Microkinetic Modeling 2: Trends across materials

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Microkinetic models can be used for screening and discovery of new materials

- Trends across reaction conditions are more accurate than individual simulations

- Trends across materials (e.g. different metals) are also more accurate than individual materials

- Trends across materials are visualized using "volcano plots" of catalytic activity as a function of reactivity descriptors
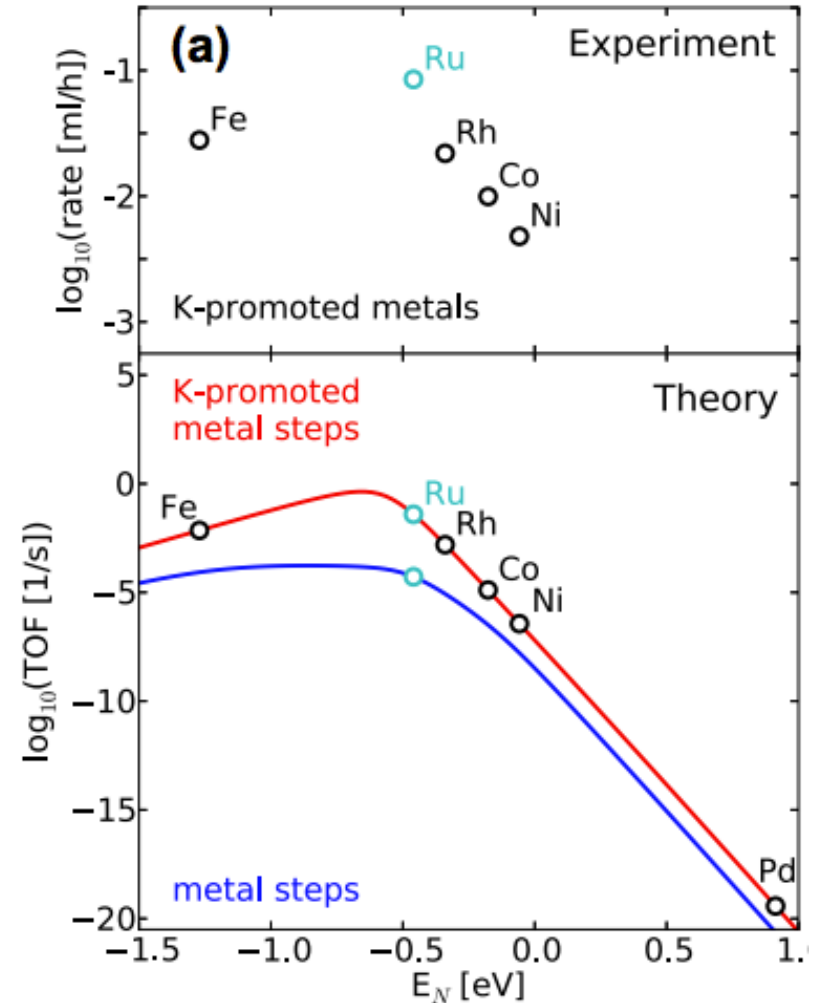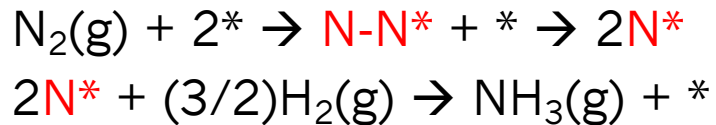
Start simple: One-step Ammonia Synthesis

MECHANISM:

Assume N_2 dissociation is rate-limiting

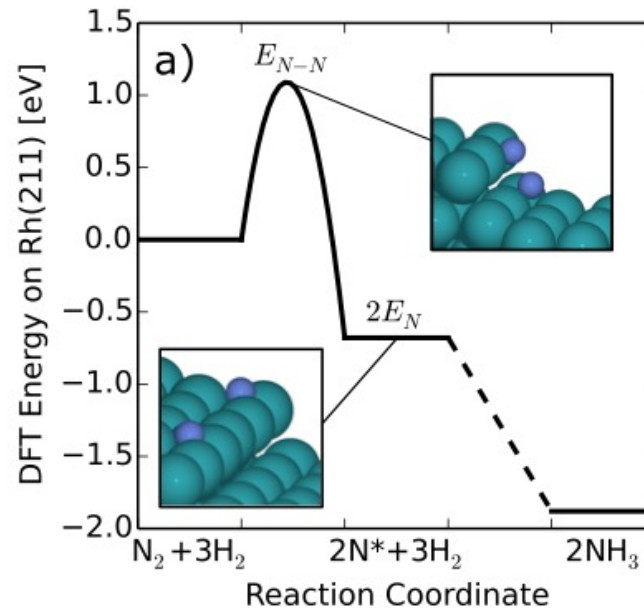Assume equilibrium between adsorbed $N*$ and ammonia

$N_2(g) + 2* \rightarrow N\text{-}N* + * \rightarrow 2N*$
$2N* + (3/2)H_2(g) \rightarrow NH_3(g) + *$

SURFACE MODEL:
$* =$ single active site
Mean-field kinetics

$r_1 = k_1 P_{N2}\theta_*\theta_* - k_{-1}\theta_N$
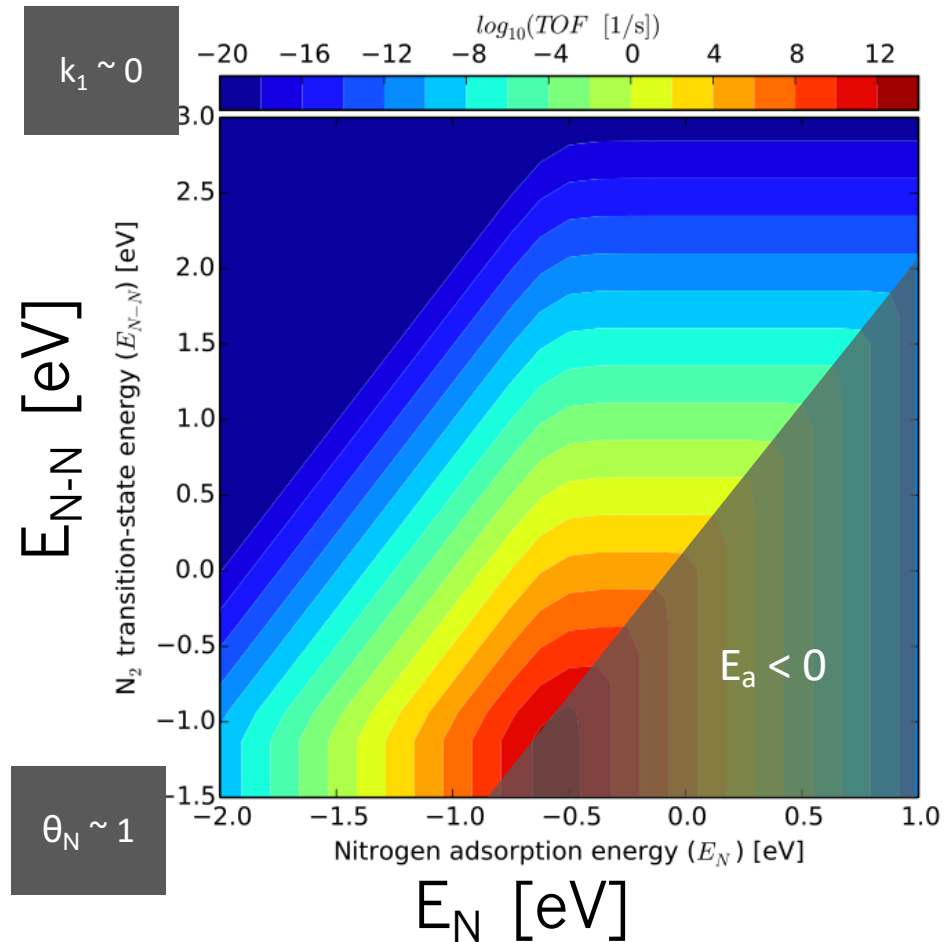$\theta_N = (P_{NH3}\theta_*)/(K_2 P_{H2}^{3/2})$
$\theta_* = 1 - \theta_N$

a)

For a single material (e.g. Rh(211) we could compute these two parameters and evaluate the turnover frequency

For a given temperature and pressure the model has 2 free parameters:

E_N and $E_{N\text{-}N}$

$E_N \rightarrow K_2$
$E_{N\text{-}N} - 2E_{N2} \rightarrow k_1$
$E_{N\text{-}N} - 2E_N \rightarrow k_1$
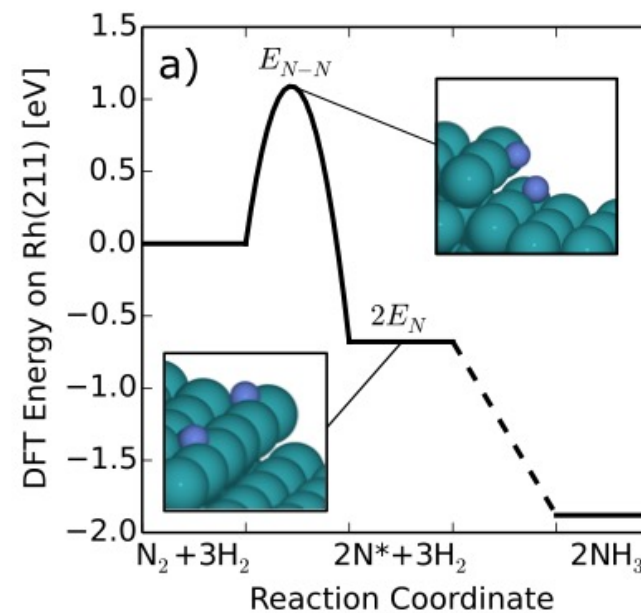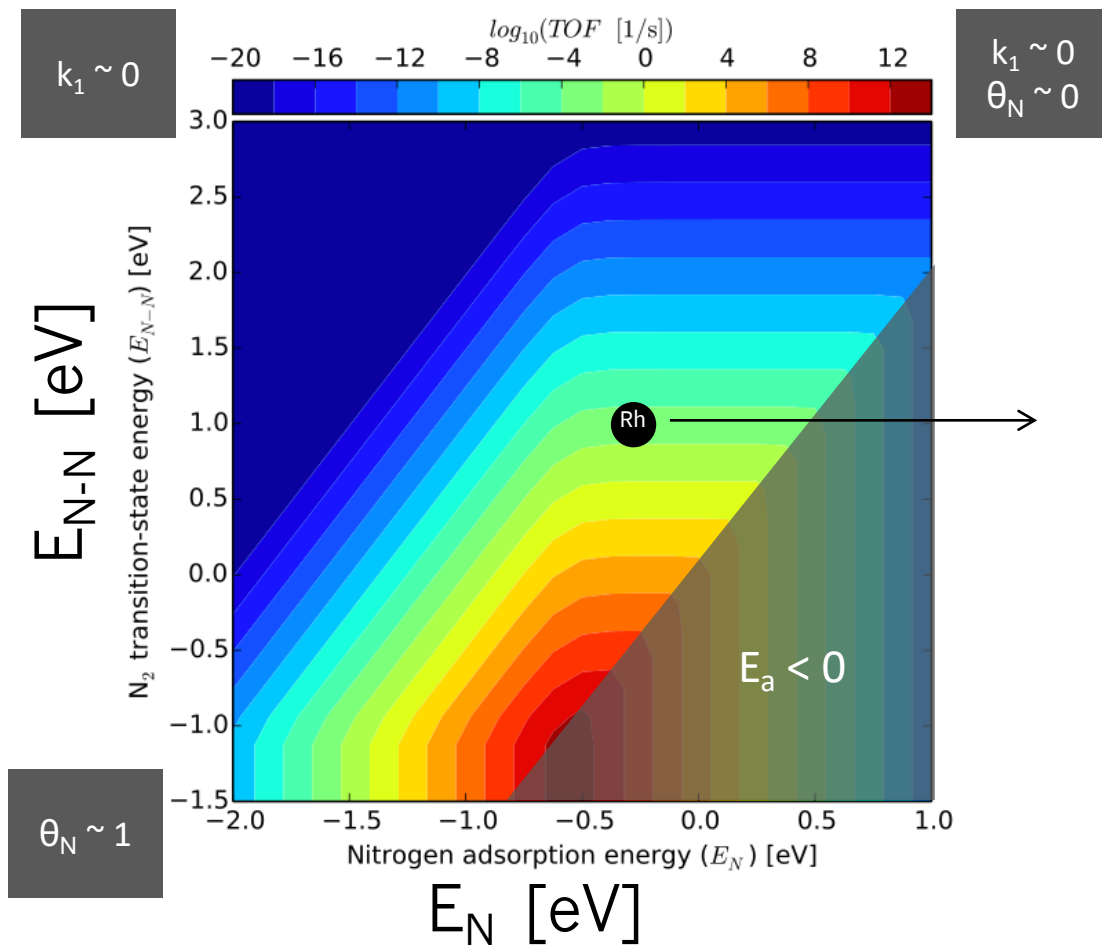
All activity can be mapped out

- Mechanism:
  - $N_2(g) + 2* \rightarrow$ N-N* + * $\rightarrow$ 2N*
  - 2N* + (3/2)$H_2(g) \rightarrow NH_3(g)$ + *
- Equations for rate:
  - $r_1 = k_1 P_{N2}\theta_*\theta_* - k_{-1}\theta_N$
  - $\theta_N = (P_{NH3}\theta_*)/(K_2 P_{H2}^{3/2})$
  - $\theta_* = 1 - \theta_N$

What is the active site?

A specific active site is a point on this "map"

$k_1 \sim 0$

$k_1 \sim 0$
$\theta_N \sim 0$

$E_{N\text{-}N}$ [eV]

$\theta_N \sim 1$

E_N [eV]

$E_a < 0$

Rh

a) E_{N-N}

$2E_N$

$N_2 + 3H_2$ $2N^* + 3H_2$ $2NH_3$

Reaction Coordinate

Vojvodic, A.J. Medford et al., Chem. Phys. Lett. 598, 108–112 (2014).

Other materials can be added to the map
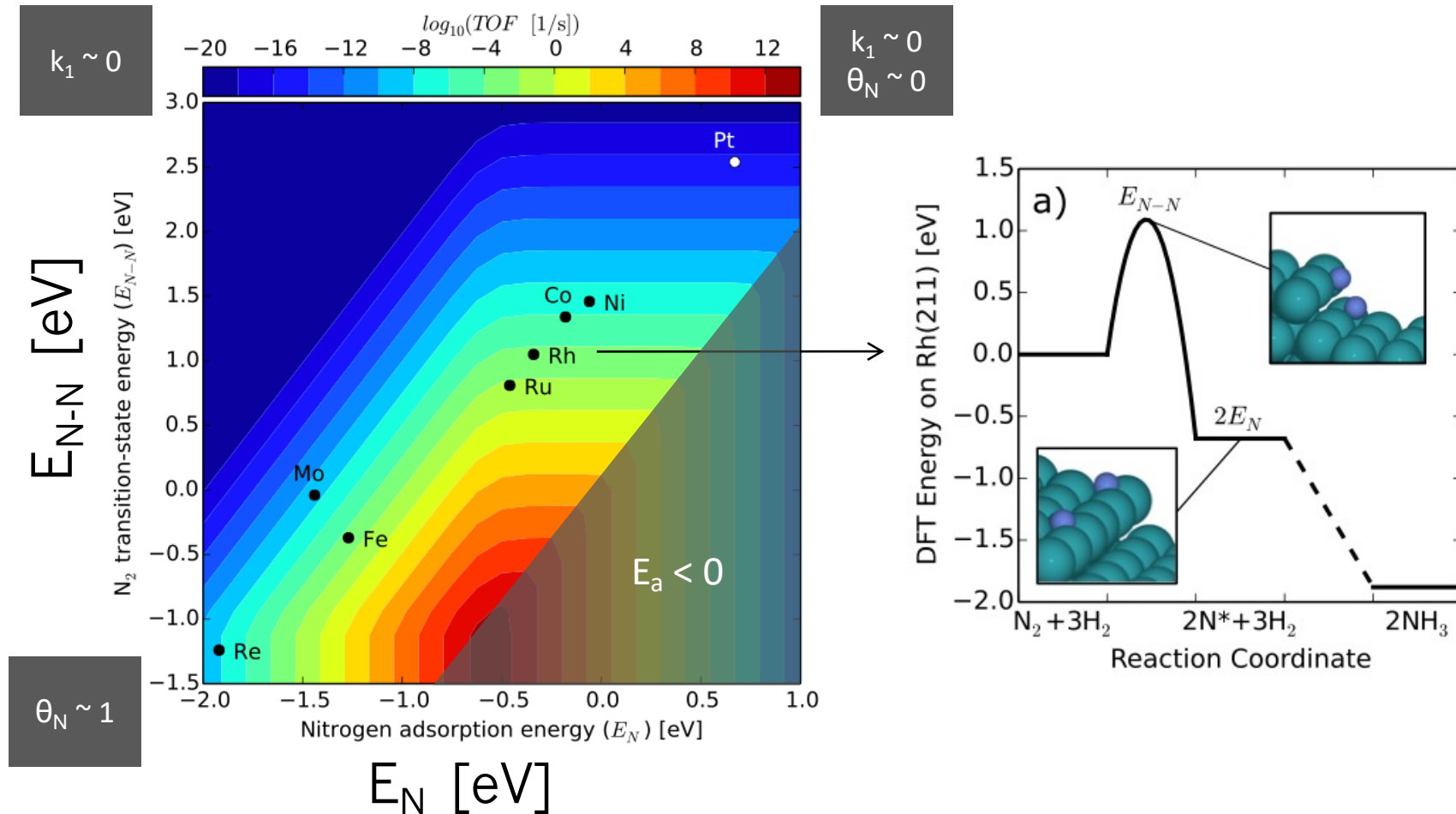
Each point represents two DFT calculations

A. Vojvodic, A.J. Medford et al., Chem. Phys. Lett. 598, 108–112 (2014).

Correlations between energies enable "dimensional reduction"
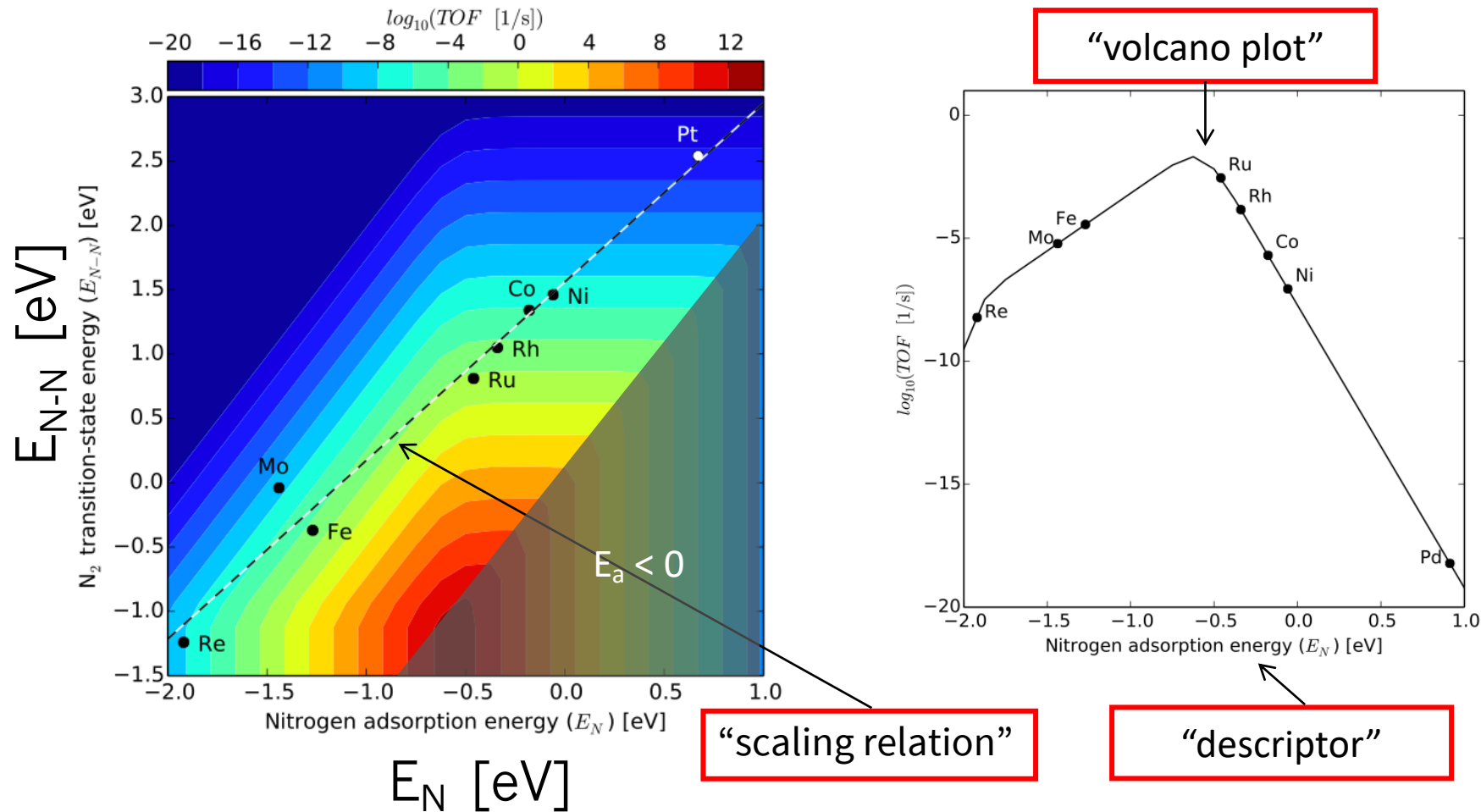
- Instead of assuming an active site, we assume a class of active sites (or active site "motif")
- The "scaling relations" allow interpolation between activity of materials with a given motif

