"Ammonia synthesis: A Bio-inspired dream or reality?"

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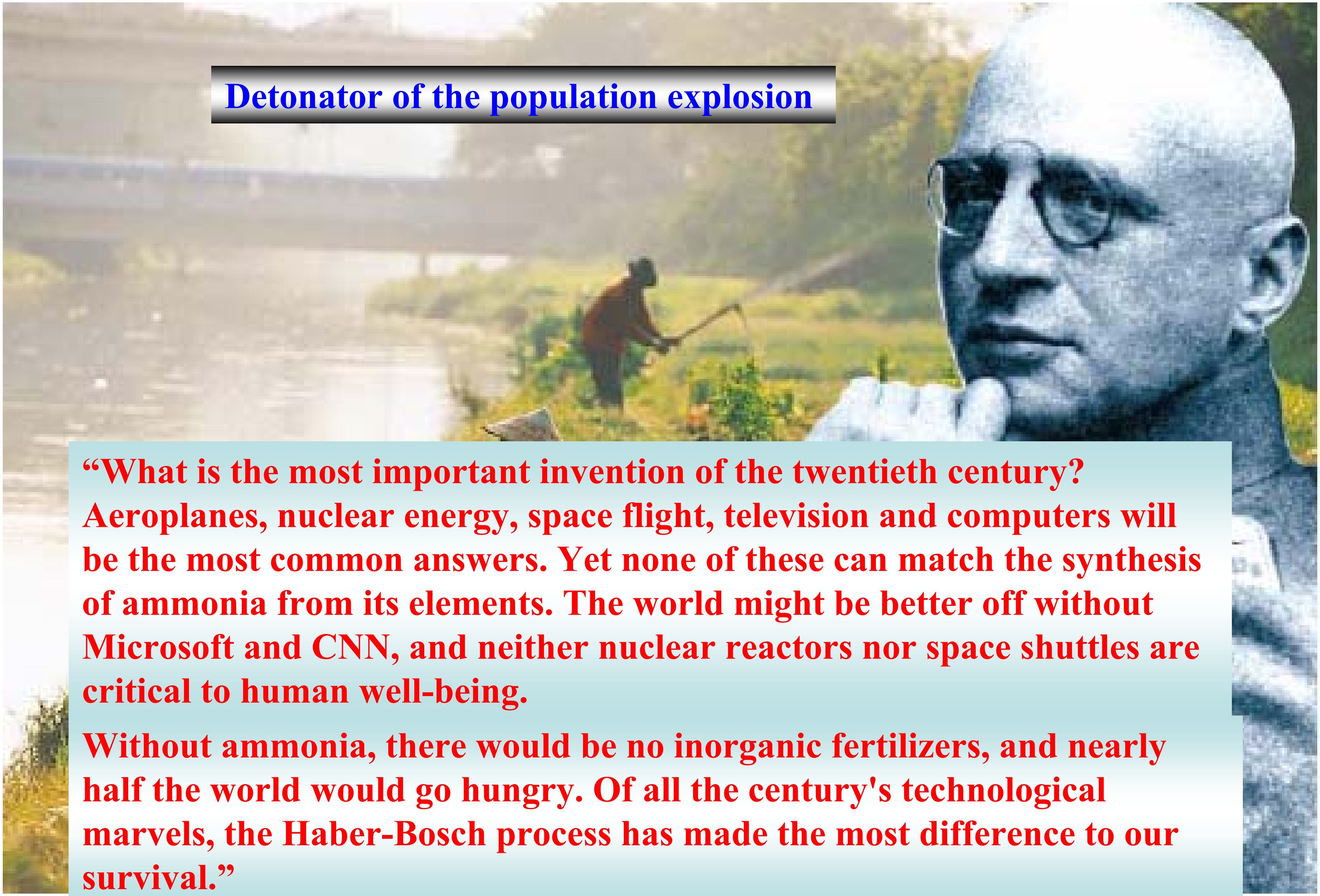


Detonator of the population explosion

"What is the most important invention of the twentieth century? Aeroplanes, nuclear energy, space flight, television and computers will be the most common answers. Yet none of these can match the synthesis of ammonia from its elements. The world might be better off without Microsoft and CNN, and neither nuclear reactors nor space shuttles are critical to human well-being.

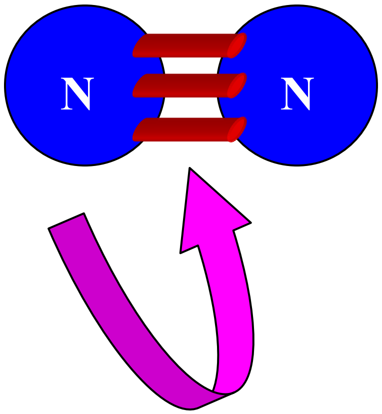
Without ammonia, there would be no inorganic fertilizers, and nearly half the world would go hungry. Of all the century's technological marvels, the Haber-Bosch process has made the most difference to our survival."

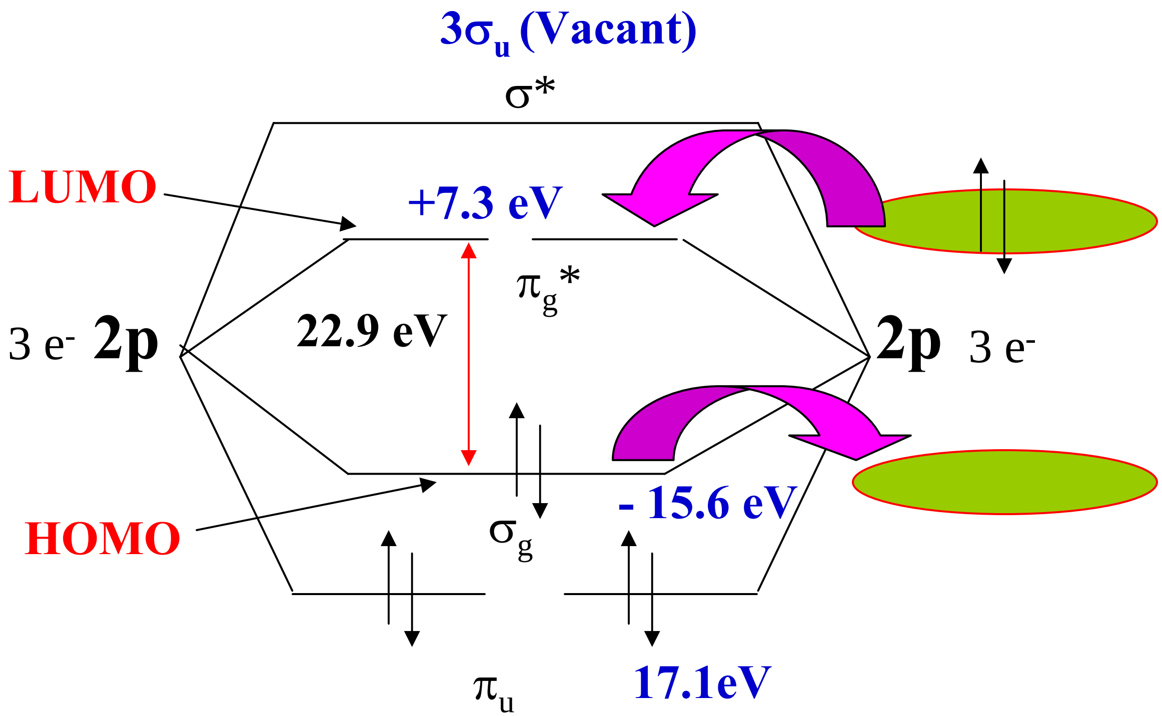
Vaclav Smil, *Nature* 400, 415 (29 July 1999)

Contents

- Why ammonia synthesis is so important?
- Why it is very difficult?
- What are the stumbling blocks?
- Present crisis?
- How and what should be tried?
- What is the role of nature?
- Relevance of cluster systems?
- “S” is it beyond a poison?
- Eco-friendly methodologies

Chemistry of N_2 fixation





First e- reduction is -3 V

Classification of the metals and semi-metals according to the chemical reactivity of their surfaces

Li	Be											B	C
Na	Mg							D				Al	Si
K	Ca	(Sc)	Ti	(V)	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
Rb	Sr	Y	Zr	Nb	Mo	(Tc)	(Ru)	Rh	Pd	Ag	Cd	In	Sn
Cs	Ba	La	(Hf)	Ta	W	Re	(Os)	Ir	Pt	Au	Hg	Tl	Pb
	C		A			B		E					

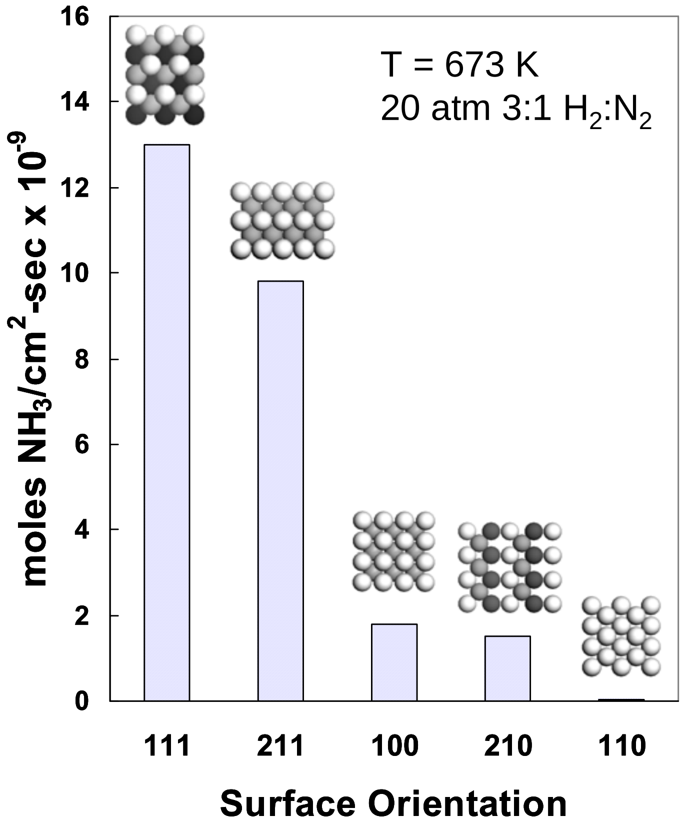
J.Chatt, General L.M. da Camara Pina and R.L.Richards, New trends in the chemistry of Nitrogen fixation (Academic press) London, (1980) Chapter 1.

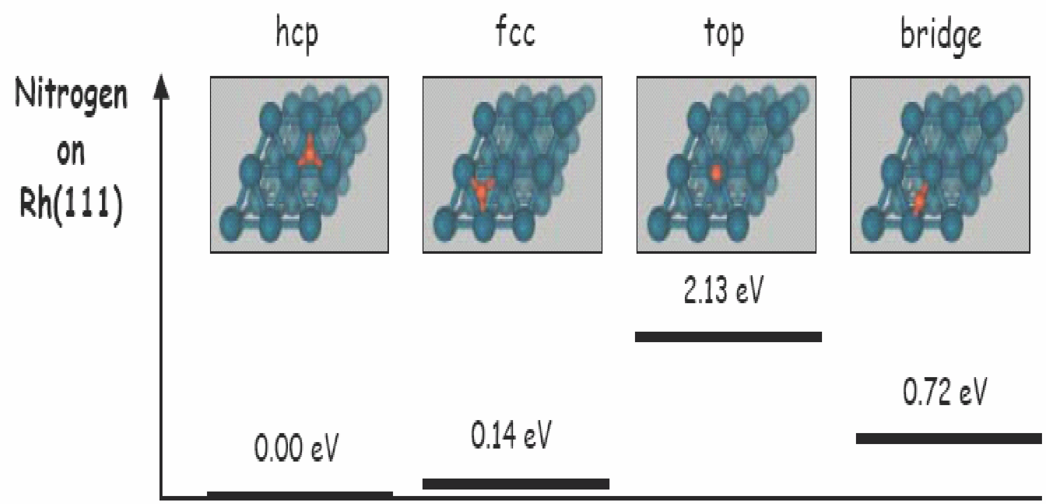
Chemisorption of gases by metals

Metals	Reacting gases				
	O_2	CO	H_2	CO_2	N_2
Group A	3	3	3	3	3
Group B	3	3	3	3	2
Group C	3	3	2 or 3	3	2
Group D	3	3	3	3	1
Group E	3	3	3	1 or 0	1 or 0
Cu	3	1	0	?	0
Ag	2 or 3	0	0	?	0
Au	0	1	0	?	0
B	3 or 2	3 or 2	3 or 2	?	3 or 2
Al	3	3	0	?	0
Si,Ge	3	0	2	2 or 3	0
K	3	0	0	?	0
Other metals	3	0	0	?	0

