Microwave Catalytic Synthesis of Ammonia for Energy Storage and Transformation

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Background:

- Hydrogen Energy
  - Clean combustion;
  - Bountiful in supply;
  - Low volumetric energy density – difficult to transport.
- Significance of Ammonia
  - Important raw material of fertilizers and pharmaceutical products;
  - Energy-dense hydrogen carrier.

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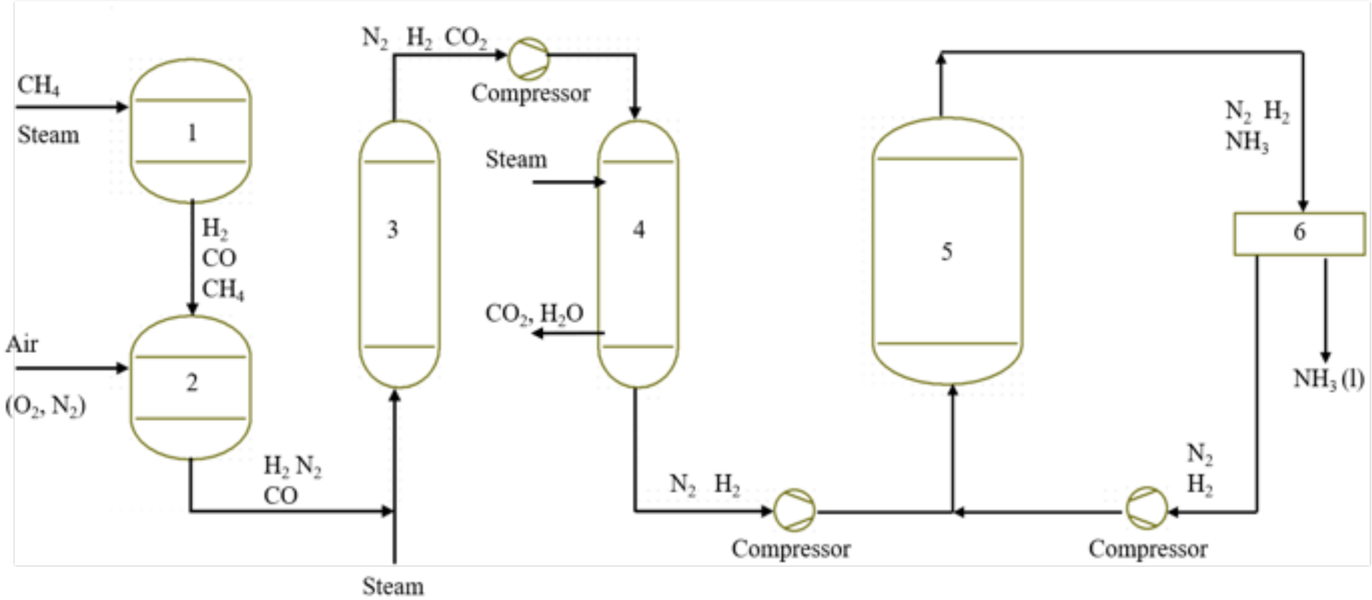
Source: 1: APNews: https://www.apnews.com/bd4f217666964b6984b77501a34d62a1
2: Economic Times: https://economictimes.indiatimes.com/news/science/hydrogen-cars-for-masses-one-step-closer-to-reality/articleshow/61736337.cms

Commercial Ammonia Plant: Haber-Bosch Process (~1000 ton per day)



Unit operations: 1: methane steam reforming reactor; 2: methane oxidative reforming reactor; 3: Catalytic water-gas shift reactor; 4: pressure swing adsorption of CO_2; 5: Haber-Bosch ammonia synthesis reactor (high temperature, high pressure); 6: condenser.

