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Chemical Catalysis for Bioenergy

An Introduction to Programmable Catalysis for Chemical Energy Technology

Paul J. Dauenhauer
University of Minnesota
January 29, 2025

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Today's Speaker

Paul J. Dauenhauer
University of Minnesota

Center for Programmable Energy Catalysis

An Introduction to Programmable Catalysis for Chemical Energy Technology

Paul J. Dauenhauer

University of Minnesota

Wednesday, January 29, 2025

U.S. Department of ENERGY

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Public Disclosure of Conflicts of Interest

PRIVATE FUNDING

Paul Dauenhauer is the **co-founder of, and holds equity in**, Sironix Renewables, a company that holds the license to manufacture and sell OFS surfactants. The University of Minnesota also has equity and royalty interests in Sironix. These interests have been reviewed and managed by the University of Minnesota in accordance with its Conflict of Interest policies.

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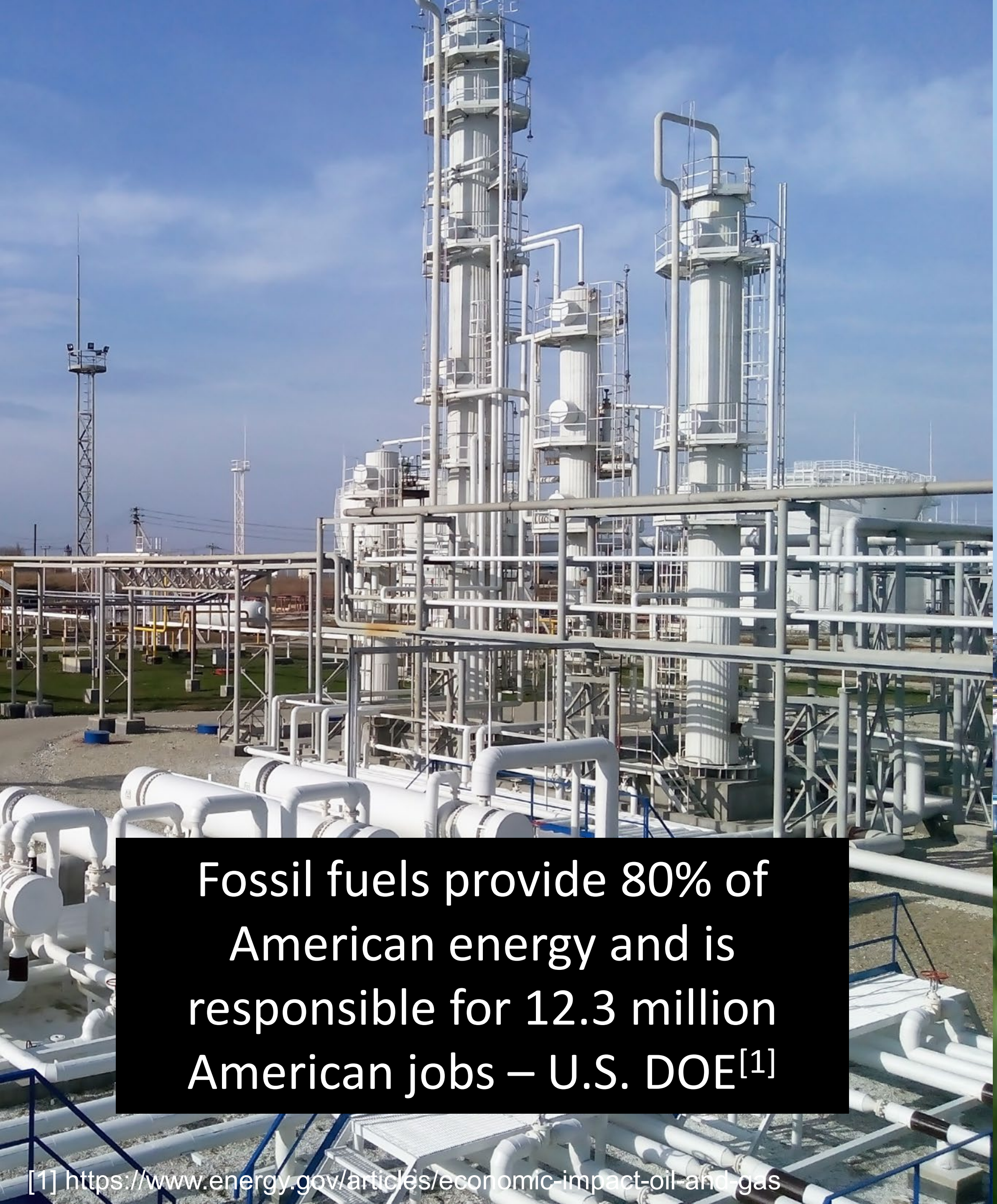


Fossil fuels provide 80% of American energy and is responsible for 12.3 million American jobs – U.S. DOE[1]

Agriculture, food, and related industries contributed roughly $1.537 trillion to U.S. gross domestic product (GDP) in 2023 – USDA[2]

[1] https://www.energy.gov/articles/economic-impact-oil-and-gas

[2] https://z.umn.edu/a431

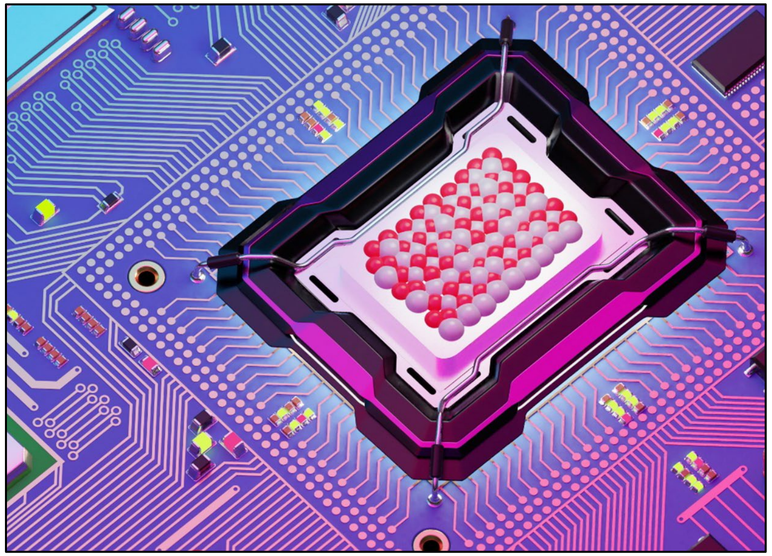
The Big Opportunity for Catalysis & Energy

What "disruptive technologies" will change our future? (My opinion)

Artificial Intelligence

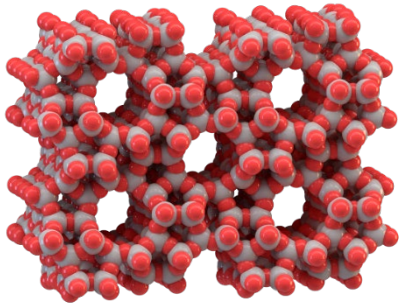
Quantum Computing

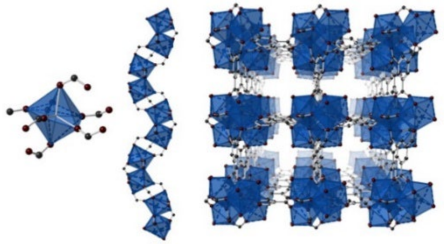
Programmable Catalysis (This Webinar)

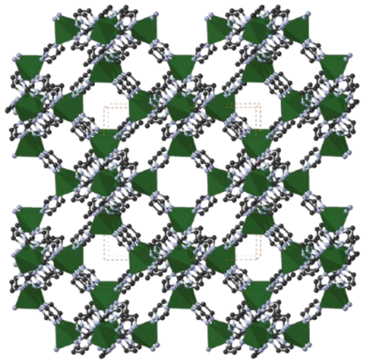


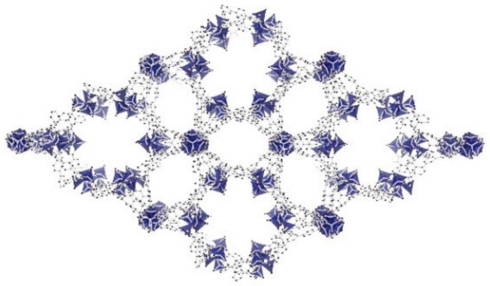
The Limits of *Structure-Function in Catalysis*

Advanced Materials

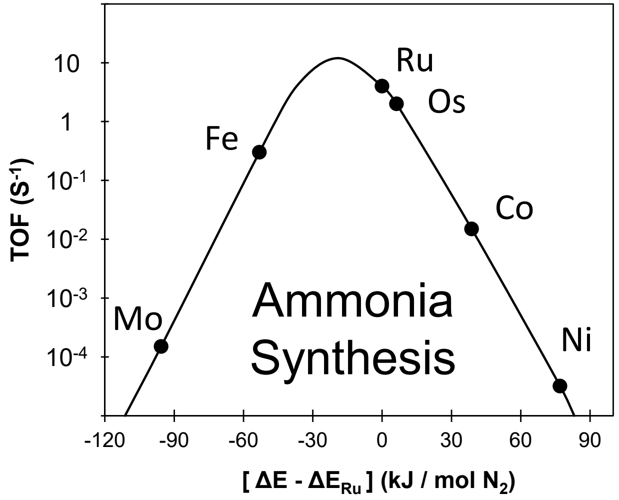


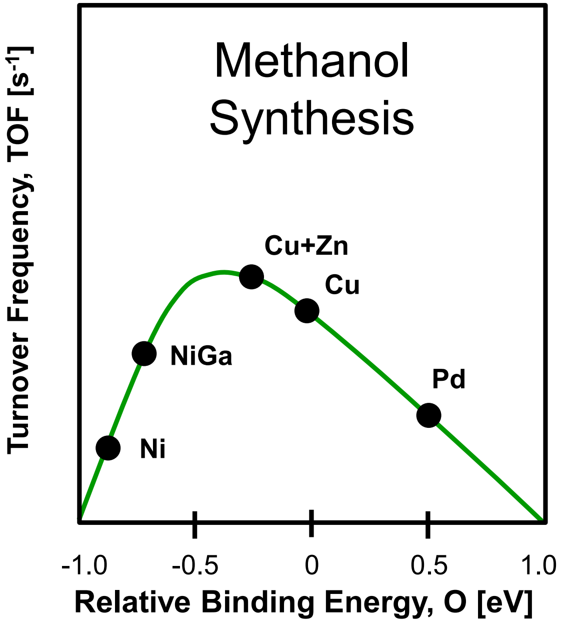


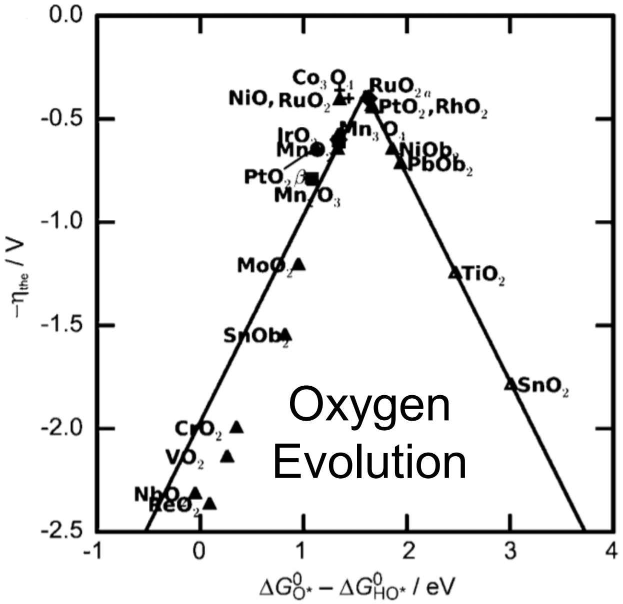




Almost all of the key reactions of interest to energy are limited by the Sabatier Principle





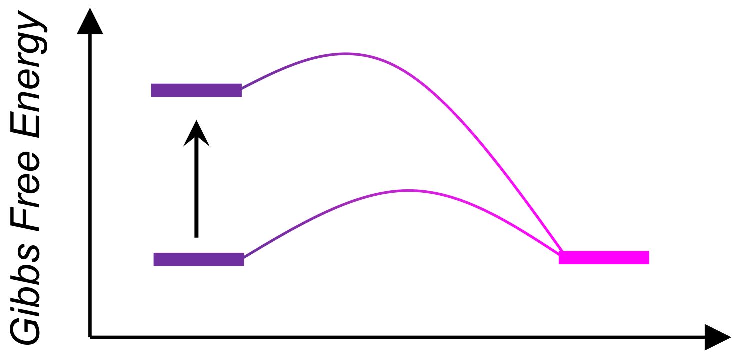


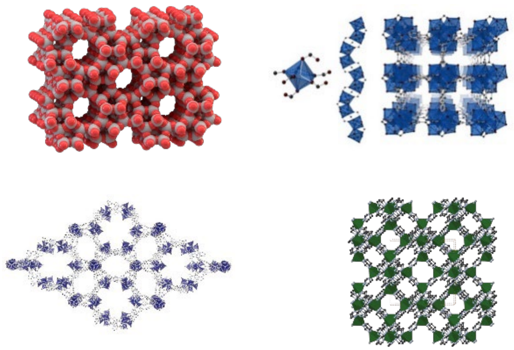
ChemCatChem **2011**, 3, 1159 – 1165.

New Catalyst Function: Dynamic Free Energy

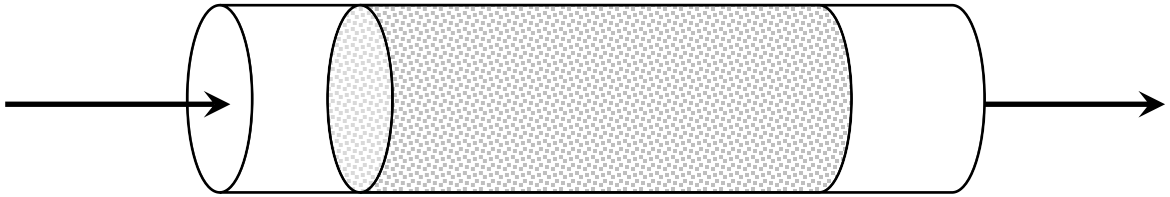
Catalytically Convert Reactant A to Product B

<u>Conventional Strategy 1</u>: Put in energy to raise Gibbs Free Energy of A (e.g., higher temperature)



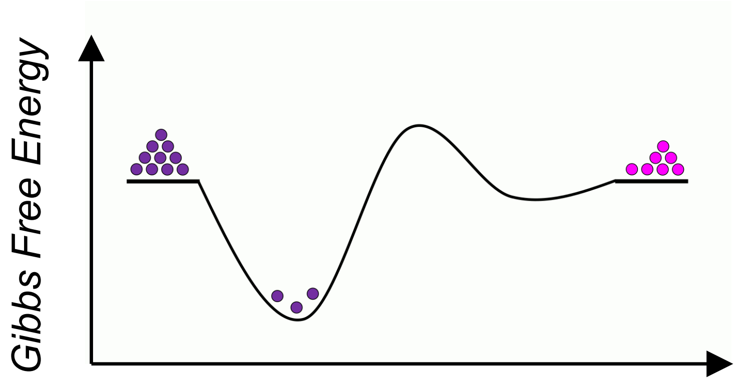


Reactant A



Product B

<u>New Strategy 2</u>: Put in energy to drive reactants to products via the surface



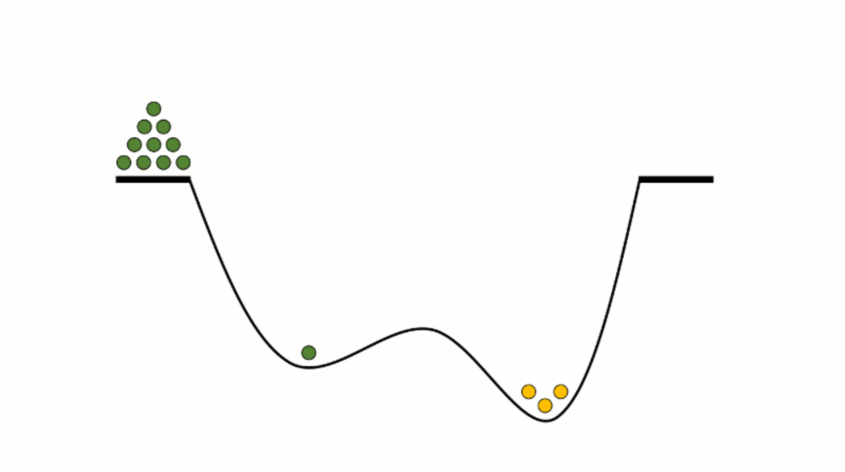
How do we design these catalytic pumps?

Oscillating Catalytic Ratchet

The ratchet mechanism preferentially moves molecules in one direction

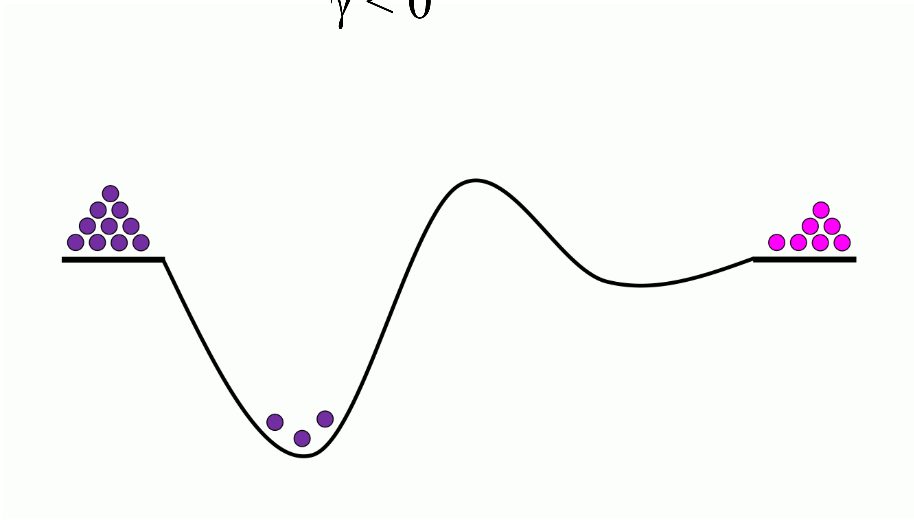
Positive Scaling

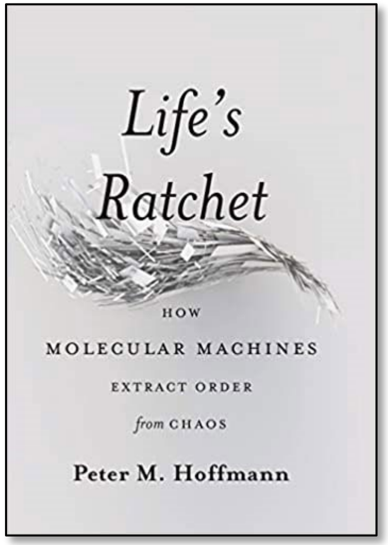
$\gamma > 1$



Negative Scaling

$\gamma < 0$





Book: "Life's Ratchet", by Professor Peter Hoffmann

[1] M.A. Ardagh, et al. *Cat. Sci. Tech.* 2019, 9, 5058. DOI: 10.1039/C9CY01543D

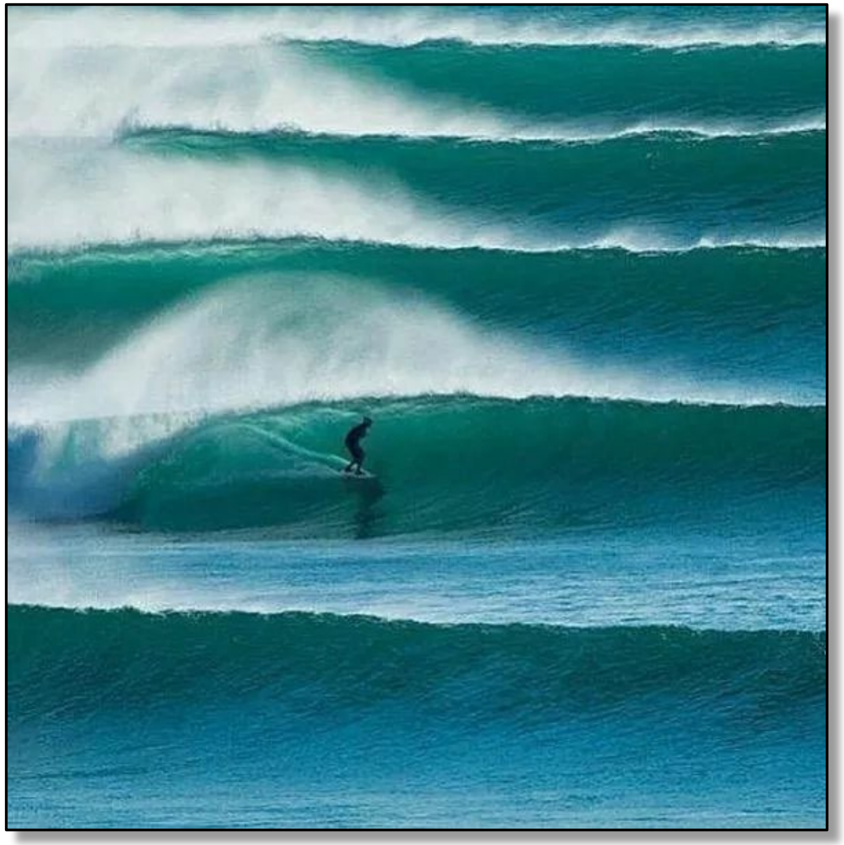
Static versus Programmable Catalysis

Static Catalysis

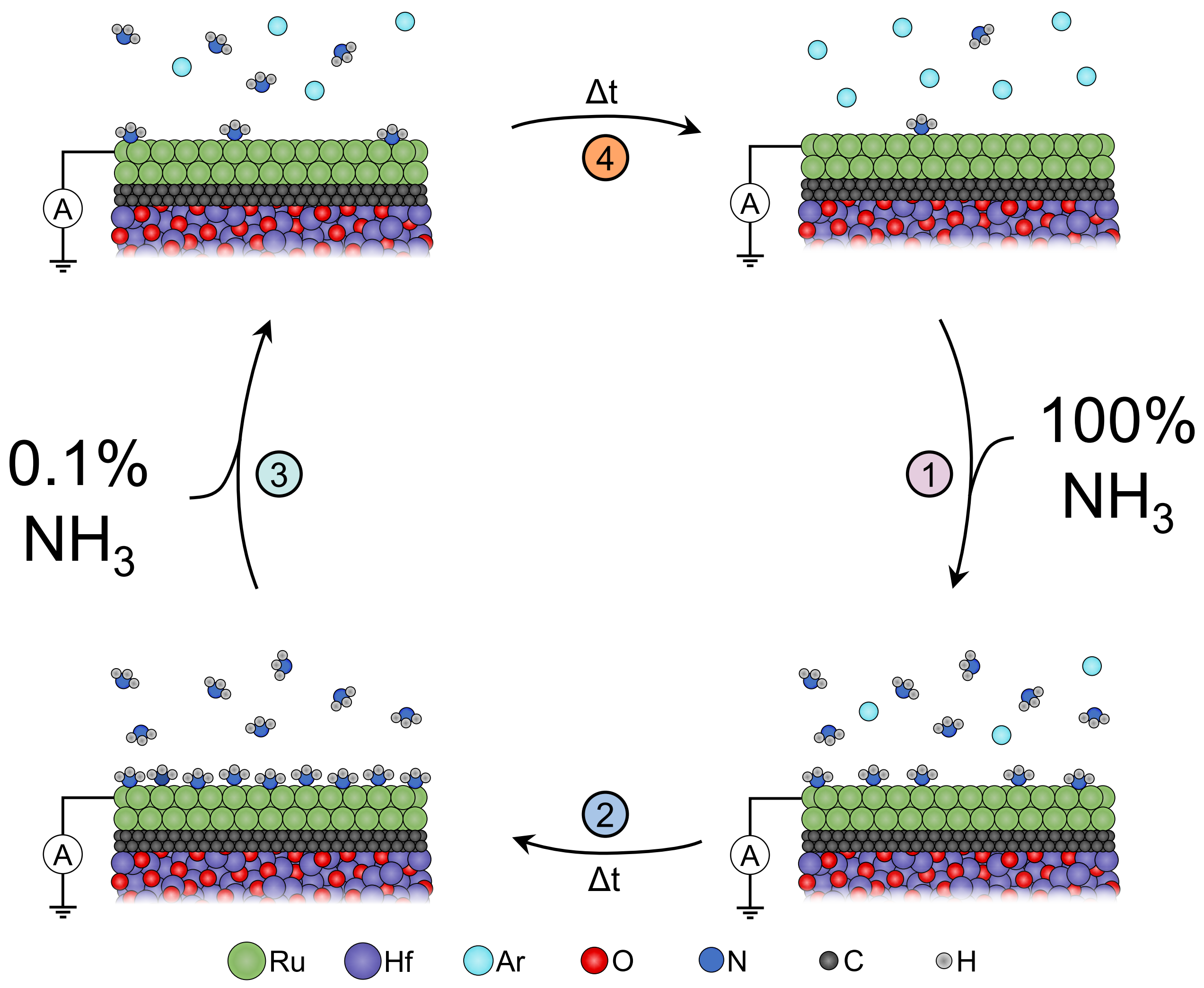
Molecules fall down the free energy gradient

