# Energy-Efficient Catalysts For Green Ammonia Synthesis

Associate Professor Franck Natali
CSO & Founder Director Liquium, New Zealand
Breakthrough Energy Innovator Fellow
School of Chemical and Physical Sciences
Te Herenga Waka—Victoria University of Wellington

TUESDAY SEPTEMBER 28, Session 6:  Energy sustainability I 1:30PM – 3:10PM

# HEAVY INDUSTRY MANUFACTURING

**FROM 51 BILLION TONS PER YEAR TO ZERO**

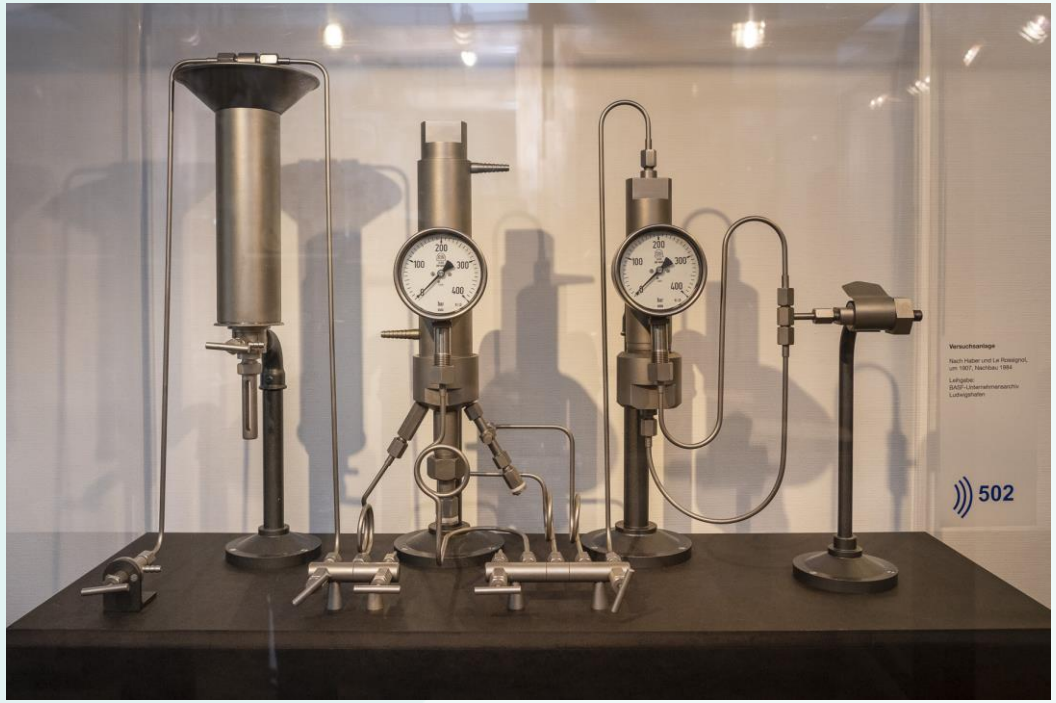
# HEAVY INDUSTRY MANUFACTURING

## AMMONIA: SYNTHETIC FERTILISERS

### Haber-Bosch process

"Of all the century's technological marvels, the Haber-Bosch process has made the most difference to our survival" Vaclav Smil

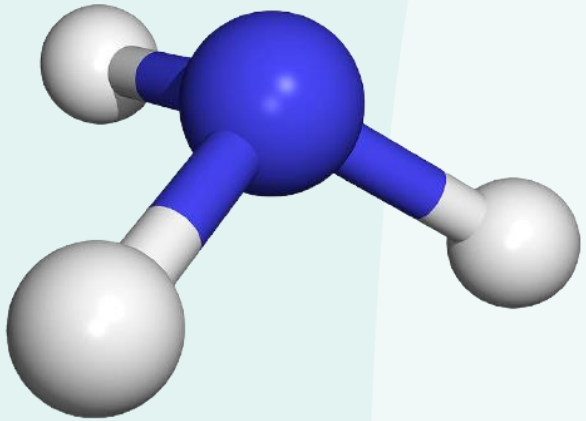
**1920 – Teaspoon of ammonia per day**




**~2000 – >> 5000 tonnes of ammonia per day**

# AMMONIA SYNTHESIS

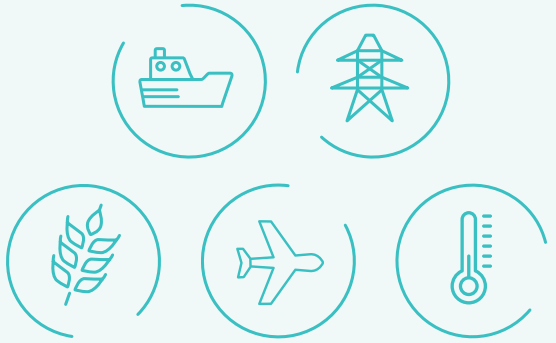
## INTRODUCTION



Ammonia: $NH_3$

$N_2 + H_2$

$NH_3$ is one of largest chemical processes (Haber-Bosh) on the planet



For every tonne of $NH_3$ produced, three tonnes of $CO_2$ are emitted

~ 1 billion tons of $CO_2$ per year

# AMMONIA SYNTHESIS

## PROCESS CHALLENGES OF GREEN AMMONIA PRODUCTION

### The Problem

**Ammonia is hard to make!!**

$$N_2 + 3H_2 \underset{}{\overset{\text{catalyst}}{\rightleftharpoons}} 2NH_3$$

**Industrial Haber Bosch Process**

Iron or ruthenium metals as catalysts

High pressure (150-400 Bar)

High temperature (400-600°C)

### Our Solution

A new catalyst platform for green ammonia

**Our Catalysts**

Lower pressure (<100 Bar)

Lower temperature (<400°C)

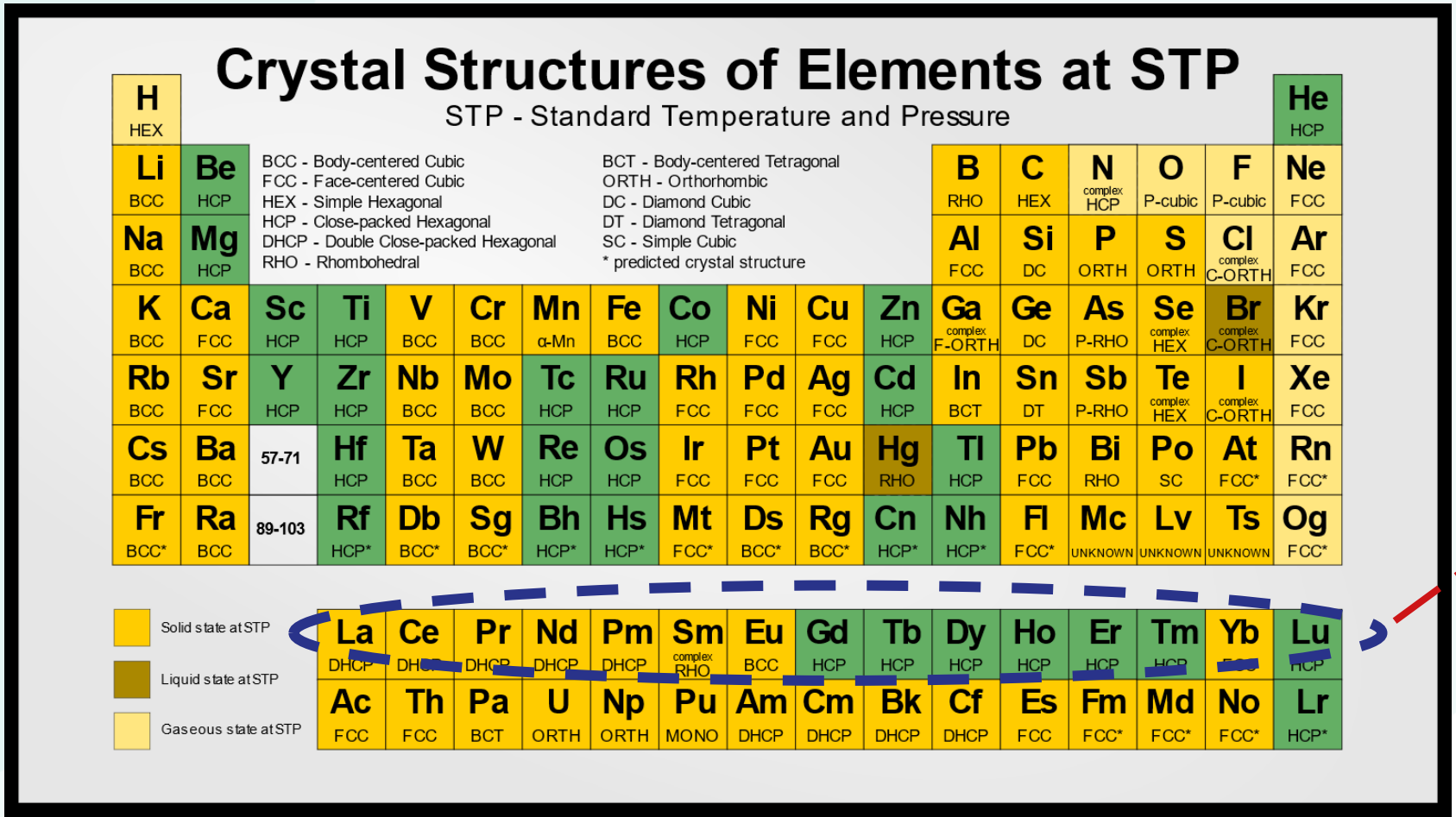
Alignment with renewable energy

*In My Presentation: Rate-limited step by $N_2$ breaking*

# AMMONIA PROCESS AT THE ATOMIC SCALE

## THE CATALYST: THE CHALLENGE

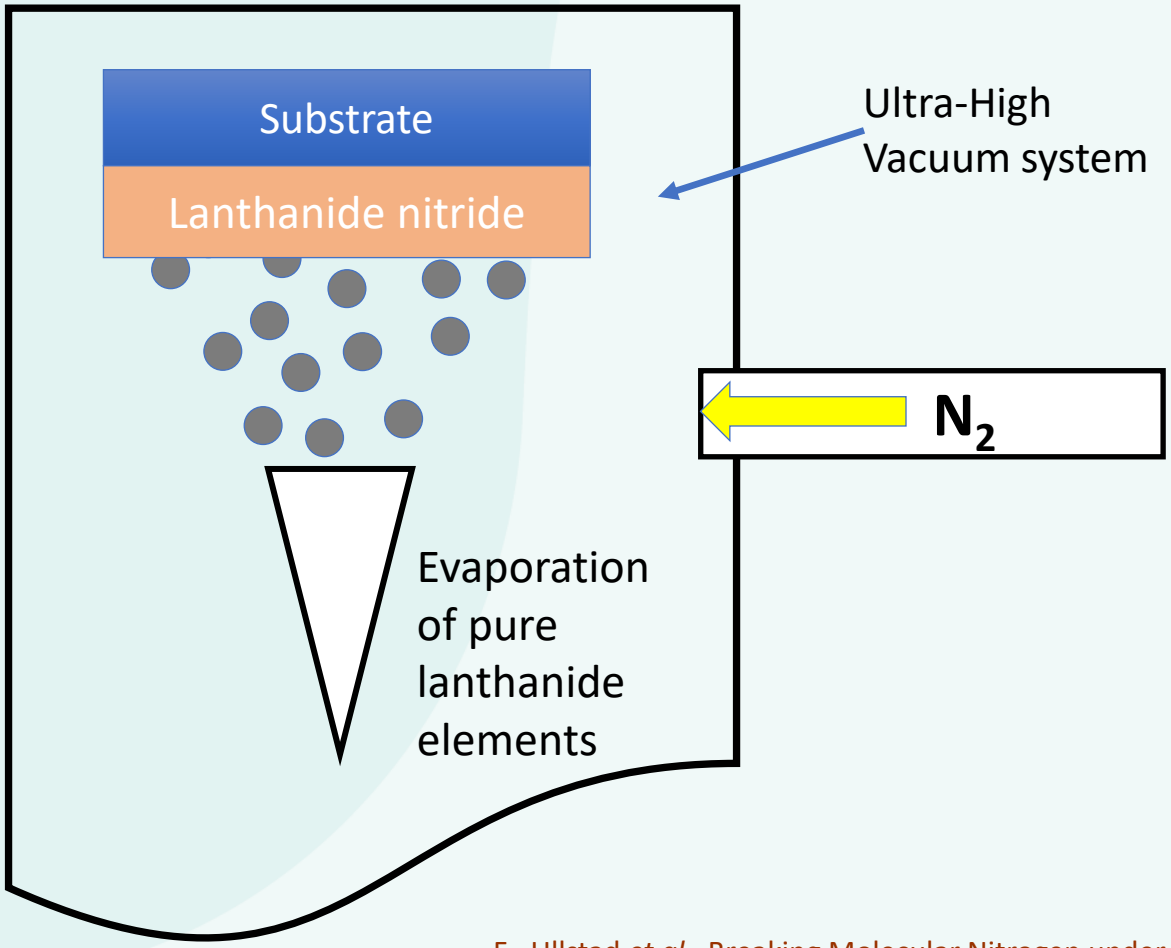
The Scientific Journey: a material that can break molecular nitrogen at mild temperature and pressure