Volcano plots illustrate the "Sabatier Principle"
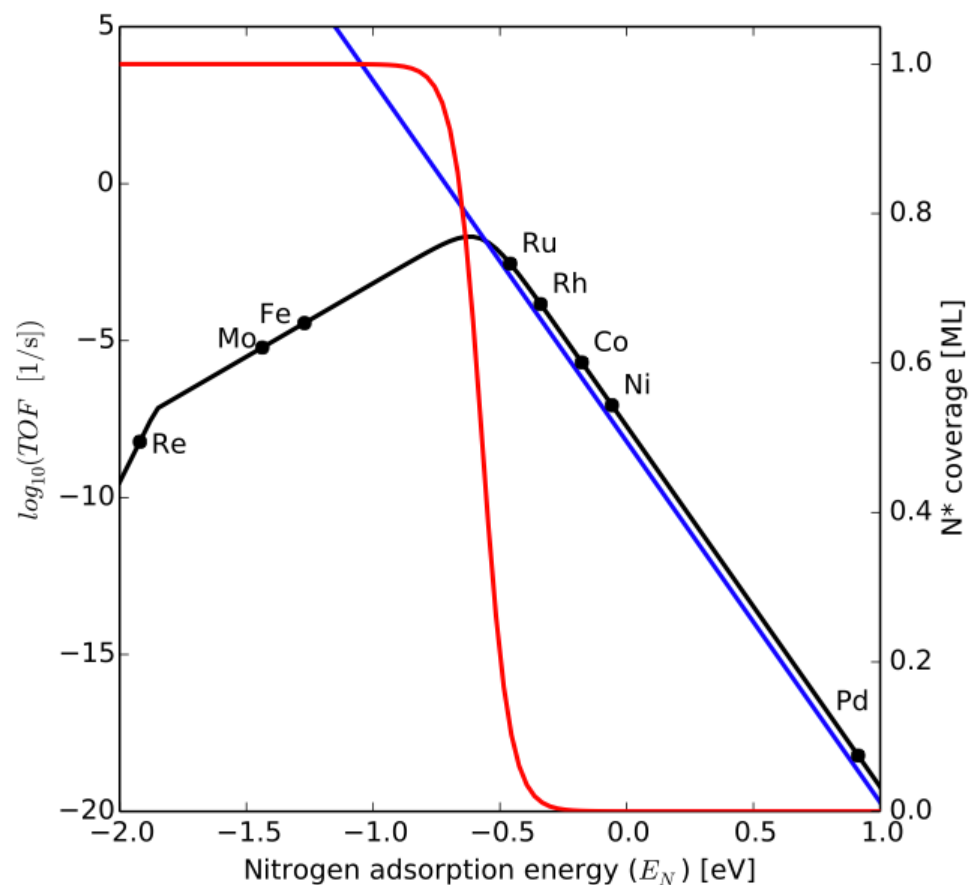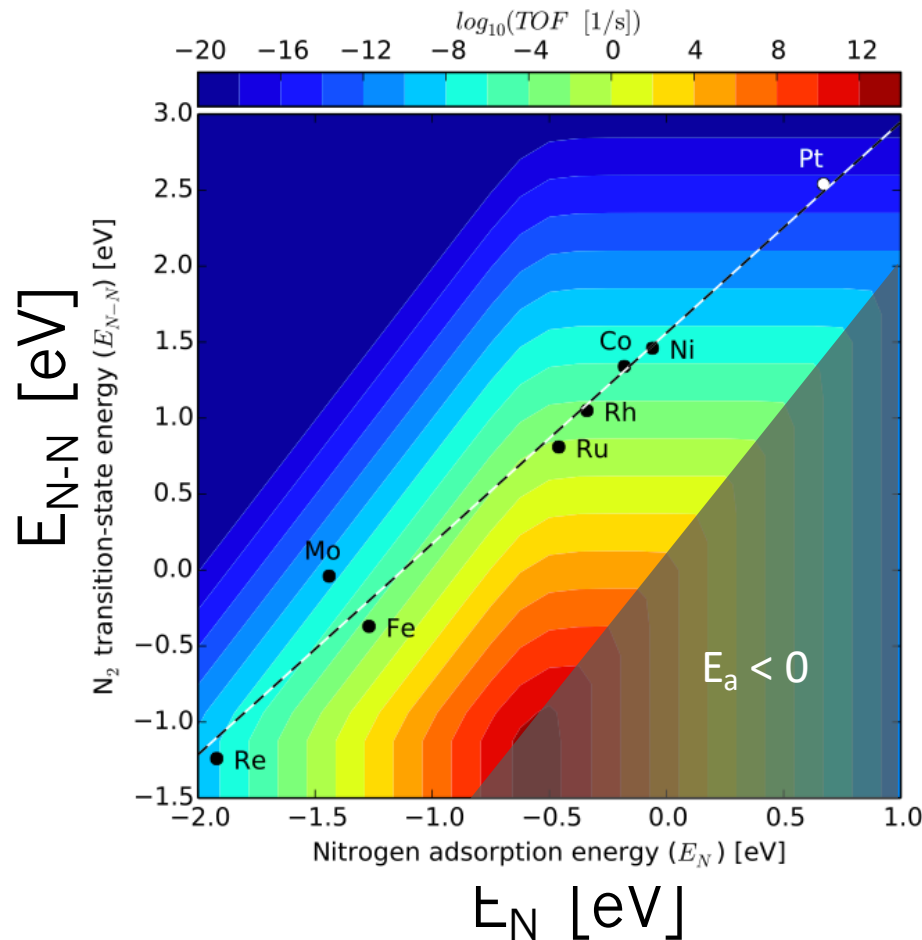

The optimum catalytic surface should bind intermediates "just right"

- Too strong → catalyst will be poisoned by intermediates
- Too weak → catalyst will not be able to bind intermediates or break bonds

- Materials screening can be accomplished by calculating a single quantity (E_N) for each candidate

$$r \sim k(1-\theta_N)^2$$

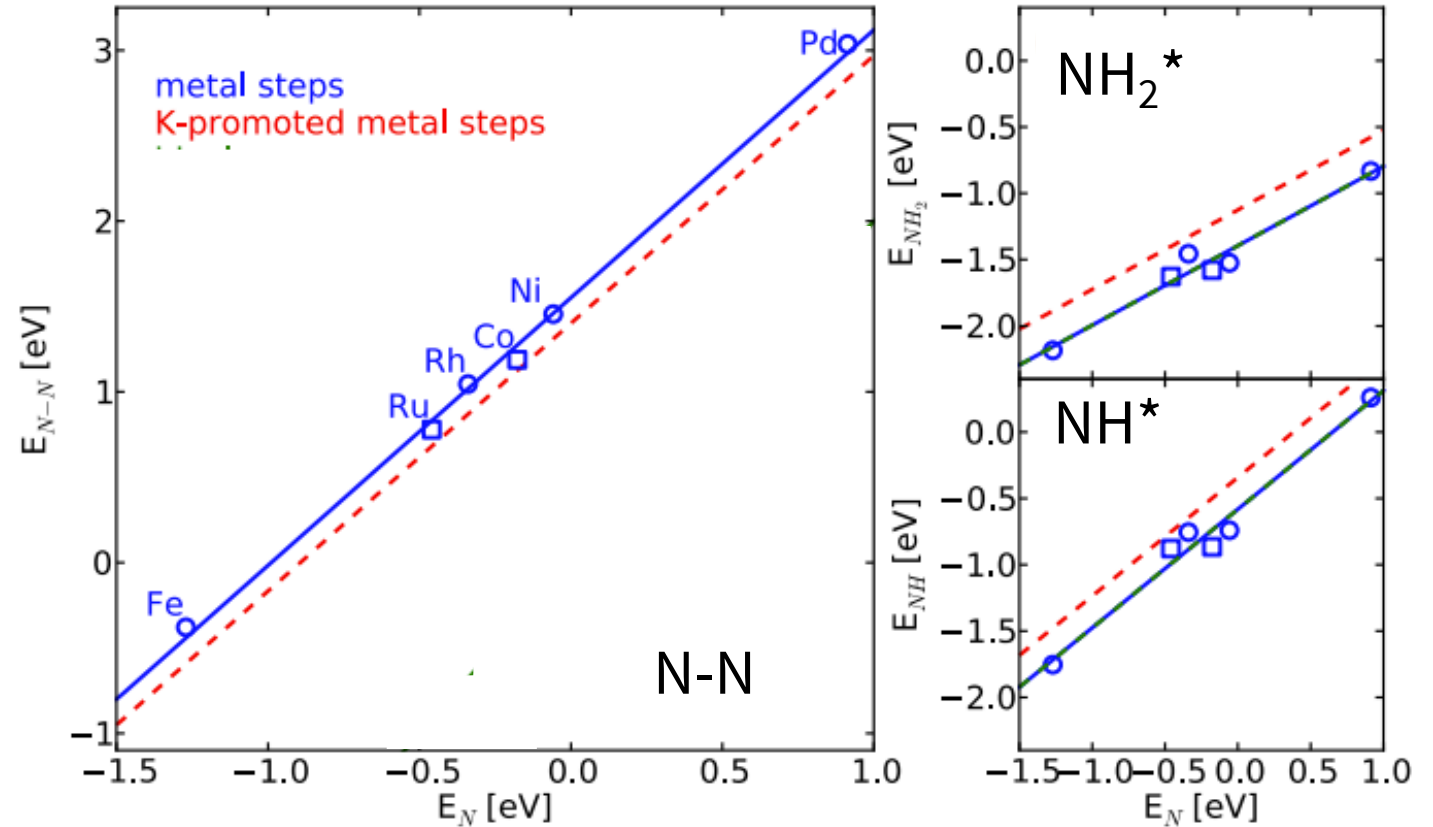# Scaling relations are a blessing and a curse

