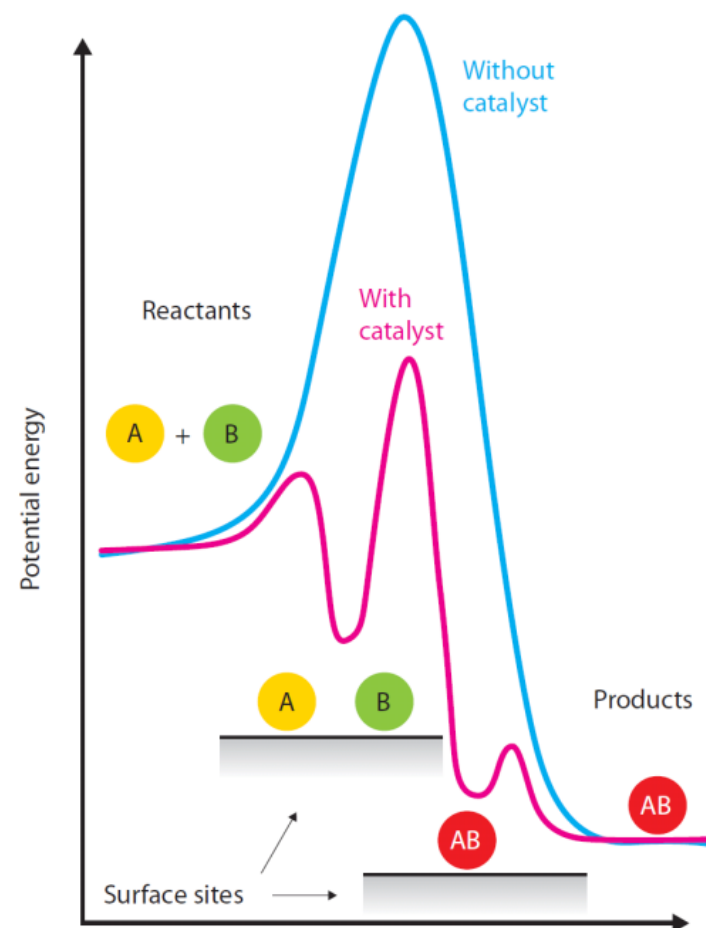


Towards Catalyst Design Rules

Jens Nørskov

norskov@stanford.edu

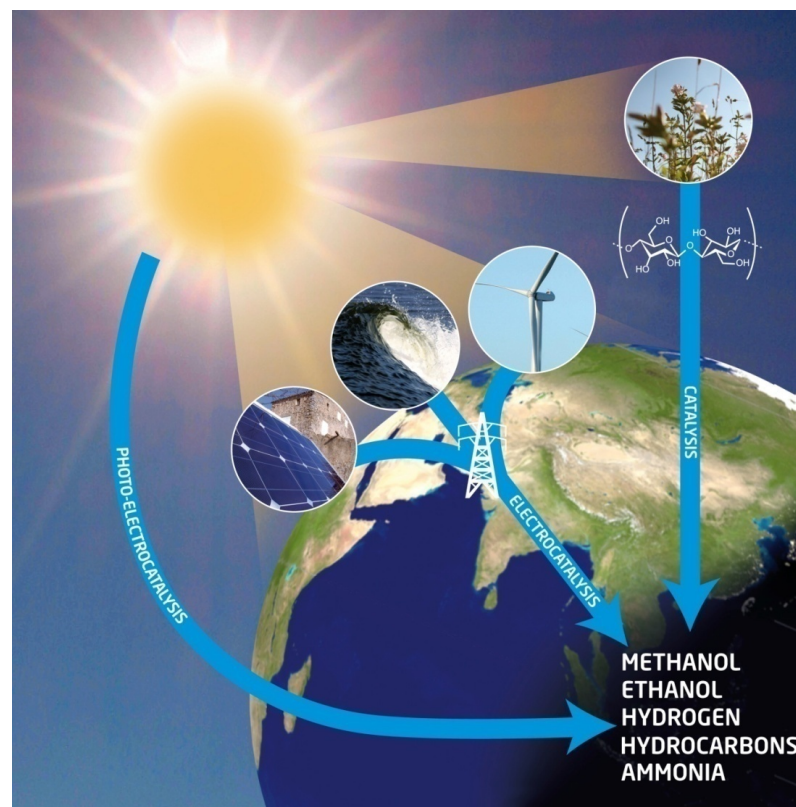


Why catalysis?



Control of chemical processes:

- >10% of GNP
- ~10% of energy use
- ~90% of chemicals and materials production dependent on catalysis
- Sustainable fuels and chemicals only possible w. new catalysts

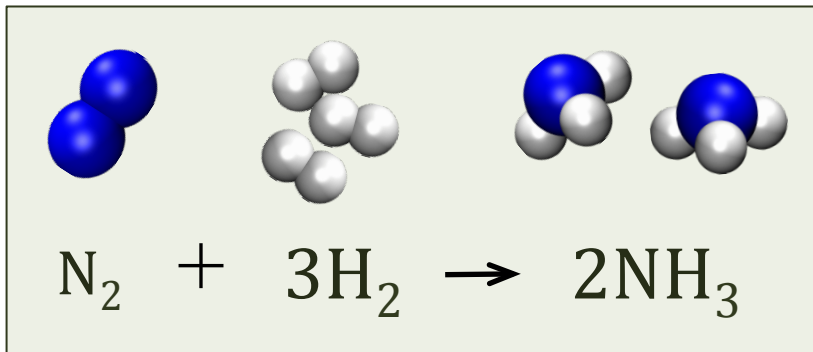


Ammonia Synthesis

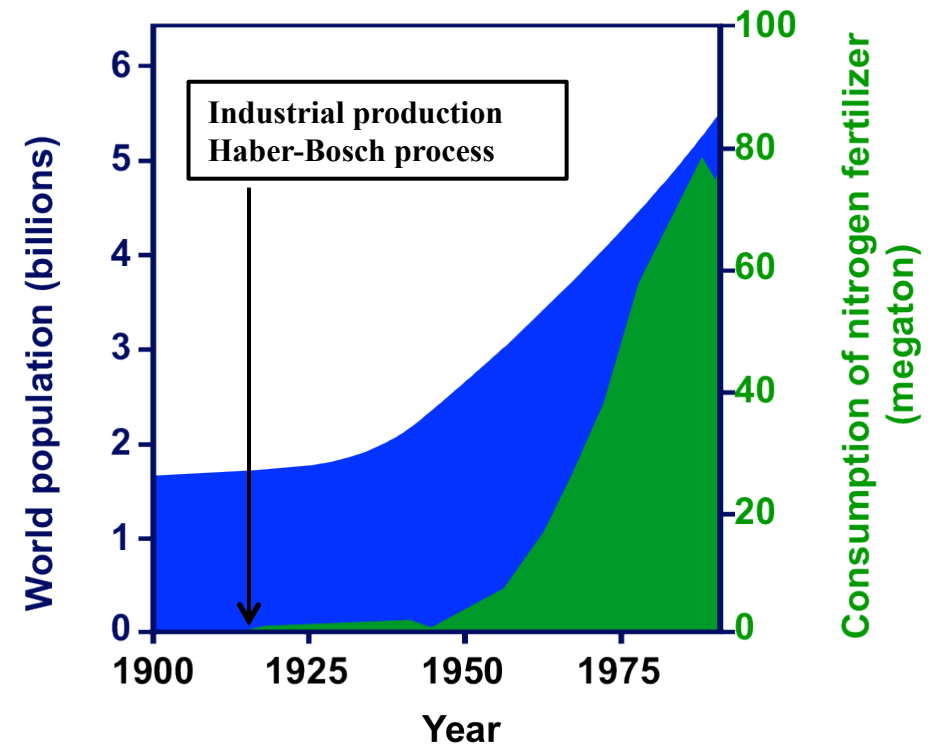


“Most important discovery in 20th century”

Smil, Nature **400**, 415 (1999)

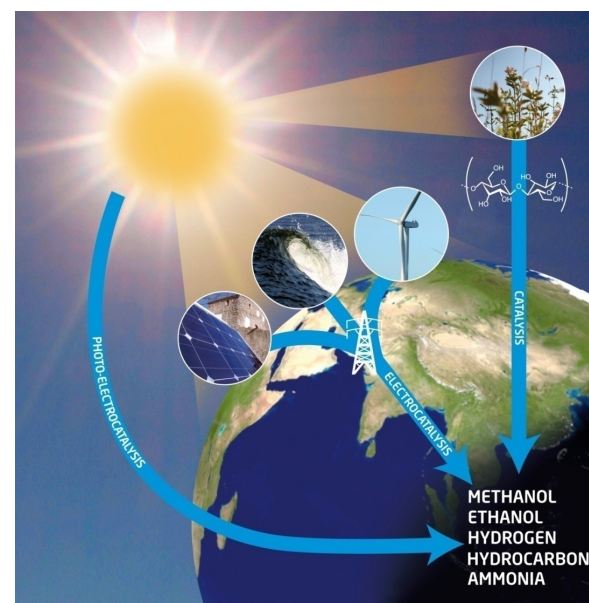
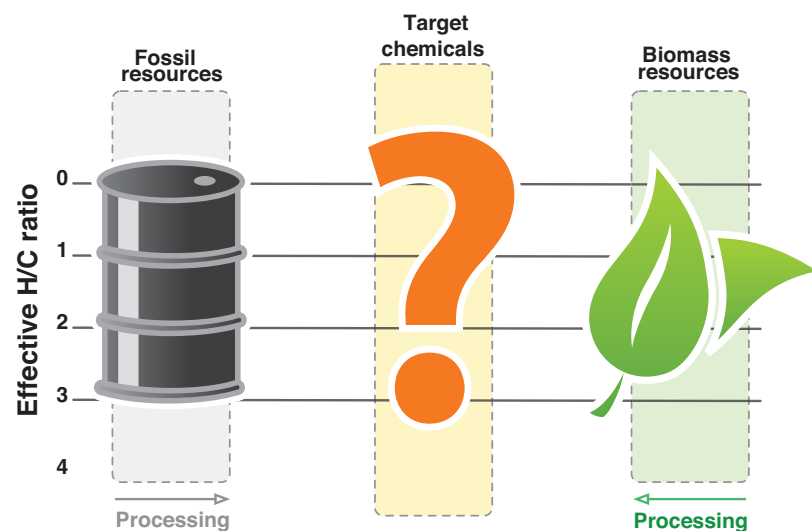


- 1-2% of all energy use in world



The need for a new chemistry

Need technology for production of chemicals, incl. fuels,
that does not rely on fossil feedstocks



The need for a new chemistry



Current technology is extremely wasteful

Subsector	Quantity produced ton product per year	Product Value US \$ per kg	E-factor (kg waste/kg product)
Oil Refining	$10^6 - 10^8$	<5	< 0.1
Bulk Chemicals	$10^4 - 10^6$	1-10	< 1 to 5
Fine Chemicals	$10^2 - 10^4$	$10 - 10^3$	5 to > 50
Pharmaceuticals	$10 - 10^3$	$10^2 - 10^6$	25 to 100

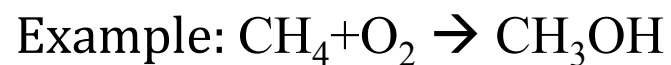


Sheldon, Chemtech, March 1994, p38

The need for a new chemistry



Many processes do not have a catalyst

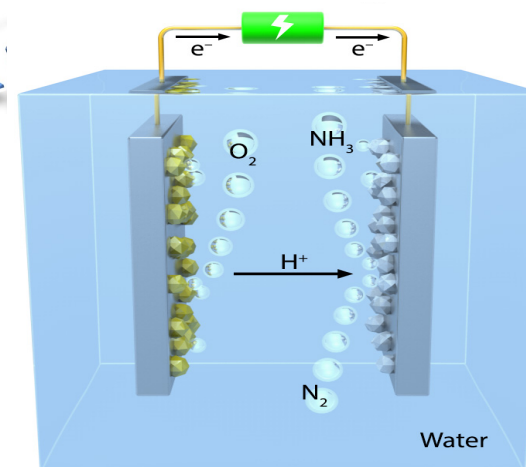
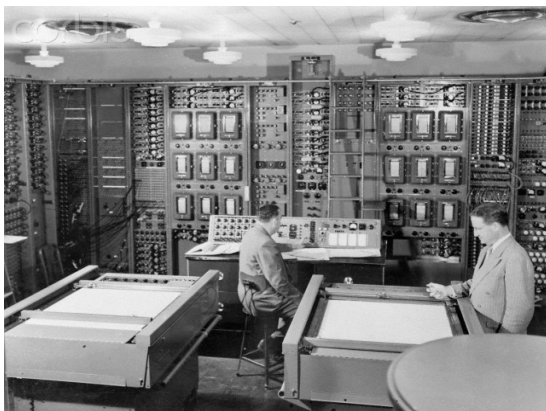


NYTimes.com

The need for a new chemistry



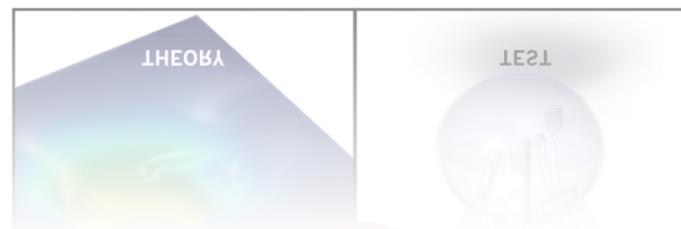
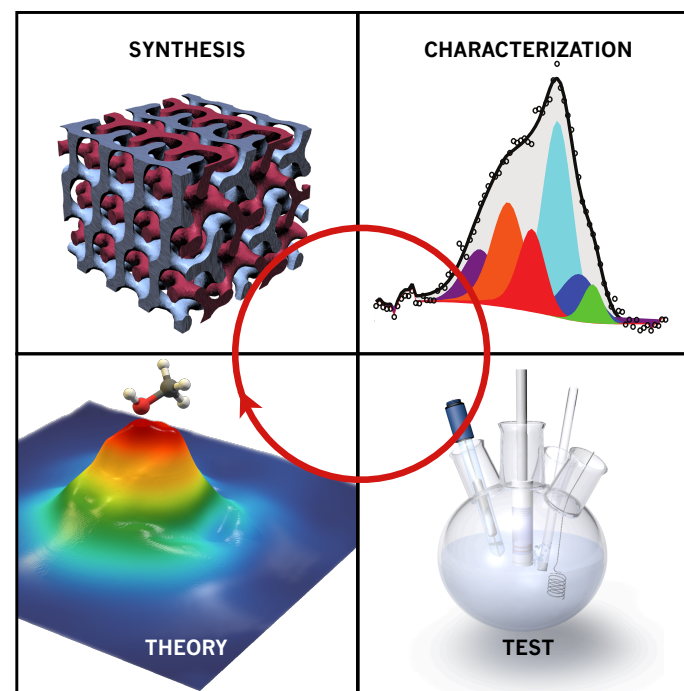
Decentralized production



Catalyst design strategy



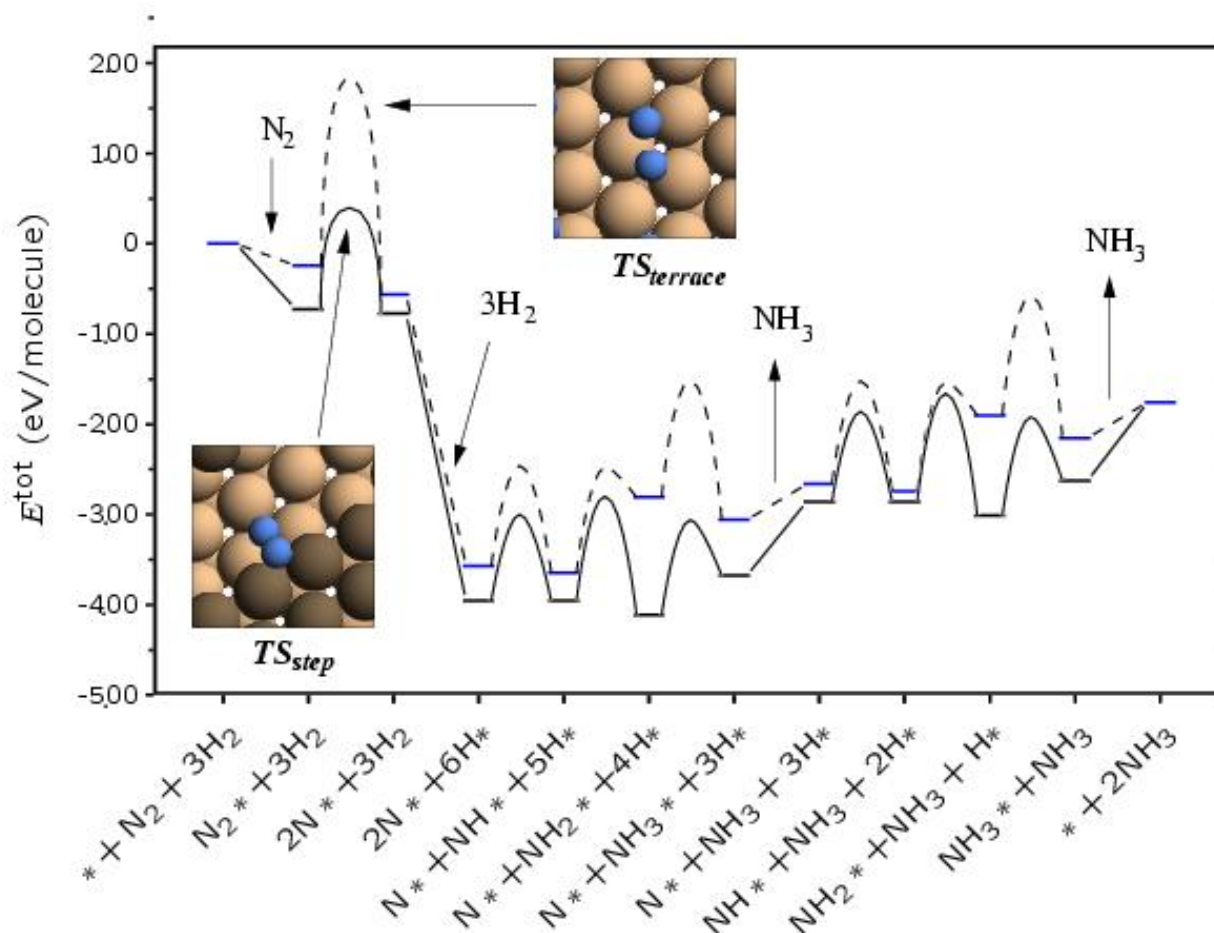
1. Develop a theory of catalysis that extracts the most important descriptors of catalytic rates
2. Find optimum rate and selectivity criteria
3. Use computers to search for leads
4. Include feedback from experiment



