SOUTH DAKOTA SCHOOL OF MINES

CARREON LAB

Ammonia yield enhancement by hydrogen sink effect during plasma catalysis

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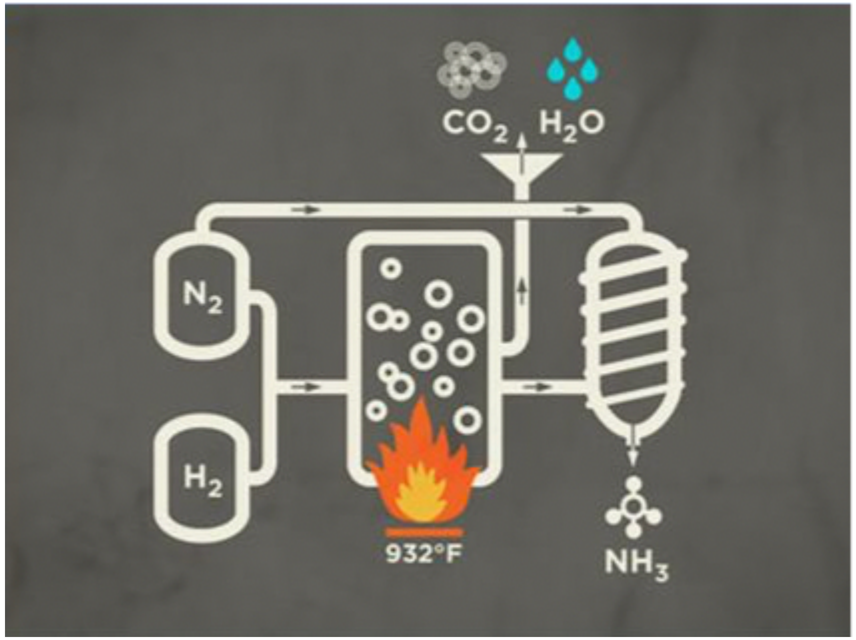
Nitrogen Fixation: Background

- Nitrogen makes 78 % of the Earth's atmosphere, important element for *growth* of plants and living organisms on Earth.

- Before nitrogen can be used, the strong triple bond of N2 must be broken and atomic nitrogen must be chemically bonded with other elements such as hydrogen through N-fixation process.

- An important artificial mean for fixing atmospheric nitrogen: the Haber-Bosch process.



Haber-Bosch Process by numbers

3H2 +N2 ↔2NH3

157.3 million:
Metric tons of NH_3 produced worldwide in 2010

451 million:
Metric tons of CO_2 emitted by NH_3synthesis worldwide in 2010.

~1%:
Percentage of global CO_2 emissions that come from NH_3 synthesis.

450-600 °C and 150-350 bar:
in the presence of the right catalyst

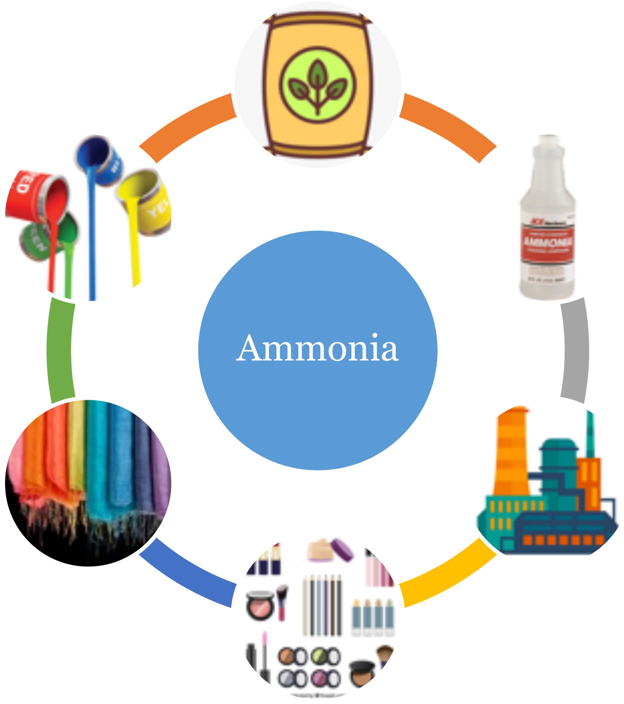
40% of today's global population:
sustained by this process

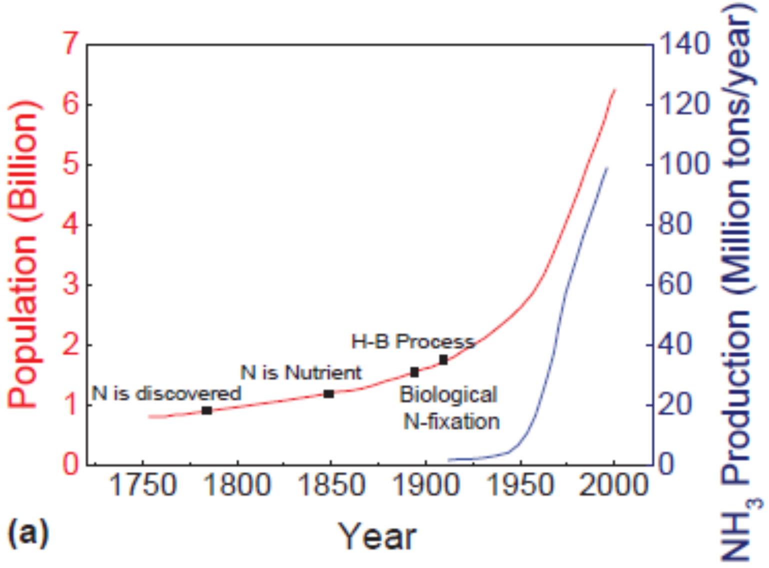
2-3% of world's natural gas output:
Chemical industry most energy-intensive process

Sources: Institute for Industrial Productivity

Ammonia

- Ammonia, is the second highest industrially produced chemical, is used in many different forms, ranging from nitric acid to hydrogen cyanide and used for large scale applications in chemistry, e.g. fertilizer.
- Ammonia has an irreplaceable role in chemical industry.
- Ammonia can be employed as an efficient hydrogen carrier.





Patil, B. S. ***Doctoral Thesis***, Technische Universiteit Eindhoven *(**2017**)*.

Ammonia Reaction

The overall reaction for ammonia production is:

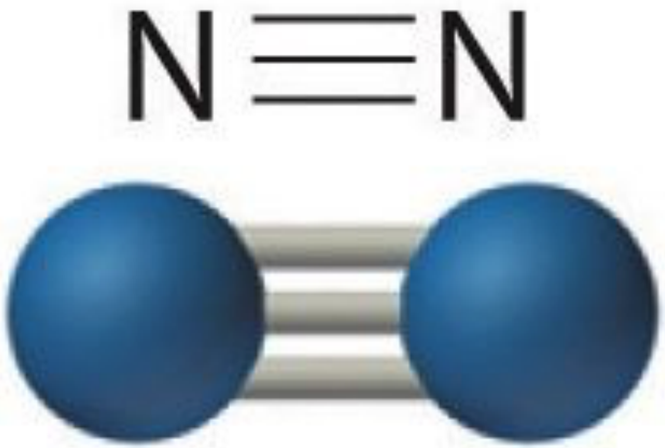
$$3H_2 + N_2 \leftrightarrow 2NH_3, \quad H_{298} = -10.97 \text{ kcal/mol.}$$

- The reaction enthalpy indicates that the reaction is thermodynamically favored at low temperature.
- However, the critical elementary step of N_2 dissociation presents a large free energy of activation, even on widely used heterogenous catalysts.
- High temperature is needed to overcome the barrier, but this forces the use of high pressure to make the equilibrium favor the reaction again via Le Chatelier principle.

The triple Nitrogen bond

- The kinetic stability of the N2 triple bond ultimately makes the "fixation" of nitrogen an energy intensive process.

- It is difficult to dissociate the triple bond of nitrogen because the molecule does not readily accept or donate electrons.

