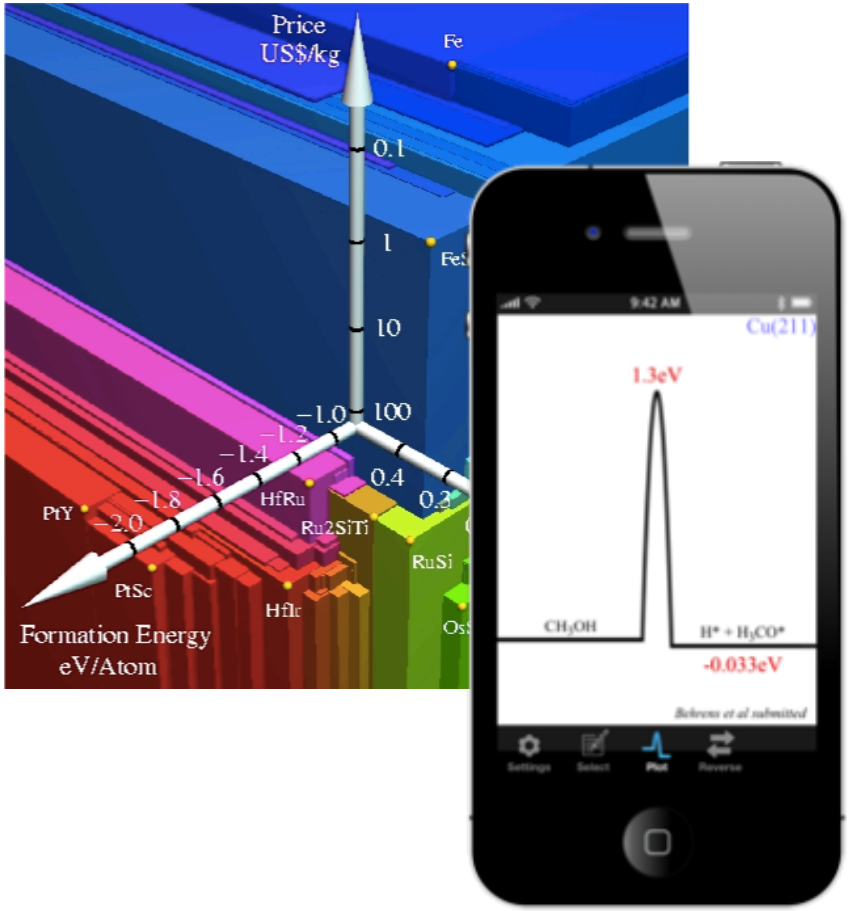
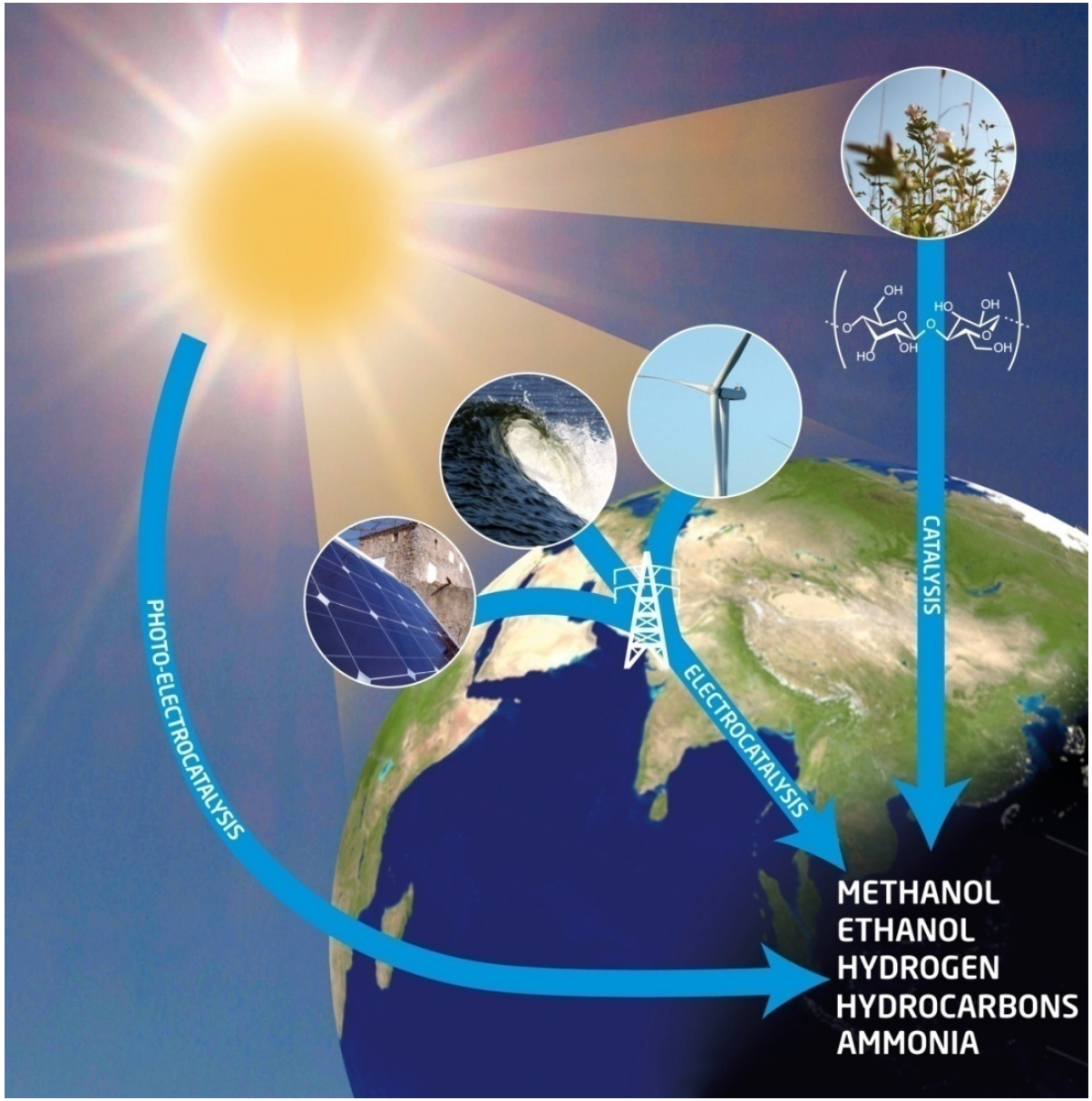
Materials Discovery for Catalysis

Thomas Bligaard
bligaard@slac.stanford.edu



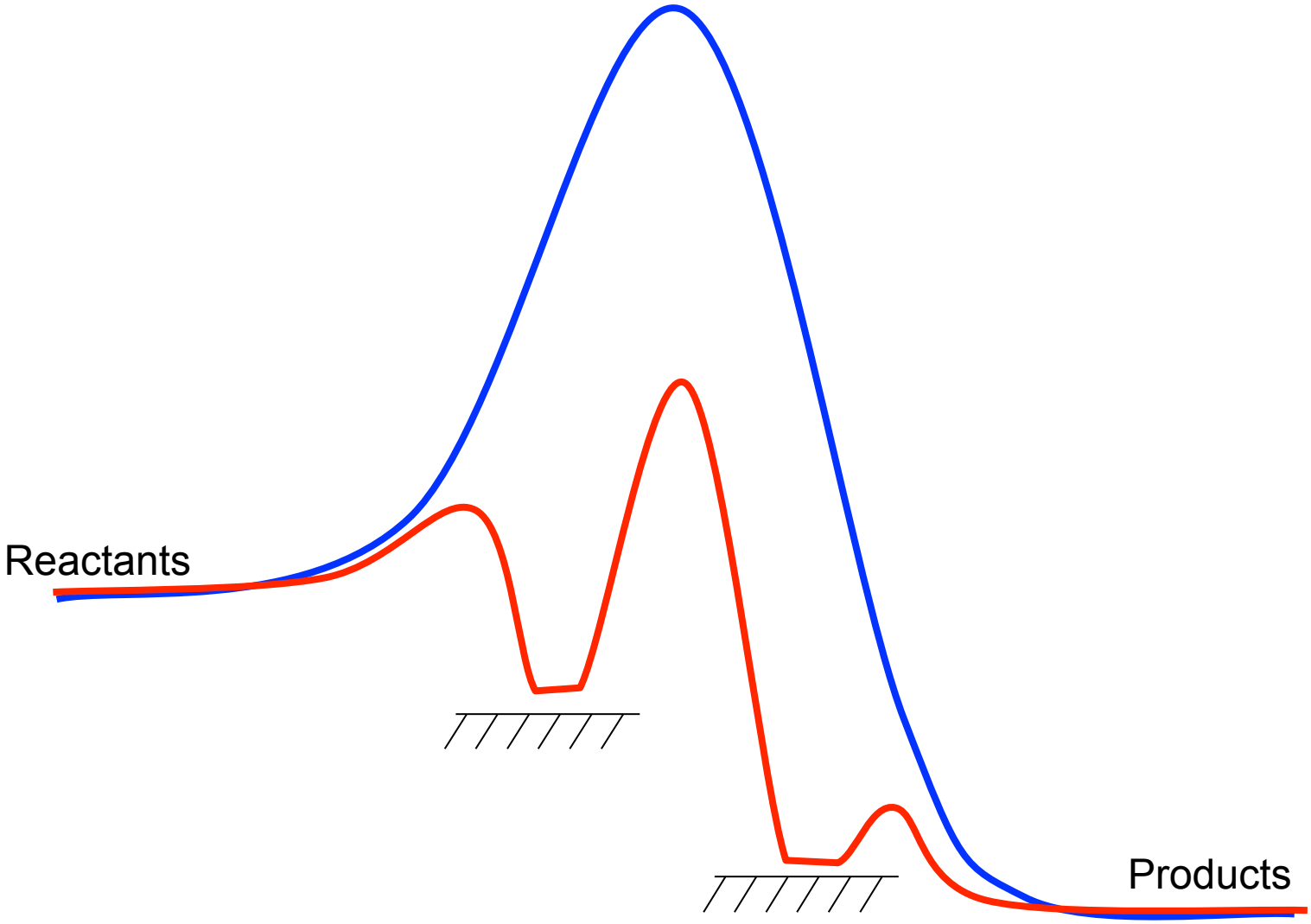
SUNCAT
CENTER FOR INTERFACE SCIENCE AND CATALYSIS
U.S. DEPARTMENT OF ENERGY
Office of Science
SLAC
NATIONAL ACCELERATOR LABORATORY

Sustainable energy conversion

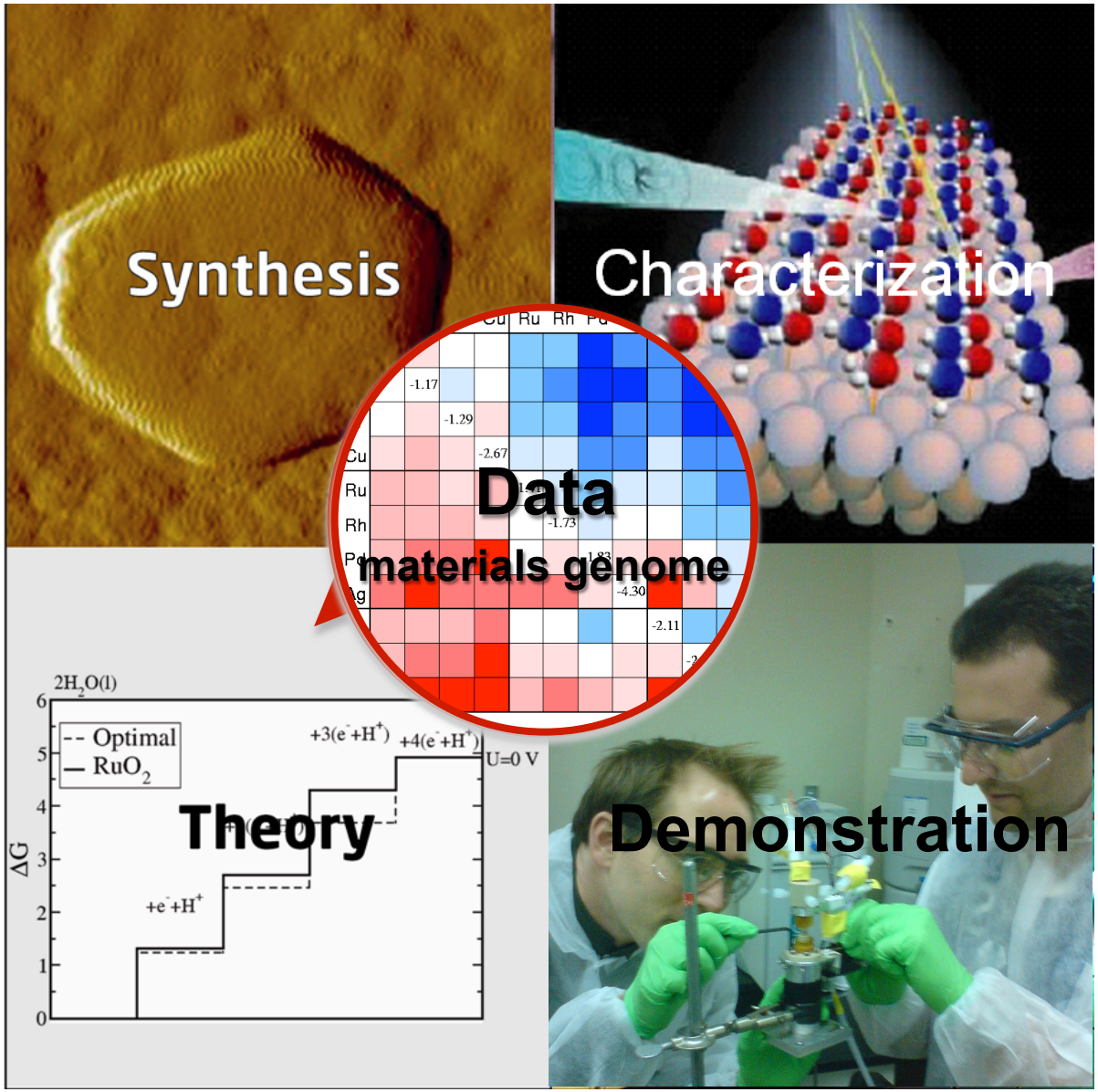


Nørskov, Bligaard
Angewandte Chemie Int. Ed
52, 776 (2013)

Heterogeneously catalytic materials



Integrated approach to catalyst and process discovery



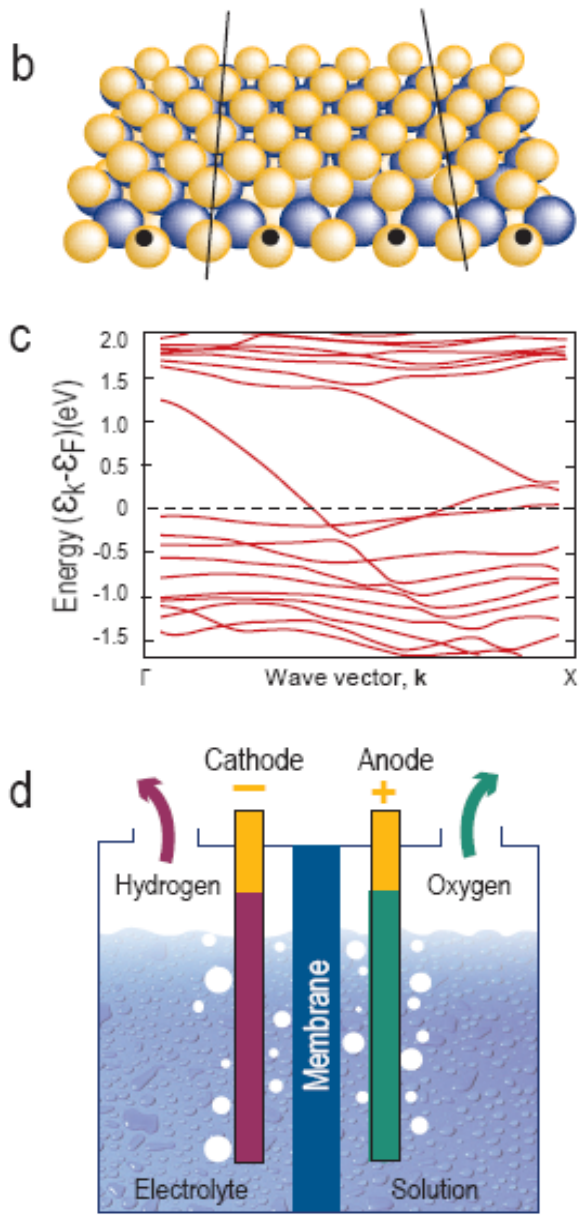
Nørskov, Bligaard
Angewandte Chemie Int. Ed
52, 776 (2013)

