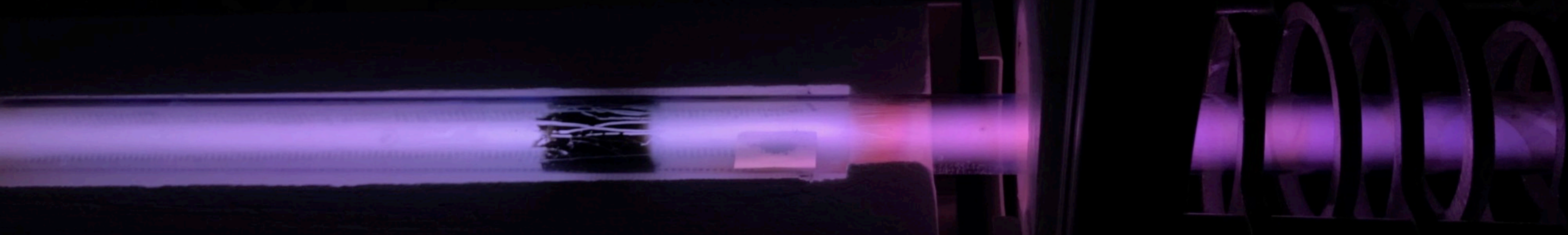


Ammonia Synthesis via Radiofrequency Plasma Catalysis

Javishk Shah, Weizong Wang, Annemie Bogaerts and Maria L. Carreon

2018 AIChE Annual Conference

NH3+ Energy Topical Conference

October 31, 2018

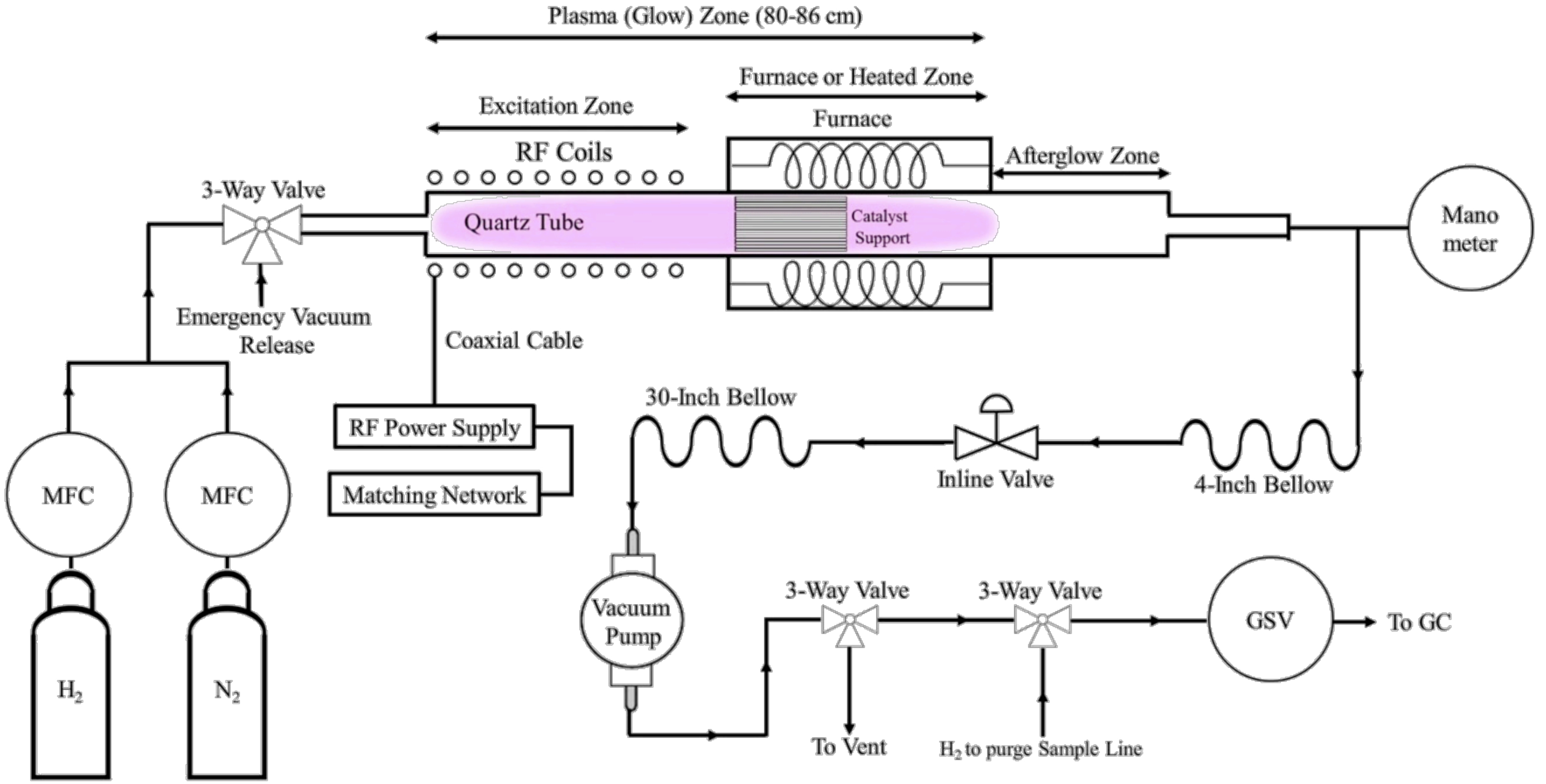
Ammonia Synthesis by Plasma Route

- Small-scale synthesis
- No catalyst poisoning
- Shift in rate limiting step
- Can operate on renewable sources