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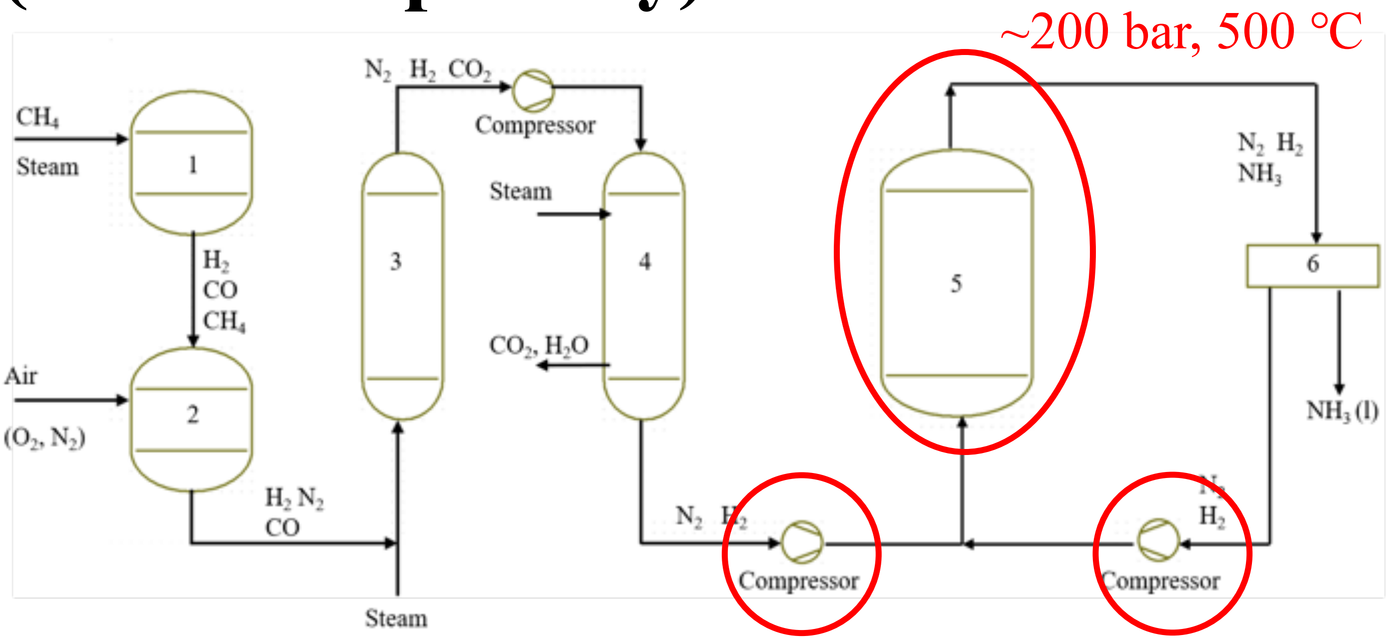

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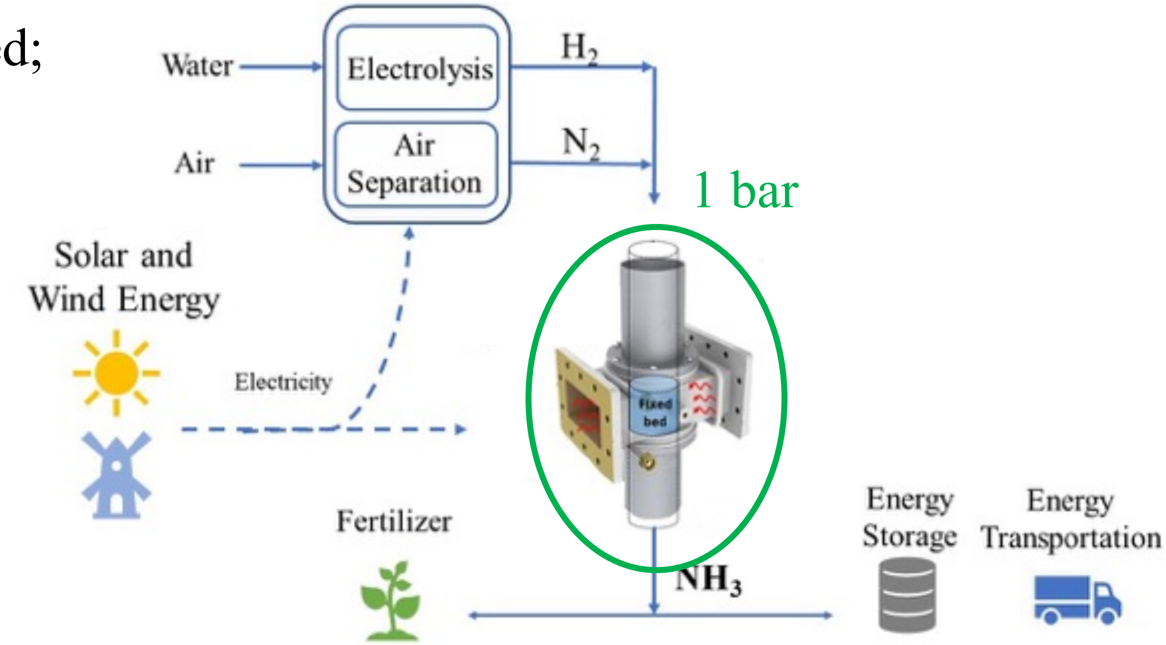
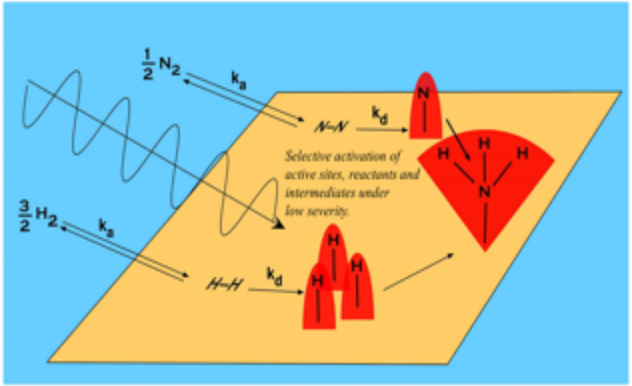
Designed Ammonia Synthesis under Atmospheric Pressure

