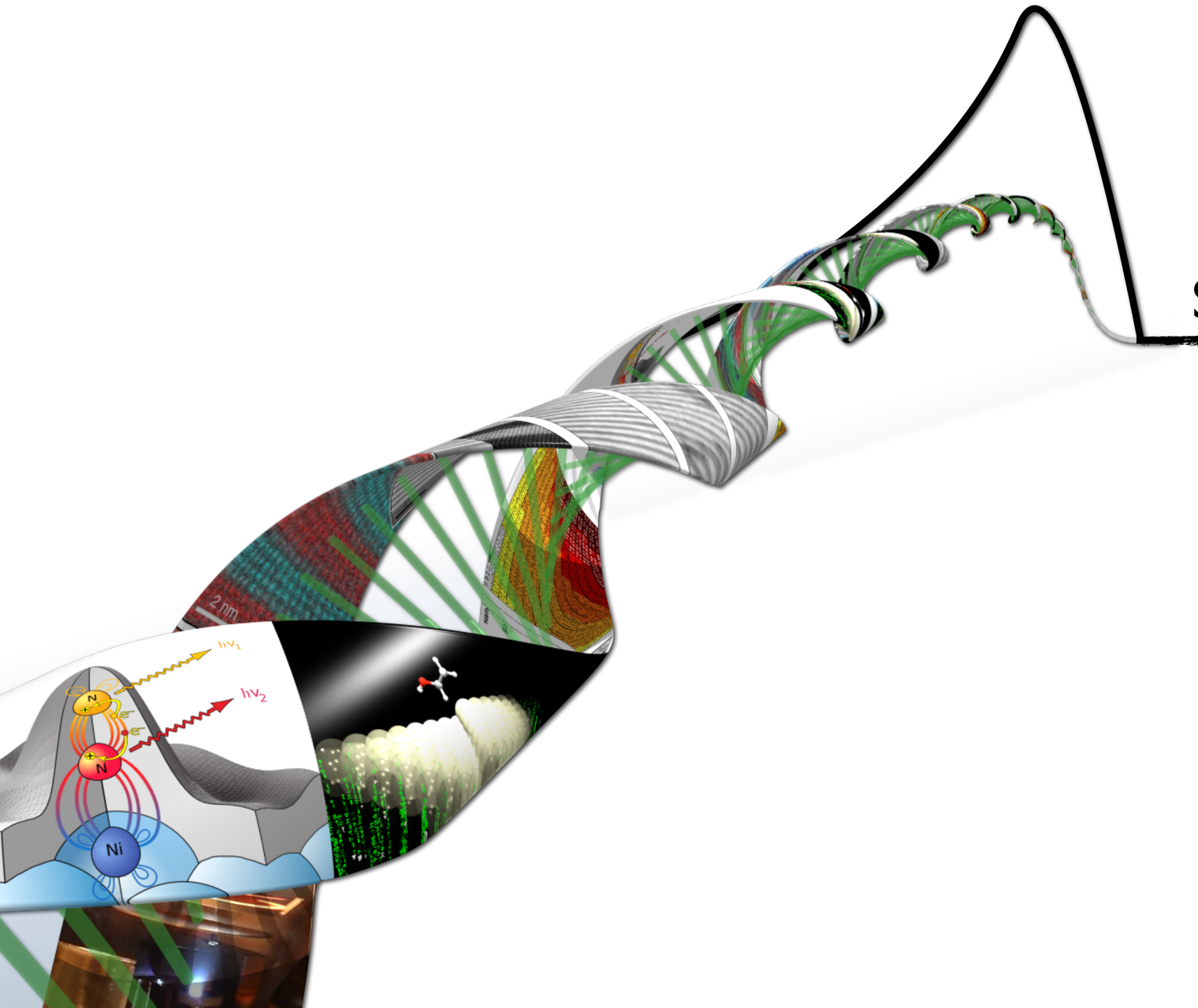
SUNCAT
CENTER FOR INTERFACE SCIENCE AND CATALYSIS

SLAC
NATIONAL ACCELERATOR LABORATORY



Scaling Relations: A Computational Approach to Catalyst Search

Aleksandra Vojvodic

The "Control Age"

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We now stand at the brink of a "Control Age" that could spark revolutionary changes in how we inhabit our planet, paving the way to a bright and sustainable future for us all. *

- How to design energy- & atom-efficient synthesis of new materials with tailored properties to reduce environmental impact?
  - Computer guided catalyst and materials design rooted in fundamental understanding
  - Search for the "materials genome"

* Directing Matter and Energy: Five Challenges for Science and the Imagination, Basic Energy Sciences Report, U.S. DOE (2009).

Catalysts and Real Materials

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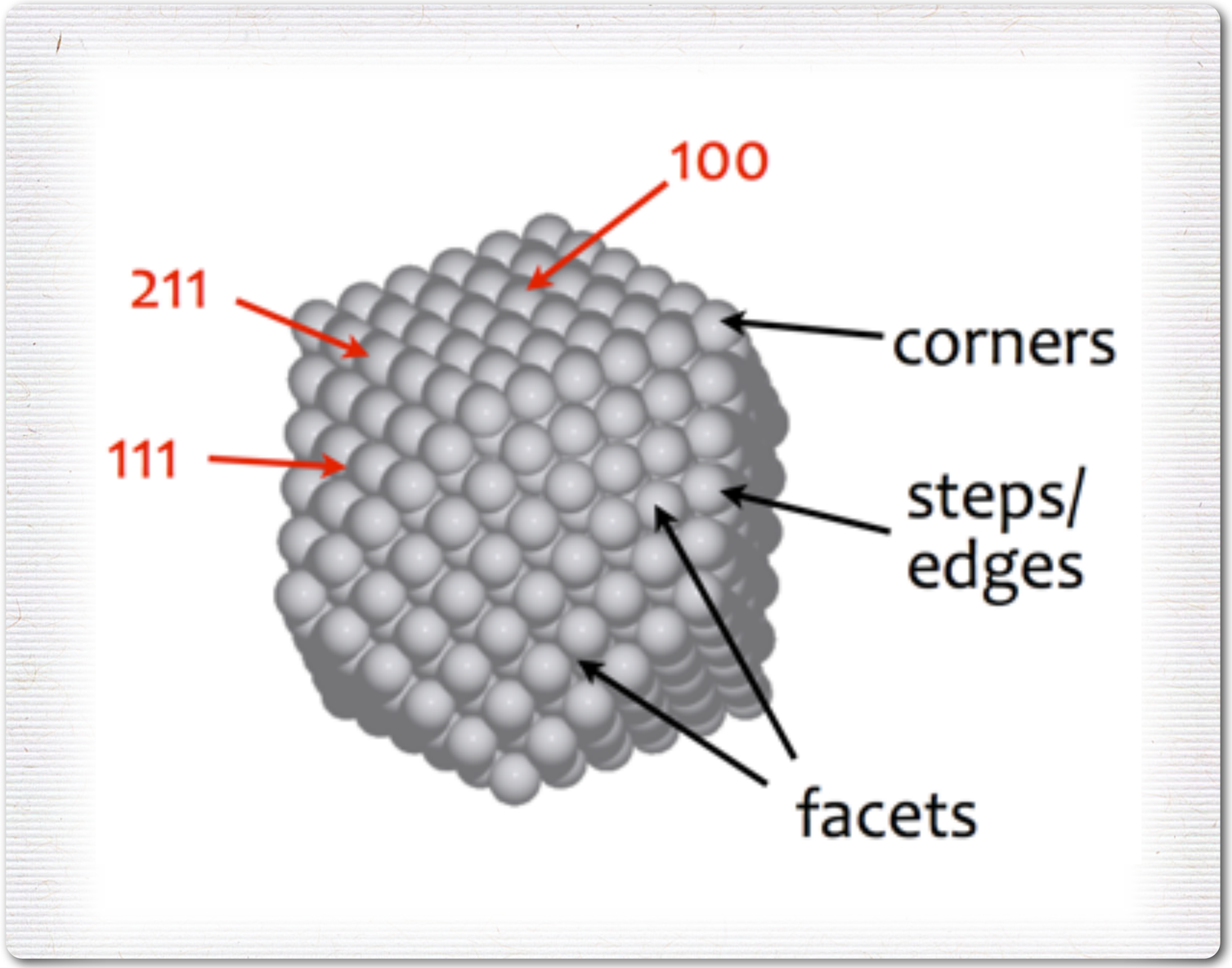
Nano-particles:

- Finite size
- Many facets
- Steps/Edges
- Corners
- Defects
- Support



Validity of Surface Science Approach

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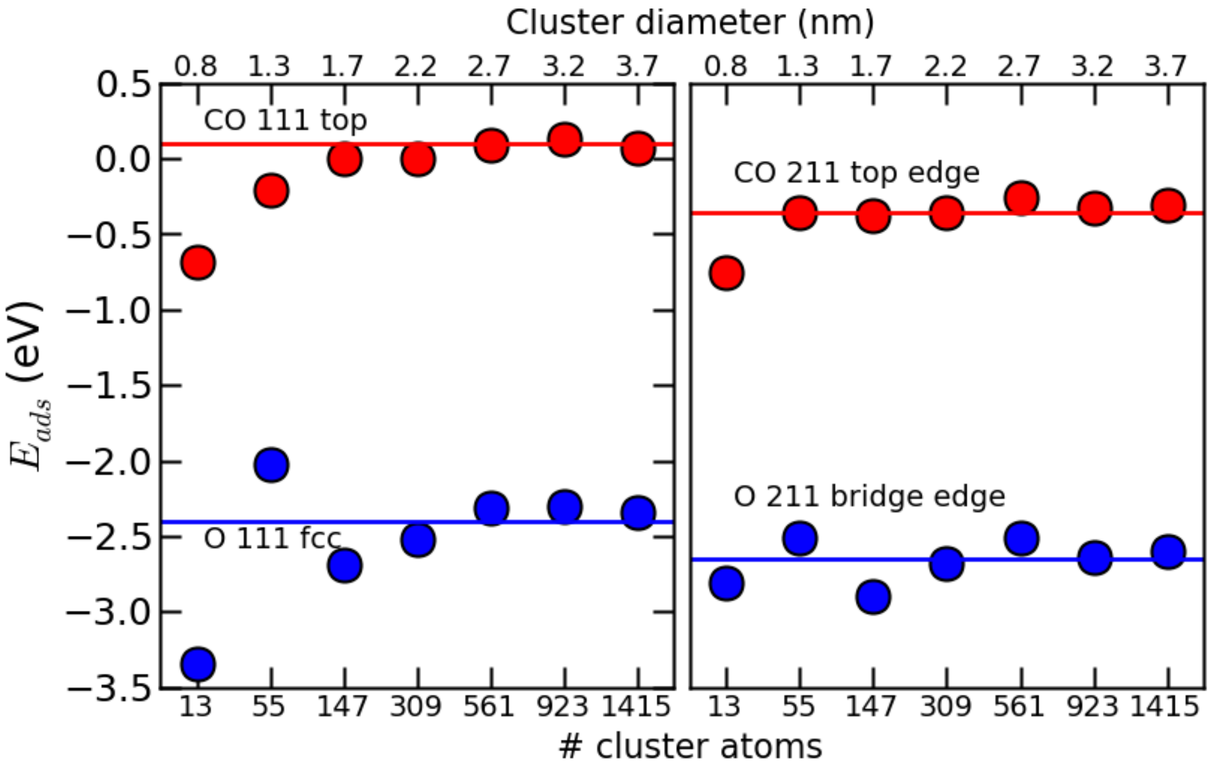
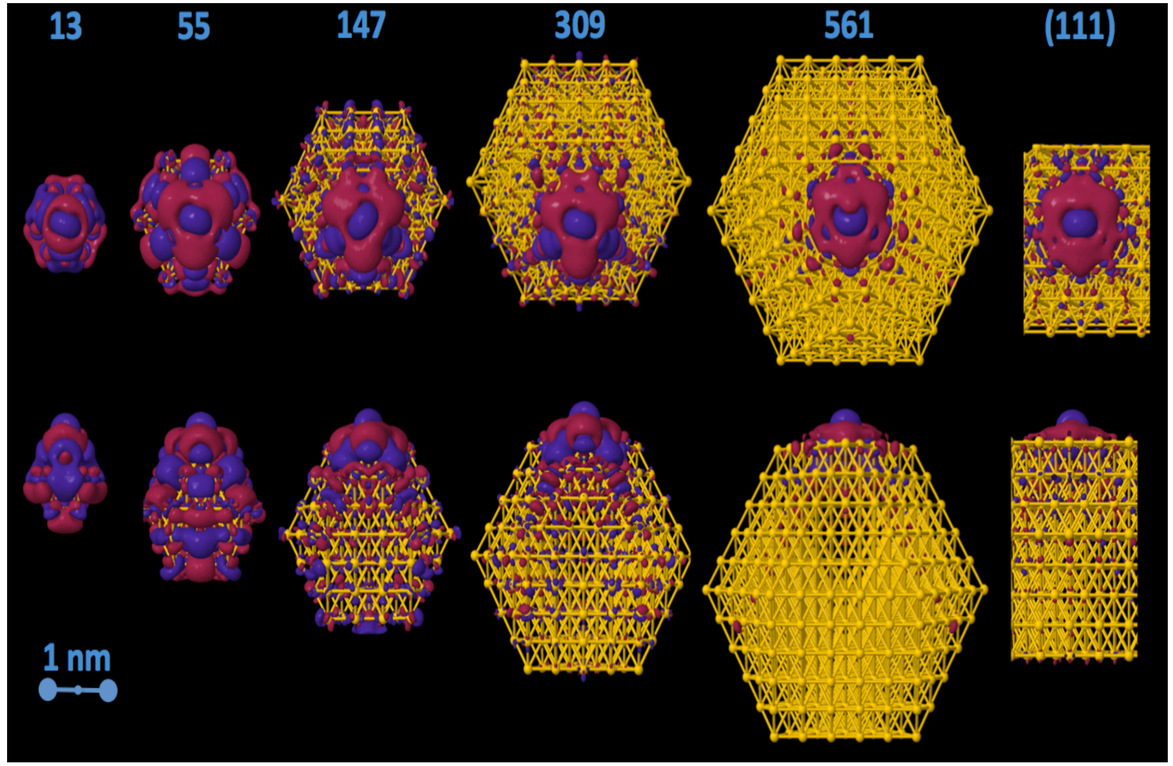
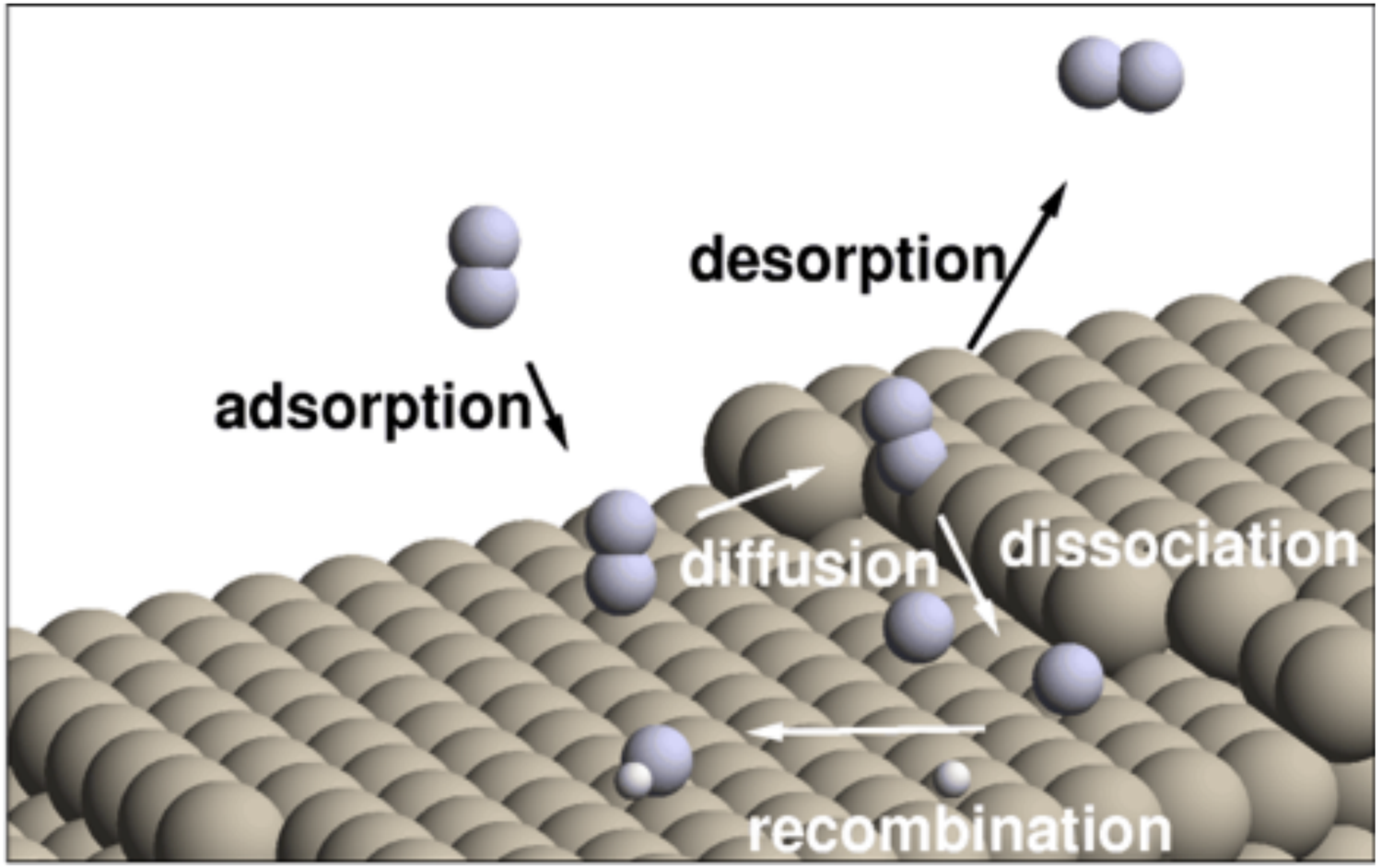
adsorption on Au nano-particles



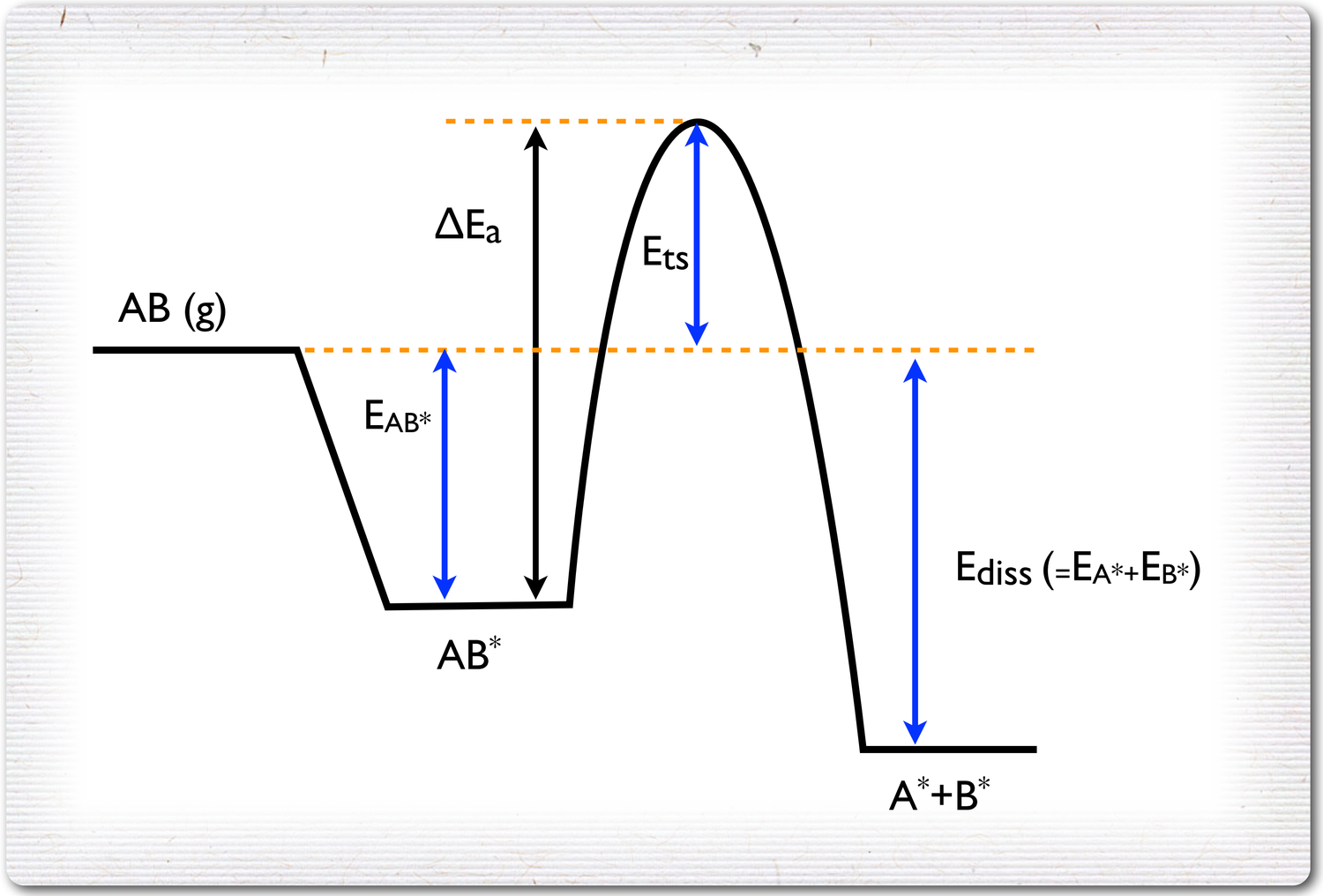


A. Larsen, J. Kleis, K.Thygesen, J. K.Nørskov, K. Jacobsen, Phys. Rev. B 1, **84** (2011)

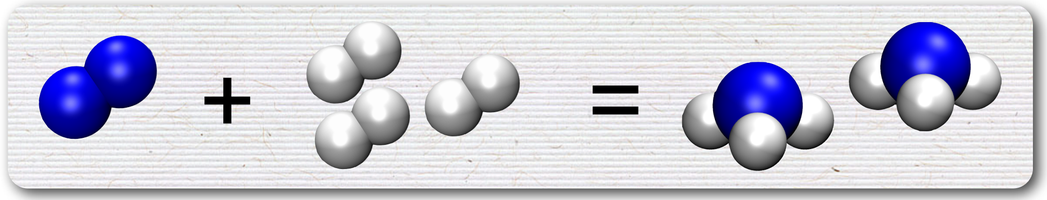
Elementary Surface Reaction Steps

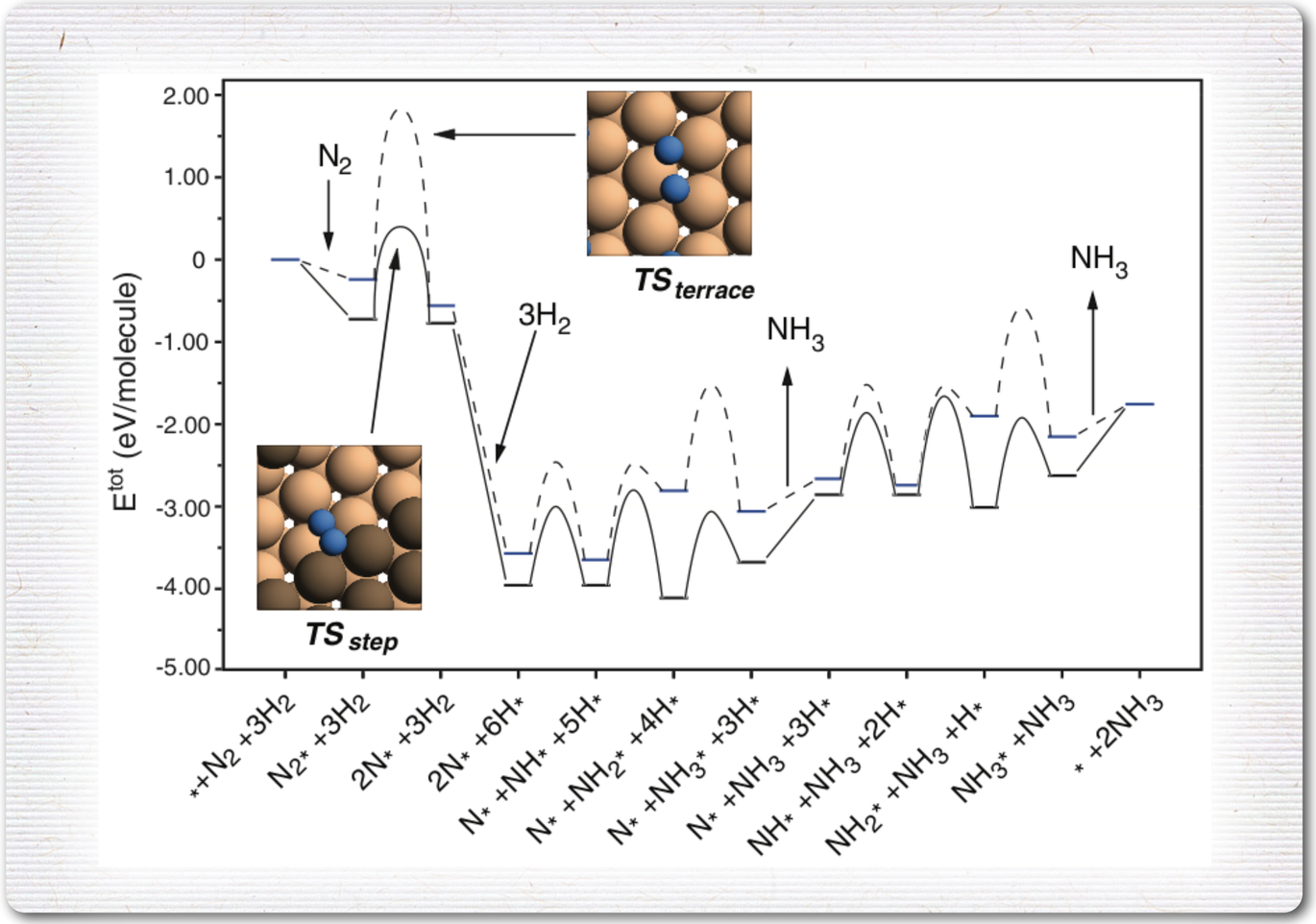


Key Ingredients to Surface Reactions: Adsorption and Barriers



Ammonia Synthesis, Stepped Ru(0001) Surface





K. Honkala *et al.*, Science **307**, 555 (2005)

- Overall reaction

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

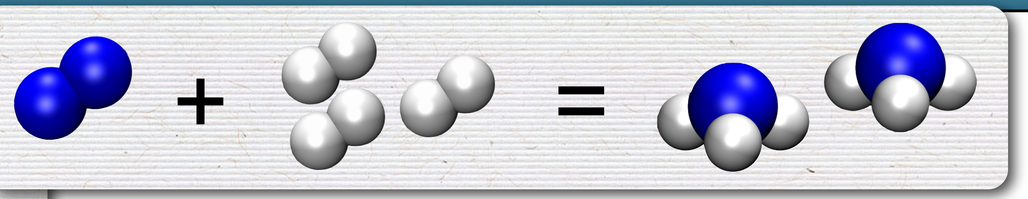
- Elementary steps

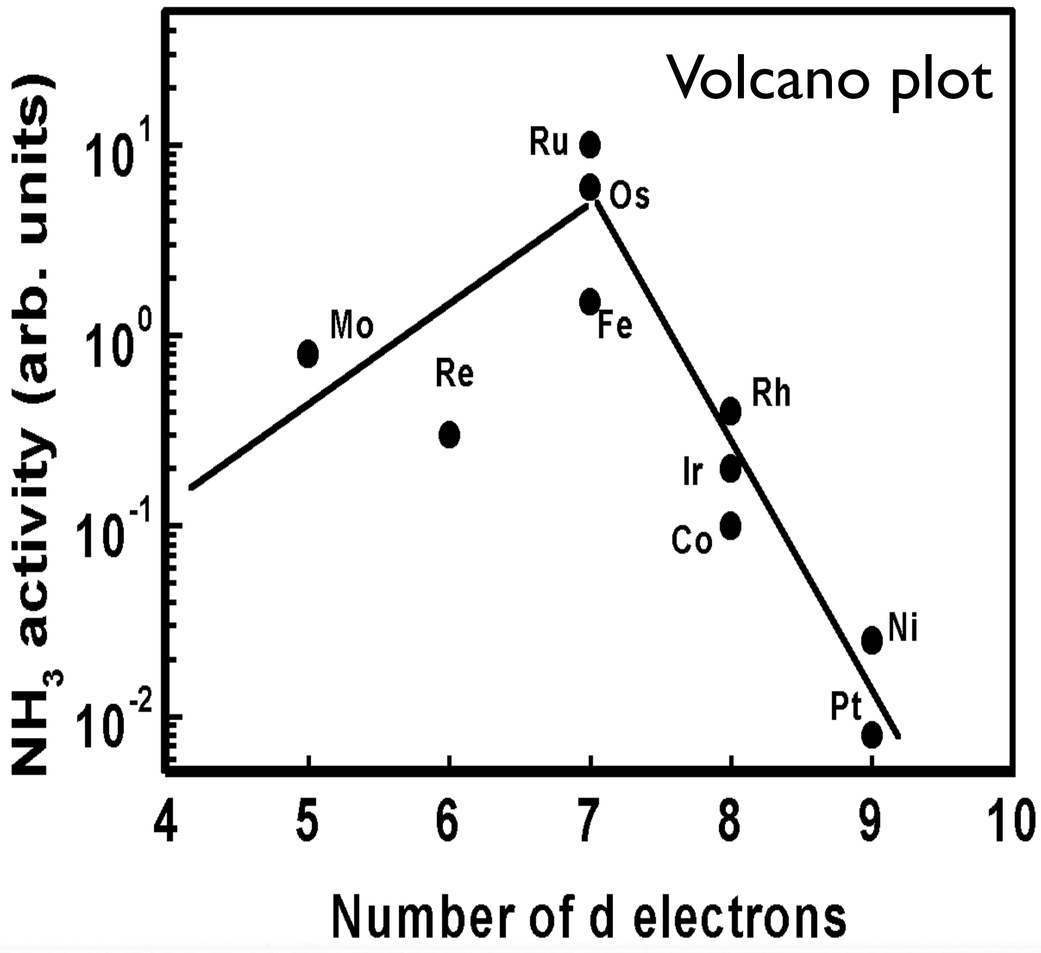
$$N_2(g) + 2^* \rightleftarrows 2N^* \qquad \text{RDS}$$
$$H_2(g) + 2^* \rightleftarrows 2H^*$$
$$N^* + H^* \rightleftarrows NH^*$$
$$NH^* + H^* \rightleftarrows NH_2^*$$
$$NH_2^* + H^* \rightleftarrows NH_3^*$$
$$NH_3^* \rightleftarrows NH_3(g)$$

- Rate of reaction

$$R = R_1 = k_1 p_{N_2} \theta_*^2 (1 - \gamma)$$

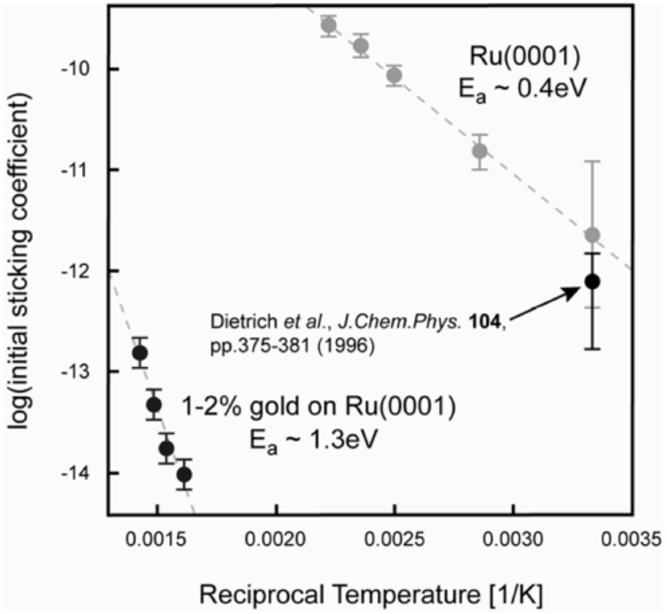
What About Other Catalysts?





