Accelerating mechanism development for heterogeneous catalysis

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Virtual

Exascale Catalytic Chemistry

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Outline

- Introduction to the ECC project and team
- Automated microkinetic mechanism generation
- Automated reaction path search on surfaces
- Summary

The Exascale Catalytic Chemistry (ECC) project

Goal

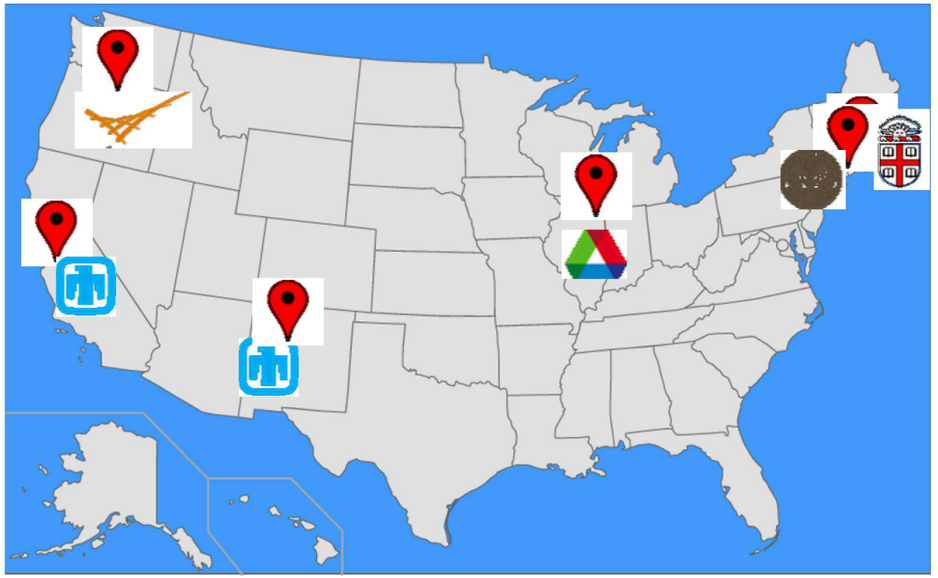
Develop an exascale-ready software ecosystem that enables the characterization of catalytic processes faster and more accurately.

Target systems

Catalytic systems on ideal catalysts with coupled gas-phase and heterogeneous chemistry.

Argonne National Laboratory

Pacific Northwest National Laboratory



Brown University
Northeastern University

Sandia National Laboratories

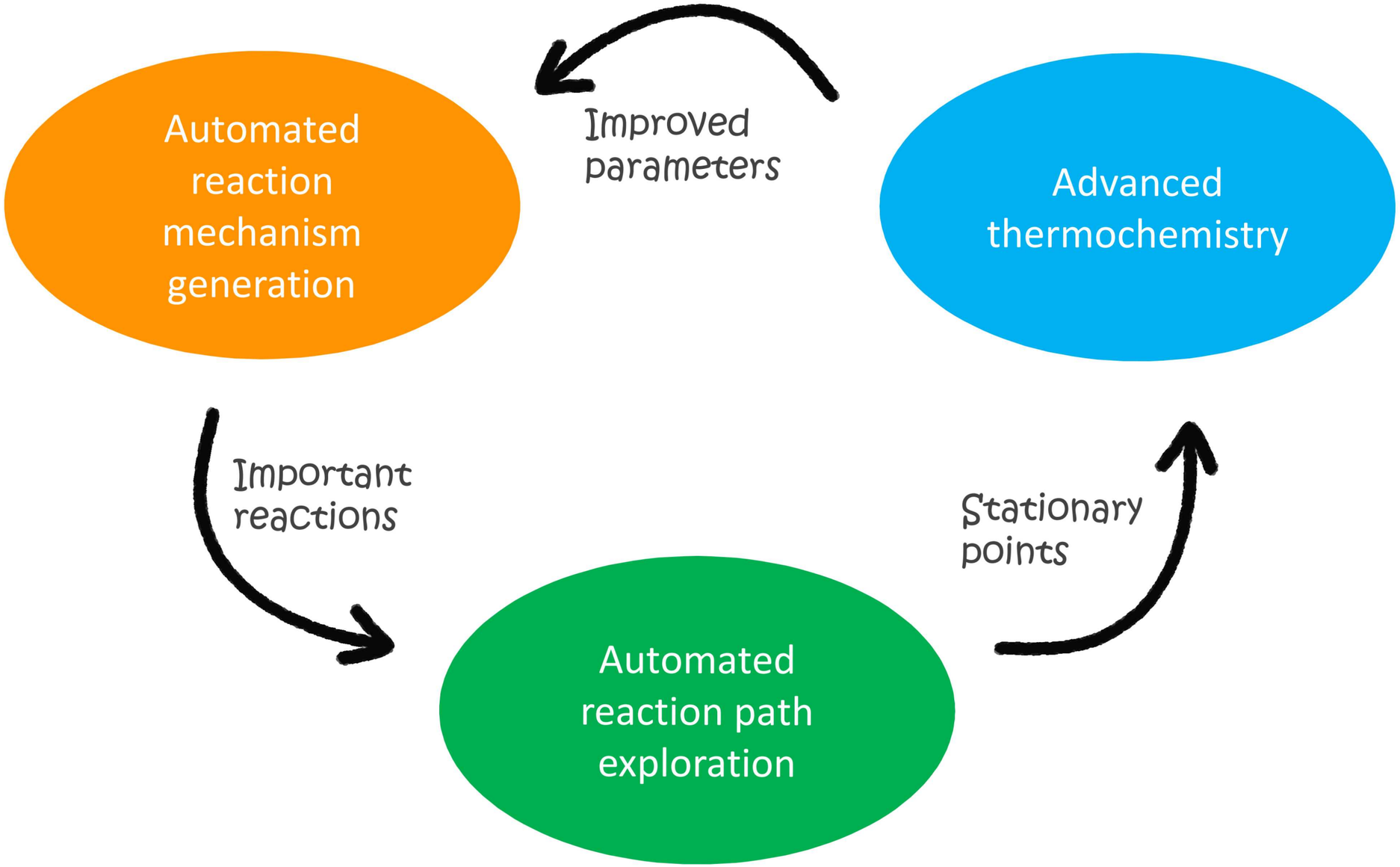
https://ecc-project.sandia.gov

Funding

2017-2021

US Department of Energy, Basic Energy Sciences, Computational and Theoretical Chemistry program