Theory of catalysis – Dealing with complexity



Ammonia synthesis over Ru



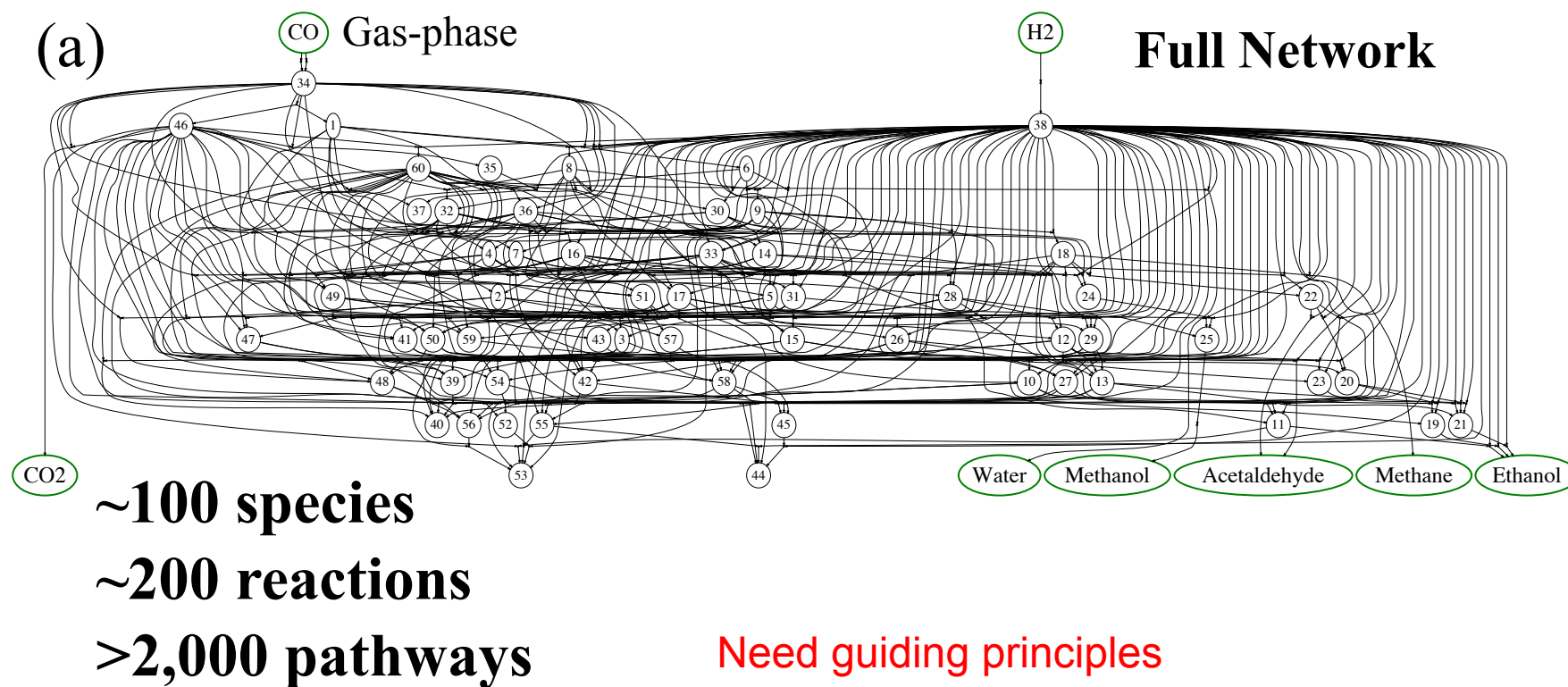
14 relevant
energy
descriptors

Honkala, Remediakis, Logadottir, Nørskov, Hellmann,
Dahl, Carlsson, Christensen, Science **307**, 555 (2005)

Dealing with complexity



CO (and CO₂) hydrogenation



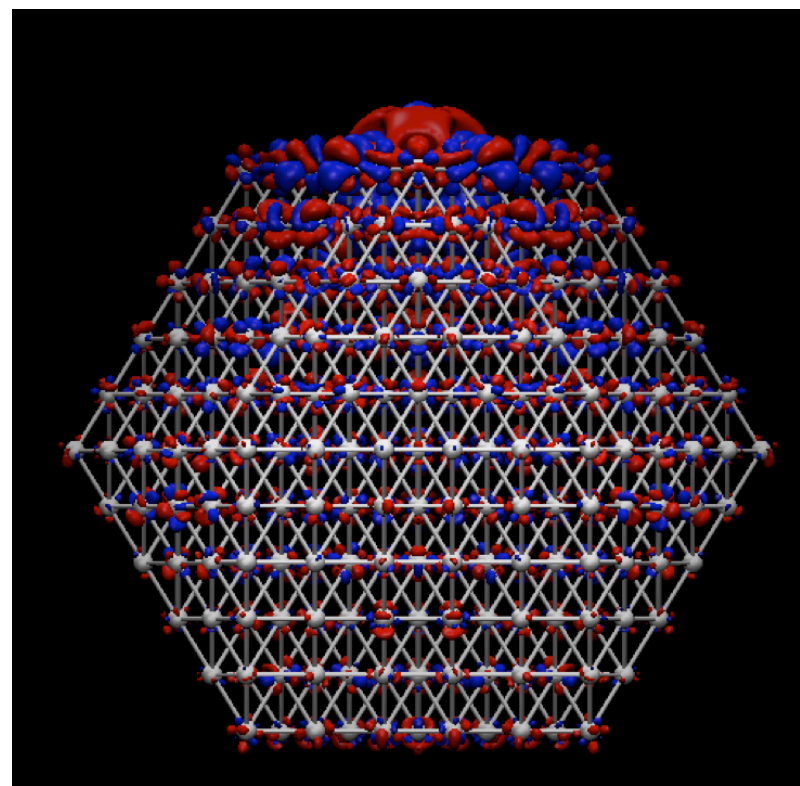
Ulissi, Medford, Bligaard, Nørskov (2016)
Yang, Medford, Liu, Studt, Bligaard, Bent, Nørskov, JACS (2016)

The approach – complexity reduction



Theory of transition metal heterogeneous catalysis

1. Understand *intrinsic* activity/selectivity of surfaces
2. Add effects of
 - Finite size
 - Additives
 - Support
 -
3. Test model by making predictions
 - Design rules



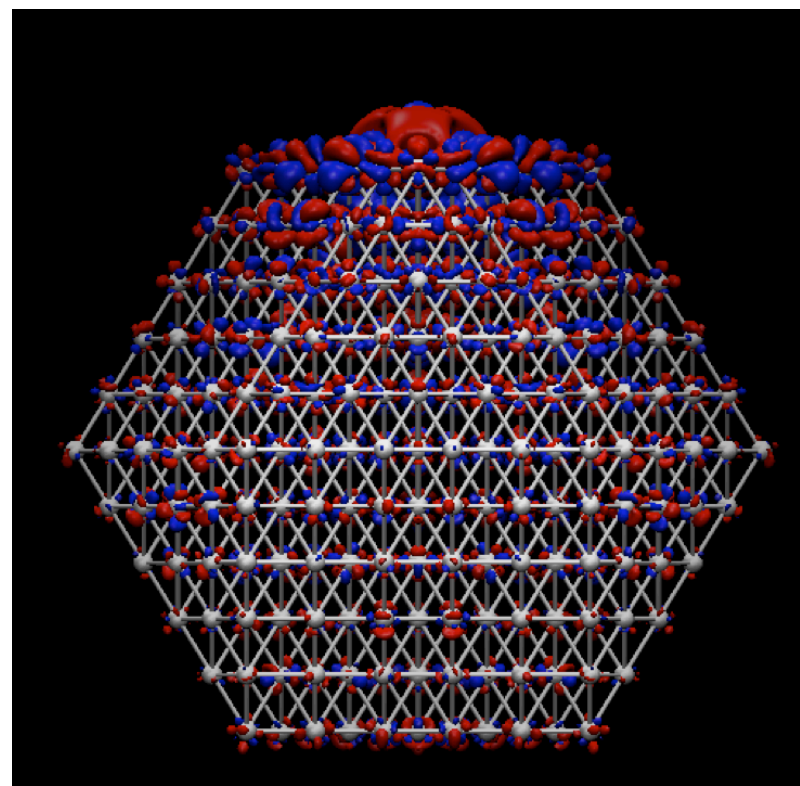
Li, Larsen, Romero, Morozov, Glinsvad, Abild-Pedersen, Greeley, Jacobsen, Nørskov, J. Phys. Chem. Lett., **4**, 222 (2013).

Outline



Theory of transition metal heterogeneous catalysis

- Introduction to scaling relations
 - Simple example: NH_3 synthesis
- Activity and selectivity maps
 - Generalization to more more complex reactions
- Catalyst Design Strategies
 - The optimum descriptor
 - Beyond known scaling relations

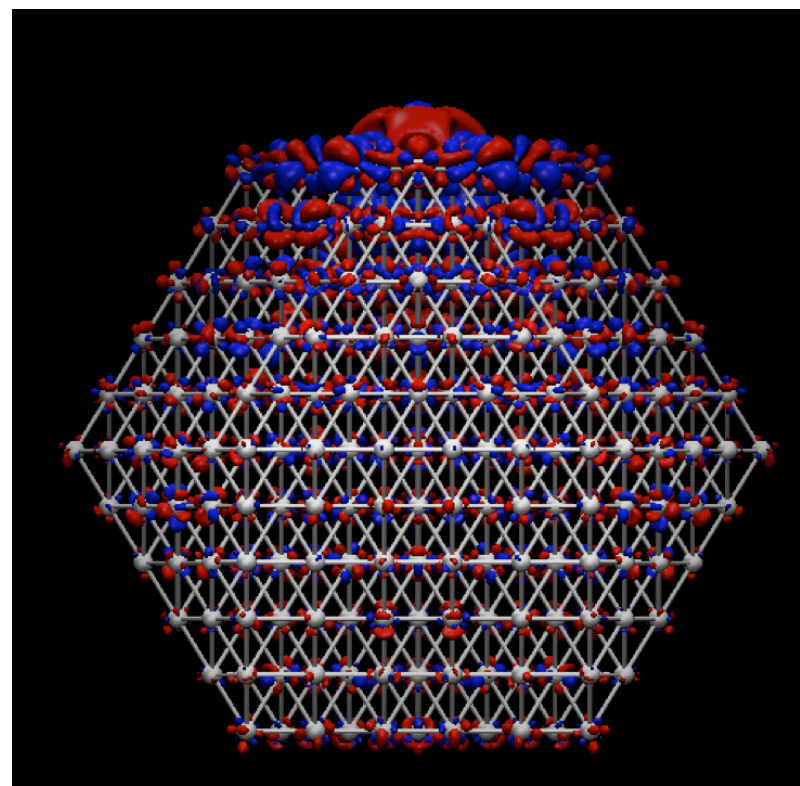


Outline



Theory of transition metal heterogeneous catalysis

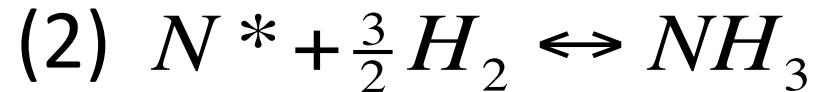
- Introduction to scaling relations
 - Simple example: NH_3 synthesis
- Activity and selectivity maps
 - Generalization to more more complex reactions
- Catalyst Design Strategies
 - The optimum descriptor
 - Beyond known scaling relations



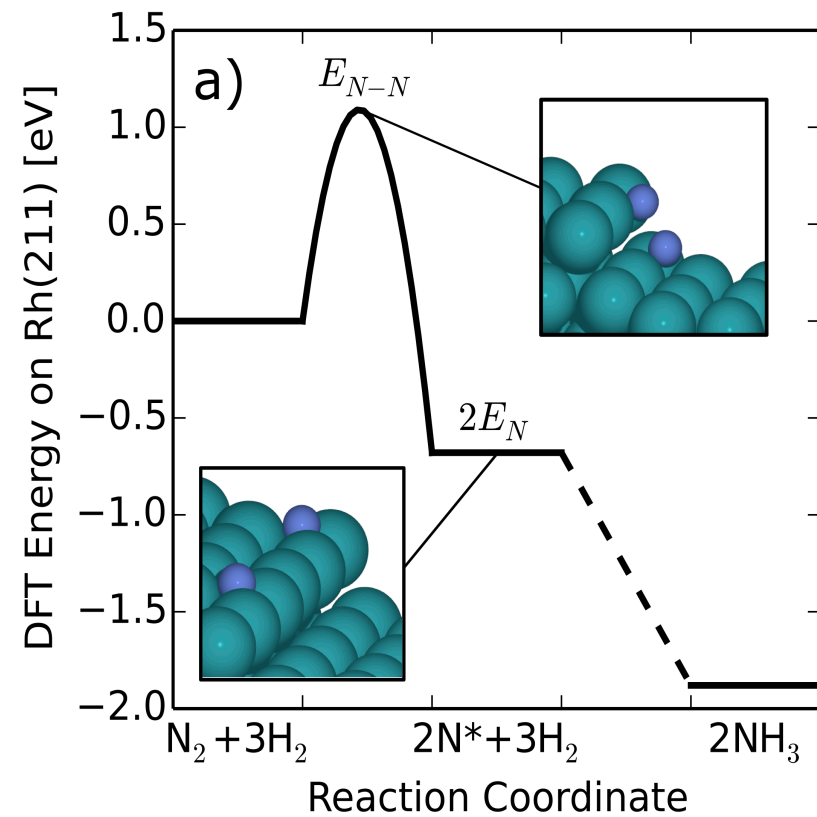
Simple model of Ammonia synthesis



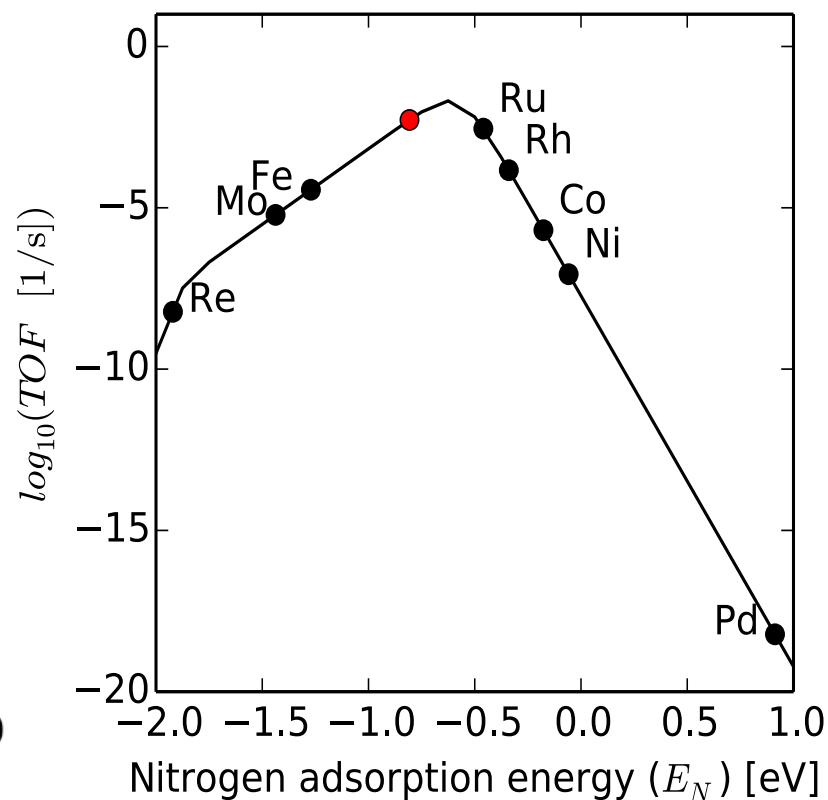
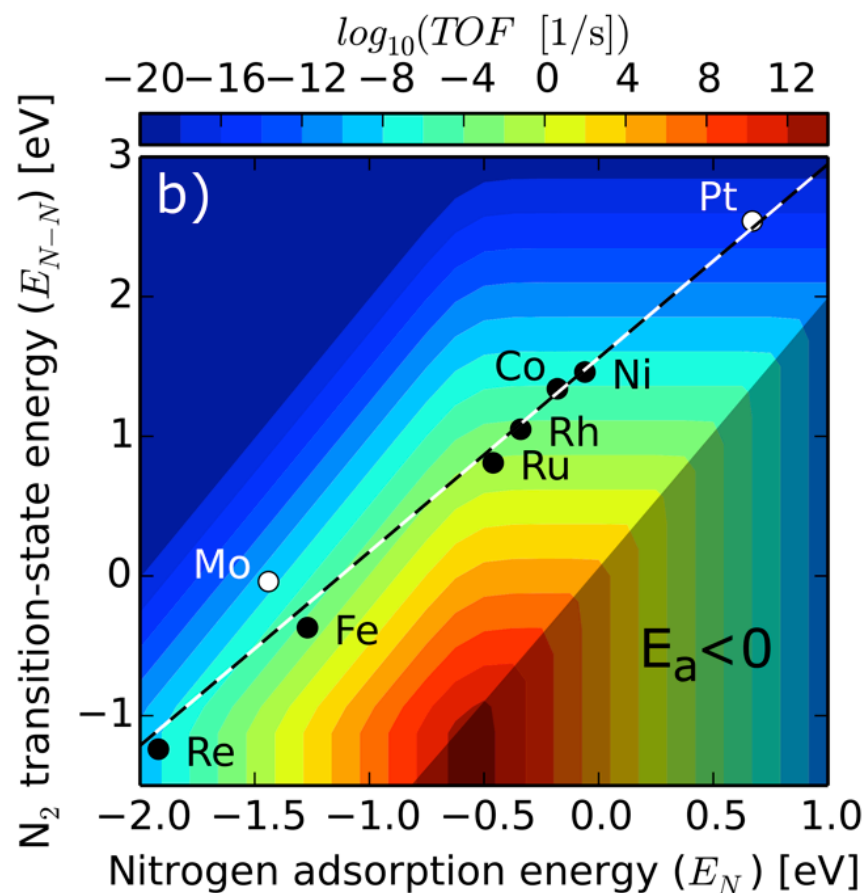
Mechanism:



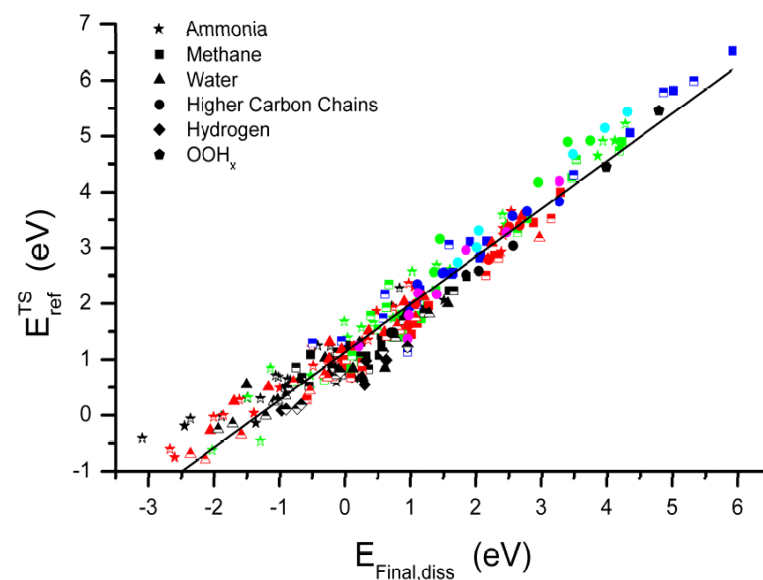
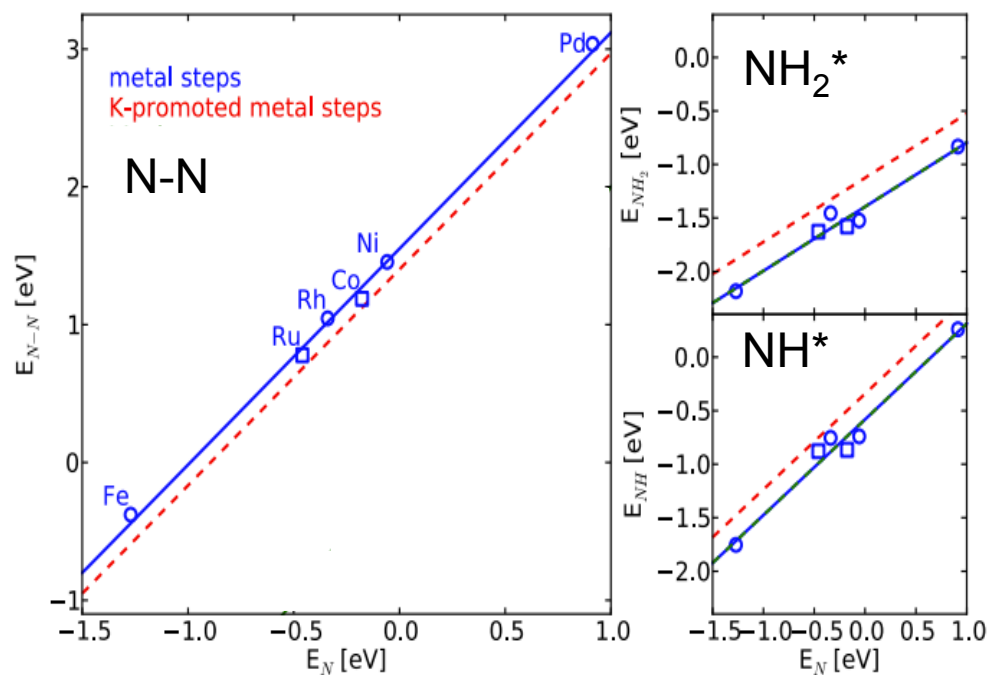
(1) is rate determining



Descriptors: from two to one



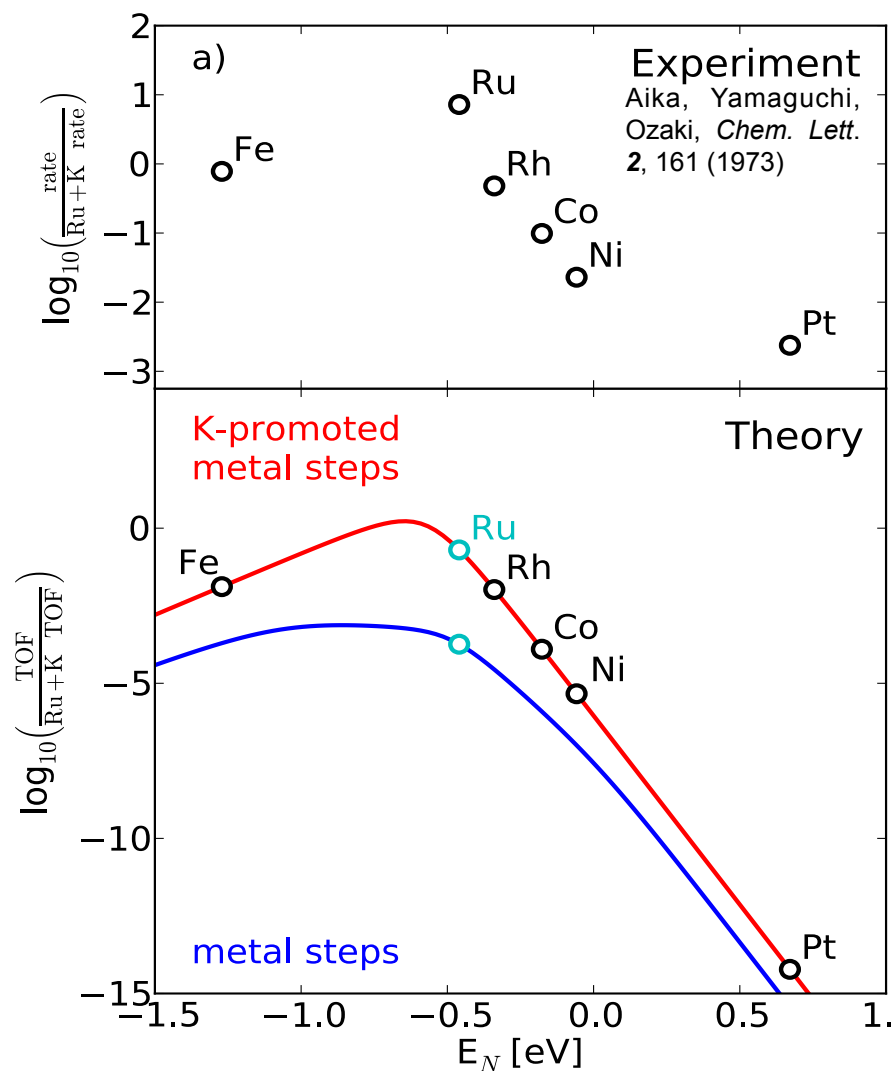
More scaling relations; ammonia synthesis



Vojvodic, A. J. Medford, Khan, Studt, Abild-Pedersen, Bligaard, Nørskov, CPL **598**, 108 (2014)

Wang, Petzold, Tripkovic, Kleis, Howalt, Skulason, Fernandez, Hvolbæk, Jones, Toftelund, Falsig, Björketun, Studt, Abild-Pedersen, Rossmeisl, Nørskov, Bligaard, PCCP **13**, 20760 (2011)

Full model, theory vs. experiment

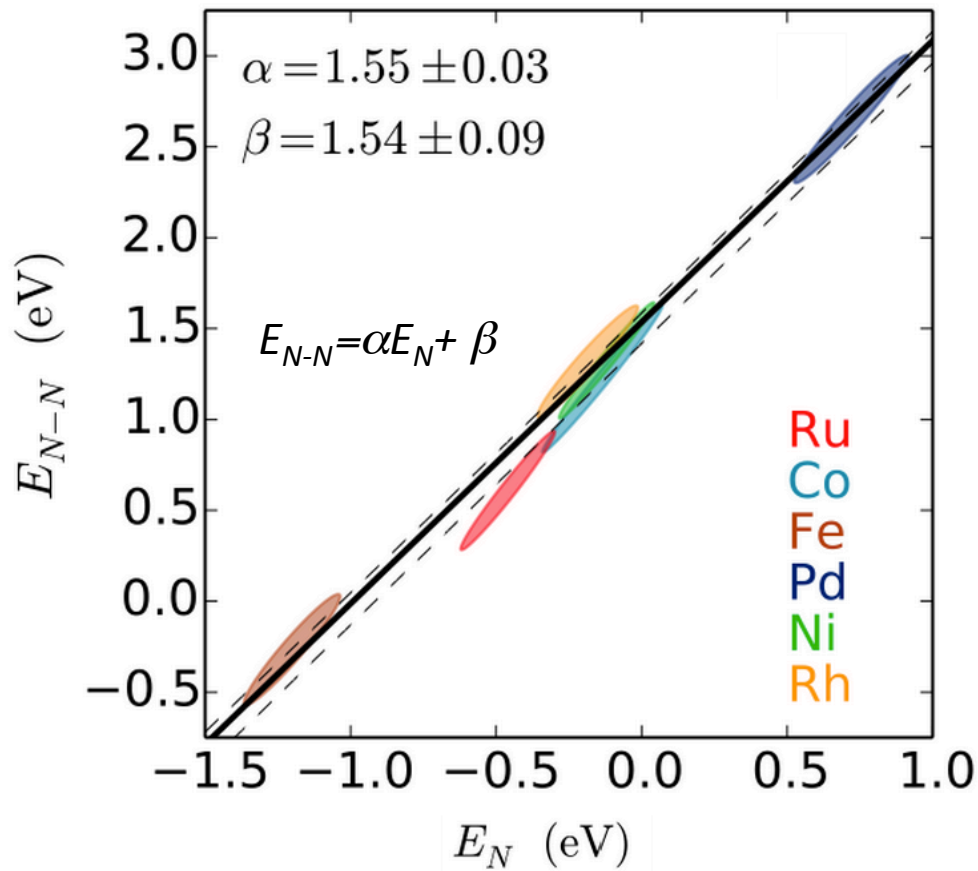


Vojvodic, Medford, Studdt, Abild-Pedersen, Kahn, Bligaard, Nørskov,
Chem. Phys. Lett. **598**, 108 (2014)

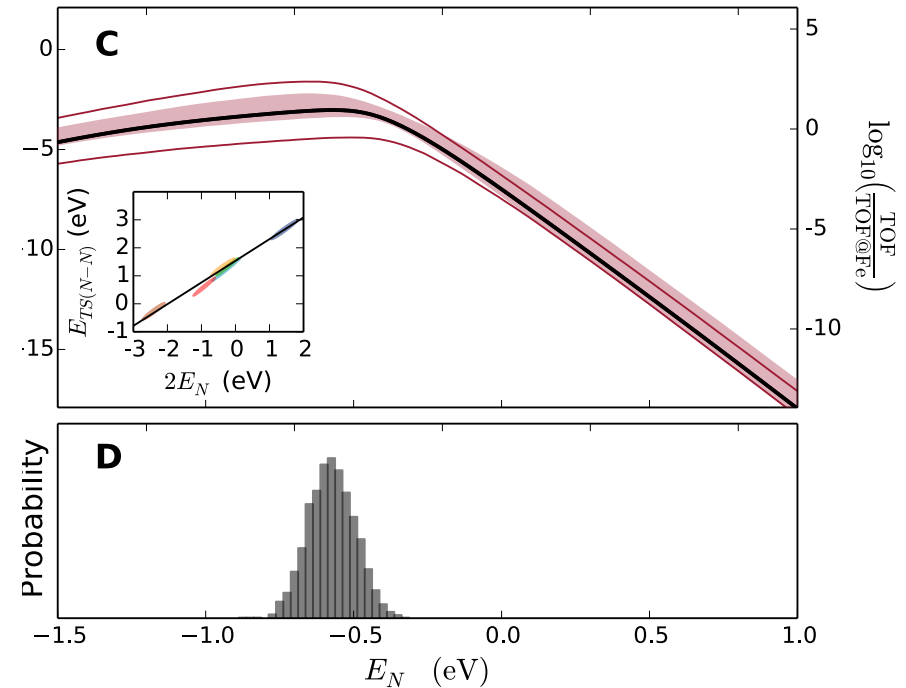
Quantifying DFT errors



Scaling relation



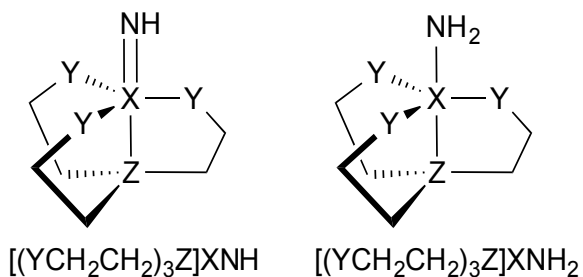
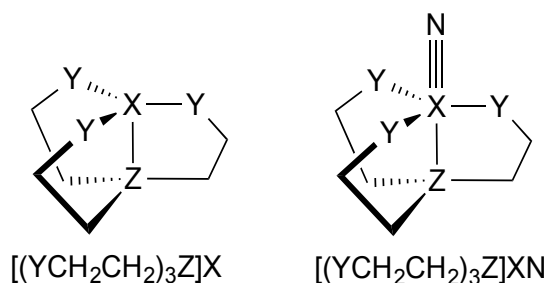
Activity map



Scaling in hom. catalysis

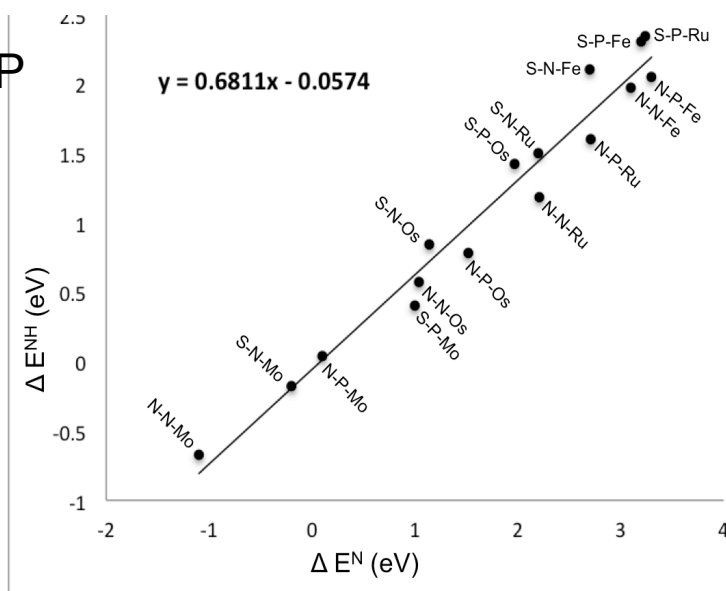
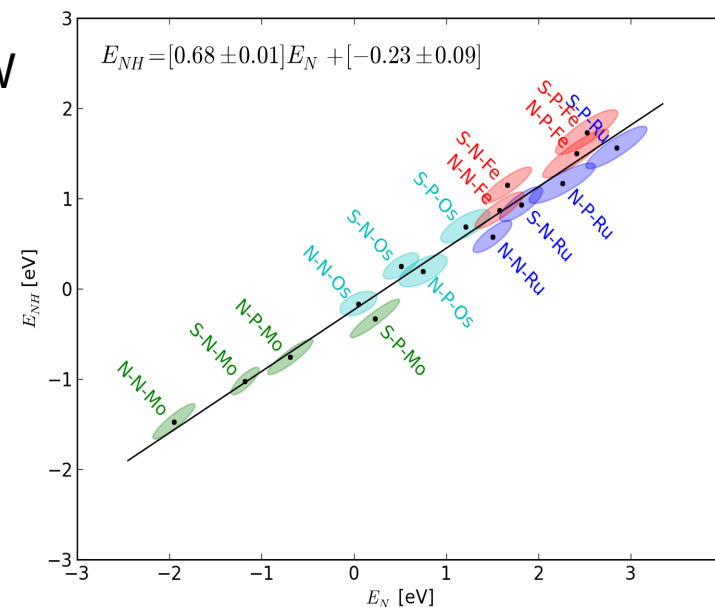


