Microkinetic Modeling 1:
Individual Catalyst Material

A.J. Medford

Georgia Institute of Technology

6/17/2022

iCoMSE Summer School

What is a "microkinetic model"?

- Constructed from **elementary steps** of a reaction mechanism
  - Typically, no "*a priori*" assumption of a rate-limiting step
- Alternative types of kinetic models:
  - "Power law" kinetics: Empirical fit to experimental data
  - "Lumped" kinetics: Many elementary steps are grouped together
- Derived from "master equation" for time evolution of probability that molecules react into different states
  - Probability of elementary processes are governed by rate constants
  - Numerous approximations typically needed to make solution tractable
  - Various solution techniques can be used (e.g. kinetic Monte Carlo, ODE solvers)
- Many approximations are typically employed
  - Mean field: probability is proportional to concentration (well-mixed)
  - Pseudo steady-state: surface coverages at steady-state
  - Neglect/approximate coverage effects: rate constants are independent of coverage (or use some approximate form)
  - Rate-limiting step assumption: sometimes used to solve analytically

$$\frac{dP(S_i)}{dt} = \sum_j \left(A_{ji}P(S_j) - A_{ij}P(S_i) \right)$$

$$\frac{dC_j}{dt} = \sum_i s_{ij} \left(k_i^+ \prod_r C_r - k_i^- \prod_p C_p \right)$$

Remainder of the talk focused on the case where these assumptions are made

Pre-requisites for a microkinetic model

- Reaction mechanism or network:
  - All elementary steps that connect the products and reactants
  - Note that this may include parallel/competing pathways (multiple mechanisms)
- Active site (rate constants)
  - Atomic structure of the surface site where reaction occurs
  - Adsorption configuration of initial/final/transition states
  - Alternatively, rate constants may be determined from model fitting
    - Difficult or impossible to rigorously fit complex mechanisms to steady-state data
- **These are critical assumptions!**
  - Even the most accurate quantum mechanical calculation will yield incorrect predictions if the mechanism and active site are not correctly defined.
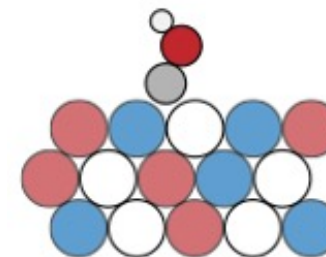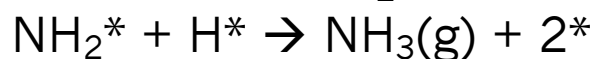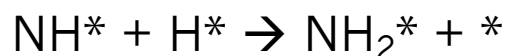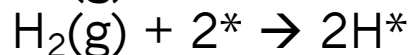
$$\underbrace{\frac{\mathrm{d}C_j}{\mathrm{d}t} = \sum_i}_{\text{mechanism}} s_{ij} \left(\overbrace{k_i^+}^{\text{active site}} \underbrace{\prod_r C_r}_{\text{mechanism}} -k_i^- \prod_p C_p \right)$$
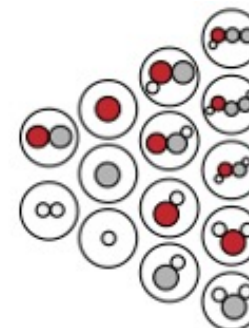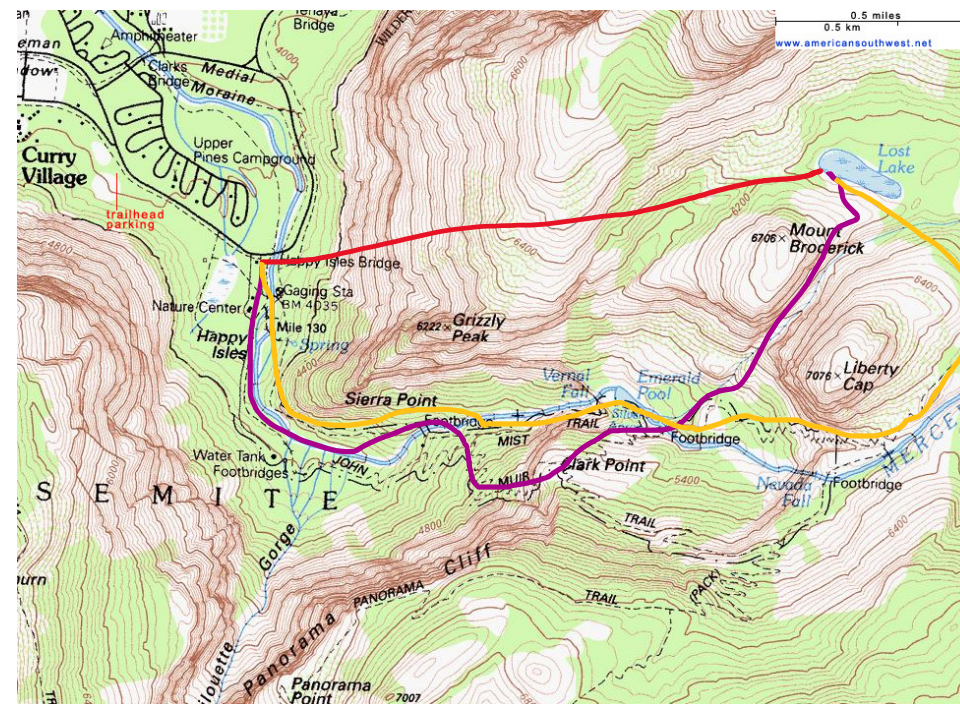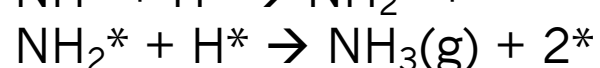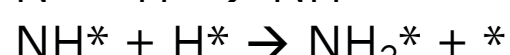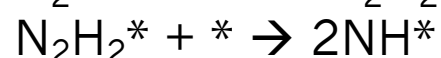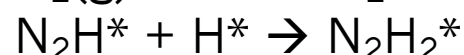
Determining reaction mechanisms