3: Unactivated adsorption, 2 : activated adsorption, 1: activated adsorption at lower temp., 0: No adsorption ? unknown

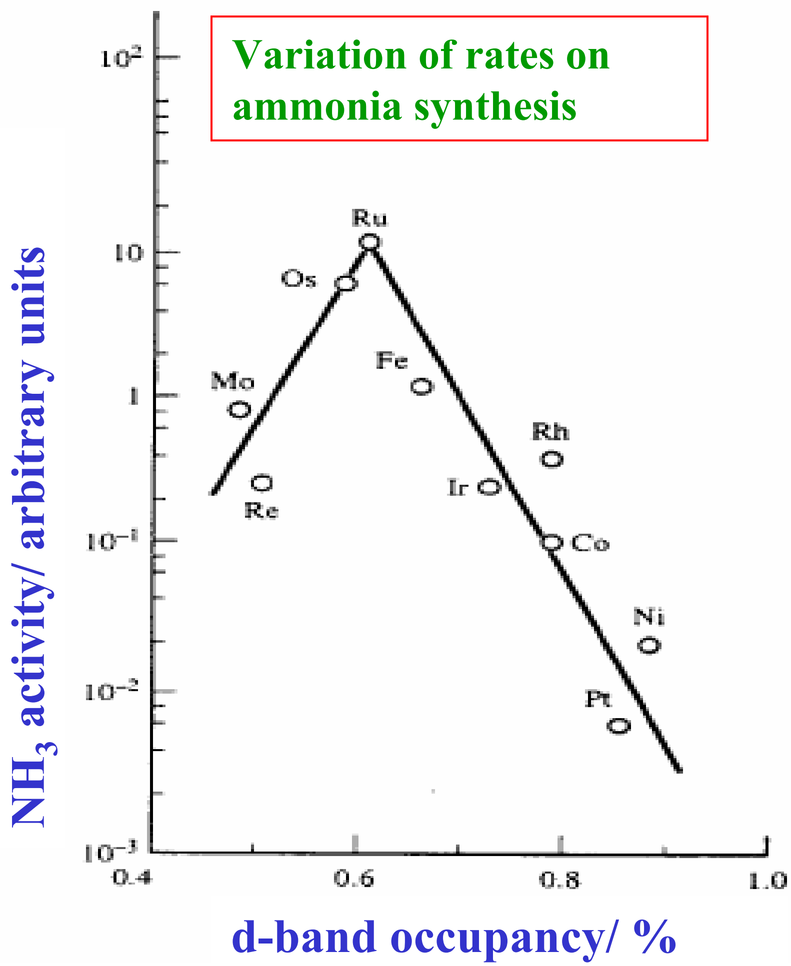
The rate is dependent on surface structure



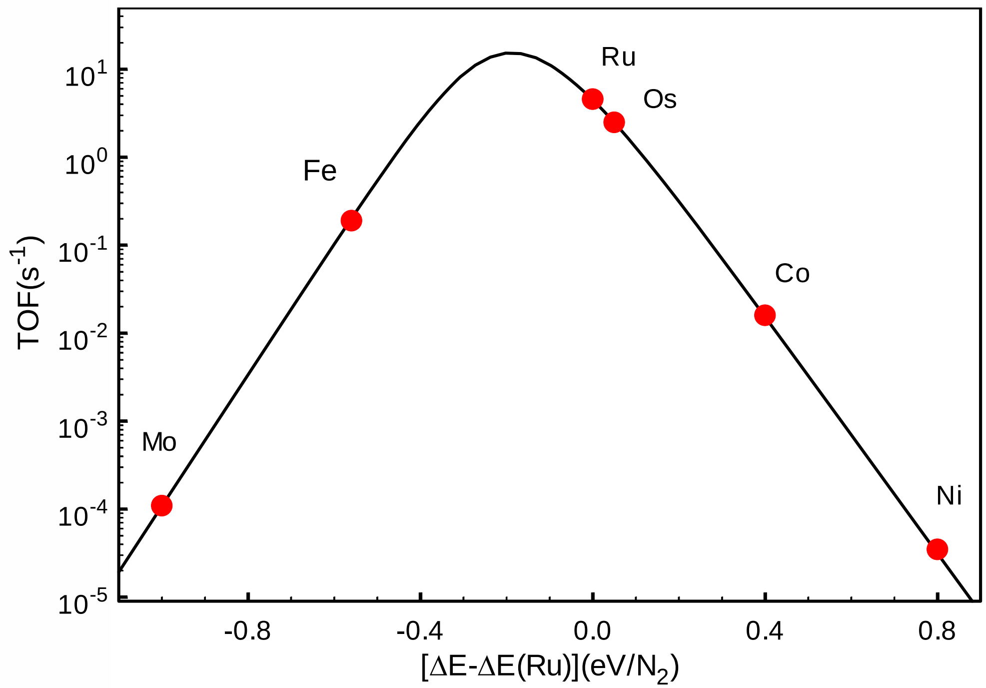


Atoms prefer high coordination

Strongin D.R., J. Carrazza, S.R Bare and G.A. Somorjai, *J. Catal.* 103 (1987) 213



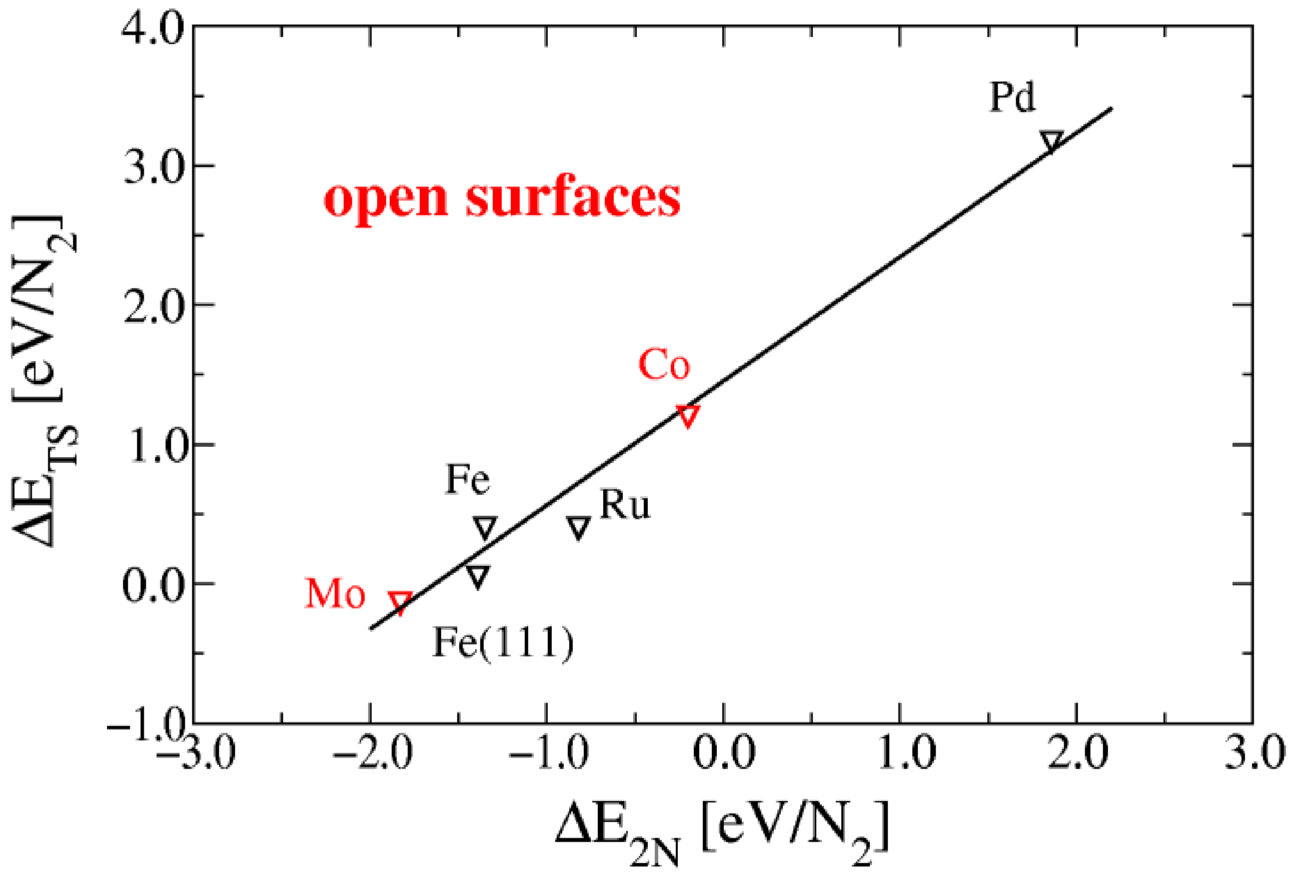
Calculated ammonia synthesis rates
400 °C, 50 bar, H_2:N_2=3:1, 5% NH_3



Jacobsen etal., *J. Catal*. 205, (2002) 382-387

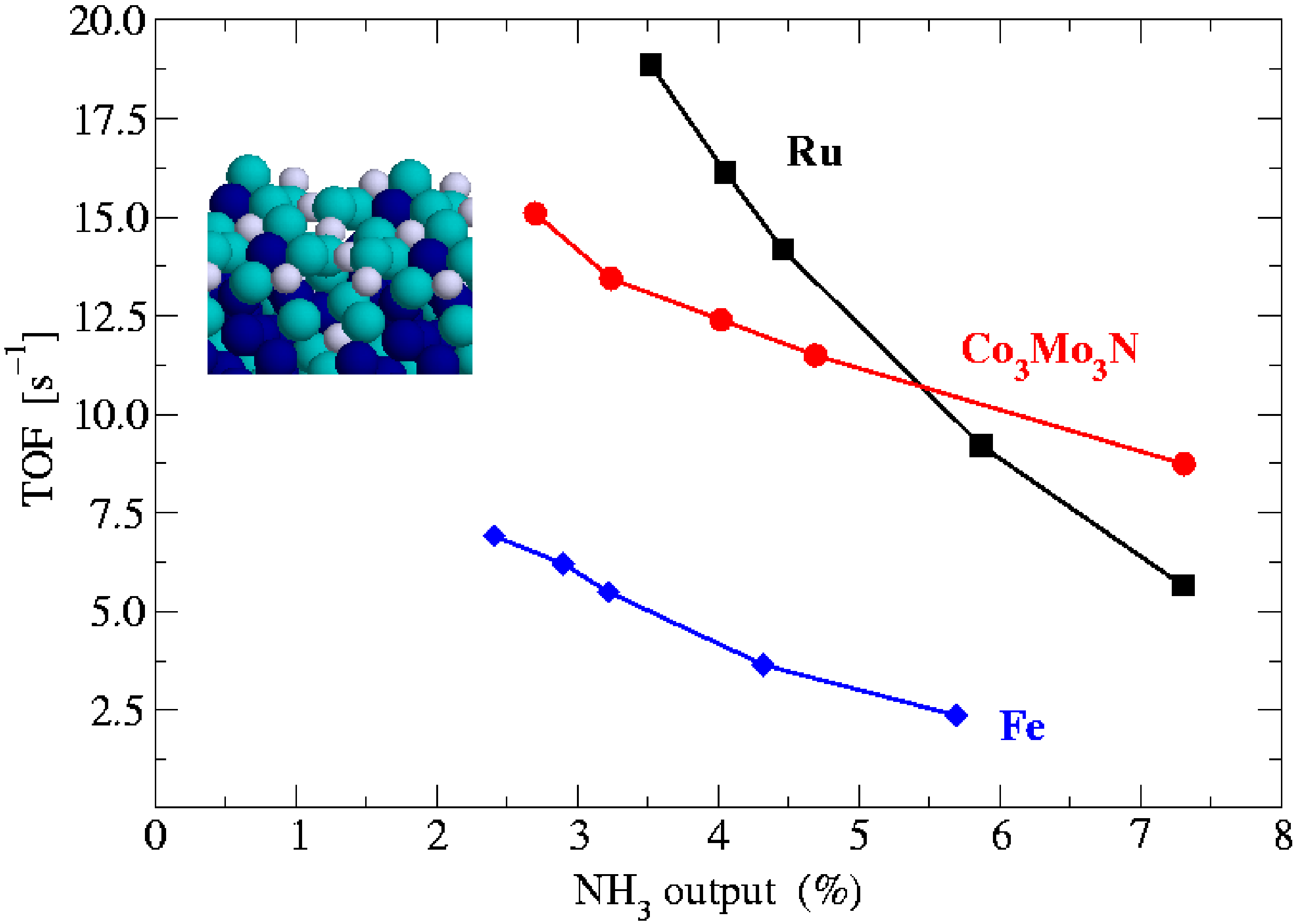
Ozaki, A. and K. Aika, *Catalytic Activation of Dinitrogen*, in *Catalysis: Science and Technology*, J.R. Anderson and M. Boudart, Editors. 1981, Springer Verlag: New York. p. 87-158.

