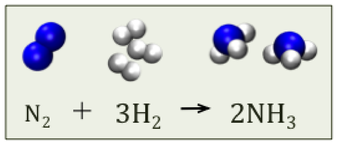
Fertilizers and Fuels from Air!

Souvik Mandal, Rachel N. Allen, Jessica D. Malcolm, and Alan S. Goldman*

Department of Chemistry and Chemical Biology Rutgers, The State University of New Jersey, Piscataway, NJ

Q: What was the most important invention of the 20th century?



A: The Haber-Bosch process.

Fe-based catalyst
high pressure
ca. 400 °C

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

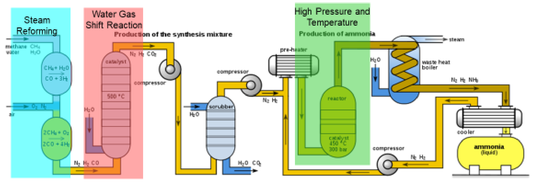
Approx. 25% of total is due to this inefficiency. Even at 200 atm we get only 14% yield at equilibrium! Wastes huge amounts of energy.

Some of the simplest possible molecules (reactants and products).
But a very difficult reaction…..
approx. 2% of human energy use

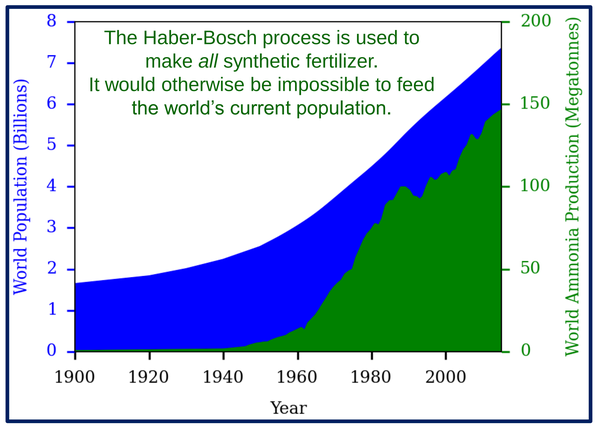
Haber Bosch (HB) process

$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$ (Fe/Ru on Al_2O_3, 450 °C, 200 atm)

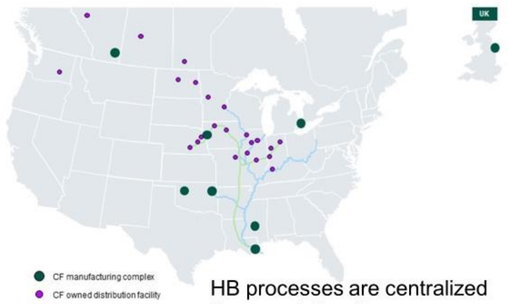
H_2 is derived from fossil fuel
2% global CO_2 emissions
Only 15% efficiency per cycle
Ca. 2% of human energy use



NH_3 is a potential alternative green fuel (zero carbon emission) if it could be produced using renewable energy

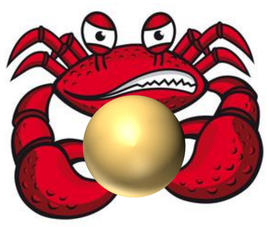


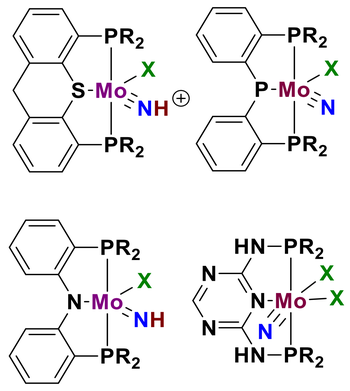
Centralized HB process



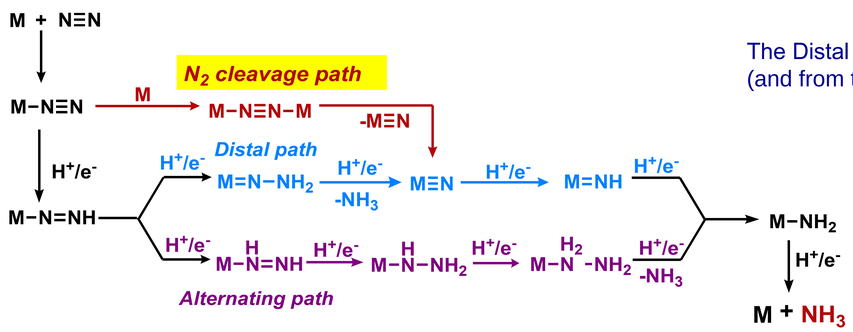
HB processes are centralized
Transportation ?
Decentralized economy

Pincer ligands and metal complexes

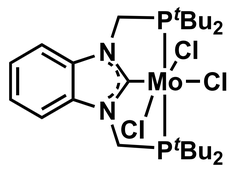




Traditionally, N_2 reduction is approached via two routes: the "Alternating" and "Distal" pathways.
Both involve *very high energy intermediates* like M-NH=NH and M≡N-NH_2.



