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Plasma-Enhanced Catalysis: A Detailed Study of Surface Interactions Between Low-Temperature Plasma and Catalytic Materials

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Abstract

The goal of this research is to provide fundamental molecular insights into how plasmas modify surface catalytic chemistry and how these modifications can be exploited to control selectivity and efficiency during gas reforming. In this work, a novel plasma Fourier transform infrared spectroscopy/mass spectrometry (FTIR/MS) platform was developed to measure how atmospheric-pressure plasmas affect the adsorption/desorption and reactions that occur on various catalysts. Complementary studies were also conducted using inelastic neutron scattering at Oak Ridge National Laboratory to reveal reduction intermediates produced by plasma activation. Continued work with the continuous flow DBD catalysis reactor revealed the conversion and kinetics of plasma activation on ammonia synthesis, including the impact of catalysts on the DBD itself and how the DBD can promote conversion that extends beyond thermal equilibrium. Both atomistic simulations and microkinetic analysis were used to assess the underlying physical and chemical phenomena. Finally, the team published multiple comprehensive reviews of plasma-catalysis, primarily focusing on hydrocarbon reforming and ammonia synthesis.

Journal Articles Published and Submitted

[1] Herrera, F.A., Brown, G.H., Barboun, P., Turan, N., Mehta, P., Schneider, W.F., Hicks, J.C. and Go, D.B., 2019. The impact of transition metal catalysts on macroscopic dielectric barrier discharge (DBD) characteristics in an ammonia synthesis plasma catalysis reactor. *Journal of Physics D: Applied Physics*, 52(22), p.224002. (*appears in Special Issue on Nitrogen Fixation in Plasma: From Fundamentals to Sustainability*)

[2] Barboun, P., Mehta, P., Herrera, F.A., Go, D.B., Schneider, W.F. and Hicks, J.C., 2019. Distinguishing plasma contributions to catalyst performance in plasma-assisted ammonia synthesis. *ACS Sustainable Chemistry & Engineering*, 7(9), pp.8621-8630.

[3] Mehta, P., Barboun, P., Go, D.B., Hicks, J.C. and Schneider, W.F., 2019. Catalysis enabled by plasma activation of strong chemical bonds: A review. *ACS Energy Letters*, *4*(5), pp.1115-1133. (*invited review*)

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[8] Barboun, P.M., Daemen, L., Waitt, C., Wu, Z., Schneider, W.F., and Hicks, J.C., Inelastic neutron scattering observation of plasma-promoted nitrogen reduction intermediates on Ni/γ-Al_2O_3. *ACS Energy Letters* – in revision

[9] Turan, N., Saeidi-Javash, M., Chen, J., Zeng, M., Zhang, Y., and Go, D.B., Atmospheric pressure and ambient temperature plasma jet sintering of aerosol jet printed silver nanoparticles. *ACS Applied Materials & Interfaces* – in revision

1. Project Overview and Objectives

Catalyst systems are important to many defense-oriented applications such as catalyst-enabled power generation (*e.g.*, fuel cells). Furthermore, many defense-related technologies integrally exploit catalysis in their function, such as the production of essential chemicals and fuels using thermal catalysis. Ultimately, developing new ways to control catalytic processes to exert control over selectivity and energy efficiency will dramatically impact the United States' defense and security systems – from the scale of individual military vehicles to the entire energy economy of the United States. Non-thermal plasmas offer a unique way to inject energy into a reacting system to promote the reaction and exert control. Furthermore, plasma-catalyst interactions that capitalize on plasma-injected energy offer the opportunity to profoundly reshape the way we approach catalysis. We propose utilizing plasma-enhanced catalytic systems as a novel approach to chemical processing focusing on hydrocarbon gas reforming and nitrogen fixation as model systems.

The goal of this research program is to provide fundamental molecular insights into how plasmas modify surface catalytic chemistry and how these modifications can be exploited to control selectivity and efficiency of gas reforming.

Objective 1: In Objective 1, we will develop and characterize an *in situ* and *operando* plasma FTIR/MS platform. We will build both diffuse reflectance (DRIFTS) and attenuated total reflectance (ATR-IR) configurations so that we have a breadth of options for exploring specific surface chemistries. We will conduct detailed characterization of the plasma source(s) to ensure that it reflects the plasma conditions found in our existing tube reactor system. Using electrical measurements, optical emission spectroscopy (OES), and MS, we will analyze the plasma behavior in the FTIR/MS system and correlate these to FTIR measurements.

