

Theory, Applications, and Tools for Multiscale Kinetic Modeling

Microkinetics Fundamentals

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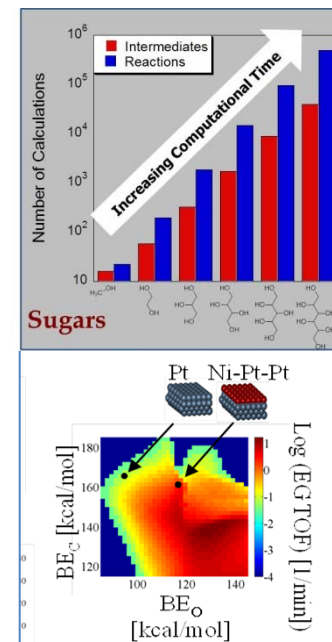
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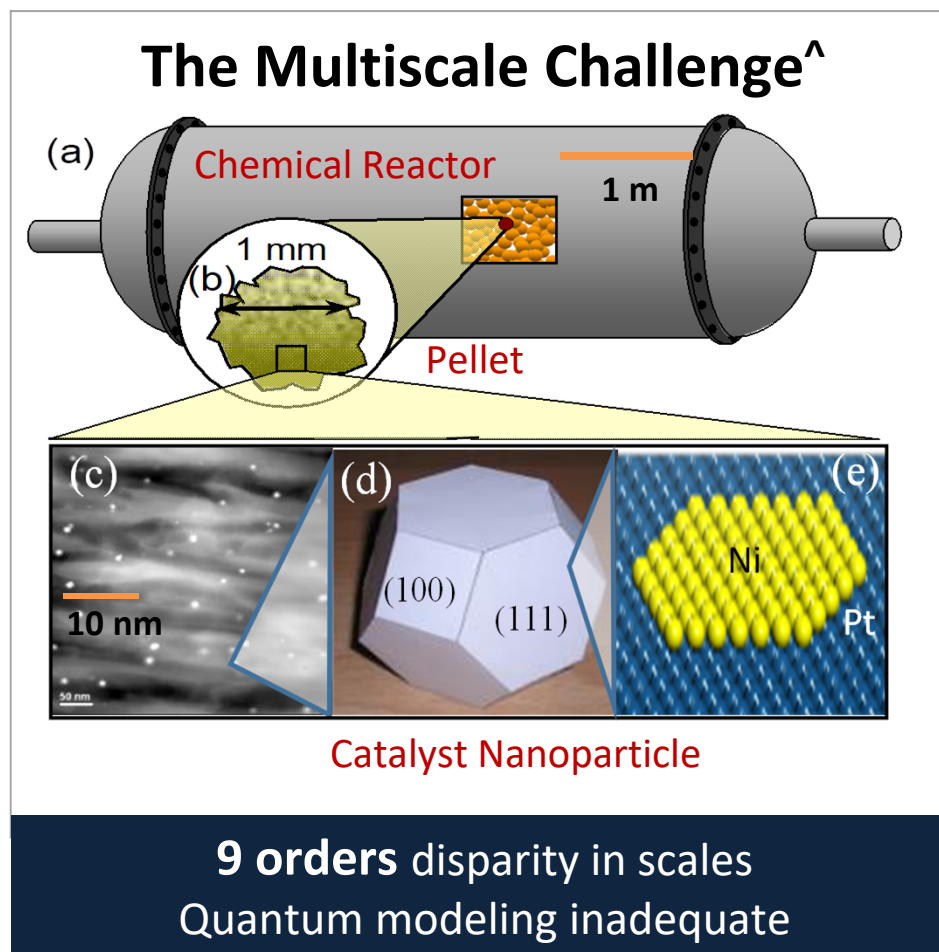
Catalysis Center for Energy Innovation (CCEI)



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Multiscaling



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



Outline

- Types of catalytic kinetic models: Empirical, LH, MKM
- Microkinetic modeling (MKM)
 - Governing mean field eqs
 - Solution methods
 - Analysis
- Parametrization of MKM
 - Overview
 - First principles
 - Semi-empirical estimation methods
 - Lateral interactions
 - Thermodynamic consistency; referencing
- MKM uses
 - Reactor design, analysis, catalyst discovery, design of experiments
- Accuracy; predictive ability; UQ
- Limitations of MF models; Kinetic Monte Carlo



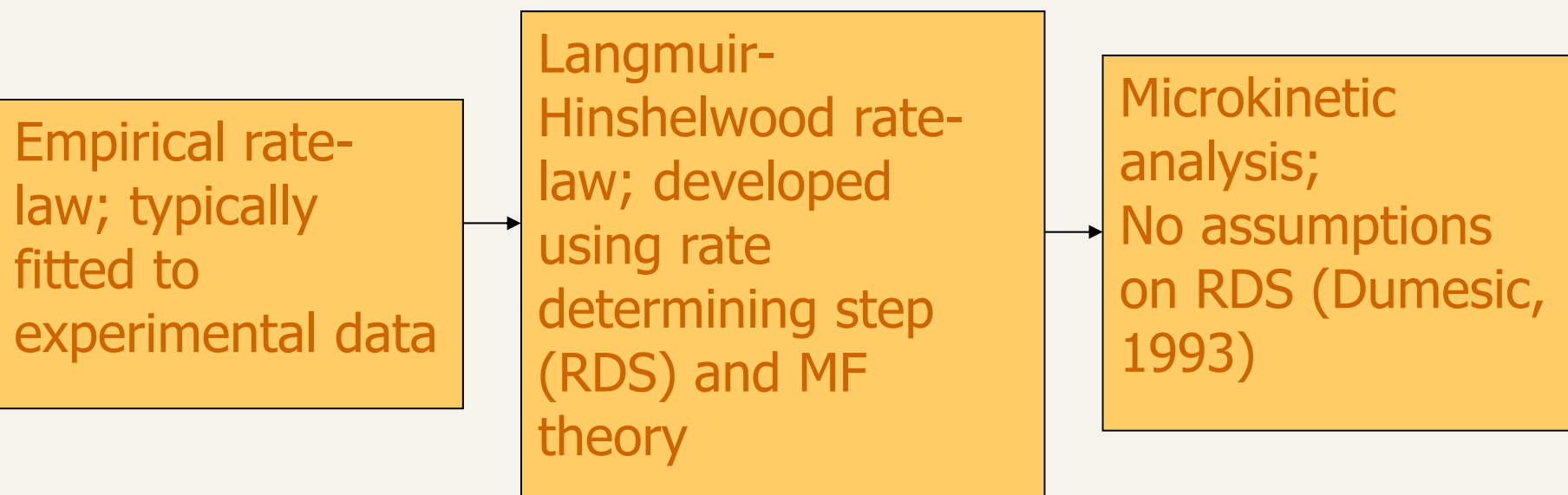
Recommended Reading

- 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
- M. Saliccioli, 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).



Surface Reaction Rate Calculation Paradigm

- Hierarchy of calculation of surface reaction rates



Complexity, Accuracy and Predictability



Global Reaction Rate Expression

- Reaction $A+B \rightarrow \text{Products}$
- Typical power-law 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

Scatter in Published Data

How do we explain the scatter in data?

Example: CH₄ Catalytic Combustion on Pt

Investigator	E _a (kcal/mol)	a _{CH₄}	b _{O₂}
Yao (Ind. Eng. Chem. Prod. Res. Dev., 1980)	21	1.0	-0.6
Lam & Trimm (Chem. Eng. Sci., 1980)	18/40	1.0	1.0/0.75
Aube & Sapoundijev (CCE, 2000)	13 (lowest)	1.0	
Firth & Holland (Trans. Faraday Soc., 1969)	48 (highest)	1.0	
Niwa et al. (App. Cat, 1983)	29	0.9	0.0
Aryafar & Zaera (Cat. Lett, 1997)	32	1.1	-0.1
Song et al. (Combust. Flame, 1991)	33	1.0	0.5

- Literature rate expressions (mostly under 'fuel-rich' conditions) indicate scatter in activation energies and rxn orders
- Is the scatter a result of (1) different operating conditions and surface area, (2) catalyst preparation, (3) fitting procedure, (4) bad data quality, or (5) inadequacy of power-law kinetics?



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Langmuir-Hinshelwood Rate Expressions

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
 - Temppkin 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

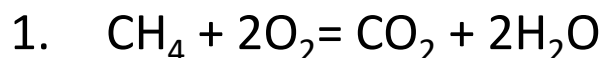


LH Rates on Rh

Overall rxn (CPOX): $\text{CH}_4 + 1/2\text{O}_2 = \text{CO} + 2\text{H}_2$

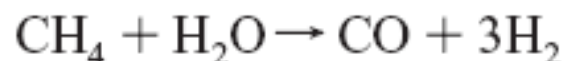
Overall rxns (hypothesized?)

1. CH_4 total oxidation (combustion)



$$r_{\text{TO}} = \frac{k_{\text{TO}} \cdot P_{\text{CH}_4}}{(1 + K_{\text{H}_2\text{O}}^{\text{ads}} \cdot P_{\text{H}_2\text{O}})^2}$$

2. Steam reforming of CH_4



$$r_{\text{SR}} = \frac{k_{\text{SR}} \cdot P_{\text{CH}_4} \cdot (1 - \eta_{\text{SR}})}{(1 + K_{\text{O}_2}^{\text{ads}} \cdot P_{\text{O}_2} + K_{\text{CO}}^{\text{ads}} \cdot P_{\text{CO}})^2}$$

3. CO_2 -reforming of CH_4



$$r_{\text{CO}_2\text{-R}} = \frac{k_{\text{CO}_2\text{-R}} \cdot P_{\text{CH}_4} \cdot (1 - \eta_{\text{CO}_2\text{-R}})}{(1 + K_{\text{O}_2}^{\text{ads}} \cdot P_{\text{O}_2} + K_{\text{CO}}^{\text{ads}} \cdot P_{\text{CO}})^2}$$

4. RWGS



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

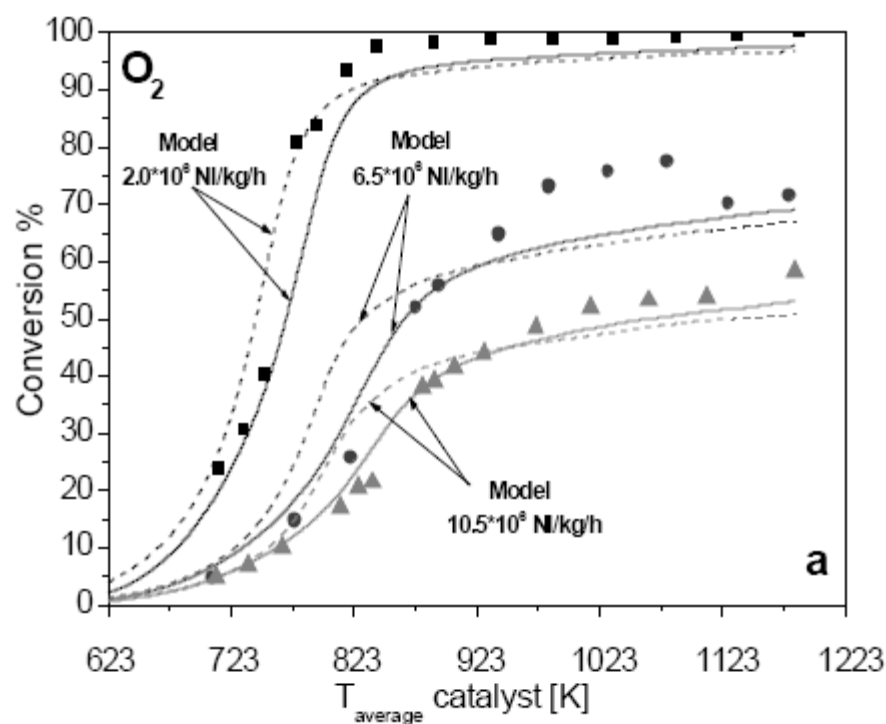
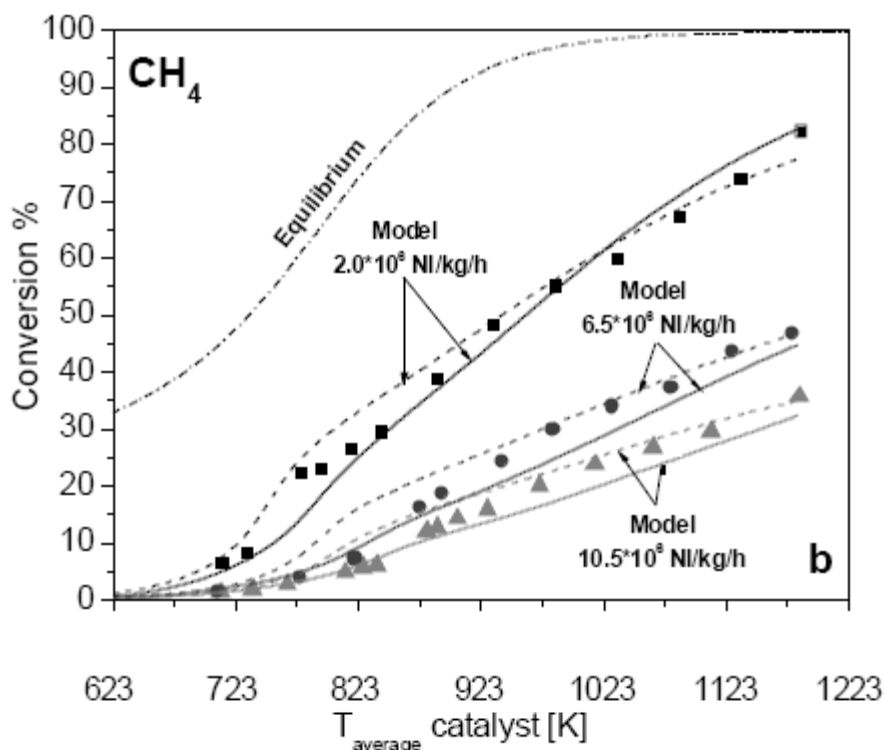
η = distance from equilibrium

