Nitride-Based Step Catalysis for Ammonia Synthesis at Atmospheric Pressure

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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
NH₃ Synthesis via Solar Thermochemical Cycle

1. N₂
   Mn -> MnₐNₐ

2. P = 1 atm.

3. CH₄
   H₂O
   MnO
   Mn
   MnₐNₐ
   NH₃!!

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 NH₃ 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: $600 \, ^\circ C \leq T \leq 1000 \, ^\circ C$
- **Find Optimum Reaction Time**

\[
\[
\frac{5}{2} \text{Mn}_\text{s} + \frac{1}{2} \text{N}_2\text{(g)} \leftrightarrow \frac{1}{2} \text{Mn}_5\text{N}_2\text{(s)} \tag{1A}
\]
\[
4\text{Mn}_\text{s} + \frac{1}{2} \text{N}_2\text{(g)} \leftrightarrow \text{Mn}_4\text{N}_\text{(s)} \tag{1B}
\]
Max Nitrogen Fixation Occurs at 800 °C and 120 min

\[
\frac{5}{2} \text{Mn}(s) + \frac{1}{2} \text{N}_2(g) \leftrightarrow \frac{1}{2} \text{Mn}_5\text{N}_2(s)
\]
\[
4\text{Mn}(s) + \frac{1}{2} \text{N}_2(g) \leftrightarrow 1\text{Mn}_4\text{N}(s)
\]

\[\Delta H_{\text{Rxn}}^{800^\circ C} = -91.0 \text{ kJ mol}^{-1}\]
\[\Delta G_{\text{Rxn}}^{800^\circ C} = -64.3 \text{ kJ mol}^{-1}\]  
1A

\[\Delta H_{\text{Rxn}}^{800^\circ C} = -110.6 \text{ kJ mol}^{-1}\]
\[\Delta G_{\text{Rxn}}^{800^\circ C} = -61.0 \text{ kJ mol}^{-1}\]  
1B

Mn-Nitride Mixture at Optimal:
- \(\text{Mn}_6\text{N}_{2.58}\)-rich
- w/ \(\text{Mn}_4\text{N}\) also

Nitrogen Content in Solid Product

Weight % Nitrogen Fixed

![Diagram](image)
Experimental Method: Ammonia Synthesis – Rxn #2

\[
\frac{1}{2} \text{Mn}_5\text{N}_2(s) + \frac{5}{2} \text{H}_2\text{O}(v) \leftrightarrow \frac{5}{2} \text{MnO}(s) + \text{NH}_3(g) + \text{H}_2(g)
\]

\[\Delta H_{\text{Rxn}}^{500^\circ C} = -302.4 \text{ kJ mol}^{-1}\]

\[\Delta G_{\text{Rxn}}^{500^\circ C} = -230.5 \text{ kJ mol}^{-1}\]
Alkali-Metal ‘Promotor’ Improves NH$_3$ Yield

**Equation:**

\[
\text{Mn}_a\text{N}_b + \text{H}_2\text{O} \rightarrow \text{MnO} + \text{NH}_3
\]

**Graph:**

- **NH$_3$ Yield** [mol NH$_3$/mol N$_\text{Lat}$]
- **Time (min)**
- **Na Promotor:** 0.542
- **No Promotor:** 0.037
Expt. Method: Metal Oxide Reduction – Rxn #3

\[
\frac{5}{2} \text{MnO}_s + \frac{5}{2} \text{CH}_4(g) \leftrightarrow \frac{5}{2} \text{Mn}(s) + \frac{5}{2} \text{CO}(g) + 5\text{H}_2(g)
\]

\[\Delta H^{1150°C}_{\text{Rxn}} = 916 \text{ kJ mol}^{-1}\]

\[\Delta G^{1150°C}_{\text{Rxn}} = -57.1 \text{ kJ mol}^{-1}\]
Partial Conversion of MnO by Dilute CH$_4$ Achieved

- $X_{\text{MnO}} = 0.371 \pm 0.072$
- $Y_{\text{Mn6N2.58}} = 0.381 \pm 0.083$
- CO$_2$ NOT Detected!
- $H_2 / CO = 29.9 \pm 6.0$ mol H$_2$ mol$^{-1}$ CO

T = 1150°C
t = 30 min

Mn$_7$C$_3$ formation an issue

Possible Solutions:
- Co-Feed CO$_2$
- Co-Feed H$_2$
What if We Could Use Renewable H₂?

Nitridation

\[
\frac{5}{2} Mn(s) + \frac{1}{2} N_2(g) \rightleftharpoons \frac{1}{2} Mn_5N_2(s)
\]

All Pressures = 1 atm.

Reduction and NH₃ Synthesis

\[
\frac{5}{2} Mn(s) + 1NH_3(g) \rightleftharpoons \frac{3}{2} H_2(g) + \frac{1}{2} Mn_5N_2(s)
\]

Concentrated Solar Radiation
N₂- H₂ Cycling Expt. Method

• Nitridation:
  ▪ 700 °C
  ▪ 30 min
  ▪ N₂ Flowrate: 2.0 ± 0.1 L min⁻¹

• Reduction:
  ▪ 700 °C
  ▪ 60 min
  ▪ H₂ Flow: 1.8 ± 0.1 L min⁻¹
NH$_3$ Yield Limited When Using Mn Alone

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

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

NH$_3$ Yield
(mol NH$_3$ mol$^{-1}$ N$_{Nitride}$)
XRD Shows Stable Reactant

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

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

Mass Fraction

Nitridation (N₂) – Reduction (H₂) Cycling Stage
Mechanistic understanding of metal nitride reduction

\[ 2N_{\text{nitride}} + 3H_2(g) \rightarrow 2NH_3(g) \text{ at } 700^\circ C \text{ and } 1 \text{ atm} \]

- On Mn$_4$N, H$_2$ dissociative adsorption is endothermic.
- Reduction of lattice N (N$_{\text{lat}}$), 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.
Modifying the properties of Mn$_4$N by doping heteroatom (M)

To modify pure Mn$_4$N 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$_4$N.

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

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Questions?

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