Interpolation in the periodic table



Jacobsen, Dahl, Clausen, Bahn, Logadottir, Nørskov, *J.Am.Chem.Soc.* 123 (2001) 8404.

Measured ammonia synthesis rates
400 °C, 50 bar, H_2:N_2=3:1

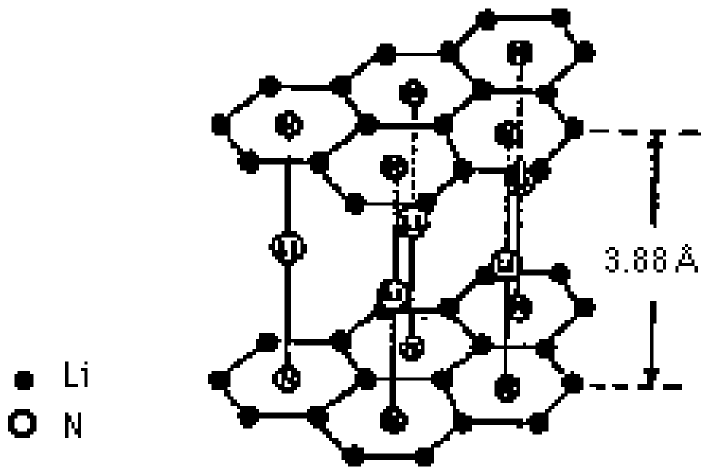


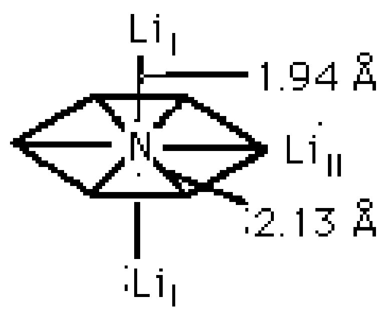
Jacobsen, Dahl, Clausen, Bahn, Logadottir, Nørskov, *J.Am.Chem.Soc.* 123 (2001) 8404.

The oxidation state of N_2 in its compounds vary from +5 to -3.

$N \longrightarrow N^{3-}$

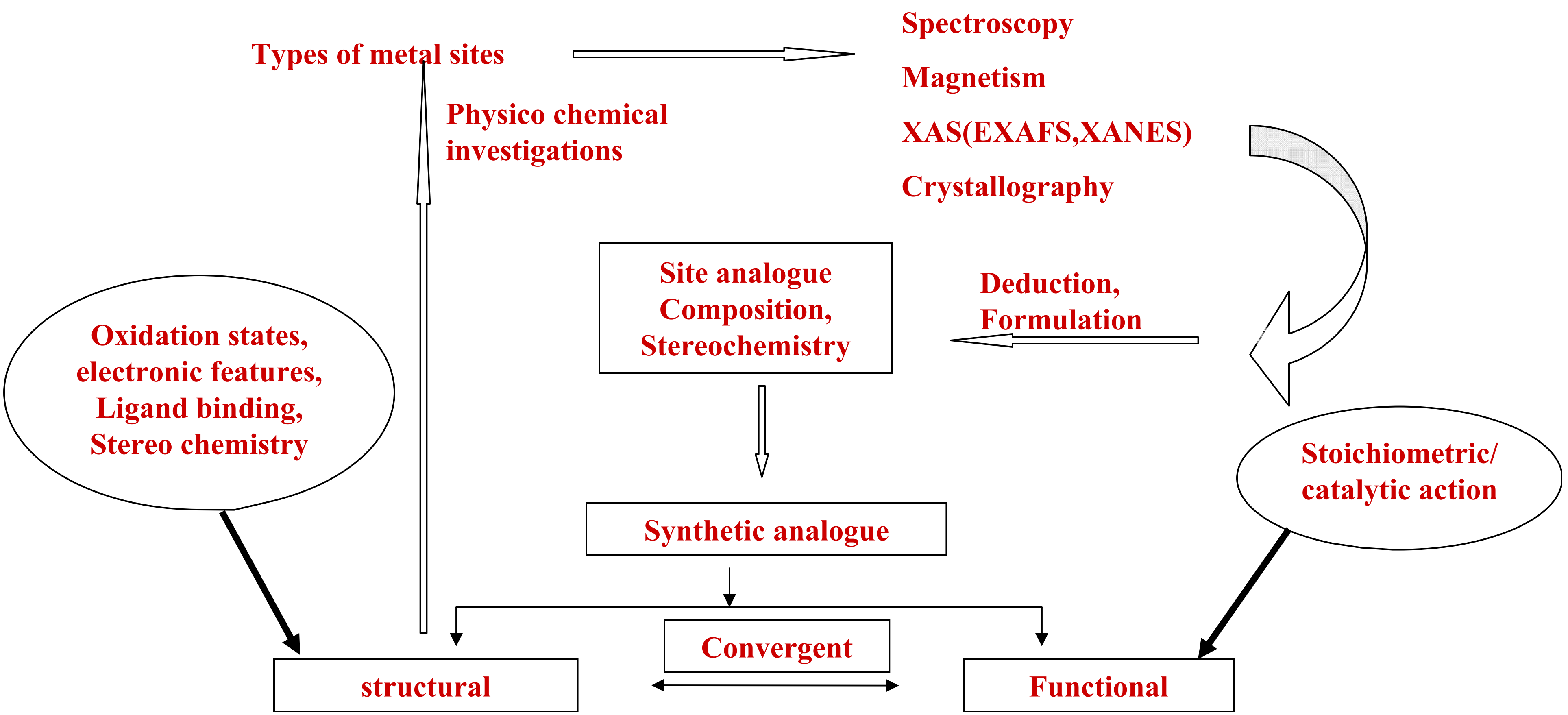
Requires lots of energy => need small cation to stablise structure.
Hence, the only Group 1 or 2 nitrides are Li_3N, and Mg_3N_2





The layer structure of Li_3N, more correctly formulated as Li[Li2N], has hexagonal Li6 nets. The nitrogen has hexagonal bipyramidal coordination, Li3N has high electrical conductivity.

Synthetic analogue approach to Metallobiomolecule active sites



Biological N_2 fixation Vs Haber process

$$N_2 + 8\,H^+ + 8\,e^- + 16\,MgATP \longrightarrow 2NH_3 + H_2 + 16MgADP + 16P_i$$

$$N_{2(g)} + 3H_{2(g)} \xrightarrow[\text{100-300atm, 400-500 °C}]{\text{Fe or Ru catalyst}} 2NH_3$$

$\Delta H° = -46.2 kJmol^{-1}$

$\Delta S° = -99 Jmol^{-1}/K^{-1}$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta G° = -8\ \text{kcal/mole}$$

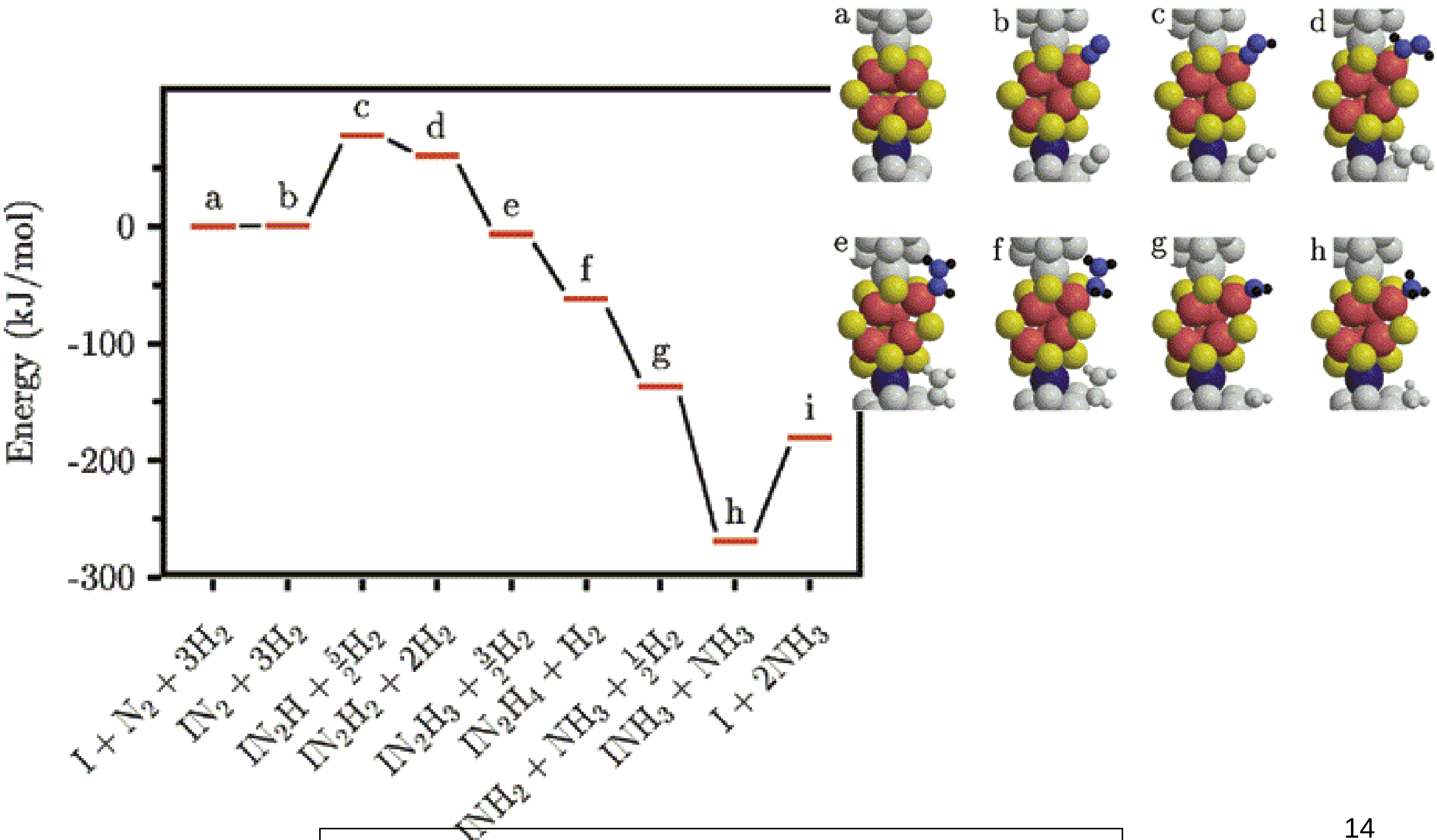
$$N_2 + H_2 \longrightarrow N_2H_2 \quad \Delta G° = +50\ \text{kcal/mole}\ (33.44\ \text{kJ/mol})$$

(approximately)

$$N_2 + 2e^- + 2H^+ \longrightarrow N_2H_2 \quad E_o = -1200\ \text{mV (approximately)}$$