Descriptor

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



S. Dahl *et al.*, Phys. Rev. Lett. **83**, 1814 (1999)

- Why is Ru good and Ni poor?
- What determines reactivity?

Dealing with Complexity

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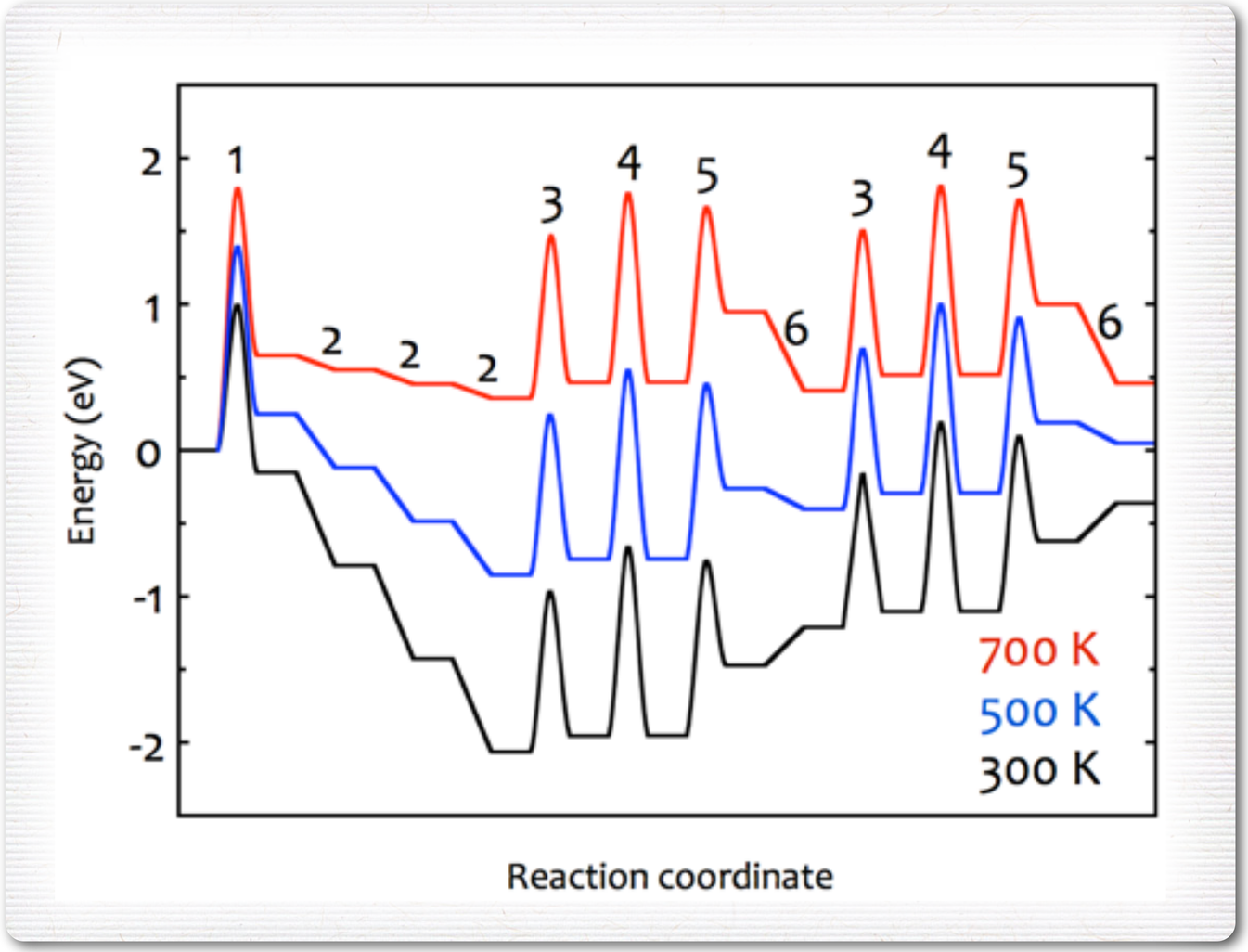
Ammonia Synthesis on Ru(0001)



1. $N_2(g) + 2^* \rightleftarrows 2N^*$
2. $H_2(g) + 2^* \rightleftarrows 2H^*$
3. $N^* + H^* \rightleftarrows NH^*$
4. $NH^* + H^* \rightleftarrows NH_2^*$
5. $NH_2^* + H^* \rightleftarrows NH_3^*$
6. $NH_3^* \rightleftarrows NH_3(g)$

+ $N_2(g) \rightleftarrows N_2^*$

- How many energetic variables are there?

Dealing with Complexity

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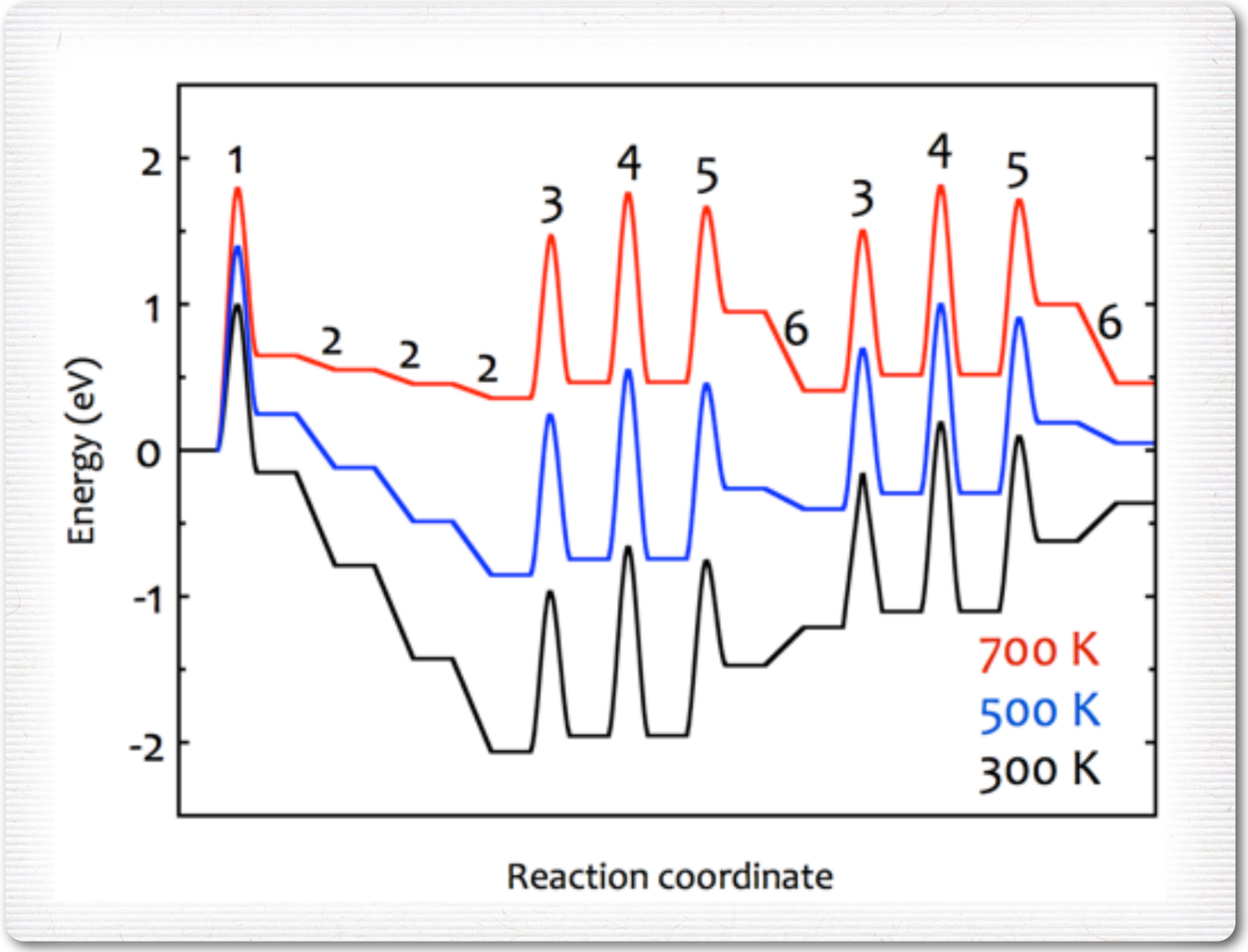
Ammonia Synthesis on Ru(0001)



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5. $NH_2^* + H^* \rightleftarrows NH_3^*$
6. $NH_3^* \rightleftarrows NH_3(g)$

\+ $N_2(g) \rightleftarrows N_2^*$

- How many energetic variables are there?

6 intermediates

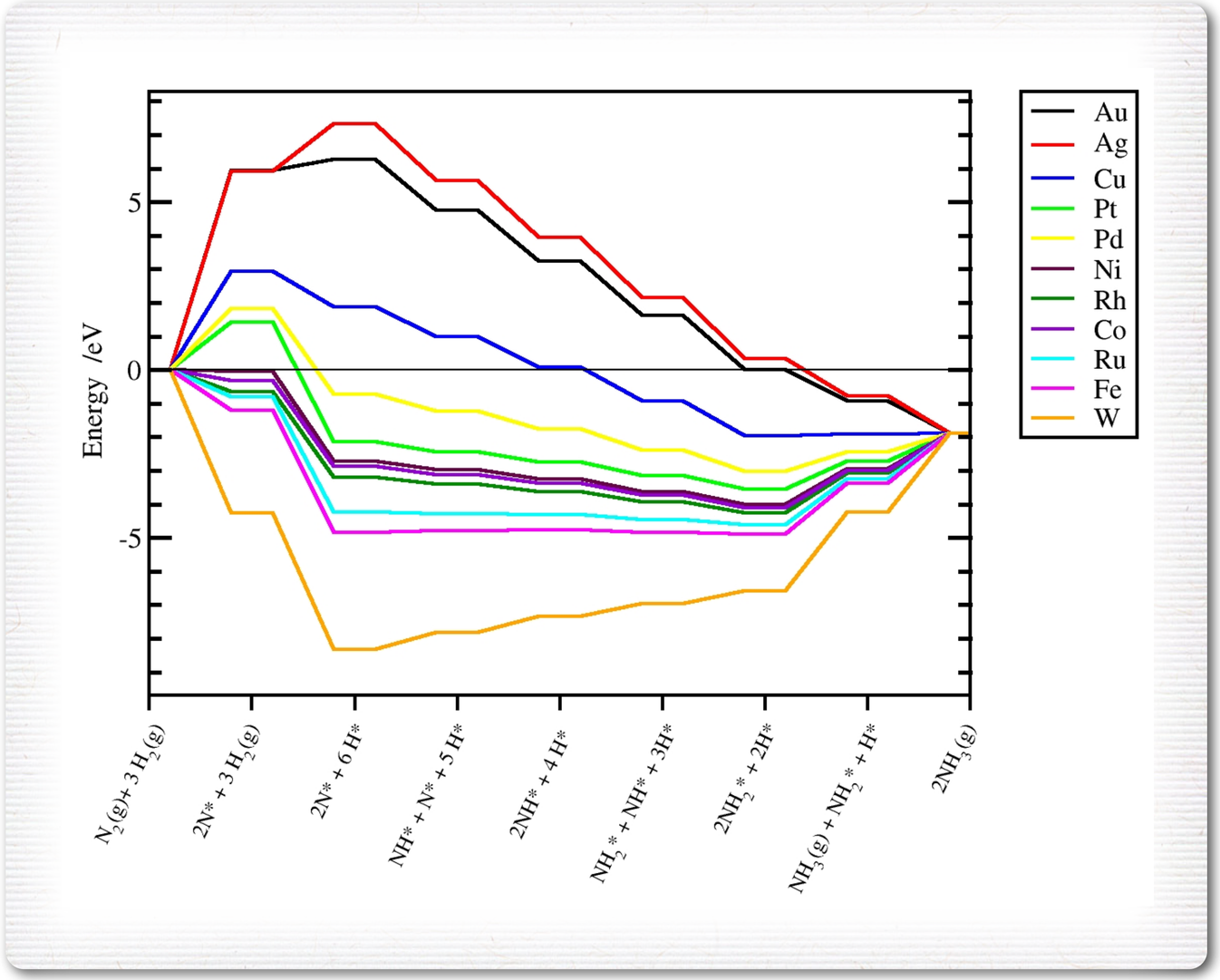
\+

6 transition states

=

12 different energy parameters

Scaling Relations



Adsorption scaling

- Relationships between bond energies of different intermediates

Brønsted-Evans-Polanyi (BEP)/ Transition state scaling

- Relationships between activation energies and reaction energies

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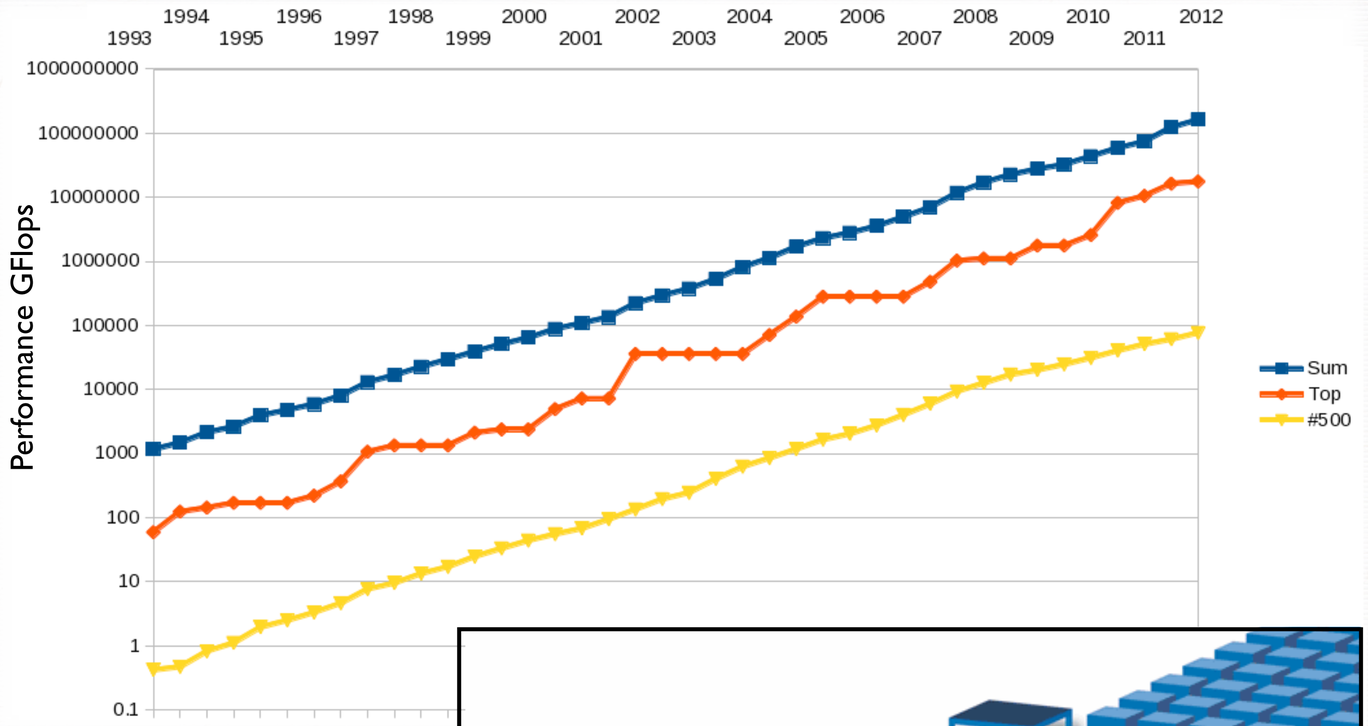
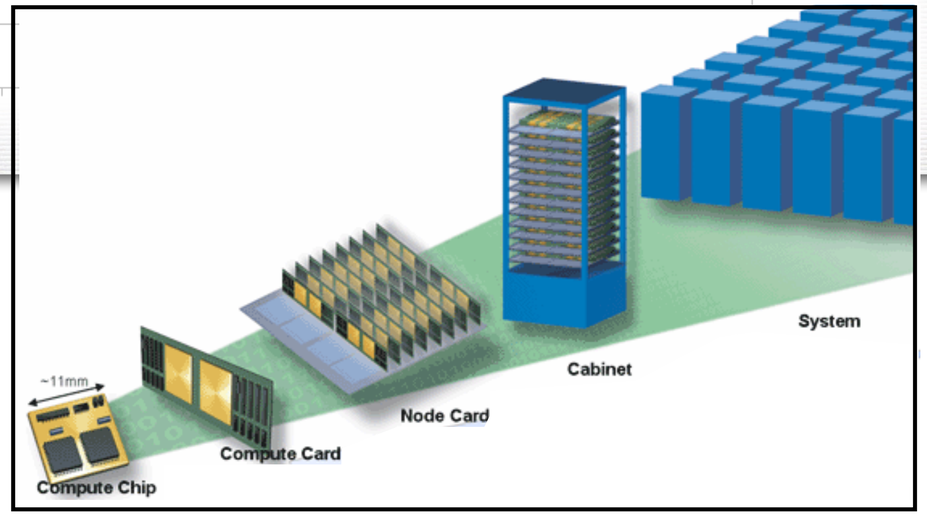
Perform Computer Experiments

Machines: Supercomputers



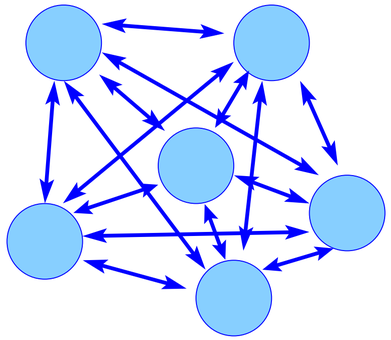
www.top500.org



SUNCAT computer cluster

Blue Gene/Q Argonne National Laboratory #4

Main Method: Density Functional Theory

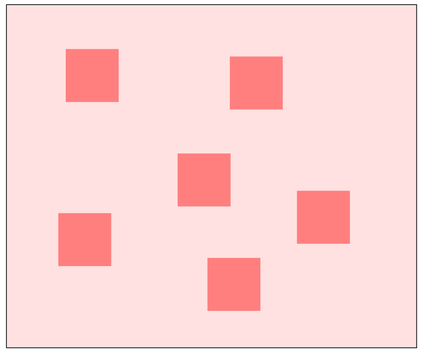


N interacting electrons
+ real potential

$$H\Psi(\mathbf{r}) = \varepsilon\Psi(\mathbf{r})$$

$$H = -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$-\sum_{i,I}\frac{Z}{|\mathbf{r}_i - \mathbf{R}_I|}$$



N non-interacting, fictitious particles + effective potential

Kohn-Sham Equations:

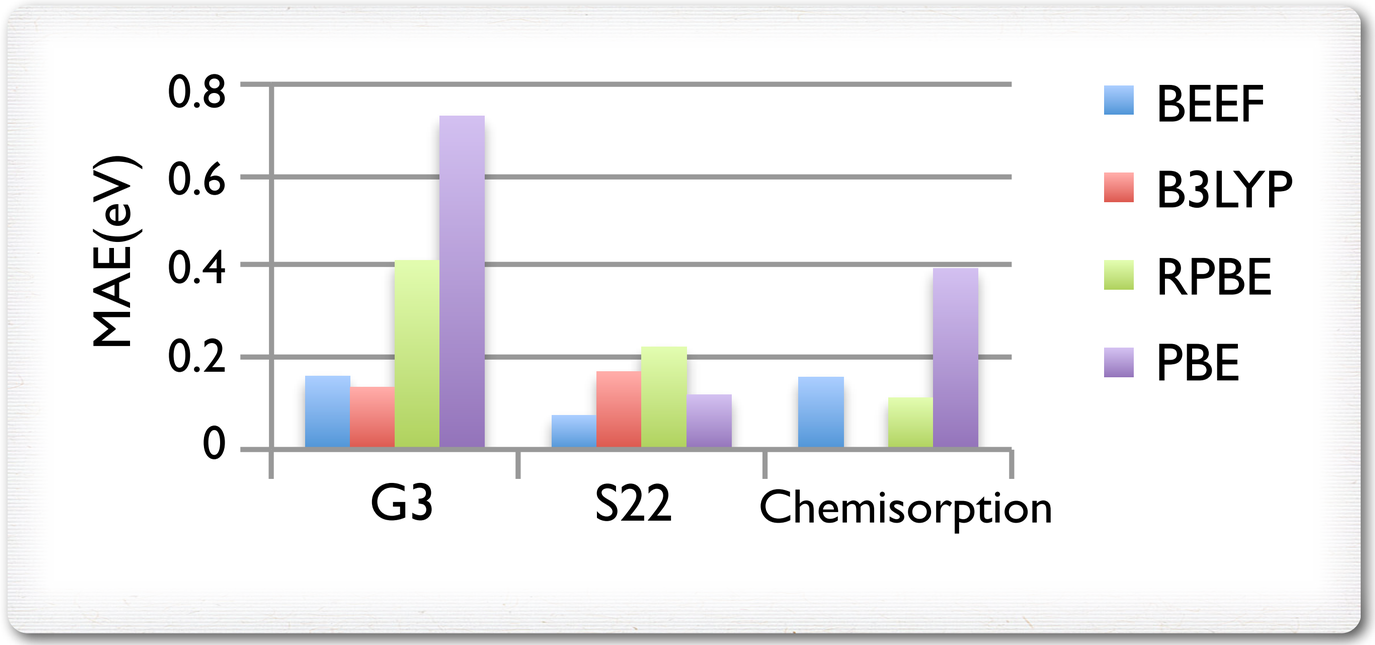
$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2$$

$$\mathrm{v_{eff}} = \mathrm{v_{ext}}(\mathbf{r}) + \mathrm{v_{Hartree}}[n(\mathbf{r})] + \mathrm{v_{xc}}[n(\mathbf{r})] \quad \text{with} \quad \mathrm{v_{xc}}[\mathrm{n}(\mathbf{r})] = \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}$$

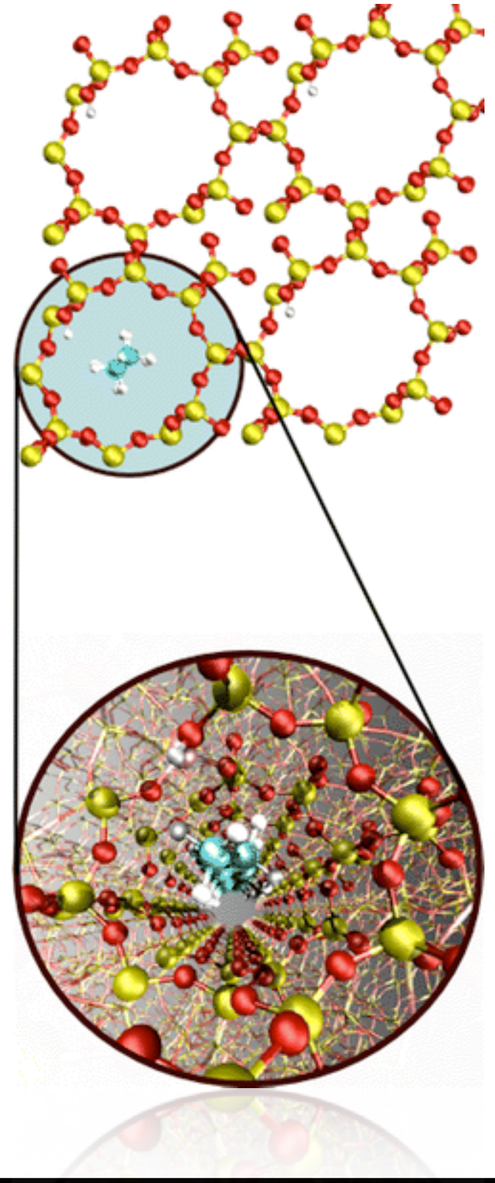
DFT Performance: "It's All in the Exchange-Correlation Functional"

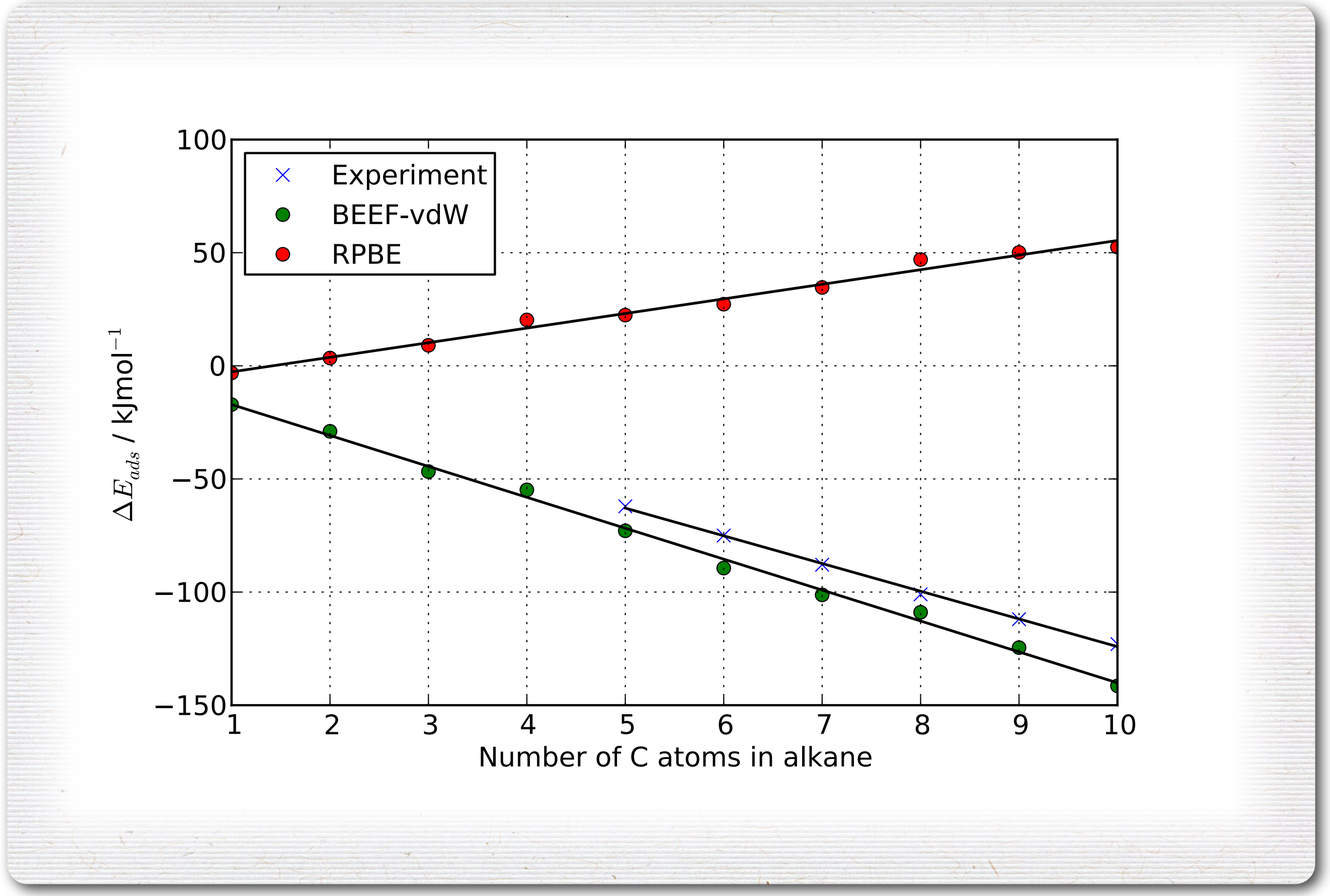
J. P. Perdew *et al.* in AIP Conf. Proc. **577** (2001),
M. A. L. Marques *et al.*, Comp. Phys. Commun. **183**, 2272 (2012).