Coupled computational tools will help accelerate mechanism development for catalysis



Let's use computers to build microkinetic mechanisms!

$$R_1 + R_2 \rightleftharpoons P$$

$$\begin{bmatrix} R_1 + R_2 \rightleftharpoons I_1 + I_2 \\ I_1 \rightleftharpoons I_3 \\ I_2 + I_3 \rightleftharpoons P \end{bmatrix}$$

- The mechanism grows exponentially with the size of the reactants/products
- The number of possible pathways to be considered is orders of magnitude higher

Code needs to

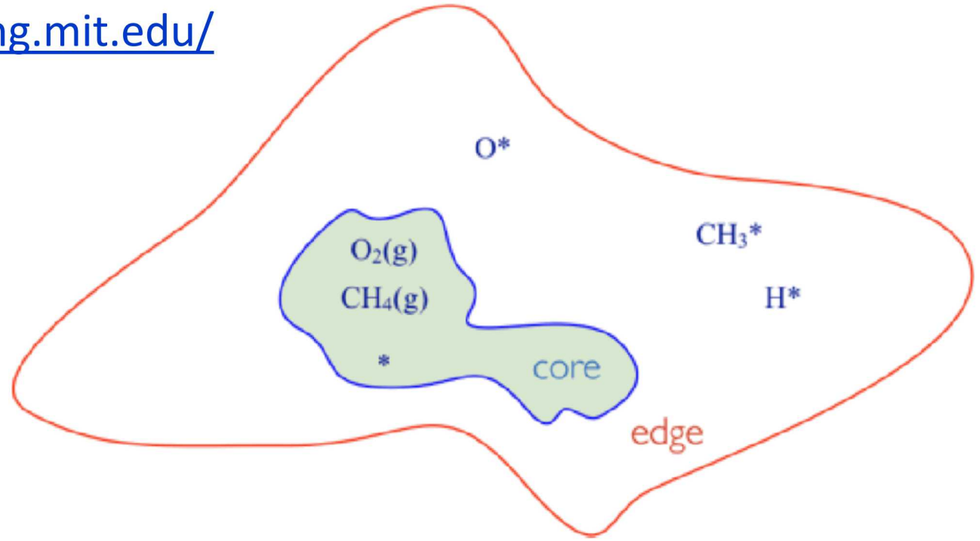
1. represent species
    - *use chemical graph theory*
2. propose new reactions
    - *use reaction families*
3. estimate thermodynamic + kinetic properties
    - *use precompiled databases and estimation methods*
4. keep only the important reactions
    - *use flux-based algorithm*

RMG-Cat

Building, running, and analyzing microkinetic models for gas/solid catalytic systems

Based upon Reaction Mechanism Generator (RMG)

- open source
- Python based
- developed for combustion
- mature (~50+ graduate-student years of development)
- https://rmg.mit.edu/



Richard H. West
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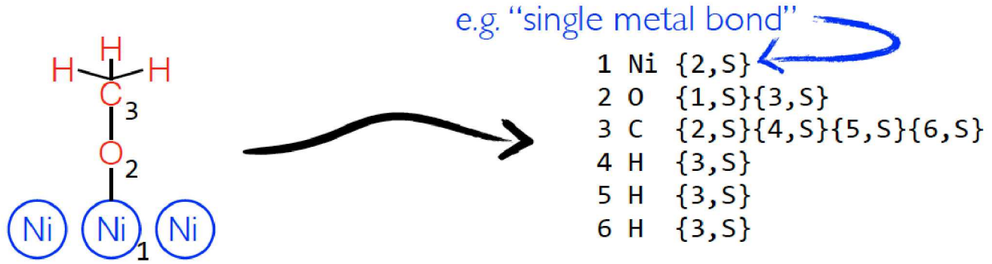
Reaction families for

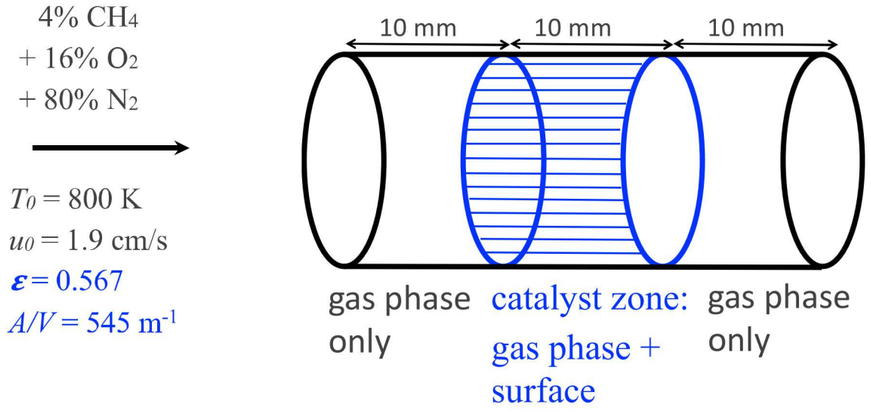
- Adsorption
- Dissociation on surfaces
- Abstraction on surfaces

