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Nitride-Based Step Catalysis for Ammonia Synthesis at Atmospheric Pressure

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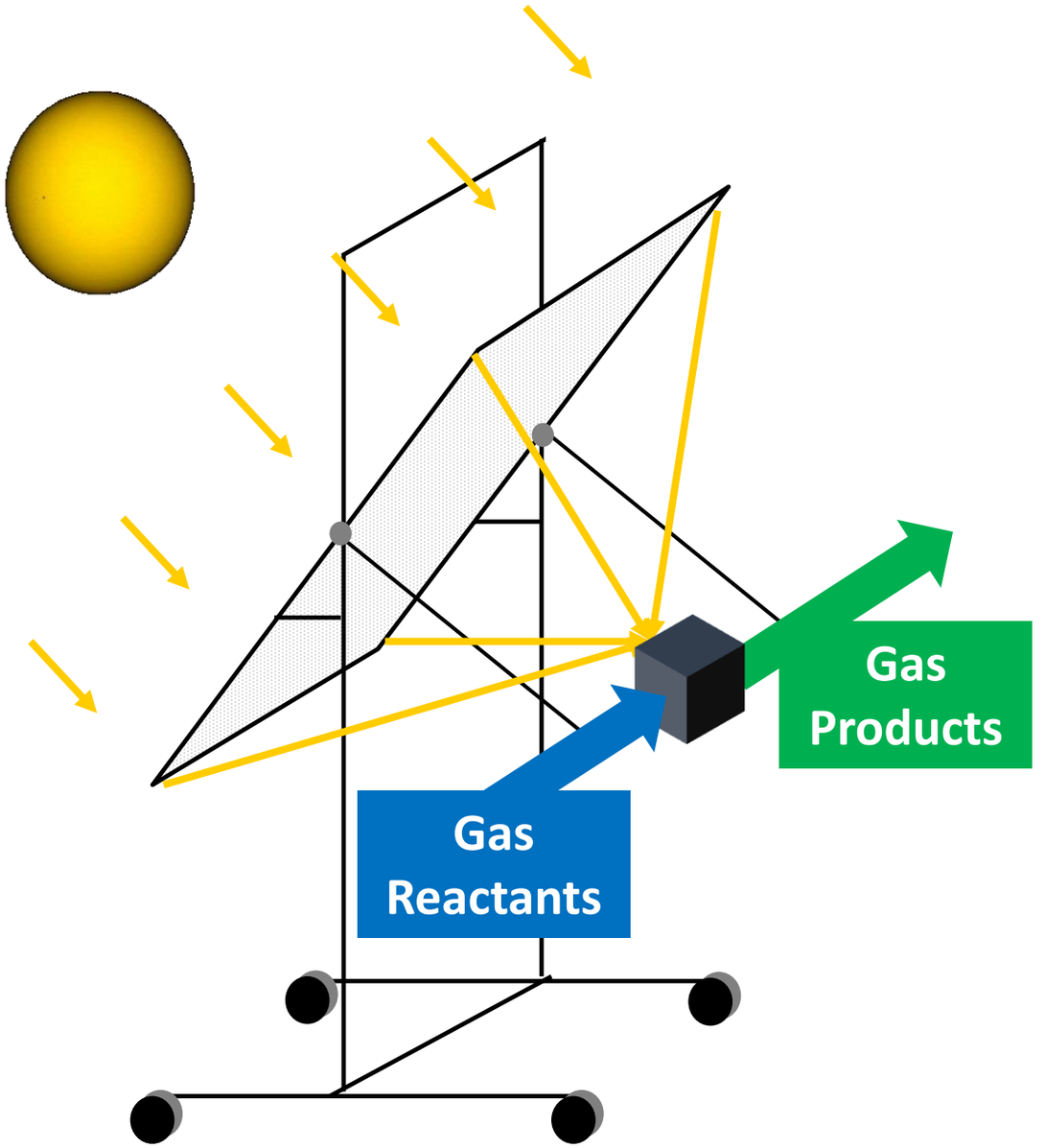
Session 730: NH_3 Fuel Synthesis II

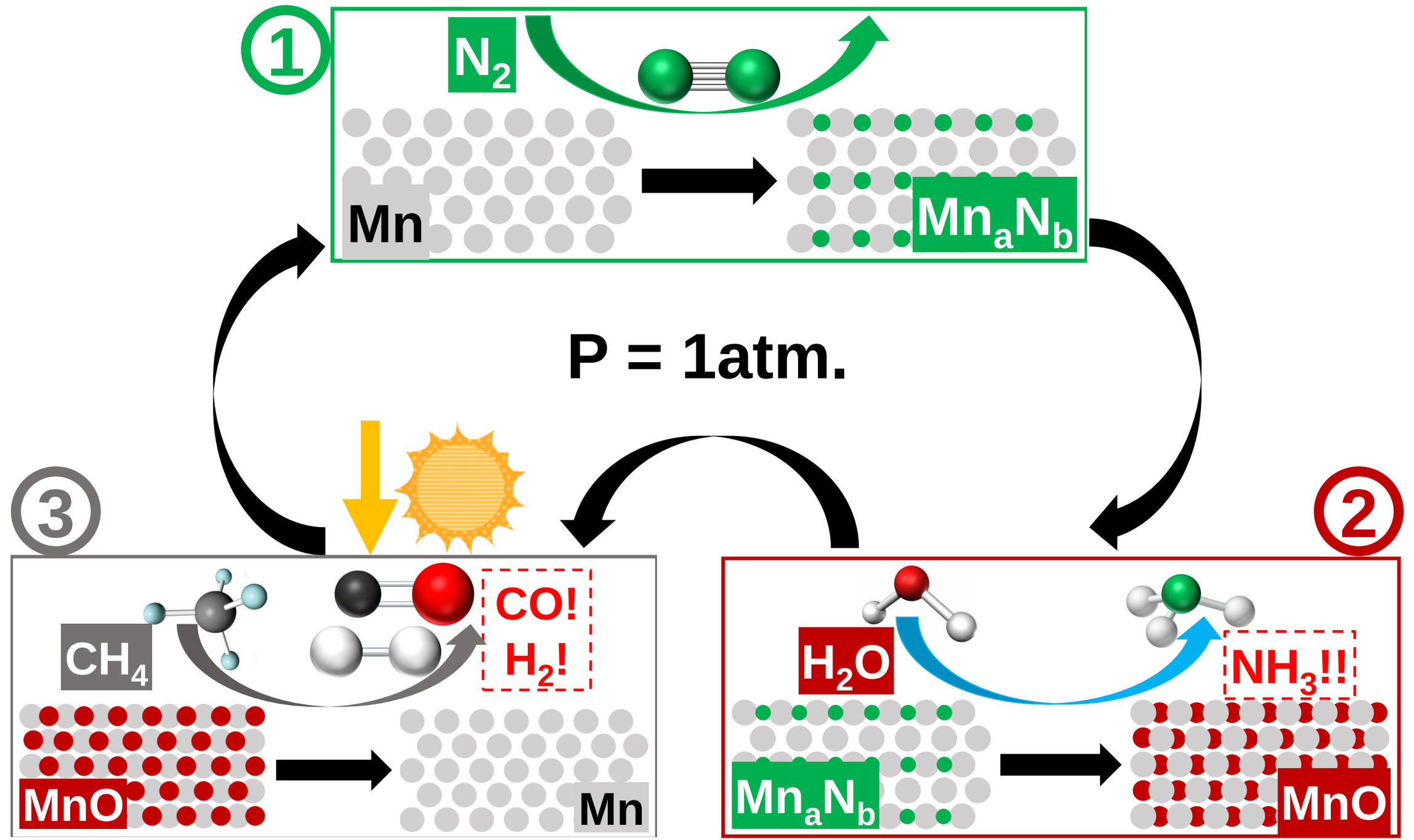
Goal: Versatile, Small Scale Solar NH_3 Synthesis

Solar Thermochemical NH_3 Synthesis

- **Possible:**
  - **Operation near atmospheric Pressure**
  - **Accommodates inherent intermittent nature of renewable energy**
  - **Reduced capital investment**
  - **Tunable/Modular**
  - **To operate near the end user**
    - **Perhaps by a single farmer**
- **Less Essential:**
  - **Transportation infrastructure**
  - **Politically stable region**
  - **Technically advanced workforce**

