SolarPACES 2022
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Talk #30208

Solar-Thermal Ammonia Production: A Renewable, Carbon-Neutral Route to Ammonia via Concentrating Solar Thermochemistry

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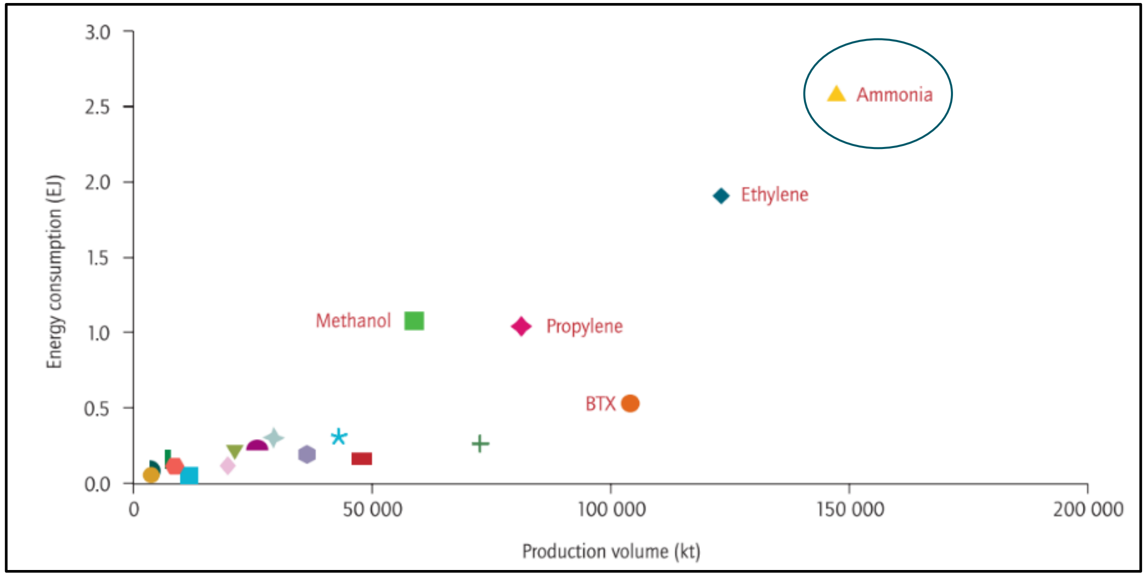
Introduction

- 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 ºC)
    - Capital-intensive and only practical with large facilities
    - Process including H_2 production is responsible for ~1.8% of global CO_2 emissions[1]
- Ammonia synthesis consumes > 1% of the total energy worldwide[2]



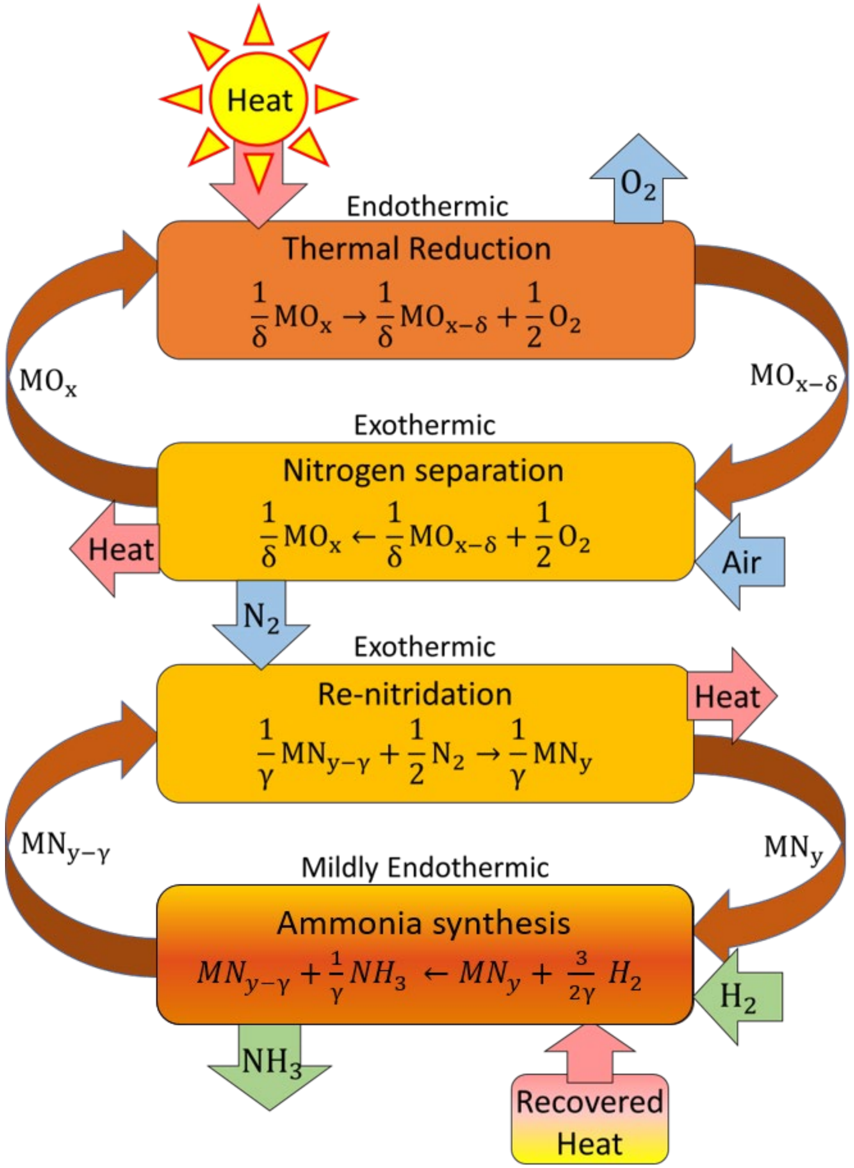
Global greenhouse gas emissions versus production volumes (2010)*

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

[1]*IEA (2013), Technology Roadmap - Energy and GHG Reductions in the Chemical Industry via Catalytic Processes, IEA, Paris https://www.iea.org/reports/technology-roadmap-energy-and-ghg-reductions-in-the-chemical-industry-via-catalytic-processes

. [2]Institute for Industrial Productivity. Industrial Efficiency Technology Database http://ietd.iipnetwork.org/content/ammonia.

