

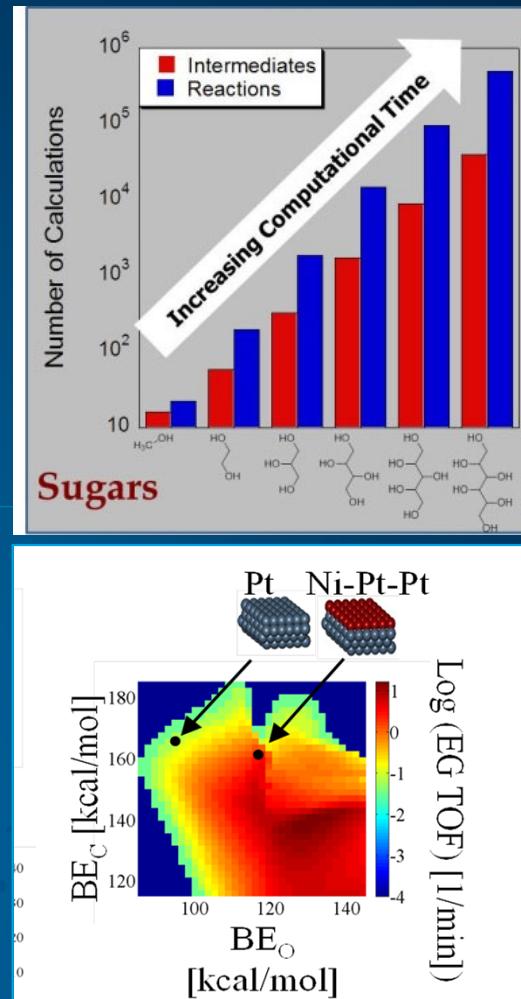
Multiscale Modeling and VLab Overview

Microkinetics Fundamentals and Applications: *Handling Complexity*

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December 11, 2023

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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



Learning Objectives



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
- 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).



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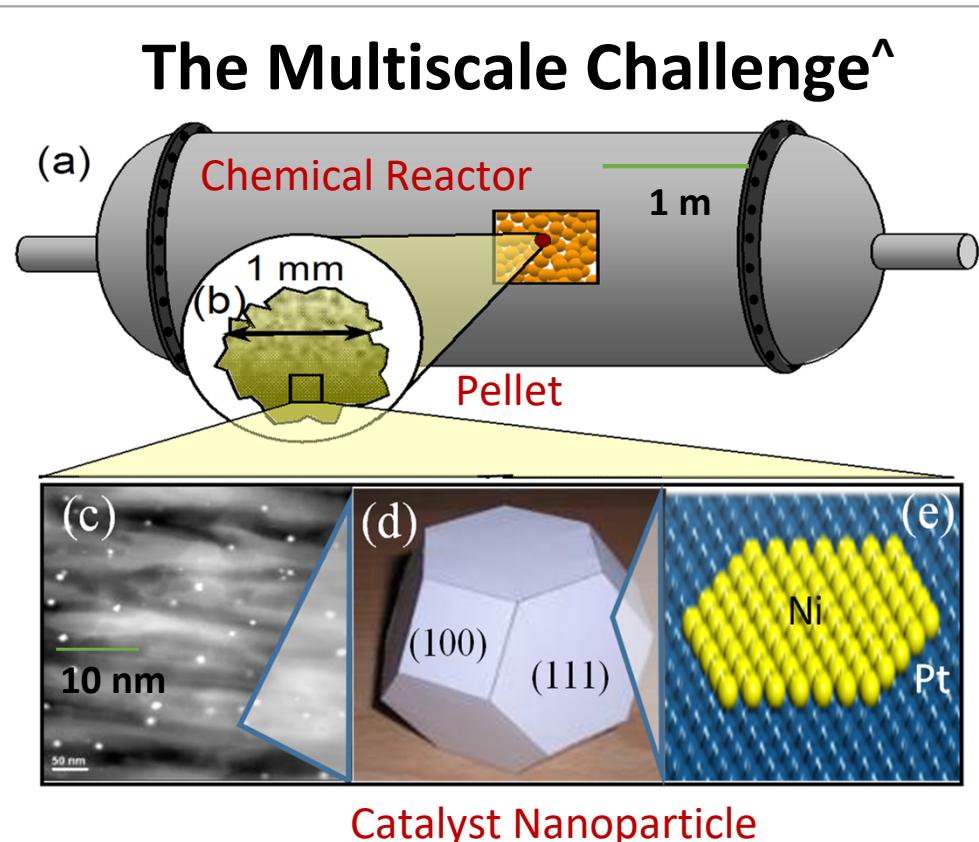


Other uses of MKMs



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_{app} , a , b contain mechanistic understanding*

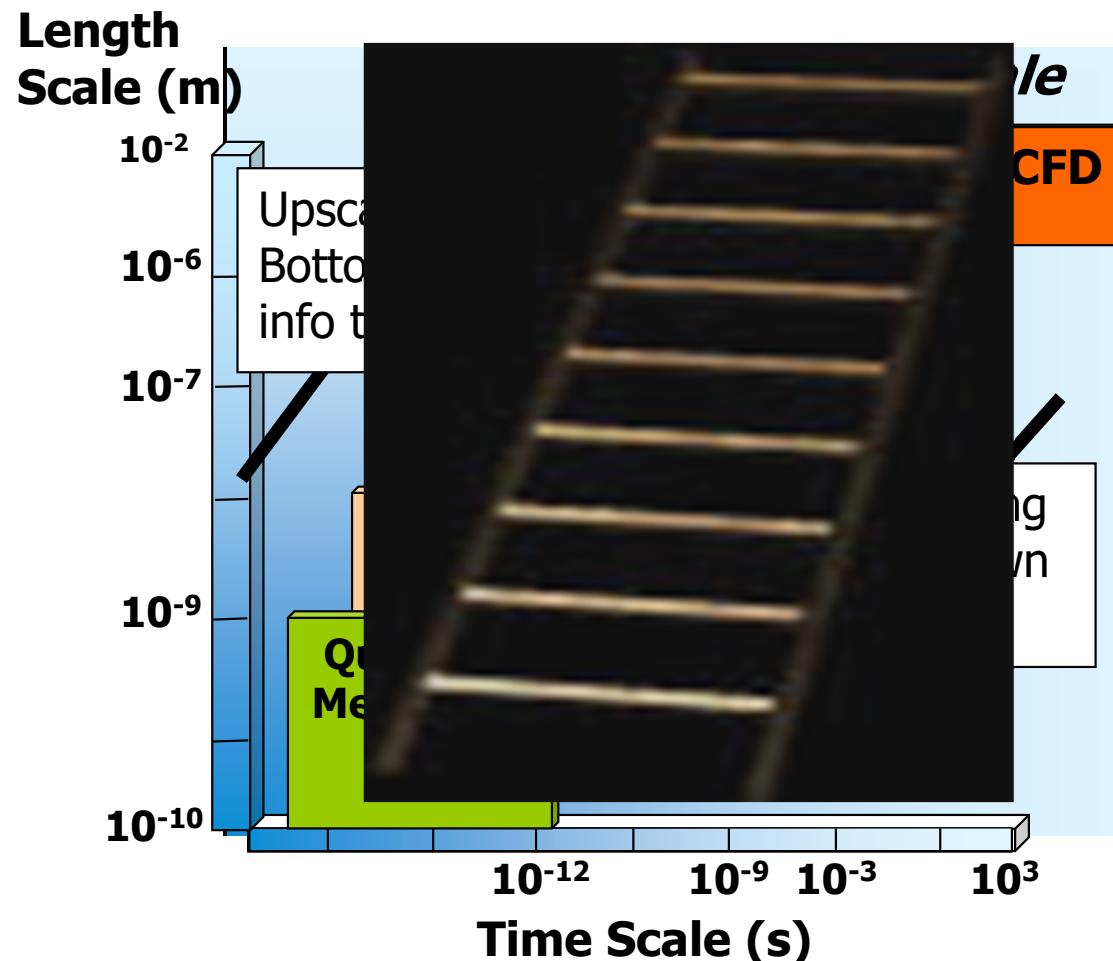


9 orders disparity in scales
Quantum modeling inadequate

[^]Vlachos, *Adv. Chem. Eng.* **30**, 1 (2005).



Modern Multiscale Simulation Paradigm



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

- **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



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



Types of Multiscale Simulation

- **Serial, one-way, or decoupled**
 - Information from a model at a smaller scale is passed onto the next scale model. Models are solved separately.
 - Examples
 - Compute activation energies and pre-exponentials by quantum mechanics and pass reaction rate constants into a CFD code (e.g., gaseous processes such as combustion, atmospheric modeling/pollutant fate, CVD, etc.)
- Most systems exhibit coupling between scales and models; Serial modeling is often an approximation
- **Co-current, two-way, or coupled**
 - Models at both (or all) scales are simultaneously solved



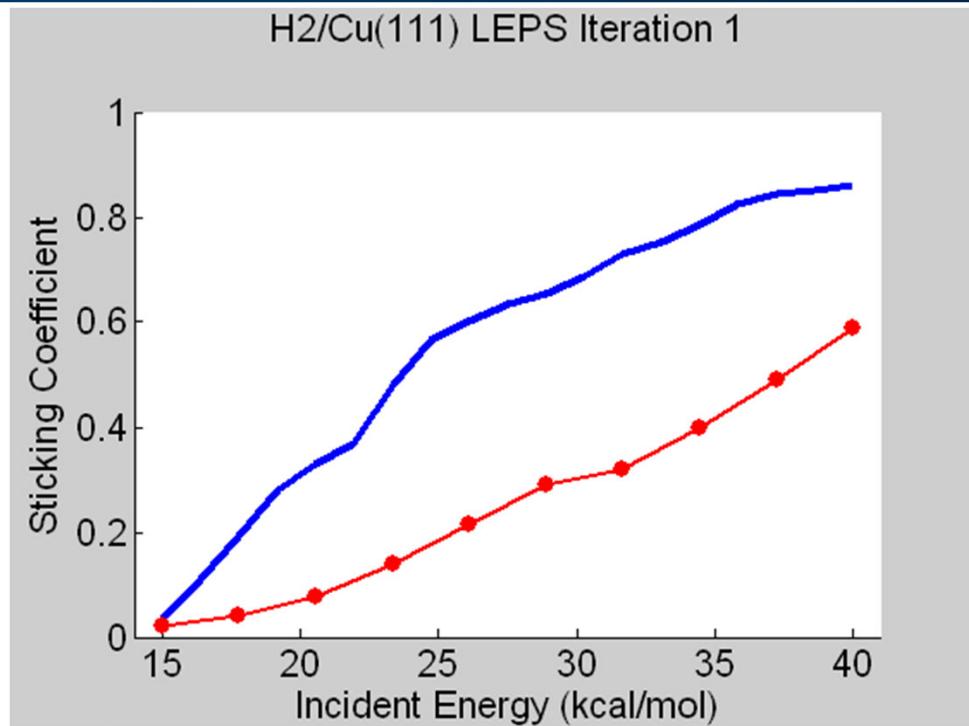
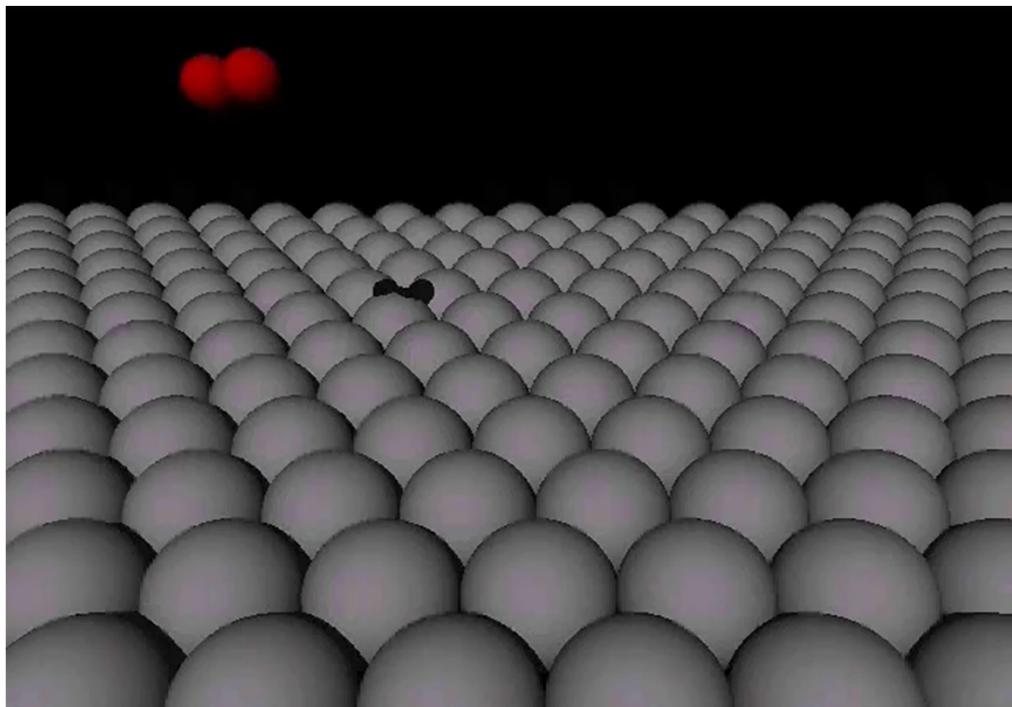
Coupled Multiscale Simulation Types

- 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



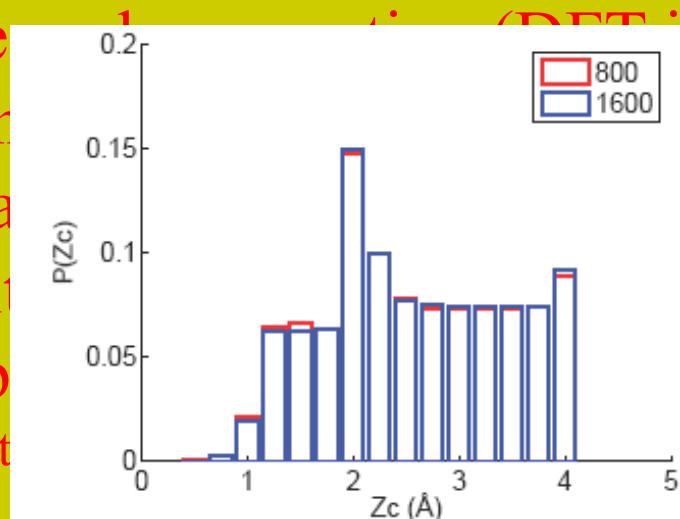
DFT/MD Hybrid Simulation

Reduction of finer scale model

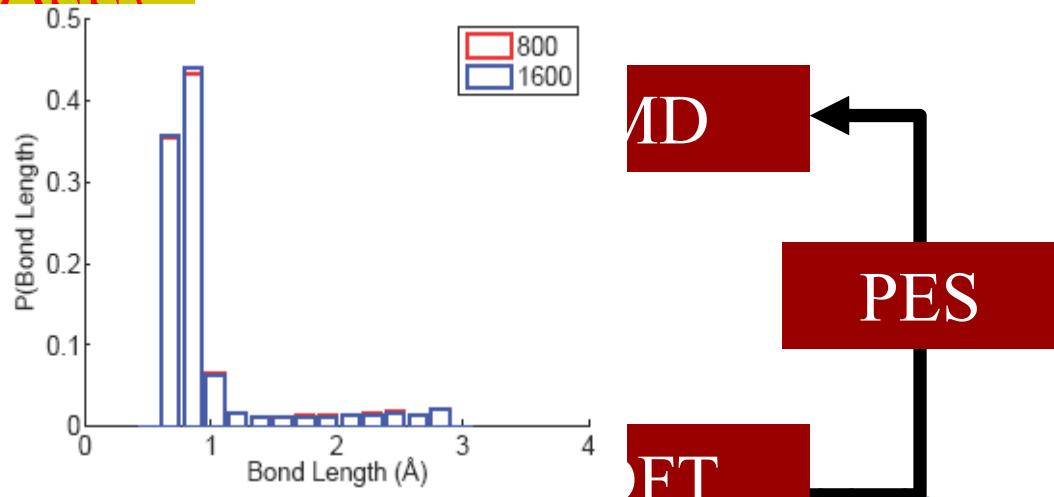


- Time
- Parame
- neural
- Addit
- samp

Ludwig et



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





Learning Objectives



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

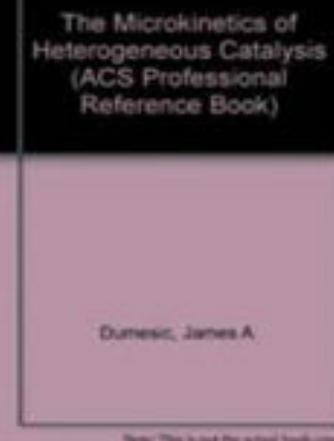
- **Overall rates; Engineering Models**

Empirical rate-law; typically fitted to experimental data

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

Elementary & Overall rates; Academic and Eng!

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_{app} and reaction orders using MKM and compare to exps



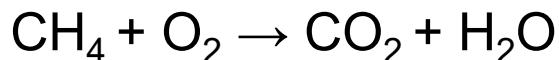
Empirical Models Considerations

- 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?

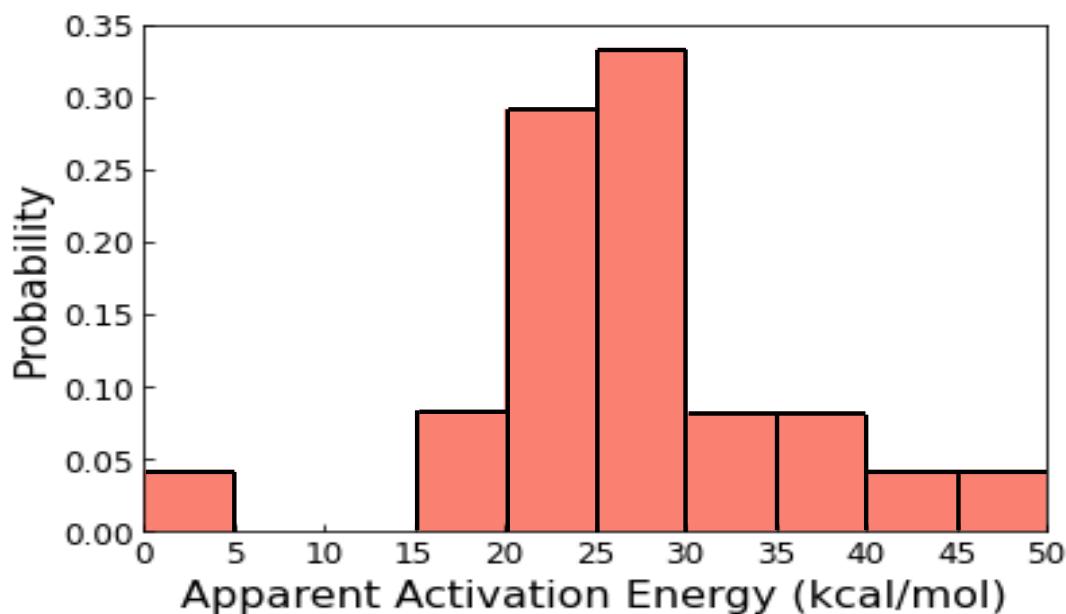


Scatter in Published Data

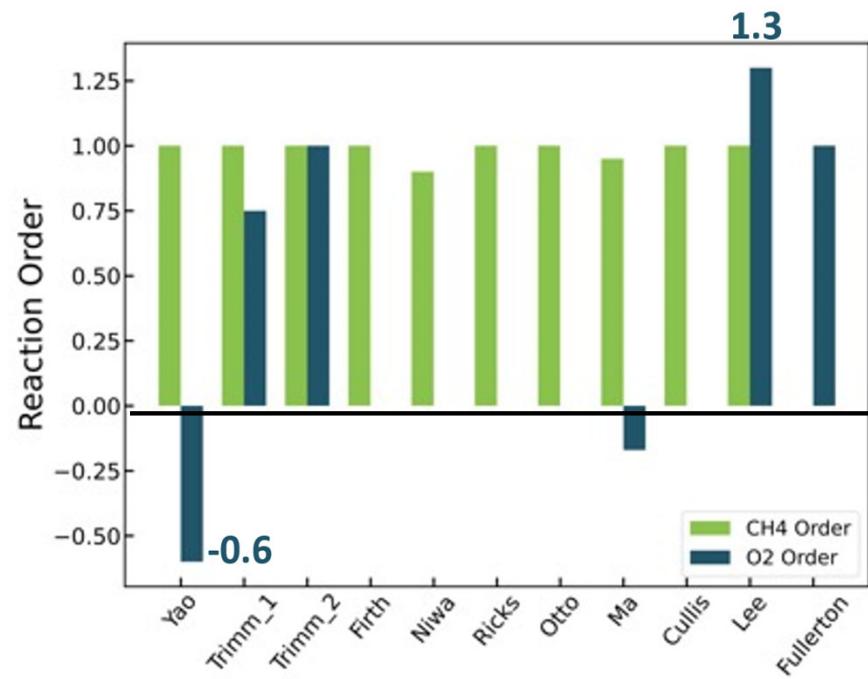
Experimental Data Collected from the Literature



Data for Fuel-Rich @ 553 K - 823 K on Pt/Al₂O₃



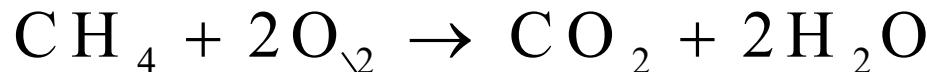
How do we explain the scatter in data?