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



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*	$100 - 21\theta_{\text{O}}$	expts, ⁵⁰⁻⁵² DFT ⁵³⁻⁵⁵
→ H ₂ O	$2.216 \cdot 10^{-1}$	39.5	→ CO*	$38.5 - 17\theta_{\text{CO}} - 3.7\theta_{\text{H}}$	expts, ^{46,56-58} DFT ^{11,59,60}
→ CO	15	6.2	→ CO ₂ *	5.2	expts, ^{61,62} UBI-QEP ⁶³
			→ H*	$62.3 - 2.5\theta_{\text{H}} - 3.7\theta_{\text{CO}}$	expts, ⁶⁴ DFT ^{11,53,65-67}
			→ OH*	$70 - 33\theta_{\text{O}} + 25\theta_{\text{H}_2\text{O}}$	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*

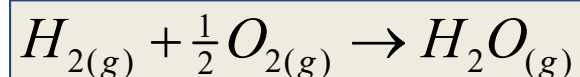
Parameters can be unphysical even if the model describes the data well!



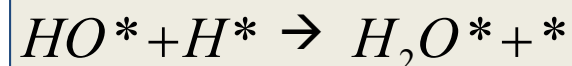
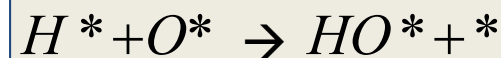
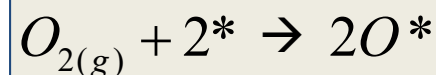
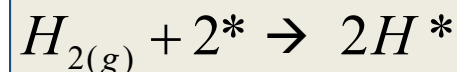
Microkinetic Modeling

- 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 multidentate 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



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Surface Species Concentration and Surface Reaction Rate

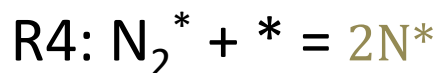
➤ Surface species concentration

- Total concentration of sites, $C_T =$ moles/cm²
- Concentration of species k, $C_k =$ moles/cm²
- $\text{Sum}(C_k) = C_T$

➤ Surface species coverage

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

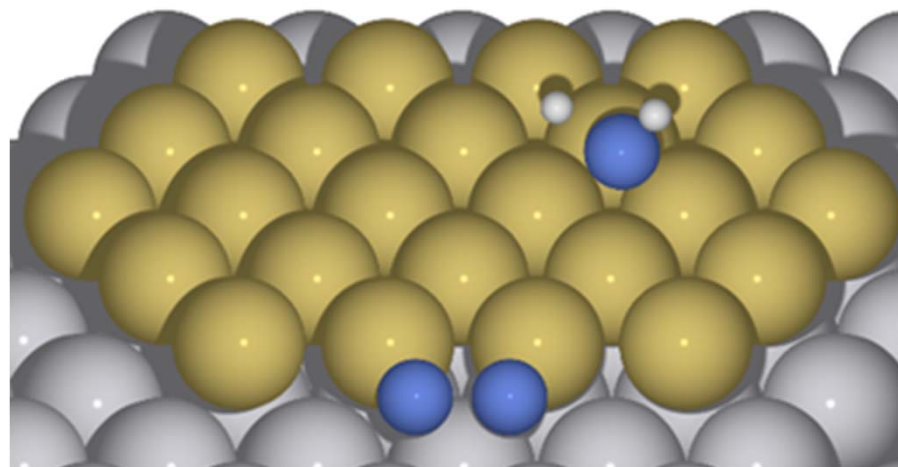
➤ Surface reaction rate



Reaction rate:

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

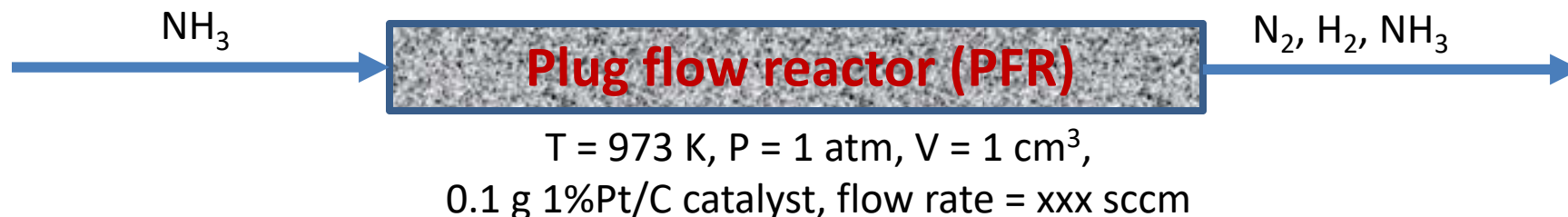
$$r_4 = k_4 \theta_{\text{N}_2} \theta^* \frac{\text{molecules}}{\text{site s}} \rightarrow \text{TOF (turnover frequency)}$$



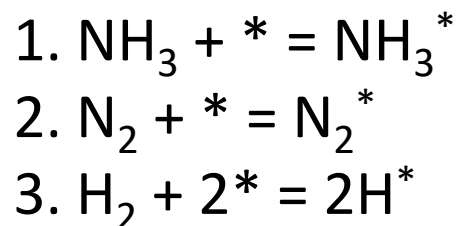


Surface Species Balance

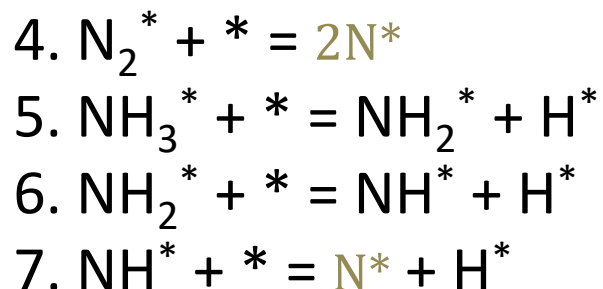
Example



Adsorption:



Surface reactions:



Balance for N^* species:

$$\frac{d[\text{N}^*]}{dt} = 2k_4[\text{N}_2^*][\text{Pt}] - 2\frac{k_4}{K_{c4}}[\text{N}^*]^2 + k_7[\text{NH}^*][\text{Pt}] - \frac{k_7}{K_{c7}}[\text{N}^*][\text{H}^*]$$

Equilibrium constants
Species conc (mol/cm²)

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

- CO₂ forms and directly goes in the gas phase; irreversible

➤ Units of pre-exps in s⁻¹ (or in cm, s, depending on reaction order)

Reactions	A ₀ (s ⁻¹) or S ₀	E _a (kcal/mol)
1 CO(g) + * → CO*	0.84 10 ⁰	0.0
2 CO* → CO(g) + *	1.250 10 ¹⁵	34.9
3 O ₂ (g) + 2* → 2O*	0.06 10 ⁰	0.0
4 2O* → O ₂ (g) + 2*	1.000 10 ¹³	51.0
5 CO* + O* → CO ₂ (g) + 2*	1.645 10 ¹⁴	24.1

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

$$\frac{d\theta_{O*}}{dt} = 2k_{O_2}^a P_t y_{O_2} \theta_*^2 - 2k_{O_2}^d \theta_{O*}^2 - k^r \theta_{CO*} \theta_{O*}$$

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

SS, one nonlinear model (after some algebra):

$$0 = 2k_{O_2}^a P_t y_{O_2} [1 - k_{CO}^a P_t y_{CO} (1 - \theta_{O*}) / (k_{CO}^a P_t y_{CO} + k_{CO}^d + k^r \theta_{O*}) - \theta_{O*}]^2 - 2k_{O_2}^d \theta_{O*}^2 - k^r k_{CO}^a P_t y_{CO} (1 - \theta_{O*}) \theta_{O*} / (k_{CO}^a P_t y_{CO} + k_{CO}^d + k^r \theta_{O*})$$

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)

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

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

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

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

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

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

- $k_i^b = k_i^f / K_i \rightarrow$ *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
- ν_{ji} = stoichiometric coef. in elementary rxn i

• 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*

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

$$\sigma_k = \sum_{i=1}^{N_r} v_{ik} r_i \quad \left[\frac{\text{gmol}}{\text{cm}^{\zeta_s}} \right] \quad \begin{array}{l} \zeta = 3 \\ \text{for homogeneous rxns} \\ \zeta = 2 \\ \text{for heterogeneous rxns} \end{array}$$

$$\tilde{\sigma}_k = \sum_{i=1}^{N_r} v_{ik} \tilde{r}_i \quad \left[\frac{\text{mlcs}}{\text{site s}} \right] \quad \begin{array}{l} \text{Turnover Frequency (TOF)} \\ \text{for heterogeneous rxns} \end{array}$$

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



I. 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 $k=1,...,K_s$ Algebraic eqs.	$0 = \sigma_k$	$0 = \tilde{\sigma}_k$

* 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

II. 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 I)*

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

Reaction Mechanism

Adsorption/Desorption:

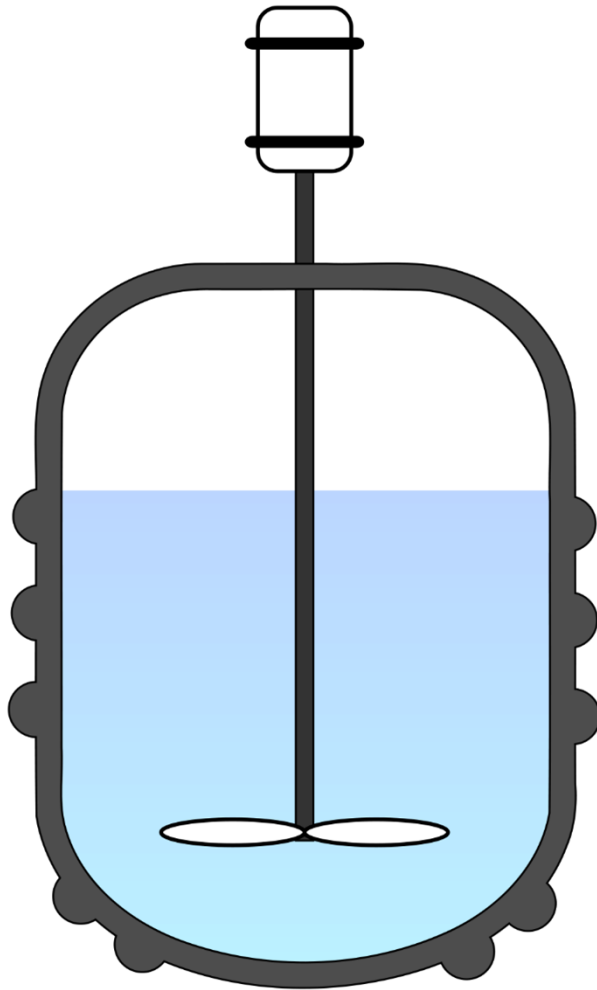
- $\text{NH}_3 + * = \text{NH}_3^*$
- $\text{N}_2 + * = \text{N}_2^*$
- $\text{H}_2 + 2* = 2\text{H}^*$

Surface reactions:

- $\text{N}_2^* + * = 2\text{N}^*$
- $\text{NH}_3^* + * = \text{NH}_2^* + \text{H}^*$
- $\text{NH}_2^* + * = \text{NH}^* + \text{H}^*$
- $\text{NH}^* + * = \text{N}^* + \text{H}^*$



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)



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 $\tilde{C}_T \sim 10^{15} [\text{sites}/\text{cm}^2]$, $C_T \sim 10^{-9} [\text{gmol of sites}/\text{cm}^2]$.