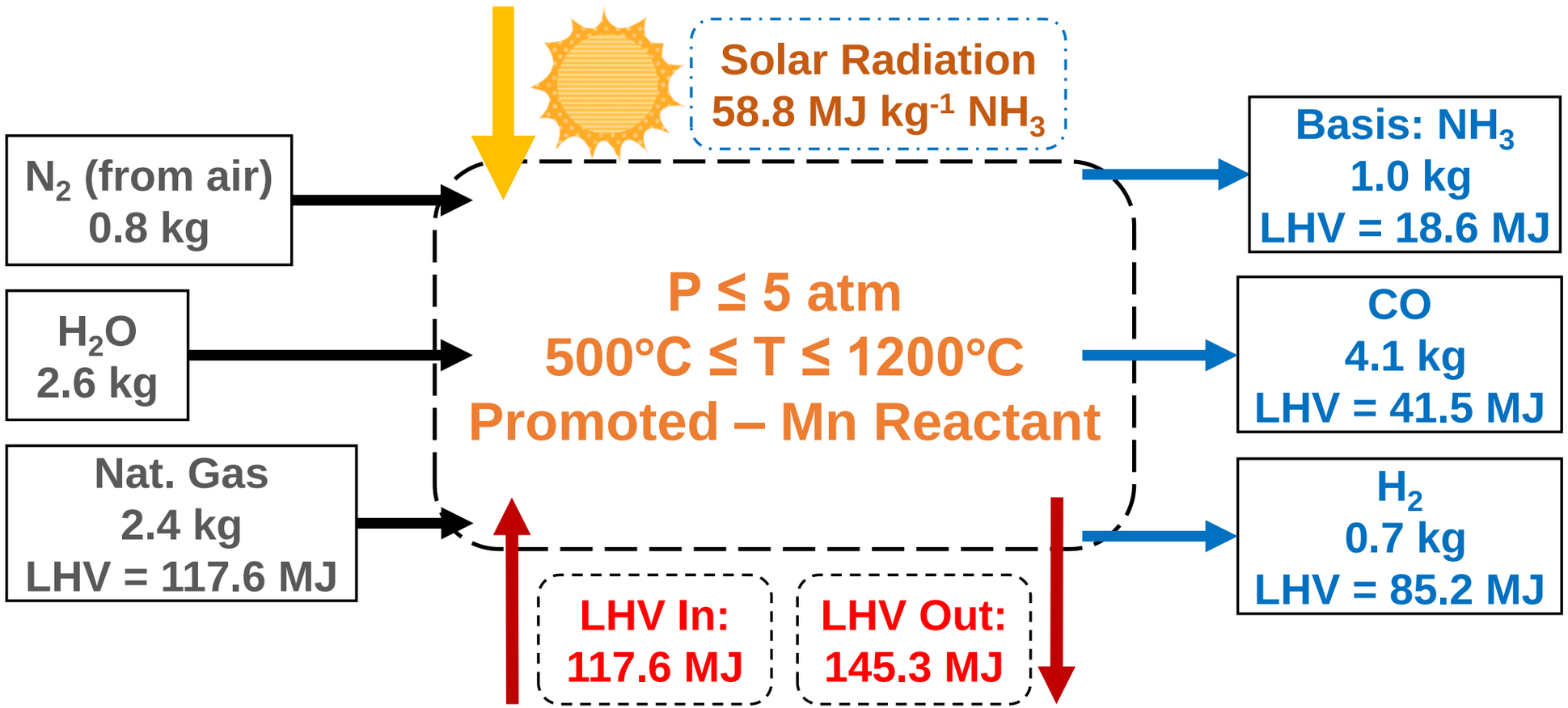


NH_3 Synthesis via Solar Thermochemical Cycle



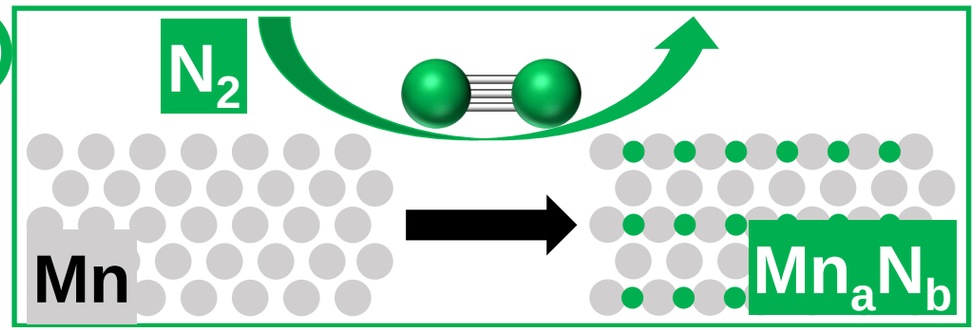
Potential Benefits of the Proposed Solar Cycle

- **Produces Valuable Syngas Co-Products**
- **LHV Upgrade in Products**
- **Solar Energy Stored as NH_3 and Syngas**
- **Operable at Pressures Near 1 atm.**
- **Possible at Smaller Economies of Scale**



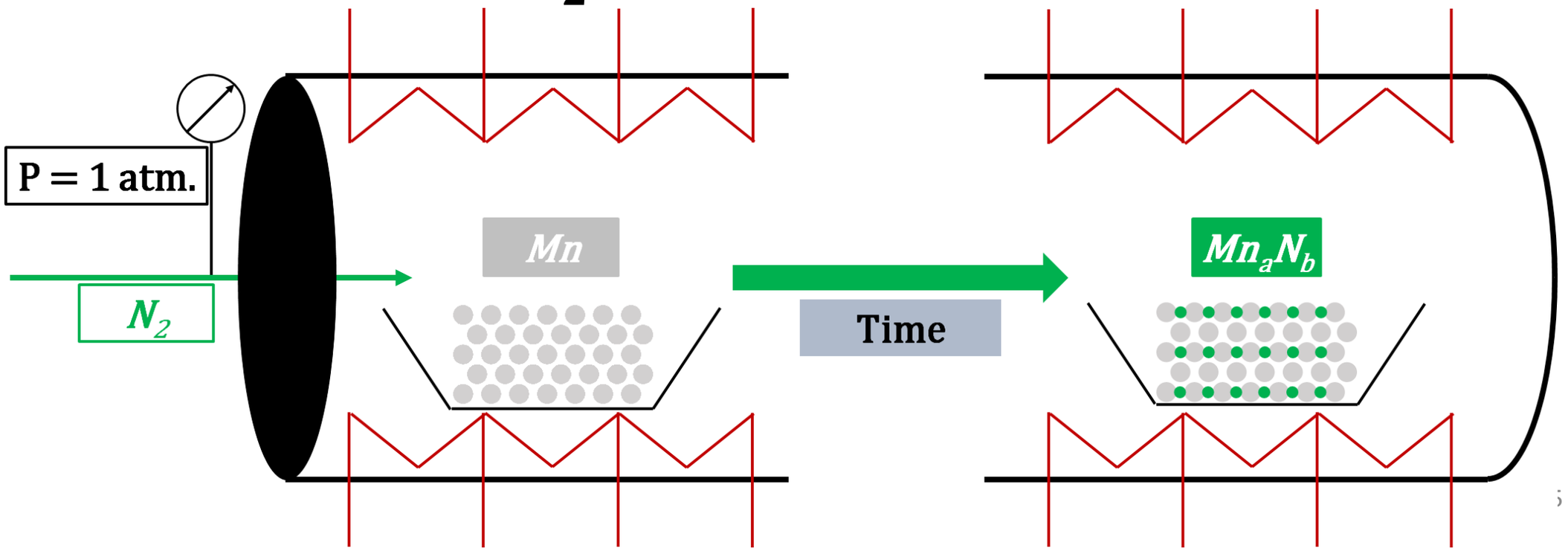
Experimental Method: Nitrogen Fixation – Rxn #1

- Goal: Max Nitrogen Fixed to Mn
- Find Optimum Rxn Temperature
  - Range: 600 °C ≤ T ≤ 1000 °C
- Find Optimum Reaction Time



$$\frac{5}{2}\mathrm{Mn_{(s)}} + \frac{1}{2}\mathrm{N_{2(g)}} \leftrightarrow \frac{1}{2}\mathrm{Mn_5N_{2(s)}} \qquad 1A$$

$$4\mathrm{Mn_{(s)}} + \frac{1}{2}\mathrm{N_{2(g)}} \leftrightarrow 1\mathrm{Mn_4N_{(s)}} \qquad 1B$$



