Catalysis in hydrogen production and storage

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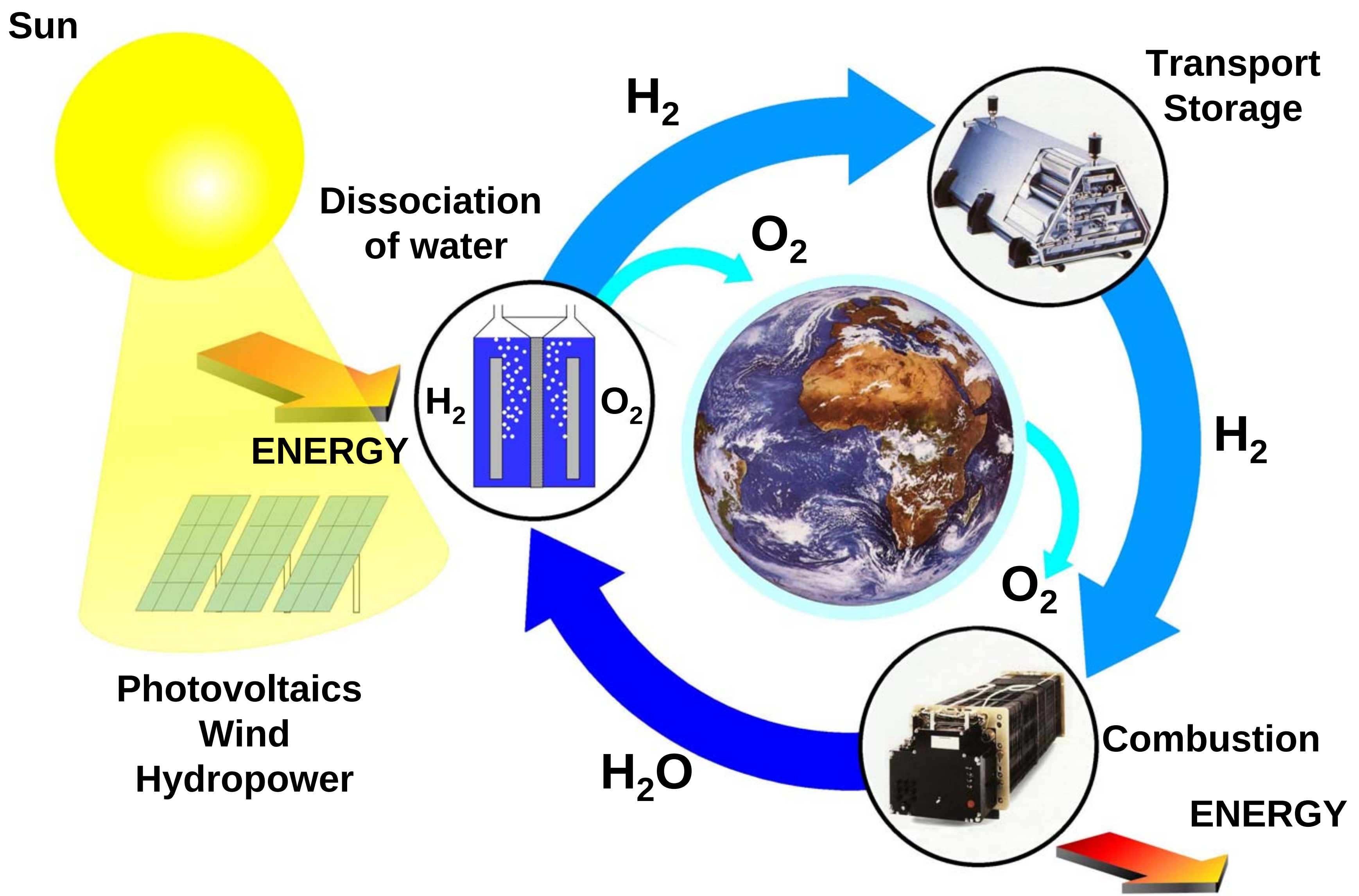
- Catalysis in hydrogen production
  - Theory: J. Rossmeisl, J. Greeley, T. Bligaard, B. Hinnemann, P.G. Moses
  - Experiment: T. Jaramillo, J. Bonde, K. Jørgensen, J. Nielsen, S.Horch, I. Chorkendorff

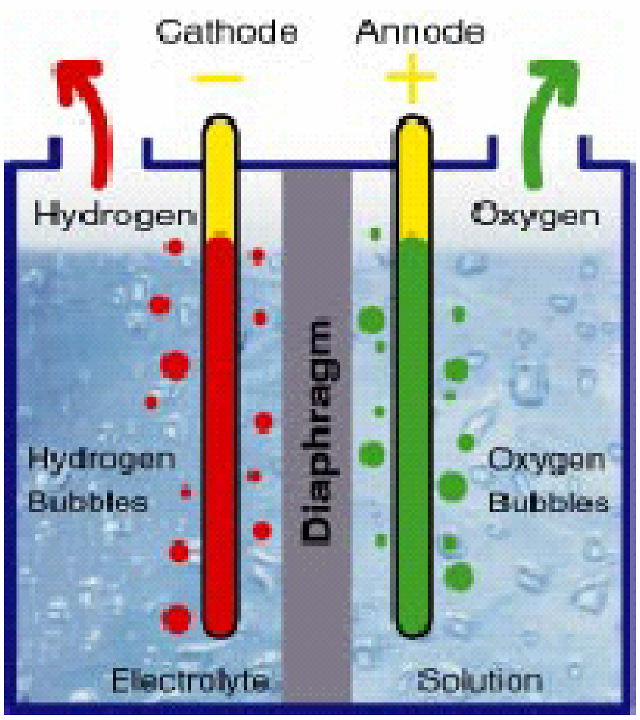
- Catalysis in hydrogen storage
  - Theory: J. Hummelshøj, T. Vegge, K. Honkala
  - Experiment: C. Christensen, T. Johannesen, R. Z. Sørensen, U. Quaade

Sustainable hydrogen production



A. Züttel, L. Schlapbach

Electrolysis



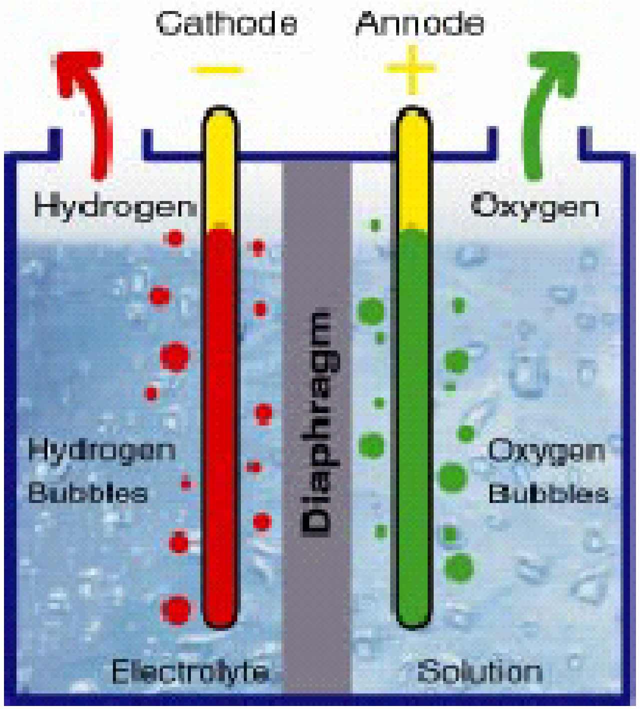
Cathode: $2(H^+ + e^-) \rightarrow H_2$

Anode: $H_2O \rightarrow \frac{1}{2} O_2 + 2 H^+$

Total: $H_2O \rightarrow \frac{1}{2} O_2 + H_2$

$\Delta G^0 = 2.46$ eV (1.23 eV/electron)

Electrolysis



Cathode: $2(H^{+}+e^{-}) \rightarrow H_2$

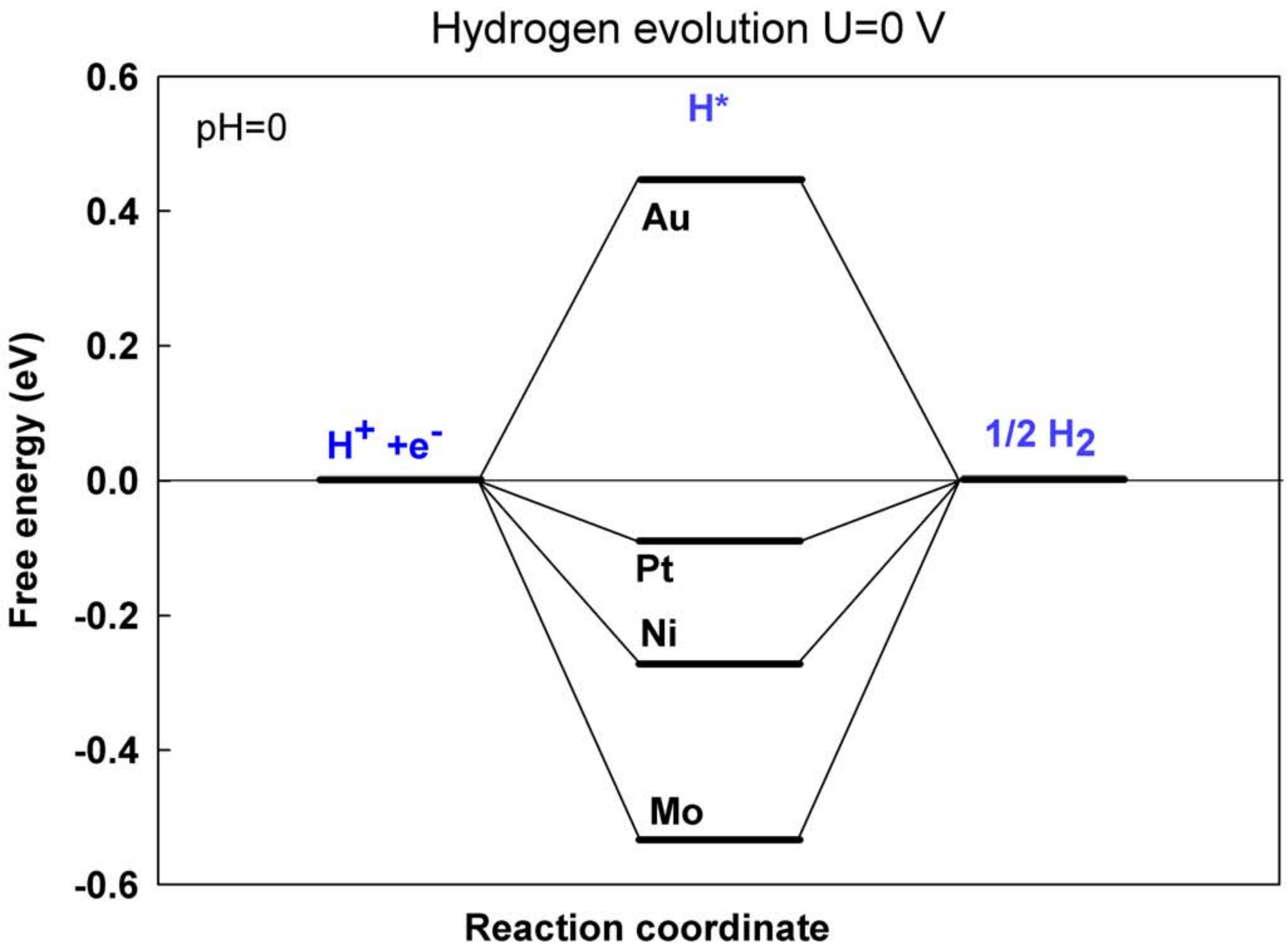
Anode: $H_2O \rightarrow ½\ O_2 + 2\ H^{+}$

