Efficient Ammonia Decomposition in a Catalytic Membrane Reactor to Enable Hydrogen Storage and Utilization

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Annual Meeting, Pittsburgh, PA

NH3 FUEL ASSOCIATION
THE KEY TO ENERGY INDEPENDENCE

Motivation and Goals

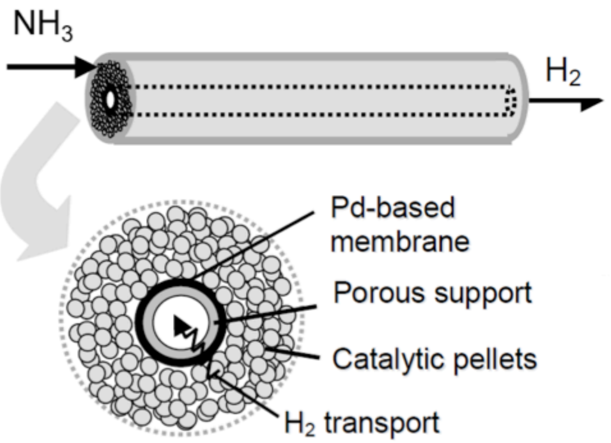
Ammonia potential carrier for H_2 fueling station

- Compressed / liquid H_2: Expensive
- High H_2 density (17.7 wt. %), existing infrastructure
- High throughput & compact system
- Minimize thermal budget
- Very high H_2 purity

Our approach: Catalytic membrane reactors

- Process Intensification: Combined reaction & separation
- Overcomes limits of conventional packed bed configuration
- Development of reactor model for analysis, scale-up

Packed Bed Membrane Reactors (PBMR)



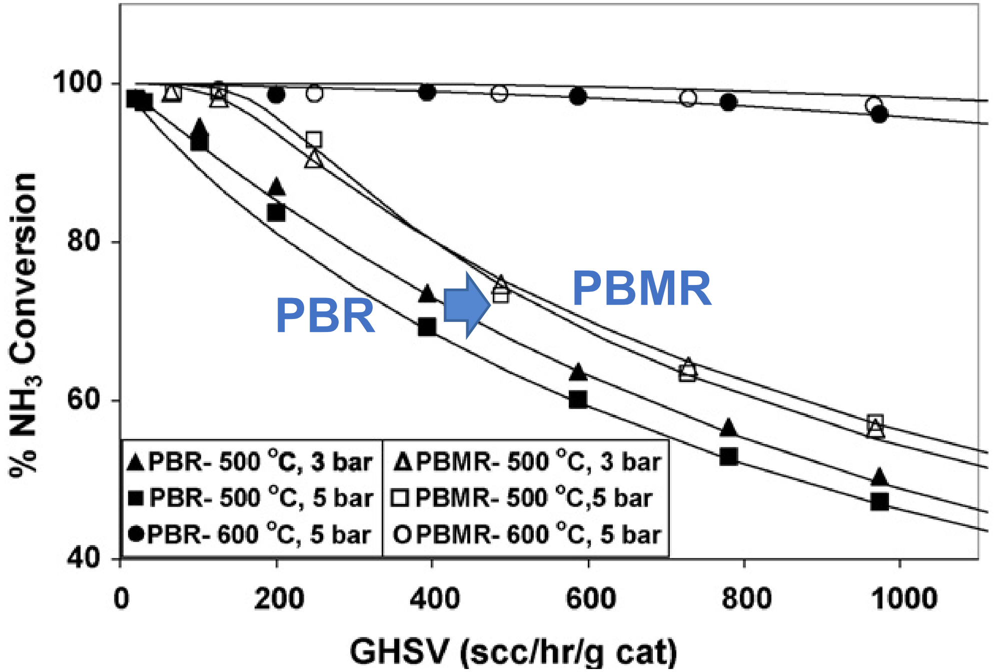
Single Tube Schematic

Conventional geometry

- Catalyst particles packed around tubular membrane
- Pd based membrane
- High permeance, high selectivity (> 99%)

Challenges

- Benefits limited
- Low flowrates, sweep gas to get complete NH_3 conversion
- Reactor model analysis: Poor radial dispersion limits permeate H_2 flux



Zhang et al. *Journal of Membrane Science* 277.1-2 (2006): 85-93.
Israni et al. *Catalysis Today* 139.4 (2009): 299-311.
Jo, Young Suk, et al. Journal of Power Sources 400 (2018): 518-526.

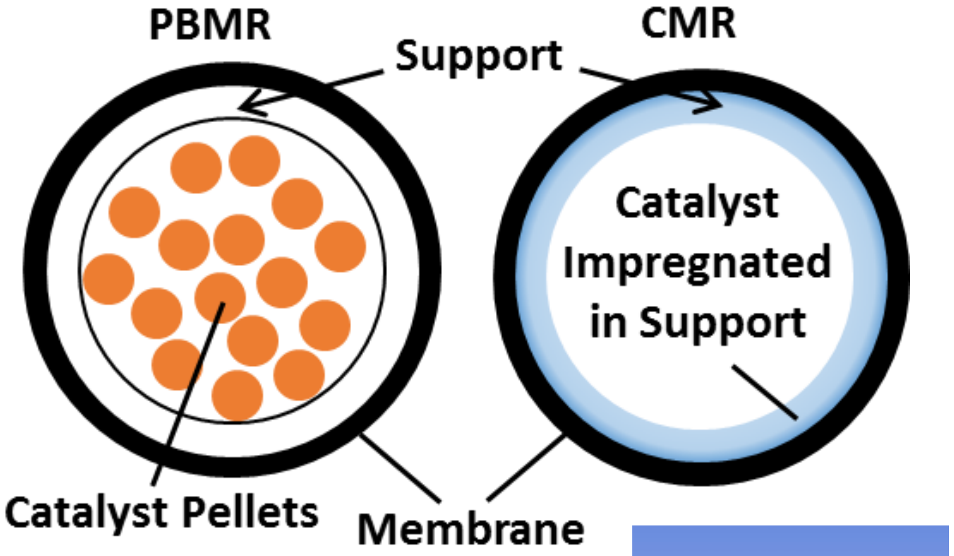
Catalytic Membrane Reactor (CMR)

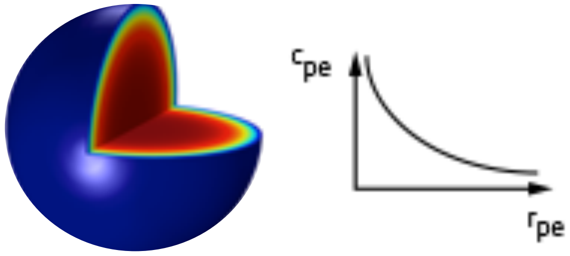
CMR: Catalyst impregnated in support

- Mitigate internal transport limitations
- Mitigate radial transport limitations
- Eliminate pressure drop, channeling

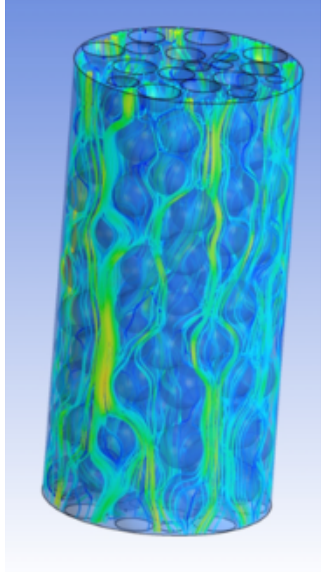
Goals: Better transport enables

- Reduced temperature operation
- Reduced catalyst loading
- Enhanced H_2 recovery





Diffusion Limitations



Channeling

CMR Preparation

Yttria-stabilized zirconia (YSZ) supports

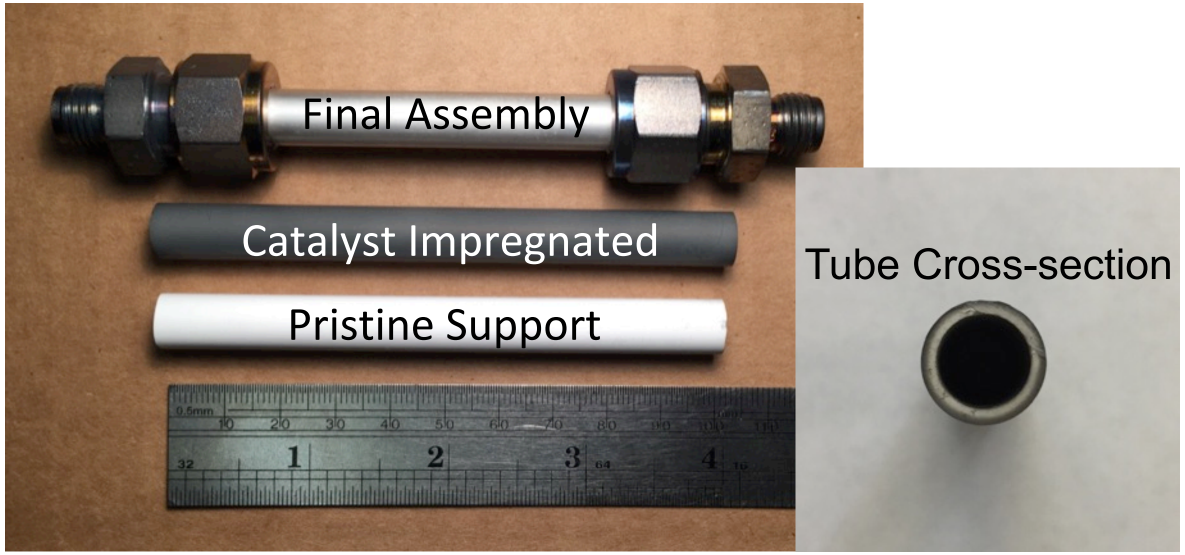
- Asymmetric structure
- Bulk: Macroporous (several microns)
- Exterior: Mesoporous (~100 nm)

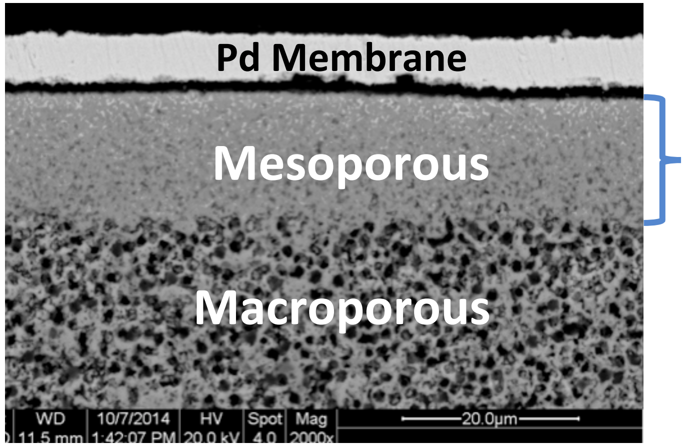
Ru catalysts loading by wet impregnation

- Applied to exterior
- 3.8 ± 2.1 nm, dispersion ~34%
- Cs promoter by impregnation

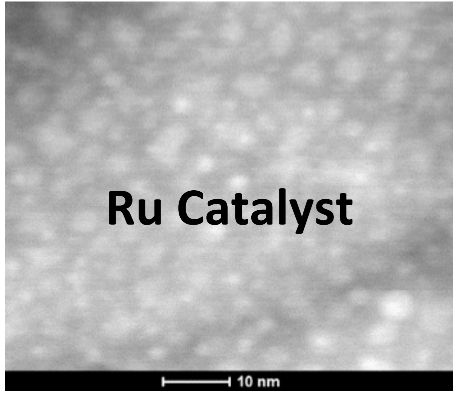
Pd Membrane

- Electroless plating, thickness ~ 6 µm
- Length = 9.3 cm, reactor Volume = 7 cm^3





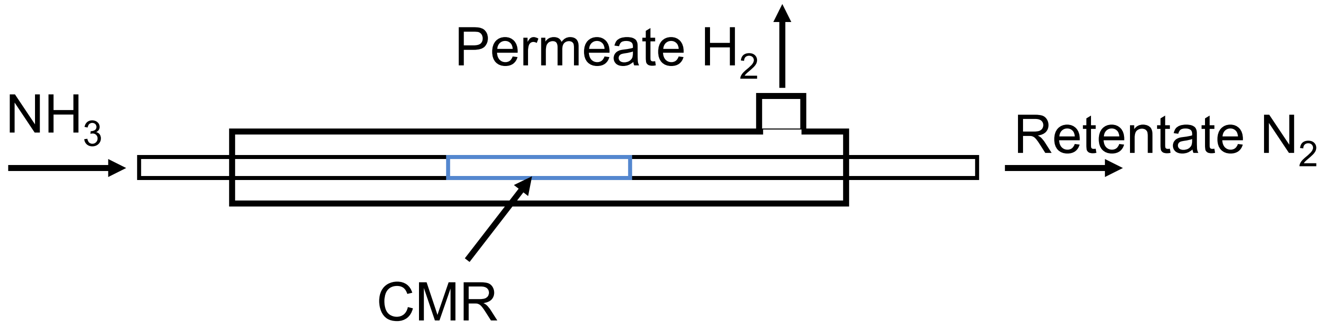
FIB - TEM



Experimental Apparatus

CMR Operation

- Compare Ru and Cs/Ru
- Vary T (350 - 450ºC),
- P (1 - 5 bar)
- NH_3 flowrate (20 – 700 sccm)



