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

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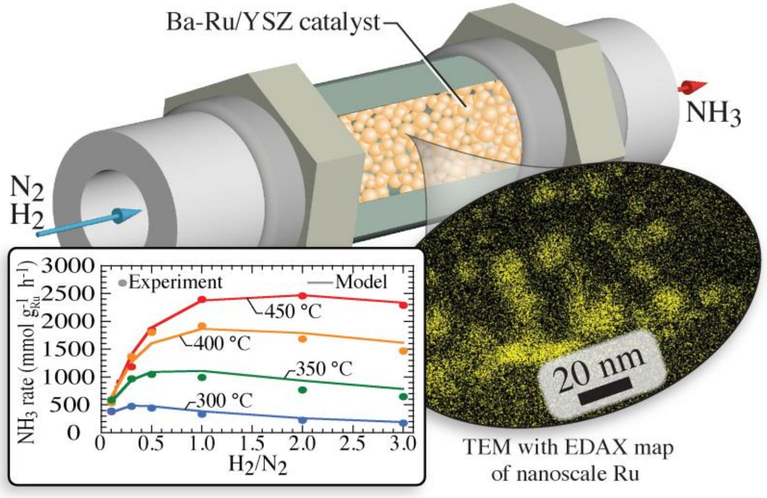

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Overview

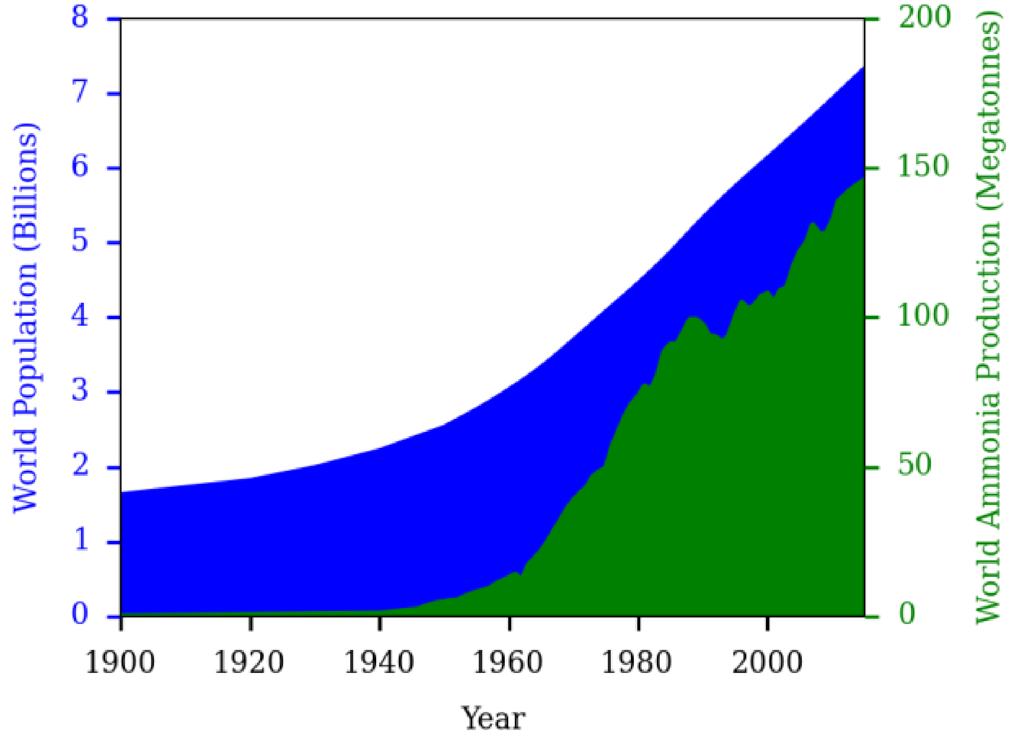
Goal: Distributed green ammonia production

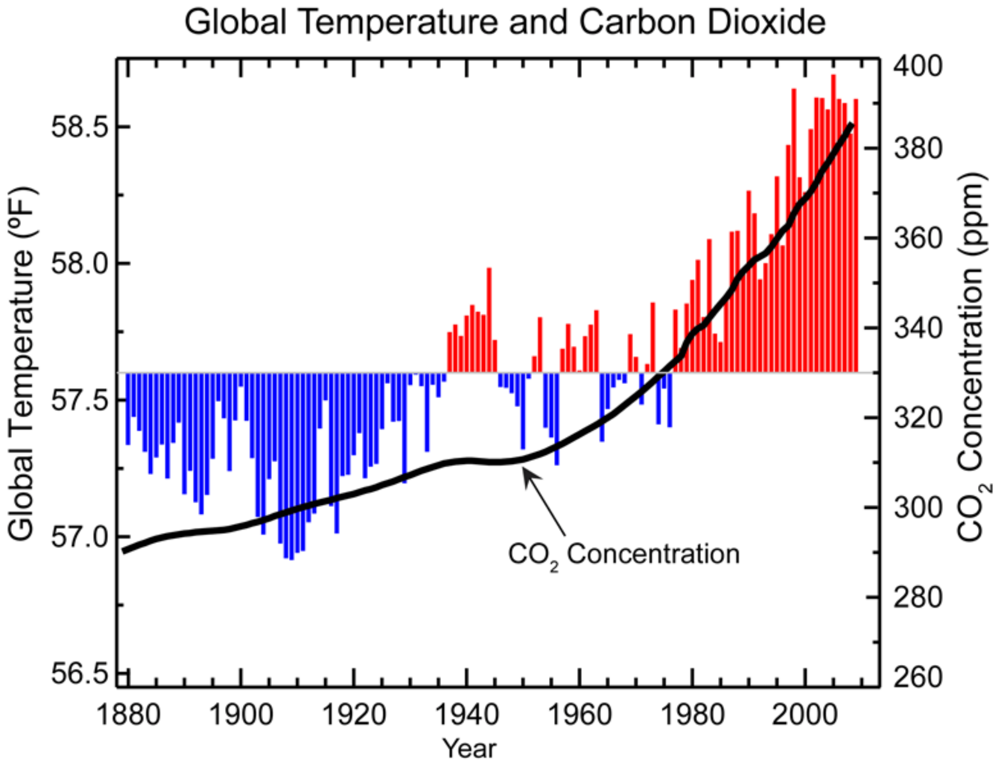
- Approach: Catalytic membrane reactors
- Focus on YSZ motivated by success for ammonia decomposition
- YSZ never investigated
- ZrO_2, rare earth oxides have been effective supports

YSZ supported Ru catalyst

- Catalyst preparation and characterization
- Baseline YSZ support vs. Al_2O_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

Ammonia & Climate Change





The Green Revolution (1960 –) powered by “brown” ammonia

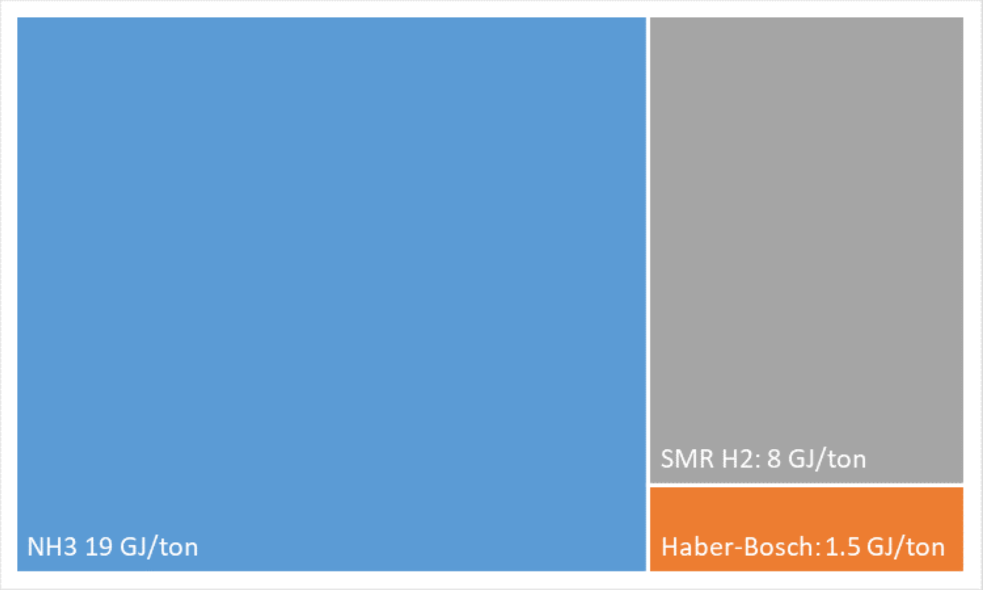
Well-correlated to anthropogenic climate change

Goal: Scalable production of “green” ammonia

Graphs from left to right: [1] *Sustainable Ammonia Synthesis–Exploring the scientific challenges associated with discovering alternative, sustainable processes for ammonia production*; US DOE Office of Science: **2016**.
[2] NOAA, national climate data center; URL: https://www.ncdc.noaa.gov/monitoring-references/faq/indicators.php

Fallacy: Haber-Bosch is inefficient

State-of-the-Art: ~28 GJ/ton NH_3



- Losses / costs / CO_2 primarily associated with hydrogen production
- Haber-Bosch CapEx intensive, does not scale down
- Renewable H_2 highly distributed

Klerke, A.; Christensen, C. H.; Nørskov, J. K.; Vegge, T., Ammonia for hydrogen storage: challenges and opportunities. *Journal of Materials Chemistry* **18** , 2304 (2008).

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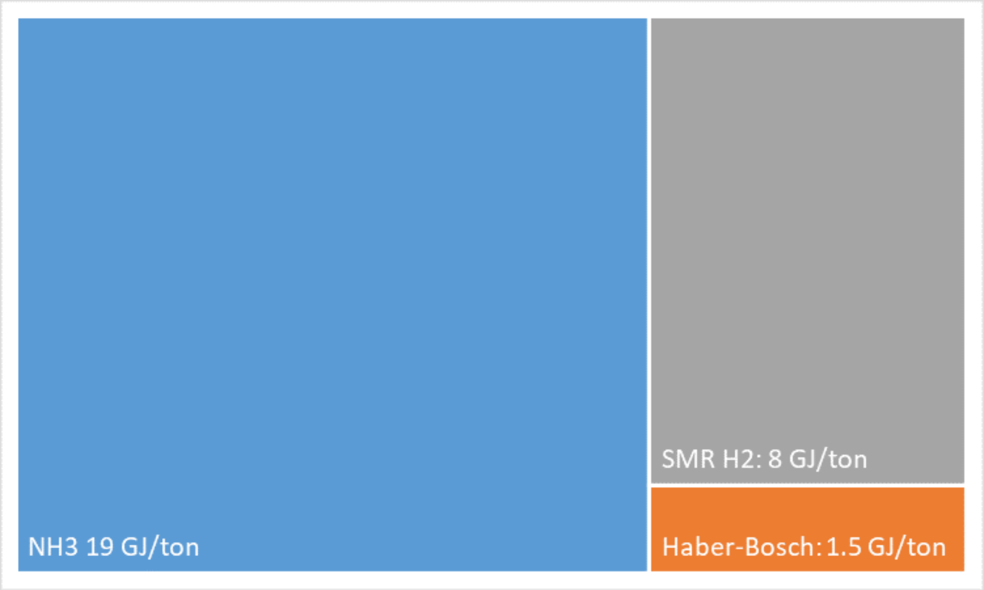

