Dense Metallic Membrane Reactor Synthesis of Ammonia at Moderate Conditions and Low Cost

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NH3 Fuel Conference
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NH_3 Synthesis II

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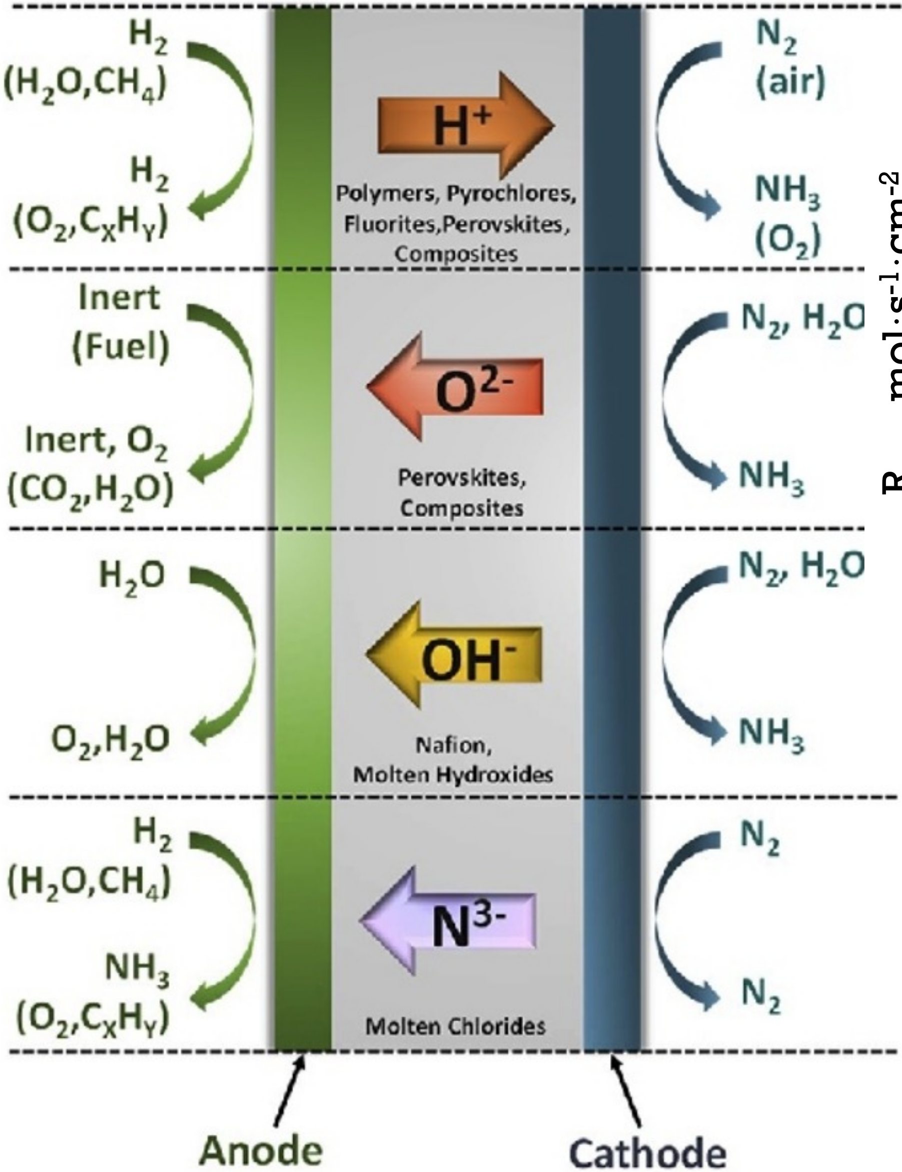
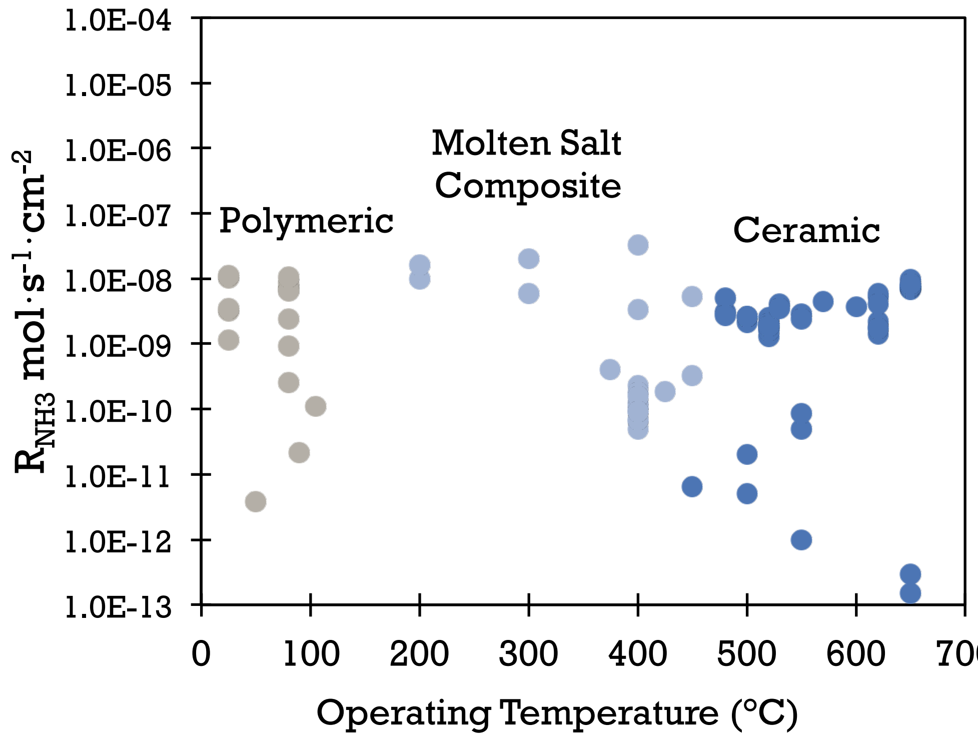
Overview

- Background
  - NH_3 Synthesis with Electrochemical Membrane
  - Dense Metallic Membranes
  - NH_3 Synthesis with Metallic Membranes
- Planar Group V Metals
- Tubular Pd Composites