Computational design at the atomic scale

Structure, composition

Electronic structure

Functionality
(Catalytic activity)



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

Three flavors of systematic "Computational Design"

A. Direct search

B. Data base screening

C. Descriptor-based search

Bligaard, Andersson, Skriver, Jacobsen, Christensen, Nørskov
Materials Research Society Bulletin **31**, 986 (2006)

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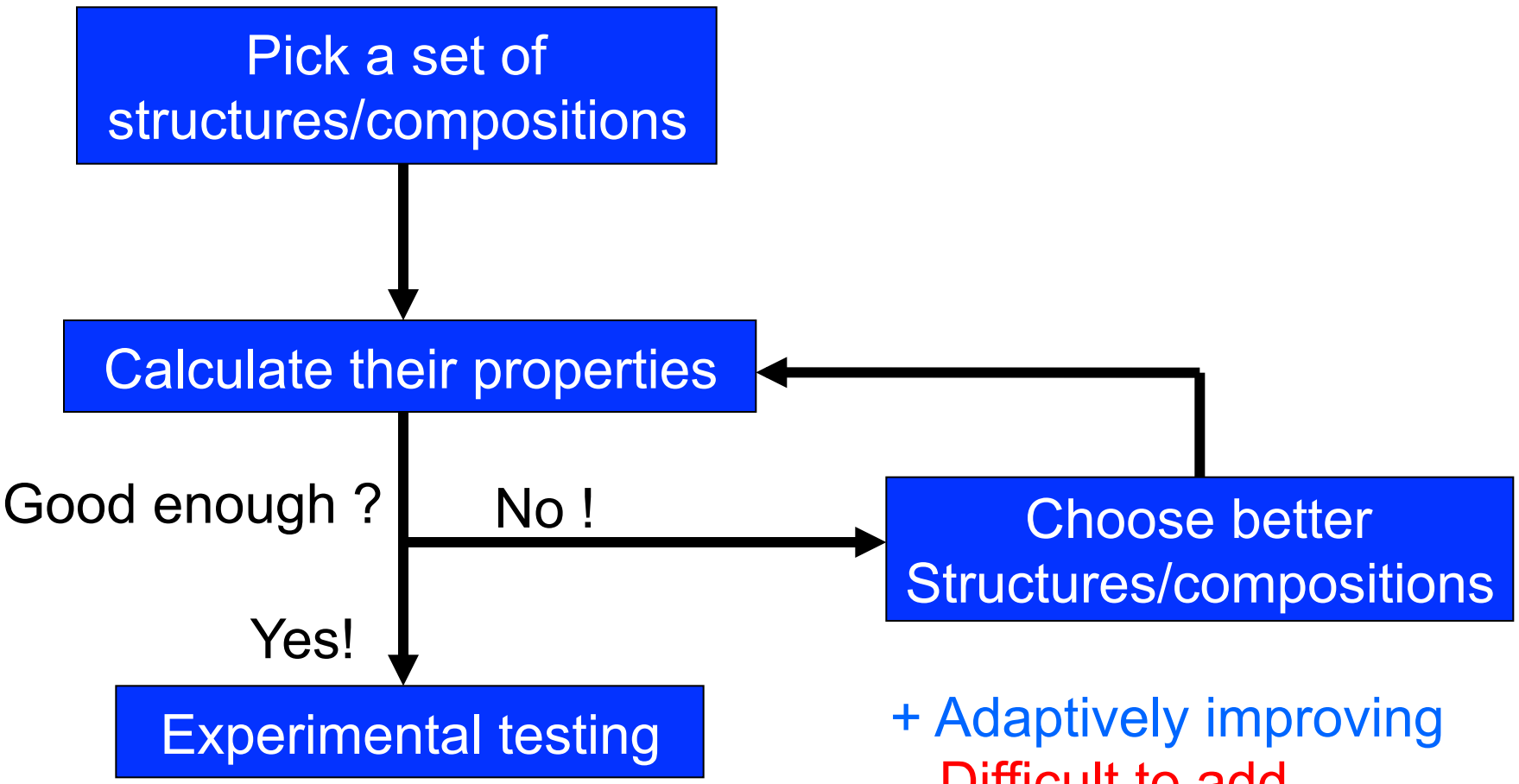
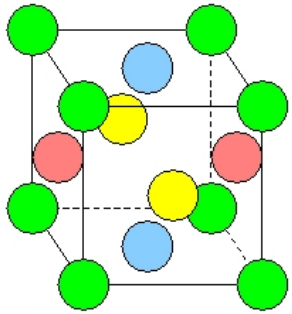
Materials Research Society Bulletin **31**, 986 (2006)

Direct Computational Search



+ Adaptively improving
- Difficult to add constraints after a run

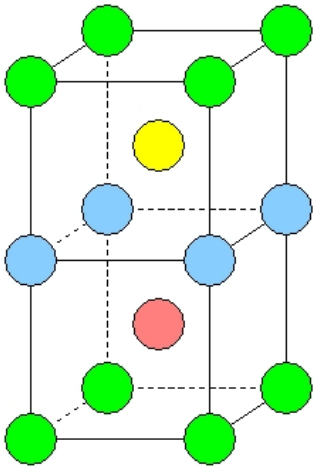
An example:
Finding the most stable quaternery alloy



fcc

- Consider only fcc- and bcc-type structures
- Consider only varations in concentration of 25%
- Include 30 transition and noble metals, Al, and Si

bcc

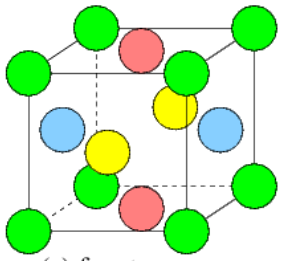


→ This ‘simple’ problem results in 192,016 different structures

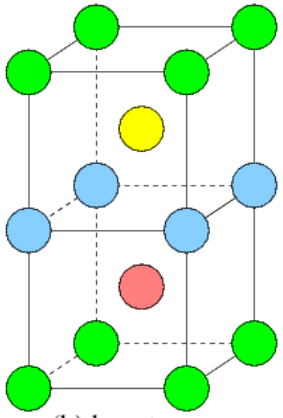
This limited search space is still too great to consider all possibilities

Evolutionary Algorithm

Four atom arrangements



(a) fcc–type

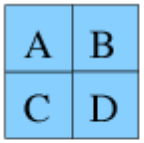


(b) bcc–type

(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



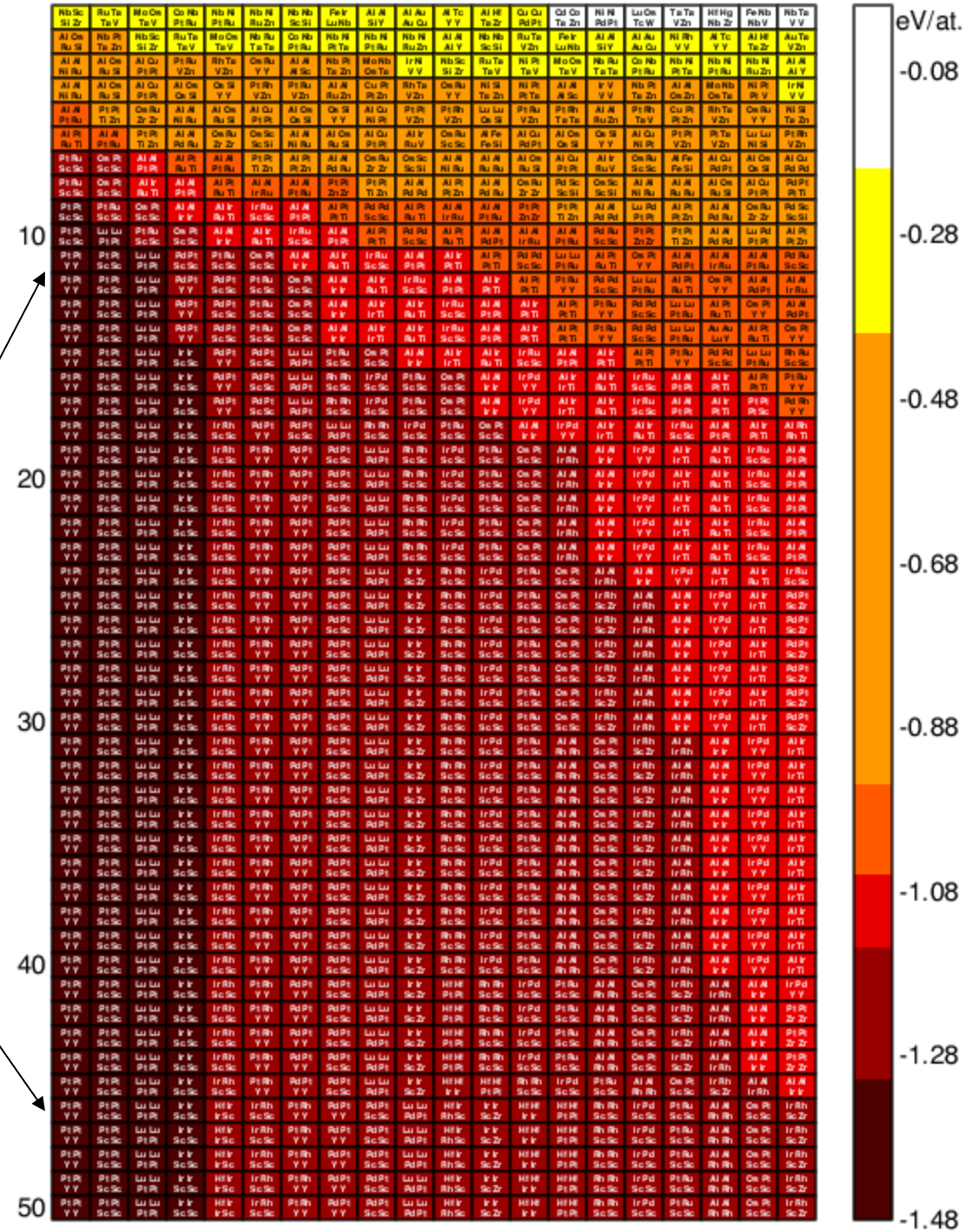
(c) Mating scheme

(d) Mutation scheme

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

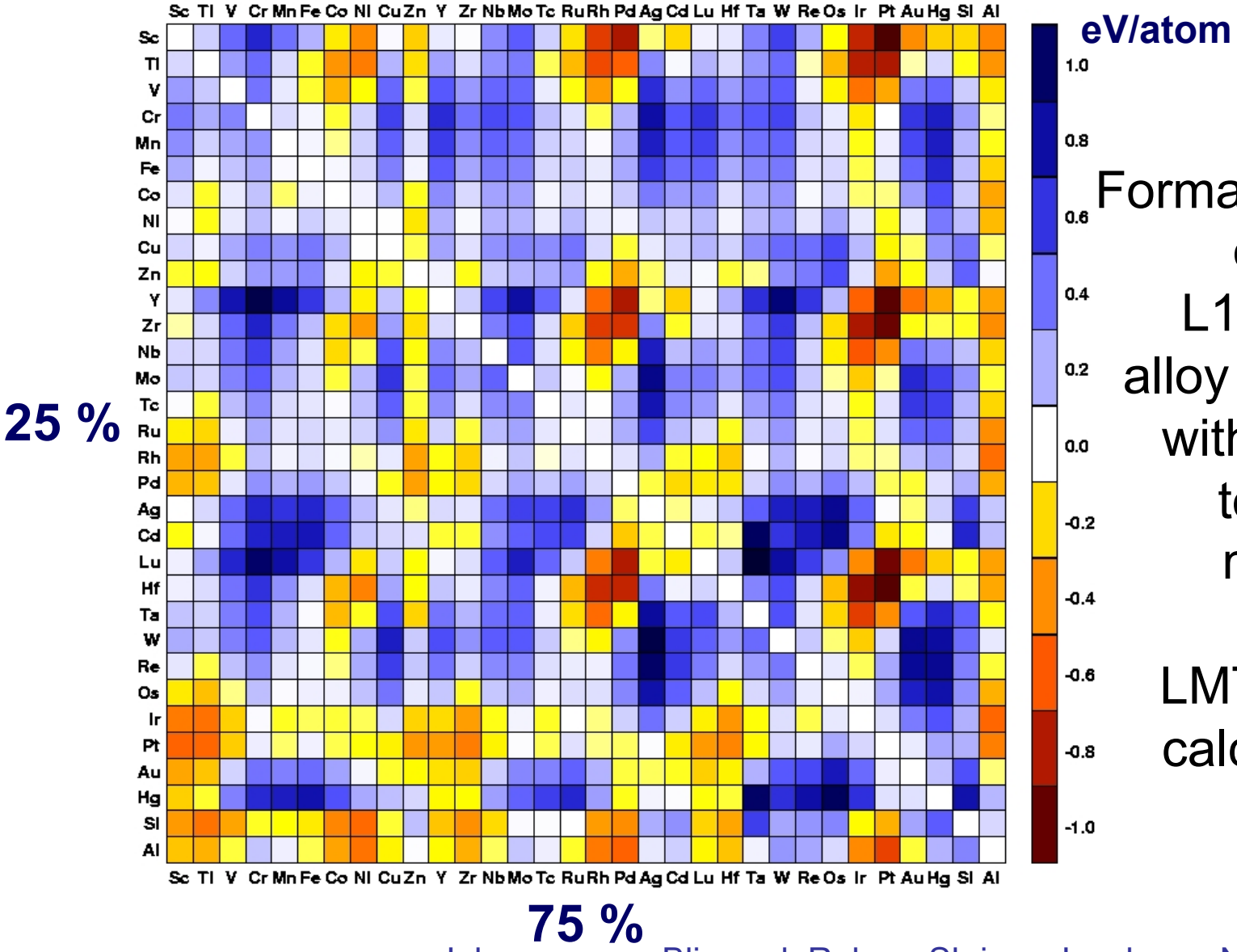
Evolutionary Algorithm

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



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

Structural stability of ordered alloys

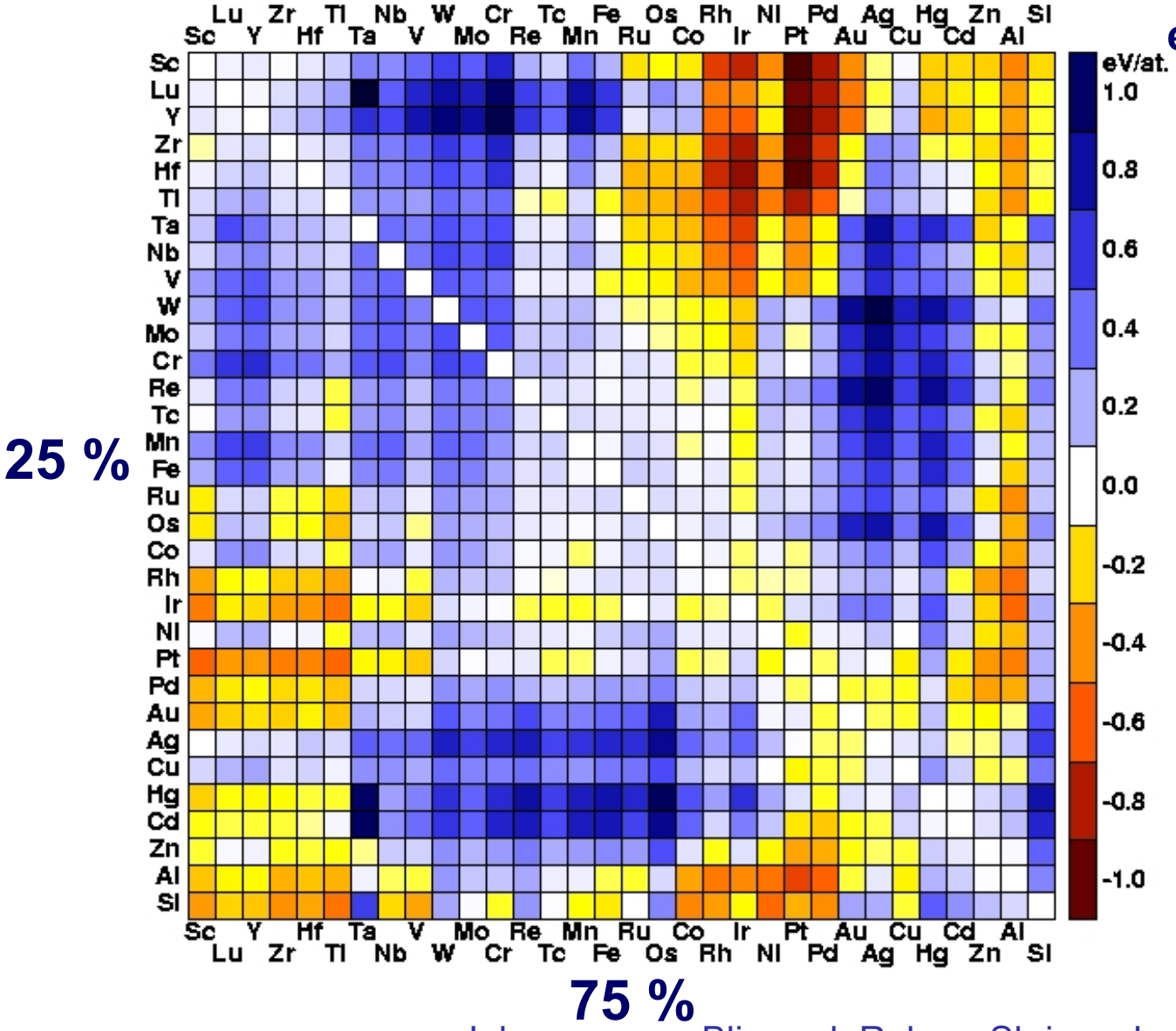


Formation energy of the $L1_2$ binary alloy structures with respect to pure metals