J. Wellendorff, *et al.*, Phys. Rev. B **85**, 23 (2012),

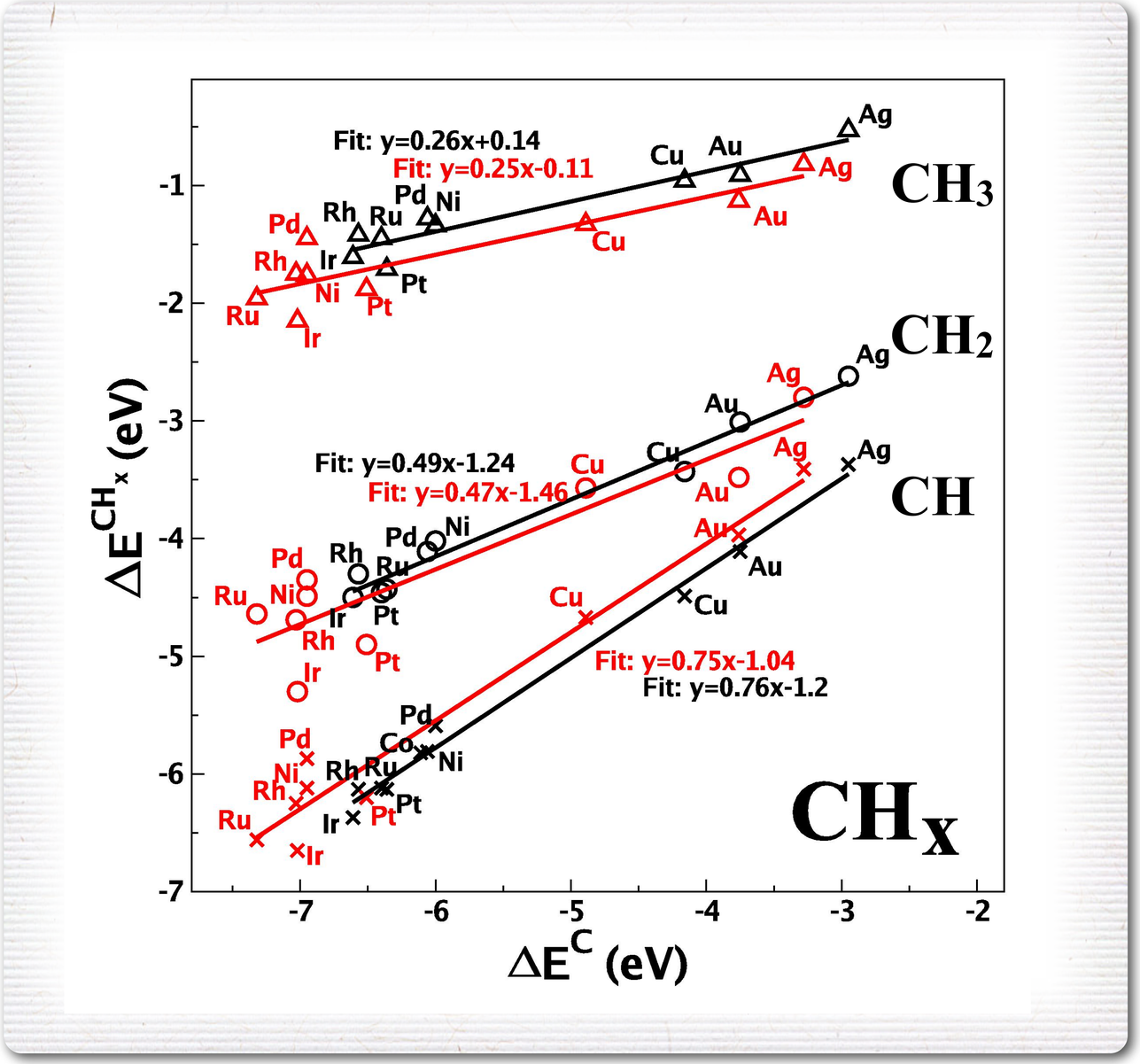
Application of BEEF: Physorption of n-alkanes in Zeolites (ZSM22)



