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

A: The Haber process.

Fe-based catalyst high pressure ca. 400 °C

\[ \text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3 \]

Some of the simplest possible molecules (reactants and products).

But a very difficult reaction... approx. 2% of human energy use

Haber Bosch (HB) process

H\(_2\) is derived from fossil fuel 2% global CO\(_2\) emissions

Only 15% efficiency per cycle Ca. 2% of human energy use

\[ \text{N}_2 \rightleftharpoons (\text{g}) \rightarrow \text{N}_2 \text{H}_3 \text{Cl} \text{MoPtBu}_2 \text{PtBu}_2 \text{MoI}_3 \text{Nishibayashi, Mo(III), 2017} \]

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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\(_2\).

\[ \text{M} + \text{N}_2 \rightarrow \text{M} = \text{N} = \text{N} = \text{M} \]

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Alternating path

Distal path

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

\[ \text{M} + \text{N}_2 \rightarrow \text{M} = \text{N}_2 \text{N} \rightarrow \text{M} = \text{N} \rightarrow \text{M} = \text{N}_2 \text{N} \rightarrow \text{M} = \text{N}_2 \text{N} \]

Best catalyst so far!!

Habermahl, Mo(III), 2017

Habermahl, Mo(III), 2019

Can we hydrogenate N\(_2\)? (the "Haber reaction")

But even the best Haber catalyst will require H\(_2\) (obtained from fossil fuel):

Net reaction:

\[ 3 \text{H}_2\text{O} + \text{N}_2 \rightarrow 3/2 \text{O}_2 + 2 \text{NH}_3 \]

"Fertilizer from air!"

Using protons and electrons, not H\(_2\), (As done by plants: the enzyme nitrogenase)

Critical Step: Bimetallic N\(_2\) cleavage

\[ 2 \text{M} + \text{N}_2 \rightarrow \text{M} = \text{N}_2 \rightarrow \text{M} + \text{N}_2 \]

Our approaches: an example of bimetallic N\(_2\) binding

Pincer ligands and metal complexes

Catalytic cycle

\[ \text{N}_2 + 6 \text{H}^+ + 6 \text{e}^- \rightarrow \text{Catalyst} \rightarrow 2 \text{NH}_3 \]

12 TON NH\(_3\)[Mo] using ethylene glycol and SmI\(_2\) as PCET reagent

Acknowledgments