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Automated Construction of Microkinetic Models with RMG-Cat for Mapping the Degree of Rate Control

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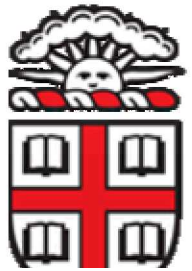
Northeastern



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Why microkinetic models?

- Microkinetic models are a collection of elementary reactions describing a complex chemical phenomena
- Traditional kinetic models simplify the chemistry by making assumptions
- Microkinetic models do **not** make *a priori* assumptions to simplify the chemistry

$$R_1 + R_2 \rightleftharpoons P$$

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

Our strategy: use computers to build the mechanism!

We have RMG for heterogeneous catalysis!

Our code is merged with the newest release of RMG version 2.4.0:

Reaction Mechanism Generator

- developed for combustion (H, C, O)
- open source, Python based
- mature (~50+ graduate-student years of development)
- recently expanded to include (N, S, Si)
- some solvent/solution effects

reactionmechanismgenerator.github.io/RMG-Py/

How do you teach a computer to think like a chemist?

- recognize when 2 or more species are the same
- predict the thermo-kinetic parameters
- find all possible elementary reactions
- determine which reactions are important
- be flexible for new reactants on novel materials

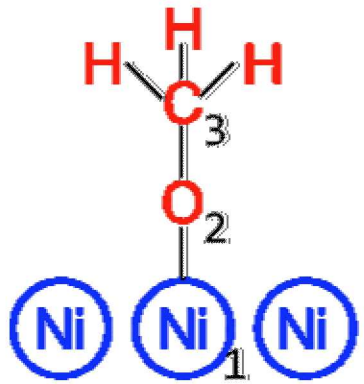
➢accomplish all of the above in a bug-free manner quicker than a grad student could!

RMG represents specie using graph theory

atom number	element	unpaired elec.	lone pair	formal charge	bonds
1	C	u0	p0	c0	{2,S}{3,S}{4,S}{5,S}
2	O	u0	p2	c0	{1,S}{6,S}
3	H	u0	p0	c0	{1,S}
4	H	u0	p0	c0	{1,S}
5	H	u0	p0	c0	{1,S}
6	H	u0	p0	c0	{2,S}

we have added new features for adsorbates

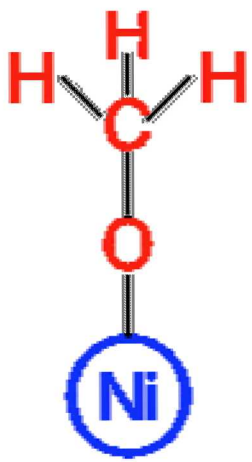
e.g. "single metal bond"



"can I find this structure in my thermo database?"

✓**recognize when 2 or more species are**

RMG-Cat estimates adsorbate thermochemistry using simple rules of thumb



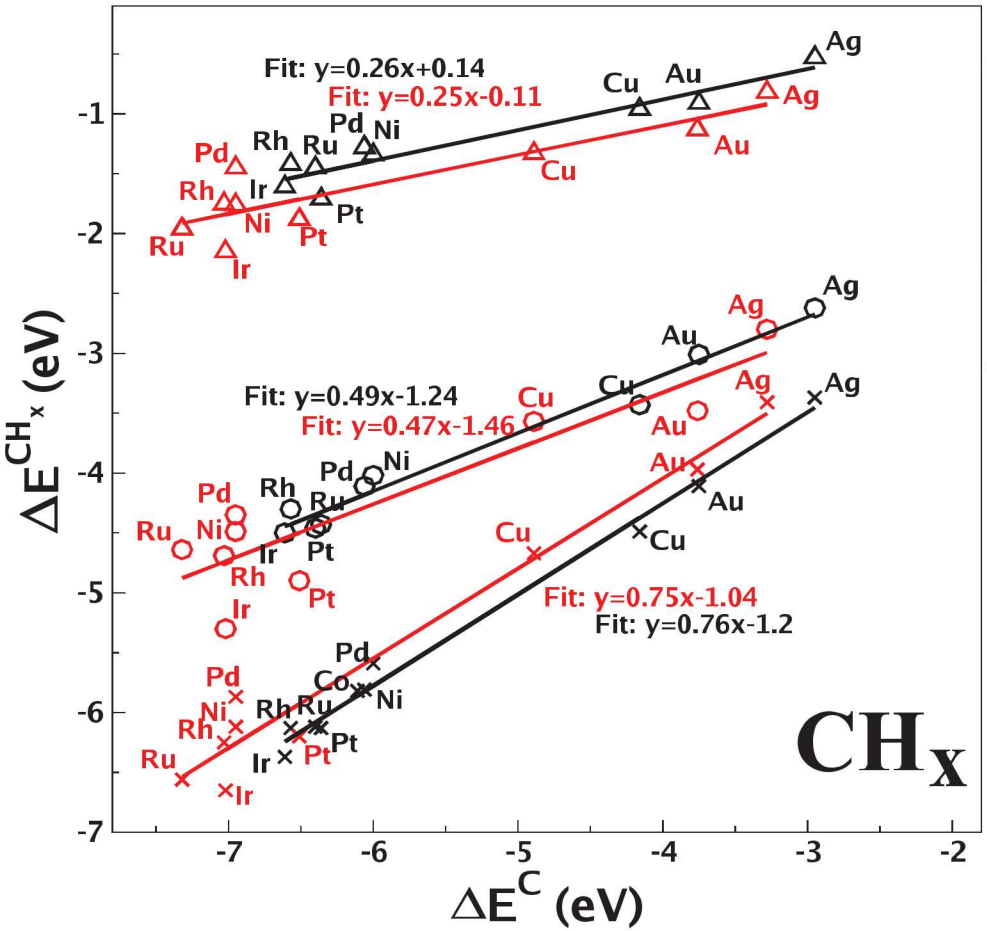
gas-phase species from database or group additivity estimate

$$\Delta_f H(298) = \Delta_f H_{gas} + \Delta H_{adsorption} + \Delta E_{binding}$$
$$\Delta S(298) = \Delta S_{gas} + \Delta S_{adsorption}$$
$$Cp(T) = Cp_{gas} + \Delta Cp_{adsorption}$$

estimated from statistical thermodynamics

✓**predict the thermodynamic parameters**

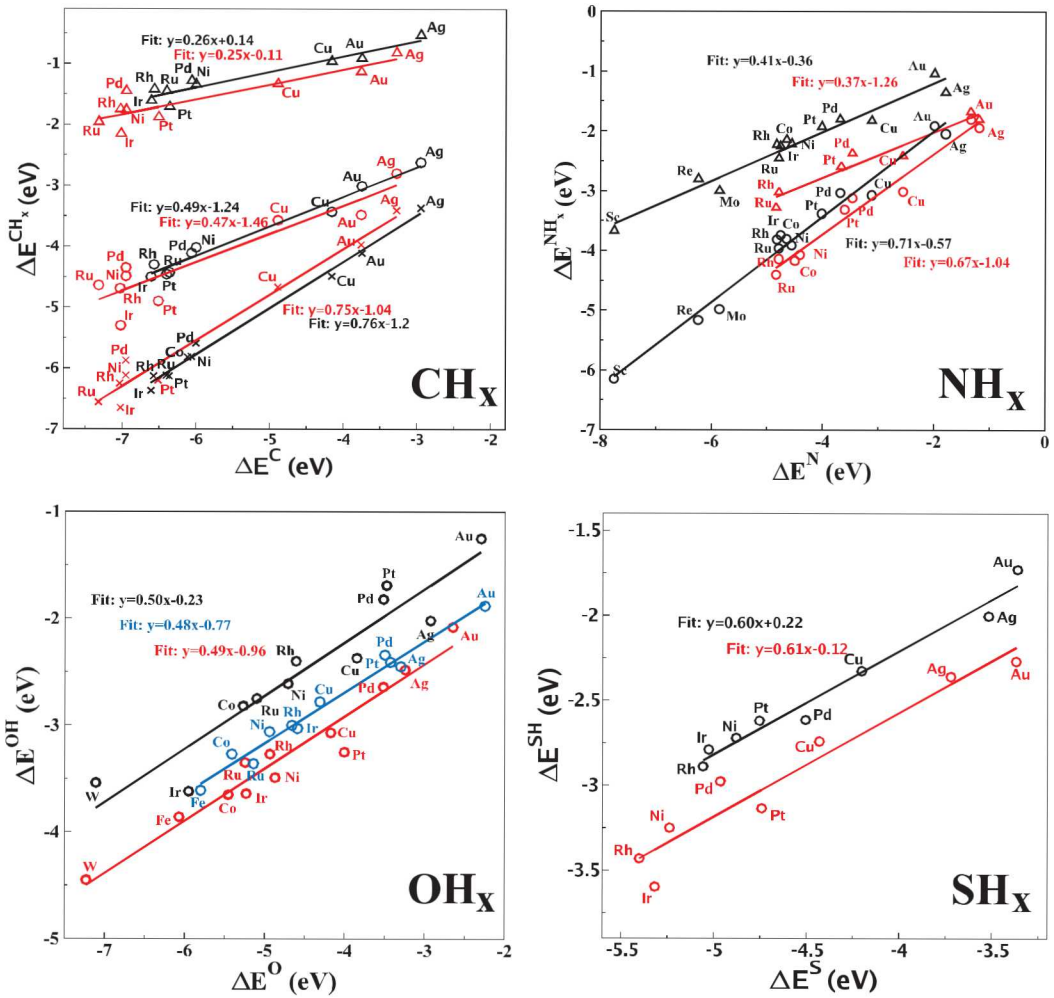
We can now estimate binding energies via linear scaling relations



Abild-Pedersen et al., Phys. Rev. Lett. (2007)

