Plasma Science and Technology
Room 315 - Session PS2-MoA

Plasma Catalysis and Synthesis

Moderators: Prof. François Reniers, Université Libre de Bruxelles, **Prof. Dr. Mohan Sankaran**, University of Illinois at Urbana-Champaign

4:00pm **PS2-MoA-11 Electrifying C1 Chemistry via Nonthermal Plasma Catalysis**, ***Tomohiro Nozaki,*** Institute of Science Tokyo, Japan **INVITED**

The growing demand for both reducing anthropogenic CO_2 emissions and utilizing CO_2 as a renewable carbon resource has accelerated global interest in circular carbon technologies. In this context, extensive efforts are being devoted to the development of next-generation chemical conversion processes capable of transforming CO_2 into value-added chemicals. Because such chemical transformations inevitably require external energy input, the integration of low-carbon energy sources, particularly renewable electricity, has become indispensable for realizing sustainable CO_2 conversion systems. Among these technologies, Plasma Catalysis - a combination of nonthermal plasma and heterogeneous catalysts - has attracted tremendous interest as a promising low-carbon technology where renewable electricity is readily coupled into chemical conversion processes [1]. In the meantime, significant challenges remain in establishing a fundamental understanding of plasma–surface interactions, reaction pathways under non-equilibrium conditions, and catalyst functions specific to plasma environments. Further advances, therefore, require not only reactor engineering and process optimization, but also the development of plasma-adapted catalytic materials and scientifically grounded reaction design methodologies. This invited lecture presents recent progress in plasma-catalytic CO_2 conversion, with particular emphasis on CO_2 methanation, as one of the most extensively studied in modern C1 chemistry for carbon recycling and mechanistically understood plasma-catalytic reactions. First, in situ FTIR and XAFS spectroscopy of CO_2 hydrogenation over Pd_2Ga/SiO_2 are discussed, which emphasizes the key role of vibrationally excited CO_2 [2]. Moreover, an Eley-Rideal-type reaction, induced by atomic hydrogen, is explained as necessary to overcome the rate-determining step (decomposition of formates) [3]. Second, a large-scale methanation is introduced, where exothermic reaction heat also promotes the methanation reaction: the bifunctional contribution of plasma catalysis, cooperative interaction between reaction heat and activated species, is clarified [4,5]. These findings are not limited to the methanation reaction but are applicable to various types of CO_2 conversion in the scope of C1 chemistry. Finally, a future perspective is presented.[1] D-Y Kim, et al., *ACS Catalysis*, **15**, 19424, 2025.[2] D-Y Kim, et al., *J Am Chem Soc*, **144**, 14140, 2022.[3] D-Y Kim, et al., *JACS Au*, **5**, 169, 2025.[4] W Zhang, et al., *Chem Eng J*, **512**, 162520, 2025.[5] W Zhang, et al., *J Ener Chem*, **115**, 858, 2026.

4:30pm **PS2-MoA-13 Methane Reforming in Nanosecond-to-Millisecond Pulsed Plasmas**, *Norleakvisoth Lim,* ***Michael Gordon,*** University of California Santa Barbara

Plasma-assisted methane reforming provides an electrified pathway for producing hydrogen and value-added hydrocarbons without direct CO_2 emissions while potentially enabling co-production of solid carbon. Here, we systematically investigate how the timescale of energy deposition governs methane plasma chemistry by examining atmospheric-pressure pulsed CH_4 discharges spanning six orders of magnitude in pulse duration, from nanoseconds to milliseconds, while maintaining comparable pulse energies of 10–50 mJ/pulse. Experiments were conducted in a coaxial flow reactor operated at low repetition frequencies (50–300 Hz) to specifically minimize pulse-to-pulse interactions. Plasma characteristics (gas temperature, electron density, presence of radicals, etc.) were quantified using electrical diagnostics and high-resolution OES, and reaction products were analyzed via online mass spectrometry.

Substantial changes in discharge physics and reaction products were observed across the ns-to-ms pulse-width range. Electron density varied from ~10^{14}–10^{18} cm^{-3} and gas temperature ranged from ~2500–5200 K, depending on pulse duration and discharge current. Short-pulse discharges (<1 µs) generated high electron densities (10^{17}–10^{18} cm^{-3}) and highly non-equilibrium conditions, where methane conversion proceeded through both electron-impact and thermal dissociation pathways. In contrast, longer pulses (>10 µs) operated at lower electron densities (10^{14}–10^{17} cm^{-3}) and were dominated primarily by thermal chemistry. Nanosecond discharges exhibited the highest total C_2 selectivity (>70%), producing approximately 17% C_2H_6, 18–20% C_2H_4, and 35% C_2H_2. Increasing pulse duration shifted product distributions toward sequential dehydrogenation pathways consistent with Kassel-type chemistry, promoting acetylene formation at the expense of ethylene and ethane.

