Adsorption Energy Correlations at the Metal-Support Boundary
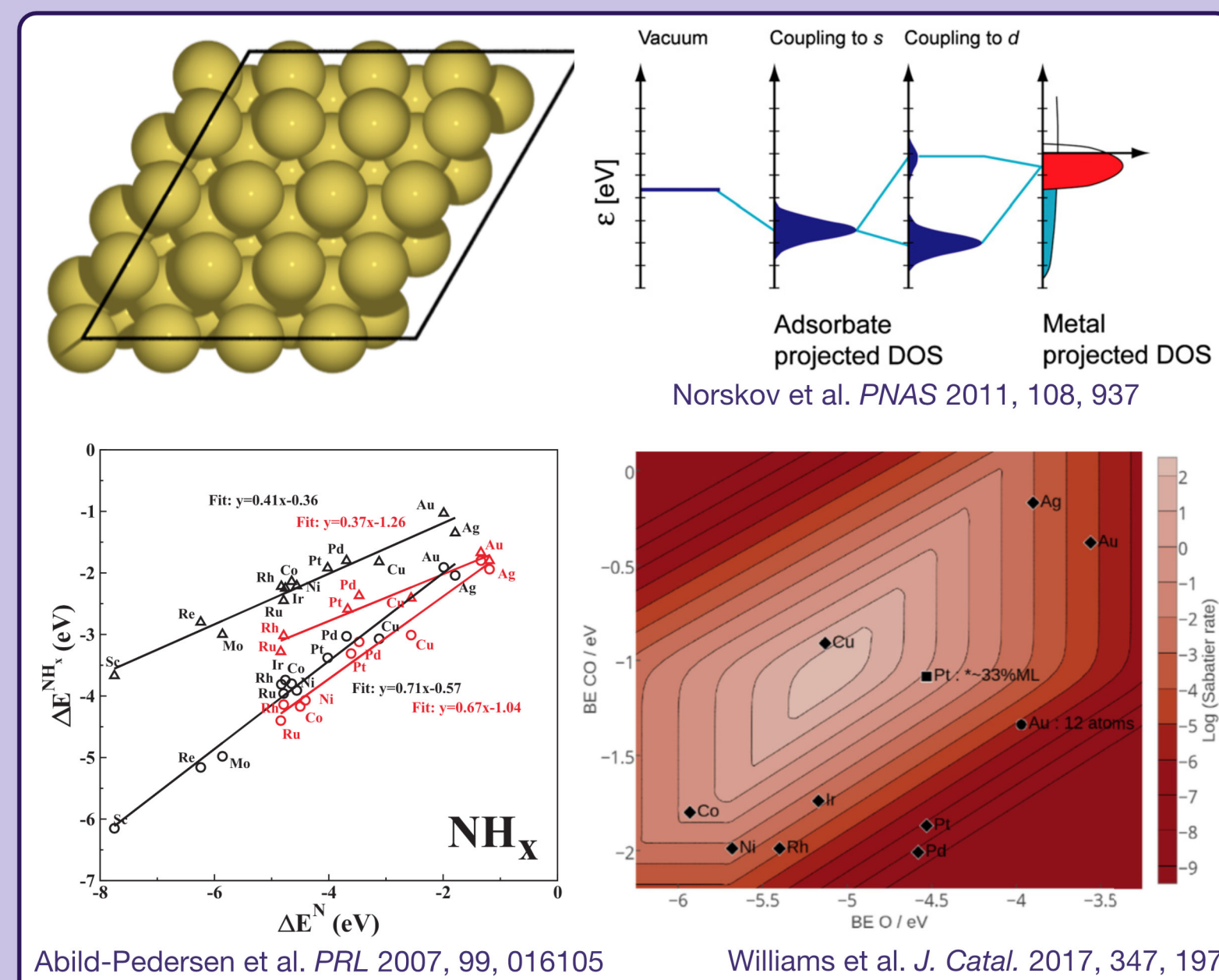
Prateek Mehta, Jeffrey Greeley, W. Nicholas Delgass, William F. Schneider*