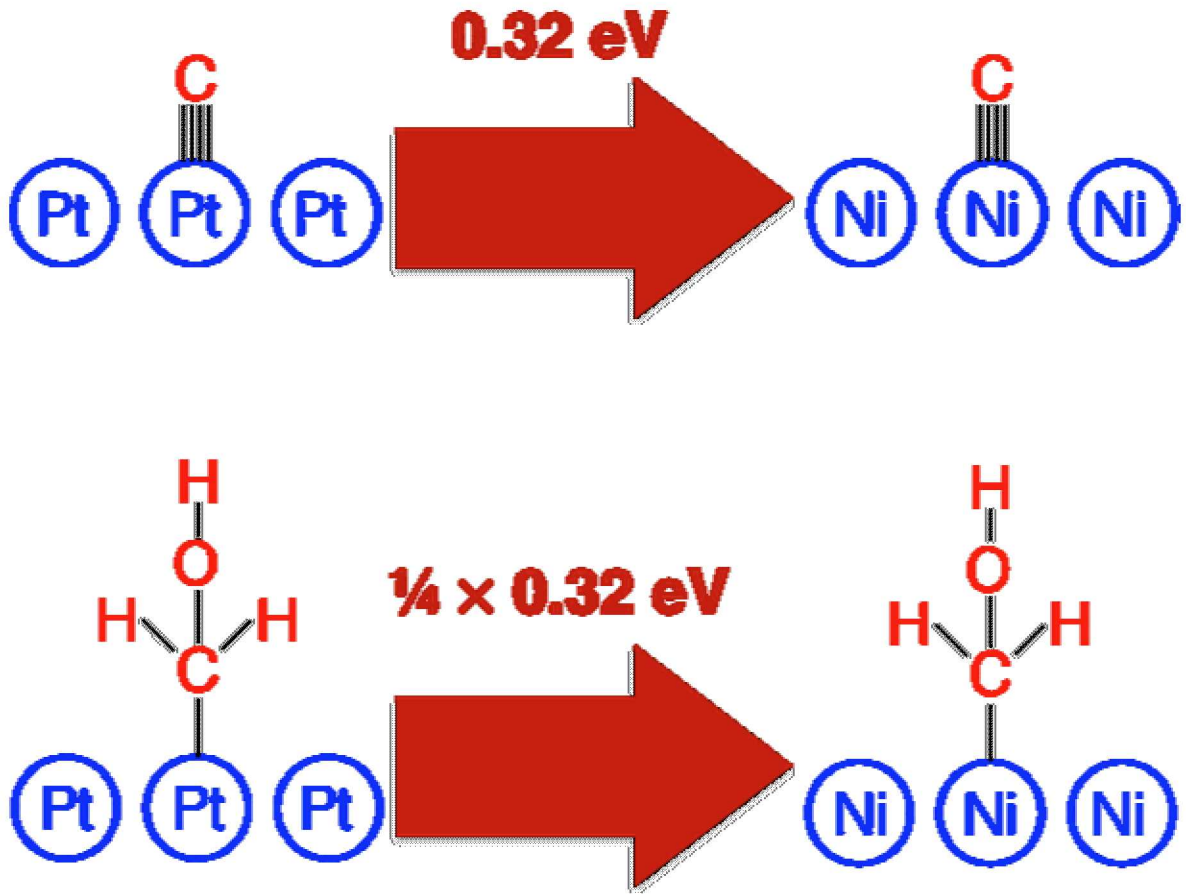
On many metals, simple rules can predict the binding energy

We can now estimate binding energies via linear scaling relations

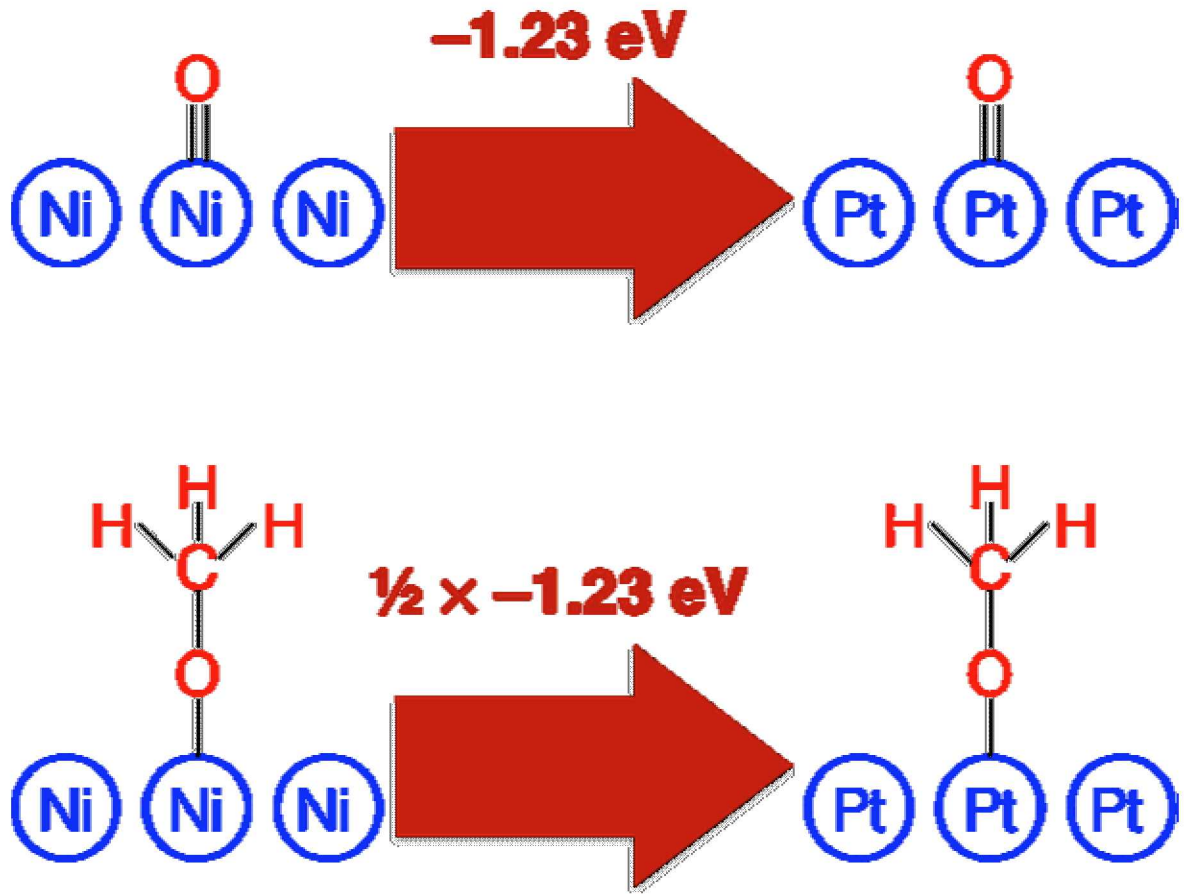


Abild-Pedersen et al., Phys. Rev. Lett. (2007)

Change in binding energy scales with normalized bond order

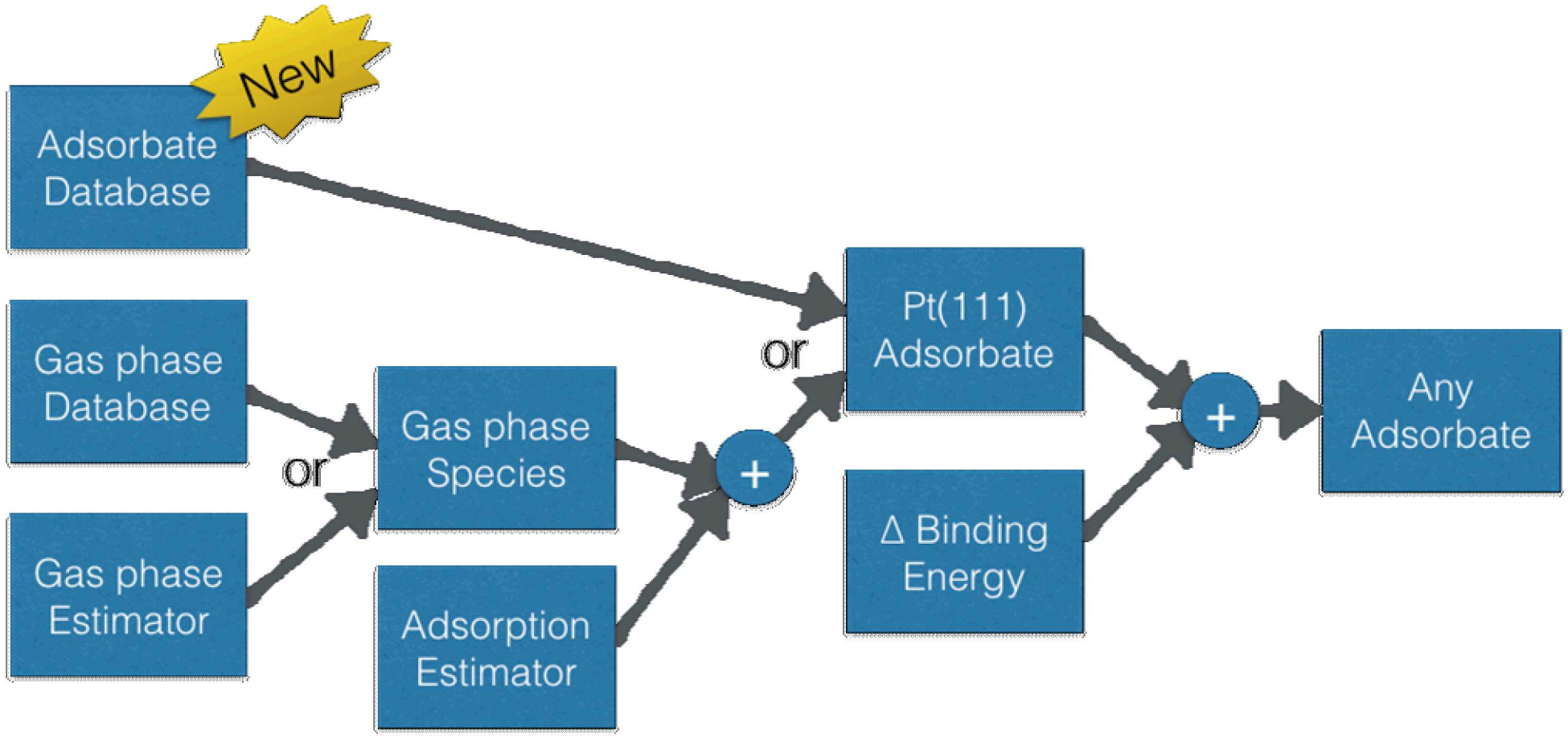


Change in binding energy scales with normalized bond order



✓**reactants on any material**

We can now estimate thermochemistry of any adsorbate



RMG uses reaction families to propose new reactions

Each species is decomposed into functional groups, and the functional groups are reacted according to templates