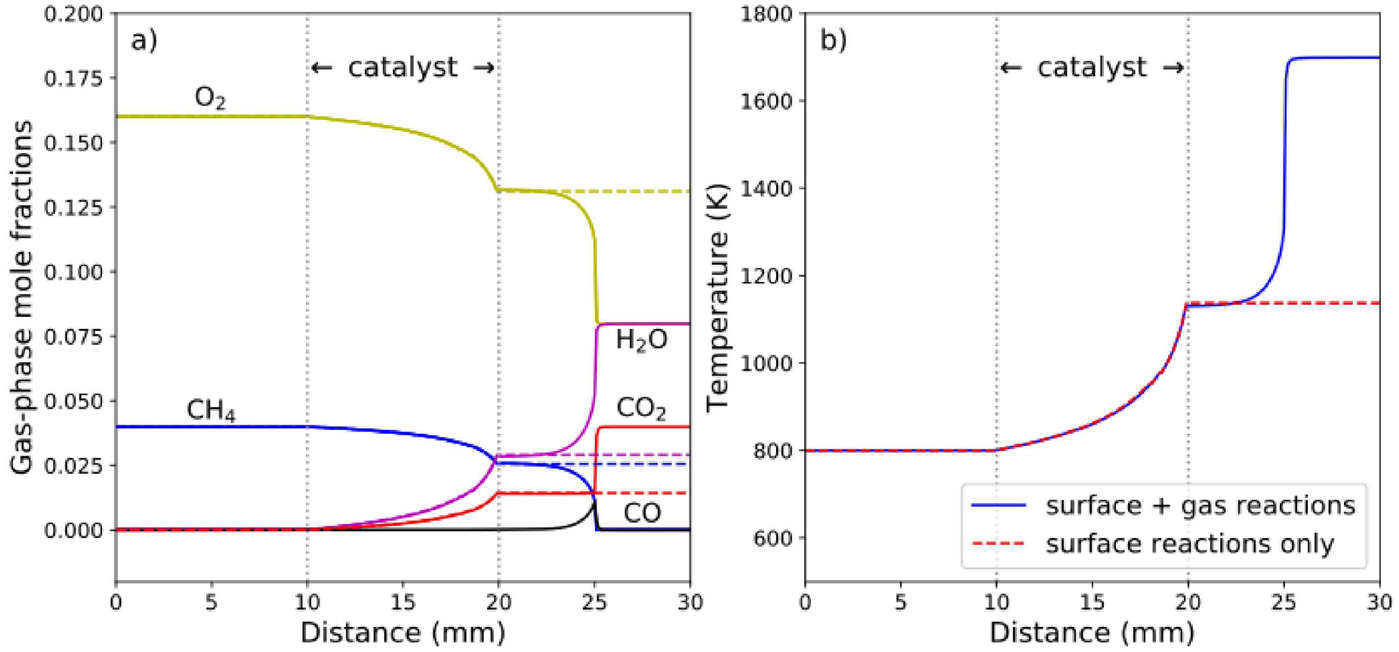


RMG-Cat can estimate thermochemistry of any adsorbate on any metal using Linear Scaling Relationships.

RMG generated a mechanism for methane oxidation on Pt(111)

- fuel lean conditions for T = 500, 1500, 1800 K & P = 1 bar
- core:
  - 21 adsorbates + 51 surface reactions
  - 38 gas-phase species + 340 reactions
- edge:
  - 196 species + 298 reactions

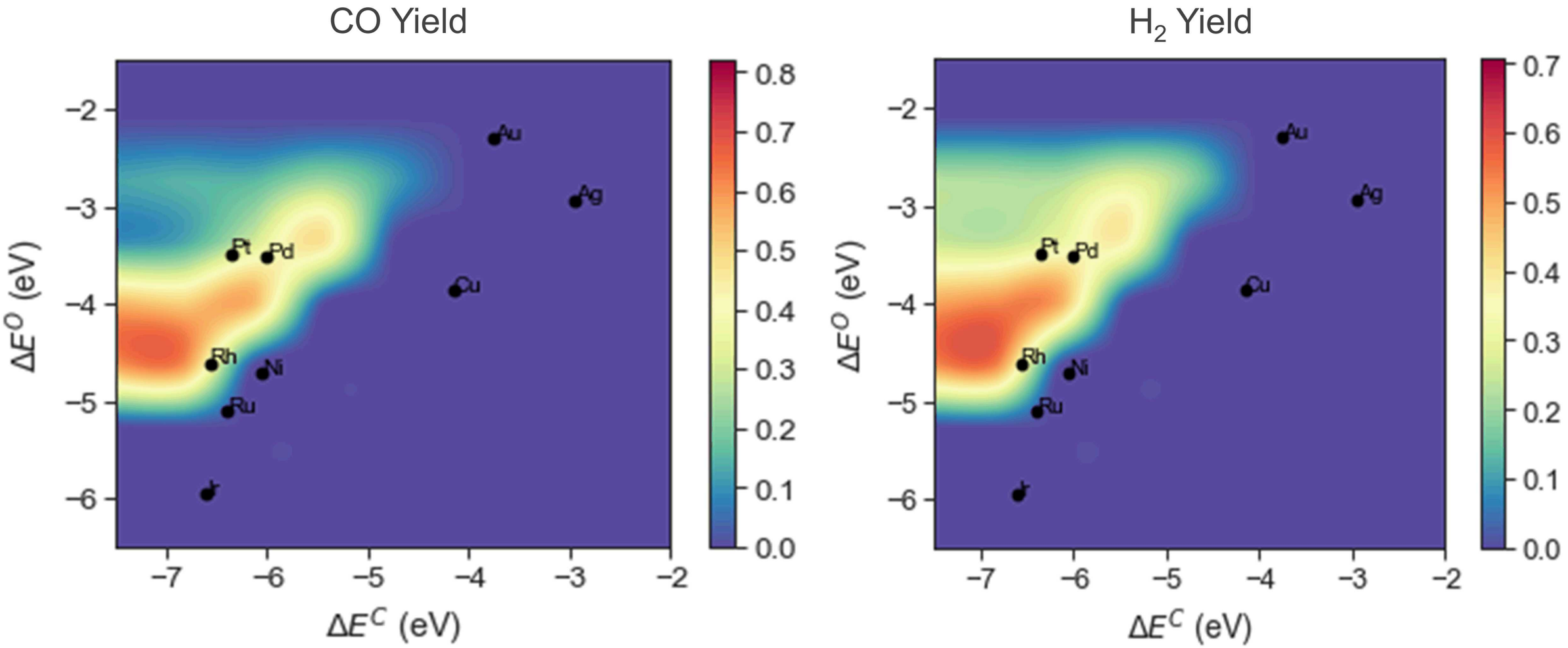




We demonstrated the coupled gas-surface capabilities of RMG.
Such coupling is necessary to predict correct behavior.