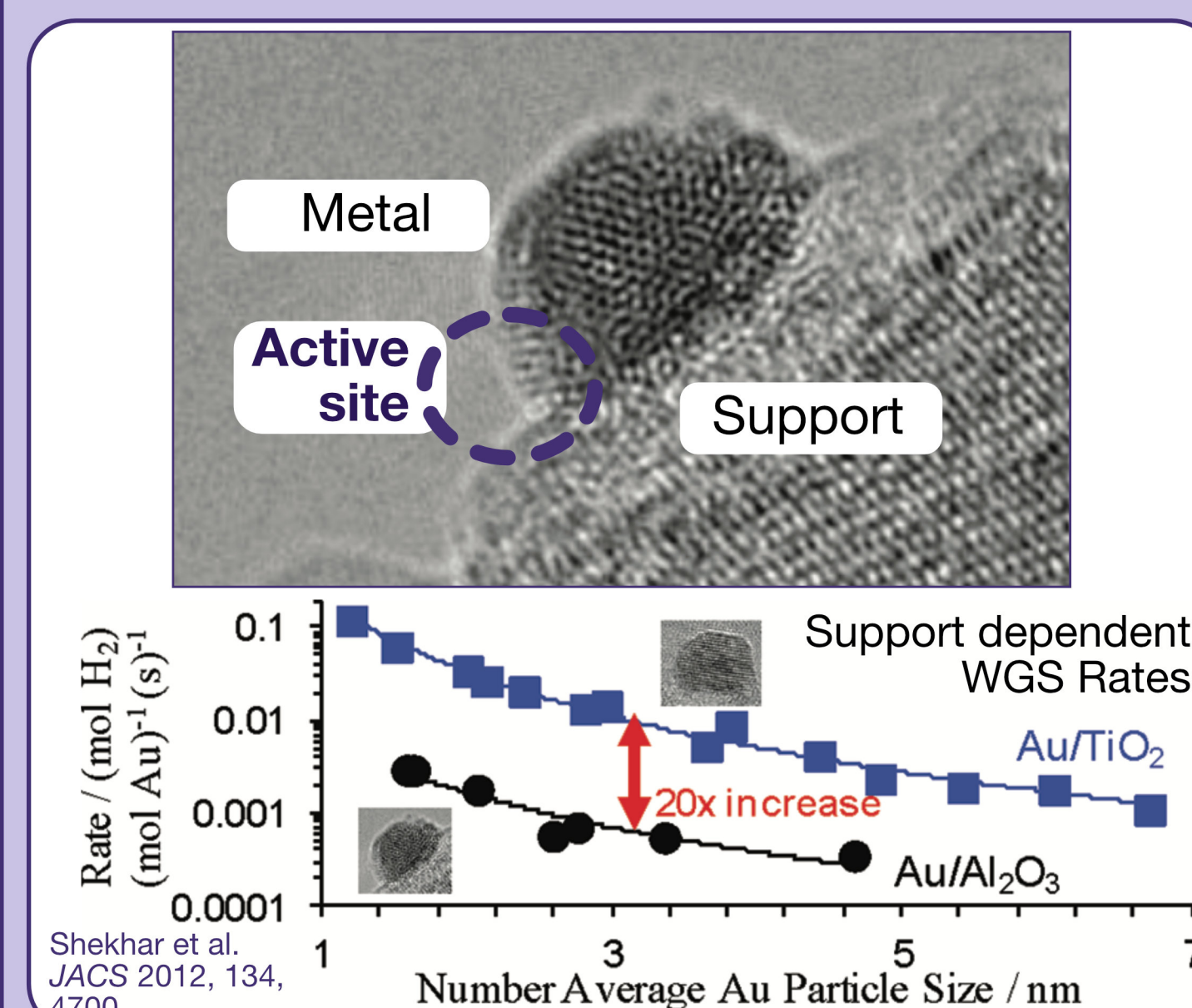COLLEGE OF ENGINEERING

Introduction

Computational approaches for modeling metal surface reactivity are well developed

Norskov et al. *PNAS* 2011, 108, 937

NH_x

Abild-Pedersen et al. *PRL* 2007, 99, 016105

Williams et al. *J. Catal.* 2017, 347, 197

Adsorption and activation energy scaling relations well established; applied for catalyst screening

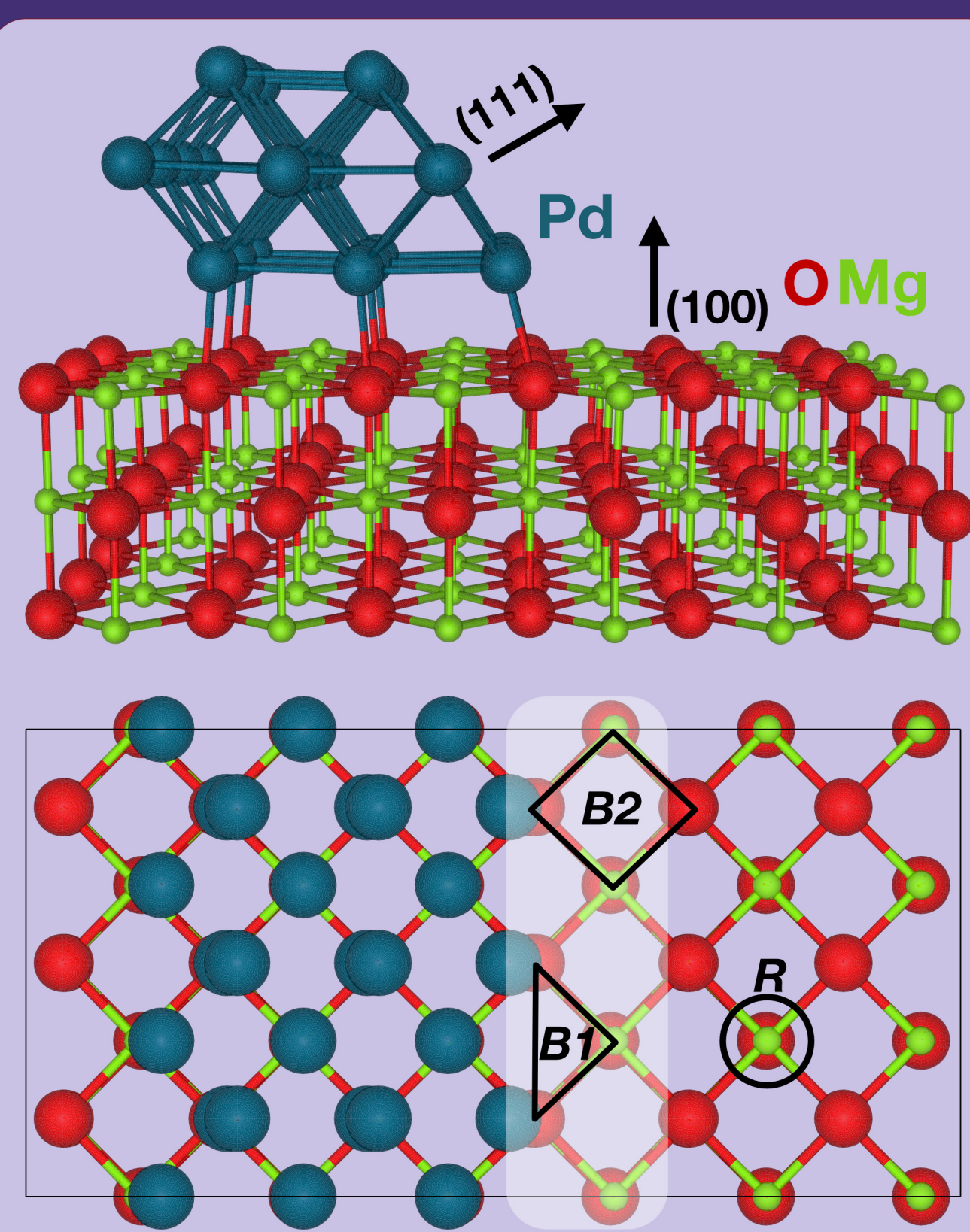Variations in reactivity explained using d-band model

But, metal nanoparticles are almost always dispersed on a support

"dual" reaction sites at metal-support boundary often proposed as active sites (CO oxidation, water gas shift, methanol synthesis)
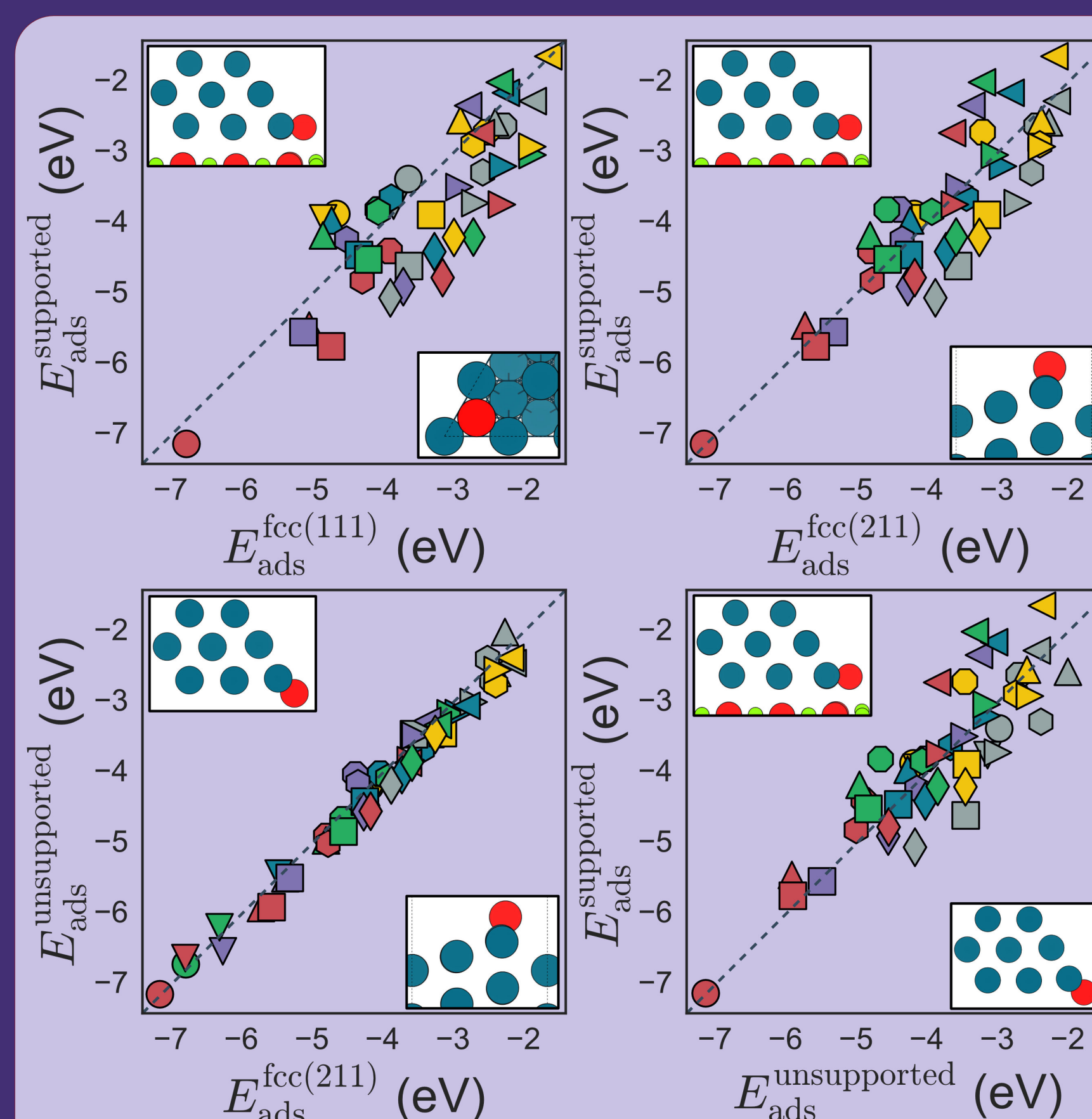
Metal
Active site
Support

Support dependent WGS Rates

Au/TiO_2

20x increase

Au/Al_2O_3

Rate /(mol H_2 (mol Au)$^{-1}$ (s)$^{-1}$)

Number Average Au Particle Size / nm

Shekhar et al. *JACS* 2012, 134, 4700

How is the reactivity of metal-support boundary sites different from pure metal sites?

M/MgO nanowire model

(111)
Pd
(100)
Mg

$E_{ads}^{supported}$ (eV)
$E_{ads}^{fcc(111)}$ (eV)
$E_{ads}^{fcc(211)}$ (eV)
$E_{ads}^{unsupported}$ (eV)

B2
B1
R

Idealized representation of boundary of large nanoparticle

Adsorbates placed at site B1

Adsorption energies at the M/MgO boundary are not captured by standard metal-only models

MgO supported metals

| Rh | Pd | Ag |
| Ir | Pt | Au |

simple atomic and hydrogen containing adsorbates

○ C ▽ CH ◁ NH_2
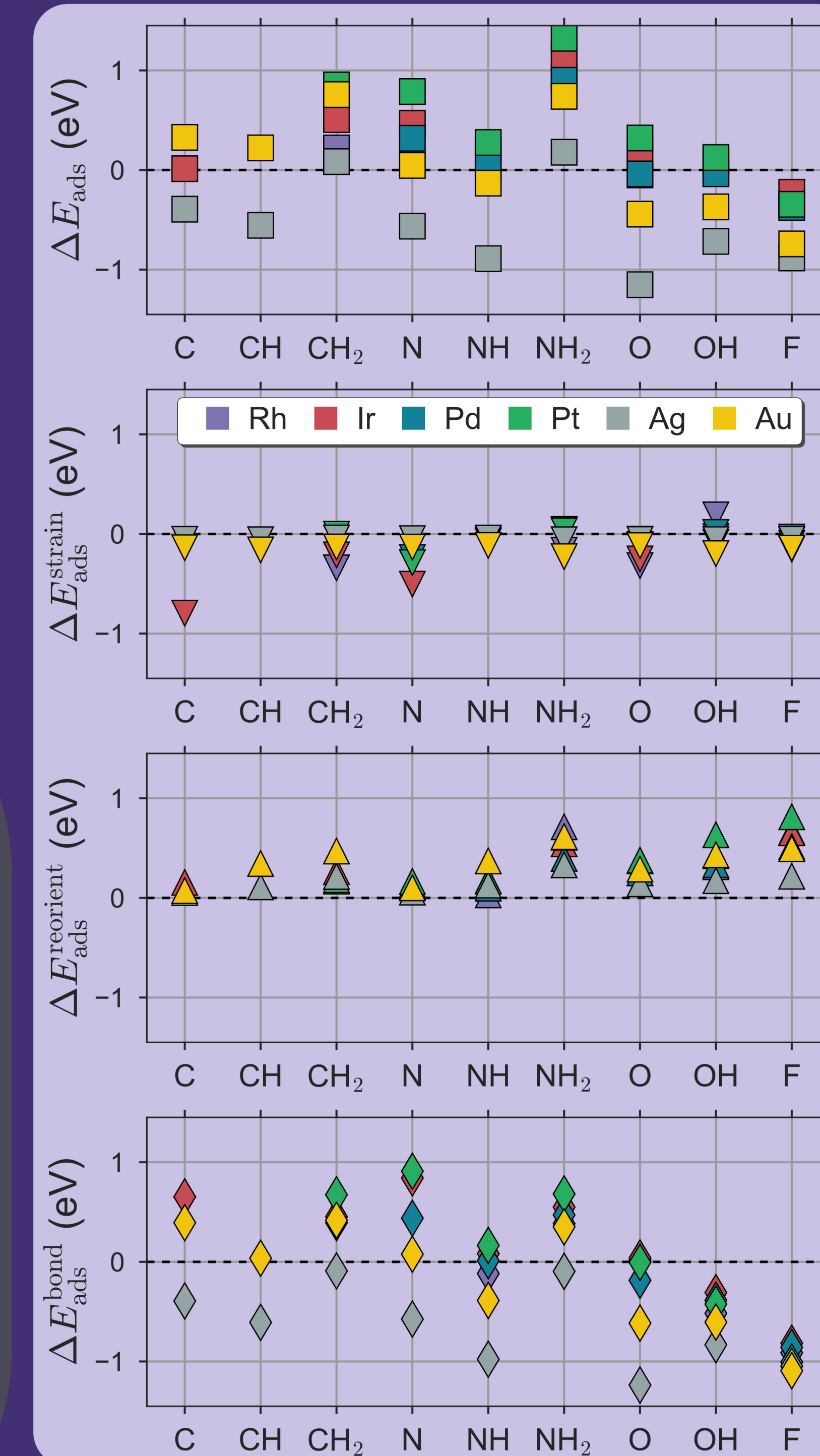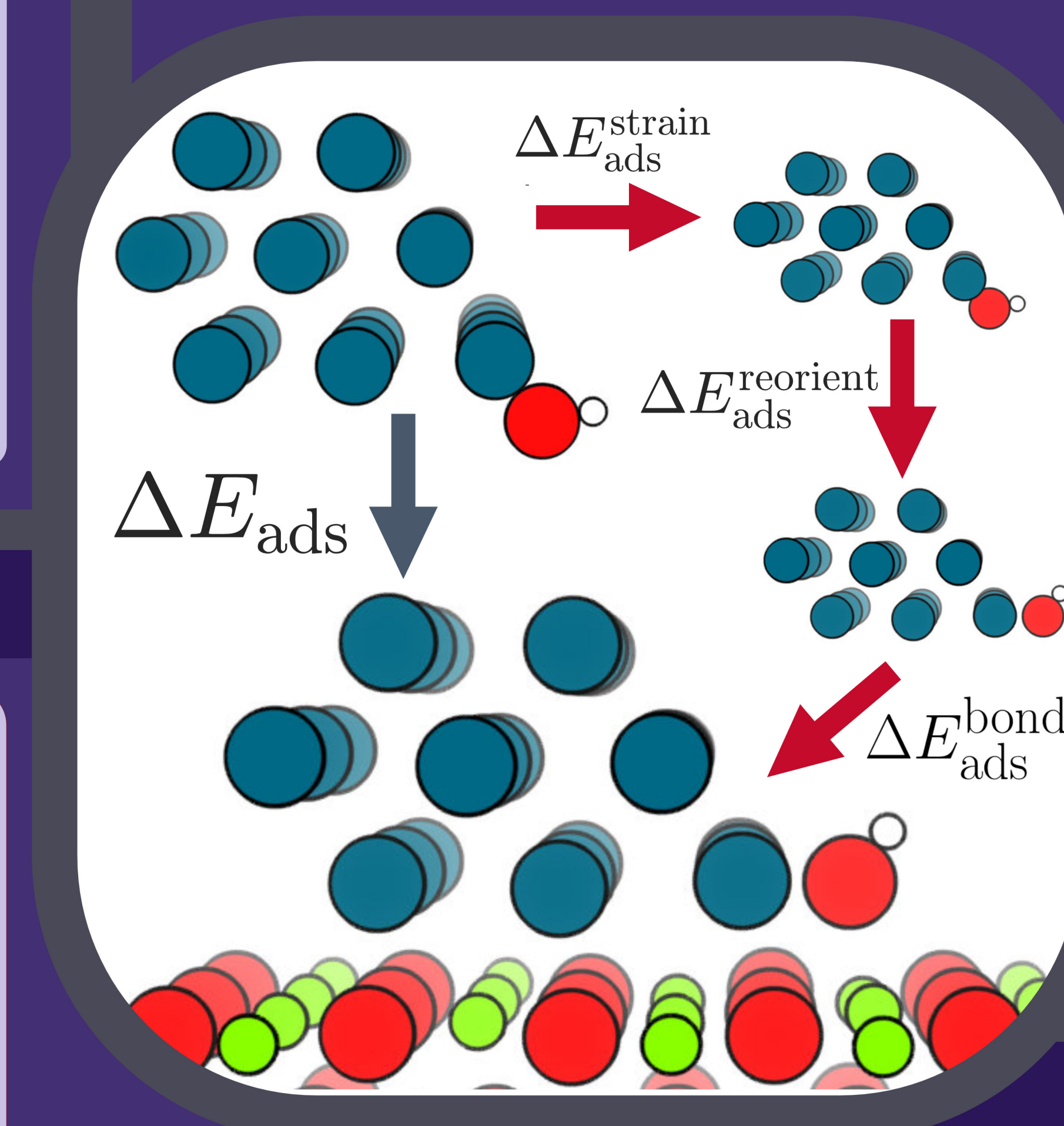△ CH ○ CH_2 ▷ OH
□ O ⬠ NH ◇ F