- Scaling relations enable dimensional reduction of problem
  - Improved intuition
  - Efficient materials screening
- Scaling relations also limit the maximum possible activity
  - Materials that "break" scaling relations can have exceptional catalytic activity

Scaling relations exist for many adsorbates

More complex reaction mechanism → more scaling relationships needed

(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) $NH_2* + H* \rightleftharpoons NH_3(g) + 2*$

A. Vojvodic, A.J. Medford et al., Chem. Phys. Lett. 598, 108–112 (2014).
K. Aika, A. Ozaki, in Catalysis: Science and Technology Volume 1 (Springer, Berlin, 1981).

Trends in activity can be compared to experiment

- Confirmation of trends in known materials is a strong indication that the model is correct

- Correlation is only semi-quantitative
  - Comparison between rates and TOF assumes active site densities are similar on all experimental catalysts

- Predicted TOF of individual materials still has very large error bar

Why should we trust trends if individual materials have large error bars?

A. Vojvodic, A.J. Medford et al., Chem. Phys. Lett. 598, 108–112 (2014).
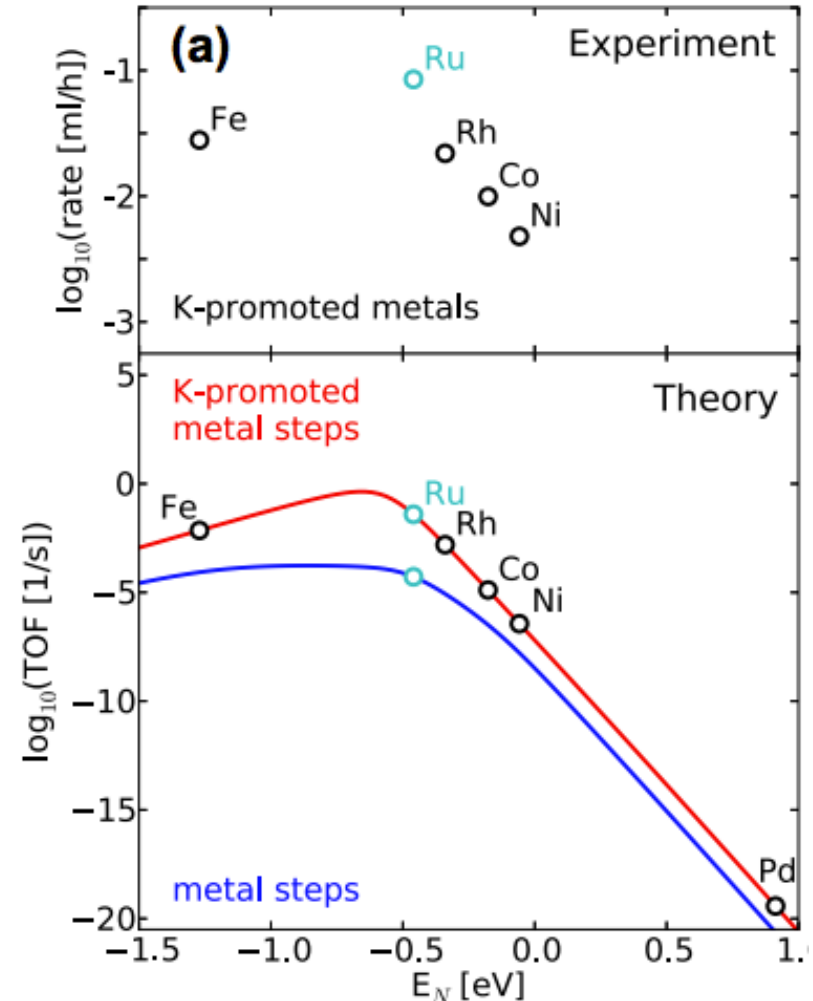
Error correlations also follow scaling relations

- BEEF-vdW functional provides error ensembles to assess the role of exchange-correlation uncertainty

- Slope and intercept of scaling relations have lower uncertainty than underlying DFT simulations

Medford et al., Science. 345, 197-200 (2014).
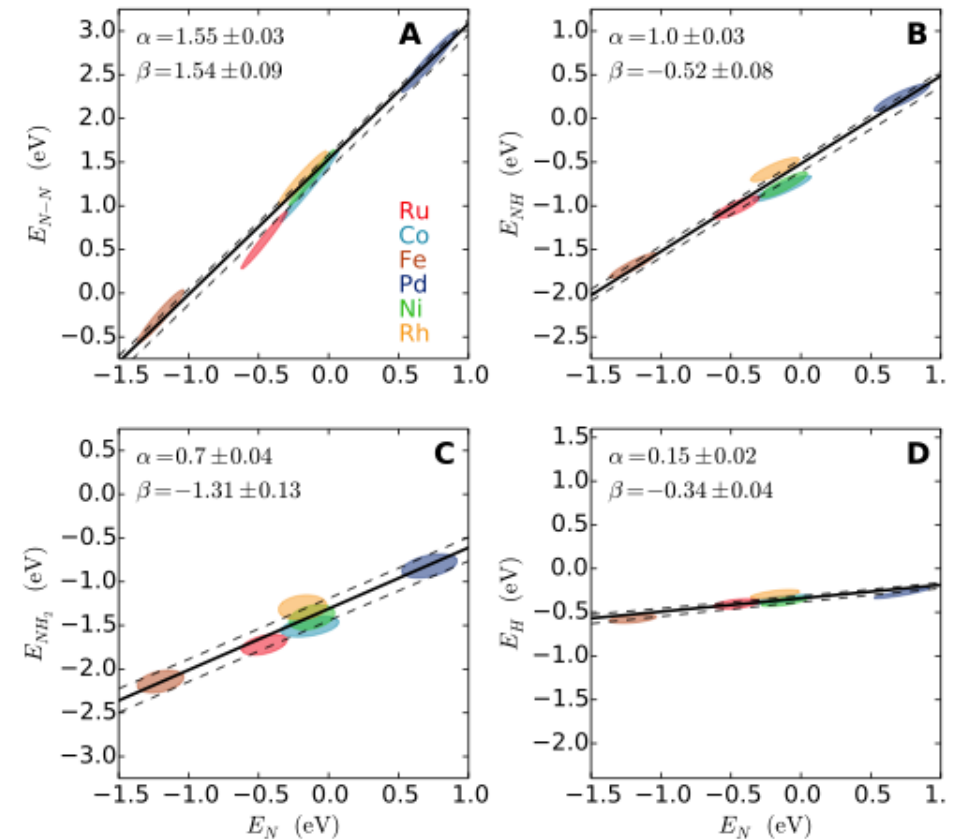
Optimum position has lower error than DFT

- Correlations in scaling relations cause cancellation of error

- Position of the optimum is well-determined, despite errors in exchange-correlation functional

- This explains why DFT is often capable of predicting new materials despite large error bars for individual materials

Medford et al., Science. 345, 197-200 (2014).
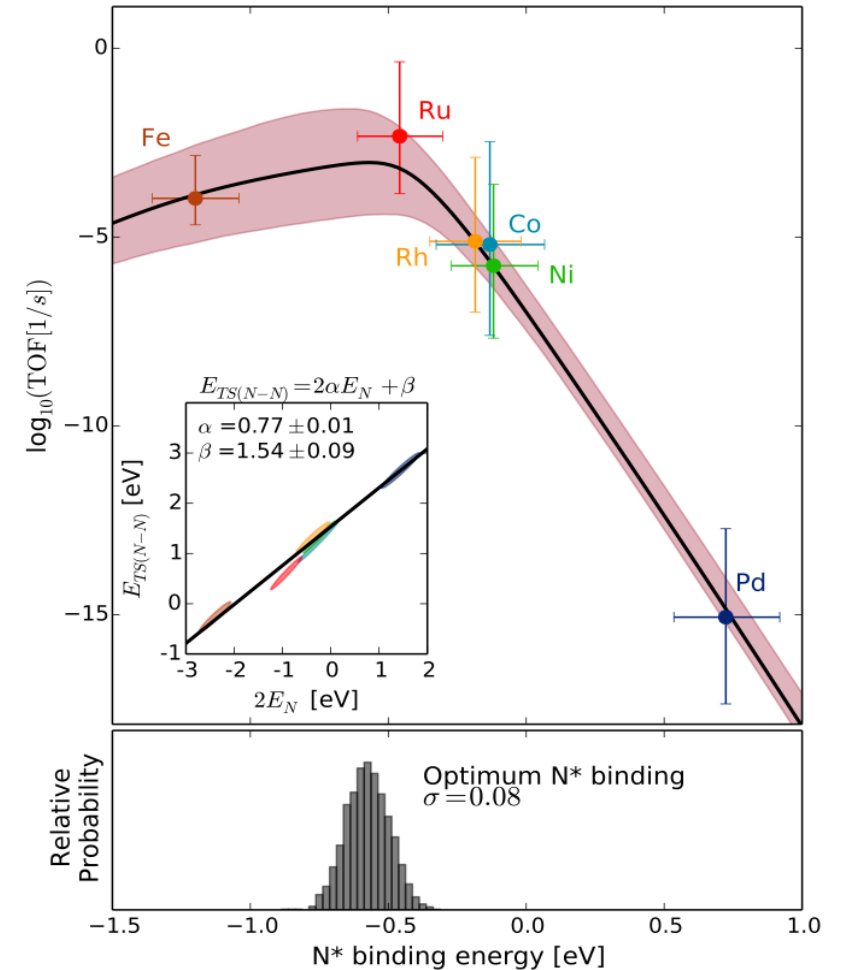
Volcano plots can be constructed for much more complex reactions