RMG has over 40 reaction families:

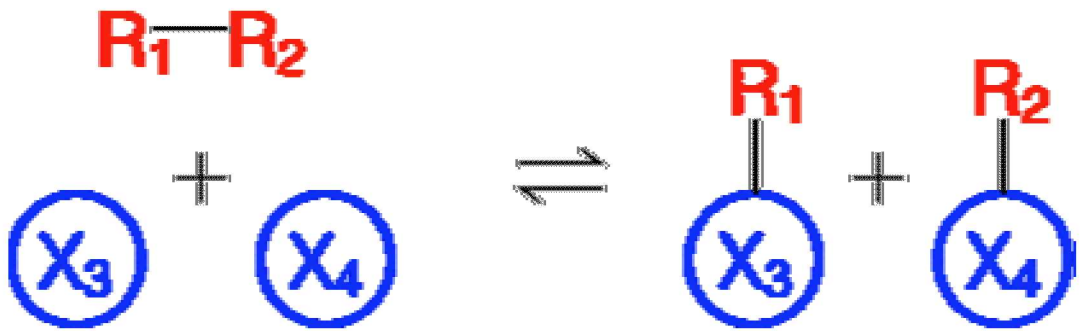
- H-abstraction
- disproportionation
- β-scission
- Diels-Alder
- Korcek
- NO_2 / ONO conversion
- cycloaddition
- etc.

RMG families specific to heterogeneous catalysis are…

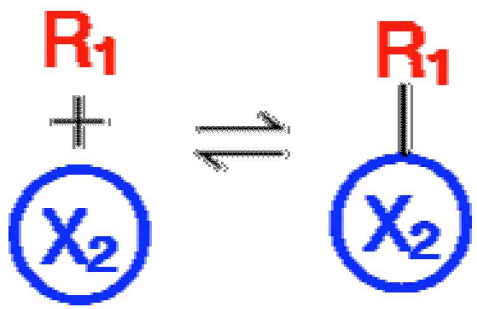
I. Adsorption

1. dissociative adsorption:

$$CH_4(g) + 2* \rightleftharpoons CH_3* + H*$$

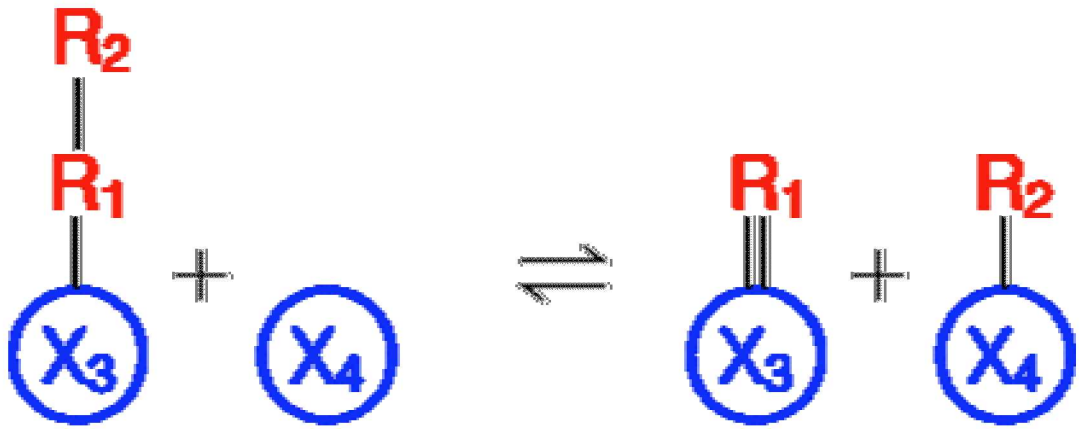


2. non-dissociative adsorption:
   - single bond: $CH_3(g) + * \rightleftharpoons CH_3*$
   - double bond: $CO(g) + * \rightleftharpoons CO*$
   - di-sigma bond: $CH_2O(g) + 2* \rightleftharpoons H_2C*O*$
   - vdW bond: $H_2O(g) + * \rightleftharpoons H_2O*$



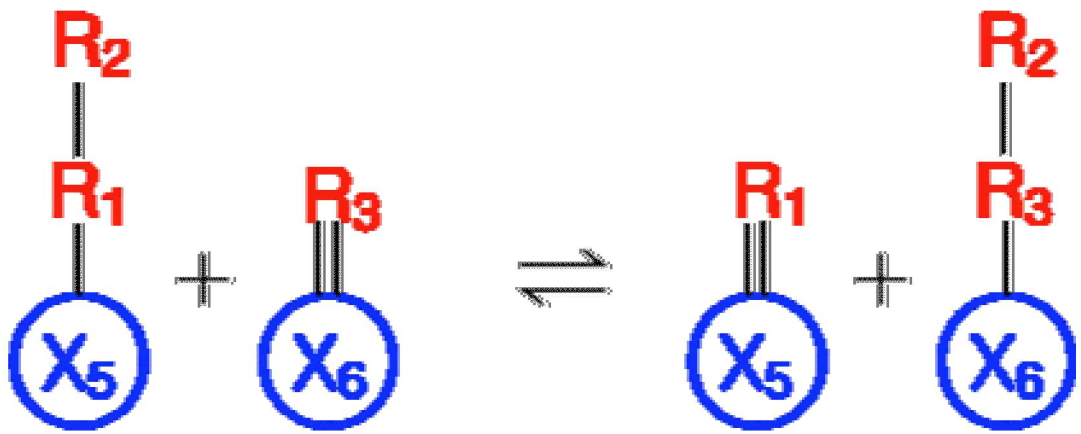
II. Dissociation

$CH_3^* + * \rightleftharpoons CH_2^* + H^*$



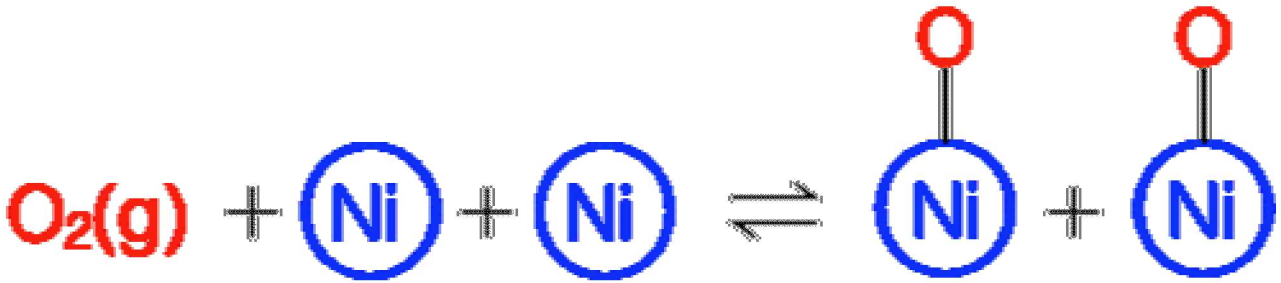
III. Abstraction

$CH_3^* + O^* \rightleftharpoons CH_2^* + OH^*$



✓**find all possible elementary reactions**

As with thermo, RMG first looks for rate coefficients in a database:



"can I find this reaction in my kinetics database?"

If not, then estimate it.