LMTO-GGA calculations

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

Pettifor stringing of the elements



Formation energy of the $L1_2$ binary alloy structures with respect to pure metals

LMTO-GGA calculations

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

“The knowledge of underlying correlations are of key importance to the efficiency of search algorithms”

Establishing reliable correlations requires large databases

Three flavors of systematic "Computational Design"

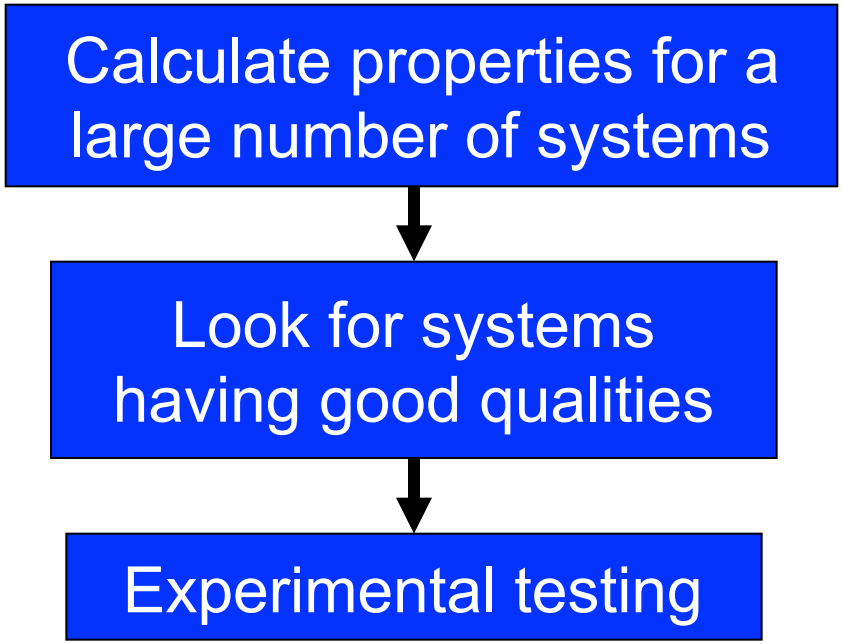
A. Direct search

B. Data base screening

C. Descriptor-based search

Bligaard, Andersson, Skriver, Jacobsen, Christensen, Nørskov
Materials Research Society Bulletin **31**, 986 (2006)

Screening of Computed Data



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

All search methods end up depending on:

Availability of reliable and transparent data

Three flavors of systematic "Computational Design"

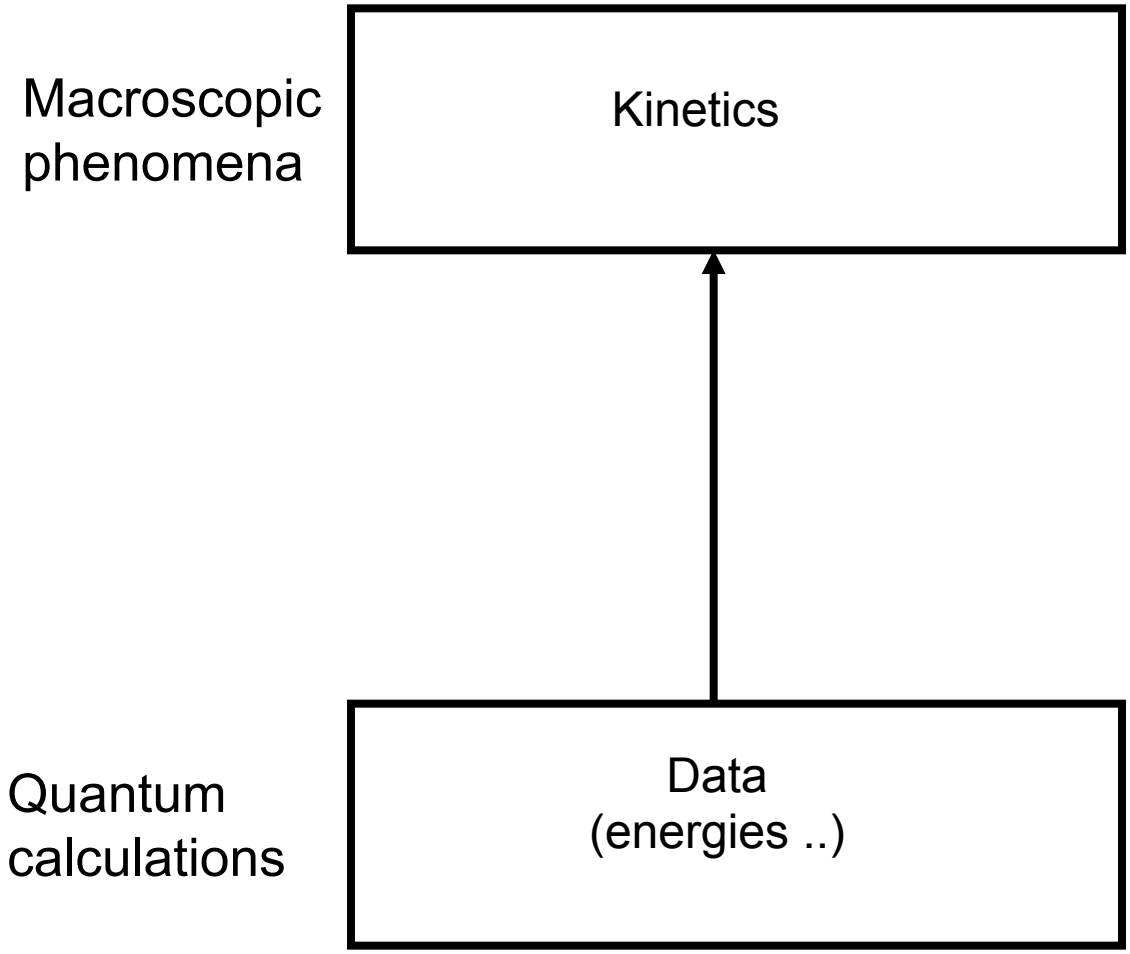
A. Direct search

B. Data base screening

C. Descriptor-based search

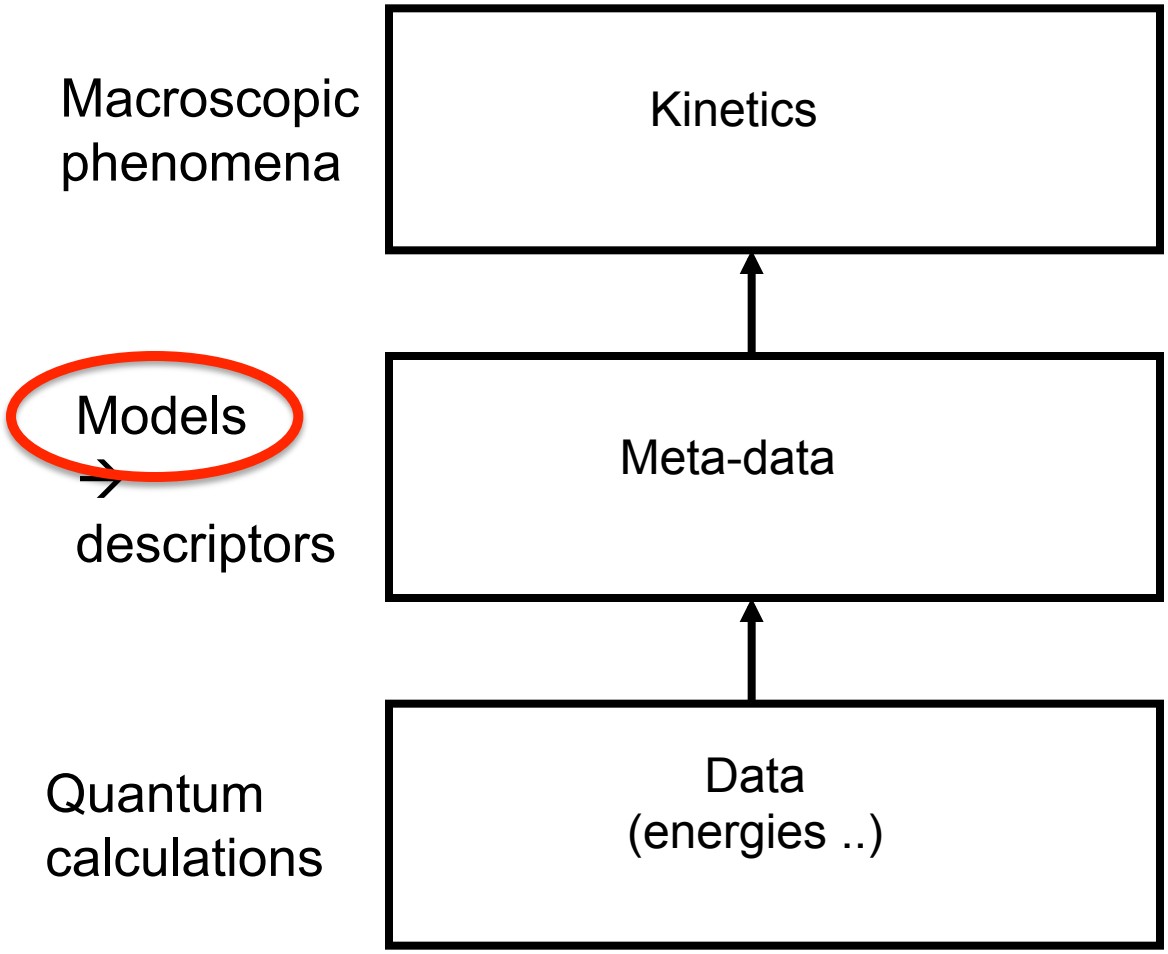
Bligaard, Andersson, Skriver, Jacobsen, Christensen, Nørskov
Materials Research Society Bulletin **31**, 986 (2006)

Design strategy



Nørskov, Abild-Pedersen, Studt, Bligaard, PNAS **108**, 937 (2011)

Design strategy



Nørskov, Abild-Pedersen, Studt, Bligaard, PNAS **108**, 937 (2011)

Steam reforming

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

Rostrup-Nielsen, Sehested, Nørskov, *Adv. Catal.* **47**, 65 (2002)

Steam reforming

Ordering of good catalysts:

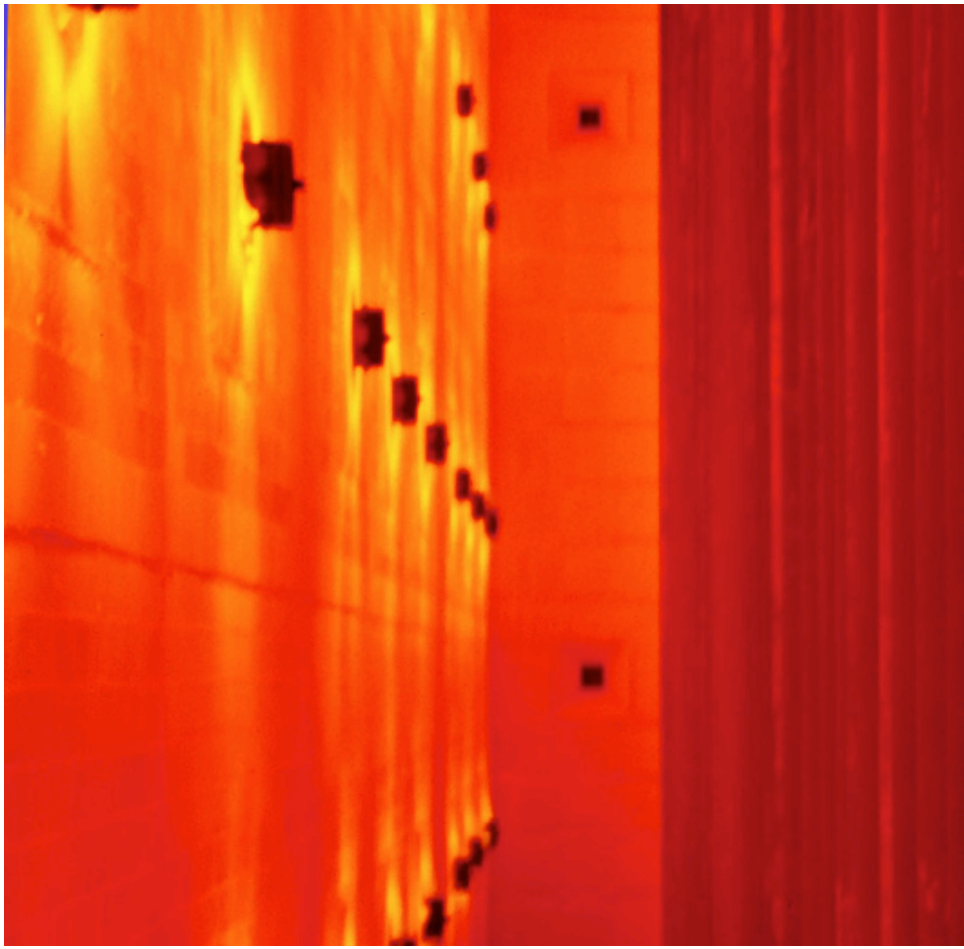
Rh, Ru > Ni, Pd, Pt > Re > NiCu > Co
(ethane SR, 773K)
Rostrup-Nielsen
J.Catal. 31, 173 (1973)

Rh, Ru > Ni > Ir > Pd, Pt > Fe, Co
(methane SR, 623K - 873K)
Kikuchi, Tanoka, Yamazaki, Morila
Bull. Jpn. Pet. Inst. 16, 95 (1974)

Ru > Rh > Ir > Pt > Pd
(methane SR, 873K - 1123K)
Qin, Lapszewicz
Catal. Today 21, 551(1994)

Pt > Ir > Rh > Ru, Ni
(methane SR, 823K - 1023K)
(Dispersion important)
Wei, Iglesia, *J. Catal.* 225, 116 (2004)
PCCP 6, 3754 (2004)
Angew. Chem. 43, 3685 (2004)