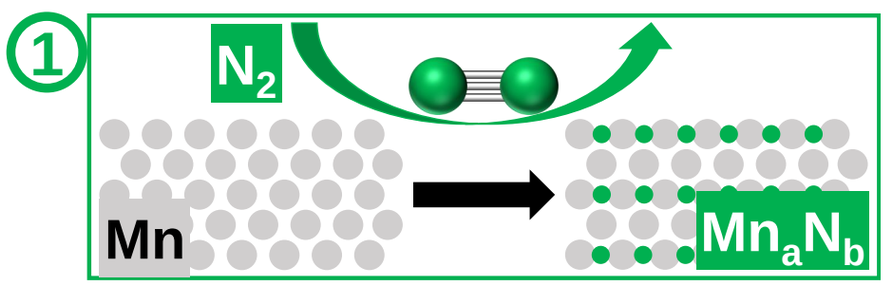
Max Nitrogen Fixation Occurs at 800 °C and 120 min

$$\frac{5}{2}Mn_{(s)} + \frac{1}{2}N_{2(g)} \leftrightarrow \frac{1}{2}Mn_5N_{2(s)} \qquad \Delta H_{Rxn}^{800°C} = -91.0\ kJ\ mol^{-1} \qquad \Delta G_{Rxn}^{800°C} = -64.3\ kJ\ mol^{-1} \qquad 1A$$

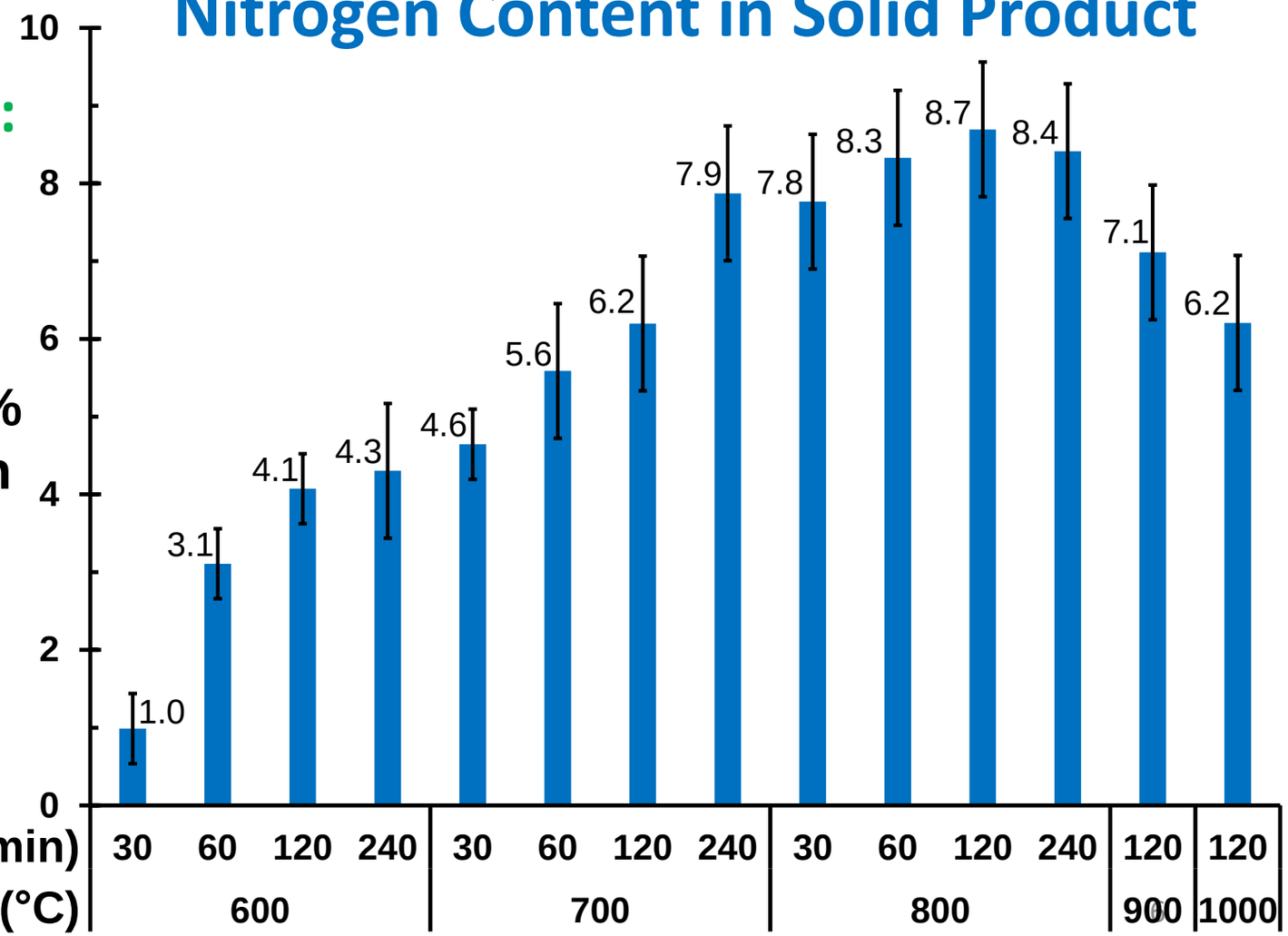
$$4Mn_{(s)} + \frac{1}{2}N_{2(g)} \leftrightarrow 1Mn_4N_{(s)} \qquad \Delta H_{Rxn}^{800°C} = -110.6\ kJ\ mol^{-1} \qquad \Delta G_{Rxn}^{800°C} = -61.0\ kJ\ mol^{-1} \qquad 1B$$

Mn-Nitride Mixture at Optimal:

- $Mn_6N_{2.58}$-rich
- w/ Mn_4N also



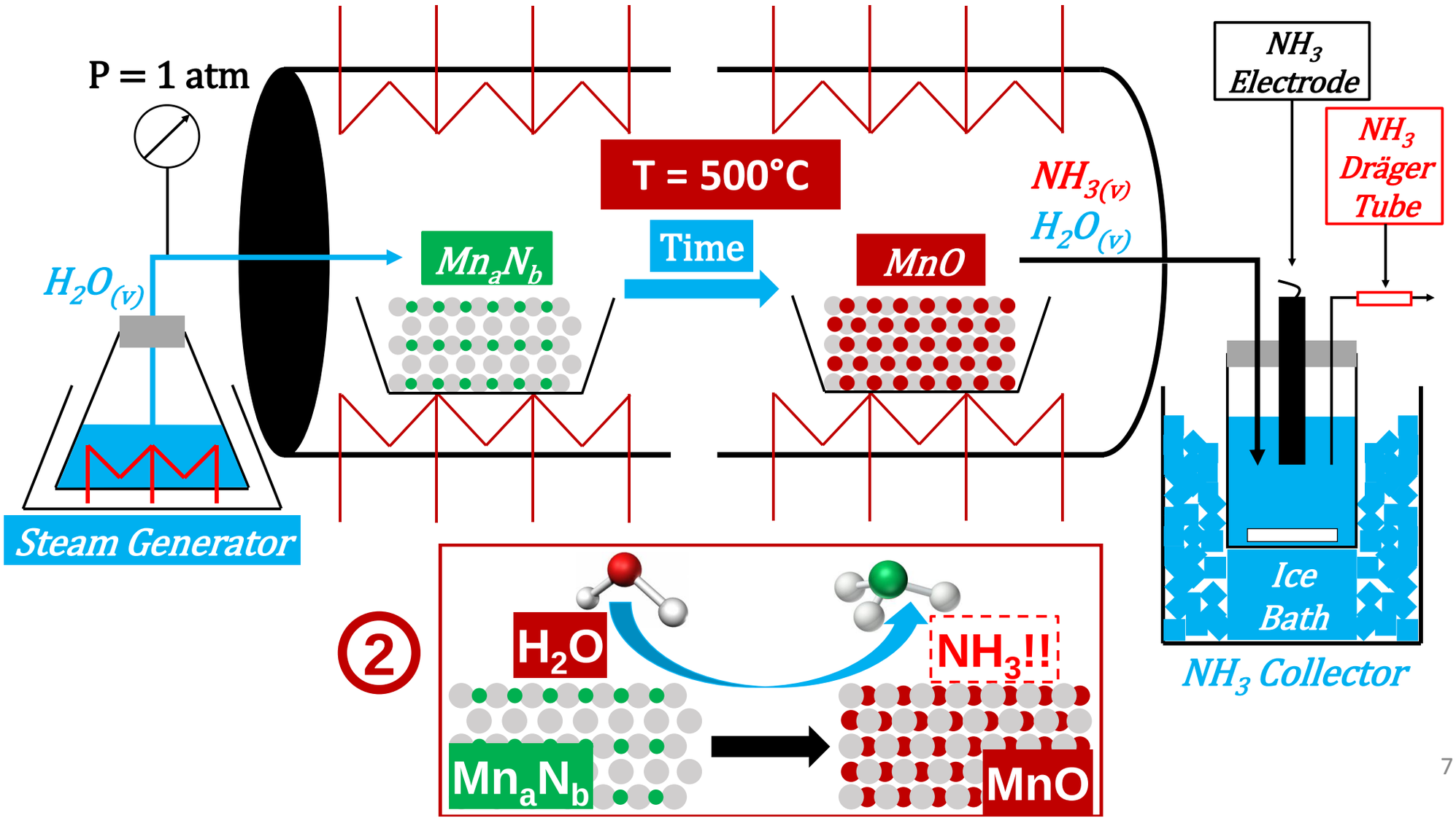
Nitrogen Content in Solid Product



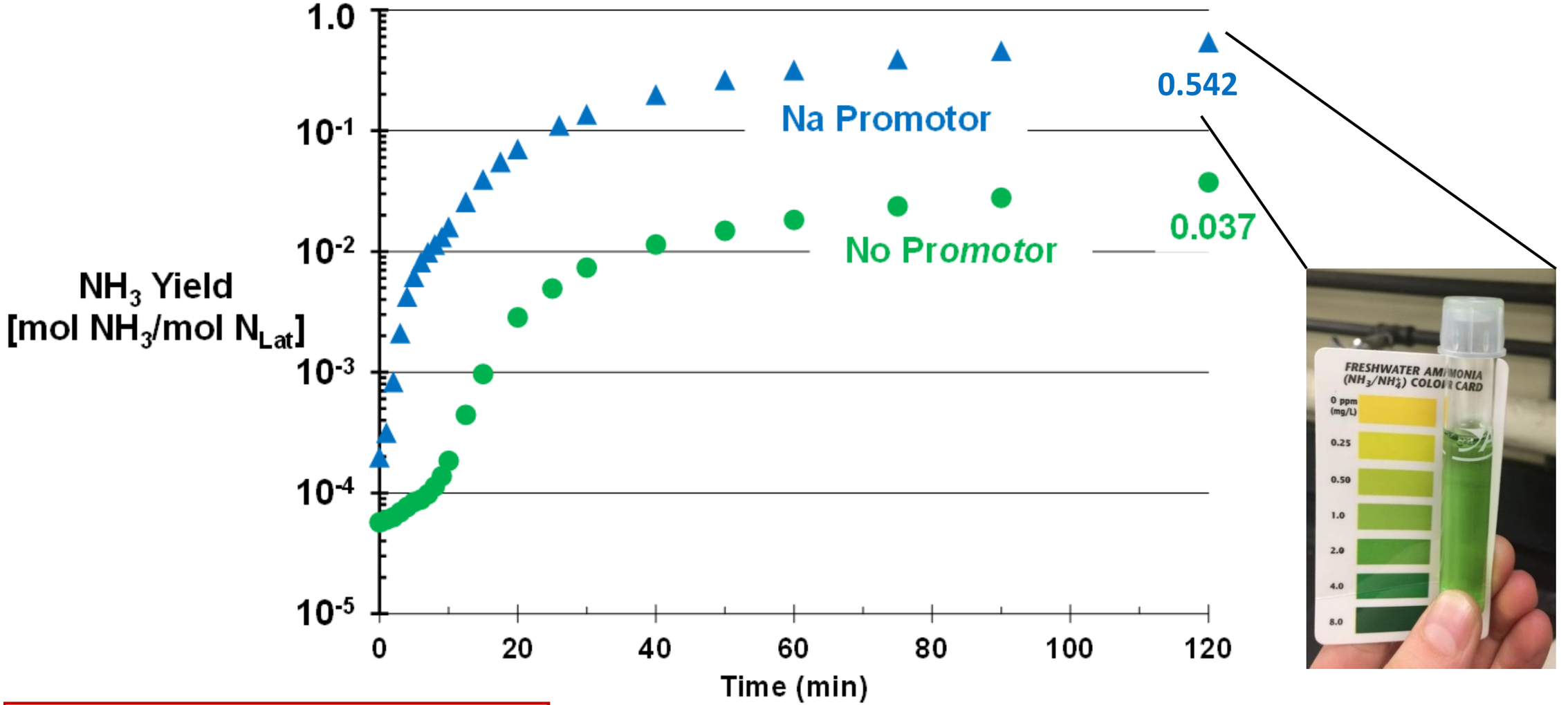
Experimental Method: Ammonia Synthesis – Rxn #2

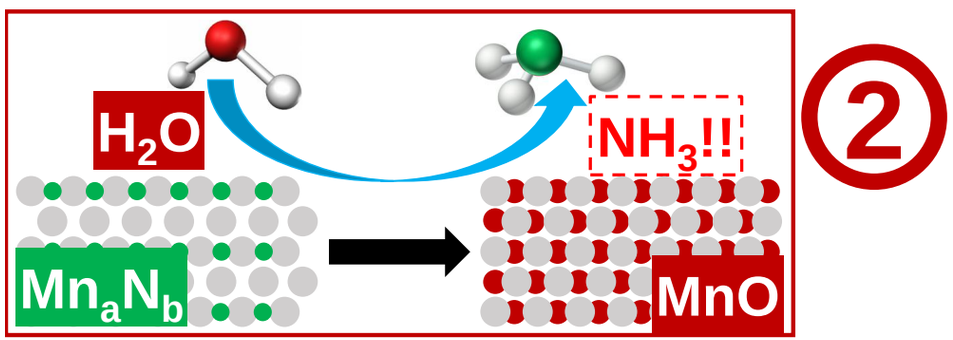
$$\frac{1}{2}\mathbf{Mn_5N_{2(s)}} + \frac{5}{2}\boldsymbol{H_2O_{(v)}} \leftrightarrow \frac{5}{2}\boldsymbol{MnO_{(s)}} + \boldsymbol{NH_{3(g)}} + \boldsymbol{H_{2(g)}}$$

$$\Delta H_{Rxn}^{500°C} = -302.4 \text{ kJ mol}^{-1} \qquad \Delta G_{Rxn}^{500°C} = -230.5 \text{ kJ mol}^{-1}$$



Alkali-Metal 'Promotor' Improves NH_3 Yield

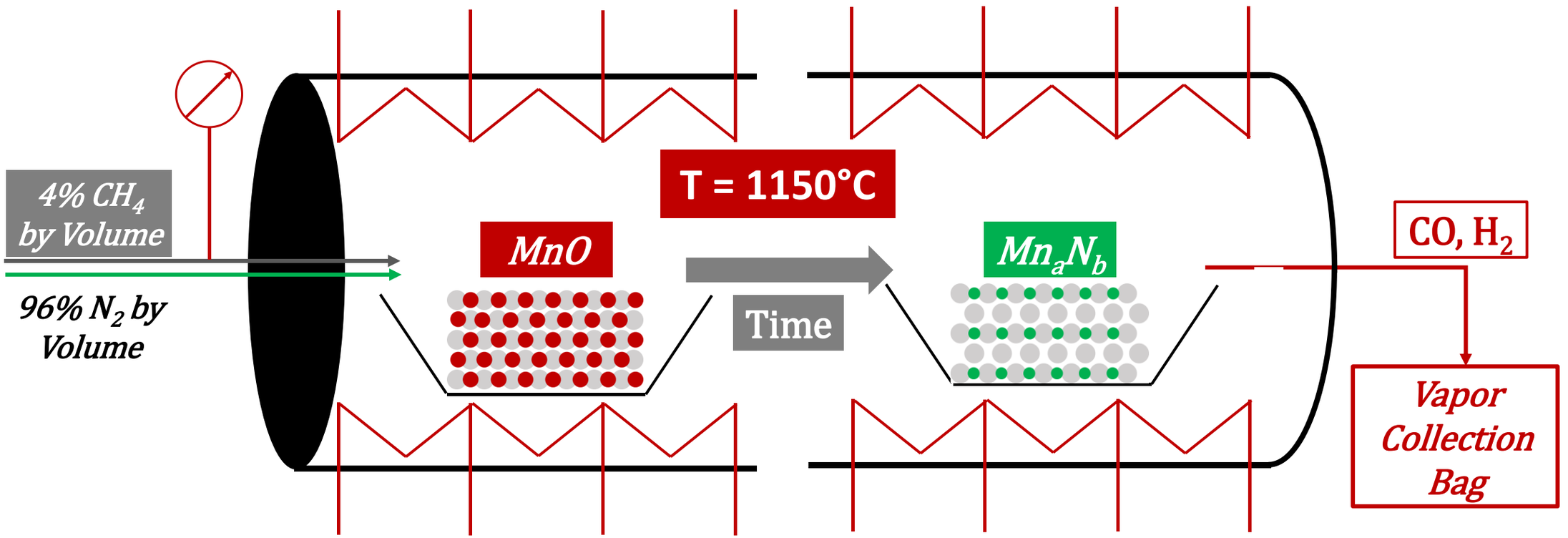




Expt. Method: Metal Oxide Reduction – Rxn #3

$$\frac{5}{2}\mathbf{Mn}O_{(s)} + \frac{5}{2}CH_{4(g)} \leftrightarrow \frac{5}{2}Mn_{(s)} + \frac{5}{2}CO_{(g)} + 5H_{2(g)}$$

$$\Delta H_{Rxn}^{1150°C} = 916 \text{ kJ mol}^{-1} \qquad \Delta G_{Rxn}^{1150°C} = -57.1 \text{ kJ mol}^{-1}$$



