Tuesday Afternoon, November 5, 2024

Plasma Science and Technology
Room 124 - Session PS-TuA

Plasma Chemistry and Catalysis II

Moderators: **Michael Gordon**, University of California at Santa Barbara, **Michael Johnson**, Naval Research Laboratory, USA

2:15pm PS-TuA-1 Nonthermal Plasmas for Advanced Nanomanufacturing, *Rebecca Anthony*, Michigan State University   **INVITED**
Advanced manufacturing strategies have immense potential to reduce time and production costs for a range of applications.Meanwhile, the multiple functionalities and small size of nanomaterials can influence the versatility and capabilities of many devices including solar cells and solid-state lighting, energy conversion technologies and batteries, wearable electronics, and coatings. Combining advanced manufacturing with nanotechnology opens the door to exciting applications based on thin films and microstructures, with on-demand tunable functionality.

One promising route to achieving advanced nanomanufacturing is to use low-temperature plasmas for synthesis of nanoparticles, together with additive manufacturing methods which are compatible with roll-to-roll or additive printing methods. Here, synthesis of nanocrystals from semiconductor materials such as Gallium Nitride (GaN), Indium Nitride (InN), Silicon, and Carbon using low-temperature flow-through plasma reactors is presented. By tuning frequency, power, pressure, and gas composition, nonthermal plasmas open the door to allowing tuning of physical nanoparticle properties including size and surface defect concentration, as observed via x-ray diffraction (XRD), transmission electron microscopy (TEM), and electron paramagnetic spin resonance (EPR). Additionally, the tunable reactor parameters open the door to controlling bonding configuration in some materials, such as carbon. This is a promising prospect, as the ratio of sp^2 / sp^3 hybridization represents significant changes in the properties of carbon materials, and in nanoparticles these changes can be paired with size-induced shifts in physical and optoelectronic properties. Nonthermal plasma synthesis can also be merged with an additive manufacturing approach to deposit tunable-property nanoparticle layers and patterns. The low-temperature synthesis of otherwise difficult-to-make semiconductor nanoparticles can thereby be uniquely paired with direct deposition onto arbitrarily chosen substrates – including temperature-sensitive materials such as polymers – for versatile deposition with on-demand property modulation.

2:45pm PS-TuA-3 Conversion of Liquid Hydrocarbons to H₂ and C₂ Olefins in AC Plasma Discharges, *Norleakvisoth Lim*, M. Gordon, UCSB Chemical Engineering
Growing concerns regarding fossil fuel depletion, coupled with efforts to transition towards sustainable and low-carbon energy sources, have prompted innovative solutions for sustainable and efficient utilization of natural resources. This has led to increasing interest in developing technologies to transform light and heavy hydrocarbons to H_2 and more valuable hydrocarbons, such as ethylene and acetylene. Direct plasma-based conversion of liquid hydrocarbons offers a new approach to hydrocarbon reforming. It leverages the high energy density of the liquid phase to achieve fast reaction rates and compact reactor design, and may enable selective production of intermediate products through quenching at the gas-liquid interface. In this work, we explore the use of low current AC discharges in liquid hydrocarbon jets (**Figure 1**) to produce gaseous hydrogen, C_2 olefins, and separable solid carbon.

This talk will examine the influence of discharge frequency, liquid jet velocity and hydrocarbon feedstock on production rates, specific energy requirements and gaseous and liquid product distributions (**Figure 2**). Direct discharges in liquid hexanes predominantly produced H_2 (56.6 mol %), C_2H_2 (23.6 mol%), C_2H_4 (13.1 mol%) and CH_4 (6.7 mol%) under 60 Hz AC frequency. As the AC frequency increased to 17.3 kHz, the energy efficiency improved by a factor of two or more, owing to the change in plasma-generated bubble formation and transport dynamics surrounding the electrode region. A single-shot multi-frame imaging system was developed for consecutive nanosecond shadowgraph acquisitions, which allows us to further investigate the changes in bubble dynamics due to discharge duration and frequency. Decrease in bubble formation/contact time was shown to improve energy efficiency. For a liquid jet flow velocity of ~270 cm/s, the specific energy requirements (SER) for H_2, C_2H_4 and C_2H_2 production were 24 kWh/kg H_2, 3.2 kWh/kg C_2H_4 and 4.9 kWh/kg C_2H_2, respectively. We also examined the reactivities and product distributions of cyclohexane, benzene, toluene and xylene (BTX) feedstocks and ultimately demonstrate the potential of using AC discharges to upgrade less valuable hydrocarbon reformate. Additional characterization of the liquid (GC-MS) and solid (SEM, TEM and Raman) products will be discussed.