- Electron impact important

Radiofrequency Discharge

- Electron Temperature – 1-15 eV
- Low pressure: 0.01 to 10 torr
- Room temperature – 400 °C
- Frequency: 100 kHz – 300 MHz
- Voltage: 1-9999 V
- Current: 0.1-100 A
- Power: 10 W – 3 kW
- Used in semiconductor industry

Schematic of In-house built reactor



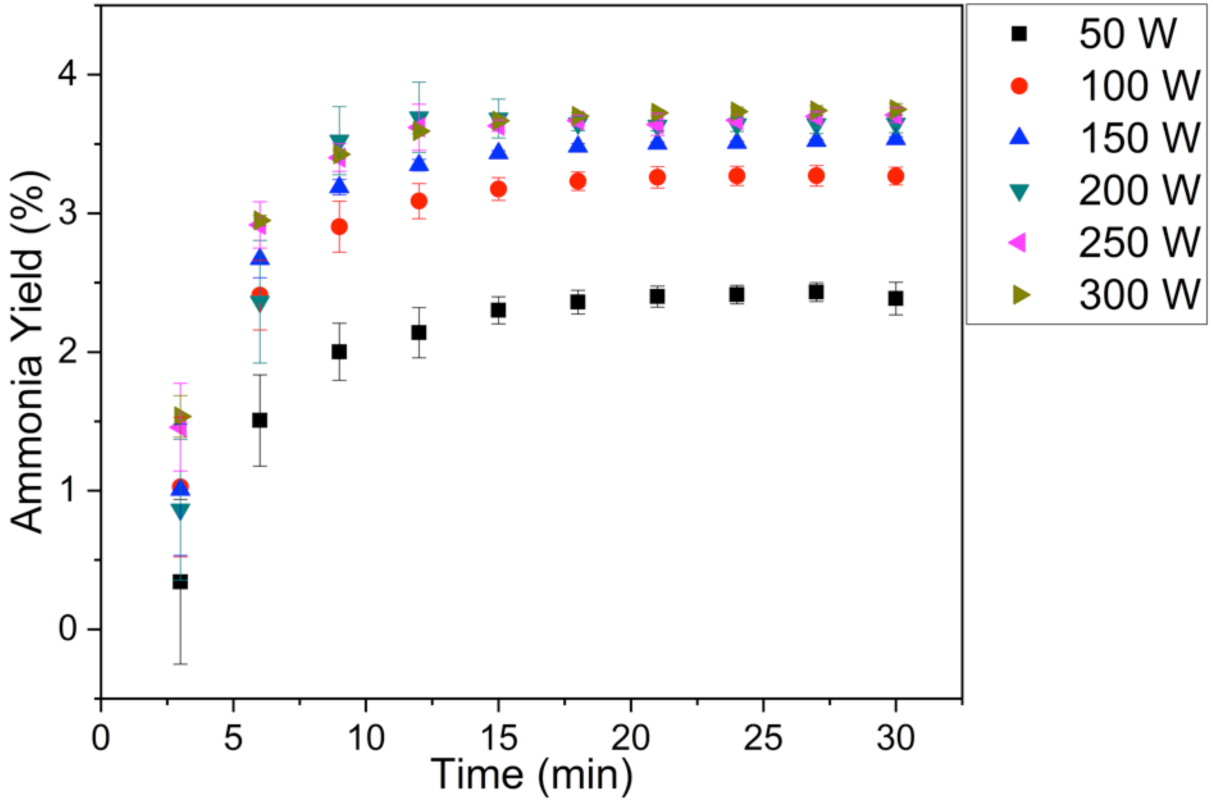
- Metal Meshes
  - Fe
  - Cu
  - Pd
  - Ag
  - Au
- Metal on Glass Tubes
  - Ga

