

COVER PAGE

Final Technical Report for DoE

Award Number: DE-SC0016543

**This Report does not contain any limitation notices.
The Government will have no liability for any disclosure or reproduction of such reports.**

Submitted by

Jason Hicks

May 22, 2019

Abstract/Executive Summary:

Ammonia (NH_3) is both a common chemical and a vital nutrient for plant life. However, the synthesis of NH_3 is energy intensive and leads to significant generation of greenhouse gases. A compelling alternative is to conduct the synthesis at ambient conditions, thus making the process more energy efficient and potentially carbon neutral. Plasmas (or gas discharges) can input electrical energy into the reactant gas mixture (N_2/H_2) to create reactive intermediates to enhance the yield of NH_3 and preclude the need for high pressures or temperatures, leading to overall better energy efficiency. Plasmas can be efficiently generated, influence reaction chemistry, and offer a number of controllable design parameters, especially in the presence of a catalyst. Despite the potential merits, plasma catalysis has not received close attention from the catalysis science community and has not benefited from the concerted coupling of synthesis, measurement, and theory-driven modeling that has been so successful in the design of thermal catalytic systems. The objectives of this project were to perform systematic plasma catalysis experiments supported by computational models that capture the molecular-scale physics and chemistry to use plasma-assisted catalysis as an alternative, scalable means to achieve the sustainable synthesis of ammonia.

DoE Final Technical Report

1. **DoE Award #:** DE-SC0016543
Recipient: *University of Notre Dame*
2. **Project Title:** Advancing Sustainable Ammonia Synthesis through Plasma-Assisted Catalysis

Principal Investigator: *Prof. Jason C. Hicks, Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556*
Email: Jhicks3@nd.edu; Phone: 574-631-3661

Co-PIs: *Prof. David B. Go; dgo@nd.edu and Prof. William F. Schneider; w Schneider@nd.edu*

3. **Date of the report:** May 25, 2019
Period covered by the report: 09/15/2016 – 09/14/2017 (plus 1-year extension)

4. Accomplishments

The primary objective of our collaborative, one-year study was to provide careful analysis and scientific basis to understand and apply plasmas to the synthesis of ammonia. The fundamental barrier to nitrogen fixation is activation of the robust N-N triple bond, and thermal catalysis requires elevated temperature and pressure to drive this activation. Therefore, alternative approaches to depositing energy into this bond and accessing net lower energy pathways to products hold significant promise for achieving fixation at more modest conditions and higher net efficiency. A plasma is an alternative, scalable means to achieve the same ends of depositing energy non-thermally and specifically to drive desired chemistry.

The project had three primary objectives.

Objective 1: Establish robust baseline assessment of NH₃ production rates and efficiency versus key reaction parameters across a series of traditional supports and catalysts.

Objective 2: Characterize the plasma and its influence on catalytic materials.

Objective 3: Deliver models that capture both the micro and molecular-scale physics and chemistry and elucidate key steps controlling performance and products.

Over the project period, the PIs have addressed these objectives and made significant breakthroughs in the plasma-assisted synthesis of ammonia. To date, the project has yielded four publications, two PhD theses, and funded a total of three graduate students.

a. *Overcoming ammonia synthesis scaling relations with plasma-enabled catalysis, P. Mehta et al., **Nature Catalysis**, 2018, Vol 1, 269–275, <https://doi.org/10.1038/s41929-018-0045-1>.*

In our first publication from this award, we hypothesized that, by depositing energy into the N₂ vibrational states, a non-thermal DBD plasma coupled with a catalyst can lower the effective barrier and increase the reaction rate without influencing either the final state or any subsequent steps in the catalysis (Figure 1).

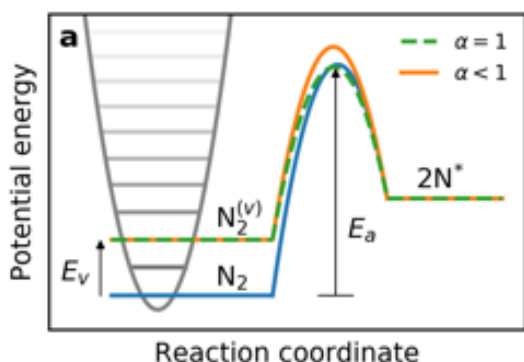


Figure 1. (a) Representative reaction path energetics for N_2 dissociation when N_2 is in the ground state (blue) or in a vibrationally excited state. The dashed green curve corresponds to a vibrational efficiency (α) of 1, and the orange curve corresponds to a vibrational efficiency less than 1. Reproduced from Mehta, Nature Catalysis 2018.

plasma-modified volcano plot. We determined that the rates in the presence of vibrational excitation are enhanced compared to the thermal rates for a given bulk temperature and pressure. This indicated that plasma-induced vibrational excitations are expected to be highly effective in promoting NH_3 synthesis. We also determined the optimal catalyst in the presence of plasma excitation is not the same as the optimal thermal catalyst. For instance, catalysts that are limited in the rate of N_2 dissociation can be enhanced (such as Co and Ni as observed in Figure 2a).

