

1 September, 2022

PC11

SOLAR-THERMAL AMMONIA PRODUCTION VIA A NITRIDE LOOPING CYCLE

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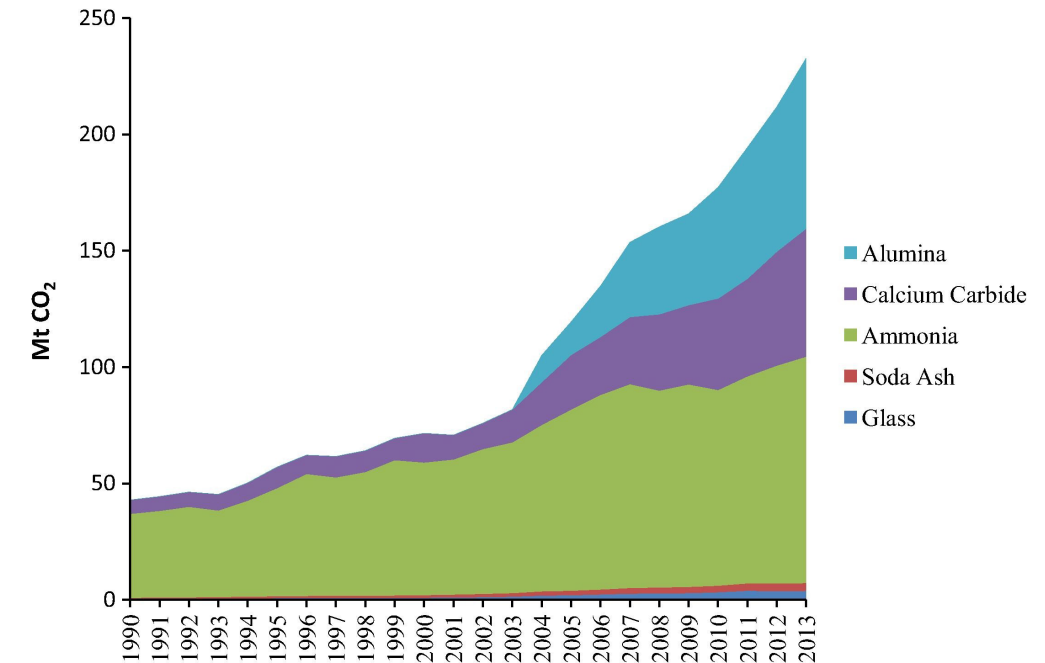
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Introduction



- 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



Industrial process emissions (China) from the production of alumina, plate glass, soda ash, ammonia and calcium carbide in 1990–2013. (Liu, Z. (2016). *Applied Energy* **166**: 239.)

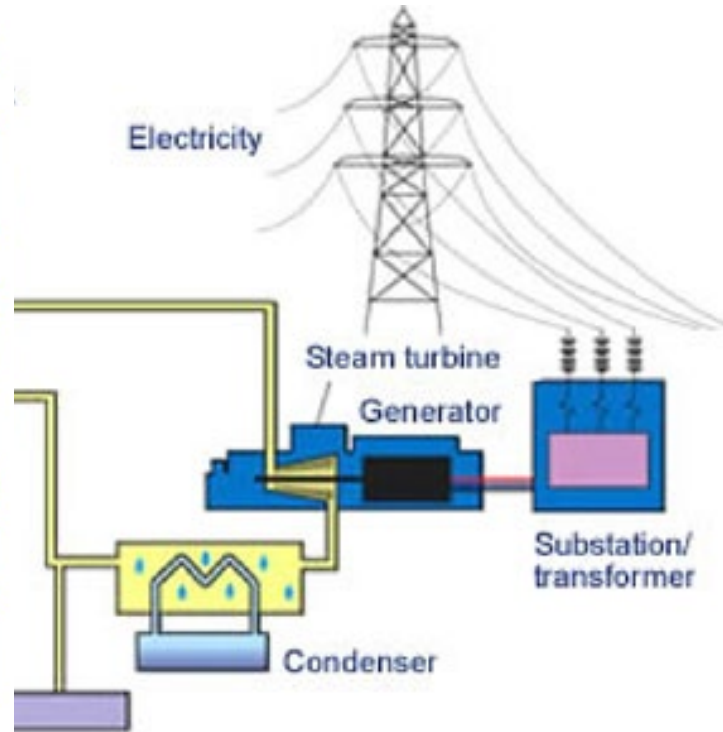
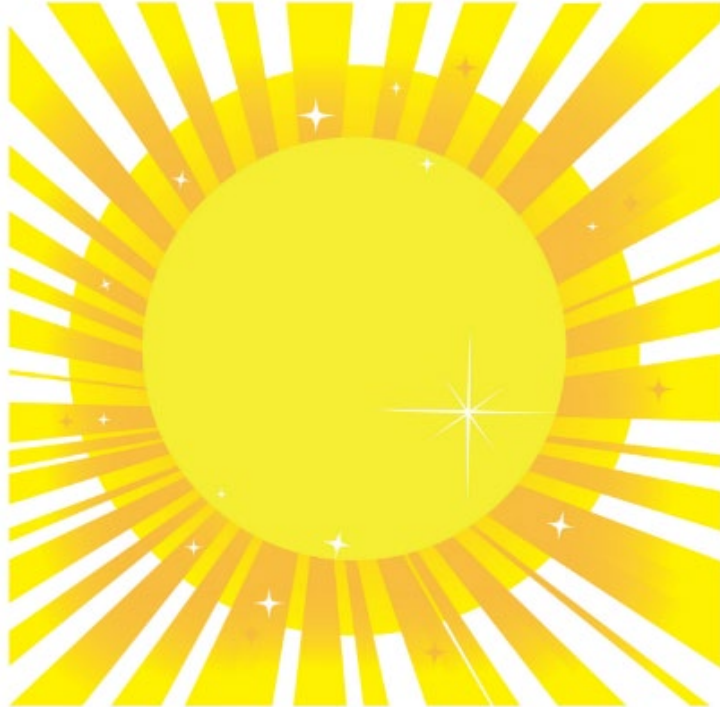
Production of NH_3 via a renewable, carbon-neutral technology powered by concentrating solar can mitigate climate and CO_2 impacts