T=1223K

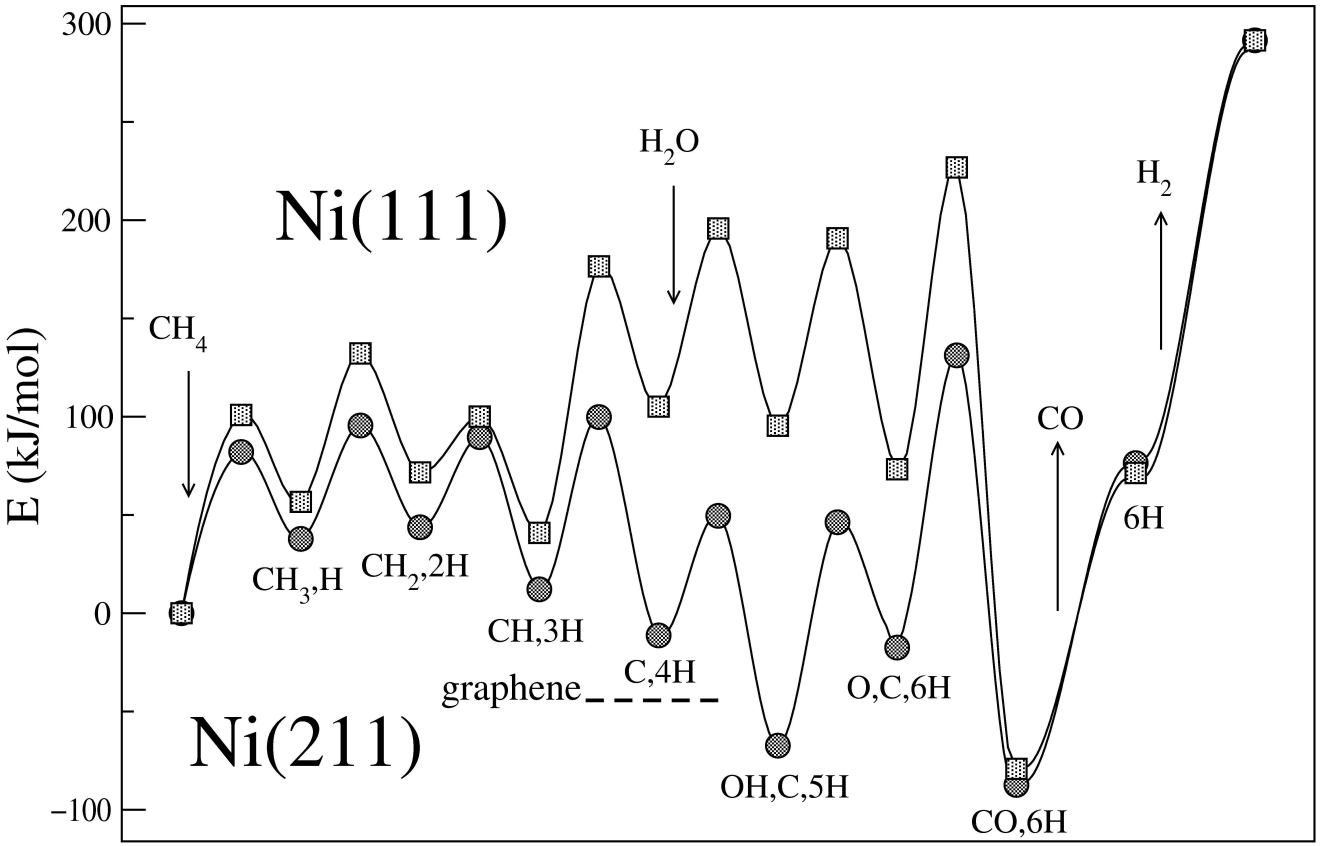


T=723K

ΔH= +206 kJ/mol
Industrial catalyst: Ni

Potential energy diagram

Steam reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$



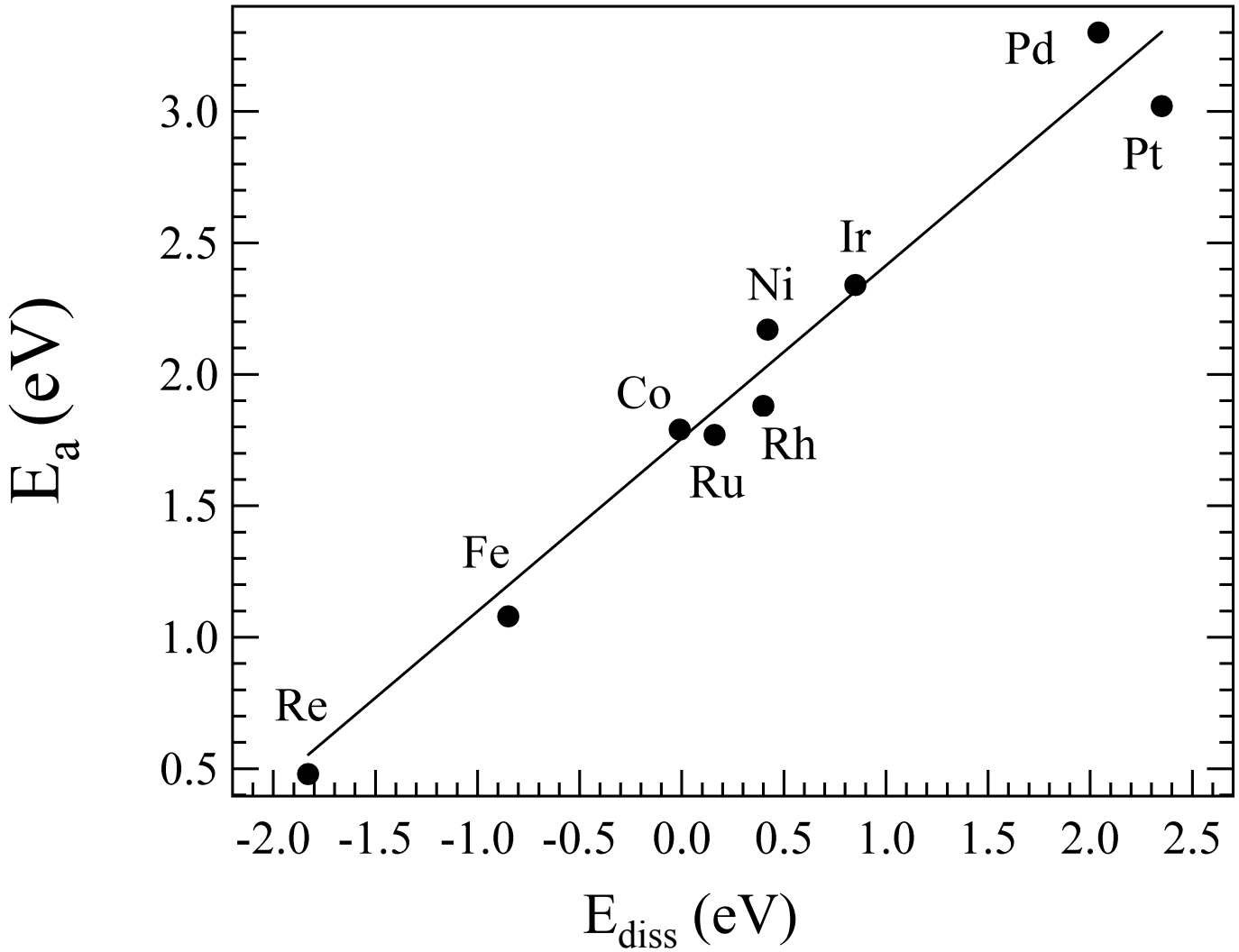
16 kinetic parameters

→ Too much complexity to give full insight

Bengaard, Nørskov, Sehested, Clausen, Nielsen, Molenbroek, Rostrup-Nielsen
J. Catal. **209**, 365 (2002)

Brønsted-Evans-Polanyi (BEP) relations:

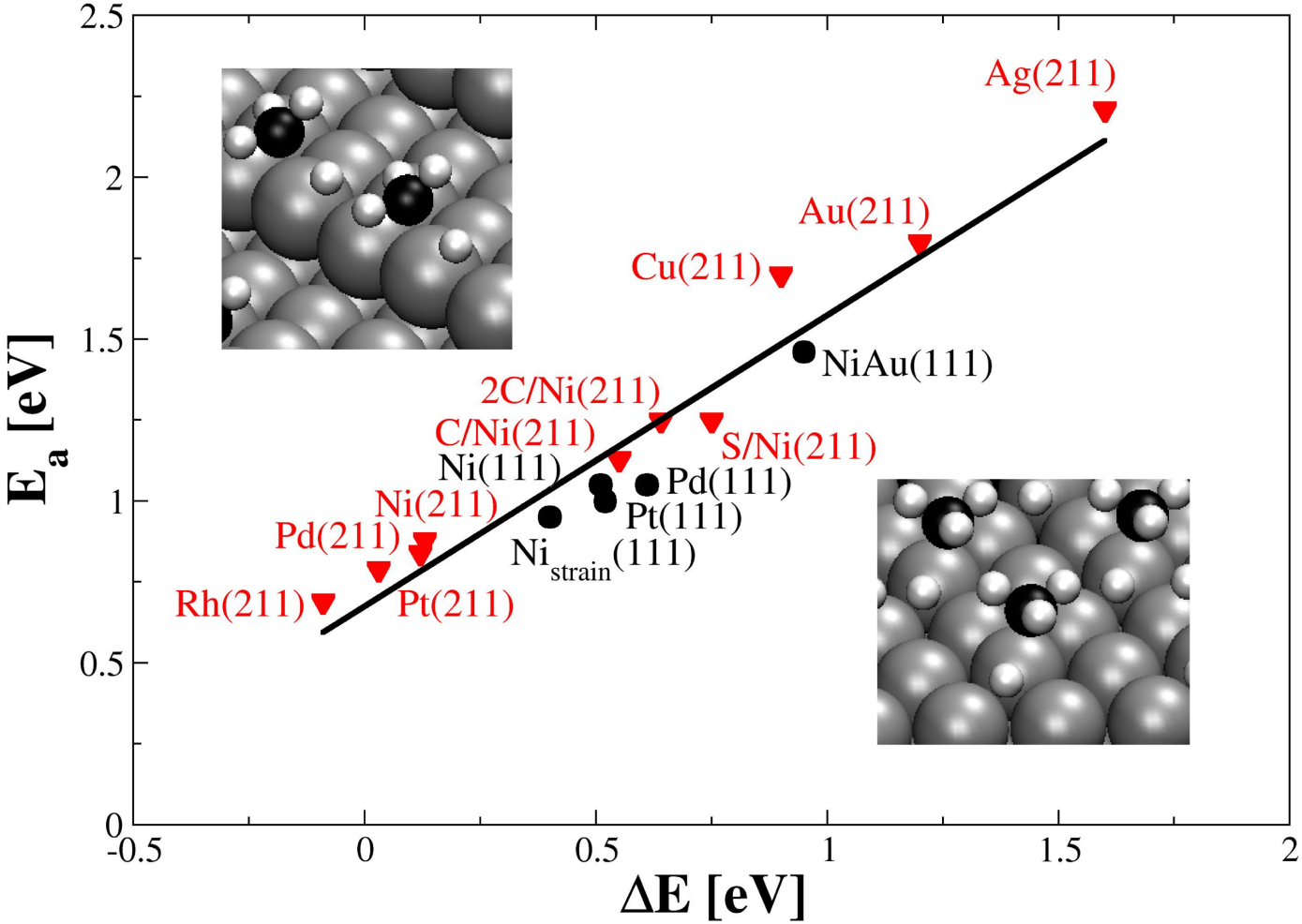
→ e.g. CO dissociation



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

Adsorption energy correlations

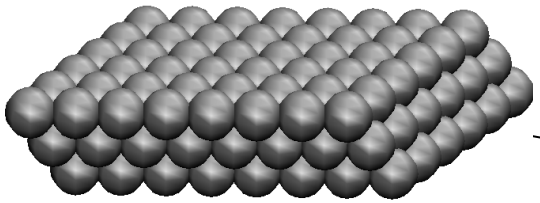
→ BEP for methane activation



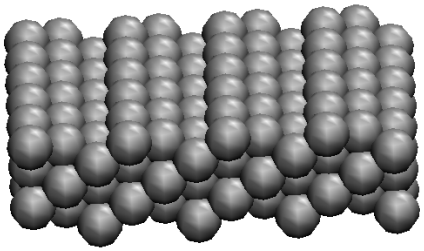
Nørskov, Bligaard, Hvolbæk, Abild-Pedersen, Chorkendorff, Christensen, *Chem. Soc. Rev.* **37**, 2163 (2008)