Energy deposition timescale produced a distinct tradeoff between selectivity and conversion. Rapid energy deposition and quenching in short-pulse plasmas favored partially dehydrogenated intermediates, whereas longer pulses improved methane conversion and process efficiency through increased reaction volume and residence time. The best overall performance was achieved near 100 µs pulse duration, yielding methane conversion energy cost as low as ~370 kJ/mol CH_4 and specific energy requirements of ~15 kWh/kg for C_2H_2 and ~40 kWh/kg for H_2, comparable to thermal plasma processes. These results demonstrate that pulse duration serves as a powerful control parameter for tuning plasma reaction pathways and optimizing selective methane conversion to hydrogen and value-added hydrocarbons.

4:45pm **PS2-MoA-14 Asymmetric Plasma-Electrocatalyst Process for Tunable Nitrogen Fixation**, ***Mohammad Ali Eslamisaray,*** Department of Nuclear, Plasma, and Radiological Engineering, University of Illinois Urbana-Champaign, Champaign, IL, USA; *Hee-Eun Kim, Xiao Su,* Department of Chemical and Biomolecular Engineering, University of Illinois Urbana-Champaign, Urbana, IL, USA; *R. Mohan Sankaran,* Department of Nuclear, Plasma, and Radiological Engineering, University of Illinois Urbana-Champaign, Champaign, IL, USA

Nitrogen-containing compounds, such as ammonia and nitrate, are critical to applications in agriculture, polymer synthesis, and biomanufacturing. Industrially, ammonia is primarily produced by the Haber-Bosch process, in which nitrogen reacts with fossil-fuel-derived hydrogen over a catalyst bed, and nitrate or nitric acid is produced by subsequent oxidation of ammonia via the Ostwald process. Both the Haber-Bosch and Ostwald processes are carried out in large, centralized manufacturing facilities with substantial capital expenditure and supporting infrastructure. Such production schemes create significant logistic and economic challenges, including transportation, safety and handling, and supply chain vulnerabilities. In addition, both processes require elevated temperatures and pressures making them incompatible with intermittent renewable energy. Recently, there has been a growing interest in sustainable and decentralized alternatives for nitrogen fixation. Electrochemical approaches have been challenged by the activation of molecular nitrogen but can efficiently reduce nitrate to ammonia. In comparison, nonthermal plasmas can react air to efficiently produce nitrate. These complementary features have been exploited in combined strategies, but only as separate reactors.

In this work, we investigated an asymmetric plasma-electrocatalyst process that directly converts air and water into tunable nitrogen products within a single reactor. Specifically, the plasma and electrocatalytic electrodes share the same electrical circuit and electrolyte, with a plasma serving as the anode and a cobalt oxide-based electrocatalyst acting as the cathode. We first evaluated the performance of the system in a single-supply configuration, in which the plasma and electrocatalyst operating conditions are coupled. We then introduced an independent cathodic bias to decouple the plasma and electrocatalyst operating conditions. With the latter configuration, we were able to demonstrate significant control over product selectivity, with final compositions ranging from nitrate-dominant to ammonia-dominant and solution pH ranging from acidic to alkaline.

5:00pm **PS2-MoA-15 Operando Spectroscopic Insights into Plasma-Driven Ammonia Synthesis via Isocyanate Intermediates**, ***Casey O'Brien,*** Texas Tech University

Coupling nonthermal N_2 plasmas with heterogeneous catalysts offers a promising route to sustainable ammonia synthesis under mild conditions. Here, we demonstrate a plasma-catalytic pathway that utilizes H_2O as a carbon-free hydrogen source and leverages trace CO_2/CO_x impurities as catalytic promoters rather than undesirable contaminants. Using a multi-modal operando spectroscopy platform capable of simultaneously probing plasma-phase species and surface-bound intermediates, we identify a distinct vibrational feature at ~2200 cm^{-1}. Isotopic labeling confirms this band arises from surface-bound isocyanate (NCO) species formed via reactions between plasma-activated nitrogen and trace CO_x present at ppm levels in commercial N_2 feeds.

