Atmospheric-Pressure Synthesis of Ammonia Using Non-Thermal Plasma with the Assistance of Ru-Based Multifunctional Catalyst

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NH3 Fuel Conference

AICHE 2017 Annual Meeting, Minneapolis, MN, USA

Non-thermal plasma (NTP)

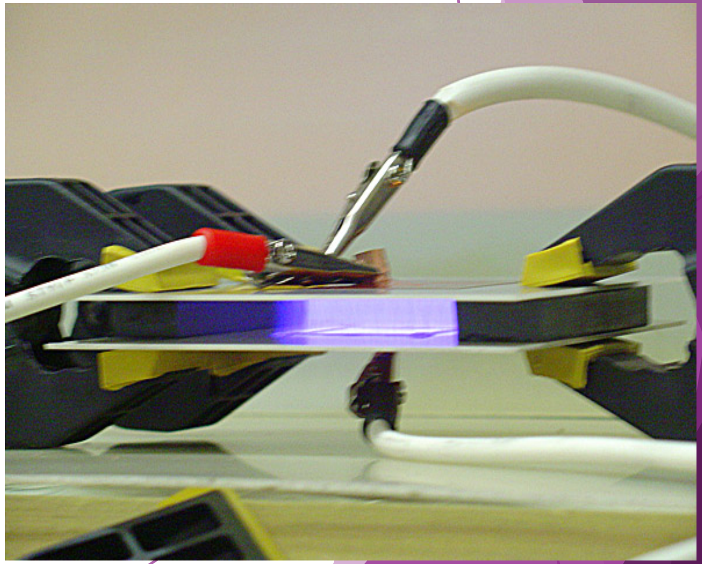
- Electrically energized matter in a gaseous state and generated through electrical discharge
- NTP species include: energetic electrons, ions, atoms and molecules, highly reactive radicals, and quanta of electromagnetic radiation (photons)
- Types of non-thermal plasma:

  Microwave-induced plasma (MIP),

  Dielectric barrier discharge (DBD) plasma,

  Gliding arc discharge plasma, etc.

Conrads & Schmidt, 2000;
C. Liu, Brown, & Meenan, 2006;
Schütze et al., 1998;
Wang et al, 2011;



Uses of non-thermal plasma (NTP)

- Gas pollutant treatment

- Biomedical applications

  (blood coagulation, wound and tissue sterilization)

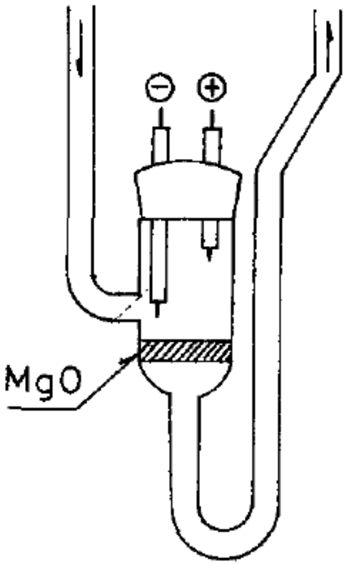
- A potential alternative to the high temperature and pressure method for the synthesis of many chemicals

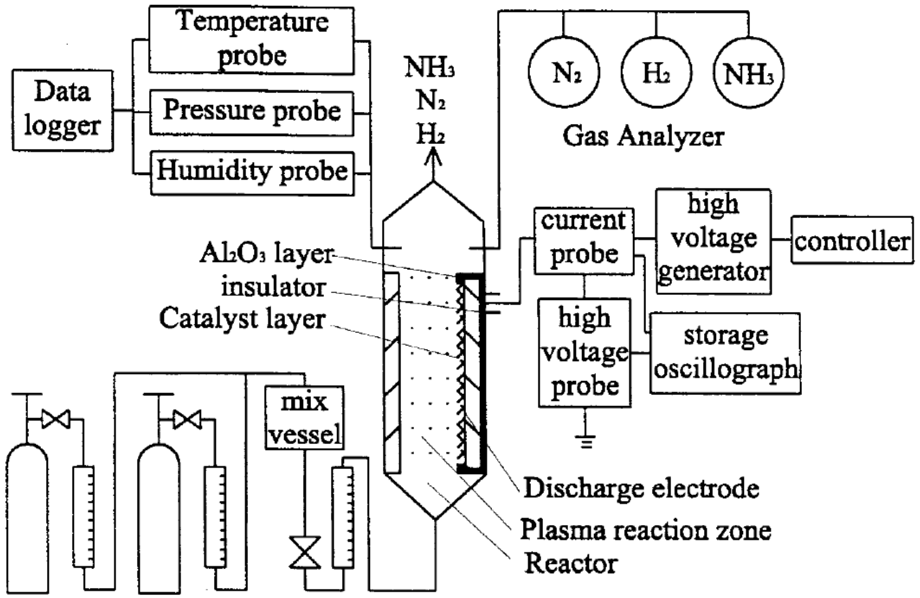
  (methane, isooctane, etc.)

- Can also be suitable for ammonia synthesis

Background: Earlier NTP reactors for NH3 synthesis

- 1980’s to 1990’s: glow DC arc discharge, microwave discharge
  - Operated under low pressure (5 to 10 Torr)
- Early 2000’s: rectangular shaped DBD