- Example: Conversion of syngas to methane, methanol, ethanol

CO + H$_2$ → CH$_4$ + CH$_3$OH + CH$_3$CH$_2$OH

- Many assumptions about mechanism
  - H-assisted CO dissociation
  - CH$_x$-CO carbon coupling
- Assume metal (211) active sites
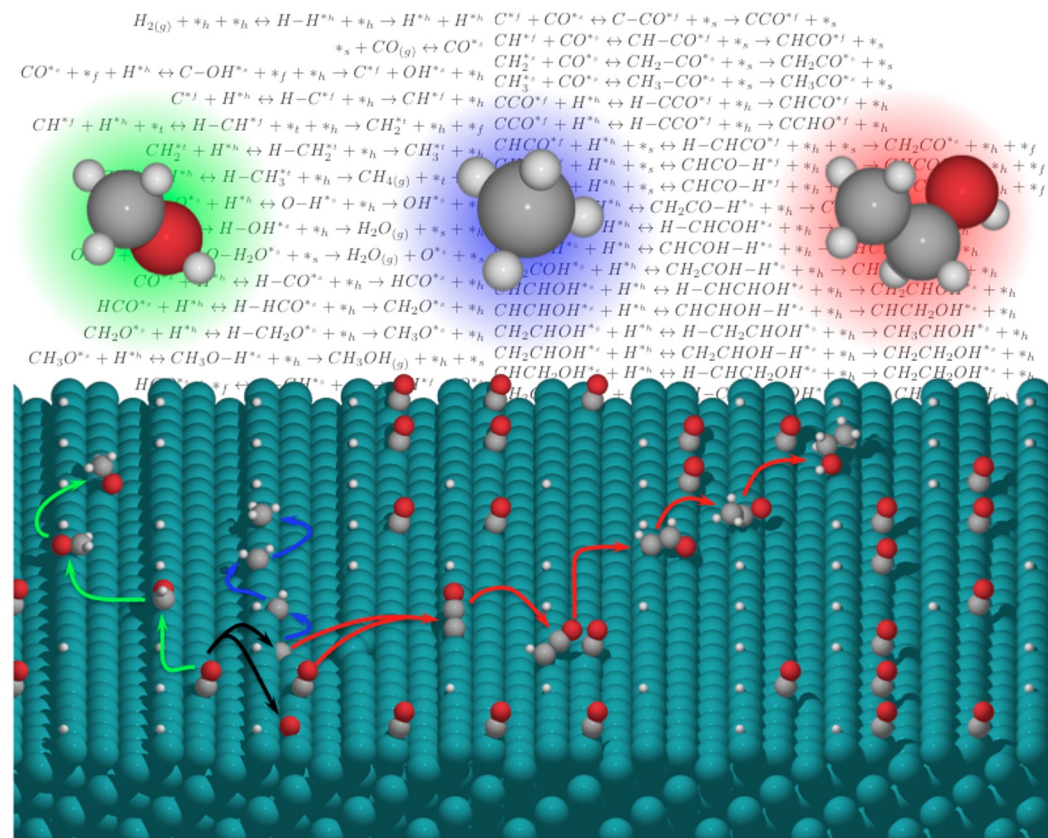
- 51 elementary steps, 30 intermediates → **81 parameters**

A. J. Medford et al. Top. Catal., vol. 57, no. 1–4, pp. 135–142, Oct. 2014.

Linear scaling relations work for many reaction types

- Scaling relations hold for all intermediates and transition-states in ethanol synthesis

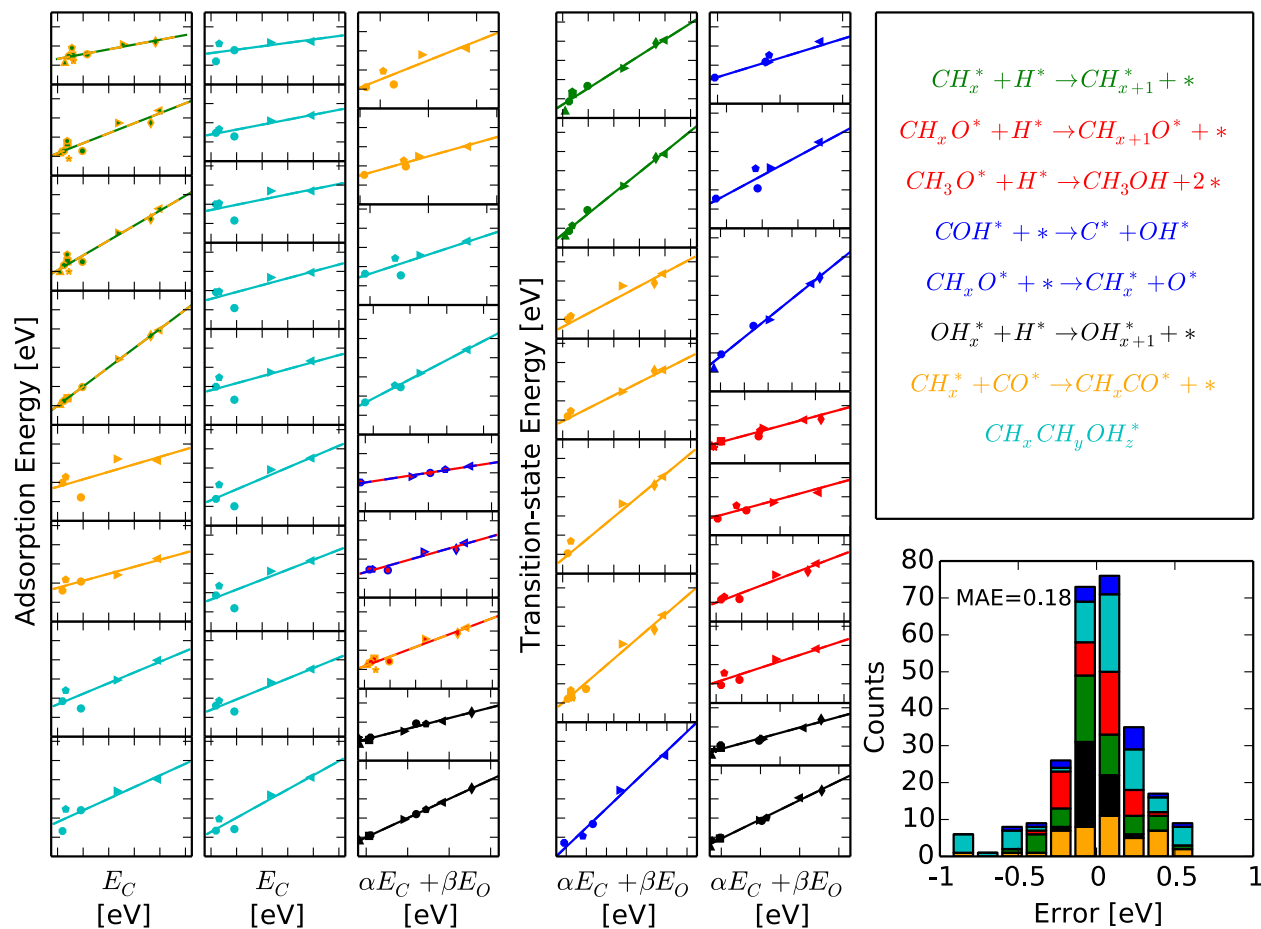- Two-dimensional scaling relations required
  - Carbon and oxygen binding are not well-correlated

- Note: linear scaling relations will break down for very complex molecules or materials
  - Active area of research to use non-linear and machine-learning models instead