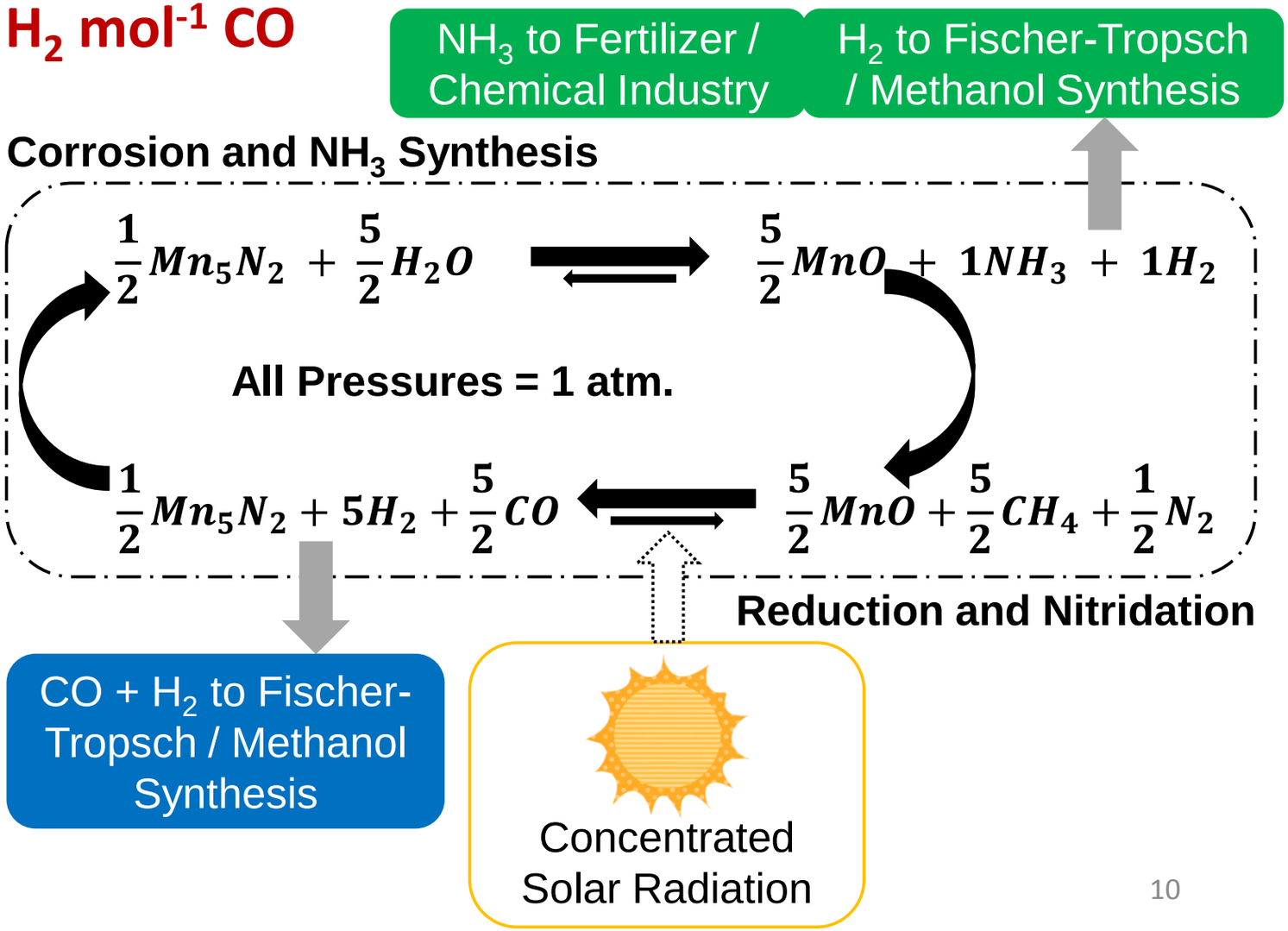
Partial Conversion of MnO by Dilute CH_4 Achieved

- $X_{MnO} = 0.371 \pm 0.072$
- $Y_{Mn6N2.58} = 0.381 \pm 0.083$
- CO_2 NOT Detected!
- H_2 / CO = 29.9 ± 6.0 mol H_2 mol^{-1} CO

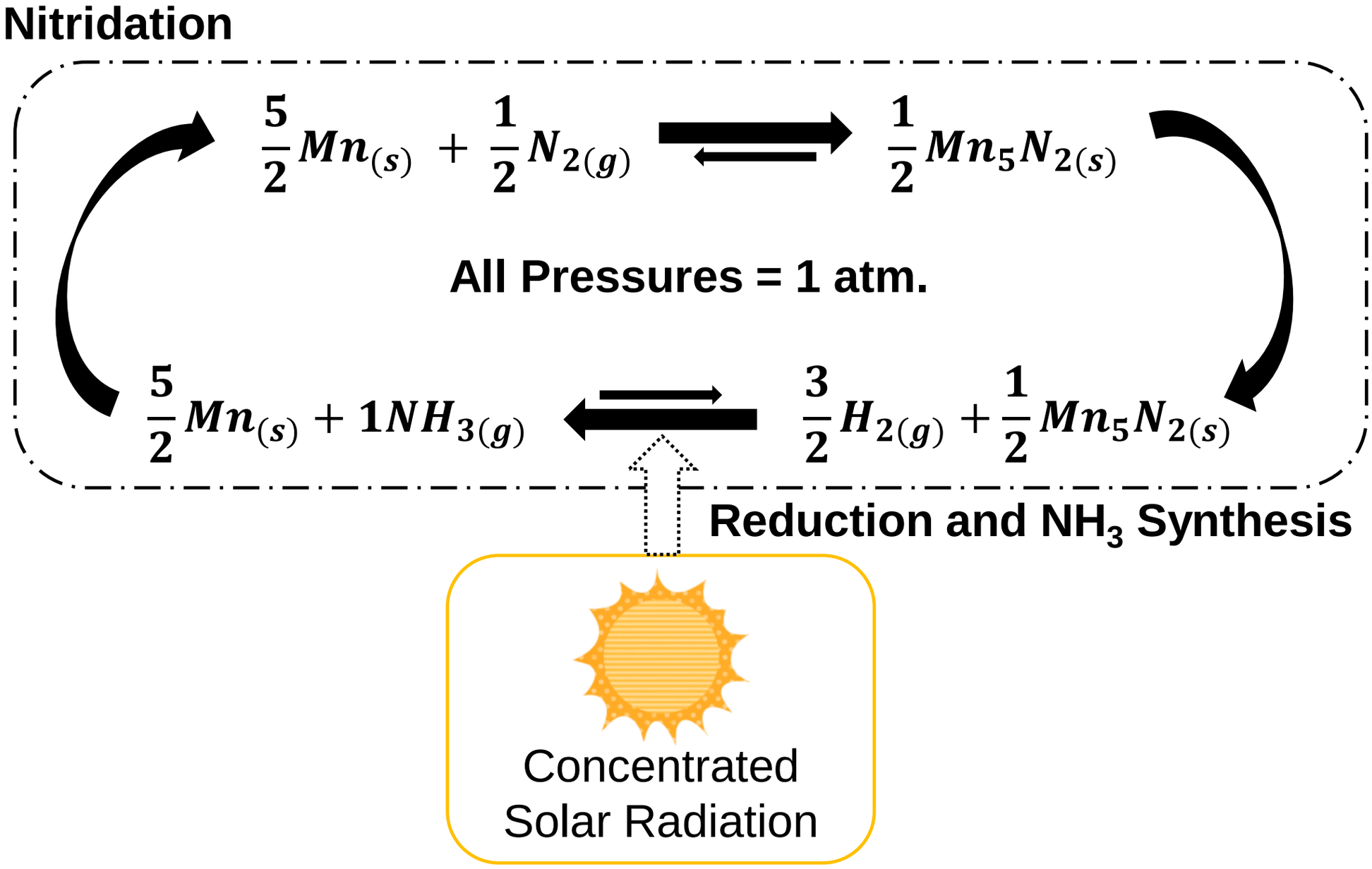
T = 1150°C
t = 30 min

Mn_7C_3 formation an issue
Possible Solutions:

- Co-Feed CO_2
- Co-Feed H_2



What if We Could Use Renewable H_2?