Electrochemical Membranes

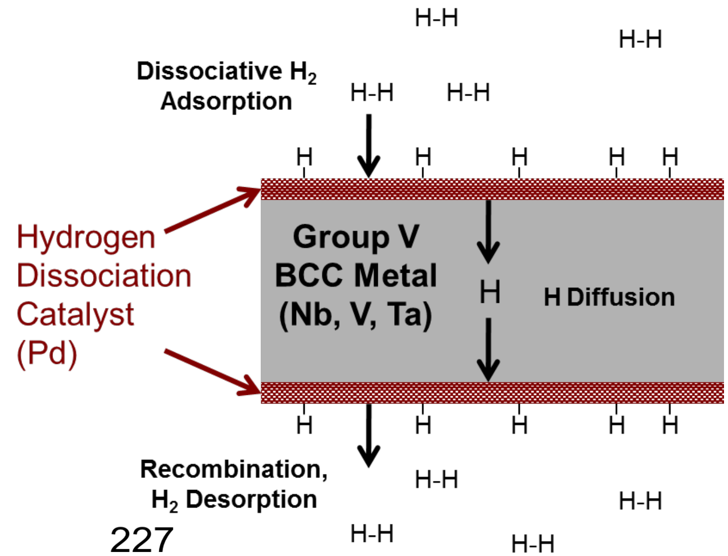


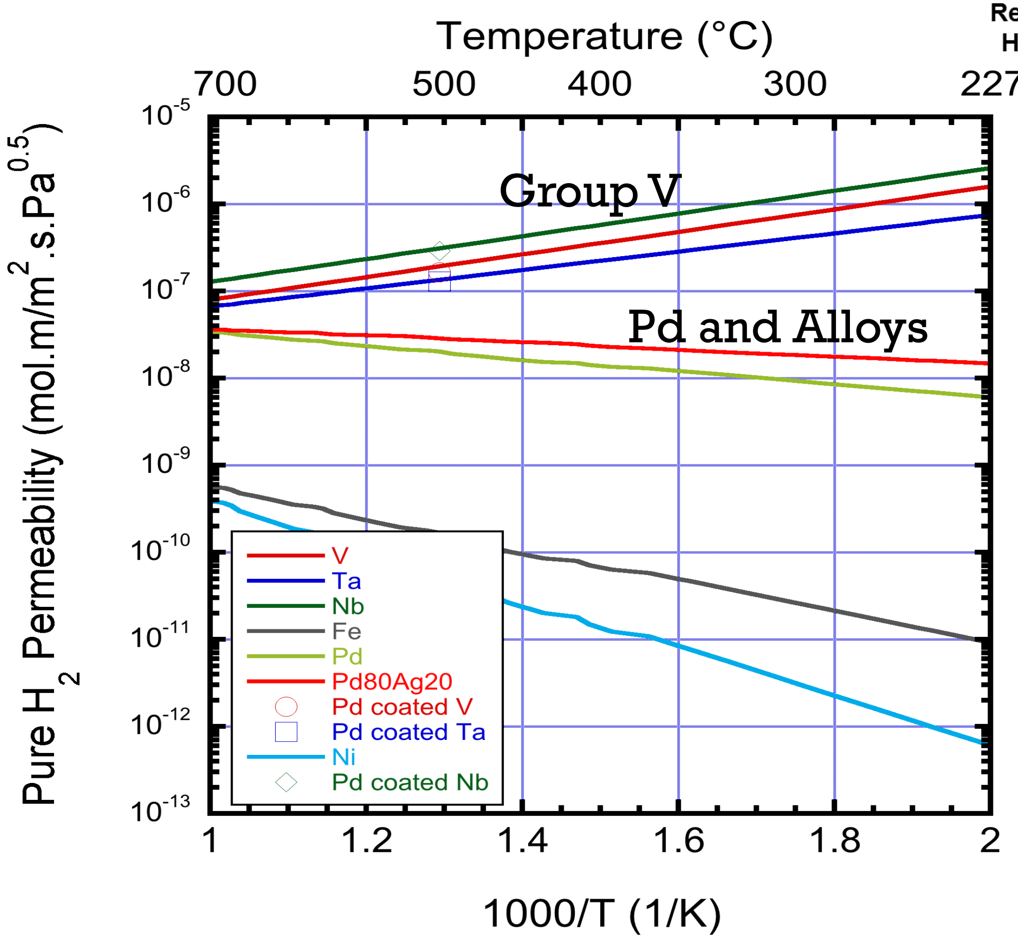


V. Kyriakou, I. Garagounis, E. Vasileiou, A. Vourros, M. Stoukides, *Progress in the Electrochemical Synthesis of Ammonia.* Catalysis Today, 2017. **286**: p. 2-13.

Dense Metals

- High H_2 permeability/flux
- Wide temperature range
- Very high theoretical selectivity
- Source of atomic H

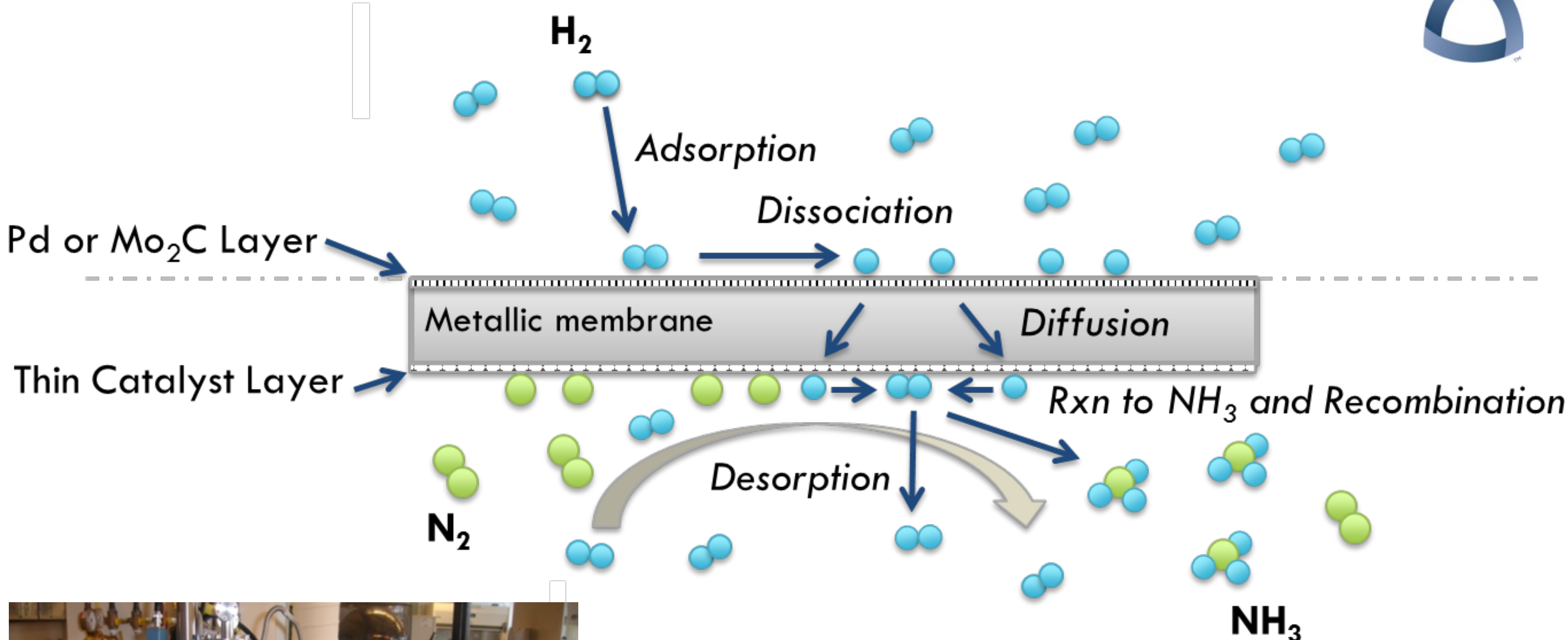




	Comparison of Membrane Cost	
Metal-alloy (wt %)	Alloy Metal Price (US$/ oz)	Membrane Cost (Alloy/ Pure Pd)
Pd	786.5	1.00
Pd-27Ag	17.95	0.74
Pd-20Au	1235.8	1.11
Pd-39Cu	0.19	0.61
V	68*	0.09
Nb	5.6*	0.007
Ta	140*	0.18

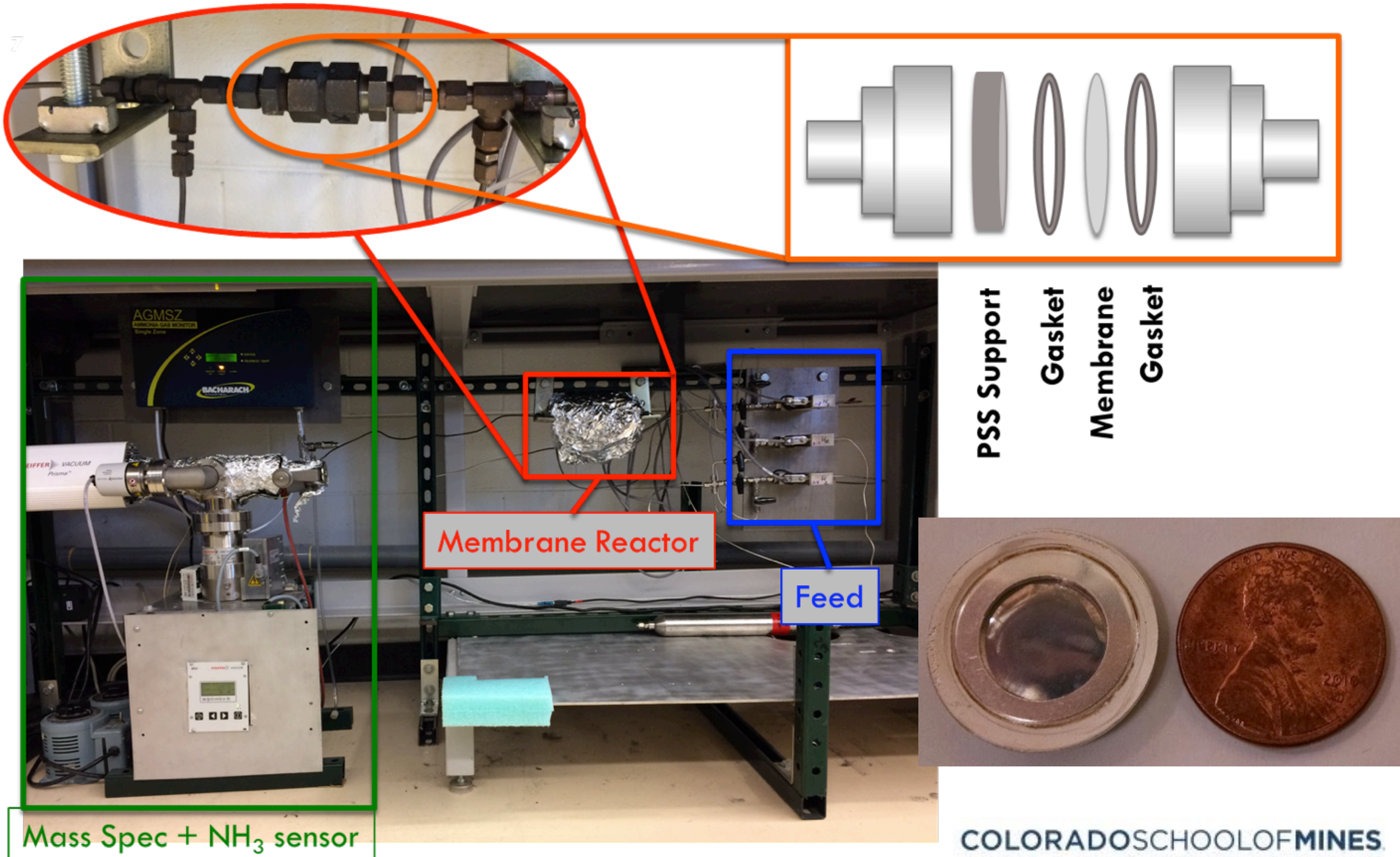
*Estimated from ore price March, 2017

NH_3 Synthesis with Metallic Membranes



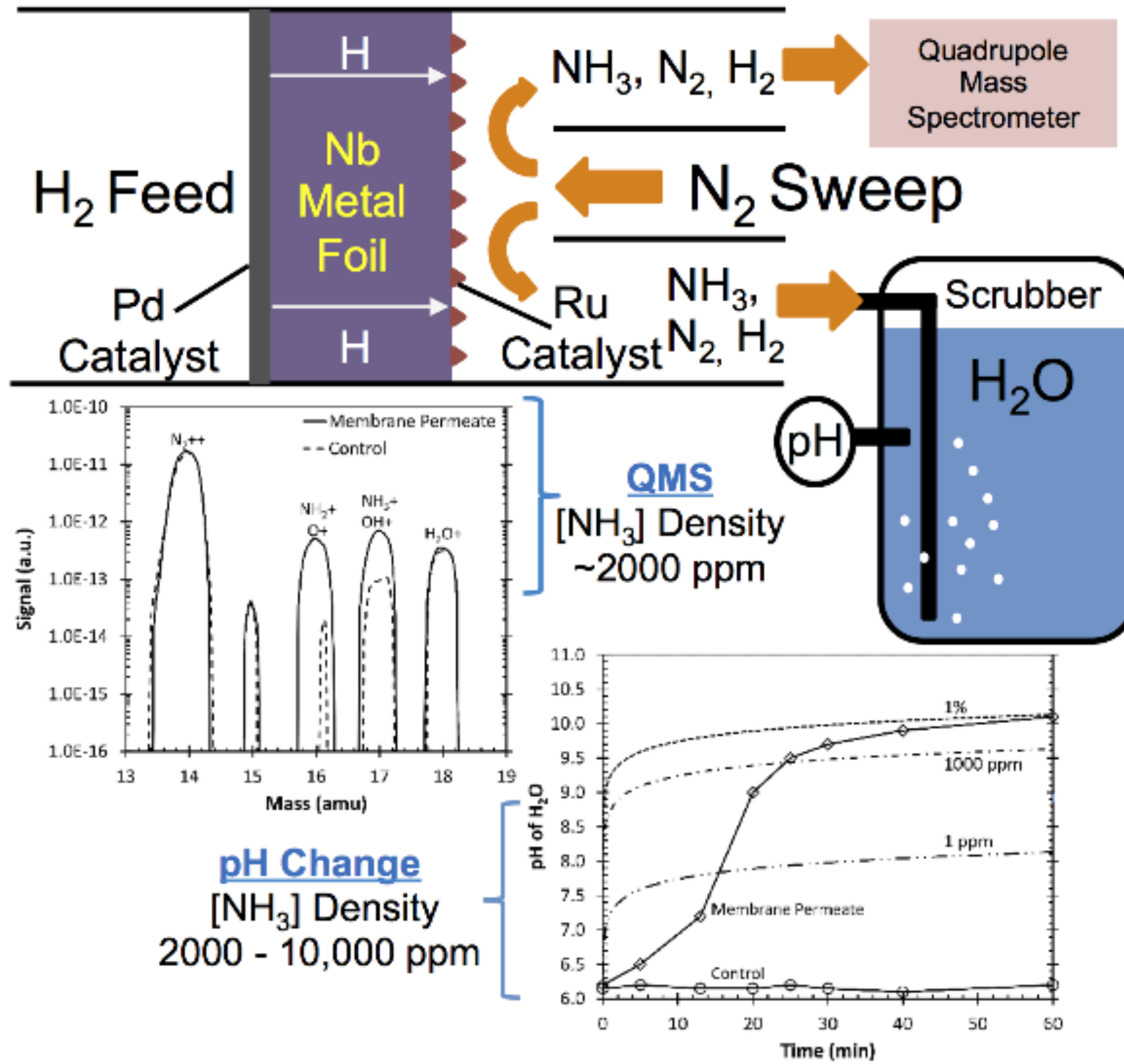
- Decouple N_2 and H_2 dissociation reactions by providing atomic hydrogen to reaction zone by permeation
- H_2 preferentially adsorbed, so gas phase H_2 inhibits the dissociation of N_2, reducing rate

Planar Group V Metals – VCR Module

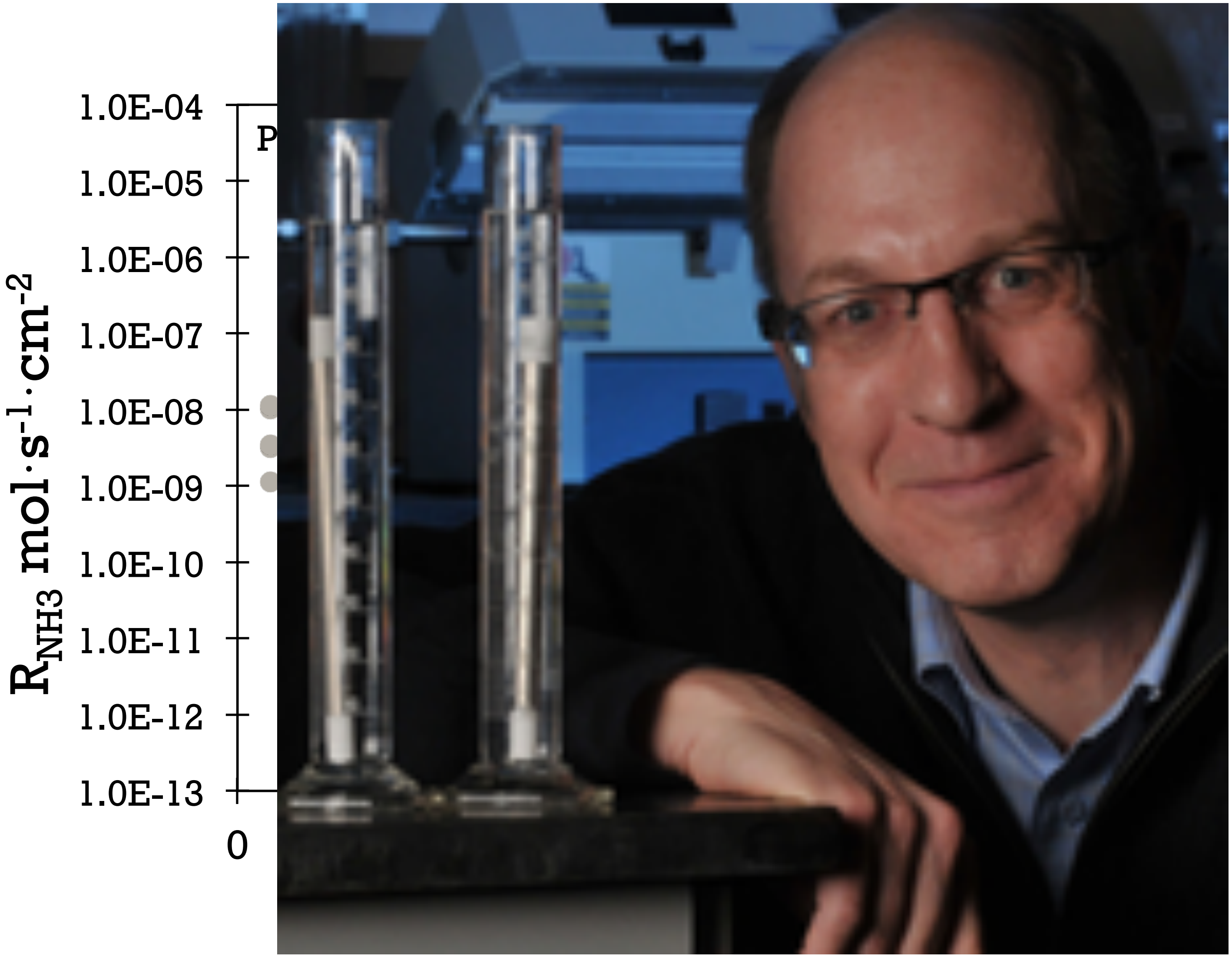


Preliminary data for NH_3 synthesis

- 100 nm Pd on 50 μm Nb foil membrane in Swagelok® VCR cell
- Ru sputtered on NH_3 synthesis side-low coverage
- NH_3 detection by MS and pH change
- Conditions: T = 500°C, P = 0.8 atm
- Rate: $6 \cdot 10^{-9}$mol/cm^2.s



