

# Multiscale Modeling and VLab Overview

## Microkinetics Fundamentals and Applications: *Handling Complexity*

Dion Vlachos

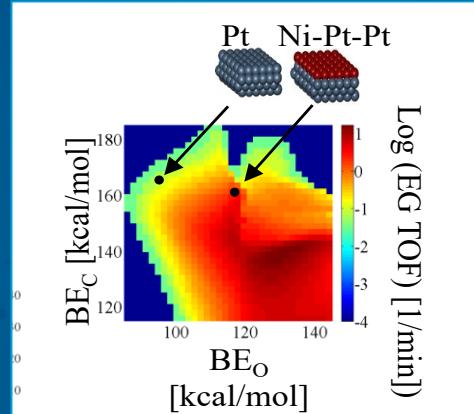
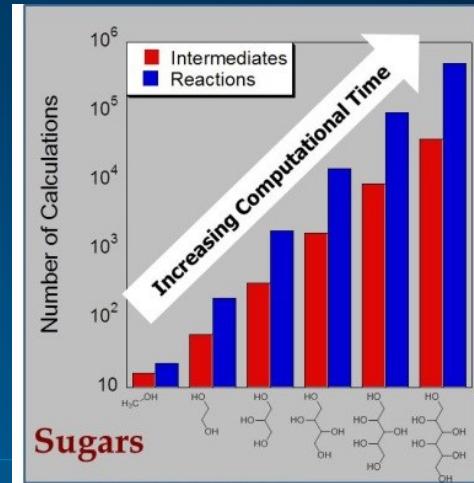
December 11, 2023

University of Delaware

Department of Chemical and Biomolecular Engineering

Center for Catalytic Science and Technology (CCST)

Catalysis Center for Energy Innovation (CCEI)





# New Topics than Previous Workshops

*Previous workshops: NAM 2019, Virtual (Globe) July 2020,  
AIChE/RAPID...*

- Introduction to multiscale modeling (brief)
- Machine learning in the multiscale workflow
- Parameter estimation, similarity, reaction networks, etc.
- Single atom catalysis
- Extensive suite of software tools and advanced database



## Multiscale modeling (brief)



## Empirical kinetic models

Assumptions and limitations



## Formulating a microkinetic model (MKM): Fundamentals

What is an MKM? How do we build it?  
How do we estimate the **reaction rates**?



## Automation and solving MKMs

Mechanism generation  
Efficient, robust simulations



## Analysis of MKMs

What can we learn?



## Other uses of MKMs



# Recommended Reading

- G. R. Wittreich, K. Alexopoulos, and D. G. Vlachos, *Microkinetic Modeling of Surface Catalysis*, in *Handbook of Materials Modeling: Applications: Current and Emerging Materials*, W. Andreoni and S. Yip, Editors. 2020, Springer International Publishing: Cham. p. 1377-1404. [https://doi.org/10.1007/978-3-319-44680-6\\_5](https://doi.org/10.1007/978-3-319-44680-6_5)
- J. E. Sutton and D. G. Vlachos, **Building large microkinetic models** with first-principles' accuracy at reduced computational cost. *Chem. Eng. Sci.* **121**, 190 (2015).
- M. Salciccioli, M. Stamatakis, S. Caratzoulas, and D. G. Vlachos, A review of **multiscale modeling** of metal-catalyzed reactions: Mechanism development for complexity and emergent behavior. *Chem. Eng. Sci.* **66**, 4319–4355 (2011). [DOI:10.1016/j.ces.2011.05.050](https://doi.org/10.1016/j.ces.2011.05.050).
- A. Chatterjee and D. G. Vlachos, An overview of spatial microscopic and accelerated **kinetic Monte Carlo methods**. *Journal of Computer-Aided Materials Design* **14**, 253 (2007).
- D. G. Vlachos, A review of **multiscale analysis**: Examples from systems biology, materials engineering, and other fluid-surface interacting systems. *Adv. Chem. Eng.* **30**, 1 (2005).
- S. R. Deshmukh et al., **From density functional theory to microchemical device homogenization**: Model prediction of hydrogen production for portable fuel cells. *Int. J. Multiscale Comp. Eng.* **2**, 221 (2004).
- S. Raimondeau and D. G. Vlachos, Recent developments on multiscale, **hierarchical modeling** of chemical reactors. *Chem. Eng. J.* **90**, 3 (2002).



## Multiscale modeling (brief)



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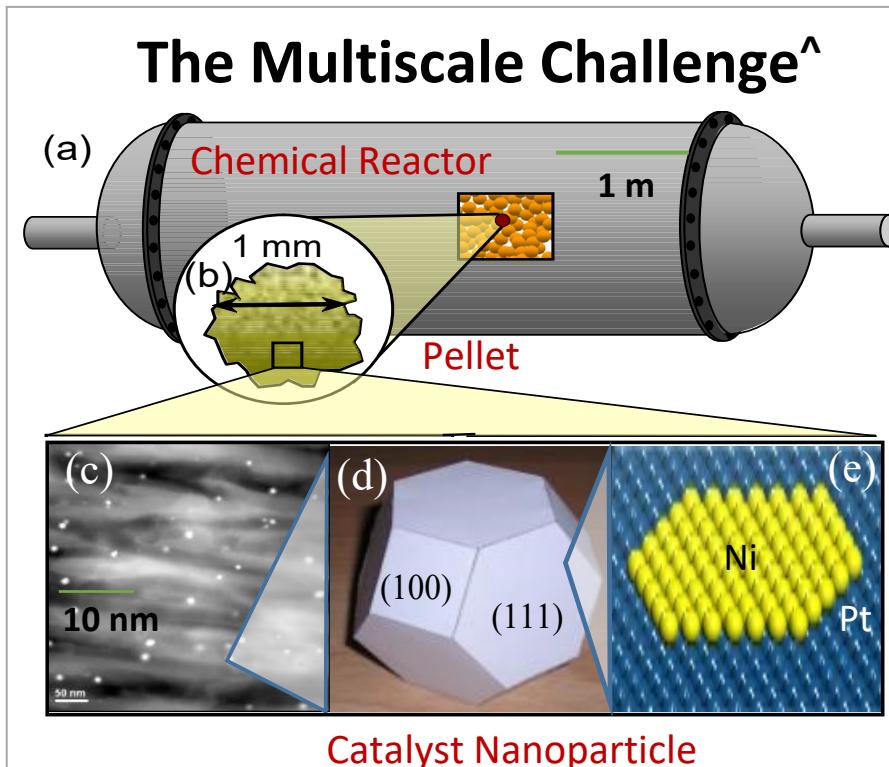
### Other uses of MKMs



# Catalytic Reactors Are Inherently Multiscale

An example of a fixed-bed reactor

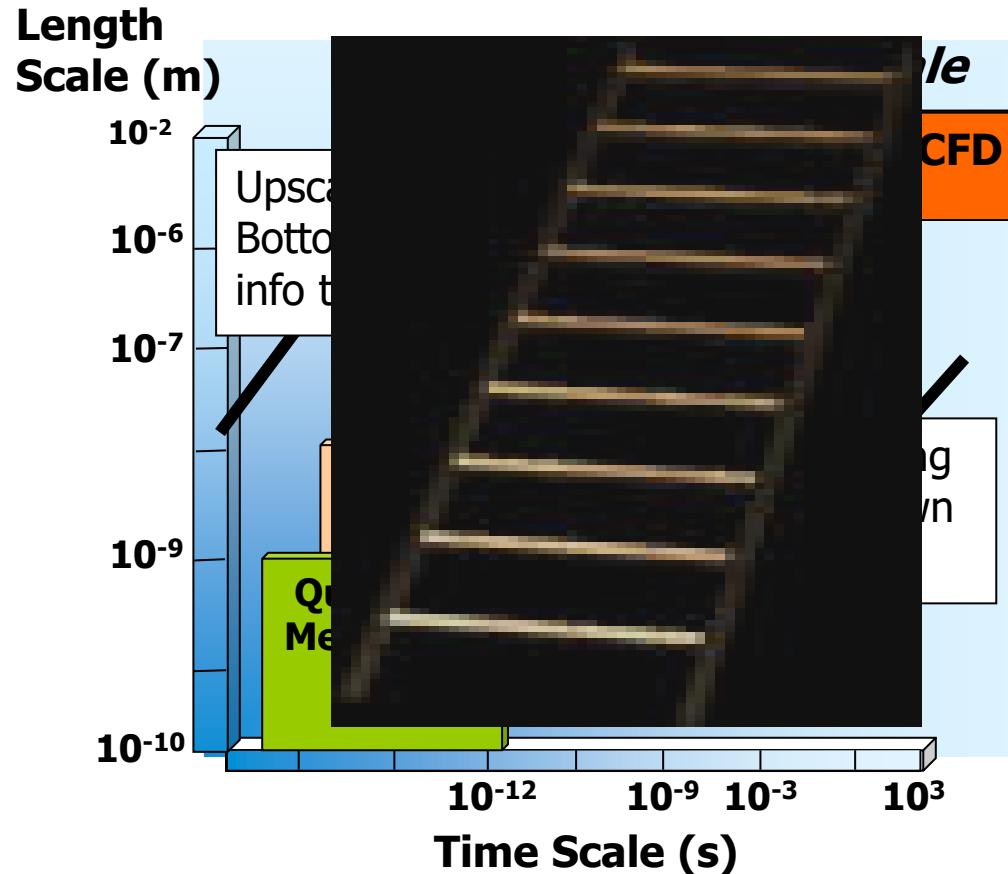
- **Fluid flow, external and internal heat and mass transfer** can be relevant
- **Reactions** typically occur on active sites within pores of materials; fluid chemistry can be relevant, e.g., homogeneous catalysts; side reactions
- **Reaction rates** couple gas (fluid) and solid phases; they are sink/source terms in conservation equations
  - *TOF is not as a good kinetic signature*
- **Kinetic experiments** eliminate flow and transport effects; isothermal
  - Kinetics:  $r = A \exp(-E_{app}/RT) C_A^a C_B^b$
  - *Kinetic signatures: E<sub>app</sub>, a, b contain mechanistic understanding*



<sup>^</sup>Vlachos, *Adv. Chem. Eng.* **30**, 1 (2005).



# Modern Multiscale Simulation Paradigm



- **Multiscale simulation:** Predict macroscopic behavior from first principles (**bottom-up**)
- Model may involve two or more models and scales
- As one goes up the ladder, degrees of freedom are left out (coarse-grained)
- **Top-down:** predict materials with certain macroscopic performance, e.g., high yield

Reviews: *Chem. Eng. J.* **90**, 3 (2002); *Adv. Chem. Eng.* **30**, 1 (2005).

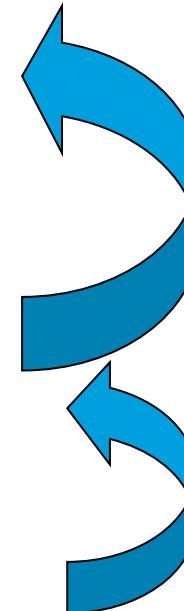


# Summary of Simulators Across Scales

- Macroscopic/Process: Computational fluid dynamics (CFD; OpenFOAM, COMSOL, Fluent/Ansys, etc.), solid mechanics (stress-strain models)
- Mesoscopic models
  - Direct simulation Monte Carlo (Bird)
  - Lattice Boltzmann
  - Brownian dynamics
  - Dissipative particle dynamics
  - Lattice Monte Carlo
- Atomistic or molecular scale models
  - Molecular dynamics, off lattice Monte Carlo
- Electronic structure/quantum (ab initio, DFT, ...)



Constitutive Eqs.  
BCs  
Rates



Paths, equil.  
Properties  
(structure,  
self-  
diffusivity)

PES, E, A



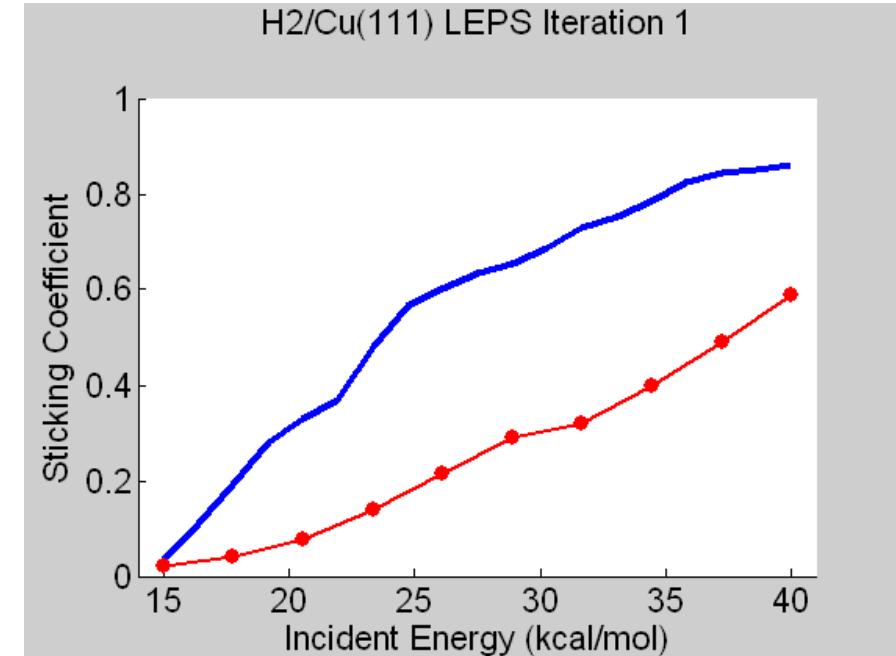
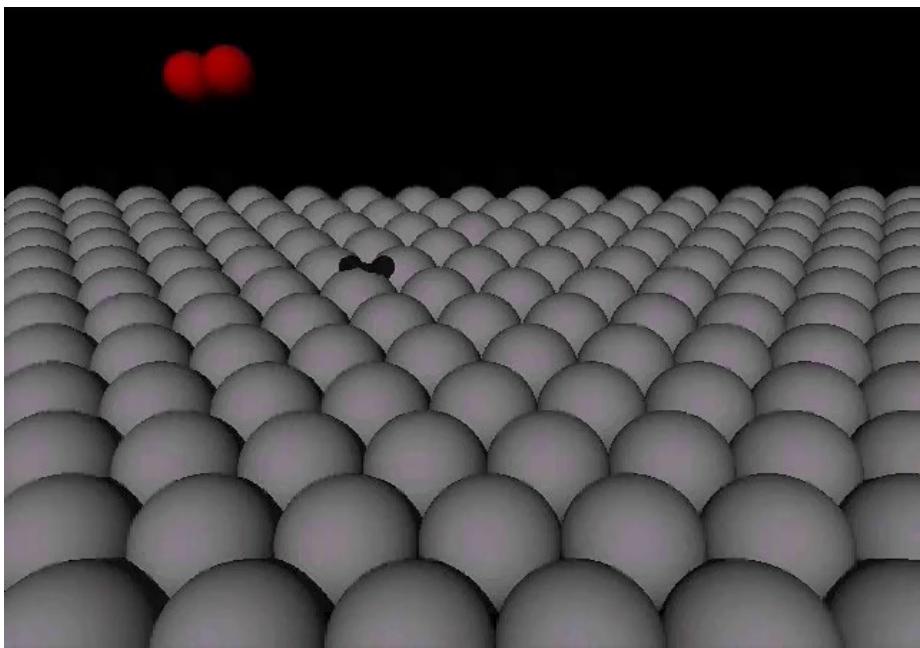
# Coupled Multiscale Simulation Types

- Phenomena and models are strongly coupled; **hybrid modeling merges models of different scales (heterogeneous multiscale modeling** per Weinan E @ Princeton; **tooth gap** model per Kevrekidis @ Hopkins)
  - Models operate over very different scales, so direct coupling is practically impossible
  - Models are often different in nature
    - Stochastic (e.g., MC, BD) vs. deterministic (e.g., ODEs, PDEs, MD)
    - Discrete (MC, MD, etc.) vs. continuum (Langevin, ODEs, PDEs, etc.)
- Develop bridges between models of various scales to enable accurate, efficient, robust, seamless hybrid coupling
  - Need to ensure conservation laws, correct noise passing
- A single model may be inadequate; suitable **coarse-graining** techniques of atomistic and quantum methods are needed
  - Model reduction, correct statistical mechanics, correct dynamics

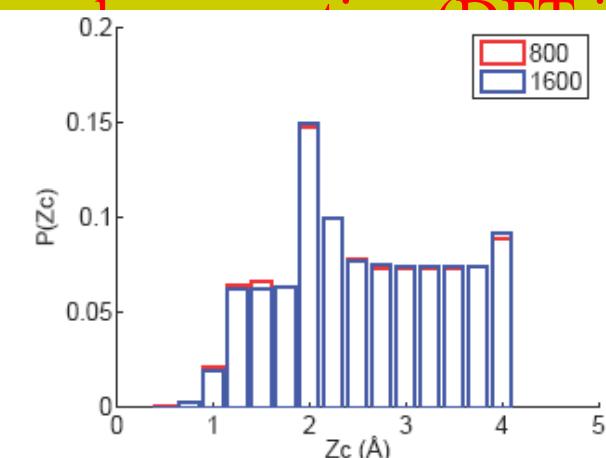


# DFT/MD Hybrid Simulation

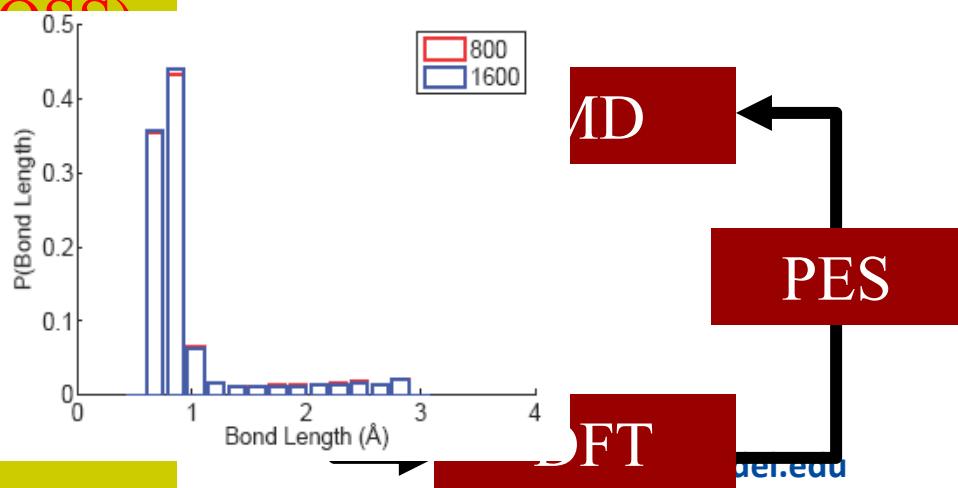
## Reduction of finer scale model



- Time
  - Parame
  - neurall
  - Additio
  - samp
- Ludwig et al.



J. Chem. Phys. 127, 154716-1-16 (2007).





## Multiscale modeling (brief)



## Empirical kinetic models

Assumptions and limitations



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## Other uses of MKMs

# Surface-reaction Rate Models

- Hierarchy of surface reaction rates

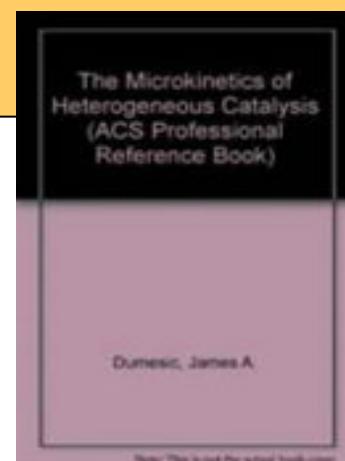
## Overall rates; Engineering Models

Elementary & Overall rates; Academic and Eng!

Empirical rate-law; typically fitted to experimental data

Langmuir-Hinshelwood rate-law; developed using rate determining step (RDS) and MF theory

Microkinetic analysis; No assumptions on RDS (Dumesic, 1993)



## Complexity, Accuracy and Predictability



Kasiraju and Vlachos, LearnCK: mass conserving neural network reduction of chemistry and species of microkinetic models. *React. Chem. Eng.*, In press (2024).  
<http://dx.doi.org/10.1039/D3RE00279A>

Machine learning



# Power Law Rate Expressions

## Global Reaction Rate Expression

- Reaction A+B → Products
- Typical power-low expression (**apparent properties**)

$$r = k_{\text{eff}} C_A^a C_B^b; k_{\text{eff}} = A_{\text{eff}} e^{-E_{\text{eff}}/RT}$$

- The parameters have no obvious physical significance\*
  - Exponents unrelated to stoichiometry
  - Apparent activation energies can be negative
- Prediction is reliable within the given experimental space
  - Can describe overall rate and heat effects
- Simple interpolation models
  - Not good for process optimization
  - Can typically describe only one set of data

\* It may be possible to deduce reduced expressions from MKMs; one can certainly estimate  $E_{\text{app}}$  and reaction orders using MKM and compare to exps

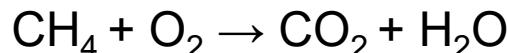


# Empirical Models Considerations

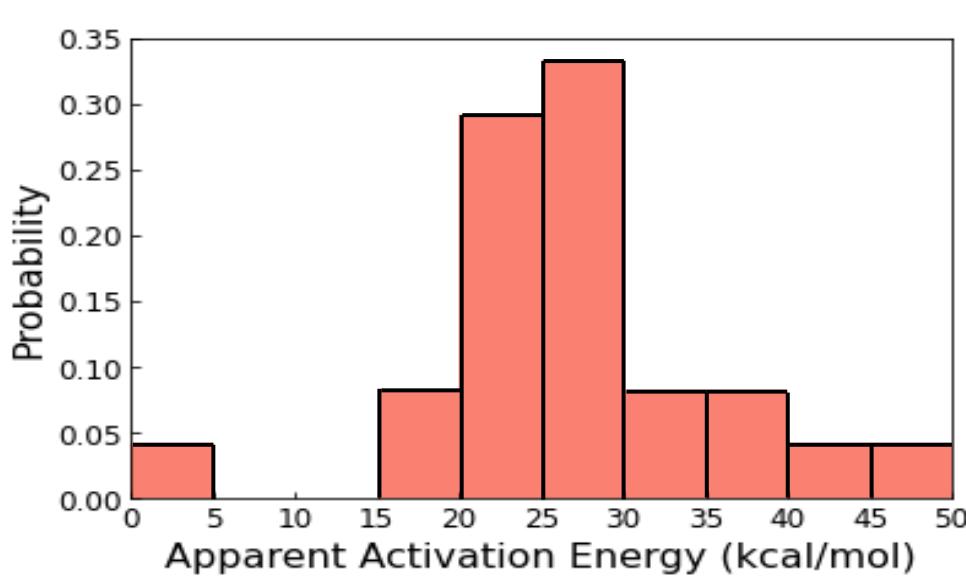
- Overall reactions to consider
  - Ammonia synthesis:  $2\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$ : one overall reaction
  - Methane steam reforming:  $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$ 
    - Water gas shift side reaction in parallel:  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$
    - Dry reforming in parallel:  $\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$
- Data to develop a model
  - How much data do we need? Whose data?
- Accuracy of these models
  - Can we extrapolate for optimization and design?