- Need elementary steps that connect reactants to products

- Number of possibilities is combinatorial with the size of molecules

- Manual strategies:
  - Chemical intuition – works well for small and simple reactions
  - Literature search – requires that a reaction is already well studied

- Example: Ammonia synthesis

$N_2(g) + 2* \rightarrow 2N*$
$H_2(g) + 2* \rightarrow 2H*$
$N* + H* \rightarrow NH* + *$ OR
$NH* + H* \rightarrow NH_2* + *$
$NH_2* + H* \rightarrow NH_3(g) + 2*$

$H_2(g) + 2* \rightarrow 2H*$
$N_2(g) + H* \rightarrow N_2H*$
$N_2H* + H* \rightarrow N_2H_2*$
$N_2H_2* + * \rightarrow 2NH*$
$N* + H* \rightarrow NH* + *$
$NH* + H* \rightarrow NH_2* + *$
$NH_2* + H* \rightarrow NH_3(g) + 2*$
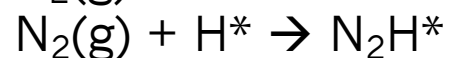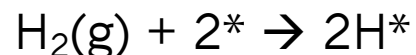
Which mechanism is correct?

Automating reaction network discovery

- Combinatorial explosion makes manual strategies difficult for complex reactions
- Several different strategies:
  - Global – enumerate everything and reduce
  - Local – start from reactants and include most important (RMG-Cat)
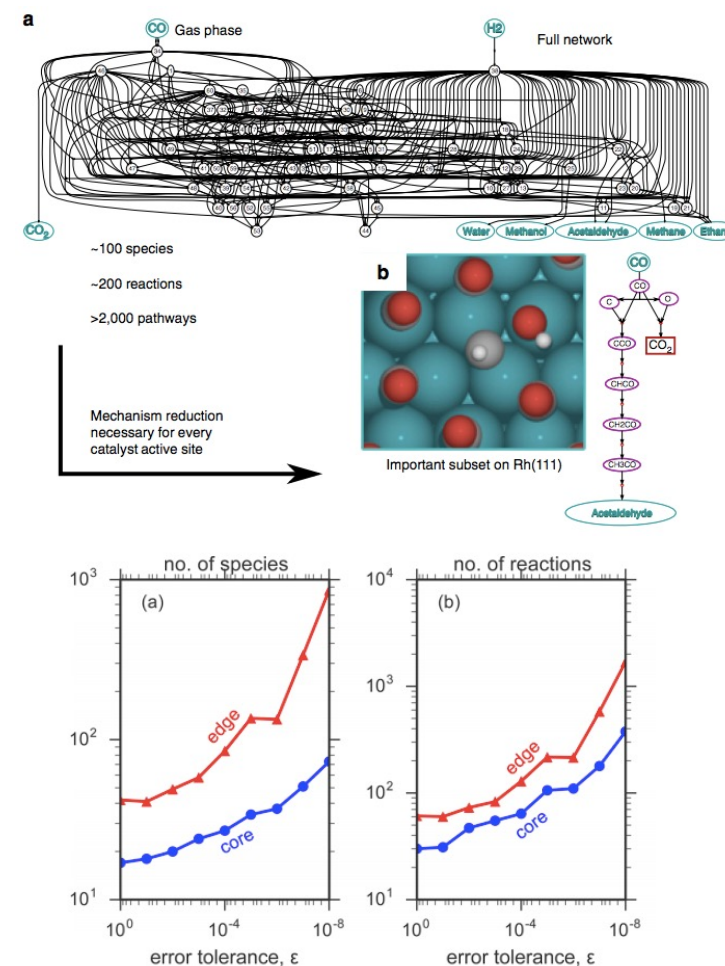- Estimates of rate constants are needed for either strategy
  - Need estimates of hundreds/thousands of rate constants
  - ML techniques are increasingly used for rapid predictions that can help identify reaction mechanisms
- Active area of research

Z. W. Ulissi, A. J. Medford, T. Bligaard, and J. K. Nørskov, Nature Communications, vol. 8, p. 14621, Mar. 2017.
C. F. Goldsmith and R. H. West. The Journal of Physical Chemistry C, vol. 121, no. 18, pp. 9970–9981, May 2017.

From reaction mechanisms to ODE's

- Each species has a formation/depletion rate governed by an ODE
  - Full mechanism is set of coupled ODE's
  - Number of ODE's is equal to the number of species
  - Each elementary step has corresponding terms in ODE's
  - All reactions are reversible in principle: $K_{eq} = \dfrac{k_f}{k_r}$
- An algebraic ``site occupation constraint'' is needed for heterogeneous catalysis
  - $\sum_i^N \theta_i = 1$ where θ_i is the coverage of species i, including free sites (*) as a species.
  - Ensures that coverage cannot exceed 1 monolayer
  - Causes ODE's to become "differential algebraic equations"

From reaction mechanisms to ODE's

- Example: Ammonia synthesis

(1) $N_2(g) + 2* \rightleftharpoons 2N*$
(2) $H_2(g) + 2* \rightleftharpoons 2H*$
(3) $N* + H* \rightleftharpoons NH* + *$
(4) $NH* + H* \rightleftharpoons NH_2* + *$
(5) $NH_2* + H* \rightleftharpoons NH_3(g) + 2*$

stoichiometry

$$\frac{dC_{N2(g)}}{dt} = k_{r,1}\theta_N^2 - k_{f,1}\theta_*^2 C_{N2(g)}$$

$$\frac{dC_{H2(g)}}{dt} = k_{r,2}\theta_H^2 - k_{f,2}\boxed{\theta_*^2 C_{H2(g)}}$$

Law of mass action in each term

$$\frac{d\theta_{N*}}{dt} = \boxed{2}k_{f,1}\theta_*^2 C_{N2(g)} - 2k_{r,1}\theta_N^2 - k_{f,3}\theta_N\theta_H + k_{r,3}\theta_{NH}\theta_*$$

$$\frac{d\theta_{NH*}}{dt} = k_{f,3}\theta_N\theta_H - k_{r,3}\theta_{NH}\theta_* + k_{r,4}\theta_{NH2}\theta_* - k_{f,4}\theta_{NH}\theta_H$$

$$\frac{d\theta_{NH2*}}{dt} = k_{f,4}\theta_{NH}\theta_H - k_{r,4}\theta_{NH2}\theta_* + k_{r,5}\theta_*^2 C_{NH3(g)} - k_{f,5}\theta_{NH2}\theta_H$$

$$\frac{d\theta_{H*}}{dt} = \boxed{2}k_{f,2}\theta_*^2 C_{H2(g)} - 2k_{r,2}\theta_H^2 + k_{r,3}\theta_{NH}\theta_* - k_{f,3}\theta_N\theta_H + k_{r,4}\theta_{NH2}\theta_* - k_{f,4}\theta_{NH}\theta_H + k_{r,5}\theta_*^2 C_{NH3(g)} - k_{f,5}\theta_{NH2}\theta_H$$

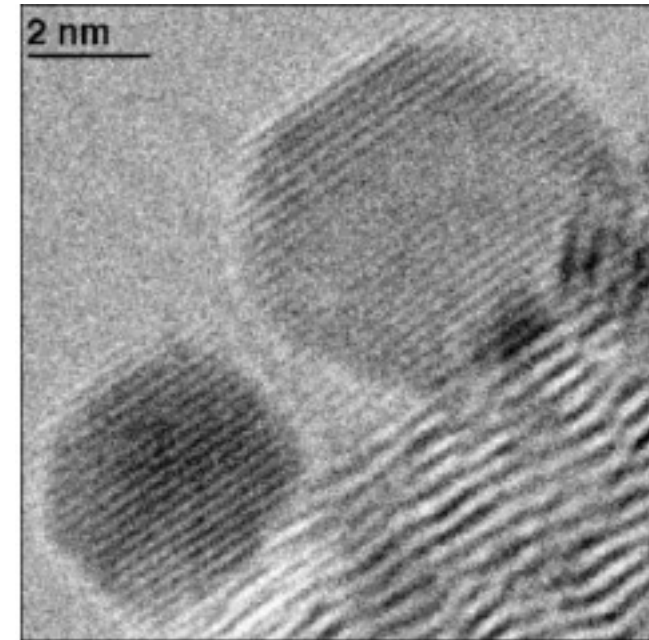$$\frac{dC_{NH3(g)}}{dt} = k_{f,5}\theta_{NH2}\theta_H - k_{r,5}\theta_*^2 C_{NH3(g)}$$

Software packages (e.g. CatMAP) typically construct these equations for you!

Site constraint $\longrightarrow$ $\theta_N + \theta_{NH} + \theta_{NH2} + \theta_H = 1$

Defining active sites

- Active sites are typically denoted with a * in heterogeneous chemical reactions

- Example: Ammonia synthesis
  - $N_2(g) + 2* \rightleftharpoons 2N*$
  - $H_2(g) + 2* \rightleftharpoons 2H*$
  - $N* + H* \rightleftharpoons NH* + *$
  - $NH* + H* \rightleftharpoons NH_2* + *$
  - $NH_2* + H* \rightleftharpoons NH_3(g) + 2*$

How should we model the active site?

Atomic resolution image of supported Ru particles for ammonia synthesis

T. W. Hansen, J. B. Wagner, P. L. Hansen, S. Dahl, H. Topsøe, and C. J. H. Jacobsen, "Atomic-Resolution in Situ Transmission Electron Microscopy of a Promoter of a Heterogeneous Catalyst," Science, vol. 294, no. 5546, pp. 1508–1510, Nov. 2001.

Defining active sites

- Detailed experiments and/or careful modeling are needed to identify the active site

- Example: Ammonia synthesis
  - $N_2(g) + 2* \rightleftharpoons 2N*$
  - $H_2(g) + 2* \rightleftharpoons 2H*$
  - $N* + H* \rightleftharpoons NH* + *$
  - $NH* + H* \rightleftharpoons NH_2* + *$
  - $NH_2* + H* \rightleftharpoons NH_3(g) + 2*$

- Step sites activate N_2

S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, I. Chorkendorff, E. Törnqvist, and J. K. Nørskov, "Role of Steps in N2 Activation on Ru(0001)," Physical Review Letters, vol. 83, no. 9, pp. 1814–1817, Aug. 1999.
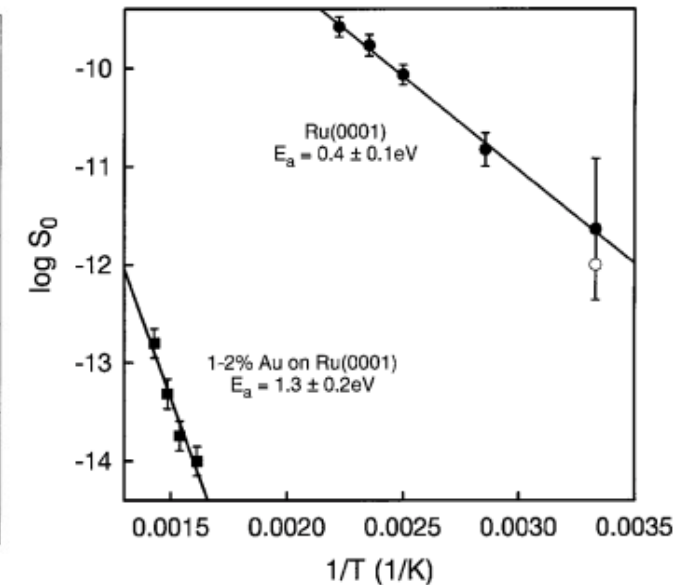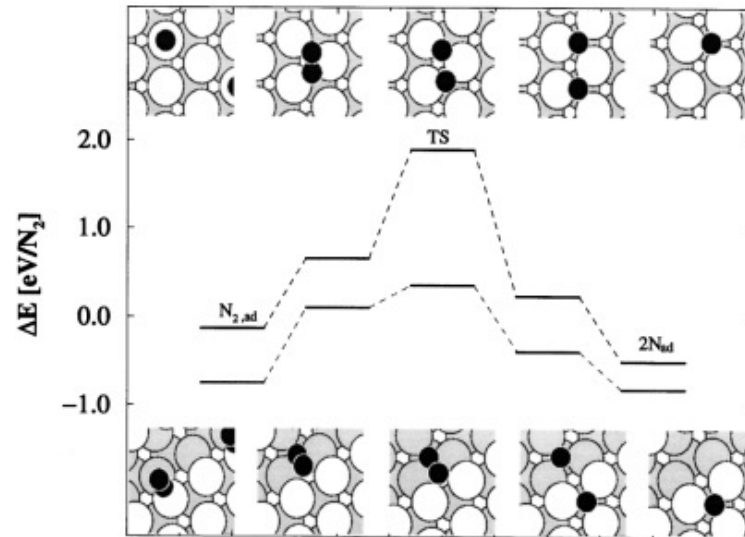
Multi-site mechanisms

- Often, a single active site type is not enough to explain activity
  - Defect sites are often important (step edges, vacancies, etc.)
  - Catalyst support may participate in the reaction
  - Neglect of coverage effects may cause sites to be incorrectly blocked
- Mean field models are not ideal for multiple active site types, but they can be included
  - Remember that you are implicitly mixing all the sites together!
  - Kinetic Monte Carlo is required to rigorously treat multiple site types

$3H_2 + N_2$

(211) lower step
N, NH

(211) upper step
N, NH, NH$_2$, H

$2NH_3$
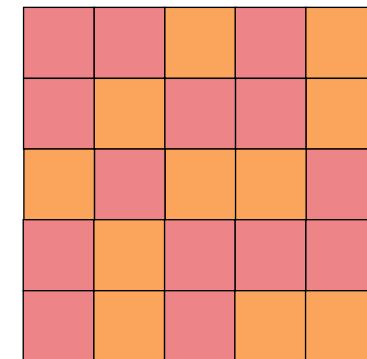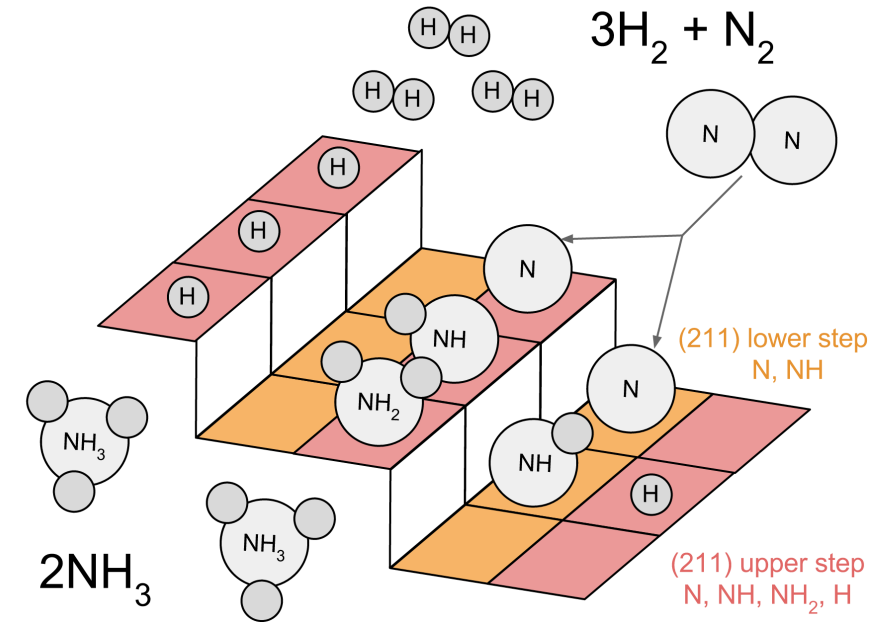
$r \sim k\theta$

From active sites to rate constants

- Transition-state theory relates activation free energy to rate constant
  - $k = \frac{k_B T}{h} \exp(\frac{-\Delta G_a}{k_B T})$ (for surface reactions)
  - $k = \frac{P}{N_A \sqrt{2\pi m k_B T}} \exp(\frac{-\Delta G_a}{k_B T})$ (for adsorption reactions)
- The key quantity is the free energy of activation (ΔG_a)
  - $\Delta G_a = G_{TS} - G_{IS}$ (forward reaction: TS = transition state, IS = initial state)
  - $\Delta G_a = G_{TS} - G_{FS}$ (reverse reaction: TS = transition state, FS = initial state)
- Free energies of initial and final state can be computed using DFT along with thermodynamic corrections to account for temperature.

Calculating Gibbs free energies

- DFT energies are the internal energy of electrons (typically at 0K). Need to add several significant corrections at finite temperature:
  - Zero-point energy + Enthalpy +Entropy
    - Zero-point energy computed from vibrational frequency calculation
- Gas-phase species:
  - Use ideal gas approximation, or tabulated/interpolated data from NIST (Shomate equation or other equation of state)
- Adsorbed species:
  - Good - assume "harmonic oscillator" partition function (requires vibrational calculation)
    - Beware of diverging entropy as frequencies go to zero!
  - Better – utilize "hindered rotor" partition function (requires vibrational calculation + parameters)
  - Best – use molecular dynamics with enhanced sampling (potential of mean force, umbrella sampling, metadynamics)
- Note that pressure corrections ($\ln(P/P_0)$) should be omitted – they are implicitly included in the law of mass action.

Ideal Gas

$$H(T) = E_{\text{elec}} + E_{\text{ZPE}} + \int_0^{\text{T}} C_P \, \mathrm{d}T$$

$$\int_0^T C_{V,\text{vib}} \mathrm{d}T = \sum_i^{\text{vib DOF}} \frac{\epsilon_i}{e^{\epsilon_i/k_B T} - 1}$$

$$S_{\text{trans}} = k_B \left\{ \ln\left[\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{k_B T}{P^\circ} \right] + \frac{5}{2} \right\}$$

Harmonic Oscillator

$$U(T) = E_{\text{elec}} + E_{\text{ZPE}} + \sum_i^{\text{harm DOF}} \frac{\epsilon_i}{e^{\epsilon_i/k_B T} - 1}$$

$$S = k_B \sum_i^{\text{harm DOF}} \left[\frac{\epsilon_i}{k_B T \left(e^{\epsilon_i/k_B T} - 1 \right)} - \ln\left(1 - e^{-\epsilon_i/k_B T} \right) \right]$$

ASE "Thermochemistry" module has these equations implemented

Reference states and corrections

- Large errors in gas-phase thermodynamics can lead to qualitative failure of microkinetic model (reaction runs in the wrong direction)
  - Common to add "corrections" to gas-phase species that have large DFT errors (O_2, CO_2, CO)
- It is common and convenient to convert "raw" DFT energies (or free energies) to "formation energies" with a common reference state
  - References are typically not IUPAC standard states
  - Reference states should not have known issues with DFT (e.g. triplet state of O_2, van der Waals in graphite)
  - Reference states do not affect reaction energies as long as no "corrections" are applied (corrected species should never be used as reference states!)
  - Assuming reasonable reference states, formation energies should generally be ~3 eV or less
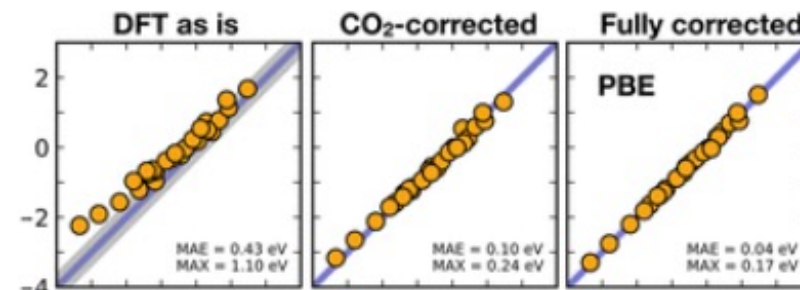
Number of atoms of element j

$$E_f = E_{DFT} - \sum_j n_j R_j$$

Reference energy of element j

CatMAP 1: Generating an input file

surface_name	site_name	species_name	formation_energy	bulk_structure	frequencies
None	gas	CH4	0	None	[]
None	gas	H2O	0	None	[]
None	gas	H2	0	None	[4401]
None	gas	CO	2.74	None	[2170]
Pt	211	CO	1.113	fcc	[]

- CatMAP requires DFT "formation energies" as input
  - Uses a tab-separated text file
- Input file includes:
  - Surface name (distinguishes different materials)
  - Site name (e.g. 111 or 211, distinguishes different active site types)
  - Species name (labels a gas-phase or adsorbed species)
  - Formation energy (DFT formation energy)
  - Bulk structure (defines bulk structure of material)
  - Frequencies (vibrational frequencies for thermo corrections)
  - Reference (to note where the energy came from)

CatMAP 1: Generating an input file

- Computing "formation energies" is always the trickiest part
  - Different from typical standard-state formation energies
  - Use DFT energies, and non-standard reference states
- For a given set of "reference states":
  - Calculate atomic "reference energies"
  - Subtract off based on stoichiometry
- Resulting energy is equivalent to the reaction energy between the "reference state" compounds and the compound of interest
- Example:
  - E_slab = -114762.254
  - E_slab+CO = -115390.445
  - E_COgas = -626.612

CatMAP 1: Generating an input file

Example: Adsorbed CO "formation" energy with different references (all energies in eV)

- E_slab = -114762.254
- E_slab+CO = -115390.445
- E_COgas = -626.612
- E_CH4gas = -231.609
- E_H2gas = -32.962
- E_H2Ogas = -496.411

- True adsorption energy:
  - E_slab+CO – E_slab – E_CO = -1.579

- Carbon reference = CO, oxygen reference = H2O
  - E_O = E_H2O – E_H2 = -463.449
  - E_C = E_CO – E_O = -163.163
  - E_CO = E_slab+CO – E_slab – E_C – E_O = -1.579

- Carbon reference = CH4, oxygen reference = H2O
  - E_O = E_H2O – E_H2 = -463.449
  - E_C = E_CH4 – 2*E_H2 = -165.685
  - E_CO = E_slab+CO – E_slab – E_C – E_O = 0.942

Why is adsorption positive with CH_4 as a reference, but negative with CO as a reference?

Note: CO + 3H2 → CH4 + H2O has a reaction energy of -2.55 eV based on these energies

CatMAP 1: Generating an input file

Example: Adsorbed CO "formation" energy with different references (all energies in eV)

- $E\_slab = -114762.254$
- $E\_slab+CO = -115390.445$
- $E\_COgas = -626.612$
- $E\_CH4gas = -231.609$
- $E\_H2gas = -32.962$
- $E\_H2Ogas = -496.411$
- $E\_slab+CH = -114943.455$

- True adsorption energy:
  - $E\_slab+CO - E\_slab - E\_CO = -1.579$

- Carbon reference = CO, oxygen reference = H2O
  - $E\_O = E\_H2O - E\_H2 = -463.449$
  - $E\_C = E\_CO - E\_O = -163.163$
  - $E\_CO = E\_slab+CO - E\_slab - E\_C - E\_O = -1.579$

- Carbon reference = CH4, oxygen reference = H2O
  - $E\_O = E\_H2O - E\_H2 = -463.449$
  - $E\_C = E\_CH4 - 2*E\_H2 = -165.685$
  - $E\_CO = E\_slab+CO - E\_slab - E\_C - E\_O = 0.942$

Calculate the "formation energy" of CH* with CO, H2, and H2O as reference states

Note: CO + 3H2 → CH4 + H2O has a reaction energy of -2.55 eV based on these energies

Accounting for coverage effects

- Standard mean-field formulation neglects lateral interactions between adsorbates
  - Rate constants do not depend on coverage
- There are approaches for parameterizing coverage-dependent rate constants
  - $k = f(\vec{\theta})$ where $\vec{\theta}$ is a vector of all coverages
  - Parameterization is (very) tricky
- Coverage dependent mean-field models can have multiple solutions
  - Convergence is often difficult
  - Results can be very sensitive to initial guesses and fitted parameters
- CatMAP includes coverage-dependent functionality, but it should be used carefully
  - Results are likely qualitative at best
  - Kinetic Monte Carlo is recommended for rigorous treatment of coverage dependence

Reaction conditions and reactor model

- Results of kinetic models depend on reaction conditions
  - Pressure/concentration of products/reactants: Le Chatlier's principle
  - Temperature: Affects rate constants exponentially (and free energies)
  - Applied potential (electrochemistry): Affects thermodynamics and kinetics of reactions (can be complex to model correctly, especially kinetics)
- Reactor model will also influence results
  - Selectivity and yield can vary a lot depending on reactor setup
- Typically, simple reactor models are used due to complexity of microkinetic equations
  - Batch reactor with fixed product/reactant concentrations (CatMAP)
  - Continuously-stirred tank reactor (CSTR)
  - Plug-flow reactor (PFR)
- Be aware of assumptions when interpreting results
  - Trends as a function of reaction condition are often most useful

Solving microkinetic models

- Rate-limiting step assumption:
  - Assume the rate of the reaction is equal to the rate of the slowest step
  - Works well for simple cases (few possible reactions → analytical solutions)
  - Difficult or impossible for more complex reactions
  - Only works if one step is much slower than all others
- Root finding (CatMAP uses this method)
  - Works for pseudo-steady state approximation (ODE's become a system of non-linear equations)
  - Requires strong initial guess in many cases (equilibrium coverages, solution from similar catalyst/condition)
  - May require "multiple precision" arithmetic to deal with stiff systems
- ODE integration
  - Provides transient response of system over time (converges to pseudo-steady state as t → infinity)
  - Computationally expensive and prone to convergence issues (especially for stiff systems)

Interpreting the output

- Microkinetic models provide a turnover frequency, not a "rate"
  - Rate will depend on the number of active sites present in the system
- Quantitative agreement is rare due to numerous factors
  - Number of active sites is hard to quantify (especially if they are defects)
  - Exchange-correlation errors are typically ~0.2 eV (~5 orders of magnitude in Arrhenius rate)
  - Errors in entropy/enthalpy may also be ~0.1 eV or larger (especially for large molecules)
  - Good fortune or fitted parameters are almost always required for quantitative agreement!
- Qualitative trends are typically much more reliable
  - Rate as a function of temperature/pressure/voltage
  - Selectivity can still be quite difficult due to strong sensitivity to energies and reactor model, but qualitative trends can still be extracted in some cases

Ammonia synthesis example

- Computed ammonia synthesis rate as a function of temperature on Ru(0001) step surface

- Rate is off by ~2 orders of magnitude compared to experiment

- Trend with temperature (and corresponding apparent activation barrier) are relatively close to experiment

Medford et al., Science. 345, 197-200 (2014).
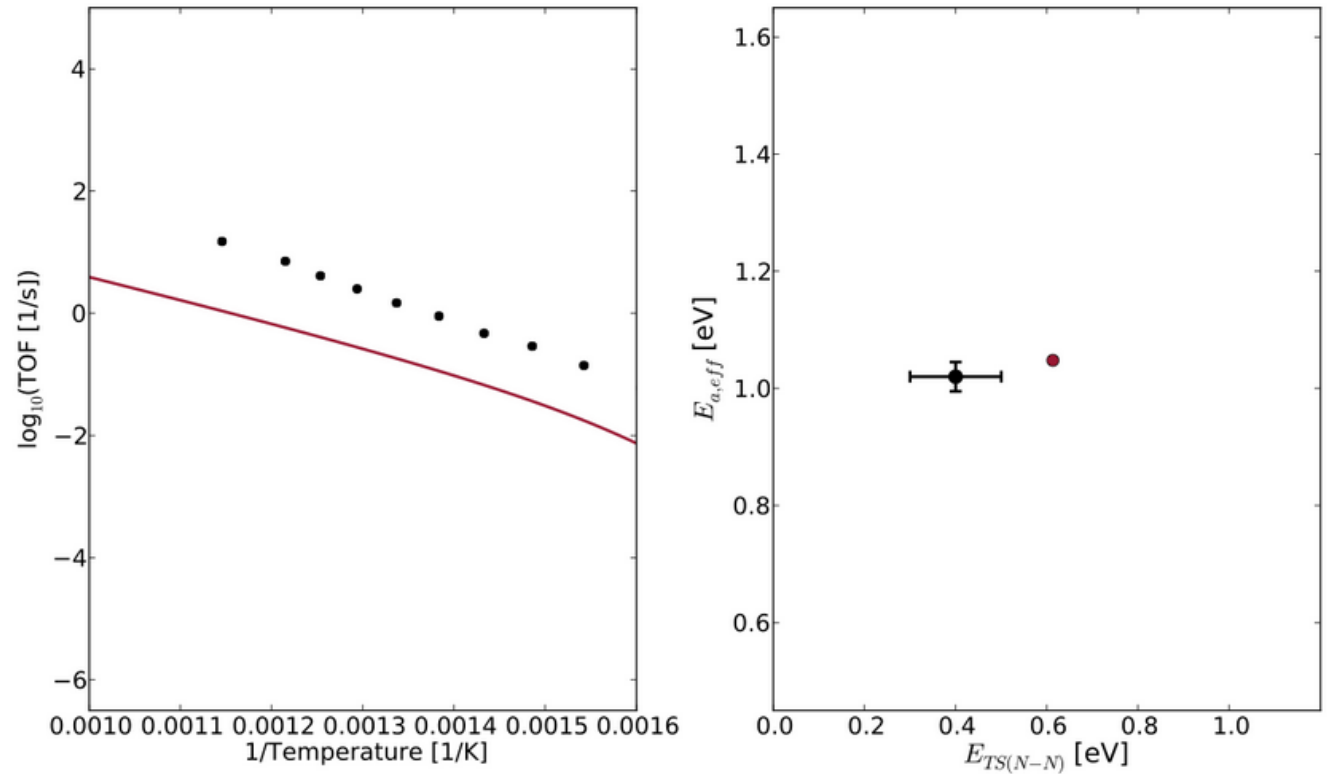
Evaluating sensitivity to exchange-correlation approximation

