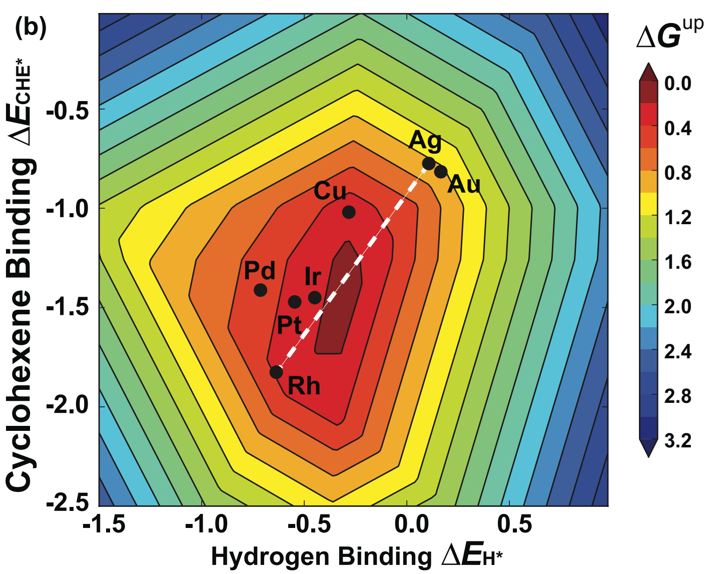
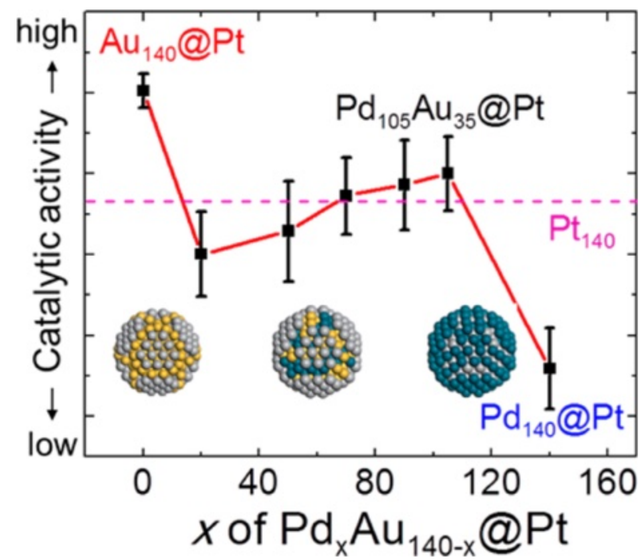
Correlating structure and function for nanoparticle catalysts

Graeme Henkelman
University of Texas at Austin

Co-workers
Liang Zhang, Zhiyao Duan, Long Luo, Hao Li, Lei Li, Hyun You Kim, and Kihyun Shin

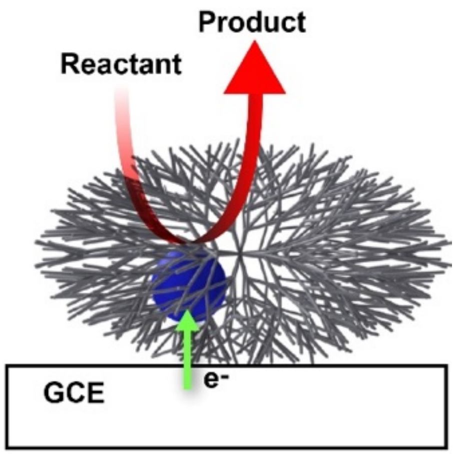


vs

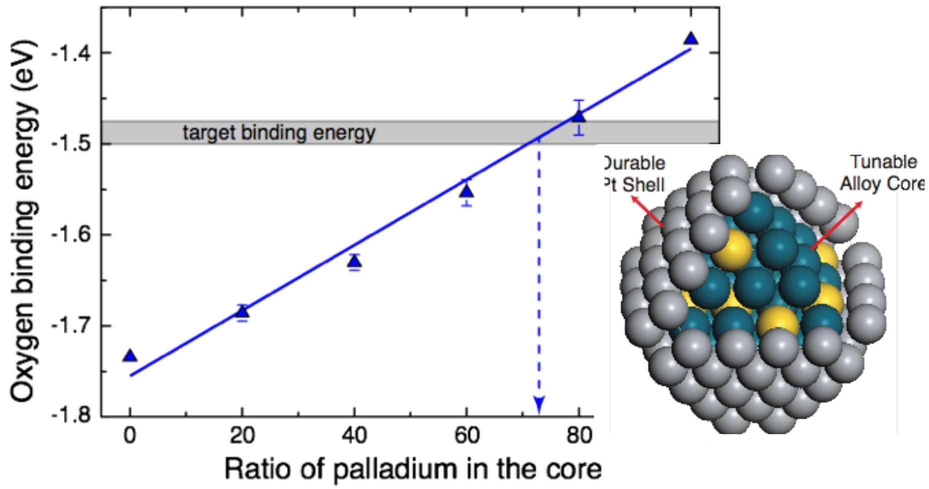


Catalyst design cycle

Evaluation

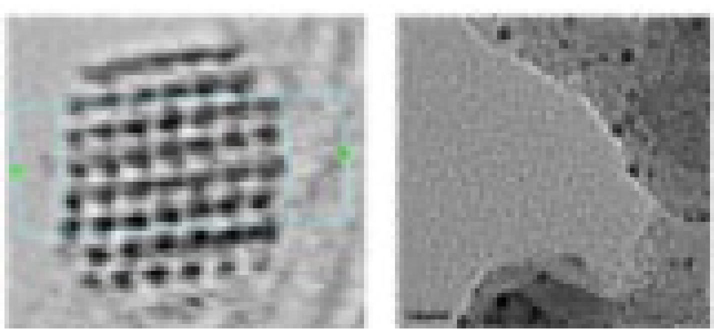


Modeling and Prediction

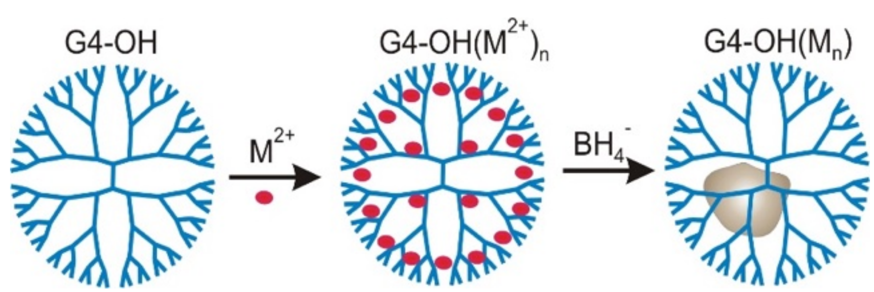


Novel Catalysts

Characterization

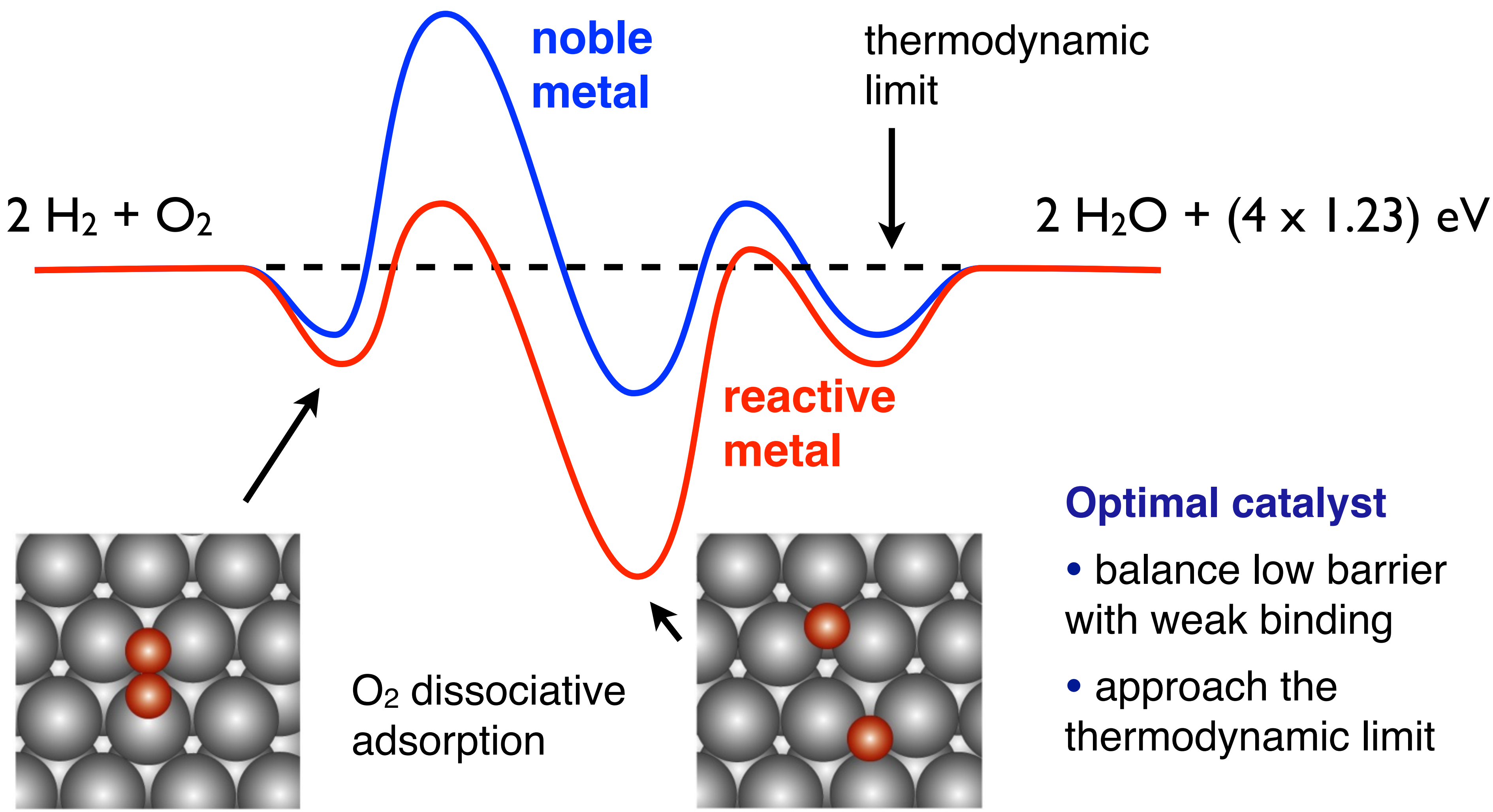


Synthesis



Modeling catalysis

Oxygen reduction: different catalysts change both the energy of saddle points and the binding energy of products

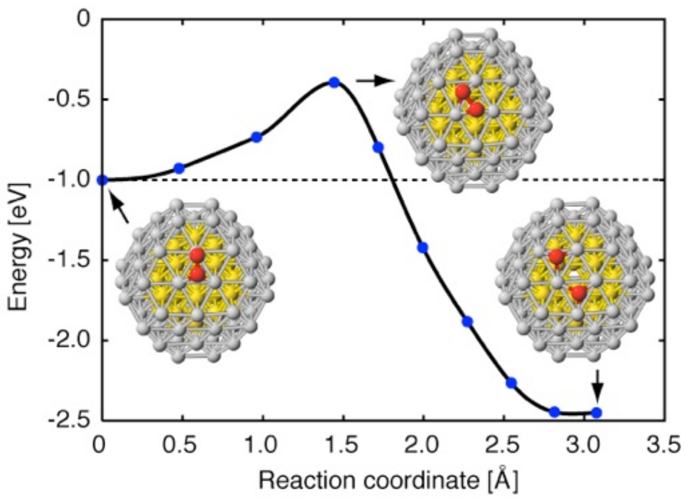


Optimal catalyst

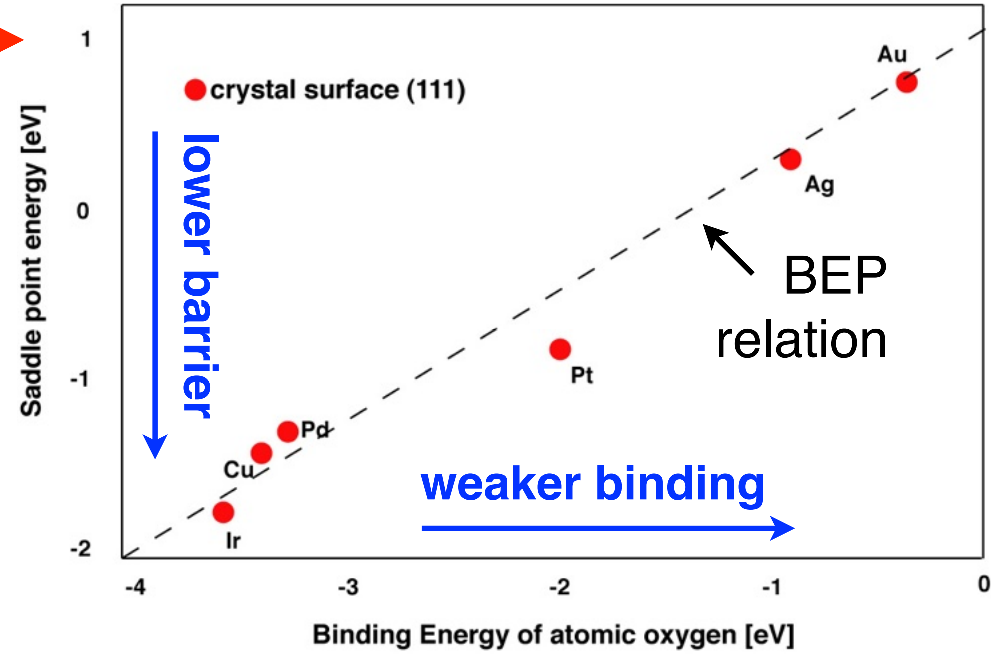
- balance low barrier with weak binding
- approach the thermodynamic limit

Brønsted-Evans-Polanyi relation

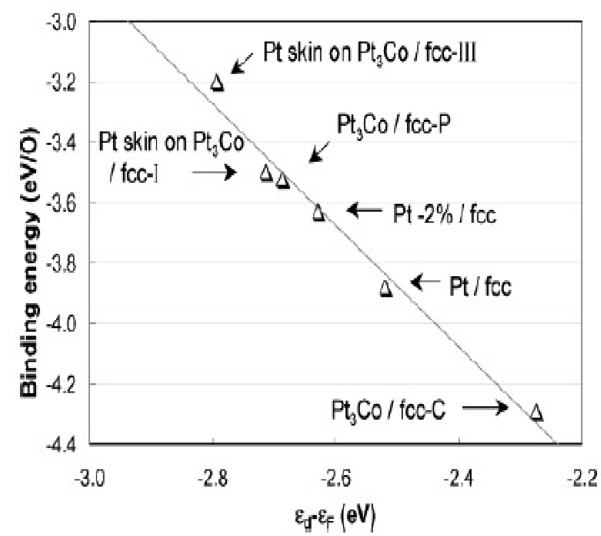
Similar catalysts: saddle point energies are linearly related to reaction energies



O_2 dissociative adsorption



Electronic structure:
Barriers and binding energies are both determined by the energy of the bonding electronic states **(*d*-band)**

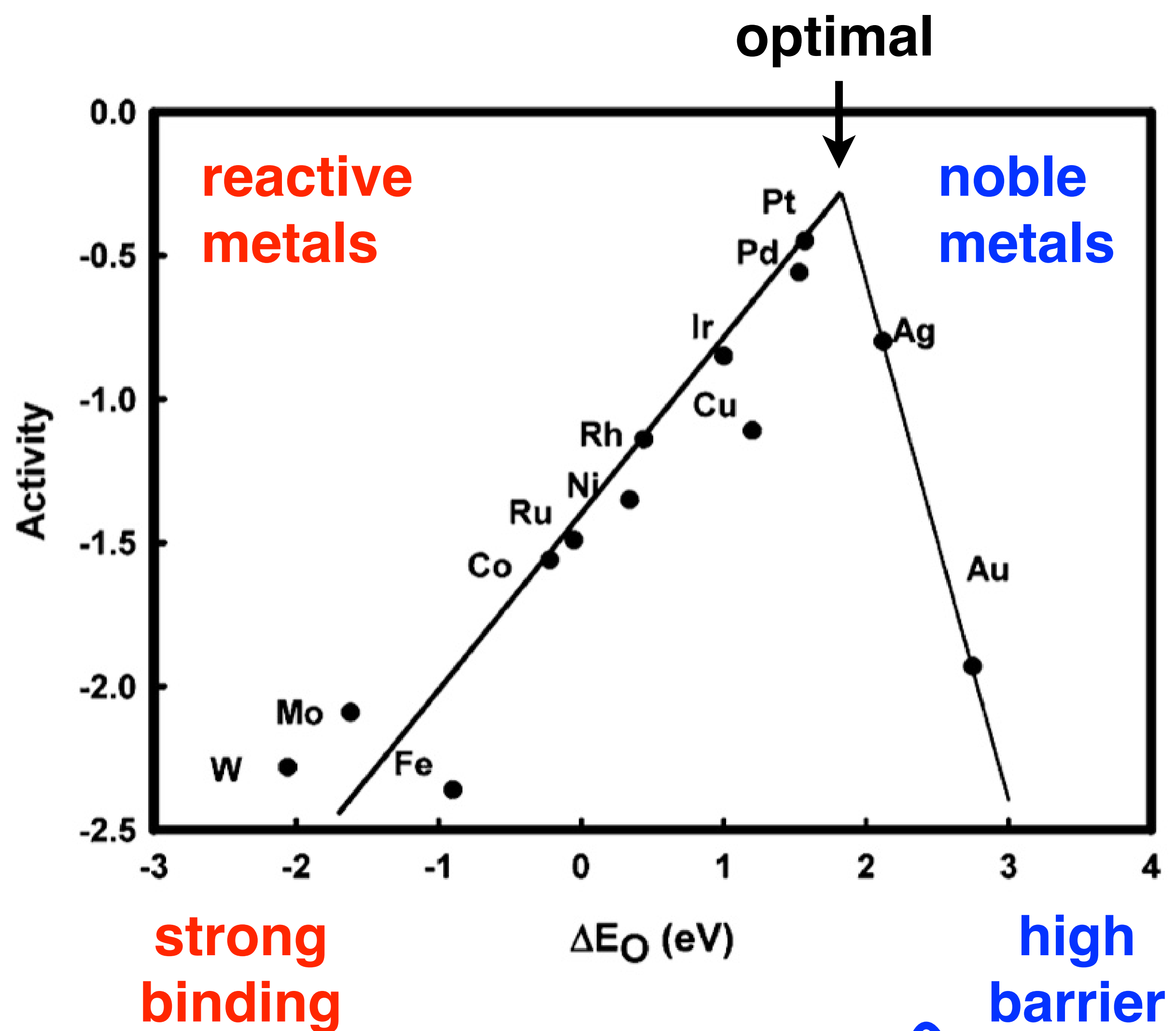


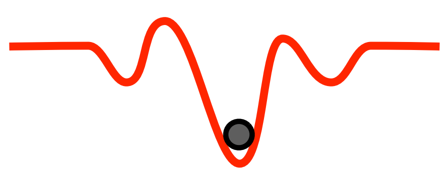
Xu, Ruban, Mavrikakis, *JACS*.**126**, 4717 (2004)
Bligaard, Nørskov, *et al.*, *J. Catal*. **224**, 206 (2004)

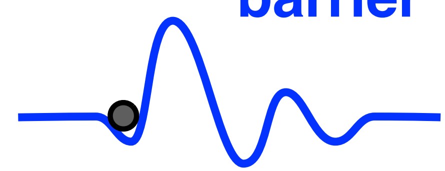
Volcano plots from reactivity descriptors

Volcano plot:
A peak in catalytic activity corresponds to the optimal balance between reactive and noble metals

Pt has the highest activity of any single transition metal catalyst for the O-reduction reaction (ORR)