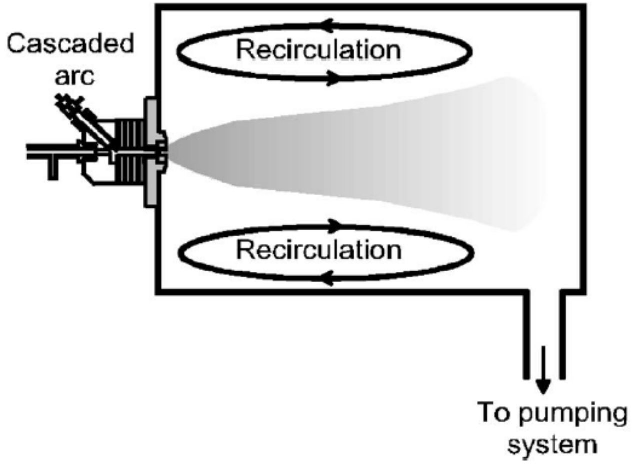


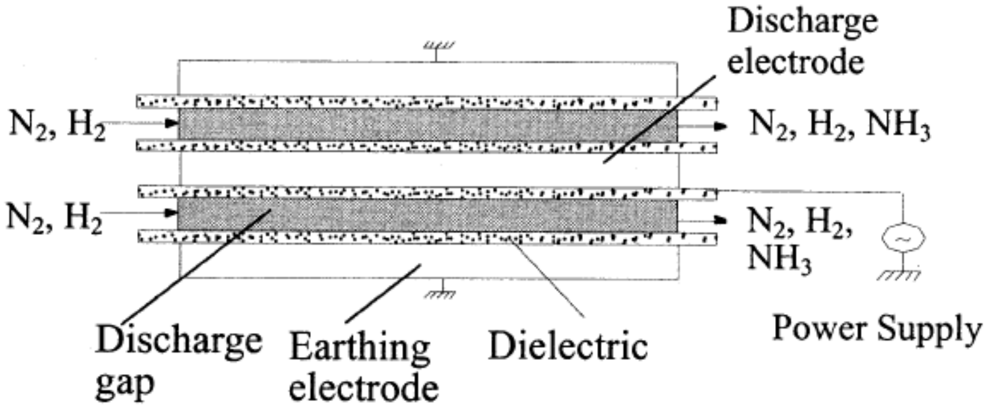


Sugiyama et al, 1986
Uyama et al, 1993
Tanaka et al, 1994
Bai et al, 2000

Background: Earlier NTP reactors for NH3 synthesis

- Cascaded arc plasma ammonia synthesis
  - Operated under vacuum conditions (0.37 Torr)
  - Semi-continuous operation
- Rectangular micron meter (gap) dielectric barrier discharge (DBD) reactors
  - Operated under atmospheric pressure
  - Continuous operation



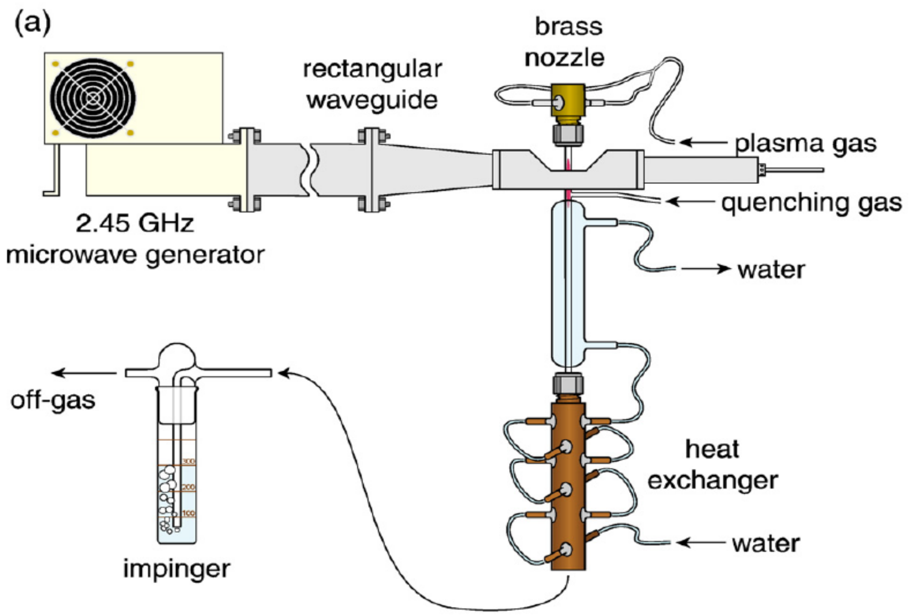


Bai et al. 2003, 2008
Van Helden et al. 2007
Florian et al., 2015.

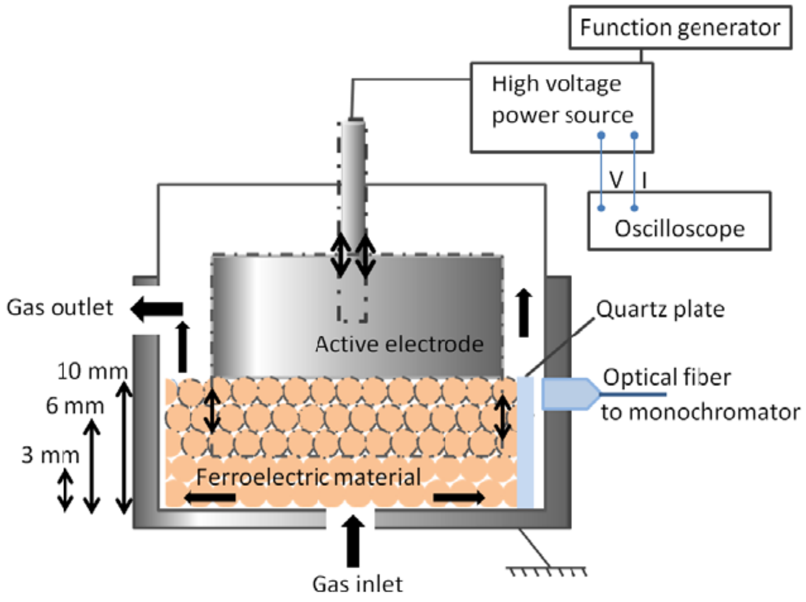
Background: Using microwave plasma reactors and using ferroelectric material for NH3 synthesis

- Achieved microwave discharge plasma at atmospheric pressure
- Continuous operation
- Temperature: 516 C to 966 C

