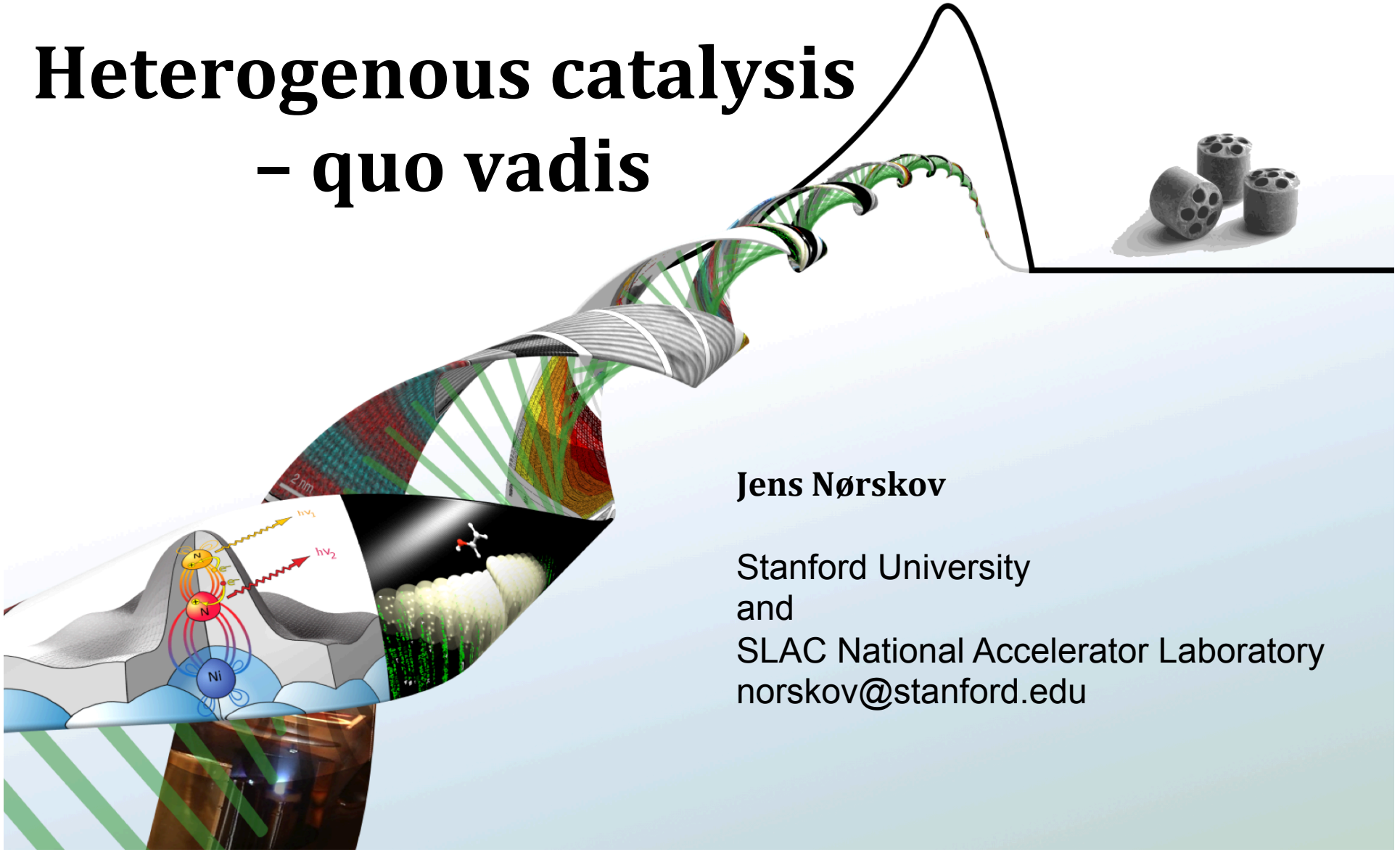
SUNCAT
CENTER FOR INTERFACE SCIENCE AND CATALYSIS

Heterogenous catalysis – quo vadis

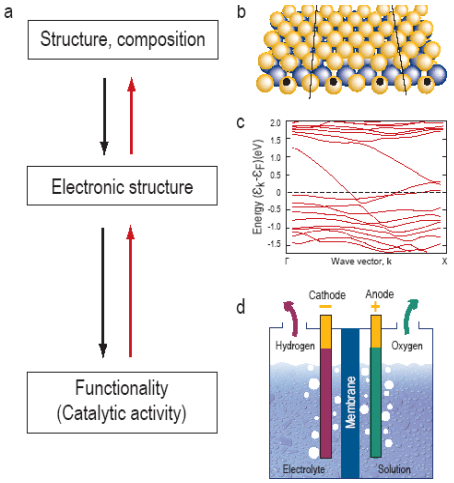


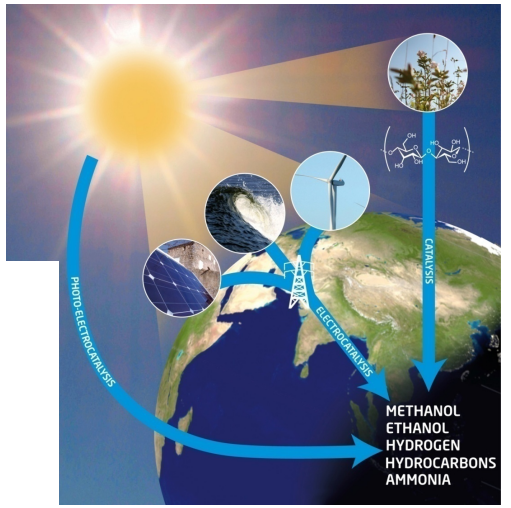
Jens Nørskov

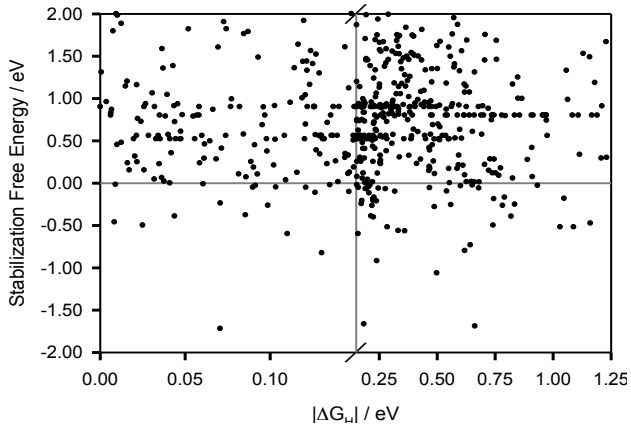
Stanford University
and
SLAC National Accelerator Laboratory
norskov@stanford.edu

Heterogeneous Catalysis – Quo Vadis

- Is catalysis important?
  - Sustainable future
- The challenge
  - Discovering the catalyst genome
- The role of modeling
  - Example: Sustainable fuel and chemicals
- Moving forward…
  - Some developments needed







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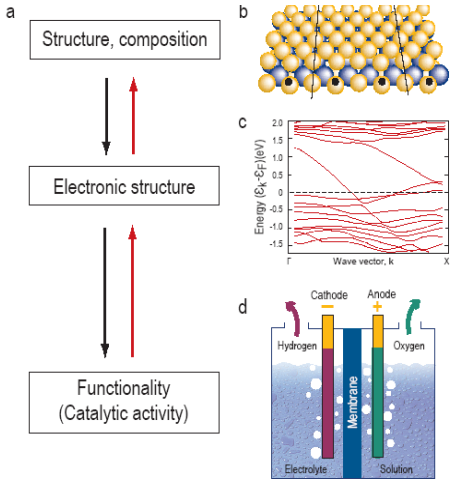
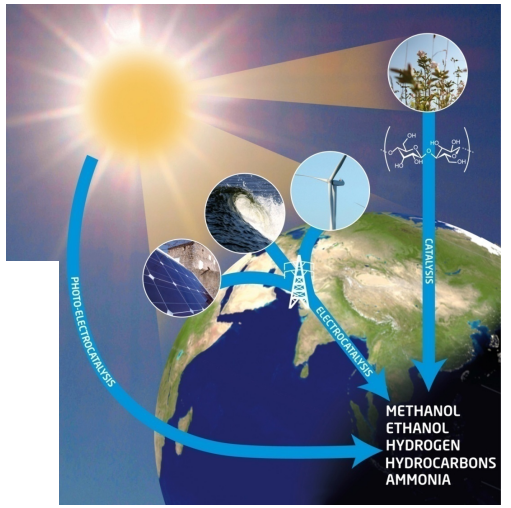
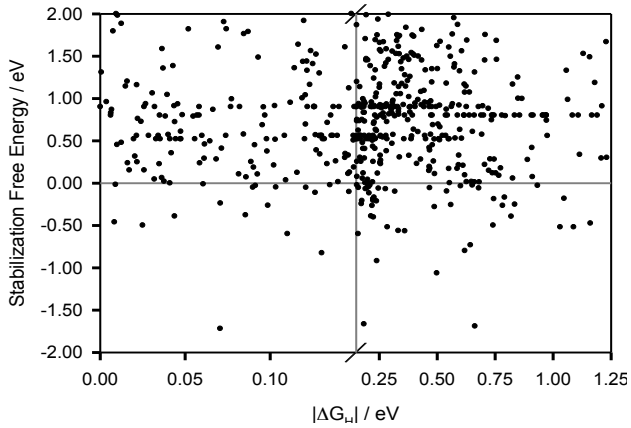
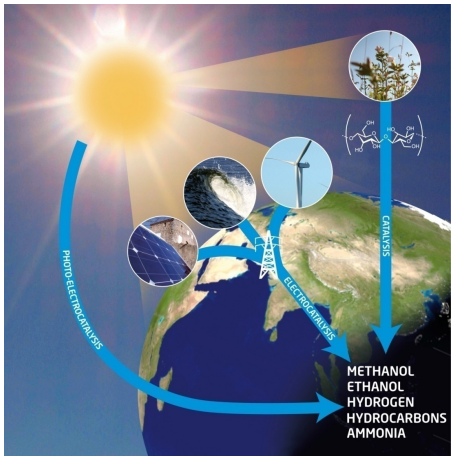