QE, BEEF-vdW



$X = Mo, Ru, Os \text{ or } Fe.$
 $Y = NH \text{ or } S.$
 $Z = N \text{ or } P.$

Jaguar, B3LYP

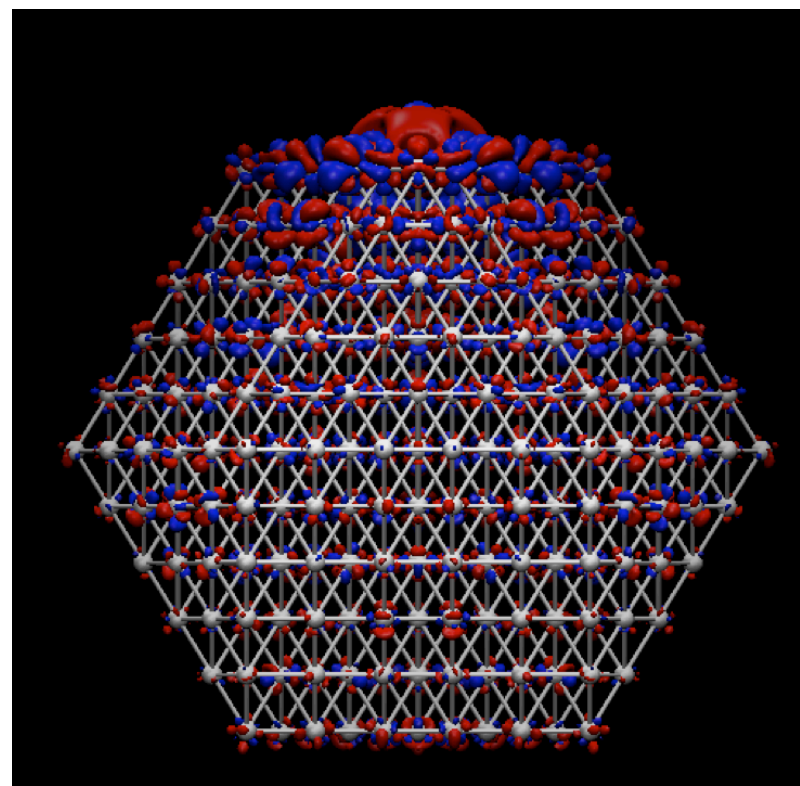


Outline



Theory of transition metal heterogeneous catalysis

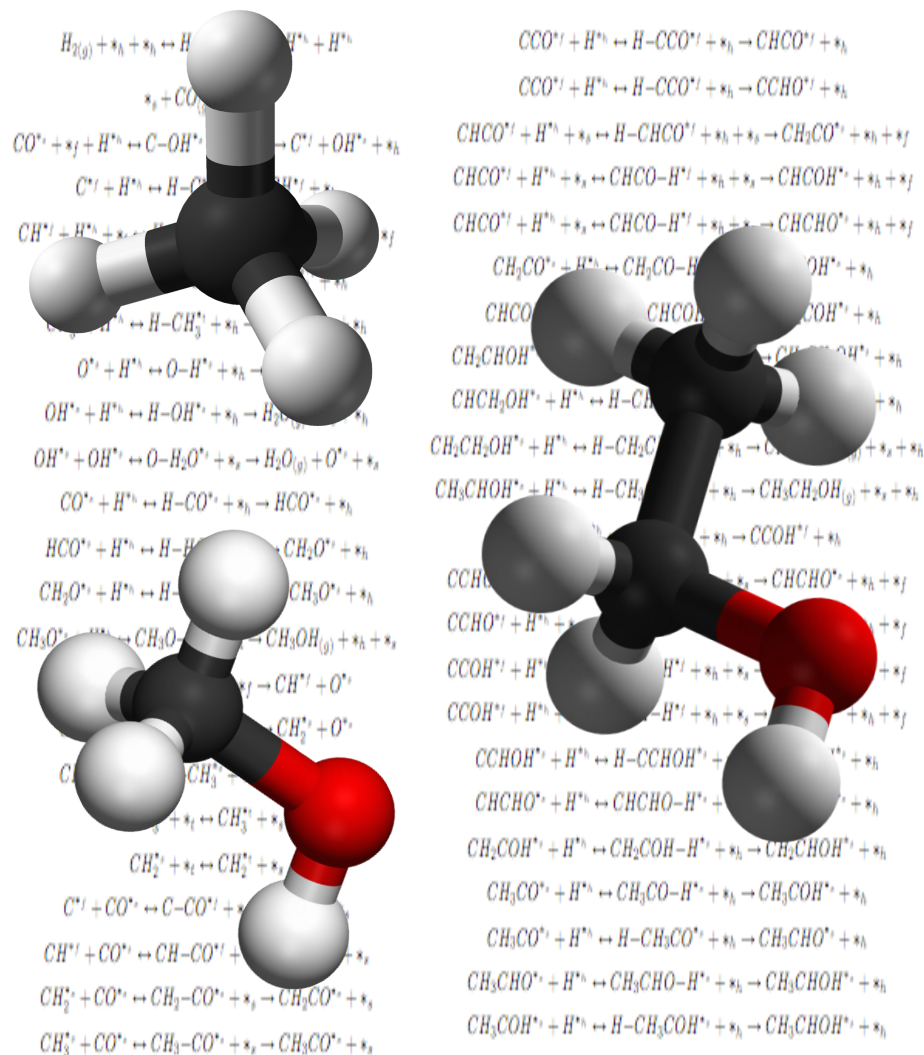
- Introduction to scaling relations
 - Simple example: NH_3 synthesis
- Activity and selectivity maps
 - Generalization to more more complex reactions
- Catalyst Design Strategies
 - The optimum descriptor
 - Beyond known scaling relations



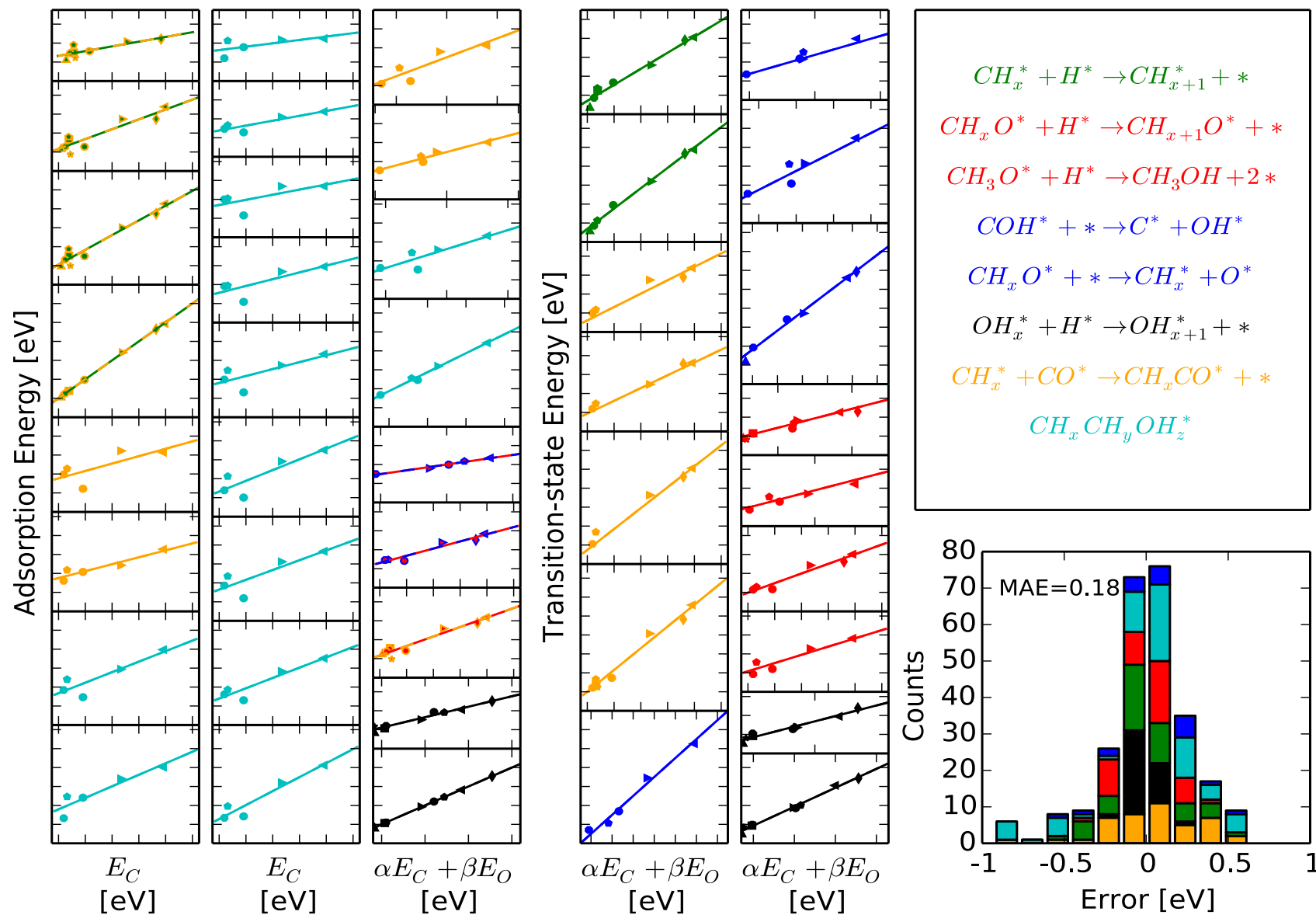
More complexity: CO hydrogenation

- Methane synthesis:
 - CO dissociation (H-assisted)
 - CH_x hydrogenation
 - OH_x hydrogenation
- Methanol synthesis:
 - CH_xO hydrogenation
 - $\text{CH}_x\text{-O}$ dissociation
- Ethanol synthesis:
 - $\text{CH}_x\text{-CO}$ coupling (CO insertion)
 - CCO backbone hydrogenated via network of 28 elementary steps

51 elementary steps, 30 intermediates $\rightarrow$ 81 parameters

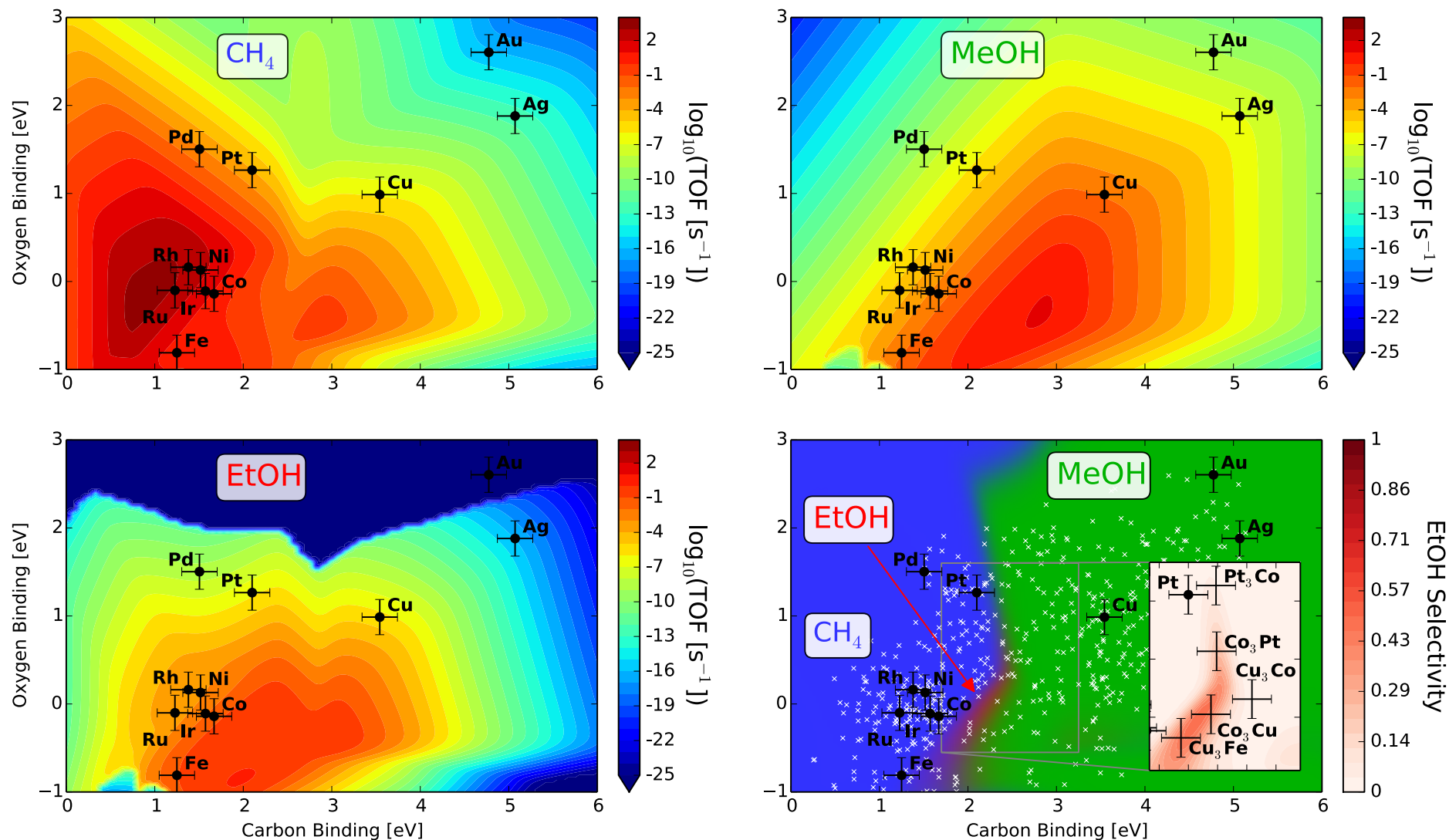


Scaling relations, EtOH synthesis



Activity and selectivity maps

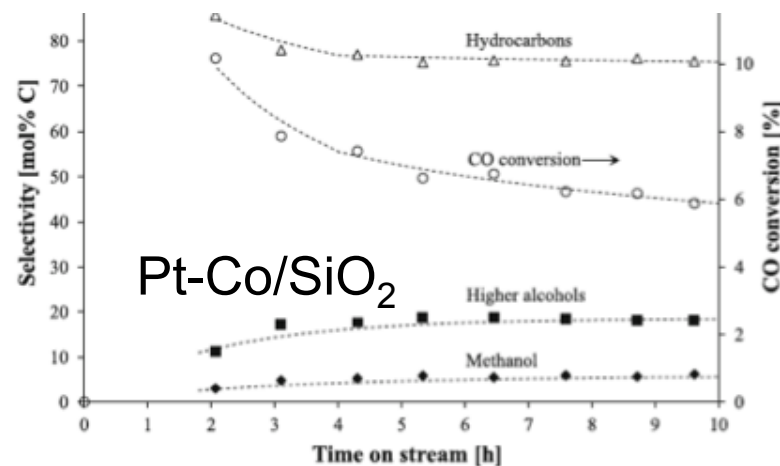
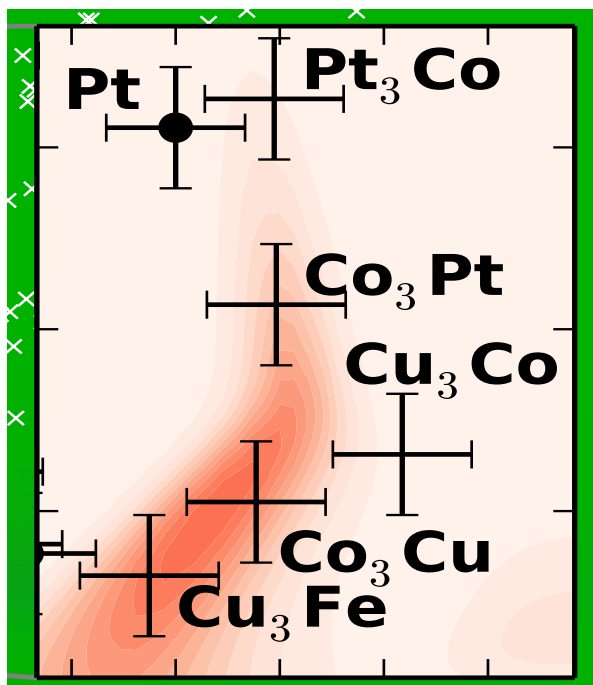
573 K, 2:1 H₂:CO, 90 bar, stepped surfaces



Comparison to experiment

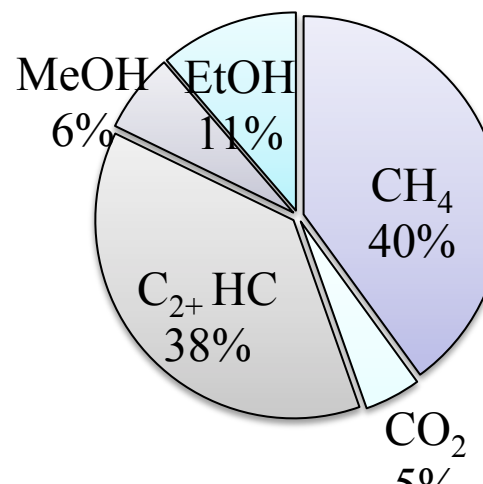


Medford, Lausche, Abild-Pedersen, Temel,
Schjodt, Nørskov, and F. Studt,
Top. Catal. **2014**, 57, 135.