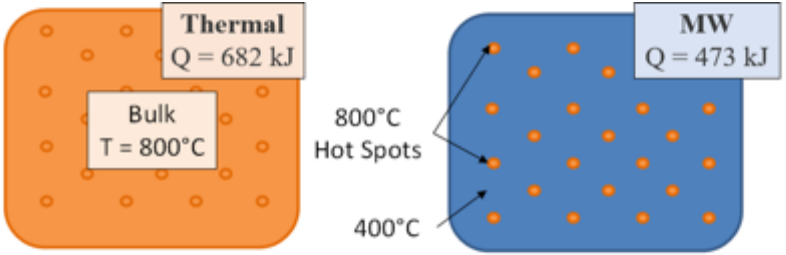
- Renewable energy is stranded;
  - Duck effect;
  - Intermittent in nature;
- Energy transformation for storage and transportation;
  - Stored as chemical energy;
  - Ammonia;

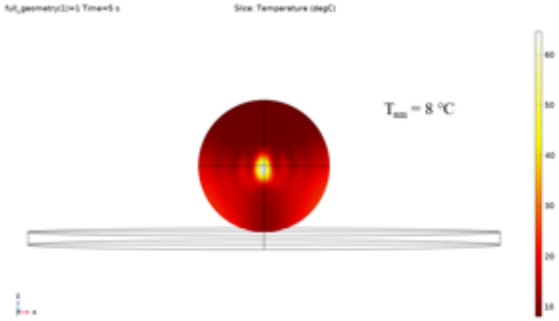


New Technology: Microwave (MW) Reactor

- Internal Heating;
- Rapid Heating;
- Selective Heating of Composite Material;
- Controllable Field Distribution (single-mode MW reactors);
- Other Non-thermal Effects.