Programmable Catalysis

Molecules are promoted by a local free energy gradient

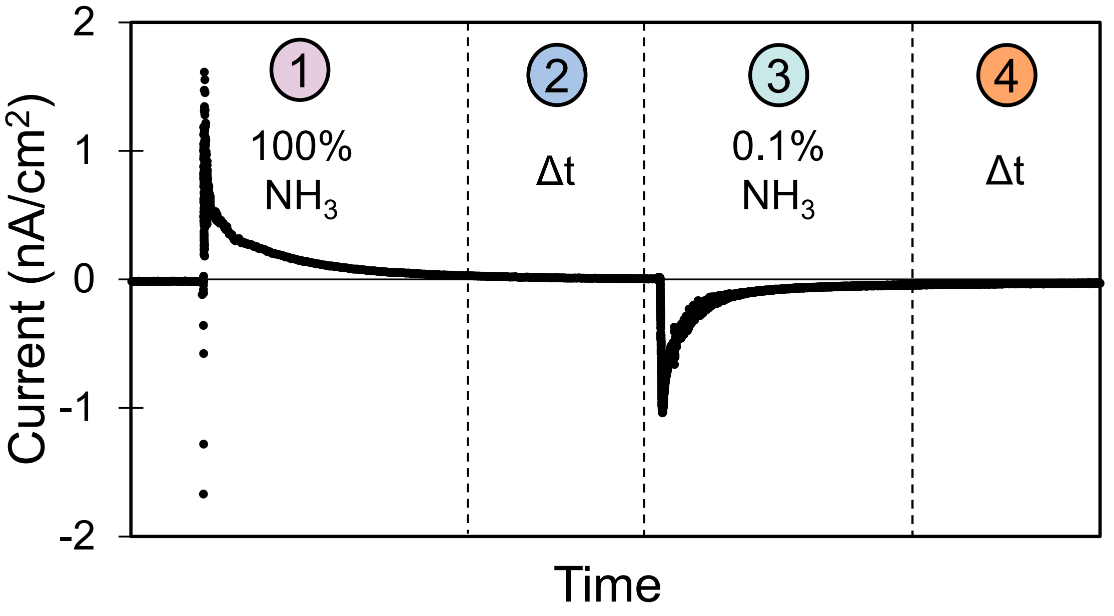


Isopotential Electron Titration (IET) – NH_3 on Ru



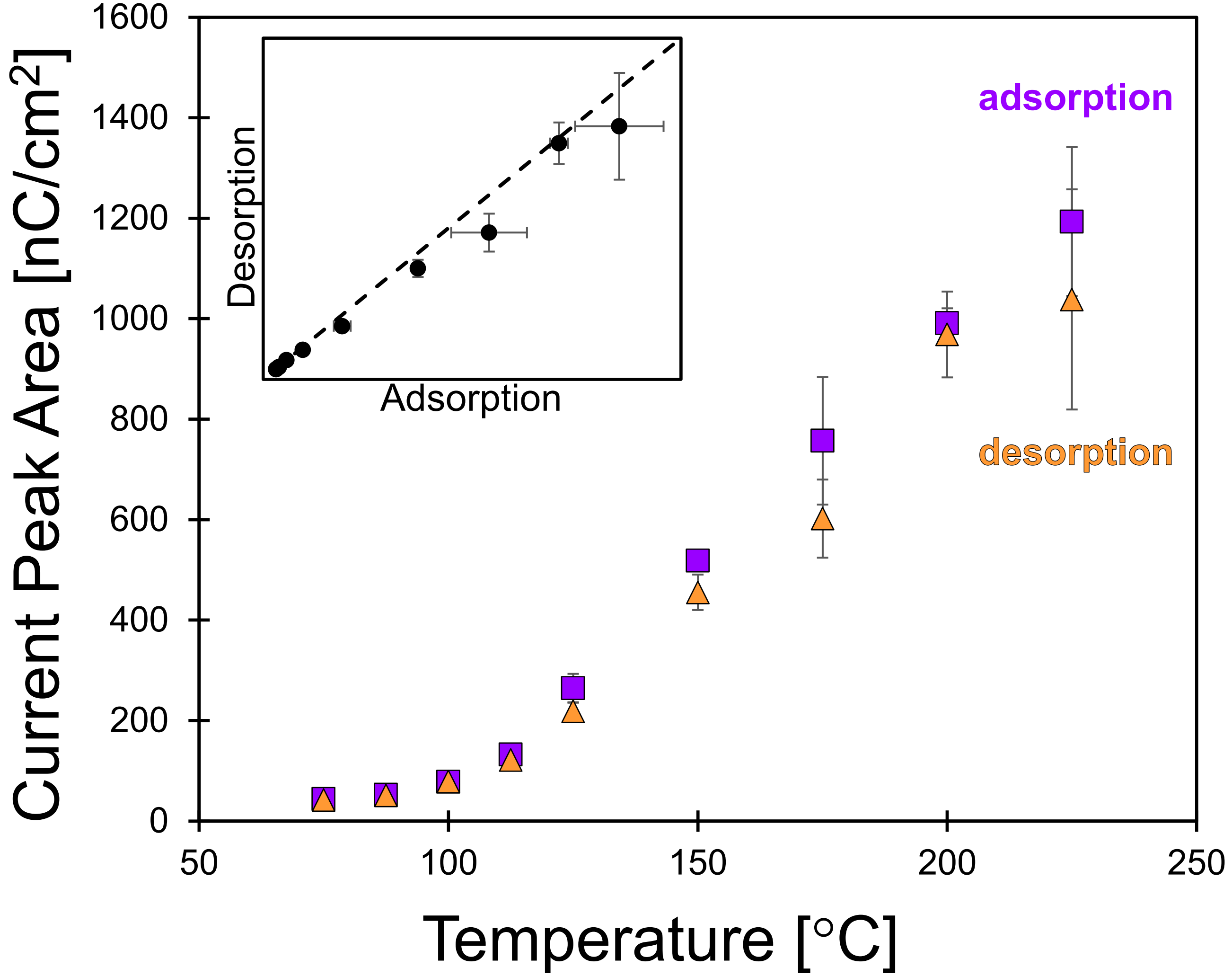
Adsorption of NH_3 adds electrons to the Ru surface

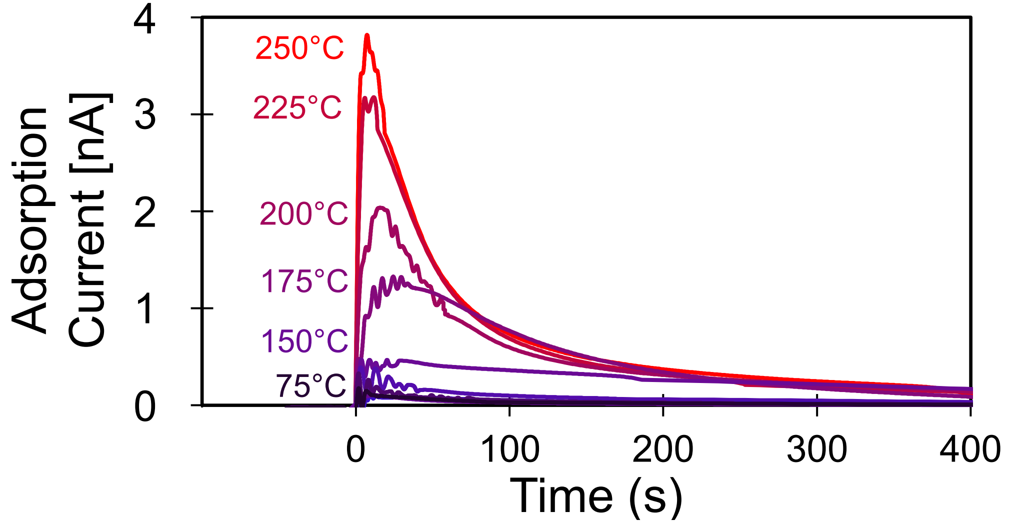
Desorption of NH_3 removes electrons from the Ru surface

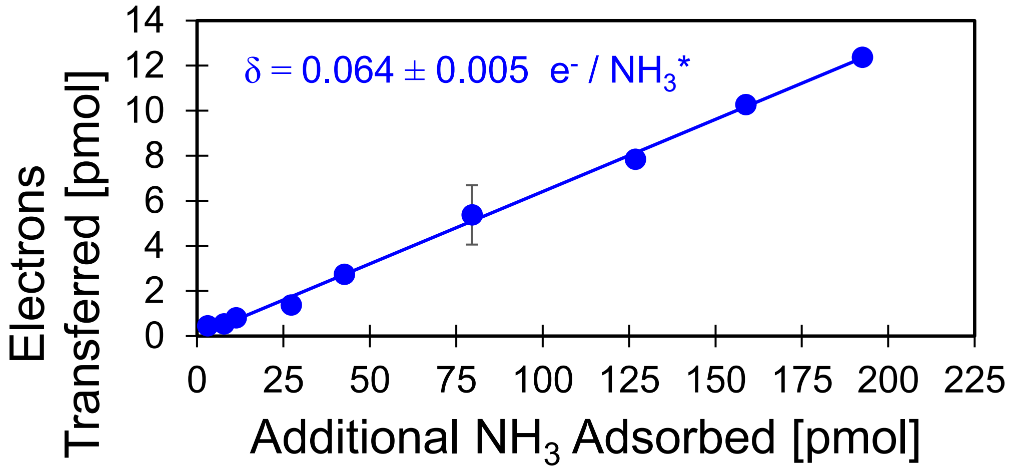


Isopotential Electron Titration (IET) – NH_3 on Ru

Adsorption of NH_3 adds 6.4% of an electron to the Ru surface





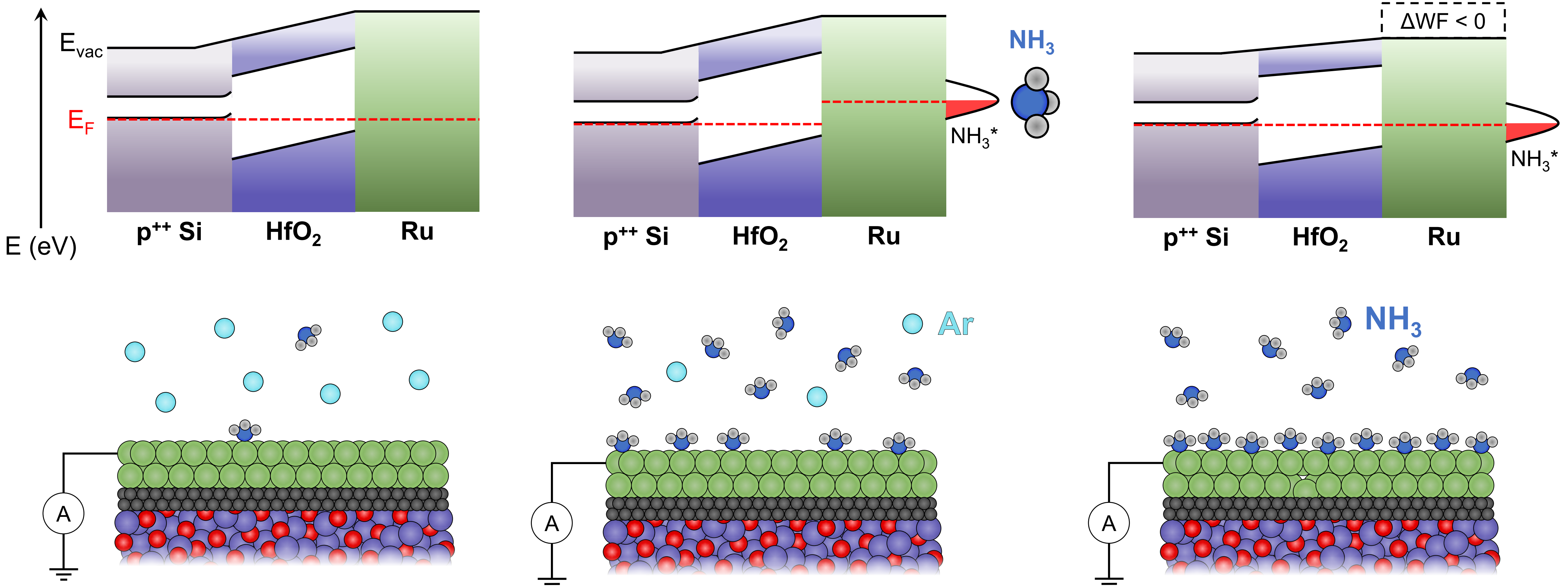


Isopotential Electron Titration (IET) – NH_3 on Ru

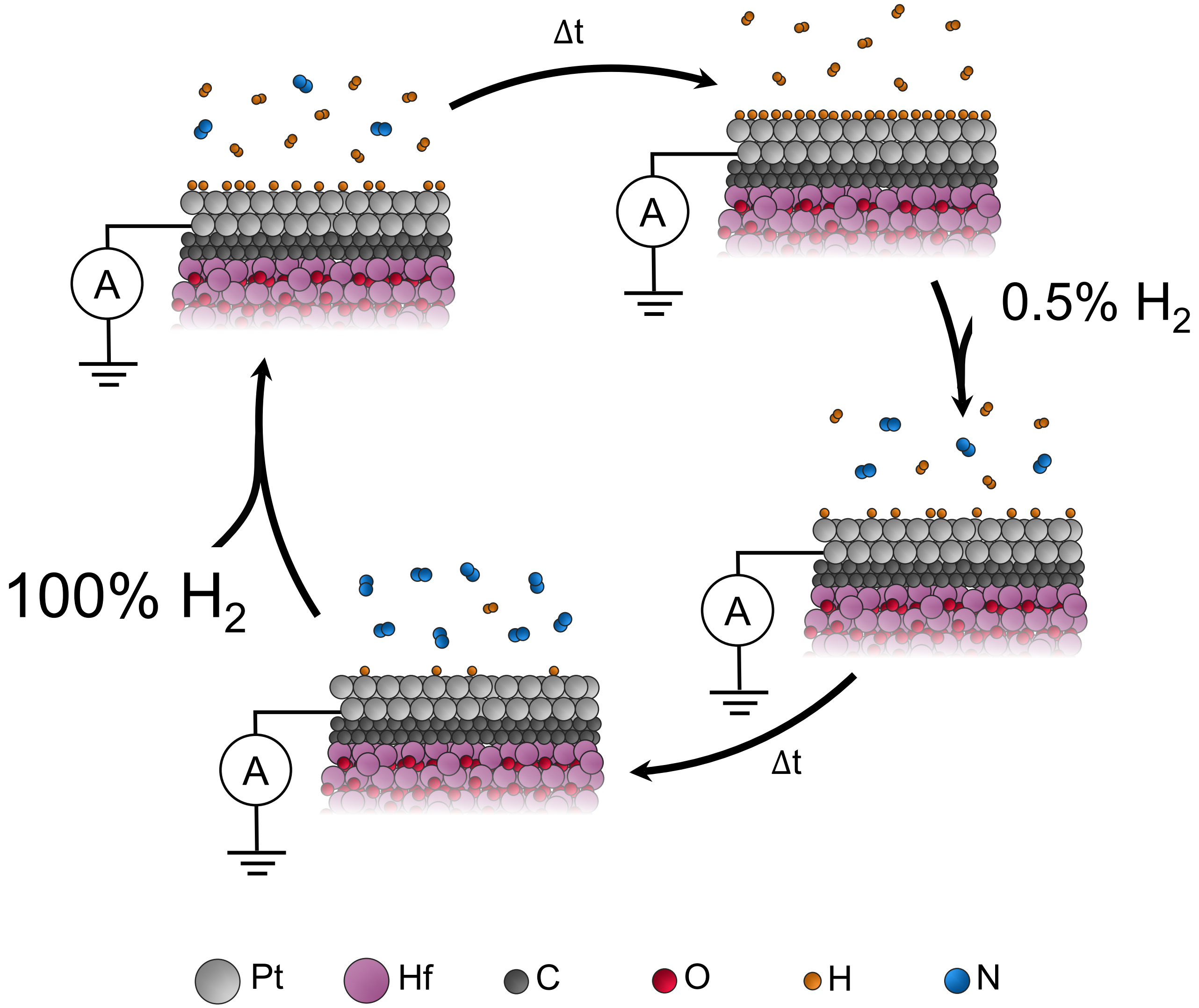
Electrochemical equilibrium between Ru and 0.1% NH_3

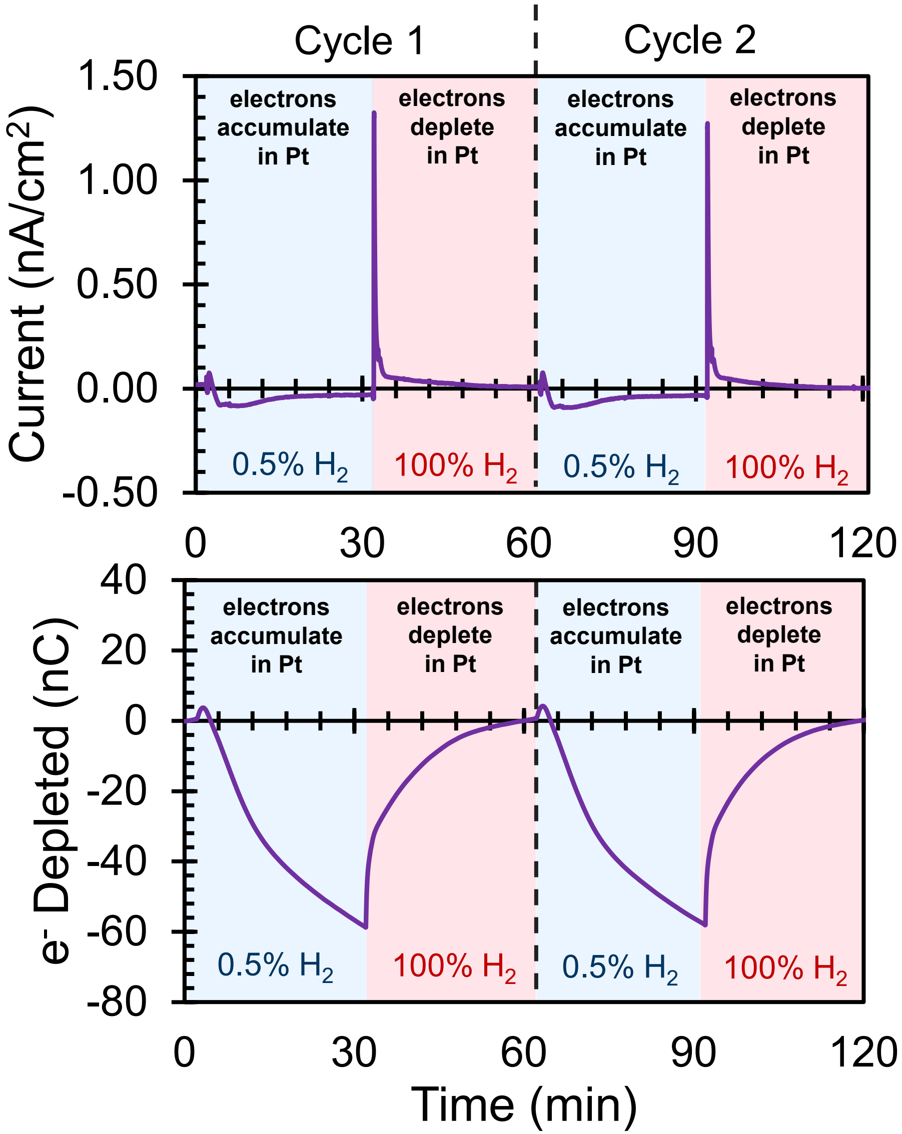
Dosing of 100% NH_3 perturbs equilibrium

Electrochemical equilibrium between Ru and 100% NH_3



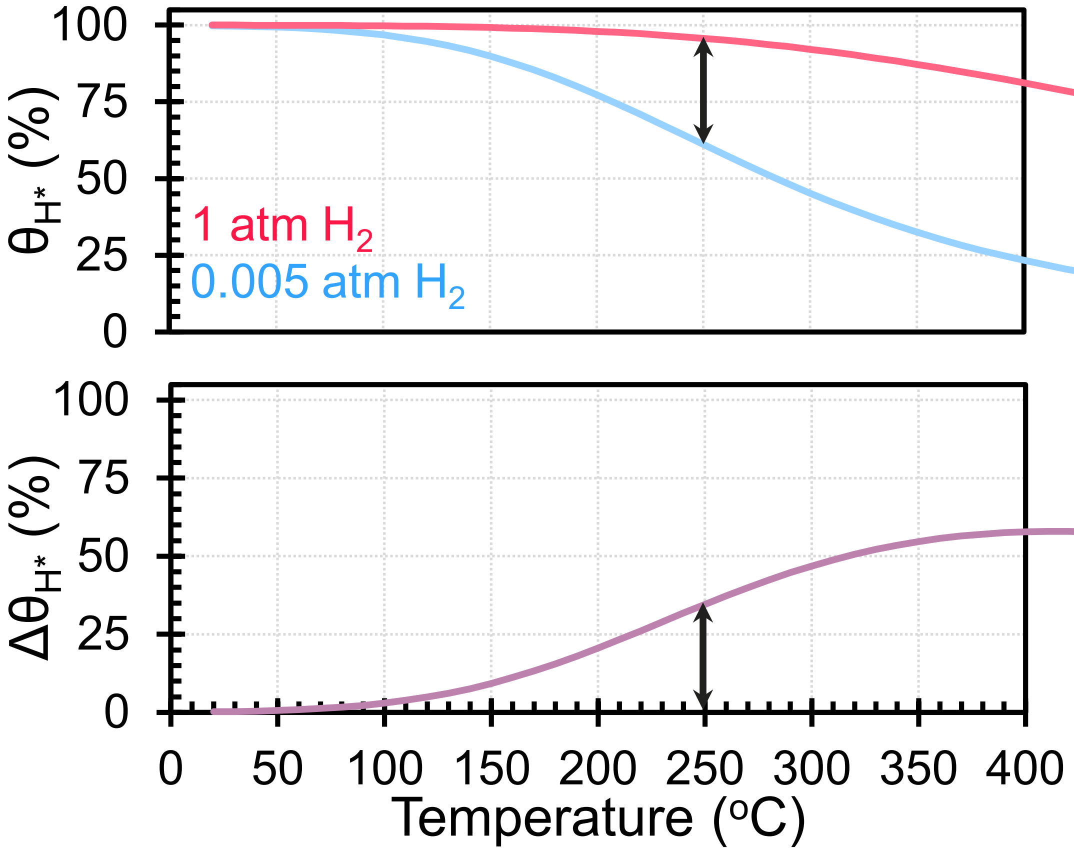
Isopotential Electron Titration (IET) – H_2 on Pt