Planar Group V Metal NH_3 Synthesis



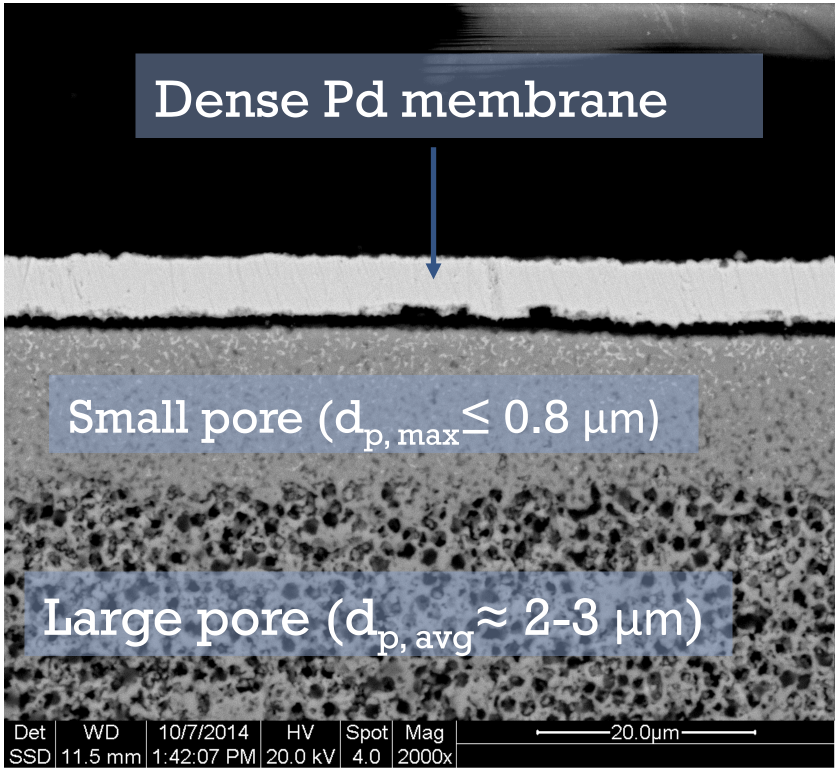
Base Metal:
V and Nb Foils

H_2 Catalyst
100 nm Pd
20 nm Mo_2C

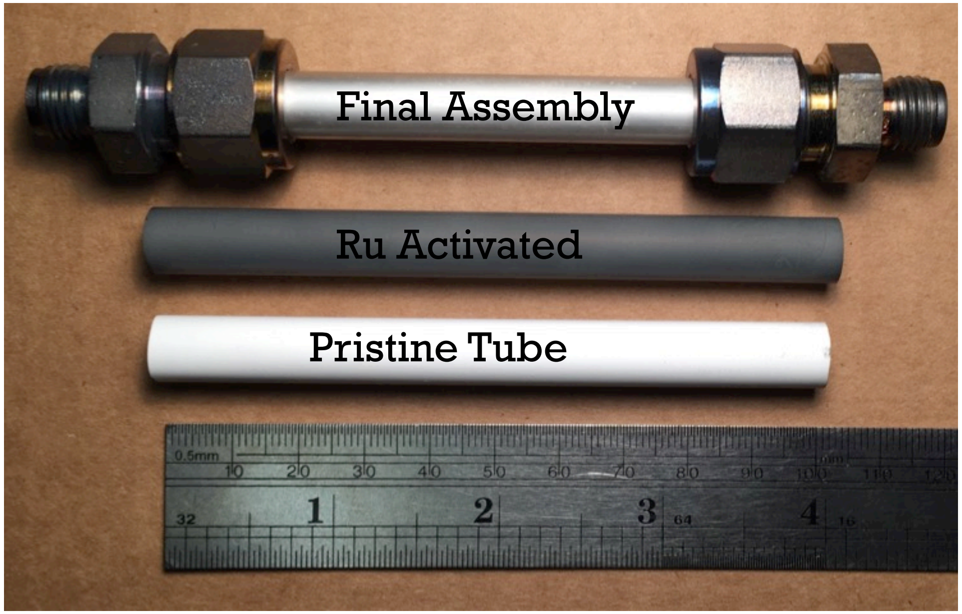
N_2 Catalyst
Ru, Mo_2C, Nb,
Ru/Mo_2C

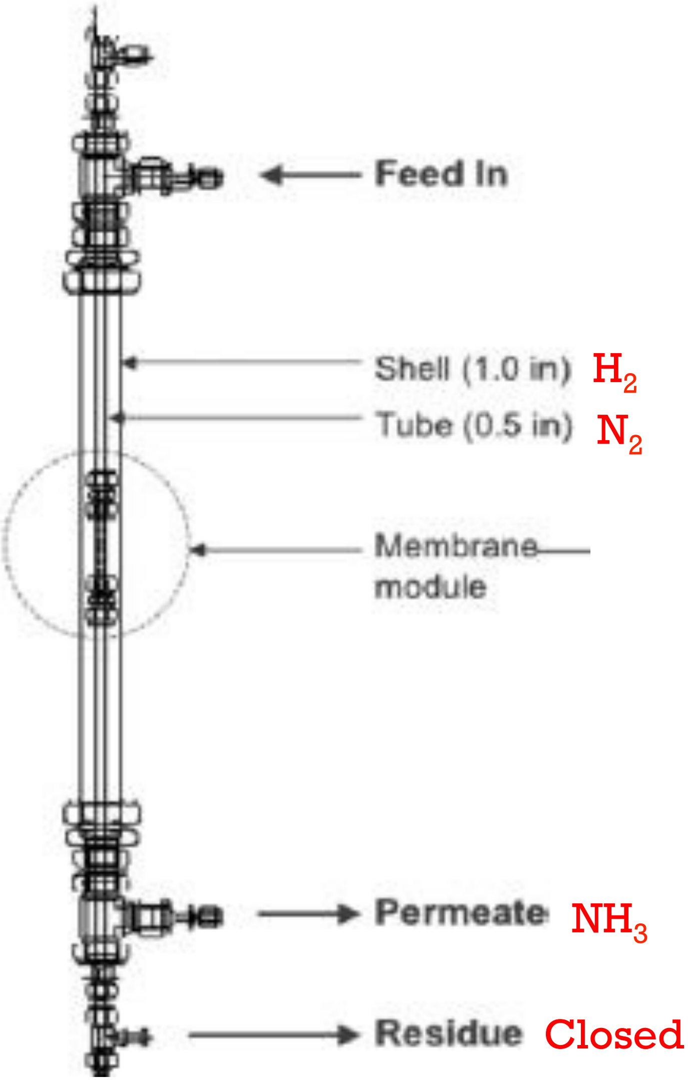
Tubular Pd Composite Membranes

- Substrate:
  - Tubular ceramic support
  - Asymmetric design
- Pd membrane:
  - Ru activated w/ & w/o Cs promoters
  - Pd electroless plating
    - 5-10 μm



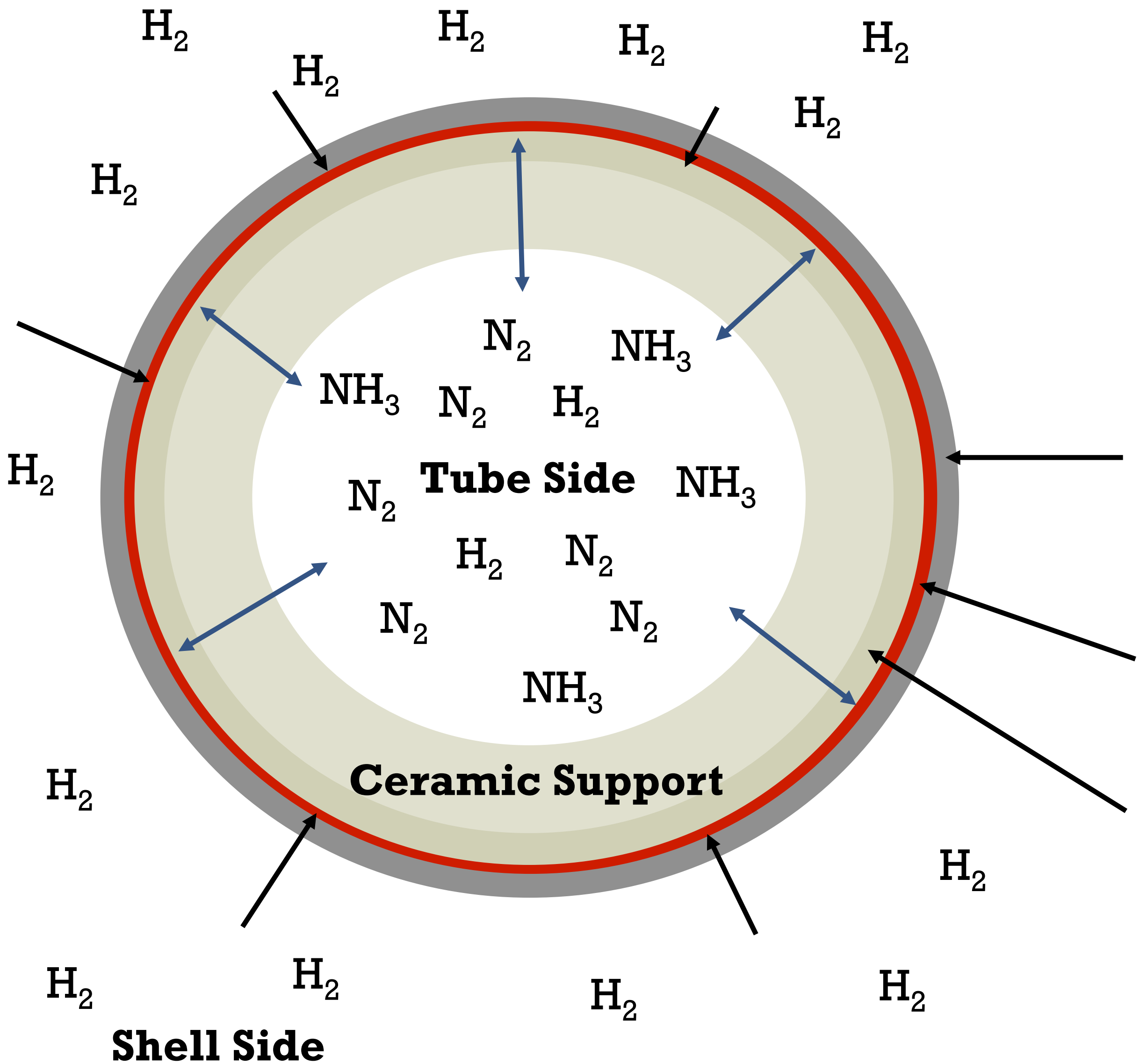
Tubular Pd Membrane NH_3 Synthesis





- Spray $RuCl_3$ solution on external surface
- Reduce in H_2 at 450 C 24 hours
- Electroless plate Pd
- Mount membrane into Swagelok fittings
- Insert into shell-and-tube reactor module

Tubular Membrane Reactor Specs



Diameter
- 1 cm

Active Length
- 8.9 cm

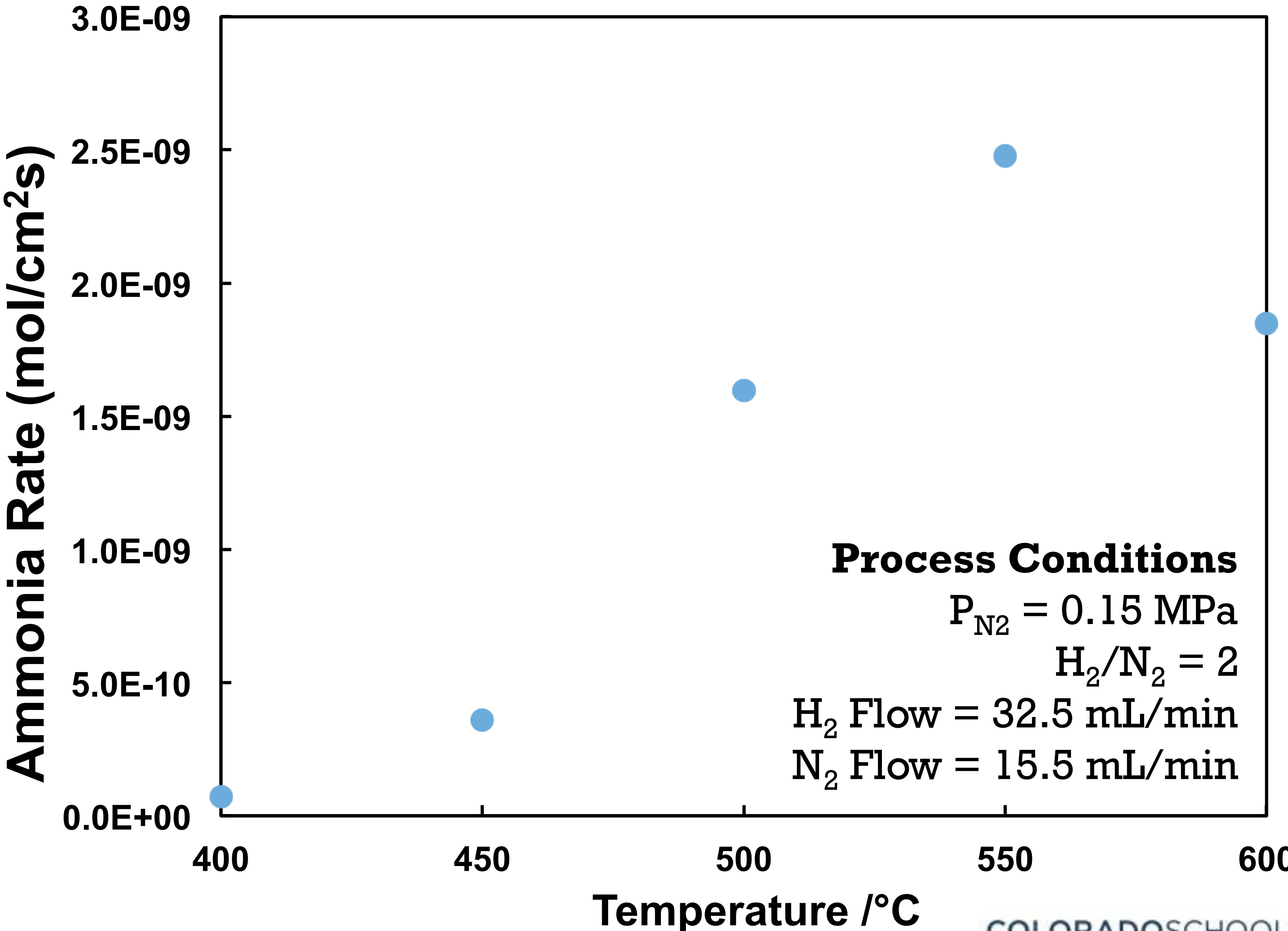
Active Surface Area
- 28 cm^2

Pd Layer
- 9.4 μm
- 317 mg

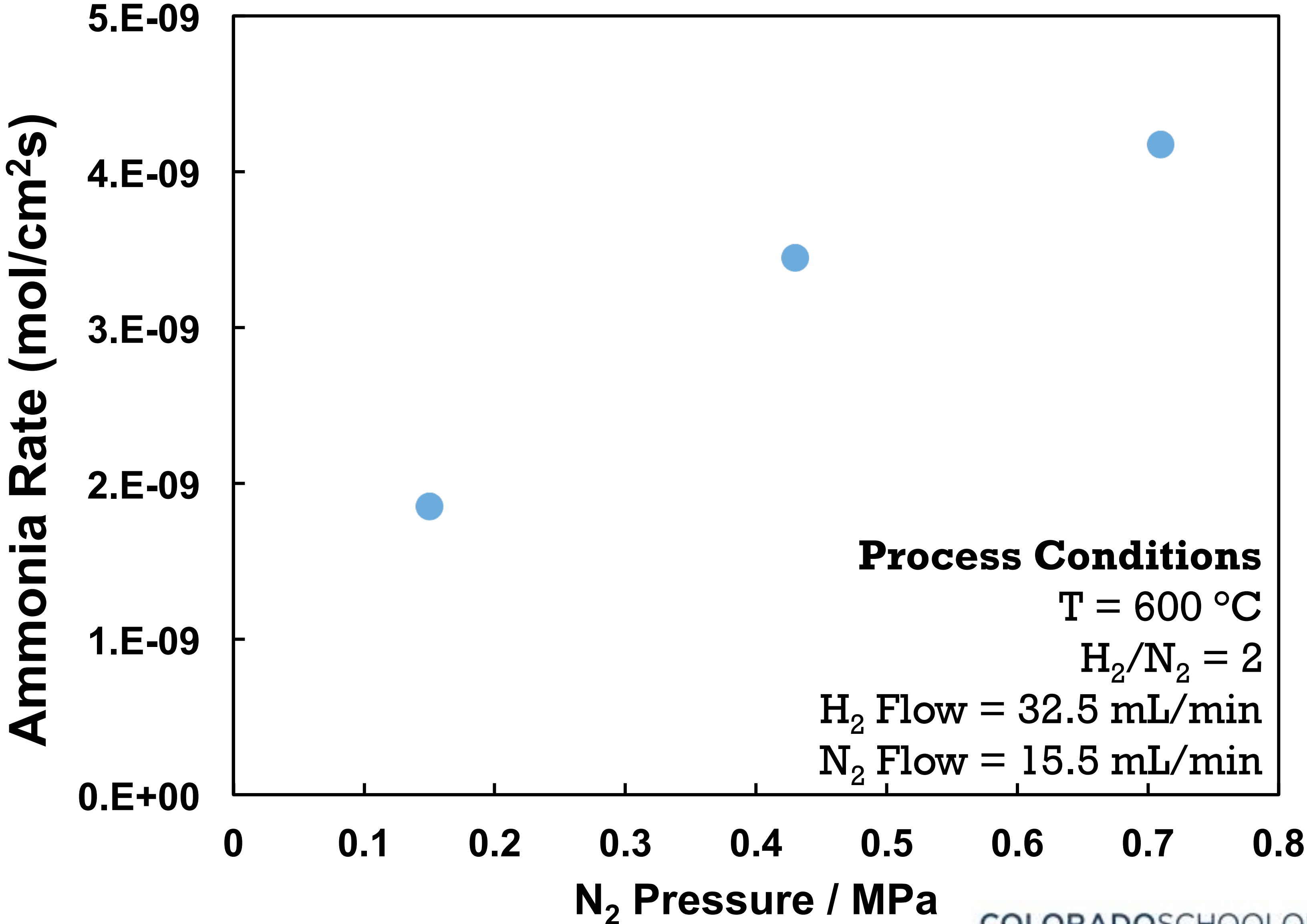
Ru Catalyst
- 6.6 mg

Cs Promoter
- 6.8 mg

Pd/Ru – Thermal Effects