Supercell PBE DFT calculations performed using VASP
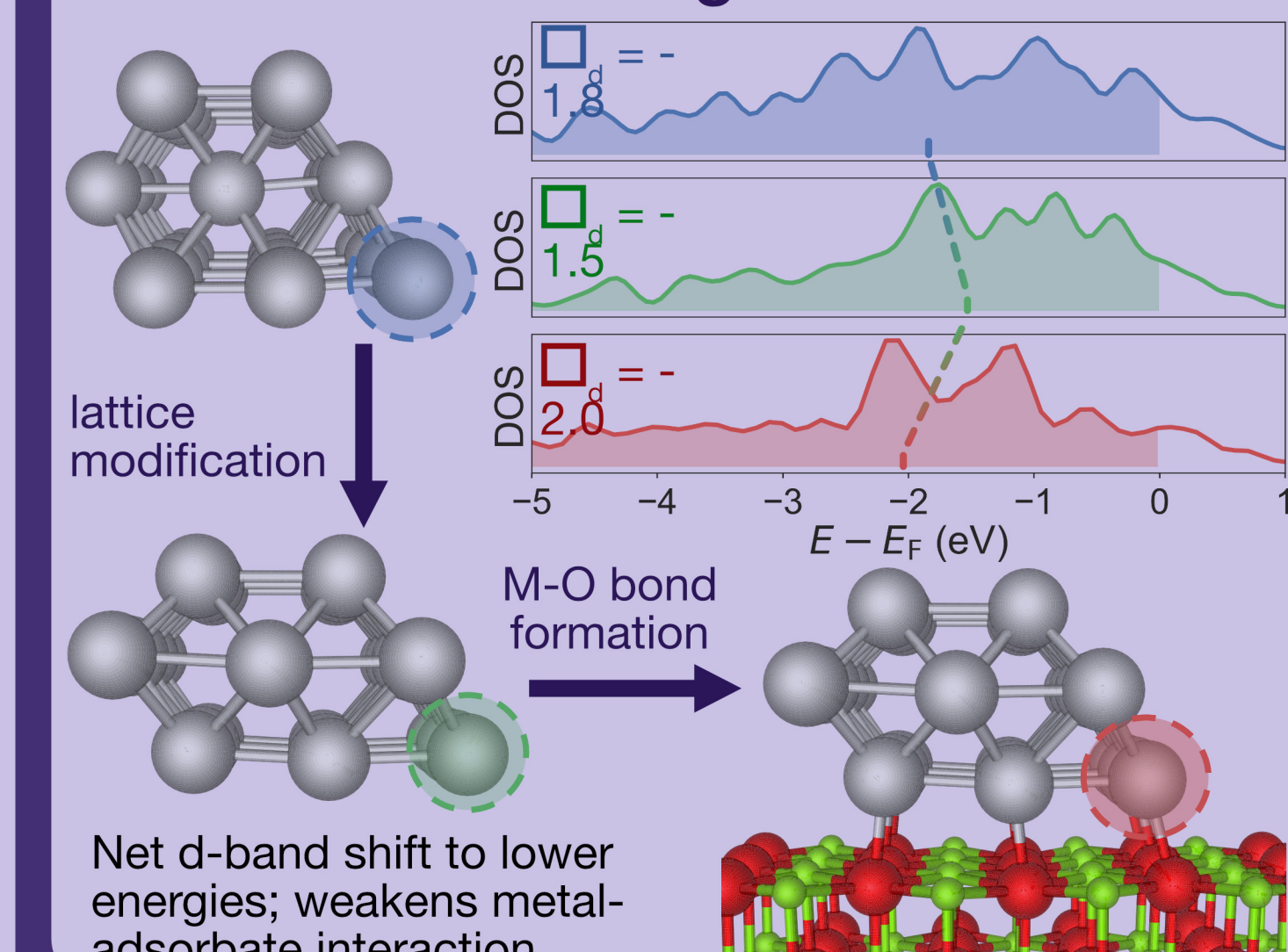
Origins of adsorption energy perturbations