Opportunity for Scalable Production

- Produced @ $150/ton
- Costs: ~$450/ton
- Difference shipping

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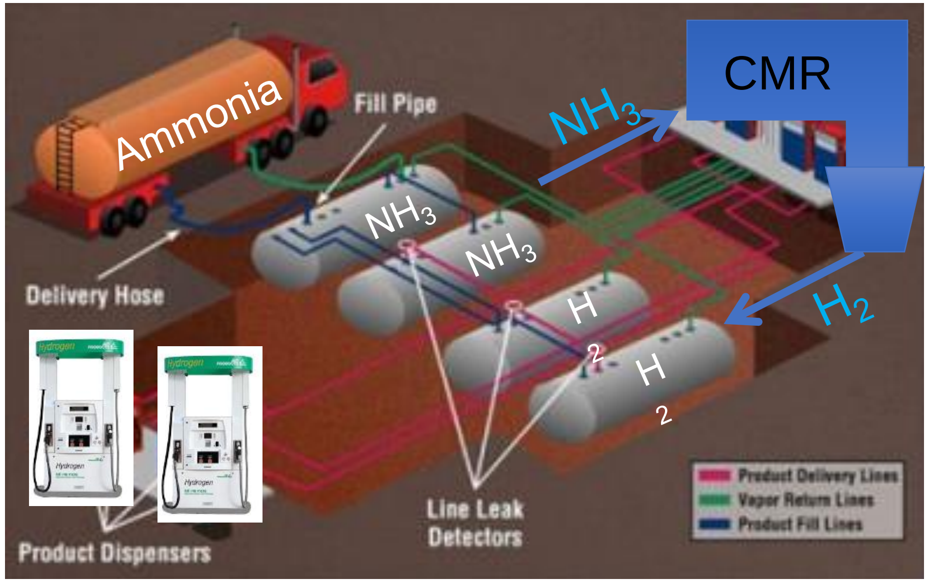
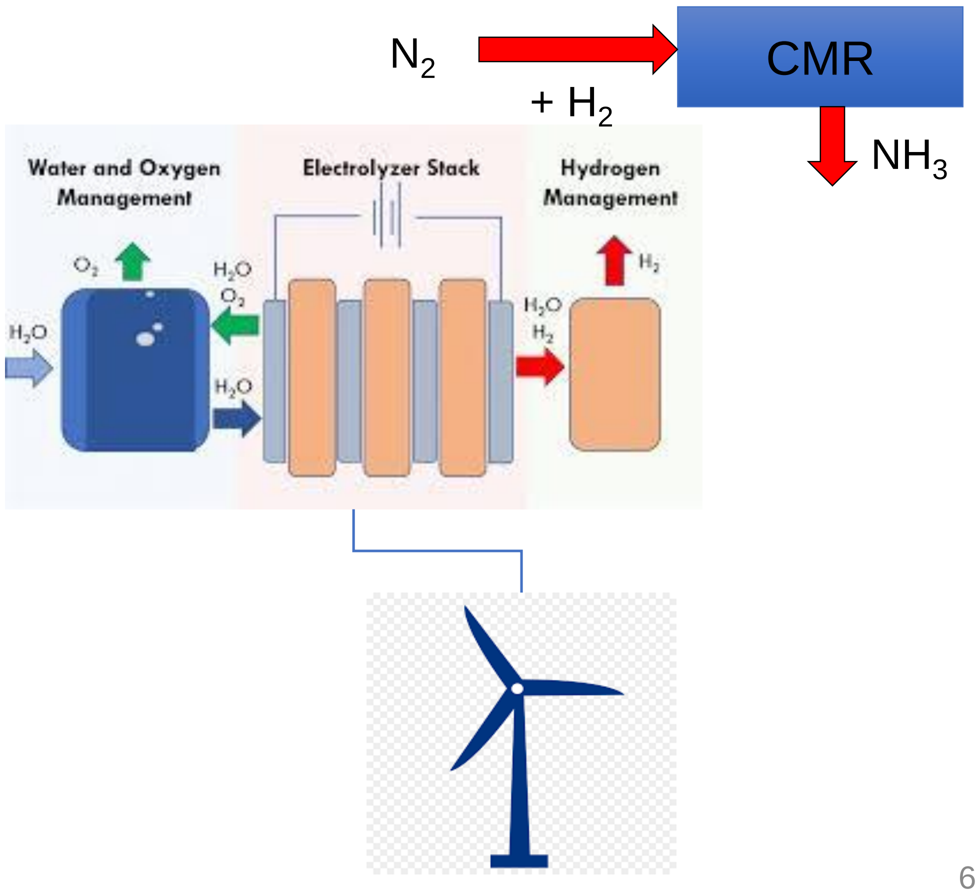
ARPA-E Concept

- Vision: Develop catalytic membrane reactor (CMR) technology for both efficient hydrogen delivery and distributed production of ammonia





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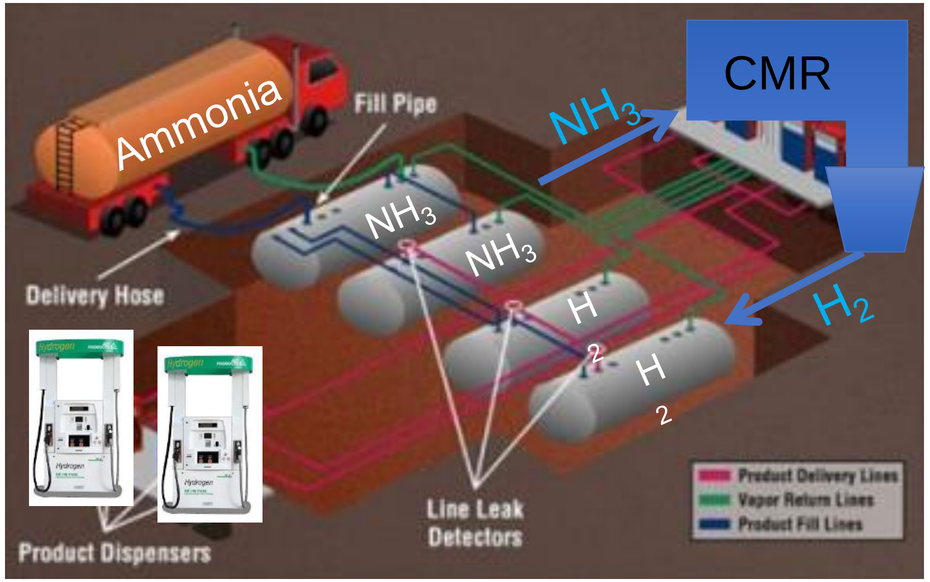
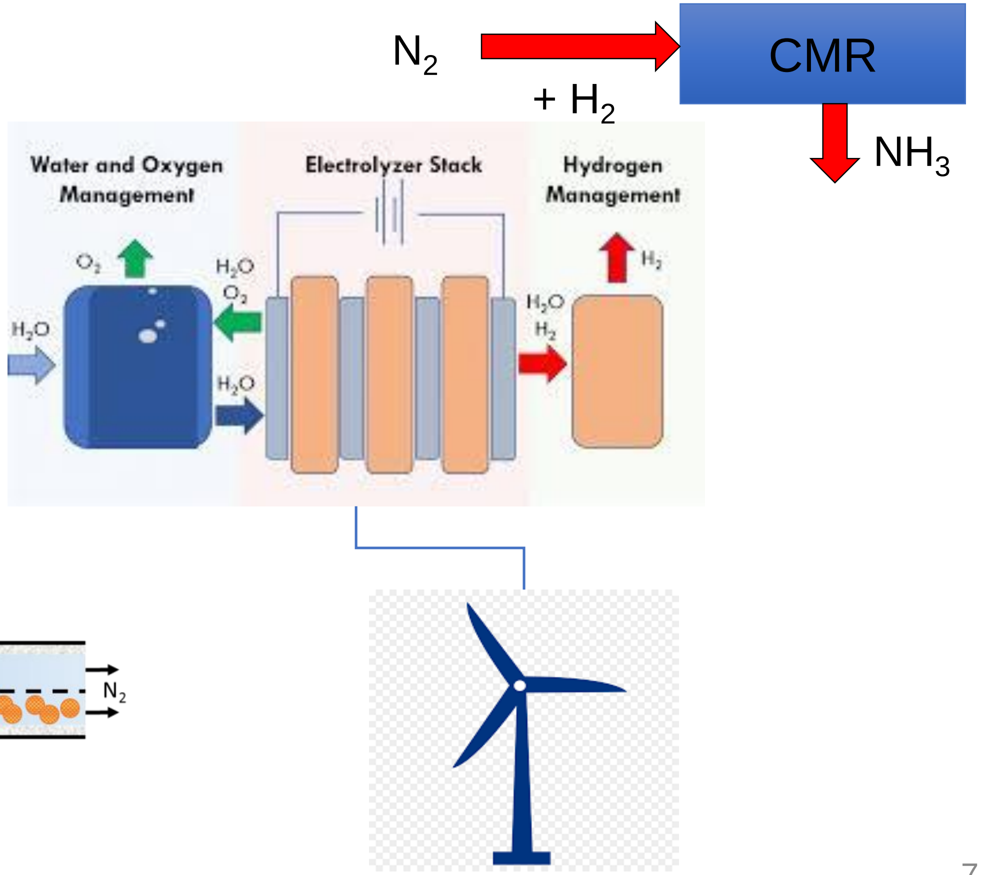
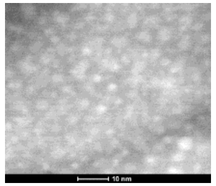
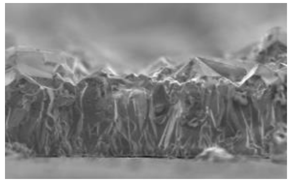


