



# Modeling reaction pathways

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November 4, 2014

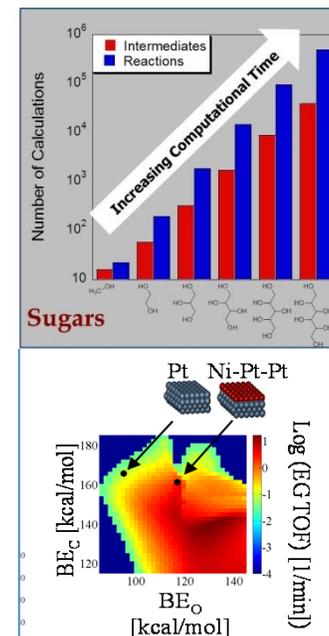
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Catalysis Center for Energy Innovation (CCEI),

an Energy Frontier Research Center



*CCEI is an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Basic Sciences*



# 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
  - Analysis
  - Catalyst discovery



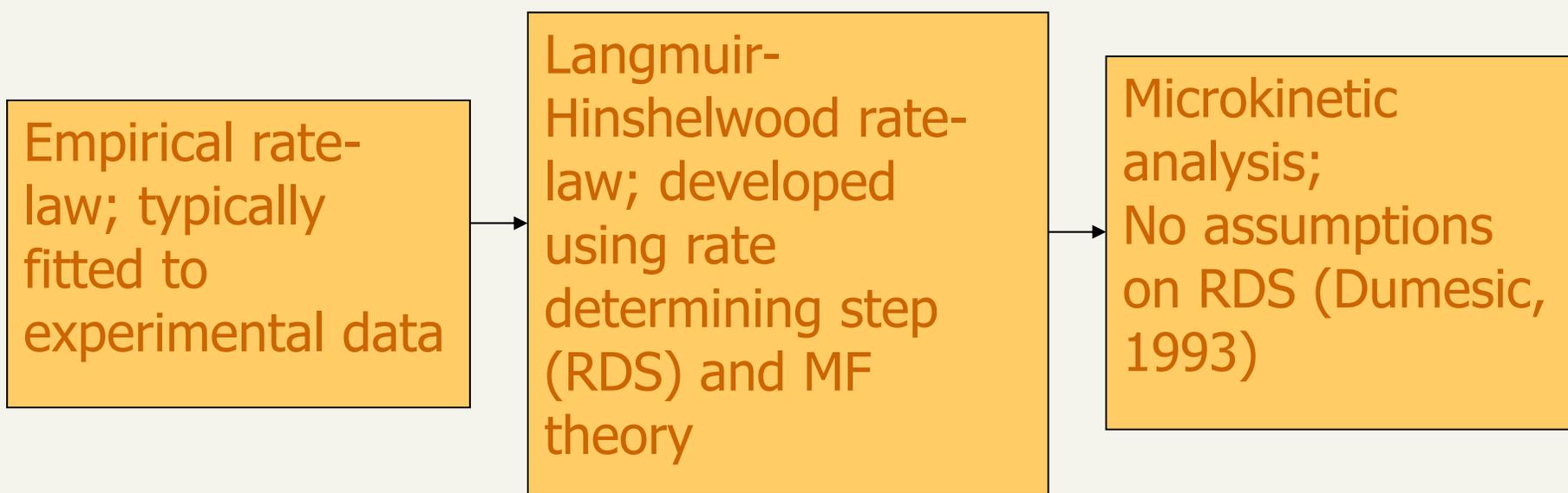
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## Surface Reaction Rate Calculation Paradigm

- Hierarchy of calculation of surface reaction rates



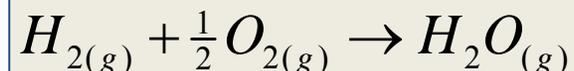
**Complexity/Reliability/Accuracy**



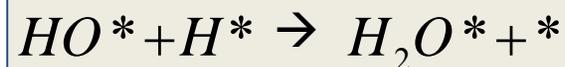
# Microkinetic Modeling

- All relevant elementary reactions
  - Written by hand or computer generated<sup>1</sup>
- No simplifying assumptions
- Rate determining step (RDS), partial equilibrium (PE), quasi-steady state (QSS), and most abundant reaction intermediate (MARI) are all computed
- Reactor + Catalyst model needed
  - Use computer software, such as surface CHEMKIN<sup>3</sup>, Cantera<sup>2</sup>, or Matlab

## An example



### *Elementary Reactions*



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

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

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

Reactor Design (commercial kinetics software)



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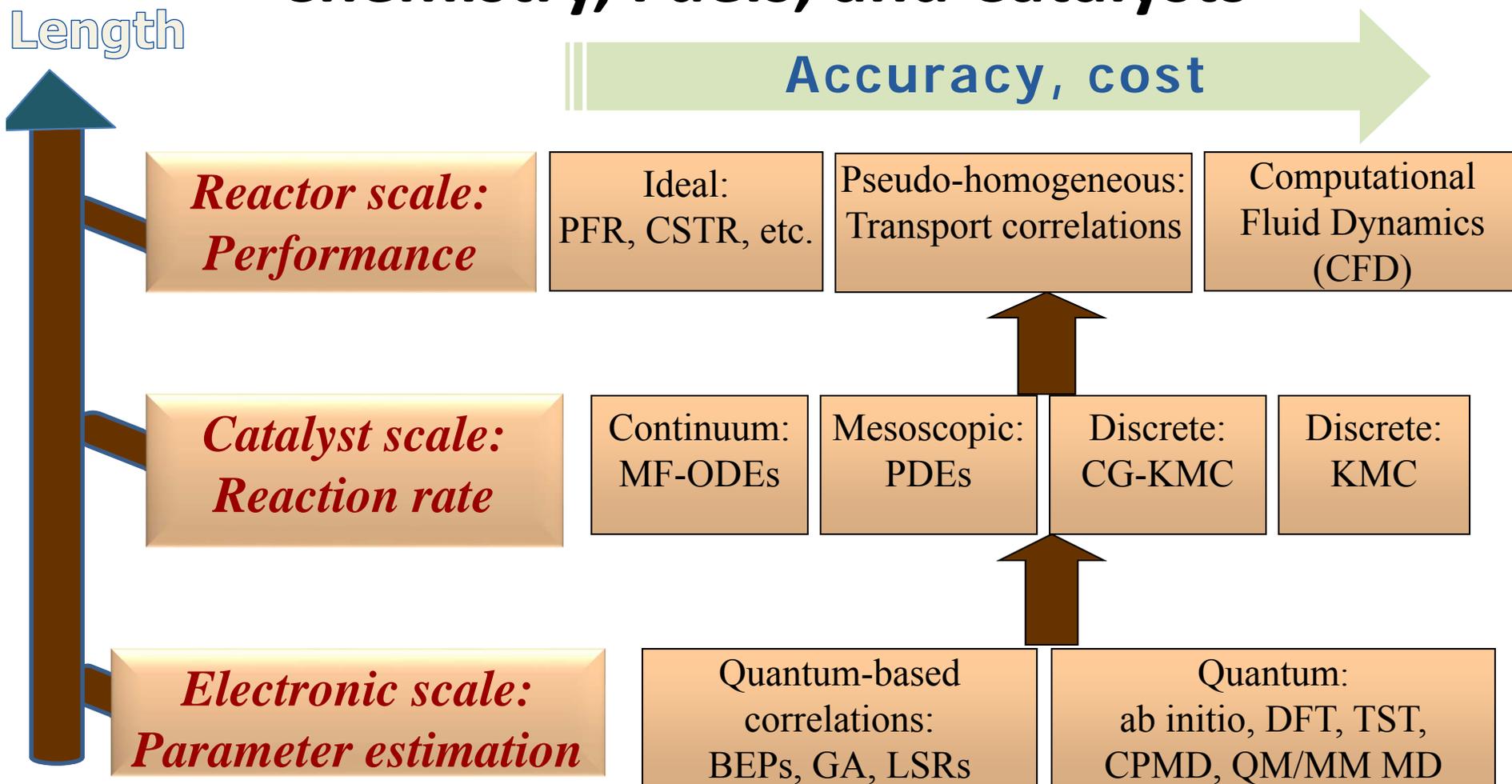
# Parameter Estimation of Microkinetic Models

- **Parameters fitted to data**
  - ✓ Inability to simultaneously predict multiple experimental sets
- **Parameters estimated with empirical methods (Bond-Order Conservation)**
  - ✓ Efficient, reasonable accuracy (2-4 kcal/mol)
  - ✓ Limited to small adsorbates
- **Density functional theory (DFT)-based semi-empirical methods**
  - ✓ Group additivity, Brønsted-Evans-Polanyi (BEP) relations
- **Parameters obtained from DFT**
  - ✓ Fairly accurate (<5 kcal/mol)
- **Hierarchical methods**
  - ✓ Empirical or semi-empirical to screen; DFT to refine (zero coverage limit)
  - ✓ Include coverage effects



# Hierarchy Enables Rapid Screening of Chemistry, Fuels, and Catalysts

Length





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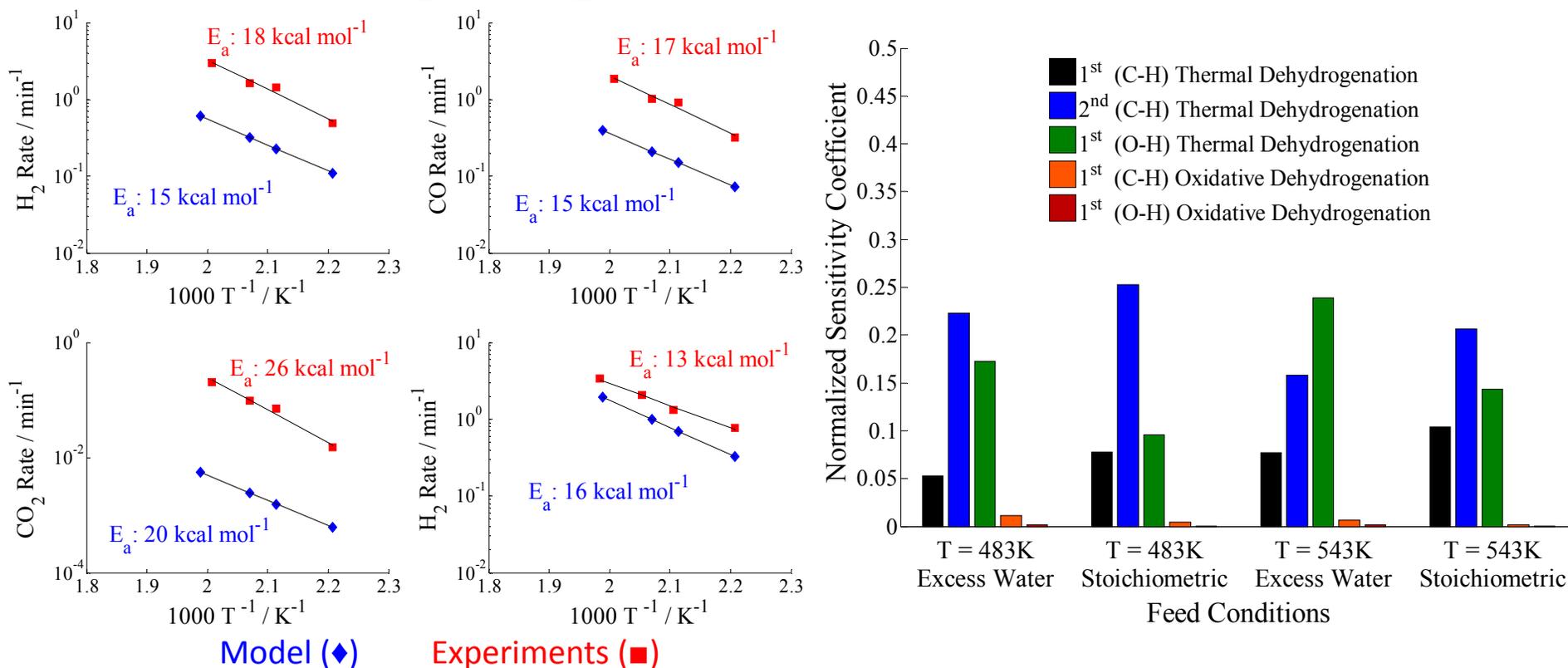


## Accuracy of MKM

- **Myth:** A microkinetic (detailed) model [even with DFT input] can quantitatively describe experimental data



# C<sub>2</sub>H<sub>6</sub>O<sub>2</sub> Steam Reforming



- Good agreement with data\*
- No parameter fitting performed

\* Kandoi et al., *J. Phys. Chem. C* **115** (4) 961 (2011)

- Thermal dehydrogenation steps are kinetically most important
- OH\*-mediated steps inactive on Pt (due to low [OH\*])

Christiansen and Vlachos, *App. Cat. A: General* **431–432**, 18 (2012).



# You Need to Ensure That MKM Captures Correctly

- Temperature effects
- Reaction orders of reactants
- Reaction orders of products  
(Effect of co-feeding products)
- Ideally the RDS is tested spectroscopically
- Ideally the MASI is tested via IR



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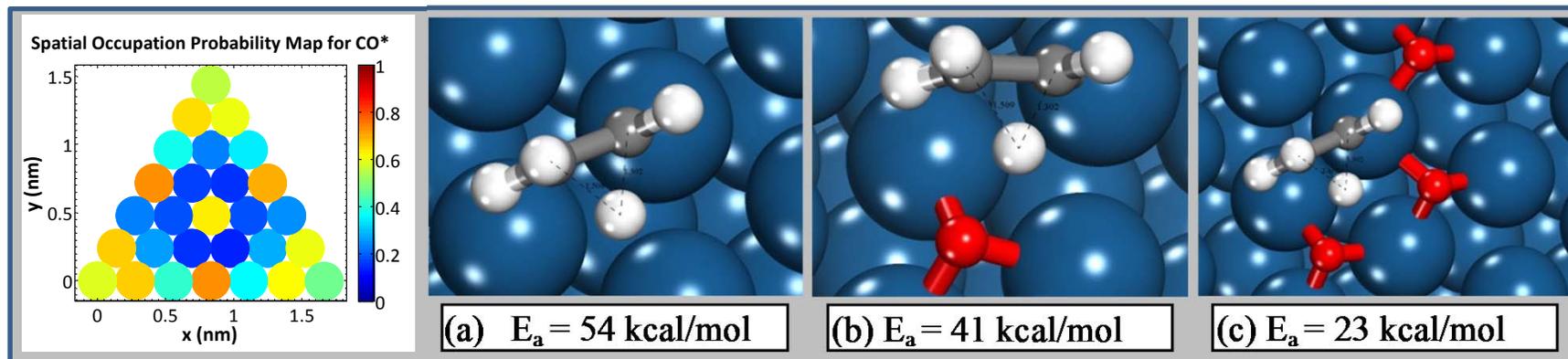


# Lateral Interactions: Estimation via Hierarchical Estimation Methodology

**Myth:** After parameterization of a microkinetic model via DFT (or semi-empirical methods), the model is correct and no further refinement is needed



## Lateral Interactions Are Typically Critical



- Adsorbate heterogeneity arises due to coverage effects
- Combinatorial problem in *a priori* estimating kinetic parameters due to coverage effects



## Hierarchical Multiscale Modeling Principle: Dealing with Size (No. of Reactions and Coverage)

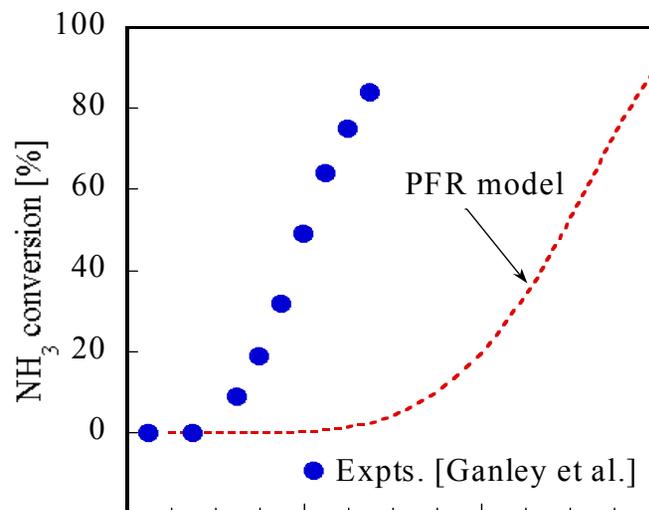
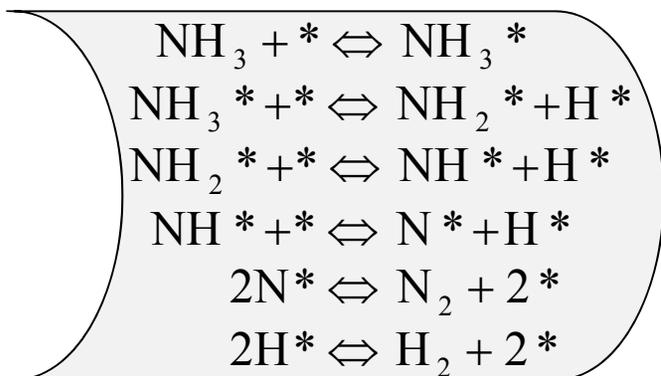
- 
- A large green L-shaped arrow pointing from the left towards the list items.
- Start with a sufficiently simple, physical model at each scale
    - Automatic mechanism generation
    - First-principles based semi-empirical parameter estimation
  - Link all models
  - Identify important scale and parameter(s)
    - Sensitivity and flux analyses
  - Use higher level theory for this scale and parameter(s)
    - Kinetically relevant steps, inclusion of coverage effects, internal diffusion, etc.
  - Iterate

**First-principles accuracy at orders of  
magnitude reduced cost**

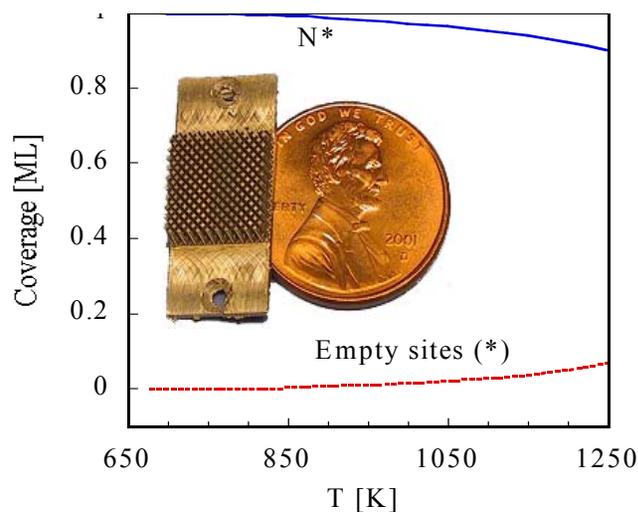


# NH<sub>3</sub> Decomposition on Ru: 2NH<sub>3</sub> = N<sub>2</sub> + 3H<sub>2</sub>

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



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

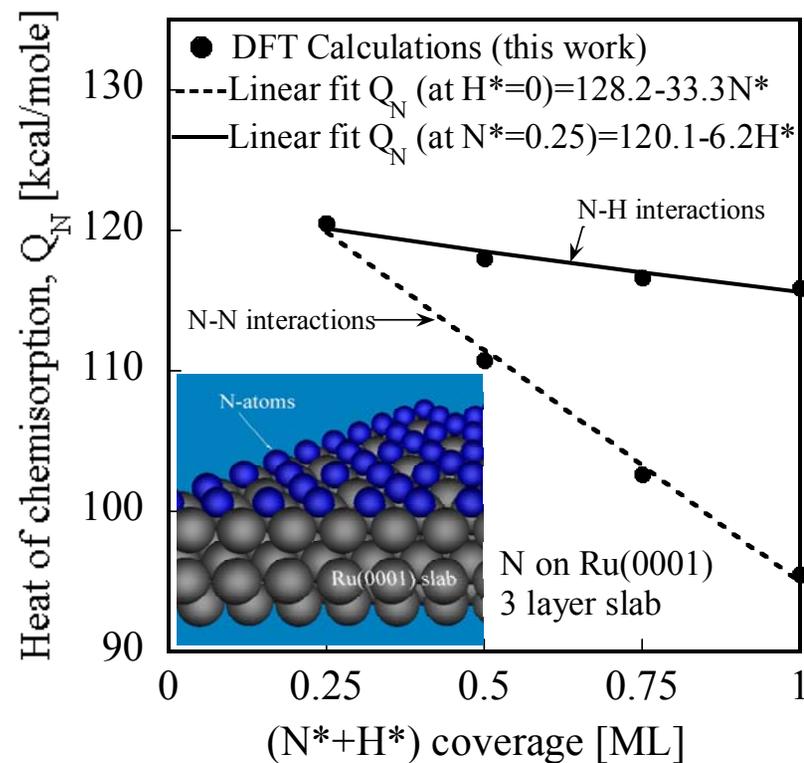




# DFT Estimates Lateral Interactions

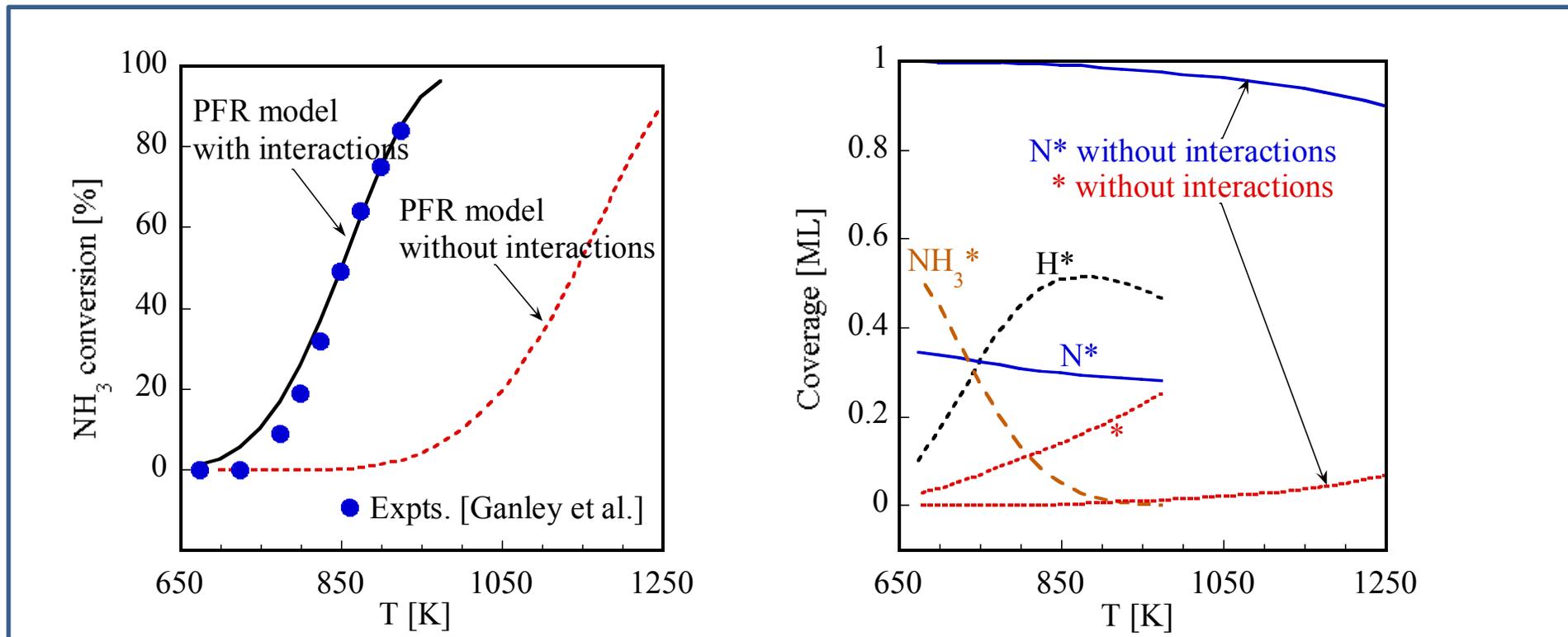
- DACAPO (solid-state electronic structure package by Hammer and coworkers\*)
- 3-Layer slab of Ru(0001)
- $2 \times 2$  unit cell
- All layers are relaxed
- Plane wave cutoff = 350eV
- 18 k-points for surface Brillouin zone
- Generalized gradient approximation (PW-91)

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





# DFT-Retrained Microkinetic Model



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

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



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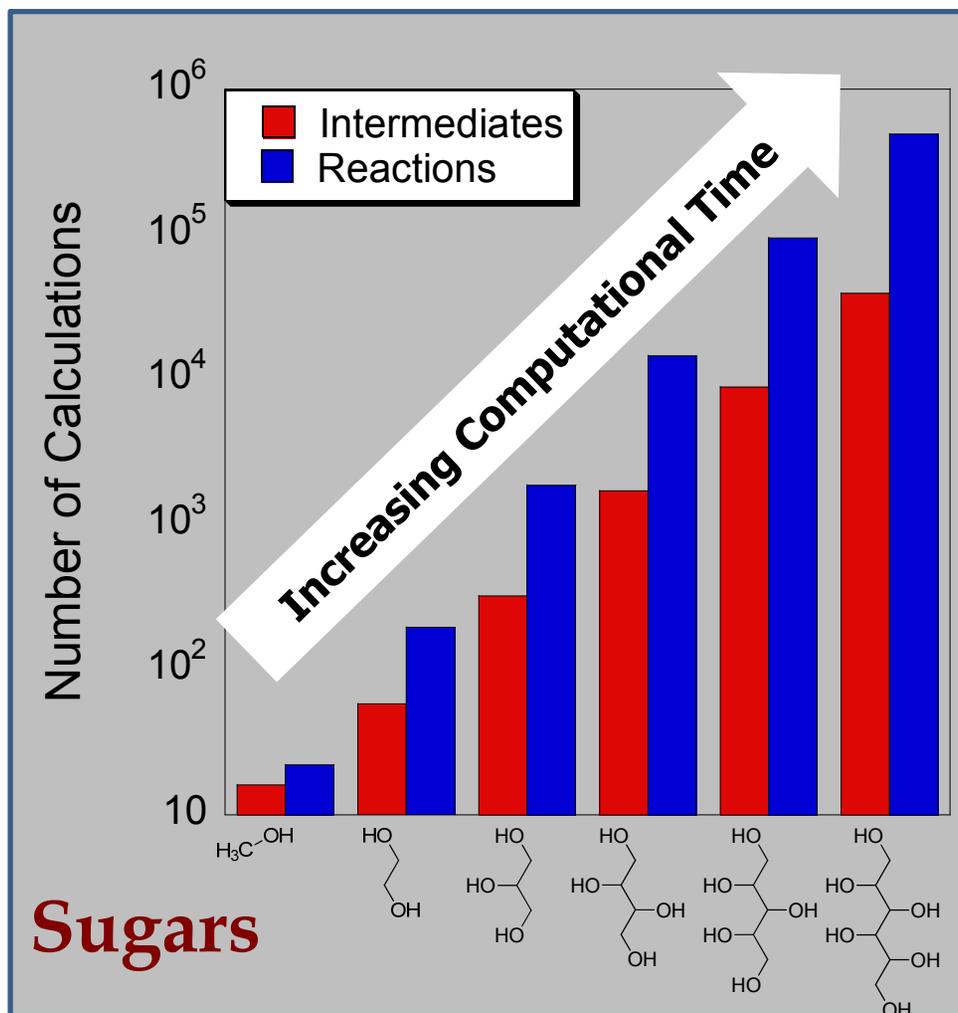


## Semi-Empirical Estimation Methods

- **Myth:** First-principles (DFT) MKM can be developed for any mechanism and feedstock
- Estimation with first-principles semi-empirical methods (FPSEM) is possible
- Refinement of important parameters is feasible



## Modeling Reactions of Large Molecules is Challenging



- Combinatorial explosion in number of calculations for first-principles (DFT) calculations
- **Semi-empirical methods** can potentially identify relevant species and reactions instantaneously
- **Major advances in systematic development of semi-empirical methods and understanding of errors**



# DFT-Based Estimation Methods

## Linear Scaling Relations

- Libraries of atomic binding energies
- Binding energies of  $AH_x$  species vs. heteroatom A valency
- Metal transferability

## Group Additivity

- Single metal thermochemistry
- Thermodynamic consistency
- Screen adsorbates

## Brønsted Evans Polanyi (BEP)

- Activation energies
- Reaction rate constants
- Screen reactions

## Microkinetic Model

- Compute rates, conversion, selectivity, abundant species
- Identify key adsorbates and reactions
- Refine thermochemistry and barriers via DFT
- Include adsorbate-adsorbate interactions

- **Surface thermochemistry** via group additivity
- Brønsted-Evans Polanyi relations for **reaction barriers** of homologous series
- Transfer thermo from one material to another (**linear scaling relations**)
- Perform high-throughput microkinetic modeling (MKM) for **materials prediction**
- Identify key steps and refine them via higher level theory

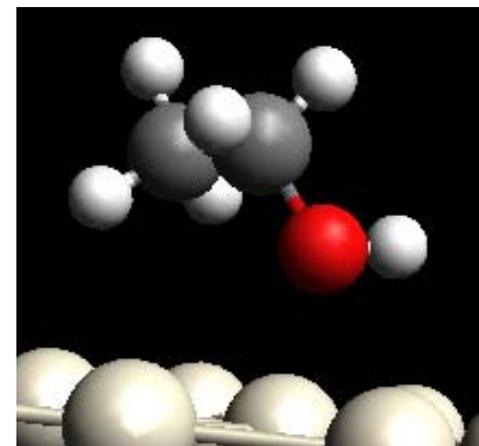
Review: Saliccioli et al., *Chem. Eng. Sci.* **66**, 4319 (2011);

Saliccioli et al., *J. Phys. Chem. C* **114**, 20155 (2010); *J. Phys. Chem. C* **116**, 1873 (2012); Sutton and Vlachos, *ACS Catal.* **2**, 1624 (2012); *J. Catal.* **297**, 202 (2013)

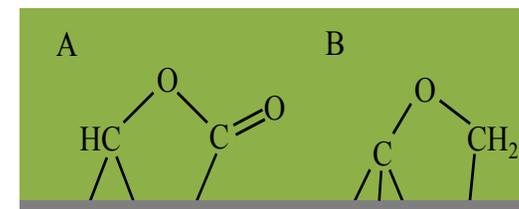
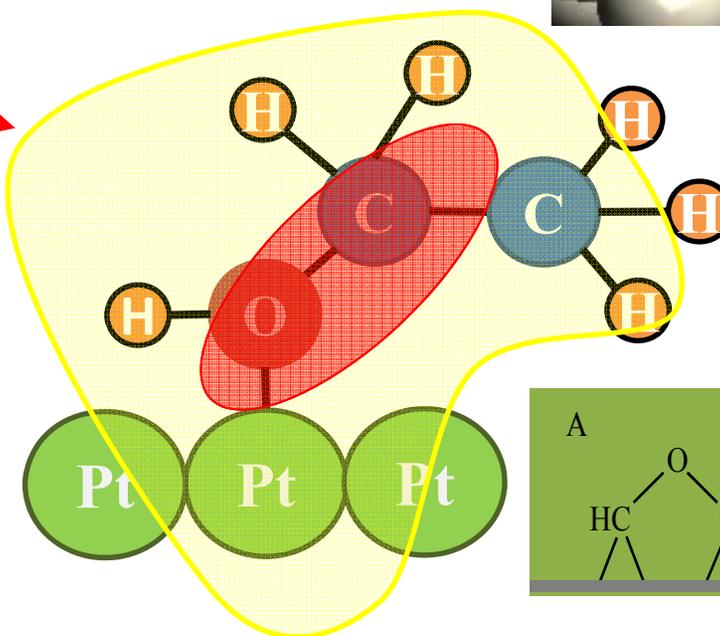


# Group Additivity for Adsorbed Species

- Binding for oxygenates traced to  $(CH_yO_x)$  groups
- Use alcohols and dehydrogenated alcohol intermediates to develop groups
- Include contributions for  $\Delta H_{f,298}$ ,  $S(T)$  and  $C_p(T)$



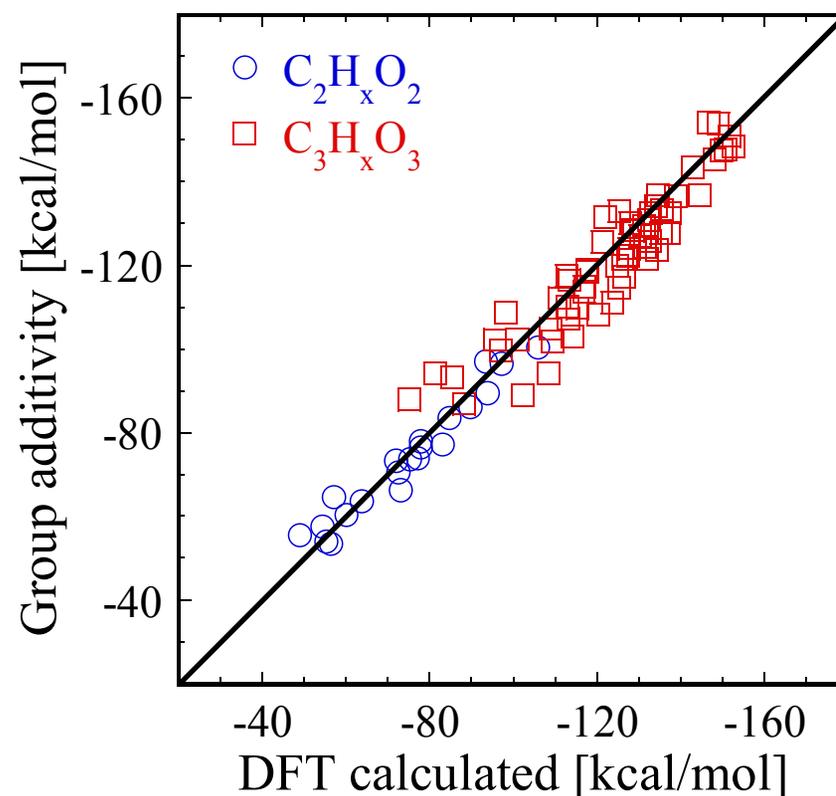
Group	$\Delta H_{f,298}$ Value [kcal/mol]
[C(C,H <sub>2</sub> )-O(M,H)]	-50.2
[C(C,H,M)-O(H)]	-46.8
[C(C,M <sub>2</sub> )-O(H)]	-39.3
[C(C,H <sub>2</sub> )-O(M)]	-26.1
[C(C,H,M)-O(M)]	-26.5
[C(C,M,M)-O(M)]	-33.4
[C(C,M)=O]	-33.4
[C(C <sub>2</sub> ,H)-O(M,H)]	-51.1
[C(C <sub>2</sub> ,M)-O(H)]	-42.9
[C(C <sub>2</sub> ,H)-O(M)]	-25.1
[C(C <sub>2</sub> ,M)-O(M)]	-23.0





# Group Additivity for Adsorbed Species

- Second-order effects included:
  - 4-member ring strain
  - Weak interactions
  - Hydrogen bonding
- Calculations of  $\Delta H_{f,298}$  of  $C_2H_xO_2$  and  $C_3H_xO_3$  species show good quantitative agreement
- **This method can be used for initial screening of larger hydrocarbons and oxygenates**

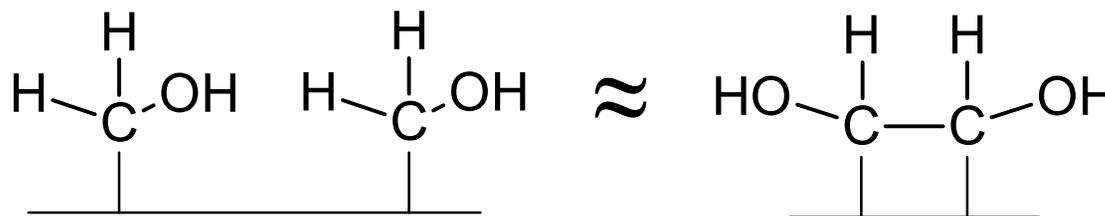
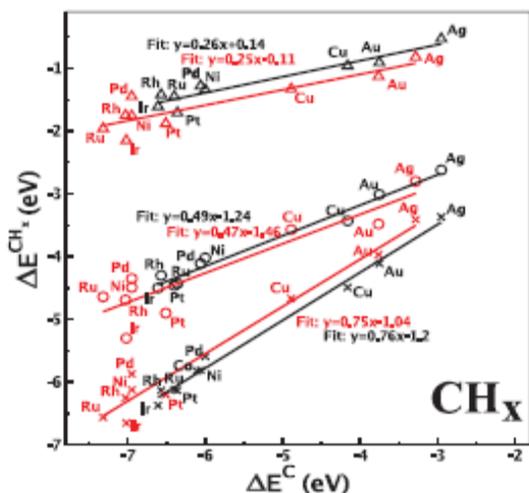