Objective 2: In Objective 2, we will characterize and quantify the effect of plasma on the adsorption/desorption of reactants and products on catalyst surfaces. Adsorption is the key first step in a catalytic reaction on solid surfaces, and it is not clear the extent to which the plasma directly impacts this step. Conversely, desorption of surface-generated products is required to sustain the catalytic cycle. Using *in situ* plasma FTIR/MS measurements and density functional theory (DFT) simulations, we will explain the roles of the plasma on adsorption/desorption of relevant light gases (e.g., CO_2, CO, CH_4, C_2H_6) on oxide supports and metal-supported catalysts.

Objective 3: In Objective 3, we will explore the impact of plasma on C-H and C-O bond activation and dissociation at catalytic surfaces; reactions important in hydrocarbon reforming. Our prior work suggested that the energy barrier for CH_4 dissociation is reduced in the presence of a plasma. Here we will directly explore the impact of the plasma on various model C-H and C-O systems in order to gain insight into the role of the plasma during hydrocarbon reforming, comparing *operando* plasma FTIR/MS measurements with DFT simulations of reaction rates.

2. Progress and Findings

2.1 Objective 1

In order to study plasma-catalyst reactions with an FTIR, we developed a dielectric barrier discharge (DBD) that can fit within the confined geometry of the DRFITS reactor (~1-5 mm) and effectively be operated while in contact with a packed bed of catalytic material [5]. We utilized a new DBD configuration to produce surface DBDs over a three-dimensional geometry within the sample holder of the DRIFTS cell. The helical surface DBD consists of an internal Kapton-enameled, silver-plated copper wire and a helically wrapped silver-plated copper wire outside (Fig. 1a). The diameter of the exposed wire is 1.01 mm. The thickness of the dielectric that covers the internal wire is 51 μm. Sinusoidal AC voltage is applied to the two wires that act as electrodes, providing a power density of 0.2-1 W/cm^3. The DBD spreads along the length of the inner wire (Fig. 1b) and can extend 7 mm. As shown in Fig. 1c and d, we can also operate the helical DBD within a packed bed of catalyst material.

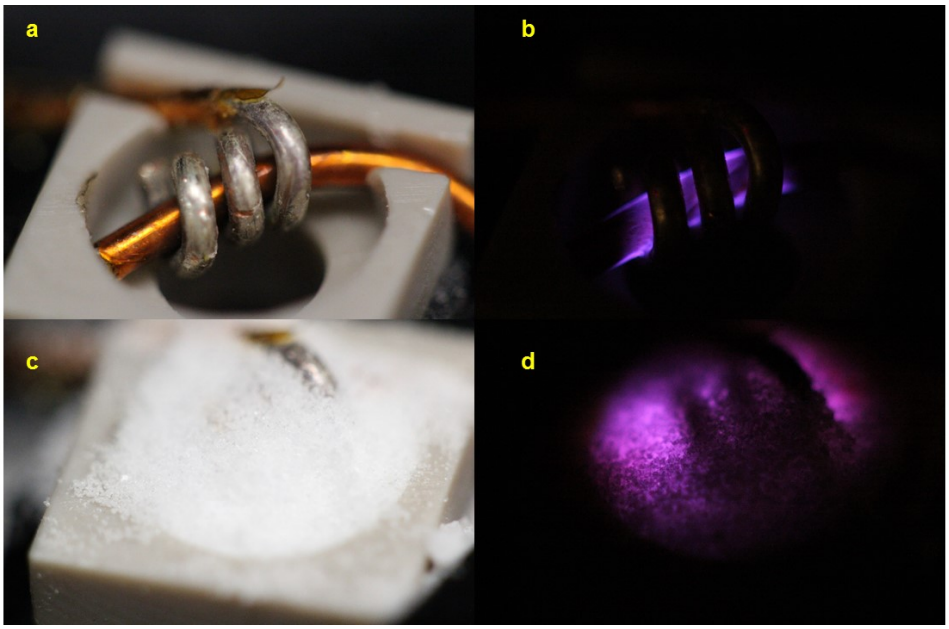

Figure 1 Photographs of (a) helical DBD device within a DRIFTS sample holder, (b) DBD generation in air showing expansion of the plasma along the Kapton covered internal wire, (c) the helical DBD device immerged in potassium bromide (KBr) powder, and (d) DBD operation within the packed bed.