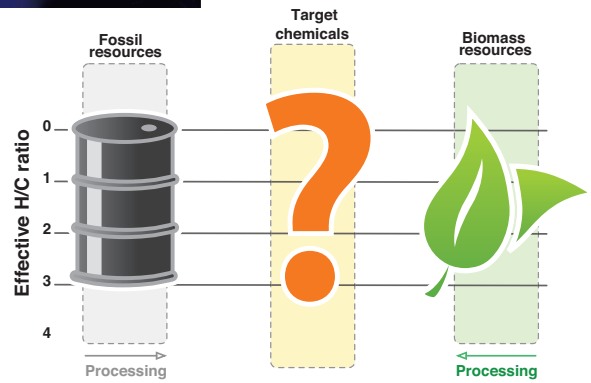


Need for catalysis research

- Catalysis for sustainable energy

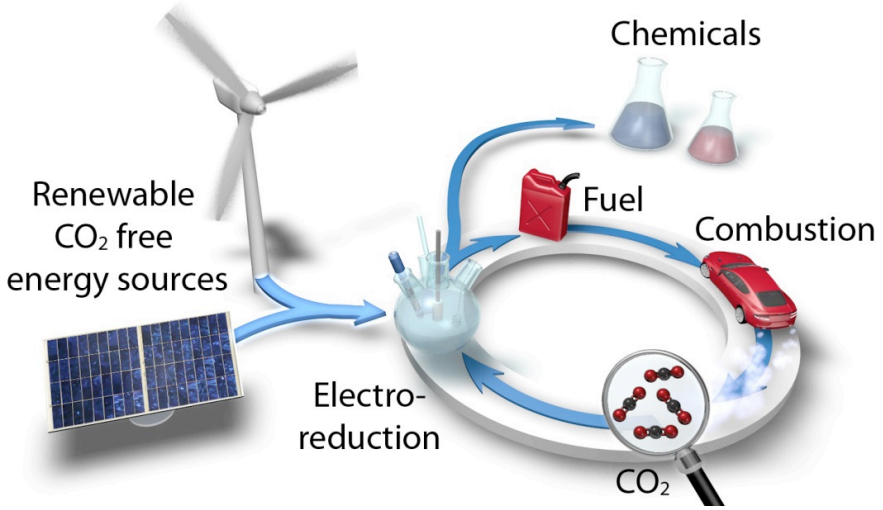


- Catalysis for sustainable chemicals

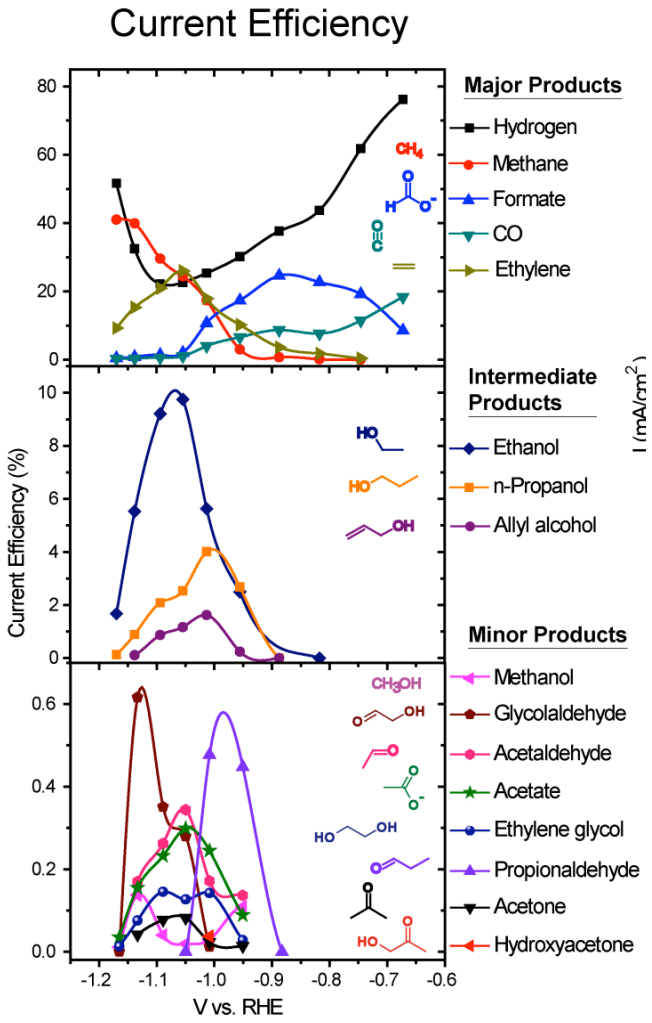


- Optimization of existing industry

Solar chemicals and fuels



Cu catalyst:



Kuhl, Cave, Abram, Saha, Kibsgaard, Jaramillo (2012)
Kuhl, Cave, Abram, Jaramillo
Energy Environ. Sci. **5**, 7050 (2012)

The problems

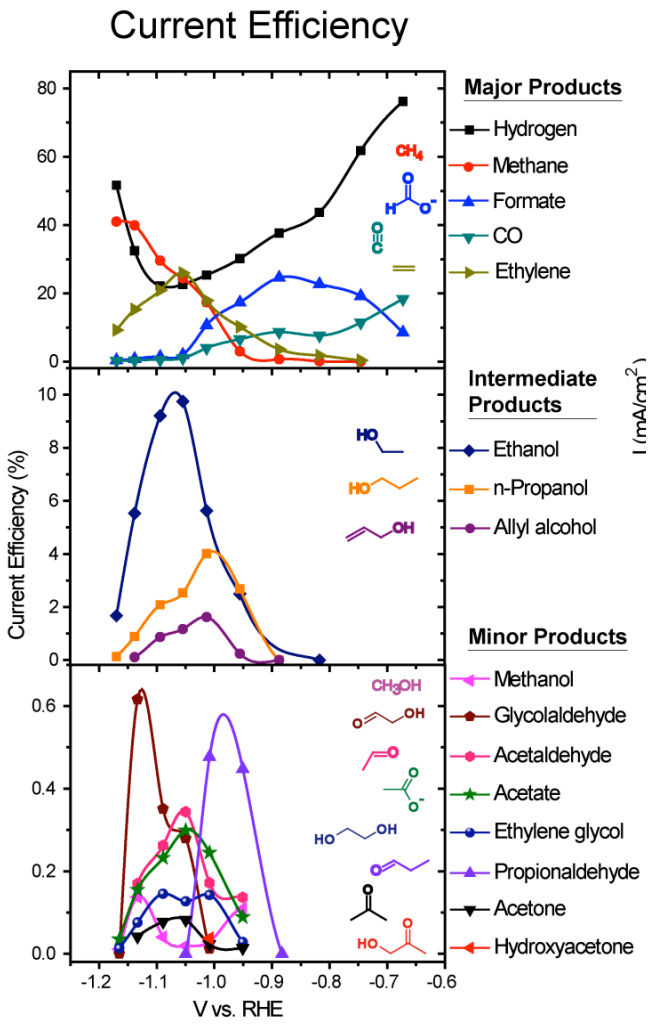
Methane formation:

$CO_2 + 8\ (H^+ + e^-) \rightarrow CH_4 + 2\ H_2O$

Very negative potential needed, ~ -0.8 V vs RHE.

