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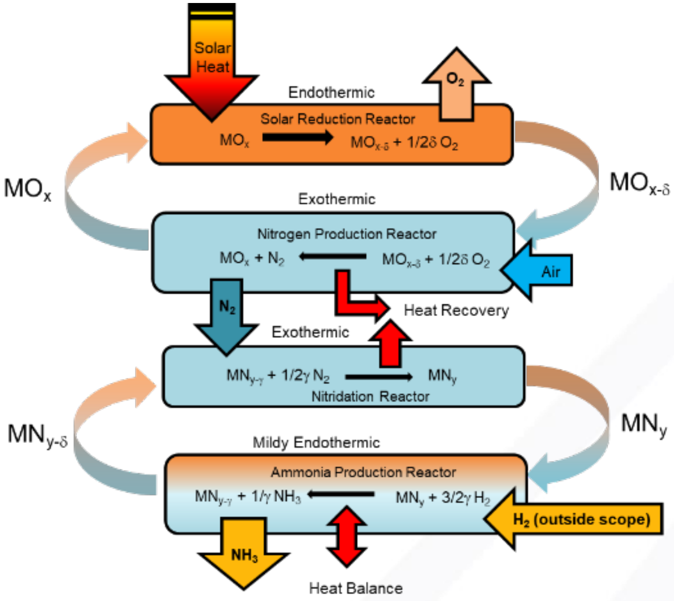

Synthesis of Metal Nitrides for Solar Thermochemical Ammonia Production (STAP)

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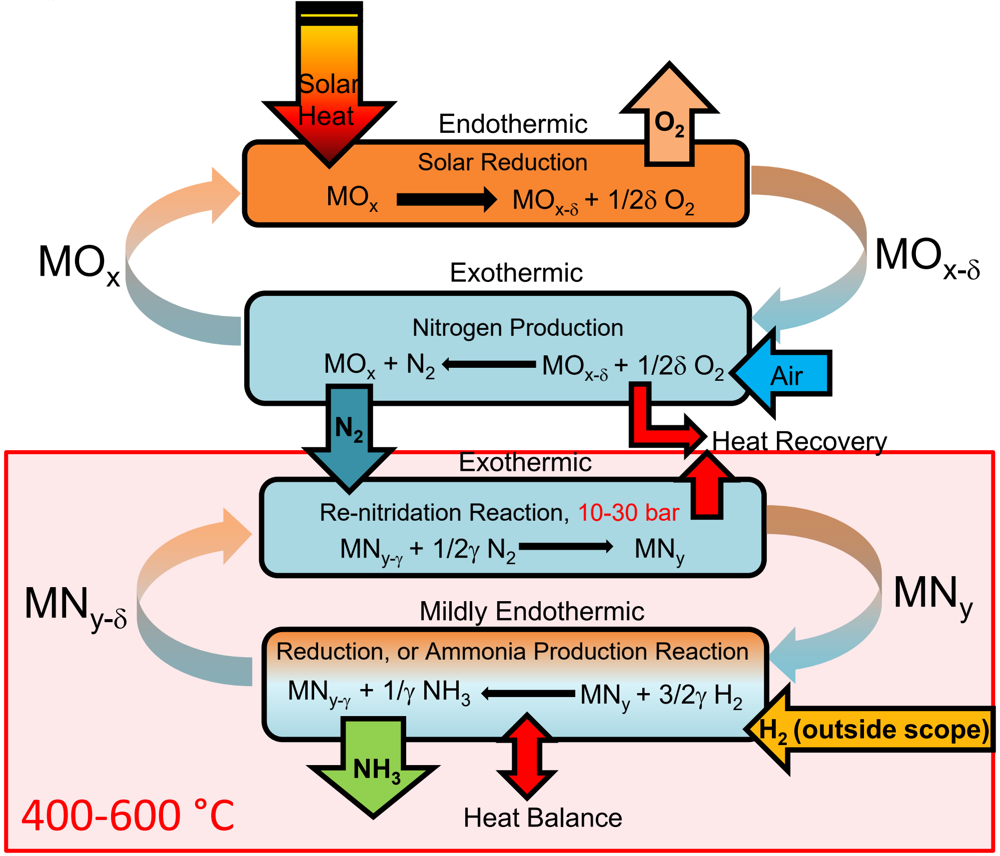
STAP Objectives – The Technology’s Critical Path

Project Objective: We propose to demonstrate the feasibility of a 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.



Innovative features of the project

- Inputs are sunlight, air, and green hydrogen; the output is ammonia
- Significantly lower pressures (10-30 bar) than Haber-Bosch (~300 bar)
- Greatly decreases or eliminates carbon footprint
- The process consumes neither the oxide nor the nitride particles, which actively participate cyclically
- Mild operating temperature (400-600 °C)

Metal Nitrides for NH_3 Production and re-nitridation reactions

Objective: seek materials to decrease the pressure (cost) at a temperature wherein kinetics are rapid, conversion improved, and selectivity high (avoid ammonia decomposition). Target operating parameters: 10-30 bar, 400-600 °C.

Mo_2N, CoN, Ni_3N, Cu_3N, etc.

Binary nitrides (AN) are unlikely to be sufficient to perform the necessary chemical looping reactions

→

Co_3Mo_3N, Fe_3Mo_3N, Ni_2Mo_3N, Co_3W_3N, etc.

Ternary nitrides (ABN) are more promising candidates to balance between NH_3 production and re-nitridation.

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

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

50% mobile lattice N

Challenge: synthesis of ternary metal nitrides

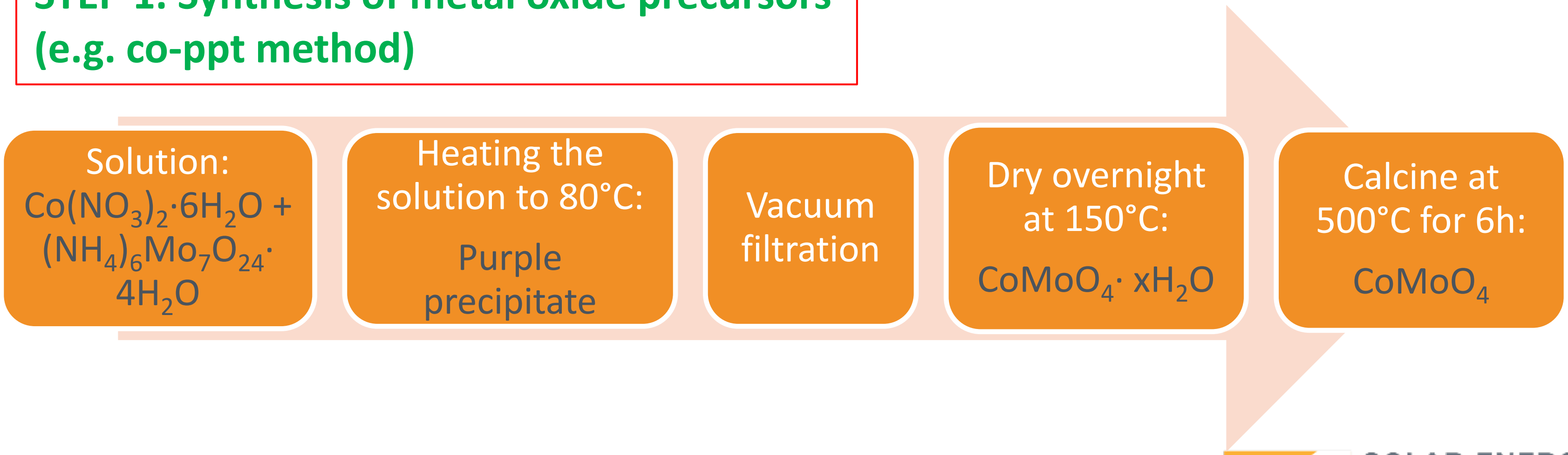
Identification and synthesis of suitable metal nitrides is the highest risk/highest reward aspect of STAP project

Synthesis of Ternary metal nitrides A-Mo-N

Method: "Ammonolysis" of A-Mo-O oxide precursors (e.g. $CoMoO_4 \rightarrow Co_3Mo_3N$)

- Does not require handling NH_3, use 10% H_2-N_2 mixture gas as nitrogen source (eased ES&H concerns)
- Relatively fast "ammonolysis" kinetics at ambient pressure (vs. direct nitridation of Co-Mo metal mixtures)
- Single-phase Co_3Mo_3N can be achieved (vs. urea glass method)
- Facile synthesis of $CoMoO_4$ oxide precursors via modified co-precipitation (co-ppt) or Pechini sol-gel methods.

STEP 1. Synthesis of metal oxide precursors (e.g. co-ppt method)



Solution: $Co(NO_3)_2{\cdot}6H_2O$ + $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$

Heating the solution to 80°C: Purple precipitate

Vacuum filtration

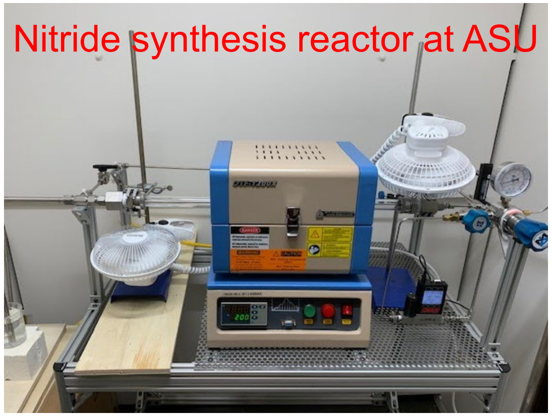
Dry overnight at 150°C: $CoMoO_4{\cdot}xH_2O$

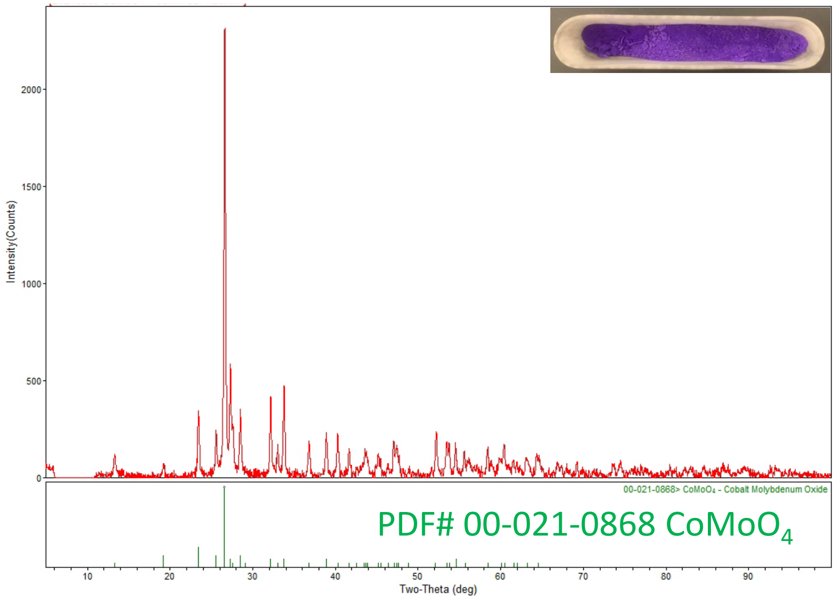
Calcine at 500°C for 6h: $CoMoO_4$

“Ammonolysis” of A-Mo-O oxide precursors (cont.)

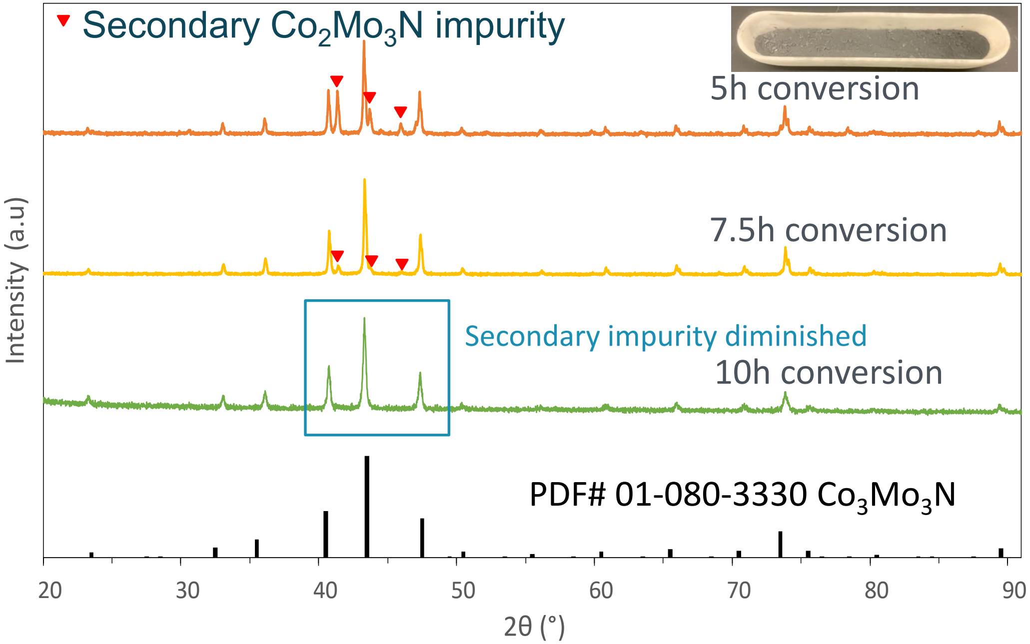
STEP 2. Nitridation of metal oxide precursors

- Single-step conversion temperature at 785 °C
- Atmosphere: 50 sccm 10% H_2 with N_2 balance
- Dwell time: 10 - 12 h
- Near single-phase Co_3Mo_3N product





Single-phase $CoMoO_4$ oxide precursor from co-ppt synthesis.



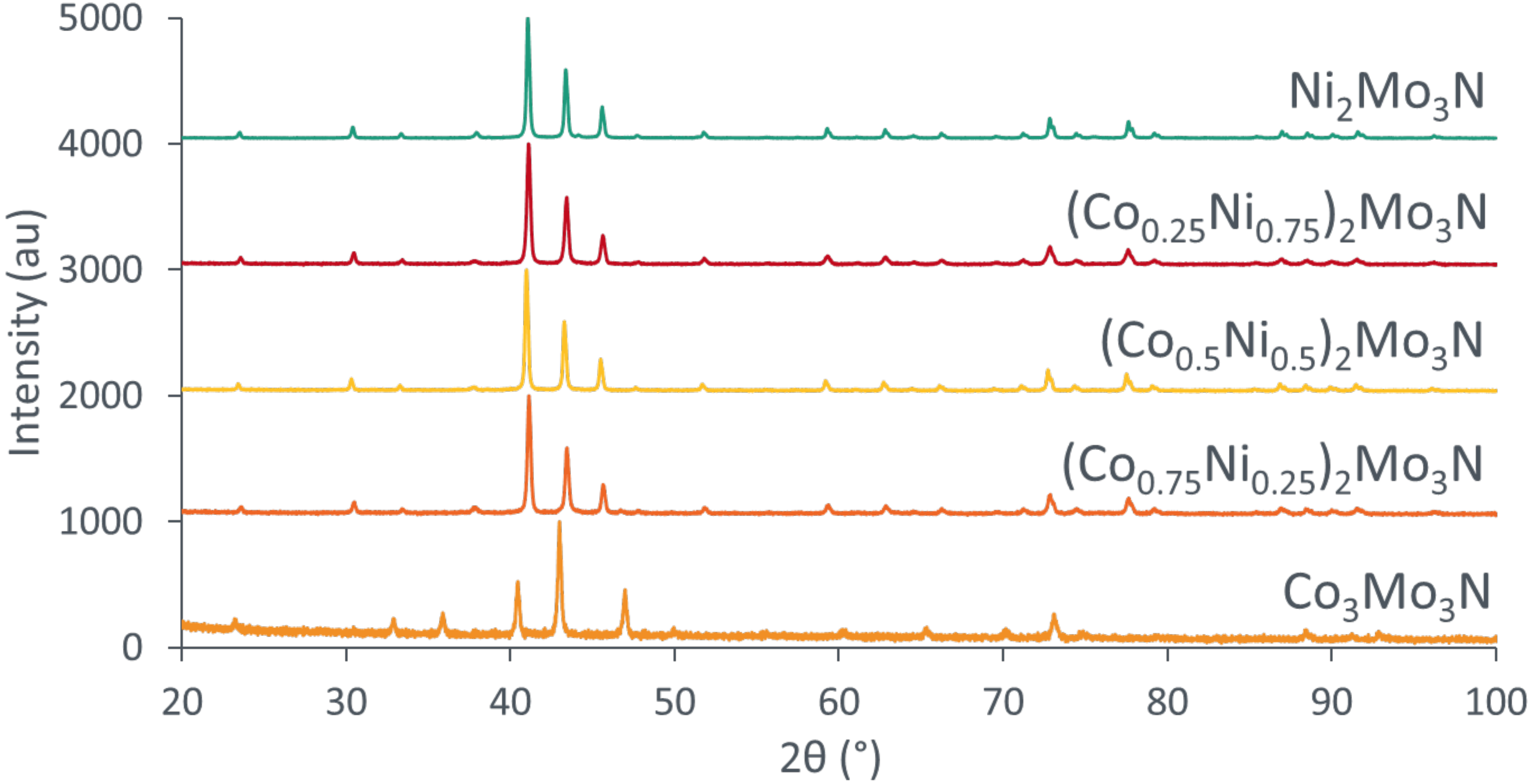
Nitride products after 5 h, 7.5 h and 10 h of nitridation.

(Fe, Co, Ni) – Mo – N quaternary nitrides

Target composition	Oxide synthesis method	Precursor oxide product	Single phase after nitridation?
Fe_3Mo_3N	Co-ppt or Pechini	$FeMoO_4$ or $Fe_2(MoO_4)_3 + Fe_2O_3$	Yes
Ni_2Mo_3N	Co-ppt or Pechini	$NiMoO_4$	Yes
$(Co_{0.25}Ni_{0.75})_2Mo_3N$	Pechini	$CoMoO_4$ + possible MoO_3	Yes
$(Co_{0.5}Ni_{0.5})_2Mo_3N$	Pechini	$NiMoO_4$ + possible MoO_3	Yes
$(Co_{0.75}Ni_{0.25})_2Mo_3N$	Pechini	$CoMoO_4$ + possible MoO_3	Yes
$(Fe_{0.25}Ni_{0.75})_2Mo_3N$	Pechini	$Fe_2(MoO_4)_3$ + possible MoO_3 + possible $NiMoO_4$	Yes
$(Fe_{0.5}Ni_{0.5})_2Mo_3N$	Pechini	$Fe_2(MoO_4)_3$ + possible MoO_3 + possible $NiMoO_4$	Yes
$(Fe_{0.75}Ni_{0.25})_2Mo_3N$	Pechini	$FeMoO_4 + NiMoO_4$	No
$(Fe_{0.25}Co_{0.75})_3Mo_3N$	Pechini	$Fe_{0.3}Co_{0.7}MoO_4$ + possible $CoMoO_4$	Yes
$(Fe_{0.5}Co_{0.5})_3Mo_3N$	Pechini	$Fe_{0.3}Co_{0.7}MoO_4$ + possible $CoMoO_4$	Yes
$(Fe_{0.75}Co_{0.25})_3Mo_3N$	Pechini	$Fe_2(MoO_4)_3 + Fe_{0.3}Co_{0.7}MoO_4$	Yes

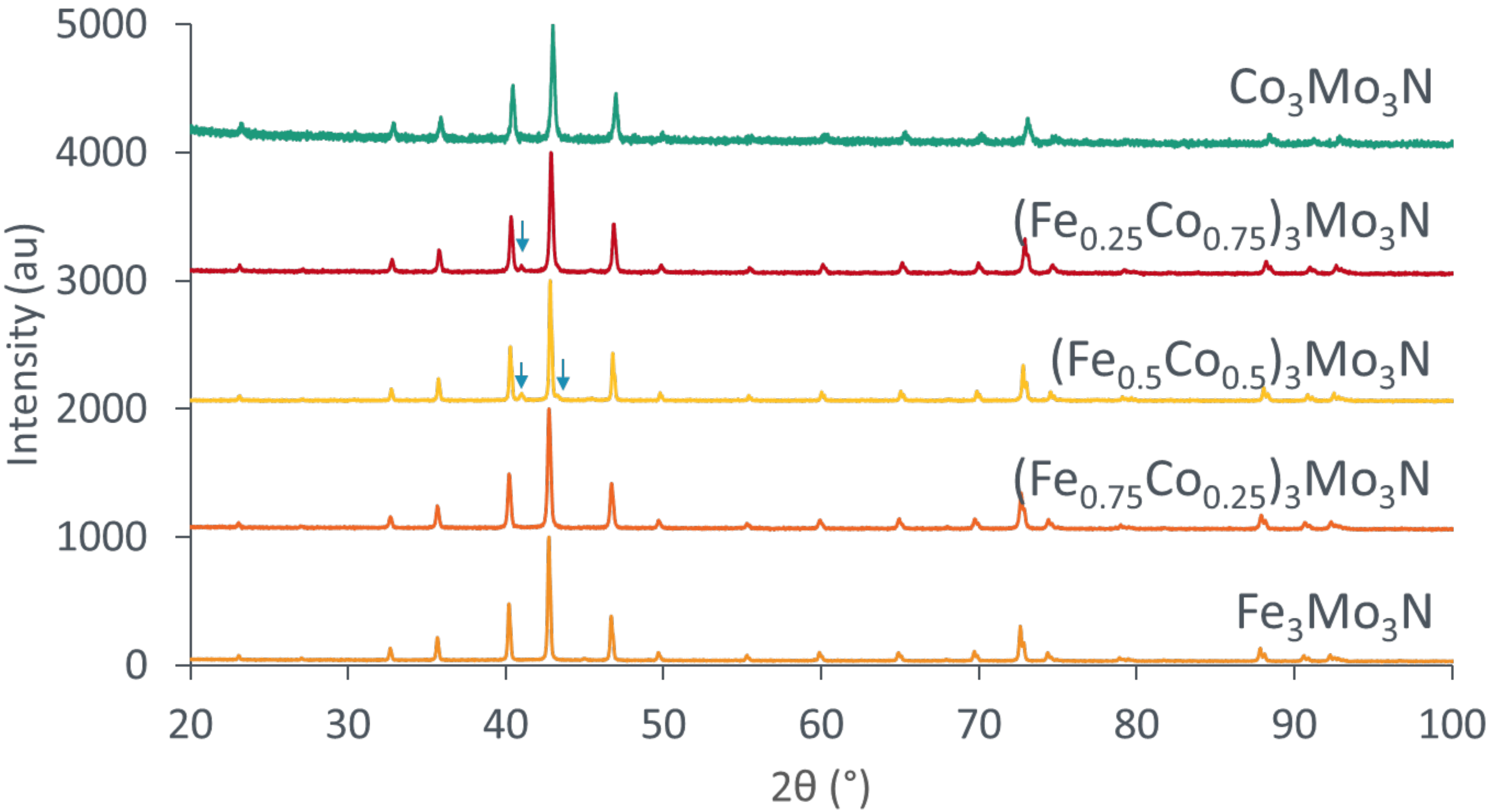
Precise control of oxide synthesis conditions not required!

$(Co_xNi_{1-x})_2Mo_3N$ Ternary and Quaternary Nitrides



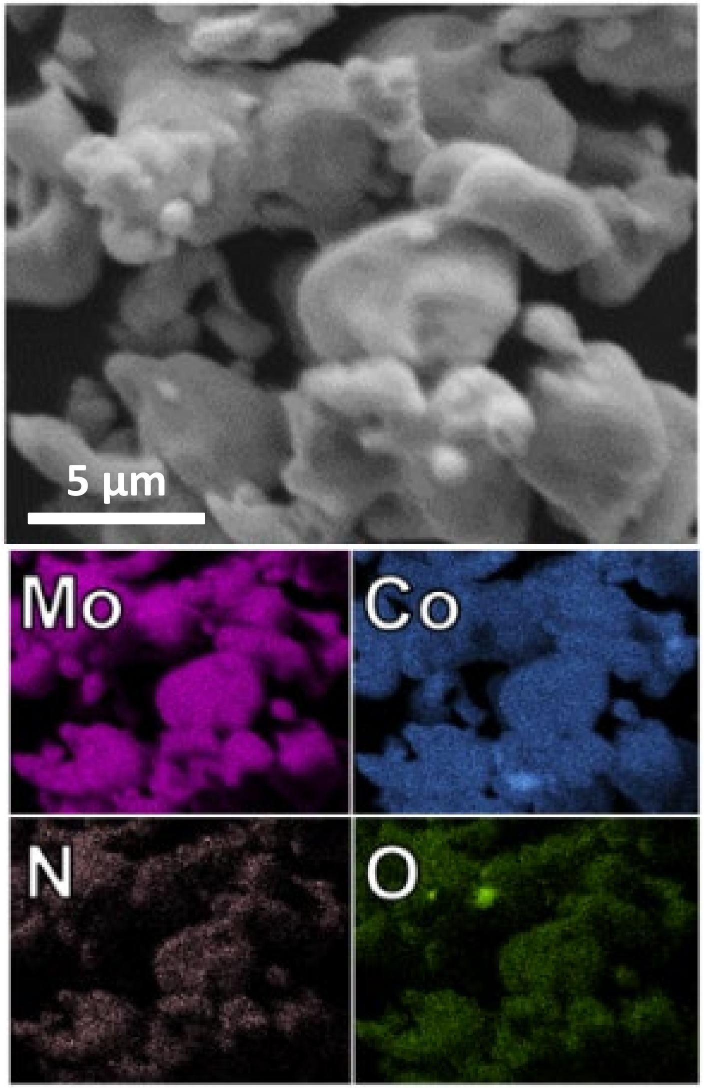
Single phase nitrides at all doping concentrations retaining the Ni_2Mo_3N ("231") crystal phase

$(Co_xFe_{1-x})_3Mo_3N$ Ternary and Quaternary Nitrides



- Small (< 5%) $(Co,Fe)_2Mo_3N$ impurity phase in 25% and 50% [Fe]

SEM-EDS of Co_3Mo_3N



Composite SEM-EDS maps for Co_3Mo_3N

- Near-uniform elemental distribution indicates no apparent phase segregation, corroborating XRD results
- Smooth particle morphology with 5-20 µm particle size distribution
- Low percentage of oxygen likely from surface passivation
  - No oxide phase observed in XRD
- XPS depth profiling may help characterize surface oxide layer (planned)

Nitride Screening System for Chemical Looping NH_3 Production

1. Reactive gas input port

   High [H_2]

2. Residual gas analyzer (RGA)

   Gas monitoring

3. Check and bypass valve

   Overpressure

4a. Heated SS outlet line

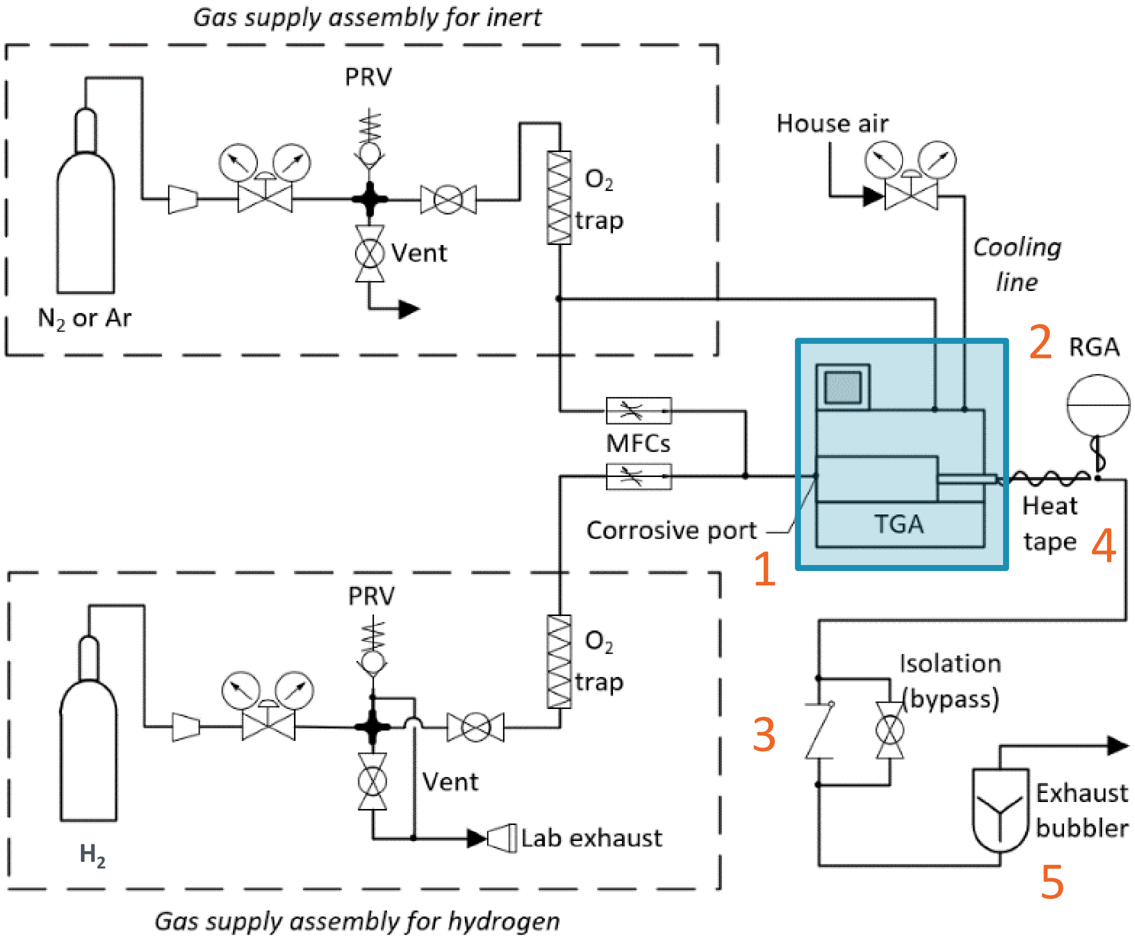
   Condensation (H_2O)

4b. Plastic outlet lines

   Adsorption (NH_3)

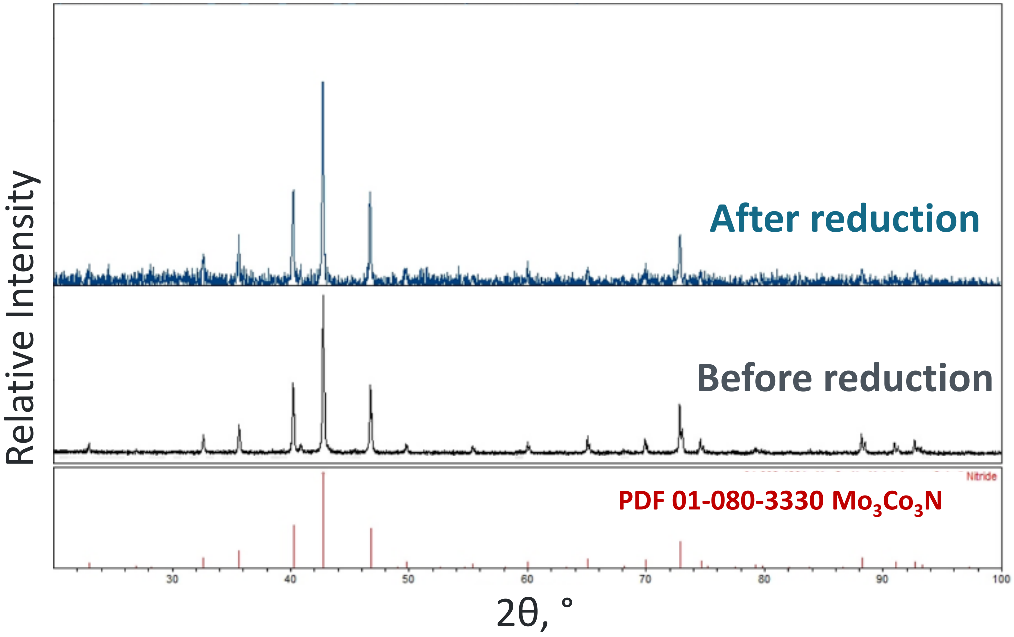
5. DI bubbler w/ice bath

   NH_3 *capture, air seal*

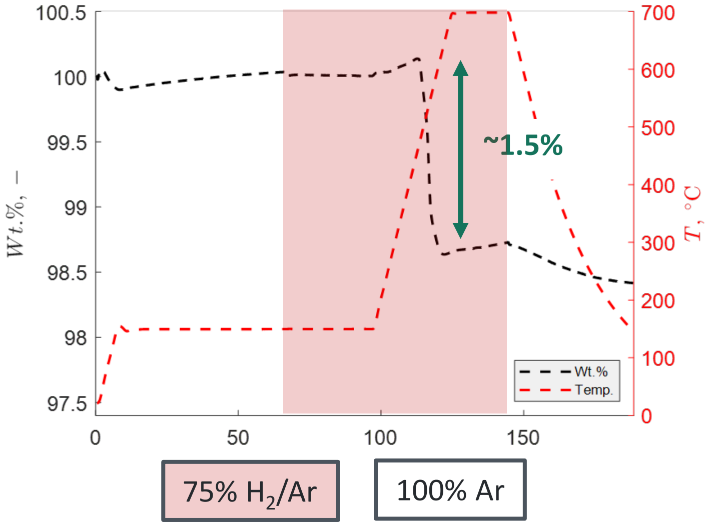


Co_3Mo_3N → Co_6Mo_6N Reduction

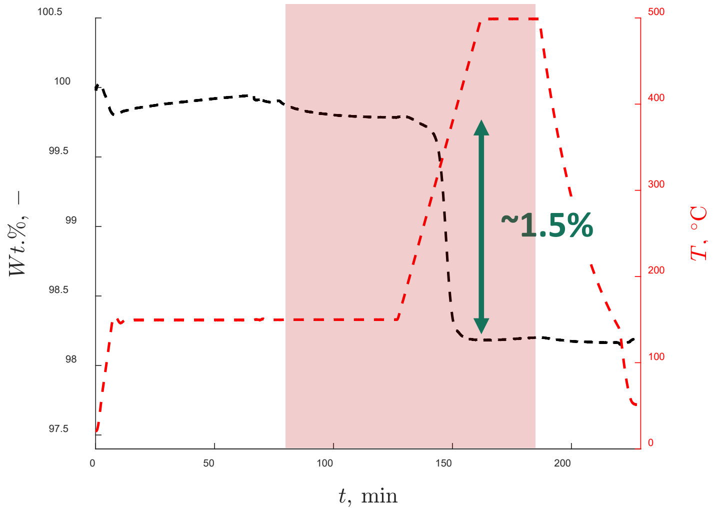
- H_2/Ar TGA reduction:
  - T = 300, 400, 500, 700 °C, 5-75% H_2
  - Rapid kinetics for T ≥ 500 °C
  - ✓ Wt. % match for 331 → 661 (1.46%)
  - ✓ No evidence of phase change on XRD
- 331 → 661 transition successful
  - Appealing kinetics and reaction temperature even at ambient pressures



700 °C



500 °C

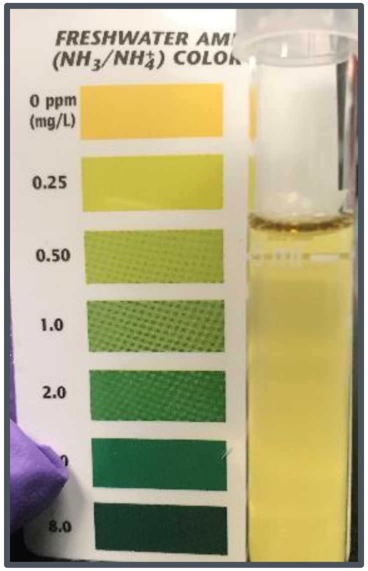


Co_3Mo_3N → Co_6Mo_6N NH_3 Detection

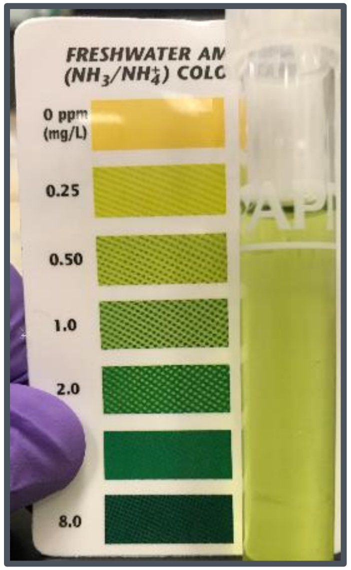
- Salicylate test kit used for semi-quantitative detection:
  - Test kit specific to NH_3
  - DI water bubbler
  - Testing before/after experiment
  - Ice bath to increase NH_3(aq) solubility
  - Test immediately after reduction -%Wt.
- Ammonia detected from CMN331 reduction
  - $[NH_{3(aq)}] = 0$ prior to reduction
  - $[NH_{3(aq)}] = 0.25 - 0.50$ ppm post-reduction
  - $[NH_{3(aq)}] = 0$ control (no sample)

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

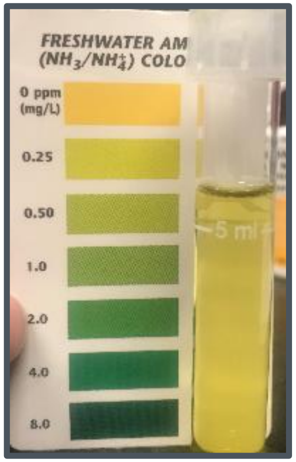
Initial bubbler



Post-reduction



Control test

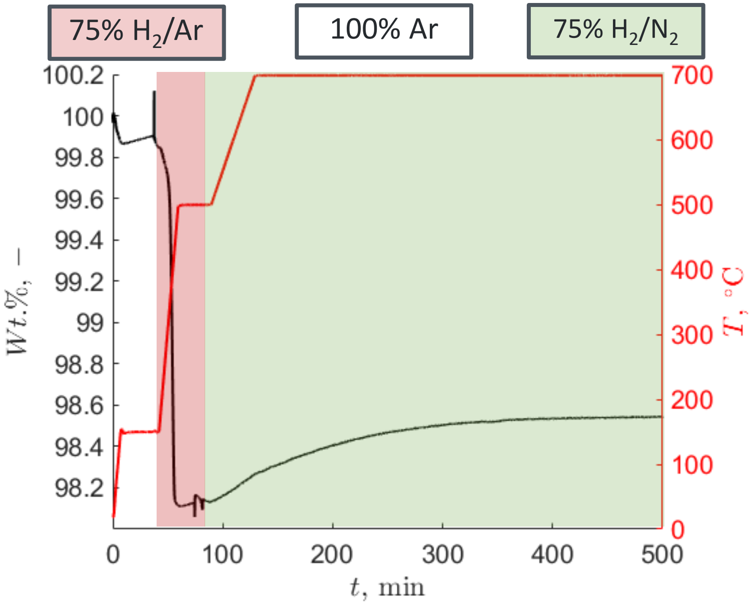


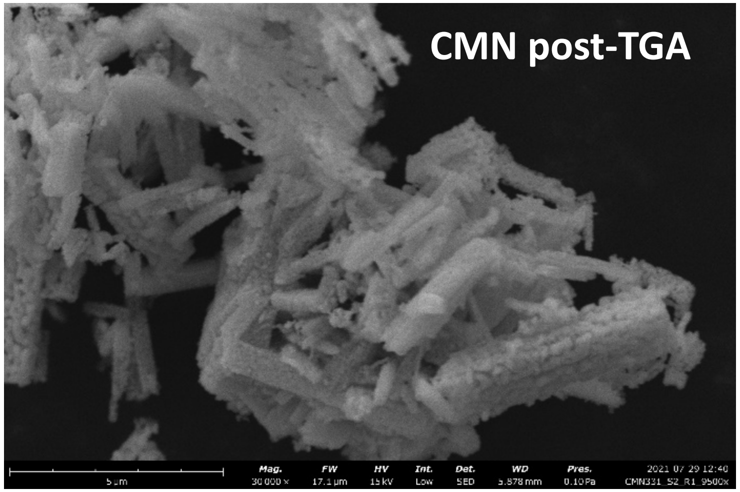
Co_6Mo_6N → Co_3Mo_3N Re-nitridation

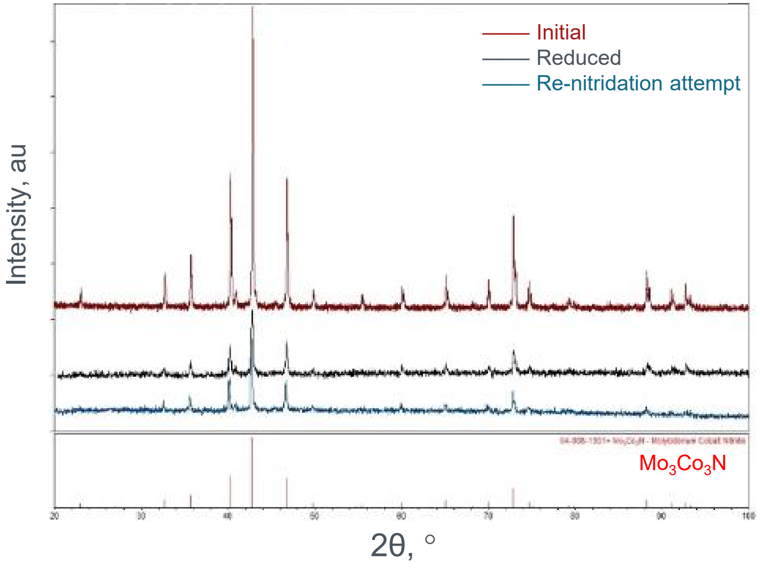
1. 100% N_2 TGA re-nitridation
   - → No apparent mass re-gain
     - → Expected at ambient pressure
       - → Require more activated N_2
         - → Use H_2/N_2 mixture gas

2. H_2/N_2 TGA re-nitridation:

- Partial re-nitridation attained
  - Maximum of 0.41% mass re-gain at 700 °C, 75% H_2/N_2







Summary and Path Forward

- Proposing a novel chemical looping mechanism to achieve a more energy-efficient green NH_3 production process compared to H-B.
- Proposing ternary/quaternary nitrides which possess thermodynamic knobs for the chemical looping NH_3 production.
- Facile synthesis of stable ternary/quaternary nitrides using EH&S-friendly and time-efficient conditions.
- Pre-screening in TGA reveals potential for NH_3 production under desirable operating conditions (low P, low T).
- Re-nitridation requires further validation.
- Demonstrate cyclic looping.

→ Expand nitride synthesis capability (substitute Mo).

→ Obtain kinetics/thermodynamics data for techno-economic models (vs. Haber-Bosch process).

→ Facilitate pressure reaction conditions suitable for chemical looping demonstration (re-nitridation at 10-30 bar).

Thank You!

STAP team:

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Arizona State University

Georgia Institute of Technology

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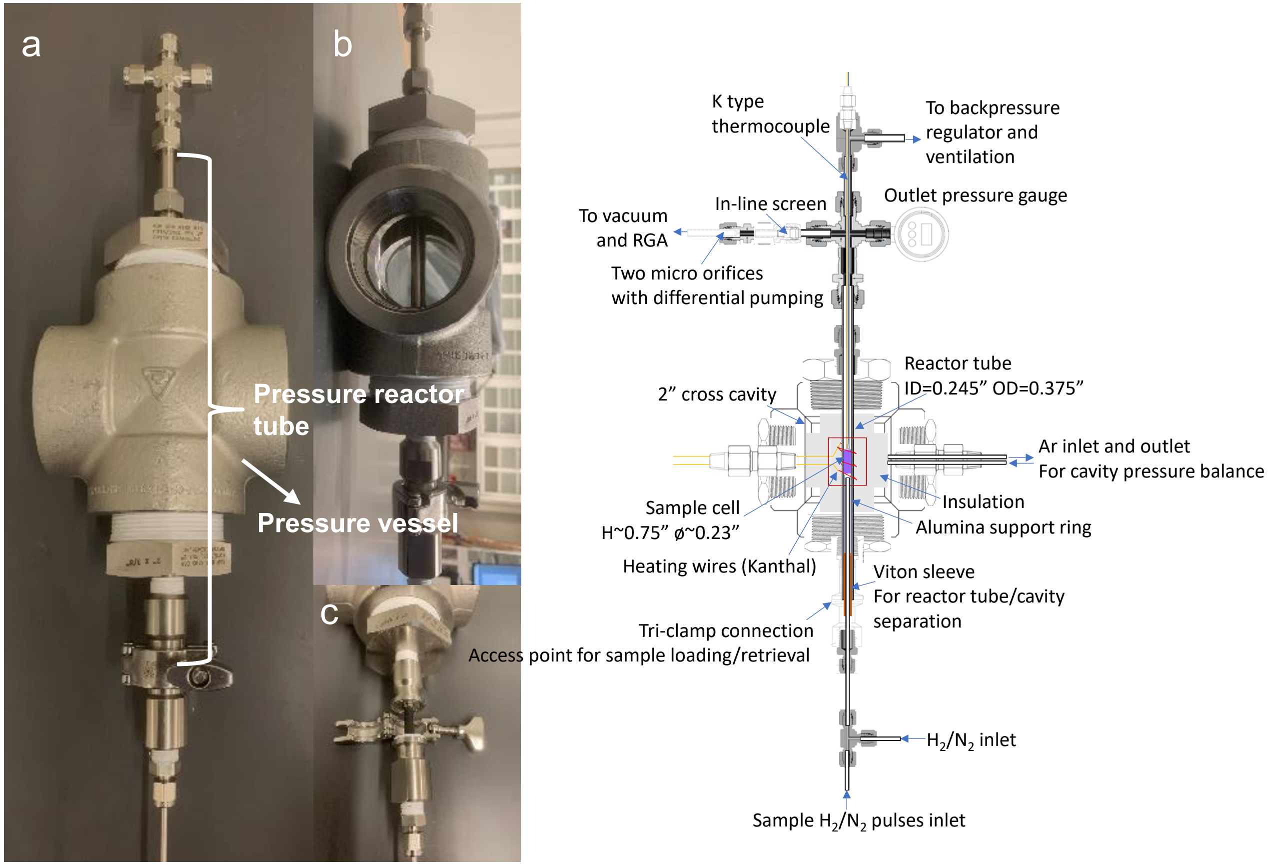

Ammonia Synthesis Reactor prototype currently under construction in ASU.

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