Total: $H_2O \rightarrow ½\ O_2 + H_2$

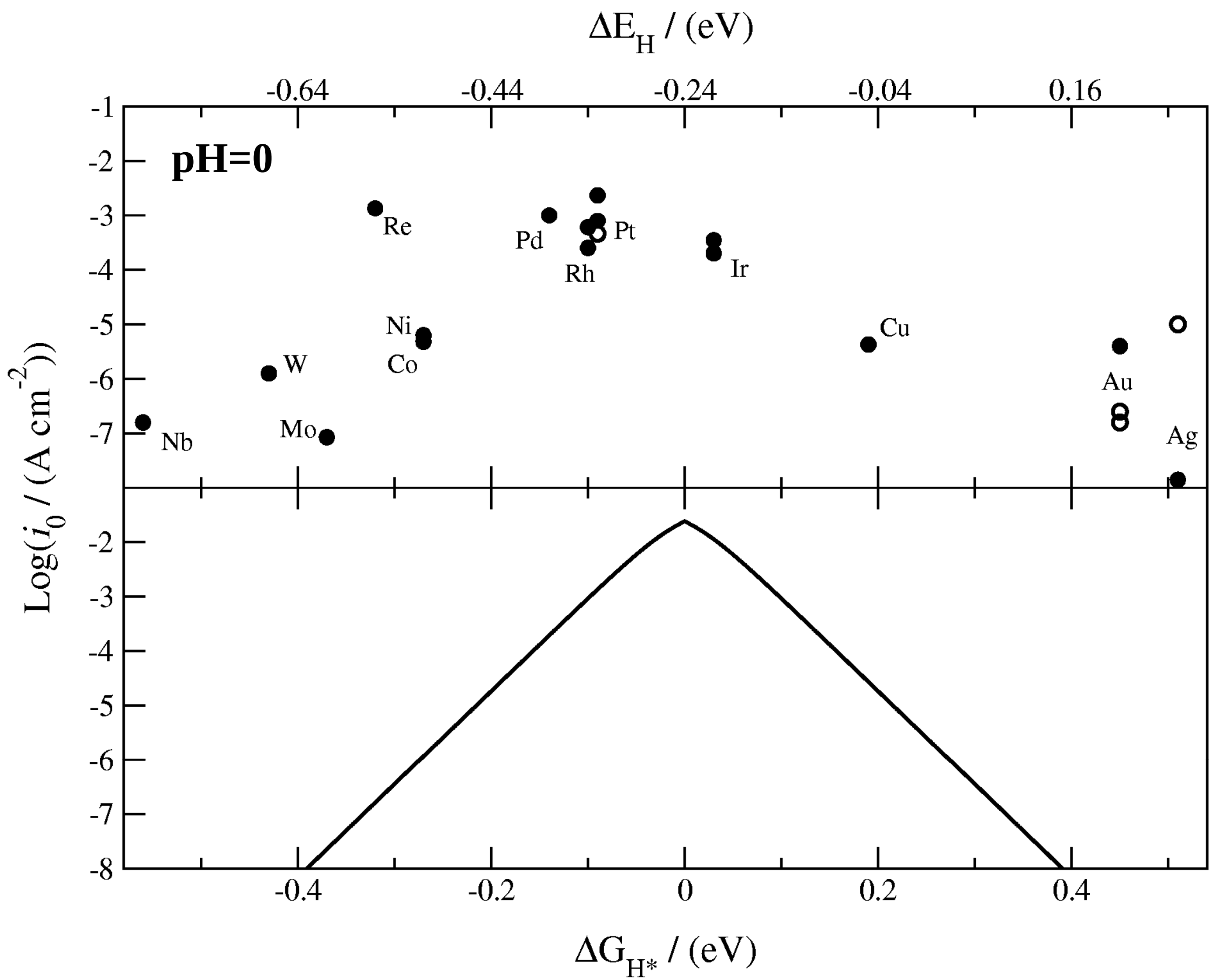
$\Delta G^0 = 2.46$ eV (1.23 eV/electron)

The hydrogen evolution process

DFT calculations give free energy of intermediates:



Using DFT energies in volcano



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

Volcanoes in electrochemistry

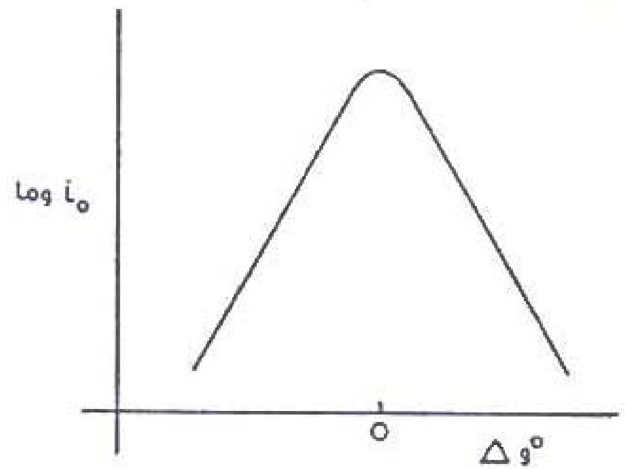
DTU

THE RATE OF ELECTROLYTIC HYDROGEN EVOLUTION AND THE HEAT OF ADSORPTION OF HYDROGEN

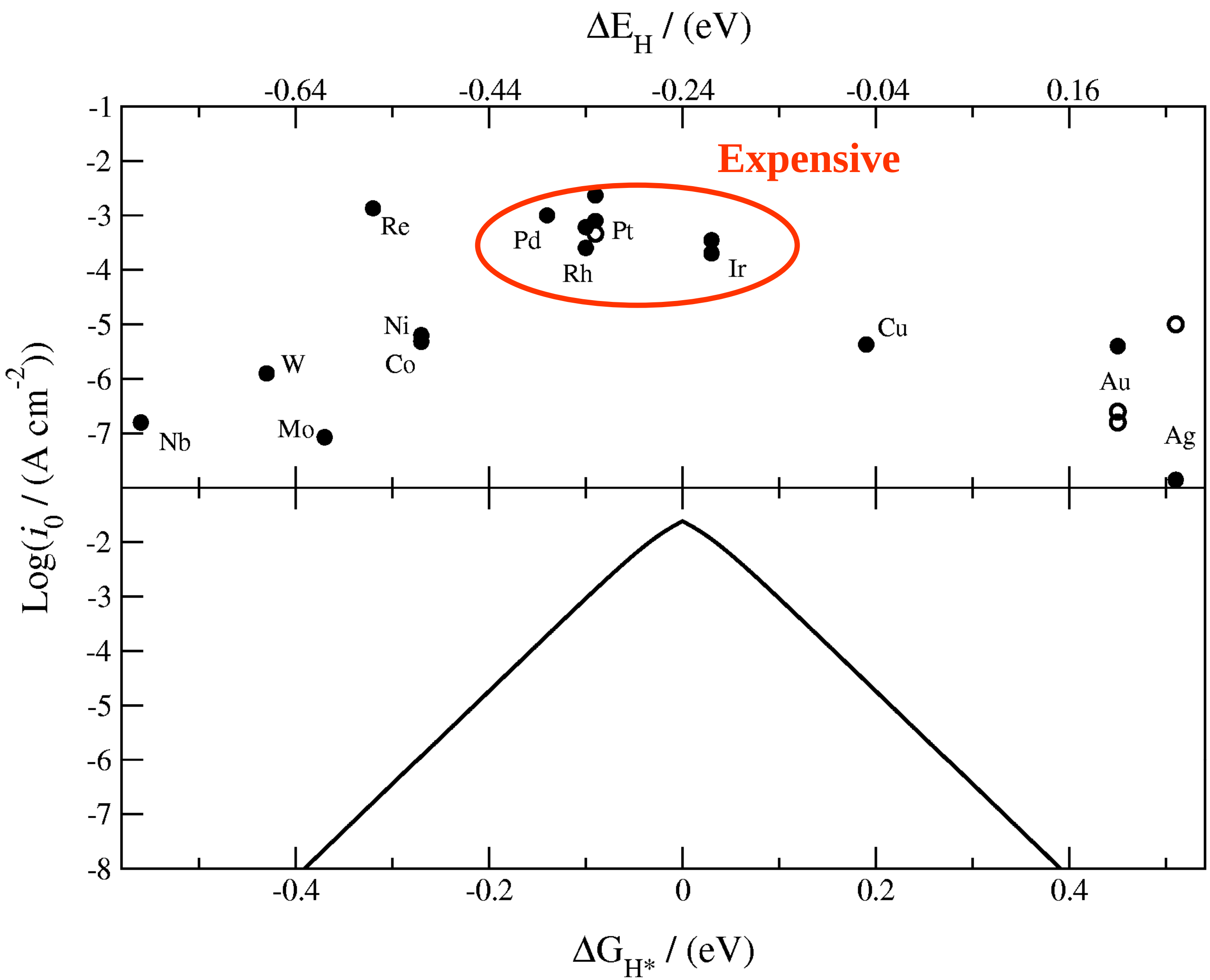
BY ROGER PARSONS
Dept. of Physical and Inorganic Chemistry, The University, Bristol 8

Received 10th December, 1957

FIG. 1.—Form of the relation between exchange current at a hydrogen electrode and the standard free energy of adsorption of hydrogen on the electrode surface, assuming that the adsorbed atoms obey a Langmuir adsorption isotherm.



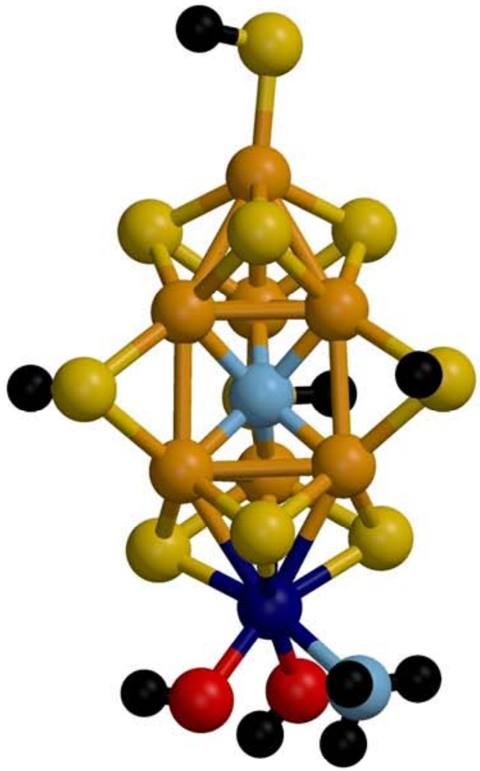
HER volcano



ΔE_H / (eV)
-0.64
-0.44
-0.24
-0.04
0.16
Expensive
Re
Pd
Pt
Rh
Ir
Ni
Co
W
Cu
Au
Nb
Mo
Ag
-1
-2
-3
-4
-5
-6
-7
-8
Log(i_0 / (A cm^-2))
-0.4
-0.2
0
0.2
0.4
ΔG_H* / (eV)

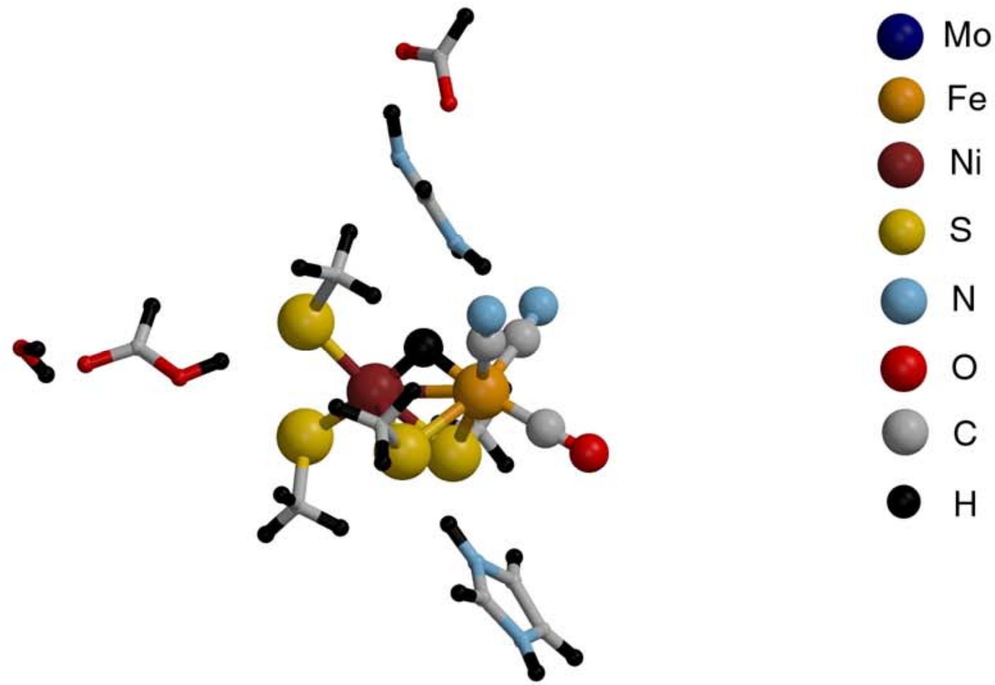
Active sites of hydrogen producing enzymes

DTU



nitrogenase

active site



hydrogenase

active site

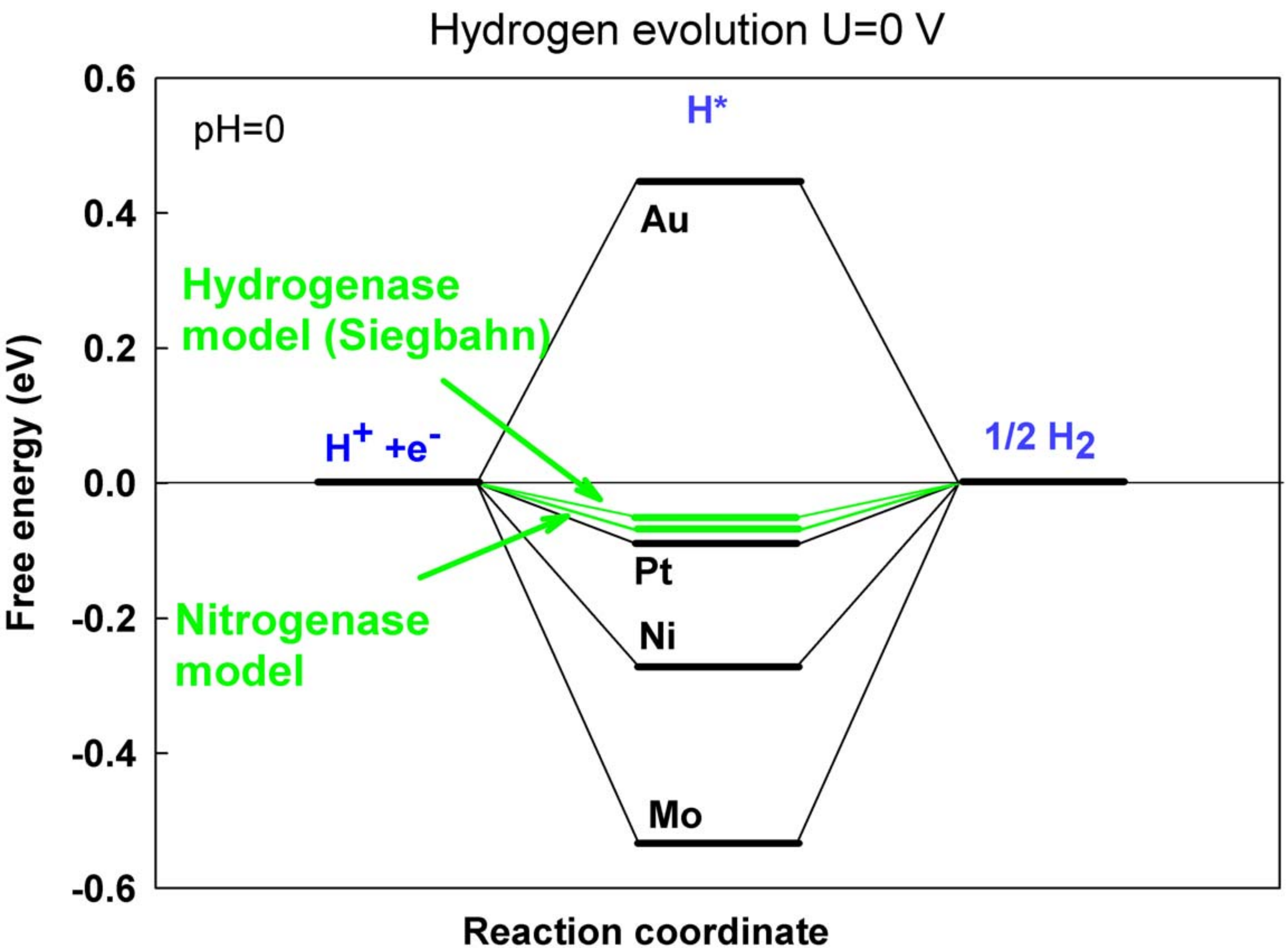
Einsle, Teczan, Andrade, Schmid, Yoshida, Howard, Rees, Science **2002**, *297*, 1696.

