



SOLAR-THERMAL AMMONIA PRODUCTION VIA A NITRIDE LOOPING CYCLE



Sandia National Laboratories

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Andrea Ambrosini

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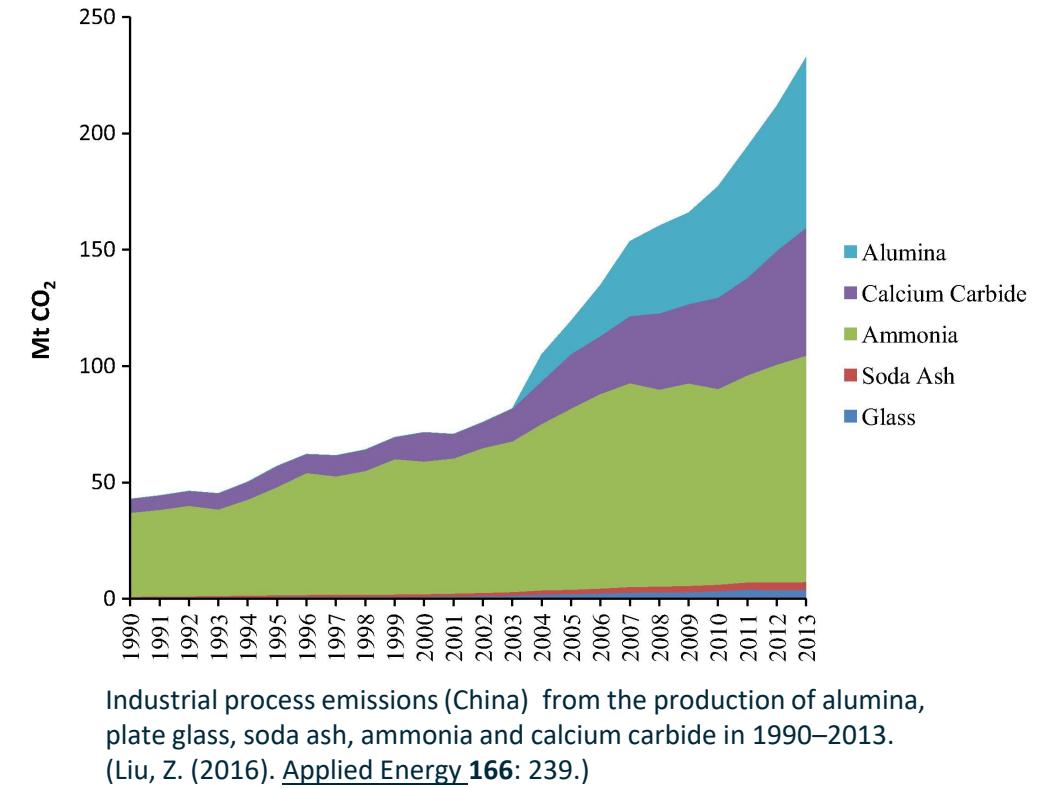
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Introduction



- Ammonia (NH_3) is an energy-dense chemical and a vital component of fertilizer
 - Also finds use as potential fuel and in CSP thermochemical energy storage
- NH_3 synthesized via the Haber-Bosch process
 - Requires high pressures (15-25 MPa) and temperatures (400-500 °C)
 - Capital-intensive and only practical with large facilities
 - Process including H_2 production is responsible for ~1.4% of global CO_2 emissions¹
- Ammonia synthesis consumes > 1% of the total energy worldwide²



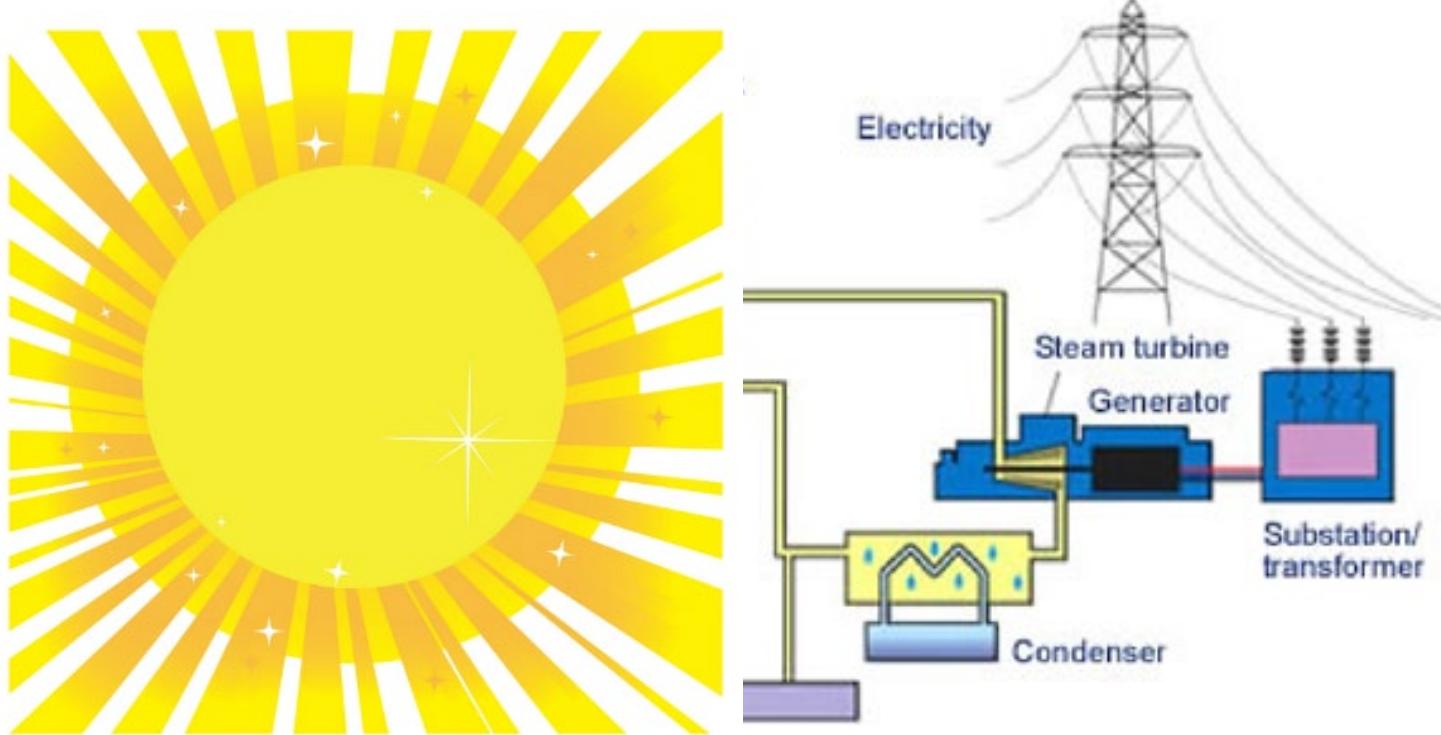
Production of NH_3 via a renewable, carbon-neutral technology powered by concentrating solar can mitigate climate and CO_2 impacts

¹Kyriakou, V., Joule **2020**, 4 (1), 142. ²Institute for Industrial Productivity. Industrial Efficiency Technology Database <http://ietd.iipnetwork.org/content/ammonia>.

What is Concentrating Solar Power (CSP)?



Conventional power plants burn fossil fuels (e.g., coal, natural gas) or use radioactive decay (nuclear power) to generate heat for the power cycle



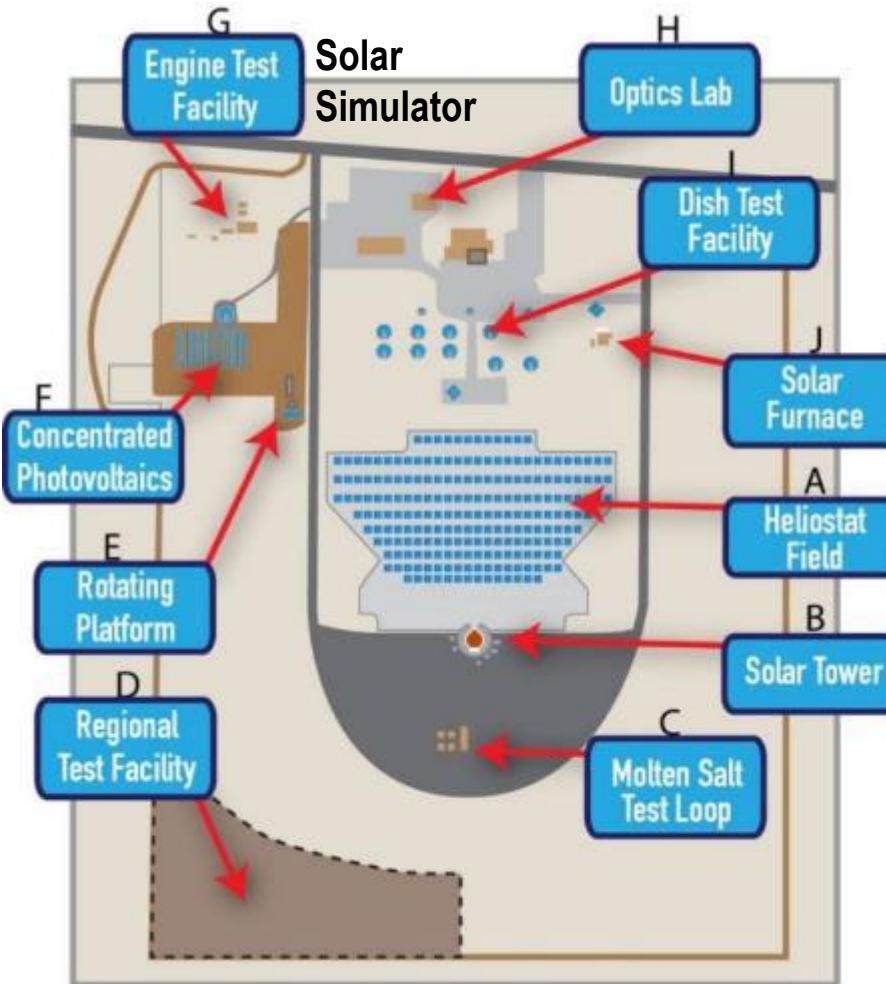
Coal-Fired Power Plant

Concentrating solar power uses mirrors to concentrate the sun's energy onto a receiver to provide heat to spin a turbine/generator to produce electricity

The National Solar Thermal Test Facility at Sandia



The NSTTF is a DOE Designated User Facility for R&D in Concentrating Solar Power Technologies

