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Mapping the Degree of Rate ~~Control~~ Sensitivity ~~Using Automated~~ Construction of Microkinetic Models with RMG-Cat

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Northeastern

BROWN

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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-Cat!

Our code is based upon RMG:

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

http://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

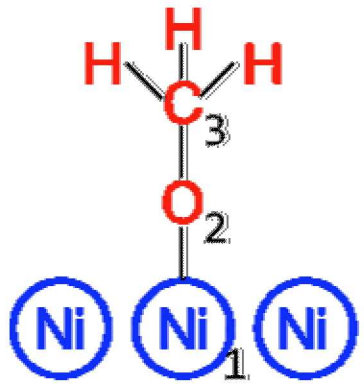
➢accomplish all of the above in a bug-free manner quicker than a grad student could!

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

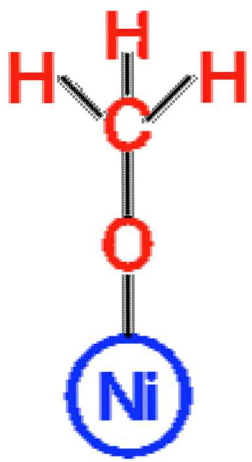
e.g. "single metal bond"



"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



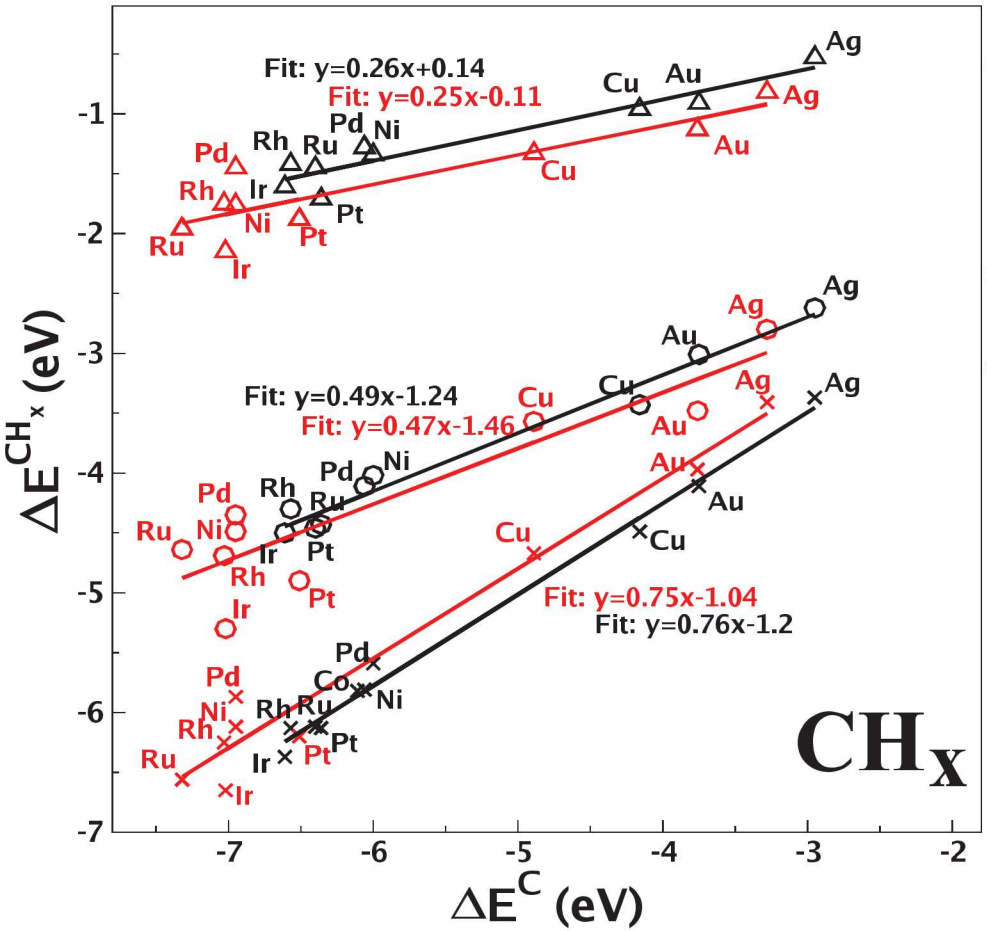
gas-phase species from database or group additivity estimate

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

estimated from statistical thermodynamics

✓**predict the thermodynamic parameters**

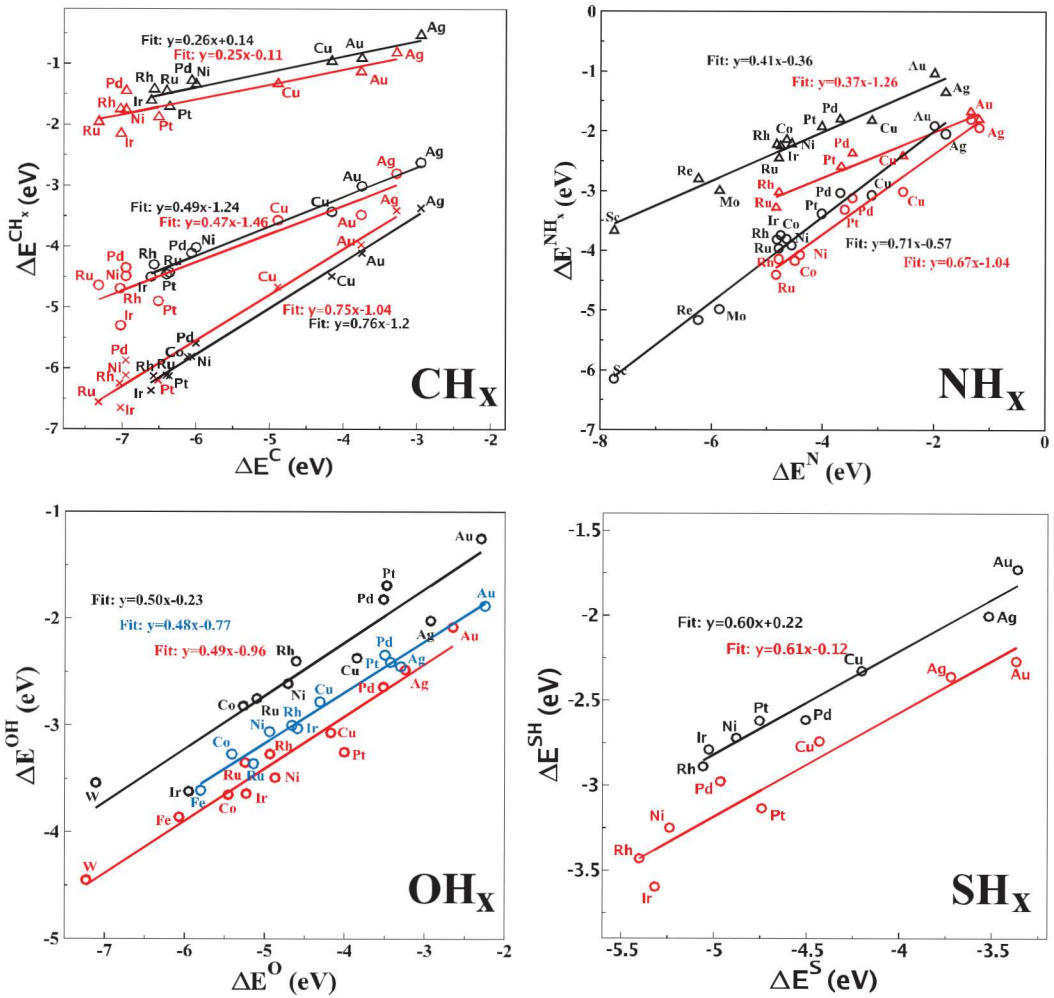
We can now estimate binding energies via linear scaling relations