$CH_x^* + H^* \rightarrow CH_{x+1}^* + *$

$CH_xO^* + H^* \rightarrow CH_{x+1}O^* + *$

$CH_3O^* + H^* \rightarrow CH_3OH + 2*$

$COH^* + * \rightarrow C^* + OH^*$

$CH_xO^* + * \rightarrow CH_x^* + O^*$

$OH_x^* + H^* \rightarrow OH_{x+1}^* + *$

$CH_x^* + CO^* \rightarrow CH_xCO^* + *$

$CH_xCH_yOH_z^*$

CatMAP facilitates construction of "volcano plots" for complex reactions
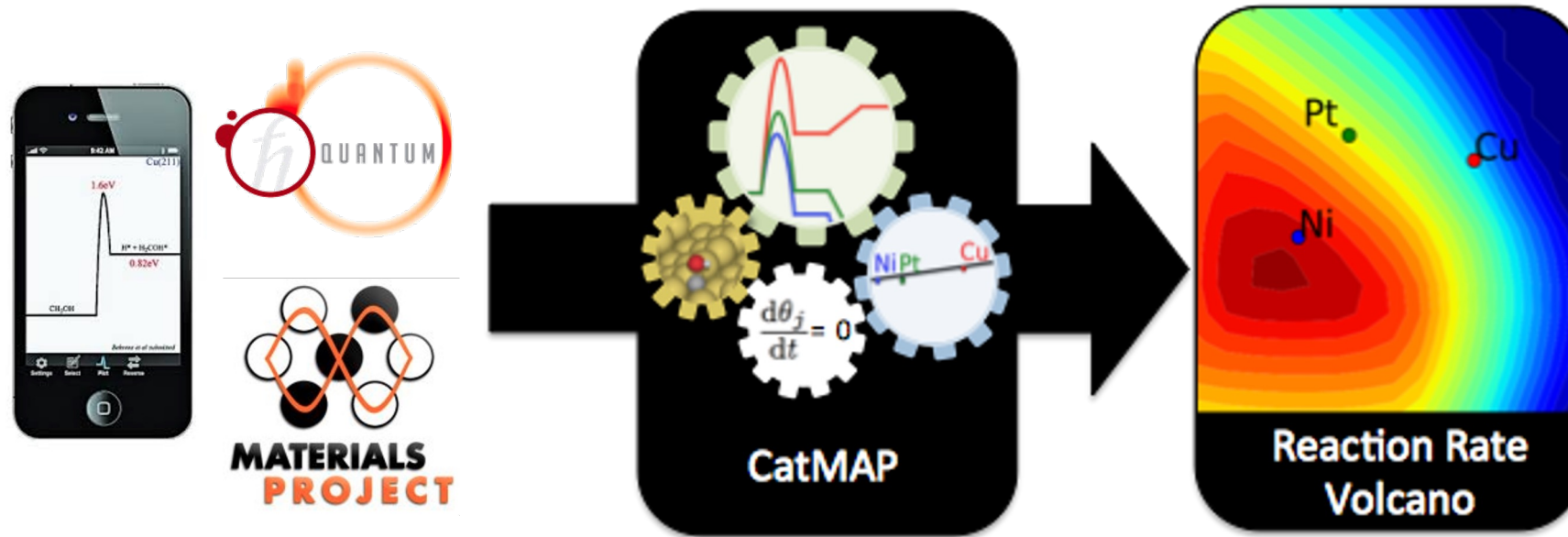
- CatMAP will:
  - Set up and solve microkinetic equations
    - Good initial guess strategies (equilibrium and nearby coverages)
  - Construct scaling relations
    - Including physical constraints and 2D scaling relations
  - Generate plots and analyses of results

Methane and methanol rates can be computed as a function of C* and O* binding
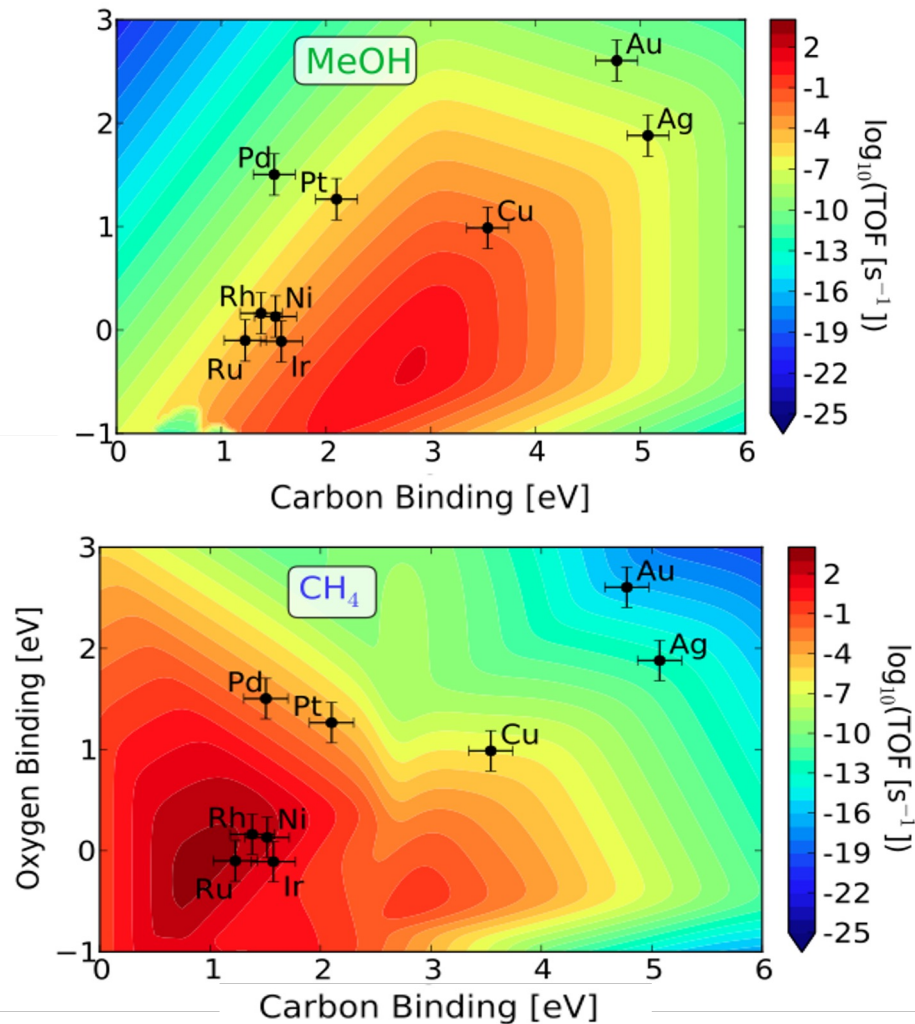
METHANOL ACTIVITY

Cu is the best elemental catalyst

METHANE ACTIVITY

- Reaction conditions:
  - T = 593 K
  - P = 90 bar
  - H_2:CO = 2
  - conversion ~ 0
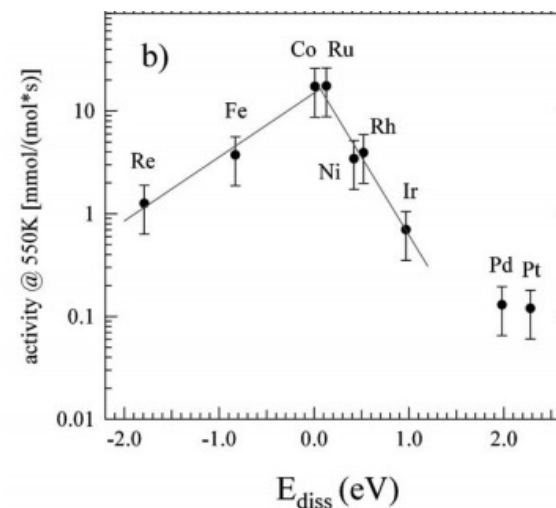
- Trends agree well with experiments

Medford, A. J., Lausche, A., Studt, F. *et al. Top. Catal.* 57:135-142 (2014).
M. P. Andersson, T. Bligaard, et al., J. Catal., vol. 239, no. 2, pp. 501–506, 2006.

Volcano plots can have multiple peaks

C-OH dissociation
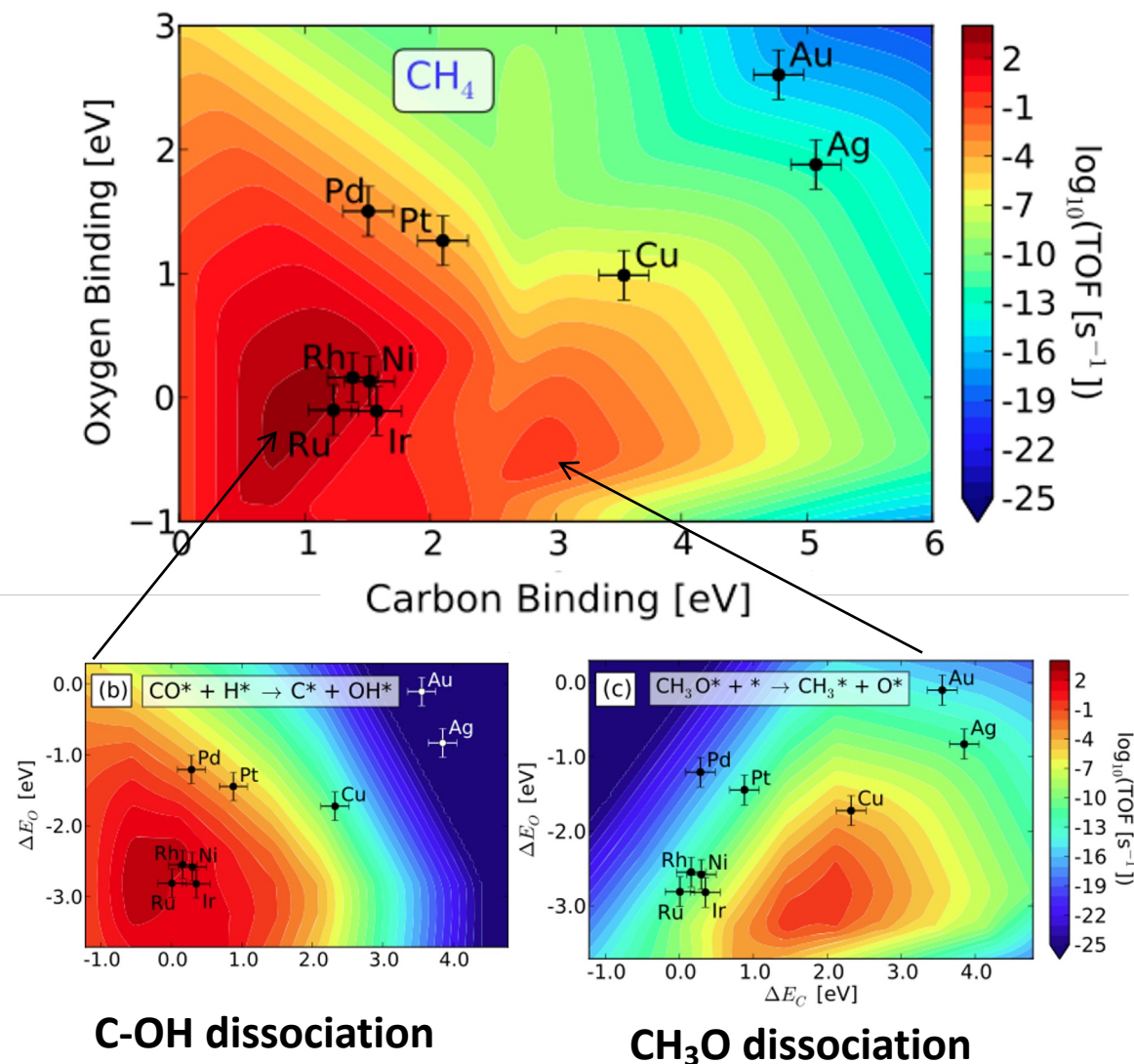
CH$_3$O dissociation

- 1 peak per mechanism
  - CO* dissociation
  - CH$_3$O* dissociation

- In theory, other peaks are present, but the rates are so low that they don't show up

- The most active mechanism may change in different regions of a volcano plot
  - Mechanisms that are not included may cause optima to be missed

Medford, A. J., Lausche, A., Studt, F. *et al. Top. Catal.* 57:135-142 (2014).