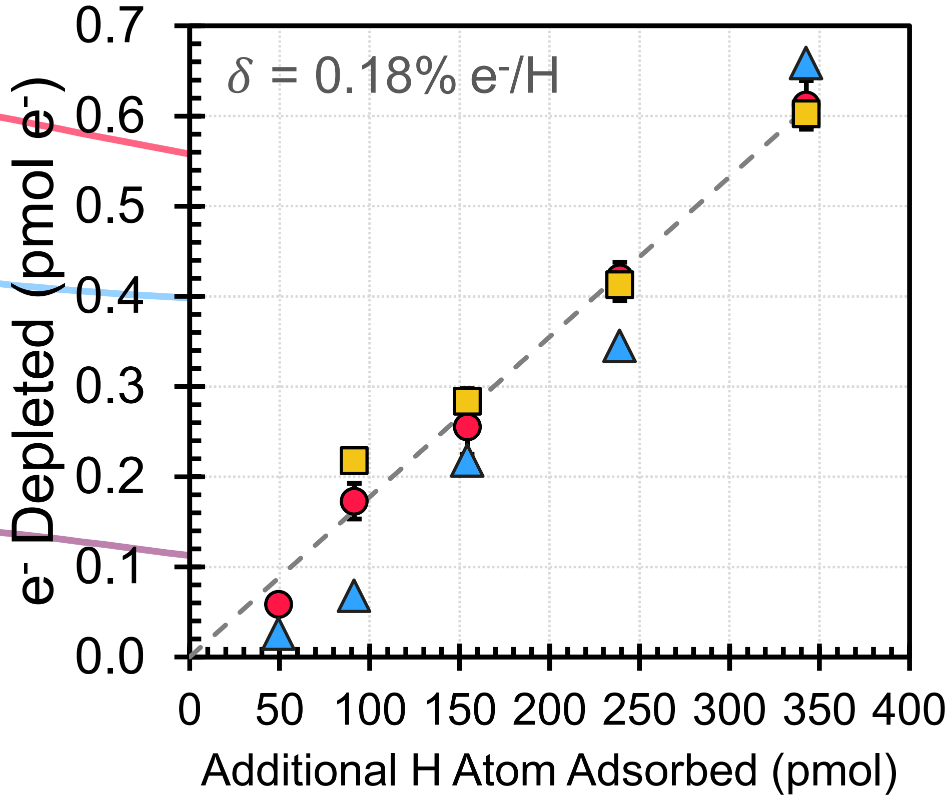


Isopotential Electron Titration – H_2 on Pt

Change in of H_2 surface coverage increases with temperature



H_2 only contributes ~0.2% of an electron to the Pt surface



Materials, Catalyst States, & Transition States

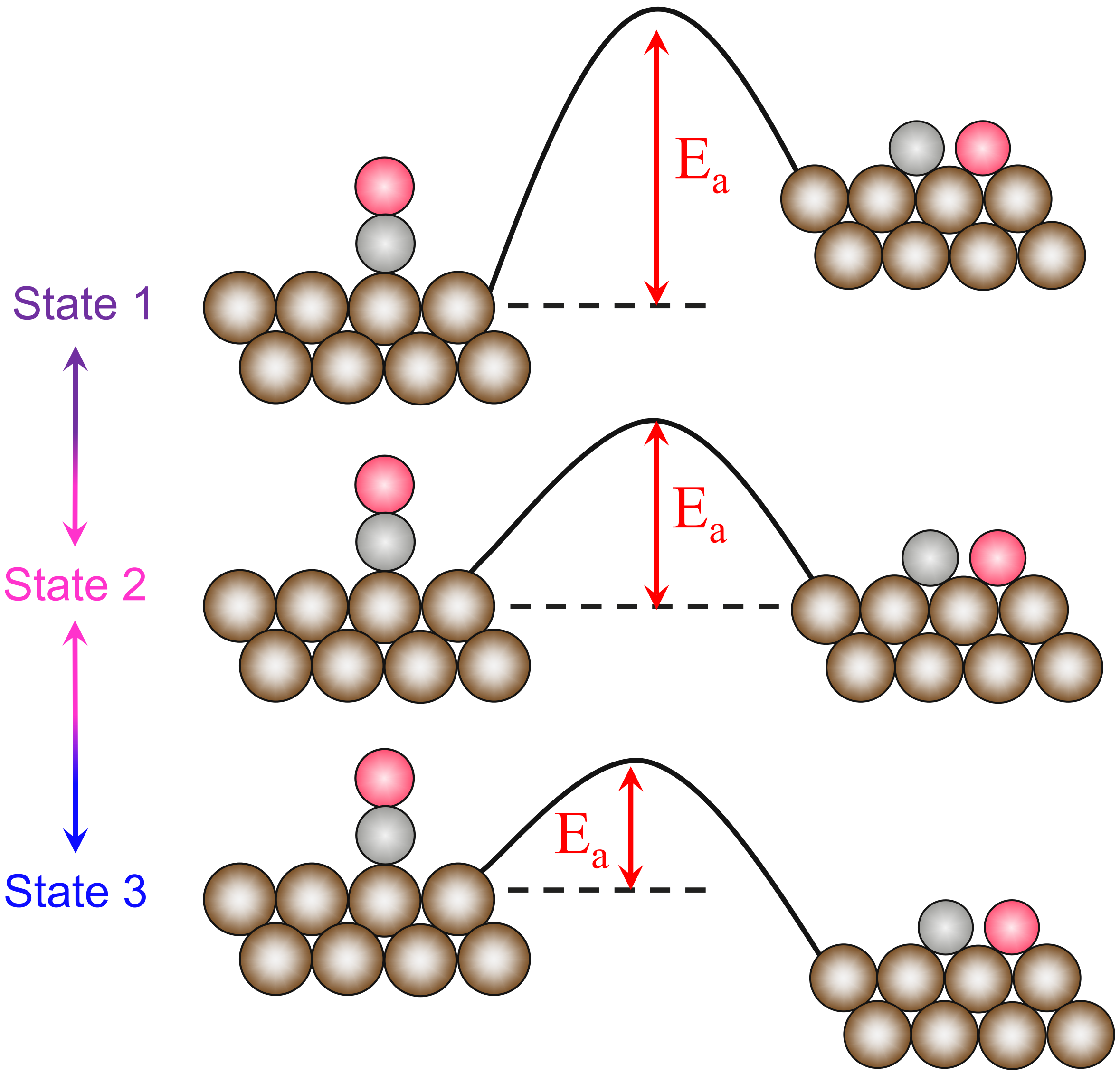
Consider a **single material** that changes in electronic state with time

Perturbation between catalyst states changes both:

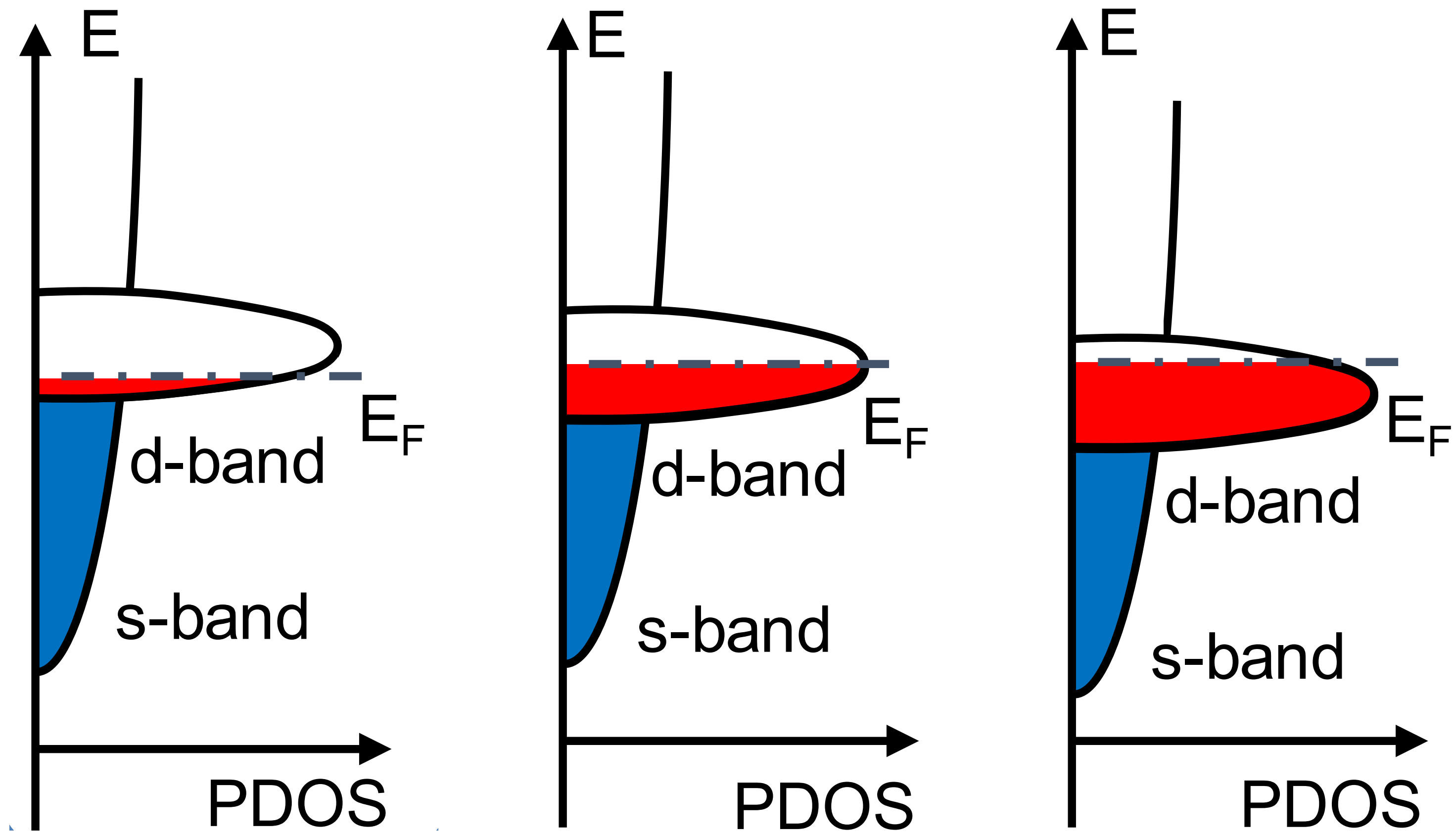
- Binding energies of surface species
- Transition state energy

Changing of energies is predicted by **linear scaling relationships**

Intermediate, Slope: γ
Intermediate, Offset: δ
Transition state, Slope: α
Transition state, Offset: β



Catalytic Condenser: A Platform Device



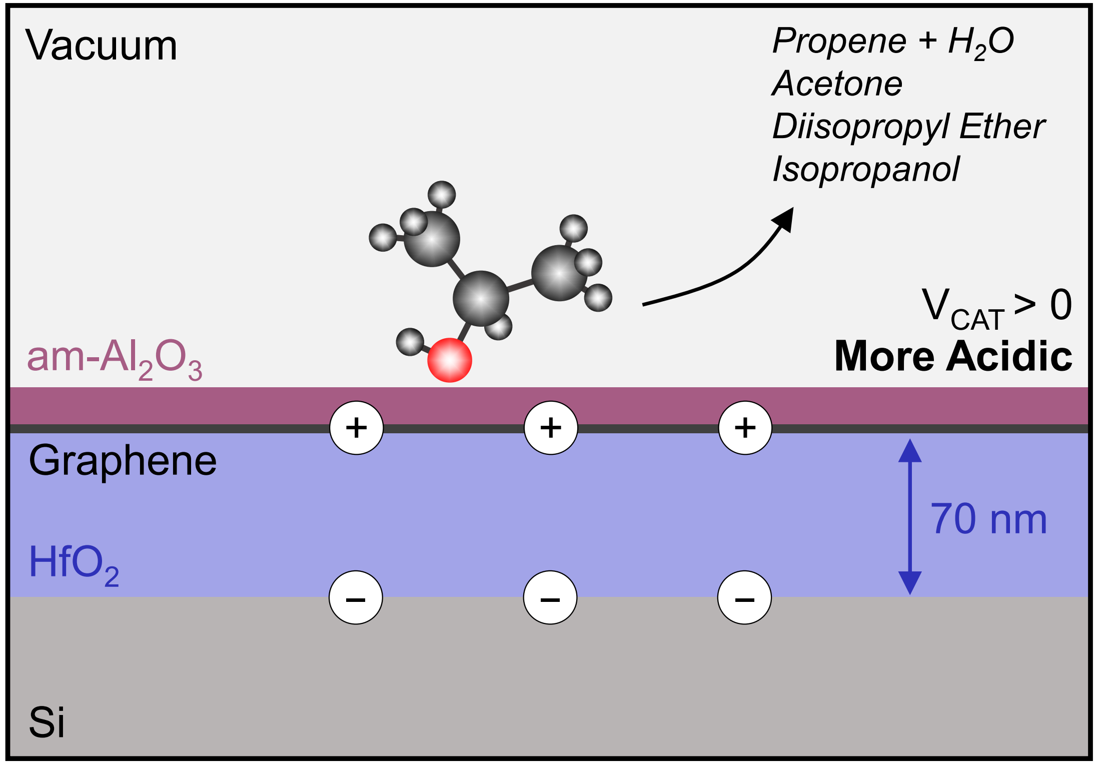
Positive Bias
$V_{CAT} > 0V$

Neutral
$V_{CAT} = 0V$

Negative
$V_{CAT} > 0V$

Catalytic Condenser: Structure - Function - Perturbation

Expanded Catalysis Ideology: Find the right structure and *perturb it effectively* for the best performance…



Device: Catalytic Condenser

Two conducting layers on either side of an electrical insulator (HfO_2)

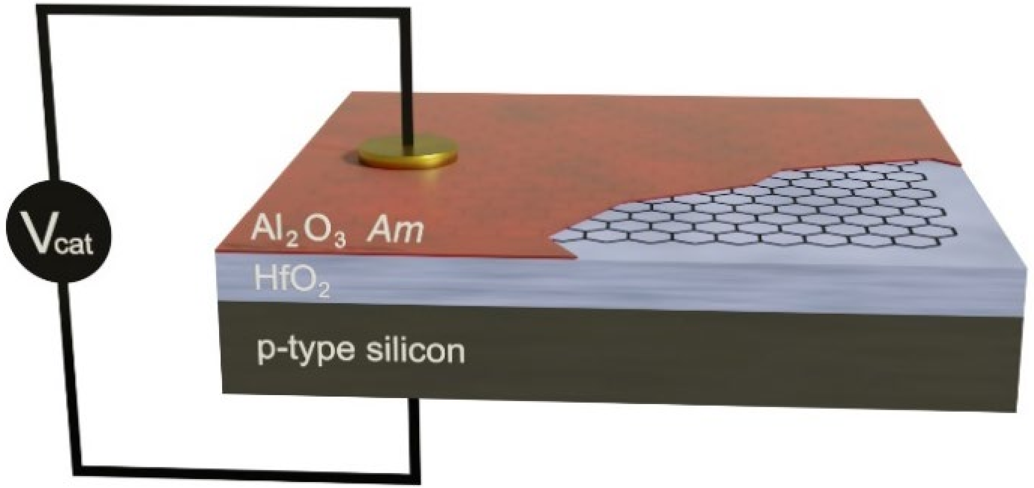
Top conducting layer (alumina & graphene) is thin

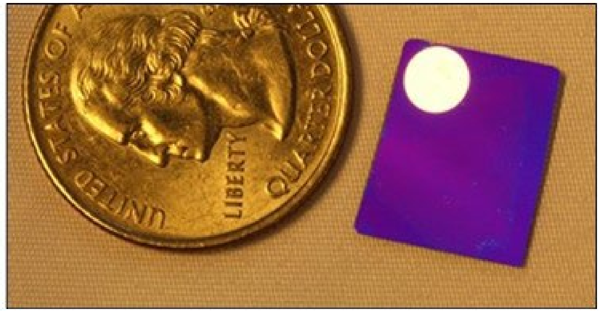
Charge in the top layer alters the electronic properties of the catalyst

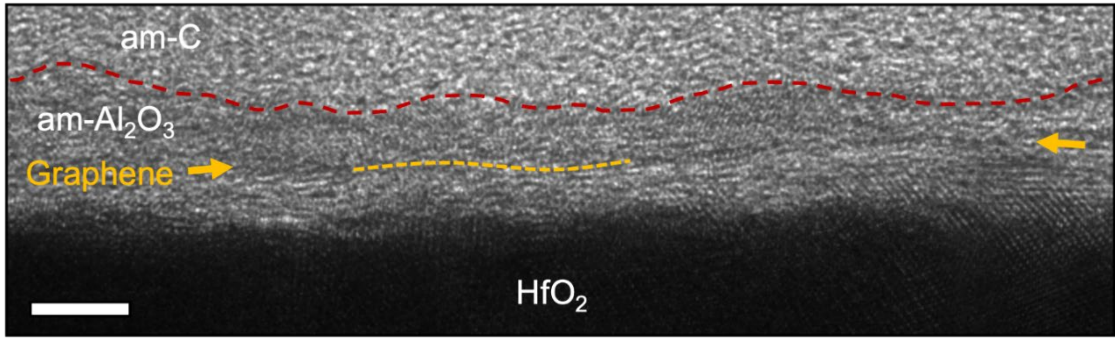
[1] *JACS Au*, 2022, DOI: 10.1021/jacsau.2c00114

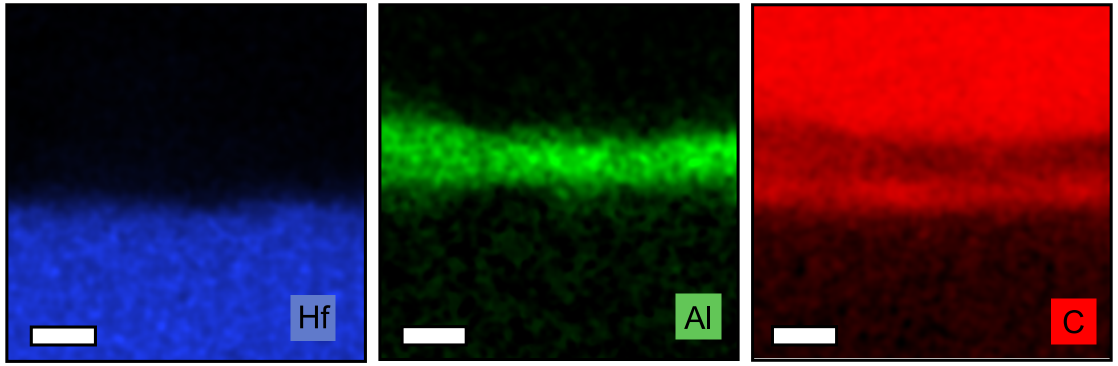
Catalytic Condenser: Design

A thin layer of graphene conducts charge to the alumina active sites





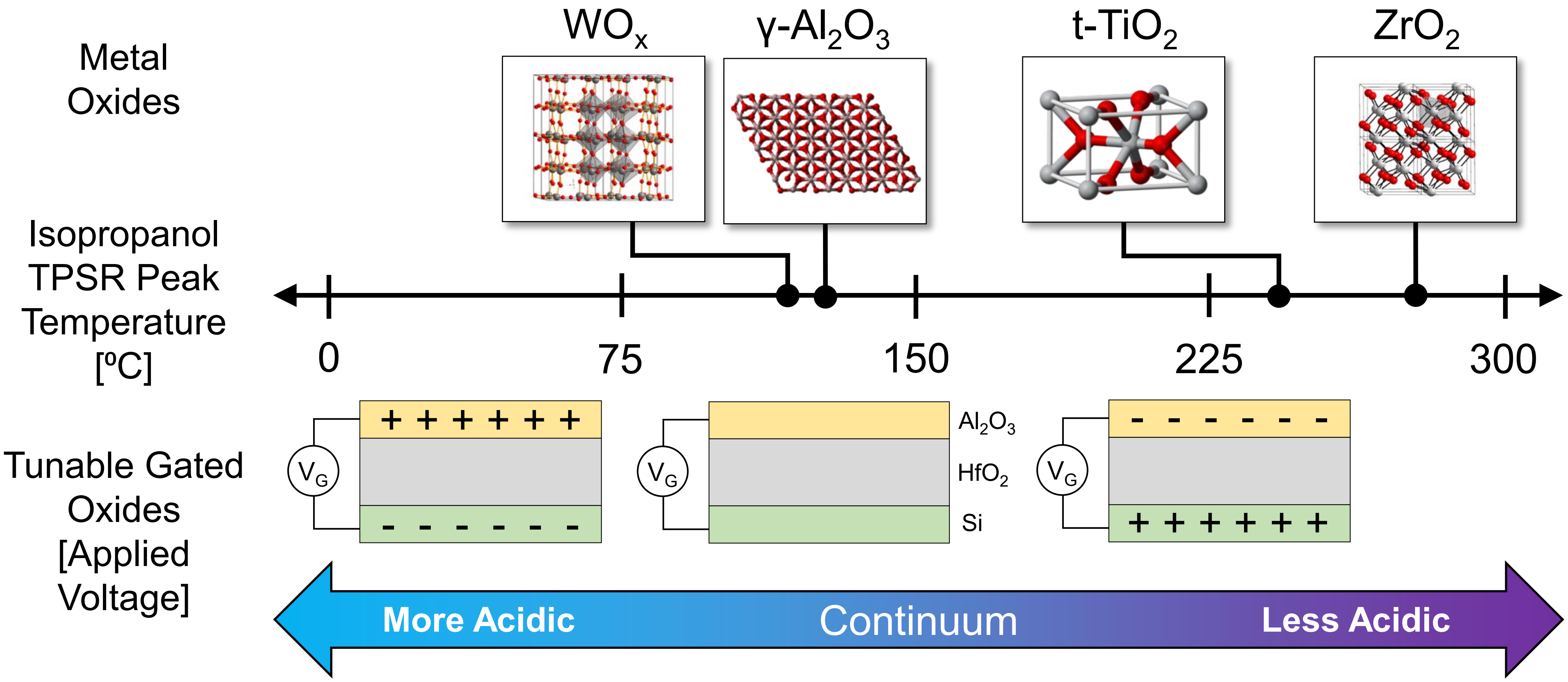




[1] *JACS Au*, 2022, DOI: 10.1021/jacsau.2c00114

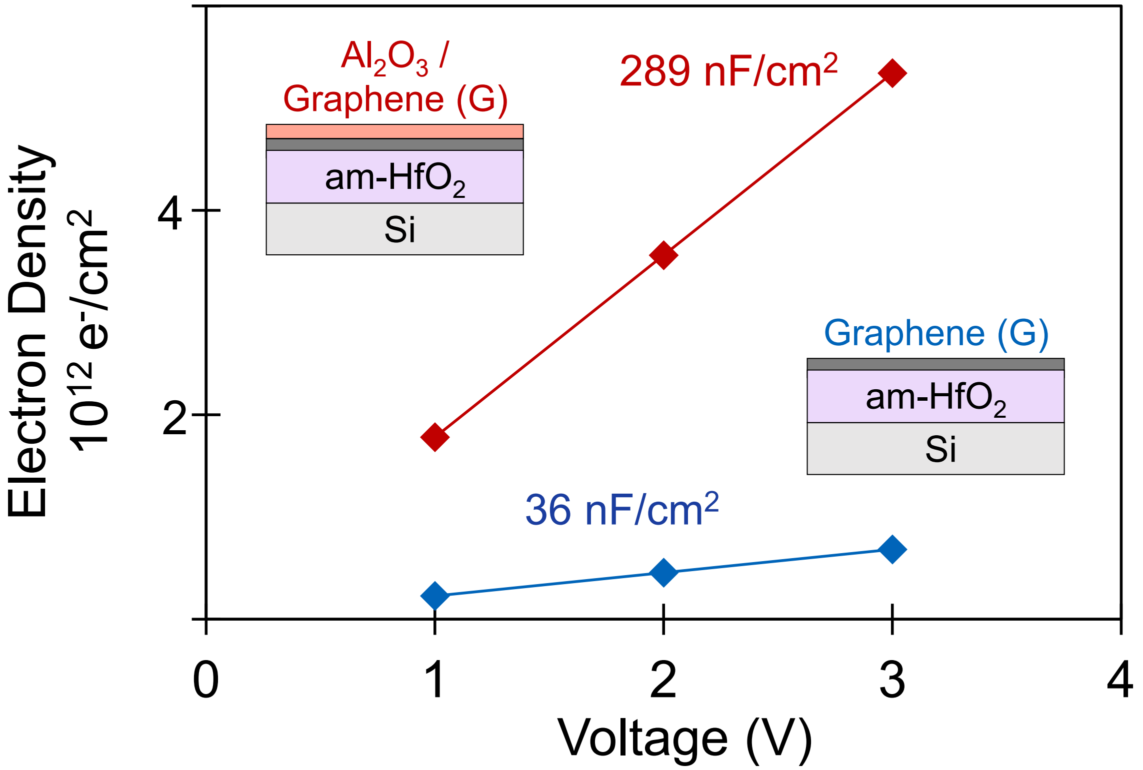
Catalytic Condenser: Isopropanol Dehydration