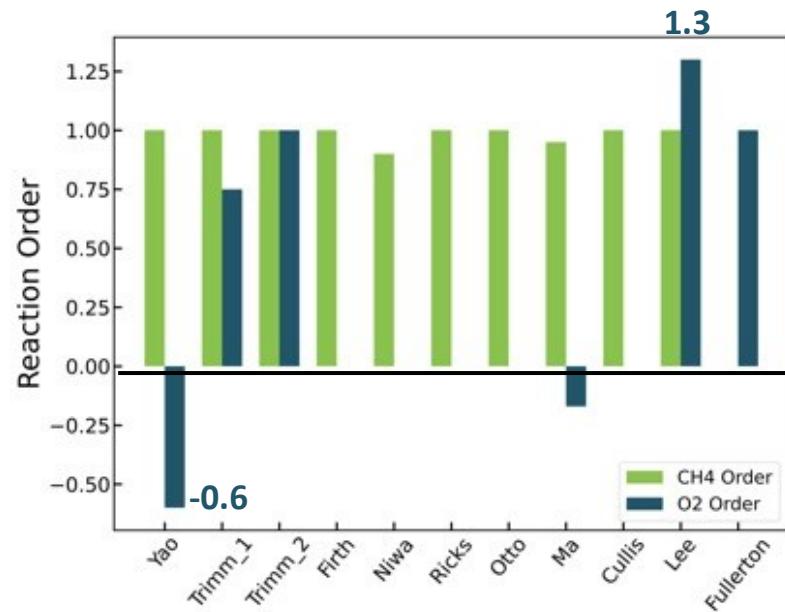
## Experimental Data Collected from the Literature



Data for Fuel-Rich @ 553 K - 823 K on Pt/Al<sub>2</sub>O<sub>3</sub>



## How do we explain the scatter in data?



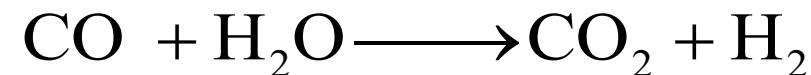
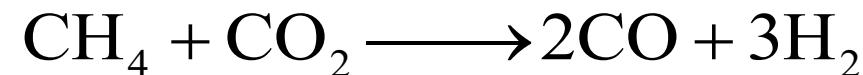
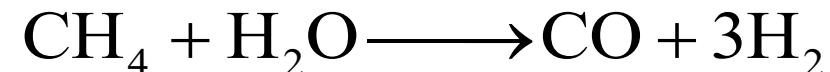
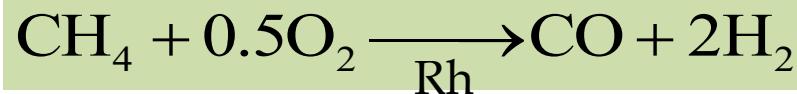
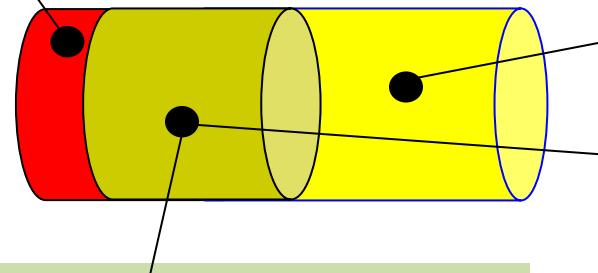
- Hypothesis: **structure sensitivity** plays a critical role
- How do you design the optimal catalyst structure?

# Stratified Partial Oxidation

## What Global Reaction(s) Occur?



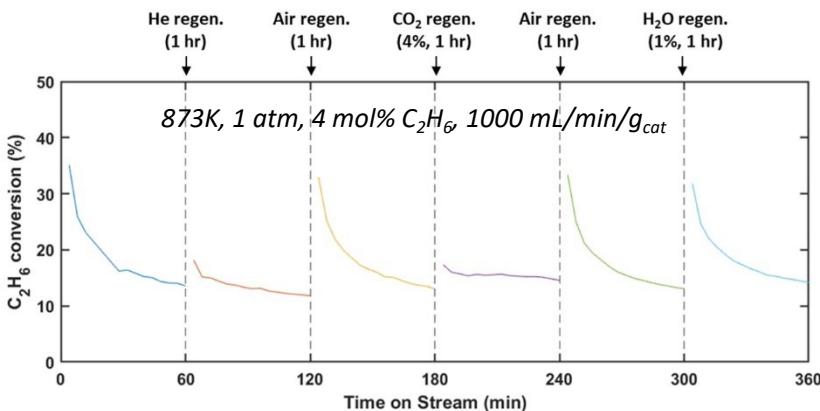
**Short Contact Time Technology of Hichman and Schmidt, 1993**



- Up to three reaction zones
- The extent of combustion vs. mixed mode zone depends on mass transfer
  - No diffusion limitations eliminate the second zone
  - Strong diffusion limitations eliminate the combustion zone
- **PI: Heat integration; in situ steam generation**
- One can control/eliminate hot spot formation

# Identification of Reaction Network from Data: Methodology

- New mechanism to explain catalyst deactivation behavior
  - Gasification:  $\text{H}_2\text{O}$  removes coke
- **Regeneration study confirms  $\text{H}_2\text{O}$  removes coke;  $\text{CO}_2$  does not**

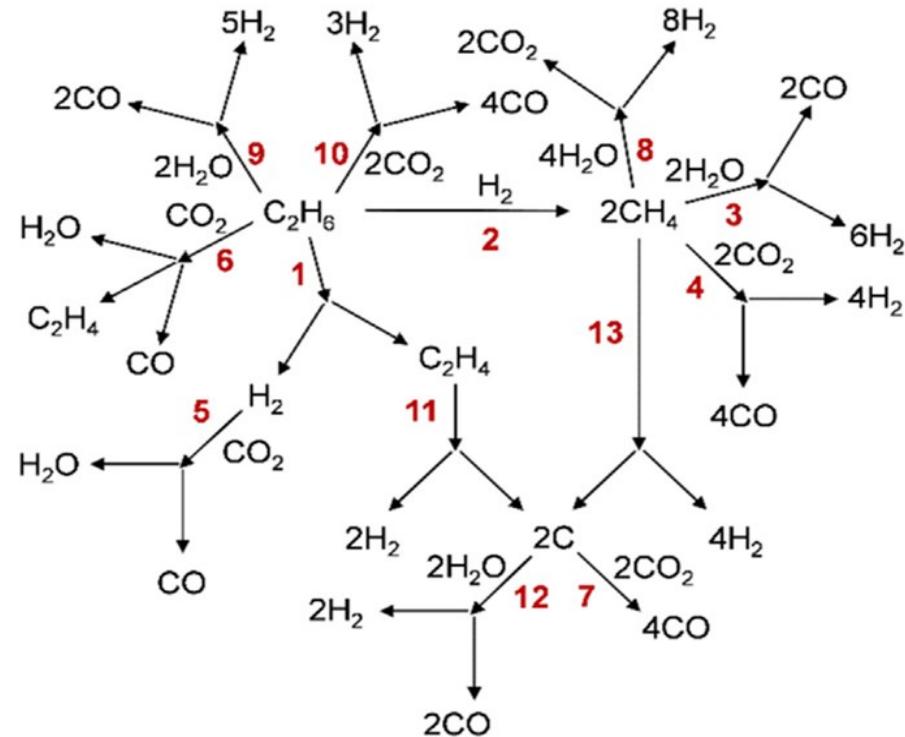


Experiments performed by Dr. Weiqi Chen.

Chen, W.\* , Cohen, M.\* , et al. *Chem. Eng. Sci.* (2021), 237, 116534

Cohen, Max et al., **Active learning of chemical reaction networks** via probabilistic graphical models and Boolean reaction circuits. *React. Chem. Eng.* **8**, 824 (2023).

Ethane oxidative dehydrogenation:  
 $\text{C}_2\text{H}_6 + \text{CO}_2 = \text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{CO}$

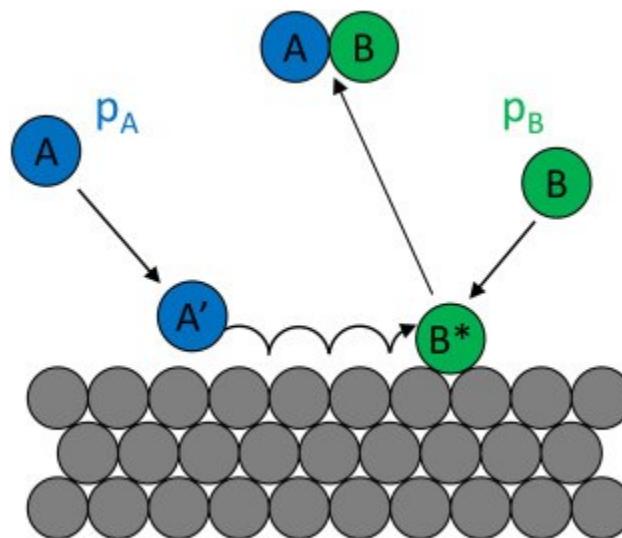


1. Ethane Dehydrogenation
2. Ethane Hydrogenolysis
5. Reverse Water-Gas Shift
- 11, 13. Hydrocarbon Coking
12. Coke gasification via  $\text{H}_2\text{O}$

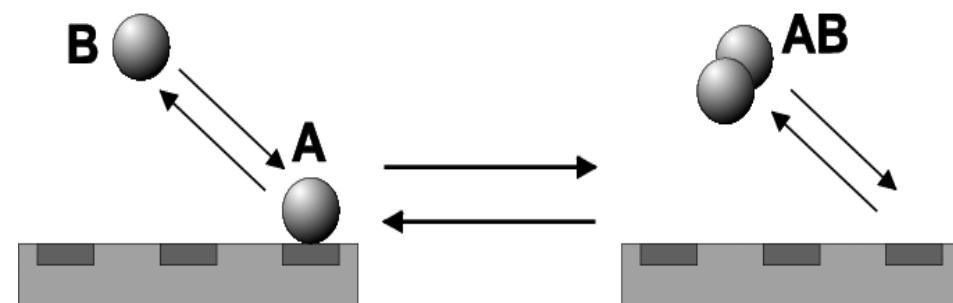
# **Langmuir-Hinshelwood Rate Expressions**

# Type of Elementary Steps

- Adsorption
- Desorption
- Surface diffusion
- Surface reactions
  - Langmuir-Hinshelwood
  - Eley-Rideal
  - Hybrid

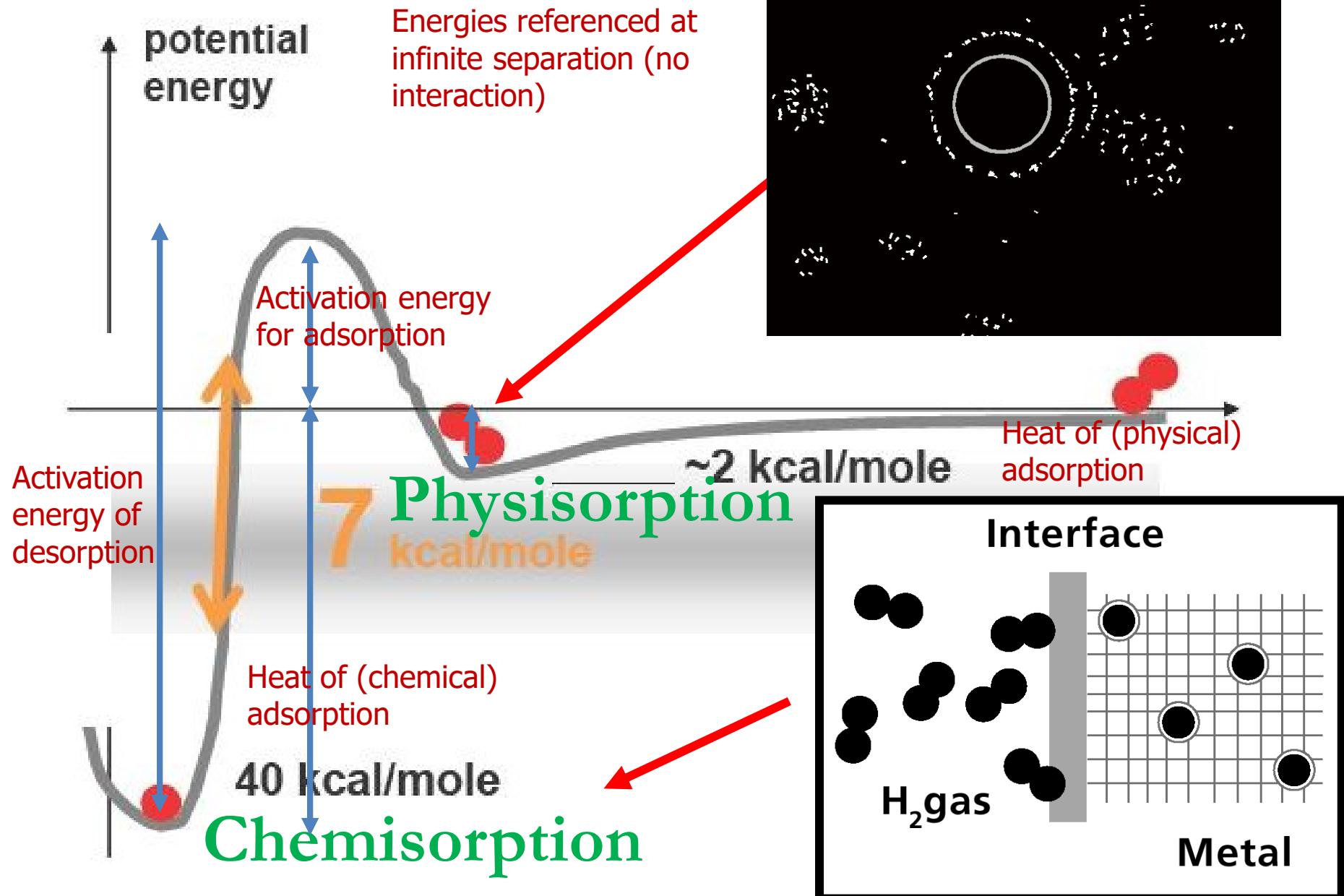


Langmuir–Hinshelwood



Eley-Rideal

# Adsorption Models



# Langmuir Key Assumptions

- All catalyst sites are equivalent
  - Extension to multiple types of sites (e.g., bimetallic, steps and terraces) is possible
- Every site is occupied by one adsorbate only (exclusion principle)
- No interactions between adsorbates
  - Tempkin isotherm can account for interactions
- Number of sites is conserved
  - One site conservation eq. for each type for multiple type of sites
  - Catalyst deactivation reduces the number of sites
- **Eley-Rideal** steps can also be part of a mechanism; they entail one gaseous species and one surface species

# Overview of LH Rate Expressions

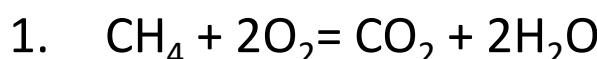
- They describe fundamentally the same elementary reactions as a MKM
- They can capture the change from positive to negative order kinetics (impossible with power law kinetics)
- LH expressions are based on ***a priori assumptions***
  - Typical assumptions: Equilibrated (fast) reactions, rate determining step (RDS), most abundant surface intermediate (MASI)
- Parameters are usually fitted on a limited number of data
- Multiple rate expressions can describe the same data
- Multiple parameters exist for the same rate expression (common optimization issue)
- Even if data is well-fitted, parameters may be unphysical
- LH expressions, even if correct, are limited to a narrow regime and cannot describe changes in RDS, MASI, etc. with operating conditions

# LH Rates on Rh

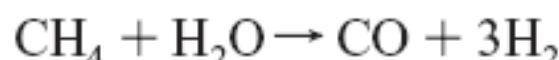


## Overall rxns (hypothesized?)

### 1. *CH<sub>4</sub> total oxidation (combustion)*



### 2. *Steam reforming of CH<sub>4</sub>*



### 3. *CO<sub>2</sub>-reforming of CH<sub>4</sub>*



### 4. *RWGS*



$$r_{TO} = \frac{k_{TO} \cdot P_{CH_4}}{(1 + K_{H,O}^{ads} \cdot P_{H,O})^2}$$

$$r_{SR} = \frac{k_{SR} \cdot P_{CH_4} \cdot (1 - \eta_{SR})}{(1 + K_{O_2}^{ads} \cdot P_{O_2} + K_{CO}^{ads} \cdot P_{CO})^2}$$

$$r_{CO_2-R} = \frac{k_{CO_2-R} \cdot P_{CH_4} \cdot (1 - \eta_{CO_2-R})}{(1 + K_{O_2}^{ads} \cdot P_{O_2} + K_{CO}^{ads} \cdot P_{CO})^2}$$

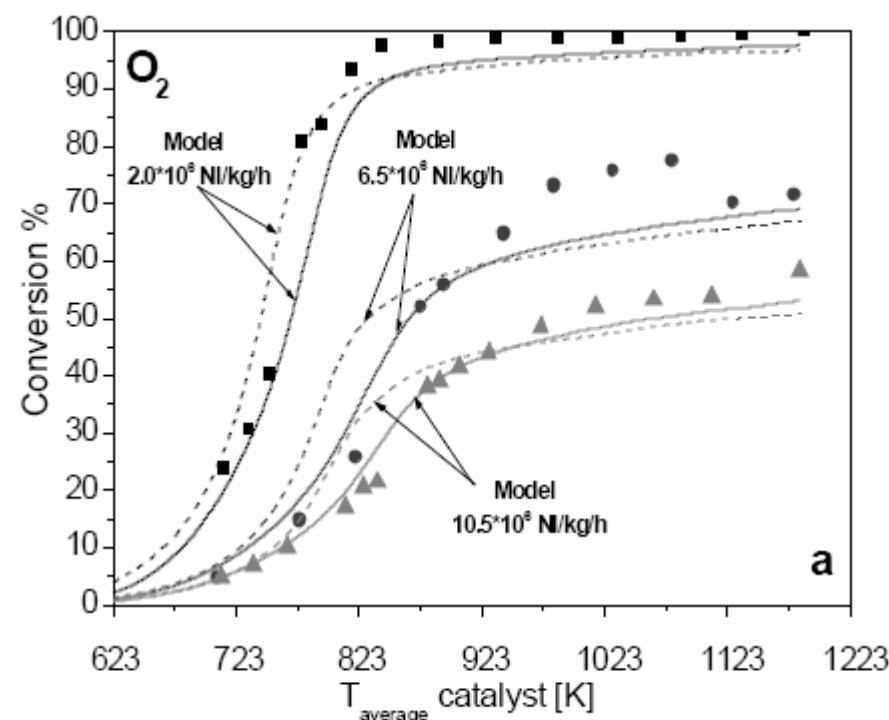
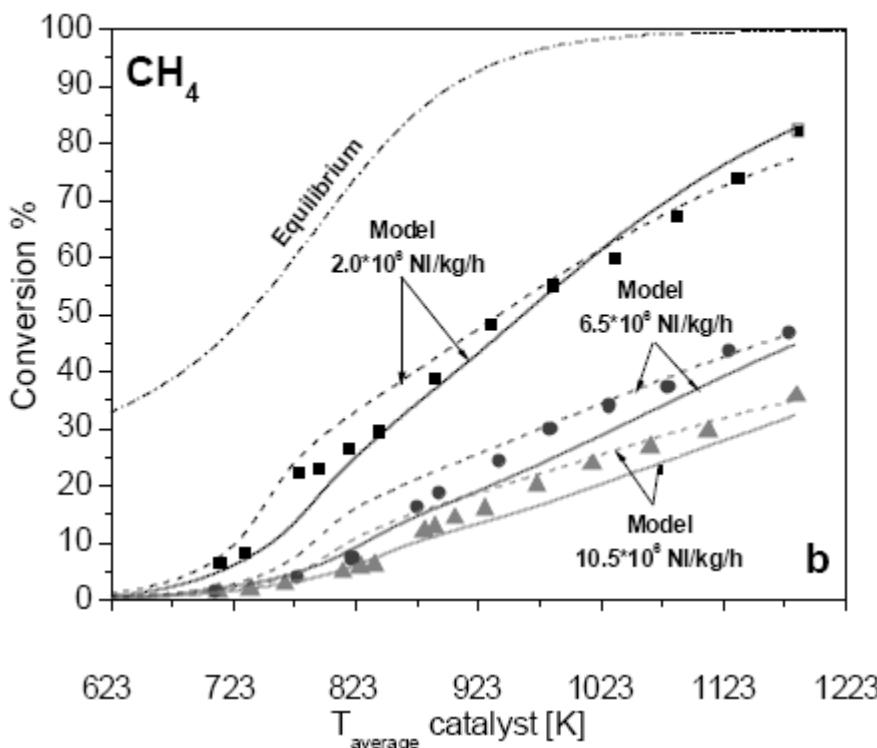
$$r_{RWGS} = \frac{k_{RWGS} \cdot P_{CO_2} \cdot P_{H_2} \cdot (1 - \eta_{RWGS})}{(1 + K_{O_2}^{ads} \cdot P_{O_2} + K_{CO}^{ads} \cdot P_{CO})^2}$$

$\eta$  = distance from equilibrium

This is the "approach to equilibrium" and should be defined mathematically. For  $aA + bB \rightleftharpoons cC + dD$ ,  $\eta = ([C]^c[D]^d)/([A]^a[B]^b)/K_{eq}$ , using instantaneous (non-equil) concentrations in the numerator.  $r = r_{fwd}([A], [B], \dots) - r_{bwd} = k_{fwd} * [A]^a * [B]^b / \{k_{fwd} * [A]^a * [B]^b - k_{bwd} * [C]^c * [D]^d\} = k_{fwd} * [A]^a * [B]^b / \{r_{fwd} / \{k_{fwd} * [A]^a * [B]^b - k_{bwd} * [C]^c * [D]^d\} / \{k_{fwd} * [A]^a * [B]^b * r_{bwd} / \{k_{bwd} * [C]^c * [D]^d\}\} = k_{fwd} * [A]^a * [B]^b * r_{fwd} / \{k_{fwd} * [A]^a * [B]^b - \eta * r_{bwd} / \{k_{bwd} * [C]^c * [D]^d\}$

# Comparison of LH Model to Data

- Process is away from equilibrium
- Model fits data fairly well
- Reactions in series are proposed
- Combustion of syngas is important



dashed lines= model w/o consecutive combustion of CO and H<sub>2</sub>;  
 solid lines= model with consecutive CO and H<sub>2</sub> combustion

## Estimated parameters

Surface adsorption	$K_{\text{ads},j}^{873 \text{ [K]}}$ [atm $^{-1}$ ]	$\Delta H_{\text{ads}}$ [kcal/mol]	species	heat of chemisorption $Q$ (kcal/mol)	selected refs
O <sub>2</sub>	42.53	13.9	O*	100 – 21 $\theta_O$	expts, <sup>50–52</sup> DFT <sup>53–55</sup>
H <sub>2</sub> O	$2.216 \cdot 10^{-1}$	39.5	CO*	38.5 – 17 $\theta_{\text{CO}} - 3.7\theta_H$	expts, <sup>46,56–58</sup> DFT <sup>11,59,60</sup>
CO	15	6.2	CO <sub>2</sub> *	5.2	expts, <sup>61,62</sup> UBI-QEP <sup>63</sup>
			H*	62.3 – 2.5 $\theta_H - 3.7\theta_{\text{CO}}$	expts, <sup>64</sup> DFT <sup>11,53,65–67</sup>
			OH*	70 – 33 $\theta_O + 25\theta_{\text{H}_2\text{O}}$	UBI-QEP, <sup>63</sup> DFT <sup>53,66</sup>
			H <sub>2</sub> O*	10.8 – 4.5 $\theta_{\text{H}_2\text{O}} + 25\theta_{\text{OH}}$	expts, <sup>68</sup> DFT <sup>53,69</sup>
			COOH*	62.2	DFT <sup>17</sup>
			HCOO** (bidentate)	69.2	DFT <sup>17</sup>
			C*	159.0	DFT <sup>17</sup>
			CH*	151.2	DFT (this work)
			CH <sub>2</sub> *	109.3	DFT (this work)
			CH <sub>3</sub> *	42.4	DFT <sup>18</sup>
			CH <sub>4</sub>	6.0	expts <sup>16</sup>
			CH <sub>3</sub> OH*	11.0	expts <sup>21</sup>
			CH <sub>3</sub> O*	35.2	DFT <sup>22</sup>
			CH <sub>2</sub> O*	22.0	DFT <sup>22</sup>
			HCO*	64.7	DFT <sup>22</sup>
			CH <sub>2</sub> OH*	56.4	DFT <sup>22</sup>

➤ *Models may fit but most often than not include unrealistic parameters*

Parameters can be unphysical even if the model describes the data well!