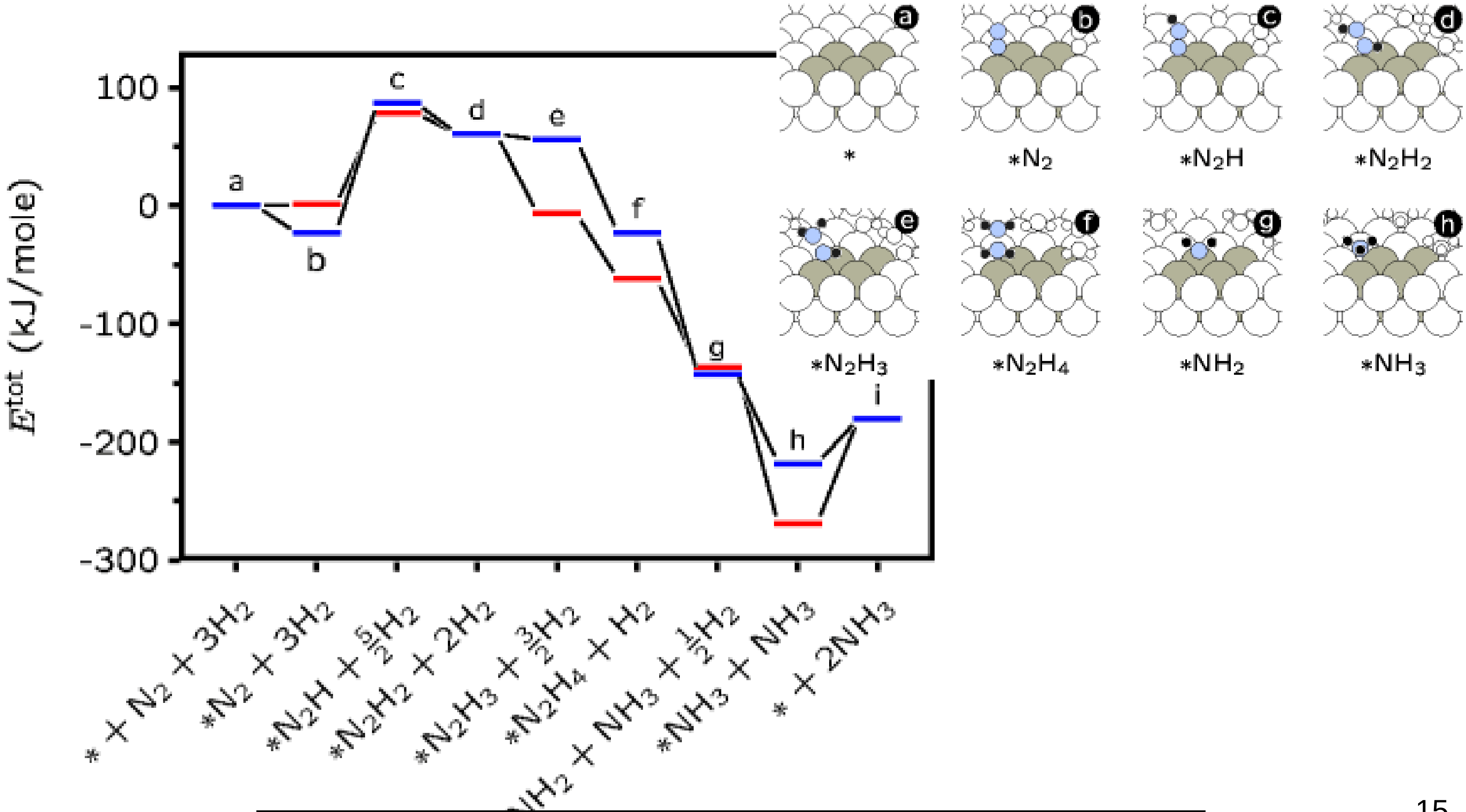
$\Delta G° = 231.6$ kJ/ mole

N_2 hydrogenation on FeMoco



Rod and Nørskov, *J.Am.Chem.Soc.*,122 (2000) 12751

Comparing the FeMoco and Ru (0001)

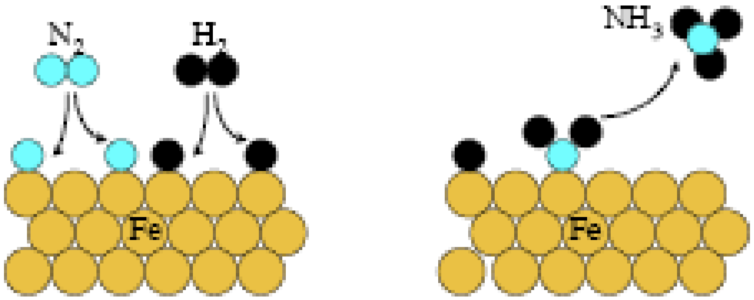


Rod, Logadottir, Nørskov, *J.Chem.Phys.*, 112 (2000) 5343

Dissociative Mechanism:

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

430 °C
150 atm.

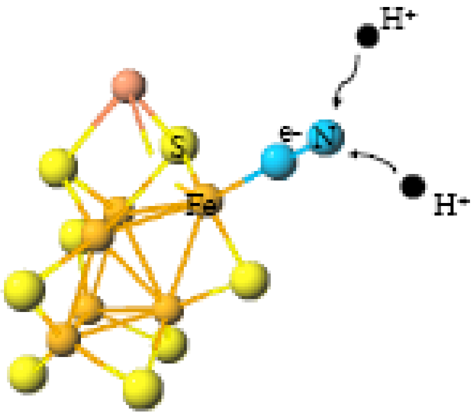


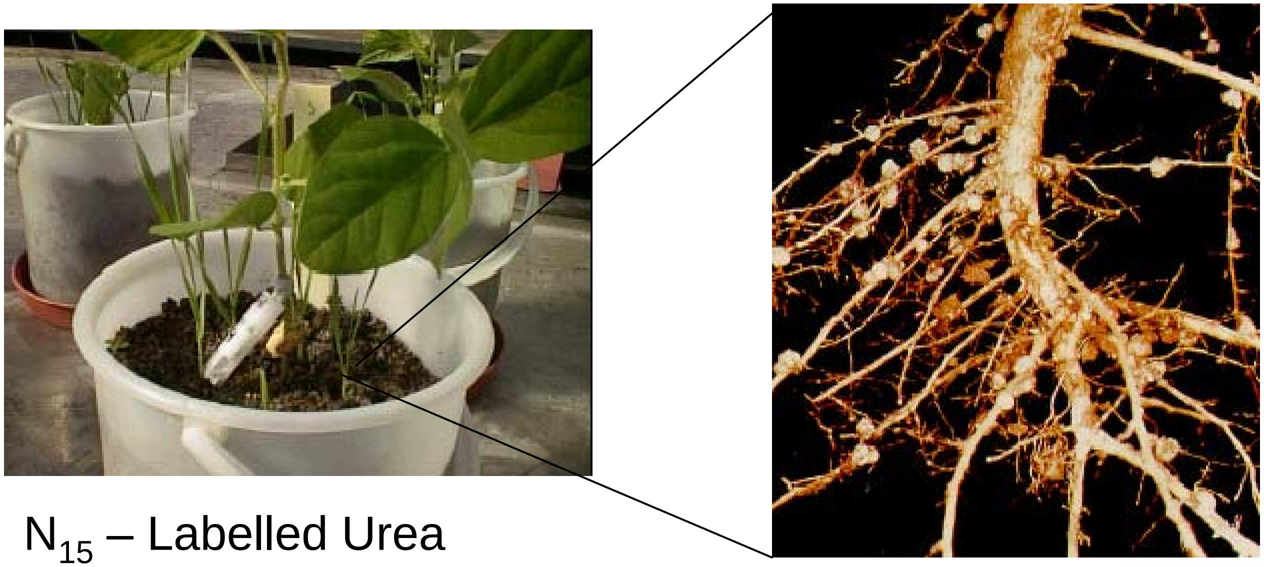
Associative Mechanism:

$$N_2 + 8H^+ + 8\ e^- \rightarrow 2NH_3 + H_2$$

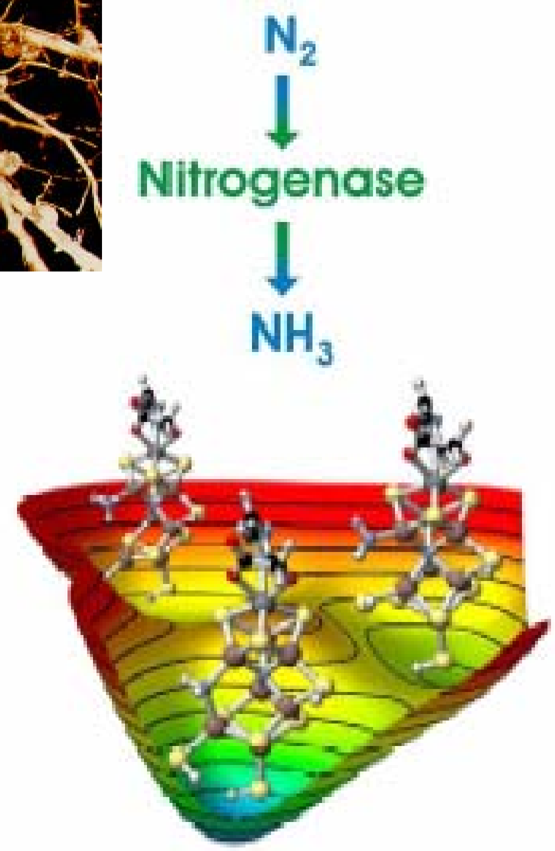
20 °C
1 atm.

16 ATP → 16 ADP
Expensive !!!





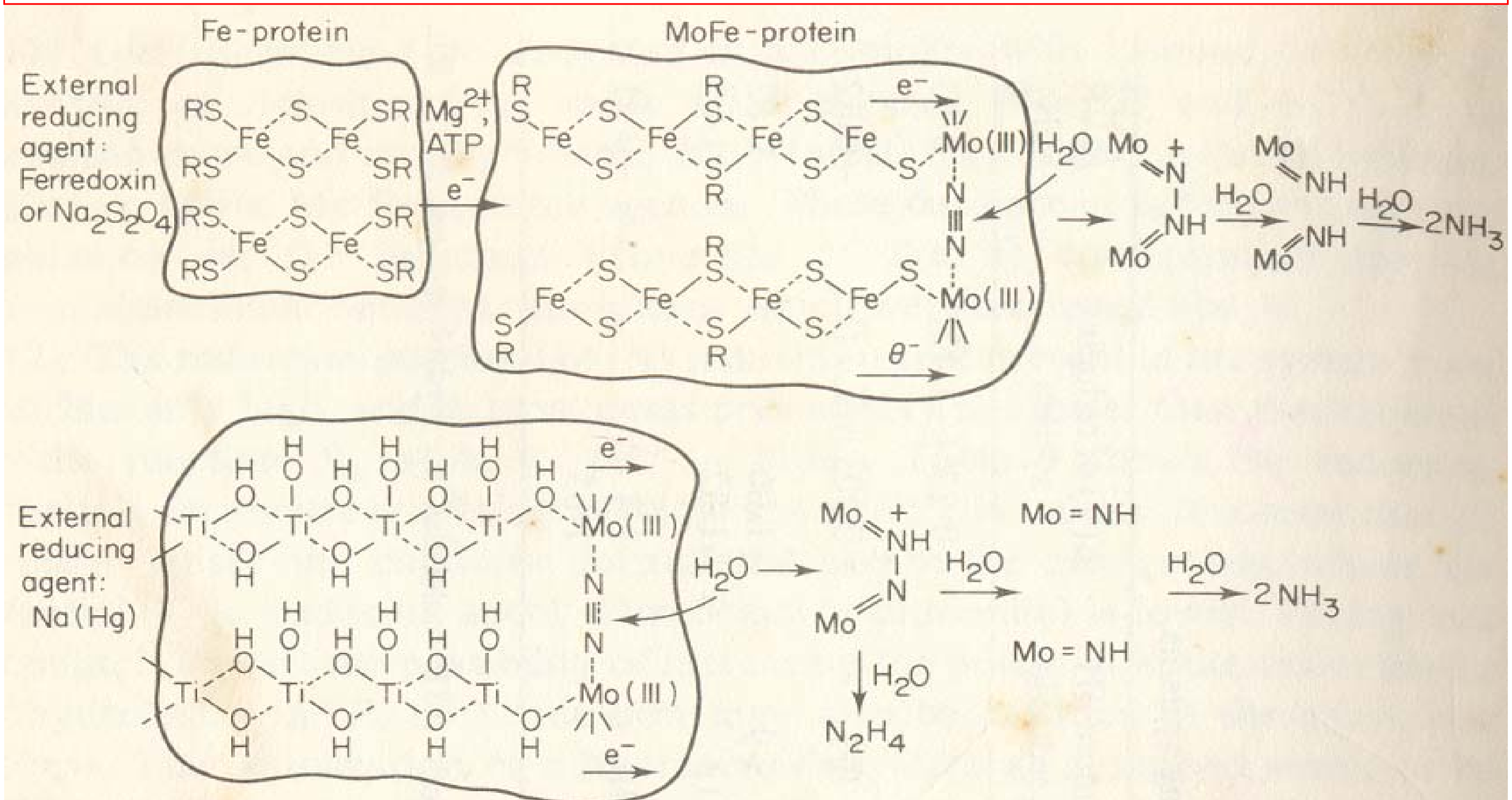
N_{15} – Labelled Urea



Nitrogenase:
Enzyme which is one of the most complex bioinorganic catalysts in nature