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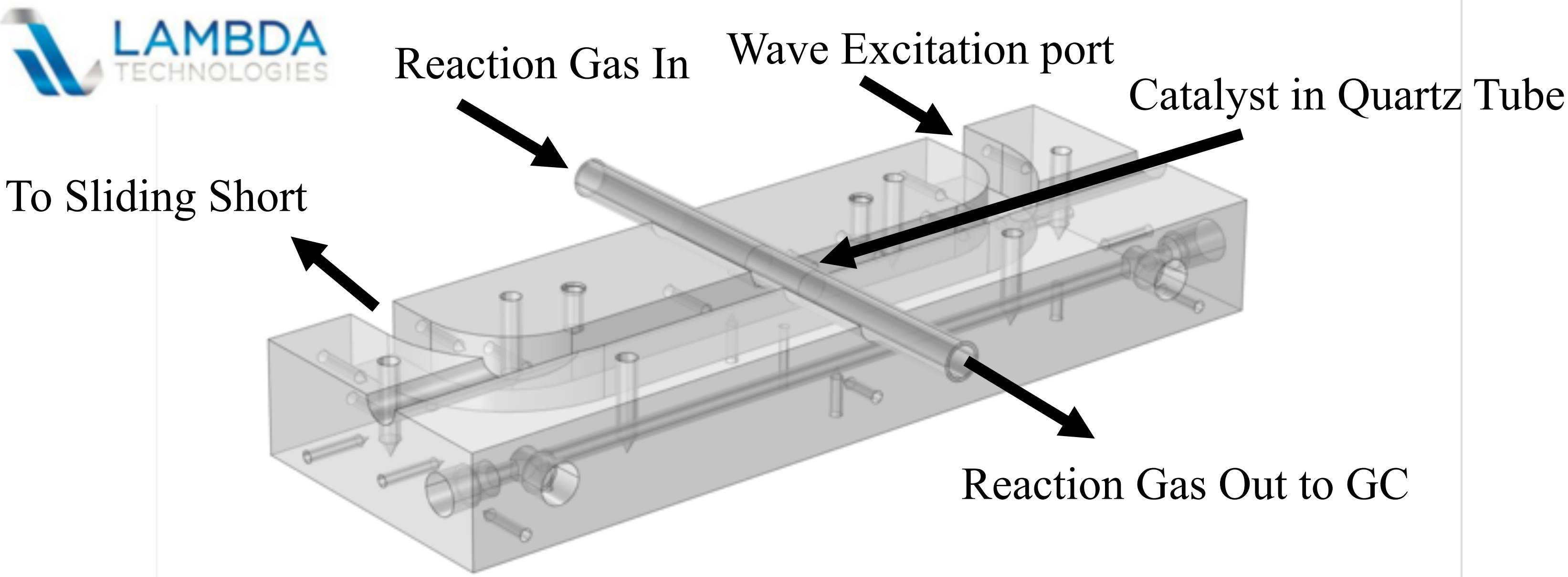
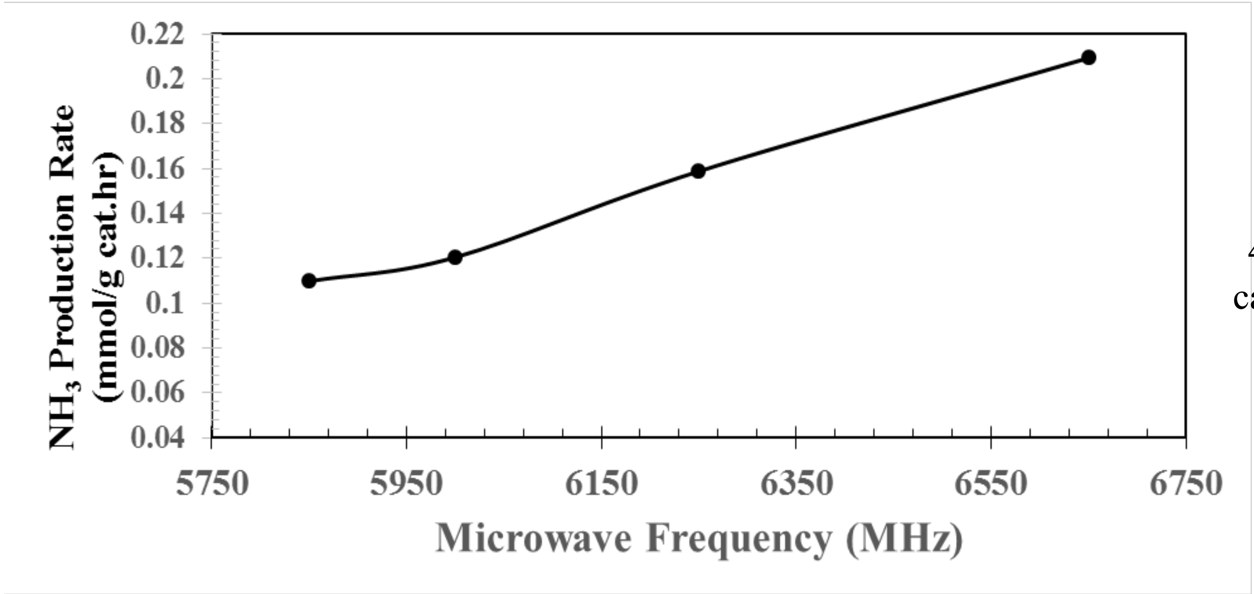


VFM MC-1330 unit (cross section) with
frequency range: 5850 – 6650 MHz (max 180 W)

Results: Ammonia Productivity of Ru/Al_2O_3 under MW irradiation



The effect of microwave frequency on the NH_3 yield. Reaction conditions: 4 wt% Ru/Al_2O_3, 280°C, 0.5 g catalyst, 0.1 MPa, GHSV=5000 h^{-1}; $N_2:H_2$ = 1:3.