Experiments were performed to determine if, and under what conditions, plasma-catalyst interactions enhance ammonia yields. These experiments were conducted in a custom-built plasma reactor that consisted of a quartz tube with a tungsten rod in the center as the inner electrode and a steel mesh wrapped around the tube for the outer electrode. The electrodes are connected to a high voltage power source to generate a non-thermal, non-equilibrium atmospheric-pressure plasma called a dielectric barrier discharge (DBD). An oscilloscope was used to monitor the electrical power deposited into the DBD. We studied five different metal catalysts (Fe, Ru, Co, Ni, and Pt) supported on $\gamma-Al_2O_3$ (5 wt %). Experiments were performed in a DBD plasma operated at 10 W. As expected based on literature reports, some NH_3 is produced when N_2 and H_2 are passed through the plasma alone (empty DBD reactor) or when N_2 and H_2 are flowed through a DBD reactor packed with $\gamma-Al_2O_3$. The

Because N_2 can be vibrationally excited by inelastic electron collisions in a plasma and vibrational-vibrational energy exchange, we performed experiments using optical emission spectroscopy (OES) to estimate the effective vibrational temperature of N_2 in an ambient pressure and temperature N_2/H_2 plasma. To obtain these results, we first constructed a reactor that allowed for the direct measurement of the activated N_2 by incorporating the OES probe into the reactor system. We determined the vibrational temperature to be on the order of 3000 K, and we used this information to predict the populations of vibrationally excited N_2 states. We combined this information with standard models from the molecular beam literature for how activation energies are modified by vibrational excitation to predict the

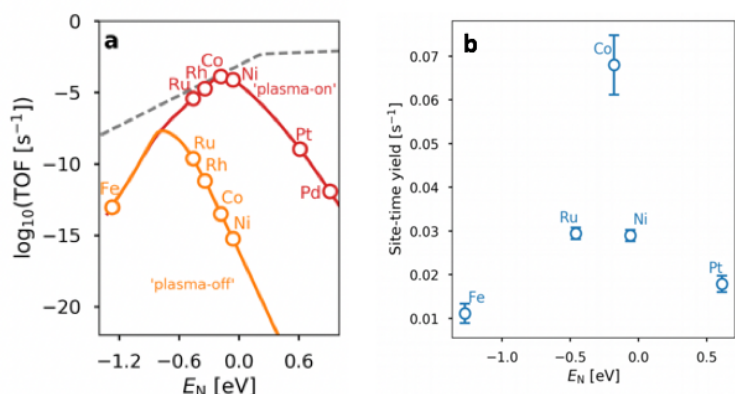


Figure 2. Comparison of N_2 VDF probability weighted ('plasma-on') and thermal ('plasma-off') ammonia synthesis rates on (a) step sites, and (b) measured ammonia site time yields in the DBD reactor. Figures reproduced from Mehta, Nature Catalysis 2018.

measured bulk temperature due to heating of the gases by the DBD was approximately 165°C, and all catalysts were verified to be inactive for thermal NH₃ synthesis at these conditions. Figure 2b shows the measured plasma-catalytic NH₃ synthesis rates after background plasma effects were removed from the yields. As can be seen, all catalysts had a positive influence on NH₃ generation at conditions much lower than those used in the commercial Haber-Bosch process. Additionally, the experimental results qualitatively track well with the “volcano” predictions of Figure 2a.

b. Distinguishing Plasma Contributions to Catalyst Performance in Plasma-Assisted Ammonia Synthesis, P. Barboun et al., *ACS Sustainable Chemistry & Engineering*, 2019, 7, 8621-8630. DOI: 10.1021/acssuschemeng.9b00406.

Plasma catalysis is a complex network of plasma phase reactions, surface catalyzed reactions, and plasma-catalyst interactions. The synergistic effects associated with the plasma and catalyst surface is of significant interest, as understanding this interaction can lead to the rational design of new materials/processes. However, the direct measurement/observation of plasma-catalyst interactions is not trivial. In this report, we performed controlled experiments of 1) plasma only ammonia production, 2) thermal catalytic ammonia synthesis, and 3) plasma-assisted catalytic ammonia synthesis in order to distinguish between the plasma and plasma-catalytic reactions. From these experiments, pathway differences between plasma-phase reactions and plasma-assisted catalysis were observed, where an overall 2nd-order dependence on the rate was observed for plasma-only reactions (1st order for both N₂ and H₂) but a 1st-order dependence on N₂ and 0th-order dependence on H₂ were observed for plasma-stimulated catalytic experiments. These findings provide further evidence of the interaction between the plasma and catalyst surface.