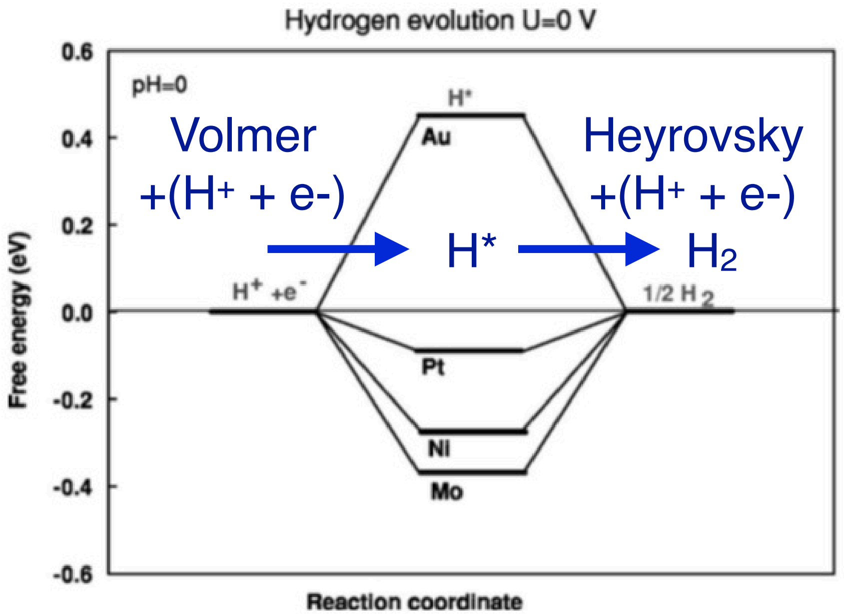




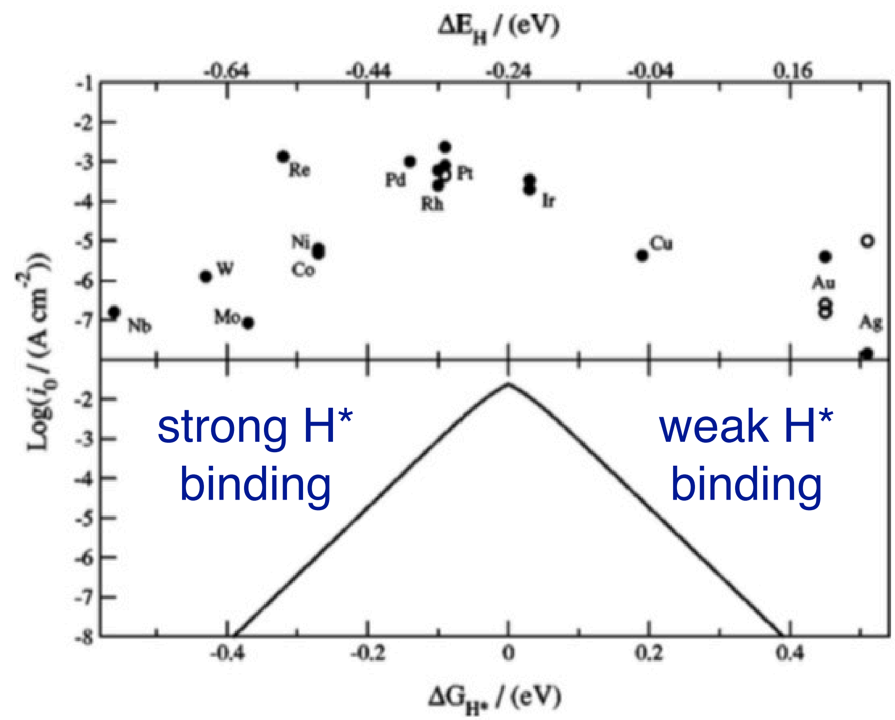


Bligaard, Nørskov, Dahl, Matthiesen, Christensen, and Schesten, *J. Catal*. **224**, 206 (2004)

Calculations and Experiments of HER



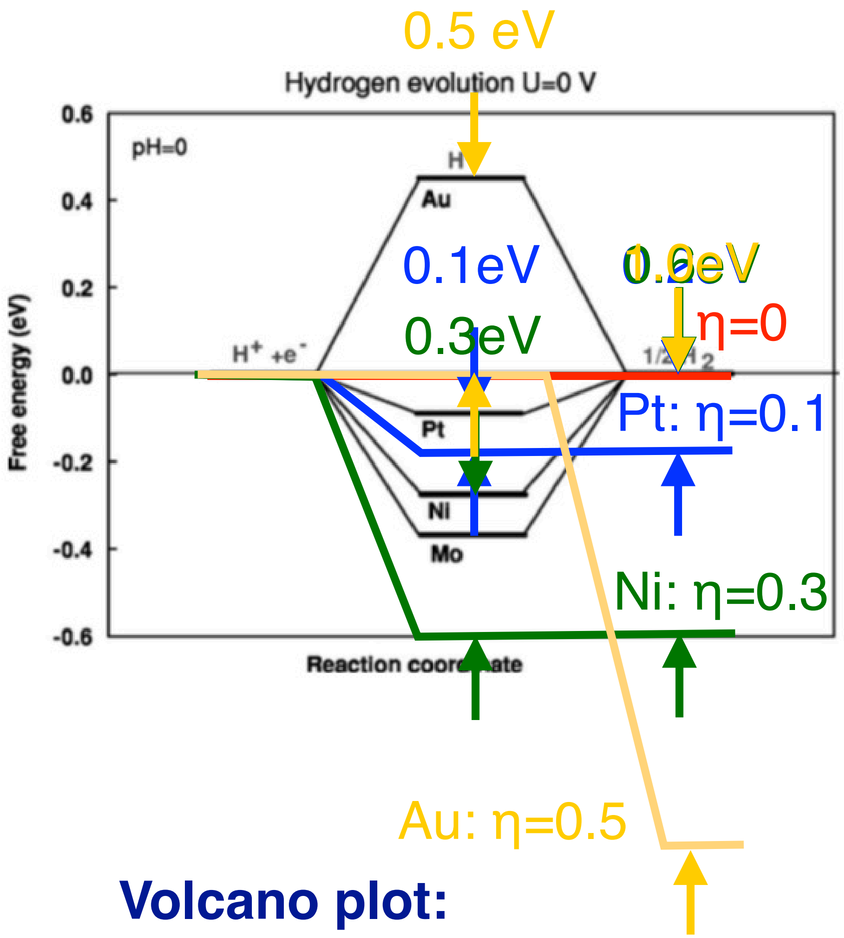
Calculations:
DFT calculations of the free energy of adsorbed H to a set of metals



Experiments:
A simple rate model, using one parameter, k_0, shows qualitative agreement with experimental data

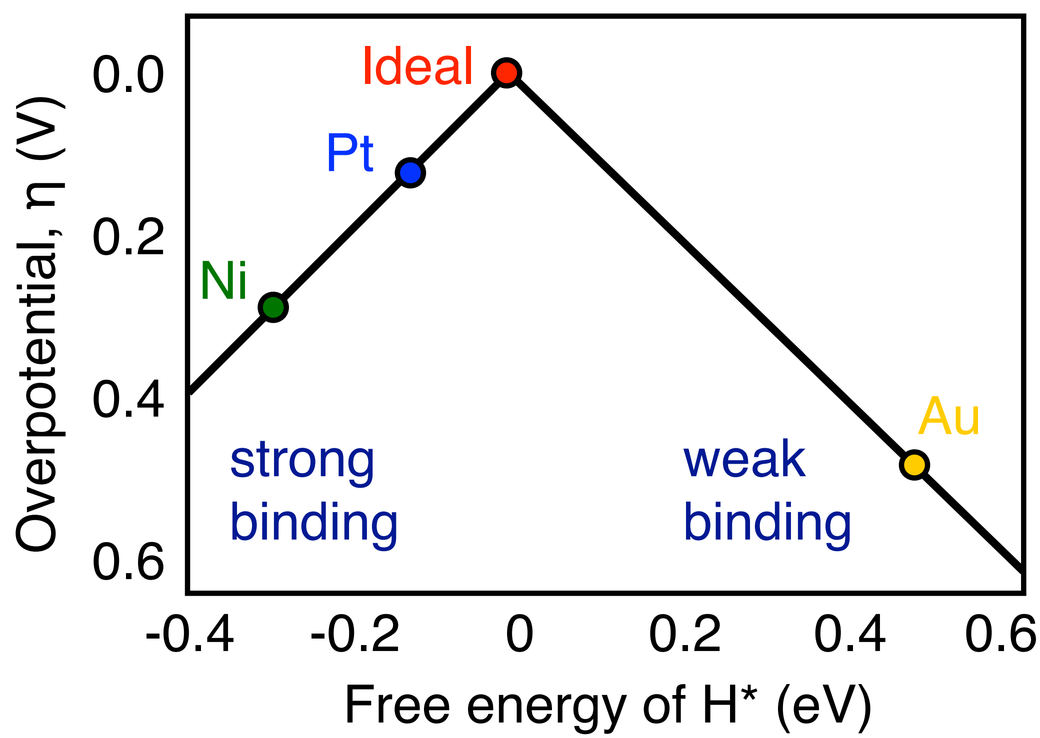
Norkov et al, *J. Electrochem. Soc.*, **152** J23-J26 (2005).

Modeling the Overpotential



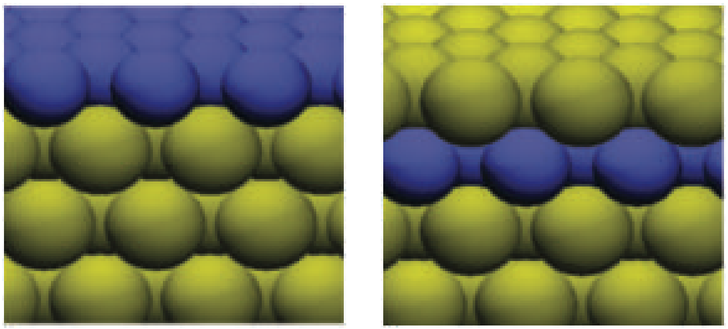
Calculations:
DFT calculations of the free energy of adsorbed H to a set of metals

Volcano plot:
In terms of an onset potential avoids an assumption of k_0 and allows for a direct comparison of experiment and theory

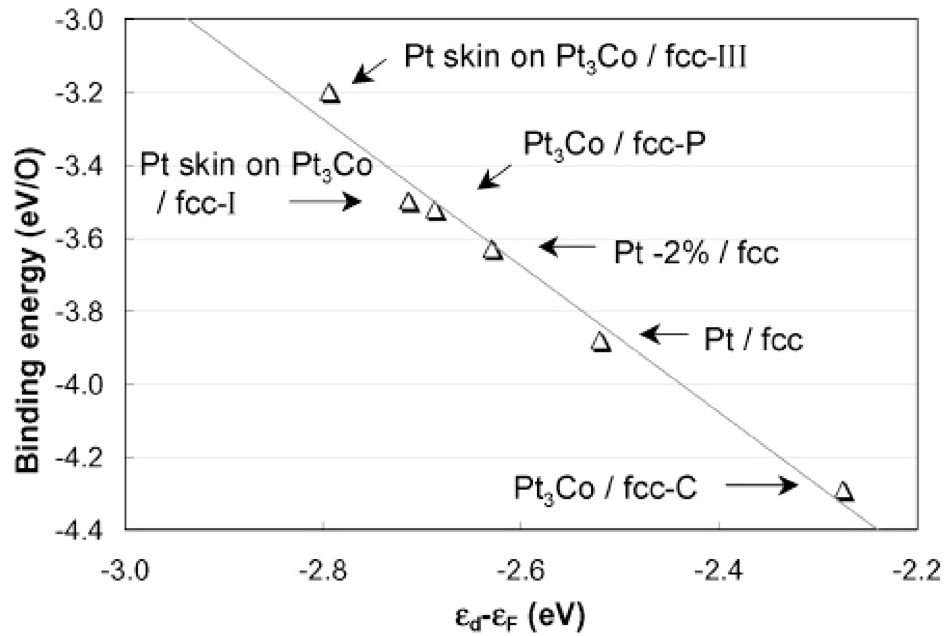


Near surface alloys for tuning catalysts

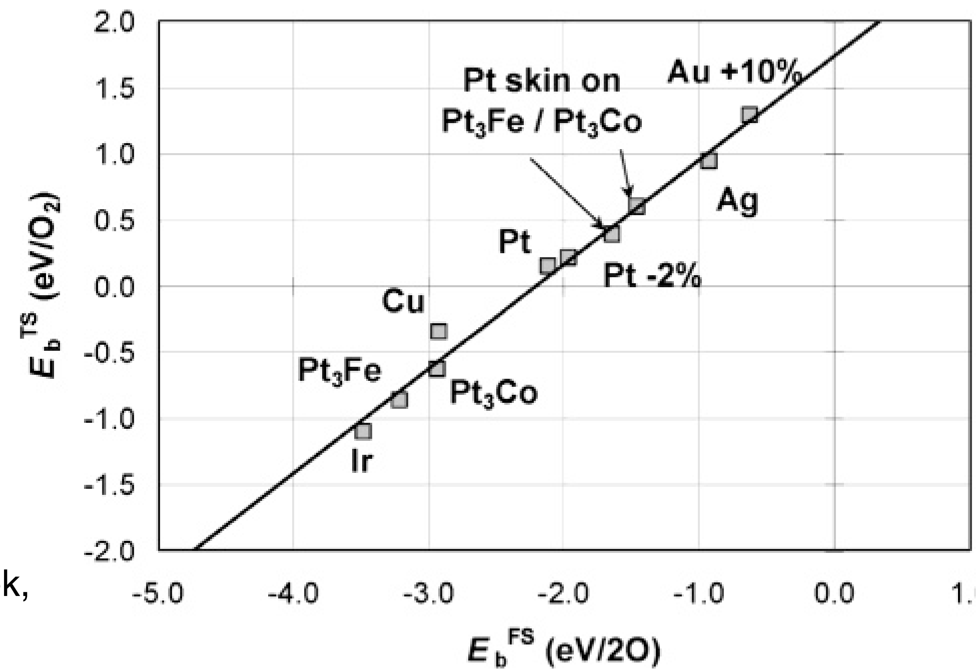
Overlayers* | Subsurface alloys



strain effect | **ligand effect**



Overlayers:
Alloy metal can wet the surface, or form a subsurface alloy

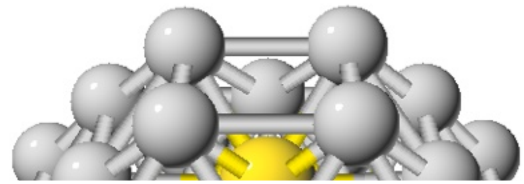


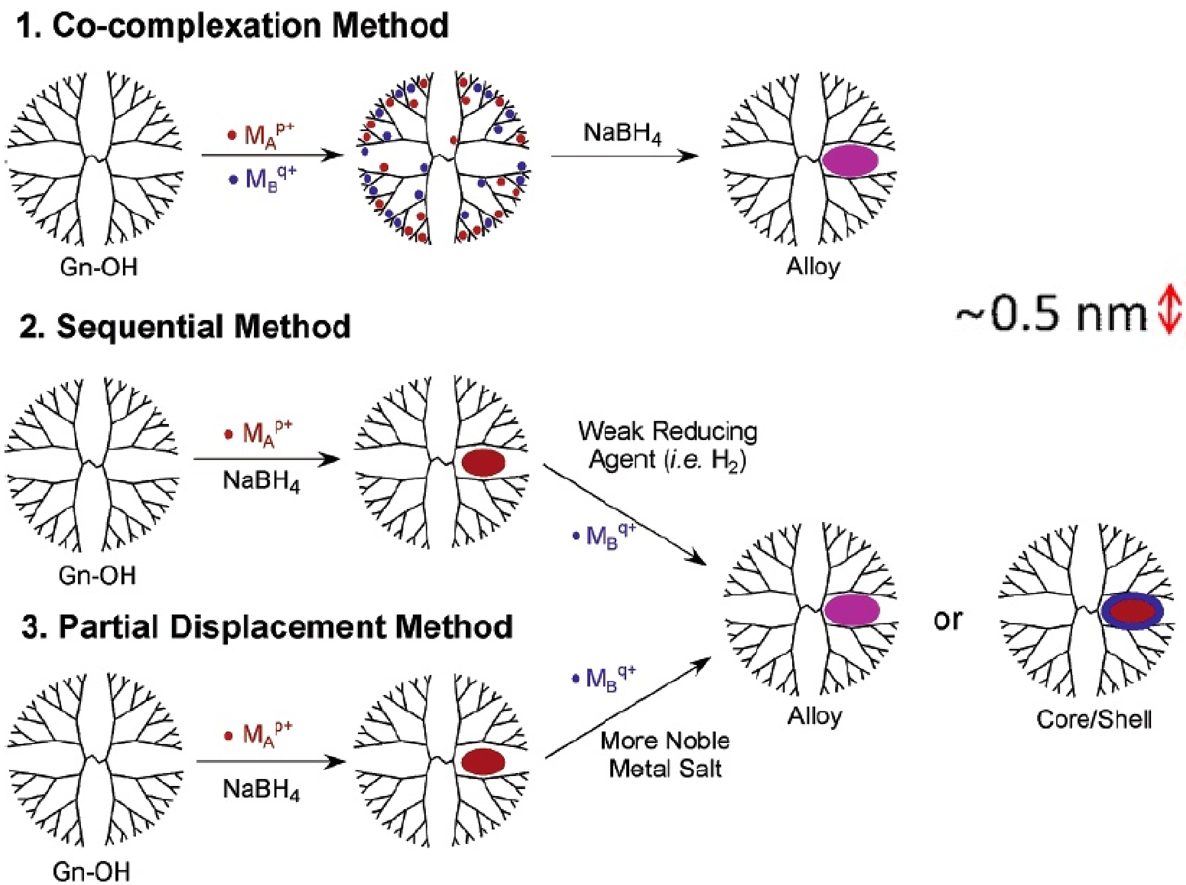
Subsurface alloys:
Change the *d*-band level (and reactivity) of the surface

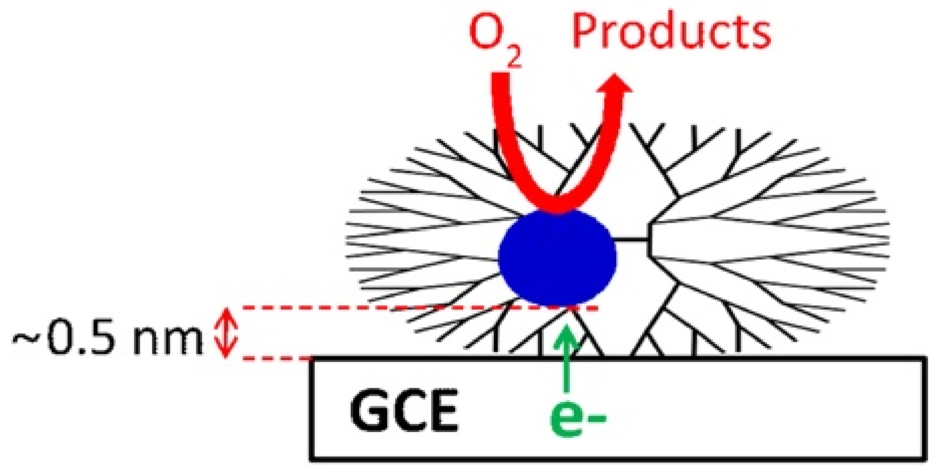
Besenbacher, Chorkendorff, Clausen, Hammer, Molenbroek, Nørskov, and Stensgaard, *Science* **279**, 1913 (1998).
Greeley and Mavrikakis, *Nature Materials* **3**, 810 (2004)

Dendrimer encapsulated nanoparticles

Dendrimer encapsulation:
make reproducible alloy or core/shell nanoparticles





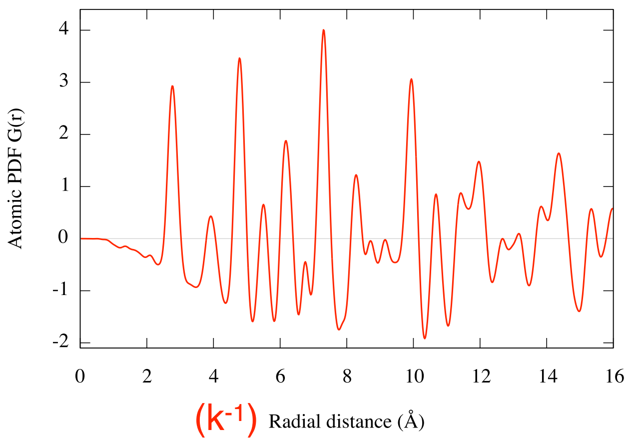


Core/shell:
use core metal to tune the reactivity of the shell

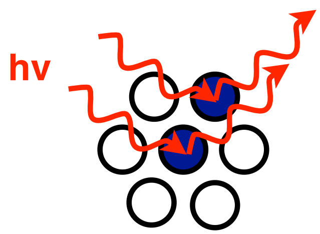
R. W. J. Scott, O. M. Wilson, S.-K. Oh, E. A. Kenik, and R. M. Crooks, *J. Am. Chem. Soc.* **126**, 15583 (2004).
O. M. Wilson, R. W. J. Scott, J. C. Garcia-Martinez, and R. M. Crooks, *J. Am. Chem. Soc.* **127**, 1015 (2005).