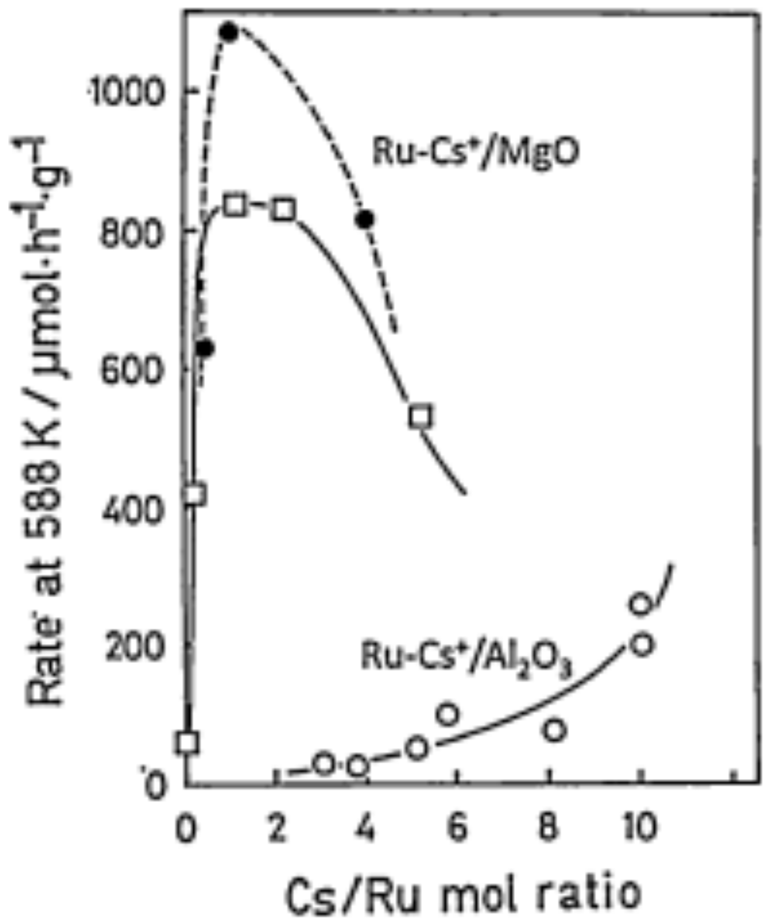
Pd/Ru – Pressure Effects



Alkaline Promoters

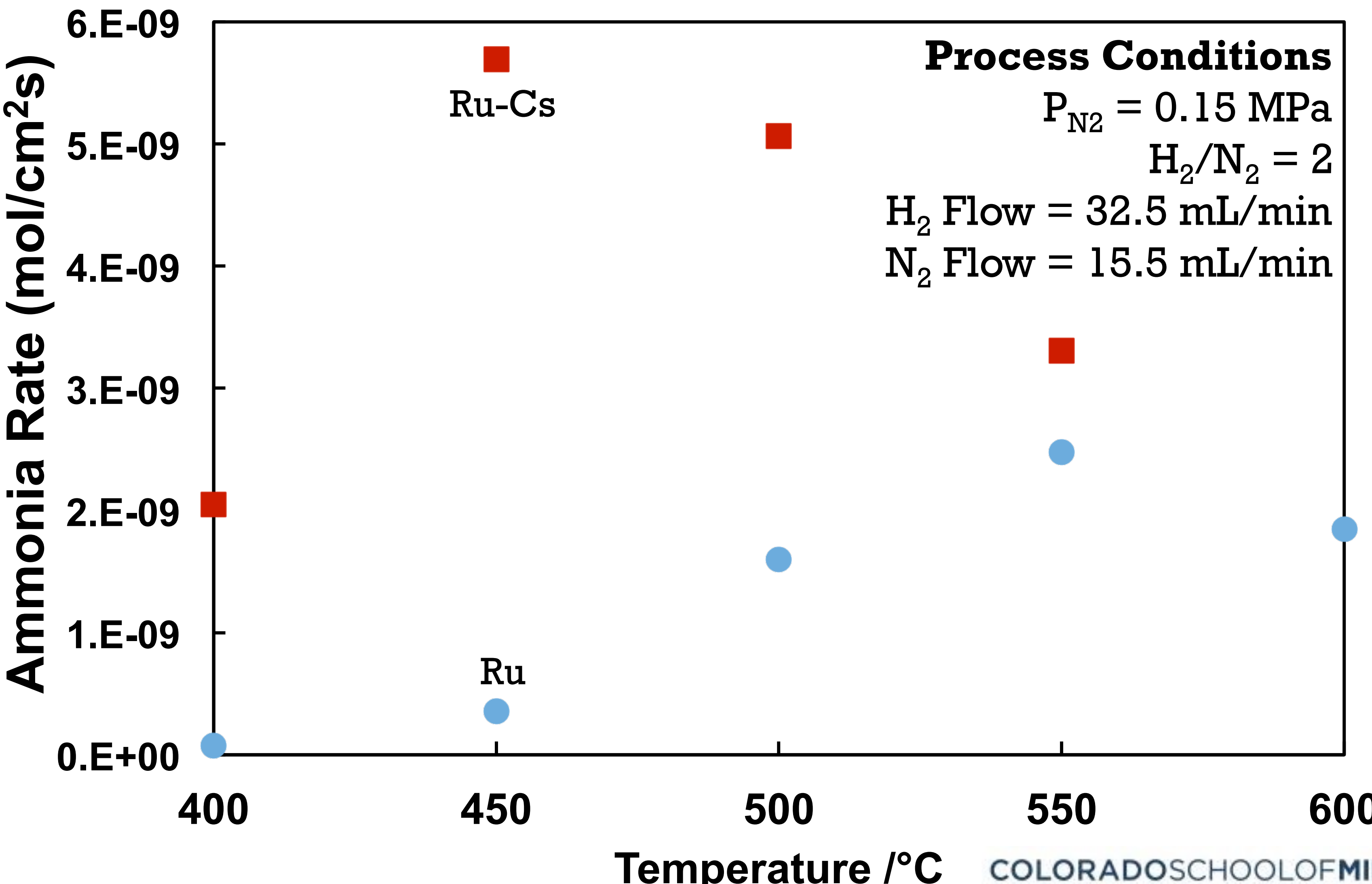
- Cs Impregnation
  - Pd/Ru membrane capped
  - Filled with $CsNO_3$ solution 30 min
  - Dried at 130 °C
  - Reduced at 450 °C ambient UHP H_2 for 24 hours

