



## Microkinetic Model Analysis

0

Energy profile analysis and energy span

1

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

2

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

3

Reaction path analysis

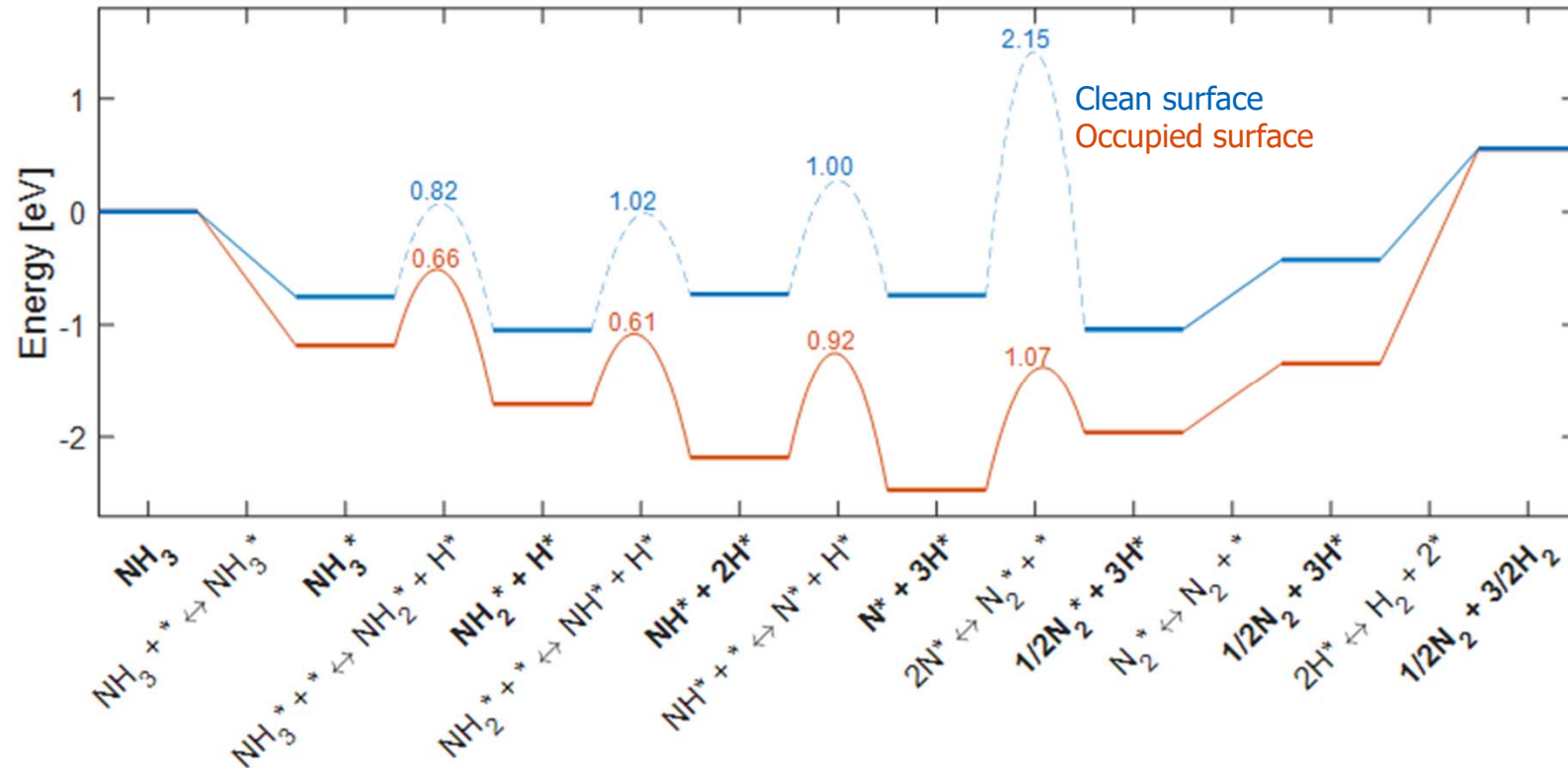
4

Sensitivity analysis



# 0. Potential Energy Analysis

<sup>1</sup>  
pMuTT



- Lowest energy path
- Activation energy
- Surface coverage impact
- Energy span

[1] Lym, J., Wittreich, G. R. and Vlachos, D. G. (2019), *Computer Physics Communications*. Elsevier B.V., 245, p. 106864.

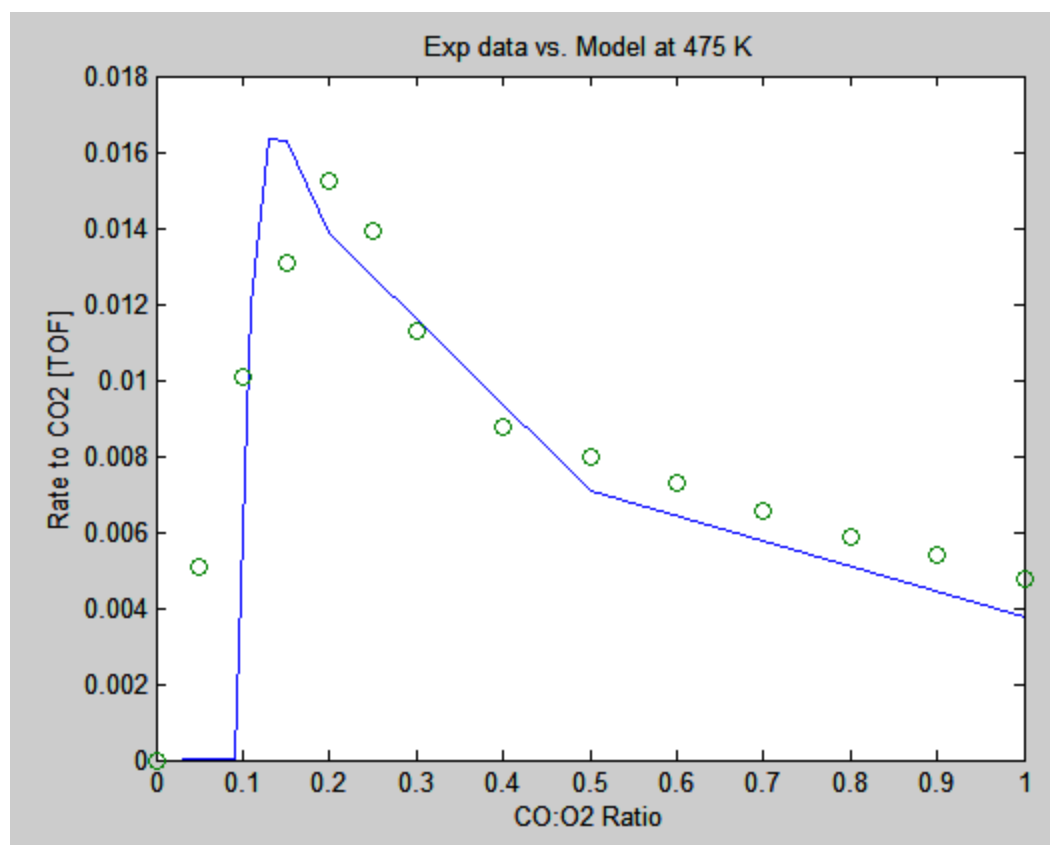
# 1. Basics: Visualization

- **Graph every component of the solution vector as a fcn of position and/or a parameter (parametric continuation)**
  - Examples of soln components: concentrations, temperature, velocity, etc.
  - Soln vs. position (e.g., x coordinate) is called a profile. Contour graphs are useful too.
  - Think about the physics by visualizing the solution. Make as many observations as possible.
  - Graphical inspection reveals lots: e.g., hot spots in a reactor, recirculation in fluid flow, the most abundant reactive intermediate (MARI), i.e., the species in excess, etc.
  - A change in the slope of the solution  $x$  vs. the parameter  $p$  usually indicates a change in the rate determining step (RDS)

# Example of CO Oxidation

## Comparison of expt. and siml.

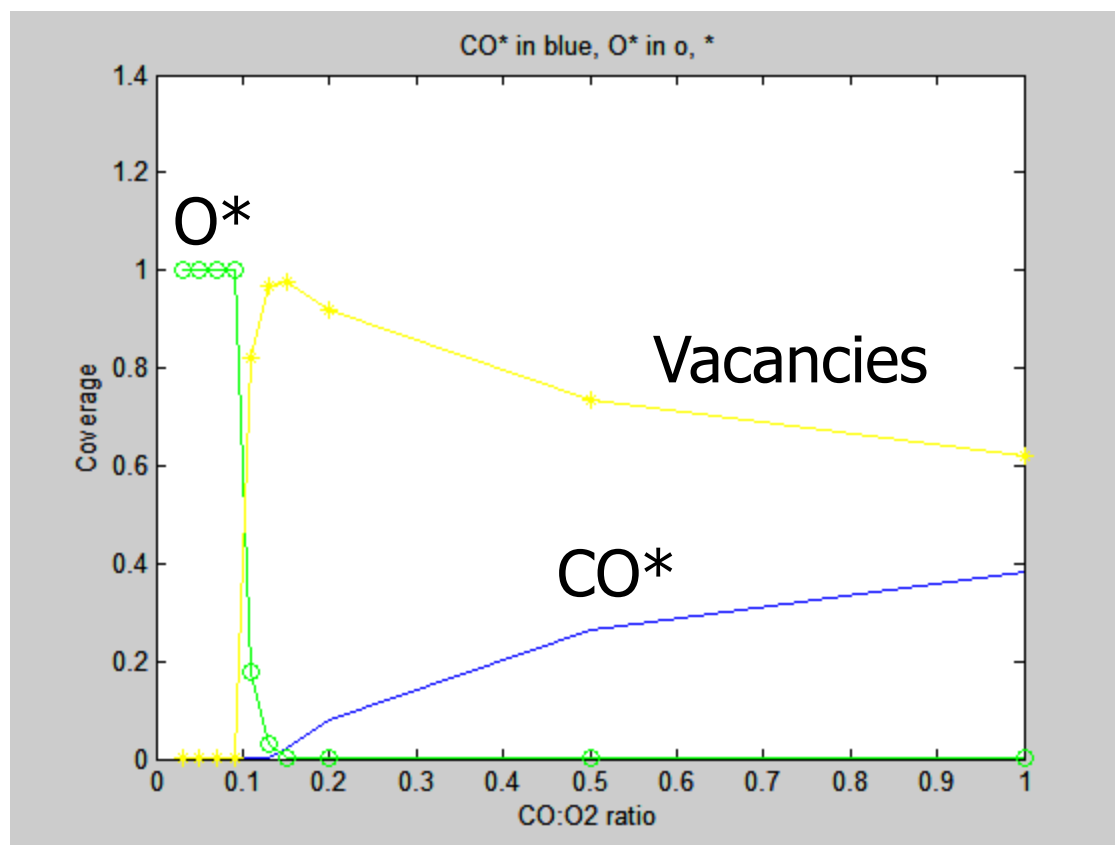
- Observations?
- What controls the value of CO:O<sub>2</sub> ratio where the max rate occurs?
- What controls the initial slope?
- Why does the rate first increase and then decrease with increasing CO:O<sub>2</sub> ratio?





## ➤ Observations?

# Example of CO Oxidation Coverages and MASI





## 2. Partial Equilibrium (PE) of a Rxn Quasi-steady State (QSS) of a Species

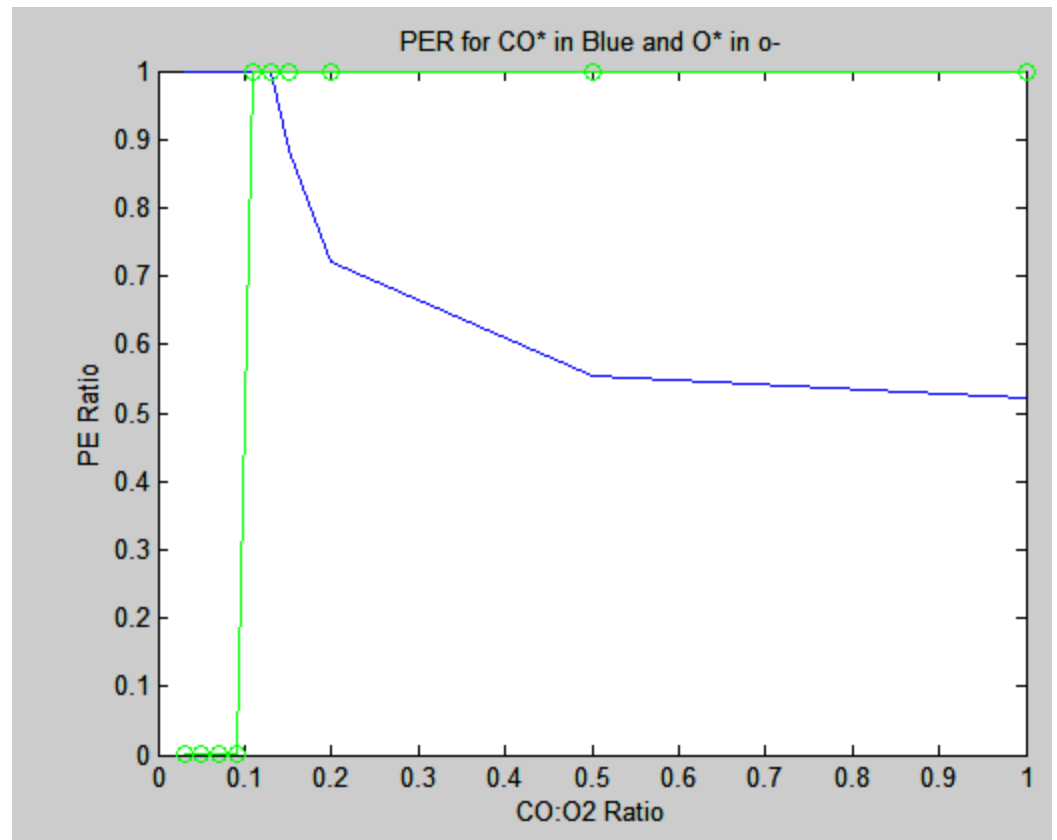
- The proposed method is based on *a posteriori analysis*
  - Performed using the solution
  - Simplify and able to visualize the reaction network
  
- **Flux analysis, reaction path analysis (RPA), or rate analysis**
  - PE is satisfied if  $r_f \sim r_b$ , or  $PEI_i = |r_{fi}| / (|r_{fi}| + |r_{bi}|) \sim 1/2$
  - PE is practically satisfied when PEI is in the range 0.45-0.55
  - Test each reversible pair
  - Slow paths are left out
  
- **QSS** is satisfied if  $dC/dt$  is small compared to other terms in the DE, e.g.,  $(dC/dt)/\text{max rate of the specific balance} \ll 1$ 
  - Test each species balance



# CO oxidation on Pt

## Partial Equil. Ratio

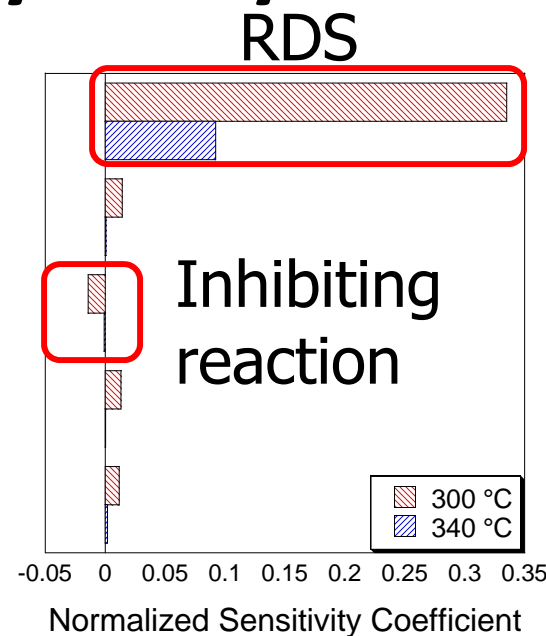
- Steady-state eqs. solved
- PE approached only at high CO:O<sub>2</sub> ratios
- Recall that PE is often assumed in ads-des steps in deriving LH expressions but this may be incorrect
  - Weakly adsorbed species, such as H<sub>2</sub>, are often in PE in the reaction network





### 3. Overview of Sensitivity Analysis

- Sensitivity analysis measures the effect of perturbing a parameter (e.g. a pre-exponential) on a response (e.g., the conversion)
- Sensitivity analysis is useful for
  - Determining a rate-controlling step
  - Subsequent parameter refinement



Determining the sensitive reactions in ethanol SR

$$NSC_i = \frac{d \ln X}{d \ln k_i}$$





## Rate-determining Step (RDS)

- Carry out **LOCAL** sensitivity analysis (SA)
  - Local or brute force can be used depending on model complexity and convenience
- More than one step can be RDS
- The RDS can change with conditions
- Obey thermodynamics for reversible processes, i.e, perturb forward and backward steps simultaneously
- **SA can provide information beyond the RDS**, i.e., which **parameters** affect which **responses**
  - RDS denotes only the reaction step that controls the reaction rate



# Brute Force SA

- Perturb each parameter and solve the system again and again
- Use finite difference approximation to compute SC
- Perturbations should be large but not too large (2%, 20%, factor of 2, 20) so changes beyond numerical accuracy but not so dramatic occur

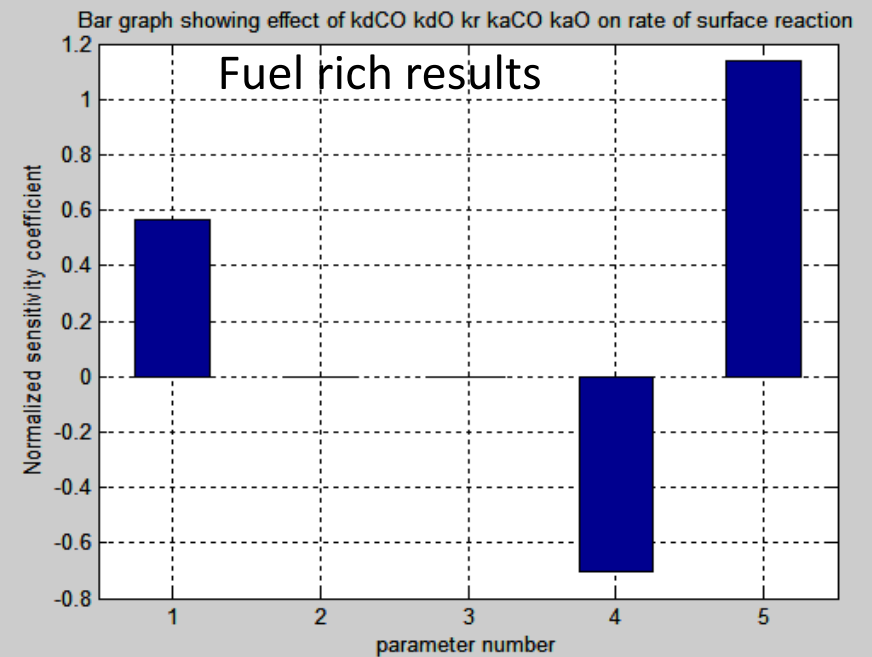
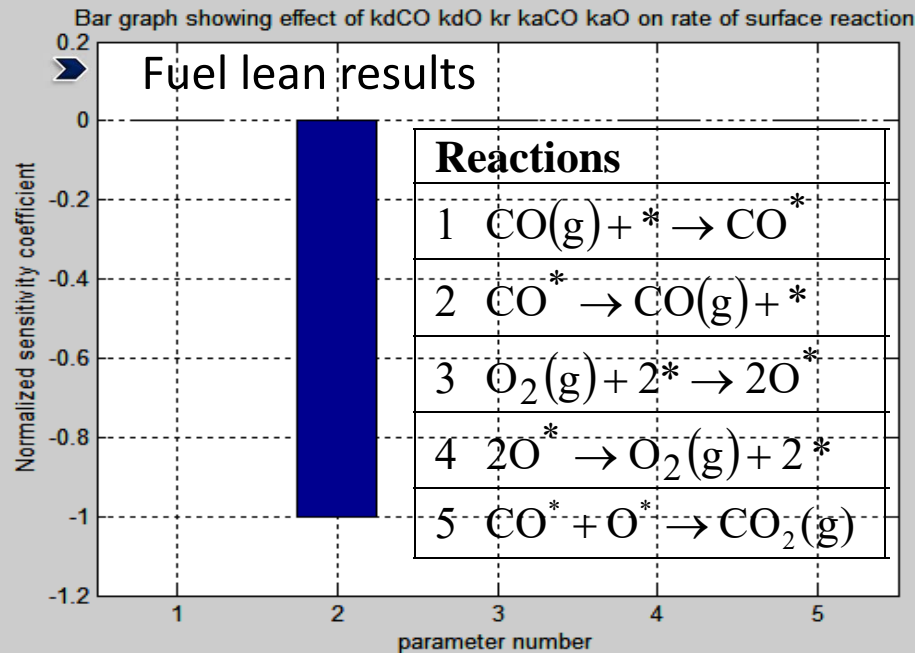
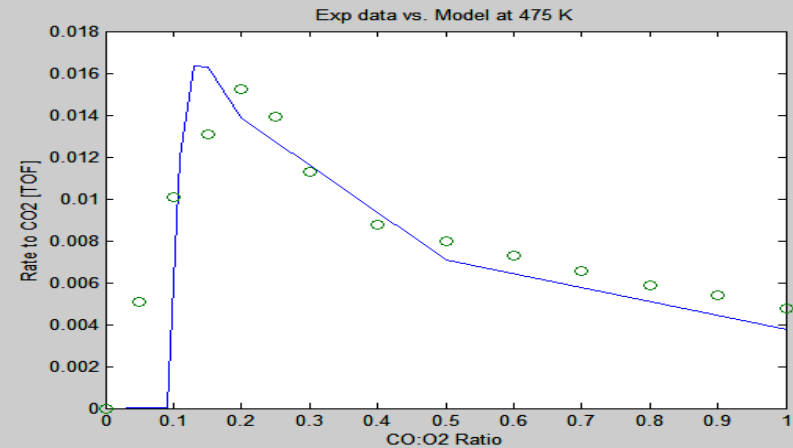
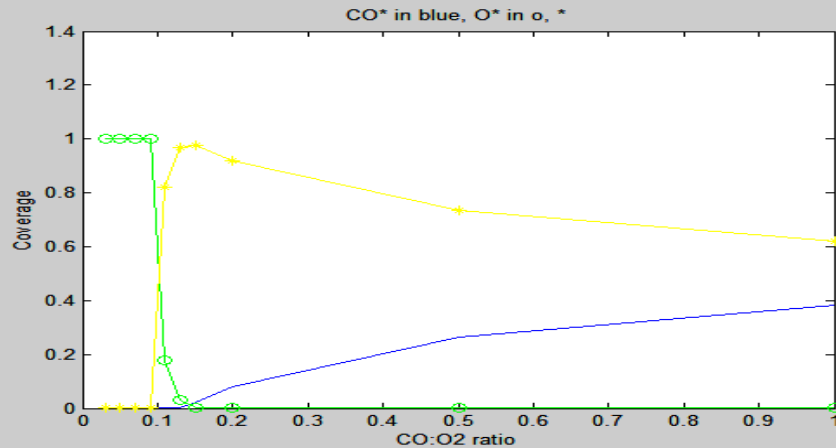
$$\text{First - order: } SC_{ij} = \frac{x_i(p_j + \Delta p_j) - x_i(p_j)}{\Delta p_j}$$

$$\text{Second - order: } SC_{ij} = \frac{x_i(p_j + \Delta p_j) - x_i(p_j - \Delta p_j)}{2\Delta p_j}$$

- Both methods (local and brute force SA) apply to linear and nonlinear problems; identical for linear problems!



# Example of CO Oxidation: SA

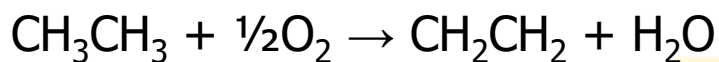


➤ Multiple reactions can be important

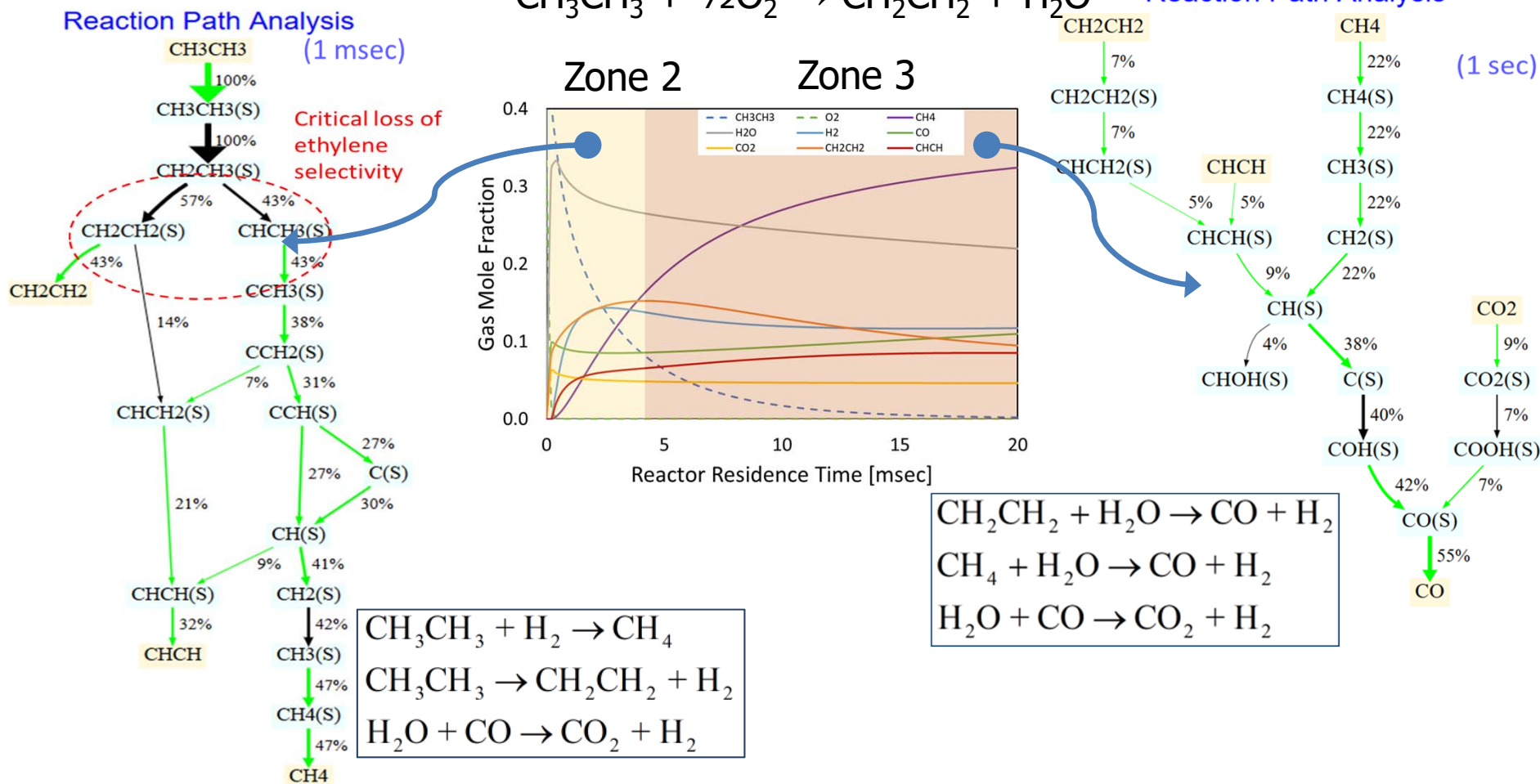


# Automated Reaction Path/Partial Equilibrium Analysis

ReNView<sup>1</sup>



Reaction Path Analysis



[1] <https://github.com/VlachosGroup/ReNView>; Gupta and Vlachos, *SoftwareX* **11**, 100442 (2020).



# Assessment of MKM

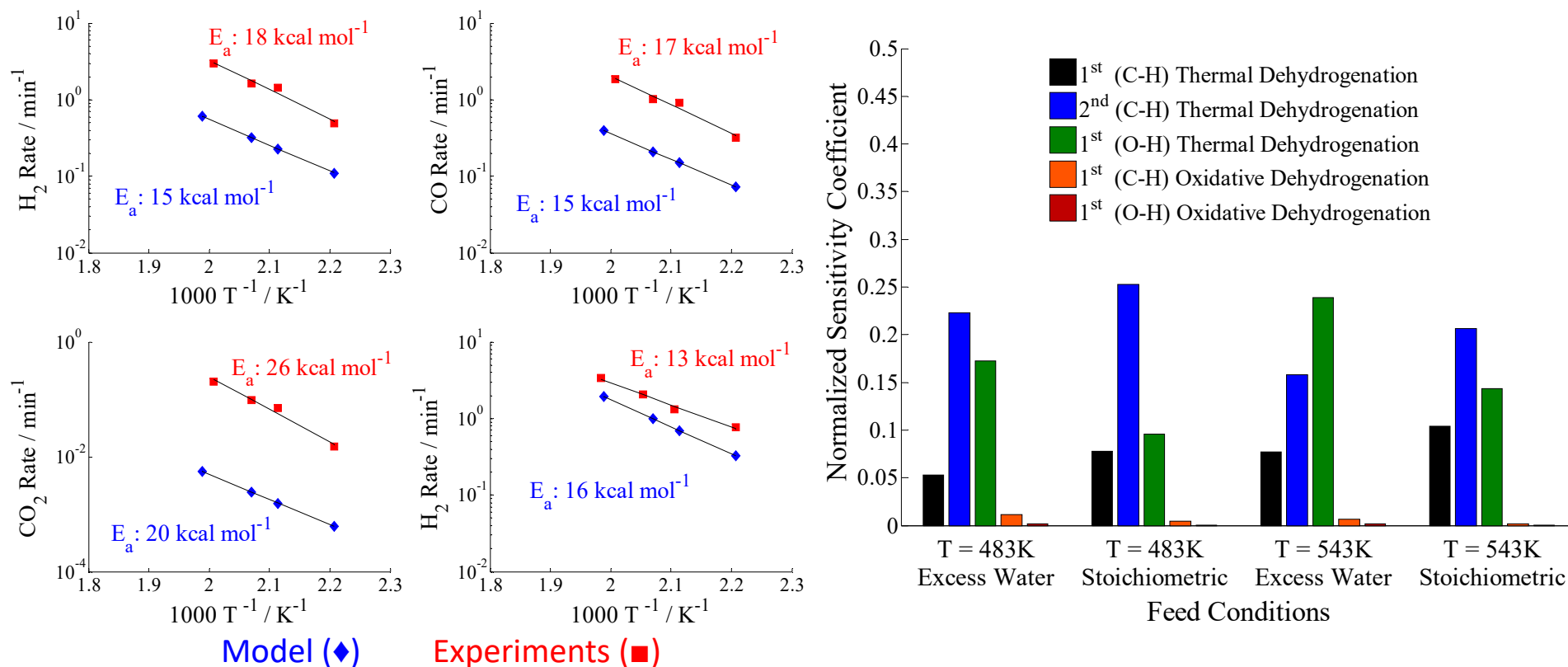
## Ensure that MKM Captures Correctly

- Temperature effects,  $E_{app}$
- 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

### Experimental data quality is essential

- Equilibrium limitations
- Transport effects
- Differential conditions (conversion <10%)
- Catalyst characterization

# 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)

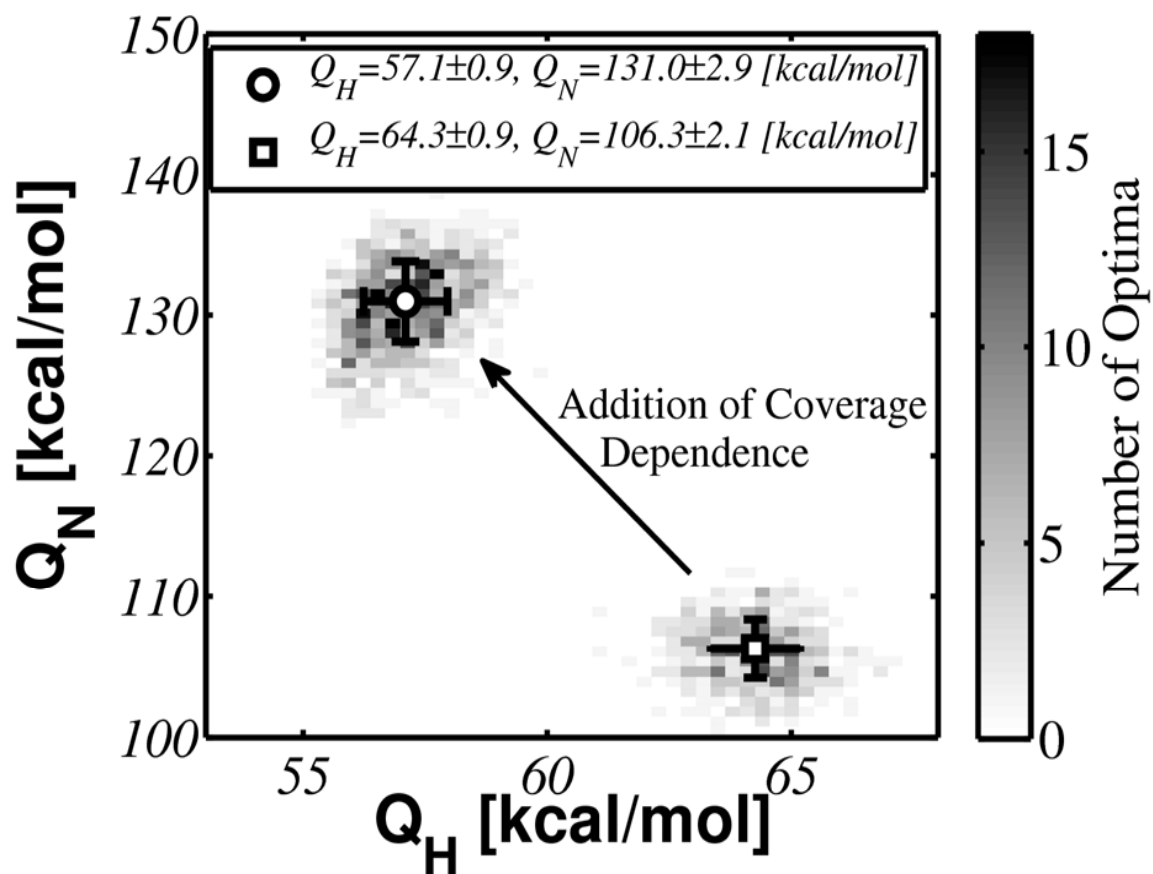
- Thermal dehydrogenation steps are kinetically most important
- OH\*-mediated steps inactive on Pt (due to low [OH\*])

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



# Uncertainty Quantification

## Effect of adsorbate-adsorbate interactions



# Uncertainty Quantification

Parametric Uncertainty



Model Uncertainty