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	$\tilde{k}_{fi} \left[\frac{\text{mlcs}}{\text{site s}} \right]$	$k'_{fi} \left[\frac{\text{gmol}}{\text{cm}^2 \text{ s}} \right]^1$	$k_{fi} \frac{1}{s} \left[\frac{\text{cm}^2}{\text{gmol}} \right]^{v_{ti}-1}$
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) $\frac{dW_k}{dz} = \frac{(\sigma_k^{\text{fluid}} + \sigma_k^{\text{surf}})M_k}{\rho u}, k=1, \dots, K_g$ $\sigma_k^{\text{surf}} = v_{\text{ads}}r_{\text{ads},k} + v_{\text{des}}r_{\text{des},k}$ typically : $v_{\text{ads}} = -1, v_{\text{des}} = 1$ (net rate of consumption) <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> $\frac{dW_k}{dt} = 0 = \frac{W_k^o - W_k}{\tau(\rho/\rho^o)} + \frac{(\sigma_k^{\text{fluid}} + \sigma_k^{\text{surf}} a)M_k}{\rho}$ <p>or $\frac{dW_k}{dt} = 0 = \frac{W_k^o - W_k}{\tau_m} + \frac{(\sigma_k^{\text{fluid}} + \sigma_k^{\text{surf}} a)M_k}{\rho},$</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)
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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

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)

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

\underline{a} is the catalyst surface area per unit volume of the reactor

Solution Methods

- Transient Problems: Stiff ODEs or DAEs
- Steady state/Analytical solution possible for toy problems

$$0 = 2k_{O_2}^a P_t y_O [1 - k_{CO}^a P_t y_{CO} (1 - \theta_{O*}) / (k_{CO}^a P_t y_{CO} + k_{CO}^d + k^r \theta_{O*}) - \theta_{O*}]^2 \\ - 2k_{O_2}^d \theta_{O*}^2 - k^r k_{CO}^a P_t y_{CO} (1 - \theta_{O*}) \theta_{O*} / (k_{CO}^a P_t y_{CO} + k_{CO}^d + k^r \theta_{O*})$$

- Steady state/Numerical method
 - Newton
 - Solve the transient model if Newton's method has difficulty to converge
 - Hybrid: Solve the transient model if Newton's method has difficulty to converge until you get close enough to SS; then switch to Newton's method

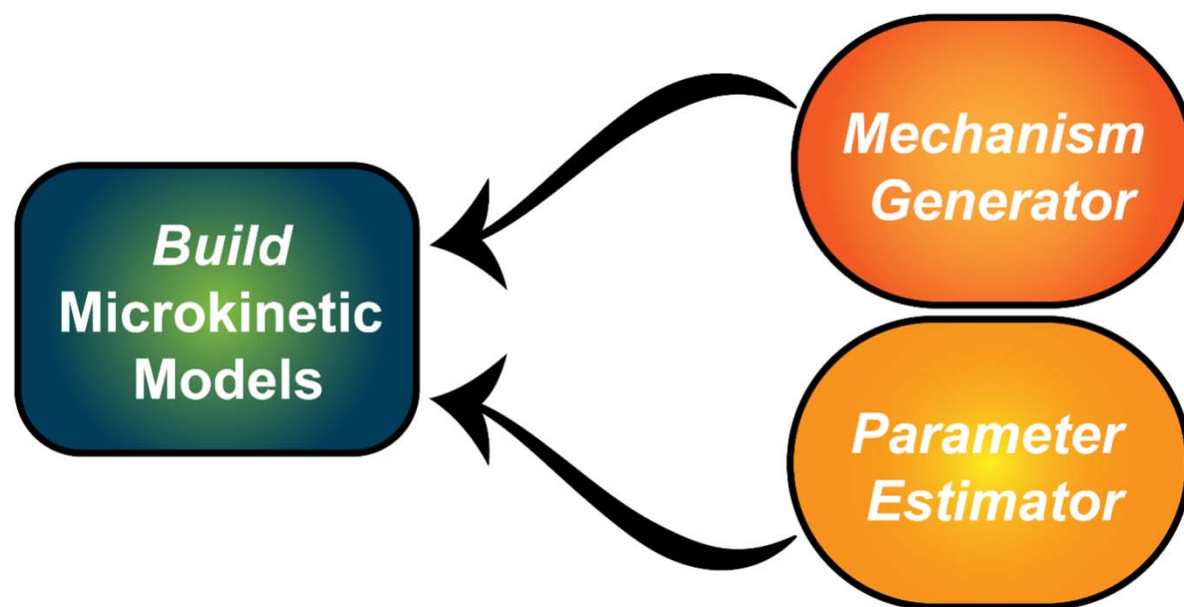


Numerical Solvers in Cantera

- Cantera is an open source software which formulates the kinetics based on supplied reactions and reactor models.
- Formulating chemical kinetics result in stiff ODEs and DAEs (lot of fast reactions coupled with few slow ones).
- High quality numerical packages to solve ODEs and DAEs are already in public domain (PETsc, SUNDIALS, Trilinos, DASPK (Fortran)).
- Cantera uses CVODES (part of SUNDIALS) to solve the ODES originating from steady state regime in PFR (as network of CSTRs) reactor model.
- The default options are BDF for solving the ODEs with Newton iterative method for linear step using dense matrix approach.
- BDF (Backward differentiation formula) is an implicit multistep method of order k , where $k \leq 5$

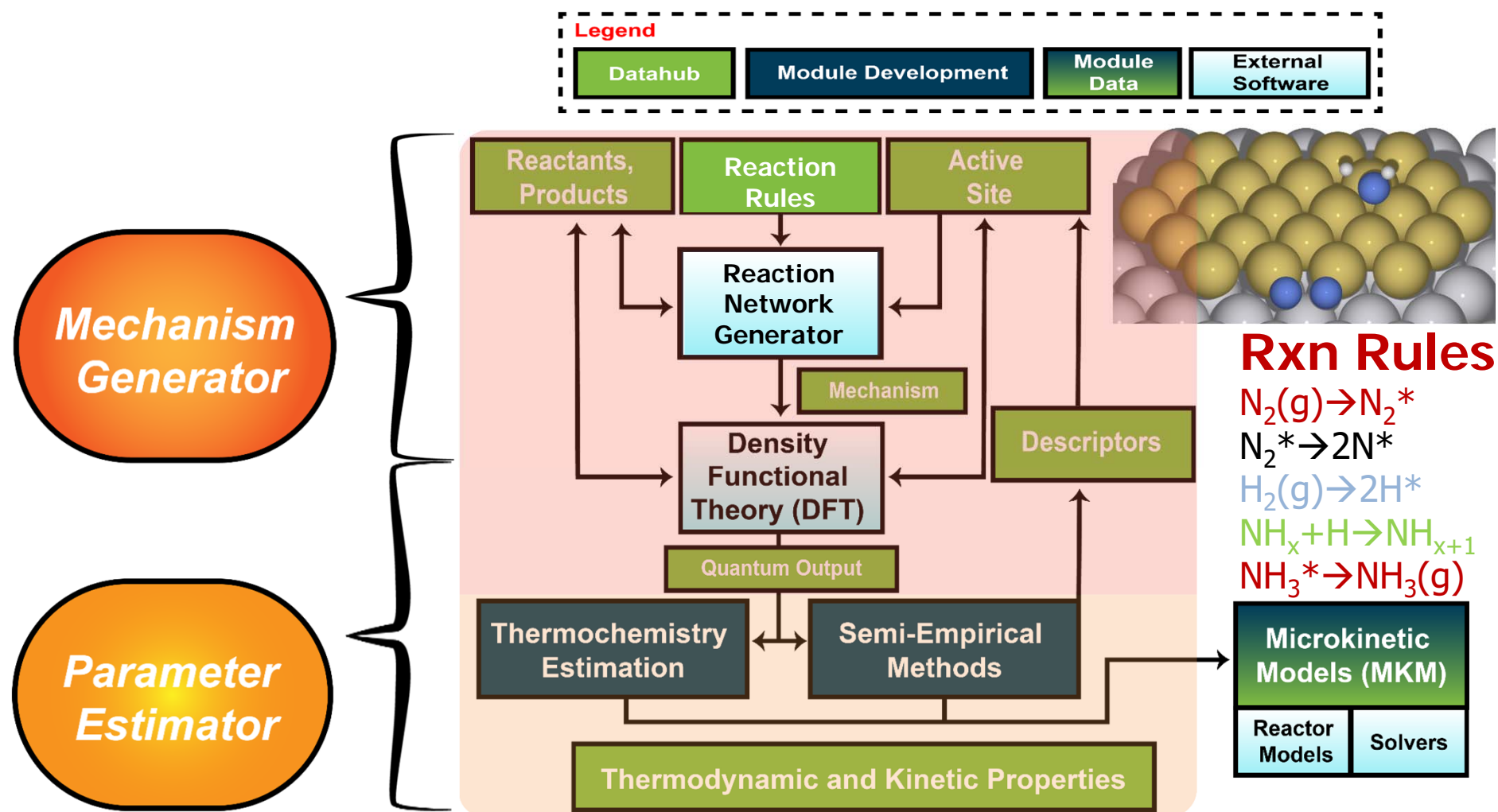


Workflow and Software Modules





Workflow and Software Modules



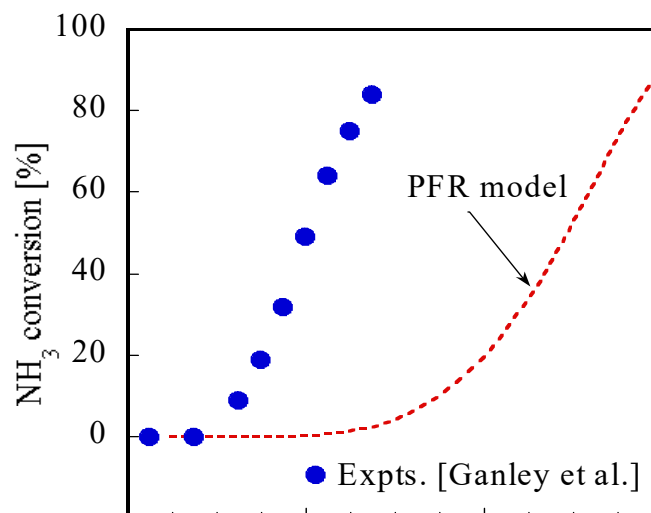
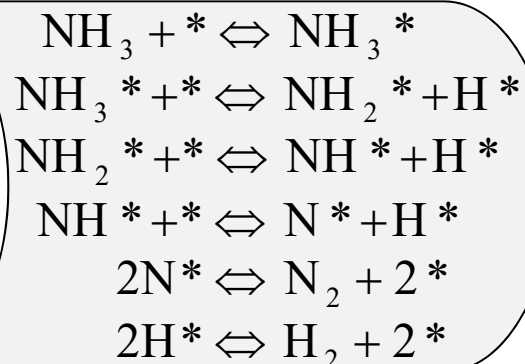


Lateral Interactions: Estimation via Hierarchical Estimation Methodology

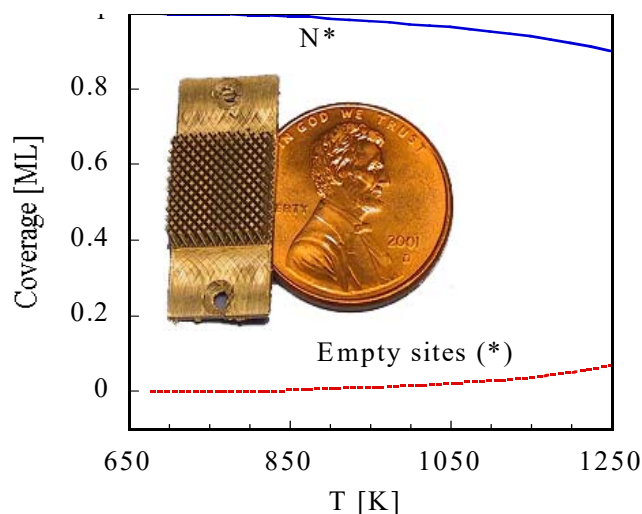
After parameterization of a microkinetic model via DFT (or semi-empirical methods), the model needs refinement to account for most abundant surface intermediates (MASI)

