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Roadmap

The 2020 plasma catalysis roadmap

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Abstract

Plasma catalysis is gaining increasing interest for various gas conversion applications, such as CO_2 conversion into value-added chemicals and fuels, CH_4 activation into hydrogen, higher hydrocarbons or oxygenates, and NH_3 synthesis. Other applications are already more established, such as for air pollution control, e.g. volatile organic compound remediation, particulate matter and NO_x removal. In addition, plasma is also very promising for catalyst synthesis and treatment. Plasma catalysis clearly has benefits over 'conventional' catalysis, as outlined in the Introduction. However, a better insight into the underlying physical and chemical processes is crucial. This can be obtained by experiments applying diagnostics, studying both the chemical processes at the catalyst surface and the physicochemical mechanisms of plasma-catalyst interactions, as well as by computer modeling. The key challenge is to design cost-effective, highly active and stable catalysts tailored to the plasma environment. Therefore, insight from thermal catalysis as well as electro- and photocatalysis is crucial. All these aspects are covered in this Roadmap paper, written by specialists in their field, presenting the state-of-the-art, the current and future challenges, as well as the advances in science and technology needed to meet these challenges.

Keywords: catalysis, CO_2 conversion, CH_4 activation, NH_3 synthesis, plasma catalysis, non-thermal plasma, air pollution control

(Some figures may appear in colour only in the online journal)

Contents

List of abbreviations

AC:	Alternating current
AFM:	Atomic force microscopy
ANN-GA:	Artificial neural network - genetic algorithm
ATR:	Attenuated total reflectance
CCS:	Cross correlation spectroscopy
CES:	Chemical energy storage
COP21:	21st Conference of the Parties
DBD:	Dielectric barrier discharge
DC:	Direct current
DFT:	Density functional theory
DRIFTS:	Diffuse reflectance infrared Fourier transform spectroscopy
DRM:	Dry reforming of methane
DRS:	Diffuse reflectance spectroscopy
ECE:	Energy conversion efficiency
EEDF:	Electron energy distribution function
EFISH:	Electric field induced second harmonic generation
EPC:	Electro- and photo-catalysis
ERC:	European Research Council
FTIR:	Fourier transform infrared
GA:	Gliding arc
HC:	Hydrocarbons
ICCD:	Intensified charged coupled device
IR:	Infrared
IPC:	In-plasma catalysis
KPI:	Key performance indicator
LCA:	Lifecycle analysis
LHV:	Lower heating value
MDA:	Methane dehydroaromatization
ML:	Machine learning
MOF:	Metal organic framework
MW:	Microwave
NO_x:	Nitrogen oxides
NOCM:	Non-oxidative coupling of methane
NTP:	Non-thermal plasma
OES:	Optical emission spectroscopy
PEC:	Photo-electrocatalytic
PIC-MCC:	Particle-in-cell-Monte Carlo collision
PID:	Proportional–integral–derivative
PM:	Particulate matter
PPC:	Post-plasma catalysis
RE:	Renewable energy
RF:	Radio-frequency
SCR:	Selective catalytic reduction
SDBD:	Surface dielectric barrier discharge
SEI:	Specific energy input
SER:	Specific energy requirement
SFG:	Sum frequency generation
SRM:	Steam reforming of methane
TALIF:	Two photon absorption laser induced fluorescence
TEA:	Techno-economic analysis
TEM:	Transmission electron microscopy
TOF:	Turnover frequency
TRL:	Technology readiness levels
UV–vis-IR:	Ultraviolet-visible-Infrared
VOC:	Volatile organic compound
WGS:	Water-gas shift
XAFS:	X-ray absorption fine structure
XPS:	X-ray photoelectron spectroscopy
XRD:	X-ray diffraction

Introduction

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This Plasma Catalysis Roadmap forms part of the special collection, 'Advances in Plasma for a Sustainable Future', published in *Journal of Physics D: Applied Physics*, and follows the same format as the '2012 and 2017 Plasma Roadmaps' [1, 2]. The intent of the Plasma Catalysis Roadmap, which is written by various experts in their field, is to provide insight into the research needs and opportunities in the rich and diverse field of plasma catalysis, as well as to establish a reference to guide decisions on investments in this emerging research field. We do not aim to provide a detailed discussion of the different aspects mentioned, as it is not a review paper, but a Roadmap, which should indicate in a concise way strategic directions for new research based on a few selected references.

The goal of applied catalysis is to promote the transformation of some feedstock into a desired product at conditions that make a process overall practically viable. Catalysis is at the heart of the chemicals and petroleum industries, and catalysis practice is highly developed and optimized. Significant opportunities remain, however, to enable chemical transformations currently inaccessible to known catalysts. In conventional catalysis, proportions and quantities of products formed (i.e. selectivity and yield) are controlled by the conditions (bulk temperature, pressures, concentrations) prevailing in the reactor and the rates of the underlying catalytic processes at those conditions. Plasma catalysis is the integration of a catalyst with a plasma to generate desired products at desired rates and at desired efficiencies that are otherwise inaccessible via conventional catalytic means.

A plasma is a (partially) ionized gas, consisting of neutral species (molecules, radicals, excited species), ions, photons and electrons. In a non-thermal plasma (NTP), or non-equilibrium plasma, the electron temperature is much greater than the temperature of the heavy species (ions and neutrals), and thus the radicals and excited species are formed at temperatures closer to ambient. This non-thermal distribution of energy offers a potential avenue to overcoming both the kinetic and thermodynamic limitations on chemical transformations of reactants into desired products. This energy, appropriately directed, can in principle drive endothermic, equilibrium-limited reactions at conditions at which equilibrium conversions are small. Similarly, the energy can accelerate reaction pathways that are kinetically slow at prevailing conditions. The highly energetic electrons in an NTP produce (rotationally, vibrationally and electronically) excited species, ions and radicals through inelastic collisions with feedstock molecules, yielding a plethora of new species and states that are inaccessible at the bulk thermal temperature. Because NTPs can contain a diverse mix of highly reactive species, they are difficult to operate in such a way as to produce single products in high yield and at high selectivity. Integration of plasma and catalysts together promises to combine the advantages of the two, to effect transformations that are currently difficult or impossible to achieve.

There is, however, a paradigm shift, often overlooked, in the concept of catalyst operations. In conventional heterogeneous catalysis, reactants chemisorb and follow some surface-mediated reaction paths that ultimately determine the types and rates of products formed. On the other hand, the NTP provides external activation, and thus the issue is different: how can the catalyst interact with these highly reactive (or energetic) species without simply quenching them and how can it provide a selective path of transformation? Thus, the conceptual mechanism of operation and control of yield and selectivity is different for thermal catalysts compared to catalysts that operate on plasma-activated reactive species. There are analogies with photo- and electro-catalysts, discussed later, but there are again differences in the mechanism of operation. Thus, catalysts well-suited for operation with plasma could be different from those for thermal catalysis and for photo-/electro-catalysis, as discussed in sections 2 and 3 of this Roadmap. A further complication is that the NTP environment may transform the catalyst itself, structurally or compositionally, from its *ex situ* form, and that the NTP environment may, through for instance charging or electric field effects, modify intrinsic surface reaction rates and/or pathways.

The key question is: why would plasma catalysis be of interest, keeping in mind the large and successful, highly-optimized field of catalysis (section 3 in this Roadmap). Although an NTP may not be selective towards targeted products, plasma provides another kind of selectivity, not present in conventional, thermal catalysis. In conventional catalysis, the reactions are thermally-driven, and thermal energy is intrinsically non-selective, i.e. by definition it equally influences all degrees of freedom of all reaction intermediates across all intermediate steps ('equipartition of energy'). In contrast, NTP causes non-thermal activation of the molecules, in the most ideal case directing energy selectively into the reaction coordinate of a single targeted elementary step, without significantly affecting the other steps [3]. Indeed, the key characteristic of NTP is that thermal equilibrium is not maintained between all degrees of freedom. In other words, plasma catalysis distinguishes itself from conventional thermal catalysis by using a different concept of 'temperature'. Typically, the bulk gas temperature in an NTP (such as a dielectric barrier discharge, DBD) is around 300–1000 K, while the electron temperature is in the order of 10^4–10^5 K (1–10 eV), and other degrees of freedom have temperatures in between these two extremes.

Of particular interest is the vibrational temperature, which is typically on the order of a few 1000 K. NTP can indeed selectively activate vibrational excitation modes in the gas molecules, depending on the reduced electric field (i.e. the ratio of the electric field and gas number density) [4, 5]. These vibrationally excited molecules may give rise to the most energy-efficient gas conversion [4, 5], but also provide more reactivity at a catalyst surface, as they experience lower barriers for dissociation at the surface. Therefore, they can even overcome intrinsic limitations on the design space accessible within a given class of heterogeneous catalysts, as nicely demonstrated in [6]. Furthermore, ions and radicals formed in the plasma can participate in alternative reaction pathways towards products, both at the catalyst surface in addition to the plasma itself. For instance, they may allow Eley–Rideal reactions to occur at the catalyst surface, alongside the Langmuir–Hinshelwood steps that dominate in thermal catalysis. To summarize, because an NTP is not characterized by a single temperature, chemical conversions are not bound by the thermodynamic equilibrium constraints of the bulk gas temperature and pressure. Finally, in addition to the lower barriers and alternative pathways provided by plasmas, other interactions are also possible between plasmas and catalysts, such as electric field effects, surface charging, hot spot formation, and morphological changes of the catalyst, as well as effects of the catalyst on the plasma characteristics [7–16], which might also lead to plasma-catalyst synergies (see further).