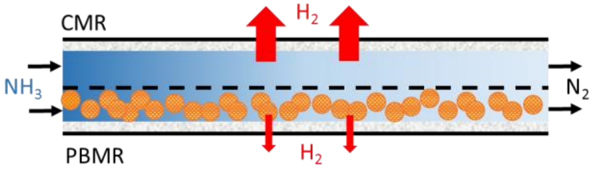




Advanced Catalysts

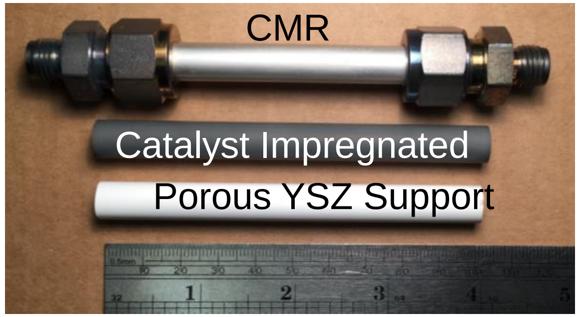


Highly Permeable Membranes

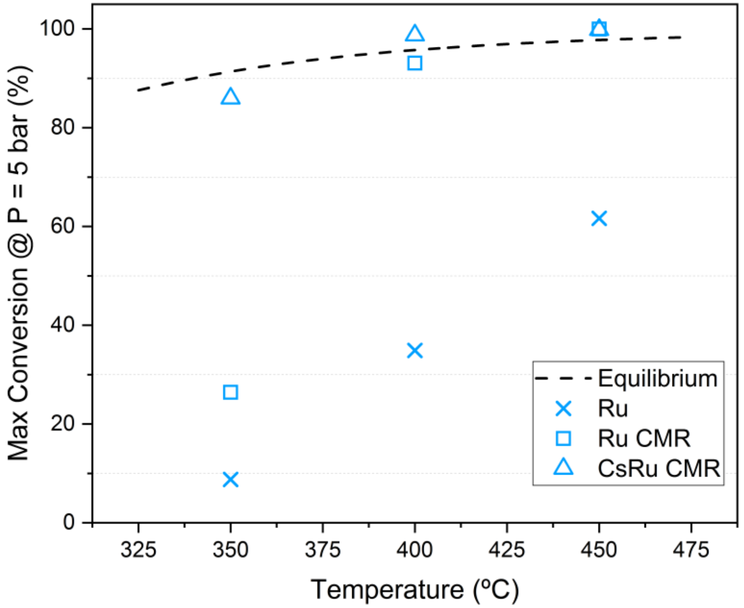


Innovative Reactor Design

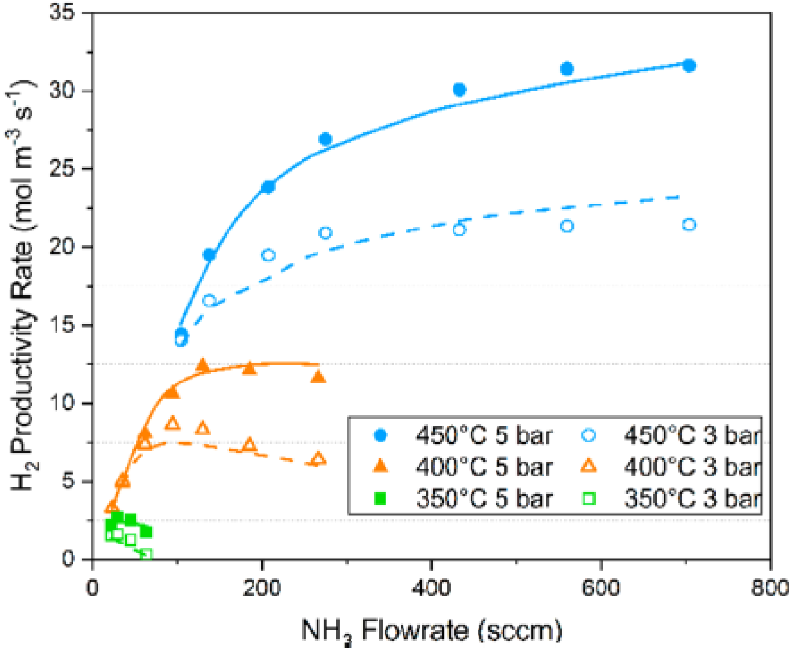
Efficient H_2 Generation from NH_3



- T < 450 °C
- >99% conversion
- Exceeds equilibrium
- High purity H_2: >99.5%
- Productivity >0.1 $g/h/cm^3$
- Reduced catalyst loading 10X
- Developed/validated 2D Model



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



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

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

Z. Zhang, S. Liguori, T. F. Fuerst, J. D. Way and C. A. Wolden, "Efficient ammonia decomposition in a catalytic membrane reactor to enable hydrogen storage and utilization", *ACS Sustainable Chemistry & Engineering* **7,** 5975 (2019).

Efficient H_2 Generation from NH_3

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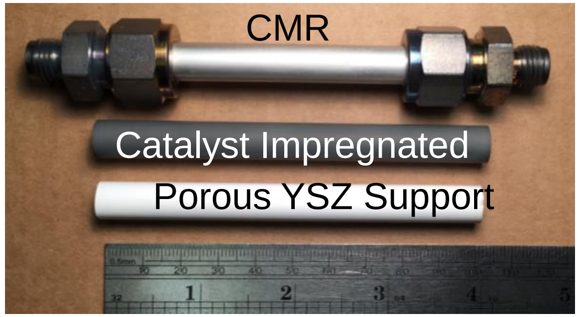

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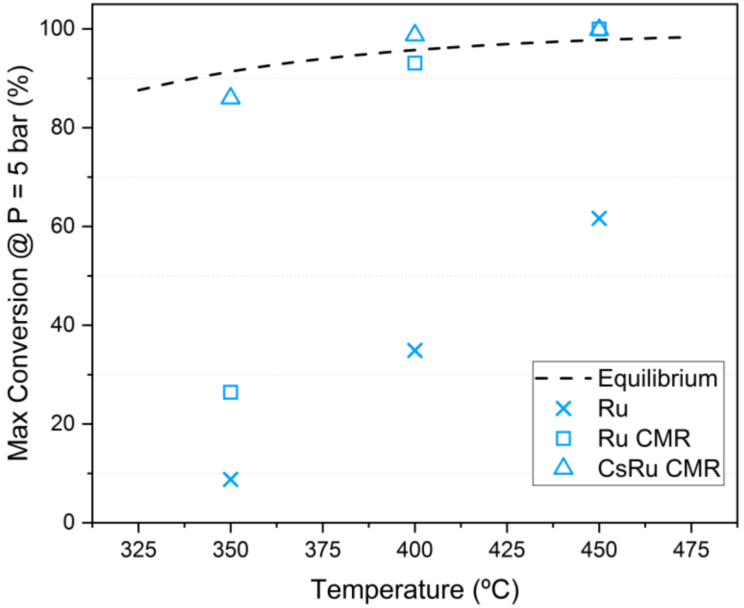

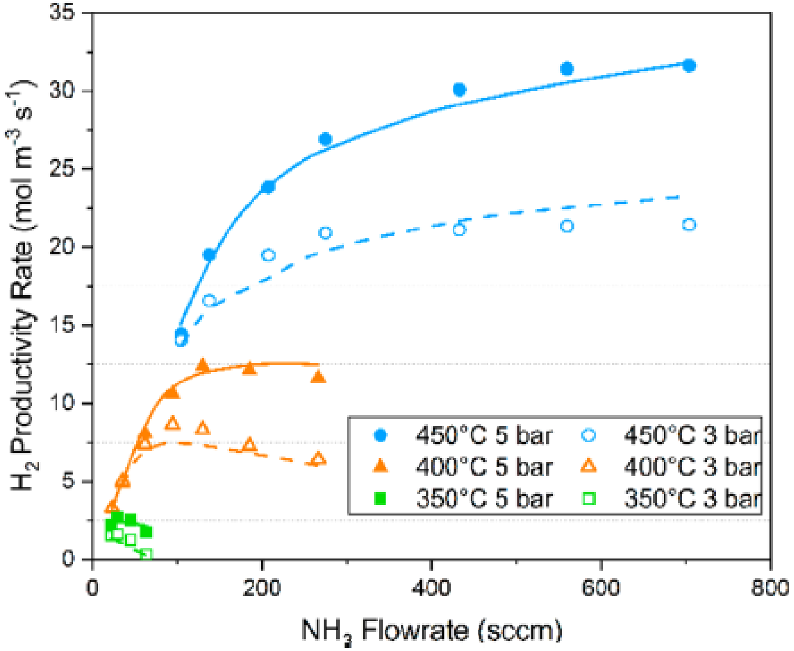

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$$\frac{\partial(\rho_i u)}{\partial z} = F_c \nu_i r - F_m W_i J_i$$

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

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

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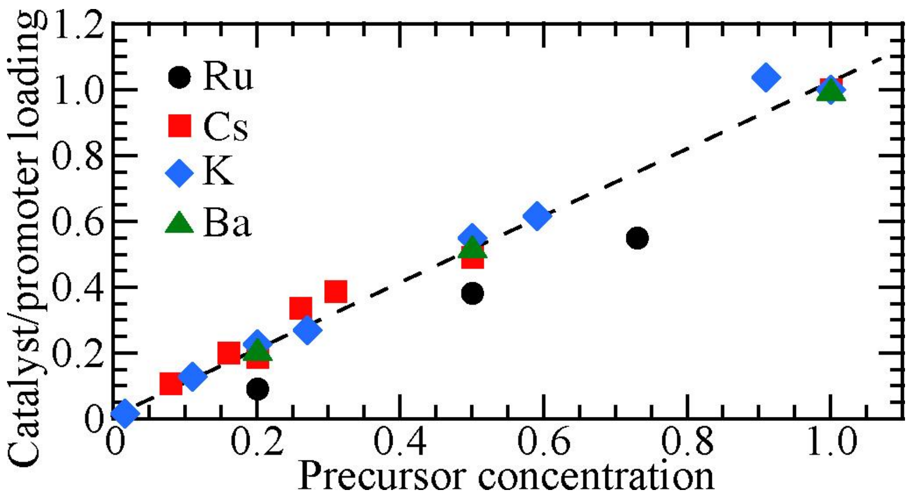
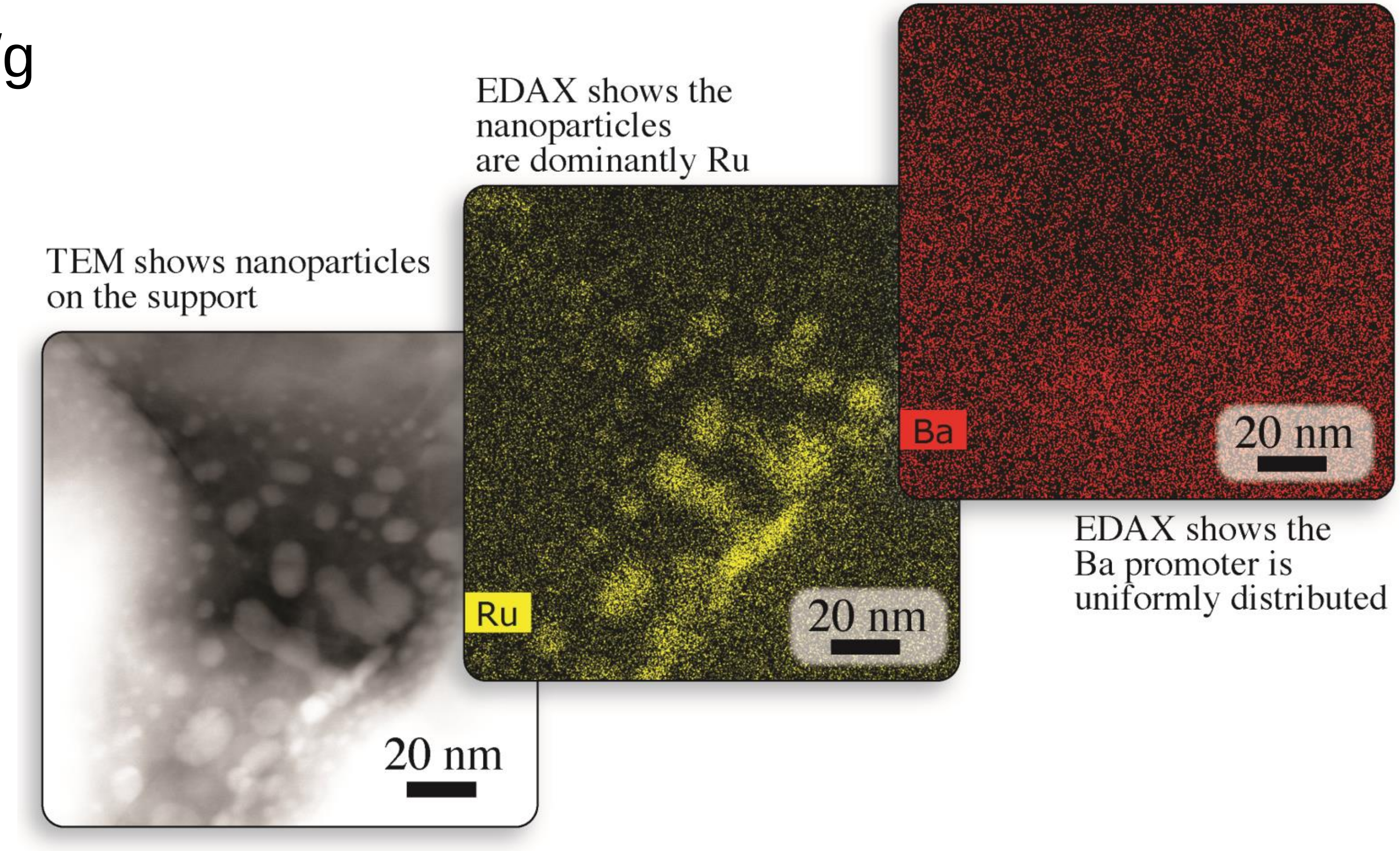
Catalyst Preparation & Characterization