We characterized the electrical properties of the helical DBD in both free space (no packed bed) and within a packed bed reactor. Various electrical parameters, including energy and power deposited, and the number and lifetime of the filaments were measured as a function of frequency. To demonstrate utilization of the device in the ATR, we explored the behavior of DBDs in two packed bed conditions – dry powdered potassium bromide (KBr) and air-exposed powdered KBr. Electrical measurements showed that in air-exposed KBr, the DBD is initially filamentary and then transitions to a homogeneous or glow mode after repeated exposures. Operation in dry KBr, however, always displayed homogenous behavior. DRIFTS measurements confirmed that the increasing plasma exposure time in the air-exposed KBr desorbed water from the KBr (Fig. 2), which led to the mode transition of the discharge.

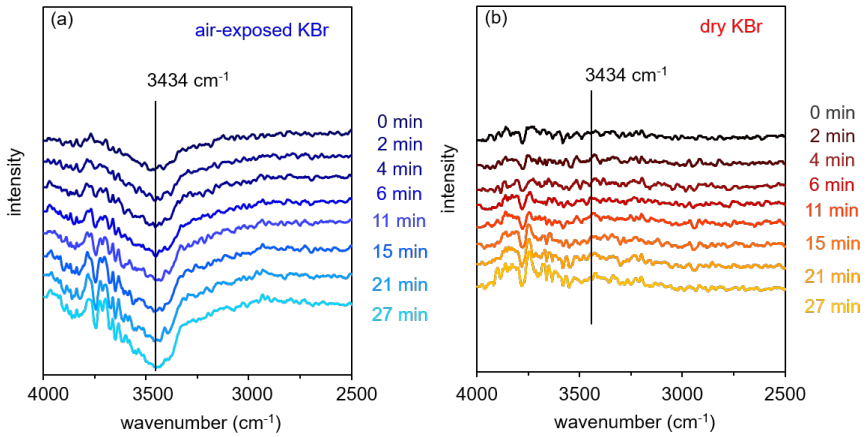

Figure 2 DRIFTS spectra for *in situ* helical DBD operation for (a) air-exposed and (b) dry KBR, where the decreasing signal at 3434 cm^{-1} is indicative of water desorption.

In parallel to developing the helical DBD, we have also developed a DBD plasma jet configuration that can be implemented in the ATR FTIR configuration (Fig. 3). However, we have focused on conducting *in situ* characterization of using the DBD plasma jet to conduct room temperature and atmospheric pressure sintering of printed silver nanoparticles [9]. Within the plasma-catalysis context, sintering is unwanted and should be avoided; sintering catalytic nanoparticles reduces their surface-to-volume ratio and can render them less active. Within the context of manufacturing often printed or powdered materials need to be sintered as a post-processing step to create a continuous material or film. Typically, this requires high-temperature and high-pressure conditions, which are not only energy intensive and time-consuming, but limits the materials that can be evaluated. Low-temperature sintering enables creating nanoparticle-based devices on delicate and flexible substrates, including plastics, papers, and even organics such as leaves and fruit (Figs. 3e and f).