We show that these NCO intermediates react readily with water vapor to produce ammonia at ambient temperature and pressure. Notably, NCO formation is observed across a broad range of metal catalysts, including Pd, Ni, Ag, Au, and Cu, with metal-dependent vibrational signatures, binding

energetics, and reaction kinetics for NCO + H_2O conversion. These results indicate that ammonia synthesis via NCO intermediates is a generalizable pathway and that both catalyst identity and gas composition can be tuned to control activity and selectivity. This work highlights the potential of plasma-catalyst coupling to access new reaction mechanisms enabled by trace species and metastable intermediates under non-equilibrium conditions.

5:15pm **PS2-MoA-16 Structural Changes of Plasma Modified Polymers for Applications in Catalytic Deconstruction**, ***Aunic Goodin***, North Carolina State University; *Sujoy Bepari,* North Carolina A&T State University; *Tridip Das,* California Institute of Technology; *Duncan Trosan,* North Carolina State University; *Zahidul Islam,* North Carolina A&T State University; *William Goddard III,* California Institute of Technology; *Debasish Kuila,* North Carolina A&T State University; *Steven Shannon,* North Carolina State University

1. **Introduction**

The disposal of plastic waste has become an increasing global challenge as single use consumer plastics continues to grow. Catalytic deconstruction is a potential method for upcycling this plastic waste, with plasma being added at different steps to improve the yields or vary/modify the products.

This work investigates the effects of a plasma pre-treatment using atmospheric pressure air plasma to pre-treat polymers prior to catalytic deconstruction. The structural changes of the polymers and the effect on the product distribution under different plasma conditions is investigated.

2. **Methods**

Plasma treatment is performed in a sealed vial with a rubber septum cap. A steel hypodermic needle is used to both deliver synthetic air and apply a high voltage in a pin-to-cup configuration. The grounding cup is made up of a copper pipe soldered to a copper plate. The vial is placed the copper “cup” with the whole assembly surrounded with a 3D printed holder to prevent arcing from the high voltage to ground. The treatment voltage, frequency, flow rate, and power are varied and the modification of polypropylene and polyethylene are investigated using XPS, FTIR, NMR, and MALDI-TOF measurements.

3. **Results and Discussion**

Plasma pre-treatment has been shown to improve yields and modify product distribution depending on the plasma parameters. Previous work has shown this trend with polypropylene and ZSM-5/SBA-15 composite catalyst [1]. The method has been shown to apply with polyethylene and a FeRu-HM catalyst to improve the yield of jet fuel (C_8-C_{16}) products. Further investigation of the structural changes of the plasma treated polymers is therefore necessary to better understand this process.

4. **Conclusion**

Through variations in plasma pre-treatment, catalytic deconstruction can be tuned to produce different product distributions. This method can be applied to other polymer based catalytic deconstruction applications but requires more understanding of the changes in the pr-treatment step.

Acknowledgement

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[1] A. Goodin *et al.*, *J. Vac. Sci. Technol. A* **44**(3), (2026).

[2] G. Pandey *et al.*, *ACS Sustain. Chem. Eng.* **14**(16), (2026).

[3] S. Chakraborty *et al.*, *J. Environ. Chem. Eng.* **13**(2), (2025).

5:30pm **PS2-MoA-17 Dynamics of Intermediates Formed from Ionizing Radiation of Aqueous Salt Solutions: A Transient Absorption Study**, ***William Maza***, US Naval Research Laboratory; *Sara Gebre,* us naval Research Laboratory; *Adam Dunkelberger,* US NAval Research Laboratory

The ionization products of laser-induced plasmas generated in water are of great interest; in particular, as they relate to plasmas generated in marine waters. However, despite the complexities involving the ionization of neat water we have endeavored to study ionization of aqueous solutions that mimic the conditions found in seawater. To simplify the strong ionization power of intense pulsed-laser interactions with seawater leading to the formation of undersea plasmas, and to provide a baseline for the study of undersea plasmas, we have begun investigating the softer ionization of aqueous salt solutions by two-photon absorption. We find that the spectra and dynamics observed from two-photon absorption of simulated seawater solutions are complex and indicate the formation of multiple meta-stable intermediates that can be temporally resolved. These include the very short lived (< 50 ns) hydroxyl radical, longer-lived hydrated electron (up to ~ 1 µs), and even longer-lived products of anion ionization like Cl_2^- and CO_2^- (> 10 µs). The presence of humic acids, meant to model dissolved organic matter typically found in seawater, further complicates our analysis. We will discuss these results and their potential significance to underwater plasma formation under similar conditions.

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