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



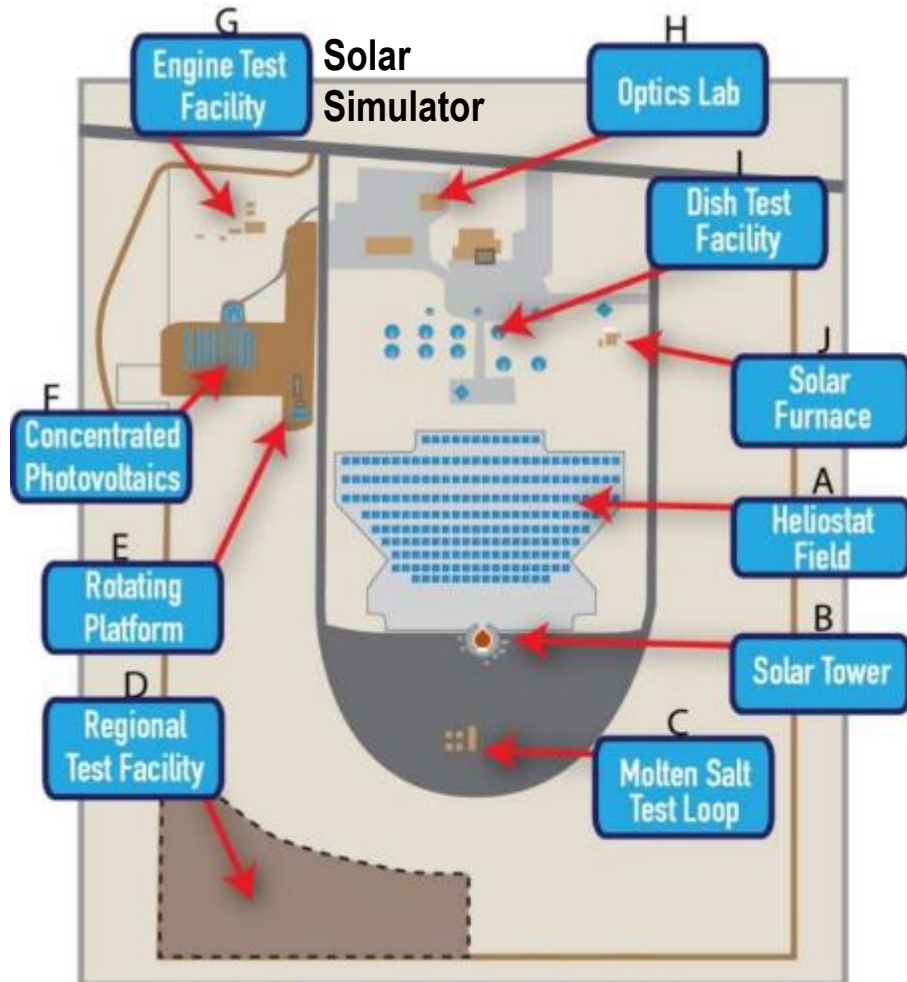
Coal-Fired Power Plant

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

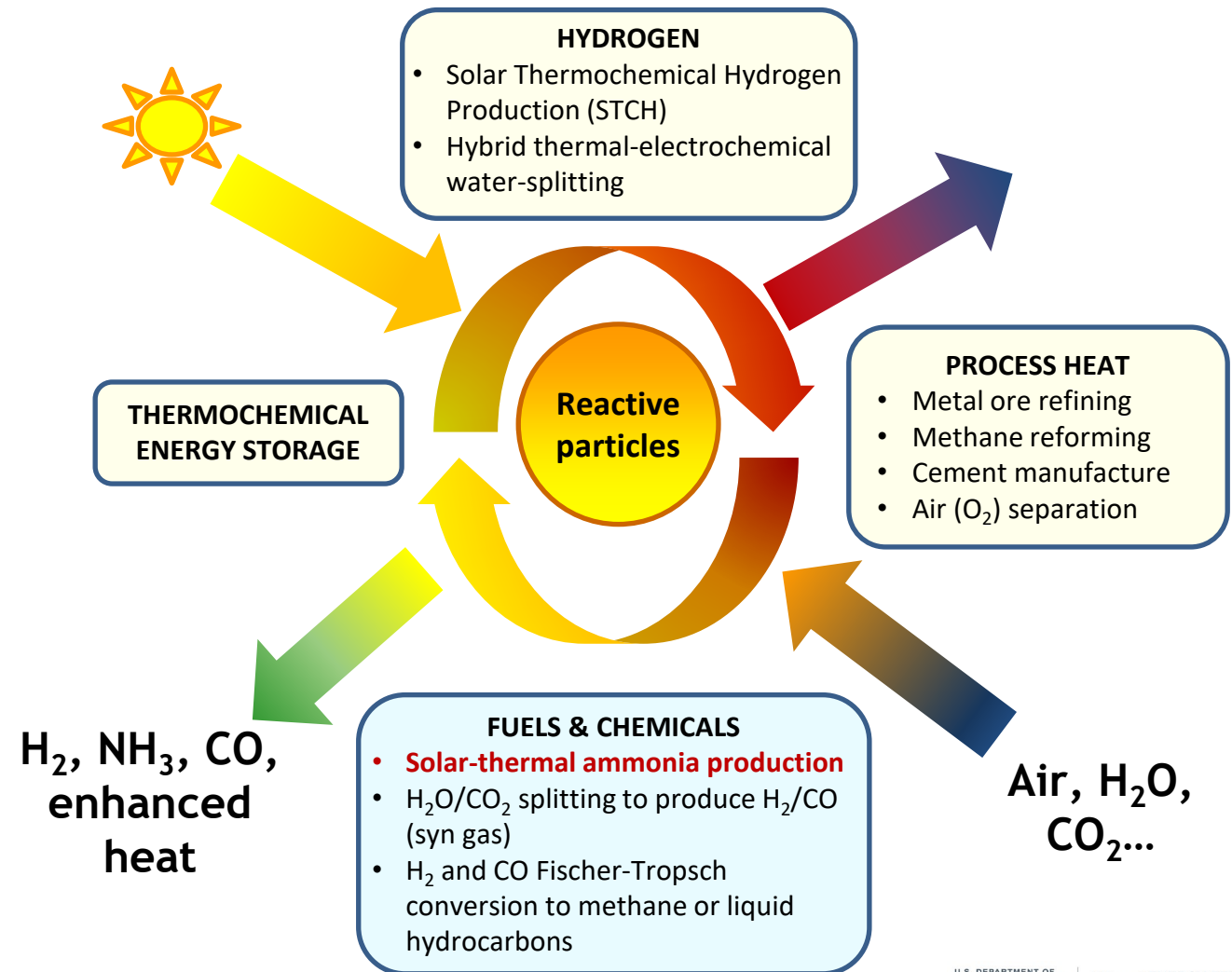


Solar Thermochemistry (STC)

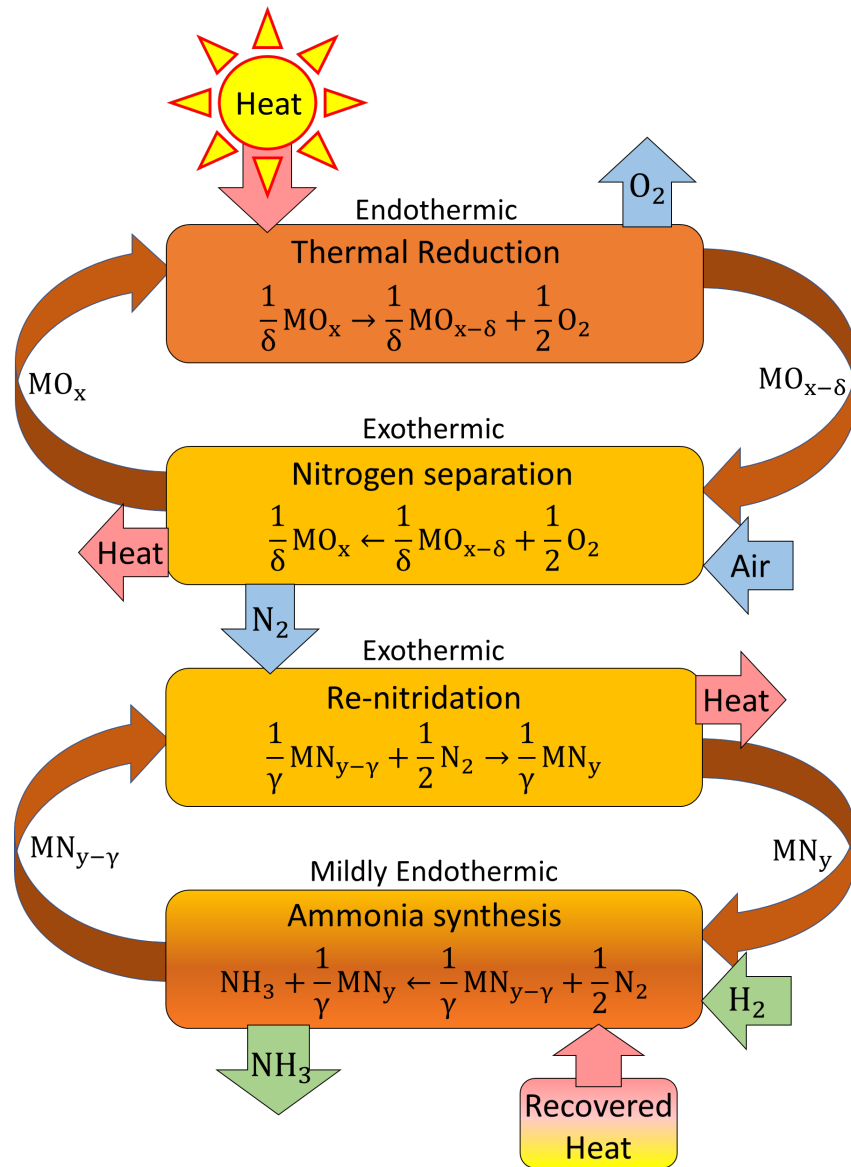


Solar thermochemistry harnesses concentrated solar heat to drive chemical reactions that would normally be energy- or resource-intensive

- 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



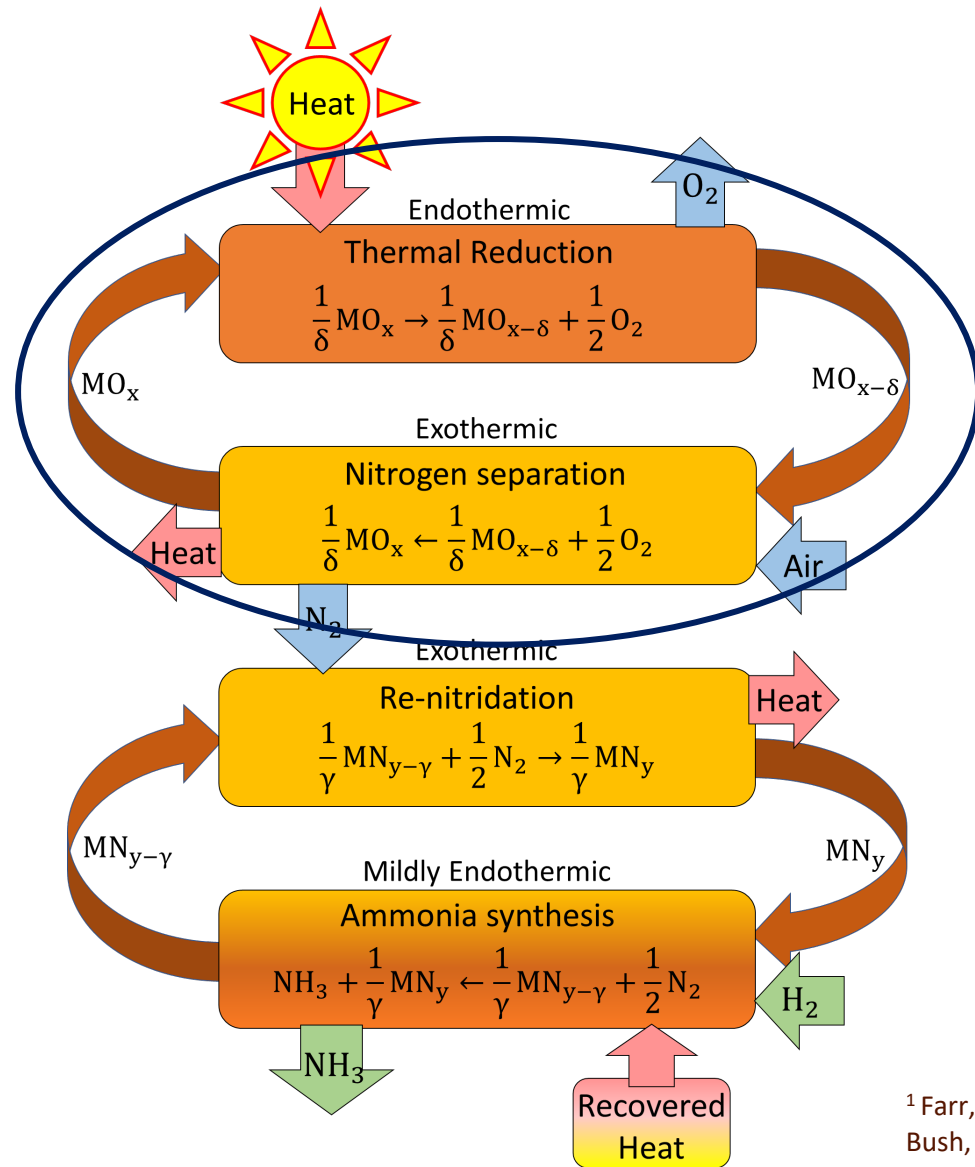
Solar Thermal Ammonia Production (STAP)