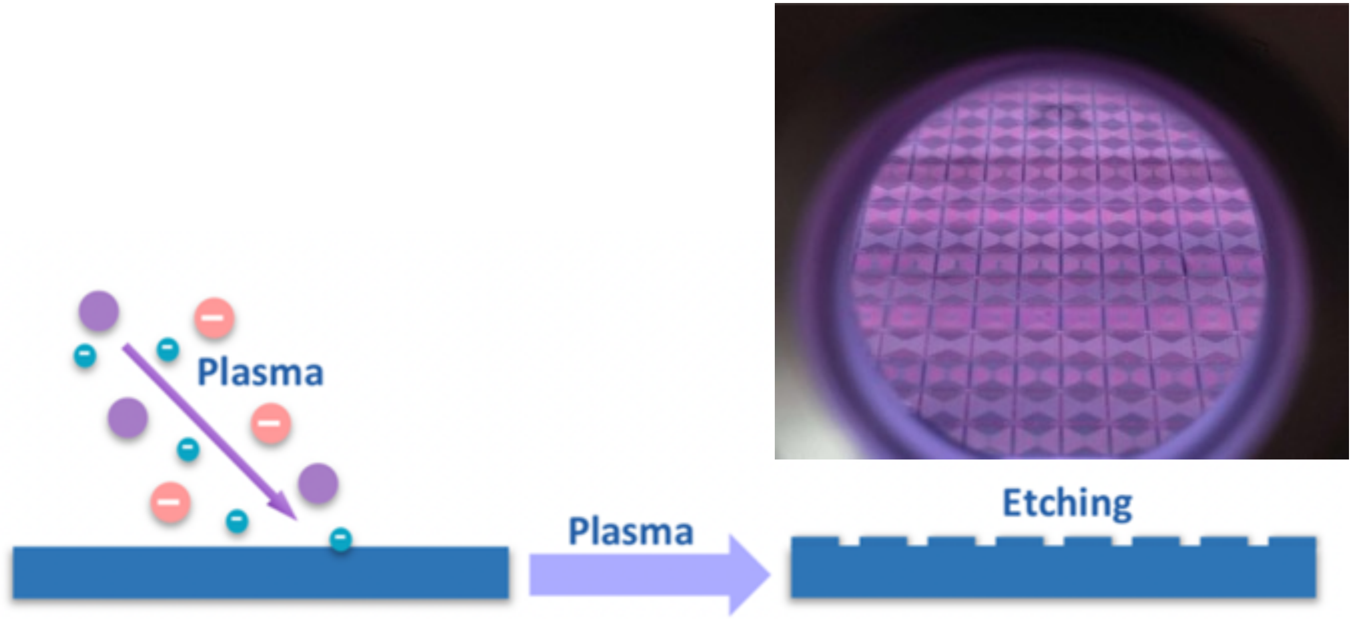


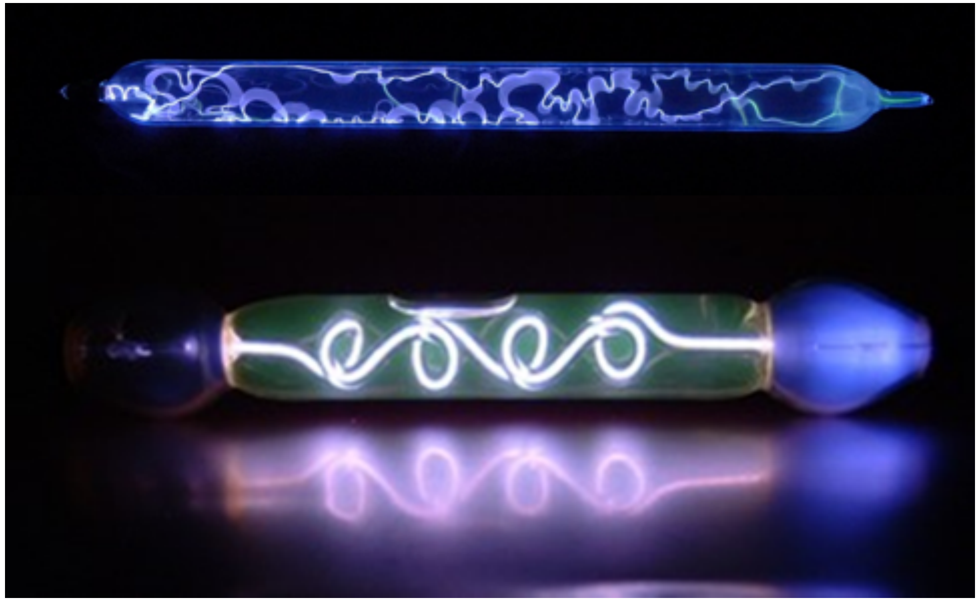
How can we dissociate the triple nitrogen bond?

Non-thermal plasma

- Electrons are usually at very high temperatures of the order of 10^5 K because of their smaller mass, whereas ions and background gas are at room temperature.

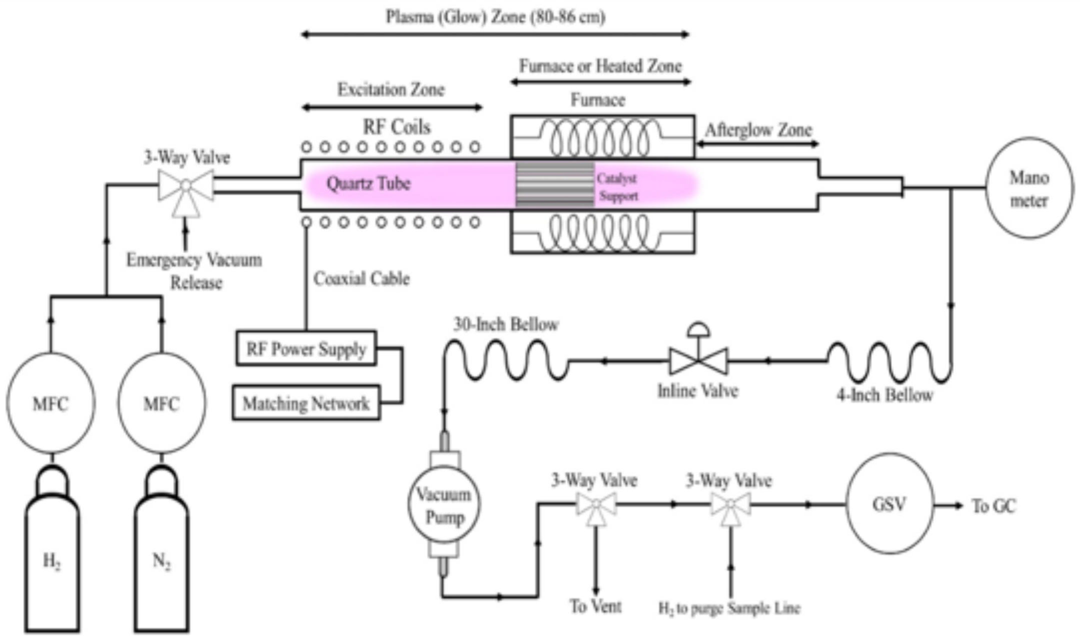
- Non-thermal plasmas commonly used for technological applications.





Non-thermal plasma synthesis of ammonia

Plasma reactor/process offers advantages such as:
(1) simple one step processes,
(2) fast on/off operation (possibility to adapt to renewable electricity sources)
(3) generally non-polluting.