3:00pm PS-TuA-4 Pulsing a Methane Discharge for Temperature Control and Better Energy Efficiency for Hydrogen Production, *Thomas Fontaine*, L. Nyssen, D. Petitjean, Université libre de Bruxelles, Belgium; N. De Geyter, Ghent University, Belgium; R. Snyders, University of Mons, Belgium; F. Reniers, Université libre de Bruxelles, Belgium
In the quest for CO_2-free energy, new fuels and energy storage media are gaining attention. The hydrogen molecule is of interest, as it presents industrial potential and can serve as an energy carrier. H_2 is mainly obtained from CH_4 steam reforming and water gas shift reactions, emitting CO_2. Cracking of CH_4 is an alternative route for H_2 production, with competitive theoretical energetical cost (standard enthalpy of the reaction at 0°C: 37.5 kJ for 1 mol of hydrogen, i.e. 7.5 times less than H_2O splitting) and no direct CO_2 emission. Various plasma processes can form H_2, but all struggle to enhance energy efficiency.

Tuning the shape of the voltage applied to the system is known to have beneficial impact on the energy efficiency, mostly by allowing a better control of the discharge energy. It is indeed well known that temperature of the discharge is a key factor, as some dehydrogenation steps are favored by higher temperatures, but elevated temperatures also lead to thermal losses. [1]

We investigate pulsing at different time scales (ms (AC pulses, called "burst"), μs, ns) in an atmospheric pressure discharge. A dielectric barrier discharge reactor is used to investigate the energy efficiency. DBD notably allows for operation with different high voltage sources. The reactor is composed of a central copper rod (high voltage electrode), a borosilicate glass tube (dielectric) and a stainless-steel mesh wrapped around the glass (ground electrode). Conversion is measured over time by mass spectrometry. Interesting conditions were further investigated by optical emission spectroscopy. Rotational temperatures during the pulses are derived from the Swan band. A T_{rot} increase is measured for shorter duty cycle in burst mode. Switching from burst to nanosecond pulses also increases T_{rot}. Impact of the pulse energy on the temperature is studied by tuning the pulse energy (voltage tuning) and the total power (frequency tuning). T_{rot} is linked to the pulse energy, but not to the total power. Conversion for same SEI through different pulse lengths is compared in identical experimental conditions, which is rarely observed in the literature. We conclude that ms and ns pulses lead to similar energy efficiencies and perform better than ms pulses.

[1]M. Scapinello *et al.*, *Chem. Eng. Process. Process Intensif.*, vol. 117, pp. 120–140, Jul. 2017, doi: 10.1016/j.cep.2017.03.024

4:00pm PS-TuA-8 Integrated Reactor Models of Diamond Growth: Advancing Towards Low-Temperature CVD, *Yuri Barsukov*, I. Kaganovich, M. Mokrov, PPPL; A. Khrabry, Princeton University
In modern diamond chemical vapor deposition (CVD) techniques, substrates are commonly exposed to temperatures above 1200K. This high-temperature requirement restricts the selection of substrate materials to those that can withstand such extreme conditions. Low-temperature diamond CVD attracts major interest because it enables broader applications, e.g., utilization of diamond materials in the architecture of three-dimensional integrated circuits.

