

## Plasma Science and Technology Division Room B131 - Session PS+SS-ThA

### Plasma Conversion and Enhanced Catalysis for Chemical Synthesis

**Moderator:** R. Mohan Sankaran, Case Western Reserve University

2:20pm **PS+SS-ThA1 Rate Limiting Factors of Low Pressure Plasma-catalytic CO<sub>2</sub> Methanation Process**, *Kazunori Koga, A. Yamamoto, K. Kamataki, N. Itagaki, M. Shiratani*, Kyushu University, Japan

The methanation of CO<sub>2</sub> attracts attention as the ways of CO<sub>2</sub> reduction and energy storage as well as space exploration. It is expected to produce rocket propellant fuels at Mars and CO<sub>2</sub> conversion in space stations. The Sabatier reaction has been employed to generate CH<sub>4</sub> from CO<sub>2</sub> and H<sub>2</sub>. Using catalysts realizes a high conversion efficiency. However, the conventional catalytic reaction starts at about 200 °C but thermal runaway occurs above 250 °C. The heat management is an important problem. A method using non-thermal plasma with catalyst allows methanation under low-temperature condition [1, 2]. Here, we studied rate-limiting steps of CO<sub>2</sub> methanation and their important parameters in the plasma-catalytic process. Experiments were carried out using a capacitively coupled plasma reactor. The electrode diameter was 50 mm and the distance between the electrodes was 6.1 mm. The Cu electrodes were employed as catalyst. We set a CO<sub>2</sub> gas flow rate between 1.0 sccm and 5.0 sccm and an H<sub>2</sub> gas flow rate between 1.0 sccm and 30 sccm. The pressure was 750 Pa. The discharge power was set in a range of 10 to 100 W. Gas composition in the discharge plasmas was measured with a quadrupole mass spectrometer. CH<sub>4</sub> yield rapidly increases with time after plasma initiation. It tends to be saturated after 200 s. From time dependence of catalyst temperature, the saturation occurs between 350 K and 370 K. The temperature shows the threshold temperature at which the rate-limiting step change from gas-phase reactions in plasma to surface reactions on the catalyst. The CH<sub>4</sub> yield increases with increasing the gas residence time. From optical emission spectroscopy, emission intensity related with CO angstrom band increase with the gas residence time but hydrogen-related emission is irrelevant to the residence time. It suggests that CO excited by plasma is responsible to the CH<sub>4</sub> yield increase. The results of H<sub>2</sub> gas flow rate dependence suggest that electron temperature is an important factor in the rate-limiting step of the gas phase reaction. I will discuss the detail mechanisms at the conference.

Work supported partly by JAXA and JST.

[1] S. Toko, et al., *Sci. Adv. Mater.* **10** (2018) 655.

[2] S. Toko, et al., *Sci. Adv. Mater.* **10** (2018) 1087.

2:40pm **PS+SS-ThA2 Radical Nitriding of Graphene Promoted by Surface Plasmon Resonance of Gold Nanoparticle Catalyst**, *Takeshi Kitajima, T. Nakano*, National Defense Academy, Japan

In recent years, catalyst activity<sup>1</sup> of graphene nitride including fuel cell catalysts has attracted attention. We apply the catalytic property<sup>2</sup> of gold nanoparticles to the surface reaction of graphene, and investigate a process that can nitride graphene while reducing the damage caused by plasma irradiation.

In this study, we compared the degree of nitridation according to the presence or absence of ion irradiation (I), light irradiation from plasma (L) and the presence or absence of gold nanoparticle catalyst (C), respectively, and discovered the presence of radical nitriding by surface plasmon resonance of gold nanoparticles.

Gold is deposited for 2 minutes by electron beam evaporation on graphite crystals in an ultra-high vacuum chamber.

It was found by AFM measurement that gold nanoparticles with a diameter of about 20 nm were formed on the graphite crystal surface by aggregation.

Next, NH<sub>3</sub>-Ar (1: 3) mixed plasma (ICP, 70 MHz, 100 W) at a pressure of 10 Pa was generated in the plasma chamber. The sample was irradiated for 10 minutes with radicals and light that passed directly or through a 30 line/inch SUS304 single mesh.

The atomic composition by XPS was examined for each irradiation condition. It was found that in the condition RLC where gold nanoparticles were generated and irradiated with radicals and light, nitridation was promoted about twice as much as plasma irradiation.

It is speculated that irradiation of gold nanoparticles with light excites plasmons to promote the nitridation reaction.

Next, Raman scattering analysis of graphene nitride was performed. Islands found on graphite were considered as graphene. Among the Raman scattering spectra, the component intensities of 2D (2690 cm<sup>-1</sup>), G (1580 cm<sup>-1</sup>) and D (1350 cm<sup>-1</sup>) were measured to evaluate the intensity ratio.