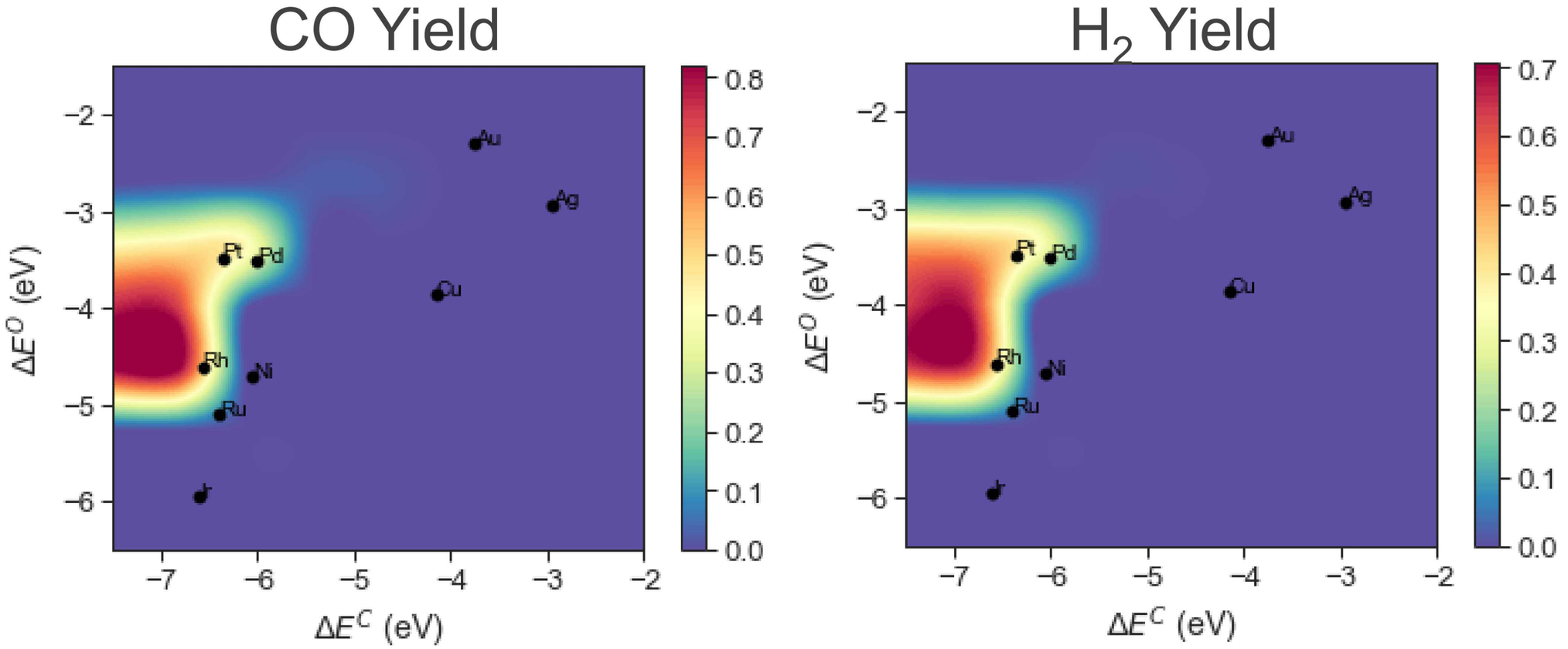
K. Blondal, J. Jelic, E. Mazeau, F. Studt, R. H. West, and C. F. Goldsmith. Computer-generated kinetics for coupled heterogeneous/homogeneous systems: A case study in catalytic combustion of methane on platinum, Indust. Eng. Chem. Res. 2019, 58, 38, 17682–17691

RMG allows systematic and automatic investigation of many metals
Example: Synthesis gas on different metal surfaces



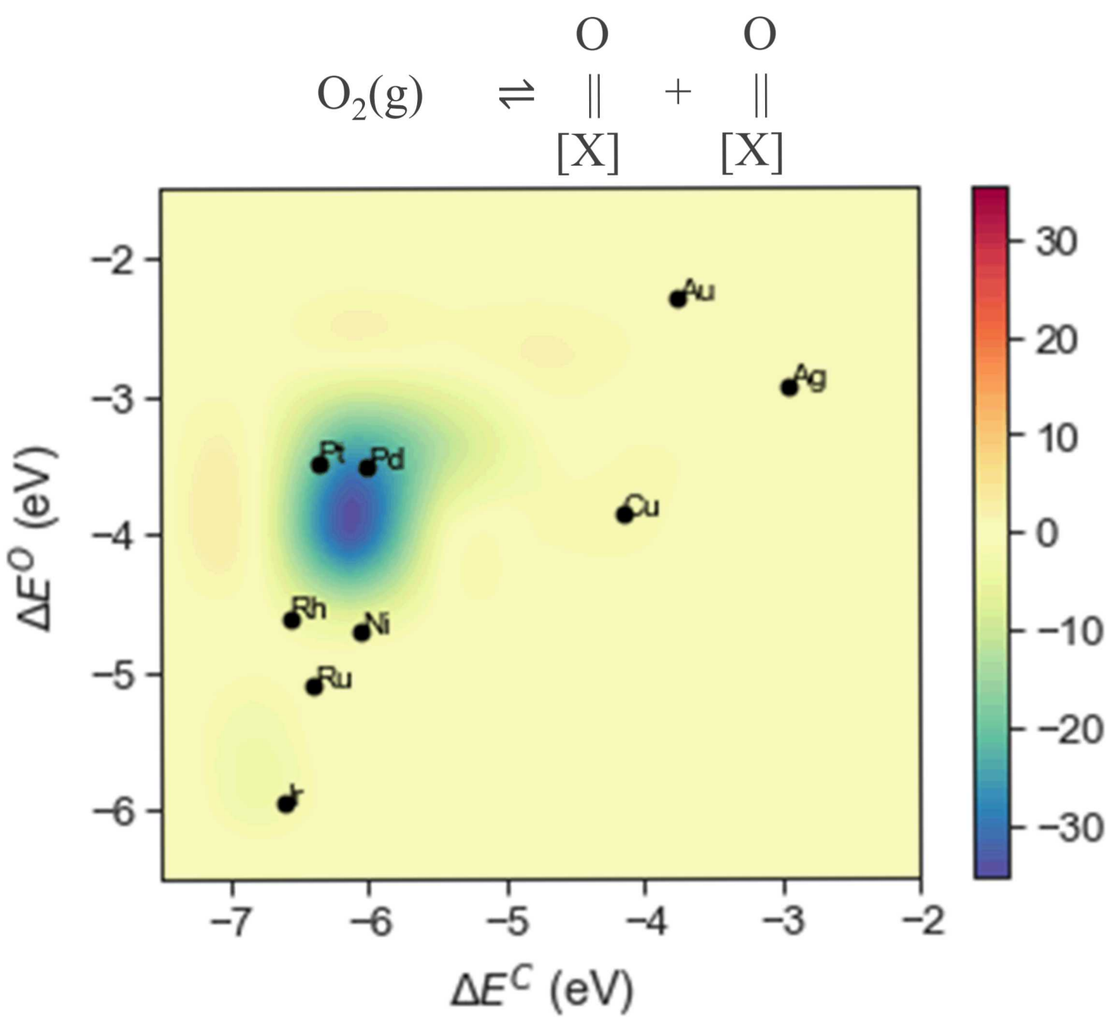
Some metals have higher selectivity but lower yield.