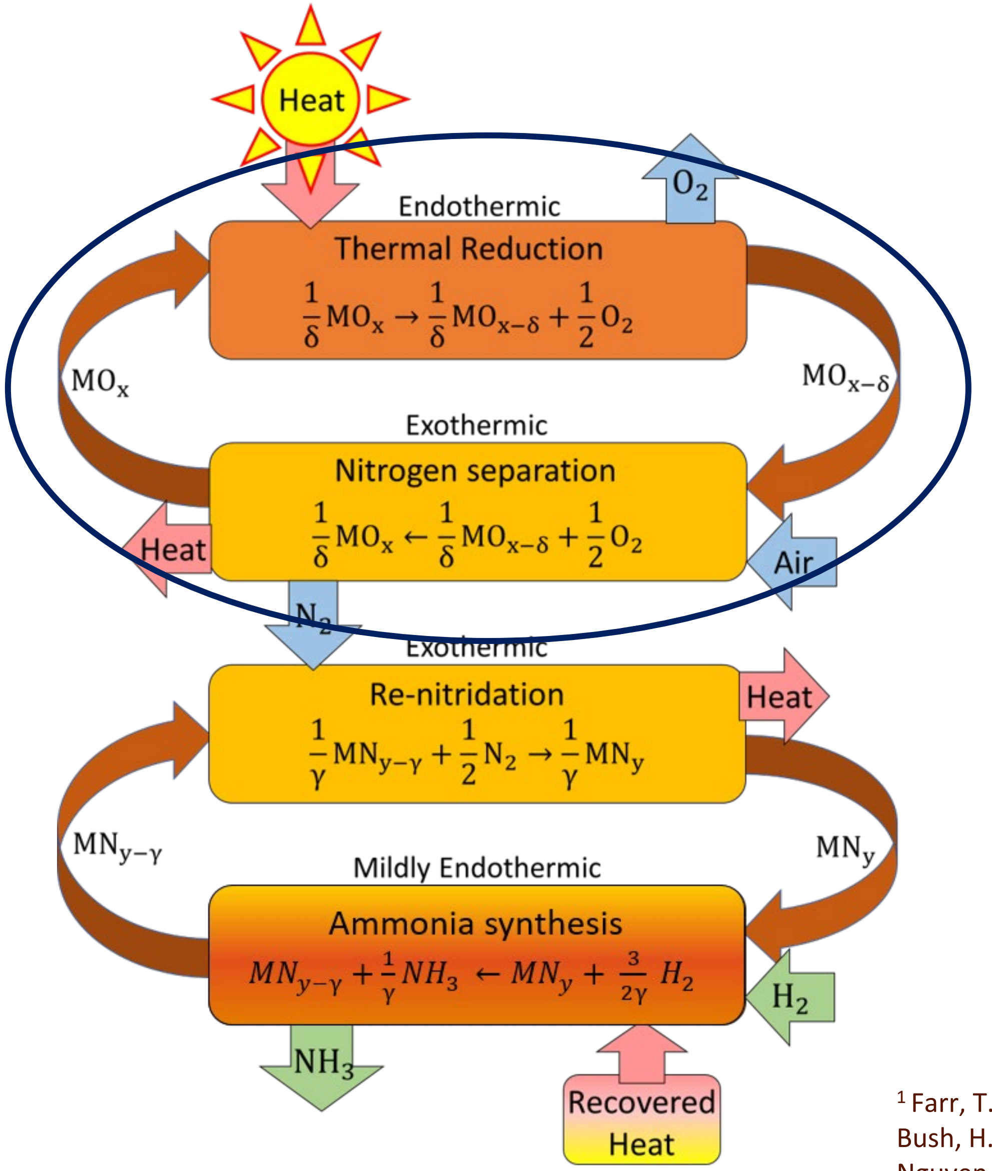
Solar Thermal Ammonia Production (STAP)



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

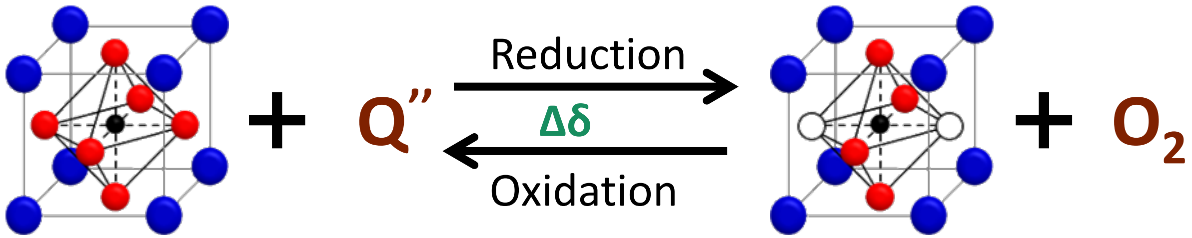
Cycle 1: Nitrogen Separation



Identify and optimize redox active metal oxide (MOx) materials for N_2 recovery via air separation[1]

- MO_x thermally reduced by concentrated solar heat to form oxygen-deficient compound, $MO_{x-\delta}$
- $MO_{x-\delta}$ reacts with O_2 in air to re-oxidize, leaving behind purified N_2

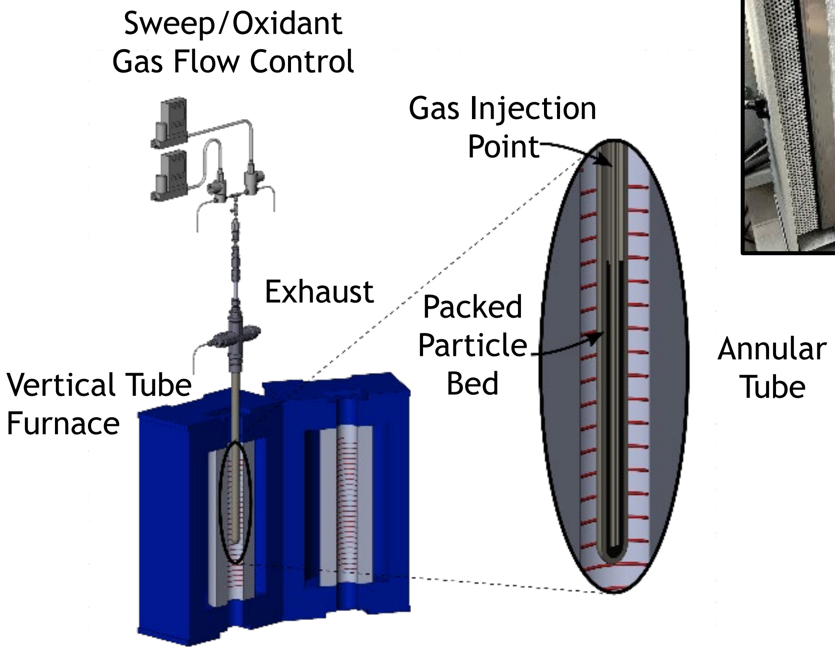
$Ba_{0.15}Sr_{0.85}FeO_{3-\delta}$ (BSF1585)



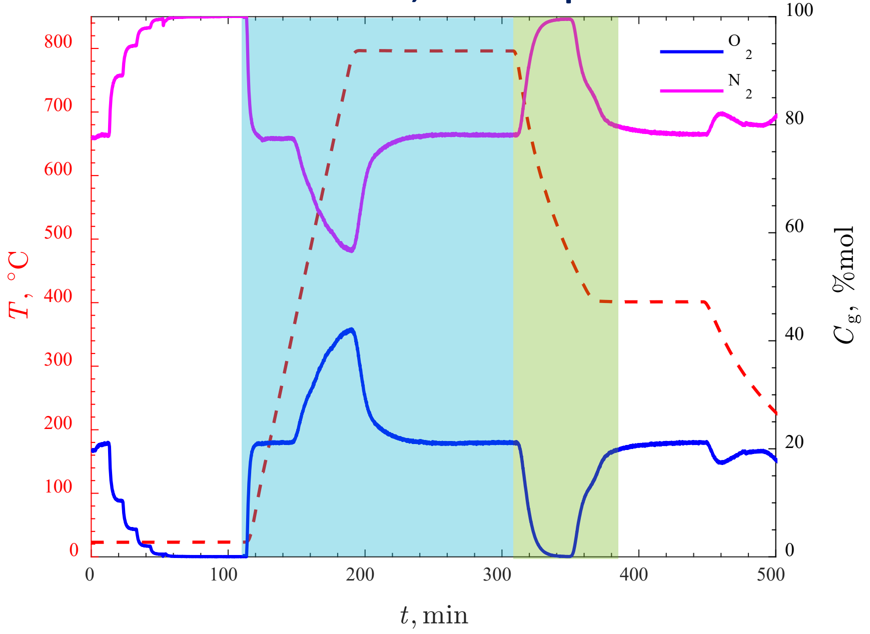
[1] Farr, T. P.; Nguyen, N. P.; Bush, H. E.; Ambrosini, A.; Loutzenhiser, P. G., *Materials* **2020,** *13* (22).
Bush, H. E.; Nguyen, N. P.; Farr, T.; Loutzenhiser, P. G.; Ambrosini, A., *Solid State Ion.* **2021,** *368, 115692.*
Nguyen, N. P.; Farr, T. P.; Bush, H. E.; Ambrosini, A.; Loutzenhiser,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

Packed Bed Reactor

- Demonstrates air separation reaction
- Stationary bed (35-40 g BSF1585) with sweep airflow
- Gas measurement via RGA calibrated for pO2 range
- Fully cyclic thermal reduction and air separation
- Multi-cycle testing
- Range of T, $\dot{V}$, pO2