Each peak of a 2D volcano plot can also be interpreted in terms of Sabatier's principle

Medford, A. J., Lausche, A., Studt, F. *et al. Top. Catal.* 57:135-142 (2014).
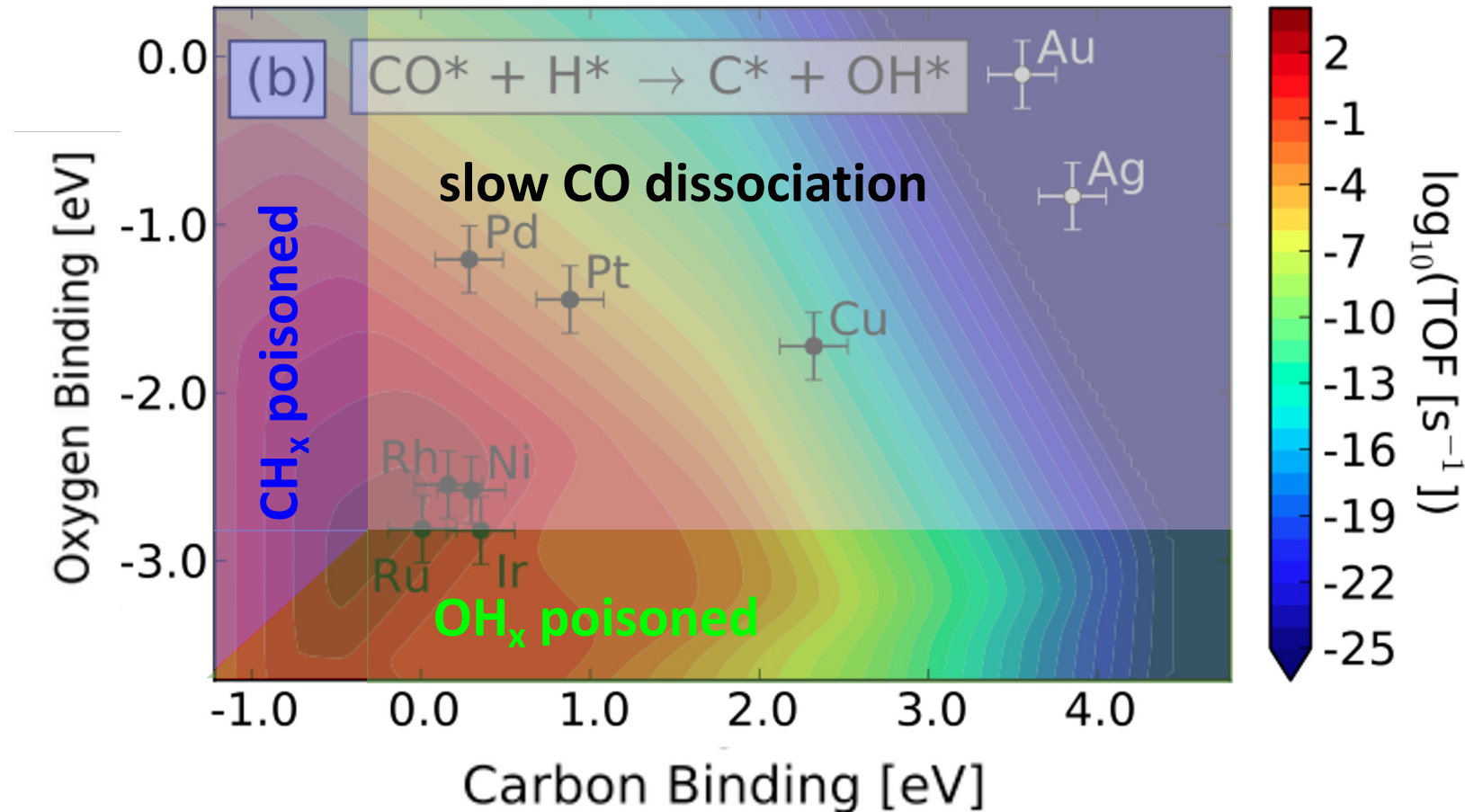
Selectivity can be approximated as a ratio of different rates
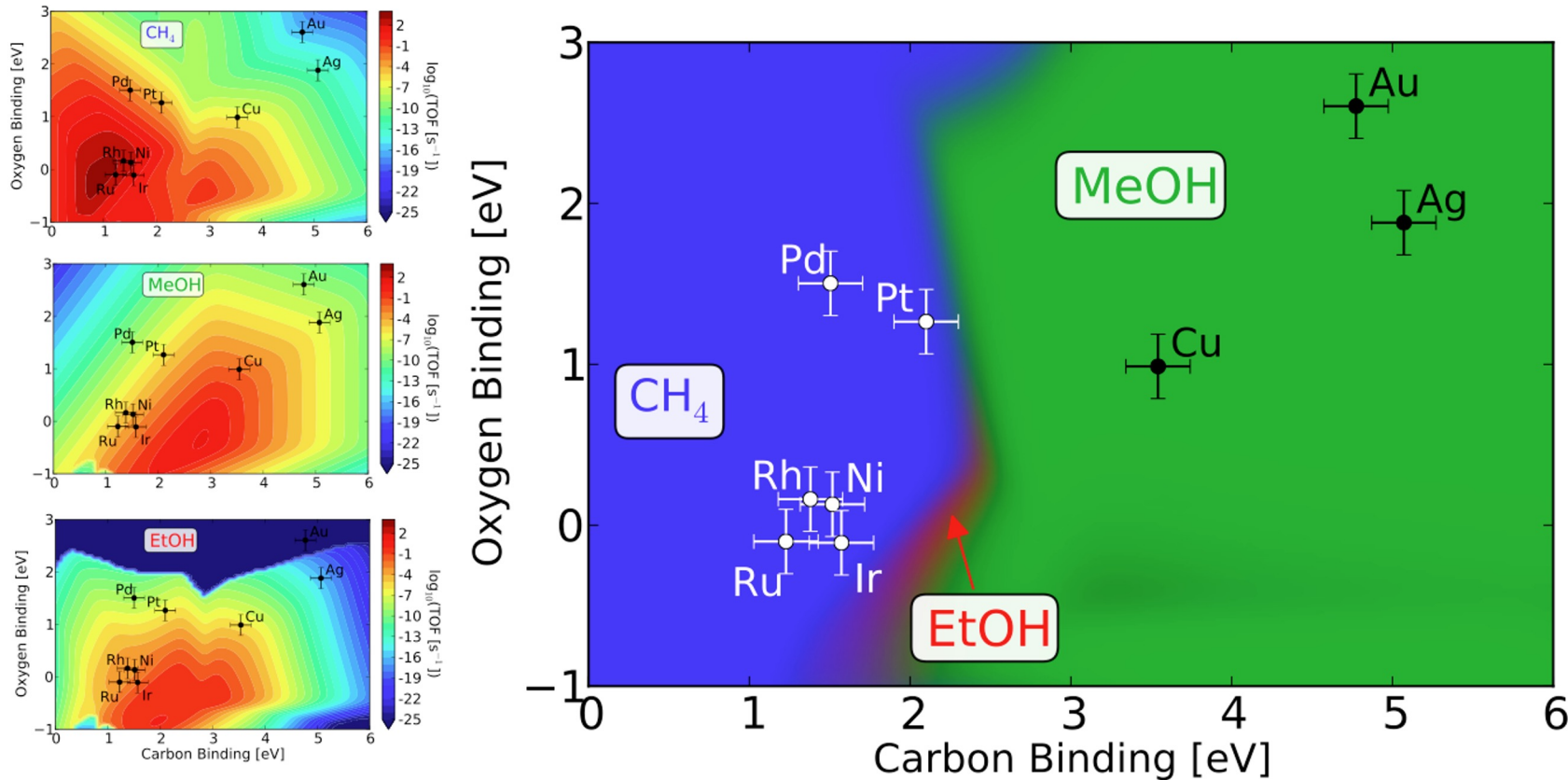
- Example: Ethanol synthesis
- Results explain difficulty in finding a single-element ethanol synthesis catalyst
- Note: This is only the selectivity at a fixed set of conditions (not at the outlet of a reactor)

Volcano plots are efficient screening tools

- Turnover frequency (or selectivity) of a new material can be approximated with 2 DFT calculations
  - C* and O* binding energies
  - Massive savings over computing 81 DFT energies for each material
- Predicted alloys include known ethanol synthesis catalyst
  - CoCu alloys
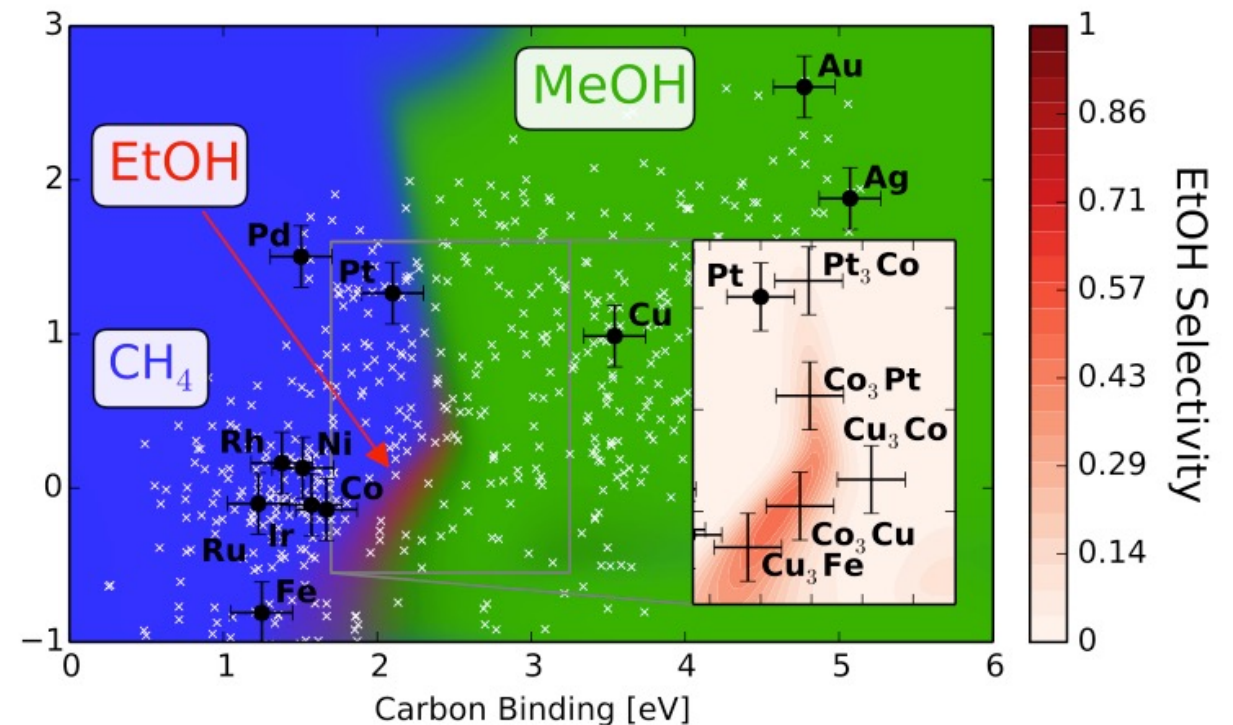
CatMAP 2: Constructing a volcano plot