Values are taken with respect to the most highly hydrogenated species in the gas phase ( $C_2H_6O_2$ ,  $C_3H_8O_2$ ) and H adsorbed on a separate slab



# Transferability Between Metals

- Molecular binding energy is linearly dependent on atomic binding energy<sup>1</sup>
- These correlations relate molecular binding energy to atomic binding energy on different surfaces
- Multidentate species can be accounted for by summing the contributions of each bond to the surface<sup>2</sup>



$$Q_M = Q_{Pt} + \sum_{A,i} (Q_{A,i,M} - Q_{A,i,Pt}) \gamma(x) + \Delta E_S + \Delta E_{ROH}$$

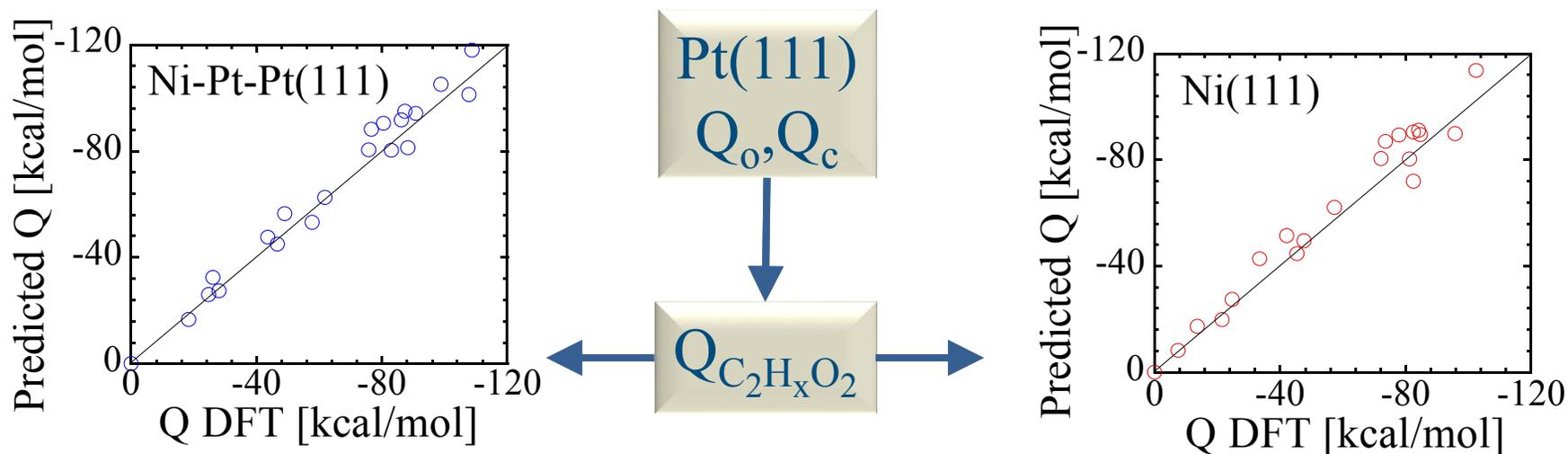
[1] Abild-Pedersen et al. *PRL* **99**, (2007)

[2] Saliciccioli, Y. Chen, and Vlachos, *J. Phys. Chem. C* **114**(47), 20155 (2010)



## Transferability Between Metals

- This scheme was validated by testing the binding energy of all  $C_2H_xO_2$  intermediates on Ni(111) and Ni-Pt-Pt(111)
- These correlations allow for metal transferability of the  $C_2H_6O_2$  decomposition mechanisms



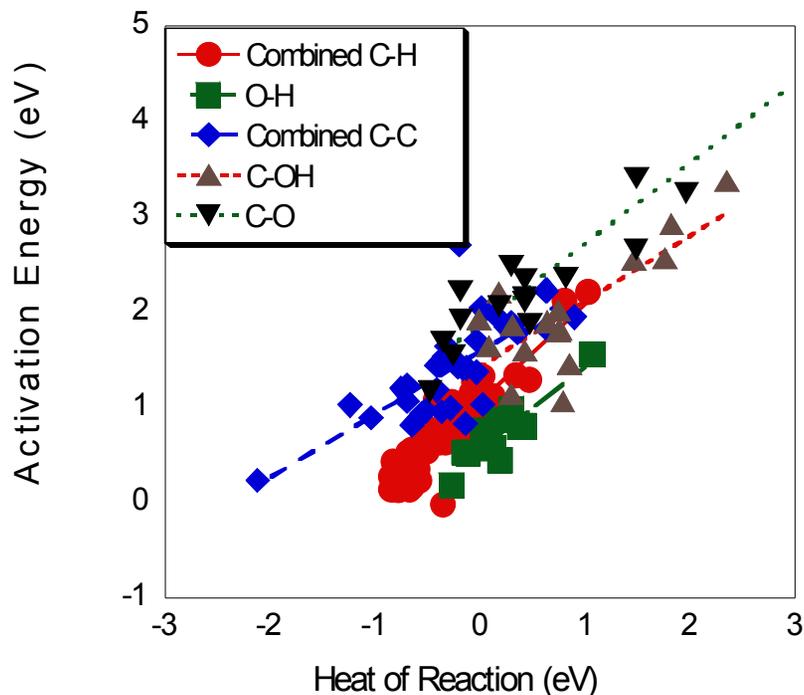


## Linear Free-Energy Relations (LFR)

- Two types of relations are found
  - Transition State Scaling (TSS)
  - Brønsted-Evans-Polanyi (BEP)
- There is reductionistic trend of combining multiple reaction types into a homologous series
  - Minimal calculations
  - Accuracy may be sacrificed
- **Connection between the two LFR types and distinct homologous series**



## Distinct Homologous Series Developed

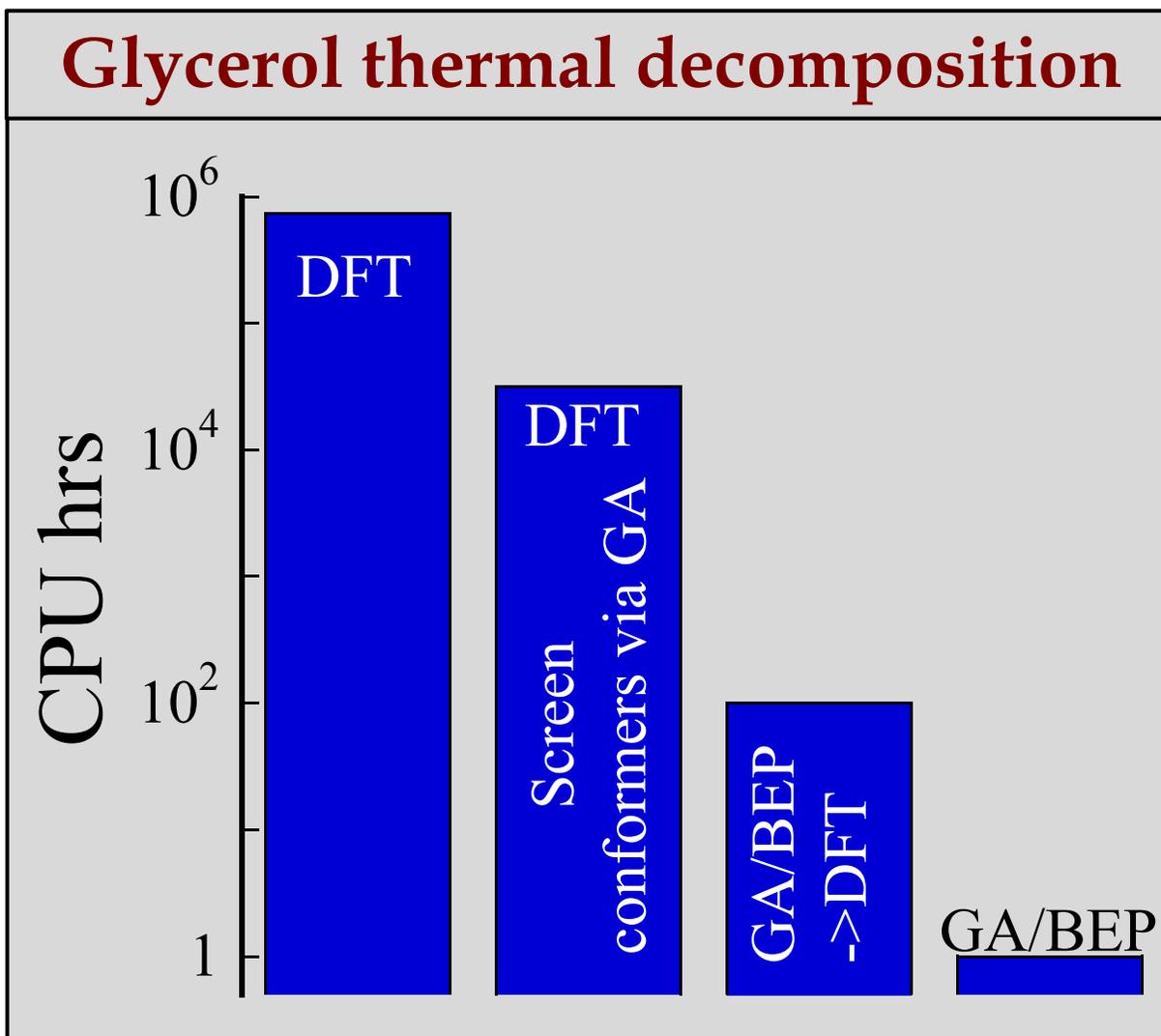


- Performed DFT calculations for methane, methanol, ethane, and ethanol
  - 45 stable intermediates and 124 transition states
- Considered C-H (a and b positions), O-H, C-C, C-O, and C-OH reactions
- Statistical tests are used



# Computational Savings from Hierarchy

- Profound computational savings
- **(Important)** information content remains the same





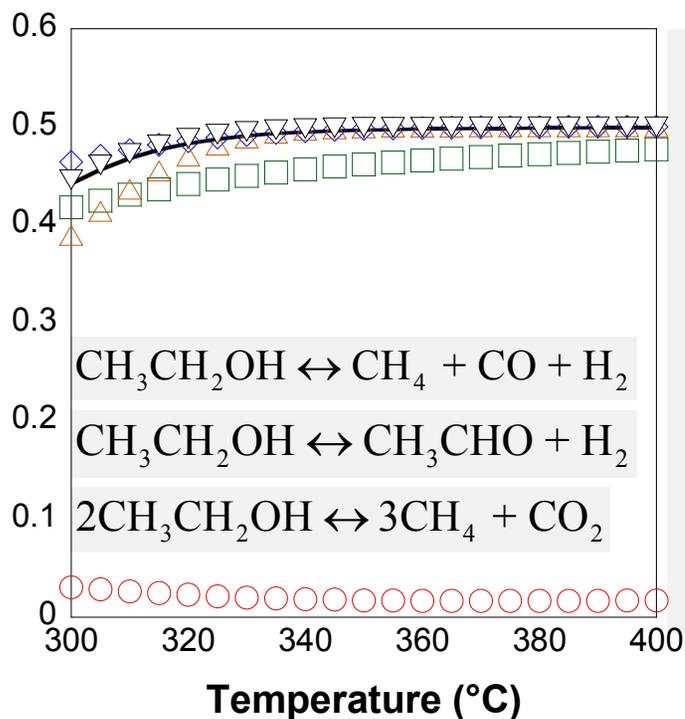
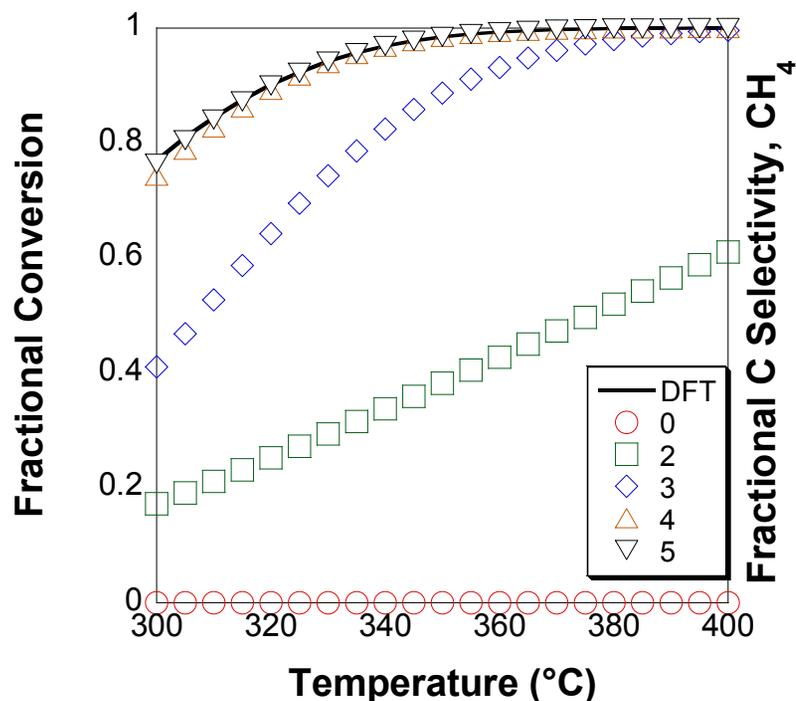
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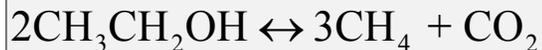
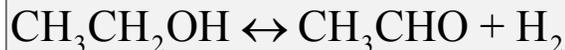
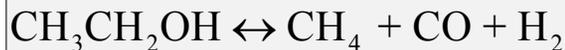


# Speed of Convergence of FPSEM Models



## Ethanol MKM/Pt

- 160 reversible reactions
- 67 gas and surface species



- It takes only a few iterations to converge the semi-empirical model to be nearly indistinguishable with the DFT-based MKM
- Interaction parameters in the first two iterations are most critical for qualitative agreement



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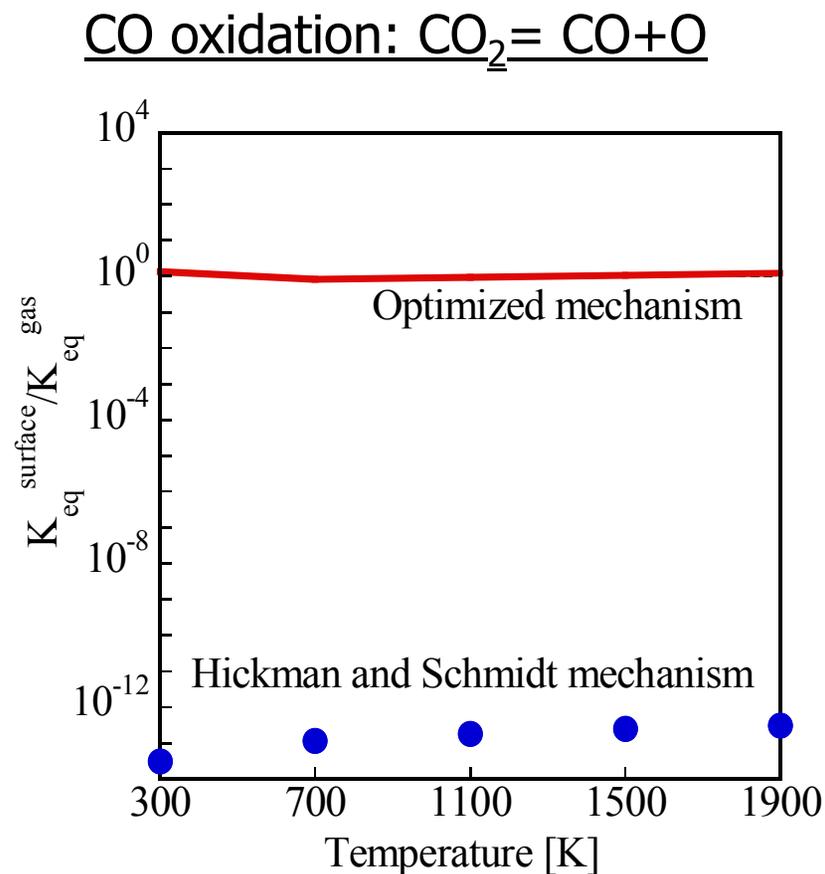
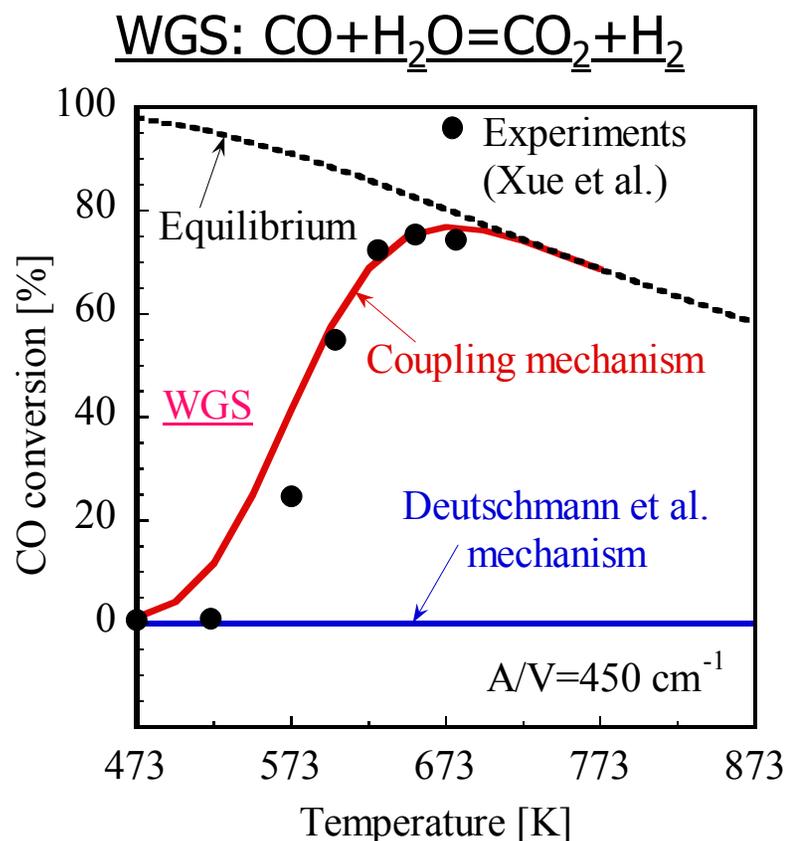


# Thermodynamic Consistency of MKM

- **Myth:** Your model is thermodynamically consistent
- A mechanism based solely on a single DFT mechanism is thermo consistent
- Challenges
  - DFT is not accurate for gas-phase thermo → overall thermo is not accurate; thus, we often mix high level ab initio data or NIST thermo data
  - Kinetic parameters are adjusted to describe data
  - Either adjustment leads to thermo inconsistencies



# Most Literature Mechanisms Are Thermodynamically Inconsistent





# Thermodynamic Loop



➤ TST  $A_{f,b} = \frac{k_B T}{h} e^{\Delta S_{f,b}/R}$

➤ Pre-exponentials of a reversible reaction

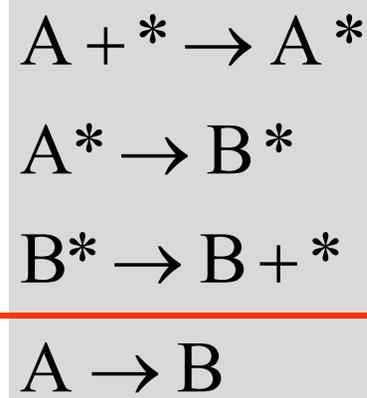
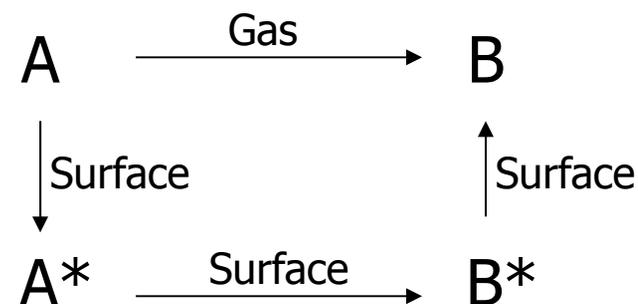
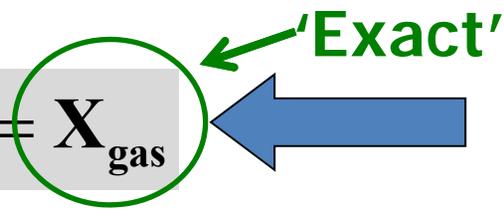
$$\frac{\Delta S}{R} = (\Delta S_b - \Delta S_f) / R = \ln A_b / A_f$$

➤ Enthalpic consistency for single reaction

$$E_f = E_b + \Delta H$$

➤ Carry out a thermodynamic loop on a state variable X:

$$X_{ads}^A + X_{surf} - X_{ads}^B = X_{gas}$$





# Linear Independence and Parameter Tuning

- For every surface reaction, one can write a corresponding gas reaction and a thermo loop
- The number of surface species usually determines the number of independent variables
- **Cannot simply change barriers or pre-exponentials to fit data without paying attention to thermo consistency**

- Mhadeshwar et al., Thermodynamic consistency in microkinetic development of surface reaction mechanisms, *Journal of Physical Chemistry B* **107**, 12721-12733 (2003).
- Saliccioli et al., A review of multiscale modeling of metal-catalyzed reactions: Mechanism development for complexity and emergent behavior, *Chem. Eng. Sci.* **66**, 4319–4355 (2011).



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## What Can We Use MKMs for?

Traditional

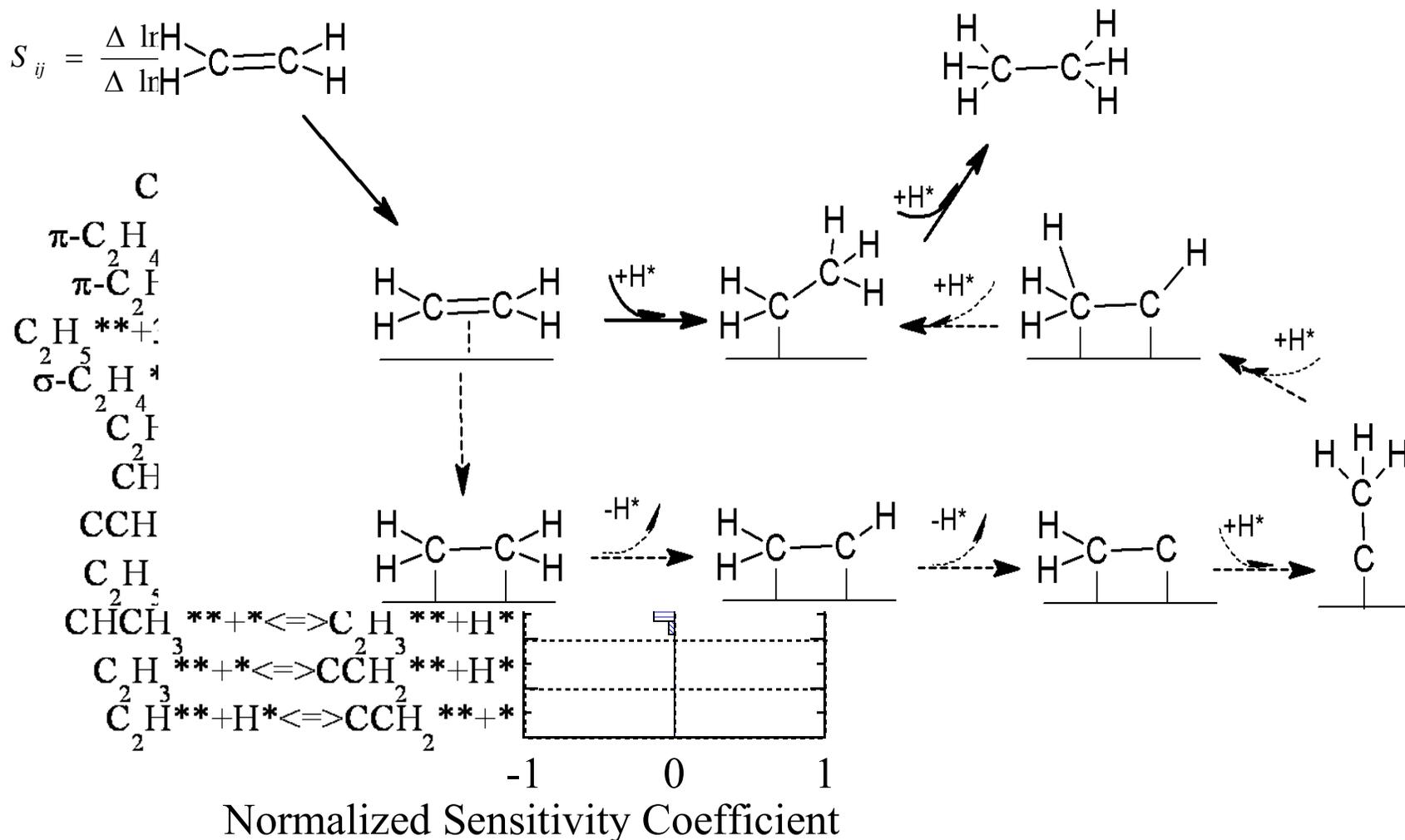
- Reconcile apparently contradictory experimental data at different conditions (TPD, steady state, various operating conditions)
- Mechanistic understanding
- Perform reactor optimization

Modern

- Model-based design of experiments to assess model
- Rational catalyst design
  - Composition
  - Size
  - Shape



# Ethylene Hydrogenation: Analysis



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

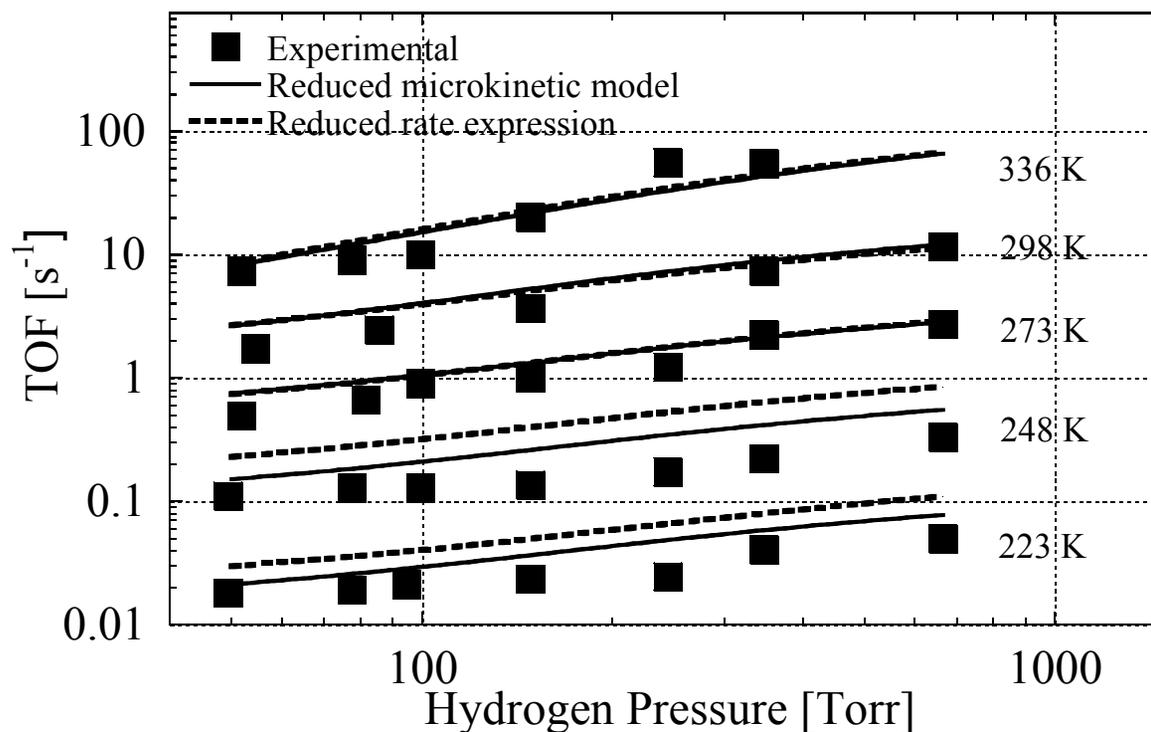




## Ethylene Hydrogenation Rate Expression

$$\text{Rate } C_2H_6 = \frac{k_6}{K_6} \theta_{C_2H_5} \theta_H - k_6 C_{C_2H_6} \theta_*^3$$