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



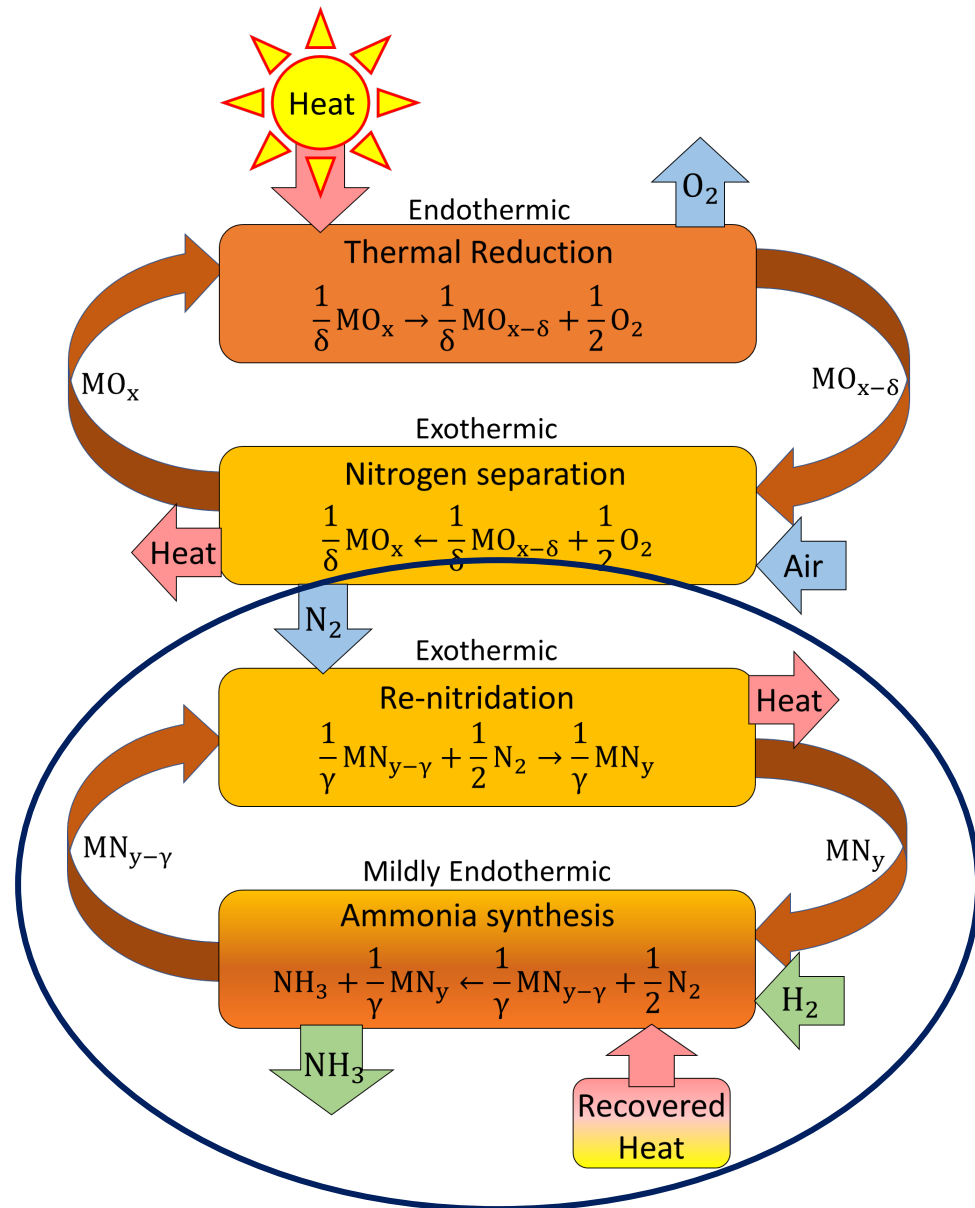
1. Nitrogen Separation: Identify and optimize redox active metal oxide (MO_x) materials for N_2 recovery via air separation¹

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.

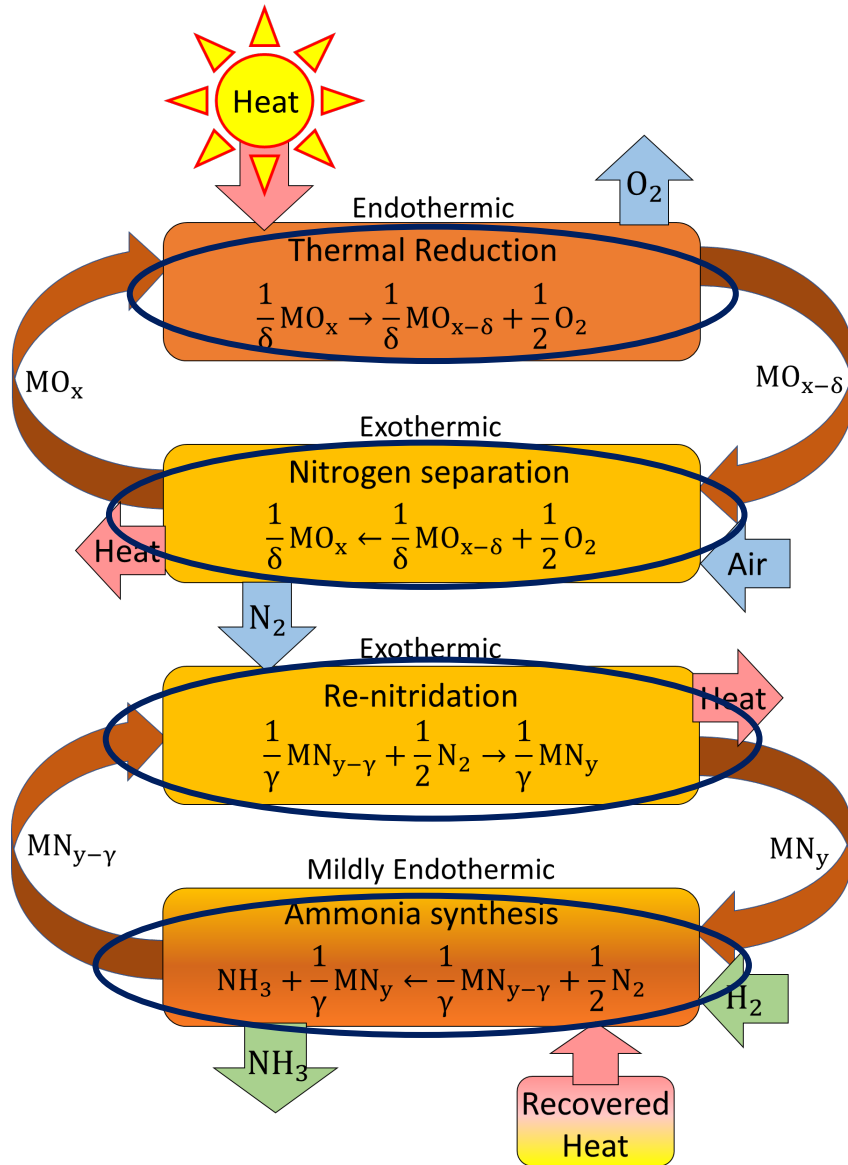
Nguyen, N. P.; Farr, T. P.; Bush, H. E.; Ambrosini, A.; Loutzenhiser, P. G., *Phys Chem Chem Phys* **2021**, 23 (35), 19280-19288.

Four Project Thrusts



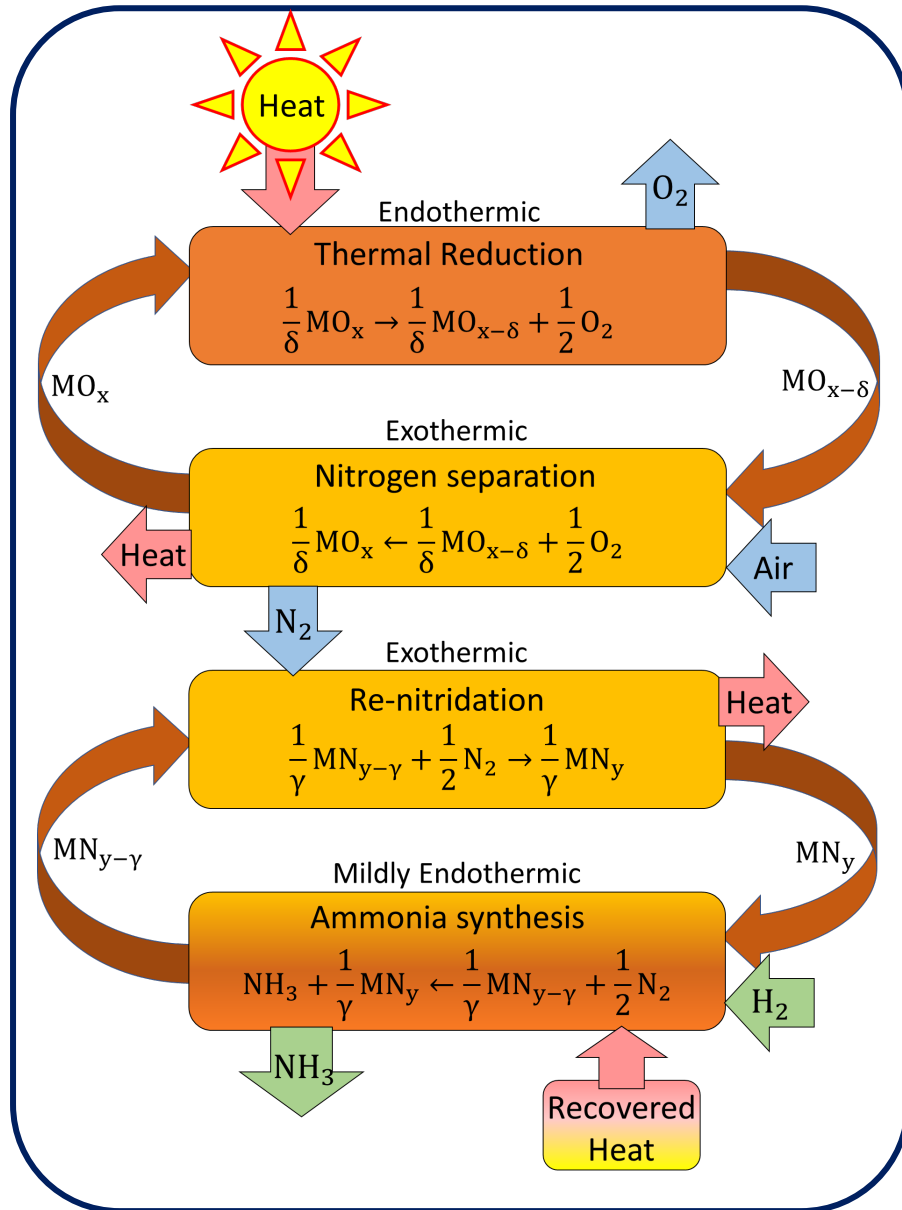
1. Nitrogen Separation: Identify and optimize redox active metal oxide (MO_x) materials for N_2 recovery via air separation¹
2. NH_3 Production: Identify and optimize “redox active” metal nitride (MN_y) materials for ammonolysis reaction