Hinnemann, Nørskov, JACS **126**, 3920 (2004)

Vollbeda, Fontecilla-Camps, Dalton Trans. 4030-3048 (2003).

Siegbahn, Blomberg, Wirstam, Crabtree Biol. Inorg. Chem. **6**, 460 (2001)

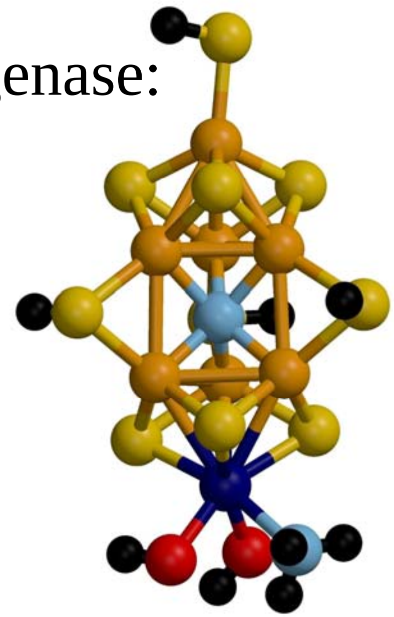
Biological hydrogen evolution



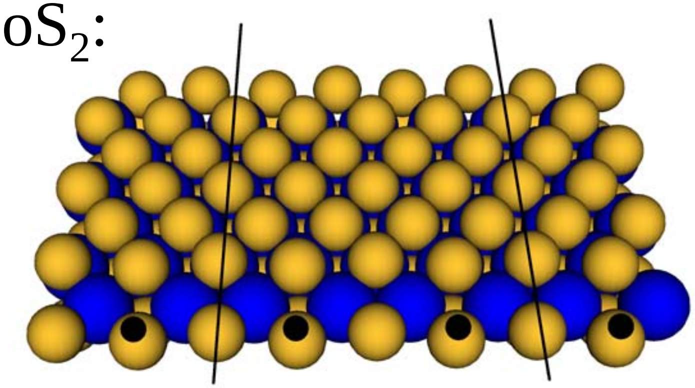
Hinnemann, Bonde, Jørgensen, Nielsen, Horch, Chorkendorff, Nørskov, JACS **127** 5308 (2005)

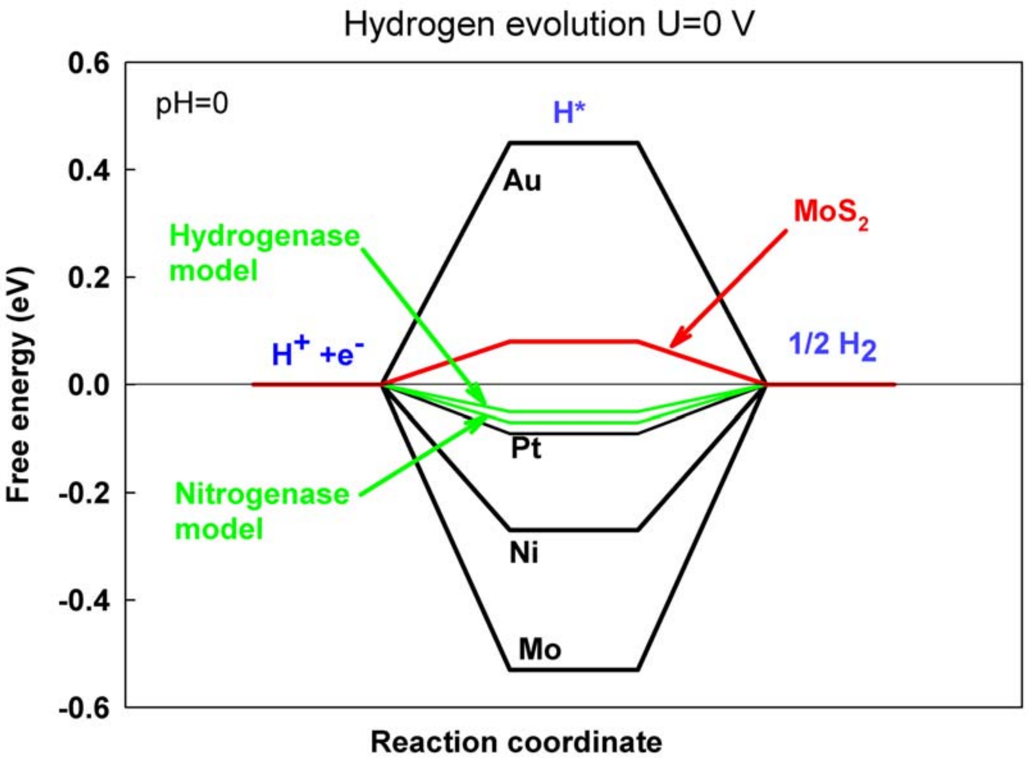
MoS_2 as HER catalyst

Nitrogenase:



MoS_2:

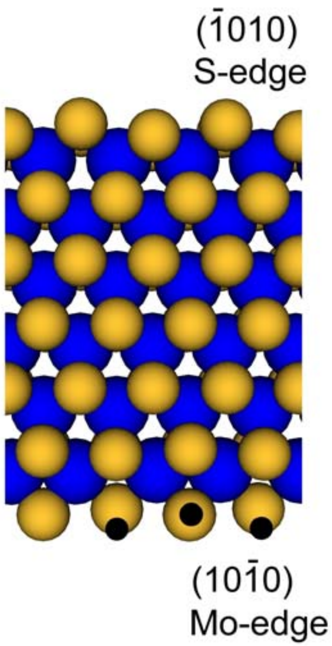


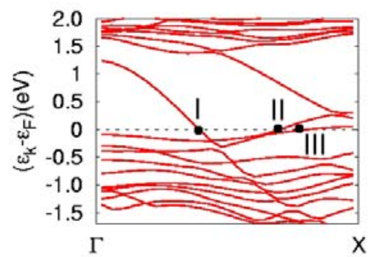


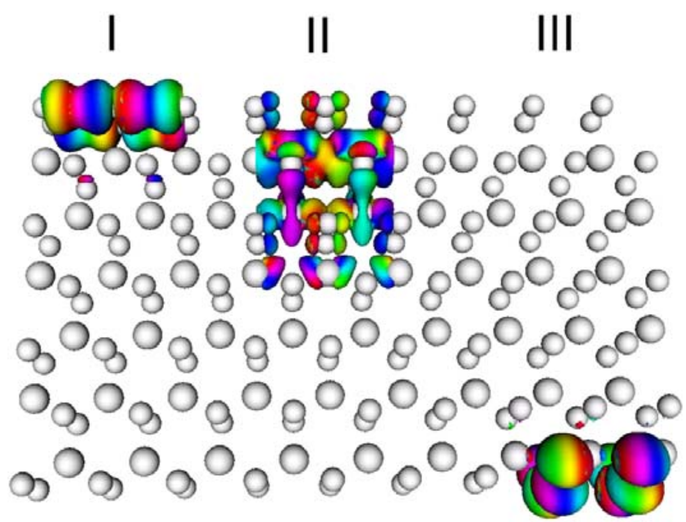
Hinnemann, Bonde, Jørgensen, Nielsen, Horch, Chorkendorff, Nørskov, JACS **127** 5308 (2005)

MoS$_2$ nanoparticles are metallic

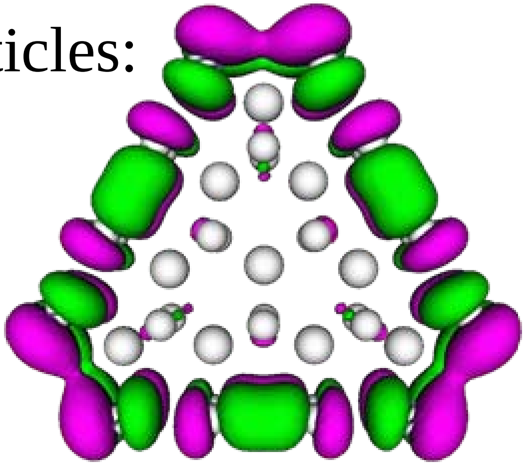
1-layer slab:

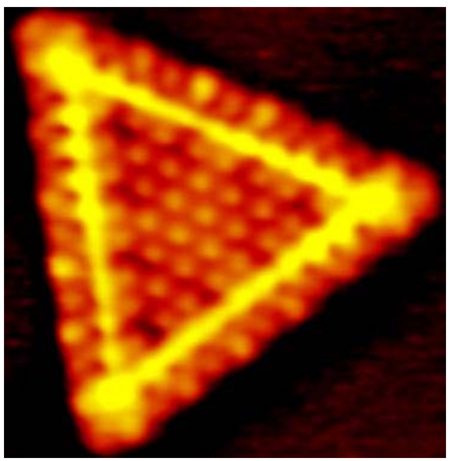






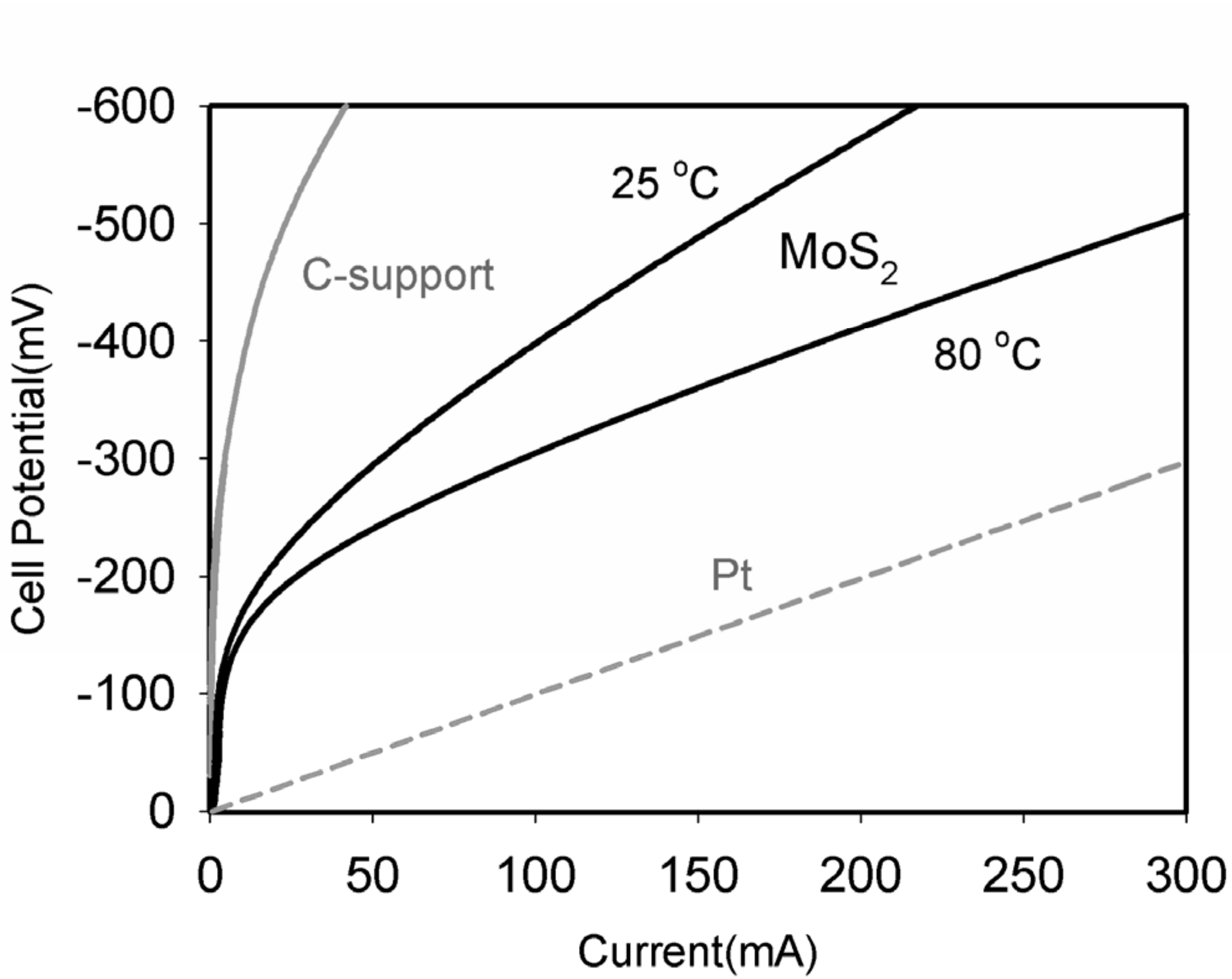
Nanoparticles:





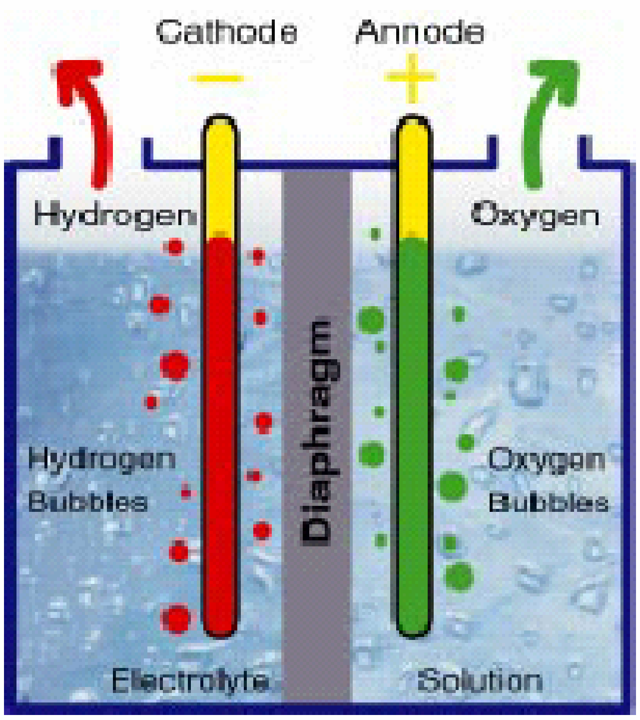
Bollinger, Lauritsen, Jacobsen, Nørskov, Helveg, Besenbacher, Phys. Rev. Lett. **87**, 196803 (2001).

MoS_2 as HER catalyst



Hinnemann, Bonde, Jørgensen, Nielsen, Horch, Chorkendorff, Nørskov, JACS **127** 5308 (2005)

Electrolysis



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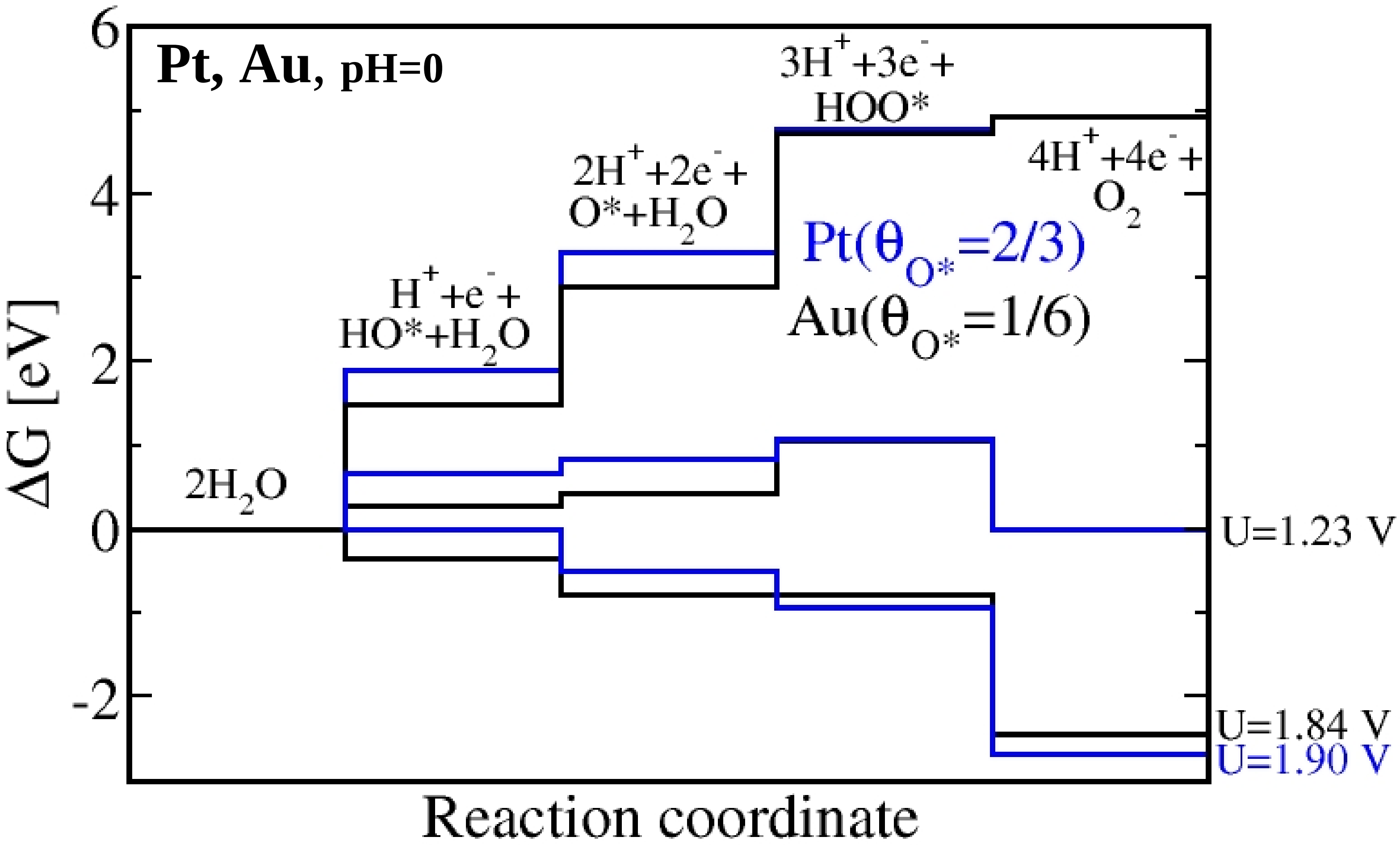
Total: $H_2O \rightarrow \frac{1}{2} O_2 + H_2$

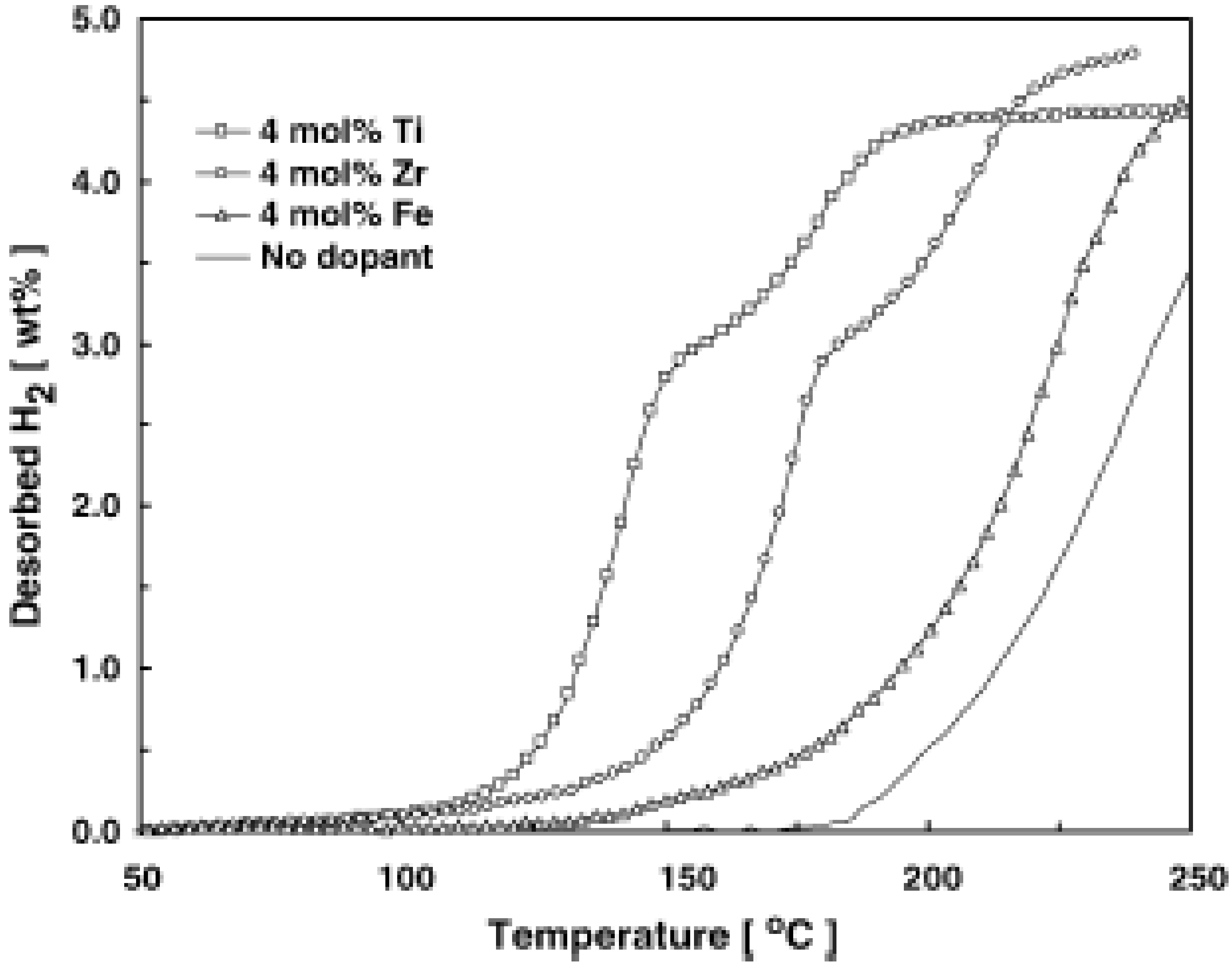
$\Delta G^0 = 2.46$ eV (1.23 eV/electron)

Water splitting at different potentials



Rossmeisl, Logadottir, Nørskov, J. Chem. Phys. **319,** 178 (2005)

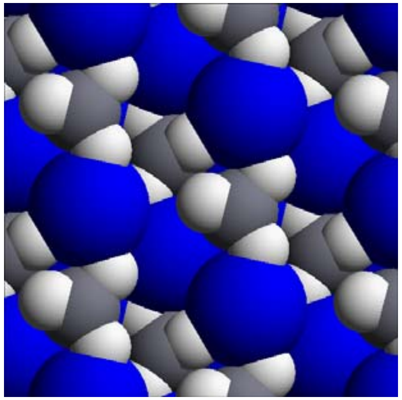
Catalyzed decomposition of $NaAlH_4$



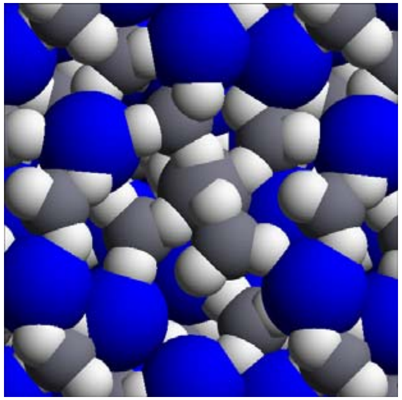
Wang, Ebner, Zidan, Ritter, J.Alloys & Comp. **391** (2005) 245

