



materials design®

# Machine Learning Meets Quantum Chemistry: Using Theory, Data, and Experiments to Design Catalysts

Siwen Wang  
Materials Design

February 2021



# Materials Design Webinar Series

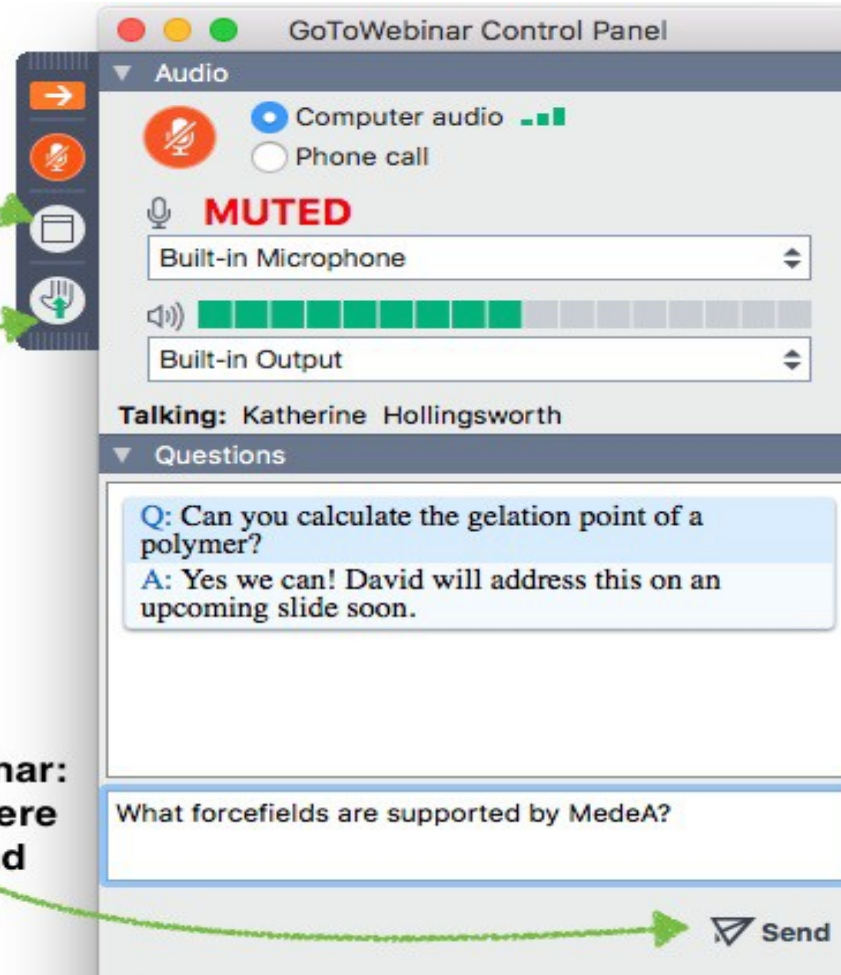
- ▶ **Each session runs several times to accommodate schedules**
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# Please Ask Questions!

**Use the raise hand icon to bring attention to your question**

**full screen**  
**during discussion:**

**any time during webinar:  
type your question here  
and then press Send**



The screenshot shows the GoToWebinar Control Panel interface. It features a sidebar on the left with icons for full screen, mute, and raise hand. The main panel is divided into sections: Audio, Talking, and Questions. The Audio section shows 'Computer audio' selected and the microphone is 'MUTED'. The Talking section shows 'Talking: Katherine Hollingsworth'. The Questions section contains a question and answer: 'Q: Can you calculate the gelation point of a polymer?' and 'A: Yes we can! David will address this on an upcoming slide soon.' Below this is a text input field with the question 'What forcefields are supported by MedeA?' and a 'Send' button.



# Webinar Speakers

***Katherine Hollingsworth***

*khollingsworth@materialsdesign.com*

***Siwen Wang***

*swang@materialsdesign.com*

***Taylor Juran***

*tjuran@materialsdesign.com*



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# Machine Learning Meets Quantum Chemistry: Using Theory, Data, and Experiments to Design Catalysts

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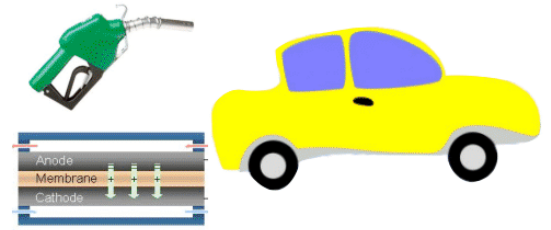
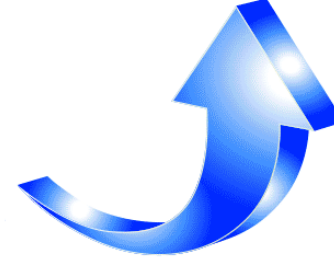
February 2021

# Why Catalysis?

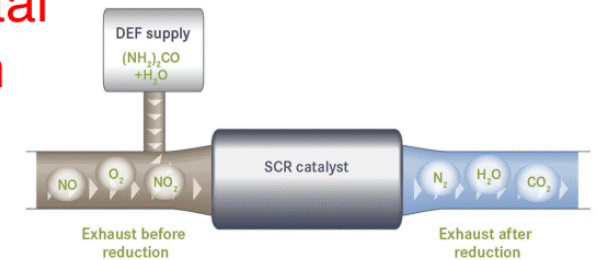


Fe 26 Iron	Co 27 Cobalt	Ni 28 Nickel	Cu 29 Copper
Ru 44 Ruthenium	Rh 45 Rhodium	Pd 46 Palladium	Ag 47 Silver
Os 76 Osmium	Ir 77 Iridium	Pt 78 Platinum	Au 79 Gold
C 6 Carbon	N 7 Nitrogen	O 8 Oxygen	

chemical/  
energy  
transformation



environmental  
remediation

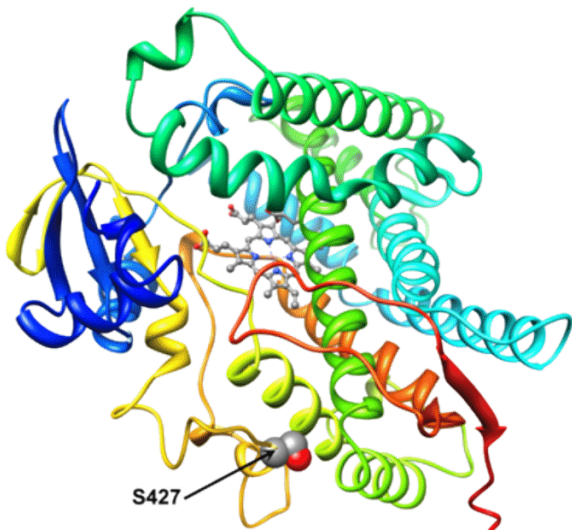
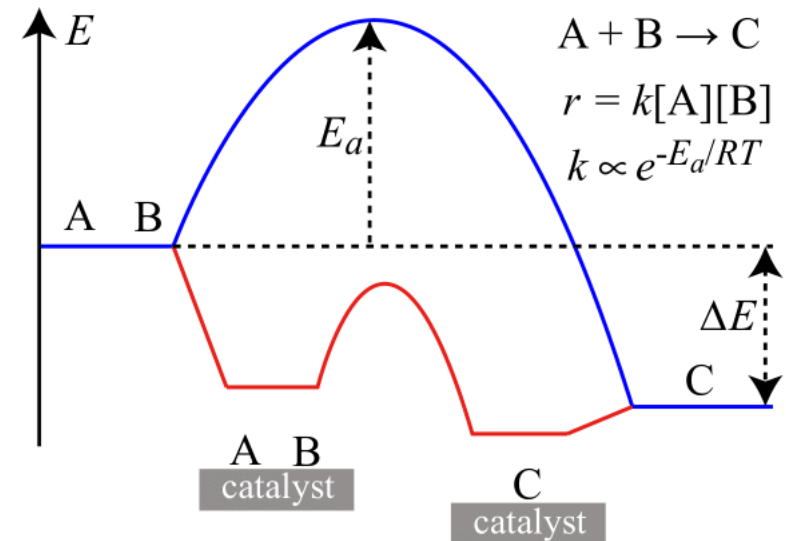


# What is Catalysis?

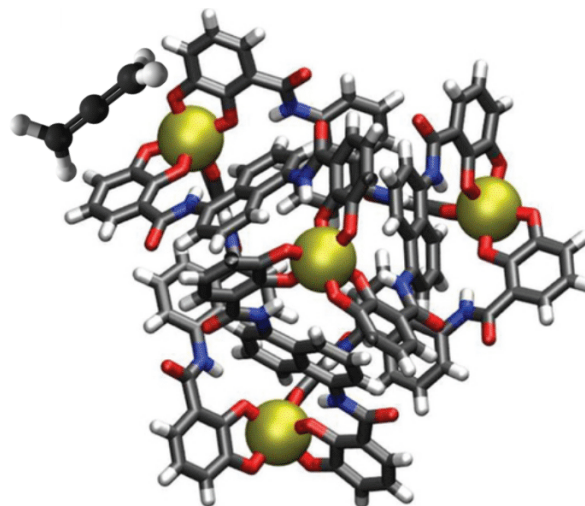
## Modern definition of catalysis

*Catalysis is the acceleration of a slowly proceeding chemical reaction through the presence of a foreign substance.*

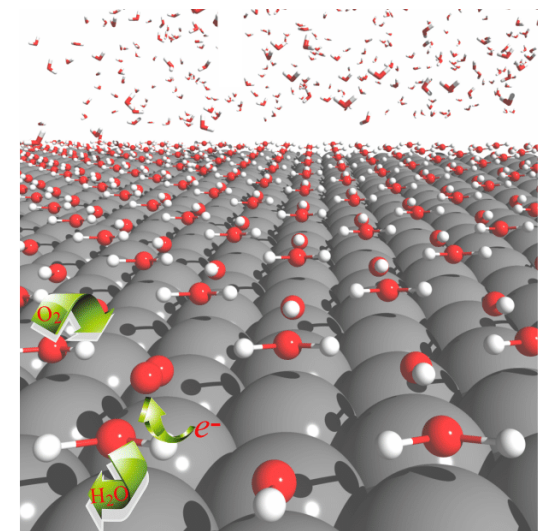
Wilhelm Ostwald 1894



Enzyme Catalysis

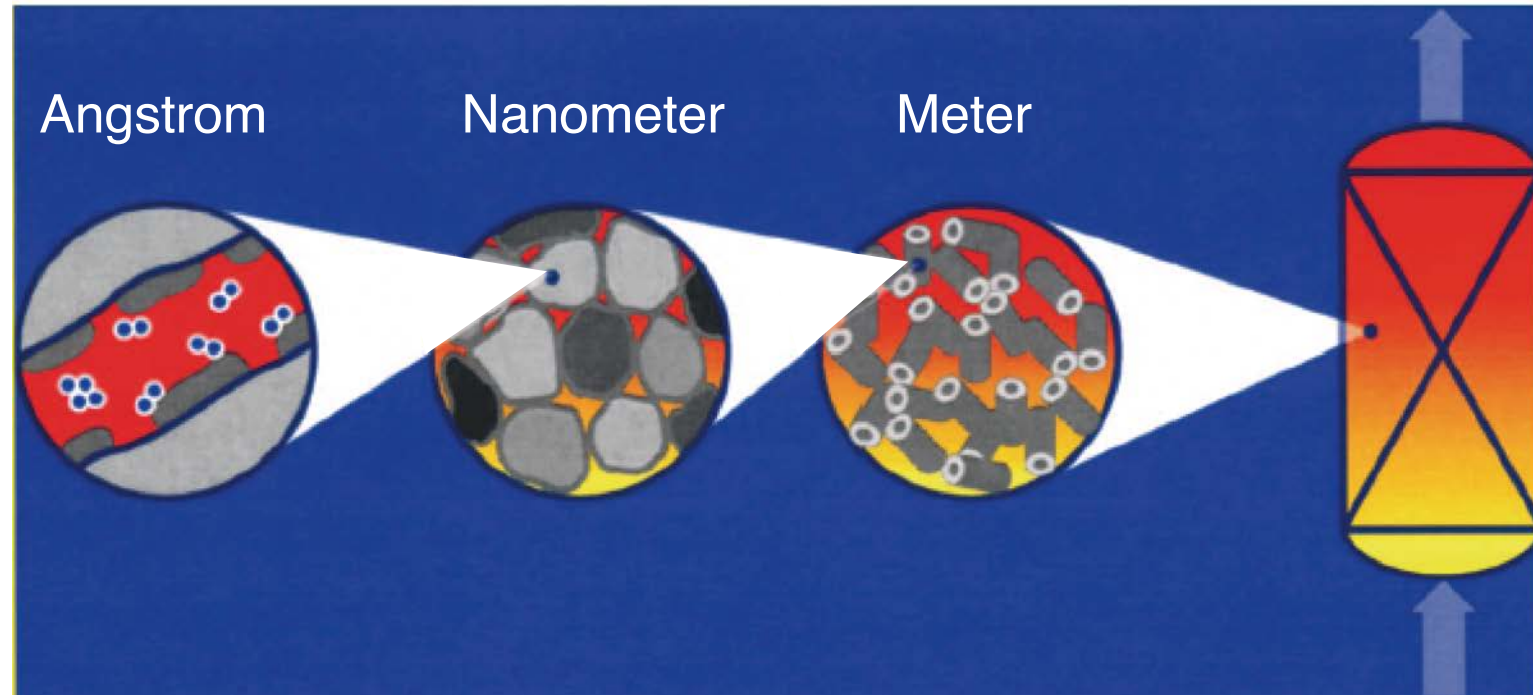


Homogeneous Catalysis

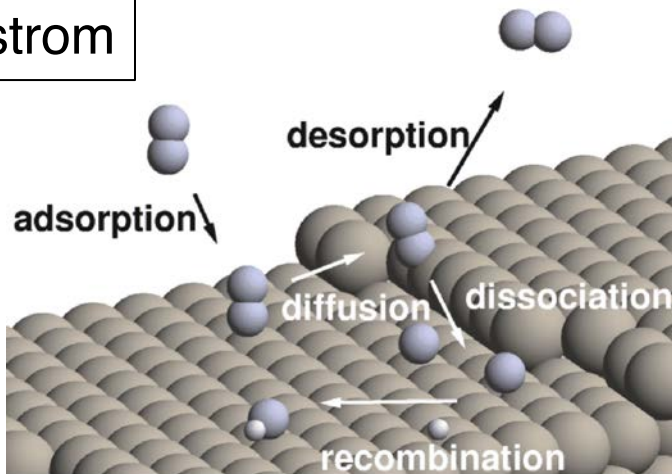


Heterogeneous Catalysis

# Time and Length Scales in Heterogeneous Catalysis

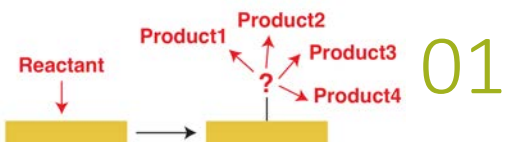


Angstrom



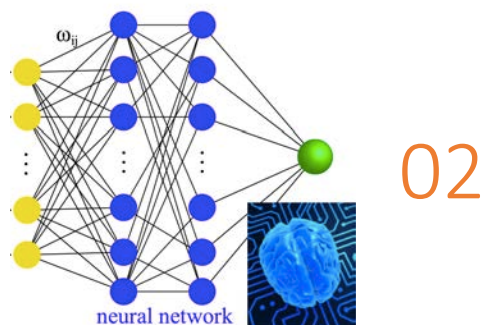
- Elementary events at molecular level control the catalytic performance.
- Understanding the surface chemical bonding is the key to catalyst design.
- Challenge: Rational design of catalytic sites with desired electronic properties.

# Outline



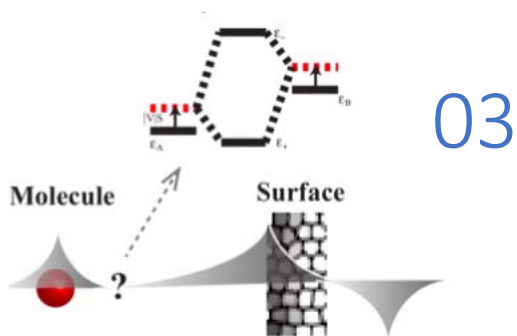
## Understand Reaction Mechanisms

Biopolymer interaction effect in  $C_2H_2$  hydrogenation reaction on Pd catalysts  
Surface strain effect in  $CO_2$  reduction reaction on AgSn/SnO<sub>x</sub> core-shell catalysts



## Accelerate Materials Discovery

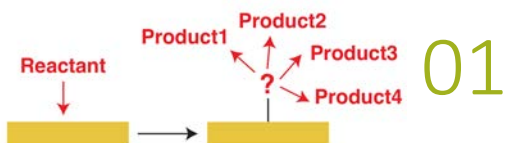
High-throughput screening of bimetallic catalysts enabled by machine learning



## Advance Catalysis Theory

What determines reactivity of catalyst

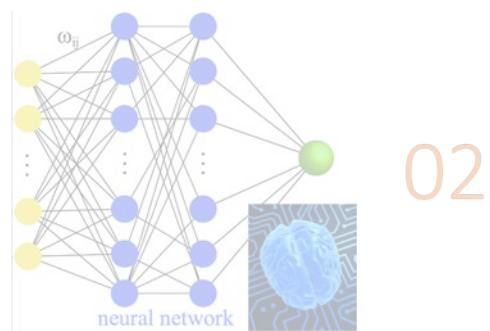
# Outline



## Understand Reaction Mechanisms

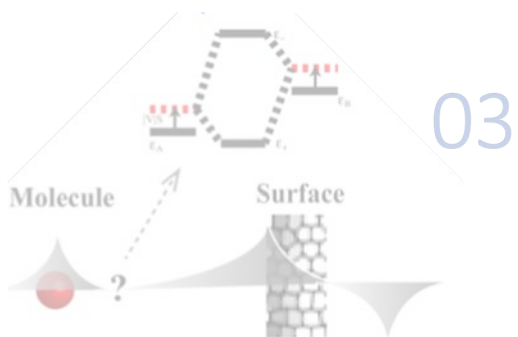
Biopolymer interaction effect in  $C_2H_2$  hydrogenation reaction on Pd catalysts

Surface strain effect in  $CO_2$  reduction reaction on AgSn/SnO<sub>x</sub> core-shell catalysts



## Accelerate Materials Discovery

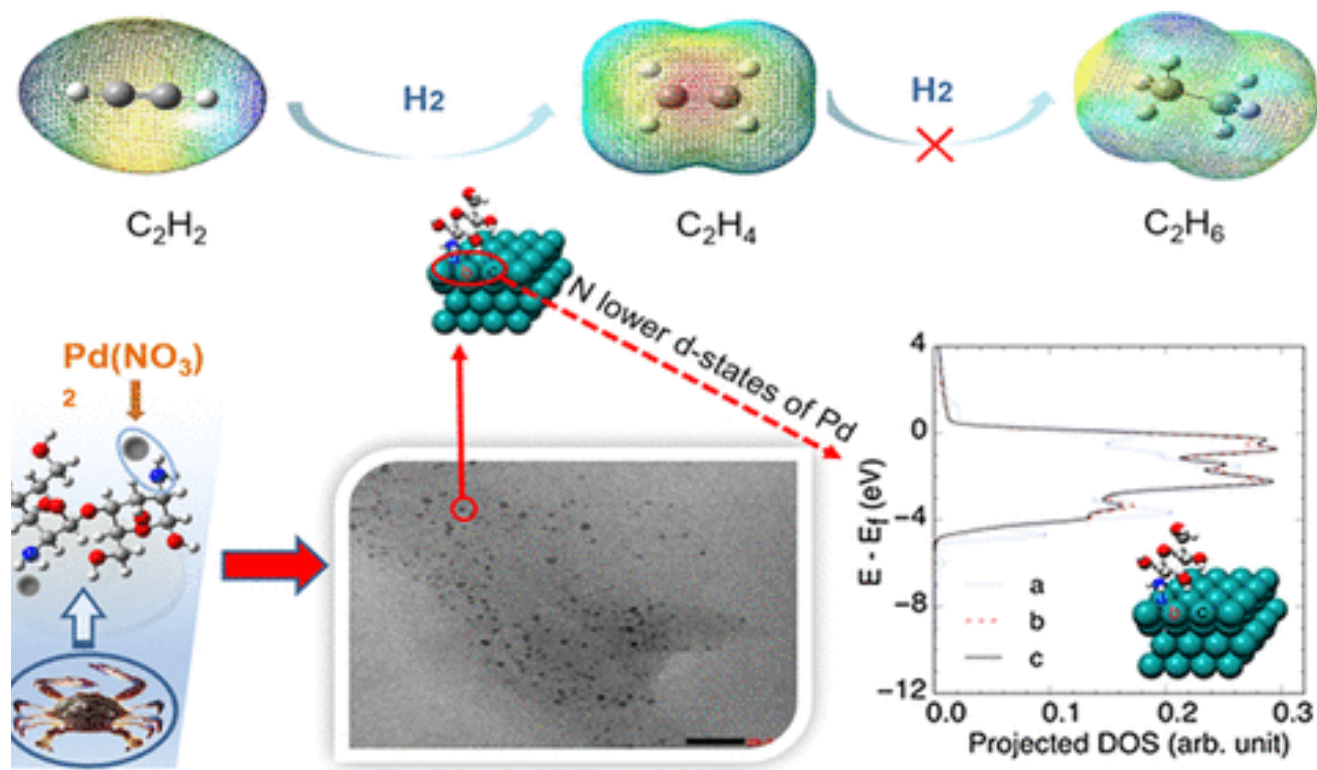
High-throughput screening of bimetallic catalysts enabled by machine learning