Christensen et al, *Catal. Lett.* **2014**, 144, 777.

Cu-Co



Mendes, J Sinder, Fleischman, Kibsgaard,
Aranda, Tjaramillo, **2016**,

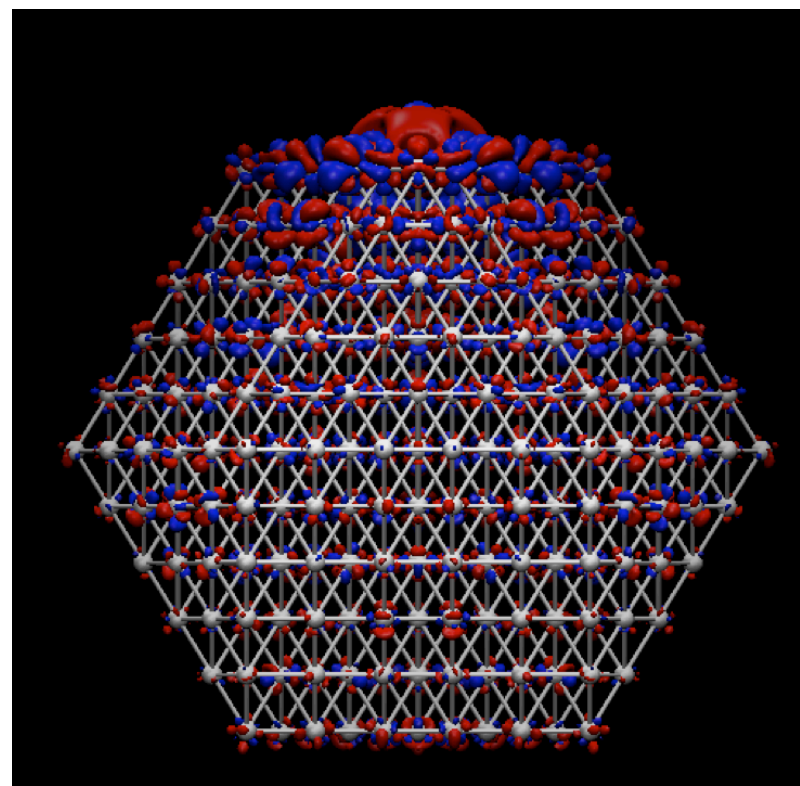
Kruse et. al. *J. Am. Chem. Soc.* **135**, 7114 (2013)
Baker, Burch, Yuqin, *Appl. Catal.* **73**, 135 (1991).
Dong et al., *Catal. Today* **147**, 158 (2009).
Mahdavi, Peyrovi, Islami, Mehr, *Appl. Catal. A Gen.* **281**, 259 (2005).

Outline



Theory of transition metal heterogeneous catalysis

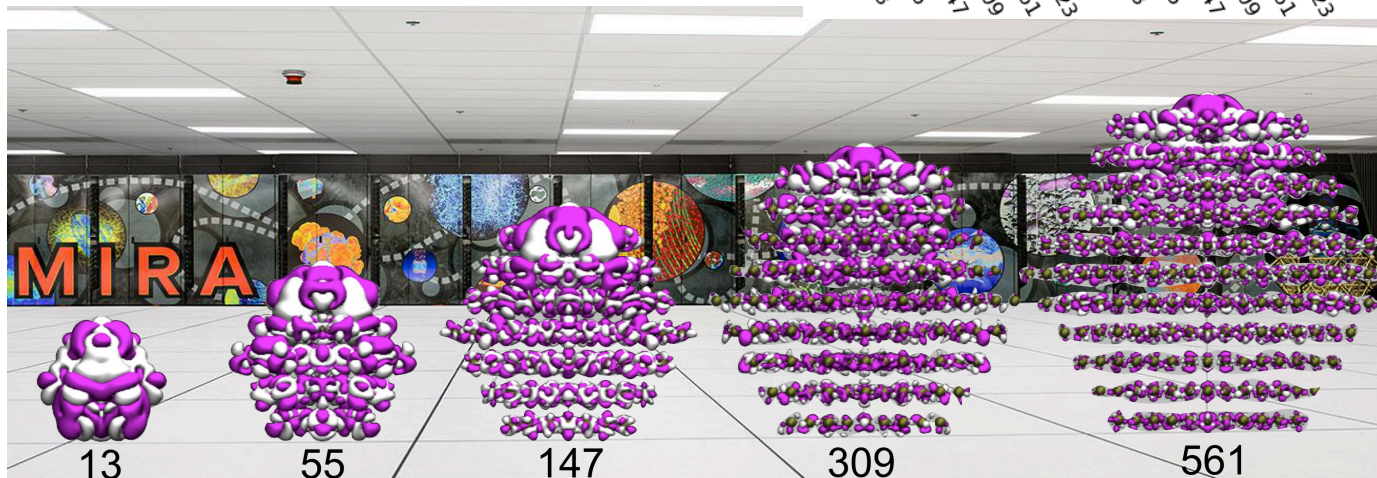
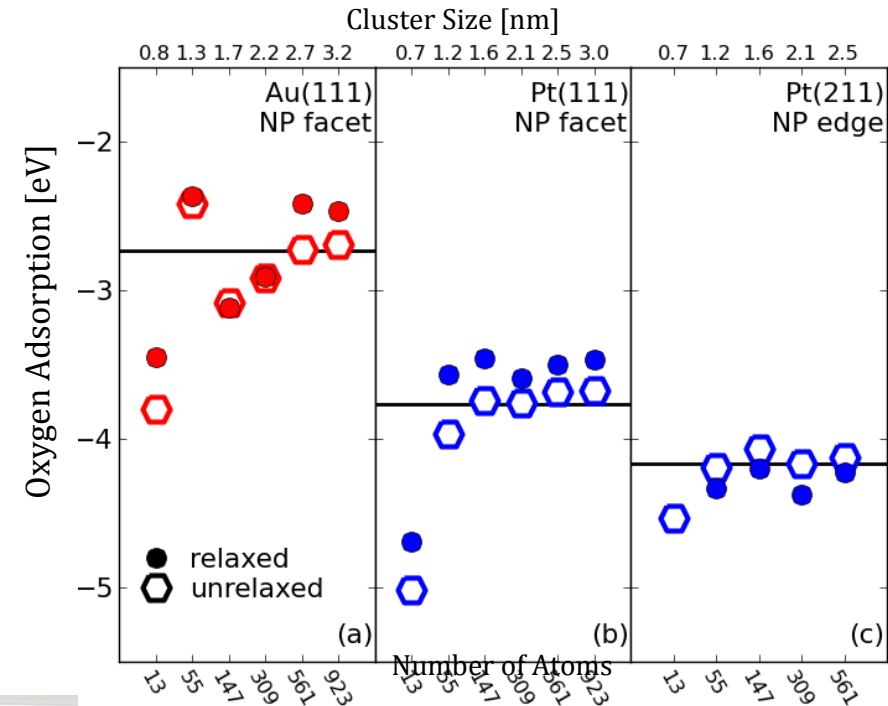
- Introduction to scaling relations
 - Simple example: NH_3 synthesis
- Activity and selectivity maps
 - Generalization to more more complex reactions
- Catalyst Design Strategies
 - The optimum descriptor
 - Beyond known scaling relations



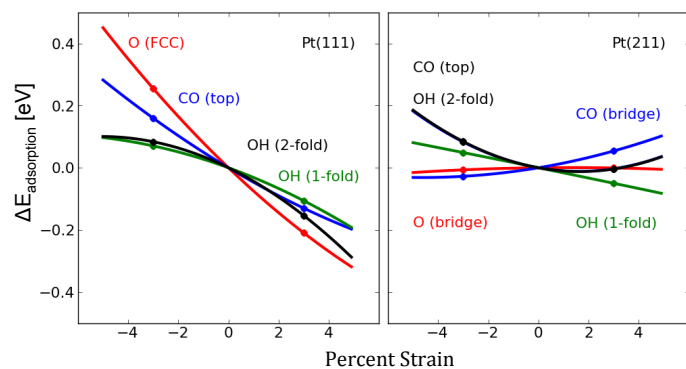
Finite-size Effects

Sources of finite-size effects

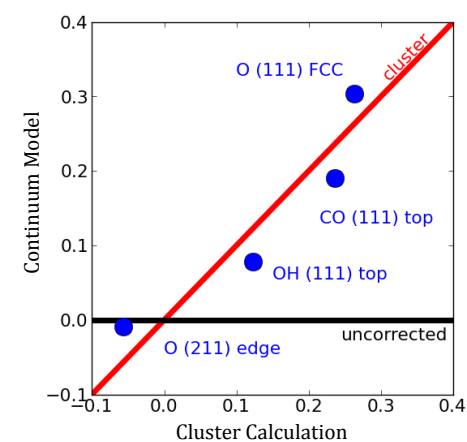
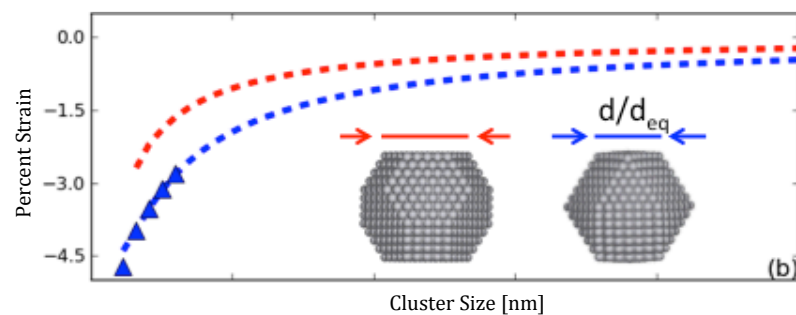
- Ratio of edge and terrace sites
- Compression of metal surface (strain)
- Quantum-size effects



Finite-size Effects



$$\Delta E(d) \approx \left. \frac{d}{ds} [\Delta E(s)] \right|_{s=0} s(d)$$

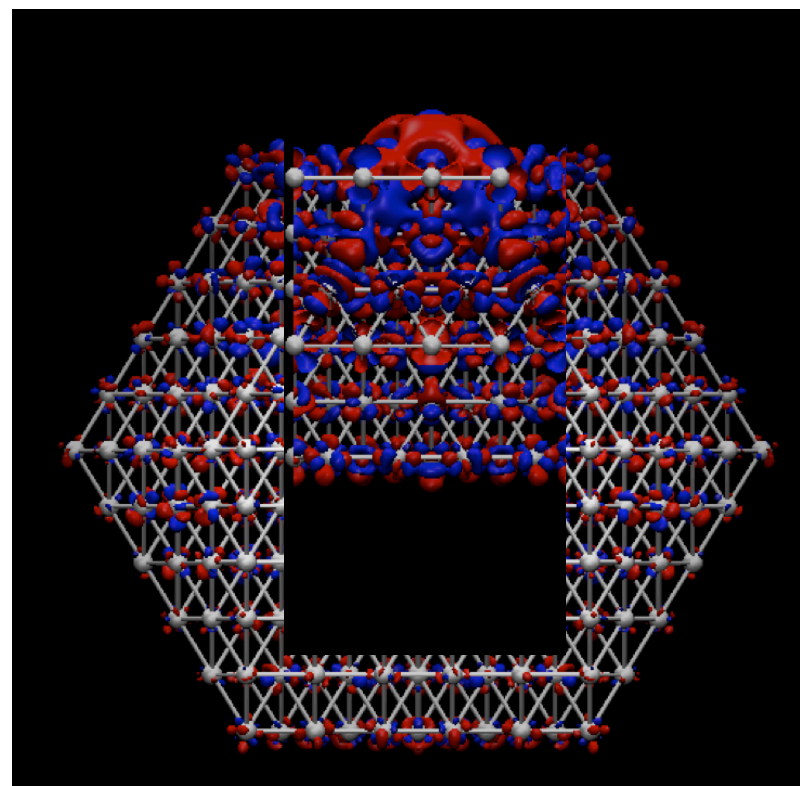


Li, Abild-Pedersen, Greeley, Nørskov, J. Phys. Chem. Lett., **6**, 3797-3801. 2015

Finite size effects

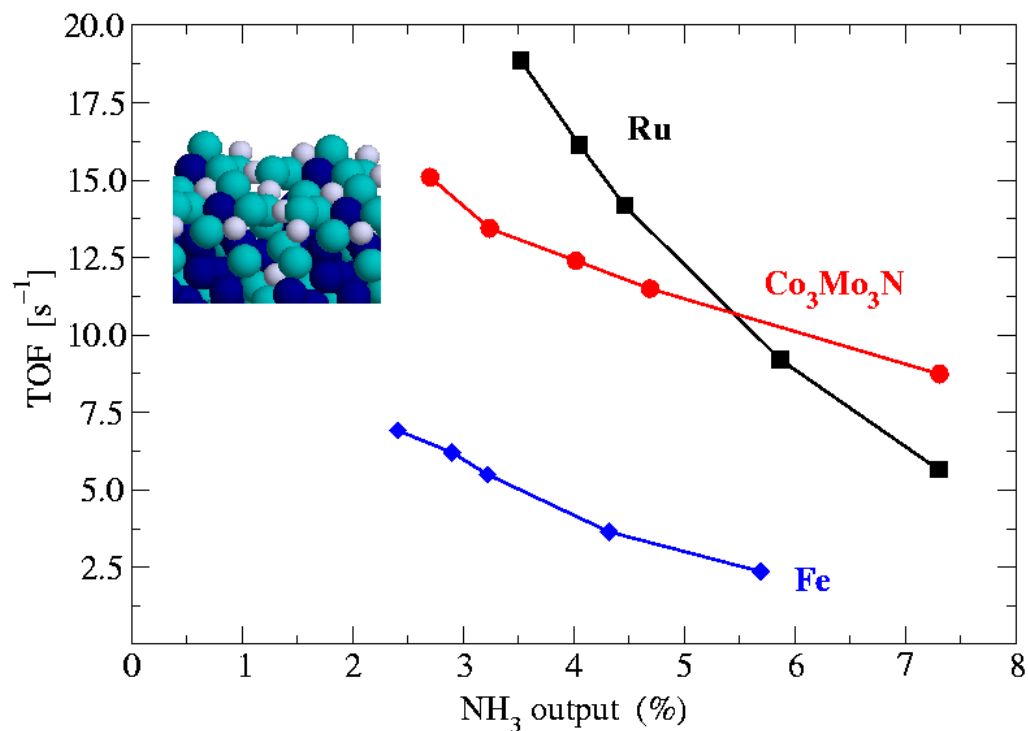
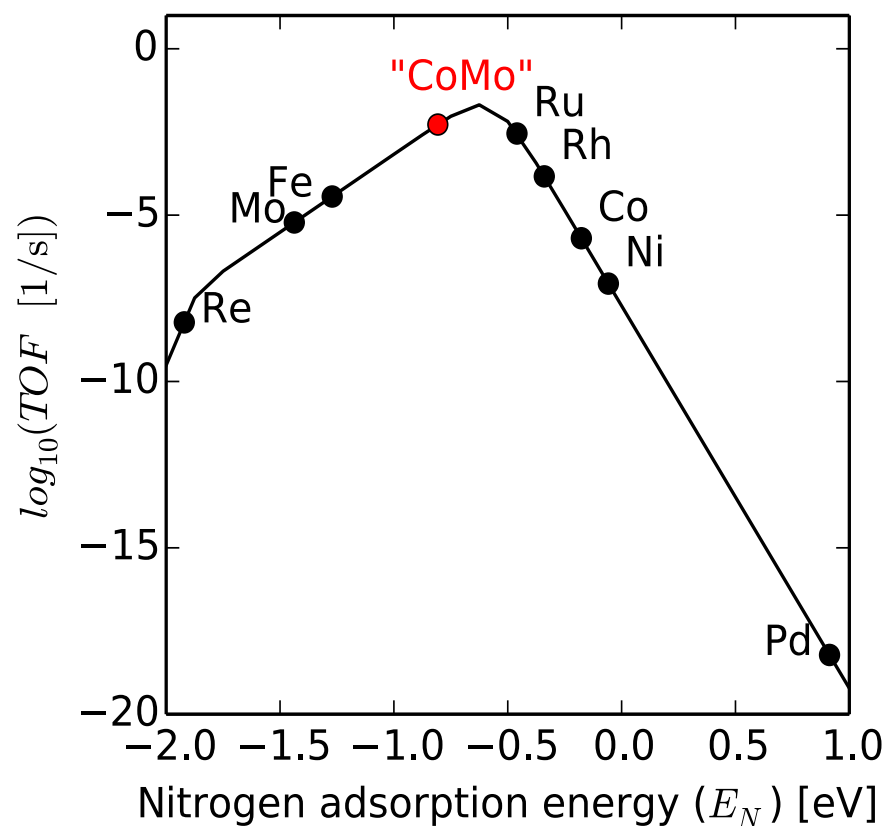


Surface chemistry
is a quite local effect...



Li, Larsen, Romero, Morozov, Glinsvad, Abild-Pedersen, Greeley,
Jacobsen, Nørskov, J. Phys. Chem. Lett., **4**, 222 (2013).