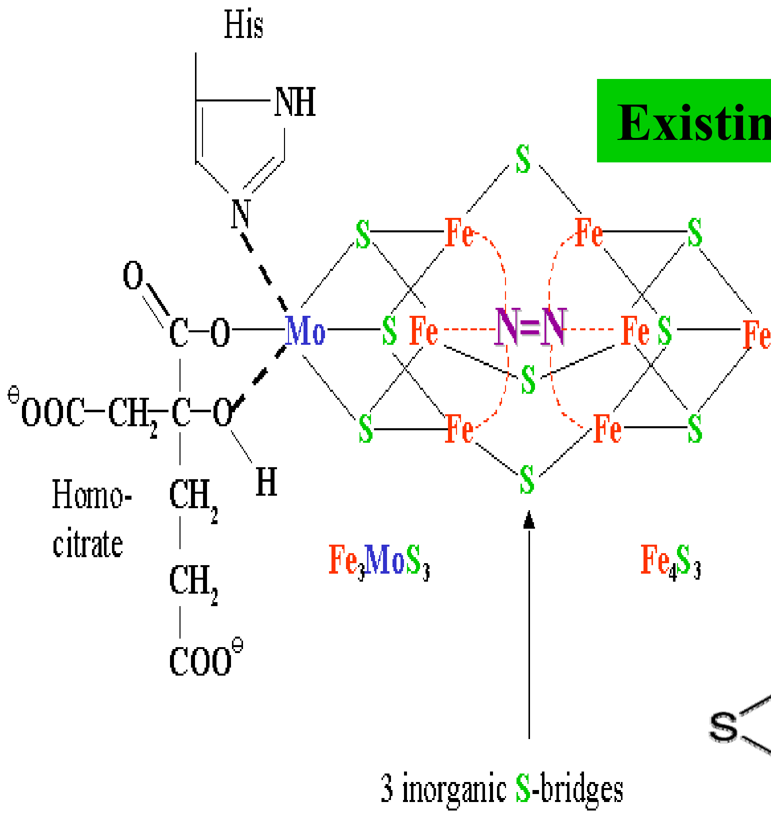
Legumes can fix more than 250 kg N/ ha^{-1}. However, the amounts of N_2 fixed can vary considerably in time and space.

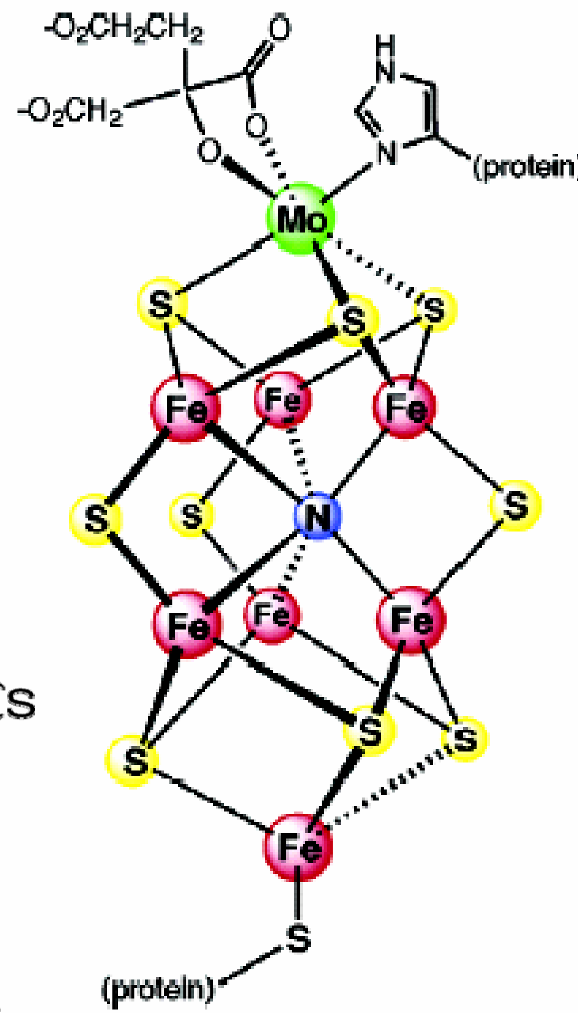
Chemical mechanism of N_2 fixation in biological and model systems

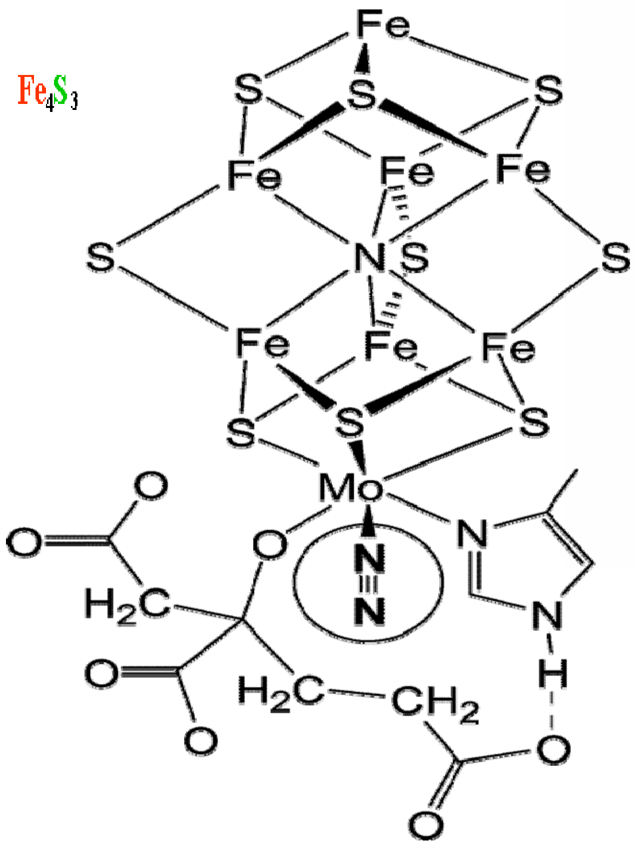


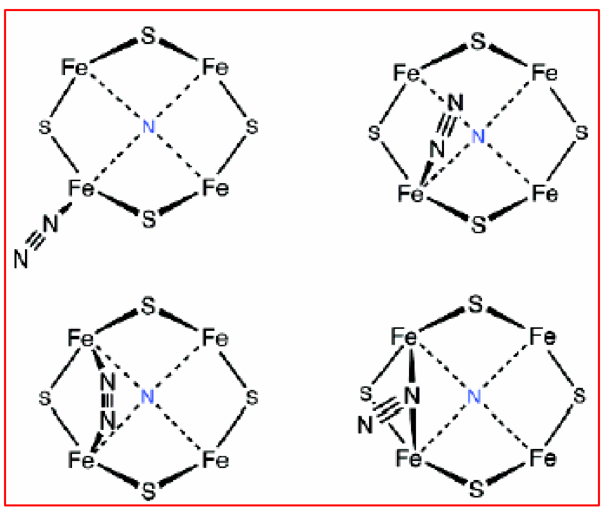
J.Chatt, General L.M. da Camara Pina and R.L.Richards, *New trends in the chemistry of Nitrogen fixation* (Academic press) London, (1980) Chapter 1.

Existing controversies

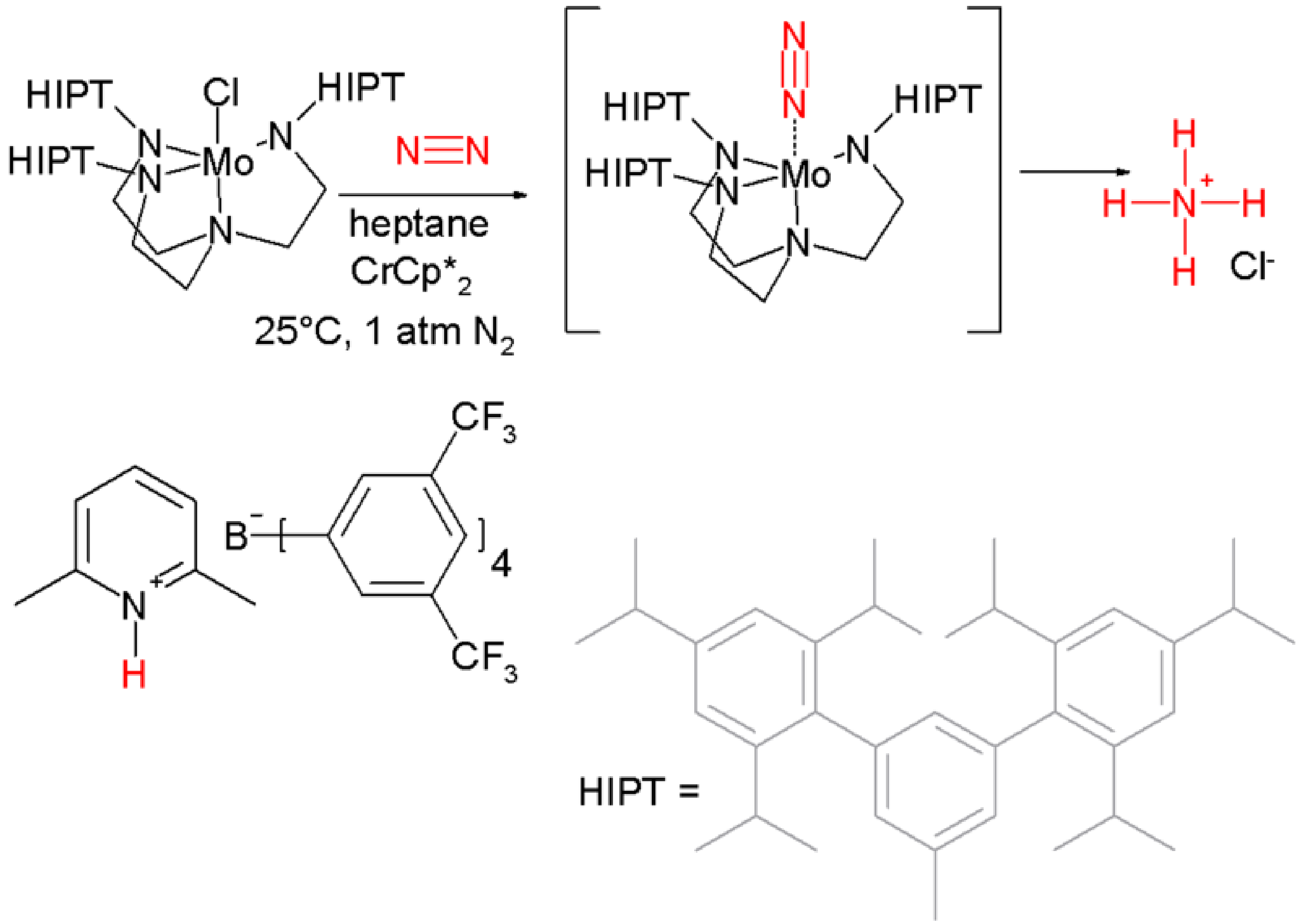








Mackay B.A. and M.D. Fryzuk, *Chem. Rev.*, 104 (2004) 385-401.



The first catalytic system converting nitrogen to ammonia at room temperature and 1 atmosphere was discovered in 2003

Unfortunately, the catalytic reduction only undergoes a few turnovers before the catalyst dies.