Reaction Conditions

- Feed
  - N_2:H_2 Ratio = 1:4
  - Total Flow = 20 sccm
- Pressure = 0.3 torr
- Temperature = 400 °C
- Plasma Power = 50-300 W
- Reflected Power < 5%
- Reaction Time = 30 minutes
- Catalyst = 1 g

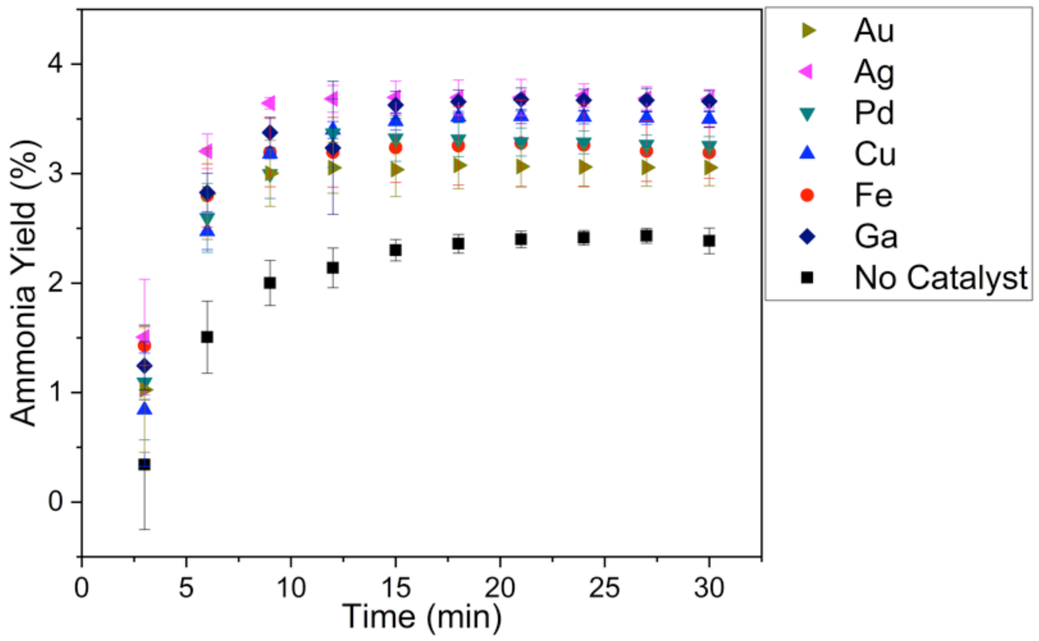
Ammonia Yield (Only Plasma)

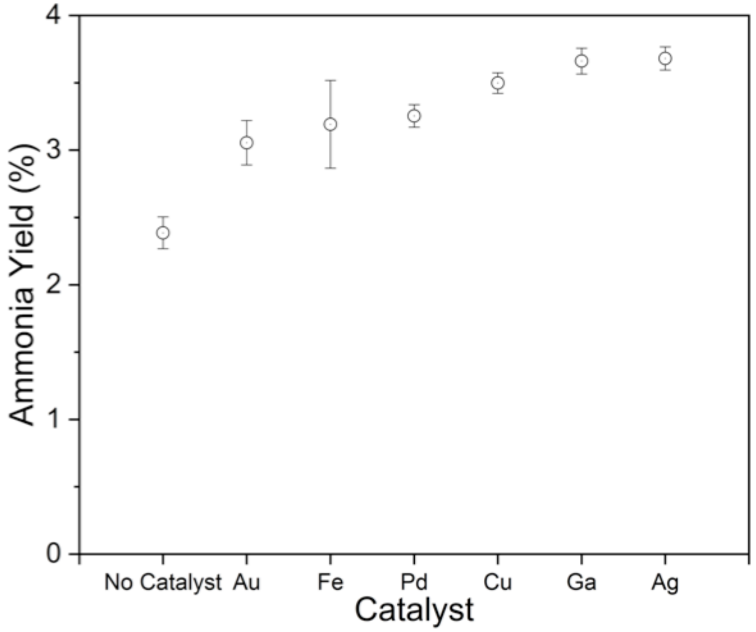
- Maximum Yield: 3.65%
- Steady state at 12 min
- No hydrazine
- Power saturation at 150 W



