

Science and Technology Facilities Council

# Catalysts for ammonia synthesis and decomposition

Tom Wood ARENHA Workshop 7<sup>th</sup> April 2022

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### Nitrogen

Obviously there is a way for nitrogen, an essential element for life, to get transformed from  $N_2$  to something useful.













Life's answer to getting nitrogen from the air: bacteria with nitrogenases

- Nitrogenases are heavily dependent on iron
- Can have Fe replace the Mo or even V
- Remarkably inorganic-looking clusters in the centres.
- Nitrogenases are responsible for around half (B) of the ammonia/nitrates that are found in soil.





There is another way that nitrogen is fixed in nature: by lightning.



 $N_2 + O_2 \rightarrow 2NO$ 

Subsequently  $2NO + O_2 \rightarrow 2NO_2$ 

And dissolved in water to give nitric acid.



The Birkeland-Eyde process (the arc process)





- The arc process was used industrially in 1900s, but phased out in the early part of the 20<sup>th</sup> century.
- A big rival was the cyanamide (Frank-Caro) process, which is a good example of chemical looping:



DR. NIKODEM CARO IN BERLIN UND DR. ADOLPH FRANK IN CHARLOTTENBURG. Verfahren zur Darstellung von Cyanverbindungen aus Carbiden.

Patentirt im Deutschen Reiche vom 31. März 1895 ab.



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Adolph Frank



Nikodem Caro





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## Nitrogen to ammonia: Haber-Bosch

Although the arc and cyanamide processes were both used in the early part of the 20<sup>th</sup> century, there was a more economical method developed then that surpassed them.



Technology

Habel, long with associates (particularly Robert le Rossigned found that osmium and uranim were excellent catalysis for making ammonia from nit ogen and hydrogen. Osmium was later replaced with lion.

00 atmospheres and 500 °C.

"The main work of the company however, was in substituting electrolytic Science and Facilities Council hydrogen, with which we conducted our experiments, for water-gas hydrogen which introduced impurities." Haber, Nobel Lecture, 1920





### Nitrogen to ammonia: T vs P

- High temperatures: required for catalytic activity, but pushes the equilibrium towards the reactants.
- In order to recover that equilibrium, high pressures are required.



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- It all comes down to the nitrogen-nitrogen triple bond.
- There's a sweet spot of just the right degree of affinity of nitrogen adsorption on the surface.

$$N_{2} + [*] \rightleftharpoons N_{2}^{*} \qquad (1)$$

$$N_{2}^{*} + [*] \rightleftharpoons 2N^{*} \qquad (2)$$

$$H_{2} + [*] \rightleftharpoons H_{2}^{*} \qquad (3)$$

$$H_{2}^{*} + [*] \rightleftharpoons 2H^{*} \qquad (4)$$

$$N^{*} + H^{*} \rightleftharpoons NH^{*} + [*] \qquad (5)$$

$$NH^{*} + H^{*} \rightleftharpoons NH_{2}^{*} + [*] \qquad (6)$$

$$NH_{2}^{*} + H^{*} \rightleftharpoons NH_{3}^{*} + [*] \qquad (7)$$

$$NH_{3}^{*} \rightleftharpoons NH_{3} + [*] \qquad (8)$$



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Alwin Mittasch 1000s of experiments

• Think synthesis but in reverse:

Nche [k]  $\Rightarrow$  plarameter which deterministic  $\forall H_{3}^{*} = NH_{3}^{*}$ Note that the product of the product o

Two possible mechanisms:

The "tungsten" mechanism, where  $r = k p_{\text{NH}_3}^{m}$ 

Acc. Chem. Res. 1988, 21, 88–94 A "New" General Mechanism of Ammonia Synthesis and Decomposition on Transition Metals

Kenzi Tamaru



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 $r = k \left(\frac{P_{\rm NH_3}^2}{P_{\rm H}^3}\right)^{\beta}$ 

(1)

(2)

(3)

(4) (5)

(6)

(7)

(8)

Titherley in 1894, in passing, noted that sodium amide decomposes ammonia catalytically.



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XLV.—Sodium, Potassium, and Lithium Amides. By ARTHUR W. TITHERLEY, B.Sc., 1851 Exhibition Scholar.

An interesting result is obtained on heating sodamide to dull redness in a boat contained in a hard glass tube, through which a current of ammonia is passing; the latter is continuously decomposed into its elements. At this comparatively low temperature, the amide is split up into nitrogen, hydrogen, and sodium, and the latter in presence of the ammonia re-forms sodamide, which is again split up. In this way an indefinite quantity of ammonia may be decomposed by a small quantity of amide; thus 0.4 gram of sodamide in the course of an hour or two gave nearly half a litre of the mixture of nitrogen and hydrogen, without showing any indication of loss of activity. The amide at the end of the experiment had mostly volatilised unchauged on to the cool upper surface of the tube.



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This result was finally picked up again about 12 years ago in our group, where it was noted that sodium amide, on heating, decomposes into its elements, *not ammonia*:

 $NaNH_2 \rightarrow \frac{1}{2}N_2 + H_2 + Na$ 

But sodium reacts with ammonia to form sodium amide and a bit of hydrogen:

 $NH_3 + Na \rightarrow NaNH_2 + \frac{1}{2}H_2$ 



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#### Hydrogen Production from Ammonia Using Sodium Amide

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- Some issues with sodium amide:
- The amide at the end of the experiment had mostly volatilised unchauged on to the cool upper surface of the tube.
- The vapour pressure of sodium is nonnegligible at temperatures above 400 °C
  - Therefore catalyst escape is very high.





- Potassium amide follows a similar path to sodium amide (it decomposes to its elements, is active, but difficult to keep in the reactor).
- Lithium amide shouldn't work, because:

 $2\text{LiNH}_2 \rightleftharpoons \text{Li}_2\text{NH} + \text{NH}_3$ 

But...





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### Ammonia to nitrogen and hydrogen



• By marrying up the flow and the mass spectrometry data, we can determine the exact stoichiometry of the catalyst at every stage of the reaction, and therefore its phase.





Paper submitted



### Conclusions

- There are several ways of decomposing and synthesising ammonia
- The mechanisms are not straightforward to determine
- In chemistry terms, new catalyst directions are seeing big advances in chemical looping and light metal hydride/amide/imide catalysts.
- Careful chemistry can mitigate problems of phase (i.e. keeping things solid).
- Very recent advances in the amide/imide catalysts have come up with a variant that is solid over the entire temperature range (i.e. no mitigations are needed).
- A word of warning: amides react with lots of things (including silica, alumina and carbon).





Figure 4. XRD patterns for: (a) the products of  $Li_2NH$  and  $SiO_2$  heated under Ar; (b)  $LiNH_2$  and  $SiO_2$  heated under Ar; (c)  $LiNH_2$  and  $SiO_2$  heated under NH<sub>3</sub>.



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