- Use ferroelectric material to produce discharge in stead of dielectric barrier
- Operated under atmospheric pressure
- Temperature: ~50 C
- Continuous operation



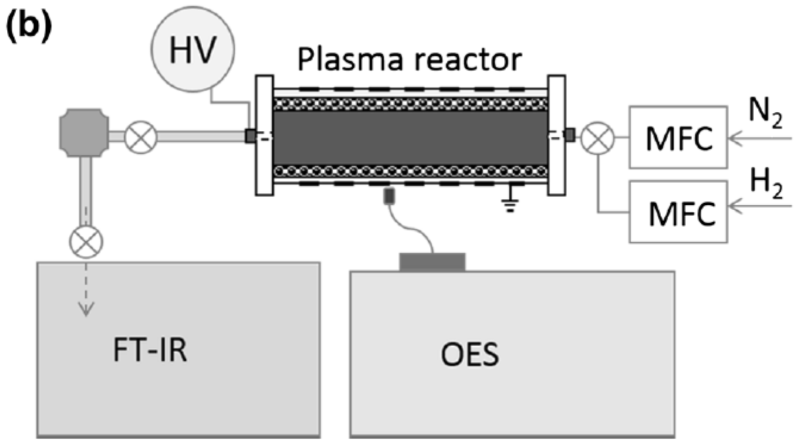
Nakajima et al. 2008

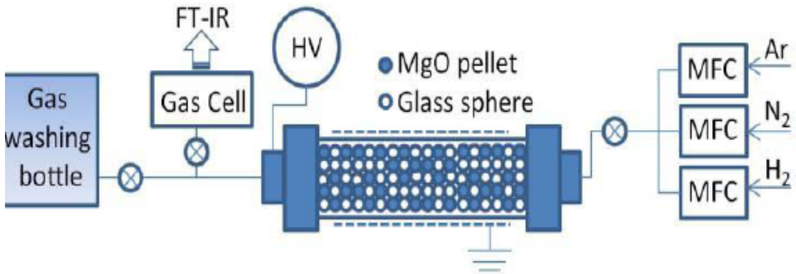


Gomez et al. 2015, 2016

Background: Using tubular NTP reactors for NH3 synthesis

- Tubular-shape NTP reactors has better energy efficiency than the other systems
- Operated under atmospheric pressure
- Temperature: ~120 C
- Continuous operation
- Various catalysts were used





Hong et al. 2014,
Hong et al. 2016

NTP for ammonia synthesis

- No fossil fuels
- Low capital cost
- NTP N-fixation has a theoretical efficiency floor of 0.2 MJ/mol, which is more efficient than the HB method of 0.48 MJ/mol
- A continuous process at atmospheric pressure
- Less land use
- Can be co-located with end users (save transporation and storage cost)
- More suitable for the distributed ammonia production in local farms

Key reactions:

$N_2^+ + H_2 \rightarrow N_2H^+ + H$

$N_2^+ + H \rightarrow N_2H^+$

$N_2H^+ + e \rightarrow NH + N$

$N + H \rightarrow NH$

$NH + H \rightarrow NH_2$

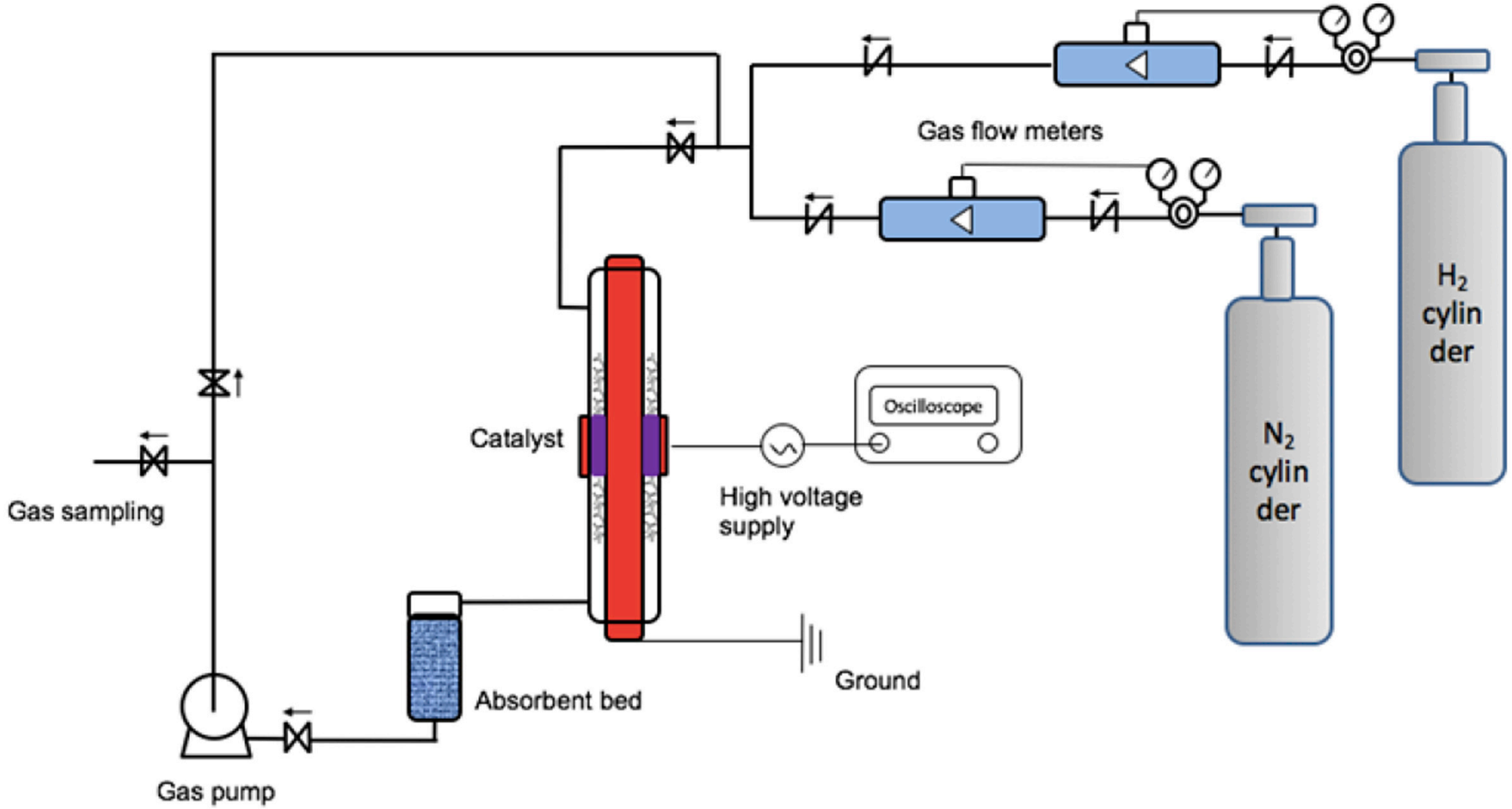
$NH + H_2 \rightarrow NH_3$

$NH + 2H \rightarrow NH_3$

$NH_2 + H \rightarrow NH_3$

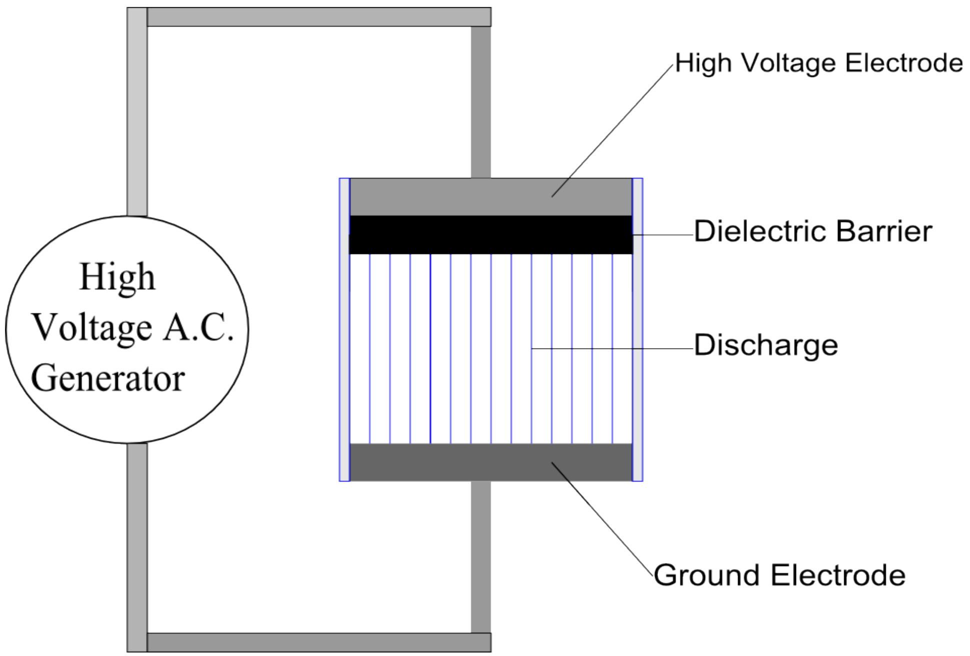
Cherkasov et al., 2015;
Patil, 2017;
Ingels and Graves, 2015

Current progress: Experimental setup



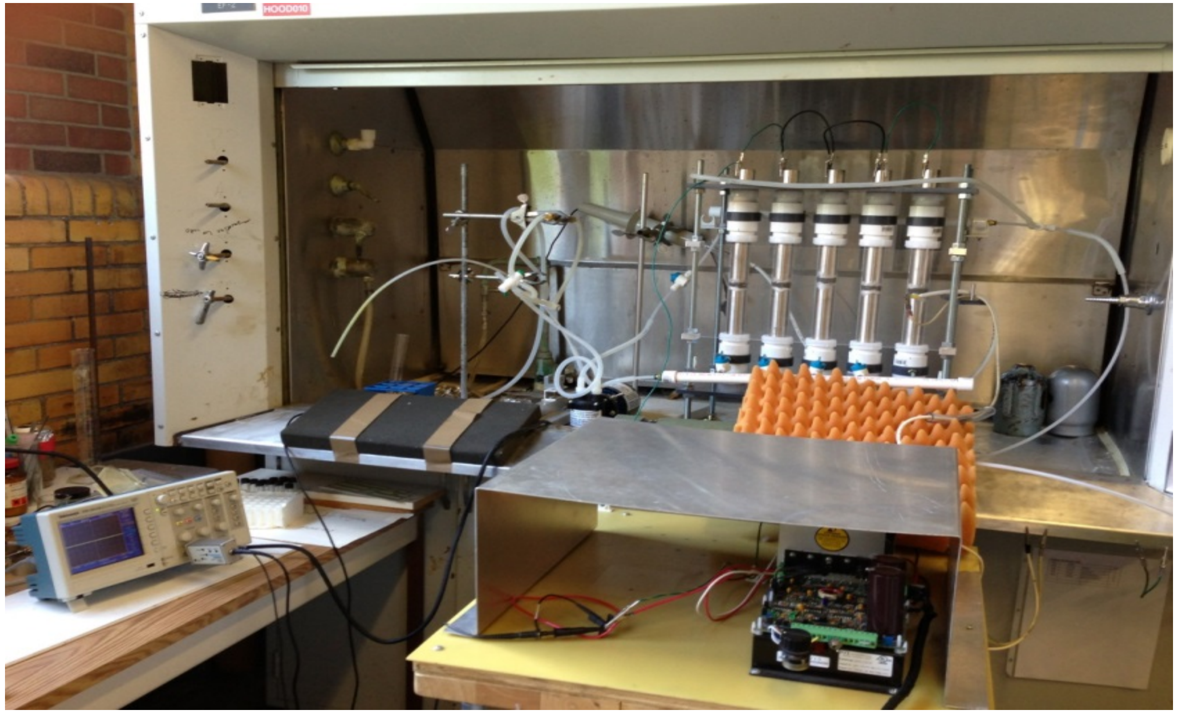
Advantages of DBD plasma

- Low operational/maintenance cost
- Greater accessibility of broad operation pressure
- A recent comparison between the DBD plasma and microwave-induced argon plasma showed that DBD plasma generates higher electron density and atomic oxygen concentration with less temperature increase.