Another obvious advantage of plasmas is that they allow conversion of the reactants using renewable energy (RE) sources rather than thermal energy, as in conventional catalysis. Thus, plasmas can drive chemical processes with RE, including chemical energy storage of RE, enabling a new low-carbon technology for chemical production and a new solution to store/transport RE. Note that microwaves or electrical heating can also be applied to use RE in chemical processes, but up to now, limited examples exist of these solutions.

Plasmas are thus another element in the portfolio of non-conventional catalysis technologies being developed, which also includes photo- and electro-catalysis. In the latter processes, however, the reaction is limited to the surface of the electrodes, and thus a 2D-like catalytic process occurs, and mass/charge transport often limits the process. In plasma catalysis, on the other hand, the full reactor volume can in principle be used, as in thermal catalysis (3D-like processes). Thus, the potential productivity is larger. In addition, electro-catalysis often relies on scarce elements like noble metals. There are also differences in the typology of reactions possible, due to the different mechanisms of conversion between plasma catalysis and photo-/electro-catalytic processes. Therefore, they are complementary, rather than competing, technologies to drive chemical processes using RE.

While energy efficiency remains an issue in some plasma catalytic processes, as illustrated in this Roadmap (especially sections 7, 8 and 9), this limitation will become less critical, thanks to the dramatic drop in electricity costs associated with RE in recent years. Indeed, the electricity cost from solar photovoltaics can be as low as \$0.03/kWh in areas (e.g. the United Arab Emirates) with good resources and enabling regulatory and institutional frameworks [17], while the cheapest electricity cost of 0.02/kWh has been achieved in large-scale hydropower projects at high-performing sites [18]. This will make electricity-driven processes, like plasma catalysis, much more attractive.

In addition, plasma allows the fast switch on/off to follow fluctuations in RE production. From this perspective, plasma catalysis has clear advantages over alternative technologies. Furthermore, plasmas (and plasma catalysis) have low investment and operating costs and can be applied on a modular basis for distributed use, as there are almost no economies of scale. Thus, plasma catalysis allows for local on-demand production schemes, which can be of particular interest for fertilizer production from air (N_2 fixation) and RE, even on individual farms, e.g. in underdeveloped countries [19] (see also section 9).

Thus, from the technological side, there is interest in developing novel industrial solutions based on RE as an alternative to the current thermal catalysis processes, but a full portfolio of technologies must be developed to drive chemical production and chemical energy storage by using RE sources, with plasma catalysis offering some points of advantage.

Plasma catalysis has the potential to address a wide range of societal needs. While, in recent years, a large effort has been devoted to the conversion of hard-to-activate molecules (N_2, CO_2, CH_4) for the reasons explained above (i.e. the production of species and the availability of pathways that are unattainable by conventional catalysis at similar temperature and pressure), plasma catalysis is used—and has been for many years—in other application fields, such as air pollution control [7–16]. Table 1 lists the molecules and target products that are under study with plasma catalysis, with some assessment of the status of development (technology readiness levels (TRLs)). More details about most of these applications can be found in sections 7–11 of this Roadmap. Note that the Roadmap does not cover all processes listed in table 1, e.g. some processes are already at a higher TRL or reflect small niche applications for now, but more information about these applications can be found in the cited references. Indeed, the Roadmap is not intended as a comprehensive review, but to pinpoint the major research needs. Nevertheless, this table demonstrates the great potential for plasma catalysis in terms of variety of molecules and suggests where emphasis should be placed in determining research priorities.

Two types of plasma catalysis can be distinguished, based on whether the catalyst is placed inside the plasma or not. The first type is called 'in-plasma catalysis' (IPC), or one-stage or single-stage catalysis, while the second type is called 'post-plasma catalysis' (PPC), or two-stage catalysis. Although various terms are used in literature, in this Roadmap, we consistently use the terms 'in-plasma catalysis' (IPC) and 'post-plasma catalysis' (PPC). IPC can only be applied in NTP devices, such as DBDs, that operate at low enough temperature (300–1000 K) for the catalyst to be inserted in the plasma region. On the other hand, so-called warm plasmas, such as (atmospheric-pressure) microwave and gliding arc discharges, typically operate at temperatures that are too high (several 1000 K) to directly insert the catalysts (unless specific fluidized-bed configurations were applied). In this case, PPC is more appropriate, and thus, only long-lived species that can escape from the plasma will interact with the catalyst, while in the case of IPC, short-lived reactive plasma species (radicals, ions, photons, electronic and vibrationally excited species) can also interact with the catalyst, giving additional possible pathways for the chemical conversions.

Table 1. Overview of molecules being converted by plasma catalysis, and the corresponding target products and technology readiness levels (TRL; see table footnote), as well as references to reviews or key papers.

Process	Reactants	Target products	TRL[a,b]	Ref
CO_2 conversion	CO_2	CO	2–3	[5]
	CO_2/H_2	CO	1–2	[5]
	CO_2/H_2	CH_4	2–3	[5]
	CO_2/H_2	Liquid fuels	2–3	[5]
	CO_2/H_2O	Syngas	1–2	[5]
	CO_2/CH_4	(see below)		
	CO_2/C_2H_6	Liquid fuels	1–2	[20]
CH_4 conversion	CH_4	H_2	2–4	[21]
	CH_4	Olefins	1–2	[21]
	CH_4/CO_2	Syngas	2–4	[3]
	CH_4/CO_2	Olefins	1–2	[3]
	CH_4/CO_2	Liquid fuels	2–3	[20]
	CH_4/O_2	Syngas	1–2	[10]
	CH_4/O_2	Methanol	1–2	[20]
	CH_4/H_2O	Syngas	1–2	[21]
	$CH_4/CO_2/H_2O$	Syngas	2–3	[21]
VOC oxidation	Nonhalogenated VOCs/air	CO_2/H_2O	6–7	[8]
	Halogenated VOCs/air	$CO_2/H_2O/HCl$ or HF	1–2	[7]
Odour control	Odour/air	Haress compounds	8–9	[22]
NH_3 synthesis	N_2/H_2	NH_3	1–2	[23]
NO_x synthesis	N_2/O_2 or air	NO/NO_2	3–5	[23]
NO_x removal	Reduction of NO_x by hydrocarbons	N_2	4–7	[24]
	Reduction of NO_x by NH_3	N_2	4–7	[24]
	NO_x oxidation	NO_2	2–4	[24]
Tar reforming	Tar	Syngas	2–3	[25]
Water gas shift reaction	CO/H_2O	CO_2/H_2	1–2	[26]
Methanol conversion	$MeOH/H_2O$	H_2	1–2	[27]
Ethanol conversion	$EtOH/H_2O$	H_2	1–2	[27]

[a] TRL: 1: basic principles observed; 2: technology concept formulated; 3: experimental proof of concept; 4: technology validated in lab; 5: technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies); 6: technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies); 7: system prototype demonstration in operational environment; 8: system complete and qualified; 9: actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space).

[b] TRLs of these processes are based on the experiences and discussion of all the authors.

The key performance indicators (KPIs) in plasma catalysis for the various applications listed in table 1 and discussed in this Roadmap are (i) conversion of reactants, (ii) product yields and selectivities, (iii) energy efficiency and energy cost, and (iv) catalyst lifetime. The state-of-the-art in these KPIs, as well as target values, e.g. for the applications to become of commercial interest, will be defined in the various application sections of this Roadmap. An important metric to calculate the energy cost and energy efficiency is the specific energy input (SEI), which is defined as the ratio of plasma power to gas flow rate. Depending on the application, the SEI or energy cost appears to be expressed in literature with different units, i.e. eV/molec, kJ/mol, MJ/mol, J/L, etc. Therefore, these typical units will also be used in the different sections of this Roadmap, depending on the application, to present the state-of-the-art, based on the corresponding literature.

As well as the applications of plasma catalysis listed in table 1, plasmas are often used to pretreat catalysts for subsequent use in the conversion process and are also increasingly important for preparing catalysts for other catalysis applications. Plasma indeed offers advantages of reduced catalyst deactivation, based on lower temperature (decreased sintering), as well as possibilities of reactivation. The possibilities and challenges of these applications are described in the final section of this Roadmap (section 12). This is highly relevant more broadly, as it illustrates how plasma affects the catalysts introduced in the reactor, which is crucial information for the plasma catalysis applications described in this Roadmap.

Despite the growing interest in plasma catalysis for various promising environmental and energy applications, as shown in table 1 and in sections 7–11 of this Roadmap, the fundamental mechanisms of plasma-catalyst interactions are not yet fully understood. It is a complex environment, as the catalyst may affect the plasma behavior, and vice versa, the plasma also affects the catalyst and catalysis mechanisms. An overview of the key mechanisms and species in the plasma phase and at the catalytic surface is presented in figure 1. Optimization of plasma catalysis involves optimization of the entire system, including the operating conditions of the plasma, the integration of plasma with catalyst, and the physical and chemical composition of the catalyst itself. As changing one of these may change others in unknown ways, the optimization becomes high dimensional, and lack of fundamental understanding of governing physical processes makes progress challenging.