## Multiscale modeling



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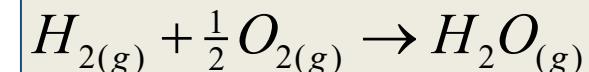
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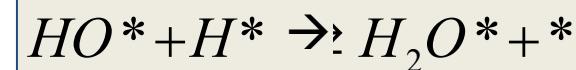
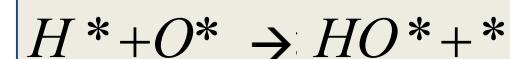
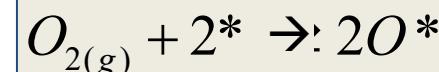
# Microkinetic Modeling

- Includes all relevant elementary reactions
  - Written by hand or computer generated<sup>1</sup>
- No simplifying assumptions re rate determining step (RDS), partial equilibrium (PE), quasi-steady state (QSS), and most abundant surface intermediate (MASI); these are all predicted rather than assumed
- Reactor + Catalyst model needed
  - Use computer software, such as surface CHEMKIN<sup>3</sup>, Cantera<sup>2</sup>, Matlab, Python, OpenMKM

## An example



### Elementary Reactions



<sup>1</sup>Ring: Rangarajan et al., *Computers & Chemical Engineering* **45**, 114 (2012).

<sup>2</sup>Cantera (Matlab Chem Kinetics Package): Goodwin et al., Cantera: An Object-oriented Software Toolkit for Chemical Kinetics, Thermodynamics, and Transport Processes. 2014.

<sup>3</sup>Chemkin (Fortran Chem Kinetics Package): Coltrin; Kee and Rupley, *Int. J. Chem. Kinet.* **23**, 1111 (1991). Coltrin; Kee and Rupley Surface CHEMKIN (Version 4. 0): A Fortran package for analyzing heterogeneous chemical kinetics at a solid-surface---gas-phase interface; SAND-90-8003B; 1991.

Reactor Design (commercial kinetics software); **OpenMKM:** <https://github.com/VlachosGroup/openmkm>

# A Reaction Mechanism

## An Example

### Reaction Mechanism

#### Adsorption/Desorption:

1.  $\text{NH}_3 + * = \text{NH}_3^*$
2.  $\text{N}_2 + * = \text{N}_2^*$
3.  $\text{H}_2 + 2* = 2\text{H}^*$

#### Surface reactions:

4.  $\text{N}_2^* + * = 2\text{N}^*$
5.  $\text{NH}_3^* + * = \text{NH}_2^* + \text{H}^*$
6.  $\text{NH}_2^* + * = \text{NH}^* + \text{H}^*$
7.  $\text{NH}^* + * = \text{N}^* + \text{H}^*$

### Points to Pay Attention

1. Molecular or dissociative adsorption
2. Number of sites involved (for multidente adsorbates)
3. Stoichiometry check
4. Which bonds break and are being made?  
→ **Reaction rule; Reaction family or homologous series (C-H, C-C, C-O)**
5. **Gas-phase species** are involved in rxtr model
6. **Surface species** are in the surface model



# GOVERNING EQUATIONS

# Surface Species Concentration and Surface Reaction Rate

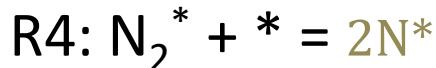
## ➤ Surface species concentration

- Total concentration of sites,  $C_T$  = moles/cm<sup>2</sup>
- Concentration of species k,  $C_k$  = moles/cm<sup>2</sup>
- $\sum(C_k) = C_T$

## ➤ Surface species coverage

- $\theta_k = C_k/C_T$  = molecules/site
  - Coverage of species k = fraction of occupied sites by species k
- $q^*$  = fraction of empty sites
- $\sum(\theta_k) = 1$

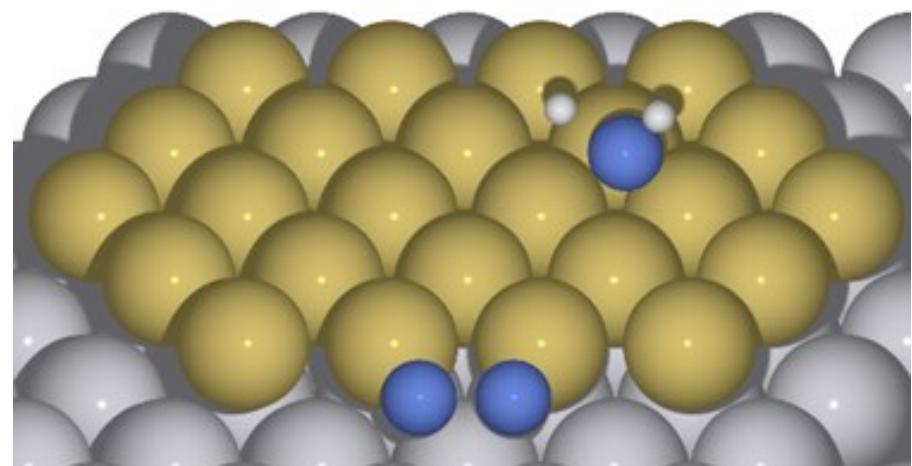
## ➤ Surface reaction rate



Reaction rate:

$$r_4 = k_4 [N_2^*][Pt] \frac{\text{moles}}{\text{cm}^2 \text{s}}$$

$$r_4 = k_4 \theta_{N2} \theta_* \frac{\text{molecules}}{\text{sites}} \rightarrow \text{TOF (turnover frequency)}$$



# Surface Species Balance

## Example



T = 973 K, P = 1 atm, V = 1 cm<sup>3</sup>,  
0.1 g 1%Pt/C catalyst, flow rate = xxx sccm

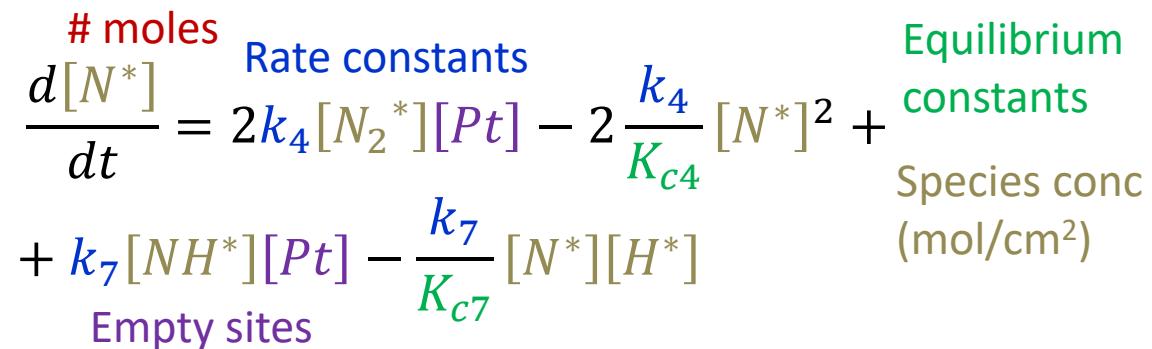
### Adsorption:

1.  $\text{NH}_3 + * \rightleftharpoons \text{NH}_3^*$
2.  $\text{N}_2 + * \rightleftharpoons \text{N}_2^*$
3.  $\text{H}_2 + 2* \rightleftharpoons 2\text{H}^*$

### Surface reactions:

4.  $\text{N}_2^* + * \rightleftharpoons 2\text{N}^*$
5.  $\text{NH}_3^* + * \rightleftharpoons \text{NH}_2^* + \text{H}^*$
6.  $\text{NH}_2^* + * \rightleftharpoons \text{NH}^* + \text{H}^*$
7.  $\text{NH}^* + * \rightleftharpoons \text{N}^* + \text{H}^*$

### Balance for N\* species:



### Parameters needed:

- Forward rate constants  $k$
- Equilibrium constants  $K_c$
- Number of catalytic sites

# Langmuir-Hinshelwood Kinetics

## MF Model for CO Oxidation

- Reactions written as irreversible steps
  - $\text{CO}_2$  forms and directly goes in the gas phase; irreversible
- Units of pre-exp's in  $\text{s}^{-1}$  (or in  $\text{cm}, \text{s}$ , depending on reaction order)

Reactions	$A_0 (\text{s}^{-1}) \text{ or } S_0$	$E_a (\text{kcal/mol})$
1 $\text{CO(g)} + * \rightarrow \text{CO}^*$	$0.84 \cdot 10^0$	0.0
2 $\text{CO}^* \rightarrow \text{CO(g)} + *$	$1.250 \cdot 10^{15}$	34.9
3 $\text{O}_2(\text{g}) + 2* \rightarrow 2\text{O}^*$	$0.06 \cdot 10^0$	0.0
4 $2\text{O}^* \rightarrow \text{O}_2(\text{g}) + 2*$	$1.000 \cdot 10^{13}$	51.0
5 $\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2(\text{g}) + 2*$	$1.645 \cdot 10^{14}$	24.1

$$\frac{d\theta_{\text{CO}^*}}{dt} = k_{\text{CO}}^a P_t y_{\text{CO}} \theta_* - k_{\text{CO}}^d \theta_{\text{CO}^*} - k^r \theta_{\text{CO}^*} \theta_{\text{O}^*}$$

$$\frac{d\theta_{\text{O}^*}}{dt} = 2k_{\text{O}_2}^a P_t y_{\text{O}} \theta_*^2 - 2k_{\text{O}_2}^d \theta_{\text{O}^*}^2 - k^r \theta_{\text{CO}^*} \theta_{\text{O}^*}$$

$$\theta_{\text{CO}^*} + \theta_{\text{O}^*} + \theta_* = 1$$

SS, one nonlinear model (after some algebra):

$$0 = 2k_{\text{O}_2}^a P_t y_{\text{O}} [1 - k_{\text{CO}}^a P_t y_{\text{CO}} (1 - \theta_{\text{O}^*}) / (k_{\text{CO}}^a P_t y_{\text{CO}} + k_{\text{CO}}^d + k^r \theta_{\text{O}^*}) - \theta_{\text{O}^*}]^2$$

$$- 2k_{\text{O}_2}^d \theta_{\text{O}^*}^2 - k^r k_{\text{CO}}^a P_t y_{\text{CO}} (1 - \theta_{\text{O}^*}) \theta_{\text{O}^*} / (k_{\text{CO}}^a P_t y_{\text{CO}} + k_{\text{CO}}^d + k^r \theta_{\text{O}^*})$$

$y_k$  = the mole fraction of gaseous species k

$k_i$  = rate constant of the i-th step

All steps are taken to be elementary

Rate constants are in TOF units

# I. Elementary Reaction Rate (Mass Action Kinetics)

- Rate of elementary reaction (forward)

$$K_s \sum_{k=1}^{K_s} v_{ik} A_k = 0$$

$$r_i = k_i \prod_{k=1, v_{ik} < 0}^K C_k^{-v_{ik}} \quad \left[ \frac{\text{gmol}}{\text{cm}^2 \text{s}} \right]$$

$$\tilde{r}_{fi} = r_{fi}/C_T = \tilde{k}_{fi} \prod_{k=1, v_{ik} < 0}^K \theta_k^{-v_{ik}} \quad \left[ \frac{\text{molecules}}{\text{site s}} \right]$$

- Reversible (net) rxn rate,  $r_i = r_i^f - r_i^b$

- $k_i^b = k_i^f / K_i \rightarrow$  Thermo Consistency at the elementary rxn level

- $k_i$  = rate const. of elementary rxn  $i$
- $C_j(\theta_j)$  = Concentration (coverage) of surface species  $j$
- $v_{ji}$  = stoichiometric coef. in elementary rxn  $i$

- Units

- Concentrations [mols/cm<sup>2</sup> of active catalyst phase], rate const.  $k$  [cm, mol, s], rate [moles/cm<sup>2</sup>/s]
- Coverage (molecules per site), rate const.  $k$  [s<sup>-1</sup>], rate [mlcs/site/s] or TOF

$$r_i = k_{fi} \prod_{k=1, v_{ik} < 0}^K C_k^{-v_{ik}} - k_{bi} \prod_{k=1, v_{ik} > 0}^K C_k^{v_{ik}}$$

$$\tilde{r}_i = \tilde{k}_{fi} \prod_{k=1, v_{ik} < 0}^K \theta_k^{-v_{ik}} - \tilde{k}_{bi} \prod_{k=1, v_{ik} > 0}^K \theta_k^{v_{ik}}$$

## II. Rate of Surface and Gaseous Species

- Chemical rxn among  $K_s$  species
- Species rate of production (or consumption); it has sign
- Estimate rate of surface species *and* gas species\*

$$\sum_{k=1}^{K_s} v_{ik} A_k = 0$$

$$\sigma_k = \sum_{i=1}^{N_r} v_{ik} r_i \quad \left[ \frac{\text{gmol}}{\text{cm}^\zeta \text{s}} \right]$$

$$\tilde{\sigma}_k = \sum_{i=1}^{N_r} v_{ik} \tilde{r}_i \quad \left[ \frac{\text{mlcs}}{\text{site s}} \right]$$

$\zeta = 3$   
for homogeneous rxns

$\zeta = 2$   
for heterogeneous rxns

Turnover Frequency (TOF)  
for heterogeneous rxns

- \* Gas species are involved only in adsorption, desorption, ER rxns, and possible gas rxns

## III.A Surface Species Conservation Model<sup>&</sup>

Coverage=fraction of occupied sites,  $\theta_k = C_k / C_T$

(1) Site conservation**	$\sum_{k=1}^{K_s} C_k = C_T$ $\left[ \frac{gmol}{cm^2} \right]$	$\sum_{k=1}^{K_s} \theta_k = 1$ $\left[ \frac{molecule}{site} \right]$
(2a) Species conservation (diffusion-reaction)*	$\frac{\partial C_k}{\partial t} = D_k \nabla^2 C_k + \sigma_k \left[ \frac{gmol}{cm^2 s} \right]$	$\frac{\partial \theta_k}{\partial t} = D_k \nabla^2 \theta_k + \tilde{\sigma}_k \left[ \frac{molecules}{site s} \right]$
(2b) Mean field Eqs.  ODEs	$\frac{dC_k}{dt} = \sigma_k \left[ \frac{gmol}{cm^2 s} \right]$	$\frac{d\theta_k}{dt} = \tilde{\sigma}_k \left[ \frac{molecules}{site s} \right]$
(2c) Steady-state $k=1, \dots, K_s$	$\theta = \sigma_k$  Algebraic eqs.	$0 = \tilde{\sigma}_k$

\* Fickian diffusion; not valid for interacting species

\*\* In the limit of fast diffusion, one can show that the site conservation can be replaced with a rate eq. for vacancies

& DAEs if site balance is used; ODEs if all species and vacancies are solved as time dependent rate eqs; algebraic eqs if steady state problem is solved

# Surface Science Models (No Fluid Model)

- TPD in UHV: desorption upon heating the crystal
  - No (re)adsorption unless at high P (not UHV); time dependent; initial coverages are needed
  - No fluid phase model is solved
  - $dT/dt = \beta$ , an ODE is added
- Molecular beam experiments: Gaseous species flux is fixed (specified in exp)  $\rightarrow P_{\text{gas species}} = \text{fixed}$ 
  - No fluid phase model is solved; adsorption happens

## III.B Fluid Phase (Reactor) Conservation Model

- This is for **gas-phase species**, i.e., for  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2$  in this example
- $\hat{\sigma}$  = adsorption-desorption of **gaseous species**: accounts for reactants, products, and intermediates (radicals) when adsorbed and desorbed; *NOT applicable to surface species (see Model III.A)*

$$\rho \frac{\partial \bar{\omega}}{\partial t} + \rho \mathbf{u} \cdot \nabla \bar{\omega} = -\nabla \cdot \hat{\mathbf{J}} + \hat{\sigma}$$

### Reaction Mechanism

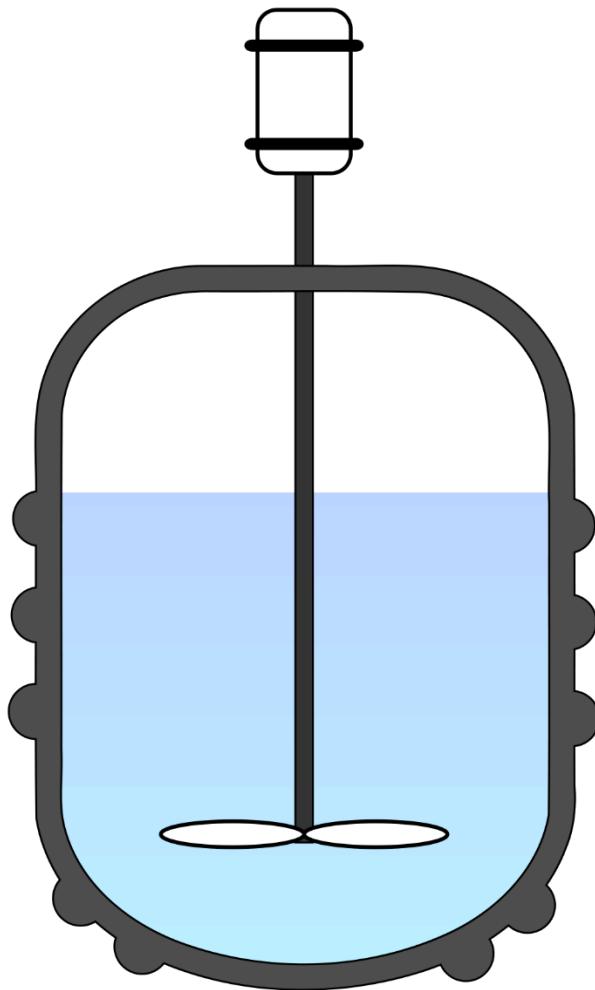
#### Adsorption/Desorption:

1.  $\text{NH}_3 + * = \text{NH}_3^*$
2.  $\text{N}_2 + * = \text{N}_2^*$
3.  $\text{H}_2 + 2* = 2\text{H}^*$

#### Surface reactions:

4.  $\text{N}_2^* + * = 2\text{N}^*$
5.  $\text{NH}_3^* + * = \text{NH}_2^* + \text{H}^*$
6.  $\text{NH}_2^* + * = \text{NH}^* + \text{H}^*$
7.  $\text{NH}^* + * = \text{N}^* + \text{H}^*$

# Batch Reactor Balances



## Mass Balance

$$\frac{dm_k}{dt} = \dot{\omega}_k W_k V$$

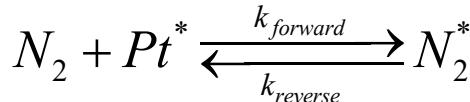
$$\frac{dY_k}{dt} = \frac{\dot{\omega}_k W_k}{\rho}$$

$$Y_k = \frac{m_k}{\sum_k m_k} = \frac{m_k}{m}$$

## Energy Balance

$$\rho c_p \frac{dT}{dt} = - \sum_{k=1}^K h_k \dot{\omega}_k W_k + \frac{\hat{h}A}{V} (T_{ext} - T)$$

## Example (Only Ads, Des, and ER Steps for Gaseous Species)



$$\dot{\omega}_{N_2^*} =$$

$$(k_{forward} [N_2] [Pt^*] - k_{reverse} [N_2^*])$$

# Rate Const. and Pre-exp Conversion Units

Table 5: Multiplication factors of rate constant and pre-exponential from  $\left[ \frac{\text{mlcs}}{\text{site s}} \right]$  into other units. Note that for  $\tilde{C}_T \sim 10^{15}$  [sites/cm<sup>2</sup>],  $C_T \sim 10^{-9}$  [gmoles of sites/cm<sup>2</sup>].

Rate	$\tilde{r}_{fi} = \tilde{k}_{fi} \prod_{k=1, v_{ik} < 0}^K \theta_k^{-v_{ik}}$	$r_{fi} = k'_{fi} \prod_{k=1, v_{ik} < 0}^K \theta_k^{-v_{ik}}$	$r_{fi} = k_{fi} \prod_{k=1, v_{ik} < 0}^K C_k^{-v_{ik}}$
Units of rate	$\left[ \frac{\text{mlcs}}{\text{site s}} \right]$	$\left[ \frac{\text{gmol}}{\text{cm}^2 \text{ s}} \right]$	$\left[ \frac{\text{gmol}}{\text{cm}^2 \text{ s}} \right]$
Variable	Coverages	Coverages	Concentrations
Rate constant	$\tilde{k}_{fi} \left[ \frac{\text{mlcs}}{\text{site s}} \right]$	$k'_{fi} \left[ \frac{\text{gmol}}{\text{cm}^2 \text{ s}} \right]^1$	$k_{fi} \frac{1}{\text{s}} \left[ \frac{\text{cm}^2}{\text{gmol}} \right]^{v_{ti}-1}$
Multiplication factor from TOF [mlcs, site, s] to [gmol, cm, s]	Unimolecular reactions, $v_{ti} = 1$	$C_T$	1
	Bimolecular reactions, $v_{ti} = 2$	$C_T$	$C_T^{-1}$

<sup>1</sup> Input units of Surface Chemkin: [1]. Surface Chemkin is a software that models complex surface kinetics. It is an ideal tool for microkinetic modeling.