Performance Metrics

- NH_3 conversion (χ_{NH_3})
- H_2 recovery (R_{H_2})
- H_2 volumetric productivity (Π_{H_2})
- H_2 purity (MS/NDIR)

$$\chi_{NH_3} = \frac{F_{NH_3,\text{in}} - F_{NH_3,\text{out}}}{F_{NH_3,\text{in}}}$$

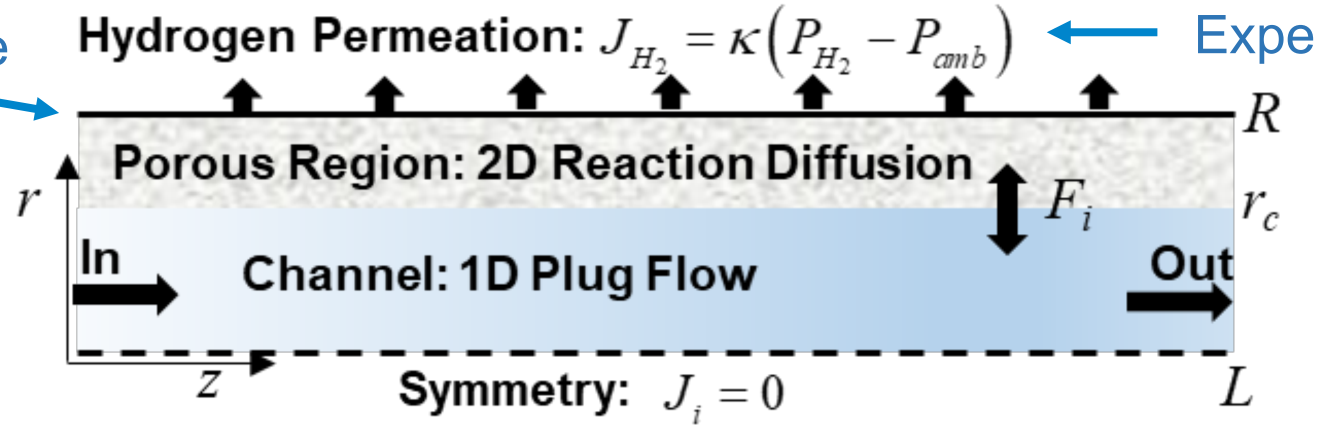
$$R_{H_2} = \frac{F_{H_2,\text{perm}}}{1.5 \times F_{NH_3,\text{in}} \times \chi_{NH_3}}$$

$$\Pi_{H_2} = \frac{F_{H_2}^{\text{perm}}}{V_r}$$

CMR Model

Pd Membrane

Experimental Permeability



Channel/lumen assumptions

- Sufficient time for radial mixing
- Axial diffusion << advection

Governing equation

*∂(ρ↓i u)/∂z =**F↓c** v↓i r− **F↓m** W↓i J↓i*

Reaction

H_2 Permeation

Porous region assumptions

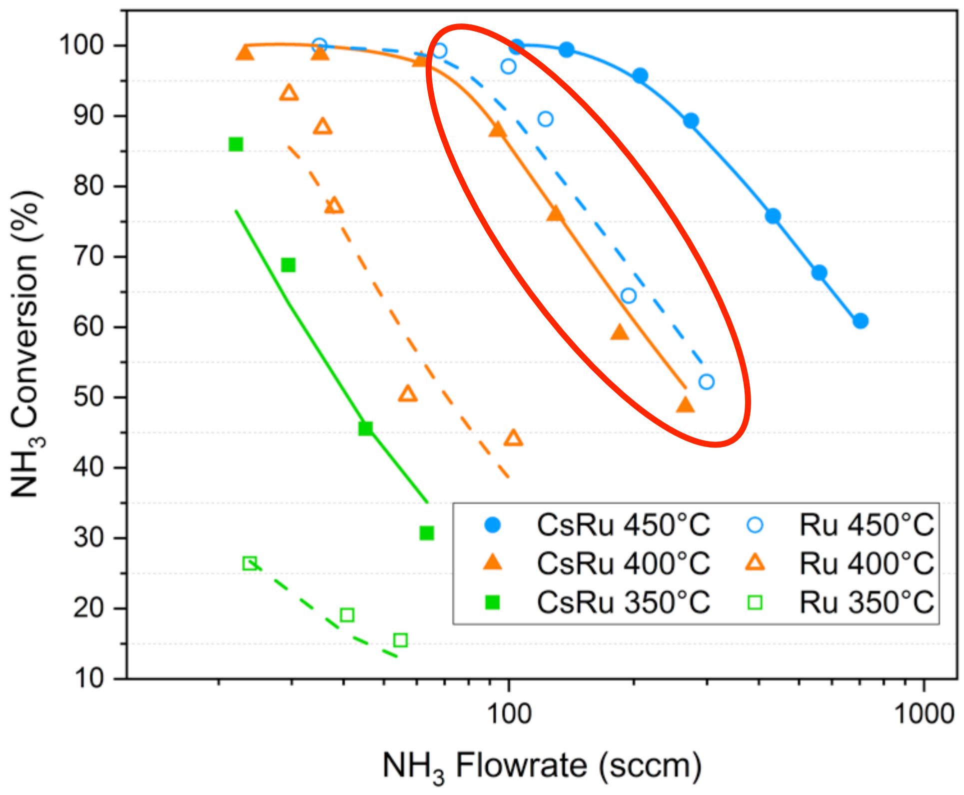
- Pressure driven flow negligible
- Bulk diffusivity, Kn < 1

Governing equation

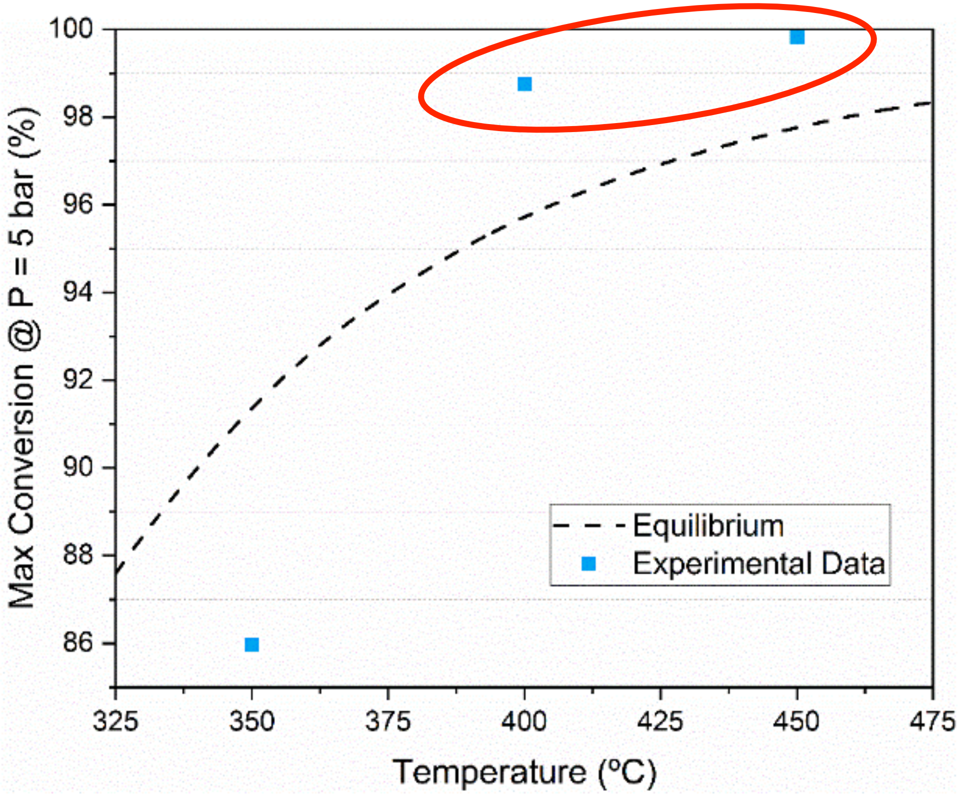
∇(D↓i ∇C↓i)= v↓i r

Impact of Cs Promoter

- Full conversion as low as T = 400ºC, exceeds equilibrium
- Cs enhances kinetics by ~50ºC
- Similar activation energy: $E_A = 160 \pm 20$ kJ/mol
- Suggests increase in active sites

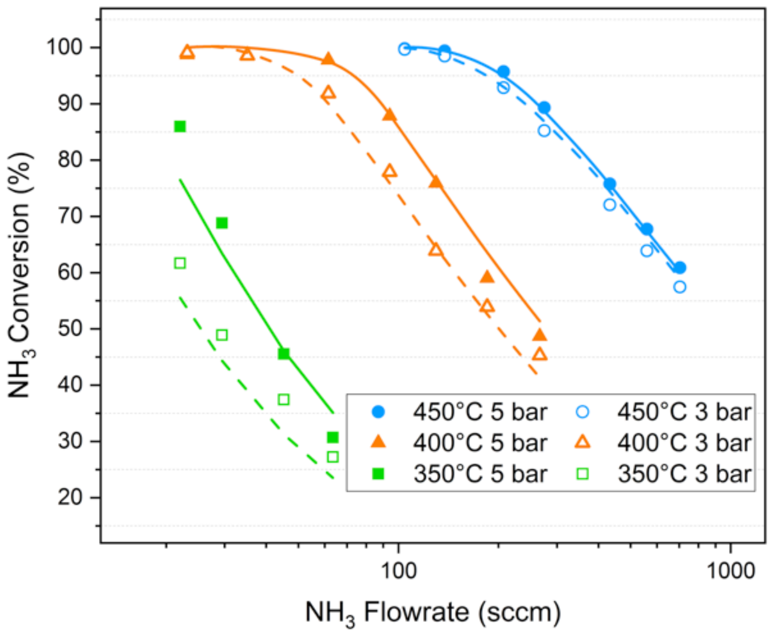


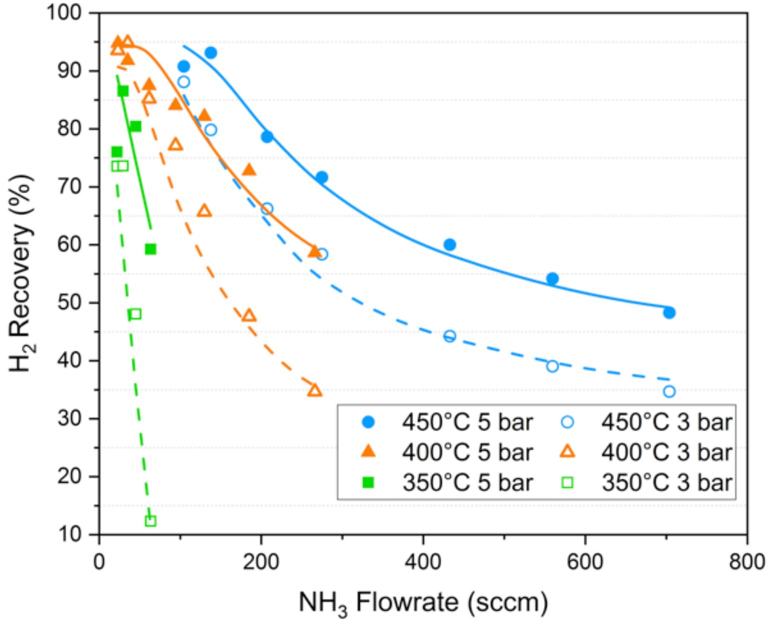
Lines from Model Prediction; Points from Experiments

