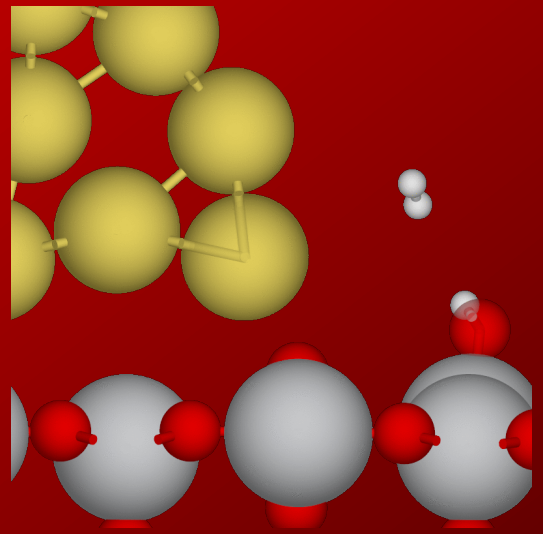
U.S. DEPARTMENT OF ENERGY

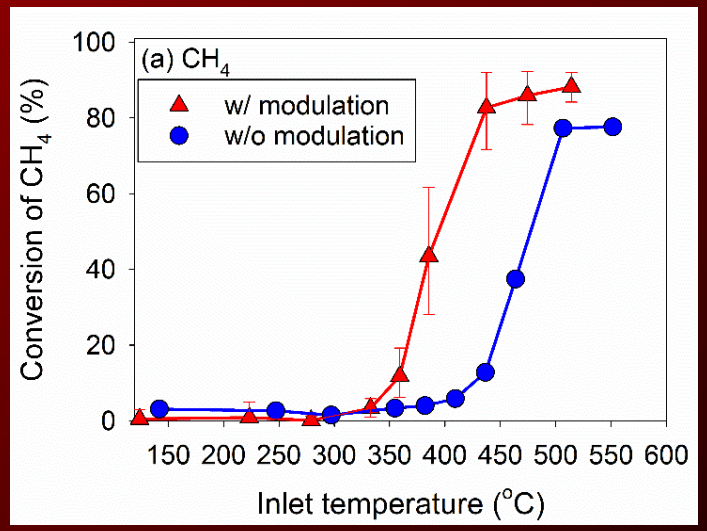
Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

DOE/EERE Advanced Manufacturing Office

Dynamic Catalyst Science Roundtable

Connecting Atomistic Modeling, Laboratory and Industrial Scales





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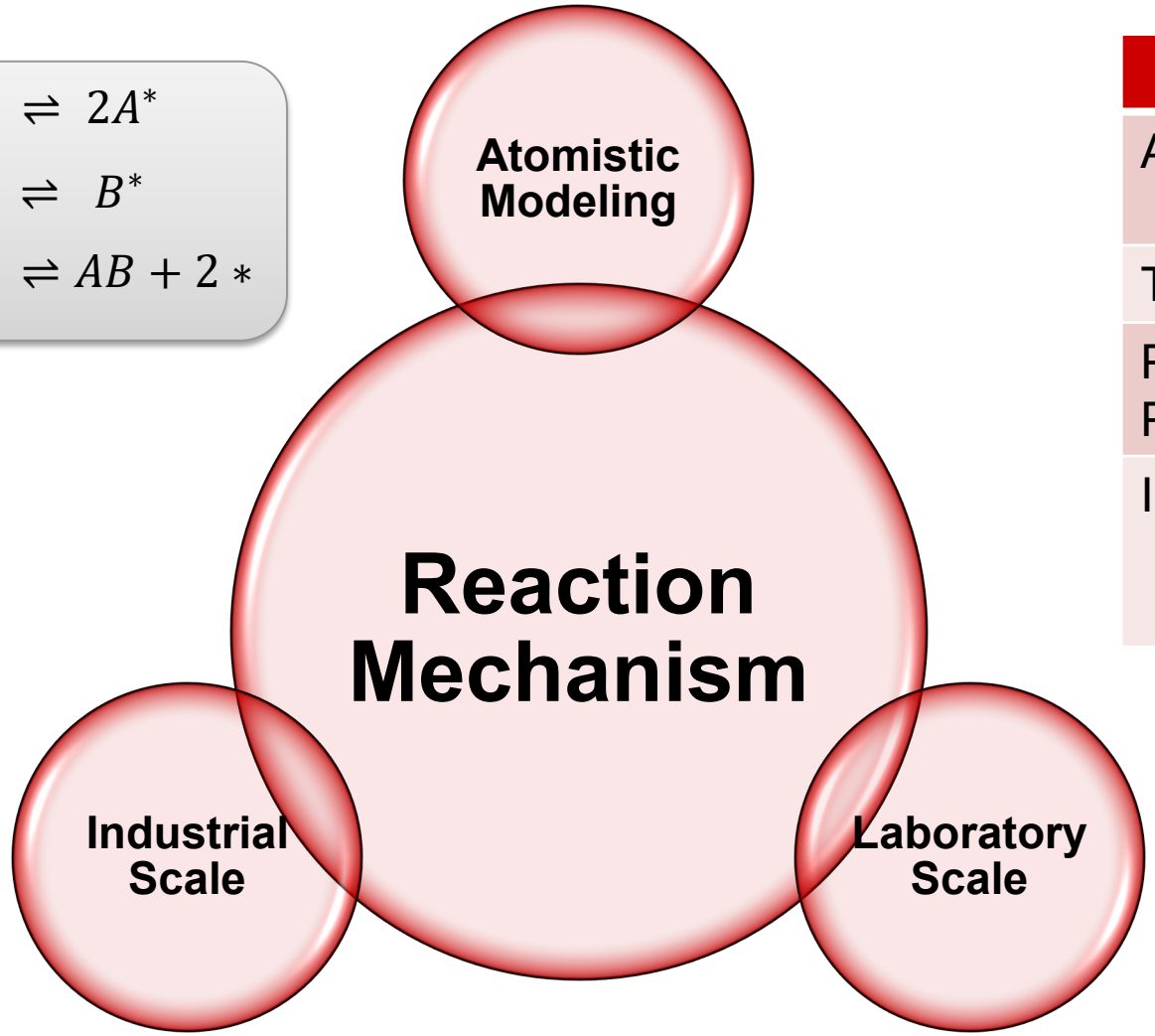
Department of Chemical & Biomolecular Engineering

Foundation of Understanding Catalysis: The Mechanism

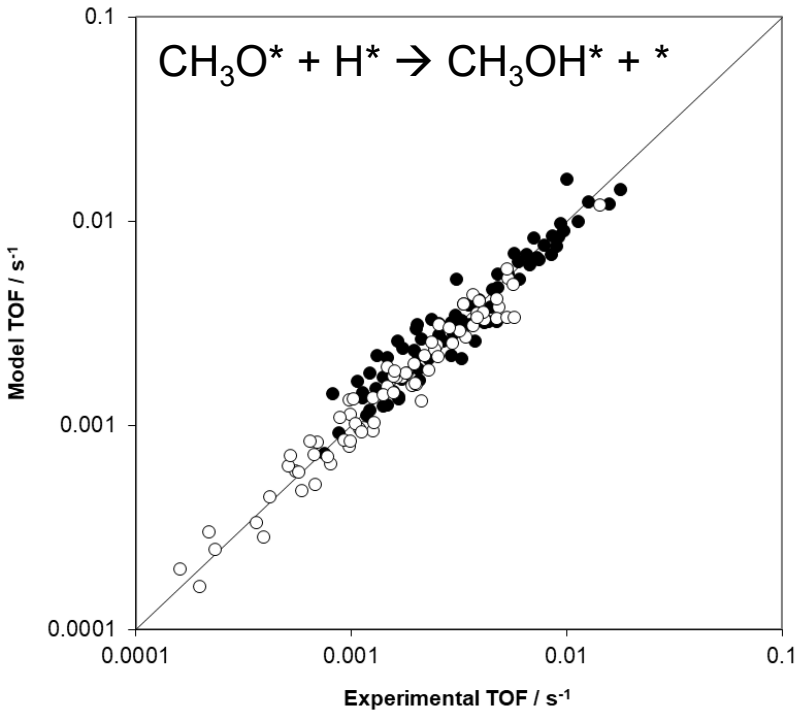
$$A_2 + 2* \rightleftharpoons 2A^*$$
$$B + * \rightleftharpoons B^*$$
$$A^* + B^* \rightleftharpoons AB + 2*$$