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

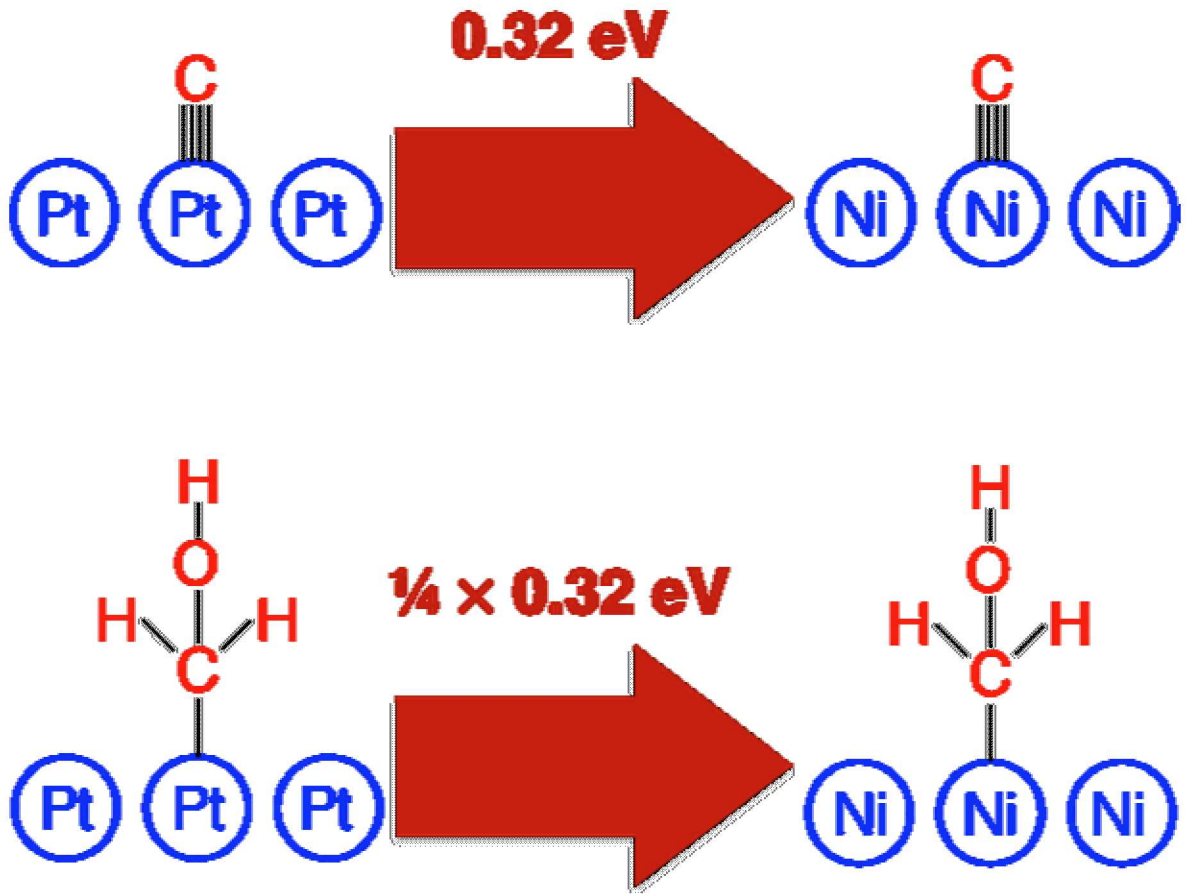
On many metals, simple rules can predict the binding energy

We can now estimate binding energies via linear scaling relations



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

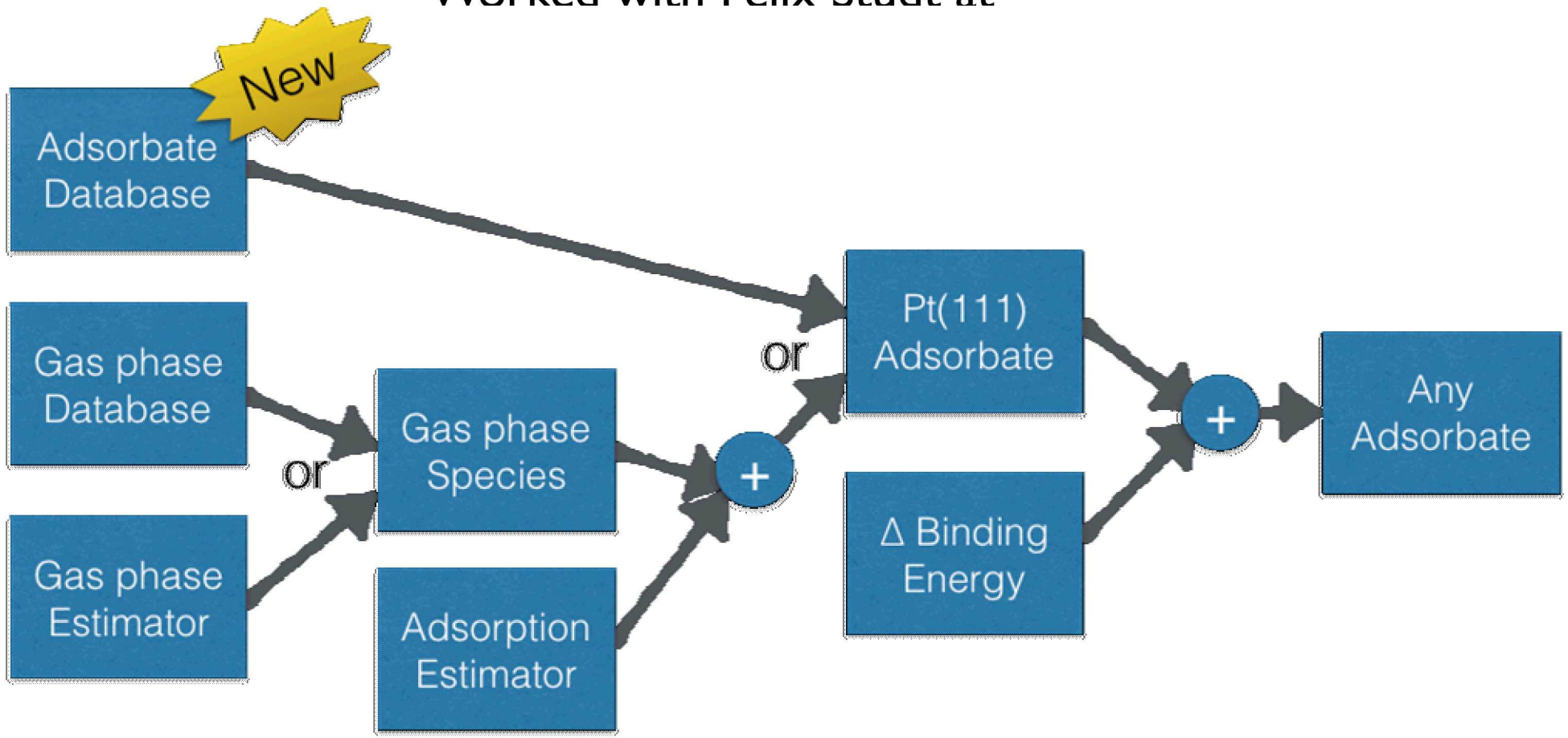
Change in binding energy scales with normalized bond order