The Distal Pathway eventually gives M≡N
(and from there it is hopefully easy!)



Best catalyst so far!!

Can we hydrogenate N_2? (the "Haber reaction")

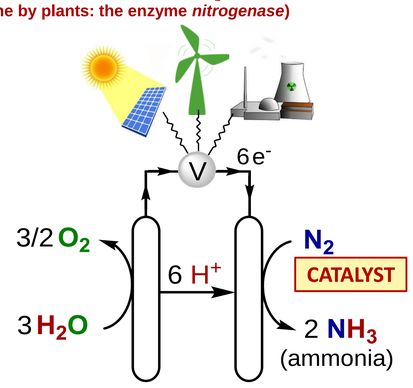
But even the best Haber catalyst will require H_2 (obtained from fossil fuel):

Can we instead obtain the H from H_2O?
Instead of making H_2, direct reduction of N_2??
--no need for H_2 *and* no inefficient Haber catalysts?

Net reaction:
3 H_2O + N_2 → 3/2 O_2 + 2 NH_3

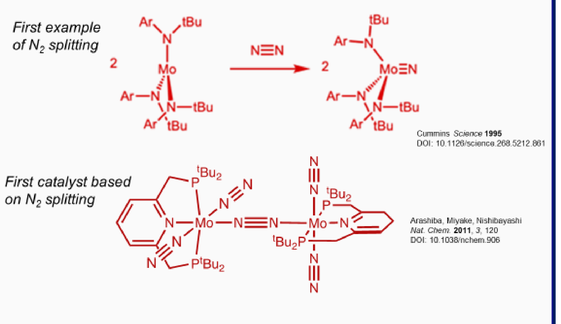
"Fertilizer from air!"

Using protons and electrons, not H_2.
(As done by plants: the enzyme *nitrogenase*)

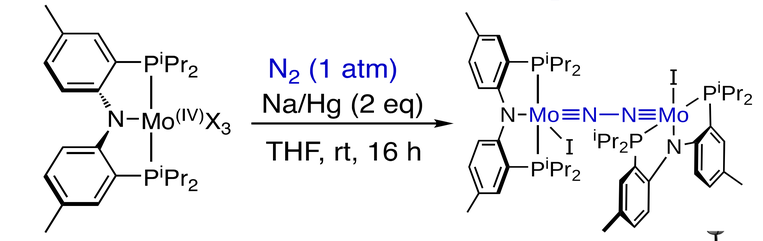


Critical Step: Bimetallic N_2 cleavage

$2\,M + N{\equiv}N \rightarrow M{-}N{\equiv}N{-}M \rightarrow M{\equiv}N + N{\equiv}M$



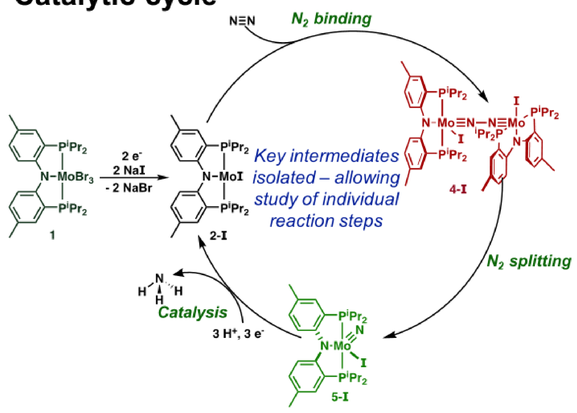
Our approaches: an example of bimetallic N_2 binding

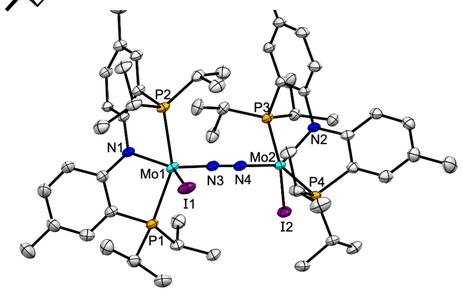


Uncommon example of 8-p-electron M≡N-N≡M system.

Diamagnetic and stable, as predicted…

Catalytic cycle





$N_2 + 6\,H^+ + 6\,e^- \xrightarrow{\text{Catalyst}} 2\,NH_3$

6 TON NH_3/[Mo]
collidinium triflate as H^+ source and $CoCp^*_2$ as reducing agent

12 TON NH_3/[Mo] using ethylene glycol and SmI_2 as PCET reagent

Acknowledgments

NSF