A First-Principles Approach to Catalytic H_2 Production and Chemistry:

Reaction Mechanisms and Identification of Promising Catalysts

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Outline

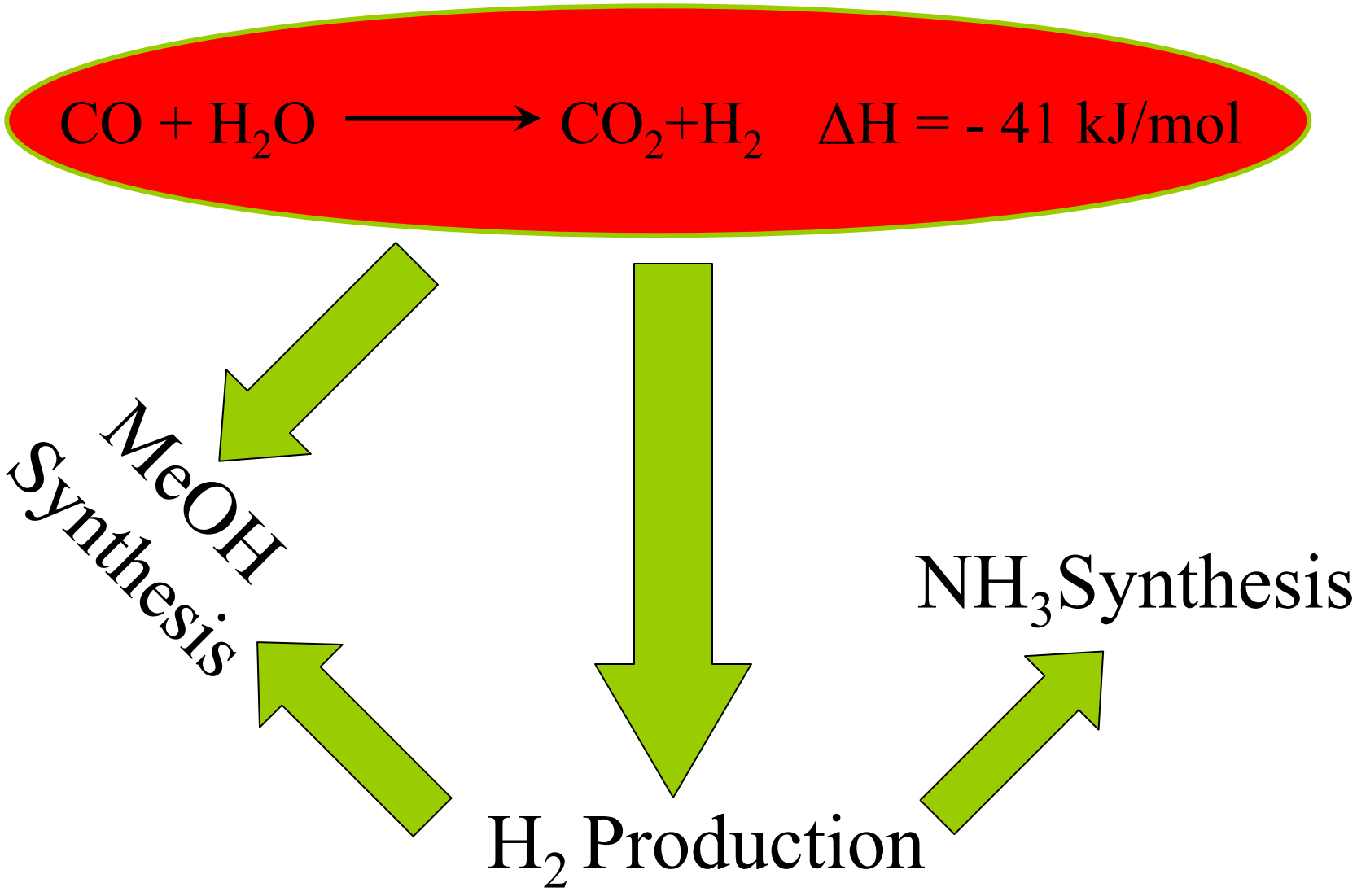
- H_2 production:
  - An alternative mechanism for the Low Temperature *Water Gas Shift* Reaction

- H_2 catalytic chemistry:
  - Identifying Promising Catalysts from 1st Principles:

    H_2 and H on Bimetallic Near Surface Alloys (NSAs)

Water Gas Shift Reaction (WGSR)

Ovesen, Stoltze, Nørskov, Campbell – J. Cat. 134, 445 (1992)
Ovesen, et.al. – J. Cat. 158, 170 (1996)
C.T. Campbell – Studies in SS and Catalysis 38, 783 (1988)