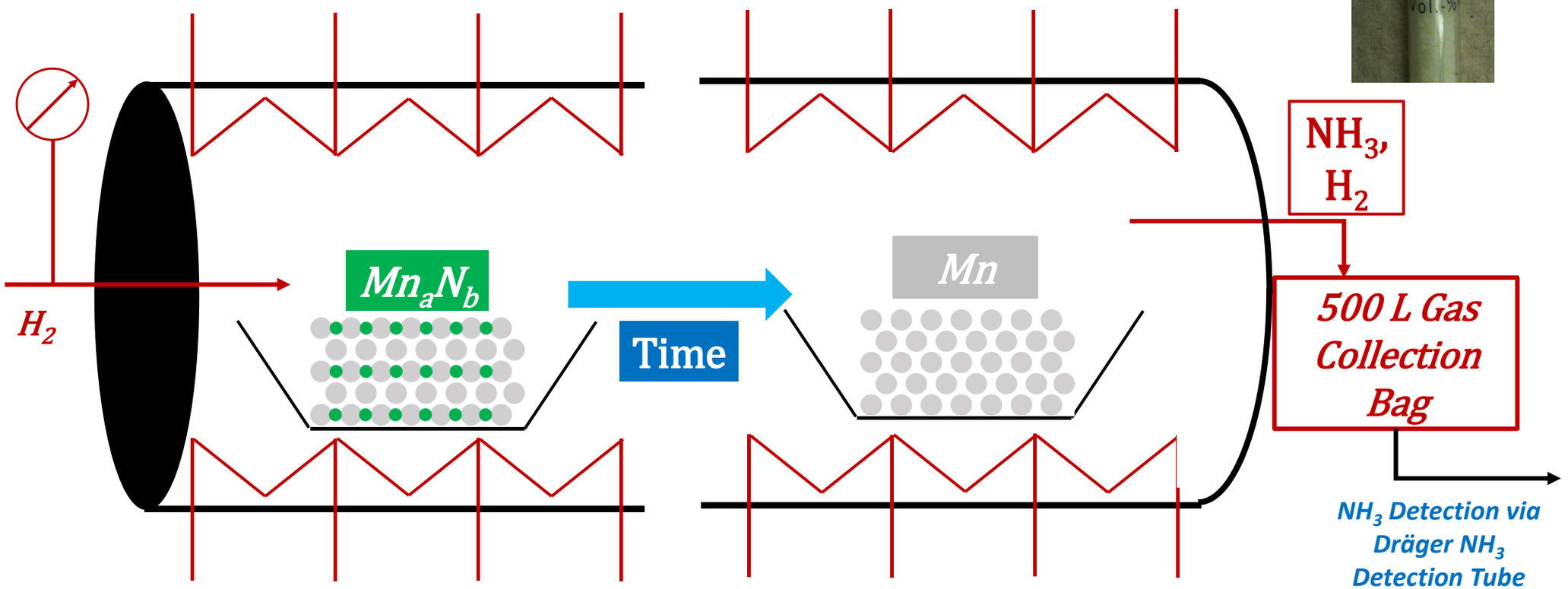


N_2- H_2 Cycling Expt. Method

- **Nitridation:**
  - **700 °C**
  - **30 min**
  - **N_2 Flowrate: 2.0 ± 0.1 L min^{-1}**
- **Reduction:**
  - **700 °C**
  - **60 min**
  - **H_2 Flow: 1.8 ± 0.1 L min^{-1}**