Four Project Thrusts



1. Nitrogen Separation: Identify and optimize redox active metal oxide (MO_x) materials for N_2 recovery via air separation¹
2. NH_3 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 N_2 separation and NH_3 synthesis bench-scale reactors; construct and test with working materials

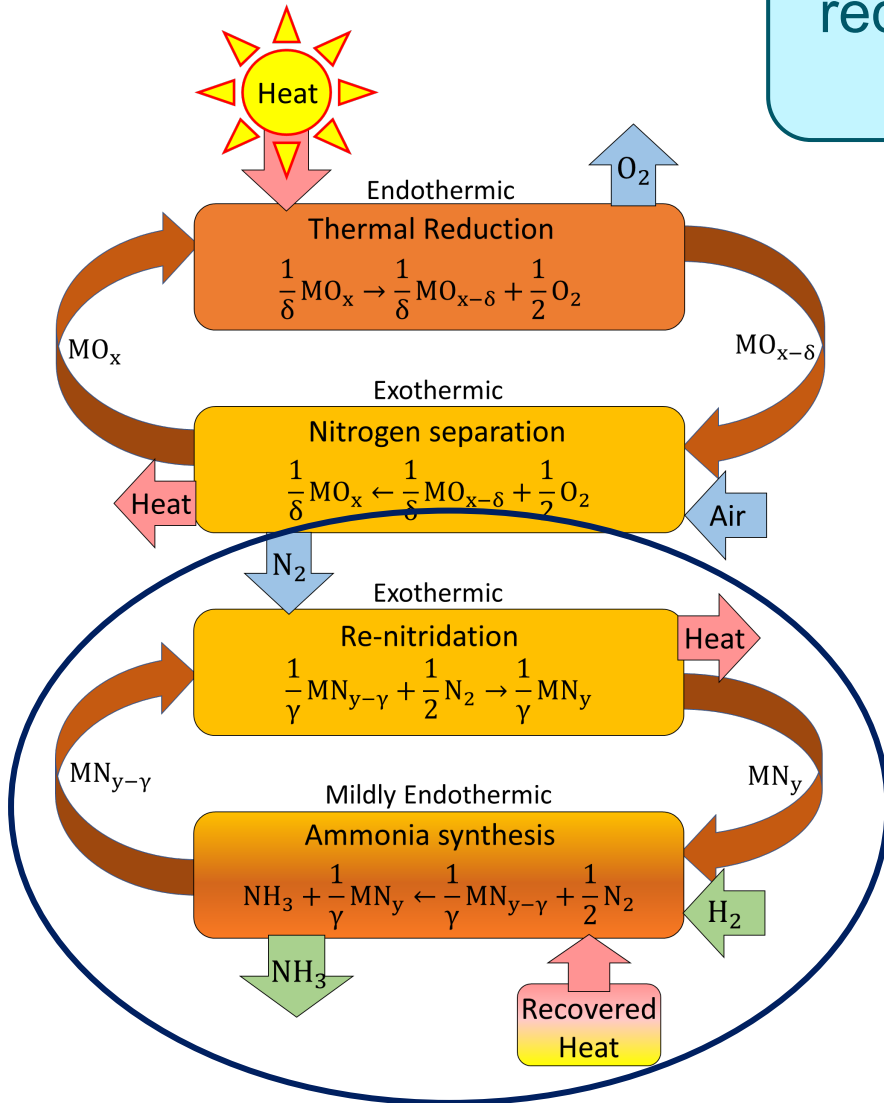
Four Project Thrusts



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



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



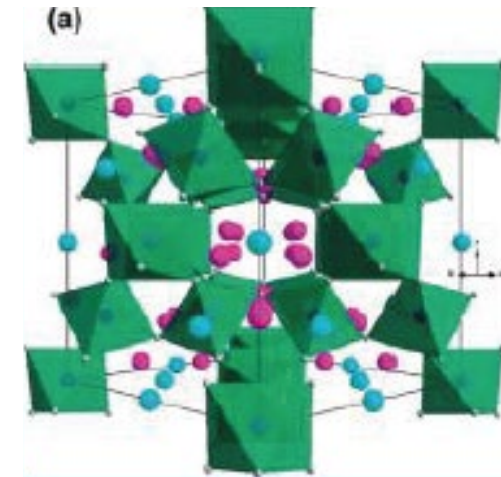
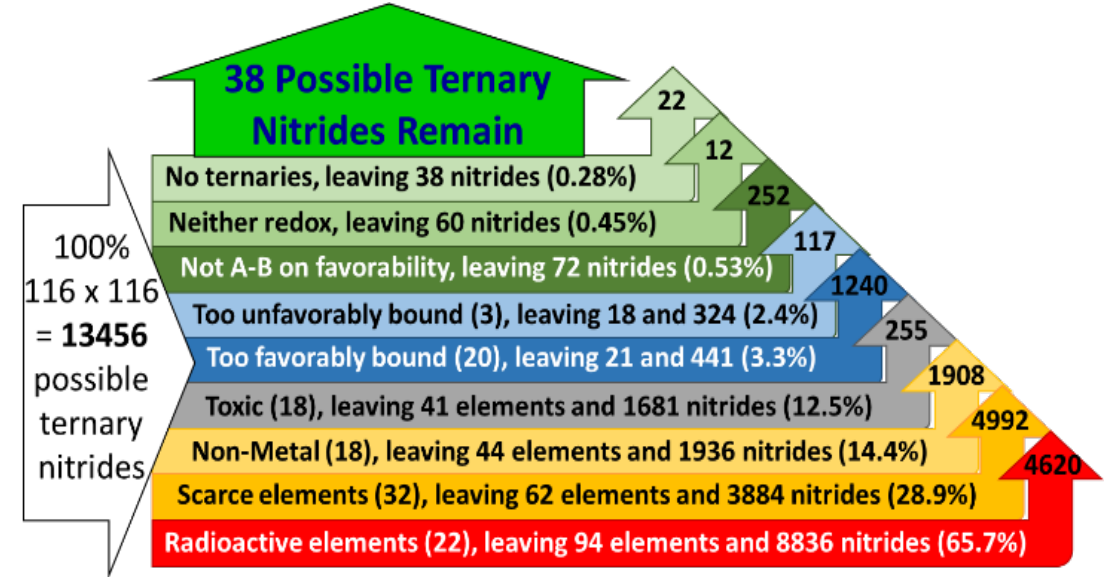
- Initial thermodynamic calculations (ASU) imply that candidate must be a ternary nitride (MM'N)

- Preliminary candidate: $\text{Co}_3\text{Mo}_3\text{N}$ (CMN331)

- Can undergo reversible phase change to CMN661, losing 50 mol% of nitrogen:

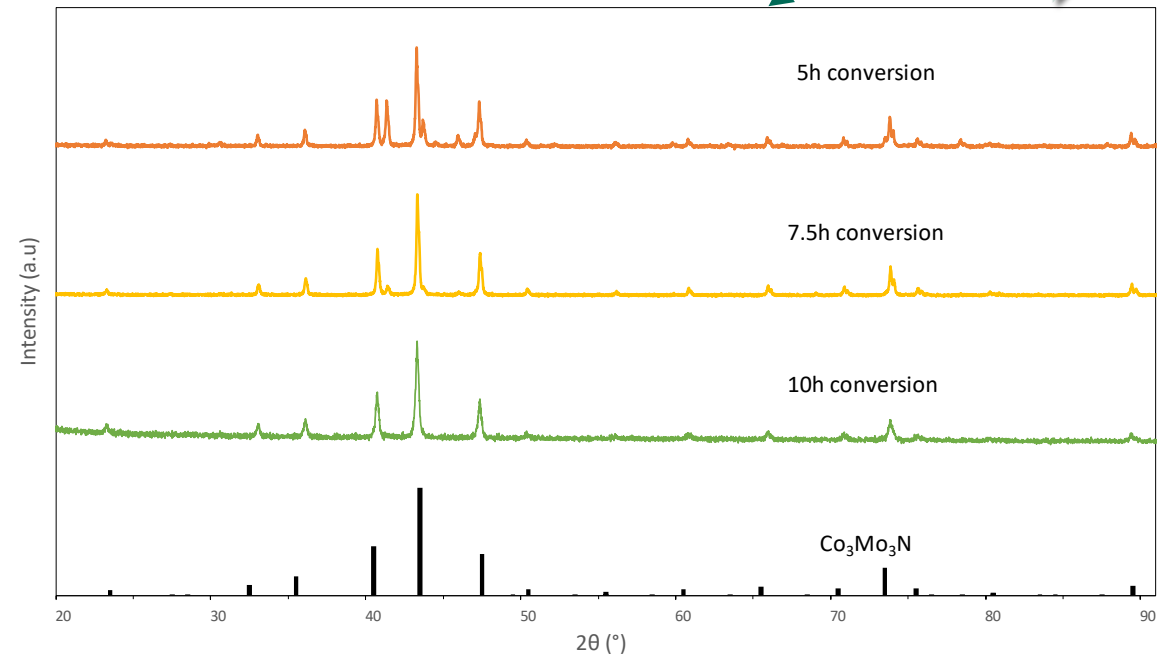
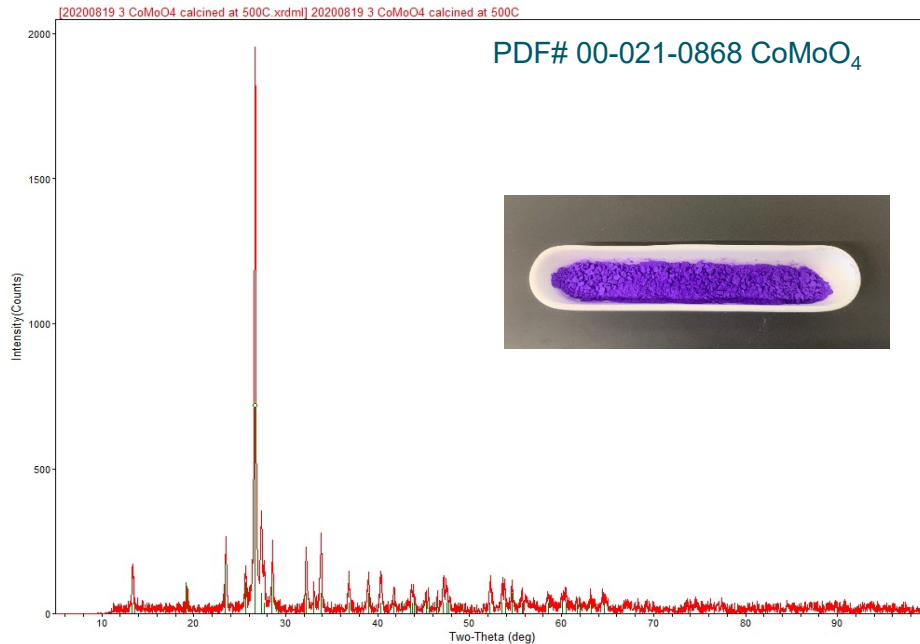
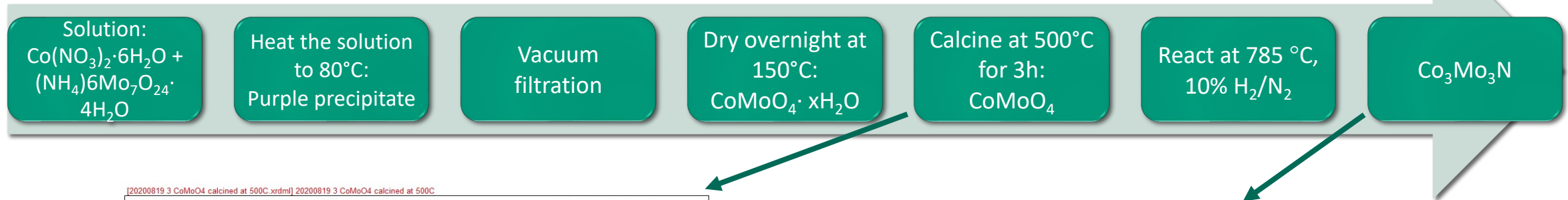


- Both phases crystallize in same space group (Fd-3m) – facilitate kinetics?
- Evidence that material can be regenerated directly by N_2



*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

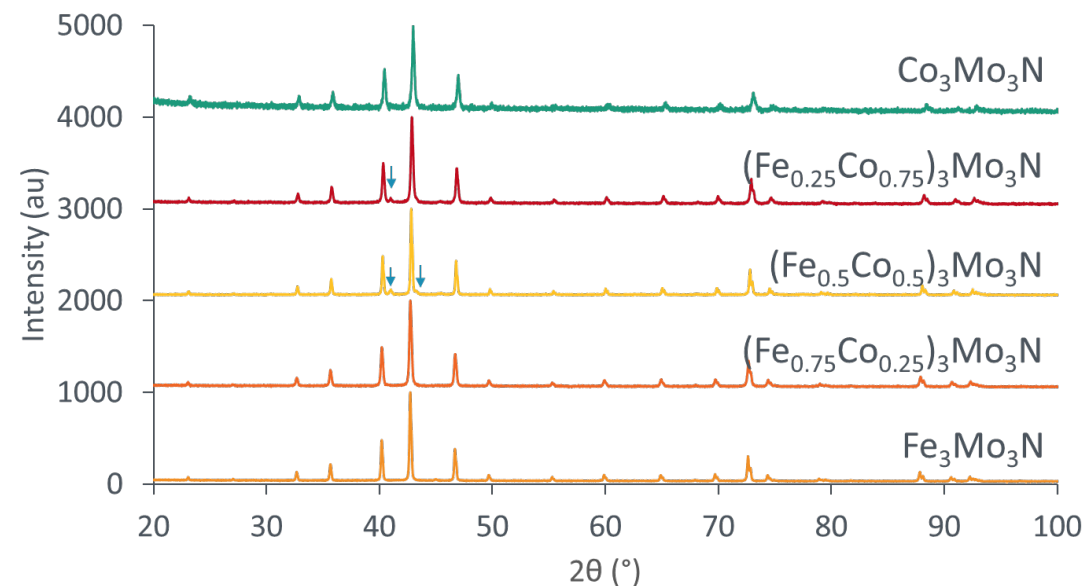
¹Hunter, S. M., et al., *Chem Mater* **2010**, 22 (9), 2898.

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



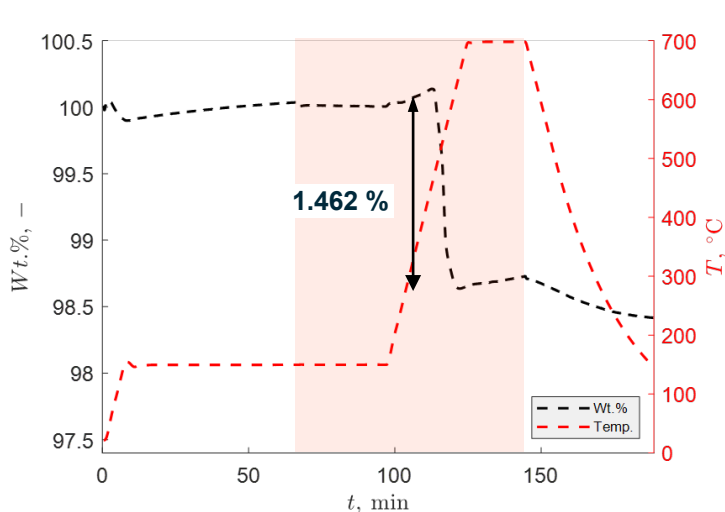
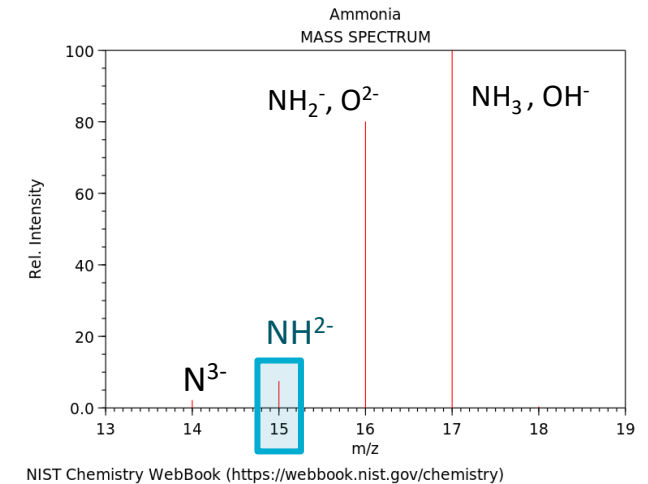
- $W > 5\%$ in Co_3Mo_3N (“331”) B-site substitution leads to phase segregation and reluctance to nitridize
- $Ni > 5\%$ in Co_3Mo_3N A-site substitution leads to phase segregation and preference of Ni_2Mo_3N (“231”) structure
- Synthesis attempts of Mn- and Zn- based ternaries didn’t yield nitrides

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

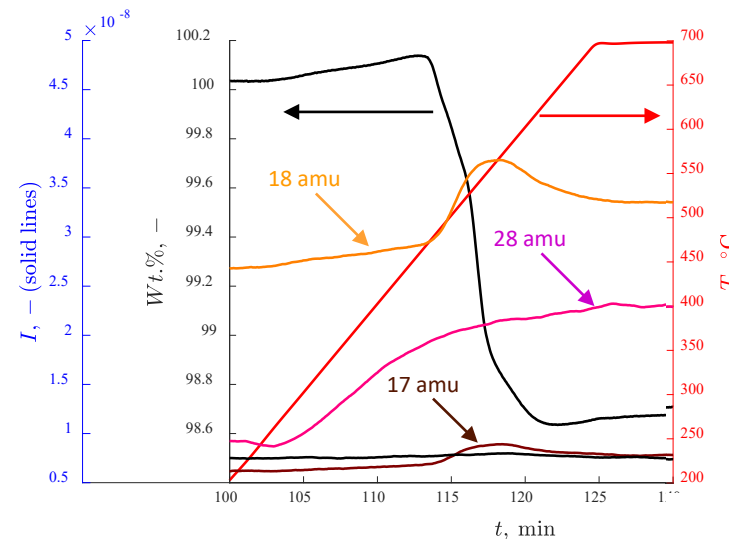


- 500-700 °C under 3:1 H_2 :Ar flow on Thermogravimetric Analyzer (TGA) connected to Residual Gas Analyzer (RGA)
- Total mass loss is close to theoretical for full conversion to $\text{Mo}_6\text{Co}_6\text{N}$ (1.46%)
- NH_3 production conf via RGA inconclusive
 - Reduction conditions (low p, high T) favor NH_3 dissociation
 - m/z overlap with H_2O , N_2 : 15 amu (NH_2^-) is the only fragment with no “competition”
- Partial solution: Test DI H_2O from bubbler using salicylate NH_3 test kit
 - Ammonia detected from CMN331 reduction compared to reference (blank) sample

Combined with RGA/XRD results, detection of NH_3 with test kit provides strong evidence of CMN331 reduction and NH_3 formation

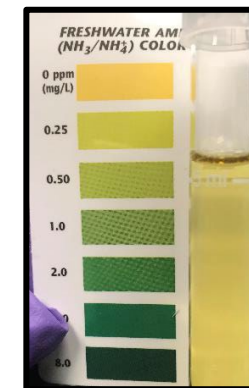


$\text{Co}_3\text{Mo}_3\text{N}$ mass loss (dashed black) and sample temperature (dashed red); 75% H_2/Ar (reducing flow) is shown as a red region.

