SAND2022-13452C

ASU LightWorks
Arizona State University


# Solar Ammonia Production via Novel Two-step Thermochemical Looping of a $Co_3Mo_3N/Co_6Mo_6N$ pair

Xiang Gao, Ivan Ermanoski, Alberto de la Calle, Andrea Ambrosini, and Ellen B. Stechel

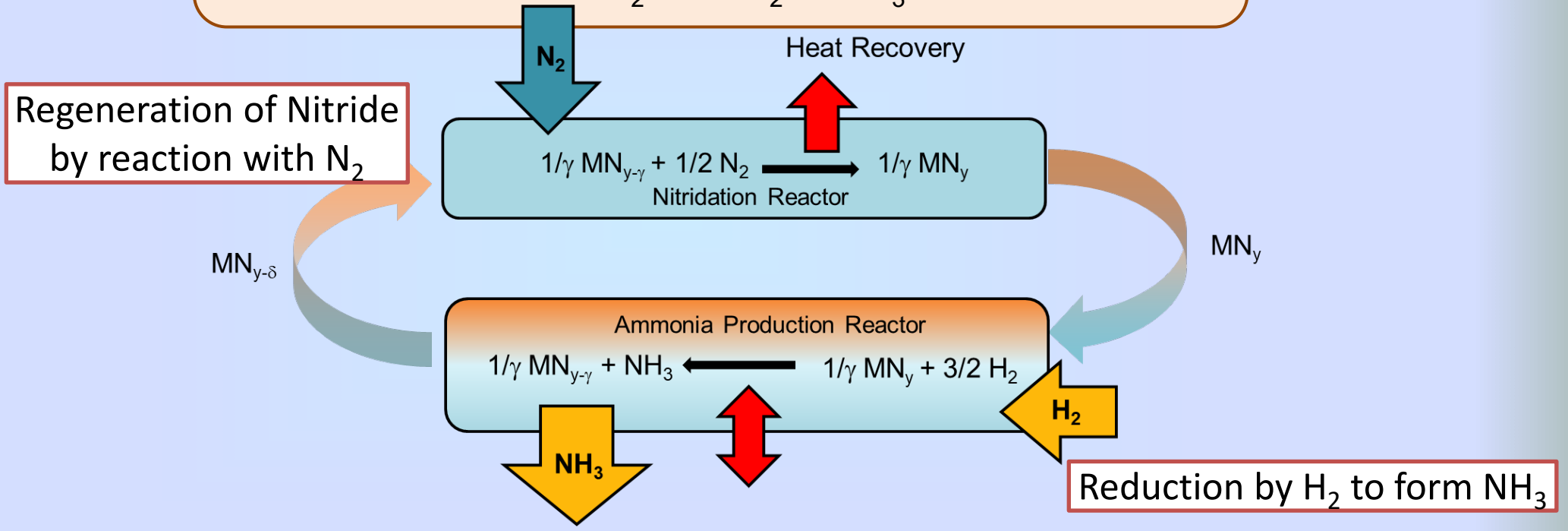
Presented by James E. Miller

**Arizona State University**

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Cyclic repetition of two reactions that sum to ammonia formation

$3/2\ H_2 + 1/2\ N_2 \rightarrow NH_3$

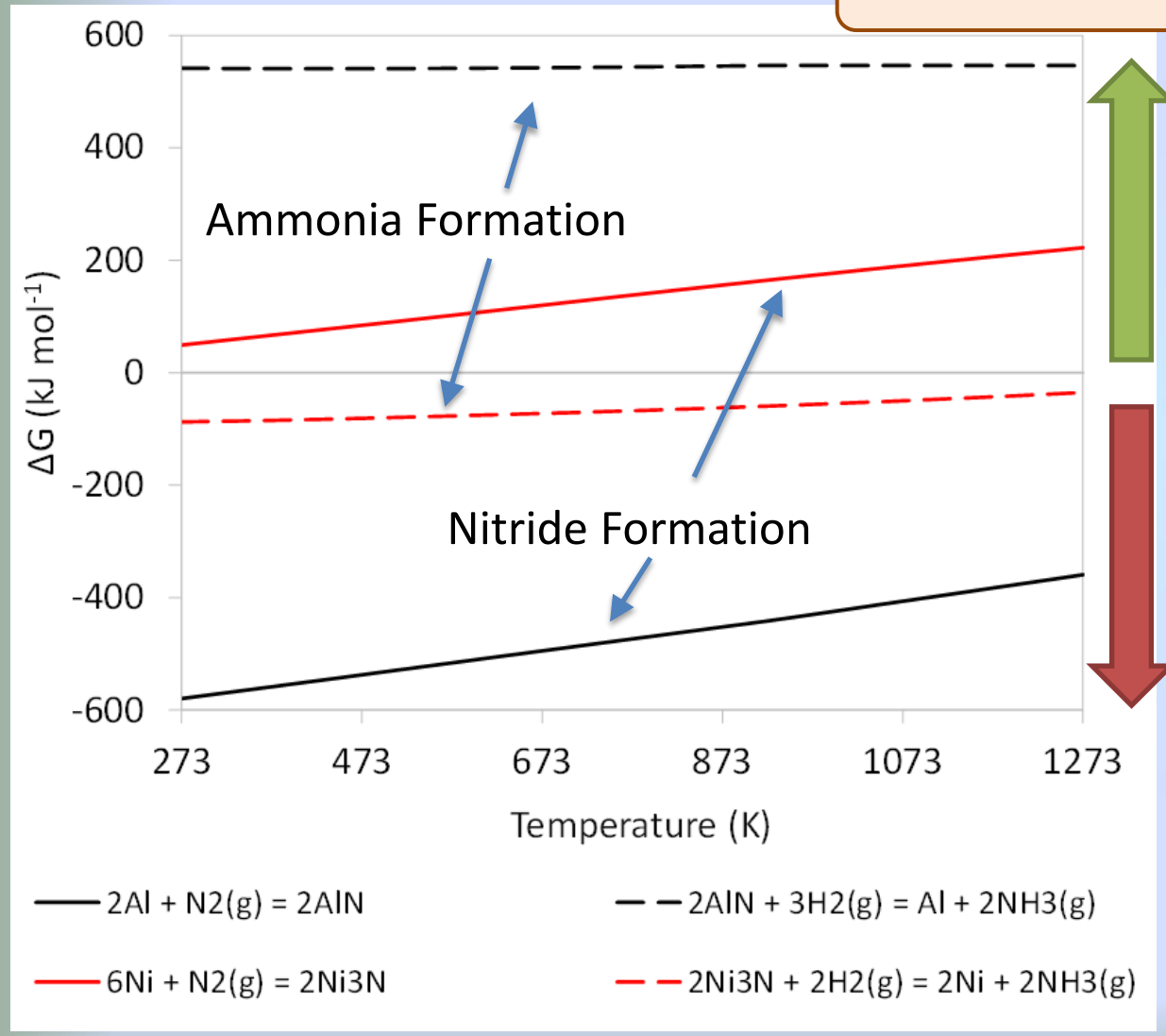



$NH_3$ Synthesis from Nitrides at lower pressure or higher temperature with good selectivity?

# Challenge: Identify and optimize a metal nitride

- Tuning the nitride thermodynamics to the reaction
- Reaction with the bulk, not (exclusively) surface-catalyzed
  - $NH_3$ dissociates (thermodynamically unfavorable relative to $H_2$+$N_2$) at high temperature
- Nitrogen diffusion in metal nitrides slow? ~~(nitrogen conductors)~~
- Nitride synthesis can be difficult – e.g. reacting under flowing $NH_3$ at high temperature

# Basic Thermodynamic Principles




- Thermodynamic of the two reactions comprising the cycle inextricably linked.

$$1/\gamma\ MN_{y-\gamma} + 1/2\ N_2 \rightarrow 1/\gamma\ Mn_y \quad (1)$$

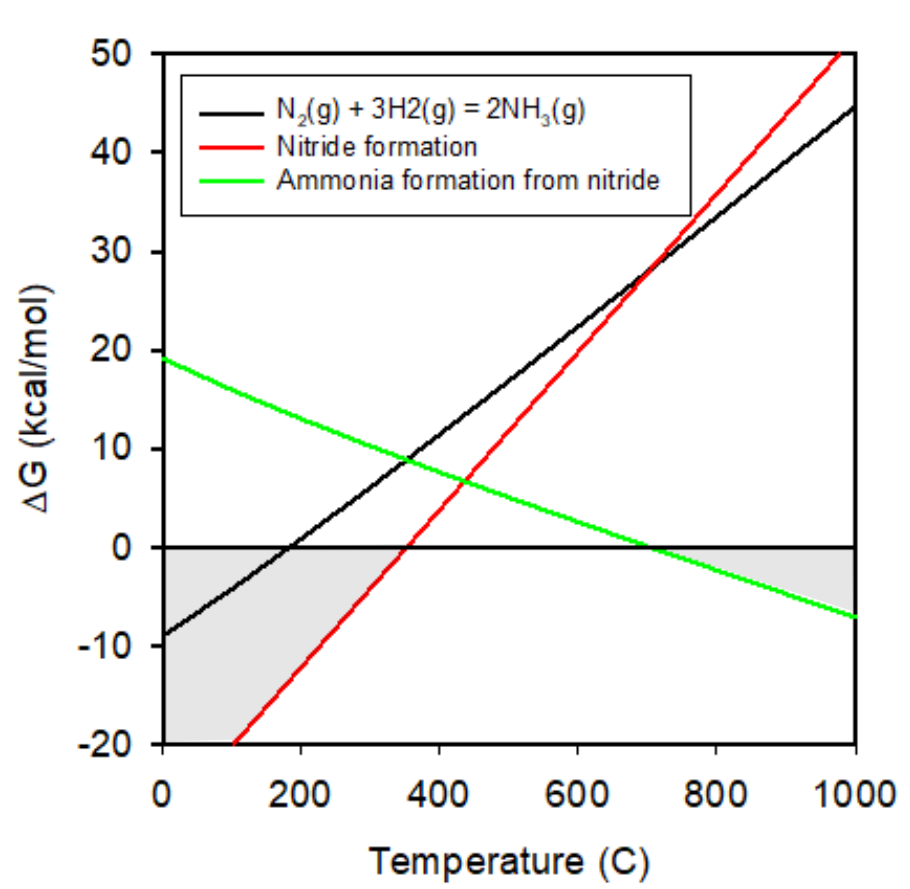
$$1/\gamma\ MN_y + 3/2\ H_2 \rightarrow 1/\gamma\ MN_{y-\gamma} + NH_3 \quad (2)$$

$$3/2\ H_2 + 1/2\ N_2 \rightarrow NH_3 \quad (3)$$

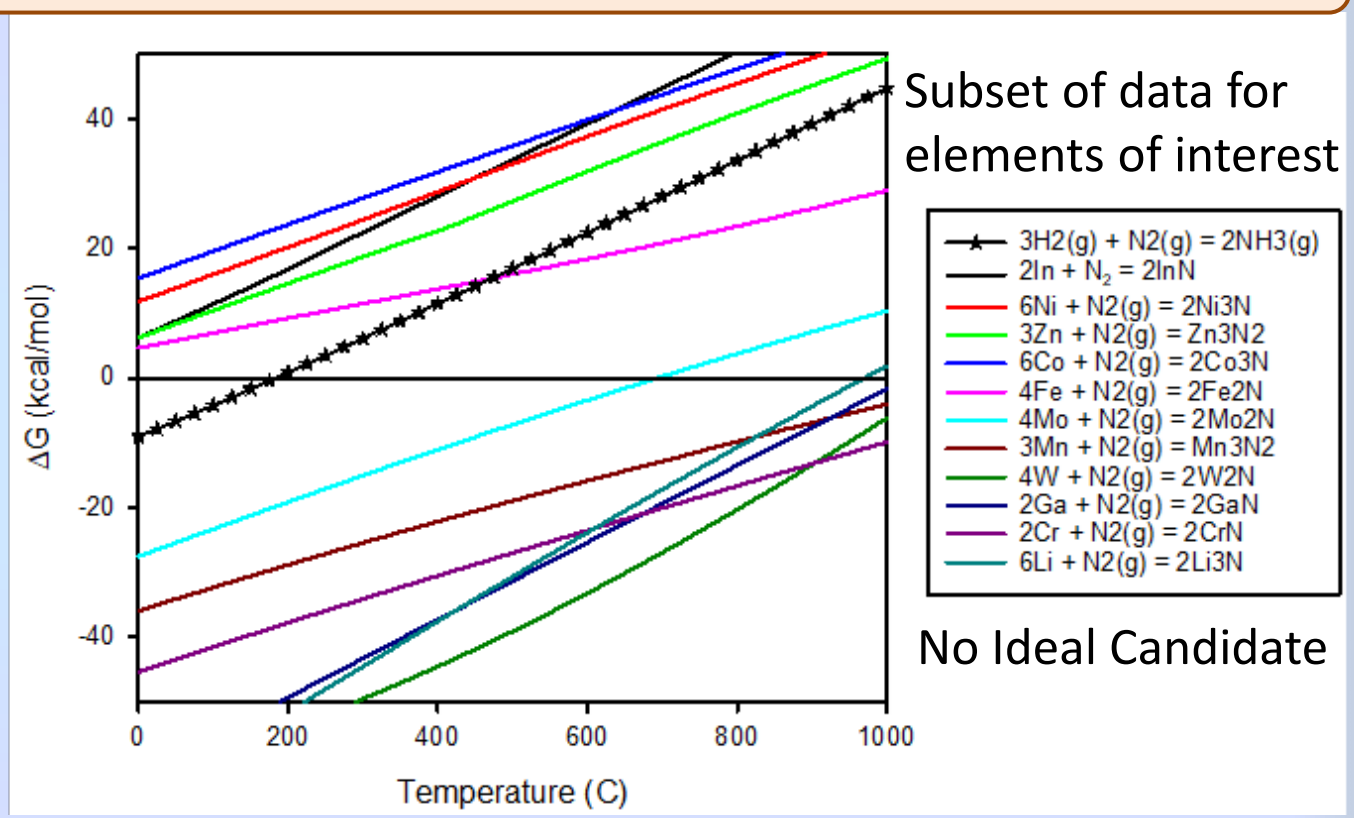
$$\Delta G_1 + \Delta G_2 = \Delta G_3$$

- The more favorable is nitridation, the less favorable is ammonia production, and vice versa.
- Ammonia formation is exothermic – unconventional for a cycle.

# Begin with Survey of Binary Nitrides & "Conventional" Cycle Construct




Rethink these cycles a bit – e.g. impact of pressure

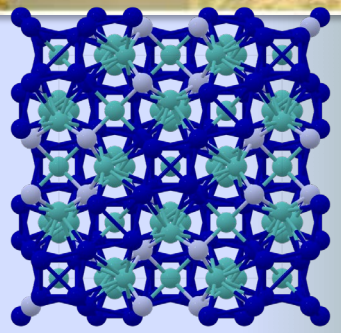



Subset of data for elements of interest

No Ideal Candidate

Ternaries (two metals) offer the opportunity to tune the thermo to that required for a two step cycle.

ASU LightWorks
Arizona State University



$Co_3Mo_3N$

Ternary Nitride Considerations

Binary Nitride Thermodynamics

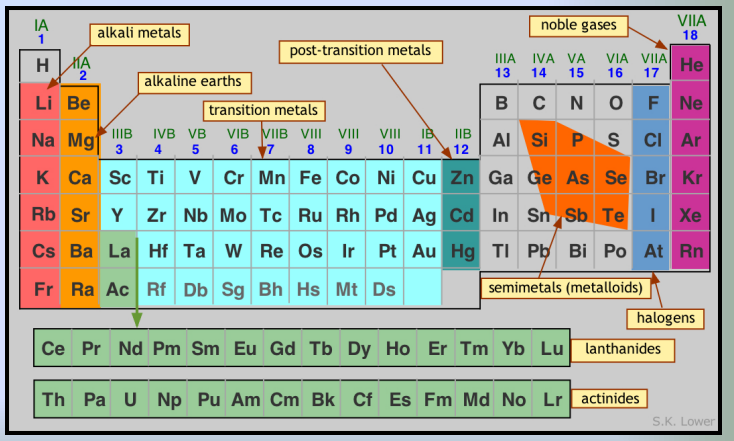
Element Considerations

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

**38 Possible Ternary Nitrides Remain**

- No ternaries, leaving 38 nitrides (0.28%) — 22
- Neither redox, leaving 60 nitrides (0.45%) — 12
- Not A-B on favorability, leaving 72 nitrides (0.53%) — 252
- Too unfavorably bound (3), leaving 18 and 324 (2.4%) — 117
- Too favorably bound (20), leaving 21 and 441 (3.3%) — 1240
- Toxic (18), leaving 41 elements and 1681 nitrides (12.5%) — 255
- Non-Metal (18), leaving 44 elements and 1936 nitrides (14.4%) — 1908
- Scarce elements (32), leaving 62 elements and 3884 nitrides (28.9%) — 4992
- Radioactive elements (22), leaving 94 elements and 8836 nitrides (65.7%) — 4620

Start with the Periodic Table



# After Ternary Considerations 38(+) Combinations of Interest

| | | | Cation Redox Active | | | | | | Cation Redox Inactive | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Element | | Cr | Fe | Mn | Mo | V | W | Ba | Ga | Li | Mg | Na | Sr |
| | kJ $mol_N^{-1}$ | | -56.3 | -13.8 | -33.1 | -60.2 | -178 | -42.8 | -137 | -83.3 | -132 | -174 | -3.94 | -135 |
| Cation Redox Active | Co | 30.5 | | 8.3 | -1.3 | -14.8 | **-73.7** | -6.1 | **-53.4** | | **-50.5** | **-71.5** | 13.3 | **-52.2** |
| | Cu | 119.3 | | | **43.1** | | | | -9.0 | 18.0 | -6.1 | -27.1 | | -7.8 |
| | Ge | 2.1 | -27.1 | -5.9 | -15.5 | | **-87.9** | | **-67.6** | | **-64.7** | **-85.7** | -0.9 | **-66.4** |
| | Ni | 22.8 | | 4.5 | -5.2 | -18.7 | **-77.5** | -10.0 | **-57.3** | | **-54.4** | **-75.4** | 9.4 | -56.1 |
| Cation Redox Inactive | Sn | 46.0 | -5.2 | | 6.4 | | | | | | | | | |
| | Zn | 38.7 | -8.8 | 12.4 | 2.8 | -10.7 | **-69.6** | | | | | | | |

$Co_3Mo_3N$ (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 $N_2$

*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.

Solution: $Co(NO_3)_2 \cdot 6H_2O$ + $(NH_4)6Mo_7O_{24} \cdot 4H_2O$

Heat the solution to 80°C: Purple precipitate

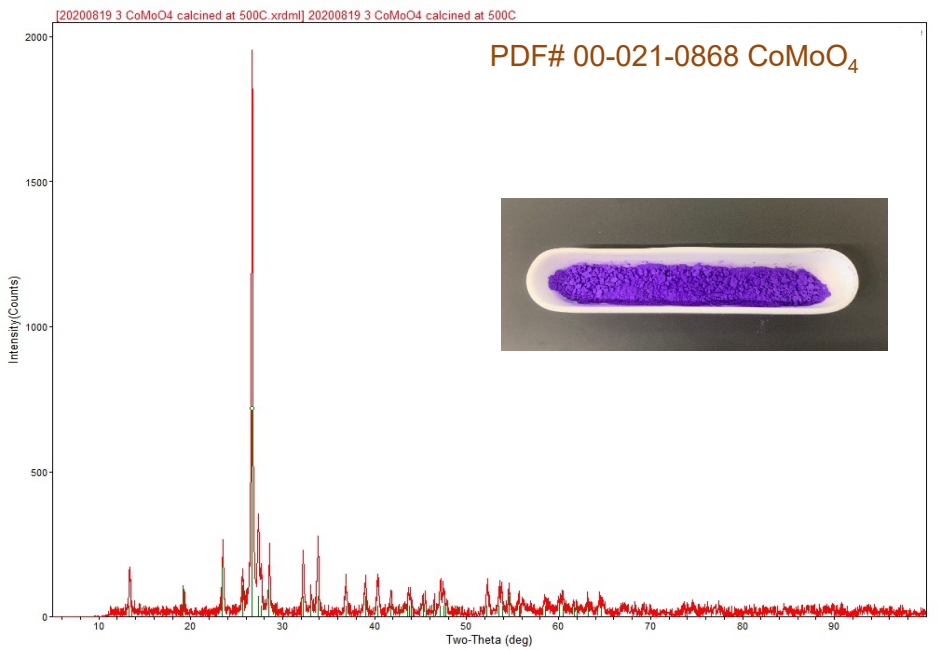
Vacuum filtration

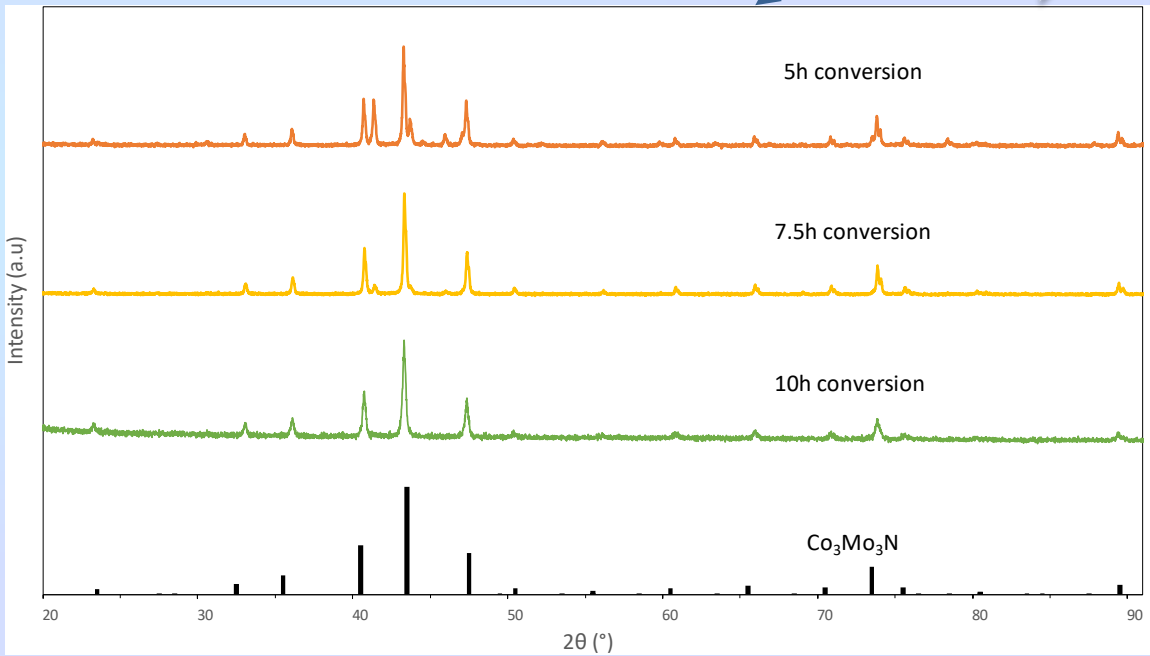
Dry overnight at 150°C: $CoMoO_4 \cdot xH_2O$

Calcine at 500°C for 3h: $CoMoO_4$

React at 785 °C, 10% $H_2/N_2$

$Co_3Mo_3N$



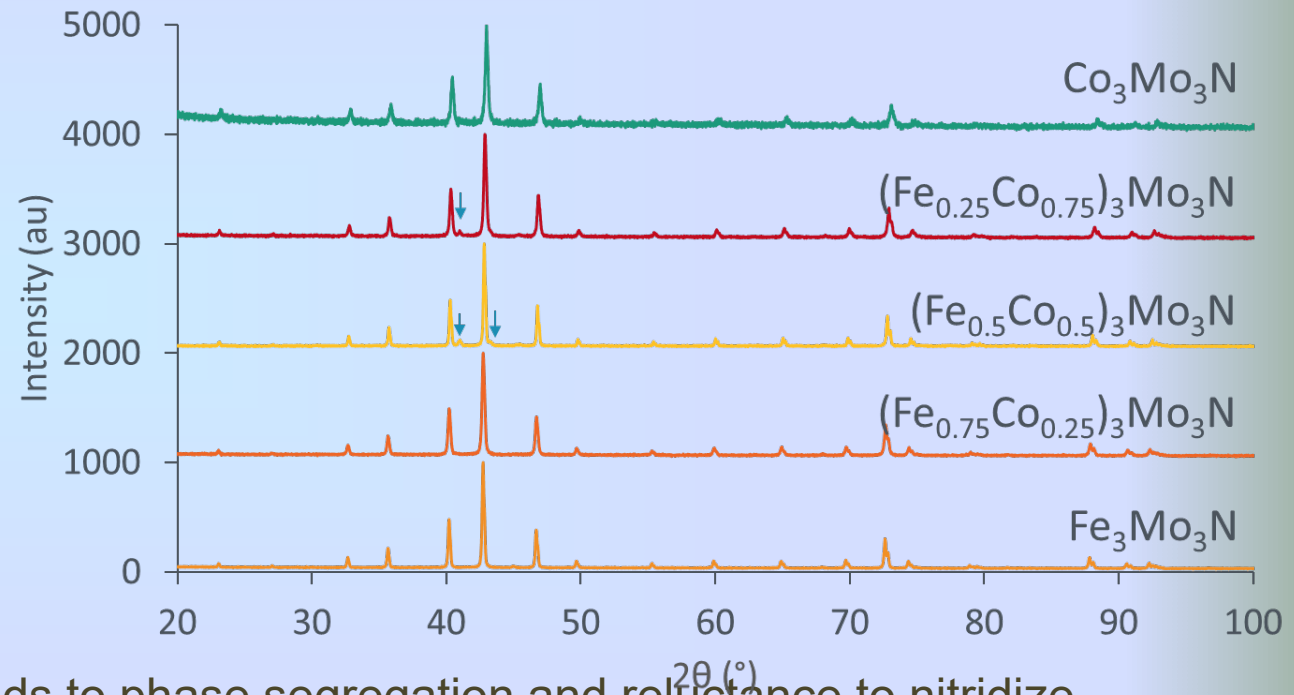

Synthesis of oxide precursor followed by nitridation in 10% $H_2$ results in single phase $Co_3Mo_3N$ (somewhat milder synthesis conditions than reported ammonolysis[1])



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

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

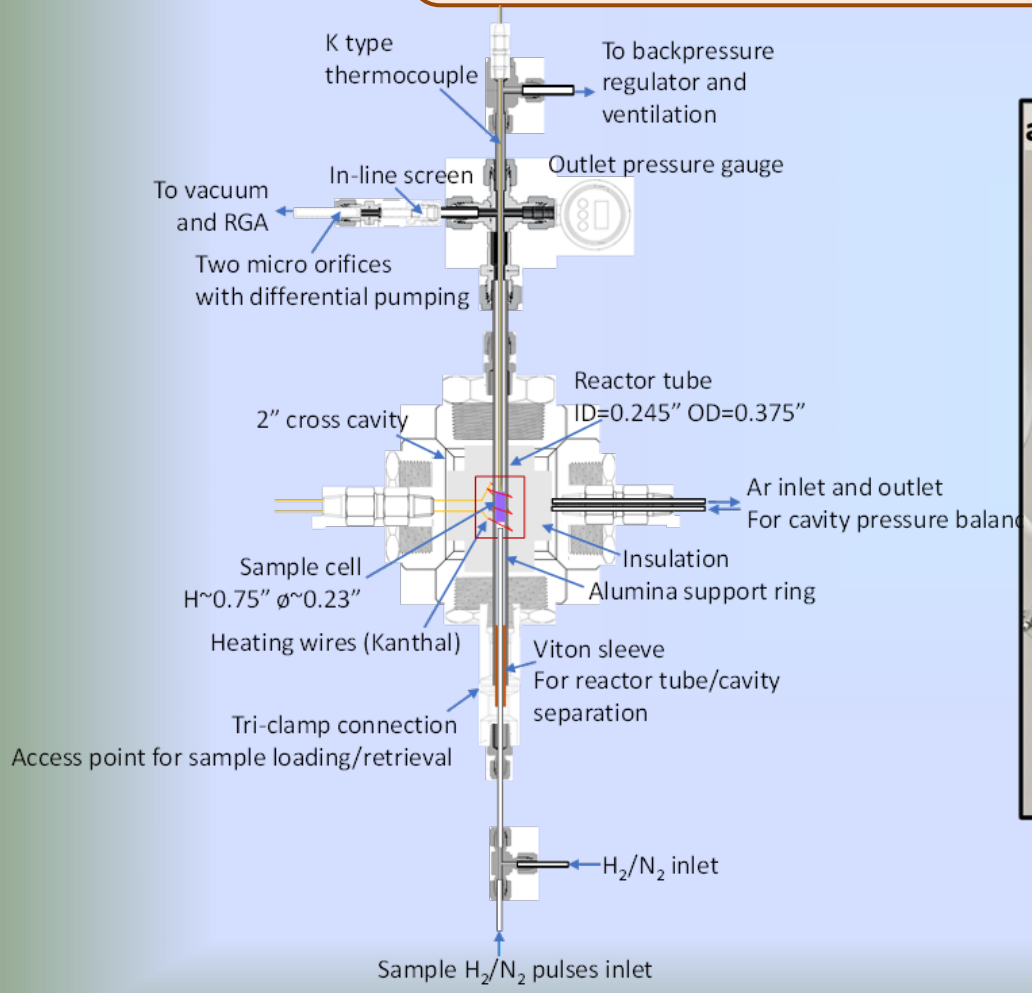
| Composition Target | Phase (> 95% via XRD) |
|---|---|
| $Co_3Mo_3N$ | 331 |
| $(Co_xNi_{1-x})_2Mo_3N$ (x = 0.25, 0.5, 0.75) | 231 |
| $Ni_2Mo_3N$ | 231 |
| $(Fe_xNi_{1-x})_2Mo_3N$ (x = 0.25, 0.5) | 231 |
| $Fe_3Mo_3N$ | 331 |
| $(Co_xFe_{1-x})_3Mo_3N$ (x = 0.25, 0.5, 0.75) | 331 |
| $Co_3(W_xMo_{1-x})_3N$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

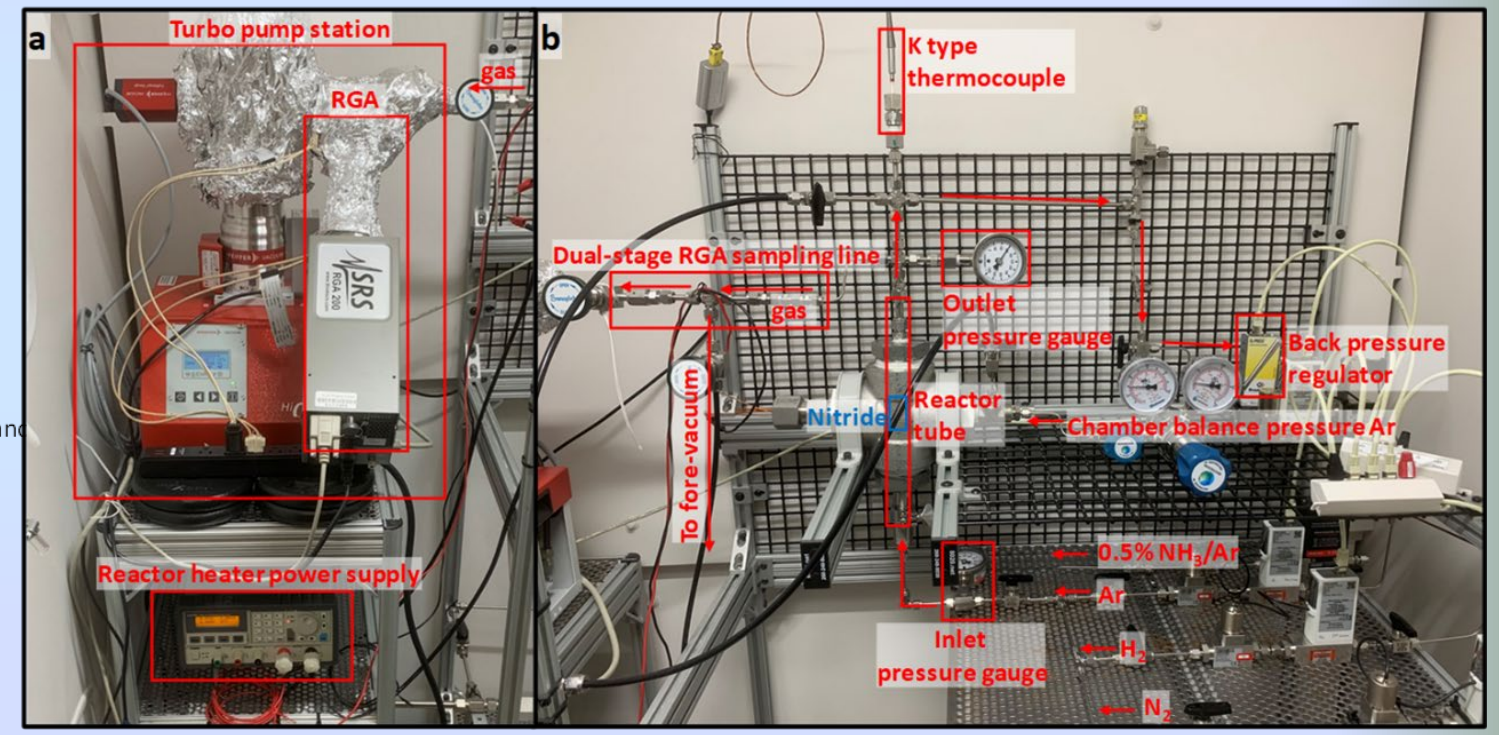



- W > 5% in $Co_3Mo_3N$ (“331”) B-site substitution leads to phase segregation and reluctance to nitridize
- Ni > 5% in $Co_3Mo_3N$ or $Fe_3Mo_3N$ A-site substitution leads to phase segregation and preference of $Ni_2Mo_3N$ (“231”) structure

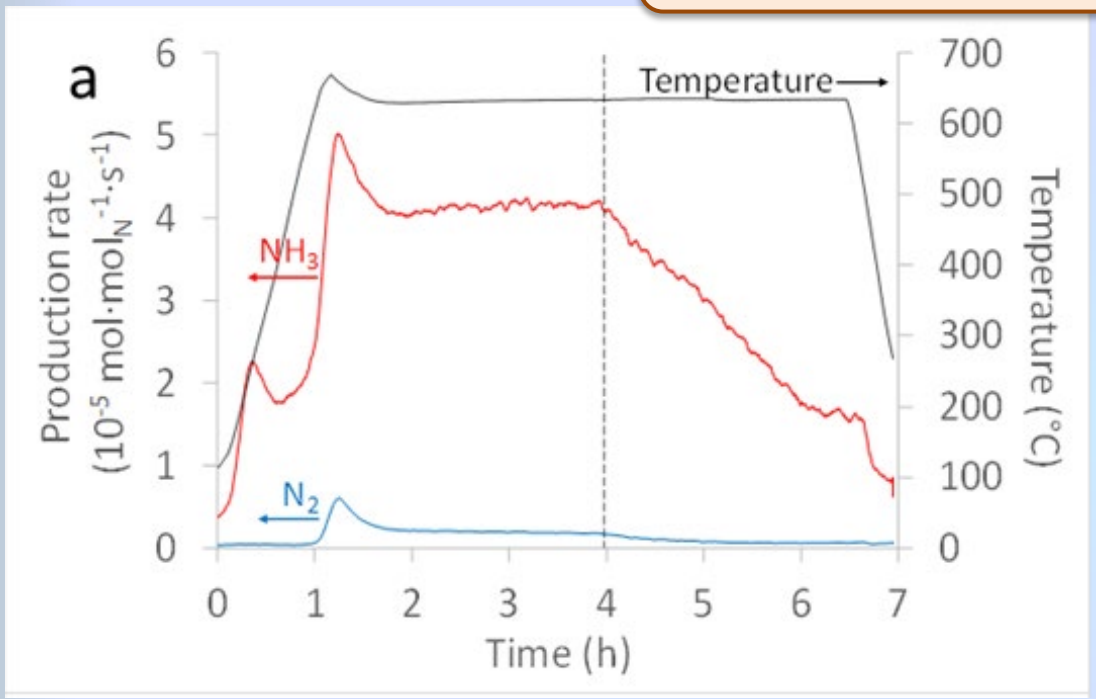
Gao, X.; Bush, H. E.; Miller, J. E.; Ermanoski, I.; Ambrosini, A.; Stechel, E. B., Synthesis and Structural Study of Substituted Ternary Nitrides for Ammonia Production. *submitted* 2022.

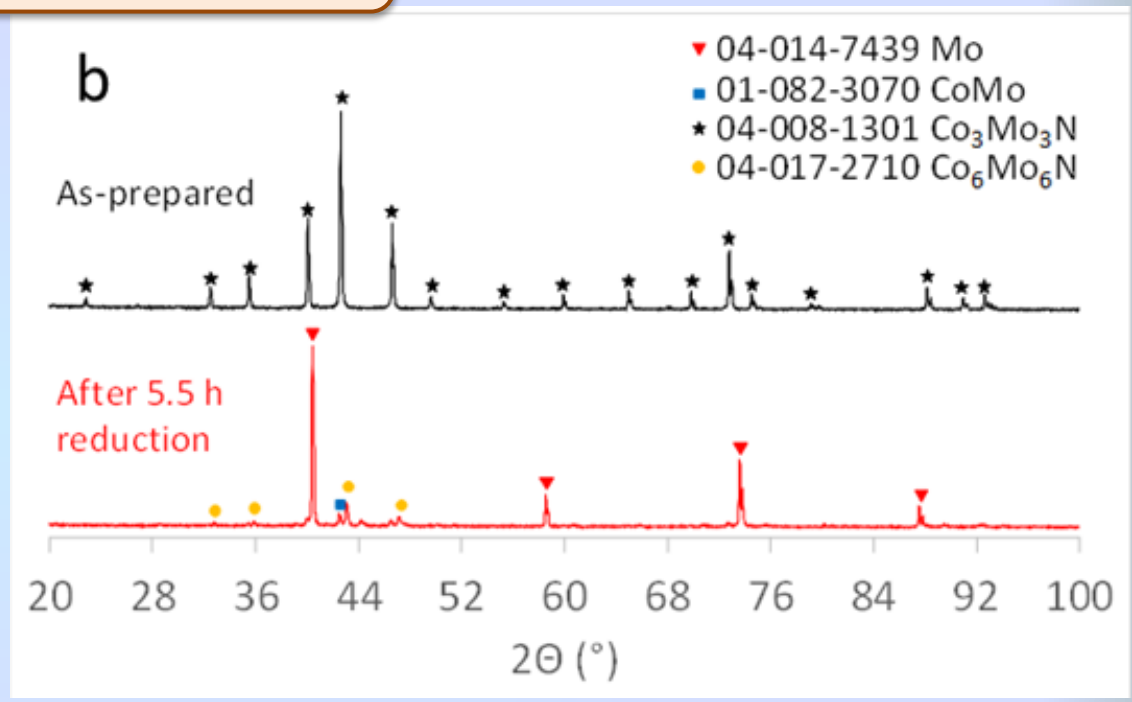
Reactor designed to perform $NH_3$ synthesis and nitridation under variable pressure and temperature, up to 30 bar and 800 °C, respectively



# Reactions of $CO_3MO_3N$




Two regions apparent in <u>extended reduction</u> experiments

Nearly constant rate – 331 (662) → 661

Linearly decreasing rate – 661 → Metal

ASU LightWorks
Arizona State University

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

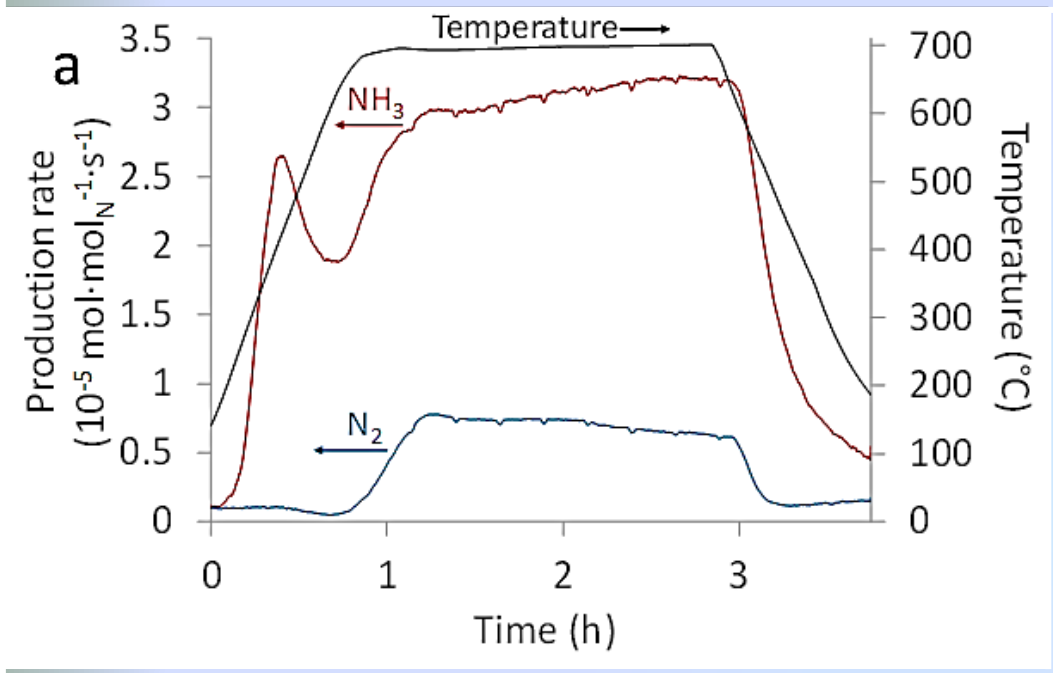
Reacted solid-state nitrogen was calculated by adding $NH_3$ yield and two times of $N_2$ yield (theoretical max CMN331→ CMN661 = 0.5)

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% |

- 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

Repetitions on single $Co_3Mo_3N$ sample – ***Reaction is cyclic***

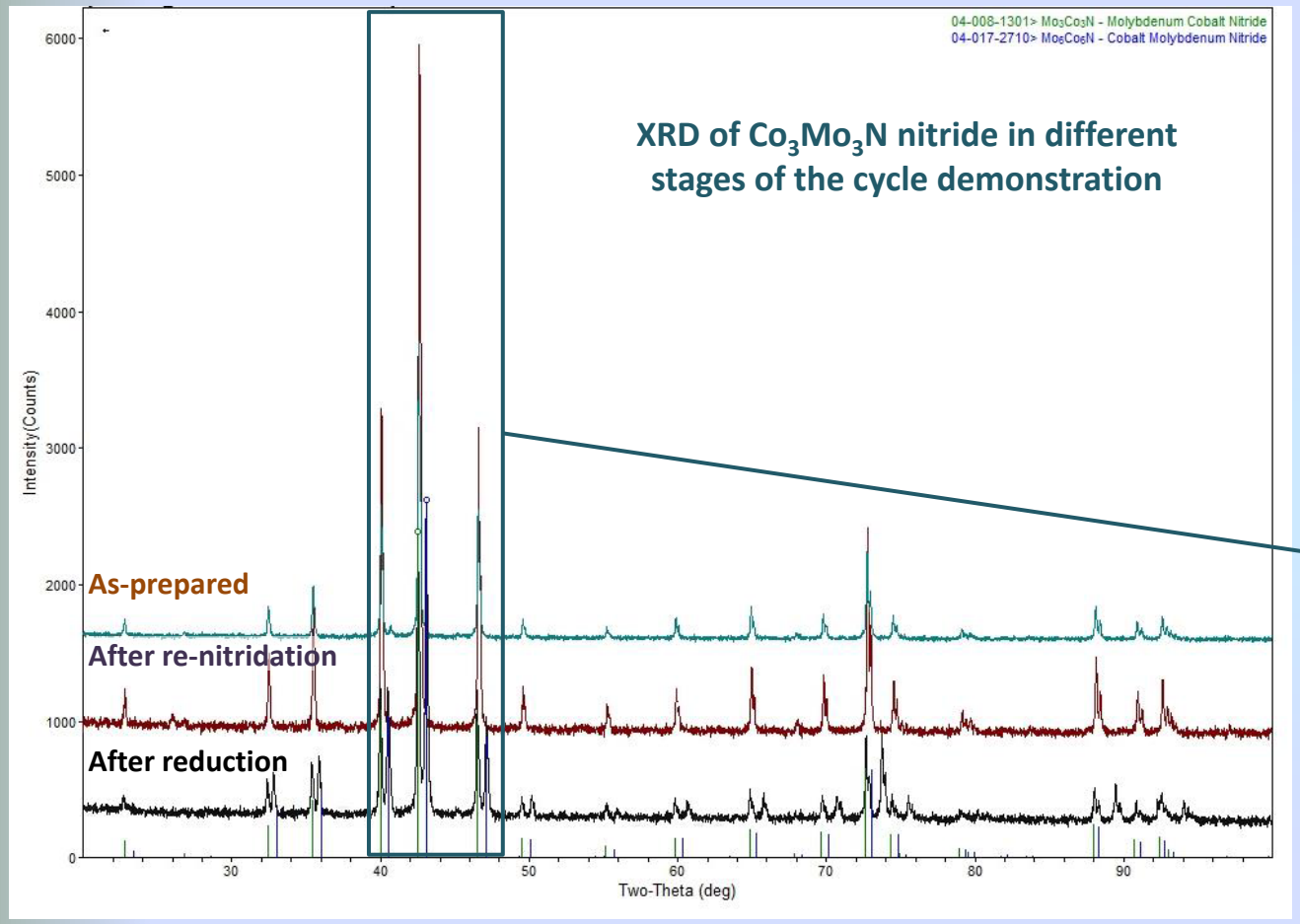


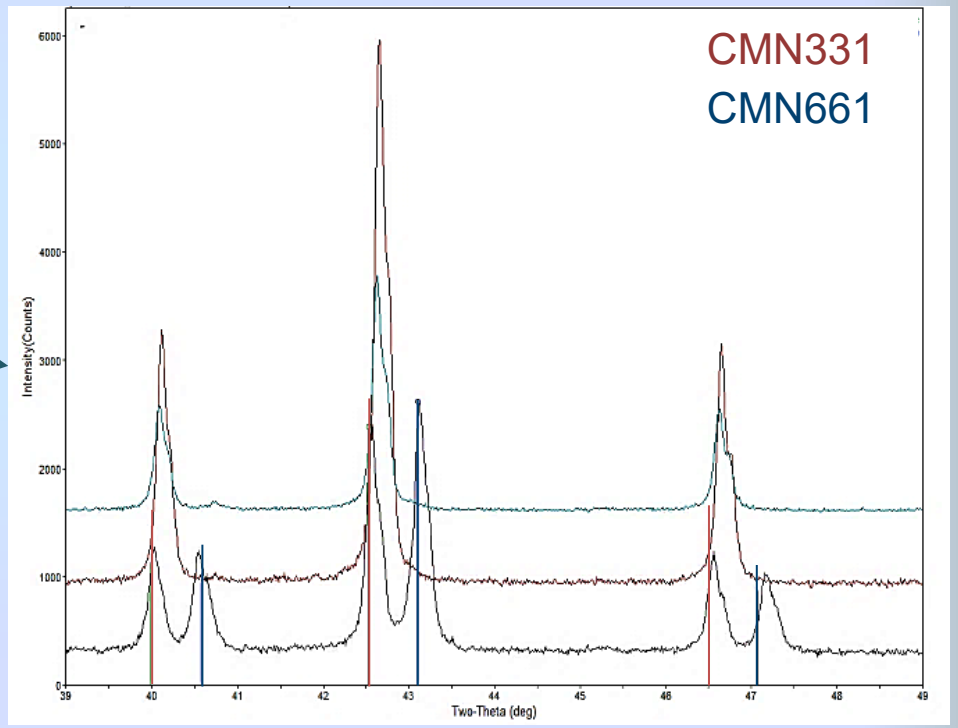

$NH_3$, $N_2$ production rates and temperature profile of representative reduction step under 100% $H_2$ (Cycle 6)

- 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)
- Production rates fairly flat in all the reduction steps with no evident dependence on the consumed solid-state nitrogen.
- Sample can be re-nitridized under 100% $N_2$ at same 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 CMN331 → CMN661 bulk reaction

## XRD Confirms Bulk Reduction and Nitridation
## CMN331 → CMN661 → CMN331




- Partial conversion to 661 after reduction (both 331 and 661 phases observed), consistent with bulk reacted nitrogen calculation of < 0.5
- Regeneration to 331 after re-nitridation with no sign of secondary phase

## Second Set of Experiments with Same Sample of CMN

| 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 $NH_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 8 | 20 | 600-720 | 0.5×5 | -- | -- | | | | |
| 9 | 15 | 600-720 | 0.5×5 | -- | -- | | | | |
| 10 | 10 | 600-720 | 0.5×5 | -- | -- | | | | |
| 11 | 5 | 600-720 | 0.5×5 | -- | -- | | | | |

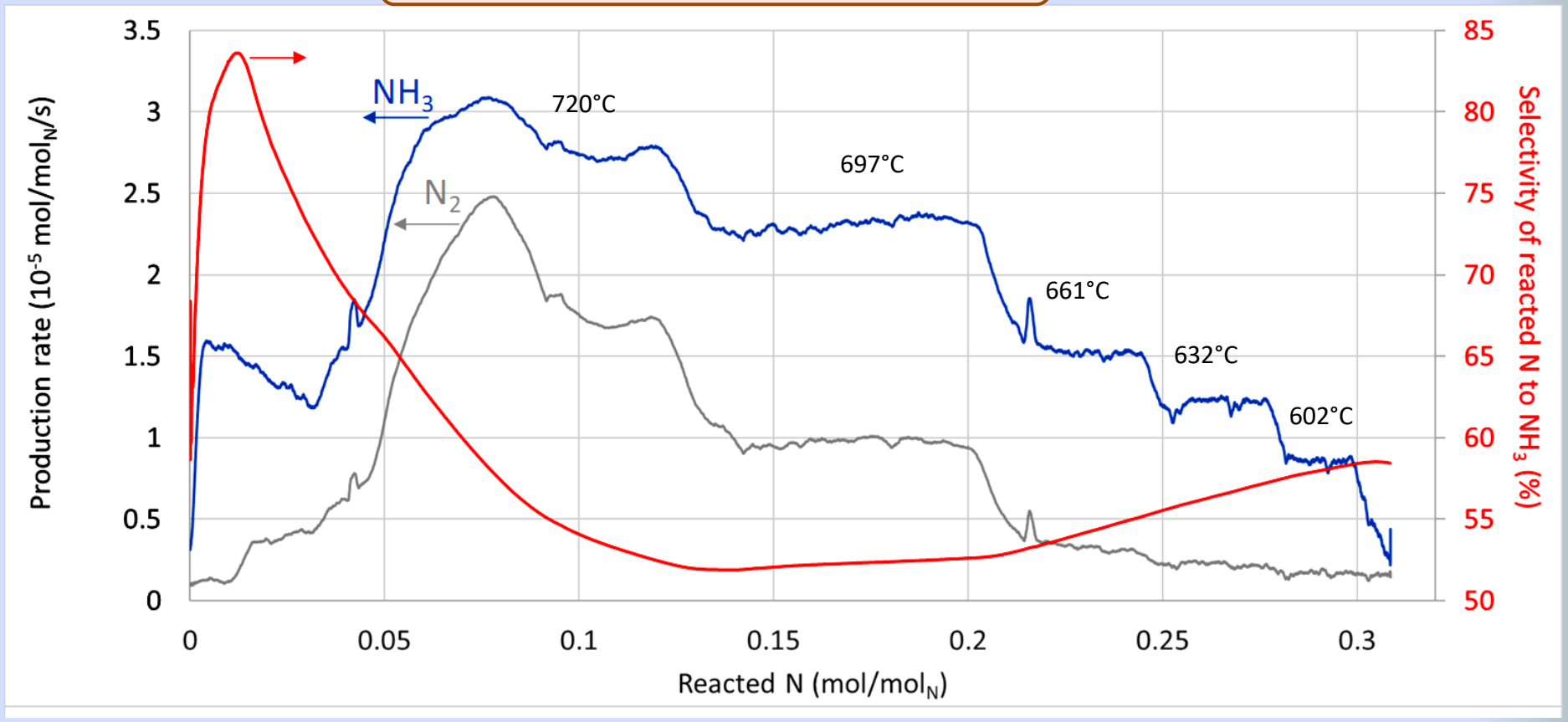
T steps at varying $pH_2$

- 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

Xiang, G., *et al,* "Sustainable Ammonia Production via a Novel Two-step Thermochemical Cycle of a $Co_3Mo_3N/Co_6Mo_6N$ pair." *in prep,* 2022.

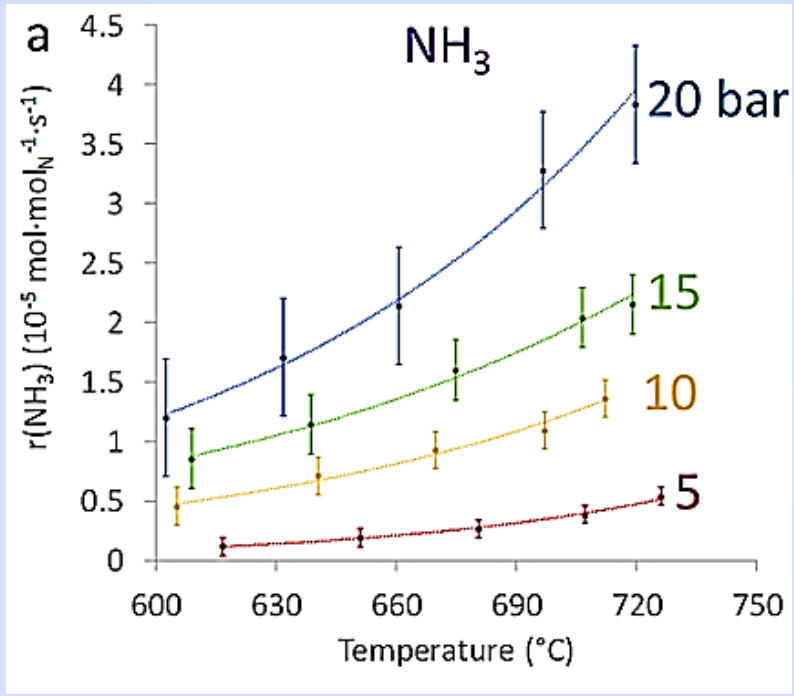
## Typical Data Set

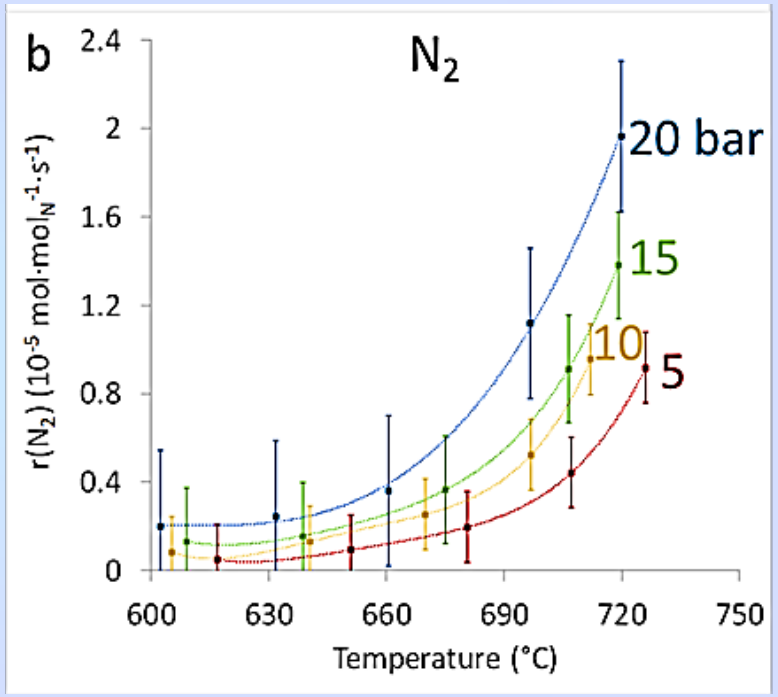
$NH_3$, $N_2$ production rates and selectivity of reacted nitrogen to $NH_3$ as a function of reacted nitrogen in a temperature stepping reduction experiment (20 bar, 100% $H_2$, 8th cycle)



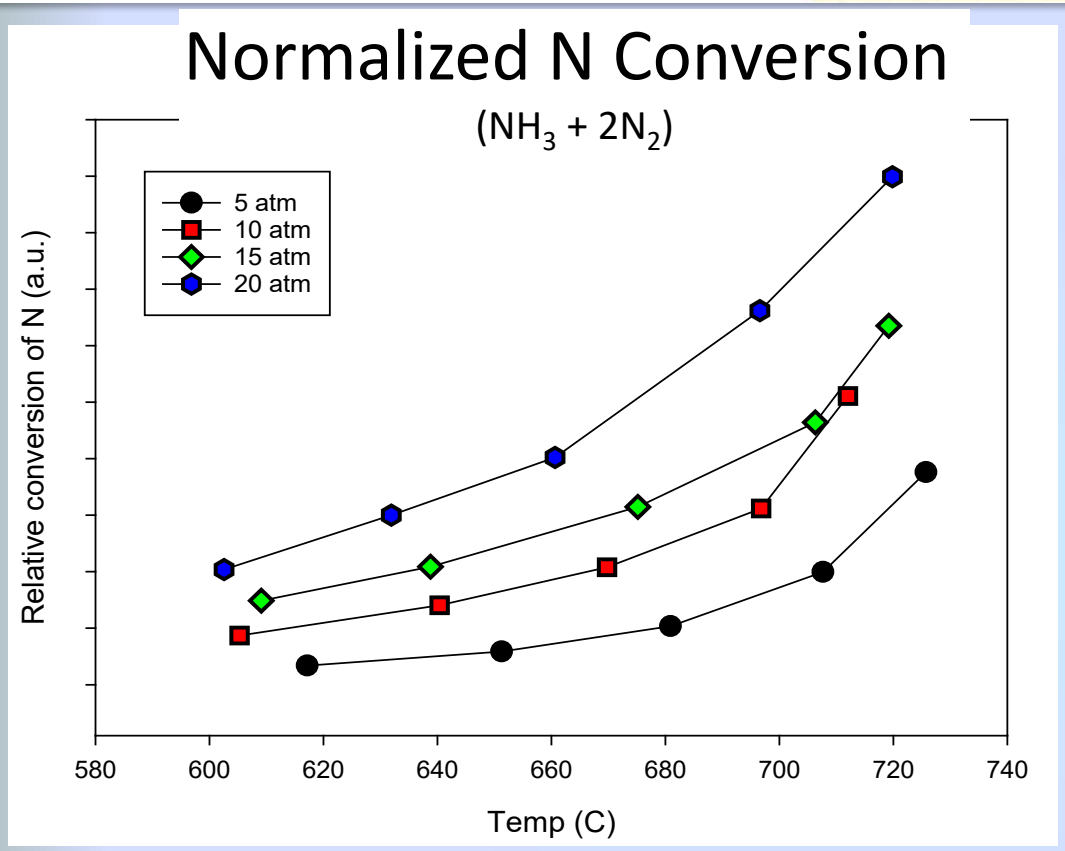

- Selectivity continuously calculated (summed) over entire run – i.e. not he instantaneous value

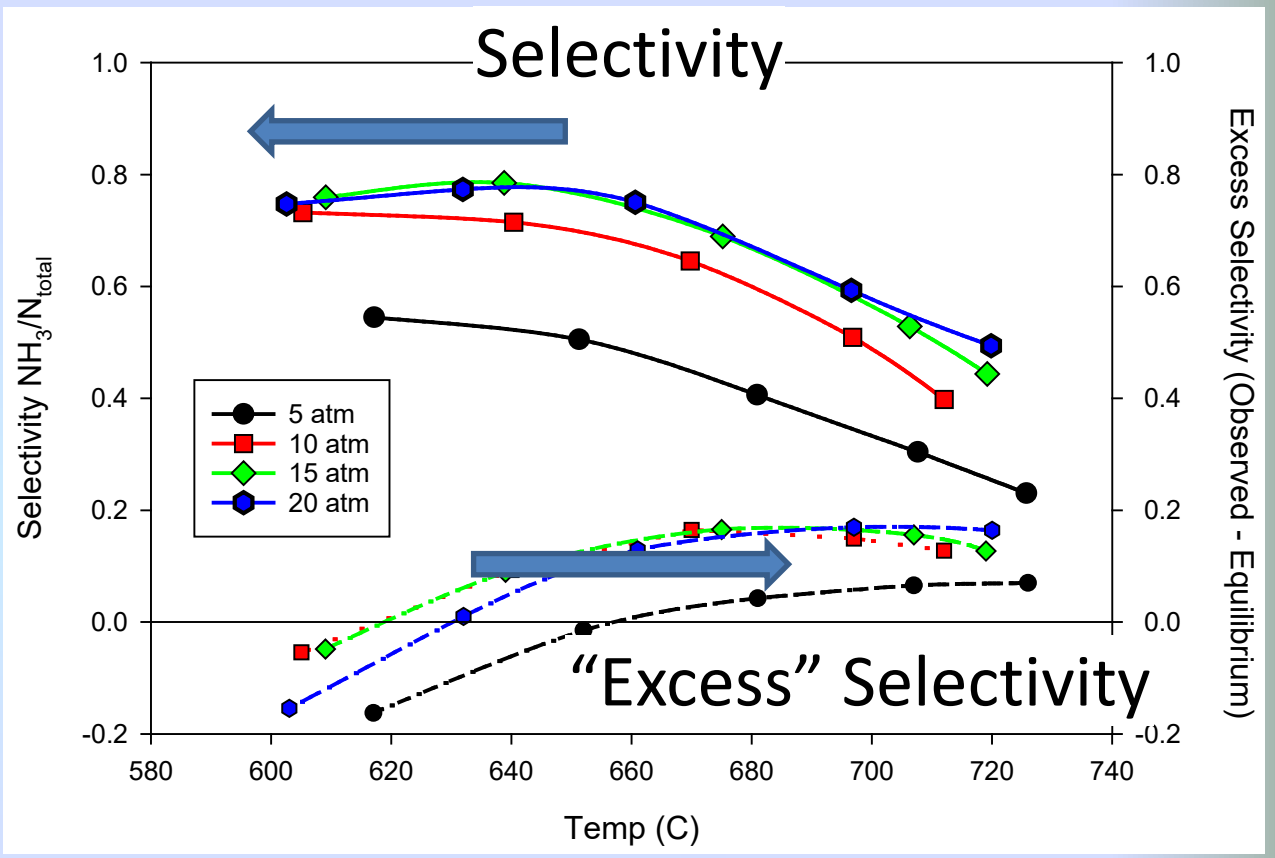
# Conversion of bulk N to $NH_3$ and $N_2$ increases with T and P




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

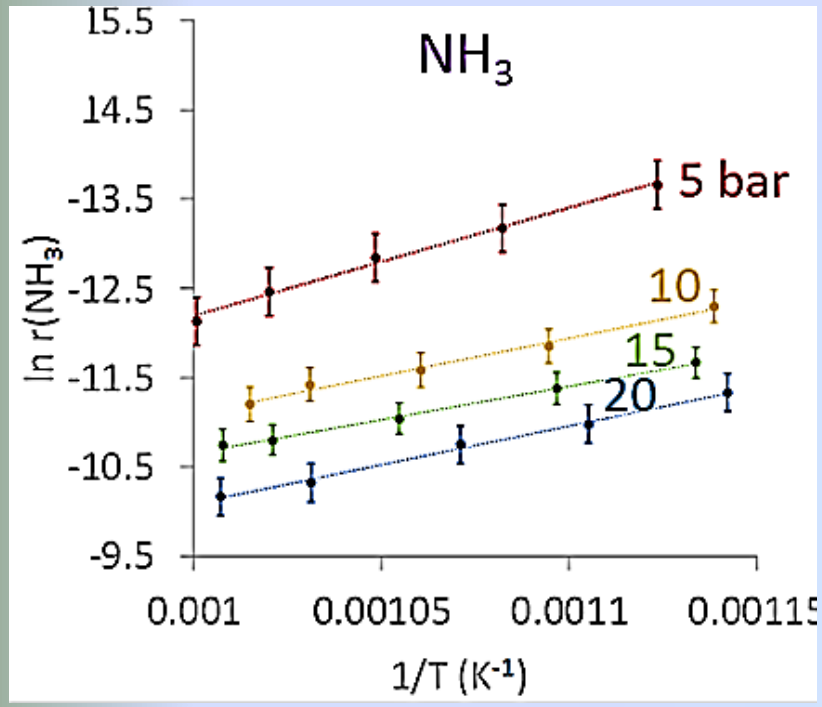


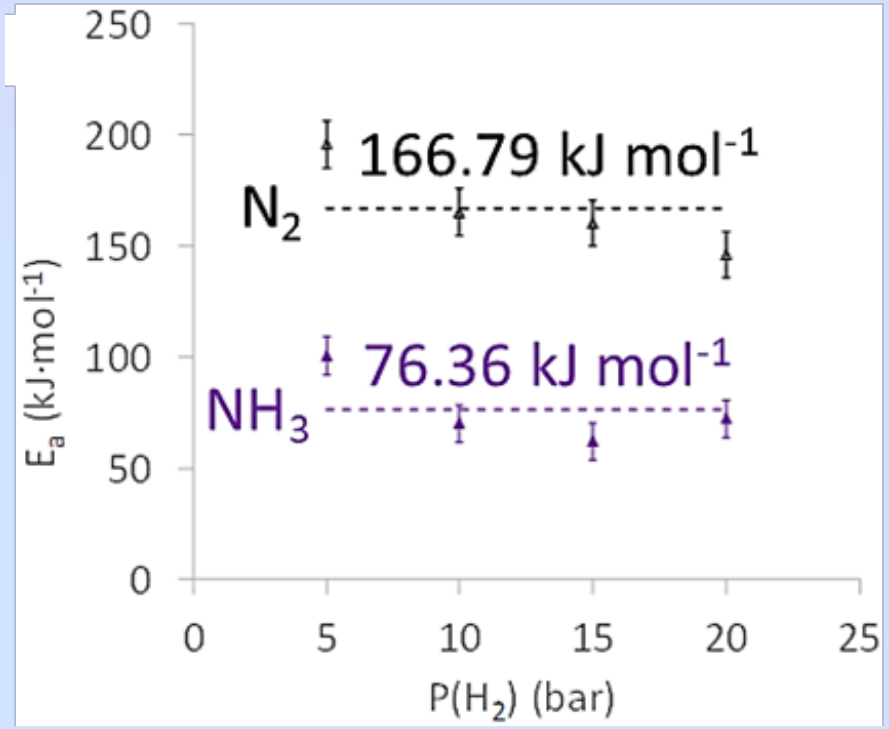



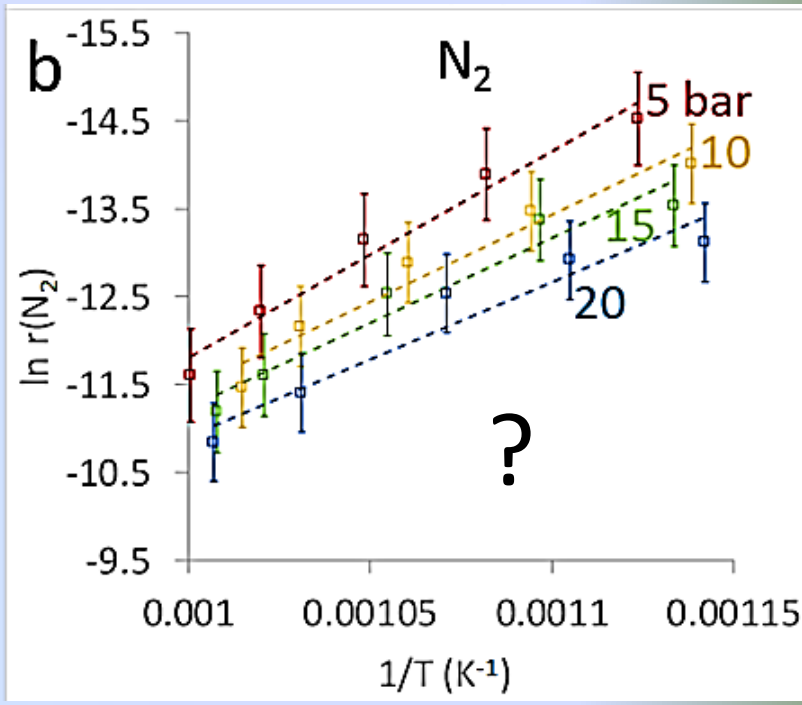

- Conversion increases with T
- $NH_3$ selectivity decreases with increasing T but exceeds expectation

~650 °C Balances Rate and Selectivity

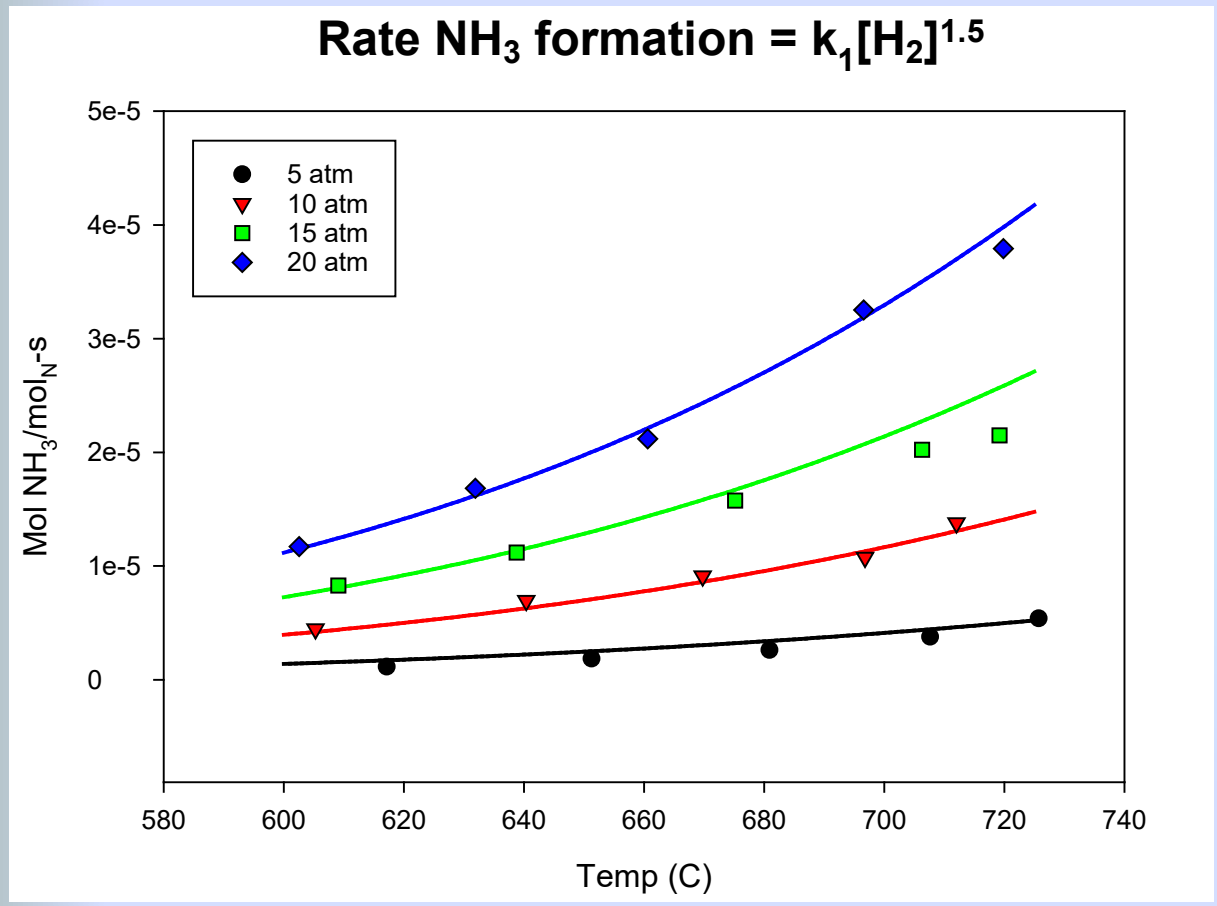
## Activation energies of $N_2$ and $NH_3$



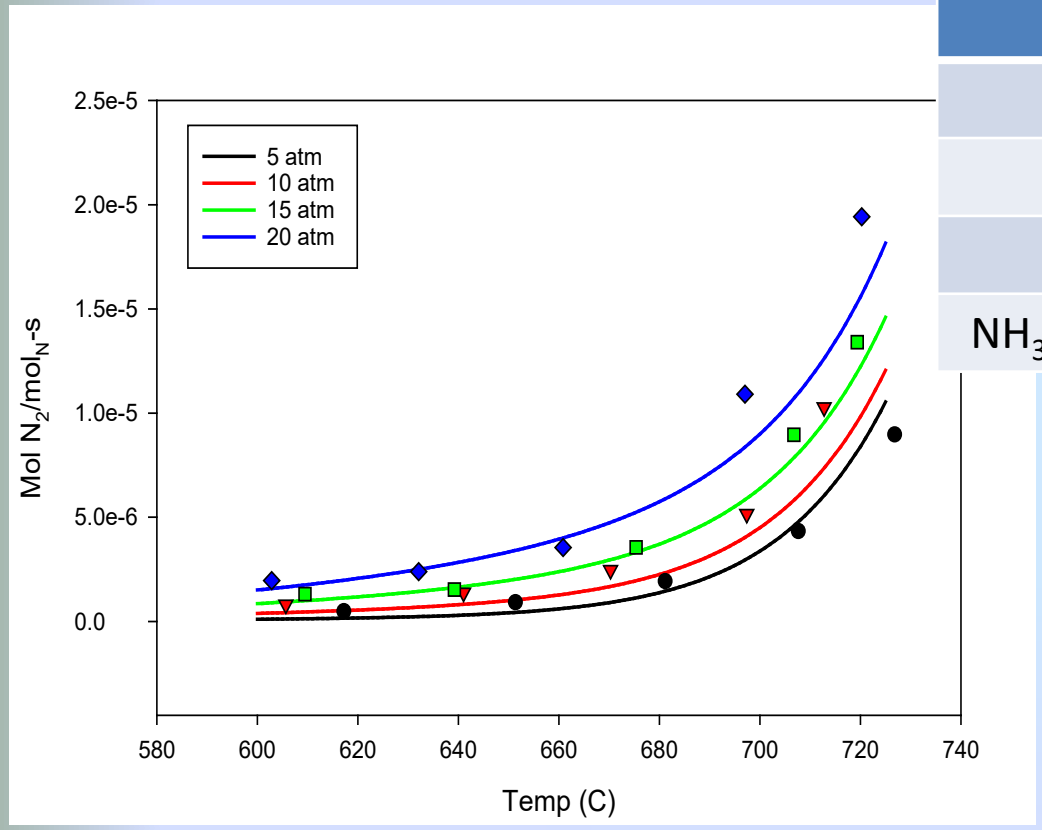




- Use caution comparing catalytic vs bulk reaction, but …
- $E_a$ ranges from 40 (HB) -120 kJ/mol for a variety of heterogeneous (HB) catalysts
- $E_a$ = 54 kJ/mol reported for Cs-promoted $Co_3Mo_3N$, T = 320-440 °C, P = 50 bar

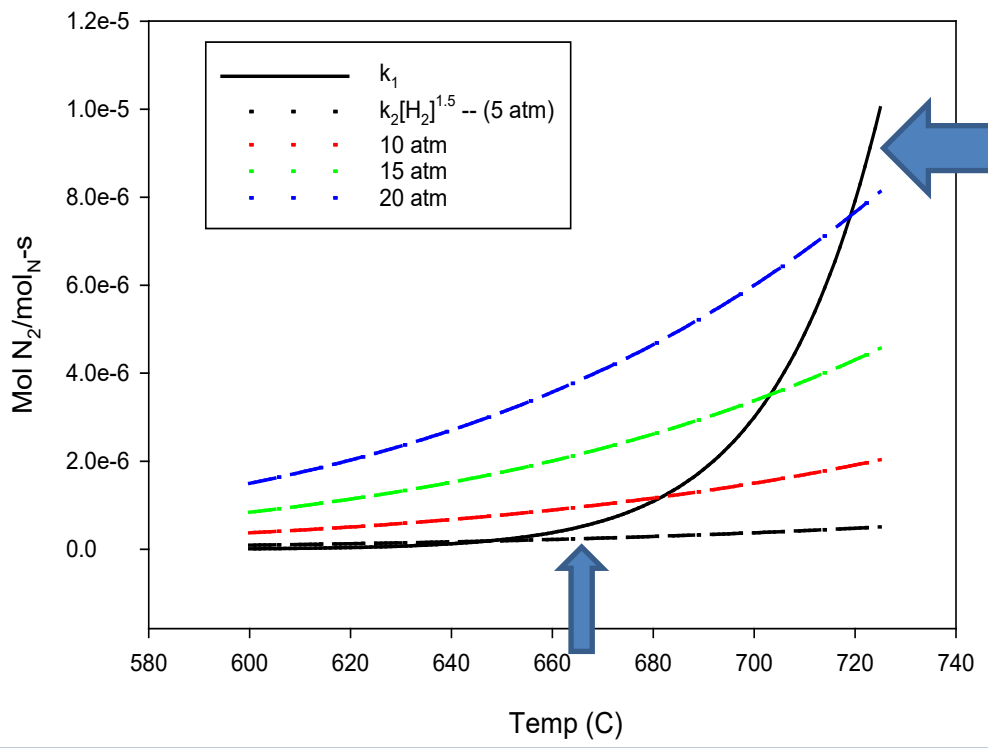



- Simple analysis consistent with multi-step mechanism for $NH_3$ formation
- (3/2 order in $H_2$)
- Favorable Energetics

| Reaction | A ($mol/mol_N$-S) | Ea (kJ/mol) | Order in [H2} |
|---|---|---|---|
| $NH_3$ | 0.00463 | 76.4 | 3/2 |
| $NH_3$ thermolysis | | ≈ 350 | |




| Reaction | A (mol/mol$_N$-S) | Ea (kJ/mol) | Order in [H2} |
|---|---|---|---|
| $NH_3$ | 0.00463 | 76.4 | 3/2 |
| N2(1) | $2.59 \times 10^{16}$ | 390 | 0 |
| N2(2) | 0.00274 | 98 | ≈ 2 |
| $NH_3$ thermolysis | | ≈ 350 | |




0 order in $H_2$

**Rate $N_2$ formation = $k_1 + k_2[H_2]^2$**

$N_2$ rates consistent with multiple pathways

- Ternary nitrides in the family $A_3B_xN$ (A=Co, Ni, Fe; B=Mo; x=2,3) identified and synthesized
- Experiments with $Co_3Mo_3N$ in Ammonia Synthesis Reactor demonstrate cyclable $NH_3$ production from bulk nitride under pure $H_2$
  - Production rates were approx. constant in all the reduction steps with no evident dependence on the consumed solid-state nitrogen up to formation of 661
  - Material can be re-nitridized under pure $N_2$ (or 10% $H_2/N_2$)
  - Bulk N utilization per reduction step averaged between 25 – 40% of the total (2-3 hours)
  - Rate equations and parameters extracted from data.
  - $NH_3$ selectivity exceeds gas phase equilibrium at higher temperatures (in a large excess of $H_2$)
  - Selectivity begins to decrease significantly above 650 C, $N_2$ production rapidly increases above 650 C seemingly due to reaction that is zero order in $H_2$ (thermal reduction of the nitride?).
- Poised to begin the systematics studies of relationships between materials and reactions

Sandia National Laboratories

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

ASU LightWorks
ARIZONA STATE UNIVERSITY

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

Georgia Tech Solar Fuels and Technology Lab

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

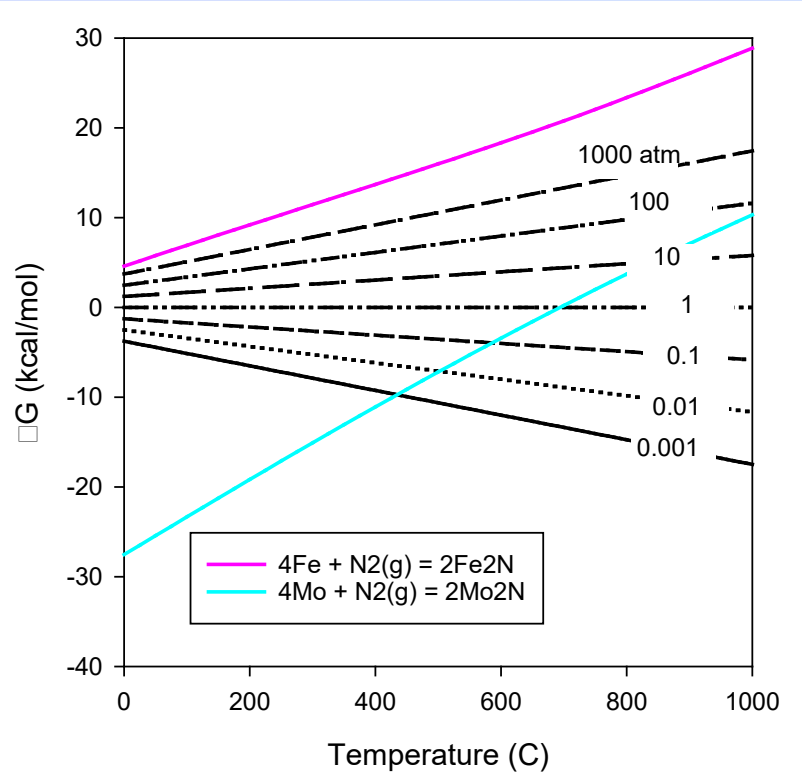
U.S. DEPARTMENT OF ENERGY

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.

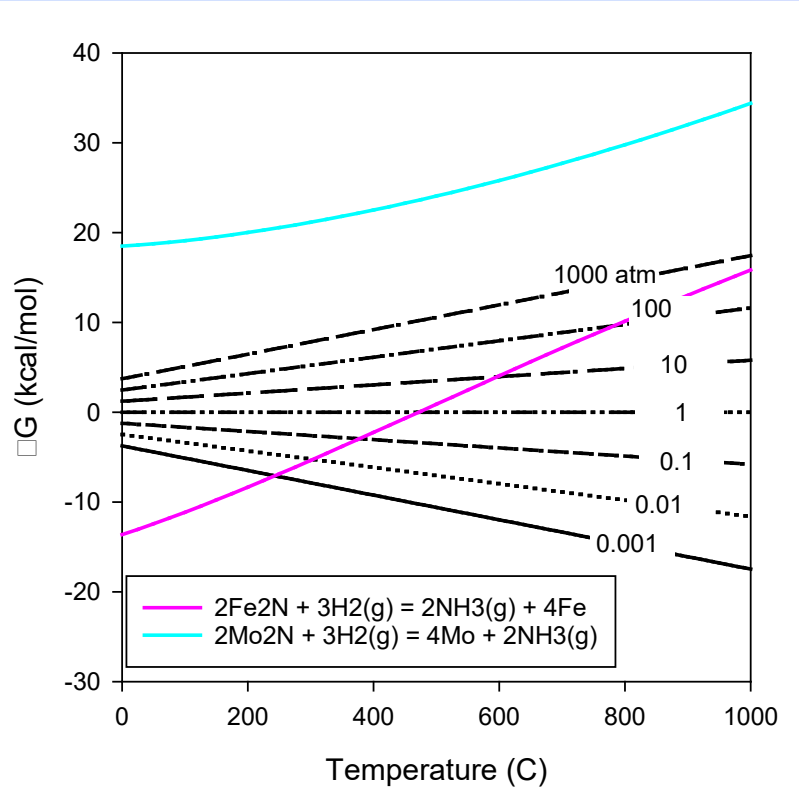
SOLAR ENERGY TECHNOLOGIES OFFICE
U.S. Department Of Energy

# Why Multiple Metals are Required

## Nitridation




## Ammonia Formation




Black lines: Equilibrium $pN_2$

Equilibrium $pH_2 = pNH_3$