Catalyzed formation/decomposition of $NaAlH_4$

$NaAlH_4(001)$



$Ti@NaAlH_4(001)+2Na^v$

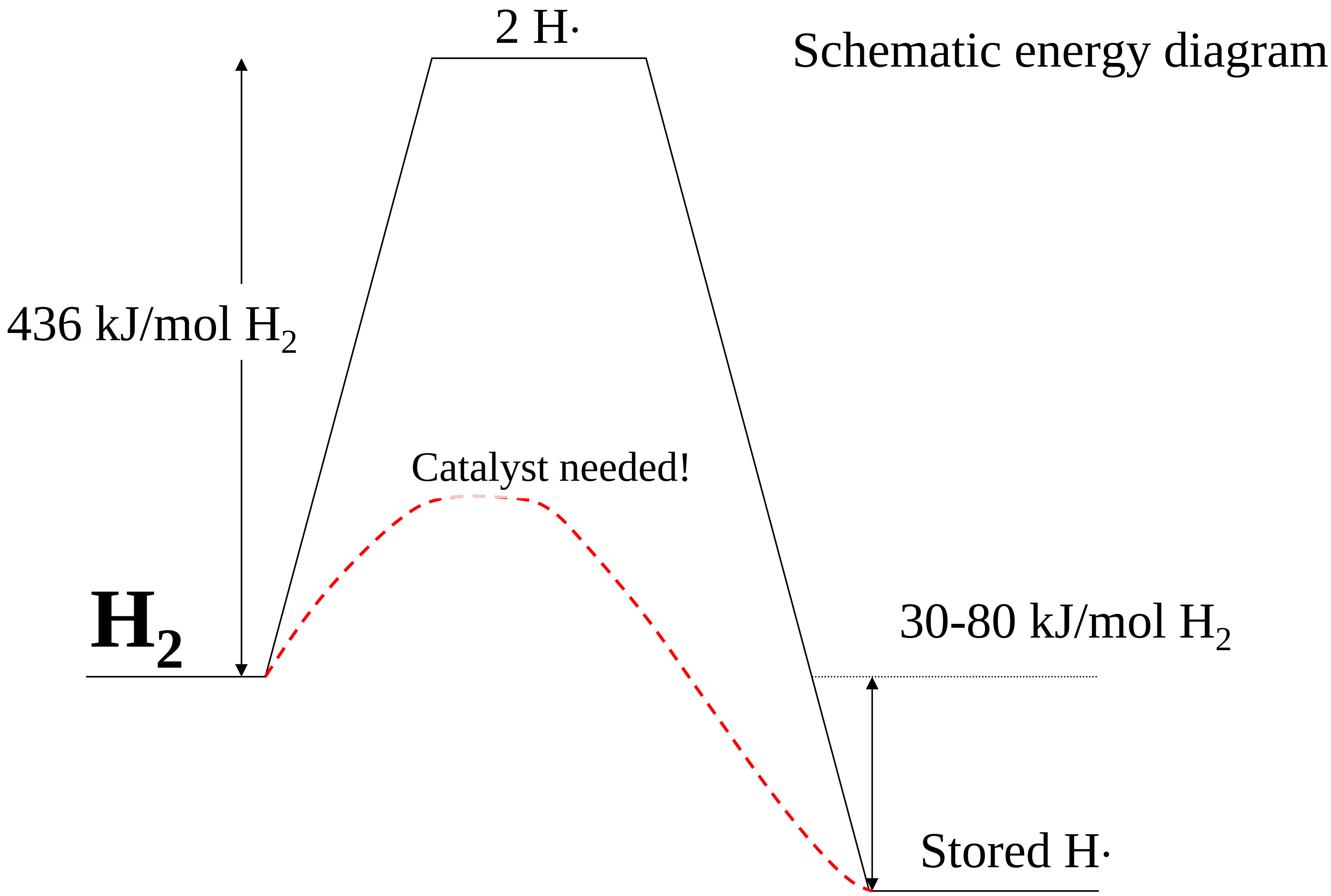


T. Vegge:

$TiCl_3$ as catalyst:

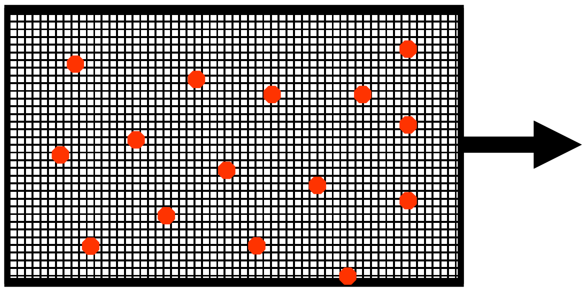
- lowers the H_2 desorption barrier
- Na/H-vacancy formation energy
- driving force: NaCl formation
- Ti- has long range effects

Activating H_2

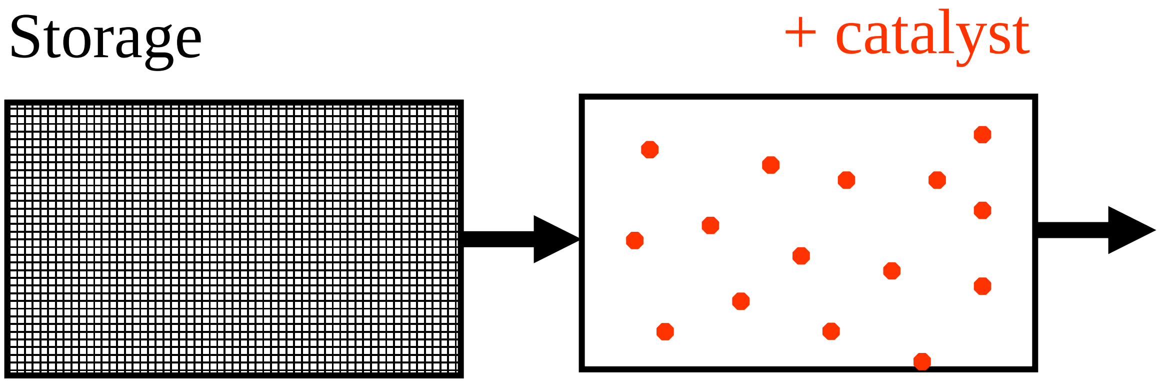


Separating storage and catalyst

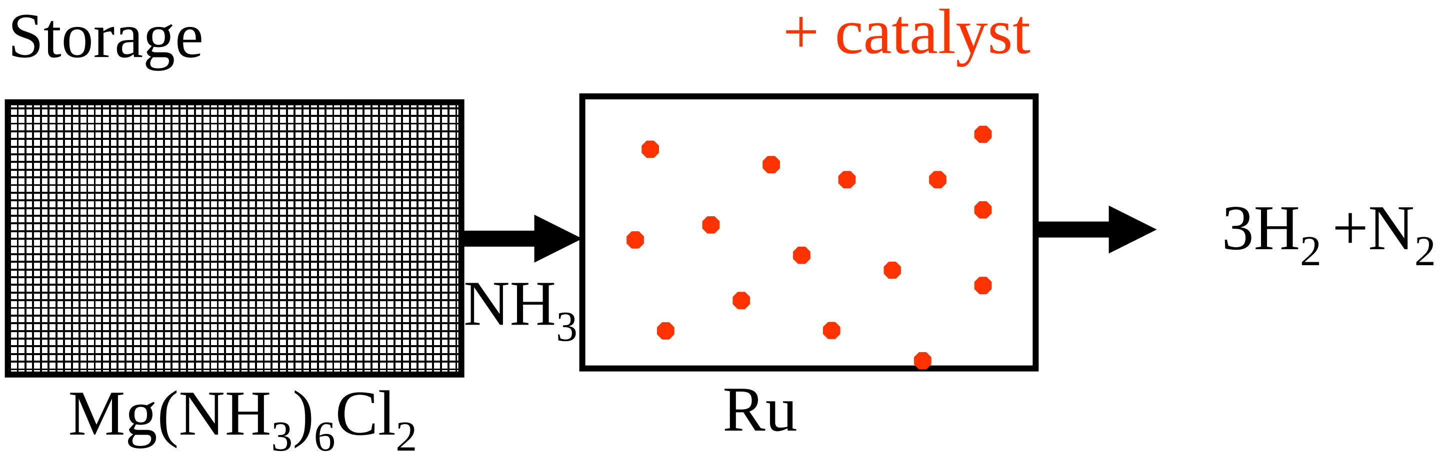
Storage + catalyst



Separating storage and catalyst



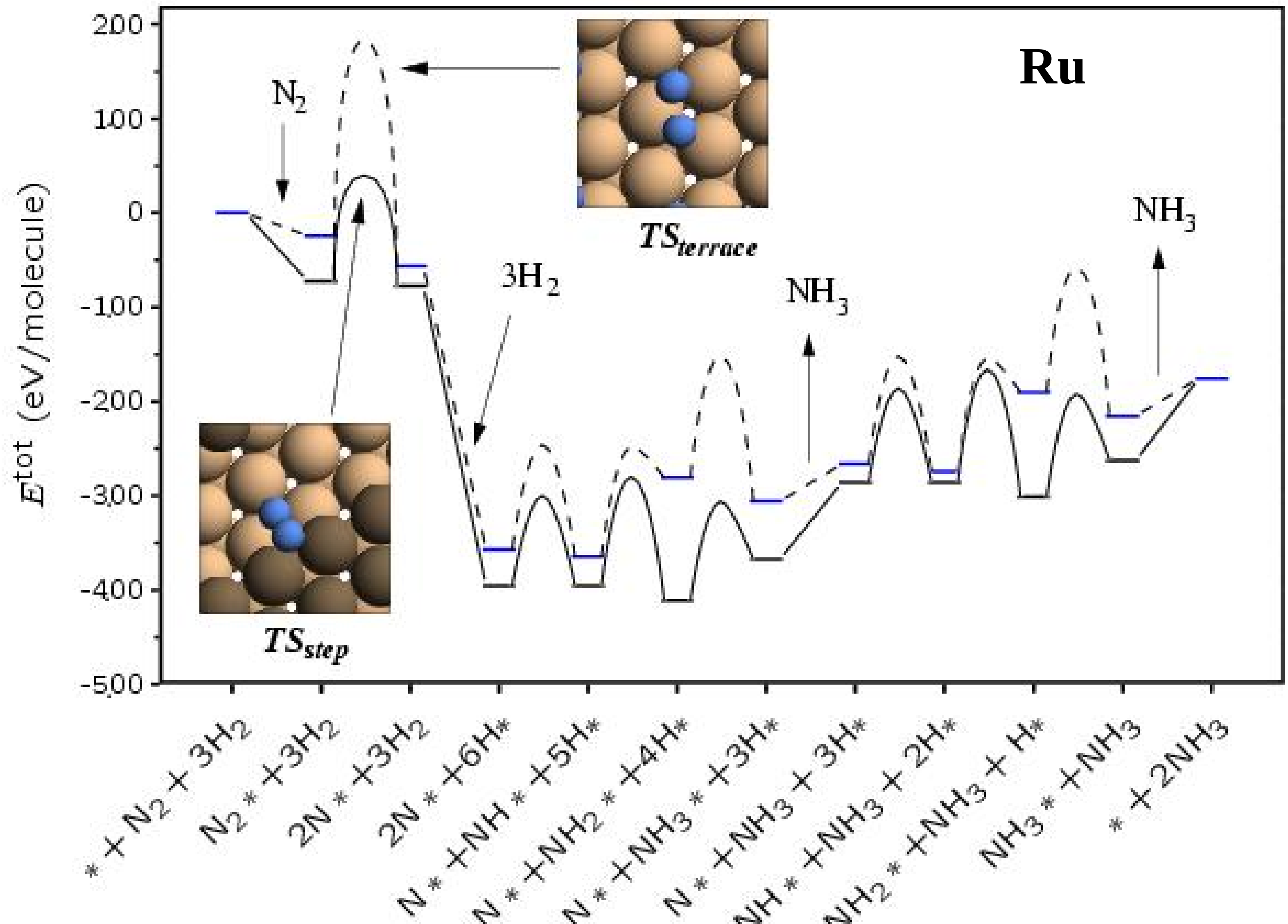
Separating storage and catalyst



One possibility: Use metal ammine complexes

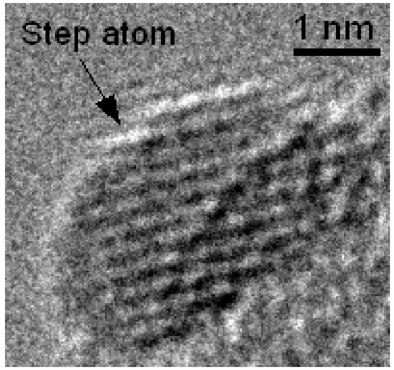
Christensen. Sørensen, Johannessen, Quaade, Honkala, Elmøe, Køhler, Nørskov, J. Mater. Chem **15**, 1406 (2005)

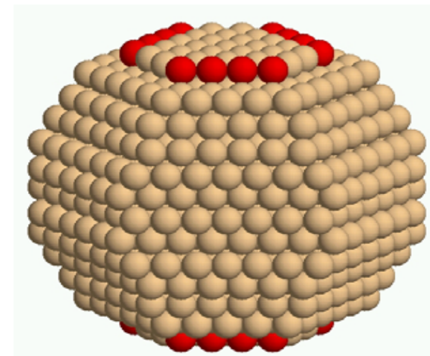
Catalyzed synthesis/decomposition of ammonia