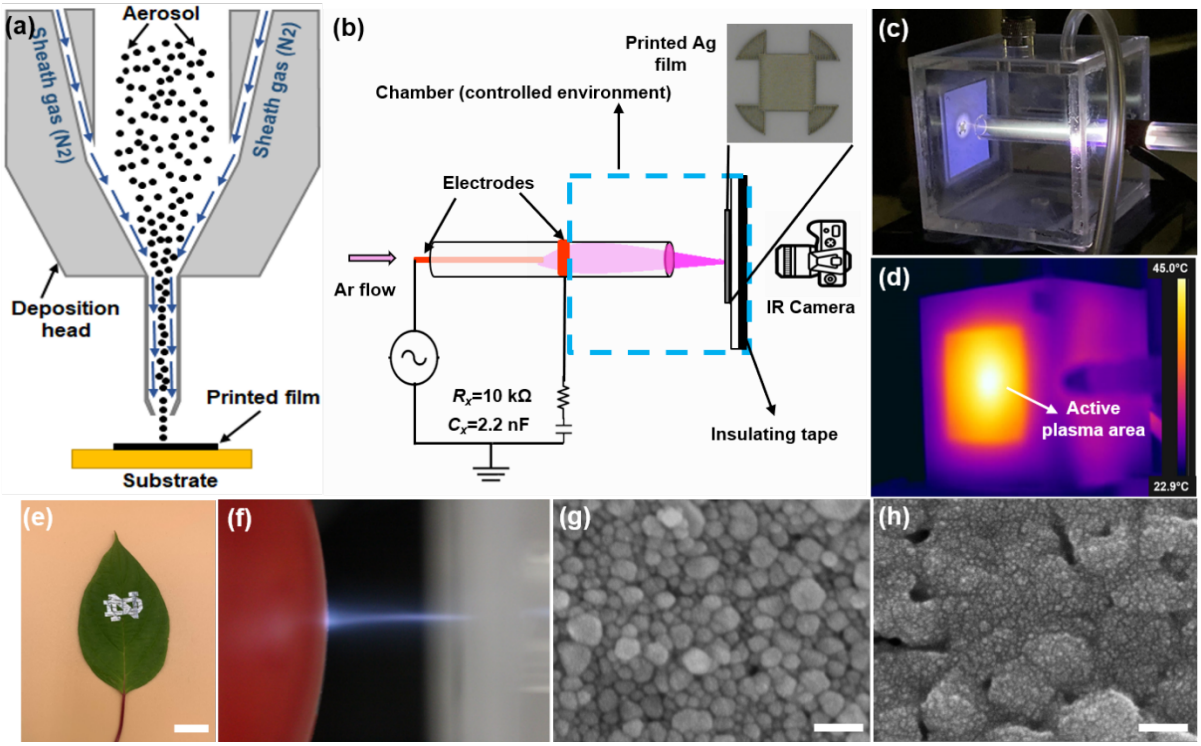

Figure 3 Atmospheric pressure and low temperature plasma sintering of the aerosol jet printed silver nanoparticle films. (a) Schematic illustration of the deposition head of the aerosol jet printer. (b) Schematic illustration of the plasma sintering setup. (c) Photograph of plasma jet impinging on PEL paper. (d) IR camera image of the test chamber showing temperature distribution during plasma exposure. (e) Aerosol jet printed University of Notre Dame logo (interlocking ND) on a leaf. Scale bar is 1 cm. (f) Argon plasma jet sintering of printed silver on a tomato. (g and h) Top-view SEM images of the printed silver nanoparticle films (g) before and (h) after plasma sintering for 100 minutes. Scale bar is 50 nm.

We demonstrated that we could successfully sinter aerosol jet-printed silver nanoparticle films (~860 nm) using a 6 W argon plasma jet in 50 minutes without exceed a substrate temperature of 48°C [9]. Figure 4 shows a representative sintering process on both glass and the filter paper PEL, where the sheet resistance of the thin film drops nearly 6 orders of magnitude in the first 20 minutes (and the corresponding conductivity increases) and then continuously decreases until saturating at close to the value of bulk silver after approximately 50 minutes. With further refinement of the process (*e.g.*, using a power of 6 W), we even showed sintering on the delicate skin of a tomato without damaging it. *In situ* optical emission spectroscopy showed that the plasma was low-energy, with an electron temperature of roughly 0.79 eV.

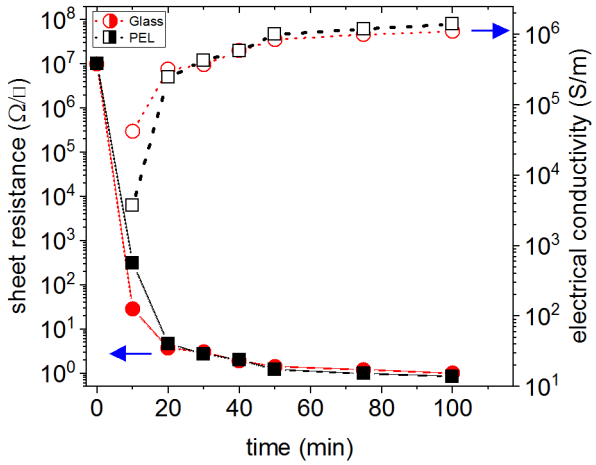

Figure 4 Sheet resistance (left axis) and electrical conductivity (right axis) of printed silver nanoparticle films as a function of plasma sintering time for glass and PEL paper substrates.

2.2 Objective 2

In order to probe the effect of the plasma on adsorbed species on a surface, a model system of carbon dioxide (CO_2) adsorbed on alumina (γ-Al_2O_3) was investigated using the helical DBD (Fig. 1) in the DRIFTS FTIR cell. Due to the acidic properties of CO_2 gas, it is well known to probe basic sites on metal oxides. In the case of solid basic oxides, such as Al_2O_3, the species formed have been well characterized by others and thus serve as a good benchmark. The primary adsorbates observed are bicarbonates (weak basic sites), bidentate carbonates (intermediate basic sites), and unidentate carbonates (strong basic sites), which can be easily distinguished with IR. The well characterized nature of this system for thermal catalysis makes it a good model for investigating the effects of a DBD on surface bound species.

