Yittria-stabilized Zirconia (YSZ) Supports for Low Temperature Ammonia Synthesis

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Overview

Goal: Distributed green ammonia production
- Approach: Catalytic membrane reactors
- Focus on YSZ motivated by success for ammonia decomposition
- YSZ never investigated
- ZrO$_2$, rare earth oxides have been effective supports

YSZ supported Ru catalyst
- Catalyst preparation and characterization
- Baseline YSZ support vs. Al$_2$O$_3$
- Understand effect of promoters (Cs / Ba / K)
- Characterize performance as a f(T, P, H$_2$/N$_2$)
- Develop and validate microkinetic model for design/scale up
The Green Revolution (1960 –) powered by “brown” ammonia
Well-correlated to anthropogenic climate change
Goal: Scalable production of “green” ammonia

Fallacy: Haber-Bosch is inefficient

State-of-the-Art: ~28 GJ/ton NH₃

- Losses / costs / CO₂ primarily associated with hydrogen production
- Haber-Bosch CapEx intensive, does not scale down
- Renewable H₂ highly distributed

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State-of-the-Art: ~28 GJ/ton NH₃

Opportunity for Scalable Production
- Produced @ $150/ton
- Costs: ~$450/ton
- Difference shipping

- Losses / costs / CO₂ primarily associated with hydrogen production
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- Renewable H₂ highly distributed

ARPA-E Concept

Vision: Develop catalytic membrane reactor (CMR) technology for both efficient hydrogen delivery and distributed production of ammonia.
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Advanced Catalysts + Highly Permeable Membranes + Innovative Reactor Design
Efficient H₂ Generation from NH₃

- T < 450 °C
- >99% conversion
- Exceeds equilibrium
- High purity H₂: >99.5%
- Productivity >0.1 g/h/cm³
- Reduced catalyst loading 10X
- Developed/validated 2D Model

\[
r = \frac{k_f \left( \frac{P_{NH_3}^2}{P_{H_2}^3} \right)^\beta - \frac{P_{N_2}}{K_{eq} \left( \frac{P_{H_2}^3}{P_{NH_3}^2} \right)^{1-\beta}}}{P_{NH_3}}
\]

\[
\frac{\partial (\rho_i u)}{\partial z} = F_c \nu_i r - F_m W_i J_i
\]

\[
\nabla (D_i \nabla C_i) = \nu_i k C_{NH_3}
\]

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Catalyst Preparation & Characterization

- YSZ (Praxair) support: low specific surface area 2.24 m$^2$/g
- Ru loading: 0.4 – 1.0 wt%
- Good dispersion (3-10 nm)
- Promoters (Cs, K, Ba)
Impact of Support & Promoters

- YSZ ~4X > Al₂O₃
- Promoters increase rate ~5 - 10X
- Cs > Ba ~ K
- Insensitive to promoter/Ru Ratio

![Graph showing the relationship between temperature and ammonia rate for different promoters](image)

- **NH₃ rate (mmol g₉Ru h⁻¹)**
  - Ru/YSZ
  - Ru/α-Al₂O₃

- **NH₃ rate (mmol g₉Ru h⁻¹)**
  - Cs/Ru = 0.3
  - K/Ru = 3.4
  - K/Ru = 0.4
  - K/Ru = 0.1
  - Ba/Ru = 1.0
  - K/Ru = 0.9
  - K/Ru = 0.5
  - K/Ru = 2.0
  - Ba/Ru = 0.5

- **Temperature (°C)**: 340, 360, 380, 400, 420, 440, 460
- **Pressure (bar)**: 0, 2, 4, 6, 8, 10
- **T = 450 °C**
- **H₂/N₂ = 3**
- **GHSV = 13,000 h⁻¹**
Transport & Equilibrium Limitations

Catalyst studies typically done at GHSV ~ 10,000 h\(^{-1}\)
SV > 72,000 mL g cat h\(^{-1}\) or GHSV > 200,000 h\(^{-1}\)
Stability

- Cs instantly activated but unstable
- Deactivation thermally activated: Attributed to low melting Cs oxide
- Ba slowly activated but highly stable
- Focus on Ru/Ba/YSZ
Microkinetic Model

Primary steps in catalytic synthesis of ammonia

G. Ertl


\[
\begin{align*}
\text{H}_2 & \leftrightarrow 2\text{H}_\text{ad}, \\
\text{N}_2 & \leftrightarrow 2\text{N}_\text{ad}, \\
\text{N}_\text{ad} + \text{H}_\text{ad} & \leftrightarrow \text{NH}_\text{ad}, \\
\text{NH}_\text{ad} + \text{H}_\text{ad} & \leftrightarrow \text{NH}_2\text{ad}, \\
\text{NH}_2\text{ad} + \text{H}_\text{ad} & \leftrightarrow \text{NH}_3\text{ad}, \\
\text{NH}_3\text{ad} & \leftrightarrow \text{NH}_3.
\end{align*}
\]

\[E^* \approx 60\]
\[\Delta H = 11\]

Fig. 8. Potential energy diagram illustrating the progress of the overall reaction. The activation energy $E^*$ depends on surface structure and coverage. Energies in kcal/mol.