# Summary of Catalyst and Reactor Models

Catalyst/ Reactor	Chemistry	Experiment/ Operation	Model	Solution method (Matlab)
Single crystal	Surface	Molecular beam; Steady state	$(1) \frac{d\theta_k}{dt} = \tilde{\sigma}_k = 0, k=1, \dots, K_s-1$ $(2) \sum_{k=1}^{K_s} \theta_k = 1$	Nonlinear algebraic solver, e.g., Newton, (fsolve)
Single crystal	Surface	TPD, TPR; Transient Note: species often in QSS	$(1) \frac{d\theta_k}{dt} = \tilde{\sigma}_k = 0, k=1, \dots, K_s-1$ $(2) \sum_{k=1}^{K_s} \theta_k = 1 \text{ or } \frac{d\theta_*}{dt} = - \sum_{k=1, k \neq *}^{K_s} \frac{d\theta_k}{dt}$ $(3) \frac{dT}{dt} = \beta$	ODE solver (ODE15s) or differential-algebraic solver, e.g., DDASL [7, 8]
Fixed bed	Fluid and/or surface	Steady	<p>No internal and external transport; Isothermal:</p> <p><u>Gas-phase</u></p> $(1) \frac{dW_k}{dz} = \frac{(\sigma_k^{\text{fluid}} + \sigma_k^{\text{surf}}) \underline{a} M_k}{\rho u}, k=1, \dots, K_g$ $\sigma_k^{\text{surf}} = v_{\text{ads}} I_{\text{ads},k} + v_{\text{des}} I_{\text{des},k}$ <p>typically: <math>v_{\text{ads}} = -1, v_{\text{des}} = 1</math> (net rate of consumption)</p> <p><u>Surface</u></p> $(2) \tilde{\sigma}_k = 0, k=1, \dots, K_s-1$ $(3) \sum_{k=1}^{K_s} \theta_k = 1$	Differential-algebraic solver, e.g., DDASL [7, 8]

# Summary of Catalyst and Reactor Models

CSTR (simplified version of fluidized bed)	Fluid and/or surface	Steady	No internal and external transport; Isothermal: <u>(1) Gas-phase</u> $\frac{dW_k}{dt} = 0 = \frac{W_k^o - W_k}{\tau(\rho/\rho^o)} + \frac{(\sigma_k^{\text{fluid}} + \sigma_k^{\text{surf}} \underline{a})M_k}{\rho}$ or $\frac{dW_k}{dt} = 0 = \frac{W_k^o - W_k}{\tau_m} + \frac{(\sigma_k^{\text{fluid}} + \sigma_k^{\text{surf}} \underline{a})M_k}{\rho},$ $k=1, \dots, K_g$  <u>Surface</u> <u>(2) <math>\tilde{\sigma}_k = 0, k=1, \dots, K_s-1</math></u> <u>(3) <math>\sum_{k=1}^{K_s} \theta_k = 1</math></u>	Nonlinear algebraic solver, e.g., Newton, (fsolve)
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# Notation

$y_k$  mass fraction of species k in the gas-phase

$z$  denotes the length of a PFR

$A_c$  is the area of the catalyst

$V_r$  is the volume of the reactor

$M_k$  is the molecular weight of species k

$\rho$  is the density of the mixture

$u$  is the velocity of the mixture

$K_g$  is the total number of gas-phase species

$K_s$  is the total number of surface species including vacancies

$\rho u$  represents the mass flux that is constant at every cross section of the PFR

$\theta_k$  is the coverage of species k

$t$  denotes the time

T is the temperature

$\sigma_k$  is the net surface rate of species k

$\omega$  is the site density

$\beta$  is the ramp rate

$\tau_m = m/\dot{m}$  is the mass-based residence time ( $m$  is mass and  $\dot{m}$  is mass flow rate)

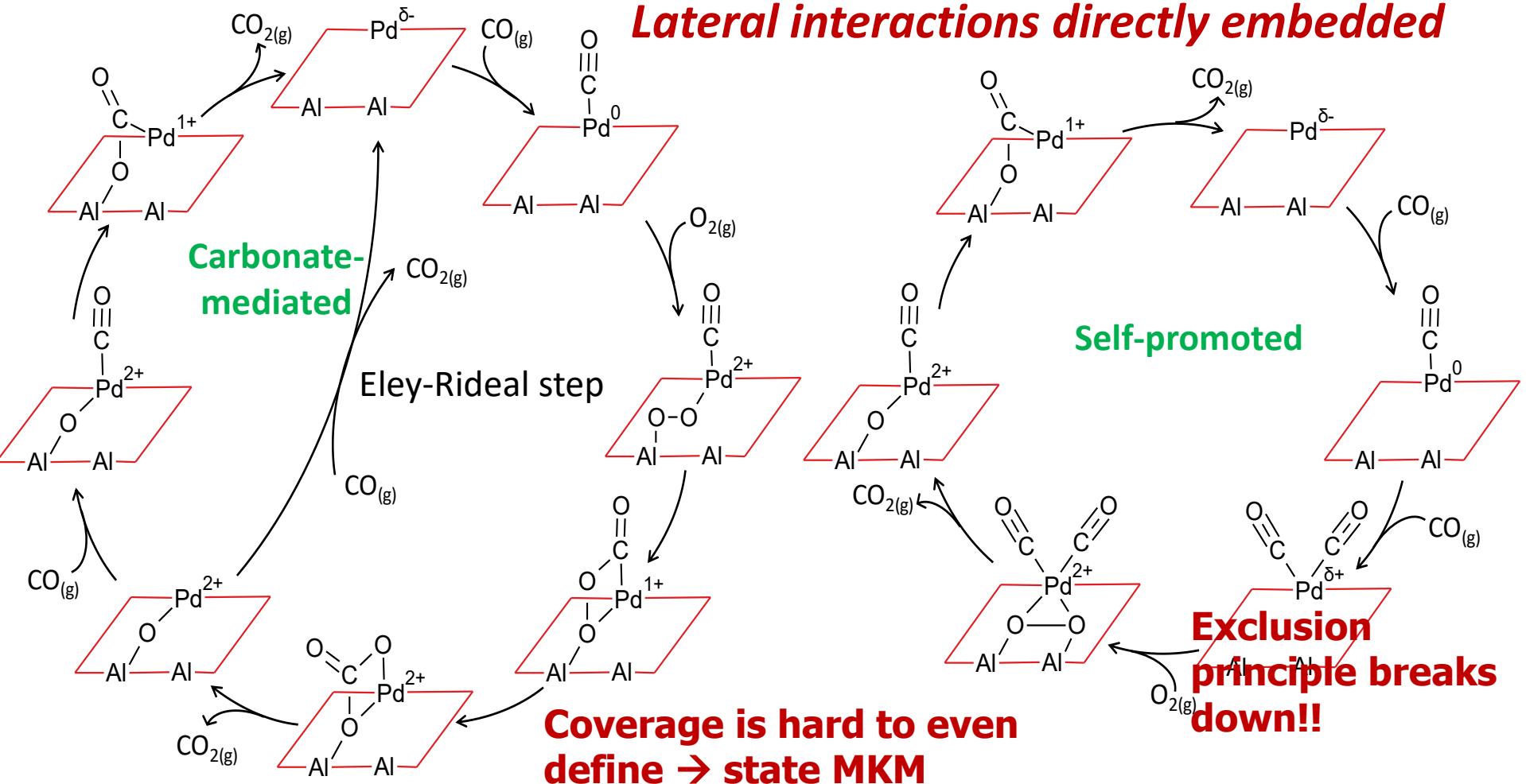
$\tau = V/q^0$  is the usual volumetric based residence time ( $V$  is volume and  $q^0$  is the entrance volumetric flow rate)

$a$  is the catalyst surface area per unit volume of the reactor



# Catalytic Cycles: CO Oxidation on SA Pd/Al<sub>2</sub>O<sub>3</sub>

*Elementary steps differ from those on NPs*  
*Lateral interactions directly embedded*



SAs cycle through multiple oxidation states!

Alexopoulos *et al.*, ACS Catal. **9**, 5002 (2019); Alexopoulos and Vlachos, Chem. Science **11**, 1469 (2020).

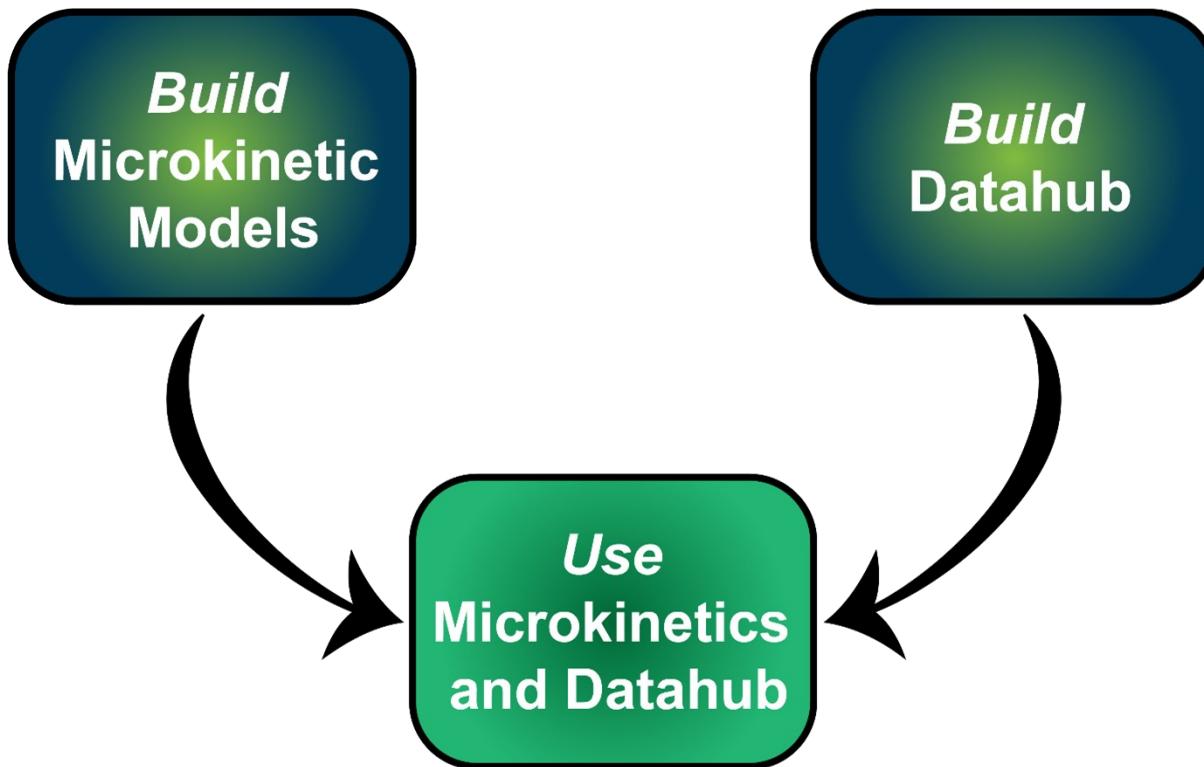


# **Automation in Building and Solving MKMs**

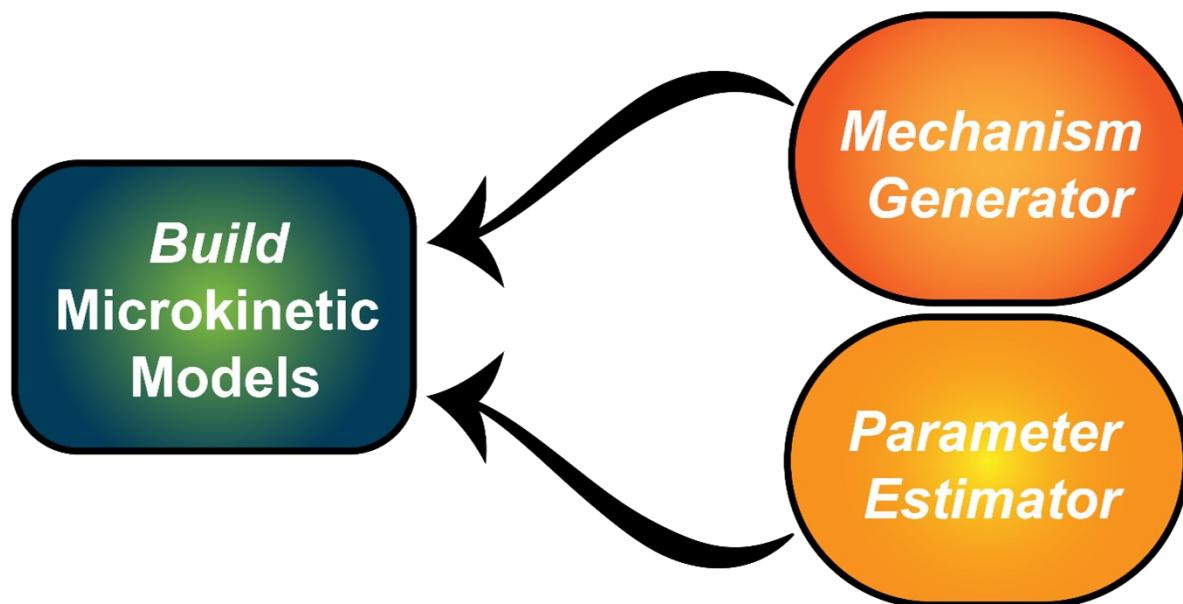
# Manual Solution

- Tedious and prone to mistakes
- Does not scale to large reaction networks (slow, missing reactions, etc.)
- Not sufficiently robust numerics; problems do not converge

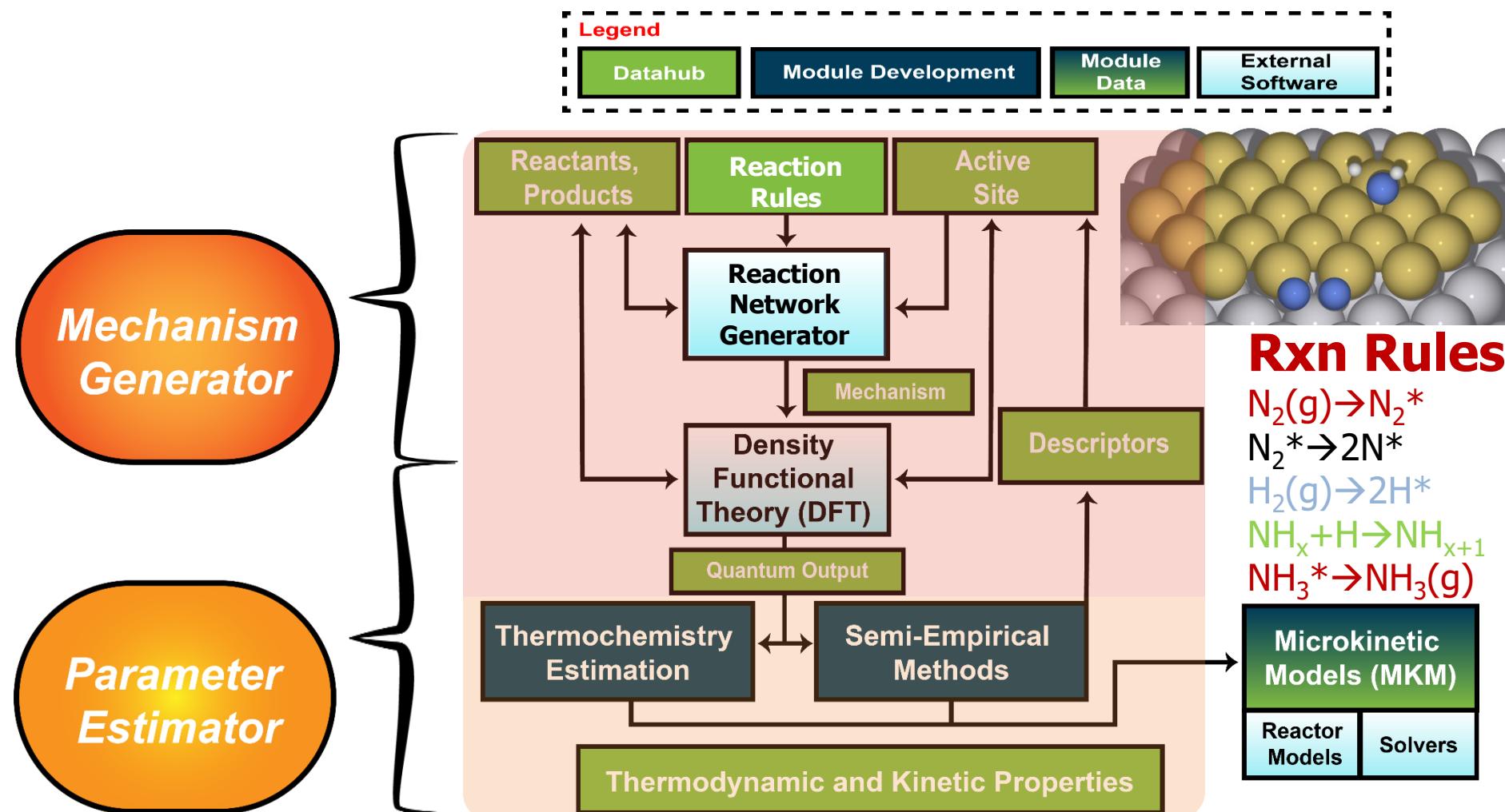
# Software Modules and Datahub



# Workflow and Software Modules

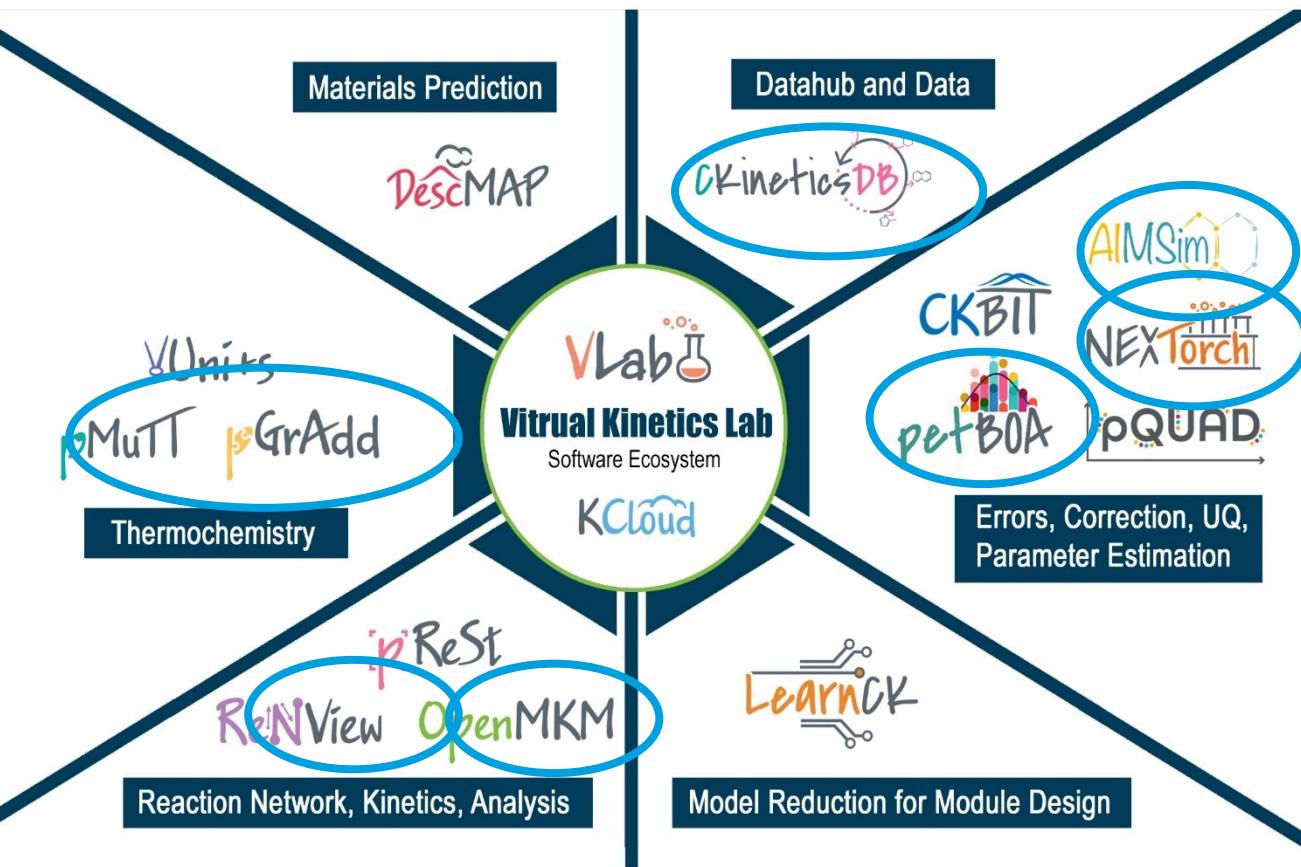


# Workflow and Software Modules





# Virtual Chemical Kinetics Lab – Vlab Overview



pMuTT

[vlachosgroup.github.io/pMuTT](https://vlachosgroup.github.io/pMuTT)

pGrAdd

[vlachosgroup.github.io/PythonGroupAdditivity](https://vlachosgroup.github.io/PythonGroupAdditivity)

vUnits

[vlachosgroup.github.io/vunits](https://vlachosgroup.github.io/vunits)

pRest

[github.com/VlachosGroup/prest](https://github.com/VlachosGroup/prest)

RenView

[github.com/VlachosGroup/renview](https://github.com/VlachosGroup/renview)

OpenMKM

[vlachosgroup.github.io/openmkm](https://vlachosgroup.github.io/openmkm)

DescMAP

[dei.udel.edu/rapid/rapid-research](https://dei.udel.edu/rapid/rapid-research)

CKineticsDB

[dei.udel.edu/rapid/rapid-research](https://dei.udel.edu/rapid/rapid-research)

AIMSim

[vlachosgroup.github.io/AIMSim](https://vlachosgroup.github.io/AIMSim)

CKBIT

[vlachosgroup.github.io/ckbit](https://vlachosgroup.github.io/ckbit)

NEXTorch

[nextorch.readthedocs.io/en/latest](https://nextorch.readthedocs.io/en/latest)

pQUAD

[vlachosgroup.github.io/pQUAD](https://vlachosgroup.github.io/pQUAD)

petBOA

[dei.udel.edu/rapid/rapid-research](https://dei.udel.edu/rapid/rapid-research)

LearnCK

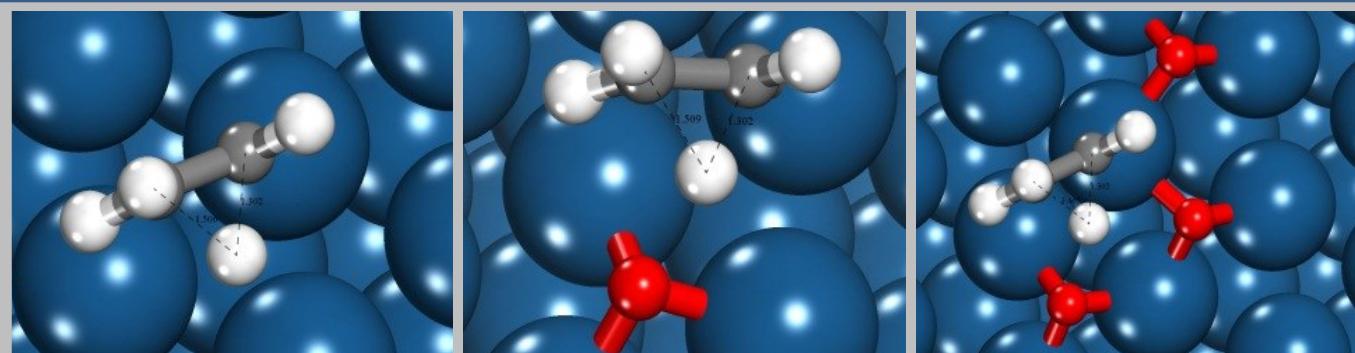
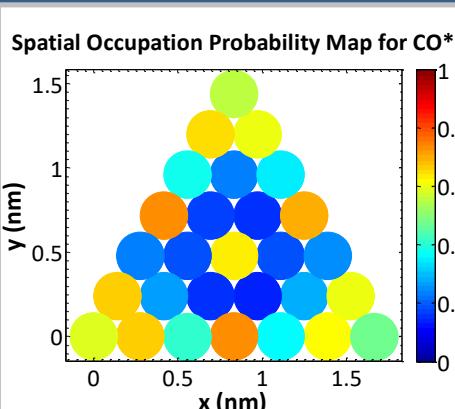
[dei.udel.edu/rapid/rapid-research](https://dei.udel.edu/rapid/rapid-research)

**Software tools for multiscale modeling**

# Lateral Interactions: Incorporation via Hierarchical Estimation Methodology

After parameterization of a microkinetic model via DFT (or semi-empirical methods), the model needs refinement to account for most abundant surface intermediates (MASI)

