SAND2021-12269C

Sandia National Laboratories

REFINING AUTOMATICALLY GENERATED MICROKINETIC MECHANISMS IN A WORKFLOW

Richard H. West[1], Chris Blais[1], Eric D. Hermes[2], Maciej Gierada[2], David H. Bross[3], C. Franklin Goldsmith[4], Eric J. Bylaska[5], Judit Zádor[2]

[1] Northeastern University; [2] Sandia National Laboratories; [3] Argonne National Laboratory; [4] Brown University; [5] Pacific Northwest National Laboratory

Overview

We couple several of our new or improved open-source tools, as we work towards a highly automated workflow to facilitate the process of constructing a microkinetic model for heterogeneous catalysis, identifying the important parameters, calculating them more accurately, and refining the model, in a loop. Our example goal is to (re)create a well-studied system: synthesis of methanol from H_2, CO, and CO_2 on Cu(111).

NWChem

NWChem is an open-source high-performance computational chemistry package that aims to provide its users with tools that are scalable both in their ability to treat large problems efficiently, and in their use of available parallel computing resources.

Sella

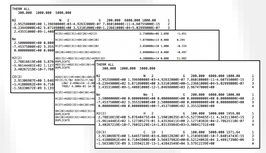
Sella is a utility for finding first order saddle points. We use iterative diagonalization to update an approximate Hessian, which both dictates progress towards the saddle point and is a preconditioner for subsequent Hessian diagonalizations. It scales better with respect to system size and converges more reliably than traditional approaches. Our open-source software can be used with more than 40 electronic structure packages for molecules, solids and other atomic systems.

Pynta

pynta is designed to automatically characterize chemical reactions relevant to heterogeneous catalysis. It spawns and processes many *ab initio* quantum chemistry calculations to study gas-phase reactions on crystal facets. It is designed to run on petascale and upcoming exascale machines, and handles embarrassingly parallel computations using the balsam workflow code.

1. Generate Mechanism

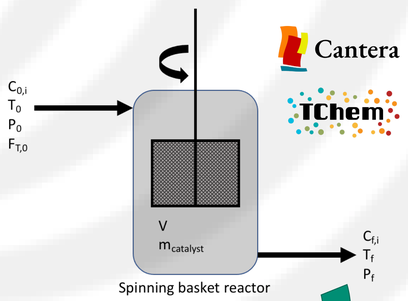
The first mechanism was generated using RMG's surface reaction families and thermo libraries, primarily consisting of data from Pt(111). Linear scaling relations for adsorbate binding energies were applied to extrapolate to the Cu(111) surface.



The kinetic model has elementary reactions in both gas phase and on the Cu surface.

2. Simulate

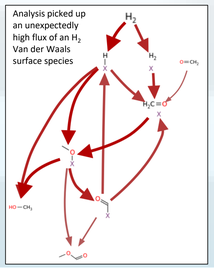
The model was used to simulate a spinning basket reactor (CSTR) at experimental conditions, using Cantera and TChem.

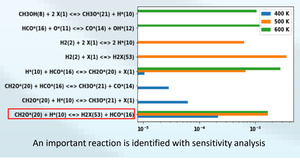


Spinning basket reactor

3. Analyze model

The simulations were analyzed using local sensitivity and Computational Singular Perturbation. The results highlighted reactions with the largest effect on the model outcome.

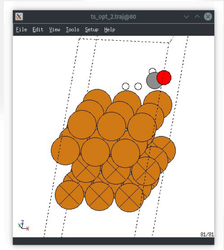




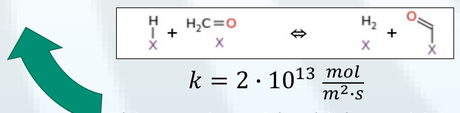
An important reaction is identified with sensitivity analysis

4. Find Saddle Point

A partial Nudged Elastic Band (NEB) calculation followed by optimization with Sella was used to find a saddle point.



A saddle point for this elementary reaction



$$k = 2 \cdot 10^{13}\ \frac{mol}{m^2 \cdot s}$$

This reaction with a high sensitivity and importance index was estimated by RMG, from a reaction family with a single (barrierless) rate rule and no training reactions.

5. Calculate Rate

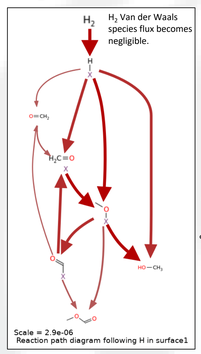
DFT calculations (at first, modest PBE with a 3x3x1 k-point mesh) and transition state theory give a rate expression to replace RMG's estimate.

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$

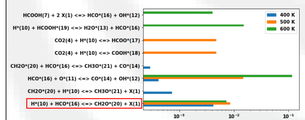
The new rate expression is much slower than RMG's first estimate, and now depends on temperature

6. Generate New Mechanism

RMG is run again with the new kinetic data, to give a new model.



The new model already performs better, and the process can be repeated to improve it further.



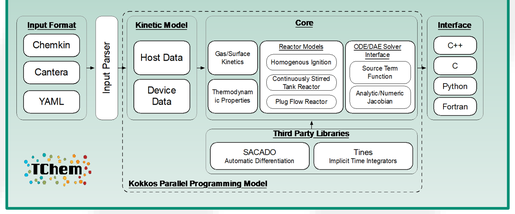
New important reactions can be identified and re-calculated

Reaction Mechanism Generator

Reaction Mechanism Generator (RMG) proposes species and reactions using reaction templates, estimates their thermodynamic and kinetic values, and selects them for the final microkinetic model based on their rates.

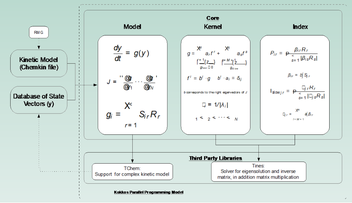
TChem

TChem is an open-source software library for solving complex computational chemistry problems and analyzing detailed chemical kinetic models.



CSPlib

CSPlib is an open-source software toolkit for the analysis of dynamical systems and chemical kinetic models, using the Computational Singular Perturbation method.



Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division, as part of the Computational Chemistry Sciences Program (Award No. 0000232253).

https://ecc-project.sandia.gov/

Sandia National Laboratories