Reaction: Isopropanol ⟷ Propene + H_2O

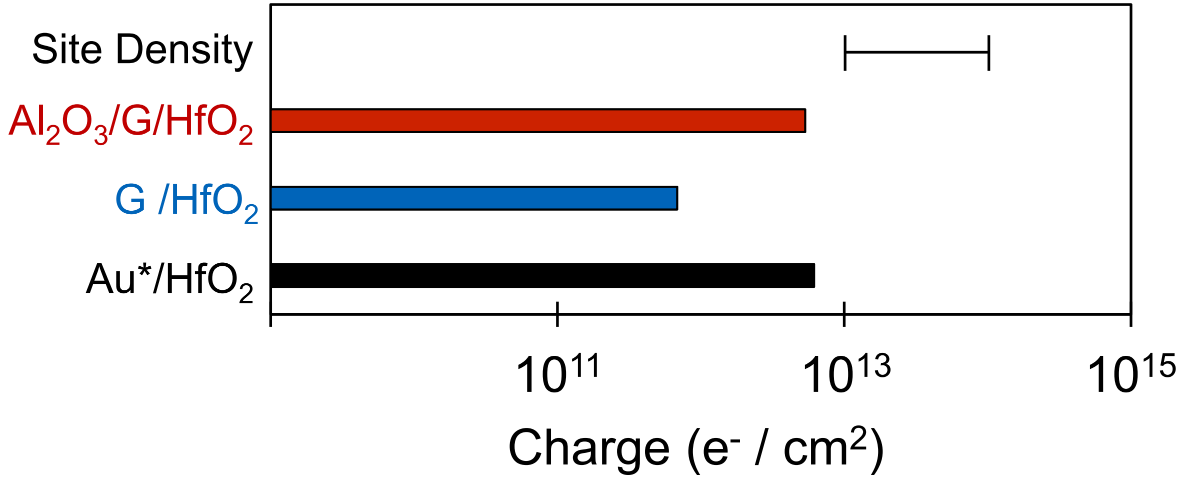


Charge Accumulation in the Catalyst

Most of the stabilized charge is in the 4 nm thick aluminum oxide catalyst layer

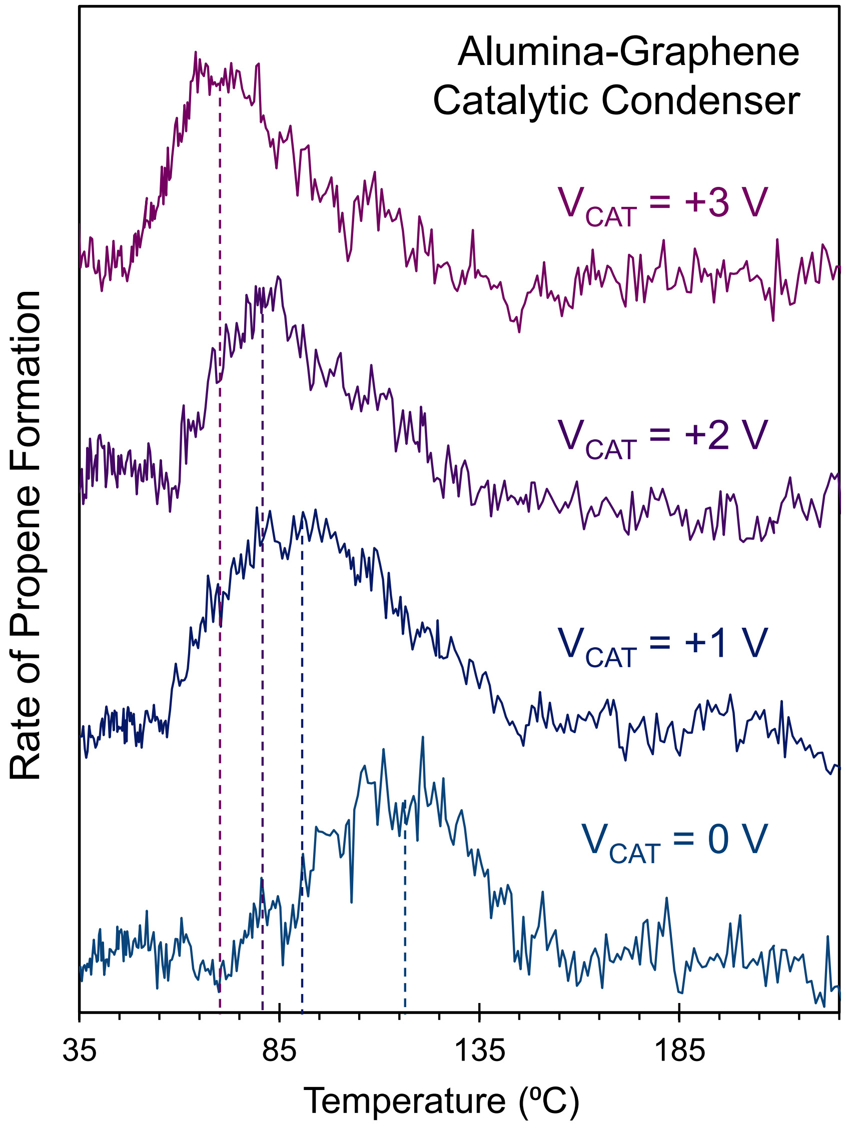


Alumina/graphene stabilizes 10X more charge than graphene alone



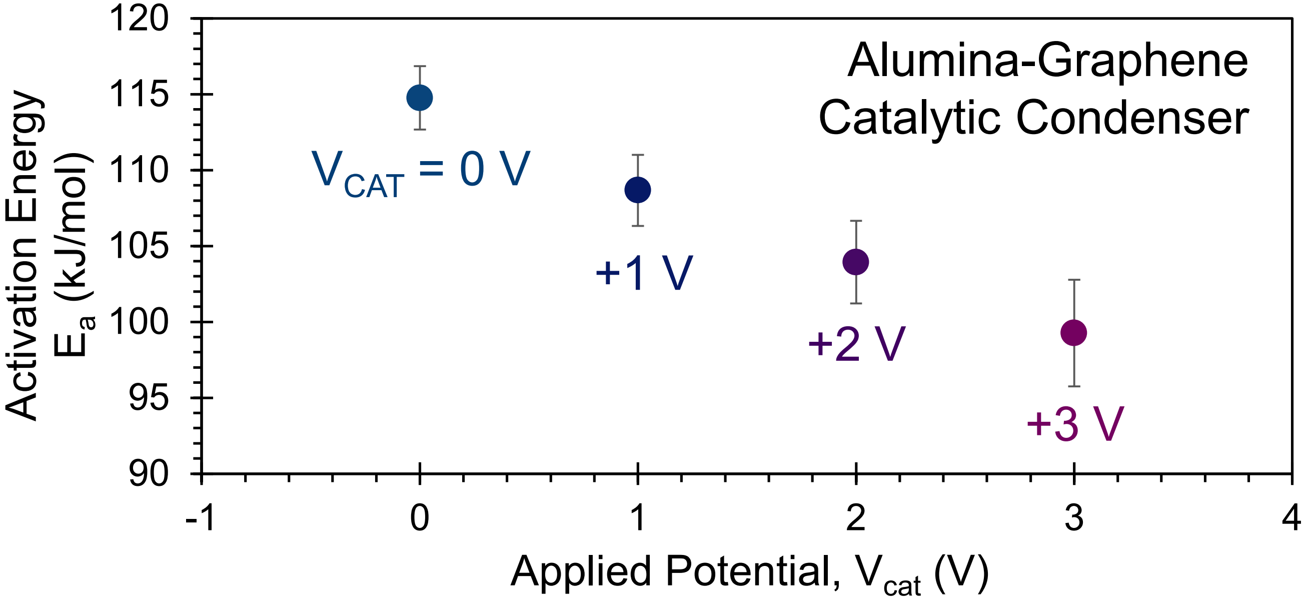
[1] *JACS Au*, 2022, DOI: 10.1021/jacsau.2c00114

Catalytic Condenser: Isopropanol Dehydration



Adding holes to alumina promotes isopropanol dehydration at lower temperatures

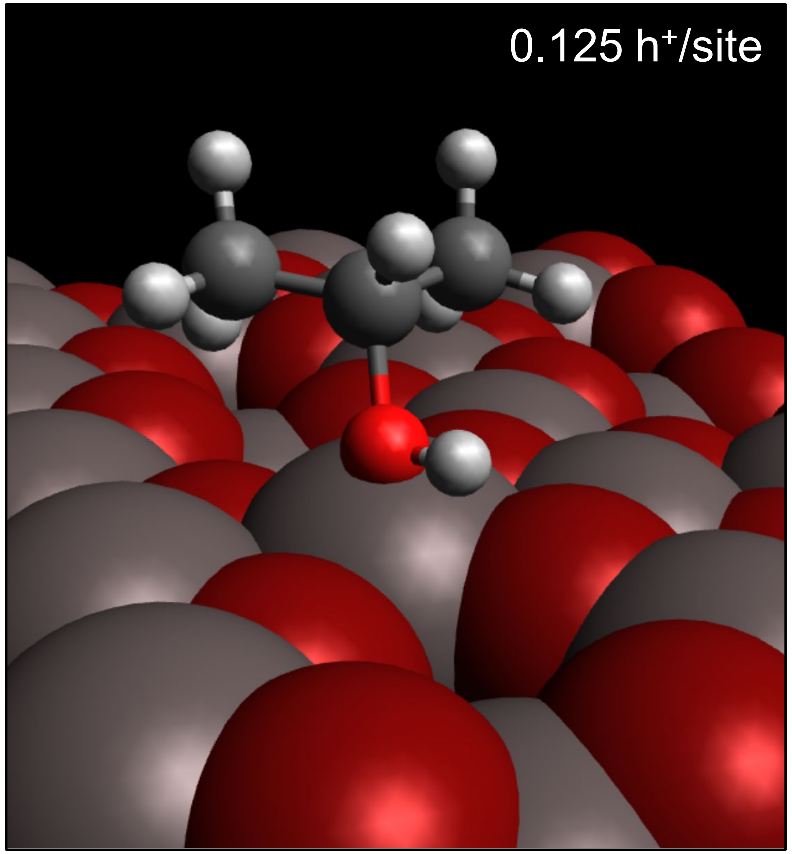
Positive bias (electron depletion) lowers the reaction barrier to form propene

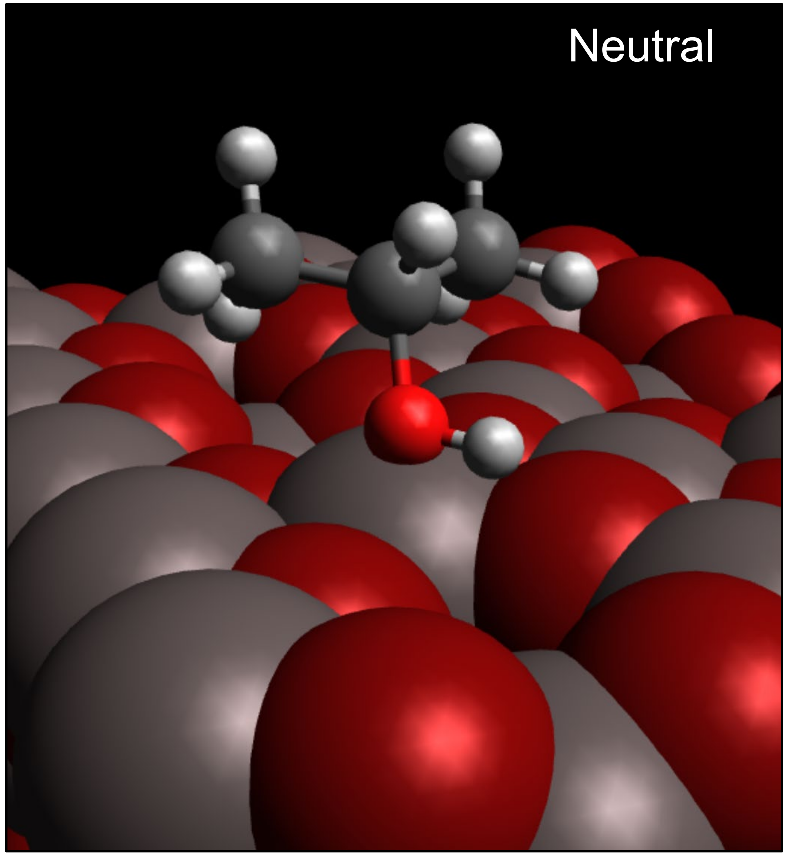


[1] *JACS Au*, 2022, DOI: 10.1021/jacsau.2c00114

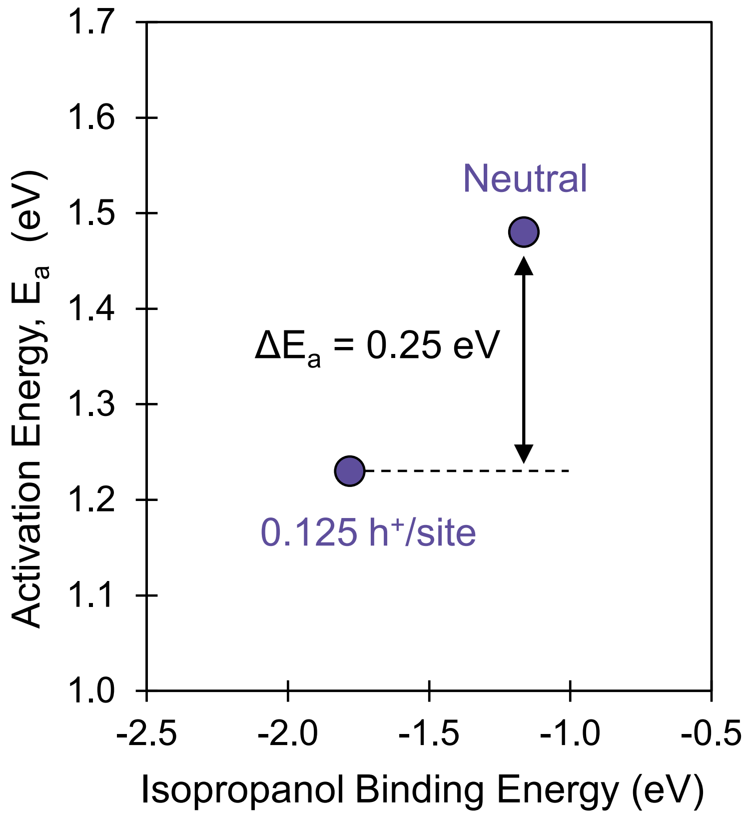
Catalytic Condenser: Isopropanol Dehydration (DFT)

Experiments and DFT indicate that about 8-10% of an electron removed per site





DFT Calculation

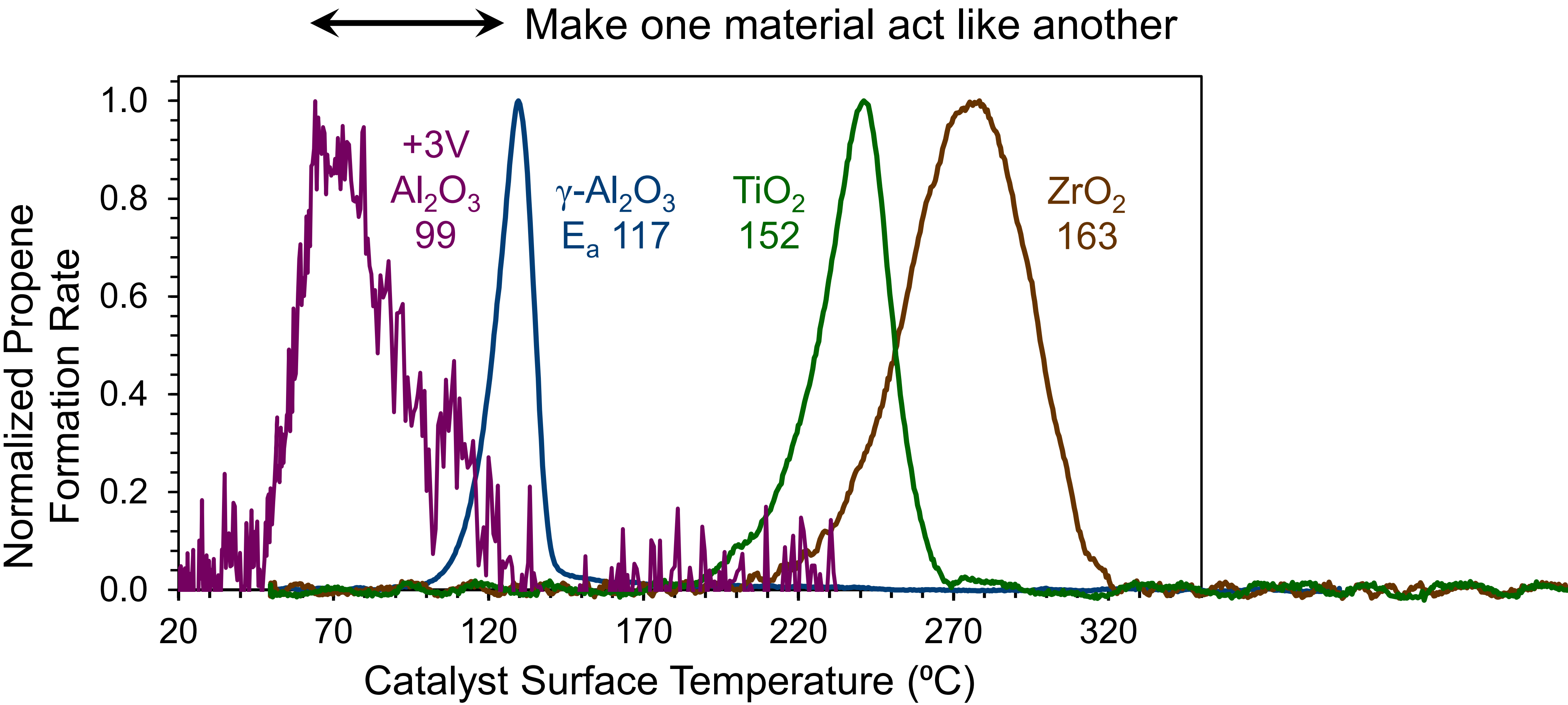


Calculations by Matt Neurock

[1] *JACS Au*, 2022, DOI: 10.1021/jacsau.2c00114

Catalytic Condenser: Isopropanol Dehydration

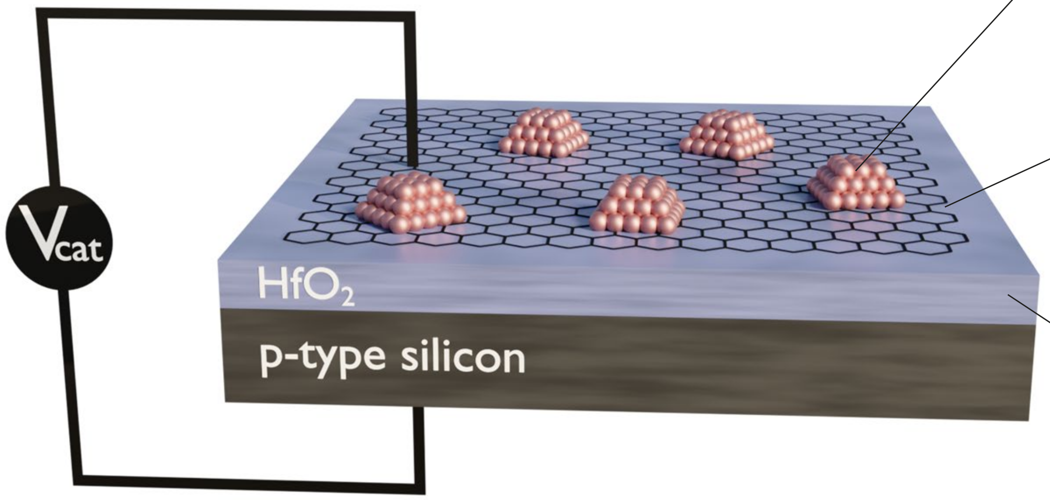
Charge condensation acts like "electronic alchemy"



[1] *JACS Au*, 2022, DOI: 10.1021/jacsau.2c00114

What can be varied on condensers?

Device Metrics
- Overall capacitance (nF/cm^2)
- Speed – corner frequency (Hz)



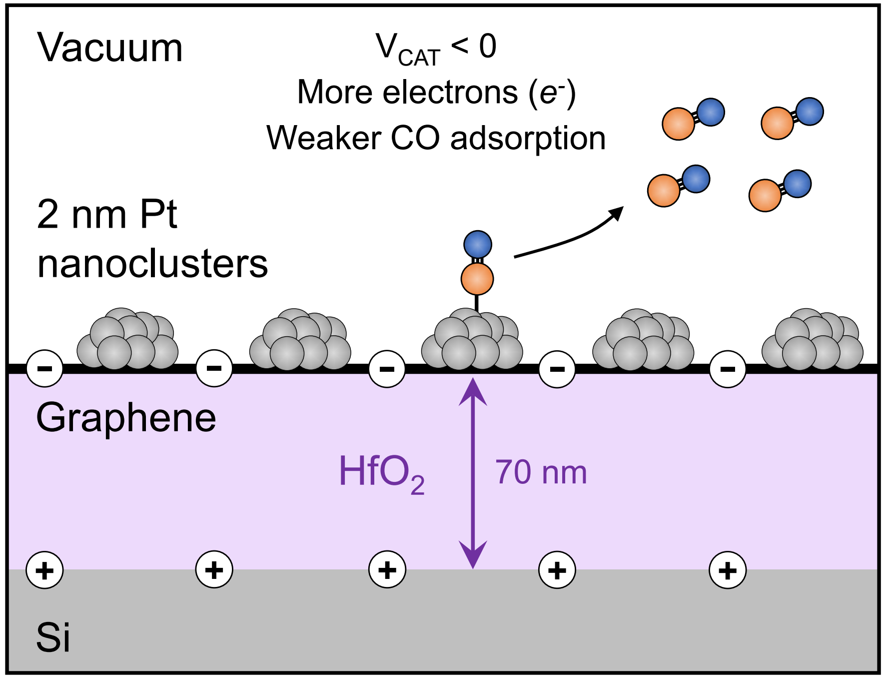
Active Site Metrics
- Charge per active site (e^- / site)

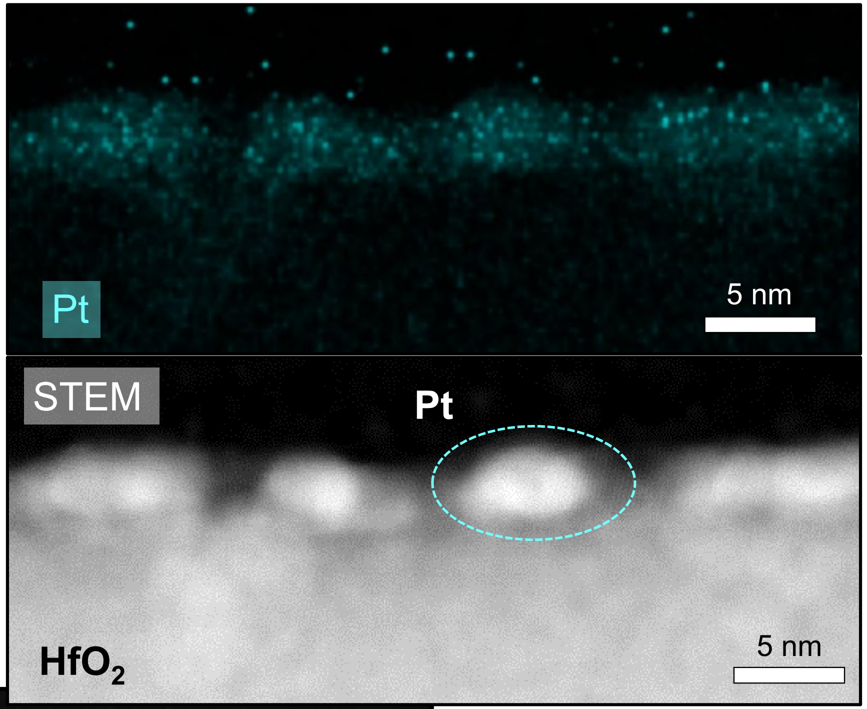
Catalyst Sites
- Composition: metals, oxides, etc.
- Site density ($1/cm^2$)
- Structure: clusters versus single atoms

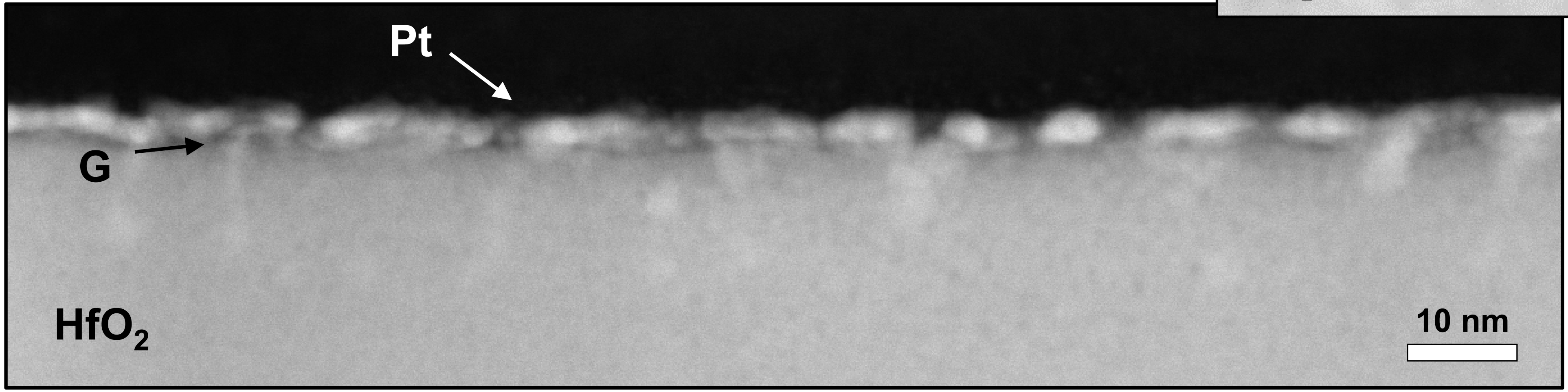
Conductive Film
- Conductance ($\mu S/cm^2$)
- Capacitance (nF/cm^2)
- Graphene, carbon, or oxide (band gap)

Dielectric Film
- Dielectric constant
- Thickness (nm) & composition
- Breakthrough voltage (V)