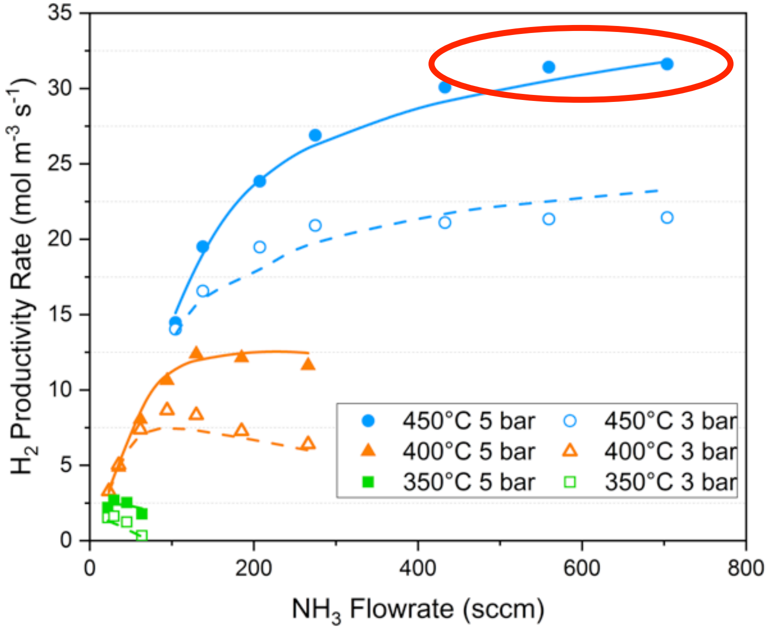


Impact of Pressure on CsRu CMR Performance

- Enhances conversion, particularly at low temperature
- Drives H_2 recovery
- Enhances H_2 volumetric productivity, > 3X higher than previous reports
- Model does an excellent job at all conditions

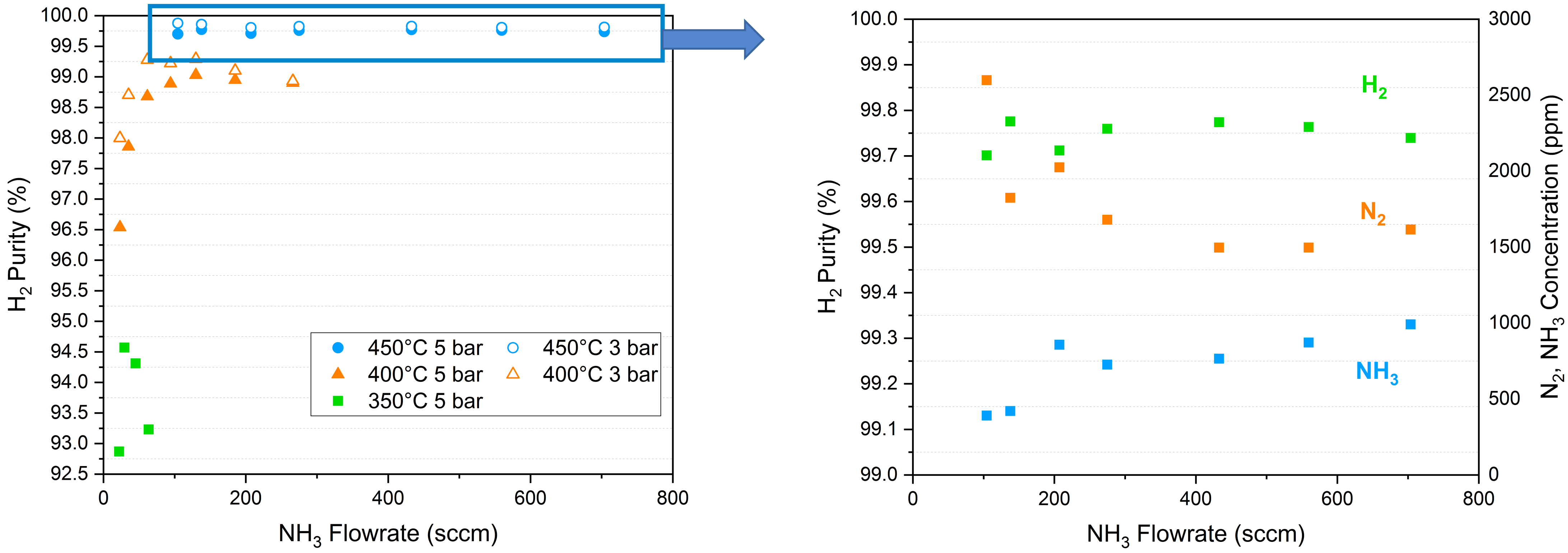






Permeate Purity

- > 99.7% at optimal conditions at low temperature
- Ammonia impurity < 1000 ppm, easily removed by absorbent
- High quality Pd membrane
- Membrane performance nominally unchanged after 680 hrs of operation



CMR vs. PBMR

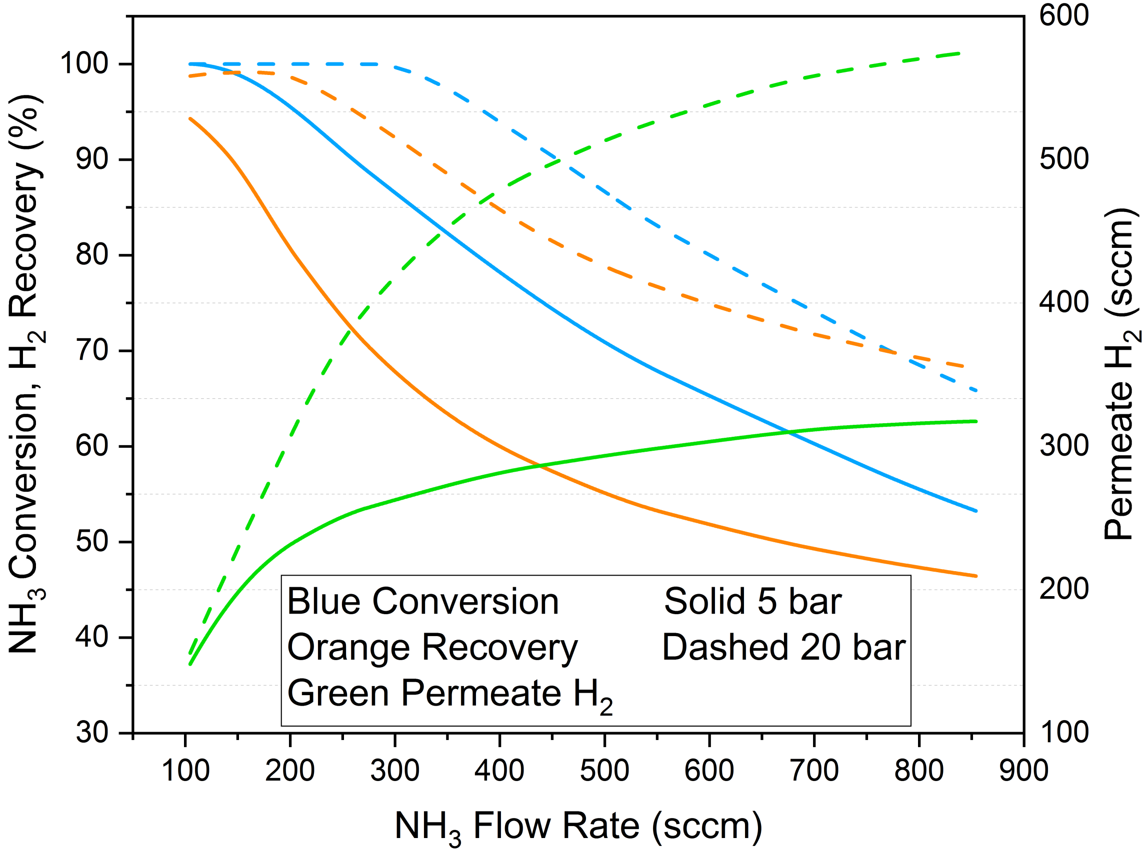
- Membranes nominally identical
- Catalyst loading reduced by 10X
- Temperature reduced > 100ºC for similar conversion
- Significant improvements in recovery, productivity

Specifications	This work		Lundin et al.
mg Ru/cm^2	1.4		11.7
Temperature (°C)	400	450	520
Pressure (bar)	5	5	3
NH_3 Flowrates (sccm)	61.3	207.3	150
NH_3 Conversion (%)	98	96	98
H_2 Purity (%)	98.7	99.7	99.2
H_2 Recovery (%)	87.5	78.6	66
H_2 Productivity (mol m^{-3} s^{-1})	8.1	23.9	3.6

Lundin et al. *Separation and Purification Technology* 172 (2017): 68-75.

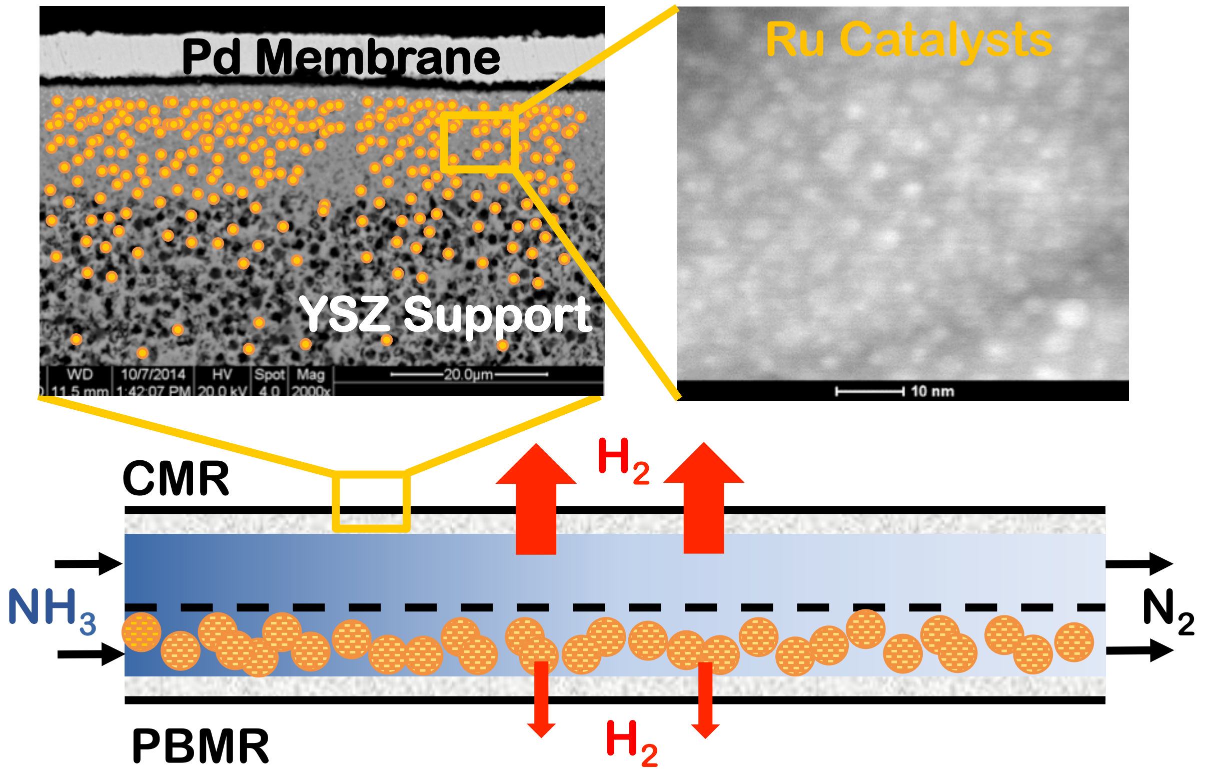
Model Optimization: Increase Pressure

- Increases NH_3 conversion by ~24% at same NH_3 flow rate
- Increases H_2 recovery by 47%
- Almost doubles highest H_2 productivity rate



Conclusions

- New configuration for CMR: Ru impregnated into H_2 permeable membrane support
- Better transport enables:
  - Reduced operating T (> 120°C)
  - Reduced catalyst loading (> 10X)
  - Enhanced H_2 productivity (> 3X)
  - Exceed equilibrium w/o sweep gas
- Developed reactor model
  - Excellent agreement w/ experiment
  - Valuable tool for scale up



