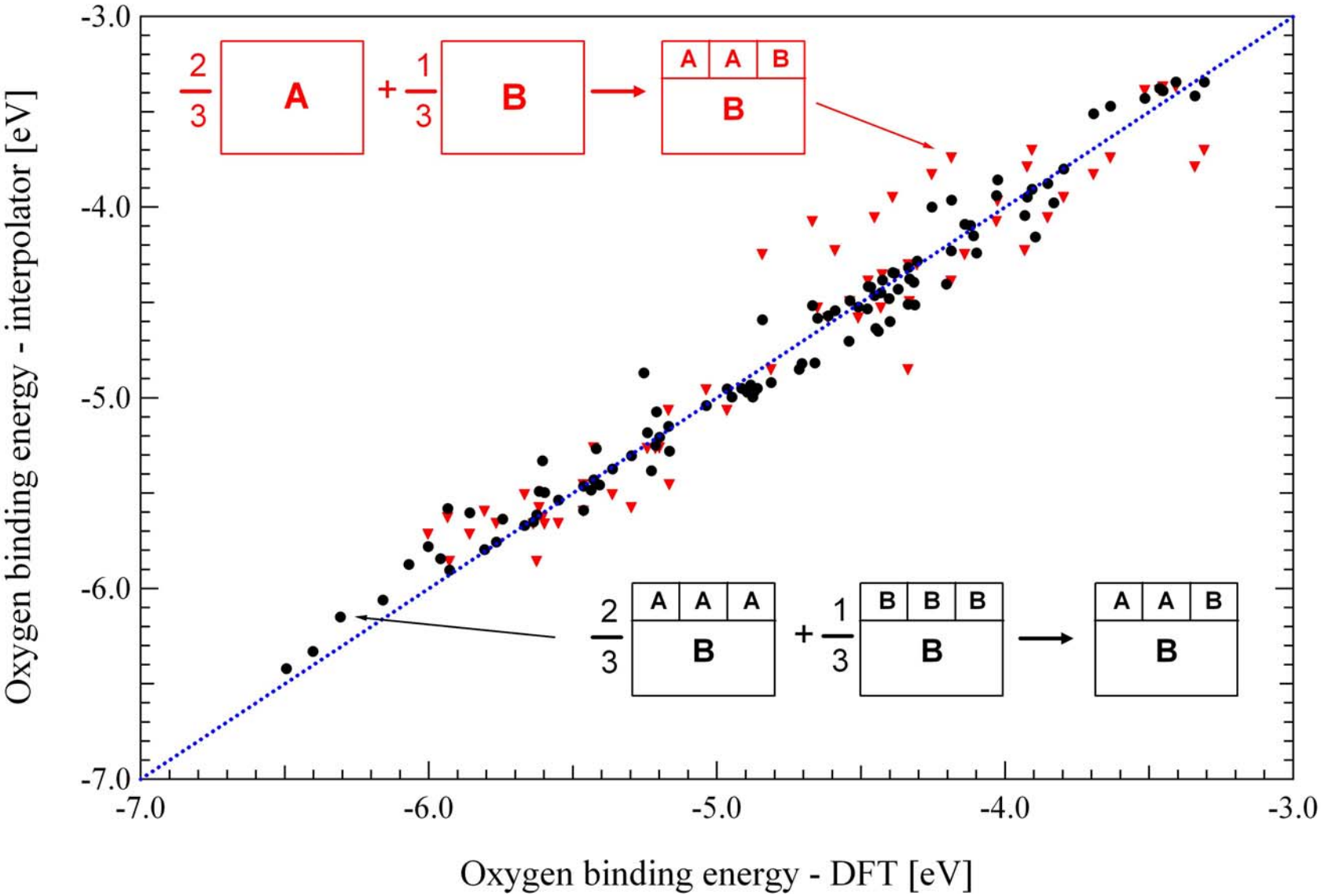
$\Delta E(A_xB_{1-x}) \sim$
$x\,\Delta E(A) + (1-x)\,\Delta E(B)$



Liu, Nørskov, Phys.Chem.Chem.Phys. **3**, 3814 (2001)

Jacobsen (Christensen), Dahl, Clausen, Bahn, Logadottir, Nørskov, JACS **123**, 404 (2001)

O adsorption – model vs DFT

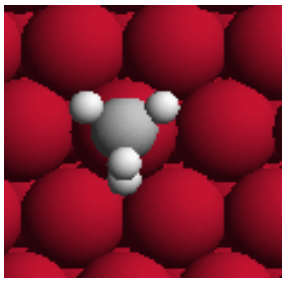


Greeley, Nørskov, Surf. Sci. **592**, 104 (2005)

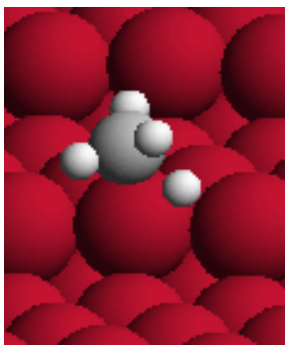
Similar trends for activation energies

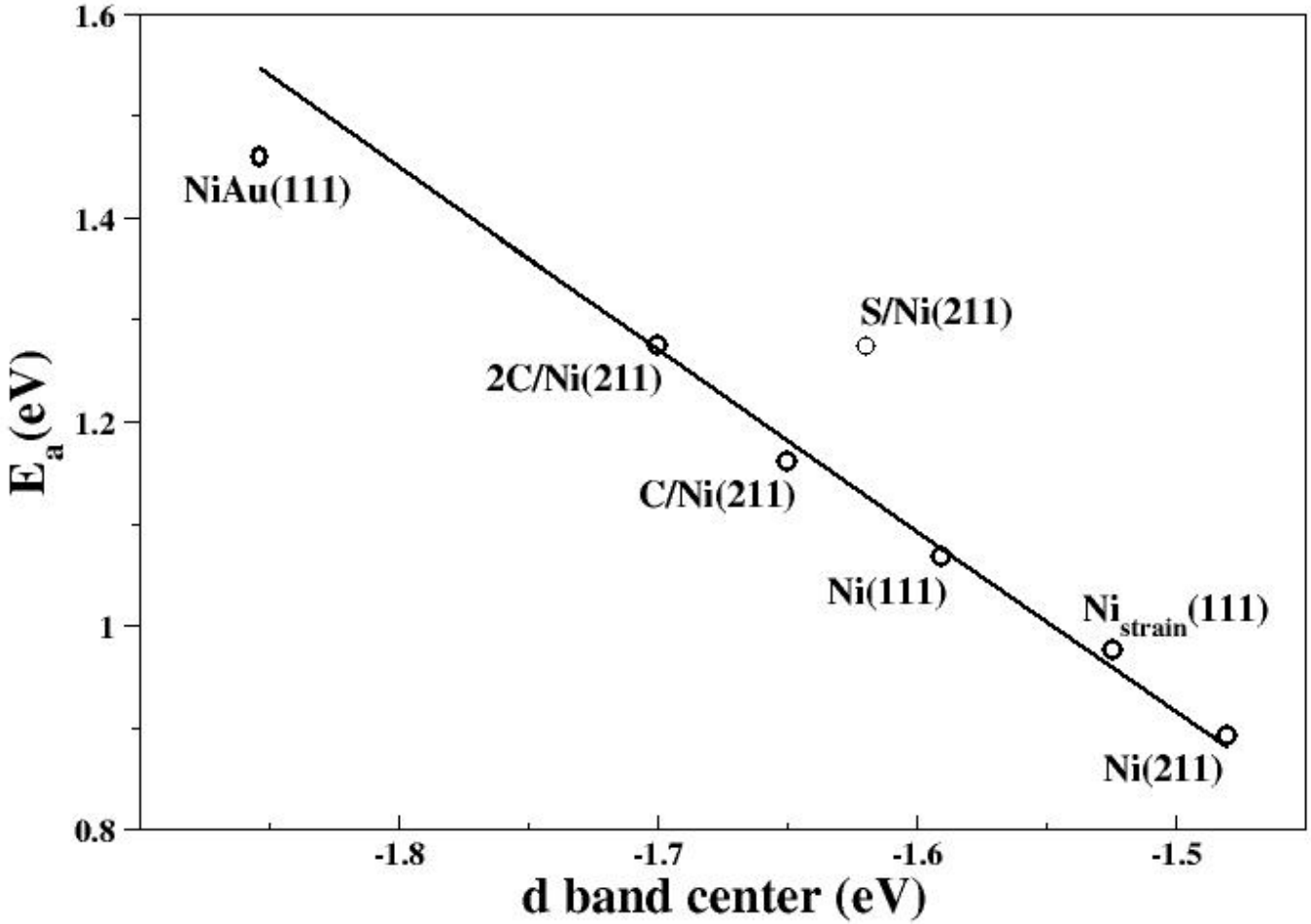
Methane dissociation on Ni surfaces

Ni(111)



Ni(211)

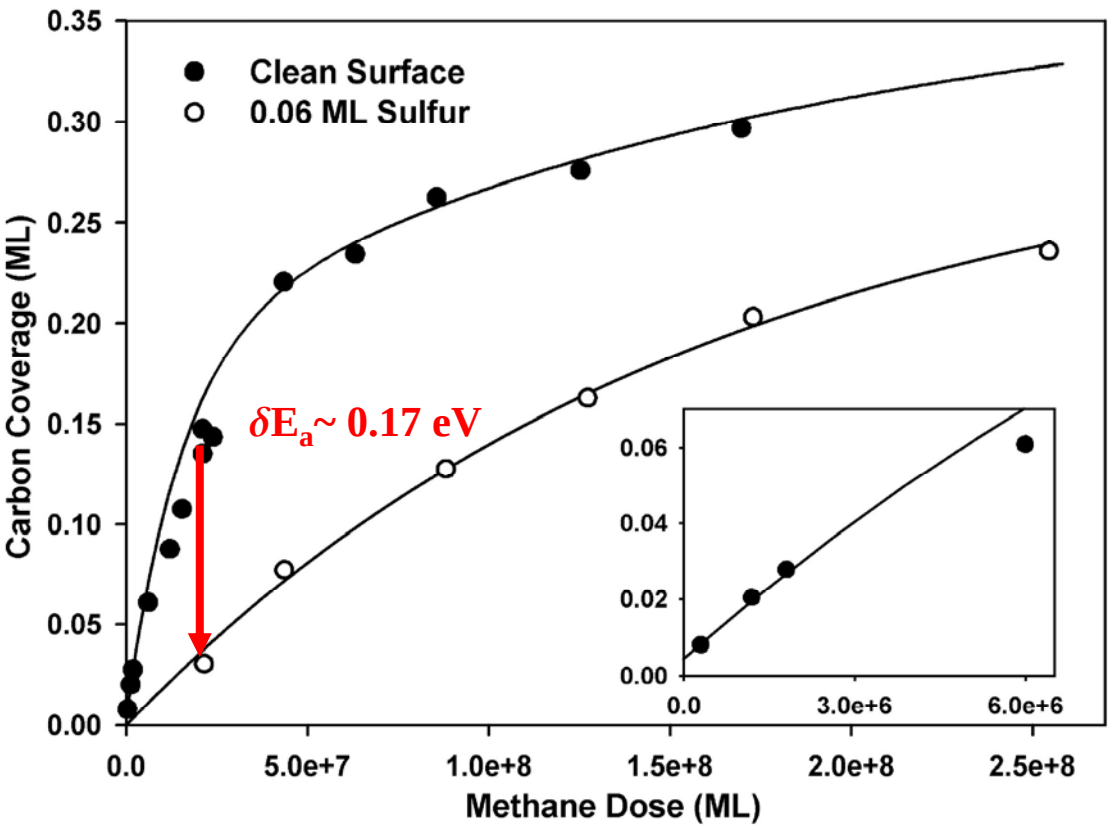


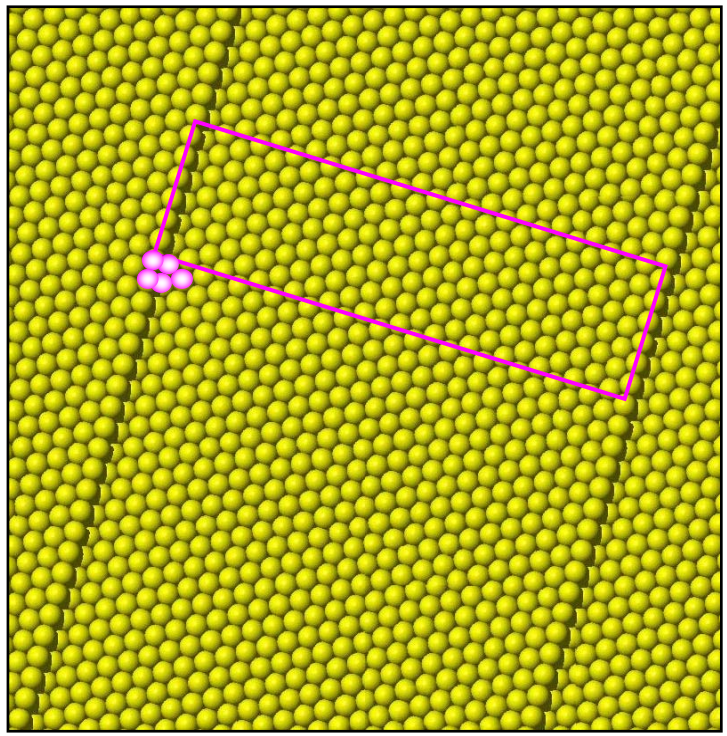


Abild-Pedersen, Greeley, Nørskov, Catal. Lett. **105**, 9 (2005)

Experimental verification

Carbon deposition at 500K vs. methane dose on a Ni(14 13 13) crystal surface.