Conrads & Schmidt, 2000;
C. Liu, Brown, & Meenan, 2006;
Schütze et al., 1998;
Wang et al, 2011;
Florian et al., 2015).

Photographs of the system



Catalyst development

- Three important factors:
  1. With or without catalyst?
  2. Catalyst shape (Disks, wires, powders, pallets)
  3. Catalyst type

     - Mono: Al2O3, MgO, Cu

     - Catalyst-support: (Ru on Al2O3, Ru on MgO, Diamon-like carbon on Al2O3)

**Transitional metals including Fe, Co, Cu and Ni demonstrated relatively high activities during plasma-assisted ammonia decomposition. (L. Wang et al., 2015)

Catalyst development

Catalyst type	Catalyst	Catalyst shape	Greatest energy efficiency	Reactor	Reference
Mono catalyst	CaO Al_2O_3; WO_3, and SiO_2-Al_2O_3	Disks	Little to no ammonia detected for Al_2O_3, WO_3, and SiO_2-Al_2O_3	glow DC arc (Batch)	(Sugiyama et al., 1986)
Mono catalyst	Iron and molybdenum	Wires	0.078 g/kWh**	Microwave	(Tanaka et al., 1994; Uyama et al., 1993)
Mono catalyst	MgO	Powders	N/A	Reactangular	(Mingdong Bai et al., 2000)
Mono catalyst	MgO and glass spheres	Pallets	N/A	Tubular	(Hong et al., 2014)
Mono catalyst	Lead zirconate titanate, BaTiO3	Pallets	0.9 g/kWh	ferroelectric discharge	(Gómez-Ramírez et al., 2015)

Catalyst development

Catalyst type	Catalyst	Catalyst shape	Greatest energy efficiency	Reactor	Reference
Catalyst-support	Ru/ Alumina	Powders	0.34 g/kWh** (5.5E-9 mol/J)	Tubular DBD	(Mizushima et al., 2004)
Catalyst-support	Nanodiamonds and diamond-like carbon coated Al2O3	Sphere powders	0.16 g/kWh	Tubular DBD	(Hong et al., 2016)

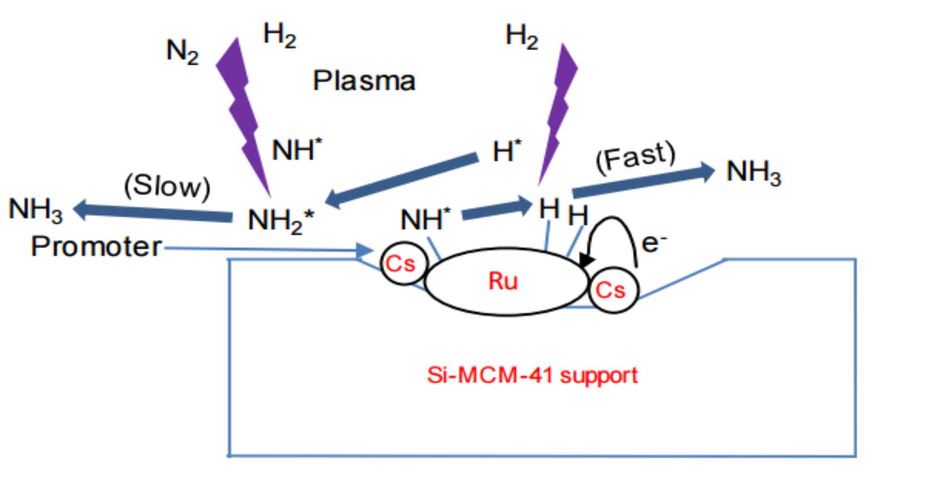
Catalyst development

Catalyst	Catalyst shape	Greatest energy efficiency	Reactors	Reference
No catalyst	N/A	N/A	Rectangular DBD	(Mindong Bai et al., 2008)
No catalyst	N/A	0.78 g/kWh**	Tubular microwave	(Nakajima & Sekiguchi, 2008)
No catalyst	N/A	1.16 g/kWh (Including HNOx species)	Tubular DBD (plasma activated nitrogen with water)	(Kubota et al., 2010)