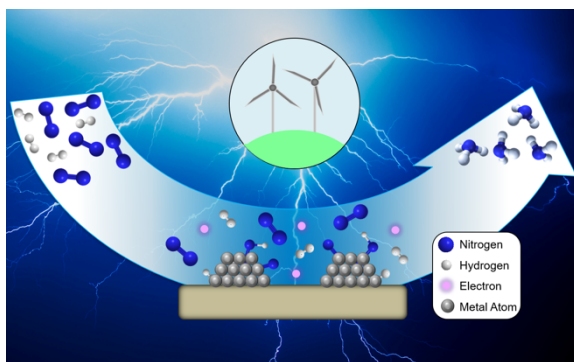


Figure 3. Low pressure and temperature plasma-assisted catalytic synthesis of ammonia. Figure reproduced from Barboun, et al., *ACS Sustainable Chemistry & Engineering*, 2019.

c. The impact of transition metal catalysts on macroscopic dielectric barrier discharge (DBD) characteristics in an ammonia synthesis plasma catalysis reactor, F. Herrera et al., *Journal of Physics D: Applied Physics*, 2019, 52 (224002), <https://doi.org/10.1088/1361-6463/ab0c58>.

In a recent study, we performed experiments to determine if the presence of a supported catalyst affects the plasma conditions and thereby alters the gas-phase production of ammonia. We explored this possibility by conducting detailed electrical and optical measurements of our N₂ and H₂ plasmas under different conditions and with different alumina-supported catalysts. While we found that the measured conversion rates were similar to our previous findings, with Co leading to the highest rate, we did not observe any changes to the macroscopic properties of the DBD plasma. From these experiments, the observed synergy is likely due plasma interactions with catalyst surface rather than the catalyst modifying the plasma phase. Microscopic measurements

of the plasma in the presence of a catalyst are underway to determine if local changes in the plasma are observed.

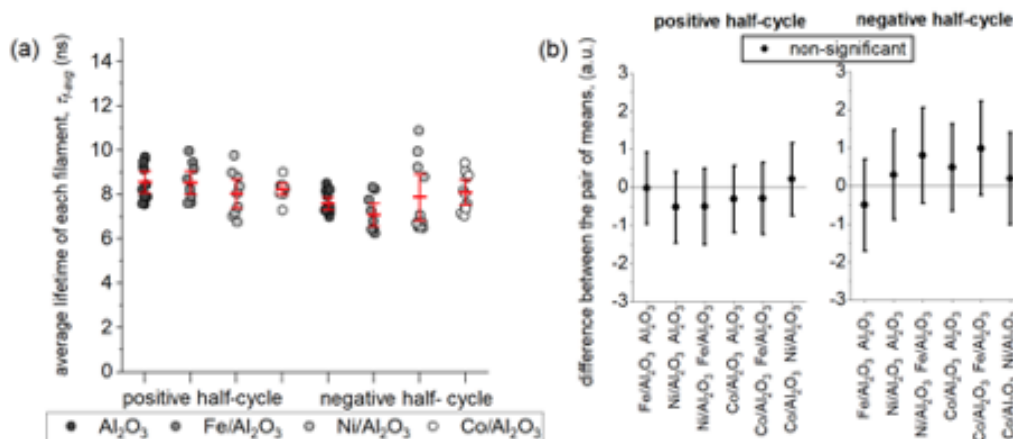


Figure 4. Extracted average lifetime of each filament per half-cycle shows a little variation between the different metal catalysts. Panel (a) shows scatter columns for average lifetime of each filament values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values. Figure reproduced from Herrera, et al., *Journal of Physics D: Applied Physics*, 2019.

5. Publications Acknowledging DOE Funding:

1. Mehta, P.; Barboun, P.; Herrera, F.; Kim, J.; Rumbach, P.; Go, D. B.; Hicks, J. C.; Schneider, W. F., *Nature Catalysis*. **1** (4), 269 (2018).
2. Mehta, P.; Barboun, P.; Go, D. B.; Hicks, J. C.; Schneider, W. F., *ACS Energy Letters*. **4** (5), 1115-1133 (2019).
3. Barboun, P.; Mehta, P.; Herrera, F.; Go, D. B.; Schneider, W. F.; Hicks, J. C., *ACS Sustainable Chemistry & Engineering*. **7** (9), 8621-8630 (2019).
4. Herrera, F.; Brown, G. H.; Barboun, P.; Turan, N.; Mehta, P.; Schneider, W. F.; Hicks, J. C.; Go, D. B., *Journal of Physics D: Applied Physics*. **52** (224002), (2019)

6. Students involved in this project

Students: Patrick Barboun, Francisco Herrera, Prateek Mehta

Francisco Herrera and Prateek Mehta both successfully defended their dissertations in the spring of 2019. Patrick Barboun is an entering 4th year doctoral candidate in the PhD program.

7. Unexpended funds

The grant is fully expended.

8. Computational Modelling

The computational details for this project can be found directly in P. Mehta et al., *Nature Catalysis*, 2018, Vol 1, 269–275, <https://doi.org/10.1038/s41929-018-0045-1>. The code to solve the microkinetic models was also provided in the supporting information of this manuscript.