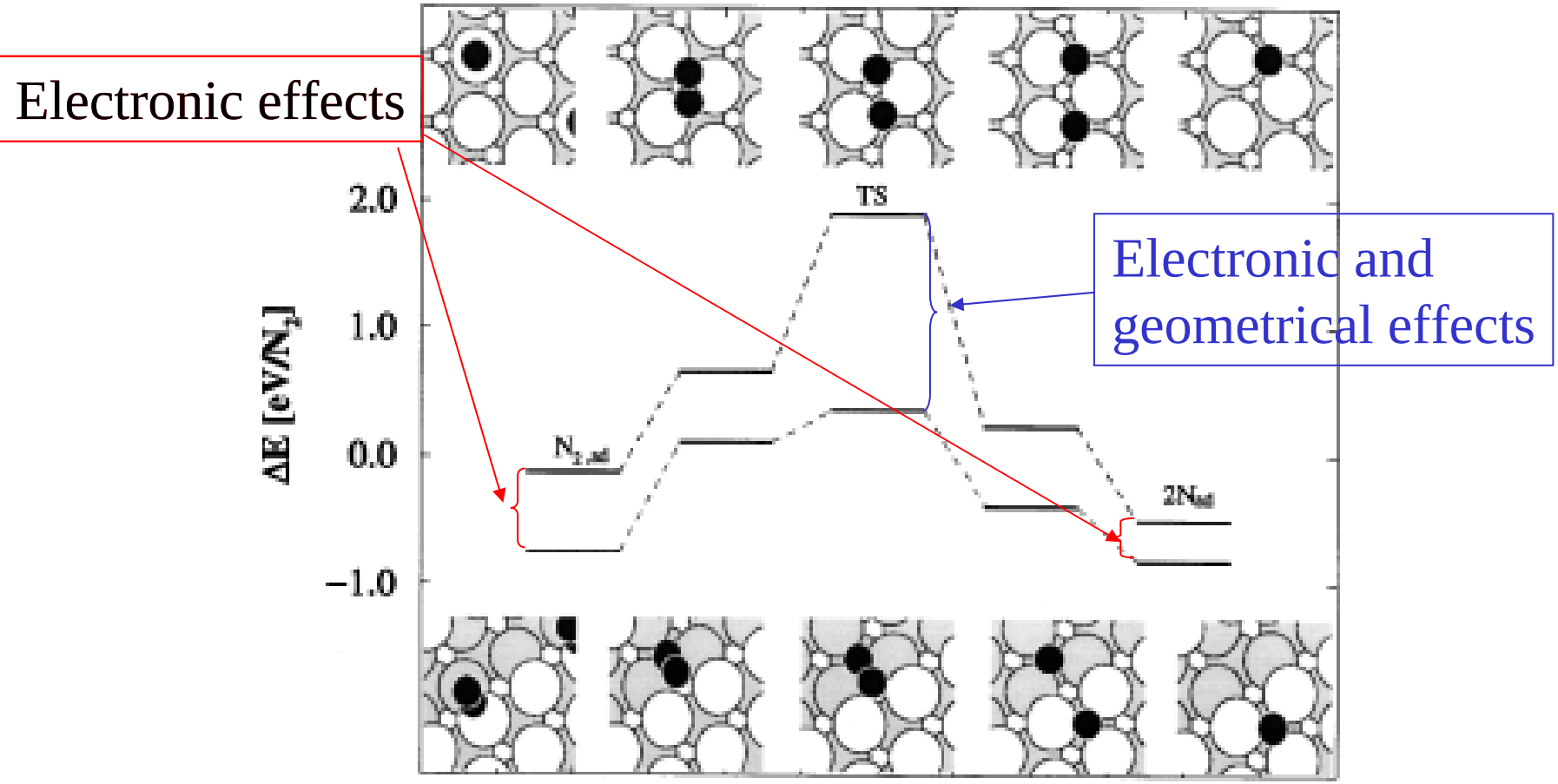


Theory: δE_a~ 0.20 eV

Abild-Pedersen, Lytken, Engbæk, Nielsen, Chorkendorff, Nørskov Surf. Sci (2005)

The electronic and geometrical factors in surface reactivity

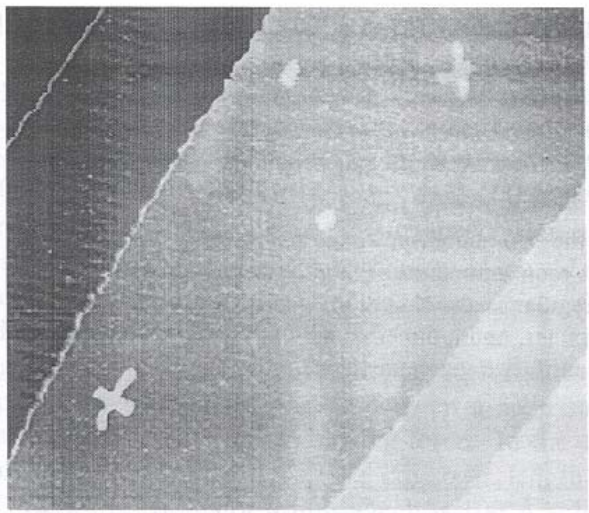
N_2 dissociation on Ru surfaces:

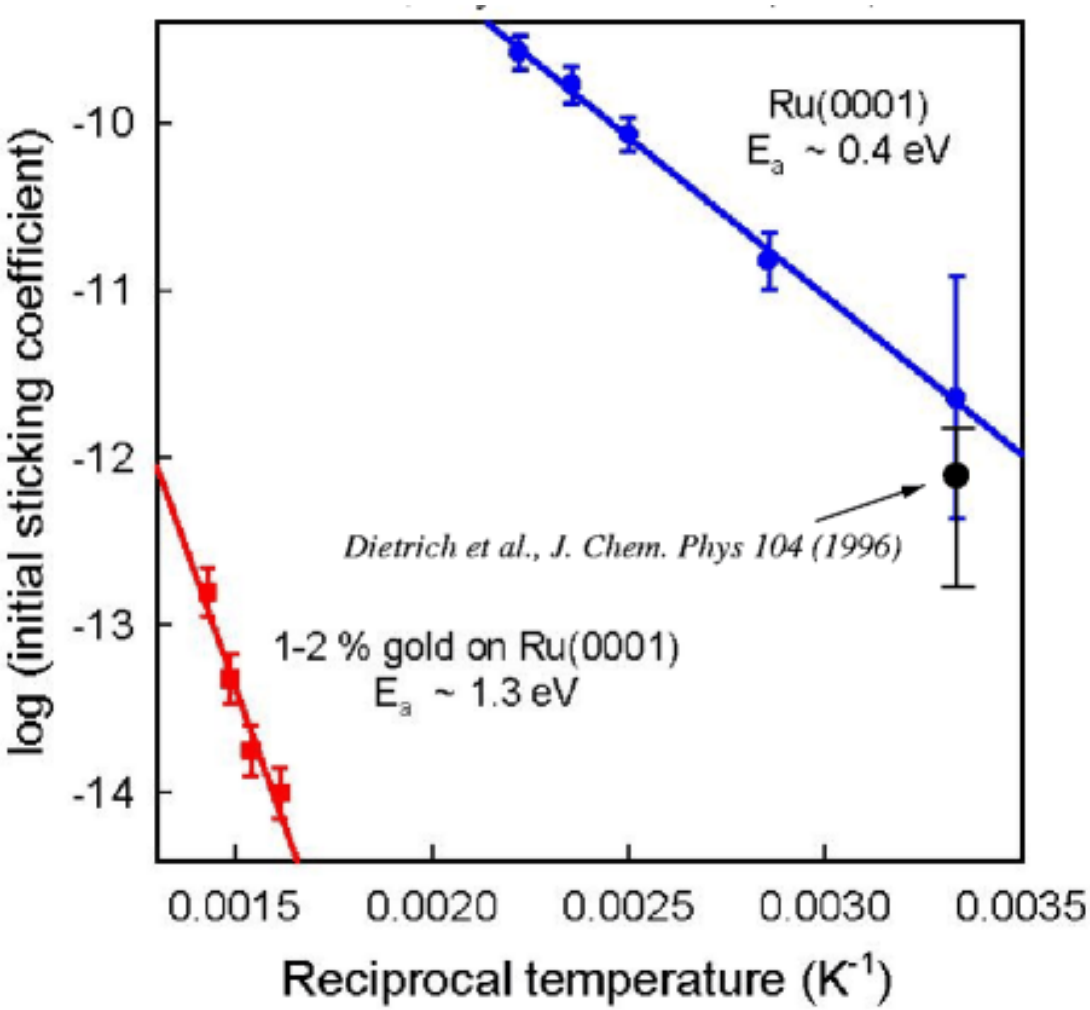


Experimental evidence for step-effect

Au decorates steps:

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





Dahl, Logadottir, Egeberg, Larsen, Chorkendorff, Törnqvist, Nørskov, Phys.Rev.Lett. **83**, 1814 (1999)

N_2 dissociation on Ru(0001)

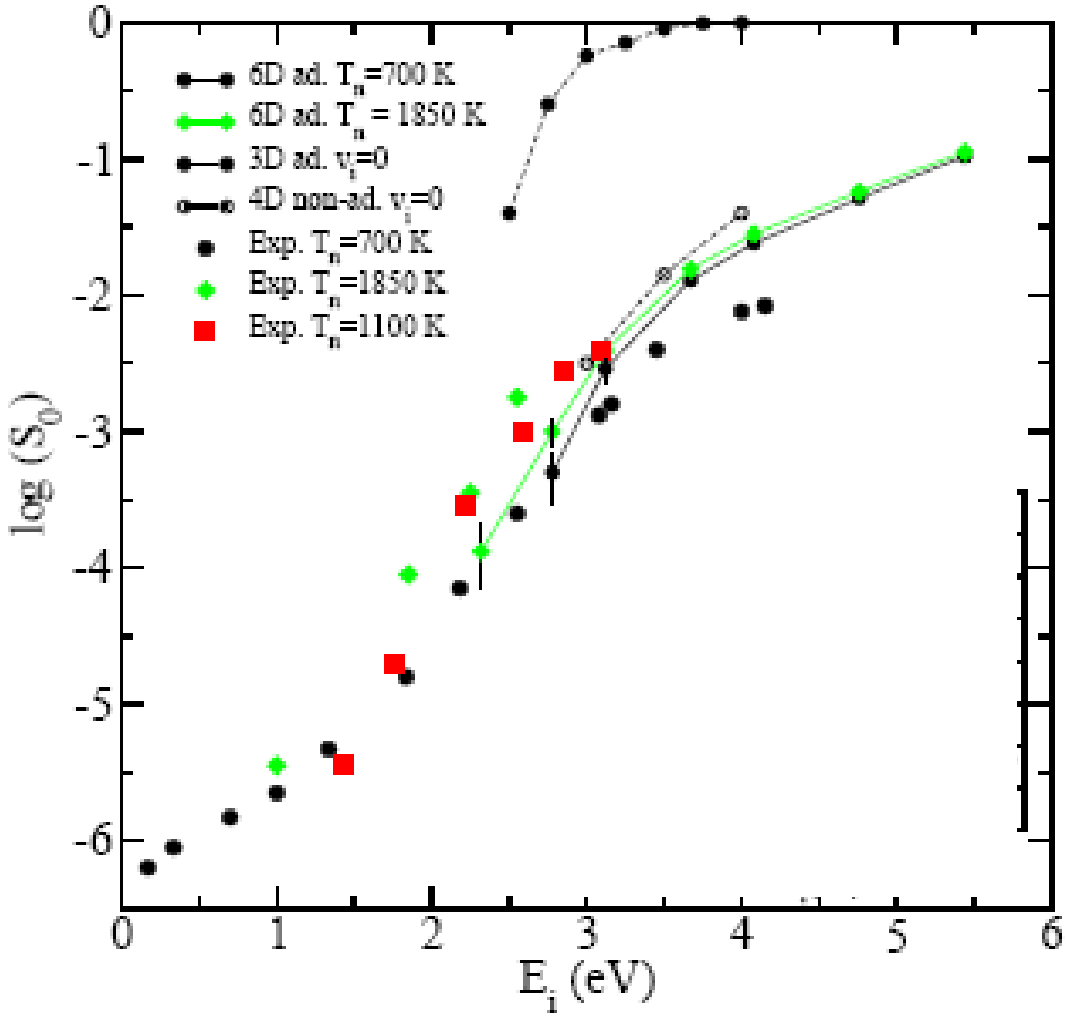
Experiments:

Romm, Katz, Koslov, Assher
JPC B **101** 2213 (1997)

Diekhoner, Mortensen, Bauer, Luntz, JCP **115**, 9028 (2001)

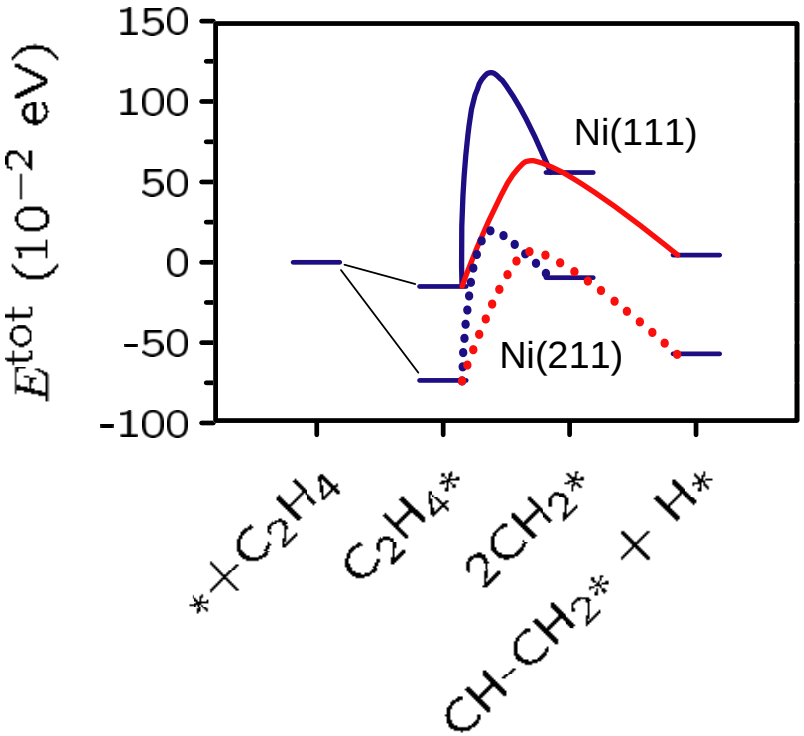
Theory:

Diaz, Vincent, Khrisnamohan, Olsen, Kroes, Honkala, Nørskov
Phys. Rev. Lett. **96,** 096102 (2006)

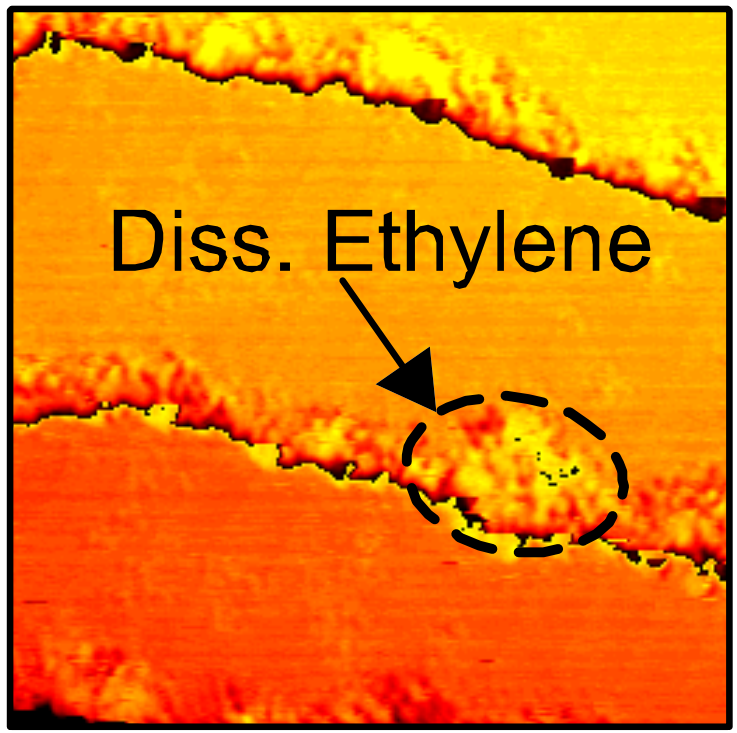


C_2H_4 dissociation Ni(111)

DFT:



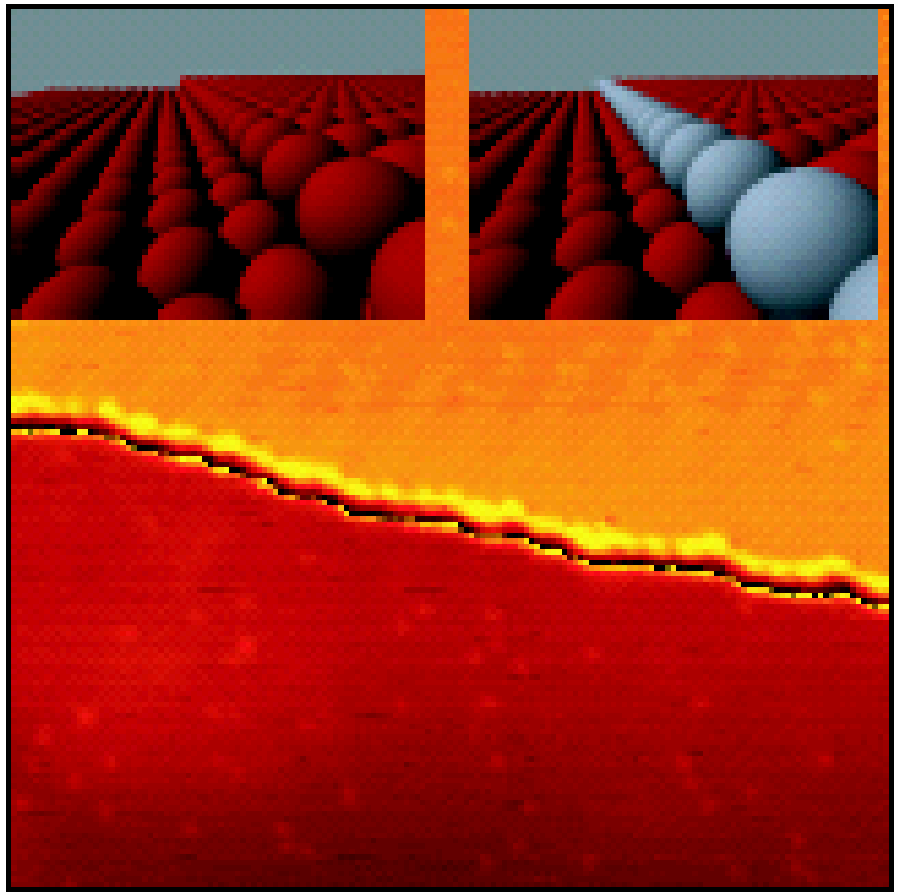
STM:



Vang, Vestergaard, Besenbacher, Dahl, Clausen, Honkala, Nørskov
Nature Mat. **4**, 160 (2005)

Step blocking I

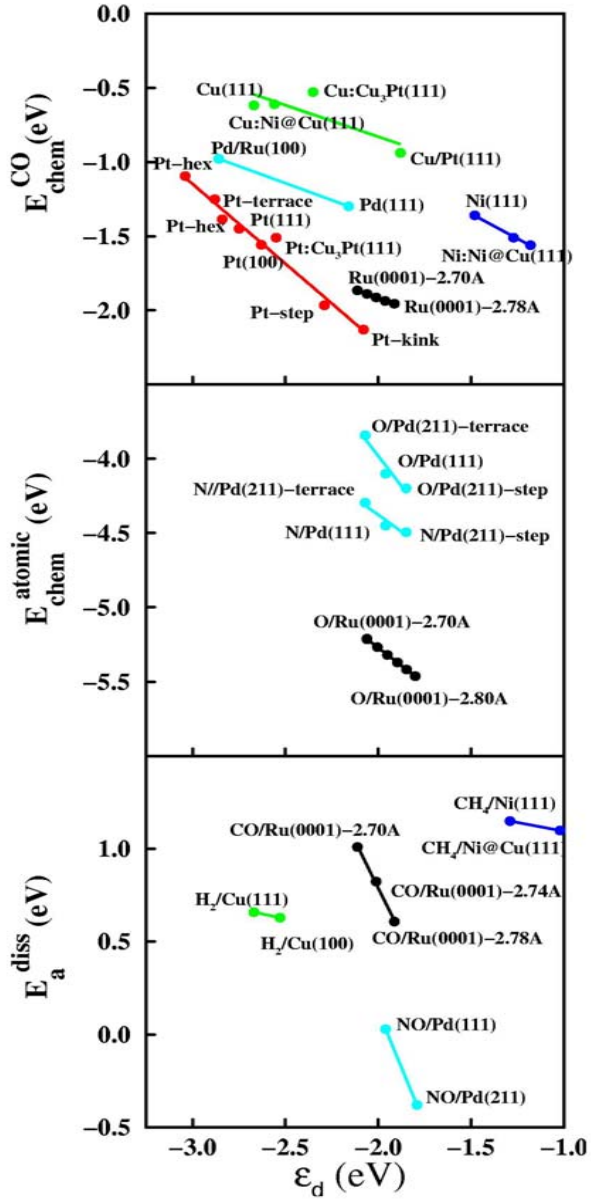
STM – Ag/Ni(111)



Vang, Vestergaard, Besenbacher, Dahl, Clausen, Honkala, Nørskov
Nature Mat. **4**, 160 (2005)

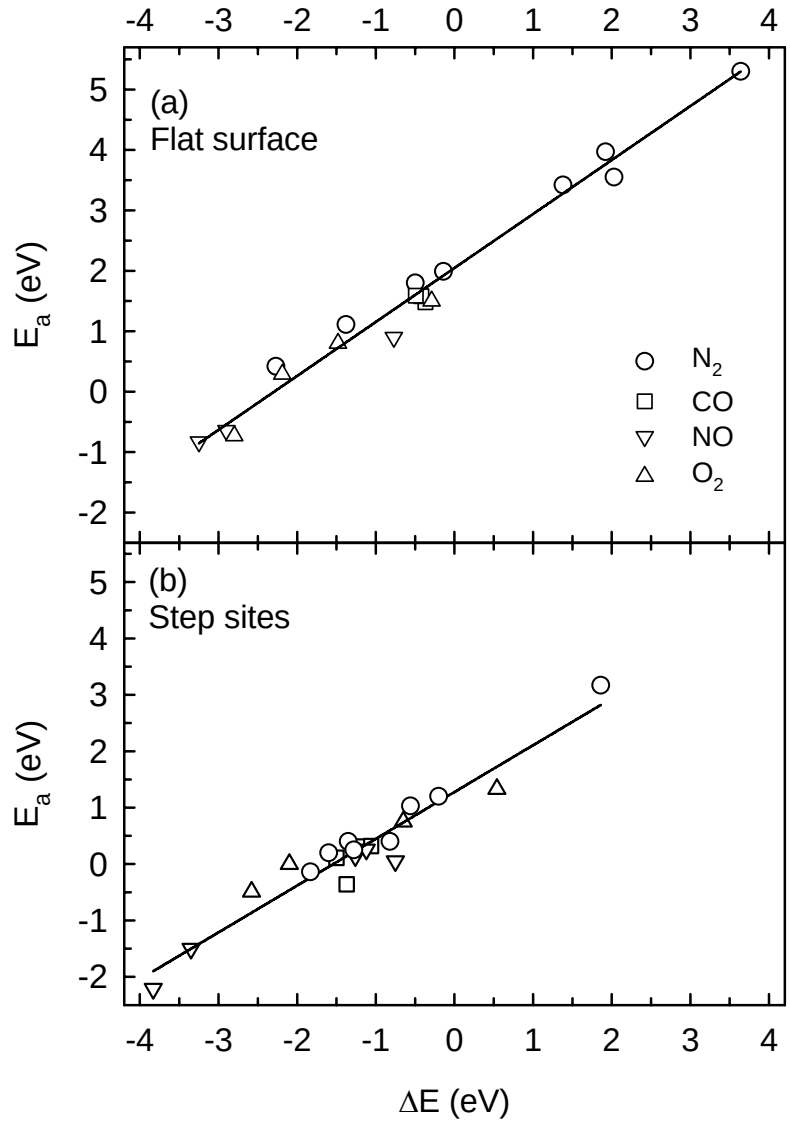
Trends for FIXED geometry

- Governed largely (but not exclusively) by d-band shifts
- Same for initial, final, and transition states

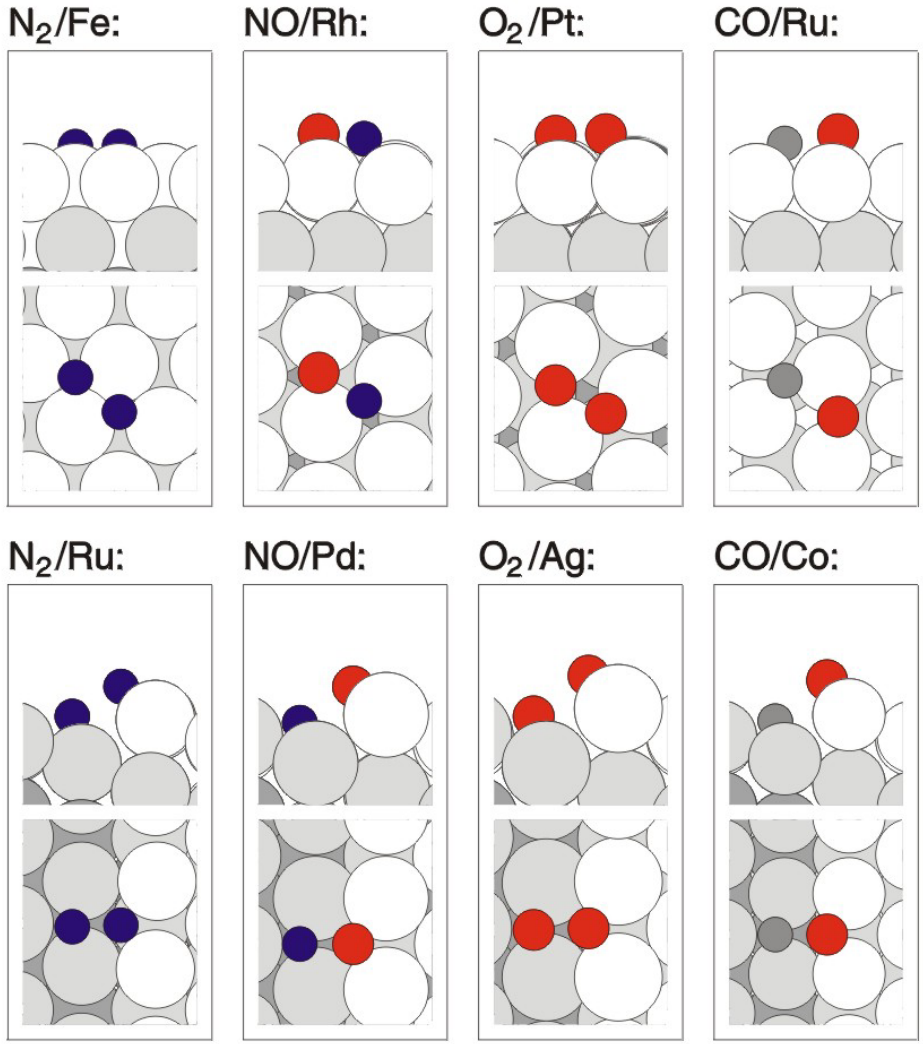


Correlations

– the Brønsted-Evans-Polanyi relation



Transition state structures



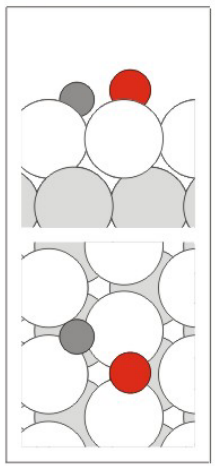
The geometrical effect– rigorous definition

For all ΔE :

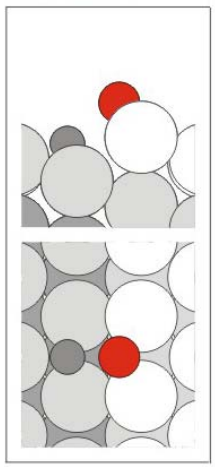
$$E_a^{close\ packed}(\Delta E) - E_a^{step}(\Delta E) \approx 1\text{eV}$$