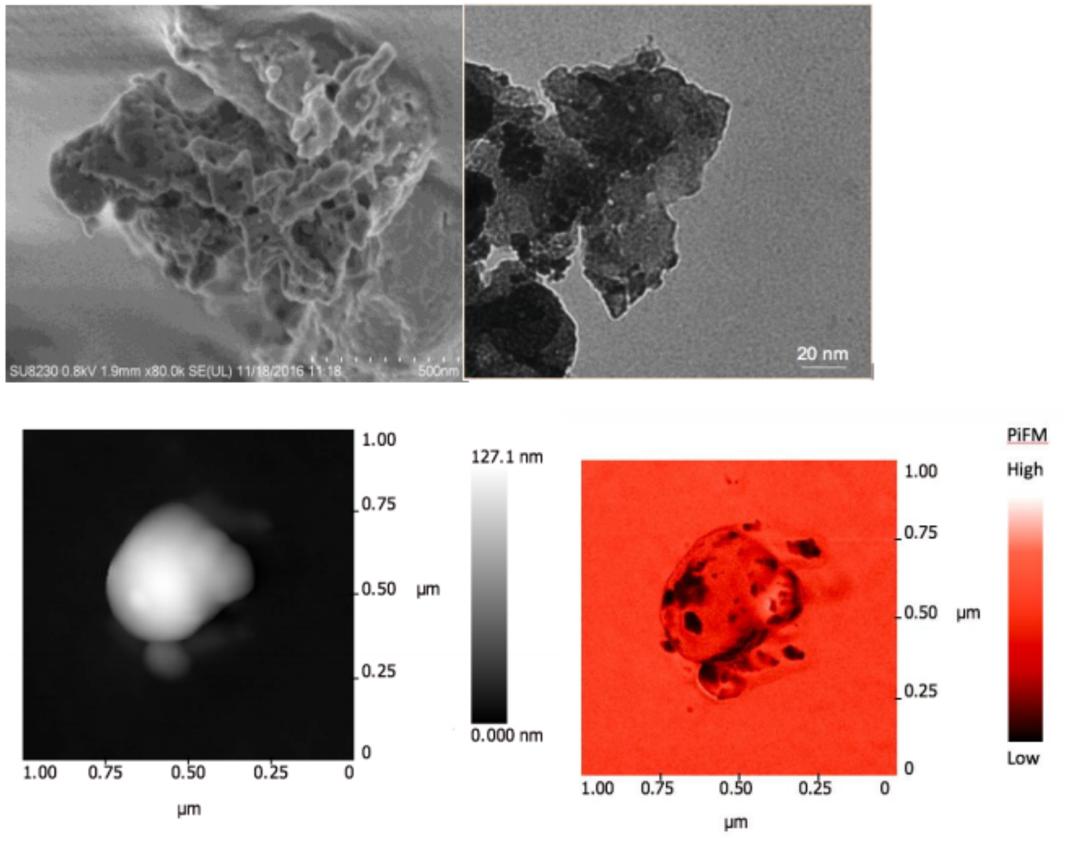
Ji et al., 2013;
L. Wang et al., 2015

Multifunctional catalyst: catalyst, promoter, and support

- Supported with non-conductive mesoporous structure
- Ruthenium catalyst and Cs, Ba promoters
- BET surface area Si-MCM-41 are in the range of 600 to 1000 m2/g, while the Ru deposited MgO catalyst are approximately 100 m2/g
- Non-conductive catalysts: increase stability and reduce catalyst shielding effects
- Catalyst preparation: Liquid impregnation -> Calcination -> Reduction in hydrogen environment

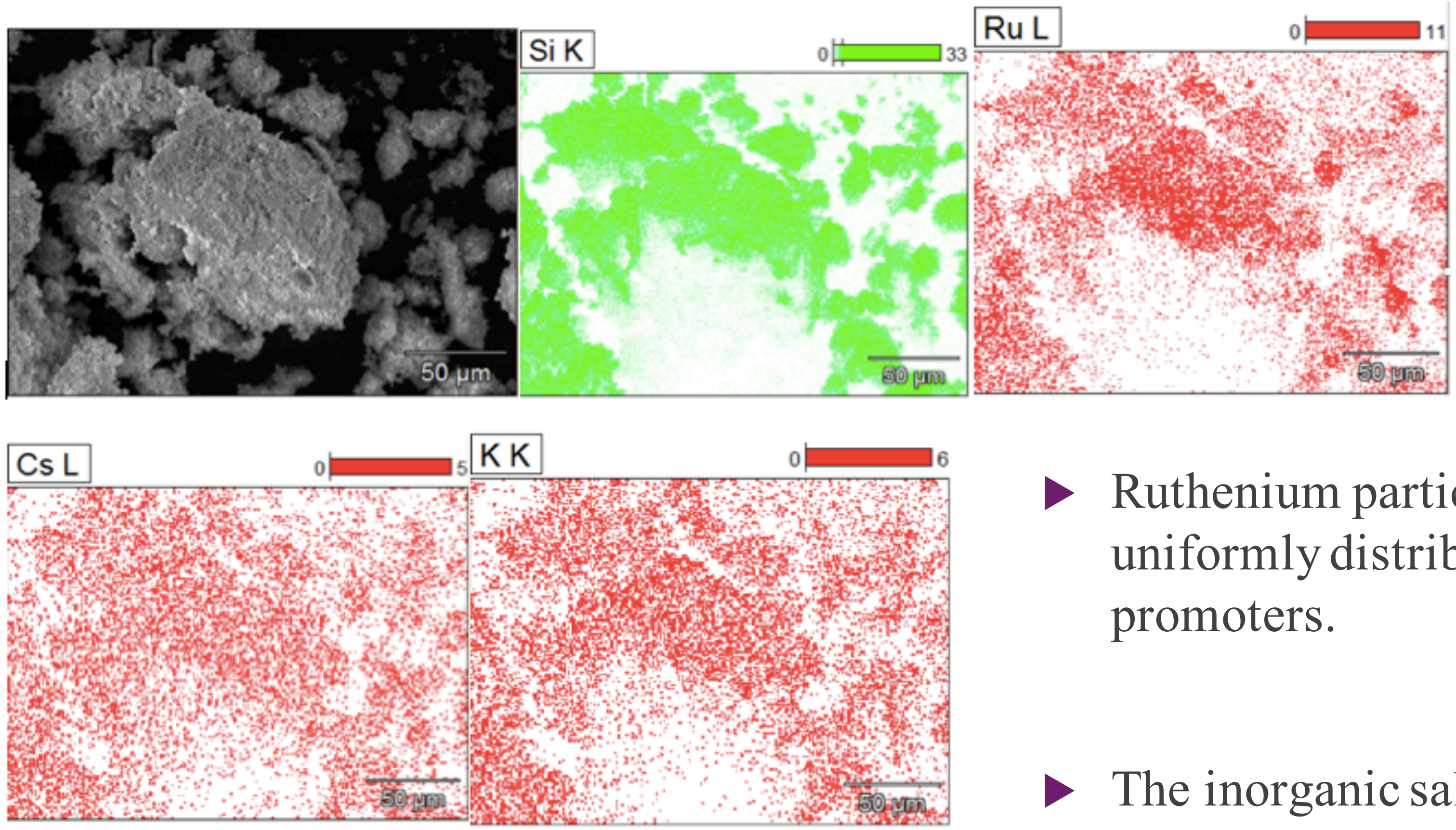


Catalyst characterization



- SEM, TEM, and AFM and Photo induced Force Microscopy (PiFM) were taken
- Pores in the material are mainly from 10 to 50 nm.
- The ruthenium particles could be deposited both inside and outside of the pores of the Si-MCM-41 support.
- After calcination, the catalyst particle sizes are around 0.5 to 2 um