$Ba_{0.15}Sr_{0.85}FeO_{3-\delta}$
800°C Reduction, 400°C Separation



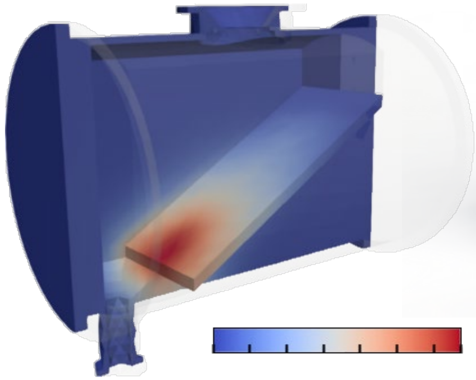
White = calibration
Blue = thermal reduction and purge
Green = air separation

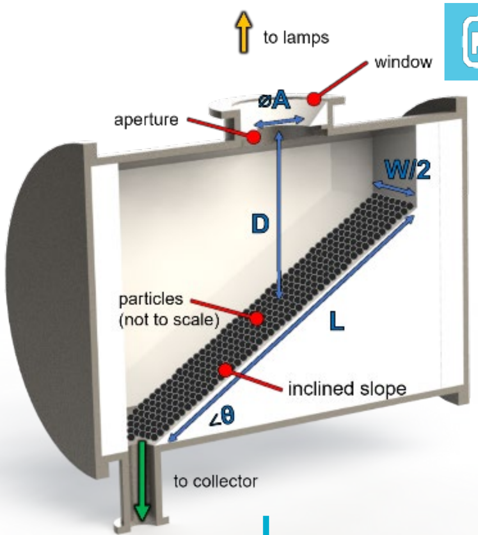
- Air separation studied via parametric analysis of reduction, air separation temperatures, multi-cycling
- Validation of heat and mass transfer flow models
- All reactions (reduction/reoxidation) performed in air
- During reoxidation step, O_2 gettered by material (BSF1585), leaving purified N_2

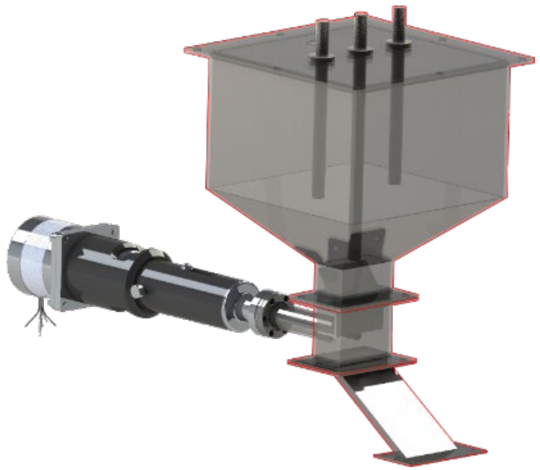
Directly Irradiated Incline Flow Reactor

- Directly irradiated cavity receiver, water cooled quartz window
- Thermal input from high flux solar simulator (HFSS)
- Flowing inclined bed of BSF1585
- Heated 5 kg hopper with linear actuator-controlled valve
- Collection and measurement of product O_2
- Load cell to measure flow rate
- Thermocouples for particle and cavity measurements

Heat Transfer Model

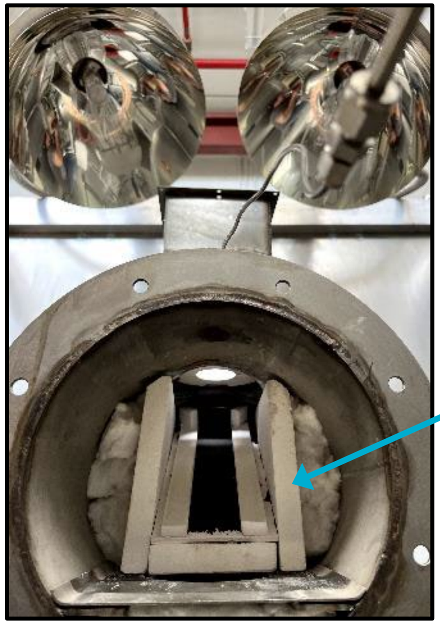






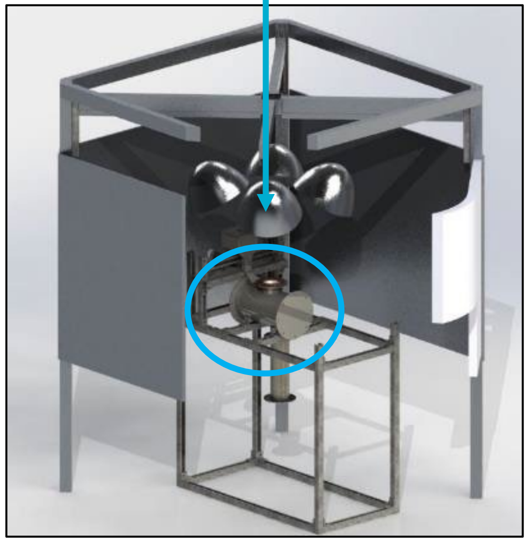
Pre-heated Hopper Design

Flow Calibration

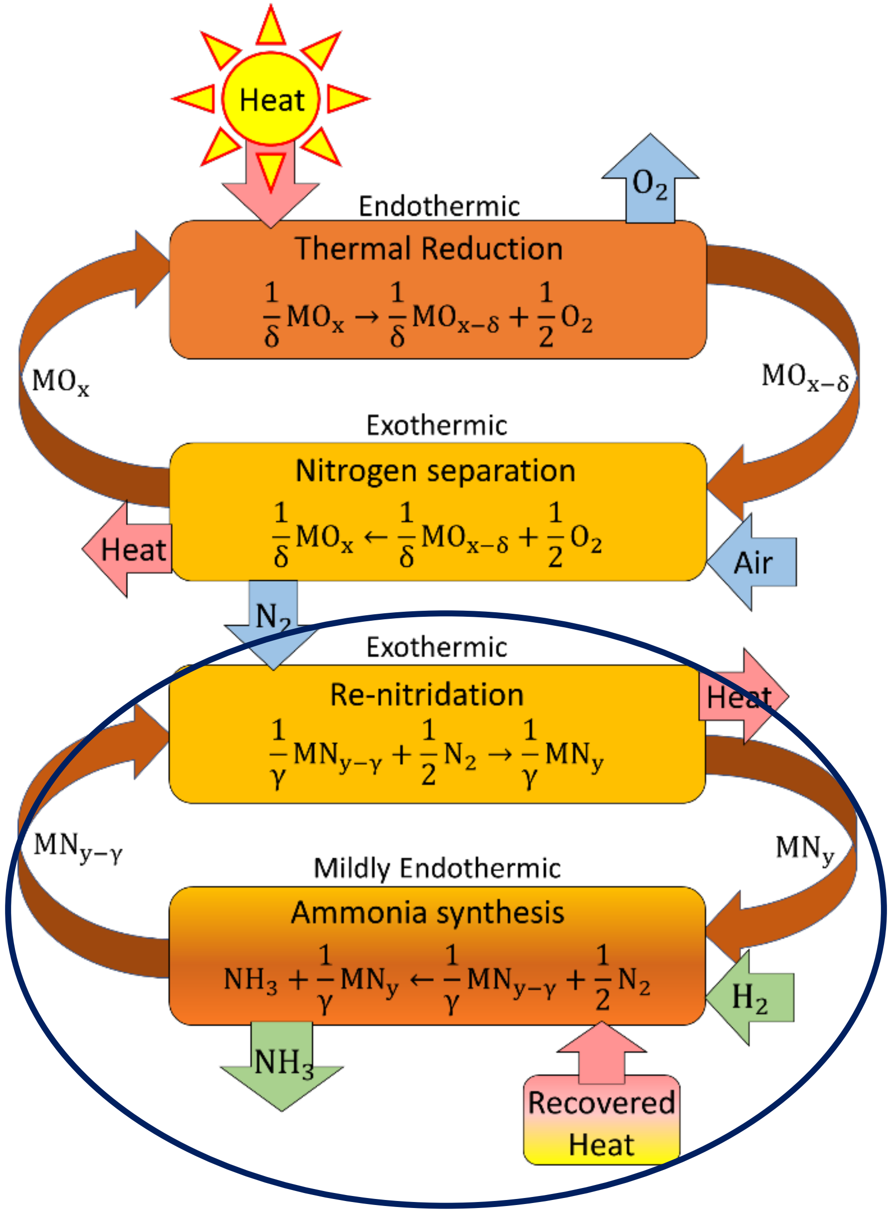


HFSS Lamps

Particle Flow



Cycle 2: NH_3 Production



Identify and optimize metal nitride material (MN_γ) that can be reduced by H_2 to produce NH_3, then re-nitridized directly by N_2 to close the cycle

- Nitride is reduced by H_2 to form $Mn_{y\text{-}\gamma}$+ NH_3, then regenerated by N_2 from 1st cycle
- Bulk reaction, not exclusively surface-catalyzed
- Nitride materials more challenging than oxide development
  - Pool of candidates much smaller
  - Thermodynamics are challenging; NH_3 dissociates at high temperature
  - Nitrogen diffusion in metal nitrides is slower and less common
  - Synthesis more complex – usually reacting under flowing NH_3 at high temperature in ammonolysis reaction

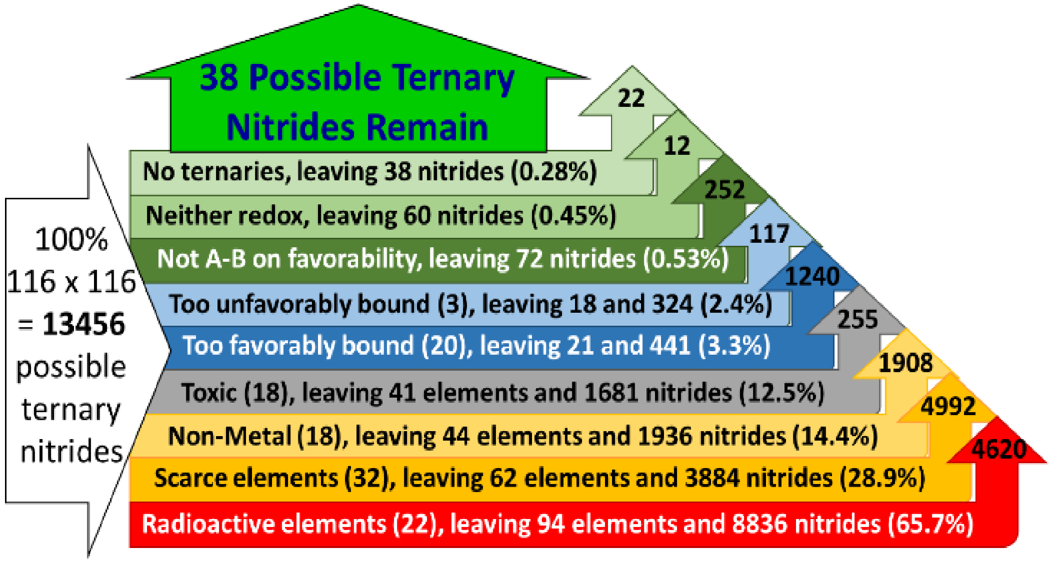
Candidate Identification

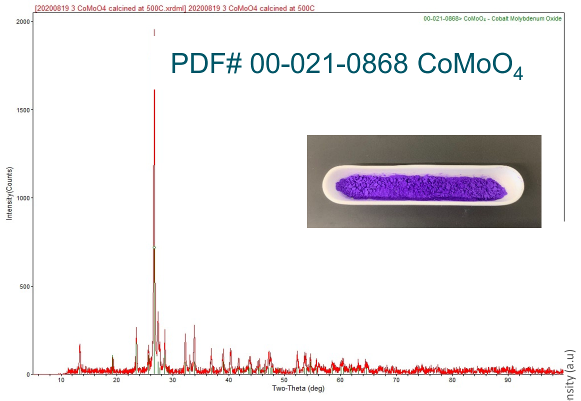
- Initial thermodynamic calculations determined that material should be at least a ternary nitride (MM'N)
- Down-selected to 38 possible ternary compounds
- Preliminary candidate: Co_3Mo_3N (CMN331)
  - Can undergo reversible phase change to CMN661, losing 50 mol% of nitrogen:

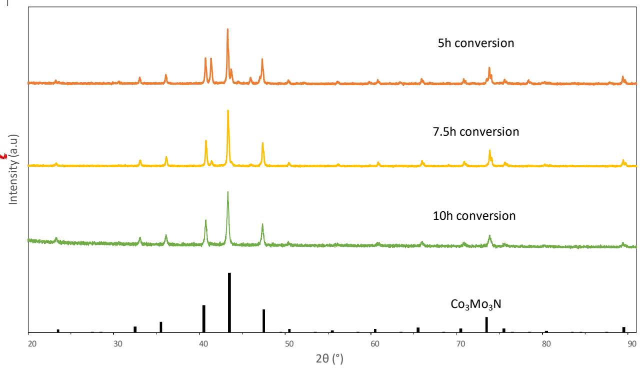
$$2Co_3Mo_3N + 3/2H_2 \rightarrow 2Co_6Mo_6N + NH_3$$

$$Co_6Mo_6N + 1/2N_2 \rightarrow 2Co_3Mo_3N$$

  - Both phases crystallize in same space group (Fd-3m) – facilitate kinetics?
  - Reports that material can be regenerated directly by N_2
  - Synthesized via oxide precursor method
- Expanded candidate pool to a family of single-phase A_3B_xN (A=Co, Ni, Fe; B=Mo, W; x = 2, 3) ternary and quaternary nitride solid solutions





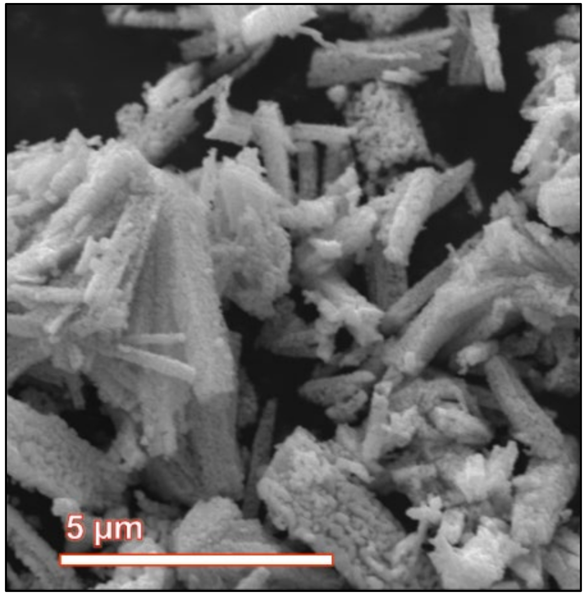


*Hunter, S.M., Mckay, D., Smith, R.J., Hargreaves, J.S.J., Gregory, D.H., 2010, Chemistry of Materials, 22(9), pp. 2898-2907.
Gregory, D.H., Hargreaves, J.S.J., Hunter, S.M., Catalysis Letters, 2011, 141(1), pp. 22-26.

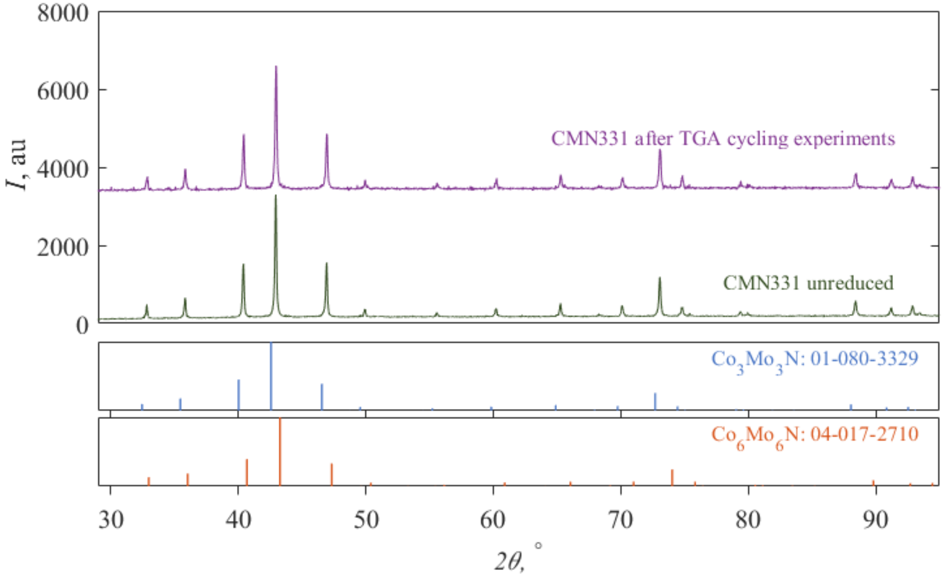
Nitride Characterization

- XRD before/after cycling for phase identification
- Elemental analysis performed using ICP-OES and CHN to identify Co3Mo3.1N1.13
- Particle surface composition investigated with XPS, SEM/EDS, and TEM identified oxide surface layer
- Oxygen detected on particles surface using XPS and EDS
  - Surface oxygen-rich layer observed