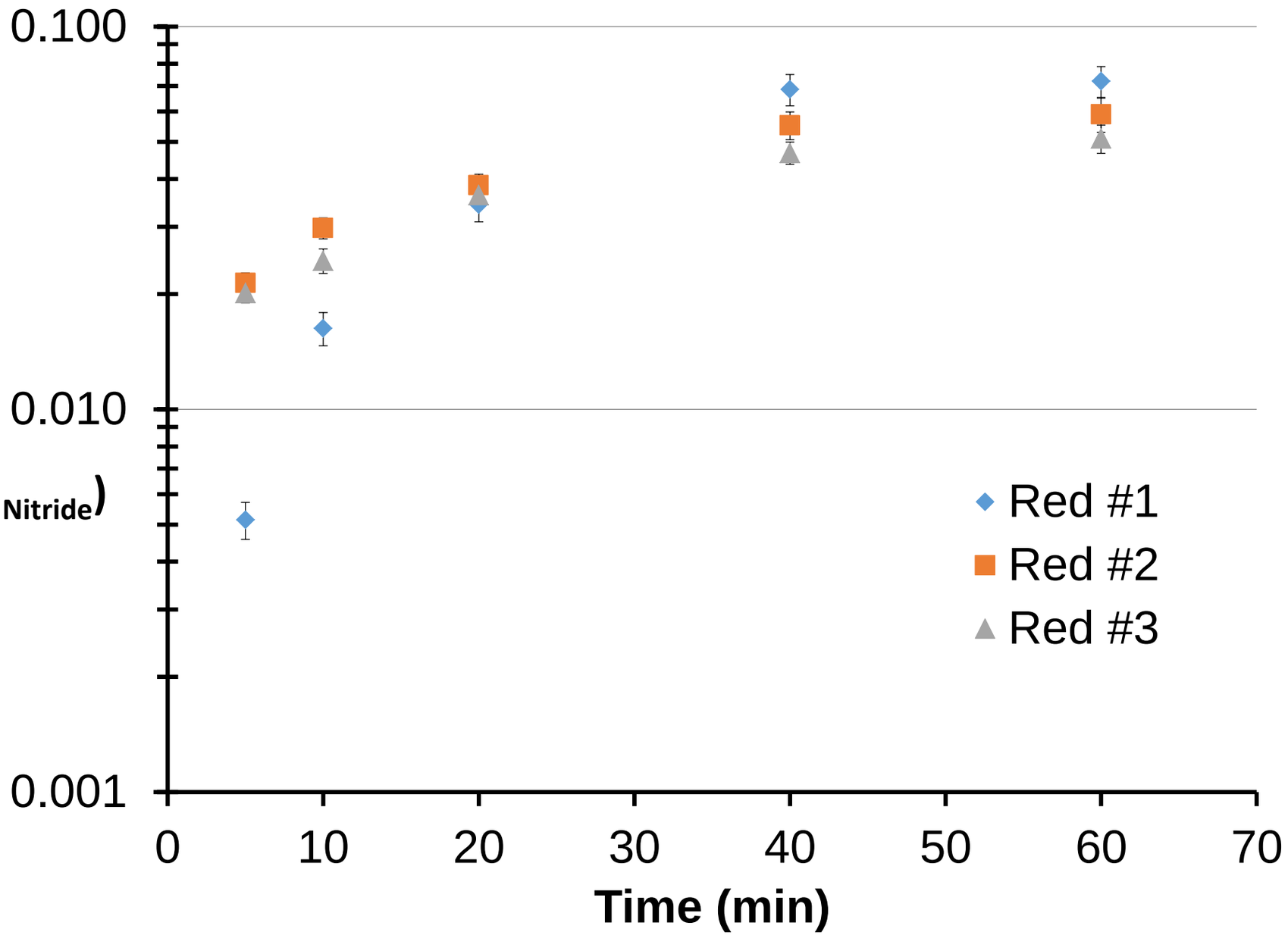
Unreacted Dräger Tube

NH_3 Confirmed



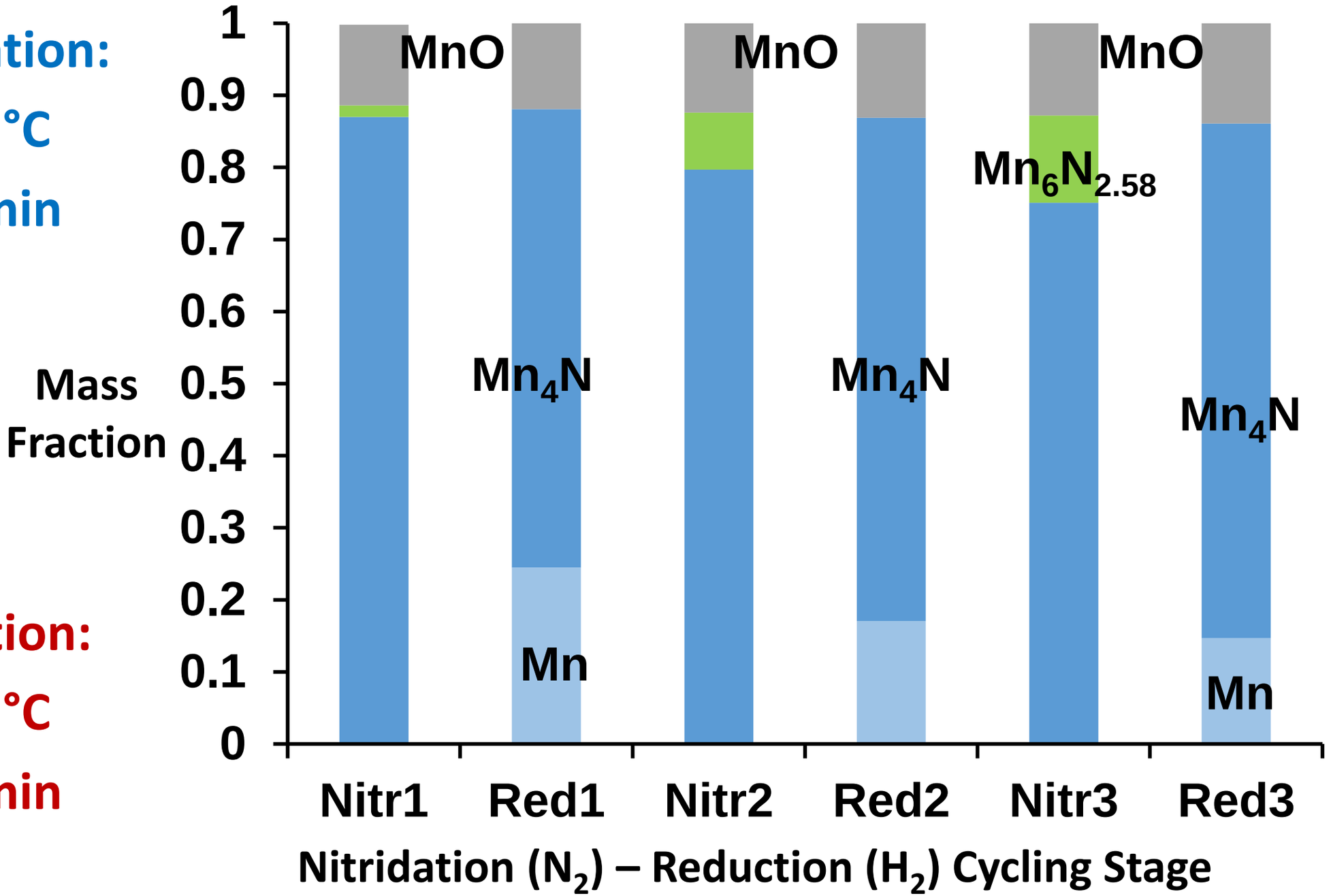
NH_3 Yield Limited When Using Mn Alone

- **Nitridation:**
  - **700 °C**
  - **30 min**
- **Reduction:**
  - **700 °C**
  - **60 min**



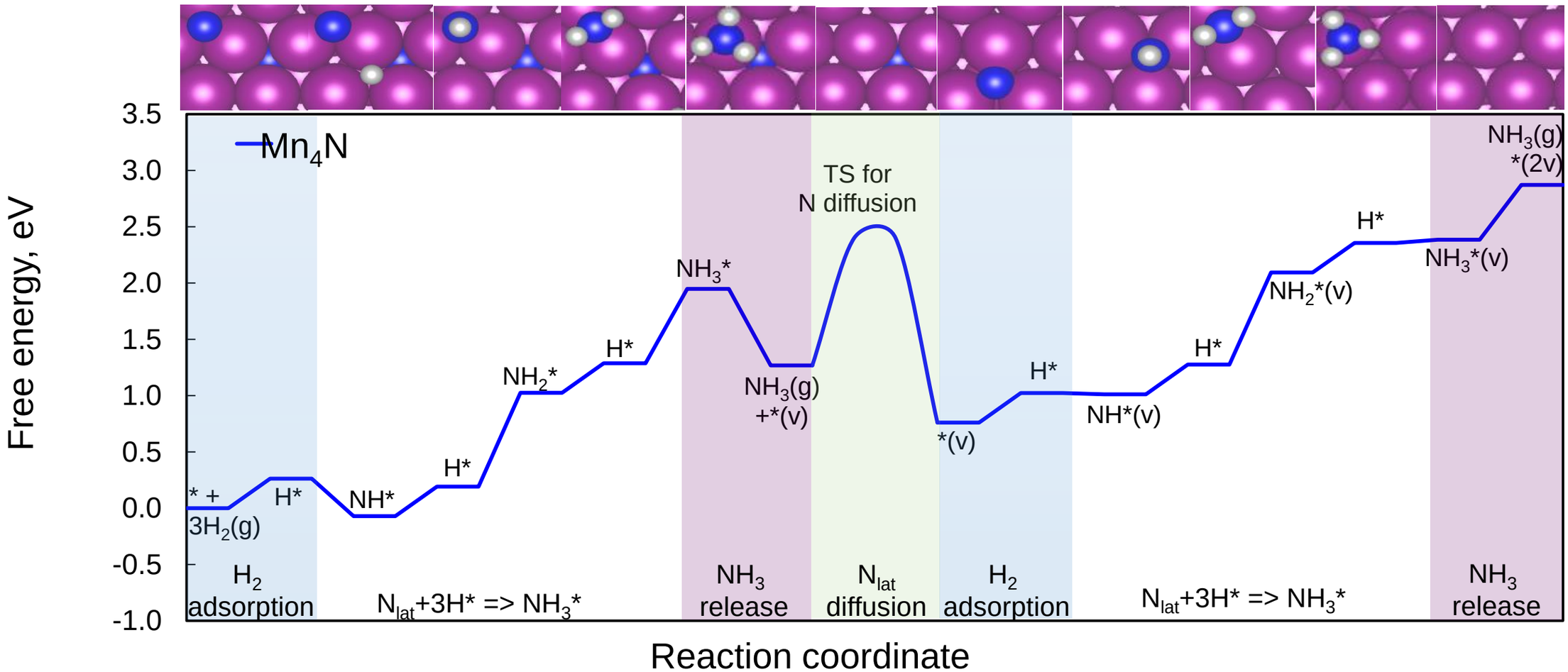
XRD Shows Stable Reactant

- **Nitridation:**
  - **700 °C**
  - **30 min**
- **Reduction:**
  - **700 °C**
  - **60 min**