## Advance Catalysis Theory

What determines reactivity of catalyst

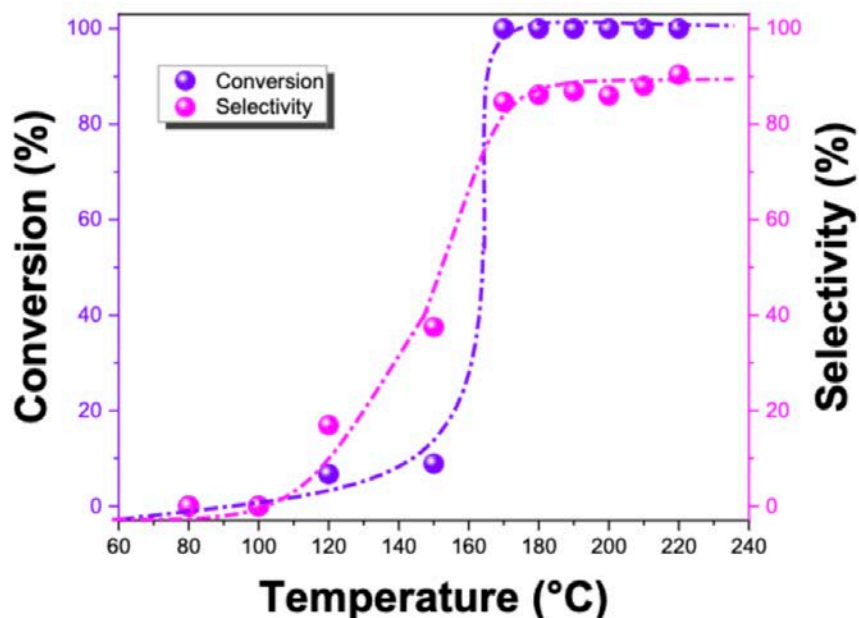
# Biopolymer Interaction Effect in $C_2H_2$ Hydrogenation Reaction on Pd Catalysts



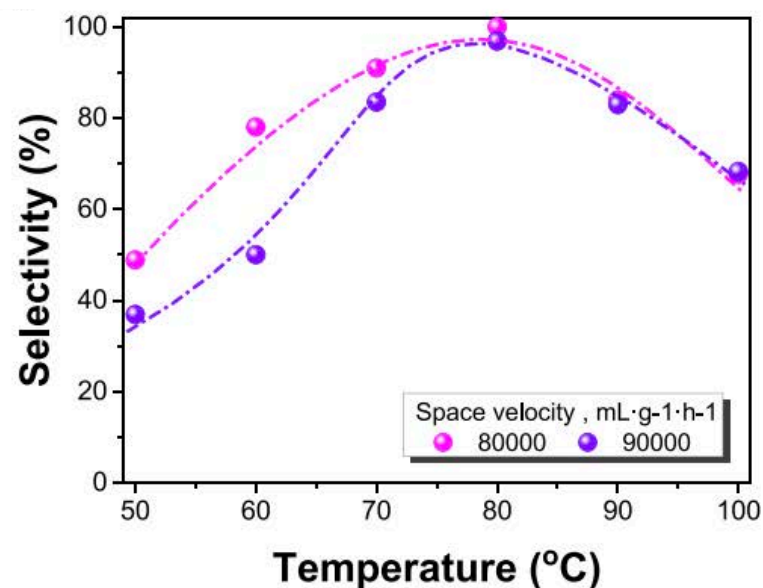
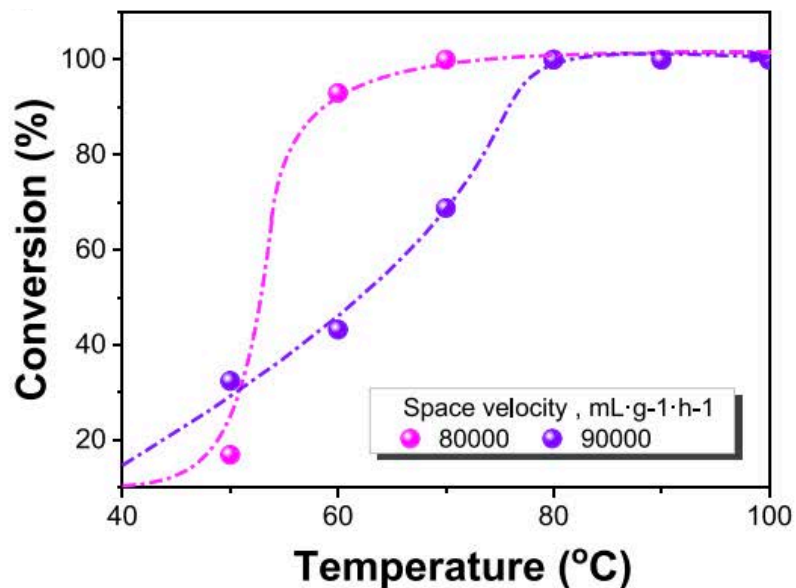
➤ Q. Guan, C. Yang, S. Wang, et al., *ACS Catal.*, 2019, 9 (12).

# Catalytic Acetylene Conversion and Ethene Selectivity

Pd



Pd + chitosan



# Workflow

Build model system

1. Retrieve Pd bulk and chitosan monomer from *MedeA* database
2. Create Pd surface with *surface builder* and *supercell builder*

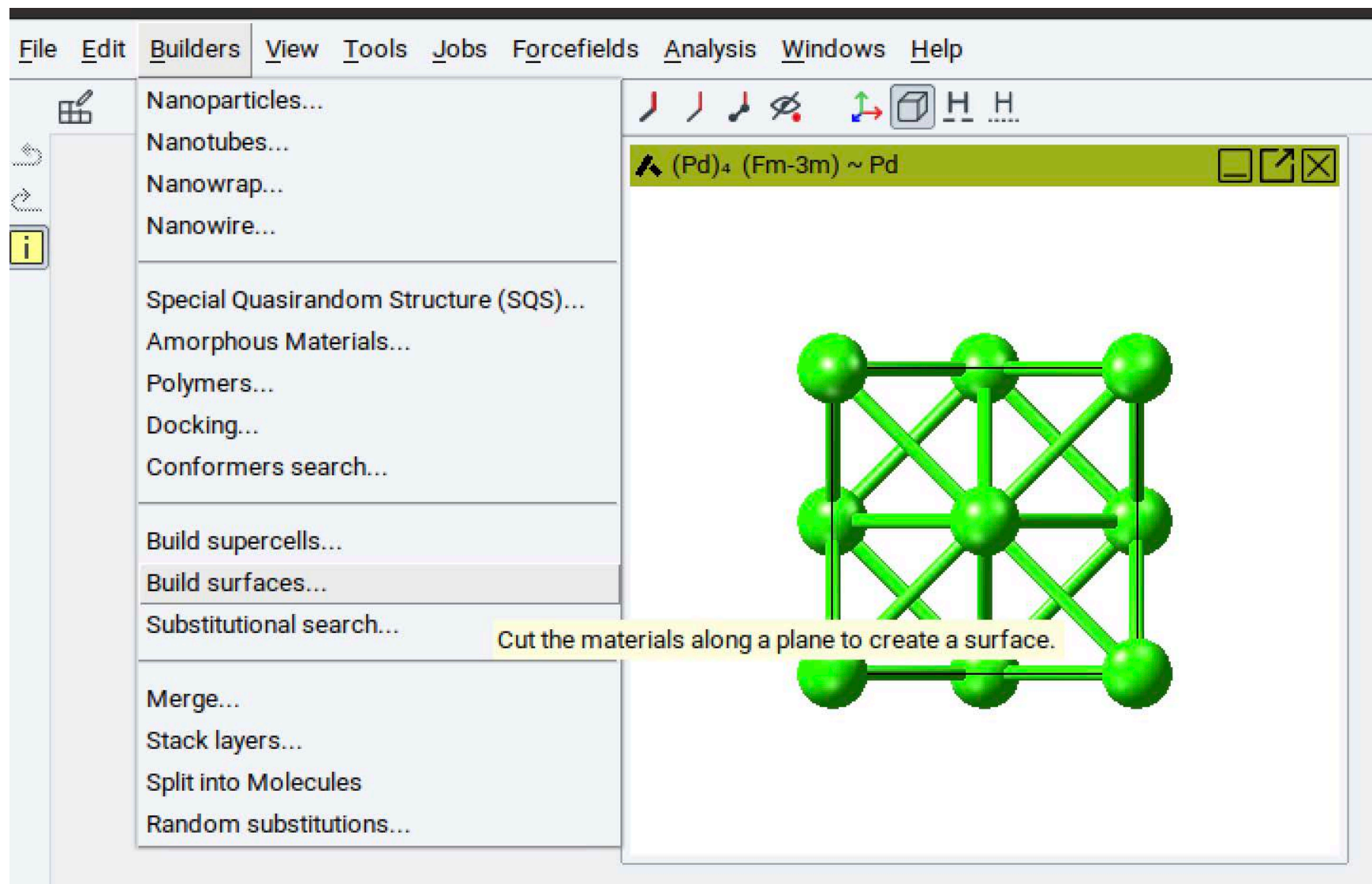
Explore reaction pathway

1. Find stable adsorption site/configuration with *MedeA Docking*
2. Calculate transition state with *MedeA Transition State Search (TSS)*

Understand chitosan effect on ethene selectivity

1. Plot potential energy diagram of  $C_2H_2$  hydrogenation
2. Calculate projected density of states onto Pd 4d with/without chitosan

# Retrieve Pd Bulk



The screenshot shows a software interface with a menu on the left and a 3D model in the center. The menu includes options like Nanoparticles..., Nanotubes..., Nanowrap..., Nanowire..., Special Quasirandom Structure (SQS)..., Amorphous Materials..., Polymers..., Docking..., Conformers search..., Build supercells..., Build surfaces..., Substitutional search..., Merge..., Stack layers..., Split into Molecules, and Random substitutions... The 3D model shows a cubic lattice structure of Pd atoms, with a tooltip indicating the material is (Pd)<sub>4</sub> (Fm-3m) ~ Pd. A yellow tooltip points to the model with the text: "Cut the materials along a plane to create a surface."

File Edit Builders View Tools Jobs Forcefields Analysis Windows Help

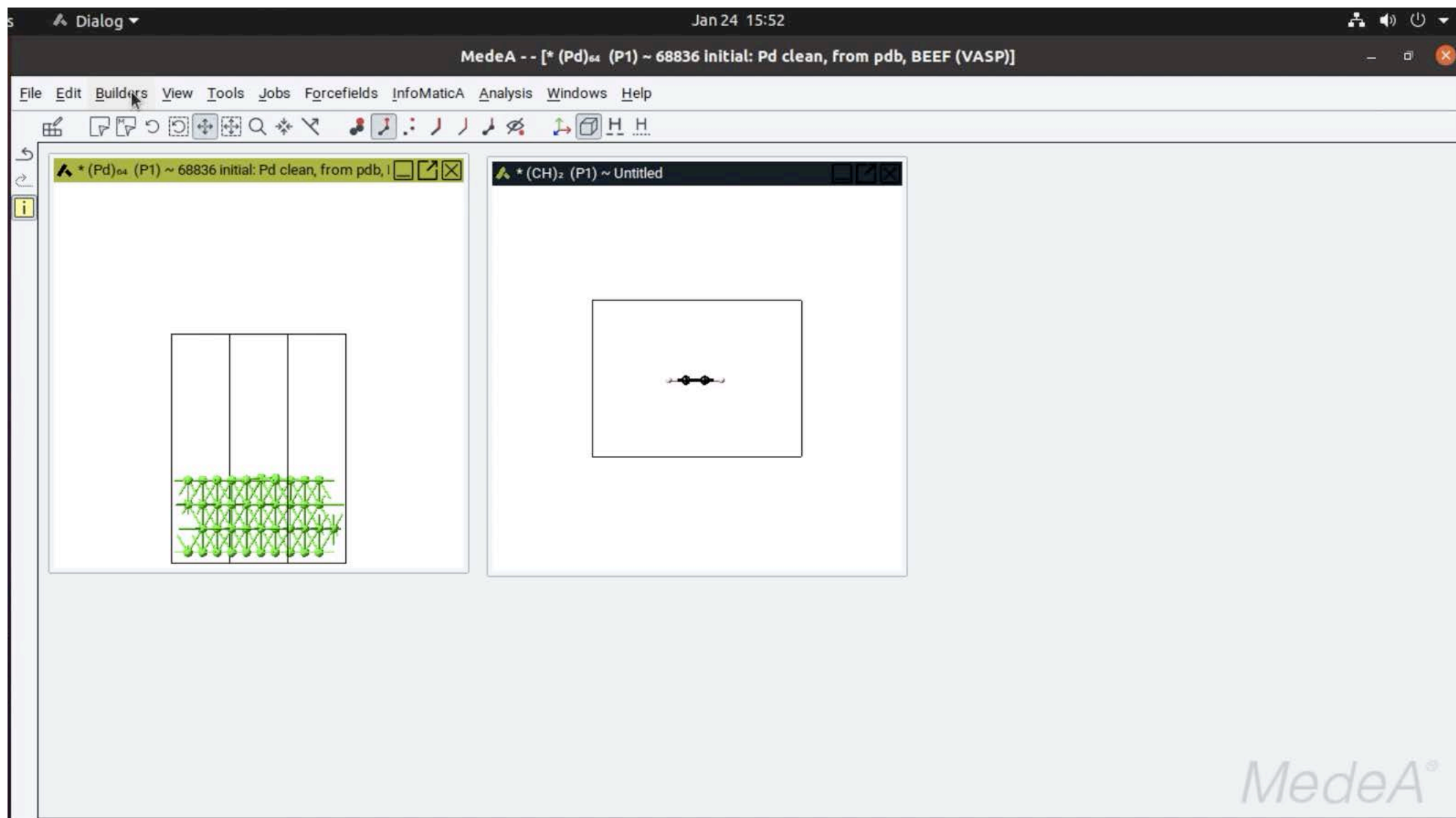
Nanoparticles...  
Nanotubes...  
Nanowrap...  
Nanowire...  
Special Quasirandom Structure (SQS)...  
Amorphous Materials...  
Polymers...  
Docking...  
Conformers search...  
Build supercells...  
Build surfaces...  
Substitutional search...  
Merge...  
Stack layers...  
Split into Molecules  
Random substitutions...

(Pd)<sub>4</sub> (Fm-3m) ~ Pd

Cut the materials along a plane to create a surface.



# Find Stable Adsorption Site Using *Docking*



# Geometry Optimization with *MedeA VASP*

MedeA : Run VASP 6

Calculation Functional/Potential SCF DOS/Optic/Tensors Band Structure Advanced/Restart Add to Input Preview Input

Type of calculation: Single Point

- Single Point
- Structure Optimization
- Molecular Dynamics
- Time-dependent Hybrid / DFT
- Quasiparticle Spectra (GW)
- Quasiparticle Spectra (Low Scaling GW)
- Accurate Energy (MP2)
- Accurate Energy (ACFDT-RPA)
- Accurate Forces (Low Scaling ACFDT-RPA)
- Electron-phonon Coupling
- MT -- Elastic Properties

Properties

- (Pseudo, difference, spin) charge density
- Total local potential
- Electron localization function
- Wave functions
- Electric field gradients
- Hyperfine parameters
- Work function (surfaces only)
- (Total, valence) charge density, Bader analysis
- Band structure
- Density of states
- Optical spectra
- Elastic constants
- Zone center phonons
- Response tensors
- NMR: chemical shifts
- Energy of formation

Solvation (for molecules or surfaces)

- Apply solvation model

External pressure: 0 GPa

Charge state: 0 e

External electrostatic field: none

Interaction

- Functional: Density functional
- DFT exchange-correlation: GGA-PBE
- Van der Waals: None
- Magnetism: Defined by model to be non-magnetic

General Setup

- Precision: Normal
- Increase planewave cutoff (cell optimizations)
- Planewave cutoff (default): 400.000 eV
- Planewave cutoff: eV
- Projection: Reciprocal space
- VASP version: standard

# Calculate Energy Barrier with *MedeA TSS*

The screenshot shows the MedeA software interface. The top menu bar includes File, Edit, Builders, View, Tools, Jobs, Forcefields, InfoMaticA, Transition State Search, Analysis, Windows, and Help. The Transition State Search menu is open, showing options: Map the reaction path and find transition states, Find transition state in a direction, Find transition states in random directions, Select Engine, and Energy Profile. Below the menu are two 3D molecular models of a Pd<sub>64</sub>C<sub>2</sub>H<sub>3</sub> system on a surface, represented by green spheres and sticks.

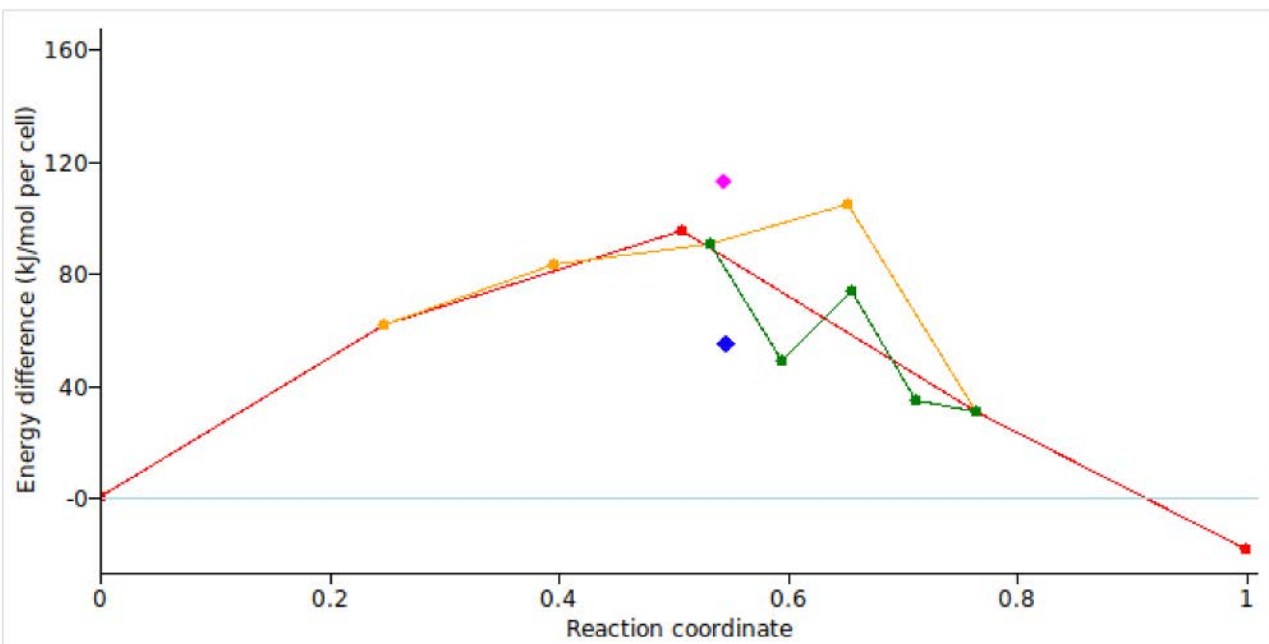
The screenshot shows the configuration window for the MedeA : VASP / Run (Nudged) Elastic Band method. The window title is "MedeA : VASP / Run (Nudged) Elastic Band". The initial configuration is "\* Pd<sub>64</sub>C<sub>2</sub>H<sub>3</sub> (P1) ~ 68886 initial: C2H3(68858), PBE, softPAW, gamma (TSS)". The final configuration is "\* Pd<sub>64</sub>C<sub>2</sub>H<sub>3</sub> (P1) ~ 68886 final: C2H3(68858), PBE, softPAW, gamma (TSS)".