Characteristics of Free N_2 and some intermediates

Species	N---N distance	ν(N-N) (cm^{-1})
Free N_2	1.0975 A°	2331
Ph-N=N-Ph	1.255 A°	1442
NH_2-NH_2	1.460 A°	1111

Different intermediates expected :

Diazene : NH=NH, Hydrazene : NH_2-NH_2

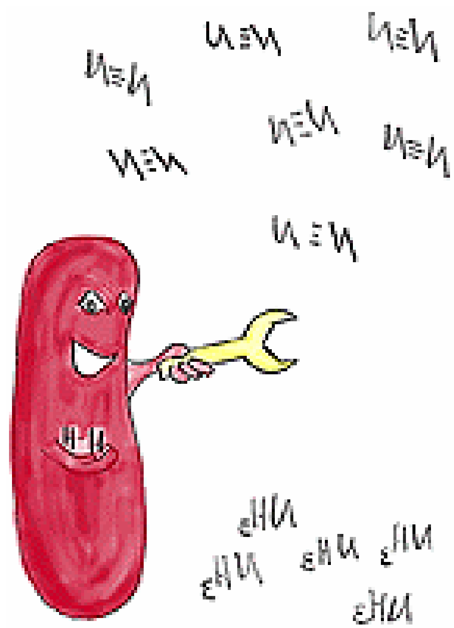
Diazenido : N_2^{-2} Hydrazido : N_2^{-4}

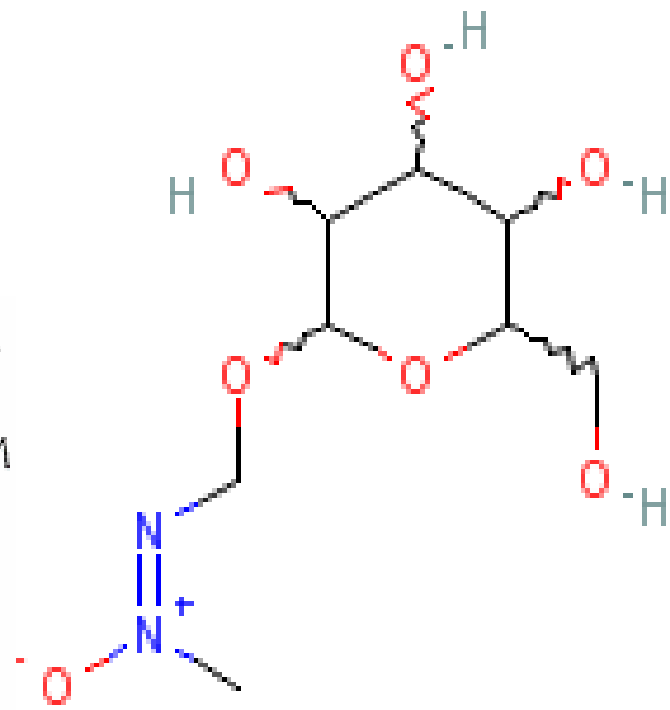
Nitrido : N^-

$1/2N_2 + 2H^+ + H_2O + e^- \longrightarrow NH_3OH^+$ E° = -1.87V

$1/2N_2 + 5/2H+ + 2e- \longrightarrow 1/2N_2H_5+$ E° = -0.23V

$1/2N_2 + 4H^+ + 3e^- \longrightarrow NH_4^+$ E° = 0.27V

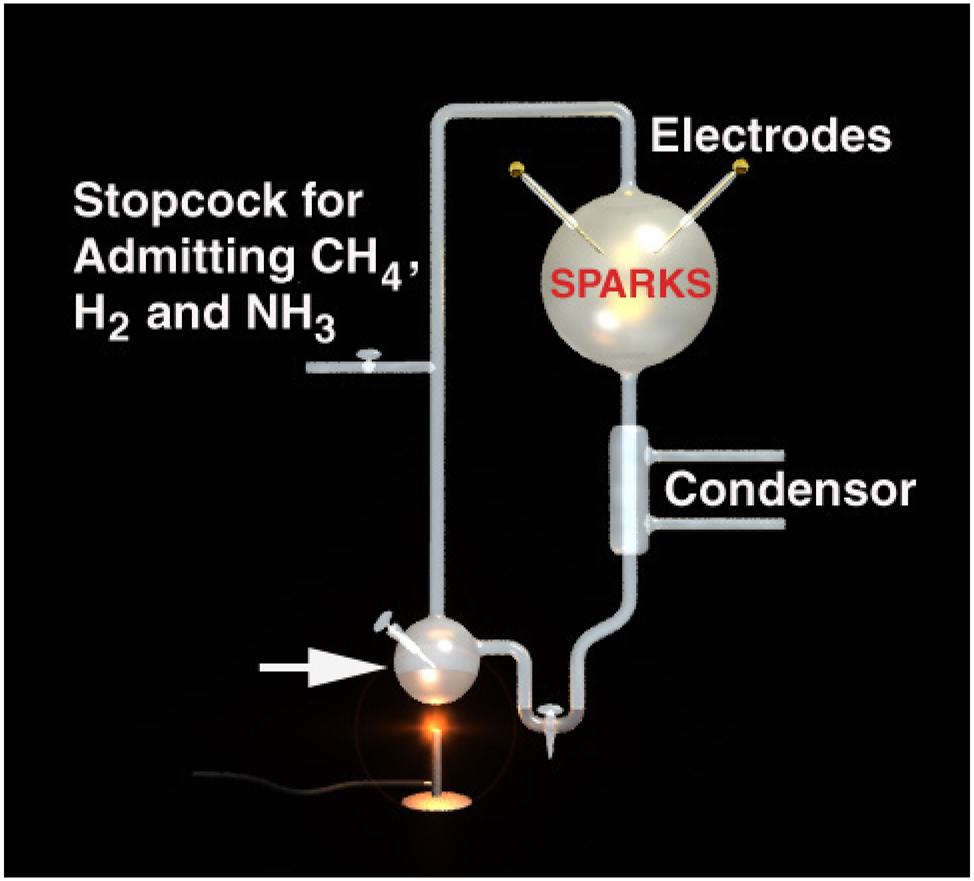


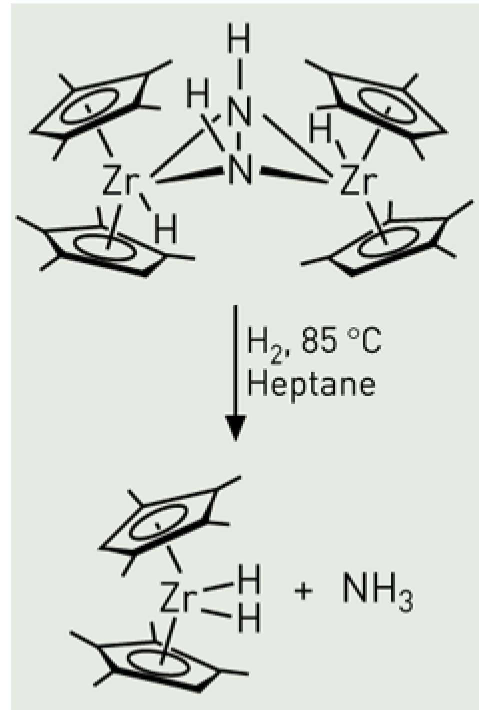


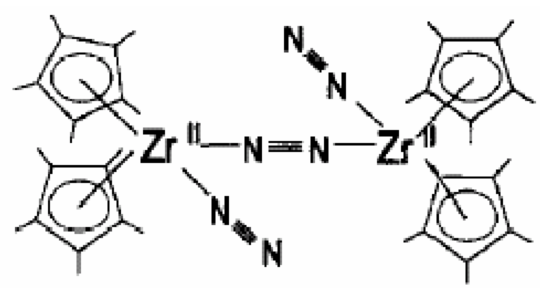
Enzyme Nitrogen fixation invitro

In porous water swollen polymer networks (Hydrogels)

Optimum oxygen pressure

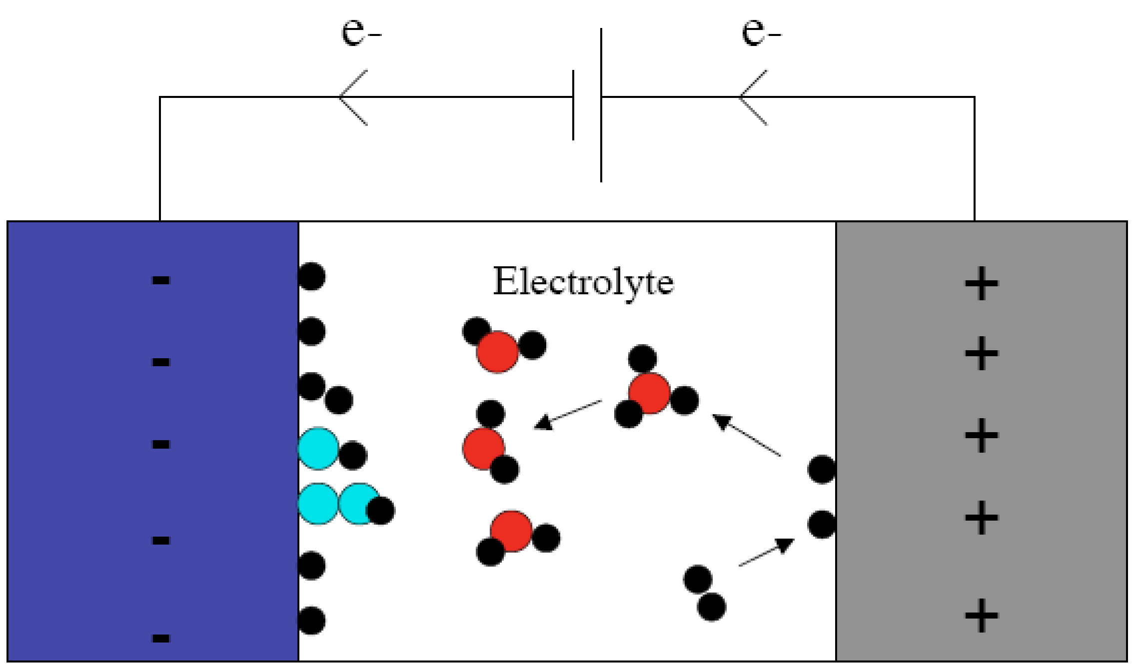






Structure of the $\{[\pi\text{-}C_5(CH_3)_5]_2Zr(N_2)\}_2N_2$ complex.