Mechanistic understanding of metal nitride reduction

$2N_{nitride}+3H_2(g) \Rightarrow 2NH_3(g)$ @ 700°C and 1 atm



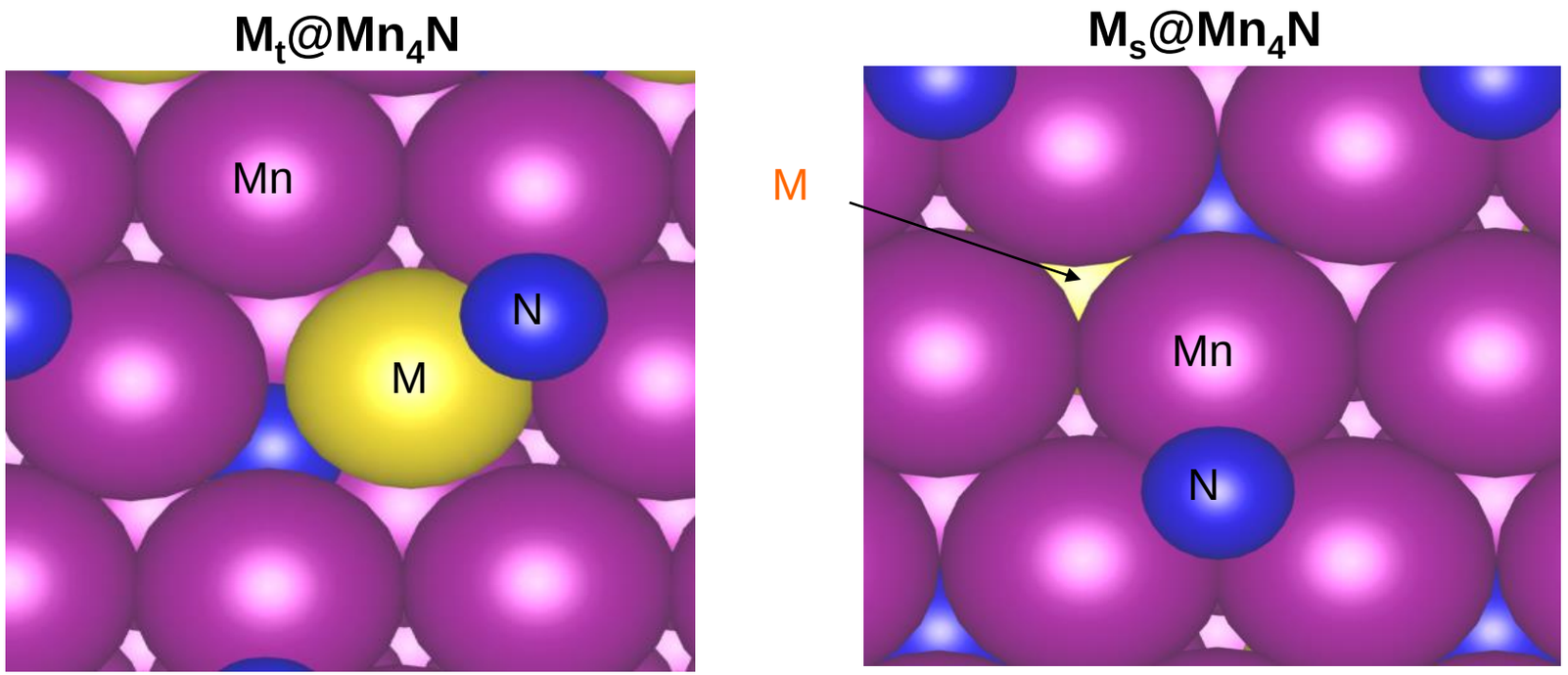
- On Mn_4N, H_2 dissociative adsorption is endothermic.
- Reduction of lattice N (N_{lat}), forming NH_3, is very endothermic.
- Diffusion energy barrier of subsurface N is 1 eV.
- Hydrogenation of the diffused subsurface N (N_{ss}) is also endothermic.

Slide provided by Dr.Bin Liu, Kansas State University, Manhattan, KS

Modifying the properties of Mn_4N by doping heteroatom (M)

To modify pure Mn_4N to facilitate NH_3 formation, it is desirable to:

- lower endothermicity (e.g., increasing H binding energy)
- lower N diffusion energy barrier.



- Heteroatom is introduced to disturb local electronic structures.
- The heteroatom is deliberately placed in the sublayer (‘s’) and the top layer (‘t’) of Mn_4N.

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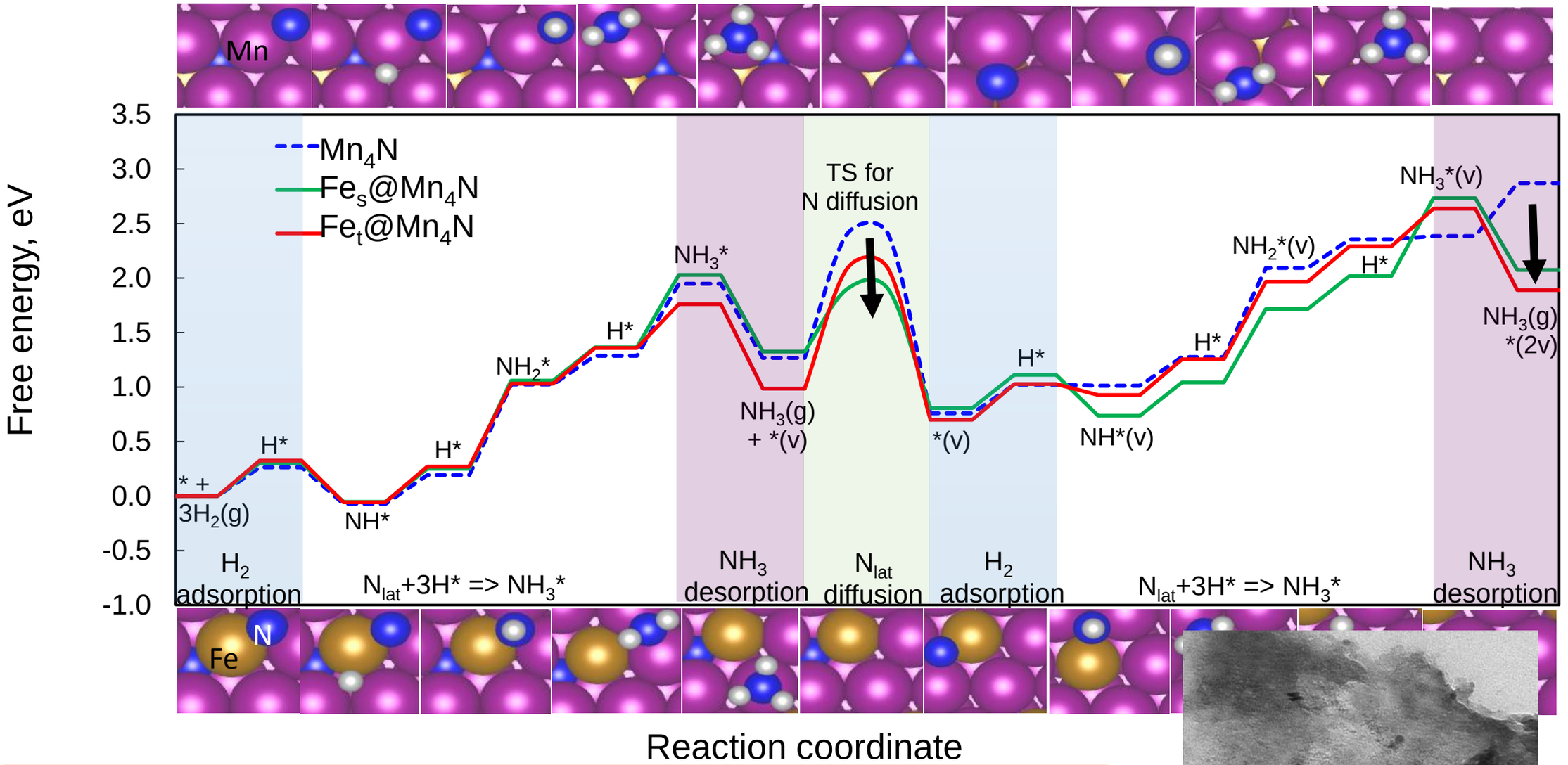
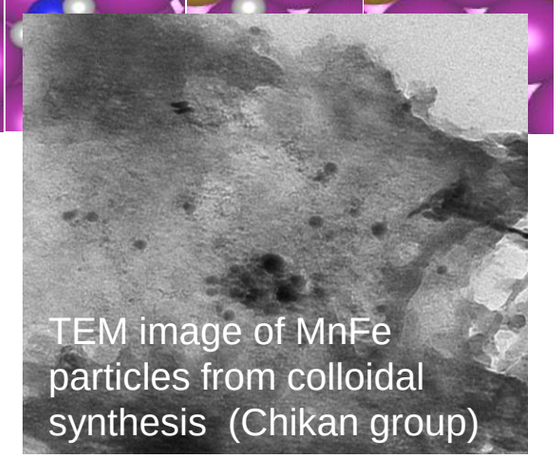
Manganese nitride reduction by doping with Fe





The N-Fe bond is expected to be weaker than N-Mn bond, and Fe dopant can:

- Lower diffusion energy barrier of subsurface N
- Lower reduction energy (when Fe is at top surface)
- However, the overall process is still quite endothermic (by > 1.5 eV).

Slide provided by Dr.Bin Liu, Kansas State University, Manhattan, KS

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Questions?

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