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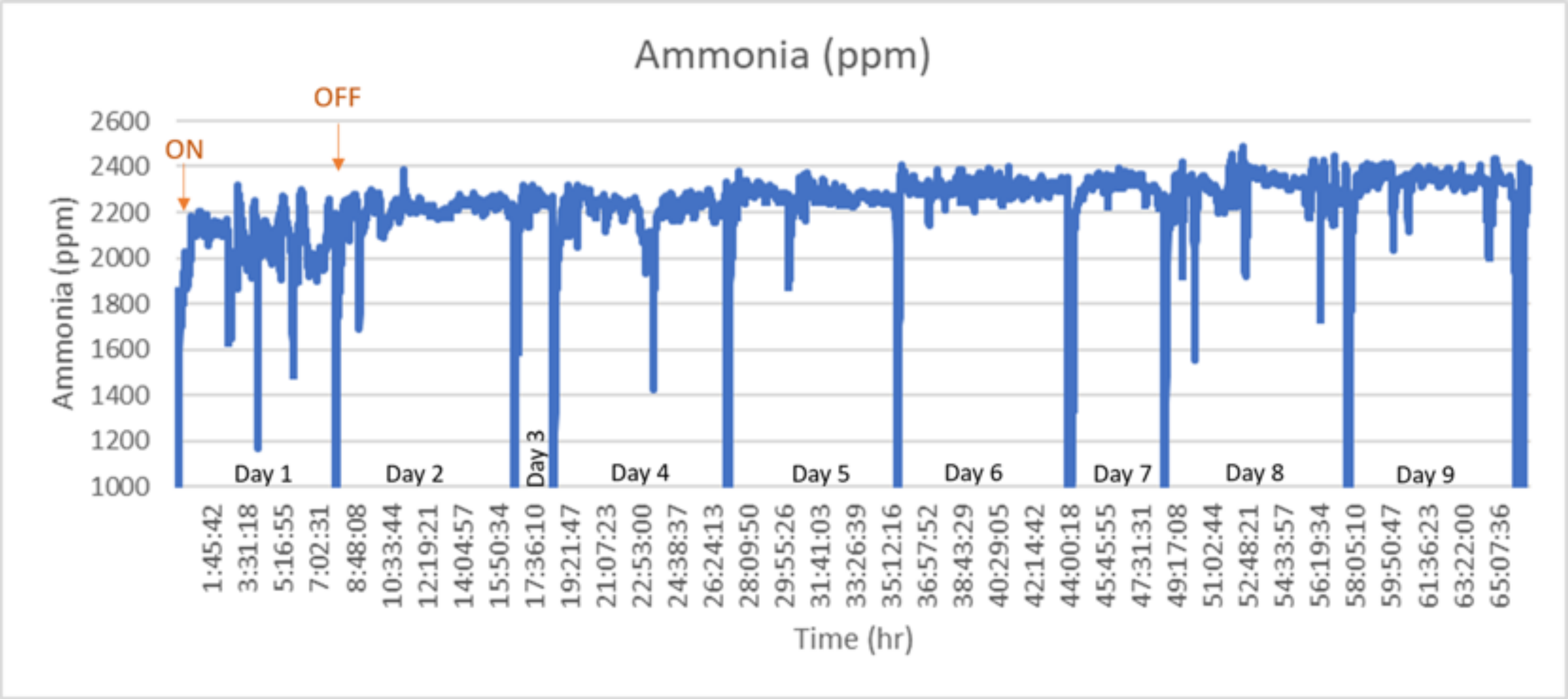
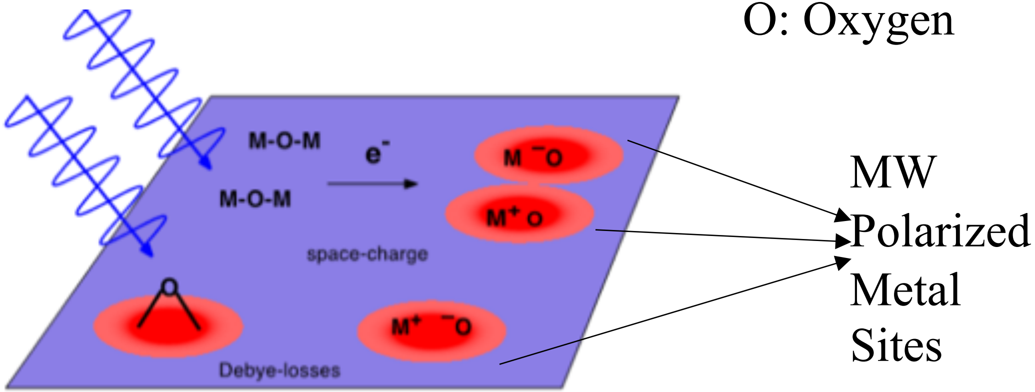
Results: Catalyst Stability



The Role of Microwave: thermal and non-thermal effects

- MW Heating (thermal)
  - kinetic energy loss due to inelastic dipole rotation and/or oscillation;
  - Changing H-field induces eddy current within conductive metal particles [1];
- Polarization (non-thermal)
  - Electric dipole formation due to displacement of electron cloud of atoms [2].
  - Field distribution