# Lateral Interactions Are Typically Critical



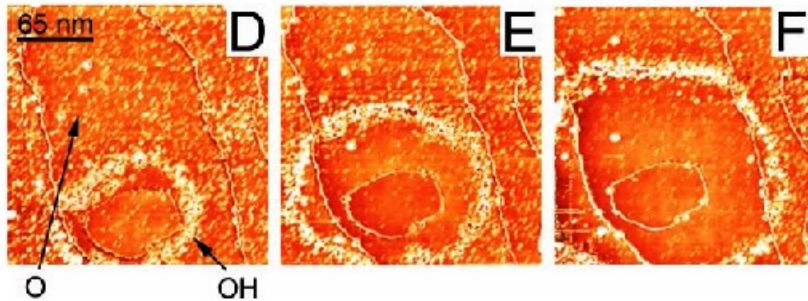
- Mean field (MF) breakdown
  - Site heterogeneity (MF can handle\*)
  - Lateral interactions (many-body effects)
  - Reaction-induced pattern formation
- KMC can handle these issues

- \*Combinatorial problem in
  - Counting the number of states
  - *a priori* estimation of kinetic parameters due to coverage effects

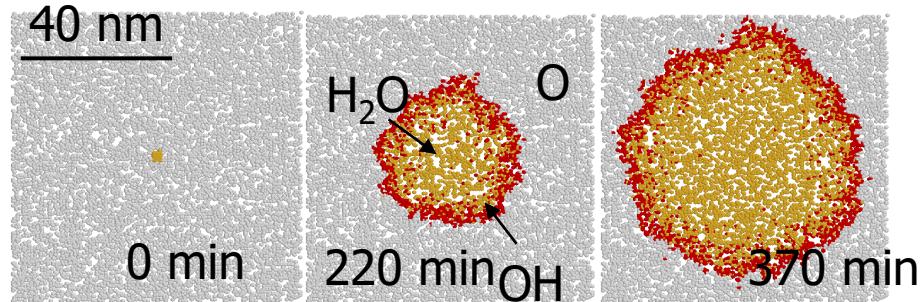


# Mean Field (MF) vs. Kinetic Monte Carlo (KMC)

- Both solve the surface species equations; they are rate calculators!!
- MF assumes a uniform distribution of adsorbates over a mesoscopic length scale;  $\text{rate} = k \theta_A \theta_B$ ; cheap solver
- KMC resolves all catalyst sites and uses site-specific probabilities to compute rate;  $\text{rate} = k_i \pi_A \pi_{B/A}$ ; expensive solver

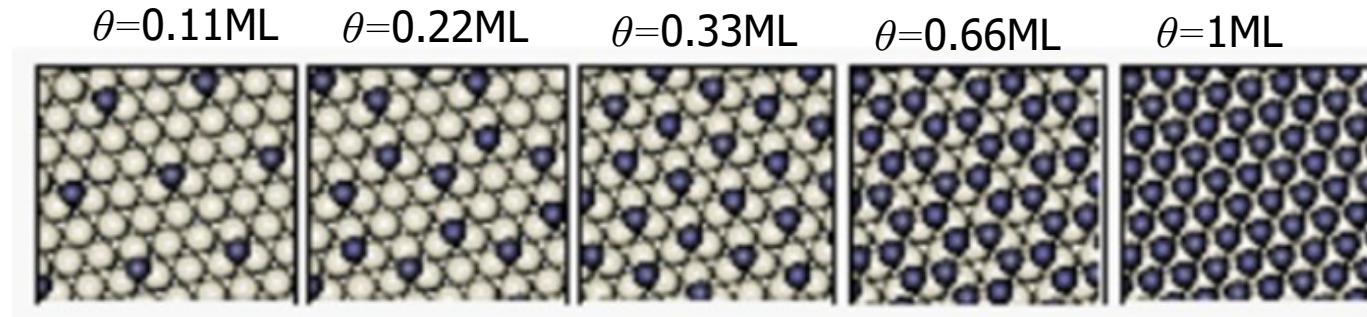


Sachs et al., Science 293, 1635 (2001)



Raimondeau and Vlachos, CES 58, 657 (2003)

# Lateral Interactions Couple Models Across Scales



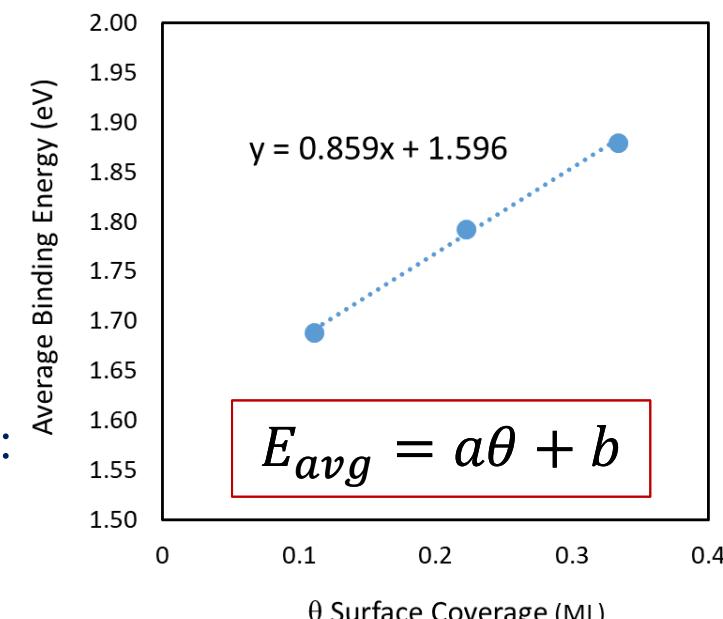
$$\text{Surface Coverage} \leftarrow \theta = \frac{n}{N_a} \quad \begin{matrix} \longrightarrow & \text{Number of adsorbates} \\ \longrightarrow & \text{Total Number of active sites} \end{matrix}$$

- DFT calculated Binding Energy:

$$E_{avg} = \frac{E_{ads+slab} - E_{slab} - nE_{gas}}{n}$$

- Required binding energy for MKM is  $E_{diff}$ :

$$E_{avg} = \frac{1}{\theta} \int_0^\theta E_{diff}(\theta) d\theta$$



Lateral interaction can be approximated by linear model

# Lateral Interactions

$$E_{avg} = \frac{E_{ads+slab} - E_{slab} - nE_{gas}}{n}$$

$$E_{avg}(\theta) = E_0 + \varepsilon\theta$$

$E_0$  : binding energy at zero coverage

$\varepsilon$  : lateral interaction parameter

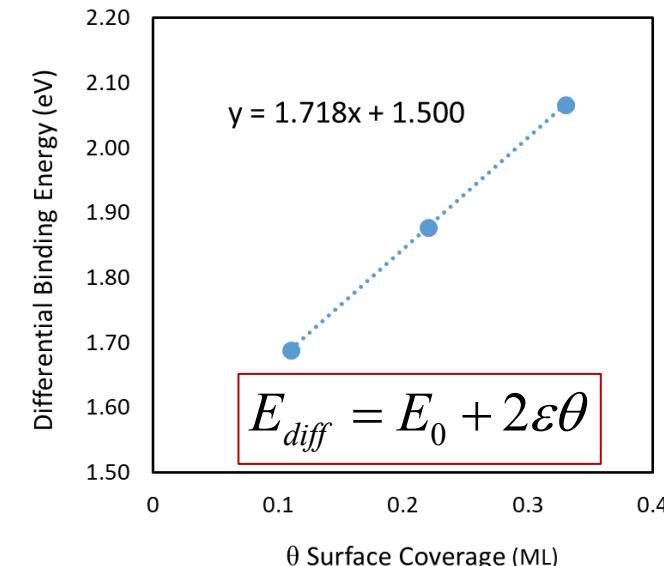
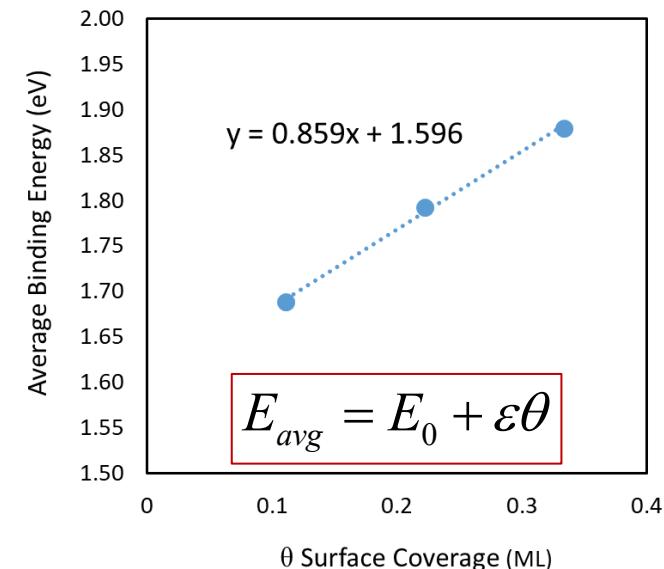
$$E_{avg} = \frac{1}{\theta} \int_0^\theta E_{diff}(\theta) d\theta$$

$$\int_0^\theta E_{diff}(\theta) d\theta = \theta \times E_{avg} = \theta E_0 + \varepsilon \theta^2 = E_{int}$$

integral

$$E_{diff}(\theta) = \frac{\partial E_{int}}{\partial \theta} = E_0 + 2\varepsilon\theta$$

$$H_{diff} = 2\varepsilon\theta + E_0 + ZPE + H_{corr}(T)$$



# Lateral Interactions

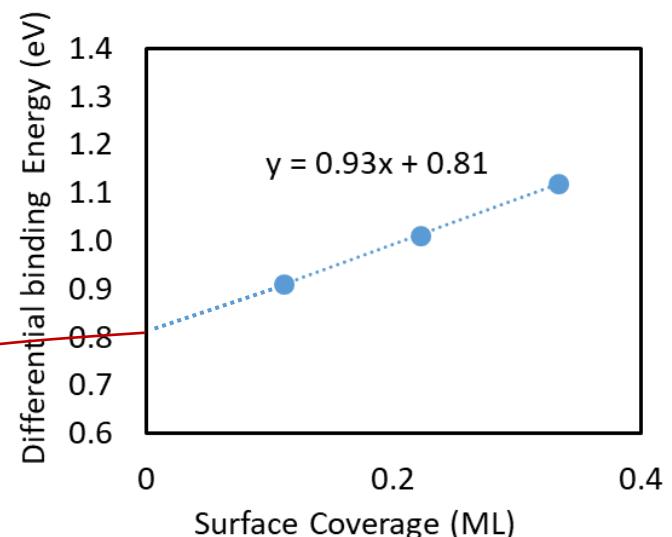
linear model:

$$E_{diff}(\theta) = E_0 + 2\epsilon\theta$$

$E_0$  : binding energy at zero coverage

$\epsilon$  : lateral interaction parameter

$E_0$

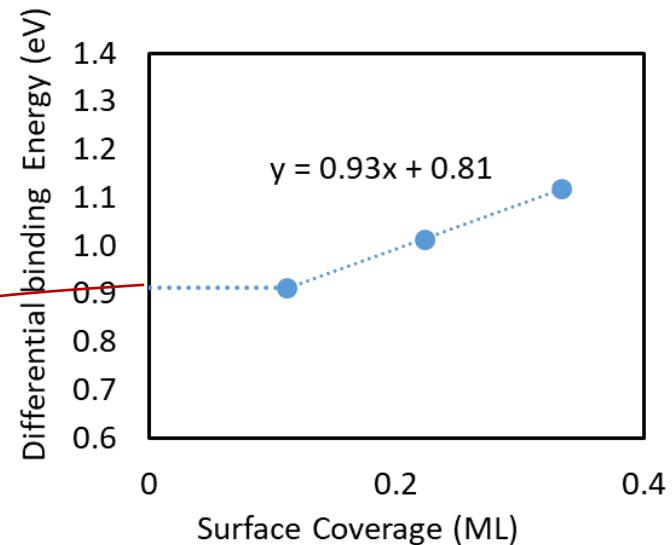


Piece-wise linear model:

$$E_{diff}(\theta) = E_0 + 2\epsilon(\theta - \theta_0) \quad \theta > 0.11$$

$$E_{diff}(\theta) = E_0 \quad \theta < 0.11$$

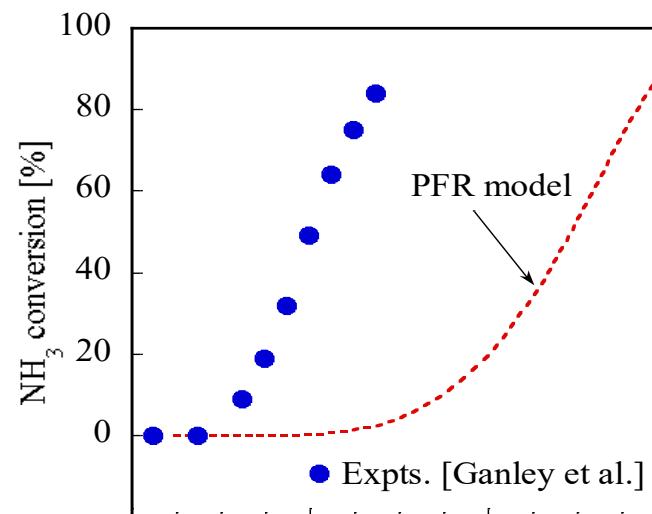
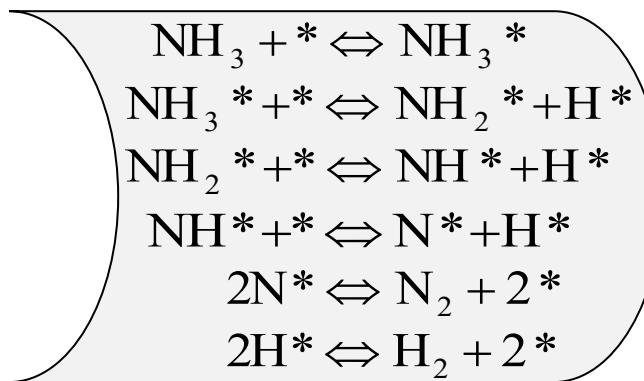
$E_0$



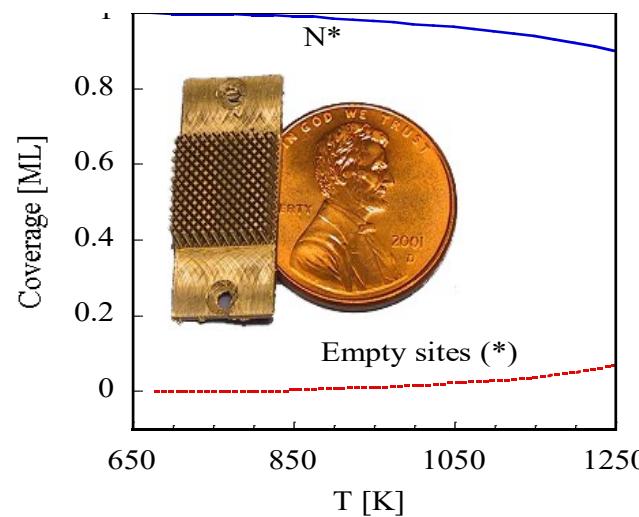
Negligible lateral interactions below threshold coverage, binding energy is constant

# NH<sub>3</sub> Decomposition on Ru: 2NH<sub>3</sub> = N<sub>2</sub> + 3H<sub>2</sub>

- NH<sub>3</sub> as a storage medium
- ‘Pure’ H<sub>2</sub> – No CO<sub>x</sub>
- A microkinetic model is build using BOC and TST
- Our microkinetic model captures the trend
- High N\* coverages



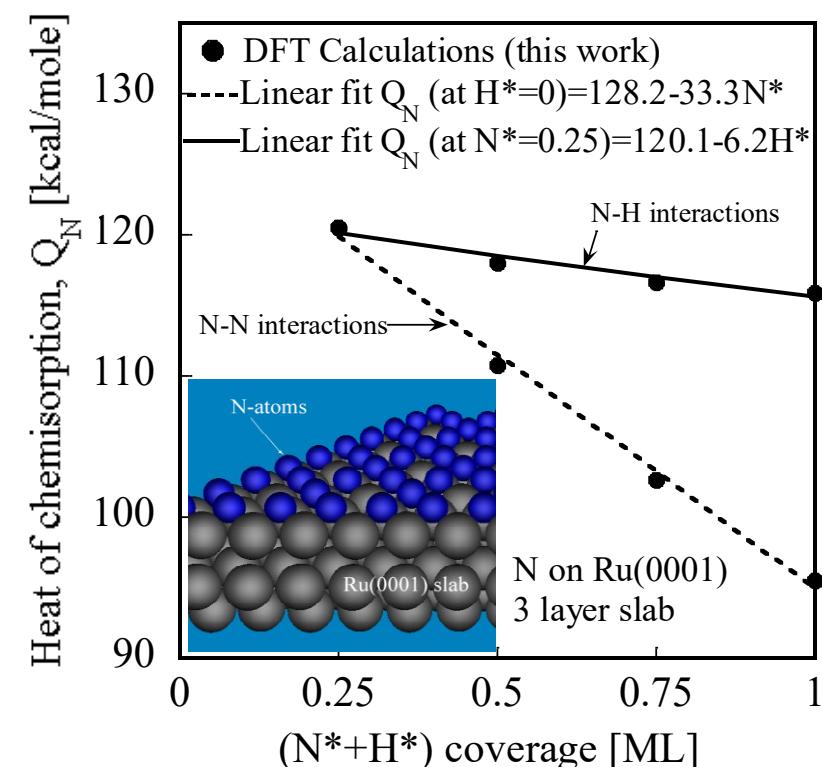
Exptl: Ganley  
et al., *AIChE J.* 2003



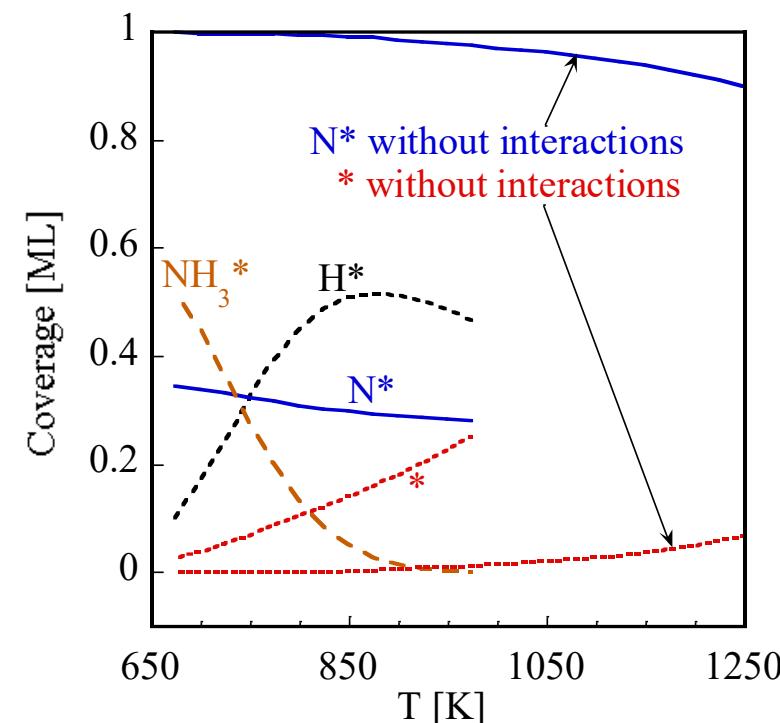
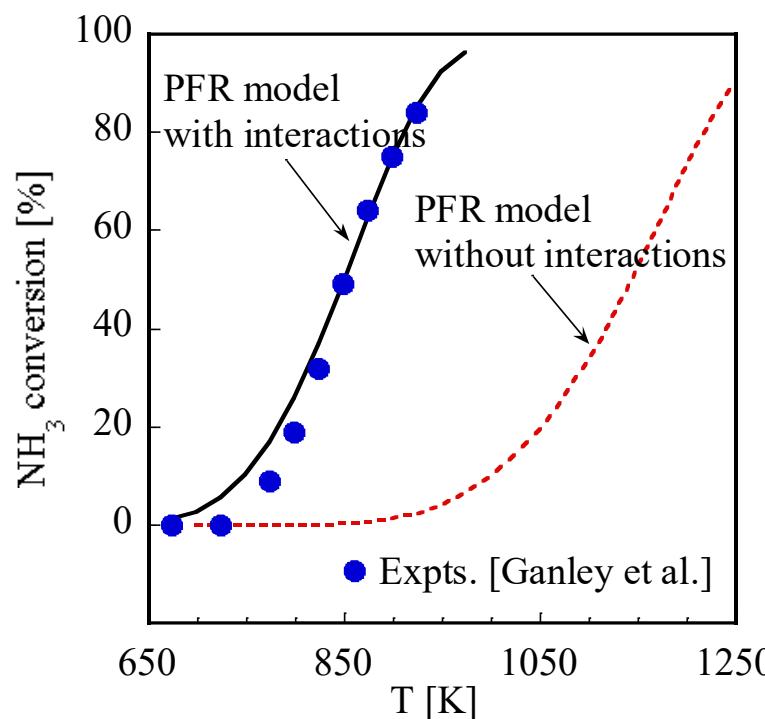
# DFT Estimates Lateral Interactions

- DACAPO (solid-state electronic structure package by Hammer and coworkers\*)
- 3-Layer slab of Ru(0001)
- $2 \times 2$  unit cell
- All layers are relaxed
- Plane wave cutoff = 350eV
- 18 k-points for surface Brillouin zone
- Generalized gradient approximation (PW-91)

\* Hammer et al., DACAPO version 2.7 (CAMP, Technical University, Denmark)



# DFT-Retrained Microkinetic Model



- H-H and N-H interactions are small
- N-N interactions completely change the chemistry
- **Extensive validation against UHV and high P data**

Exps: Ganley et al., *AIChE J.* (2004)

# Suggested Method for Including Coverage Effects and Refining MKMs in General

- Start with zero coverage heats of chemisorption of intermediates
- Solve MKM
- Identify the most abundant surface species
- Compute coverage effects via DFT
  - Single component and up to binary interactions needed
- Repeat MKM simulations and iterate if needed
- Include coverage effects on activation energy
  - Alternative: use BEPs
- Iterate



## Multiscale modeling (brief)



## Empirical kinetic models

Assumptions and limitations



## Formulating a microkinetic model (MKM): Fundamentals

What is an MKM? How do we build it?  
How do we estimate the **reaction rates**?