- BEEF-vdW functional enables sensitivity analysis through error estimation

- Rates vary by ±2 orders of magnitude based on XC approximation

- Apparent and actual activation barriers vary by ±0.3 eV (1 st. dev.)
  - Experimental observations are within theoretical error bars

- This only accounts for XC error!
  - Errors due to active site structure, thermochemistry, coverage effects, etc. may be even greater.

Medford et al., Science. 345, 197-200 (2014).
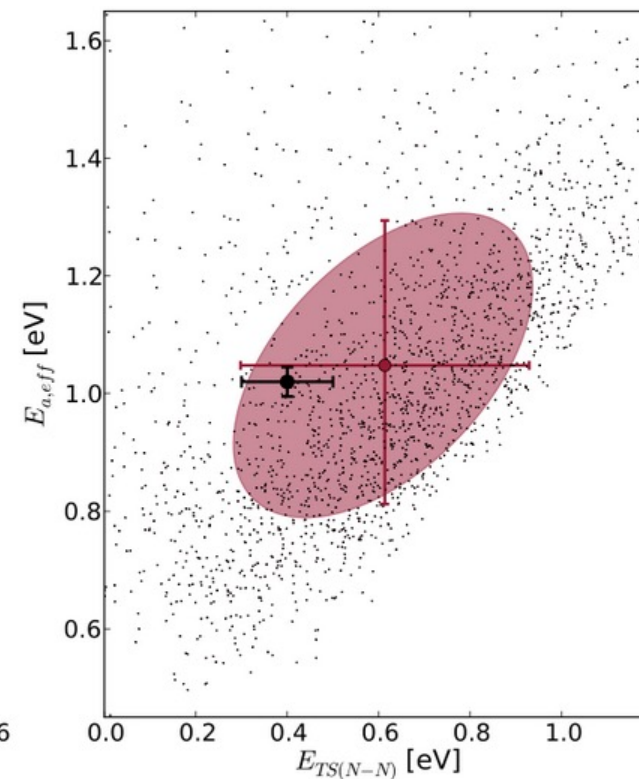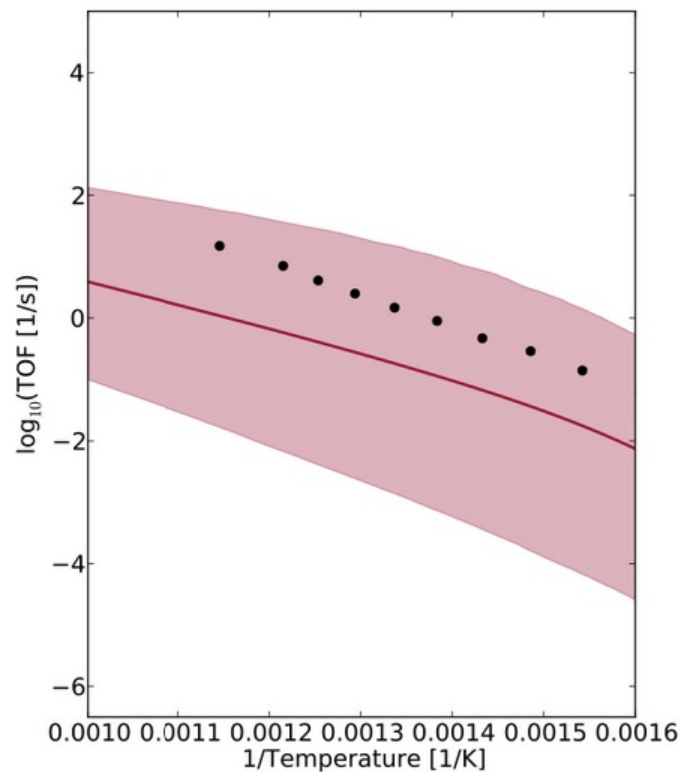
Conclusions

- Microkinetic models enable calculation of turnover frequencies from first-principles simulations

- Constructing a microkinetic model requires:
  - Description of reaction mechanism/network
  - Atomic-scale description of the active site
  - A way to calculate free energies under reaction conditions
  - Solution of a set of (stiff) coupled ODE's with an algebraic constraint