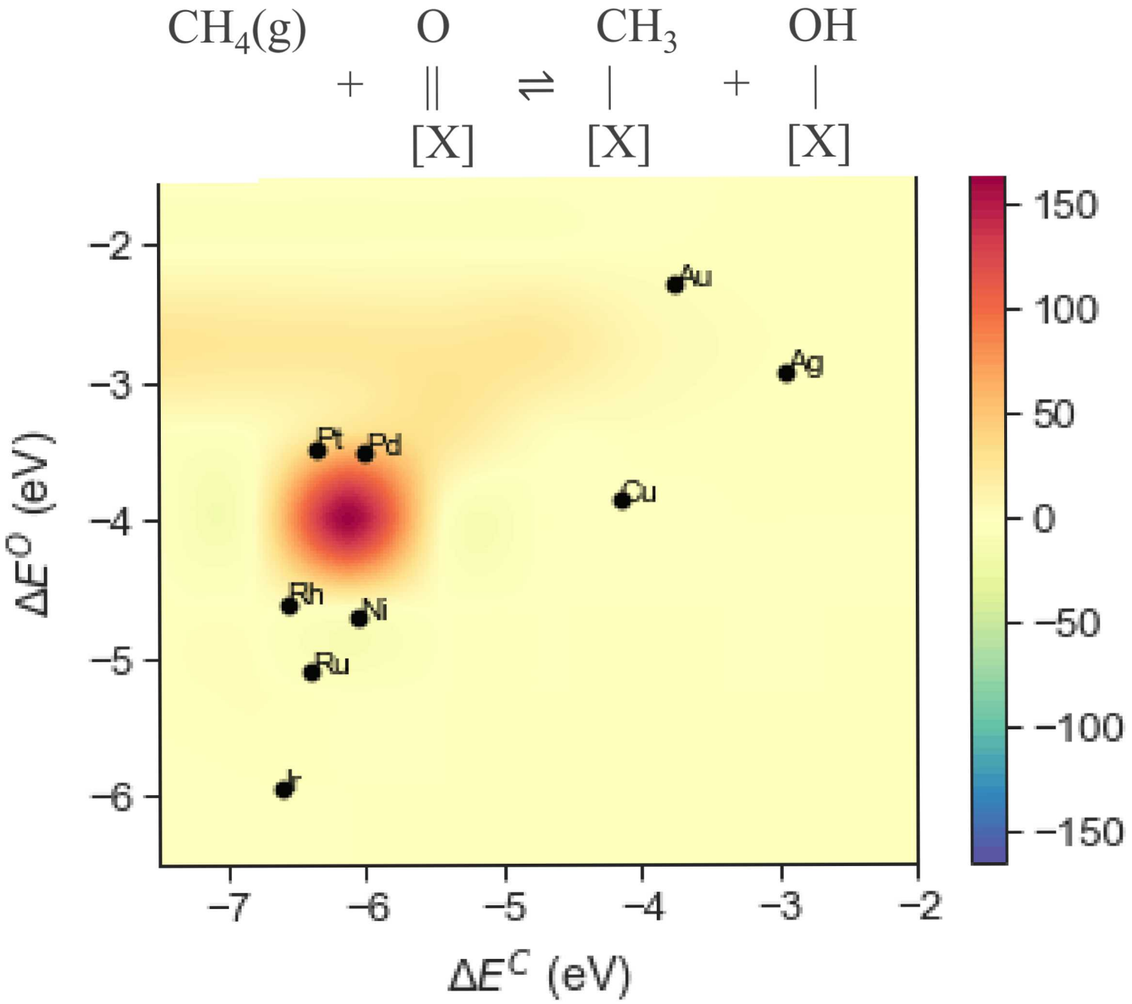
Automated investigation of the effect of the inlet composition



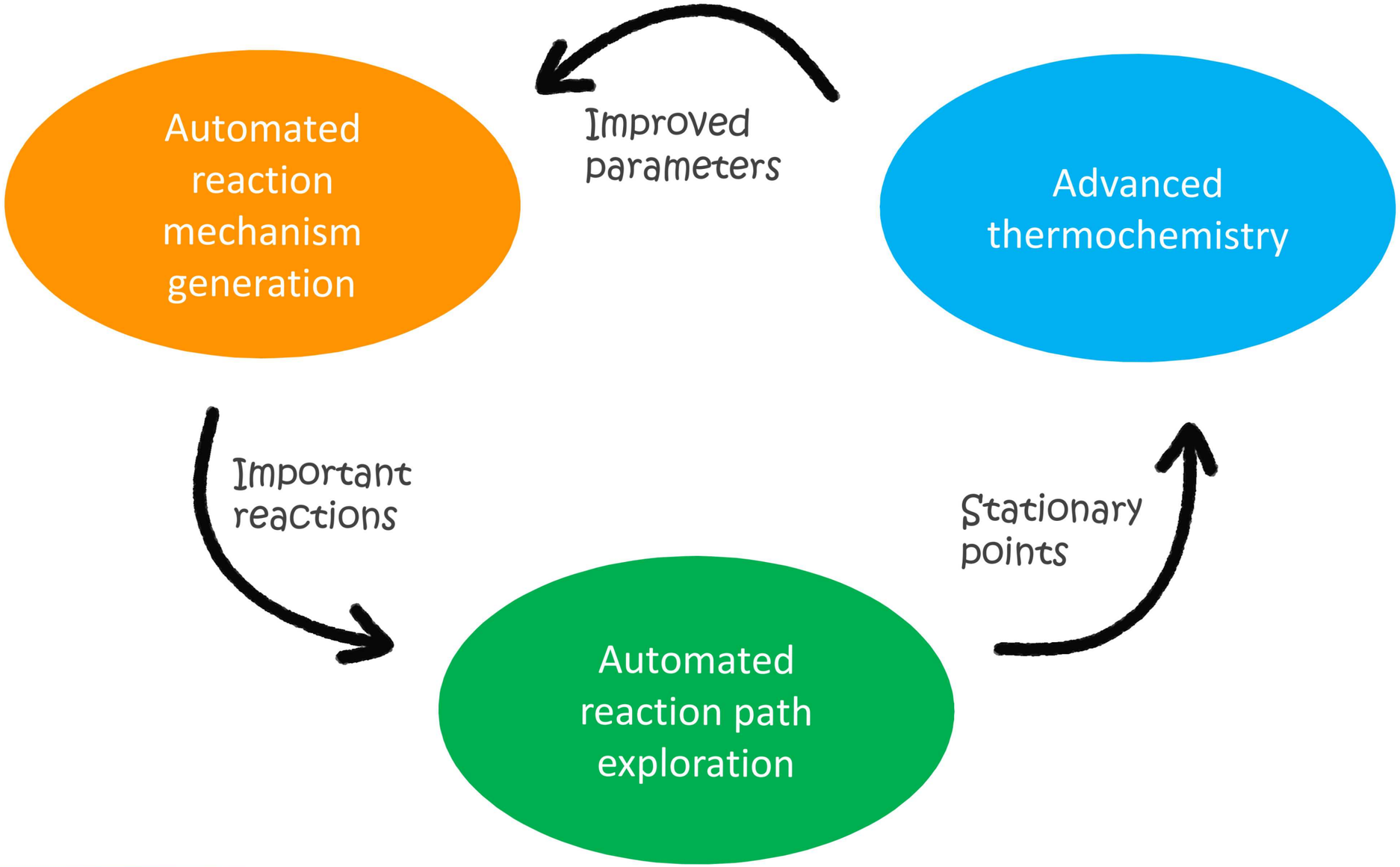
Not only does each metal affect yield,
feed gas composition does as well