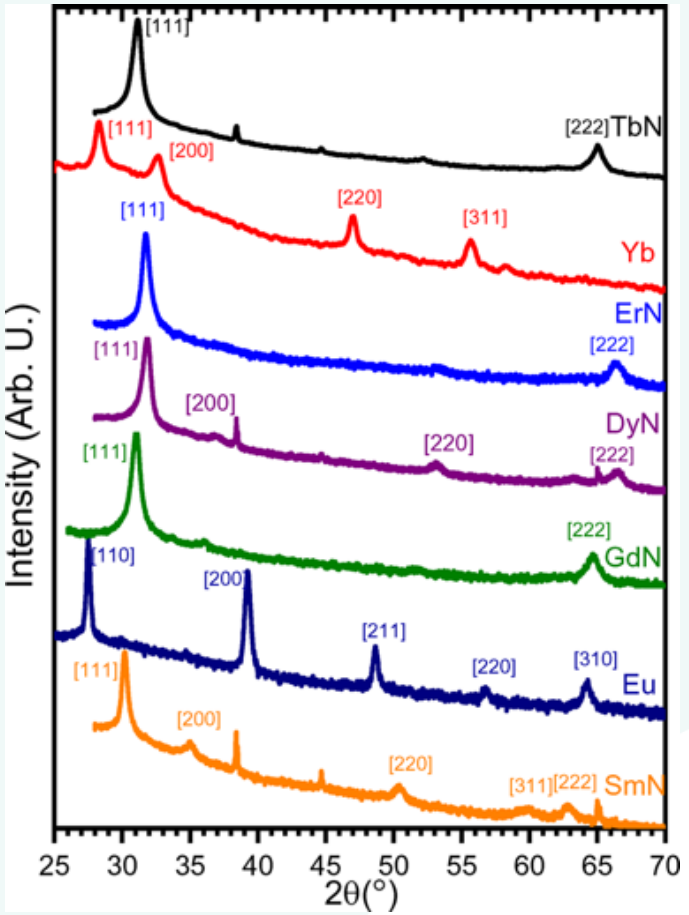
# AMMONIA SYNTHESIS

## THE JOURNEY: $NH_3$ CHEMISTRY WITH LANTHANIDE METAL

Catalytic activity of lanthanide atoms promoting the $N_2$ dissociation at room temperature & $N_2$ pressure <1 bar: growth of thin films in the presence of pure molecular $N_2$




XRD of thin films of lanthanides deposited in a nitrogen atmosphere.



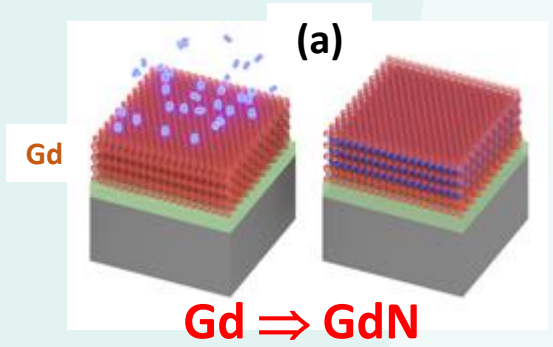

F . Ullstad *et al.*, Breaking Molecular Nitrogen under Mild Conditions with an Atomically Clean Lanthanide Surface, *ACS Omega*, 4, 5950−5954 (2019)

# AMMONIA PROCESS AT THE ATOMIC SCALE

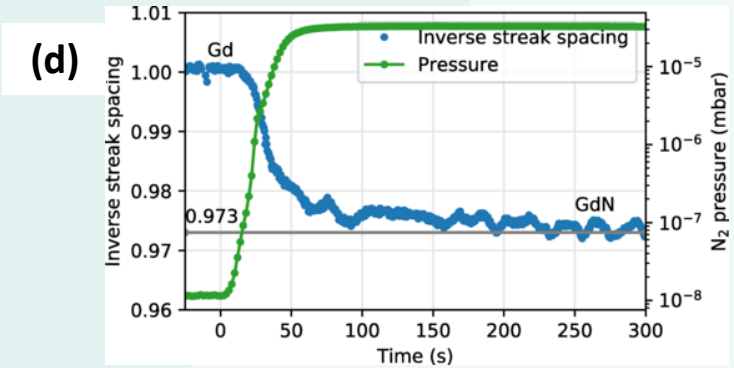
## FACILE DISSOCATION OF $N_2$ BY LANTHANIDE SURFACES

In-situ and real time monitoring of the nitridation of lanthanides - exptl results

- Steps by steps: Exposure of gadolinium layer to $N_2$ AND (3) Formation of gadolinium nitride layer








- (a) Exposure of the Gd surface to $N_2$; *at ambient temperature and $N_2$ partial pressure of 3 x $10^{-5}$ mBar.*
- (b) and (c) RHEED patterns of Gd before and after exposure to $N_2$.
- Streak spacing increases, indicating a contraction of the surface Gd lattice spacing; $a_{GdN}$ = 3.53 Å.
- (d) full nitridation of the surface within 300 seconds; relatively fast process.

Australian Synchrotron

J. Chan *et al.*, *Epitaxial growth of gadolinium and samarium thin films and their subsequent facile nitridation at ambient temperatures,* Applied Surface Science 632, 157550 (2023).

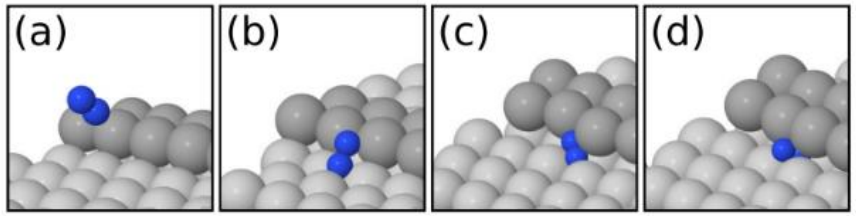
# AMMONIA SYNTHESIS

## FACILE DISSOCATION OF $N_2$ BY LANTHANIDE SURFACES

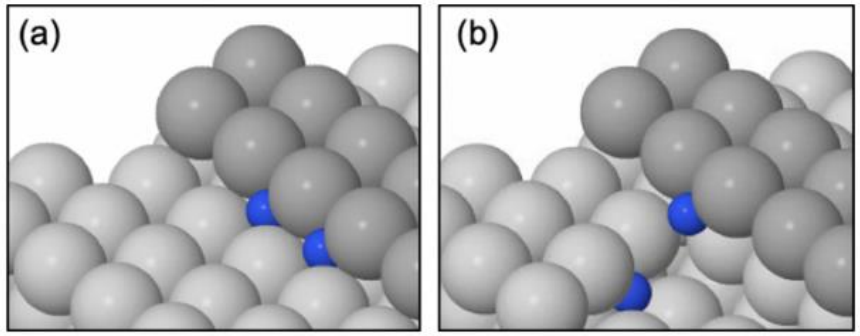
Density functional theory study of $N_2$ dissociation on pure lanthanide surfaces

- Investigated a key step in ammonia formation – $N_2$ dissociation
- Used DFT+U, which allows explicit description of *f* electrons, however, is a prohibitively slow method.
- Used DFT with "*f* in core" potentials – no explicit description of *f* electrons, but much faster than DFT+U – gives acceptable description of adsorbates
- Stable adsorption geometries of $N_2$ on lanthanides markedly different from transition metals: a different mechanism, potentially involving partial absorption of $N_2$ into the surface.