The objective of this study is to identify conditions that would allow to significantly reduce the substrate temperature for diamond CVD growth. To investigate the potential for reducing the substrate temperatures, we developed a comprehensive reaction kinetic model of (100) diamond surface growth from a CH_4/H_2 gases, which are typical feed gases [1]. This model involves 91 surface reactions, which were investigated using quantum chemistry methods. Subsequently, we integrated this reaction kinetic model with a gas-phase chemistry model of typical hot-filament and microwave reactors. The models were validated against previously reported experimental data, accurately predicting the measured diamond growth rates under various operating conditions.

Our results show that the effect of C_2H_2 on diamond growth is minor at temperatures above 1200 K, as previously reported. For temperatures below a critical value predicted by our model, C_2H_2 molecules nucleate the sp^2-phase (soot) instead of diamond, thus hampering diamond growth. At temperatures above the critical, C_2H_2 does not nucleate the sp^2-phase

(soot) and its effect on the diamond growth is not important (compared to the main precursor CH_3). However, for a low-temperature CVD regime, C_2H_2 deleteriously affects the diamond growth, and its presence in the CVD mixture is highly undesirable.

Using ab initio quantum chemistry methods coupled with a numerical plasma model, we developed an integrated model that not only reproduces the experimental results but also identifies a critical bottleneck in modern CVD reactors. Our findings suggest that an optimization of low-temperature CVD reactor design implies maximizing the CH_3 radical production and minimizing the generation of C_2H_2 and other sp and sp^2 hydrocarbons.

[1] Y. Barsukov, I. D. Kaganovich, M. Mokrov, and A. Khrabry, *Quantum Chemistry Model of Surface Reactions and Kinetic Model of Diamond Growth: Effects of CH3 Radicals and C2H2 Molecules at Low-Temperatures CVD*, (2024). https://doi.org/10.48550/ARXIV.2405.03050

4:15pm PS-TuA-9 Solid State Generated Microwave Power for Hydrogen Plasma Reduction of Iron Oxide, *Daniel Ellis, J. Rebollar,* University of Illinois Urbana-Champaign*; B. Jurczyk,* Starfire Industries*; J. Krogstad, M. Sankaran,* University of Illinois Urbana-Champaign

The reduction of iron ore is a key step in steel production. Current approaches lead to substantial carbon dioxide emission and there has been growing interest in low-temperature hydrogen plasmas that would avoid carbon-based feedstocks and lower the heating required by increasing reactivity. Microwave excitation is of particular interest because of the potential to energy efficiently generate reactive plasma species. However, microwave power is typically generated by magnetrons, which utilize rigid and bulky waveguides to couple the microwave radiation to a cavity, and the plasmas that are formed at atmospheric pressure are filamentary, hot, and confined to cavities.

Here, we studied a low-temperature, atmospheric-pressure hydrogen plasma for iron oxide reduction powered by microwave generated from solid state amplifiers. Solid state technology allows the microwave power to be transmitted by standard coaxial cables to an antenna. By configuring the antenna in a coaxial geometry where gas flow is simultaneously coupled, a plasma jet free from any surface is generated which can be used to treat a material surface downstream. To demonstrate the applicability of this unique plasma to iron oxide reduction, films of iron oxide prepared from hematite powder were prepared and treated. The effect of various process parameters, including plasma power, treatment time, distance between the plasma electrode and substrate, and feed composition, on reduction were investigated. The reduction of the iron oxide samples was evaluated ex-situ by mass loss measurements, X-ray diffraction, and scanning electron microscopy. The reduction was found to especially depend on the distance of the plasma and the concentration of molecular hydrogen in a background of argon gas. In support of these experimental results, an advection-diffusion-recombination model was developed to calculate the hydrogen radical concentration in the gas phase. The study clarifies opportunities and challenges for iron oxide reduction by low temperature plasmas.