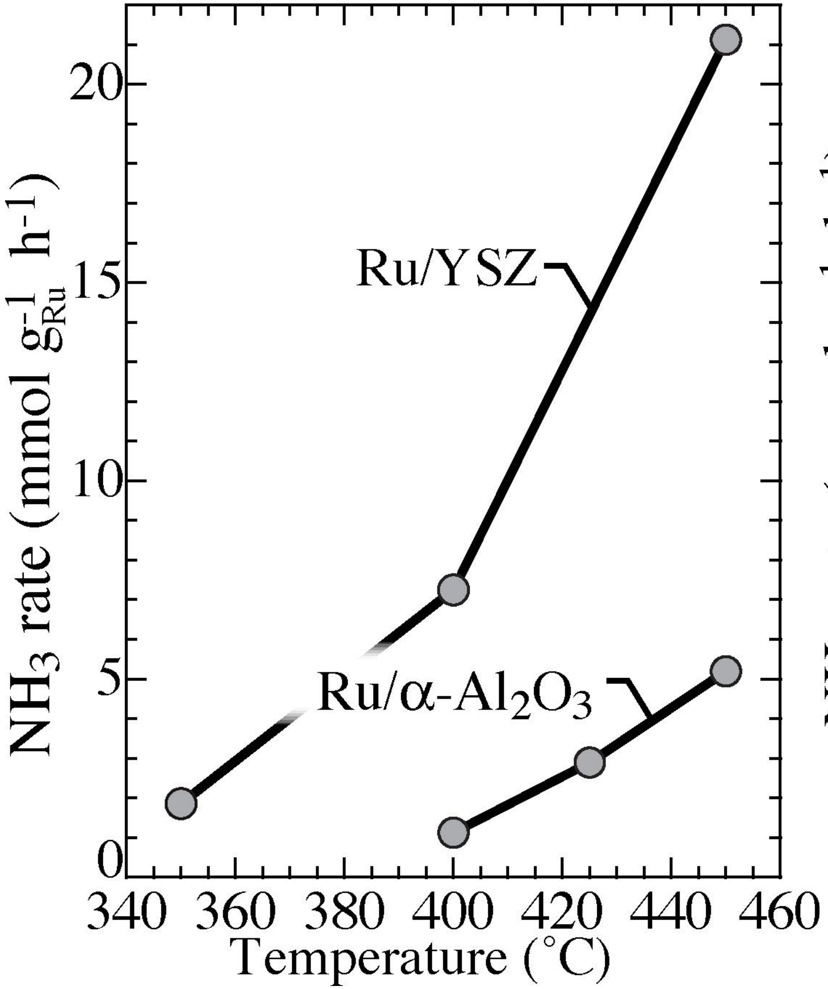
- YSZ (Praxair) support: low specific surface area 2.24 m^2/g
- Ru loading: 0.4 – 1.0 wt%
- Good dispersion (3-10 nm)
- Promoters (Cs, K, Ba)

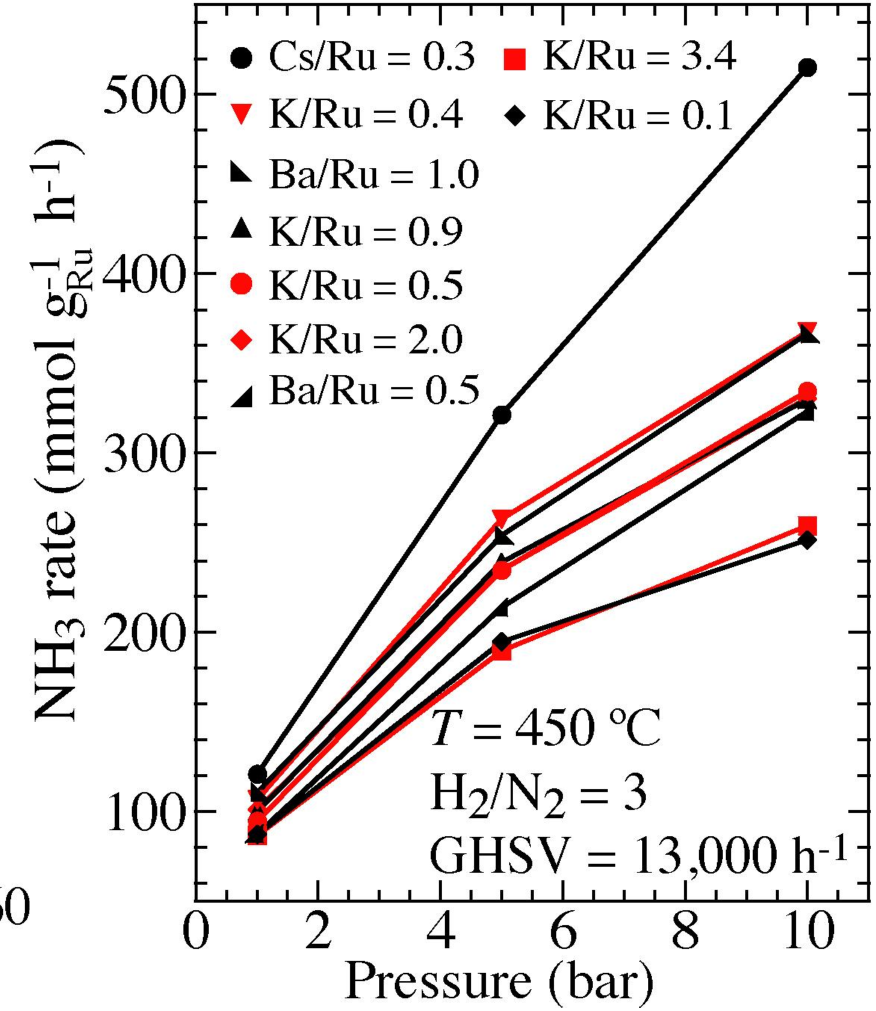




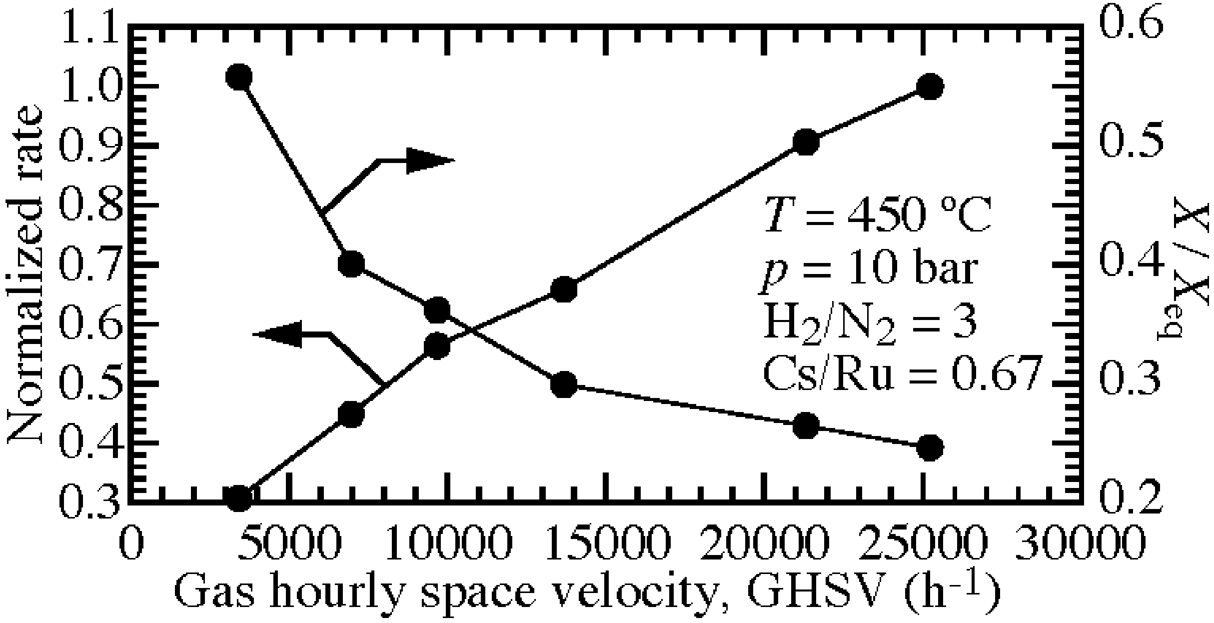
Impact of Support & Promoters

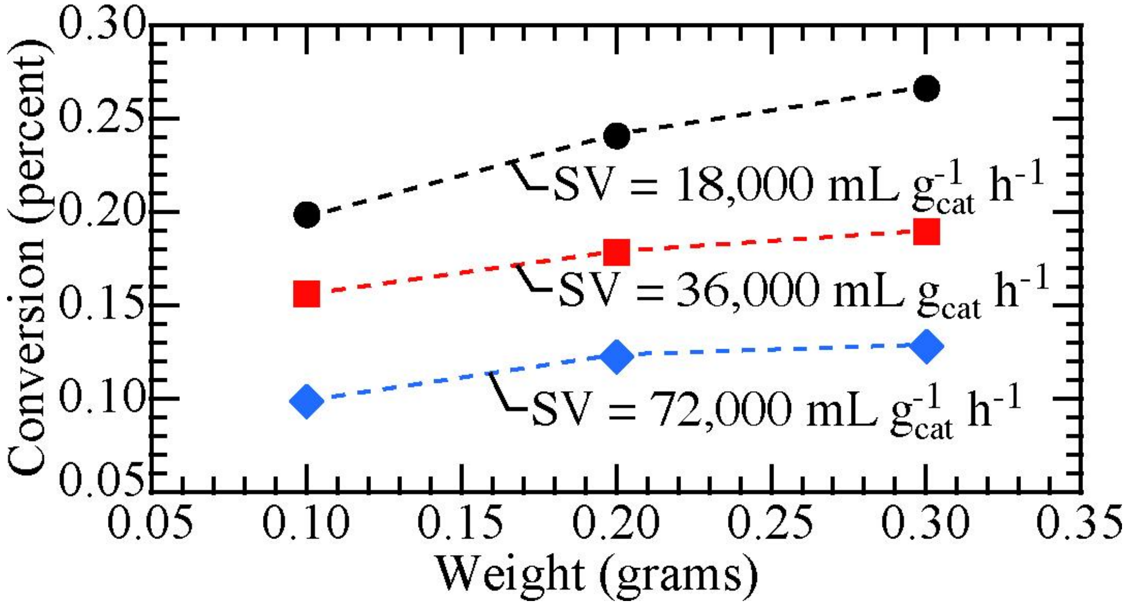
- YSZ ~4X > Al_2O_3
- Promoters increase rate ~5 - 10X
- Cs > Ba ~ K
- Insensitive to promoter/Ru Ratio