- Based on Ertl mechanism
- Innovation: Coverage-dependent activation energies
- Framework generally applicable
Microkinetic Model

Primary steps in catalytic synthesis of ammonia

G. Ertl


\[ H_2 \rightarrow 2H_{ad}, \]
\[ N_2 \rightarrow N_{2, ad} \rightarrow 2N_{s}, \]
\[ N_{s} + H_{ad} \rightarrow NH_{ad}, \]
\[ NH_{ad} + H_{ad} \rightarrow NH_{2, ad}, \]
\[ NH_{2, ad} + H_{ad} \rightarrow NH_{3, ad}, \]
\[ NH_{3, ad} \rightarrow NH_{3}. \]

Fig. 8. Potential energy diagram illustrating the progress of the overall reaction. The activation energy \( E^* \) depends on surface structure and coverage. Energies in kcal/mol.

- Based on Ertl mechanism
- Innovation: Coverage-dependent activation energies
- Framework generally applicable

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<tr>
<th>Reaction</th>
<th>( A ) (cm ( \cdot ) s)</th>
<th>( \beta )</th>
<th>( E ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ( \text{N}_2 + 2(\text{Ru}) \rightarrow \text{N}(\text{Ru}) + \text{N}(\text{Ru}) )</td>
<td>( 2.892 \times 10^{-06} )</td>
<td>0.000</td>
<td>38.949</td>
</tr>
<tr>
<td>2 ( \text{N}(\text{Ru}) + \text{N}(\text{Ru}) \rightarrow \text{N}_2 + 2(\text{Ru}) )</td>
<td>( 2.015 \times 10^{+17} )</td>
<td>-0.279</td>
<td>148.027 - 14 ( \theta_{\text{N}(\text{Ru})} )</td>
</tr>
<tr>
<td>3 ( \text{H}_2 + 2(\text{Ru}) \rightarrow \text{H}(\text{Ru}) + \text{H}(\text{Ru}) )</td>
<td>( 4.007 \times 10^{-03} )</td>
<td>0.000</td>
<td>0.0</td>
</tr>
<tr>
<td>4 ( \text{H}(\text{Ru}) + \text{H}(\text{Ru}) \rightarrow \text{H}_2 + 2(\text{Ru}) )</td>
<td>( 3.600 \times 10^{+20} )</td>
<td>0.658</td>
<td>91.948 - 2 ( \theta_{\text{H}(\text{Ru})} )</td>
</tr>
<tr>
<td>5 ( \text{NH}_3 + (\text{Ru}) \rightarrow \text{NH}_3(\text{Ru}) )</td>
<td>( 1.247 \times 10^{-05} )</td>
<td>0.000</td>
<td>0.0</td>
</tr>
<tr>
<td>6 ( \text{NH}_3(\text{Ru}) \rightarrow \text{NH}_3 + (\text{Ru}) )</td>
<td>( 2.235 \times 10^{+11} )</td>
<td>0.083</td>
<td>83.536</td>
</tr>
<tr>
<td>7 ( \text{N}(\text{Ru}) + \text{H}(\text{Ru}) \rightarrow \text{NH}(\text{Ru}) + (\text{Ru}) )</td>
<td>( 8.424 \times 10^{+20} )</td>
<td>0.000</td>
<td>83.620 - 7 ( \theta_{\text{N}(\text{Ru})} )</td>
</tr>
<tr>
<td>8 ( \text{NH}(\text{Ru}) + (\text{Ru}) \rightarrow \text{N}(\text{Ru}) + \text{H}(\text{Ru}) )</td>
<td>( 6.813 \times 10^{+19} )</td>
<td>0.207</td>
<td>30.972 - 1 ( \theta_{\text{H}(\text{Ru})} )</td>
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<tr>
<td>9 ( \text{NH}(\text{Ru}) + \text{H}(\text{Ru}) \rightarrow \text{NH}_2(\text{Ru}) + (\text{Ru}) )</td>
<td>( 4.949 \times 10^{+19} )</td>
<td>0.083</td>
<td>75.236</td>
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<tr>
<td>10 ( \text{NH}_2(\text{Ru}) + (\text{Ru}) \rightarrow \text{NH}(\text{Ru}) + \text{H}(\text{Ru}) )</td>
<td>( 8.321 \times 10^{+19} )</td>
<td>-0.083</td>
<td>15.767 - 1 ( \theta_{\text{H}(\text{Ru})} )</td>
</tr>
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<td>11 ( \text{NH}_2(\text{Ru}) + \text{H}(\text{Ru}) \rightarrow \text{NH}_3(\text{Ru}) + (\text{Ru}) )</td>
<td>( 3.886 \times 10^{+19} )</td>
<td>0.083</td>
<td>17.036</td>
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<td>12 ( \text{NH}_3(\text{Ru}) + (\text{Ru}) \rightarrow \text{NH}_2(\text{Ru}) + \text{H}(\text{Ru}) )</td>
<td>( 1.478 \times 10^{+20} )</td>
<td>0.000</td>
<td>64.980 - 1 ( \theta_{\text{H}(\text{Ru})} )</td>
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Effect of Pressure, Temperature, and $\text{H}_2/\text{N}_2$ Ratio