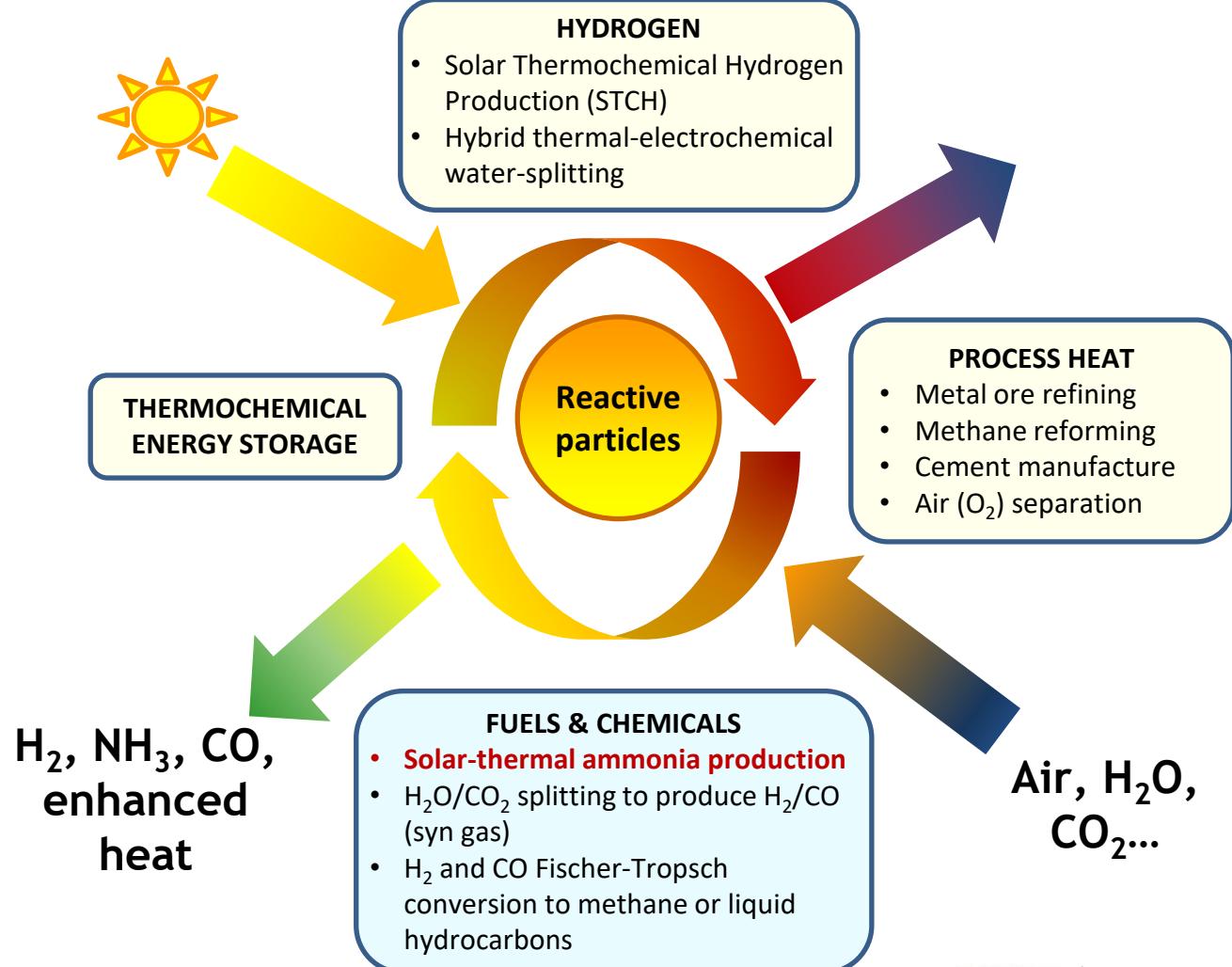


Solar Thermochemistry (STC)

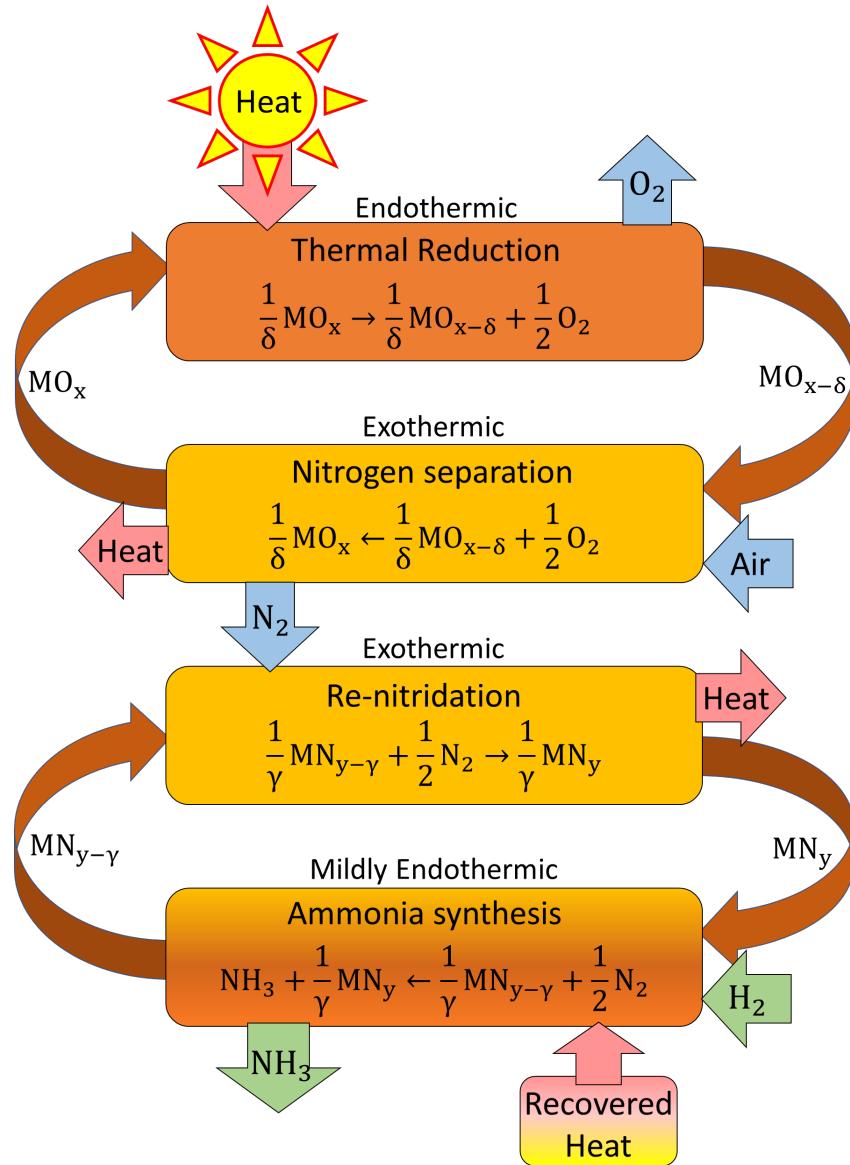


Solar thermochemistry harnesses concentrated solar heat to drive chemical reactions that would normally be energy- or resource-intensive

- High temperature applications (600-1500 °C)
- Synergistic with CSP particle technology
- Chemical and sensible heat storage
- Many technologies still low TRL
- Must increase efficiency and decrease costs to make technology more competitive



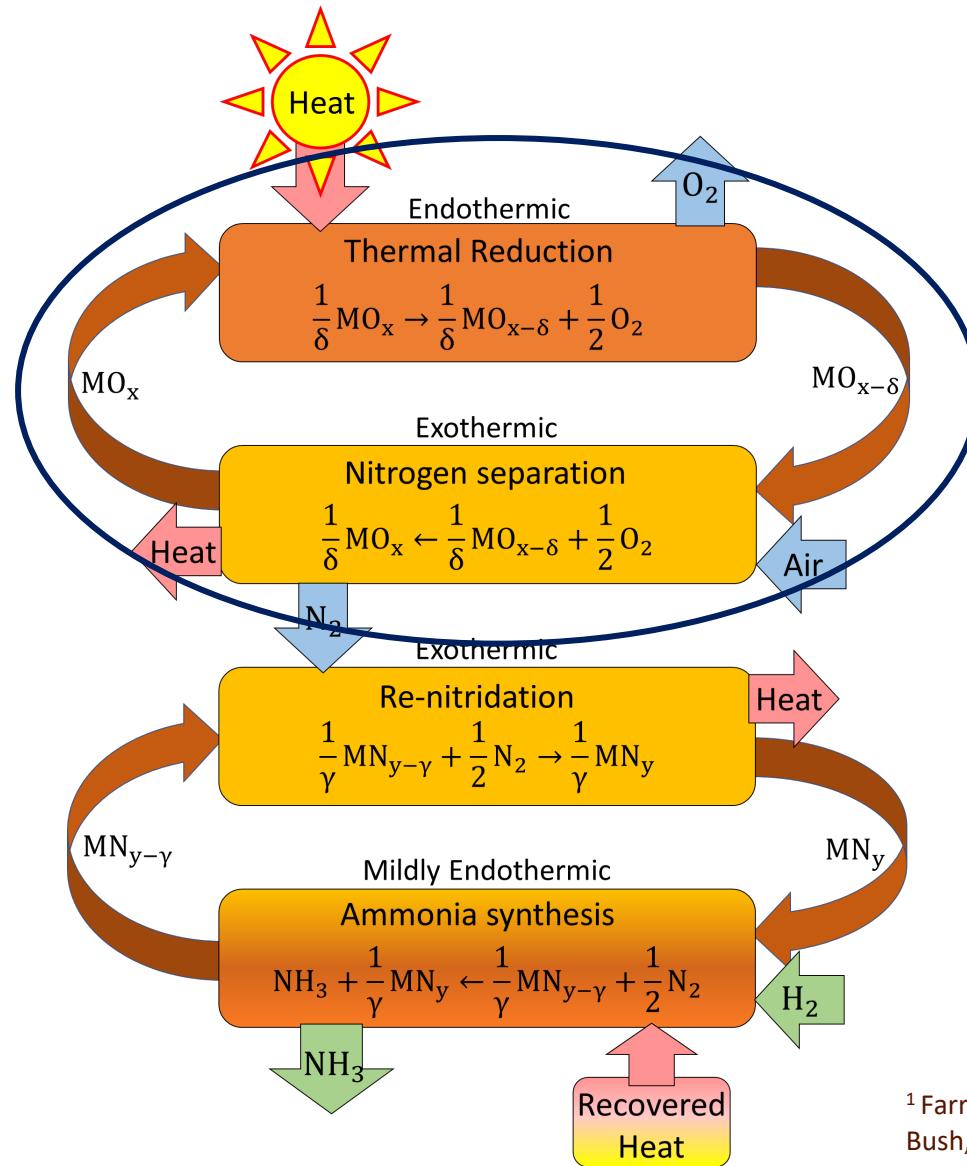
Solar Thermal Ammonia Production (STAP)