The optimum descriptor: design rules

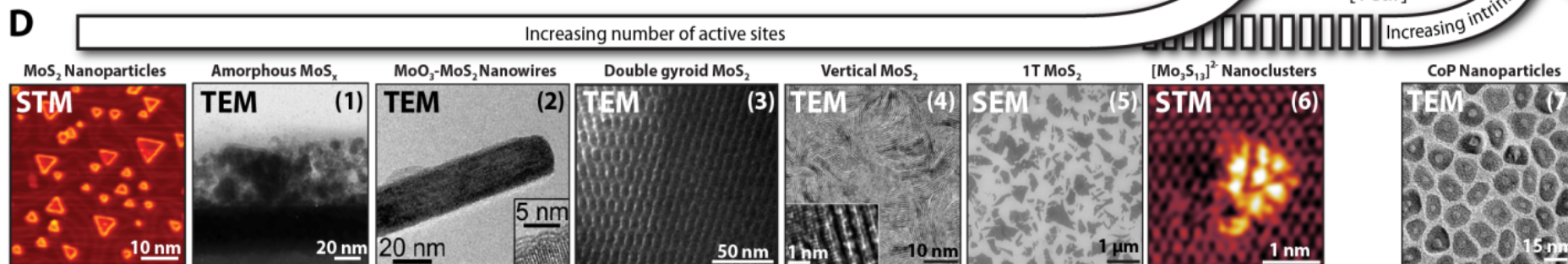
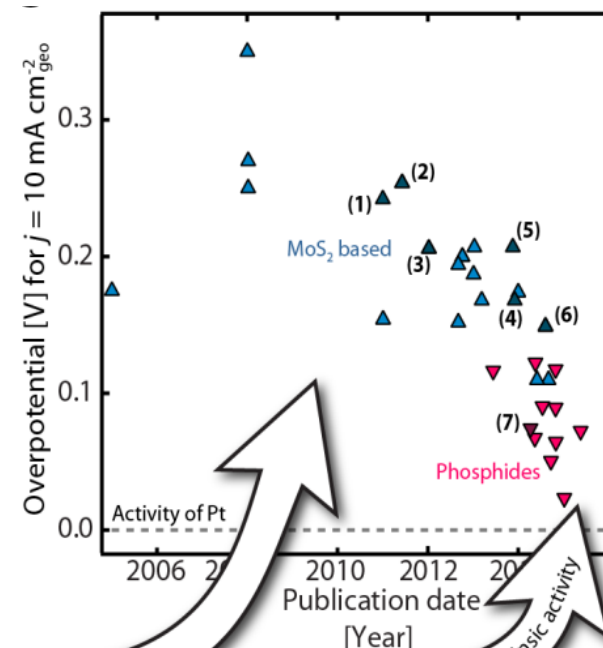
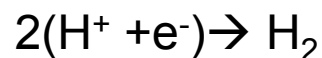
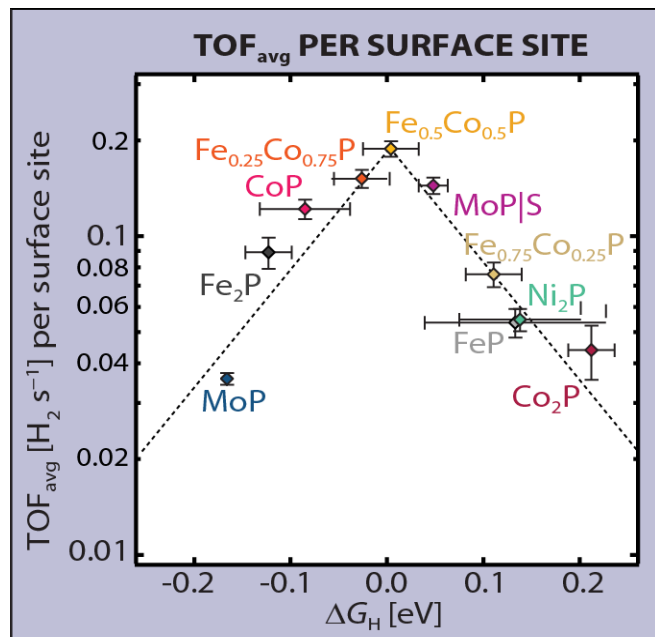


Jacobsen, Dahl, Clausen, Bahn, Logadottir,
Nørskov, JACS **123**, 8404 (2001)

New non-Pt group HER catalysts



Seh, Kibsgaard, Dickens, Chorkendorff, Norskov, Jaramillo



Jaramillo *et al.*, *Science* **317**, 100 (2007)

Chen *et al.*, *Nano Lett.* **11**, 4168 (2011)

Kibsgaard, Chen, Reinecke, Jaramillo, *Nat. Mater.* **11**, 963 (2012).

Kibsgaard, Jaramillo, Besenbacher, *Nat. Chem.* **6**, 248 (2014).

Kong *et al.*, *Nano Lett.* **13**, 1341 (2013).

Merki, Fierro, Vrubel, Hu, *Chem. Sci.* **2**, 1262 (2011).

Voiry *et al.*, *Nano Lett.* **13**, 6222-6227 (2013)

Popczun, Read, Roske, Lewis, Schaak, *Angew. Chem.* **53**, 5427 (2014).

Kibsgaard, Jaramillo, *Angew. Chem.* **53**, 14433 (2014).

Li *et al.*, *J. Am. Chem. Soc.* **133**, 7296 (2011).

Laursen *et al.*, *Energy Environ. Sci.* **8**, 1027 (2015).

Hoffert, Roberts, Bullock, Helm, *Chem. Commun.* **49**, 7767 (2013).

Benck, Hellstern, Kibsgaard, Chakthranont, Jaramillo, *ACS Catal.* **4**, 3957 (2014).

Popczun *et al.*, *J. Am. Chem. Soc.* **135**, 9267 (2013).

McEnaney *et al.*, *Chem. Mater.* **26**, 4826 (2014).

Liu *et al.*, *Angew. Chem. Int. Ed.* **53**, 6710 (2014).

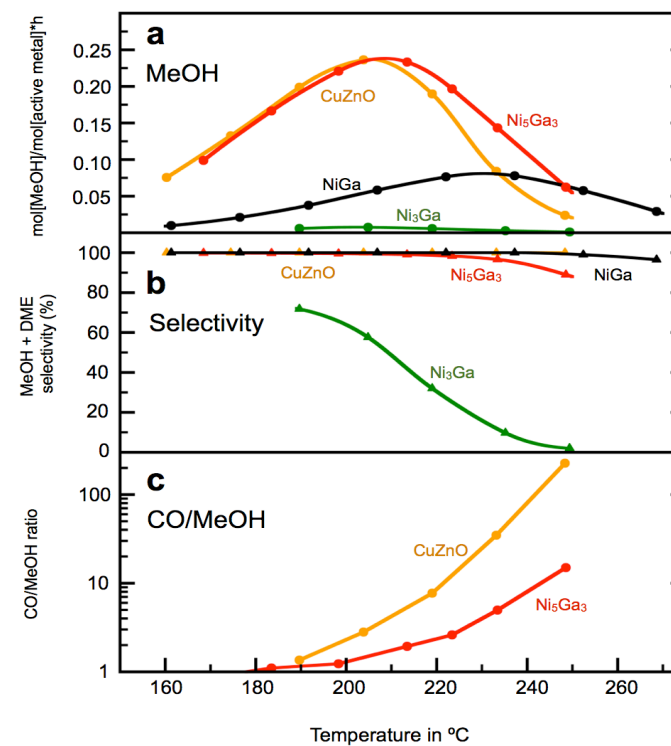
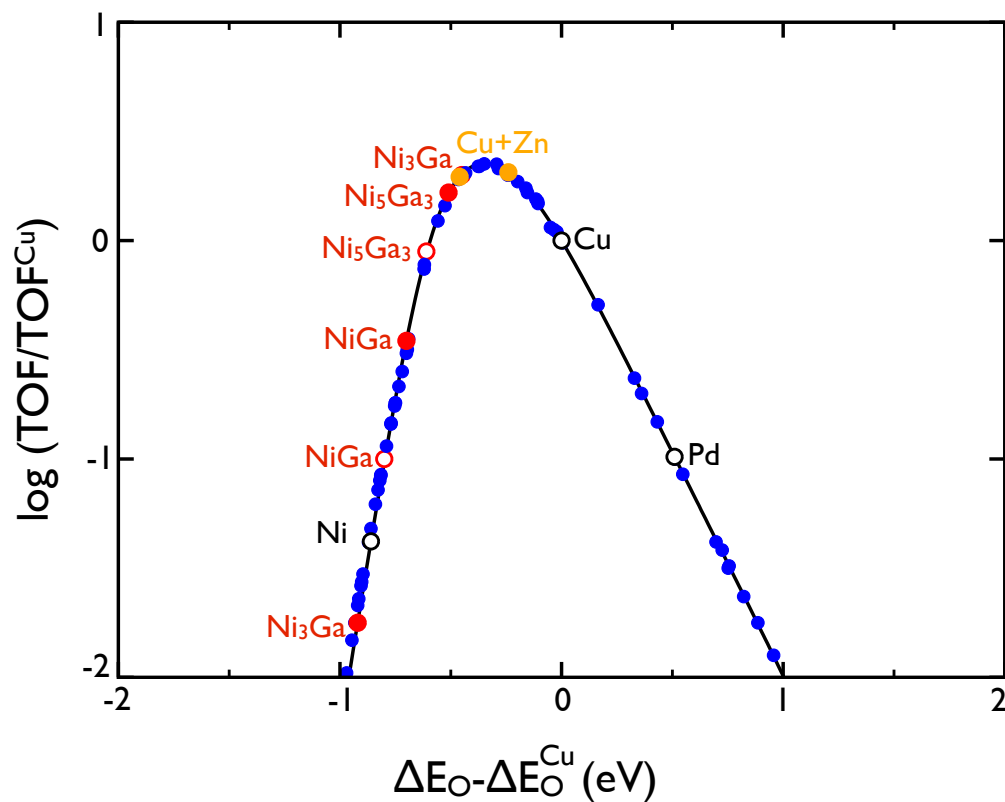
Tian, Q. Liu, A. M. Asiri, X. P. Sun, *JACS* **136**, 7587 (2014).

Hao, W. S. Yang, Z. Zhang, J. L. Tang, *Nanoscale* **7**, 11055 (2015).

Callejas *et al.*, *ACS Nano* **8**, 11101 (2014).

Kibsgaard *et al.*, *Energy Environ. Sci.* **8**, 3022 (2015).

CO₂ reduction to methanol



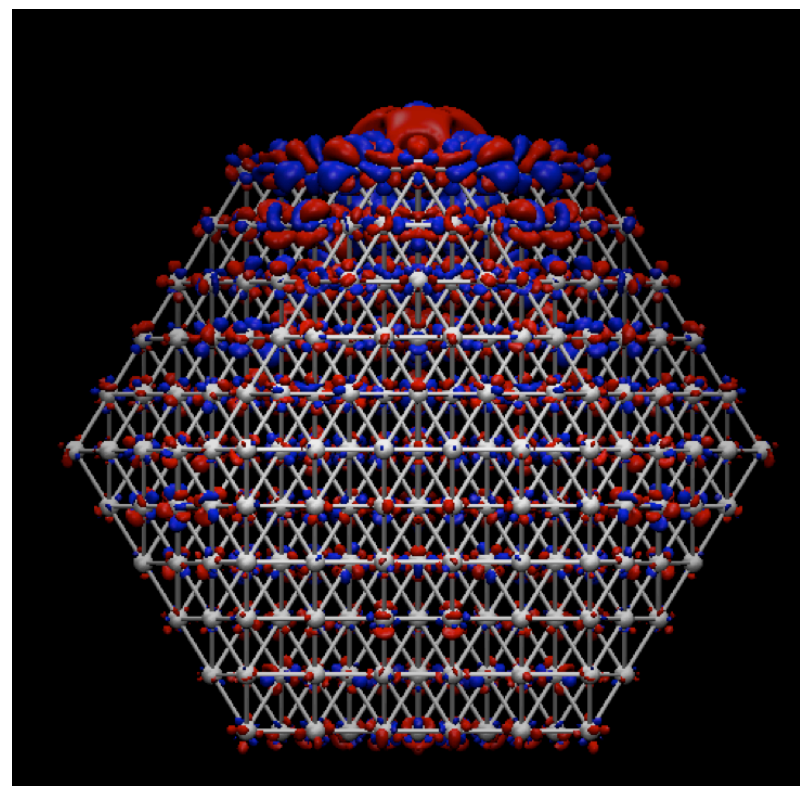
Studt, Abild-Pedersen,
Elkjær, Sharafutdinov,
Dahl, Chorkendorff,
Nørskov, Nature Chem.
(2014)

Outline



Theory of transition metal heterogeneous catalysis

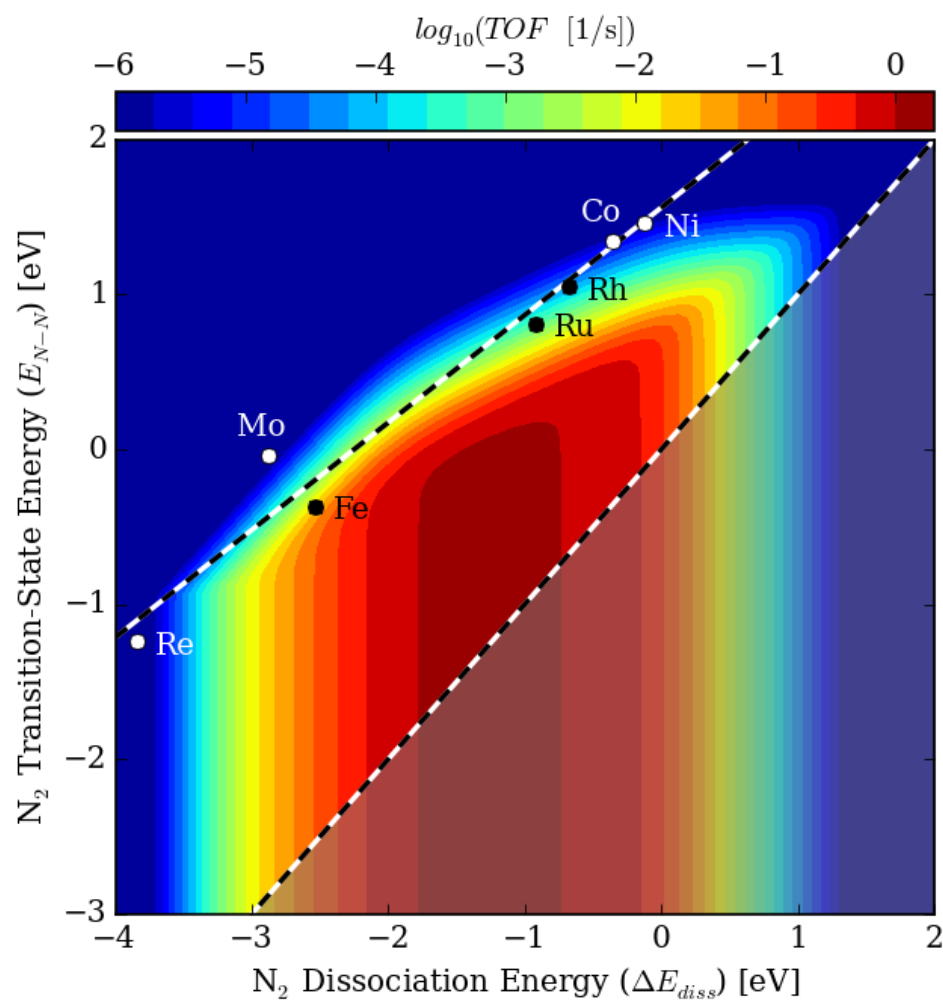
- Introduction to scaling relations
 - Simple example: NH_3 synthesis
- Activity and selectivity maps
 - Generalization to more more complex reactions
- Catalyst Design Strategies
 - The optimum descriptor
 - Beyond known scaling relations