Volcano plots for the sensitivity of a reaction on H_2 yield as a function of atomic binding energies



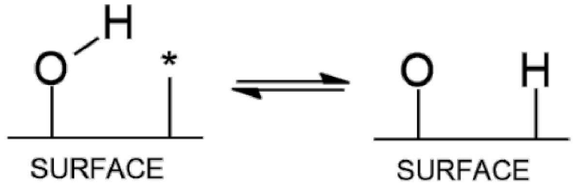


RMG-Cat works, but we have work to do



From formal catalytic reactions to *ab initio* kinetics

We need tools to take us from a proposed chemical reaction to a rate coefficient for gas/solid catalytic systems.



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Sandia postdoc

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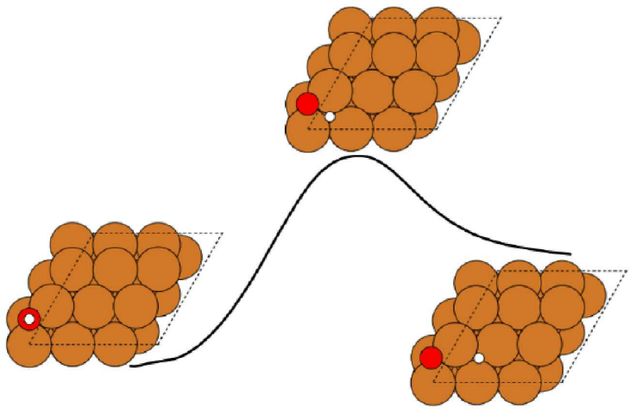
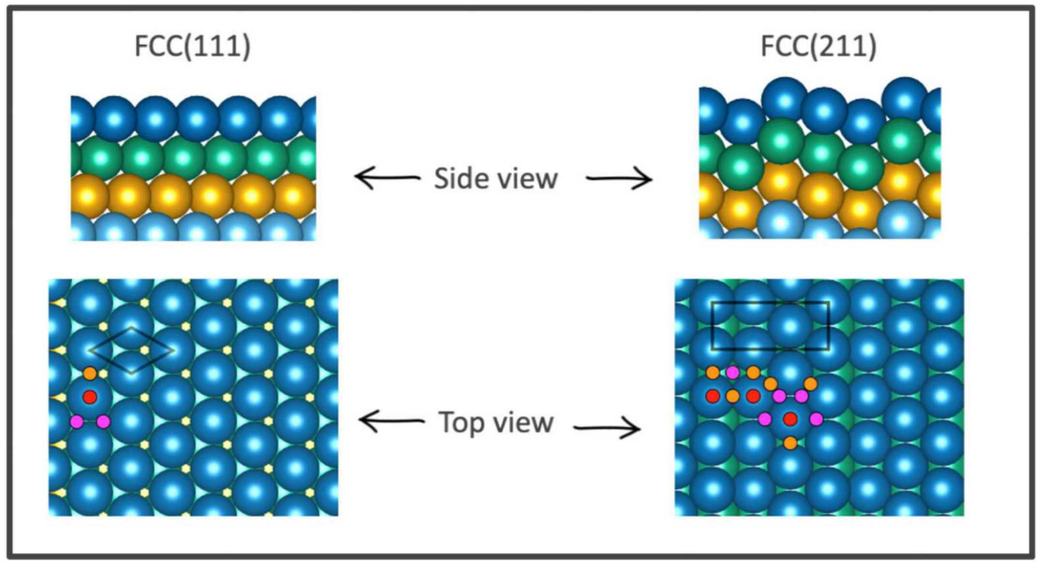
Sandia postdoc