Tools for determining nanoparticle structure

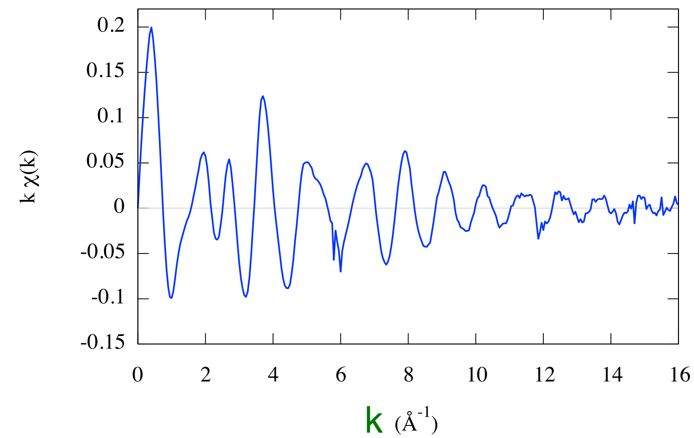
PDF (x-ray: pair distribution function)



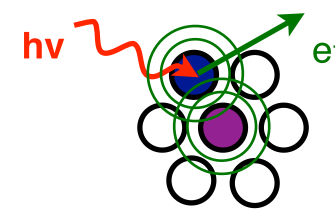
- Long range
- Total scattering



EXAFS (extended x-ray adsorption)



- Short range
- Atom identity

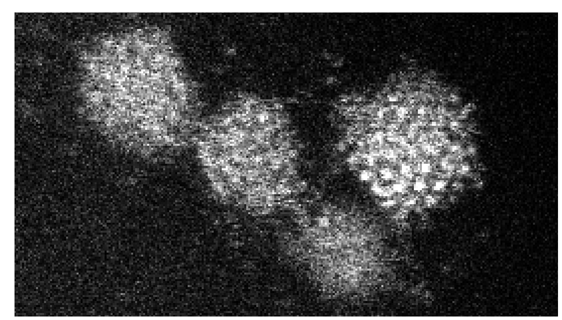


DFT (density functional theory)

$$\hat{H}\Psi = E\Psi$$

- Potential energy
- Idealized model

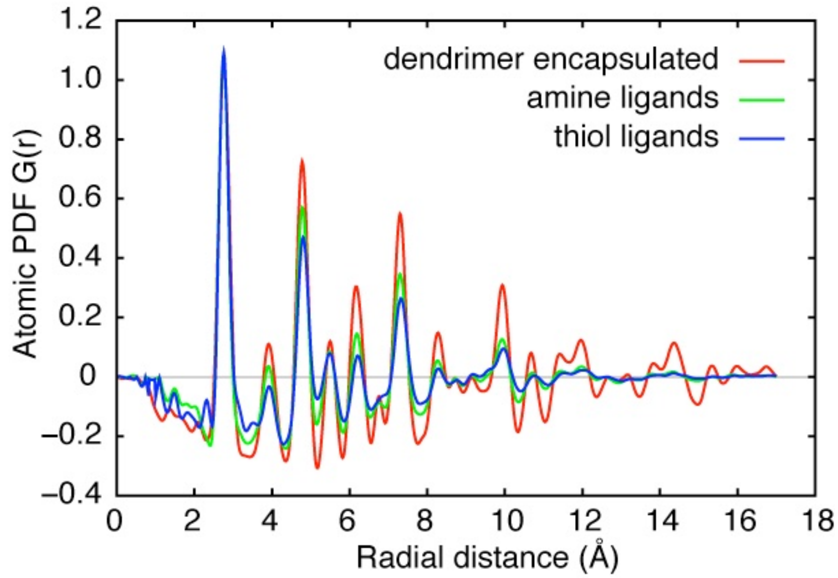
TEM (transmission electron microscopy)



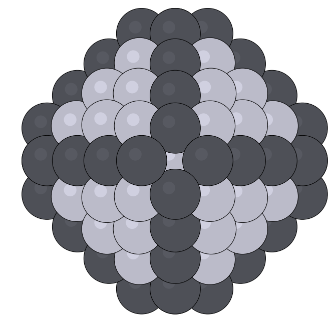
- Particle size and morphology

Structural information from X-ray scattering

Pair Distribution Function X-ray Data: Valeri Petkov



Compare experimental PDF data (G_{expt}) with that calculated from a model particle (G_{calc}):

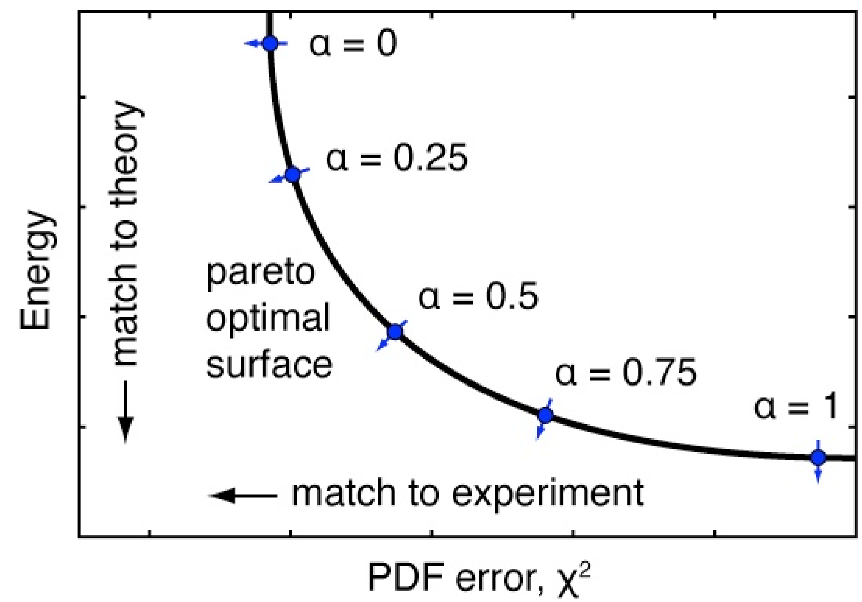


$$G_{\mathrm{calc}}(r) = \frac{A}{r}\sum_{i,j}\frac{1}{2\pi\sigma^2}e^{-\frac{(r-r_{ij})^2}{2\sigma^2}}$$

Combine error in PDF (χ^2) with the total energy (U) to give a single object function, (F):

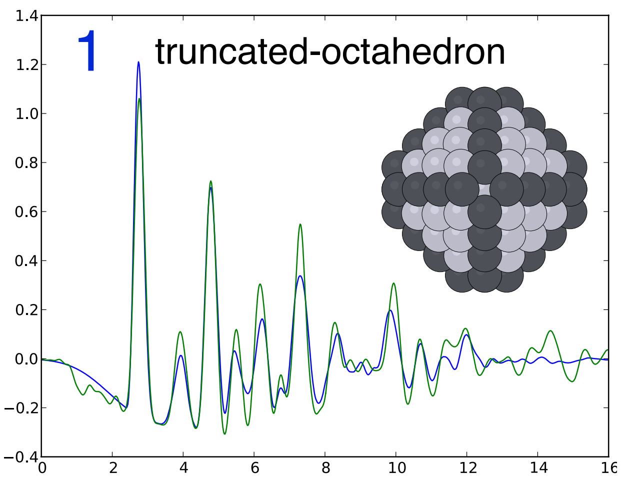
$$\chi^2 = \frac{1}{R}\int_0^R [G_{\mathrm{expt}}(r) - G_{\mathrm{calc}}(r)]^2 \mathrm{d}r$$

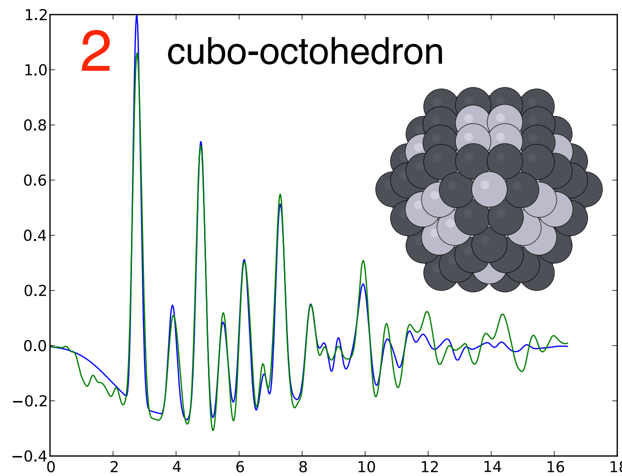
$$F = \alpha U + (1-\alpha)\chi^2$$

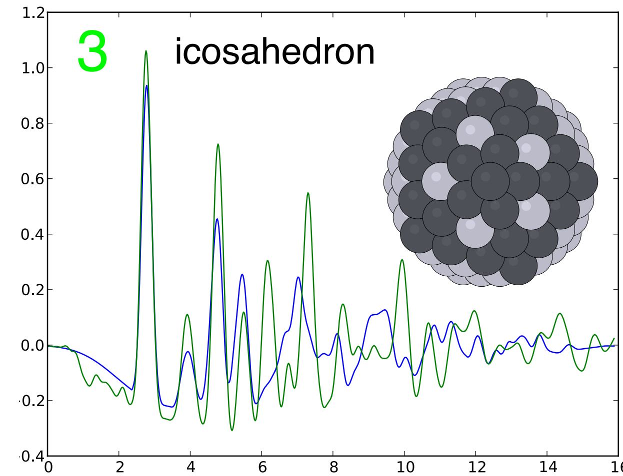


M. Welborn, W. Tang, J. Ryu, V. Petkov, and G. Henkelman, *J. Chem. Phys.* **135**, 014503 (2011).

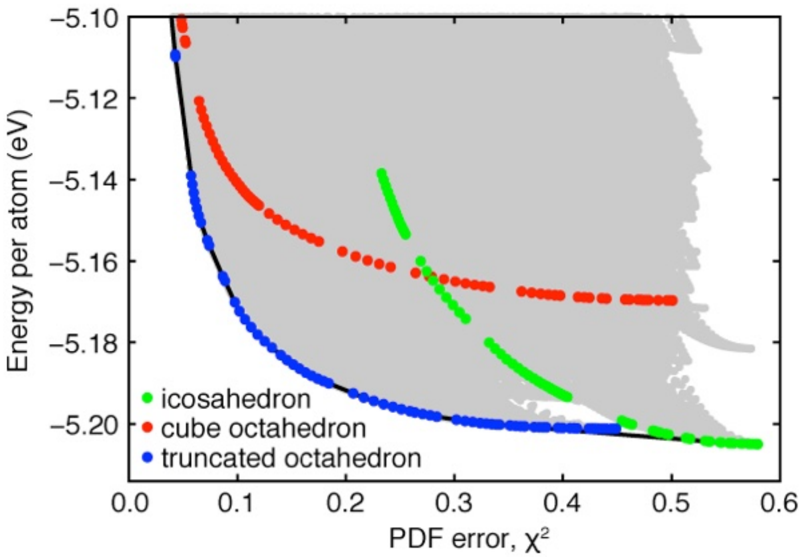
FCC crystals are the best-fit structures



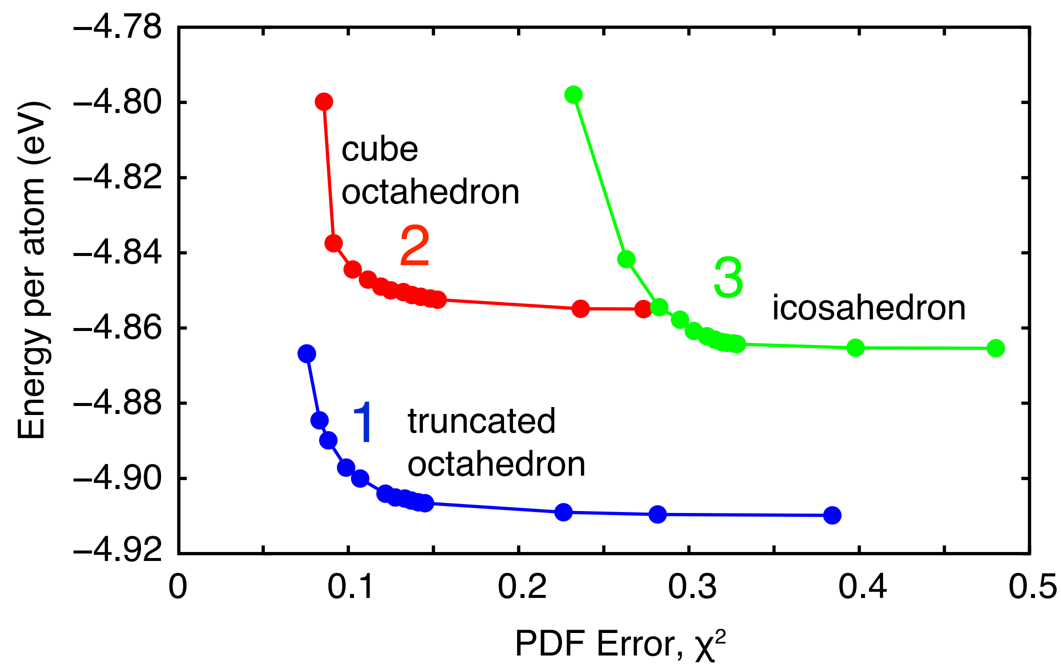




Searching a large number of conformations with an empirical (EAM) potential

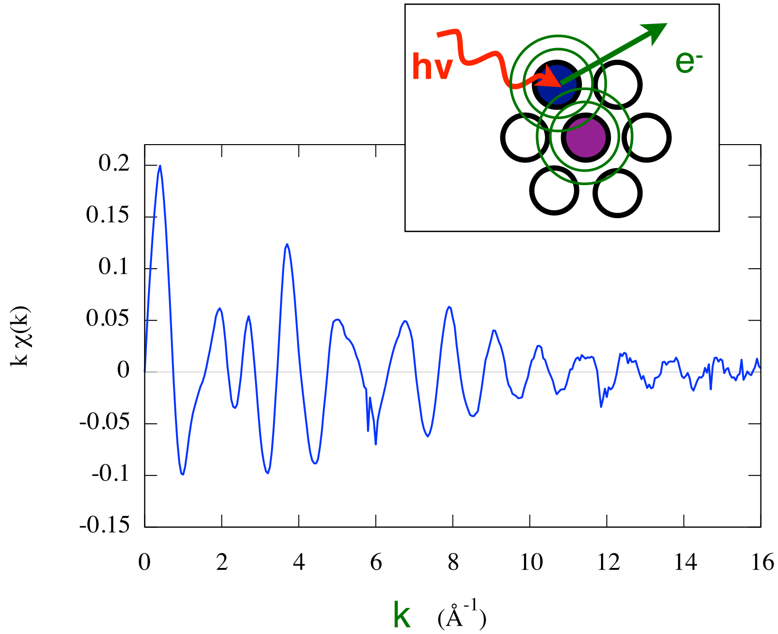


Refine with DFT: truncated octahedron (1) best fits the experimental data and has the lowest energy



EXAFS spectra and standard fitting

Experiment



Theory

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^{\,2}} \sin[2kR_j + \delta_j(k)]$$

***N* = Coordination Number**

$CN_{X\text{-}Y}$: Average number of atoms X around Y

Bulk Au: $CN_{Au\text{-}Au}$ = 12

Au_{147} NP: $CN_{Au\text{-}Au}$ = 8.98

***R* = Bond Length**

***σ²* = Debye-Waller Factor**

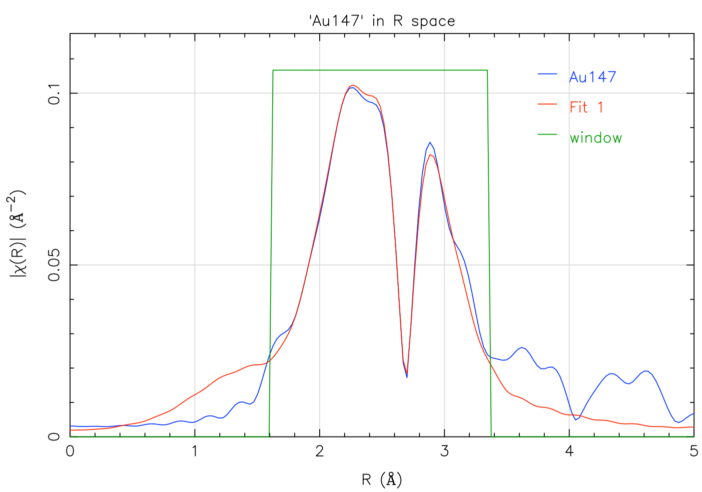
Average bond length variance

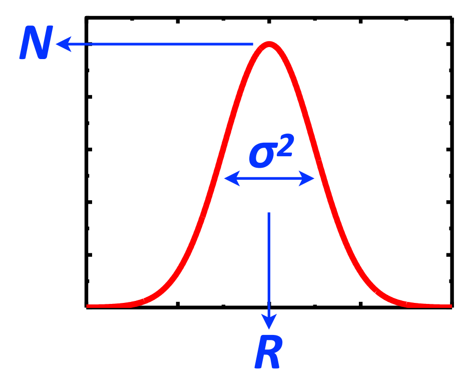
Combination of static and dynamic disorder

Fitting

Determine *N*, *R*, *σ²*

e.g. with IFEFFIT





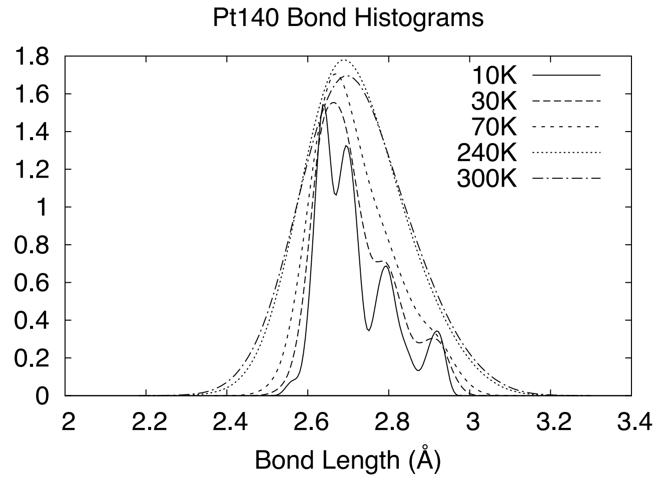
Potential problems with EXAFS fitting

Dependency between fitting parameters

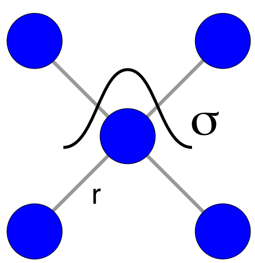
EXAFS fitting can convolute physical properties, for example, coordination number and disorder (disordered particles look like smaller bulk-like particles)

Bulk reference model can break down for nanoparticles

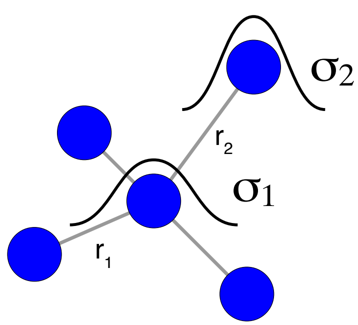
Distributions in bond lengths may be non-Gaussian, particularly at low temperatures



ordered



disordered

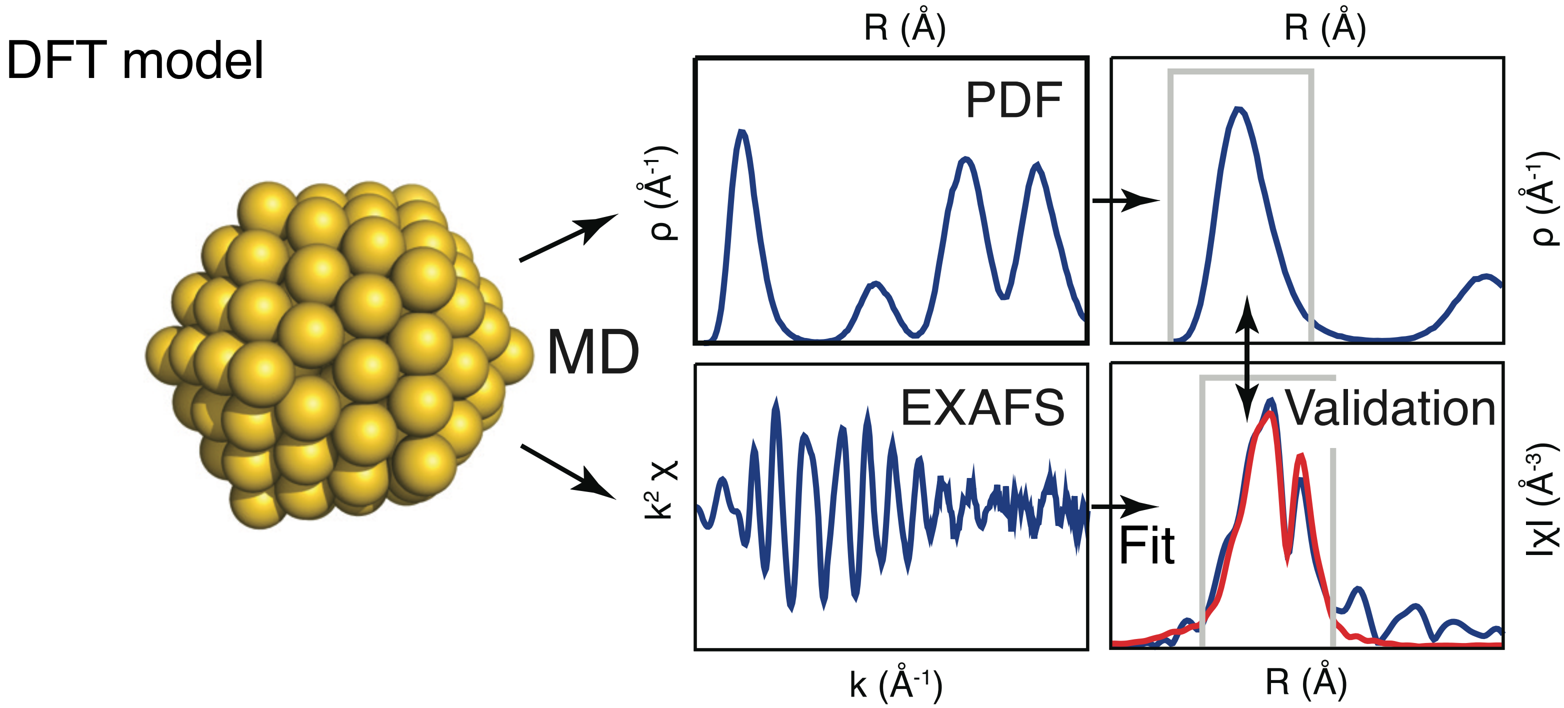


A range of Debye-Waller factors can also be found in disordered materials

A. Yevick, A. Frenkel, *Phys. Rev. B* **81**, 115451 (2010).

Self-consistency test for the fitting model

Determine the accuracy of the **fitting model** without experimental uncertainty



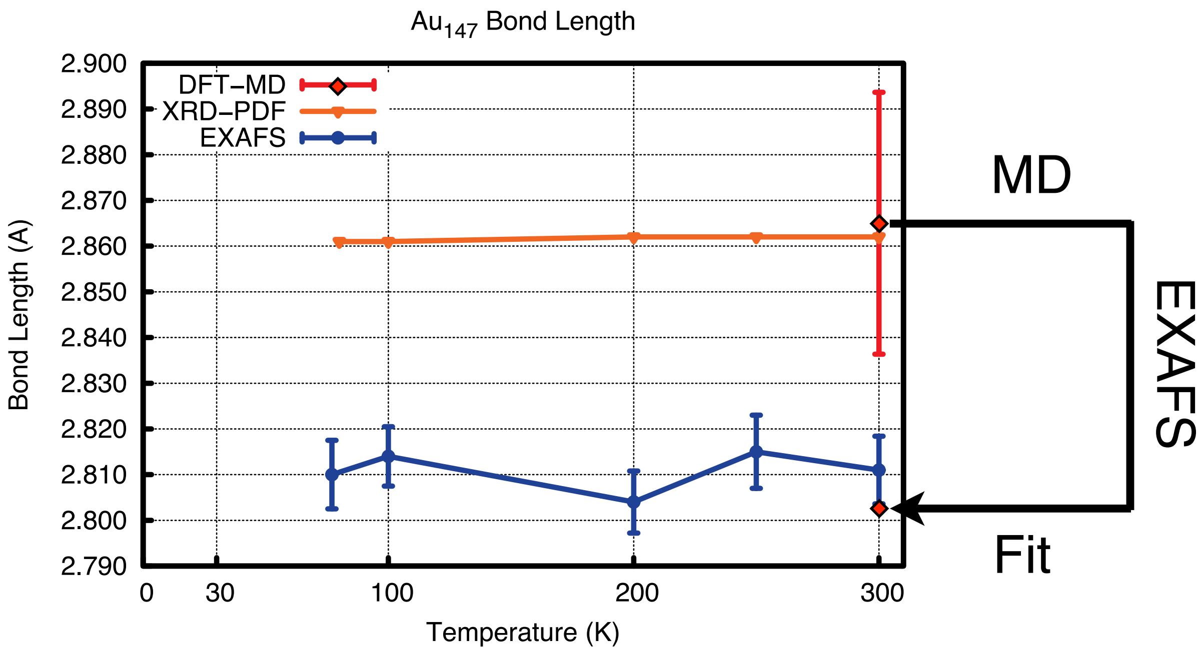
Use DFT to generate an ensemble of structures around an initial geometry.