Acknowledgement

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- Dr. David Diercks

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arpa·e

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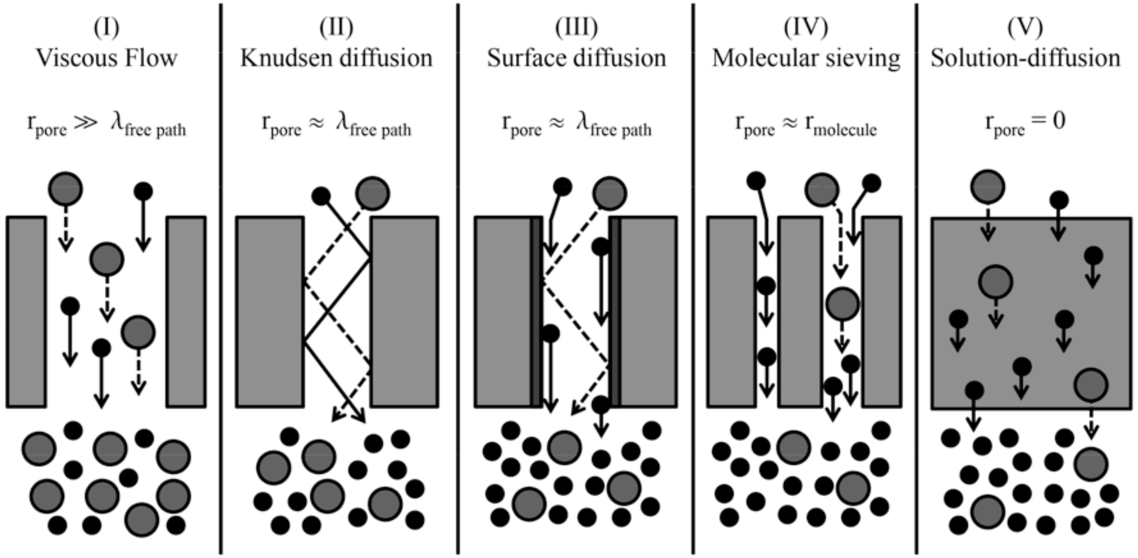
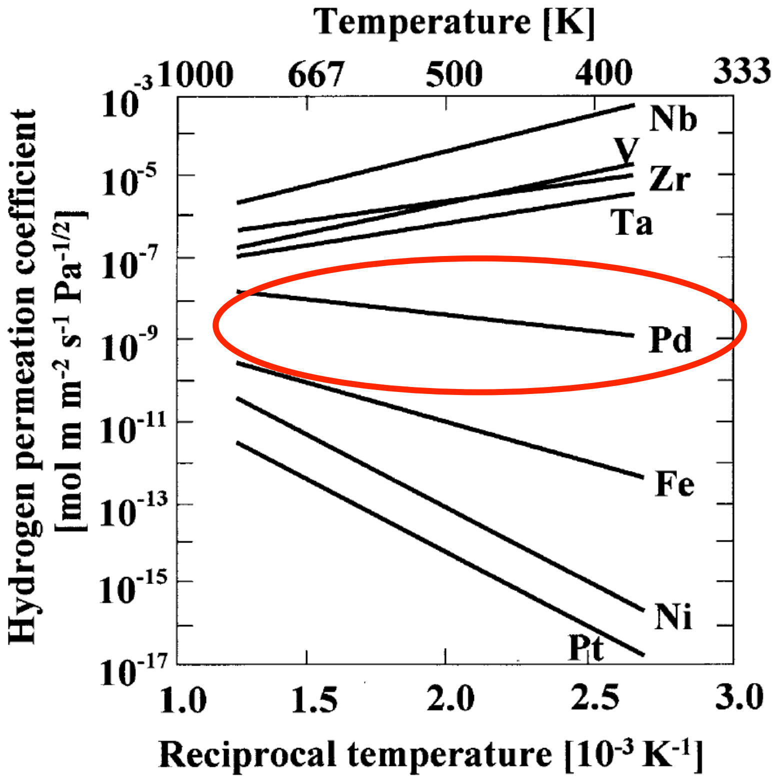
Mechanisms of gas transport





Permeability $\pi_H = S \times D$

Flux $$J = \frac{\pi_H}{L}\left(P^n_{H2,F} - P^n_{H2,P}\right)$$

1) Diffusion-limited (Sievert's Law)

n ~ 0.5

2) Adsorption/Desorption limited

n ~ 1

Pd Membrane

Pd Electroless Plating

$$2Pd(NH_3)_4^{++} + N_2H_4 + 4OH^- \rightarrow 2Pd^0 + 8NH_3 + N_2 + 4H_2O$$

Au Displacement Plating

$$3Pd^0 + 2Au^{3+} \rightarrow 3Pd^{2+} + 2Au^0$$

680 hours stable Performance

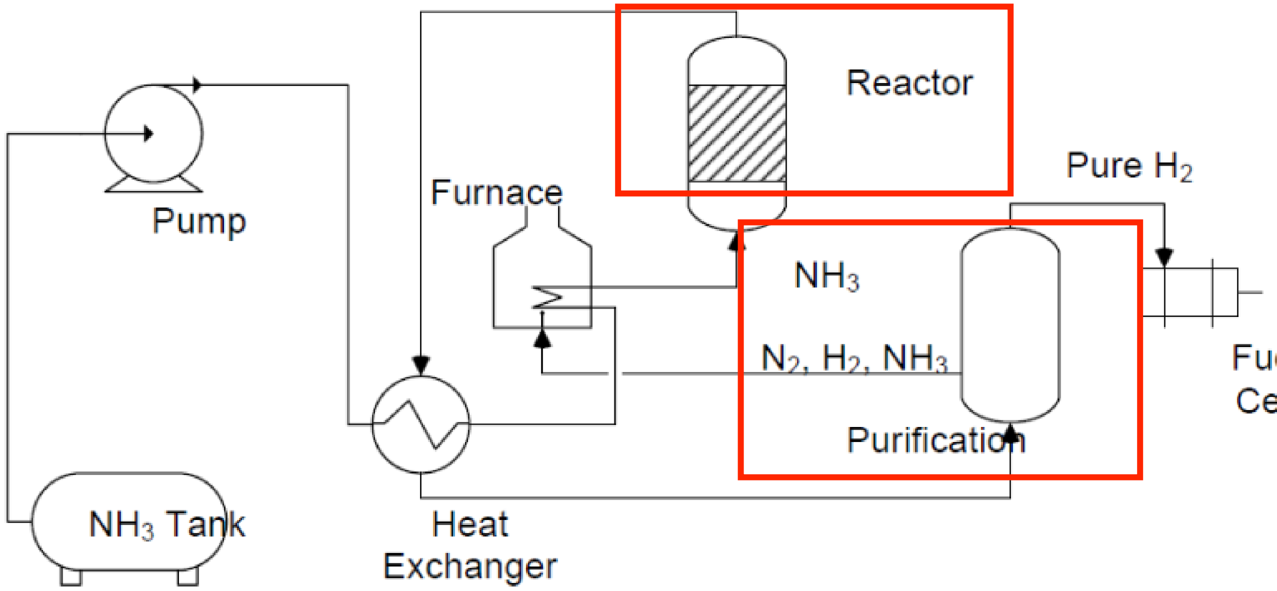
Permeance	350°C	400°C	450°C
Before ammonia decomposition test			
H_2 (mol cm^{-2} s^{-1} Pa^{-1})	4.19×10^{-11}	5.52×10^{-11}	6.46×10^{-11}
N_2 (mol cm^{-2} s^{-1} Pa^{-1})	Not measurable at 5 bar		
After ammonia decomposition test			
H_2 (mol cm^{-2} s^{-1} Pa^{-1})	6.64×10^{-11}	8.25×10^{-11}	9.91×10^{-11}
N_2 (mol cm^{-2} s^{-1} Pa^{-1})	4.42×10^{-14}	N/A	N/A

Challenges facing Ammonia Utilization

- NH_3 decomposition endothermic

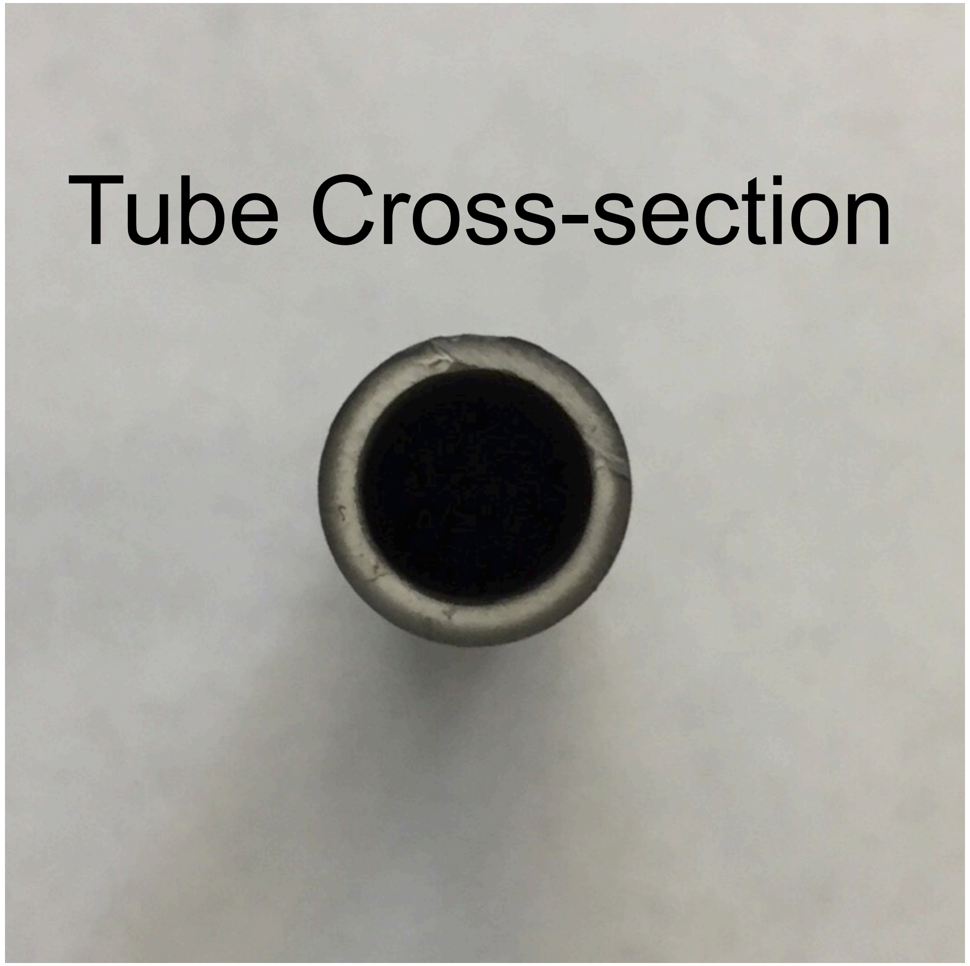
$$2NH_3 \leftrightarrow N_2 + 3H_2 \qquad \Delta H^o = 46.2\ \text{kJ/mol}\ NH_3$$

- High purity required ($NH_3 < 0.1$ ppm)
- Requires multi unit operations & high temperature

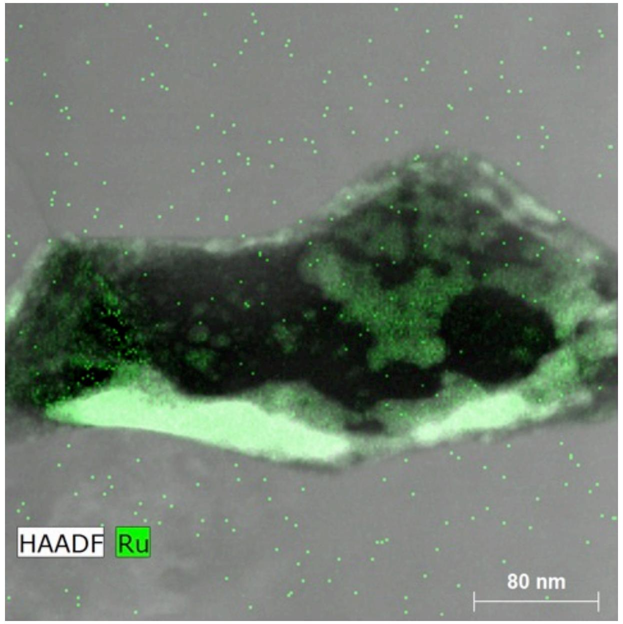


Flow chart source: DOE

Tube Cross-section



Ru Particle Characterization



Focused ion beam (FIB) Milling

- 10×10 μm cross-section of the Ru impregnated mesoporous region

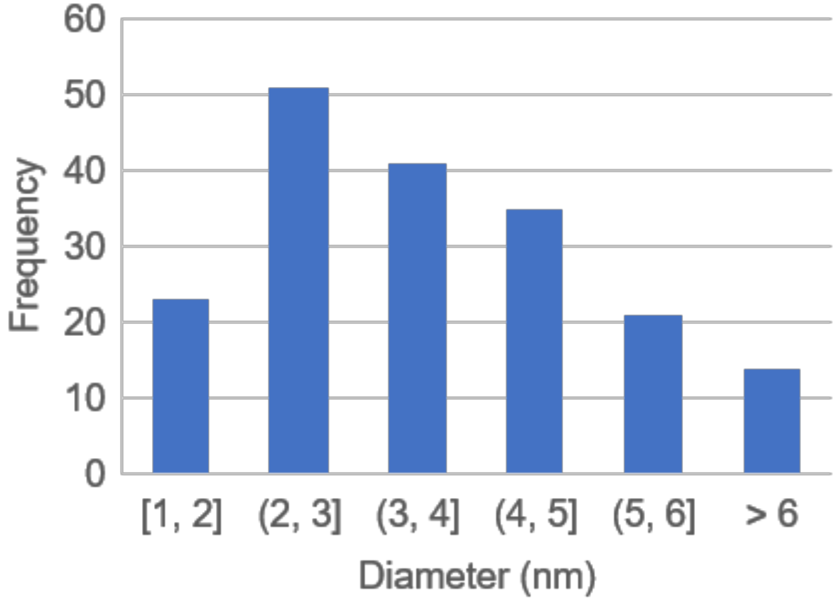
TEM

- FEI Talos F200X CTEM/STEM

Size distribution by ImageJ

Dispersion

- 34%
- $d{\downarrow}vA = 6v{\downarrow}m\ /Da{\downarrow}m$
- $v{\downarrow}m$ volume occupied by a metal atom in the bulk
- $a{\downarrow}m$ surface area occupied by an exposed surface metal atom



NH_3 Decomposition Kinetics

Conventional: Temkin-Pyzhev mechanism

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

- Typical $\beta = 0.2 - 0.4$
- Inhibited by H_2 and reverse reaction

Efficient Hydrogen Removal: Tamaru mechanism

- Typically observed at very high temp & low P_{H2}

$$r = \frac{kKP_{NH_3}}{1 + KP_{NH_3}} = k' P_{NH_3}^{\alpha}$$

- Modeled at 1st order reaction, only adjustable parameter

Temkin, M.; Pyzhev, V., *URRS* **1940,** *12*, 327-335.
Tamaru, K., *Res.* **1988,** *21* (2), 88-94.