RMG-Cat uses bond-specific BEP relations,

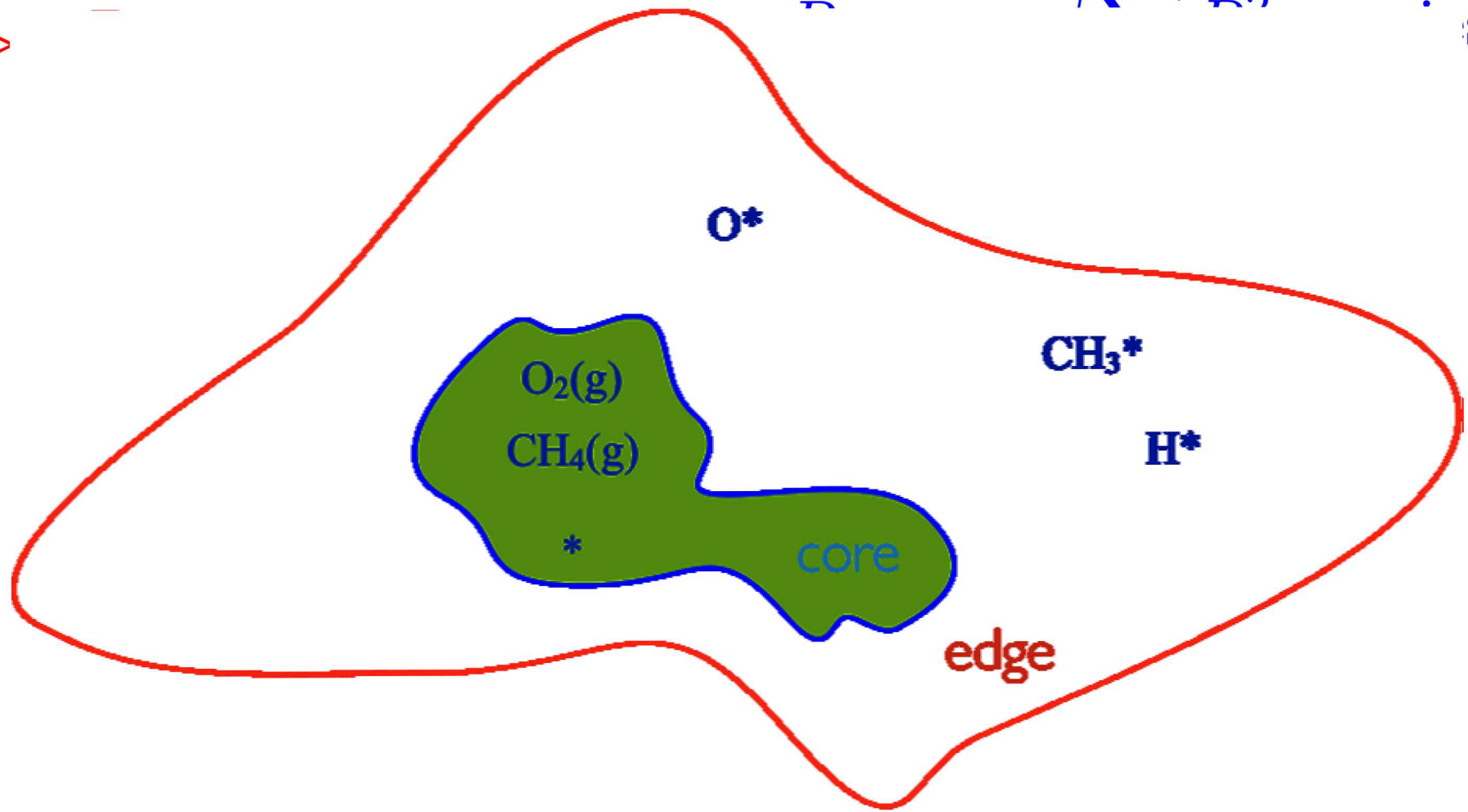
but other options are available

$$E_a = E_o + \alpha \Delta H$$

✓**predict the kinetic parameters**

To illustrate how RMG grows a mechanism, start with $CH_4(g)$, $O_2(g)$ and vacant site *

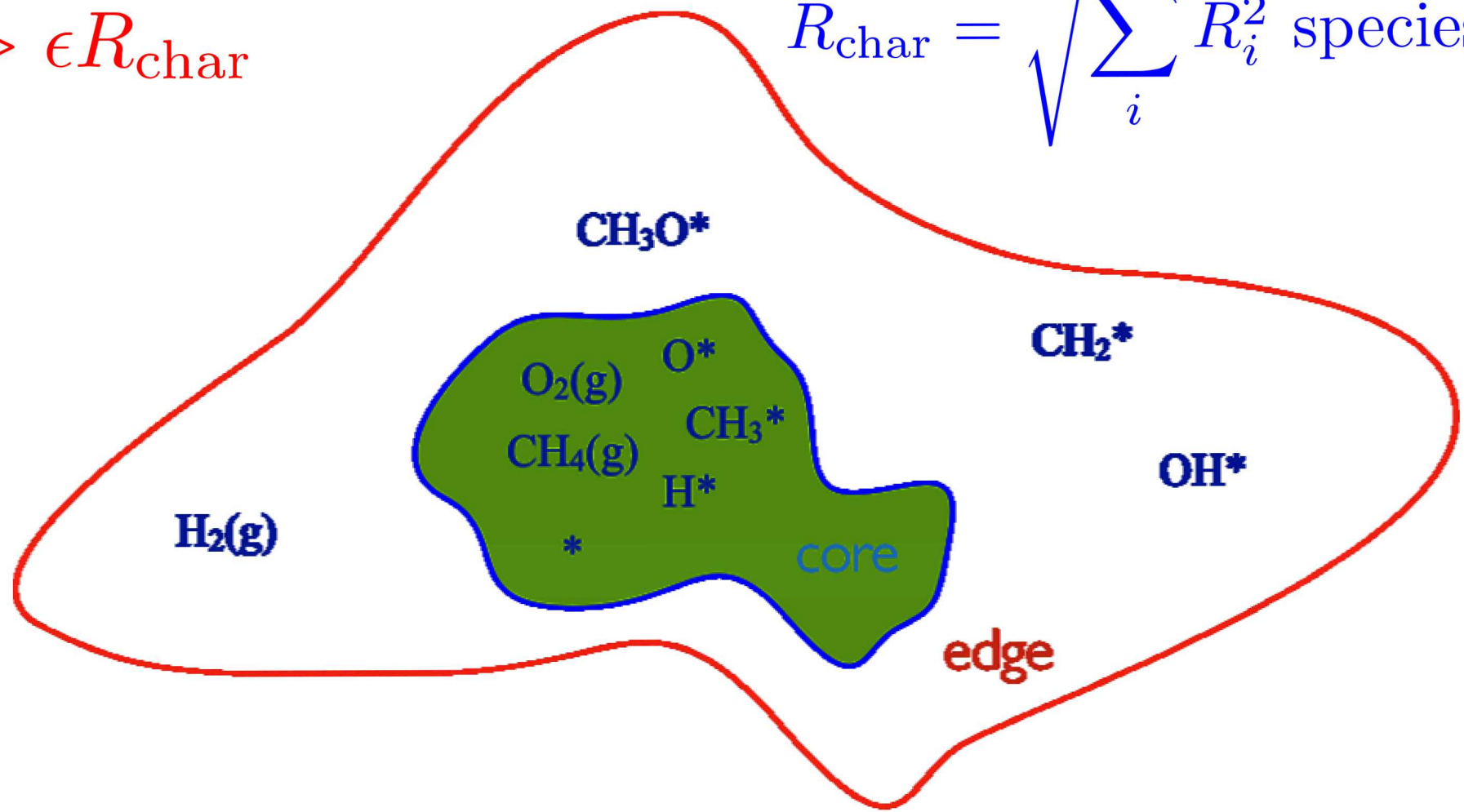
$R_{\text{edge}} >$ $\sqrt{\sum R^2}$ s $i \in$ core



Add CH_3*, H*, and O* to the core and start over

$$R_{\text{edge}} > \epsilon R_{\text{char}}$$

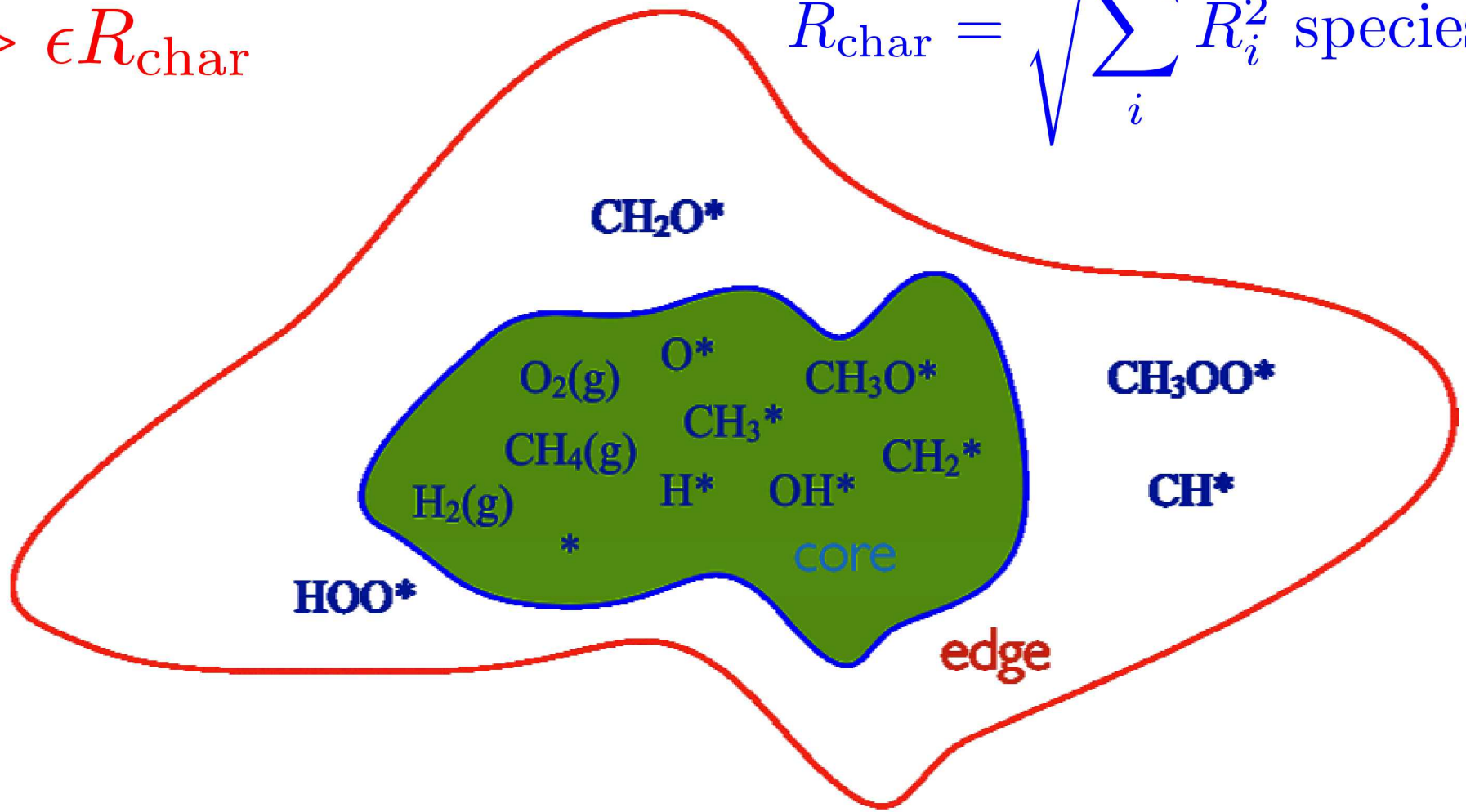
$$R_{\text{char}} = \sqrt{\sum_i R_i^2} \text{ species } i \in \text{core}$$