✓**reactants on any material**

We can now estimate thermochemistry of any adsorbate

Worked with Felix Studt at



RMG-Cat 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:

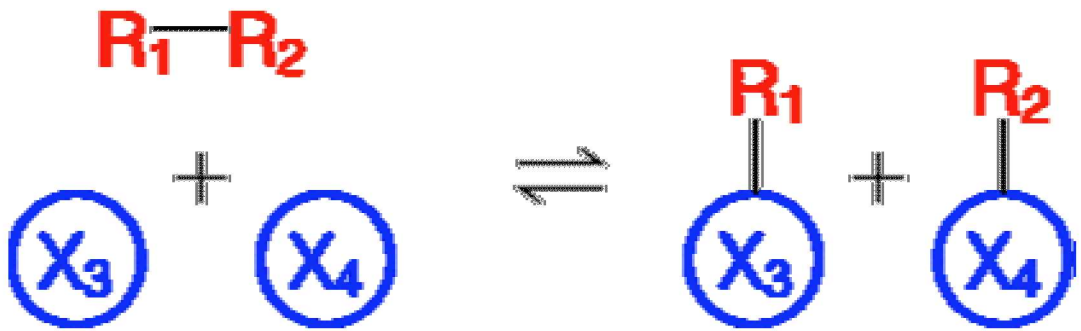
- H-abstraction
- disproportionation
- β-scission
- Diels-Alder
- Korcek
- NO_2 / ONO conversion
- cycloaddition
- etc.

RMG-Cat has some more…

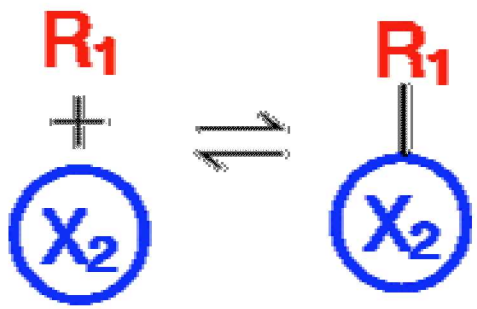
I. Adsorption

1. dissociative adsorption:

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

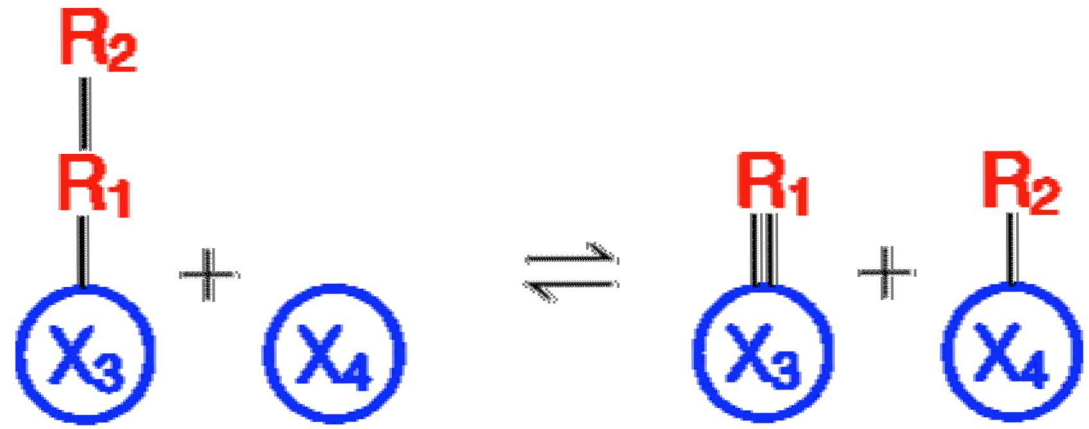


2. non-dissociative adsorption:
   - single bond: $CH_3(g) + * \rightleftharpoons CH_3*$
   - double bond: $CO(g) + * \rightleftharpoons CO*$
   - di-sigma bond: $CH_2O(g) + 2* \rightleftharpoons H_2C*O*$
   - vdW bond: $H_2O(g) + * \rightleftharpoons H_2O*$