M: Metal
O: Oxygen

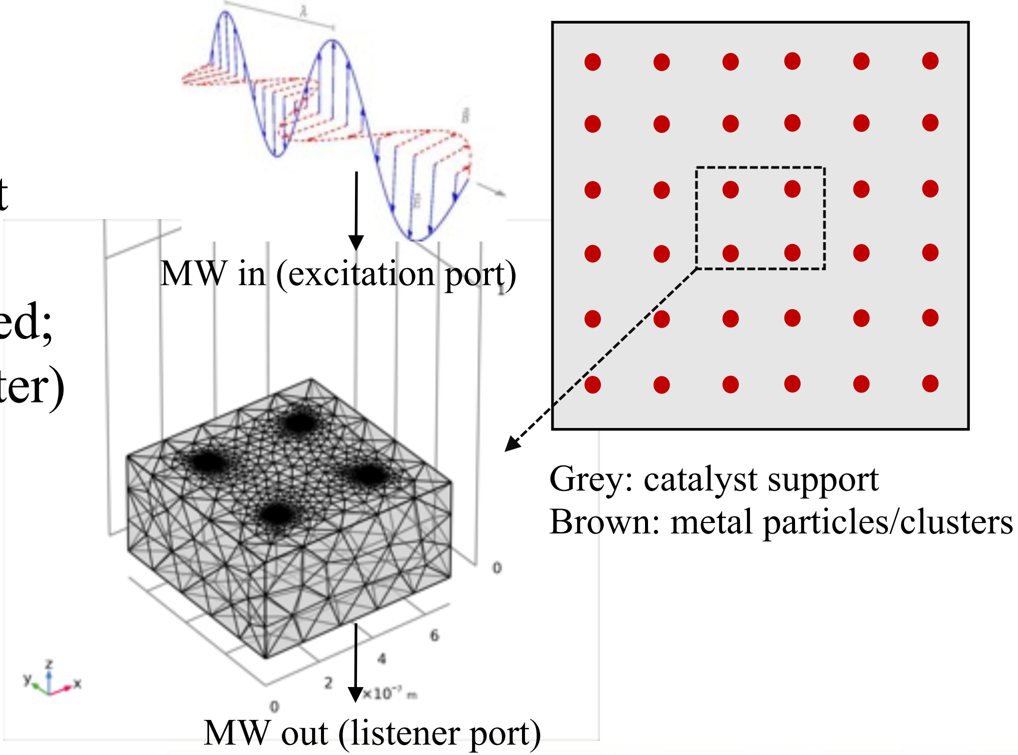


[1] A.P. Anzulevich, V.D. Buchelnikov, I. V Bychkov, D. V Louzguine-Luzgin, Microwave Penetrating and Heating of Metallic Powders, Piers 2009 Moscow Vols I Ii, Proc. 2 (2009) 844–847.
[2] National Research Council, Microwave Processing of Materials, the National Academy Press, Washington, D. C., 1994. doi:10.17226/2266.

The Role of Microwave: Finite-Element Method

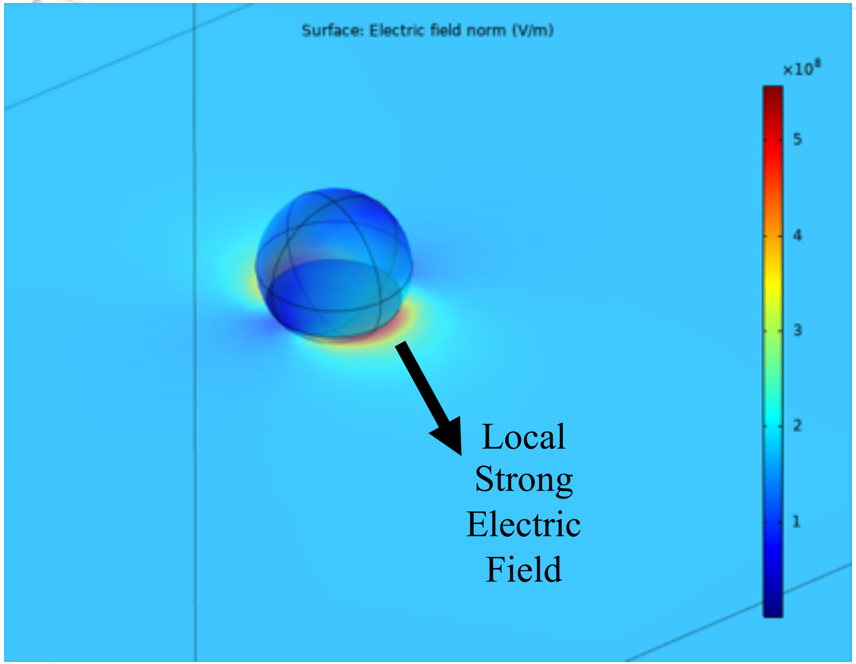
Assumptions:

- Large, continuous metal-support system;
- Metal particles are equally spaced;
- Diameter of metal particle (cluster) is 20 nm;
- Microwave in –z direction;