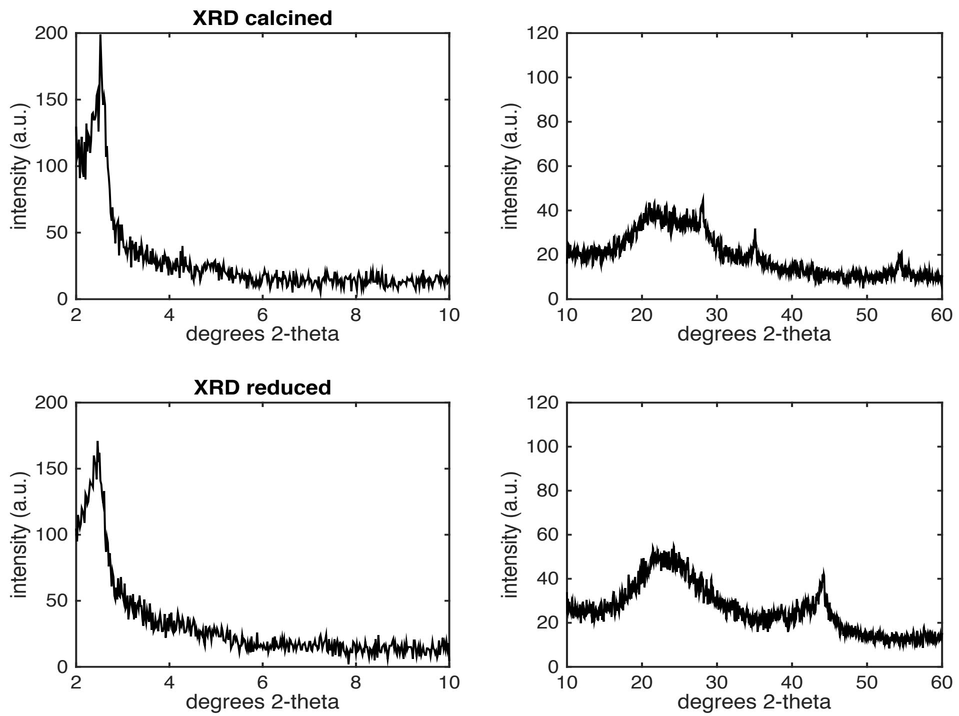
Elemental mapping



- Ruthenium particles are less uniformly distributed than the promoters.

- The inorganic salts form solution during the impregnation process while the Ru forms suspension.