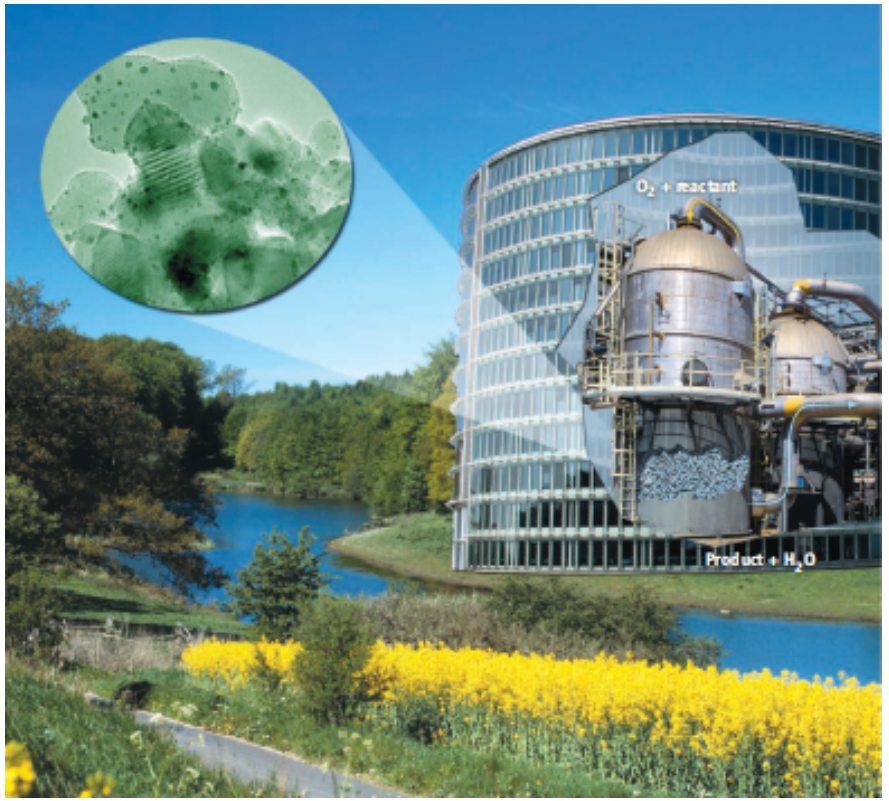
Thermodynamically, +0.17 V vs RHE should be sufficient

Cu catalyst:



Catalysis and the chemical industry

- >10% of GNP
- ~10% of energy use
- 90% dependent on catalysis
- Energy-heavy processes dominated by heterogeneous catalysis



Energy Use and Energy Intensity of the U.S. Chemical Industry
Worrell, Phylipsen, Einstein, Martin, Energy Analysis Department, LBNL

Problems

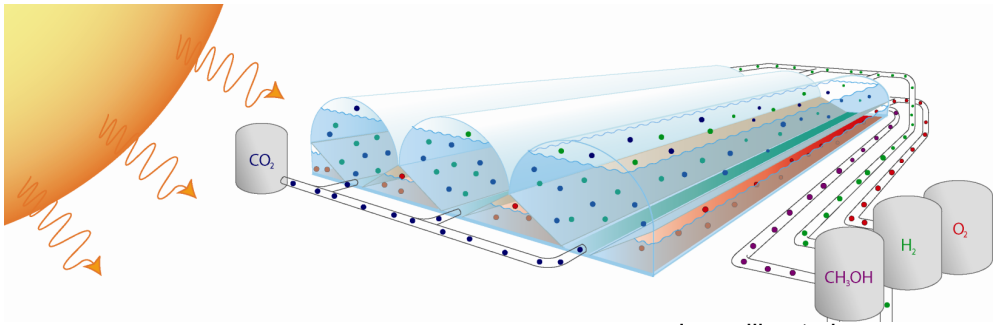
- Energy and atom efficiency
  - Activity
  - Selectivity

Subsector	**Quantity produced** kg 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 to100

- Several processes has no catalyst
  - E.g. $CH_4+O_2 \rightarrow CH_3OH$

NYTimes.com

- Distributed production
  - Completely new processes and catalysts



Jaramillo et al.

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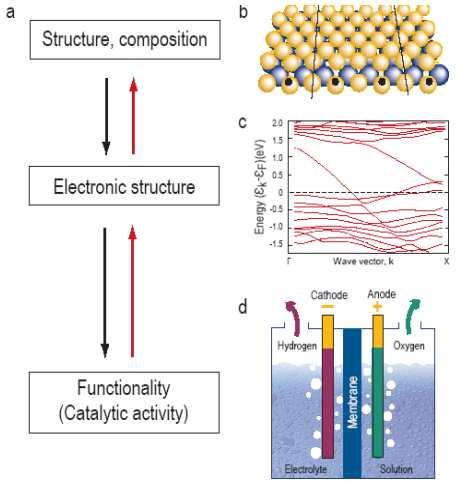
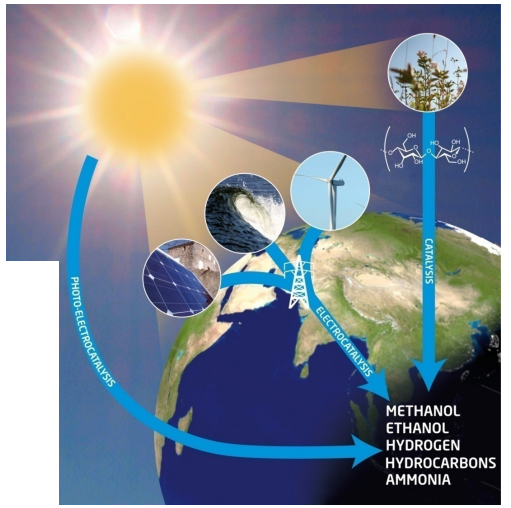
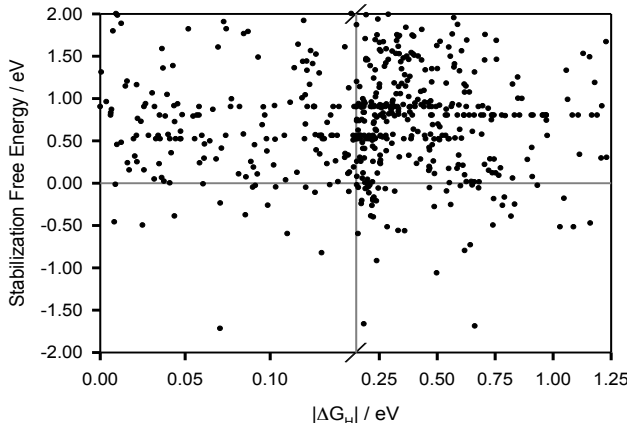
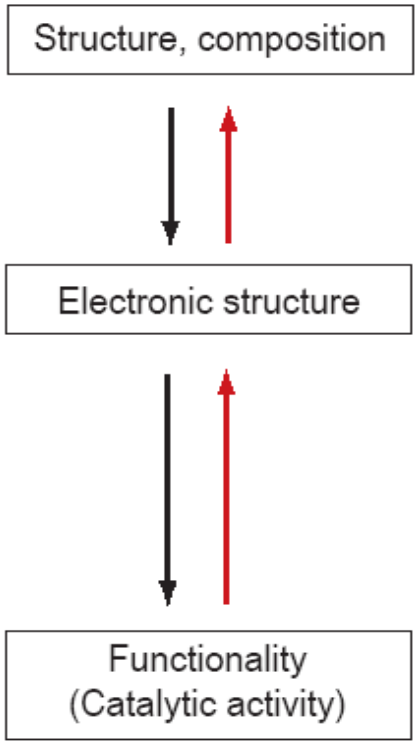