An advanced solar thermochemical looping technology to produce and store nitrogen (N_2) from air for the subsequent production of ammonia (NH_3) via an advanced two-stage process

- Inputs are sunlight, air, and hydrogen; the output is ammonia
- Significantly lower pressures than Haber-Bosch
- Greatly decreases or eliminates carbon footprint
- The process consumes neither the oxide nor the nitride particles, which actively participate cyclically

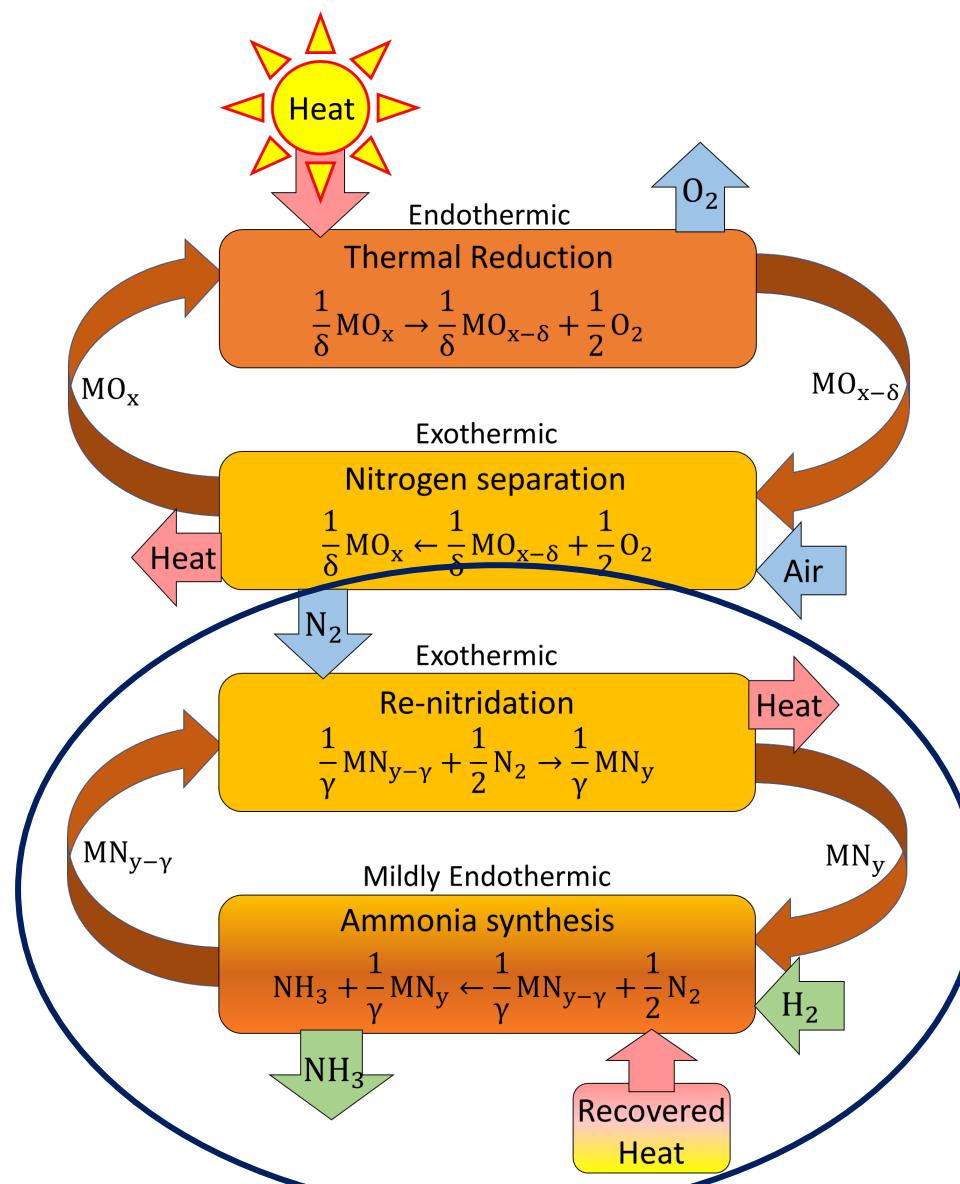
Four Project Thrusts



1. **Nitrogen Separation:** Identify and optimize redox active metal oxide (MOx) materials for N_2 recovery via air separation¹

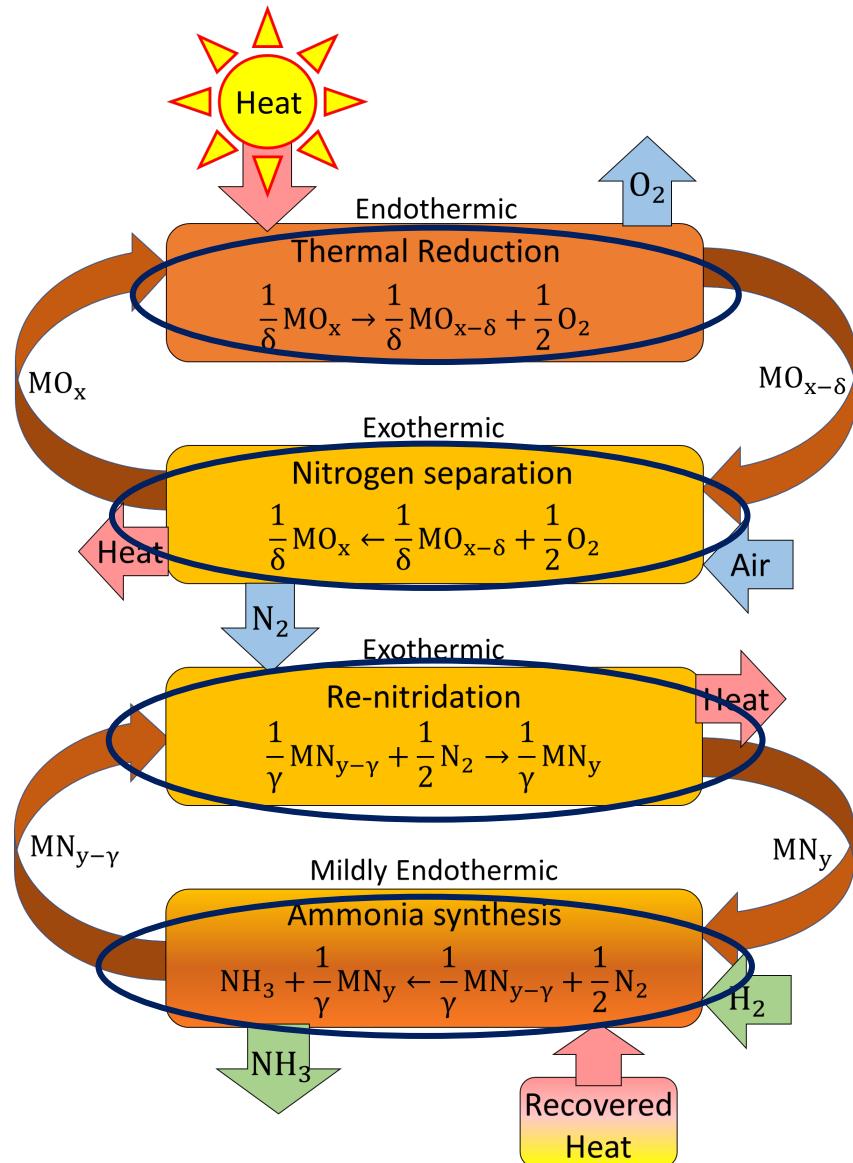
¹ Farr, T. P.; Nguyen, N. P.; Bush, H. E.; Ambrosini, A.; Loutzenhiser, P. G., *Materials* **2020**, *13* (22).
 Bush, H. E.; Nguyen, N. P.; Farr, T.; Loutzenhiser, P. G.; Ambrosini, A., *Solid State Ion.* **2021**, *368*, 115692.
 Nguyen, N. P.; Farr, T. P.; Bush, H. E.; Ambrosini, A.; Loutzenhiser, P. G., *Phys Chem Chem Phys* **2021**, *23* (35), 19280-19288.

Four Project Thrusts



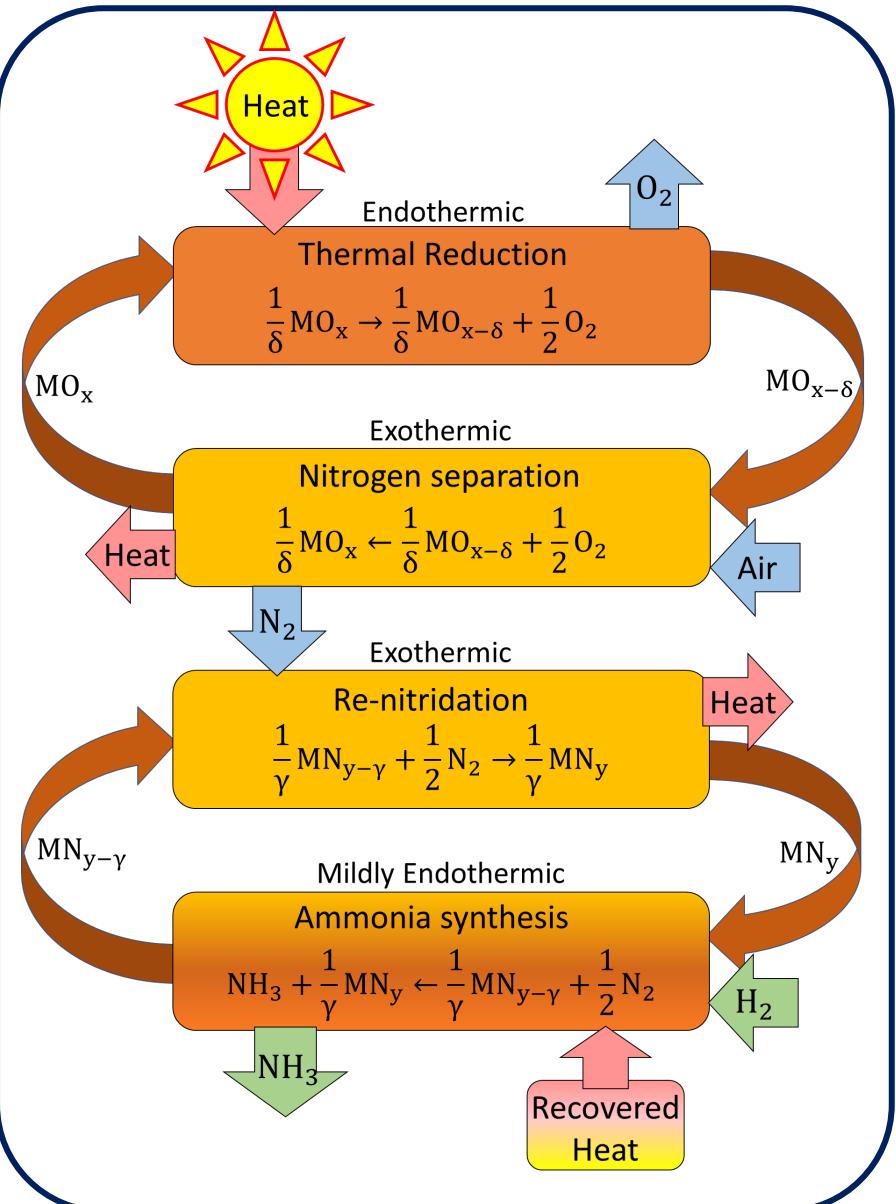
1. **Nitrogen Separation:** Identify and optimize redox active metal oxide (MO_x) materials for N₂ recovery via air separation¹
2. **NH₃ Production:** Identify and optimize “redox active” metal nitride (MN_y) materials for ammonolysis reaction