Ammonia Yield (50 W)

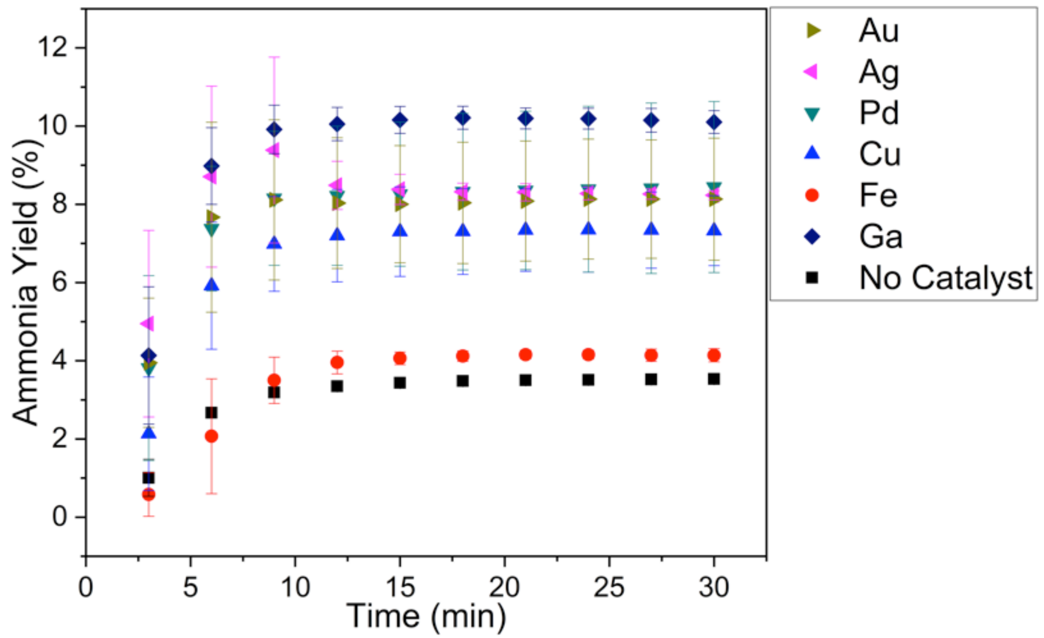
- No significant increase in catalytic activity compared to non-catalyzed reaction
- No catalyst < Au < Fe < Pd < Cu < Ga < Ag
- Highest Yield: 3.7%
- No-catalyst: 2.2%

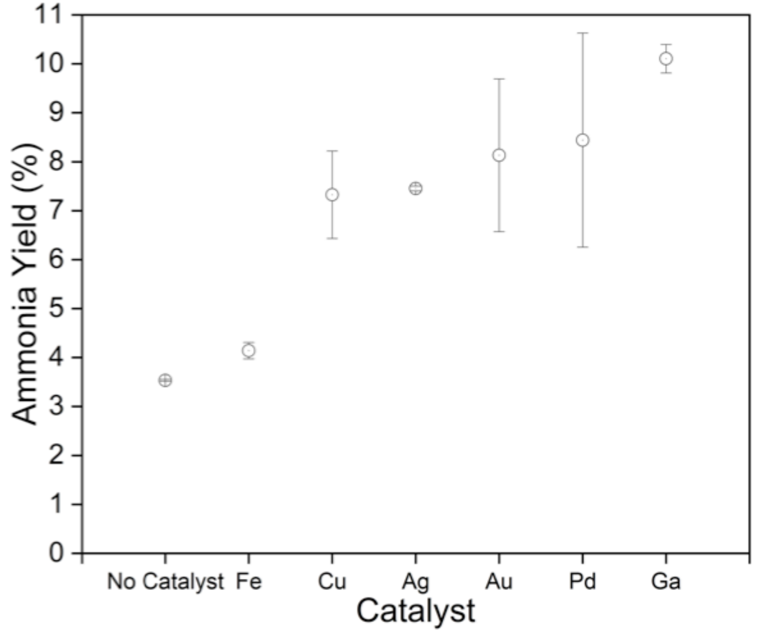




Ammonia Yield (150 W)