Stephanie Lambie and Anna Garden (University of Otago)




$N_2$ adsorbed onto stepped lanthanide surfaces




2 N adsorbed onto stepped lanthanide surfaces

L atoms – grey, N atoms – blue

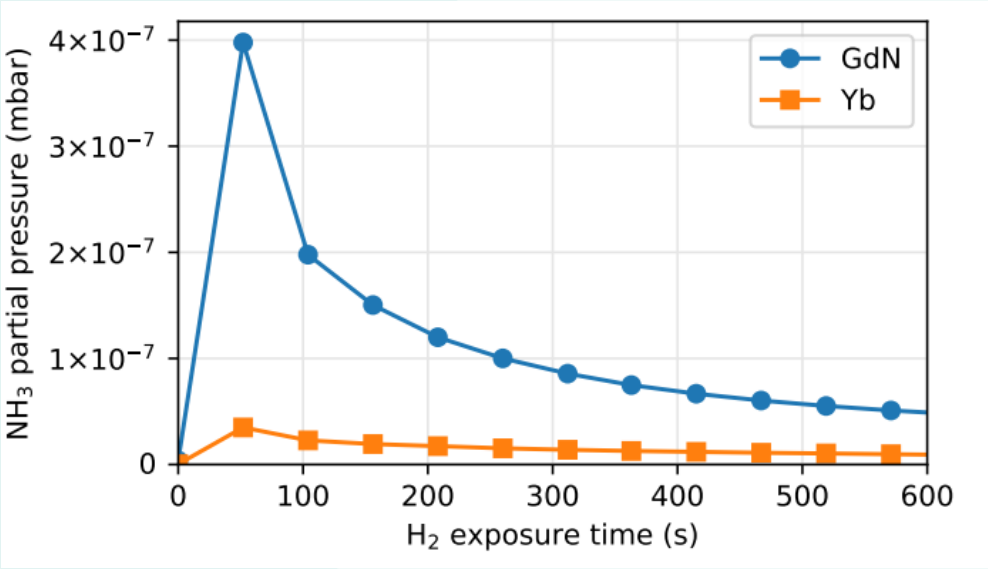
J. Chan *et al.*, *Facile dissociation of molecular nitrogen using lanthanide surfaces: Towards ambient temperature ammonia synthesis,* Phys. Rev. Materials **4**, 115003 (2020).

# AMMONIA SYNTHESIS

## TOWARDS AMBIENT TEMPERATURE AMMONIA SYNTHESIS

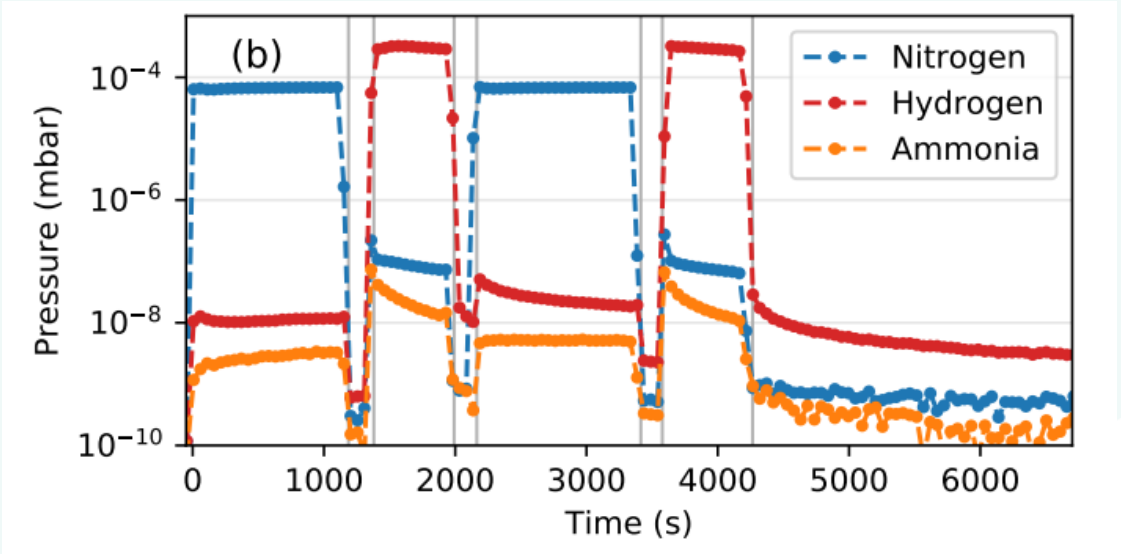
- Gadolinium metal and its subsequent nitridation, *and its subsequent exposure to $H_2$.*