In various cases, plasma-catalyst synergy has been reported, i.e. the combined effect of plasma catalysis is larger than the sum of plasma alone and catalysis alone, but this synergy is not always observed. The catalysts used are often adopted from thermal catalysis, but the optimal thermal catalysts are not necessarily also optimal in plasma catalysis, because of the intrinsically different reaction paths, as introduced before. This will be discussed further in section 3. As mentioned above, vibrationally or electronically excited species, or plasma radicals, may facilitate certain steps at the catalyst surface (e.g. dissociative adsorption), allowing other catalysts to perform better in the overall catalytic process.

To select the optimal catalyst in plasma catalysis, one option is to perform catalyst screening, which can provide useful guidelines. Accumulation of reliable data from the past, together with new data, might lead to general trends in designing catalysts for plasma catalysis, optimized for specific applications. In this respect, it would be interesting to use machine learning (ML) based on catalyst screening to train a model for catalyst optimization. However, the problem is that we do not have large amounts of experimental data yet. One option could be to collect experimental data from literature, but they cannot be directly compared, because different groups use different reactors and conditions. We would need to perform catalyst screening for a large number of catalysts, e.g. 50 or more, and not 4–5 catalysts as is now typically done in the literature.

ML and/or artificial intelligence are used already in many plasma application fields, e.g. in plasma processing applications [28] and in plasma medicine [29]. In the field of plasma catalysis, Istadi and Amin [30] developed a hybrid artificial neural network−genetic algorithm (ANN−GA) numerical technique for computational optimization of a DBD plasma reactor without and with a catalyst, used for dry reforming of methane (DRM), but the focus was on the reactor level, and not on the detailed plasma-catalytic mechanisms. Whitehead and coworkers [31] developed an automatic computer control system, with an industry standard software package, a multifunction data acquisition card, on-line fast Fourier transform infrared (FTIR) spectroscopy and adaptive proportional–integral–derivative (PID) algorithms, for real-time control of plasma conditions, to optimise NO_x removal in a packed bed DBD reactor. Likewise, Tu and coworkers developed an ANN model to better understand the role of different process parameters on the methanol removal efficiency and energy efficiency in post-plasma catalysis [32]. The catalyst composition (i.e. Mn/Ce ratio) was found to be the most important factor affecting the methanol removal efficiency. This paper illustrates that a well-trained ANN model may provide accurate and fast prediction of plasma-catalytic chemical reactions. However, in general, the use of ML in plasma catalysis is still very limited. Plasma catalysis is of course much more complicated than thermal catalysis, where ML is more common already [33]. New methodological developments in thermal catalysis modeling include global optimization techniques, *ab initio* constrained thermodynamics, biased molecular dynamics, microkinetic models of reaction networks and ML. These methods allow us to investigate how the chemical environment, pressure and temperature affect the molecular level picture of catalytic sites and catalytic reaction mechanisms [34]. Such methods could—and should—also be applied in the field of plasma catalysis. Recently, Trieschmann and coworkers used ML for plasma-surface interactions, more specifically for sputter-deposition, by coupling sputtering and gas phase transport simulations [35]. In principle, a similar methodology could be of interest for plasma-catalyst interactions and for their optimization. However, due to the complexity of plasma catalysis and the lower level of understanding with respect to thermal catalysis, we must first obtain more insight in the underlying mechanisms, before modelling can lead to real-time-control.

Next to catalyst screening, rational design of catalysts tailored to the plasma environment, based on deep insights in the underlying mechanisms, is of particular interest as a more novel approach. This however requires more fundamental studies to understand the possible synergy between plasma and catalyst.

Such insight can be obtained from *in situ* and *operando* surface characterization and carefully designed experiments to isolate specific contributions from plasma and catalyst (as described in sections 4 and 5 of this Roadmap), but also from microkinetic modeling (see section 6 in this Roadmap), which can evaluate the effect of particular plasma activation modes on specific (e.g. rate-limiting) elementary steps in catalytic reaction pathways. For instance, it was nicely demonstrated by Mehta *et al* [6] that by decoupling N_2 activation from the binding energies of adsorbed fragments, plasma catalysis can circumvent the kinetic limitations imposed by scaling relations in conventional thermal catalytic NH_3 synthesis, facilitating much higher rates and for other catalysts than those that are optimal in thermal catalysis. However, researchers in the field of plasma catalysis are only beginning to understand the underlying mechanisms and remain far from having the scientific insight needed to rationally design plasma-catalytic systems. This highlights the importance of this Roadmap: to identify the possibilities and to assemble existing knowledge, while also stressing the current and future challenges and possible ways to solve them.

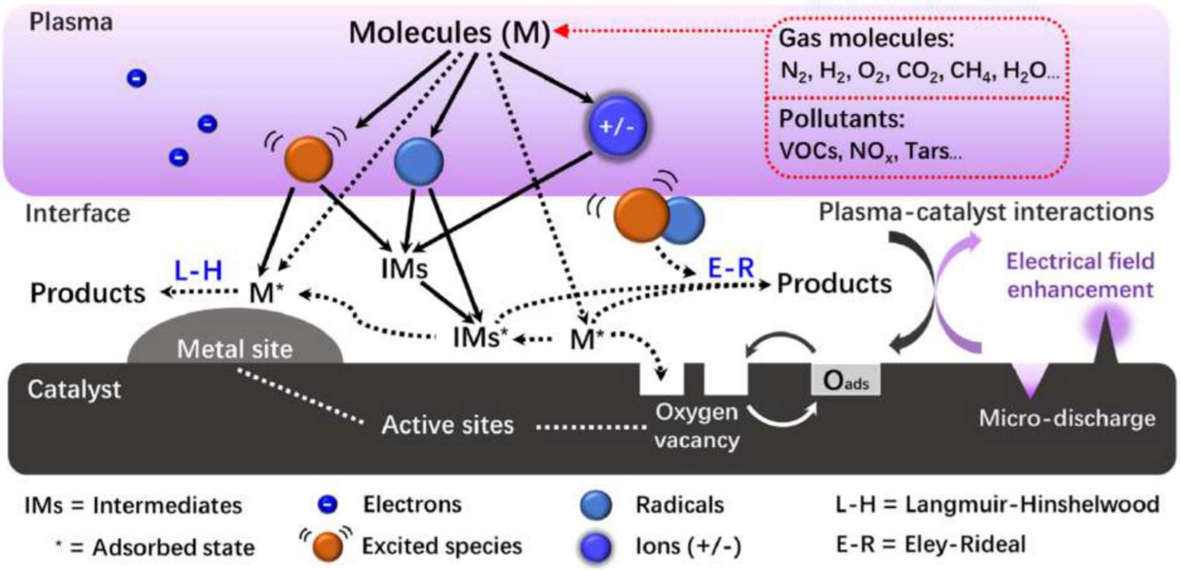

Figure 1. Overview of the key mechanisms and species in the plasma and at the catalytic surface, showing the complexity of plasma catalysis.

To summarize, a prerequisite for substantial progress in the field is a better understanding of plasma chemical processes, and particularly the reactions involving the surface-adsorbed species. For this purpose, close interaction between experiments and modeling will be needed. This better insight should pave the way for the design of plasma reactors with optimized transport of plasma species to the catalyst surface, and/or which produce an electron energy distribution function that optimizes the plasma chemistry (e.g. in terms of vibrationally excited species), as well as for the development of catalysts suited to surface reactions involving these plasma species.

Industrial heterogeneous catalysis has matured over more than a century to its current state. In contrast, research in plasma catalysis is just beginning to establish a science basis to what has been largely empirical development. Plasma catalysis will not supplant conventional catalysis, but it has the potential to supplement existing and to enable new chemical transformations, in particular those of emerging societal importance, with the growth in alternative and intermittent energy sources and the need to accommodate new chemical feedstocks. Plasma catalysis began as an outgrowth of the plasma technology community and is quickly gaining momentum in the broader catalysis community. We believe this confluence of scientific activity and societal need makes this Roadmap particularly timely.

1. Background and opportunities in plasma catalysis

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Status

There can be no doubt about the potential of plasma catalysis as a technique across a wide range of applications with the promise of considerable impact emerging in the next few years. In the 2012 Plasma Roadmap [1], plasma catalysis featured as but one of several topics related to low pressure plasma science and technology. The most recent 2017 Plasma Roadmap [2] saw plasma catalysis being established within a range of plasma topics, particularly environmental applications and plasma-assisted combustion and chemical conversion. Whilst the origins of plasma catalysis can be traced back to early gas discharge studies at the beginning of the 20th century, there was a rapid take-off of publications from 1990s, marking the beginning of the systematic and burgeoning research effort that we have today [36]. This Roadmap can be regarded as formalizing the coming of age of this research field, marking the beginning of a period when fundamental studies provide the knowledge that enables the scaling-up of the technique to exploitable processes by identifying applications where its unique advantages can be employed.