Four Project Thrusts



1. **Nitrogen Separation:** Identify and optimize redox active metal oxide (MO_x) materials for N₂ recovery via air separation¹
2. **NH₃ Production:** Identify and optimize “redox active” metal nitride (MN_y) materials for ammonolysis reaction
3. **Lab-scale Reactors Modeling, Design, and Testing:** Model and identify design parameters for N₂ separation and NH₃ synthesis bench-scale reactors; construct and test with working materials

Four Project Thrusts

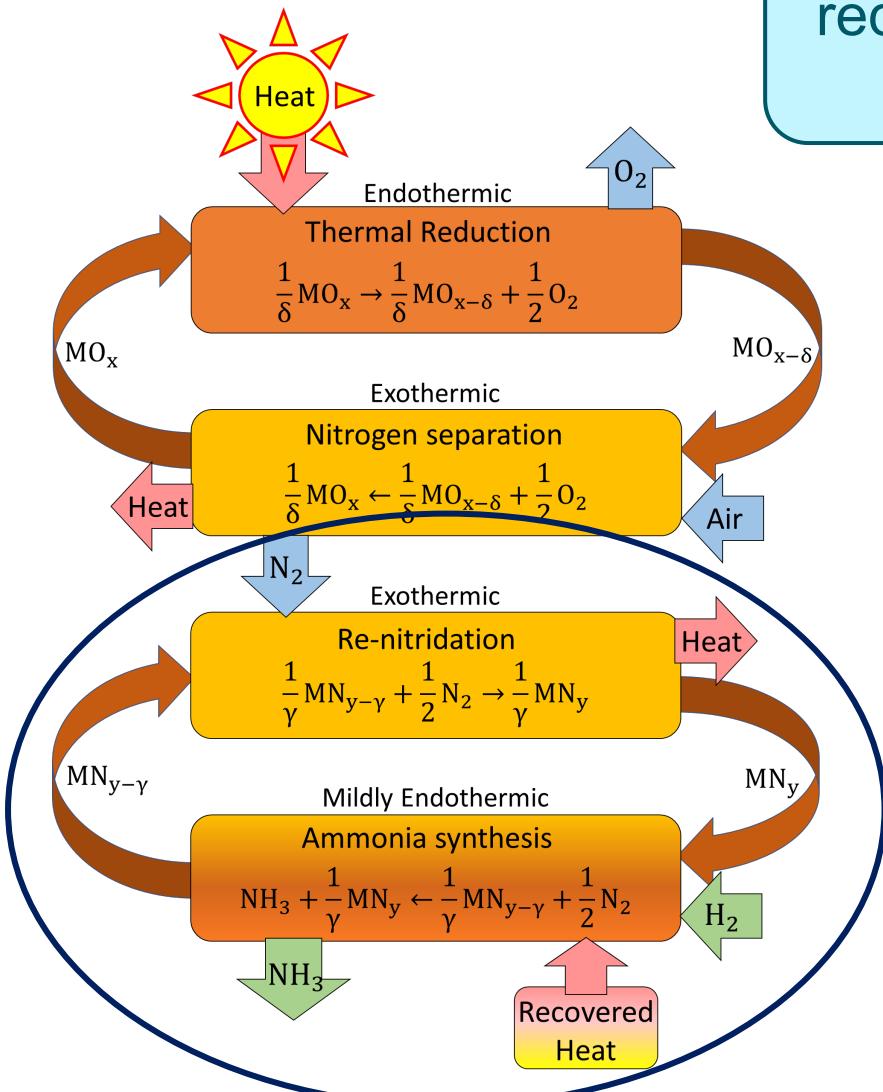


- 1. Nitrogen Separation:** Identify and optimize redox active metal oxide (MO_x) materials for N₂ recovery via air separation¹
- 2. NH₃ Production:** Identify and optimize “redox active” metal nitride (MN_y) materials for ammonolysis reaction
- 3. Lab-scale Reactors Modeling, Design, and Testing:** Model and identify design parameters for N₂ separation and NH₃ synthesis bench-scale reactors; construct and test with working materials
- 4. System and Technoeconomic Analyses:** Develop and refine *throughout the project*, systems and TE models to guide materials choices, reactor design, and determine projected cost for a scaled-up system

NH₃ Production



Identify and optimize metal nitride material (MN_y) that can be reduced by H₂ to produce NH₃, then re-nitridized directly by N₂ to close the cycle



- Nitride is reduced by H₂ to form Mn_{y-γ} + NH₃, then regenerated by N₂ from 1st cycle
- Not as straightforward as oxide development
 - Pool of candidates much smaller
 - Thermodynamics are challenging; NH₃ dissociates at high T
 - Nitrogen diffusion in metal nitrides is slower and less common
 - Synthesis more complex – usually reacting under flowing NH₃ at high T in ammonolysis reaction

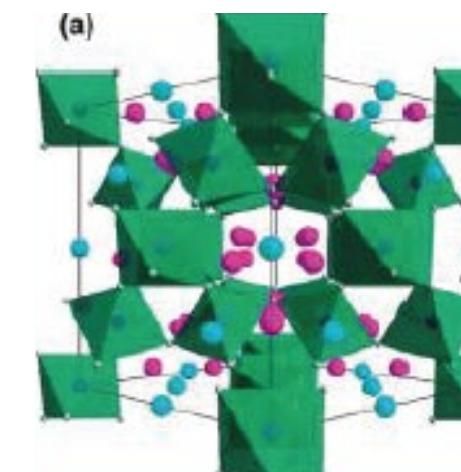
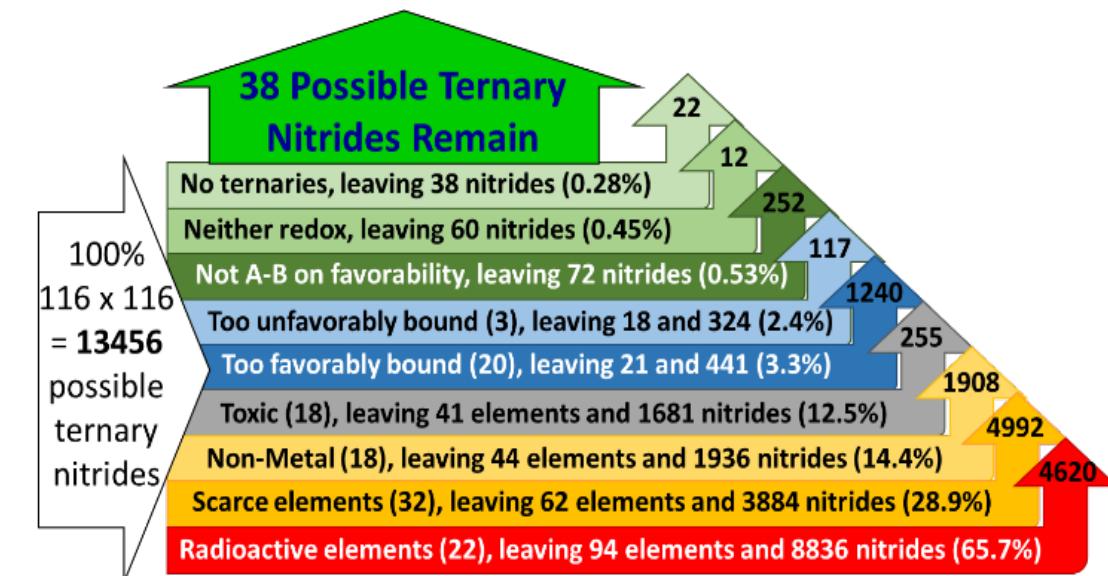
Candidate Identification



- Initial thermodynamic calculations (ASU) imply that candidate must be a ternary nitride (MM'N)
- Preliminary candidate: $\text{Co}_3\text{Mo}_3\text{N}$ (CMN331)
 - Can undergo reversible phase change to CMN661, losing 50 mol% of nitrogen:

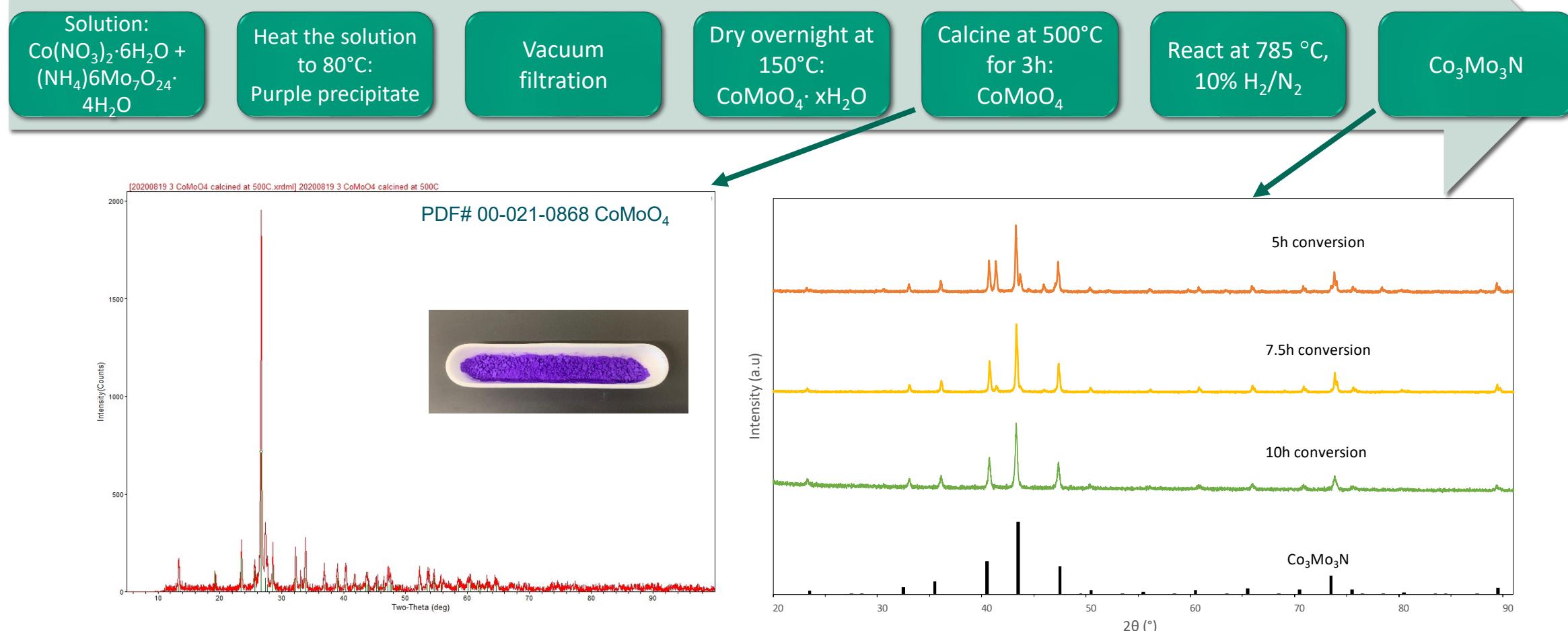


- Both phases crystallize in same space group (Fd-3m) – facilitate kinetics?
- Evidence that material can be regenerated directly by N_2



*Hunter, S.M., Mckay, D., Smith, R.J., Hargreaves, J.S.J., Gregory, D.H., 2010, Chemistry of Materials, 22(9), pp. 2898-2907.
Gregory, D.H., Hargreaves, J.S.J., Hunter, S.M., Catalysis Letters, 2011, 141(1), pp. 22-26.

Synthesis of $\text{Co}_3\text{Mo}_3\text{N}$



Synthesis of oxide precursor followed by nitridation in 10% H_2 results in single phase $\text{Co}_3\text{Mo}_3\text{N}$ under milder synthesis conditions compared to ammonolysis¹

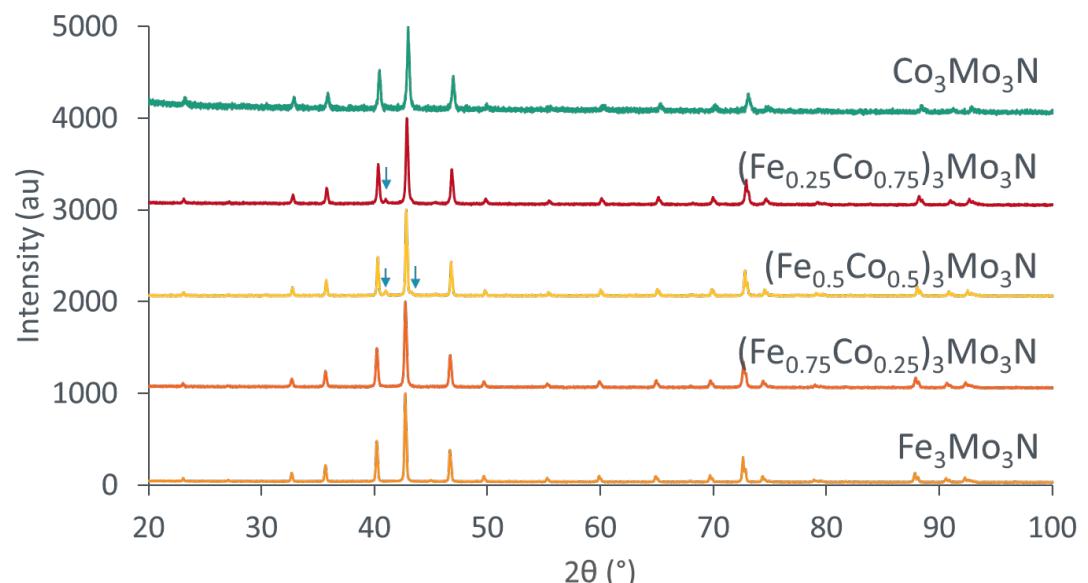
¹Hunter, S. M., et al., *Chem Mater* **2010**, 22 (9), 2898.

Expanding the Materials Space



A family of single-phase A_3B_xN ($A=Co, Ni, Fe$; $B=Mo, W$; $x = 2, 3$) ternary and quaternary nitride solid solutions synthesized

Composition Target	Phase (> 95% via XRD)
Co_3Mo_3N	331
$(Co_xNi_{1-x})_2Mo_3N$ ($x = 0.25, 0.5, 0.75$)	231
Ni_2Mo_3N	231
$(Fe_xNi_{1-x})_2Mo_3N$ ($x = 0.25, 0.5$)	231
Fe_3Mo_3N	331
$(Co_xFe_{1-x})_3Mo_3N$ ($x = 0.25, 0.5, 0.75$)	331
$Co_3(W_xMo_{1-x})_3N$ ($x = 0.005 - 0.05$)	331
$(Ni_xCo_{1-x})_3Mo_3N$ ($x = 0.005 - 0.05$)	331



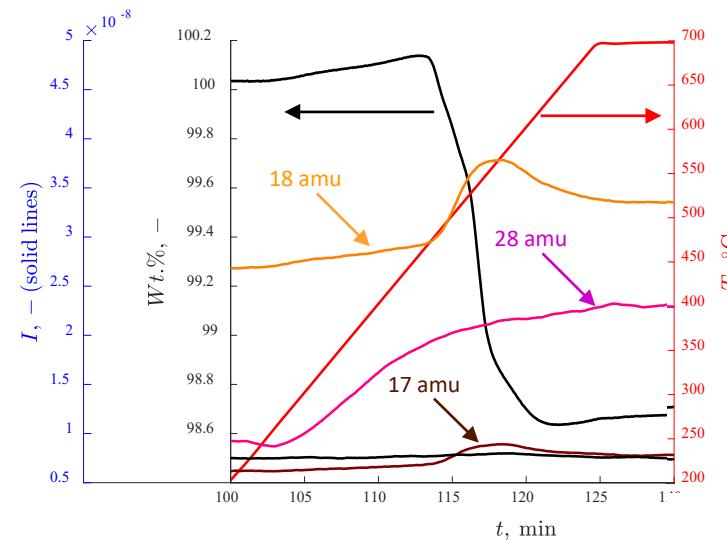
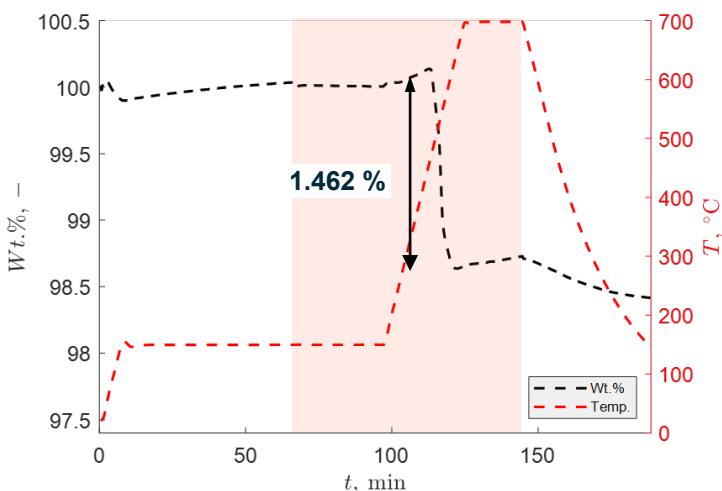
- W > 5% in Co_3Mo_3N ("331") B-site substitution leads to phase segregation and reluctance to nitridize
- Ni > 5% in Co_3Mo_3N A-site substitution leads to phase segregation and preference of Ni_2Mo_3N ("231") structure
- Synthesis attempts of Mn- and Zn- based ternaries didn't yield nitrides

$\text{Co}_3\text{Mo}_3\text{N} \rightarrow \text{Co}_6\text{Mo}_6\text{N}$ Reduction via TGA

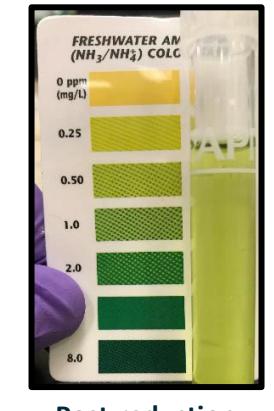
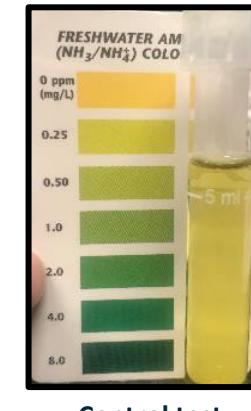
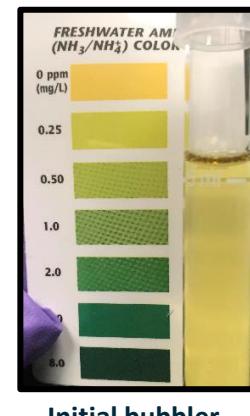
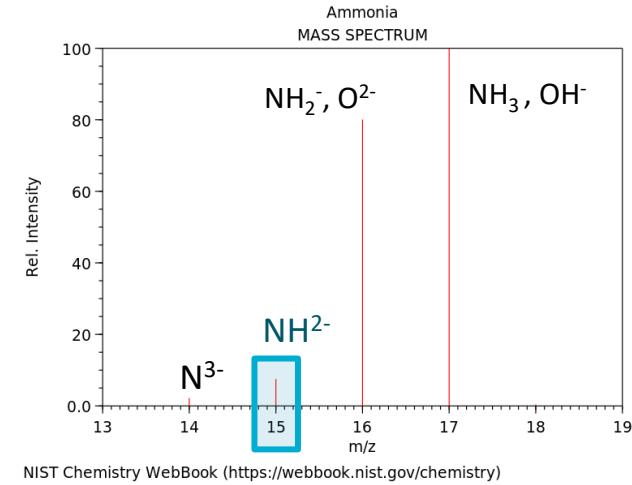


- 500-700 °C under 3:1 H₂:Ar flow on Thermogravimetric Analyzer (TGA) connected to Residual Gas Analyzer (RGA)
- Total mass loss is close to theoretical for full conversion to Mo₆Co₆N (1.46%)
- NH₃ production conf via RGA inconclusive
 - Reduction conditions (low p, high T) favor NH₃ dissociation
 - m/z overlap with H₂O, N₂: 15 amu (NH²⁻) is the only fragment with no “competition”
- Partial solution: Test DI H₂O from bubbler using salicylate NH₃ test kit
 - Ammonia detected from CMN331 reduction compared to reference (blank) sample