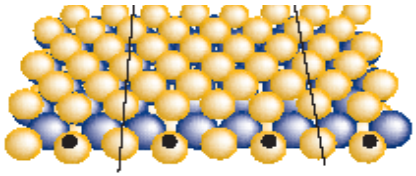


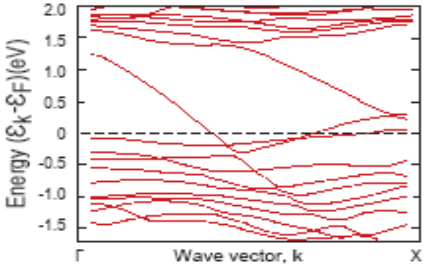


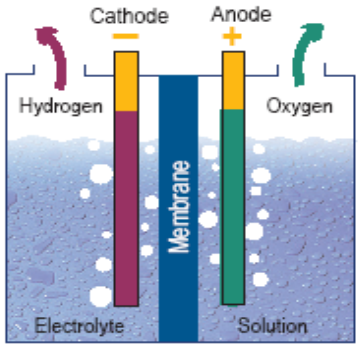
The search for the catalyst genome

The instructions defining the catalytic properties of a material

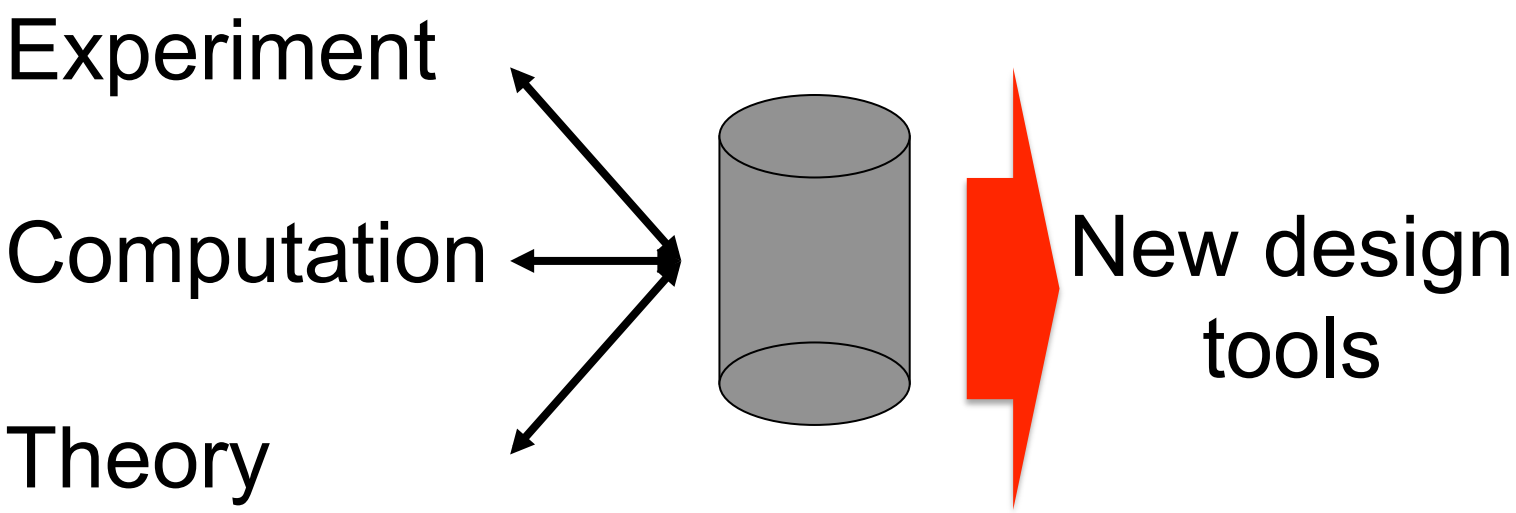








Accelerated catalyst design



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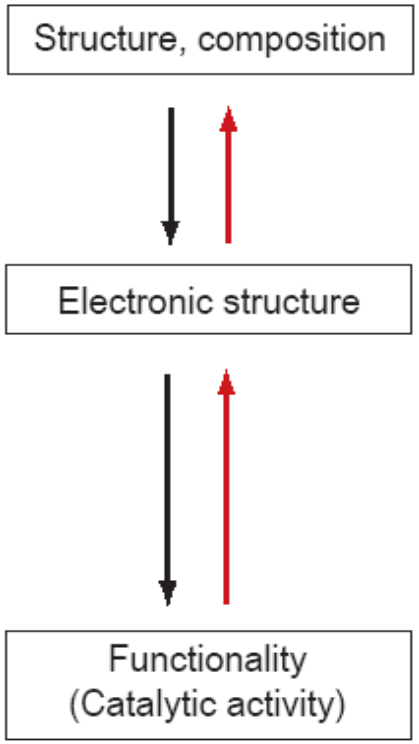
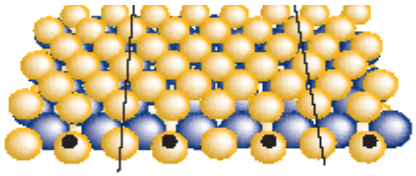
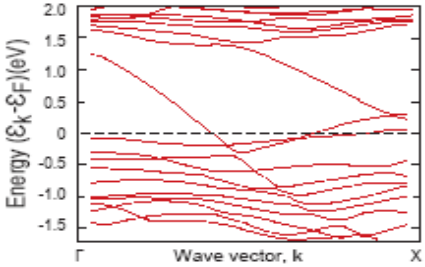
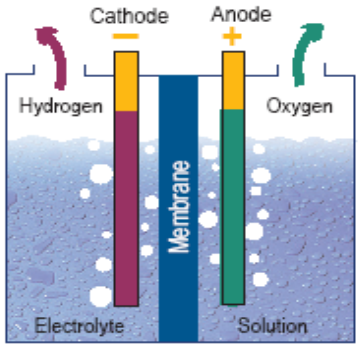
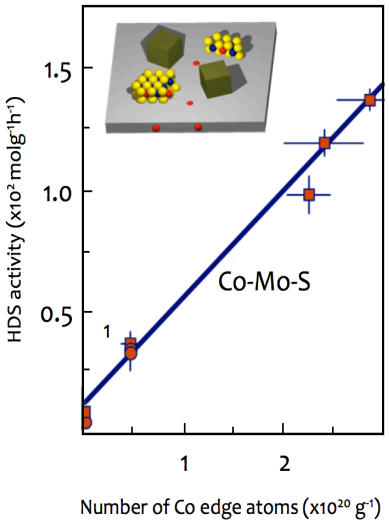




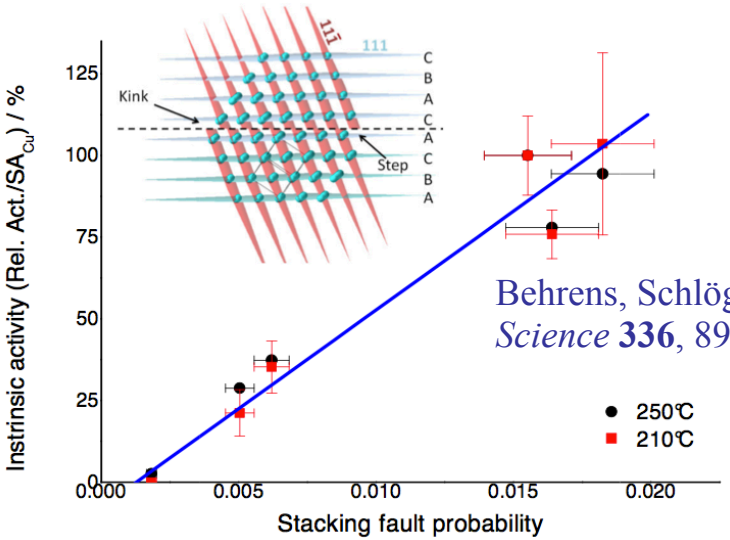




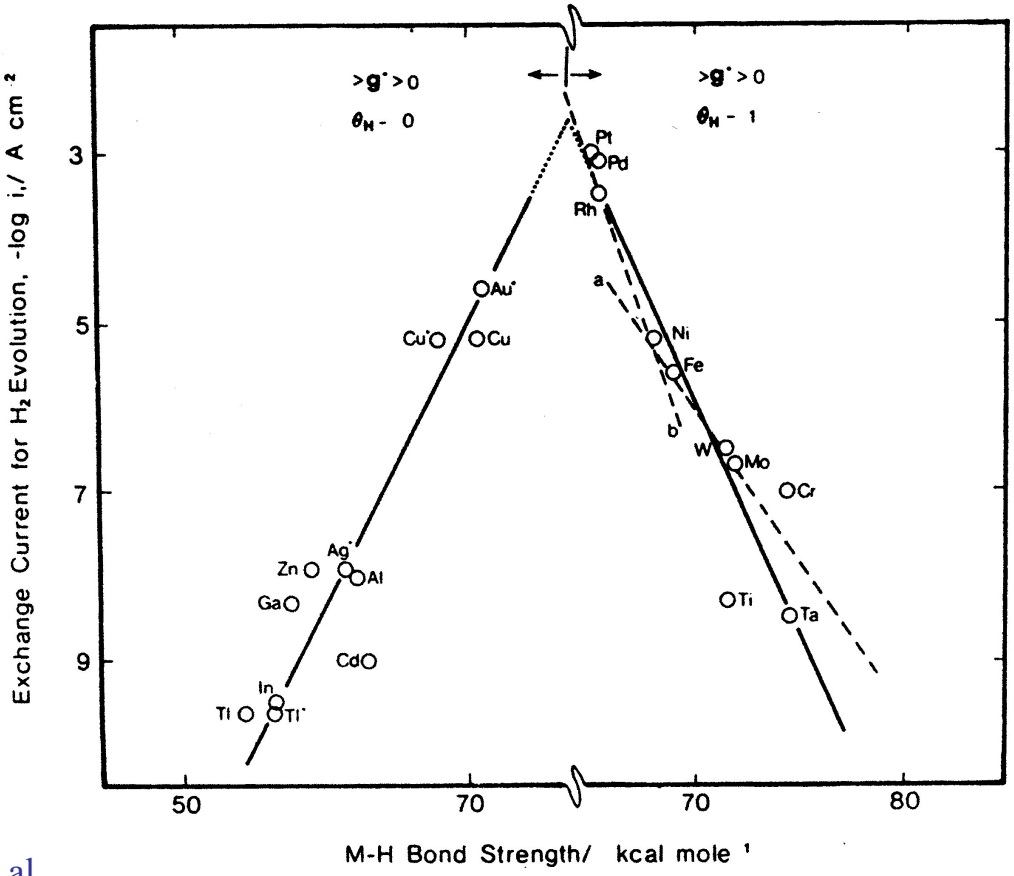
… as old as the field itself



Topsøe, Candia, Clausen (1984)