Channel 1D Plug Flow

Assumptions

- Isothermal
- $d/L \ll ReSc \ll L/d$
- Competing time scale analysis
  - Left bound: Axial diffusion << advection
  - Right bound: $\tau{\downarrow}r,d \ll \tau{\downarrow}f$

Dimensionless numbers

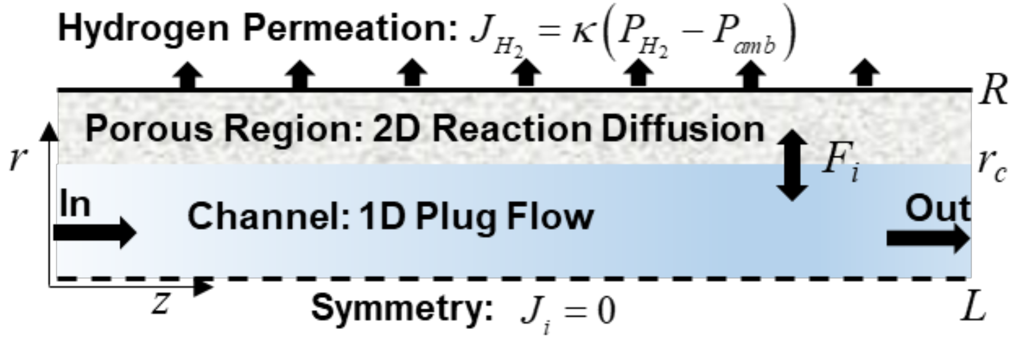
- Reynolds # (Da)
  - $Re{\downarrow}d = ud{\downarrow}i\,/\nu$
  - $Re{\downarrow}L = uL/\nu$
- Schmidt # (Sc)
  - $Sc = \nu/D$

Governing equation

$\partial(\rho{\downarrow}i\,u)/\partial z = F{\downarrow}c\,v{\downarrow}i\,r - F{\downarrow}m\,W{\downarrow}i\,J{\downarrow}i$

$F{\downarrow}c = P{\downarrow}e\,/A\,F{\downarrow}c\uparrow' = P{\downarrow}e\,2\pi Rdrdz/A2\pi r{\downarrow}c\,dz$ the ratio of the volume of the catalytic active region to the channel geometric surface

$F{\downarrow}m = 2\pi Rdz/2\pi r{\downarrow}c\,dz$ the area ratio of the membrane to the channel geometric surface



$r{\downarrow}c$ = 0.13 cm
R = 0.5 cm
L = 6.6 cm

Porous Media 2D Reaction-Diffusion

4 BCs required (N_2 and NH_3)

- Left wall (Inlet): $P = P_0$
- Right wall (Outlet): $\partial P / \partial z = 0$
- Interface (Symmetry): $P = P_0$
- Upper wall (No flux): $\partial P / \partial z = 0$

Solving order

- Given/assume volumetric reaction rate ($P_1(z)$) in the porous media
- Solve for $\rho_1 u$, $\rho_2 u$, $\rho_3 u$, and get x_1, x_2, x_3 in the channel
- Solve for ρ using ideal gas law
- Get ρ_1, ρ_2, ρ_3 ($P_{0,i}$ at the interface)
- Solve equations system in the porous media

Chapman-Enskog relation for D_{AB}

$$D_{AB} = 0.0018583 \sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \frac{1}{P \sigma_{AB}^2 \Omega_{D,AB}}, \ [cm^2/s]$$

σ_{AB}, [Å], $\sigma_{AB} = 0.5(\sigma_A + \sigma_B)$

$\Omega_{D,AB}$, collison integral, $f\left(kT/\varepsilon_{AB}\right)$, $\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}$

Mixture-averaged D

$$D_{im} = \frac{1 - y_i}{\sum_{j=1, j \neq i}^{n} y_j / D_{kj}}$$

$$D_{im}^e = \frac{\epsilon}{\tau} D_{im}$$

Dimensionless number Analysis

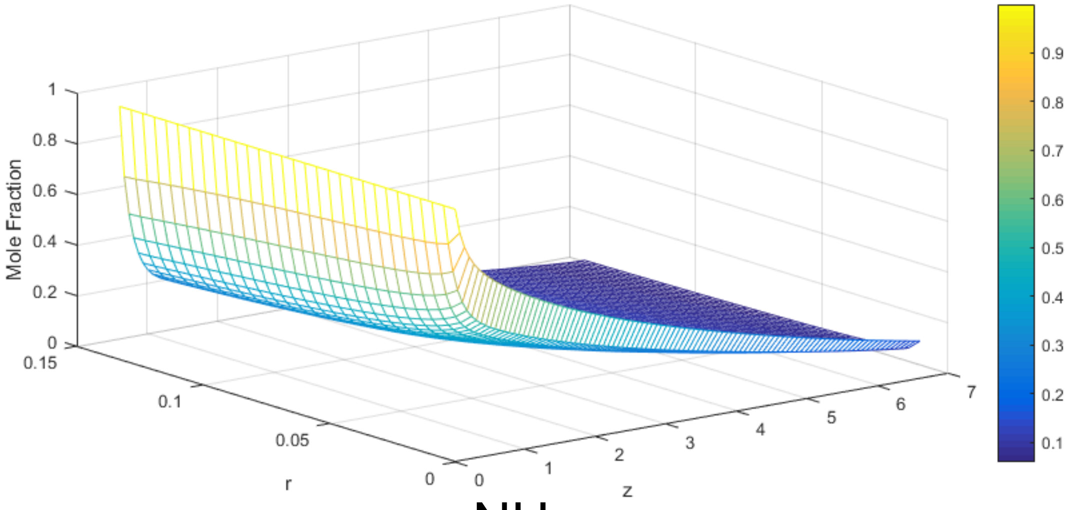
Timescale

- Flow time
  - $\tau_f = L/v_{NH_3, in}$
- Reaction time
  - $\tau_r = 1/k$ (1st order rate)
- Permeation time
  - $\tau_p = c_{NH_3, in} V_r / J_{H_2} A_m$
- Radial dispersion time
  - $\tau_d = (R - r_c)^2 / D_{H_2}$
- Axial diffusion time
  - $\tau_L = L^2 / D$

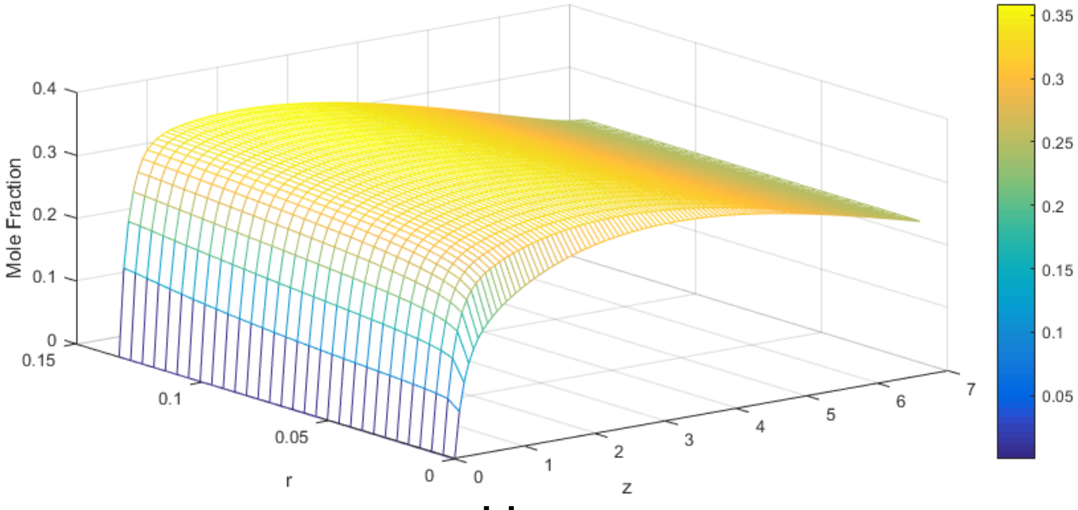
Dimensionless numbers

- Damkohler # (Da)
  - $Da = \tau_f / \tau_r$
  - Da >> 1, meaning high conversion
- Transverse Peclet # (Pe_t)
  - $Pe_t = \tau_d / \tau_f$
  - Pe_t >> 1, radial diffusion is slow
- $Pe_t \, Da = \tau_d / \tau_r$
  - $Pe_t \, Da$ >> 1, enough time for reaction