Figure 5 shows IR spectra of CO_2 adsorbed on γ-Al_2O_3. For each experiment, Al_2O_3 was diluted in potassium bromide (KBr) powder and pretreated in flowing nitrogen (N_2) at 250°C for 1 hr in order to remove physisorbed and chemisorbed species from the surface. Subsequently, 30 sccm of pure CO_2 was flowed over the sample at 50°C to adsorb the gas onto the surface. The excess gas phase CO_2 was then purged from the cell with an inert gas, N_2 in the case of the thermally treated sample and He in the case of the plasma treated sample. Figure 3a shows spectra collected at increasing temperatures. All three adsorbate configurations are observed, with the bicarbonate features being the most intense. At 150°C, significant reductions in bicarbonate feature

intensity is observed, which is expected due to the weak binding of bicarbonate species, whereas at 250°C substantial reduction of all features is observed.

Figure 3b shows spectra collected in the plasma-modified cell but without the DBD active, with a low power helical DBD, and with a higher power DBD. In the plasma-modified cell with no DBD active, features associated with the various surface carbonate species are observed as in the thermal cell, though unidentate carbonates are difficult to identify due to the reduction in signal-to-noise ratio. However, upon igniting the DBD, bicarbonate features disappear almost entirely, while bidentate carbonate features largely remain. This shows that the introduction of a DBD can facilitate the desorption of surface species, which has been observed in other studies, but may also indicate that the plasma's selectivity towards which species desorb may be different than thermal desorption. Ongoing studies will focus on isolating and explaining this effect.

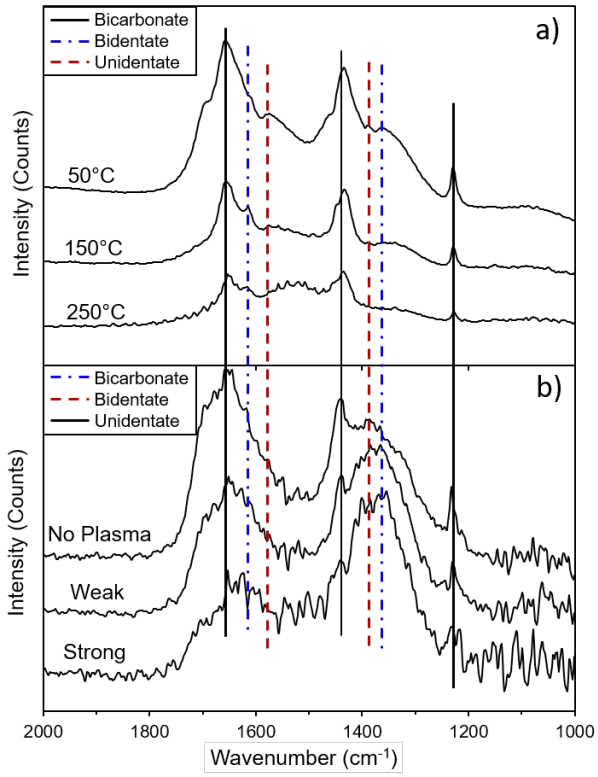

Figure 5 IR spectra of adsorbed CO_2 on γ-Al_2O_3 as a) the temperature is increased in N2 or b) a He plasma is generated in the packed bed. CO_2 was adsorbed on the surface by flowing pure CO_2 over Al_2O_3 for 30 min before purging the cell with N_2 (thermal case) or He (plasma case). Spectra are the result of averaging 256 scans at a resolution of 4 cm^{-1}.

To complement these FTIR studies, we developed a DBD reactor cell for integration into the VISION spectrometer at Oak Ridge National Laboratory (ORNL) [8]. We specifically use inelastic neutron scattering (INS) to study alumina-supported nickel (Ni/γ-Al_2O_3) particles after treatment with nitrogen (N_2) and hydrogen (H_2) plasmas, which corresponds to ammonia (NH_3) synthesis from N_2 and H_2. INS experiments revealed the presence of NH_x species and hydrides on Ni sites after exposure to sequential nitrogen and hydrogen plasma treatments. By using a

sequential approach, we separated nitrogen and hydrogen exposure and excluded the presence of plasma-phase reactions (Fig. 6).