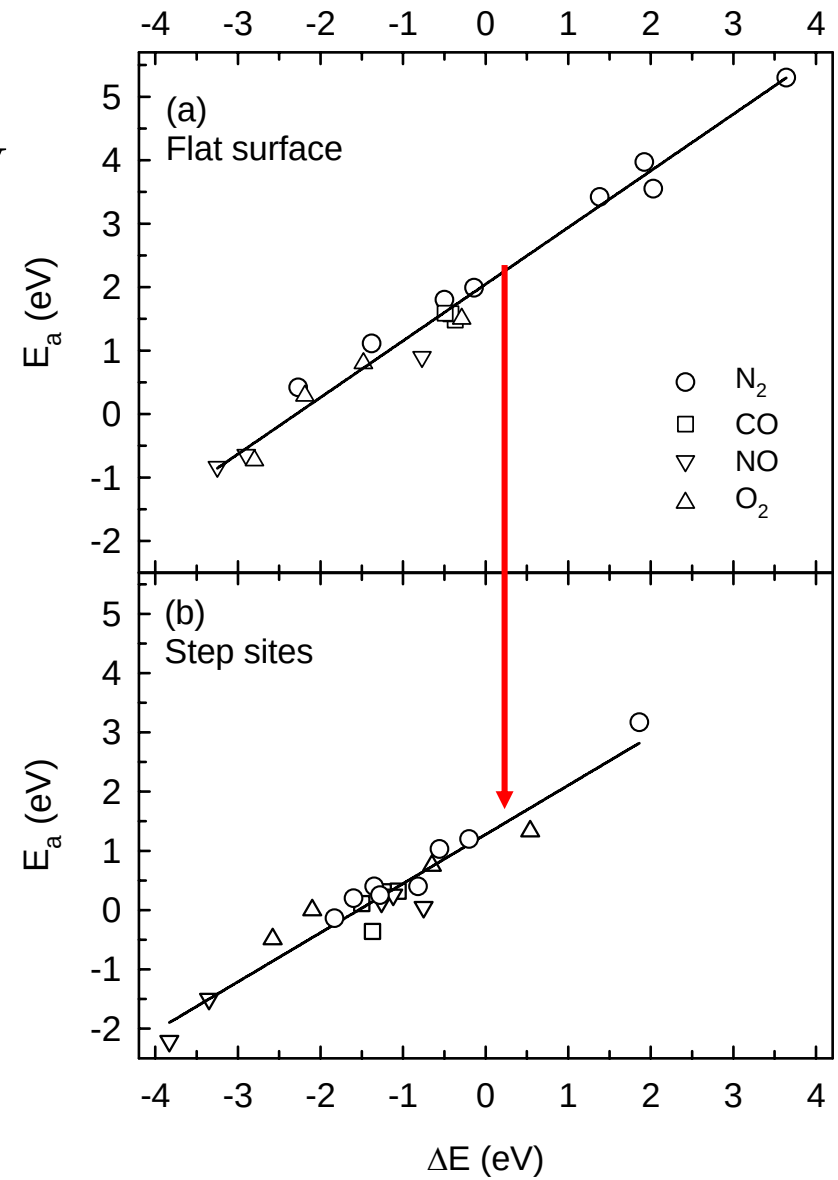
=> Steps (much) more reactive

CO/Ru:



CO/Co:

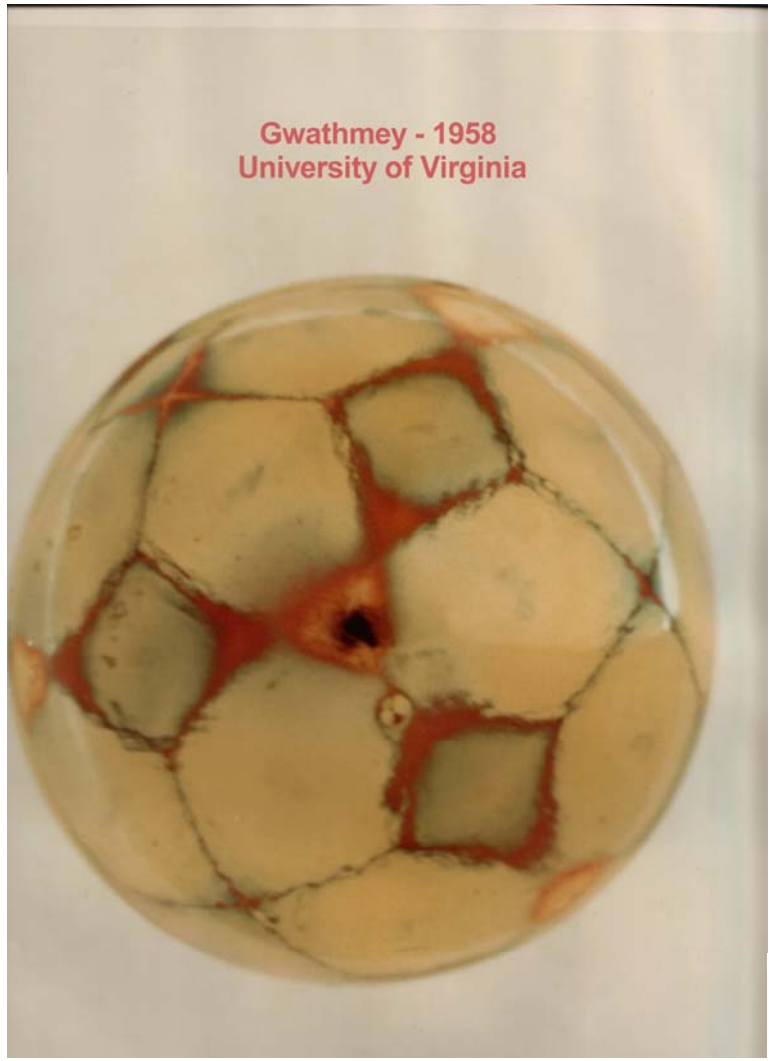




Same for other geometries, which can stabilize TS

The geometrical effect – long history

- Taylor, *Proc. R. Soc. London Ser. A* **108,** 105 (1925).
- Gwathmey, Cunningham, *Adv. Catal.* **10,** 57 (1958).
- Somorjai, *Surface Chemistry and Catalysis* (Wiley, New York, 1994).
- Yates, *J. Vac. Sci. Technol. A* **13,** 1359 (1995).
- Zambelli, Wintterlinn, Trost, Ertl, *Science* **273,** 1690 (1996).
- Dahl *et al.* , *Phys. Rev. Lett.* **83,** 1814 (1999)
- Zubkov *et al.* , *Surf. Sci.* **526,** 57–71 (2003).
- ……



Which is the best catalyst?

Ammonia synthesis :

$N_2+3H_2 \rightarrow 2NH_3$ (Ru, Fe, (Os))

Fischer Tropsch synthesis, methanation:

$nCO+(2n+1)H_2 \rightarrow C_nH_{2n+2}+nH_2O$ (Co, Ru, Rh, Ni)

NO reduction:

$2NO+2H_2 \rightarrow N_2+2H_2O$ (Pt, Pd, Rh)

Oxidation:

$O_2+2X \rightarrow 2XO$ (Pt, Pd, Ag)

……..

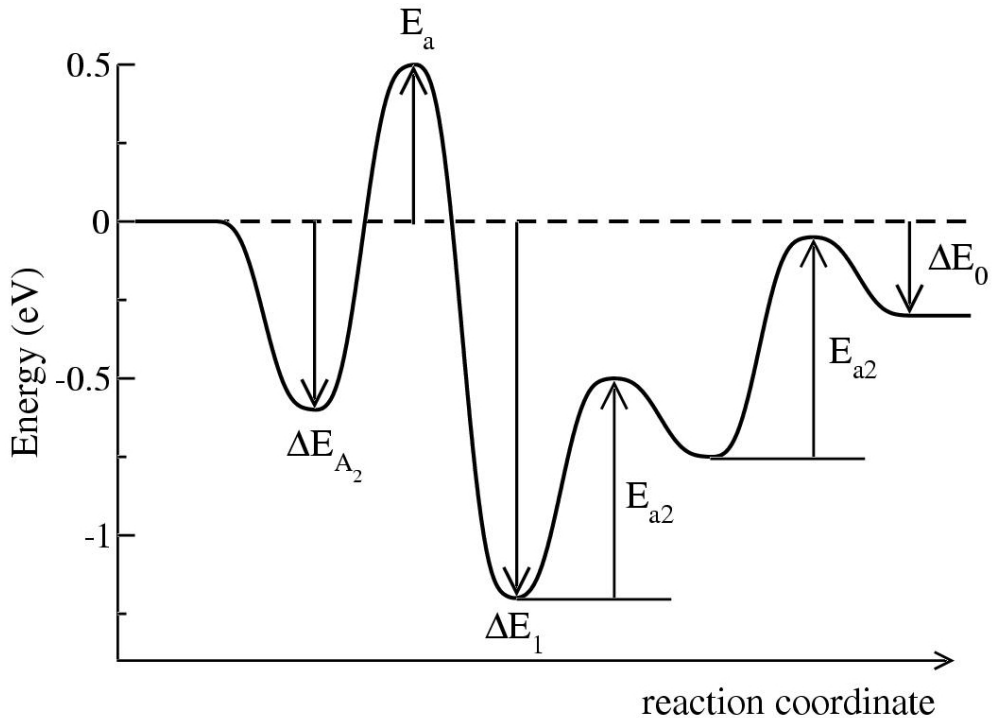
Simple kinetics + BEP

1: $A_2 + 2^* \rightarrow 2A^*$

2: $A^* + B \rightarrow AB + ^*$

$$E_a = \alpha_1 \Delta E_1 + \beta_1$$

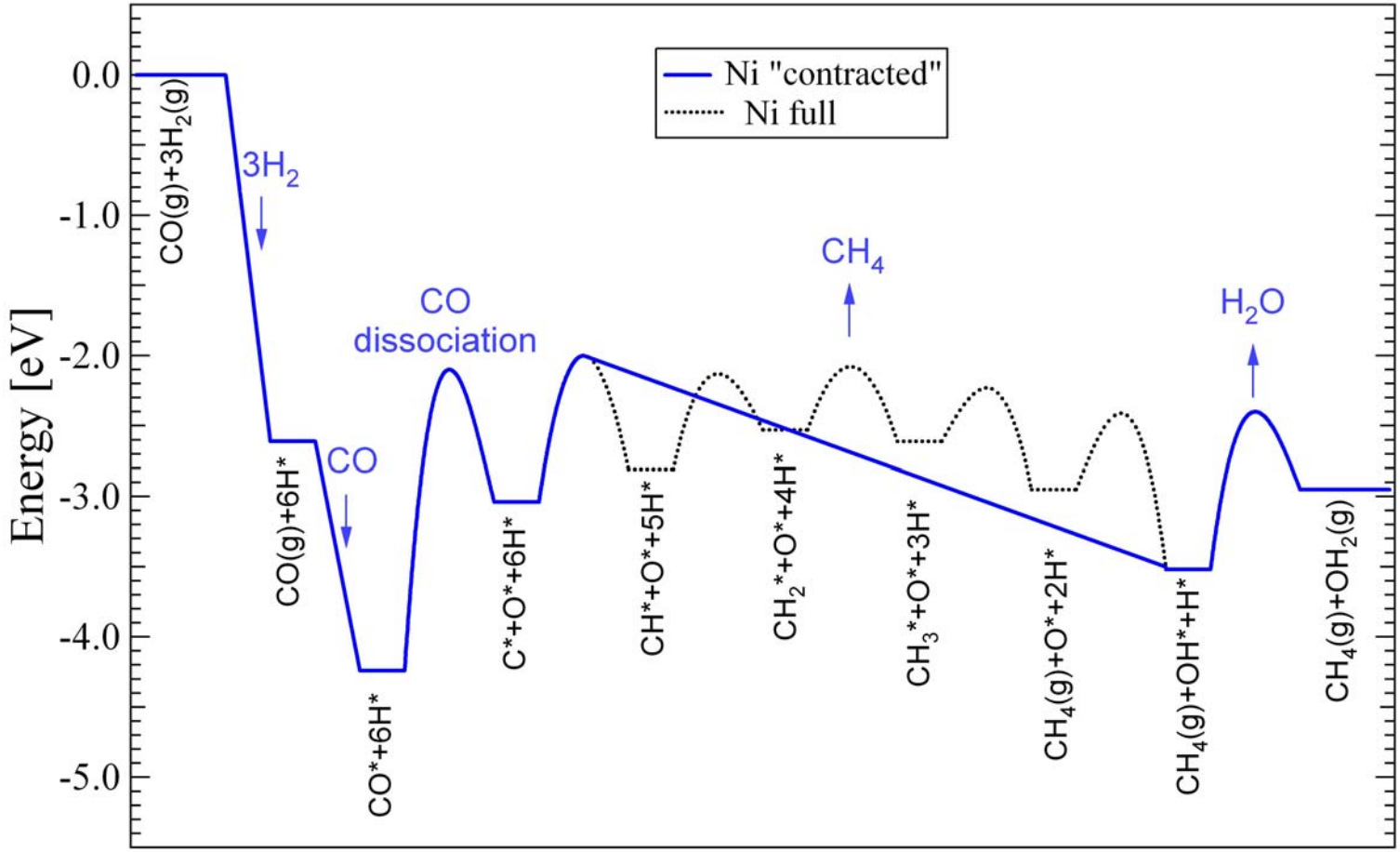
$$E_{a2} = \alpha_2 \Delta E_1 + \beta_2$$