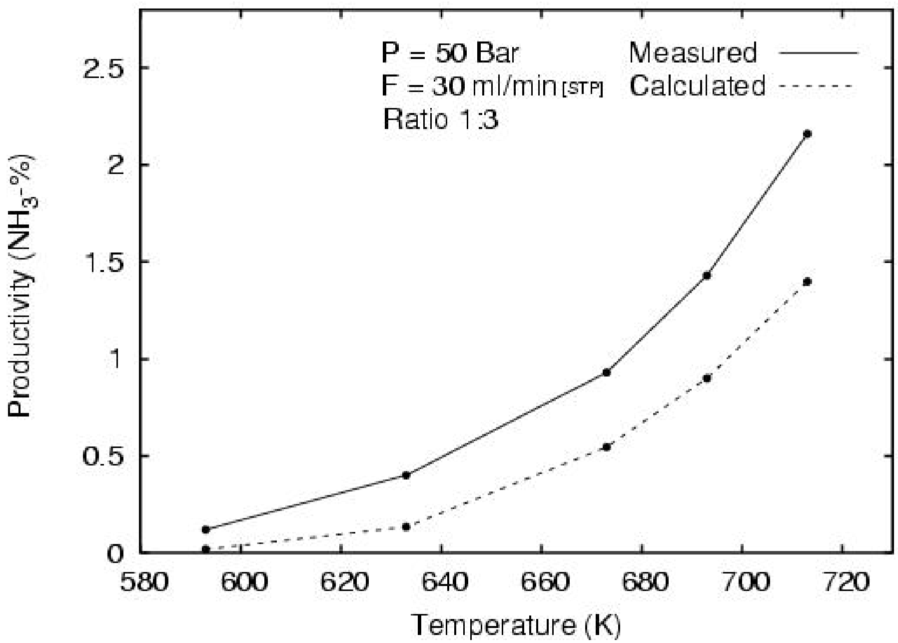


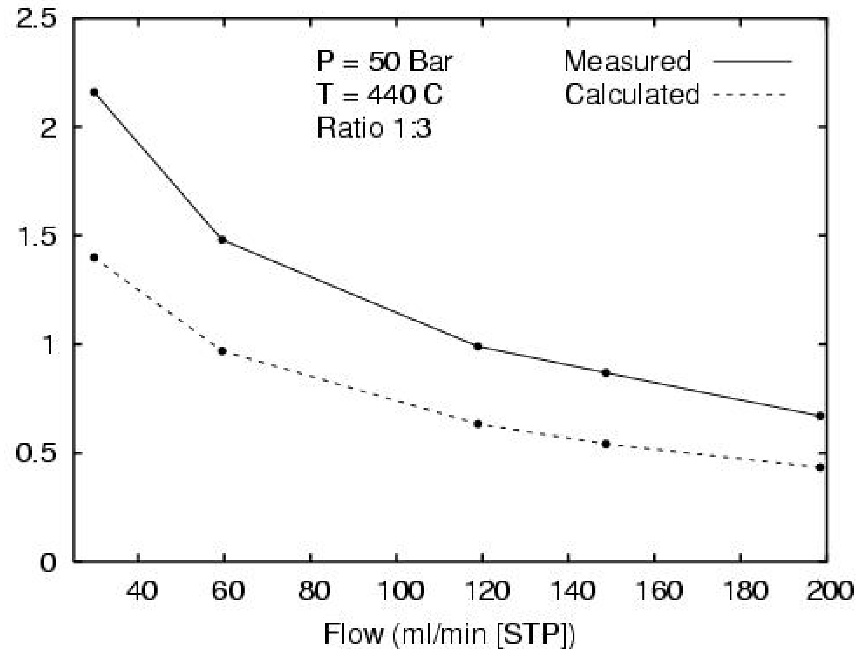
Logadottir, Nørskov, J. Catal. **220**, 273 (2003)

Ab initio kinetics – Ru catalysts



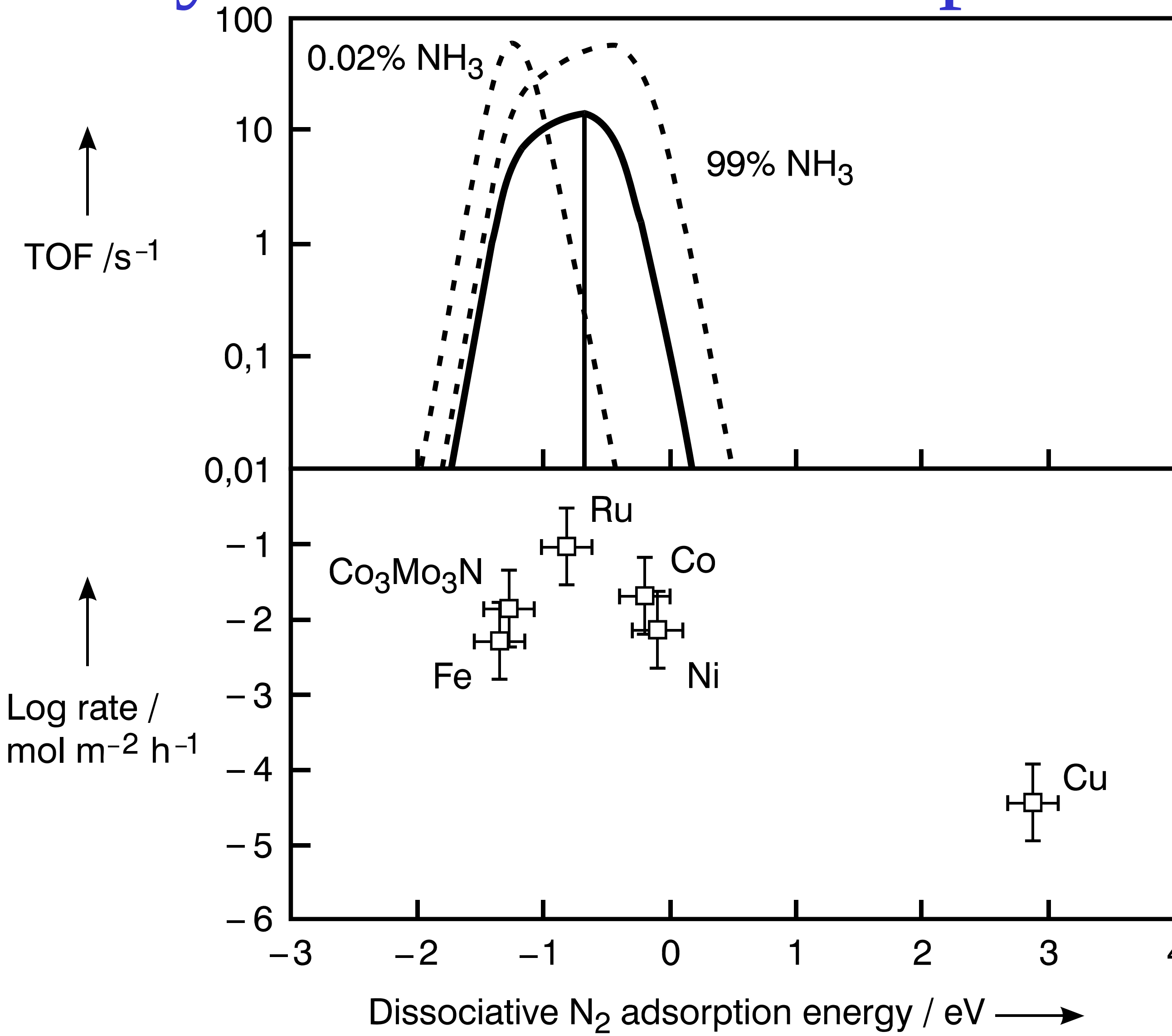






Honkala, Remediakis, Logadottir, Nørskov, Hellmann, Dahl, Carlsson, Christensen, Science **307**,555 (2005)

Optimal catalyst for ammonia synthesis and decomposition



Boisen, Dahl, Nørskov, Christensen, J. Catal **230**, 318 (2005)

Metal ammine chemistry – the $MgCl_2$-NH_3 system

$$MgCl_2(s) + NH_3(g) \rightleftharpoons Mg(NH_3)Cl_2(s), \quad \Delta H = 87.0\, kJ/mol\ NH_3$$

$$Mg(NH_3)Cl_2(s) + NH_3(g) \rightleftharpoons Mg(NH_3)_2Cl_2(s), \quad \Delta H = 74.9\, kJ/mol\ NH_3$$

$$Mg(NH_3)_2Cl_2(s) + 4NH_3(g) \rightleftharpoons Mg(NH_3)_6Cl_2(s), \quad \Delta H = 55.6\, kJ/mol\ NH_3$$

$$Average\ desorption\ enthalpy:\ 42.7 \frac{kJ}{mol\ H_2}$$

A. Werner, "On the constitution and configuration of higher-order compounds", 1913.

E. Lepinasse and B. Spinner, Rev. Int. Froid, 1994, 17, 309.

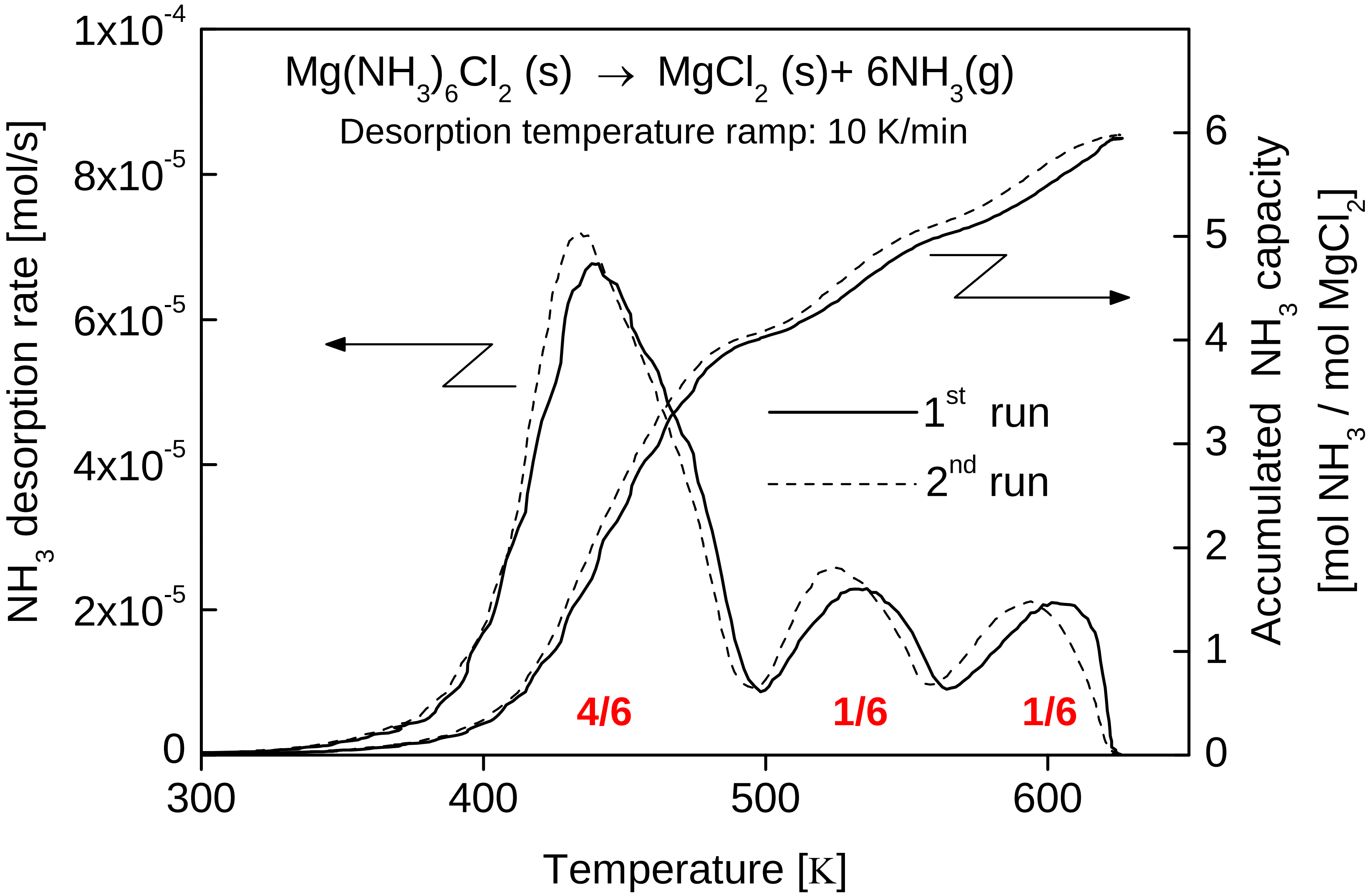
Bulk properties

$MgCl_2$:	2325 kg/m^3 ;	40,9 cm^3/mol
$Mg(NH_3)_6Cl_2$:	1252 kg/m^3 ;	157,4 cm^3/mol

The ammonia content

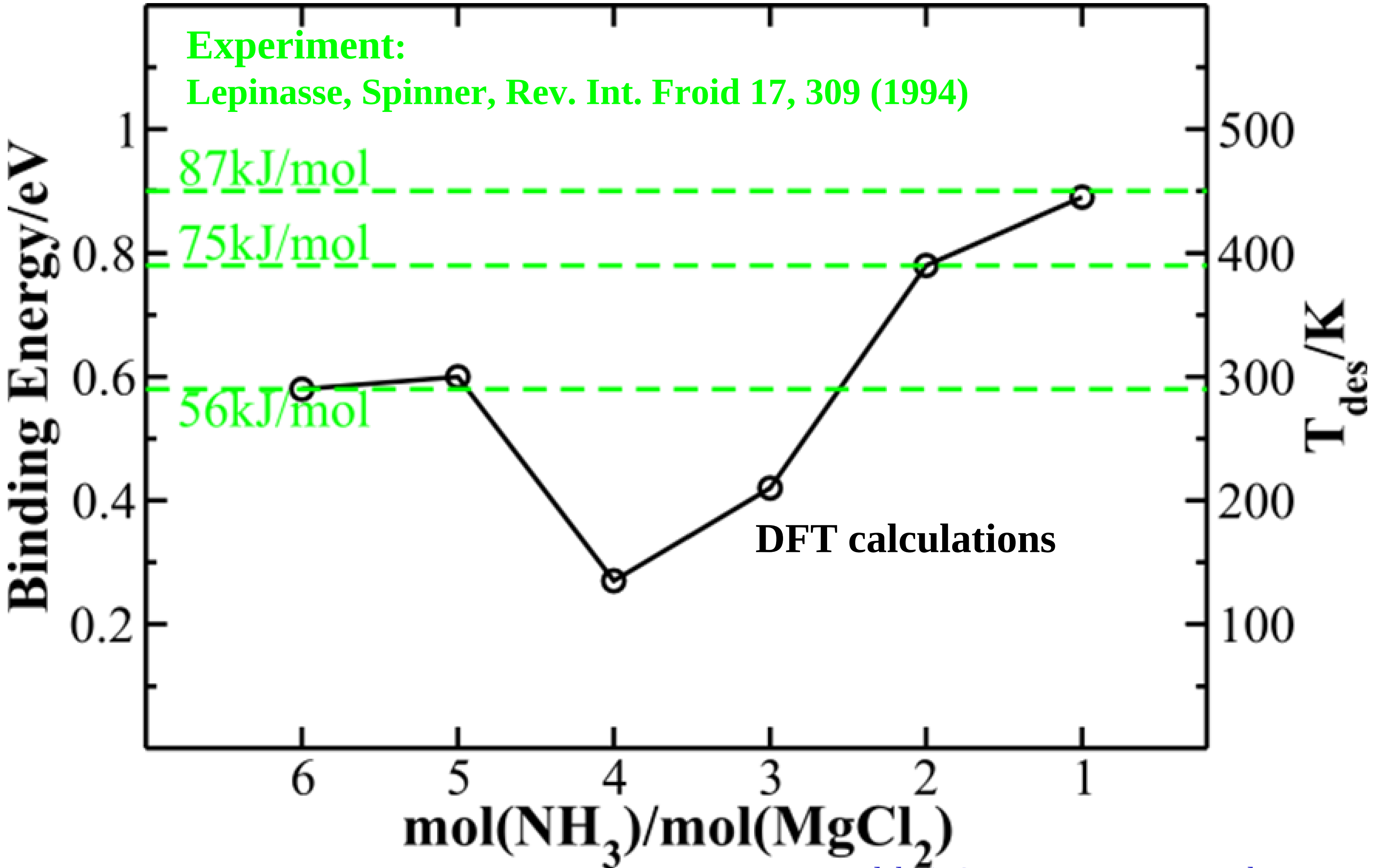
$Mg(NH_3)_6Cl_2$:	38.1 kmol NH_3/m^3
Liquid ammonia:	40.1 kmol NH_3/m^3