The configuration window is divided into several sections:

- Map Reaction Path** (Configurations):
  - Step 1: Map the reaction path using the elastic band method
  - Settings for step 1:
    - Refine the transition states for: all identified saddle points
    - Number of images: 3
    - Convergence: 0.1 eV/Ang
    - Maximum number of steps: 50
    - Start from wave functions of previous iteration
  - Image initialization for step 1:
    - Initial images from: linear interpolation
    - Interpolation range: full range
    - Translation criterion: 0.5
    - Suppress net atom movements
- Step 2: Refine the transition state(s) Using Elastic Band Methods
- Parameters for step 2:
  - Number of images: 1
  - Convergence: 0.1 eV/Ang
- Step 3: Refine the transition state(s) using the RMM-DIIS minimizer

The title bar at the bottom reads: "Title: Pd64C2H3 (P1) ~ 68886 initial: C2H3(68858), PBE, softPAW, gamma (TSS) (TSS)". There are "Run" and "Close" buttons at the bottom right.

# Energy Profile (Transition State Search)



Select images for custom profile

Show profile: Select image: Unselect all

Profile	0	1	2	3	4
<input checked="" type="checkbox"/> neb0	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
<input checked="" type="checkbox"/> neb1	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
<input checked="" type="checkbox"/> neb2	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
<input checked="" type="checkbox"/> TS refined					
<input checked="" type="checkbox"/> TS final					

Create profile

Custom profiles

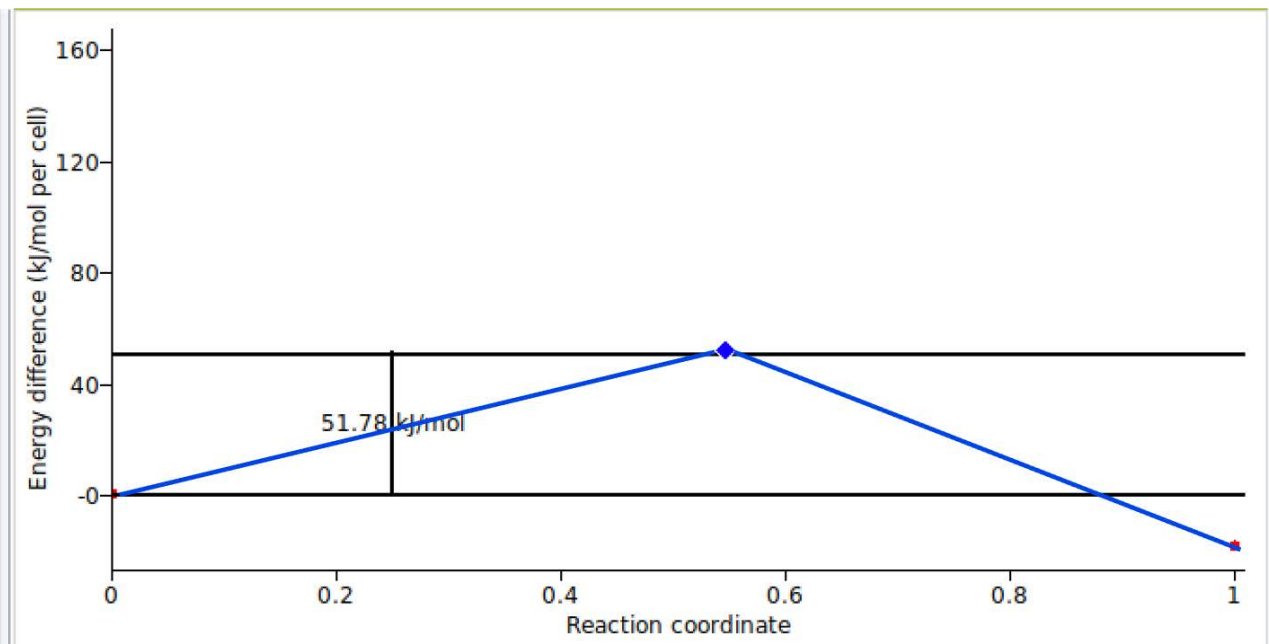
Display options

Type: optimized coordinate / energy

Measuring lines

Show images of selected profile

Animate selected custom profiles



Select images for custom profile

Show profile: Select image: Select all

Profile	0	1	2	3	4
<input type="checkbox"/> neb0	<input checked="" type="checkbox"/>				<input checked="" type="checkbox"/>
<input type="checkbox"/> neb1					
<input type="checkbox"/> neb2					
<input type="checkbox"/> TS refined					
<input checked="" type="checkbox"/> TS final					

Create profile

Custom profiles

Profile1

Display options

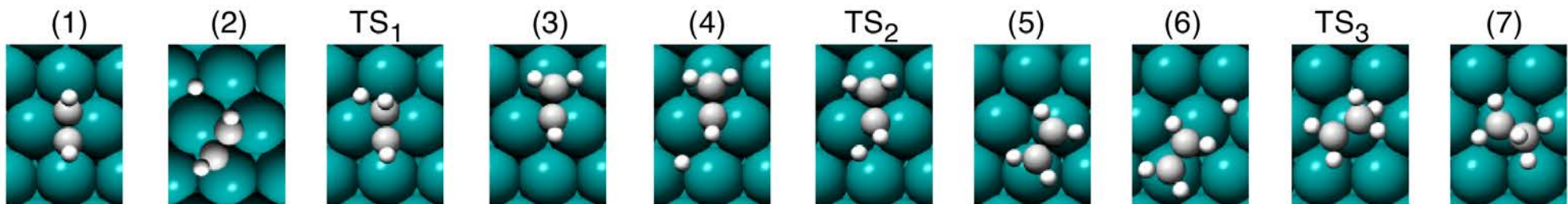
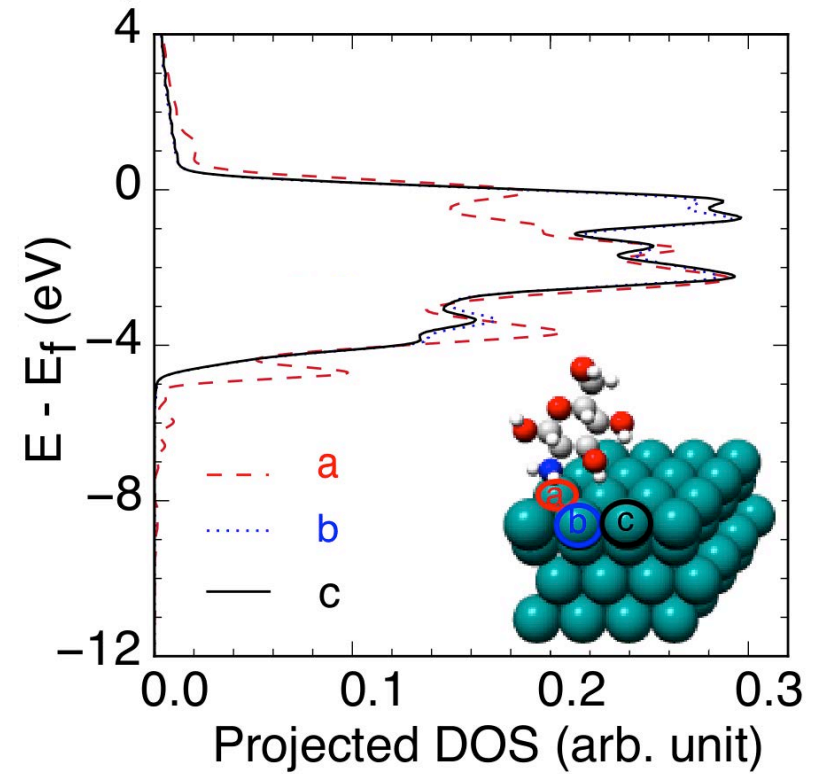
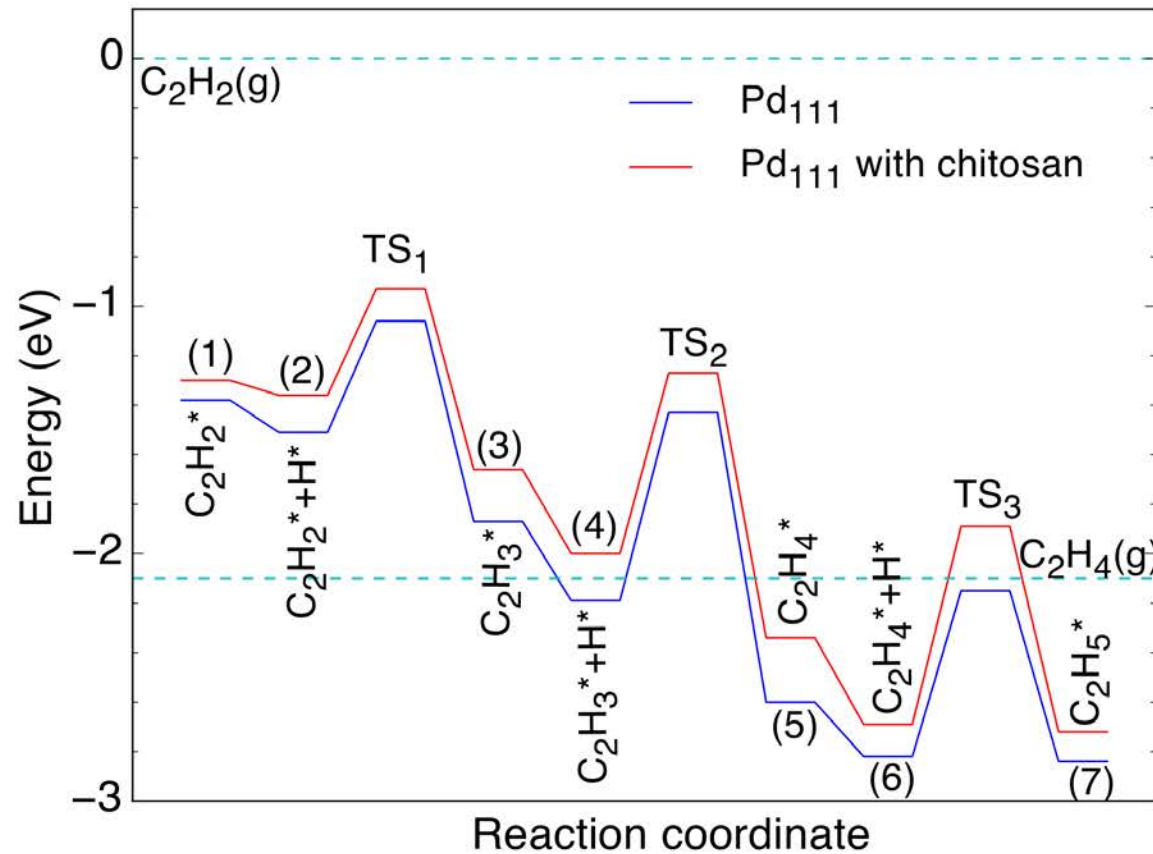
Type: optimized coordinate / energy

Measuring lines

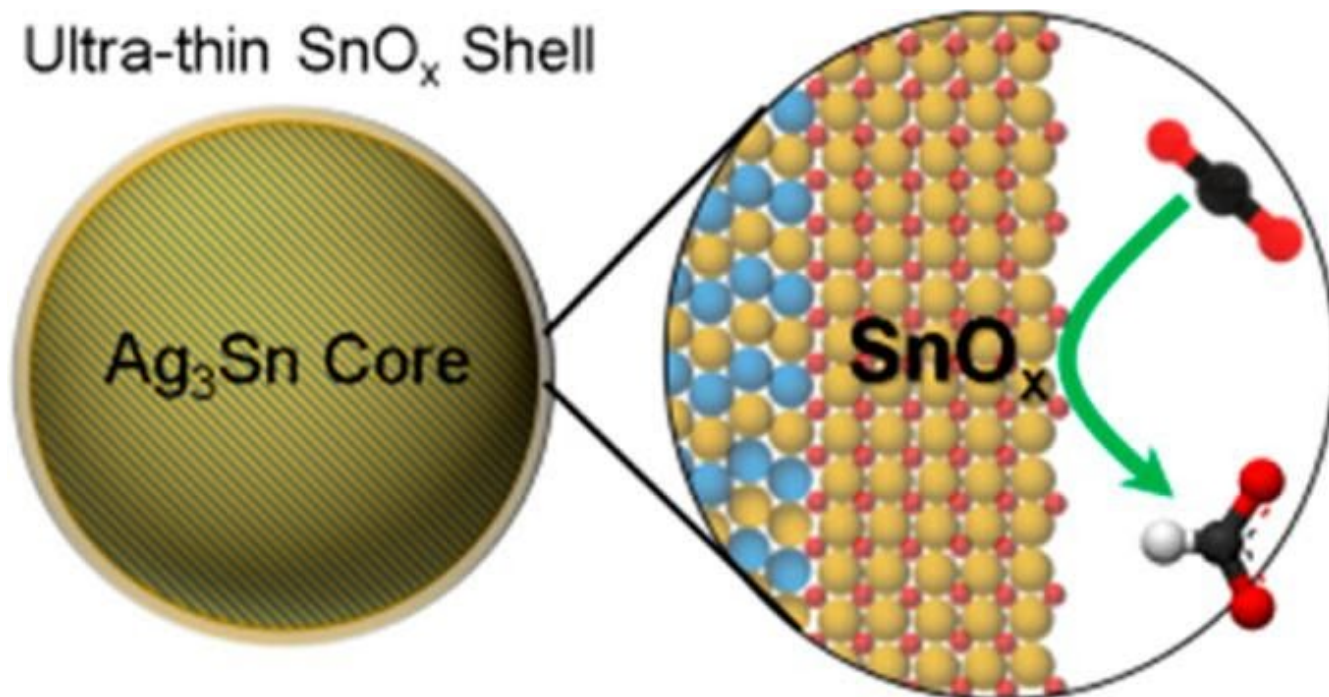
Show images of selected profile

Animate selected custom profiles

# Potential Energy Diagram of C<sub>2</sub>H<sub>2</sub> Hydrogenation and Projected DOS

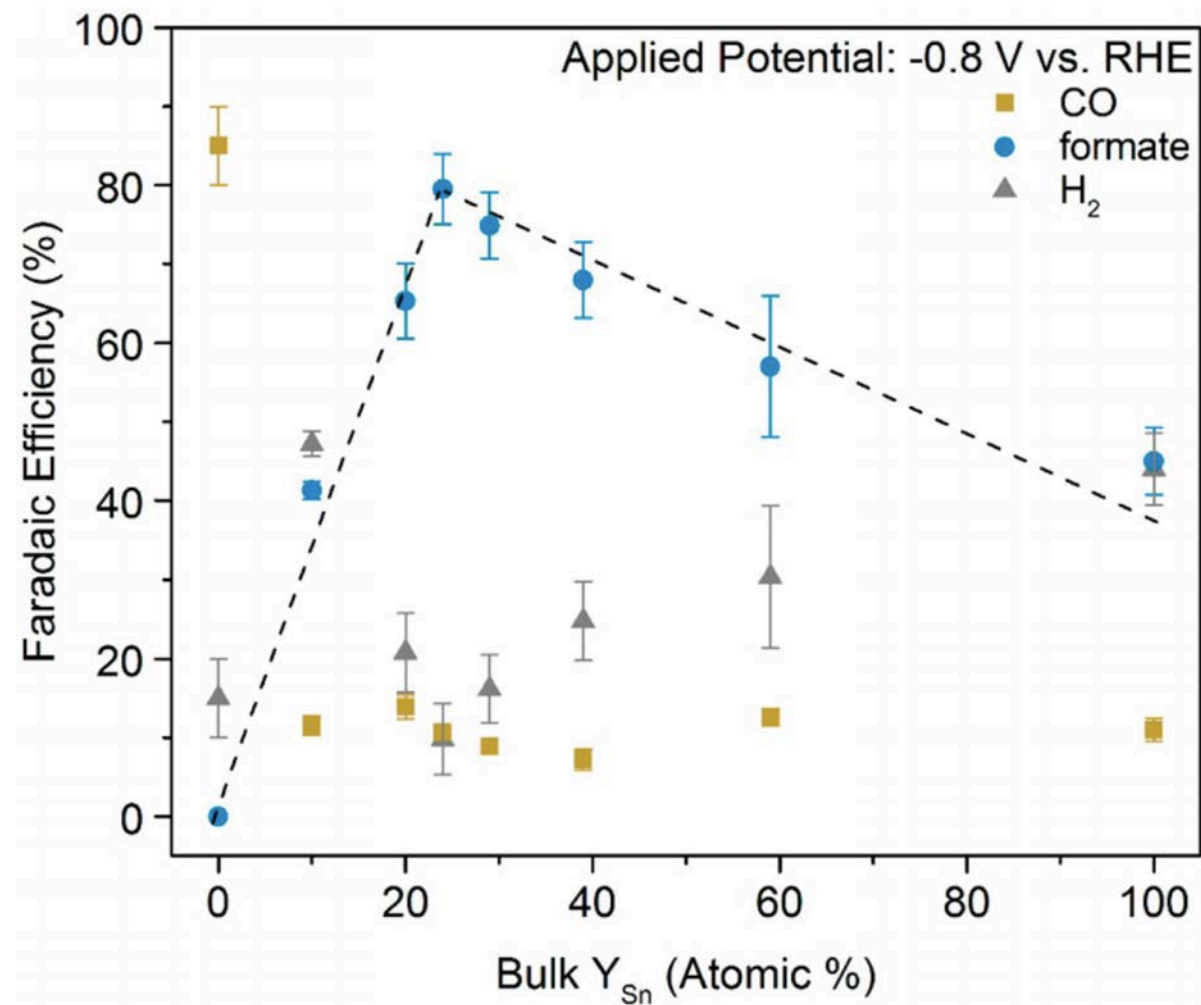
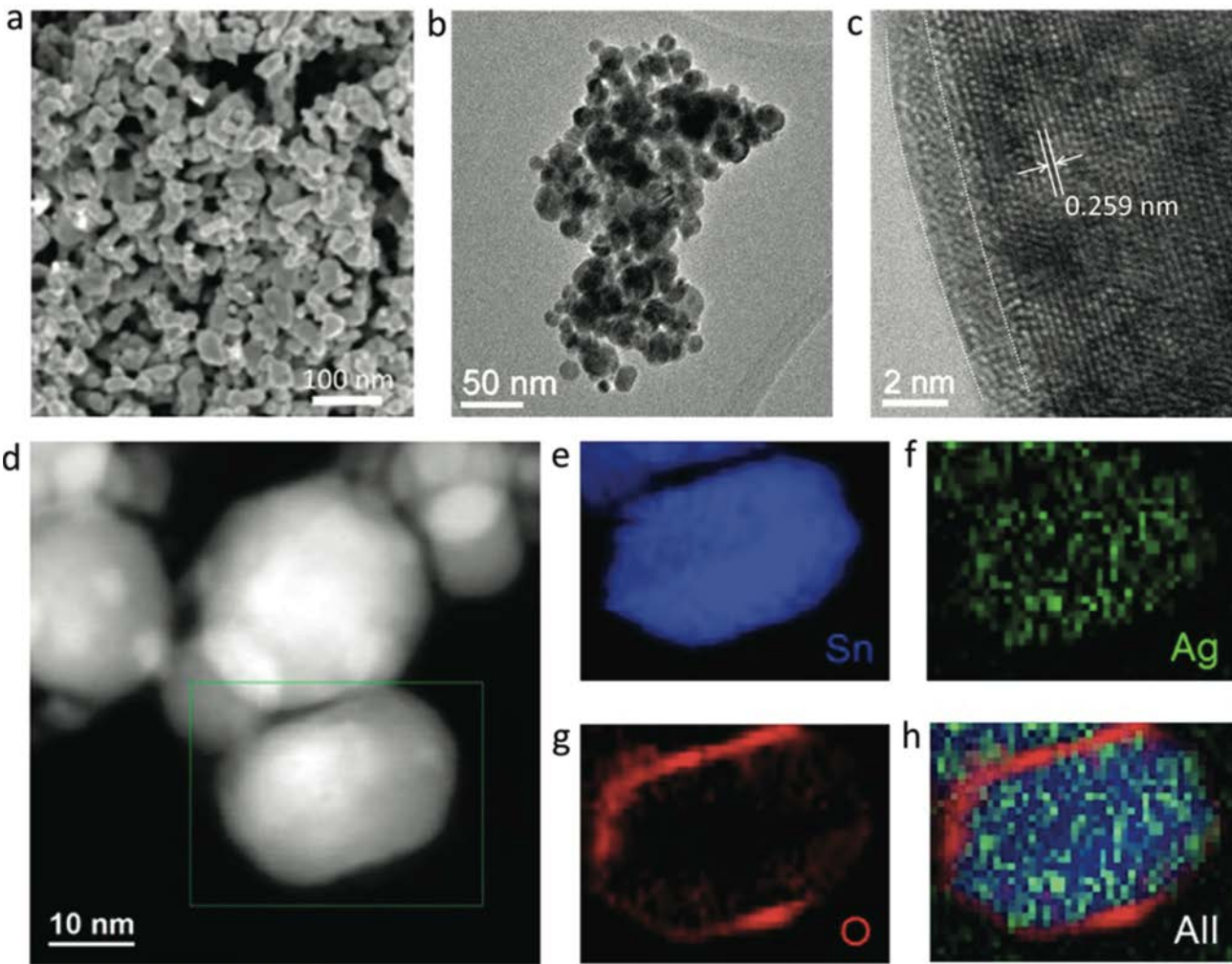