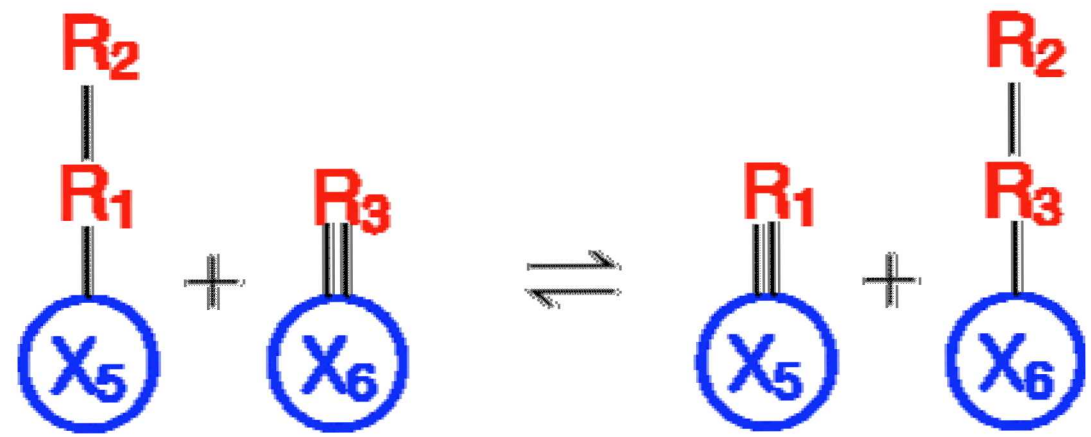
II. Dissociation

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

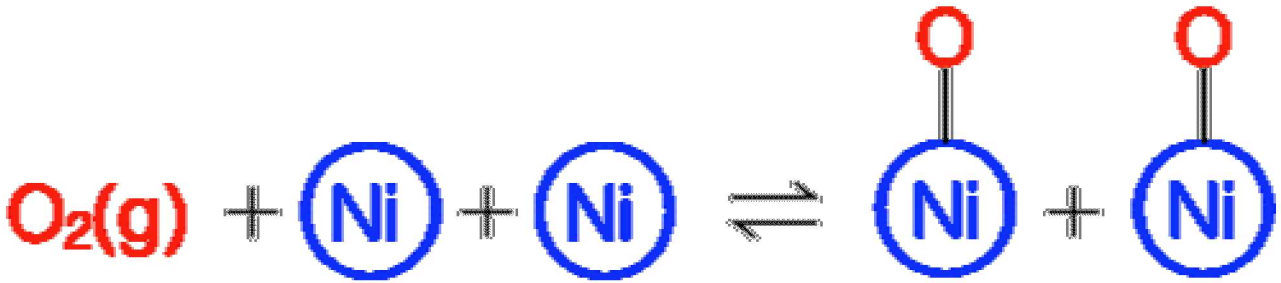


III. Abstraction

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



As with thermo, RMG-Cat 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,

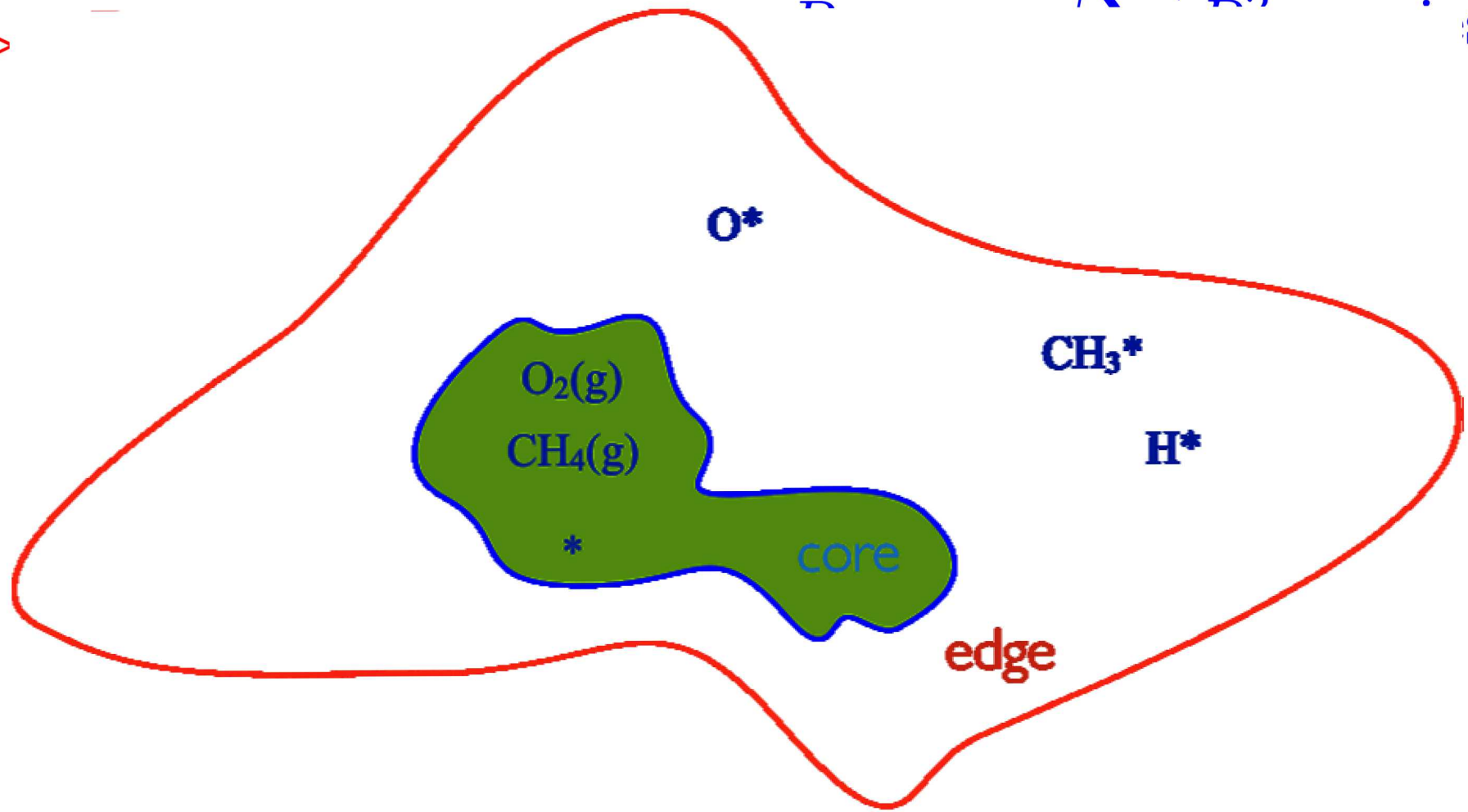
but other options are available

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