**Optimal $\text{H}_2/\text{N}_2$ ratio**
- less than stoichiometric
- Balance between $\text{N}_2/\text{H}_2$ adsorption
- Shift to stoichiometric at high T

**Pressure dependence**
- ~linear at optimal ratio
- Significant rates as low as $T = 300^\circ\text{C}$

**Membrane Synthesis**
- Low T operation
- Low $\text{H}_2/\text{N}_2$ ratios beneficial for separation

*Models provide accurate predictions over wide operating conditions*
Competition between $\text{H}_2/\text{N}_2$ Adsorption

$T = 300^\circ \text{C}$

$T = 450^\circ \text{C}$
Role of YSZ, Ba: XPS

Ru 3d position
- Metal: 280.2
- YSZ: 280.1
- YSZ/Ba: 279.8

Peak @ 275.8 eV
- Ru-Ba Complex?
- Role?
Comparison with Literature

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Specific rates highest reported to date for Ru-based catalyst
Activation energy (46 kJ/mol) among lowest reported to date
Validated coverage-dependent microkinetic model

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Acknowledgements

Colleagues

• Drs. Thomas F. Fuerst (INL), Simona Ligouri (WPI)
• Lucy Fitzgerald (UCD), Sarah Livingston (CSM)
• Ryan Gasvoda (CSM)

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• ARPA-E DE-AR0000808
• ARPA-E DE-AR0001004
• NSF CBET-1512172
Catalytic Membrane Reactor (CMR)

Challenges with conventional PBMR
- Benefits rather limited
- Limited by poor transport

CMR: Catalyst impregnated in support
- Mitigate internal transport limitations
- Mitigate radial transport limitations
- Eliminate pressure drop, channeling
CMR: Ammonia Synthesis

CMR vs Haber Bosch
- CapEx effective: less use of heat exchanger
- Less compressor: Low H₂/N₂ ratio enables less recycle stream

Ammonia separation along reaction enables:
- Increased synthesis rate: kinetics limited by ammonia adsorption
- Overcome thermodynamic limitations
Reforming step dominates H₂ production cost

Reforming step (800-900°C, ~30 bar), >67% energy loss in NH₃ production

Role of YSZ, Ba: XPS

Comparison with Ba-Ru/YSZ

- Ba-Ru/YSZ 2X > Cs-Fe/γ-Alumina

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<td>47.5</td>
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<tr>
<td>Fe-YSZ</td>
<td>68.5</td>
</tr>
<tr>
<td>Fe/α-alumina</td>
<td>70.7</td>
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<tr>
<td>Fe/γ-alumina</td>
<td>73.1</td>
</tr>
<tr>
<td>Cs0.1-Fe/γ-alumina</td>
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<tr>
<td>Ba0.1-Fe/γ-alumina</td>
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Reaction conditions: 350 - 450°C, H₂/N₂ = 3, P = 10 barg

Reaction conditions: 450°C, H₂/N₂ = 3
Cs-Fe/γ-Alumina: Effect of H$_2$/N$_2$

- Optimal H$_2$/N$_2$ doesn’t shift with T

![Graph showing the effect of H$_2$/N$_2$ ratio on NH$_3$ rate for different temperatures.](image)