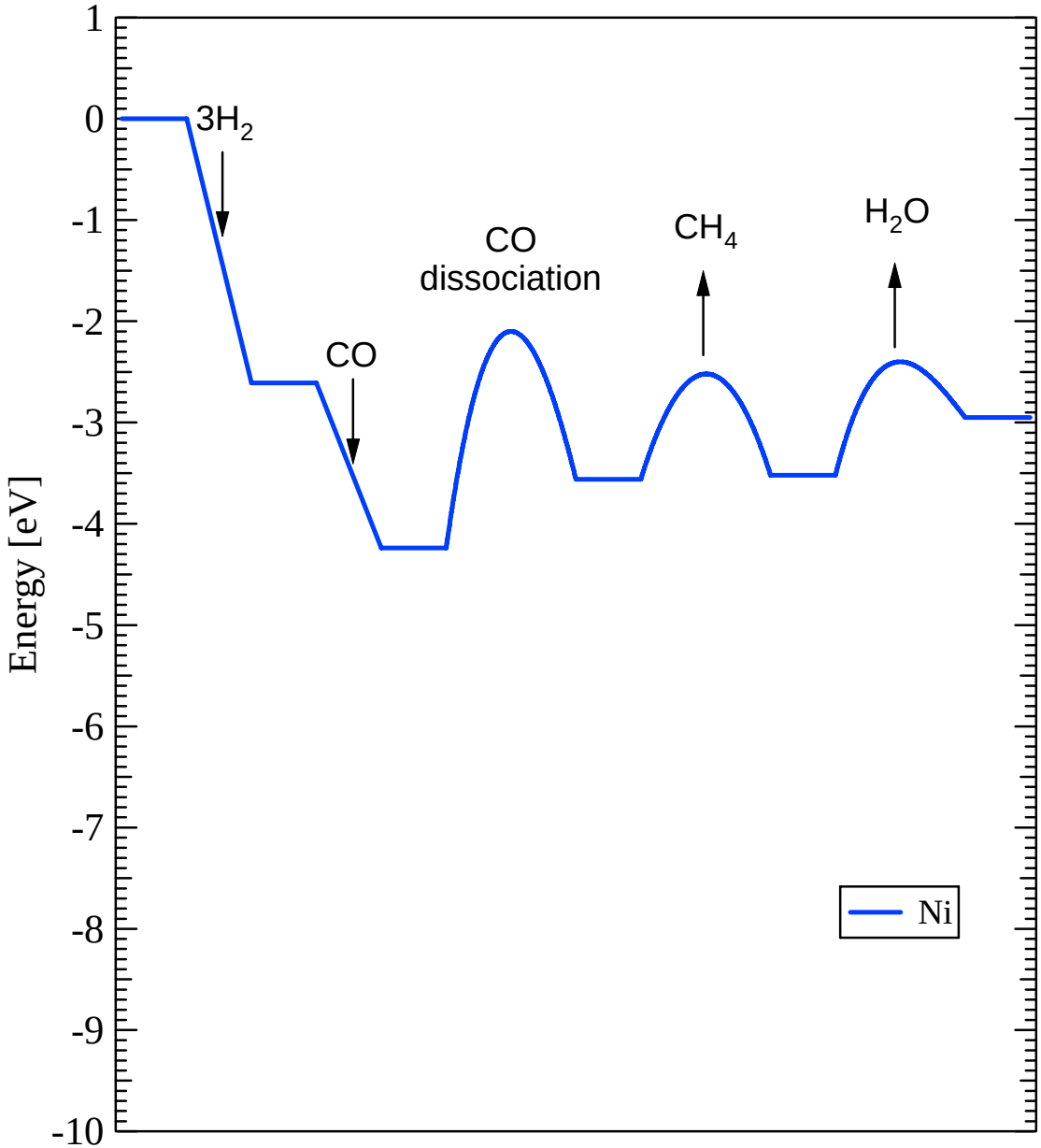
Bligaard, Nørskov, Dahl, Matthiesen, Christensen, Sehested, J. Catal. **224**, 206 (2004)

Example: Methanation

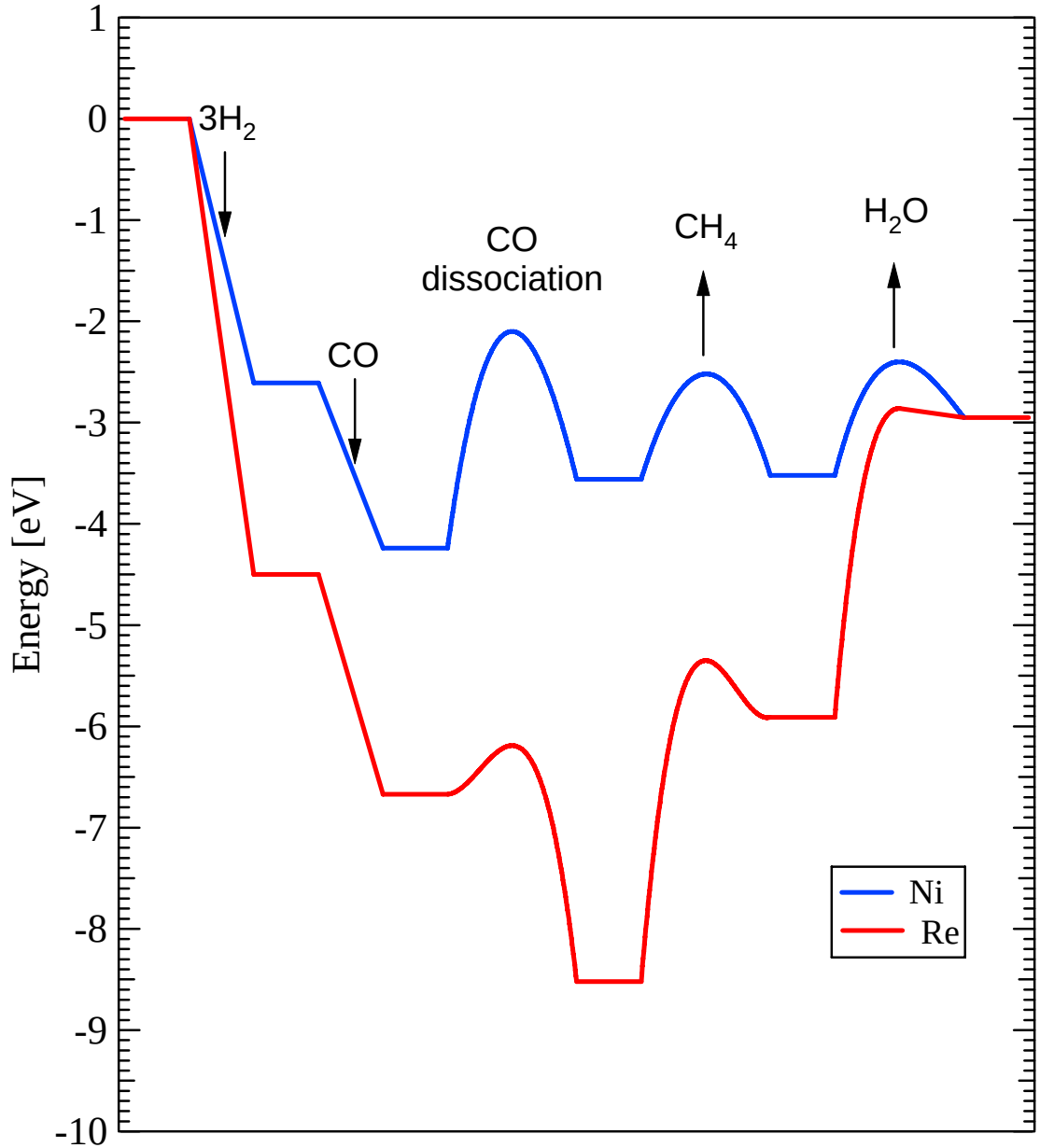
$CO+3H_2 \rightarrow CH_4+H_2O$



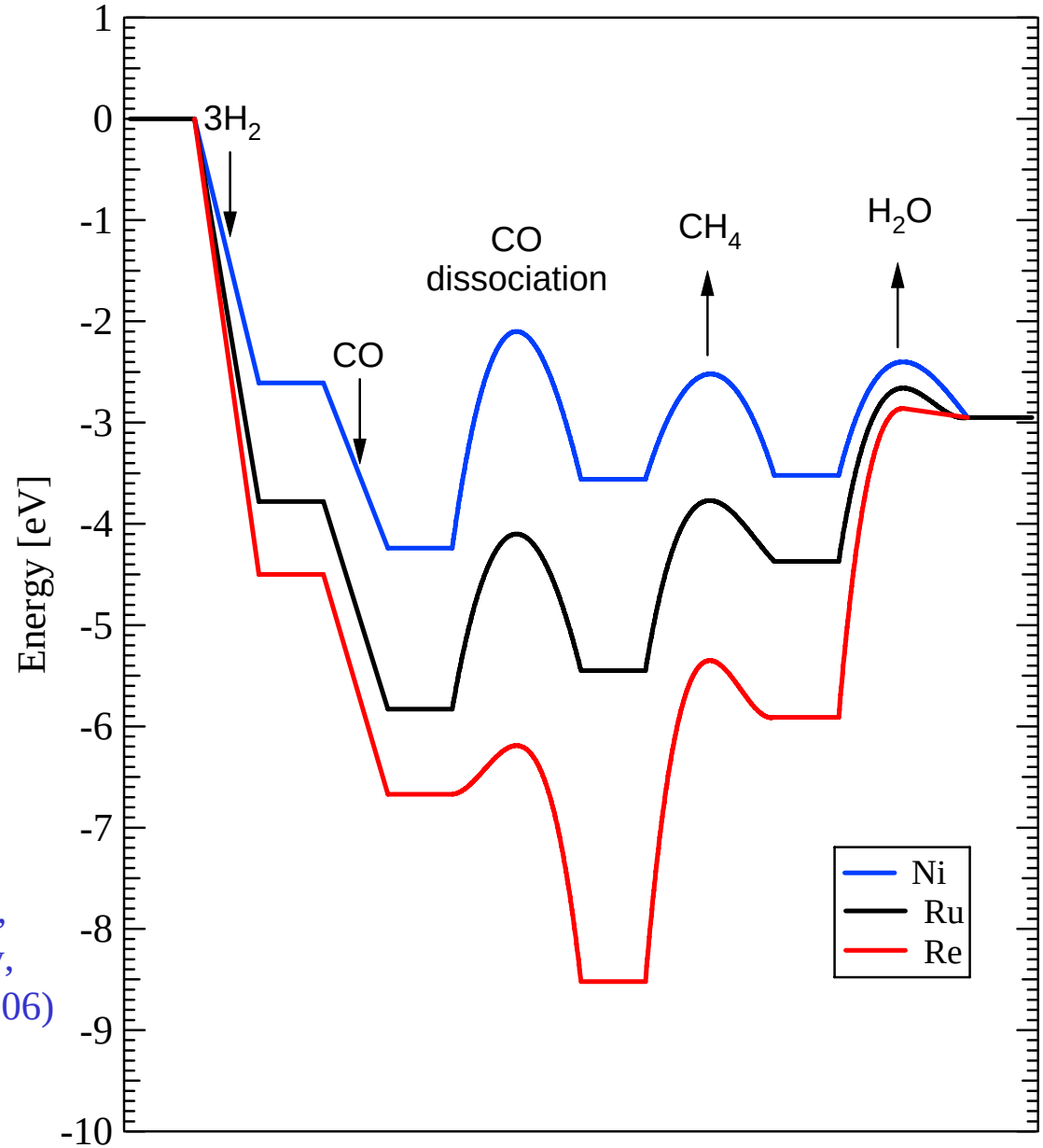
Methanation, Ni



Methanation, Ni, Re



Methanation, Ni, Re, Ru



Andersson, Bligaard, Kustov, Greeley, Johannessen, Larsen, Christensen, Nørskov, J. Catal. **239**, 501 (2006)