Transport & Equilibrium Limitations



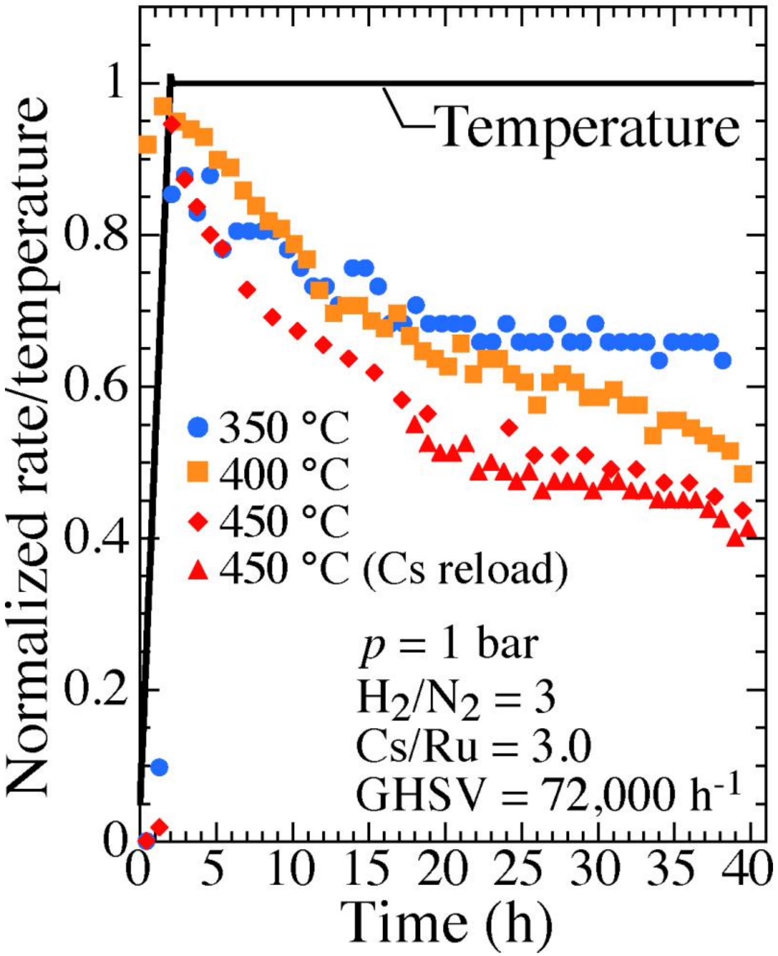


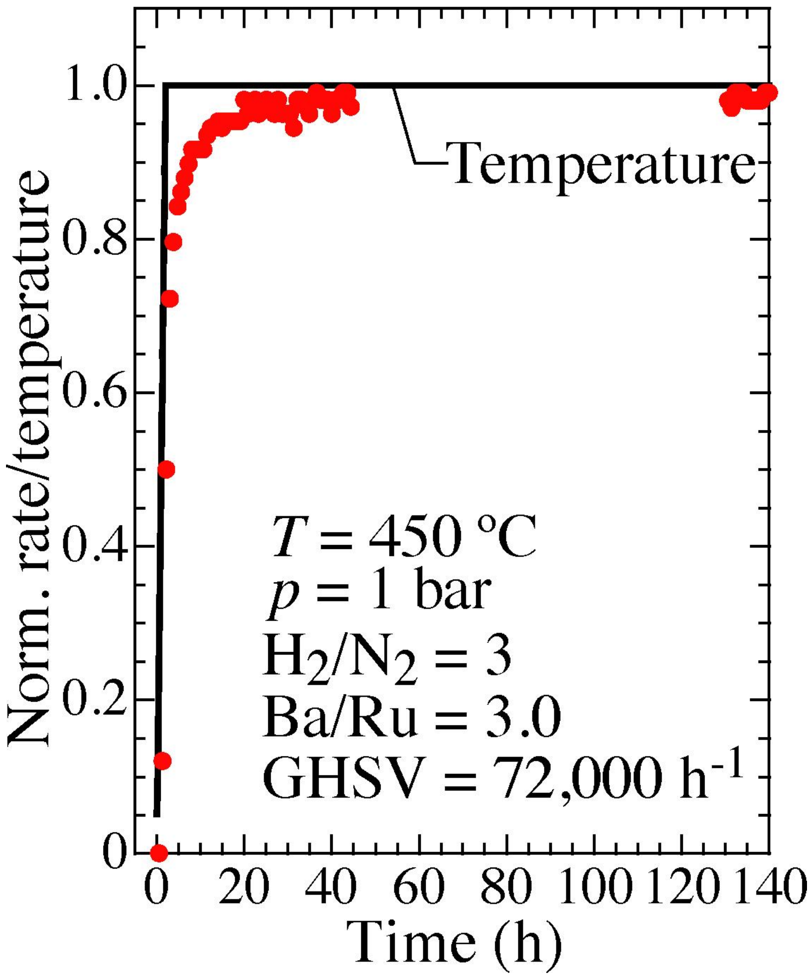
Catalyst studies typically done at GHSV ~ 10,000 h^{-1}

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**



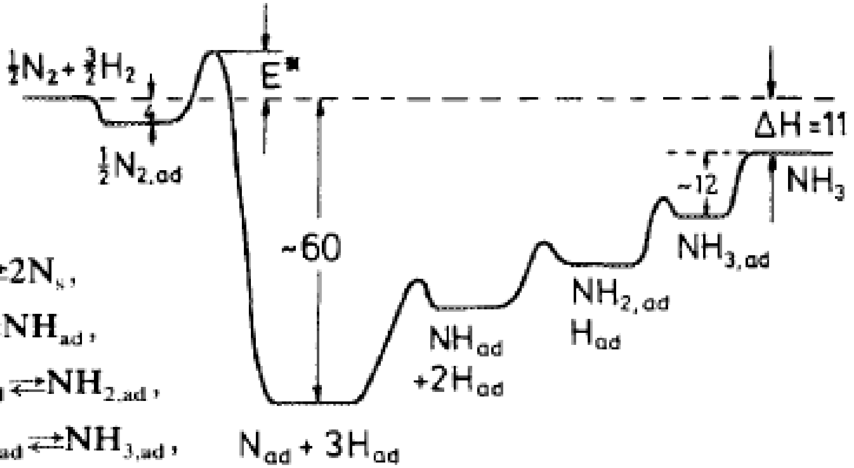


Microkinetic Model

Primary steps in catalytic synthesis of ammonia

G. Ertl

Journal of Vacuum Science & Technology A 1, 1247 (1983)



$H_2 \rightleftarrows 2H_{ad}$,

$N_2 \rightleftarrows N_{2,ad} \rightleftarrows 2N_s$,

$N_s + H_{ad} \rightleftarrows NH_{ad}$,

$NH_{ad} + H_{ad} \rightleftarrows NH_{2,ad}$,

$NH_{2,ad} + H_{ad} \rightleftarrows NH_{3,ad}$,

$NH_{3,ad} \rightleftarrows NH_3$.

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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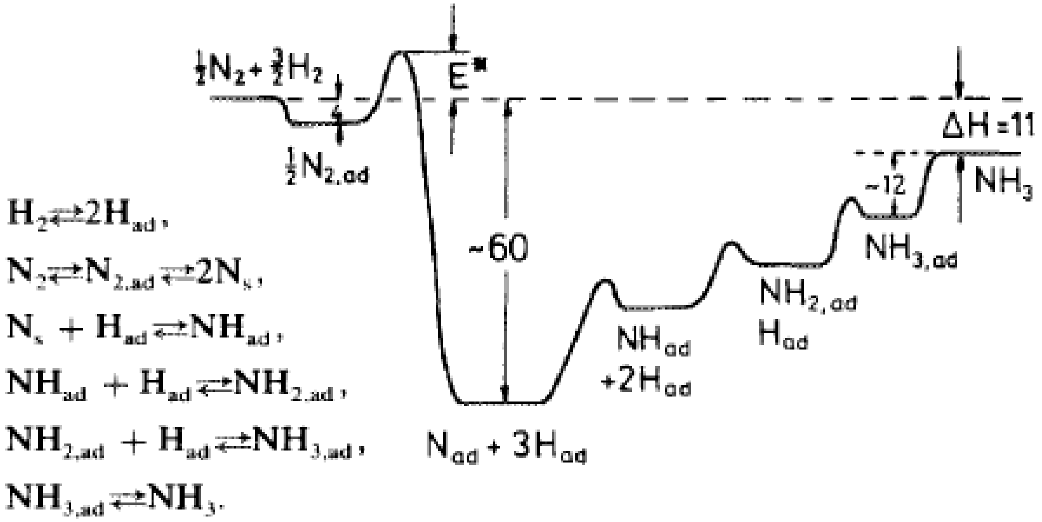


FIG. 8. Potential energy diagram illustrating the progress of the overall reaction. The activation energy E^* depends on surface structure and coverage. Energies in kcal/mol.

	Reaction	A (cm, s)	β	E ($kJ\ mol^{-1}$)
1	$N_2 + 2(Ru) \rightarrow N(Ru) + N(Ru)$ (Sticking coefficient)	2.892×10^{-06}	0.000	38.949
2	$N(Ru) + N(Ru) \rightarrow N_2 + 2(Ru)$	$2.015 \times 10^{+17}$	-0.279	$148.027 - 14\ \theta_{N(Ru)}$
3	$H_2 + 2(Ru) \rightarrow H(Ru) + H(Ru)$ (Sticking coefficient)	4.007×10^{-03}	0.000	0.0
4	$H(Ru) + H(Ru) \rightarrow H_2 + 2(Ru)$	$3.600 \times 10^{+20}$	0.658	$91.948 - 2\ \theta_{H(Ru)}$
5	$NH_3 + (Ru) \rightarrow NH_3(Ru)$ (Sticking coefficient)	1.247×10^{-05}	0.000	0.0
6	$NH_3(Ru) \rightarrow NH_3 + (Ru)$	$2.235 \times 10^{+11}$	0.083	83.536
7	$N(Ru) + H(Ru) \rightarrow NH(Ru) + (Ru)$	$8.424 \times 10^{+20}$	0.000	$83.620 - 7\ \theta_{N(Ru)}$
8	$NH(Ru) + (Ru) \rightarrow N(Ru) + H(Ru)$	$6.813 \times 10^{+19}$	0.207	$30.972 - 1\ \theta_{H(Ru)}$
9	$NH(Ru) + H(Ru) \rightarrow NH_2(Ru) + (Ru)$	$4.949 \times 10^{+19}$	0.083	75.236
10	$NH_2(Ru) + (Ru) \rightarrow NH(Ru) + H(Ru)$	$8.321 \times 10^{+19}$	-0.083	$15.767 - 1\ \theta_{H(Ru)}$
11	$NH_2(Ru) + H(Ru) \rightarrow NH_3(Ru) + (Ru)$	$3.886 \times 10^{+19}$	0.083	17.036
12	$NH_3(Ru) + (Ru) \rightarrow NH_2(Ru) + H(Ru)$	$1.478 \times 10^{+20}$	0.000	$64.980 - 1\ \theta_{H(Ru)}$

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

Effect of Pressure, Temperature, and H_2/N_2 Ratio

Optimal H_2/N_2 ratio

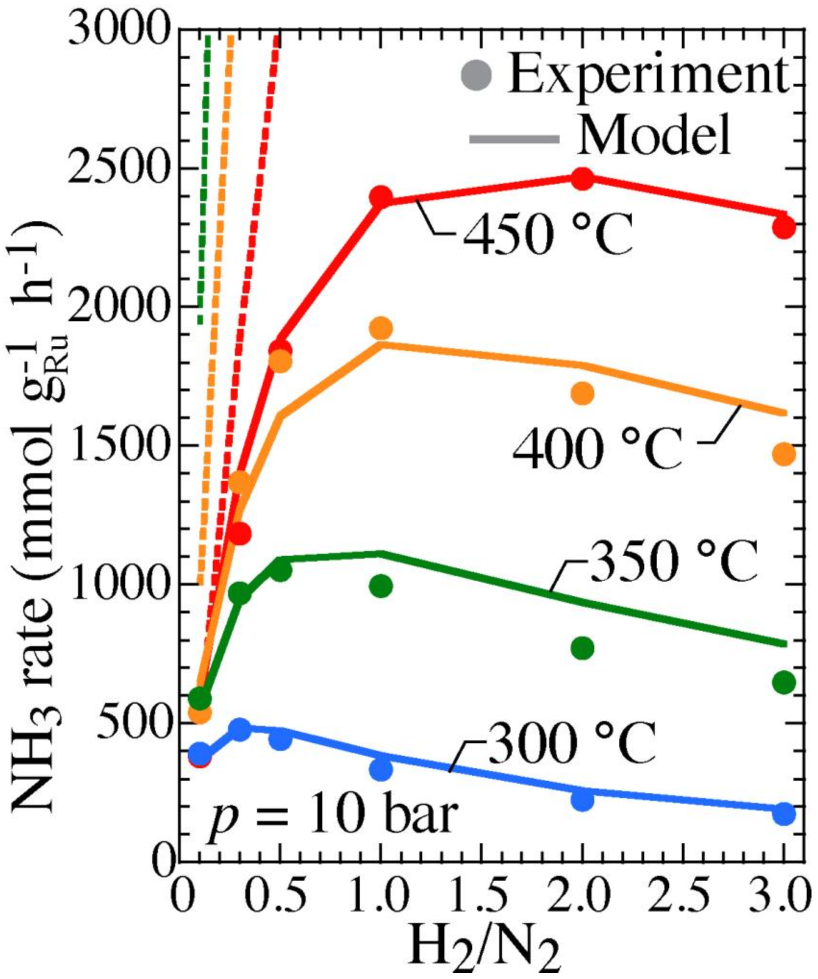
- less than stoichiometric
- Balance between N_2/H_2 adsorption
- Shift to stoichiometric at high T