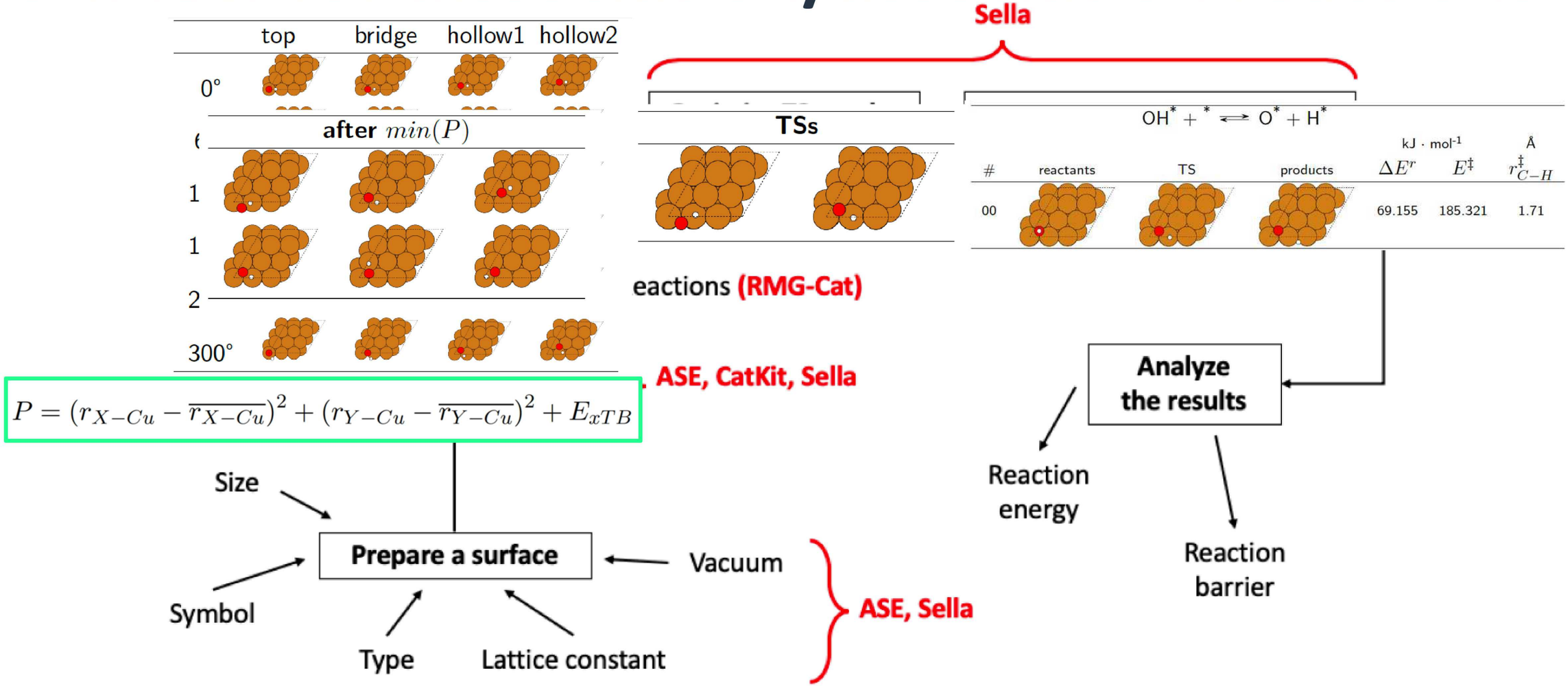
RMG reaction representation

```
- index: 0
reaction: OHX + X <=> OX + HX
reaction_family: Surface_Abstraction
reactant: |
multiplicity -187
1 *1 O u0 p0 c0 {2,S} {4,S}
2 *2 H u0 p0 c0 {1,S}
3 *3 X u0 p0 c0
4    X u0 p0 c0 {1,S}
product: |
multiplicity -187
1 *1 O u0 p0 c0 {4,S}
2 *2 H u0 p0 c0 {3,S}
3 *3 X u0 p0 c0 {2,S}
4    X u0 p0 c0 {1,S}
```





Workflow for dissociation/association reactions



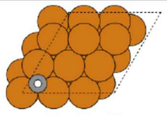
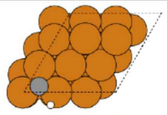
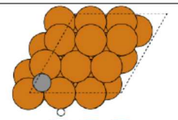
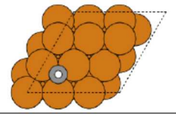
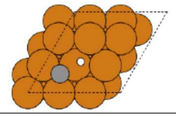
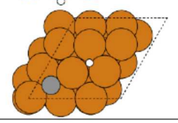
The workflow is ASE based.
Symmetrically equivalent structures are filtered between steps.
Geometry optimization is done with Sella, our own optimizer.

https://github.com/grimme-lab/xtb
https://gitlab.com/ase/ase
https://github.com/SUNCAT-Center/CatKit
https://github.com/zadorlab/sella

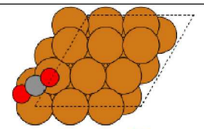
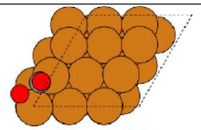
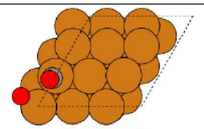
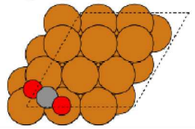
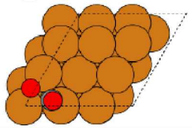
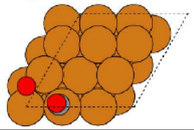
Hermes, E. D.; Sargsyan, K.; Najm, H. N.; Zádor, J., *J. Chem. Theory Comp.* **2019,** *15* 6536-6549.

Further examples

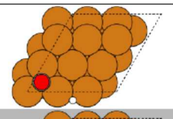
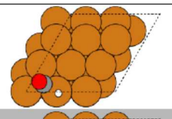
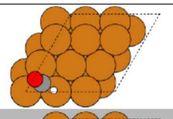
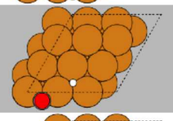
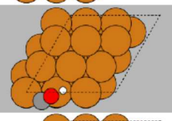
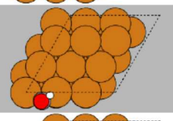
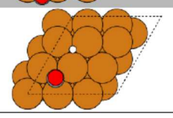
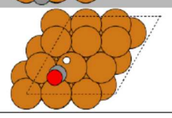
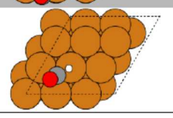
$CH^* + {}^* \rightleftharpoons C^* + H^*$

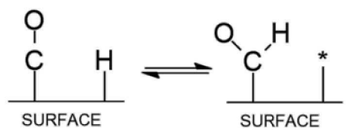
#	reactants	TS	products	ΔE^r (kJ · mol^{-1})	$E^{\ddagger}$ (kJ · mol^{-1})	$r^{\ddagger}_{C-H}$ (Å)
00				132.836	183.297	1.82
01				117.379	197.932	2.00