Behrens, Schlögl et al., *Science* **336**, 893 (2012)

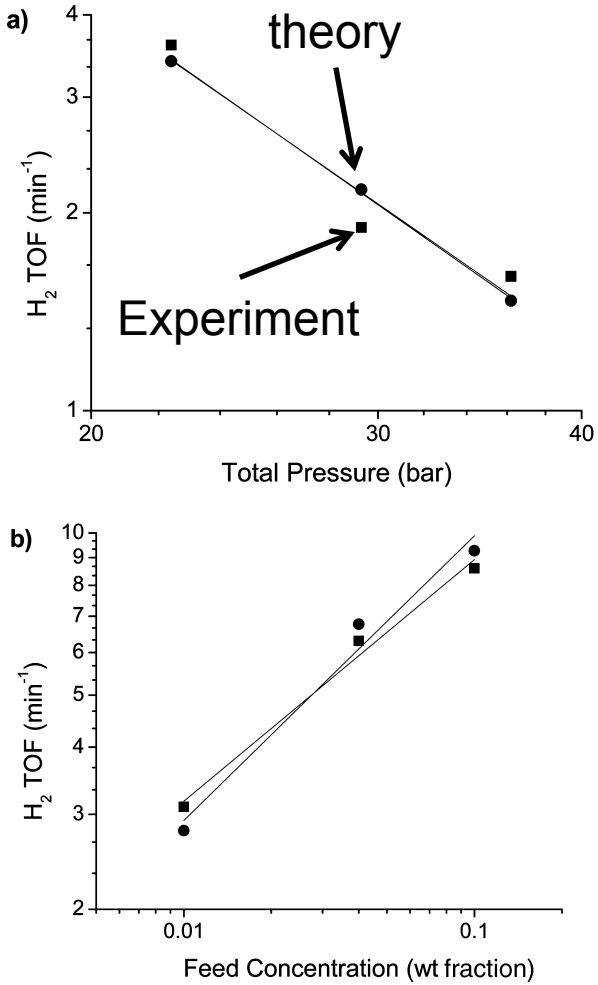


Trasatti, J. Electroanal. Chem. **39**, 163 (1972)

O'M Bockris, Reddy, Gamboa-Aldeco, *Modern Electrochemistry* 2A (2000)

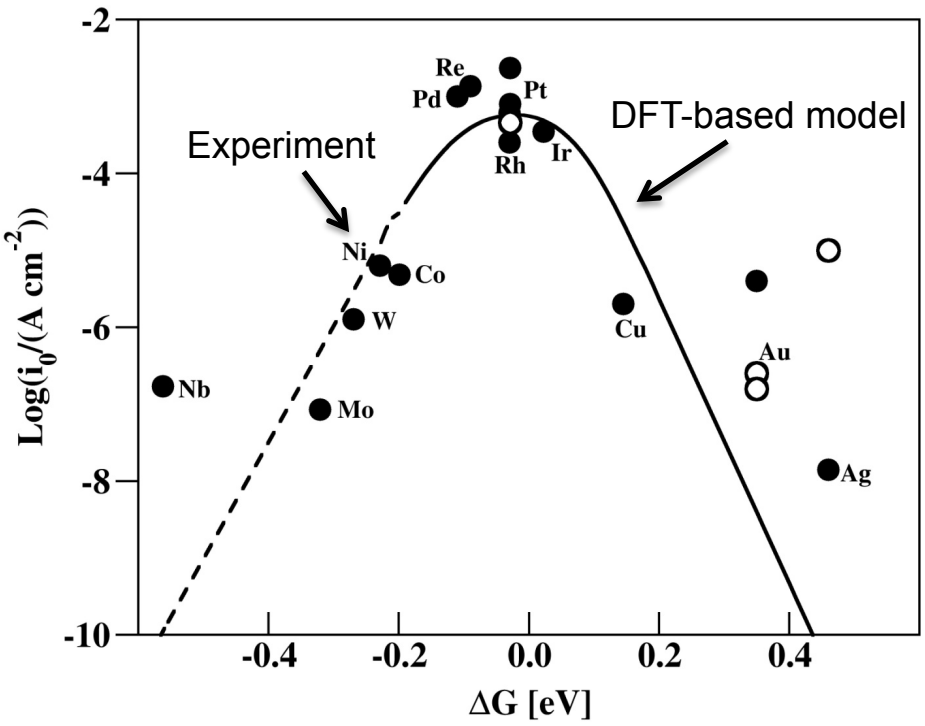
… so what's new

Ethylene Glycol Reforming over Platinum



Kandoi; Greeley; Simonetti; Shabaker; Dumesic; Mavrikakis; J. Phys. Chem. C **115**, 961 (2011)

Trends in hydrogen evolution rates



Calculated free energy of H adsorption

Nørskov, Bligaard, Logadottir, Kitchin, Chen, Pandelov, Stimming, JES **152,** J23, (2005)

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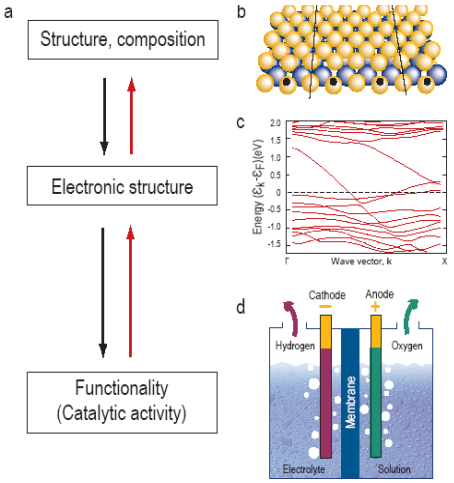
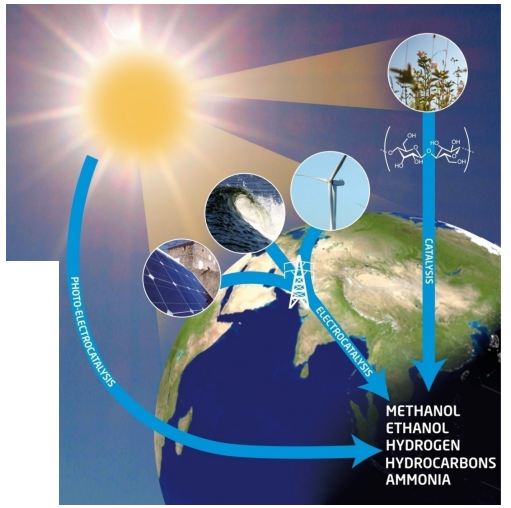
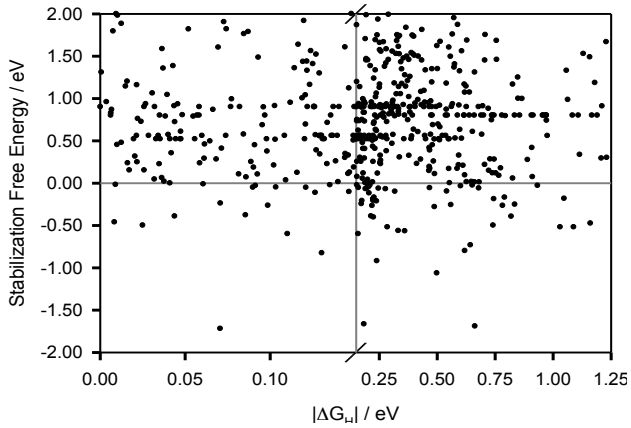