# Surface Strain Effect in CO<sub>2</sub> Reduction Reaction on AgSn/SnO<sub>x</sub> Core-Shell Catalysts



- *W. Luc, C. Collins, S. Wang, et al., J. Am. Chem. Soc., 2017, 139 (5).*
- *S. Wang, J. Wang, and H. Xin, Green Energy & Environment, 2017, 2(2), 168.*

# Direct Imaging of AgSn/SnO<sub>x</sub> Core-Shell Nanoparticles and CO<sub>2</sub> Reduction Efficiency



# Workflow

Build model system

1. Retrieve SnO bulk from *MedeA* database *InfoMaticA*®
2. Create SnO (101) surface with surface builder and supercell builder

Probing stability of SnO<sub>x</sub> surfaces

1. Calculate free formation energy of SnO<sub>x</sub> surfaces as function of different operating potentials

Apply strain to SnO<sub>x</sub> surface

1. Compress/Expand SnO<sub>x</sub> surface with structure editing tool
2. Calculate SnO<sub>x</sub> surface with different strains in one flowchart

# Retrieve SnO Bulk from *InfoMaticA*

MedeA InfoMaticA: Search

File Edit Options

ID	completeness	space group name H-M	sum	structural	name systematic
COD.110002C	Missing Atoms	Cmc21	O Sn	Sn O	Tin (II) oxide - red modification
COD.901214C	Complete	P4/nmm01	O Sn	O Sn	
COD.9011217	Complete	P4/nmm01	O Sn	O Sn	
COD.900895E	Complete	P4/nmm01	O Sn	SnO	
COD.720647C	Complete	P4/nmm02	O Sn	O Sn	?
COD.4124667	Complete	P4/nmm01	O Sn	O Sn	Sn O
COD.110103E	Missing Atoms	Cmc21	O Sn	Sn O	Tin (II) oxide - red modification

Search Criteria Detailed Information Coordinates Geometry Coordination Pair Correlation Powder pattern

Require that  is

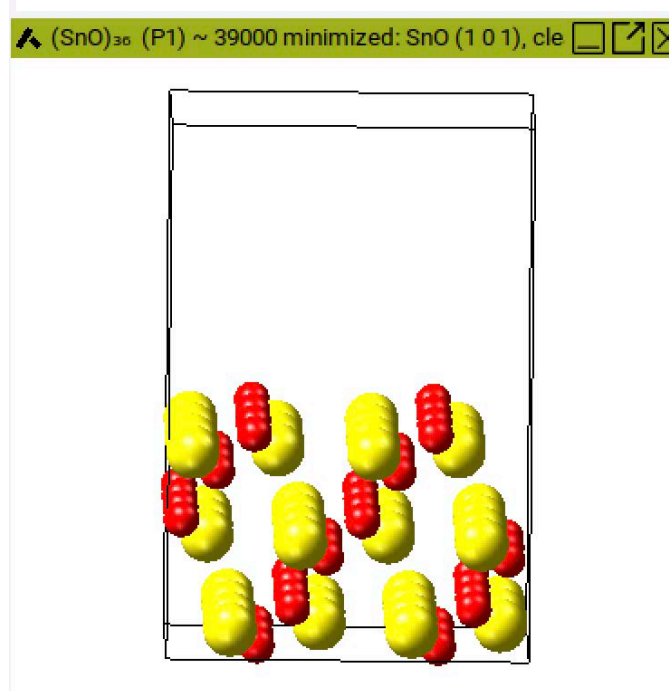
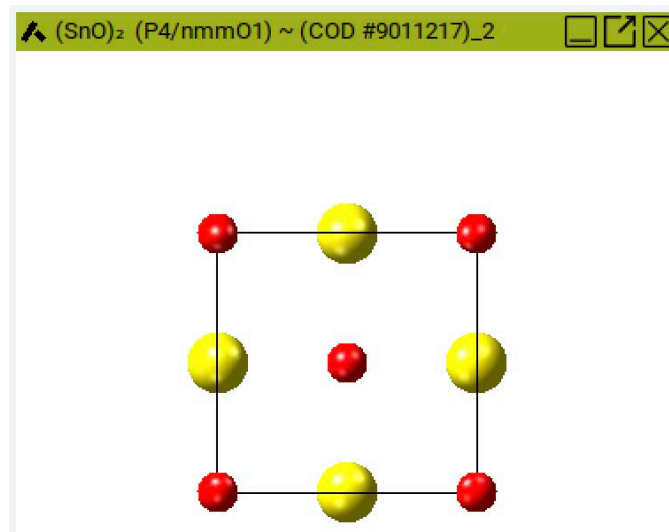
Require that

- database ID
- formula
- number of elements
- structural completeness
- author
- title
- systematic name
- mineral name
- remark

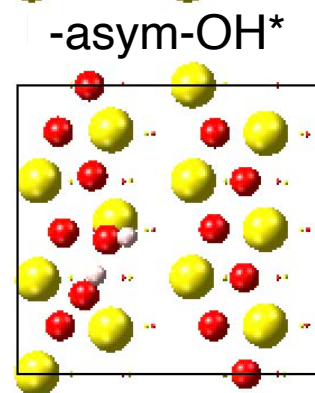
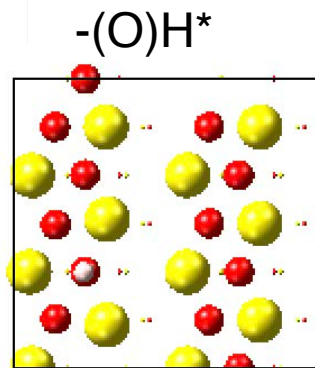
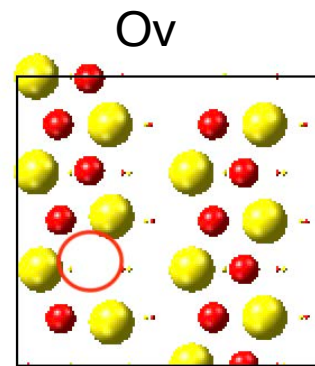
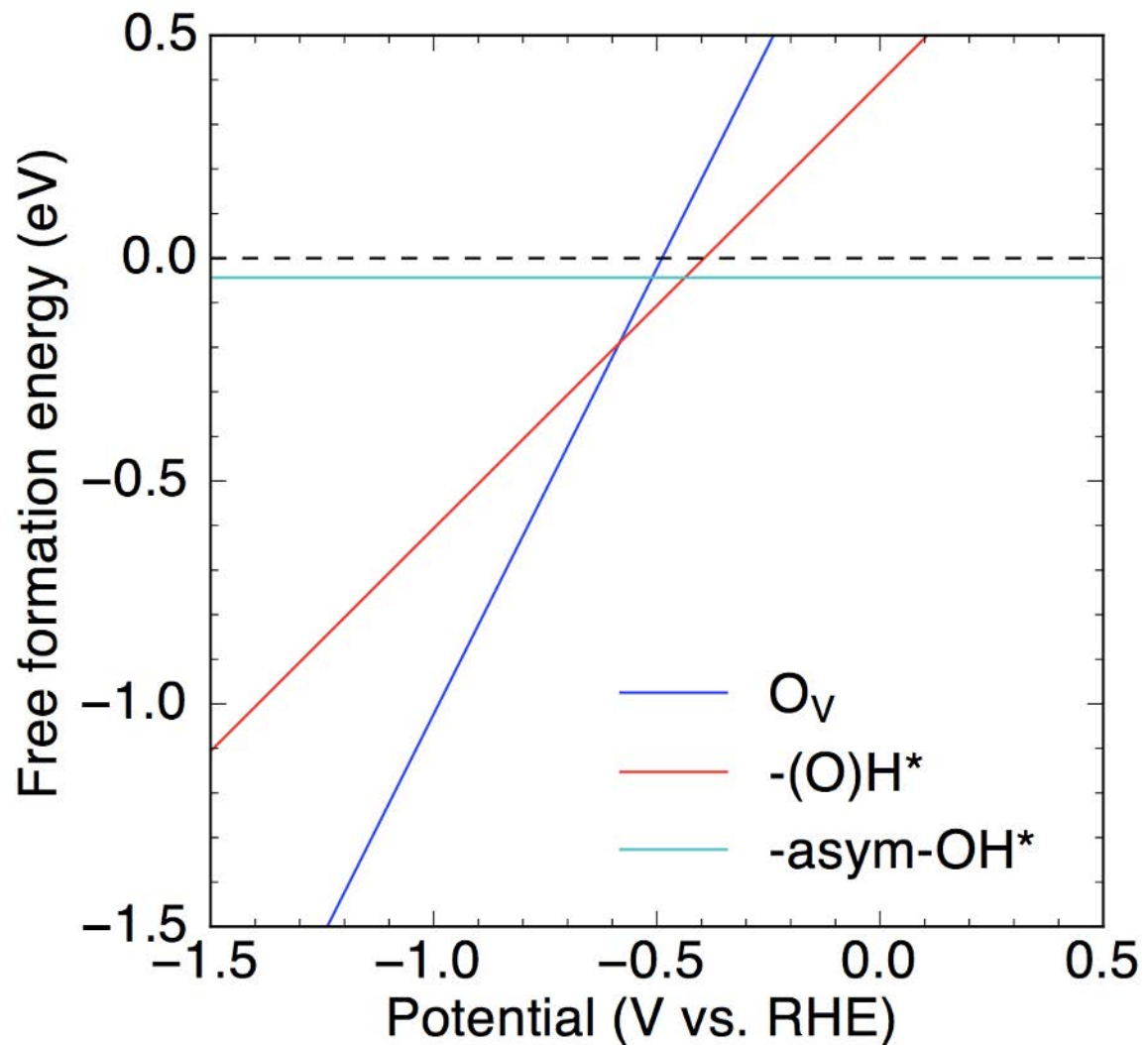
Run search Clear

Displaying 7 of 7 hits

Advanced



# Probing Stability of SnO<sub>x</sub> Surfaces



Two H<sup>+</sup>/e<sup>-</sup> transfer:



One H<sup>+</sup>/e<sup>-</sup> transfer:



H<sub>2</sub>O dissociation:



# Gibbs Free Energy for Bulk and Surface

Electronic energy = 0.00 kJ/mol (set to zero since reference energies are unavailable)  
 PV term = 8.01 kJ/mol  
 Zero-point energy = 8.62 kJ/mol

## Thermodynamic functions:

- Cv: heat capacity
- E(T)-E(0): change in vibrational internal energy from 0 K
- S(T): vibrational entropy
- (A(T)-E(0)): change in the vibrational Helmholtz free energy
- E(T): change in vibrational internal energy plus the ZPE
- A(T): internal energy plus vibrational Helmholtz energy
- alpha: coefficient of linear thermal expansion

### Electronic contributions:

	Empirical Formula SnO	Cell (SnO) <sub>36</sub>
VASP Energy	-11.352005	-408.672189 eV
=	-1095.302	-39430.862 kJ/mol

T K	Cv J/K/mol	E(T)-E(0) kJ/mol	S(T) J/K/mol	-(A(T)-E(0)) kJ/mol	E(T) kJ/mol	A(T) kJ/mol
0	0.0000	0.0000	0.0000	-0.0000	8.6195	8.6195
1	0.0052	0.0000	0.0019	-0.0000	8.6195	8.6195
2	0.0160	0.0000	0.0086	0.0000	8.6196	8.6195
3	0.0325	0.0000	0.0180	0.0000	8.6196	8.6195
4	0.0545	0.0001	0.0302	0.0000	8.6196	8.6195
5	0.0830	0.0001	0.0453	0.0001	8.6197	8.6195
10	0.4135	0.0012	0.1820	0.0006	8.6208	8.6190
15	1.2417	0.0051	0.4881	0.0022	8.6247	8.6174
20	2.5196	0.0144	1.0121	0.0058	8.6339	8.6137
25	4.0375	0.0307	1.7346	0.0126	8.6503	8.6069
30	5.6428	0.0549	2.6121	0.0235	8.6745	8.5961
35	7.2533	0.0872	3.6031	0.0389	8.7067	8.5806
40	8.8284	0.1274	4.6750	0.0596	8.7469	8.5599
45	10.3501	0.1754	5.8033	0.0858	8.7949	8.5338
50	11.8126	0.2308	6.9700	0.1177	8.8503	8.5018
55	13.2169	0.2934	8.1622	0.1555	8.9129	8.4640
60	14.5667	0.3629	9.3705	0.1994	8.9824	8.4202
65	15.8671	0.4390	10.5881	0.2493	9.0585	8.3703
70	17.1224	0.5215	11.8102	0.3052	9.1410	8.3143
75	18.3367	0.6101	13.0331	0.3674	9.2297	8.2522
80	19.5124	0.7048	14.2543	0.4356	9.3243	8.1840
85	20.6516	0.8052	15.4716	0.5099	9.4247	8.1097
90	21.7552	0.9112	16.6834	0.5903	9.5308	8.0293
95	22.8239	1.0227	17.8884	0.6767	9.6422	7.9428
100	23.8577	1.1394	19.0856	0.7692	9.7589	7.8504
:	:	:	:	:	:	:
2800	49.6722	130.9391	164.8746	330.7067	139.5587	-322.0872
2850	49.6752	133.4228	165.7537	338.9724	142.0423	-330.3529
2900	49.6780	135.9066	166.6177	347.2818	144.5262	-338.6622
2950	49.6807	138.3906	167.4670	355.6339	147.0101	-347.0143
3000	49.6832	140.8746	168.3020	364.0281	149.4942	-355.4086

$$\text{Gibbs: } G(T) = U + \text{ZPE} + \text{PV} - \text{TS}(T)$$

### Computational hydrogen electrode



$$\text{at } 0\text{V: } G[\text{H}^+ + \text{e}^-] = G[\text{H}_2]/2$$

$$\Delta G(\text{V}) = \Delta G_0 + eV$$

# Gibbs Free Energy for Gas Phase Molecule

Mode	Symmetry	Frequency (1/cm)	IR Intensity (km/mol)	Reduced mass (u)	Force constant (mDyne/Ang)
1	PI	656.5615	67.1636	12.8774	3.2706
2	PI	656.5615	67.1636	12.8774	3.2706
3	SG	1407.4617	0.0000	15.9949	18.6683
4	SG	2374.5040	918.7885	12.8774	42.7783

Temperature (K): 298.150

Pressure (atm): 1.00000

	Hartree	kcal/mol	kJ/Mol
Zero-point vibrational energy:	0.011607	7.284	30.47
Thermal correction to energy:	0.014238	8.934	37.38
Thermal correction to enthalpy:	0.015182	9.527	39.86
Thermal correction to Gibbs free energy:	-0.009745	-6.115	-25.59
Sum of electronic and zero-point energy:	-187.503346	-117660.140	-492290.03
Sum of electronic and thermal energy:	-187.500715	-117658.489	-492283.12
Sum of electronic and thermal enthalpy:	-187.499771	-117657.897	-492280.64
Sum of electronic and thermal free energy:	-187.524698	-117673.539	-492346.09

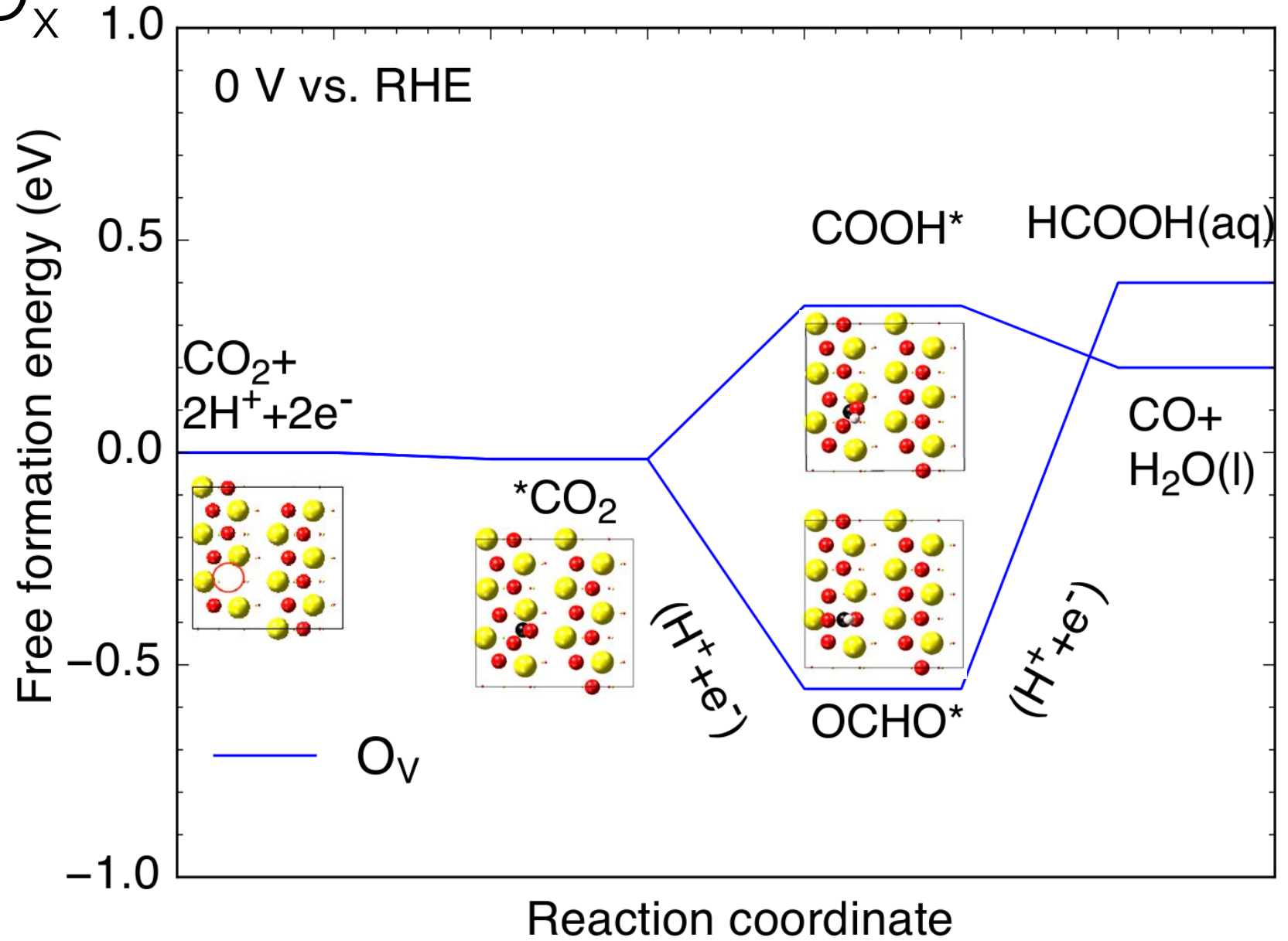
$$E0 = E_{elec} + ZPE$$

$$E = E0 + E_{vib} + E_{rot} + E_{trans}$$

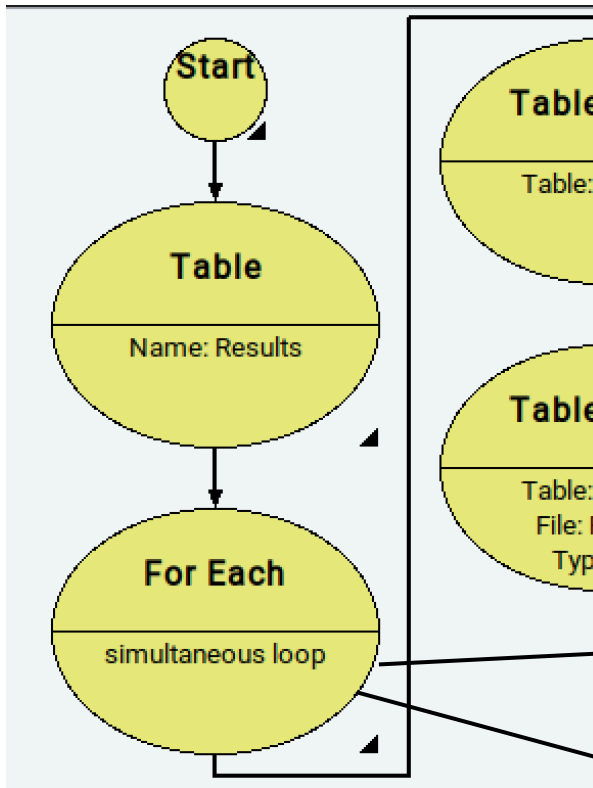
$$H = E + RT$$

$$G = H - TS$$

# Free Energy Pathway of CO<sub>2</sub> Reduction on Ov/SnO<sub>x</sub>



# Strain Effect on Ov/SnO<sub>x</sub> with *MedeA HT*



## Stage 3: Print Table Results

Constraint	Energy eV
-6.929000	-418.001809
-4.602000	-423.138229
-2.275000	-426.323908
0.051000	-427.960296
2.378000	-428.431143
4.705000	-427.986867
7.032000	-426.655596

Edit ForEach stage 1

Values

0.051 2.378 4.705 7.032

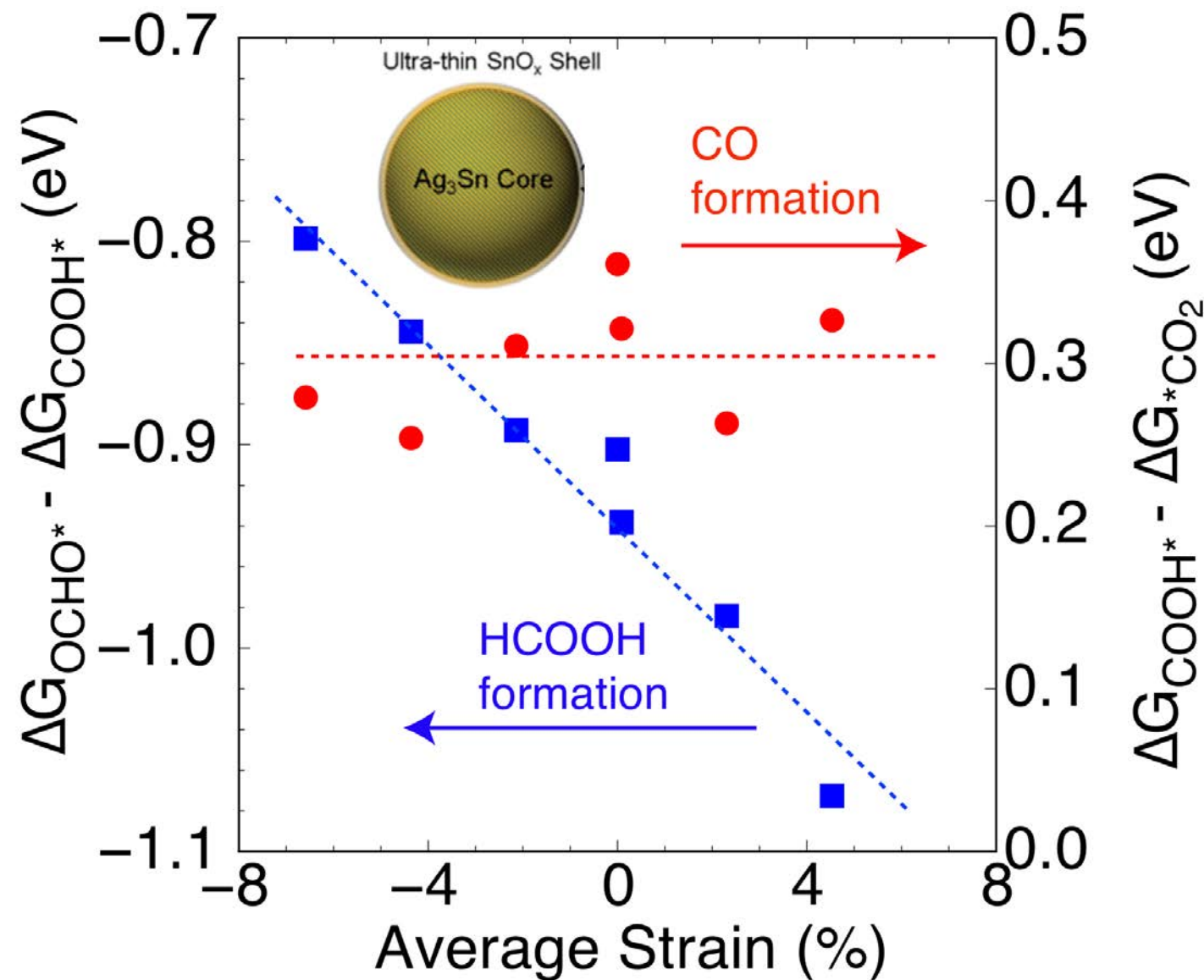
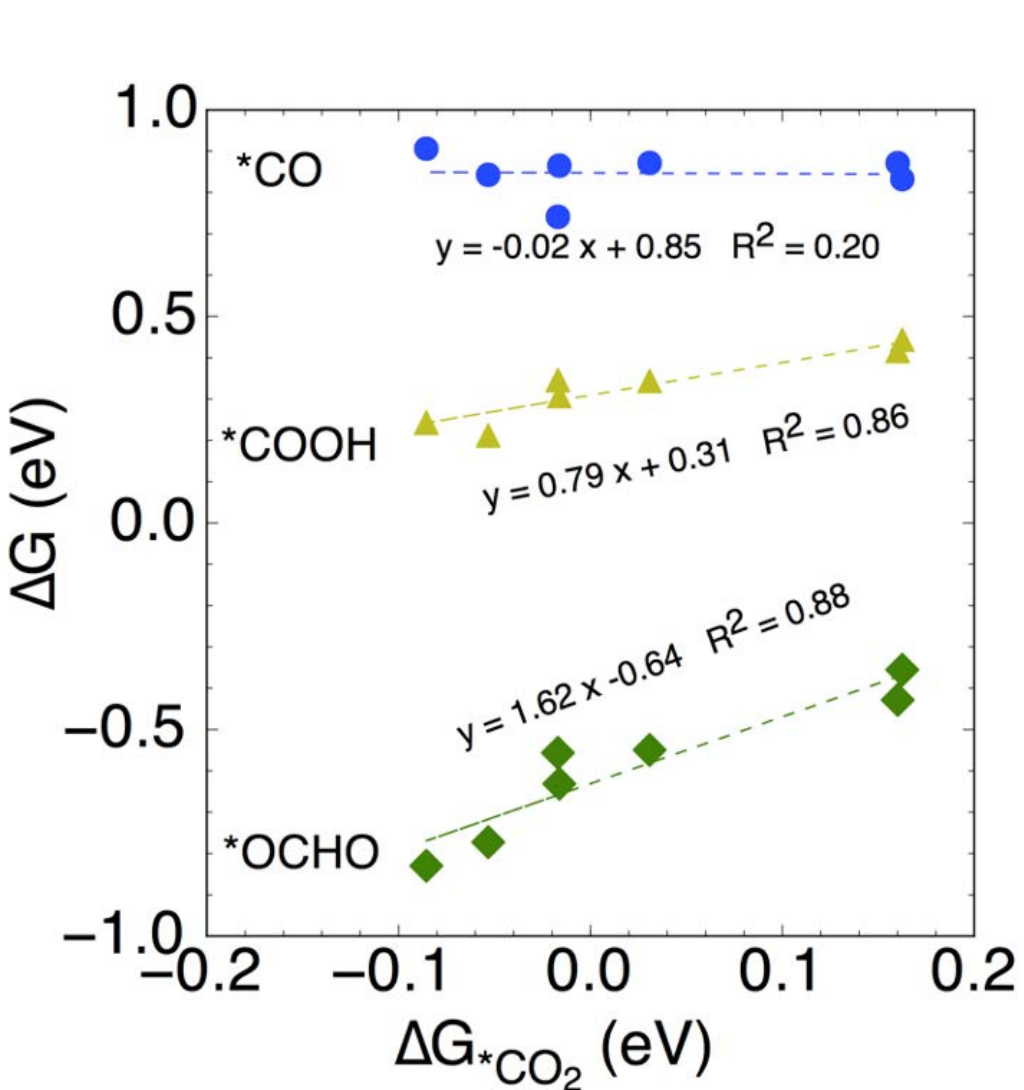
03-7.656 -5.508 -3.360 -1.213

VASP 6

Table: Add Row

Table: Results  
ta: \$X\_strain  
\$Electronic\_calc

# Strain as an Origin of Improved Efficiency



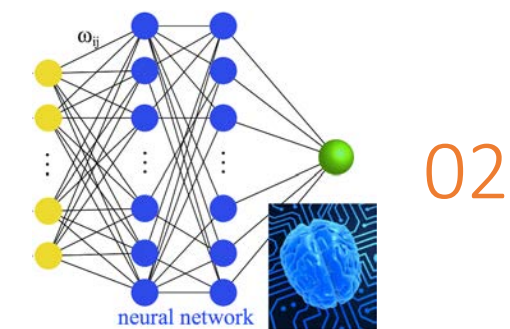
# Outline



## Understand Reaction Mechanisms

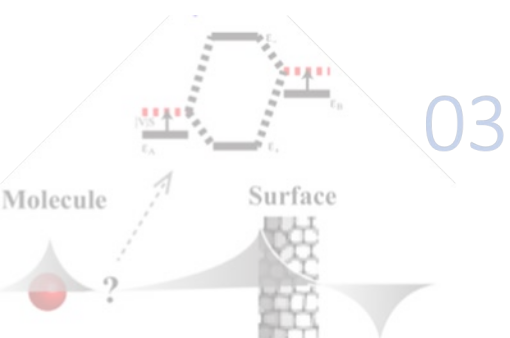
Biopolymer interaction effect in  $C_2H_2$  hydrogenation reaction on Pd catalysts

Surface strain effect in  $CO_2$  reduction reaction on AgSn/SnO<sub>x</sub> core-shell catalysts



## Accelerate Materials Discovery

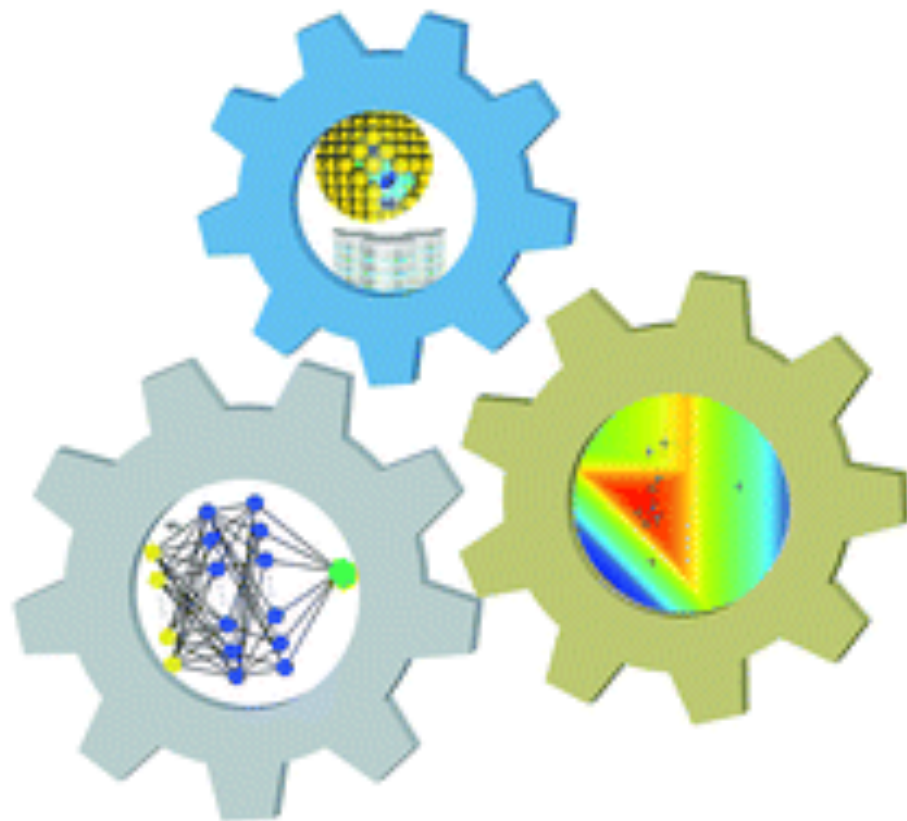
High-throughput screening of bimetallic catalysts enabled by machine learning



## Advance Catalysis Theory

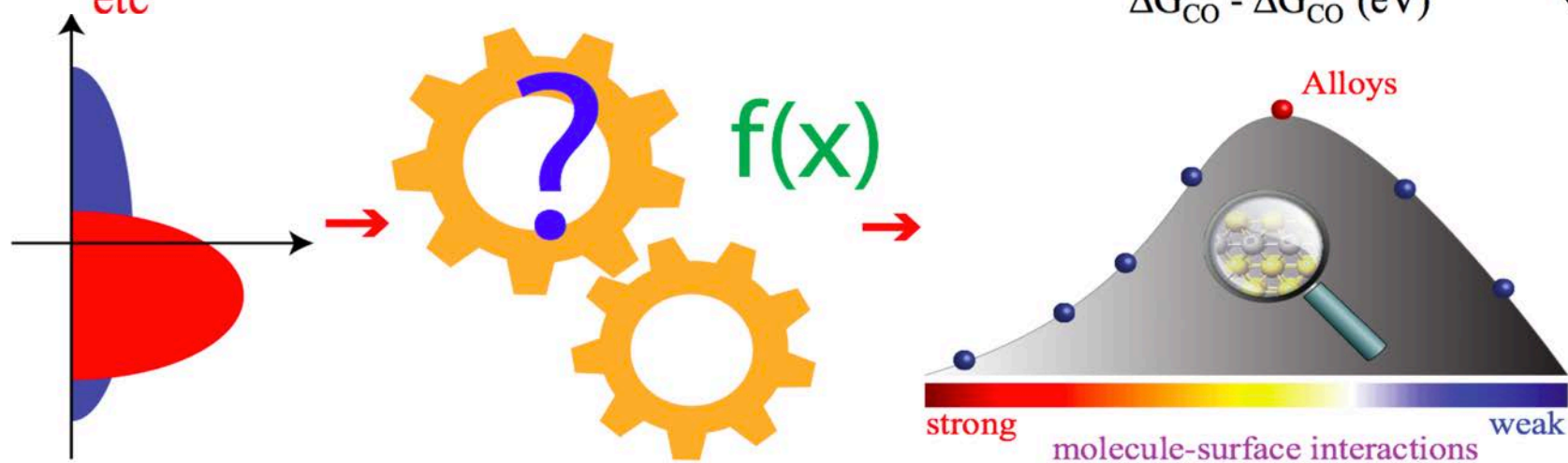
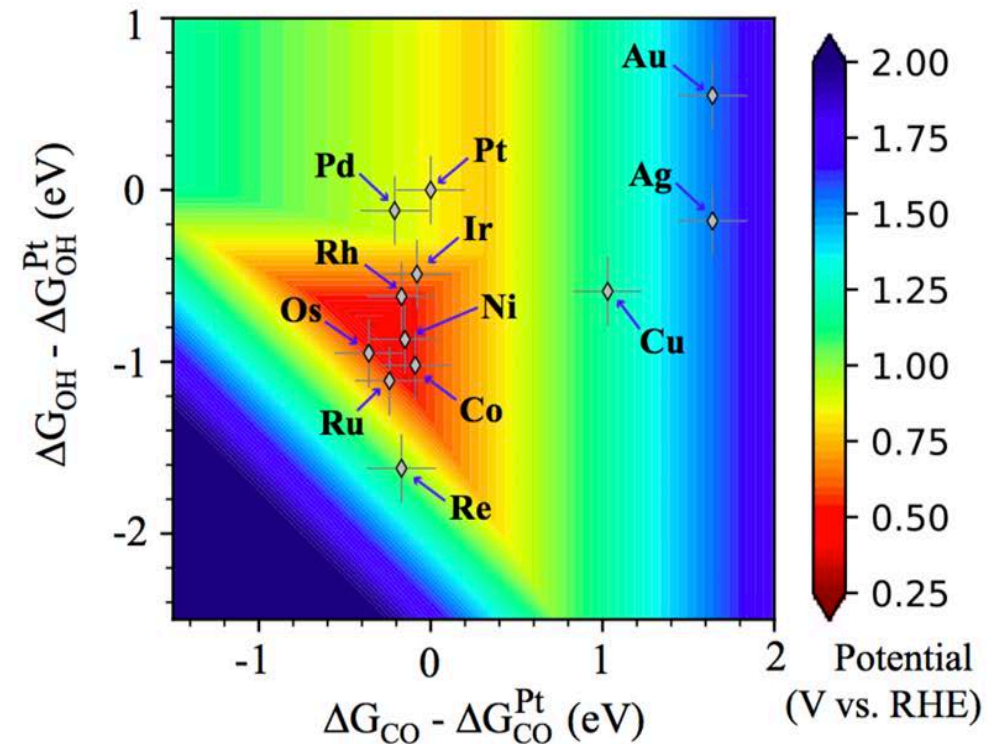
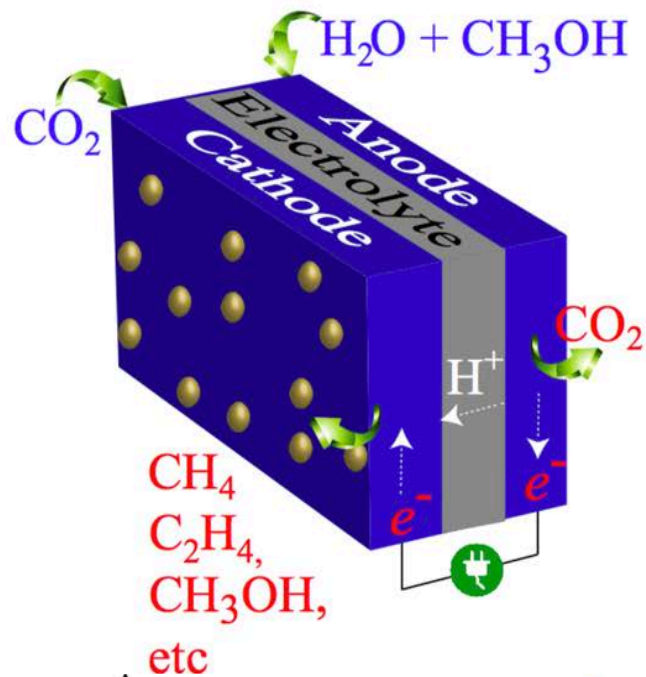
What determines reactivity of catalyst