✓**predict the kinetic parameters**

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

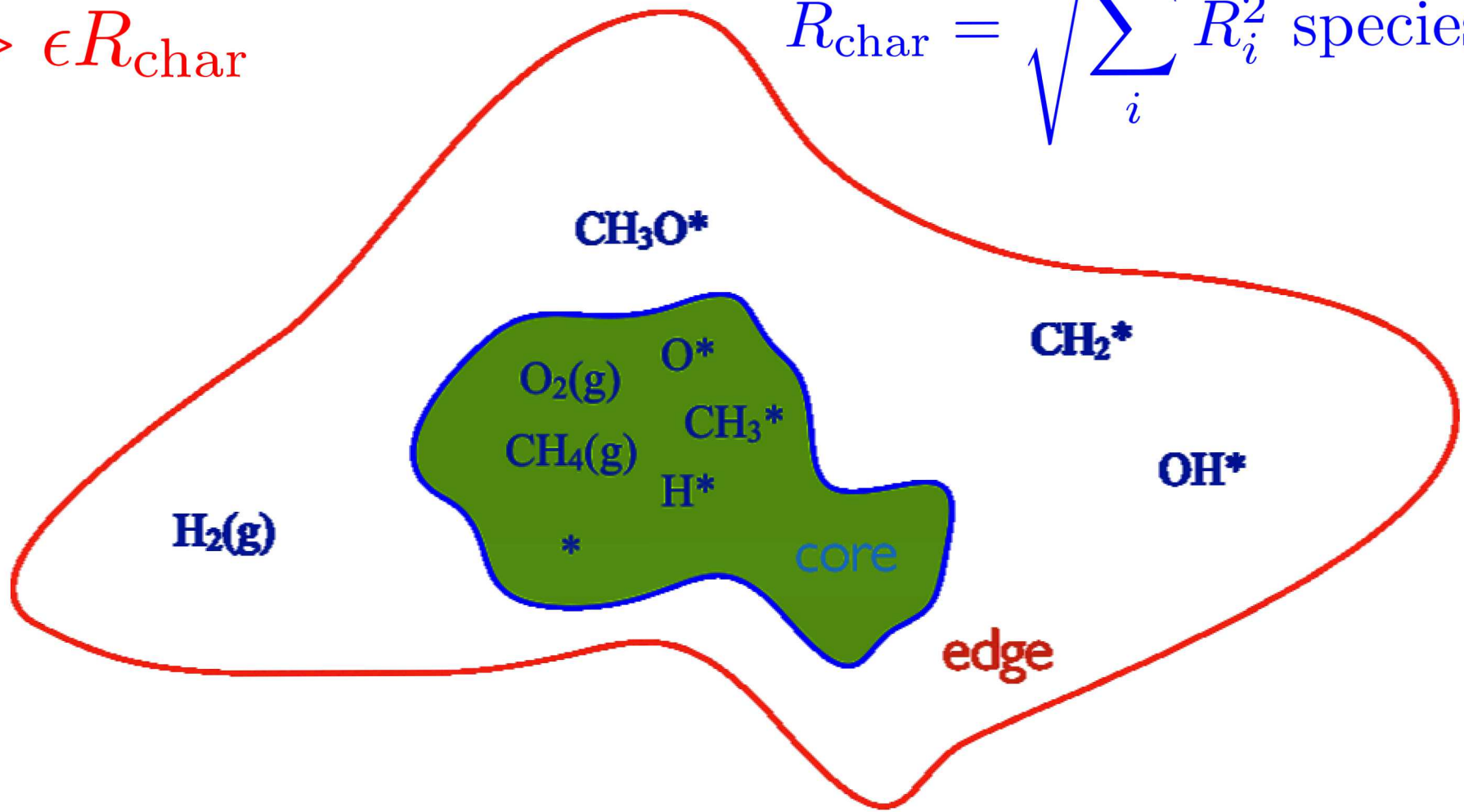
$R_{\text{edge}} >$ $\sqrt{\sum R^2}$ s $i \in$ core



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

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

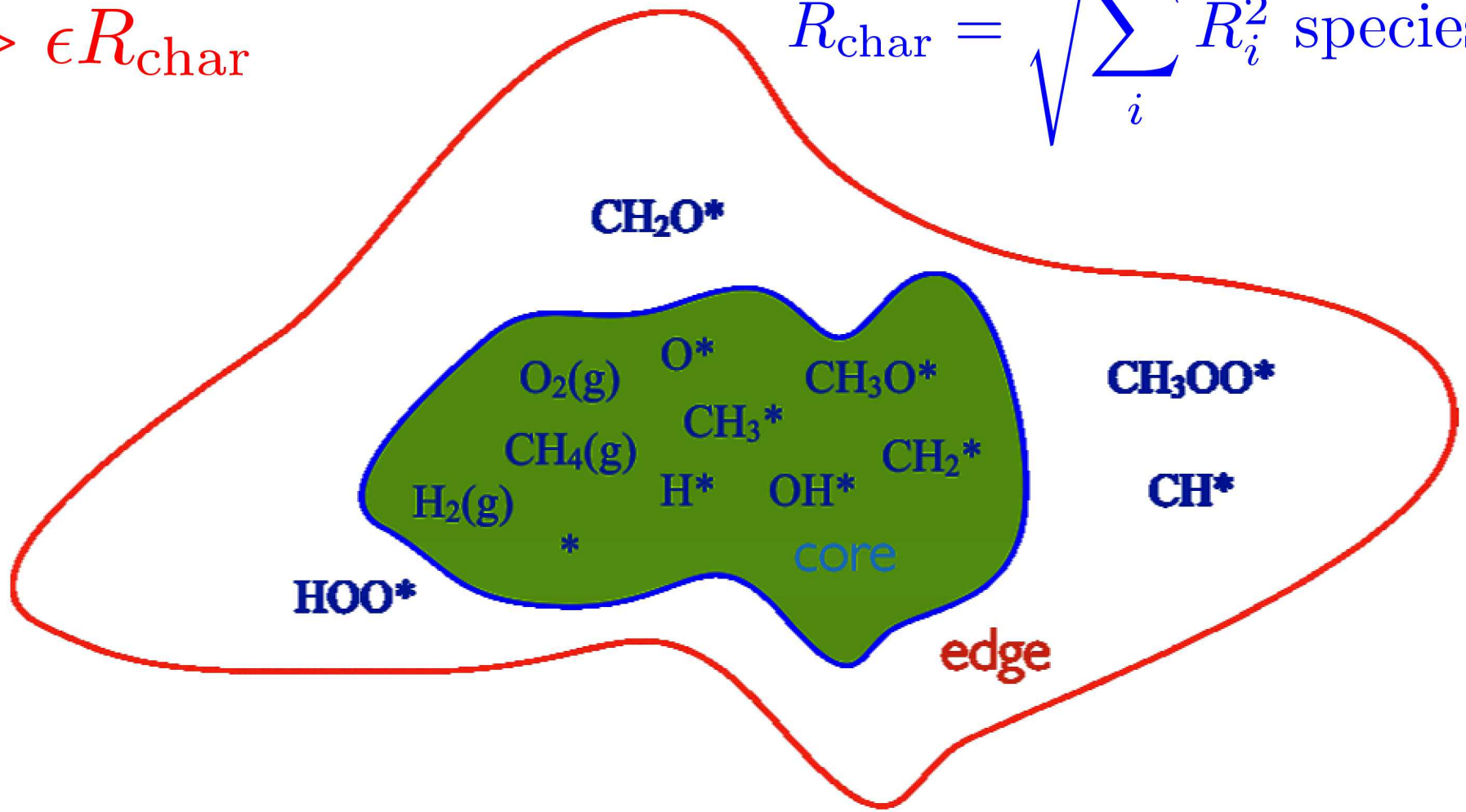
$$R_{\text{char}} = \sqrt{\sum_i R_i^2} \text{ species } i \in \text{core}$$



