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Plasma catalytic production of ammonia: An exploration of reaction mechanisms and process optimization

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Ammonia synthesis via non-thermal plasma-catalytic processes has the potential to become a viable method of producing green ammonia due to the non-equilibrium nature of plasma, whereby the bulk gas remains near room temperature whilst the electrons are highly energetic with energies in the range 1-10 eV. If combined with a renewable energy source, plasma-catalytic ammonia production could also be a key player in boosting the hydrogen economy, reducing greenhouse gas emissions. Ammonia is an important chemical, most commonly known for its use as a fertilizer; it is also an excellent hydrogen storage molecule due to the 1:3 (N:H) ratio of NH_3 and can be transported using existing natural gas infrastructure. Plasma processes are highly versatile and scalable, making them useful in isolated regions as well as on an industrial scale. They can easily be scaled by altering the discharge volume or, if larger scale operation is required, modular systems of multiple reactors can be employed. The quick start-up and shut-down time of this electrical process make this technology useful for combining with renewable energy, where fluctuations readily occur.

However, current plasma systems have low NH_3 yields and energy efficiencies. Although an increase in these properties is achievable by combining a catalyst with the plasma, energy efficiencies remain an order of magnitude too low for the process to be viable. Furthermore, interactions between the plasma and catalyst, that determine which species are present and the reaction pathways, are largely unknown. Generally, catalysts are selected based on their activity in the thermal process; however, it is known that catalysts behave differently in plasma compared to when heated in a thermal reactor. Novel approaches are therefore required to uncover plasma-catalyst interactions and hence enhance reaction performance through process optimization.

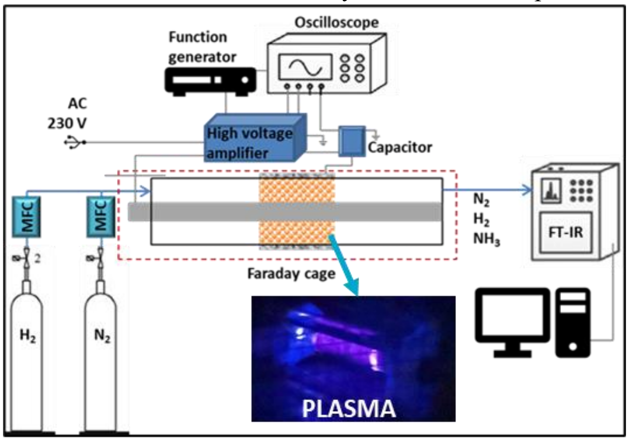

Figure 1. Process setup for the plasma catalytic production of ammonia; a DBD reactor is used to test various catalysts. This is operated at 10 kV and 1 kHz.

This presentation will address various approaches to increase NH_3 yield and energy efficiency, such as reactor design and catalyst design, along with the benefit of in-situ studies and the role they play in process optimization.

Several novel catalysts containing nitrogen and hydrogen groups shall be presented and their activity discussed in terms of reaction mechanism. These catalysts are thought to follow the Mars–Van Krevelen mechanism, which has a lower energy barrier than the conventional Langmuir–Hinshelwood mechanism that usually dominates this process[1]. Two types of catalyst are considered – oxynitride-hydrides and an amine-containing catalyst.

To understand plasma-catalyst interactions and inform process optimization, a variety of techniques can be carried out. In-situ techniques, such as in-situ FTIR, are required to detect important surface adsorbed species which can indicate the reaction mechanisms. This data can help us create highly active catalysts. The plasma process can also be simulated. Our kinetic model[2] is one of the most extensive models available for non-thermal plasmas interacting with a surface. The model can be used to gain deeper insights into experimental data[3], which can inform the catalyst and reactor design.

References

[1] M. Kitano *et al.*, *J. Am. Chem. Soc.*, **141**, pp. 20344–20353, 2019.
[2] J. Hong, S. Pancheshnyi, E. Tam, J. J. Lowke, S. Prawer, and A. B. Murphy, *J. Phys. D Appl. Phys.*, **51**, p. 109501, 2018.
[3] L. R. Winter, B. Ashford, J. Hong, A. B. Murphy, and J. G. Chen, *ACS Catal.*, **10**, no. 24, pp. 14763–14774, 2020.