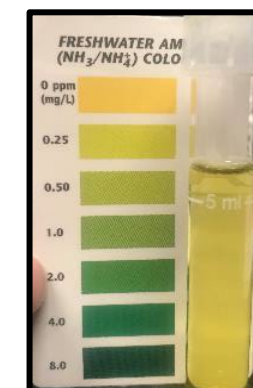


Corresponding RGA of CMN331

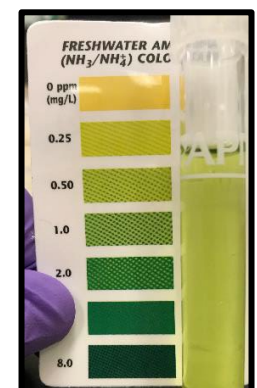
1ST SYMPOSIUM ON AMMONIA ENERGY



Initial bubbler



Control test

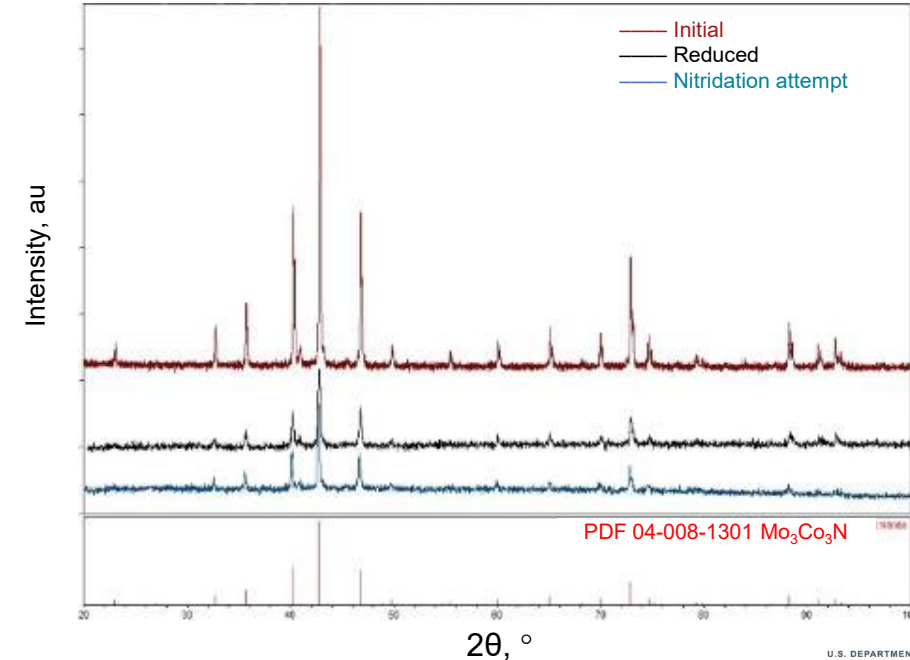
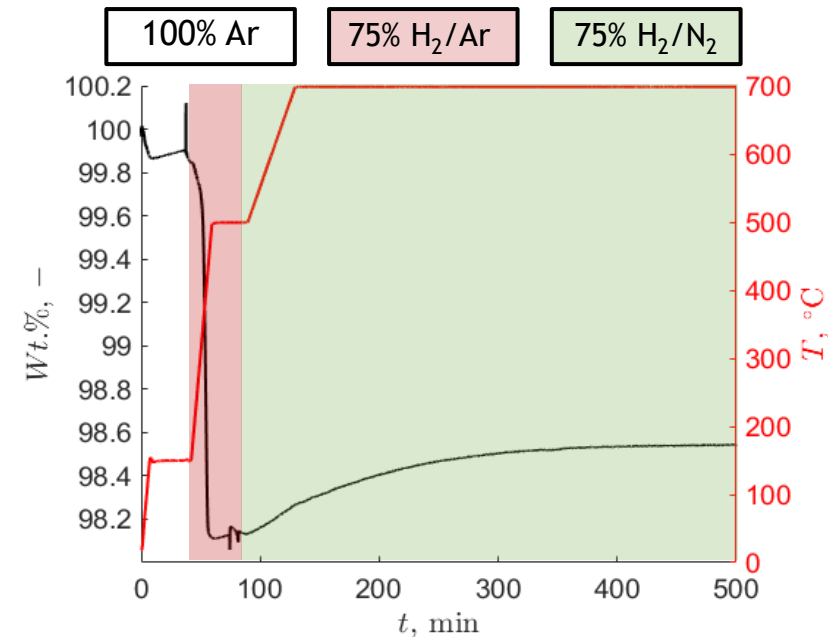


Post-reduction

CMN66I → 33I: 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

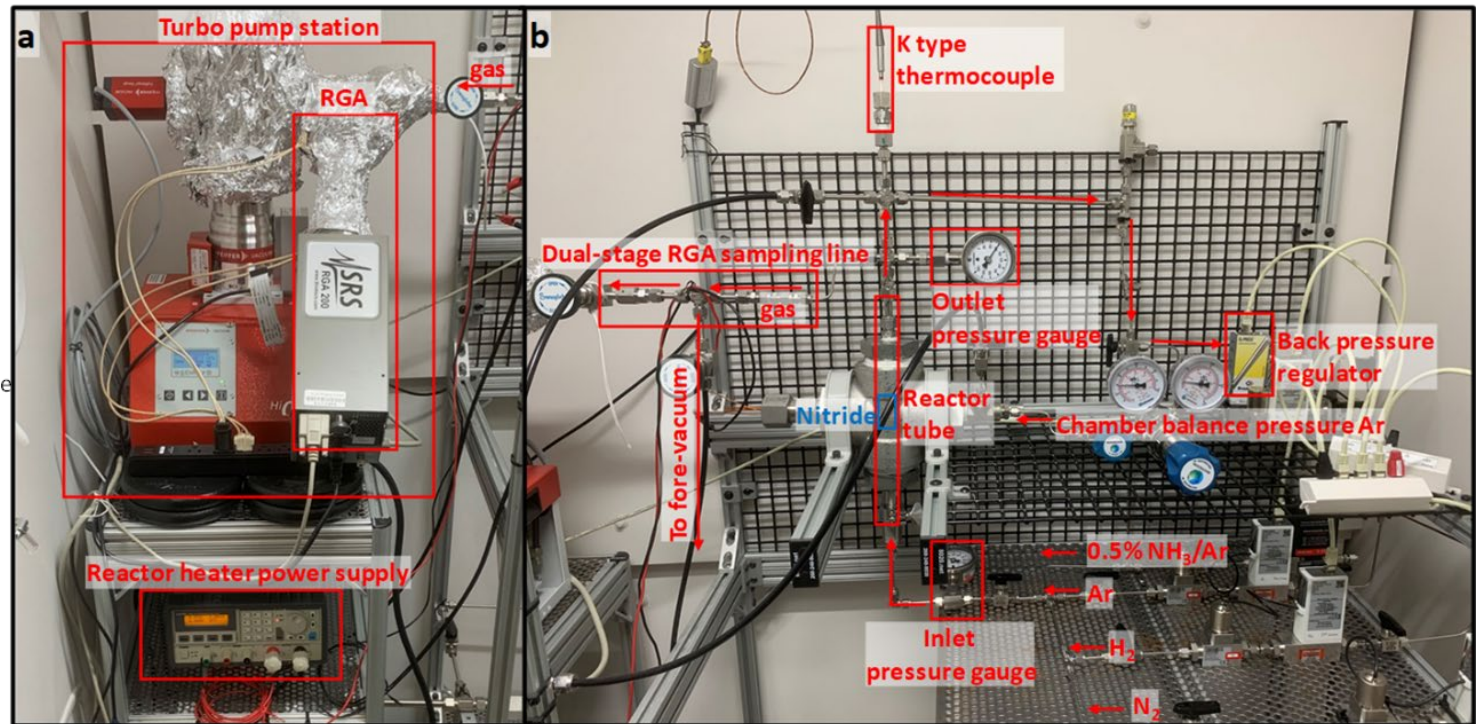
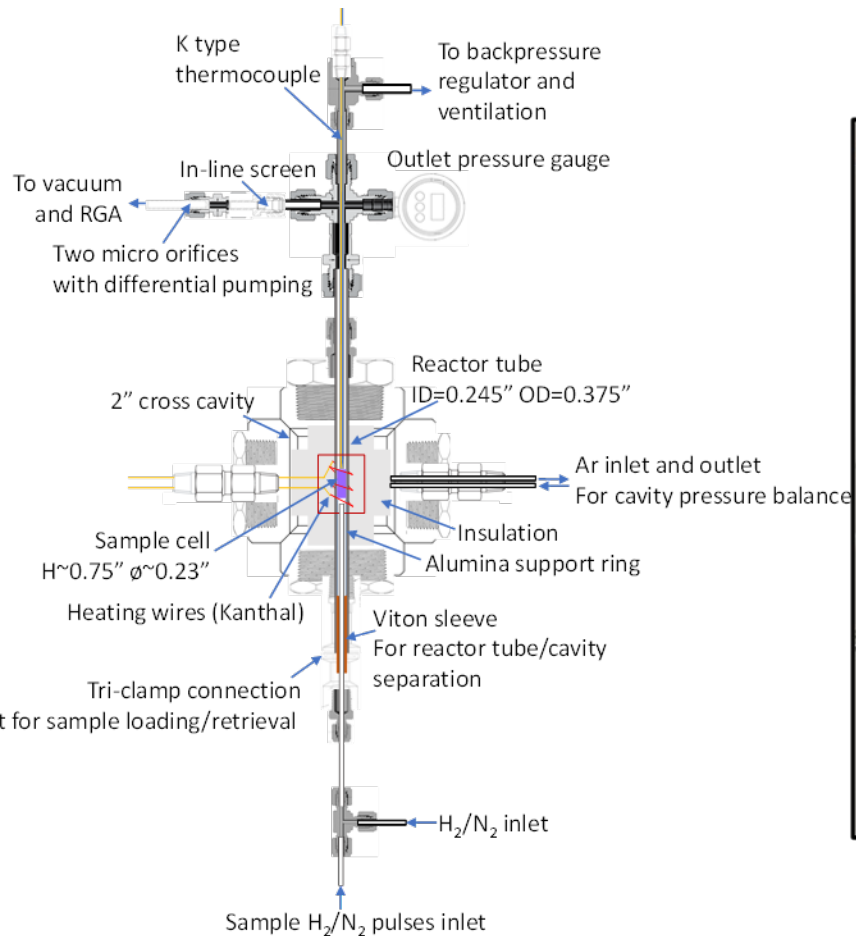
Full re-nitridation not favorable under ambient conditions