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

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

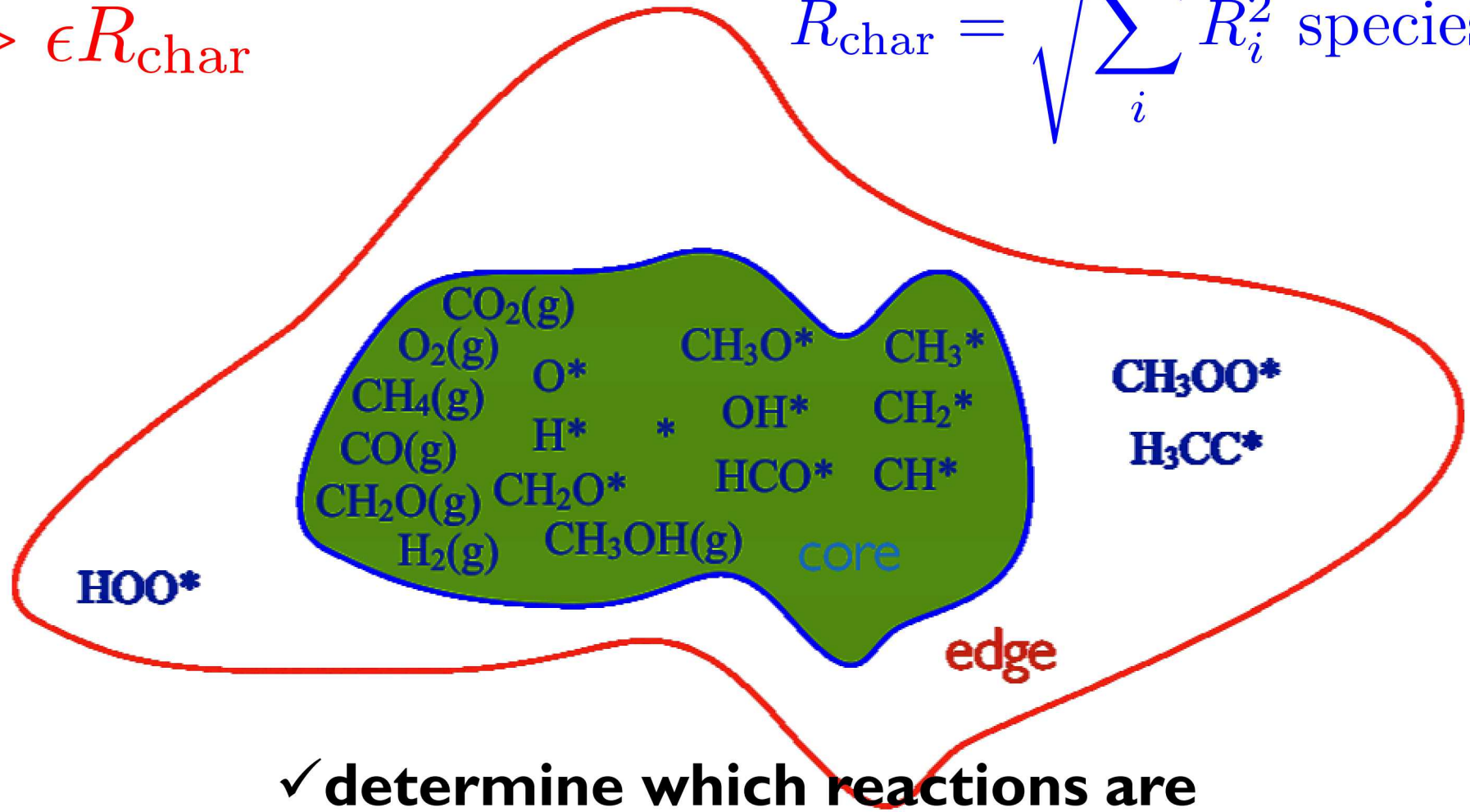
$R_{\text{char}} = \sqrt{\sum_i R_i^2}$ species $i \in$ core



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



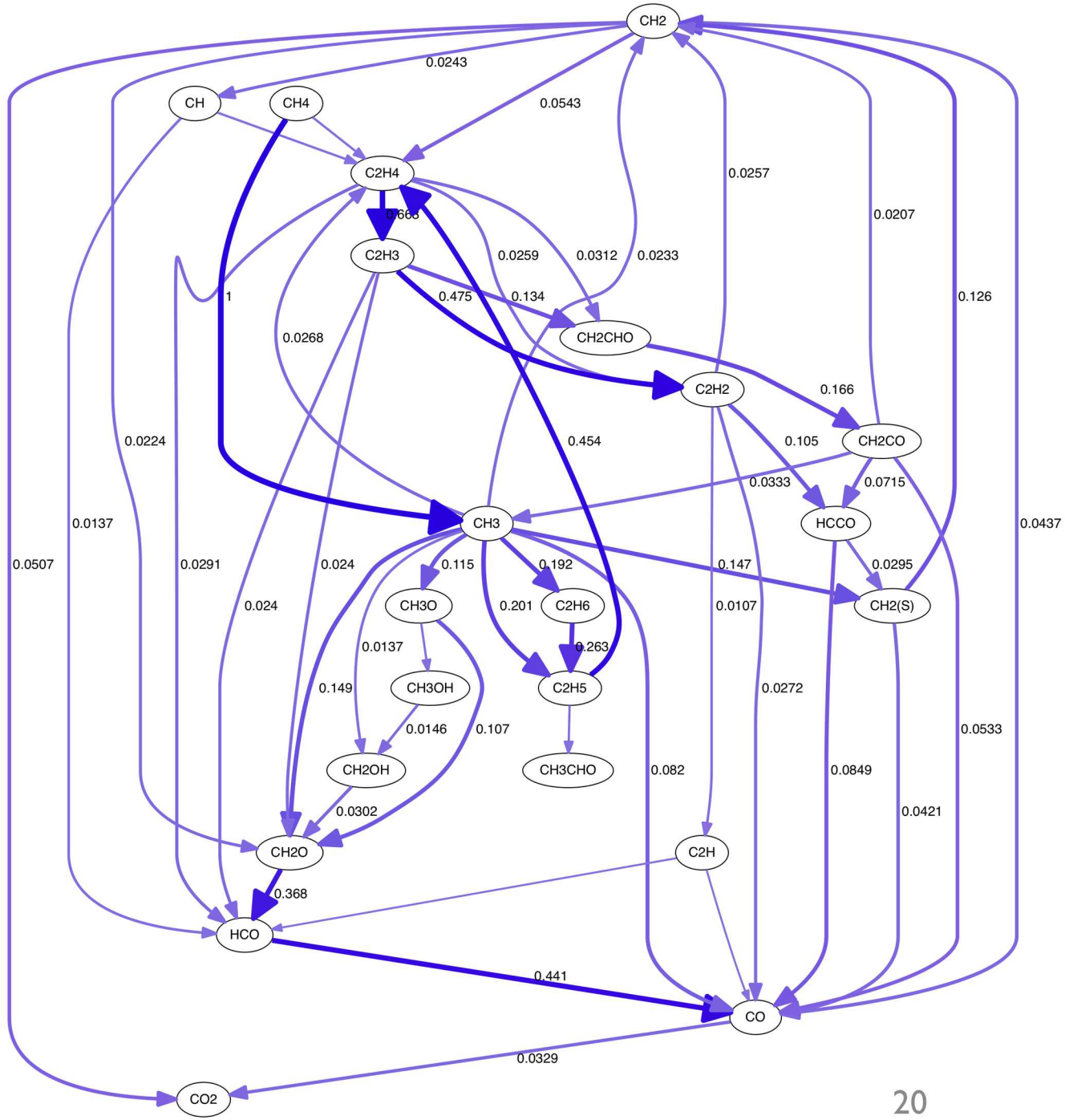
✓**determine which reactions are important**

