Early Transition Metal Carbides and Nitrides for Ammonia Synthesis

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Thermochemical Process for Ammonia Synthesis

Major challenges [1]
- Inefficient

Opportunity
Alternative catalysts

Approach
Bifunctional catalyst [3]

N≡N 941 kJ/mol
H—H 432 kJ/mol
N—H 391 kJ/mol

Strongly bound

Weakly bound

Bifunctional catalyst

Applications in heterogeneous catalysis [1]:

- Hydrogenation
- Isomerization
- Hydrogenolysis
- Methanation

Material properties [1,2]:

- Similar to ceramics in terms of strength and hardness
- Similar to precious metals for electronic properties
- High surface area

Ternary Nitrides for Ammonia Synthesis

Volcano Plot of for Ammonia Synthesis

Model conditions:
400 °C, 50 bar, 3:1 balance of H₂:N₂

Co-Mo catalyst at optimum ammonia synthesis adsorption energy [1]

Ternary Mo₂N Comparison

Experimental conditions:
400 °C, 1 bar, 3:1 balance of H₂:N₂

Co₃Mo₃N catalyst resulted in highest ammonia production levels [2]

Carbides for Ammonia Synthesis

Comparing Mo$_2$C and Mo$_2$N

Gap in body of knowledge: ternary Mo$_2$C-based material for ammonia synthesis

Both phases of the Mo$_2$C resulted in higher production rates than the Mo$_2$N [1]

Hypothesis

Bifunctional catalyst with metal domains for N-N activation and support domains for nitrogen hydrogenation will be highly active for low-temperature ammonia synthesis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Kojima SA [1]</th>
<th>Thompson</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo₂C</td>
<td>32</td>
<td>91</td>
</tr>
<tr>
<td>Co₃Mo₃N</td>
<td>52</td>
<td>-</td>
</tr>
<tr>
<td>Co/Mo₂N</td>
<td>-</td>
<td>132</td>
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</table>

Different metals on the support would allow us to design the surface of the catalyst to optimize ammonia production

Experimental Methods

Synthesis and Metal Loading

- Ammonium paramolybdate (125 – 250 μm)
- Temperature programmed reaction
- 0.5 ML Metal deposition
- Passivate with 1% O₂/He flow, > 5 hours

Selected metals: Fe, Ru, Co

Characterization

- X-ray diffraction (XRD): crystal structure
- N₂ physisorption: BET surface area calculation

Performance

- Temperature programmed reaction: NH₃ production rate
- Reaction conditions: ramp from 40 – 800 °C under 25% N₂/H₂
- Mass spectrometer
Material Characterization

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m² g⁻¹)</th>
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<tr>
<td>Mo₂C</td>
<td>91</td>
</tr>
<tr>
<td>Fe/Mo₂C</td>
<td>65</td>
</tr>
<tr>
<td>Ru/Mo₂C</td>
<td>65</td>
</tr>
<tr>
<td>Co/Mo₂C</td>
<td>85</td>
</tr>
<tr>
<td>Mo₂N</td>
<td>159</td>
</tr>
<tr>
<td>Fe/Mo₂N</td>
<td>117</td>
</tr>
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<td>Ru/Mo₂N</td>
<td>126</td>
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- Nitrides tend to have higher surface area than carbides
- Depositing metal on the carbide and nitride retains the high surface area of the catalyst

Comparing Nitrides to Carbides

Conditions:

- Mass of catalyst: ~100 mg
- Benchmark pretreatment: 3 hours, H2, 400 °C
- Nitride pretreatment: 1 hour, 25% N2/H2, 600 °C
- Carbide pretreatment: 4 hours, 15% CH4/H2, 590 °C
- Flow rate of reactants: 60 ml/min
- Temperature Ramp: 40 - 800 °C, 1 atm

Baseline was ran with N2 and resulted in a flat line.
Comparing Nitrides to Carbides

Conditions:
- Mass of catalyst: ~100 mg
- Benchmark pretreatment: 3 hours, H₂, 400 °C
- Nitride pretreatment: 1 hour, 25% N₂/H₂, 600 °C
- Carbide pretreatment: 4 hours, 15% CH₄/H₂, 590 °C
- Flow rate of reactants: 60 mL/min
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Baseline was ran with N₂ and resulted in a flat line.

Mo₂N has an ammonia production site at 80 °C and higher production levels than the 5% Fe/Al₂O₃.