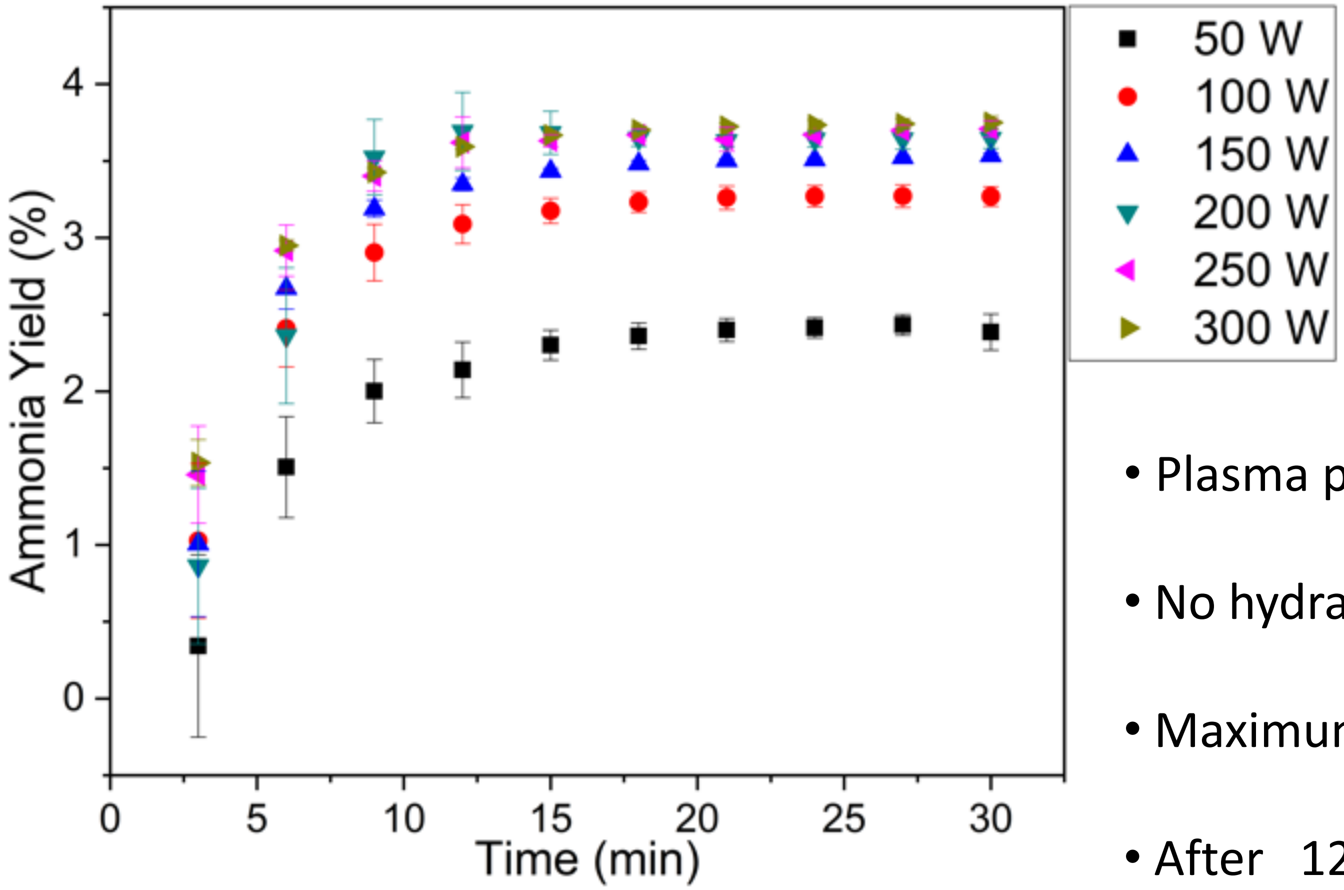
- Feed
  - N_2:H_2 Ratio = 1:4
  - Total Flow = 20 sccm
- Pressure = 0.26 torr
- Temperature = 400 °C
- Plasma Power = 300 W
- Reflected Power < 5%
- Reaction Time = 30 minutes
- Catalyst = 1g

Metals:

Ni, Sn, Au, Ag, In, Pd, Cu, Ga, Fe

Alloys:
Rich Ga alloys

Ammonia yield (only plasma, 400 ℃)



- Plasma power saturation observed above 150-200 W.
- No hydrazine detected.
- Maximum yield of 3.75% at 200W-300W, after 12 minutes.
- After 12 minutes of plasma initiation constant yield is observed.

Ammonia Yield, Energy yield and energy cost for metals

Catalyst	T_m (K)	NH_3 Yield (%)	Energy Yield ($g\text{-}NH_3/kWh$)	Energy Cost (MJ/mol)	Binding Energy on Surface (in Bulk) (kJ/mol)	
					N	*H*
Ni	1728	34.1	0.41	147	-446 (-376)	-266 (-207)
Sn	505	28.8	0.35	174	-	-
Au[a]	1338	19.1	0.22	263	-168 (-42)	-193 (-100)
Ag[a]	1235	18.6	0.22	271	-155 (-130)	-197 (-153)
In[a]	430	17.7	0.22	283	-	-
Pd[a]	1828	17.6	0.21	285	-396 (-317)	-270 (-215)
Cu[a]	1358	16.7	0.20	301	-296 (-247)	-231 (-174)
Ga[a]	303	11.2	0.14	451	-410 (-389)	-172 (-139)
Fe[a]	1811	9.5	0.12	532	-705 (-213)	-323 (-82)
[a]**Metals also run in our previous work.** J. Shah, W. Wang, A. Bogaerts, Maria L. Carreon*, *ACS Appl. Energy Mater.* 2018, *1*, 4824-4839. J. Shah, J. Harrison, Maria L. Carreon*, *Catalysts* 2018, *8*, 437.						
Data from Haber-Bosch Process						
Fe[c,d]	1811	8-15%	500	0.5	-705 (-213)	-323 (-82)
[c]**Reference:** H.-H. Kim, Y. Teramoto, A. Ogata, H. Takagi, T. Nanba, *Plasma Chem. Plasma Process.* **2016**, *36*, 45-72. [d]To achieve such yields a minimum production capacity of 100 ton/day is required. The process occurs at high temperature(450-600°C) & High Pressure (150-350 bar). The major limitation in this process is scaling down & catalyst regeneration (Iron).						

- All metals tested outperformed Fe.
- Under plasma conditions, ammonia formation favored in coinage metals not traditional: **Cu, Ag, Au,** (have hard time activating N≡N bond.)
- N and H DFT calculated binding energies (surface and bulk) as a measure of the tendency of each catalyst to adsorb and dissolve atomic N and H initially formed in the plasma.

Ammonia % yield vs H_α relative intensity

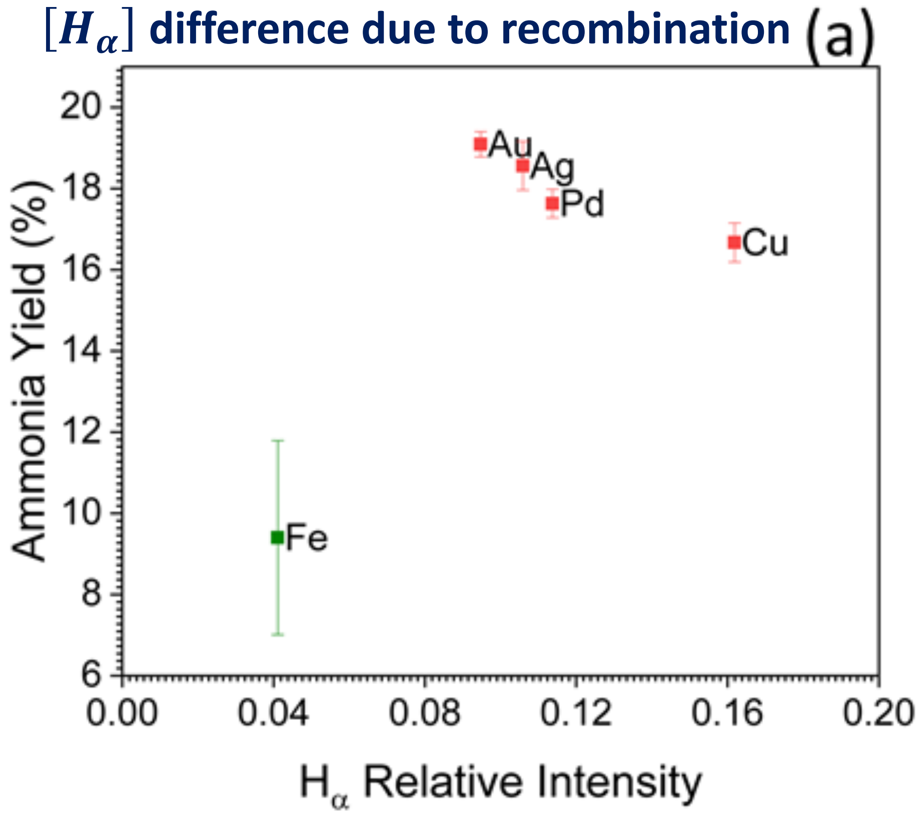
- Relative intensity H_α: ratio of H_α peak intensity in the presence and absence of catalyst *or* relative gas-phase $[H_\alpha]$ when a catalyst is used compared to when not.