Scaling relations: CH_x vs. C

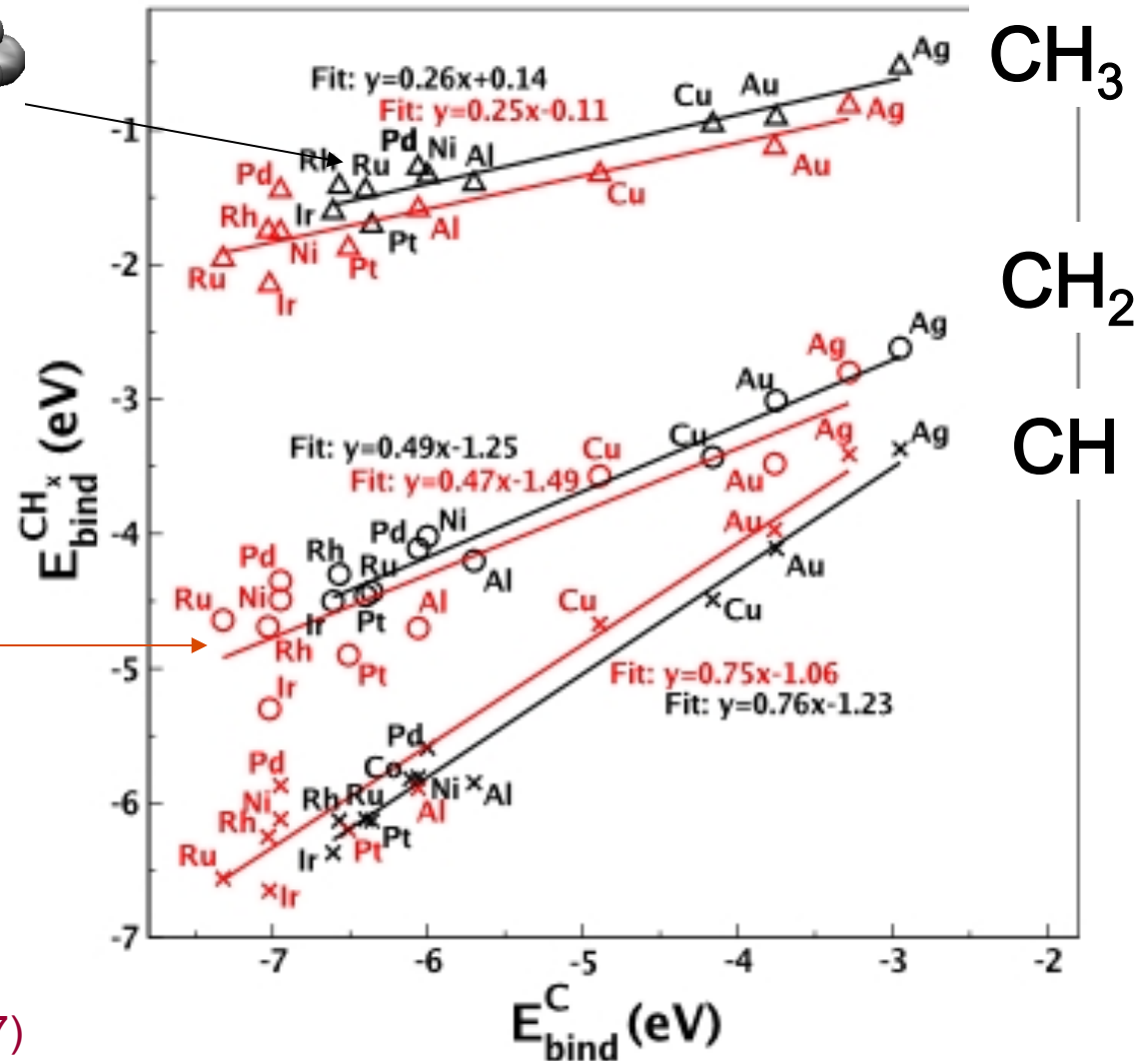
Close-packed surfaces



Stepped surfaces

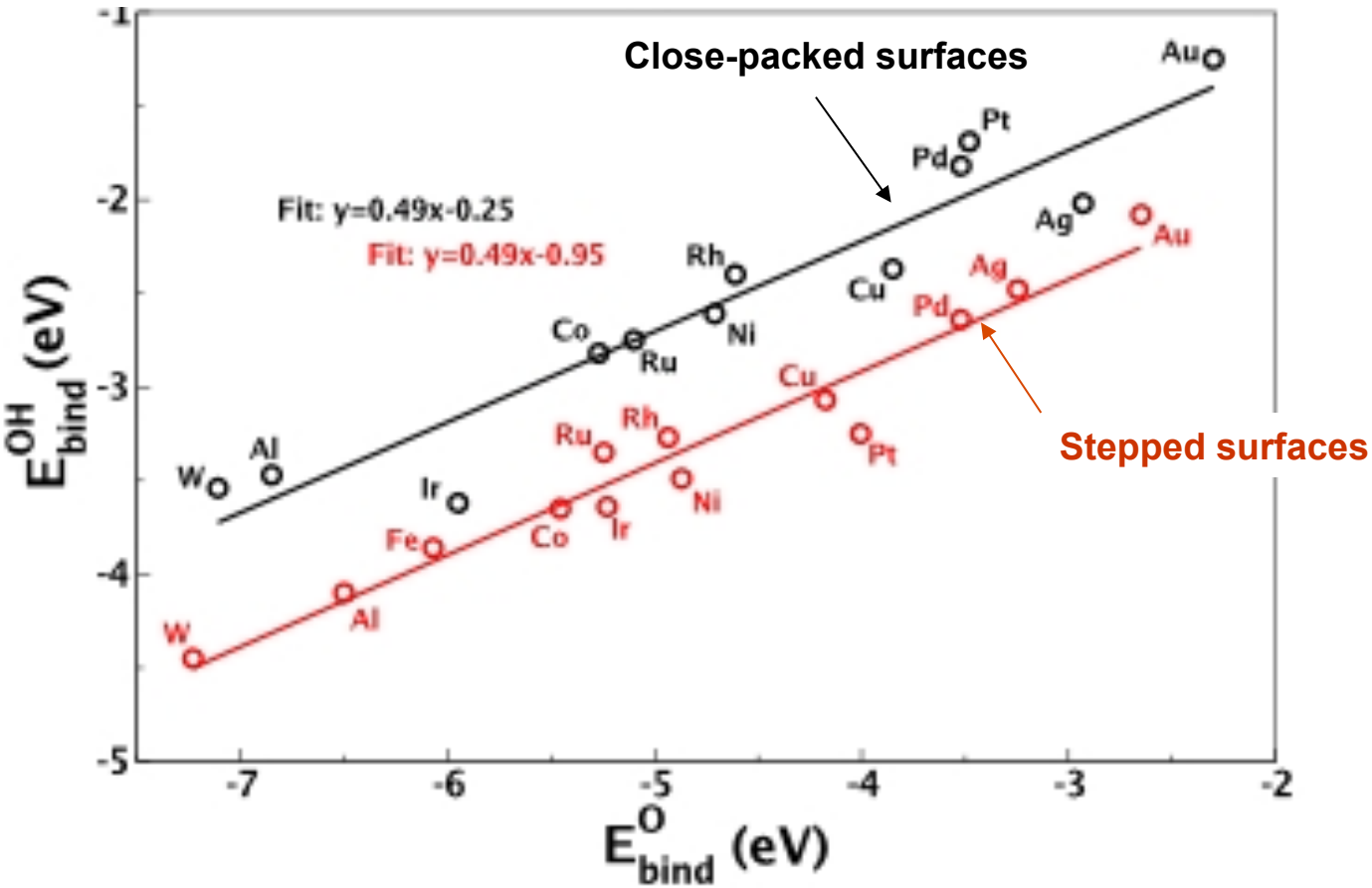


CH_x adsorption energies



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

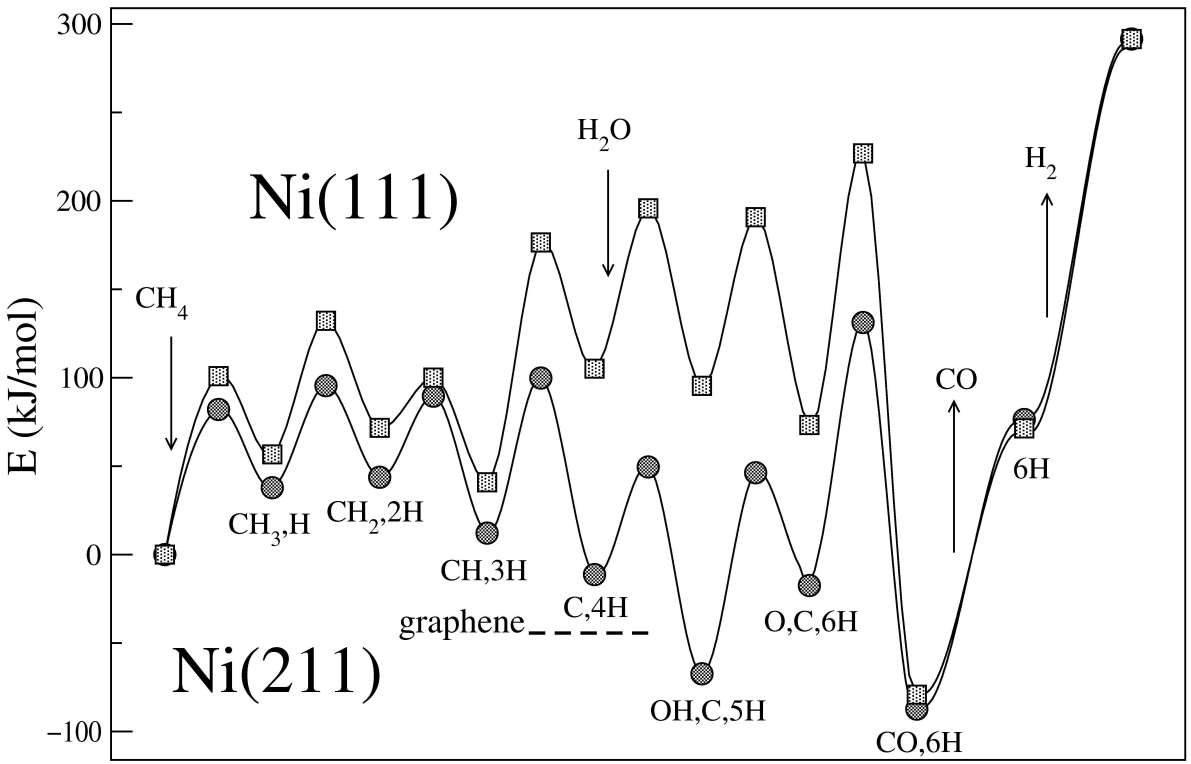
Scaling relations: OH vs. O



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

Descriptors of catalytic activity

Steam reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$



16 kinetic parameters

→

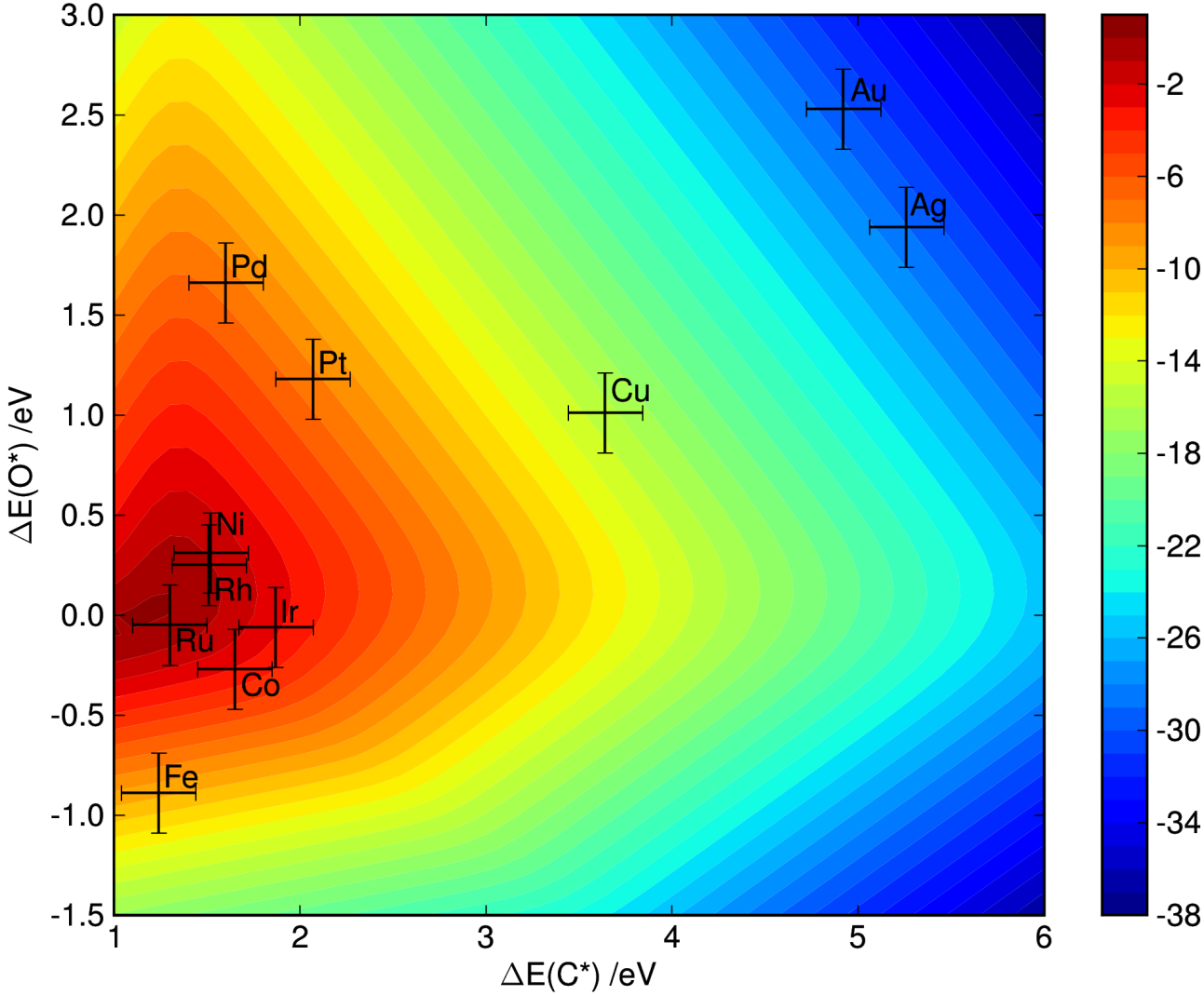
2 independent parameters

(ΔE_C, ΔE_O)

Jones, Jakobsen, Shim, Kleis, Andersson, Rossmeisl, Abild-Pedersen, Bligaard, Helveg, Hinnemann, Rostrup-Nielsen, Chorkendorff, Sehested, Nørskov, *J.Catal.* **259**, 147 (2008)

The steam reforming activity volcano

→ suggests the "classical wisdom" holds



Log_{10}(TOF) as $f(E_O,E_C)$ at
T = 773K
P = 1 bar
10% conversion

The error bars represents an estimated 0.2 eV uncertainty on the adsorption energies

Jones, Jakobsen, Shim, Kleis, Andersson, Rossmeisl, Abild-Pedersen, Bligaard, Helveg, Hinnemann, Rostrup-Nielsen, Chorkendorff, Sehested, Nørskov, *J. Catal.* **259**, 147 (2008)

Measured reaction rates vs. dispersion

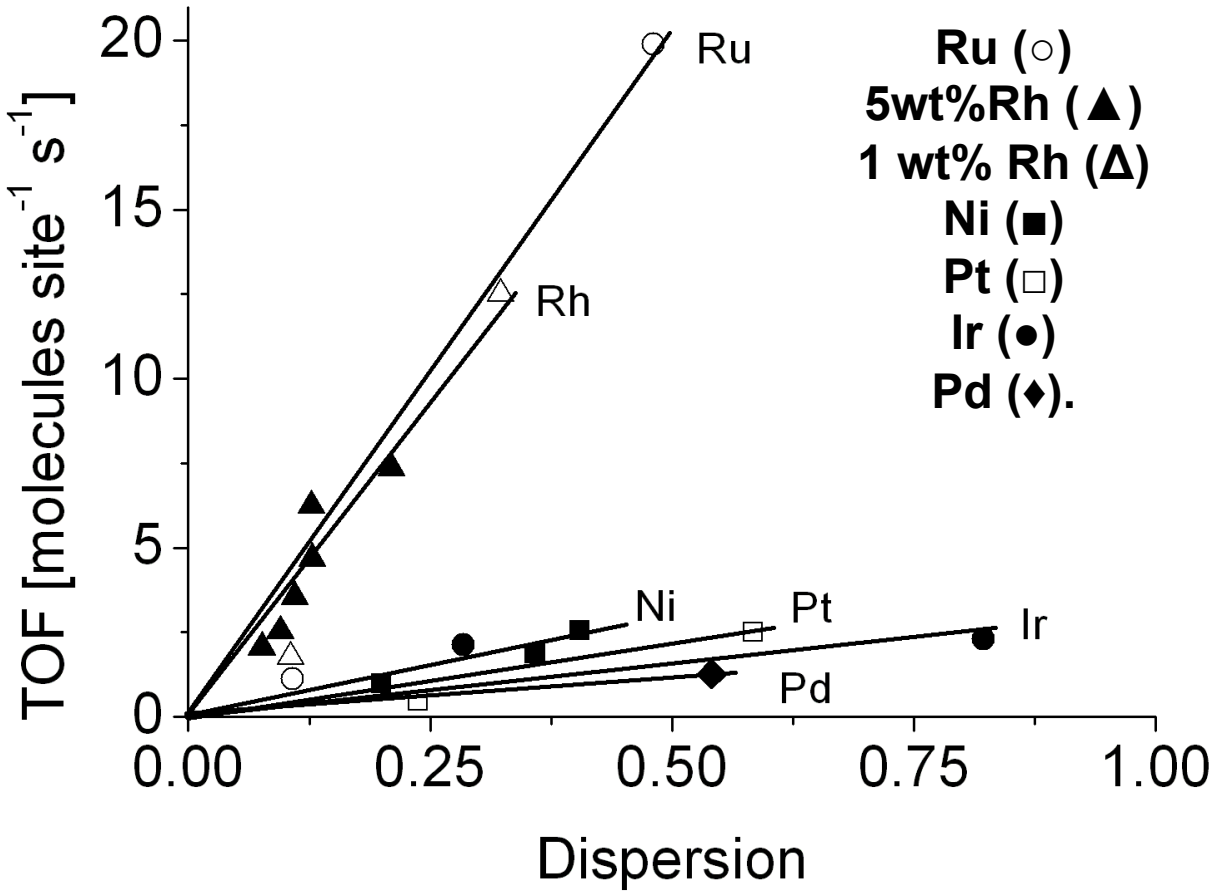
→ 773K, 0.19 bar CH_4, 0.74 bar H_2O, 0.07 bar H_2

Theory:

Ru > Rh > Ni > Ir >Pt~Pd

Experiments:

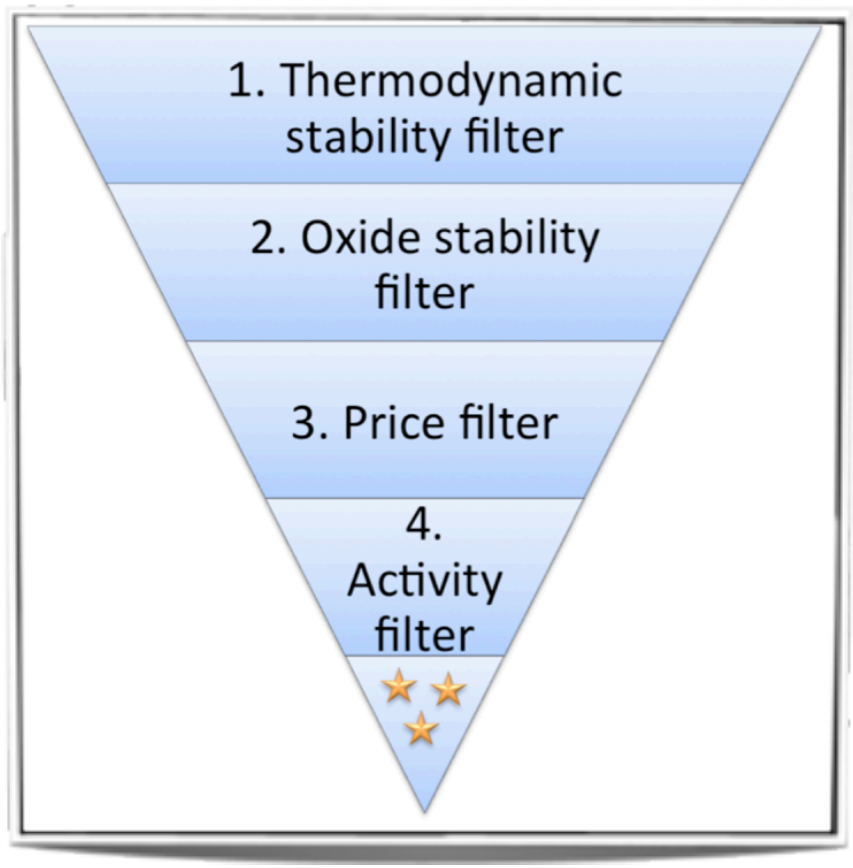
Ru~Rh > Ni~Ir~Pt~Pd

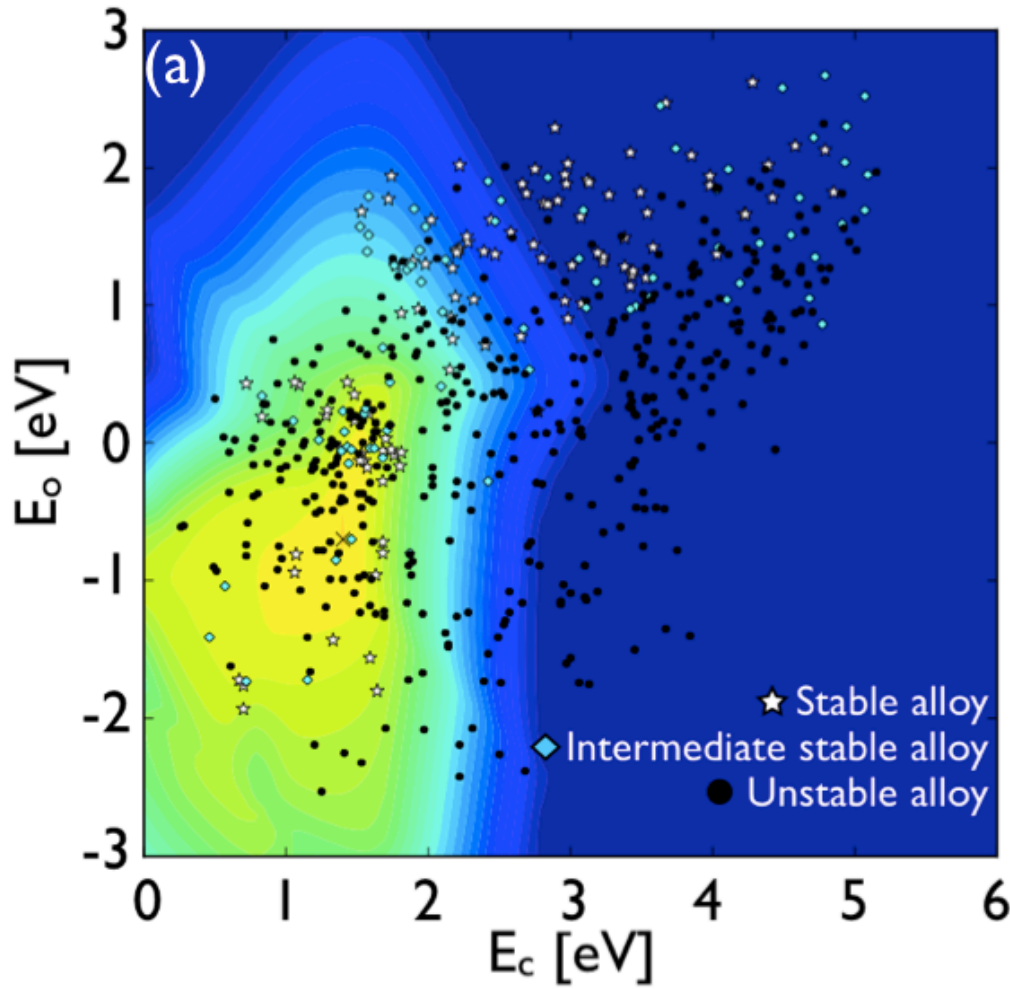


Jones, Jakobsen, Shim, Kleis, Andersson, Rossmeisl, Abild-Pedersen, Bligaard, Helveg, Hinnemann, Rostrup-Nielsen, Chorkendorff, Sehested, Nørskov, *J. Catal.* **259**, 147 (2008)

Computational design hierarchy

→ Catalyst filtering

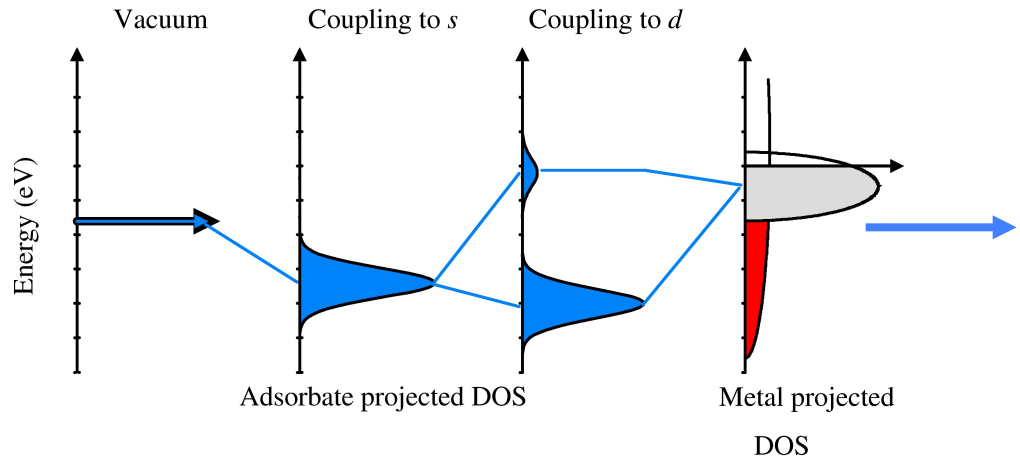


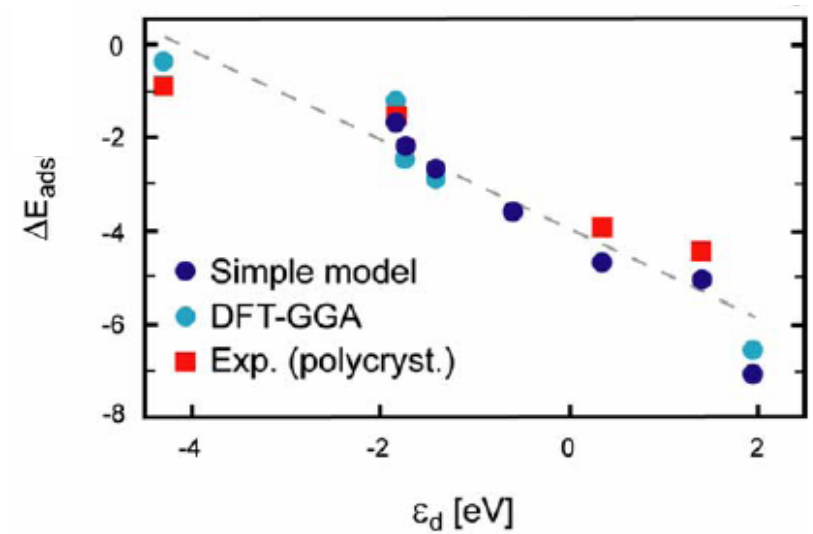


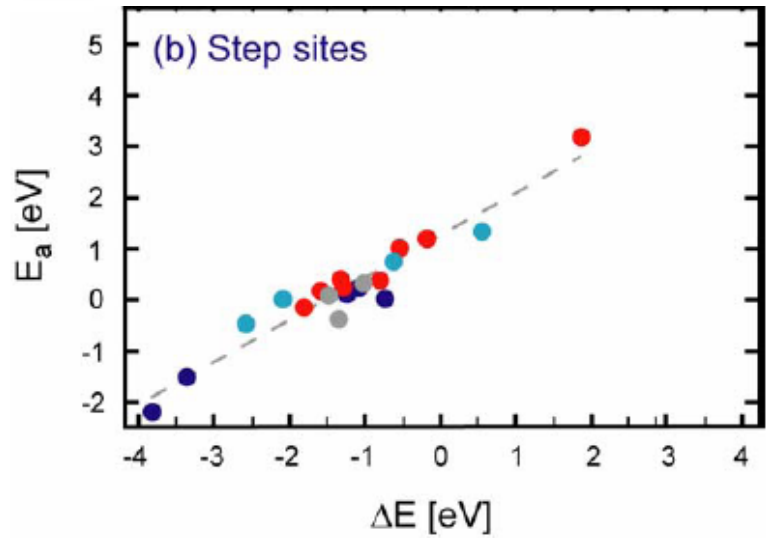
Xu, Lausche, Wang, Khan, Abild-Pedersen, Studt, Nørskov, Bligaard, *New J. of Physics* (2013)

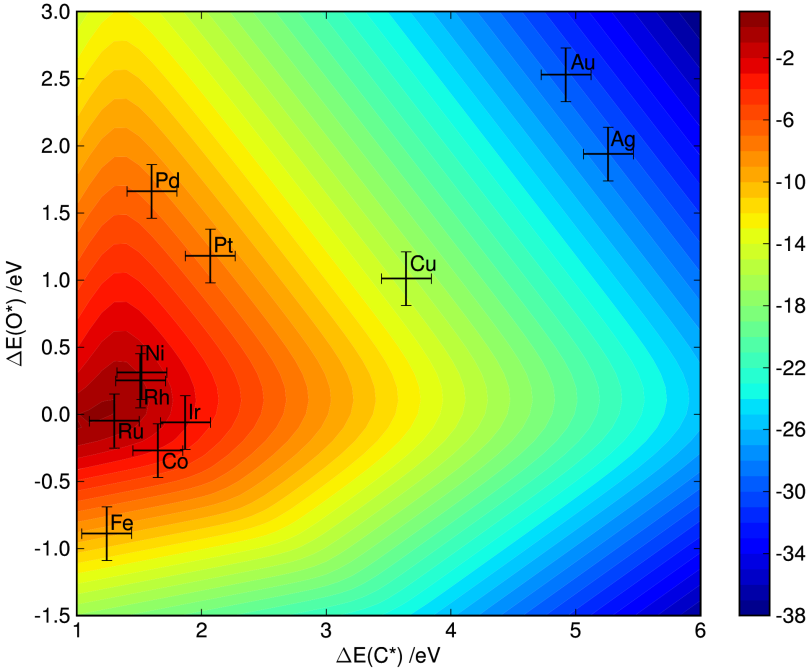
A "Standard Model"
- for descriptor-based catalysis trends