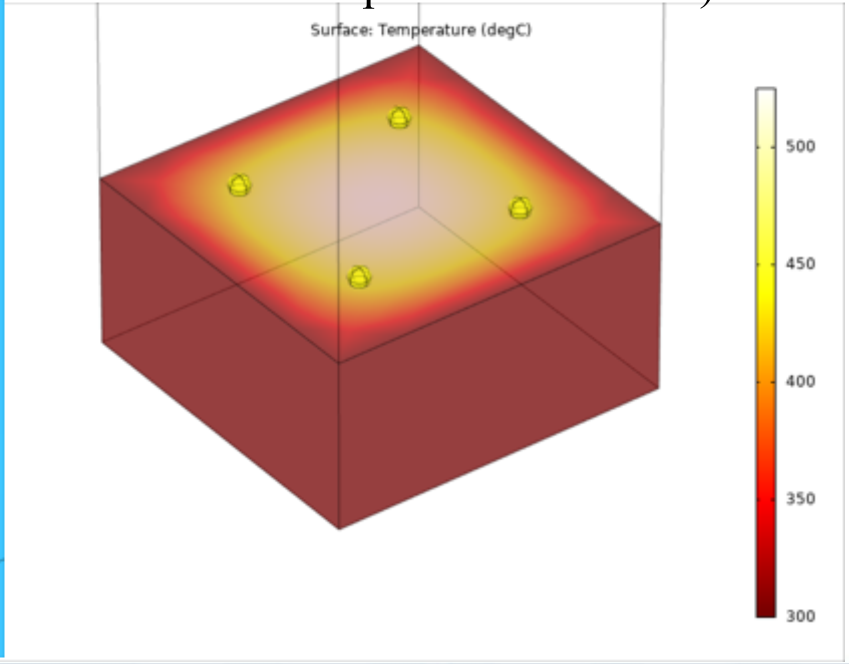


The Role of Microwave: Finite-Element Method

Electric Field Distribution (V/m)

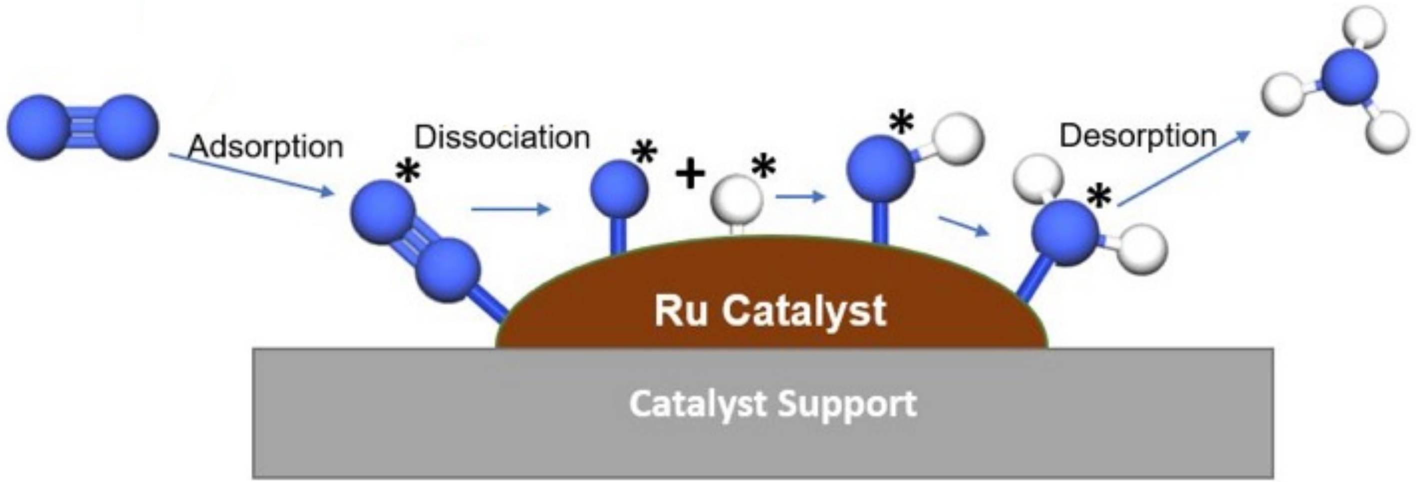


Temperature Distribution (^{o}C) (bulk temperature = 300 ^{o}C)