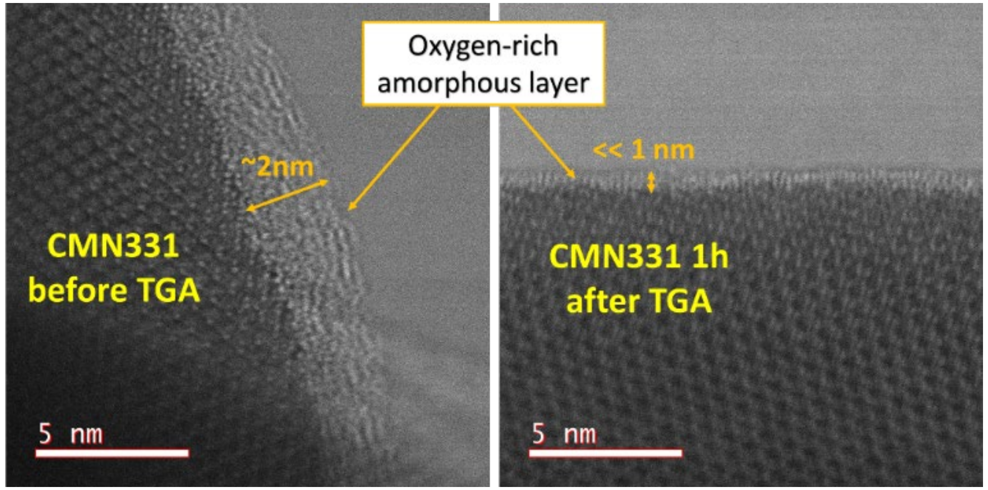
CMN331 particle morphology



XRD of CMN331 before and after reaction



TEM images of CMN331 particle



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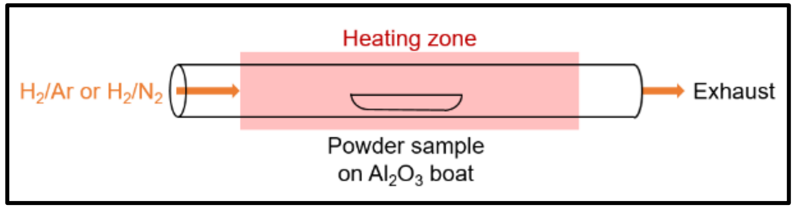
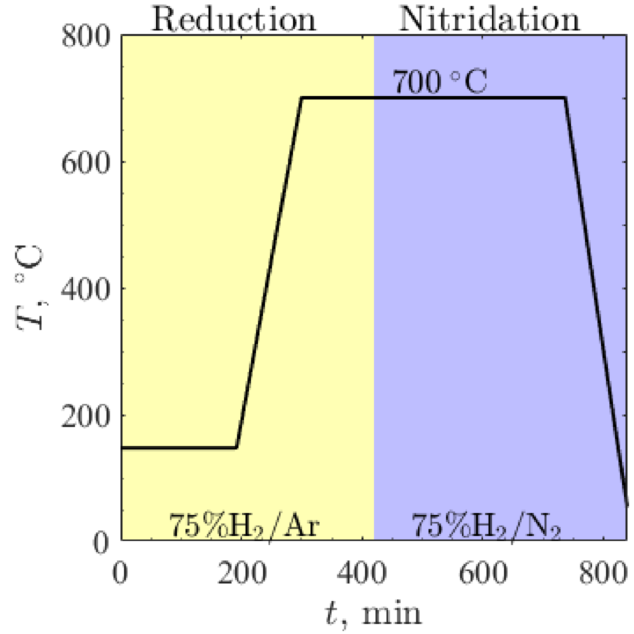
Nitride Reactivity at Ambient Pressure

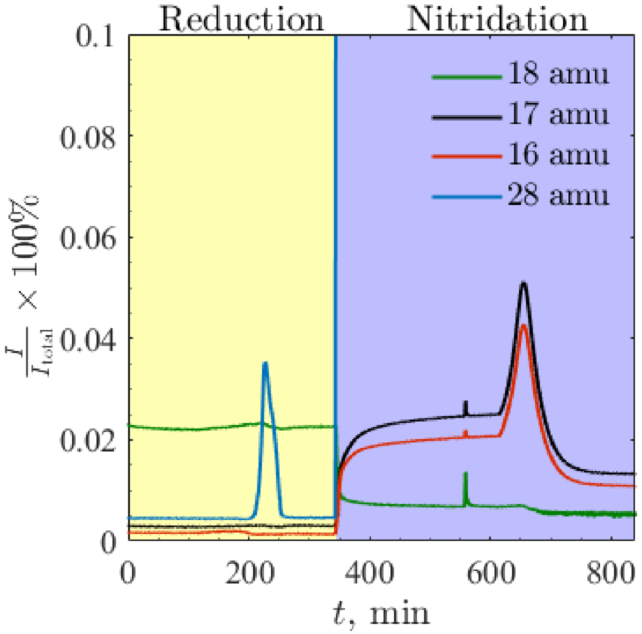
- Series of reductions/re-nitridations performed at varying T and P_{H2}
- Performed in TGA (low P_{H2}) and tube furnace (high P_{H2}, below)
- NH_3 detected under both reduction and re-nitridation, *under certain conditions*
  - Catalytic + bulk behavior?
- Does nitride activity differ under pressure?