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 NH_3 yield and two times of N_2 yield (theoretical max $\text{CMN331} \rightarrow \text{CMN661} = 0.5$)

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

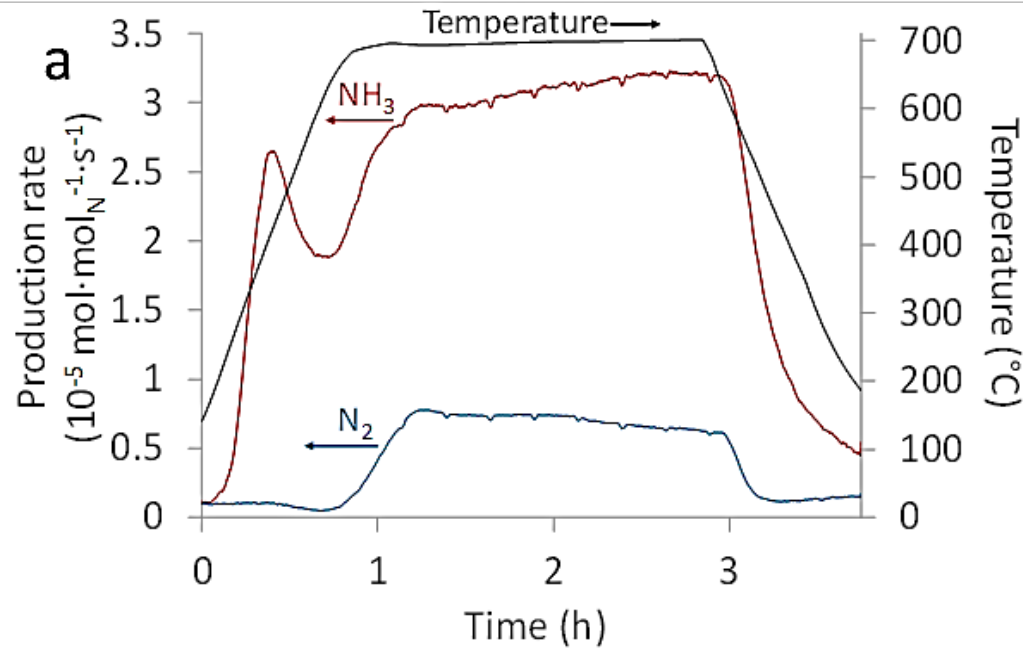
Reduction step	$P(\text{H}_2)$ bar	T_{hold} °C	t_{hold} h	Steady $r(\text{NH}_3)$ $10^{-5} \text{ mol mol}_N^{-1} \text{ s}^{-1}$	Steady $r(\text{N}_2)$ $10^{-5} \text{ mol mol}_N^{-1} \text{ s}^{-1}$	NH_3 yield mol/mol_N	N_2 yield mol/mol_N	Reacted solid-state nitrogen mol mol_N^{-1}	Selectivity to 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 ,
 $p\text{H}_2$, t)

- 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

All cycles on same $\text{Co}_3\text{Mo}_3\text{N}$ sample – *Reaction is cyclic*

Ammonia Production and Re-nitridation of CCM33 I

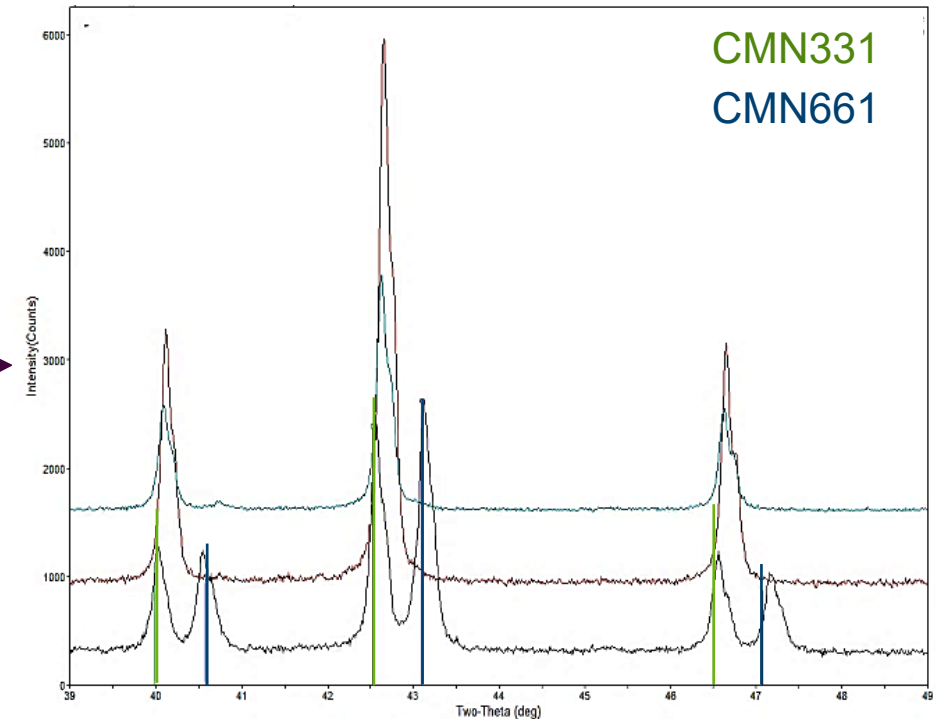
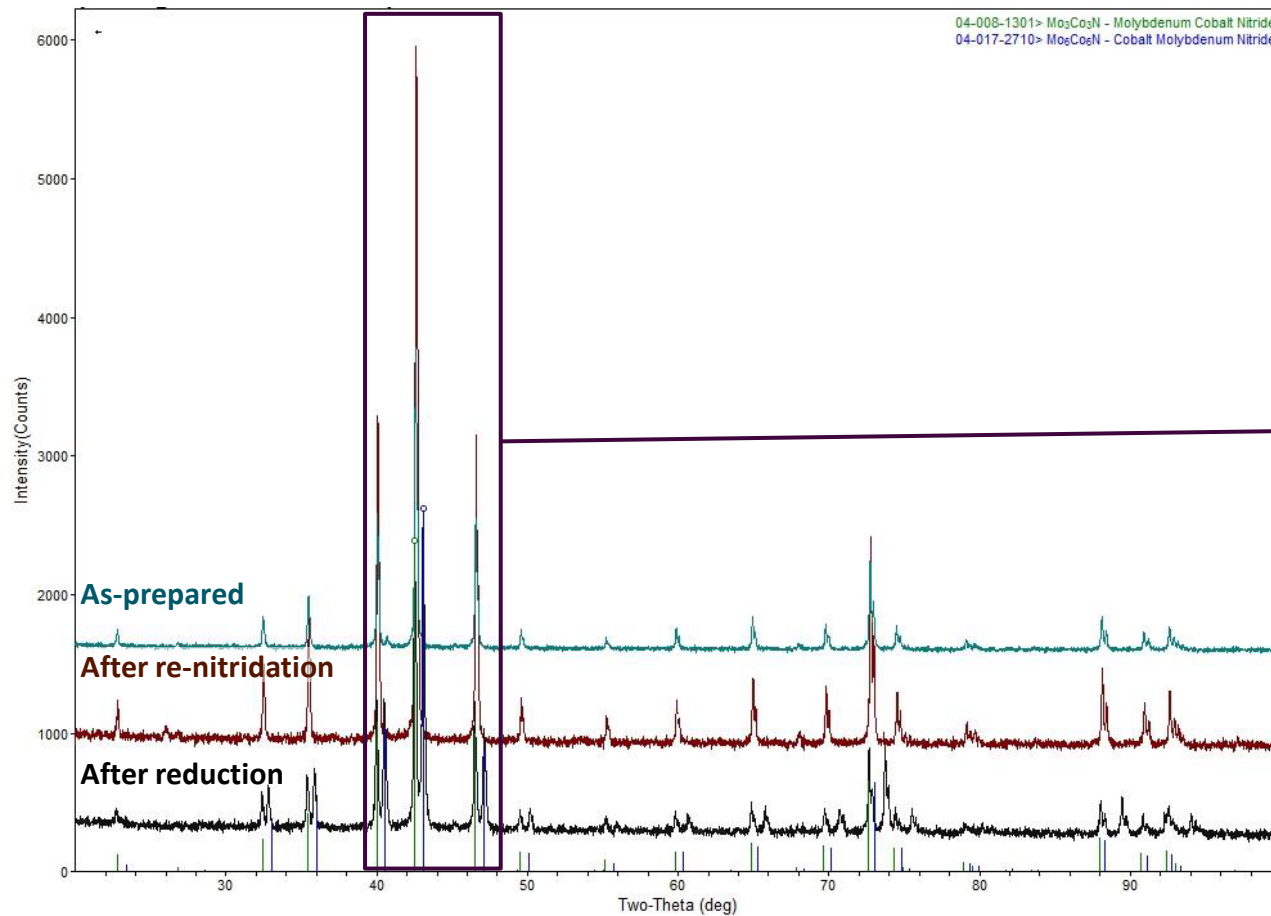