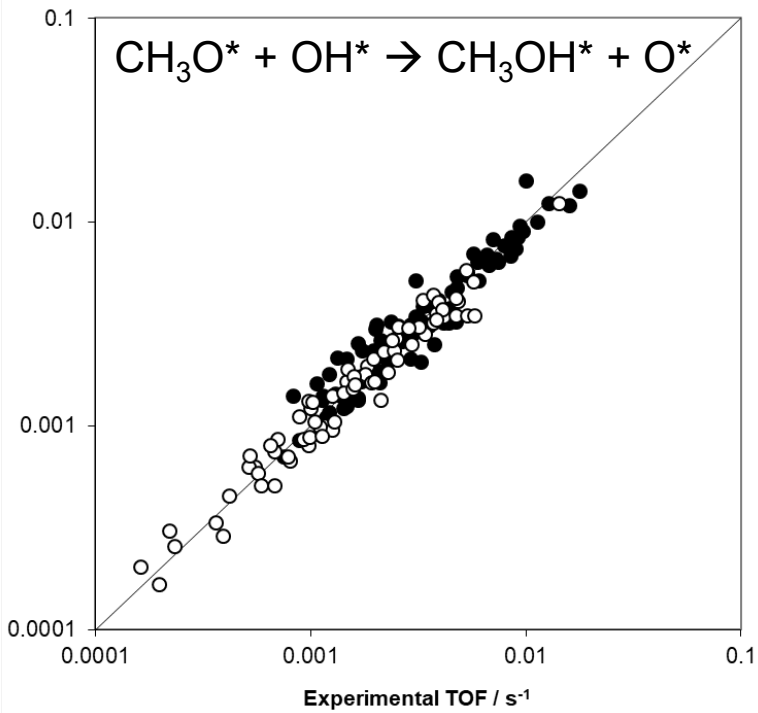
	Steady-state	Transient
Active site '*'	Static	Dynamically formed
Temperature	E_{app}	TPD, TPR
Partial Pressure	Reaction order	Pulse response
Isotopes	Kinetic isotope effects	SSITKA
	Scalar values	Time resolved information

Problem of fitting steady-state data

"do not use"



…corrected/refitted/improved



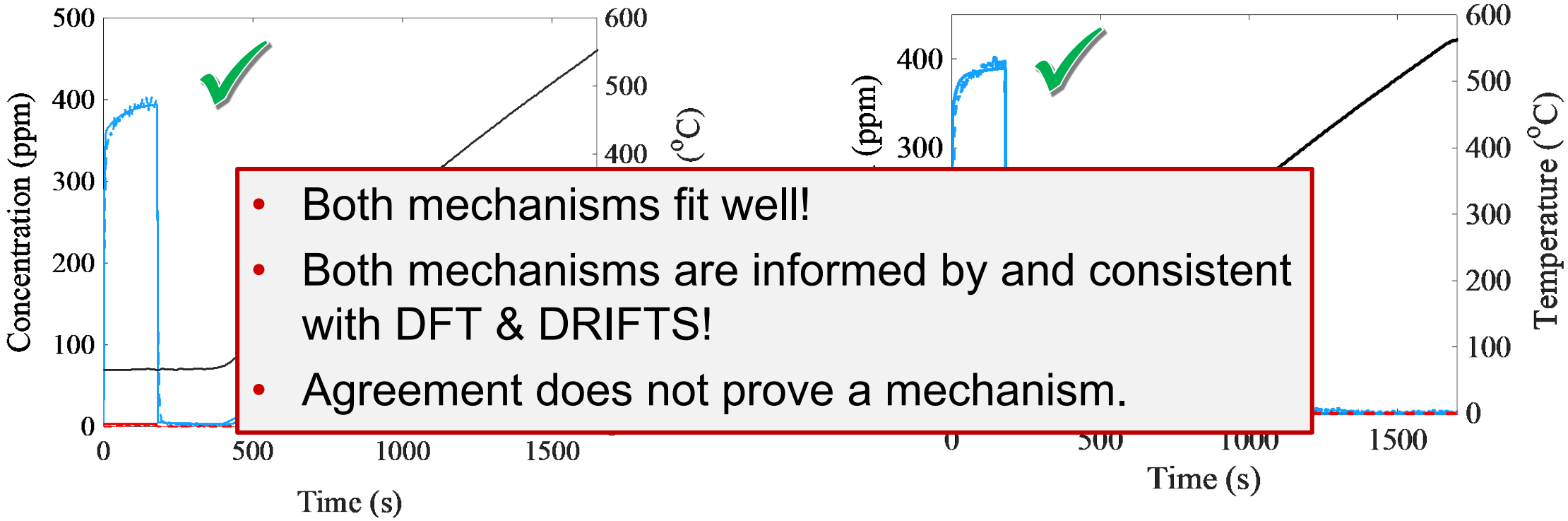
- > 20 intermediates and ca. 50 reaction steps
- Multiple parallel reaction pathways
- *"Any"* mechanism or set of parameters fits…

Grabow, Mavrikakis, *ACS Catal.* **1,** 365–384 (2011)

Fitting with limited transient data

Scheme I: $Z^-[PdOH]^+, Z^-Pd^{2+}Z^-$ and Z^-Pd^+ with Z^-Pd^+ as the strongest NO binding site.

Scheme II: NO reduction of PdO_2 to PdO with nitrate formation.

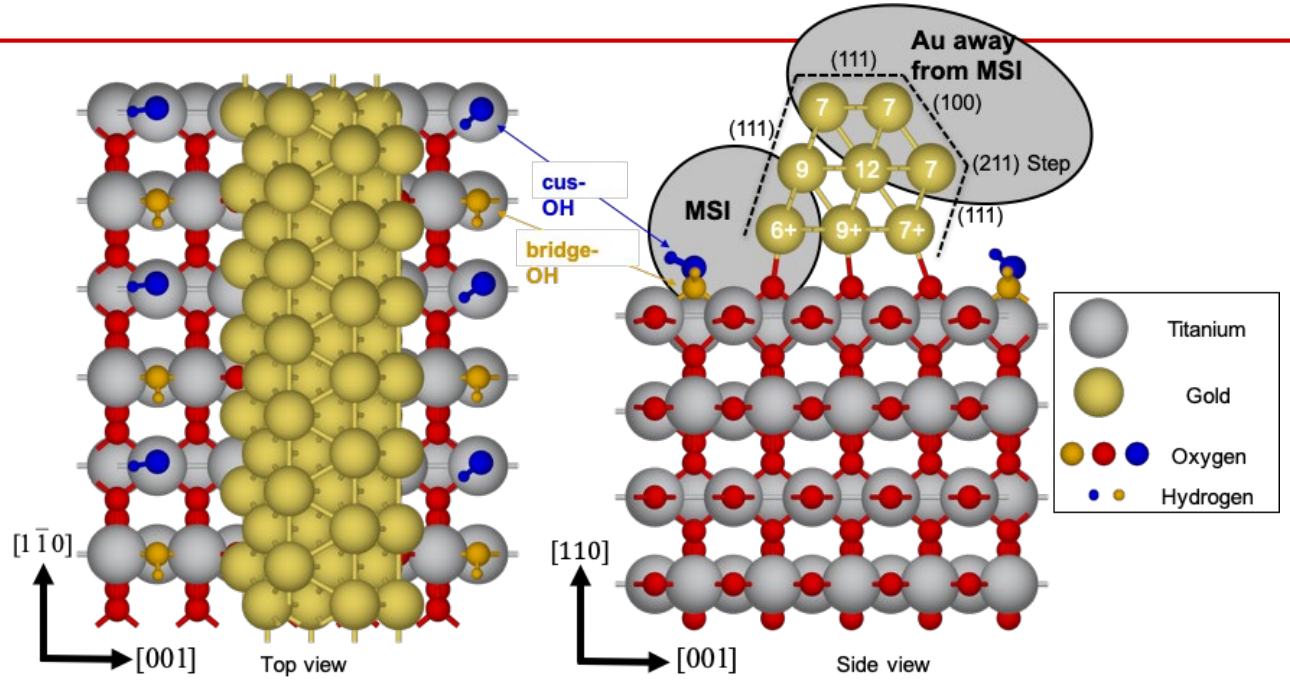


- Both mechanisms fit well!
- Both mechanisms are informed by and consistent with DFT & DRIFTS!
- Agreement does not prove a mechanism.

Experimental and modeling results of NO_x uptake at 80°C and TPD on Pd(1%)/H-ZSM-5 for wet-feed (7% H_2O) and feed flowrate of 2500 sccm.