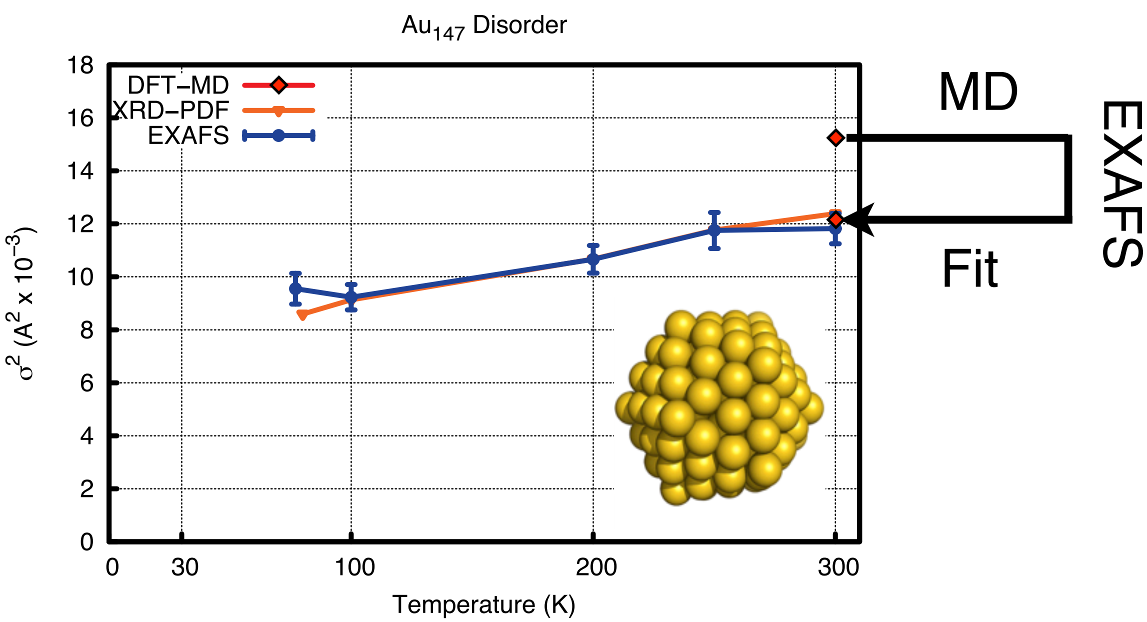
Do a full EXAFS calculation, using FEFF, for each configuration in the ensemble.

Compare fit values to direct ensemble averages: $\langle r \rangle, \sigma^2, N, c_3, c_4$

S. T. Chill, R. M. Anderson, D. F. Yancey, A. I. Frenkel, R. M. Crooks, and G. Henkelman, *ACS Nano* **9**, 4036 (2015).

Problems for Au nanoparticles

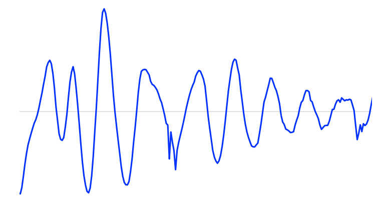




Molecular Dynamics

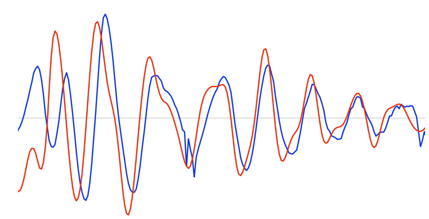
$$\langle r \rangle, \sigma^2, N, c_3, c_4$$

$\langle \chi(k) \rangle$



Simulate EXAFS

Fit $\langle \chi(k) \rangle$



Compare fit values to known ensemble averages.

Thiol-induced disorder in Au nanoparticles

Experimental vs Theoretical (MD-DFT) Analysis

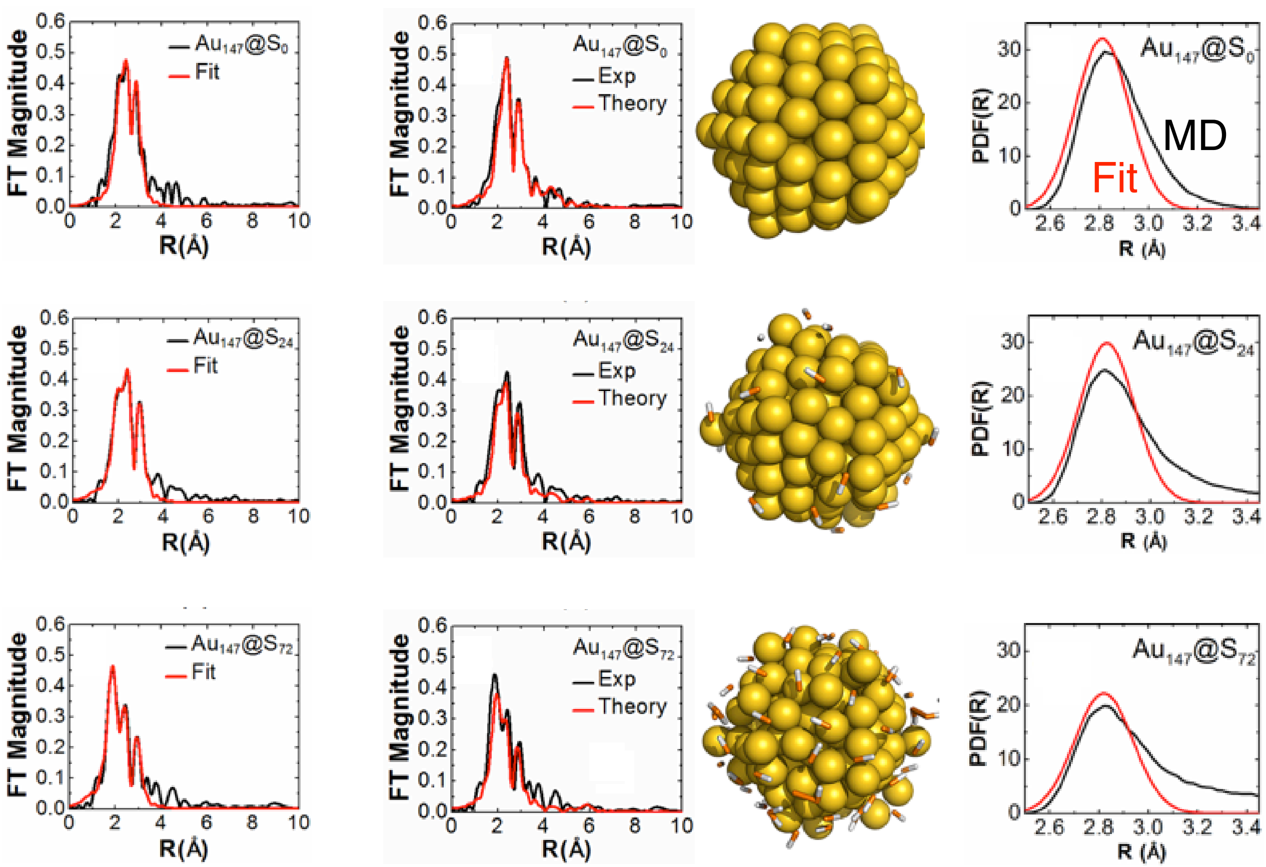
Change surface disorder with increasing thiol ligands (**N**)

Experimental EXAFS + Fit	Theoretical MD -> EXAFS	MD vs. Fit bond lengths

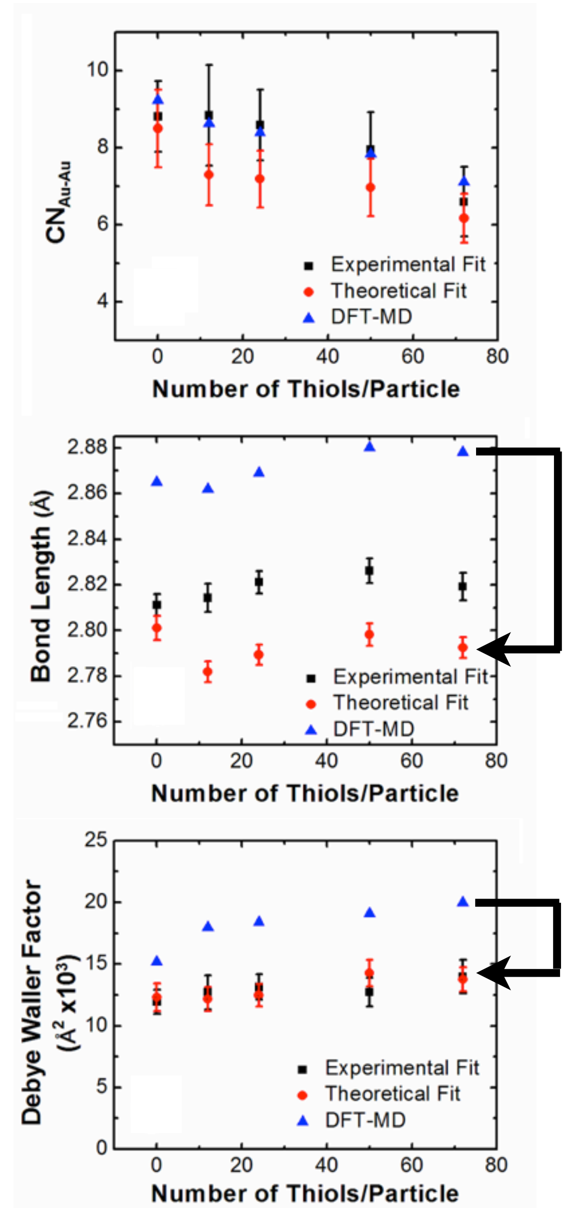
N=0

N=24

N=72

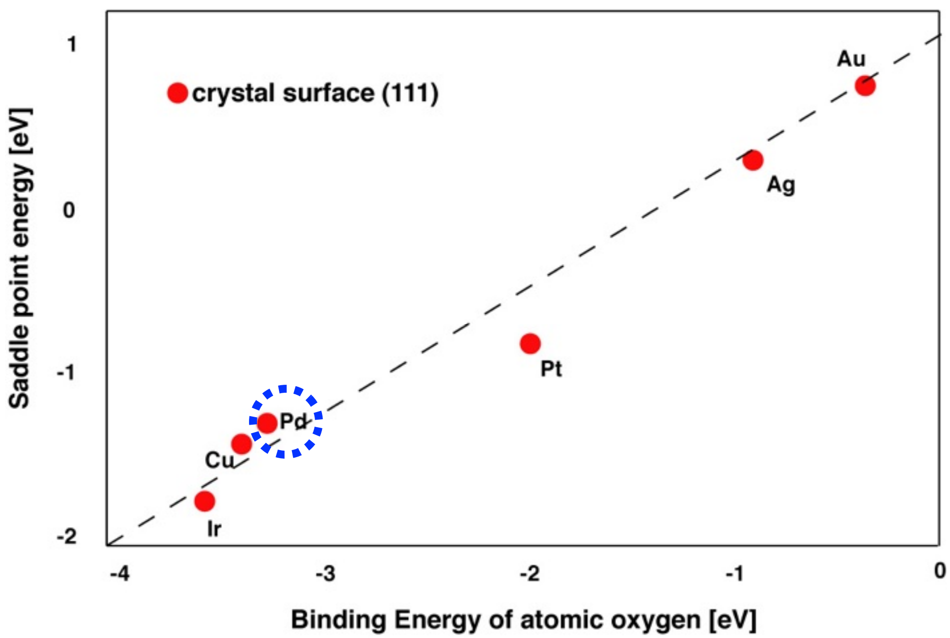


Fitted Model Values



D. F. Yancey, S. T. Chill, L. Zhang, A. I. Frenkel, G. Henkelman, and R. M. Crooks, *Chem. Sci.* **4**, 2912-2921 (2013).

First attempt: ORR on Pd-shell nanoparticles



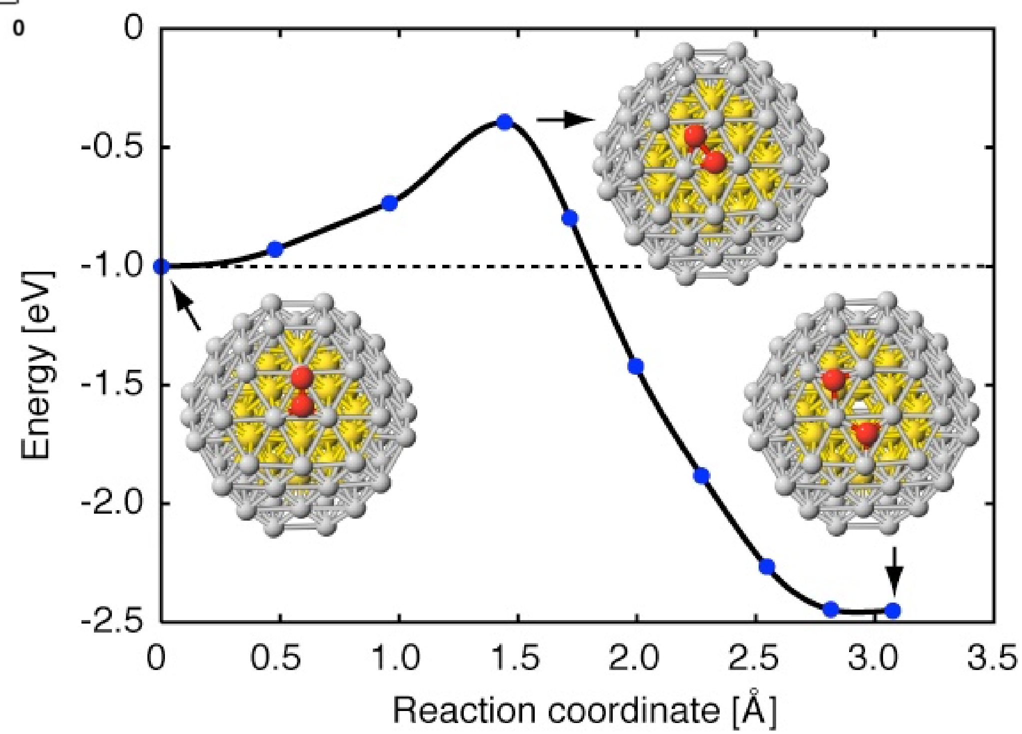
Choose **Pd shell** because it is close to Pt

See how the **core metal** changes the ORR on the shell

A **truncated octahedral** structure has the lowest energy in vacuum

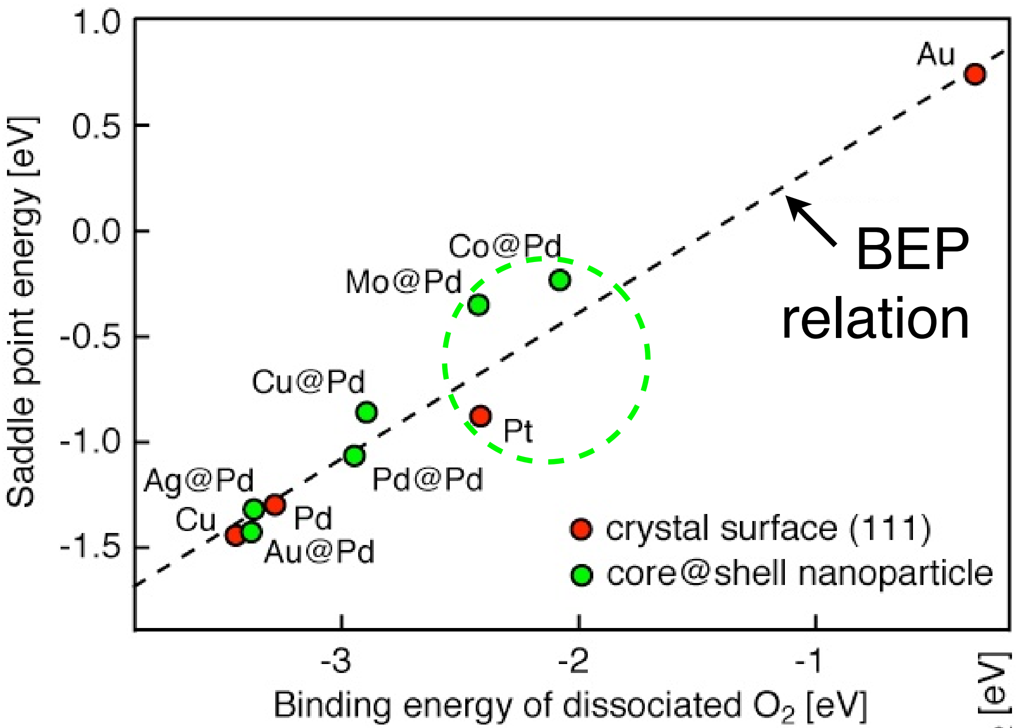
Reaction are assumed to take place on the **(111) facet**; this is the lowest energy, and most noble surface

E=0 is O_2 in gas phase



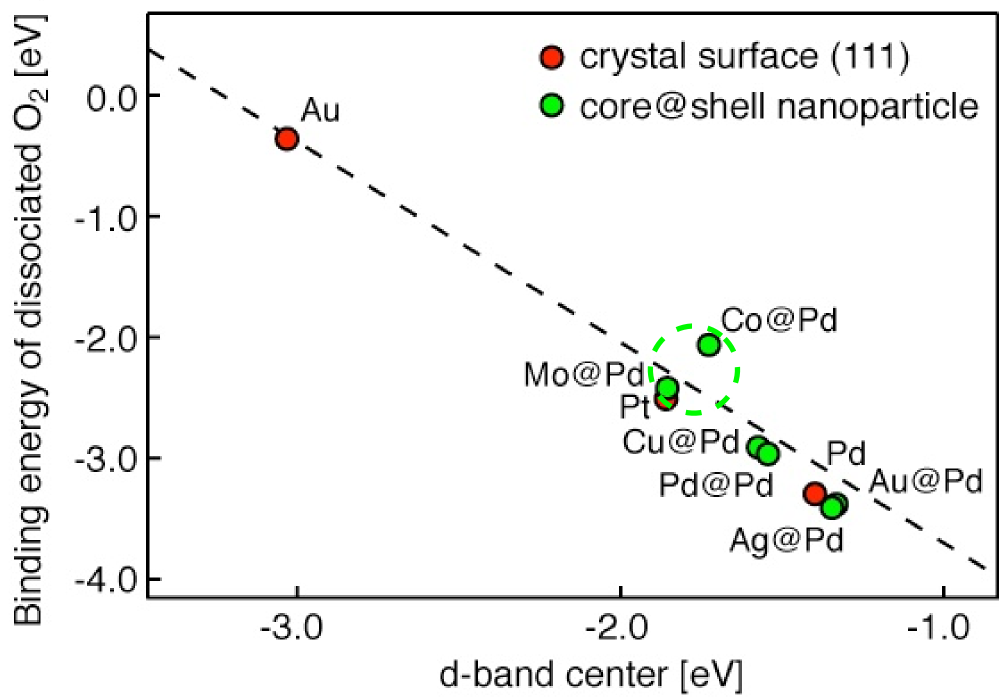
W. Tang and G. Henkelman, *J. Chem. Phys.* **130**, 194504 (2009).