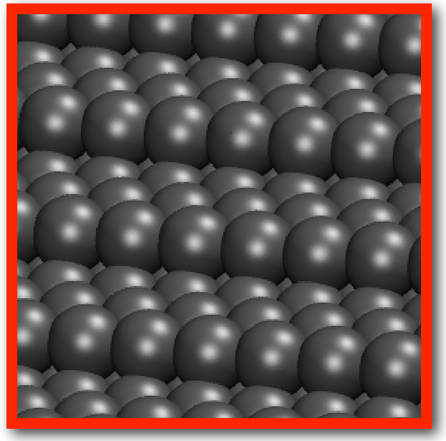


R. Brogaard, P. G. Moses, J. K. Nørskov, Catal. Lett. **142**, 1057 (2012).

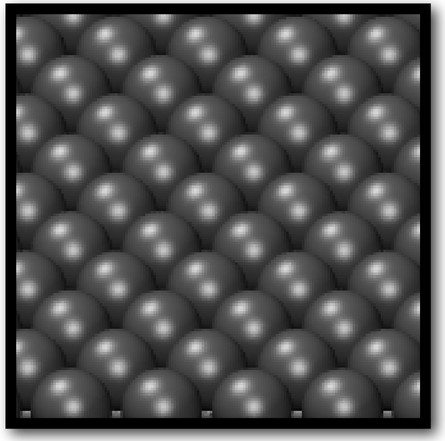
Computer Experiments I

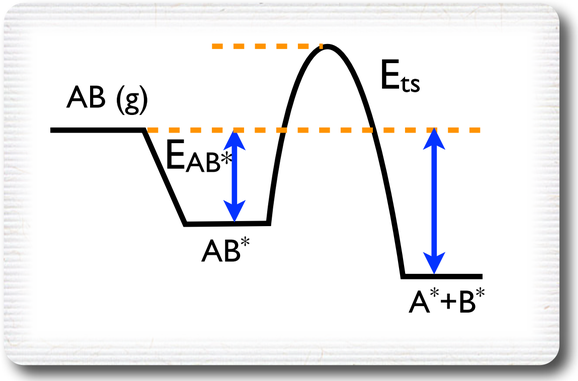


stepped surface



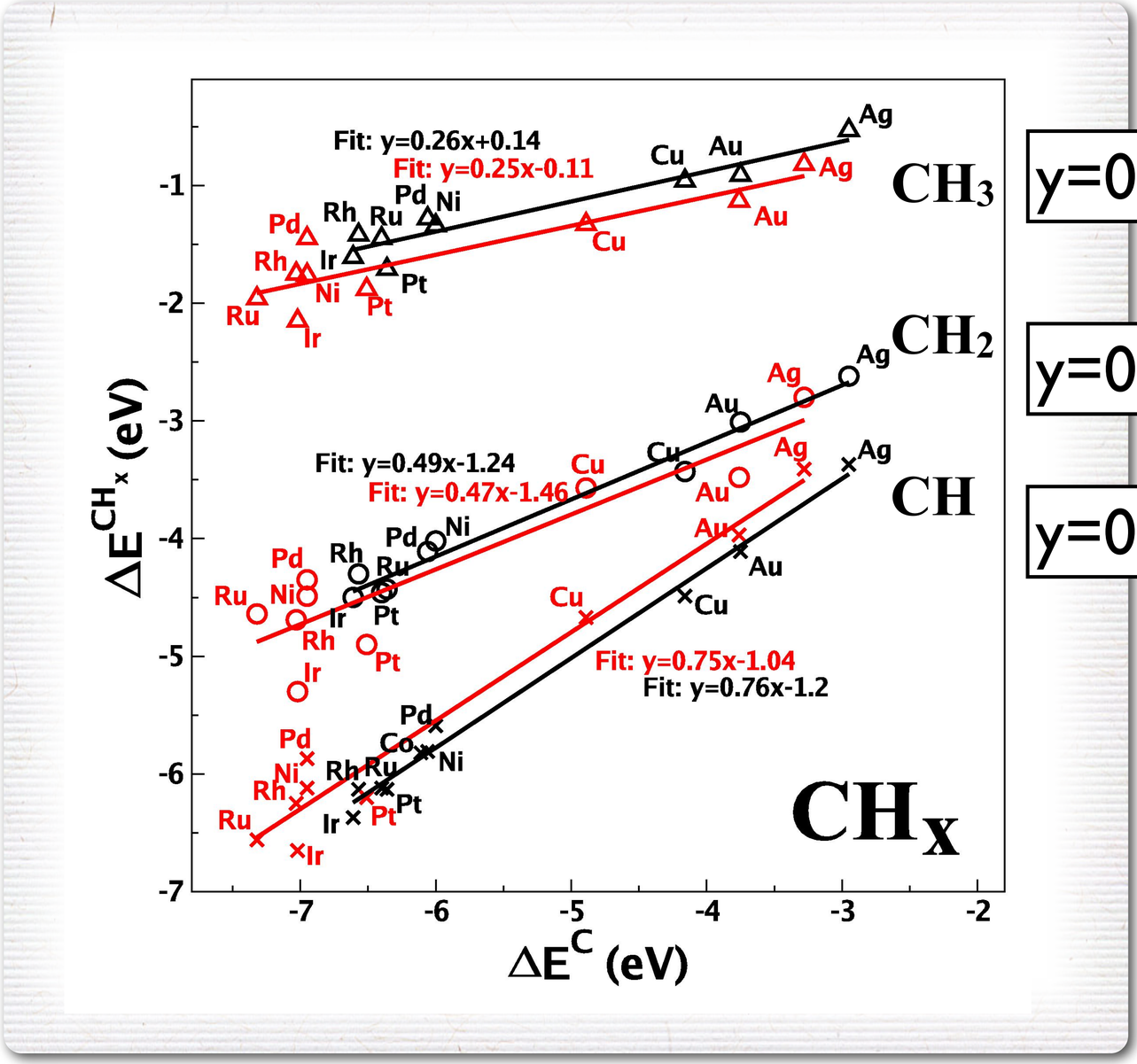
close-packed surface





F. Abild-Pedersen, *et al.*, Phys. Rev. Lett. **99**, 016105 (2007).

Computer Experiments I



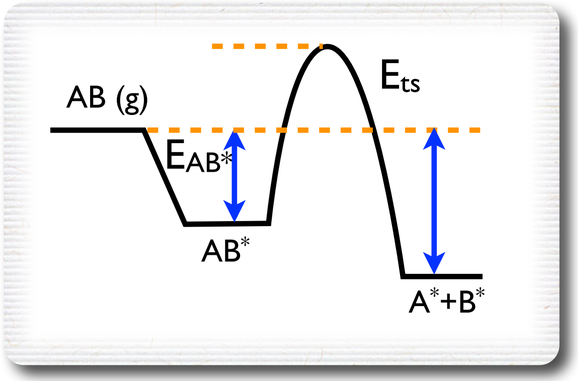
stepped surface

close-packed surface

y=0.26x+0.14

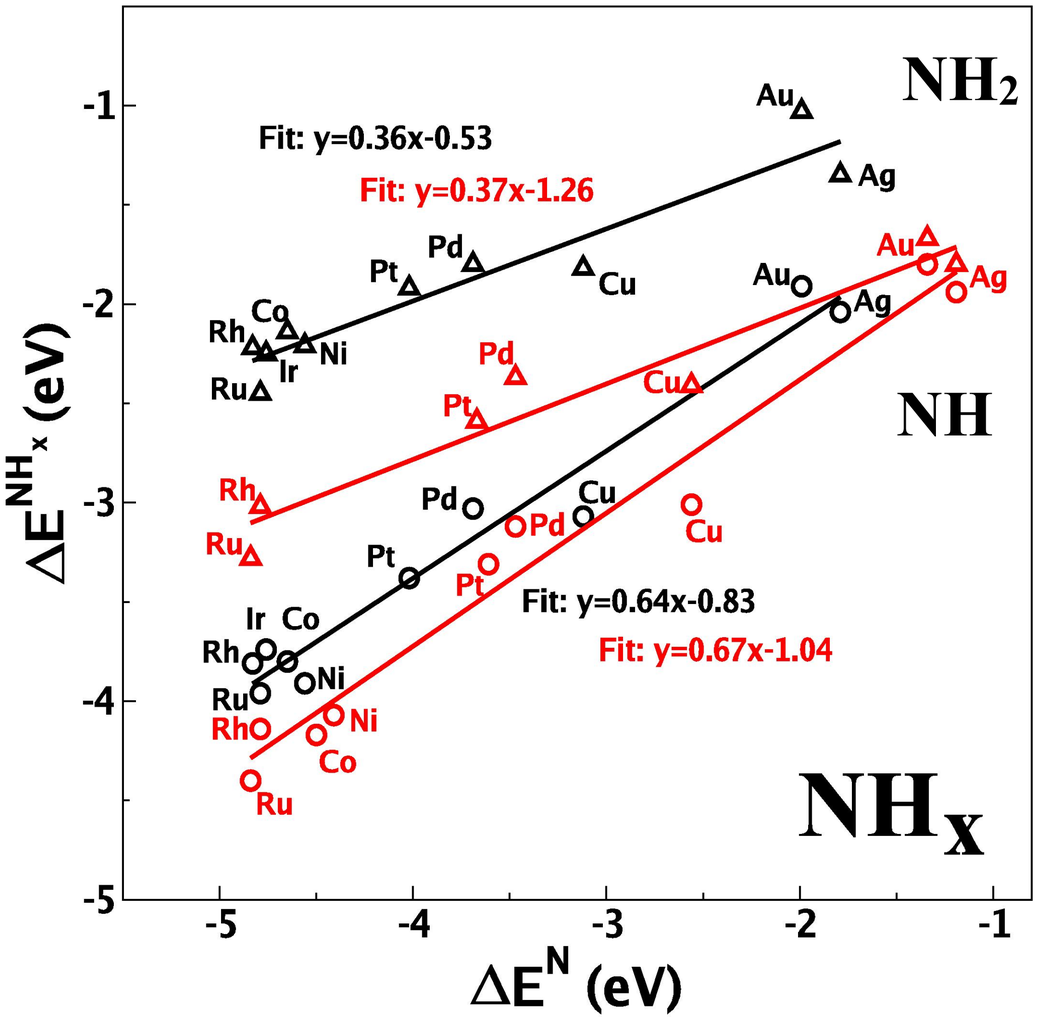
y=0.49x-1.24

y=0.76x-1.04

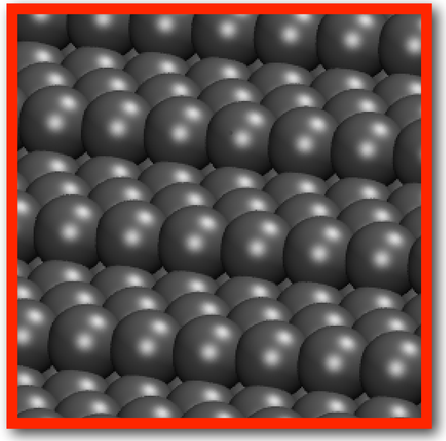


F. Abild-Pedersen, *et al.*, Phys. Rev. Lett. **99**, 016105 (2007).

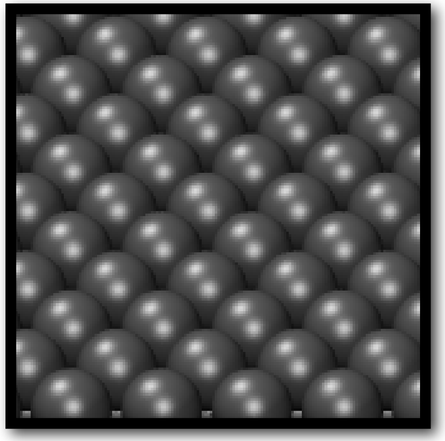
Computer Experiments II

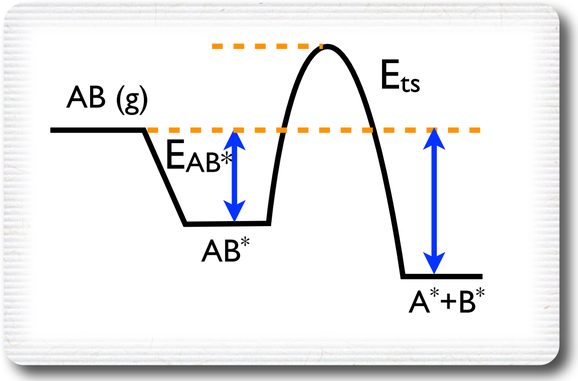


stepped surface



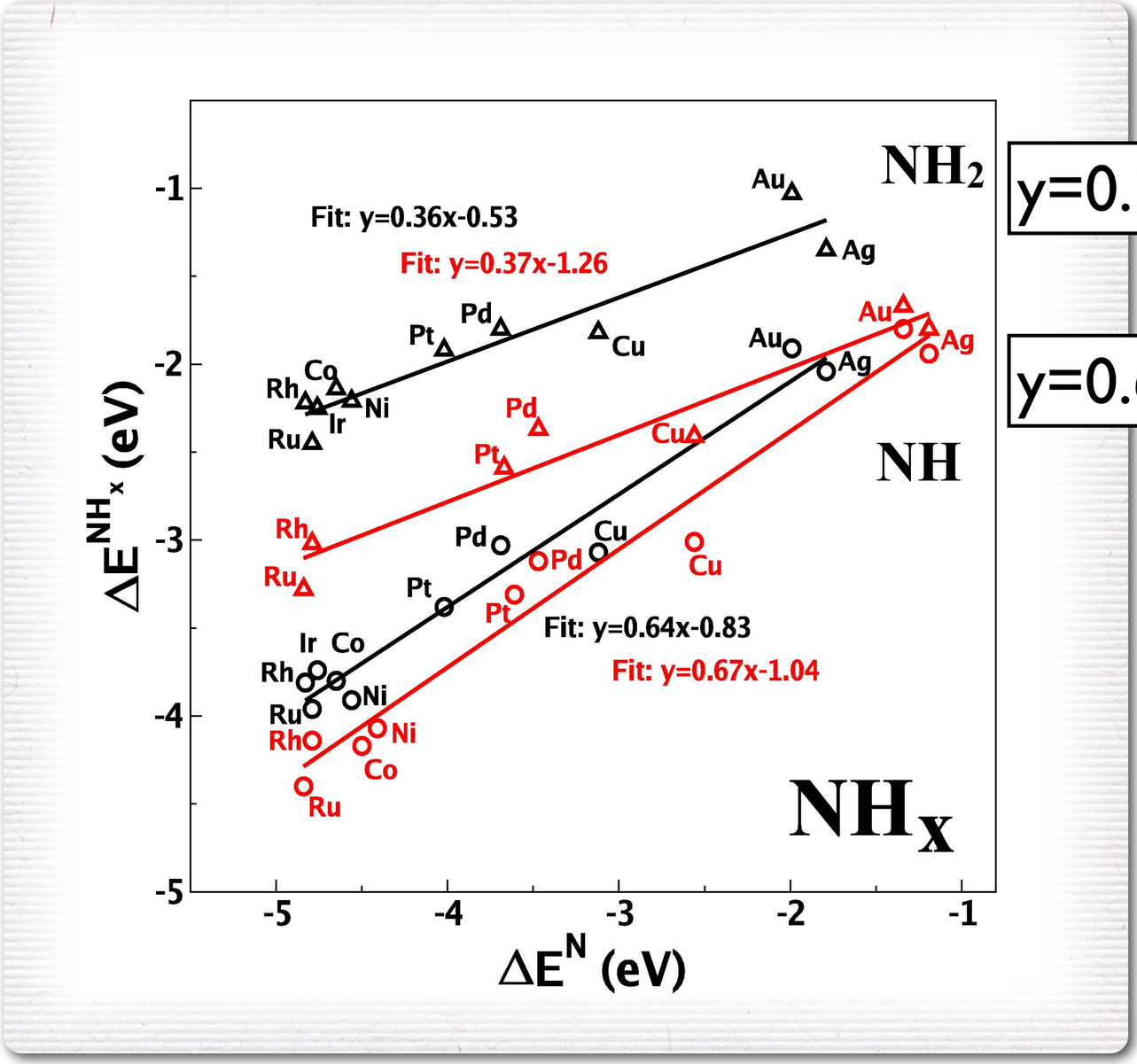
close-packed surface





F. Abild-Pedersen, *et al.*, Phys. Rev. Lett. **99**, 016105 (2007).

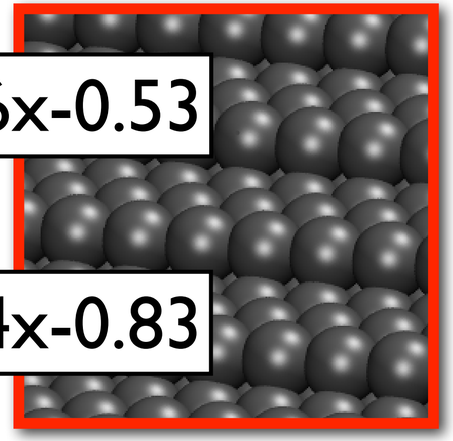
Computer Experiments II



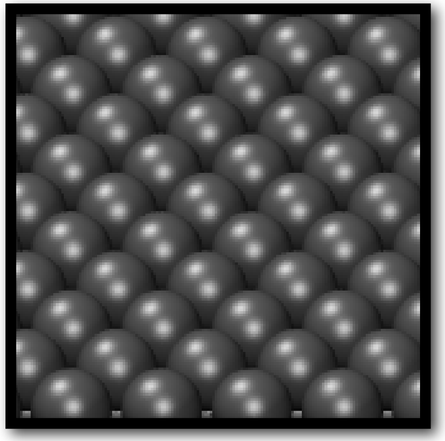
y=0.36x-0.53

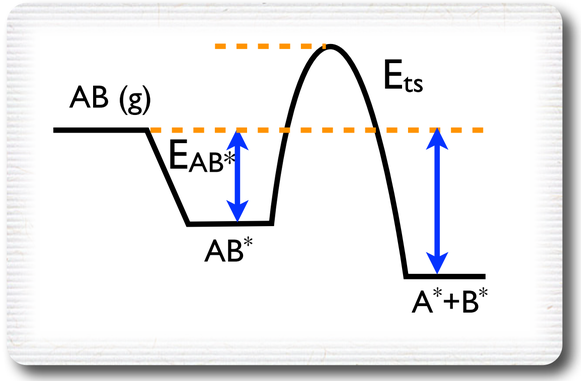
y=0.64x-0.83

stepped surface



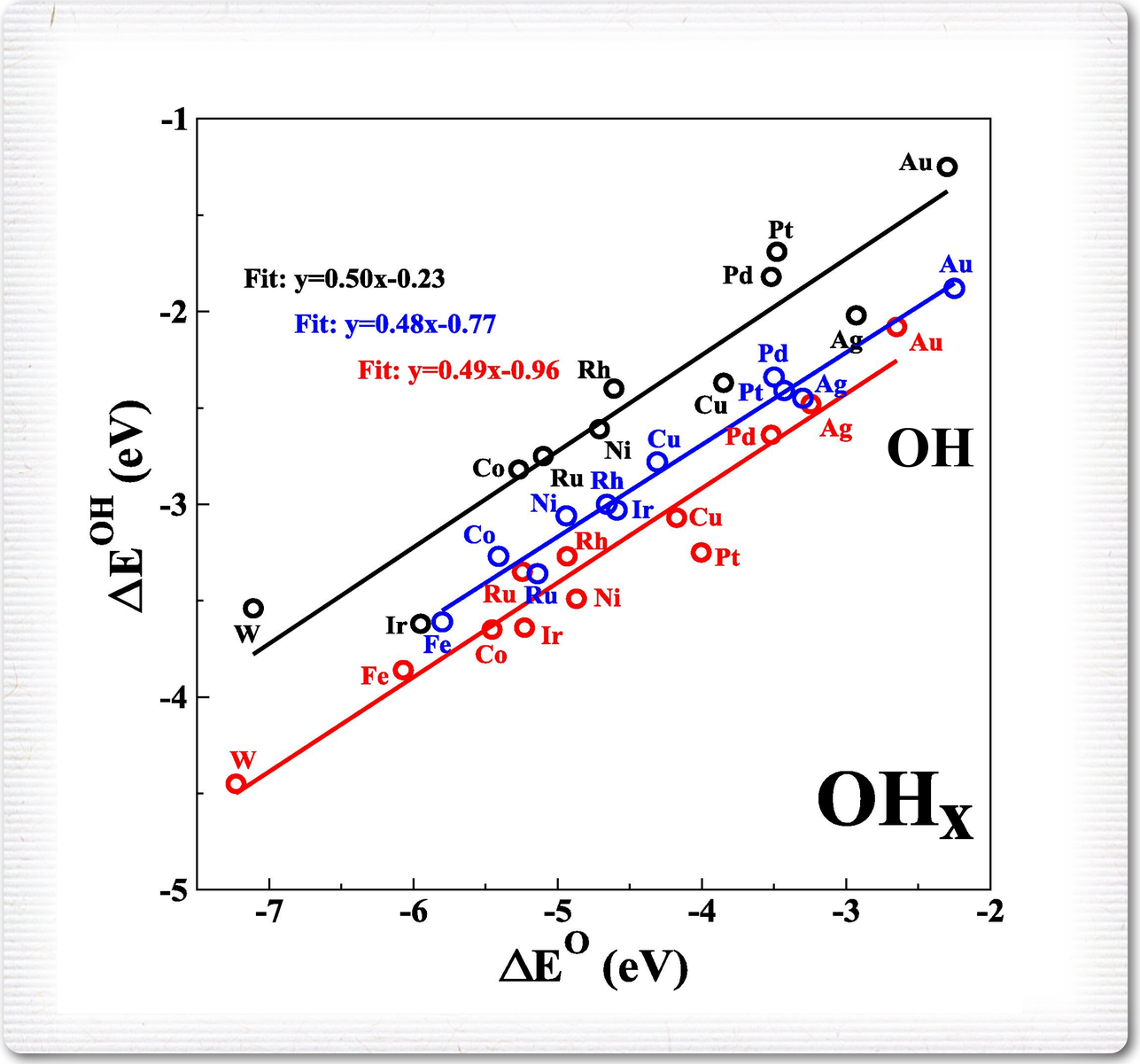
close-packed surface



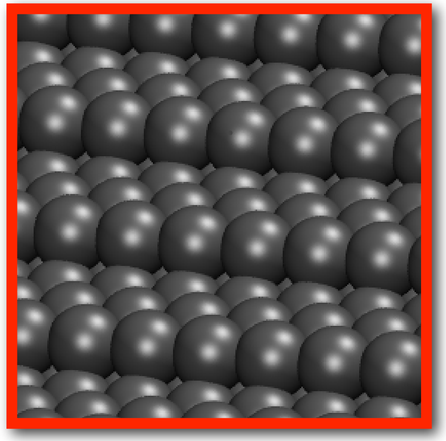


F. Abild-Pedersen, *et al.*, Phys. Rev. Lett. **99**, 016105 (2007).

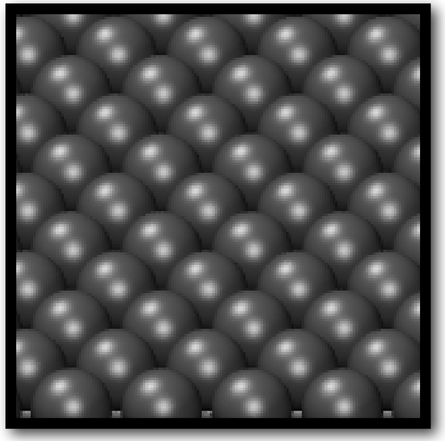
Computer Experiments III

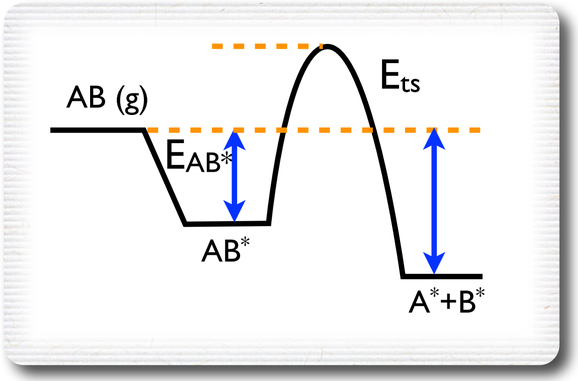


stepped surface



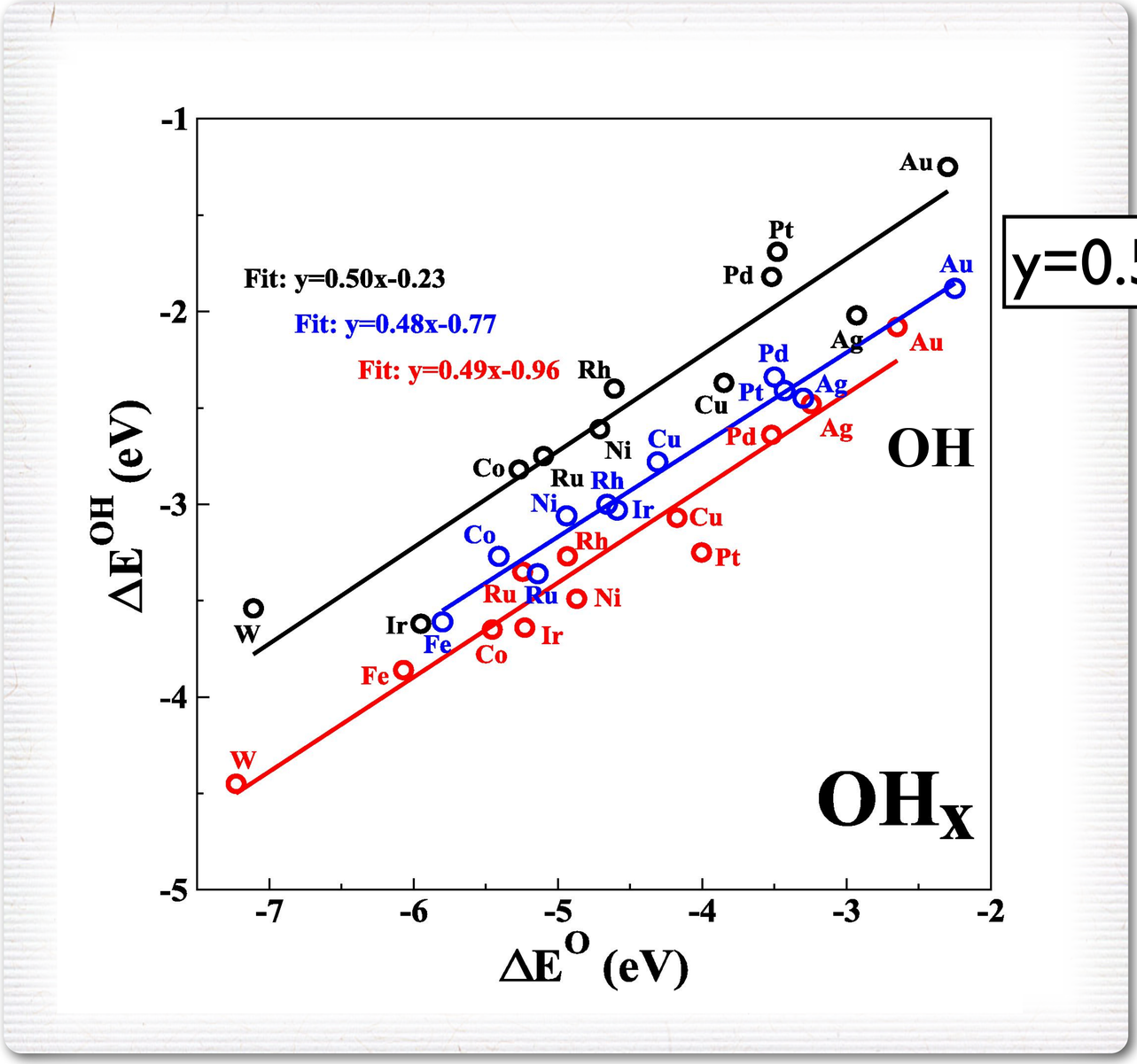
close-packed surface





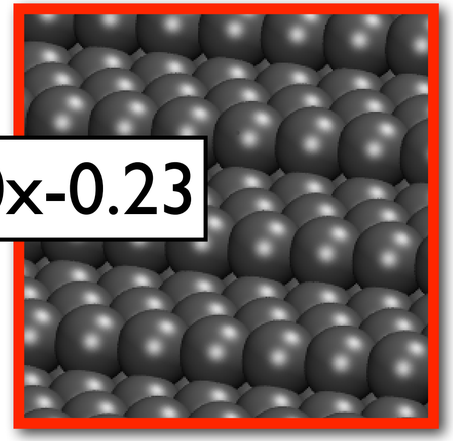
F. Abild-Pedersen, *et al.*, Phys. Rev. Lett. **99**, 016105 (2007).

Computer Experiments III

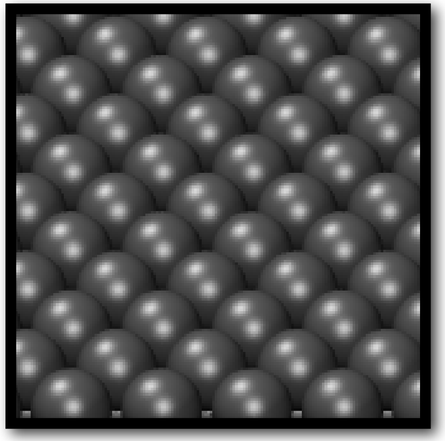


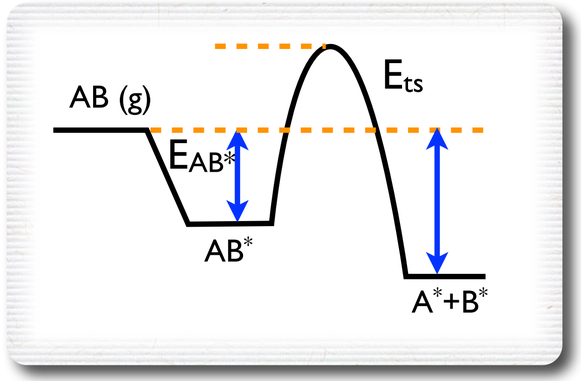
y=0.50x-0.23

stepped surface



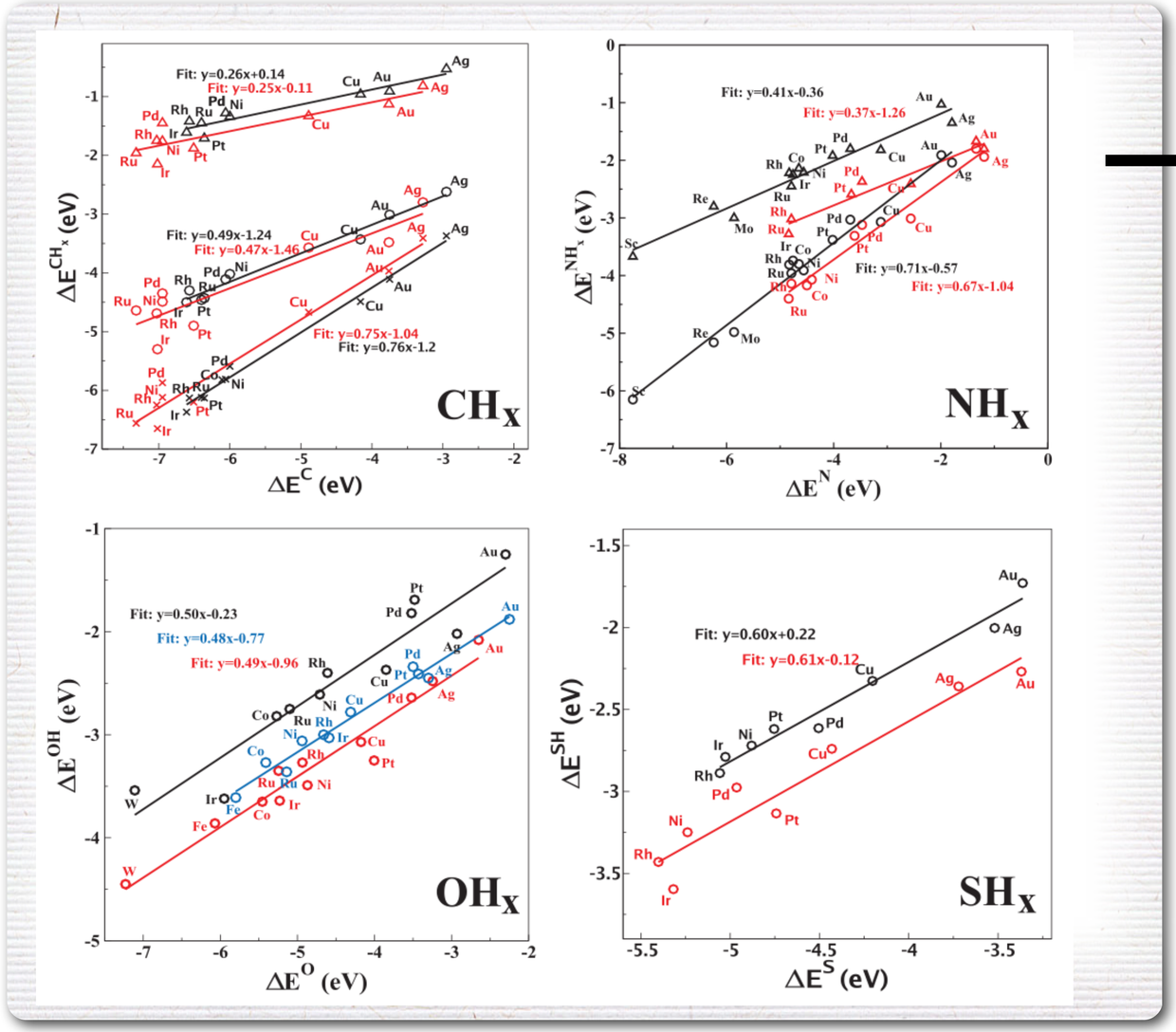
close-packed surface





F. Abild-Pedersen, *et al.*, Phys. Rev. Lett. **99**, 016105 (2007).

Adsorption Scaling Relations



$$\Delta E^{\mathrm{AH}_x} = \gamma(x)\Delta E^{\mathrm{A}} + \xi$$

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

Atom A:

- Valency: $x_{\max}$
- # H atoms attached: x
- # bonds to surface: $x_{\mathrm{surf}} = \gamma x_{\max}$

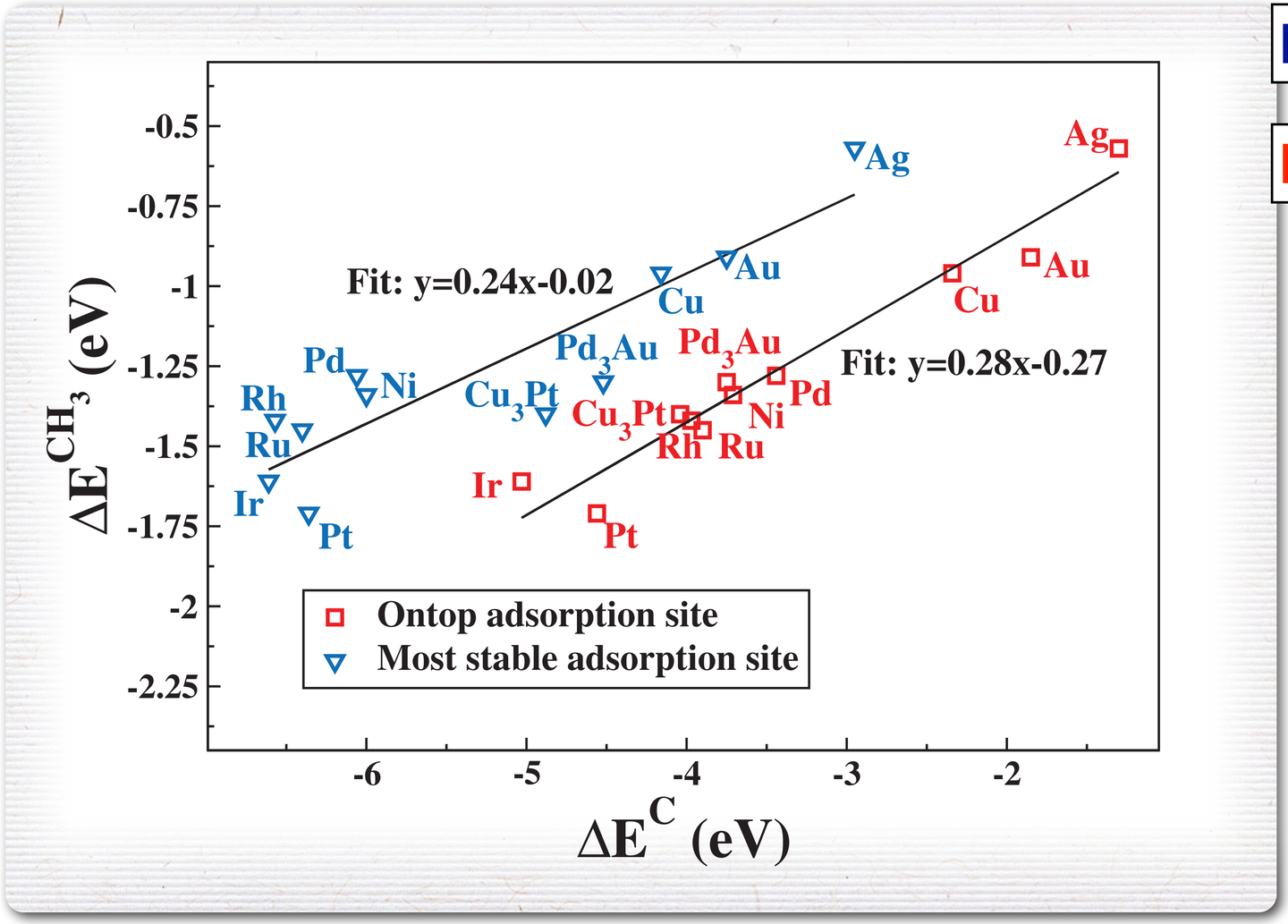
Bond order conservation

$$\gamma x_{\max} + x = x_{\max}$$

$$\Leftrightarrow$$

$$\gamma = \frac{x_{\max} - x}{x_{\max}}$$

Adsorption Site and Scaling Relations



MAE=0.13eV

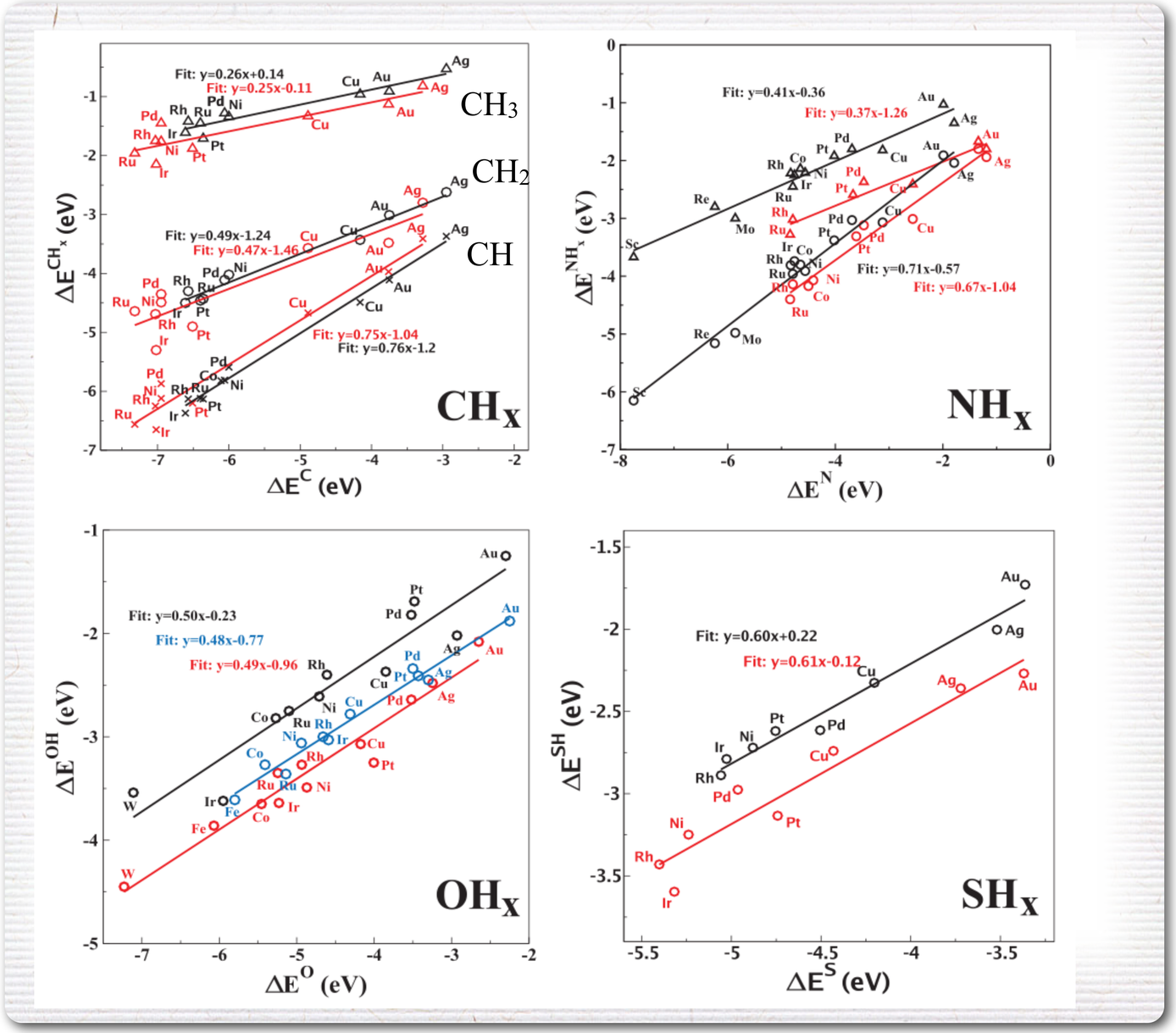
MAE=0.06eV

adsorbate	preferred adsorption site
CH_3	1-fold
CH_2	2-fold
CH	3-fold
C	3-fold

C	1-fold

Overall scaling independent of adsorption geometry and details of bonding ⇒ more general explanation

Origin of Adsorption Scaling Relations



$$\Delta E^{\mathrm{AH}_x} = \gamma(x)\Delta E^{\mathrm{A}} + \xi$$

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

=

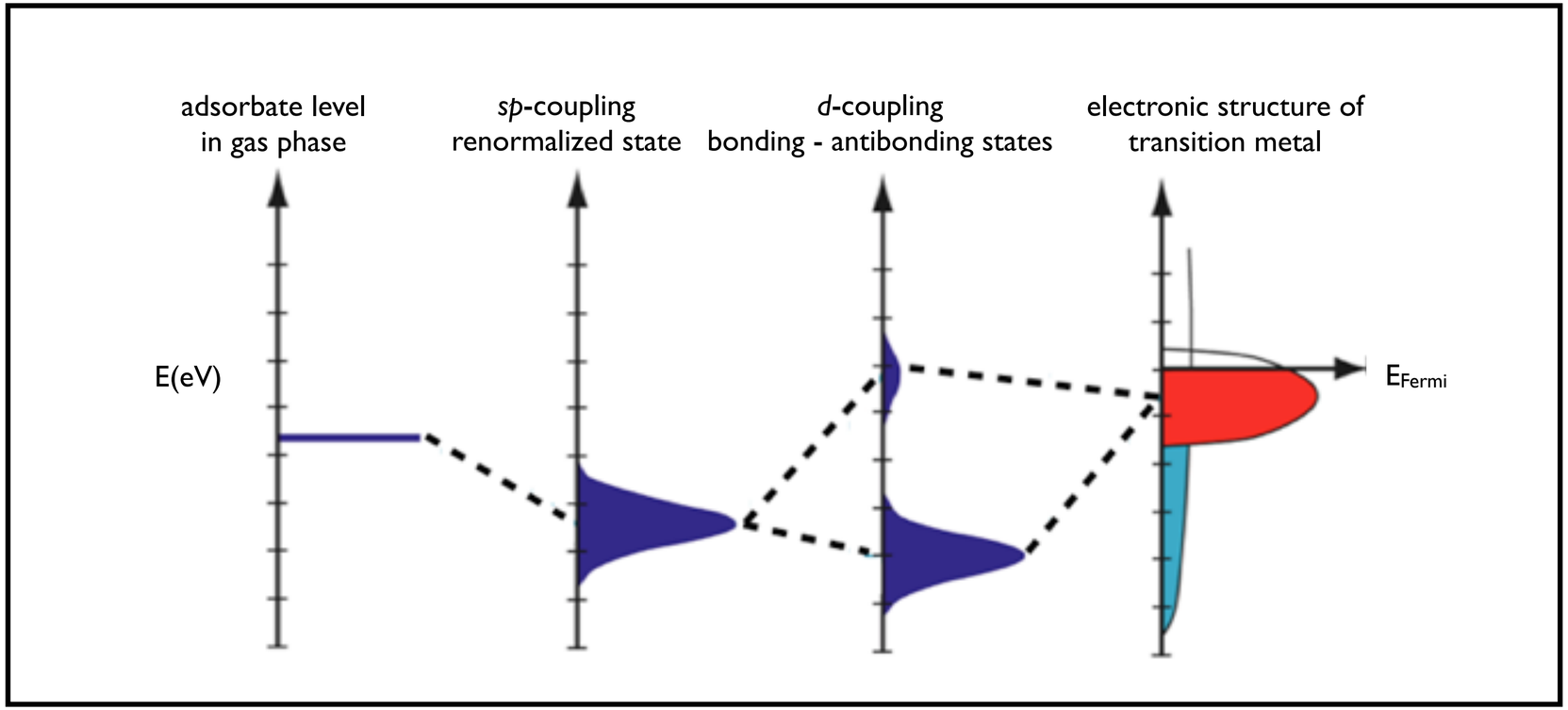
d-band model

+

Effective medium theory

F. Abild-Pedersen, *et al.*, Phys. Rev. Lett. **99**, 016105 (2007).

The d-band Model of Chemical Bonding on Metal Surfaces



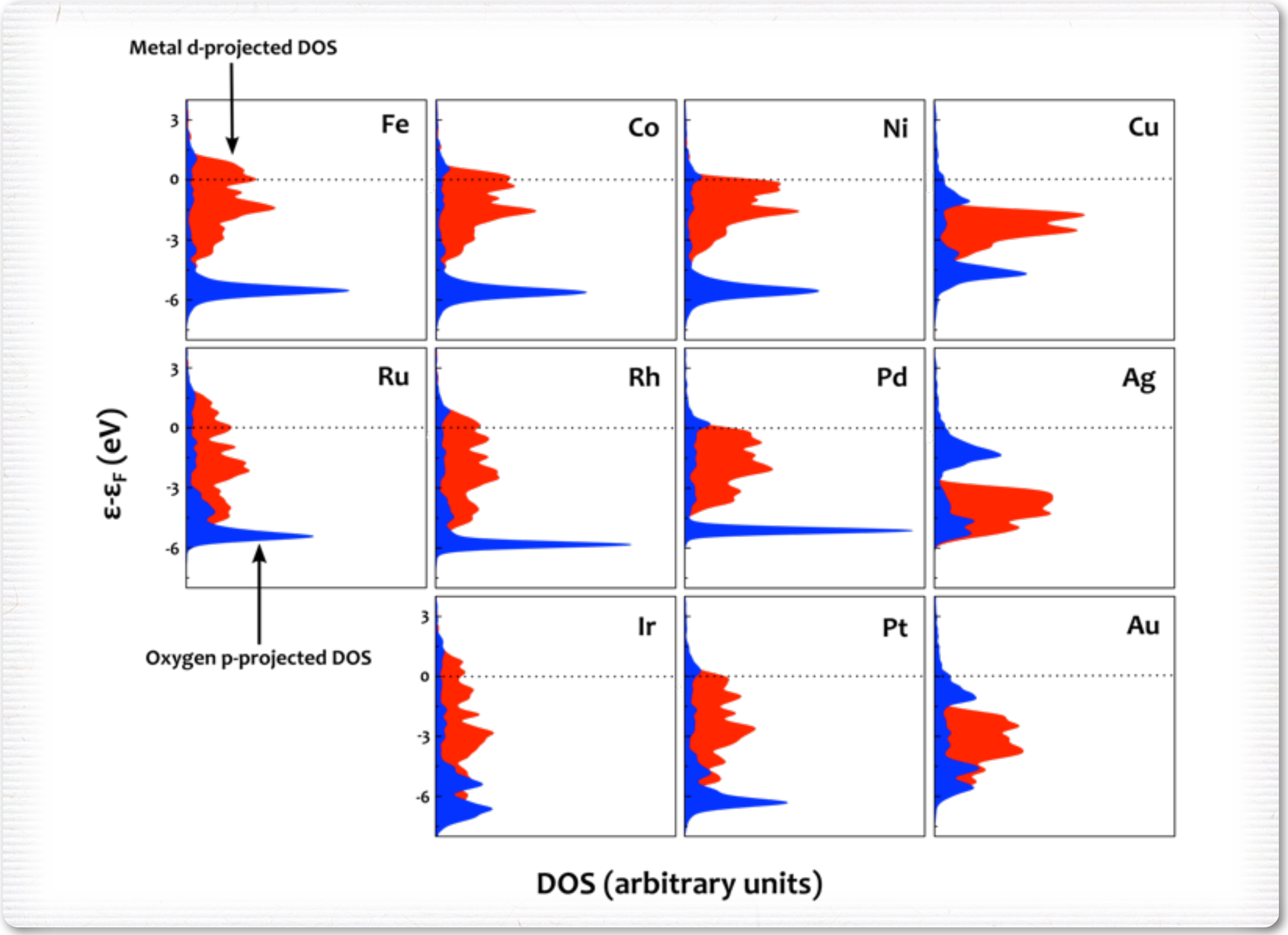
$$\Delta E_{ads} = \Delta E_{sp} + \Delta E_d \longrightarrow \Delta E_d = -2(1-f)\frac{V_{ad}^2}{|\varepsilon_d - \varepsilon_a|} + 2(1+f)\alpha V_{ad}^2$$