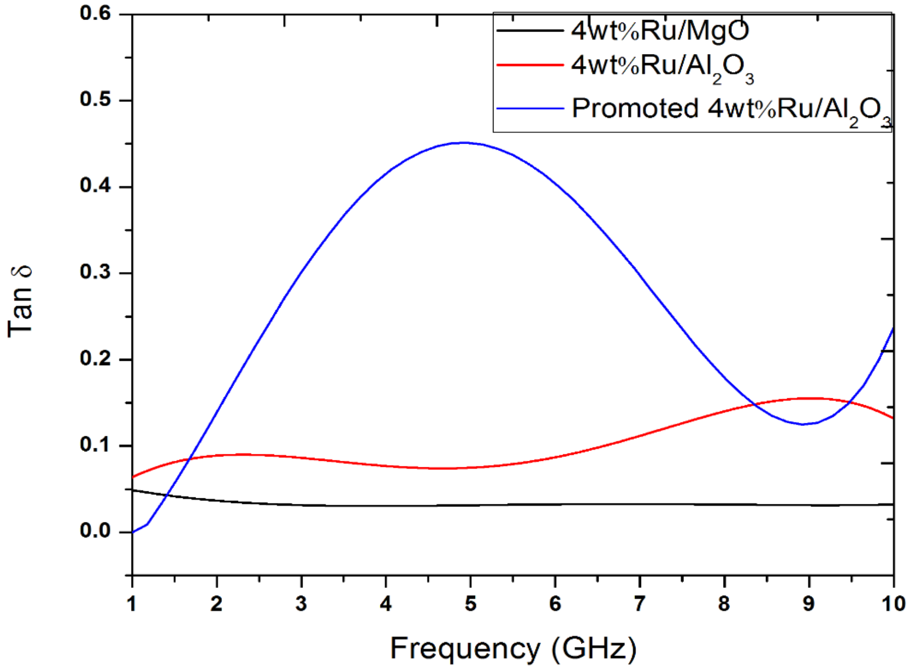


Software: COMSOL Multiphysics (version 5.4). Modules: RF, Heat Transfer

How Microwave Assists Ammonia Synthesis:



Results: Electromagnetic Properties Measurement



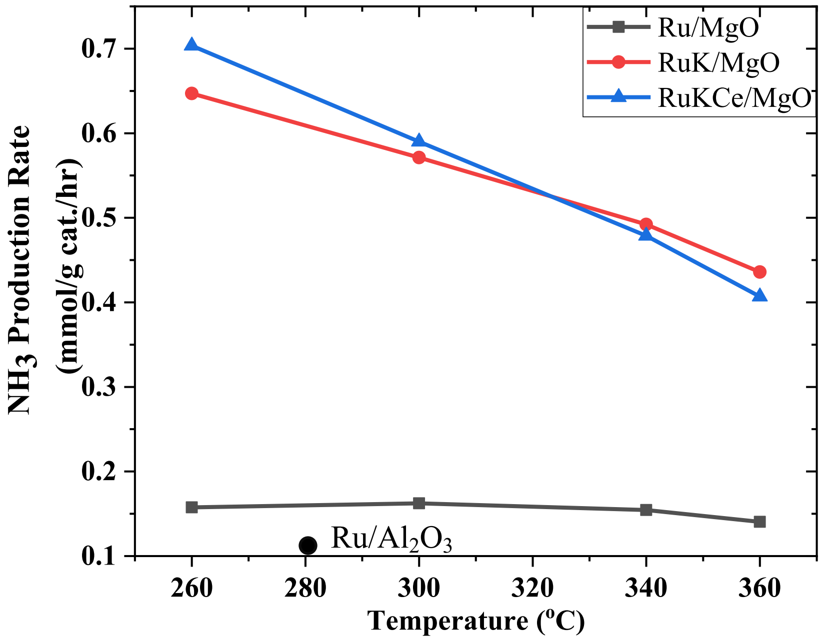
$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

- The lossiness of the material.

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$$

- Real part: how much microwave energy can be absorbed by dipoles.
- Imaginary part: the inelastic component that how much energy is loss and transformed to heat.

Results: Support and Promoter Effects



The effect of temperature and promoters on the NH_3 yield. Reaction conditions: 0.1 MPa, Frequency = 5850 MHz, GHSV=5000 h^{-1}.

- 0.4 g MgO catalyst and 0.1 g SiC, physical mixture.
- Using MgO support increases ammonia production rate;
- Adding K and Ce promoters boosts the ammonia production

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Conclusion Remarks:

- Microwave irradiation allows ammonia synthesis process be carried out under atmospheric pressure and low temperature;
- The performance of Ru-based catalyst was stable under both continuous operation and simulated power interruption performed under repeatedly start-up and shutdown mode.
- Microwave assists ammonia synthesis in both thermal and nonthermal manners:
  - Thermal: microwave can heat the catalyst material (composite material) selectively, forming "hot spots";
  - Nonthermal: microwave induces local strong E-field which potentially assists N_2 dissociation on the metal particle sites;
- Adding promotors K and Ce to Ru/MgO enhances ammonia production rate.

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    - Dr. Yan Luo (previous)
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  - Dr. Dushyant Shekhawat
  - Dr. Christina Wildfire
- **Pacific Northwest National Laboratory**
  - Robert A. Dagle
- **Florida State University**
  - Dr. Albert Stiegman

- A special thank to Dr. Terence Musho for assistance on FEM model build-up.

Microwave Assisted Catalytic Conversion of Ethane to Aromatics for a More Efficient Approach over a Conventional Fixed Bed Reactor

Presenter: Brandon Robinson (Oral)
Time: 1:24 – 1:42 pm, Nov. 12th (Tuesday)
Section: 308 - Advances in Methane Coupling Reaction and Aromatization
Location: Hyatt Regency Orlando, Challenger 41/42.

Microwave Catalytic Reactor for Converting Light Alkane to Aromatics

Presenter: Xinwei Bai (Poster)
Time: 3:30 – 5:00 pm, Nov. 13th (Wednesday)
Section: 560 - Poster Session: Catalysis and Reaction Engineering Division
Location: Hyatt Regency Orlando, Regency Ballroom R/S, #560DY