BEP relationship for nanoparticles



Pd-shell nanoparticles:
follow a BEP relationship as the core metal is changed

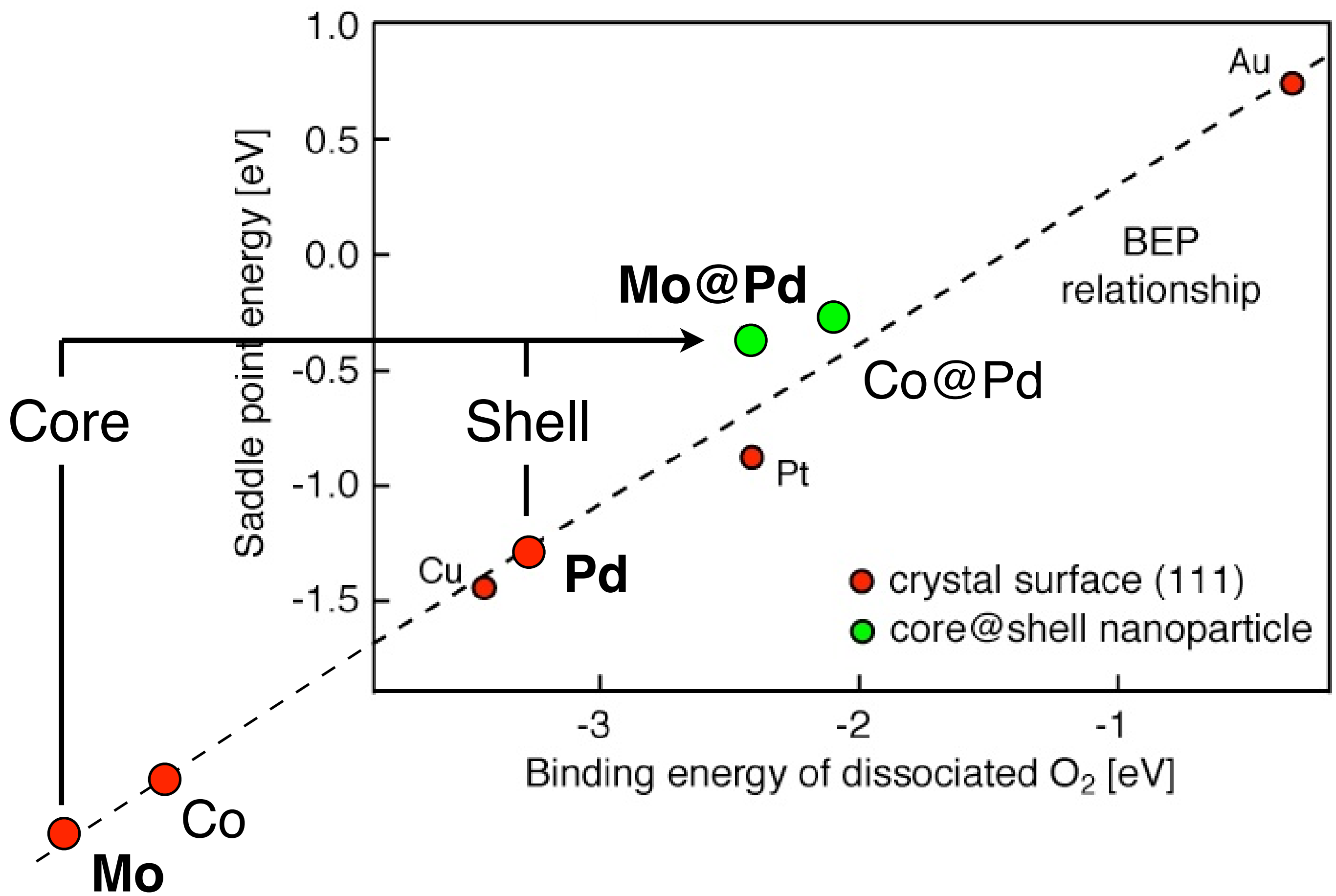
d-band center of the shell:
is a good measure of the barrier and binding for the ORR



Tune the Pd shell to be like Pt by choosing a non-noble core metal

Activity is not intermediate to the core and shell

A **Pd shell** particle, combined with a ***less*** nobel metal core, results in a particle with a shell that is ***more*** noble than Pd

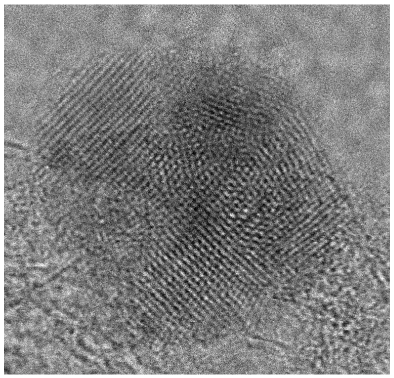


Possibility: can a core-shell particle be constructed from non-noble metals that reacts like a noble metal?

Experimental tests: Stability is important

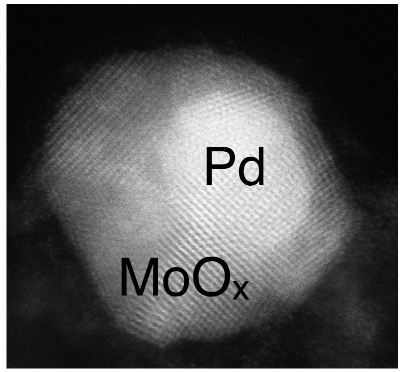
Synthesis: Keith Stevenson's group

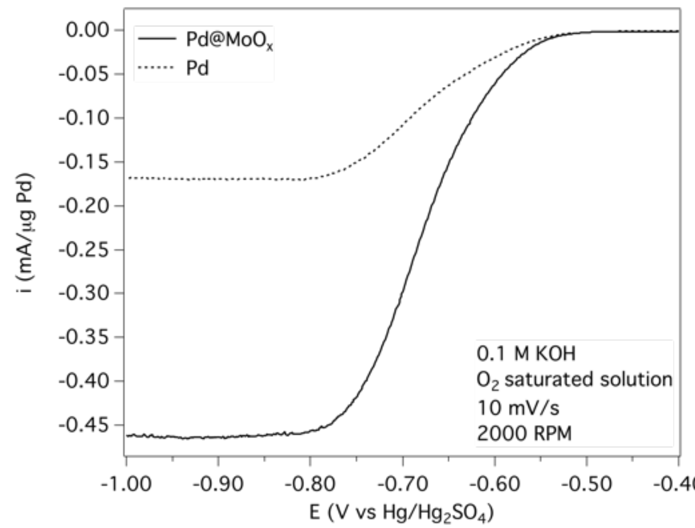
Mo@Pd are found to form a Pd@MoO_x structure

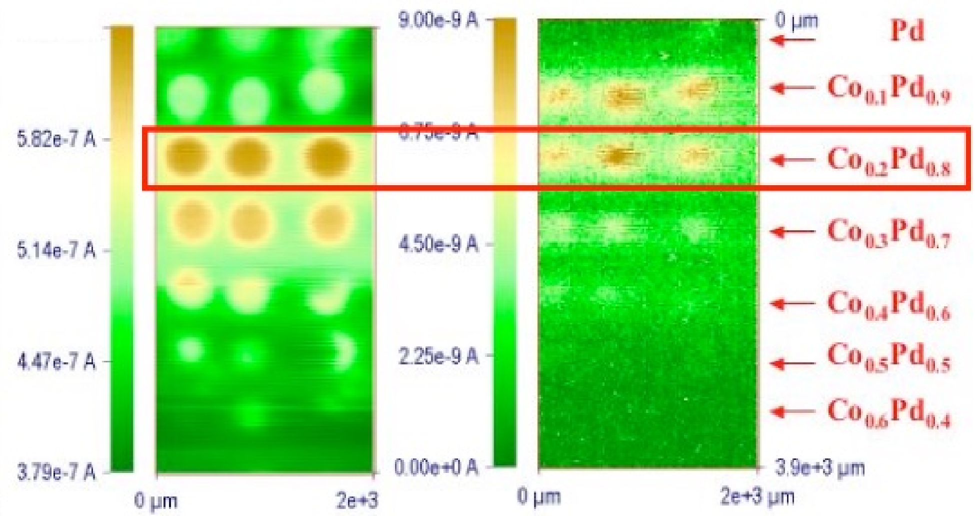


HRTEM

HAADF







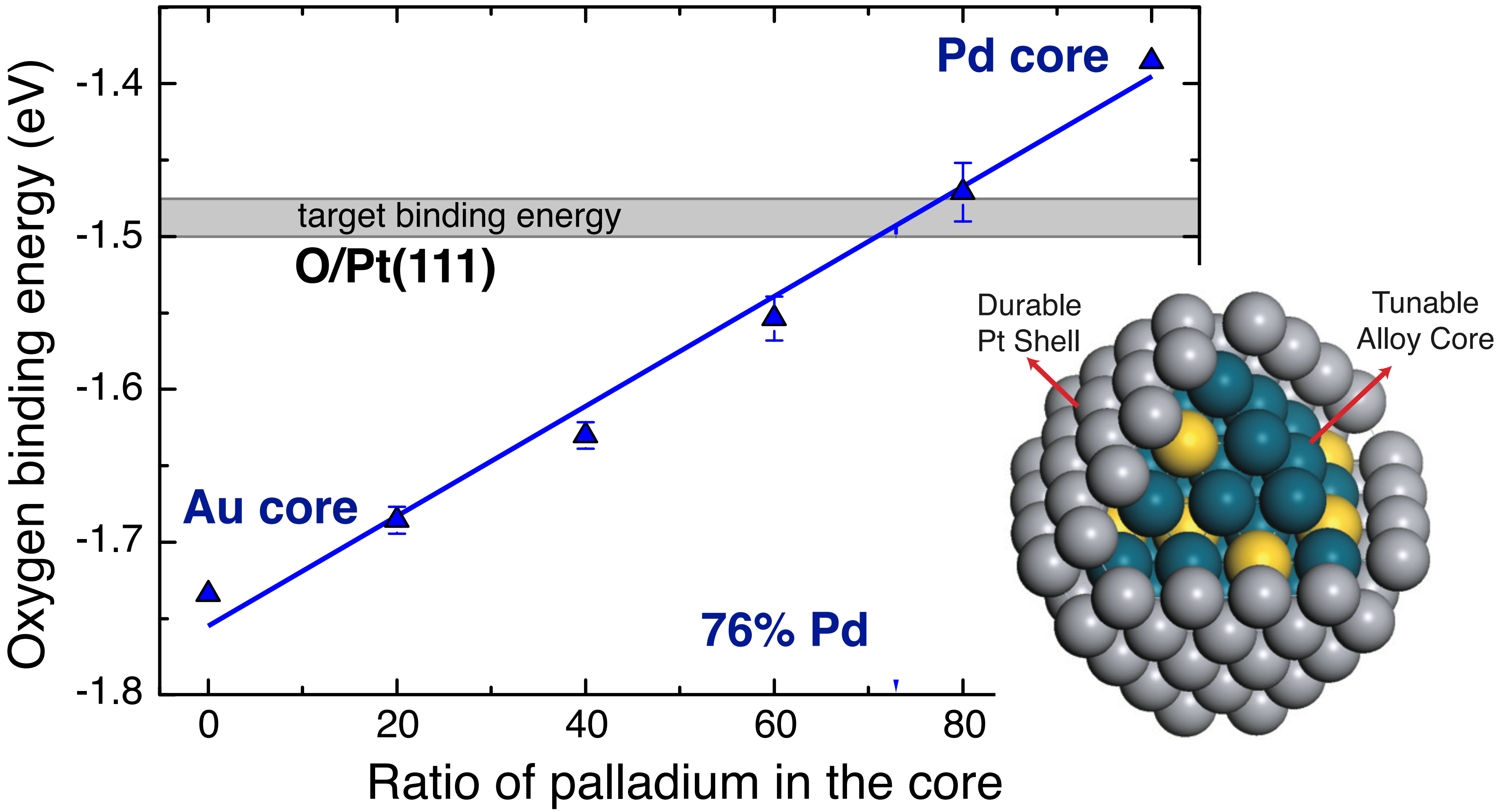
E_S = 0.45 V vs. HRE E_S = 0.7 V vs. HRE

Scanning electrochemical microscopy: Allen Bard's group

While Co@Pd particles are not stable, de-alloyed Co/Pd bulk samples are seen to be highly active for the oxygen reduction reaction.

Example I: Tuning a Pd/Au alloy @ Pt particle

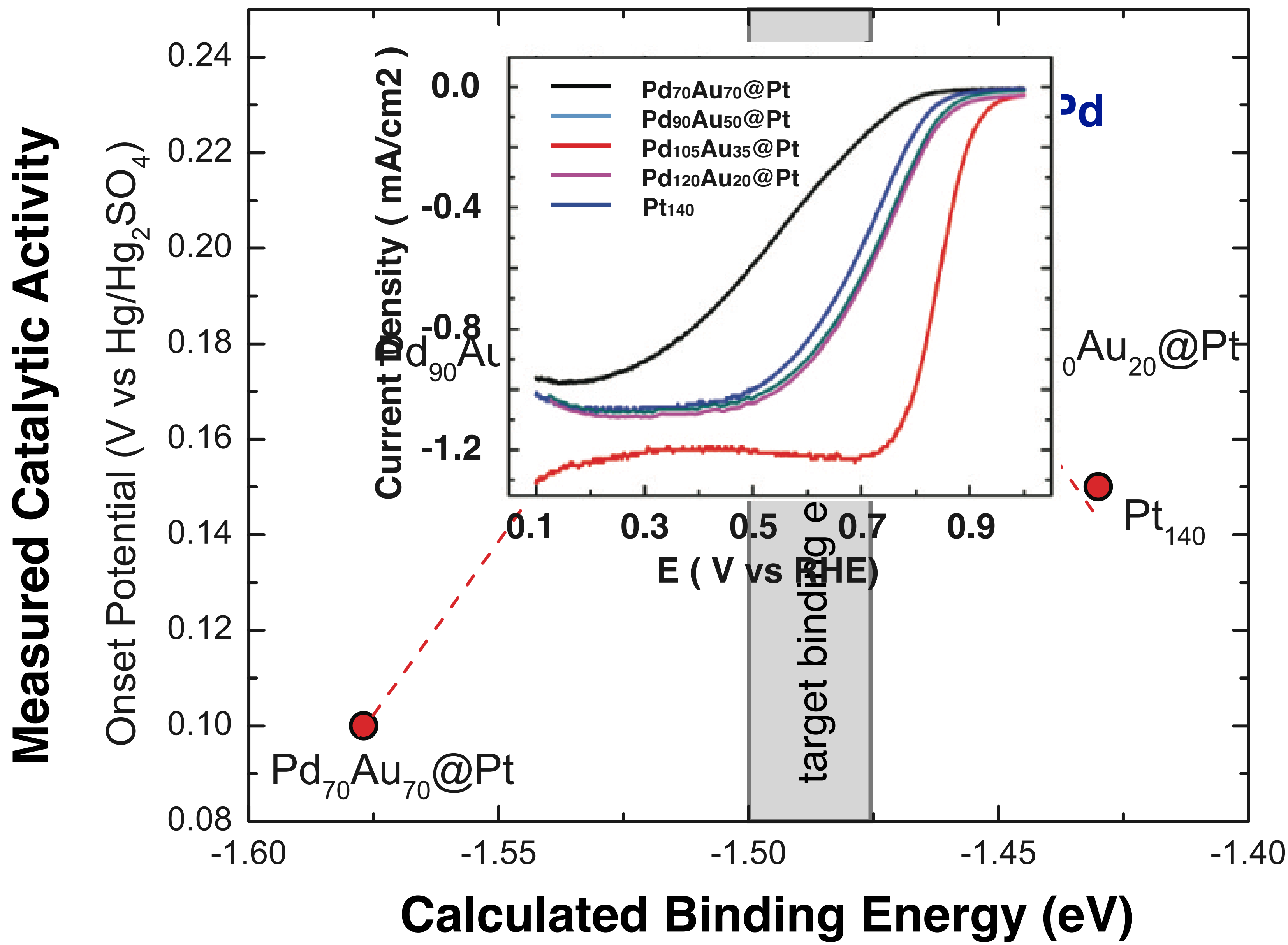
Tune the activity of a particle shell with the core composition.