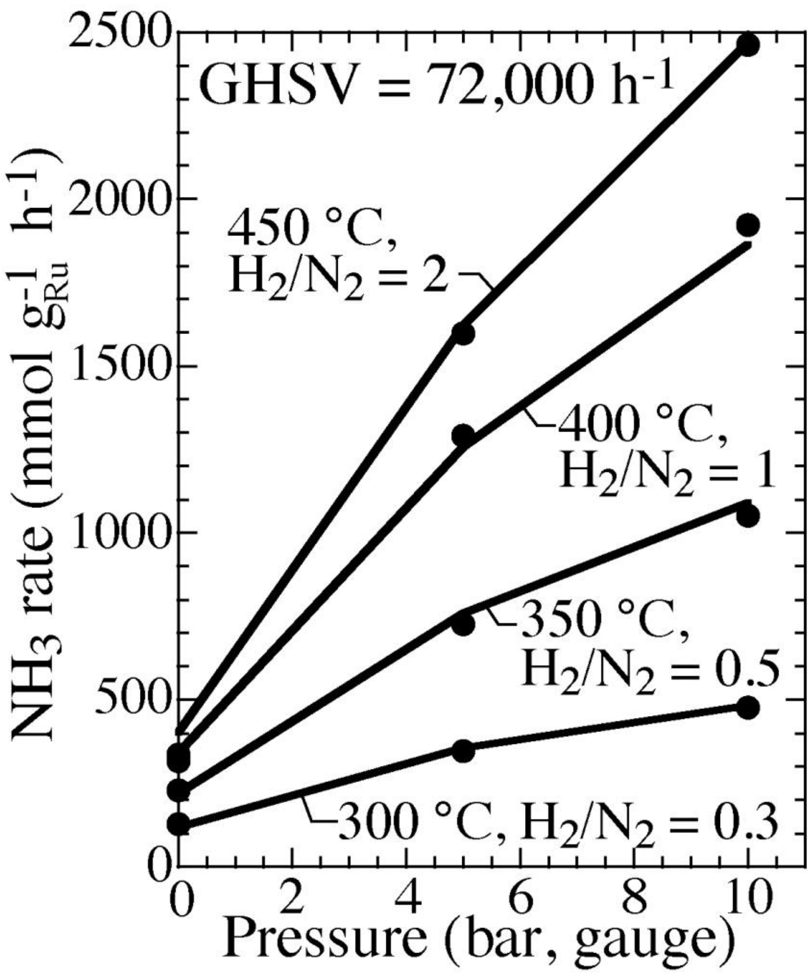
Pressure dependence

- ~linear at optimal ratio
- Significant rates as low as T = 300ºC

Membrane Synthesis

- Low T operation
- Low H_2/N_2 ratios beneficial for separation



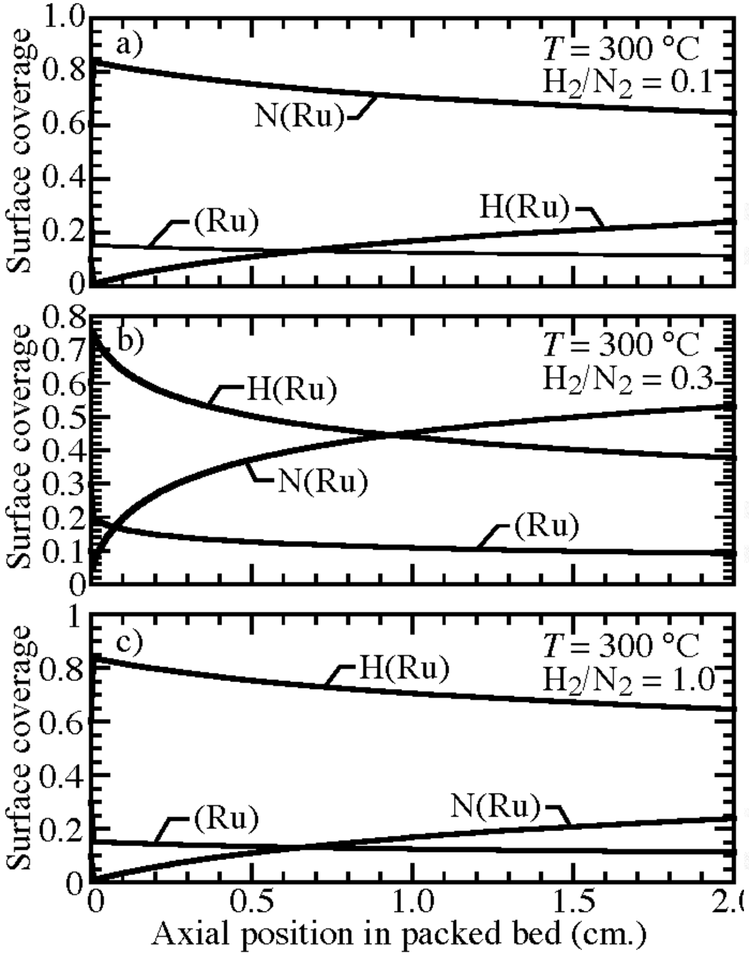


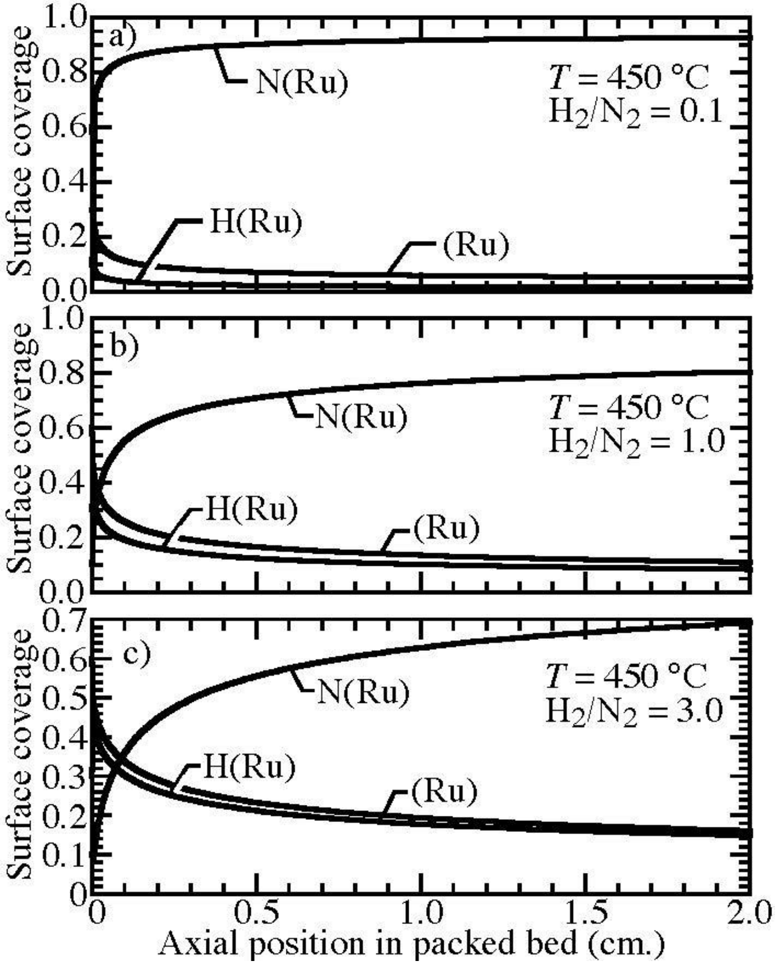
Models provide accurate predictions over wide operating conditions