Under RLC conditions, the I2D / IG ratio has not dropped significantly. It can be seen that the structural change of the graphene island due to ion bombardment is prevented. Furthermore, the ID / IG ratio is higher than in plasma irradiation (RIL), and it can be confirmed that nitrogen doping has progressed more. From the above, it is considered that the catalytic activity of the gold nanoparticles is expressed by the effect of surface plasmon excitation, and the formation of graphene nitride with low damage by radicals becomes possible.

1. Haibo Wang, Thandavarayan Maiyalagan, and Xin Wang, *ACS Catalysis* **2**, 781 (2012).

2. Marie-Christine Daniel and Didier Astruc, *Chemical Reviews* **104**, 293 (2004).

3:00pm **PS+SS-ThA3 Plasma-assisted Catalysis: Exploring the Effects of Plasma Stimulation on Catalyst Performance**, *Jason C. Hicks*, University of Notre Dame

Plasmas create incredibly reactive chemical environments and have a long history in chemical synthesis and removal of volatile organic compounds.[1-2] Plasmas can be generated in the presence of a catalyst (plasma-assisted catalysis) to increase conversions and improve the selectivity to desired products. Our research in the area of plasma-assisted catalysis is focused on the ability to control the catalyst performance by tuning the plasma environment or plasma-catalyst interactions.[3-4] We have been particularly interested in the use of non-thermal plasmas for C-H and N<sub>2</sub> activation via dry reforming of methane and ammonia synthesis reactions, respectively. Specifically, this presentation will focus on 1) the reaction regime where catalyst-plasma interactions are observed for these reactions, 2) the various catalyst-plasma interactions observed, and 3) the role of the plasma in enhancing reaction efficiency. This presentation will highlight our recent progress in controlling plasma-catalyst interactions to enhance reaction efficiency.

(1) Neyts, E. C.; Ostrikov, K.; Sunkara, M. K.; Bogaerts, A. *Chem. Rev.* **2015**, *115* (24)

(2) Mehta, P.; Barboun, P.; Go, D. B.; Hicks, J. C.; Schneider, W. F. *ACS Energy Lett.* **2019** *5*, (4)

(3) Mehta, P.; Barboun, P.; Herrera, F. A.; Kim, J.; Rumbach, P.; Go, D. B.; Hicks, J. C.; Schneider, W. F. *Nat. Catal.* **2018**, No. 4.

(4) Barboun, P. Mehta, P. Herrera, F.A. Go, D.B. Schneider, W.F. Hicks, J.C. *ACS Sus Chem & Eng*, **2019**, accepted.

4:00pm **PS+SS-ThA6 A Plasma-aerosol Droplet Reactor for the Synthesis of Ammonia from Nitrogen and Water**, *Joseph Toth, D.J. Lacks, J. Renner, R.M. Sankaran*, Case Western Reserve University

Alternative approaches are sought to the high-pressure, high-temperature Haber-Bosch (H-B) process for nitrogen fixation in order to enable distributed synthesis from renewable feedstocks. A potentially promising reactive strategy is plasma excitation which was historically the first method to fix nitrogen by reacting nitrogen and oxygen in air. More recently, plasmas have been combined with solid catalyst materials to synthesize ammonia at atmospheric pressure and lower temperatures than the H-B process. However, most of these reactions still require hydrogen gas which remains linked to fossil fuels and leads to both high cost and environmental consequences.

Here, we present a novel plasma-aerosol droplet reactor to synthesize ammonia from nitrogen and water at atmospheric pressure and near room temperature. Introducing the water as droplets instead of water vapor increases the throughput that can be achieved and also simplifies the system, eliminating the need for heated lines to avoid condensation on the walls. The plasma was formed as a dielectric barrier discharge inside a quartz tube with an outer ring electrode and an inner wire electrode. The water droplets were generated using a commercial nebulizer via a high nitrogen flow rate causing a Venturi effect which siphoned the water into the gas stream. The products were collected by bubbling the gas effluent leaving the reactor through a concentrated sulfuric acid bath and condensing in a second trap chilled to -40 °C. The ammonia was then measured by the o-phthalaldehyde colometric assay technique. The ammonia production rate was found to be a function of the power and

# Thursday Afternoon, October 24, 2019

flow rate with production rates up to 600  $\mu\text{g/hr}$  at 70 W. Controls were run with an argon plasma and with no water droplets to verify that no ammonia was produced without both nitrogen and water. In addition to ammonia, we also tested for nitrites/nitrates ( $\text{NO}_x$ ) and measured up to 3000  $\mu\text{g/hr}$  total production rate. The efficiency, power consumption, and potential reaction mechanisms will also be discussed.