Optimal core composition is predicted to be 3 Pd / 1 Au

L. Zhang and G. Henkelman, *J. Phys. Chem. C* **116**, 20860-20865 (2012).

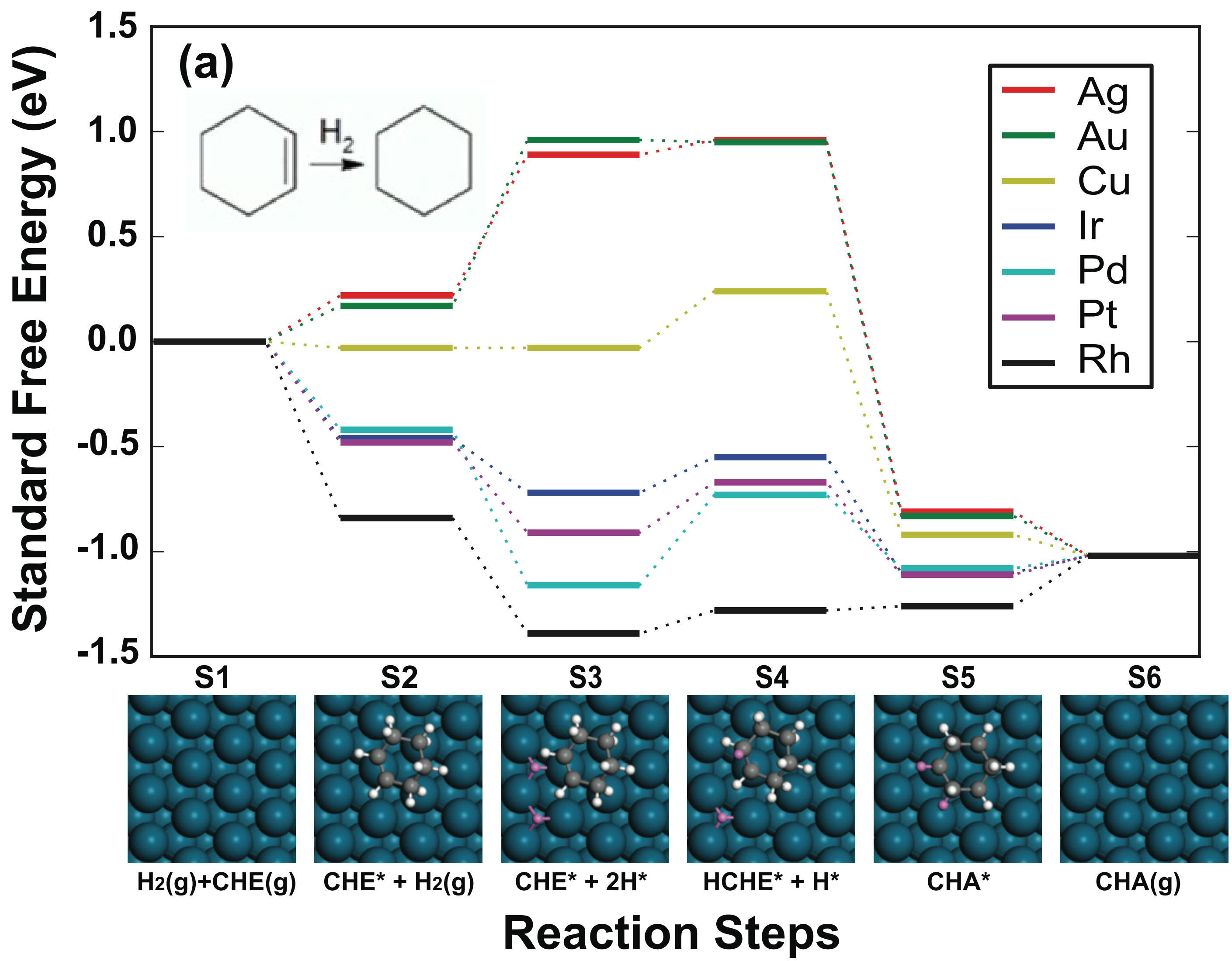
Experimental validation



L. Zhang, R. Iyyamperumal, D. F. Yancey, R. M. Crooks, and G. Henkelman, *ACS Nano* **7**, 9168-9172 (2013).

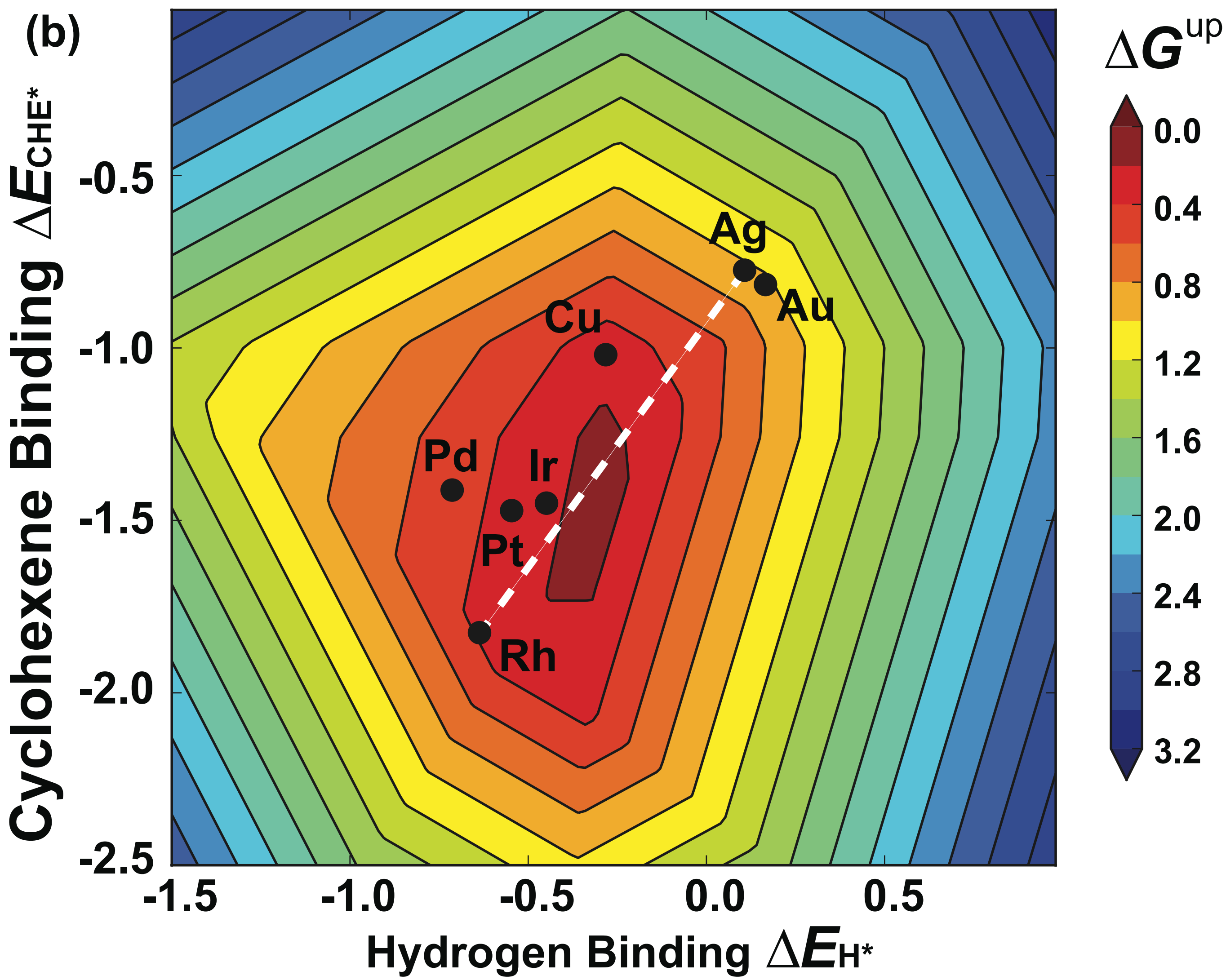
Example II: Cyclohexene hydrogenation

Reaction Mechanism: elementary steps follow BEP relationships for pure metals



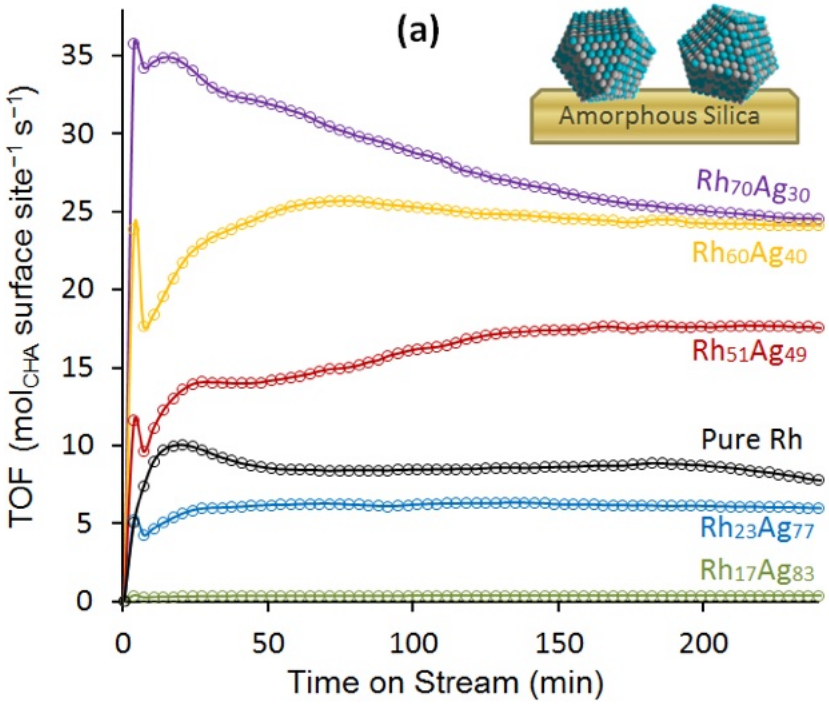
Scaling relations + Microkinetic model

= Volcano Plot:

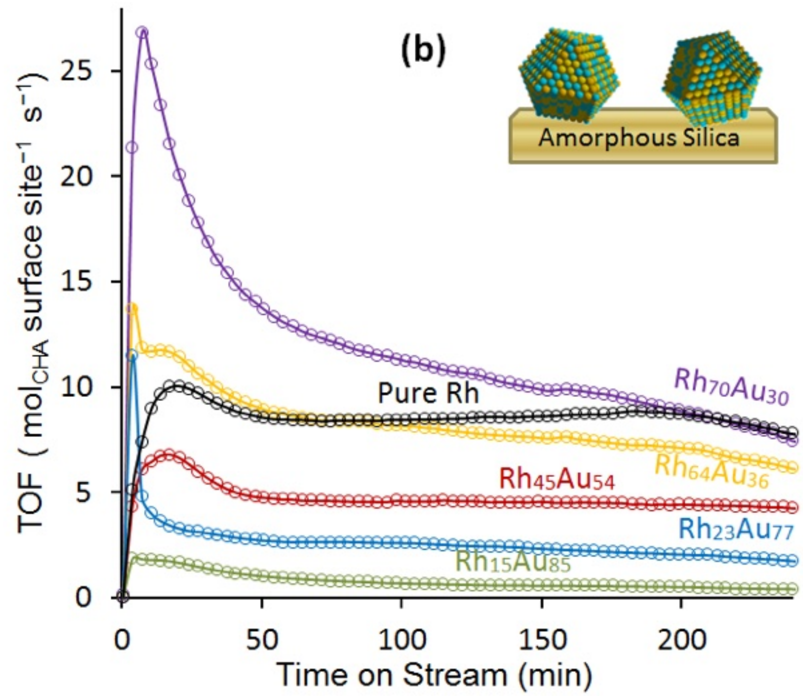


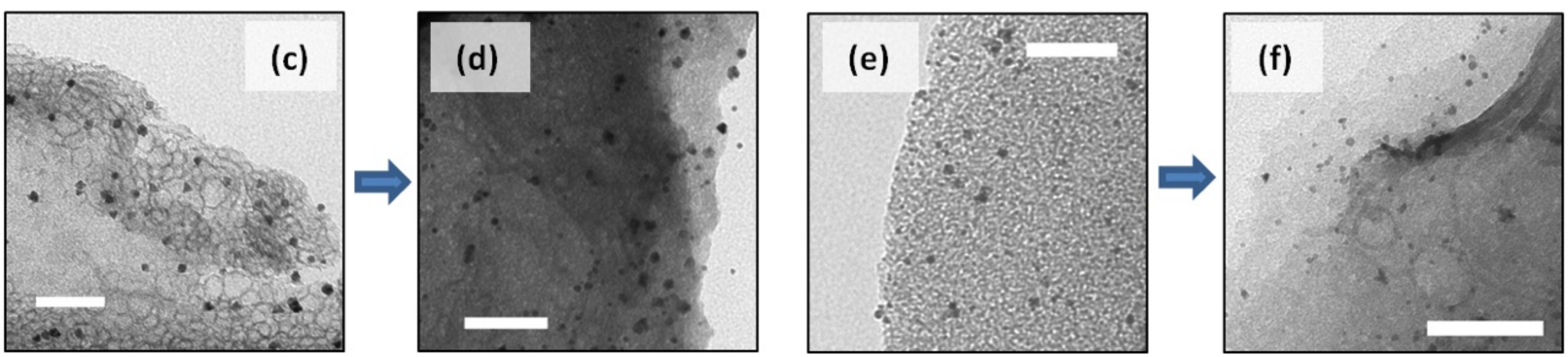
Experiments: Turn over frequency

Rh/Ag



Rh/Au

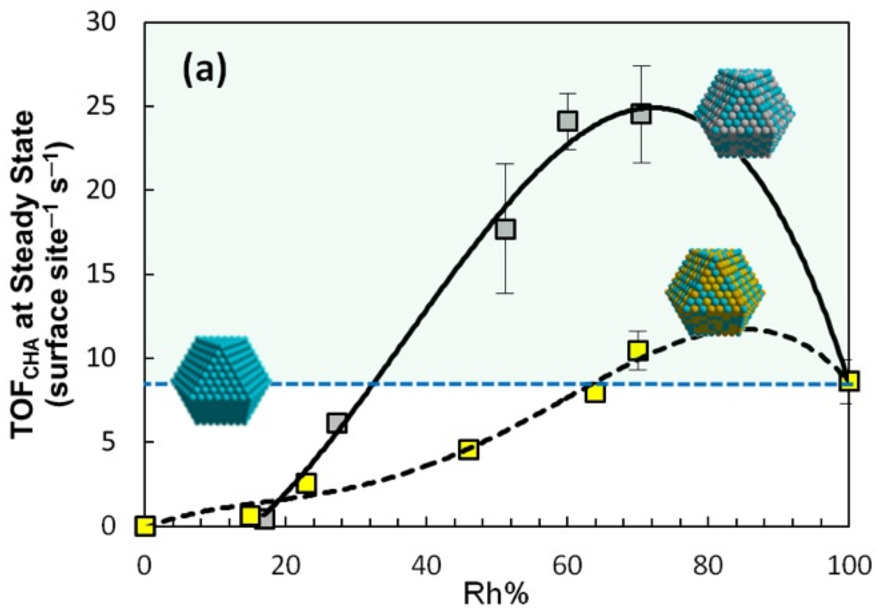




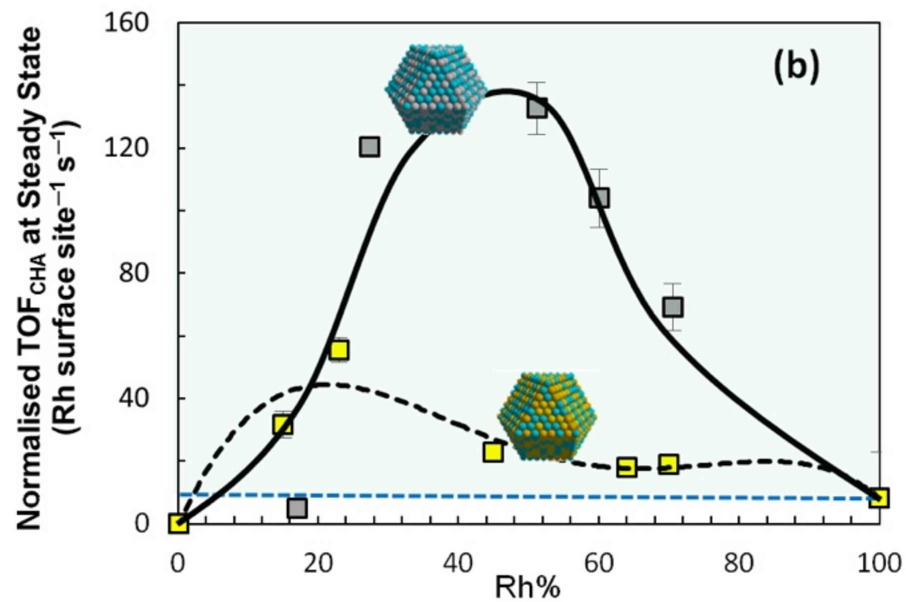
Experiments: Catalytic activity

Highest activity: found when Au or Ag is alloyed with Rh

Specific activity



Specific activity / Rh atom

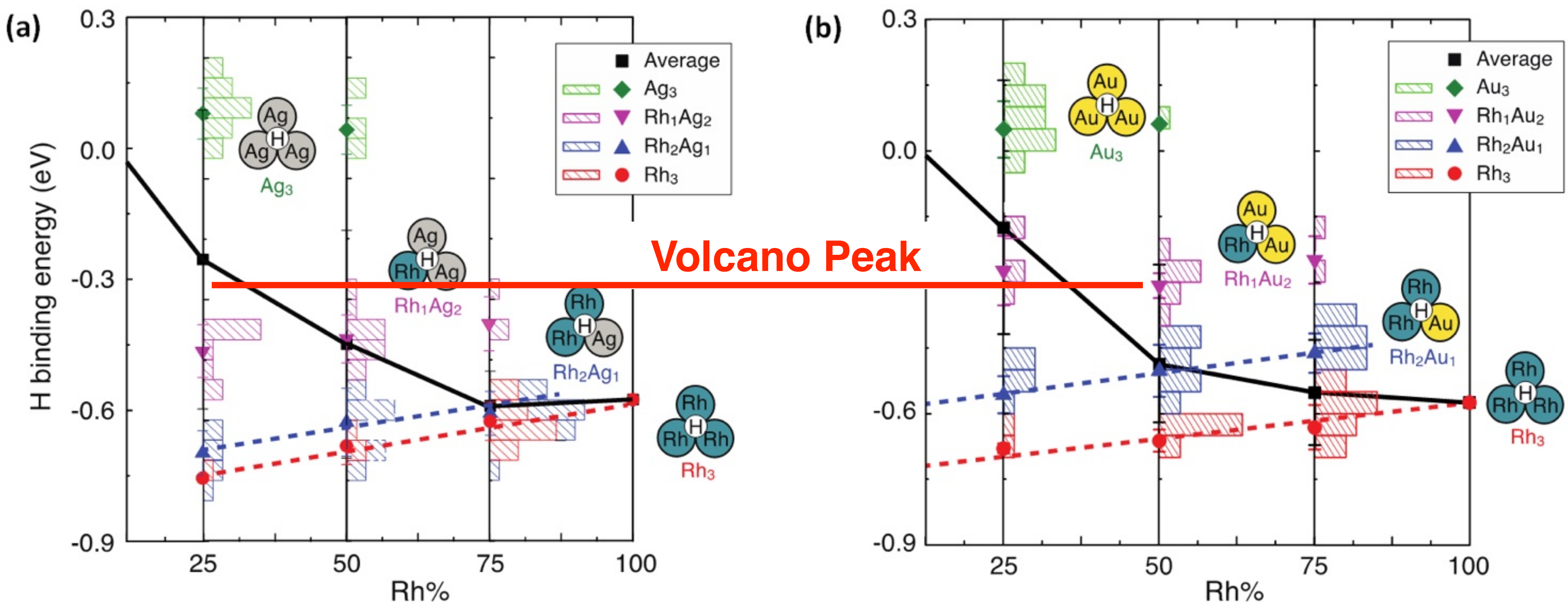


S. García, L. Zhang, G. W. Piburn, G. Henkelman, and S. M. Humphrey, *ACS Nano* **8**, 11512-11521 (2014).

Calculations of H binding to Alloys

Alloying: can tune the H binding energy to the optimal value

Rh/Ag **Rh/Au**

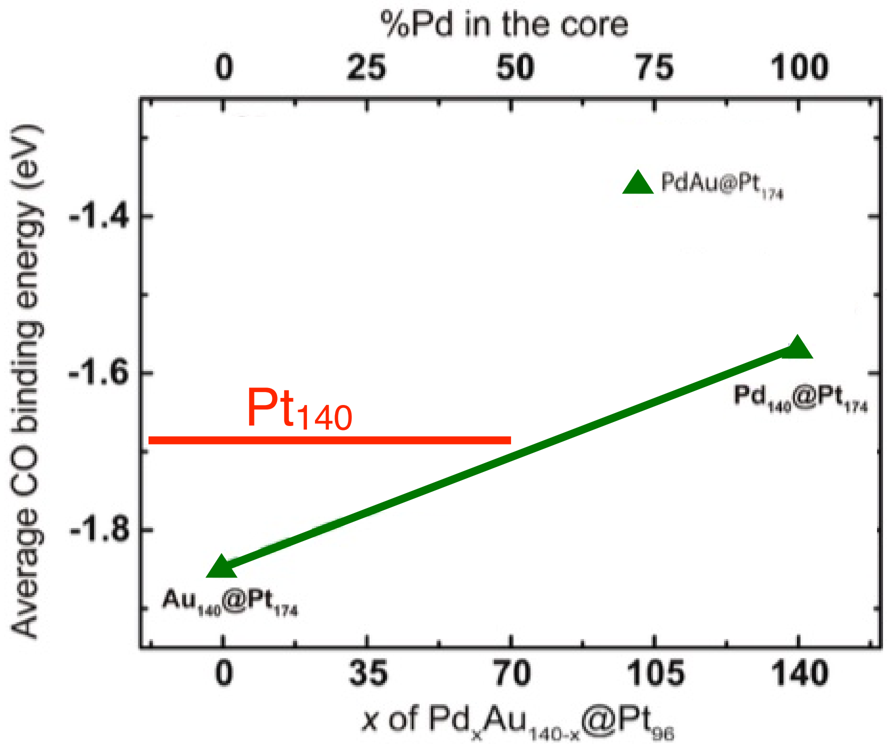


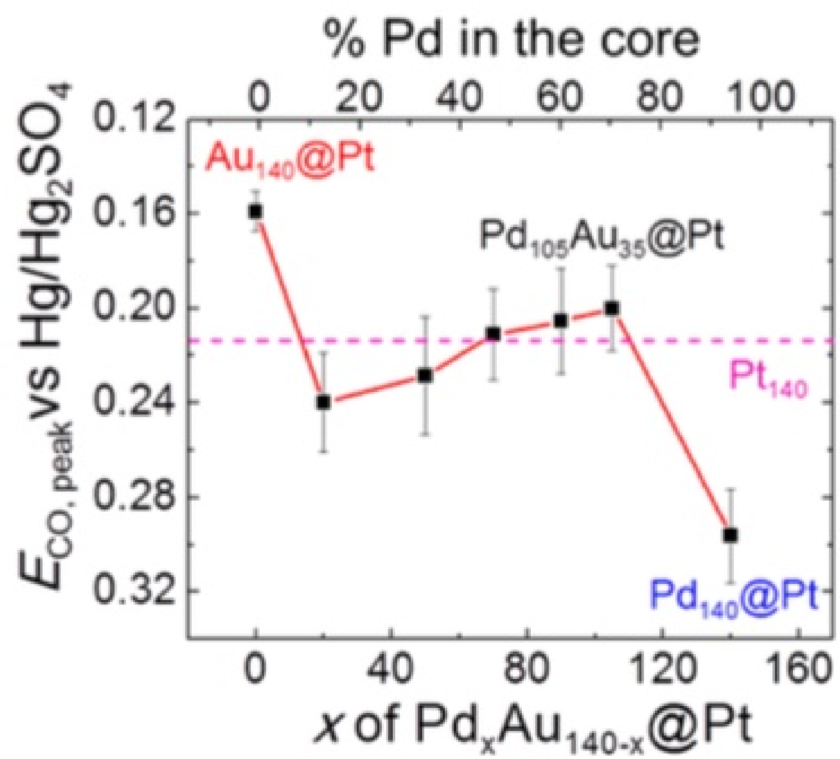
S. García, L. Zhang, G. W. Piburn, G. Henkelman, and S. M. Humphrey, *ACS Nano* **8**, 11512-11521 (2014).