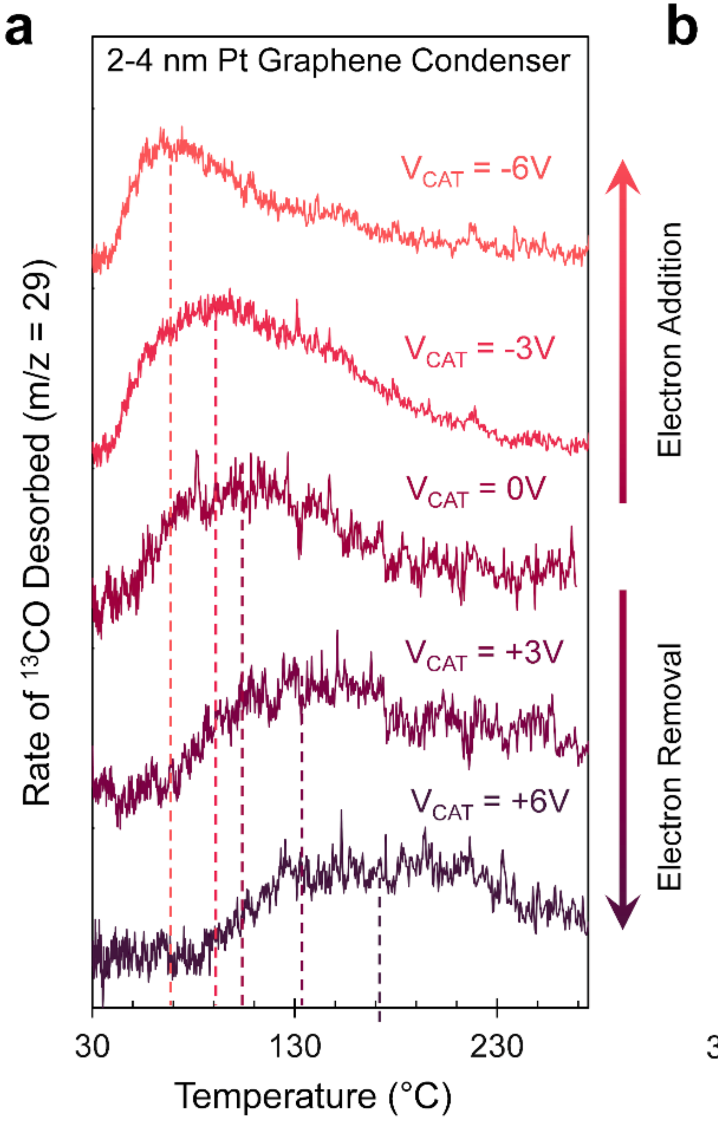
Platinum / Graphene Catalytic Condenser



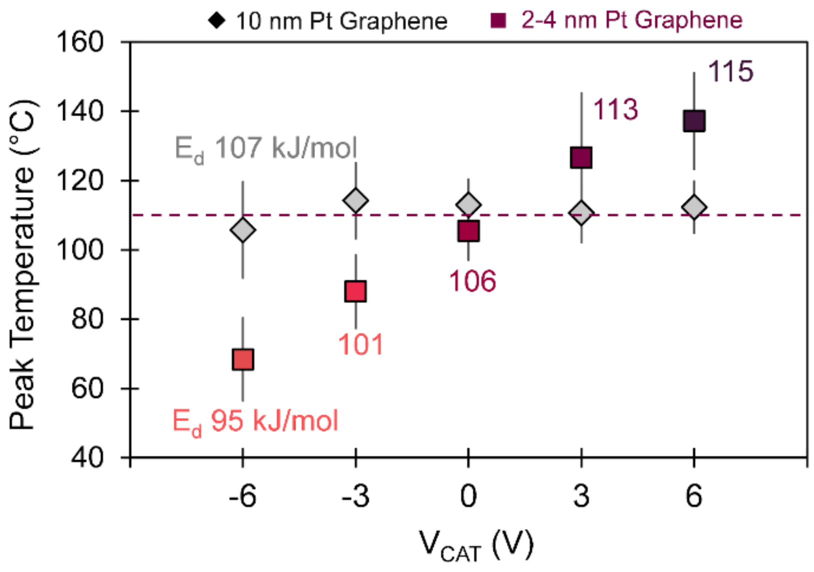




Carbon Monoxide Temperature Programmed Desorption



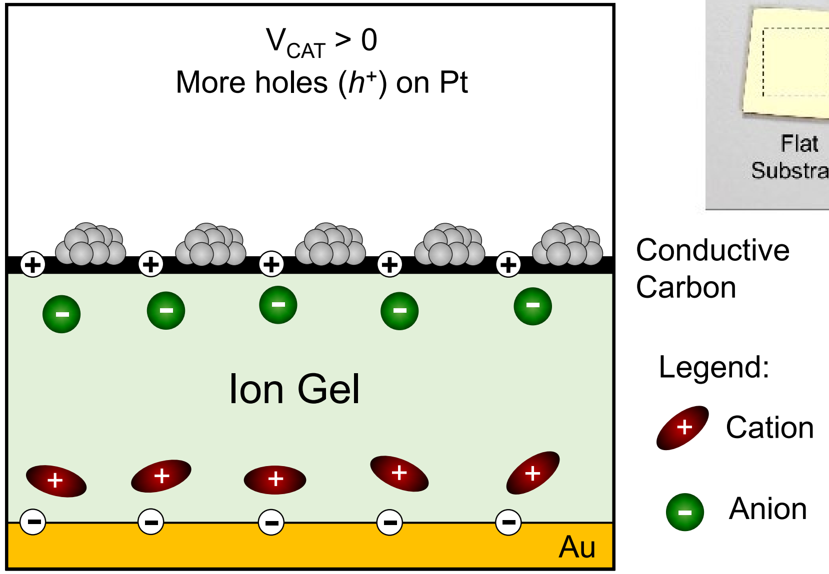
Modulation of the applied potential shifts the binding energy of carbon monoxide on Pt by ~20 kJ/mole

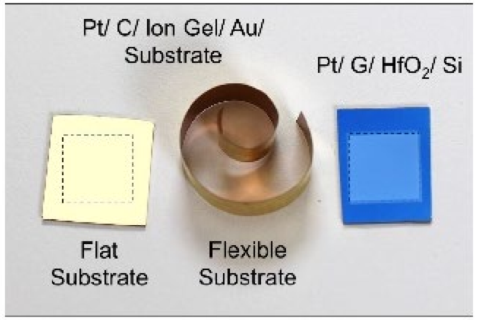


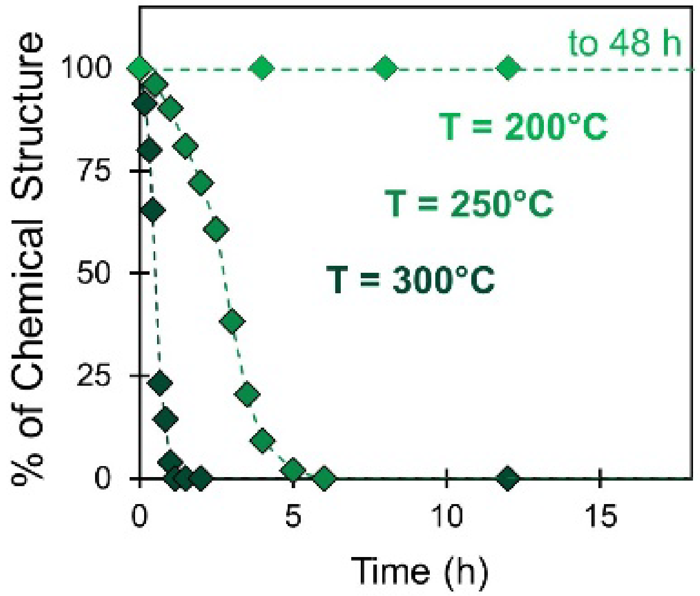
Ion Gel Condensers: Design & Function

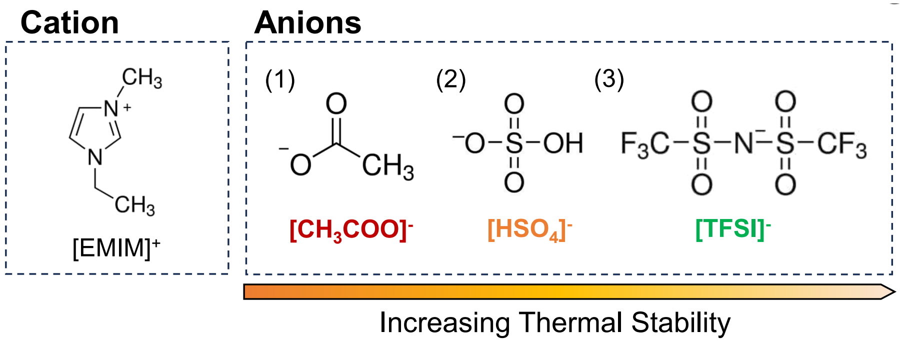
Ion Gels are composites of ionic liquids and polymers

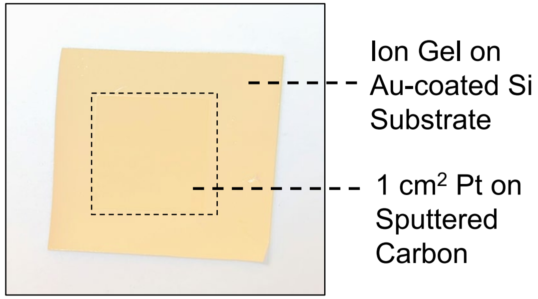
- Mobile ions provide charge stabilization
- Flexible gel is deposited via coating methods
- Ion gel is thermally stable up to 200 °C





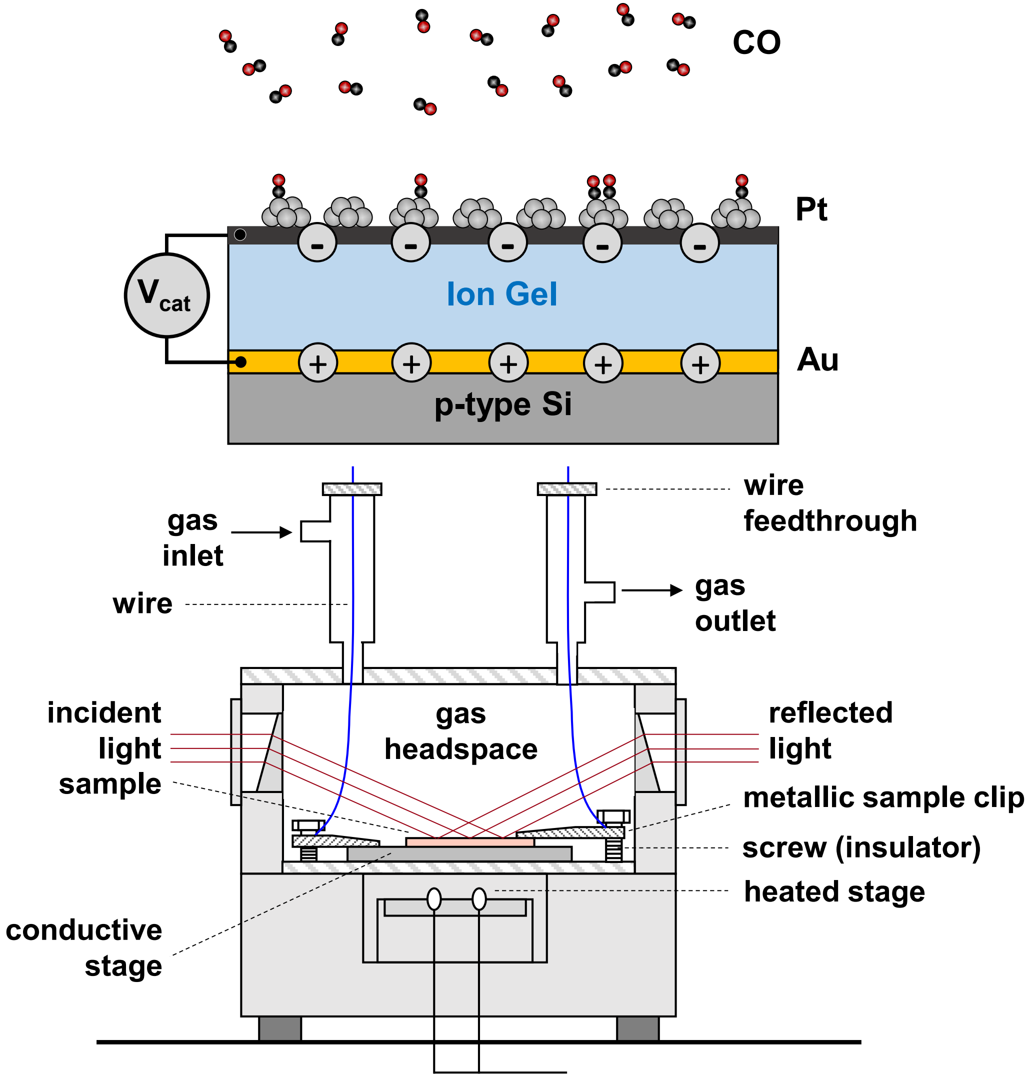




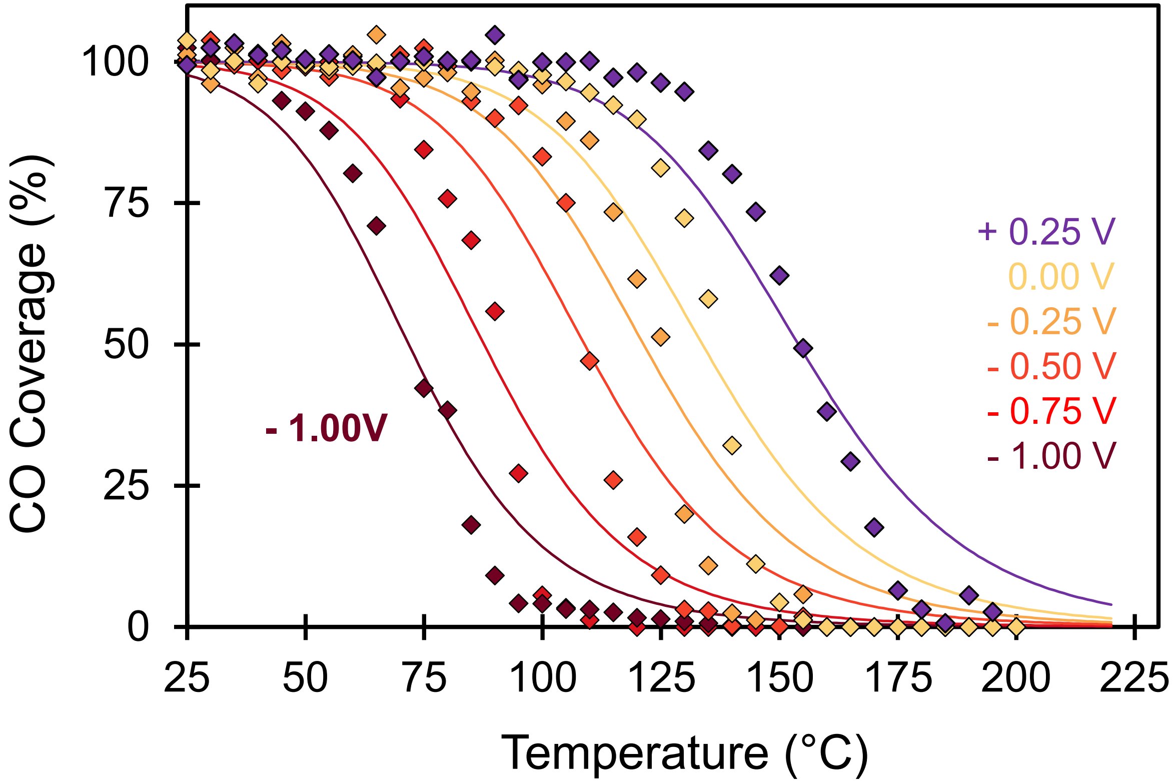


[1] ***ACS Nano***, 2024, 18(1), 983-995.

Pt/C Ion Gel Condenser: CO Binding with IR Spectroscopy



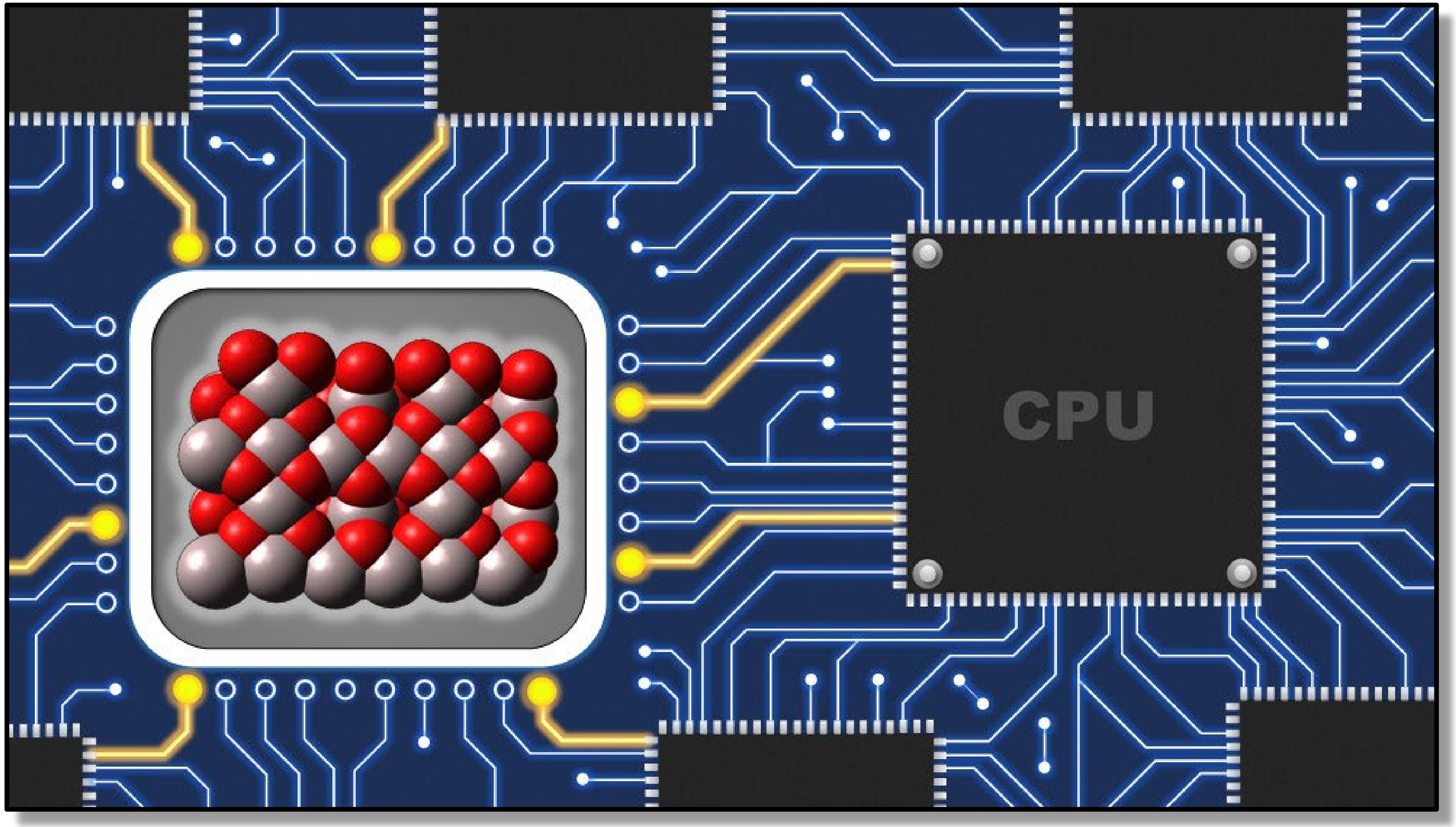
Change in ~16 kJ/mol



[1] **ACS Nano**, 2024, 18(1), 983-995.

Programs of Programmable Catalysts

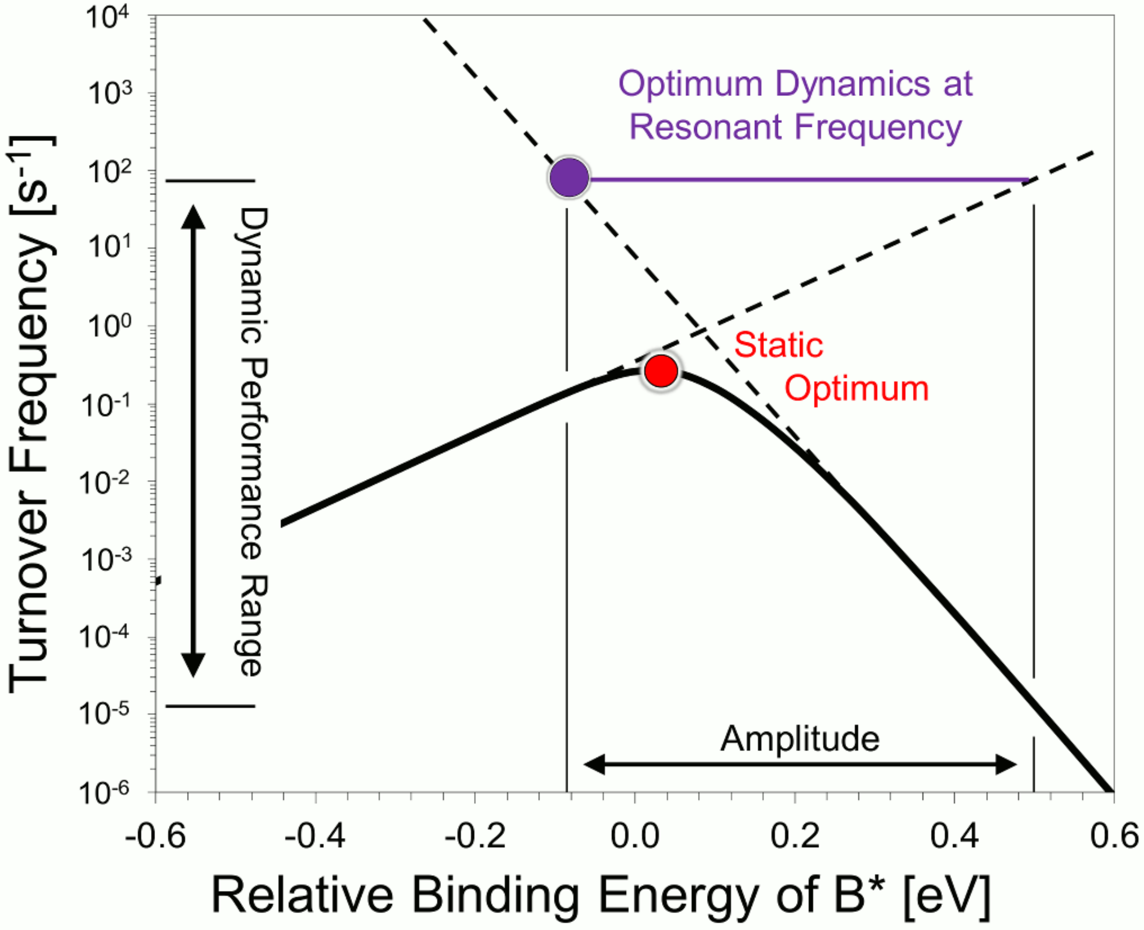
What program should I give to the catalyst?