## Automation and solving MKMs

Mechanism generation  
Efficient, robust simulations



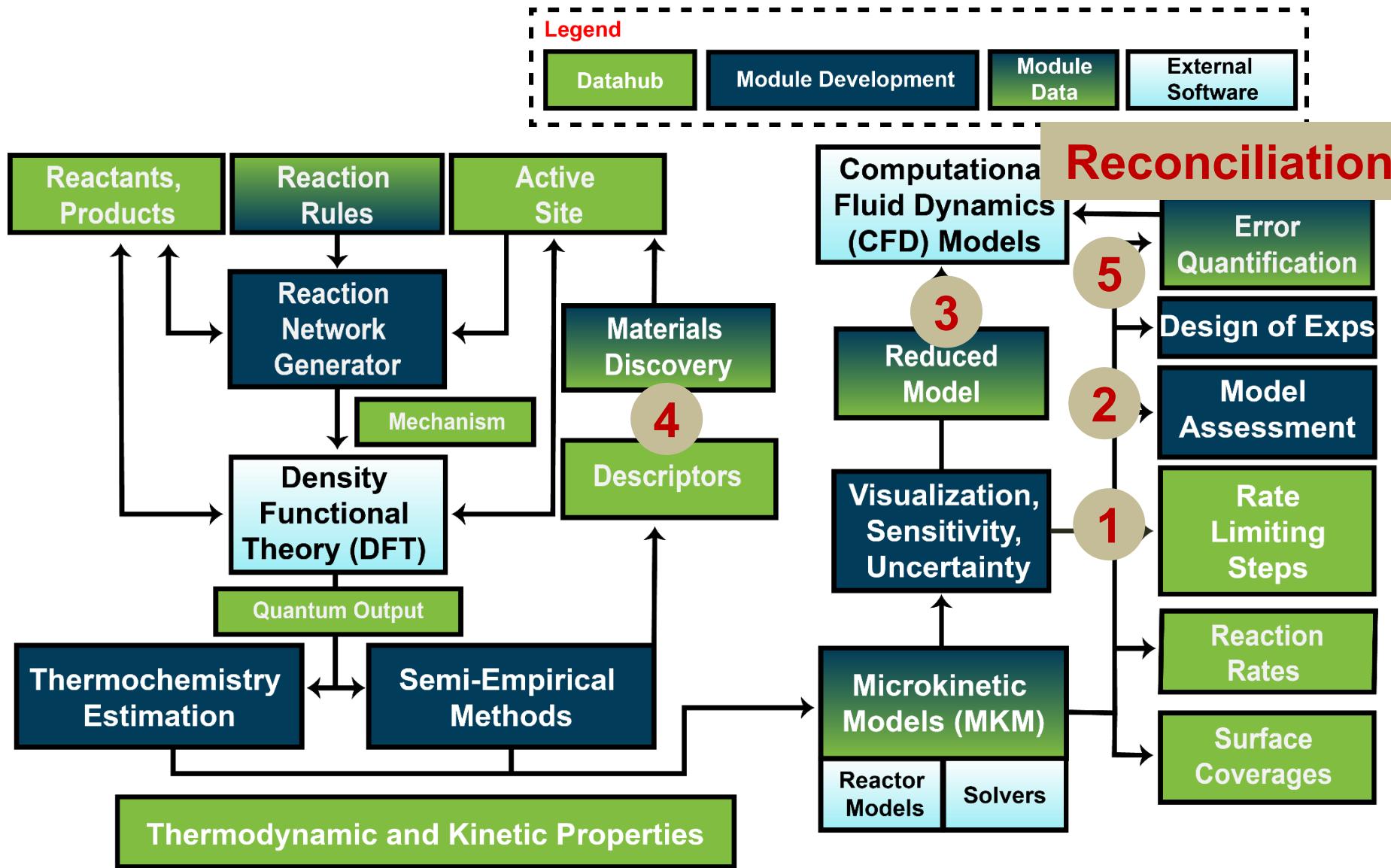
## Analysis of MKMs

What can we learn?

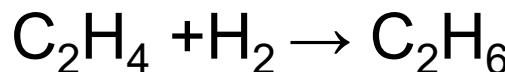


## Other uses of MKMs

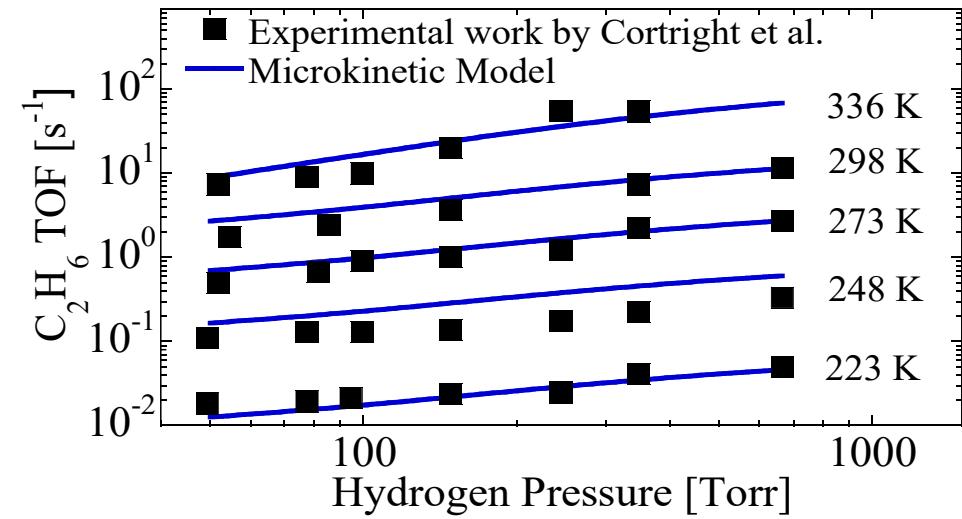
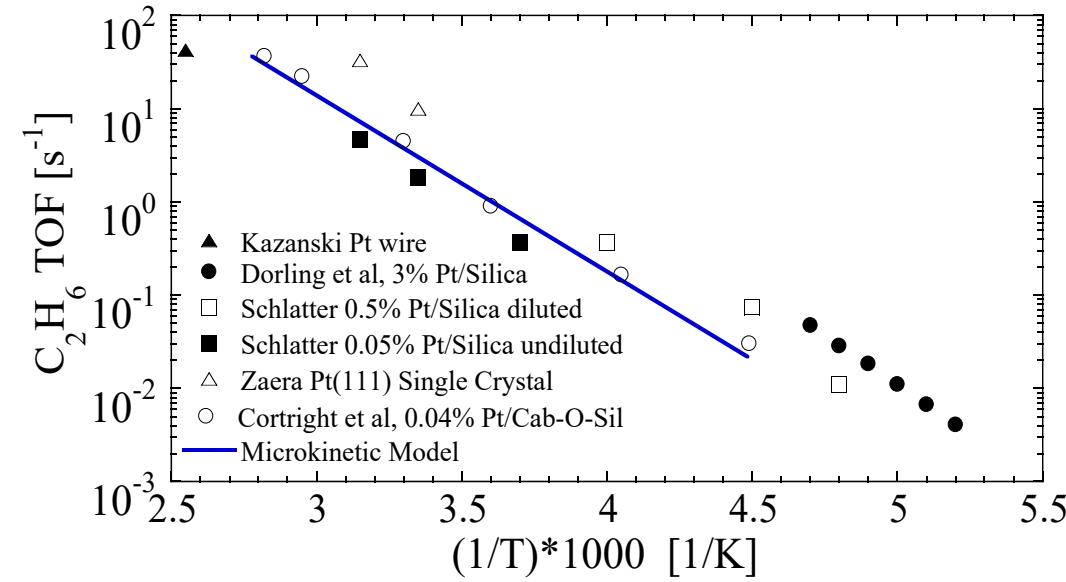
# Workflow and Software Modules



# Ethylene Hydrogenation



- Entire mechanism consists of 32 reversible elementary reactions
- Only C2 chemistry is active for hydrogenation of ethylene
- Model captures experimental data well over wide range of temperatures and hydrogen pressures

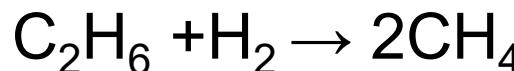


Experimental data from:

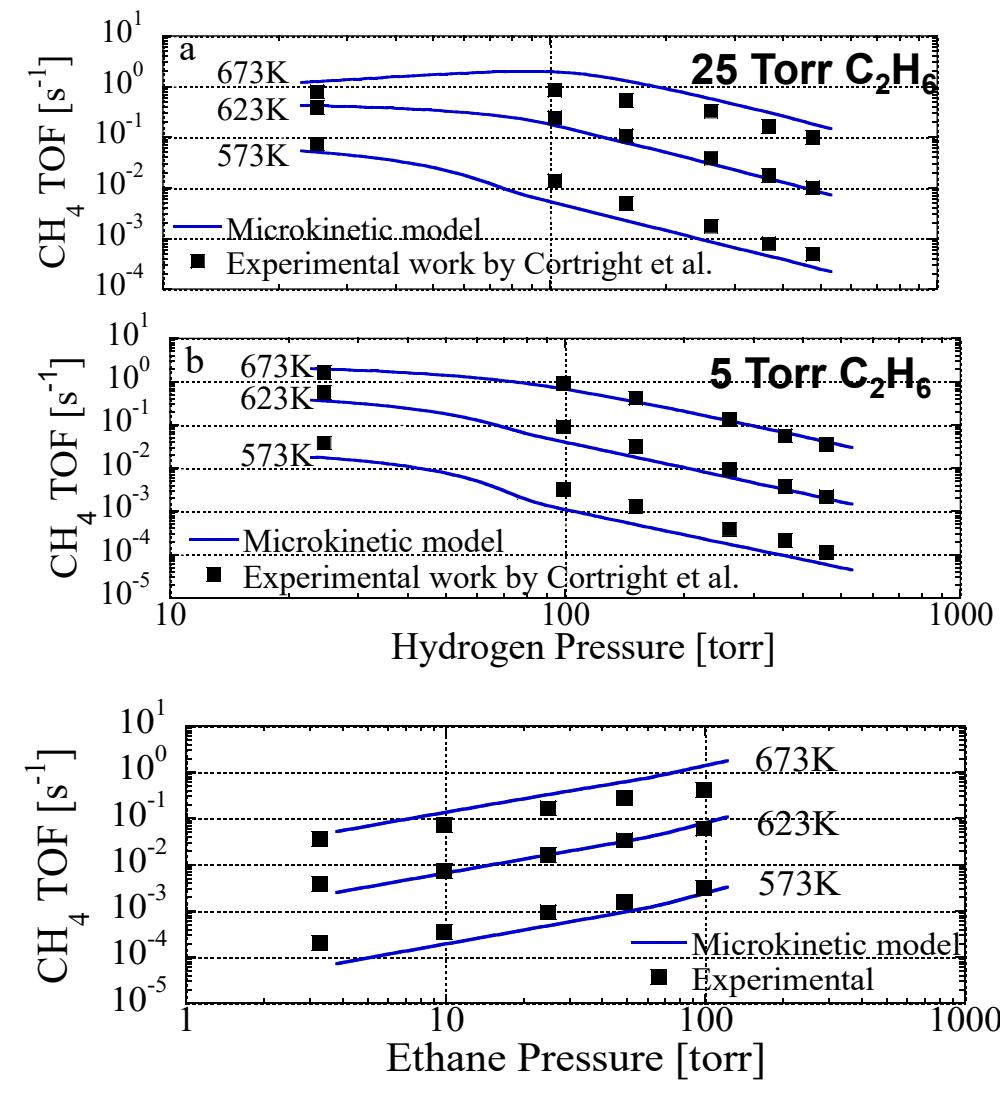
Cortright et al., J. Cat. 127 (1991) 342-353

Modeling: Salciccioli et al., Ind. Eng. Chem. Res. 50, 28 (2011).

# Ethane Hydrogenolysis



- Entire mechanism consists of 32 reversible elementary reactions
- Model captures experimental data well over wide range of temperatures and hydrogen pressures

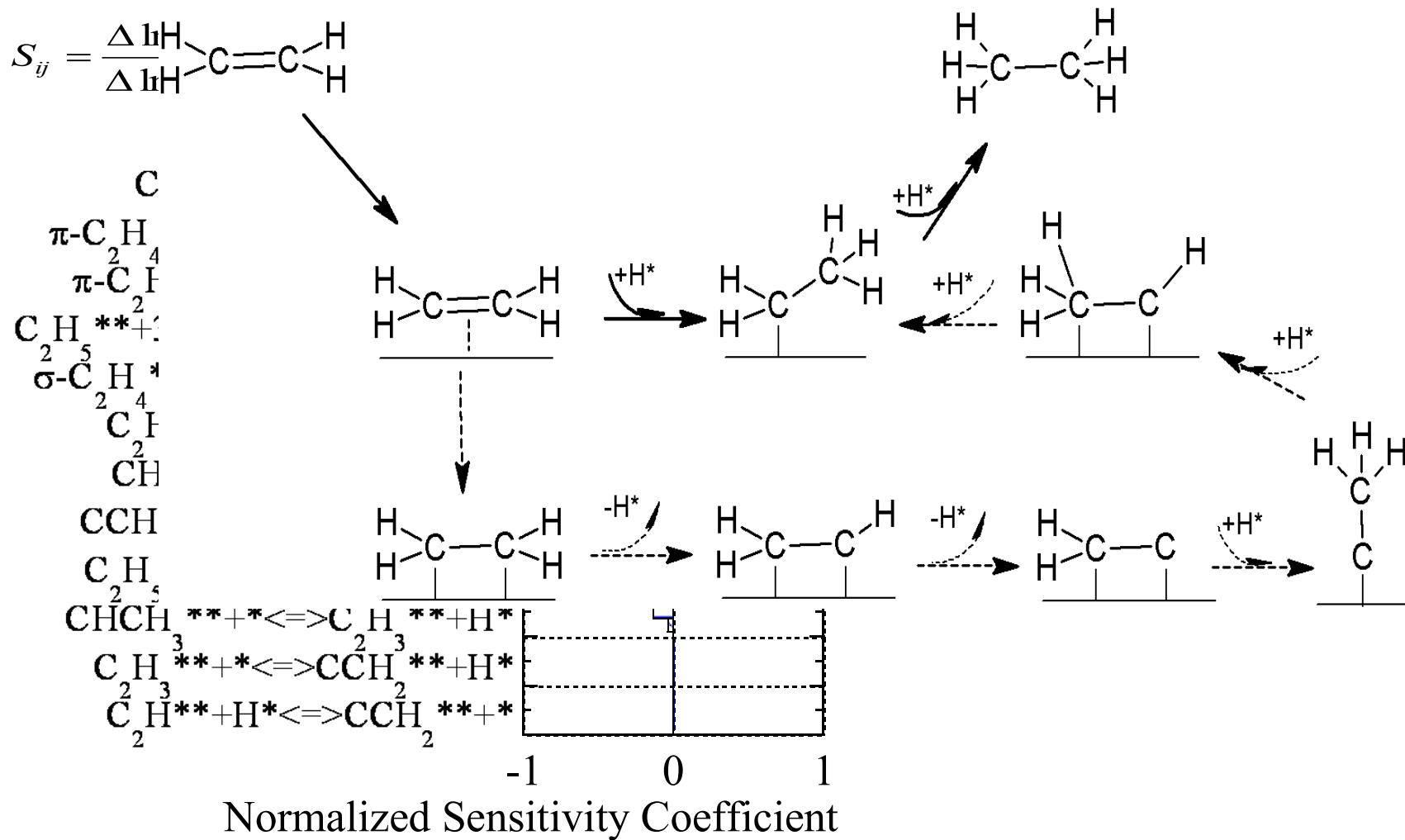


Experimental data from:

Cortright et al., Cat. Today 53 (1999) 395-406

Modeling: Salciccioli et al., Ind. Eng. Chem. Res. 50, 28 (2011).

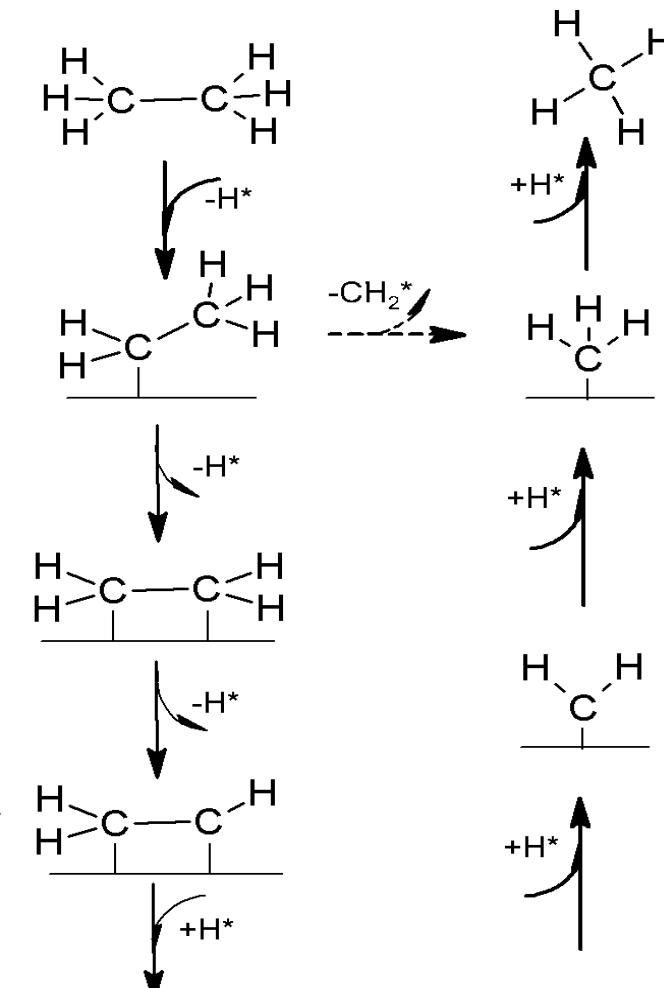
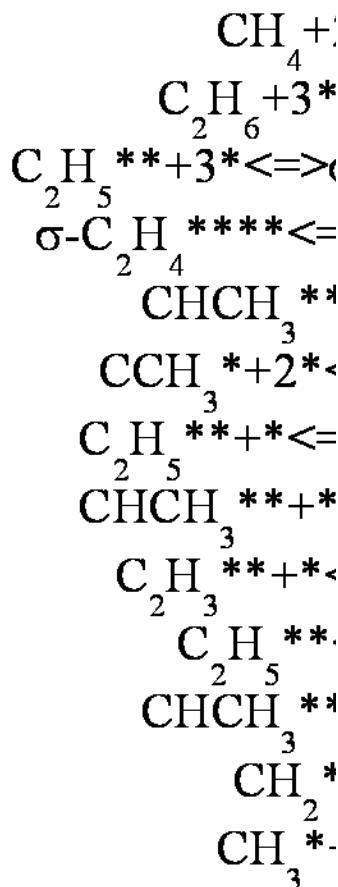
# Ethylene Hydrogenation: Analysis



Salciccioli et al., *Ind. Eng. Chem. Res.* **50**, 28 (2011).

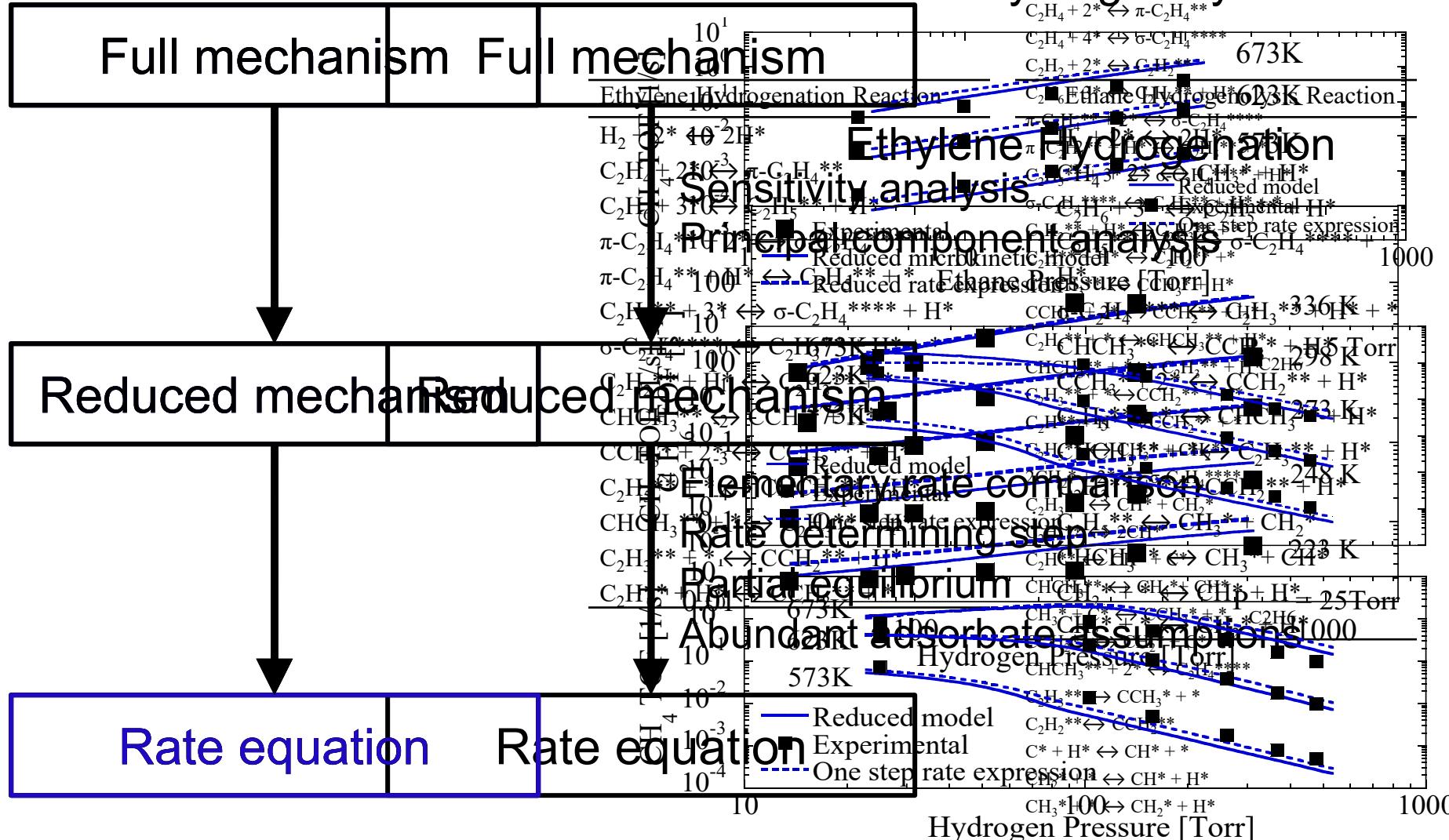
Hydrogenation rxns are rate controlling ( $\pi\text{-C}_2\text{H}_4^{**} \rightarrow \text{C}_2\text{H}_5^{**}$ ,  $\text{C}_2\text{H}_5^{**} \rightarrow \text{C}_2\text{H}_6$ )

# Ethane Hydrogenolysis: Analysis



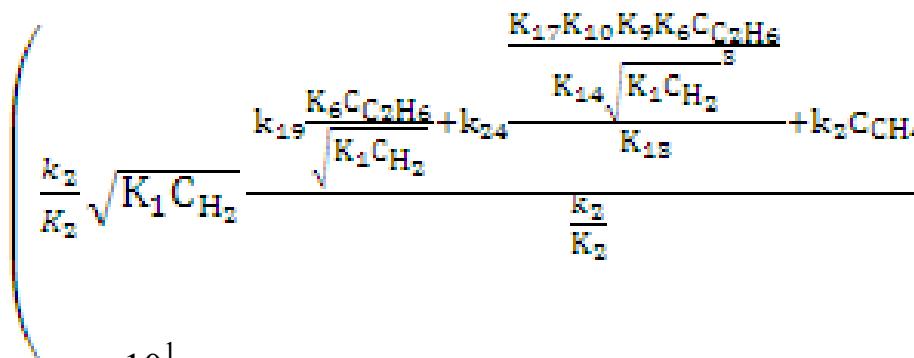
C-C bond cleaving reactions are rate controlling  
( $\text{C}_2\text{H}_5^{\bullet\bullet} \rightarrow \text{CH}_3^* + \text{CH}_2^*$  and  $\text{CHCH}_3^{\bullet\bullet} \rightarrow \text{CH}_3^* + \text{CH}^*$  )