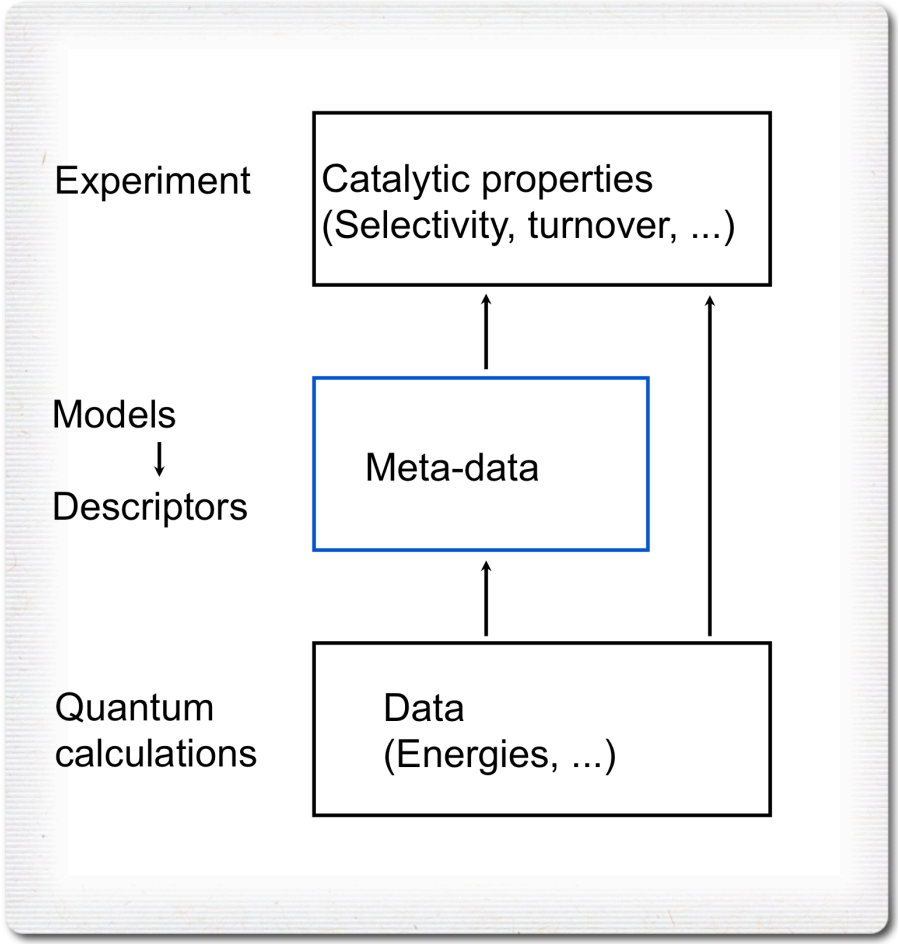




The role of modeling

In conjunction w. experiments:

- Identification of reaction mechanisms
- Understanding of trends
- Identification of the active site
- Discovery of correlations
- Discovery of descriptors
- Catalyst discovery tools
-



Large-scale production

Methanol Synthesis

50 bar, 550 K

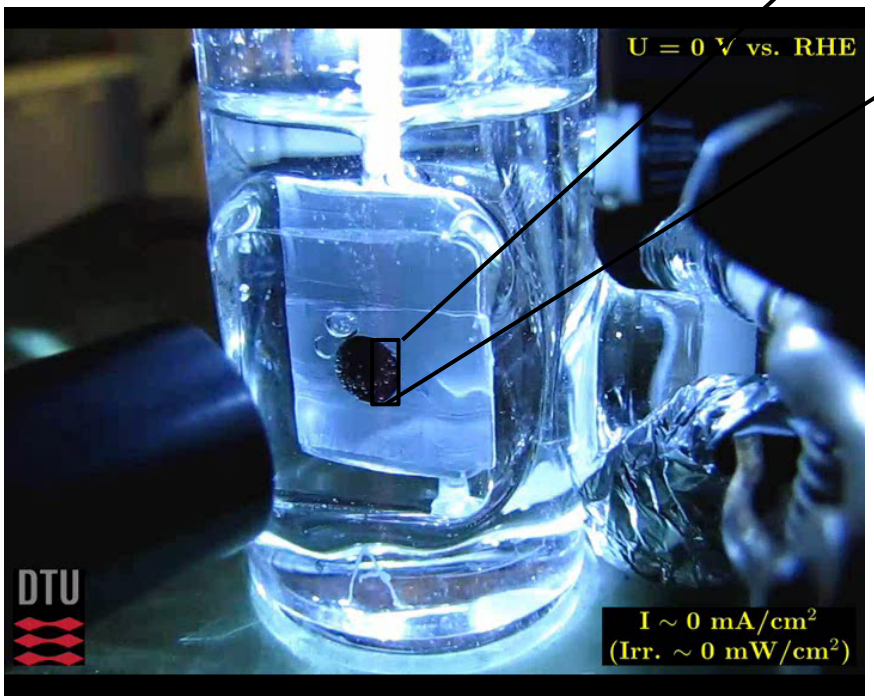
Ammonia synthesis

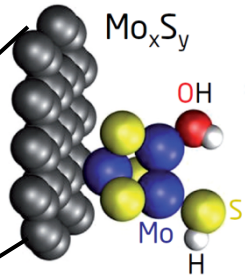
100 bar, 700 K

Is small-scale production possible?

Sustainable fuels and chemicals

Sustainable H_2 production





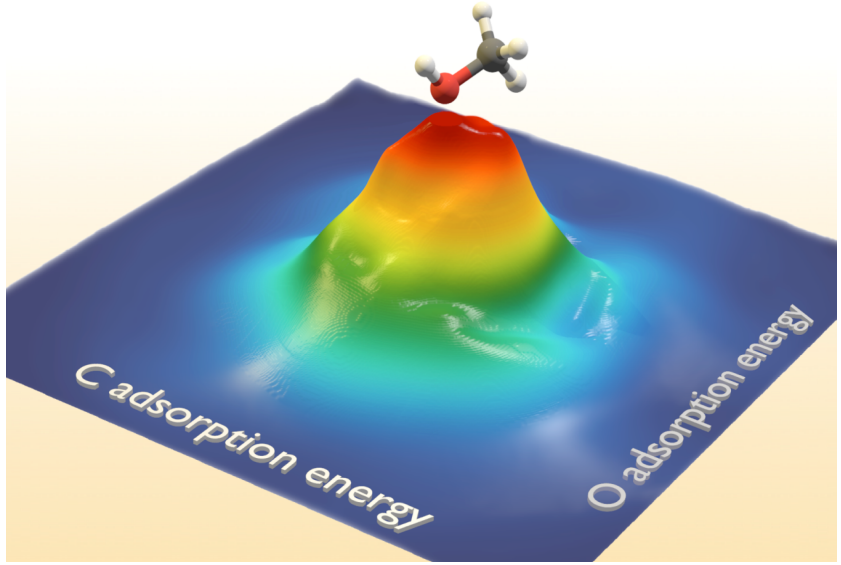
$+ CO_2 \rightarrow CH_3OH + H_2O$

$+ N_2 \rightarrow NH_3$

Hou, Abrams, Vesborg, Bjorketun, Herbst, Bech, Setti, Damsgaard, Hansen, Rossmeisl, Dahl, Nørskov, Chorkendorff, Nature Mat. **10**, 434 (2011)

Low pressure CO_2 and N_2 reduction

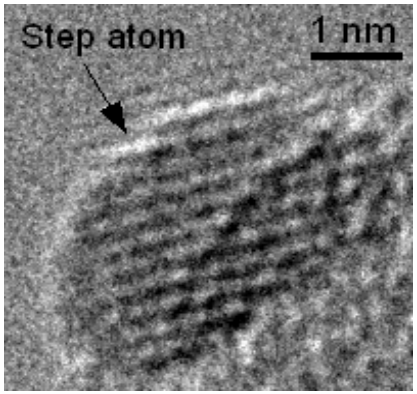
- N_2 reduction
  - Why high T and p?
  - Understanding trends
  - The ideal catalyst
- CO_2 reduction
  - Understanding trends
  - Catalyst design
- Direct electrochemical CO_2 reduction?
  - Understanding trends
  - Design principles
  - Comparison to enzymes