Add CH_3O^*, OH^*, CH_2^*, and $H_2(g)$ to the core and start over

$R_{\text{edge}} > \epsilon R_{\text{char}}$

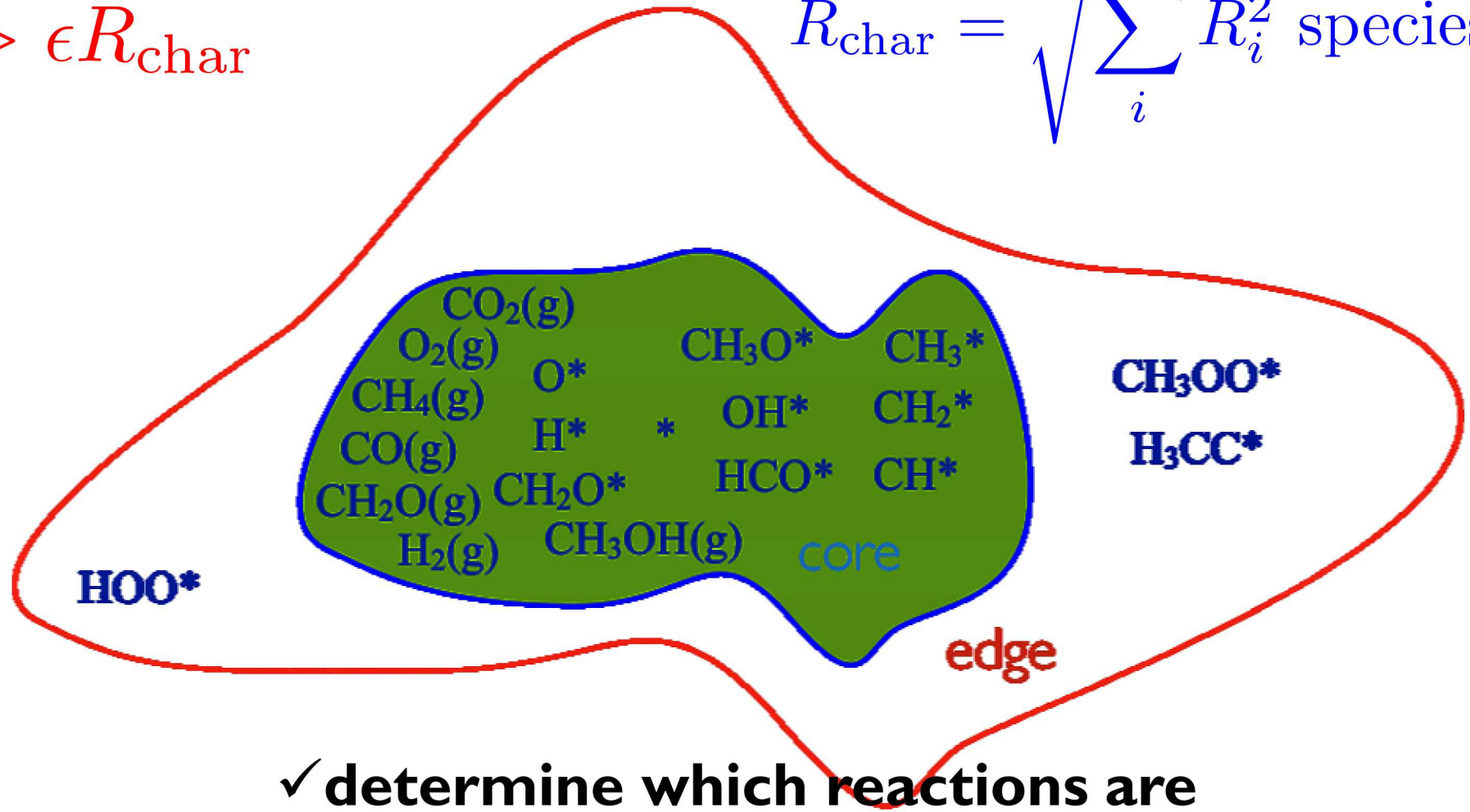
$R_{\text{char}} = \sqrt{\sum_i R_i^2}$ species $i \in$ core



Continue to select species with high fluxes, and leave slow species on the edge

$R_{\text{edge}} > \epsilon R_{\text{char}}$

$R_{\text{char}} = \sqrt{\sum_i R_i^2}$ species $i \in$ core



✓**determine which reactions are important**

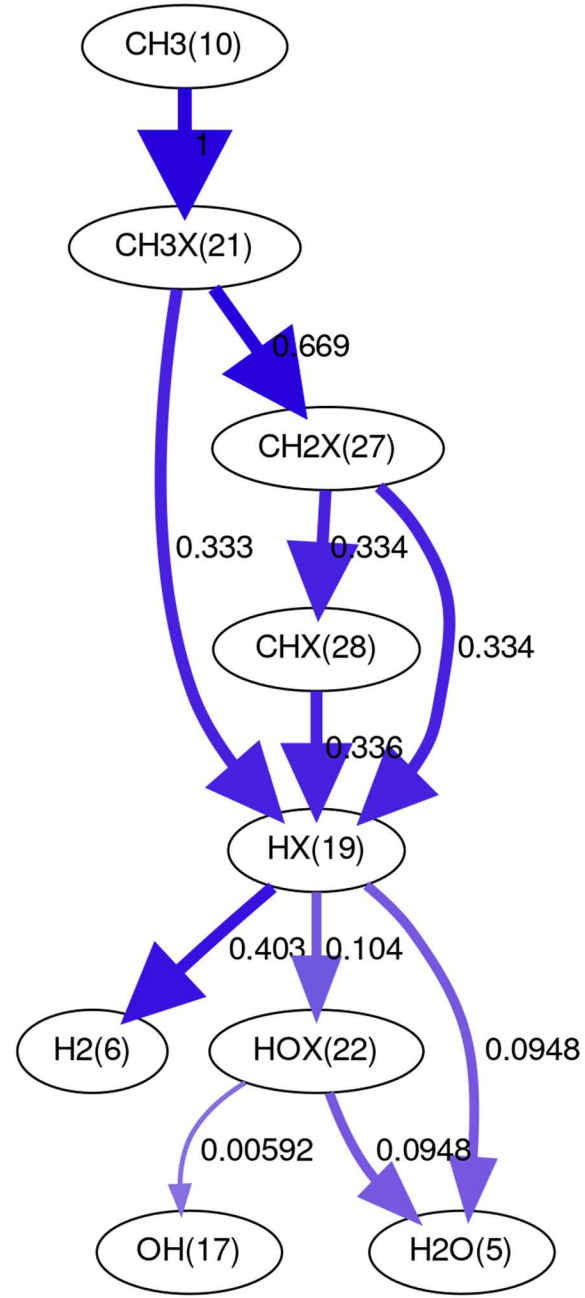
Catalytic Partial Oxidation (CPOX) of methane

- Reaction of O_2 with hydrocarbons to produce a hydrogen-rich synthesis gas
  - a mixture of hydrogen and carbon monoxide

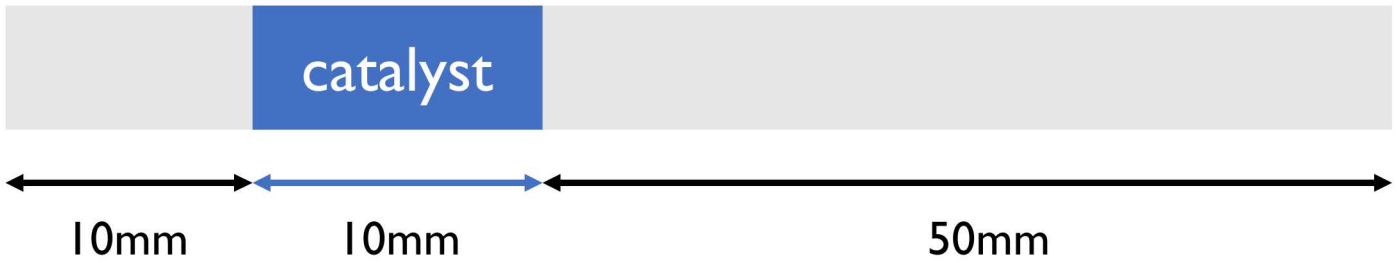
$$CH_4 + O_2 \rightleftharpoons CO + H_2$$

- Extremely important in industry
- Energy conversion with fewer pollutants than coal