- Expected to be primarily reduced by:

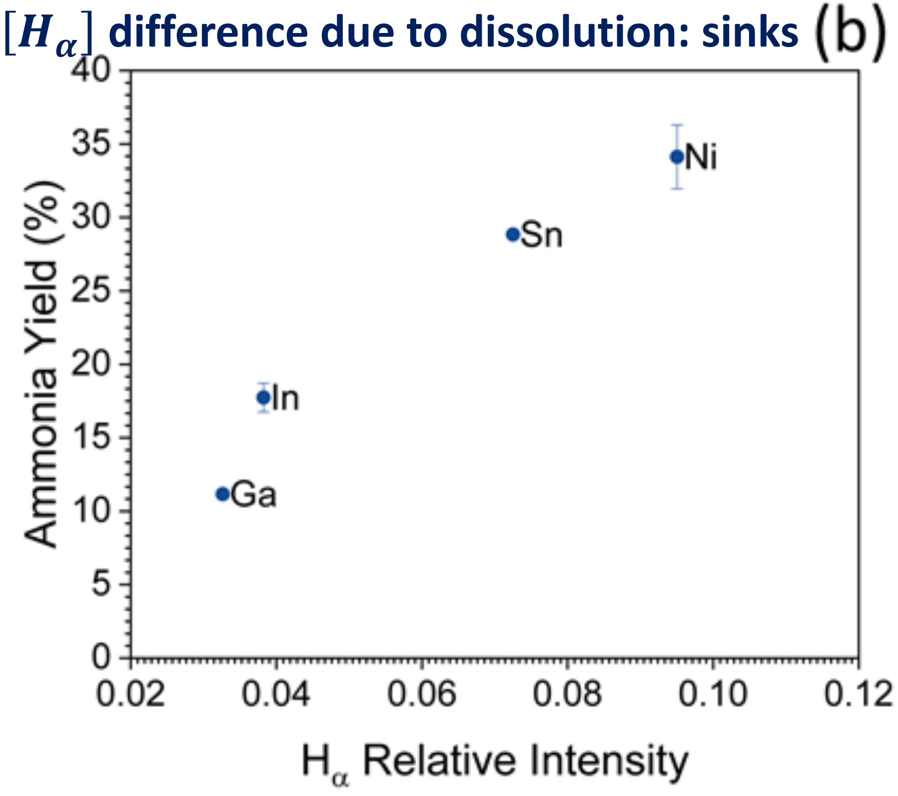
(1) Atomic H adsorption on the catalyst surface and dissolution in the bulk (more pronounced for hydrogen sink),

(2) H recombination to form $H_{2(g)}$ (some H recombination in the gas, most recombination involves the catalyst)

$[H_\alpha]$ difference due to recombination



$[H_\alpha]$ difference due to dissolution: sinks



Trends based on comparison of experimental results with DFT

<u>**Category I:**</u> [H_α] changes due to H **recombination** at surface.

(Cu, Ag, Au, Fe) <u>low tendency to dissolve H</u> in the bulk (***binding energies for H in bulk***).

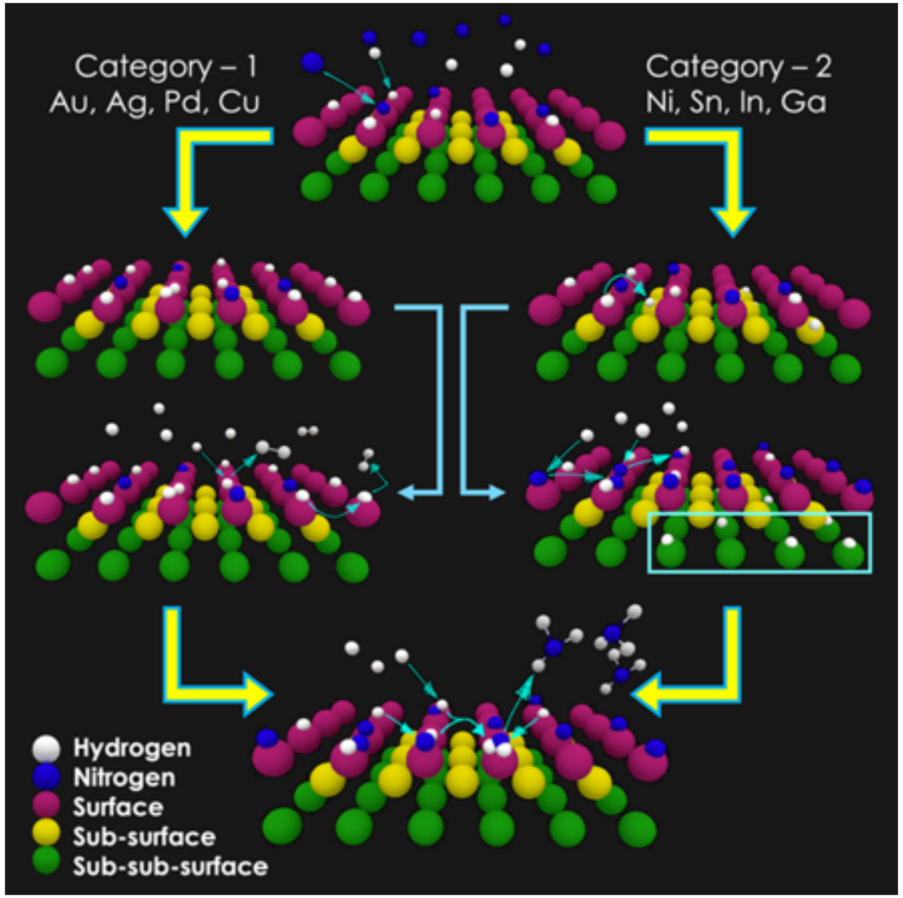
<u>Nitrophilic</u>: Fe <u>Nitrophobic</u>: Cu, Ag, Au.

<u>Nitrophobic metals:</u> [H_α] *inversely correlates* with ammonia yield.

[H_α] directly correlates with binding strength of H on the catalyst surface:

Au < Ag < Cu

(***higher H binding strength hinders H recombination, higher*** **[H_α] for Cu**)



<u>**Category II:**</u> [H_α] changes due to **dissolution** of atomic H.

[H_α] ***lower than* category I** ("hydrogen sink" behavior). Better sink, lower [H_α] in the gas.

Slow down recombination → controlling factor ***not H recombination.***

[H_α] *directly correlates* with ammonia yield.

[H_α] correlates with MP & nitride tendency formation:

Ga > In > Sn > Ni

affect N availability for ammonia-leading reactions (***controlling factor***).

<u>**Ni high yield due to its ability to act as a sink for H while maintaining N* available for reaction!**</u>

Proposed reaction pathway

- Atomic N and H most relevant species for our system (***confirmed by emission spectra at plasma-catalysts interface***)

Activation energies (kJ/mol) for potential NH_x forming reactions estimated from scaling relationships

Metal	$N^* + H_{(g)} = NH^*$	$N^* + H^* = NH^*$	$NH^* + H^* = NH_2^*$
Ni	20	95	133
Sn	-	-	-
Au	10	71	84
Ag	9	85	84
In	-	-	-
Pd	18	45	131
Cu	15	94	108
Ga	19	85	100
Fe	27	129	176

- NH* formation estimated barrier via E-R between N* and $H_{(g)}$ significantly lower (***likely NH* primarily formed by E-R***).
- Zero-dimensional continuous model: E-R reactions contribute less than 1% to NH_2^* formation. **(Ref.1)**

(1) Shah, Javishk, Wang, Weizong, Bogaerts, Annemie, Carreon, Maria L., Ammonia synthesis by radio frequency plasma catalysis: revealing the underlying mechanisms. ACS Applied Energy Materials, 2018, 1 (9), 4824-4839.*

Proposed reaction pathway

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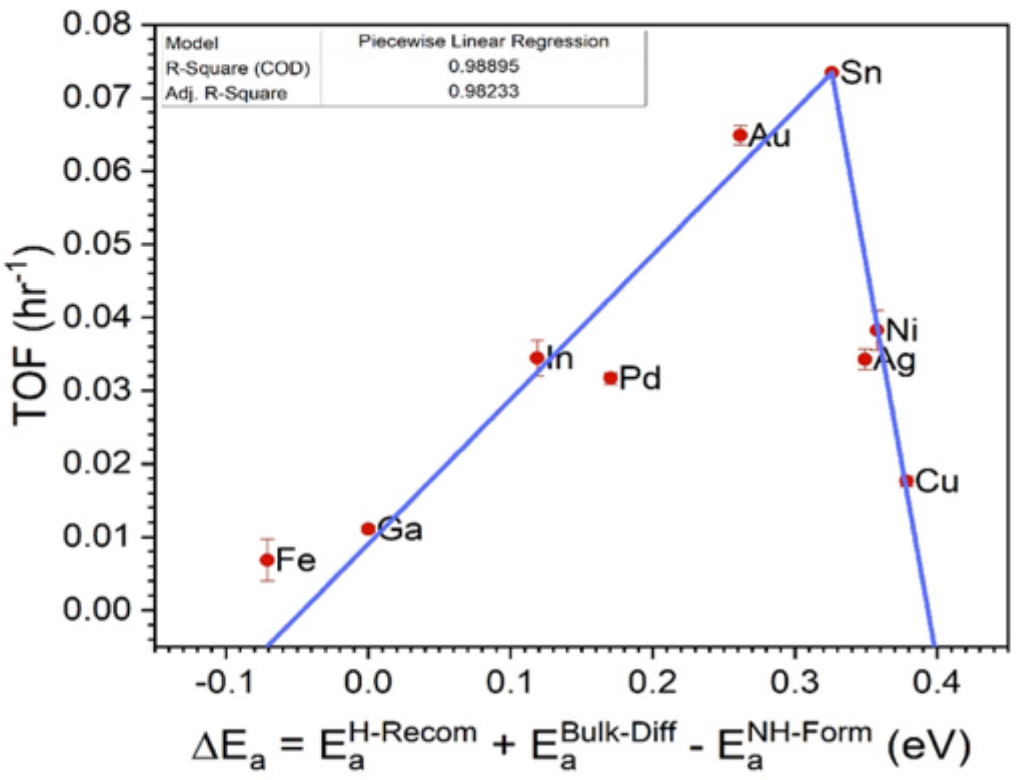
Subtracted activation energy of desired reaction from the total activation energy of undesired reactions

(**Activation energy of H_2 recombination** + **Activation energy of Bulk diffusion**) – **Activation energy of N-H formation**.



Vacuum discharges N-H formation via E-R, is competing with **H_2 formation via E-R** and **H-bulk diffusion**.

Molten Alloy Catalysts Activity

- Ga-rich alloys (Ga "hydrogen sink" desirable behavior).
- Exception: Zn 3.6%, Cu 2.5%, and Al 1.7%, ***all other Ga alloys outperformed pure Ga.***

Catalyst	Solute Metal (mass%)	T_m (K)	NH_3 Yield (%)	Energy Yield (g-NH_3/kWh)	Energy Cost (MJ/mol)
Pd	5.0	473	25.4	0.31	199
In[a]	20.0	336	20.9	0.25	242
Pd	2.5	420	19.9	0.24	253
Au	3.0	400	17.7	0.22	285
Sn	10.0	298	16.7	0.20	301
Zn	20.0	415	16.3	0.20	309
Sn	30.0	345	16.2	0.20	311
Ag	4.0	400	15.6	0.19	324
Sn	13.5	294	15.3	0.19	330
Cu	1.5	410	14.8	0.18	341
Al	5.0	430	13.5	0.16	373
Ag	3.0	299	13.1	0.16	385
			Ga: 11.1	**0.11**	**450**
Zn	3.6	298	11.2	0.14	449
Cu	2.5	485	6.8	0.08	746
Al	1.7	300	6.1	0.07	829

The 5% Pd-Ga alloy

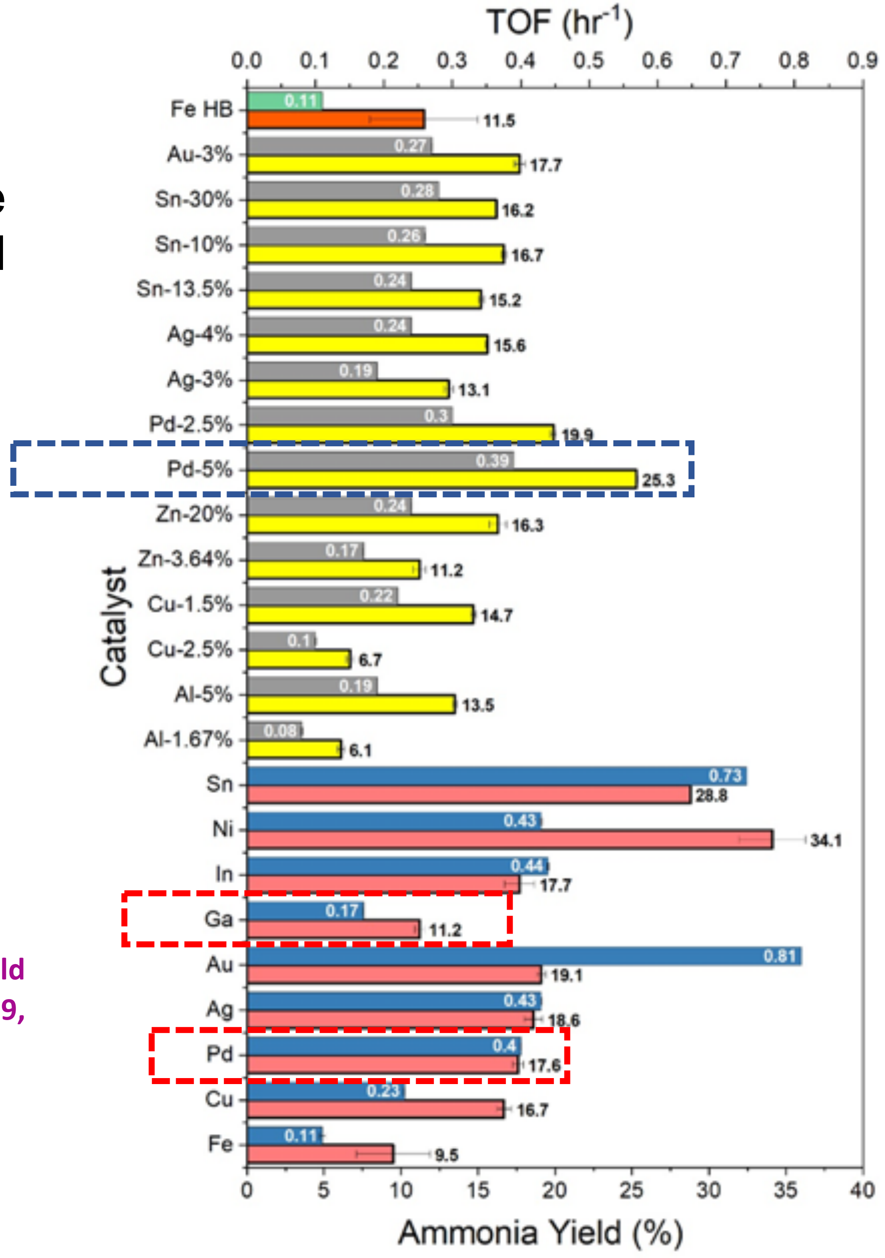
Pd 5% alloy yield of **25.3 %** higher only Ga **11.2%** only Pd **17.6%**

Expensive metals desirable characteristics can be matched/surpassed by alloying low-melting point metals with small quantities of expensive “promoters.”

5% **Pd addition increase H affinity**, **Pd affinity for N** and **tendency to form nitride low.**

Diffusion from surface to subsurface easy as in **Ga** (catalyst liquid at reaction conditions, easier than in pure Pd)

All these factors may be responsible for the alloy synergy!



Shah Javishk, Gorky, Psarras Peter, Seong Bomsaerah, Gomez-Gualdron Diego, Carreon Maria L.* Ammonia yield enhancement by hydrogen sink effect during plasma catalysis. *ChemCatChem.* 2019, *In press* (https://doi.org/10.1002/cctc.201901769)

Summary

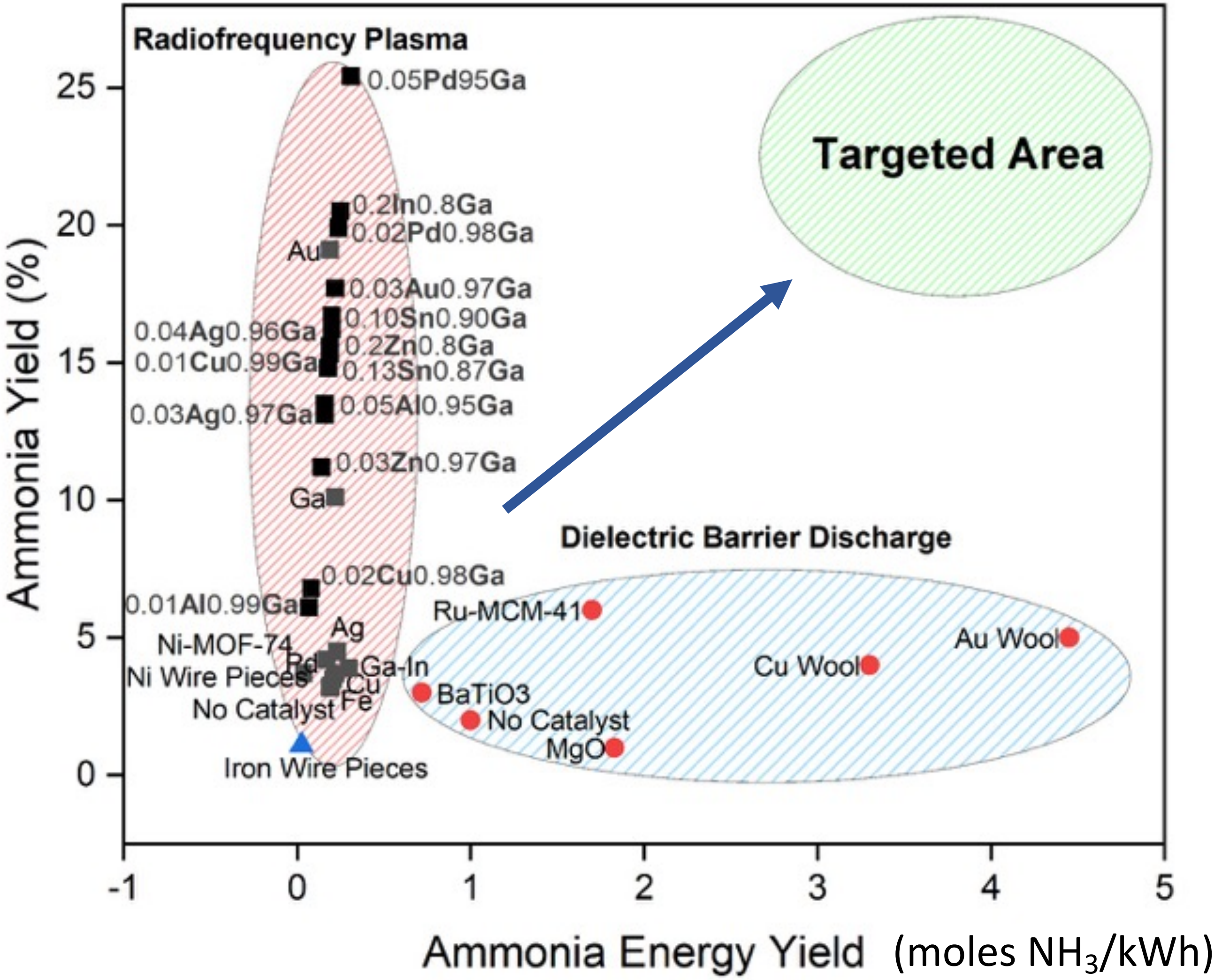
1) **Metals not traditionally** used in industrial scale, thermo-catalytic ammonia synthesis were shown to have **higher catalytic activity** when used under plasma conditions (compared to the traditional Fe catalyst).

2) The **non-traditional metals** include both **nitrophobic and molten-state metals**, presenting a relative activity as follows: **Ni > Sn > Au > Ag > In > Pd > Cu > Ga**.

3) The potential to **further improve catalytic performance** was demonstrated by experiments with **Ga alloys**, as some alloys **exhibited catalytic activity superior** (25-50% for Ga-Pd and Ga-In) to their constituent elements.

4) **More thorough theoretical and experimental mechanistic studies** (challenging as they may be) are needed to **provide a rational platform** to exploit the full potential of plasma-catalysis technology for ammonia synthesis.

Outlook



- The employment of **engineered catalysts** that can lead to better yields can have a beneficial impact in the energy efficiency.

Acknowledgements

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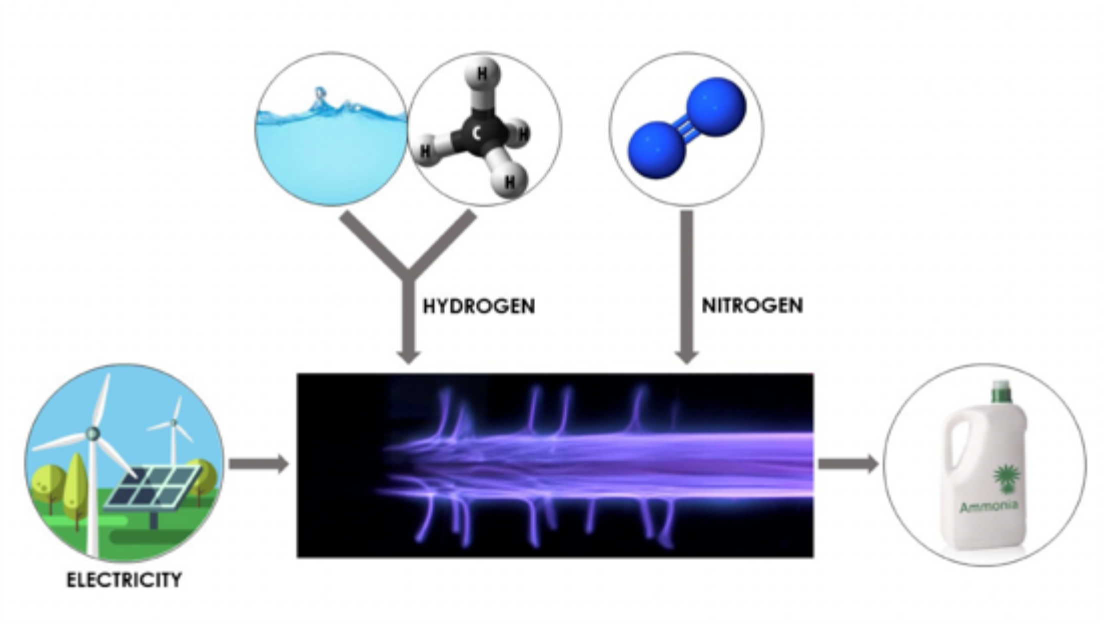
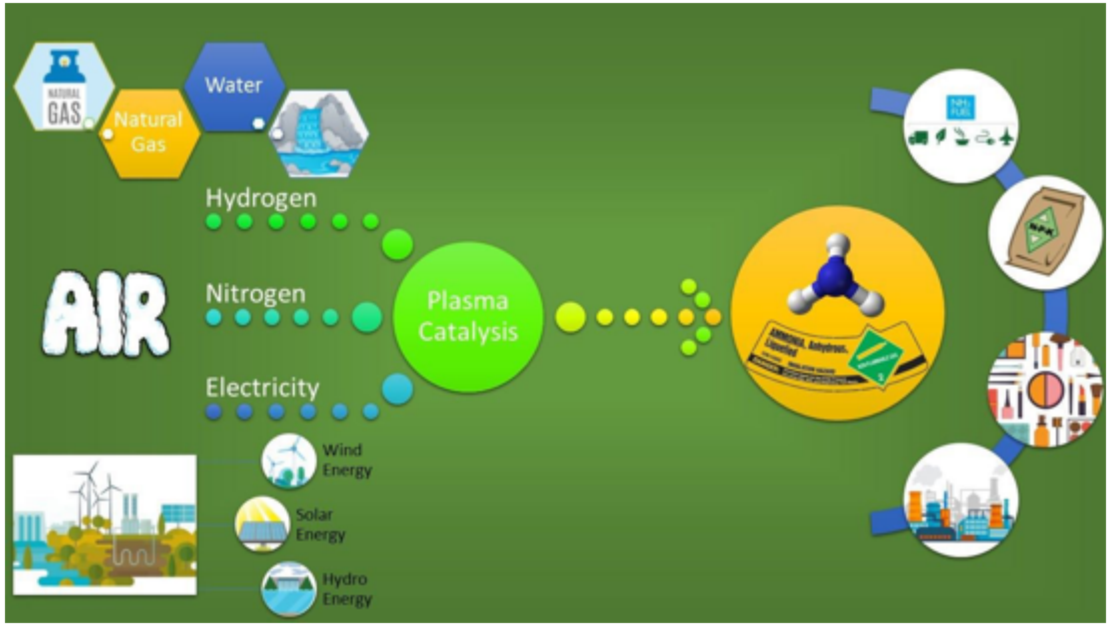
EXTRA SLIDES



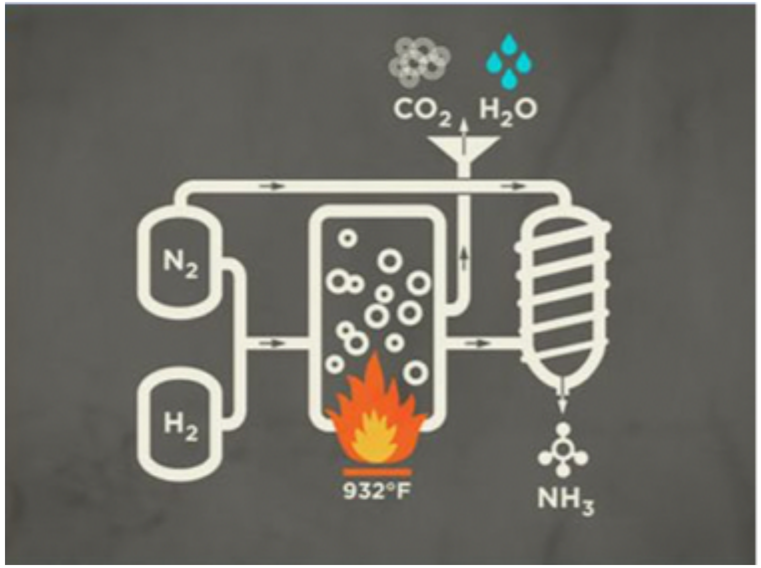


Nitrogen Fixation: Background

- Nitrogen makes 78.08% of the Earth's atmosphere, and is an important element for growth of plants and living organisms on Earth.

- Before nitrogen can be used, the strong triple bond of N_2 must be broken and atomic nitrogen must be chemically bonded with other elements such as hydrogen through N-fixation process.

- An important artificial mean for fixing atmospheric nitrogen the Haber-Bosch process.



Haber-Bosch Process

- Nitrogen is fixed at large scale through the "Haber-Bosch ammonia synthesis process" via reaction of nitrogen with hydrogen at 450-600 ℃ and 150-350 bar in the presence of a catalyst.

- This process sustains 40% of today's global population.

- Global ammonia production projected to be ~ 249. 4 million tons per year in 2018.

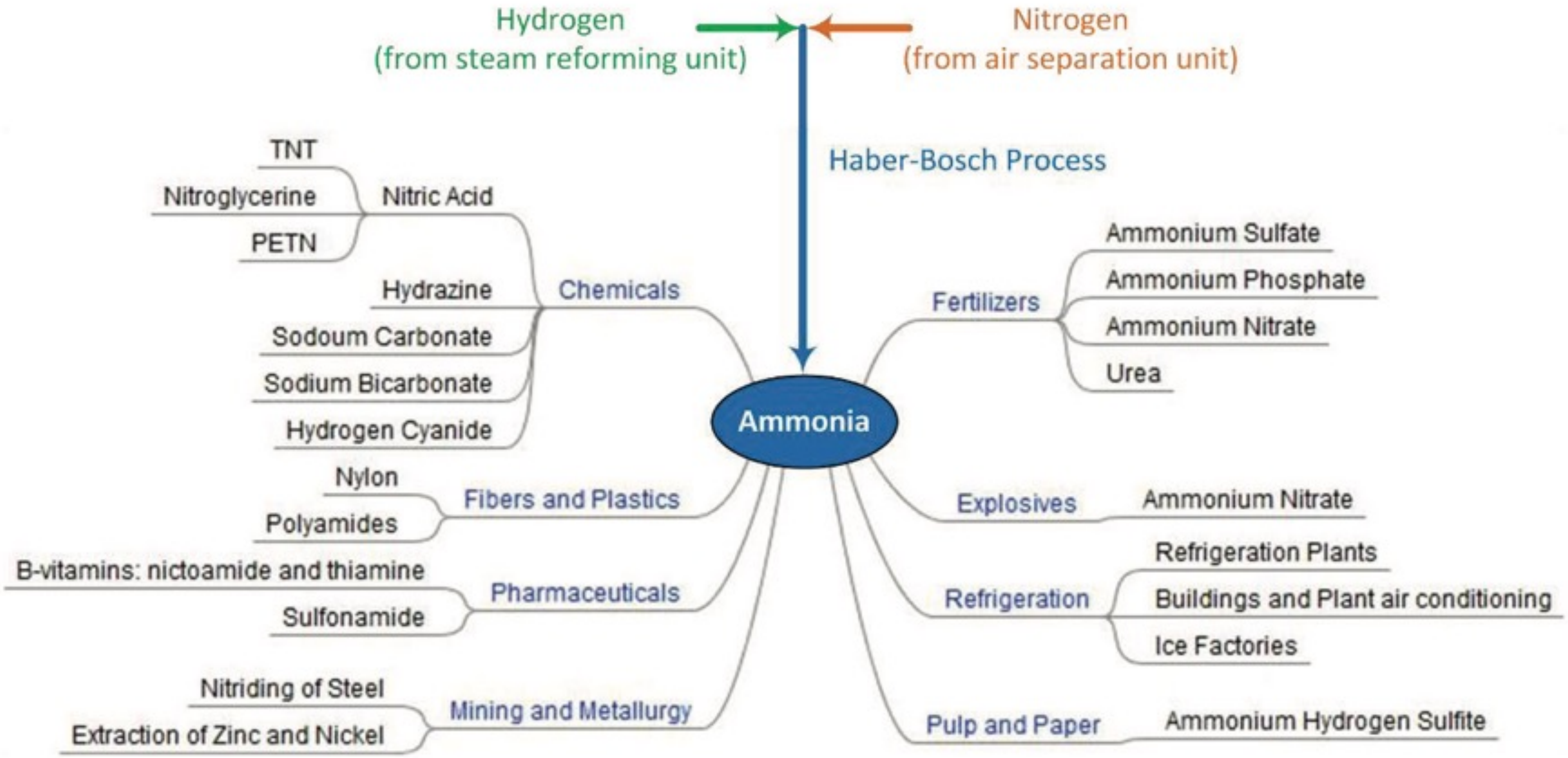
- The H-B process is the most energy-intensive process in the chemical industry.

- The Haber-Bosch process consumes 1-2% of the world's energy, uses 2-3% of the world's natural gas output, and emits over 300 million metric tons of CO2 each year.

$$3H_2 + N_2 \leftrightarrow 2NH_3$$

Ammonia uses

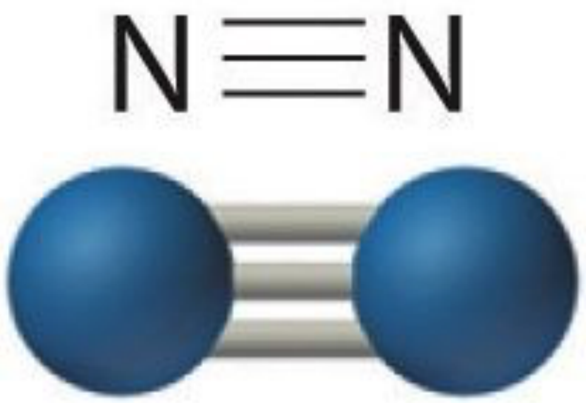
- Ammonia, is the second highest industrially produced chemical, and has an irreplaceable role in the chemical industry.



The triple Nitrogen bond

- The kinetic stability of the N_2 triple bond ultimately makes the “fixation” of nitrogen an energy intensive process.

- It is difficult to dissociate the triple bond of nitrogen because the molecule does not readily accept or donate electrons.



Non-thermal plasma can help in the dissociation of the strong triple N_2 bond!