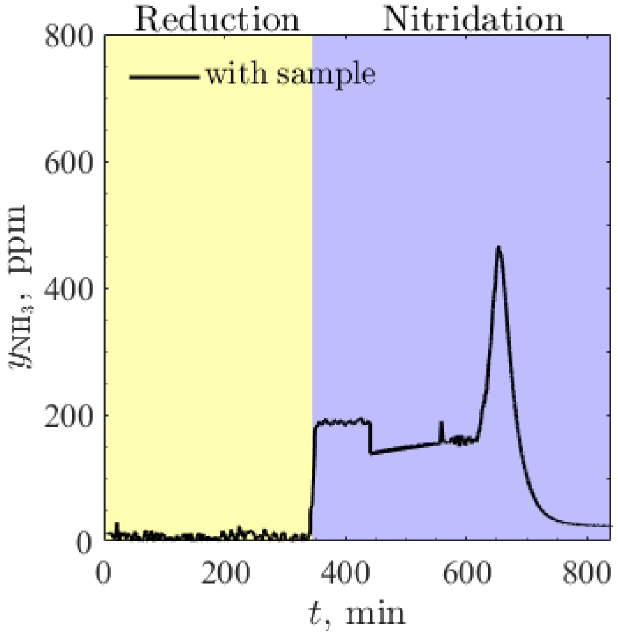
Experimental conditions



RGA

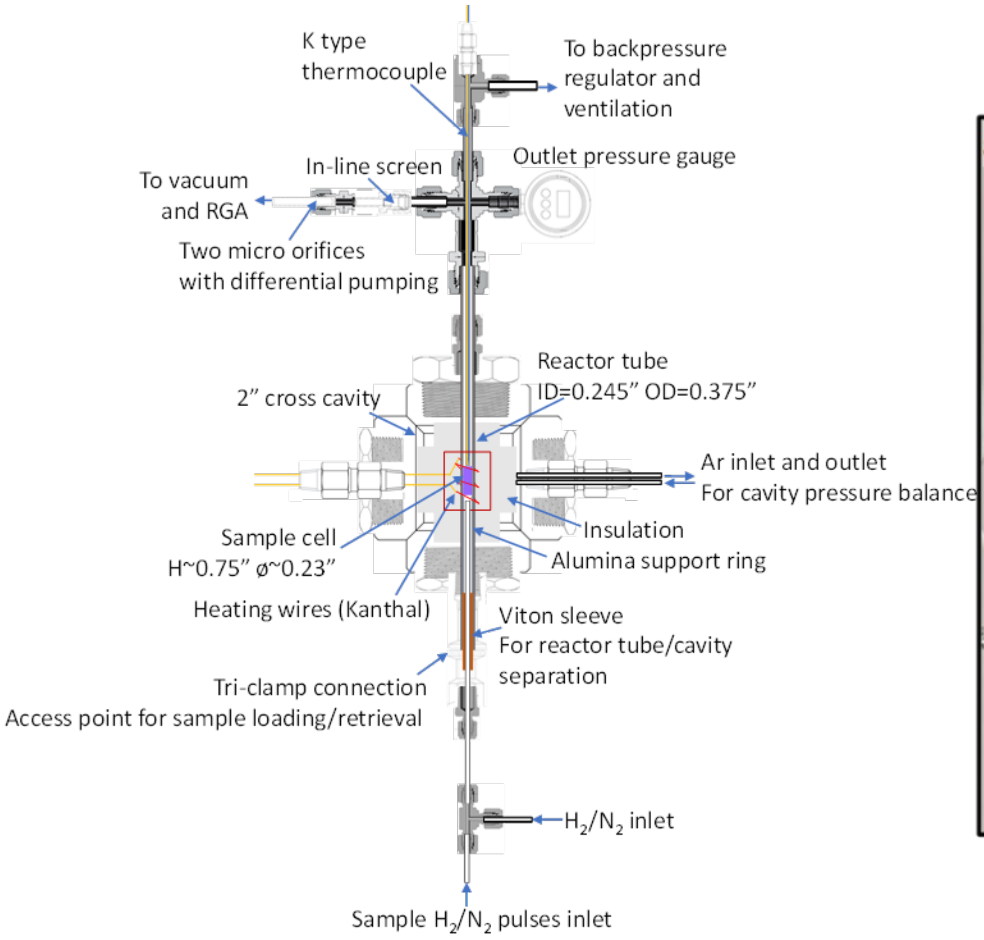


Detected NH_3

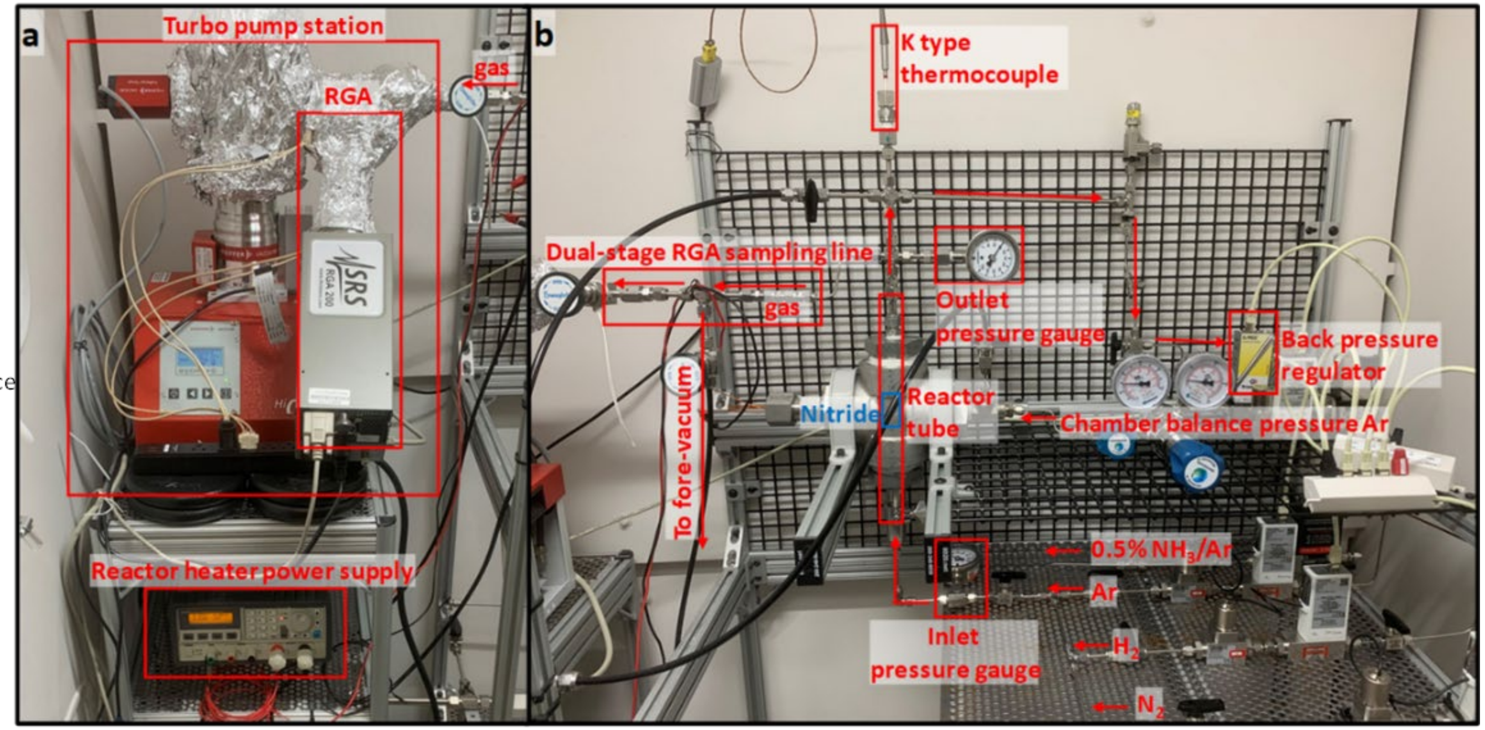


Ammonia Synthesis Reactor (ASR)

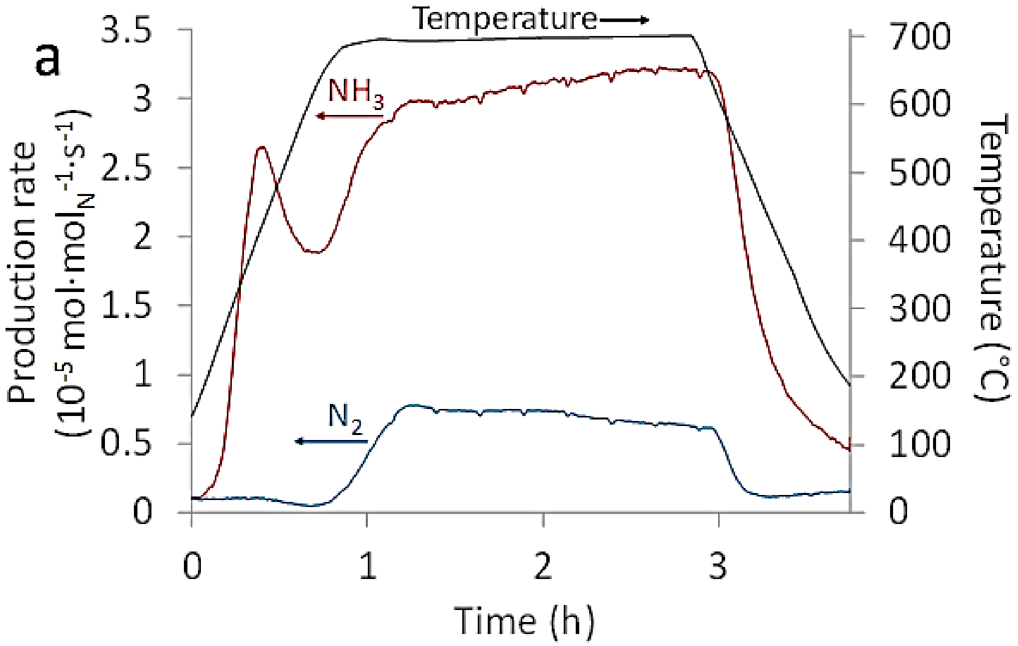
Reactor designed to perform NH_3 synthesis and nitride re-nitridation reaction under variable pressure and temperature, up to 30 bar and 800 °C, respectively