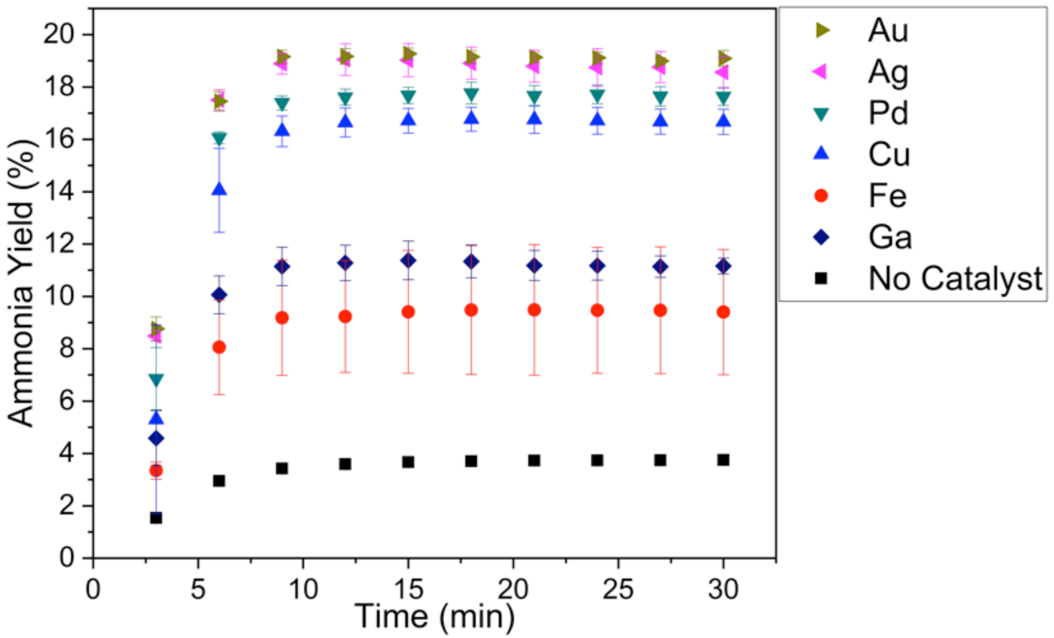
- Maximum Yield: 10.1%
- No Plasma: 3.1%
- No Catalyst < Fe < Cu < Ag < Au < Pd < Ga
- Best Catalyst Molten Ga

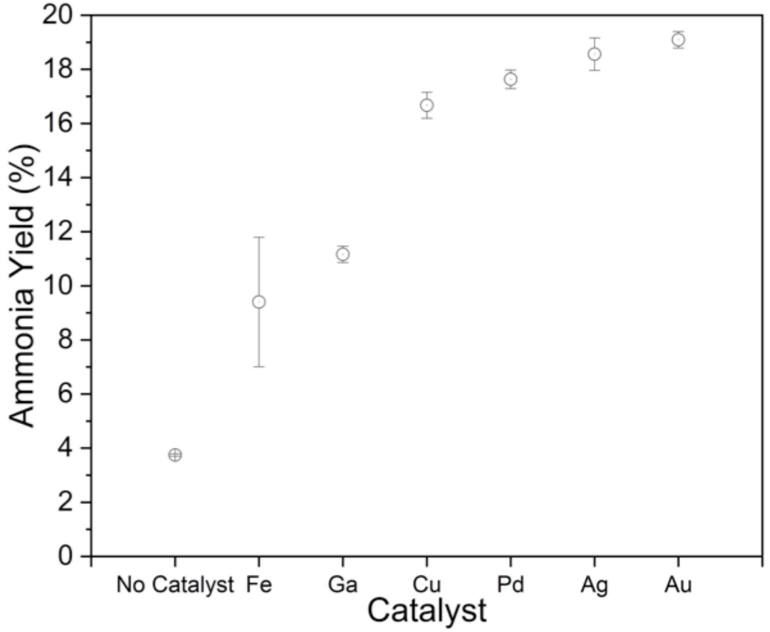




Ammonia Yield (300 W)