Historically, the origins of the component parts of plasma and catalysis can be traced back respectively to the work of Geissler and Davy in the 19th century. This was closely followed by Faraday who did pioneering work on both gas discharges and heterogeneous catalysis [36] paving the way for the serendipitous union of the two techniques a century later. This has led to work such as that in figure 2 where different catalysts show significantly increased activity when used in a plasma or discharge environment, showing that catalysis with low temperature plasma activation can often be more effective than conventional thermal activation [37] and can even give rise to a synergistic coupling, as discussed in the Introduction.

The different descriptors applied to plasma catalysis (e.g. plasma-enhanced, plasma-assisted, plasma-activated or plasma-driven catalysis and also plasma catalyst coupling) are not just semantic variations, but reflect our present uncertainty about whether the dominant benefit in the coupling comes from the plasma enhancement of catalytic processing where a few key steps in the mechanism of traditional catalysts can be slightly modified, or whether greater enhancements come from operating in regions that are far removed from what is optimal for thermal operation, as noted by Mehta *et al* [3]

Current and future challenges and opportunities

There is now a large amount of research activity with experiments achieving a high degree of sophistication. The range of plasma reactors used is increasing, although dielectric barrier discharge (DBD) systems still dominate. Presently, the vast majority of studies are laboratory-scale, with low gas flow rates (typically <1–5 l min^{-1}) using small amounts of catalyst, although gliding arc and microwave plasma systems offer prospects of higher throughputs for a single reactor whilst other designs will need multiple reactors in parallel to achieve this.

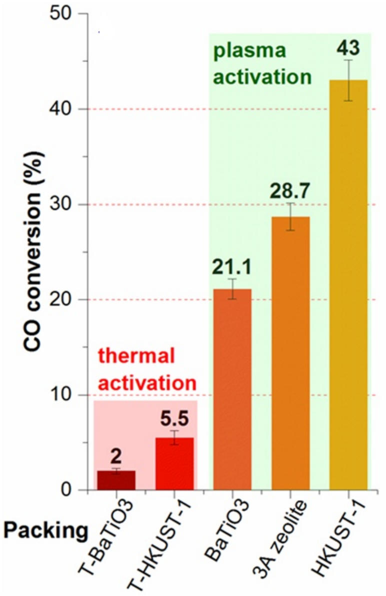

Figure 2. CO conversions of the water-gas shift reaction for a DBD packed-bed reactor using barium titanate, 3A zeolite and the MOF, HKUST-1 packing by thermal (at 100 °C) and plasma activation. Adapted by permission from Springer Nature Customer Service GmbH: Nature Catalysis [37] Copyright (2019).

Plasma catalysis is a multi-parameter process with a high degree of coupling between the parameters that we must understand. Systematic measurements are needed of the effect of all the electrical, mechanical, chemical, physical, gas dynamic and thermodynamic parameters on the outcomes of the processing to be able to gain the understanding necessary to inform the design processes required to take our promising laboratory results to the next level. Figure 3 presents in diagrammatic form an iterative methodology for making progress in the field, beginning with a better understanding of the underlying plasma chemical processes in the gas and surface phase and their interface using simulation to inform experiment. This will provide design input for developing optimized and novel plasma-catalyst reactors leading to an insight into how these processes might be scaled-up and commercialized.

It is also important that the resulting information is transferable from a specific experiment into the whole field. This is challenging because differences resulting from constructional details, materials used and their states are non-trivial. The catalysts may be films, powders, pellets, foams and may be pure or incorporate other materials. This affects their physical and chemical behavior. Moreover, the form, size and electrical properties of the materials cause varying interactions with the plasma, causing local electric field variations that may modify the catalytic reactions. Since small differences in conditions can sometimes result in significantly different outcomes, the conditions used in different studies must be made explicit. The

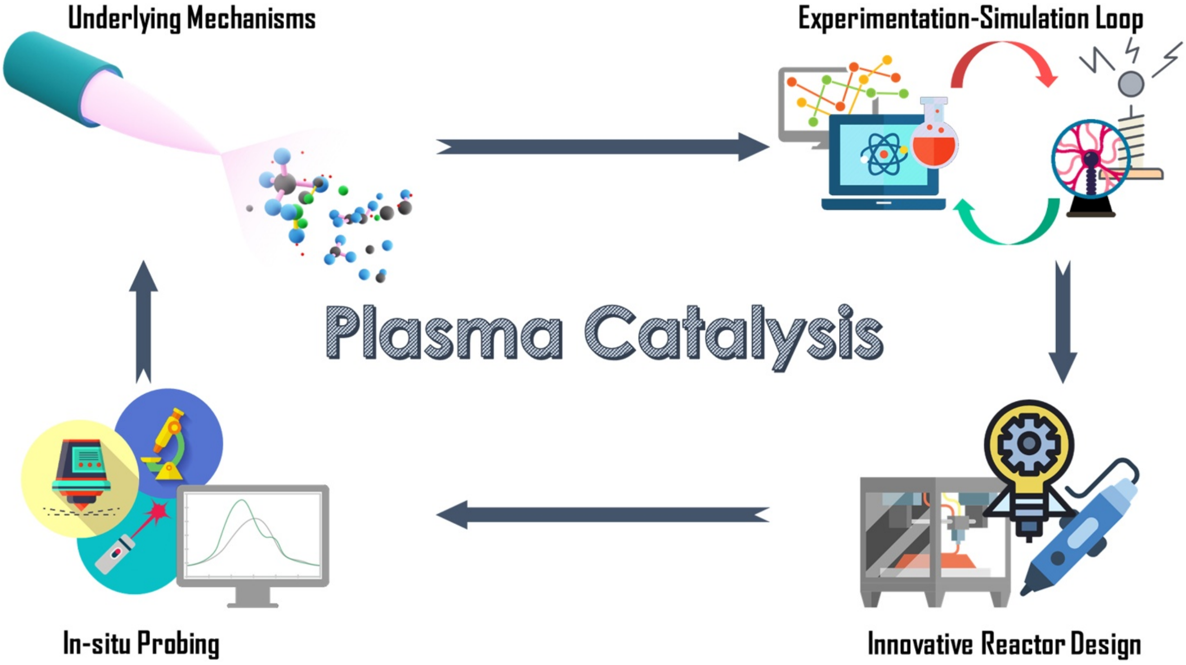

Figure 3. Elements needed to advance the field of plasma catalysis.

use of agreed, standard reactor designs and operating conditions between different research centers would aid progress by removing such uncertainties.

Advances in science and technology to realize potential opportunities

The multidisciplinary nature of plasma catalysis implies that most progress is going to be made by research groups or consortia where the disciplines of physics, chemistry, materials science, computation, mechanical, electrical and chemical engineering are found. There is encouraging evidence that plasma scientists are actively engaging with those synthesizing and designing catalysts; essential if plasma catalysis cannot just gain access to novel materials, but can also engage in establishing the design criteria for catalysts specifically for plasma activation. New categories of catalysts, such as metal organic frameworks (MOFs), have recently been used successfully in plasma experiments [37] (figure 2) giving increased efficiency and demonstrating how a new range of materials with low temperature stability can be used as catalysts.

We must embrace novel instrumentation from surface and analytical science and spectroscopy to utilize a wide range of diagnostics for plasma experiments with the necessary time and spatial resolution, ranging from sub-nanosecond to minutes and sub-nanometer to meter, probing all phases of the processing (gas, solid and interfacial). Examples include *insitu* x-ray absorption fine structure (XAFS) for monitoring structural changes of the catalyst during plasma catalysis [38] and other plasma diagnostics such as those described in section 4. These tools will help to discern the mechanisms for plasma-catalyst interactions, yielding detailed information against which to validate modelling. Modelling and simulations must provide more realistic representations of the plasma-catalytic process, with models of increased sophistication aided by the use of increased computing power and extended databases of kinetic and structural properties.

It is important that the performance of a plasma catalysis process is benchmarked not just against other plasma catalysis experiments but also against existing and emerging technologies, as has been done for CO_2 conversion [5] and nitrogen fixation [39]. The commercial viability of any potential plasma-catalytic process needs to be demonstrated taking into account full life costs, including costs of capital, catalysts and separation of products using techno-economic analysis [40, 41]. Such studies for plasma systems indicate, at least for the energy intensive nitrogen fixation process, that plasma processing can become competitive with conventional processes for small scale systems but that the most critical factor is the energy efficiency of the plasma reactor and that an efficient heat recovery design is key to increasing the efficiency. Such processes can even become profitable when the electrical power comes from a renewable source. The incorporation of a catalyst into such systems can significantly improve the energy efficiency in the best cases.

It is unrealistic to believe that plasma catalysis can ever be scaled-up to compete with well-established large scale commercial processes based on thermal catalysis that are the basis of chemical plants for the production of, for example, hydrogen and ammonia. Indeed, as explained in the Introduction, attention must be focused on applications that utilize the unique features of plasma catalysis especially focusing on small scale set ups. Plasma-catalyst systems can be constructed to be mobile and provide short-term response to situations requiring clean-up for spillage or waste; they can be integrated into existing ventilation systems to treat odors or contaminated air; and they can be distributed to provide local facilities in remote locations to manufacture fertilizers on demand using renewable energy, thereby minimizing transportation costs. Rather than contemplating large scale manufacturing of bulk chemical or fuels, plasma catalysis may be better suited to the production of high value products in small quantities, perhaps using techniques of plasma flow chemistry with microfluidic chip-based synthesis [42] which only now needs the incorporation of a catalyst as proposed in 2007 by the late academic and industrialist Ulrich Kogelschatz, a pioneer of plasma processing [43].