large and constant

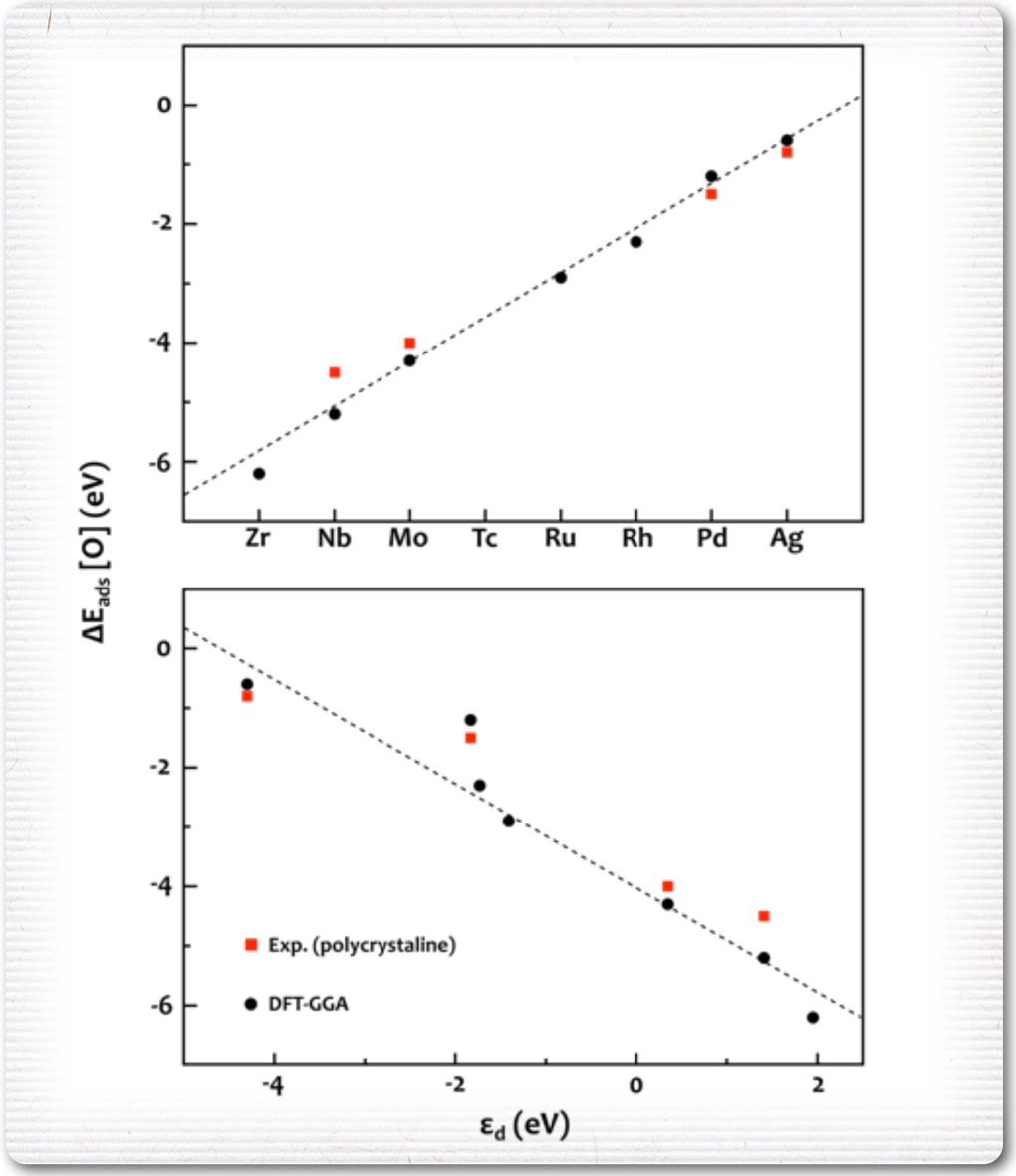
small and varies

B. Hammer *et al.*, Surf. Sci. **343**, 211 (1995); Nature **376**, 238 (1995); Adv. Catal. **45**, 71 (2000).

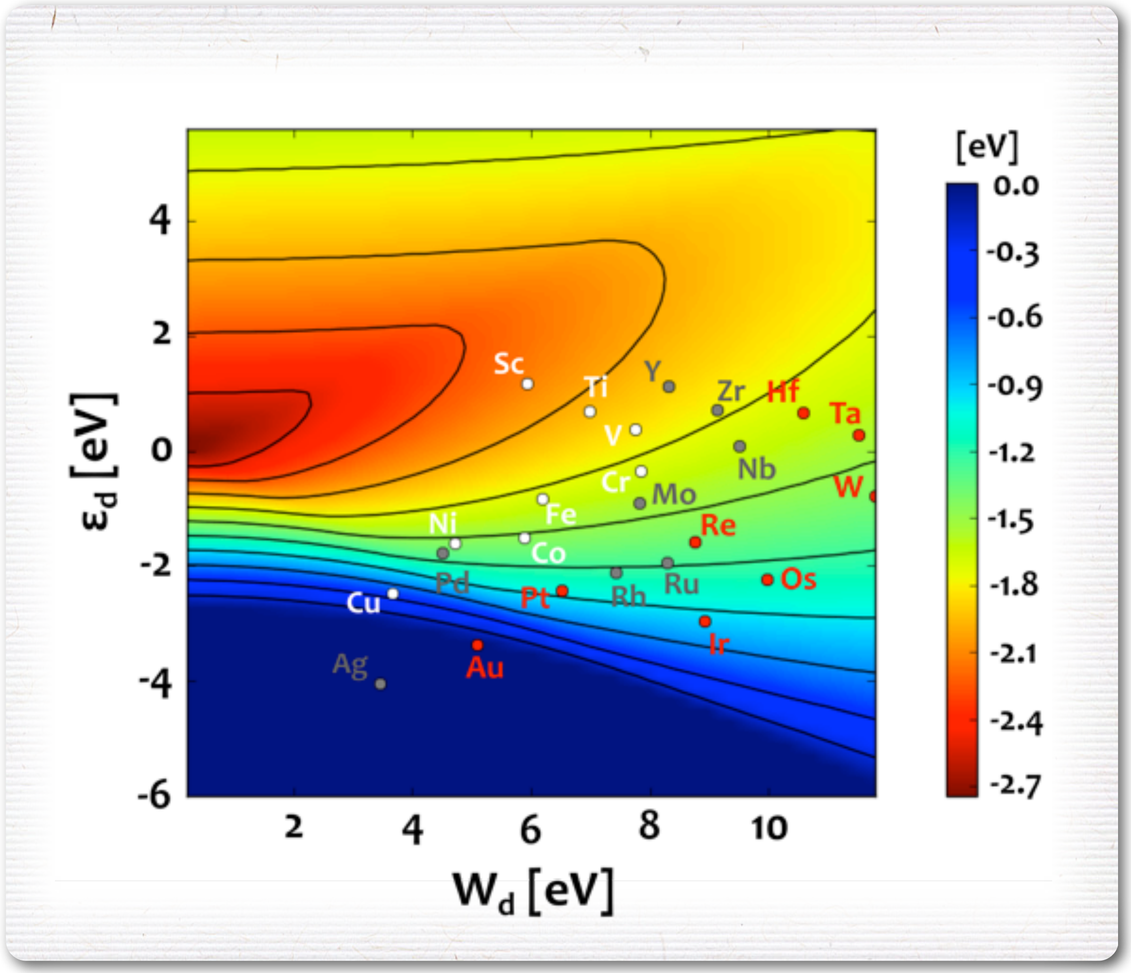
Calculated Density of States



Variations in O Adsorption Energies



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



A. Vojvodic, J. K Nørskov, F. Abild-Pedersen, Top. Catal, accepted (2013).

"d-band model part"

From d-band model: variations between metals depend on ΔE_d

$$\Delta E^{\mathrm{A}} = \Delta E^{\mathrm{A}}_{sp} + \Delta E^{\mathrm{A}}_{d}$$

$$\Delta E^{\mathrm{AH}_x}(x) = \Delta E^{\mathrm{AH}_x}_{sp} + \Delta E^{\mathrm{AH}_x}_{d}$$

Assume

$$\Delta E^{\mathrm{AH}_x}_{d}(x) = \gamma(x)\Delta E^{\mathrm{A}}_{d} \Rightarrow$$

$$\begin{aligned}\Delta E^{\mathrm{AH}_x}(x) &= \gamma(x)\Delta E^{\mathrm{A}}_{d} + \Delta E^{\mathrm{AH}_x}_{sp} \\ &= \gamma(x)\Delta E^{\mathrm{A}}_{d} + \Delta E^{\mathrm{AH}_x}_{sp} - \gamma(x)\Delta E^{\mathrm{A}}_{sp} + \gamma(x)\Delta E^{\mathrm{A}}_{sp} \\ &\equiv \gamma(x)\Delta E^{\mathrm{A}} + \xi\end{aligned}$$

read off from figure for each AH_x/A combination

metal independent

“Effective medium part”

$$\Delta E_d = \Delta E_d^{hyb} + \Delta E_d^{orth}$$

In the weak coupling limit $\Delta E_d^{hyb} \propto \Delta E_d^{orth} \propto V_{ad}^2$, where V_{ad}^2 is the coupling strength between the adsorbate and the metal *d*-states.

$V_{ad}^2(\{r_{a_i}\})$ function of the number of metal neighbors and their distance to the adsorbate.

Add H atoms to the central C, N, O or S *i.e.* $x \nearrow \Rightarrow$

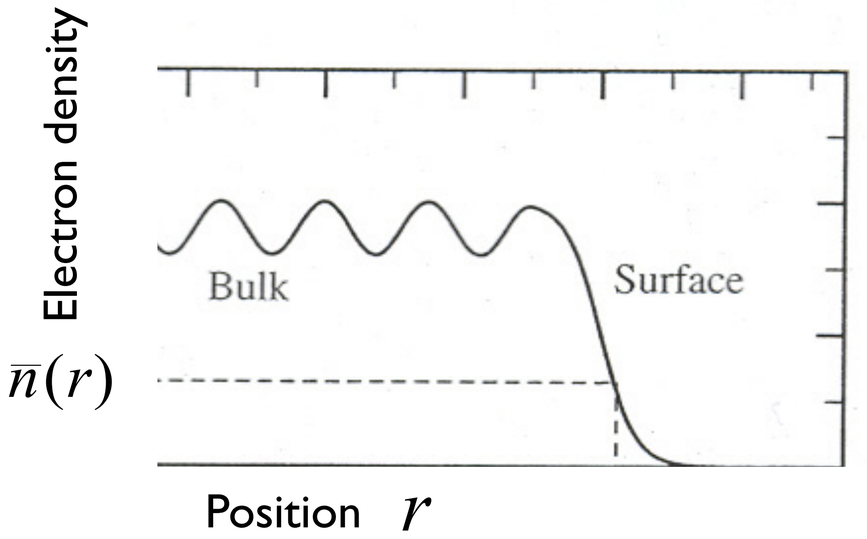
- $r_{a_i} \nearrow$
- $V_{ad}^2(\{r_{a_i}\}) \searrow$

sp-coupling determines the adsorption bond lengths r_{a_i}

Use effective medium theory (EMT)

"Effective medium part"

- Interaction of atom A with atoms in the vicinity ≈ interaction of A with a homogeneous electron gas (effective medium) of a density given by a spherical average n of the nearby atoms. $\Delta E = \Delta E_{hom}(n)$.
- $\Delta E_{hom}(n)$ has a minimum for a particular electron density $n_0 \Rightarrow$ Equilibrium geometry is the position where A experiences $n = n_0$

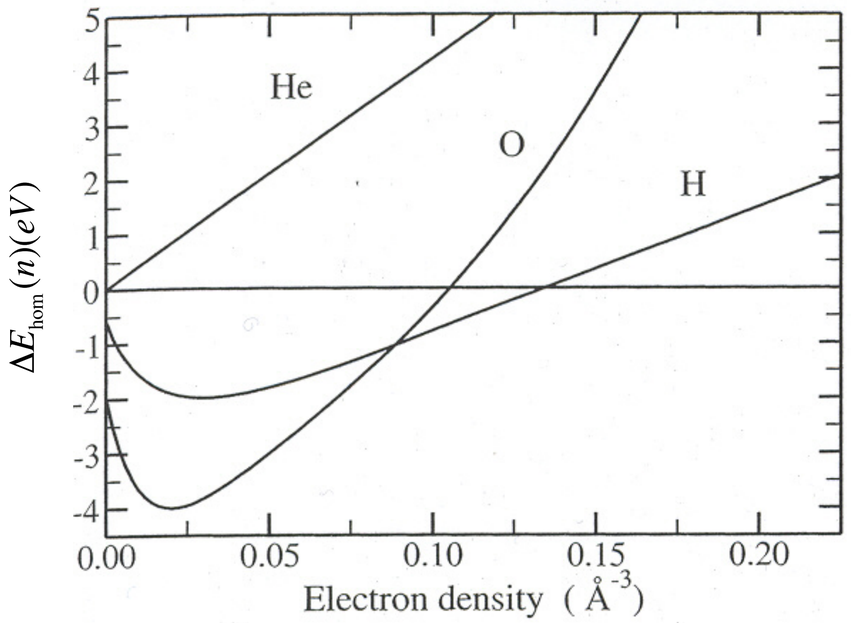


Surface electron density n_{surf} needed for $n = n_0 \searrow$ as $x \nearrow$

$\Rightarrow n_{surf} = \frac{x_{max} - x}{x_{max}} n_0 = \gamma(x) n_0$

Assumption: *d*-states have approximately the same decay length as the *sp*-states $\Rightarrow V_{ad}^2$ scales with n_{surf}

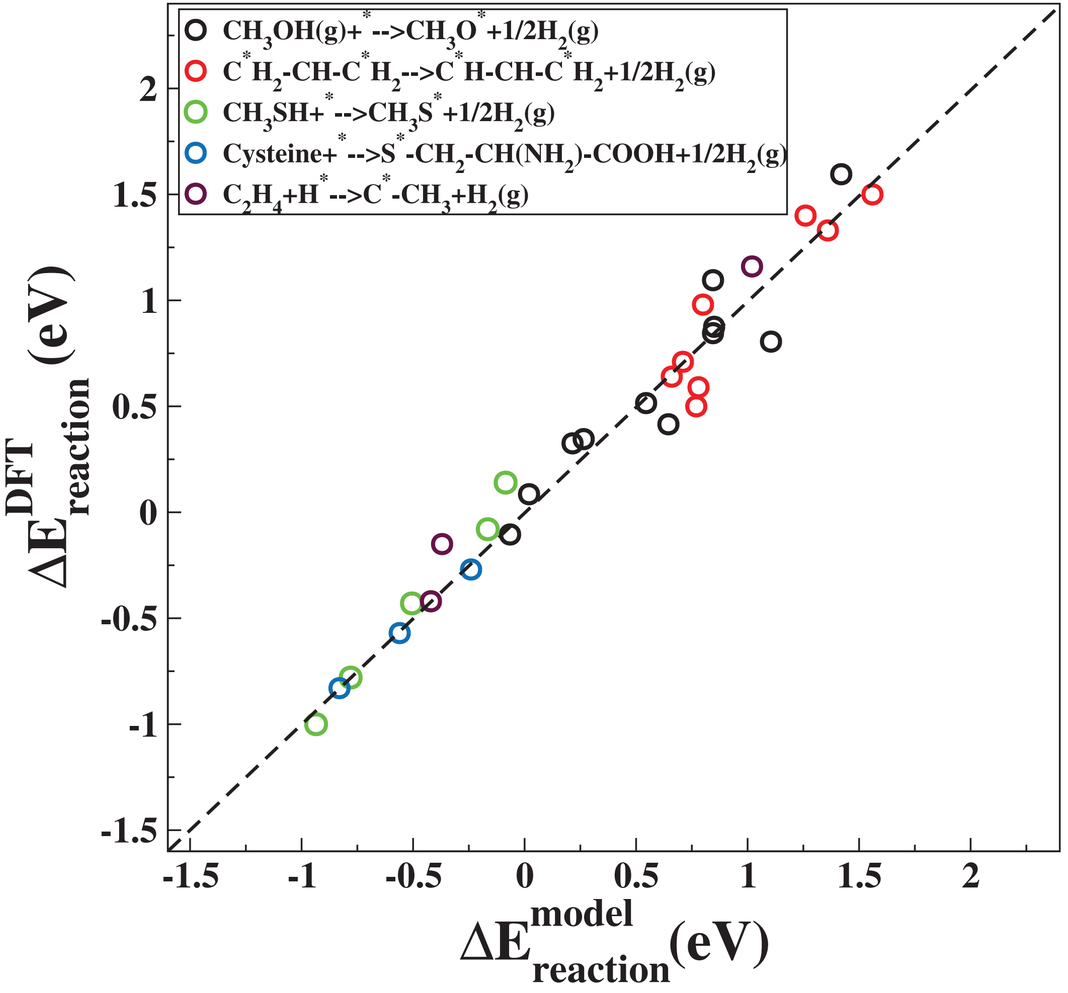
$\Delta E_d \propto V_{ad}^2 \propto n_{surf}(x) \propto \frac{x_{max} - x}{x_{max}} = \gamma(x)$



Prediction of Reaction Energies Based on Adsorption Scaling

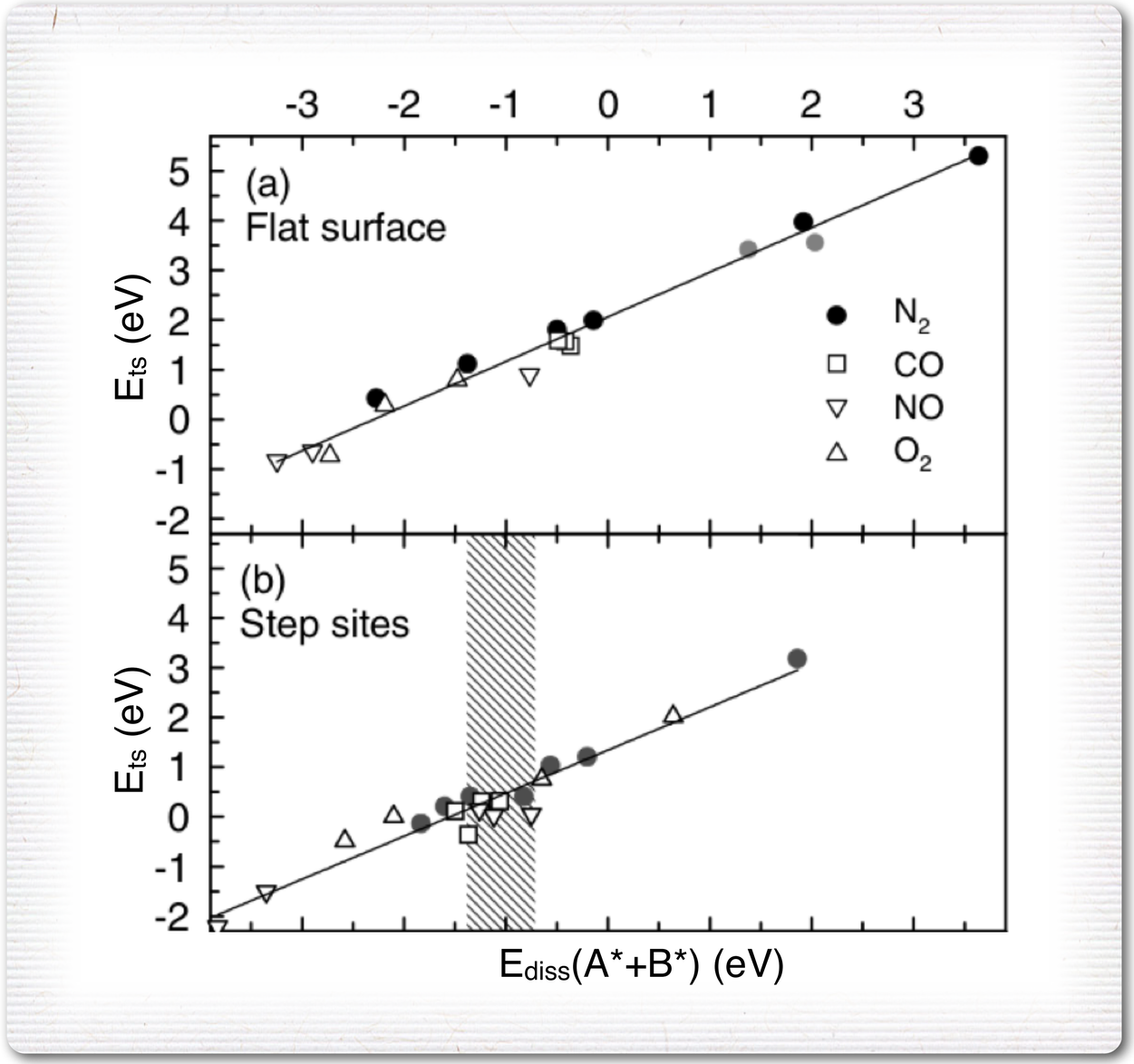
For any (de)hydrogenation reaction of molecules bonding to a TM surface via C, H, O or S atoms estimate the reaction energy ΔE for all TM's just by knowing ΔE for one TM.

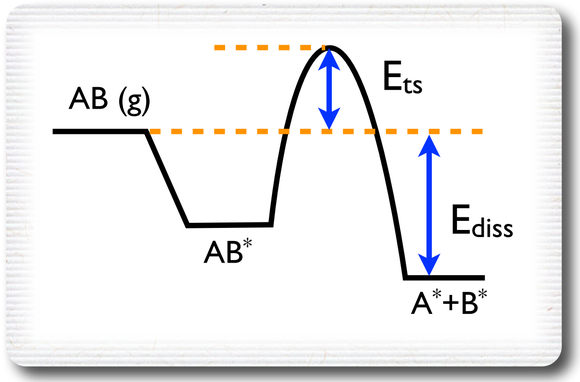
$$\Delta E = \sum_{i=1}^{N} (\gamma_i \Delta E^{A_i}) + \Delta\xi$$



F. Abild-Pedersen, *et al.*, Phys. Rev. Lett. **99**, 016105 (2007).

Reducing Complexity: BEP/Transition State Scaling Relations



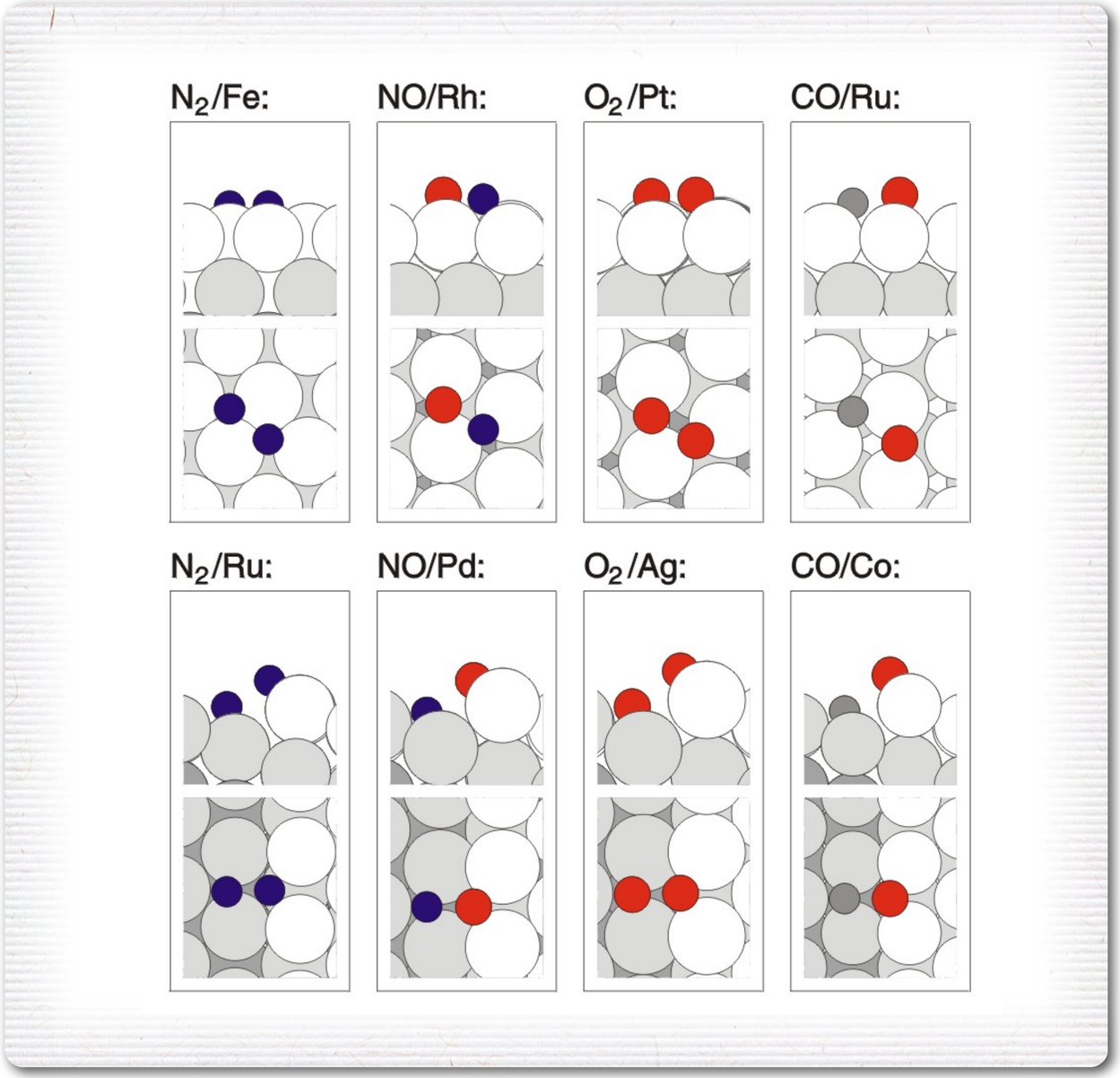


$$E_{\mathrm{ts}} = \gamma \Delta E_{\mathrm{diss}} + \xi$$

Relations are active site dependent

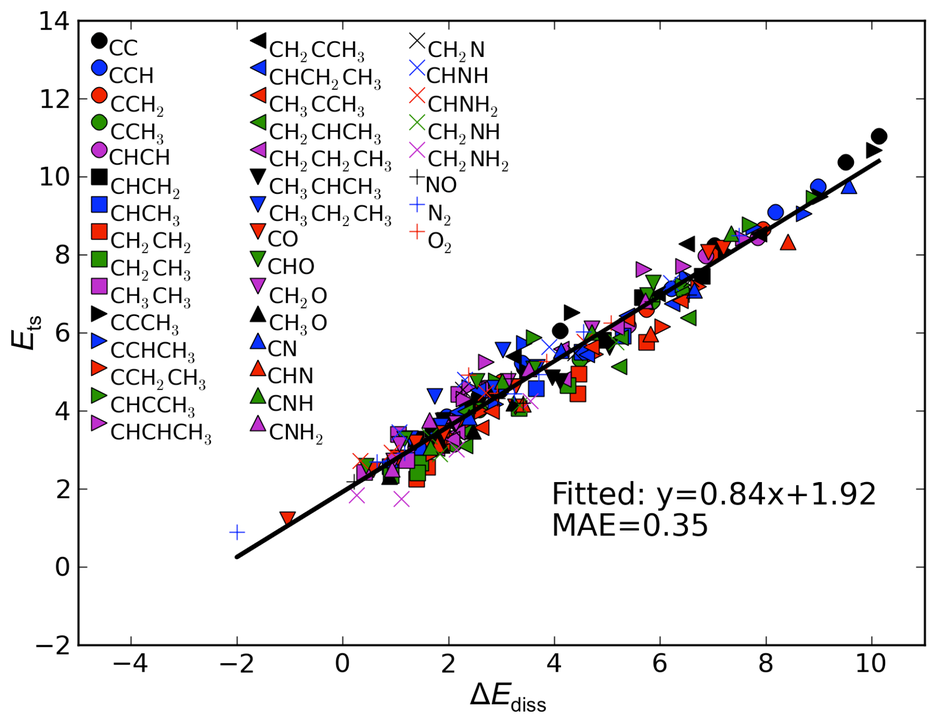
J. K. Nørskov *et al.*, J. Catal. **209**, 275 (2002).