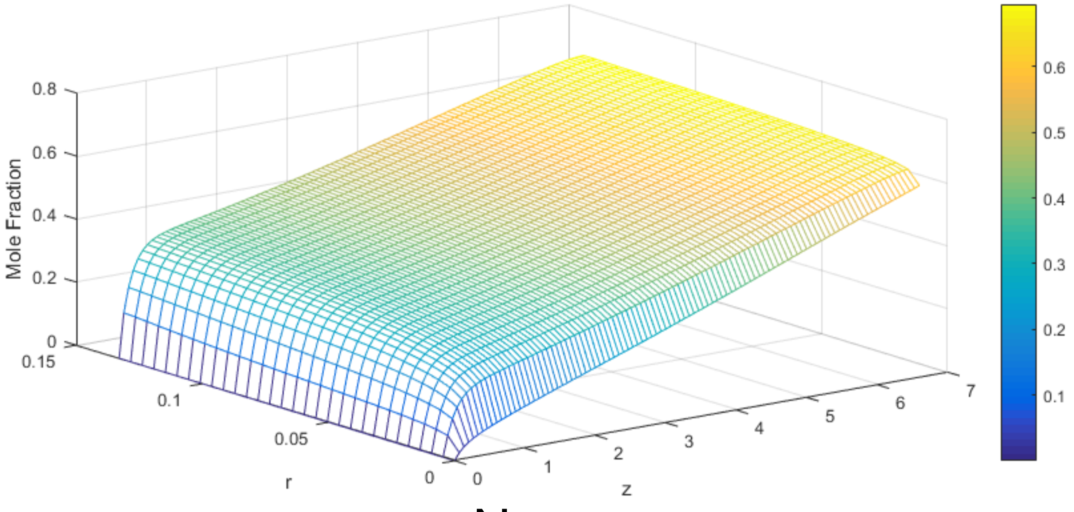
Porous Media 2D Composition Profile



NH_3



H_2



N_2

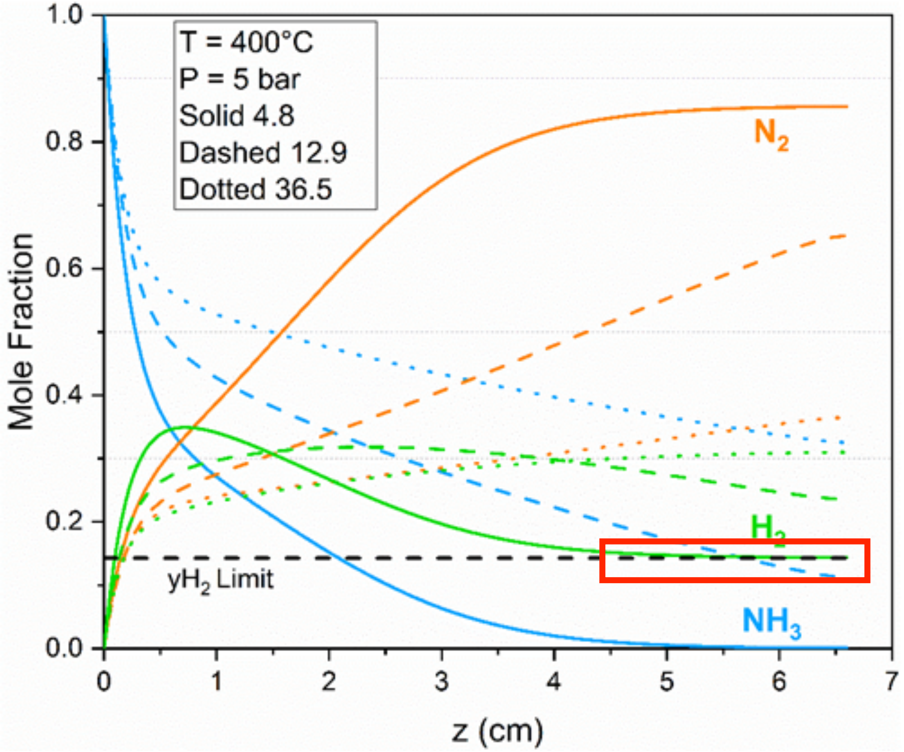
Ru as the catalyst at 450°C and 5 bar

Spatial discretization: 300 × 133

Model: Kinetic vs. Permeation Limited Regimes

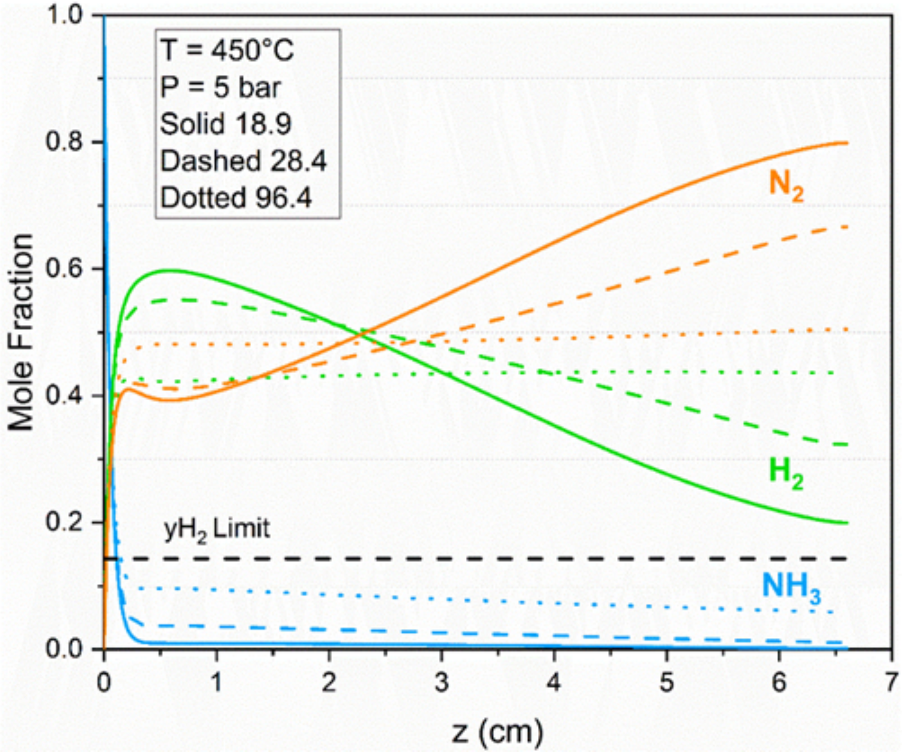
Kinetic limited

- H_2 permeation reaches limit at low NH_3 flowrate
- Low NH_3 conversion limits H_2 productivity rate

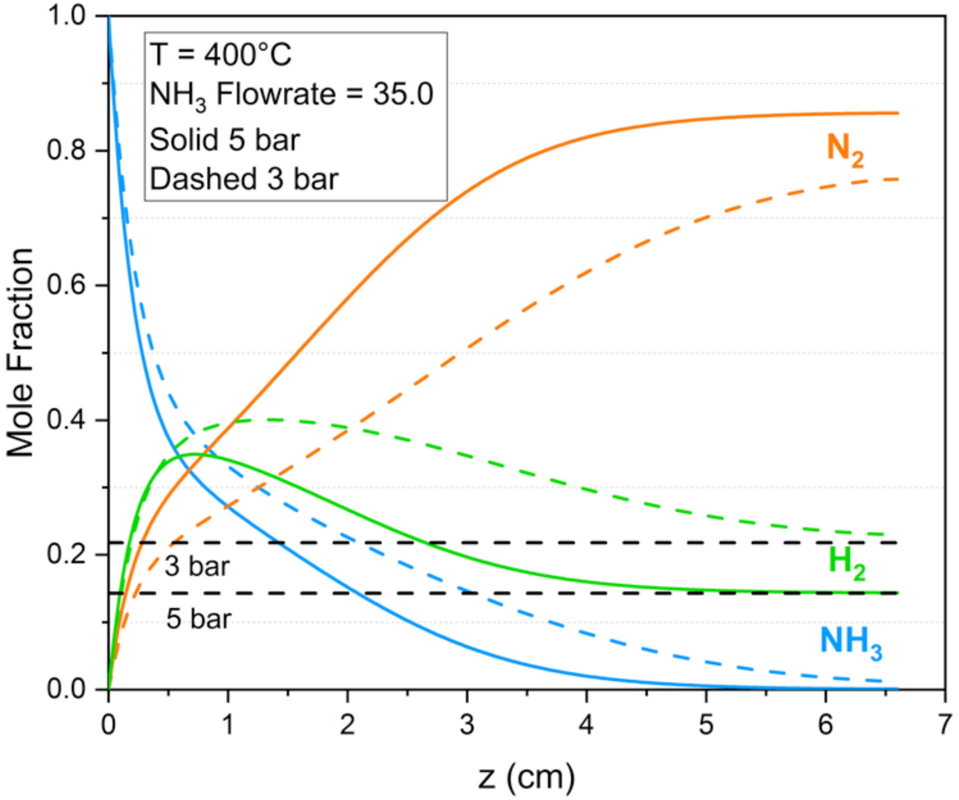


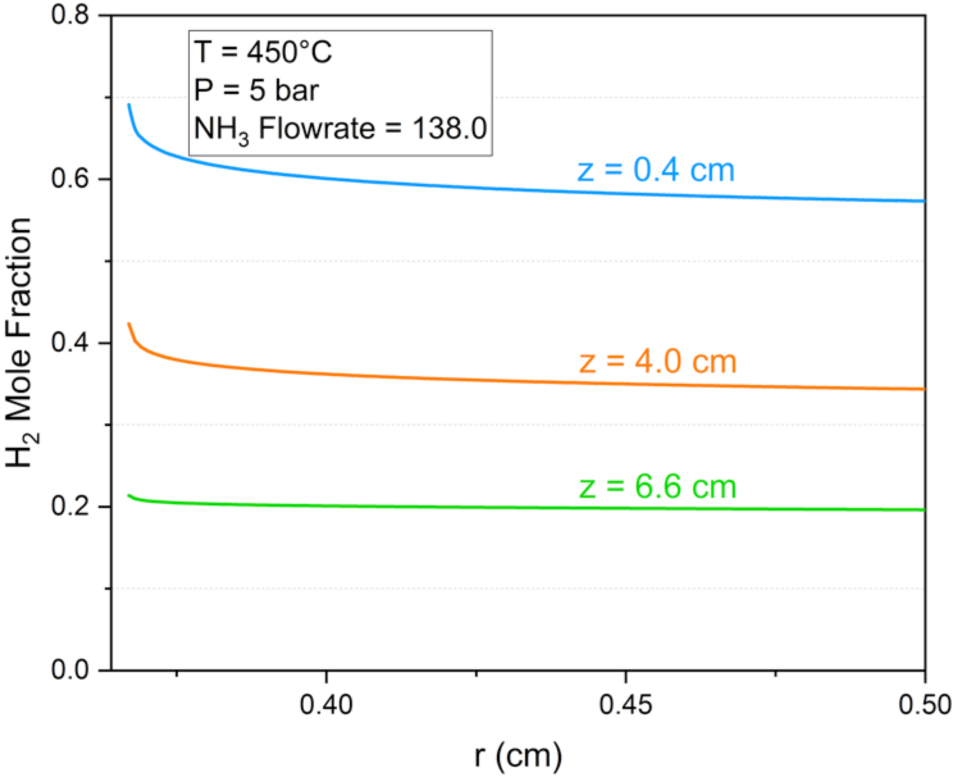
Permeation limited

- Enhanced catalytic activity at high T
- Membrane permeance/pressure driving force limits H_2 productivity rate



Model: Pressure Impact and Radial Dispersion





E_A: Ru vs. CsRu

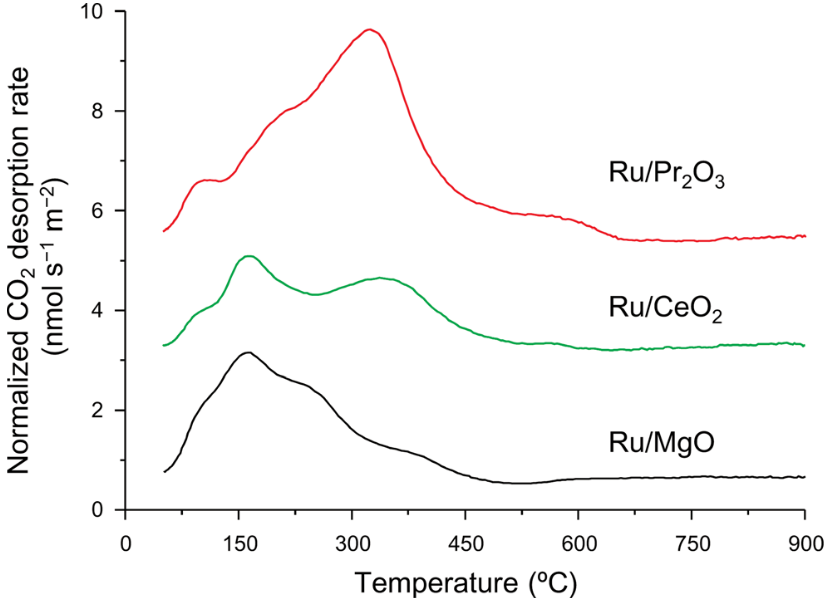
- The impact of promoter varies with supports
- High E_A suggests N_2 desorption as RDS
- High NH_3 pressure used in this study
- Narrow temperature range

Catalyst/Support	Ea (kJ/mol)
Ru/K-ZrO_2-KOH	47.2
K-Ru/K-ZrO_2-KOH	47.5
Ru/CNTs	96.7
Cs-Ru/CNTs	59.3
Ru/Al_2O_3	117
Ba-Ru/C	158

CO_2 TPD

Basics

- Detector: MS
- Different adsorption conditions of the same molecule
    - Desorption T differences of molecules desorbing different sites at the surface, e.g. terraces vs. steps.



Sato, Katsutoshi, et al. *Chemical science* 8.1 (2017): 674-679.