Concluding remarks

Across many fronts, research in plasma catalysis has advanced significantly during the last 5–10 years. There are many more active researchers and groups, several major international, multidisciplinary research programmes are under way and many talented young people are being trained in the field. Some of these people will carry on their careers in academic research but employment opportunities are now also emerging within companies that either supply plasma-based products or that support plasma research and its infrastructure; many of these are small to medium sized enterprises, often spin-outs from universities. As yet, products based on plasma catalysis are relatively rare and it is still important to ensure that any barriers or bottlenecks preventing progress on scaling up laboratory-derived processes are identified and overcome to realize the opportunities that exist for translating research in plasma catalysis into society benefiting technologies.

2. Role of electro- and photo-catalysis in designing plasma-catalysts

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Status

Electro- and photo-catalysis (EPC) indicates using catalysts which operate in the presence of a surface charge generated by application of an external potential/current or due to charge separation induced by light adsorption [44]. The term catalysis indicates that there is a specific role of catalytic sites present in the electrode to induce modifications in the reaction rates (activity) or paths of transformation (selectivity) with respect to the corresponding electro- or photo-chemical transformations [45]. EPC is a scientific area of very fast-growing research interest [46], due to the relevance for addressing energy and chemistry transition [47].

EPC is part of the portfolio of new technologies which should be developed to address the challenges of electrifying chemical production and to develop efficient energy vectors to store/transport renewable energy (see Introduction) [48]. EPC could thus be a benchmark for comparison of plasma catalysis processes. However, large R&D effort is still necessary to provide reliable quantitative bases for their comparison [49]. There is an important additional motivation. As commented in the Introduction, the interaction mechanisms of reactants with solid catalysts are significantly different between plasma catalysis and thermal catalysis. On the other hand, localized charges and species, like electrons, are present in EPC, creating closer mechanistic aspects with plasma catalysis. Therefore, this section emphasises the concept that associates EPC with plasma catalysis, and provides clues to understand the reaction mechanisms. The integration of electro- and/or photo-catalysis and plasma in a single system also allows relevant synergies. This is an area still scarcely investigated, but it is the function of a Roadmap to define new R&D directions, rather than providing only the state-of-the-art.

EPC has been investigated for a long time [50] with a new impetus on research, derived from the recent efforts in substituting fossil fuels and direct use of renewable energy sources [51]. With respect to the past main uses of EPC (fuels cells, water electrolyzers, photocatalytic degradation of pollutants), the current focus is on reactions where the control of selectivity is the main issue. Examples are the selective reduction of CO_2 to fuels and chemicals, the conversion of biomass-based platform molecules and the direct synthesis of NH_3 from N_2 and H_2O [48, 52, 53]. A new design for electrodes, devices and operations is required with respect to past applications. Combining EPC functionalities in a single device is a new direction, in order to develop photo-electrocatalytic (PEC) devices often indicated as artificial leaf or artificial photosynthesis systems [54].

The reaction mechanism in both electro- and photo-catalysis, in a simplified description, is associated with the presence of localized charges on the surface and the creation of an electrical field within the solid and at the interface. The reactants interact with these charges through electron- and/or energy-transfer processes, often generating charged molecules which react further with these surface charges. A Helmholtz layer is generated at the interface with the solid, and an electrical field is generated within the solid, as a consequence of these surface charges. The difference between electro/photo catalytic versus chemical processes lies in the presence of chemisorption and surface catalytic processes that significantly modify the paths of transformation. However, there is increasing evidence that the nature of the catalytic sites, particularly in nanoparticles, changes in the presence of these surface charges and electrical field. Thus, the photo-induced processes or the application of a surface potential induces a change in the nature of the catalyst itself, which is often the key factor for the photo/electro-catalytic behaviour. However, the study of these aspects is still at a very early stage [51].

In plasma catalysis, excited and charged species are generated by non-thermal plasma, and the reactivity derives from the interaction of these excited and charged species with the solid catalyst. Thus, rather than neutral molecules such as in thermal catalysis, charged and/or highly excited species react with the solid catalysts. This interaction also generates localized charges on the solid, with effects similar to those mentioned for EPC. There are thus closer analogies in the mechanisms between plasma catalysis and EPC, than with respect to thermal catalysis. While in plasma catalysis a thermal catalyst (active in the target reaction) is often used in combination with plasma [13], the above considerations clearly remark that EPC could instead be a more rational approach. Thus, EPC offers a model for understanding the processes occurring on the surface of the catalyst in the presence of a non-thermal plasma and could provide also new options to foster a synergy between the plasma-generated species and the catalysts.

Figure 4 reports, for example, the photocatalytic processes (in water and CO_2 conversion) occurring in a semiconductor such as TiO_2 upon charge generation by light adsorption, an effect that could be enhanced by surface plasma resonance in the presence of gold nanoparticles. The excited species generated in this photocatalytic process could react with the plasma-generated excited species, or they could directly interact with the surface charges on the photocatalysts, or with surface phonons generated by a plasmonic effect. All these effects could be potentially enhanced when nanodischarges are generated within the porous TiO_2 semiconductor.

There are also additional reasons to associate EPC and plasma catalysis. Thermal catalysis occurs in the whole volume of the reactor occupied by the catalyst, and the diffusion rate of molecules is often enough to guarantee diffusion in the whole volume of the catalyst pellet. EPC processes occur instead essentially at the surface of the electro- or photo-active material, where microporosity typically negatively affects the performances. This is similar to plasma catalysis, except when the plasma could be generated within the catalyst itself. The latter, however, is stated to be only possible for catalyst pores

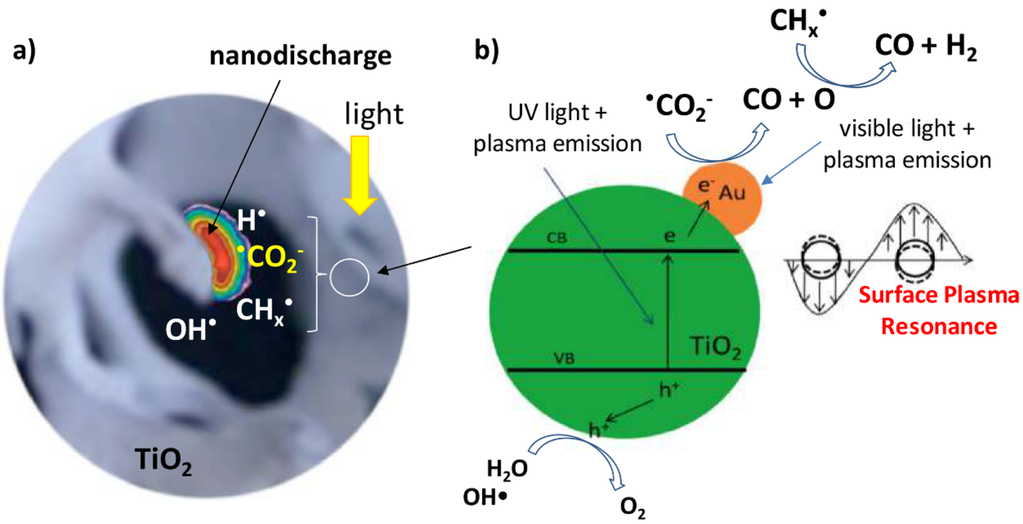

Figure 4. (a) Simplified scheme of the process of nanodischarge within a porous (foam-type) TiO_2 material and (b) photocatalytic processes (in water and CO_2 conversion) occurring in TiO_2 upon charge generation by light adsorption, with indication also of the effect related to surface plasma resonance in the presence of gold nanoparticles. Note: nanodischarge does not indicate here a true discharge mechanism, but the generation of radical and excited species within nanocavities due to charge emissions at nanotipcs. Reproduced from [12]. © IOP Publishing Ltd. All rights reserved.

larger than several 100 nm, i.e. the Debye length, as predicted from modelling [55]. Nevertheless, this solution is potentially attractive to overcome the current limitations in terms of realizing an effective synergy between plasma and catalysis and improve the overall performance.