Catalytic Partial Oxidation (CPOX)

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

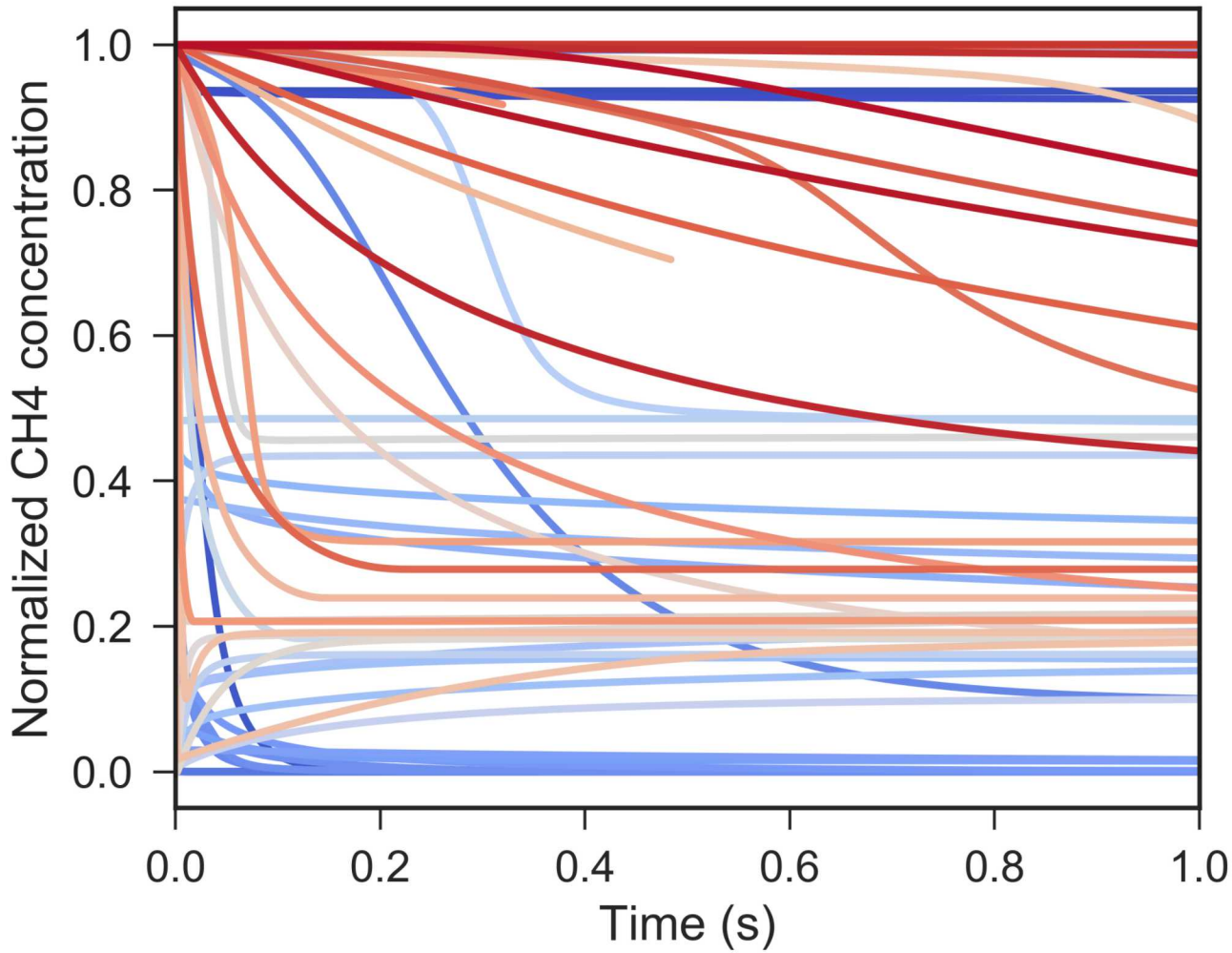
$$CH_4 + O_2 \rightleftharpoons CO + H_2$$

- Extremely important in industry



Scale = 8.2
Reaction path diagram following C

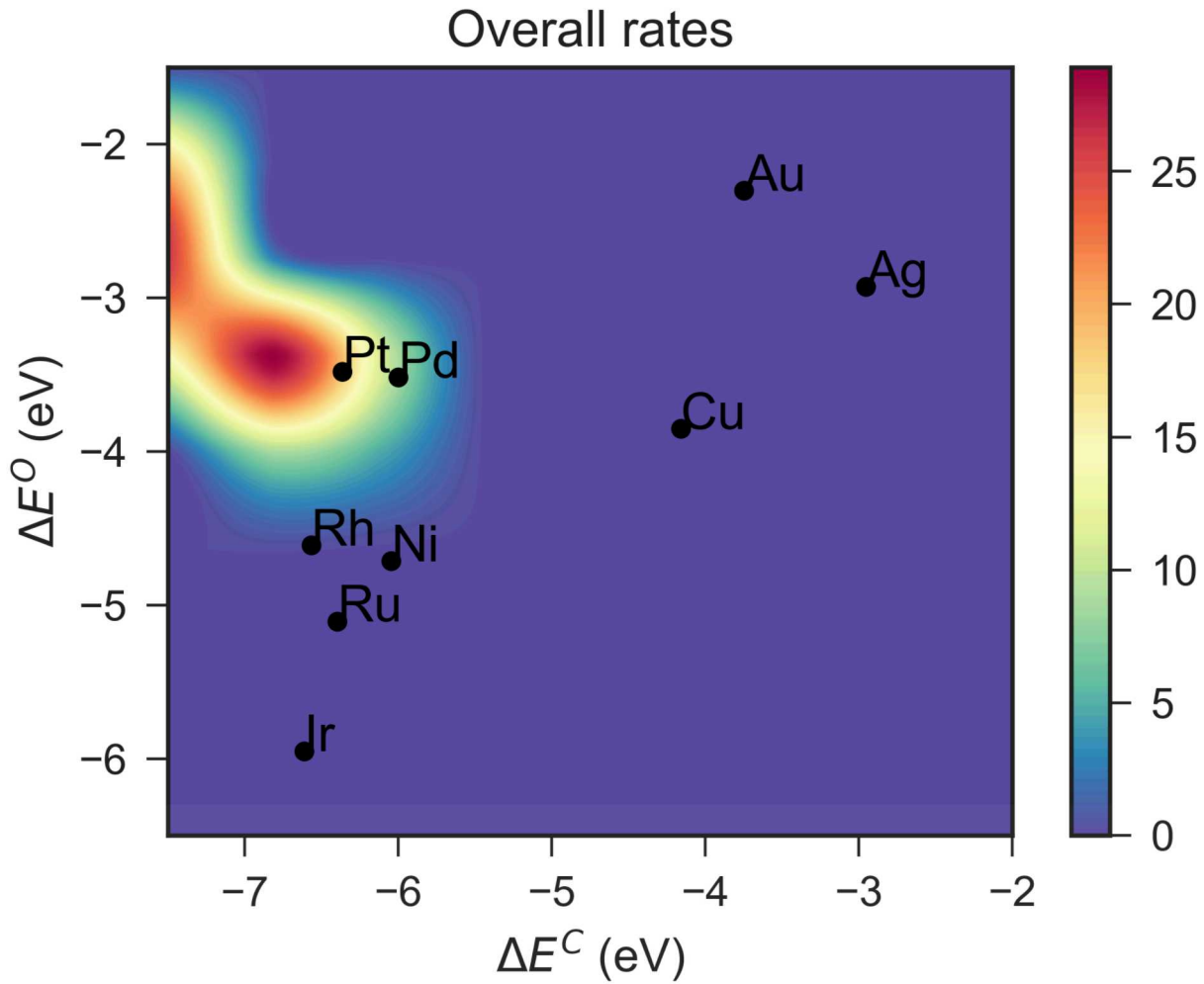
$CH_4 + O_2 \rightsquigarrow CO + H_2 + \ldots$ simulated on many alternative surfaces