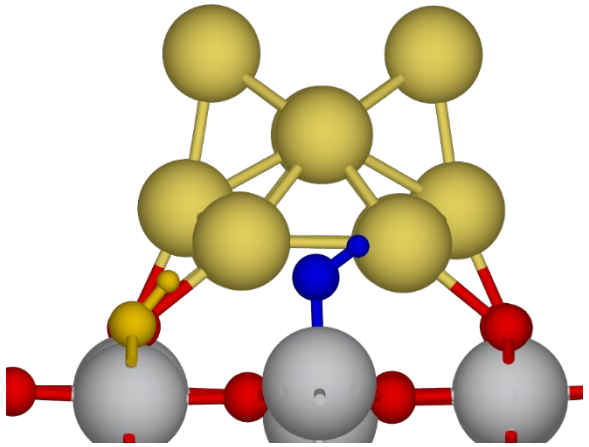
M. Ambast, K. Karinshak, B. Md. Mushfikur Rahman, L. C. Grabow, and M. P. Harold, accepted in Applied Catalysis B, 2020

Atomistic modeling hinges on the description of an active site



Nanorod
large & slow
rigid
epitaxial strain

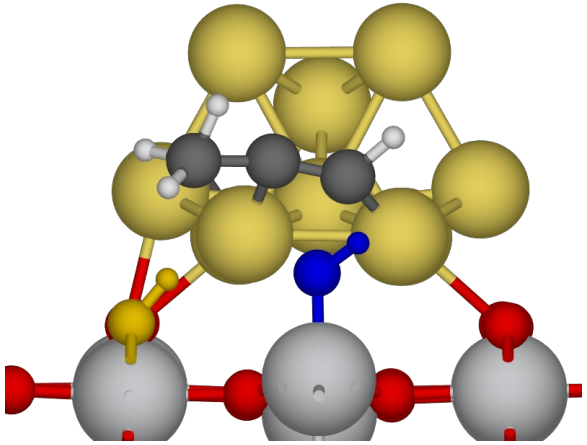
How should we model the active site of a supported metal catalyst?

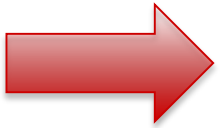


Cluster
small & fast
high mobility
strain free

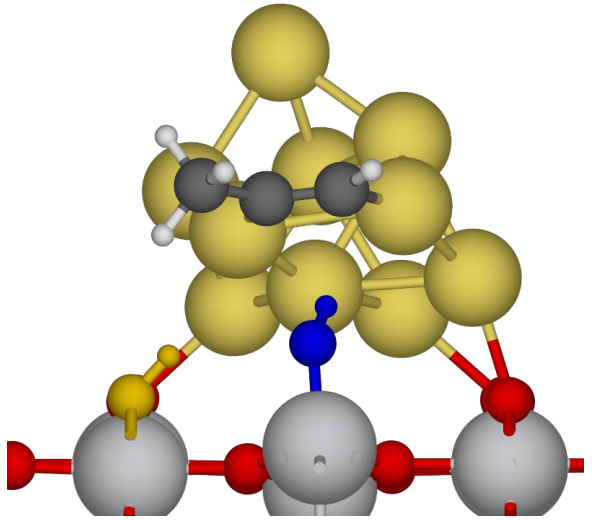
High mobility of small gold clusters

Initial guess





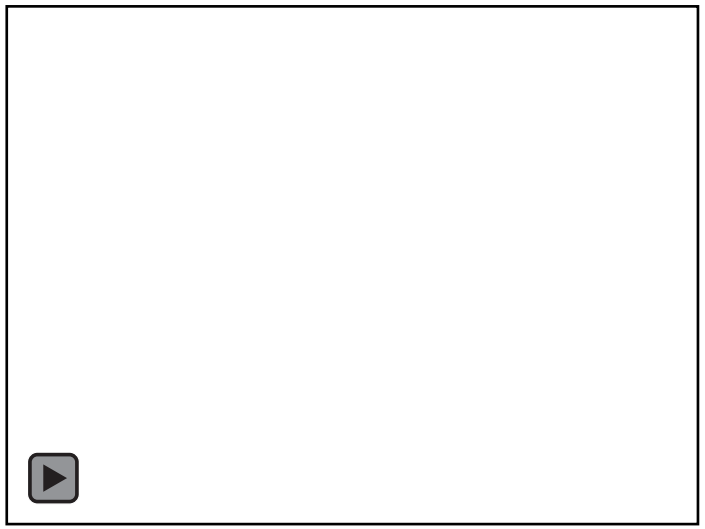
Optimized configuration

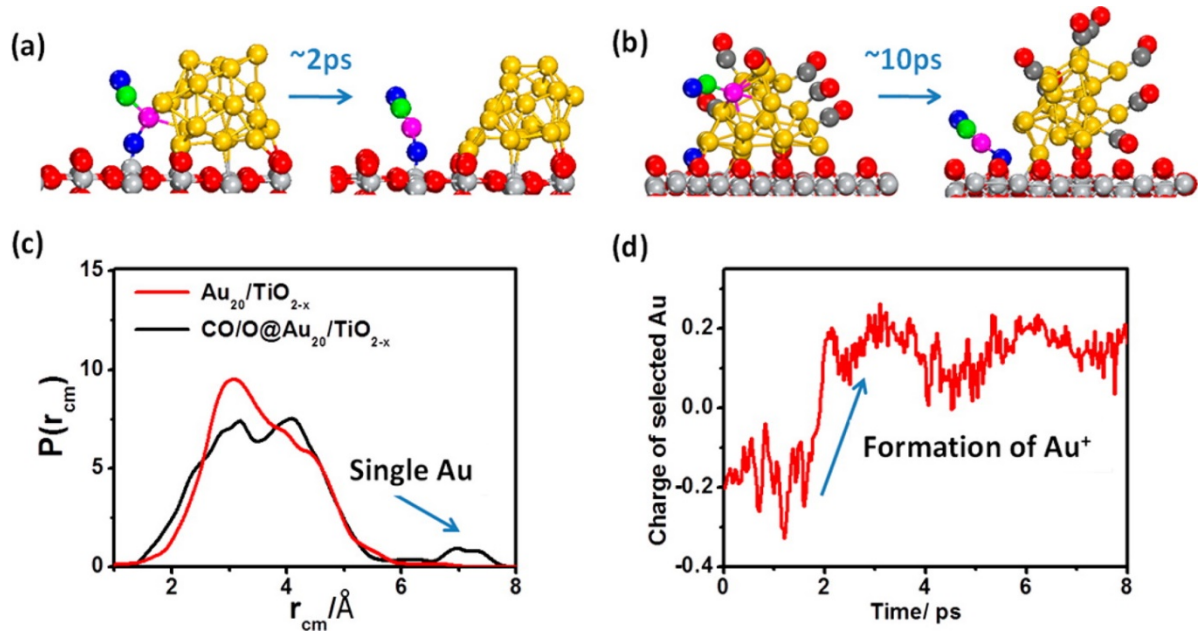


- Substantial restructuring of Au cluster upon propyne adsorption.
- Active sites are *not* well defined at the atomic scale!

Dynamic (transient) formation of active sites

(Low level) ***Ab Initio*** **Molecular Dynamics captures transient formation of active sites.**