Thermal decomposition



Christensen. Sørensen, Johannessen, Quaade, Honkala, Elmøe, Køhler, Nørskov, J. Mater. Chem **15**, 1406 (2005)

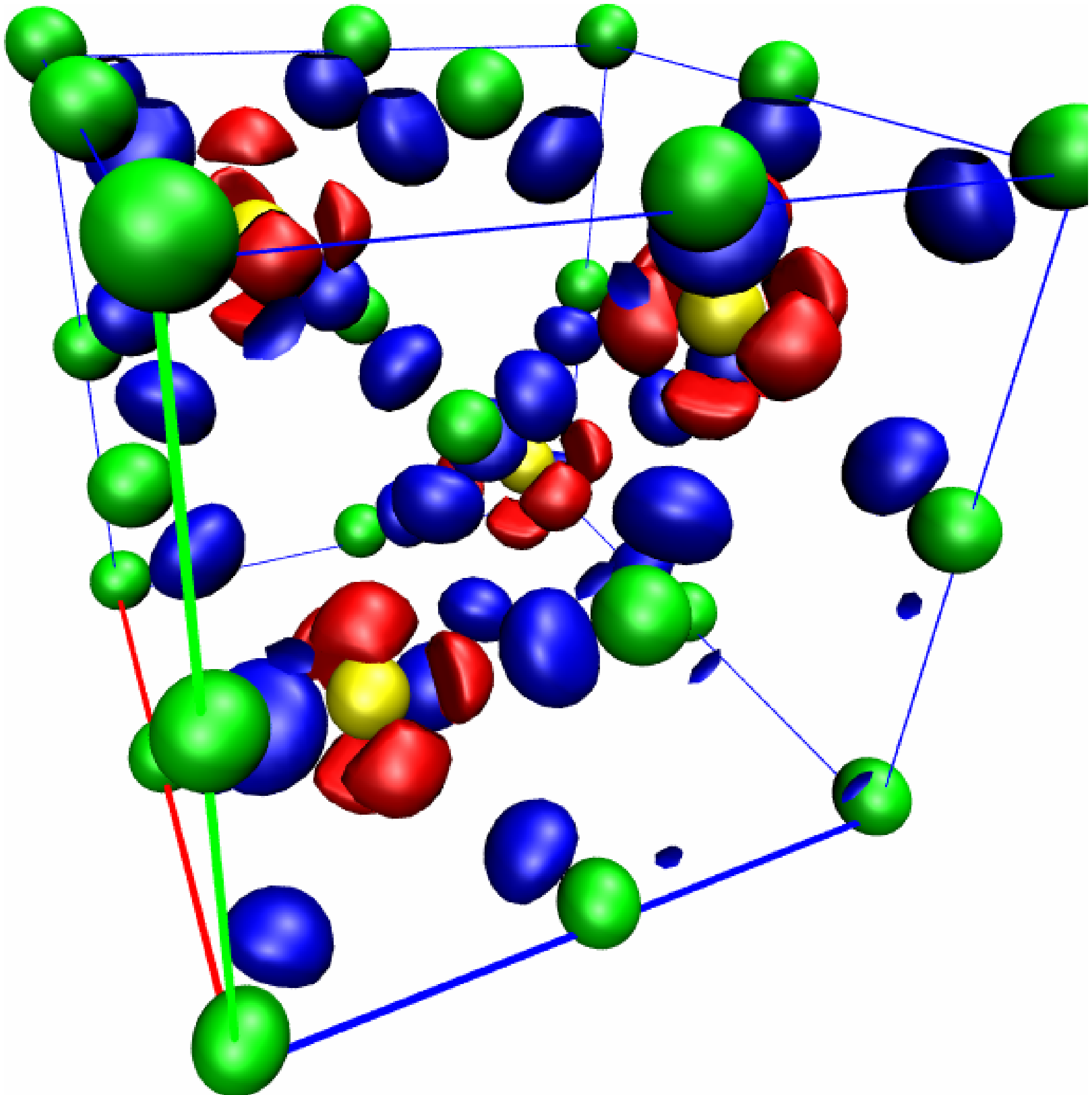
Decomposition of $Mg(NH_3)_6Cl_2$



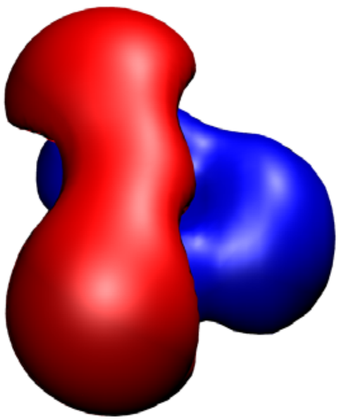
Hummelshøj, Sørensen, Kustova, Johannessen, Nørskov, Christensen, JACS **16**, 66 (2006)

Bonding in metal ammines

$MgCl_2$ in $Mg(NH_3)_6Cl_2$ structure

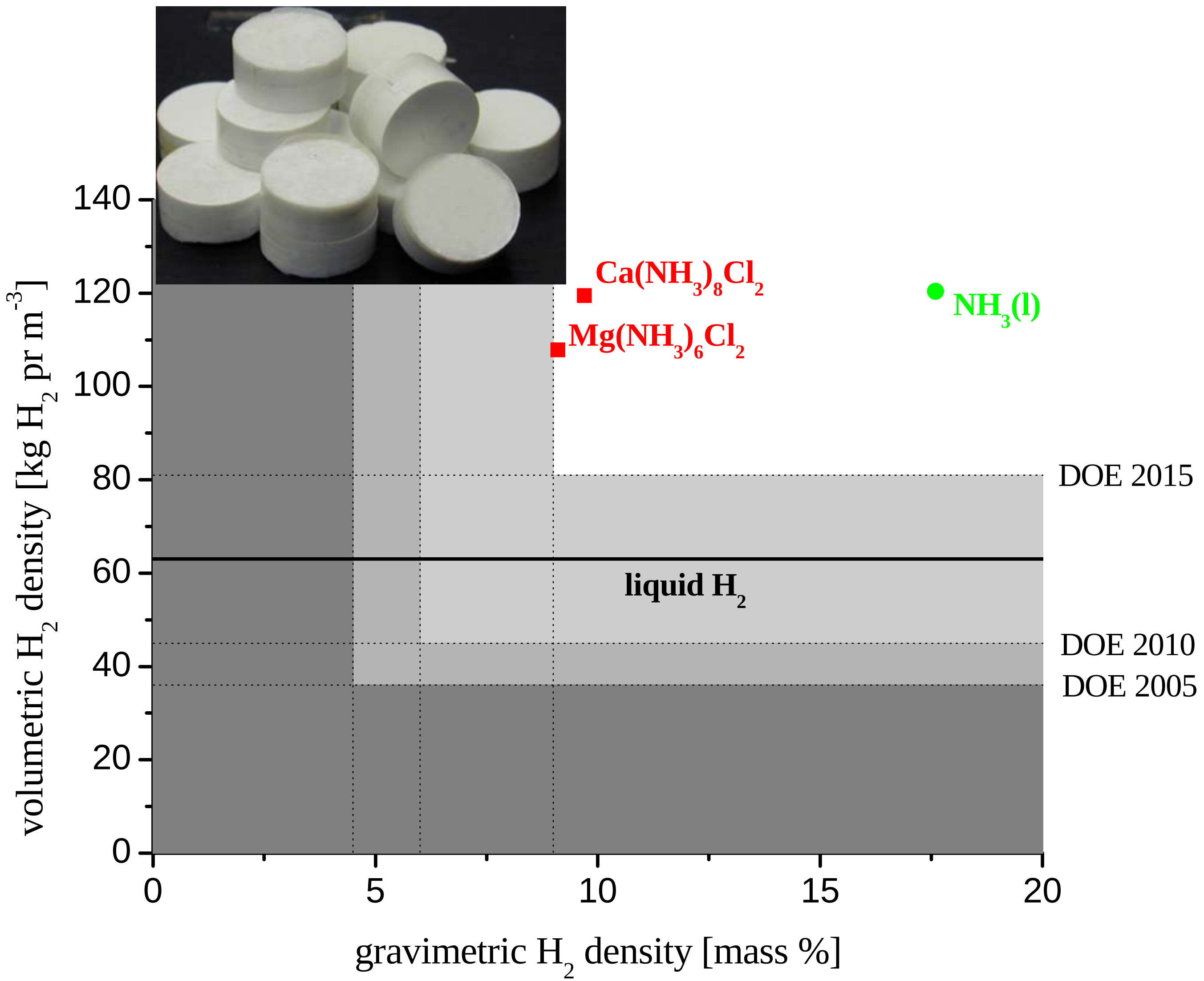


H_3-N

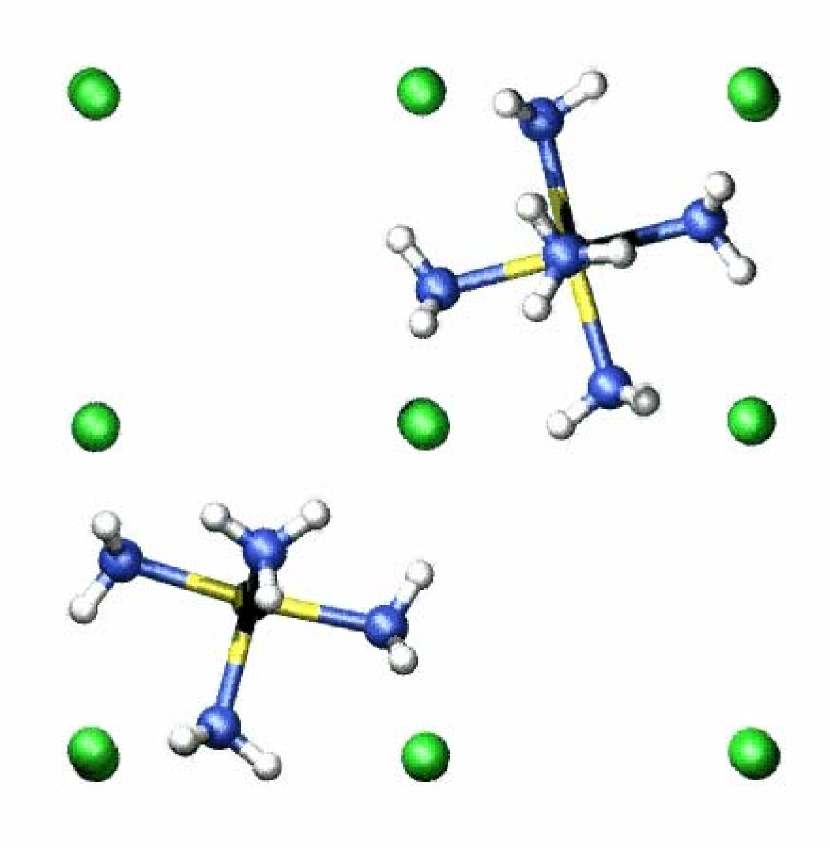


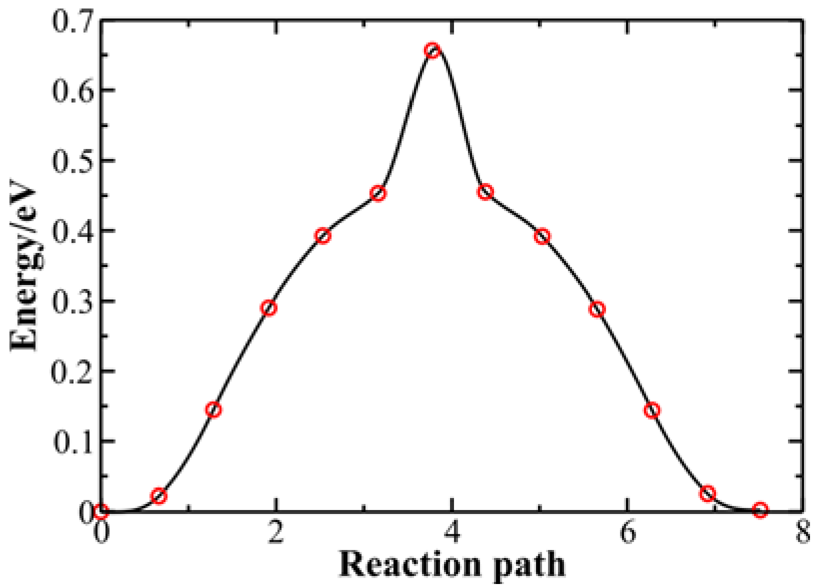
Hummelshøj, Vegge, Nørskov (2006)