Partial pressure of ammonia is detected




- Gadolinium metal – *Cycling $H_2$ and $N_2$.*

Reproducibility of the cycling process

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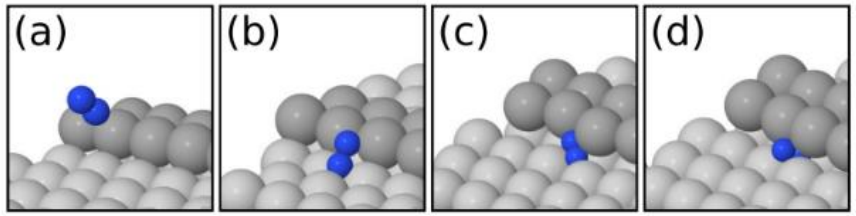


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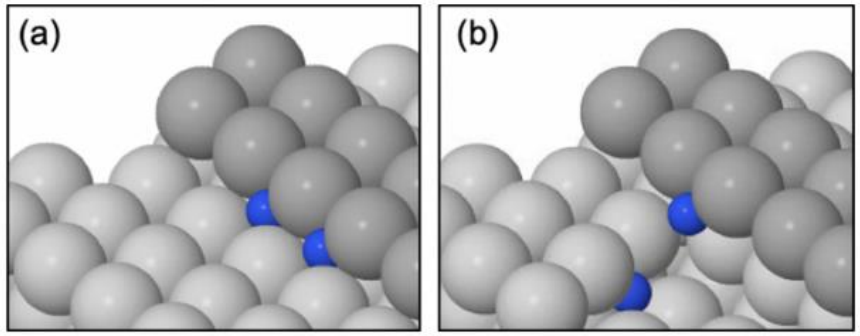


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# AMMONIA SYNTHESIS

## WHAT'S NEXT

- $NH_3$ production at room temperature &low pressure demonstrated using thin films.
- Not appropriate for kinetic & thermodynamic studies and not industrially relevant!
  ⇒ Powders ⇒ Pellets
- Dedicated $NH_3$ synthesis reactor needed!

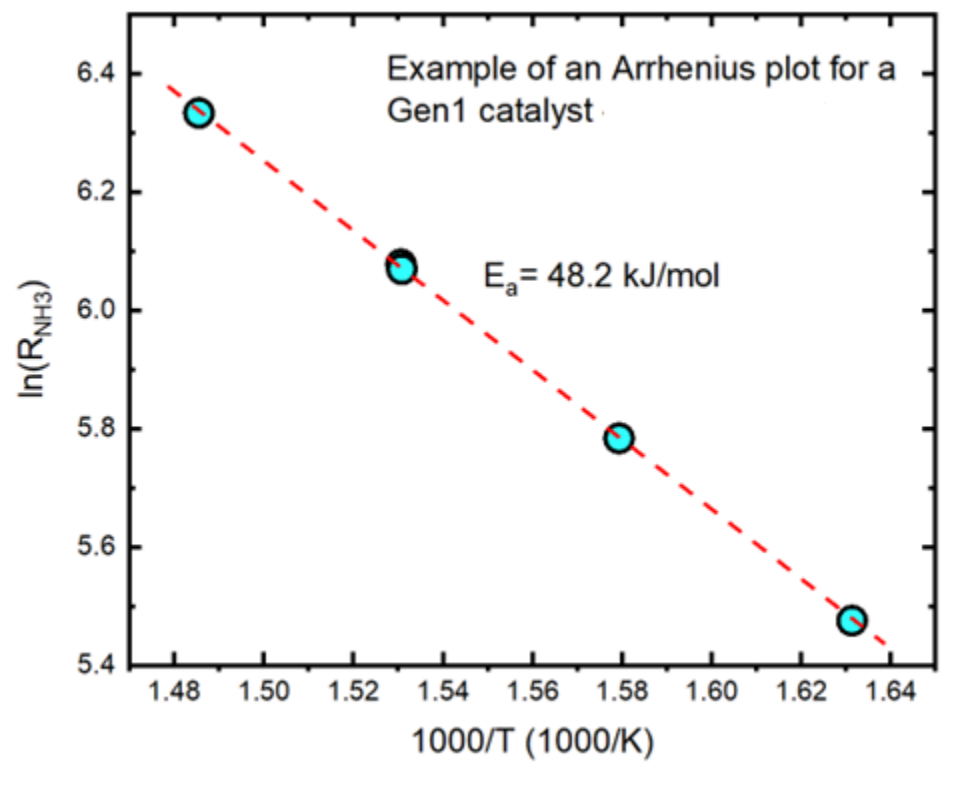

liquium

Spinout from Victoria University of Wellington

# AMMONIA SYNTHESIS

## KINETICS STUDY: ACTIVATION ENERGY

*A catalyst with lower apparent activation energy performs better at lower temperature!*




