



PLASMA-CATALYST INTERACTION MECHANISMS FOR CO₂ RECYCLING AND MOLECULE CONVERSION

O. Guaitella¹, D. Sadi¹, S. Bravo¹, B. Berdugo¹, M. Budde¹, D. Pai¹, T. Silva², V. Guerra²

¹ *Laboratoire de Physique des Plasmas, CNRS, Sorbonne Université, École Polytechnique, Institut Polytechnique de Paris - PALAISEAU (France)*

² *Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa - LISBOA (Portugal), olivier.guaitella@lpp.polytechnique.fr*

Plasma catalysis offers a promising avenue for creating energy-efficient CO₂ recycling processes. By activating CO₂ through dissociation or vibrational and electronic excitation, plasma can enhance the yield of desired products, while the catalyst can enhance the selectivity in processes such as methanation, methanol synthesis, and DRM. However, the direct dissociation of CO₂ by plasma is not always energy-efficient, and the role of CO₂'s excited states and dissociation products remains unclear [1].

Advancing plasma catalysis research requires tools that enable precise quantitative comparisons of data across different research groups. One possibility to study these complex systems is to establish standards and databases, similar to practices in conventional catalysis, for instance, but adapted to the specificities of plasmas. In this vein, the PIONEER European project has initiated a database focused on CO₂ conversion performance through plasma catalysis [2]. However, the lack of fundamental understanding of the plasma-catalyst interaction makes it difficult to define the most relevant parameters for meaningful comparisons between various plasma-catalytic systems. Moreover, the catalysts typically used in plasma catalysis are often those developed for thermal catalysis, which may not be optimal for efficiently using the short-lived species generated by plasma. To maximize the benefits of cold plasma, it is crucial to separate the chemical kinetics of the gas phase from surface processes and understand how plasma can alter the catalyst itself, necessitating *in situ* measurements.

In this study, various low-pressure plasma reactor configurations were employed to validate step-by-step kinetic models of plasmas, particularly for CO₂/H₂ and CO₂/CH₄ systems. Batch reactors with pulsed radiofrequency sources were used to constrain the characteristic times of the primary chemical reactions. Once the gas phase kinetics are understood, the same plasma sources can be used to assess their impact on catalytic surfaces. In particular, simple materials known for their oxygen mobility, such as CeO₂ and YSZ pellets, were exposed directly to plasma to conduct time-resolved infrared absorption and *in situ* Raman measurements. These measurements allowed the study of carbonate formation on the material surfaces and the creation of oxygen vacancies within the materials. The combination of detailed characterization of the plasma kinetics and the surface evolution in a single system proves to be a powerful approach to understanding the microscopic mechanisms of the plasma-catalyst interaction.

References:

- [1] Bogaerts, Annemie, et al. "Foundations of plasma catalysis for environmental applications." *Plasma Sources Science and Technology* 31.5 (2022): 053002
- [2] Salden, Antoine, et al. "Meta-analysis of CO₂ conversion, energy efficiency, and other performance data of plasma-catalysis reactors with the open access PIONEER database." *Journal of Energy Chemistry* 86 (2023): 318-342.