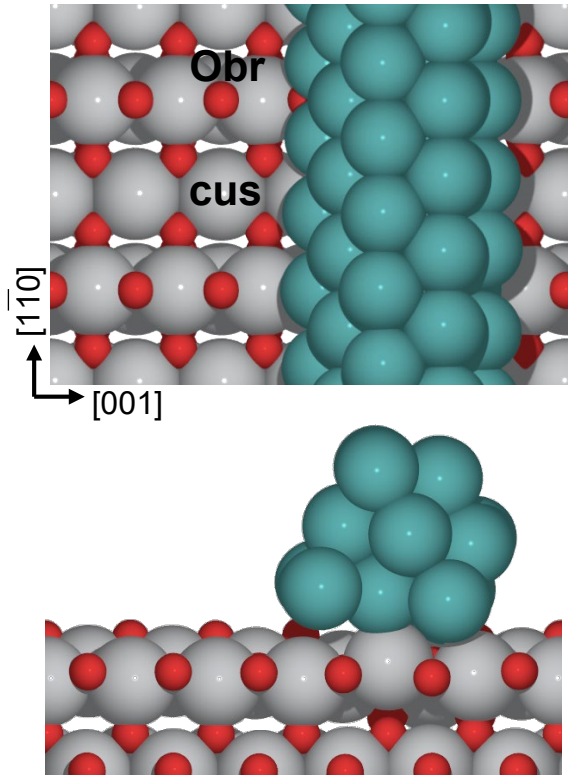




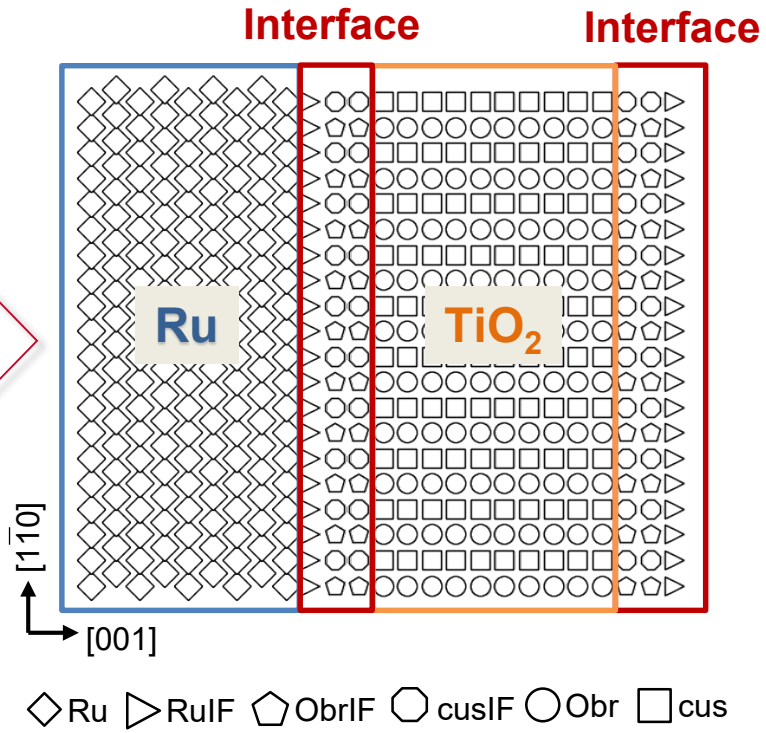
Wang, Cantu, Lee, Li, Glezakou, Rousseau, *J. Am. Chem. Soc.* **2016**, *138* (33), 10467–10476

First-principles lattice kinetic Monte Carlo model

DFT model:



Lattice configuration in kMC:



Overall reaction:

$$C_6H_4CH_3OH(g) + H_2(g) \leftrightarrow C_6H_5CH_3(g) + H_2O(g)$$

Major elementary steps:

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

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

$$H_2O* + * \leftrightarrow H* + OH*$$

$$H_2O* + O* \leftrightarrow 2OH*$$

$$OH* + * \leftrightarrow O* + H*$$

$$C_6H_4CH_3OH(g) + * \leftrightarrow C_6H_4CH_3OH*$$

$$C_6H_5CH_3(g) + * \leftrightarrow C_6H_5CH_3*$$

$$C_6H_4CH_3OH* + * \leftrightarrow C_6H_4CH_3* + OH*$$

$$C_6H_4CH_3OH* + H* \leftrightarrow C_6H_4CH_3* + H_2O*$$

$$C_6H_4CH_3OH* + H_2O \leftrightarrow C_6H_4CH_3* + OH* + H_2O(g)$$

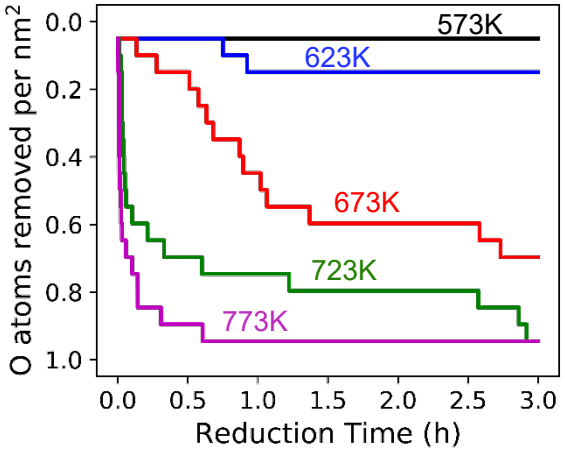
$$C_6H_4CH_3* + H* \leftrightarrow C_6H_5CH_3* + *$$

$$A* + * \leftrightarrow * + A*$$

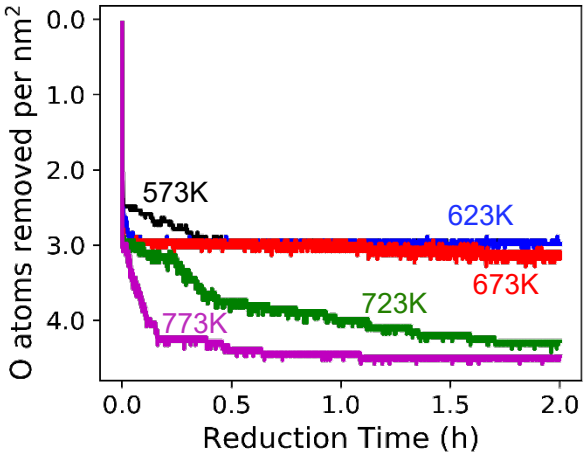
$$A* + B* \leftrightarrow B* + A*$$

Reduction rate enhancement by H_2 activation at the interface

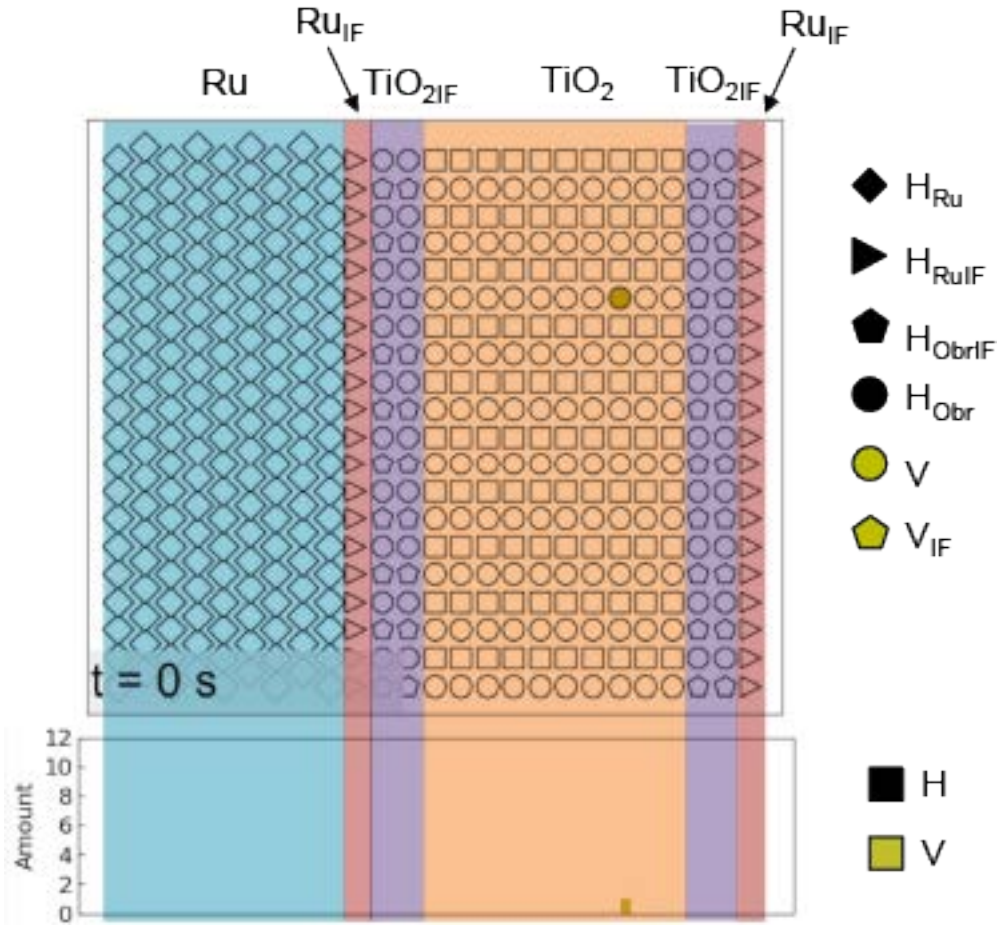
TiO_2:



Ru/TiO_2:

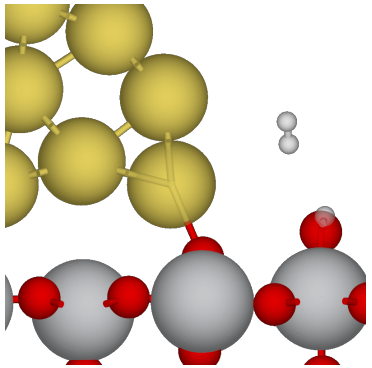


Surface evolution during Ru/TiO_2 reduction at 723 K

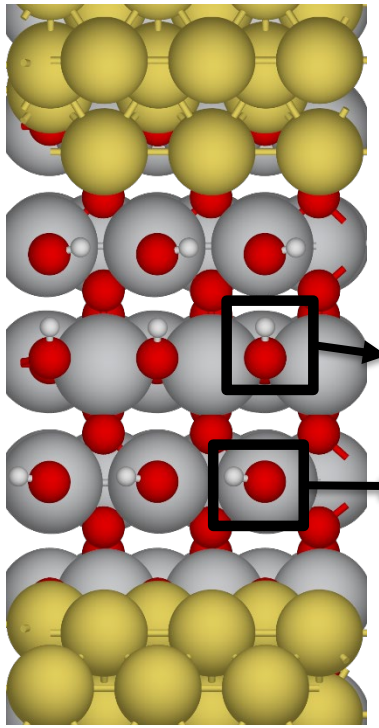


The devil is in the detail

Exothermic
H_2 dissociation



E_a = 0.53 eV
ΔE = -0.67 eV



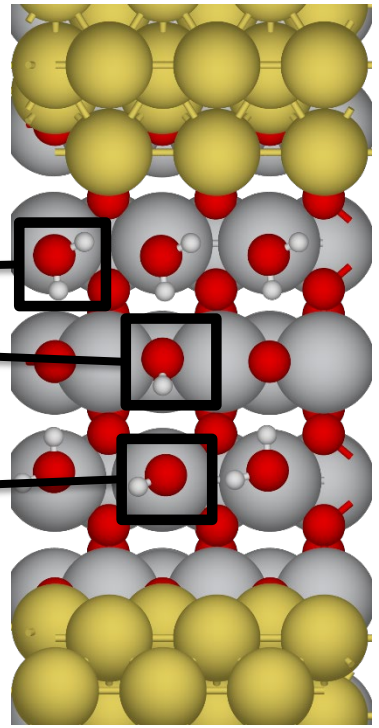
cus - H_2O

bridge - OH

cus - OH

3 dissociated H_2O; 3 additional cus-OH

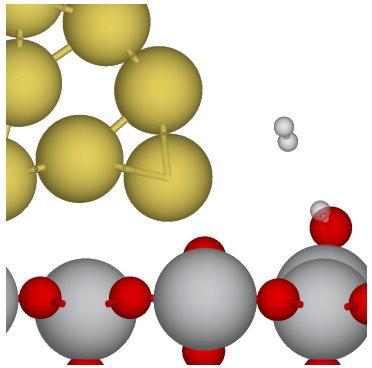
Charge unbalanced system, but regular



5 molecular H_2O; 1 dissociated H_2O

Charge balanced system, but irregular

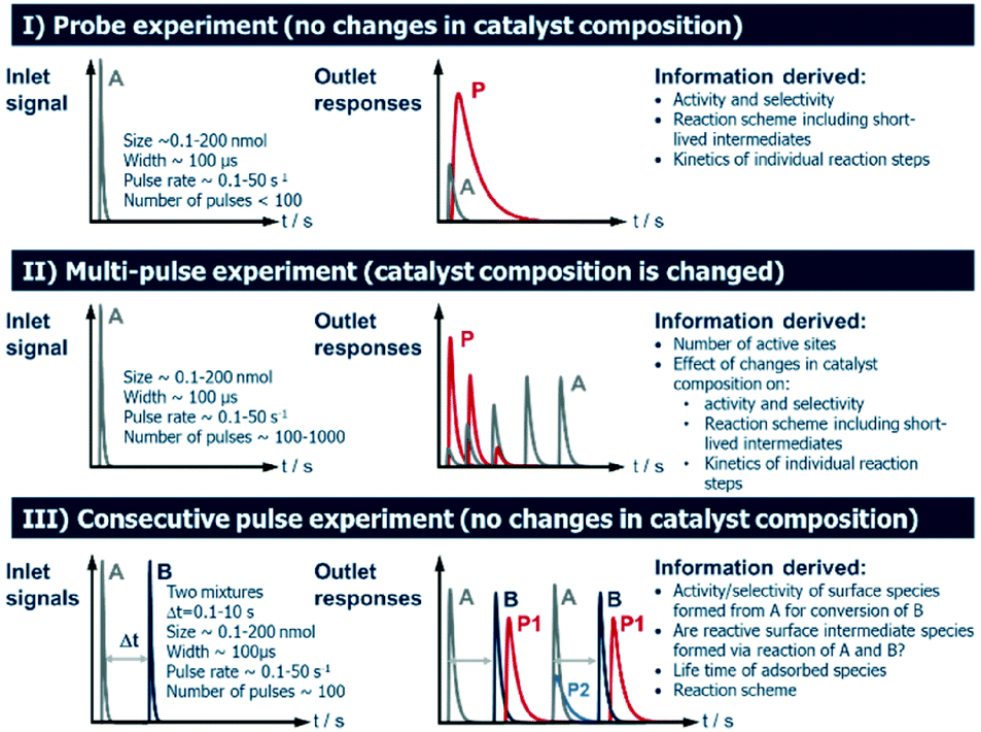
Endothermic
H_2 dissociation



E_a = 1.08 eV
ΔE = 0.42 eV

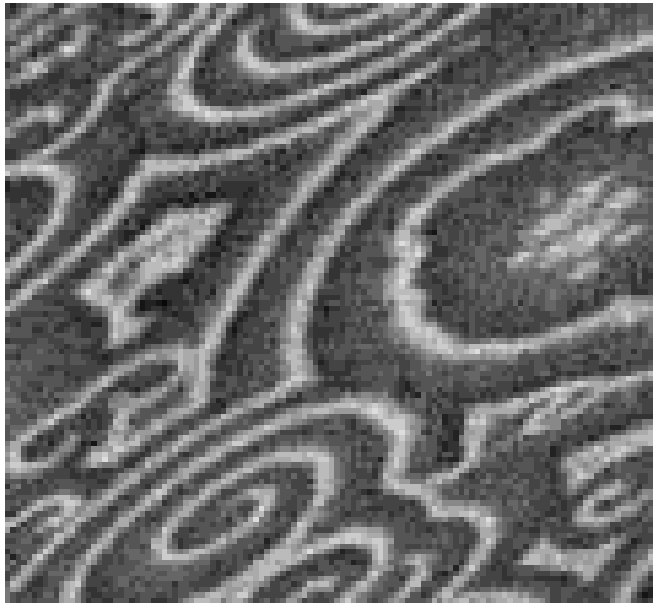
Temporal Analysis of Products (TAP)

	Steady-state	Transient	TAP
Active site '*'	Static	Dynamically formed	✓
Temperature	E_{app}	TPD, TPR	✓
Partial Pressure	Reaction order	Pulse response	✓ ✓
Isotopes	Kinetic isotope effects	SSITKA	✓

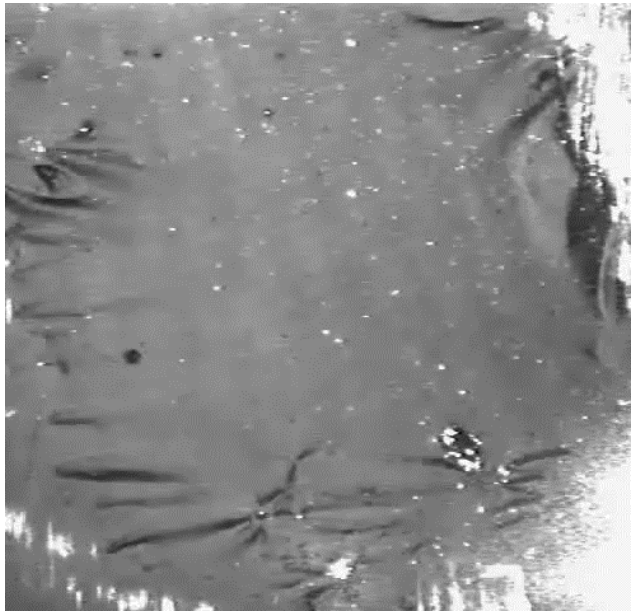


Morgan, K.; Maguire, N.; Fushimi, R.; Gleaves, J. T.; Goguet, A.; Harold, M. P.; Kondratenko, E. V.; Menon, U.; Schuurman, Y.; Yablonsky, G. S. Forty Years of Temporal Analysis of Products. *Catal. Sci. Technol.* **2017**, *7* (12), 2416–2439.

Dynamics in catalysis: Intrinsic (atomic scale)



Pt(110); $P(O_2) = 4\times10^{-4}$ mbar,
$p(CO) = 1.2\times10^{-4}$ mbar,
T = 548 K, 360×360 μm.