Combined with RGA/XRD results, detection of NH₃ with test kit provides strong evidence of CMN331 reduction and NH₃ formation



IST SYMPOSIUM ON AMMONIA ENERGY

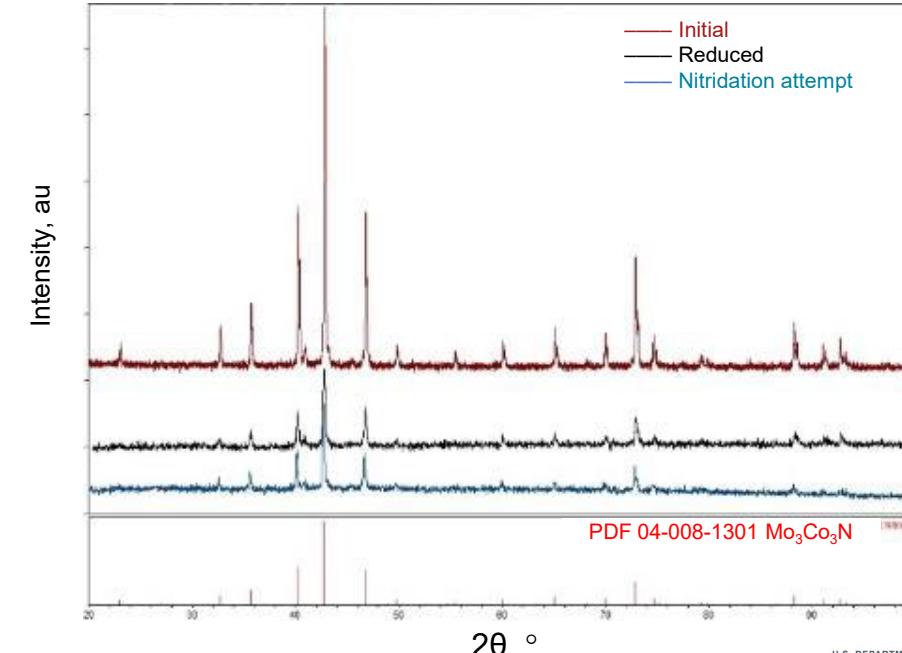
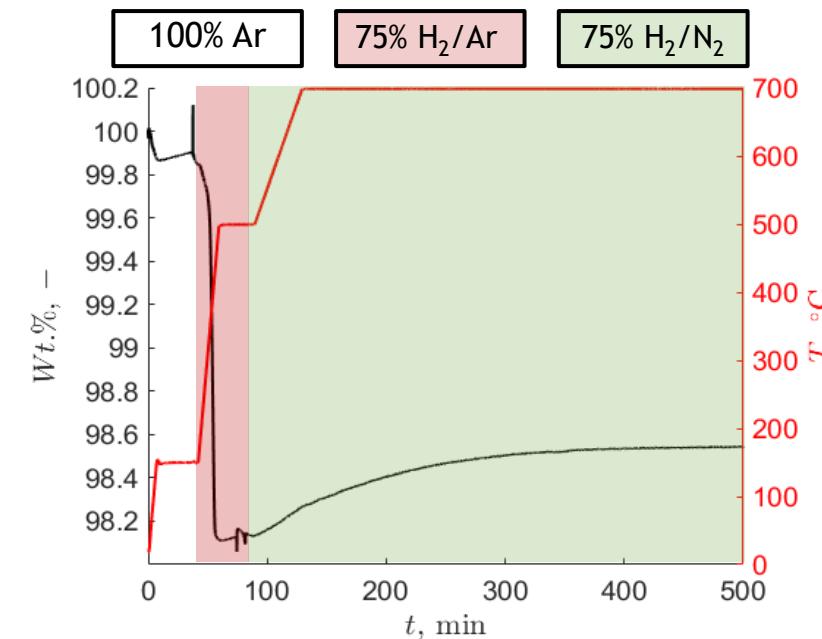


CMN66 I → 33 I: Re-nitridation



- H_2/N_2 TGA reduction at varying T and $[\text{H}_2]$
- Minimal re-nitridation attained
 - Maximum of 0.41% at 700 °C, 75% H_2/N_2
 - No change in observed in XRD (right)
- $[\text{H}_2] > 0\%$ necessary
 - Acts as a getter for residual O_2
 - “Runaway” linear mass gain under pure N_2
 - Potential oxidation from small O_2 impurity in sweep

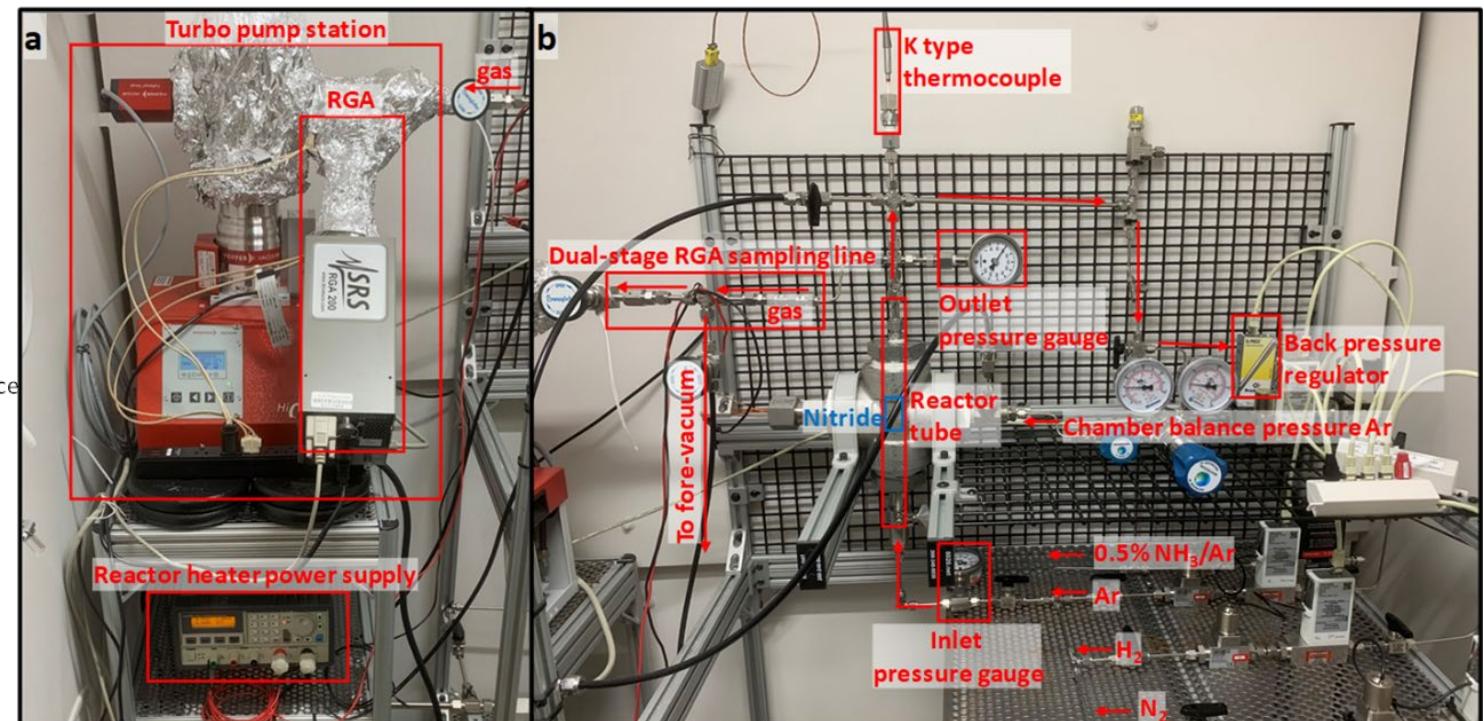
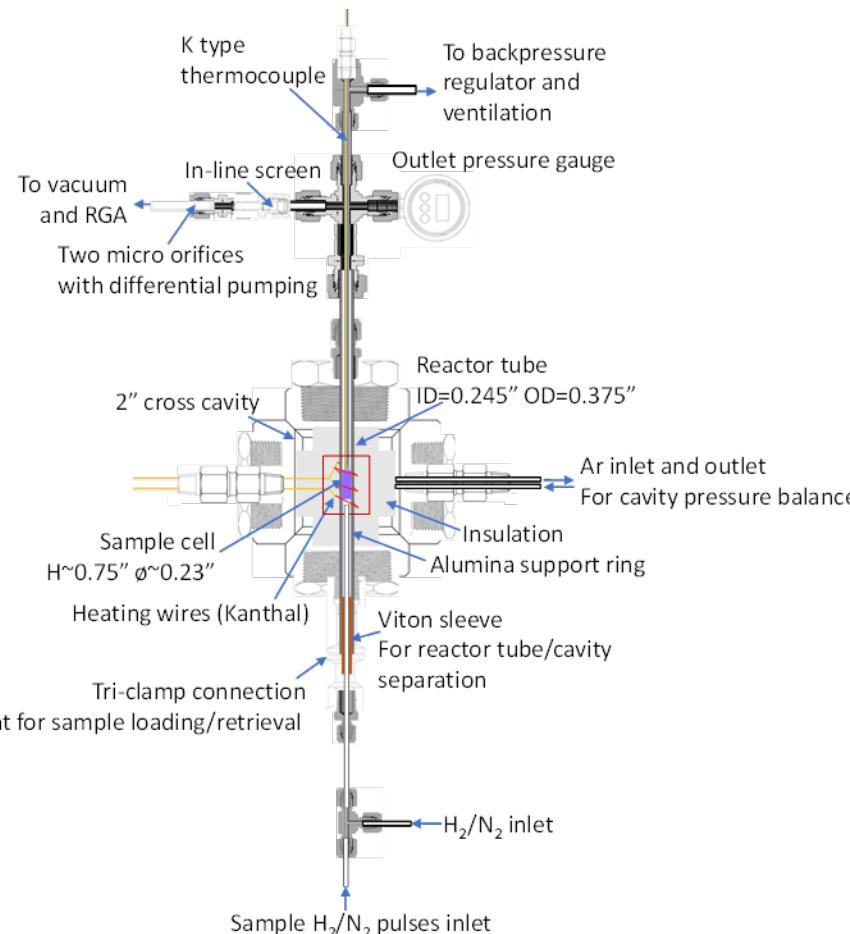
Full re-nitridation not favorable under ambient conditions