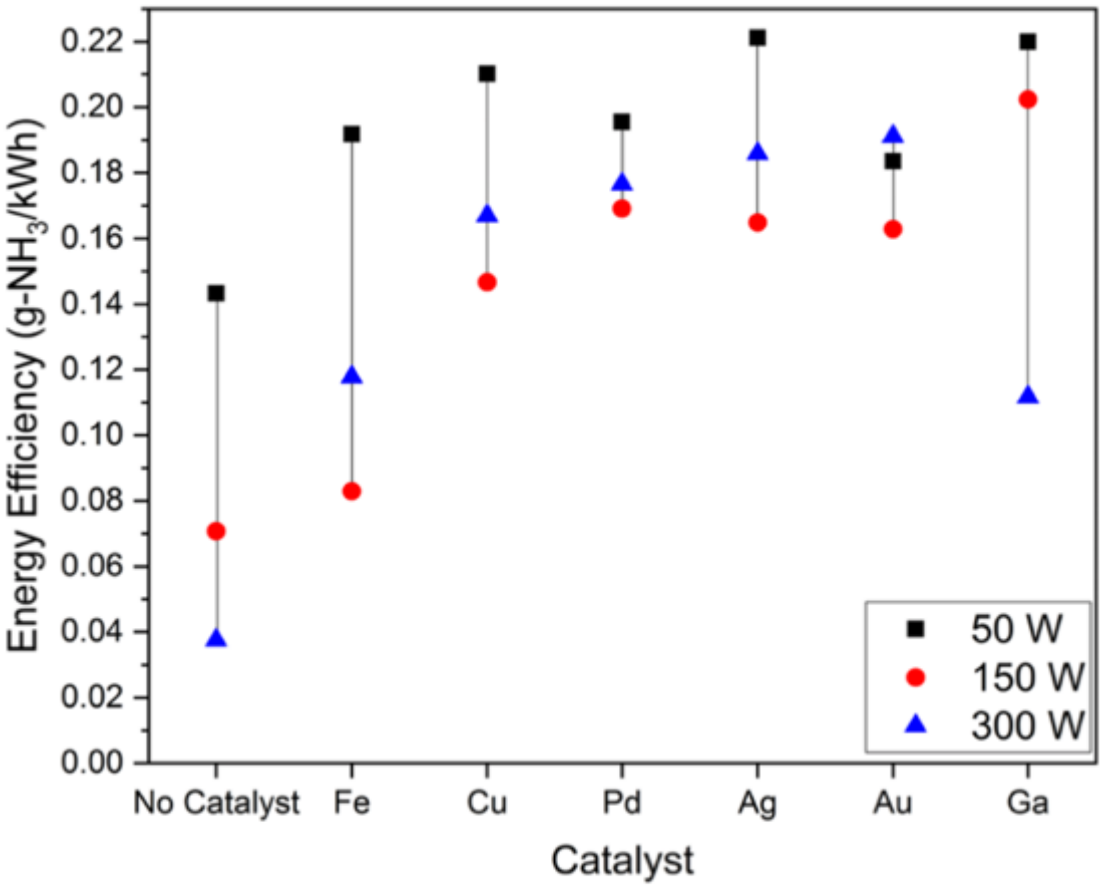
Energy efficiency

- Contrary to the ammonia yield, the highest energy efficiencies were mainly observed at 50 W.

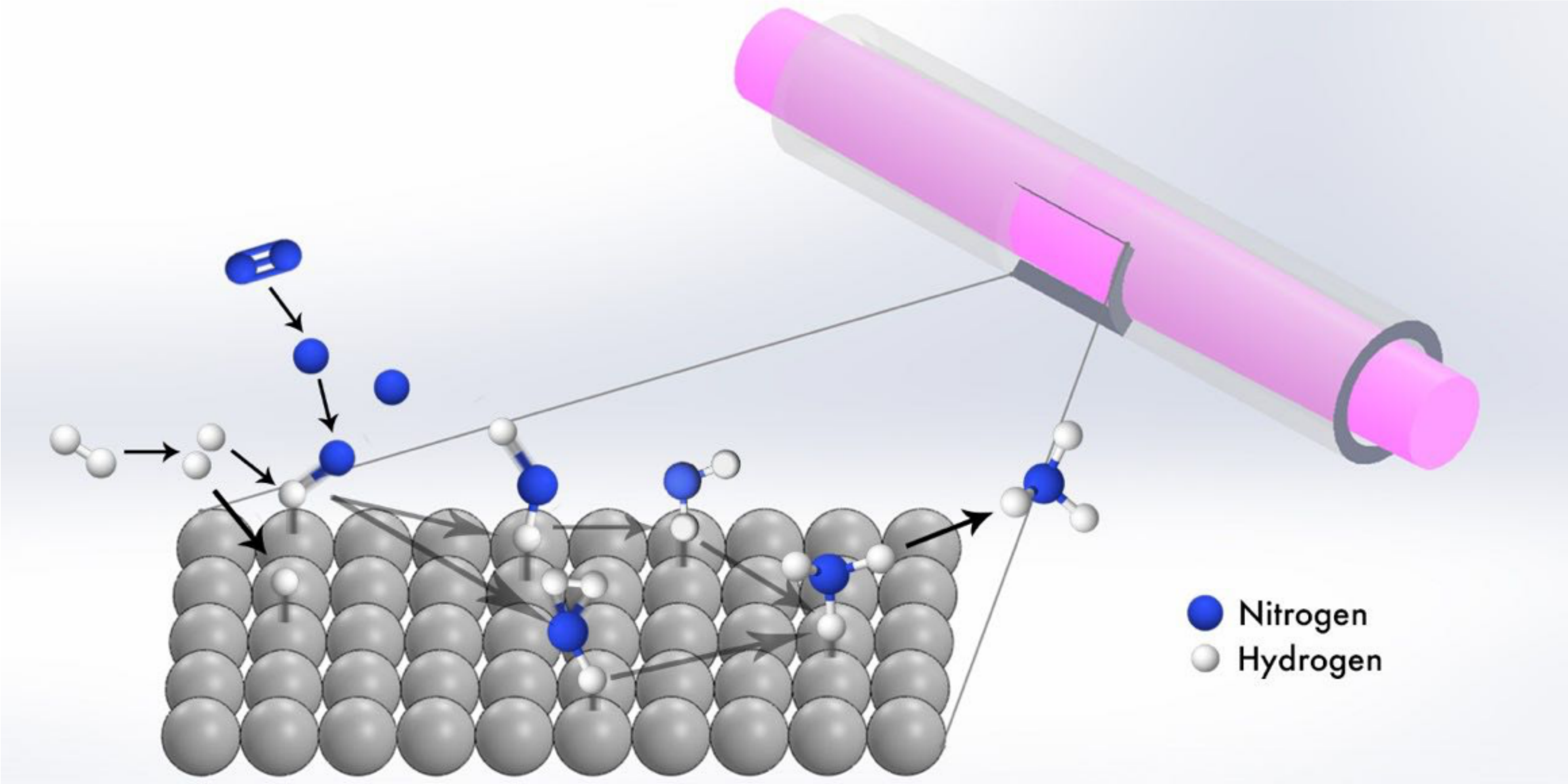
- In general, the metal meshes exhibited highest energy efficiency at 50 W followed by 300 W.

- Comparing with other reports on RF low pressure plasmas the energy efficiency has improved from 0.012 g-NH3/kWh to ≈ 0.2 g-NH3/kWh with changing the catalyst from Fe to Ga (150W) in this work.

- The energy efficiency of plasma catalytic synthesis of ammonia typically is in the range of 0.03-4.45 g- NH3/kWh.



Simplified reaction pathway



Benchmarking with other plasma processes

Plasma	Year	Catalyst	NH_3 Yield	Energy Yield (g-NH_3/kWh)*	Energy Cost (MJ/mol)**	Ref.
Radio frequency	1993	Iron wires	-----	0.025	856.2	43
	2018	No Catalyst	3.7%	0.04	1343	This Study
		Gallium	11.2%	0.11	451	
		Iron Mesh	11.8%	0.12	428	
		Copper Mesh	16.7%	0.17	302	
		Palladium Mesh	17.6%	0.18	285	
		Silver Mesh	18.6%	0.19	271	
		Gold Mesh	19.1%	0.19	264	
DBD	2017	Ru over γ-Al_2O_3	1.4%	-	32	1
	2017	$BaTiO_3$ beads or Porous Ni Catalyst	9%	-	81	41
	2017	Ru-MCM-41	0.1%	1.7	27	67
	2017	Wool-like Gold	4.72%	4.45	93	63
	2017	PZT Powder	7%	-	408	40
	2016	Wool-like Copper	3.5%	3.3	93	38
	2015	$BaTiO_3$ / PZT	2.75%	0.72	136	37
	2008	No Catalyst	0.8%	1	-	68
	2003 and 2008	MgO	0.63%	1.83	-	30, 68
Pulsed	2017	Mg promoted Ruthenium over Alumina	-	35.7	1.71	64
AC	2017	Mg promoted Ruthenium over Alumina	-	9.8-11.5	5.32	64
Microwave	2008	No Catalyst	0.00025%	0.03	-	33

- Typical experiments in DBD plasma have usually been carried out at a total flow rate of ≈100 ml/min which is 5 times the flow rate used in this study.