Pt(100); $P(O_2) = 1\times10^{-2}$ mbar,
$p(CO) = 1.85\times10^{-3}$ mbar, T = 528 K
***f* ≈ 0.2 Hz**

$$\frac{dx}{dt} = \alpha_1 x - \alpha_2 xy, \quad \frac{dy}{dt} = \beta_1 xy - \beta_2 y$$

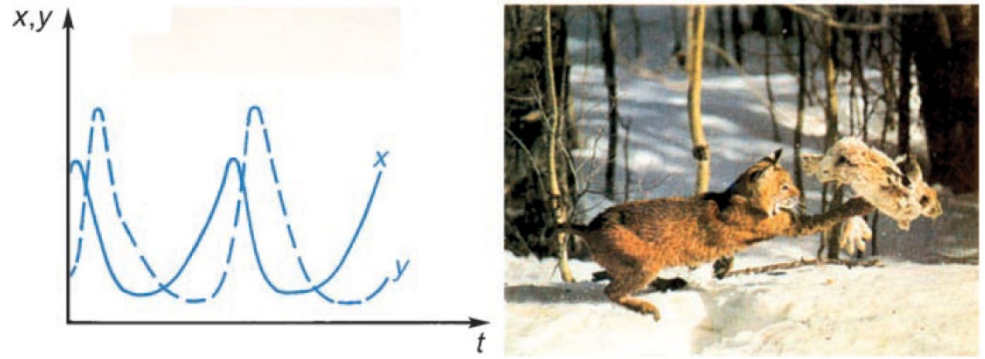


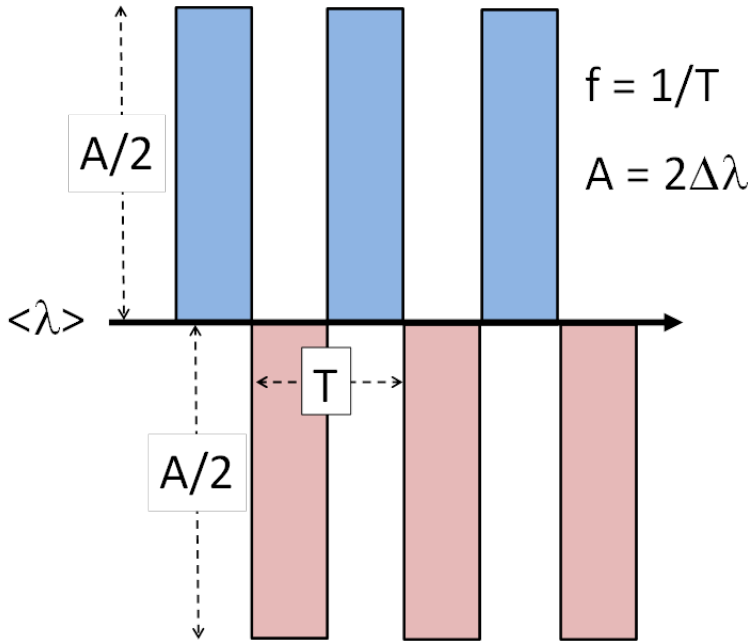
Figure 17. The Lotka–Volterra model describing the observation in Figure 16.

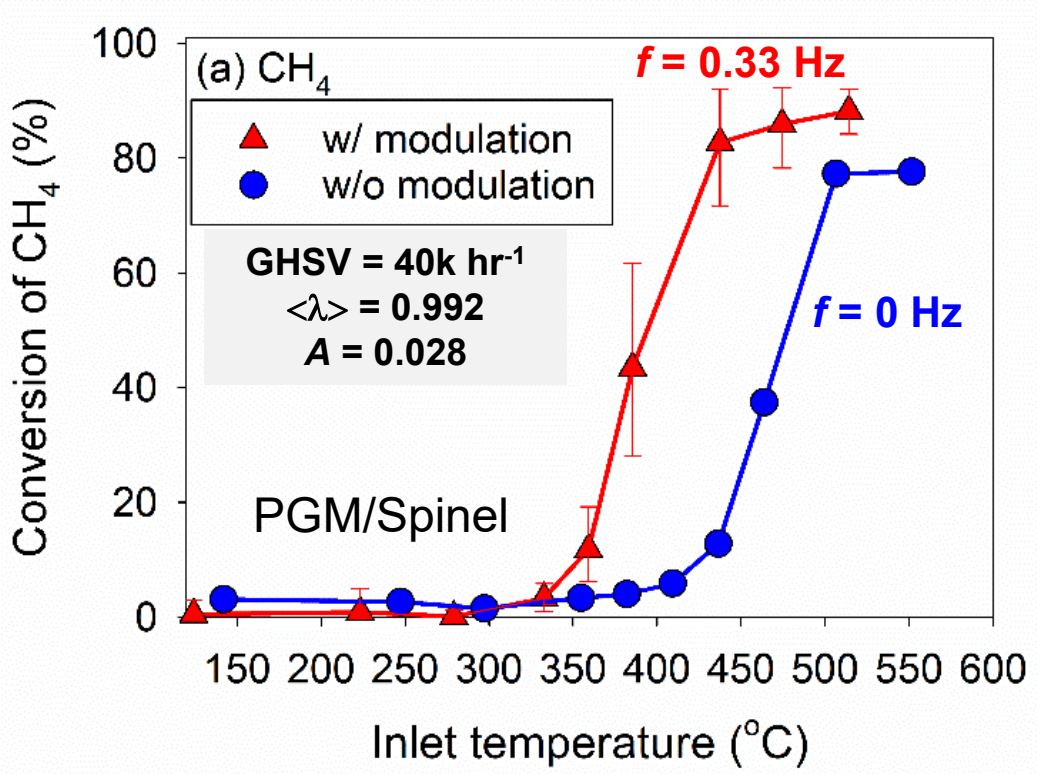
- Dynamics at surfaces at the atomic scale are well documented.
- Controlled by surface coverage, e.g., oxygen rich/lean

Ertl, G. *Angew. Chemie Int. Ed.* **47,** 3524–3535 (2008).

Dynamics in catalysis: Externally imposed (lab scale)

Example:
Vehicle exhaust emission control. Engine operation dictates lean/rich cycles.