# Model Reduction to Rate Expressions

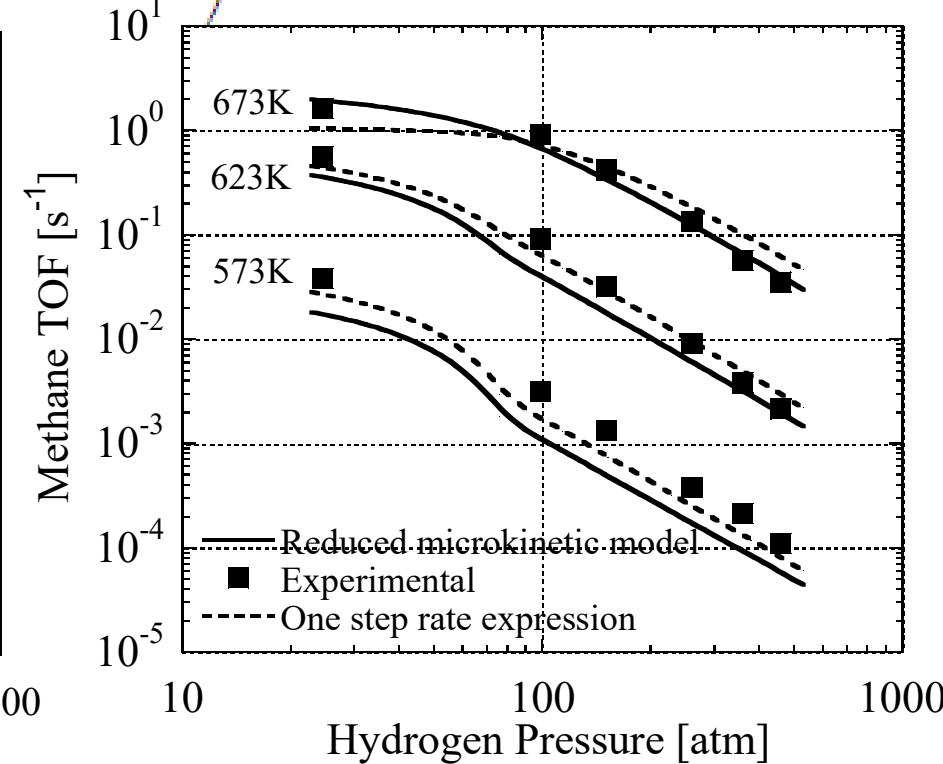
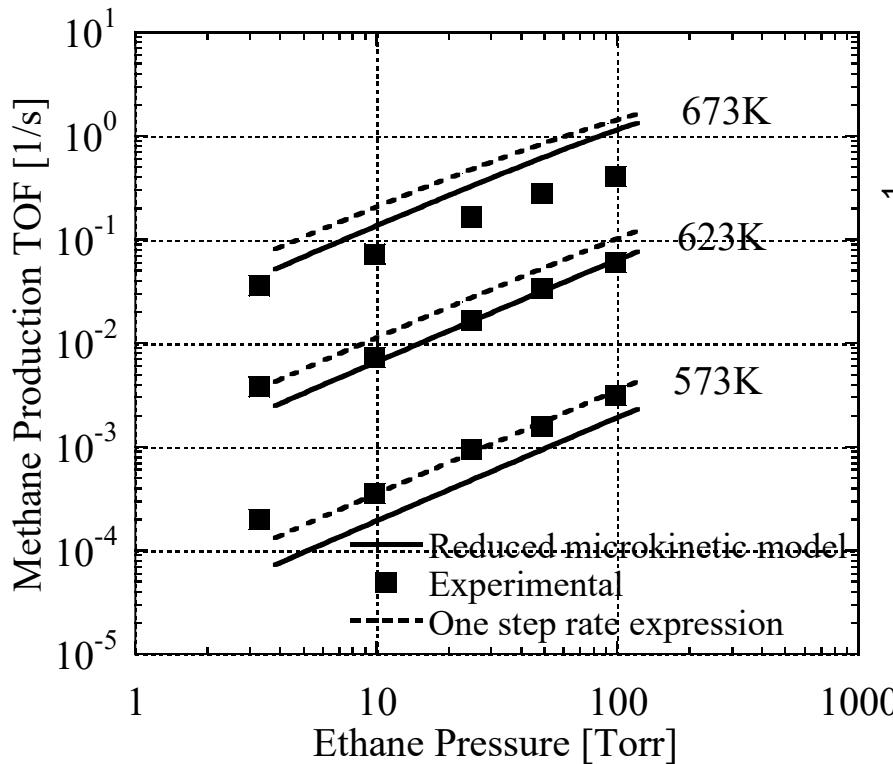


# Ethane Hydrogenolysis Rate Expression

*Hydrogenolysis Rate =*



$$= k_2 C_{CH_4} \left( \frac{1}{1 + \sqrt{\frac{K_1 C_{H_2}}{K_2}} + \frac{K_{17} K_{10} K_9 K_6 C_{C_2H_6}}{s}} \right)^2$$



# Microkinetic Model Analysis Workflow Summary

0

Energy profile analysis and energy span

1

Visualization of solution vs. time or distance or vs. a parameter

2

Partial equilibrium of reactions,  $PEI = r_f / (r_f + r_b) \sim 0.45-0.55$

3

Reaction path analysis

4

Sensitivity analysis



# Active Site Identification

## MKM Analysis

*Agreement is remarkable; Site sensitive chem*

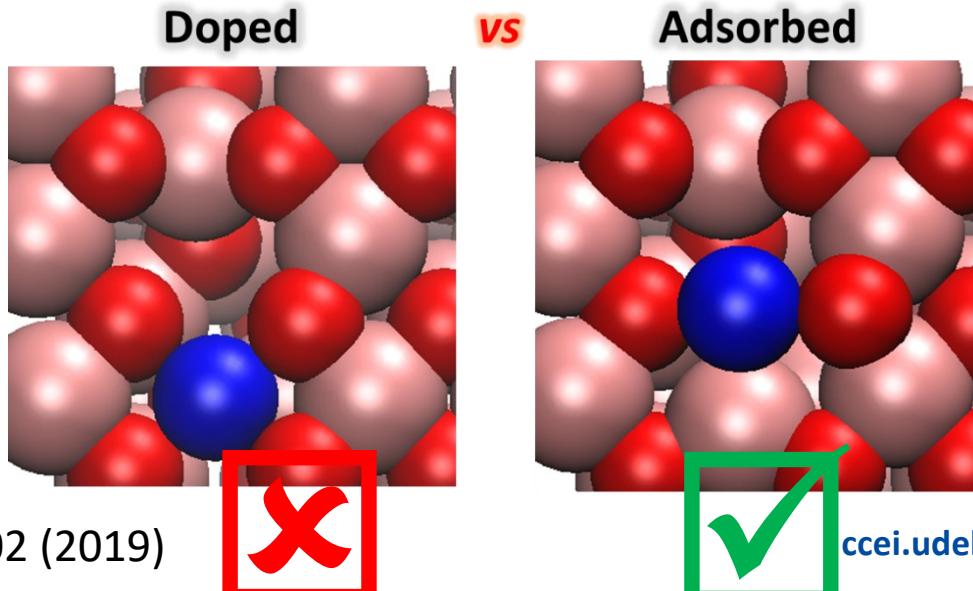
	TOF (s <sup>-1</sup> ) <sup>b</sup>	Reaction orders at 343 K <sup>c</sup>			
	343 K	398 K	CO	O <sub>2</sub>	
1 <sup>st</sup> run <sup>a</sup>	Experiments	3.8 10 <sup>-4</sup>	1.6 10 <sup>-3</sup>	-0.20	0.18
2 <sup>nd</sup> run <sup>a</sup>		9.7 10 <sup>-5</sup>	2.4 10 <sup>-4</sup>	-1.20	0.84
Pd <sub>1</sub> <sup>ads</sup>	MKM (this work) <sup>Error</sup>	1.9 10 <sup>-5</sup>	O(10)	6.1 10 <sup>-4</sup>	O(1)
Pd <sub>1</sub> <sup>doped</sup>	MKM (this work) <sup>d</sup>	5.1 10 <sup>2</sup>	7.2 10 <sup>2</sup>	-0.87	0.16
			1.00	0.00	

<sup>a</sup> Experiments, Peterson et al.

<sup>b</sup> p<sub>CO</sub> ≈ p<sub>O<sub>2</sub></sub> ≈ 8 Torr

<sup>c</sup> p<sub>CO</sub> = 14-52 torr, p<sub>O<sub>2</sub></sub> = 7-28 Torr

<sup>d</sup> Mars van Krevelen mechanism





# Active Site Identification Degree of Pd Sintering

The reaction orders can ‘track’ the fraction of single Pd atoms vs. NPs

$$\overline{TOF} = w_{SA} TOF_{SA} + w_{NP} TOF_{NP} \quad (1)$$

$$\overline{n_{O2}} = \frac{d \ln \overline{TOF}}{d \ln p_{O2}} = n_{O2,NP} + \frac{w_{SA} TOF_{SA}}{\overline{TOF}} (n_{O2,SA} - n_{O2,NP}) \quad (2)$$

$$w_{SA} = \frac{\overline{TOF}}{TOF_{SA}} \frac{(\overline{n_{O2}} - n_{O2,NP})}{(n_{O2,SA} - n_{O2,NP})} \quad (3) \qquad w_{NP} = 1 - w_{SA} \quad (4)$$

Exptl data: 343 K,  $\overline{TOF} = 9.7 \cdot 10^{-5} \text{ s}^{-1}$ ,  $\overline{n_{O2}} = 0.84$ ,  $n_{O2,NP} = 1$

Comp data: 343 K,  $TOF_{SA} = 1.9 \cdot 10^{-5} \text{ s}^{-1}$ ,  $n_{O2,SA} = 0.16$

Eq.3 gives:  $w_{SA} = 0.97$ , and eq.4:  $w_{NP} = 0.03$

***Pd sintering is minimal at low reaction temperatures***  
***Reaction order very sensitive kinetic signature of active site***

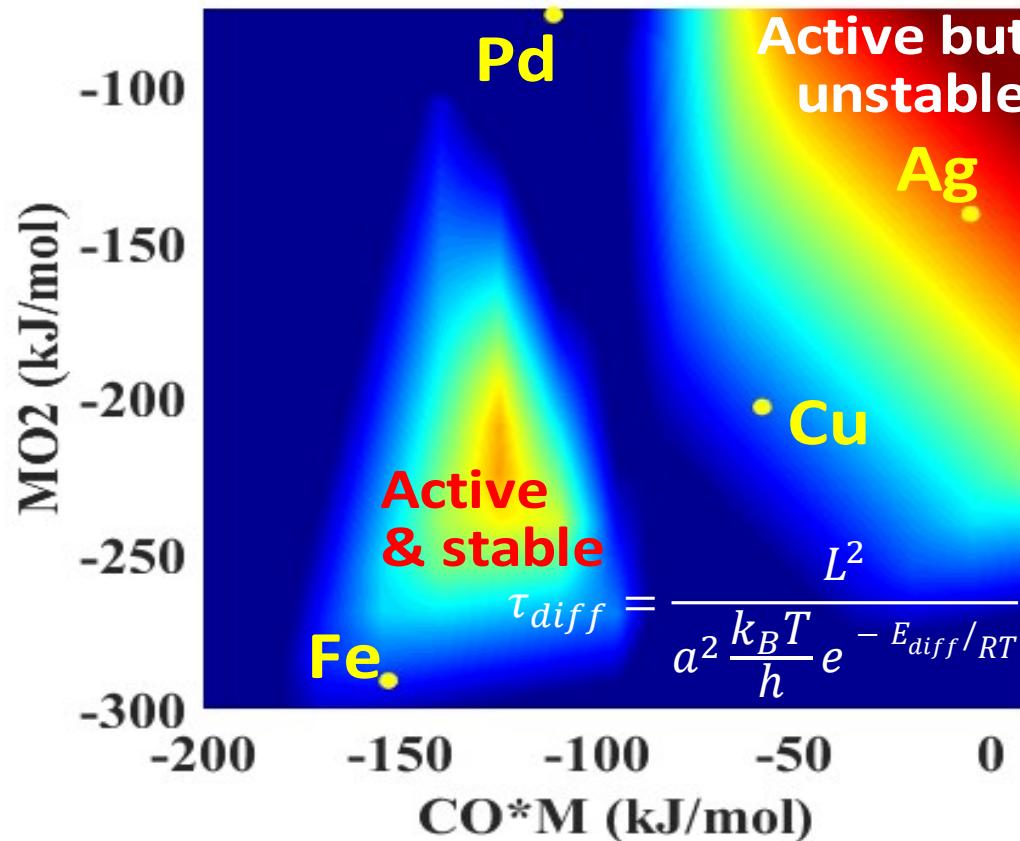


# Reactivity and Stability Map for CO Oxidation

M1/Al<sub>2</sub>O<sub>3</sub>

p<sub>CO</sub> = p<sub>O<sub>2</sub></sub> = 0.1 bar

T = 400 K

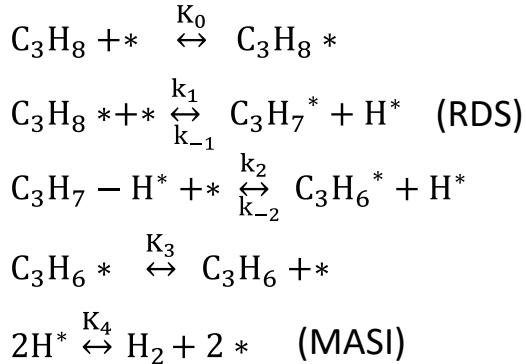


- Kinetically most abundant state MO<sub>x</sub>(CO)<sub>n</sub> during the catalytic cycle changes with metal
- Stability depends on the most abundant state

## Reduced Model vs. MKM

Overall reaction on Pt(111):  $C_3H_8 \rightleftharpoons C_3H_6 + H_2$

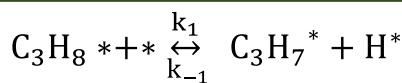
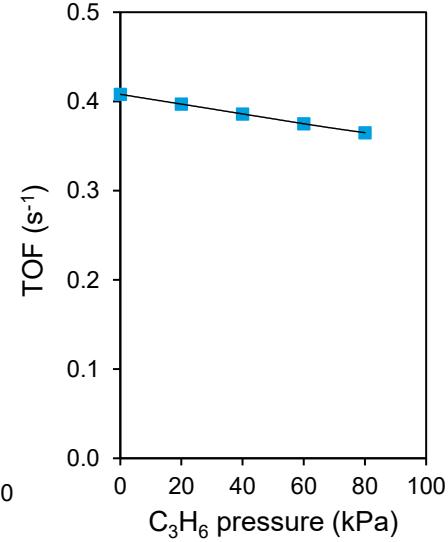
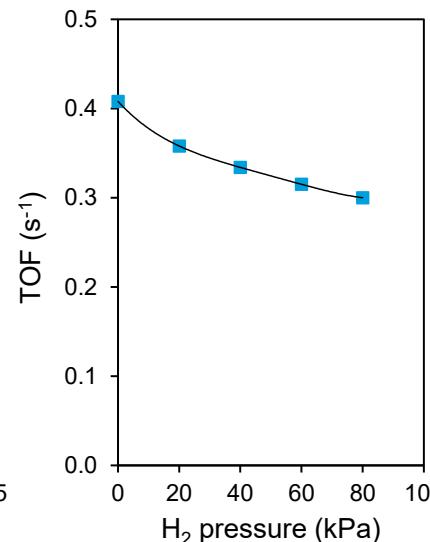
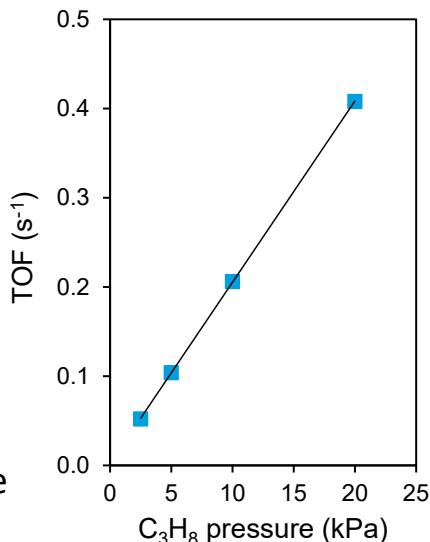
### Elementary Steps



- Cofeeding  $H_2$  or  $C_3H_6$  inhibits rate by surface coverage and the reverse reaction of C-H activation

- Reduced model:

$$\frac{r}{[*]_0} = \frac{K_0 k_1 p_{C_3H_8} - \frac{k_{-1}}{K_2 K_3 K_4} p_{C_3H_6} p_{H_2}}{1 + \left(\frac{p_{H_2}}{K_4}\right)^{\frac{1}{2}}}$$



- Without  $H_2$ :

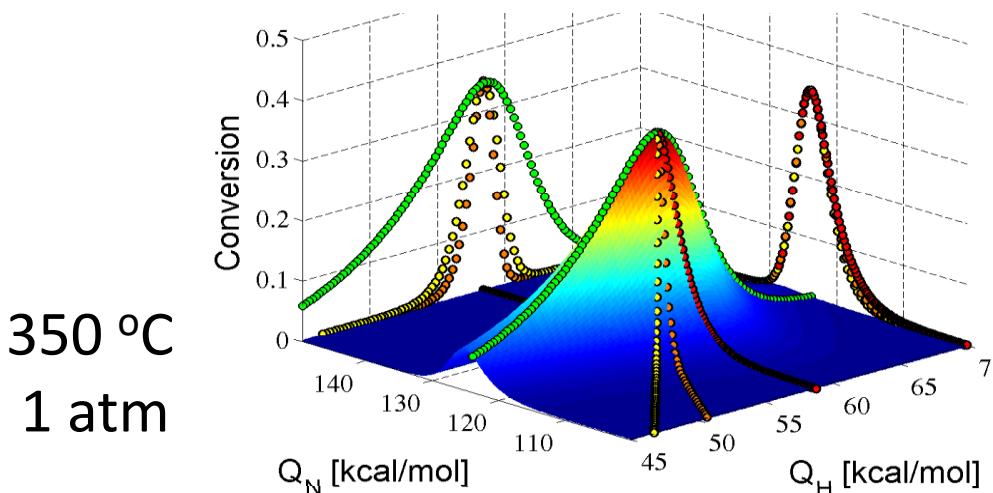
$$\frac{r}{[*]_0} = K_0 k_1 p_{C_3H_8}$$

P <sub>H<sub>2</sub></sub> (kPa)	PE ratio	θ <sub>H<sub>2</sub></sub>
0	1.00	3.0%
20	0.95	12.0%
40	0.91	16.0%
60	0.87	18.8%
80	0.85	21.1%

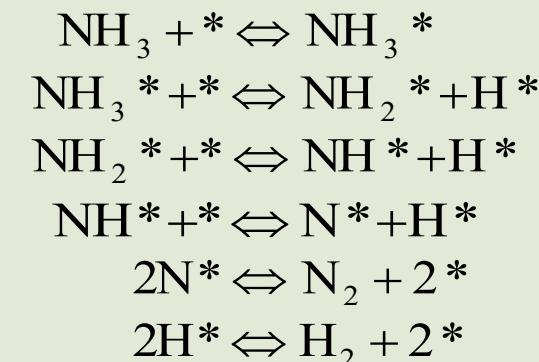
P <sub>H<sub>2</sub></sub> (kPa)	PE ratio	θ <sub>C<sub>3</sub>H<sub>6</sub></sub>
0	1.00	1.2E-7
20	0.94	2.3E-6
40	0.90	4.6E-6
60	0.86	6.8E-6
80	0.82	9.1E-6

Partial Equilibrium (PE) Ratio =  $\frac{r_f}{r_f + r_r}$  • Simple power law!