# High-throughput Screening of Bimetallic Catalysts Enabled by Machine Learning

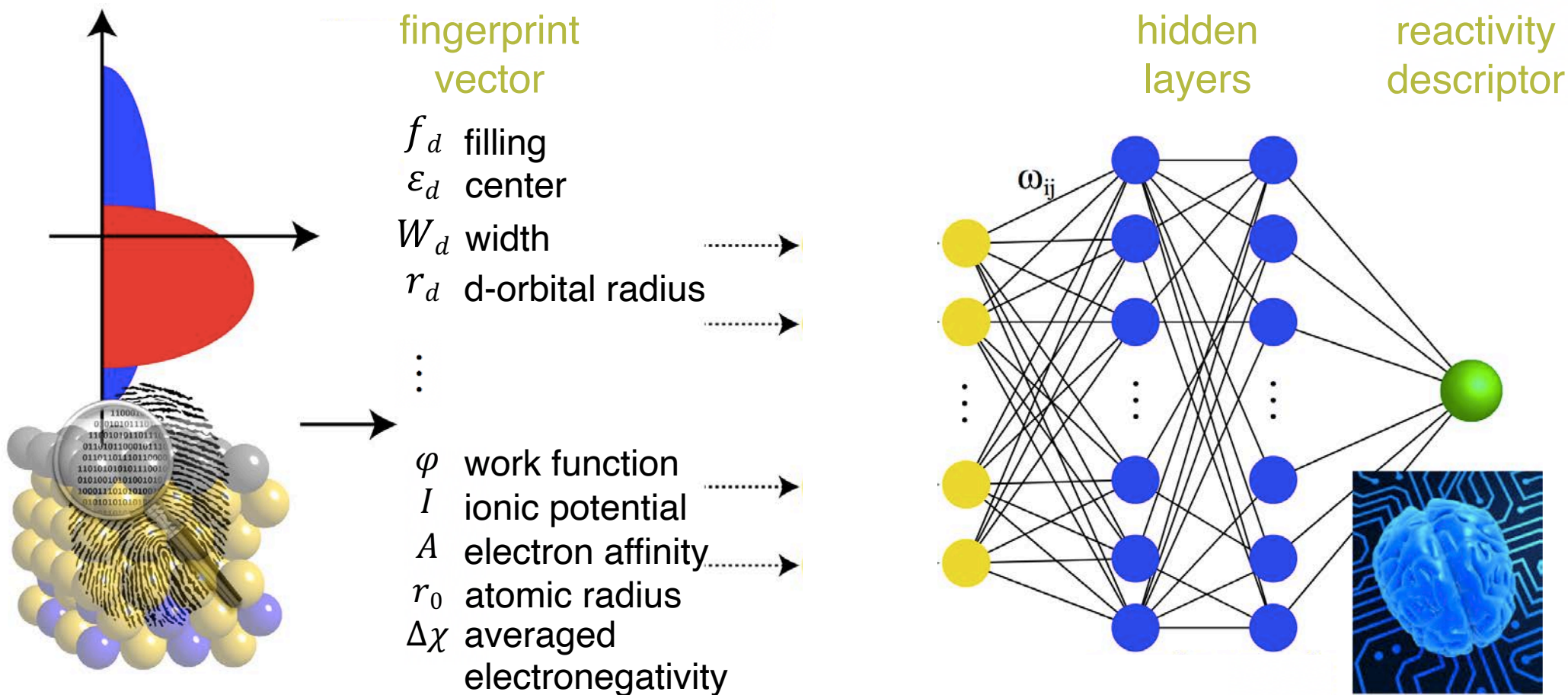


- *Z. Li, S. Wang, et al., J. Mater. Chem. A, 2017, 5, 24131.*

# Design Bifunctional Alloy Catalysts for DMFCs

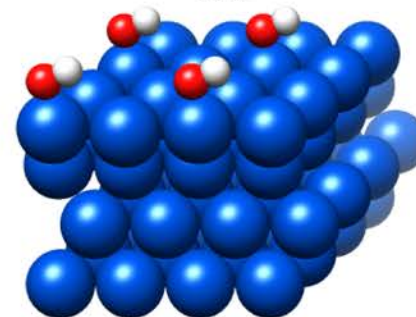
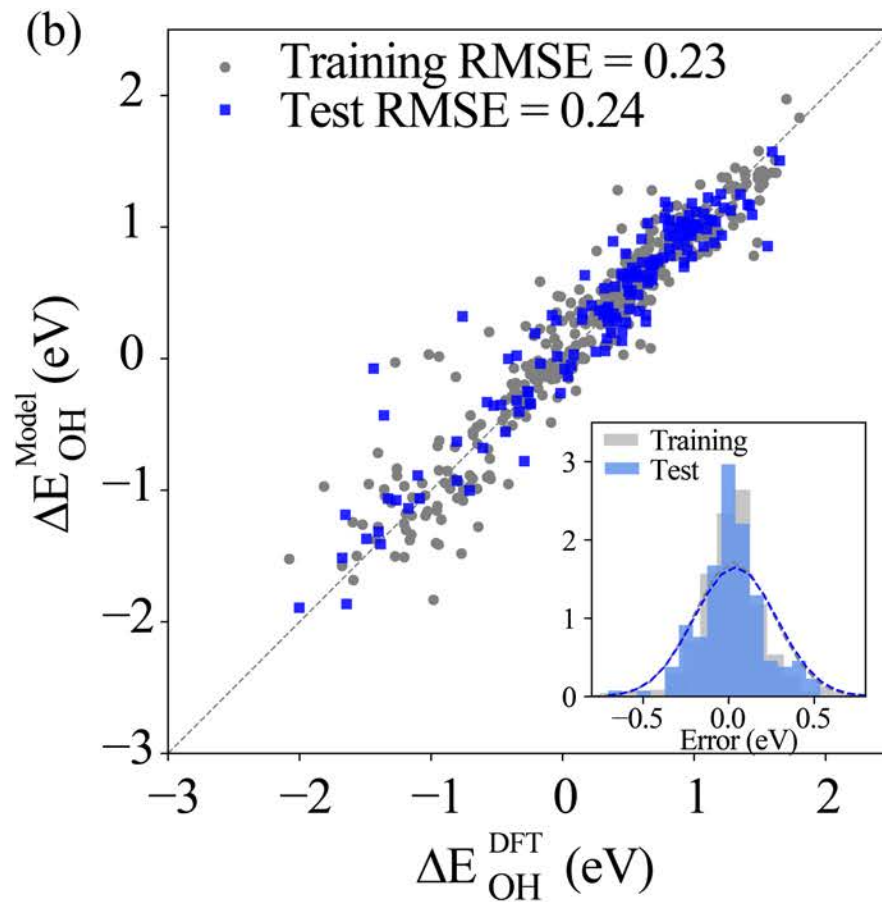
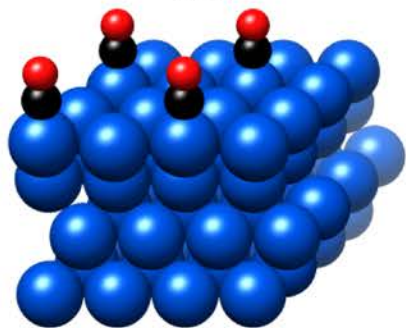
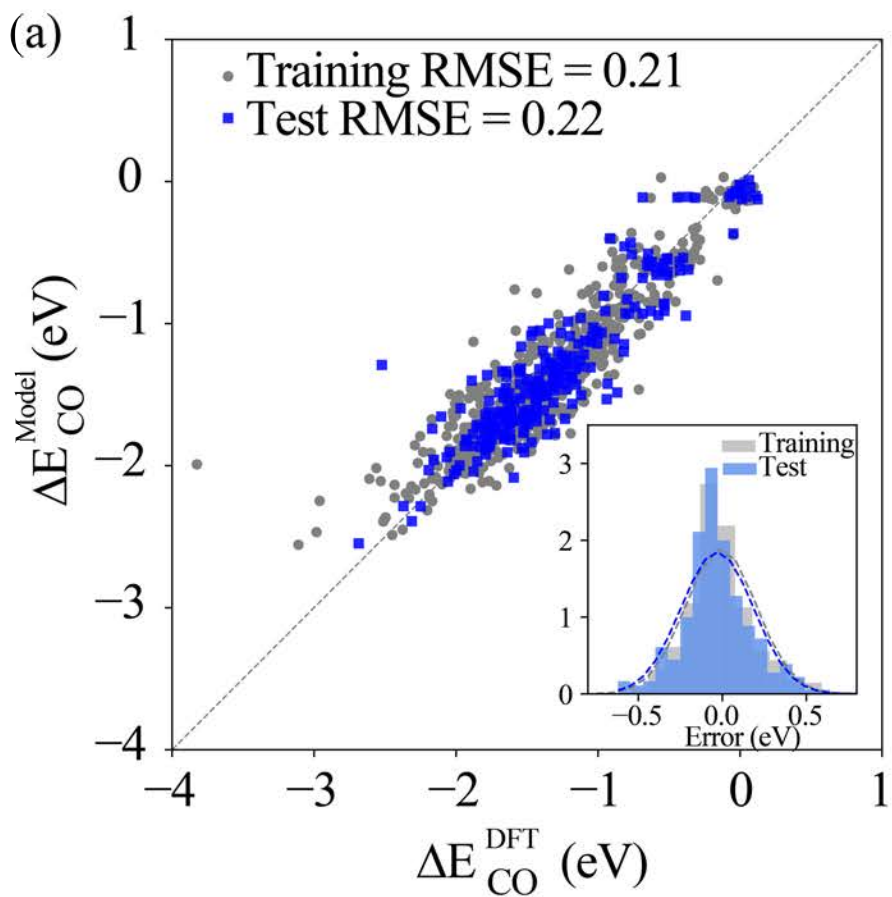


# Site Representation Inspired by the $d$ -band Theory

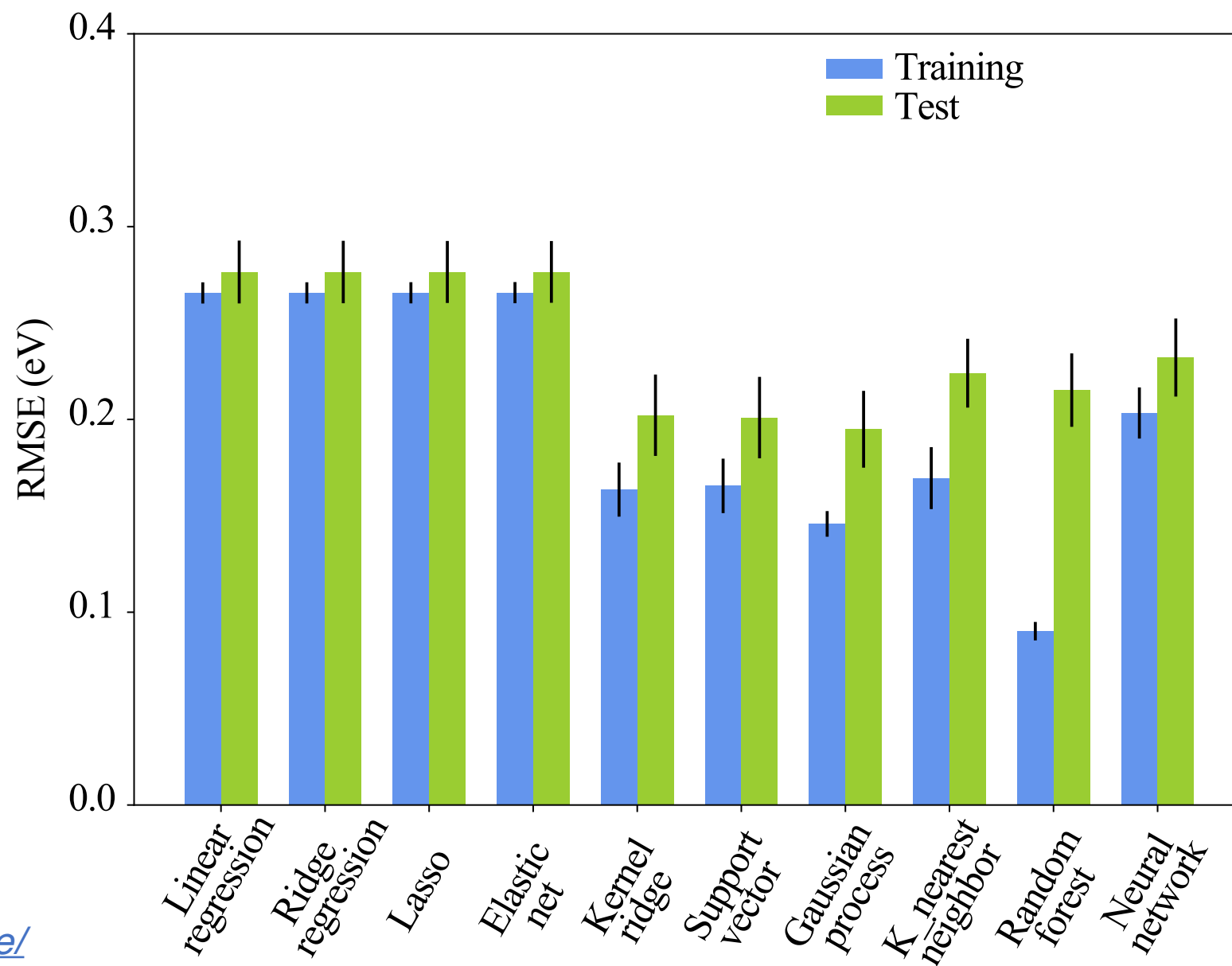


- Material properties of clean alloy surfaces are reduced to fingerprint vectors.
- Inputs are then mapped to reactivity descriptors through an artificial neural network.

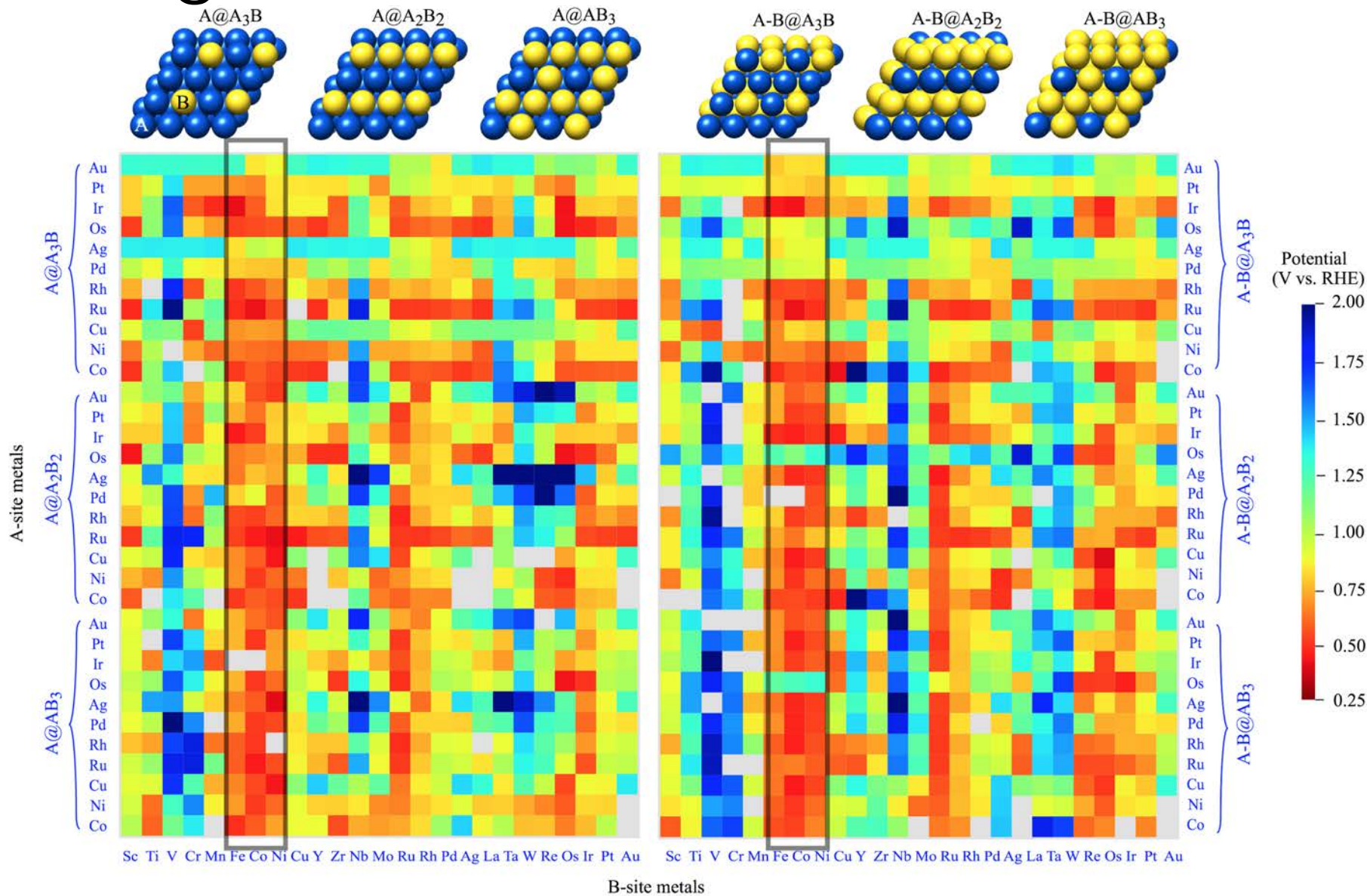
# Neural Network Model Development



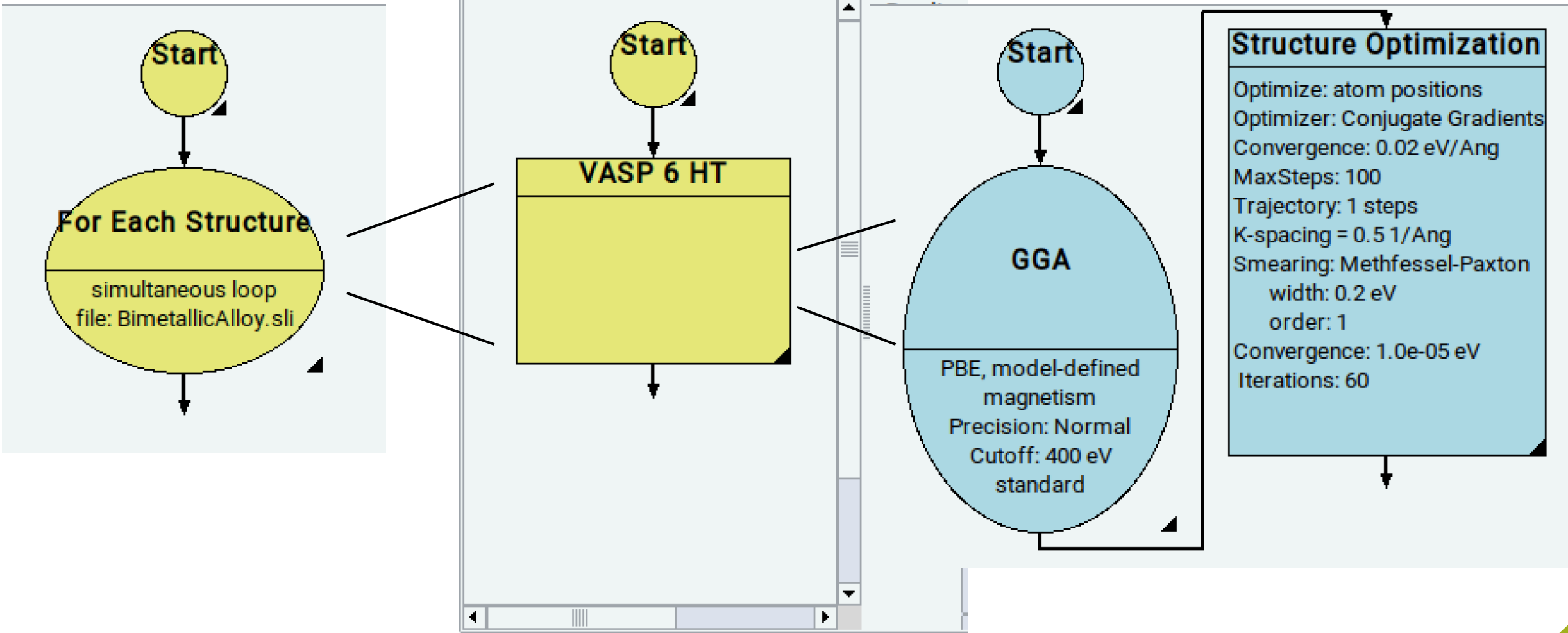
# Alternative Machine Learning Models



# Predicting New Alloys Using Machine Learning Models

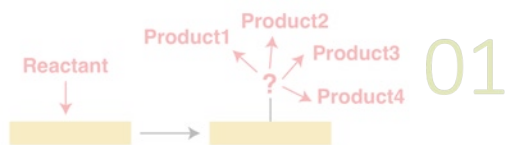


# Optimize Structures with *MedeA* High-throughput Module



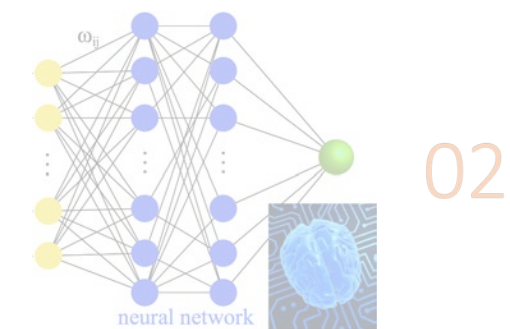
Run the different loop iterations simultaneously