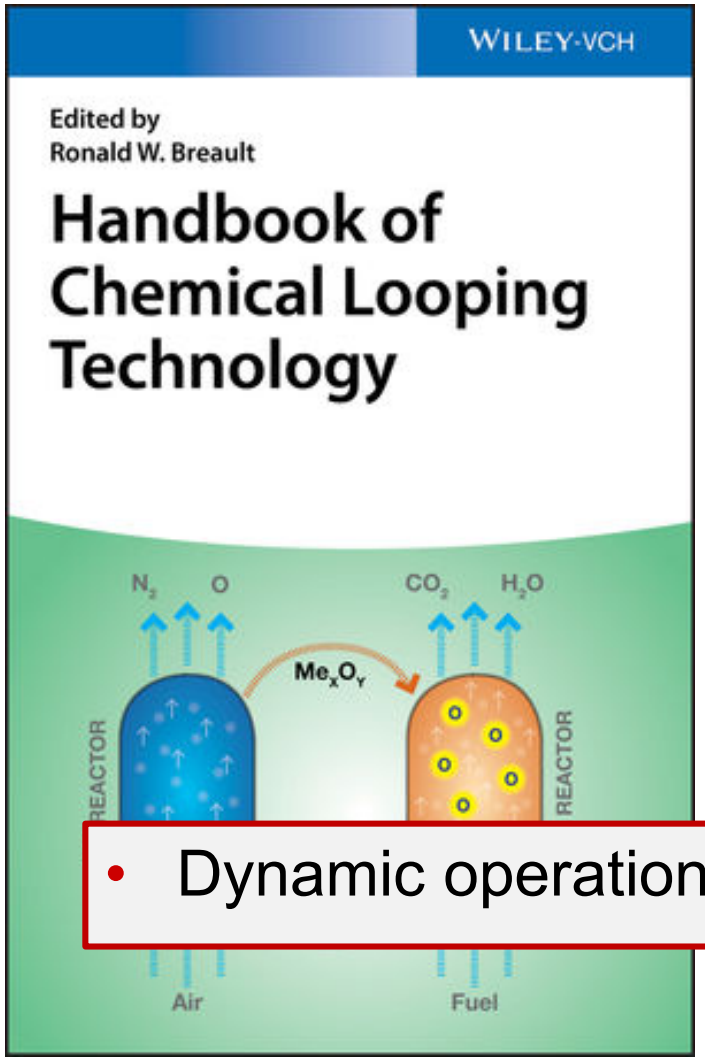


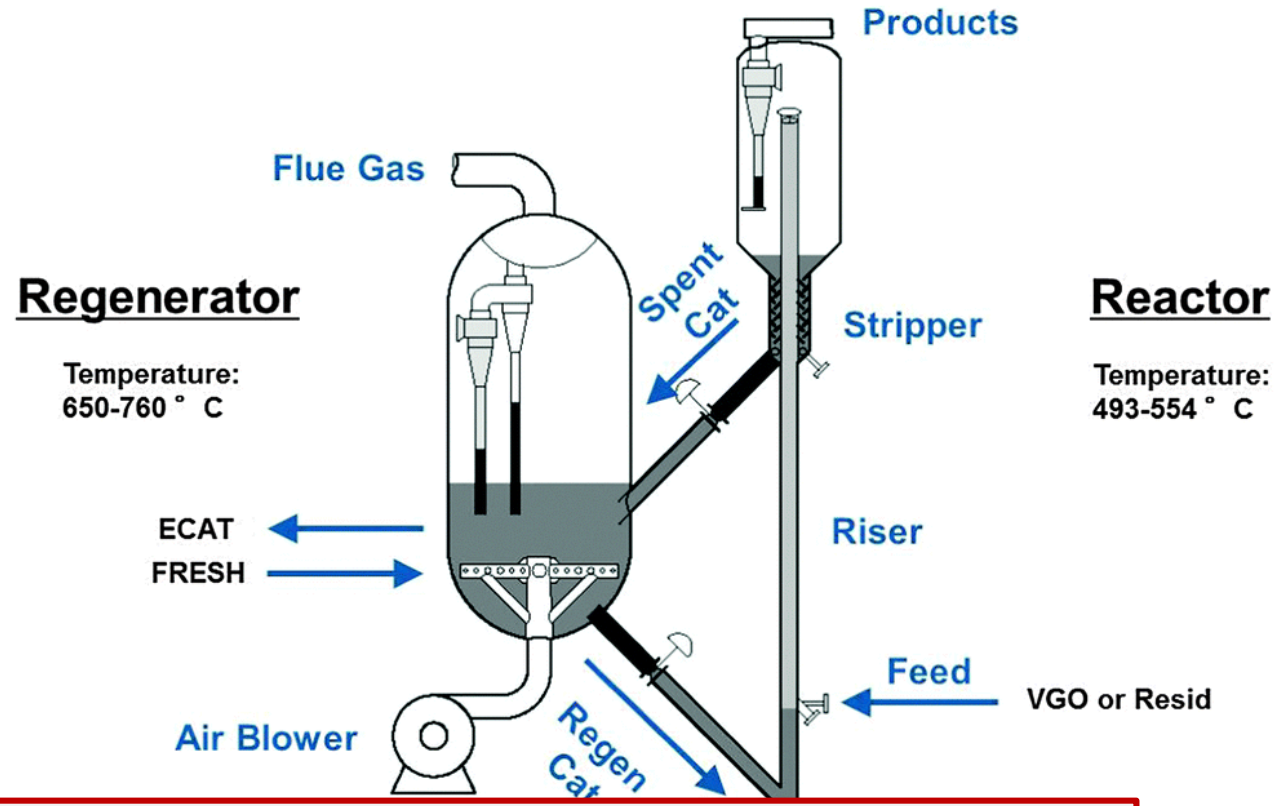


- CH_4 oxidation light-off temperature is substantially reduced when cycling between lean/rich conditions.

Data courtesy of Dr. Harold

Dynamics in catalysis: Intentionally introduced (industrial scale)

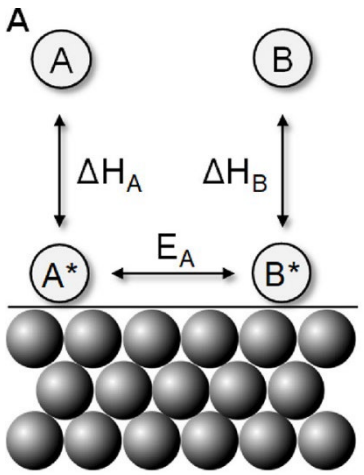


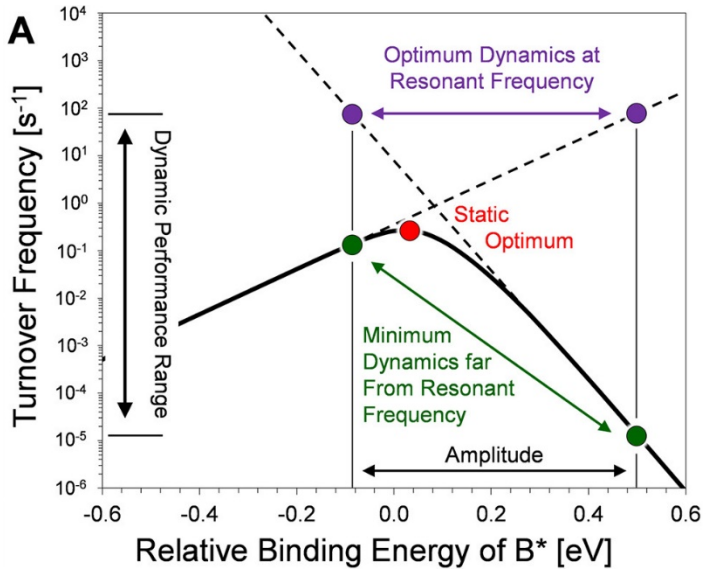


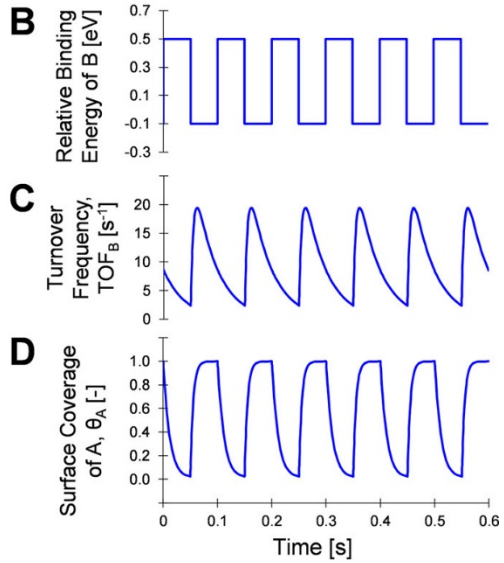
- Dynamic operation at long time scales is already an industrial reality.

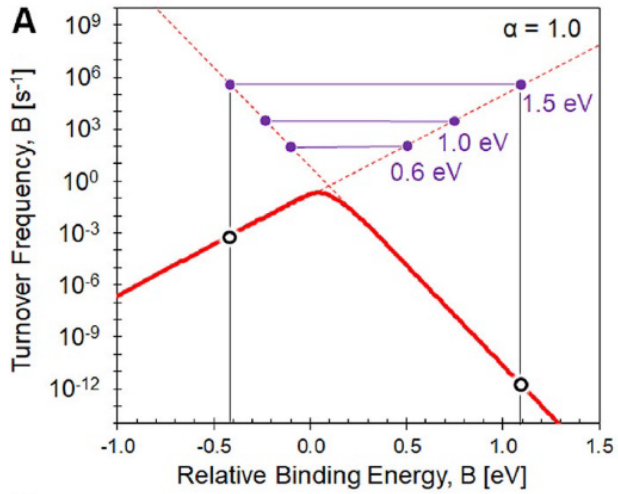
Vogt, E. T. C., Weckhuysen, B. M. *Chem. Soc. Rev.* **44,** 7342–7370 (2015)

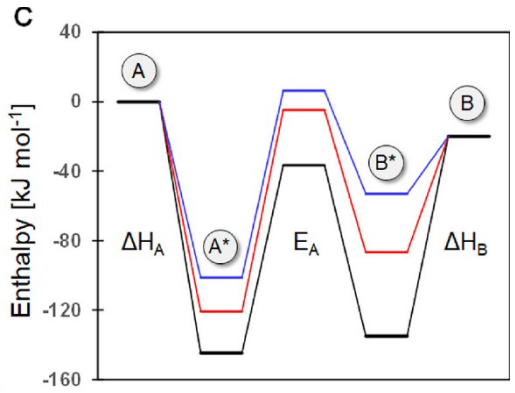
Dynamics in catalysis: Intentionally introduced (atomic scale)?