When the details matter: Part I

Calculations: 2 nm Au/Pd@Pt particles show a smooth change in the CO binding energy with core composition

Experiments: 1.7 nm Au/Pd@Pt particles show an unusual non-linear CO stripping potential with core composition



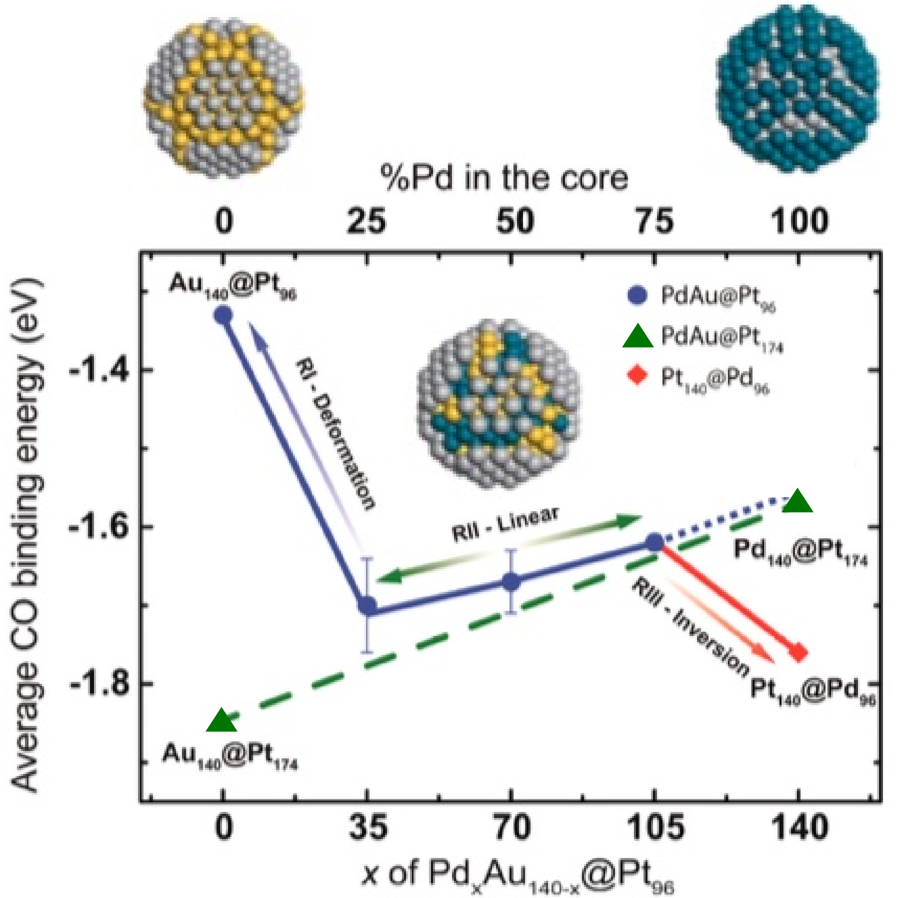


When the details matter: Part I

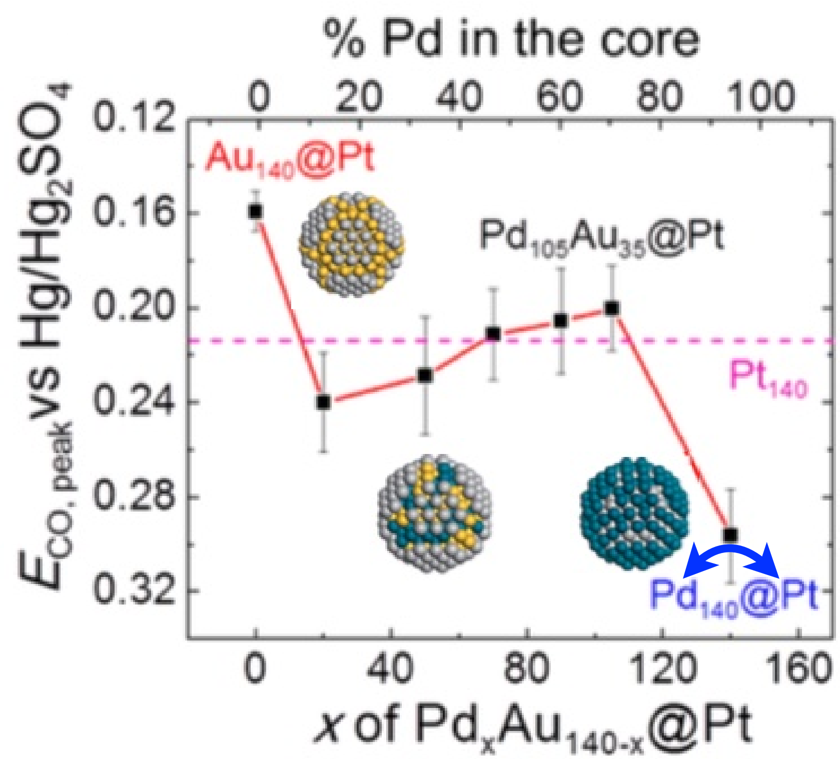
Calculations: 1.7 nm Au/Pd@Pt

deform at Au-rich core

invert for Pd-rich core



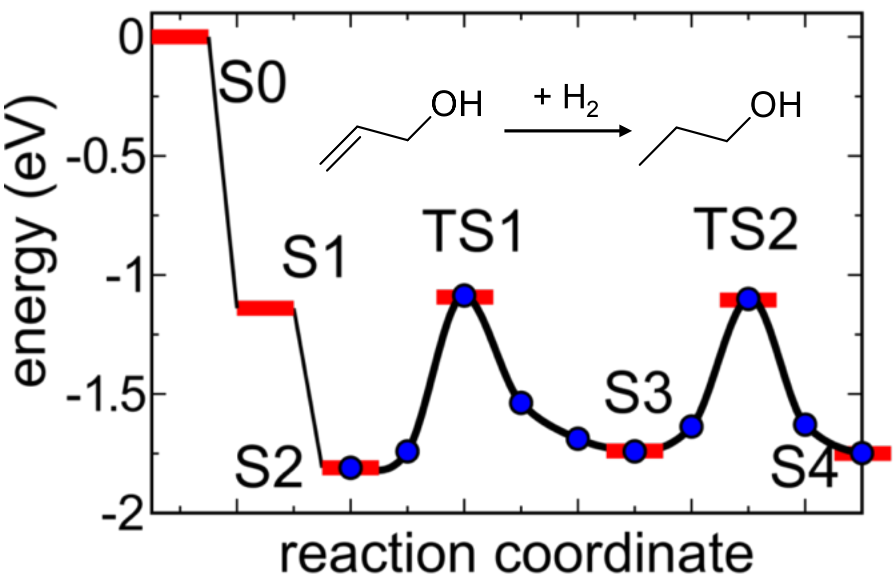
Experiments: 1.7 nm Au/Pd@Pt particles show an unusual non-linear CO stripping potential with core composition

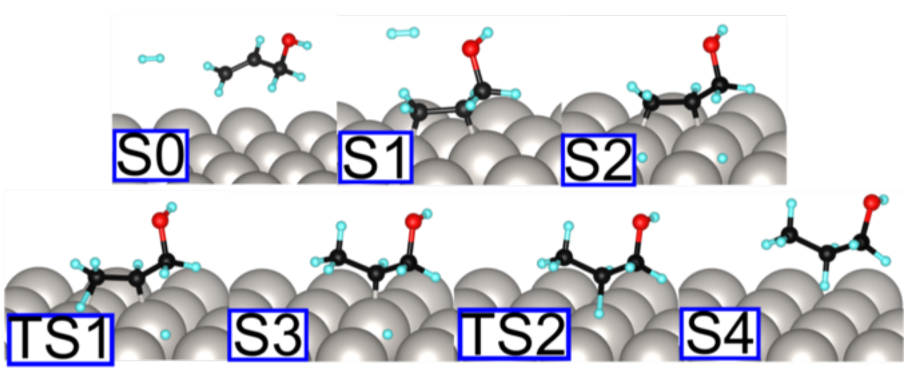


L. Luo, L. Zhang, G. Henkelman, and R. M. Crooks, *J. Phys. Chem. Lett.* **6**, 2562-2568 (2015).

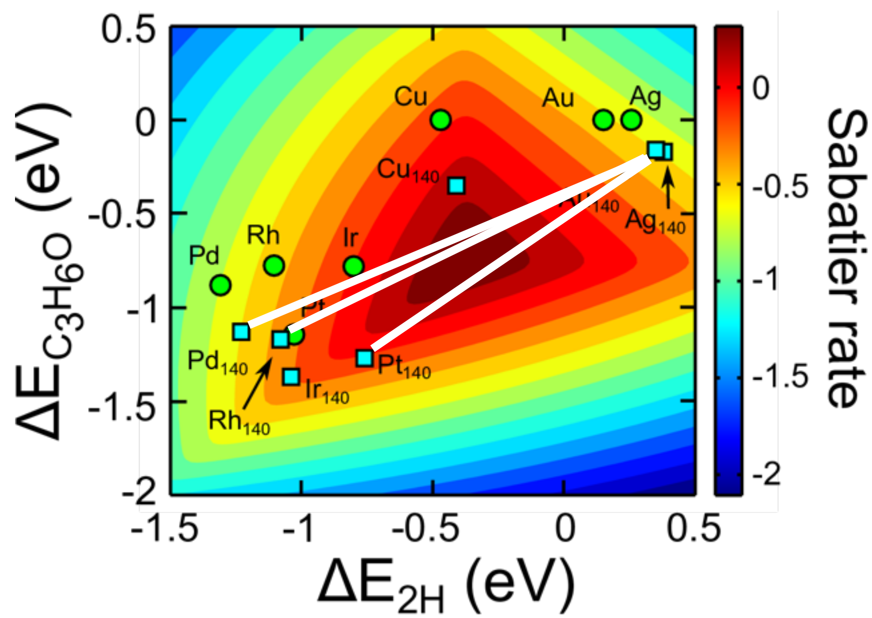
When the details matter: Part II

Allyl alcohol hydrogenation: on metal surfaces

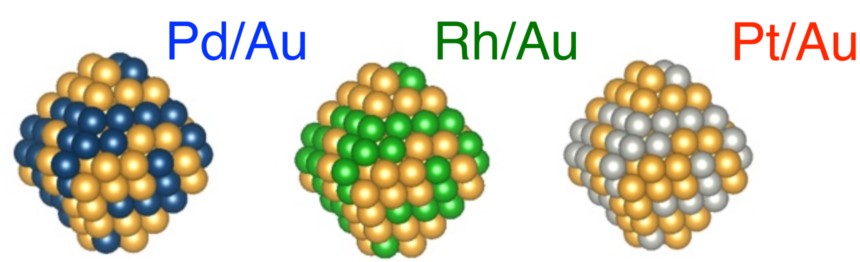




Descriptors: H and Allyl Alcohol binding energies

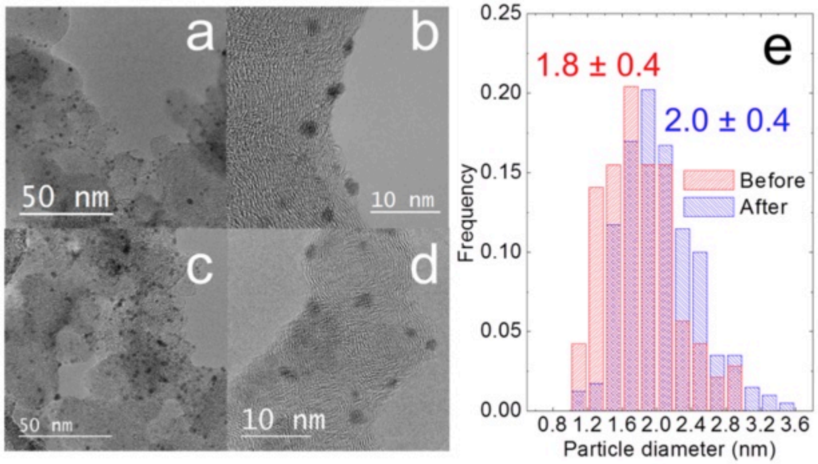


Can particles be tuned for hydrogenation by alloying?

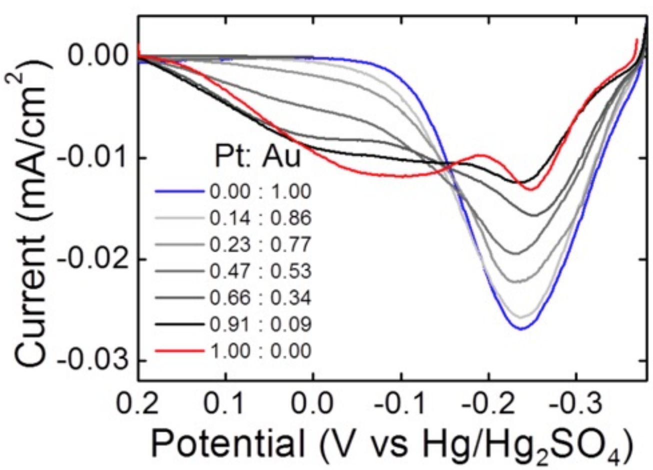


Experiments

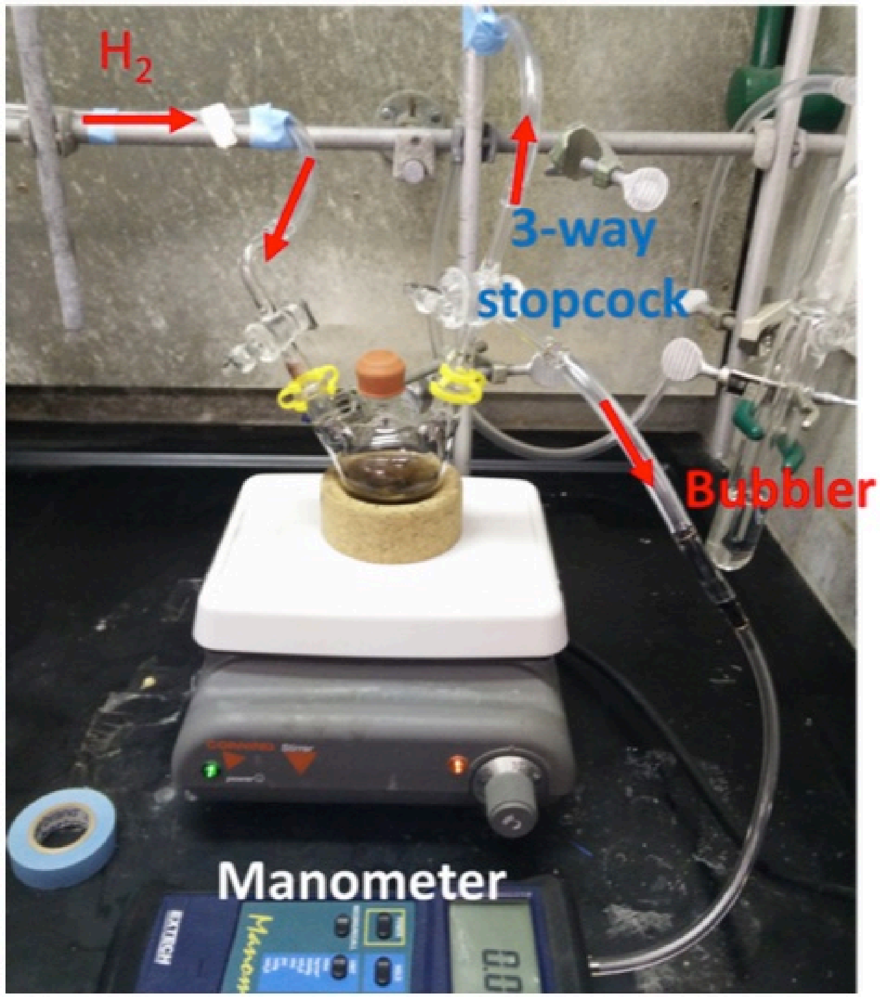
DENs size distribution: TEM



Alloys: Cu UPD stripping

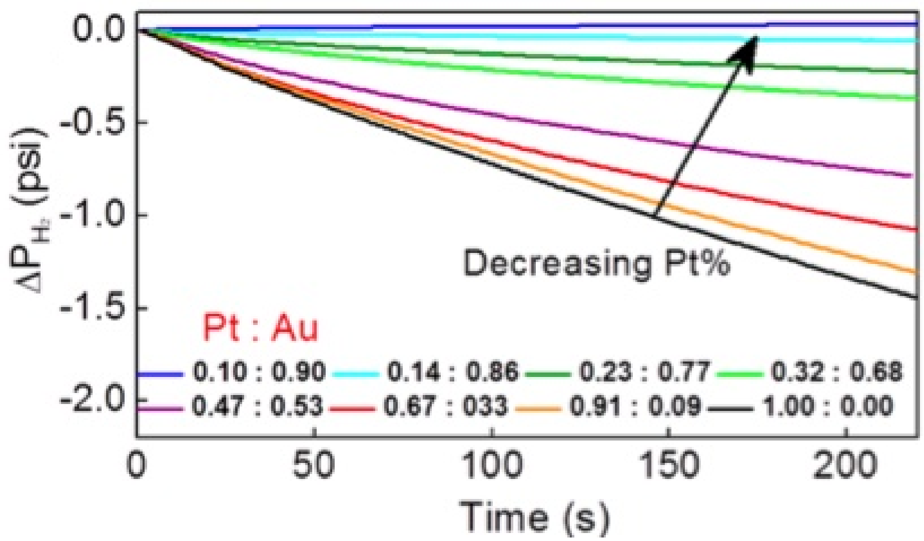


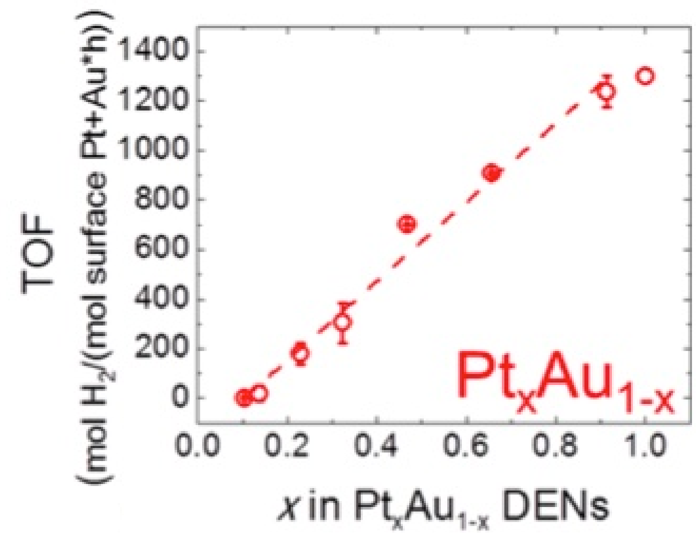
Catalytic activity: Measure the change in H_2 pressure over time

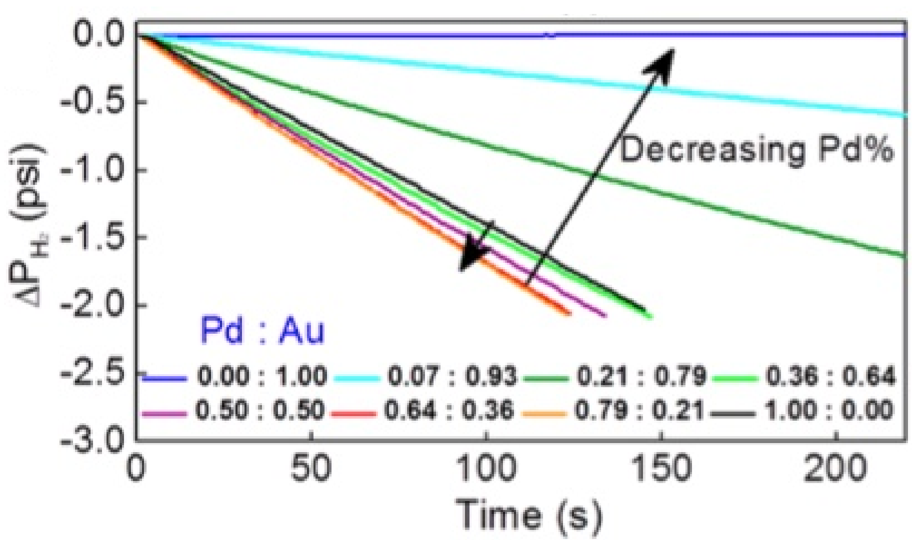


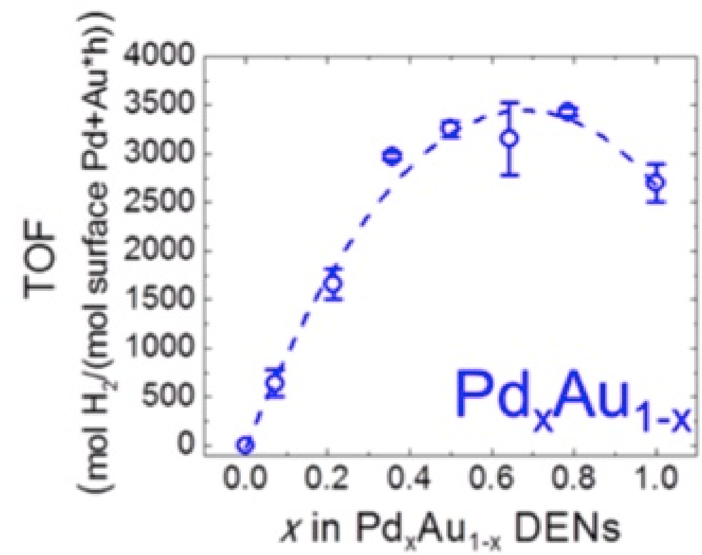
Experimental results

Pd/Au alloys have enhanced activity; **Pt/Au** do not!