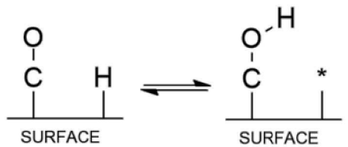
$CO^* + O^* \rightleftharpoons CO_2^* + {}^*$

	reactants	TS	products	ΔE^r	$E^{\ddagger}$	$r^{\ddagger}_{C-O}$
00				-111.682	50.449	1.77
01				-118.958	46.756	1.82

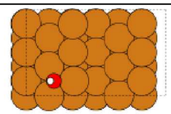
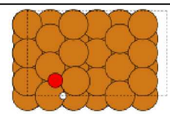
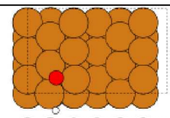
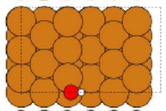
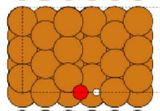
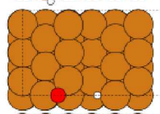
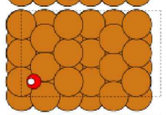
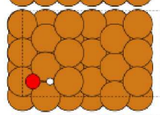
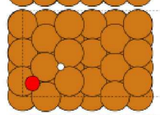
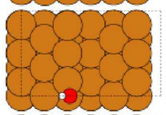
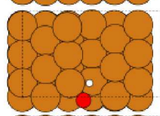
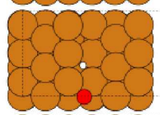
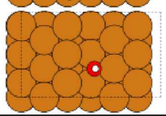
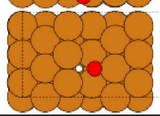
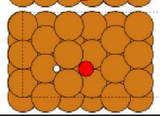
$CO^* + H^* \rightleftharpoons HCO^* + {}^*$

#	reactants	TS	products	ΔE^r (kJ · mol^{-1})	$E^{\ddagger}$ (kJ · mol^{-1})	$r^{\ddagger}_{X-H}$ (Å)
00				93.809	103.403	1.52
01				123.530	223.419	1.28
02				86.842	96.120	1.41



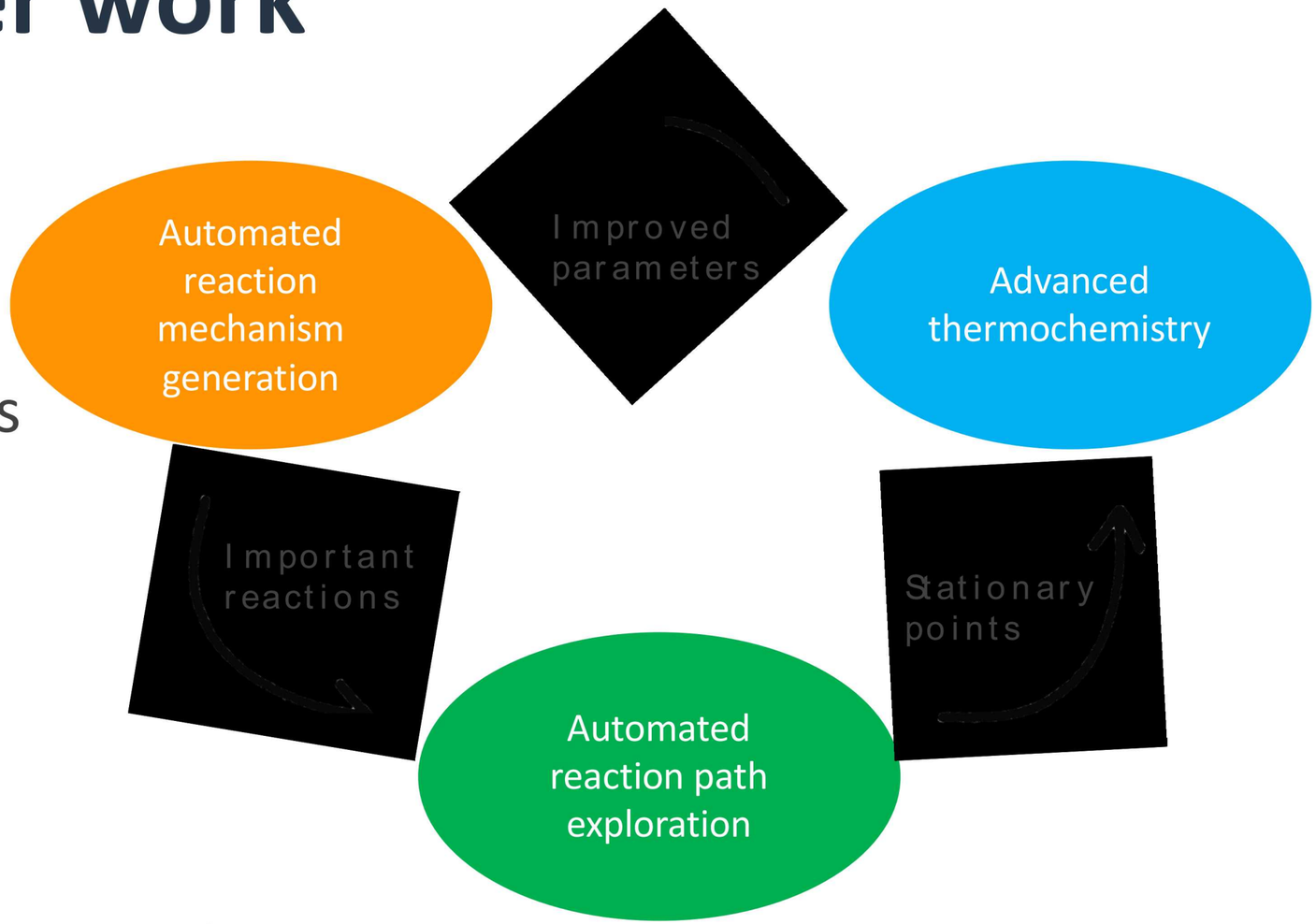


$OH^* + {}^* \rightleftharpoons H^* + O^*$

#	reactants	TS	products	ΔE^r (kJ · mol^{-1})	$E^{\ddagger}$ (kJ · mol^{-1})	$r^{\ddagger}_{X-H}$ (Å)
03				69.598	157.963	1.57
05				95.090	148.133	1.69
07				63.890	150.247	1.55
08				114.593	200.130	1.64
11				23.954	107.021	1.53

Summary and further work

- Coverage dependence
- Bifunctional materials, oxides
- Kinetic Monte Carlo simulations



- Extend methodology to other reaction types
- Scale the code