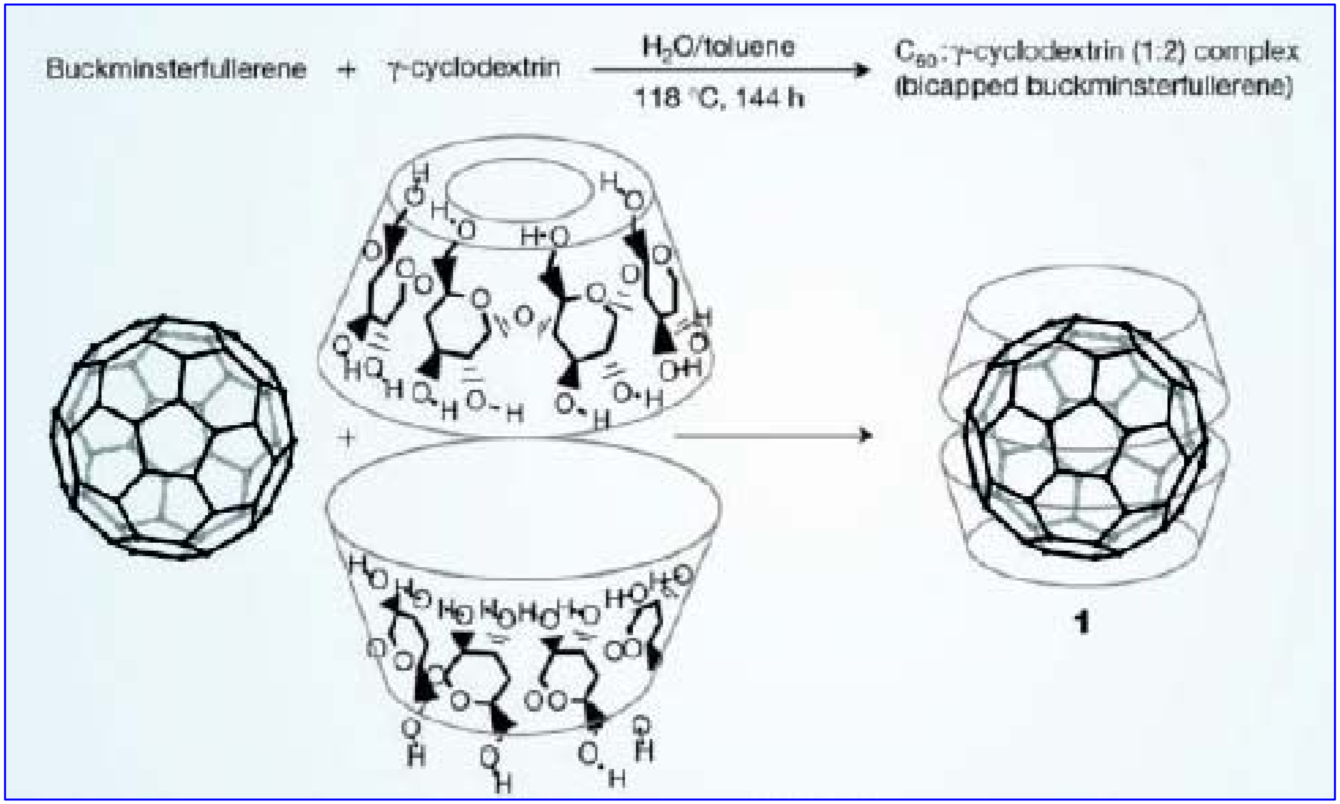
Ammonia Synthesis at Low-Temperature

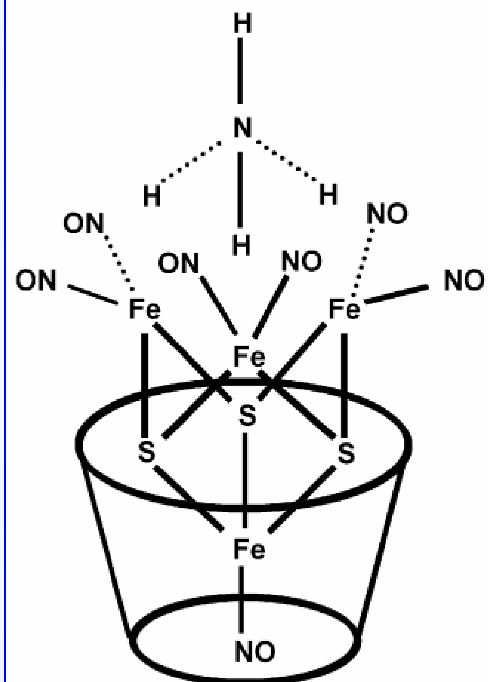


$N_2 + 6H^+ + 6e^- \leftrightarrow 2NH_3 + H_2$

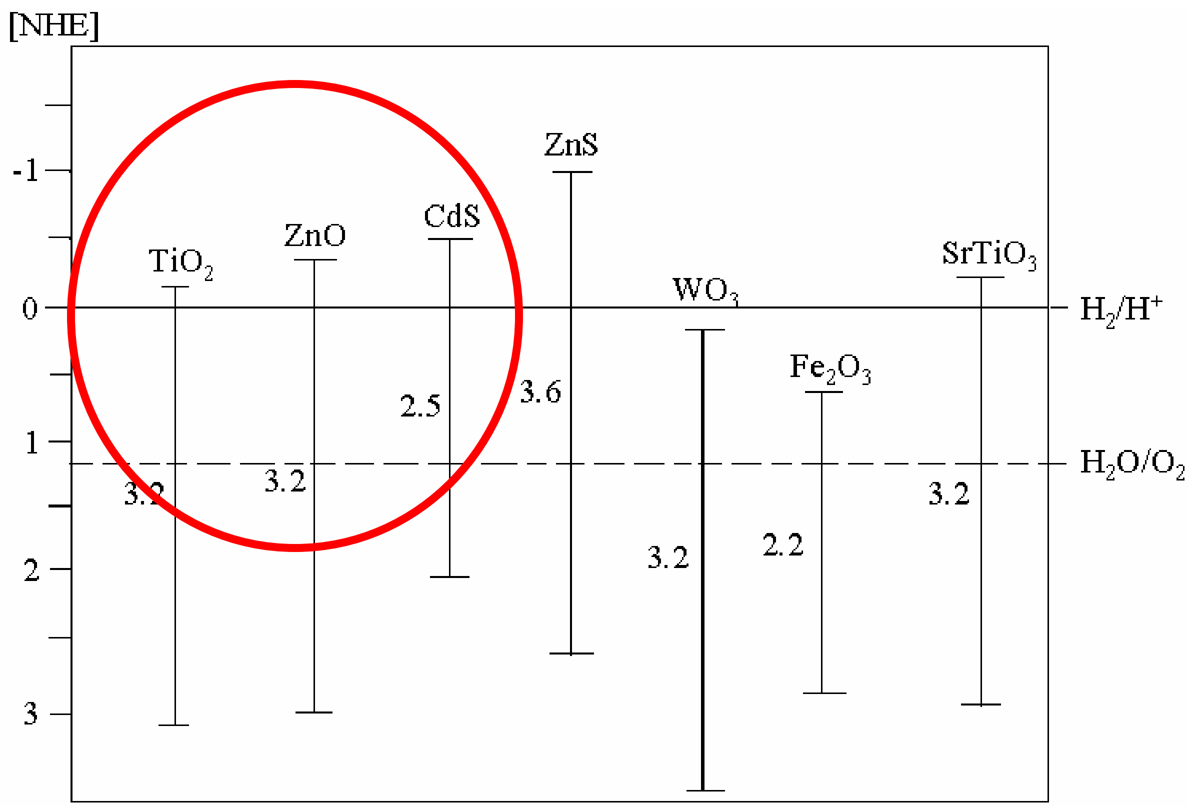
$H_2 \leftrightarrow 2H^+ + 2e^-$

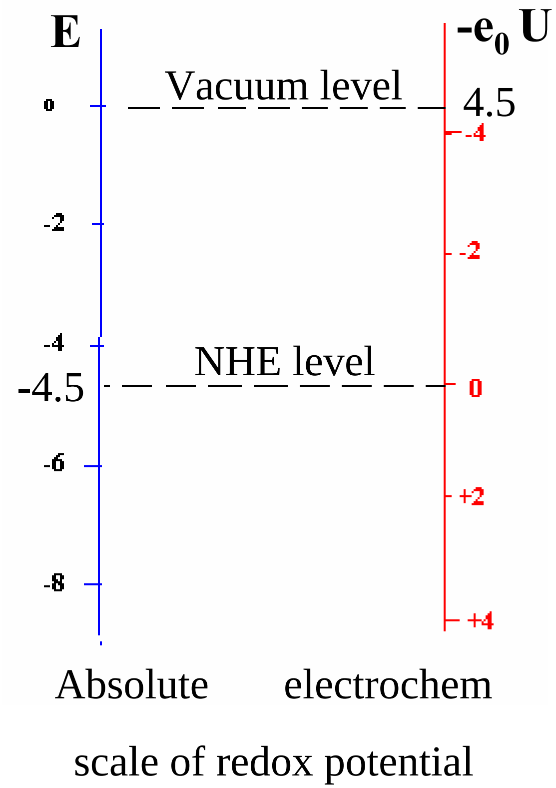
Non metal system for nitrogen fixation





Redox potential

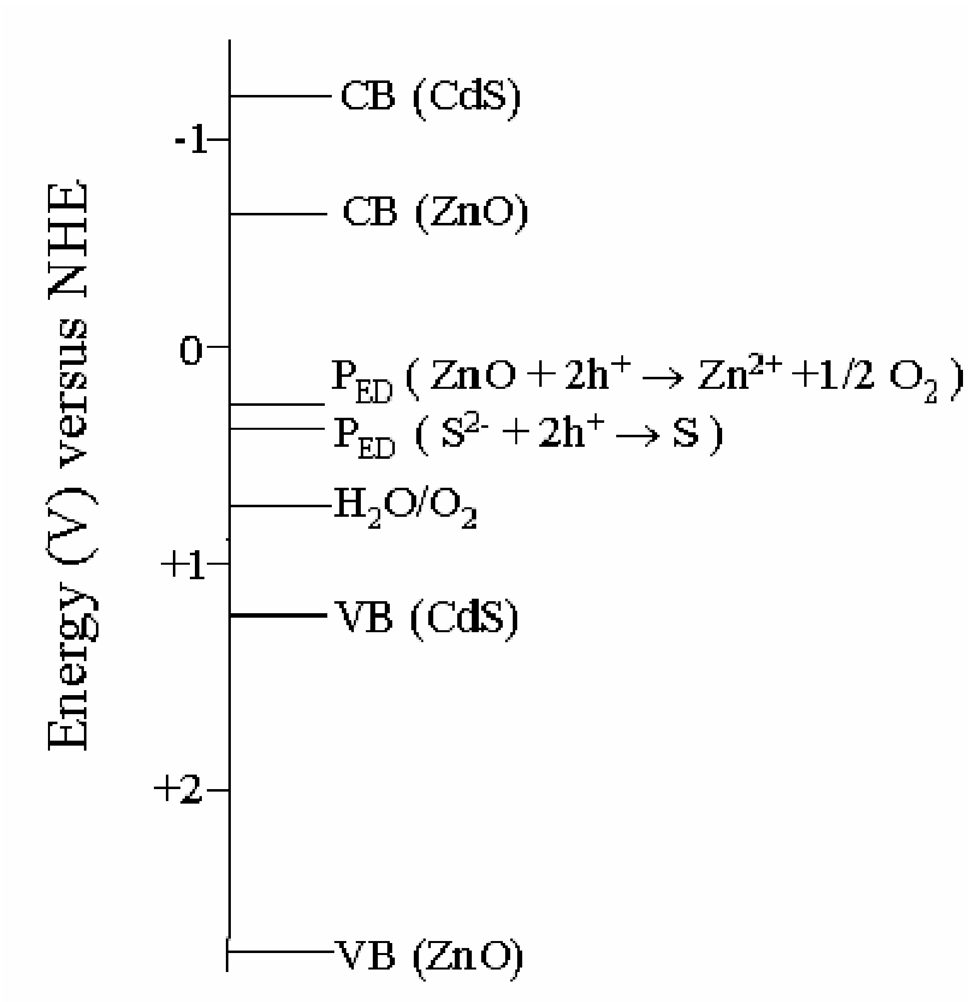




Conversion of Electrochemical scale to the Solid state scale

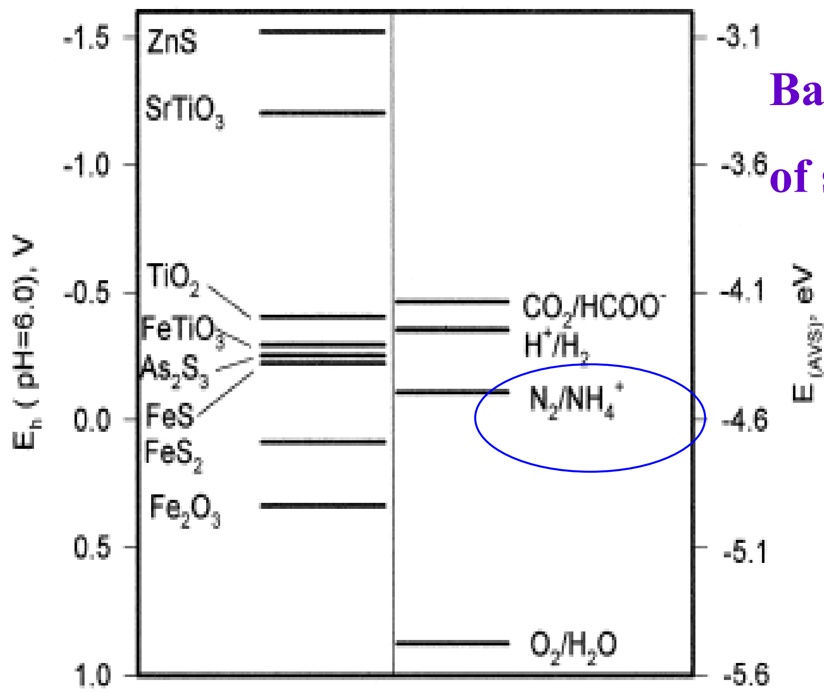
$$E_{F,redox} = -4.5 \text{ eV} - e_o E_{redox}$$