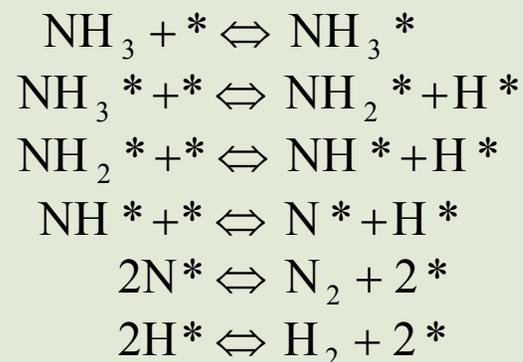
Due to multiple abundant adsorbates, the reduced rate expression is too complex for a closed form equation



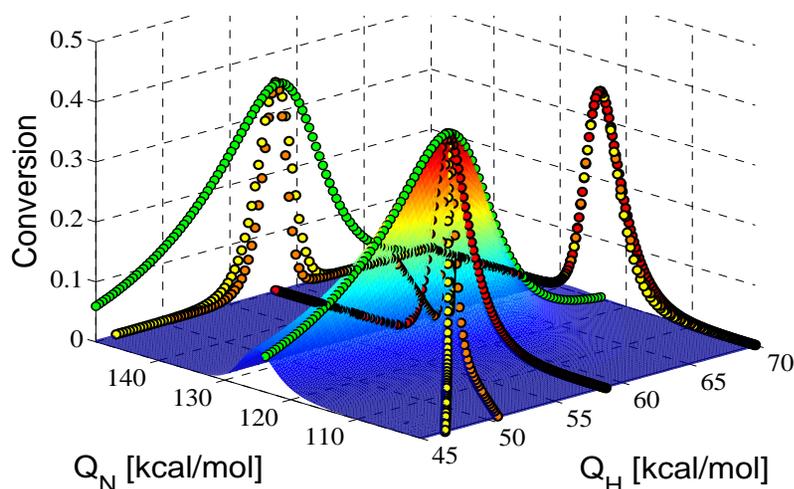


# High Throughput Multiscale Model-based Catalyst Design

## NH<sub>3</sub> decomposition



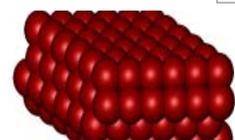
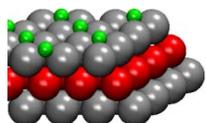
350 °C  
1 atm



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

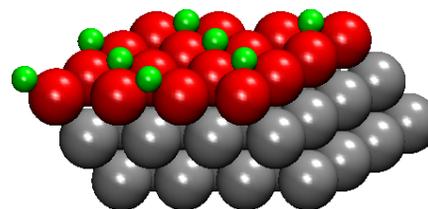


# Identifying Bimetallic Catalysts

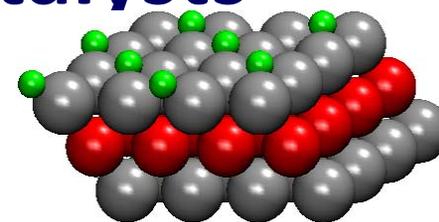


Metals	$BE_N$ (kcal/mol)
PtTiPt	56.5
PtVPt	59.5
PtCrPt	72.6
PtMnPt	84.9
PtFePt	83.9
PtCoPt	87.0
PtNiPt	89.8
<b>NiPtPt</b>	<b>137.5</b>
CoPtPt	159.9
FePtPt	169.9
MnPtPt	162.2
CrPtPt	166.5
VPtPt	184.1
TiPtPt	191.5

Pt 102.1  
Ni 113.8

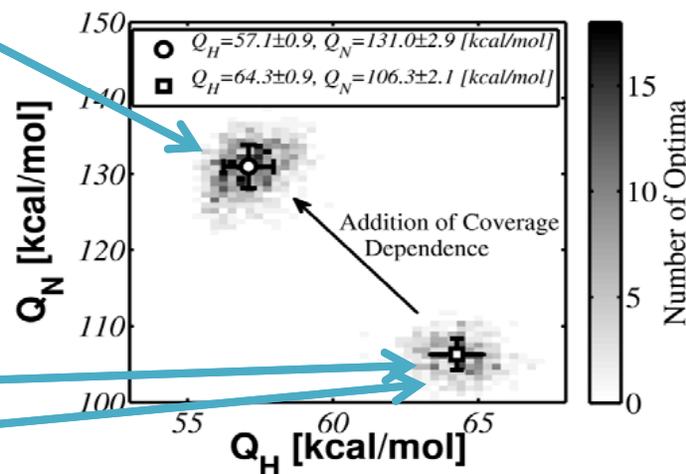


Surface



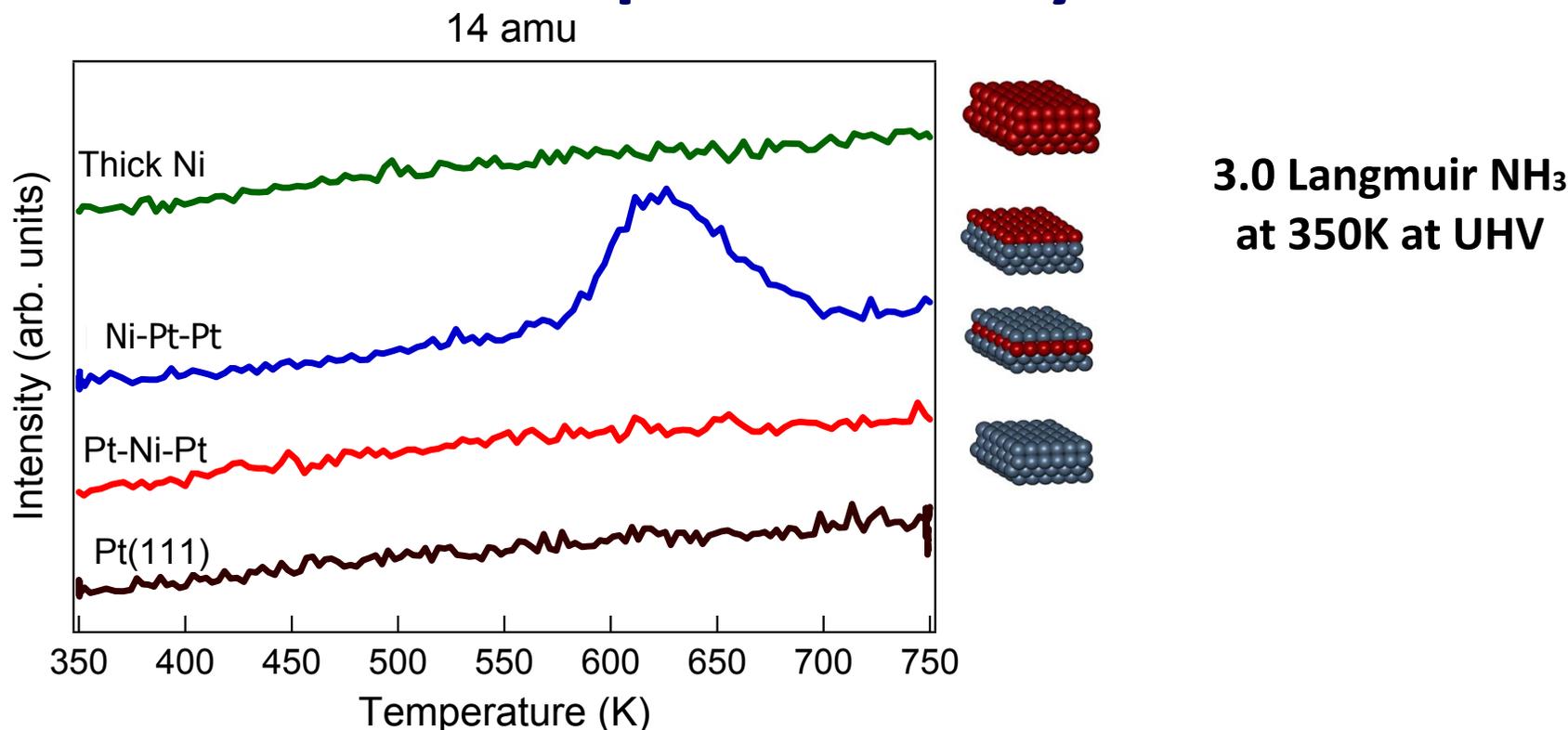
Sub-surface

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





# Emergent Behavior Verified Experimentally



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

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



**End**