Microwave Catalytic Synthesis of Ammonia for Energy Storage and Transformation

Xinwei Bai, Yuxin Wang, Dushyant Shekhawat, Christina Wildfire, Albert E. Stiegman, Robert A. Dagle and Jianli Hu

1 Department of Chemical and Biomedical Engineering, West Virginia University, Morgantown, WV
2 US Department of Energy, National Energy Technology Laboratory, Morgantown, WV
3 Department of Chemistry, Florida State University, Tallahassee, FL
4 Pacific Northwest National Laboratory, Richland, WA
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.

Source: 1: APNews: https://www.apnews.com/bd4f217666964b6984b77501a34d62a1
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 CO₂; 5: Haber-Bosch ammonia synthesis reactor (high temperature, high pressure); 6: condenser.
Commercial Ammonia Plant: Haber-Bosch Process (~1000 ton per day)

~200 bar, 500 °C

Unit operations: 1: methane steam reforming reactor; 2: methane oxidative reforming reactor; 3: Catalytic water-gas shift reactor; 4: pressure swing adsorption of CO₂; 5: Haber-Bosch ammonia synthesis reactor (high temperature, high pressure); 6: condenser.
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.
New Technology: Microwave (MW) Reactor

VFM MC-1330 unit (cross section) with frequency range: 5850 – 6650 MHz (max 180 W)
Results: Ammonia Productivity of Ru/Al$_2$O$_3$ under MW irradiation

The effect of microwave frequency on the NH$_3$ yield.

Reaction conditions:
4 wt%Ru/Al$_2$O$_3$, 280°C, 0.5 g catalyst, 0.1 MPa, GHSV=5000 h$^{-1}$; N$_2$:H$_2$ = 1:3.
Results: Catalyst Stability

The catalytic performance stability of 4 wt% Ru/Al$_2$O$_3$ catalyst:
(a) under continuous operation; (b) under intermittent power supply. Reaction conditions: 280 ℃, 0.1 MPa, 0.5 g catalyst, 0.5 g catalyst, 6650 MHz, GHSV=5000 h$^{-1}$.

Each data point represents the ammonia production rate at the end of each cycle.
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

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 (°C) (bulk temperature = 300 °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.
The effect of temperature and promoters on the NH₃ 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
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 N₂ dissociation on the metal particle sites;
• Adding promoters K and Ce to Ru/MgO enhances ammonia production rate.
Acknowledgement:

- **Hu’s Research Group @ WVU**
  - Advisor: Dr. Jianli Hu;
  - Post-docs:
    - Dr. Yuxin Wang
    - Dr. Yan Luo (previous)
  - And all other group members

- **National Energy Technology Laboratory**
  - Dr. Victor Abdelsayed
  - 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