Transition State Structures

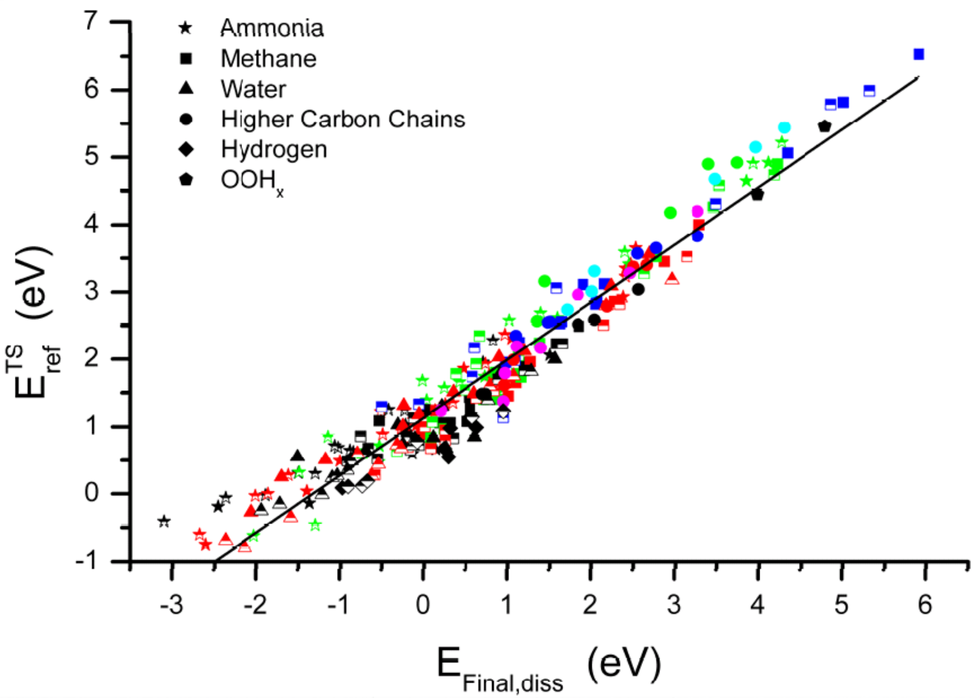


More BEP/Transition State Scaling Relations

C-C, C-O, C-N ... bond breaking



C-H, O-H, N-H ... bond breaking



S. Wang, *et al*, Catal. Lett. **141**, 370 (2011).

S. Wang, *et al*, Phys. Chem. Chem. Phys. **13**, 20760 (2011).

Dealing with Complexity of Ammonia Synthesis

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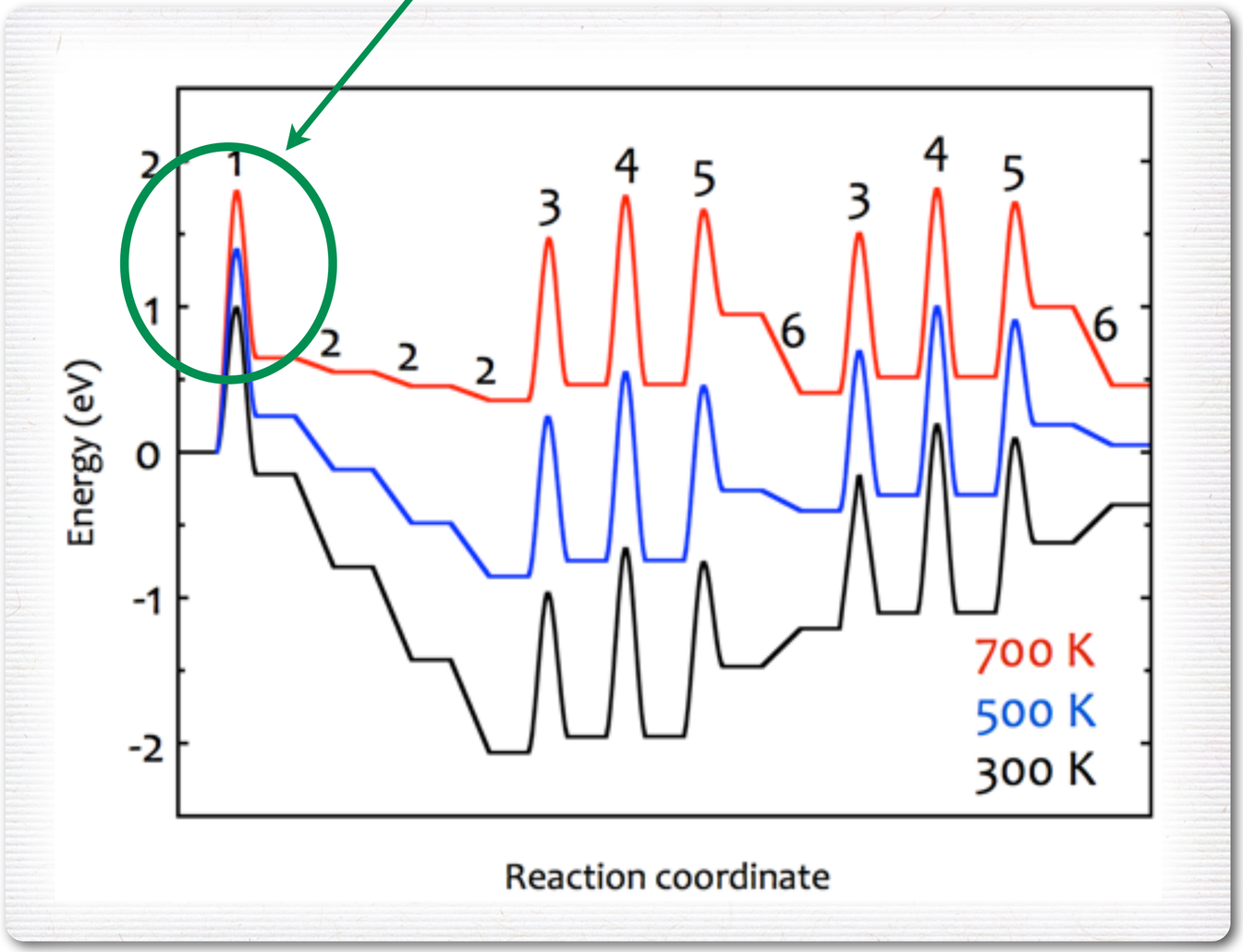
N_2 dissociation is rate determining step



1. $N_2(g) + 2^* \rightleftarrows 2N^*$
2. $H_2(g) + 2^* \rightleftarrows 2H^*$
3. $N^* + H^* \rightleftarrows NH^*$
4. $NH^* + H^* \rightleftarrows NH_2^*$
5. $NH_2^* + H^* \rightleftarrows NH_3^*$
6. $NH_3^* \rightleftarrows NH_3(g)$

+ $N_2(g) \rightleftarrows N_2^*$

- How many energetic variables are there?

6 intermediates

+

6 transition states

=

12 different energy parameters

Dissociation of A_2 is Rate Determining Step

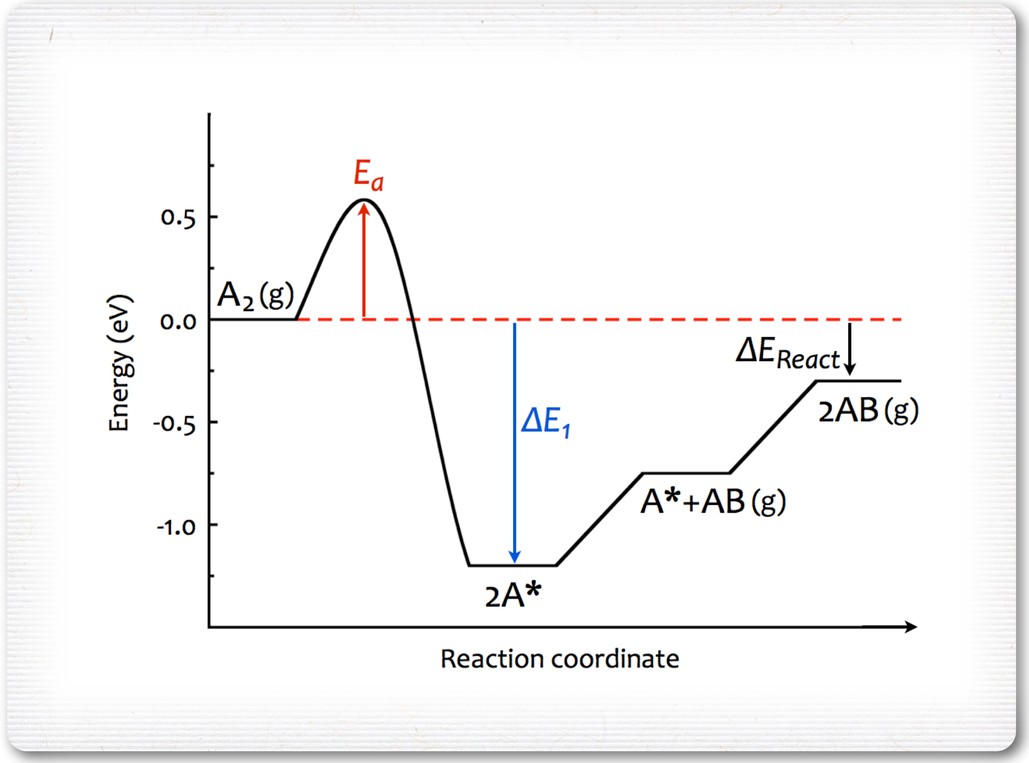
$$R(T,p) = k_1 p_{A_2} \theta_*^2 (1-\gamma)$$

$$k_1 = \frac{k_B T}{h} e^{-\Delta S_a / k_B} e^{-E_a / k_B T}$$

$$\gamma = \frac{p_{AB}^2}{K_{eq} p_{A_2} p_B^2}$$

$$\theta_* = \frac{1}{1 + \sqrt{K_1 p_{A_2} \gamma}}$$

$$K_1 = e^{-\Delta G_1^\circ / k_B T}$$



Invoke BEP relations

$$E_{a_1} = \gamma \Delta E_1 + \xi \equiv E_a(2E_N)$$

$$R(T,p) = k_1 p_{A_2} \theta_*^2 (1-\gamma)$$

$$k_1 = \frac{k_B T}{h} e^{-\Delta S_a / k_B} e^{-E_a / k_B T} = k_1(\Delta E_1)$$

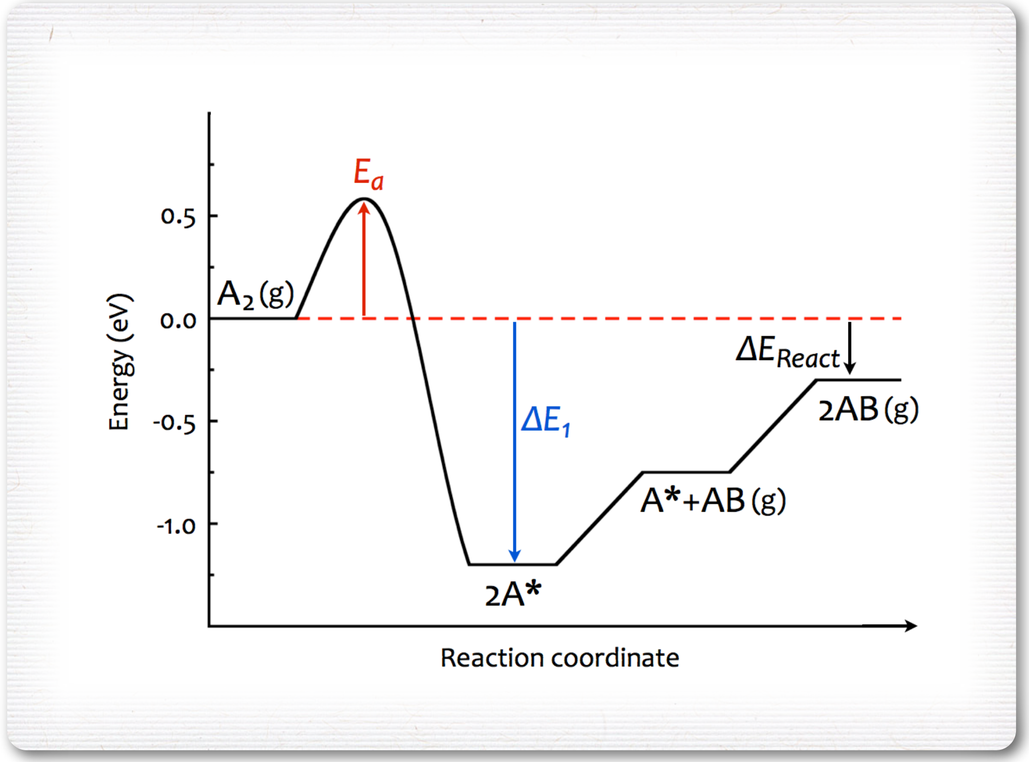
$$\gamma = \frac{p_{AB}^2}{K_{eq} p_{A_2} p_B^2}$$

$$\theta_* = \frac{1}{1 + \sqrt{K_1 p_{A_2} \gamma}}$$

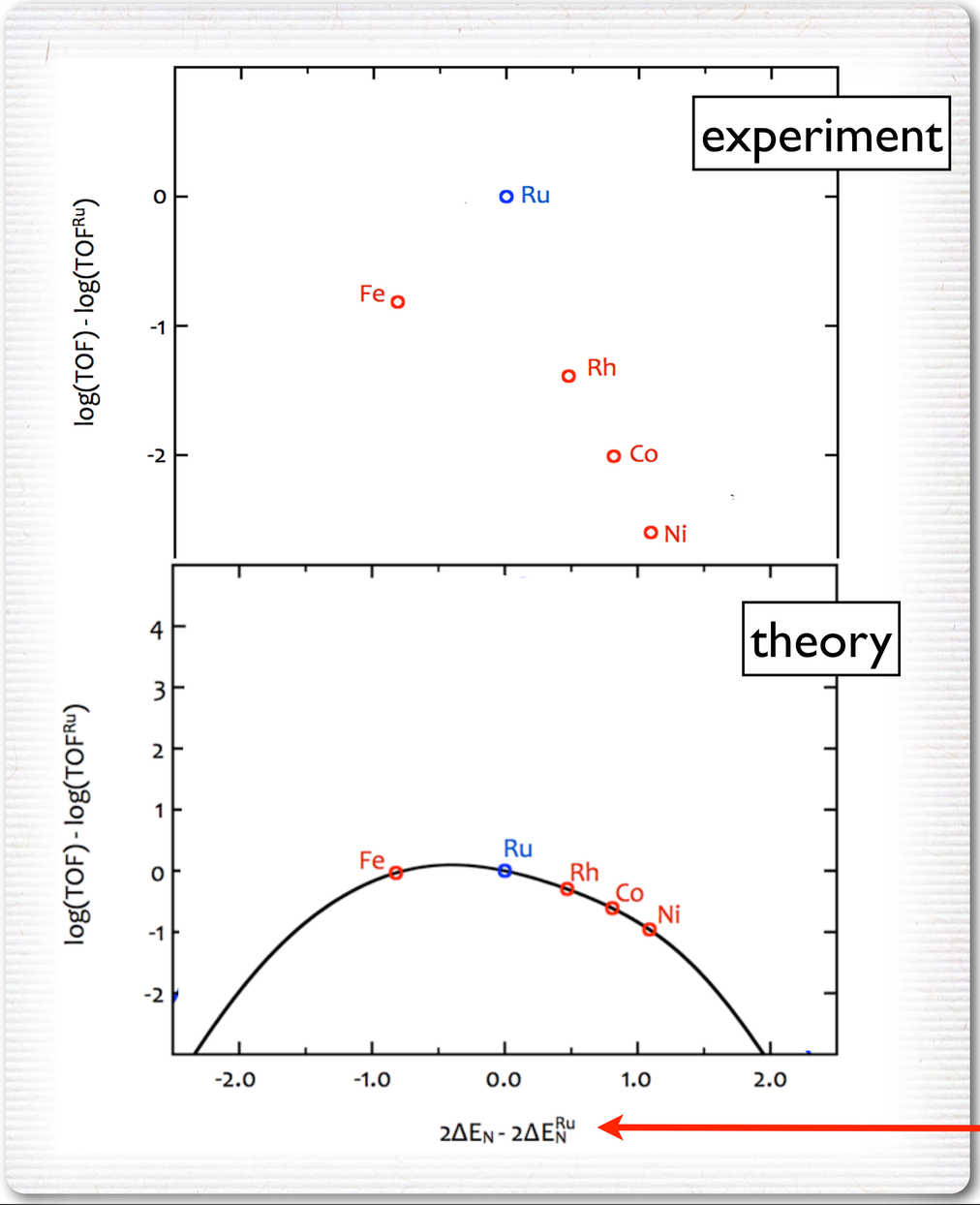
$$K_1 = e^{-\Delta G_1^\circ / k_B T} = K_1(\Delta E_1)$$

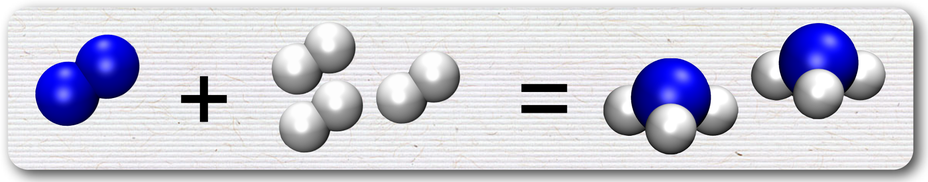
descriptor

$$\Delta E_1 = 2E_N$$



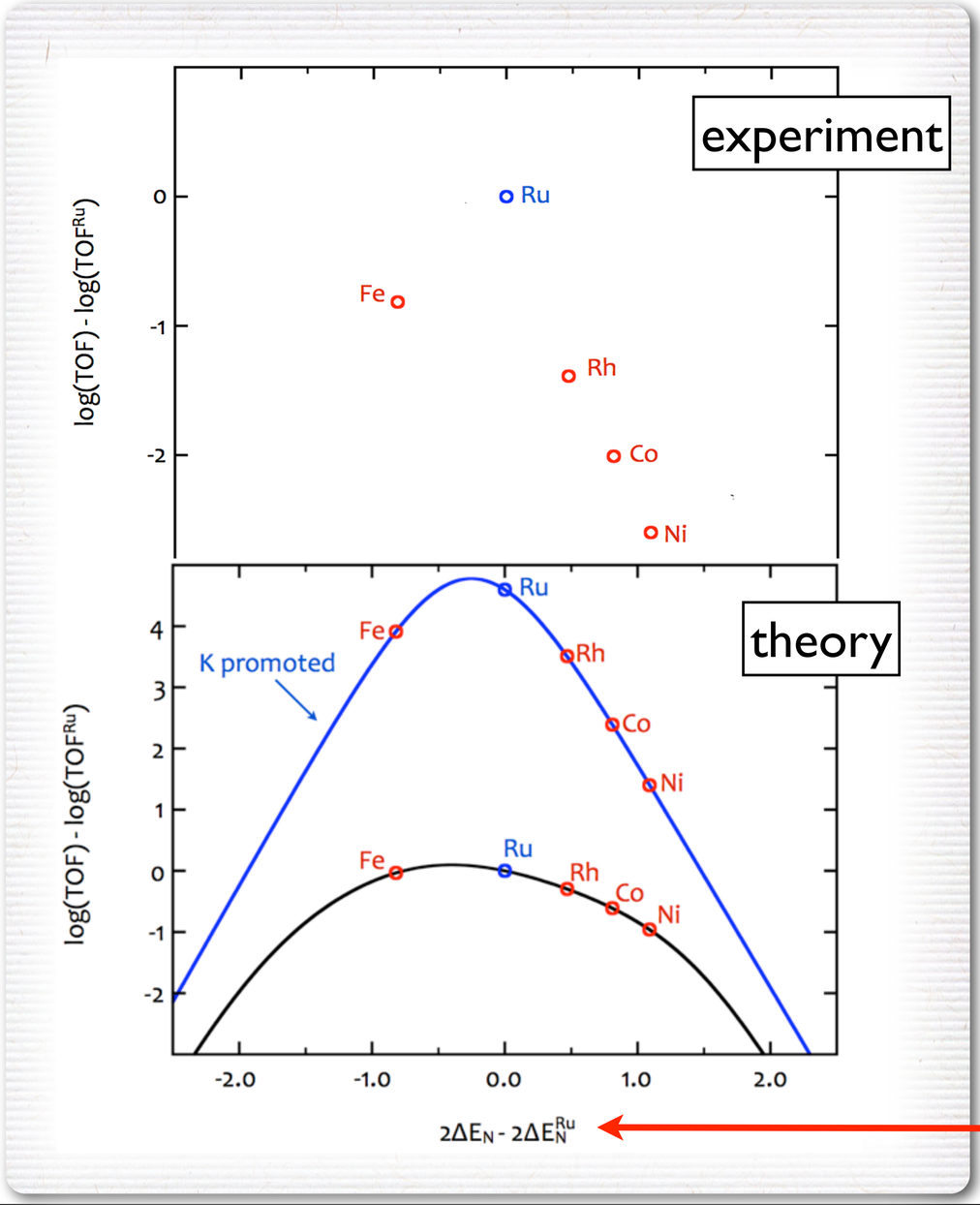
Volcano for Ammonia Synthesis

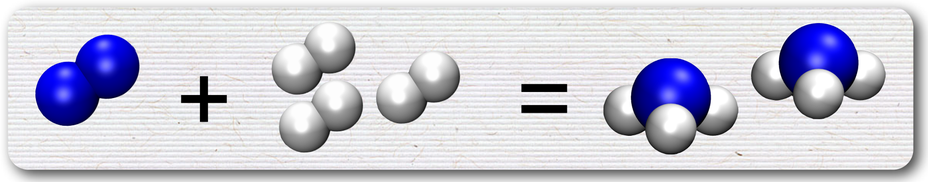




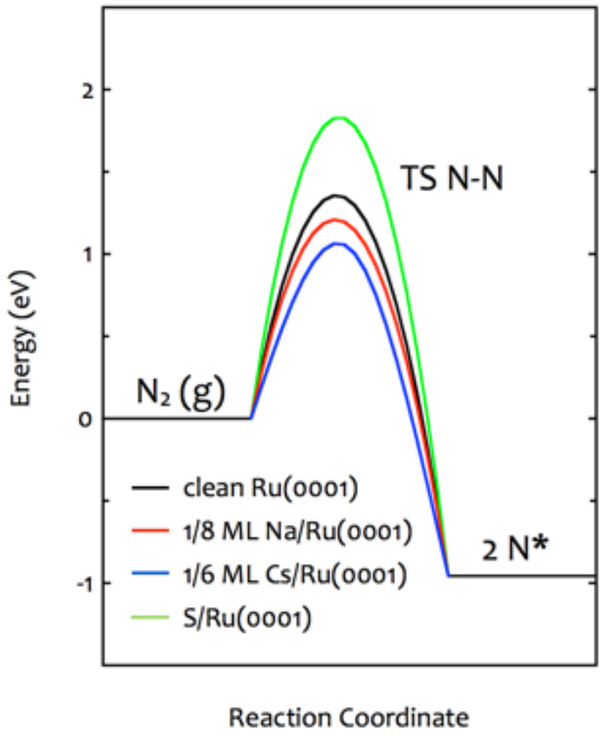
Descriptor $\Delta E_1 = 2E_N$

Volcano for Ammonia Synthesis



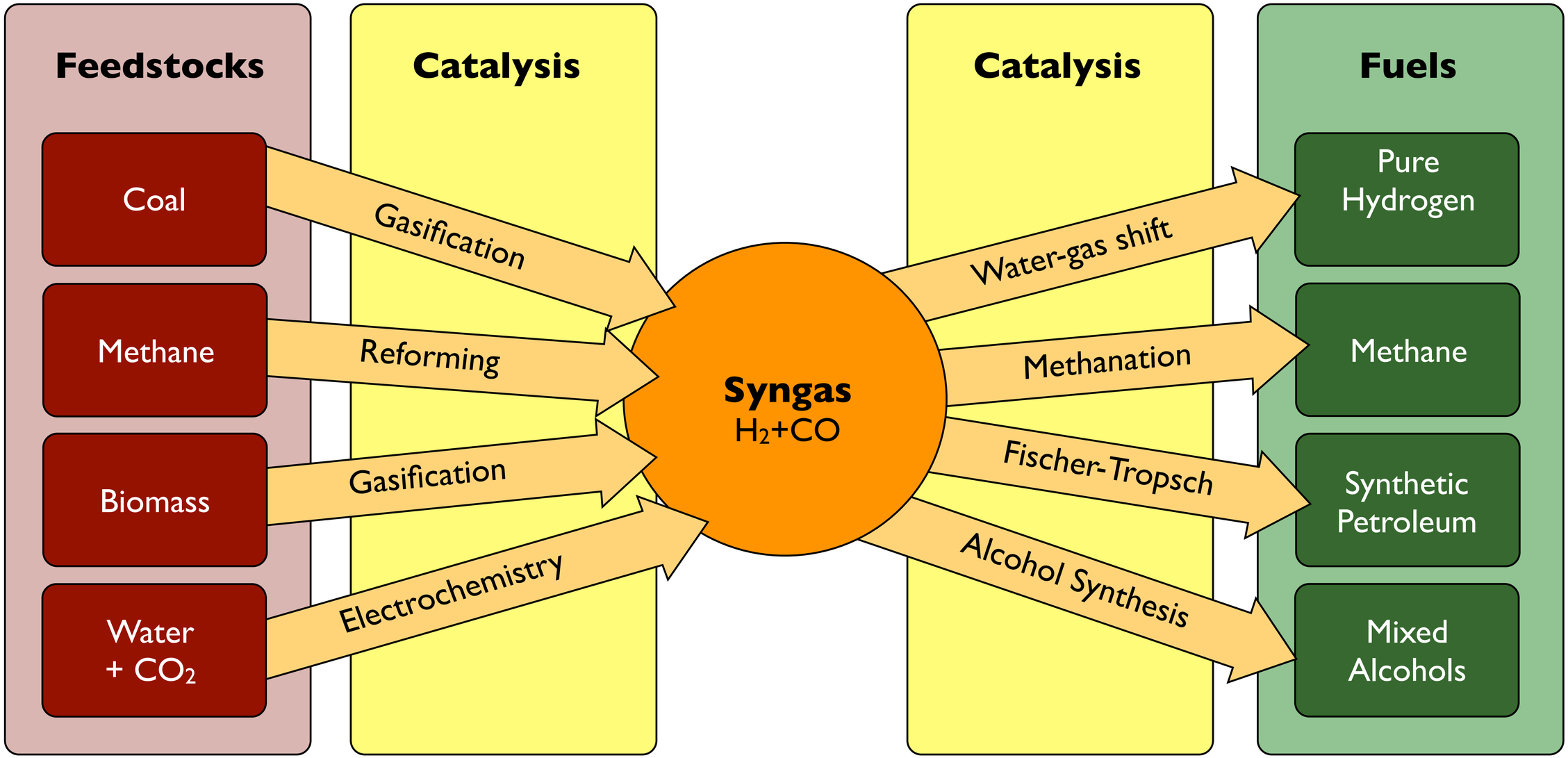


effect of alkali promotion



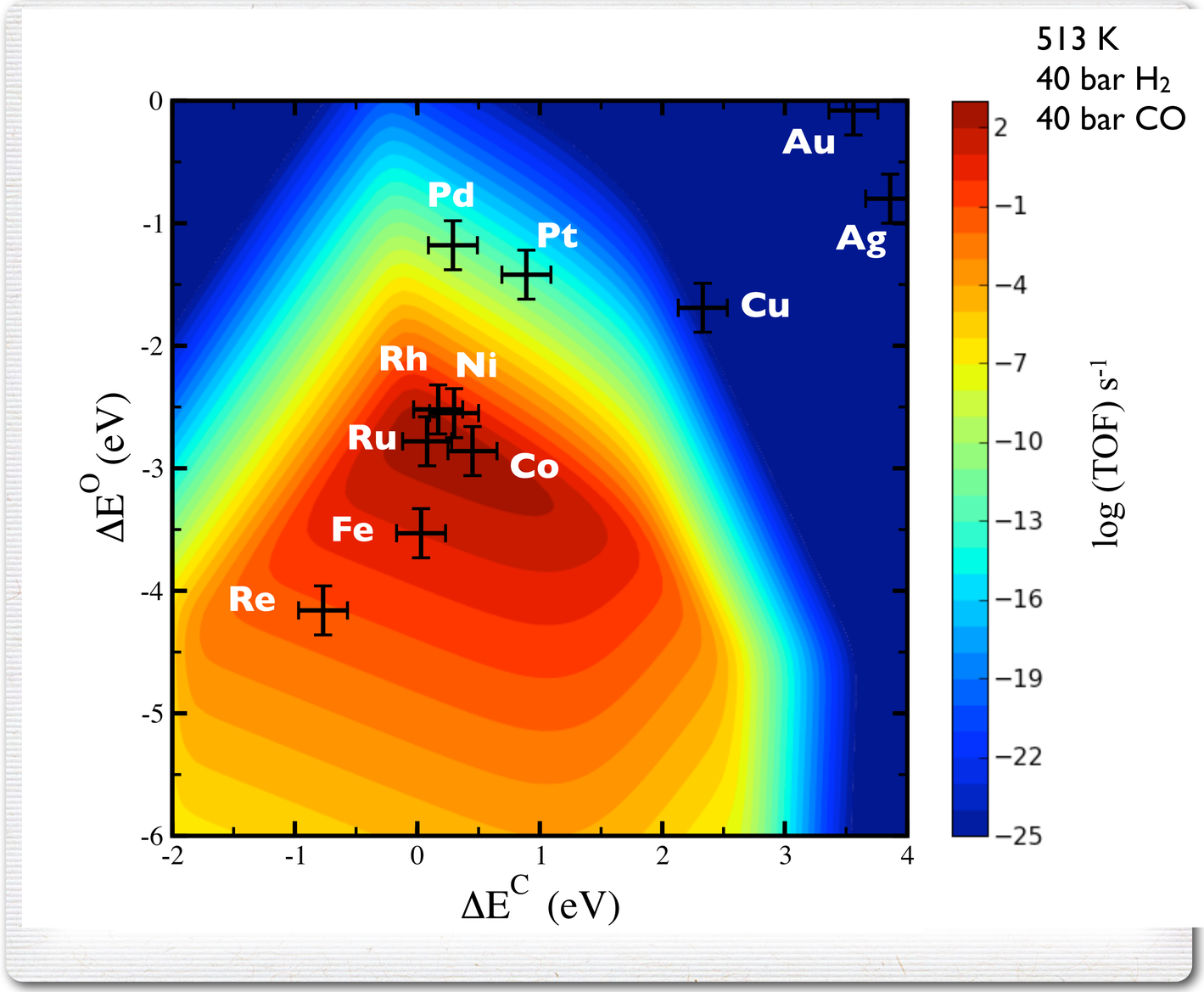
Descriptor $\Delta E_1 = 2E_N$

Motivation: Syngas Conversion

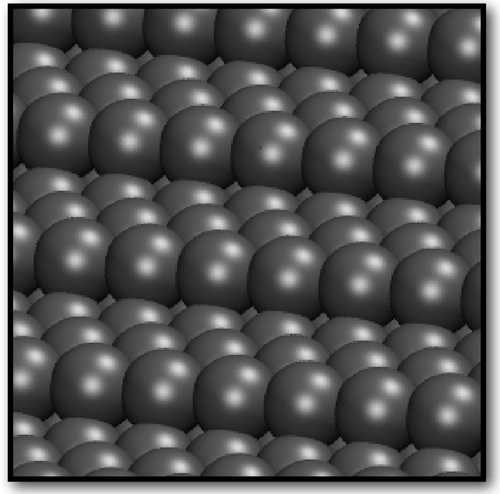


"Anything can be gasified"