Reaction Mechanisms

$CO(g) + * \rightarrow CO*$

$H_2O(g) + * \rightarrow H_2O*$

$H_2O* + * \rightarrow OH* + H*$

Red-ox Mechanism

$OH* + * \rightarrow O* + H*$

$OH* + OH* \rightarrow H_2O* + O*$

$CO* + O* \rightarrow CO_2* + *$

Carboxyl Mechanism

$CO* + OH* \rightarrow COOH* + *$

$COOH* + * \rightarrow CO_2* + H*$

$COOH* + OH* \rightarrow CO_2* + H_2O*$

$COOH* + O* \rightarrow CO_2* + OH*$

$H* + H* \rightarrow H_2(g) + 2*$

$CO_2* \rightarrow CO_2(g) + *$

Formate Reactions

$CO_2* + H* \rightarrow HCOO**$

$CO_2* + H_2O* + * \rightarrow HCOO** + OH*$

$CO_2* + OH* + * \rightarrow HCOO** + O*$

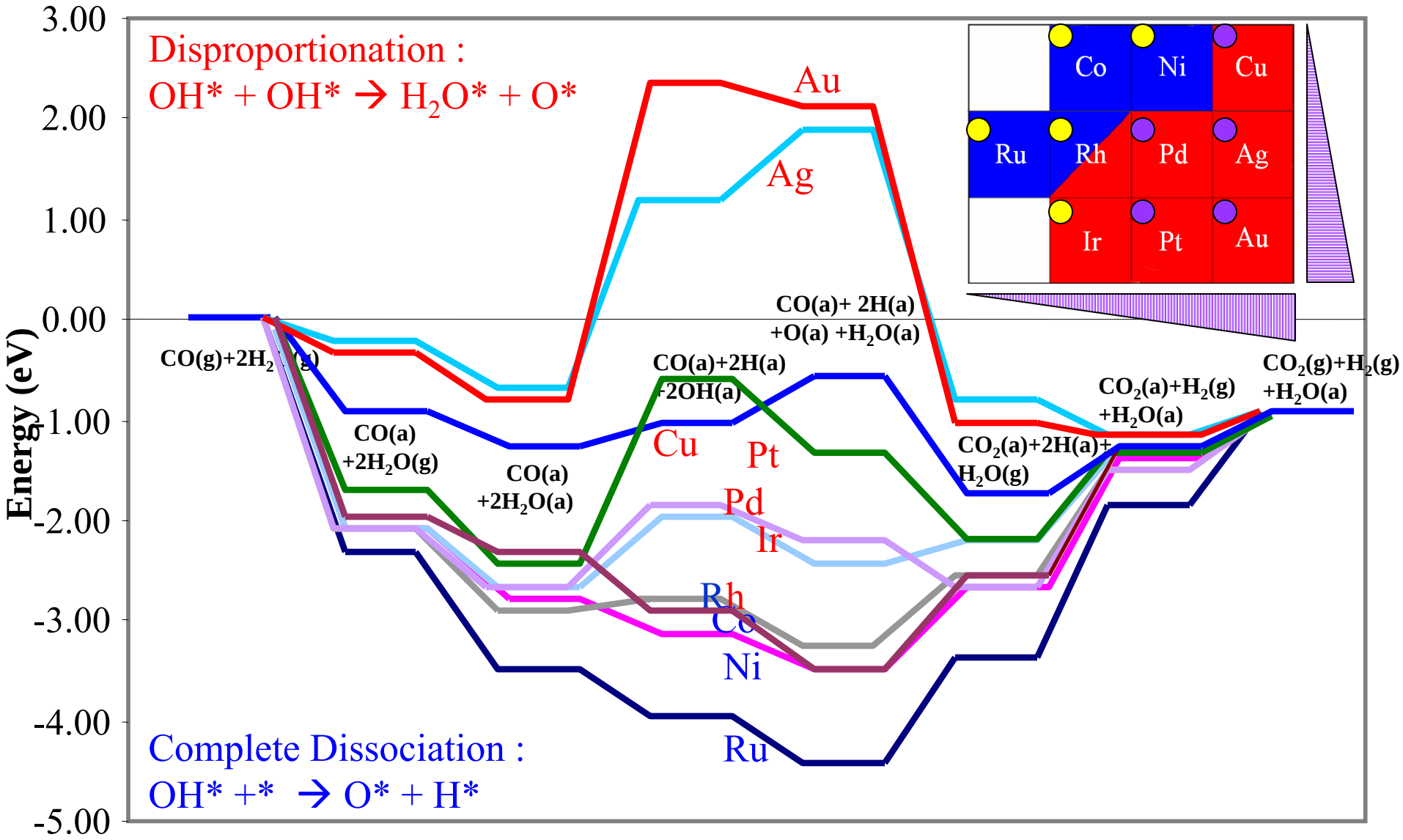
Methods

- Density Functional Theory – DACAPO total energy code [1,2]
- Periodic self-consistent PW91-GGA [3]
- Ultra-soft Vanderbilt pseudo-potentials [4]
- Plane wave basis sets with 25-Ry kinetic energy cut-off
- Spin polarization as needed
- Four-metal-layer slabs; (2x2) unit cell; top two layers relaxed
- First Brillouin zone sampled at 18 *k*-points
- Nudged Elastic Band method for reaction paths [5]

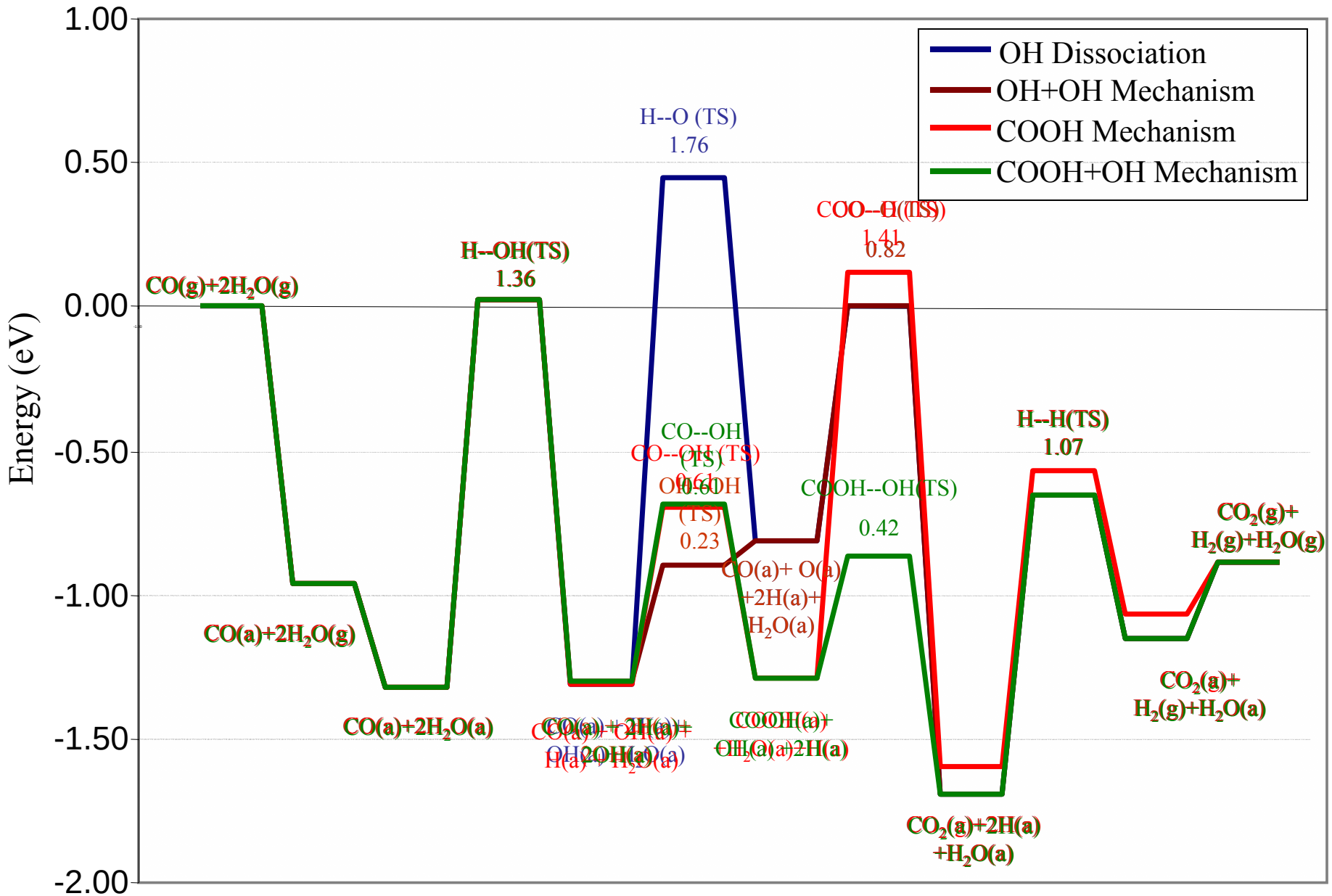
1. B. Hammer, L. B. Hansen, J. K. Nørskov, *Phys. Rev. B* 59, **1999**, 7413.
2. J. Greeley, J. K. Nørskov, M. Mavrikakis, *Annu. Rev. Phys. Chem.* 53, **2002**, 319.
3. J. P. Perdew *et al.*, *Phys. Rev. B* 46, **1992**, 6671.
4. D. H. Vanderbilt, *Phys. Rev. B* 41, **1990**, 7892.
5. G. Henkelman, H. Jónsson, *J. Chem. Phys.* 113, **2000**, 9978.

Thermochemistry of WGS on TM(111)