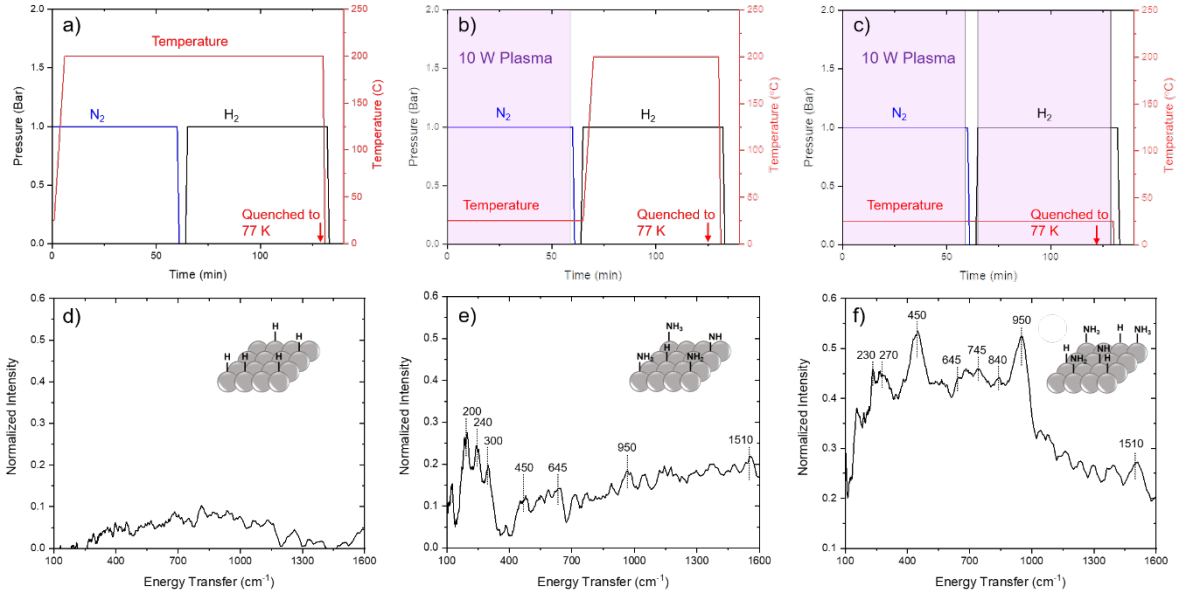

Figure 6 Graphical representation of the plasma and thermal treatments: thermal N_2 followed by thermal H_2 (a), 10 W plasma N_2 followed by thermal H_2 (b), and 10 W plasma N_2 followed by 10 W plasma H_2 (c). Background subtracted INS spectra of thermal N_2/thermal H_2 treatments (d), plasma N_2/thermal H_2 treatments (e), and plasma N_2/plasma H_2 treatments (f).

We also used atomistic simulations to produce computed synthetic INS spectra of NH_3, NH_2 and NH adsorbates in order to assign the measured INS peaks and gain further insight. Figure 7 shows measured (Figs. 7a and b) and computed (Figs. 7c and d) INS spectra. On the left, only H_2 exposure (both plasma and thermal) was used to isolate the presence of hydrides. The plasma treatment shows the presence of hydrides that are not produced under thermal conditions. On the right, we show sequential N_2/H_2 exposures, where the H_2 exposure was either an H_2 plasma or under thermal H_2 conditions. These experiments provided spectroscopic evidence that NHx species are formed and present on the Ni catalyst after N_2 plasma stimulation followed by either H_2 thermal or plasma H_2 exposure. Ultimately, by separating nitrogen and hydrogen treatments, the INS studies confirm that NHx species can be formed through thermal hydrogenation of adsorbed nitrogen generated by the plasma, even on metals where nitrogen adsorption is less favorable, such as on Ni [8].