# Outline



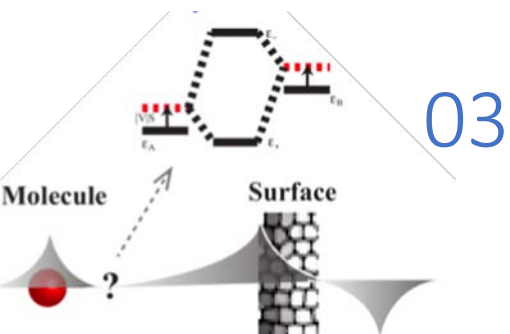
## Understand Reaction Mechanisms

Biopolymer interaction effect in  $C_2H_2$  hydrogenation reaction on Pd catalysts  
Surface strain effect in  $CO_2$  reduction reaction on AgSn/SnO<sub>x</sub> core-shell catalysts



## Accelerate Materials Discovery

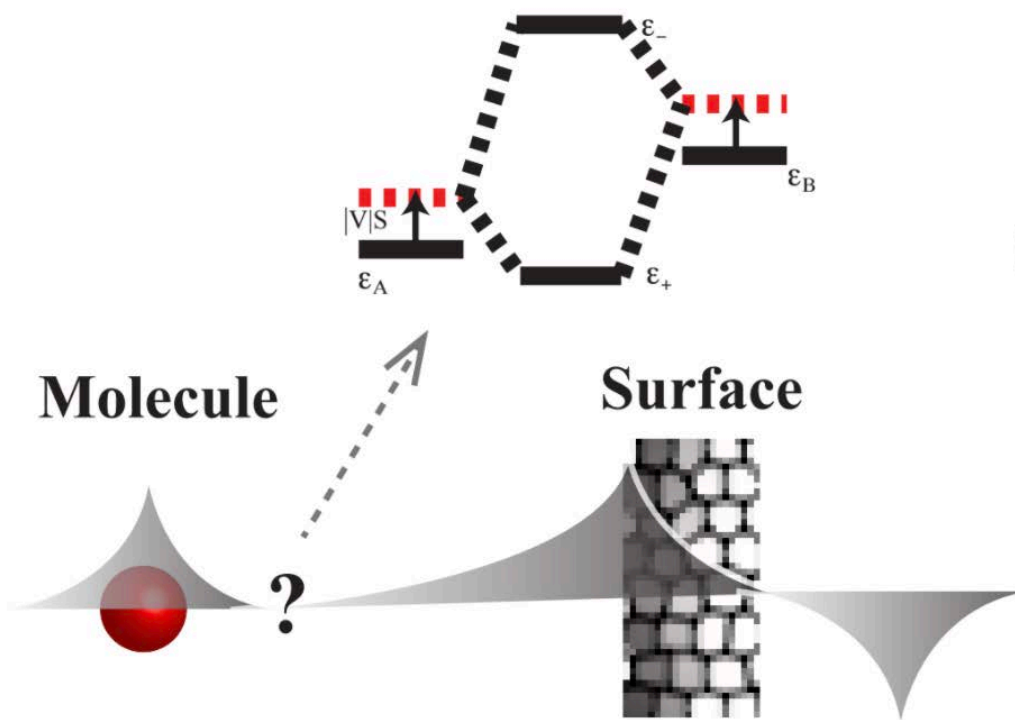
High-throughput screening of bimetallic catalysts enabled by machine learning



## Advance Catalysis Theory

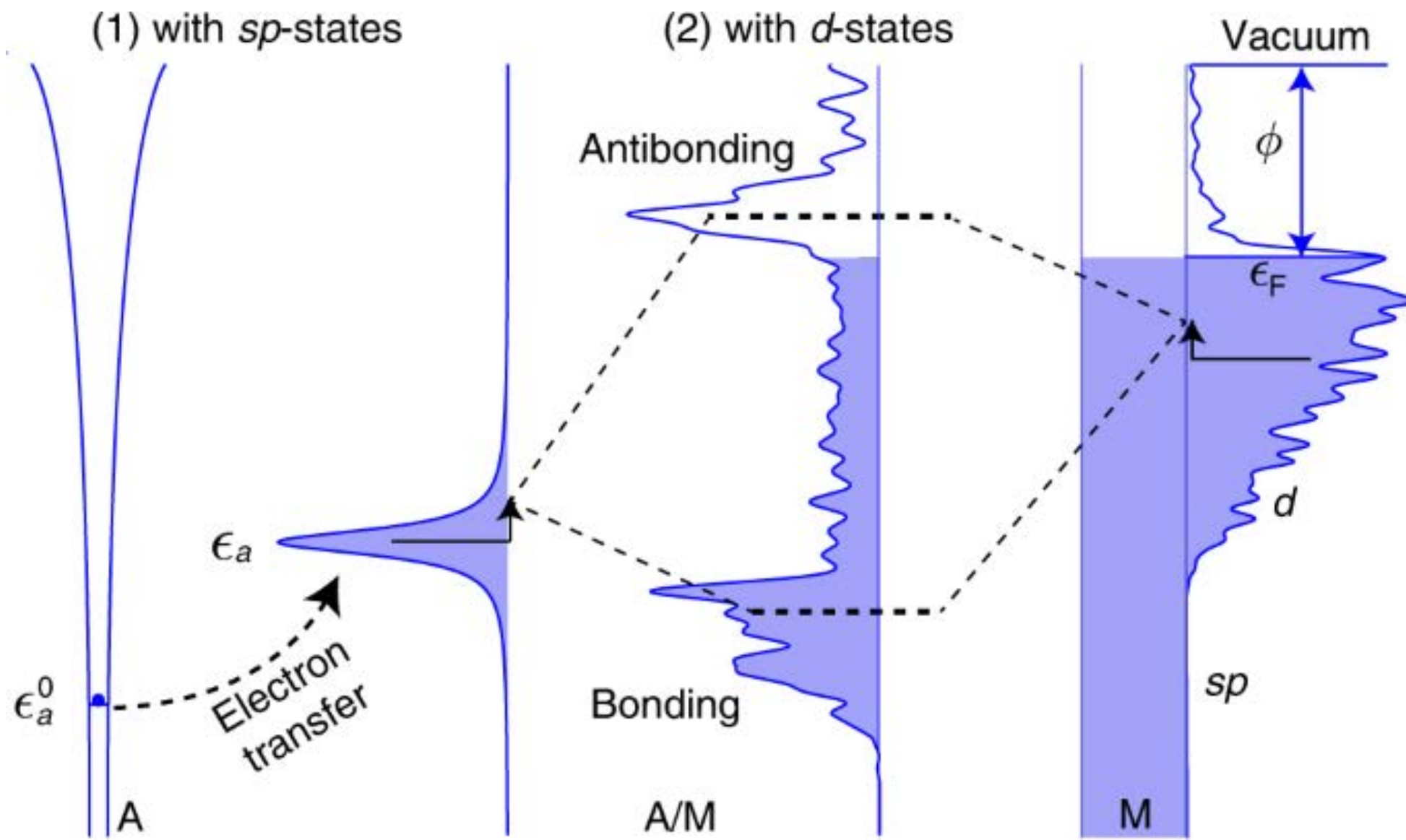
What determines reactivity of catalyst

# Bayesian Learning of Chemisorption for Bridging the Complexity of Electronic Descriptors



➤ **S. Wang, et al., Nat Commun 11, 6132 (2020).**

# $d$ -band Reactivity Theory



# Central Equations of $d$ -band Reactivity Theory

$$\hat{H} = \sum_{\sigma} \left\{ \epsilon_{a\sigma} n_{a\sigma} + \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} n_{\mathbf{k}\sigma} + \sum_{\mathbf{k}} (V_{a\mathbf{k}} c_{\mathbf{k}\sigma}^{\dagger} c_{a\sigma} + H.c.) \right\}$$

Green's  
Function  
Approach

$$(I\epsilon - H^{\sigma} + i\delta)G^{\sigma}(\epsilon) = I$$

$$G_{aa}^{\sigma}(\epsilon) = \left[ \epsilon - \epsilon_{\sigma} - \sum_{\mathbf{k}} \frac{|V_{a\mathbf{k}}|^2}{\epsilon - \epsilon_{\mathbf{k}} + i\delta} \right]^{-1}$$

$$= [\epsilon - \epsilon_{\sigma} - \Lambda(\epsilon) + i\Delta(\epsilon)]^{-1}$$

$$\Delta(\epsilon) = -Im \sum_{\mathbf{k}} [|V_{a\mathbf{k}}|^2 / (\epsilon - \epsilon_{\mathbf{k}} + i\delta)]$$

$$= \pi \sum_{\mathbf{k}} |V_{a\mathbf{k}}|^2 \delta(\epsilon - \epsilon_{\mathbf{k}})$$

$$\Lambda(\epsilon) = \frac{P}{\pi} \int_{-\infty}^{\infty} \frac{\Delta(\epsilon') d\epsilon'}{\epsilon - \epsilon'}$$

$$\rho_a(\epsilon) = \frac{1}{\pi} \frac{\Delta(\epsilon)}{[\epsilon - (\epsilon_a + \Lambda(\epsilon))]^2 + \Delta(\epsilon)^2}$$

$$\Delta E = \boxed{\Delta E_0} + \frac{2}{\pi} \int_{-\infty}^{\epsilon_F} \tan^{-1} \left[ \frac{\Delta(\epsilon)}{\epsilon - \epsilon_a - \Lambda(\epsilon)} \right] d\epsilon - \frac{2}{\pi} \int_{-\infty}^{\epsilon_F} \tan^{-1} \left[ \frac{\Delta_0(\epsilon)}{\epsilon - \epsilon_a} \right] d\epsilon + \boxed{2(\langle \tilde{n}_a \rangle + f) \alpha \beta V_{ad}^2}$$

$\Delta E_d^{hyb}$

$\Delta E_d^{orth}$

# Unknown Parameters in the $d$ -band Reactivity Theory

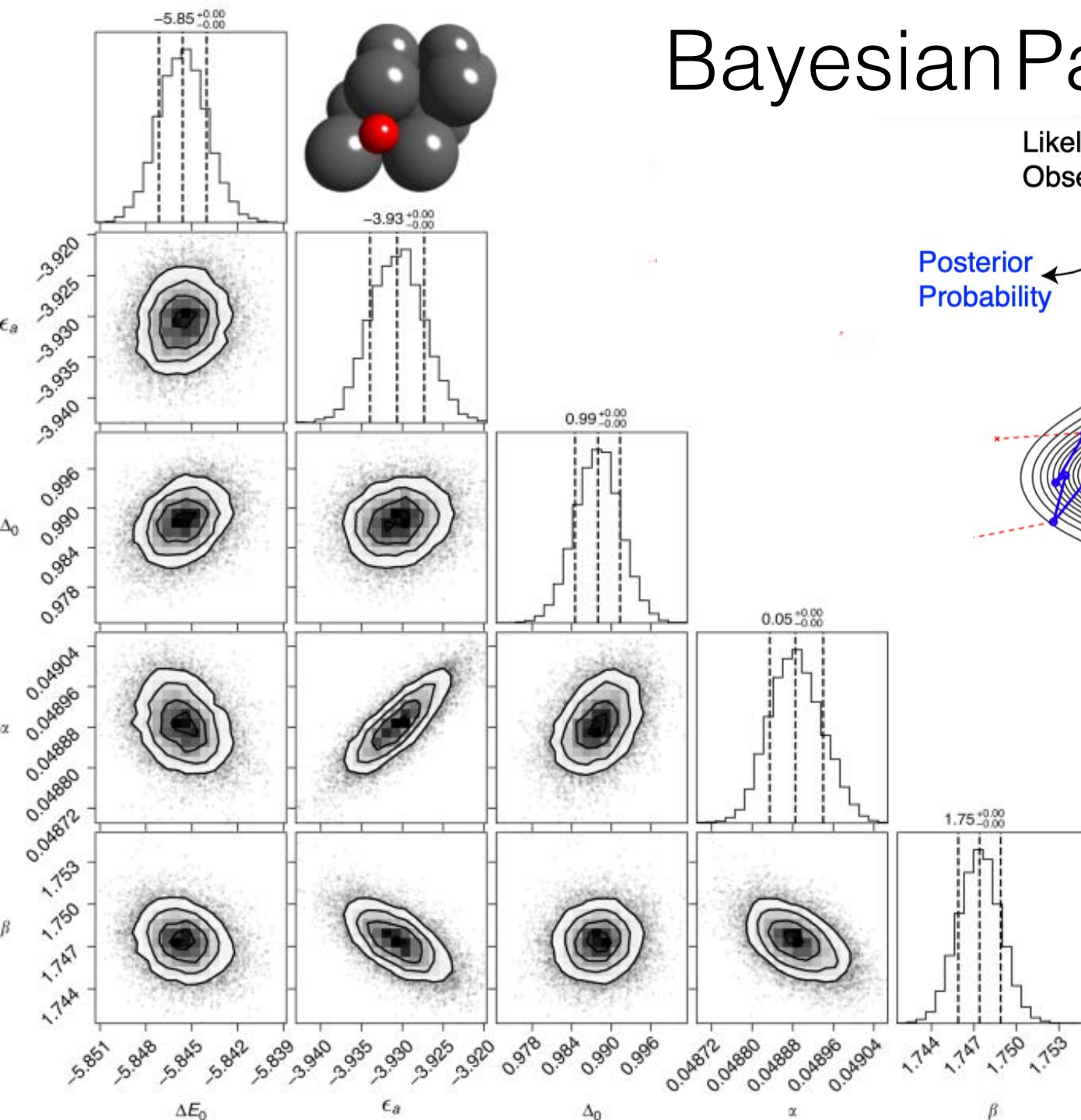
$$\rho_a(\epsilon) = \frac{1}{\pi} \frac{\Delta(\epsilon)}{[\epsilon - (\epsilon_a + \Lambda(\epsilon))]^2 + \Delta(\epsilon)^2}$$

$$\Delta E_{sp} \quad \Delta E_0 + \frac{2}{\pi} \int_{-\infty}^{\epsilon_F} \tan^{-1} \left[ \frac{\Delta(\epsilon)}{\epsilon - \epsilon_a - \Lambda(\epsilon)} \right] d\epsilon - \frac{2}{\pi} \int_{-\infty}^{\epsilon_F} \tan^{-1} \left[ \frac{\Delta_0(\epsilon)}{\epsilon - \epsilon_a} \right] d\epsilon + 2(\langle \tilde{n}_a \rangle + f) \alpha \beta V_{ad}^2$$

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

- $\Delta E_0$  : energy change due to the interaction of the unperturbed adsorbate orbital(s) with the delocalized  $sp$ -states
- $\epsilon_a$  : adsorbate resonance energy relative to the Fermi level
- $\Delta_0$  : chemisorption function contributed from delocalized  $sp$ -states
- $\alpha$  : orbital overlap coefficient
- $\beta$  : denotes the orbital coupling coefficient