Methanation Volcano ($CO+3H_2 \Rightarrow CH_4+H_2O$)



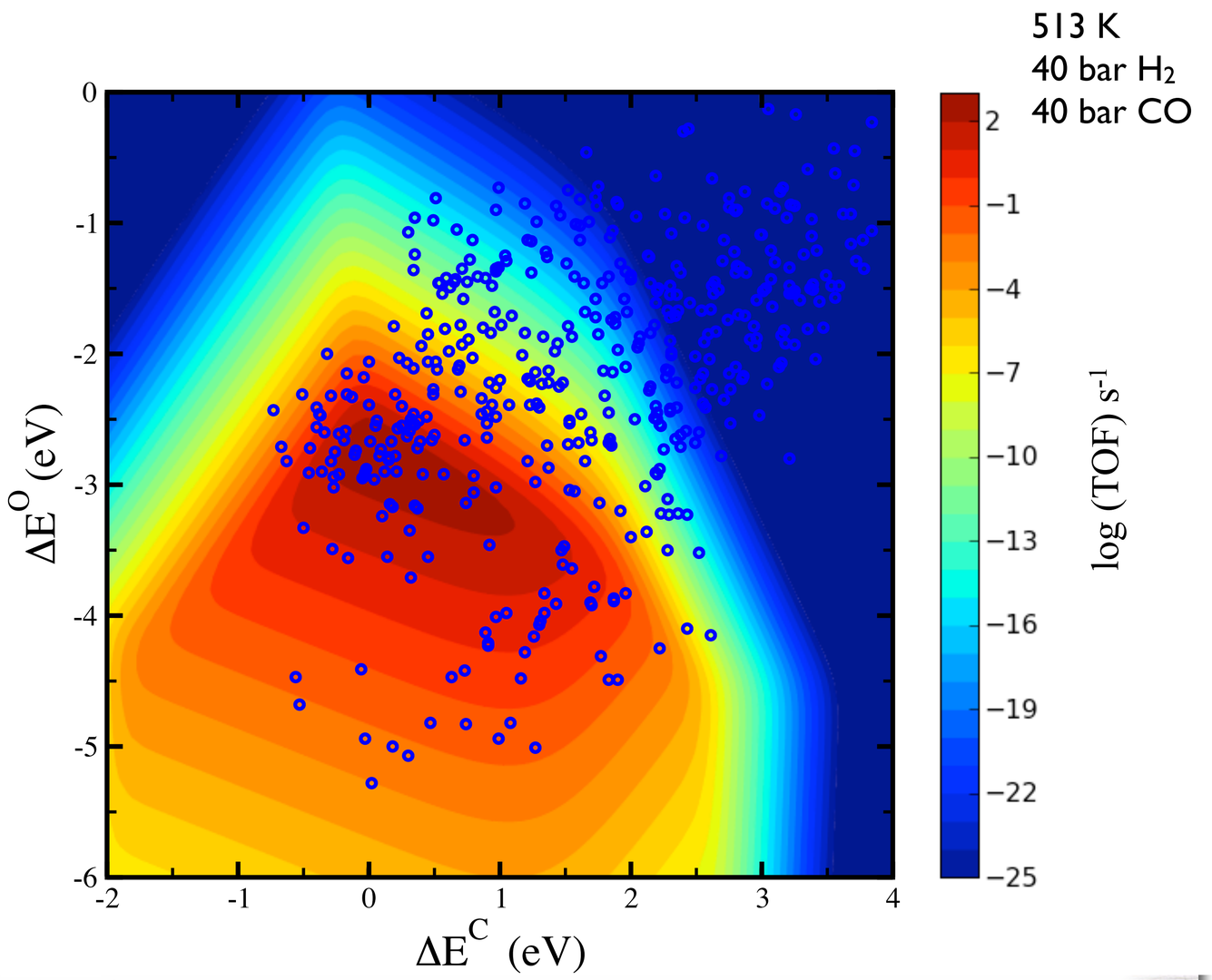
211 monometallic surface



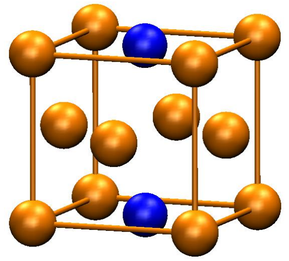
- C & O adsorption energies are descriptors
- CO dissociation = RDS
- Ru, Co highest activity
- Rh, Ni, Fe also have high activity

J. K. Nørskov, *et. al.* Proc. Nat. Acad. Sci. USA **108**, 937 (2011).

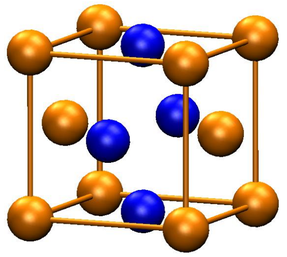
Finding Methanation Catalyst Leads



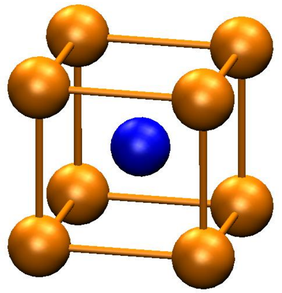
211 bimetallic surfaces



A_3B L_{12}



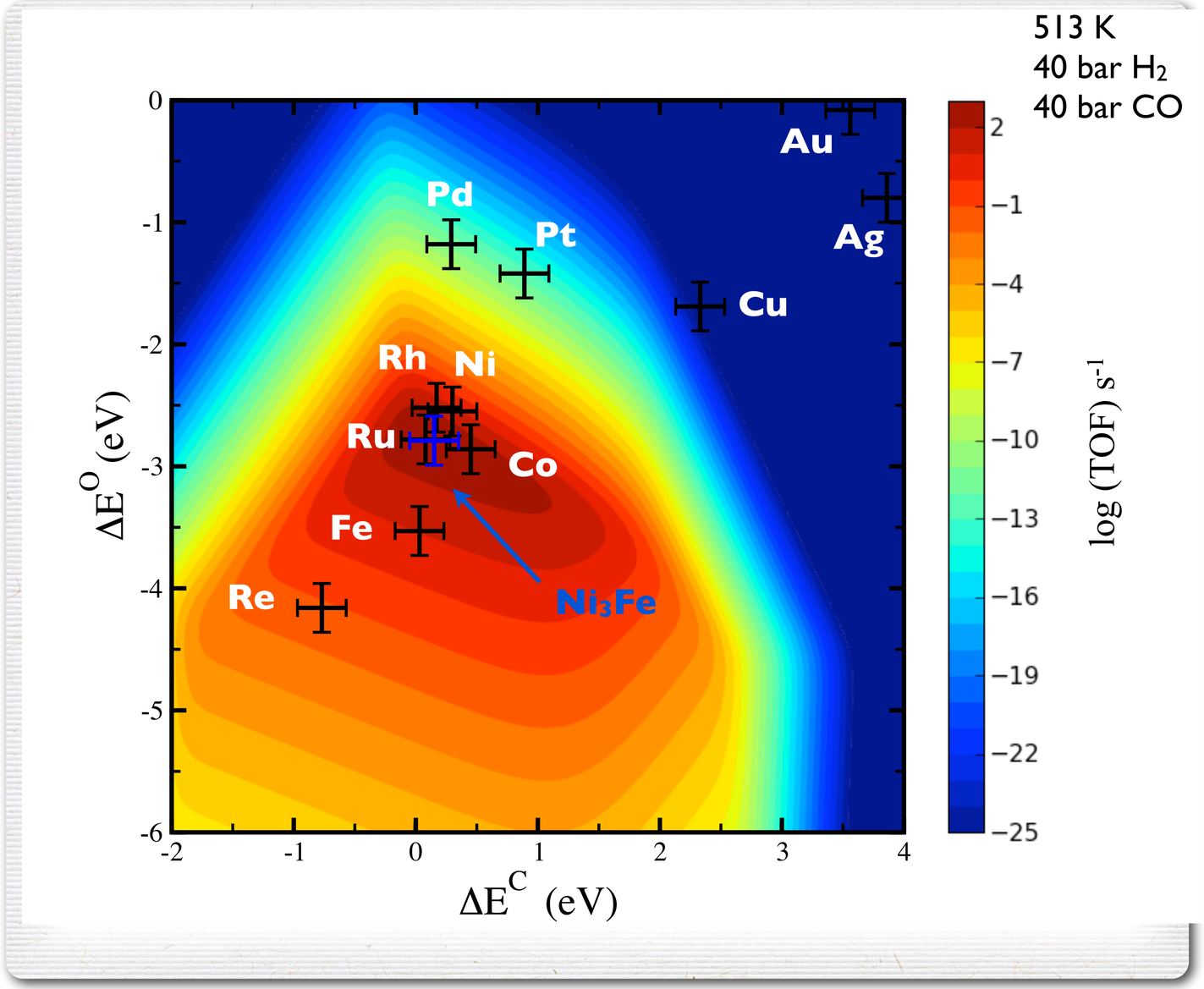
A_5B_3 L_{10}



AB BCC-B_2

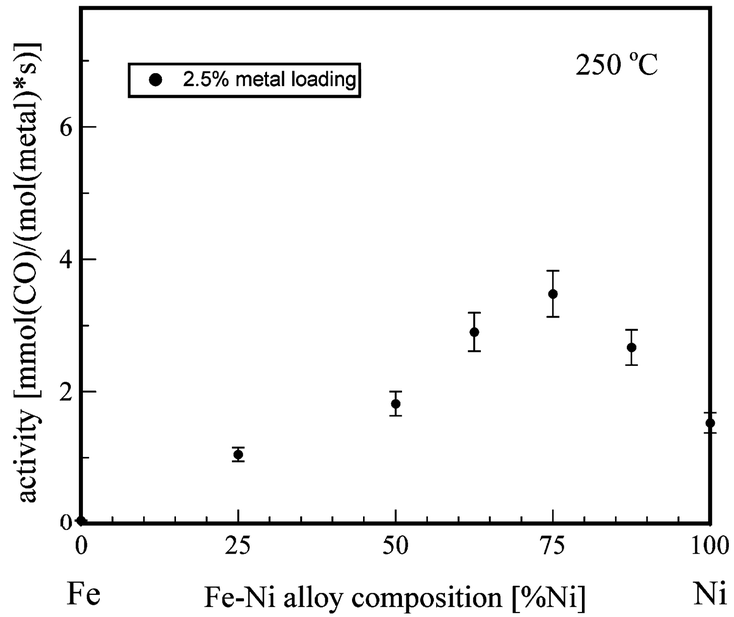
screening of 4400 systems

Identification of Ni_3Fe as Methanation Catalyst



J. K. Nørskov, *et. al.* Proc. Nat. Acad. Sci. USA **108**, 937 (2011).

Screening + Paretto analysis => Ni_3Fe



M. Andersson, *et. al.* J. Catal. **239**, 501 (2006).

The Industrial $Cu/ZnO/Al_2O_3$ Methanol Catalyst

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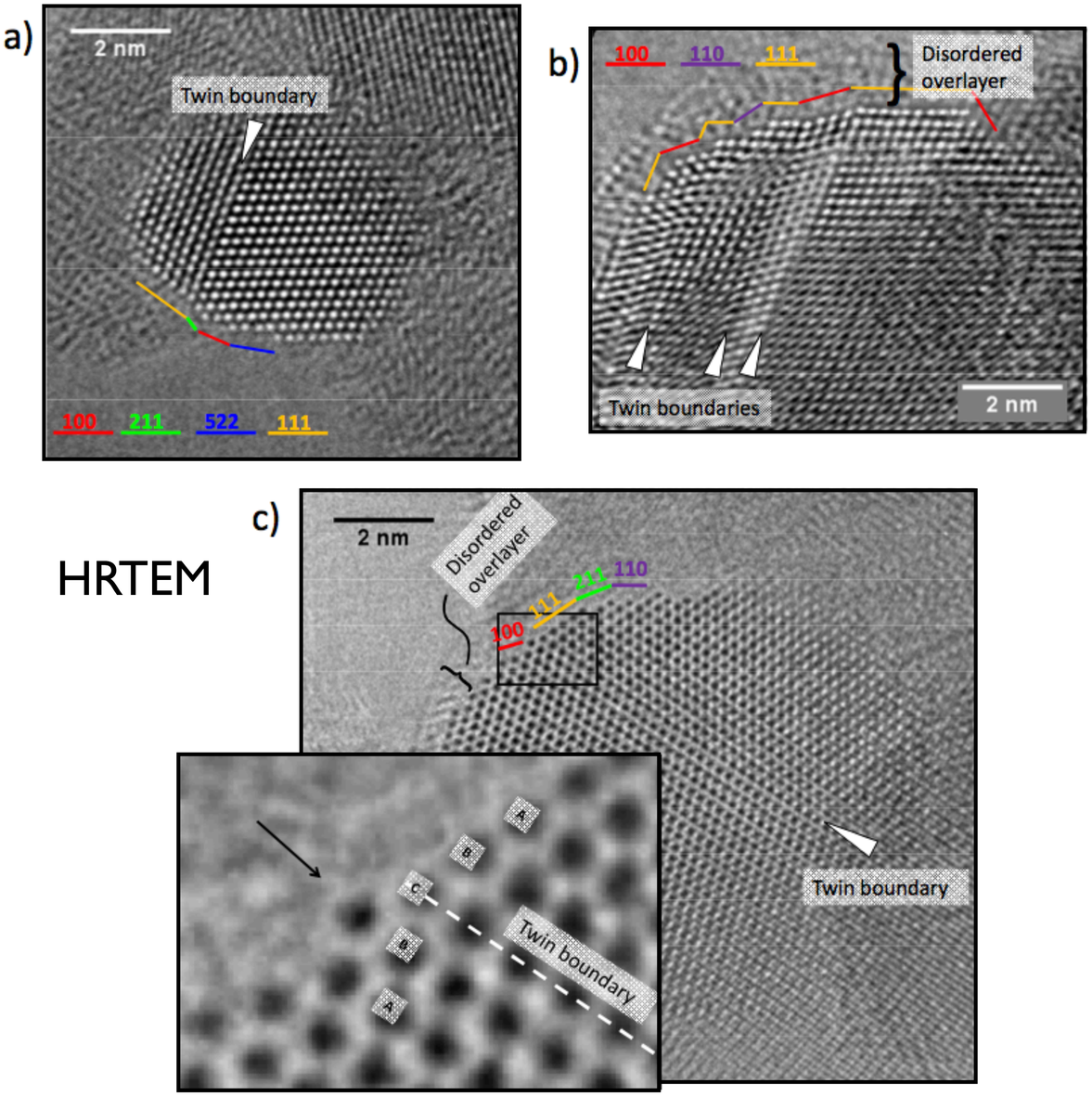
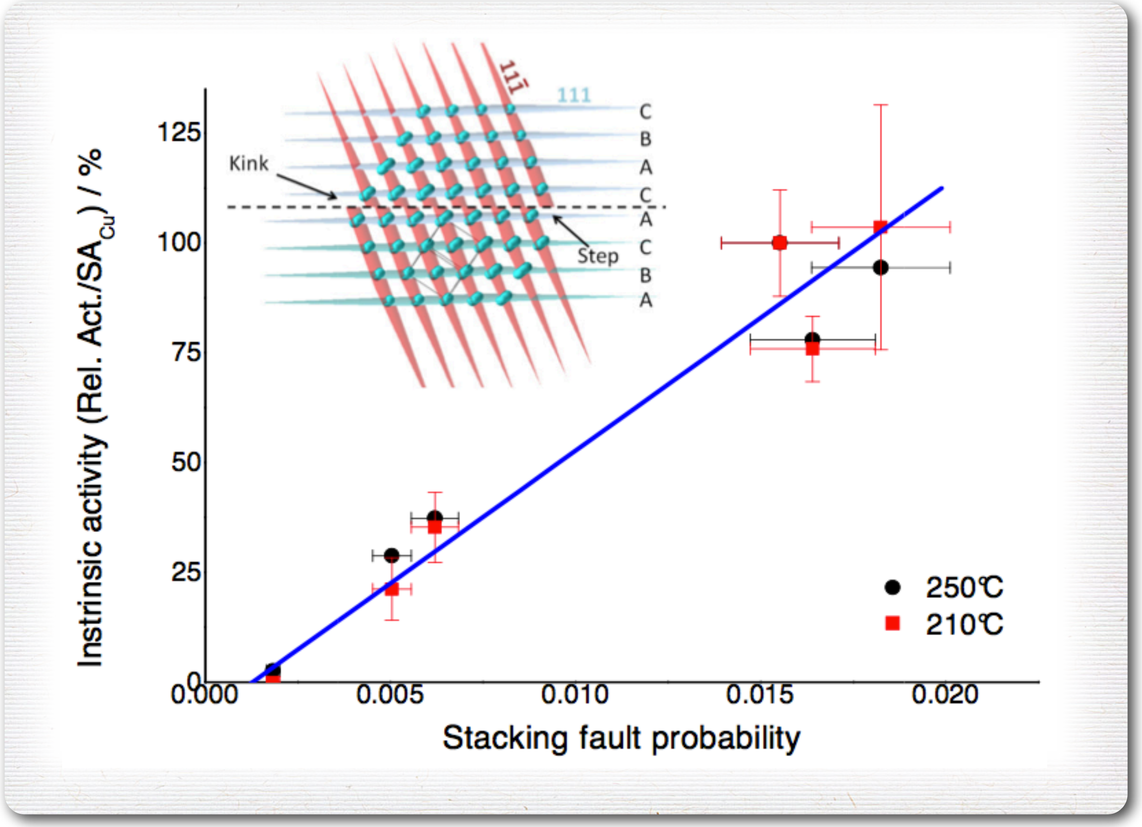
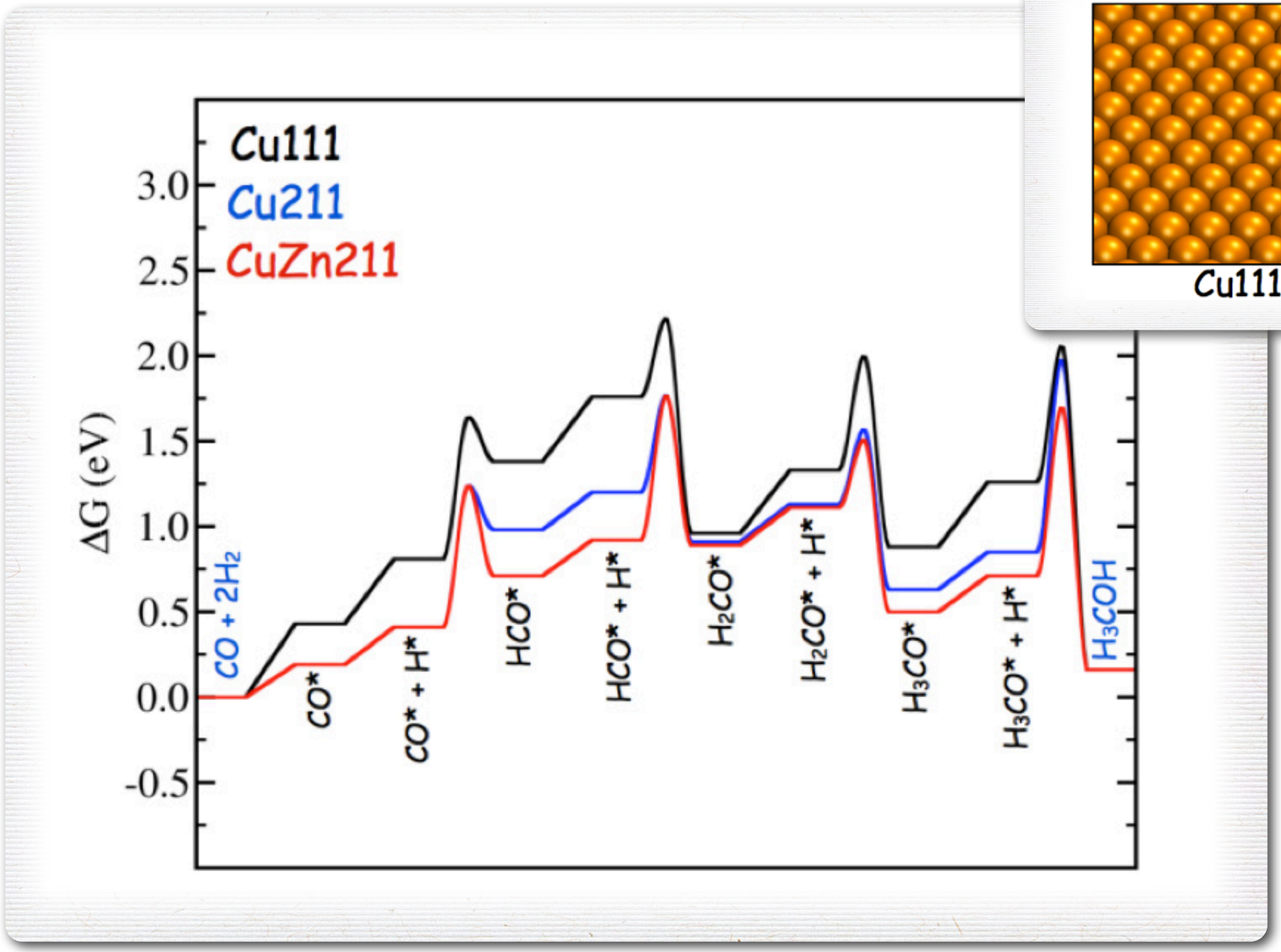


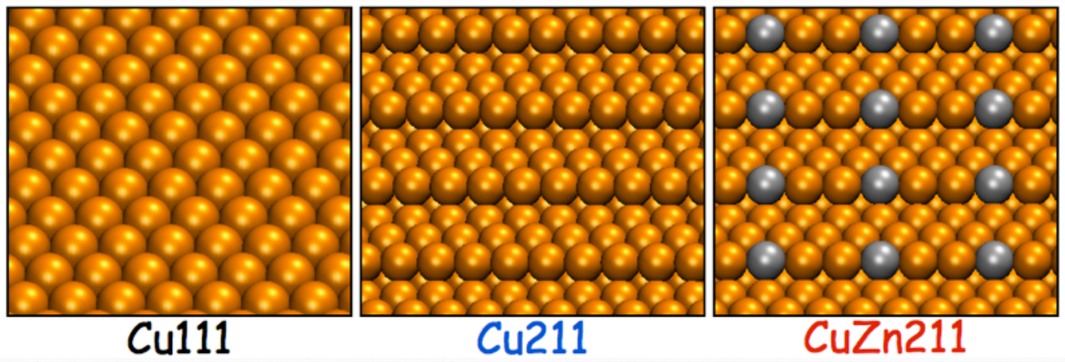


- no correlation btw Cu surface area and activity
- only Cu has low activity => need ZnO
- stacking faults => surface defects (steps/kinks ...)
- correlation btw amount of defects and activity

M. Behrens, *et. al.* Science **336**, 893 (2012).

Reaction Path for CO + 2H_2 => H_3COH

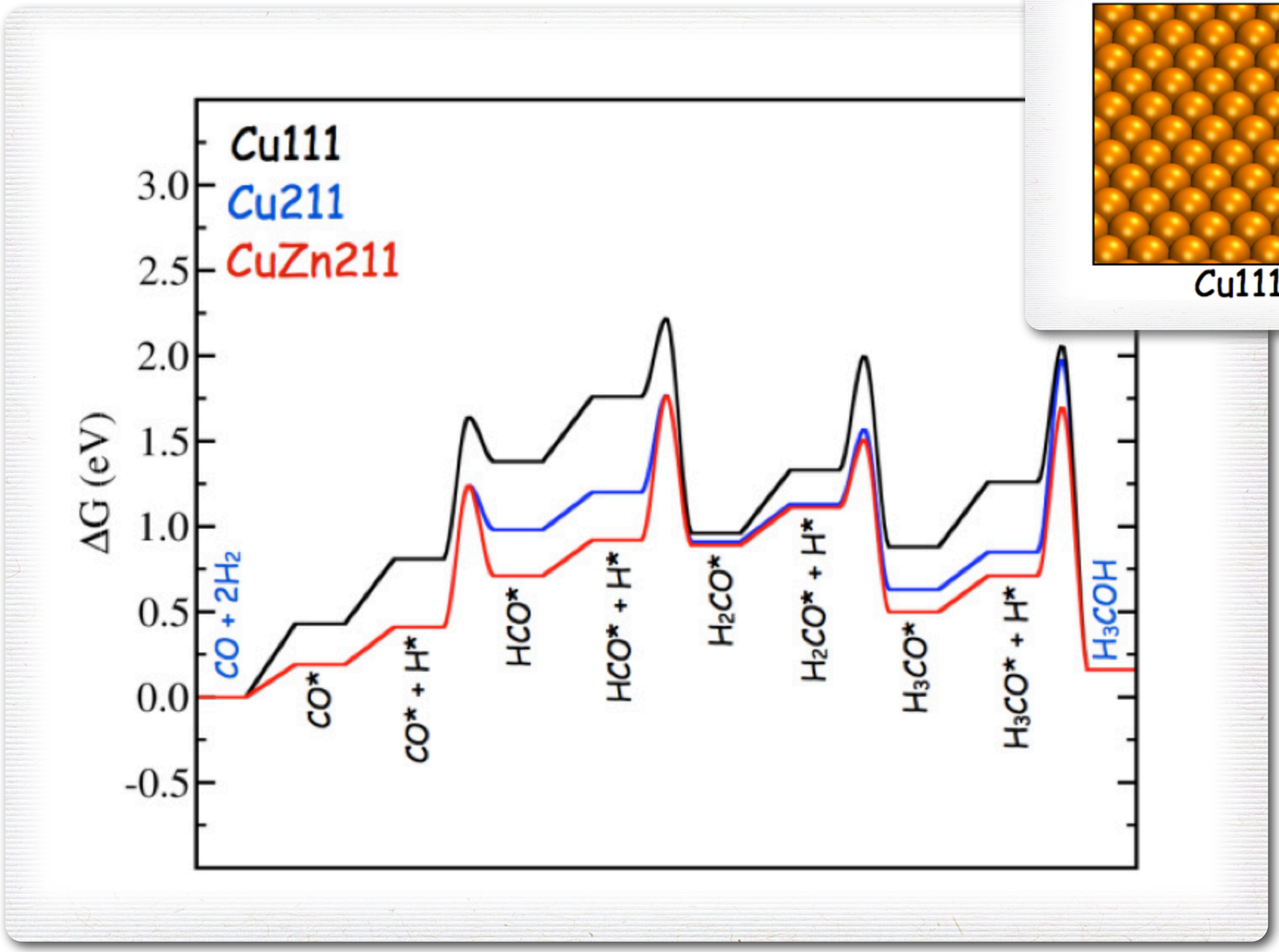


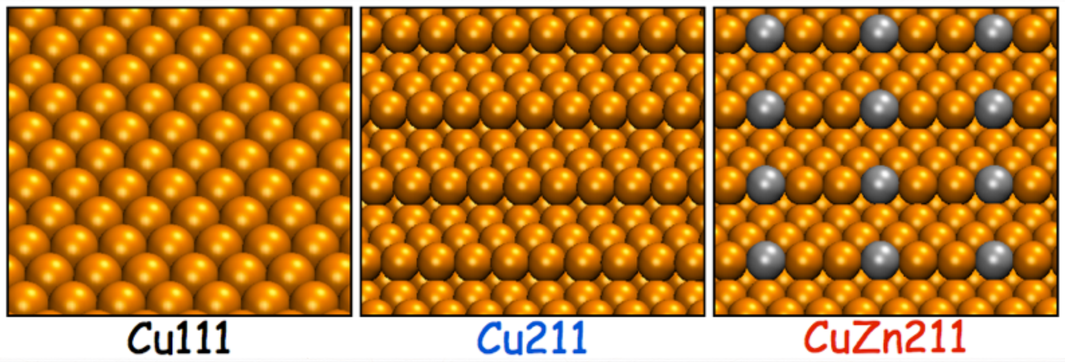


order of activity
CuZn(211) > Cu(211) > Cu(111).