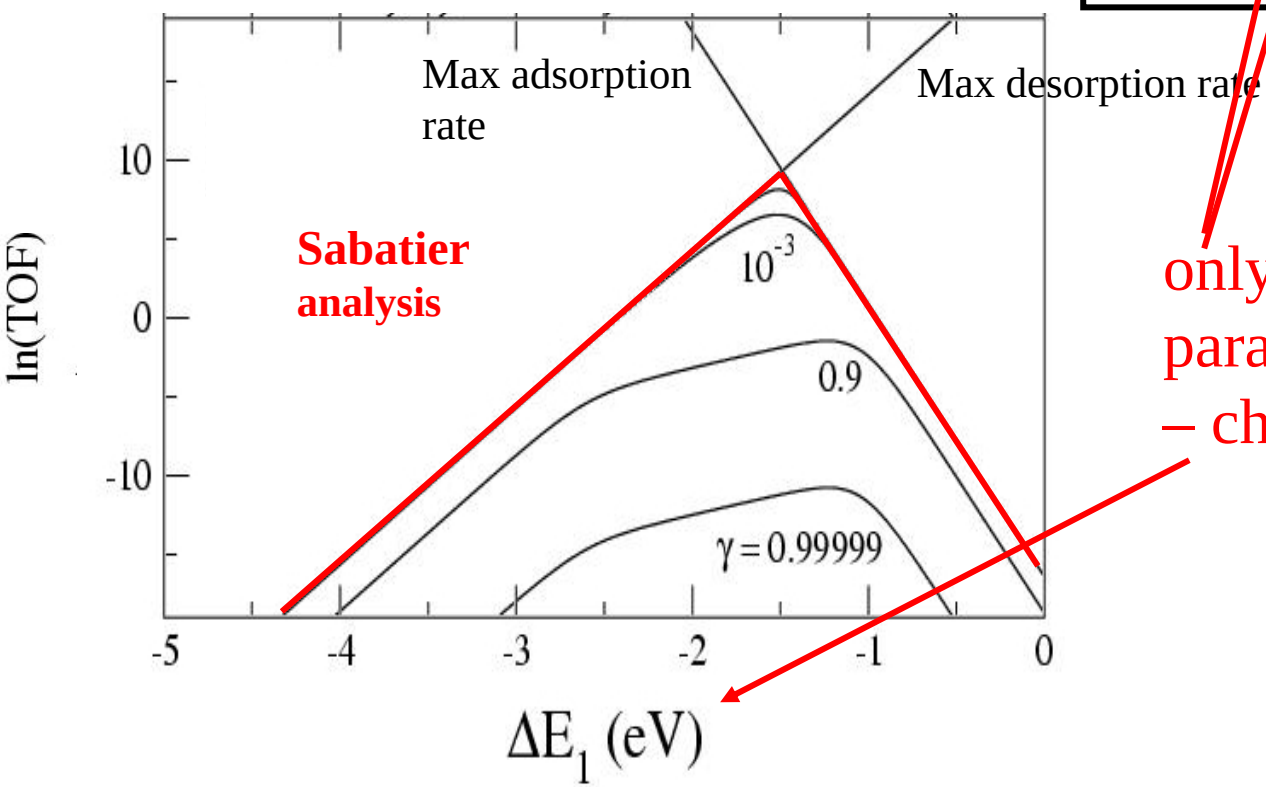
Sabatier analysis

$A_2 + 2^* \rightarrow 2A^*$

$A^* + B \rightarrow AB + ^*$

$$E_a = \alpha_1 \Delta E_1 + \beta_1$$

$$E_{a2} = \alpha_2 \Delta E_1 + \beta_2$$

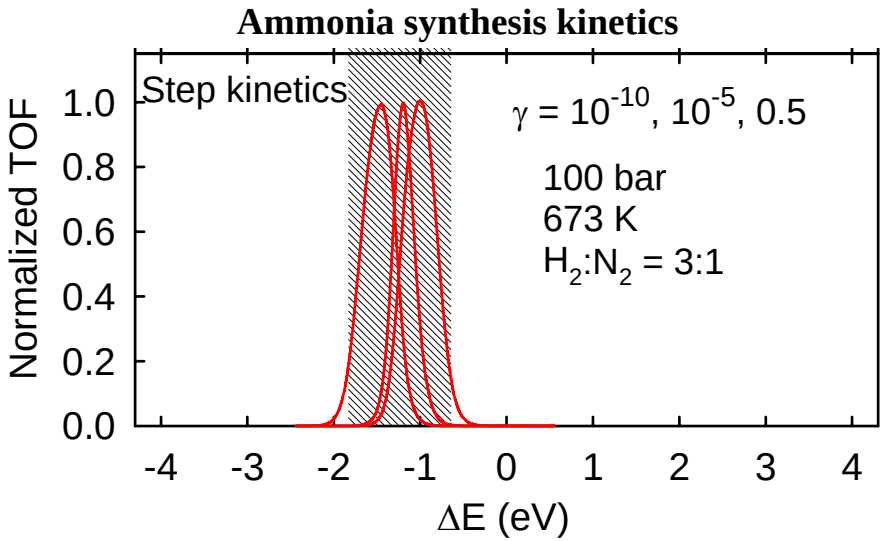


only independent parameter – characterizes catalyst!

P. Sabatier, Berichte der Deutschen Chemische Gesellshaft **44,** 1984 (1911)
Bligaard, Nørskov, Dahl, Matthiesen, Christensen, Sehested, J. Catal. **224**, 206 (2004)

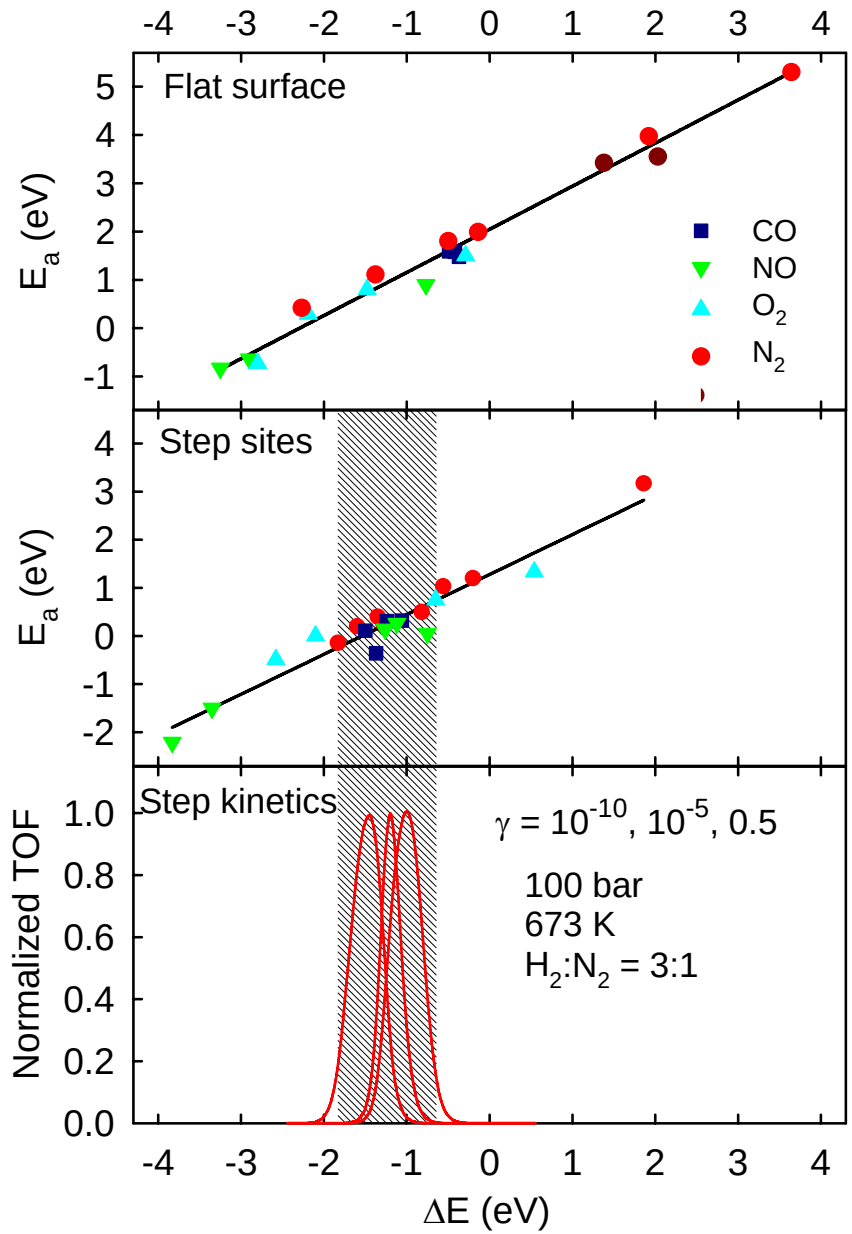
BEP+kinetics – simple models:

- The dissociative chemisorption energy ΔE is a good descriptor



- Volcano curve results
- Volcano is broad (~0.5 eV) – self-regulating
- Maximum in range $\Delta E = -1 -> -2$ eV

Understanding trends in catalytic activity

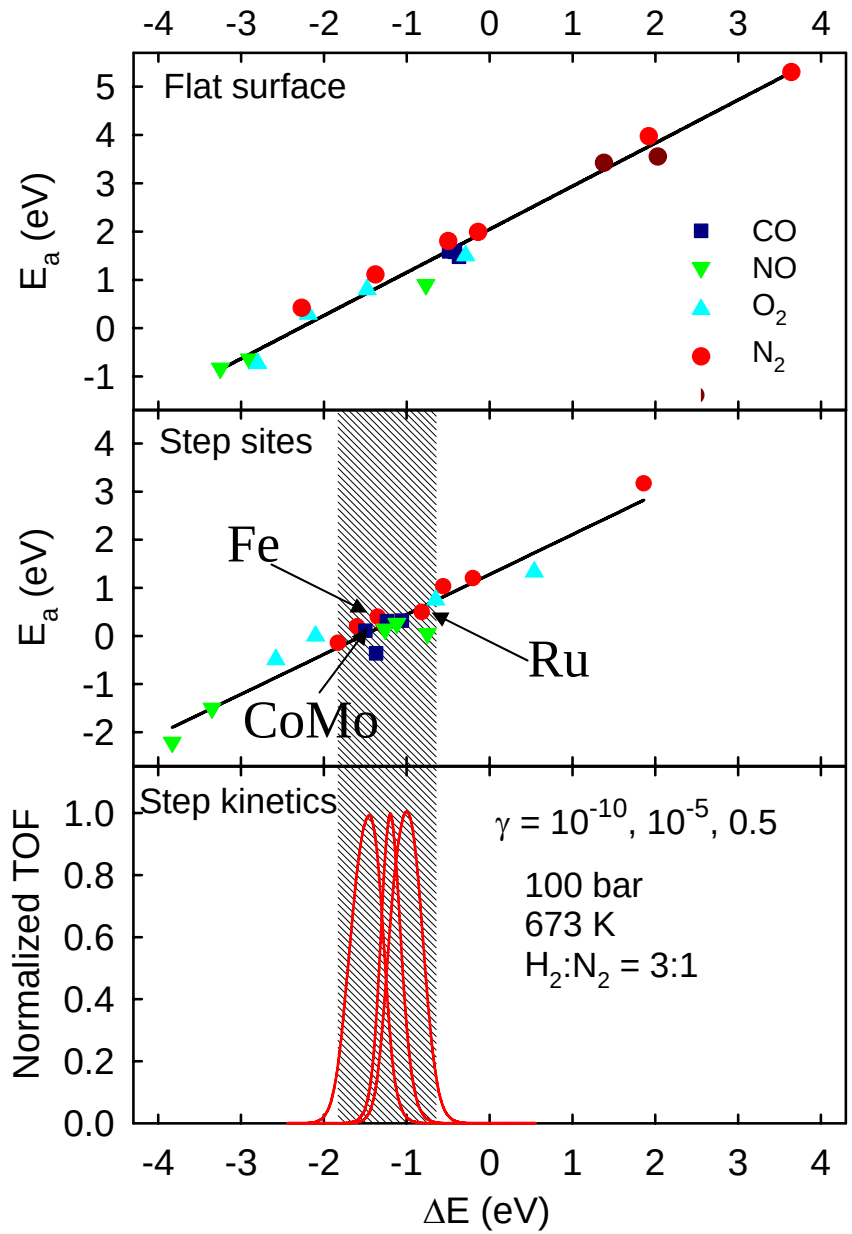


Nørskov, Logadottir, Bligaard, Bahn, Hansen, Bollinger, Bengaard, Hammer, Sljivancanin Mavrikakis, Xu, Dahl, Jacobsen
J.Catal. **209**, 275 (2002)

Understanding trends in catalytic activity

Ammonia synthesis :

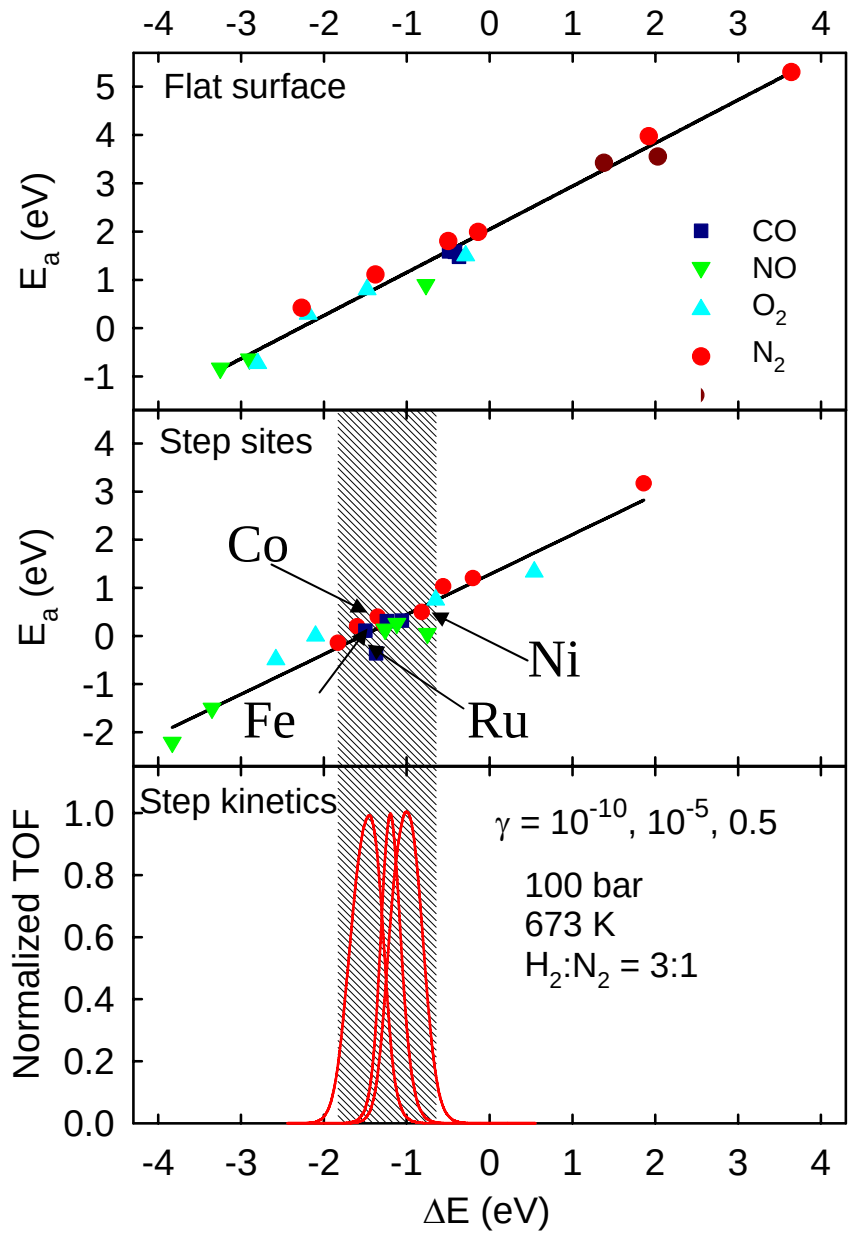
$N_2 + 3H_2 \rightarrow 2NH_3$



Understanding trends in catalytic activity

Fischer Tropsch synthesis and methanation:

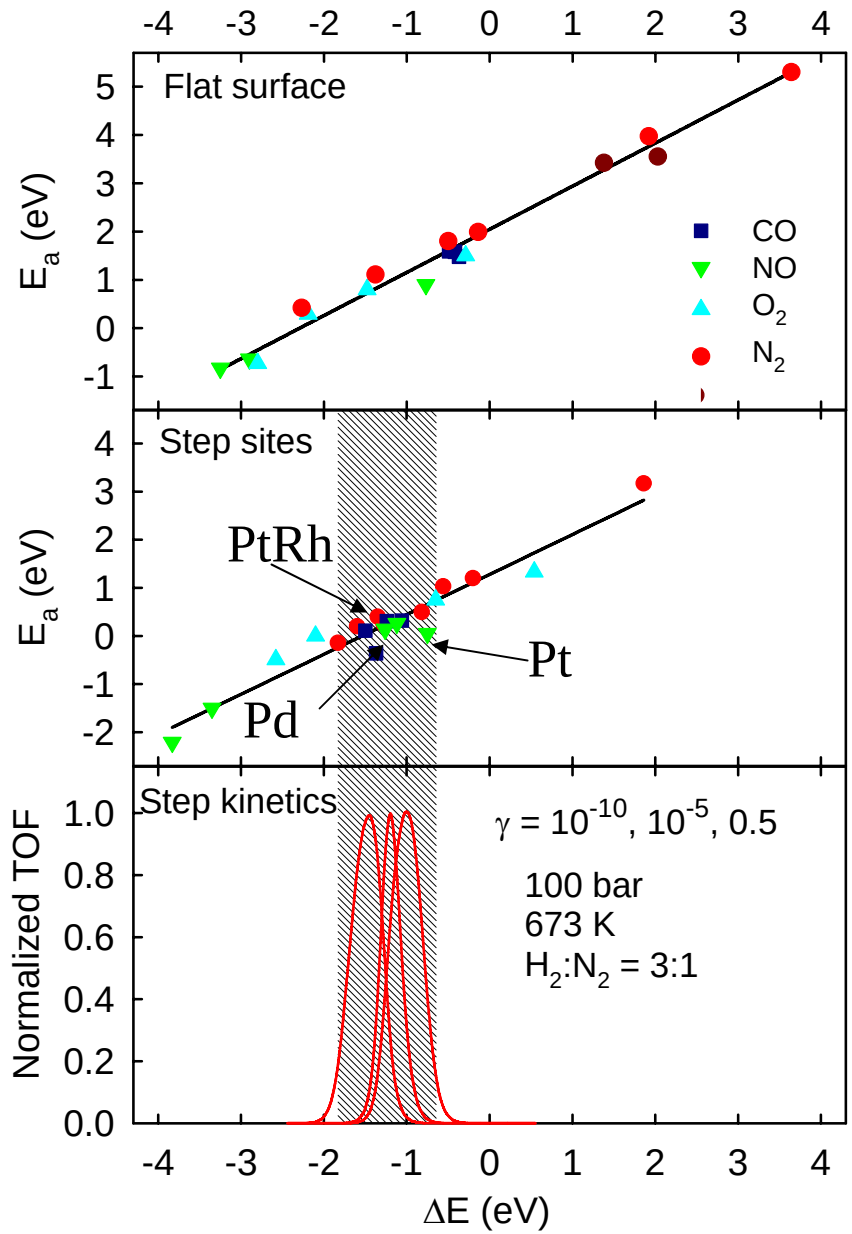
$nCO+(2n+1)H_2 \rightarrow C_nH_{2n+2}+nH_2O$



Understanding trends in catalytic activity

NO reduction:

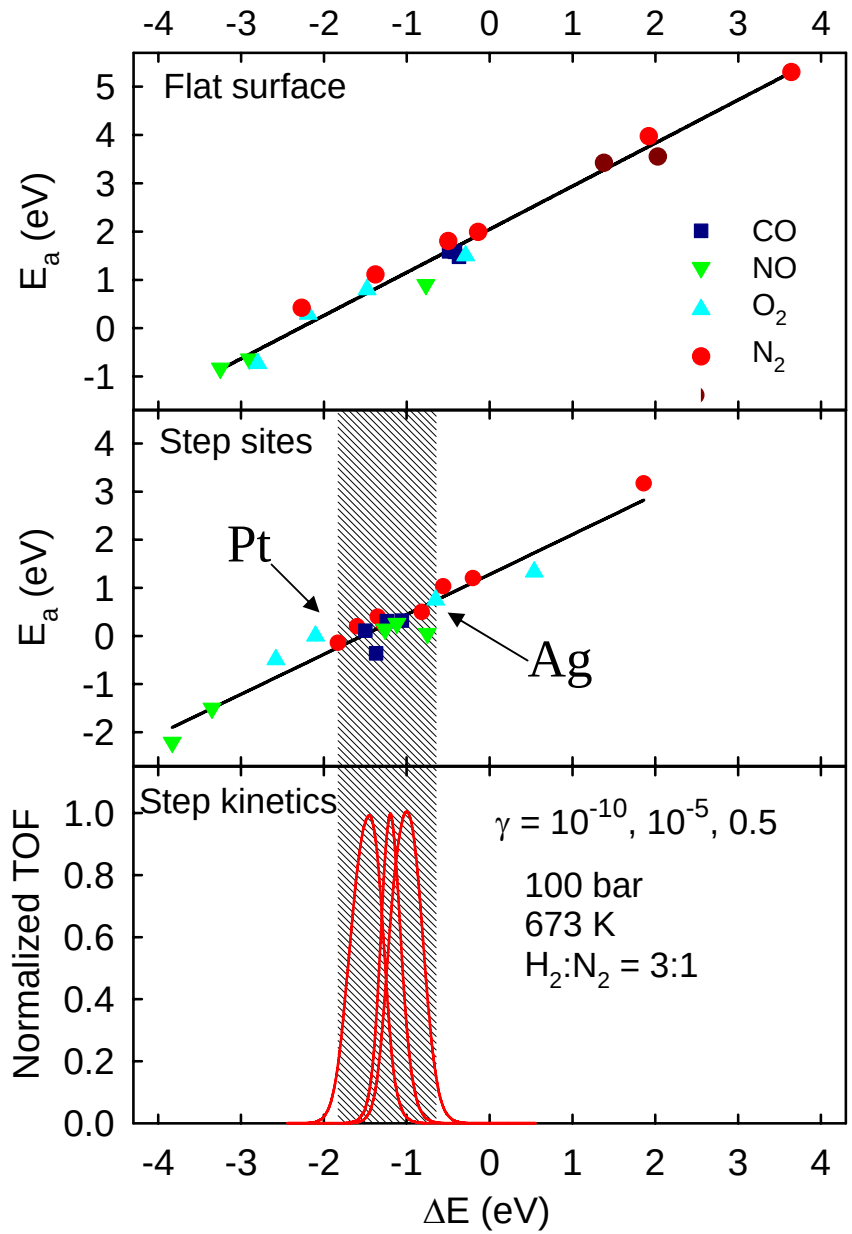
$2NO+2H_2 \rightarrow N_2+2H_2O$



Understanding trends in catalytic activity

Oxidation:

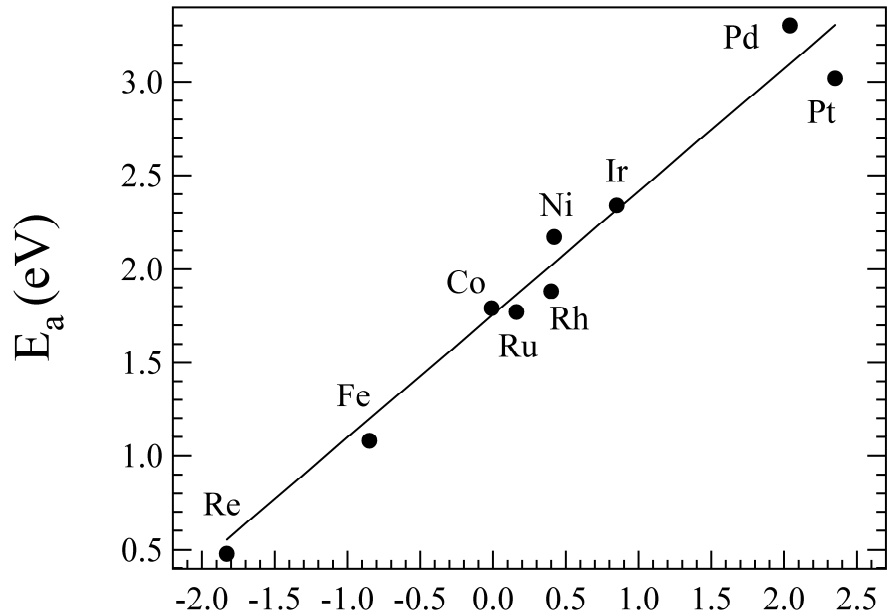
$O_2 + 2X \rightarrow 2XO$



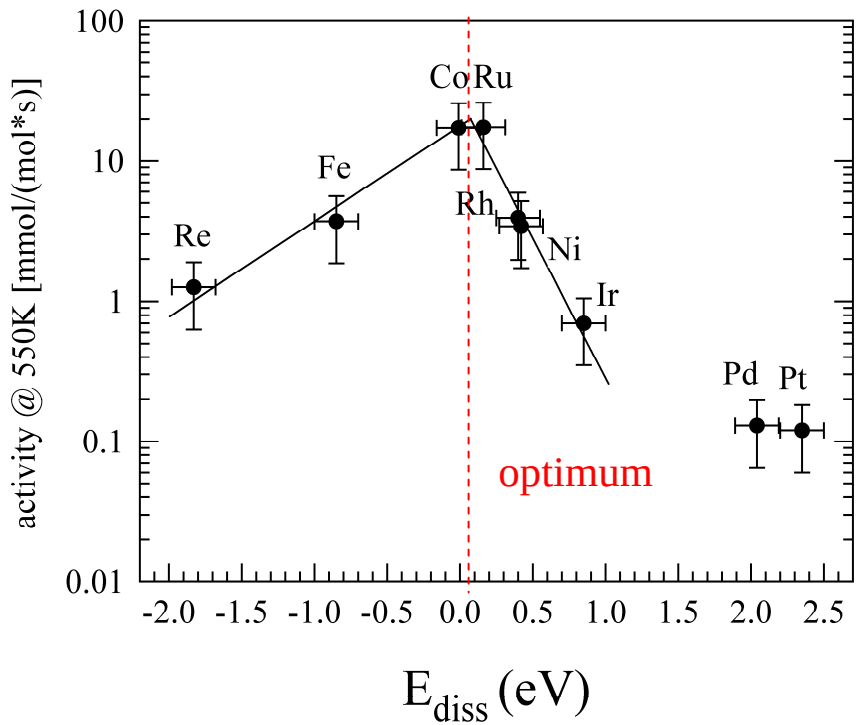
Screening for new catalysts on the computer?

- Determine descriptor for activity
- Calculate value for a range of systems
  - full DFT calculations
  - model
- Include other important factors
  - price
  - stability
  - selectivity
  - …..
- Synthesis and test of selected catalysts

Methanation



E_{diss} is a good descriptor
For catalytic activity

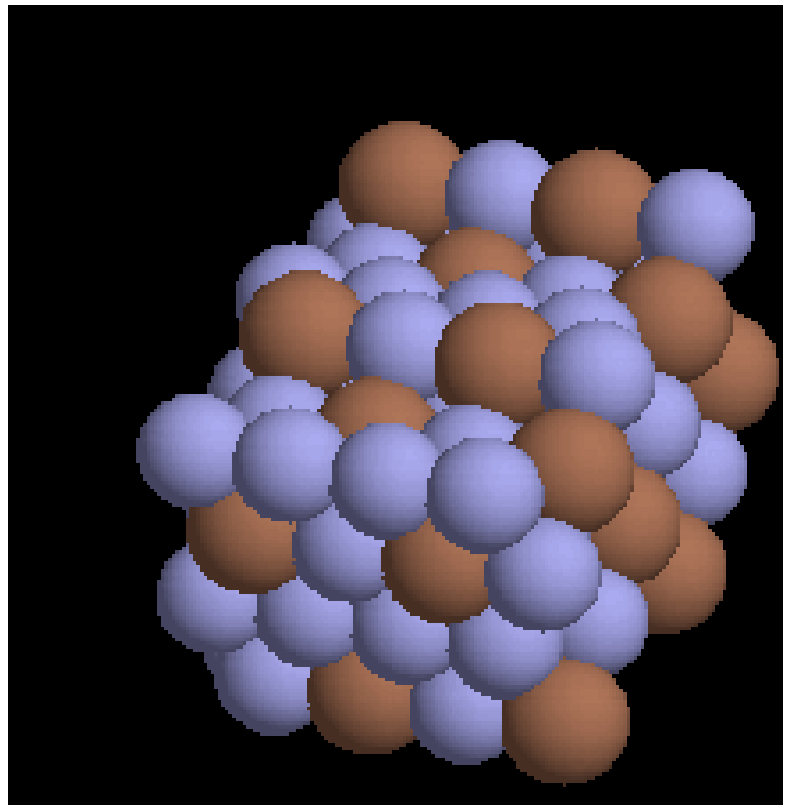


Bligaard, Nørskov, Dahl, Matthiesen, Christensen, Sehested, J.Catal. **224**, 206 (2004)