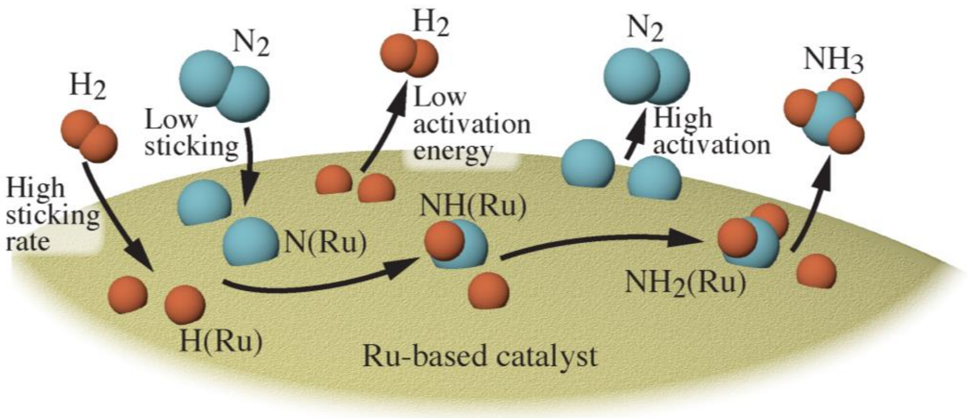
Competition between H_2/N_2 Adsorption

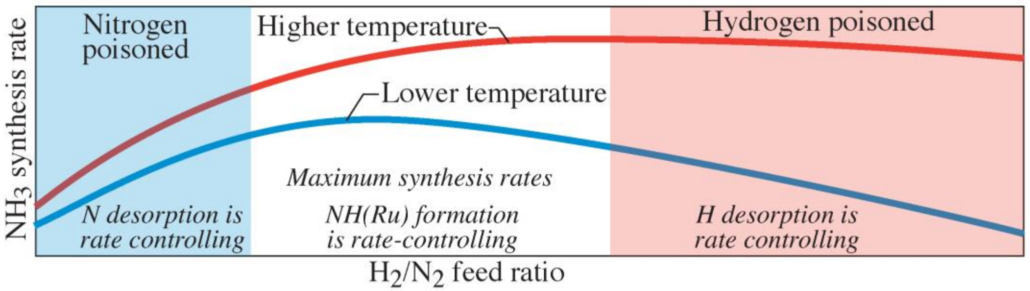
T = 300ºC

T = 450ºC

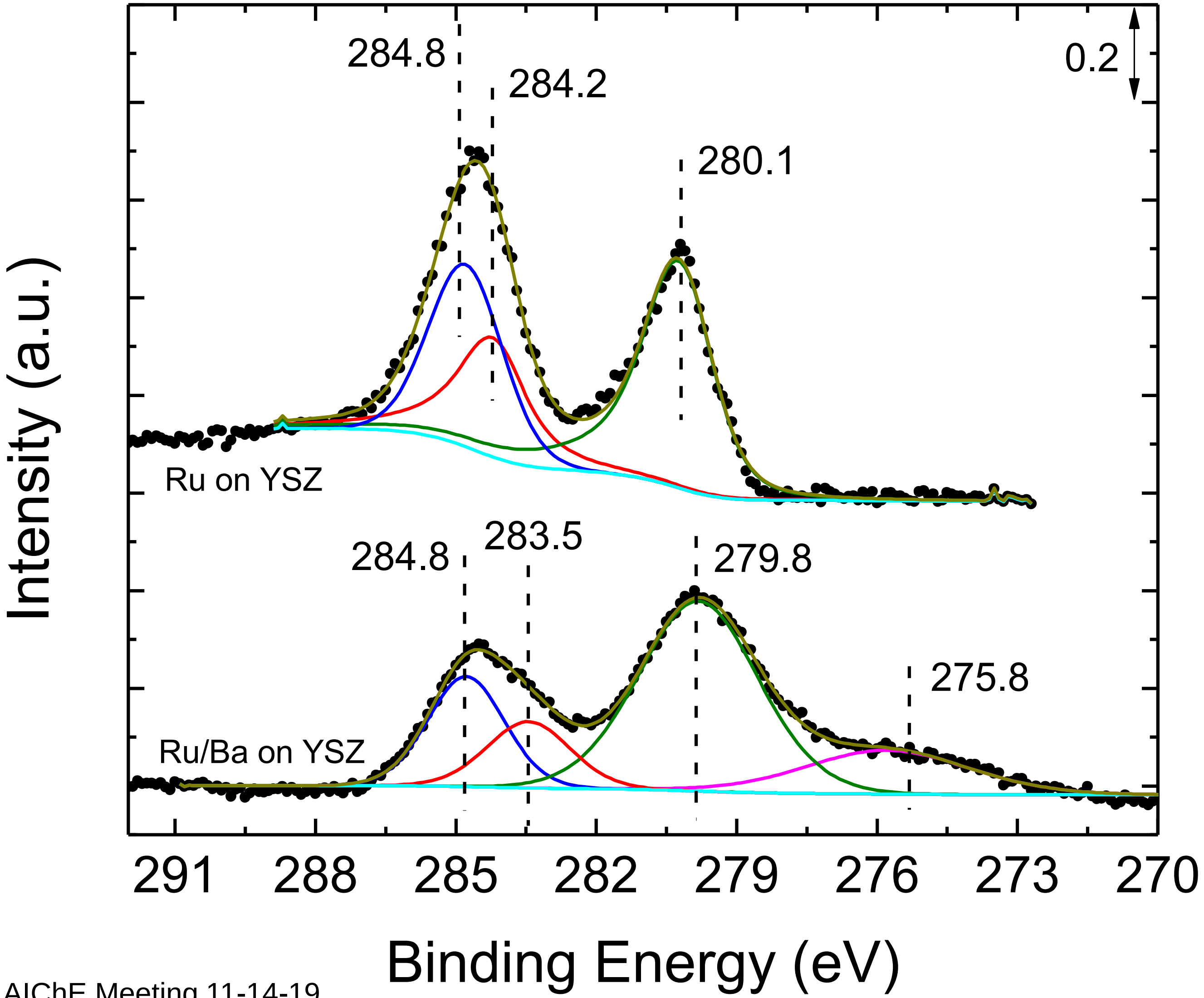








Role of YSZ, Ba: XPS



Ru 3d position

- Metal: 280.2
- YSZ: 280.1
- YSZ/Ba: 279.8

Peak @275.8 eV

- Ru-Ba Complex?
- Role?

Comparison with Literature

Support/ Promoter	wt. % Ru	T °C	P bar	H_2/N_2	GHSV ml $gcat^{-1}$ h^{-1}	Rate mmol gRu^{-1} h^{-1}	Reference
Pr_2O_3	5	400	10	3	18,000	380	Sato et al. *Chem. Sci.*, 8:674, 2017
Electride	1.2	400	10	3	18,000	667	Kitano et al., *Nature Chem.*, 4:934, 2012
$La_{0.5}Pr_{0.5}O_{1.75}$	5	400	10	3	72,000	1204	Ogura et al., *ACS Sus. Chem. Eng.*, 6:17258, 2018
Pr_2O_3	5	400	10	3	72,000	908	Ogura et al., *ACS Sus. Chem. Eng.*, 6:17258, 2018
$BaTiO_{2.51}H_{0.49}$	0.86	400	50.1	3	66,000	3349	Tang et al., Adv. Energy Mater., 8:1801772, 2018
$BaTiO_{2.51}H_{0.49}$	4.3	400	50.1	3	66,000	481	Tang et al., Adv. Energy Mater., 8:1801772, 2018
YSZ/Cs	0.46	400	10.8	3	4,222	372	Zhang et al., Present work
YSZ/Cs	0.46	400	10.8	1	4,222	615	Zhang et al., Present work
YSZ/Ba	1.05	400	10	3	72,000	1410	Zhang et al., Present work

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

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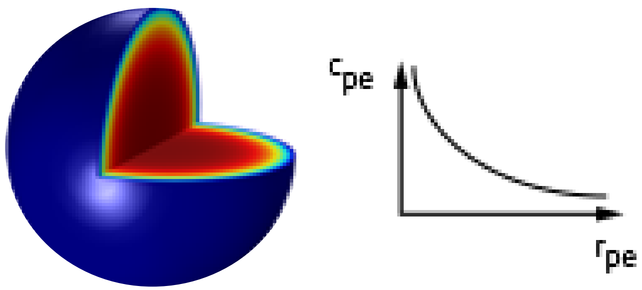
U.S. DEPARTMENT OF ENERGY

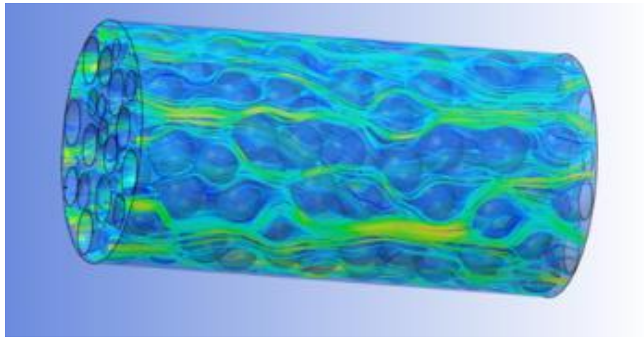
National Science Foundation
WHERE DISCOVERIES BEGIN

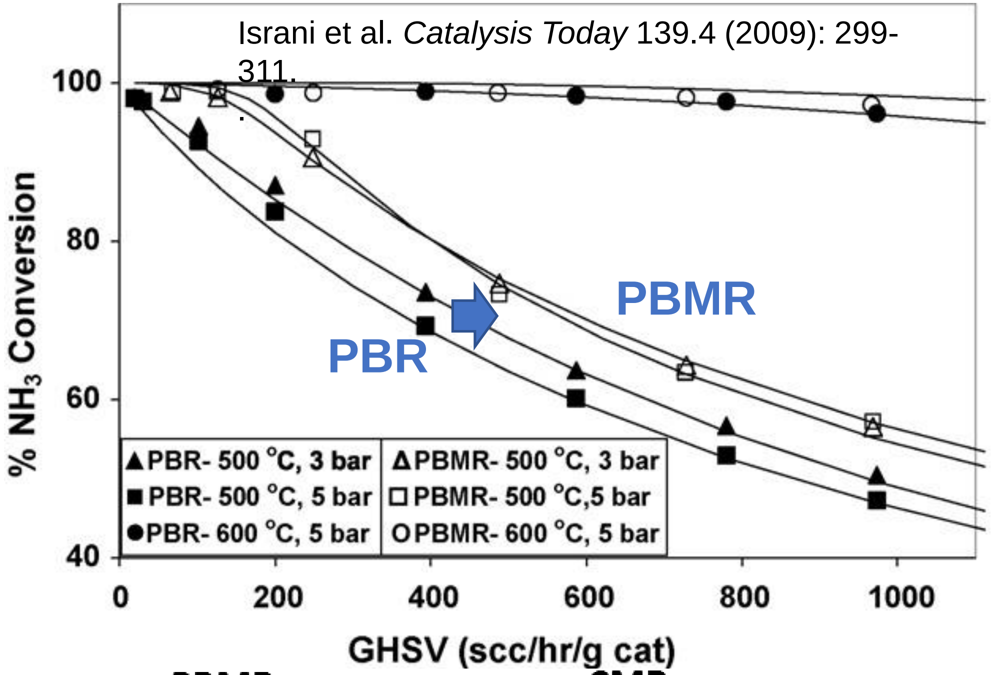
Catalytic Membrane Reactor (CMR)