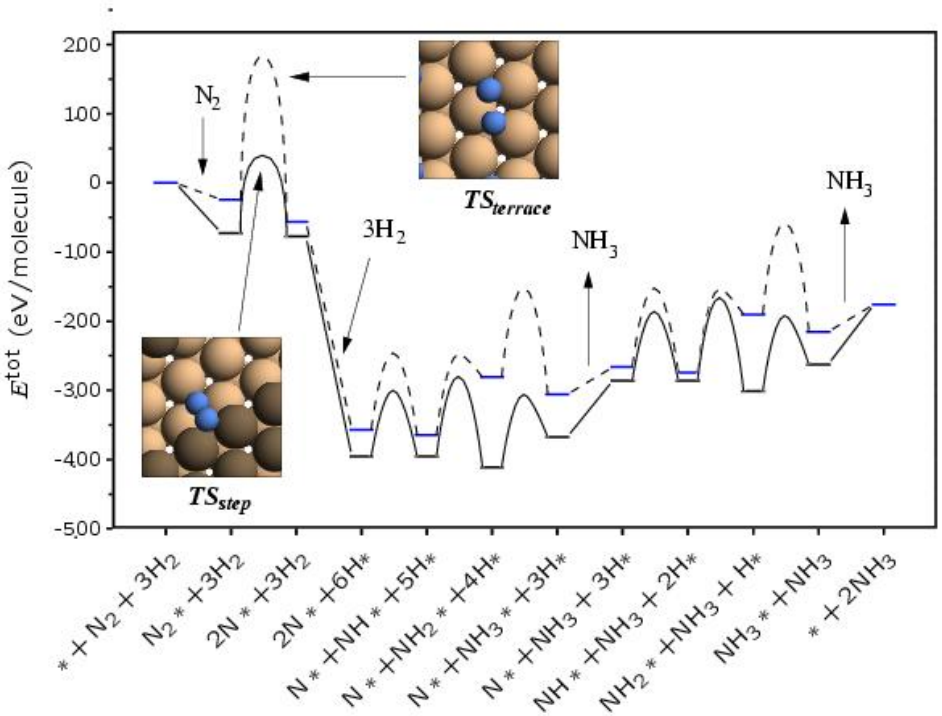


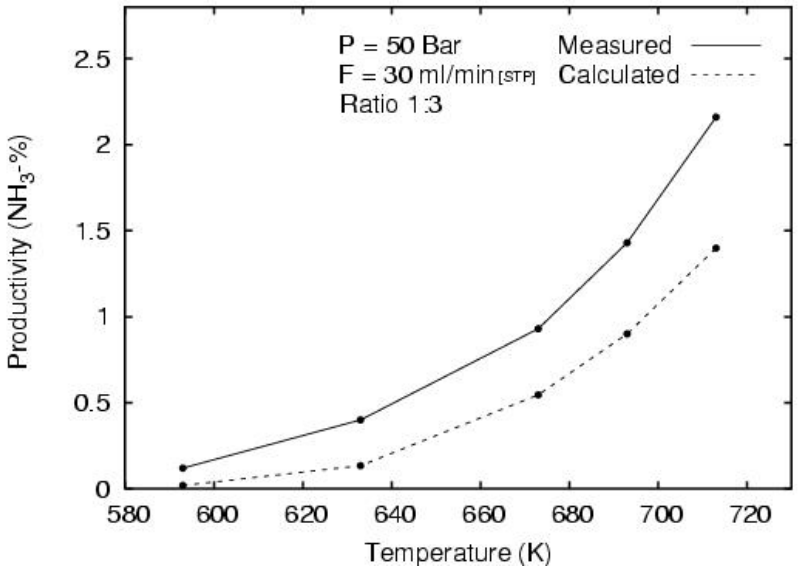
N_2 reduction over Ru

DFT (RPBE) calculations:

- Steps are active sites
- Good agreement w. experiment







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

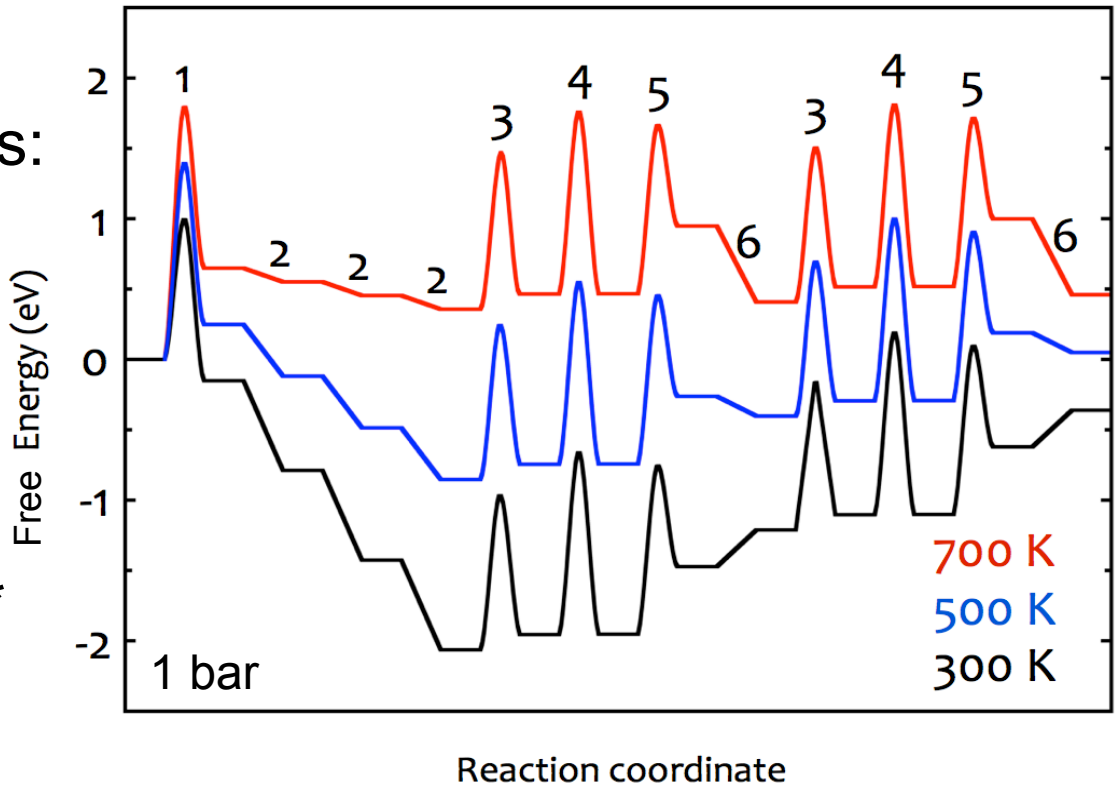
Why high T?

Ammonia synthesis, Ru step

$N_2 + 3\ H_2 \rightarrow 2\ NH_3$,

Elementary reaction steps:

(1) $N_2 + 2\ * \rightarrow 2\ N*$
(2) $H_2 + 2\ * \rightarrow 2\ H*$
(3) $N* + H* \rightarrow NH* + *$
(4) $NH* + H* \rightarrow NH_2* + *$
(5) $NH_2* + H* \rightarrow NH_3* + *$
(6) $NH\text{-}_3* \rightarrow NH_3 + *$