[1] *JACS Au*, 2022, DOI: 10.1021/jacsau.2c00114

Catalytic Resonance Theory

A catalytic reaction occurs on a surface with oscillating binding energy



Tunable quantity is the binding energy of surface intermediates: A* and B*

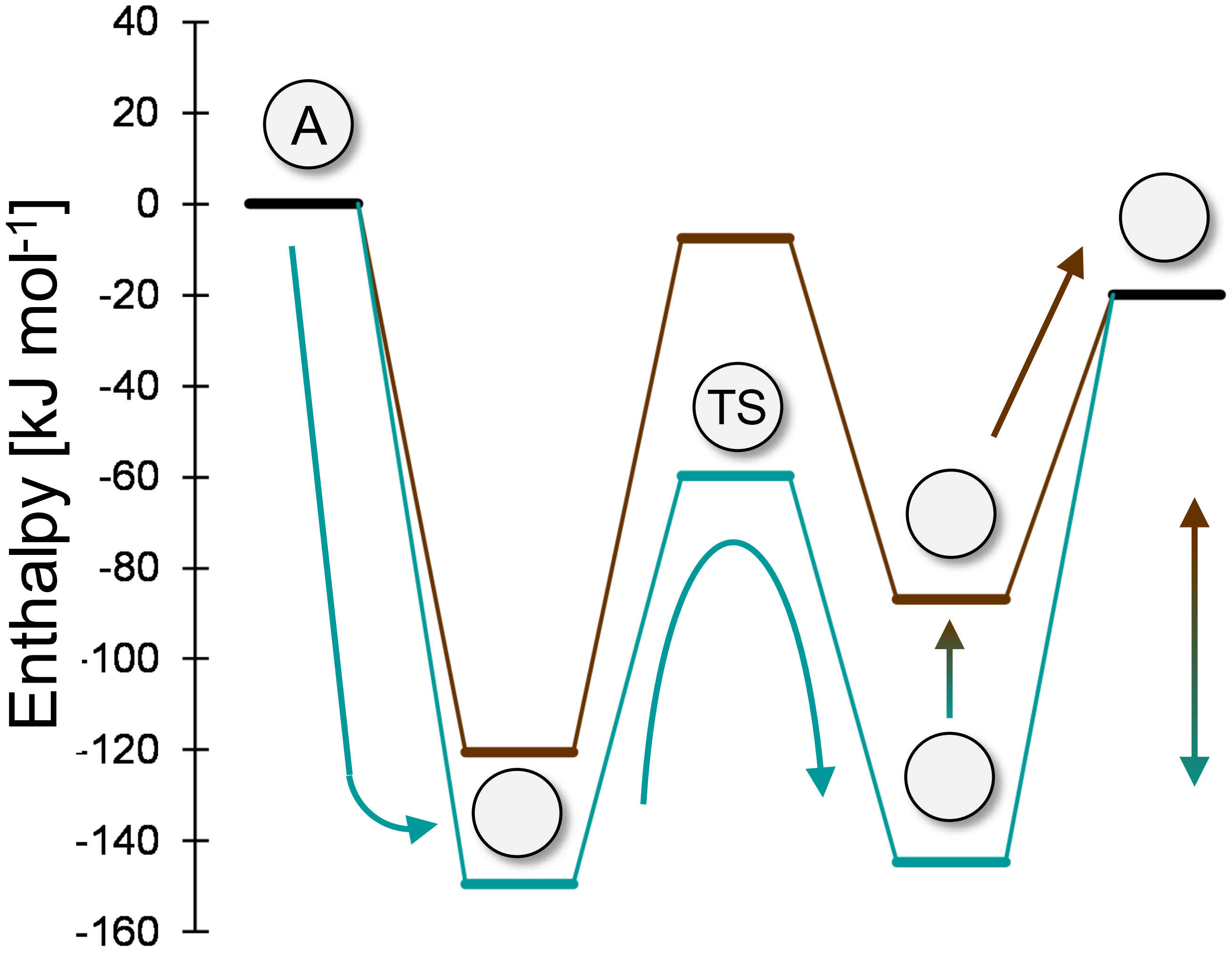
Amplitude is variation in binding energy

Frequency is the rate at which binding energy variation occurs

[1] M.A. Ardagh, et al. *ACS Catalysis,* 2019, 9(8), 6929. DOI: 10.1021/acscatal.9b01606

Approach: Programmable Catalysis

A catalytic reaction occurs on a surface with defined oscillating binding energy



- Reactant A adsorbs to form A*
- A* reacts to form B*
- B* is lifted from state 1 to state 2 & desorbs
- Surface resets to state 1

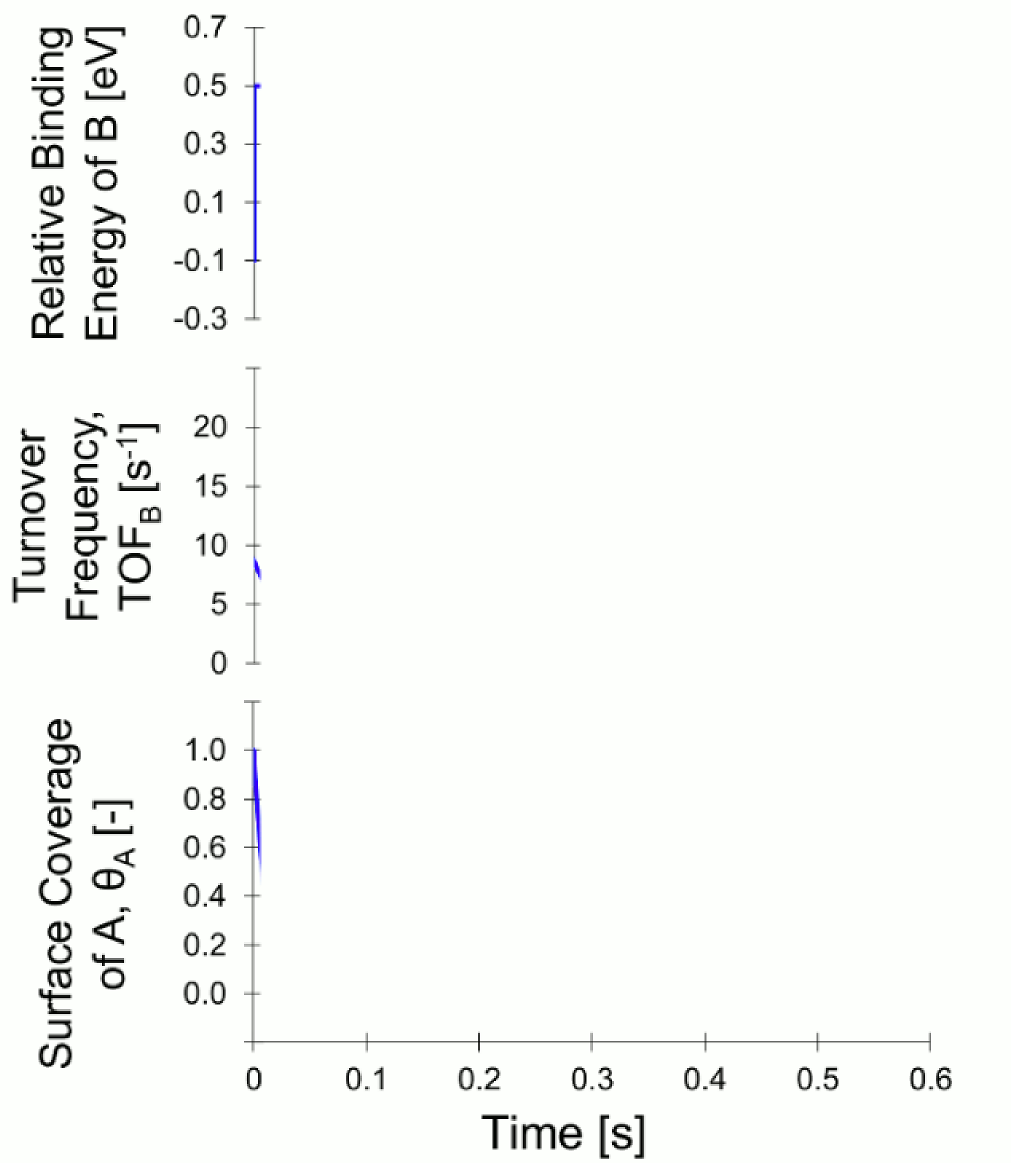
[1] M.A. Ardagh, et al. *ACS Catalysis*, 2019, 9(8), 6929. DOI: 10.1021/acscatal.9b01606

Dynamic Catalysis: Square Wave Simulation

Binding energy of B flips from high to low

Instantaneous reaction rate spikes when binding energy flips to weak state

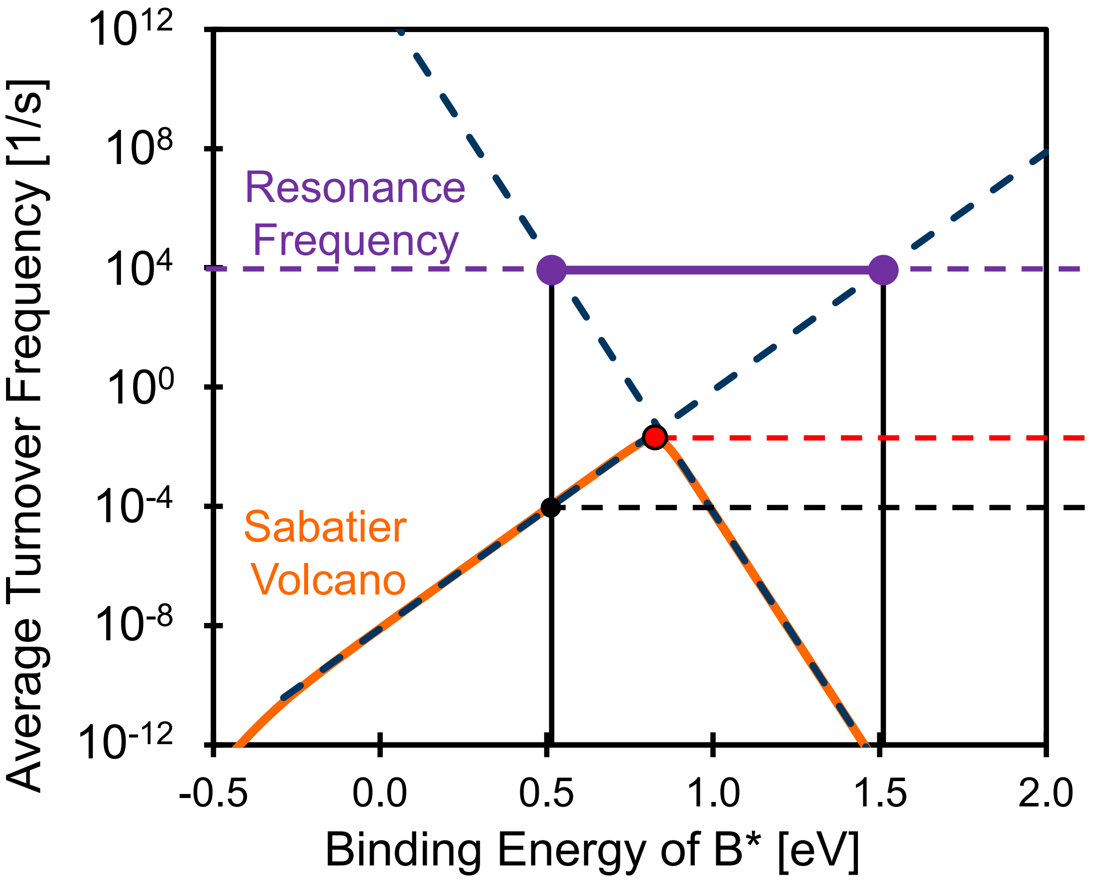
Surface flips completely between 100% coverage of A* and B*



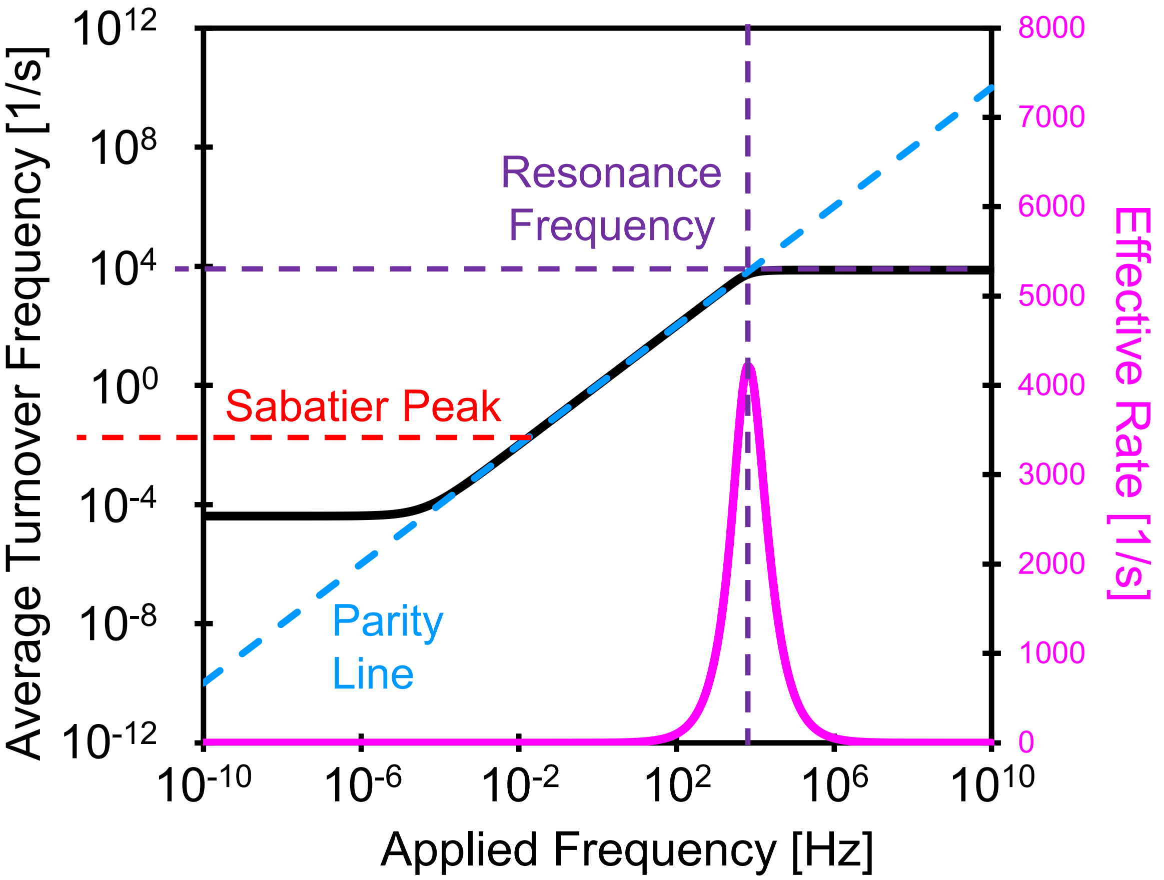
[1] M.A. Ardagh, et al. *ACS Catalysis,* 2019, 9(8), 6929. DOI: 10.1021/acscatal.9b01606

Effective Rate: Catalytic Resonance *Frequency*

The resonance frequency exists where the applied amplitude matches the change in binding energy of the inverted volcano



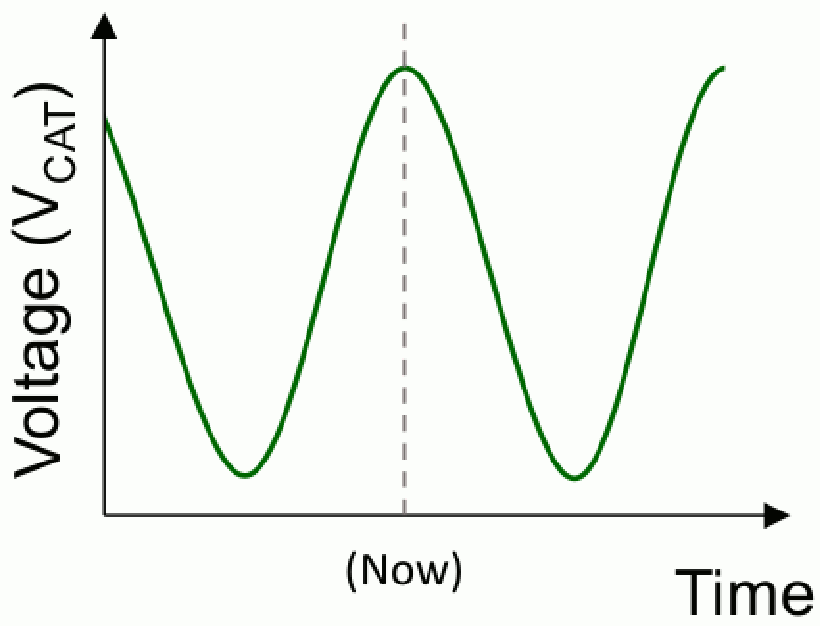
The resonance frequency exists with a maximum in effective rate (pink)

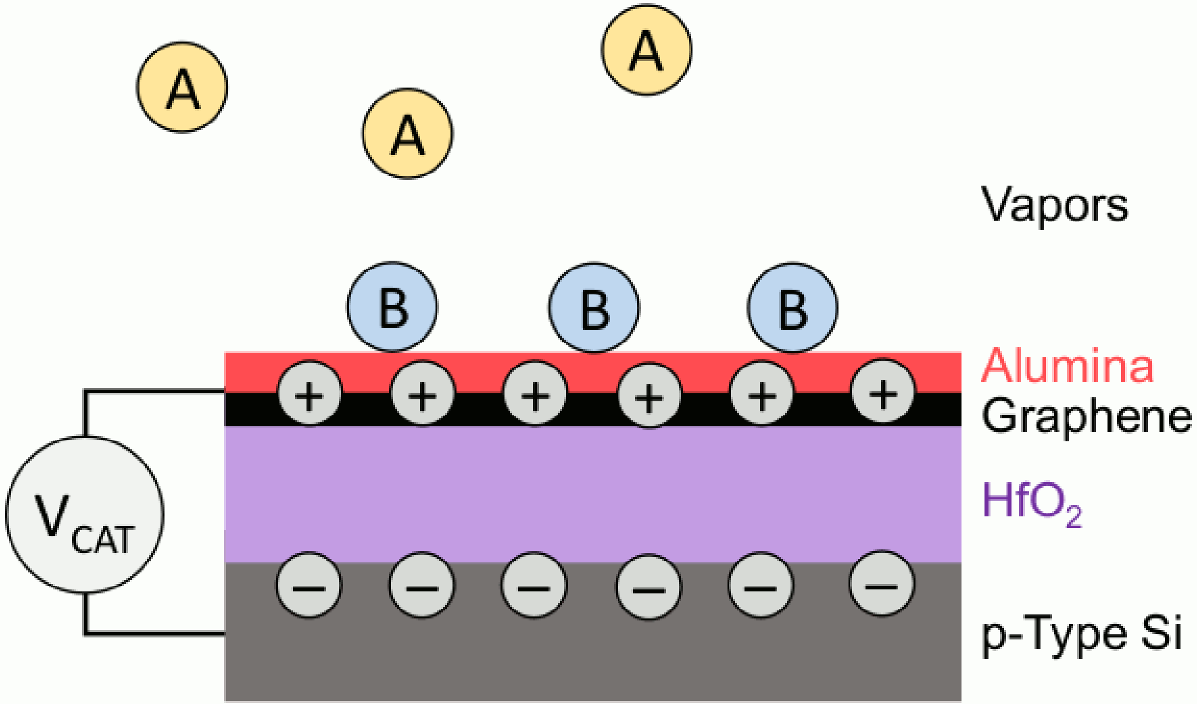


Programmable Catalyst: Forced Dynamics

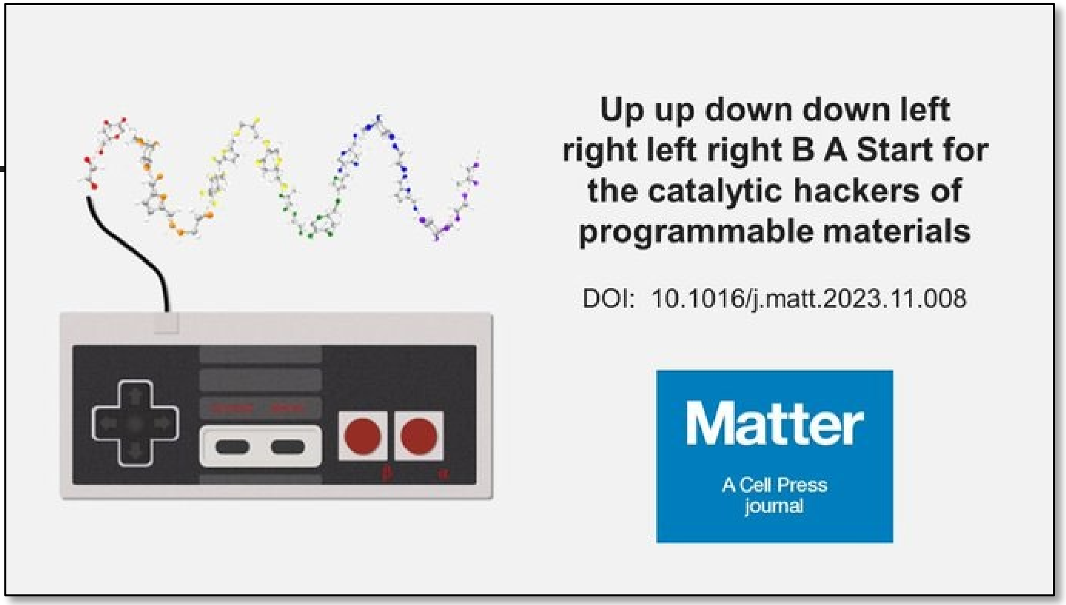
Fast (1000 Hz) and powerful (dH > 0.4 eV) condensers provide new opportunities for programmable catalysts

"Program"

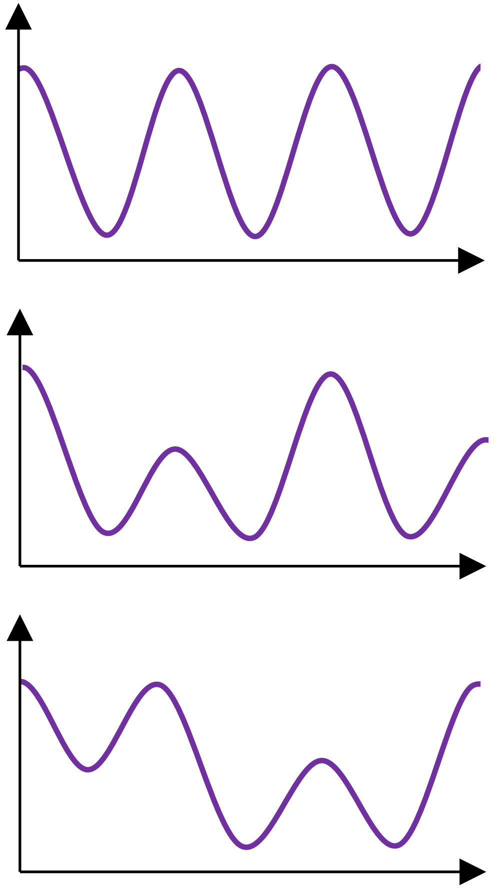


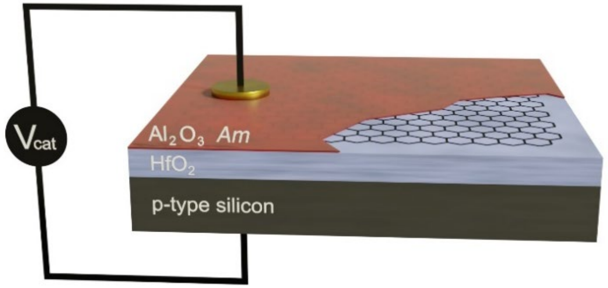


Writing Catalyst Programs



Program Options





Programmable Catalyst

RATE

Selectivity

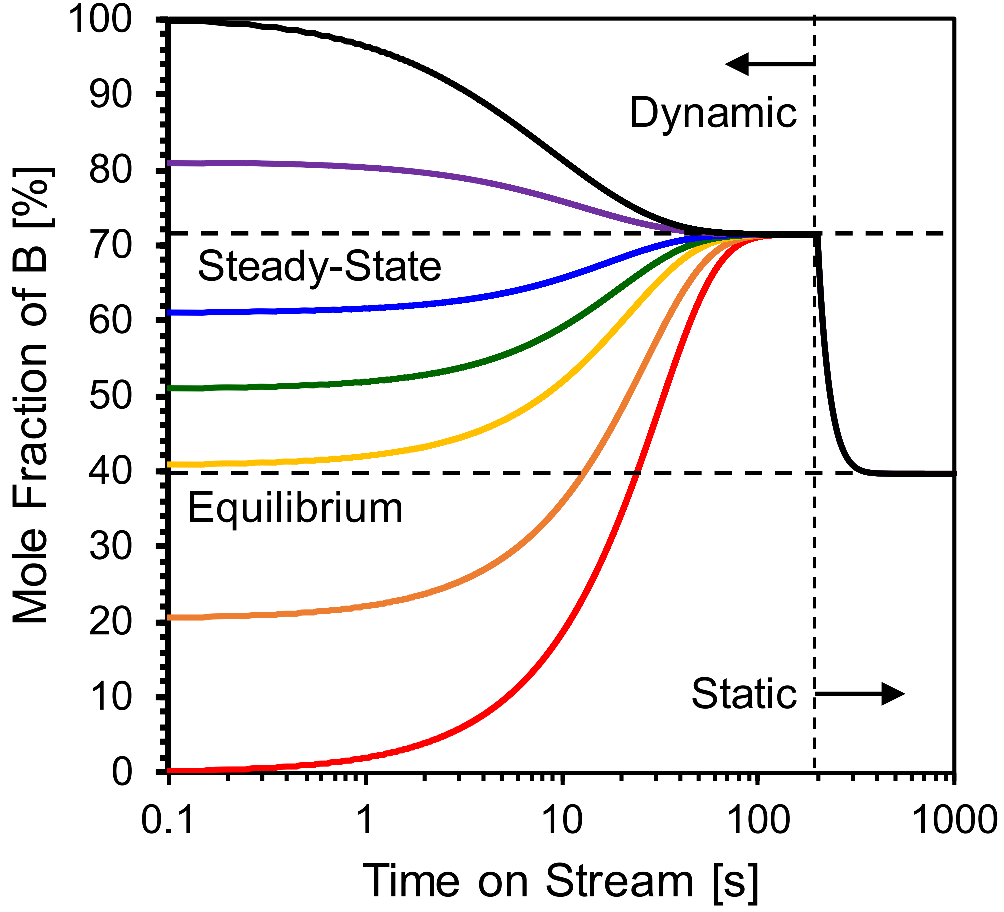
Selectivity

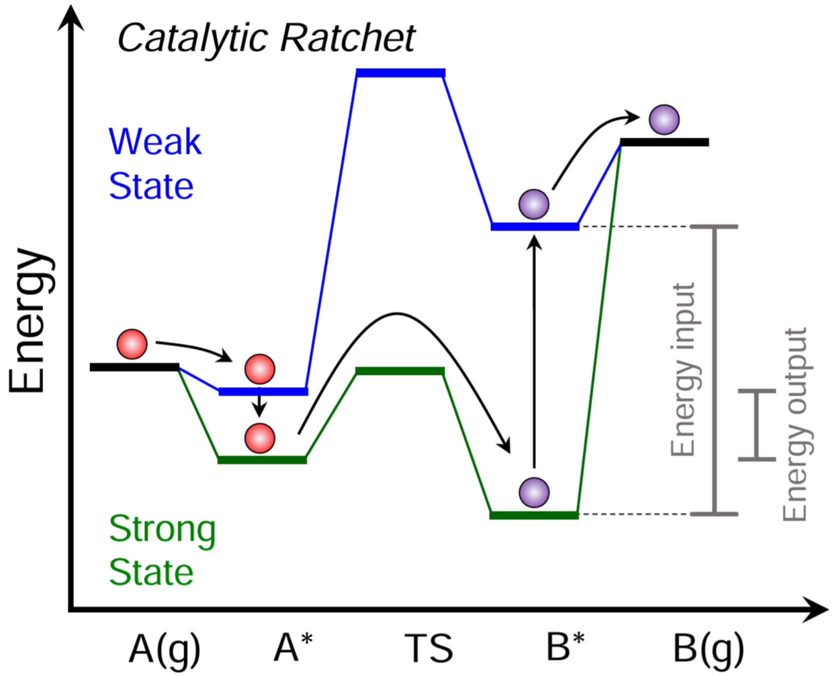
Selectivity

Conversion

Programmable Catalysis: Non-Equilibrium Steady-State

Under dynamic conditions, reactions proceed to steady state different from equilibrium