P= 6 bar, Temperatures= 400ºC, 380ºC, 360ºC, 340ºC

**Article**

**Extended Data Table 2 | Kinetic parameters of selected catalysts**

| Catalyst | *Ea* (kJ·mol$^{-1}$) |
|---|---|
| Ni/LaN NPs | 57.5 |
| Ni/LaN bulk | 60.4 |
| $Co_3Mo_3N$ | 56 |
| Co/C12A7:e$^-$ | 49.5 |
| Fe-cat. (KM1) | 70 |
| LaRuSi | 40.4 |
| Ru/Ba-Ca$(NH_2)_2$ | 59.4 |
| Cs-Ru/MgO | 124.3 |

T.-N. Ye, *et al.*, *Vacancy-enabled $N_2$ activation for ammonia synthesis on an Ni-loaded catalyst*, Nature **583**, 391 (2020).

Collaboration with Ass. Prof. Alex Yip, University of Canterbury

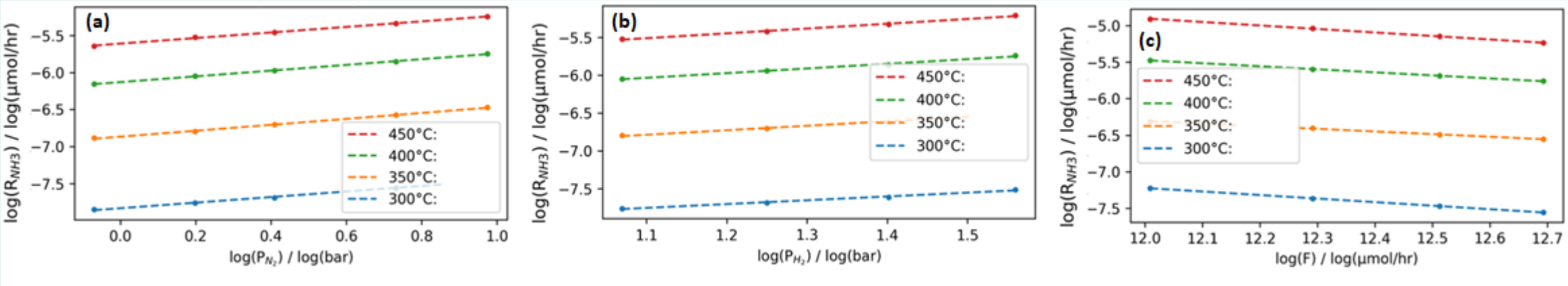
# AMMONIA SYNTHESIS

## KINETICS STUDY: REACTION ORDERS

Reaction order for $NH_3$ synthesis reaction:

$$R_{NH_3} = kP_{N2}^{\alpha}P_{H2}^{\beta}P_{NH3}^{\gamma}$$

Quantity of ammonia produced $R_{NH_3}$ during the reaction is measured for different partial pressures and temperatures.




$N_2$ order ($\alpha$) ≈ 0.90

Indicates dissociative nitrogen chemisorption is the main rate limiting step

$H_2$ order ($\beta$) ≈ 1.35

No strong inhibition of the reaction due to hydrogen adsorption: No hydrogen poisoning

$NH_3$ order ($\gamma$) ≈ -1.33

Contribution from reverse reaction: $NH_3$ decomposition

Collaboration with Ass. Prof. Alex Yip, University of Canterbury

# CONCLUSION

- Unique and strong fundamental knowledge in lanthanide materials catalyst development, laying the foundation for meaningful R&D decisions and actions as we are scaling up our chemical process.
- Synthesised >20 catalysts, with successive catalyst generations focusing successfully on improved air-stability formulation and pelletised to an industrially relevant form factor.
- Kinetic studies allowing us to be uniquely positioned for making a timely and significant contribution in low-temperature and low-pressure ammonia synthesis.