M. Behrens, *et. al.* Science **336**, 893 (2012).

Reaction Path for CO + 2H_2 => H_3COH





order of activity
CuZn(211) > Cu(211) > Cu(111).

Extend to other metal surfaces => correlations

M. Behrens, *et. al.* Science **336**, 893 (2012).

Scaling Relations for CO Hydrogenation

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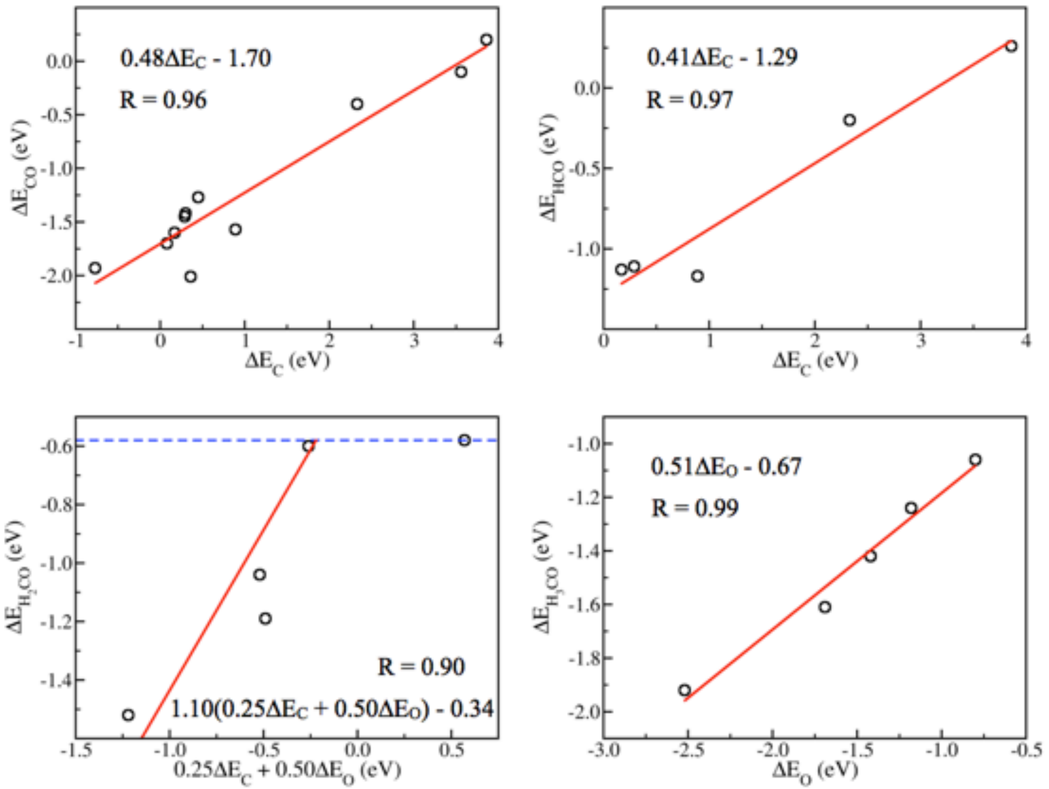
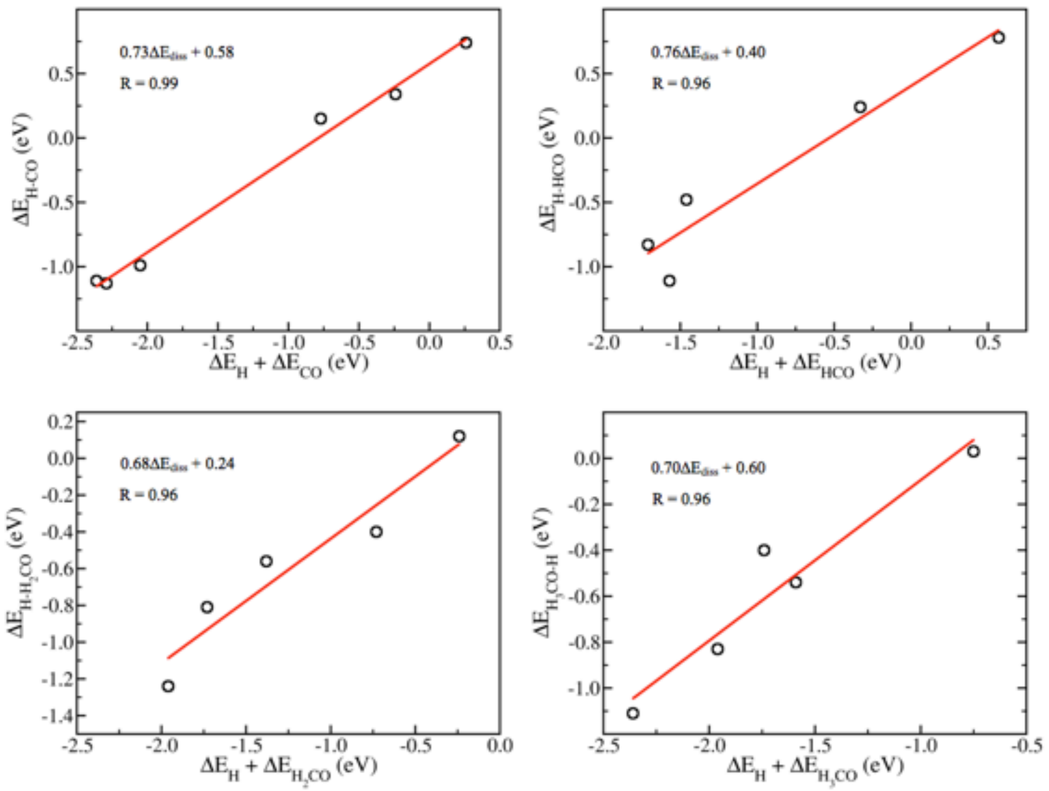
adsorption energies



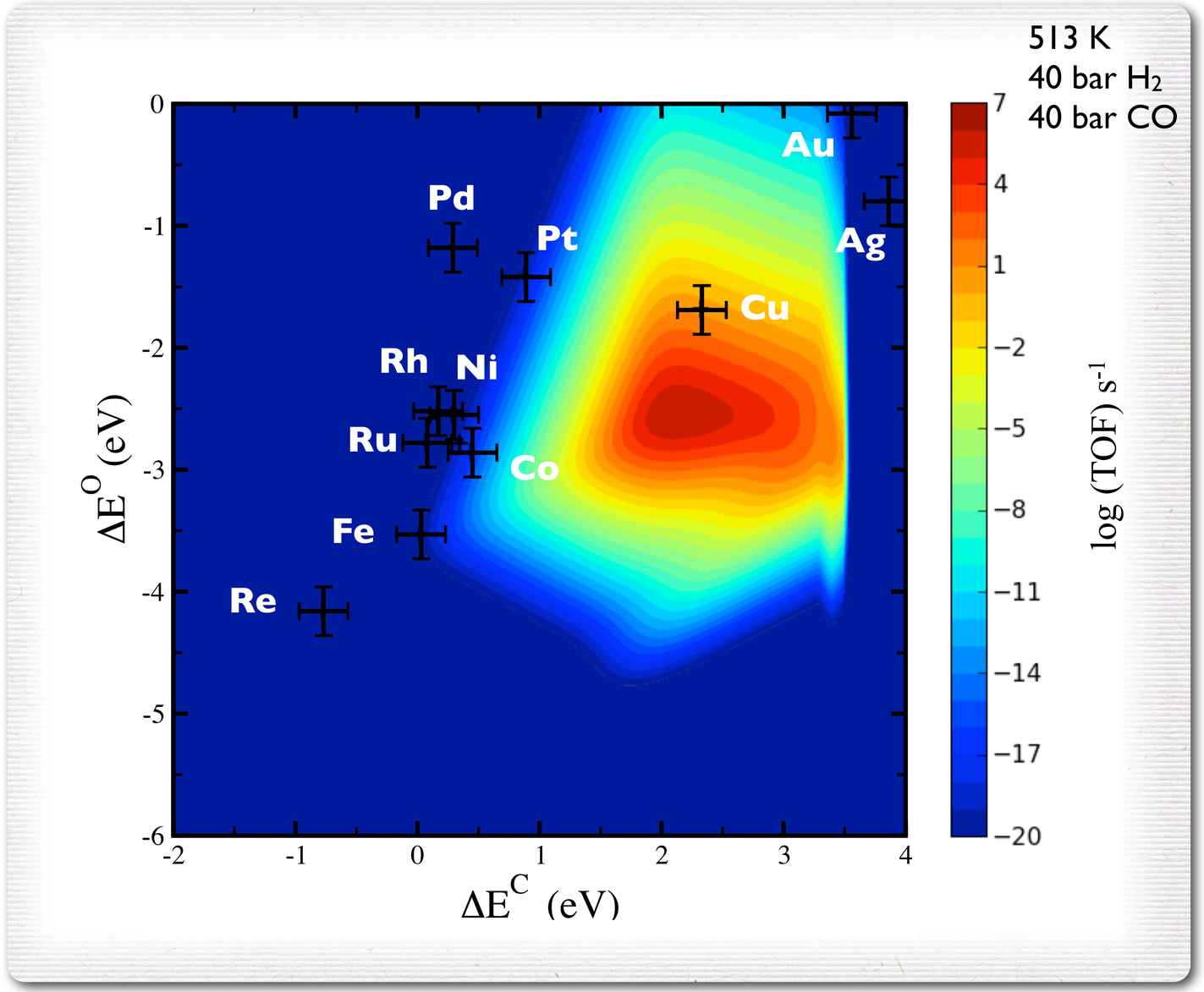
transition state energies



C & O adsorption energies only descriptors

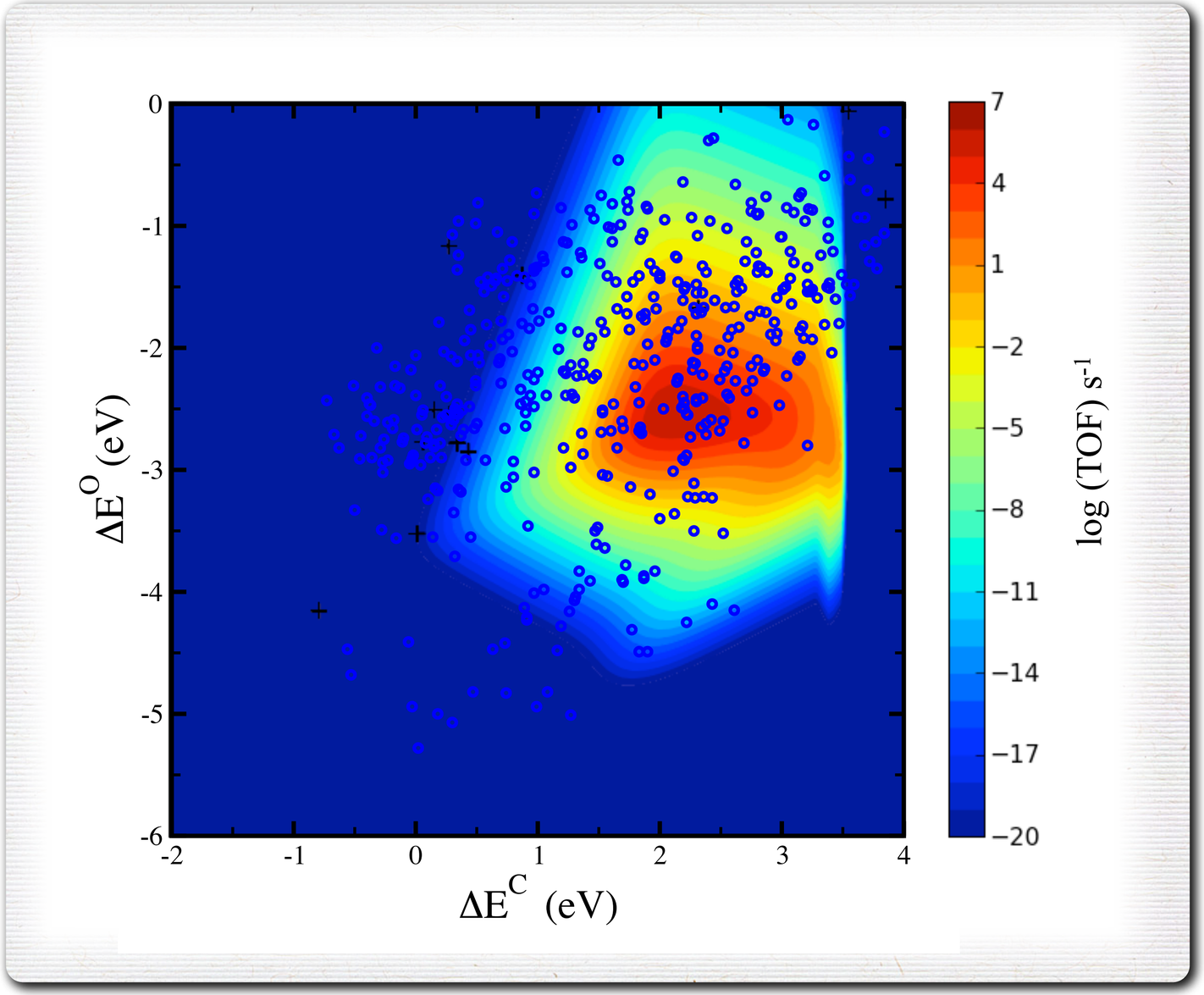
F. Studt, *et. al.* J. Catal. **293**, 51 (2012).

Methanol Volcano ($CO + 2H_2 \Rightarrow CH_3OH$)



F. Studt, *et. al.* J. Catal. **293**, 51 (2012).

Finding Methanol Catalyst Leads



- same data points as for methanation
- screening can be reused for many reactions

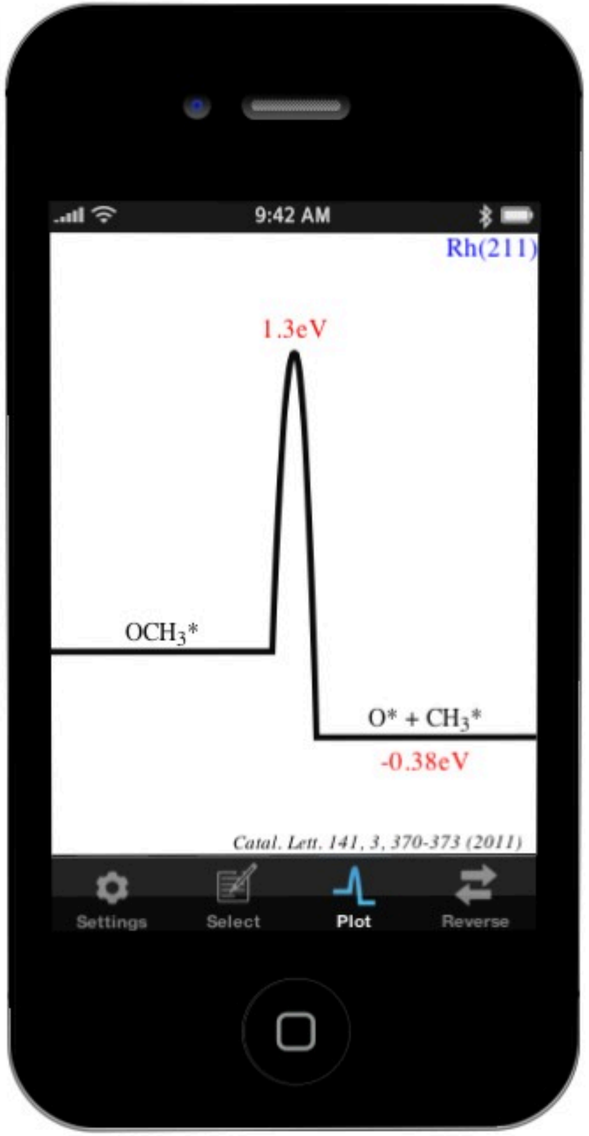
↓

Database

SUNCAT

http://suncat.stanford.edu/catapp/

- ~1500 DFT calculated adsorption and activation energies
- Published data
- Consistent sets of results
- Free web application tool
- Runs in any modern web browser without plug-ins



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CatApp Publication

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http://suncat.stanford.edu/catapp/

Angewandte And Finally

Web Applications

DOI: 10.1002/anie.201107947

CatApp: A Web Application for Surface Chemistry and Heterogeneous Catalysis**

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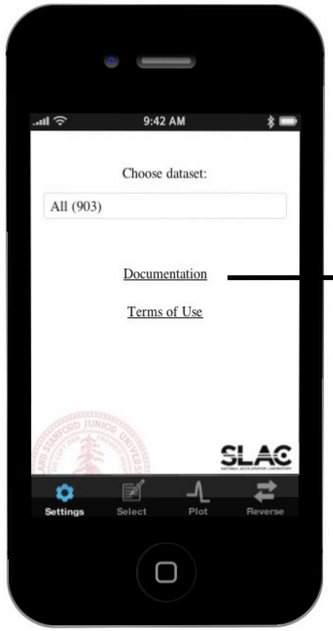
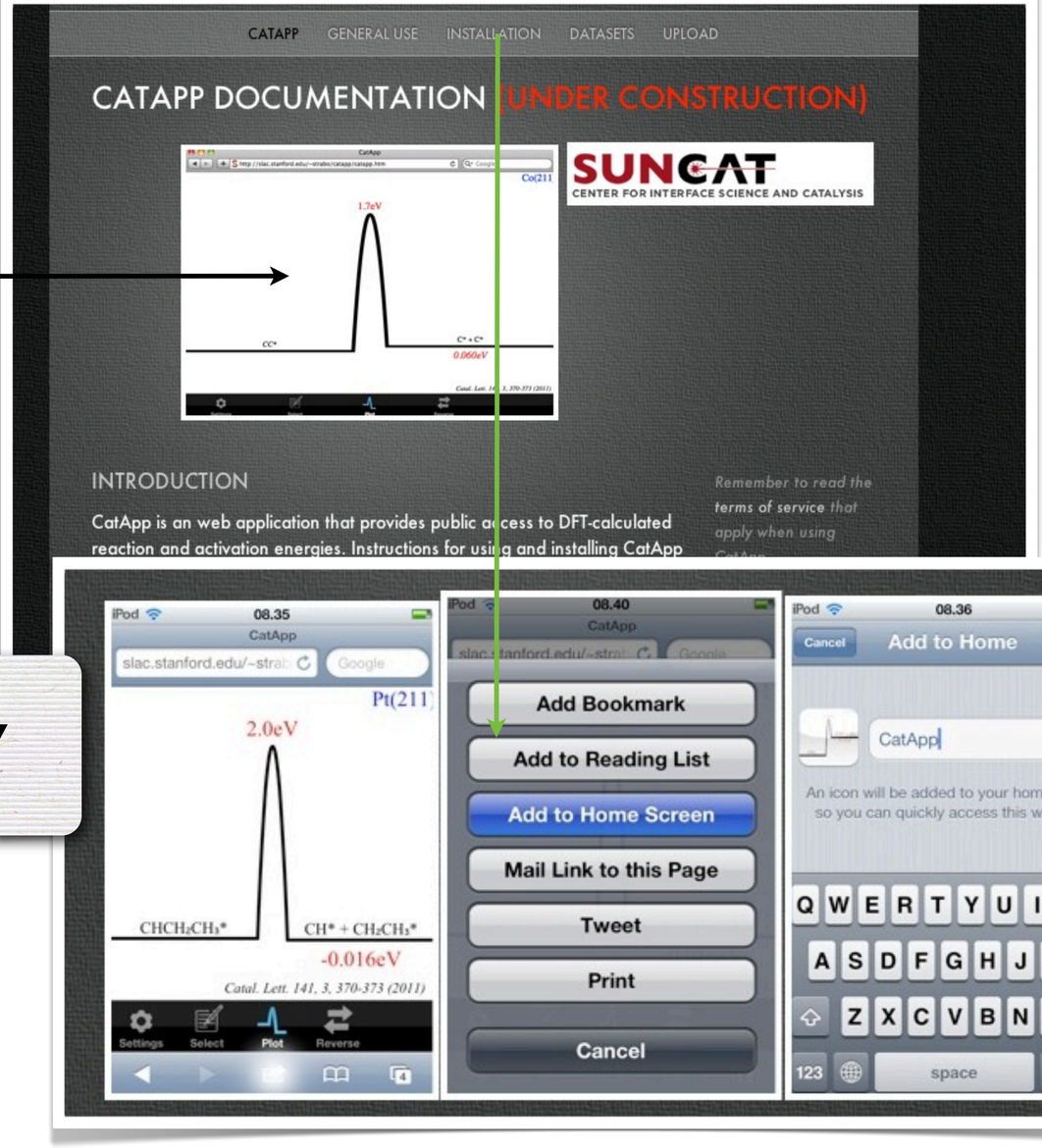
CatApp Installation





http://suncat.stanford.edu/catapp/

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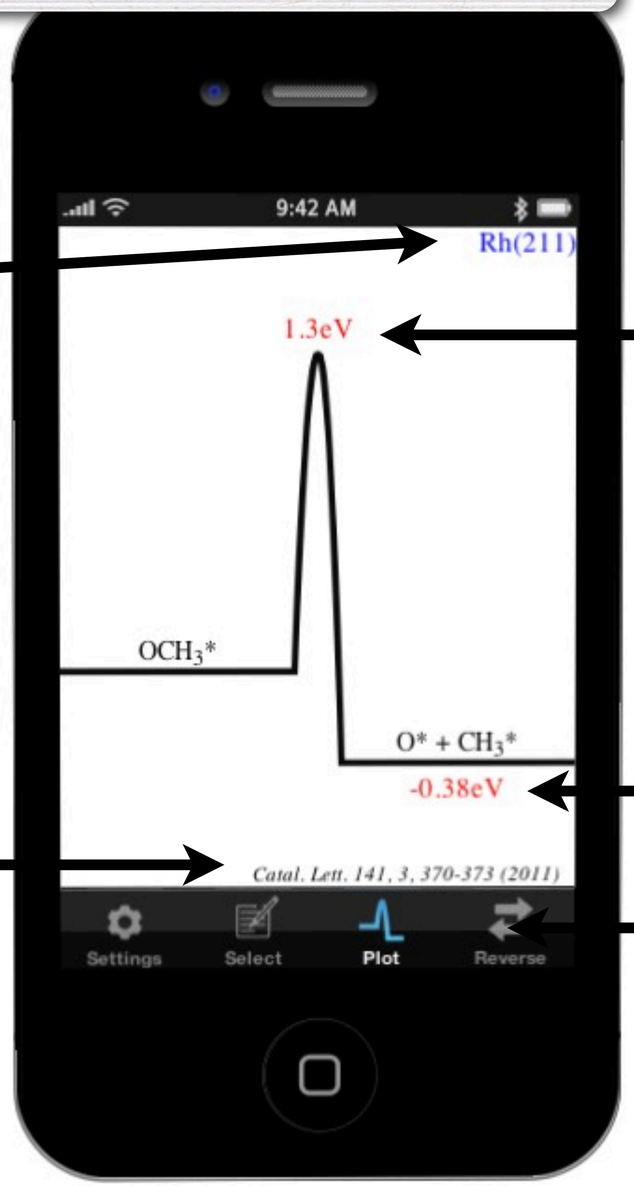


Change surface

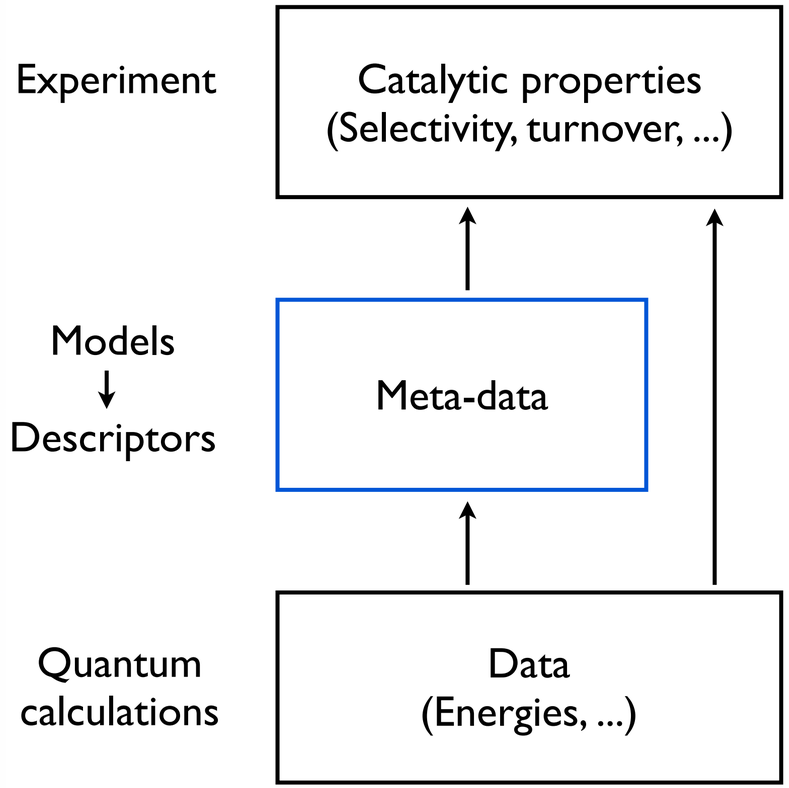
Activation energy

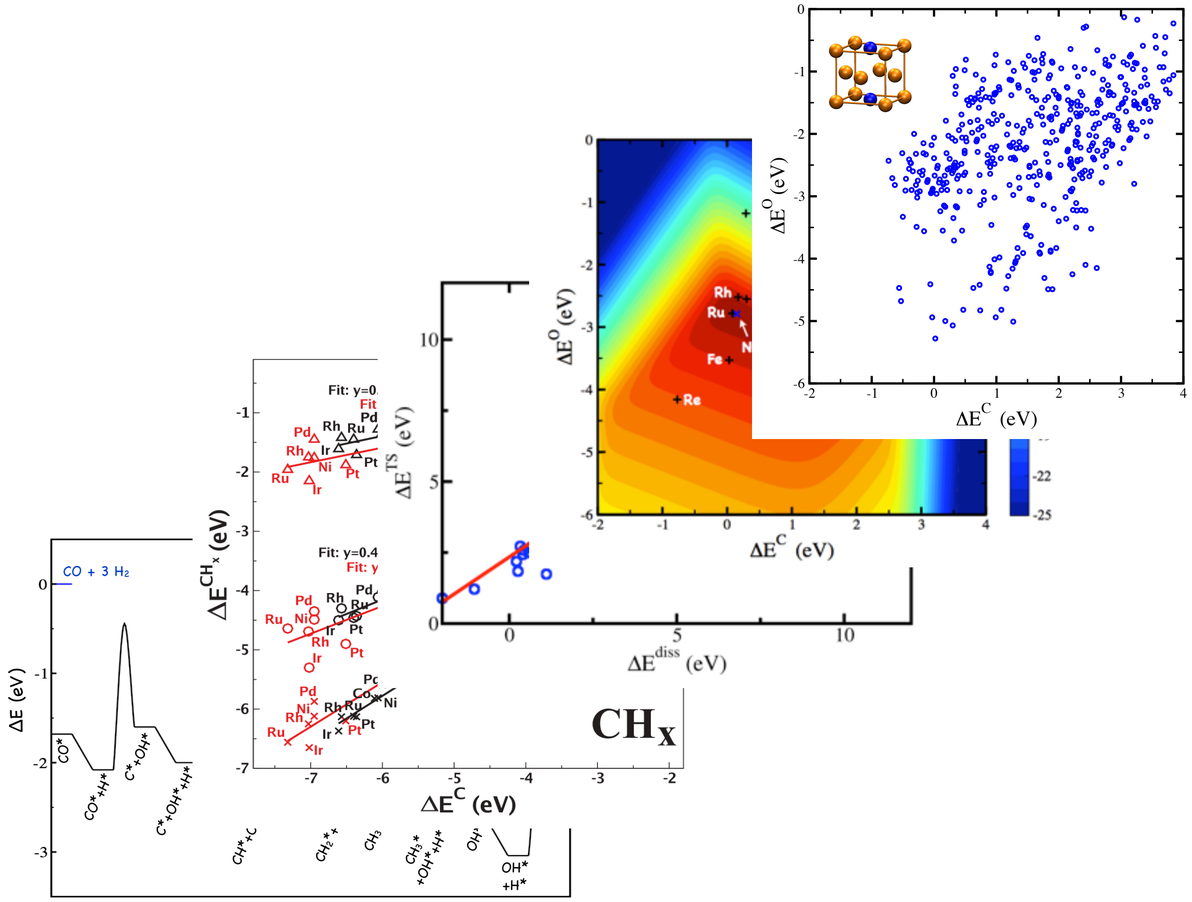
Reaction energy

Link to publication

Reverse reaction

Design Principle





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- Handbook of Surface Science Vol 2, Electronic Structure, Eds, K. Horn, M. Scheffler