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

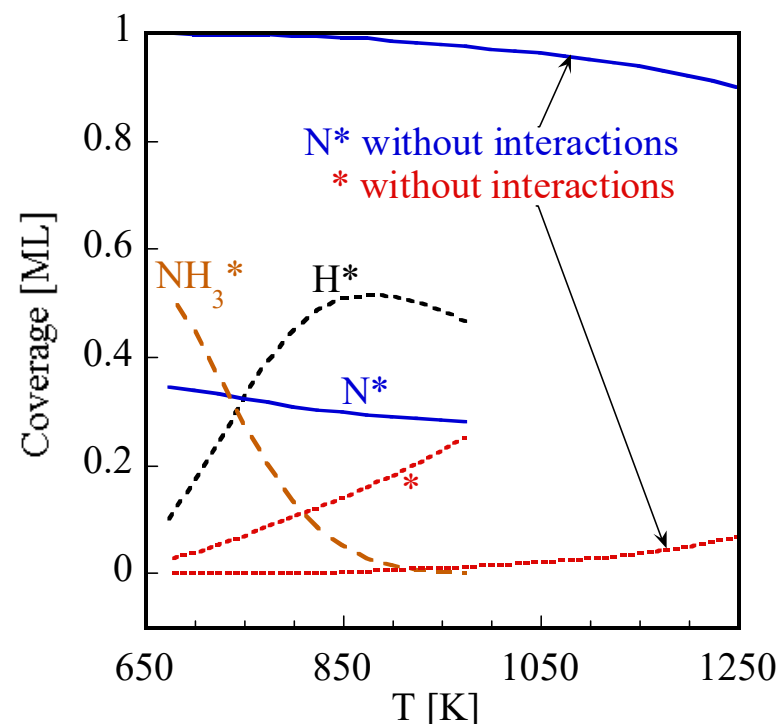
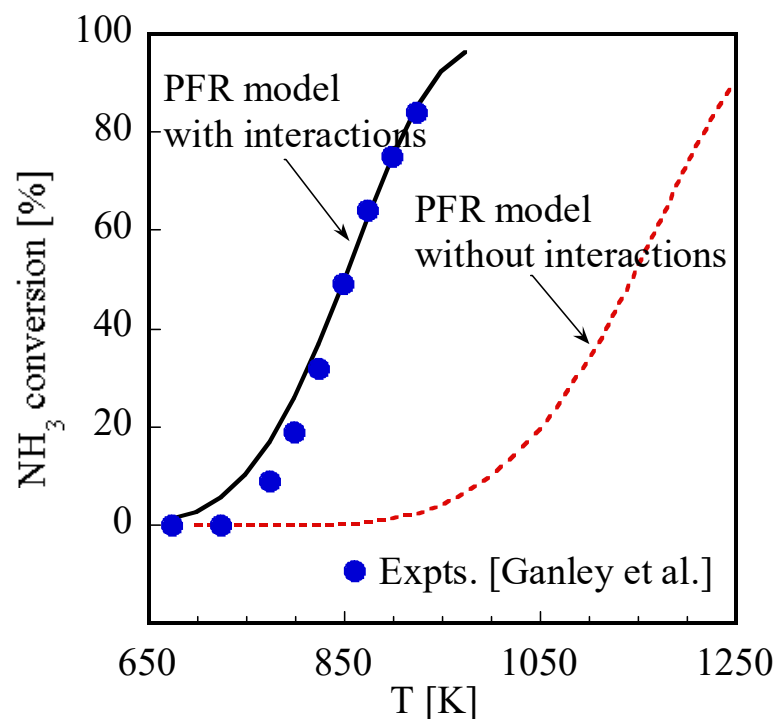
- NH₃ as a storage medium
- 'Pure' H₂ – No CO_x
- A microkinetic model is build using BOC and TST
- Our microkinetic model captures the trend
- High N* coverages



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



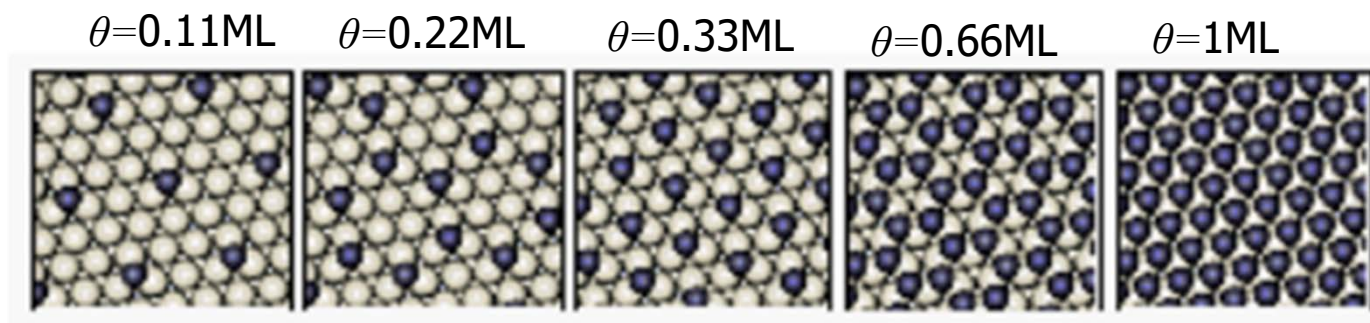
DFT-Retrained Microkinetic Model



- 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)

Lateral Interactions

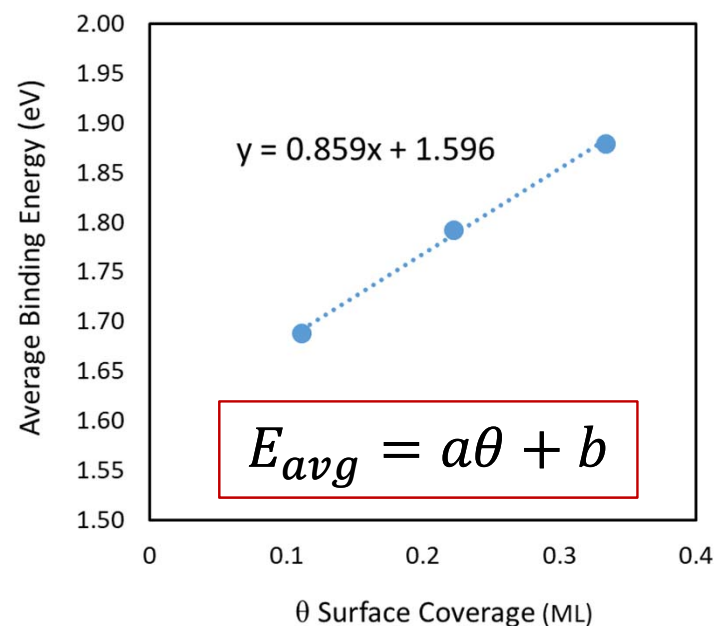

$$\text{Surface Coverage} \leftarrow \theta = \frac{n}{N_a} \begin{matrix} \rightarrow \text{Number of adsorbates} \\ \rightarrow \text{Total Number of active sites} \end{matrix}$$

- 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

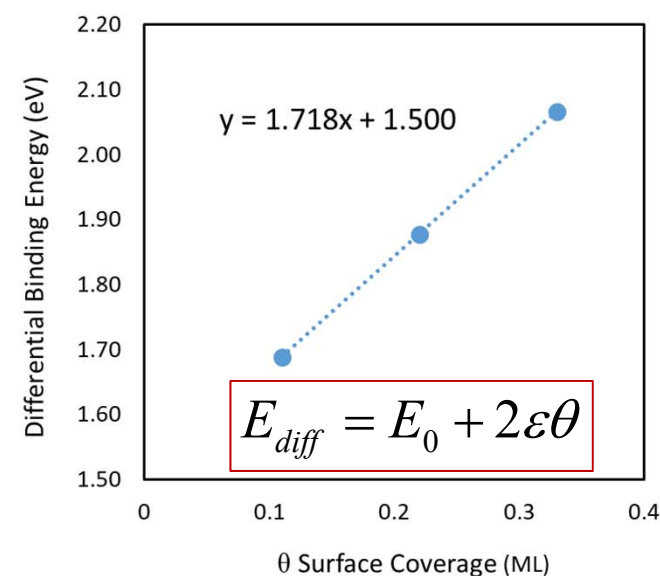
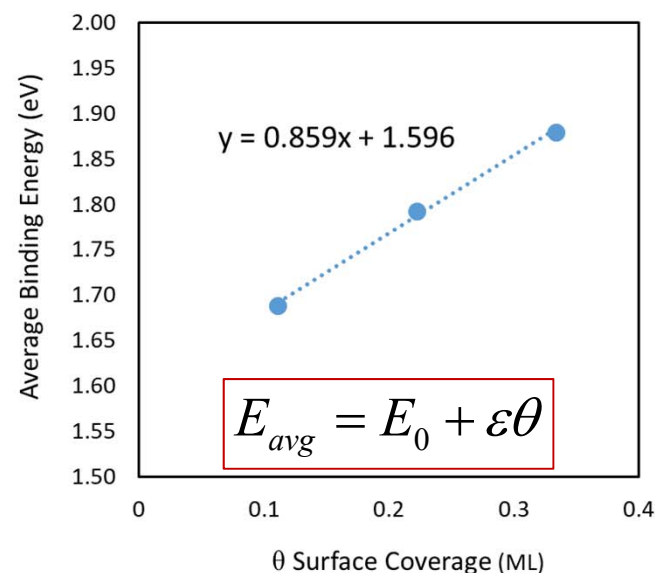
$$E_{avg} = \frac{1}{\theta} \int_0^\theta E_{diff}(\theta) d\theta$$

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

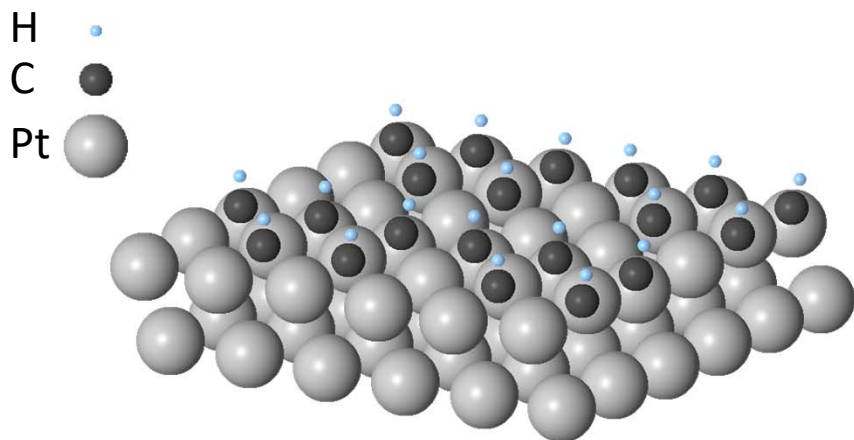
integral

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

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



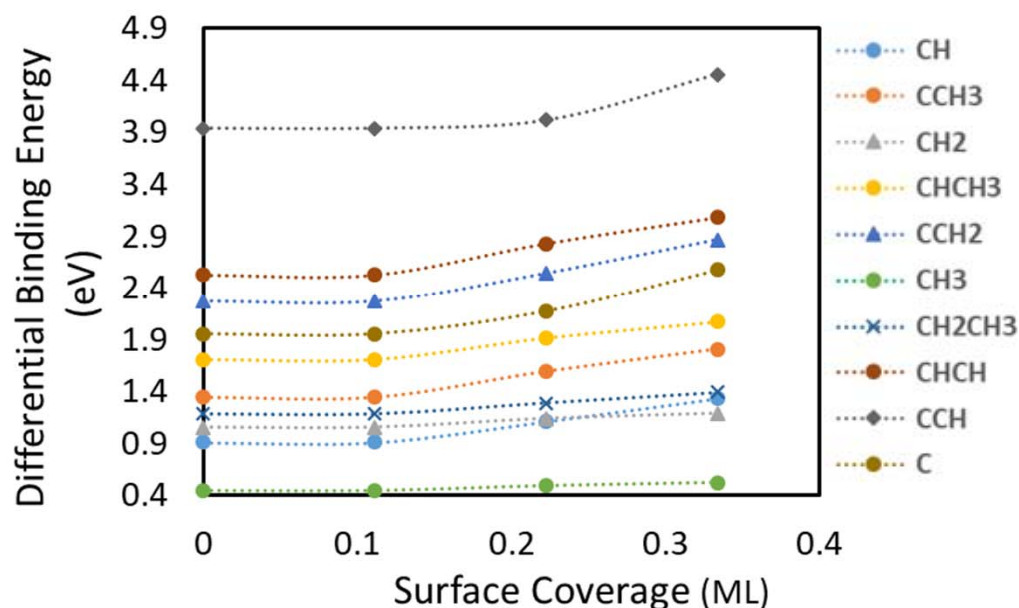
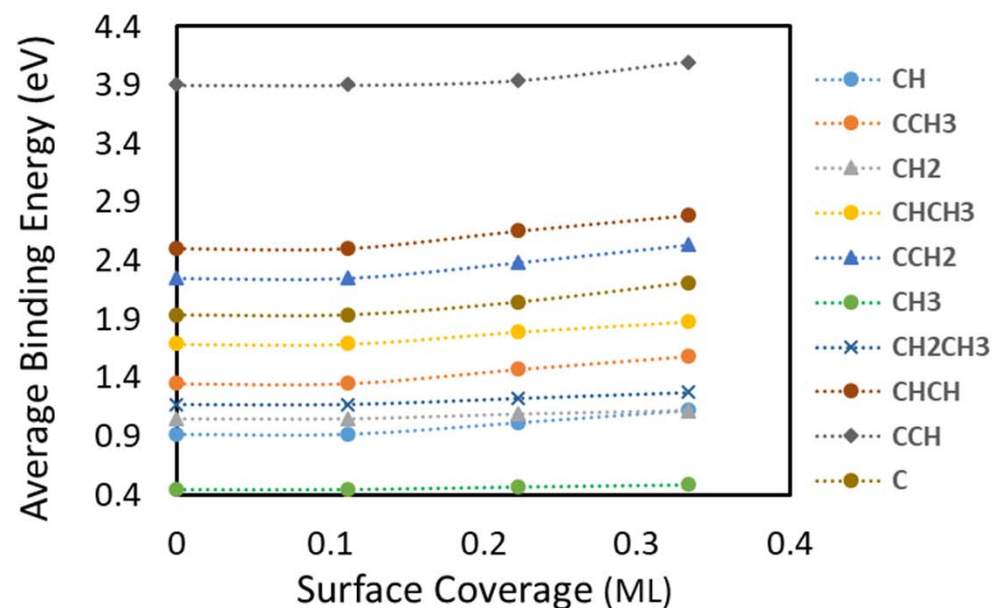
Lateral interactions: Piecewise Linear Model