- Example: CO oxidation
  - CO(g) + * $\rightarrow$ CO*
  - O_2(g) + 2* $\rightarrow$ 2O*
  - CO* + O* $\rightarrow$ CO^2(g) + 2*
- Input file taken from pre-computed DFT values
  - See tutorial 1 to learn to create an input file
- CatMAP reaction syntax:
  - * or _s: denotes "standard" active site (labeled *s*)
  - *_x or _x denotes active site type "x"
  - _g denotes gas-phase
  - -> represents reaction (all reactions assumed reversible)
  - Activated reaction has a transition-state (IS <-> TS -> FS)
  - Example:
    - **O2_g + 2* <-> O-O* + * -> 2O***
- Transition-states must be defined in the input file!

```
surface_name   site_name   species_name   formation_energy   bulk_structure  frequencies ot
None     gas CO2 2.45    None    [1333,2349,667,667] [] "Angew. Chem. Int. Ed., 47, 4835 (2008
None     gas CO  2.74    None    [2170] [] "Energy Environ. Sci., 3, 1311–1315 (2010)"
None     gas O2  5.42    None    [1580] [] "Falsig et al (2012)"
Ru  111 O  -0.07  fcc [] [] "Falsig et al (2012)"
Ni  111 O   0.35  fcc [] [] "Falsig et al (2012)"
Rh  111 O   0.55  fcc [] [] "Falsig et al (2012)"
Cu  111 O   1.07  fcc [] [] "Falsig et al (2012)"
Pd  111 O   1.55  fcc [] [] "Falsig et al (2012)"
Pt  111 O   1.62  fcc [] [] "Falsig et al (2012)"
Ag  111 O   2.05  fcc [] [] "Falsig et al (2012)"
Au  111 O   2.61  fcc [] [] "Falsig et al (2012)"
Ru  111 CO  1.3 fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Rh  111 CO  1.34    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Pd  111 CO  1.55    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Ni  111 CO  1.63    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Pt  111 CO  1.7 fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Cu  111 CO  2.58    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Ag  111 CO  2.99    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Au  111 CO  3.04    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Ru  111 O-CO    2.53    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Rh  111 O-CO    3.1 fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Ni  111 O-CO    3.25    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Pt  111 O-CO    4.04    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Cu  111 O-CO    4.18    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Pd  111 O-CO    4.2 fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Ag  111 O-CO    5.05    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Au  111 O-CO    5.74    fcc [] [] "Angew. Chem. Int. Ed., 47, 4835 (2008)"
Ag  111 O-O 5.98    fcc [] [] "Falsig et al (2012)"
Au  111 O-O 7.22    fcc [] [] "Falsig et al (2012)"
Cu  111 O-O 4.74    fcc [] [] "Falsig et al (2012)"
Pt  111 O-O 5.35    fcc [] [] "Falsig et al (2012)"
Rh  111 O-O 3.79    fcc [] [] "Falsig et al (2012)"
Ru  111 O-O 3.34    fcc [] [] "Falsig et al (2012)"
Pd  111 O-O 5.34    fcc [] [] "Falsig et al (2012)"
```

Exercise: Write the CatMAP reactions for the other two elementary steps.

CatMAP 2: Constructing a volcano plot

- Required inputs:
    - Input file (with all DFT energies, species names, etc.)
    - Mechanism (in CatMAP plain text syntax)
    - Surface types (must match input file)
    - Descriptor names (which species to use as descriptors)
    - Descriptor ranges/resolution (defines the grid to map over)
    - Temperature and pressure of gases
    - Thermodynamic model to use for enthalpy/entropy
    - Site names (must match input file)
    - Scaling constraints (improves scaling relations with few data points)
    - Precision and tolerance (for the root finding algorithm)

```python
rxn_expressions = [

            '*_s + CO_g -> CO*',
            '2*_s + O2_g <-> O-O* + *_s -> 2O*',
            'CO* +   O* <-> O-CO* + * -> CO2_g + 2*',

            ]
```

```python
descriptor_ranges = [[-1,3],[-0.5,4]]

resolution = 15
```

```python
scaling_constraint_dict = {
            'O_s':['+',0,None],
            'CO_s':[0,'+',None],
            'O-CO_s':'initial_state',
            'O-O_s':'final_state',
            }
```

CatMAP 2: Output of tutorial
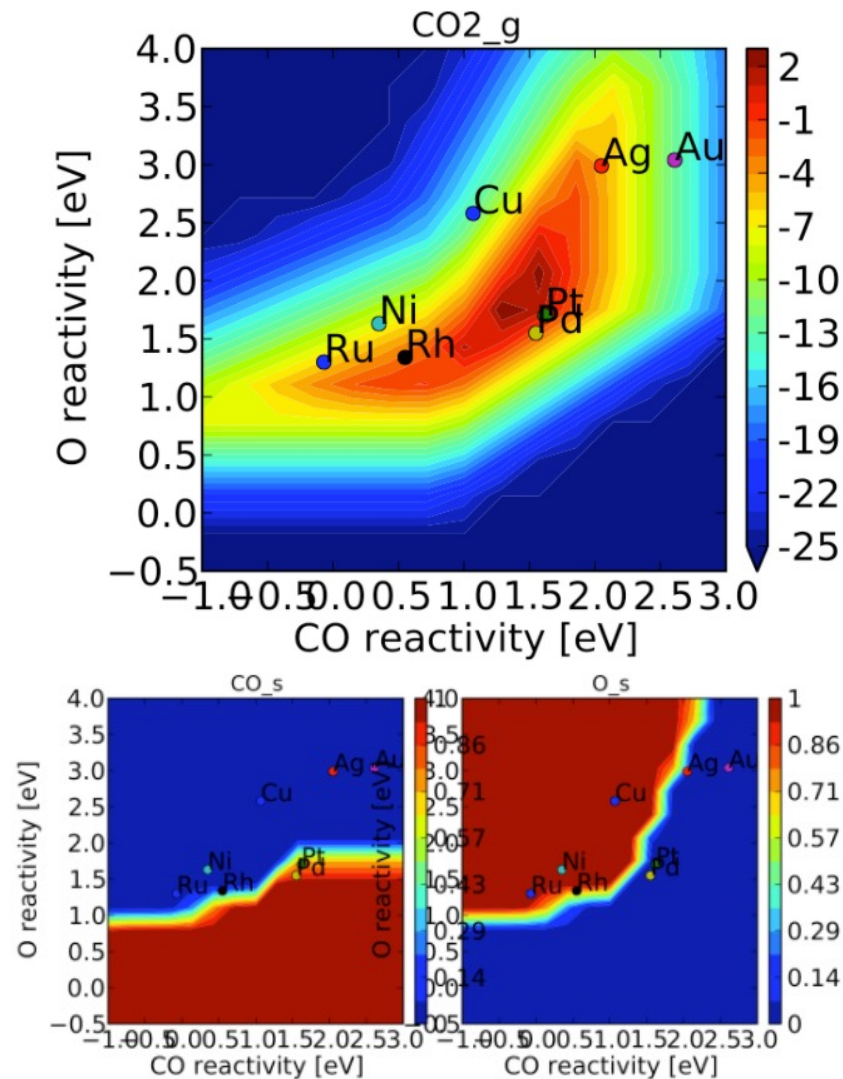
- Volcano plot showing CO_2 production rate

- Coverage "maps" to help interpret the results

- All raw data can also be accessed and post-processed using other tools

  - See "Topic" in documentation on "Accessing and reformatting output"

Why use CatMAP?

- It may be challenging, but it is easier than constructing models from scratch (especially for complex mechanisms)

- Many tutorials and sample input files available to learn basic usage

- Improve reproducibility in microkinetic modeling research
  - If you publish a paper with CatMAP, please include the input files in the SI!

- A platform for implementing, testing, and improving features available in volcano plot construction
  - Lots of advanced (though sometimes poorly tested) features

Additional CatMAP features

- Multi-site models (see Tutorial 3)
  - Utilize multiple active site types within a single reaction mechanism
- Thermodynamic "descriptors"
  - Map out TOF of a single catalyst over a range of reaction conditions
- Adsorbate-adsorbate interactions
  - Allow rate constants to depend on coverage (beware of convergence and sensitivity issues)
- Electrochemistry
  - Calculate rate as a function of voltage, or volcano plots at a fixed voltage

See "Topics" and "Examples" to learn more about these features

Conclusions

- Microkinetic models combined with scaling relations lead to "volcano plots" that represent Sabatier's principle

- Constructing a volcano plot requires:
  - Description of reaction mechanism/network
  - Active site "motif" with many possible compositions (e.g. metal (211) sites)
  - Calculated free energies of all intermediates and transition-states for a number of representative active sites (e.g. 5 single-element transition metal (211) surfaces)
  - Scaling relations (or other functions) that accurately predict all adsorption energies across all materials as a function of 1-2 independent variables
  - Solving many microkinetic models over a range of parameter values