Current and future challenges

The following main future R&D topics in plasma catalysis can be identified from the analogy with EPC:

- There are currently too limited and not systematic fundamental studies of the surface processes involving the interaction of plasma-generated excited reactant species and a solid catalyst. This includes, among other aspects, the modification of the catalyst itself derived from the interaction with plasma and how this influences the paths of transformation. It is necessary to understand the analogies and differences with respect to EPC, and whether possible synergies of operations can be realized. This knowledge-driven approach will offer clues to overcome the current main limits in plasma catalysis processes, related to both efficiency and control of the selectivity.
- New areas of fundamental investigation can be identified based on the possible analogy between EPC and plasma catalysis: (i) how local electric field enhancements (in relation to catalyst nano-morphology and charge distribution) could determine the path of transformation and thus selectivity, (ii) how modifications in the electron energy distribution in the solid catalyst derived from the application of an electrical potential or from photo-induced charge-separation processes could synergistically promote the interaction and selective conversion of plasma-generated reactant species (thus both productivity and selectivity), (iii) how the creation of metastable states in the solid catalyst derived from the interaction with the plasma could promote the behavior of plasma catalysts (this effect depends on nanoparticle characteristics and will also be important regarding stability), and (iv) how the effects induced on the catalyst by the radiation emitted by non-thermal plasmas (NTPs) could induce changes in the behavior (with implications on the design of catalysts). All of these are novel areas for which no, or very limited, literature examples could be indicated.
- The application of an electrical potential to a solid catalyst or the creation of charge separation (light-induced processes in semiconductors) alter the mechanistic modalities of interaction of plasma-generated species with the catalysts. Among the relevant possible effects, we can cite the following: (i) modifications in the nature/rate of the adsorption/desorption steps of reactants and intermediates, (ii) dynamic reconstruction/modification of the active sites, (iii) alteration of the sticking coefficients and diffusion processes inside the porous catalysts, and (iv) formation of strongly adsorbed species, including their role in relation to poisoning and coking effects.
- In photo-catalysis, a growing area of interest is associated with plasmonic photo-catalysts. The controlled modification of semiconductors by specific metal nanoparticles (the most common case is the plasmonic gold-modified TiO_2 photocatalytic system) induces strong surface phonons (collective lattice vibrations) by light absorption in the visible region. These phonons induce field enhancement or charge transfer effects which can have significant influence on the photocatalytic behavior [56]. It is possible (in principle) to design these systems to induce a positive coupling of these surface phonons with the vibrationally excited molecules generated by NTP. This is an alternative, potentially breakthrough, mechanism to induce an enhanced and controlled interaction between the (photo)catalyst and

excited species generated by NTP. This possibility has also scarcely been investigated in literature.

- The above considerations remark the need of a specific and tailored design of catalysts to obtain efficient and synergetic plasma-catalytic operations. This would require also new plasma reactor devices, to couple effectively EPC and plasma catalysis, for example. This creates new challenges for the scale-up of plasma-catalysis processes and their exploitation because higher productivity (at least 5–10 times higher), selectivity (>80%) and energy efficiency (>60–70%) is required for industrialization.

Advances in science and technology to meet challenges

The challenges indicated above require us to go significantly beyond the current state of the art. Not specifically-designed catalysts are still often used in combination with NTP, with the catalyst placed either inside or downstream to the volume where plasma generation occurs. These are the in-plasma catalysis (IPC) or post-plasma catalysis (PPC) configurations indicated in the introduction section. In the PPC case, only long-lived species that can escape from the plasma will interact with the catalyst. This is different from the first case, where the short-lived reactive plasma species (radicals, ions, photons, electronic and vibrationally excited species) can in principle interact with the catalyst. However, often they are simply quenched, and in general they are so reactive to be not able to diffuse effectively inside the catalyst pellets. In principle, generating these species by a nanodischarge inside the porous catalysts (thus, within porous or cavities of nanometric dimensions, from about 1 to 20 nm) could solve the problem, but there are still questions whether and how this could be possible (see above). Nevertheless, this is potentially one of the grand challenges for plasma catalysis to move from lab to application and meet the above targets of productivity, selectivity and energy efficiency. Figure 5 schematically illustrates this concept of passing from conventional to nanoscale plasma catalysis, i.e. in a confined space, with the possibility also of nanodischarge generated within the pore structure of the catalyst (in the 1–20 nm range). Note that the concept of nanodischarge is not a true discharge within a nanopore, but an alternative mechanism occurring within nanopores (see note in figure 4).

This challenge cannot be met by a trial-and-error approach and it is thus necessary to combine fundamental studies and modelling with tailored experiments. The latter should span from nano-scale (catalyst level) to macro-scale (reactor level). The analogy with EPC provides indications on how to design better experiments for this understanding. New catalytic materials and new reactors are necessary for this purpose.

Small void spaces inside a packing material affect the electric field strength, and this effect would be enhanced further in EPC-type materials. The enhancement can also lead to a change in the discharge characteristics, which can be different from those present in the bulk region. Local inhomogeneities in charge distribution are further promoted by application of an electrical potential. The high intensity of the electric field can also lead to the production of different species that are not observed in the bulk. By inserting a dielectric material in a discharge region, a shift in the discharge type, for example from a filamentary regime to a mixed filamentary/surface discharge, is expected.

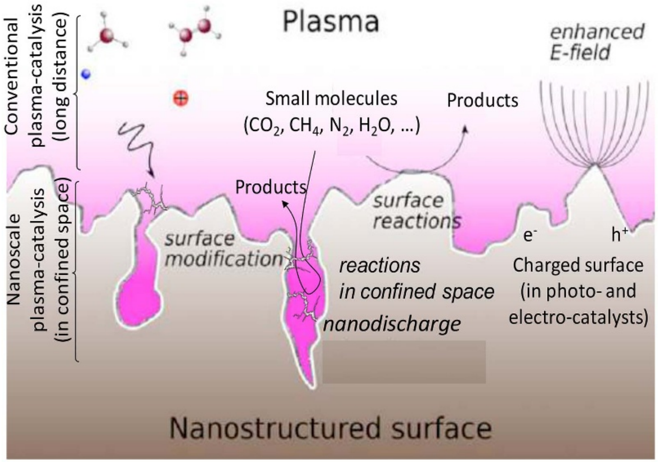

Figure 5. From conventional plasma catalysis (long distance interaction) to nanoscale plasma catalysis (in confined nanospace; from about 1 to 20 nm range) and plasma catalysis interaction with charged catalyst surface. See note on figure 4 for nanodischarge concept. Adapted with permission from [12].

Controlling nano-scale discharge processes require the capability to realize tailored preparations of the catalytic electrodes (see section 12). Realizing specific nanostructured electrodes is also the prerequisite to achieve precise and robust structure activity and selectivity relationships. These electrodes should also be stable and allow cost-effective operations.

Advanced theoretical models for NTP interaction with the catalysts should be related to the catalyst nanostructure (figure 5). In parallel, advanced reactors to maximize synergy and reduce energy requirements associated with the systems should be developed. They should allow tailored fluidodynamic on nano-/micro-scale, reactor modelling and development taking advance of discharge generation at nano-/micro-scale, and operations with short-cycle operations to optimize performances and energy efficiency.

Spatio-temporal resolved characterizations for NTP and its interaction with EPC will offer new clues for understanding and advancing kinetic modelling. Together with other diagnostic methods (see sections 4 and 5), they will allow to understand the dynamics of gas, surface and catalyst changes as a function of conditions of NTP generation and of the electro- and photo-induced processes occurring on the electrode.

Concluding remarks

Plasma catalysis, together with EPC, is a part of the portfolio of technologies to develop new processes for the two areas of fast-growing relevance (also industrial) of the so-called electrification of chemical production and distributed production of energy vectors to store/long-distance transport renewable energy. EPC is in principle a benchmark for comparing plasma catalysis solutions with alternative possibilities. However, all these technologies are still at too early a stage of development to allow a reliable comparison. Investment in R&D on both EPC and plasma catalysis is thus necessary first. However, for plasma catalysis this development requires us to have a conceptually new research approach, along the lines identified above as grand challenge.

A prerequisite is to realize a better fundamental understanding of the synergies between EPC with NTP, and then to develop effective working systems which implement this synergy in moving from the lab to industrial scale. Accelerating this procedure from idea to innovation in plasma catalysis is the crucial issue.

Acknowledgments

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3. Leveraging knowledge from thermal catalysis to plasma catalysis

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Status

The interest of plasma physicists in plasma catalysis was boosted in the 50s [14], stemming from undesired interactions of plasma with materials to contain them. On the other hand, interest from the catalysis community originates not only from the potential benefits that arise from having activated species in a plasma in contact with a catalyst, but also from the wish to understand high temperature catalysis, e.g. oxidative coupling of methane [57] and oxidative cracking of higher alkanes with Li-MgO catalysts [58]. These reactions rely on catalytic radical generation, followed by gas-phase radical chain reactions and termination both in gas phase as well as via secondary interactions on the catalyst. The advantage of plasma catalysis in general is that reactions become possible at mild conditions that are normally not suitable because of kinetic and/or thermodynamic reasons, as has been reported, e.g. for ammonia synthesis [6] and water-gas shift (WGS) reaction [37]. Furthermore, the load of the reactor can be changed much faster than in thermal catalytic operation.

Typically, 90% of all processes in the chemical industry use catalysts and therefore optimization of catalysts and process conditions is of utmost importance to limit costs as well as footprint. Intrinsic kinetic information is required, i.e. in the absence of any mass and heat transfer limitations. In practice, two approaches can be distinguished for catalyst development and optimization. First, exploration by high throughput trial-and-error testing of catalysts in lab-scale equipment is used, often supported by intuition and experience. Second, science-based development contributes to increasing extent. Micro-kinetic schemes are developed based on reaction mechanisms, describing how intermediate species on the catalyst are converted. In addition to kinetic information, this method relies on detailed catalysts characterization, mechanistic research, e.g. using *in situ* and operando characterization techniques [59], as well as theoretical chemistry [60, 61]. This information typically results in hypotheses on the critical steps on the catalyst surface, determining activity, selectivity and stability. Several reviews are available for further reading [62, 63].

The science field of heterogeneous catalysis ranges from molecular aspects to design of reactors, considering temperature and concentration gradients inside reactors and catalyst particles, aiming at optimal design of reactors, catalysts and reaction conditions. Application of these concepts for plasma catalysis is often missing and will be discussed further below.