6.4 mg Cs
1.4:1 Cs-Ru Mole Ratio

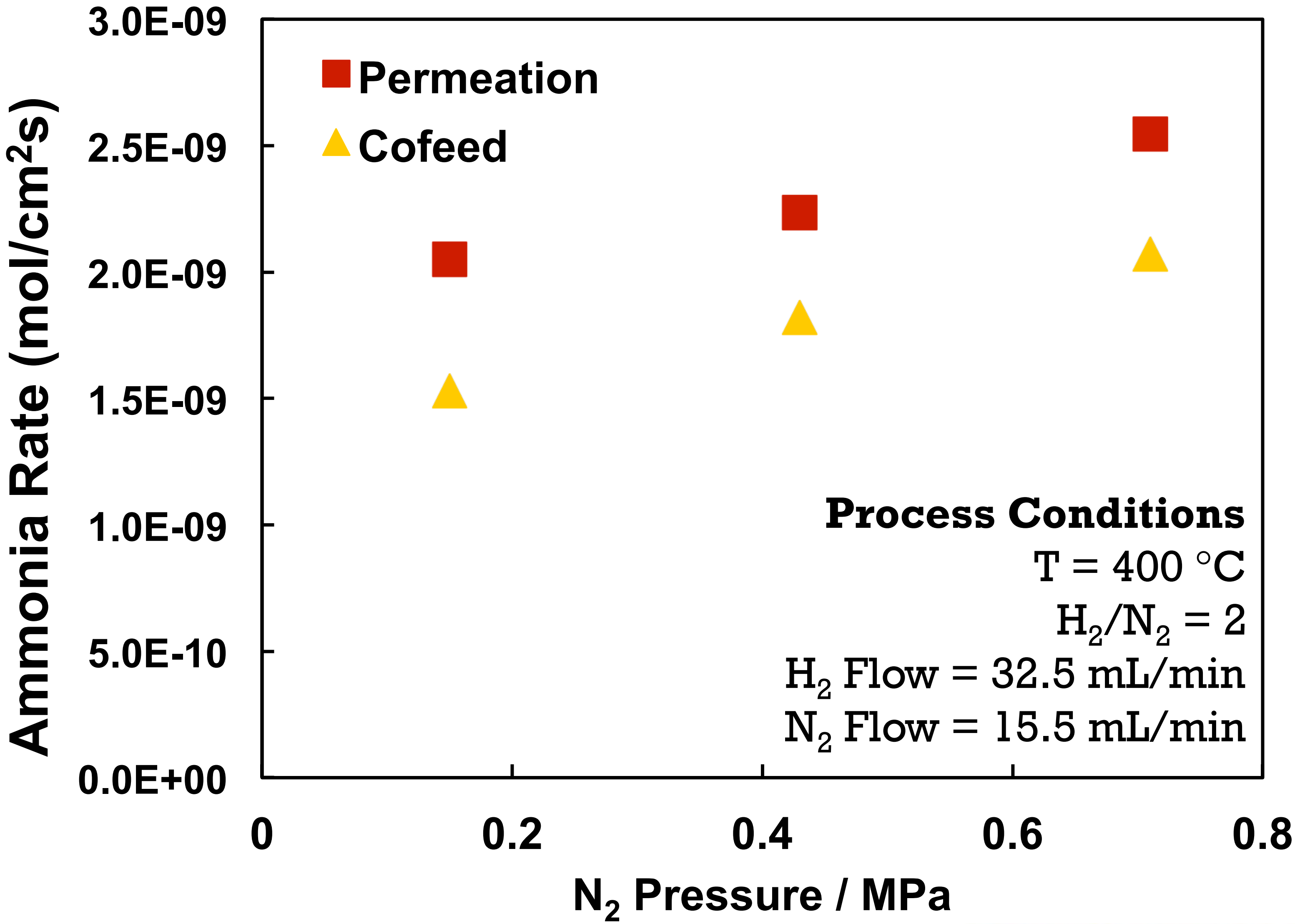


K. Aika, *Role of alkali promoter in ammonia synthesis over ruthenium catalysts – Effect on reaction mechanism.* Catalysis Today, 2013, 286 p: 14-20

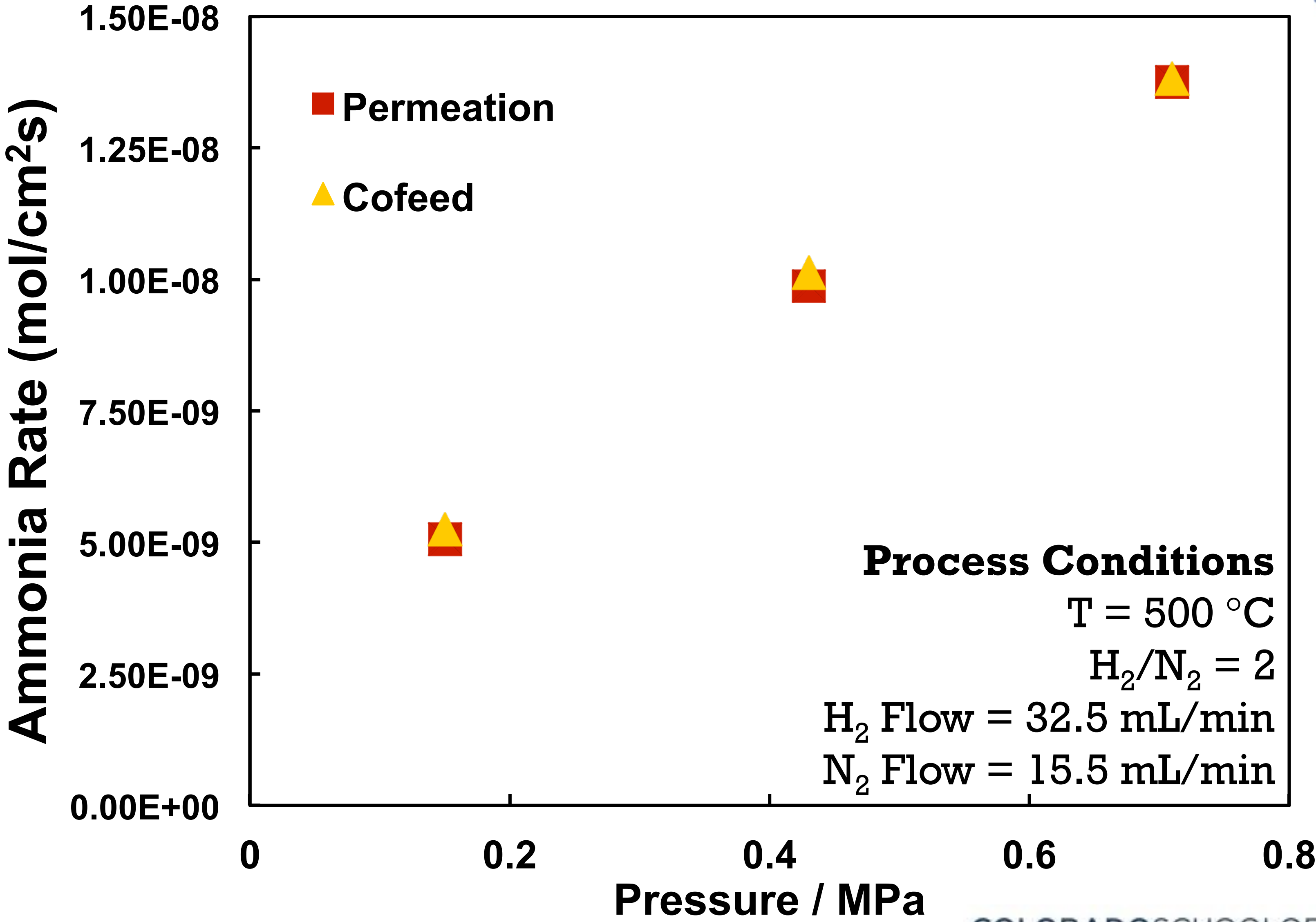
Pd/Ru-Cs - Thermal Effects



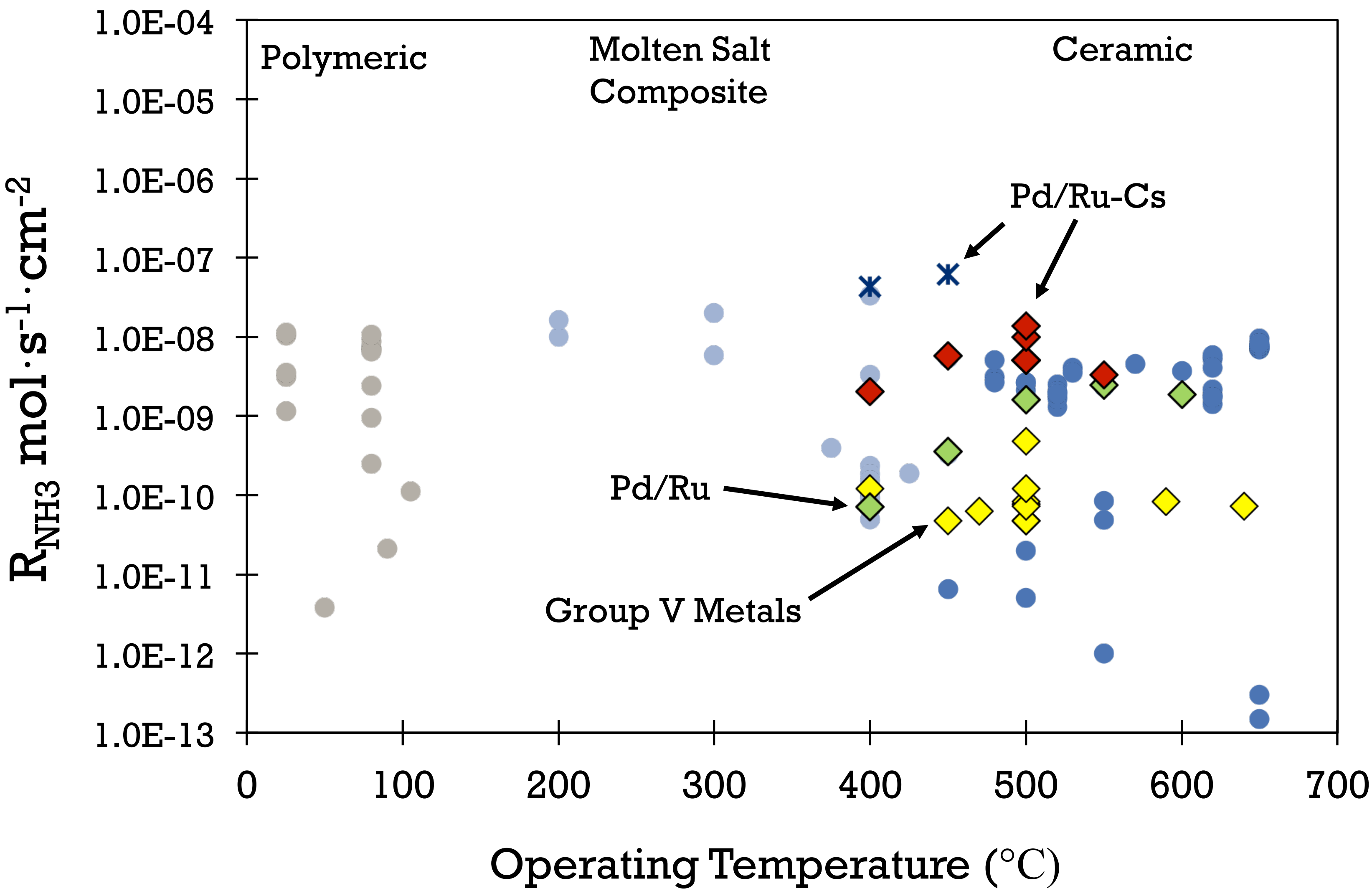
Pd/Ru-Cs – Pressure Effects 400°C



Pd/Ru-Cs – Pressure Effects 500°C



Membrane Comparison



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Conclusions

- Low rates measured with planar Group V metals
- Pd composites offer high surface area supports
- Addition of Cs promoters improves rate at lower temps
- Enhancements up to 34% for MR configuration versus cofed reactor