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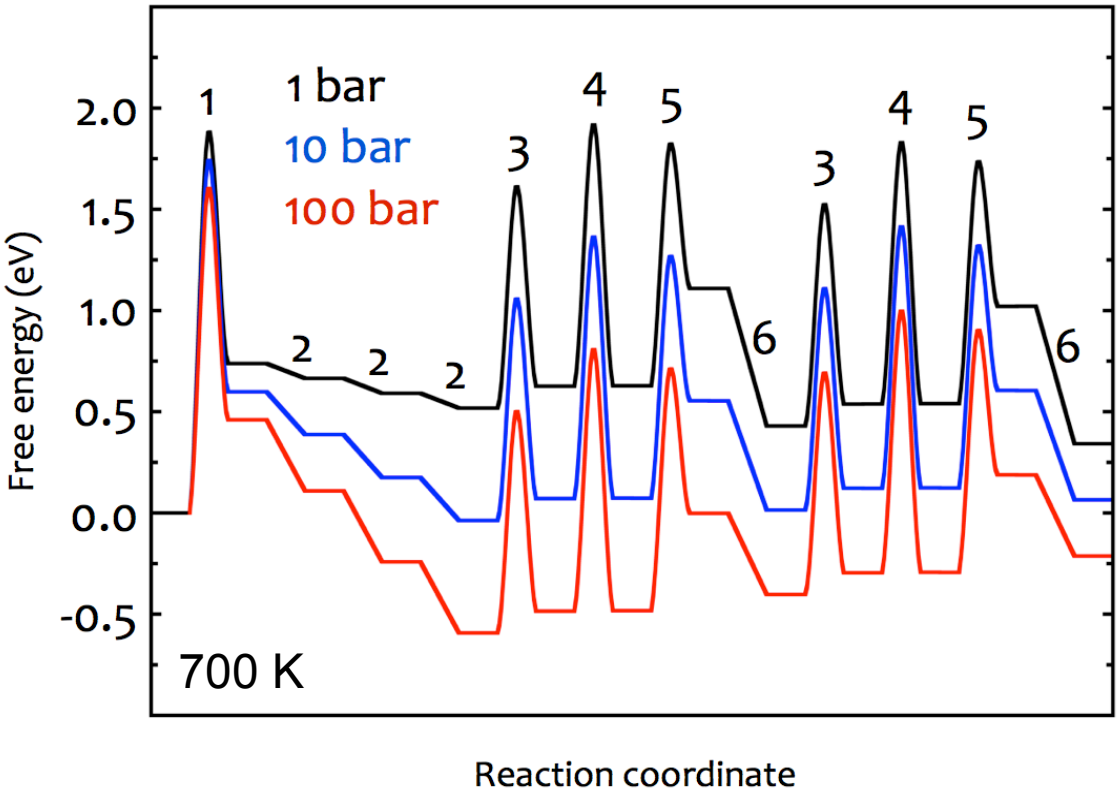
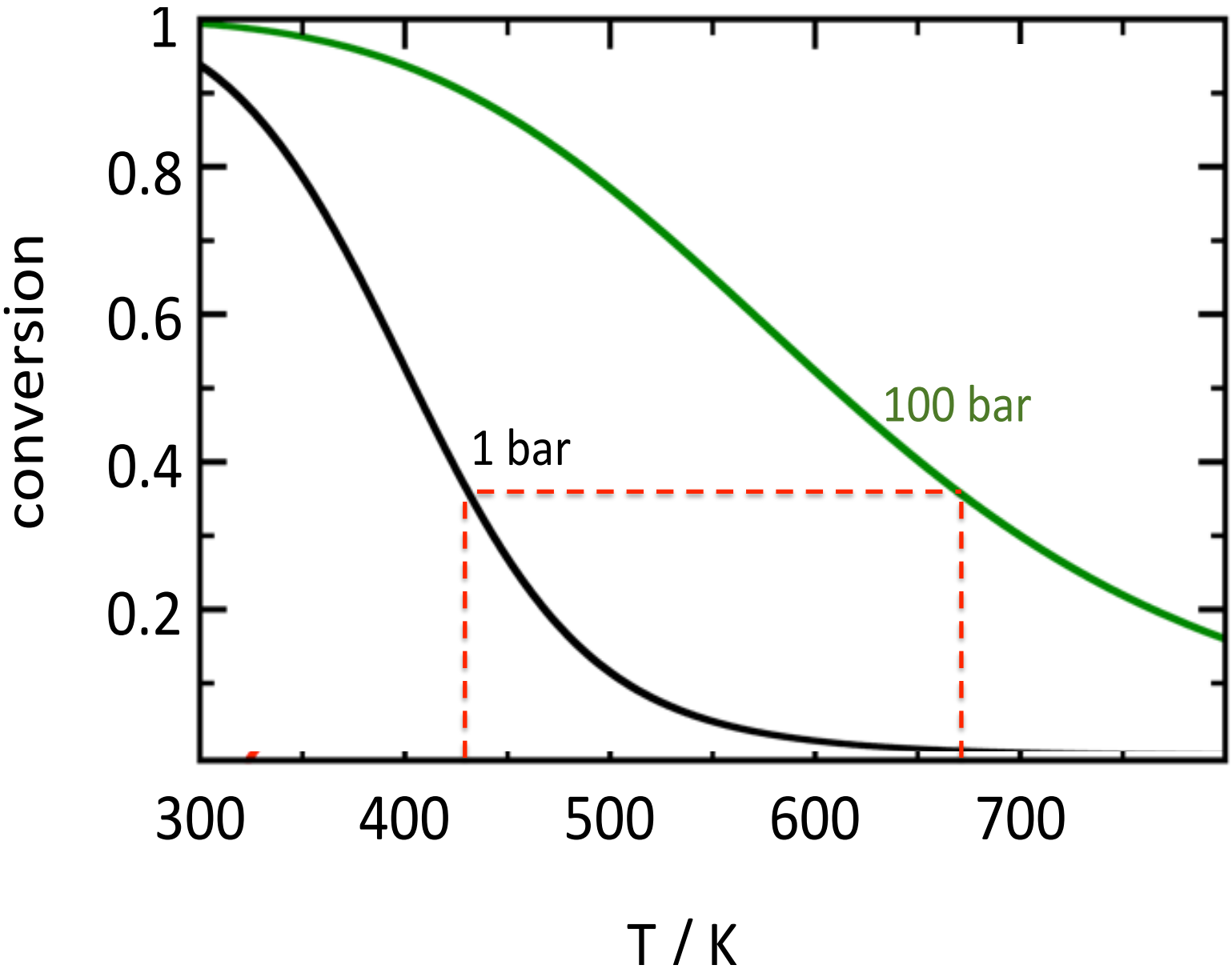
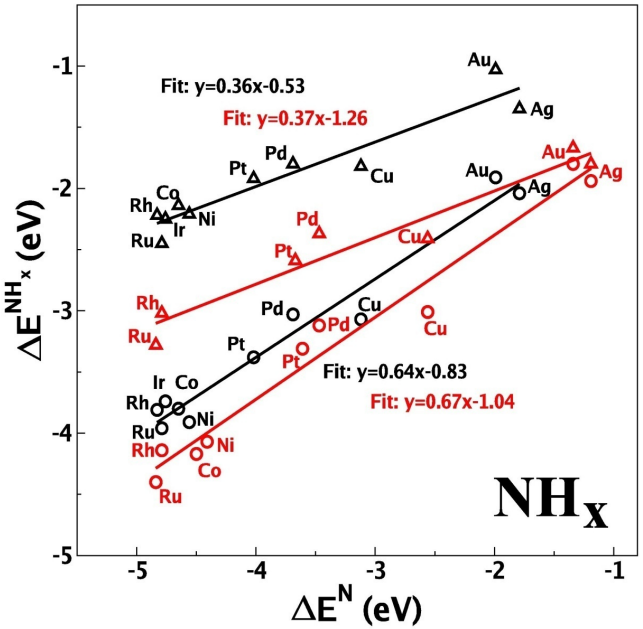


Equilibrium conversion

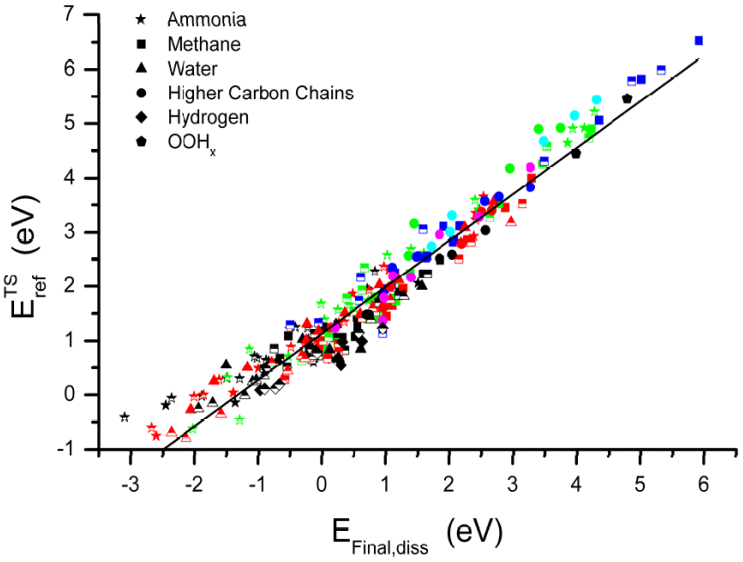


Reducing complexity – scaling relations

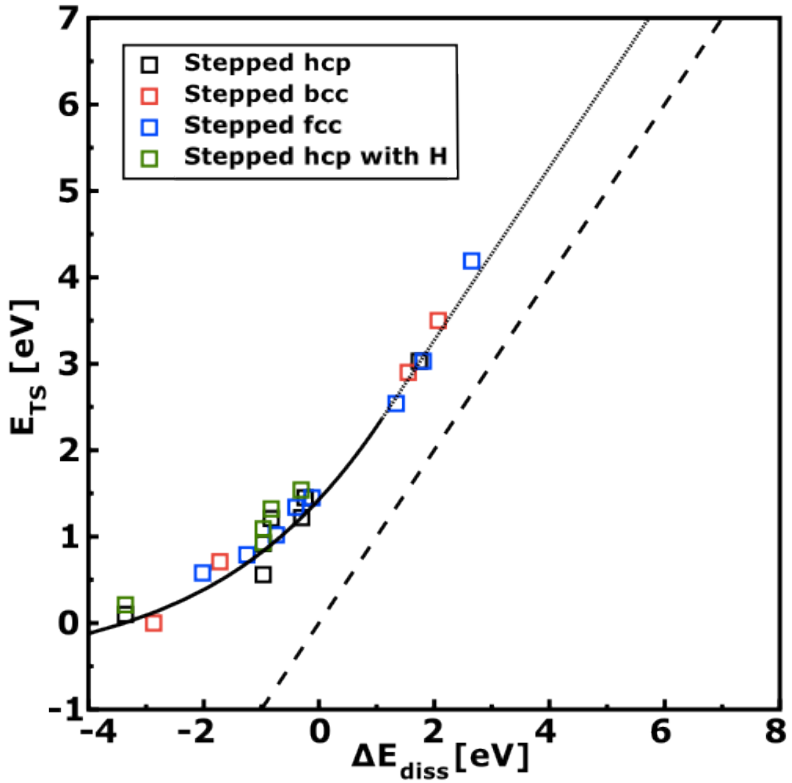
NH_x ads.



NH_x diss.



N_2 diss.



Vojvodic, Studt, Abild-Pedersen, Kahn, Bligaard, Nørskov (2013)

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