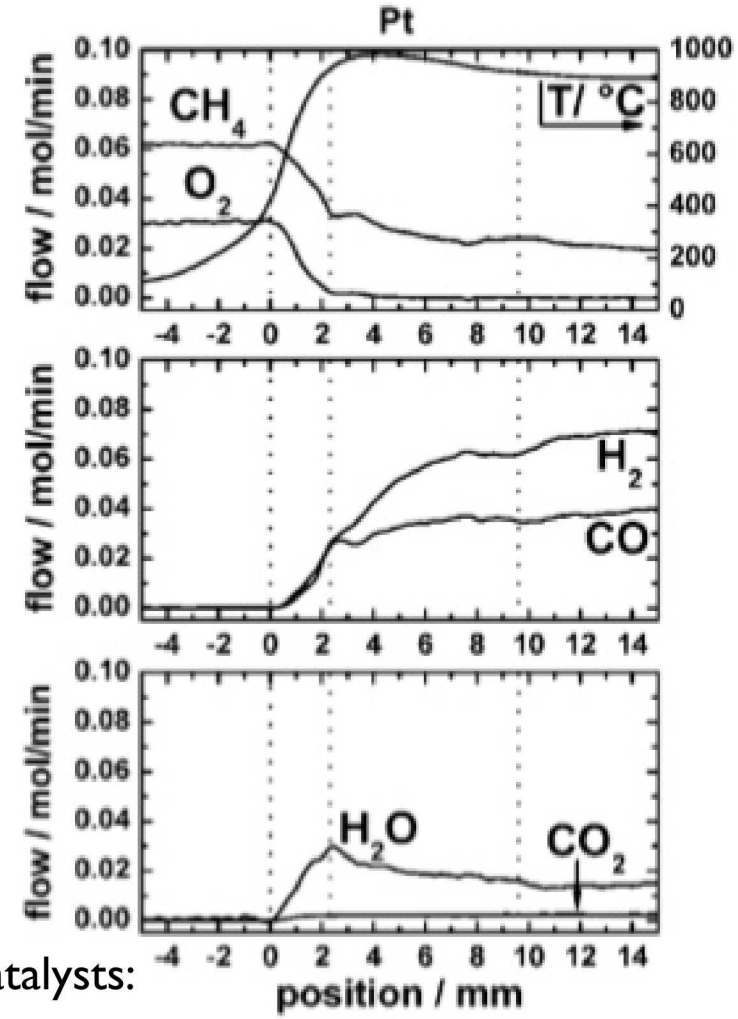
Can we find a better catalyst?



CPOX using Pt coated foam monolith

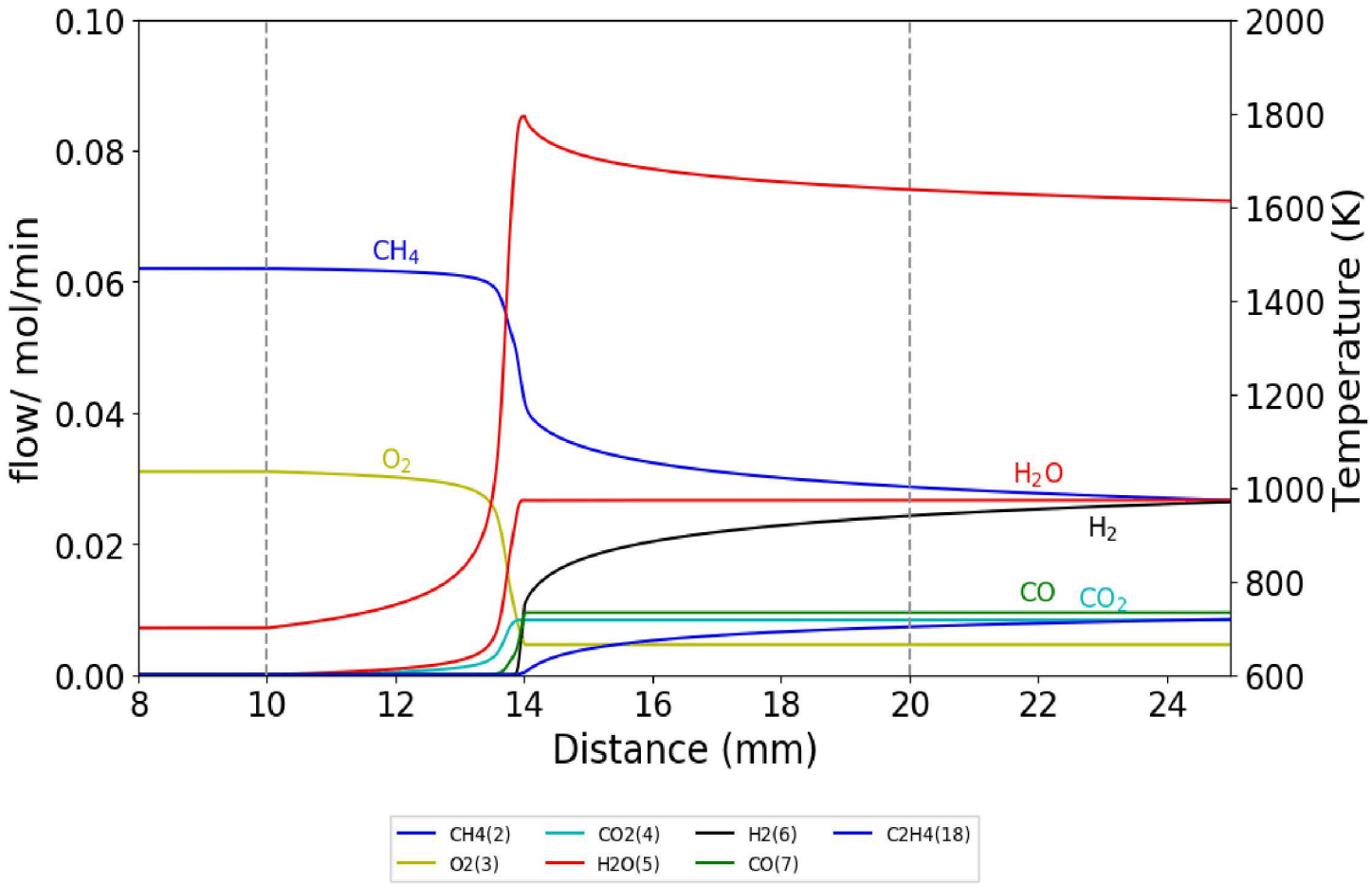


- ✓Thermo database is based on Pt(111)
- Constant inlet flow rate 0.208 mol/min
- Figure shows steady state profile through the tube
- Inlet atomic carbon/oxygen stoichiometry of 1.0



Horn, R., et al. "Methane catalytic partial oxidation on autothermal Rh and Pt foam catalysts: Oxidation and reforming zones, transport effects, and approach to thermodynamic equilibrium." Journal of Catalysis 249.2 (2007): 380-393. doi:10.1016/j.jcat.2007.05.011

CPOX simulated on Pt(111)



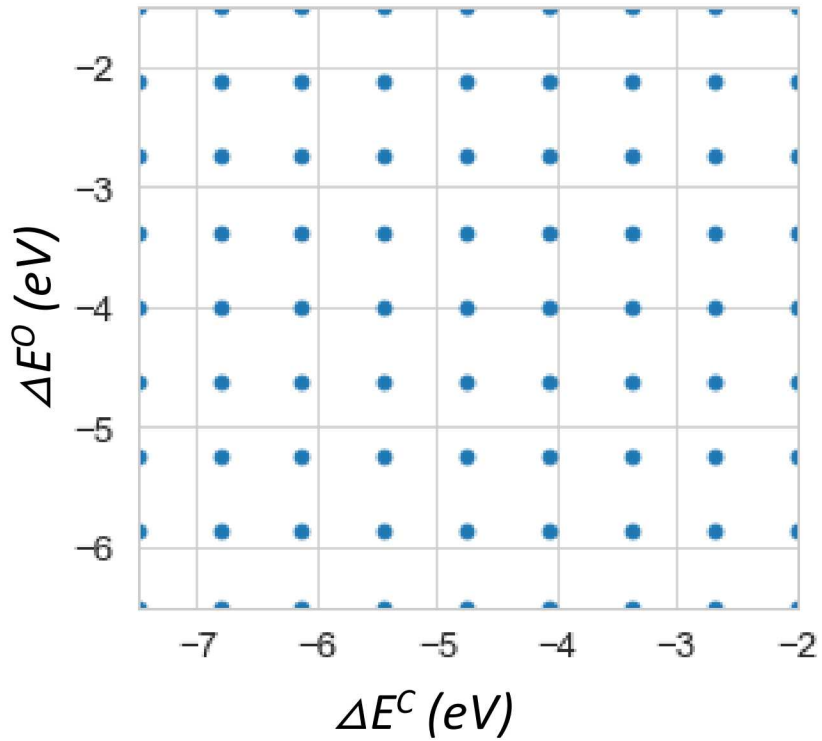
- Does not include diffusion or conduction
- All calculations are based on Pt(111), where experimental values were not
- See both partial and full oxidation

✓ Simulation matches experimental well enough to use LSRs to start simulations on different types of metals

Experiment replicated from Horn et al., J. Catalysis (2007)