Dense metallic H_2 membrane reactors promising for NH_3 synthesis

Acknowledgments

- Membrane Research Group
  - Prof. Colin Wolden
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  - Dr. Sean-Thomas Lundin
  - Zhenyu Zhang

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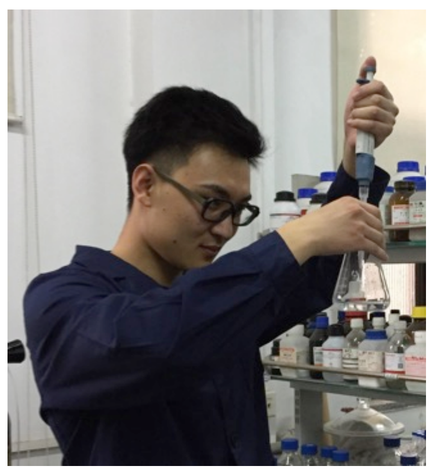
CHANGING WHAT'S POSSIBLE



Extra Slides

Future work NH_3 synthesis

- Design novel membrane configuration to maximize contact of catalyst to metallic membrane
- Some possibilities from ceramic filter manufacturers
  - http://www.tami-industries.com/industrial-products/inside-ceramtm/
  - High surface area/volume ratio, $\leq 1000\ m^2/m^3$

External diameter (mm): ø 25 | ø 41

External diameter Ø 25 L=1178 mm*							
Number of channels:	07	08	11	19	23	39	93
Hydraulic diameter:	6	6	4.6	3.5	3.5	2.5	1.6
Area (sqm):	0.16	0.20	0.25	0.25	0.35	0.50	0.60
Available cut-offs**:	MFT/UF/ Fine UF	MFT/UF/ Fine UF	MFT/UF	MFT/UF/ Fine UF	MFT/UF/ Fine UF	MFT/UF/ Fine UF	MFT/UF

* Available lengths: 580, 850, 1020, 1178 mm.

Fabrication procedure

- Pd electroless plating

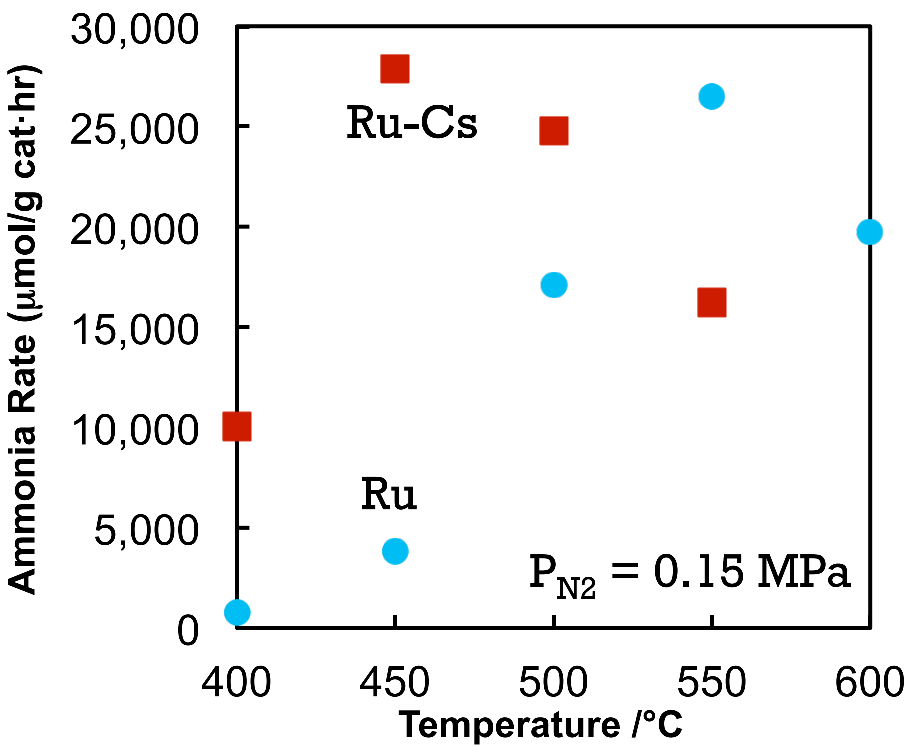
$$2Pd\left(NH_3\right)_4^{++} + N_2H_4 + 4OH^- \rightarrow 2Pd^0 + 8NH_3 + N_2 + 4H_2O$$

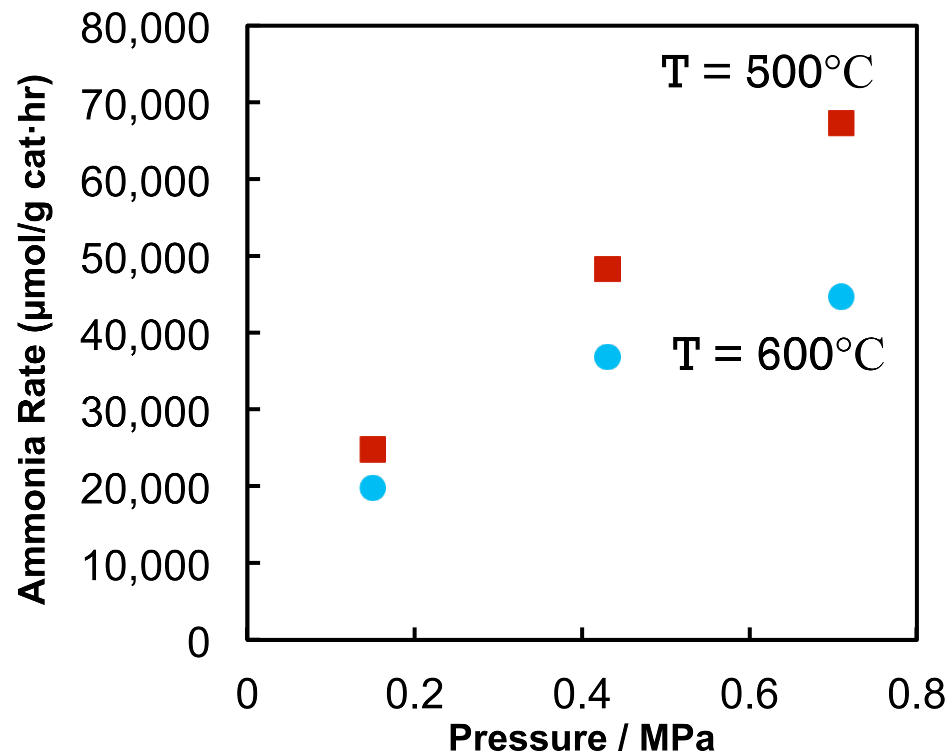
- Problem: Bubbles adhering to surface leads to porous microstructure
  - Agitate with a shaker
  - Flow plating solution over tube
- Problem: Insufficient agitation
  - Lower plating temperature
  - Sonicated water bath

Catalysis Comparison

Rate Units

μmol NH_3 per g Ru (and Cs) per hr





Appl, M., *Ammonia: Principles and Industrial Practice* 1999: Wiley-VCH.

Corrected rate Rate μmol/ gcat•h	Promoters	Support	Cat. Wt%	GHSV (h^{-1})	H2/N2	Pressure (Mpa)	Temperature (°C)	Rate μmol/ gcat•h	NH3 concentration
380000	N/A	Pr_2O_3	5	62,100	3	1	400	19,000	4.8% (Thermo 7.9%)
675000	N/A	$[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$ (Ru/ C12A7:e^-)	1.2	unknown	3	1	400	8,100	2.10%
150000	N/A	$[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$ (Ru/ C12A7:e^-)	4	unknown	3	1	400	6,000	1.50%
89010.99	Ba	AC	9.1	unknown	3	1	400	8,100	2.10%
200000	Cs	MgO	6	unknown	3	1	400	12,000	3.00%
227295.9	K	MgO	3.92	10,000	3	3	400	8,910	1.36%
17600	N/A	MgO	5	5,000	3	3	400	880	unknwon
29200	N/A	CeO_2	5	5,000	3	3	400	1,460	unknwon
54881.27	K	Al_2O_3	3.79	10,000	3	3	400	2,080	0.42%
unknown	K	AC	4	10,000	3	3	400	unknown	3.92%
292105.3	N/A	ZrO_2-KOH	3.8	10,000	3	3	400	11,100	3.95%
114248.7	K	ZrO_2	3.86	10,000	3	3	400	4,410	1.58%
26873.39	N/A	ZrO_2	3.87	10,000	3	3	400	1,040	0.50%
unknown	Ba-K	AC	Ba 2.6 Ru 2.6 K 9.1	10,000	3	10	400	unknown	23.10%

Corrected rate using active amount of catalysts excluding supports