Piece-wise linear model:

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

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





Outline

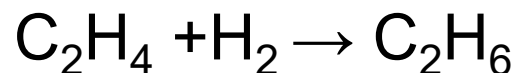
- Types of catalytic kinetic models and microkinetic modeling
- Overview of parameter estimation methods and scales
- Accuracy
- Lateral interactions
- Semi-empirical methods
- Thermodynamic consistency
- MKM uses
 - Reactor design, analysis, catalyst discovery
- Kinetic Monte Carlo

What Can We Use MKMs for?

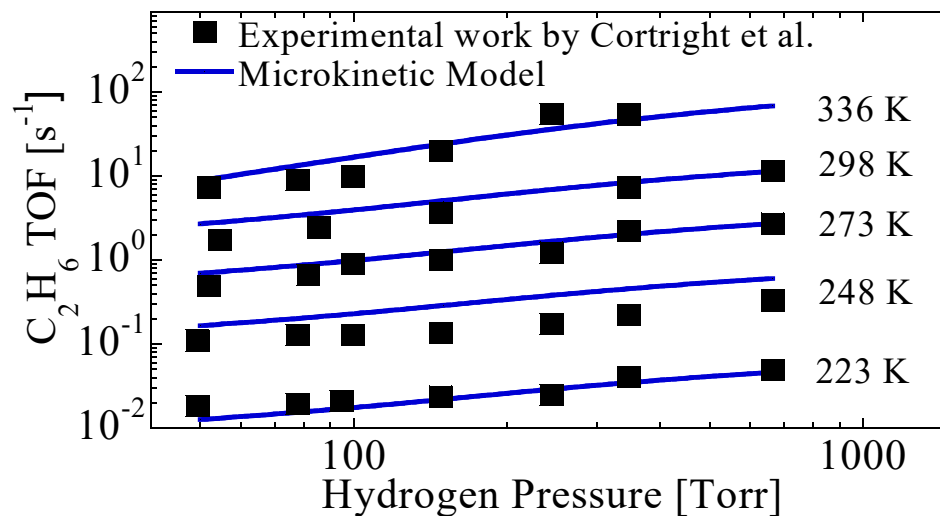
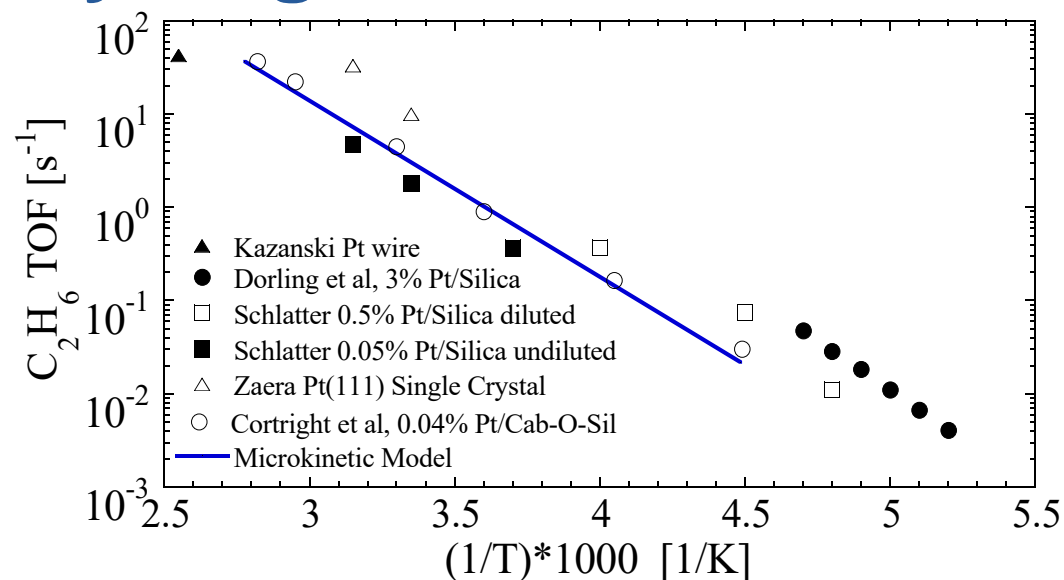
- Traditional**
 - Reconcile apparently contradictory experimental data at different conditions (TPD, steady state, various operating conditions)
 - Mechanistic understanding
 - Perform reactor design and optimization
- Modern**
 - Model-based design of experiments to assess model*
 - Rational catalyst design
 - Composition
 - Size
 - Shape

*Prasad et al., *Chem. Eng. Sci.* **65**, 240 (2010); *IECR* **48**, 5255 (2009);
Prasad and Vlachos, *IECR* **47**, 6555 (2008).

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

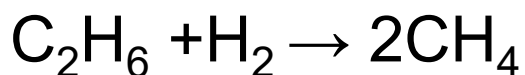


Experimental data from:

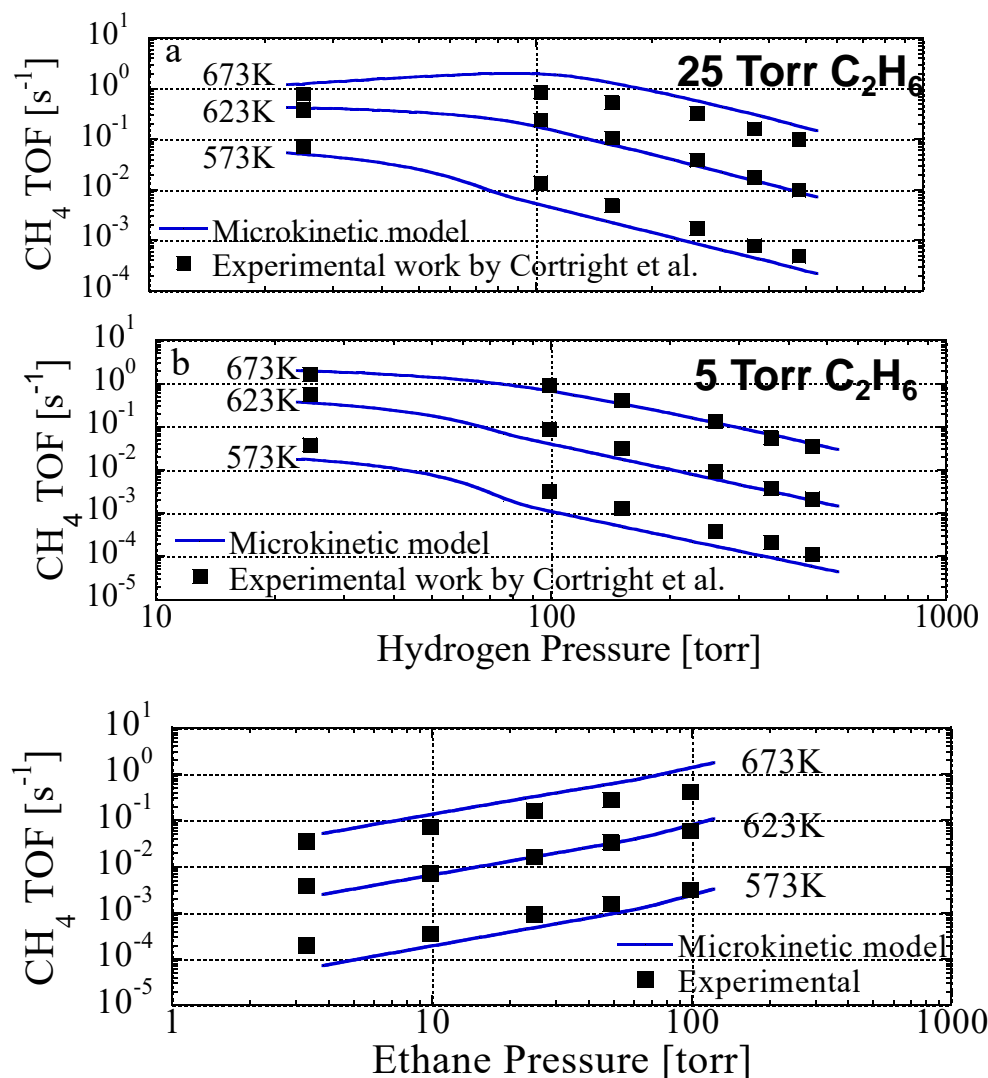
Cortright et al., J. Cat. 127 (1991) 342-353

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

Mechanisms of Hydrogenolysis of Ethane

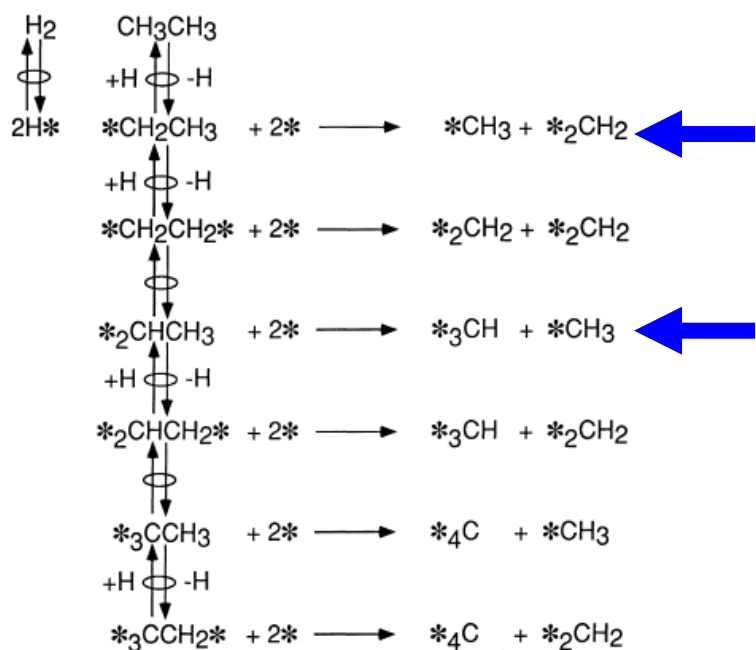


Fig. 1. Proposed reaction pathways for ethane hydrogenolysis over platinum.

- Sinfelt and co-workers⁽¹⁾ suggested that the rate-determining step may involve highly dehydrogenated C_2H_x species
- Dumesic and co-workers proposed C-C cleavage reactions take place via CH_2CH_3 and CHCH_3 over Pt⁽²⁾
- Limitations of previous mechanisms
 - Isomerization reactions are proposed to be key steps but their rates are unknown
 - Paths are incomplete

(1) Sinfelt, J. H.; Yates, D. J. C. *Journal of Catalysis* 8, 82, (1967).

(2) Cortright, R. D.; Watwe, R. M.; Spiewak, B. E.; Dumesic, J. A. *Catalysis Today* 53, 395 (1999).