Current and future challenges

The combination of plasma and catalysis has shown synergy but also enormous complexity as described in other contributions in this Roadmap. This complexity means that research questions and well-developed scientific approaches in the field of heterogeneous catalysis are still in their infancy for plasma catalysis. How to select catalysts for plasma catalysis? Most work reported so far has been performed with catalysts that are also active under thermal conditions, while dielectric materials have also been used frequently, influencing the electrical local electrical field and the local electron energy distribution, locally intensifying the plasma.

Description of catalytic reactors is based on kinetic data and local concentrations and temperatures at the active sites of the catalyst, as reviewed recently in [64]. Can we implement the same approach in plasma-catalysis? This requires a description of transport of highly unstable species, locally generated at an ill-defined location inside the plasma reactor, to the catalyst particles as well as inside the catalyst particles, in order to reach the active sites. A similar question on heat transfer is pending, but actually, an overarching question is how to deal with temperature in a non-thermal plasma (NTP) catalytic reactor in the first place.

Advances in science and technology to meet challenges

Three cases can be distinguished when discussing how to select catalysts. Case 1 involves operation of the catalyst downstream of the plasma, termed post-plasma catalysis (PPC) [65]. Cases 2 and 3 deal with in-plasma catalysis (IPC) with different types of activation of reactants, i.e. mild pre-activation via excitation-vibration versus activation via dissociation of molecules, e.g. to radicals in the plasma.

PPC is only relevant for relatively stable species, i.e. unconverted reactants, product molecules formed in the upstream plasma and possible relatively stable activated species, e.g. OH radicals [66]. Obviously, this situation allows for independent description of the plasma reactor and catalytic reactor. Also, catalyst selection and optimization is feasible following the usual methods in catalysis and intuitive catalyst selection seems appropriate; a typical example is oxidation of organic pollutants via formation of O_3. The only exemption would be if long-lived excited species would play a dominant role.

IPC implies interaction of relatively unstable species with the catalyst surface, also causing complex mutual influence of plasma and the catalyst [6, 14]. If the reaction is thermodynamically hill down ($\Delta G < 0$), the reaction rate can be enhanced via mild vibrational pre-excitation as schematically shown in figure 6. Please note that any possible change in the energy of the activated complex [12] is not considered. The rate-determining step is enhanced and possibly, but not necessarily, another elementary reaction step becomes rate determining. The optimal catalyst is likely to shift slightly in the periodic table, because decreasing the apparent activation barrier

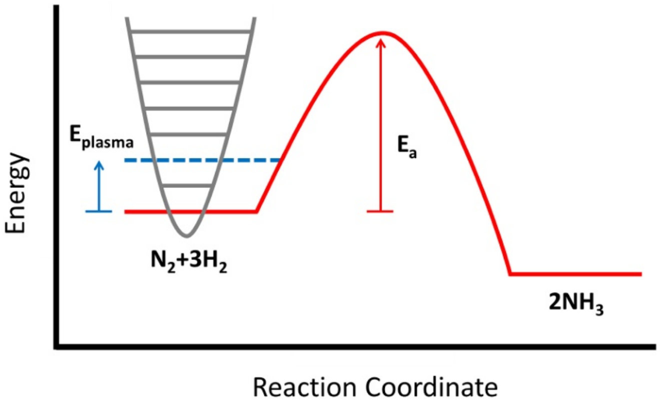

Figure 6. Energy plot of mild pre-activation via vibration excitation in the case of an exothermic reaction.

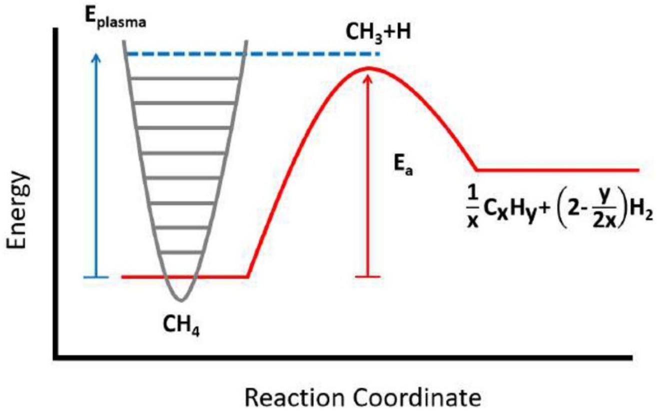

Figure 7. Energy plot of plasma activation via formation of radicals or ions via bond-breaking in the plasma in case of a reaction that is endothermic, or even thermodynamically forbidden.

enables operation at lower temperature and/or catalysts interacting relatively weakly with reactants and products are preferred. This case has been theoretically described by Mehta *et al* [6] for ammonia synthesis from N_2 and has also been reported for CH_4 dry reforming [67].

Reactions thermodynamically uphillup ($\Delta G > 0$) and/or strongly endothermic (figure 7) require strong plasma pre-activation via bond breaking in the plasma, either via vibrational excitation or direct electronic activation, forming radicals and ions. Typical examples are dry reforming and steam reforming of methane over Ni or Pt catalyst; the equilibrium conversion at mild temperatures, e.g. below 800 K, is very low and high conversion is obtained at temperatures between 1100 K and 1300 K, thanks to the fact that entropy increases. Plasma operation via formation of radicals enables conversion at temperatures as low as ambient. The catalyst of choice is however completely different from thermal catalysis, as any catalyst is also active for the backward reaction, which is clearly undesired when surpassing thermodynamic equilibrium. Therefore, the catalyst should be inactive for the target reaction and should only optimize the product distribution by enhancing favorable downhill reactions of activated species or favorable consecutive reactions of products, thereby suppressing formation of unfavorable products.

Intrinsic kinetic information requires experiments with well-defined concentrations and temperature at the active sites. In an IPC reactor, activated species are generated in the plasma intra-particles spaces in the bed. Plasma can be generated only in pores larger than a few 100 nm [14, 66, 68], but it should be noted that the majority of the pores in catalysts are usually smaller then 10 nm. Both identification of the type of activated species as well as the local concentration in the bed are generally not available; further progress in *in situ* probing as well as plasma modelling is required. In addition, diffusion of activated species to active sites in smaller pores is required, keeping in mind that the diffusion distance is limited by the short lifetime compared to ground-state molecules. The diffusion distance of relatively stable OH radicals is estimated typically 50 micron, whereas for oxygen radicals this would be typically 1 micron [14, 66]. Unfortunately, information on the lifetime of many activated species is not available. Therefore, the contribution of the catalyst is determined by the external surface area of the catalyst, i.e. the surface area of the outer surface of the catalyst support particles that constitute the fixed bed. This can be established based on the correlation between reaction rate and both internal and external surface area [69]. Structuring of catalysts, e.g. in catalytic wall reactors, is therefore a promising proposition, maximizing the external surface area and surface area of macrospores, quite similar to the suggestion to apply 3D electrodes in section 2.

Concluding remarks

In short, catalyst selection and optimization via data on reaction kinetics make sense for PPC exclusively and not for IPC with today's knowledge. IPC via vibrational excitation requires catalysts that are similar but not identical to usual catalysts, whereas radically different catalysts are required when excitation proceeds via radicals and especially when thermodynamic equilibrium is to be surpassed.

This can guide optimization of catalyst performance, i.e. conversion, selectivity and stability, in combination with NTP plasma. Also, energy efficiency is extremely important. Comparison with today's catalytic processes requires process design with similar heat integration, quite different from the usual methods to evaluate energy efficiencies of plasma reactors. In addition, if electrification of the chemical industry is to happen as part of the energy transition, reactors are heated using cheap renewable electrical energy in future, e.g. for endothermic processes like steam reforming of methane [70]. In that scenario, plasma reactors could become very attractive, intensifying catalytic chemistry in combination with electrical heating.

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4. *In situ* diagnostics and experimental approaches

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Status

As discussed in the previous sections, the complexity of the mechanisms of plasma-catalyst interaction is such that plasma catalysis as a field of science is still in its infancy. The majority of the work published to date evaluates reactor output performances of selected catalysts. Most of the time, these studies are carried out in packed bed dielectric barrier discharges (DBDs) with a limited number of catalytic materials, often developed for thermal catalysis. These works have shown the existence of plasma-catalyst synergy for specific conditions (as shown in section 1). It is imperative we transition to optimize plasma-catalyst coupling for various applications of molecule conversion based on an increased understanding and ideally with a more systematic approach involving catalyst screening. To enable such studies, we will have to extend current approaches and develop new diagnostics and experimental setups to overcome some of the current inherent limitations.

Firstly, as explained in the previous sections, materials developed for thermal catalysis are rarely the most suitable to be effective in a plasma, especially for in-plasma catalysis (IPC) (see section 3). Secondly, filamentary DBDs, which remain to date the most frequently used plasma source, intrinsically generate strong spatial-temporal gradients (with randomly distributed plasma filaments developing in a few ns over a few hundred microns), that are highly dependent on operating regimes and are not favorable for allowing comparisons from one study to another. Moreover, many studies focus on the performance obtained in terms of conversion, yield or selectivity, without providing sufficient information on a detailed characterization of both the plasma source and the surface state of the materials used, making comparison between results obtained in different research groups challenging. Finally, IPC systems aiming at the highest conversion efficiencies are often also the most difficult systems to compare with numerical models, because they involve many coupled processes in fluid mechanics, heat transport, surface and plasma chemistry, diffusion regimes in the material, etc.