Arizona State University



Ammonia Production and Re-nitridation of CMN331



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 °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 with no side-reactions observed
  - P = 20 bar, T = 700 °C for both reactions

Results imply that lattice nitrogen participates in NH_3 production in reversible CCM331 → CCM661 bulk reaction

Co_3Mo_3N 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 CMN331→ CMN661 = 0.5)

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

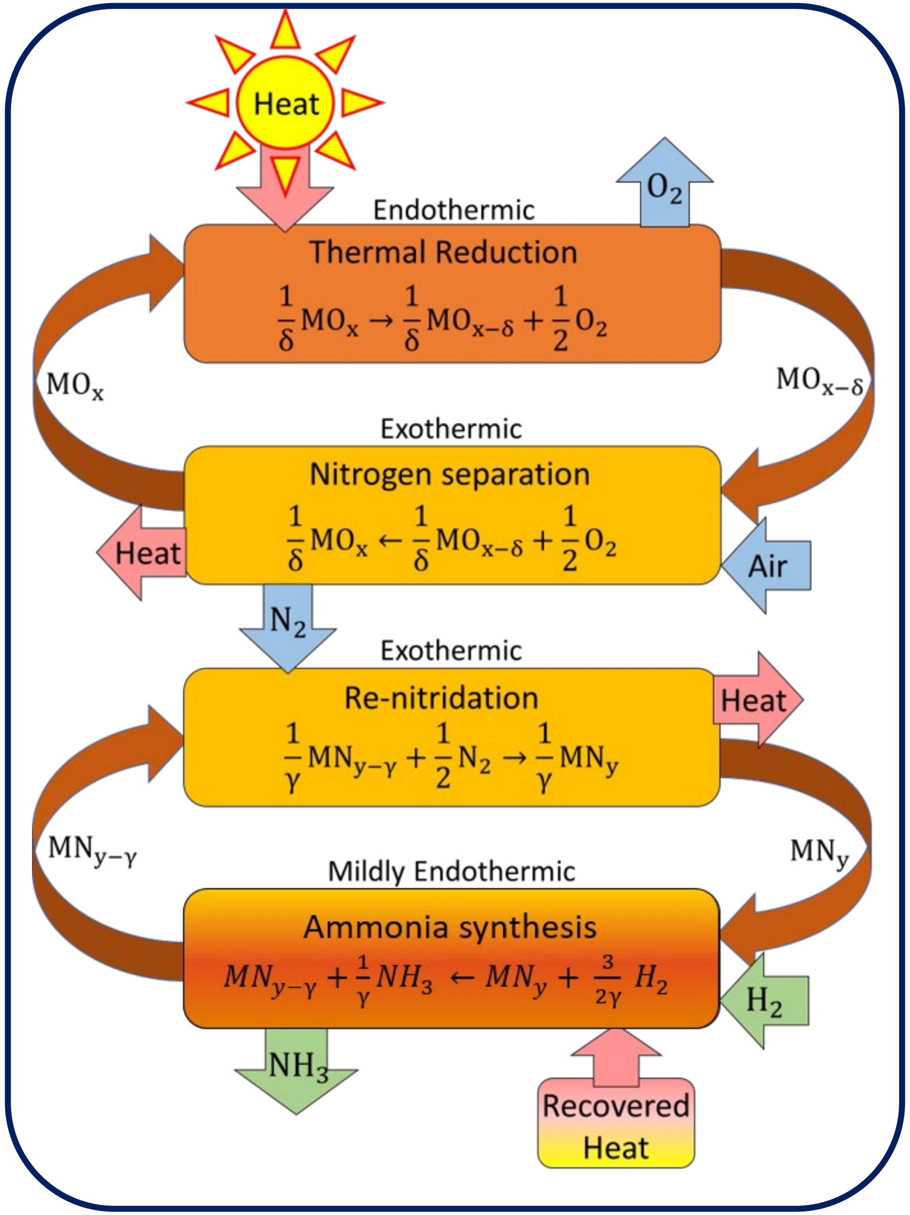
Reduction step	$P(H_2)$ bar	T_{hold} °C	t_{hold} h	Steady $r(NH_3)$ 10^{-5} mol mol_N^{-1} s^{-1}	Steady $r(N_2)$ 10^{-5} mol mol_N^{-1} s^{-1}	NH_3 yield mol/mol_N	N_2 yield mol/ mol_N	Reacted solid-state nitrogen mol mol_N^{-1}	Selectivity to NH_3
2	20	700	2	2.32	0.455	0.121	0.0610	0.243	49.8%
3	20	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, pH_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

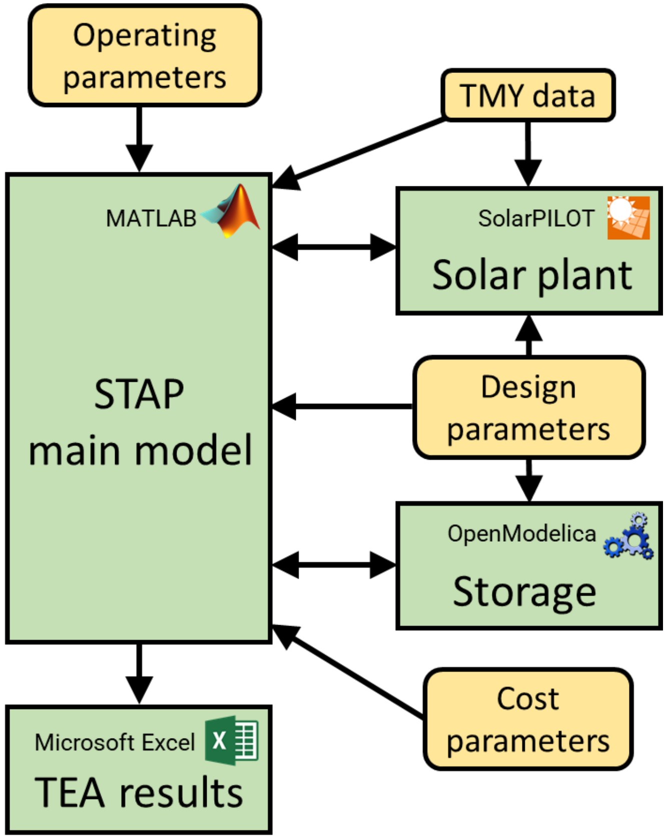
All cycles on same Co_3Mo_3N sample – ***Reaction is cyclic***

System and Technoeconomic Analyses



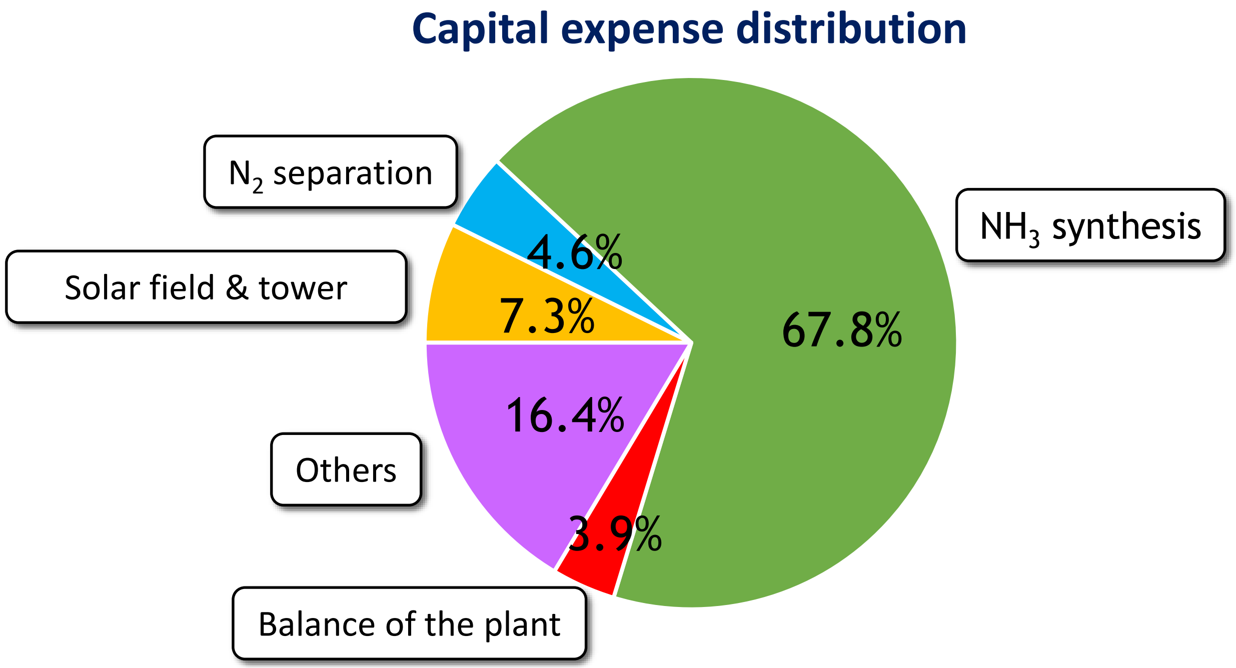
Develop and refine systems and technoeconomic models to guide materials choices, reactor design, and determine projected cost for a scaled-up system