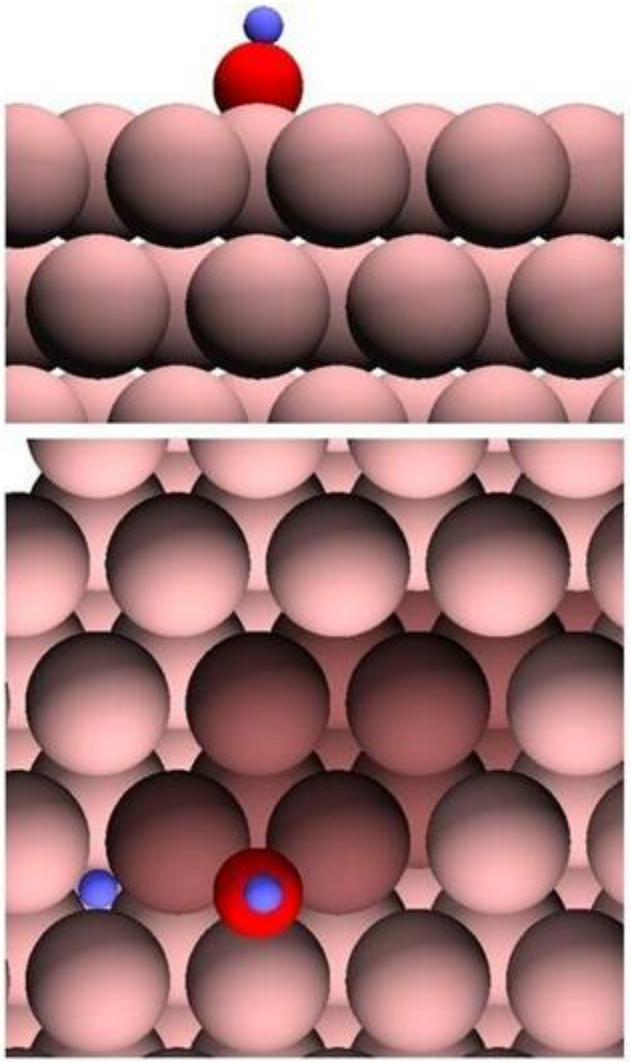
Redox Mechanism

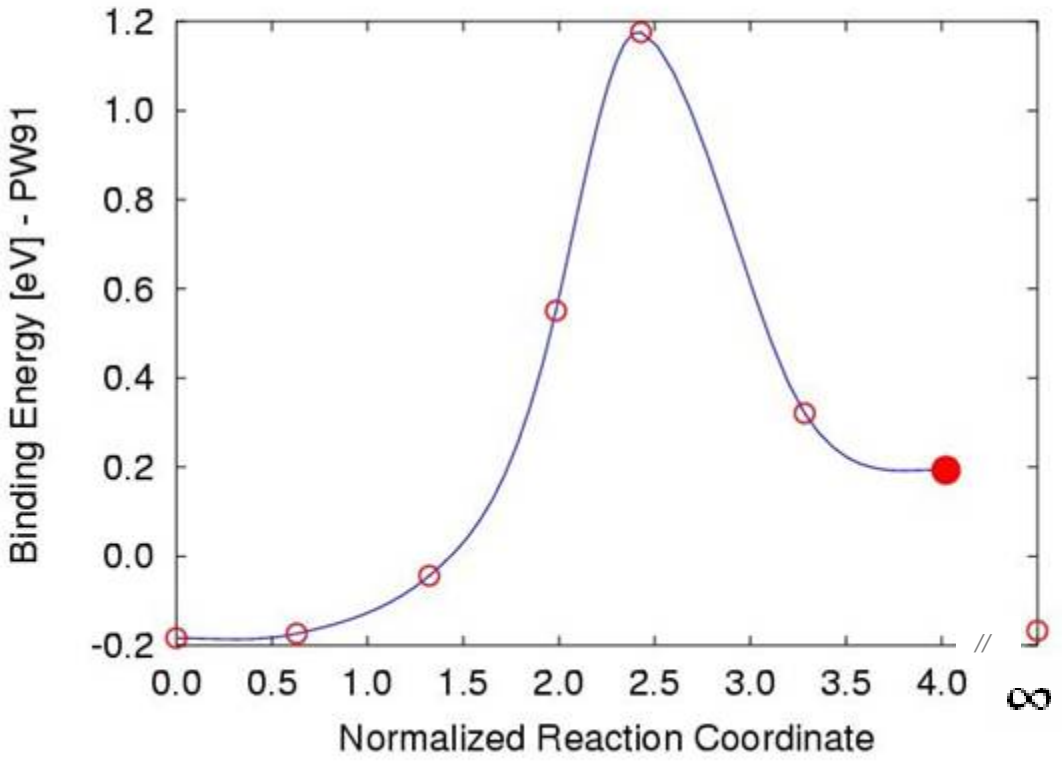


PES for Water Gas Shift Reaction on Cu(111)

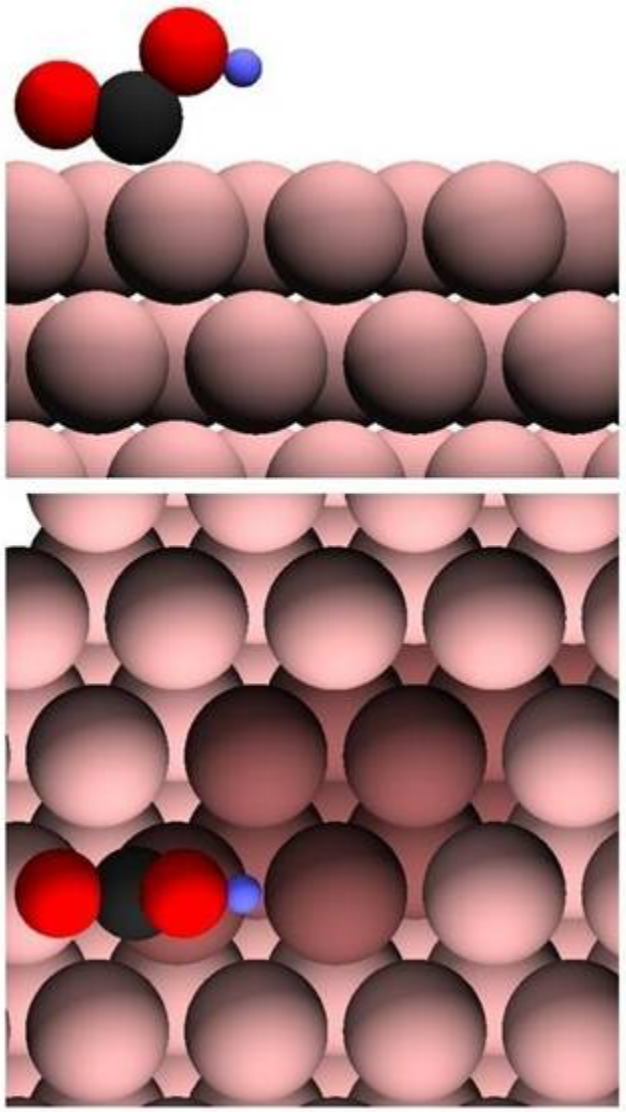


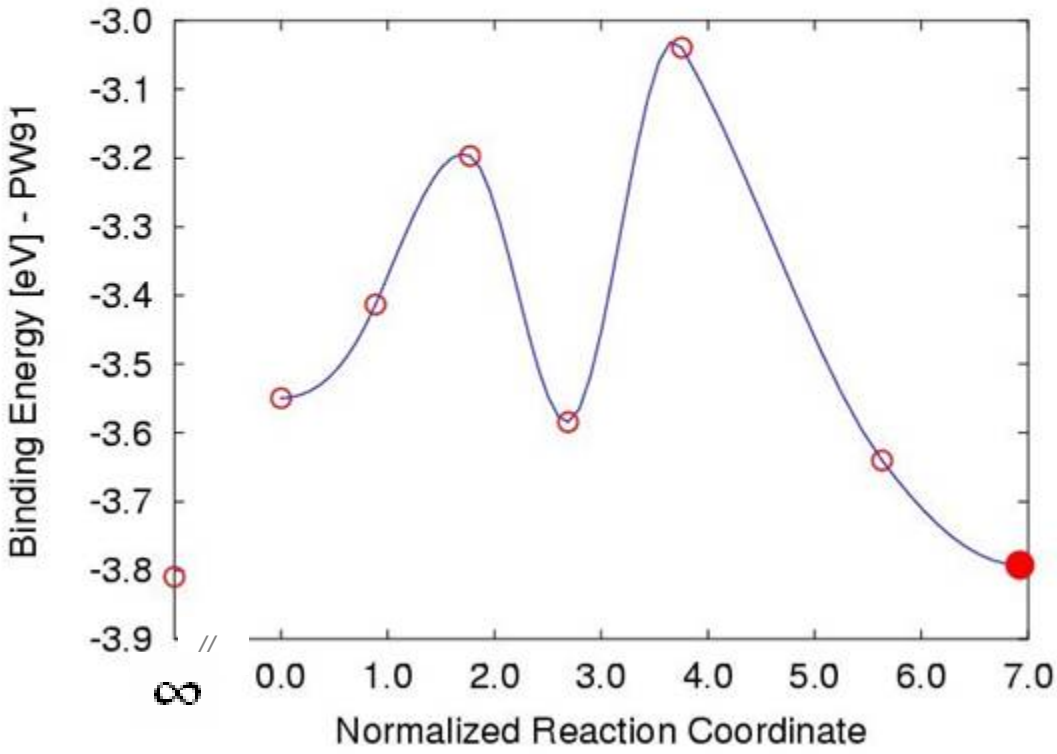
H_2O Dissociation on Cu(111)



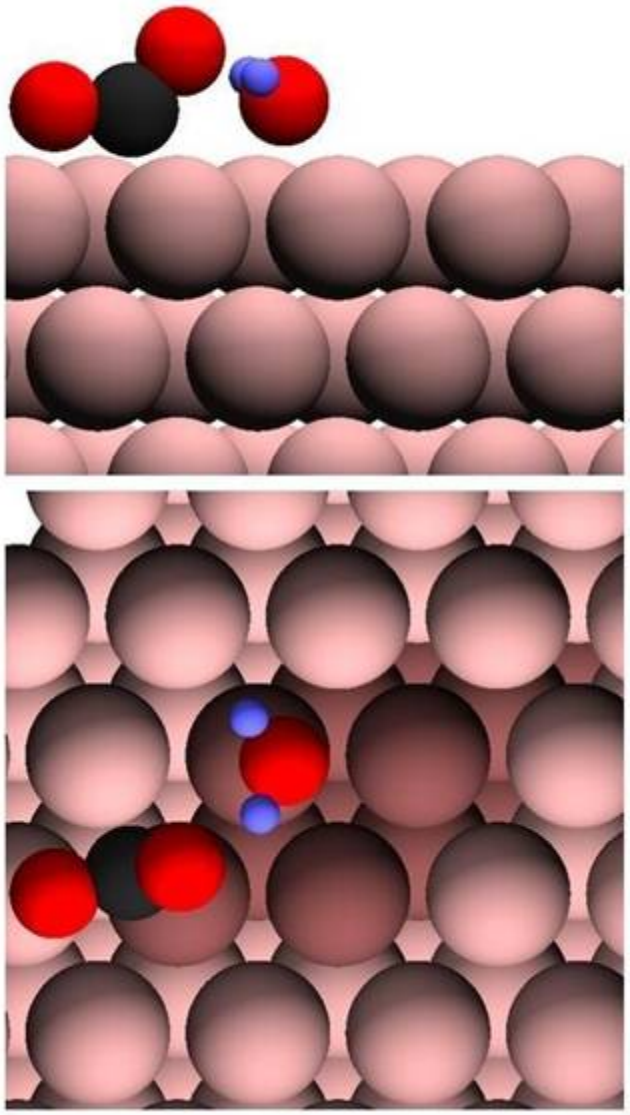


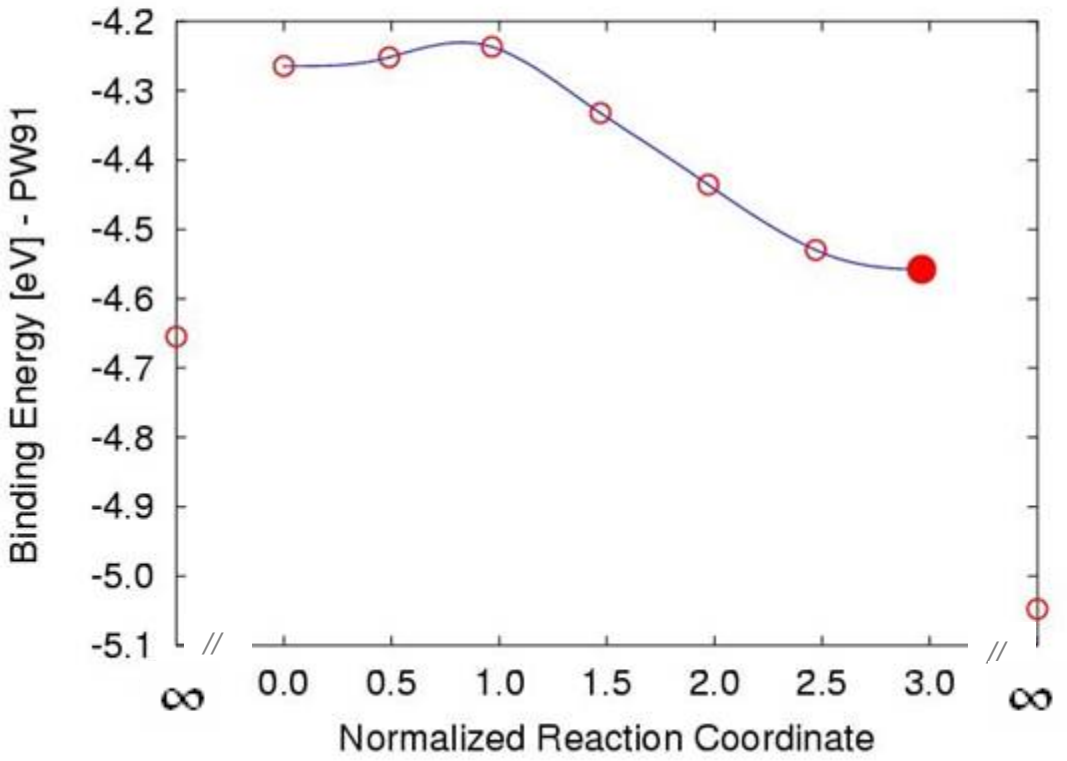
Carboxyl Formation on Cu(111)





COOH + OH reaction on Cu(111)





WGSR/Cu Mechanism: Key points

• WGSR mainly proceeds via *COOH intermediate*, which decomposes via the COOH+OH reaction.

• *H_2O Activation* is the *RCS*.

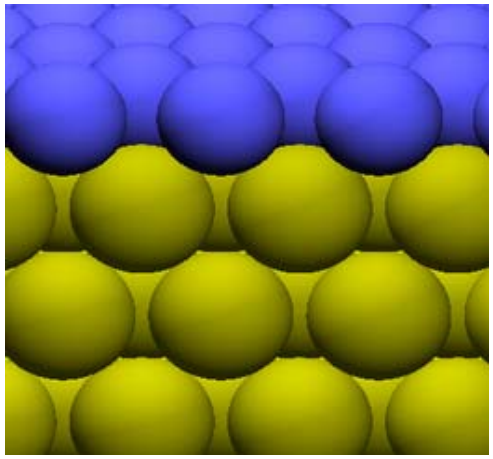
• *Formate*, a stable *spectator* species, is formed from CO_2* and H*. Formate formation is equilibrated with CO_2 and H*.

• The combination of *DFT* and *Microkinetics* shows that we can fairly accurately predict experimental WGSR rates directly from *First Principles*.