Ammonia Synthesis Reactor (ASR)



Reactor designed to perform NH_3 synthesis and nitride re-nitridation reaction under variable pressure and temperature, up to 30 bar and 800 °C, respectively



ASR Cycle Results



Steady production rates were calculated using averages of the last 10 min of stabilized rate data before cool-down

Reacted solid-state nitrogen was calculated by adding NH₃ yield and two times of N₂ yield (theoretical max CMN331 → CMN661 = 0.5)

Selectivity to NH₃ was calculated by percentage of NH₃ yield in the reacted solid-state nitrogen

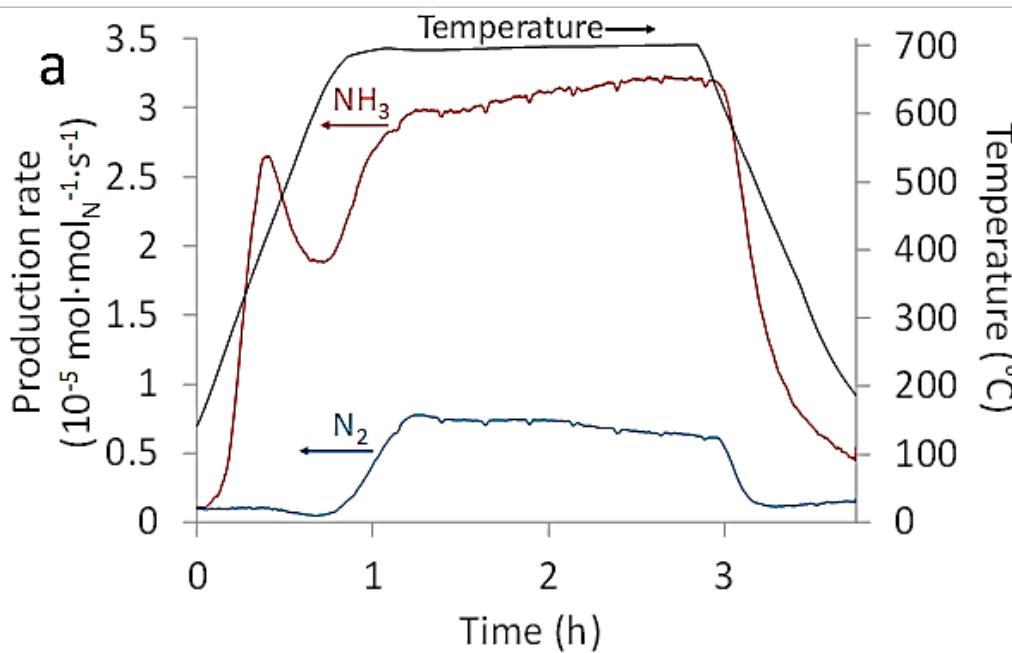
Reduction step	P(H ₂) bar	T _{hold} °C	t _{hold} h	Steady r(NH ₃) 10 ⁻⁵ mol mol _N ⁻¹ s ⁻¹	Steady r(N ₂) 10 ⁻⁵ mol mol _N ⁻¹ s ⁻¹	NH ₃ yield mol/mol _N	N ₂ yield mol/mol _N	Reacted solid-state nitrogen mol mol _N ⁻¹	Selectivity to NH ₃
2	20	700	2	2.32	0.455	0.121	0.0610	0.243	49.8%
3	20	700	2	2.93	0.923	0.151	0.111	0.372	40.5%
4	20	700	2	4.27	0.985	0.271	0.113	0.498	54.5%
5	20	700	2	2.86	0.413	0.154	0.0496	0.253	60.8%
6	20	700	2	3.20	0.643	0.183	0.0742	0.331	55.2%
7	20	700	2	3.29	0.792	0.225	0.0842	0.393	57.2%
8	20	600-720	0.5×5	--	--	0.180	0.0641	0.308	58.4%
9	15	600-720	0.5×5	--	--	0.148	0.0510	0.250	59.1%
10	10	600-720	0.5×5	--	--	0.0995	0.0506	0.201	49.6%
11	5	600-720	0.5×5	--	--	0.0428	0.0382	0.119	35.9%

Cycling runs (constant T, pH₂, t)

- All re-nitridation steps were performed with 20 bar of 10% H₂/N₂ at 700 °C
- Sample held at 5 sccm H₂ / 15 sccm Ar overnight, 1.2 atm, 120 °C

All cycles on same Co₃Mo₃N sample – **Reaction is cyclic**

Ammonia Production and Re-nitridation of CCM33I

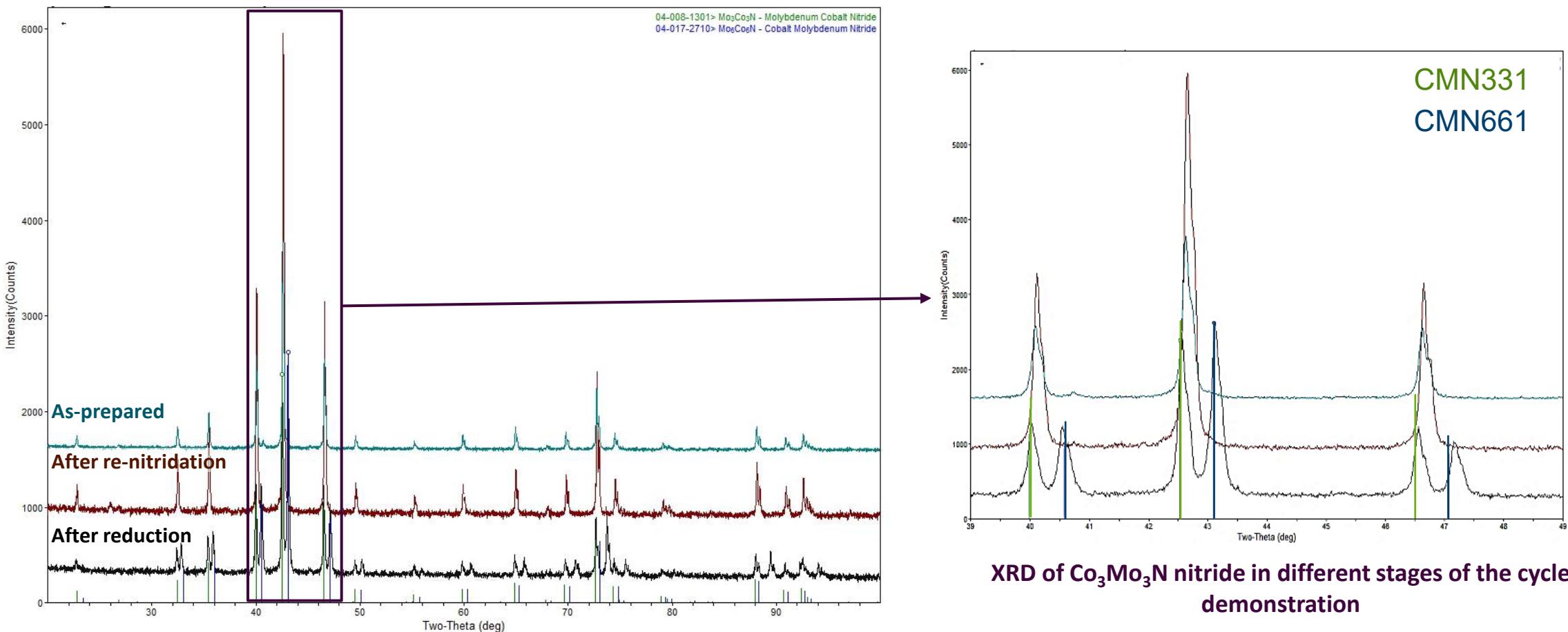


NH_3 , N_2 production rates and temperature profile of representative reduction step under 100% H_2 (Cycle 6)

- Initial NH_3 peak assumed to be hydrogenation of surface adsorbed N_2
- At $T > 600 \text{ }^{\circ}\text{C}$, consistent co-production of NH_3 and N_2 in 100% H_2 (no external N_2 feed)
- Sample can be re-nitridized under 100% N_2 at same with no side-reactions observed
 - $P = 20 \text{ bar}$, $T = 700 \text{ }^{\circ}\text{C}$ for both reactions
- Production rates fairly flat in all the reduction steps with no evident dependence on the consumed solid-state nitrogen, as would be expected from catalytic Mars-van Krevelen mechanism

Results show that lattice nitrogen participates in NH_3 production in reversible CCM33I \rightarrow CCM661 bulk reaction

Powder X-ray Diffraction



- Partial conversion to 661 after reduction (both 331 and 661 phases observed), consistent with bulk reacted N analysis of < 0.5
 - Reaction mechanism requires additional experimentation
- Regeneration to 331 after re-nitridation with no sign of secondary phase

ASR Cycle Results



Steady production rates were calculated using averages of the last 10 min of stabilized rate data before cool-down

Reacted solid-state nitrogen was calculated by adding NH_3 yield and two times of N_2 yield

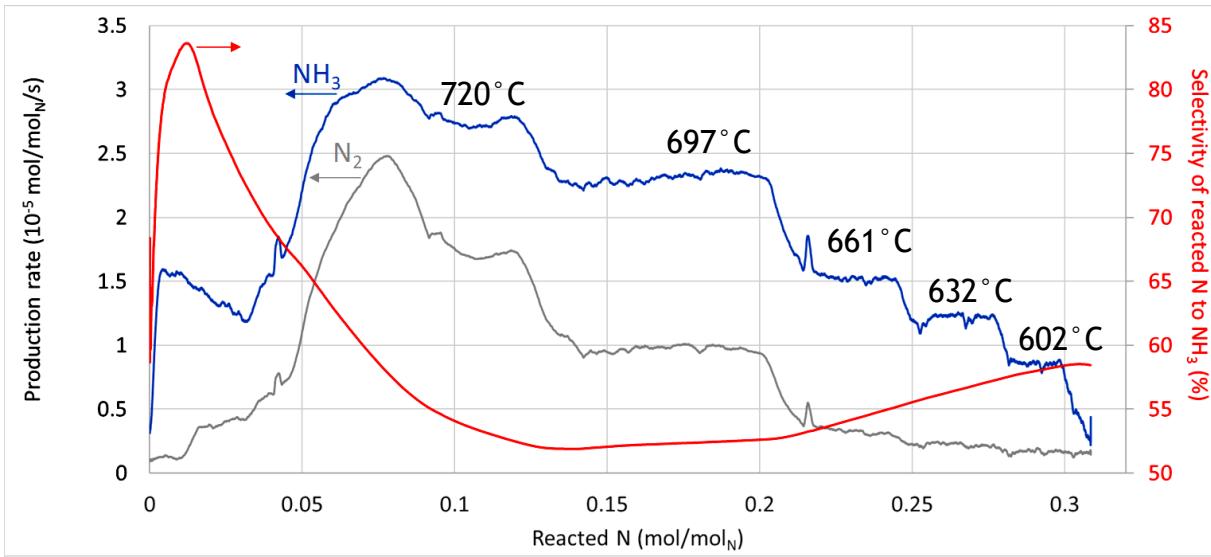
Selectivity to NH_3 was calculated by percentage of NH_3 yield in the reacted solid-state nitrogen