Looking for exceptions to the rule



Ammonia synthesis

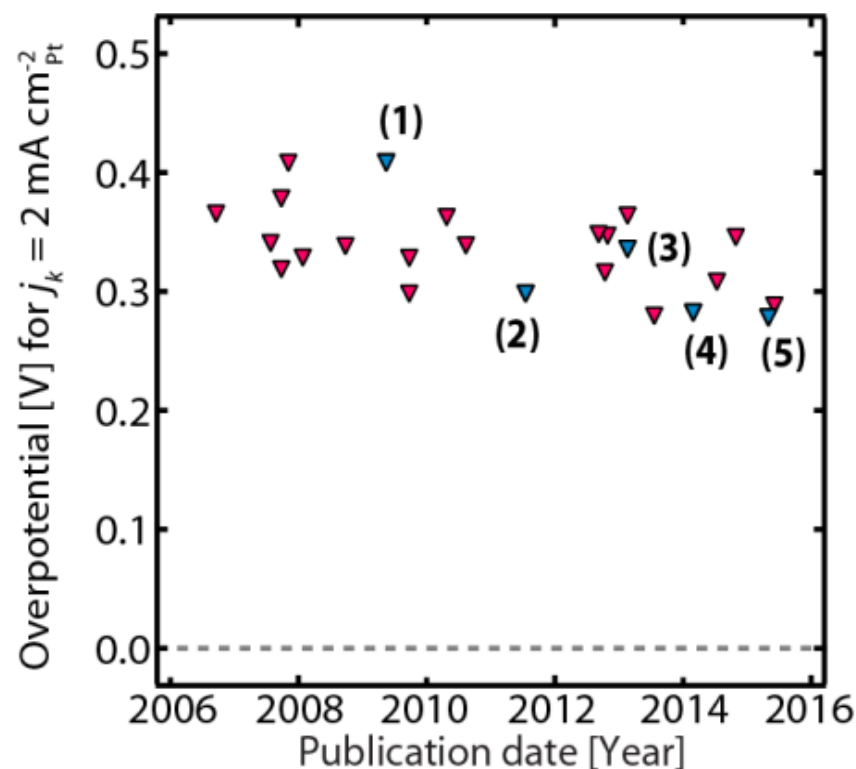
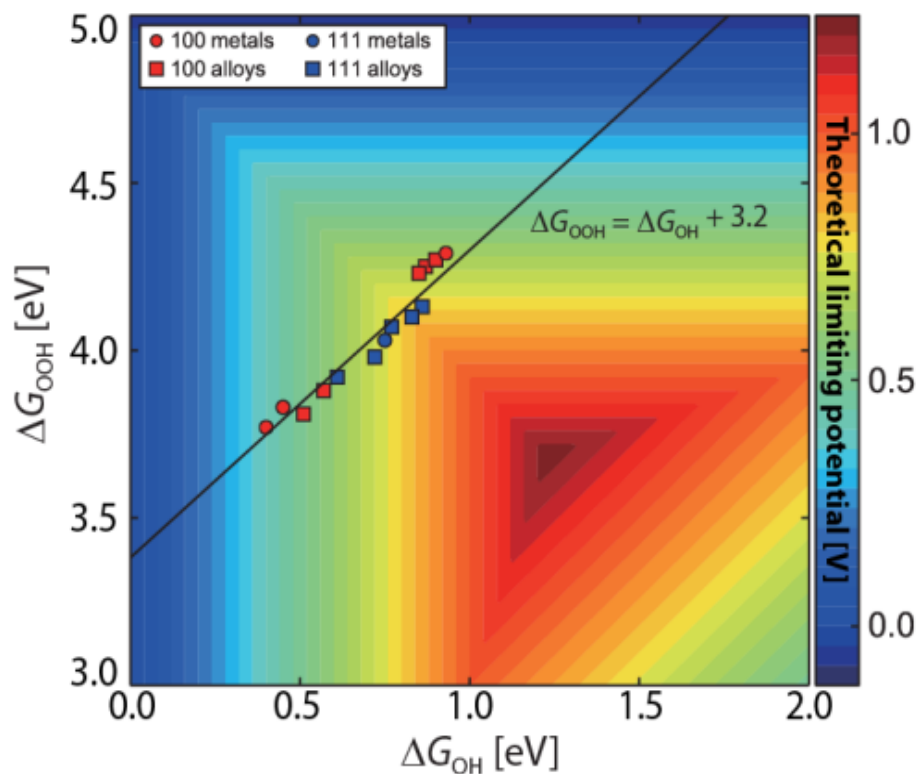


The need for a paradigm shift



ORR

Seh, Kibsgaard, Dickins, Chorkendorff, Nørskov, Jaramillo



Viswanathan, Hansen, Rossmeisl, Nørskov, ACS Catal. **2**, 1654 (2012)
 Vojvodic, Nørskov, Natl. Science Review (2015)
 Montoya, Vojvodic, Nørskov (2015)

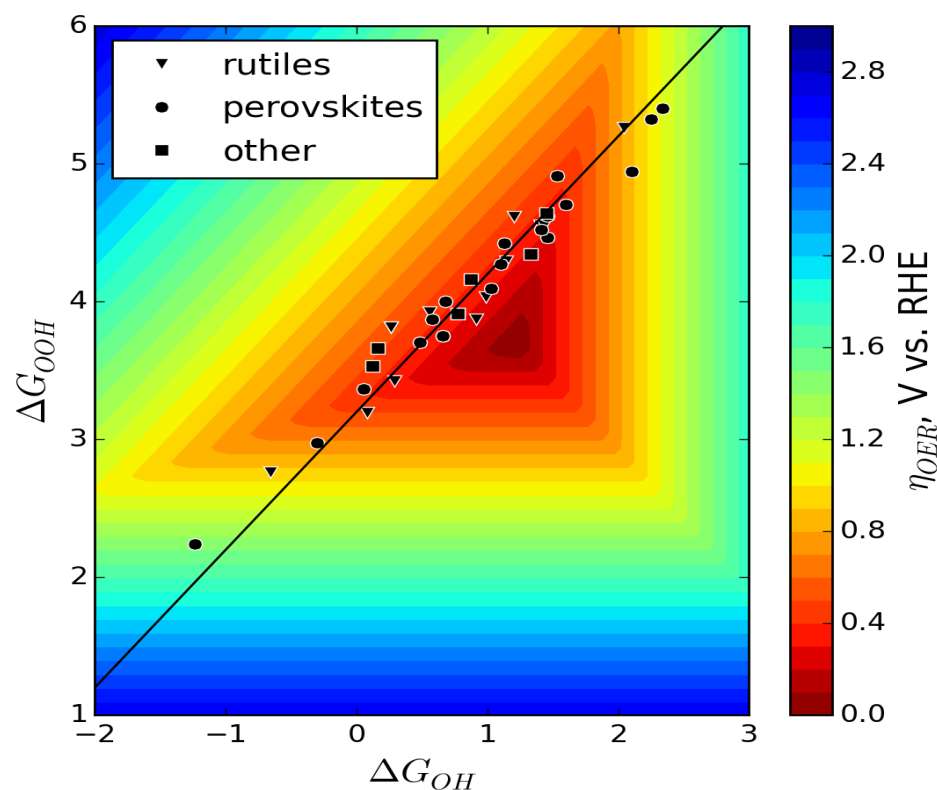
Peng, Yang, J. Am. Chem. Soc. **131**, 7542 (2009)
 Guo et al., Angew. Chem. Int. Ed. **52**, 3465 (2013).
 Huang et al., Science **348**, 1230 (2015).
 Chen et al. Science **343**, 1339 (2014).
 Wang et al., J. Am. Chem. Soc. **133**, 14396 (2011).
 Cui et al., Nano Lett. **12**, 5885 (2012).
 Mani, Srivastava, Strasser, J. Phys. Chem. C **112**, 2770 (2008)
 Srivastava et al., Angew. Chem. Int. Ed. **46**, 8988 (2007).
 Wang et al., Nano Lett. **12**, 5230 (2012).
 Wang et al., Nat. Mater. **12**, 81 (2013).
 Chen et al., J. Am. Chem. Soc. **130**, 13818 (2008).
 Shao, Sasaki, Liu, Adzic, Z. Phys. Chem. **221**, 1175 (2007).
 Sasaki, L. Zhang, Adzic, Phys. Chem. Chem. Phys. **10**, 159 (2008)

The need for a paradigm shift



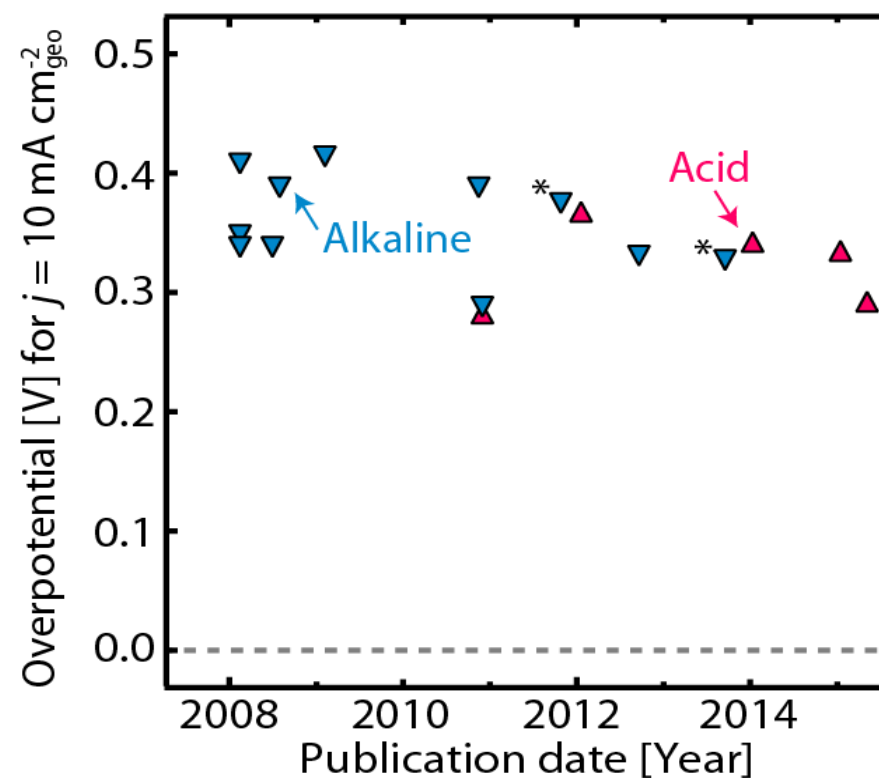
OER

Seh, Kibsgaard, Dickins, Chorkendorff, Norskov, Jaramillo



Vojvodic, Nørskov, Natl. Science Review (2015)

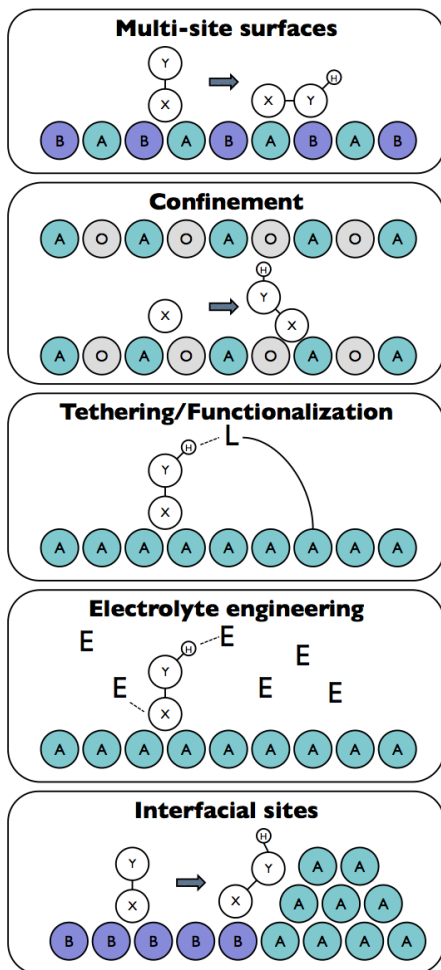
B



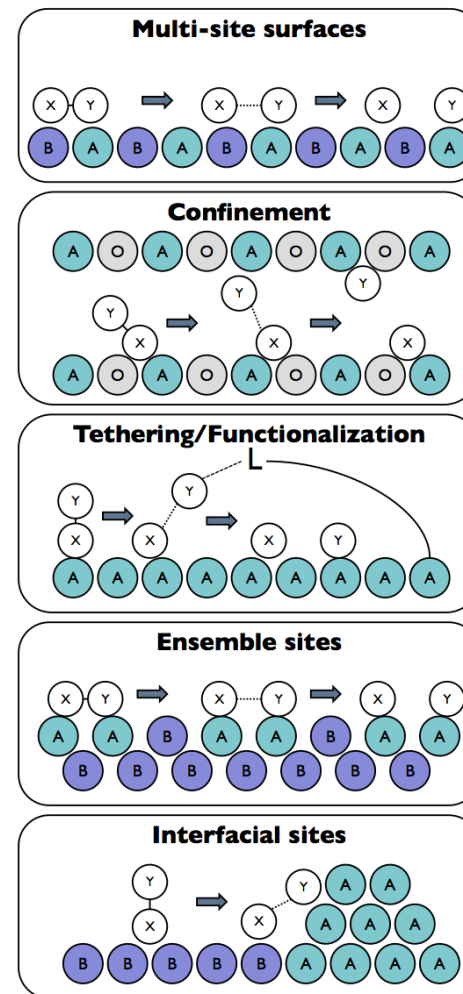
Lee, Suntivich, May, Perry, Shao-Horn, *J. Phys. Chem. Lett.* **3**, 399 (2012).
 Bernicke *et al.*, *Chemsuschem* **8**, 1908 (2015)
 Hong Nhan *et al.*, *Angew. Chem. Int. Ed.* **54**, 2975 (2015)
 McCrory *et al.*, *J. Am. Chem. Soc.* **137**, 4347 (2015)
 McCrory, Jung, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.* **135**, 16977 (2013)
 Trotochaud, Ranney, Williams, Boettcher, *J. Am. Chem. Soc.* **134**, 17253 (2012)
 D. Friebel *et al.*, *J. Am. Chem. Soc.* **137**, 1305 (2015)
 Liang *et al.*, *Nat. Mater.* **10**, 780 (2011)
 Bajdich, Garcia-Mota, Vojvodic, Norskov, Bell, *J. Am. Chem. Soc.* **135**, 13521 (2013)

The challenge

Finding strategies to circumvent scaling – nano-structuring

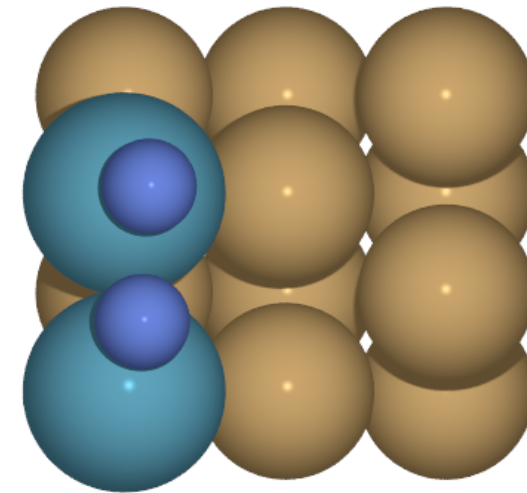
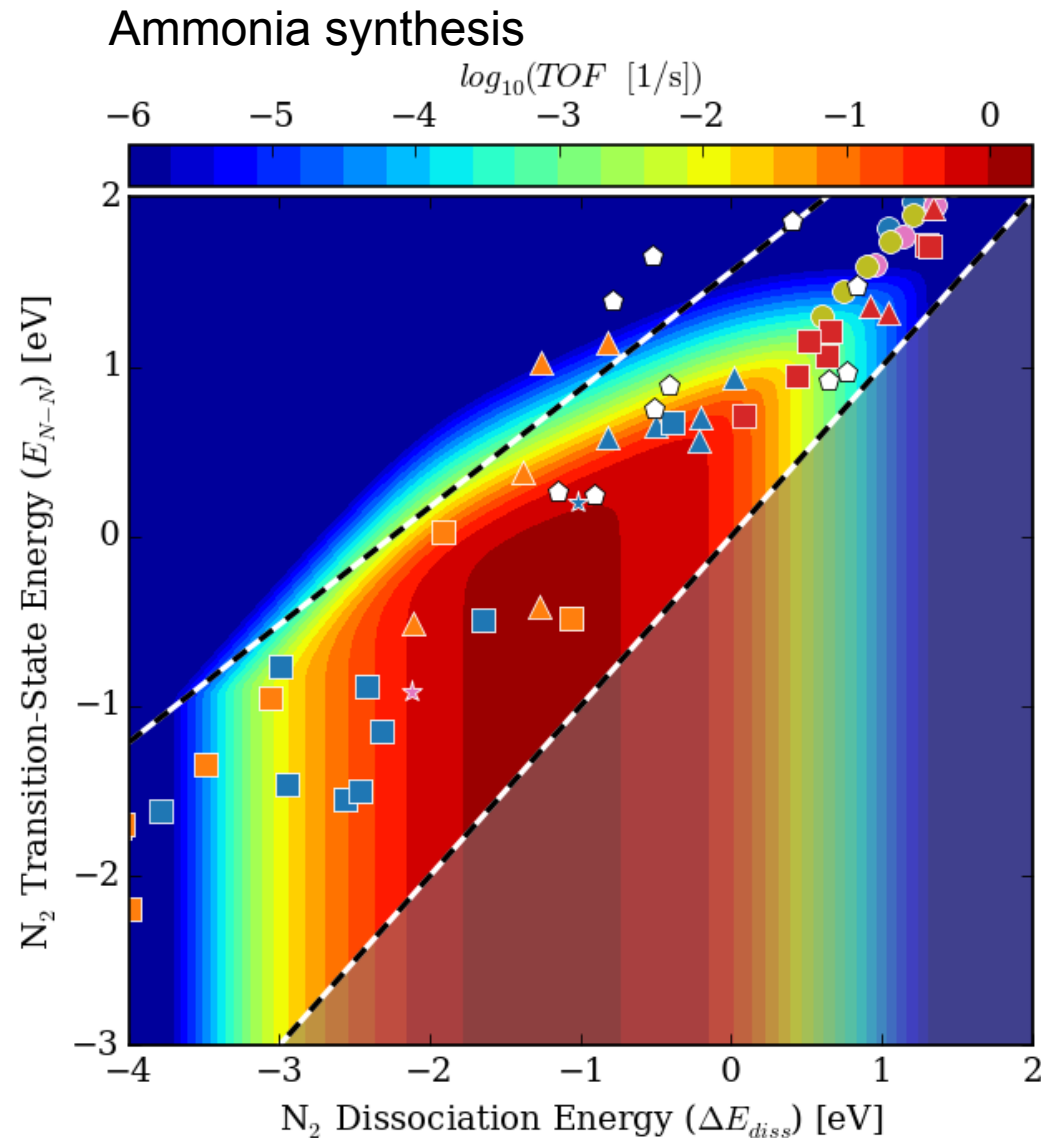


