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Introduction to understanding and new approaches to create synergy between catalysis and plasma themed collection

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Plasma catalysis has emerged as a highly promising and rapidly evolving field to address grand challenges in energy and

sustainability. Plasma is a partially ionized gas, which contains electrons, various types of ions, radicals, and excited species alongside ground state molecules. Hence, it exhibits great reactivity at mild conditions (room temperature and atmospheric pressure), as the electrons activate the gas molecules. However, due to its high reactivity, it is not selective and thus produces a plethora of different species. The proper combination and integration of plasma with catalytic materials can target the selective production of desired compounds.

for many years for air pollution control (e.g., volatile organic compound (VOC) removal), for which commercial devices are already available (see e.g., ref. 1), but in recent years it is also gaining increasing interest for sustainable chemistry, like CO₂ and/or CH₄ conversion, NH₃ and NO_x synthesis, although these applications remain largely in the research phase. Indeed, some papers report plasma-catalyst synergy, in which the combination of plasma catalysis yields better performance than the sum of plasma and catalysis separately, but this synergy is not always observed, and

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Annemie Bogaerts

Annemie Bogaerts obtained her PhD in chemistry in 1996. She is full professor at the University of Antwerp since 2012. She founded her research group PLASMANT in 2004, which currently counts about 50 members. Her research focuses on plasma chemistry, plasma reactor design and plasma-surface interactions by experiments and modelling for various applications, but mostly for sustainable chemistry (including plasma catalysis) and cancer treatment. She has above 700 peer-reviewed publications, which are highly cited (H-index = 110 in Google Scholar) and above 280 invited lectures. She has an ERC Synergy Grant together with G. Centi.



Gabriele Centi

Gabriele Centi has been a full professor at the University of Messina (Italy) since 1995. He founded the CASPE (Catalysis for Sustainable Production and Energy), which currently counts about 40 members. His research focuses on catalysis (heterogeneous, photo-, electro- and plasma catalysis) and the development/assessment of sustainable technologies and processes, covering multiple aspects from fundamentals to application and engineering. He has over 650 peer-reviewed publications, which are highly cited (H-index = 100 in Google Scholar) and nearly 300 invited lectures. He coordinates the ERC Synergy Grant SCOPE, to which A. Bogaerts is a principal investigator (PI).



sometimes plasma catalysis even performs worse than plasma-only operation. This illustrates that more research is needed to better understand the underlying plasma-catalyst interactions, possibly leading to synergy. Better insight is indeed crucial to overcome the current challenges, like limited energy efficiency, product yield and selectivity.

This themed collection aims to advance our understanding of the underlying mechanisms in plasma catalysis, by modelling and experiments. It illustrates the advanced status of plasma catalysis for VOC removal (showing *e.g.*, nearly 100% selective conversion of toluene into CO₂), but also discusses the challenges in sustainable chemistry applications, where plasma-catalyst synergy is often limited.

One challenge is the limited insight into the optimal catalyst materials for plasma catalysis. Due to the reactive environment, *i.e.*, the presence of radicals, ions, electrons and excited species, the underlying processes in plasma catalysis are different from thermal catalysis, so the best thermal catalyst is not necessarily the best in plasma catalysis. For instance, in the case of dry reforming of methane (DRM), modelling suggested that metal catalysts may scavenge the plasma radicals, and the latter recombine back into the reactants, rather than into the desired products.² Other materials, like metal oxides, could perhaps be more suitable for plasma-catalyst synergy, for instance if they trap O radicals (by means of oxygen-vacancies), so that the latter cannot recombine with CO back into CO₂. However, more research is

needed to elucidate the exact mechanisms. Furthermore, metals introduced in a plasma may not remain metallic, and can become metal oxides, and *vice versa*. One paper in this themed collection discusses the role of oxygen mobility in ZrO₂ for plasma-catalytic DRM (<https://doi.org/10.1039/D5EY00069F>).

Another way to enhance plasma-catalyst synergy may be to better tune the plasma conditions to the catalyst's needs. While radicals are the dominant species at typical plasma catalysis conditions, they might simply be scavenged at the catalyst surface, while vibrationally excited molecules might enhance catalytic reactions, by lowering the barrier for dissociative adsorption. One of the papers in this themed collection discusses the latter mechanism and presents a formula to account for this "vibrational efficacy" (<https://doi.org/10.1039/D5EY00062A>), which turns out to be much higher than predicted with the Fridman-Macheret α -model, commonly used up to now in microkinetic plasma-catalyst modeling.³ Furthermore, other "plasma aspects", like electric fields or ions/electrons, may also affect catalytic reactions. Computer simulations, like density functional theory (DFT), can help to gain better insights into such effects, and the increasing amount of DFT data from thermal catalysis may help improve our understanding of plasma catalysis. To illustrate this, another paper in this themed collection (<https://doi.org/10.1039/D4EY00256C>) presents interpretable transfer learning from thermal to plasma catalysis, to elucidate the role of

electro- and photo-effects (such as electric field and surface charges) in plasma catalysis.

Another challenge in plasma-catalyst synergy, which may explain why plasma catalysis is not always better than plasma-only, is that physical effects of the catalyst (modifying the plasma discharge characteristics) may be hiding possible chemical-catalytic effects, or that the plasma chemistry is too dominant, due to limited plasma-catalyst interaction (too large void space). All these challenges, as well as possible solutions (like other plasma-catalyst configurations) are discussed in a perspective paper published in this themed collection (<https://doi.org/10.1039/D5EY00027K>).

Most research activities have focused on so-called in-plasma catalysis, where the catalyst is placed directly inside the plasma reactor, and can react with the (short-lived) plasma species, such as radicals and excited species, as discussed above. This combination makes use of cold plasmas (room temperature or slightly above), such as dielectric barrier discharges. However, the catalyst can also be placed after the plasma reactor, in post-plasma catalysis. This combination has great potential in combination with so-called warm or thermal plasmas, like gliding arc, microwave or nanosecond-pulsed plasma, where the hot effluent gas can activate the catalyst, thus without the need of extra heating, as illustrated in several papers of this themed collection.

Finally, it is worth mentioning that the combination of plasma with materials, in a broader sense than only catalysts, such as sorption materials or membranes or a post-plasma carbon bed, is quite promising and can lead to significant performance enhancements compared to plasma-only, by product removal and avoiding the back-reactions (recombination of products back into the reactants).

Overall, we believe the novel insights and results presented in this themed collection will help move the community to the next step in applying plasma catalysis to open new avenues for carbon-free, sustainable energy and chemical production.



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