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

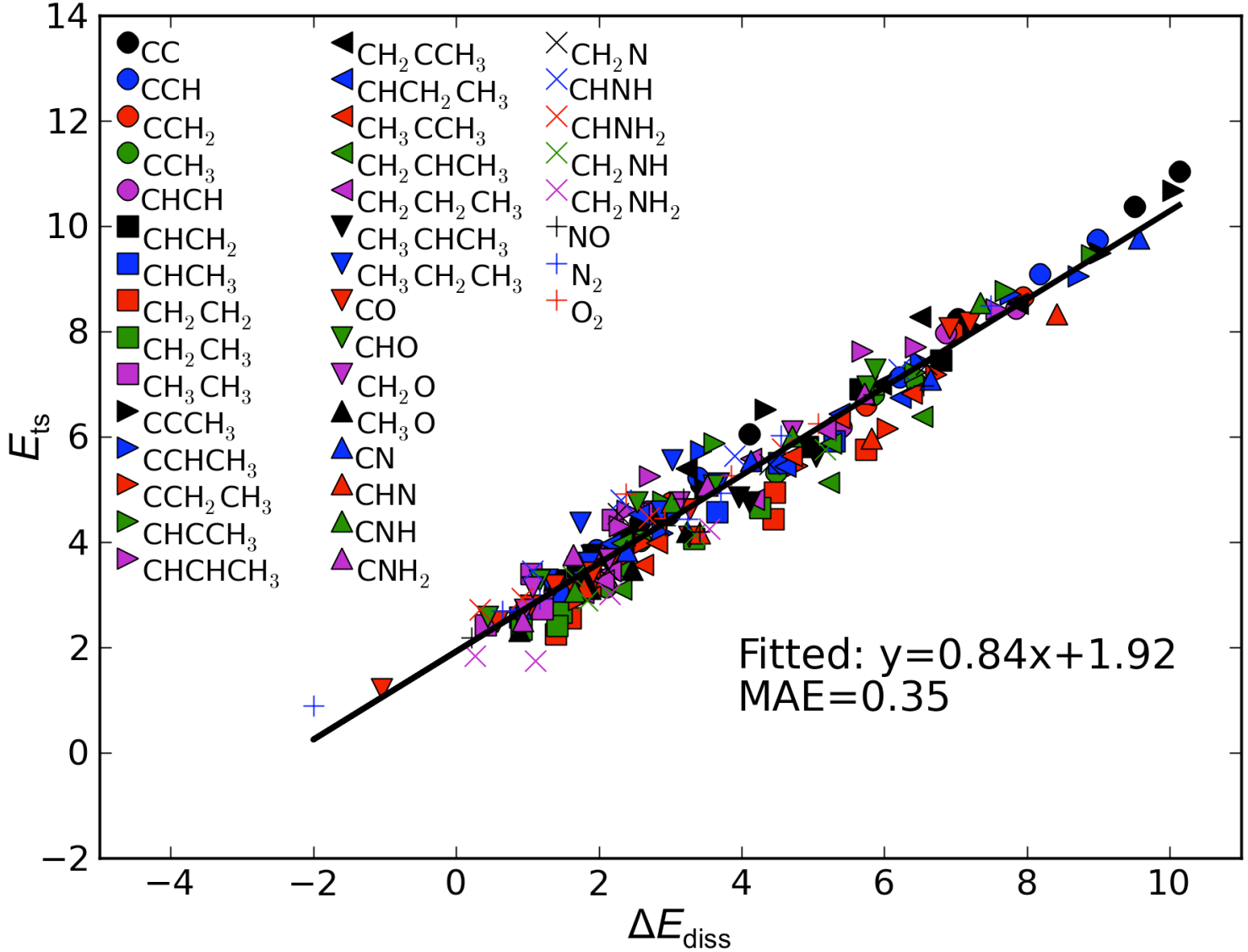






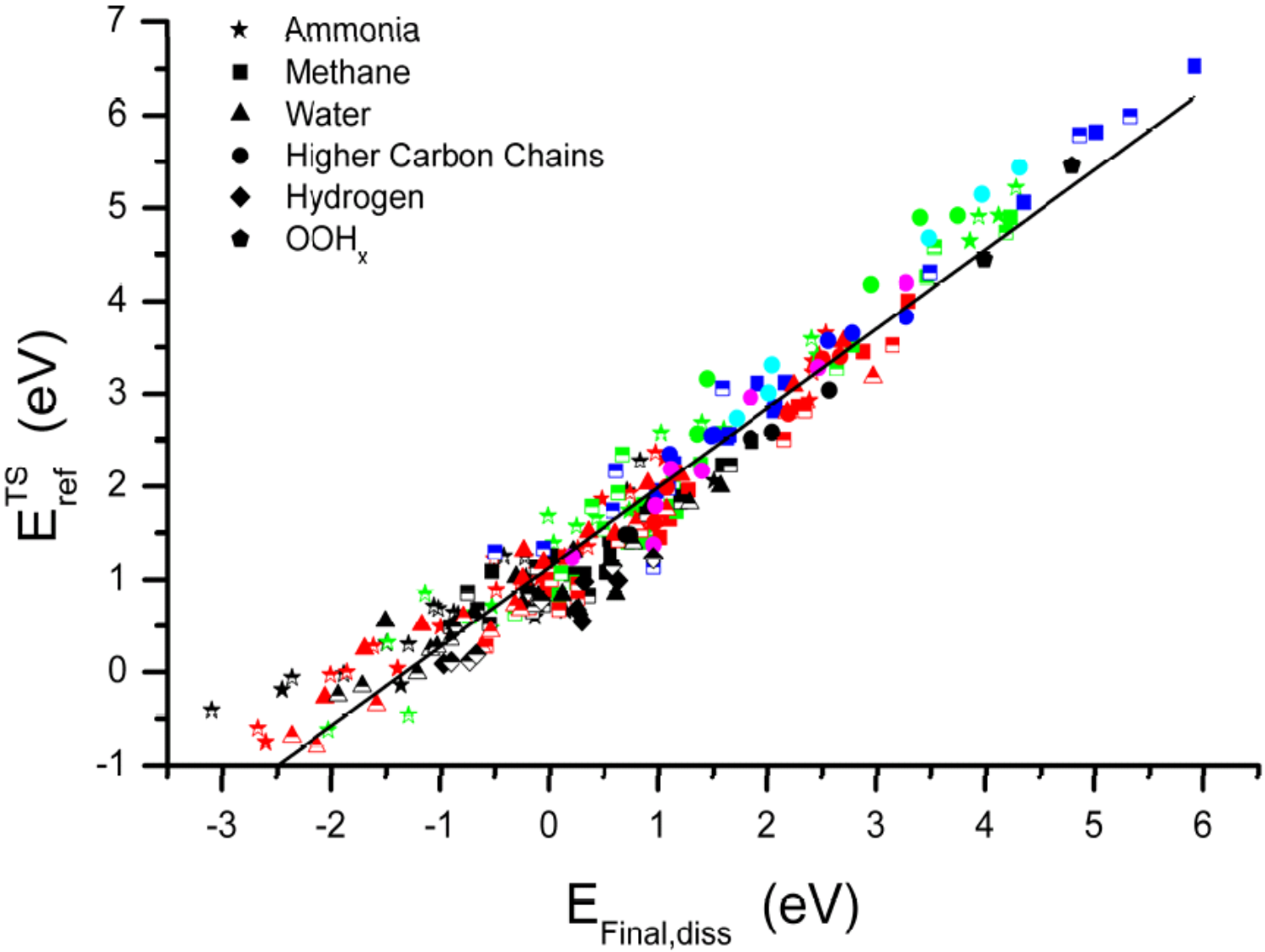


BEPs for covalent scission/TMs



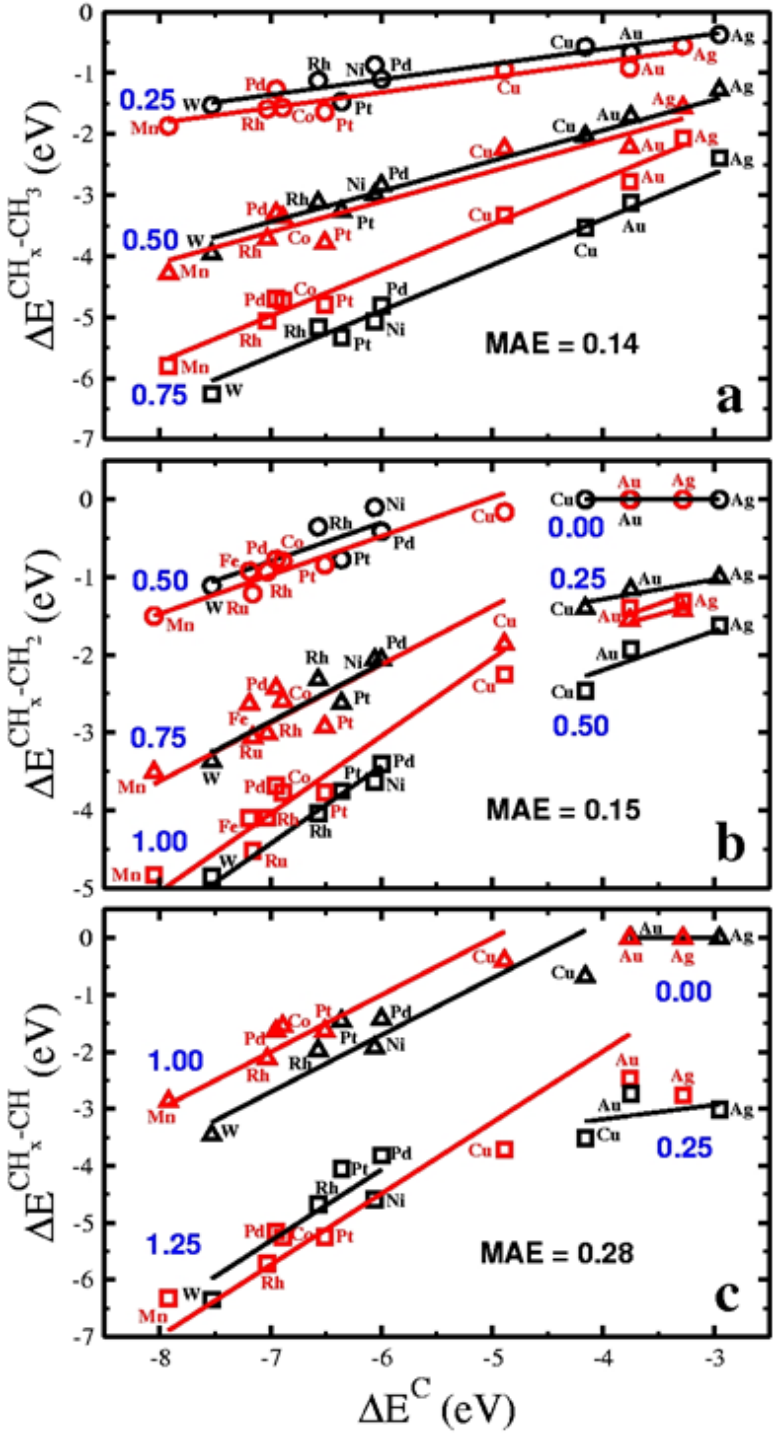
Wang, Temel, Shen, Jones, Grabow, Studt, Bligaard
Abild-Pedersen, Christensen, Nørskov, *Catal. Lett.* (2010)

BEPs dehydrogenation/TMs



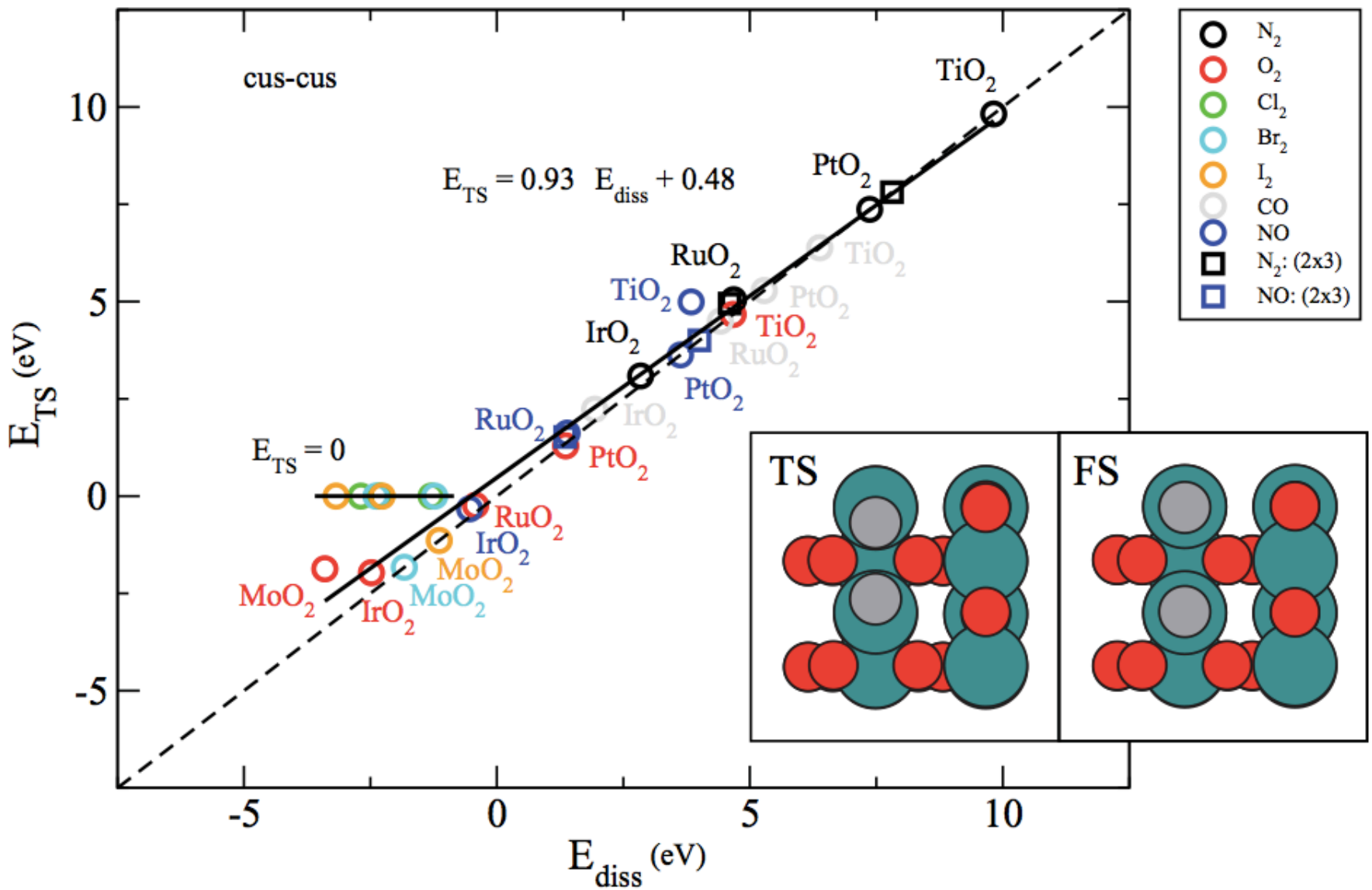
Wang, Petzold, Tripkovic, Kleis, Howalt, Skulason, Fernandez, Hvolbæk, Jones, Toftelund, Falsig, Björketun, Studt, Abild-Pedersen, Rossmeisl, Nørskov, Bligaard, *PCCP (2011)*

Unsaturated hydrocarbons



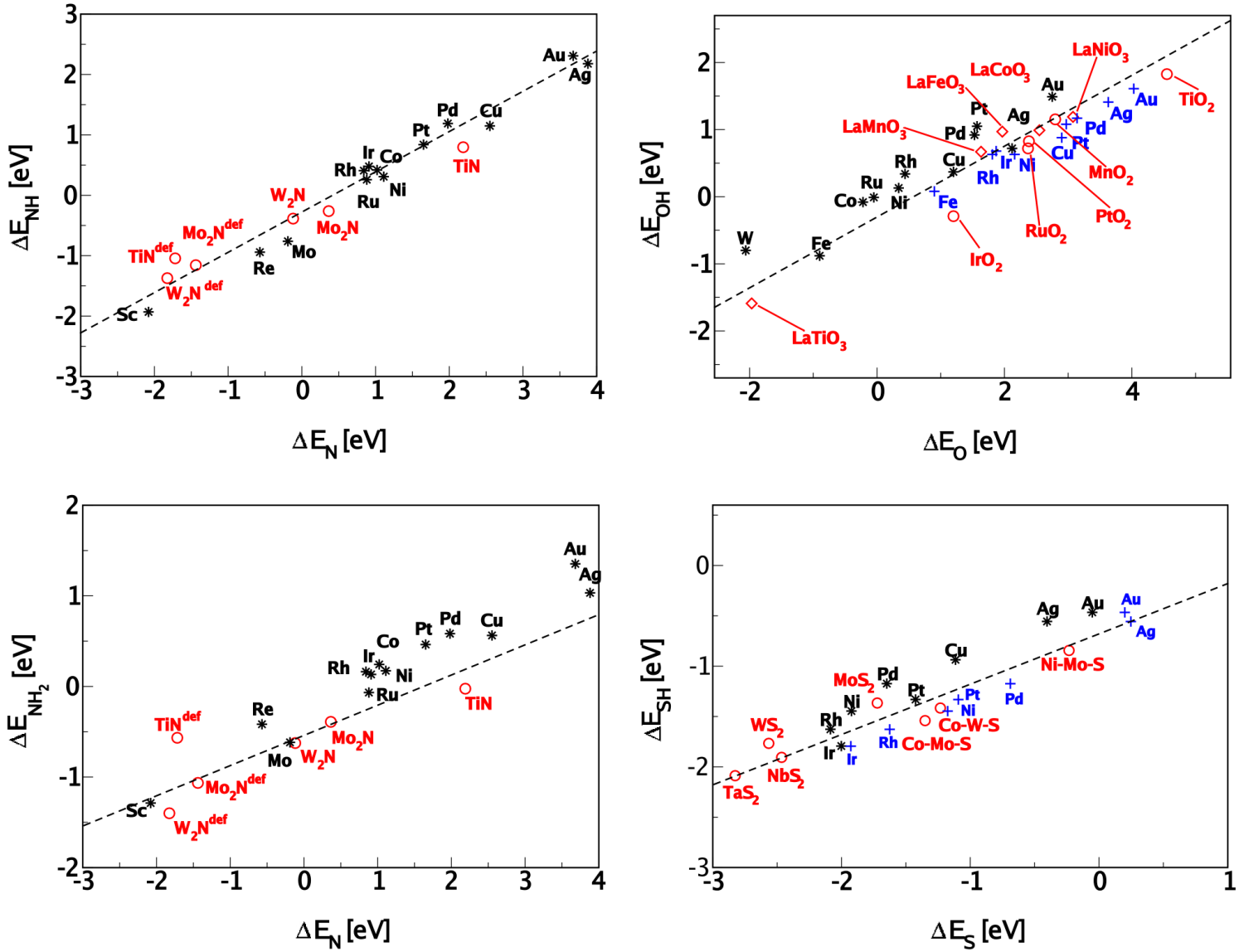
Jones, Studt, Abild-Pedersen, Nørskov, Bligaard, *Chem. Eng. Sci.* (2011)

BEPs for scission over rutile oxides



Vojvodic, Calle-Vallejo, Guo, Wang, Toftelund, Studt, Martínez, Shen, Man, Rossmeisl, Bligaard, Nørskov, Abild-Pedersen, *J. Chem. Phys.* **134**, 244509 (2011)

Scaling over oxides, nitrides, and sulfides



Fernández, Moses, Toftelund, Hansen, Martínez, Abild-Pedersen, Kleis, Hinnemann, Rossmeisl, Bligaard, Nørskov, *Angew. Chem. Int. Ed.* **47**, 4683 (2008)

Computationally "found" heterogeneous catalysts

- Steam reforming — Besenbacher et al., *Science* **279**, 1913 (1998)
- Ammonia synthesis — Jacobsen et al., *J. Am. Chem. Soc.* **123**, 8404 (2001)
- Hydro-desulfurization — Toulhoat et al., *J. Catal.* **216**, 63 (2003)
- CO-tolerant FC anodes — Strasser et al., *Phys. Chem. B* **107**, 11013 (2003)
- Ethylene oxide — Linic et al., *J. Catal.* **224**, 489 (2004)
- Hydrogen activation — Greeley & Mavrikakis, *Nature Materials* **3**, 810 (2004)
- Methanation — Andersson et al., *J. Catal.* **239**, 501 (2006)
  Sehested et al., *Top. Catal.* **45**, 9 (2007)
- Hydrogen evolution — Greeley et al., *Nature Materials* **5**, 909 (2006)
  Jaramillo et al., *Science* **317**, 100 (2007)
- Preferential CO oxidation — Alayoglu et al., *Nature Materials* **7**, 333 (2008)
- Selective acetylene hydrogenation — Studt et al., *Science* **320**, 1320 (2008)
- Electro-reduction of oxygen — Greeley, Rossmeisl, et al. *Nature Chem.* (2009)
- ……

"Towards the computational design of solid catalysts"
J.K. Nørskov, T. Bligaard, J. Rossmeisl, C.H. Christensen
Nature Chemistry **1**, 37-46 (2009)

The Grand Challenge in Catalysis Informatics:

Availability of reliable data

(more stringent than data-rich)

Challenges for data-rich catalysis informatics

- Reproducibility
- Ensuring high quality of data
- Duplication of effort
- The “leaving group-member” problem
- Acceleration through sharing

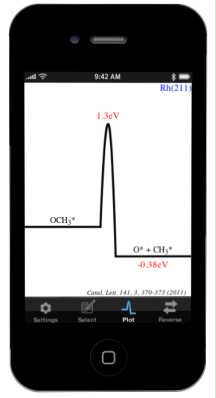
→ These are also opportunities - but requires some “Business Process Re-engineering”