4:30pm PS-TuA-10 Plasma Synthesis of Hydrogen from Ethanol Solution: A Mechanistic Study, *D. Lojen, T. Fontaine, L. Nyssen, N. Roy,* Université Libre de Bruxelles, Belgium*; R. Snyders,* Universite de Mons, Belgium*; N. De Geyter,* Ghent University, Belgium*; François Reniers,* Université libre de Bruxelles, Belgium

Routes to produce hydrogen at low energy cost and without emission of carbon dioxide are extensively studied nowadays, going from methane splitting (either thermal or plasma) to water electrolysis. In a previous preliminary study, we showed that production of hydrogen from liquid ethanol could be a possible route of interest, although the energy cost was still too high. In this paper, we present new results of the plasma induced splitting of liquid ethanol, using a nanopulsed generator. The plasma reactor consists of a 6 pin-to-plate electrode geometry, with the plate electrode being submerged in an ethanol-water solution. The gaseous products of reaction were analysed and quantified by atmospheric mass spectrometry (Hiden), after appropriate calibration, and the discharge is characterized using a high speed Photron camera, electrical measurements, and optical emission spectrometry. Ethanol – water solutions of different concentrations and liquid thicknesses have been investigated. In our previous study we focused on the drastic effect of the liquid thickness on the plasma regime (DBD-like for high thicknesses, hot plasma for small thicknesses). Here we focus on the hot plasma regime. We show that, together with hydrogen, valuable gaseous byproducts are formed, namely acetylene, ethylene, and carbon monoxide, most often without any detectable CO_2 release. Compared to methane splitting, the deposition of solid carbon on the electrodes is also strongly reduced. OES characterization of the plasma reveals that the plasma temperature, the electron density and the electron average energy depend on the composition of the solution. The amount of hydrogen produced as a function of the solution composition is also investigated, leading to a proposed mechanism for hydrogen formation in such conditions.

Acknowledgements:

4:45pm PS-TuA-11 Study of Plasma-Catalyst Surface Interactions for Coking Reduction, *Michael Hinshelwood, G. Oehrlein,* University of Maryland, College Park

Methane reforming is important for the production of both pure hydrogen and syngas (H_2 + CO) which can be used to produce other valuable chemicals. Dry methane reforming (DRM) with CO_2 is a promising technique for converting greenhouse gases into syngas. However, catalyst deactivation by carbon deposition on the catalyst surface (coking) is an issue. Non-thermal plasma may be a useful technique for mitigating coke formation in DRM performed at atmospheric pressure. Reactive species generated by the plasma may react with coke deposits, regenerating the catalyst. To better understand this plasma-surface interaction, we use in-situ IR spectroscopy techniques with a remote plasma-catalysis setup. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is used to probe surface adsorbates formed during the reaction, while Fourier Transform Infrared Spectroscopy (FTIR) is used to quantify the product species downstream of the reaction. A nickel catalyst supported by SiO_2/Al_2O_3, commonly used for dry reforming reactions, is used as a test material. By exposing the catalyst to Ar/CH_4 plasma, or just Ar/CH_4 at elevated temperatures, the catalyst's dry-reforming activity is reduced, and a lower product concentration is measured downstream. Surface characterization under the same conditions reveals a growth of adsorbed C-H species, CH_2 (2930 cm^{-1}) and CH_3 (2960 cm^{-1}, 2860 cm^{-1}), suggesting that they are responsible for this deactivation. Subsequent exposure to Ar/CO_2 plasma results in the removal of the adsorbed CH_n surface species on the timescale of minutes. The experimental setup allows for variation of the catalyst temperature to test the reactivity of the plasma produced flux with surface carbon at different temperatures. CH_n removal is seen to be more effective at high temperatures and plasma powers, suggesting a synergistic effect of temperature and reactive species flux to the surface. At lower plasma powers or catalyst temperatures, both the removal rate and amount removed are less. For surface cleaning experiments using high temperature and high plasma power, the bulk of the CH_n removal takes place during the first minutes of CO_2 plasma exposure. By comparing the effect of CO_2 plasma on surface CH_n to its effect on the subsequent dry reforming performance, the potential of plasma to reduce catalytic deactivation during dry reforming will be demonstrated. Increased understanding of this time-dependent relationship will help inform future development of plasma enhanced DRM systems.

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