Challenges with conventional PBMR

- Benefits rather limited
- Limited by poor transport

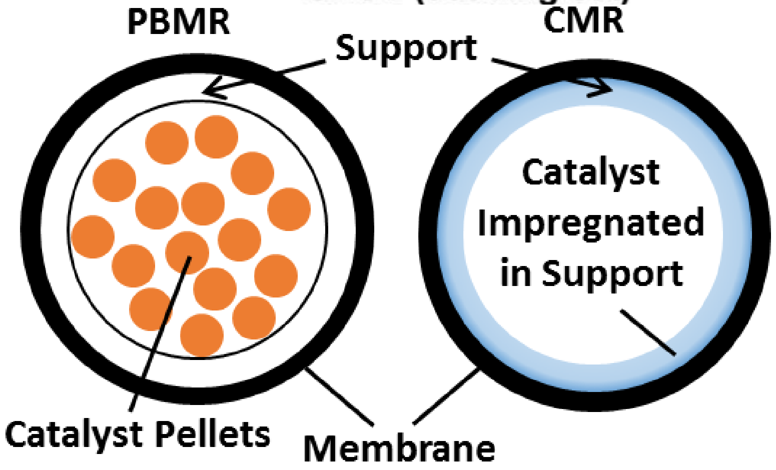




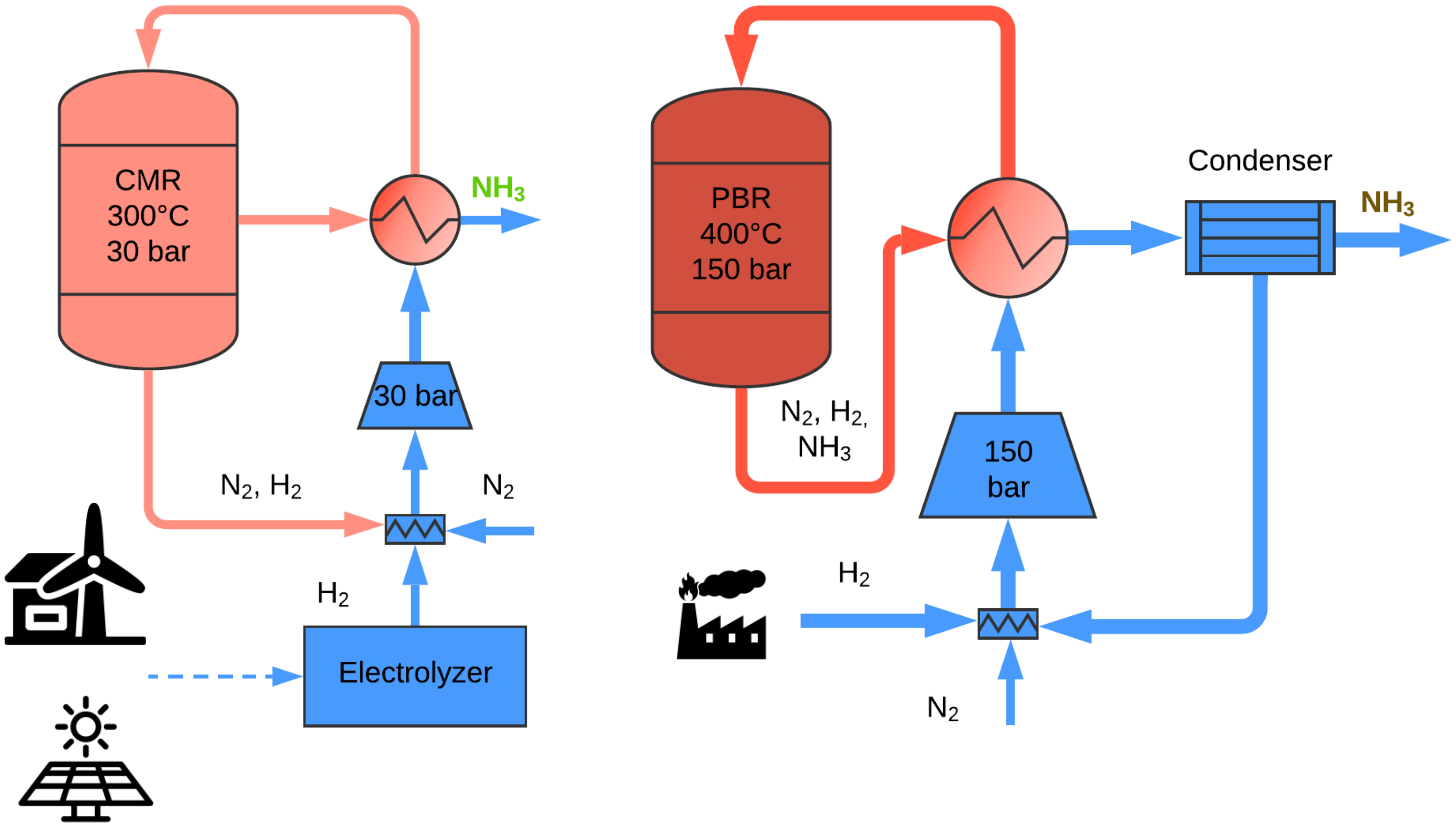


CMR: Catalyst impregnated in support

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



CMR: Ammonia Synthesis



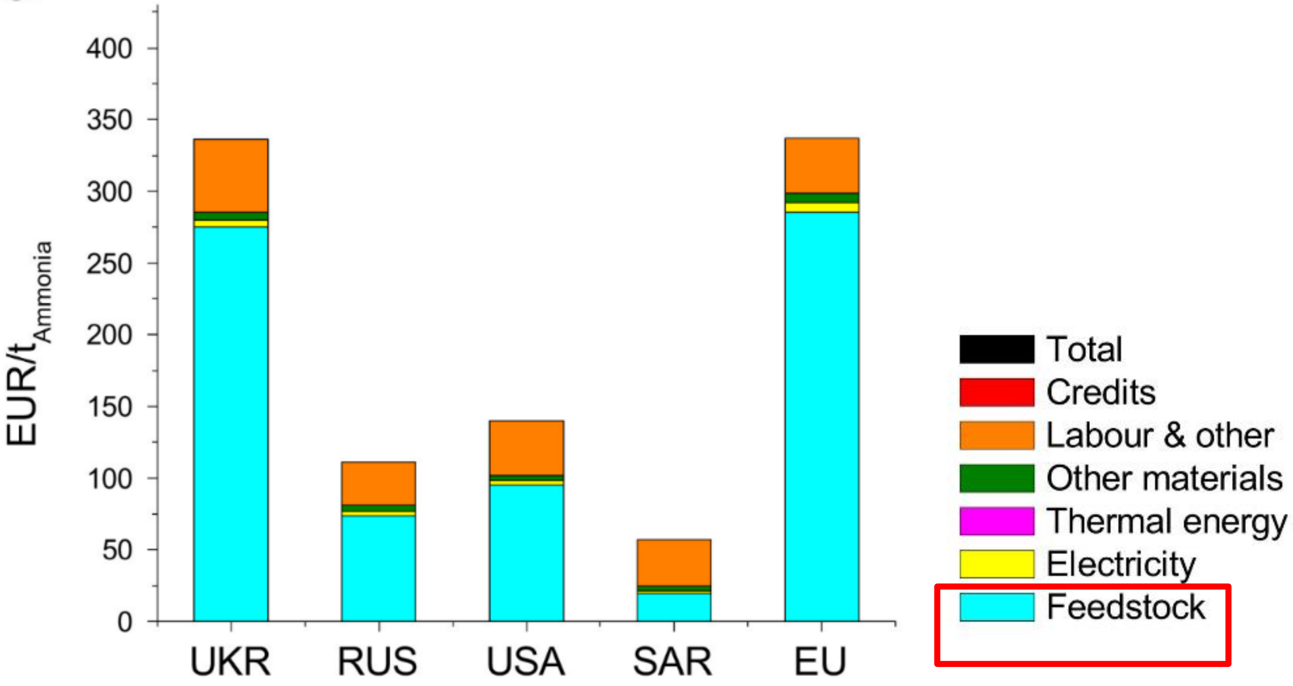
CMR vs Haber Bosch

- CapEx effective: less use of heat exchanger
- Less compressor: Low H_2/N_2 ratio enables less recycle stream

Ammonia separation along reaction enables:

- Increased synthesis rate: kinetics limited by ammonia adsorption
- Overcome thermodynamic limitations

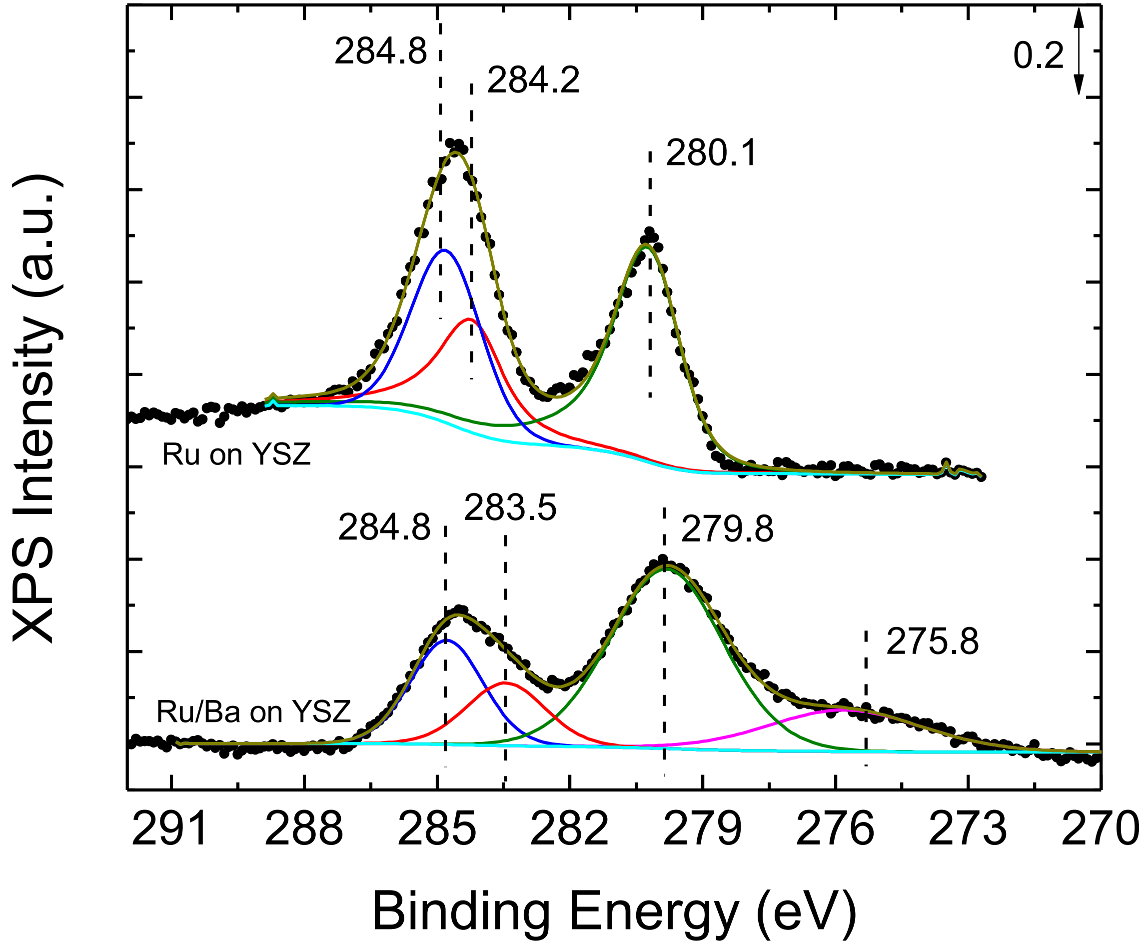
Reforming step dominates H_2 production cost

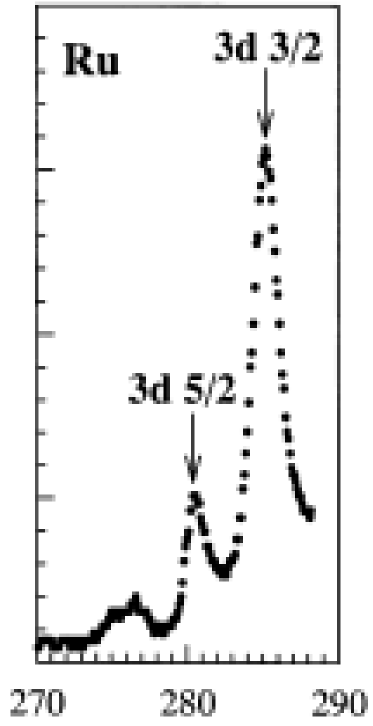


Reforming step (800-900°C, ~30 bar), >67% energy loss in NH_3 production

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

Role of YSZ, Ba: XPS



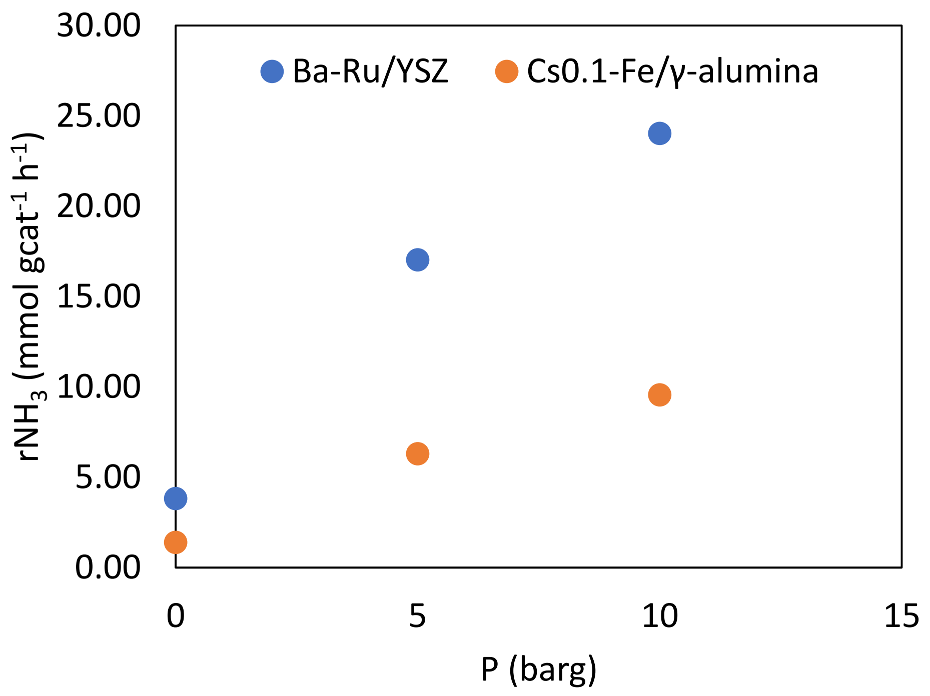


XPS spectrum of $NaBa_3Ru_2O_{10}$

Samata, Hiroaki, Amane Mishiro, Sadamasa Sawada, Yujiro Nagata, Takayuki Uchida, Masahiro Kai, Masao Ohtsuka, and Ming Der Lan. "Crystal growth and properties of new ruthenium oxides." *Journal of Physics and Chemistry of Solids* 59, no. 9 (1998): 1445-1452.

Comparison with Ba-Ru/YSZ

- Ba-Ru/YSZ 2X > Cs-Fe/γ-Alumina



Reaction conditions: 450°C, H_2/N_2 = 3

Catalyst	Ea (kJ/mol)
Ba-Ru/YSZ	**47.5**
Fe-YSZ	68.5
Fe/α-alumina	70.7
Fe/γ-alumina	73.1
Cs0.1-Fe/γ-alumina	**44.8**
Ba0.1-Fe/γ-alumina	51.7

Reaction conditions: 350 - 450°C, H_2/N_2 = 3, P = 10 barg

Cs-Fe/γ-Alumina: Effect of H_2/N_2

- Optimal H_2/N_2 doesn't shift with T