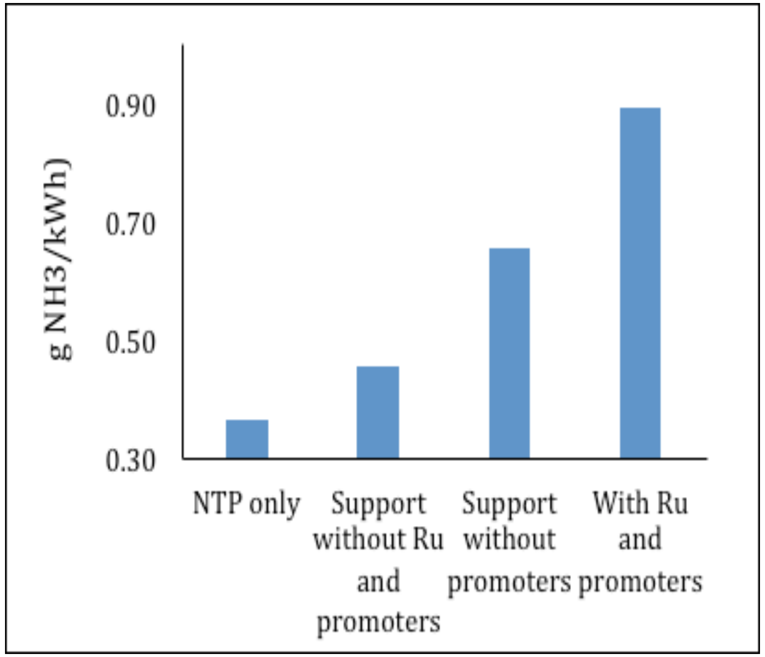
X-ray diffraction

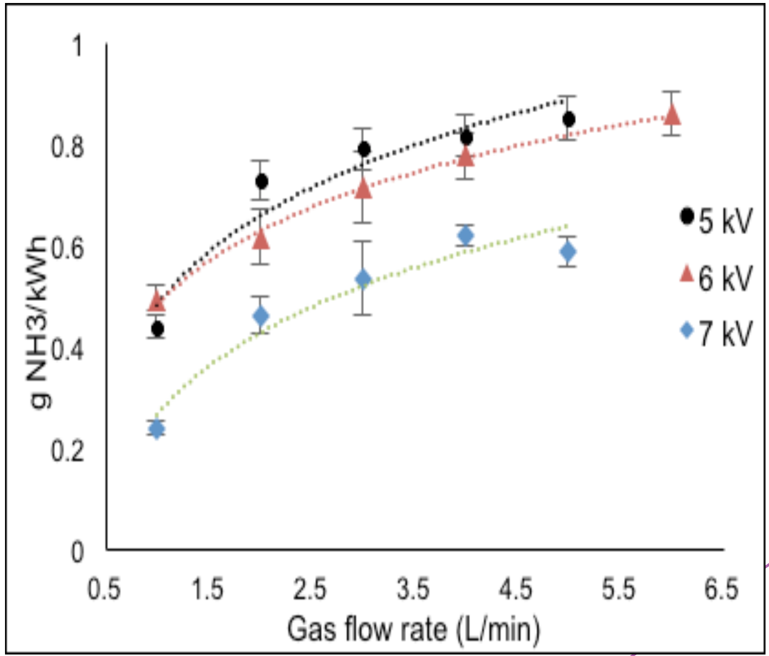


- The catalyst is amorphous
- Slight decrease in the intensity of the peak with a 2-theta value of around 2 shows that although slightly destroyed and deformed from the Ru complex, the pore shape within the Si-MCM-41 structure is largely retained after calcination and H2 reduction
- Ru in the reduced catalyst replaces Ru2O3 in the calcined catalyst

Results

- The temperature range of the experiments were between 100 °C to 150 °C, which was far less than the temperature required for the Haber Bosch process.
- Ru catalyst and promoters can lead to approximately 3 times increase of the synthesis efficiency to the process.
- Since the plasma synthesis reaction is a rapid process, it is reasonable that the higher flow rate leads to greater amount of ammonia produced, and therefore greater synthesis efficiency.



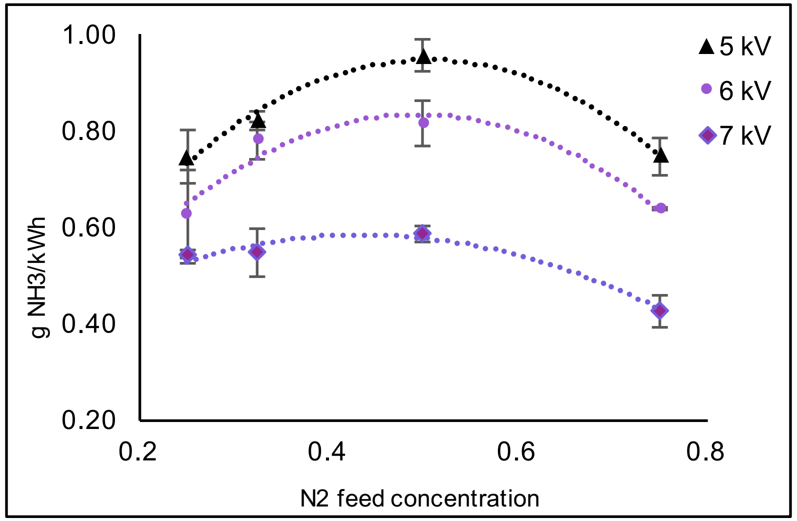


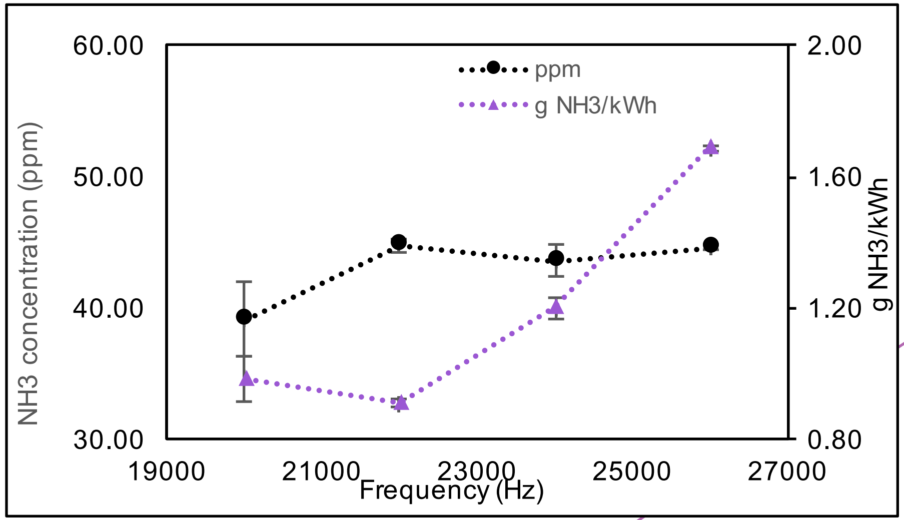
Results

- Highest energy efficiency: 1.7 g NH_3/kWh Achieved at 5000V and 26,000 Hz

- The resonance effect of the dielectric barrier discharge can contribute to the homogeneity of the discharge, which can further increase synthesis efficiency at higher frequency conditions

- Optimum gas flow rates: N_2:H_2=3:1 for MgO support, and 1:1 for mesoporous supports (Peng et al. *Plasma Chemistry and Plasma Processing*, 2016)





Conclusions and future plan

- Identified key factors for this project:
  1. Specific energy input
  2. Catalyst selection and its synergistic effects with plasma
  3. Prevention of back reactions
- Greatest energy efficiency achieved so far is 1.7 g/kWh at 0.05% N_2
- Higher frequencies helps increase efficiency for the tubular reactors and catalyst used for the current study
- Results needs to be improved to be comparable with the HB process
- Investigate to avoid or reduce the decomposition of ammonia after being synthesized

Acknowelegement

- Funding for this project was provided in part by the Minnesota Environment and Natural Resources Trust Fund as recommended by the Legislative-Citizen Commission on Minnesota Resources (LCCMR)
- Part of the synthesis study was supported by Minnesota's Discovery, Research, and Innovation Economy (MnDRIVE)
- Parts of this work were carried out in the Characterization Facility, University of Minnesota, which receives partial support from National Science Foundation (NSF) through the Materials Research Science and Engineering Centers (MRSEC) program.
- The PiFM images Molecular Vista (California, USA) for the assistance on taking the AFM and PiFM images.

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