Integration completed in a single MATLAB script that communicates with other support software to perform the simulation



Techno-economic analysis

- NH_3 yield and cycle time have a high impact on the total cost of the plant
- The nitride cost is the most significant system expense, accounting for more than the 50% of the total CapEx, but it is also the most uncertain variable



Costs Calculation	Units	Value
Heliostat field	$	3,975,900.50
Tower	$	6,251,716.68
Receiver	$	1,009,800.00
OX reactor	$	336,600.00
Lift	$	259,740.16
Storage tanks ST1 & ST2	$	1,344,389.90
MO particles	$	3,551,288.54
Storage tank ST3 and material	$	834,750.51
Heat Exchangers	$	1,550,681.99
Turboexpander	$	283,220.00
Power Block	$	2,758,295.81
Separation NH3	$	107,307.00
Separation N2/H2	$	-
AS & RN Reactors	$	3,326,583.31
MN particles	$	91,336,698.62
Subtotal direct cost	**$**	**116,926,973.02**
Contingency	$	8,184,888.11
Total direct cost	**$**	**125,111,861.14**
Land cost	$	1,007,571.02
EPC and owner cost	$	13,762,304.72
Total indirect cost	**$**	**14,769,875.74**
Total CapEx	**$**	**139,881,736.88**
OpEx (fixed)	$/y	2,797,634.74
Particle loss	$/y	355,128.85
Additional heat	$/y	-
OpEx (variable)	$/y	355,128.85
Total OpEx	**$/y**	**3,507,892.45**
Total revenue	**$/y**	**474,058.12**
LCOA w/o H_2	**$/tonne**	**213.11**

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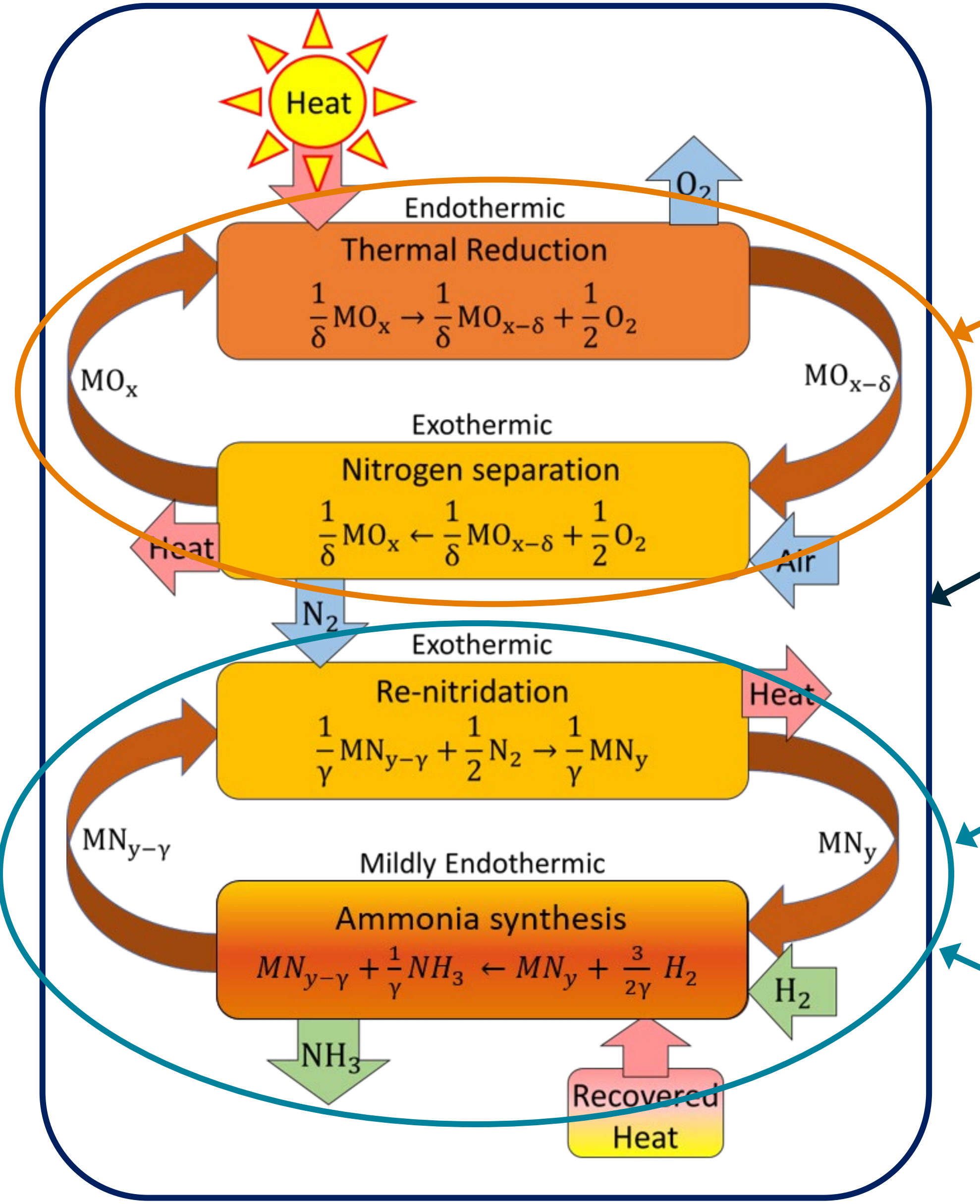
Upcoming STAP SolarPACES Talks



Evan Bush: "Demonstration of a Solar Air Separation Process to Produce High-Purity N_2 via $Ba_{0.15}Sr_{0.85}FeO_{3-\delta}$ Reduction/Oxidation Cycles," Wednesday, 17:40 (Today!)

Alberto de la Calle: "Techno-Economic Analysis of Solar-Thermal Ammonia Production," Friday, 8:30

Ty Nguyen: "Investigation of Co_3Mo_3N Reduction/Re-nitridation Extents as a Function of Temperature and N_2 Partial Pressure for Solar Thermochemical NH_3 Production," Friday, 9:10

James Miller: "Solar Ammonia Production via Novel Two-step Thermochemical Looping of a Co_3Mo_3N/Co_6Mo_6N pair," Friday, 9:50

Summary

- Solar Thermal Ammonia Production has potential to produce green ammonia using CSP, air, and water
- Air separation to purify N_2 was successfully demonstrated with BSF1585 in packed bed reactor; on-sun reduction reactor under construction
- Metal nitrides (MN_y) were successfully synthesized and characterized under both ambient and pressurized conditions
  - Co_3Mo_3N shown to successfully produce NH_3 when exposed to pure H_2 at pressures between 5 – 20 bar 600 – 750 °C
    - Reaction with pure H_2 ensures nitrogen source is bulk Mn_y
    - Performance is cyclic
  - Ambient reaction experiments imply there may be a catalytic aspect as well
- Technoeconomic and systems analyses show a path towards scale-up

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