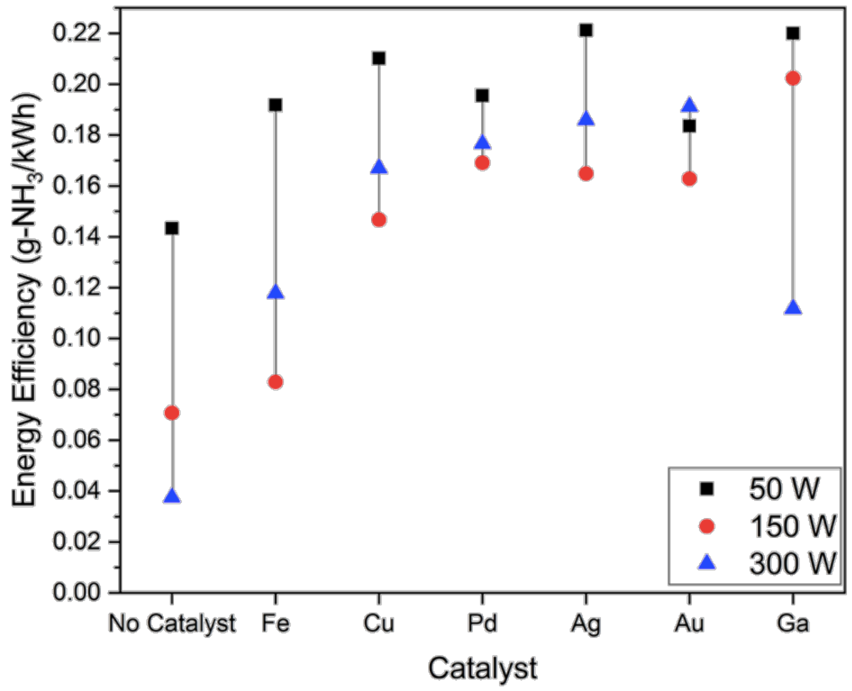
- Maximum Yield: 19.1%
- No Plasma: 3.7%
- No Catalyst < Fe < Ga < Cu < Pd < Ag < Au
- Shift in Ga activity due to tendency to form stable nitride