Goal:

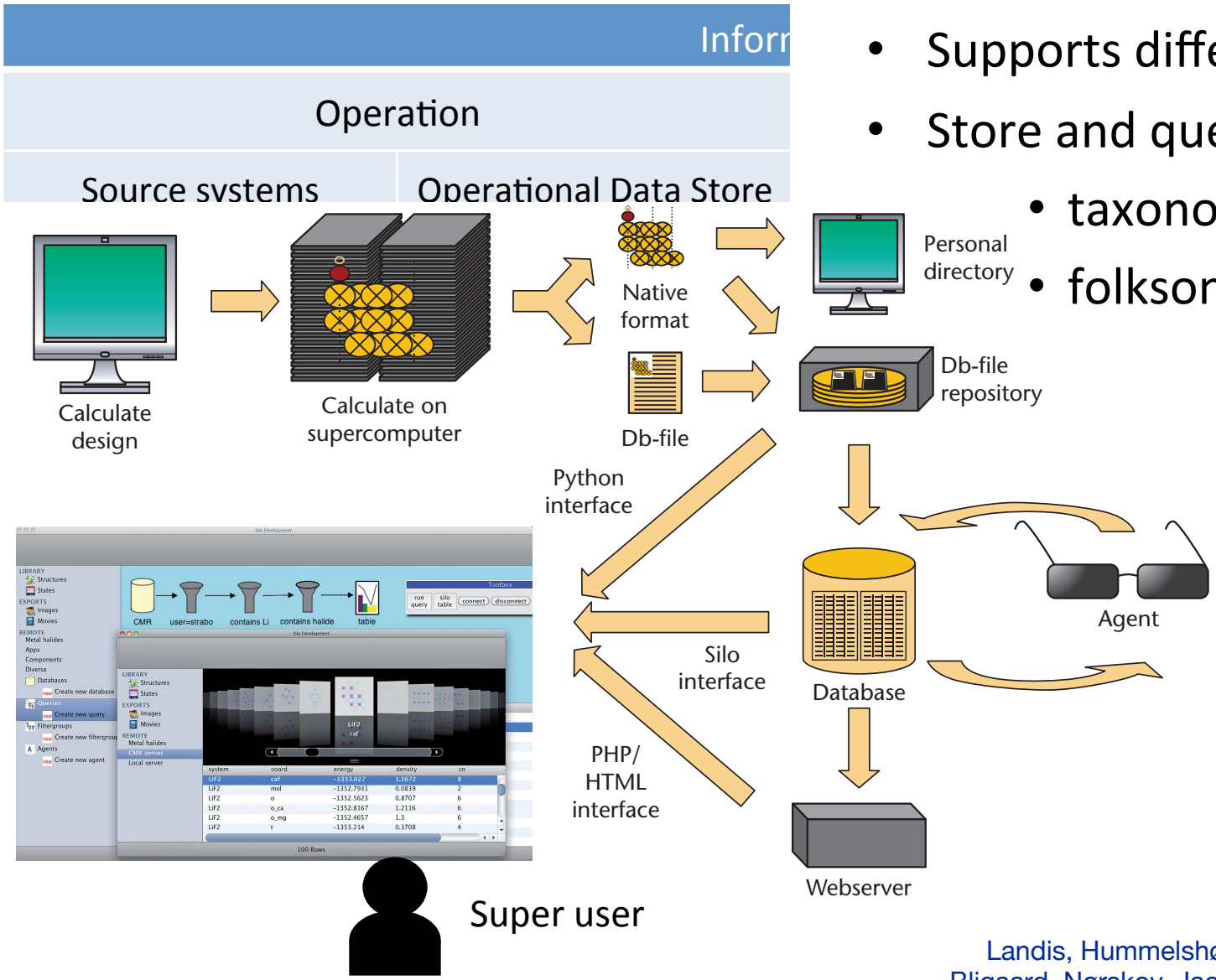
To establish an open repository of high quality electronic structure calculations of relevance for materials (and especially catalyst) design,

which is searchable, scalable, and allows facile comparison and analysis across electronic structure codes.

Informatics has four parts

Informatics			
Operation		Presentation	
Source systems	Operational Data Store	Analytical Data Store	Analytical Applications
VASP, GPAW!, QUANTUMESPRESSO, ASE	File system COMPUTATIONAL MATERIALS REPOSITORY		
Produce	Manage	Integrate	Analyze

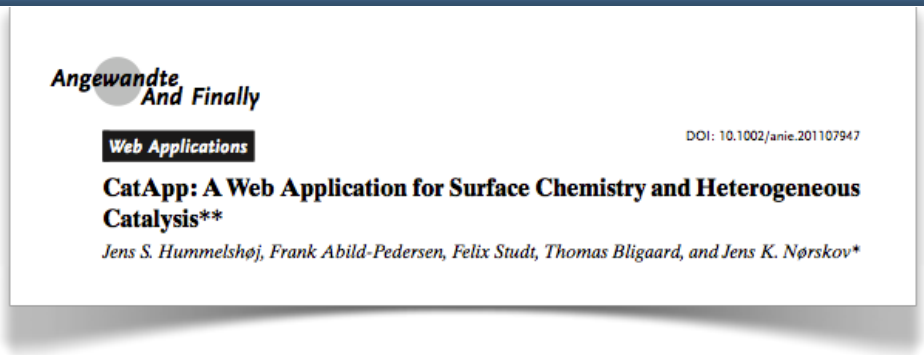
CMR provides a database for super users



- Supports different codes
- Store and query any result
  - taxonomy
  - folksonomy

Landis, Hummelshøj, Nestorov, Greeley, Dulak, Bligaard, Nørskov, Jacobsen, CiSE 14, 6, p 51 (2012)

CatApp enables sharing of elementary surface reactions


Angewandte And Finally

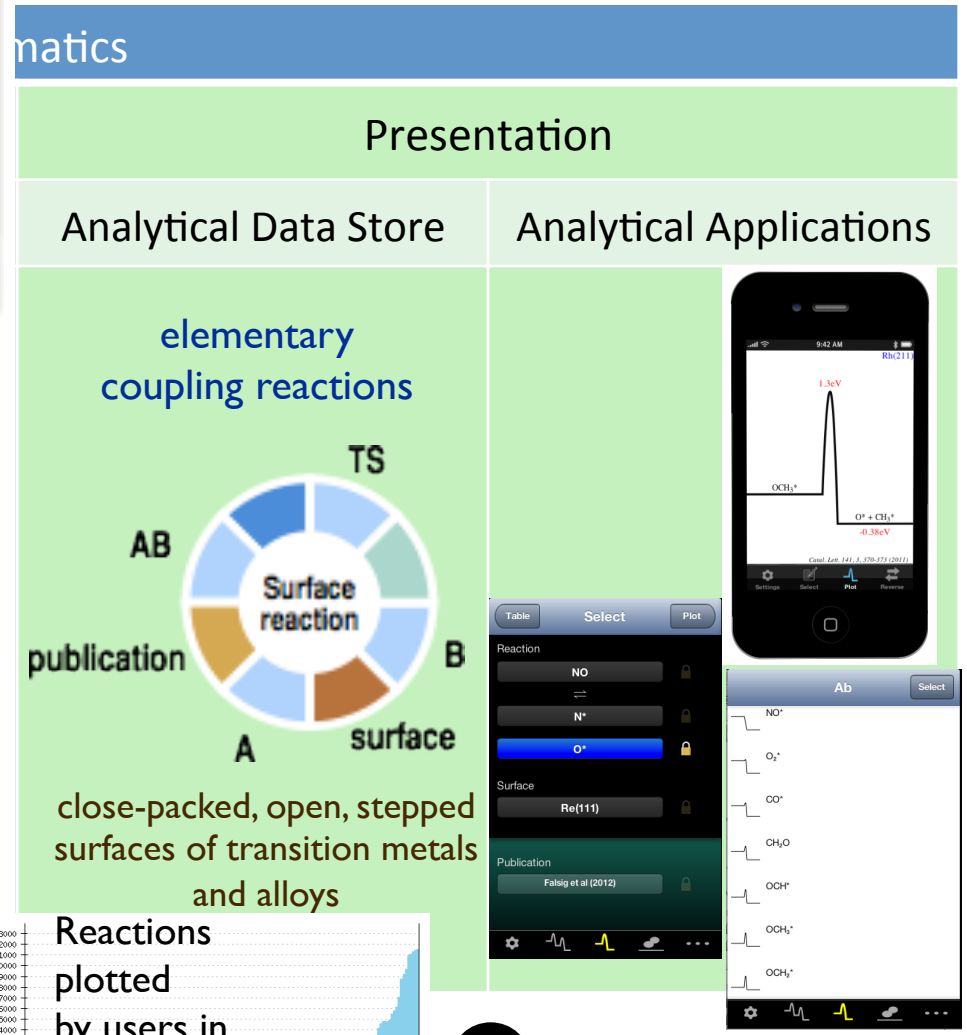
Web Applications

DOI: 10.1002/anie.201107947

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

*Jens S. Hummelshøj, Frank Abild-Pedersen, Felix Studt, Thomas Bligaard, and Jens K. Nørskov**

- ~4500 reactions
- Link to publications
- Versatile coupling reaction
- Upload
- Offline privacy
- Ready for future extensions
- Used in research and education

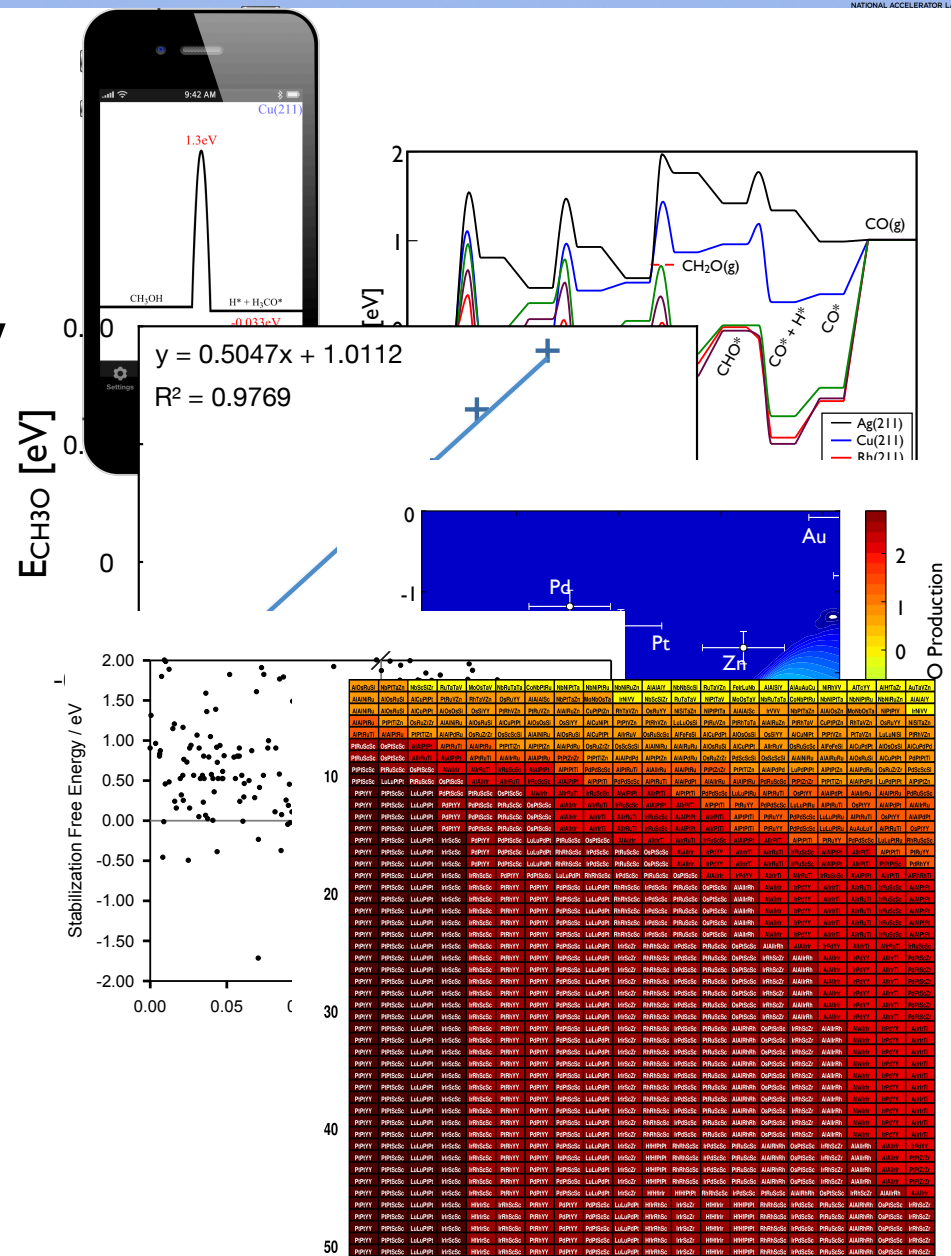


Lausche, Hummelshøj, Abild-Pedersen, Studt, Nørskov, *J. Catal.* **291**, 133 (2012)
Xu, Lausche, Wang, Khan, Abild-Pedersen, Studt, Nørskov, Bligaard, J. Catal. *(2013)*

New informatics tools in catalysis

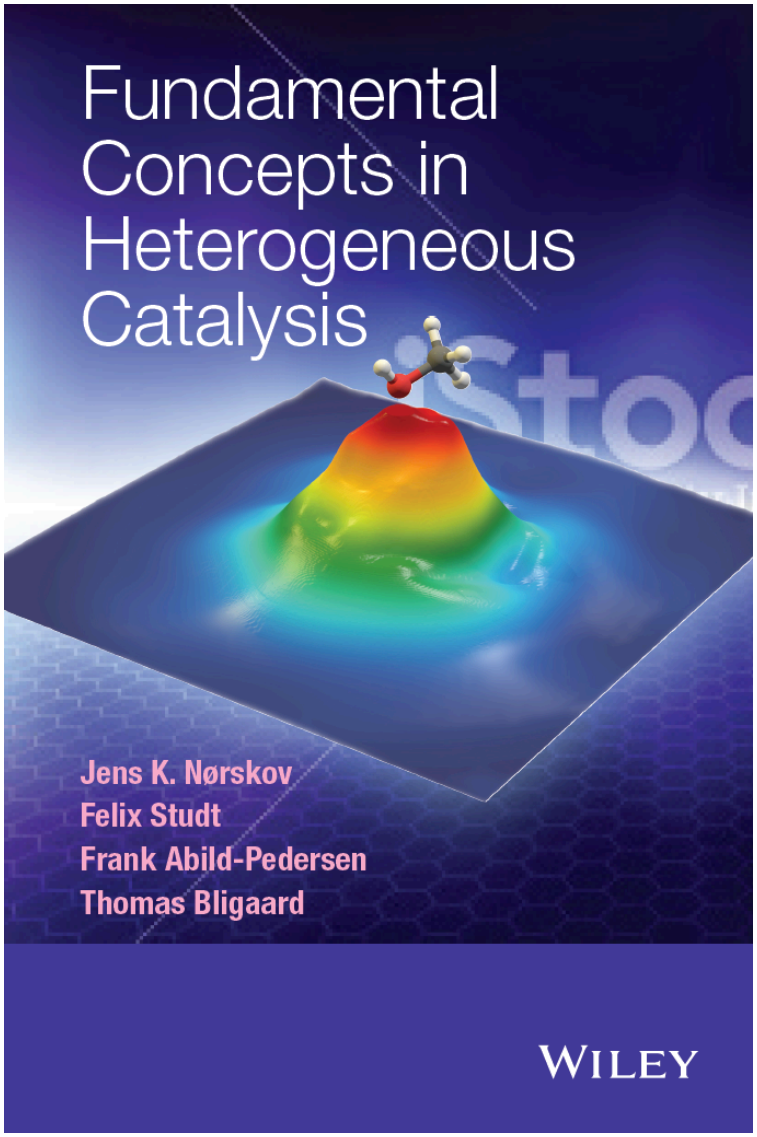
From data-poor to data-rich:

- Easy access to data
- Easy access to papers
- Outlining the potential energy diagrams
- Links to structures, vibrational spectra, XPS …..
- Discovering correlations in data
- Overview of trends
- Coupling of different databases
- Data mining
- Free your imagination ….



Publicity

Now available
from Wiley!



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Thanks !