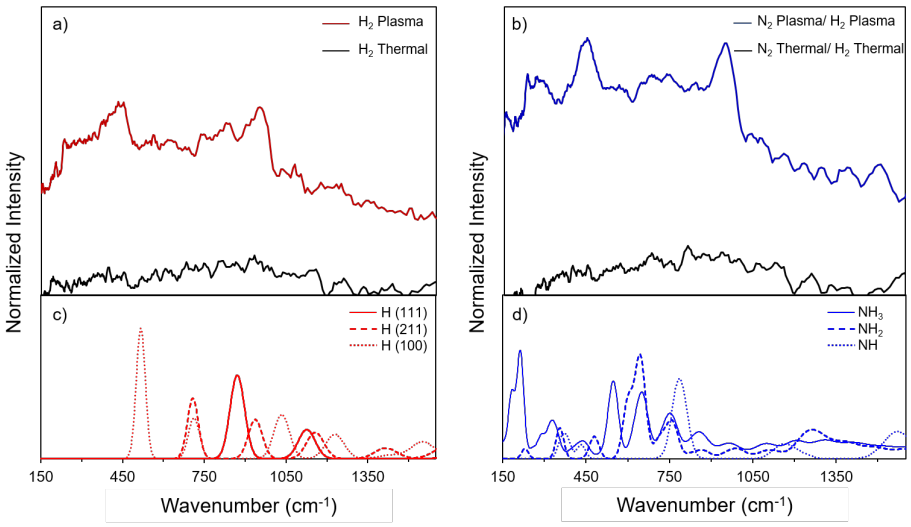

Figure 7 Experimental INS spectrum of 5% Ni/γ-Al_2O_3 exposed to a) both plasma (red) and thermal (black) hydrogen treatments, b) sequential treatments of 10 W N_2 plasma then 10 W H_2 plasma (replotted spectrum from Figure 1f) for 1 hour exposure (blue) and sequential thermal treatments of N_2 then H_2 (black). Calculated vibrational spectra for c) various surface hydrides on Ni (111), (211), and (100) facets and d) NHx species on Ni (211).

2.3 Objective 3

We have continued to use our continuous-flow DBD catalytic reactor in order to study the chemistry of plasma catalysis, expanding on our prior AFOSR-sponsored work (FA9550-14-1-0041) [1][2][4]. In our prior work, we found that catalyst performance in a plasma catalysis reactor is not what is expected from thermal catalysis theory; that is, catalyst design for plasma catalysis is different from thermal catalysis. Our results for ammonia synthesis showed that cobalt (Co) produced the highest initial rates compared to ruthenium (Ru), nickel (Ni), platinum (Pt), and iron (Fe). We have since conducted a thorough quantitative kinetic study of these catalysts to fully characterize their rates and their rate order dependence. We have developed ways to properly account for and normalize the data to isolate the effect of the catalyst independent of the DBD itself in order to properly measure the forward rates for the plasma-catalyst interaction. Among our various findings, we found that the specific energy input (SEI), which is defined as the energy input by the plasma per molecule of gas, is a good descriptor of plasma-based ammonia synthesis, but that the introduction of a catalyst breaks SEI scaling [2].

One of the unknowns about plasma catalysis is the relative impact of the plasma modifying the catalyst activity as opposed to the catalyst modifying the properties of, and thus chemical processes in, the plasma. To assess this, we conducted a comprehensive characterization of the DBD in the plasma catalysis reactor, including both electrical and optical properties. After a thorough statistical analysis, we found that there was no evidence that different catalyst materials (Co, Ni, Fe) affect the plasma differently; that is, different catalysts do not alter the macroscopic properties of the plasma. This result supports the hypothesis that the measured enhancement in catalytic rates is due to the plasma affecting the catalytic process rather than the catalyst affecting gas-phase chemistry [1].

In addition to the atomistic simulations described above and shown in Fig. 7, we complement these experiments by constructing microkinetic models of plasma-catalysis in order to study the kinetics. In particular, there was a very interesting experimental observation using our continuous-flow reactor where ammonia synthesis was enhanced 'beyond' that achievable by thermal equilibrium, as shown in Fig. 8. Importantly this observation was catalyst-dependent. First, it was observed even in the absence of a metal catalyst, when only using γ-Al_2O_3. This was then enhanced by platinum (Pt) but reverts back to equilibrium when using Ni [4].

