Plasma Chemistry and Catalysis

P. Navascués[1], J. Garrido-García[1], M. Oliva-Ramírez[1, 2], J. Cotrino[1, 2], A. González-Elipe[1], Gómez-Ramírez A.[1, 2,*]

[1] *Laboratory of Nanotechnology on Surfaces and Plasma. Instituto de Ciencia de Materiales de Sevilla (CSIC-Universidad de Sevilla), Avda. Américo Vespucio 49, E-41092 Seville, Spain*

[2] *Departamento de Física Atómica, Molecular y Nuclear, Universidad de Sevilla, Avda. Reina Mercedes, E-41012 Seville, Spain*

(*) anamgr@us.es

Since the discovery of the ozonizer by Siemens in 1857 [1], [2], plasma has been used to carry out several chemical processes of high interest, such as hydrocarbon reforming, synthesis of high-value-added chemicals (hydrogen, ammonia), and elimination of pollutants (VOCs, CO2). In the late 1990s and throughout the first two decades of the 21st century, many studies have been published incorporating classical catalysts into plasma reactors, leading to the establishment of the term “plasma catalysis” within the community [3]. The objective behind the inclusion of catalysts in plasma reactors is to enhance the energy efficiency and chemical yield of the processes, aiming to achieve synergies between plasma-assisted chemistry and the classical catalytic effect of catalysts in contact with plasma. Numerous studies have been conducted to analyze the synergistic effect of plasma catalysis in processes of significant environmental importance (such as CO_2 elimination, greenhouse gas conversion, NO_x and NH_3 synthesis, water decontamination, etc.) as well as those of energetic interest (including H_2 synthesis, CH_4 conversion, alcohol production, etc.).[4], [5] Different authors have analysed, both experimentally and theoretically, the possible mechanisms that take place in the plasma in the presence of catalysts, leading to an increase in process performance. For this purpose, operational parameters of plasma reactors are usually varied, among which temperature, operating voltages, gas flow and type of barrier materials stand out. Currently, numerous works are still being published on this topic, and it is an area of great interest in the field of plasma chemistry, with one of the highlights being the recent controversy over the real role of catalysts during plasma-assisted processes. [6], [7] Recent studies have demonstrated that the synergistic effect [5], [8] found is not due to a classical catalytic effect (or if so, it is of second order), but rather to the modifications that the inclusion of metallic particles has on the electrical properties of the discharge. Although those results would depend greatly on the type of process under study (they will not be the same for hydrocarbon reforming as for ammonia synthesis) they open a debate of great interest in the scientific community.

In this talk, we will focus on the ammonia synthesis process carried out in a packed-bed plasma reactor, including a classical ruthenium (Ru) catalyst -used in conventional thermal methods- in the ferroelectric packed-bed barrier, aiming to increase the yields and energy efficiencies of the process. We will analyse the ammonia synthesis process in the presence/absence of the Ru catalyst, and working at two different temperatures, ambient and 190°C (at which purely catalytic effects could be expected). We will address the study of the catalyst's effect on plasma properties, analysing current curves through the reactor, power consumption, energy efficiency, and simulating the possible effects of incorporating the metallic catalyst into the packed bed. Our results demonstrate, for the first time in the literature up to our knowledge, that the reported synergy is not due to a classical catalytic effect but rather to the modifications that the inclusion of metallic particles (classical catalysts) has on the plasma. Additionally, it is shown that purely chemical catalytic effects are negligible during plasma-assisted NH_3 synthesis. Our conclusions reveal that the use of classical metallic catalysts, which are highly expensive, is not a good strategy for increasing the energy efficiency of the plasma-assisted ammonia synthesis. These results are highly significant in the field of plasma catalysis, where it has traditionally been assumed that the found synergy is due to catalytic effects, implying that the catalytic effect is responsible for the increased reaction yield.

[1] W. Siemens, 'Ueber die elektrostatische Induction und die Verzögerung des Stroms in Flaschendrähten', *Ann Phys*, vol. 178, no. 9, pp. 66–122, Jan. 1857, doi: https://doi.org/10.1002/andp.18571780905.
[2] U. Kogelschatz, 'Dielectric-Barrier Discharges: Their History, Discharge Physics, and Industrial Applications', *Plasma Chemistry and Plasma Processing*, vol. 23, no. 1, pp. 1–46, 2003, doi: 10.1023/A:1022470901385.
[3] A. Bogaerts *et al.*, 'The 2020 plasma catalysis roadmap', *J Phys D Appl Phys*, vol. 53, no. 44, p. 443001, 2020, doi: 10.1088/1361-6463/ab9048.
[4] A. Bogaerts, E. C. Neyts, O. Guaitella, and A. B. Murphy, 'Foundations of plasma catalysis for environmental applications', *Plasma Sources Sci Technol*, vol. 31, no. 5, p. 053002, 2022, doi: 10.1088/1361-6595/ac5f8e.
[5] C. Yan *et al.*, 'Recent Advances in Plasma Catalysis', *The Journal of Physical Chemistry C*, vol. 126, no. 23, pp. 9611–9614, Jun. 2022, doi: 10.1021/acs.jpcc.2c03062.
[6] C. Ndayirinde *et al.*, 'Plasma-catalytic ammonia synthesis: Packed catalysts act as plasma modifiers', *Catal Today*, vol. 419, p. 114156, 2023, doi: https://doi.org/10.1016/j.cattod.2023.114156.
[7] P. Navascués, J. Garrido-García, J. Cotrino, A. R. González-Elipe, and A. Gómez-Ramírez, 'Incorporation of a Metal Catalyst for the Ammonia Synthesis in a Ferroelectric Packed-Bed Plasma Reactor: Does It Really Matter?', *ACS Sustain Chem Eng*, vol. 11, no. 9, pp. 3621–3632, Mar. 2023, doi: 10.1021/acssuschemeng.2c05877.
[8] A. Bogaerts, E. C. Neyts, O. Guaitella, and A. B. Murphy, 'Foundations of plasma catalysis for environmental applications', *Plasma Sources Sci Technol*, vol. 31, no. 5, p. 053002, 2022, doi: 10.1088/1361-6595/ac5f8e.

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