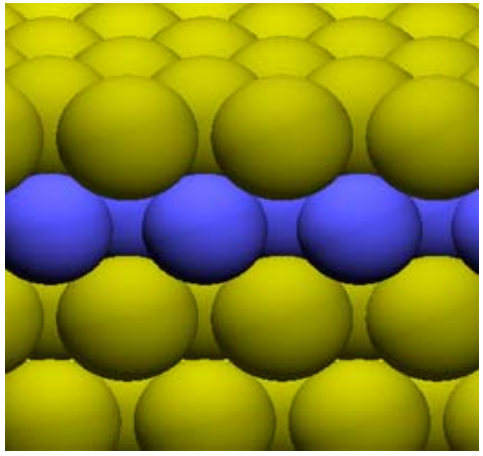
Ideal Bimetallic Near Surface Alloys

- Segregation properties of two metals are critical
- Consider two special classes:
  - Overlayers
  - Subsurface Alloys

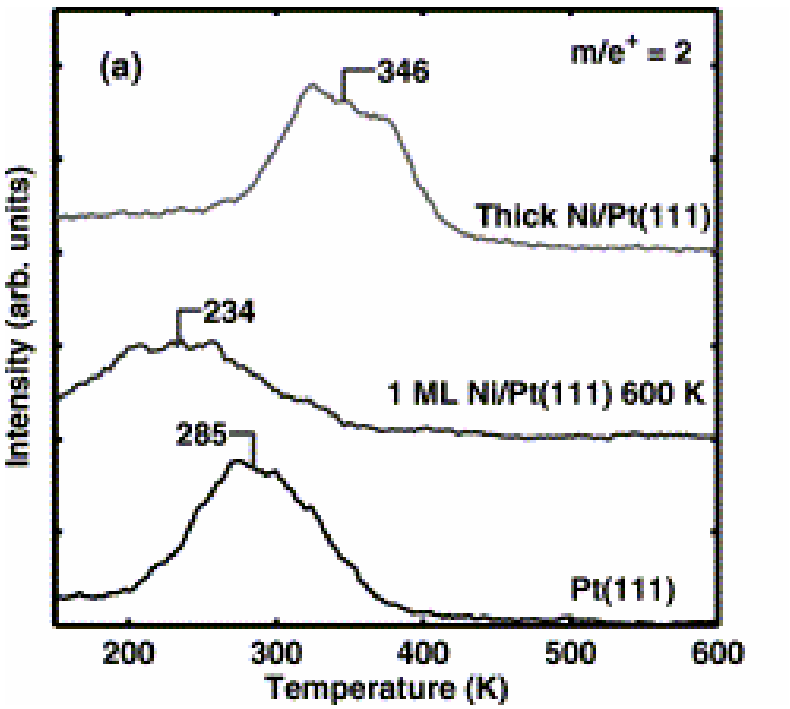
Overlayers*



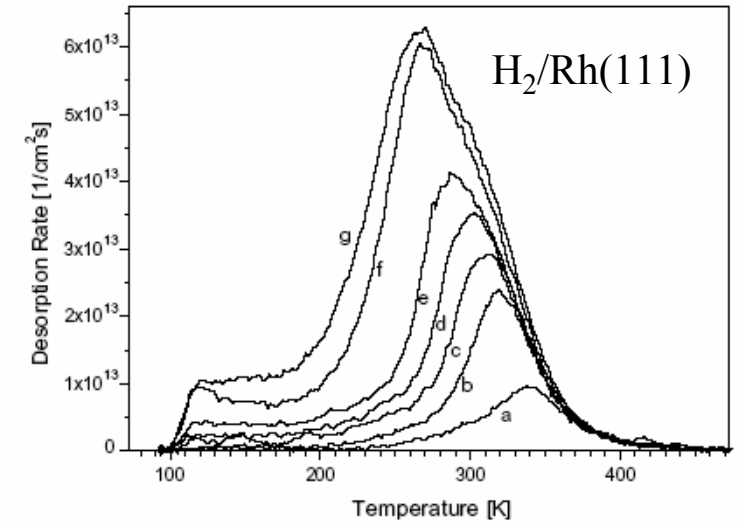
Subsurface Alloys

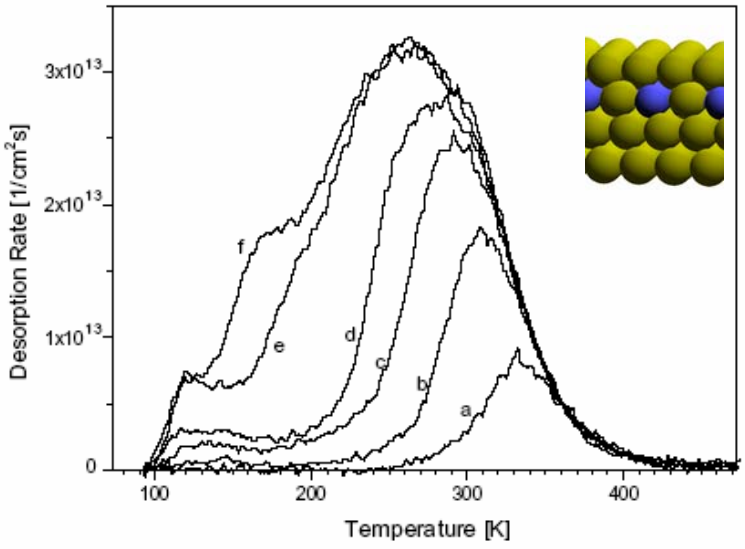


Hydrogen on NSA's



[1]Ni/Pt(111)



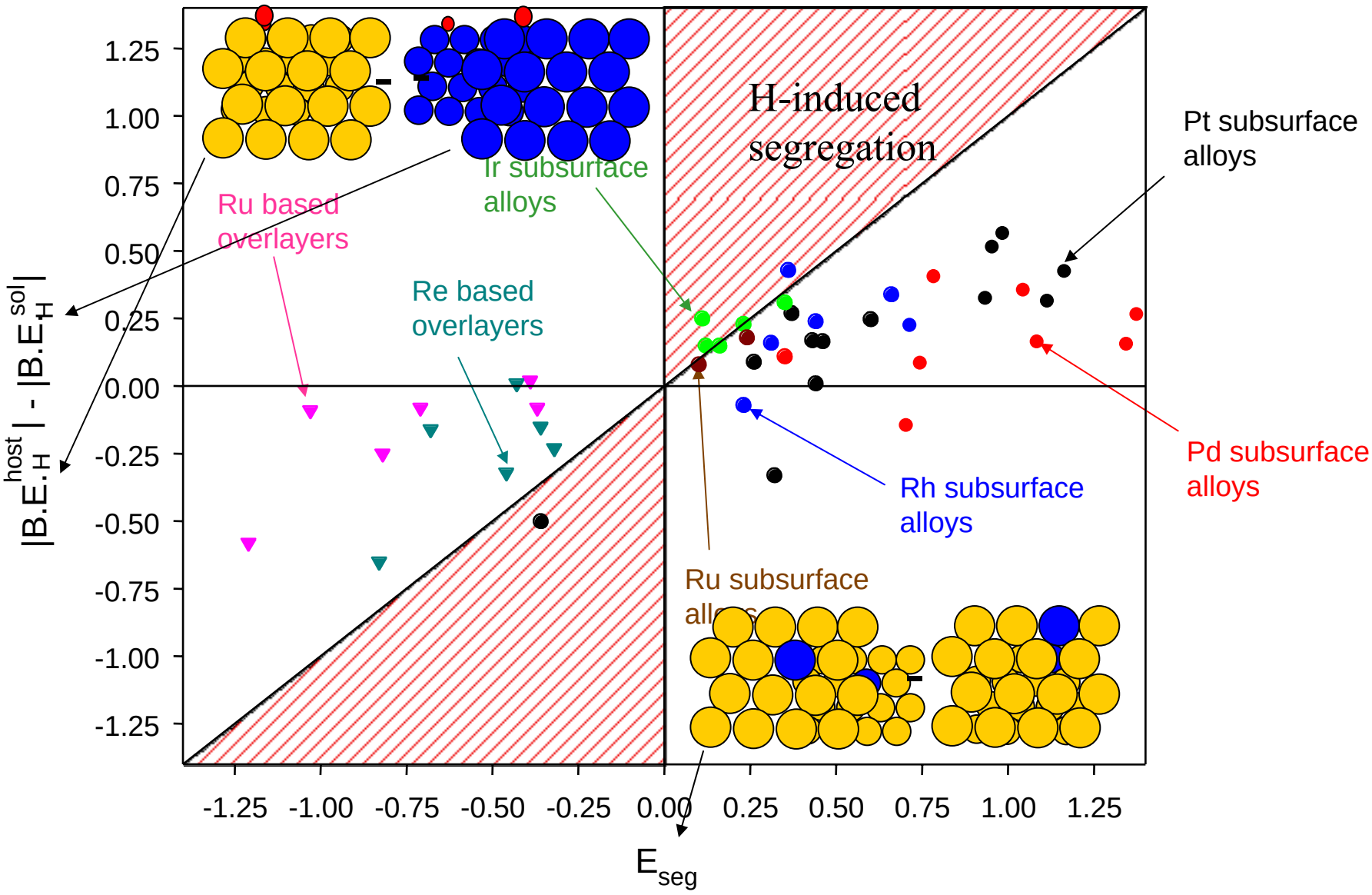


[2]V/Rh(111)

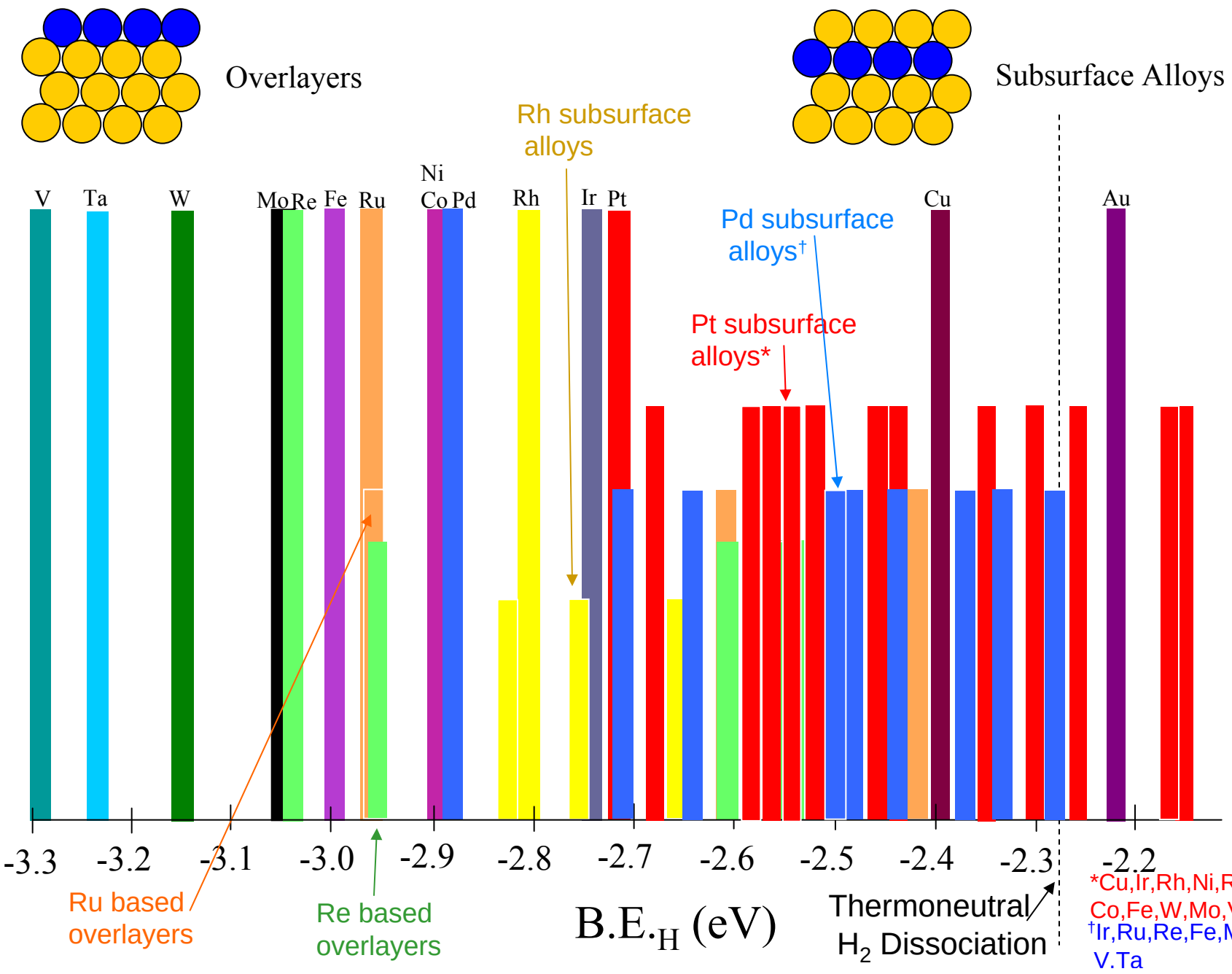
1. J. Kitchen, N. Khan, M. Barteau, J. Chen, B. Yashhinskiy, and T. Madey, Surf. Sci. **544** (2003) 295

2. R. Schennach, G. Krenn, B. Klötzer, K. Rendulic, Surf. Sci. **540** (2003) 237

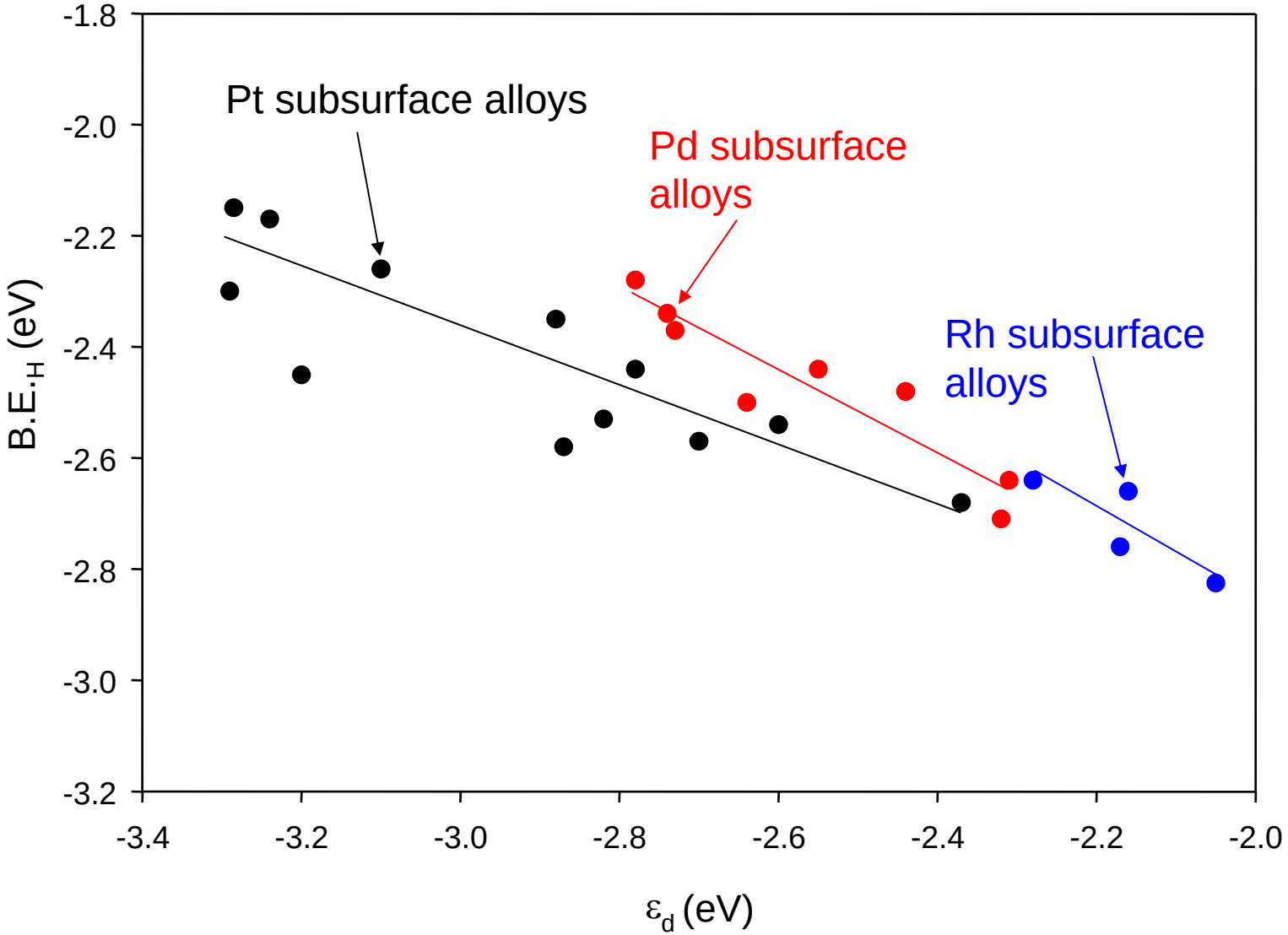
Stability of NSA's with respect to Hydrogen-induced Segregation



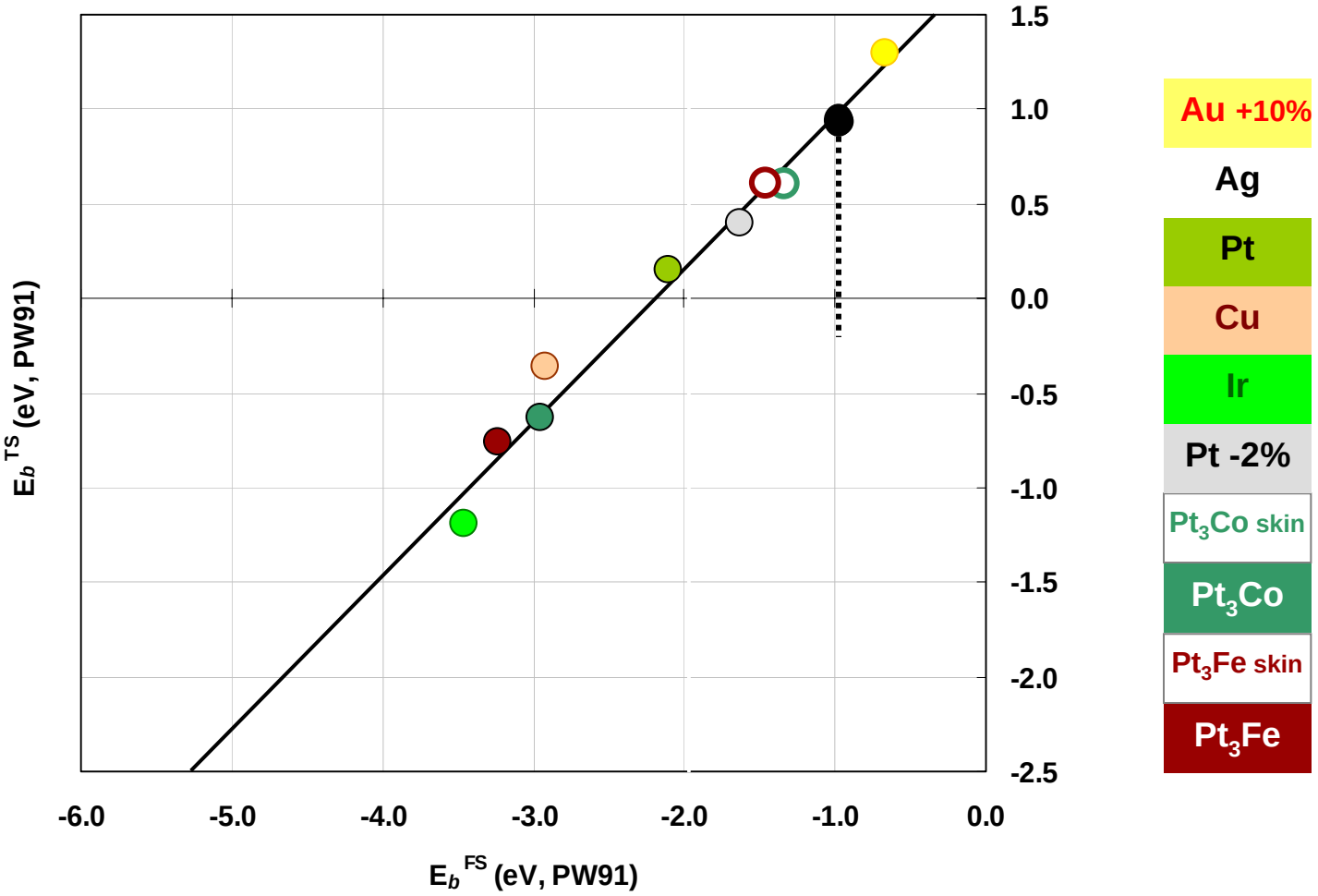
H Binding Energy Spectrum



Correlation of $B.E._H$ with Clean Surface Properties



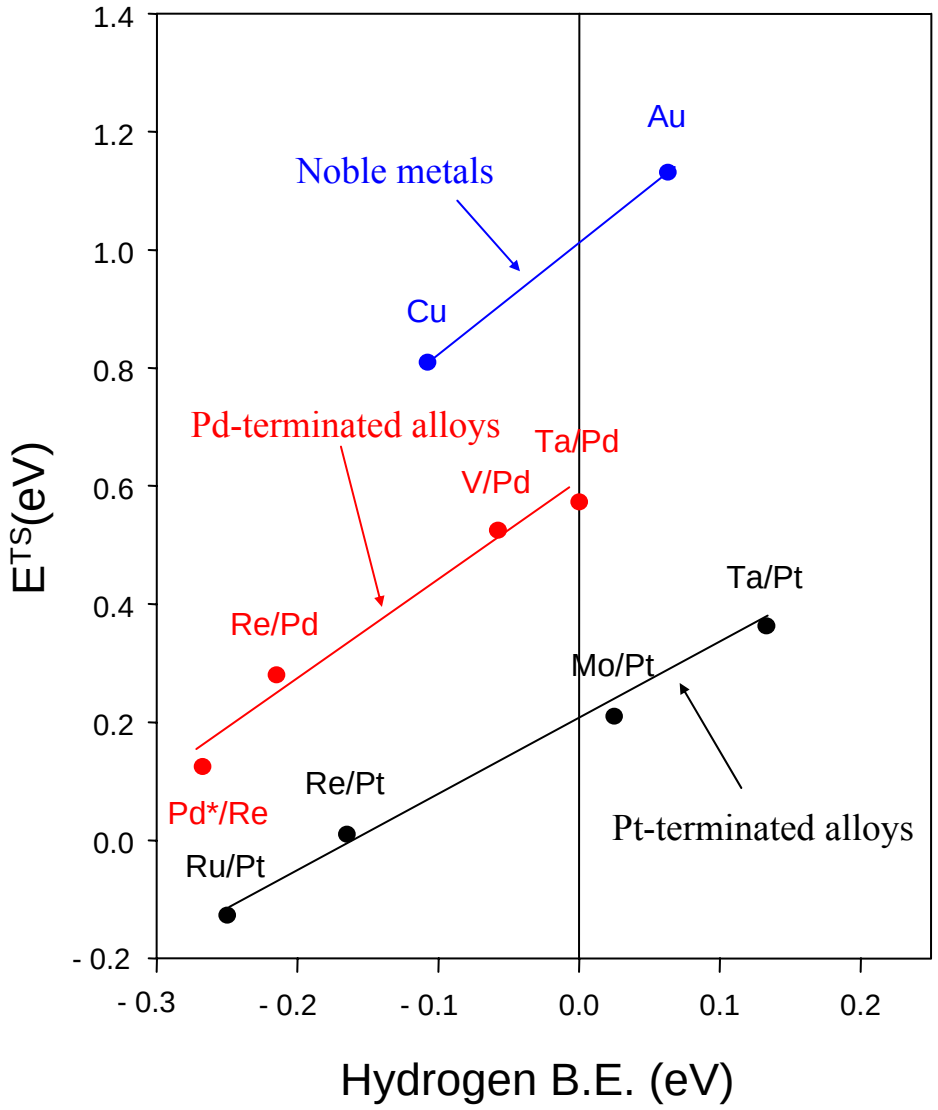
O_2 dissociation: Does E_b^{TS} follow E_b^{FS}?



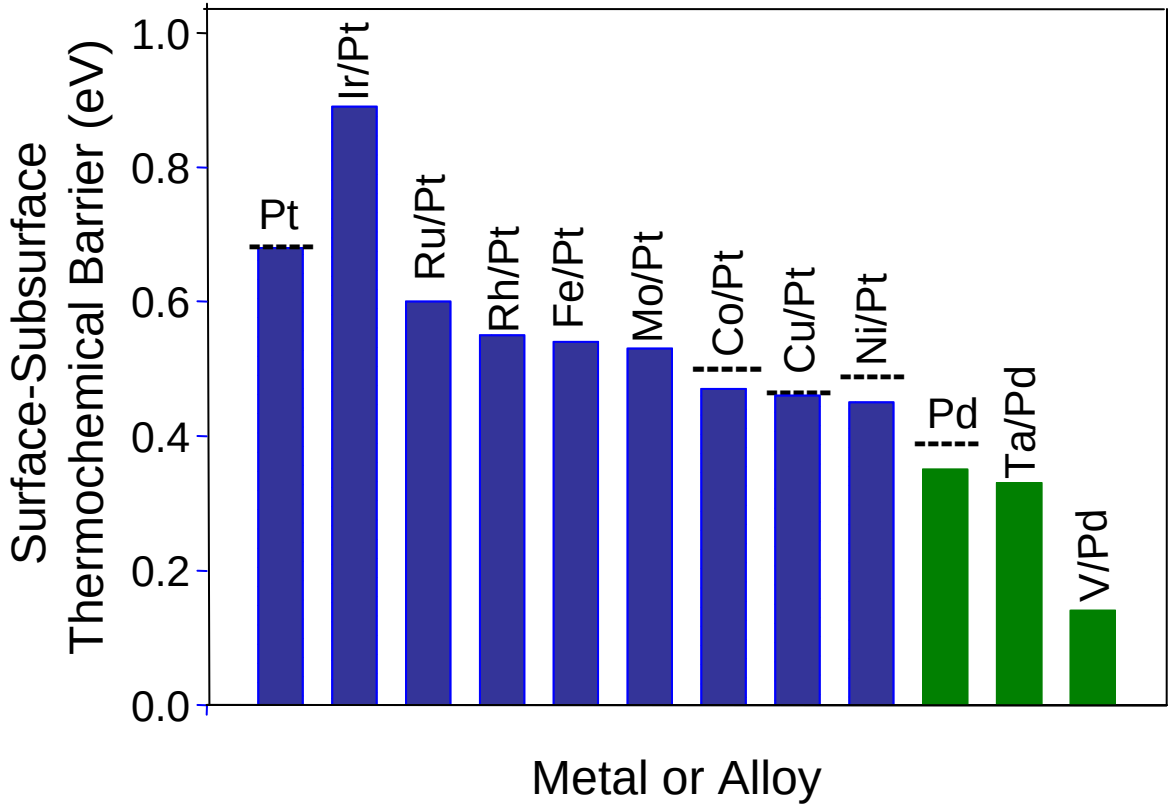
Y. Xu, A. V. Ruban, M. Mavrikakis, *JACS* 126, 4717 (2004).

BEP Plot for H_2 Dissociation on NSA's

J. Greeley, M. Mavrikakis, *Nature Materials* 3, 810 (2004)



Surface to *Subsurface* Diffusion of H
Thermochemical Barrier



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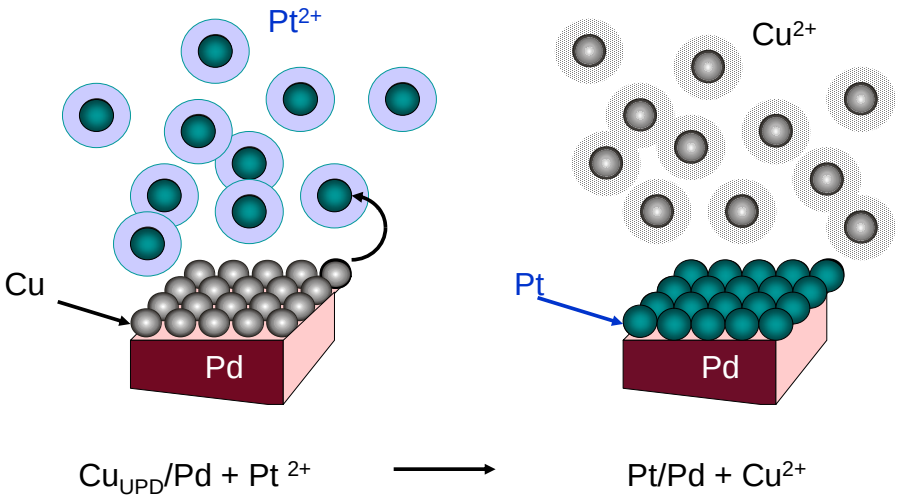
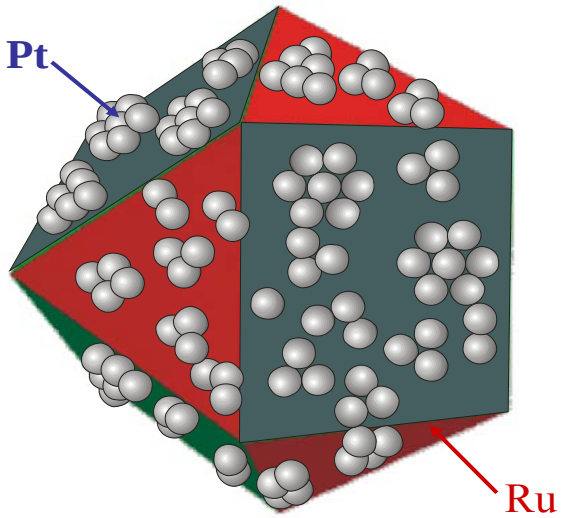
Metal monolayer deposition by galvanic displacement of a less noble metal monolayer deposited at underpotentials



Brankovic, S. R.; Wang, J. X.; Adzic, R. R. *Surf. Sci.* **2001**, *474*, L173

Zhang, J.; Vukmirovic, M.; Xu, Y.; Mavrikakis, M.; Adzic, R. R. *Angew. Chem. Int. Ed.* (*in press*).

Electroless (spontaneous) deposition of one metal on another metal



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NSA's - Summary

- First-Principles Methods can help with identifying promising bimetallic NSAs with interesting catalytic properties

- Example:
  1. H and H_2 on NSA's: Fine-tuning BE_H is possible
  2. Some NSA's:
     - 2.1. Activate H_2 easily AND bind atomic H weakly → useful for highly selective low T H-transfer reactions
     - 2.2. Allow easy H diffusion into the bulk (catalysis of H-storage)

- Developing Catalyst Preparation Techniques with Layer-by-Layer control of metal deposition (ALD-like) is critical for making the desired NSAs

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