Experimental Method

- CO_2 adsorption at 50°C, after H_2 reduction at 400°C for 1 hour
- CO_2 desorption 50-700°C, 10°C/min
- Desorption rate vs. T
- Brian Trewyn Lab at Chemistry Department

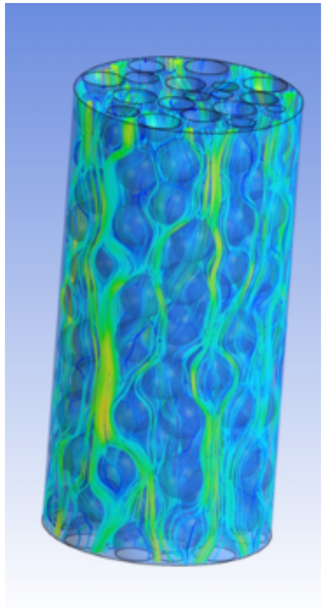
$r=Ae^{-E_a^{des}/RT}c^{\alpha}$

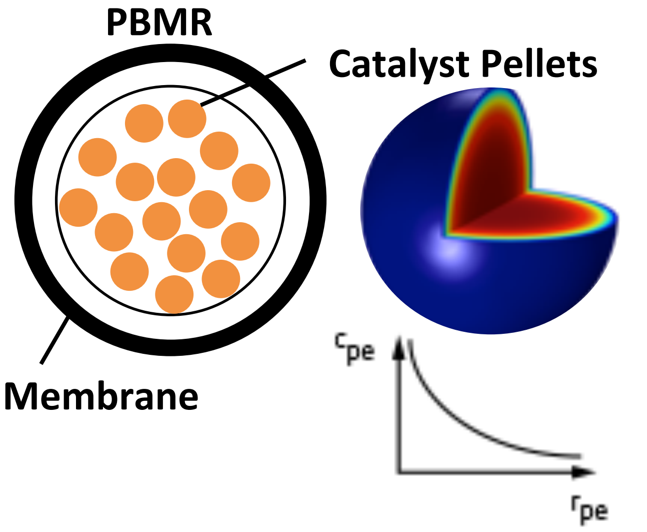
- as E_a^{des} (the activation energy for desorption) increases, T_p (the peak temperature) increases

Transport Limitations

Packed Bed

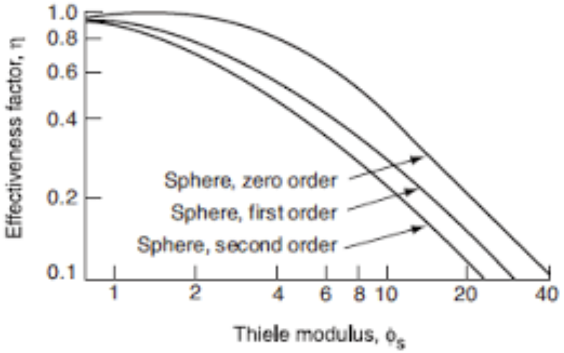
- Pressure Drop
- Channeling & Dispersion
- Radial Transport Limitations





Diffusion Limitations

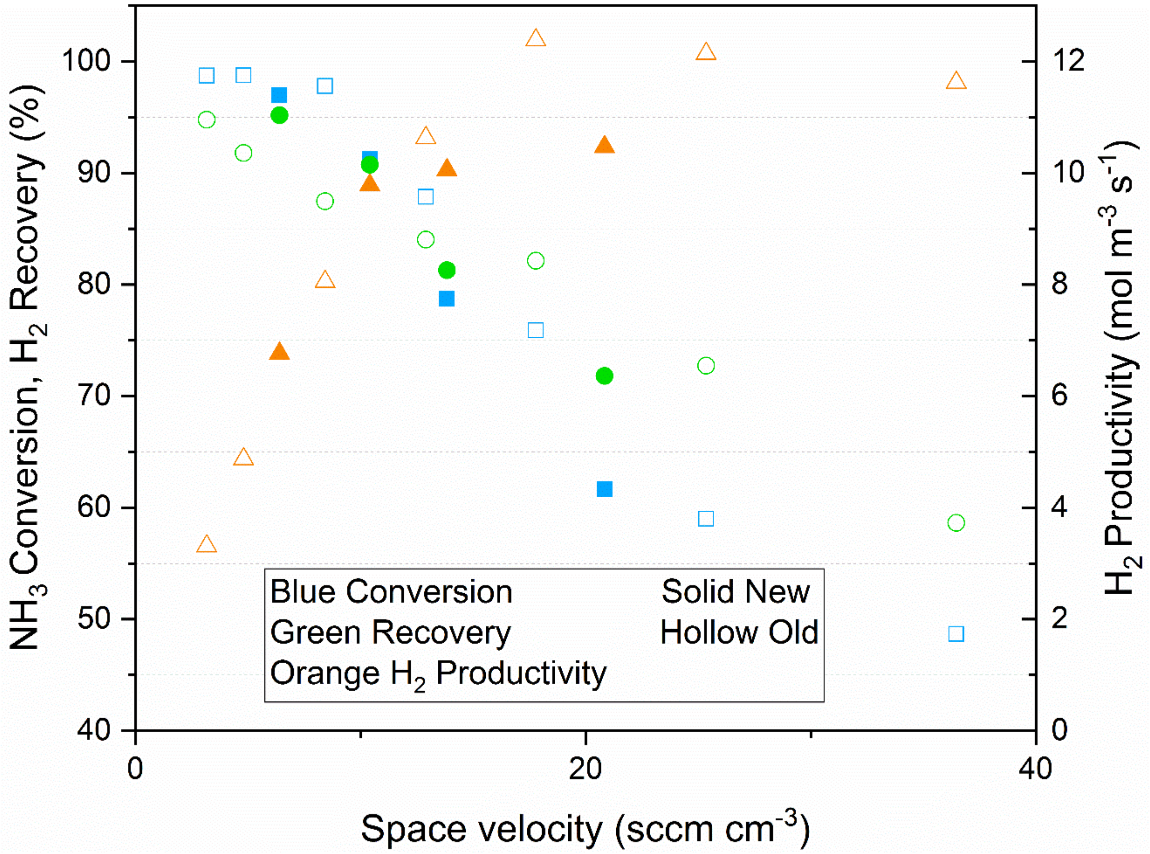
$$\Delta p = \frac{150\mu u_0 L_b}{D_p^2}\frac{(1-\varepsilon)^2}{\varepsilon^3} + \frac{1.75\rho u_0^2 L_b}{D_p}\frac{(1-\varepsilon)}{\varepsilon^3}$$



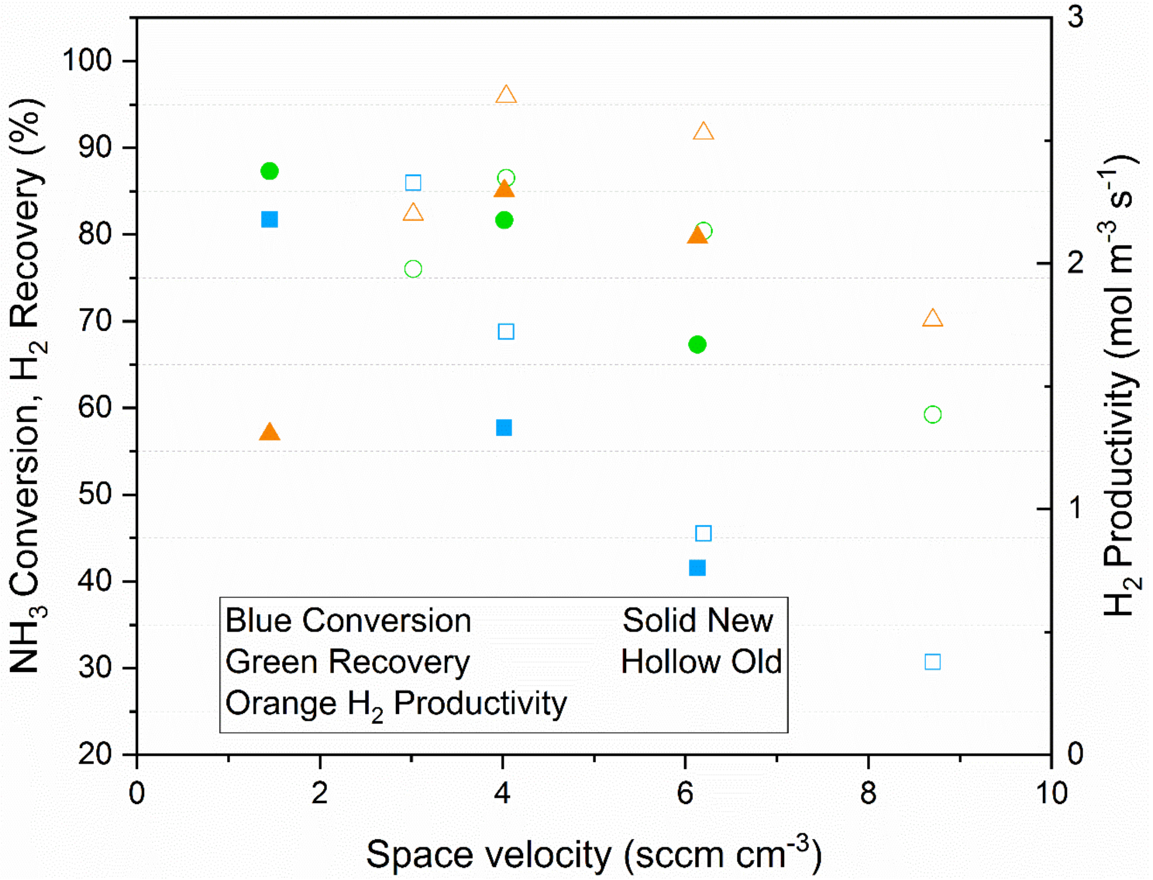
Reproducibility Test

T: 350 & 400°C P: 5 bar

400°C



350°C



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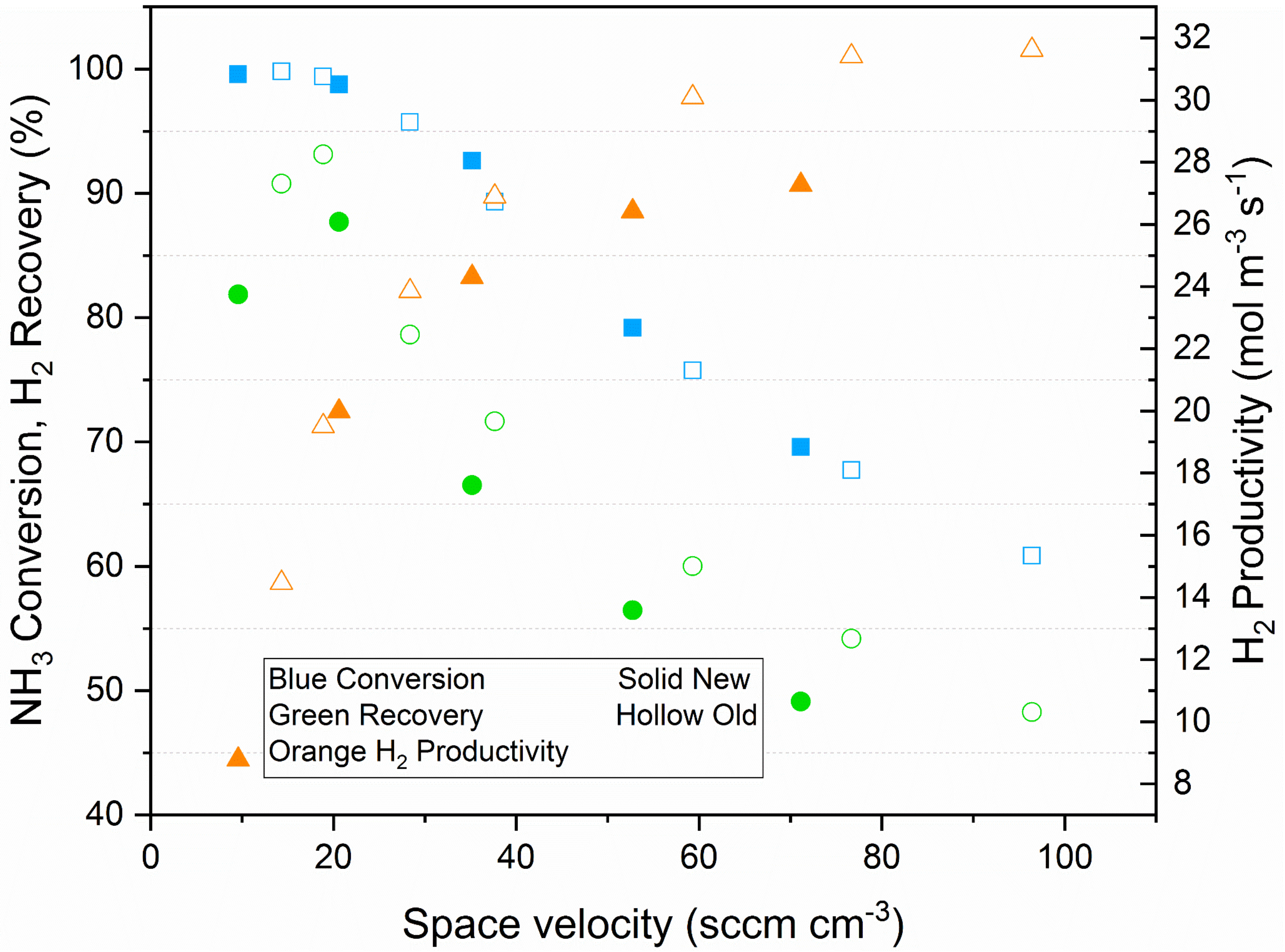
Reproducibility Test