Compacting into a solid



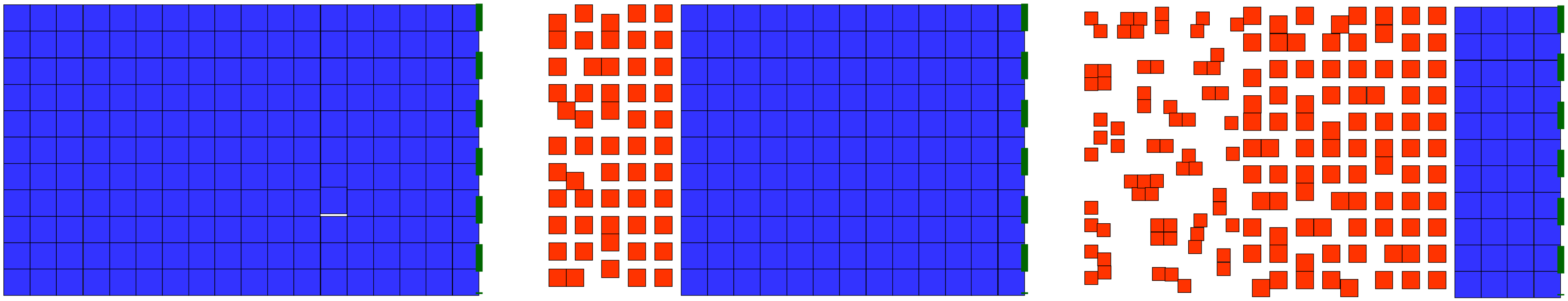
Diffusion in metal ammines

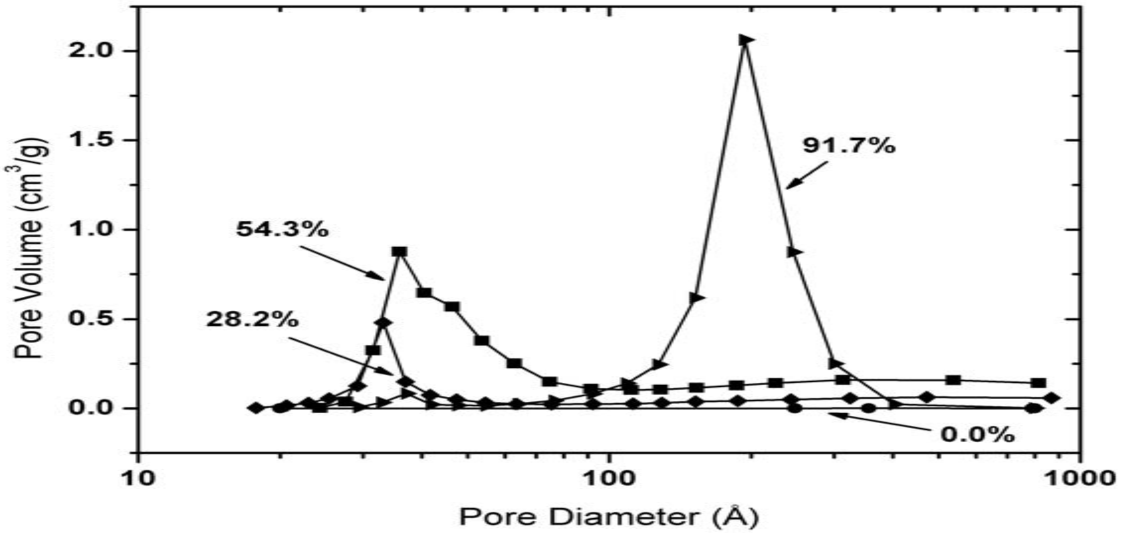




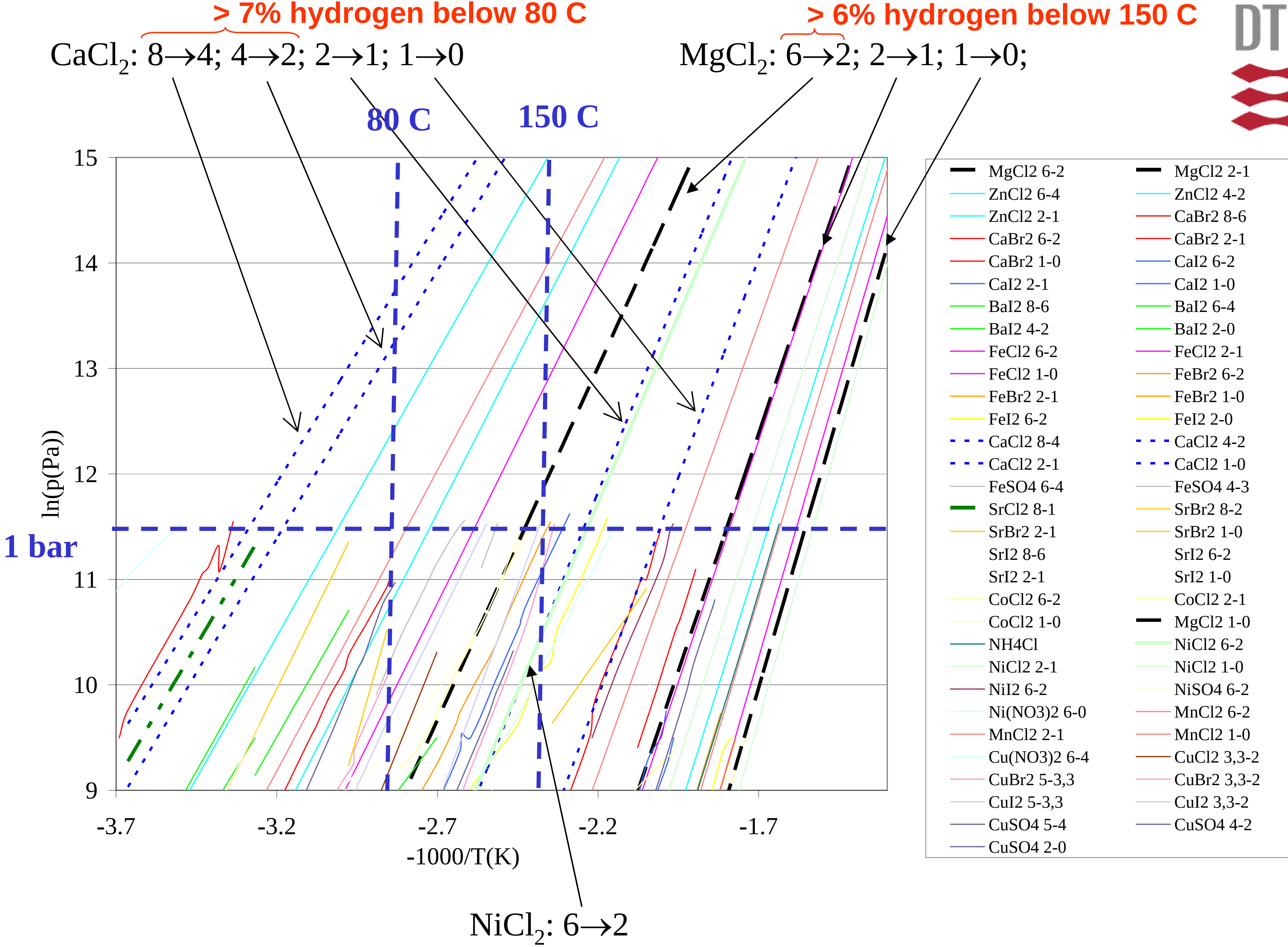
Hummelshøj, Vegge, Nørskov (2006)

Pore development in dense ammine units



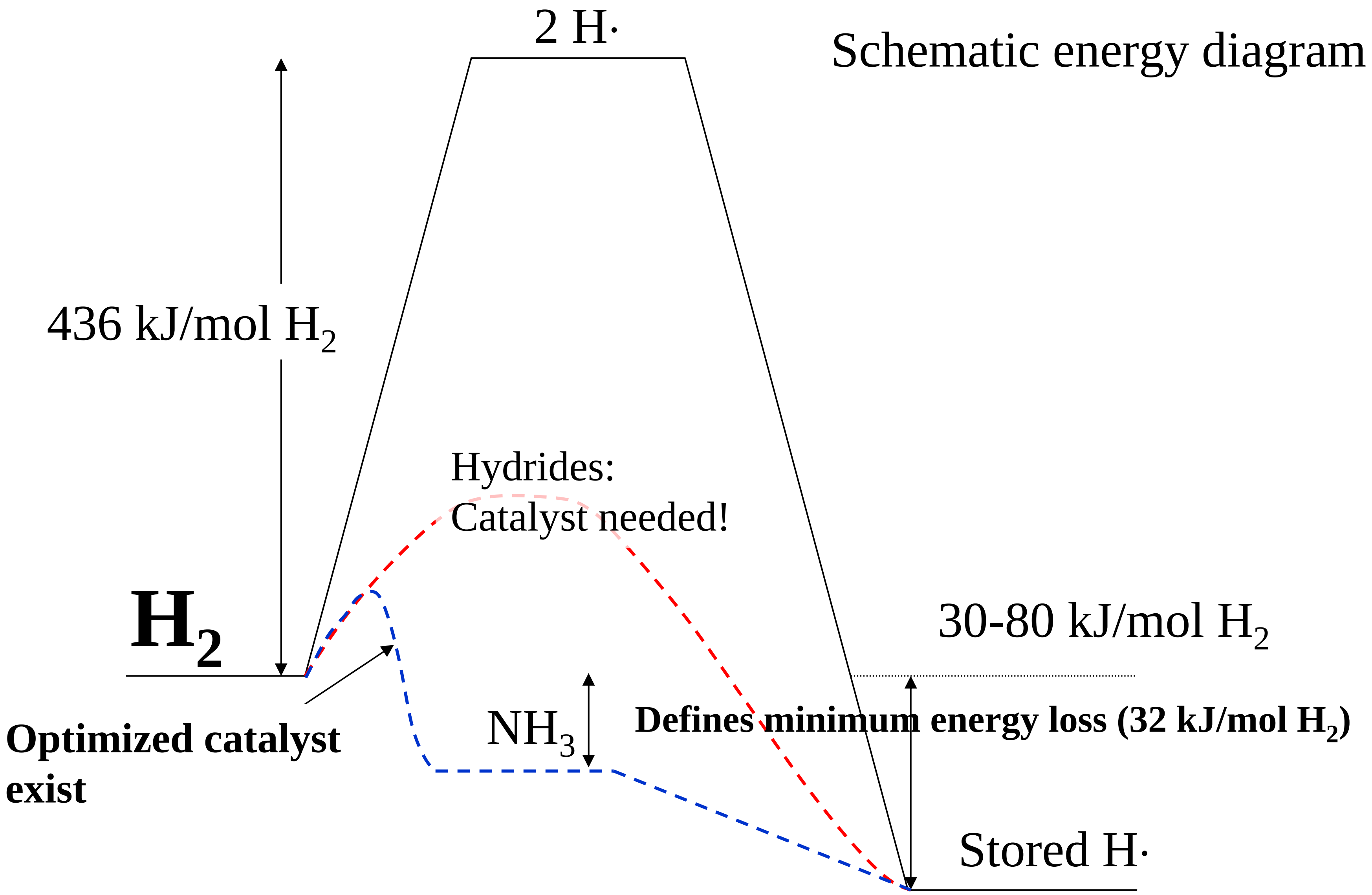


Hummelshøj, Sørensen, Kustova, Johannessen, Nørskov, Christensen, JACS **16**, 66 (2006)



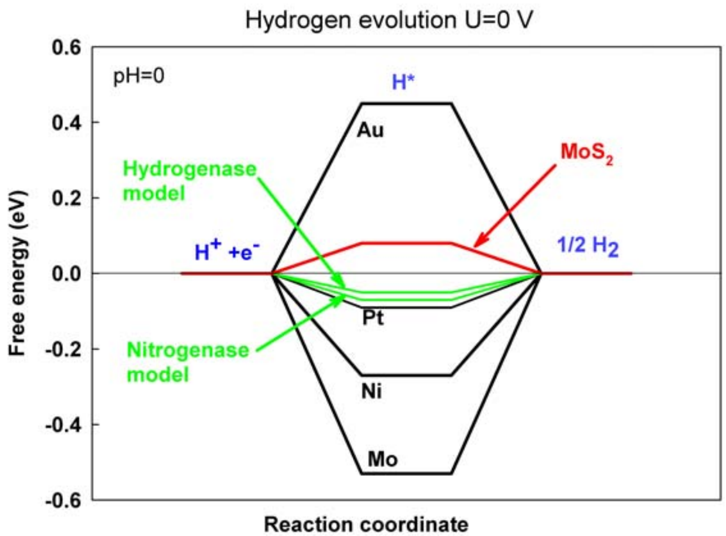
Data from: Lepinasse, Spinner, Rev. Int. Froid **17**, 309 (1994)

Activating H_2



Catalysis in hydrogen production and storage

- Catalysis in hydrogen production
  - Understanding of trends in hydrogen and oxygen evolution
  - Towards computational design
  - Inspiration from nature



- Catalysis in hydrogen storage
  - H_2 activation important
  - Alternative combinations of storage medium and catalyst