Peterson, Nørskov, J. Phys. Chem. Lett. **3**, 251 (2012)

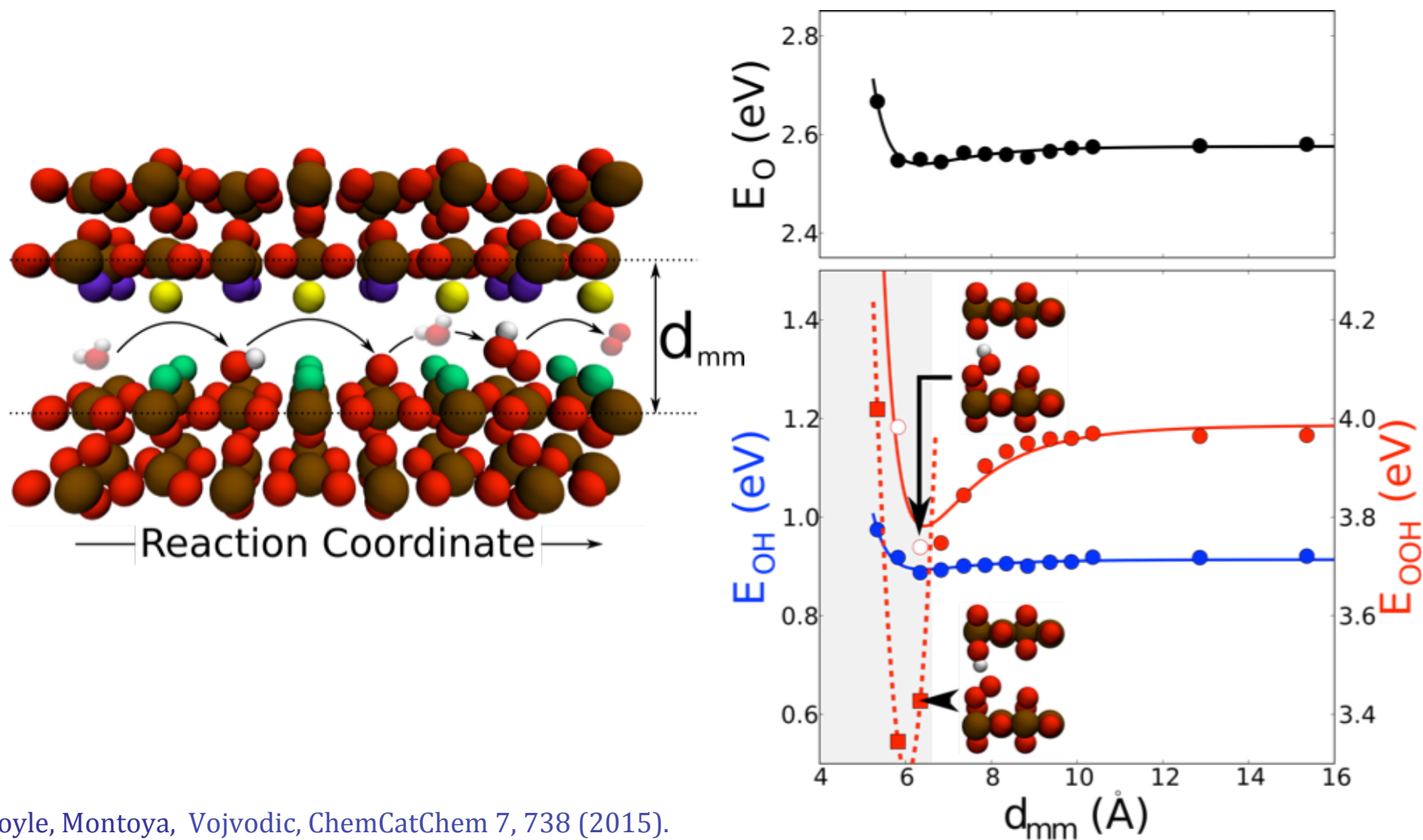


Vojvodic, Nørskov, National Science Review (2015)
Montoya, Vojvodic, Nørskov (2015)

Looking for exceptions to the rule

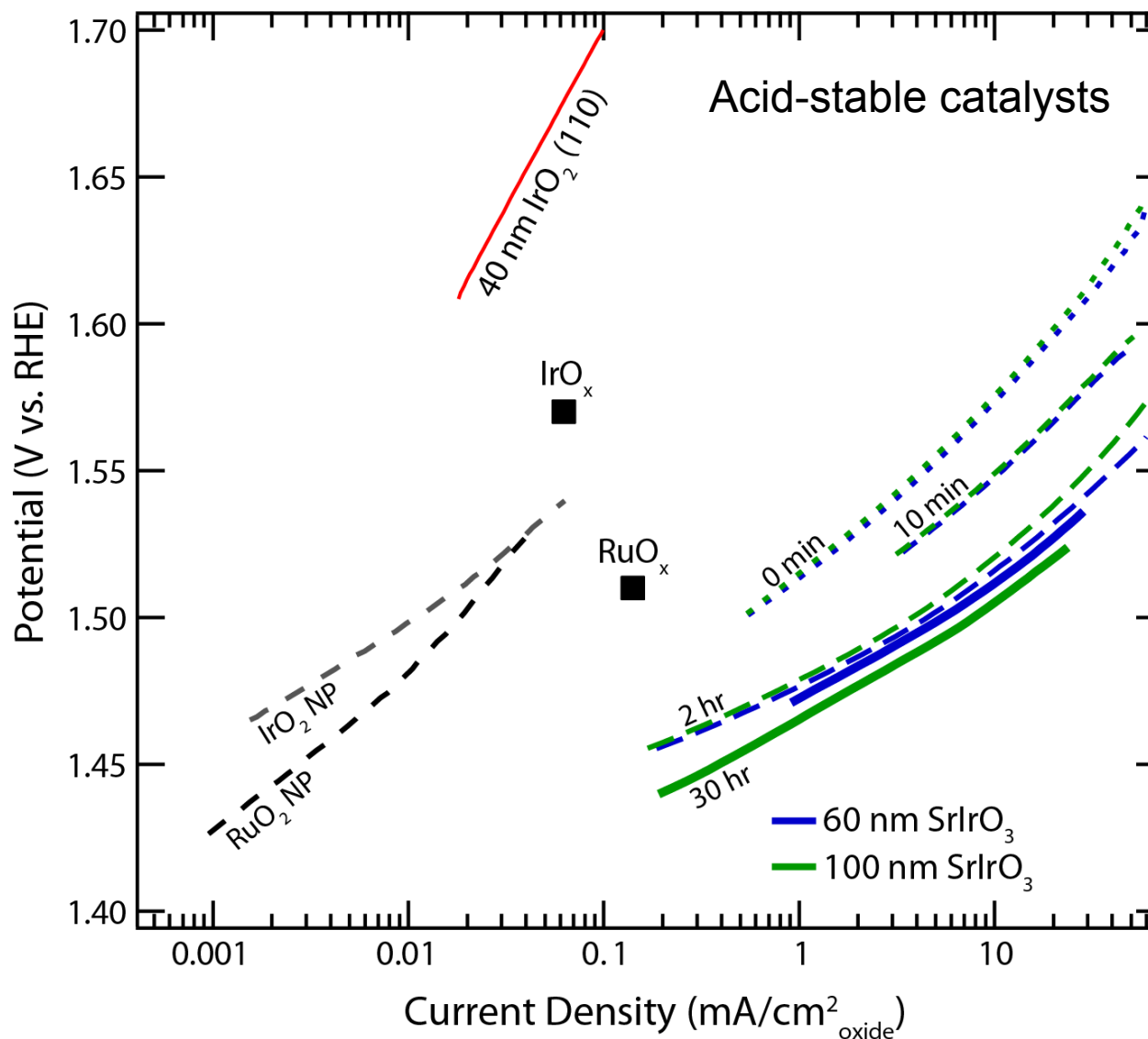


Confinement: 2D -> 3D Active Sites

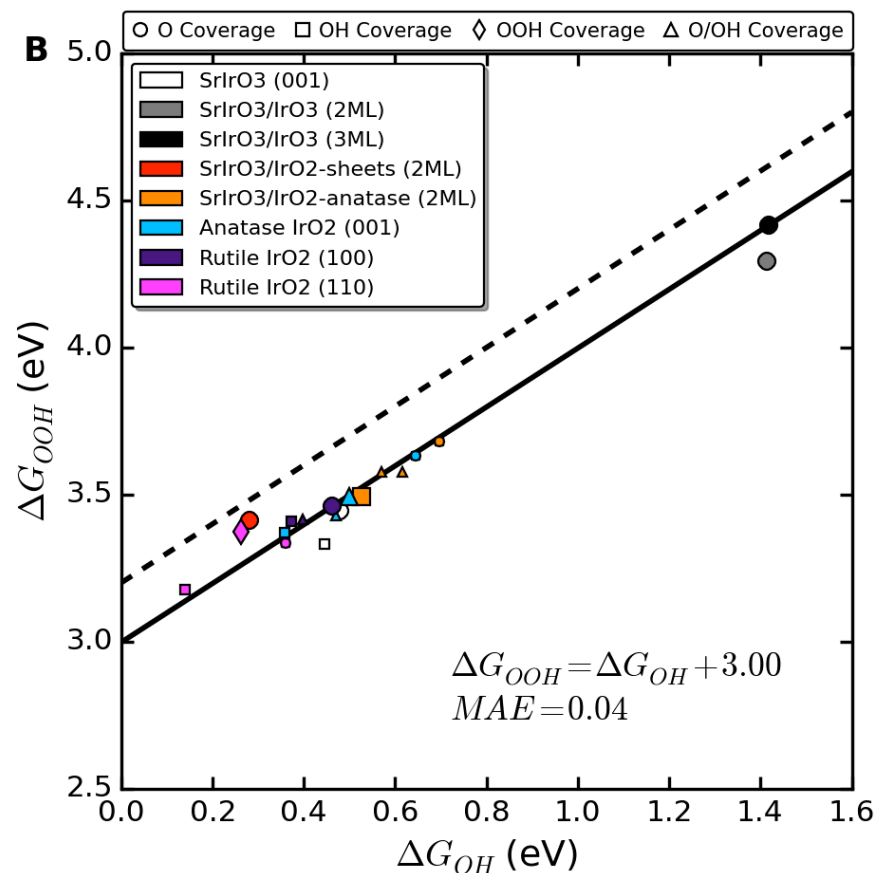


Doyle, Montoya, Vojvodic, ChemCatChem 7, 738 (2015).

A new OER Catalyst



Reasonably favorable scaling



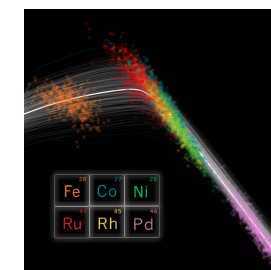
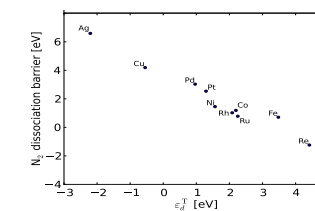
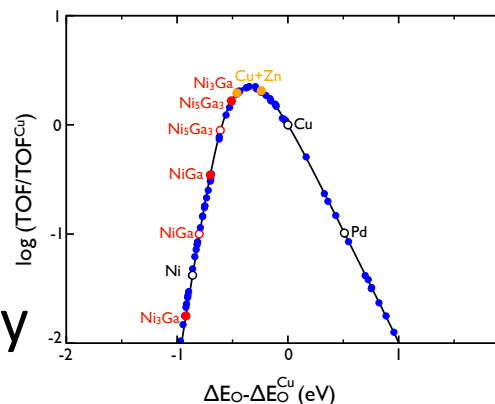
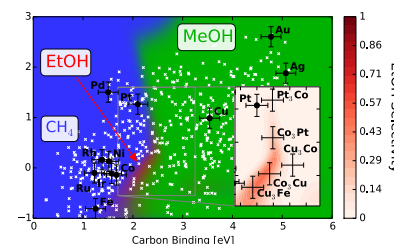
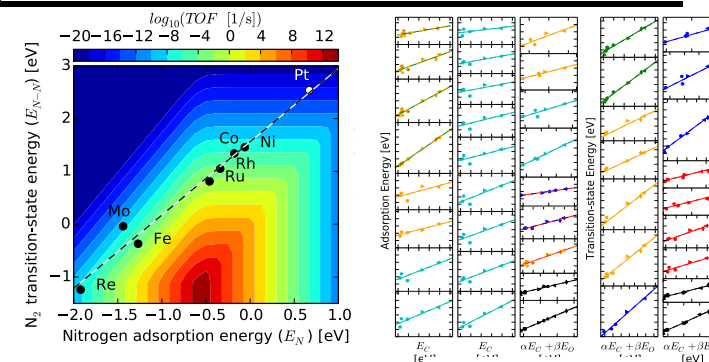
Seitz, Dickens, Nishio, Hikita, Montoya, Doyle, Kirk, Vojvodic, Hwang, Norskov, Jaramillo (2016)

Elements of a theory of heterogeneous catalysis



A quantitative model of rates + concepts to understand trends

- Rate[reaction conditions, catalyst]
- Scaling relations define mapping: catalyst $\rightarrow$ descriptors:
- Rate[reaction conditions, descriptors]
- Scaling relations[active site structure]
- Descriptor values[electronic structure, active site(s)]
- Guidance for new catalysts and processes in descriptor space
- Guidance with estimated accuracy



Funding

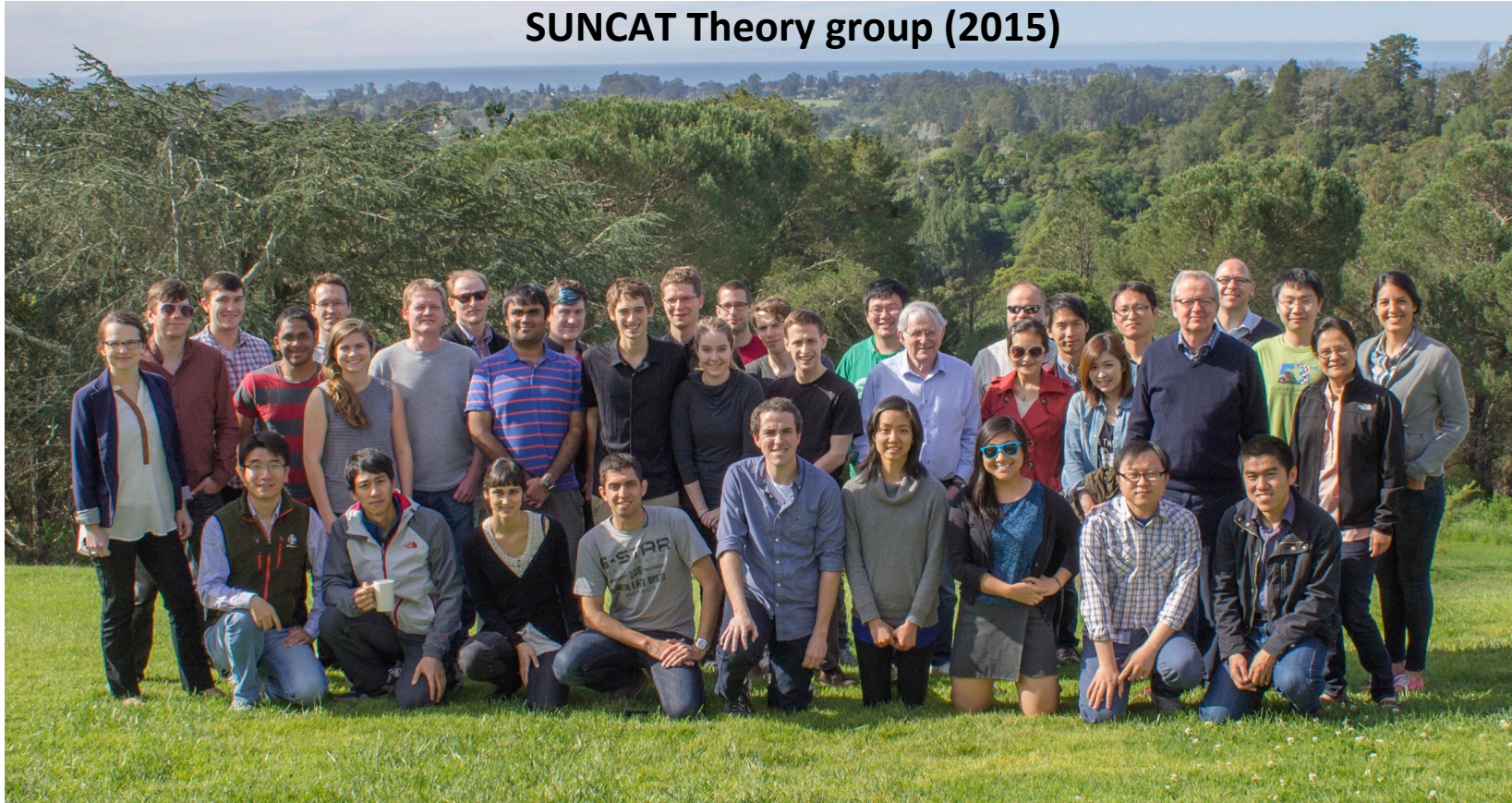


- U.S. Department of Energy, Office of Basic Energy Sciences

Thanks to



SUNCAT Theory group (2015)



Jaramillo et al., Bent et al., *Stanford University*

Chorkendorff et al., Jensen et al., Jacobsen et al. *Technical University of Denmark*

Rossmeisl, *Copenhagen University*; Greeley, *Purdue University*