NH_3 , N_2 production rates and temperature profile of representative reduction step under 100% H_2 (Cycle 6)

- Initial NH_3 peak assumed to be hydrogenation of surface adsorbed N_2
- At $T > 600^{\circ}\text{C}$, 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
 - $P = 20 \text{ bar}$, $T = 700^{\circ}\text{C}$ 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 $\text{CCM331} \rightarrow \text{CCM661}$ bulk reaction

Powder X-ray Diffraction



XRD of $\text{Co}_3\text{Mo}_3\text{N}$ nitride in different stages of the cycle demonstration

- 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

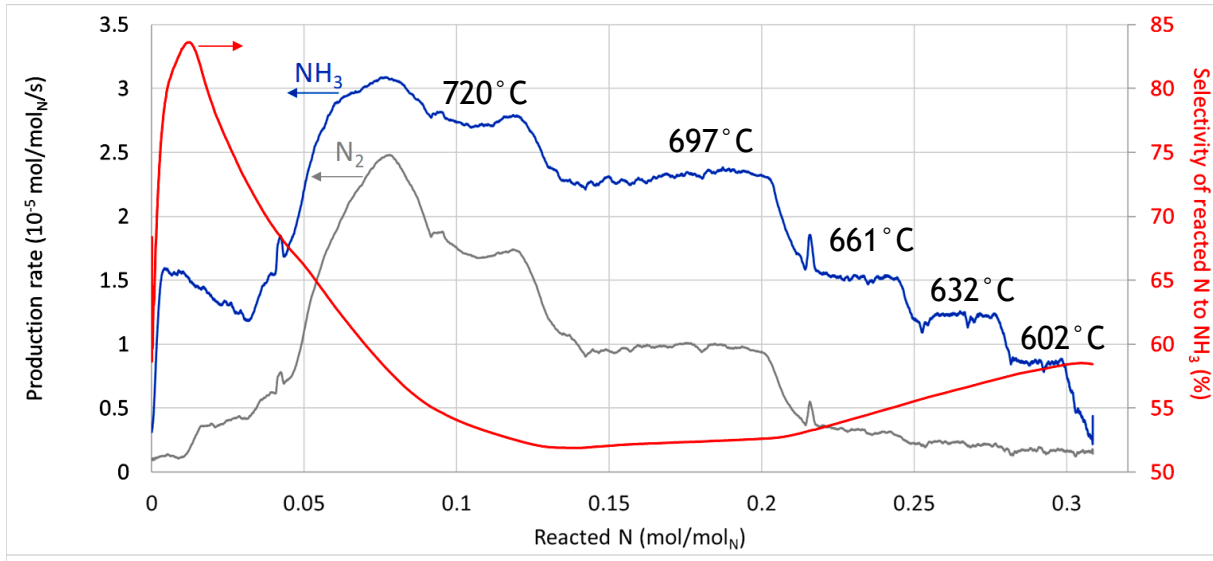
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T steps at varying pH_2

- 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

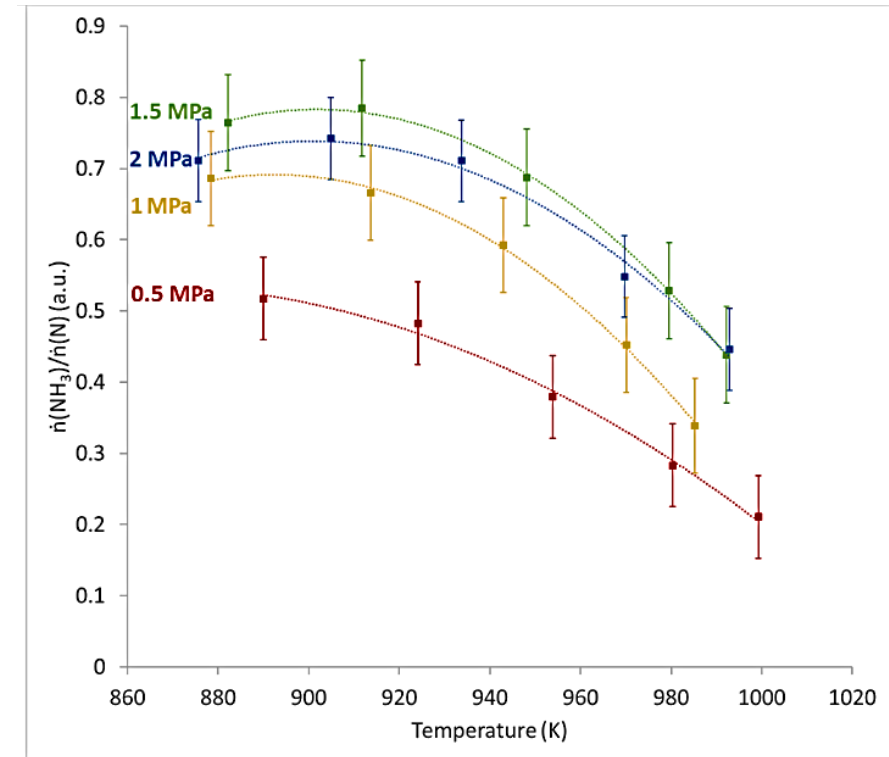
Temperature Step Reduction



NH₃, N₂ production rates and selectivity of reacted nitrogen to NH₃ as a function of reacted nitrogen in a temperature stepping reduction experiment (20 bar, 100% H₂, 8th cycle)

- NH₃ 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 NH₃ rates while keeping selectivity to NH₃ high

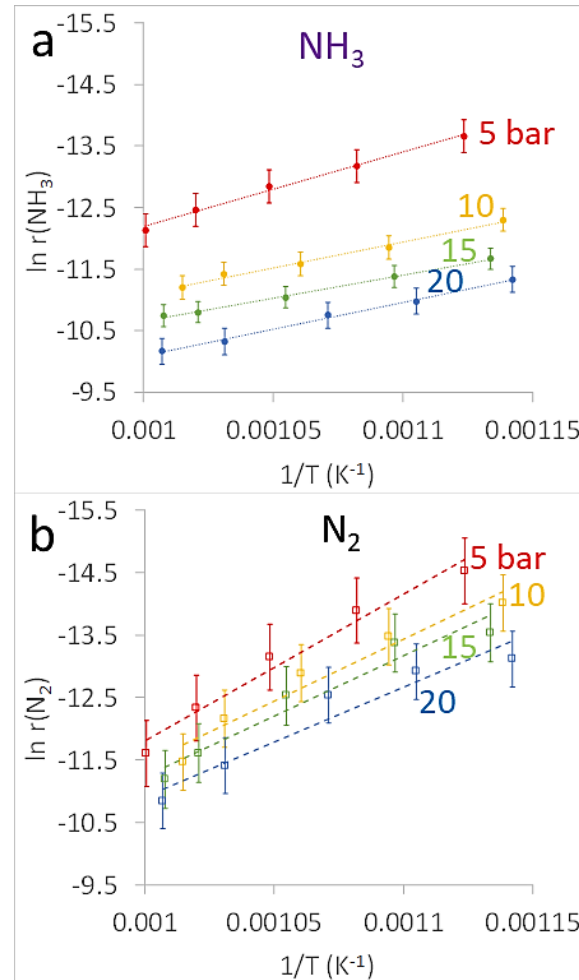


NH₃ selectivity as a function of temperature at varying P_{H₂}

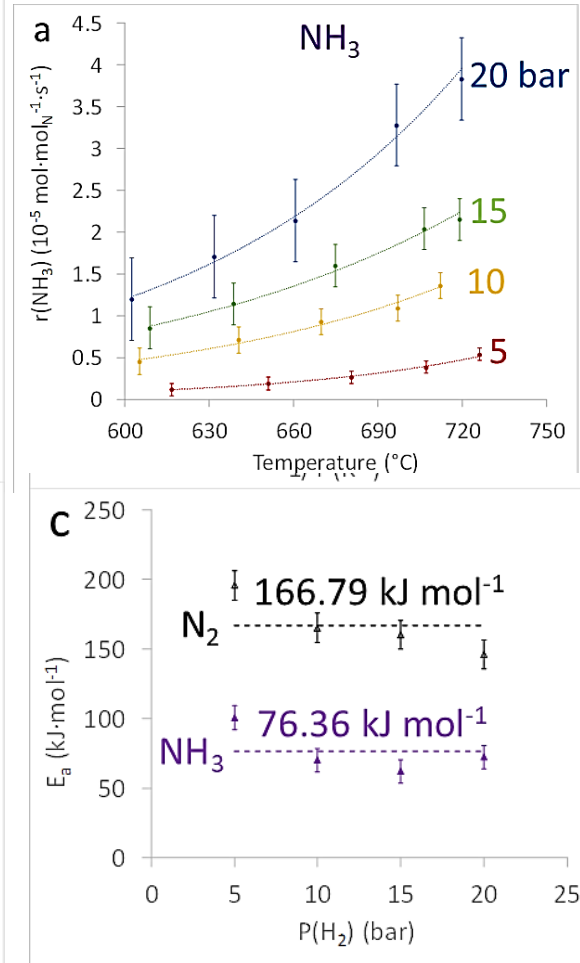
Determination of Activation Energy



- 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



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



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

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



- 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

Acknowledgements



Kevin Albrecht, H. Evan Bush, Matthew W. Kury, Tania Rivas, Madeline Finale, Luis Garcia Maldonado



Ellen B. Stechel (PI, ASU), James E. Miller, Ivan Ermanoski, Xiang Michael Gao, Alberto de la Calle, Alicia Bayon Sandoval, Nathaniel Anbar, Syed Shakeel and Jarett Prince



Peter Loutzenhiser (PI, GIT), Nhu “Ty” Nguyen, Tyler Farr, Shaspreet Singh



This work is supported by the U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technologies Office (SETO) Award Number DE-EE0034250.





THANK YOU FOR YOUR ATTENTION