# High Throughput Multiscale Model-based Catalyst Design



NH<sub>3</sub> decomposition



- Search is done on **atomic descriptors** while running the full chemistry and reactor models
- Optimal catalyst properties are identified

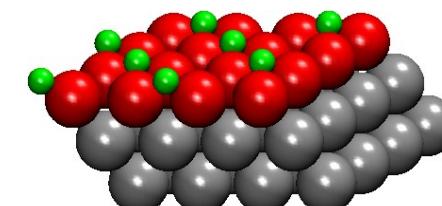
# Identifying Bimetallic Catalysts

Metals	BE <sub>N</sub> (kcal/mol)
PtTiPt	56.5
PtVPt	59.5
PtCrPt	72.6
PtMnPt	84.9
PtFePt	83.9
PtCoPt	87.0
PtNiPt	89.8
<b>NiPtPt</b>	<b>137.5</b>
CoPtPt	159.9
FePtPt	169.9
MnPtPt	162.2
CrPtPt	166.5
VPtPt	184.1
TiPtPt	191.5

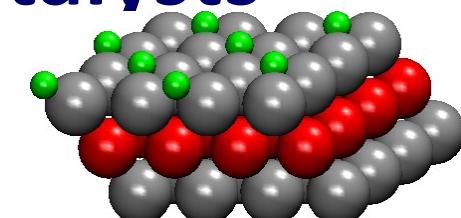
Pt      Ni

102.1

113.8

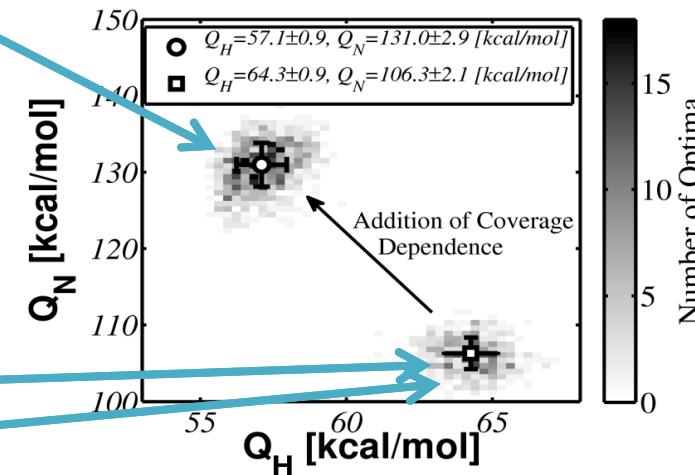


Surface

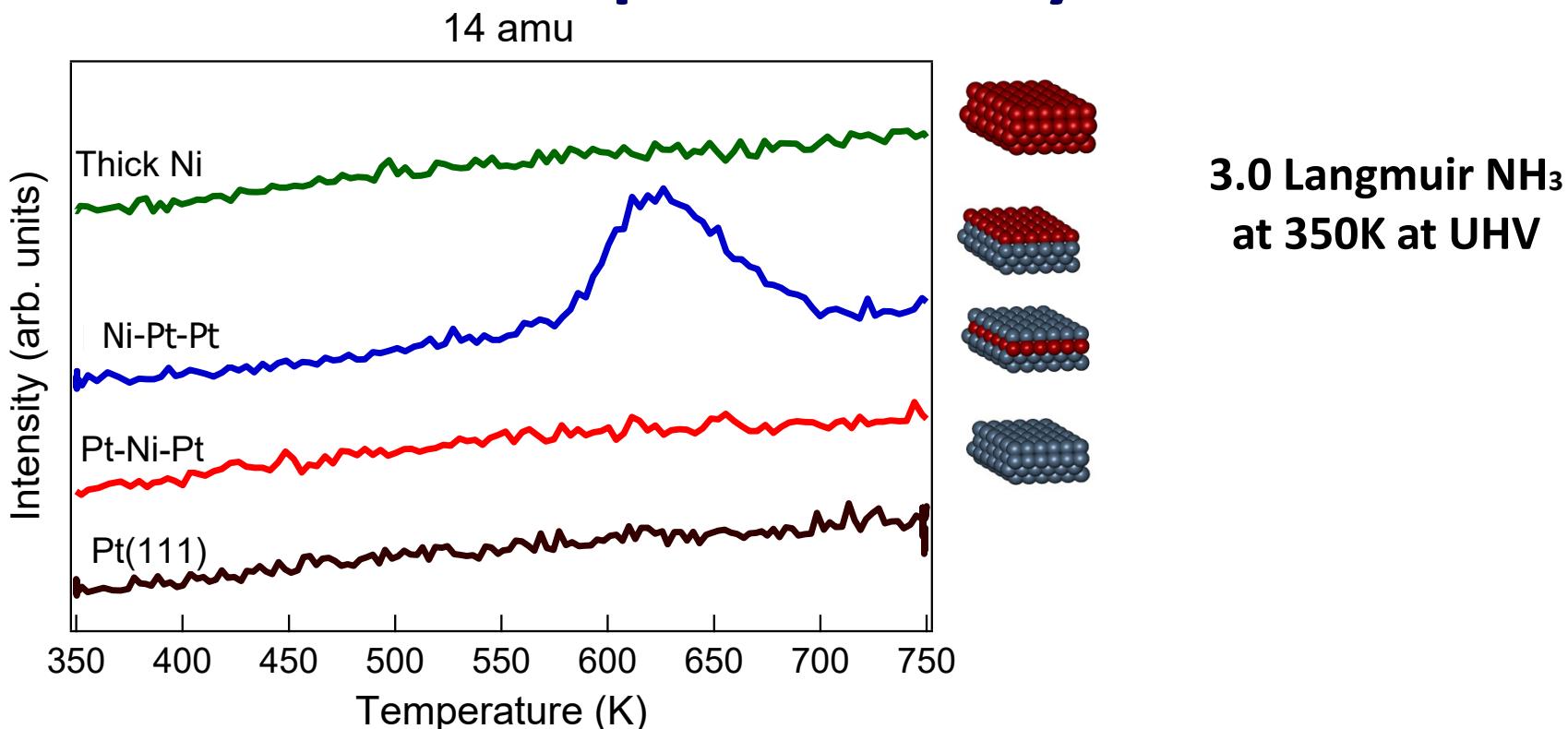


Sub-surface

- Optimum heat of chemisorption of N of ~130 kcal/mol
- NiPtPt is a good prospective bimetallic surface



# Emergent Behavior Verified Experimentally



- Ammonia decomposes on Ni-Pt
- No decomposition on other surfaces
- N-Pt is the most active catalyst

# Descriptor-based Microkinetic Analysis Package (DescMAP)



- Complex reactor parameters allowed
- Descriptors can be chosen using PCA and L1O CV linear regression
- Supports a wide array of empirical and semi-empirical relationships
- Leverages existing VLab software packages for increased functionality



# Microstructure Can Profoundly Impact Activity

## Beyond Mean Field



### ARTICLE

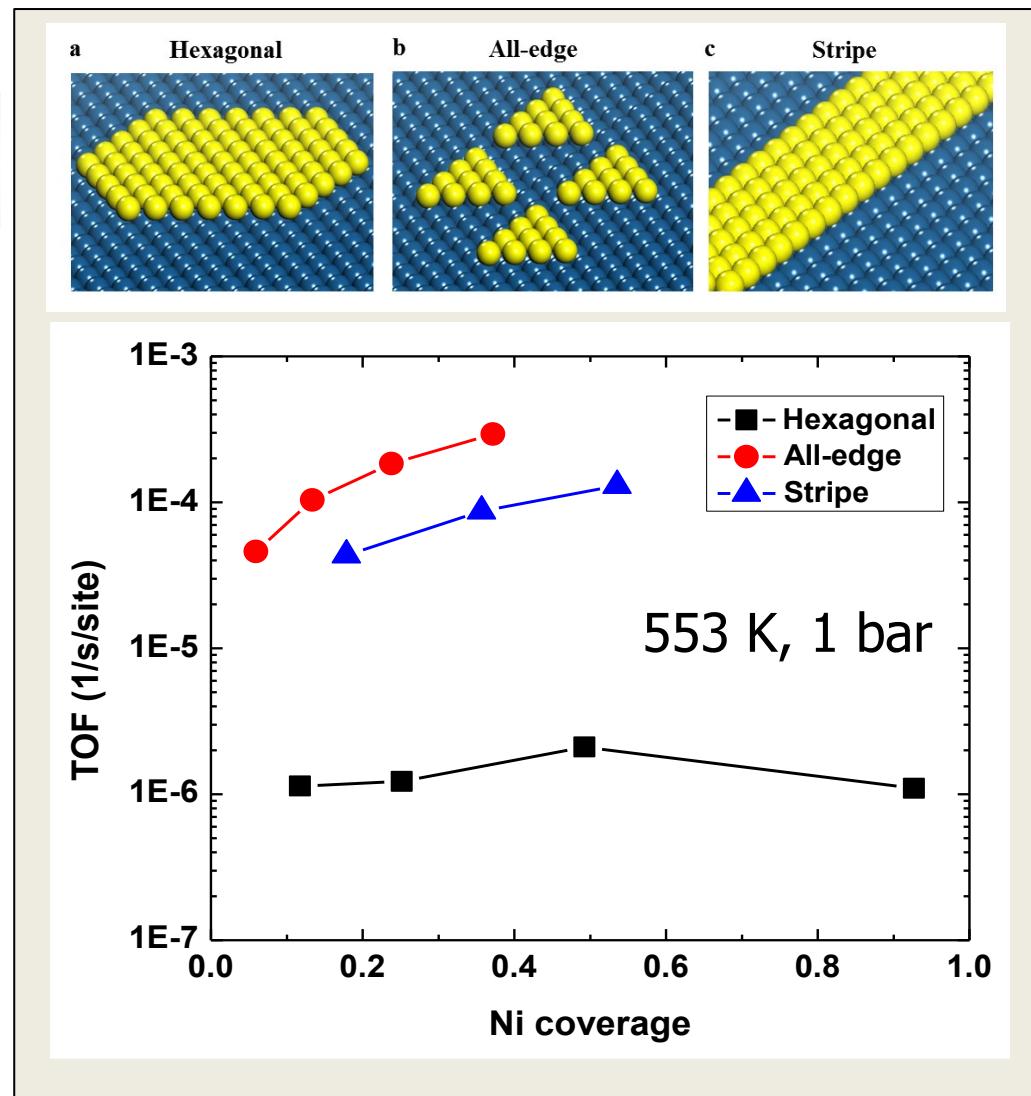
Received 17 Jan 2015 | Accepted 12 Sep 2015 | Published 7 Oct 2015

DOI: 10.1038/ncomms9619 OPEN

Patched bimetallic surfaces are active catalysts for ammonia decomposition

Wei Guo<sup>1,2,3</sup> & Dionisios G. Vlachos<sup>1</sup>

- How do we determine the active site?
- How do we predict the optimal catalyst structure?
  - Shape, size, spatial arrangement in multifunctional materials

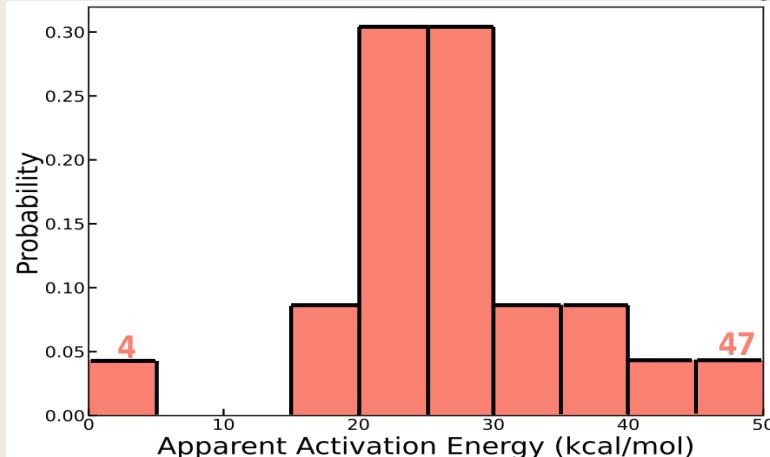


# Beyond Parametric UQ: Structure Sensitivity-based UQ

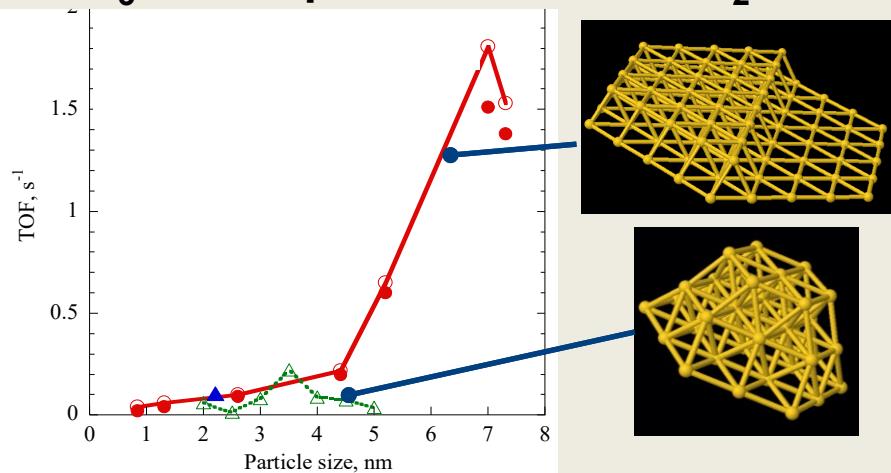
- Huge variation in experimental data
  - Why?
- Structure sensitivity can be leveraged for making improved catalysts
  - How can we predict it?

Zong, Xue and Vlachos, Reconciling experimental catalytic data stemming from structure sensitivity. *Chem. Sci.* **14**, 4337 (2023).

Methane combustion on Pt/Al<sub>2</sub>O<sub>3</sub>

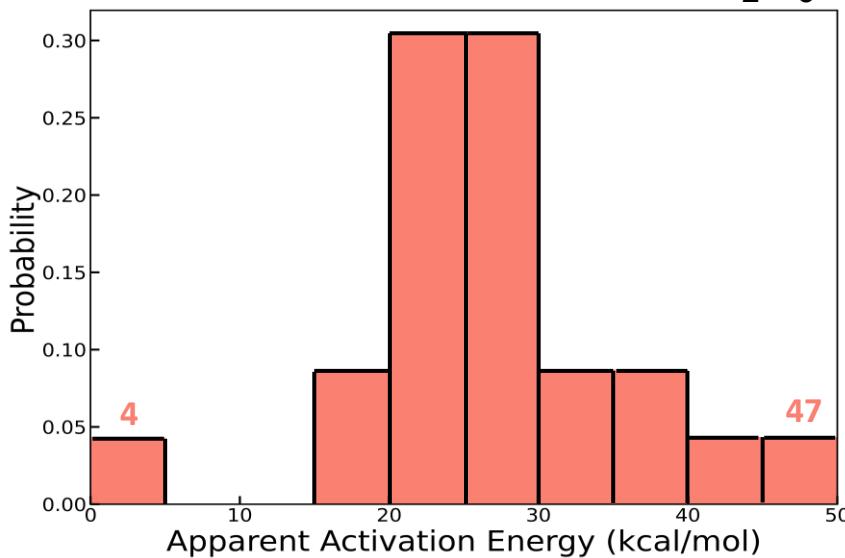


NH<sub>3</sub> decomposition on Ru/TiO<sub>2</sub>

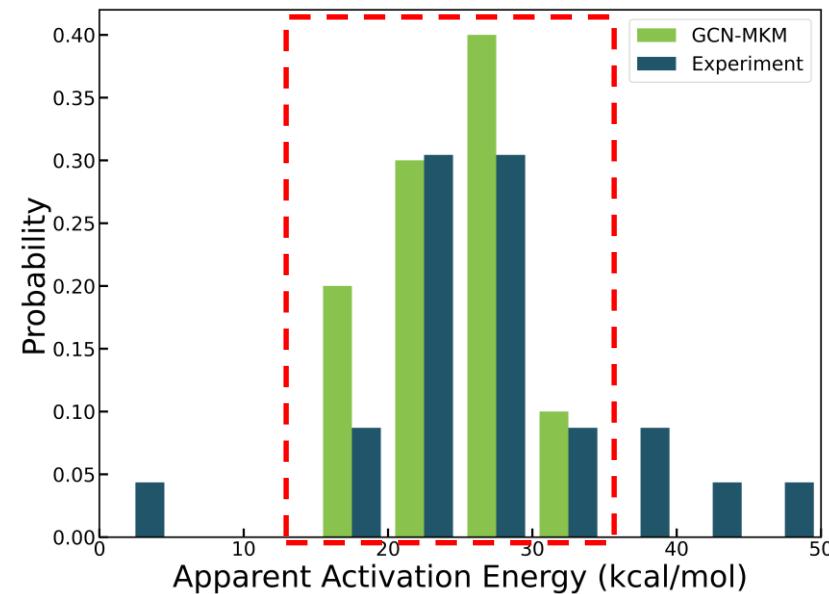


# Closing the Gap with Experiments/Data Quality

Methane combustion on Pt/Al<sub>2</sub>O<sub>3</sub>



Comparison to Experimental Data

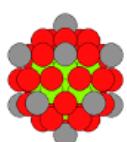


Apparent activation energies mostly fall between **20 to 30 kcal/mol** and consistent with **experimental** observations

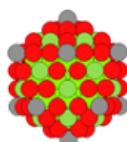
# Nanoparticle Size Effects

## Icosahedral Nanoparticles

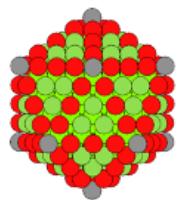
1.11 nm Pt55



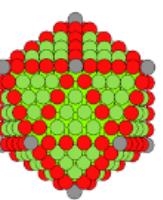
1.66 nm Pt147



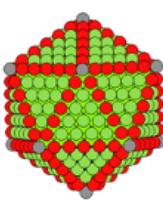
2.22 nm Pt309



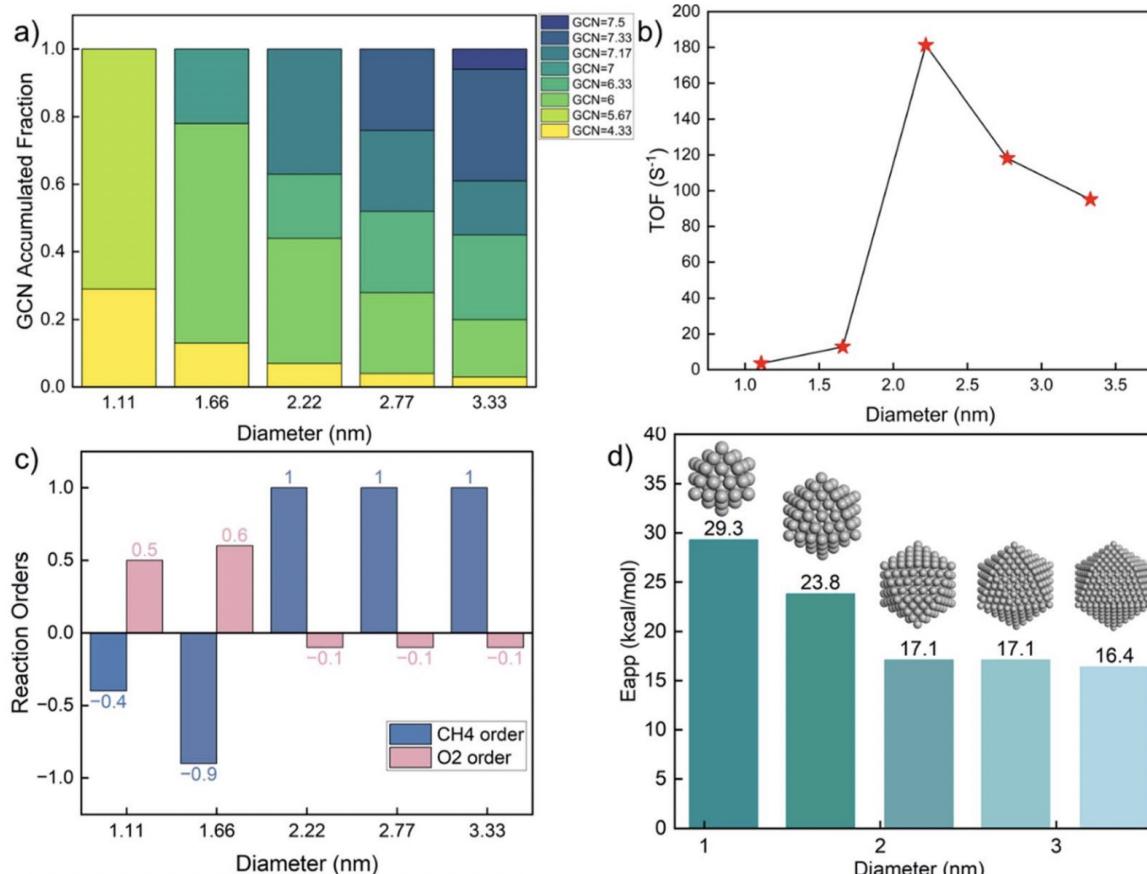
2.77 nm Pt561



3.33 nm Pt923

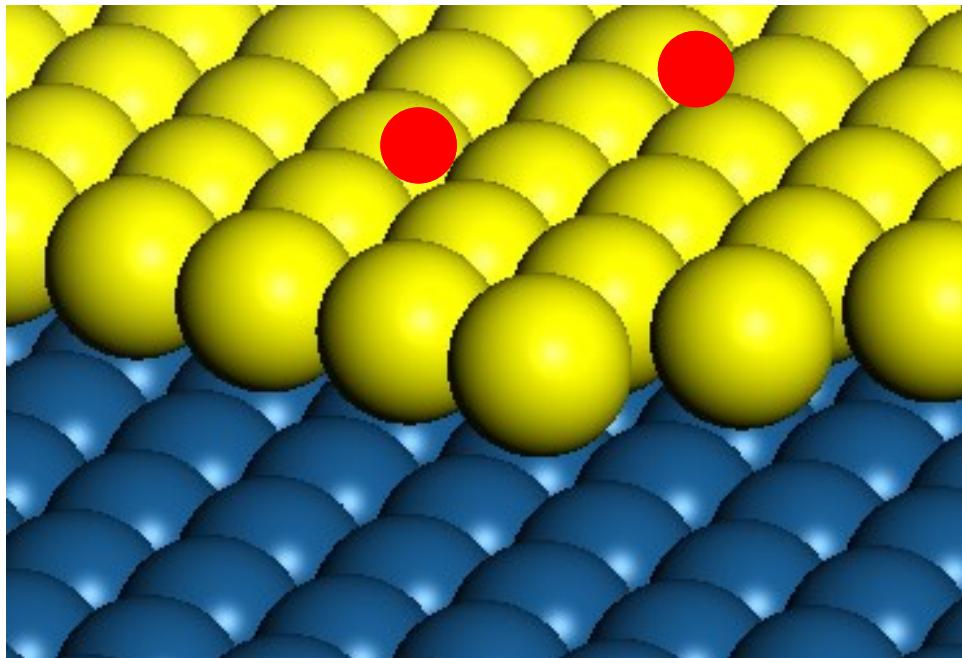


- ✓ Small nanoparticles are **undercoordinated** with limited types of GCNs on the surface
- ✓ Large nanoparticles have more diverse reaction sites



- ✓ As nanoparticle diameter grows larger than **2 nm**, the kinetic performance becomes different

# Schematic of Overall Process on Bimetallics: Minimum Energy Path Thinking

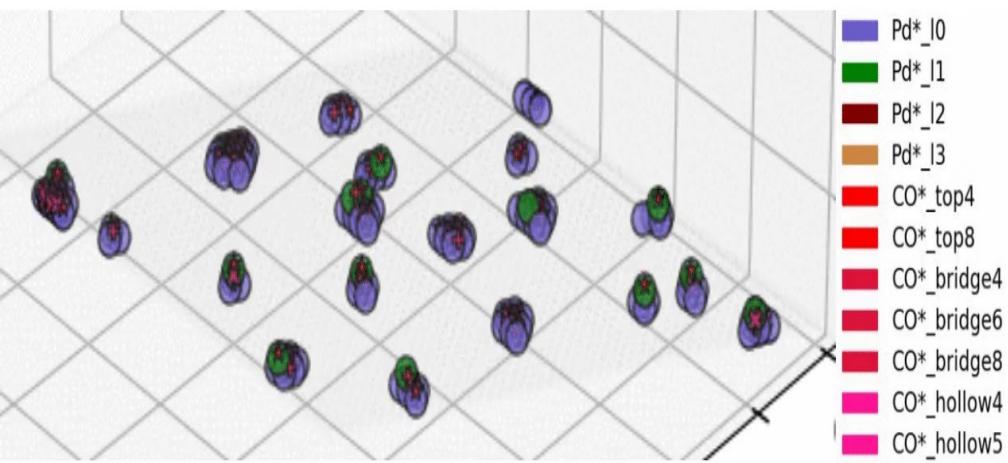


- Ni/Pt serves as a reservoir of N due to strong binding
- N diffuses at interfacial sites invoking steps and Pt terraces and associates and desorbs from there



# Catalysts are Heterogeneous and Dynamic

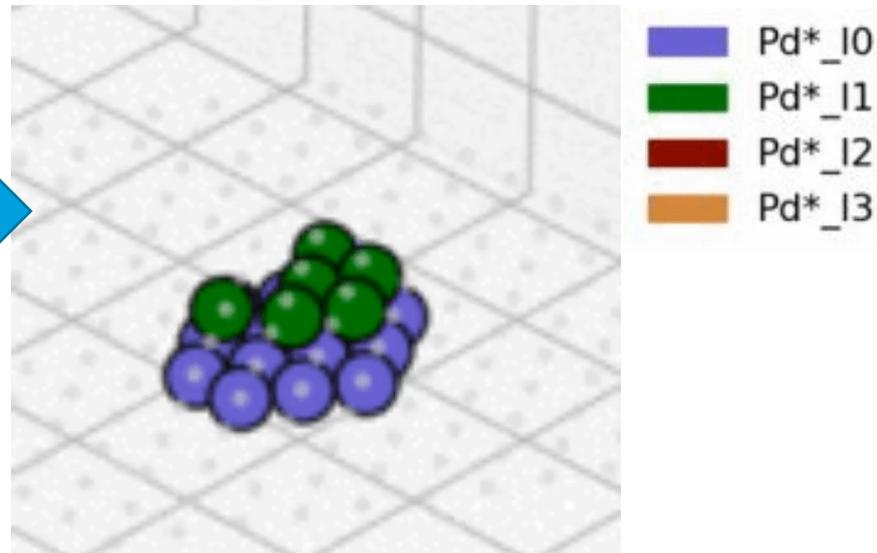
Time: 7.195e+01 sec



Exposure to 0.1 bar of CO; 300 K

Pd<sub>20</sub> relaxes to a bilayer cluster fast; 300 K

Time: 2.386e-07 sec



# END