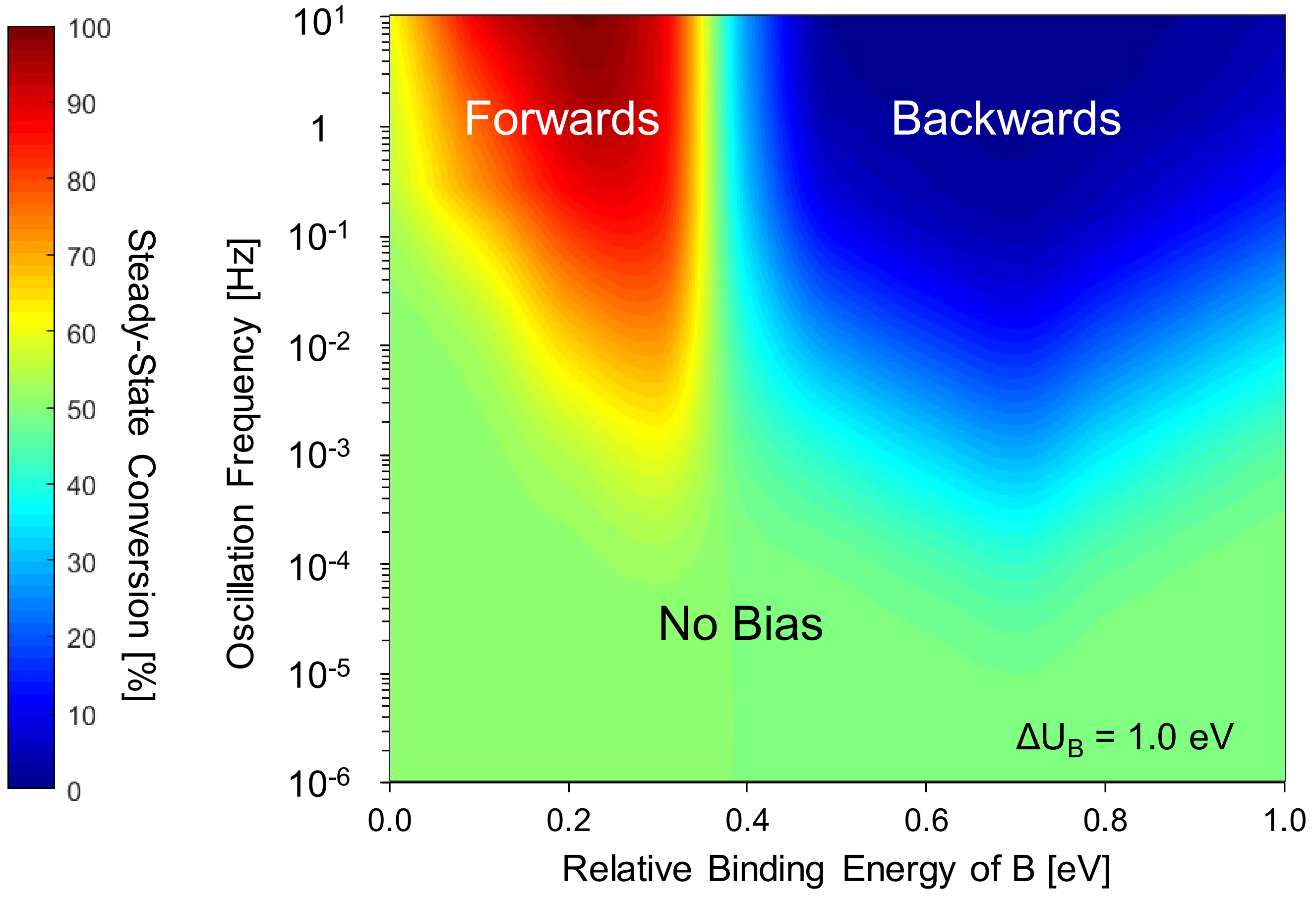


CONDITIONS: T ~ 300 °C, P_{TOT} ~ 100 bar
α ~ 0.6, β ~ 102 kJ/mol, γ ~ 2.0, δ ~ 1.4 eV
f ~ 1000 Hz square, ΔU ~ 0.2 eV

[1] M.A. Ardagh, et al. *Cat. Sci. Tech.* 2019, 9, 5058. DOI: 10.1039/C9CY01543D

The Dynamics Mechanism – Directionality

Selection of imposed surface oscillation tunes reaction conversion away from equilibrium



The A-to-B reaction in a batch reactor operating to achieve steady state

Green represents equilibrium (X_A ~ 50%)

<u>Direction predictable by metric: λ</u>

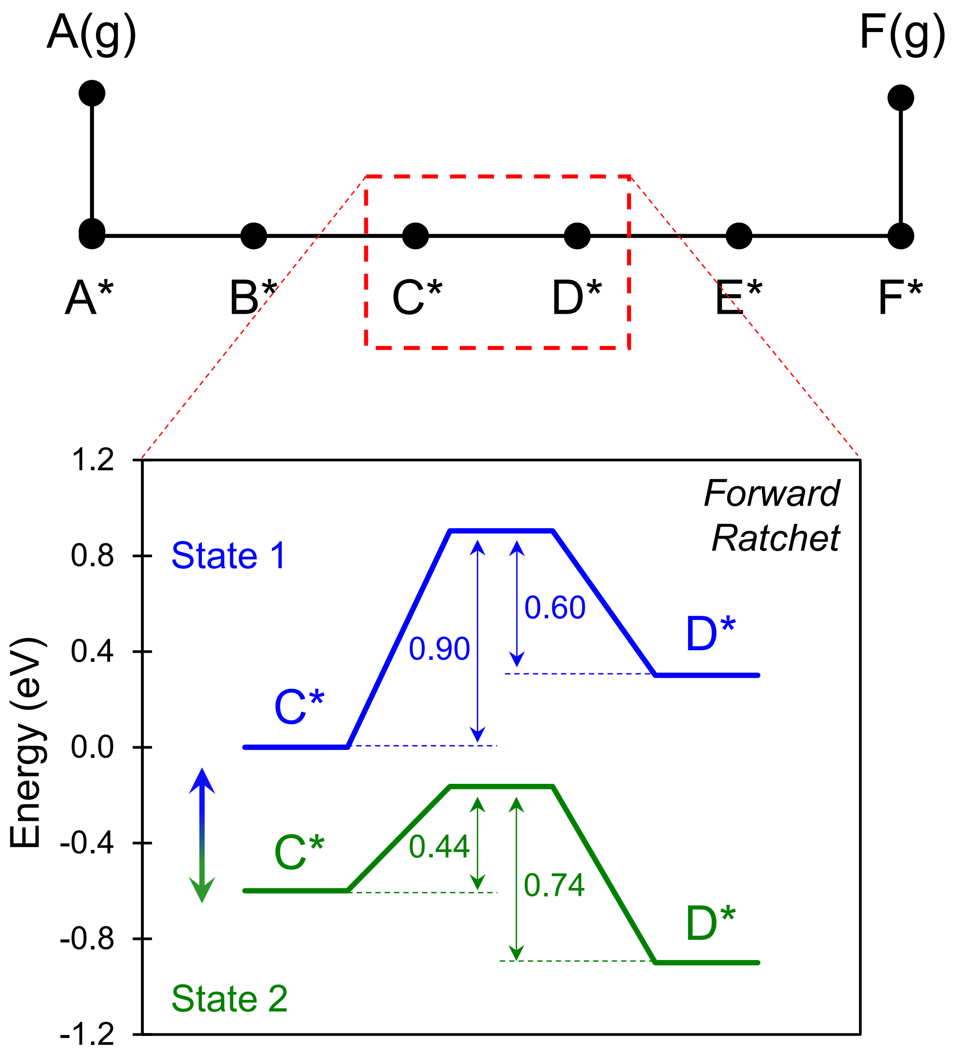
$$\lambda = \frac{\left(k_{1,blue} D_B + k_{1,green}(1 - D_B)\right)}{\left(k_{-1,blue} D_B + k_{-1,green}(1 - D_B)\right)}$$

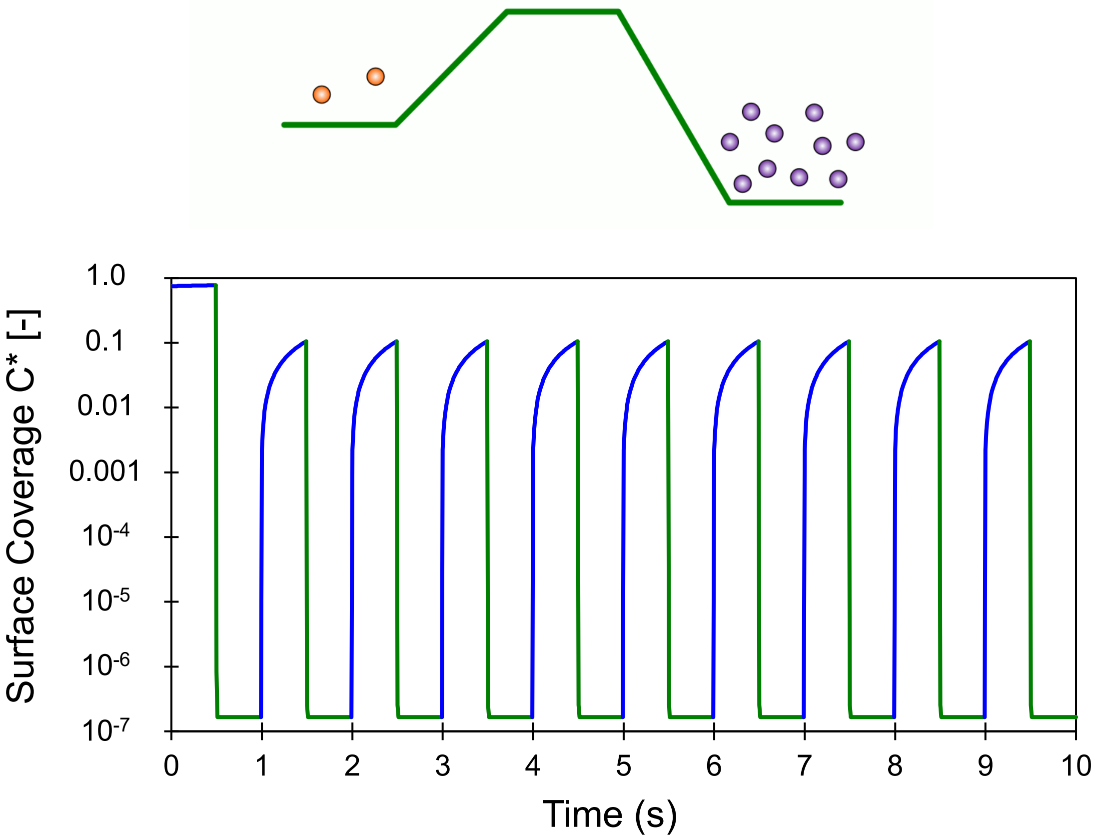
$$\lambda = \sum_j \tau_j k_{1,j} \ / \ \sum_j \tau_j k_{-1,j}$$

Batch reactor conditions: 150 °C, initial reactor composition of 100 bar pure A, ΔH_{rxn} ~ 0 kJ mol^{-1}, α ~ 0.6, β ~ 102 kJ mol^{-1}, $\gamma_{B\text{-}A}$ ~ 0.5, and δ ~ 1.4 eV.

[1] M.A. Ardagh, et al. *Cat. Sci. Tech.* 2019, 9, 5058. DOI: 10.1039/C9CY01543D

Programmable Catalytic Ratchet: Basic Unit of Dynamic Chemistry



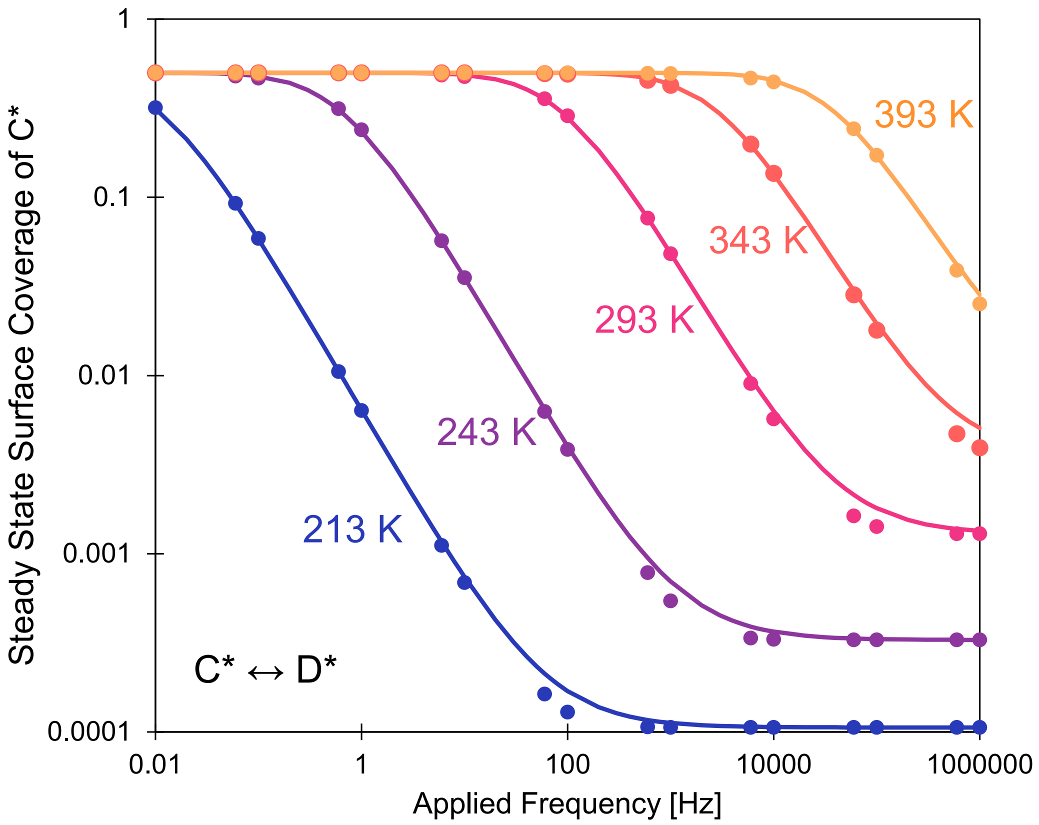


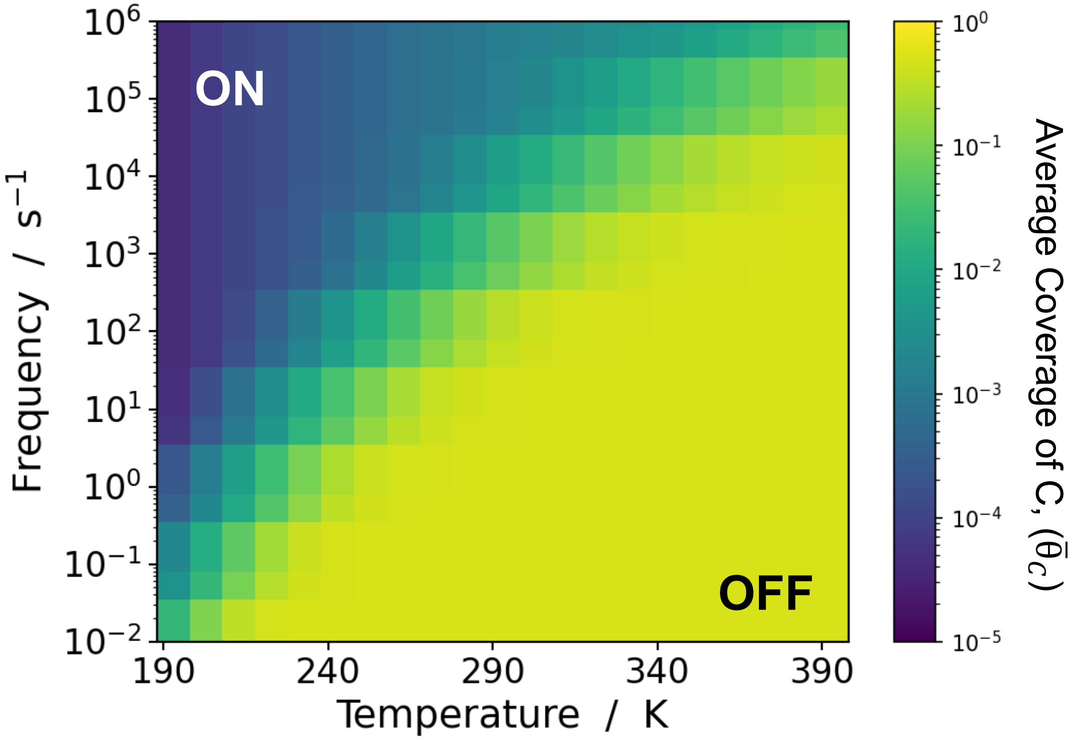
[1] ***Chem. Sci.***, 2024,**15**, 13872-13888

Programmable Catalytic Ratchet: Basic Unit of Dynamic Chemistry

$$\bar{\theta}_{C,Avg} = \bar{\theta}_{C,eq} + \left(\frac{1}{(1 + k_{II}\,\tau_{II}/4)^2}\right)\left(\frac{1}{1+\lambda} - \bar{\theta}_{C,eq}\right)$$

Elementary catalytic ratchets operate in two states:
(1) OFF at low frequency, (2) ON at high frequency



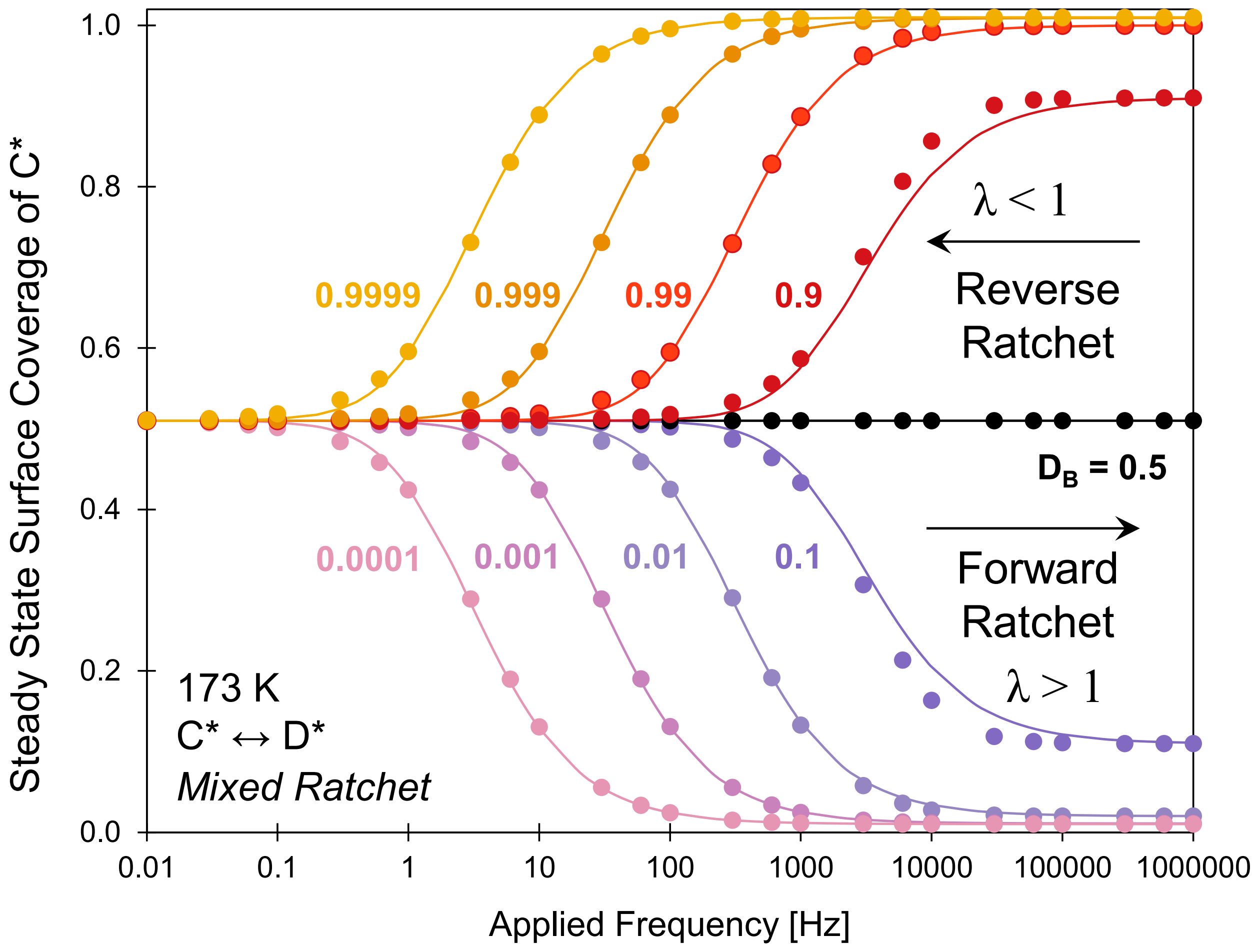


($\alpha = 0.78$, $\beta = 0.67$ eV, $\gamma_{D/C} = 2.0$, $\delta_{C\text{-}D} = 0.3$, $\Delta BE_C = 0.6$ eV)

[1] ***Chem. Sci.***, 2024,**15**, 13872-13888

Three Characteristics of Catalytic Elementary Ratchets

($\alpha = 0.5$, $\beta = 0.375$ eV, $\gamma_{D/C} = 2.0$, $\delta_{C\text{-}D} = 0.25$, $\Delta BE_C = 0.5$ eV)



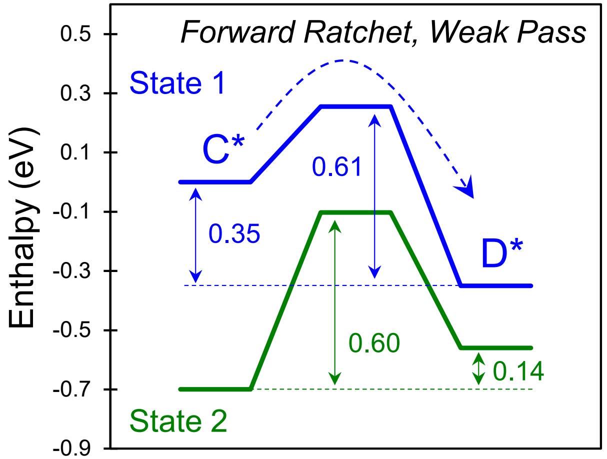
(1) Ratchet Directionality (forward vs reverse)

$$\lambda = \frac{\left(k_{1,blue}D_B + k_{1,green}(1-D_B)\right)}{\left(k_{-1,blue}D_B + k_{-1,green}(1-D_B)\right)}$$

(2) Cutoff Frequency (ON vs OFF)

$$f_c = \frac{k_{II}D_{II}}{4(\sqrt{2}-1)}$$

(3) Pass Condition (weak vs strong)