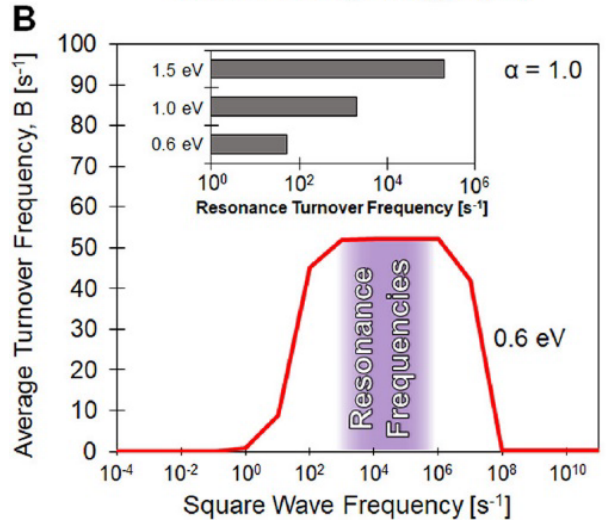








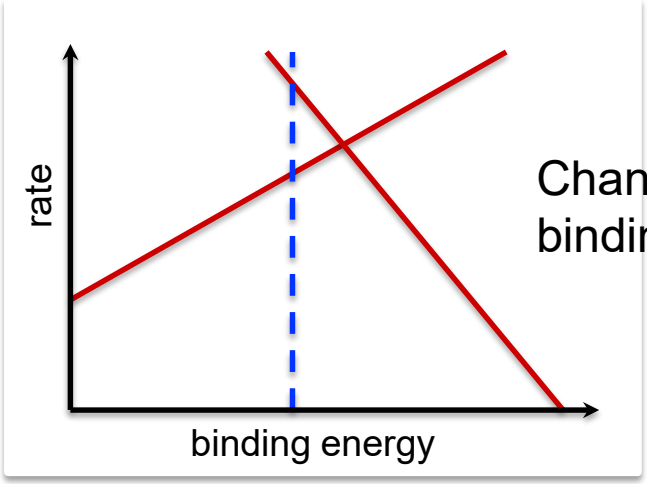
Dynamic Catalysis – The *catalyst binding energy* changes as a square wave below the resonant frequency (*f* = 10 Hz), (D) resulting in maximum and minimum surface coverage of surface intermediates B* and A*; (C) loading and unloading of B from the surface produces transient B production rates.



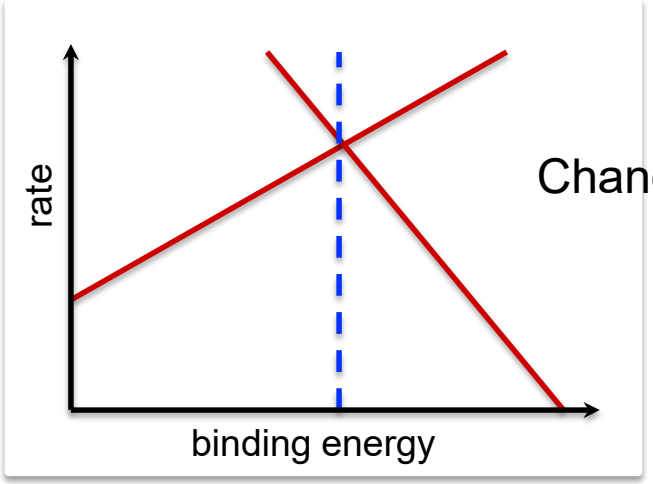
Ardagh, M. A., Abdelrahman, O. A. & Dauenhauer, P. J. *ACS Catal.* **9,** 6929–6937 (2019)

Dynamics in catalysis: Practical opportunities

- Modifying the binding properties of a catalyst at ~10 Hz is challenging
  - Alternating electric fields
  - Mechanical strain
- Changing chemical potentials, i.e. reaction conditions, is more practical
  - Partial pressure variations, pulsing
  - Local heating, fast temperature switching
  - Vibrational excitation by intermittent light exposure, microwaves, etc.



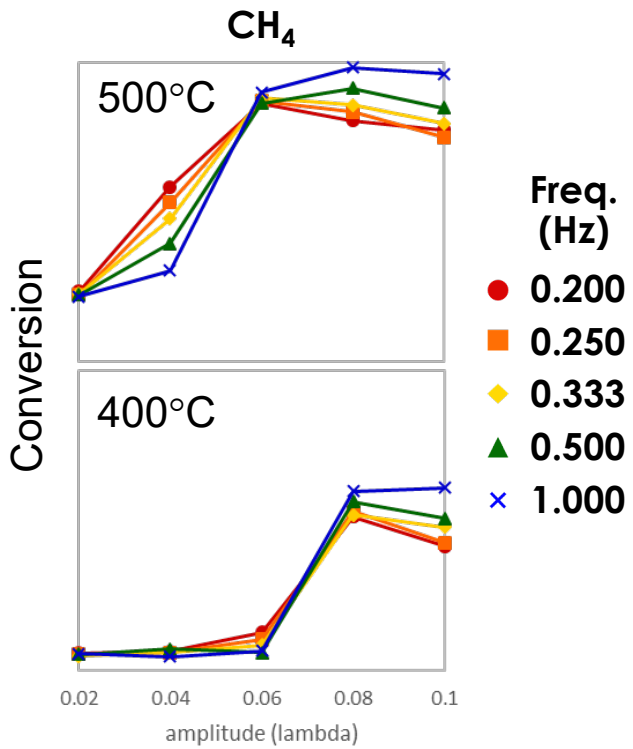
Change in binding energy



Change in $\mu(T,P)$

Transient kinetic characterization

- Need for mathematical framework
  - When is resonance behavior expected?
  - How does the characteristic frequency relate to the temperature-dependent rate constants in the reaction network?
  - Can we use this to identify rate determining steps?
  - Does it relate to the lifetime of transiently formed intermediates or active sites?
- Opportunities for new kinetic characterization approaches
  - Amplitude, frequency modulation at different temperature
  - Characteristic frequencies (*cf*. resonance)
  - Can this be used to determine a turn over frequency without counting or defining active sites?



Courtesy of Dr. Josh Pihl

Outlook

- Time-resolved, transient, dynamic information is much richer and contains mechanistic information that is not available from steady-state data.
- Can provide more rigorous tests and benchmarks for mechanism-based kinetic models.
- Robust kinetic models can span multiple length scales ranging from the atomic scale, over the lab scale to the industrial scale.

Convergence of length scales

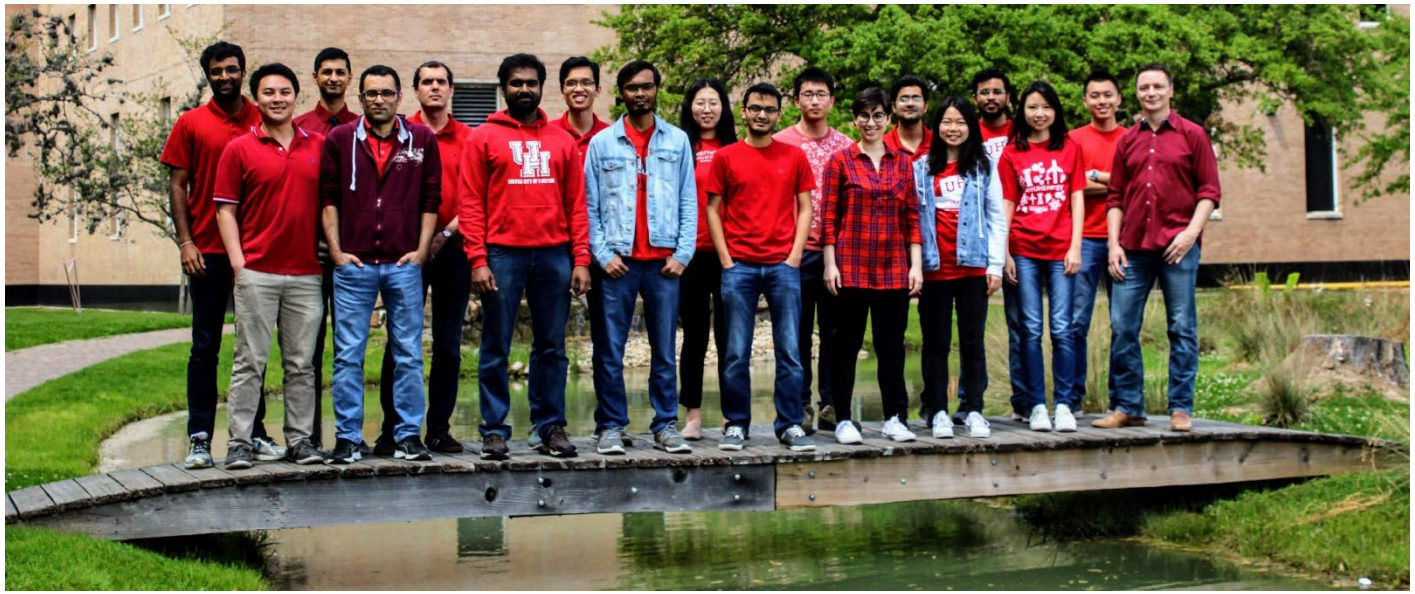
- Dynamic reaction conditions
  - intrinsic to the reaction system;
  - in response to external constraints, or
  - introduced on purpose

offer interesting opportunities.

- Dynamic reaction network analysis
- Increased activity or selectivity
- Attractive for small scale, distributed manufacturing.

Novel mechanistic knowledge with practical relevance

Acknowledgments



Financial Support

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NSF

Computing Resources

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