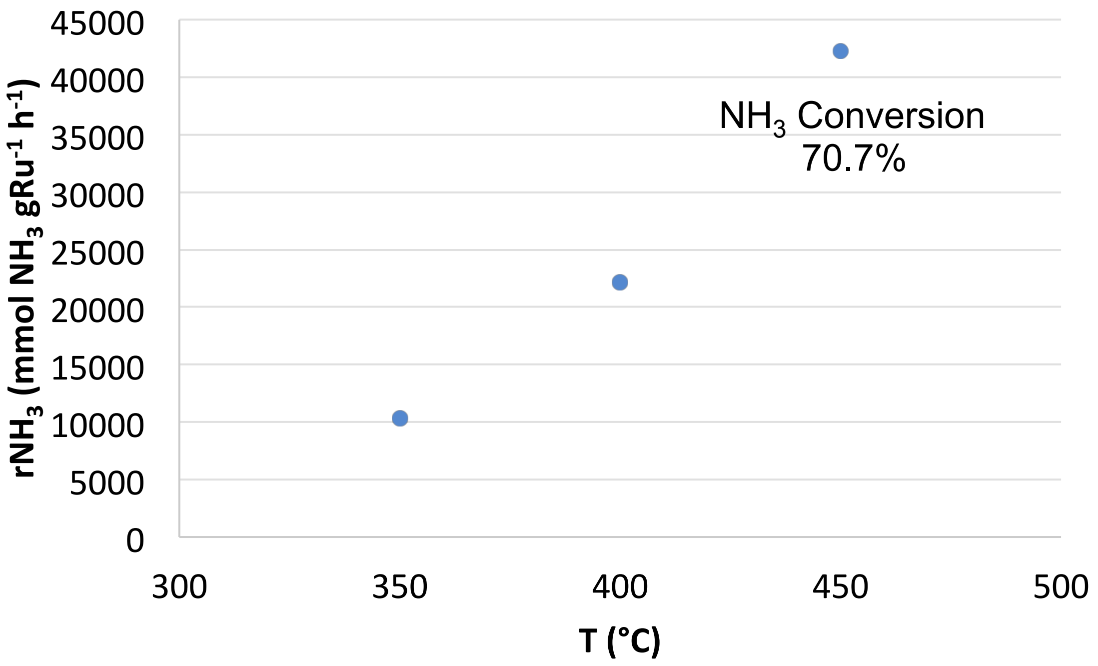
T: 450°C P: 5 bar

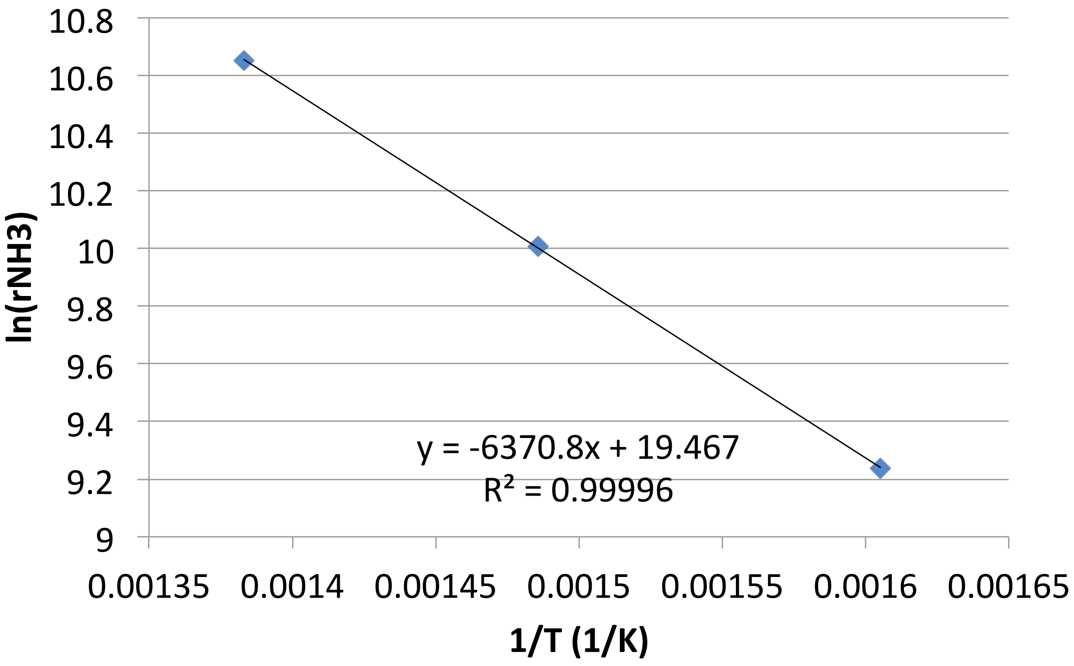


NH_3 Decomposition Ea – Pure Ru

Vary Temp

- Cross flow, atmospheric pressure, GHSV 14,000 h^{-1}
- Ea 53.0 kJ/mol

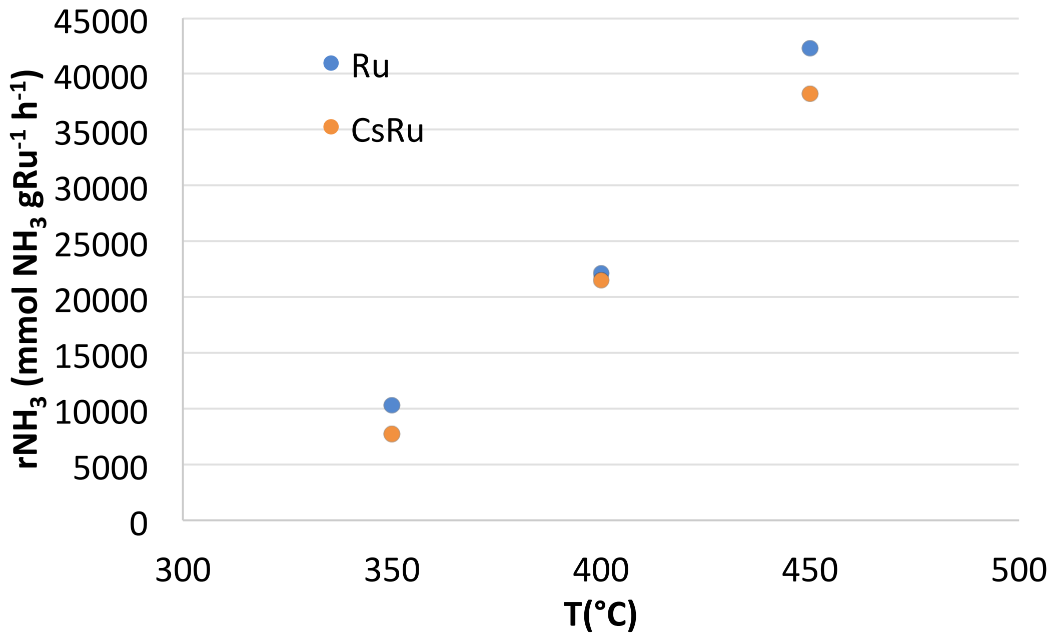


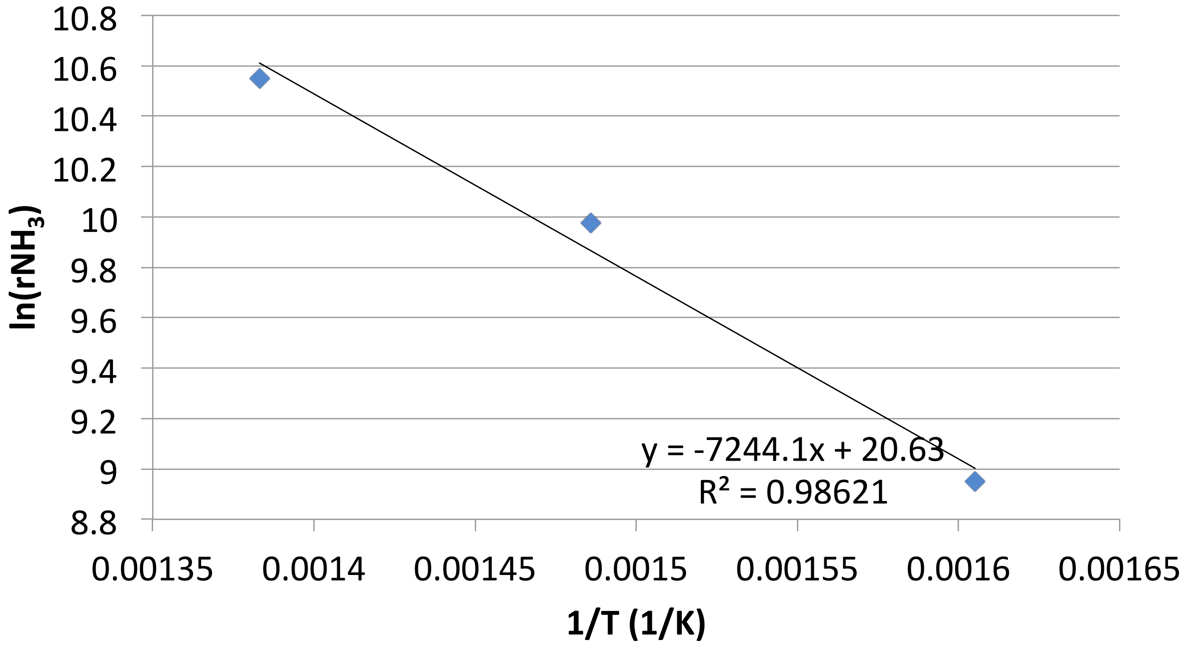


NH_3 Decomposition Ea – Cs/Ru

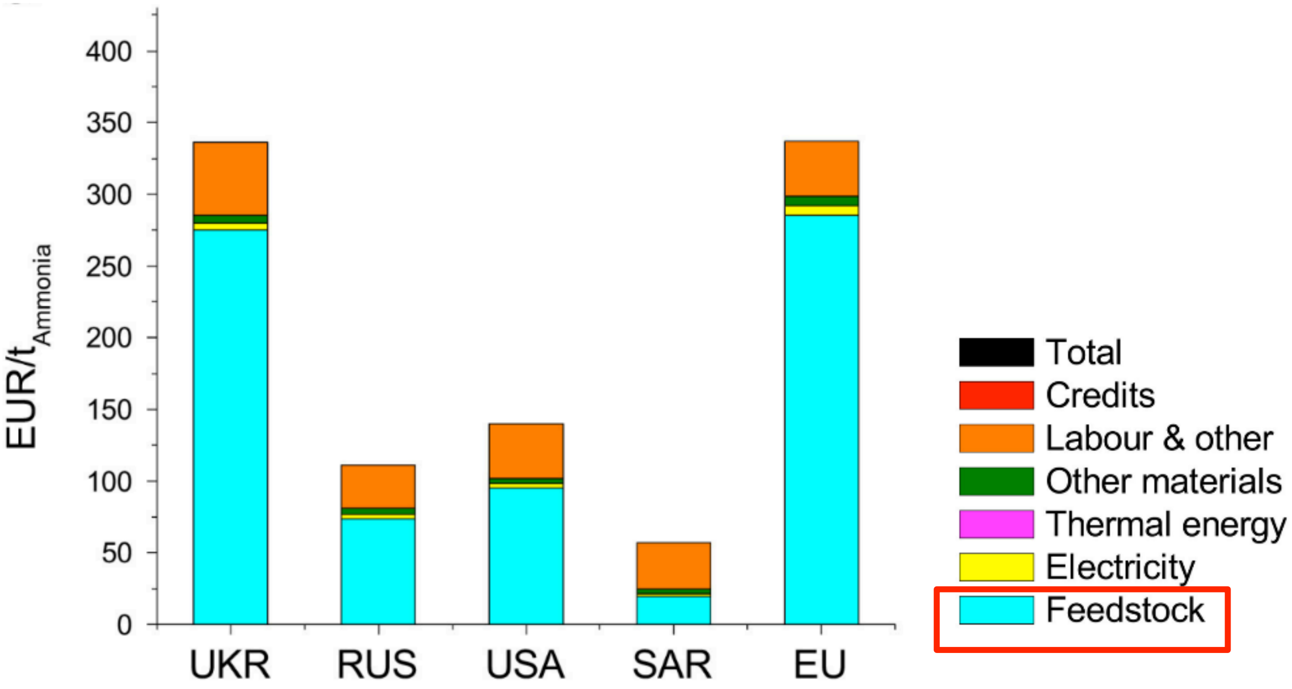
Vary Temp

- Cross flow, atmospheric pressure, GHSV 14,000 h^{-1}
- Ea 60.2 kJ/mol





Reforming step dominates H_2 production cost



Reforming step (800-900°C, ~30 bar), >67% energy loss in NH_3 production

*Angewandte Chemie International Edition*42.18 (2003): 2004-2008.
Renewable and Sustainable Energy Reviews 68 (2017): 1205-1212.