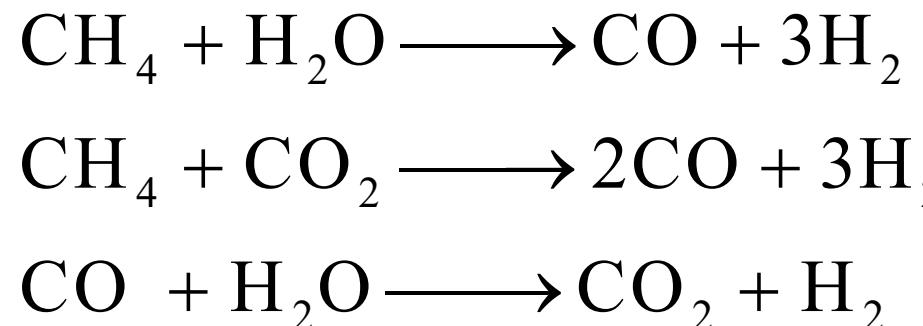
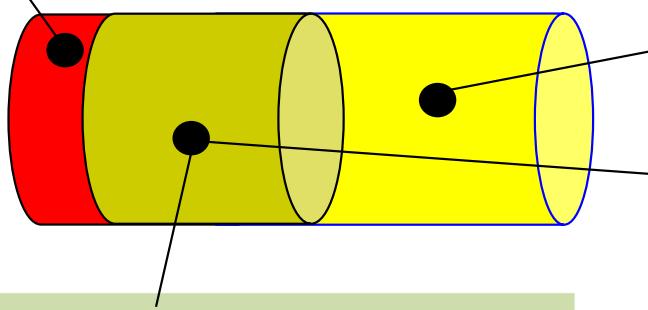
- Hypothesis: **structure sensitivity** plays a critical role
- How do you design the optimal catalyst structure?

Stratified Partial Oxidation

What Global Reaction(s) Occur?



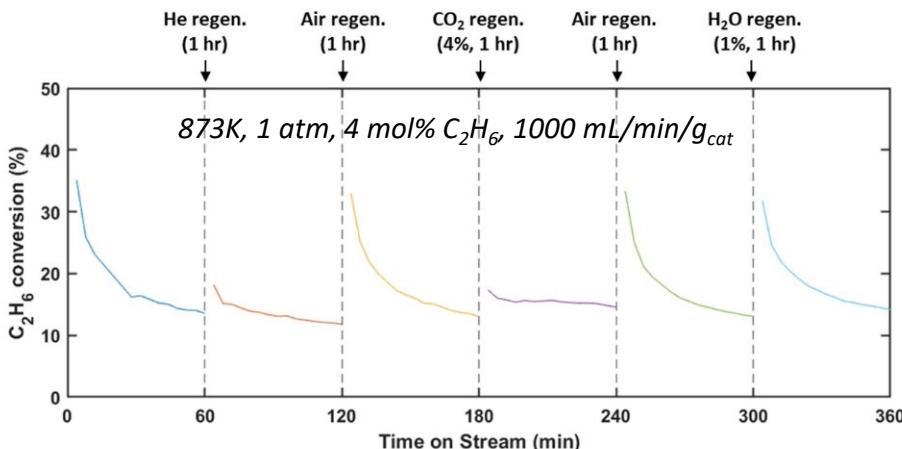
Short Contact Time Technology of Hichman and Schmidt, 1993



- 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: H_2O removes coke
- **Regeneration study confirms H_2O removes coke; CO_2 does not**

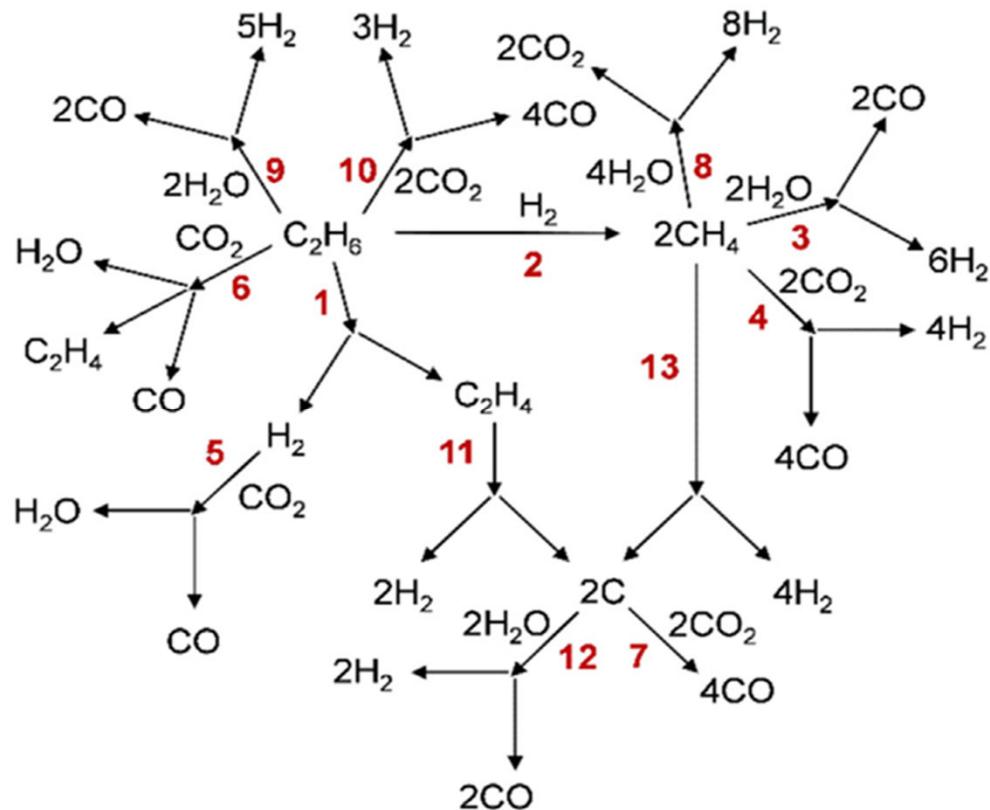


Experiments performed by Dr. Weiqi Chen.

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



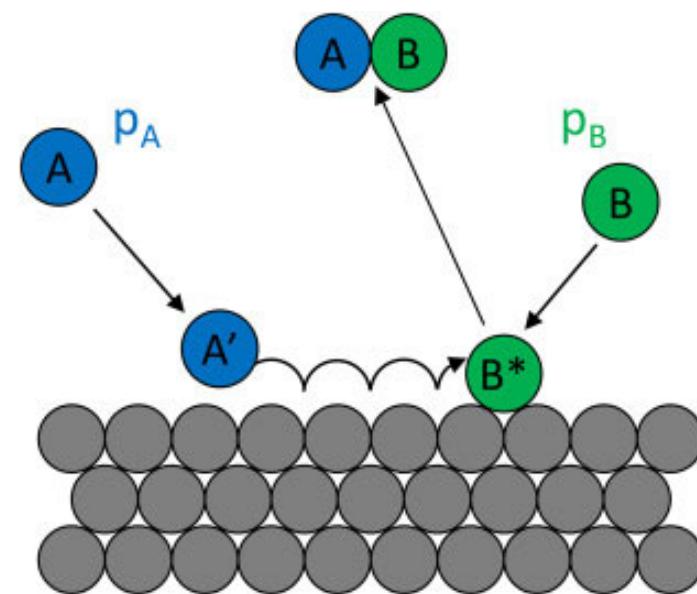
1. Ethane Dehydrogenation
2. Ethane Hydrogenolysis
5. Reverse Water-Gas Shift
- 11, 13. Hydrocarbon Coking
12. Coke gasification via H_2O



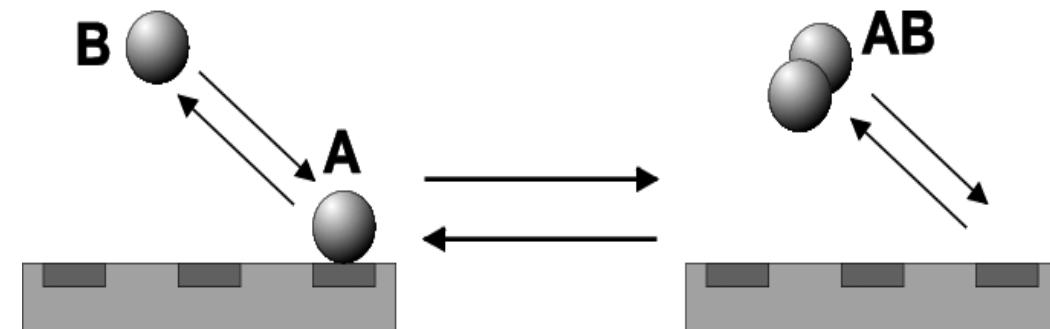
Langmuir-Hinshelwood Rate Expressions

Type of Elementary Steps

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

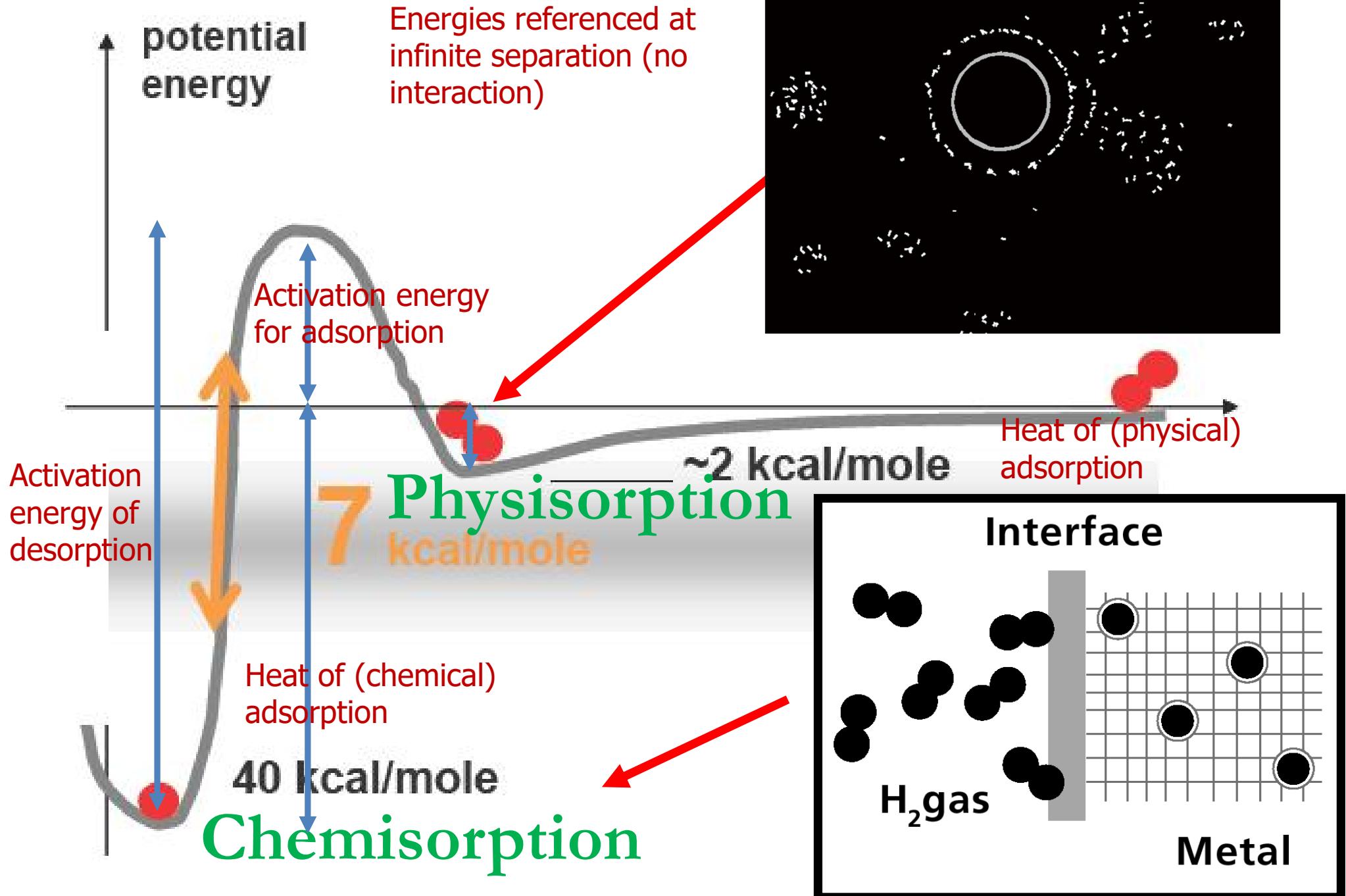


Langmuir–Hinshelwood



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

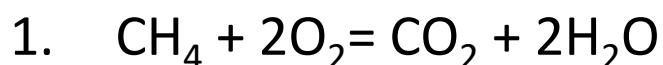


LH Rates on Rh



Overall rxns (hypothesized?)

1. *CH₄ total oxidation (combustion)*



$$r_{TO} = \frac{k_{TO} \cdot P_{\text{CH}_4}}{(1 + K_{H,O}^{\text{ads}} \cdot P_{H,O})^2}$$

2. *Steam reforming of CH₄*



$$r_{SR} = \frac{k_{SR} \cdot P_{\text{CH}_4} \cdot (1 - \eta_{SR})}{(1 + K_{O_2}^{\text{ads}} \cdot P_{O_2} + K_{CO}^{\text{ads}} \cdot P_{CO})^2}$$

3. *CO₂-reforming of CH₄*



$$r_{CO_2-R} = \frac{k_{CO_2-R} \cdot P_{\text{CH}_4} \cdot (1 - \eta_{CO_2-R})}{(1 + K_{O_2}^{\text{ads}} \cdot P_{O_2} + K_{CO}^{\text{ads}} \cdot P_{CO})^2}$$

4. *RWGS*



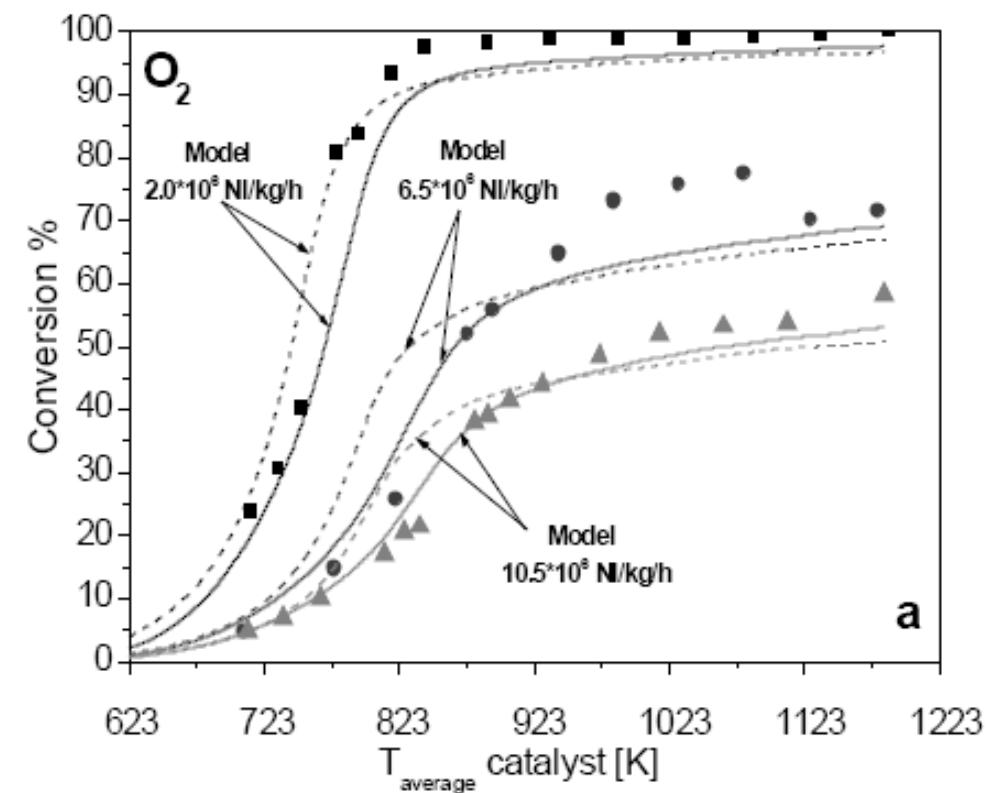
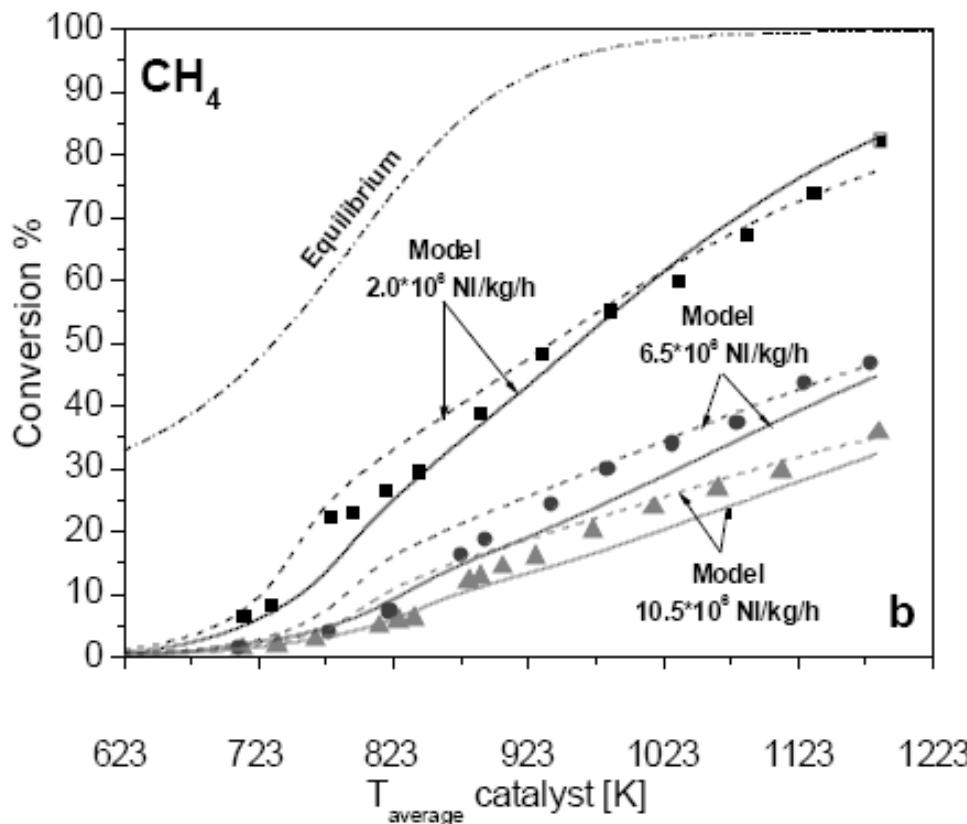
$$r_{RWGS} = \frac{k_{RWGS} \cdot P_{\text{CO}_2} \cdot P_{\text{H}_2} \cdot (1 - \eta_{RWGS})}{(1 + K_{O_2}^{\text{ads}} \cdot P_{O_2} + K_{CO}^{\text{ads}} \cdot P_{CO})^2}$$

η = distance from equilibrium

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

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 H₂;
solid lines = model with consecutive CO and H₂ combustion

Parameters & Model Adequacy

Estimated parameters

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

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

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



Learning Objectives



Multiscale modeling



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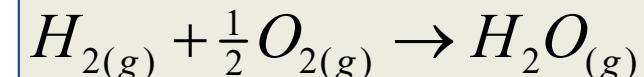


Other uses of MKMs

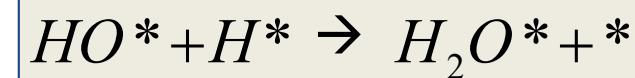


- Includes all relevant elementary reactions
 - Written by hand or computer generated¹
- No simplifying assumptions re rate determining step (RDS), partial equilibrium (PE), quasi-steady state (QSS), and most abundant surface intermediate (MASI); these are all predicted rather than assumed
- Reactor + Catalyst model needed
 - Use computer software, such as surface CHEMKIN³, Cantera², Matlab, Python, OpenMKM

An example



Elementary Reactions



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

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

³Chemkin (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

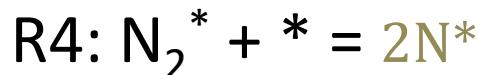
➤ Surface species concentration

- Total concentration of sites, C_T = moles/cm²
- Concentration of species k, C_k = moles/cm²

➤ 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
- $\text{Sum}(\theta_k) = 1$

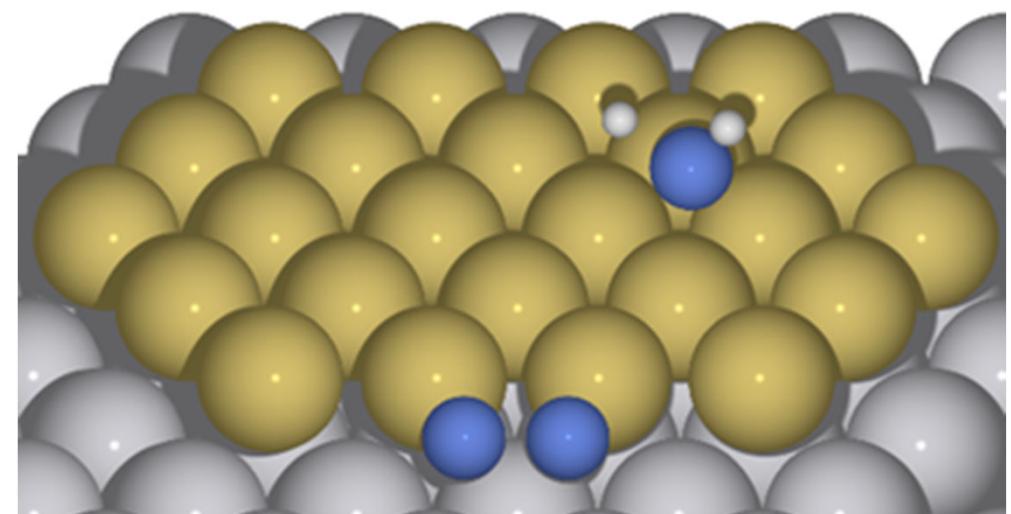
➤ Surface reaction rate



Reaction rate:

$$r_4 = k_4 [\text{N}_2^*][\text{Pt}] \frac{\text{moles}}{\text{cm}^2 \text{s}}$$

$$r_4 = k_4 \theta_{\text{N}2} \theta_* \frac{\text{molecules}}{\text{sites}} \rightarrow \text{TOF (turnover frequency)}$$



Surface Species Balance

Example



T = 973 K, P = 1 atm, V = 1 cm³,
0.1 g 1%Pt/C catalyst, flow rate = xxx sccm

Adsorption:

1. NH₃ + * = NH₃*
2. N₂ + * = N₂*
3. H₂ + 2* = 2H*

Surface reactions:

4. N₂* + * = 2N*
5. NH₃* + * = NH₂* + H*
6. NH₂* + * = NH* + H*
7. NH* + * = N* + H*

Balance for N* species:

$$\frac{d[N^*]}{dt} = \text{# moles Rate constants } d[N^*] = 2k_4[N_2^*][Pt] - 2\frac{k_4}{K_{c4}}[N^*]^2 + \text{ Equilibrium constants } + k_7[NH^*][Pt] - \frac{k_7}{K_{c7}}[N^*][H^*] \text{ Species conc (mol/cm}^2\text{)} \\ \text{Empty sites}$$

Parameters needed:

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



- Reactions written as irreversible steps
 - CO_2 forms and directly goes in the gas phase; irreversible
- Units of pre-exps in s^{-1} (or in cm, s, depending on reaction order)



Langmuir-Hinshelwood Kinetics

MF Model for CO Oxidation

| Reactions | $A_o (\text{s}^{-1}) \text{ or } S_o$ | $E_a (\text{kcal/mol})$ |
|---|---------------------------------------|-------------------------|
| 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 ith 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)

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

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

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

- 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

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

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

- Units

- Concentrations [mols/cm² of active catalyst phase], rate const. k [cm, mol, s], rate [moles/cm²/s]
- Coverage (molecules per site), rate const. k [s⁻¹], rate [mlcs/site/s] or TOF

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*

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

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

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

$\zeta = 3$
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&

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

| (1) Site conservation** | $\sum_{k=1}^{K_s} C_k = C_T \quad \left[\frac{gmol}{cm^2} \right]$ | $\sum_{k=1}^{K_s} \theta_k = 1 \quad \left[\frac{molecule}{site} \right]$ |
|--|--|---|
| (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 $k=1, \dots, K_s$ Algebraic eqs. | $\theta = \sigma_k$ | $0 = \tilde{\sigma}_k$ |

* 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 NH_3 , N_2 , and 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

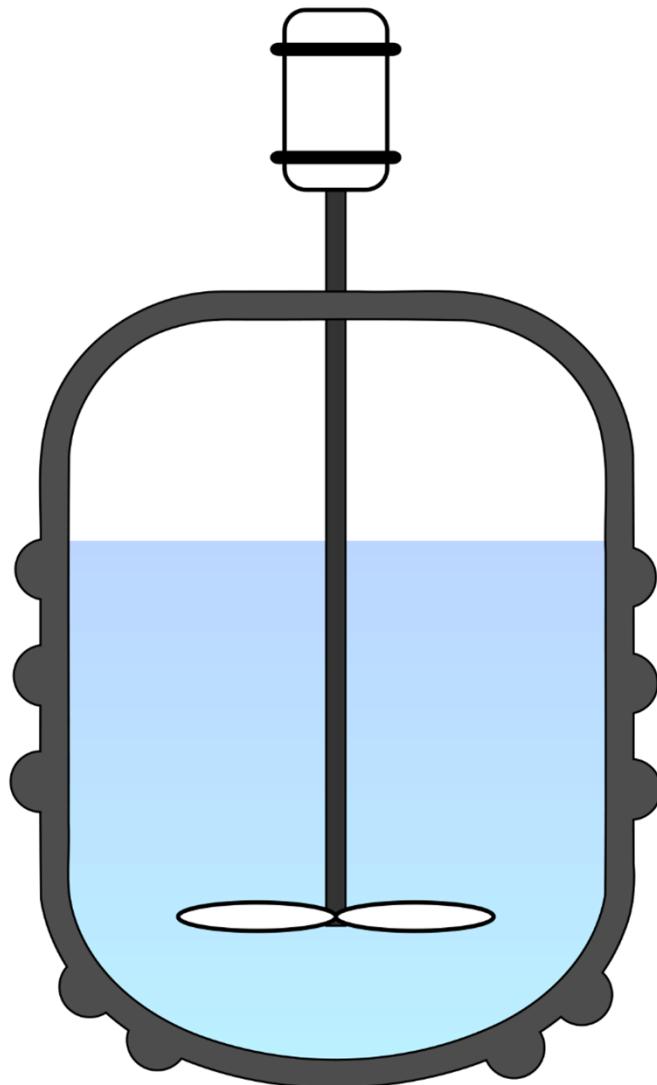
Adsorption/Desorption:

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

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

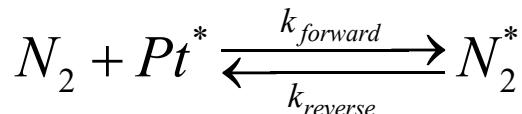
$$\frac{dY_k}{dt} = \frac{\dot{\omega}_k W_k}{\rho}$$

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

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)



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

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

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/cm²], $C_T \sim 10^{-9}$ [gmoles of sites/cm²].

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

¹ 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) $\sum_{k=1}^{K_s} \theta_k = 1$ 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 | No internal and external transport; Isothermal: <u>Gas-phase</u> (1) $\frac{dW_k}{dz} = \frac{(\sigma_k^{\text{fluid}} + \sigma_k^{\text{surf}} a) M_k}{\rho u}, k=1, \dots, K_g$ $\sigma_k^{\text{surf}} = v_{\text{ads}} r_{\text{ads},k} + v_{\text{des}} r_{\text{des},k}$ typically : $v_{\text{ads}} = -1, v_{\text{des}} = 1$ <u>Surface</u> (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 | <p>No internal and external transport; Isothermal:</p> <p>(1) <u>Gas-phase</u></p> $\frac{dW_k}{dt} = 0 = \frac{W_k^o - W_k}{\tau(\rho / \rho^o)} + \frac{(\sigma_k^{\text{fluid}} + \sigma_k^{\text{surf}} \underline{a}) M_k}{\rho}$ <p>or $\frac{dW_k}{dt} = 0 = \frac{W_k^o - W_k}{\tau_m} + \frac{(\sigma_k^{\text{fluid}} + \sigma_k^{\text{surf}} \underline{a}) M_k}{\rho}$,</p> <p>$k=1, \dots, K_g$</p> <p><u>Surface</u></p> <p>(2) $\tilde{\sigma}_k = 0, k=1, \dots, K_s-1$</p> <p>(3) $\sum_{k=1}^{K_s} \theta_k = 1$</p> | Nonlinear algebraic solver, e.g., Newton, (fsolve) |
|--|----------------------------|--------|---|--|

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

ρ 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

ρu represents the mass flux that is constant at every cross section of the PFR

θ_k is the coverage of species k

t denotes the time

T is the temperature

σ_k is the net surface rate of species k

ω is the site density

β 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



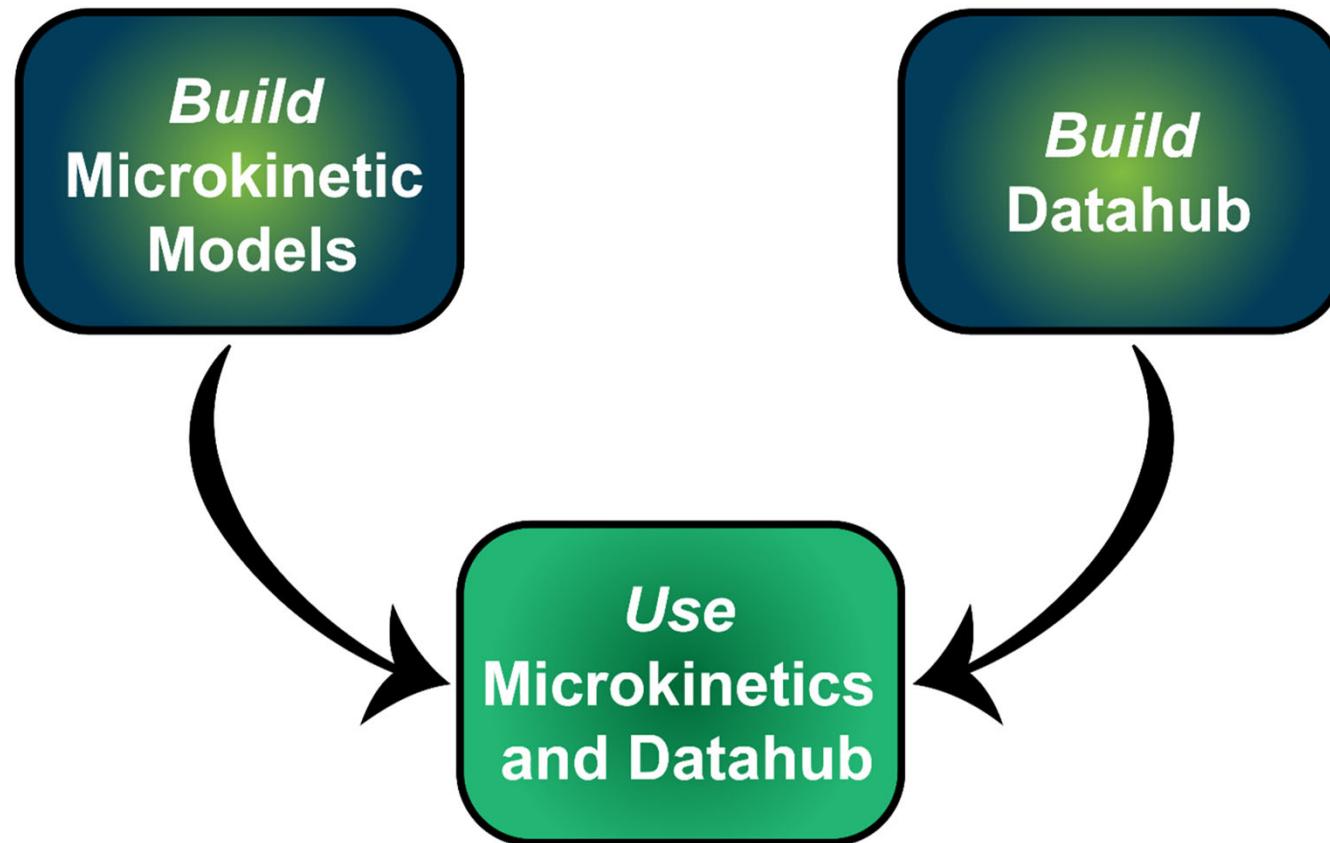
Automation in Building and Solving MKMs



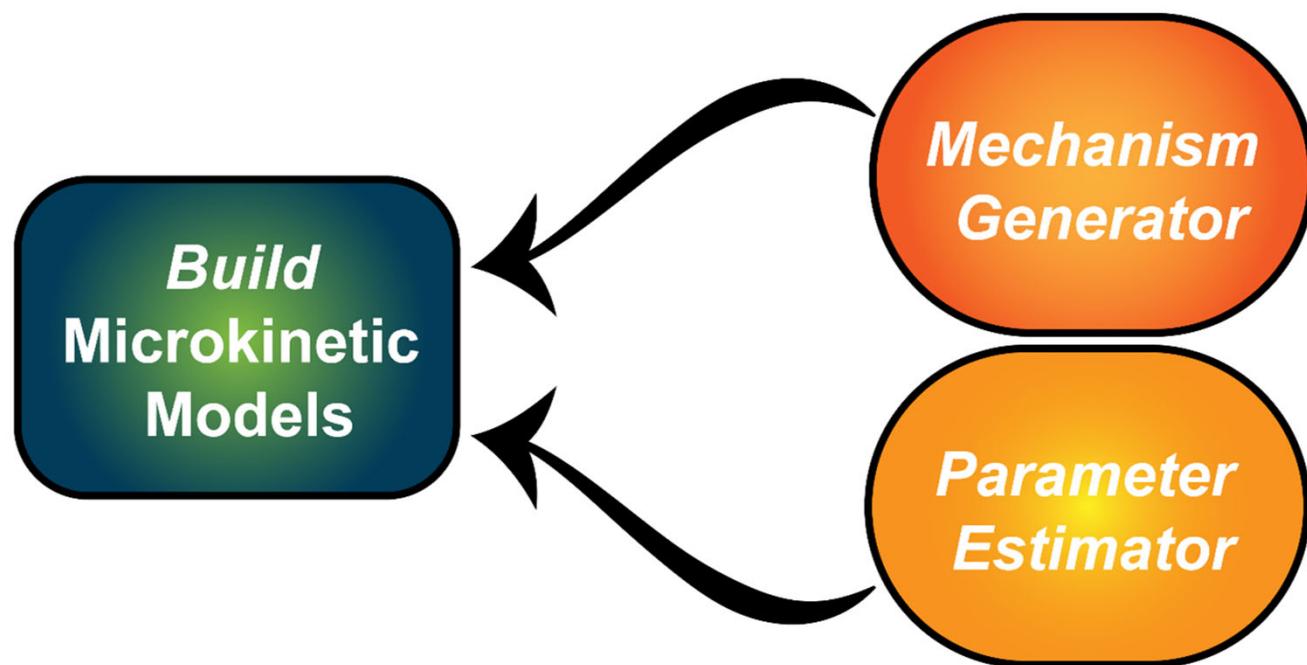
Manual Solution

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

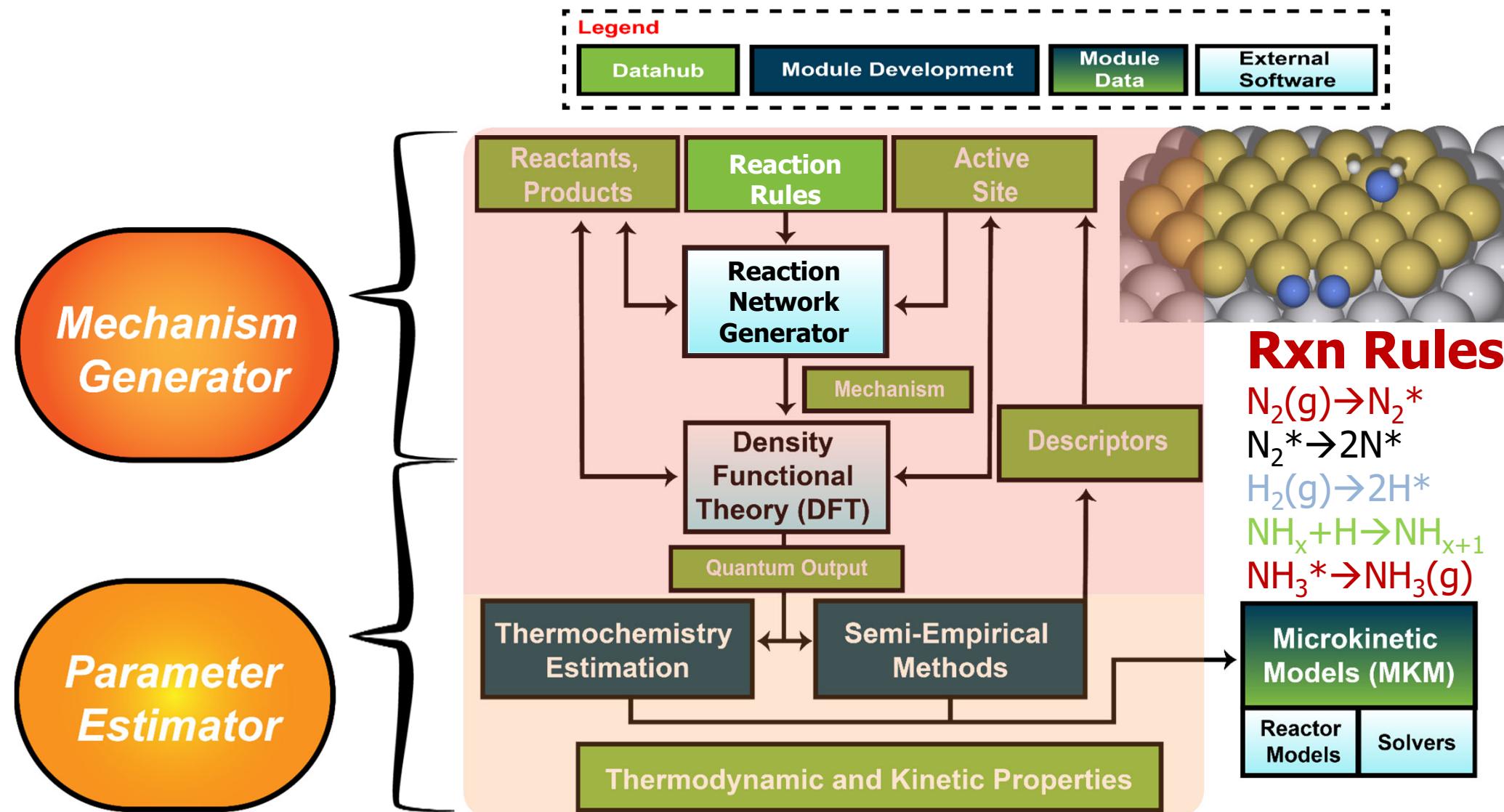
Software Modules and Datahub



Workflow and Software Modules

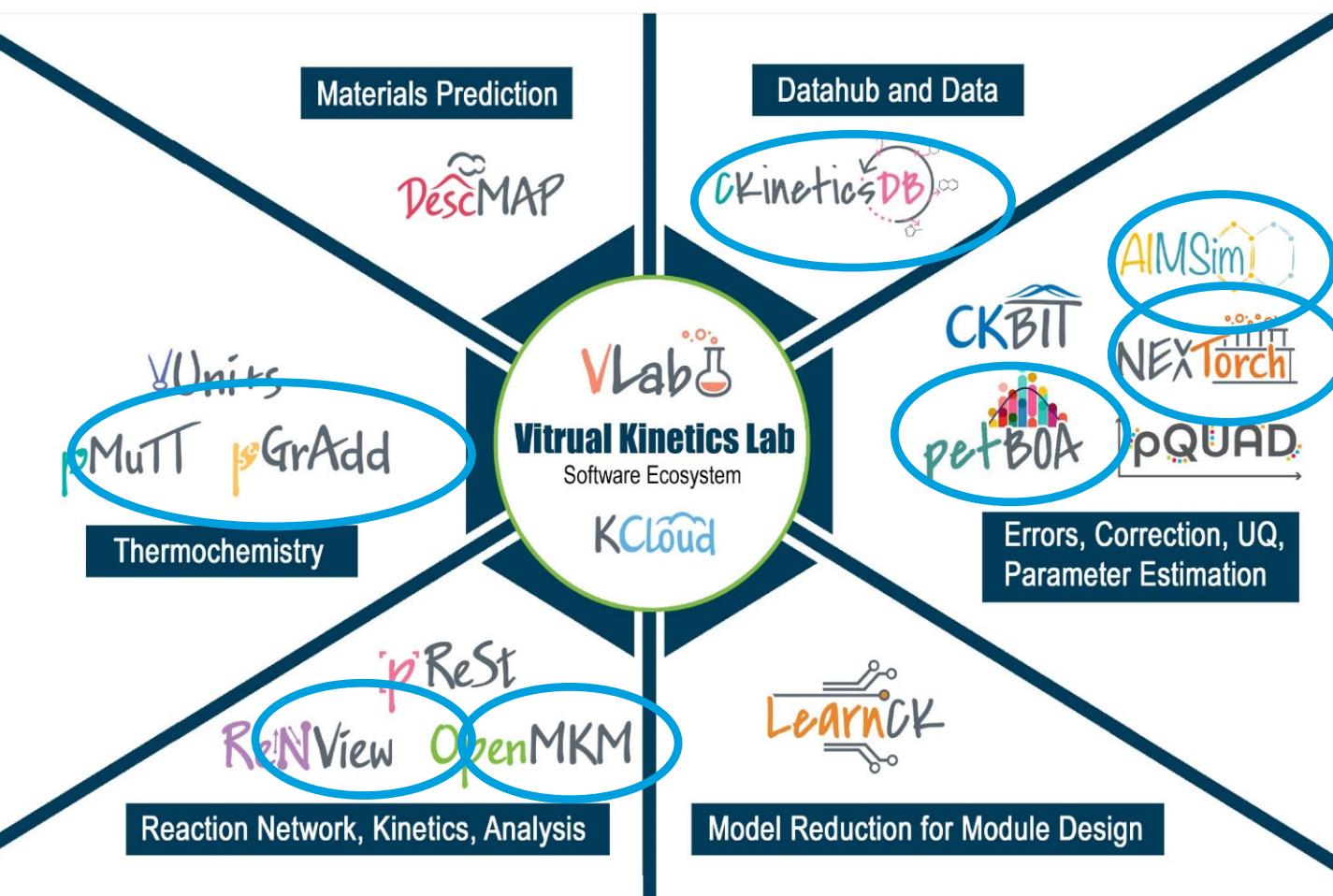


Workflow and Software Modules





Virtual Chemical Kinetics Lab – Vlab Overview



Software tools for multiscale modeling

| | |
|-------------|---|
| pMuTT | vlachosgroup.github.io/pMuTT |
| GrAdd | vlachosgroup.github.io/PythonGroupAdditivity |
| vUnits | vlachosgroup.github.io/vunits |
| pReSt | github.com/VlachosGroup/prest |
| ReNView | github.com/VlachosGroup/review |
| OpenMKM | vlachosgroup.github.io/openmkm |
| DescMAP | dei.udel.edu/rapid/rapid-research |
| CKineticsDB | dei.udel.edu/rapid/rapid-research |
| AIMSim | vlachosgroup.github.io/AIMSim |
| CKBIT | vlachosgroup.github.io/ckbit |
| NEXTorch | nextorch.readthedocs.io/en/latest |
| pQUAD | vlachosgroup.github.io/pQUAD |
| petBOA | dei.udel.edu/rapid/rapid-research |
| LearnCK | dei.udel.edu/rapid/rapid-research |



Learning Objectives



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



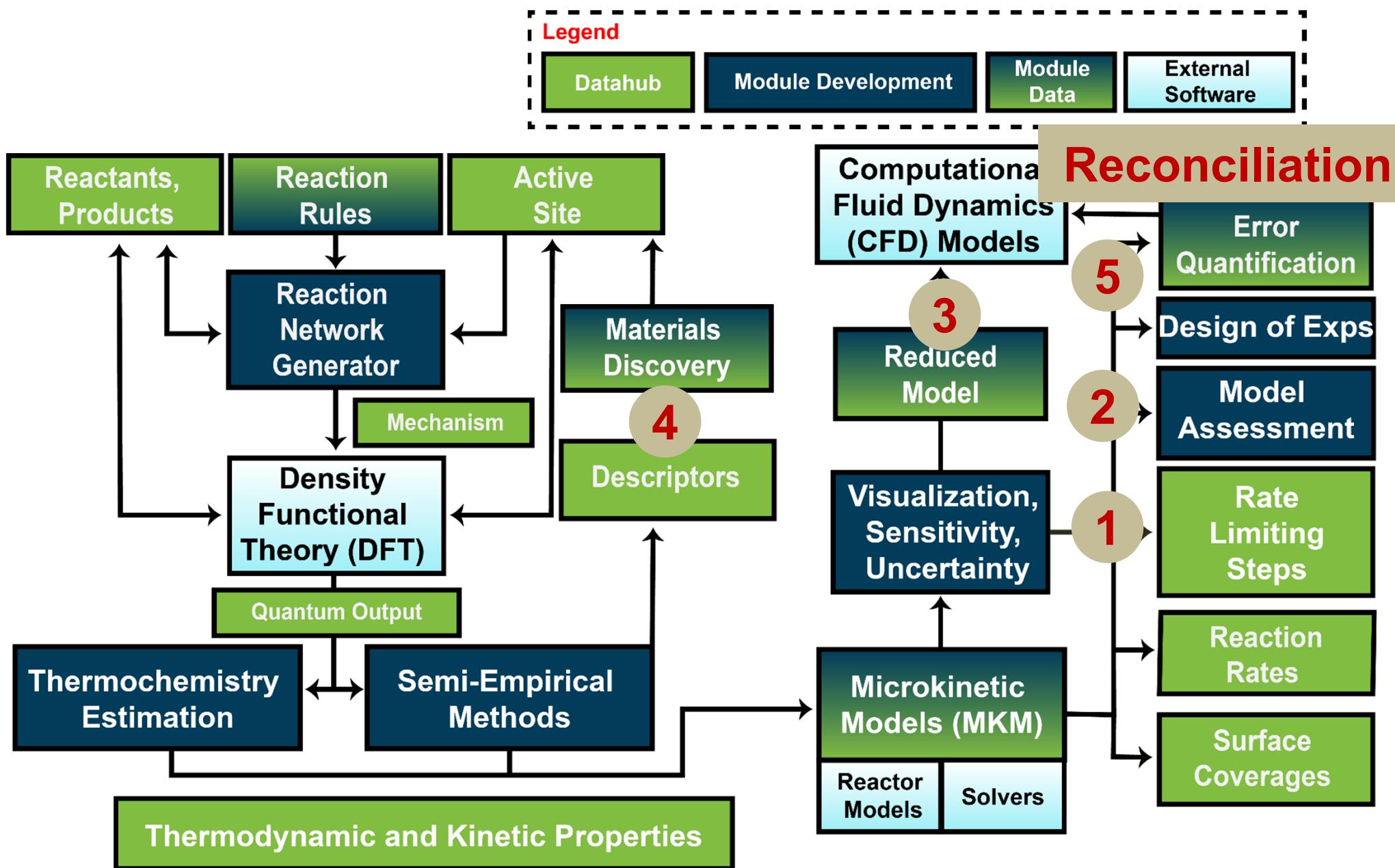
Analysis of MKMs

What can we learn?



Other uses of MKMs

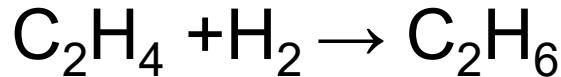
Workflow and Software Modules



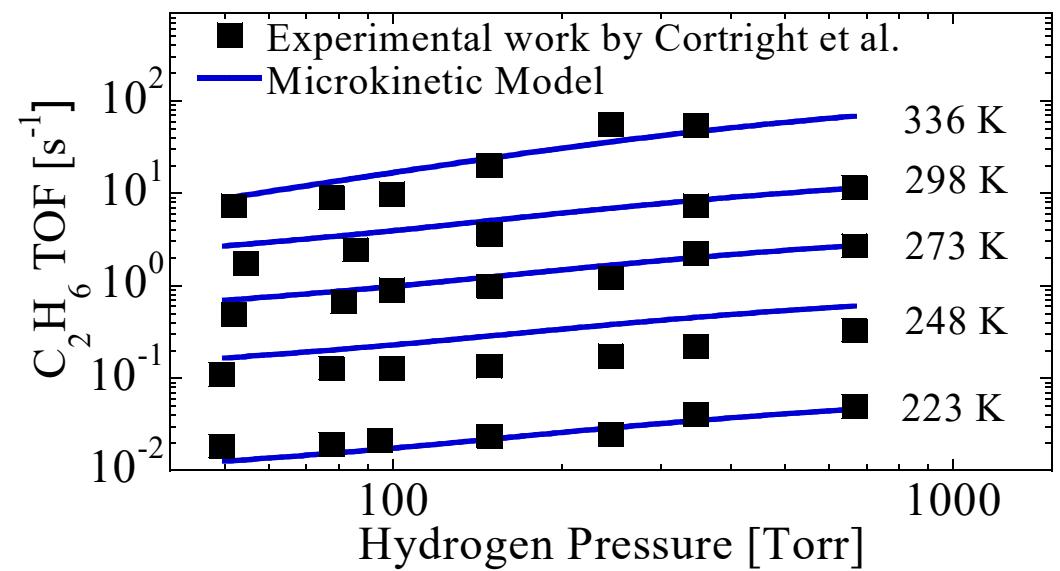
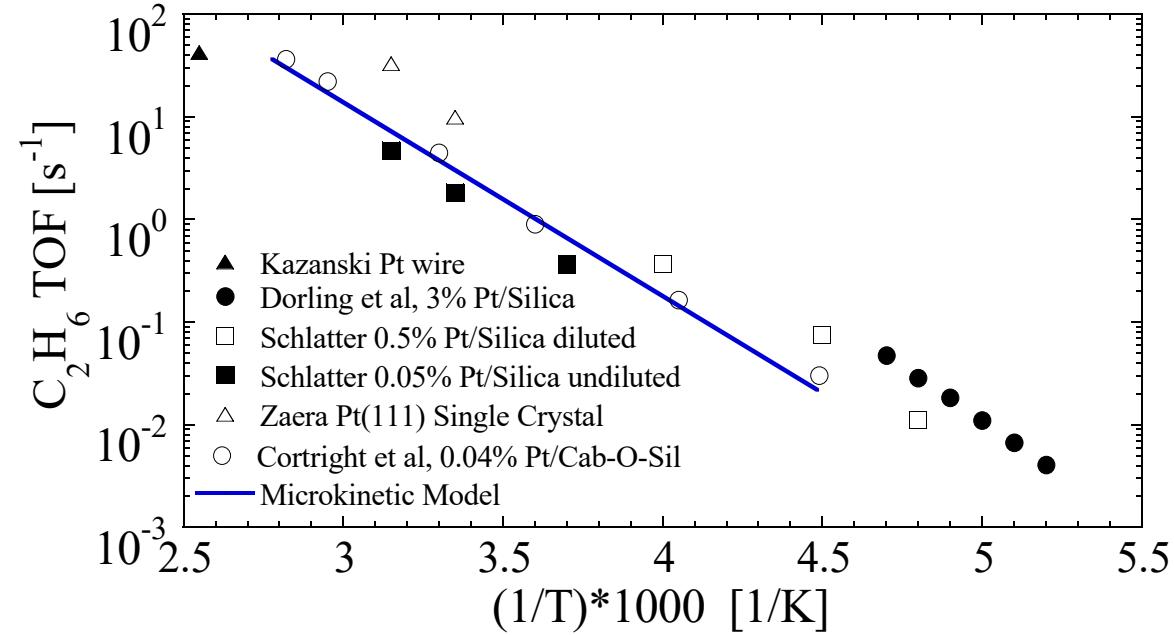
Analysis of MKM Data

Mechanism Reduction and
MKM-based Overall Rate
Expressions

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

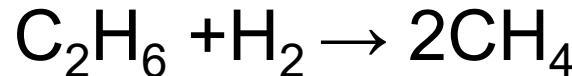


Experimental data from:

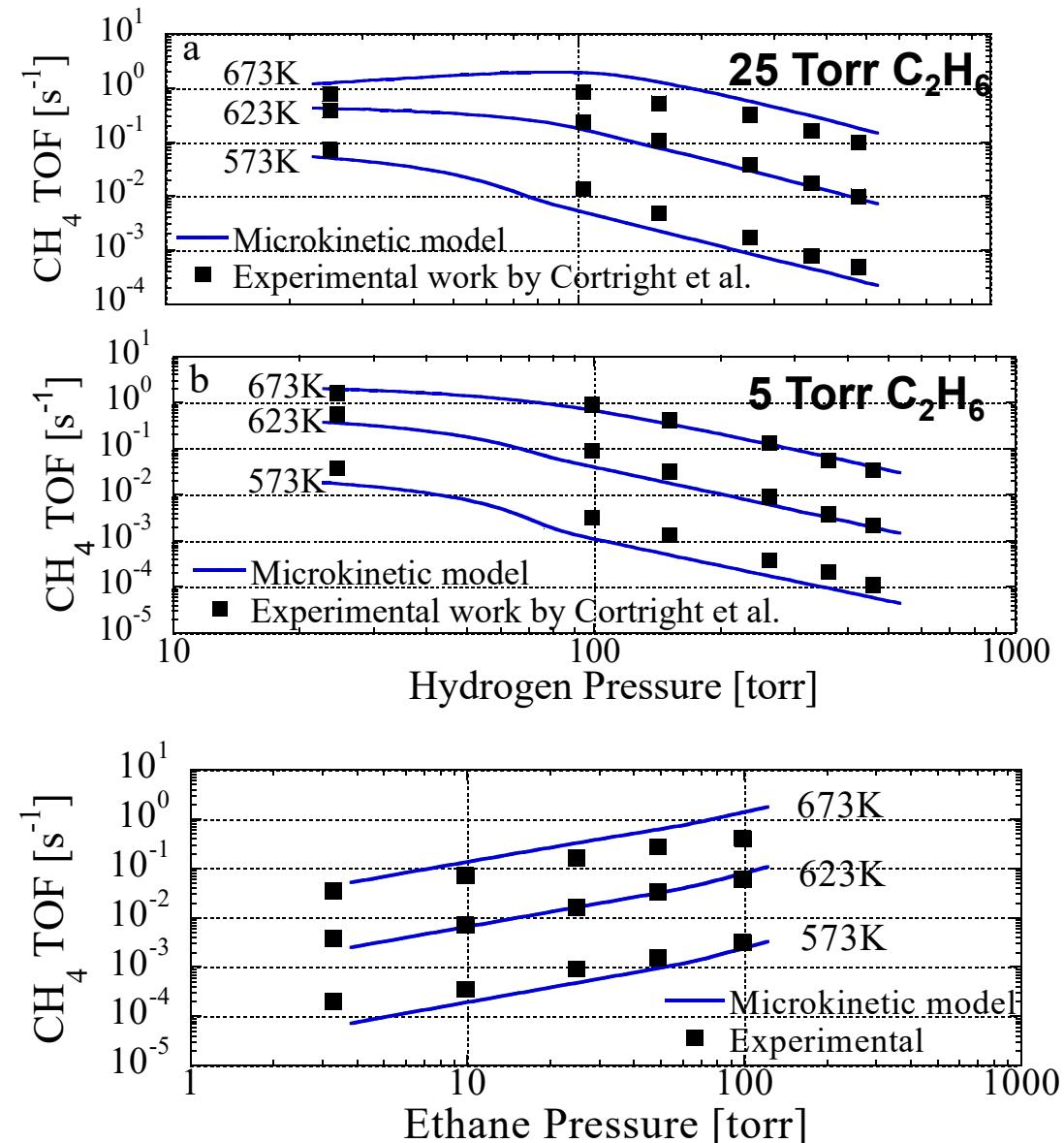
Cortright et al., J. Cat. 127 (1991) 342-353

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

Ethane Hydrogenolysis



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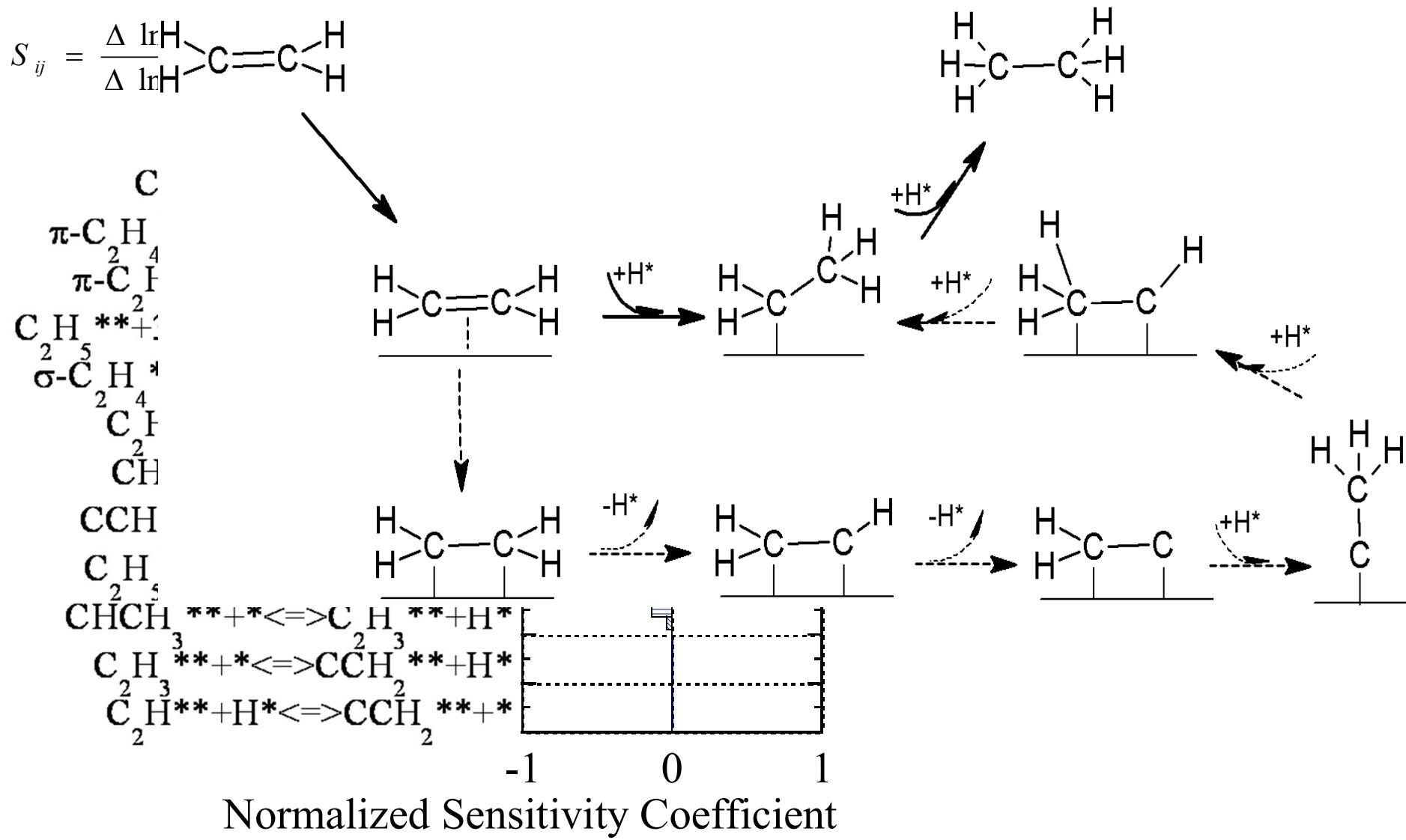


Experimental data from:

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

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

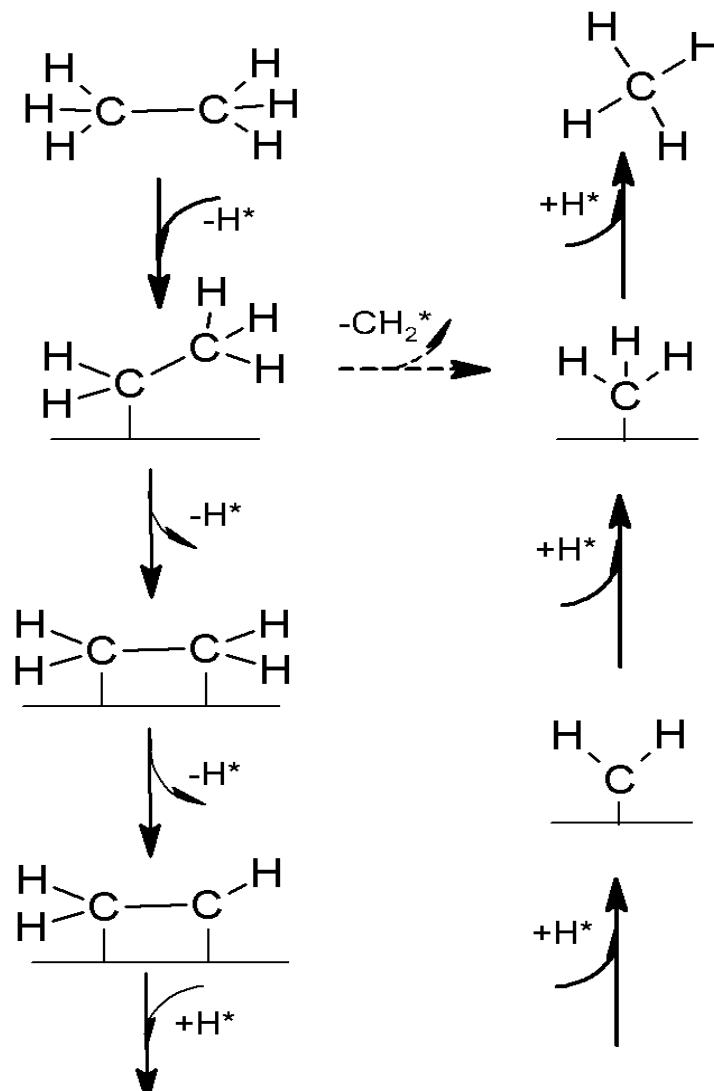
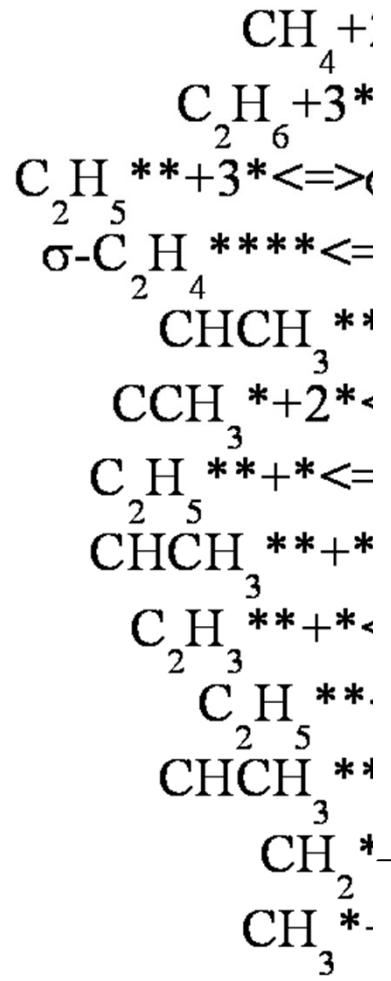
Ethylene Hydrogenation: Analysis



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

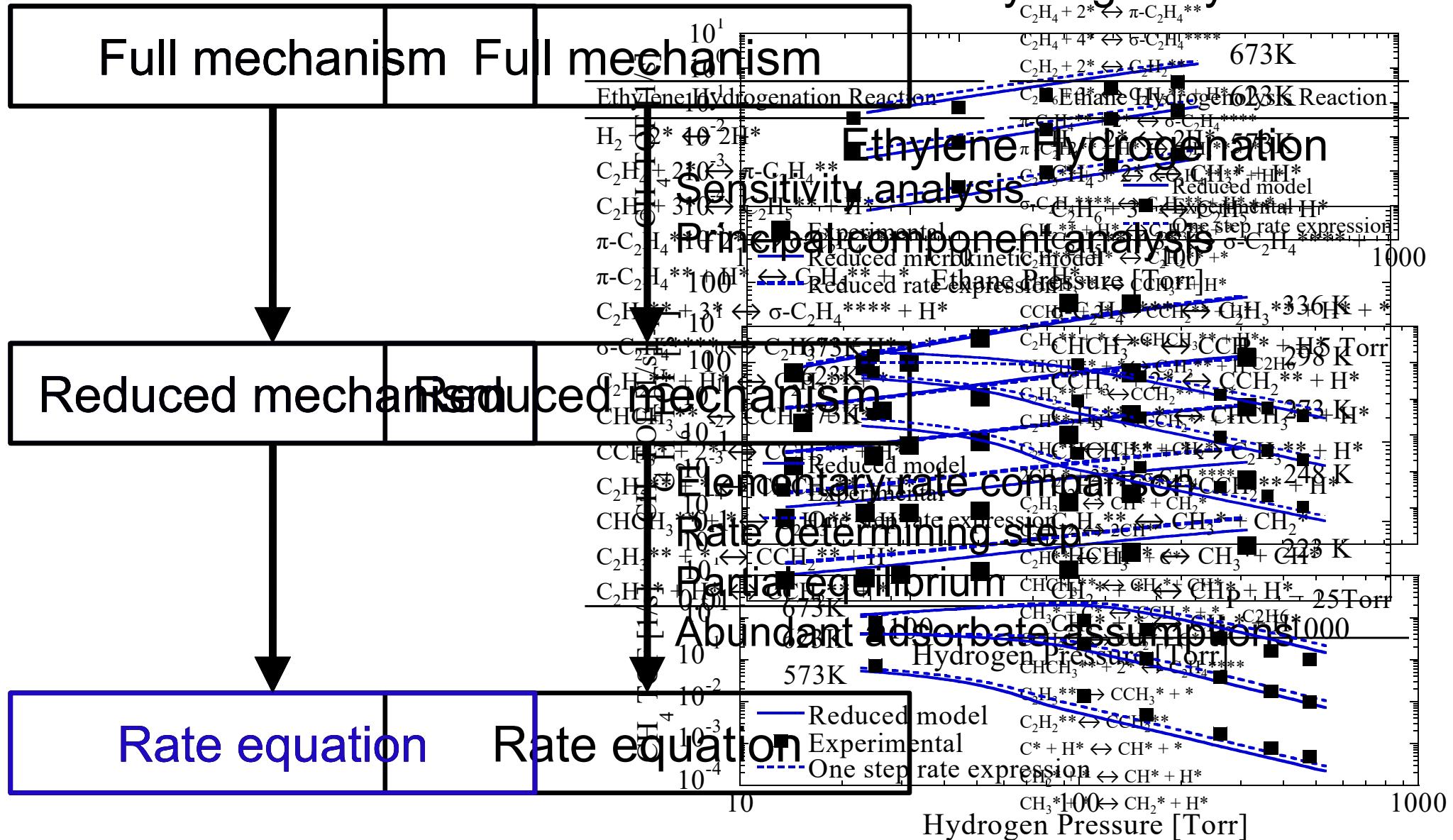
Hydrogenation rxns are rate controlling ($\pi\text{-C}_2\text{H}_4^{**} \rightarrow \text{C}_2\text{H}_5^{**}$, $\text{C}_2\text{H}_5^{**} \rightarrow \text{C}_2\text{H}_6$)

Ethane Hydrogenolysis: Analysis



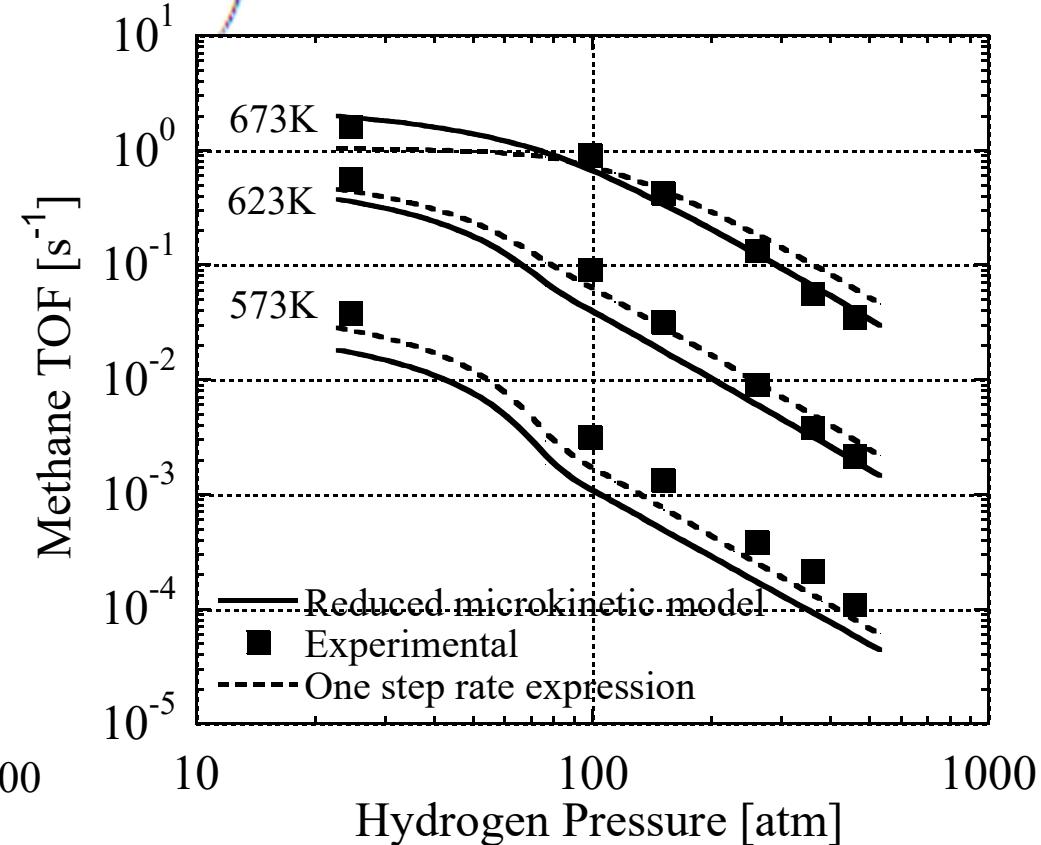
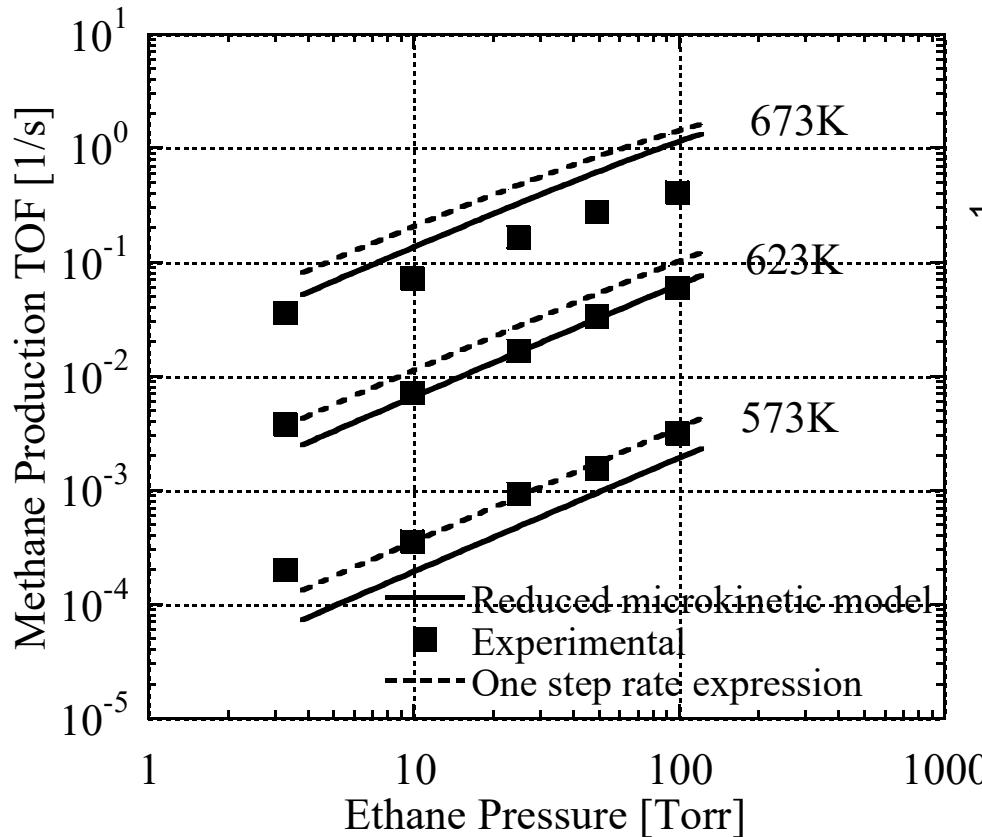
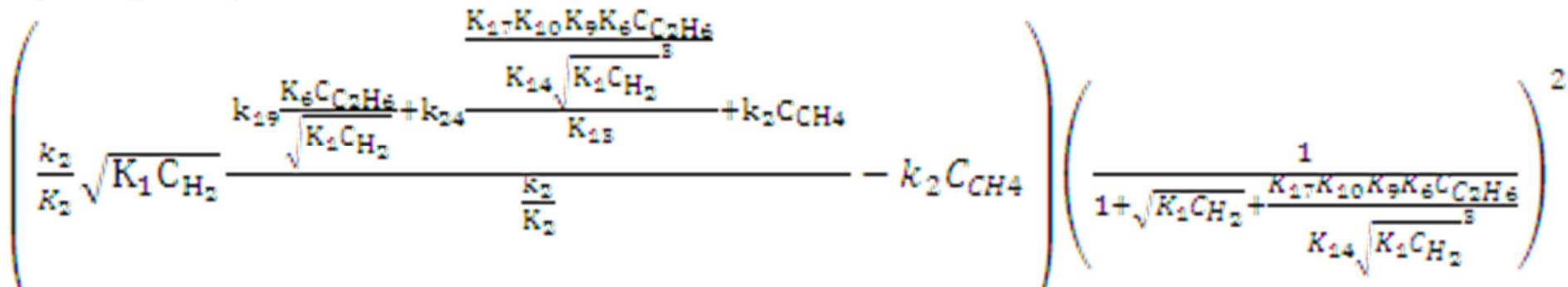
C-C bond cleaving reactions are rate controlling
($\text{C}_2\text{H}_5^{**} \rightarrow \text{CH}_3^* + \text{CH}_2^*$ and $\text{CHCH}_3^{**} \rightarrow \text{CH}_3^* + \text{CH}^*$)

Model Reduction to Rate Expressions



Ethane Hydrogenolysis Rate Expression

Hydrogenolysis Rate =



Microkinetic Model Analysis Workflow Summary

- 0 Energy profile analysis and energy span
- 1 Graph 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: Visualize network
- 4 Sensitivity analysis

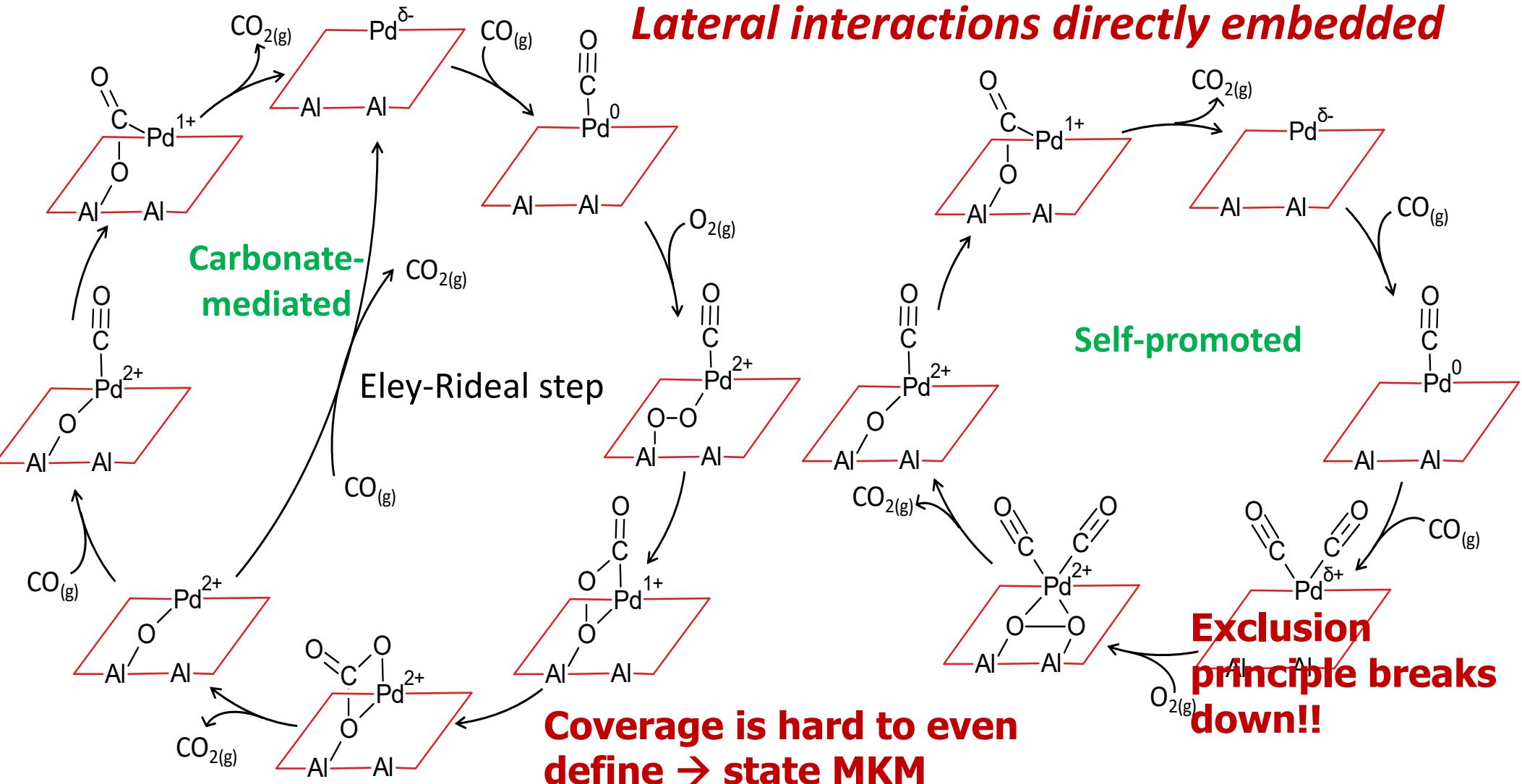
Single Atom Catalysts: State-based MKM

Mechanisms, Active Site
Determination, Rate
Expressions, Cat Dynamics



Catalytic Cycles: CO Oxidation on SA Pd/ Al_2O_3

*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).



Active Site Identification

MKM Analysis

Agreement is remarkable; Site sensitive chem

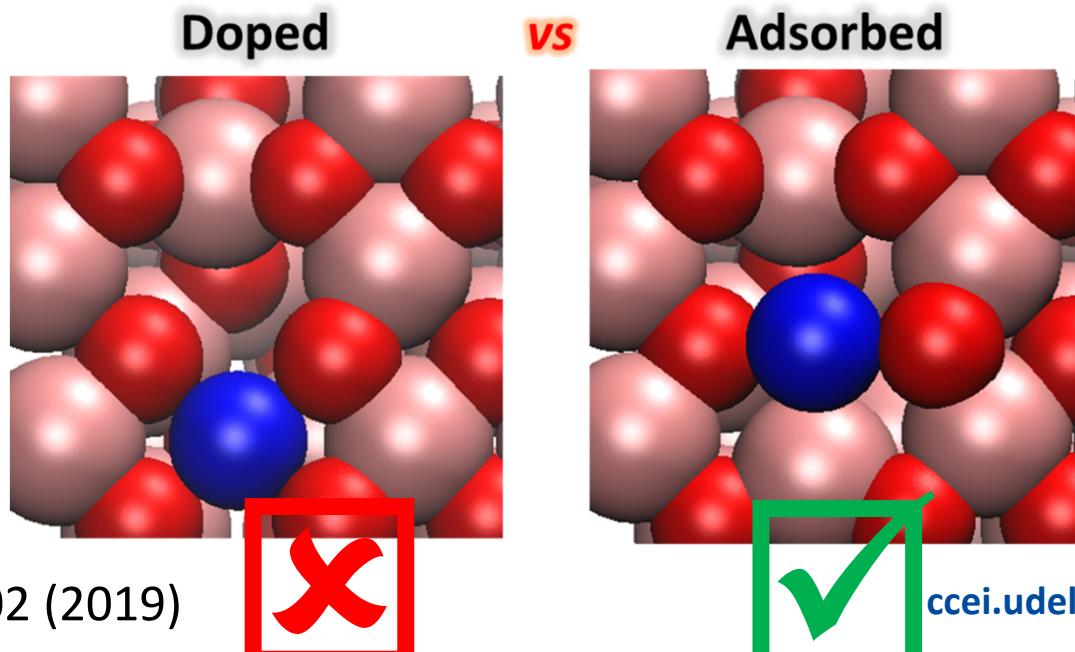
| | | TOF (s^{-1}) ^b | | Reaction orders at 343 K ^c | |
|----------------------------------|---------------------------------|-------------------------------------|------------------------------------|---------------------------------------|----------------|
| | | 343 K | 398 K | CO | O ₂ |
| 1 st run ^a | Experiments | $3.8 \cdot 10^{-4}$ 4x | $1.6 \cdot 10^{-3}$ 10x | -0.20 | 0.18 |
| 2 nd run ^a | | $9.7 \cdot 10^{-5}$ | $2.4 \cdot 10^{-4}$ | -1.20 | 0.84 |
| Pd ₁ ^{ads} | MKM (this work) Error | $1.9 \cdot 10^{-5}$ O(10) | $6.1 \cdot 10^{-4}$ O(1) | -0.87 | 0.16 |
| Pd ₁ ^{doped} | MKM (this work) ^d | $5.1 \cdot 10^2$ | $7.2 \cdot 10^2$ | 1.00 | 0.00 |

^a Experiments, Peterson et al.

^b p_{CO} ≈ p_{O₂} ≈ 8 Torr

^c p_{CO} = 14-52 torr, p_{O₂} = 7-28 Torr

^d Mars van Krevelen mechanism





Active Site Identification

Degree of Pd Sintering

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

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

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

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

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

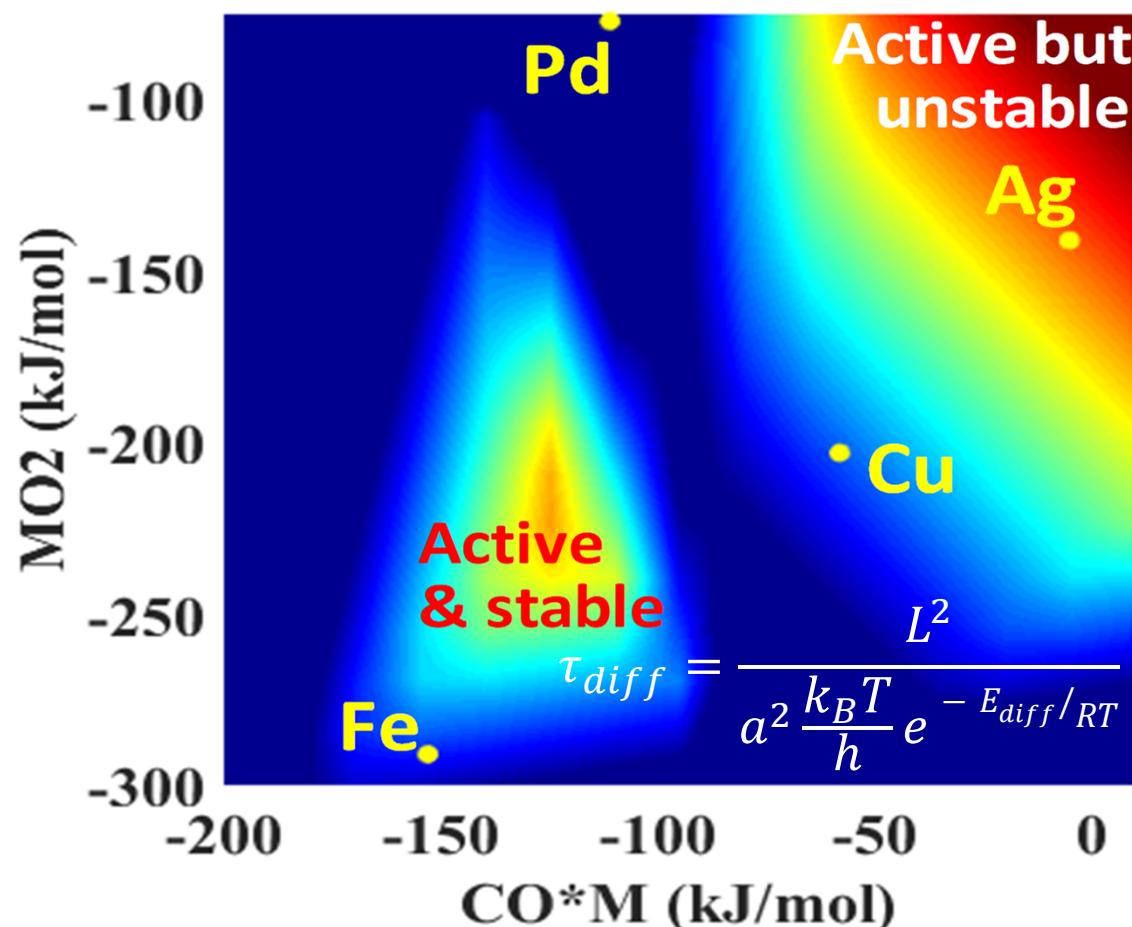


Reactivity and Stability Map for CO Oxidation

M1/Al₂O₃

p_{CO} = p_{O₂} = 0.1 bar

T = 400 K

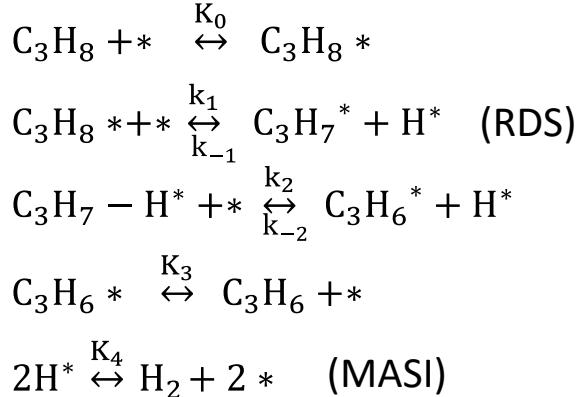


- Kinetically most abundant state MO_x(CO)_n during the catalytic cycle changes with metal
- Stability depends on the most abundant state

Reduced Model vs. MKM

Overall reaction on Pt(111): $\text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2$

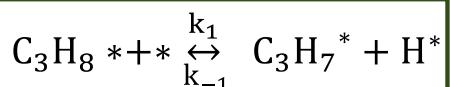
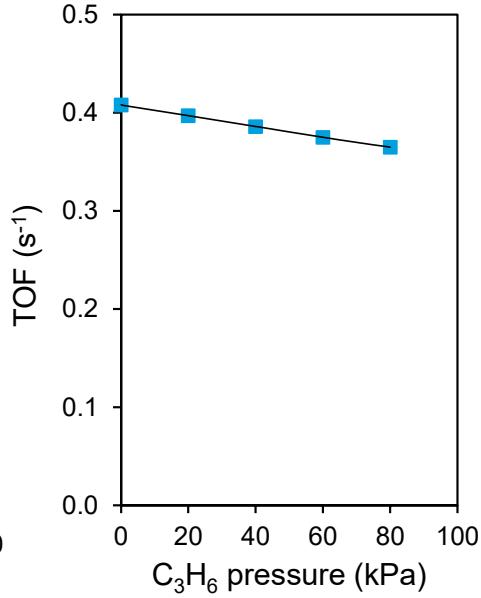
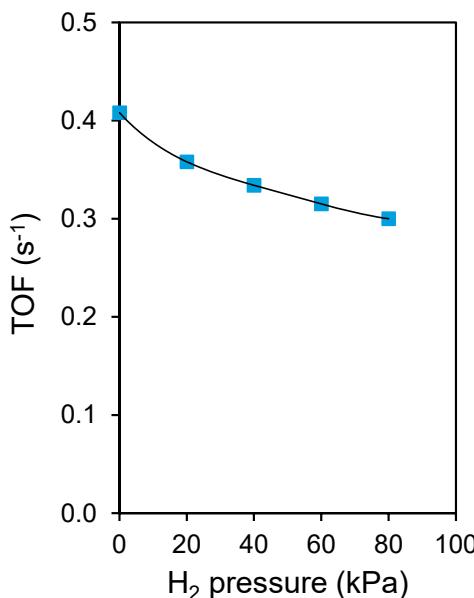
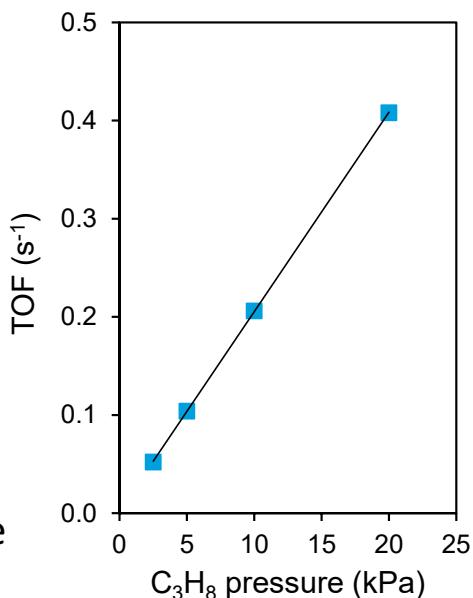
Elementary Steps



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

- Reduced model:

$$\frac{r}{[*]_0} = \frac{K_0 k_1 p_{\text{C}_3\text{H}_8} - \frac{k_{-1}}{K_2 K_3 K_4} p_{\text{C}_3\text{H}_6} p_{\text{H}_2}}{1 + \left(\frac{p_{\text{H}_2}}{K_4}\right)^{\frac{1}{2}}}$$



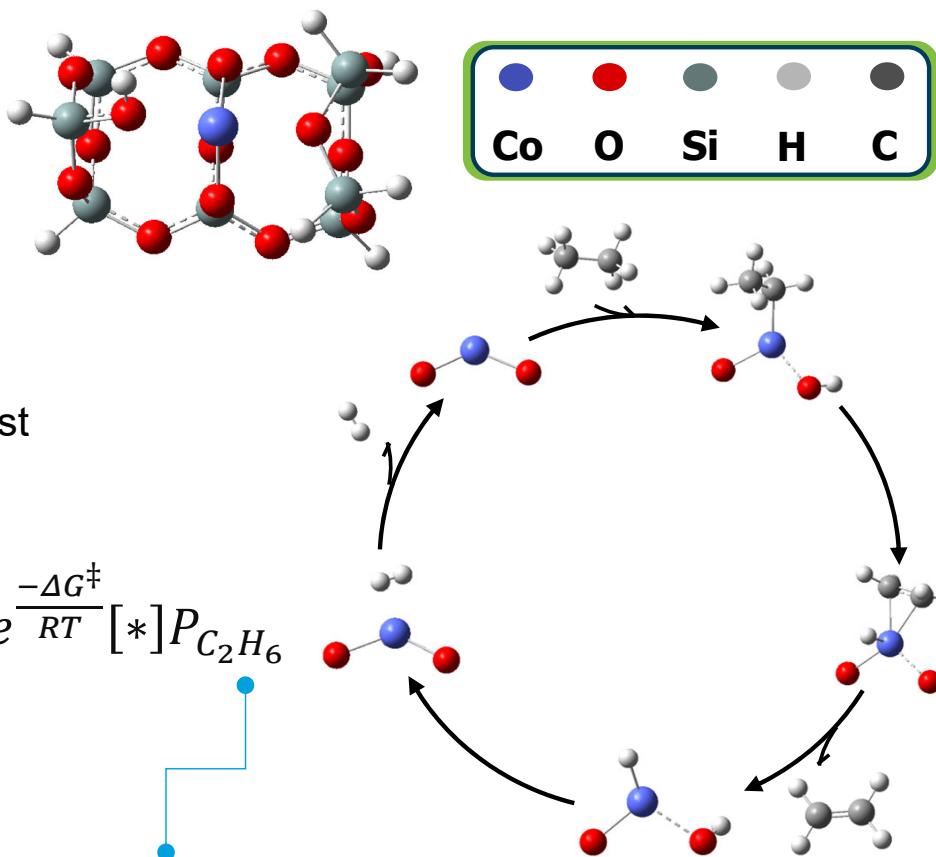
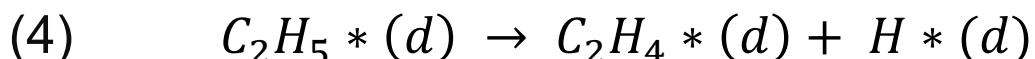
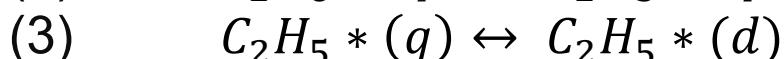
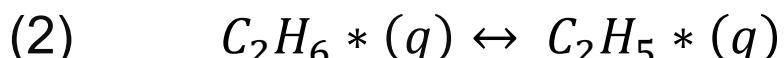
- Without H_2 :

$$\frac{r}{[*]_0} = K_0 k_1 p_{\text{C}_3\text{H}_8}$$

| P_{H_2} (kPa) | PE ratio | θ_{H_2} |
|------------------------|----------|-----------------------|
| 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_{H_2} (kPa) | PE ratio | $\theta_{\text{C}_3\text{H}_6}$ |
|------------------------|----------|---------------------------------|
| 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!

Ethane Dehydrogenation over SA of Co/SiO₂

Step (4) is the RDS; other steps are quasi-equilibrated; 'q' is a quartet and 'd' is a doublet spin. The resting state of the catalyst is the active site.

Reduced rate expression

$$r_{eff} = K_1 K_2 K_3 \frac{k_B T}{h} e^{\frac{-(G_{TS} - G_{C_2H_5*(d)})}{RT}} [*] P_{C_2H_6} = \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{RT}} [*] P_{C_2H_6}$$

K_1, K_2, K_3 are equilibrium constants

[*] is the available active site density

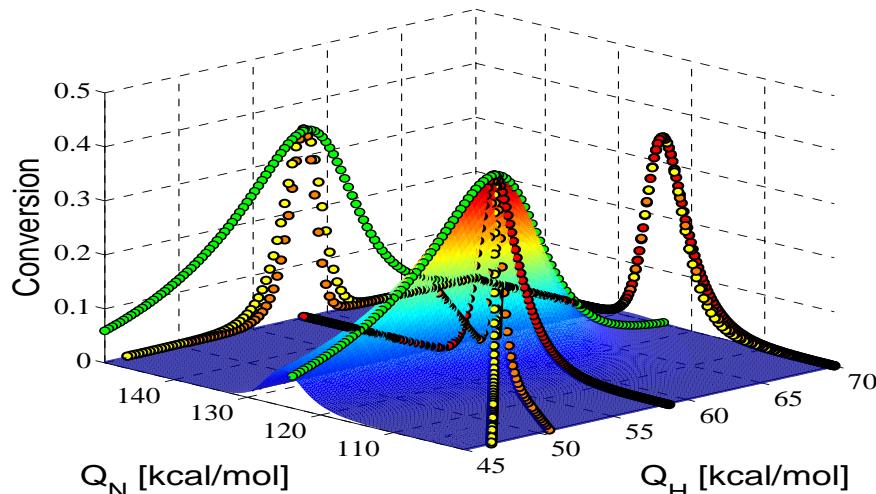
Simple power law!

Catalyst Prediction

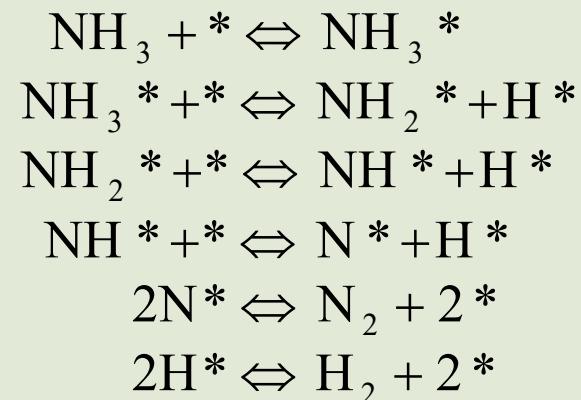
Heat Maps (Composition)
Optimum Particle Size,
Shape, Structure
Sensitivity

High Throughput Multiscale Model-based Catalyst Design

350 °C
1 atm



NH₃ decomposition



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

Identifying Bimetallic Catalysts

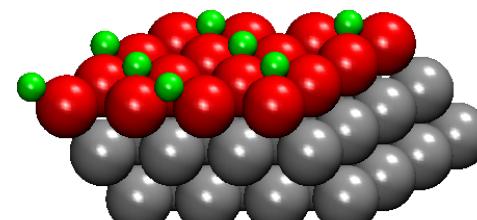
| Metals | BE _N (kcal/mol) |
|---------------|----------------------------|
| PtTiPt | 56.5 |
| PtVPT | 59.5 |
| PtCrPt | 72.6 |
| PtMnPt | 84.9 |
| PtFePt | 83.9 |
| PtCoPt | 87.0 |
| PtNiPt | 89.8 |
| NiPtPt | 137.5 |
| CoPtPt | 159.9 |
| FePtPt | 169.9 |
| MnPtPt | 162.2 |
| CrPtPt | 166.5 |
| VPtPt | 184.1 |
| TiPtPt | 191.5 |

Pt

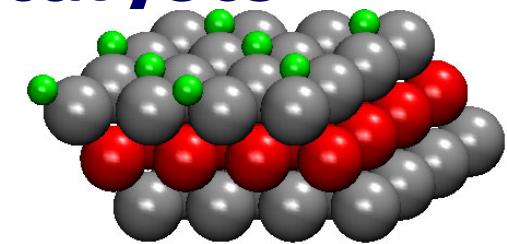
Ni

102.1

113.8

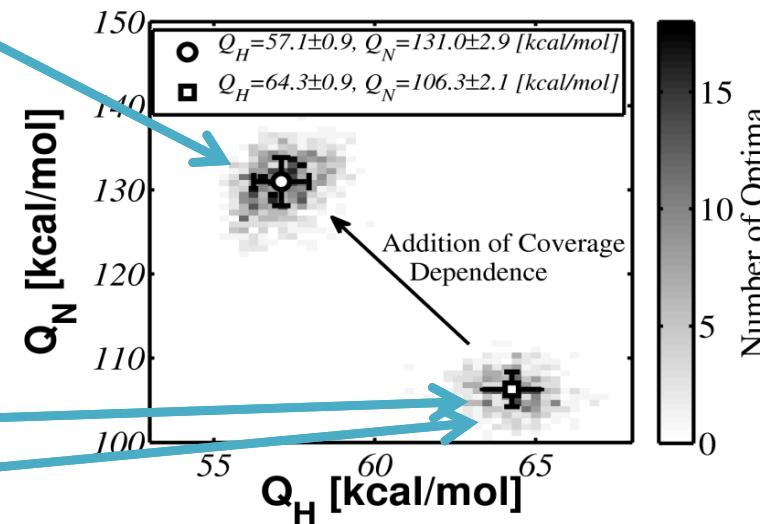


Surface

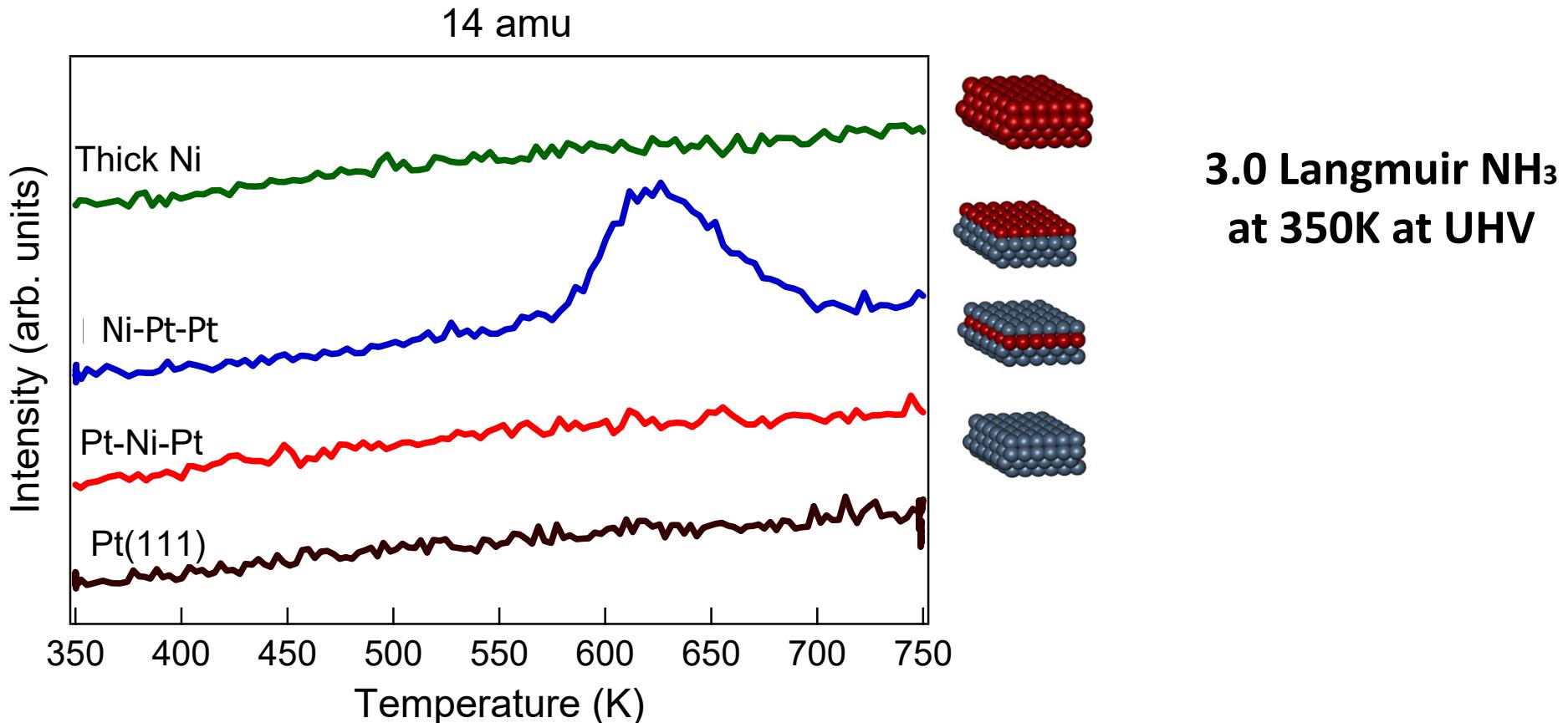


Sub-surface

- 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

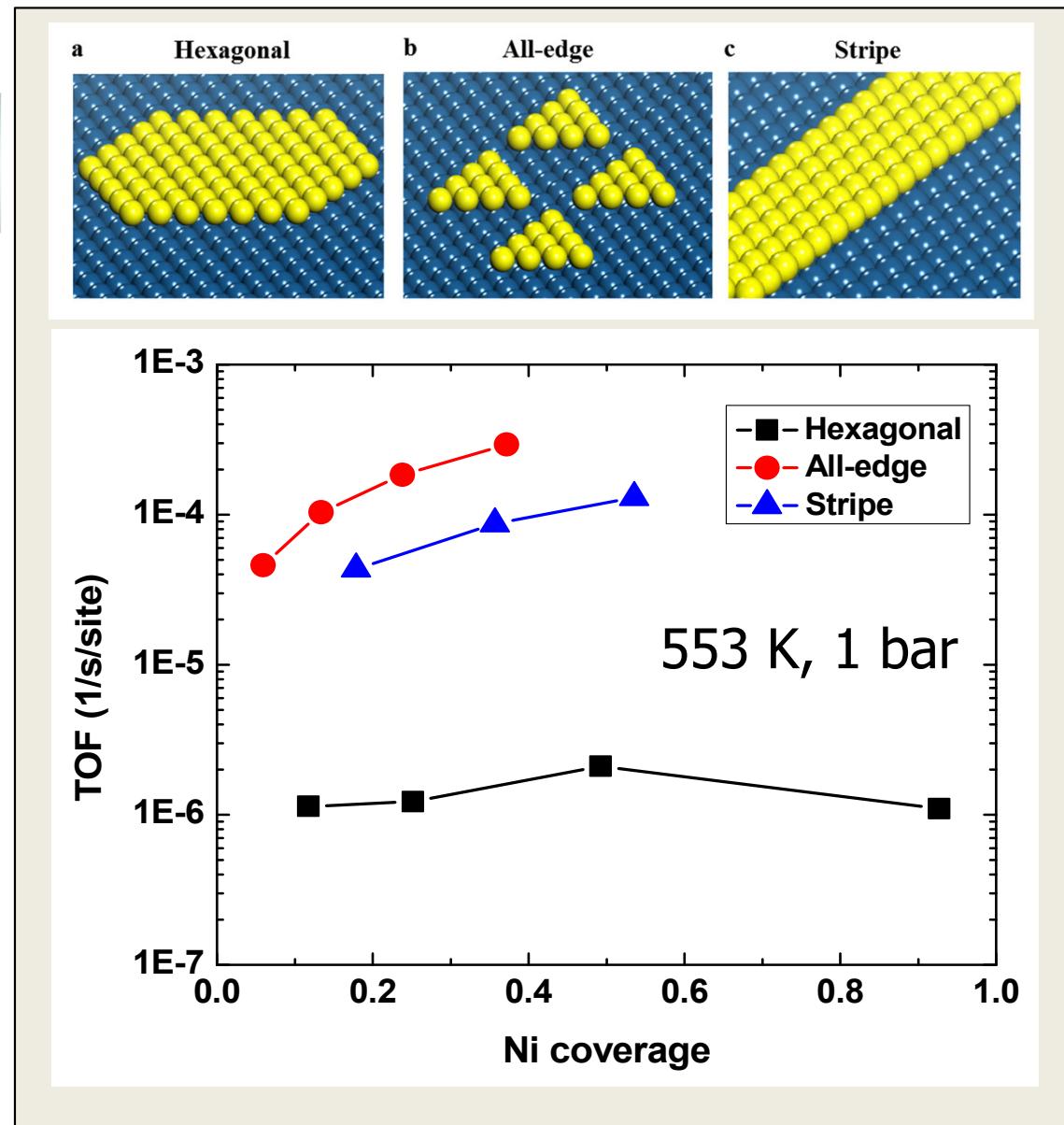
Received 17 Jan 2015 | Accepted 12 Sep 2015 | Published 7 Oct 2015

DOI: 10.1038/ncomms9619 OPEN

Patched bimetallic surfaces are active catalysts for ammonia decomposition

Wei Guo^{1,2,3} & Dionisios G. Vlachos¹

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

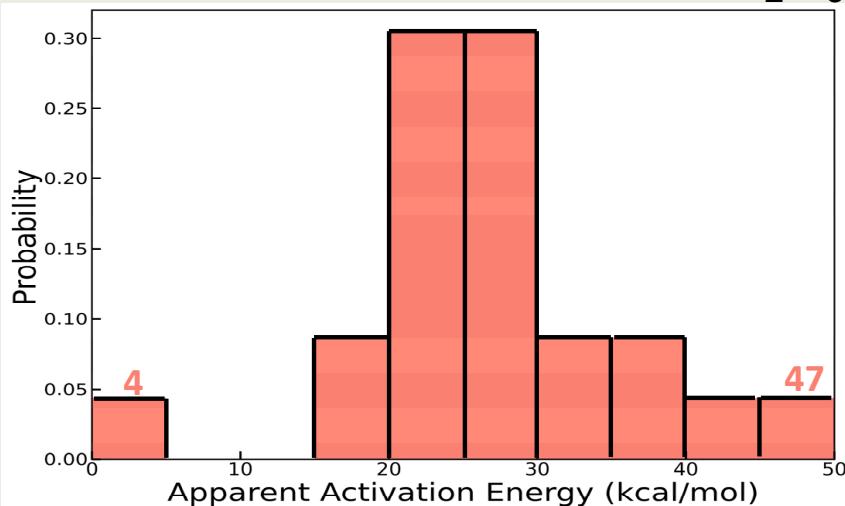


Beyond Parametric UQ: Structure Sensitivity-based UQ

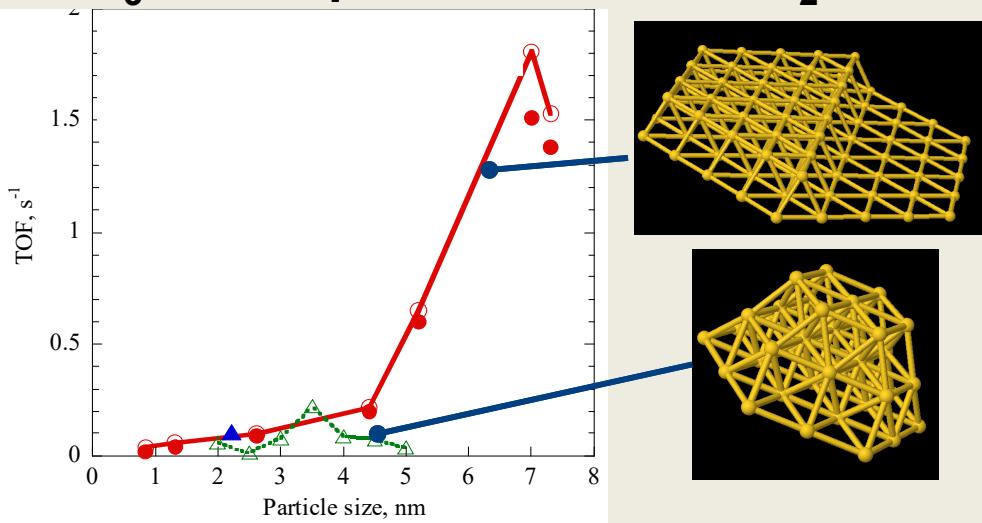
- Huge variation in experimental data
 - Why?
- Structure sensitivity can be leveraged for making improved catalysts
 - How can we predict it?

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

Methane combustion on Pt/Al₂O₃

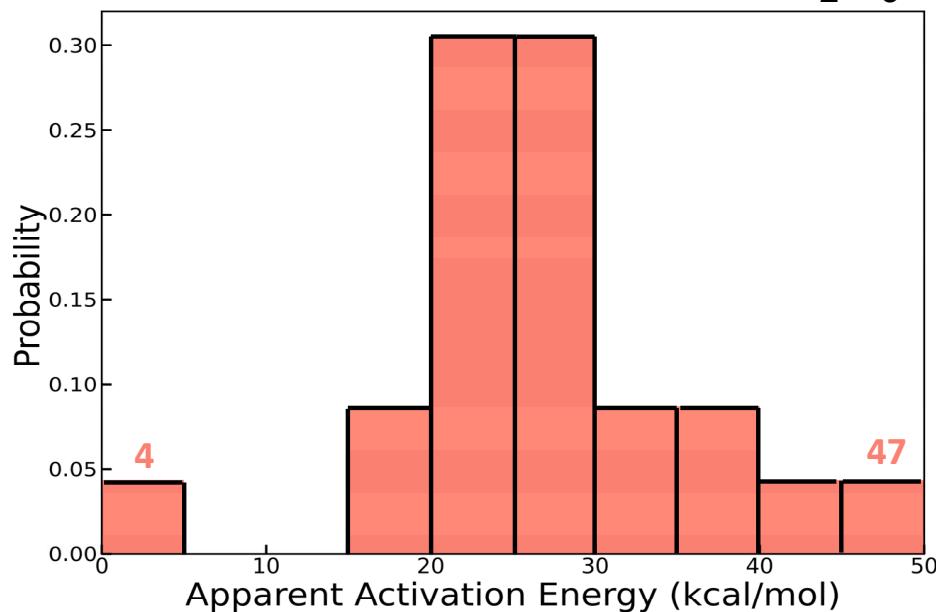


NH₃ decomposition on Ru/TiO₂

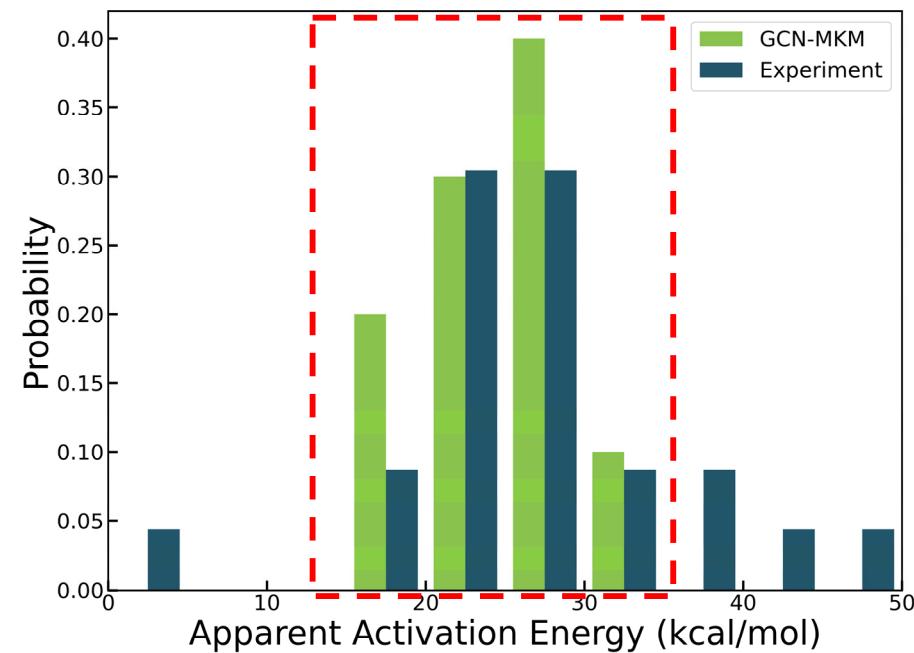


Closing the Gap with Experiments/Data Quality

Methane combustion on Pt/Al₂O₃



Comparison to Experimental Data

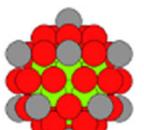


Apparent activation energies mostly fall between **20 to 30 kcal/mol** and consistent with **experimental observations**

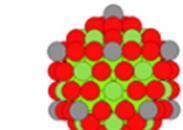
Nanoparticle Size Effects

Icosahedral Nanoparticles

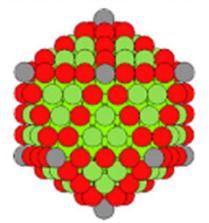
1.11 nm Pt55



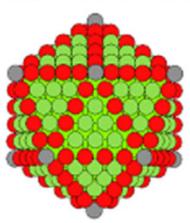
1.66 nm Pt147



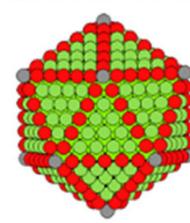
2.22 nm Pt309



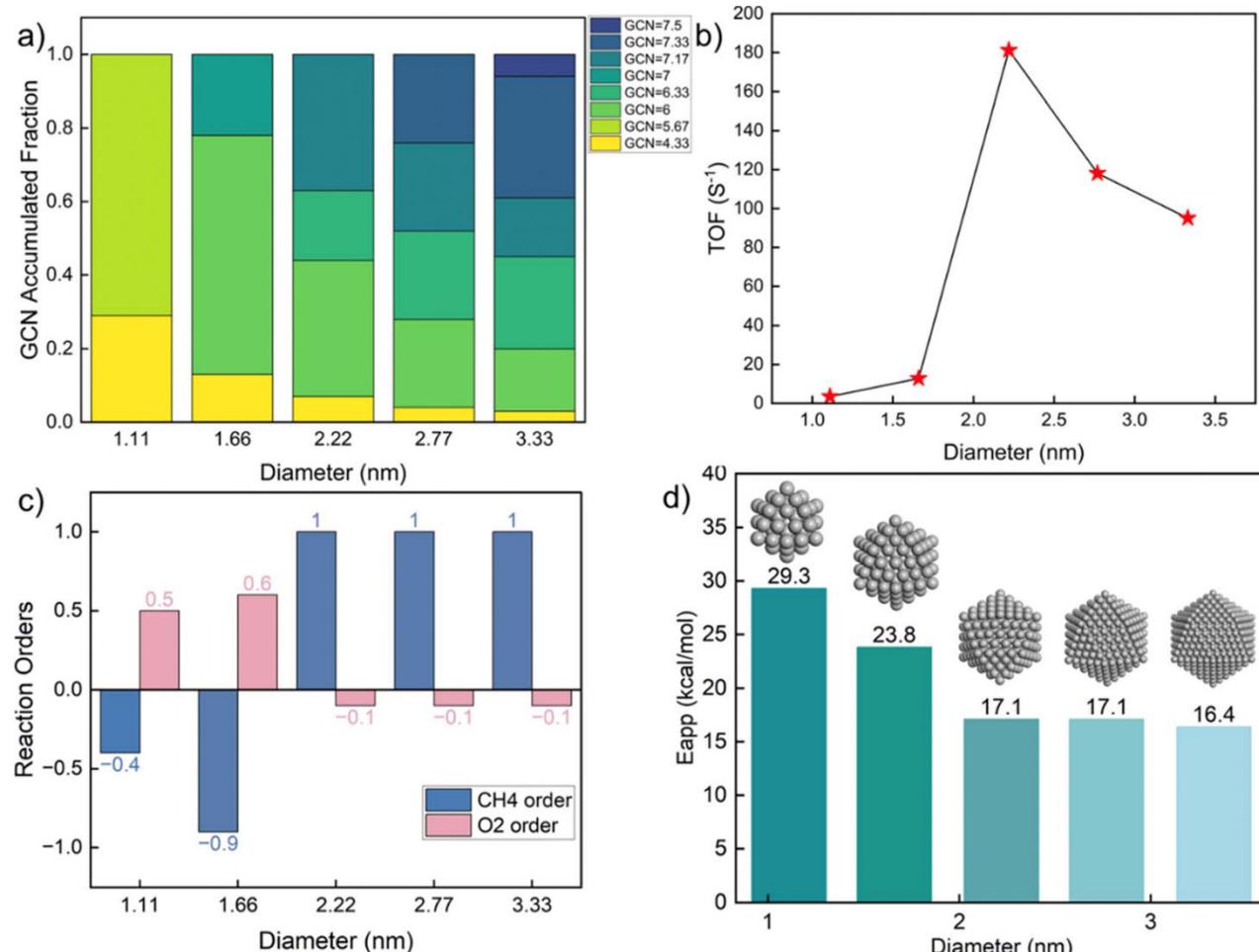
2.77 nm Pt561



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

Lateral Interactions

Failure of Mean Field MKMs

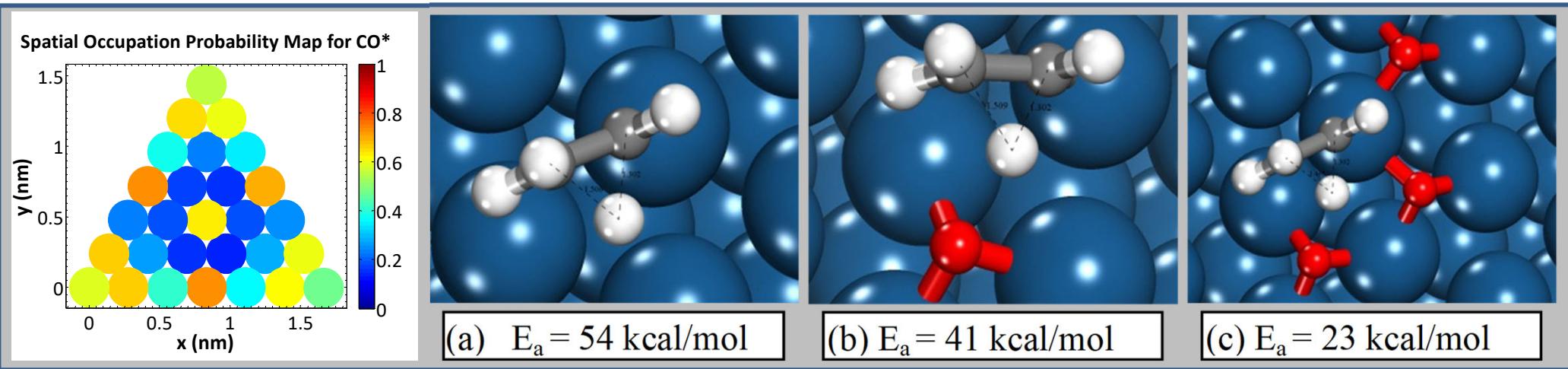
Kinetic Monte Carlo (Intro)



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



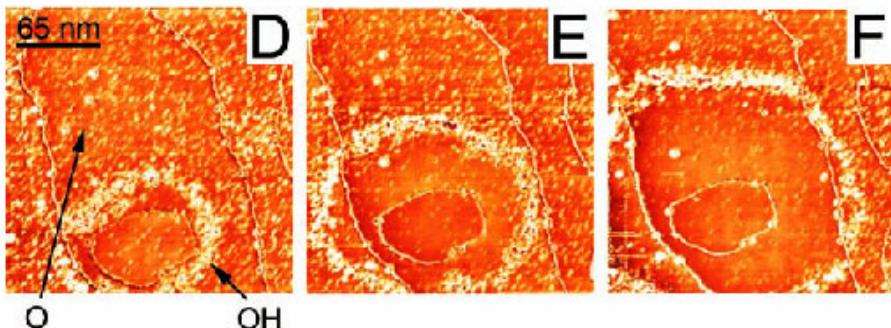
- **Mean field (MF) breakdown**
 - Site heterogeneity (MF can handle*)
 - Lateral interactions (many-body effects)
 - Reaction-induced pattern formation
- **KMC can handle these issues**

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

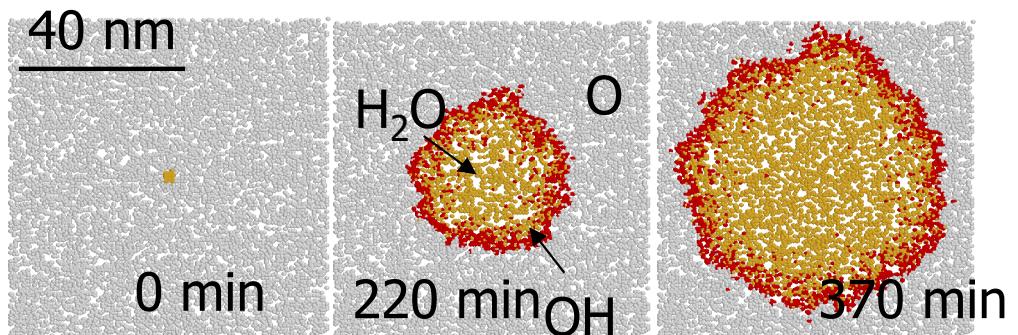


Mean Field (MF) vs. Kinetic Monte Carlo (KMC)

- 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

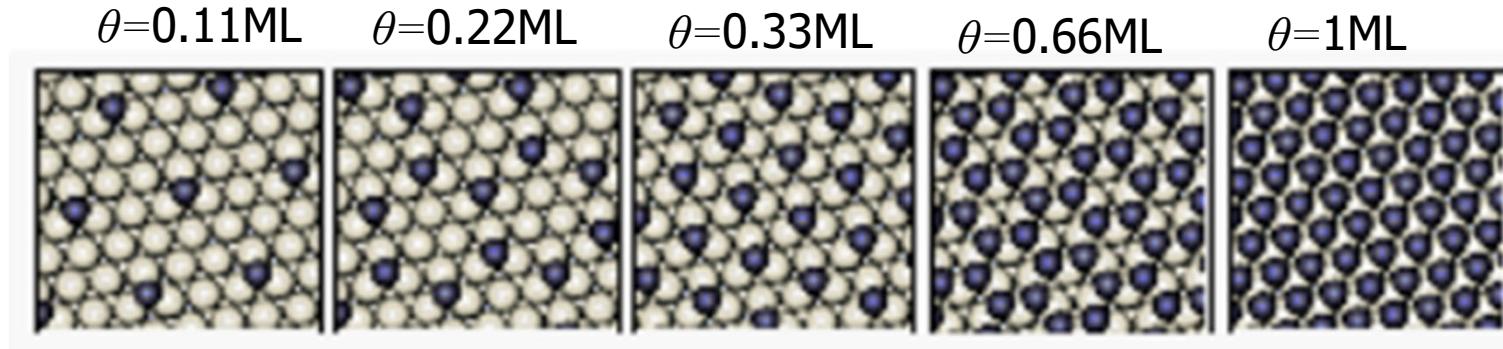


Sachs et al., Science 293, 1635 (2001)



Raimondeau and Vlachos, CES 58, 657 (2003)

Lateral Interactions Couple Models Across Scales



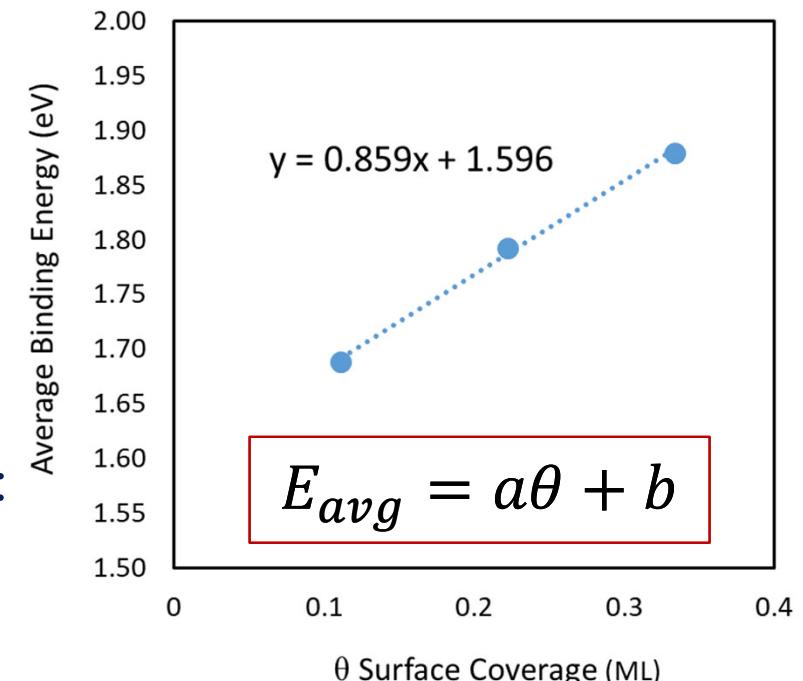
$$\text{Surface Coverage} \leftarrow \theta = \frac{n}{N_a} \quad \begin{matrix} \longrightarrow & \text{Number of adsorbates} \\ \longrightarrow & \text{Total Number of active sites} \end{matrix}$$