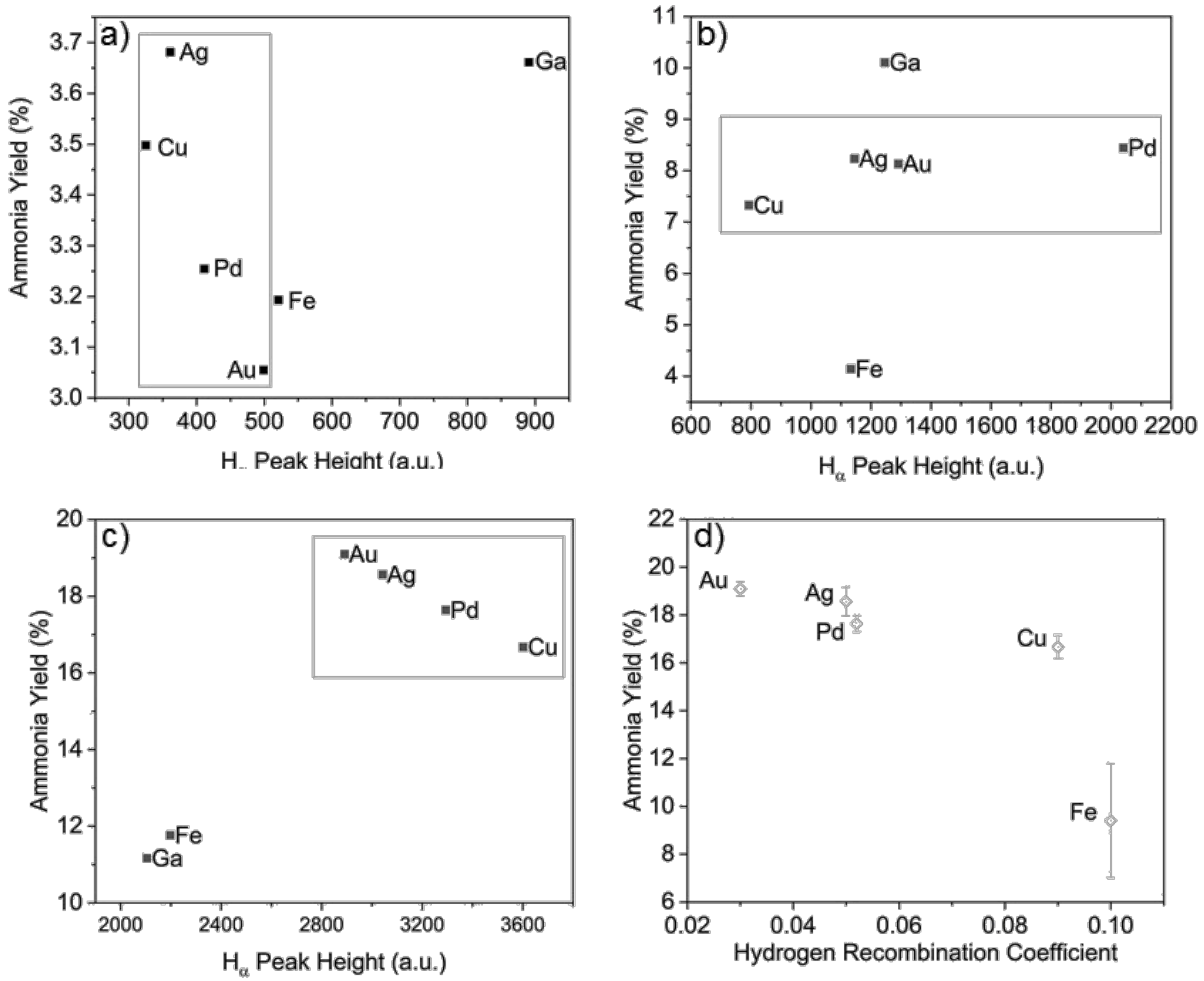
Energy Yield

- Haber-Bosch Process: 500 g-NH_3/kWh
- Plasma Processes: 0.01-3 g-NH_3/kWh
- Our case: 0.22 g-NH_3/kWh
- Highest energy yield: Ga (50W)
- Ga improved efficiency by 200% at 150 W as compared to Fe



Hydrogen Species Dependence

- Reasonable correlation between hydrogen recombination coefficients and ammonia yield at 300 W
- Obtained experimental data confirmed with simulation