Overall support effect on adsorption energy is non-systematic; individual adsorption energy perturbations vary systematically

- ΔE_{ads}^{strain} enhances adsorption strength
- $\Delta E_{ads}^{reorient}$ is a steric energy penalty
- $\Delta E_{ads}^{bond} = \Delta E_{ads}^{ligand} + \Delta E_{ads}^{redox}$
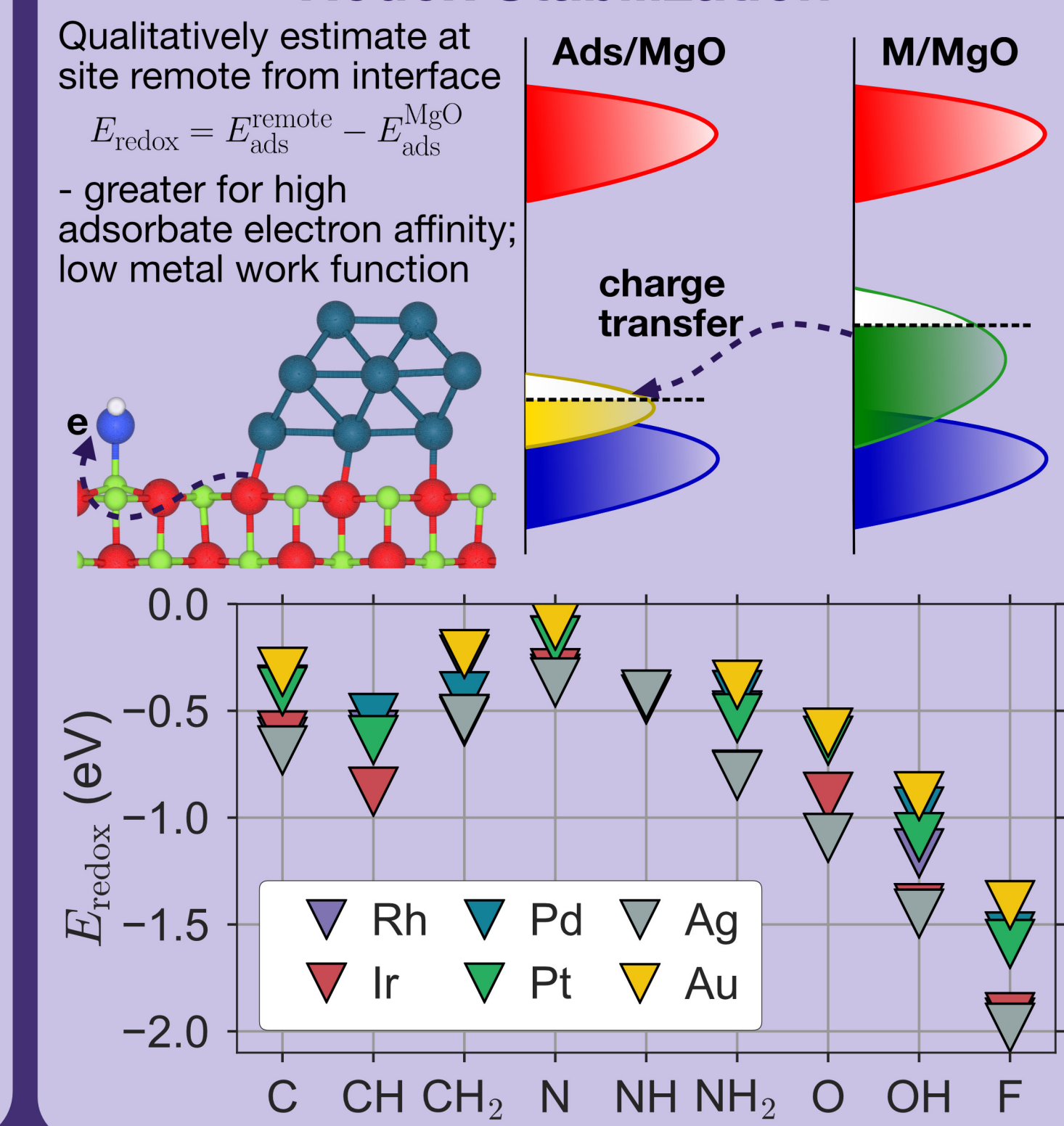- ligand effect weakens adsorption; redox effect strengthens adsorption

Main graphic: The overall support effect on the adsorption energy decomposes into strain, reorientation, and bonding effects

ΔE_{ads} (eV)
ΔE_{ads}^{strain} (eV)
$\Delta E_{ads}^{reorient}$ (eV)
ΔE_{ads}^{bond} (eV)

Rh Ir Pd Pt Ag Au

ΔE_{ads}^{strain}
$\Delta E_{ads}^{reorient}$
ΔE_{ads}^{bond}

C CH CH_2 N NH NH_2 O OH F

Strain and Ligand Effects

DOS 1.8
DOS 1.5
DOS 2.0

$E - E_F$ (eV)

lattice modification

Net d-band shift to lower energies; weakens metal-adsorbate interaction

M-O bond formation

Redox Stabilization

Qualitatively estimate at site remote from interface

$E_{redox} = E_{ads}^{remote} - E_{ads}^{MgO}$

- greater for high adsorbate electron affinity; low metal work function

Ads/MgO M/MgO

charge transfer

E_{redox} (eV)

C CH CH_2 N NH NH_2 O OH F

Rh Pd Ag
Ir Pt Au

Significance

Results guide both the the construction of interface models and predictions of reactivity

- identify systems most likely to show deviations from metal-only models

Departures from scaling relations possible at interface

- individual metal data points shifted; occasionally become outliers
- computational screening based on metal-only correlations might misidentify optimal catalysts or miss promising candidates

y = 0.48x - 0.91
y = 0.41x - 1.29

Au
Ag
Pt
Pd
Rh
Ir

E_{ads}^{OH}
E_{ads}^{O}

y = 0.34x - 1.62
y = 0.37x - 0.65

$E_{ads}^{NH_2}$
E_{ads}^{N}