Computational screening

All A_xB_{1-x} alloys, x=0,0.25,0.5,0.75,1

A,B=Ni,Pd,Pt,Co,Rh,Ir,Fe,Ru,Re

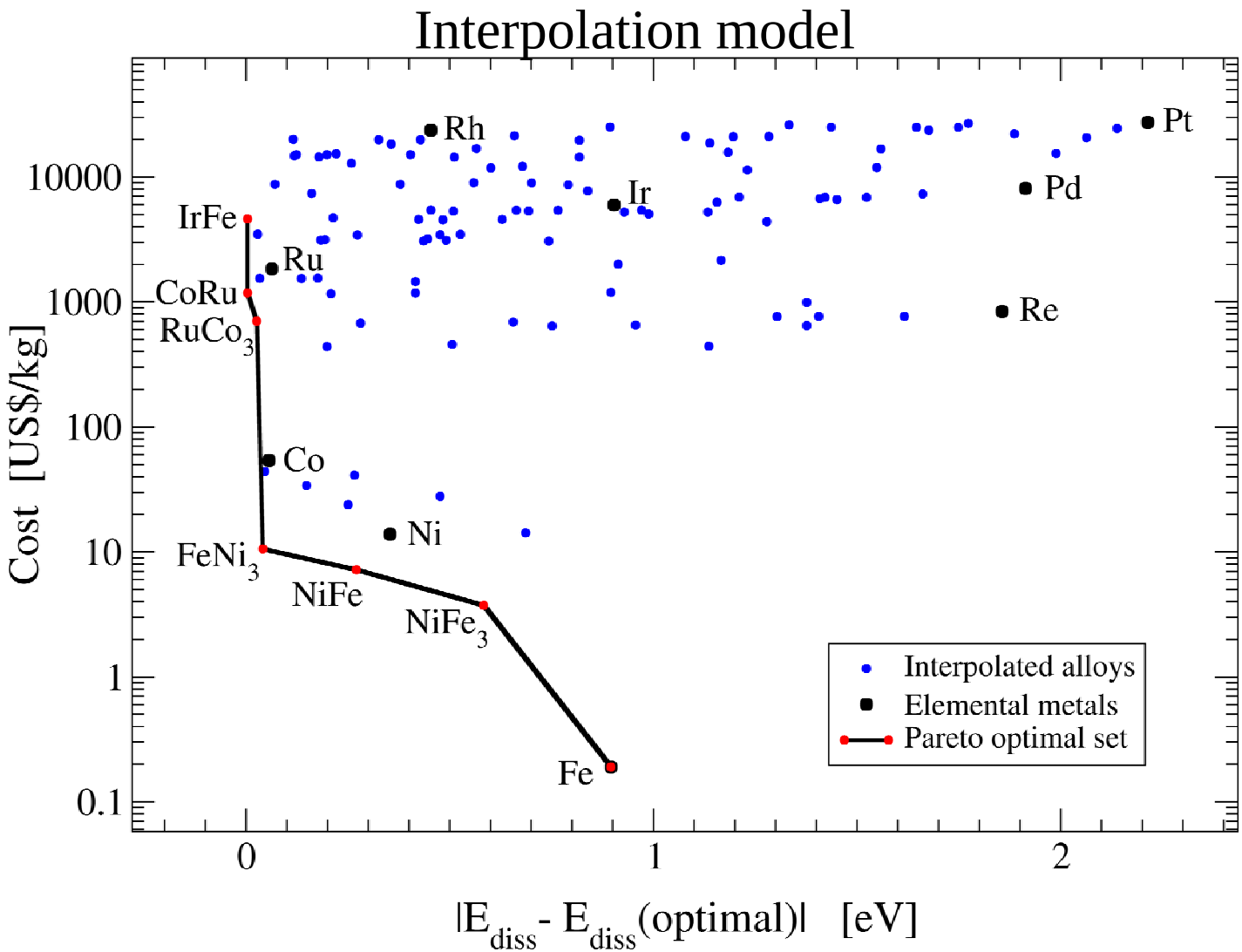


Important parameters:

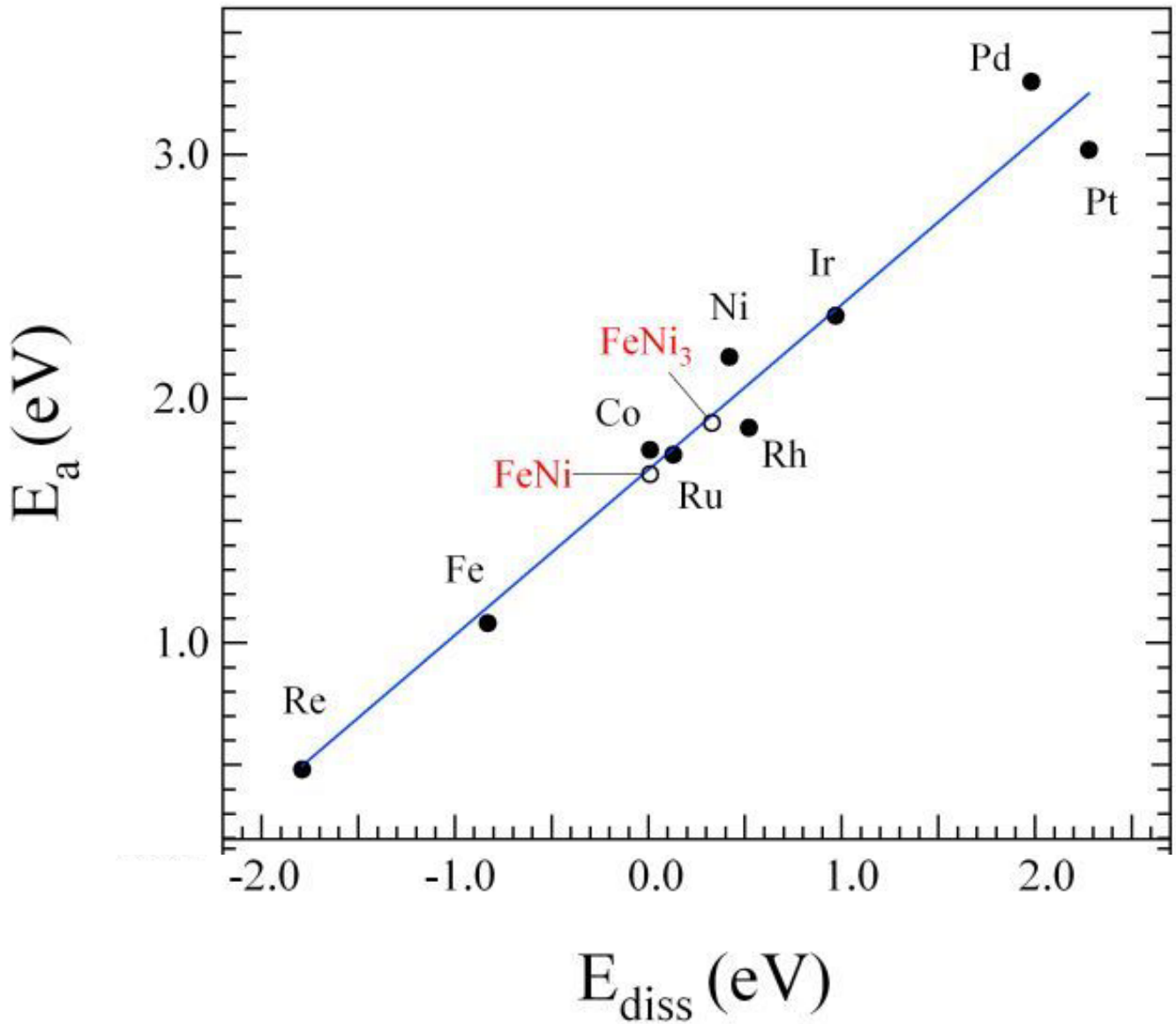
- Catalytic activity (E_{diss})
- Stability (disordering, sintering)
- Price
- ….

Andersson, Bligaard, Kustov, Greeley, Johannessen, Larsen, Christensen, Nørskov, J. Catal. **239**, 501 (2006)

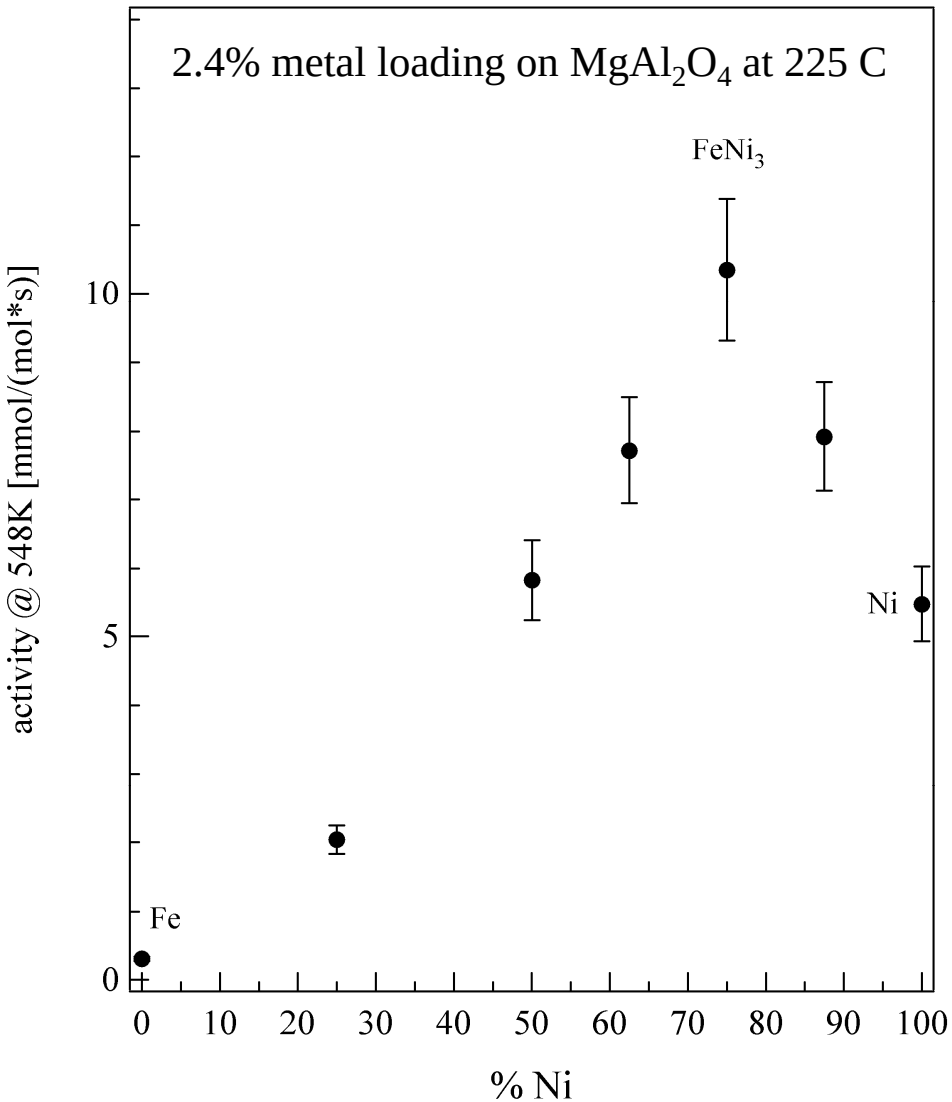
The Pareto-optimal catalysts



The Fe-Ni alloys in detail



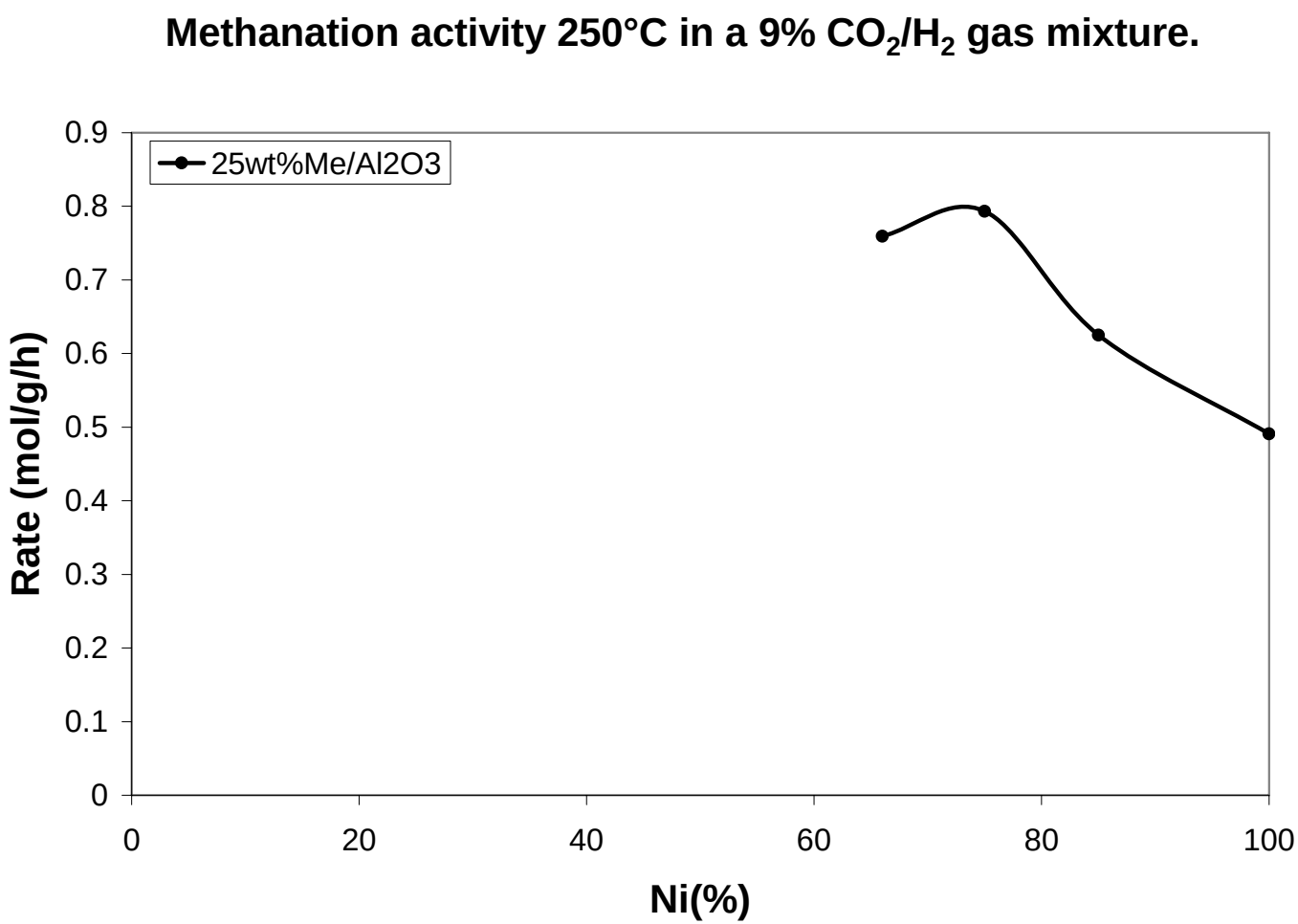
Synthesis and test



Andersson, Bligaard, Kustov, Greeley, Johannessen, Larsen, Christensen, Nørskov,

J. Catal. **239**, 501 (2006)

Towards industrial conditions



Jens Sehested et al. Haldor Topsøe A/S (2006)

Important concepts
– reactivity of transition metal surfaces

- Electronic effects can be rationalized in d band model
- Geometrical effects can be huge
- BEP relations widespread
- Overall trends in reactivity can be described in volcano relationships