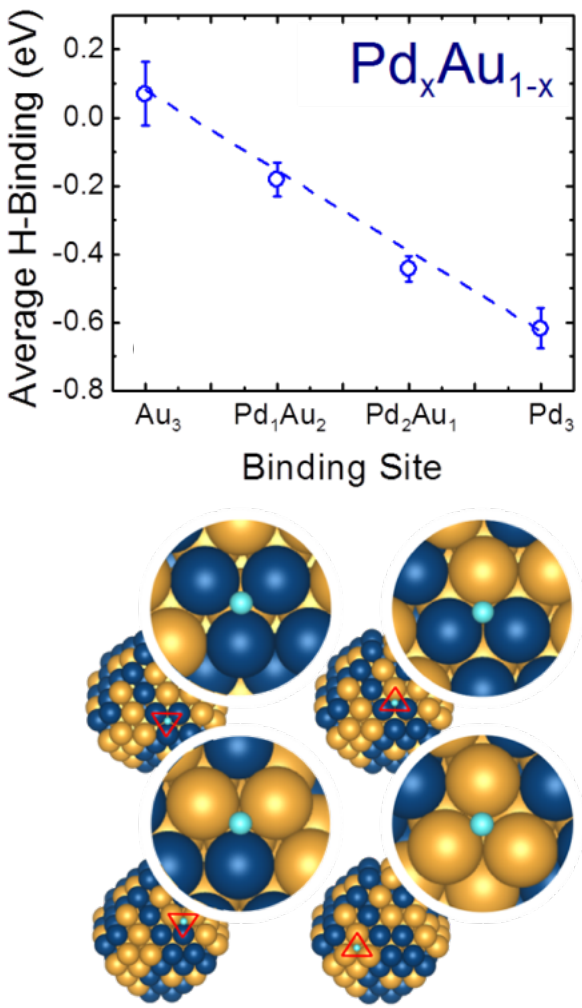


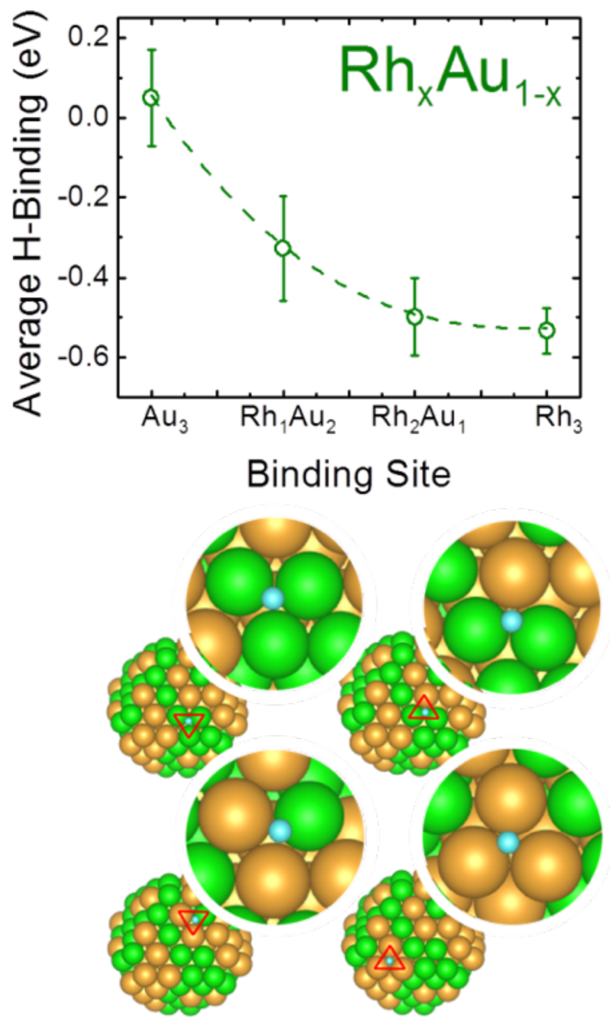


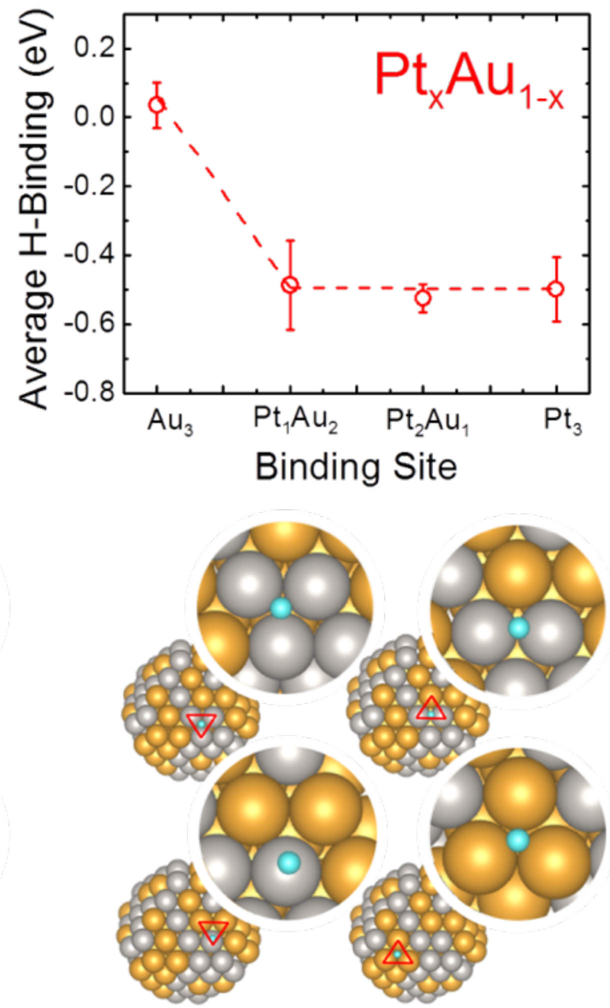




Different trends in H binding energies







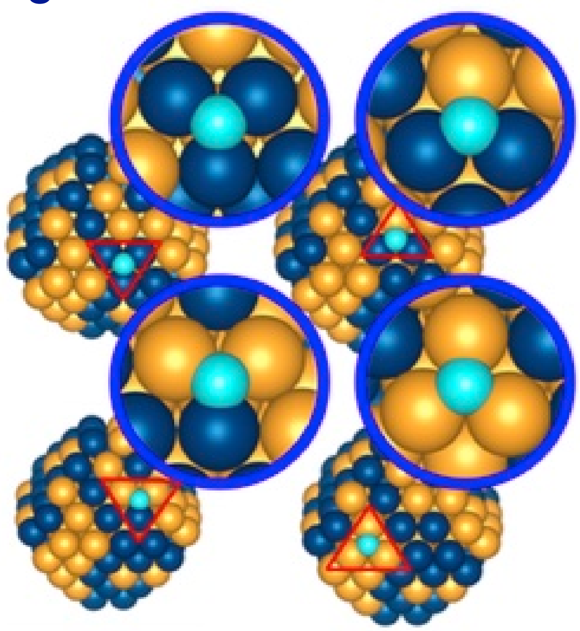
Linear tunability

Non-linear tunability

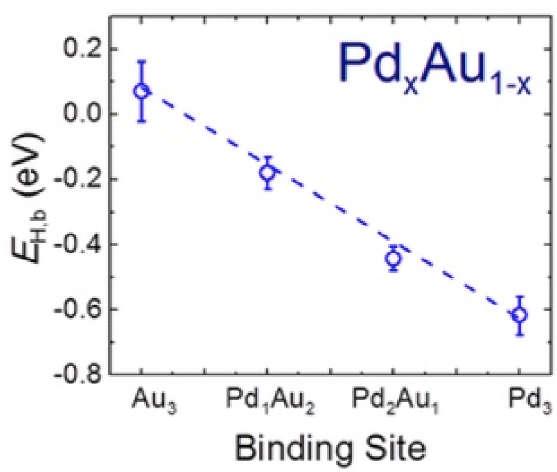
No tunability

What makes an alloy tunable?

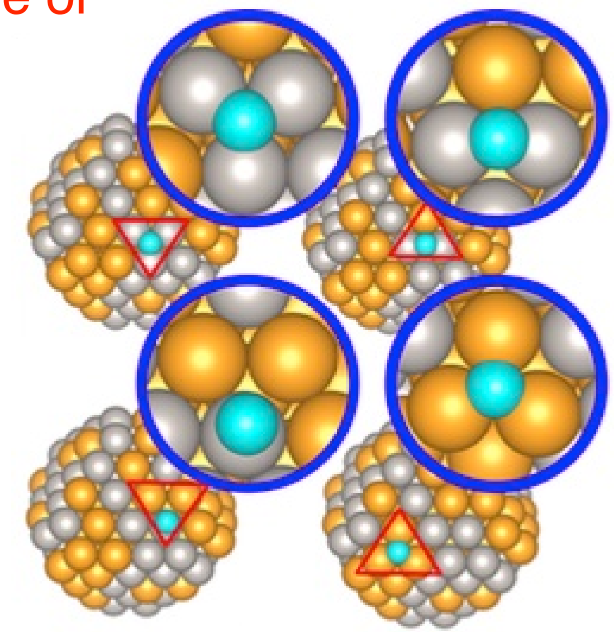
Pd/Au: Mixed metal hollow binding site



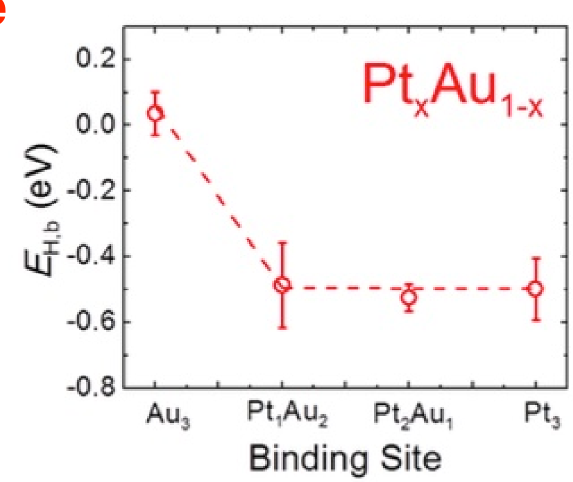
Tunable Binding



Pt/Au: binds to Pt; hollow, bridge or top site

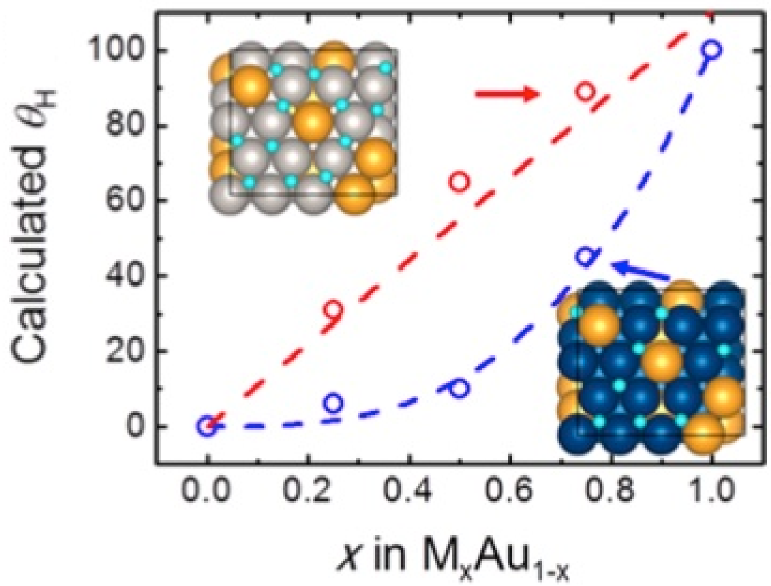


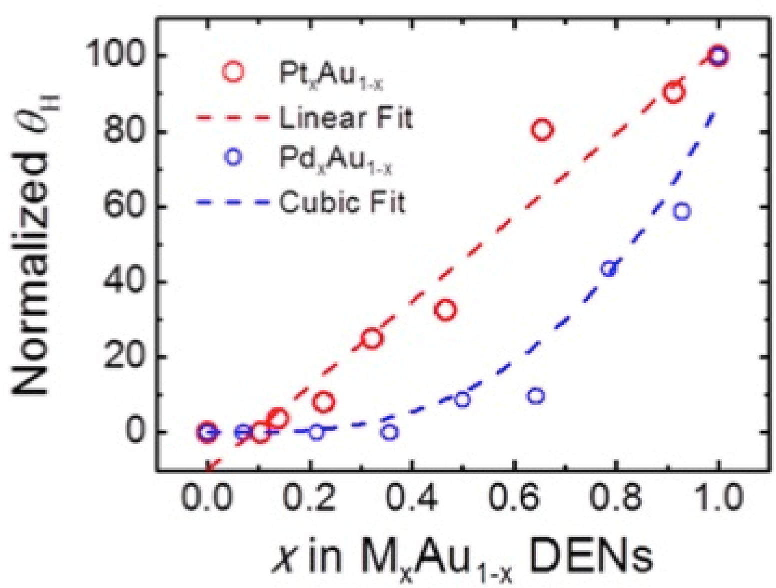
Non-Tunable Binding



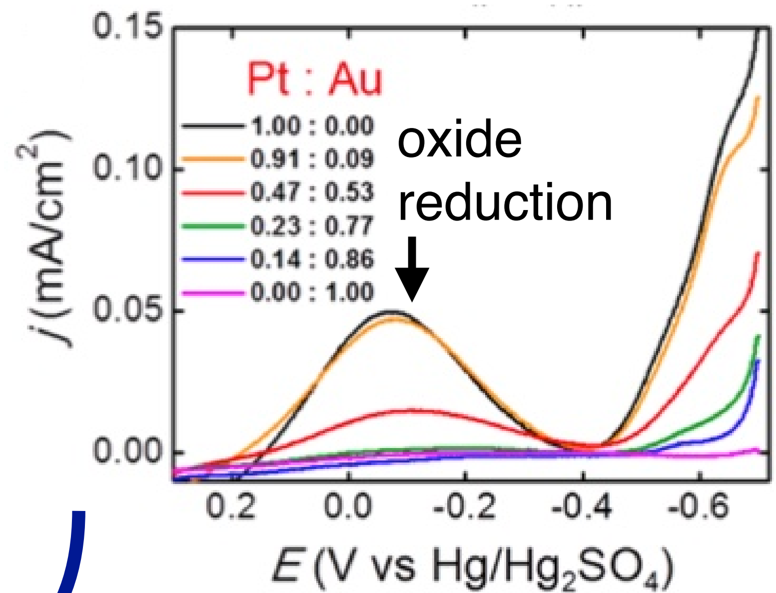
Comparison to Experiment: H coverage

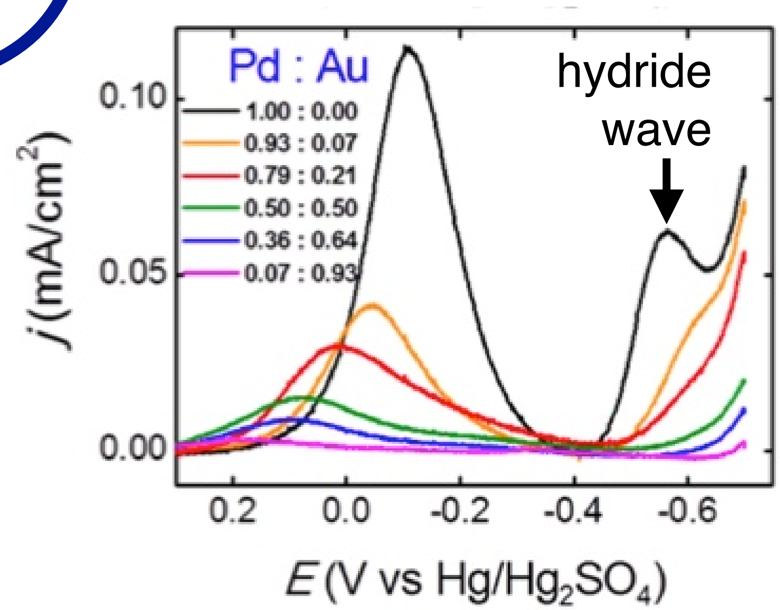
Calculations of H coverage





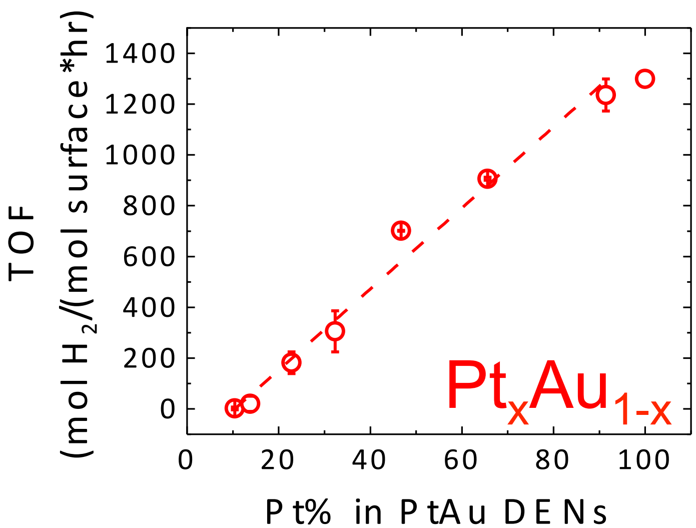
Measurements of H coverage

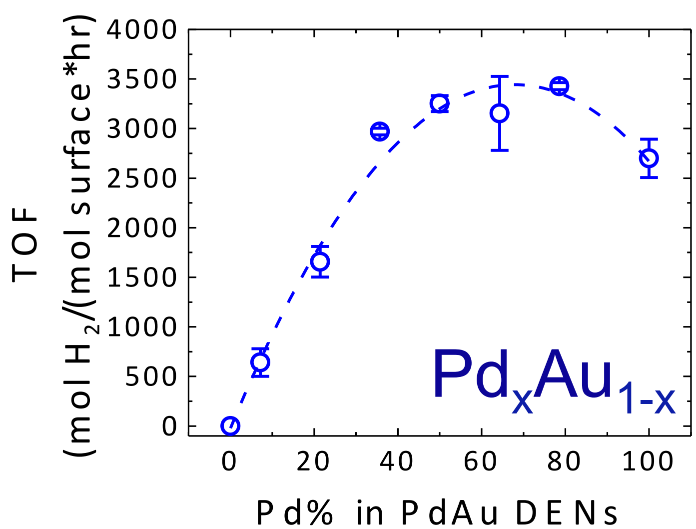




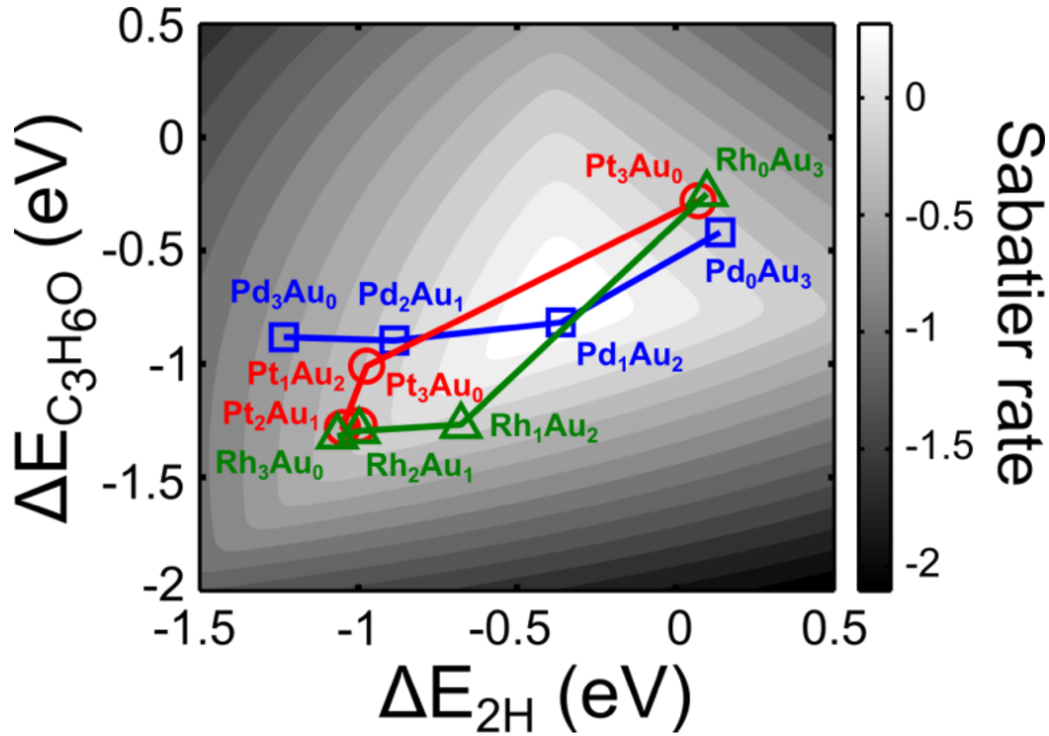
Comparison to Experiment: Activity

Experiments





Theory: but with the details



Pt/Au alloys : basically no improvement

Rh/Au alloys: some improvement

Pd/Au alloys: significant improvement

L. Luo, Z. Duan, H. Li, J. Kim, G. Henkelman, and R. M. Crooks, *J. Am. Chem. Soc.* **139**, 5538-5546 (2017).

Main Points

- An integration of theoretical and experimental tools is a promising way forward for the development of new catalytic systems.
- Reactivity descriptors provide a very powerful way of predicting catalytic activity; sometimes, however, the specific details of the catalytic system can be critically important for understanding structure-function relationships.

Research Group