- 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

ε : lateral interaction parameter

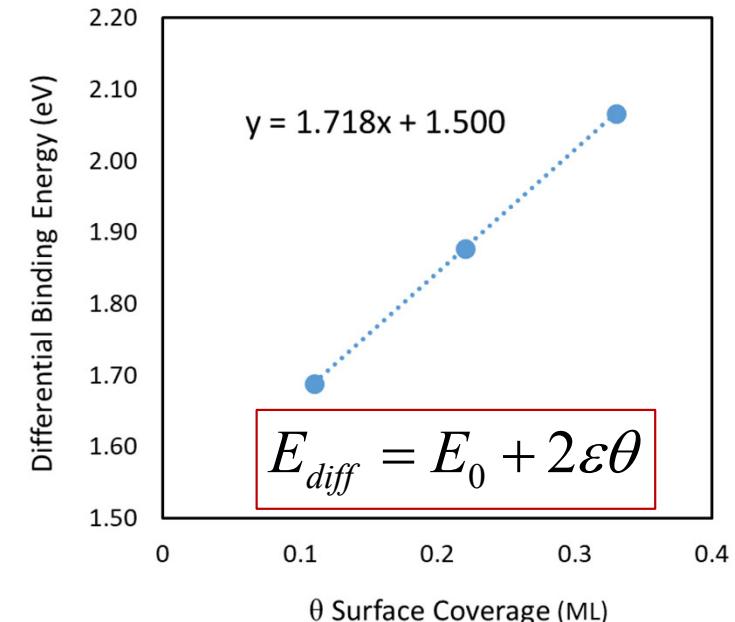
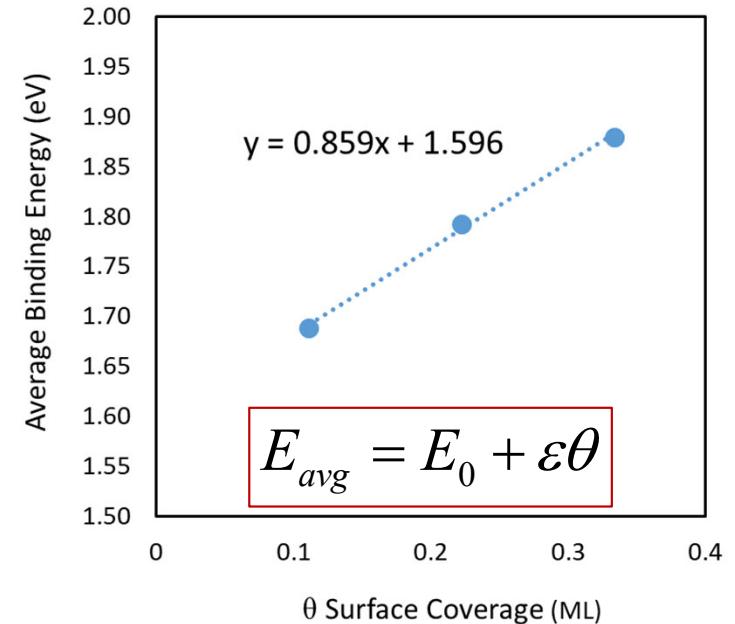
$$E_{avg} = \frac{1}{\theta} \int_0^\theta E_{diff}(\theta) d\theta$$

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

integral

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

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



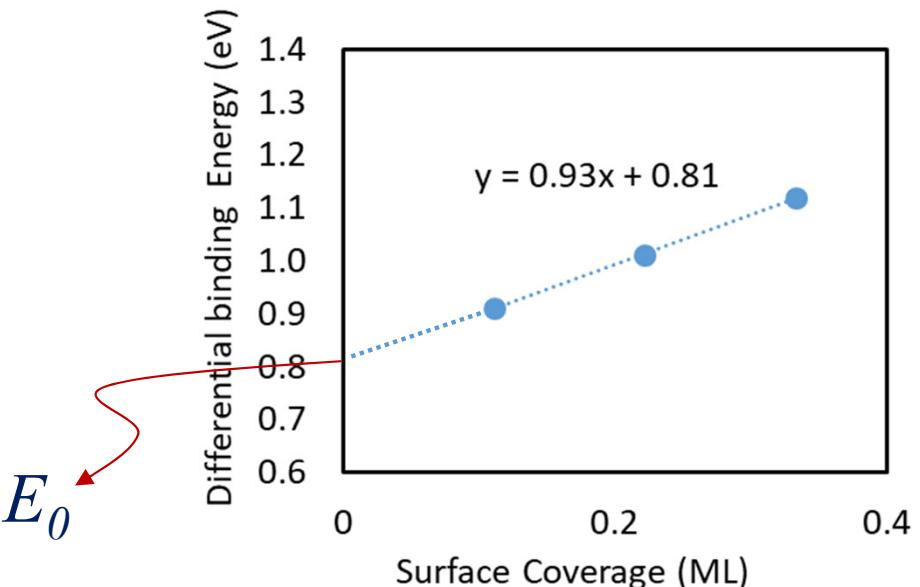
Lateral Interactions

linear model:

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

E_0 : binding energy at zero coverage

ε : lateral interaction parameter

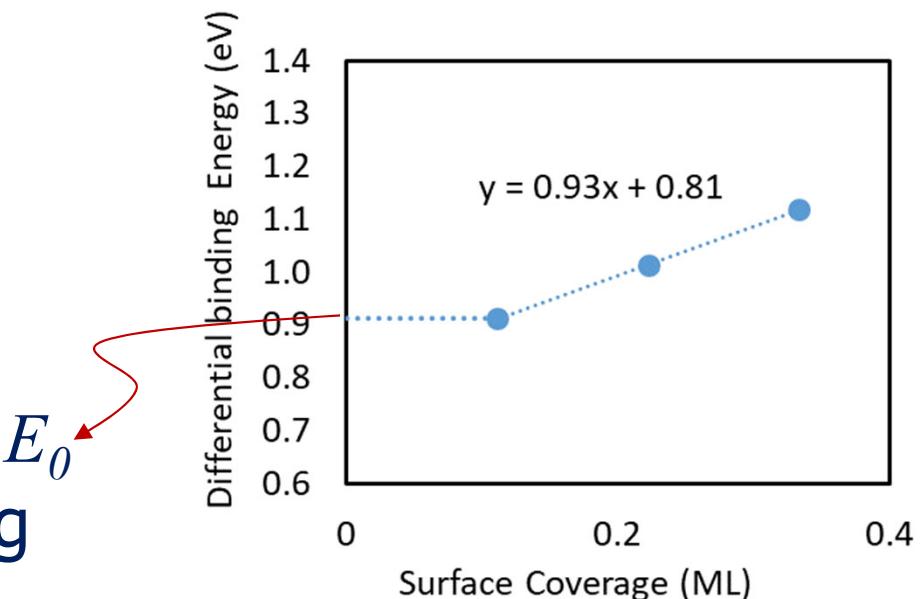


Piece-wise linear model:

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

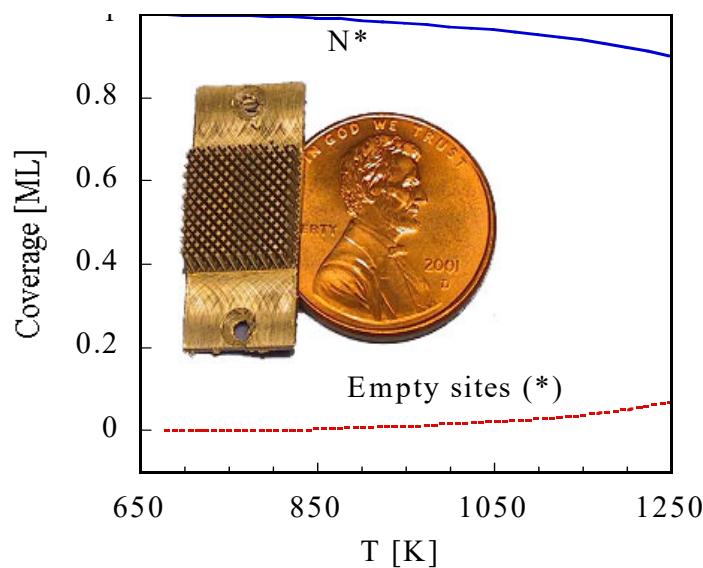
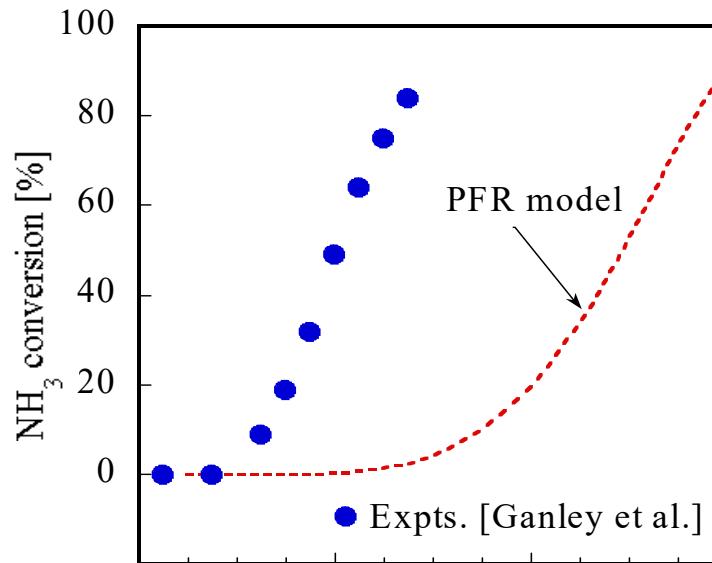
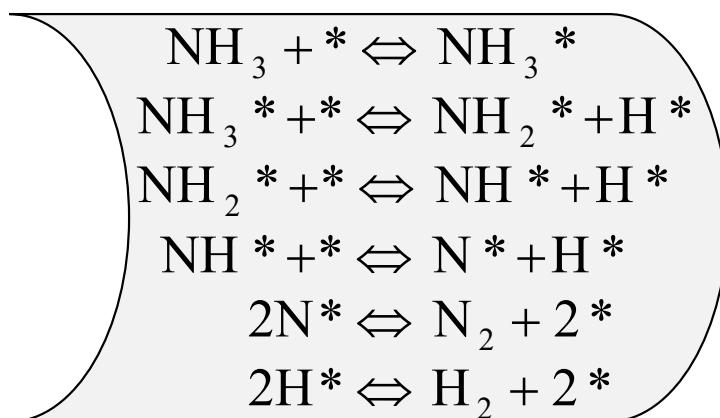
$$E_{diff}(\theta) = E_0 \quad \theta < 0.11$$

Negligible lateral interactions below threshold coverage, binding energy is constant



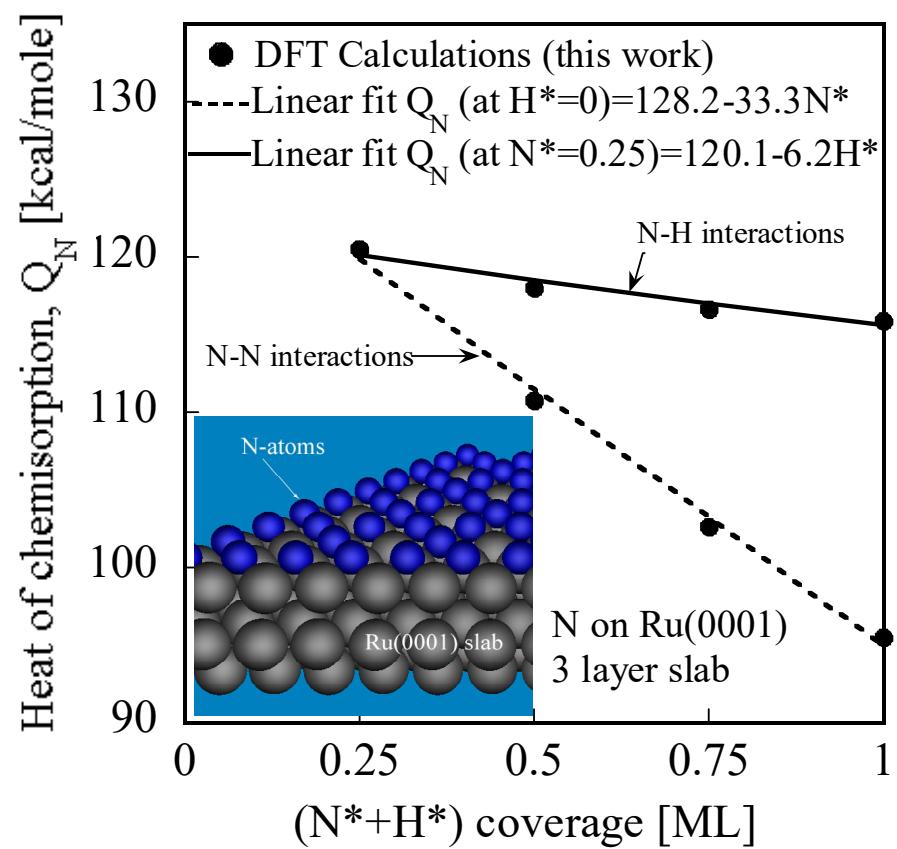
NH₃ Decomposition on Ru: 2NH₃ = N₂ + 3H₂

- NH₃ as a storage medium
- ‘Pure’ H₂ – No CO_x
- A microkinetic model is build using BOC and TST
- Our microkinetic model captures the trend
- High N* coverages



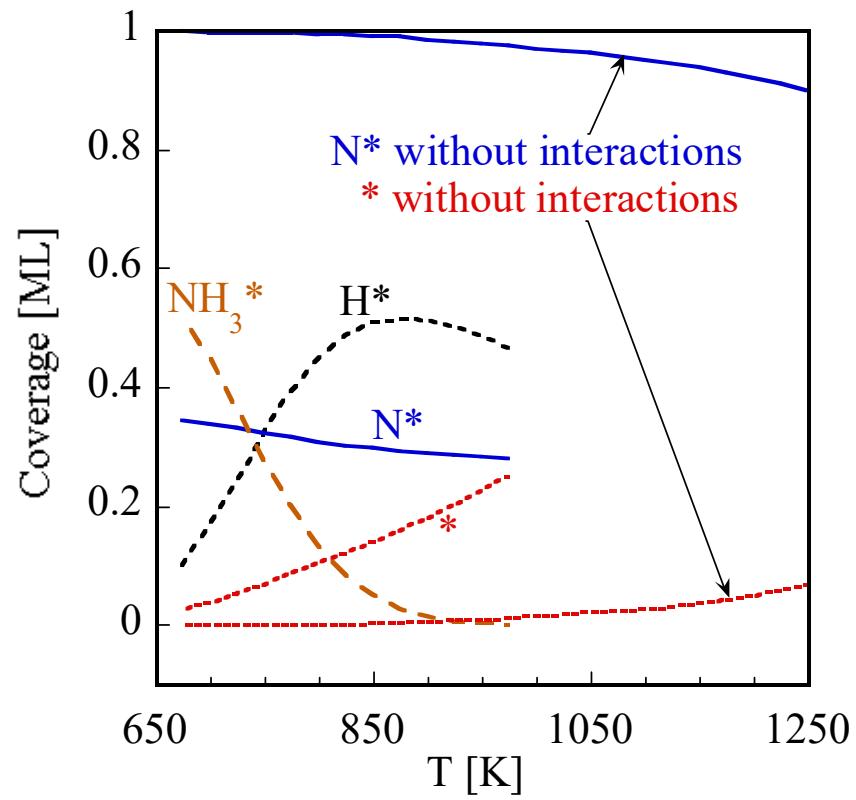
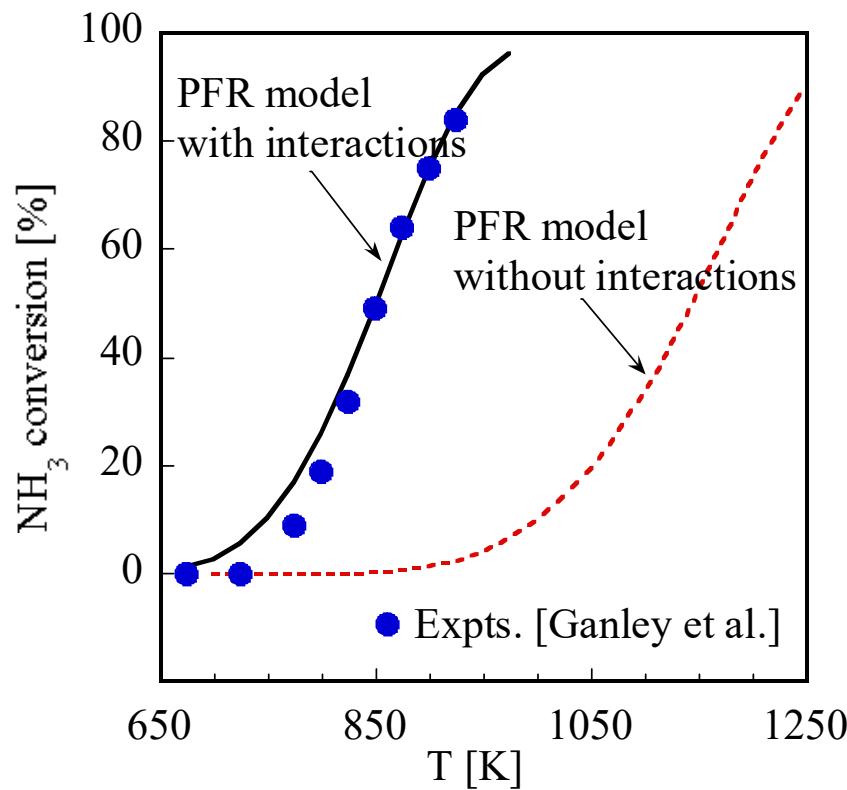
DFT Estimates Lateral Interactions

- DACAPO (solid-state electronic structure package by Hammer and coworkers*)
- 3-Layer slab of Ru(0001)
- 2×2 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

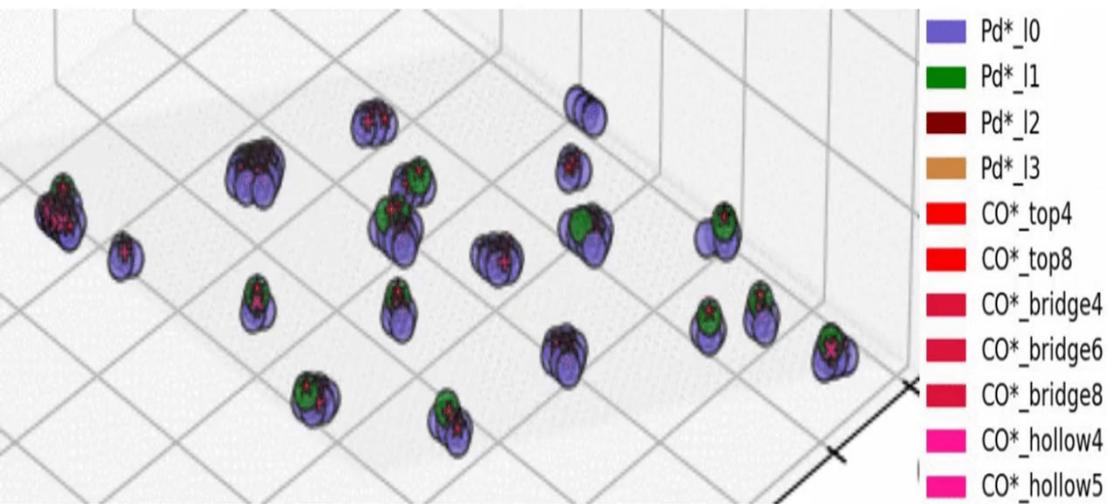
Catalyst Dynamics

An Example



Catalysts are Heterogeneous and Dynamic

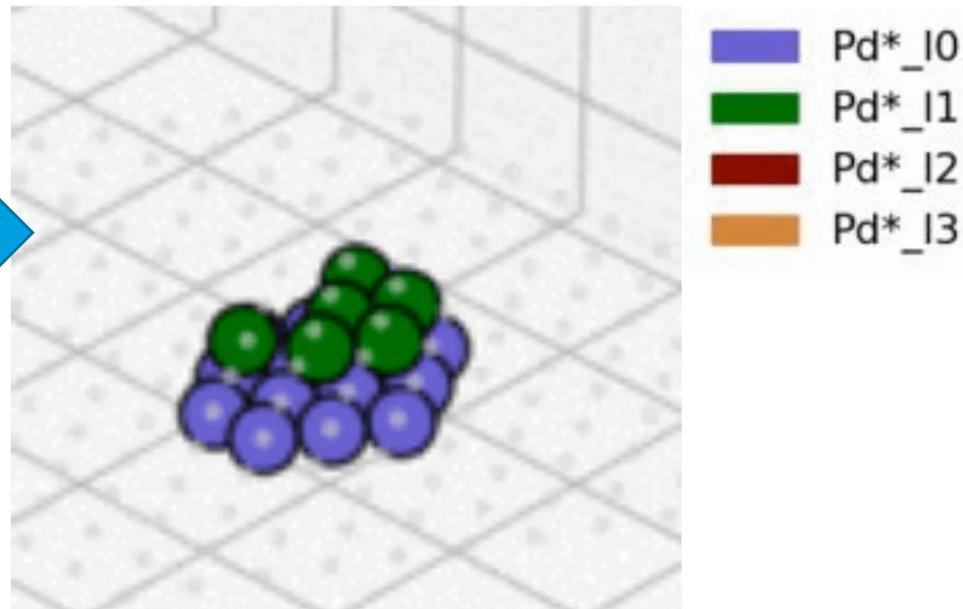
Time: 7.195e+01 sec



Exposure to 0.1 bar of CO; 300 K

Pd₂₀ relaxes to a bilayer cluster fast; 300 K

Time: 2.386e-07 sec





Summary of Learnings



Multiscale modeling

Types: One-way vs. co-current (Hybrid)
Iterative; Hierarchical



Empirical kinetic models

Assumptions and limitations



Formulating a microkinetic model (MKM): Fundamentals

Elementary steps; One phase=catalyst;
other phase=gas; solve simultaneously



Automation and solving MKMs

Mechanism generation
Efficient, robust simulations



Analysis of MKMs

Coverages, fluxes, network, partial equilibrium, RDS, parametric studies



Other uses of MKMs

Reduction for CFD (reactor optimization);
Reconciliation with and design of experiments;
structure sensitivity; material prediction

END

Thanks for Attending