Reduction step	$P(\text{H}_2)$ bar	T_{hold} °C	t_{hold} h	Steady $r(\text{NH}_3)$ $10^{-5} \text{ mol mol}_{\text{N}}^{-1} \text{ s}^{-1}$	Steady $r(\text{N}_2)$ $10^{-5} \text{ mol mol}_{\text{N}}^{-1} \text{ s}^{-1}$	NH_3 yield $\text{mol/mol}_{\text{N}}$	N_2 yield $\text{mol/mol}_{\text{N}}$	Reacted solid-state nitrogen $\text{mol mol}_{\text{N}}^{-1}$	Selectivity to NH_3
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T steps at varying pH_2

- All re-nitridation steps were performed with 20 bar of 10% H_2/N_2 at 700 °C
- Sample held at 5 sccm H_2 / 15 sccm Ar overnight, 1.2 atm, 120 °C
- Selectivity for Cycles 8-11 calculated over entire run

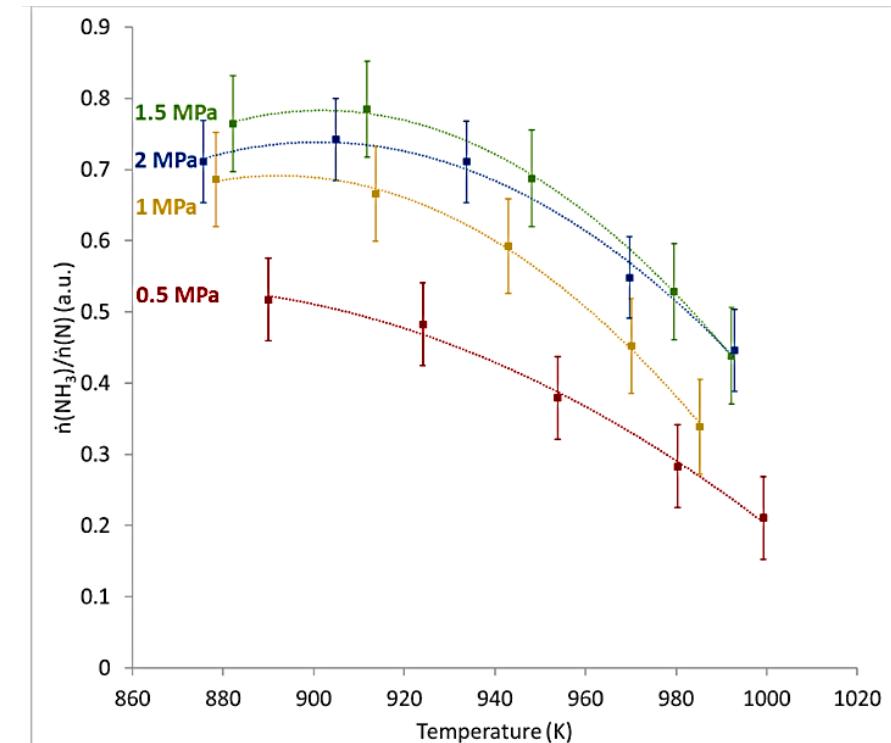
Temperature Step Reduction



NH_3 , N_2 production rates and selectivity of reacted nitrogen to NH_3 as a function of reacted nitrogen in a temperature stepping reduction experiment (20 bar, 100% H_2 , 8th cycle)

- NH_3 selectivity decreases with increasing T
- Production rates drop dramatically when $T < 600$ °C
- Haber–Bosch process reported conversion rate of ~ 10–15% at $T = 425$ –450 °C, $P > 100$ atm

~650 °C ensures sufficient NH_3 rates while keeping selectivity to NH_3 high

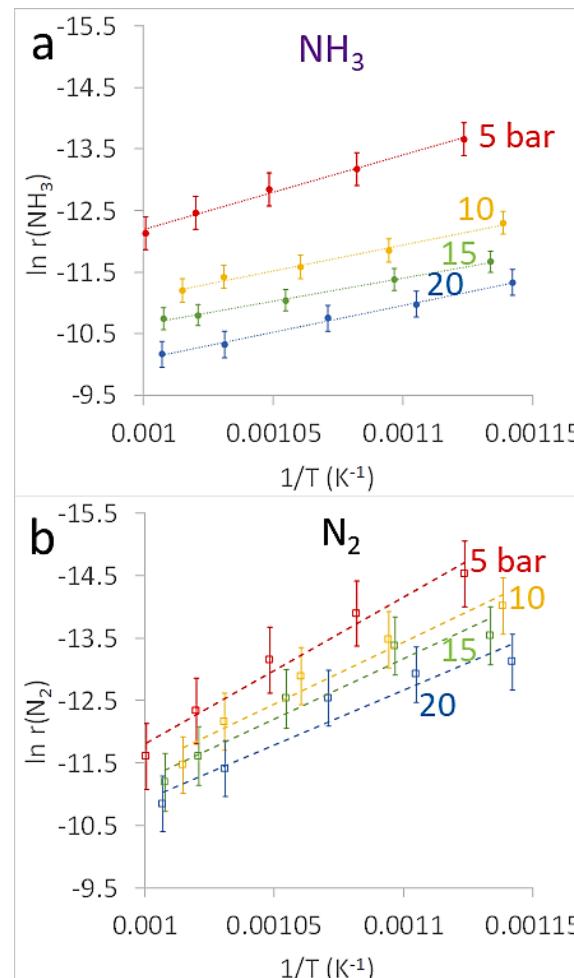


NH_3 selectivity as a function of temperature at varying PH_2

Determination of Activation Energy

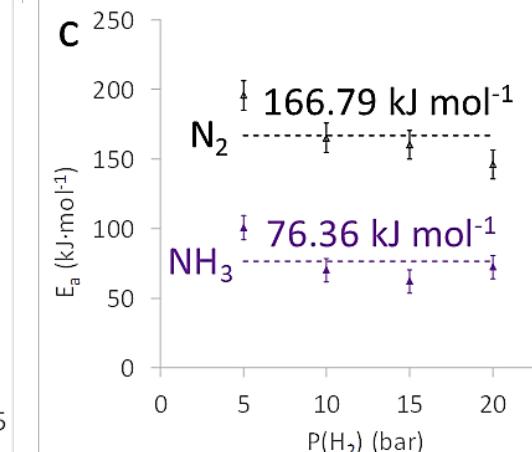
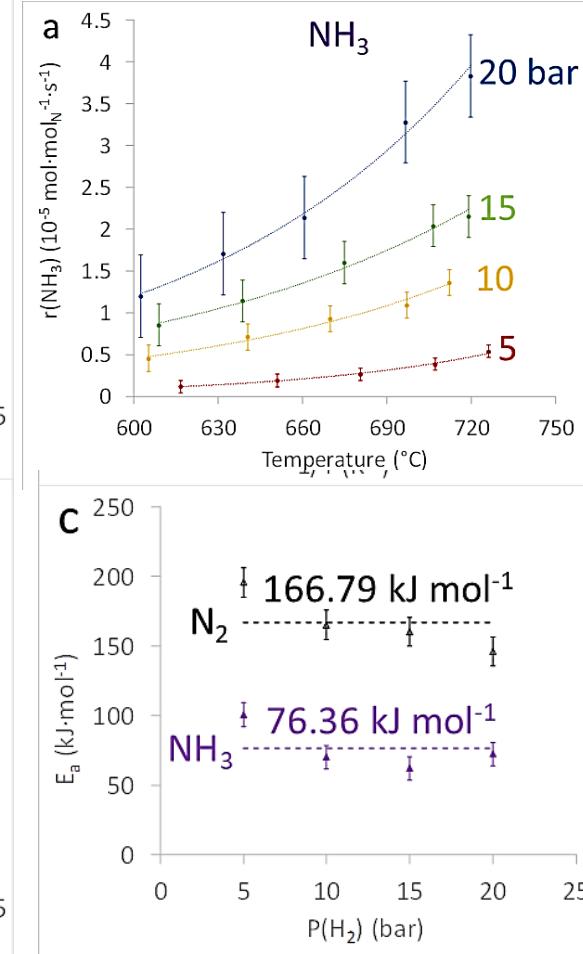


- E_a ranges from 40 (HB) -120 kJ/mol for a variety of heterogeneous catalysts
- $E_a = 54$ kJ/mol reported for Cs-promoted $\text{Co}_3\text{Mo}_3\text{N}$ at constant conversion using the activity data at $T = 320\text{-}440$ °C, $P = 50$ bar
- Current (unoptimized) reduction rates order of magnitude lower than reported CNM catalysts
- Difficult to directly compare catalyst vs bulk reaction



Activation energies for NH_3 and N_2 formation evaluated from the Arrhenius equation, at varying pressures

NH_3 production rates as a function of T and $P(\text{H}_2)$



NH_3 production demonstrated at slightly higher T and much lower P (~650 °C, ~20 bar) compared to H-B (~450 °C, ~200 bar)

Conclusions



- Solar Thermal Ammonia Production has the potential to synthesize ammonia in a green, renewable process that can greatly reduce the carbon footprint left by conventional Haber-Bosch reaction
- Ternary nitrides in the family A_3B_xN ($A=Co, Ni, Fe$; $B=Mo$; $x=2,3$) identified as a potential candidate for NH_3 production
- Experiments with Co_3Mo_3N in Ammonia Synthesis Reactor demonstrate cyclable NH_3 production from bulk nitride under pure H_2
 - Production rates were fairly flat in all the reduction steps with no evident dependence on the consumed solid-state nitrogen, as would be expected from catalytic Mars-van Krevelen mechanism
 - Material can be re-nitridized under pure N_2
- Bulk nitrogen per reduction step average between 25 – 40% of the total solid-state nitrogen
- Selectivity to NH_3 stabilized at 55 – 60% per cycle
- Production rates (NH_3 and N_2) become apparent above 600 °C at $P(H_2) = 0.5 – 2$ bar
- Optimal point of operation to keep selectivity high without compromising NH_3 rates currently estimated at 650 °C and 1.5 - 2 bar
- Next steps: optimize production rates, examine effect of N_2 addition in NH_3 synthesis reaction, test additional ternary nitrides

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THANK YOU FOR YOUR ATTENTION