Figure 1 illustrates the chemical reaction network for the formation of ethane from ethene and hydrogen. The diagram shows the following species and their corresponding sensitivity coefficients (S_{ij}):

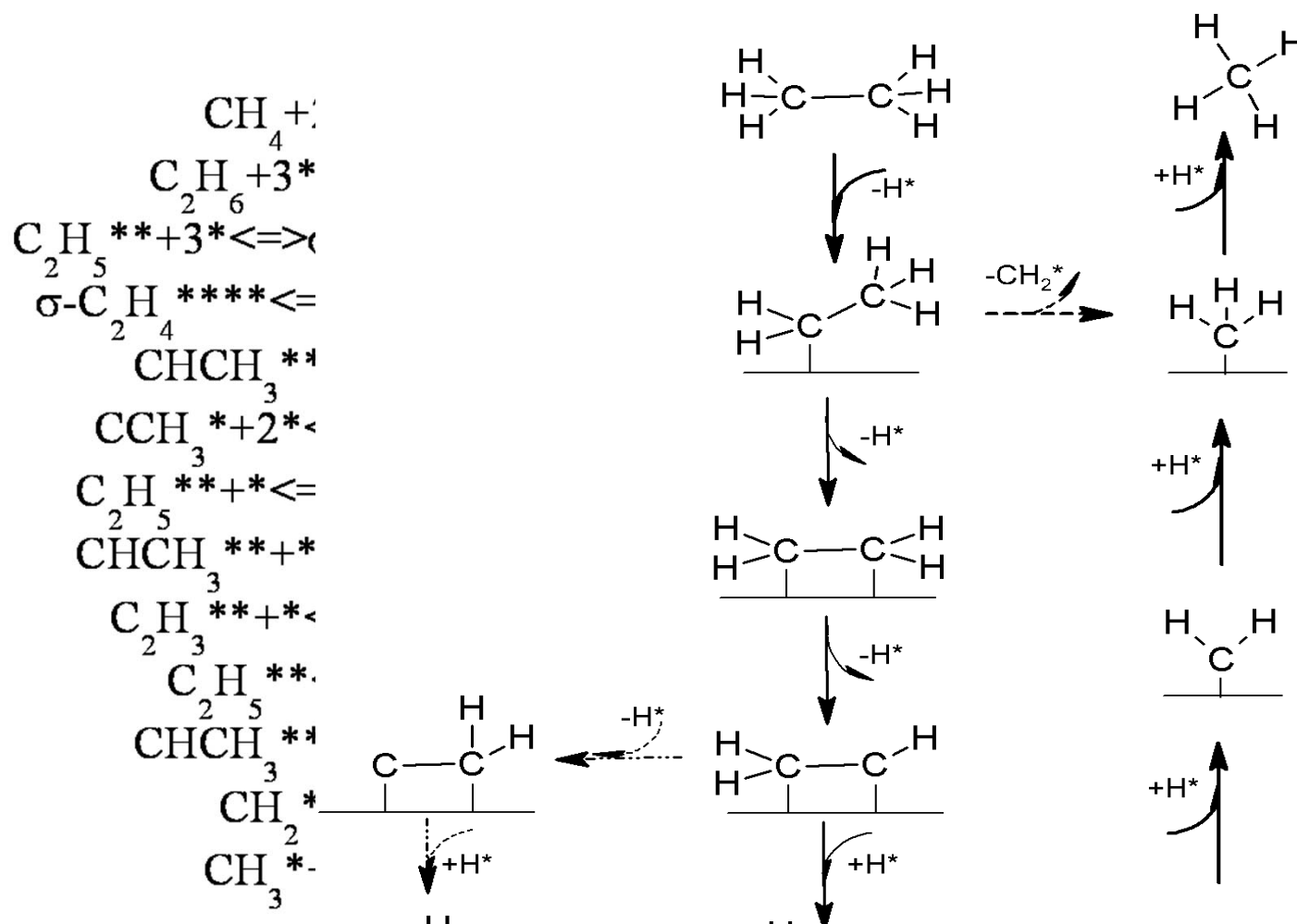
- $\pi\text{-C}_2\text{H}_4$ (Ethene): $S_{ij} = \frac{\Delta \ln H}{\Delta \ln H}$
- $\pi\text{-C}_2\text{H}_3$ (Ethyl radical)
- $\sigma\text{-C}_2\text{H}_5$ (Ethane)
- C_2H_3 (Ethyl radical)
- C_2H_4 (Ethene)
- C_2H_5 (Ethyl radical)
- C_2H_6 (Ethane)
- C_2H_7 (Ethyl radical)
- C_2H_8 (Ethane)
- C_2H_9 (Ethyl radical)
- C_2H_{10} (Ethane)
- C_2H_{11} (Ethyl radical)
- C_2H_{12} (Ethane)
- C_2H_{13} (Ethyl radical)
- C_2H_{14} (Ethane)
- C_2H_{15} (Ethyl radical)
- C_2H_{16} (Ethane)
- C_2H_{17} (Ethyl radical)
- C_2H_{18} (Ethane)
- C_2H_{19} (Ethyl radical)
- C_2H_{20} (Ethane)
- C_2H_{21} (Ethyl radical)
- C_2H_{22} (Ethane)
- C_2H_{23} (Ethyl radical)
- C_2H_{24} (Ethane)
- C_2H_{25} (Ethyl radical)
- C_2H_{26} (Ethane)
- C_2H_{27} (Ethyl radical)
- C_2H_{28} (Ethane)
- C_2H_{29} (Ethyl radical)
- C_2H_{30} (Ethane)
- C_2H_{31} (Ethyl radical)
- C_2H_{32} (Ethane)
- C_2H_{33} (Ethyl radical)
- C_2H_{34} (Ethane)
- C_2H_{35} (Ethyl radical)
- C_2H_{36} (Ethane)
- C_2H_{37} (Ethyl radical)
- C_2H_{38} (Ethane)
- C_2H_{39} (Ethyl radical)
- C_2H_{40} (Ethane)
- C_2H_{41} (Ethyl radical)
- C_2H_{42} (Ethane)
- C_2H_{43} (Ethyl radical)
- C_2H_{44} (Ethane)
- C_2H_{45} (Ethyl radical)
- C_2H_{46} (Ethane)
- C_2H_{47} (Ethyl radical)
- C_2H_{48} (Ethane)
- C_2H_{49} (Ethyl radical)
- C_2H_{50} (Ethane)
- C_2H_{51} (Ethyl radical)
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- C_2H_{65} (Ethyl radical)
- C_2H_{66} (Ethane)
- C_2H_{67} (Ethyl radical)
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- C_2H_{72} (Ethane)
- C_2H_{73} (Ethyl radical)
- C_2H_{74} (Ethane)
- C_2H_{75} (Ethyl radical)
- C_2H_{76} (Ethane)
- C_2H_{77} (Ethyl radical)
- C_2H_{78} (Ethane)
- C_2H_{79} (Ethyl radical)
- C_2H_{80} (Ethane)
- C_2H_{81} (Ethyl radical)
- C_2H_{82} (Ethane)
- C_2H_{83} (Ethyl radical)
- C_2H_{84} (Ethane)
- C_2H_{85} (Ethyl radical)
- C_2H_{86} (Ethane)
- C_2H_{87} (Ethyl radical)
- C_2H_{88} (Ethane)
- C_2H_{89} (Ethyl radical)
- C_2H_{90} (Ethane)
- C_2H_{91} (Ethyl radical)
- C_2H_{92} (Ethane)
- C_2H_{93} (Ethyl radical)
- C_2H_{94} (Ethane)
- C_2H_{95} (Ethyl radical)
- C_2H_{96} (Ethane)
- C_2H_{97} (Ethyl radical)
- C_2H_{98} (Ethane)
- C_2H_{99} (Ethyl radical)
- C_2H_{100} (Ethane)

The diagram also shows the reaction network for the formation of ethane from ethene and hydrogen, including the following steps:

- $\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_5$
- $\text{C}_2\text{H}_5 + \text{H} \rightarrow \text{C}_2\text{H}_6$
- $\text{C}_2\text{H}_6 + \text{H} \rightarrow \text{C}_2\text{H}_7$
- $\text{C}_2\text{H}_7 + \text{H} \rightarrow \text{C}_2\text{H}_8$
- $\text{C}_2\text{H}_8 + \text{H} \rightarrow \text{C}_2\text{H}_9$
- $\text{C}_2\text{H}_9 + \text{H} \rightarrow \text{C}_2\text{H}_{10}$
- $\text{C}_2\text{H}_{10} + \text{H} \rightarrow \text{C}_2\text{H}_{11}$
- $\text{C}_2\text{H}_{11} + \text{H} \rightarrow \text{C}_2\text{H}_{12}$
- $\text{C}_2\text{H}_{12} + \text{H} \rightarrow \text{C}_2\text{H}_{13}$
- $\text{C}_2\text{H}_{13} + \text{H} \rightarrow \text{C}_2\text{H}_{14}$
- $\text{C}_2\text{H}_{14} + \text{H} \rightarrow \text{C}_2\text{H}_{15}$
- $\text{C}_2\text{H}_{15} + \text{H} \rightarrow \text{C}_2\text{H}_{16}$
- $\text{C}_2\text{H}_{16} + \text{H} \rightarrow \text{C}_2\text{H}_{17}$
- $\text{C}_2\text{H}_{17} + \text{H} \rightarrow \text{C}_2\text{H}_{18}$
- $\text{C}_2\text{H}_{18} + \text{H} \rightarrow \text{C}_2\text{H}_{19}$
- $\text{C}_2\text{H}_{19} + \text{H} \rightarrow \text{C}_2\text{H}_{20}$
- $\text{C}_2\text{H}_{20} + \text{H} \rightarrow \text{C}_2\text{H}_{21}$
- $\text{C}_2\text{H}_{21} + \text{H} \rightarrow \text{C}_2\text{H}_{22}$
- $\text{C}_2\text{H}_{22} + \text{H} \rightarrow \text{C}_2\text{H}_{23}$
- $\text{C}_2\text{H}_{23} + \text{H} \rightarrow \text{C}_2\text{H}_{24}$
- $\text{C}_2\text{H}_{24} + \text{H} \rightarrow \text{C}_2\text{H}_{25}$
- $\text{C}_2\text{H}_{25} + \text{H} \rightarrow \text{C}_2\text{H}_{26}$
- $\text{C}_2\text{H}_{26} + \text{H} \rightarrow \text{C}_2\text{H}_{27}$
- $\text{C}_2\text{H}_{27} + \text{H} \rightarrow \text{C}_2\text{H}_{28}$
- $\text{C}_2\text{H}_{28} + \text{H} \rightarrow \text{C}_2\text{H}_{29}$
- $\text{C}_2\text{H}_{29} + \text{H} \rightarrow \text{C}_2\text{H}_{30}$
- $\text{C}_2\text{H}_{30} + \text{H} \rightarrow \text{C}_2\text{H}_{31}$
- $\text{C}_2\text{H}_{31} + \text{H} \rightarrow \text{C}_2\text{H}_{32}$
- $\text{C$

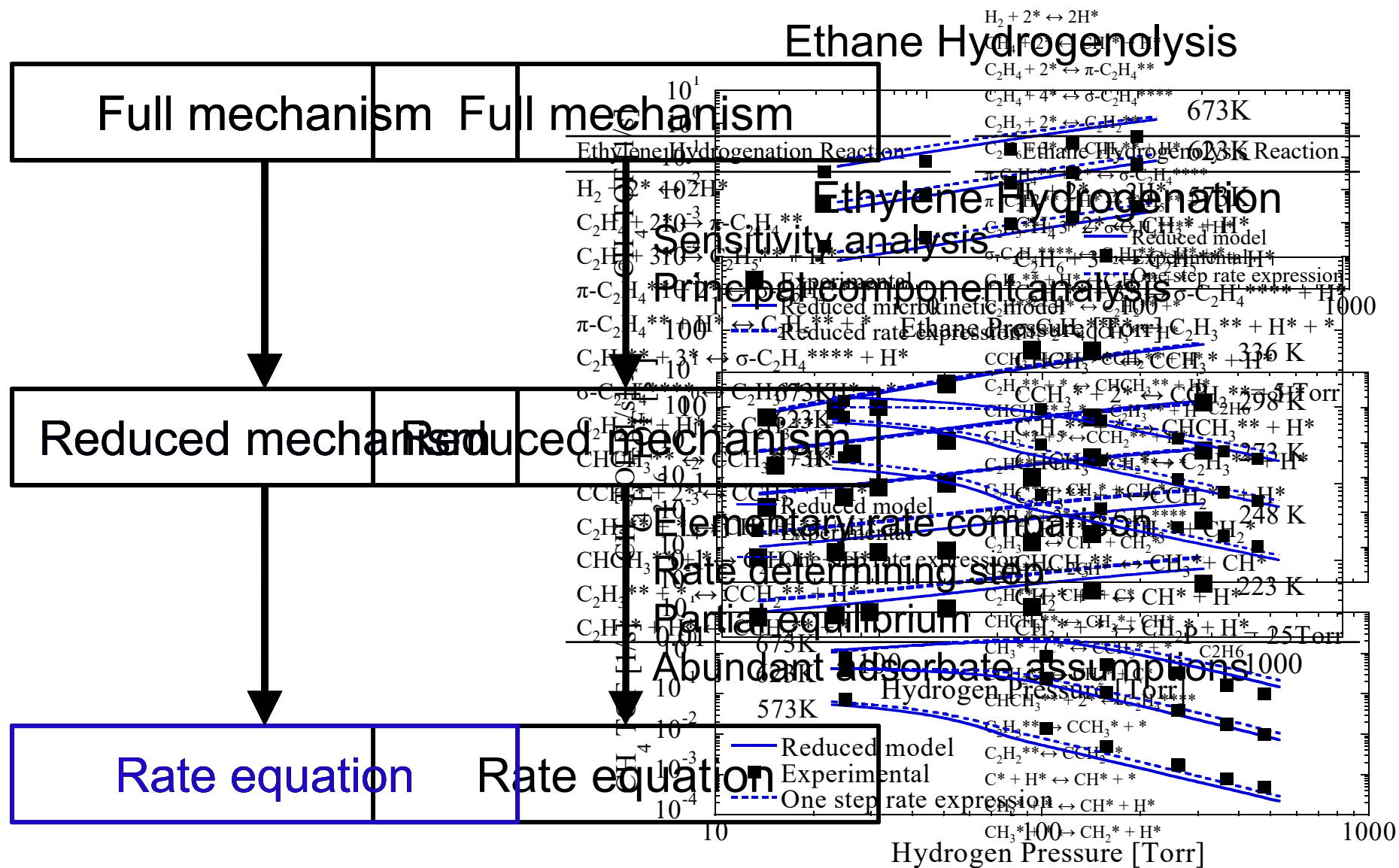
Hydrogenation rxns are rate controlling ($n\text{-C}_2\text{H}_4^{**} \rightarrow \text{C}_2\text{H}_5^{**}$, $\text{C}_2\text{H}_5^{**} \rightarrow \text{C}_2\text{H}_6$)