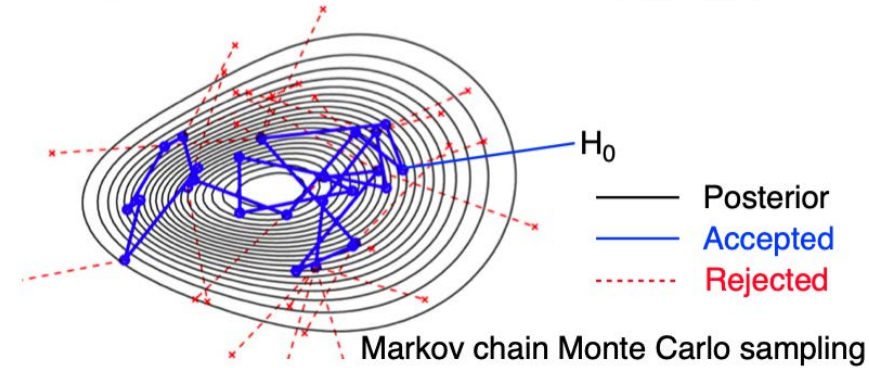
# Bayesian Parameterization



Likelihood of Observation  $\leftarrow$  Prior Probability

$$p(H|E) = \frac{p(E|H) \times p(H)}{p(E)}$$

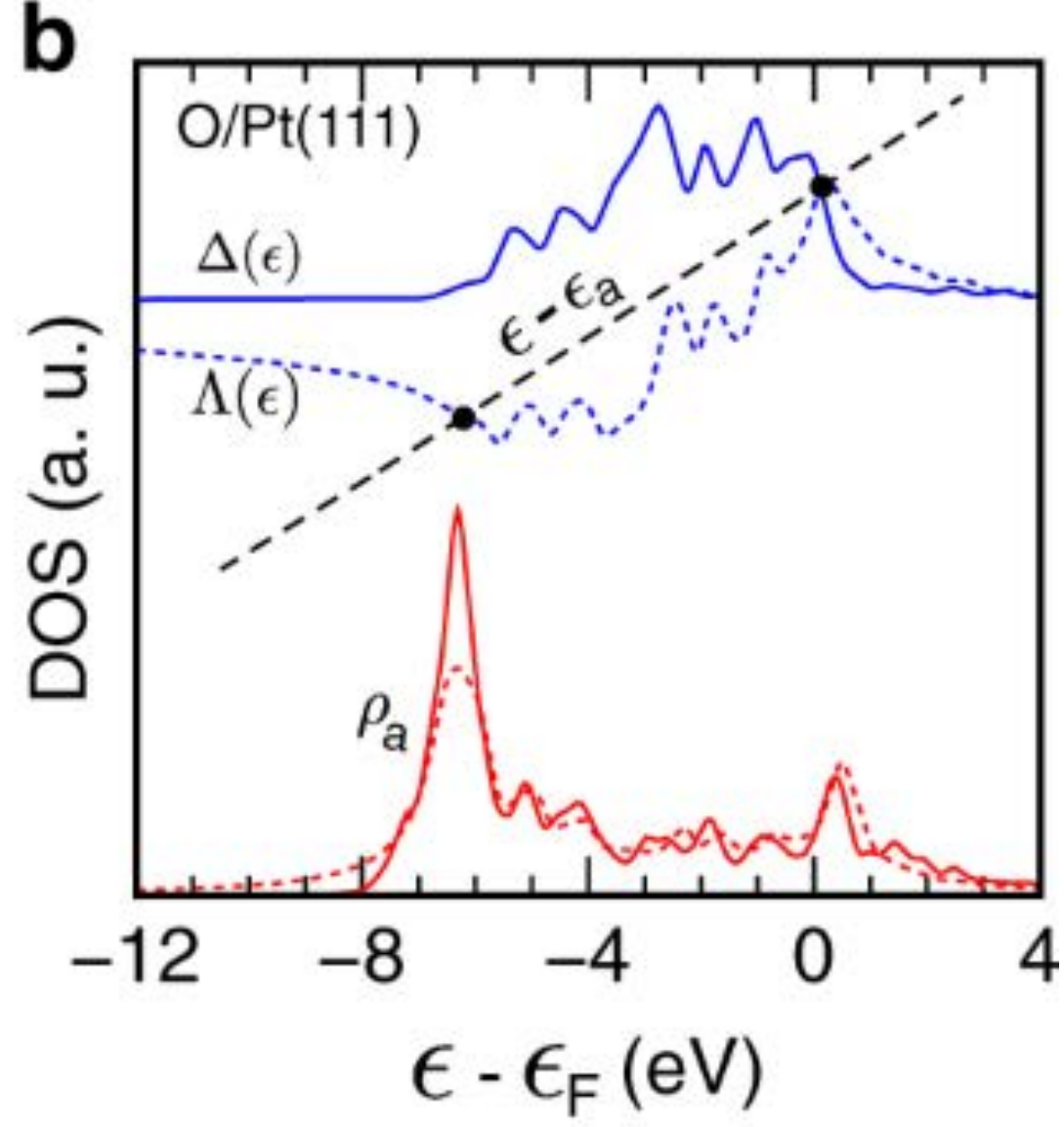
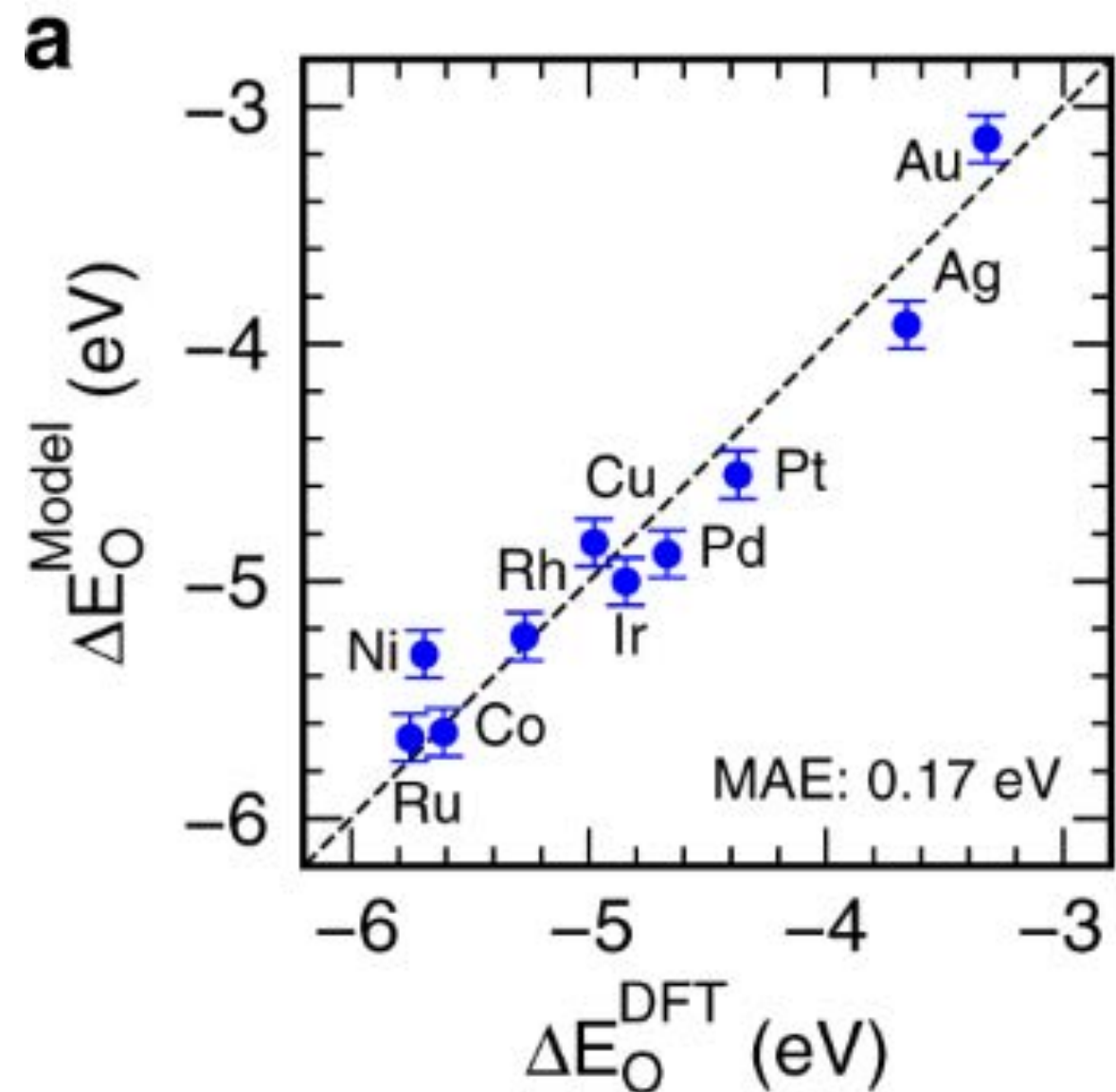
Posterior Probability  $\leftarrow$  Normalizing Constant



- Independent of initial guess.
- Less prone to trapping at local minima.

<https://github.com/hlxin/bayeschem>

# Adsorption Properties of O/M(111) Using Learned Parameters



# Interaction Energy and DOS Calculation within *MedeA*



$$BE = E_{A^*} - E_* - E_A$$

MedeA : Run VASP 6

Calculation Functional/Potential SCF DOS/Optic/Tensors Band Structure Advanced/Restart Add to Input Preview Input

Type of calculation

Properties

<input type="checkbox"/> (Pseudo, difference, spin) charge density	<input type="checkbox"/> (Total, valence) charge density, Bader analysis
<input type="checkbox"/> Total local potential	<input type="checkbox"/> Band structure
<input type="checkbox"/> Electron localization function	<input checked="" type="checkbox"/> Density of states
<input type="checkbox"/> Wave functions	<input type="checkbox"/> Optical spectra
<input type="checkbox"/> Electric field gradients	<input type="checkbox"/> Elastic constants
<input type="checkbox"/> Hyperfine parameters	<input type="checkbox"/> Zone center phonons
<input type="checkbox"/> Work function (surfaces only)	<input type="checkbox"/> Response tensors
	<input type="checkbox"/> NMR: chemical shifts
	<input type="checkbox"/> Energy of formation

Solvation (for molecules or surfaces)

Apply solvation model

External pressure:  GPa

Charge state:  e

External electrostatic field

Interaction

Functional

DFT exchange-correlation

Van der Waals

Magnetism  to be non-magnetic

General Setup

Precision

Increase planewave cutoff (cell optimizations)

Planewave cutoff (default):  eV

Planewave cutoff:

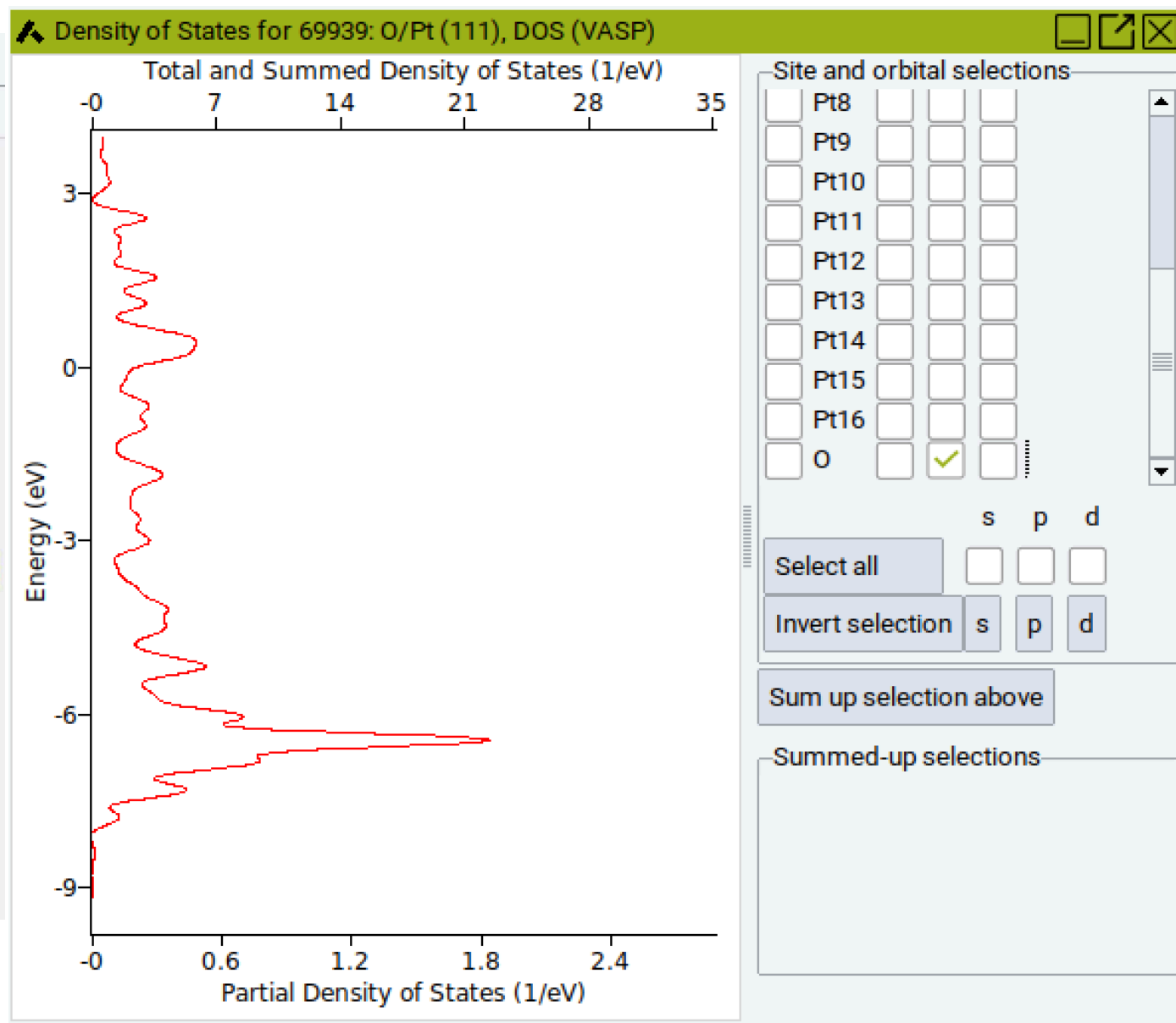
Projection

VASP version

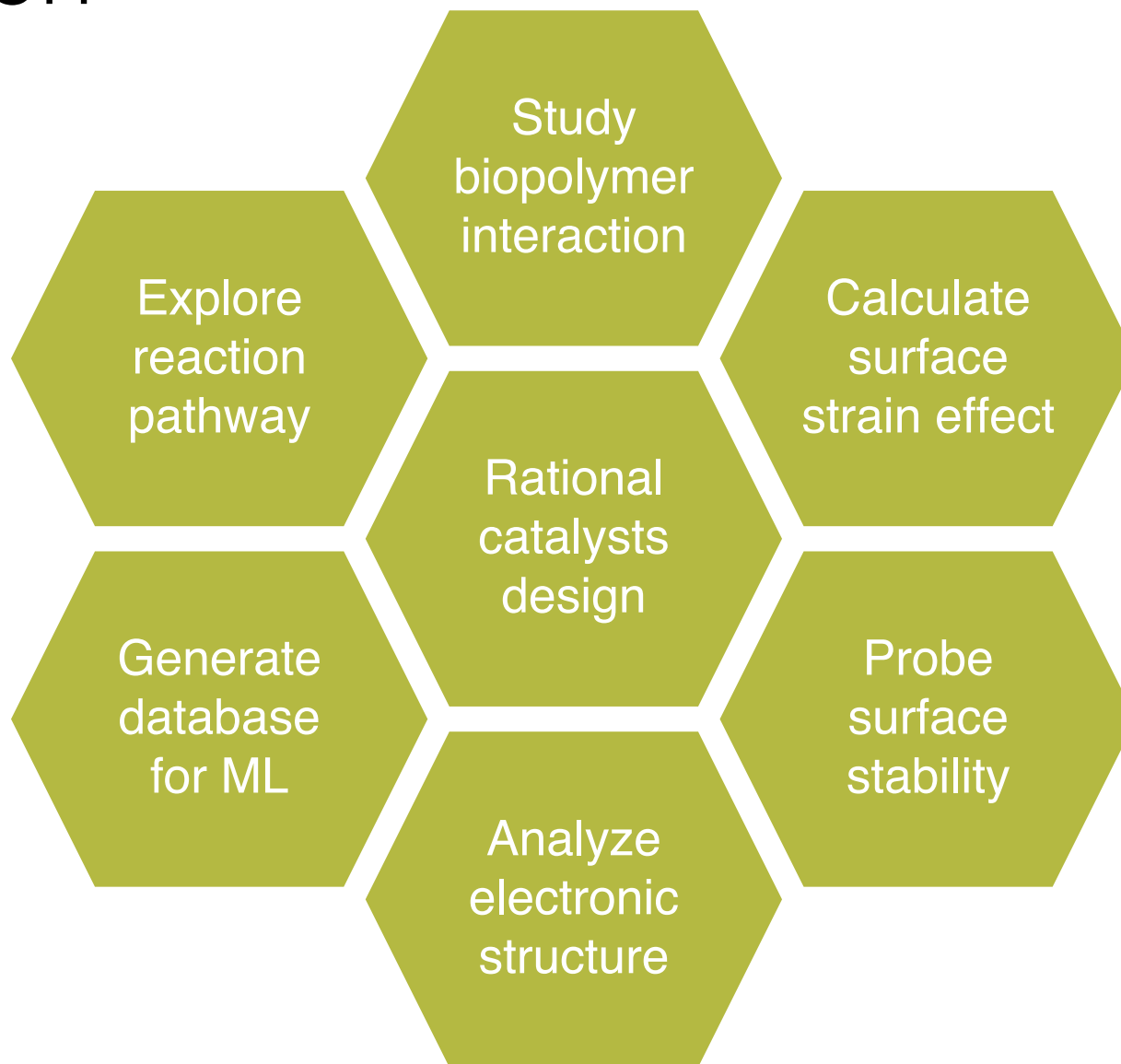
# Analysis Tool for Density of States

Analysis Windows Help

- Geometric Analysis
- Trajectories
- UNCLE Binary Ground State Diagram
- UNCLE Monte Carlo Temperature Profile
- IR / Raman Spectra
- UV / Vis Spectra
- Phonon Dispersion
- Phonon Density of States
- Thermodynamic Functions
- Band Structure
- Density of States
- Optical Spectra
- Total Charge Der Plot the density of states from a previous calculation
- Total Valence Charge Density
- Difference Charge Density
- Magnetization Density
- Pseudo Charge Density
- Electron Localization Function
- Total Local Potential
- Orbitals
- VaspView



# Conclusion



# Online Training and Demo

Orbital Level Understanding of Adsorbate-Surface Interactions in Catalysis

Next Thursday, February 11, 2021

USA/EUROPE:

10:00 am PST/1:00 pm EST

7:00 pm CEST

Register for the training:

<https://register.gotowebinar.com/rt/9025371295921111054>

\*Training open to everyone



# Design Catalysts

- ▶ MedeA modules mentioned in today's webinar

<https://www.materialsdesign.com/compute-engines>

<https://www.materialsdesign.com/analysis-tools>

[MedeA Environment](#)

[MedeA VASP](#)

[MedeA HT](#)

[MedeA Phonon](#)

[MedeA Gaussian](#)

[MedeA Transition State Search \(TSS\)](#)

- ▶ Webinar: Live and Recorded  
<https://www.materialsdesign.com/webinars>

- ▶ Publications  
<https://www.materialsdesign.com/Publications>

- ▶ Application Notes  
<https://www.materialsdesign.com/application-notes>

- ▶ For questions or comments contact:

Katherine Hollingsworth

[khollingsworth@materialsdesign.com](mailto:khollingsworth@materialsdesign.com)

# Question and Answer Session



***Dr. Siwen Wang***

*Materials Design*



***Dr. Taylor Juran***

*Materials Design*

# Questions about Materials Design Webinars

***Katherine Hollingsworth***

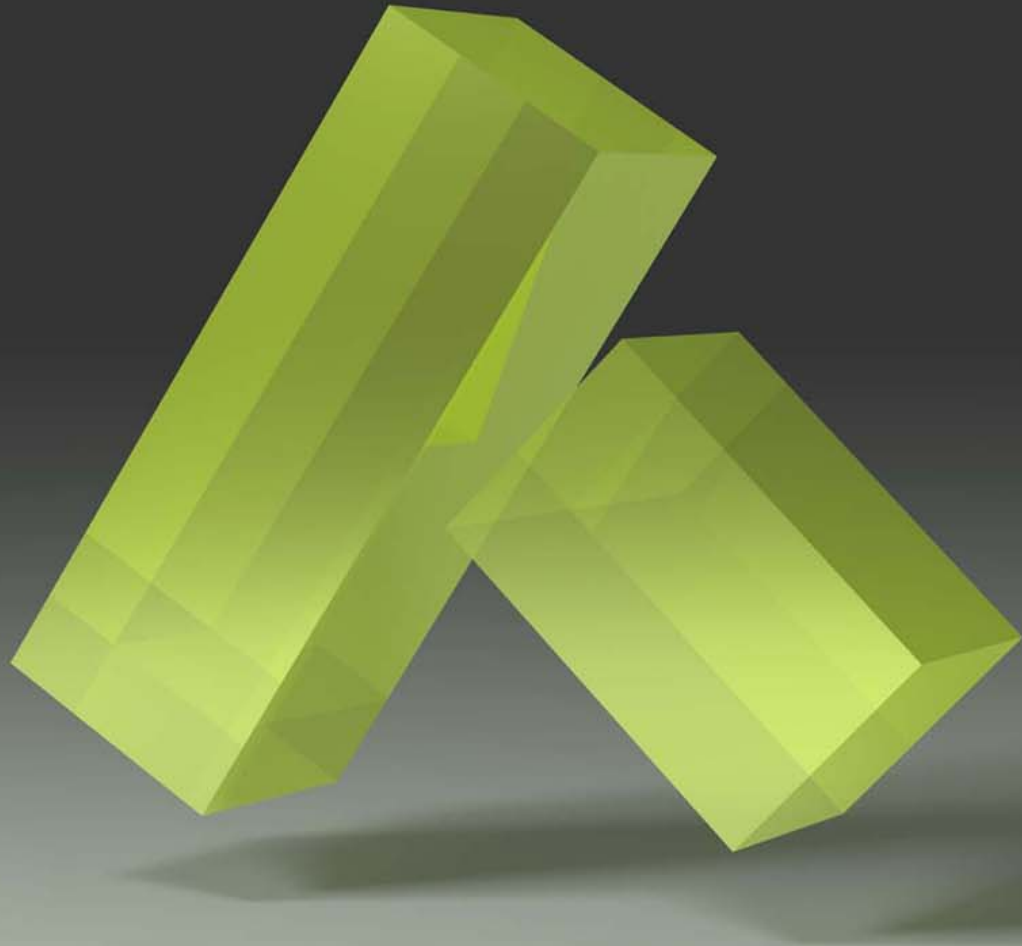
*khollingsworth@materialsdesign.com*



**materials design**

*info@materialsdesign.com*

*www.materialsdesign.com*



# *Medea*

Innovation by Simulation