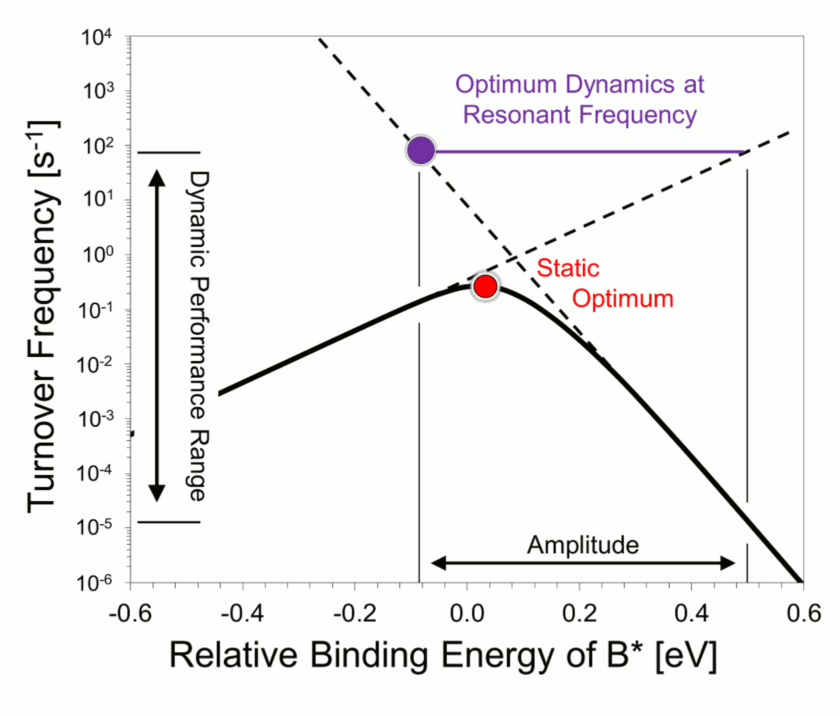


[1] ***Chem. Sci.***, 2024,**15**, 13872-13888

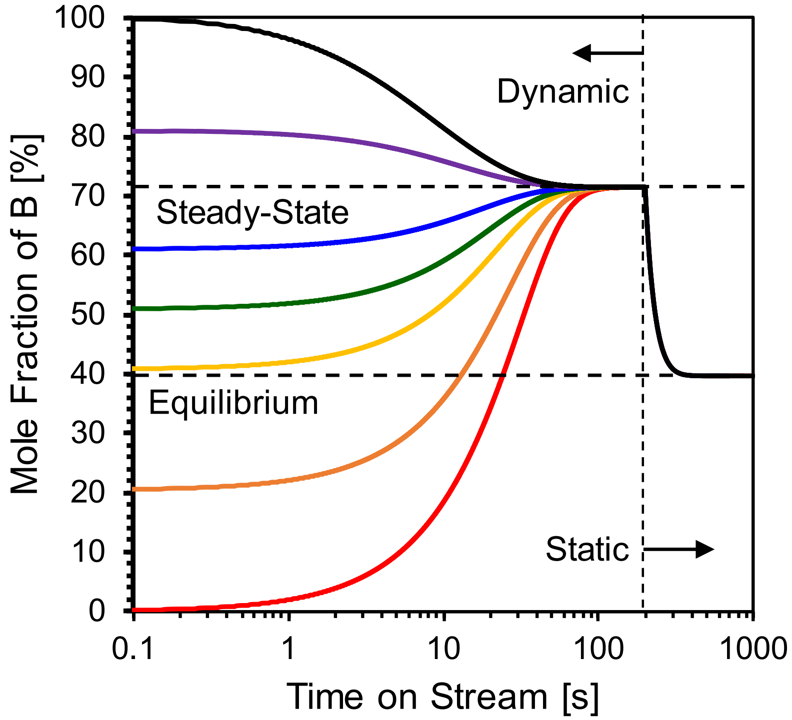
Disruption: Catalytic Resonance Theory

A theory of the catalytic mechanics of reacting molecules
on active sites that change with time

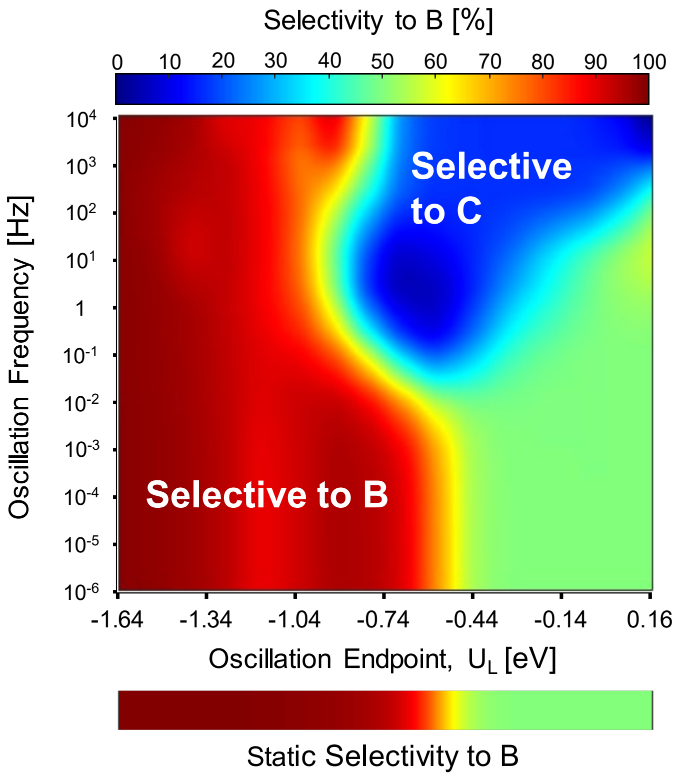
Accelerate catalytic reactions orders of magnitude beyond Sabatier limit[1]



Drive catalytic reactions away from equilibrium[2]



Perfectly control selectivity to products in branched reactions[3]
B(g) ← A(g) → C(g)

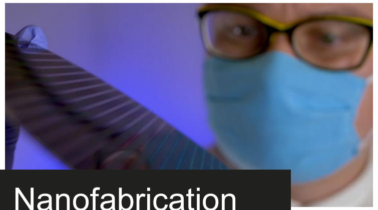


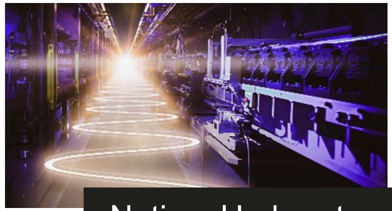
[1] *ACS Catalysis*, 2019, 9(8), 6929, [2] *Cat. Sci. Tech.* 2019, 9, 5058, [3] *Chem. Sci.*, 2020, 11, 3501

Convergence of Research for Programmable Catalysis

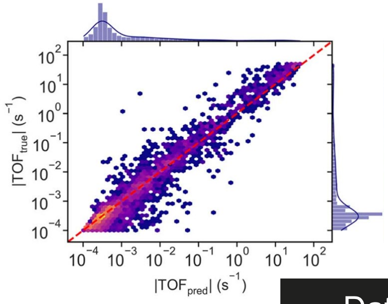
The emerging field of programmable catalysis must address four convergent research efforts

Programmable Catalyst Synthesis and Characterization
How do we make and characterize catalysts that can change with time?

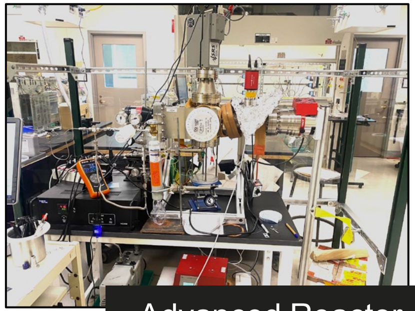

Nanofabrication


National Laboratory X-ray Source

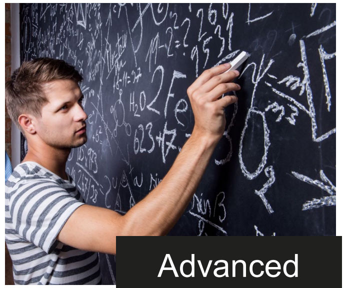
Programmable Catalyst Experiments
How do we evaluate programmable catalysts within reactors?

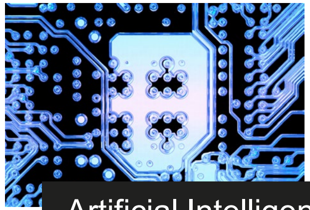


Data Science

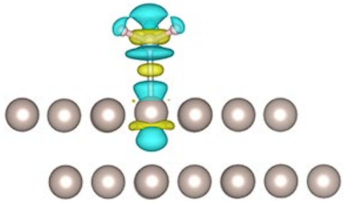

Advanced Reactor Design

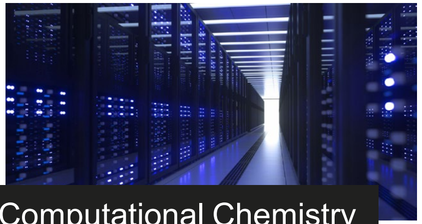
Catalytic Resonance Theory
Fundamentals behaviors of molecules on dynamic surfaces


Advanced Mathematics


Artificial Intelligence

Programmable Surface Reactions
How do we model and optimize programmable surface reactions?


Molecular Modeling

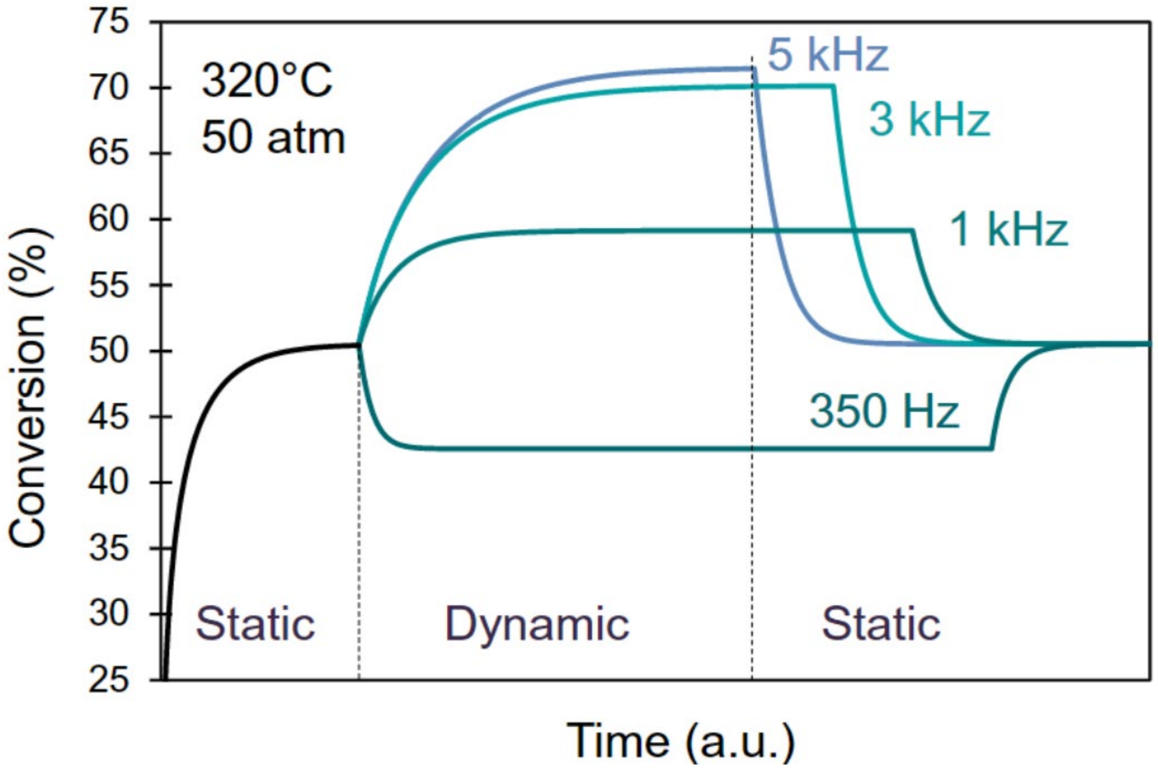

Computational Chemistry with DOE Resources

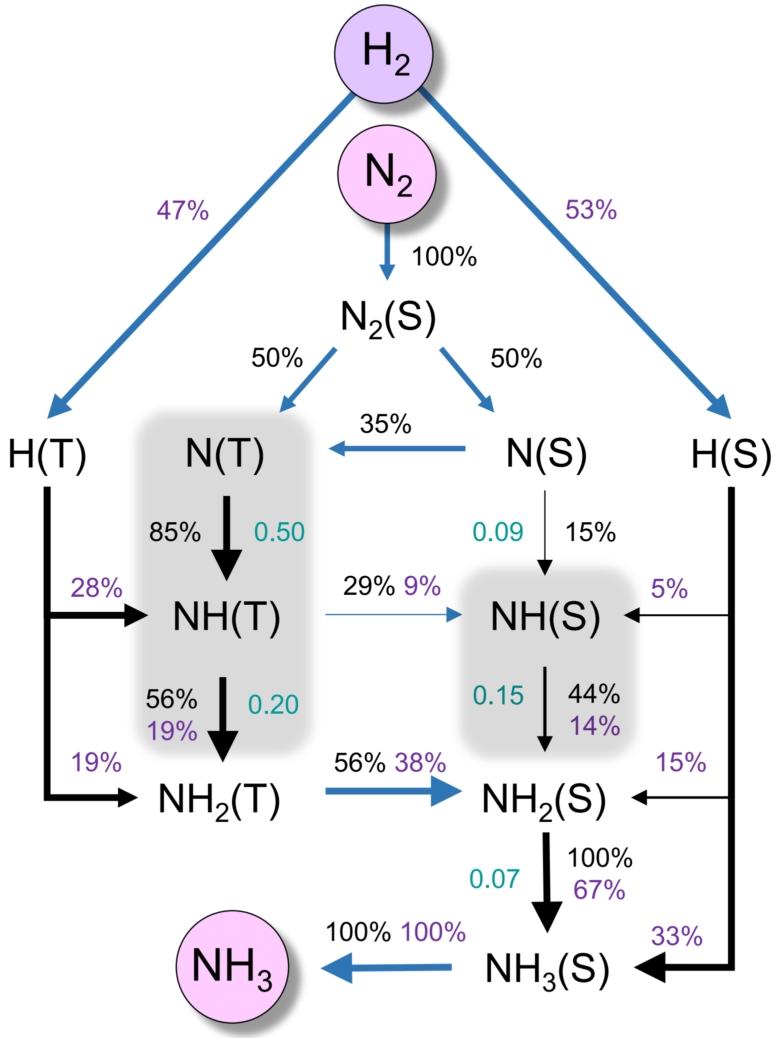
Programmable Catalysis

What happens with a network of catalytic ratchets? (Ammonia)

Different frequencies achieve higher/lower steady state of ammonia synthesis

Dynamic strain of ruthenium

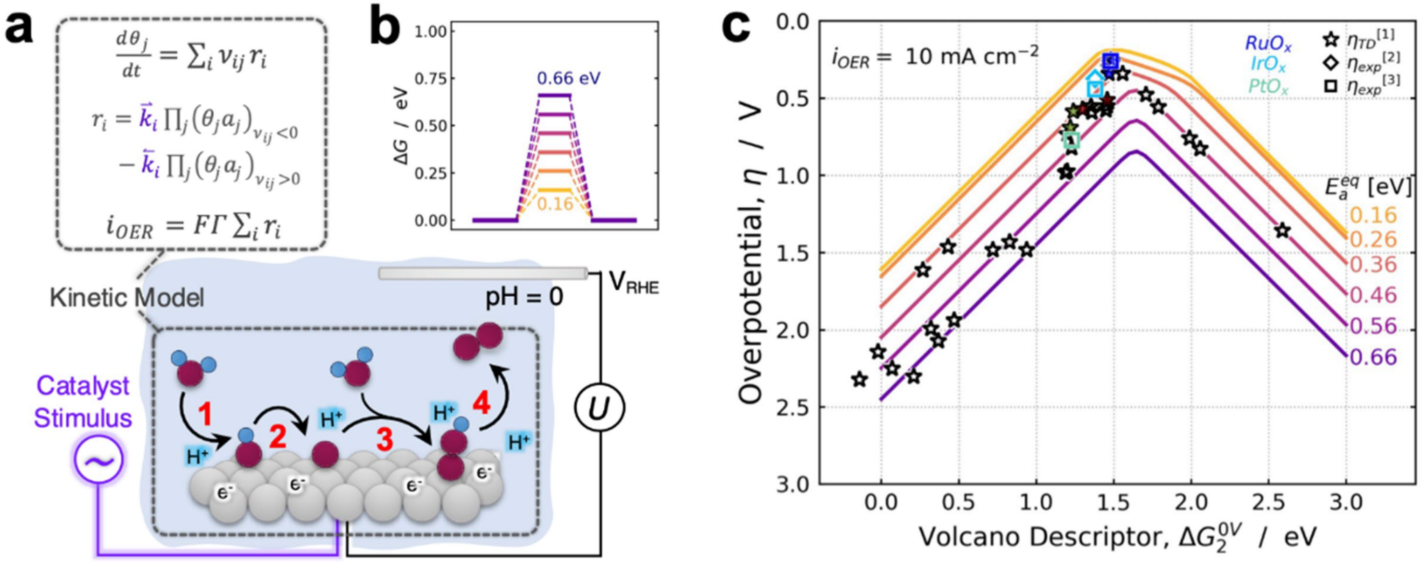


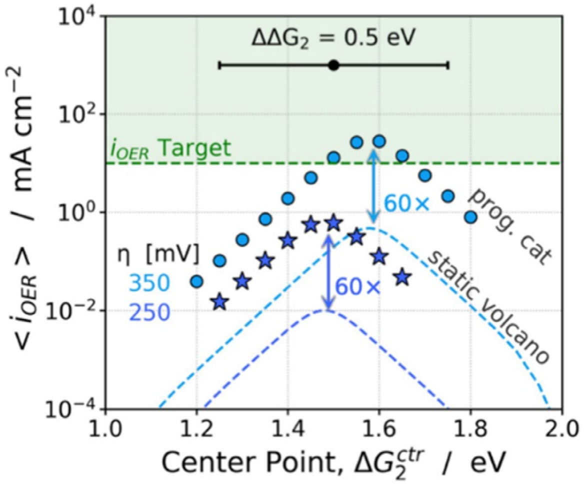


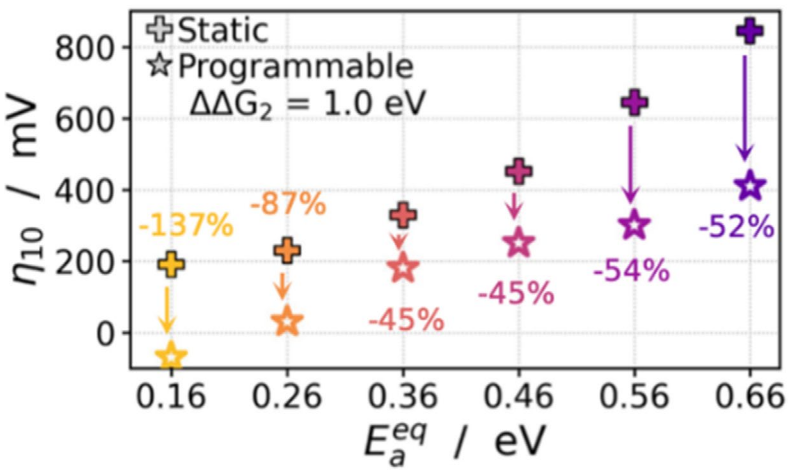
[1] *Science Advances*, 2022, 8(4)

Example: Oxygen Evolution Reaction (OER)

Dr. Sallye Gathmann







The Oxygen Evolution Reaction (OER) is the controlling chemistry of water splitting

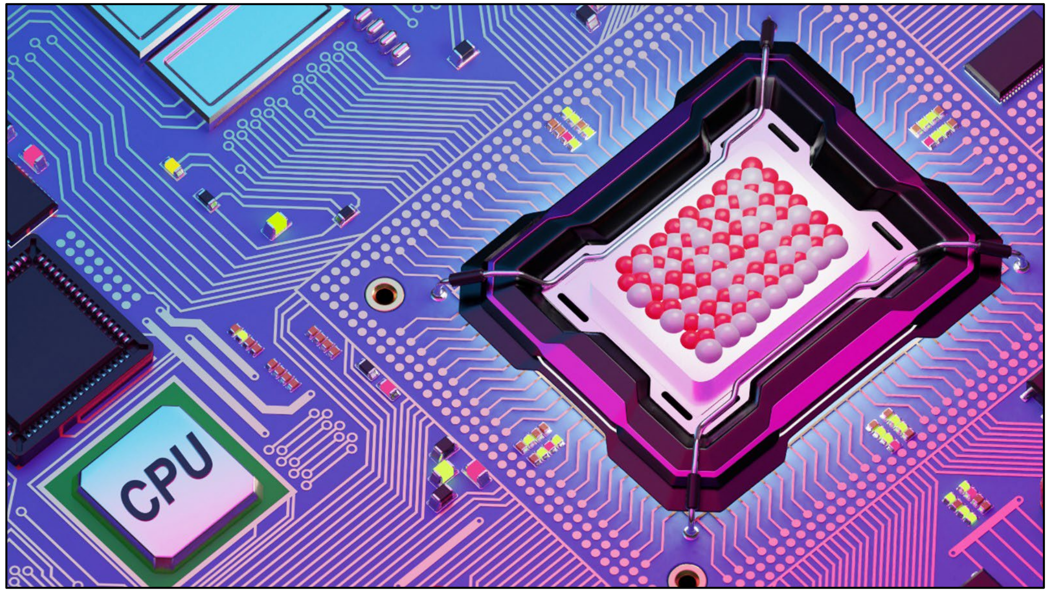
(c) OER forms a conventional Sabatier volcano

Oscillation of the catalytic surface:

- accelerates OER beyond the catalytic rate target (above Sabatier)
- dramatically reduces the required overpotential

[1] *ACS Energy Letters*, 2024, 2024, 9, 2013-2023. DOI: 10.1021/acsenergylett.4c00365

Programmable Catalysis: Path Forward



Combine:
(i) Chemistry
(ii) Perturbation
(iii) Material

→

Implement:
(i) Build
(ii) Optimize
(iii) Test

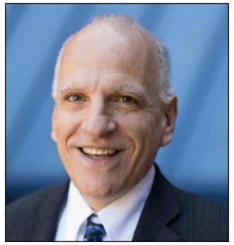
Key Step Forward: Catalyst dynamics is a *strategy* for achieving breakthrough catalytic performance

Benefit: Rate enhancement and reaction selectivity control for products

Massive targets:
- Selective Natural Gas Conversion
- Fertilizer Production
- Plastic Precursor Synthesis
- Energy Storage

This technology is just getting started…

Acknowledgements

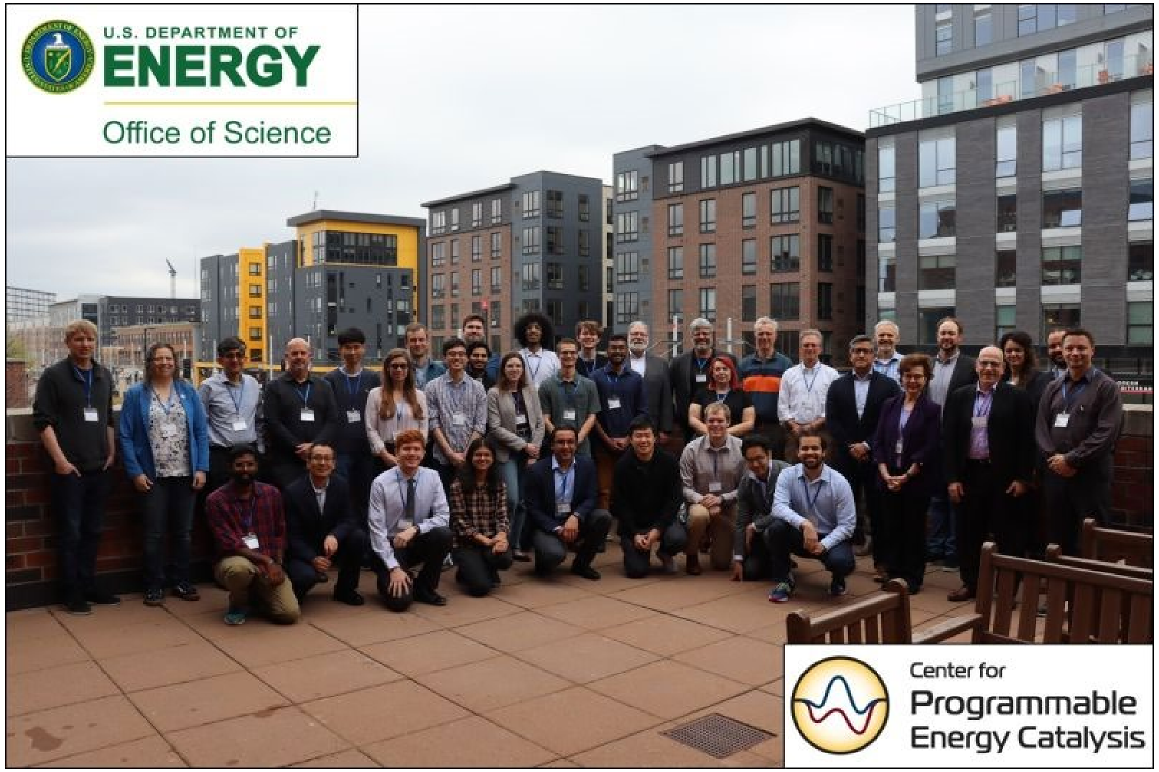










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