Four major sites for ammonia synthesis on bare Mo₂N.
Comparing Nitrides to Carbides

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Mo2N has an ammonia production site at 80 °C and higher production levels than the 5% Fe/Al2O3

Four major sites for ammonia synthesis on bare Mo2N

High levels of ammonia production for bare Mo2C at high temperatures
Catalyst Performance – M/Mo$_2$N

Fe/Mo$_2$N

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>NH$_3$ Concentration (a.u.)</th>
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<tr>
<td>80</td>
<td>0.05</td>
</tr>
<tr>
<td>230</td>
<td>0.15</td>
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<td>350</td>
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Comparison M/Mo$_2$N

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![Graph showing NH$_3$ Concentration vs Temperature for Ru/Mo$_2$N and Comparison M/Mo$_2$N](image)
**Catalyst Performance – M/Mo$_2$N**

**Conditions:**
- Mass of catalyst: ~100 mg
- Benchmark pretreatment: 3 hours, H$_2$, 400 °C
- Nitride pretreatment: 1 hour, 25% N$_2$/H$_2$, 600 °C
- Flow rate of reactants: 60 mL/min
- Temperature Ramp: 40 - 800 °C, 1 atm
Catalyst Performance – M/Mo₂C

Mo₂C

- Mo₂C does not display ammonia production at lower temperatures but it shows higher rates at typical reaction temperatures

Conditions:
- Mass of catalyst: ~100 mg
- Carbide pretreatment: 4 hours, 15% CH₄/H₂, 590 °C
- Flow rate of reactants: 60 mL/min
- Temperature Ramp: 40 - 800 °C, 1 atm
Catalyst Performance – M/Mo$_2$C

**CondiIons:**
- Mass of catalyst: ~100 mg
- Carbide pretreatment: 4 hours, 15% CH$_4$/H$_2$, 590 °C
- Flow rate of reactants: 60 mL/min
- Temperature Ramp: 40 - 800 °C, 1 atm

**Comparison M/Mo$_2$C**

**NH$_3$ Concentration (a.u.)**

- Fe/Mo$_2$C
  - 300 °C
  - 510 °C
  - 730 °C

- Mo$_2$C

**Temperature (°C)**

- 0 200 400 600 800
Catalyst Performance – M/Mo₂C

Conditions:
- Mass of catalyst: ~100 mg
- Carbide pretreatment: 4 hours, 15% CH₄/H₂, 590 °C
- Flow rate of reactants: 60 mL/min
- Temperature Ramp: 40 - 800 °C, 1 atm
Catalyst Results – M/Mo$_2$C

**Conditions:**
- Mass of catalyst: ~100 mg
- Carbide pretreatment: 4 hours, 15% CH$_4$/H$_2$, 590 °C
- Flow rate of reactants: 60 mL/min
- Temperature Ramp: 40 - 800 °C, 1 atm

Co/Mo$_2$C

<table>
<thead>
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<tr>
<td>80</td>
<td>0.7</td>
</tr>
<tr>
<td>110</td>
<td>0.6</td>
</tr>
<tr>
<td>490</td>
<td>0.5</td>
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Comparison M/Mo$_2$C

**Graph:**
- Mo$_2$C
- Fe/Mo$_2$C
- Ru/Mo$_2$C
- Co/Mo$_2$C

**Temperature (°C):**
- 0 - 800

**NH$_3$ Concentration (a.u.):**
- 0 - 0.7
Conclusion

Confirm hypothesis:
• Bare Mo$_2$N are better than bare Mo$_2$C at temperatures as low as 80 °C
• Metals deposited on Mo$_2$N affected different types of sites
• Deposition of the metal on Mo$_2$C produced two new active sites for ammonia synthesis
• Co/Mo$_2$C is the most promising catalyst for low temperature ammonia production

Future works:
• Kinetic studies of promising catalysts in flow reactor
Acknowledgements

Wei-Chung Wen
Sarah Paleg
Thompson Group
Questions?
Ammonia Synthesis

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

- **85% Fertilizer**
- **Others**
  - **Nitric Acid**
  - **Polyamides**

- Temperature: 400 – 500 °C
- Pressure: 150 – 300 bars
- Catalyst: Fe-based \( \text{Al}_2\text{O}_3 \)

- In spite of developing insight in the field, industrial standards are still the same as those discovered at the beginning of the 20th century \[1\]

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\[2\] Uses for Ammonia, CIEC Promoting Science at the University of York, York, UK \textbf{2014}.
\[3\] Pattabathula, V., Richardson, J. \textit{CEP} \textbf{2016}.
Catalyst Designs

Ternary Nitride Synthesis [1]

- Molybdenum Precursor
- Metal Impregnation
- Nitridization

Metal-Loading Synthesis [2]

- Molybdenum Precursor
- Nitridization
- Metal Impregnation
- Bifunctional active sites on the surface

Catalyst Performance – M/Mo$_2$N

Mo$_2$N displays ammonia production at temperatures as low as 80 °C

Optimal production levels between 200 – 400 °C ➔ many of the experimental conditions might not be appropriate for this material

Conditions:
- Mass of catalyst: ~100 mg
- Benchmark pretreatment: 3 hours, H2, 400 °C
- Nitride pretreatment: 1 hour, 25% N$_2$/H$_2$, 600 °C
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