**4:20pm PS+SS-ThA7 Plasma-assisted Nitrogen Fixation by Water: Development and Evaluation of Hybrid Membrane Based Plasma-Electrochemical Reactor**, *R. Sharma, Richard M.C.M. van de Sanden, H. Patel, V. Kyriakou, U. Mushtaq*, Dutch Institute for Fundamental Energy, Netherlands; *A. Pandiyan*, Dutch Institute for Fundamental Energy; *S. Welzel, M.N. Tsampas*, Dutch Institute for Fundamental Energy, Netherlands

The worldwide energy crisis and environmental issues have greatly driven the current research on exploring and efficiently utilizing the environmentally-friendly and sustainable energy sources<sup>1</sup>. Most sustainable sources such as solar and wind energy are in principle able to meet the global energy demand. Nevertheless, they are intermittent and require new concepts of conversion and storage of electricity. Storing energy in form of chemical bonds is considered as an effective option for long term storage. Thus there is quest of developing effective processes for converting electrical energy into molecules.

In this context, nitrogen fixation is unquestionably one of the most important chemical conversion process since it converts  $\text{N}_2$  into molecules of high energy (e.g.  $\text{NH}_3$ ,  $\text{NO}$ )<sup>2</sup>. However, contemporary chemical industry for nitrogen fixation imposes great concerns about the environmental sustainability in terms of immense energy consumption and burdened emissions profile. Nevertheless, plasma-technology has been receiving renewed attention as an alternative “green” approach for  $\text{N}_2$  activation which is one of the fundamental requirement for nitrogen fixation.

Up to now solutions were mainly sought on material axis, however recent theoretical studies have revealed that there are intrinsic limitations of catalysis (i.e. scaling relationships) which keep the processes far from the optimum performance. In this work, we will present a unique solution to the aforementioned limitations by employing a hybrid type reactor consisting of a plasma reactor and solid state water electrolyzers with oxygen ion<sup>3</sup> or proton conducting membranes. Unlike conventional plasma catalysis that requires the co-activation of reactants, in the proposed alternative approach, electrolyzers provide reacting species on catalysts with a controllable manner while a radiofrequency plasma is used to increase the reactivity of  $\text{N}_2$ . Such spatial separation of  $\text{N}_2$  dissociation and catalytic formation of the target molecules provides truly independent parameters to optimise the nitrogen fixation process. One aided benefit of the proposed approach is that both technologies, i.e. water electrolyser and plasma activation, utilize base molecules ( $\text{N}_2$  and  $\text{H}_2\text{O}$ ) and can be directly powered by renewable electricity. Such a scheme may be a stepping stone to zero carbon footprint processes. Moreover, the advantages of proposed approach will be also compared to conventional plasma catalysis or pure plasma processes.

## References

- [1] Chu et al, Nat. Mater., 16 (2017), 16
- [2] Patil et al, Catal. Today, 256 (2015), 49
- [3] Tsampas et al, Catal. Sci. Technol., 5 (2015) 4884

**4:40pm PS+SS-ThA8 Plasma-Assisted Ammonia Synthesis in Hybrid Plasma-Catalysis DBD Reactors**, *Z. Chen, X. Yang, Y. Ju, S. Sundaresan, Bruce E. Koel*, Princeton University **INVITED**

Solar and wind power are creating increasingly large amounts of electricity, and an important question is how can we take advantage of the expanding increase of renewable electricity for catalysis? One approach is plasma-assisted catalysis, which utilizes excited gaseous molecules or new reactive species formed in a (non-equilibrium, low temperature) gas discharge plasma, along with a catalyst to enable increases in the activity and selectivity for carrying out desirable chemical reactions. A significant challenge in plasma-catalysis hybrid systems is to achieve the strongest synergistic interactions between the plasma and catalyst to increase performance and overall energy efficiency. We report on two types of dielectric barrier discharge (DBD) reactors (with a coaxial tube and parallel plates) that have been used to screen catalytic effects of different metal surfaces and supported catalysts in plasma-catalysis hybrid systems at near atmospheric pressure, utilizing both AC and nanosecond pulsed discharges. We observed strong synergistic effects between non-equilibrium plasma and catalysts for both  $\text{NH}_3$  synthesis and methane coupling reactions. We