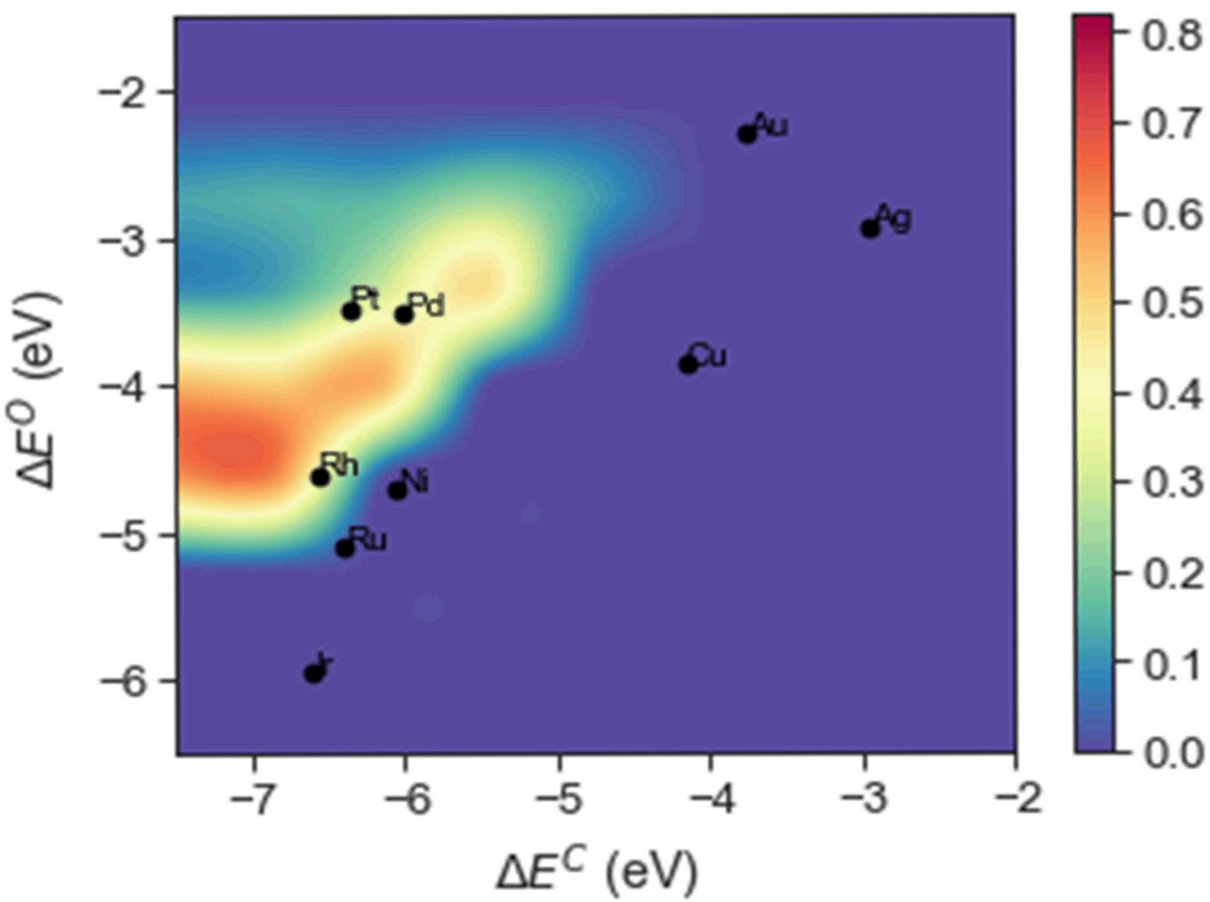
How can we tell which metal is best?

- Ran simulations on 81 different metal surfaces for different atomic carbon and oxygen binding energies
  - ✓Extract selectivities, yields, conversions, maximum temperatures, etc.

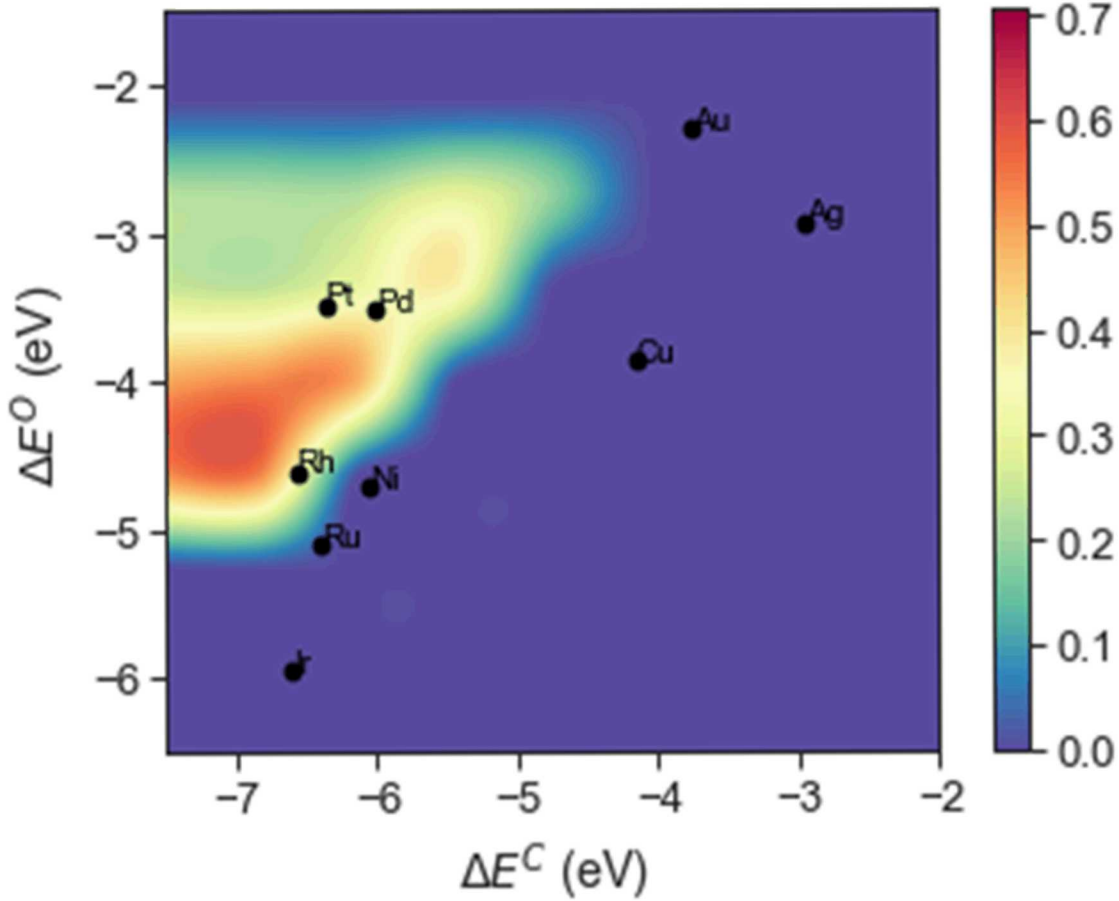


Synthesis gas on different metal surfaces

CO Yield



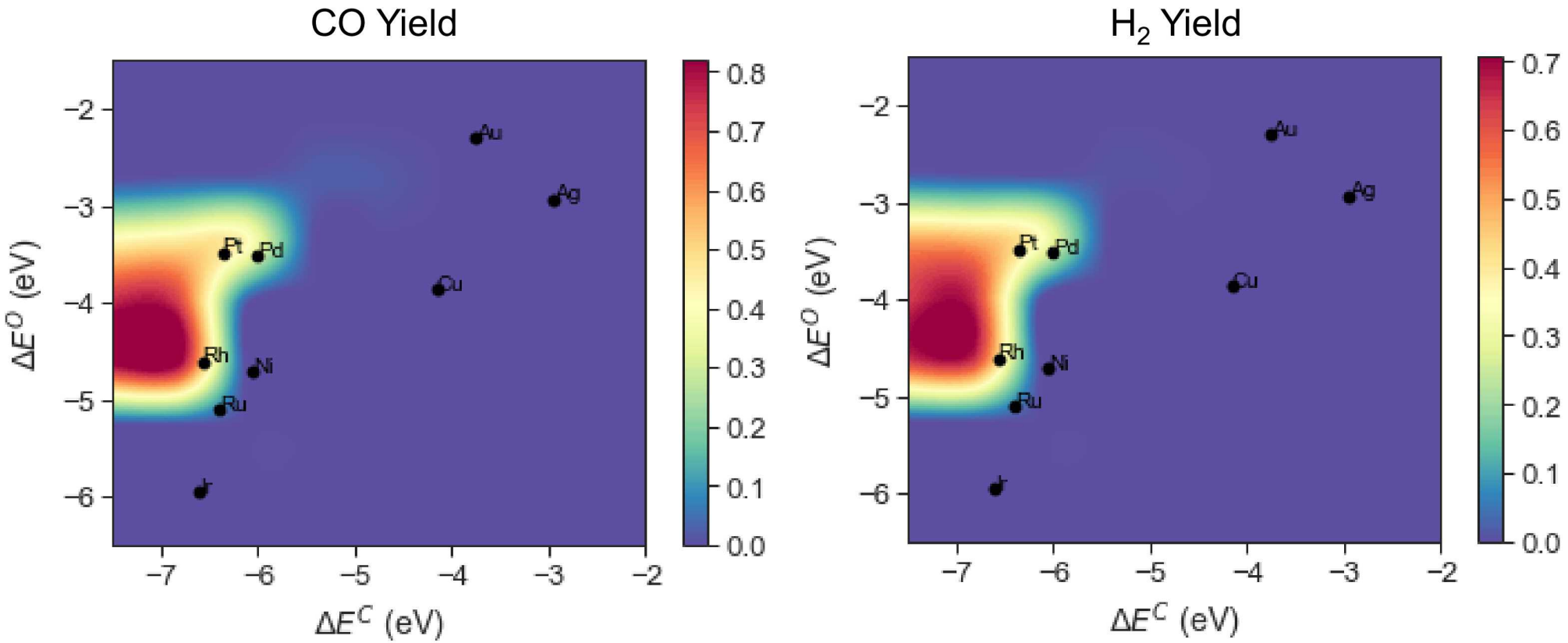
H_2 Yield



Some metals have higher selectivity but lower yield.

What happens if the inlet ratio is changed?