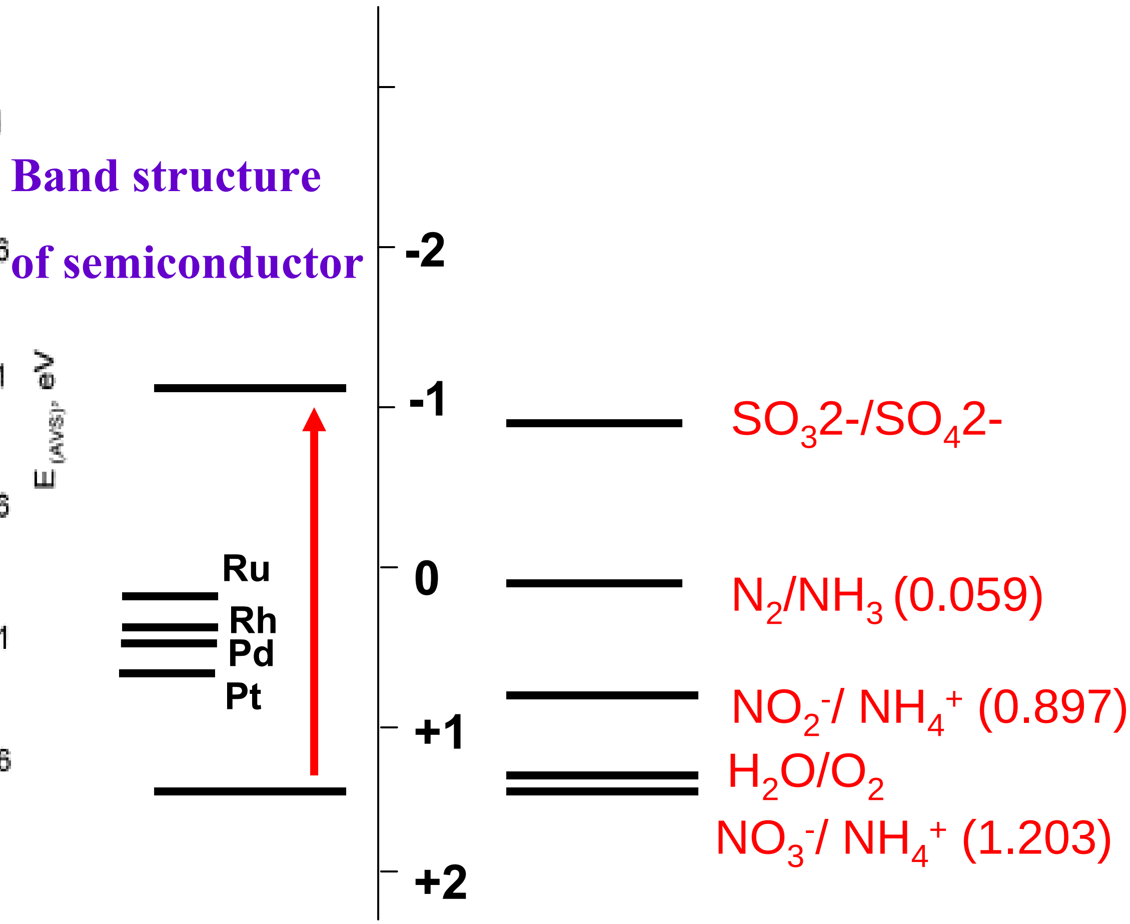
Photo corrosion

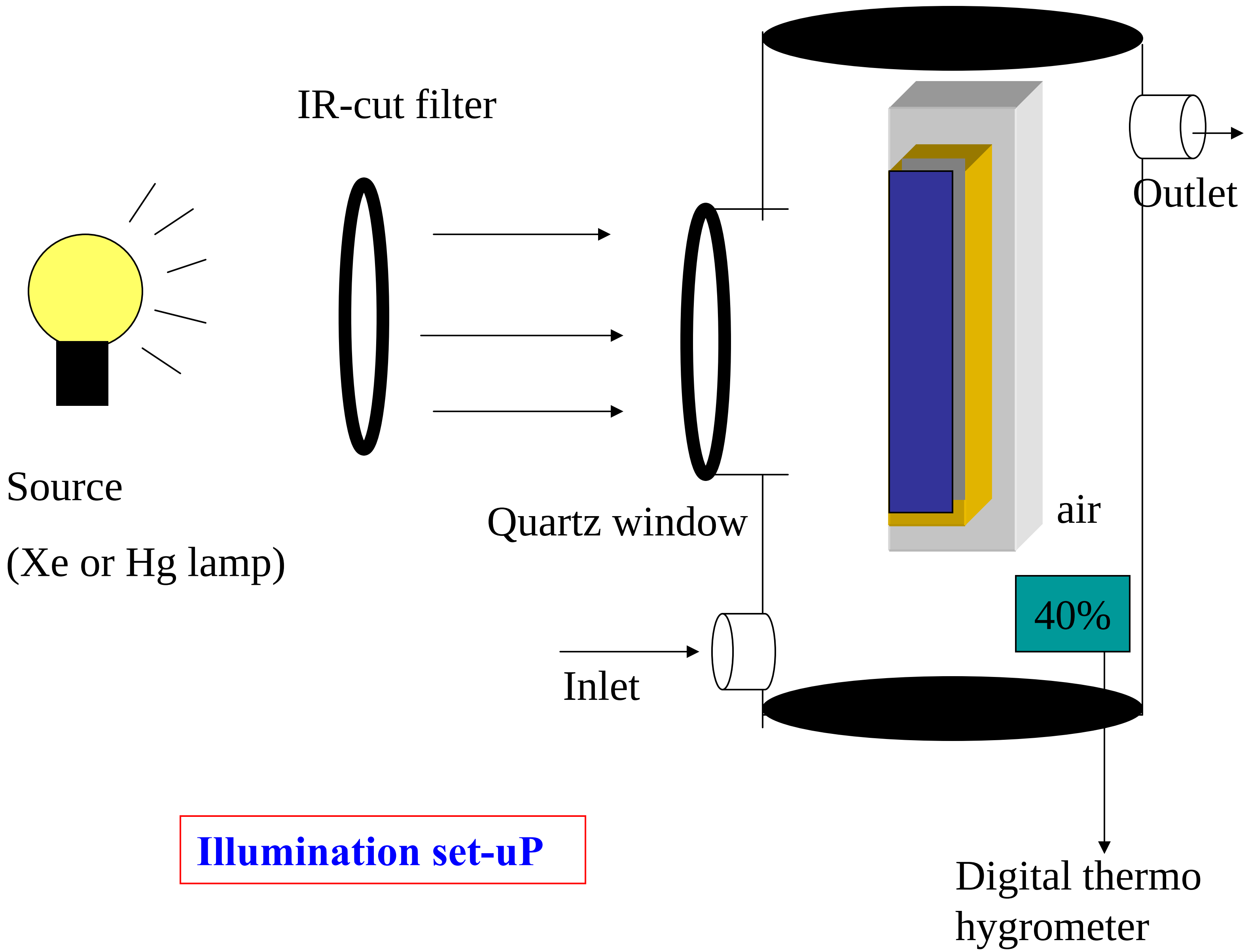


- CdS, ZnS, ZnO undergo photo corrosion
- Activity decrease as the time increases
- S deposition on the catalyst surface reduce the light absorption ability of the catalyst.

Choice of Materials for catalysis







Illumination set-uP

A possible prebiotic formation of ammonia from dinitrogen on iron sulfide surfaces

" Pyrite pulled " N_2 fixation ← FeS surfaces
H_2 source : H_2S

A broad range of reduction , addition and oxidation reactions that require transition metal sulphides as either catalysts or reaction participants.

Nitrogen-fixing bacteria

$N_2 \rightarrow NH_3$

K = 1.7 x 10^8 tons per year

nitrogenase enzyme

atmospheric pressure = (10^5 Pa)

ambient temperature = (273–323 K)

Primordial inorganic substitute for the enzyme nitrogenase

Atmospheric nitrogen pressure

Temperatures of the order of 70–80 °C

Mild and comparable to biological processes.

The driving forces of the overall reaction are the oxidation of iron sulfide to iron disulfide and the formation of hydrogen from H_2S

Aqueous suspensions of MoIII, TiII, VII, MnII, and TaIII hydroxides have been reported to reduce N_2 at pressures of approximately 10^7 Pa.

New approach ……….

$$FeS\,(s) + H_2S\,(aq) \rightarrow FeS_2\,(s) + H_2\,(g) \text{ ------- } (1)$$

$\Delta G° = -38.6$ KJ/mol

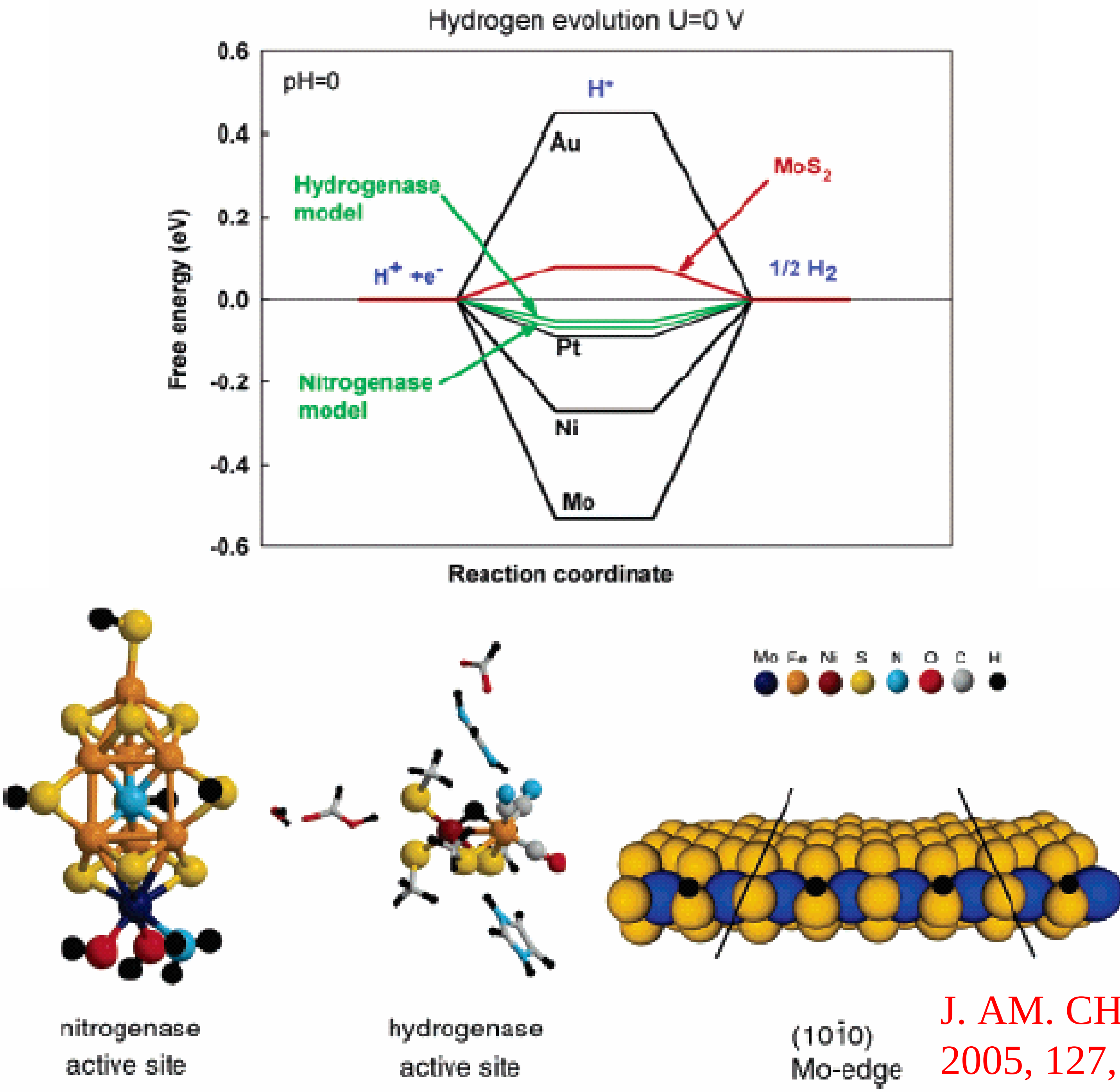
$E° = -600$ mv

pH = 6.5

$$N_2\,(g) + 3\,FeS + 3\,H_2S\,(aq) \rightarrow 3\,FeS_2\,(s) + 2\,NH_3\,(g) \text{ --- } (2)$$

Logic → Moderate reduction potential according to reaction (1)

Thermodynamic calculations show that the redox system <u>$FeS–H_2S$ / FeS_2</u> is able to reduce dissolved molecular nitrogen to ammonia.



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Thank you !