Major Reactions

$e^- + N_2 \rightarrow e^- + N + N$

$e^- + H_2 \rightarrow e^- + H + H$

$H + F_s \rightarrow H_s$

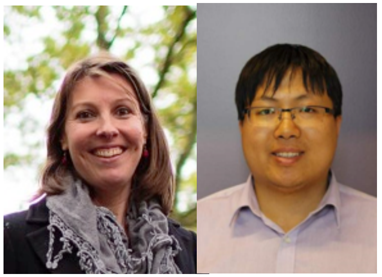
$N + F_s \rightarrow N_s$

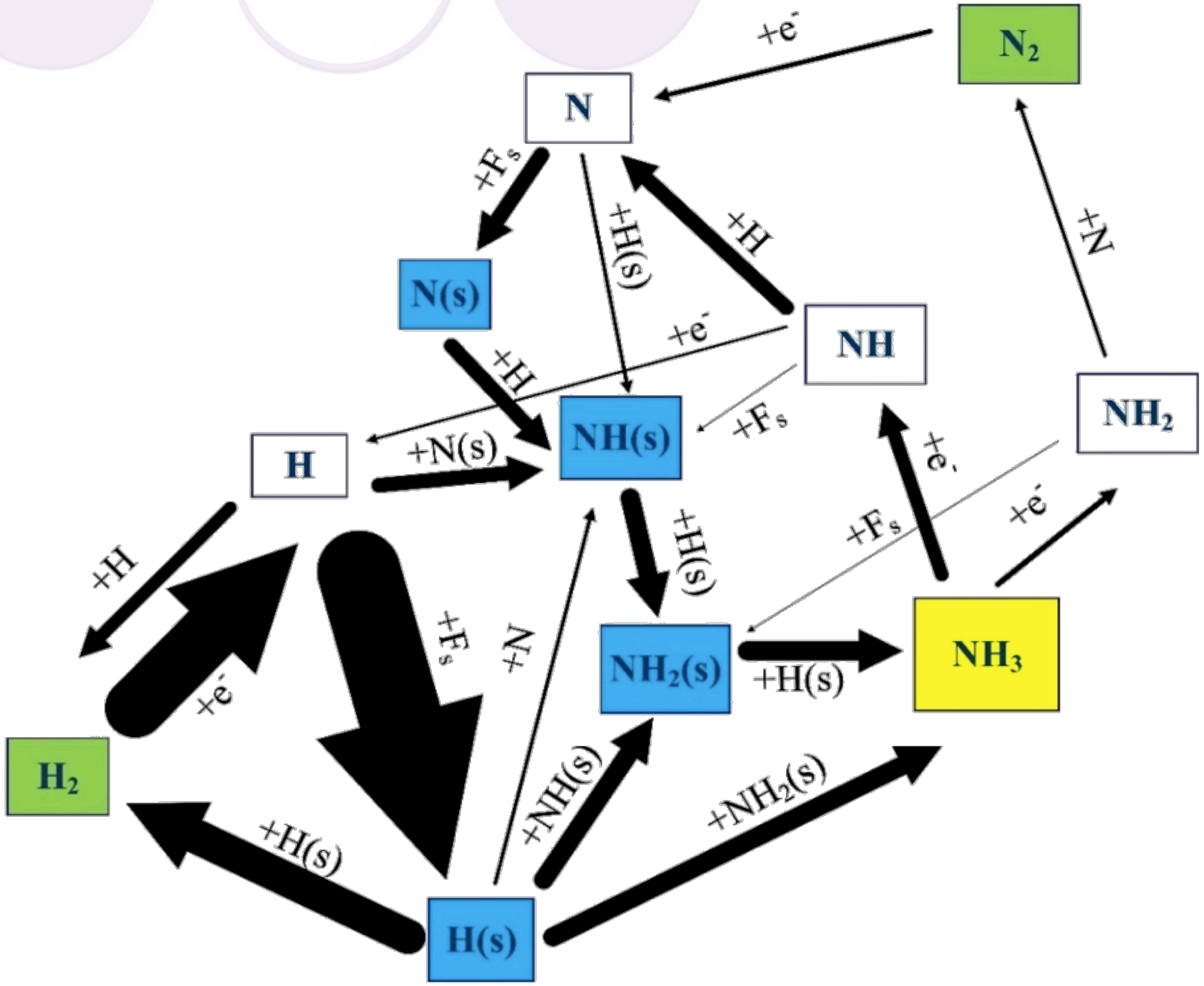
$N + H_s \rightarrow NH_s$

$NH_s + H_s \rightarrow NH_{2s} + F_s$

$NH_{2s} + H_s \rightarrow NH_3 + F_s$

$e^- + NH_3 \rightarrow e^- + NH_2 + H$





Dr. Annemie Bogaerts
Dr. Weizong Wang
Universiteit Antwerpen

Shah, Javishk, Weizong Wang, Annemie Bogaerts and Maria L. Carreon. "Ammonia Synthesis by Radio Frequency Plasma Catalysis: Revealing the Underlying Mechanisms.", ACS Appl. Energy Mater., 2018, 1 (9), pp 4824–4839

Summary

- RF plasma lead to unprecedented yields as compared to previous works
- We explore a molten catalyst, Ga which has never been explored for ammonia synthesis
- Plasma-catalyst synergy overcome the wall-plasma synergy leading to high ammonia yield
- The reaction happen on the catalyst surface than on the wall
- We observe a direct dependence of ammonia yield on hydrogen recombination coefficient and H_α species concentration.

Acknowledgements

Faculty

- Dr. Maria Carreon
- Dr. Annemie Bogaerts
- Dr. Weizong Wang

Departments/Universities

- Russell School of Chemical Engineering
- The University of Tulsa Graduate School
- Office of Research and Sponsored Programs
- PLASMANT, University of Antwerp

Thank You!

Energy Yield Calculations

- The electrical efficiency of the power supply is assumed to be 50% (average of 40-60%).
- 1 sccm = 7.45×10^{-4} m mol/s
- 1 h = 3600 s
- 1 g = 1000 mg
- Mass of ammonia = M_{NH3} = 17 g/mol
- x = flow rate of formed NH_3 in sccm
- y = energy yield in g-NH_3/h
- z = energy yield in g-NH_3/kWh

$$Energy\ Yield = Ammonia\ Flow\ Rate / Input\ Power$$

where, $Input\ Power = Plasma\ Power / Electrical\ Efficiency$

$$y_{g-NH_3/h} = x\ sccm * 7.435 * 10^{-4} * M_{NH_3} * 3600/1000$$

$$z_{g-NH_3/kWh} = y_{g-NH_3/h} * 1/Input\ Power\ (kW)$$

Energy Cost Calculations

- Molar mass of ammonia = 17 g/mol
- 1 kWh = 3.6 MJ
- Electrical efficiency of power supply = 0.5 (see above)
- z = Energy yield of ammonia production in g-NH_3/kWh

$$Energy\ Cost(MJ/mol) = 17 * 3.6/z * 0.5$$

GC Calibration

Serial Number	Nitrogen Flow (sccm)	Ammonia Flow (sccm)
1	4	0
2	1.75	2.25
3	2	2
4	0	4