Synthesis gas yield for different inlet gas flows



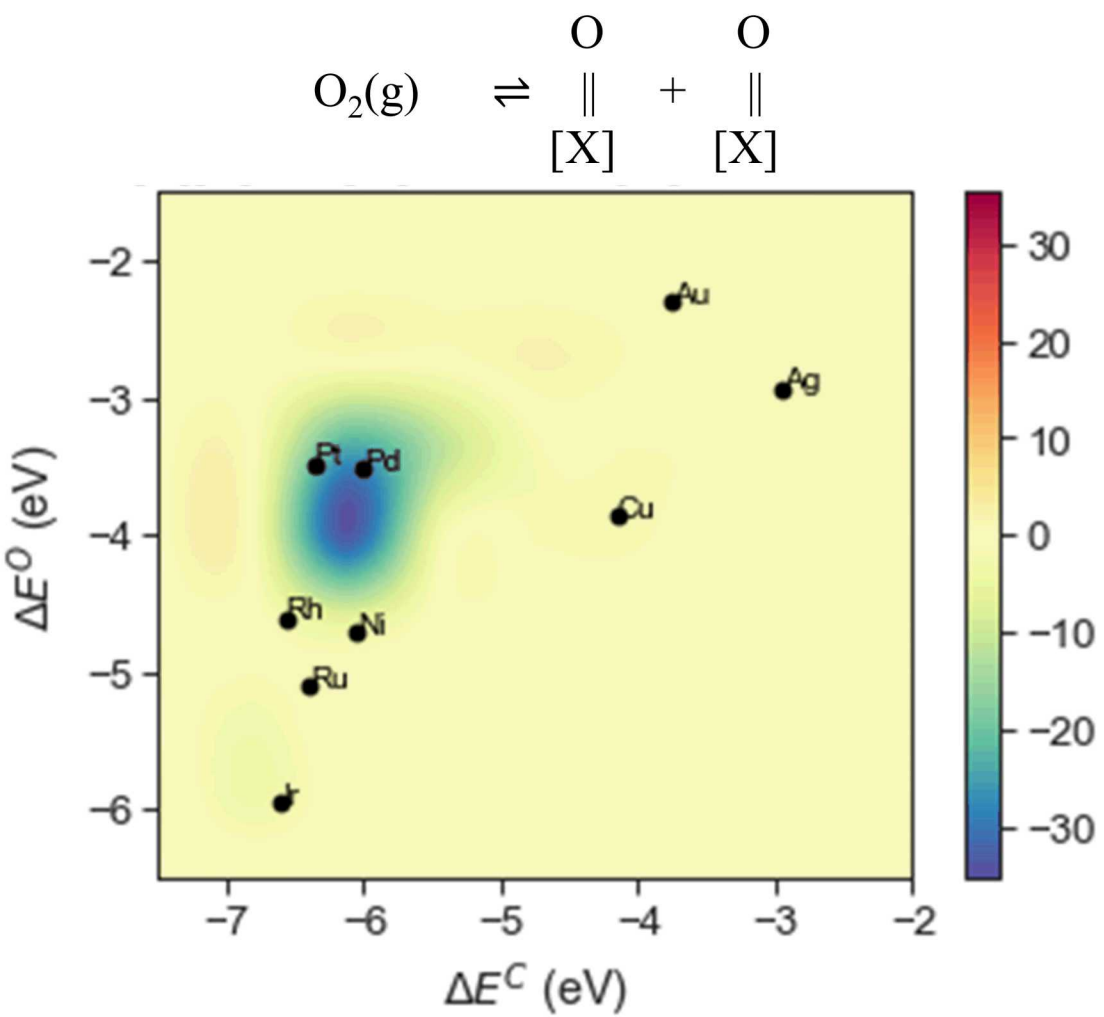
Not only does each metal affect yield,
feed gas composition does as well

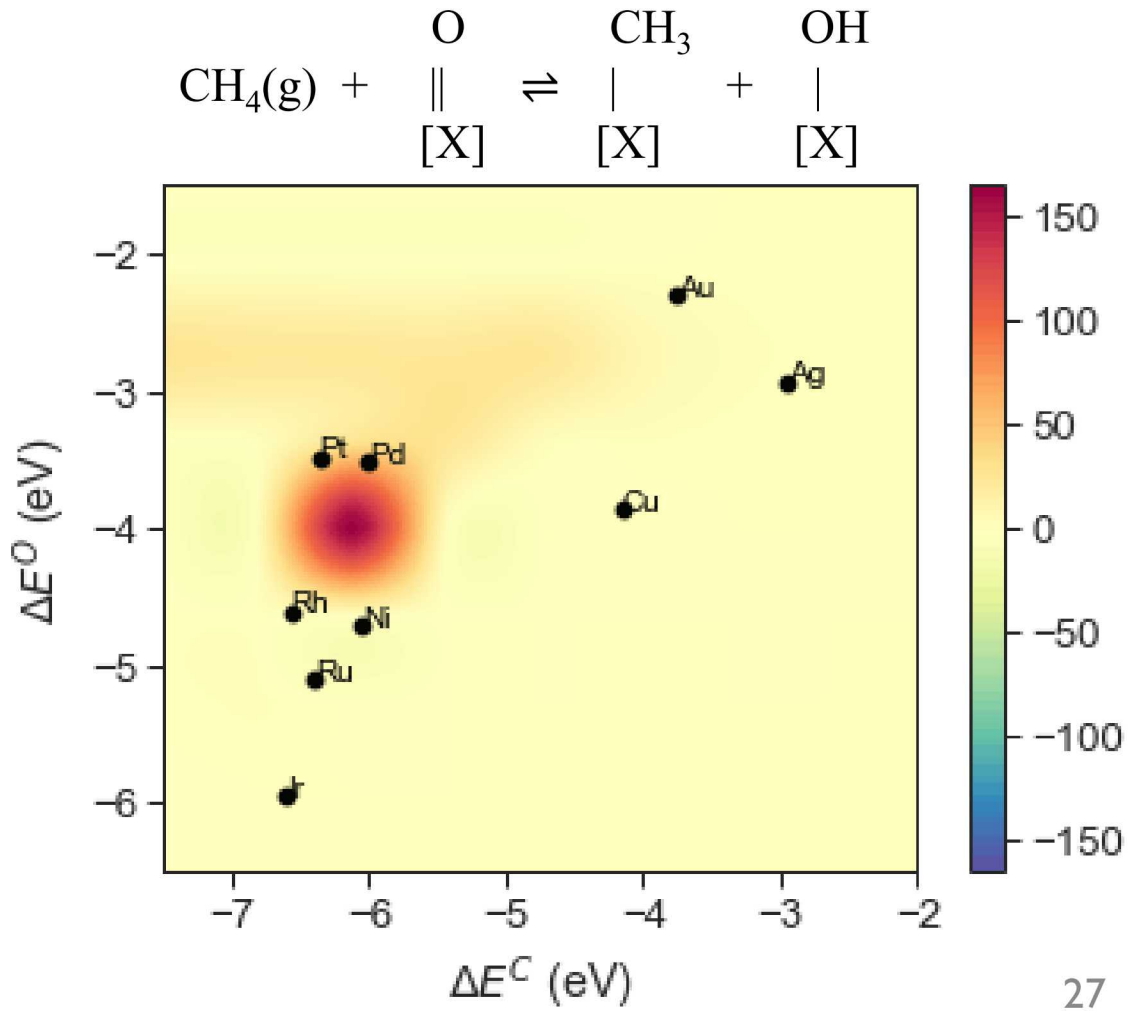
How can we tell which reaction is limiting?

- For each surface simulation, we changed the rate of **each reaction** in the simulation by 1%, one at a time
  - ✓Which reactions are most **rate limiting** (sensitive) on certain metals

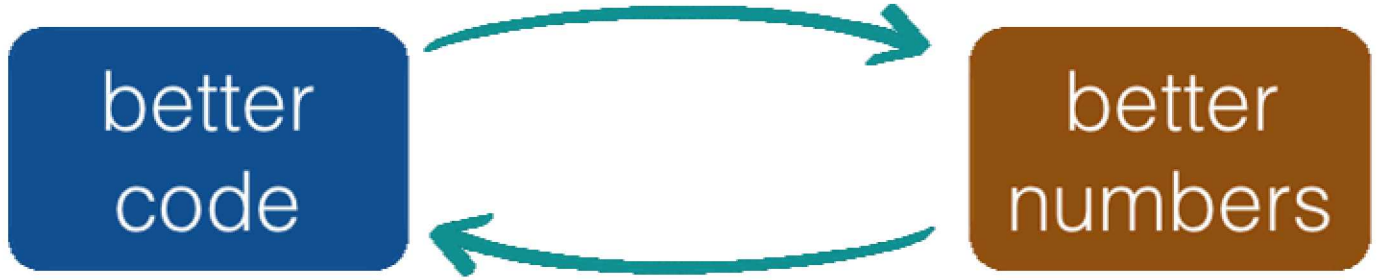
$$\text{Sensitivity} = (X_{\text{H2 yield}} - X_{\text{H2 yield after perturbation}}) \,/\, (X_{\text{H2 yield}} * 0.01)$$

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 a lot of work to do



- Systematic coverage dependence
- Uncertainty quantification
- Kinetic Monte Carlo simulations

- Add more reaction families
  - *Bi-dentate*
  - *Eely-Rideal*
- Kinetics calculations

Want to learn more?

- Read about it
  - *J. Phys. Chem. C*, 2017, *121* (18), pp 9970–9981
    DOI: 10.1021/acs.jpcc.7b02133
- Download it
  - DOI: 10.5281/zenodo.290119 (software)
  - DOI: 10.5281/zenodo.290120 (database)
- Develop it!
  - https://github.com/cfgoldsmith/RMG-Py/tree/cat
  - https://github.com/cfgoldsmith/RMG-database/tree/cat

Contributions

- Built a CPOX model on Pt and validated it with experiments
- Expanded CPOX model on other catalysts using linear scaling relations
- Evaluated syn gas yields, selectivities, and conversions for different inlet ratios
- Conducted sensitivity analyses to target important reactions on different catalysts to see chemistry changes and why that would affect amount of syn gas
- Our model suggests a catalyst with an elemental C binding energy of -6.125 eV and O -4.000 eV gives highest yield, and further research is suggested

owledgements:

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