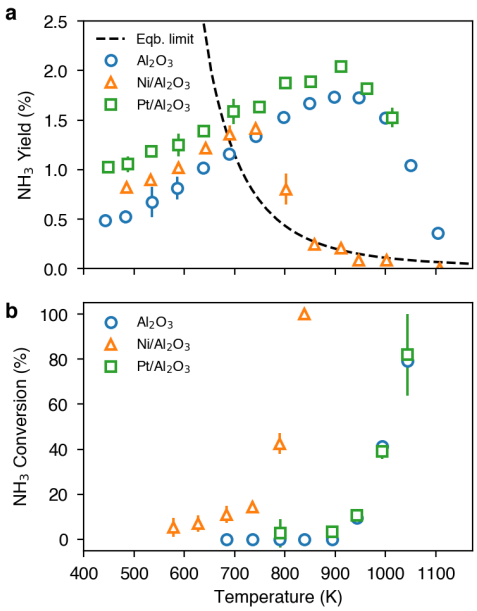

Figure 8 Ammonia synthesis and decomposition temperature-sweep experiments. (a) Plasma-catalytic ammonia yields in a DBD reactor packed with Al_2O_3, Ni/γ-Al_2O_3, and Pt/γ-Al_2O_3. Reaction conditions: total inlet flow rate = 40 mL min−1, N_2:H_2 = 2:1. (b) NH_3 conversion in thermal ammonia decomposition experiments over γ-Al2O_3, Ni/γ-Al2O_3, and Pt/γ-Al2O_3. Reaction conditions: Inlet flow rate = 40 mL min^{-1}. Inlet gas composition: 0.5% NH_3, 9.5% He, and balance of 2:1

Microkinetic modeling showed that while the plasma itself drove the yield beyond equilibrium, the behavior of the catalysts depended on its nitrogen (N) binding effectiveness, as shown in Fig. 9, which reproduced the general behavior shown in Fig. 8a. The stronger the N binding energy of the catalysts (Fig. 9a), the more it drives the thermal reaction, which pushes the NH_3 production toward thermal equilibrium. When the binding energy is weaker (Fig. 9b,c), however, the competition favors plasma behavior and is catalyst-dependent [4].

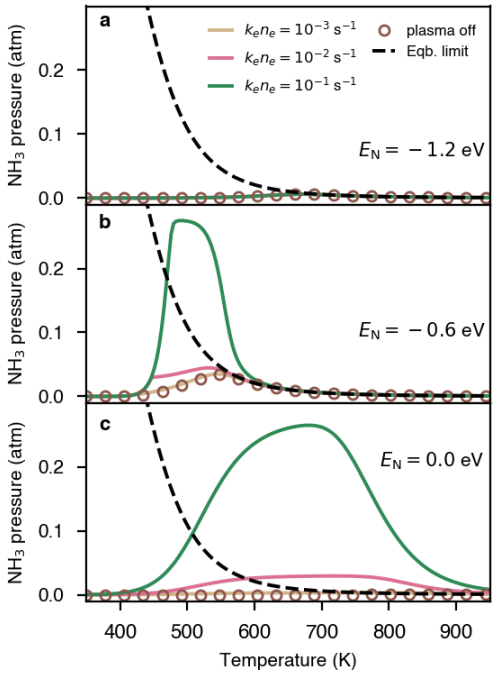

Figure 9 Modeled steady-state NH_3 partial pressures in plasma- enhanced catalytic operation as a function of bulk temperature and rate of plasma-excitation. Catalysts characterized by (a) strong ($E_N = -1.2$ eV), (b) intermediate ($E_N = -0.6$ eV), and (c) weak ($E_N = 0.0$ eV) nitrogen binding energies. For each catalyst, steady-state thermal (plasma-off) and plasma-on (for three values of $k_e n_e$) partial pressures of NH_3 are plotted. Plasma-excitation is assumed to reduce the barrier for N_2 dissociation by 1 eV.

3. Conclusions and Future Outlook

In summary, our research team has utilized a wide variety of techniques to reveal how plasmas and catalysts can favorably interact to outperform either plasma-based or catalyst-based chemistry alone. We have exploited both *in situ* and bulk reactor measurements, and complemented these with plasma measurements and computational modeling, to address specific fundamental questions, such as what is the key plasma activation in ammonia synthesis. One of the most intriguing results, however, was the side project on plasma jet sintering. Surprisingly, non-thermal plasmas can effectively sinter nanoparticles at ambient temperatures. In catalysis, however, such sintering must be avoided. To that end, the fundamental questions persists – in plasma catalysis, does the plasma also modify the catalyst itself?

The current working hypothesis for plasma jet sintering is that bombarding ions promote surface diffusion of atoms between nanoparticles, which can lead to their agglomeration. In thermal catalysis, it is known that surface diffusion can occur in oxide-support/metal catalyst systems. Furthermore, oxide coating on nanoparticle catalysis can have a positive effect, including enhancing the selectivity of the catalyst. A natural next direction for this research is to use our plasma jet and continuous flow reactor systems to specifically study plasma-promoted surface diffusion in oxide-support/metal catalyst powders leading to oxide-metal interactions that can be tailored to promote or inhibit catalytic activity. Such experimental studies could also be enhanced by modeling, including kinetic Monte Carlo studies.