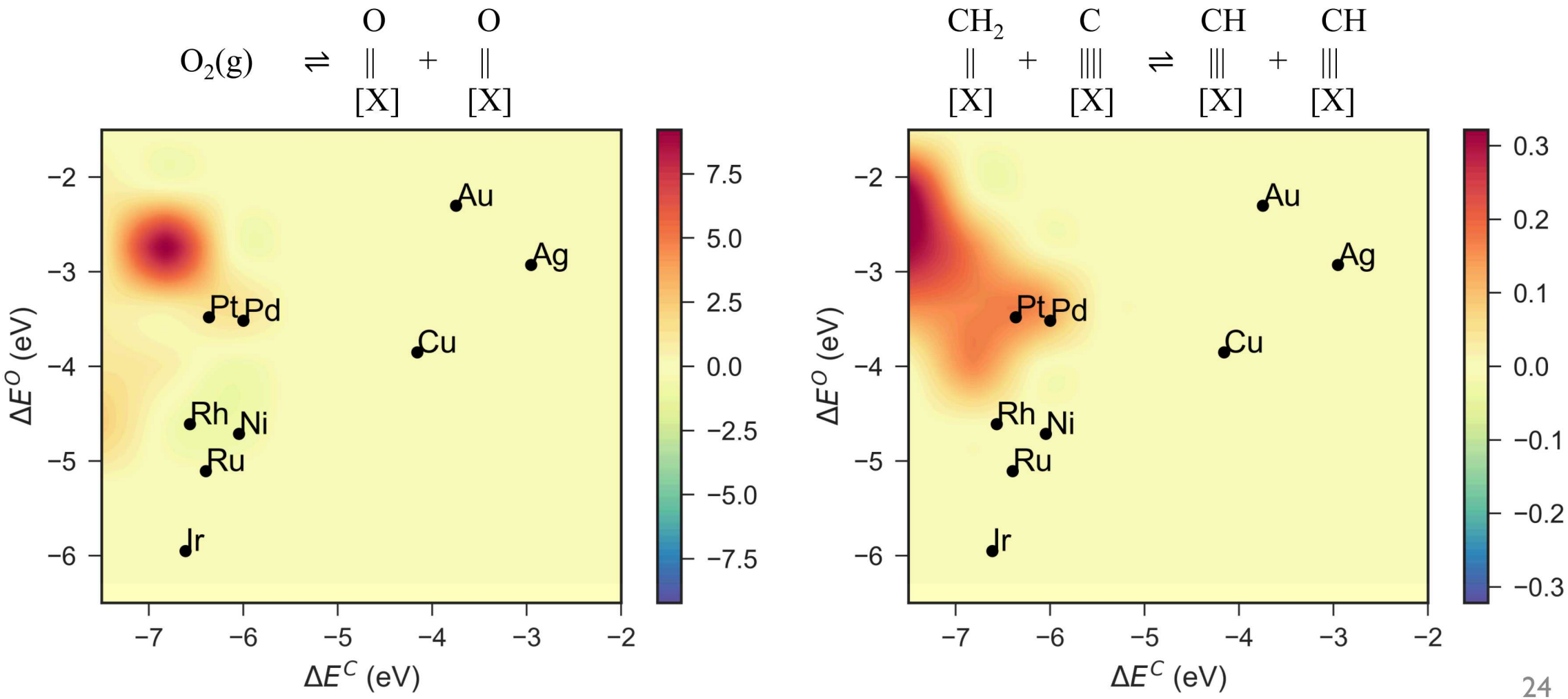
How can we tell what is sensitive?

- Ran simulations on 81 different metal surfaces
  - ✓Overall rate: time to reach 95% completion
  - ✓Which metals will be best for this reaction
- For each surface simulation, we changed the rate of **each reaction** in the simulation by 1%, one at a time
  - ✓New overall rate: new time to reach 95% completion
  - ✓Which reactions are most **rate limiting** (sensitive) on certain metals

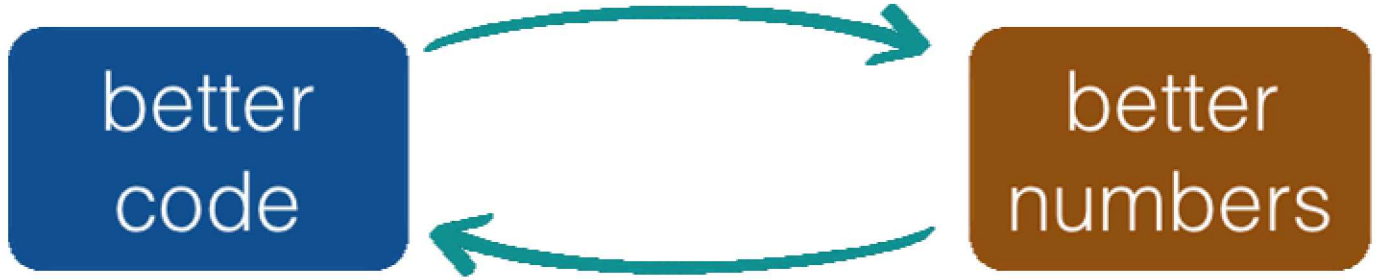
Volcano plot for the overall "rate" for time to reach 95% completion as a function of atomic binding energies



Volcano plots for the sensitivity a reaction 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*
- Kinetics calculations

Questions?

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- Franklin Goldsmith: franklin_goldsmith@brown.edu
- Richard West: r.west@northeastern.edu

Collaborators Welcome!

Acknowledgements: