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2021 SolarPACES

TUE-2C: Solar Fuels and Chemical Commodities

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Metal Nitride Materials for Solar-Thermal Ammonia Production

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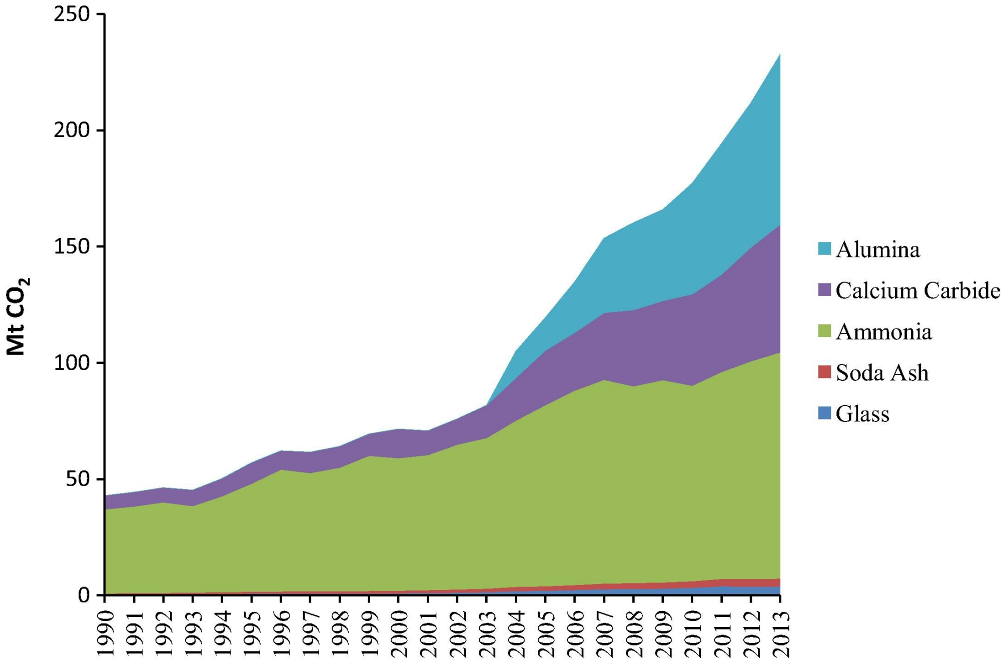
Sandia National Laboratories

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 ~1.4% of global CO_2 emissions[1]
- Ammonia synthesis consumes > 1% of the total energy worldwide[2]



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

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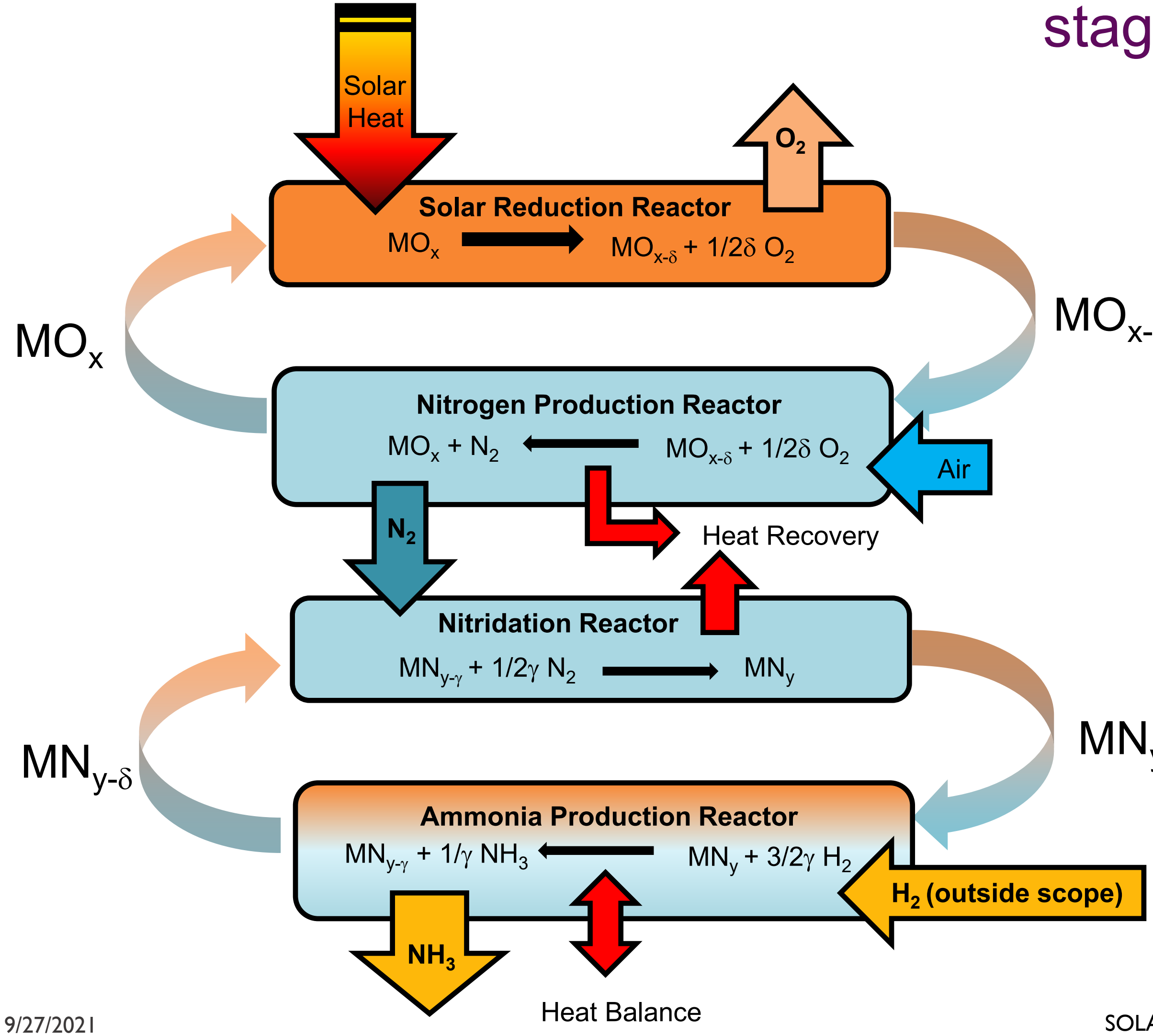
[1] Kyriakou, V., *Joule* **2020,** *4* (1), 142. [2] Institute for Industrial Productivity. Industrial Efficiency Technology Database http://ietd.iipnetwork.org/content/ammonia.

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



Solar Heat

O_2

Solar Reduction Reactor

$MO_x \rightarrow MO_{x-\delta} + 1/2\delta\ O_2$

MO_x

$MO_{x-\delta}$

Nitrogen Production Reactor

$MO_x + N_2 \leftarrow MO_{x-\delta} + 1/2\delta\ O_2$

Air

N_2

Heat Recovery

Nitridation Reactor

$MN_{y-\gamma} + 1/2\gamma\ N_2 \rightarrow MN_y$

$MN_{y-\delta}$

MN_y

Ammonia Production Reactor

$MN_{y-\gamma} + 1/\gamma\ NH_3 \leftarrow MN_y + 3/2\gamma\ H_2$

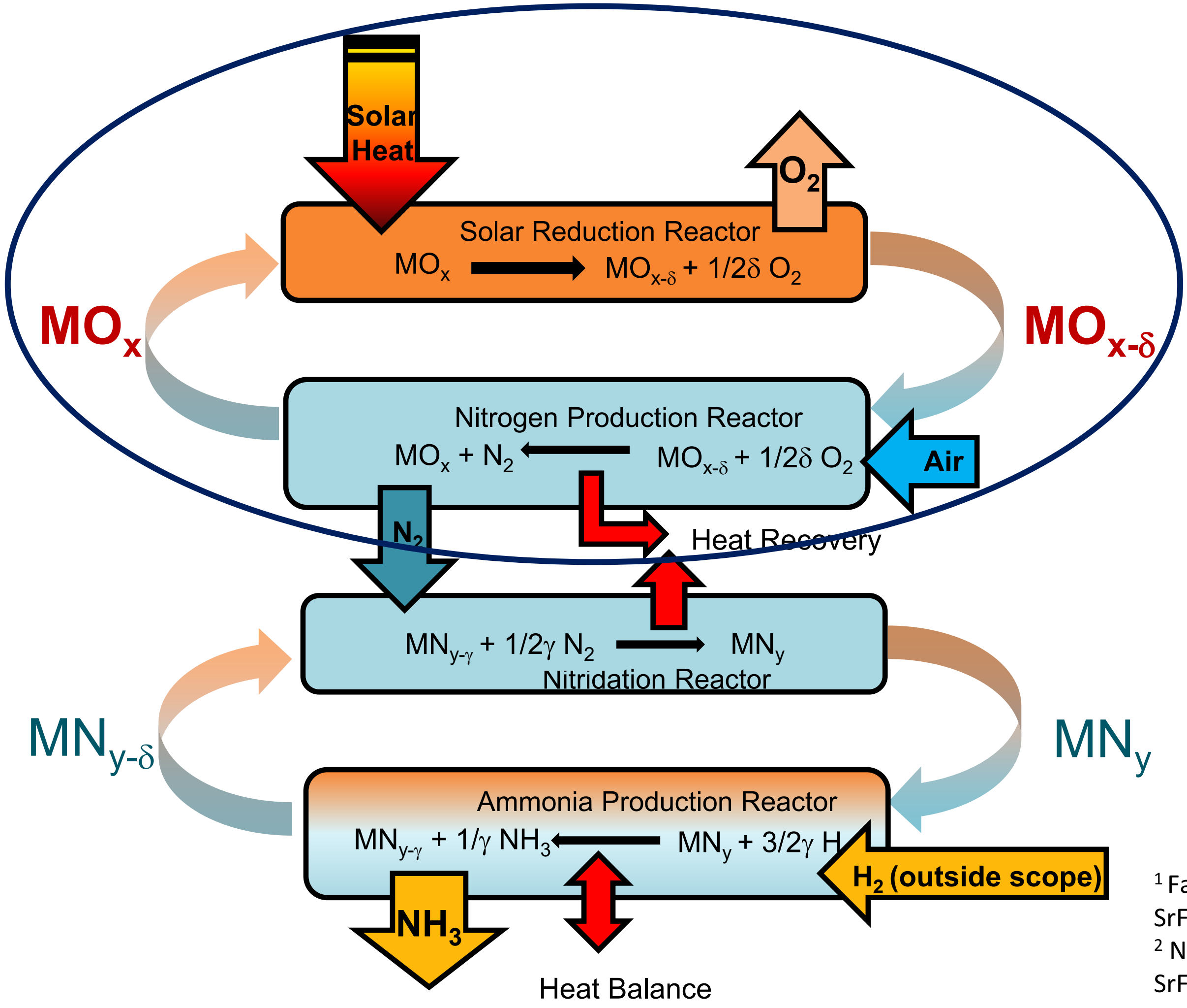
H_2 (outside scope)

NH_3

Heat Balance

- 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



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H_2 (outside scope)

NH_3

Heat Balance

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

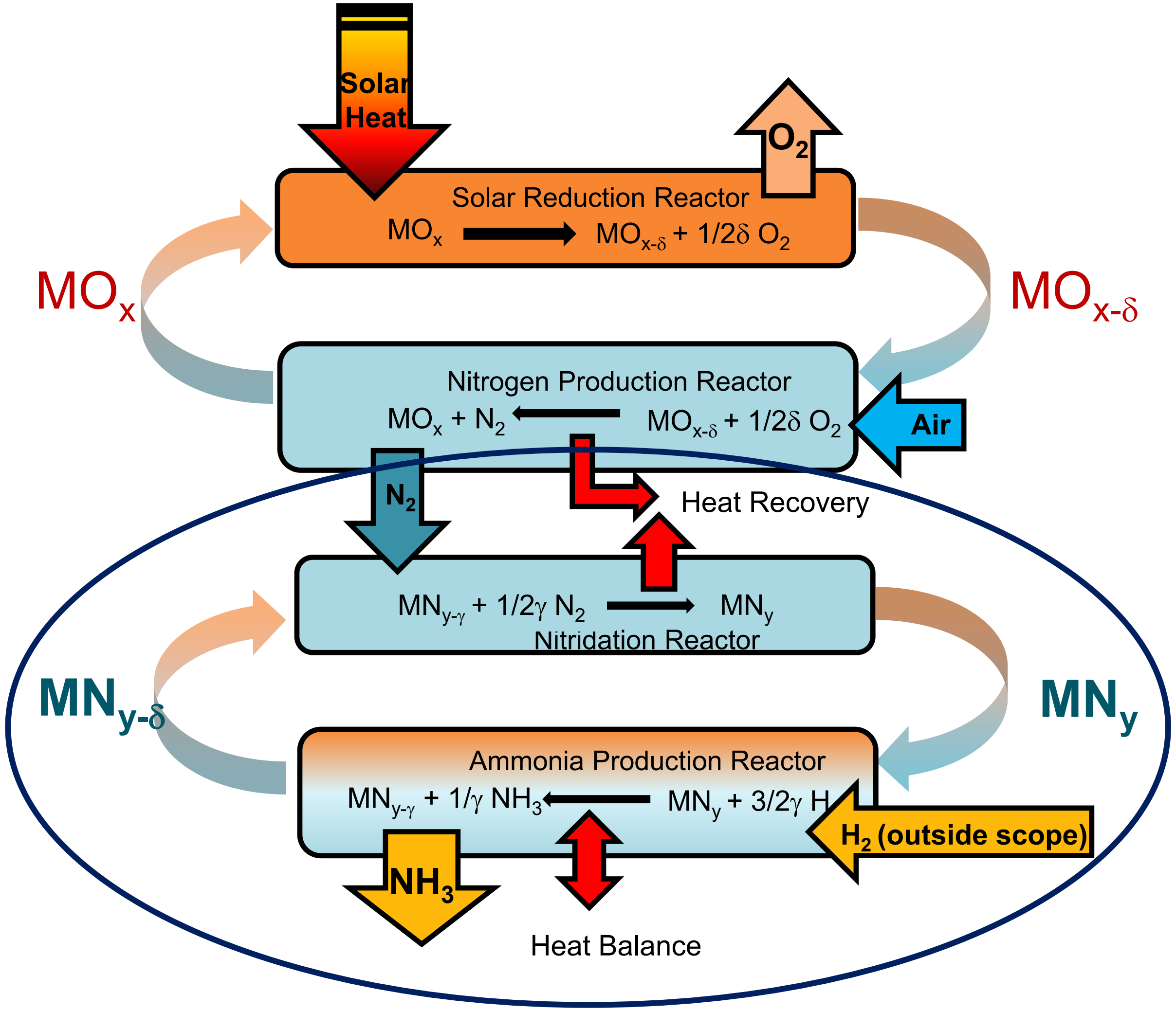
Rate Limiting Mechanism(s) Determination of $SrFeO_{3-\delta}$ and $(Ba,La)_{0.15}Sr_{0.85}FeO_{3-\delta}$ Perovskite Reduction/Oxidation Reactions for Air Separation via Two-step Solar Thermochemical Cycles

Nhu P. Nguyen, Georgia Institute of Technology (Thurs 2A)

[1] Farr, T. P.; Nguyen, N. P.; Bush, H. E.; Ambrosini, A.; Loutzenhiser, P. G., "An A- and B-Site Substitutional Study of SrFeO3-δ Perovskites for Solar Thermochemical Air Separation." *Materials* **2020,** *13* (22).

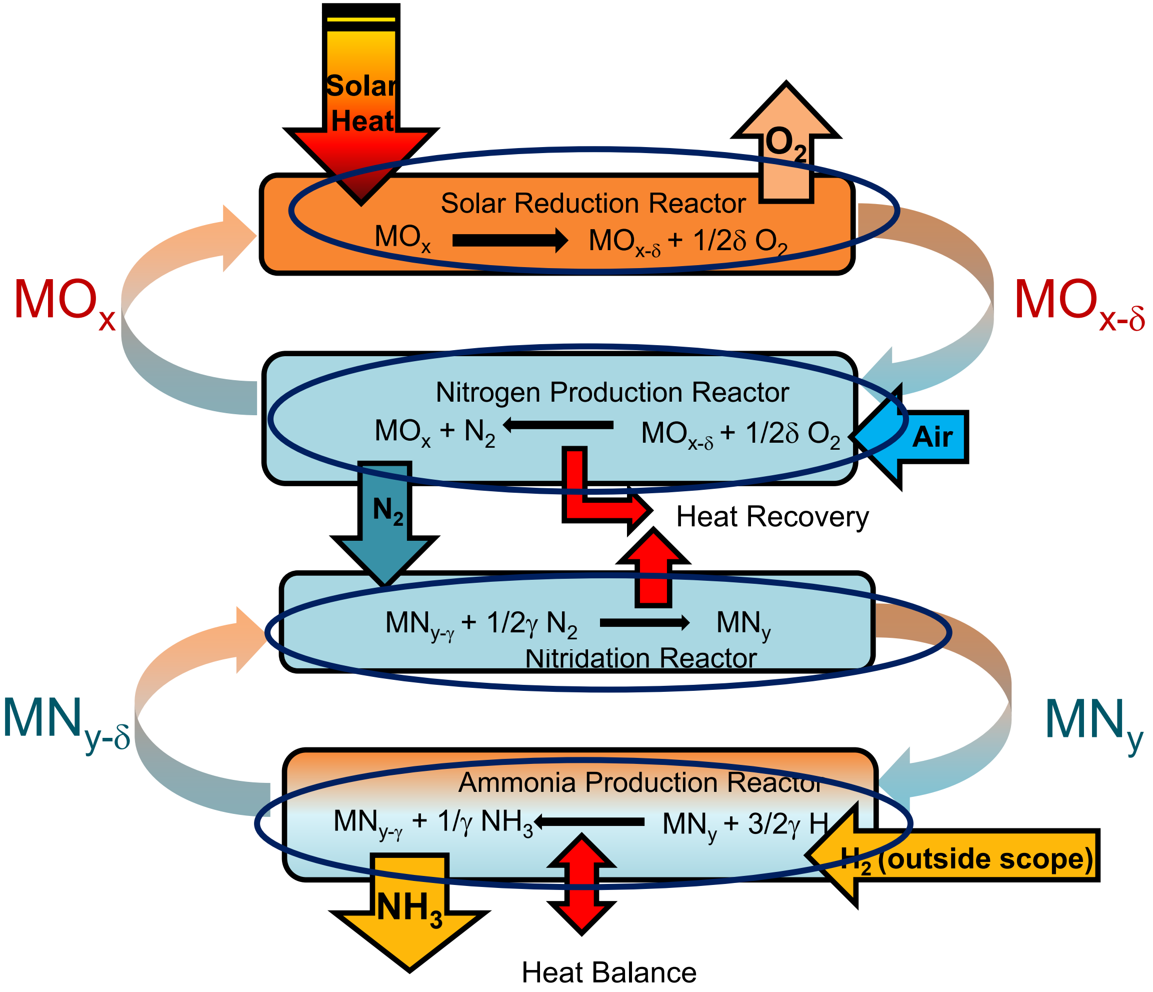
[2] Nguyen, Farr, Bush, Ambrosini, Loutzenhiser, "Air separation via two-step solar thermochemical cycles based on SrFeO3-δ and (Ba,La)0.15Sr0.85FeO3-δ perovskite reduction/oxidation reactions to produce N2: Rate limiting mechanism(s) determination.", submitted to Phys Chem Chem Phys, *in review*.

Four Project Thrusts



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

Four Project Thrusts



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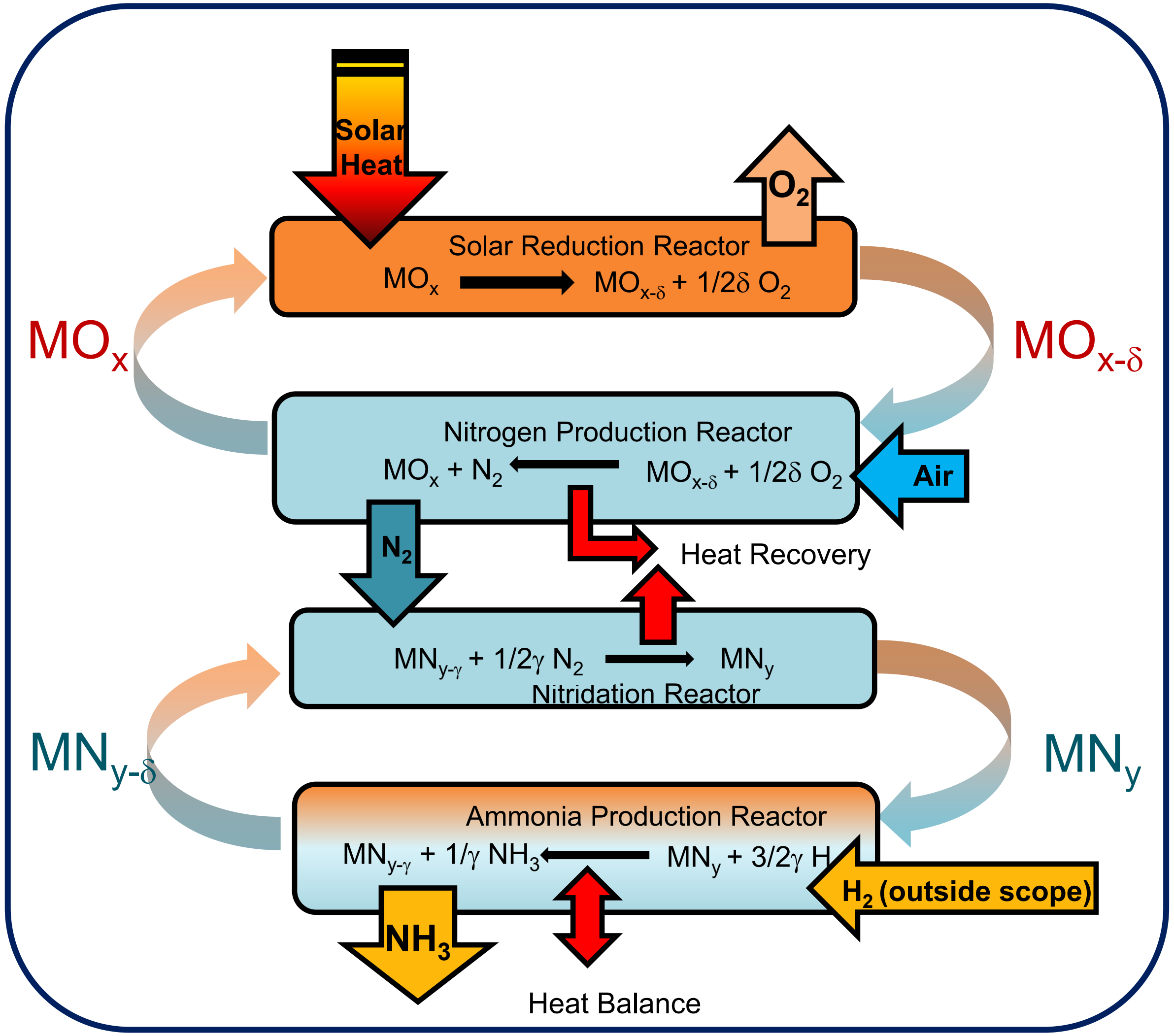
3. Lab-scale Reactors Modeling, Design, and Testing: Model and identify design parameters for N_2 separation and NH_3 synthesis bench-scale reactors; construct and test with working materials

Design and Operation of Reactors for Solar Thermochemical Air Separation for Ammonia Synthesis

H. Evan Bush, Sandia National Laboratories (Thurs 2A)

Four Project Thrusts



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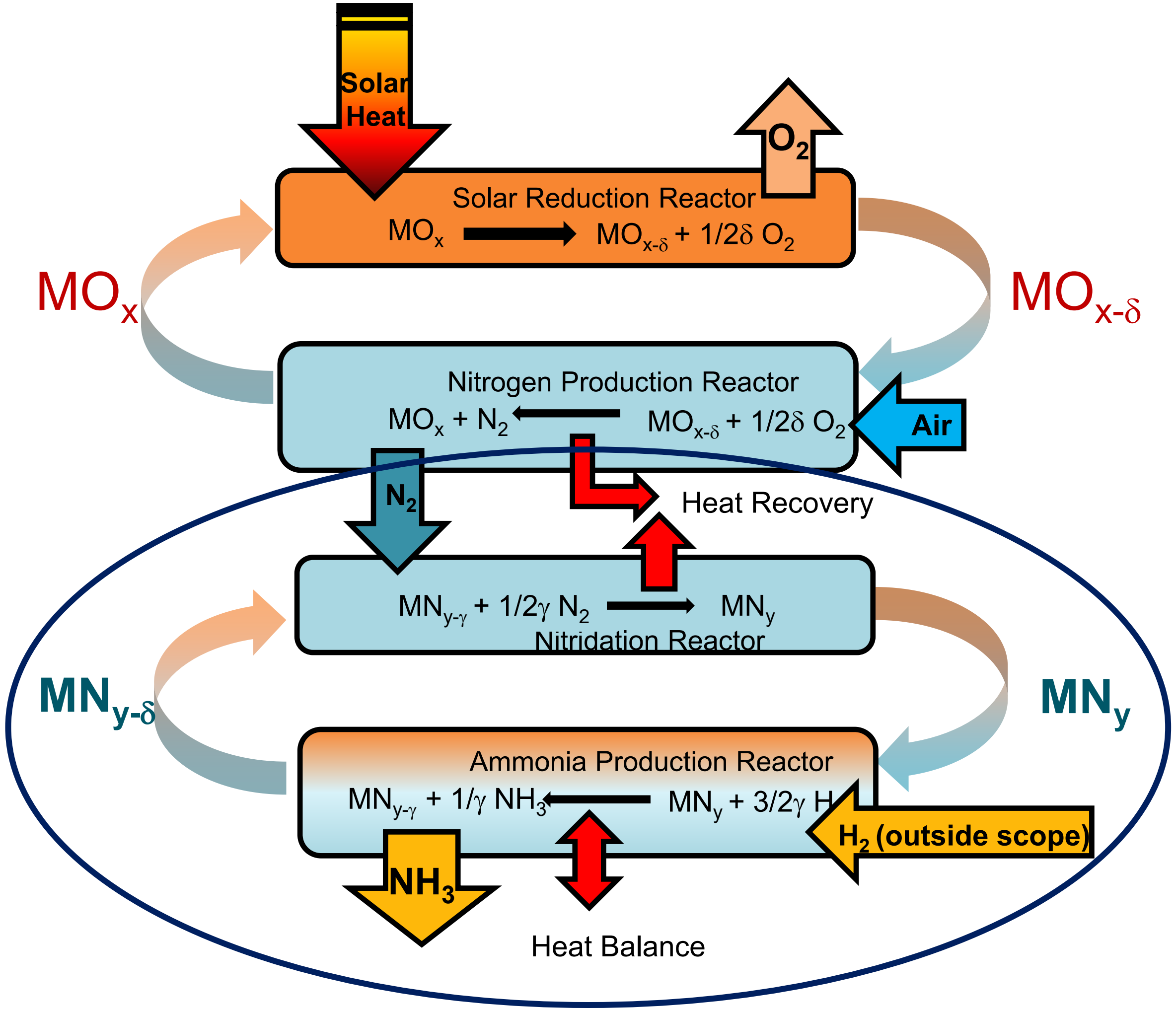
Solar-Thermal Ammonia Production: System Design and Techno-economic Analysis

Alberto de la Calle, Arizona State University (Tues 2C)

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

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



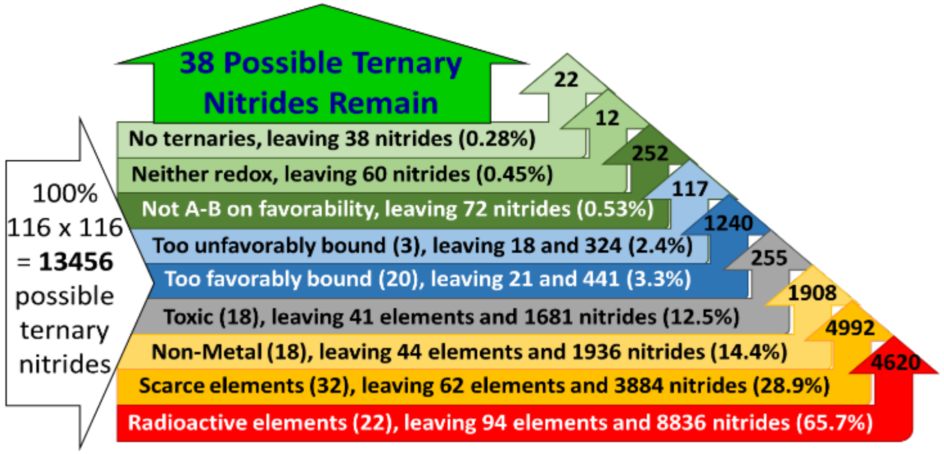
- Nitride is reduced by H_2 to form $Mn_{y-\gamma}$+ NH_3, then regenerated by N_2 from 1st cycle
- Not as straightforward as oxide development
  - Pool of candidates much smaller
  - Thermodynamics are challenging; NH_3 dissociates at high T
  - Nitrogen diffusion in metal nitrides is slower and less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

Co_3Mo_3N

- Initial thermodynamic calculations (ASU) imply that candidate must be a ternary nitride (MM'N)
- Preliminary candidate: Co_3Mo_3N (CMN331)
  - CMN331 can undergo reversible phase change to CMN661, reversibly losing 50 mol% of nitrogen:

$$Co_3Mo_3N \leftarrow\rightarrow Co_6Mo_6N$$

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



100% 116 x 116 = **13456** possible ternary nitrides

38 Possible Ternary Nitrides Remain

No ternaries, leaving 38 nitrides (0.28%)

Neither redox, leaving 60 nitrides (0.45%)

Not A-B on favorability, leaving 72 nitrides (0.53%)

Too unfavorably bound (3), leaving 18 and 324 (2.4%)

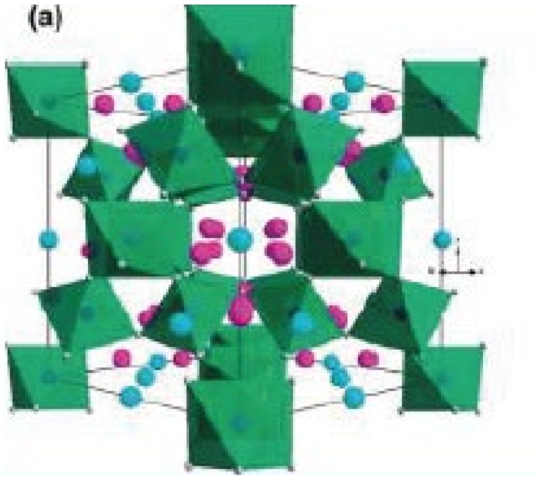
Too favorably bound (20), leaving 21 and 441 (3.3%)

Toxic (18), leaving 41 elements and 1681 nitrides (12.5%)

Non-Metal (18), leaving 44 elements and 1936 nitrides (14.4%)

Scarce elements (32), leaving 62 elements and 3884 nitrides (28.9%)

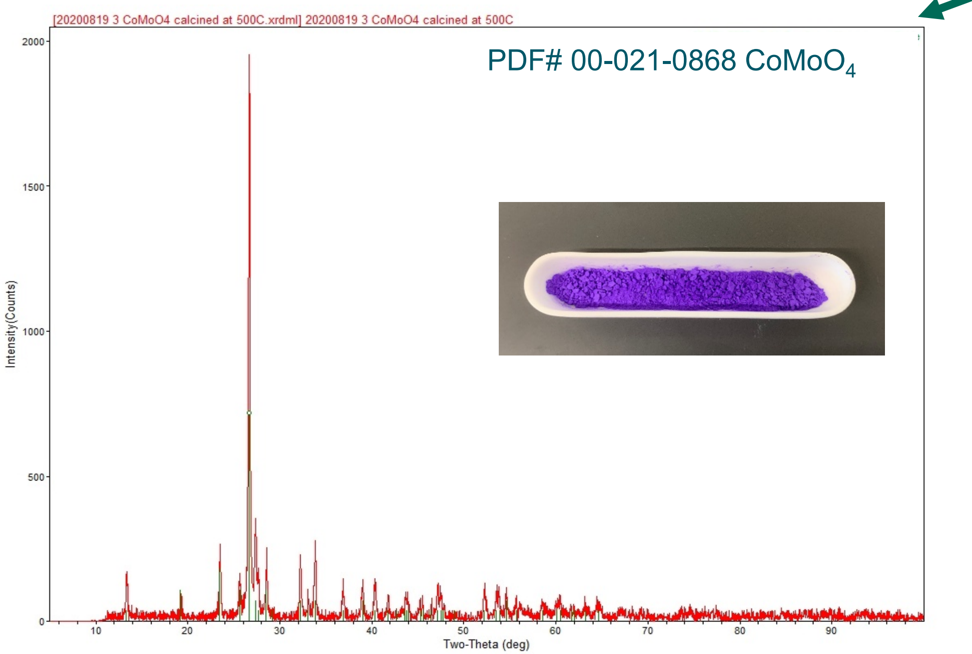
Radioactive elements (22), leaving 94 elements and 8836 nitrides (65.7%)

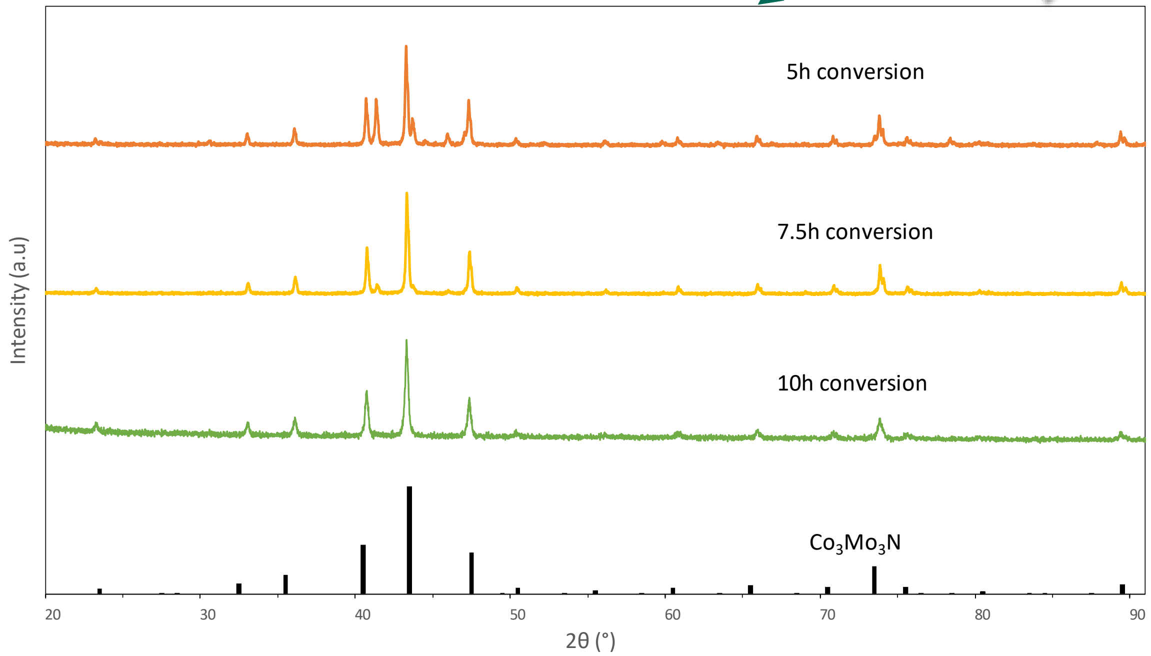


*Hunter, S.M., Mckay, D., Smith, R.J., Hargreaves, J.S.J., Gregory, D.H., 2010, Chemistry of Materials, 22(9), pp. 2898-2907.
Gregory, D.H., Hargreaves, J.S.J., Hunter, S.M., Catalysis Letters, 2011, 141(1), pp. 22-26.

Synthesis of Co_3Mo_3N

- Solution: $Co(NO_3)_2{\cdot}6H_2O$ + $(NH_4)6Mo_7O_{24}{\cdot}4H_2O$
- Heat the solution: Purple precipitate
- Vacuum filtration
- Dry overnight $CoMoO_4{\cdot}\ xH_2O$
- Calcine: $CoMoO_4$
- at 78React5 °C, 10% H_2/N_2
- Co_3Mo_3N



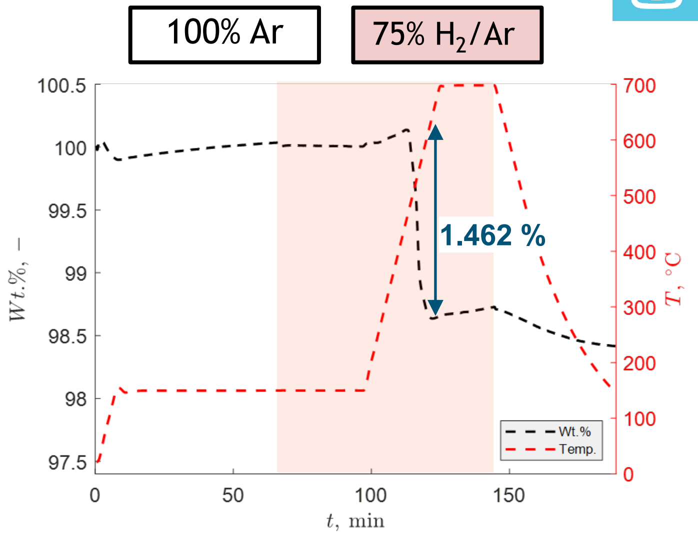


Synthesis of oxide precursor followed by nitridation in 10% H_2 for 10 hours results in single phase Co_3Mo_3N under milder synthesis conditions compared to ammonolysis[1]

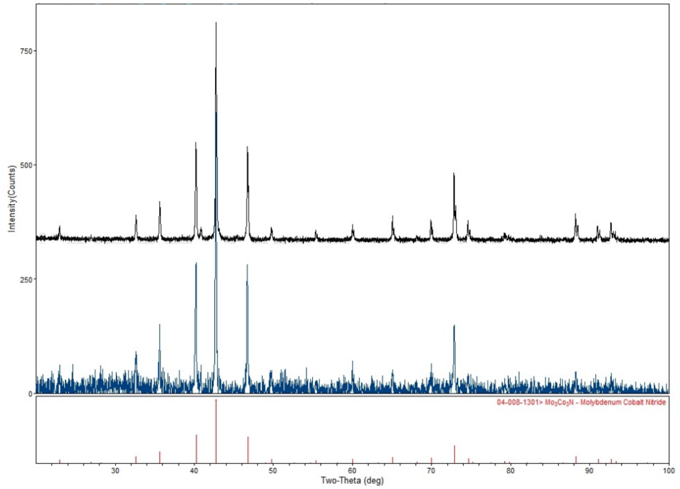
[1] Hunter, S. M., et al., *Chem Mater* **2010,** *22* (9), 2898.

Co_3Mo_3N → Co_6Mo_6N Reaction

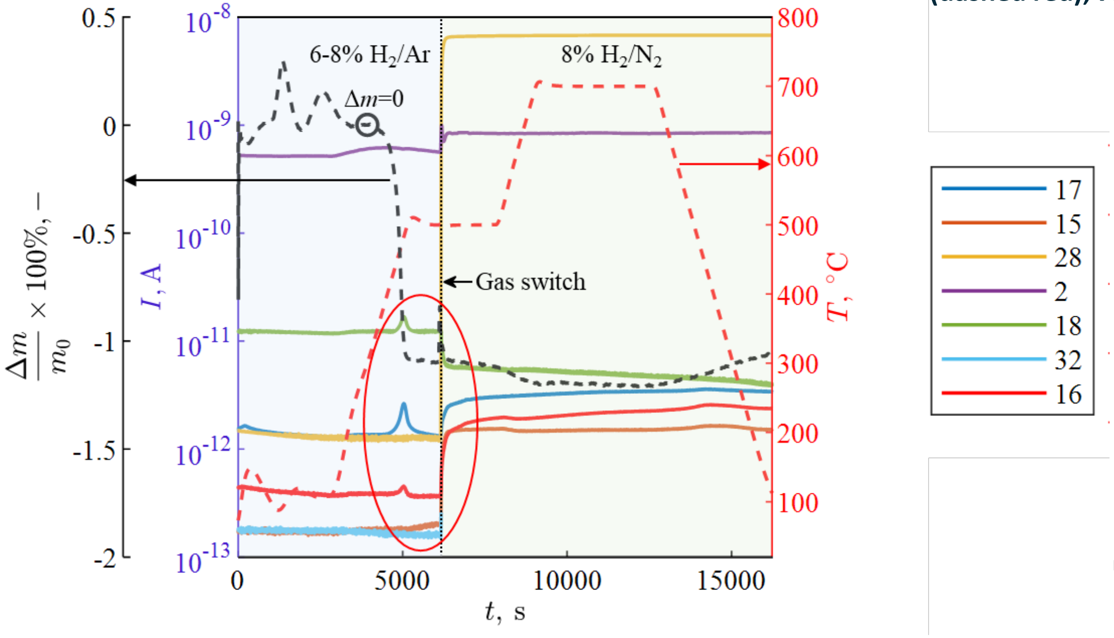
- Rapid kinetics for T ≥ 500 °C
- Reducible for wide range of T, $[H_2]$
- Total mass loss is close to theoretical for full conversion to Co_6Mo_6N (1.46%)
- XRD shows no change in structure (expected); no secondary phases detected
- NH_3 formation detected by RGA
  - Difficult to quantify due to m/z overlap with H_2O, N_2
  - Reduction conditions favor NH_3 dissociation



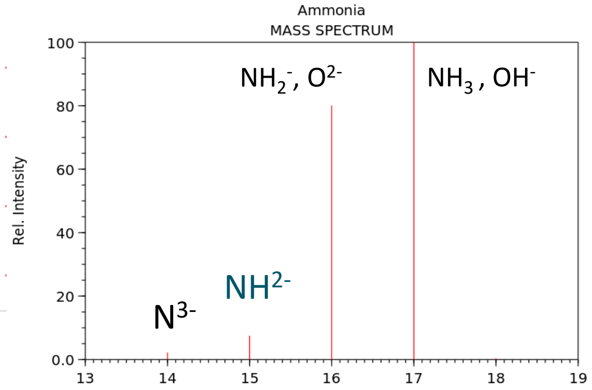
Co_3Mo_3N mass loss (dashed black) and sample temperature (dashed red); 75% H_2/Ar (reducing flow) is shown as a red region.



XRD peaks of Co_3Mo_3N sample before (black) and after (after) reduction in TGA under 75% H_2/Ar up to 700 °C



RGA of CMN331; reduction under 6-8% H_2/Ar at 500 C (Georgia Tech)

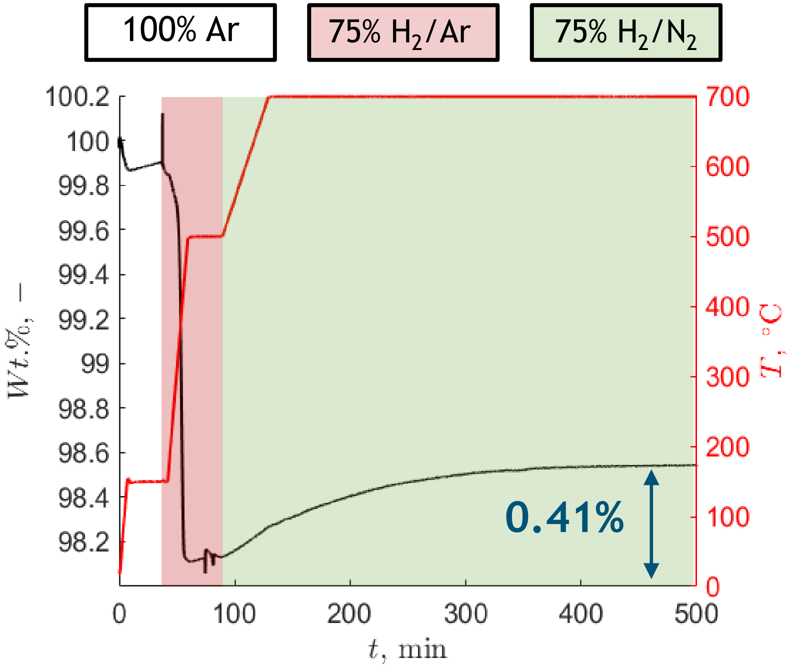


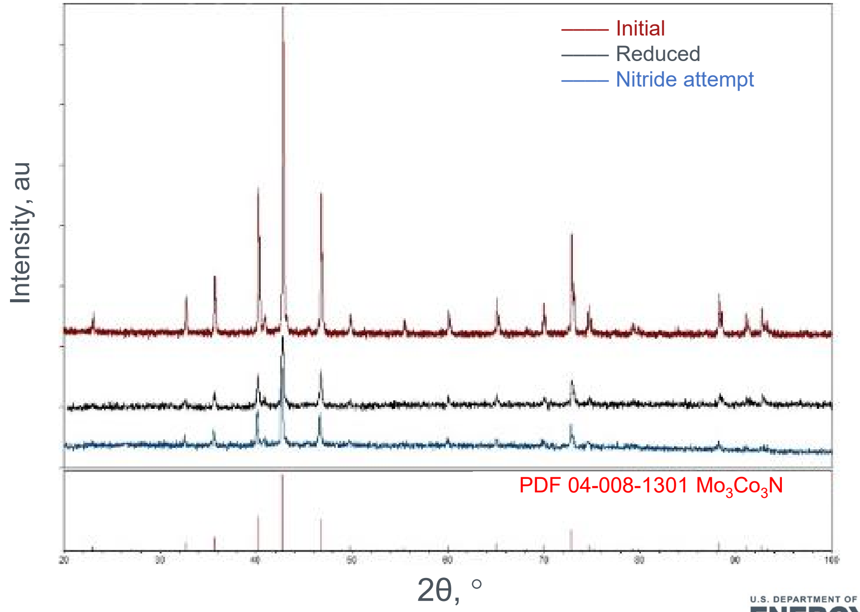
NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

NH_3 fragmentation pattern

CMN661→331: Re-nitridation

- H_2/N_2 TGA reduction at varying T and $[H_2]$
- Partial re-nitridation attained
  - Maximum of 0.41% weight gain at 700 °C, 75% H_2/N_2
    - Corresponds to ~ 35% of complete re-nitridation
  - Increased with $[H_2]$ > 1%
  - No improvement for small induced overpressure
  - No change in observed in XRD (right)
- $[H_2]$ > 0% necessary; cannot re-nitride in pure N_2
  - “Runaway” linear mass gain under pure N_2
    - Potential oxidation from small O_2 impurity in sweep
    - Phase change, potential Co-oxide formation (not shown)





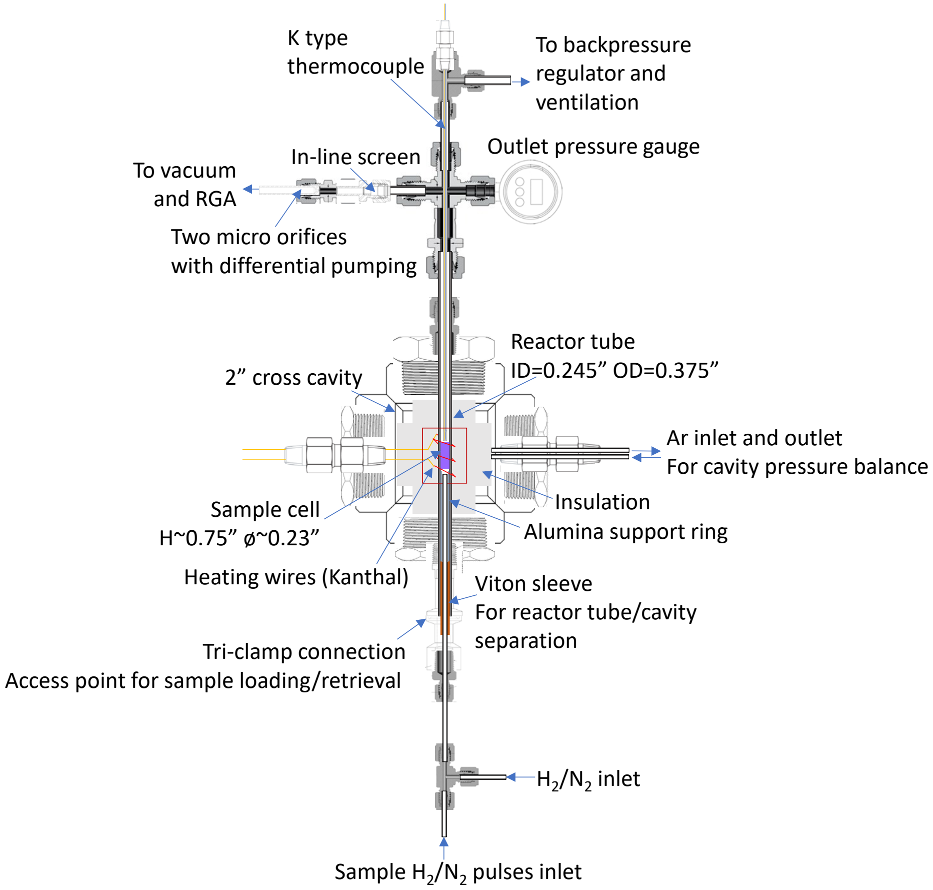
Extending Nitride Candidate Pool

Composition Target	Single Phase? (> 95% via XRD)
Co_3Mo_3N	Yes
$(Co_xNi_{1-x})_2Mo_3N$ (x = 0.25, 0.5, 0.75)	Yes
Ni_2Mo_3N	Yes
$(Fe_xNi_{1-x})_2Mo_3N$ (x = 0.25, 0.5, 0.75)	Yes (except x = 0.75)
Fe_3Mo_3N	Yes
$(Co_xFe_{1-x})_3Mo_3N$ (x = 0.25, 0.5, 0.75)	Yes
$Fe_3(W_{0.25}Mo_{0.75})_3N$	No
$Co_3(W_yMo_{1-y})_3N$ (y=0.1, 0.25, 0.5, 0.75)	No

Composition Target	Single Phase? (> 95% via XRD)
Fe_3W_3N	No
Ni_2W_3N	No
Co_3W_3N	No
$CoMnN_2$	No
$MnMoN_2$	No
Mn_2FeN_2	No
Zn_3MoN_4	No

- Attempted both A-site and B-site substitution
- (Ni,Fe,Co)Mo_3N compounds form almost complete solid solutions
- W tends to reduce to metal before other cations in B-site W-substituted nitrides
- Conversely, MnOx precursor reluctant to reduce completely, frustrating synthesis of Mn-nitrides
- Testing on the single phase materials underway

Ammonia Synthesis Reactor (ASU)



- NH_3 synthesis and re-nitridation reactions are achieved in one reactor cyclically by switching between pressurized H_2 and N_2 inlet gas flows
- Operation up to 800°C and 30 bar
  - Encourage more efficient re-nitridation
  - Discourage NH_3 decomposition post-synthesis
  - Broaden reaction conditions to access difficult to synthesis nitrides, e.g. W- and Mn- nitrides

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
- Co_3Mo_3N has been identified as a potential candidate for ammonia production
  - Synthesized via oxide precursor synthesis followed by nitridation under 10% H_2/N_2
  - Synthesis method can be extended to other candidate nitrides
- $Co_3Mo_3N \rightarrow Co_6Mo_6N$ reduction demonstrated on TGA with rapid kinetics
  - Formation of NH_3 qualitatively observed, but not quantitatively determined
  - Material retains crystal structure; no secondary phases observed in XRD
- Partial re-nitridation back to CMN331 of ~35% of max nitridation observed
  - Reaction parameters in TGA differ from experimental conditions in literature
  - Experiments at Georgia Tech better mimic re-nitridation conditions with more sensitive, quantitative analytical techniques (GC-MS)
- ASU NH_3 synthesis/re-nitridation reactor under development that will permit experiments (reduction/re-nitridation) under precisely controlled T, pH_2

Acknowledgements

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