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

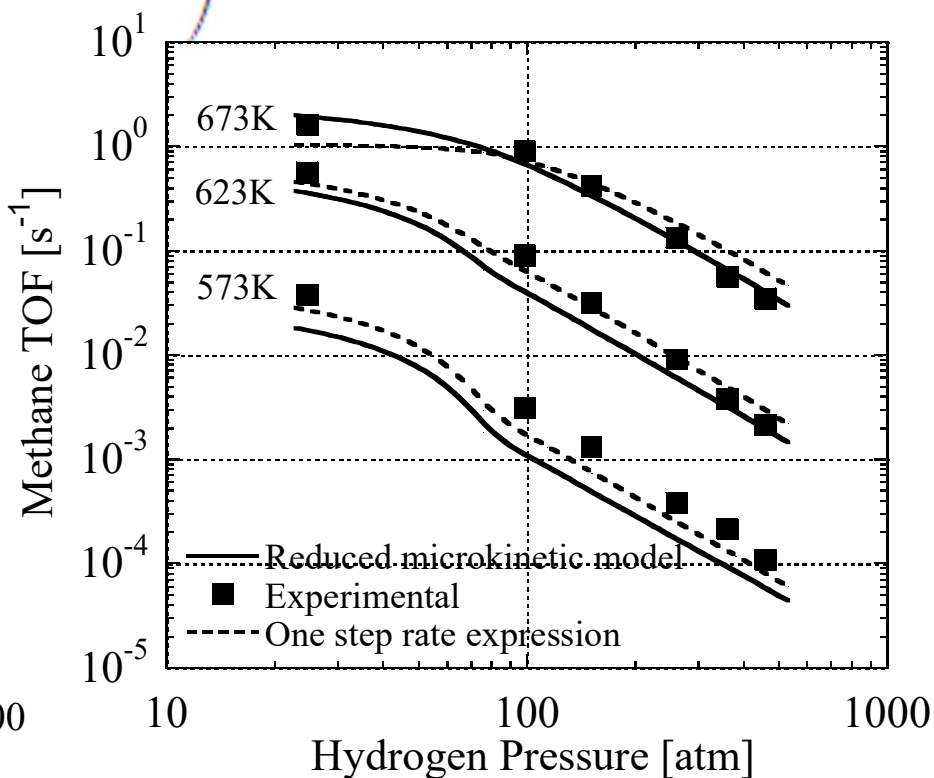
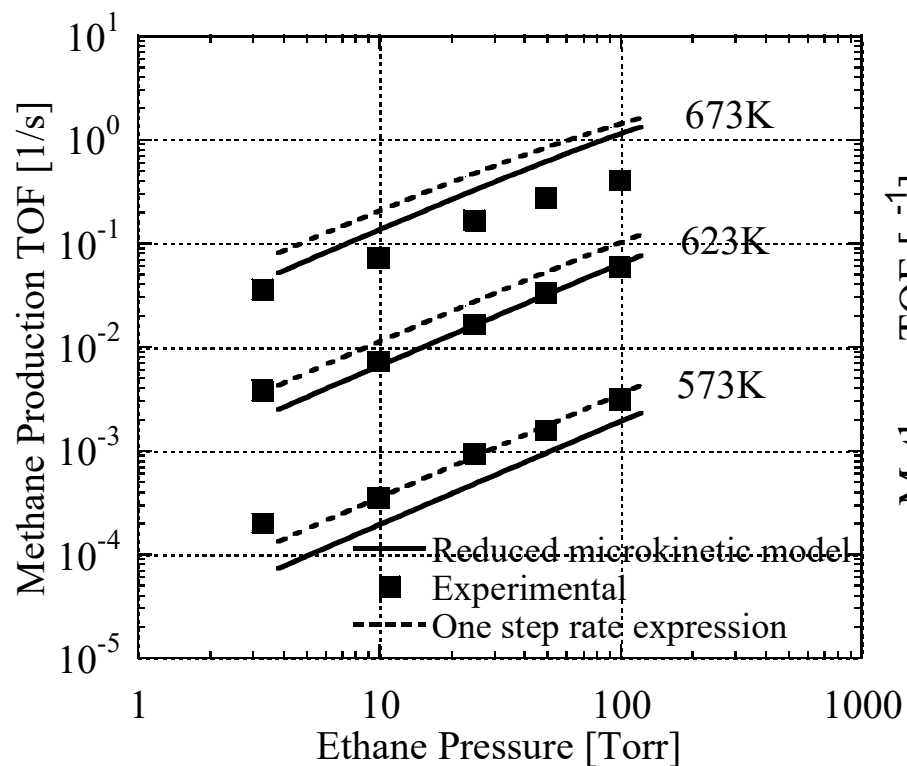


Saliccioli et al., *Ind. Eng. Chem. Res.* **50**, 28 (2011).

Ethane Hydrogenolysis Rate Expression

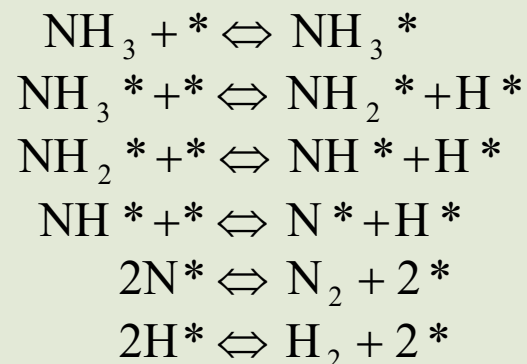
Hydrogenolysis Rate =

$$\left(\frac{\frac{k_2}{K_2} \sqrt{K_1 C_{H_2}}}{\frac{k_{19} \frac{K_6 C_{C_2H_6}}{\sqrt{K_1 C_{H_2}}} + k_{24} \frac{K_{14} \sqrt{K_1 C_{H_2}}}{K_{13}} + k_2 C_{CH_4}} - \frac{k_2}{K_2}} \right) \left(\frac{1}{1 + \sqrt{K_1 C_{H_2}} + \frac{K_{17} K_{10} K_9 K_6 C_{C_2H_6}}{K_{14} \sqrt{K_1 C_{H_2}}}} \right)^2$$

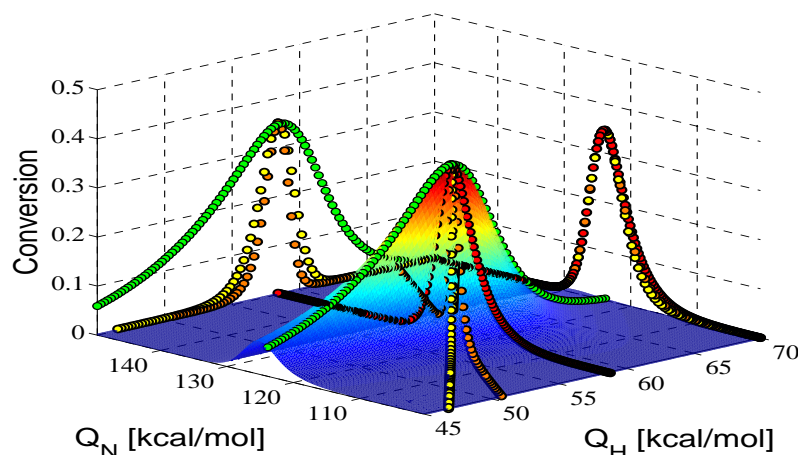


High Throughput Multiscale Model-based Catalyst Design

NH₃ decomposition

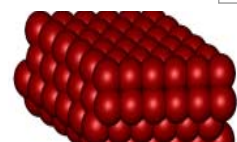
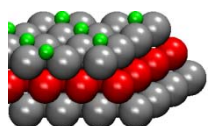


350 °C
1 atm



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

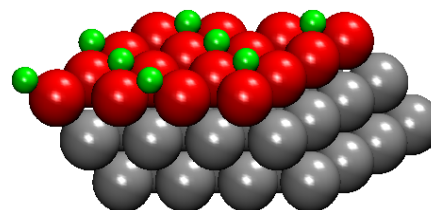
Identifying Bimetallic Catalysts



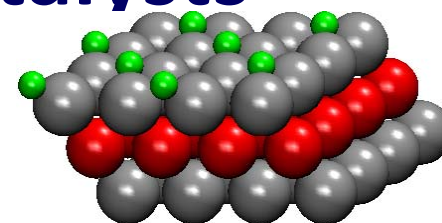
Metals	BE_N (kcal/mol)
PtTiPt	56.5
PtVPt	59.5
PtCrPt	72.6
PtMnPt	84.9
PtFePt	83.9
PtCoPt	87.0
PtNiPt	89.8
NiPtPt	137.5
CoPtPt	159.9
FePtPt	169.9
MnPtPt	162.2
CrPtPt	166.5
VPtPt	184.1
TiPtPt	191.5

Pt
Ni

102.1
113.8

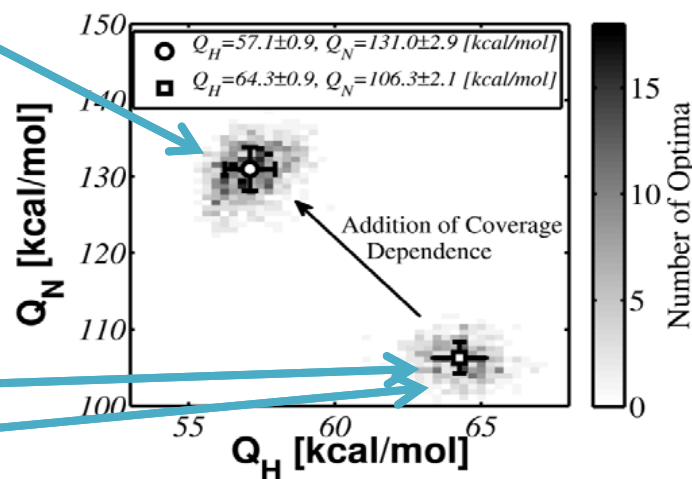


Surface

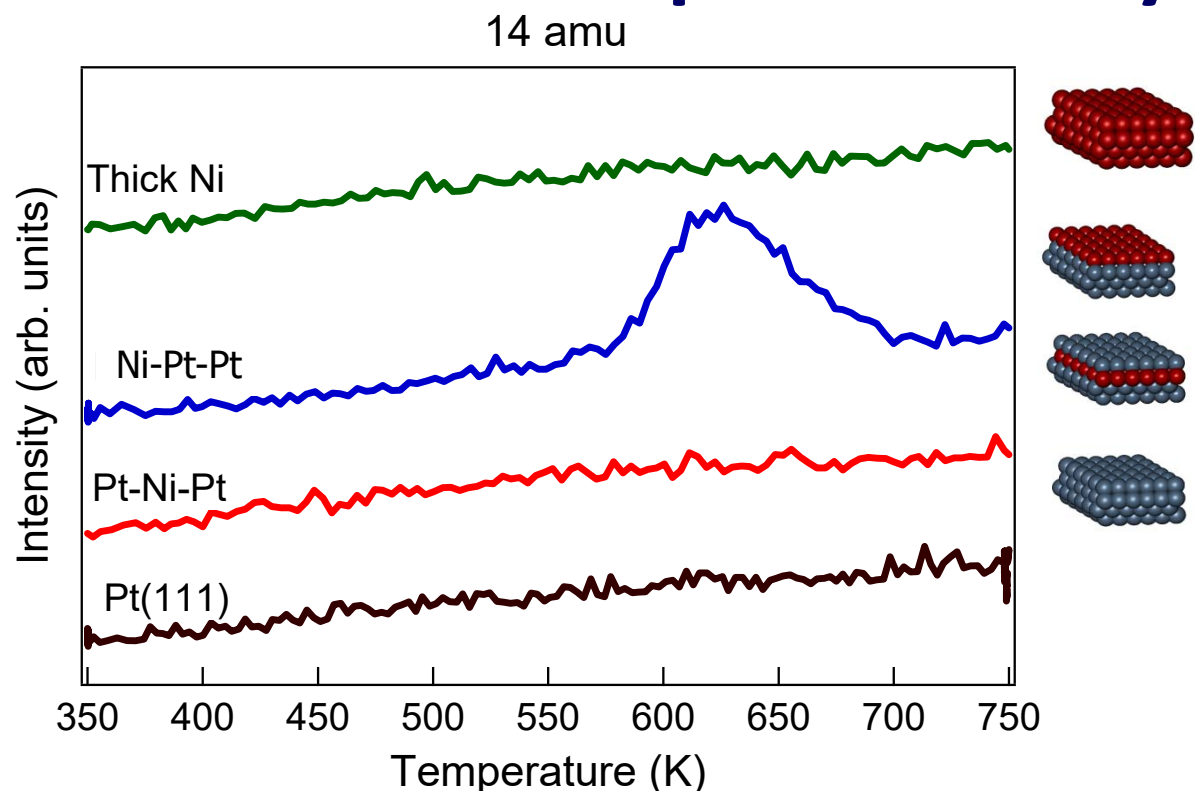


Sub-surface

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



Emergent Behavior Verified Experimentally



3.0 Langmuir NH_3
at 350K at UHV

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

Hansgen, Chen, and Vlachos, *Nature Chem.* 2, 484-489 (2010)



Descriptor-based Microkinetic Analysis Package (DescMAP)

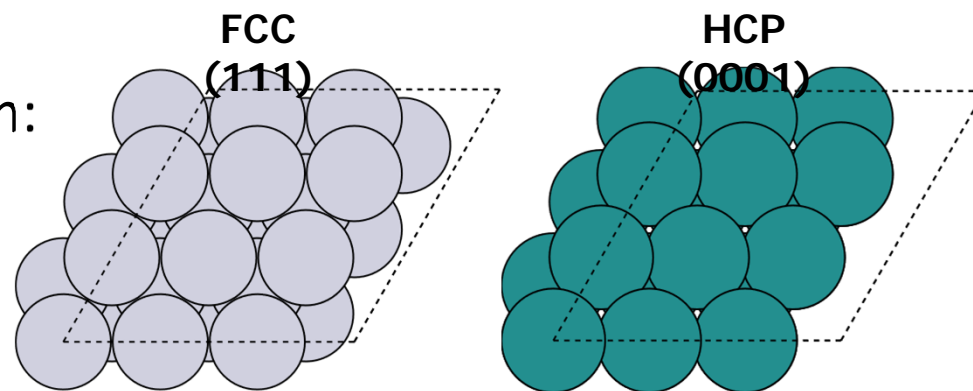
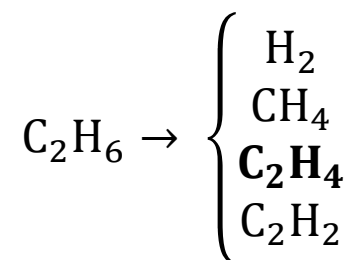


- Complex reactor parameters allowed
- Descriptors can be chosen using PCA and L10 CV linear regression
- Supports a wide array of empirical and semi-empirical relationships
- Leverages existing VLab software packages for increased functionality



Case Study: Non-Oxidative Dehydrogenation over Metal Catalysts

- System uses several empirical relationships (LSRs, BEPs, GA, lateral interactions)
- Has multiple quantities of interest:
 - Conversion of C_2H_6
 - Selectivity of C_2H_4
- Relatively simple mechanism:
 - 24 species
 - 31 elementary steps
- Considering FCC (111) and HCP (0001) metal catalysts





DescMAP Modules

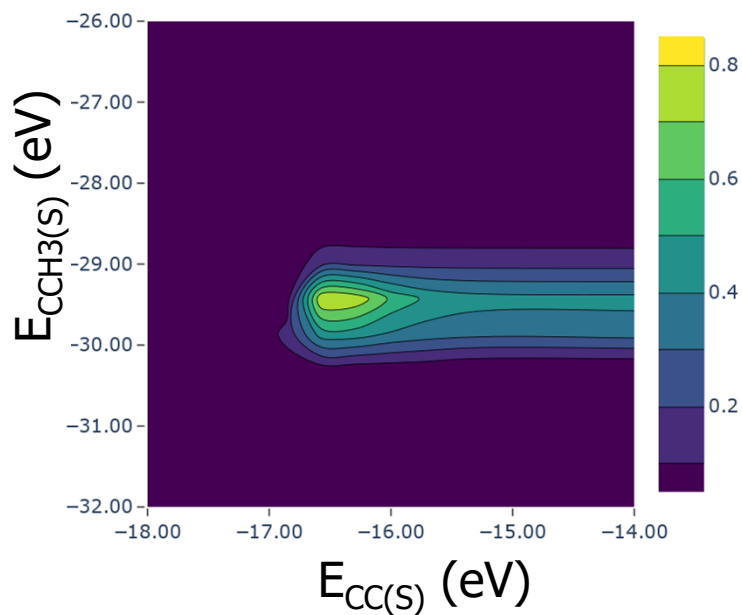




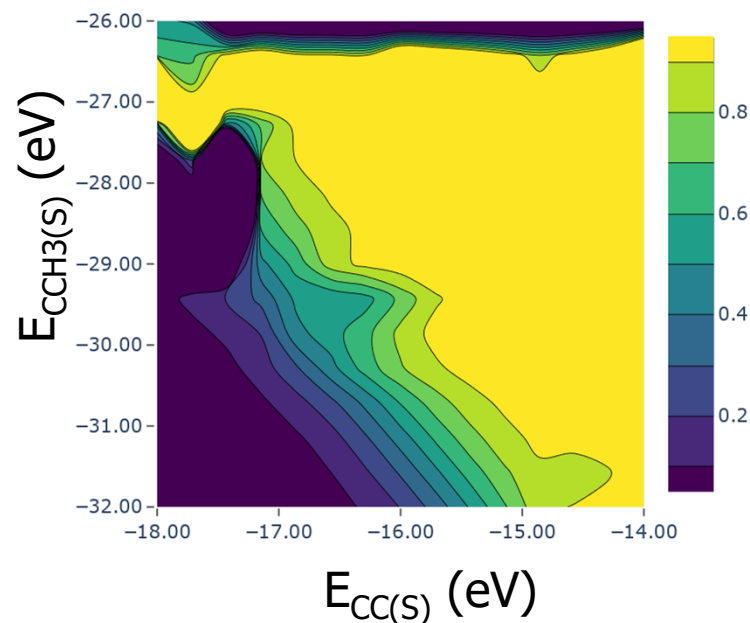
Volcano Heatmaps For Ethane Conversion and Ethylene Selectivity



Fractional C_2H_6 Conversion



Fractional C_2H_4 Selectivity





Literature Data Annotated Onto Volcano Curve

Setup

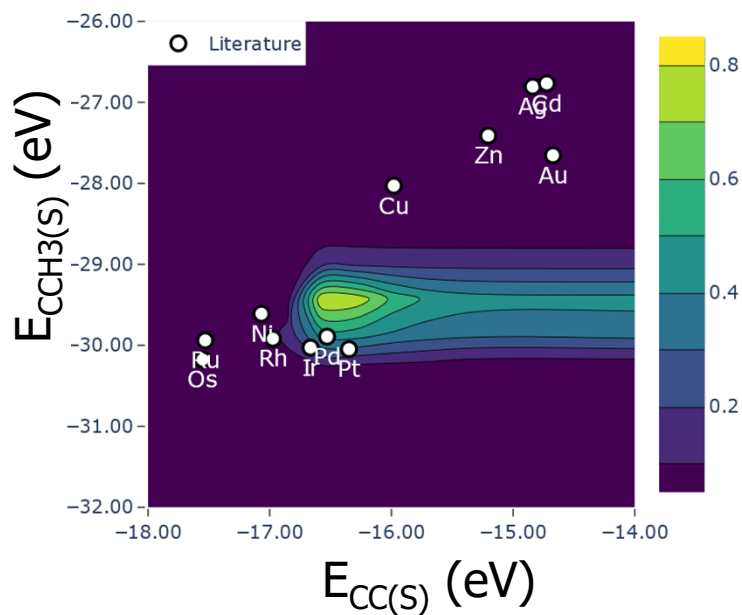
Descriptor
Selection

Descriptor
Sampling

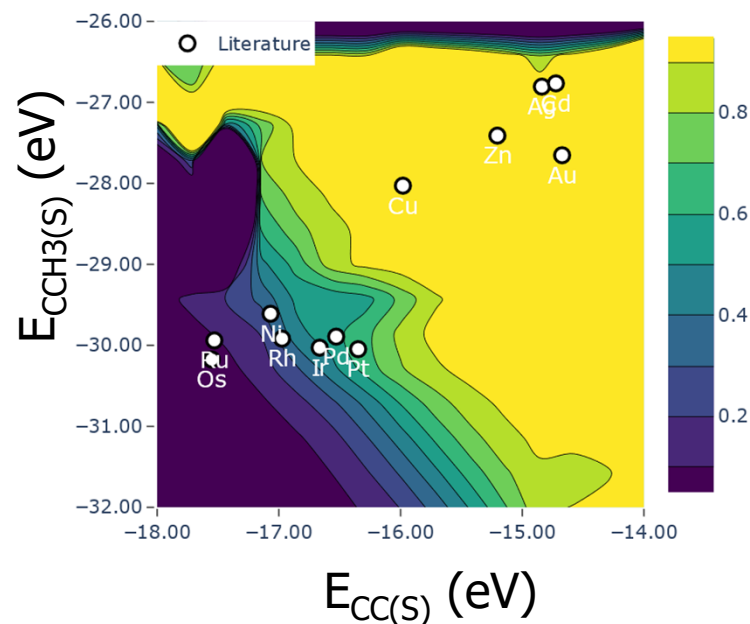
Microkinetic
Modeling

Analysis

Fractional C_2H_6 Conversion



Fractional C_2H_4 Selectivity



Prediction Intervals Suggest Catalyst Design Space

Setup

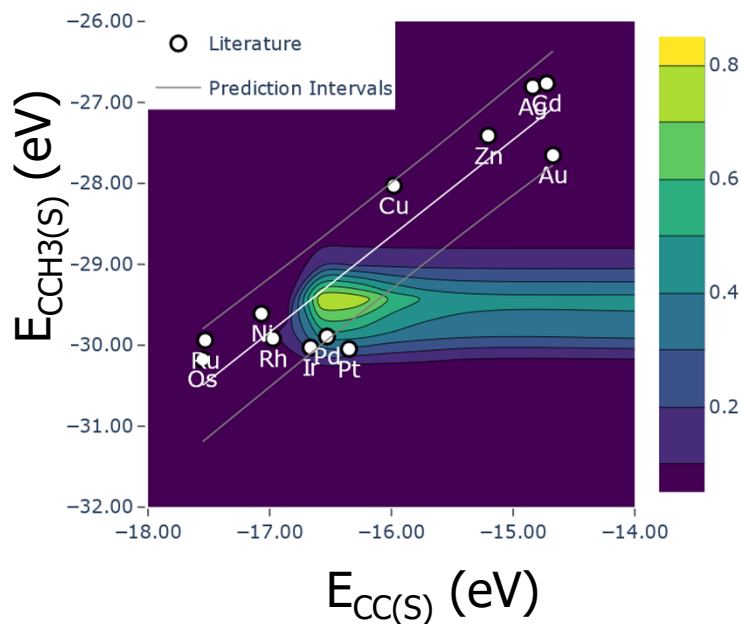
Descriptor
Selection

Descriptor
Sampling

Microkinetic
Modeling

Analysis

Fractional C_2H_6 Conversion



Fractional C_2H_4 Selectivity