compared the performance for ammonia synthesis of catalysts using active metals (Pd, Pt, and Fe) or less active metals (Au, Ag, and Cu) or their alloys. We found that the metal-nitrogen (M-N) bond energy was not the only parameter governing the catalytic activity for  $\text{NH}_3$  synthesis in plasma. Better catalytic activity could be achieved by bimetallic catalysts that contained catalytic sites for both  $\text{N}_2^*$  dissociation and hydrogenation of M-N bonds, leading to our observations of a highly active PdFe catalyst for  $\text{NH}_3$  synthesis in plasma. In addition, we will also report briefly about results in  $\text{CO}_2$  reforming of methane in the coaxial reactor, where we found that under thermal only conditions, PtFe/ $\text{Al}_2\text{O}_3$  catalyzed mainly the formation of CO and  $\text{H}_2$ , but with the plasma on, the selectivity shifted to methane coupling reactions. Interestingly, an Ag/ $\text{Al}_2\text{O}_3$  catalyst with an AC discharge demonstrated 100% selectivity to  $\text{CH}_4$  coupling reactions at 350 °C. Methane coupling using the plasma-catalysis reactor at low temperatures and pressures mainly produced higher hydrocarbons, suggesting a potential route for converting cheap and abundant methane gas into high value hydrocarbons and fuels.

**5:20pm PS+SS-ThA10 Efforts towards Plasma-assisted Catalysis: Elucidating Gas-phase Energetics, Kinetics, and Surface Interactions**, *Angela Hanna, E.R. Fisher*, Colorado State University

With increasing concern about environmental health and climate change, there is a greater need to investigate fundamental reactivity of pollutant species. Improving the effectiveness of substrates used in vehicular emissions abatement hinges on the ability to discern the contributions of gas-phase species in surface reactions. A fundamental understanding of interactions between plasma species is essential to characterizing complex plasma chemistry phenomena. Inductively-coupled  $\text{N}_x\text{O}_y$  plasma systems were investigated to determine possible synergisms between precursor chemistry and gas-surface interface reactions with a variety of catalytic substrates (i.e., Pt substrates and zeolites). The impact of adding dilute amounts of water vapor to the gas feed was also systematically explored. Precursor chemistry was probed via gas-phase diagnostics; time-resolved optical emission data elucidated NO (g) and  $\text{N}_2$ (g) production kinetics from  $\text{N}_x\text{O}_y$  source gases, whereas steady-state emission and absorbance data provide information regarding energy partitioning between rotational and vibrational degrees of freedom. The presence of micro-structured catalysts within the plasma significantly decreases excited  $\text{N}_2$  vibrational temperature, suggesting these materials promote vibrational relaxation within the discharge. Our unique Imaging of Radicals Interacting with Surfaces (IRIS) allows us to probe the gas-surface interface and provides evidence of how plasma species synergistically interact with catalytic substrates. In addition to evaluating the spectroscopic characteristics of the discharge ( $\text{N}_x\text{O}_y$ ), we have assessed material morphology and chemical composition before and after plasma exposure. The porous network of zeolite substrates was maintained after prolonged plasma exposure, although surface etching of oxygen or N-doping occurred at different plasma operating conditions. This holistic experimental approach, combining gas-phase diagnostics, IRIS, and robust materials characterization will be essential to realizing the potential of plasma assisted catalysis for pollution remediation.

## Author Index

### **Bold page numbers indicate presenter**

— C —

Chen, Z.: PS+SS-ThA8, **2**

— F —

Fisher, E.R.: PS+SS-ThA10, **2**

— H —

Hanna, A.R.: PS+SS-ThA10, **2**

Hicks, J.C.: PS+SS-ThA3, **1**

— I —

Itagaki, N.: PS+SS-ThA1, **1**

— J —

Ju, Y.: PS+SS-ThA8, **2**

— K —

Kamataki, K.: PS+SS-ThA1, **1**

Kitajima, T.: PS+SS-ThA2, **1**

Koel, B.E.: PS+SS-ThA8, **2**

Koga, K.: PS+SS-ThA1, **1**

Kyriakou, V.: PS+SS-ThA7, **2**

— L —

Lacks, D.J.: PS+SS-ThA6, **1**

— M —

Mushtaq, U.: PS+SS-ThA7, **2**

— N —

Nakano, T.: PS+SS-ThA2, **1**

— P —

Pandiyan, A.: PS+SS-ThA7, **2**

Patel, H.: PS+SS-ThA7, **2**

— R —

Renner, J.: PS+SS-ThA6, **1**

— S —

Sankaran, R.M.: PS+SS-ThA6, **1**

Sharma, R.: PS+SS-ThA7, **2**

Shiratani, M.: PS+SS-ThA1, **1**

Sundaresan, S.: PS+SS-ThA8, **2**

— T —

Toth, J.R.: PS+SS-ThA6, **1**

Tsampas, M.N.: PS+SS-ThA7, **2**

— V —

van de Sanden, M.C.M.: PS+SS-ThA7, **2**

— W —

Welzel, S.: PS+SS-ThA7, **2**

— Y —

Yamamoto, A.: PS+SS-ThA1, **1**

Yang, X.: PS+SS-ThA8, **2**