In order to make significant progress in the development of plasma catalysis, it would therefore be important on the one hand to systematize the measurement of basic parameters in plasma catalysis coupling reactors (e.g. gas temperature when the plasma is ignited), and on the other hand to develop a broader set of diagnostics enabling experiments dedicated to the understanding of individual fundamental mechanisms of plasma-catalyst synergy. *In situ* diagnostics of plasma-catalyst interactions are just emerging [71–76]. The further development and implementation of *in situ* measurements in configurations coupling plasma and catalysts are crucial to enable progress in the plasma catalysis field as they will enable us: (i) to understand the operating regimes necessary for a meaningful and reproducible comparison of materials, for example by redefining appropriately the concept of 'active sites', (ii) to provide essential constraints and validation of numerical models on individual mechanisms of charge deposition, local heating, adsorbed species, and radical densities, (iii) to develop new materials that are truly aimed at making use of the non-equilibrium properties of plasma (for instance by taking advantage of changes in adsorption energy in the presence of a strong electric field, by using vibrational and/or electronic excitation, or by optimizing radical diffusion as a function of the lifetime of these species), and finally (iv) to bring indisputable evidence of the conditions under which the plasma-catalyst synergy cannot be achieved by electro-, photo-, or thermal catalysis and therefore to define its true complementarity with other technologies.

Current and future challenges

A specificity of plasma catalysis is the extremely wide amplitude of the characteristic time scales that must be considered, from electron kinetics and electric fields varying over sub-nanosecond times to phenomena of poisoning or structural change of the catalyst that can take hours, as shown in figure 8 (taken from [71]). Therefore, a semantic difference often made in thermal catalysis between *in situ* and *operando* measurements deserves to be commented on in the context of plasma catalysis. *Operando* measurements consist of monitoring the evolution over time of the products at the output of the reactor (which requires plug-flow configurations) in order to link changes in gas composition to modifications of surface properties measured *in situ* while running the catalytic reactor in 'realistic' working conditions. For all *in situ* measurements discussed below, it is obviously very valuable to know the final composition of the gas. Nevertheless, the direct correlation with the temporal evolutions observed *in situ* can only be made with the slowest phenomena occurring in plasma catalysis, because of the limitation imposed by the transit time of the gas in the post-discharge to reach the measurement point. In addition, plasma-catalyst interactions constitute a strong coupling between the plasma and the catalyst with two-way interactions where both the catalyst modifies the plasma and vice versa. This requires that for plasma it is necessary to combine *in situ* surface characterization with *in situ* gas phase plasma characterization.

At present, *in situ* measurements performed for plasma catalysis are limited to (i) fast imaging (with intensified charged coupled device (ICCD) cameras, see section 5) to follow the morphology of plasma filaments on catalytic surfaces, and (ii) broadband infrared absorption with Fourier transform infrared (FTIR) (whether in diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [72], transmission [73] or attenuated total reflectance (ATR) [74] configurations) to monitor adsorbed infrared (IR) active molecules on materials under plasma exposure. However, in recent years, significant progress has been made in developing or adapting methods for *in situ* characterization of atmospheric

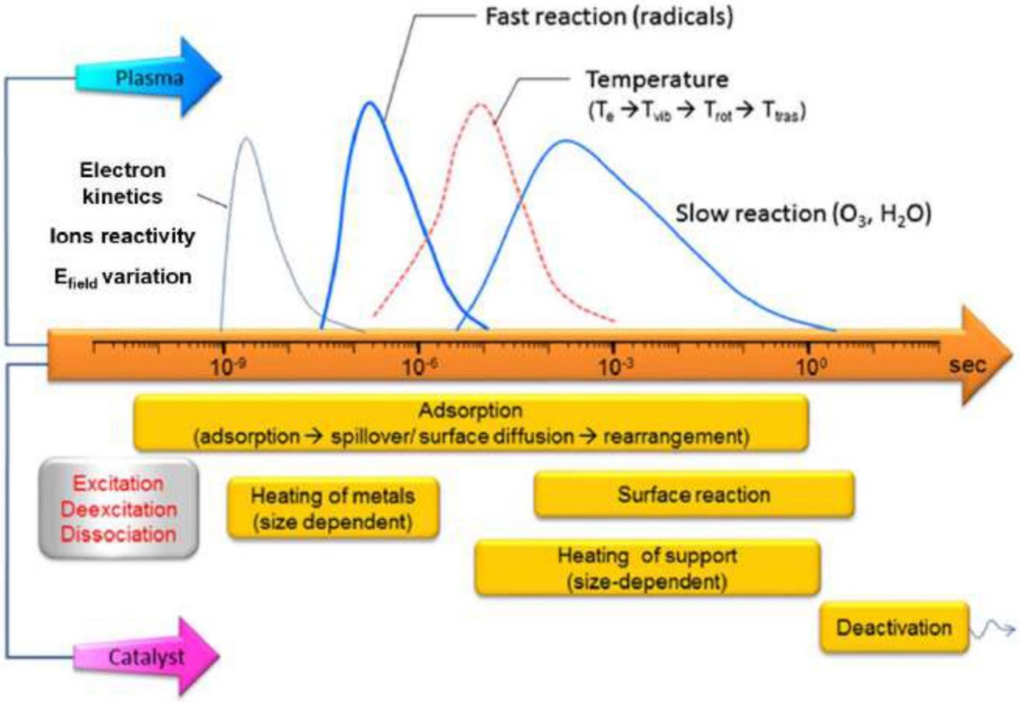

Figure 8. Different time scales important in plasma catalysis. Adapted by permission from Springer Nature Customer Service Centre GmbH: Plasma Chemistry and Plasma Processing [71] Copyright (2016).

pressure filamentary plasmas on the one hand, including electric field induced second harmonic generation (EFISH), ps-two photon absorption laser induced fluorescence (ps-TALIF), Rayleigh/Raman/Thomson scattering, Mueller polarimetry, and operando measurements in thermal catalysis on the other hand, including ultraviolet-visible-infrared (UV–vis-IR), Raman, x-ray diffraction (XRD) and absorption. Many of these techniques could be implemented and would provide valuable information when applied to configurations coupling plasma and catalysts, even if this would require making concessions on the type of plasma or materials used to perform these techniques. We can therefore distinguish four main types of experimental approaches that would all bring valuable complementary information:

(i) The development of more systematic methodologies and *in situ* monitoring of both the plasma and the catalyst surface evolution in the IPC DBD packed bed reactors to allow better data comparisons.
(ii) The study of reproducible and spatially constrained filamentary discharges, allowing for advanced diagnostics that typically can be implemented with time resolutions of ns or less, but require signal accumulation, directly in the filaments in contact with catalytic materials.
(iii) The use of homogeneous discharges (direct current (DC), radio-frequency (RF), microwave (MW) at reduced pressure) allowing for detailed and quantitative characterization of the plasma phase in contact with catalysts.
(iv) Performing fundamental experiments dedicated to the determination of basic data on surface reactions, such as vibrational quenching and radical recombination probabilities on surfaces, and adsorption energies of species in the presence of a strong electric field.

The combination of all these approaches will help in identifying interaction mechanisms at different spatio-temporal scales, allow the identification of decisive synergy mechanisms, and provide data of varying degrees of complexity to validate the different types of numerical models that will be explained in section 6, from 0D plasma kinetic models to fully coupled multiphysics 3D models. Some of these approaches have already been initiated by various groups but require a broader implementation including a further development and improvements by addressing some of the challenges detailed below.

Advances in science and technology needed to meet these challenges

(i) Packed bed DBD reactors are easy to implement and have proven their efficiency for some gas conversion applications. Therefore, their study remains important but would benefit from guidelines on required information to enable a more detailed comparison of the results generated by the research community. Among the basic characterization, fast imaging and statistics on current peaks could be performed in addition to the usual Lissajous power measurement as an assessment of spatio-temporal distribution of filaments over different materials. Similarly, such studies could be complemented with a set of catalyst surface characterization results using common ex-situ techniques such as atomic force microscopy (AFM), transmission electron microscopy (TEM), XRD, x-ray photoelectron spectroscopy (XPS), etc, both before and after plasma exposure, to establish the structure of the catalyst used and report permanent plasma-induced changes in the catalyst structure. These techniques require expensive equipment that might not be available in a single research group. Hence, a priority should be to more strongly engage in multidisciplinary collaborative research between experts in plasma and catalysis. The gas and surface temperature inside the IPC when igniting the plasma is a crucial parameter that should be reported for any plasma catalysis experiment. Standard techniques involve optical emission spectroscopy (OES) [75], optical probes, or IR thermometric cameras on surfaces with known emissivity for instance. OES can also be used to measure vibrational temperatures if the emitting electronic states are in equilibrium with ground states [76].

Standardized plasma sources, or batches of identical and well-characterized catalysts would also be very useful to share among groups with complementary expertise, to use them as reference for assessing the efficiency of new materials or plasma sources. This would be an important step towards benchmarking approaches as already done in thermal catalysis [77], even if the intrinsic inhomogeneities of packed bed DBDs still make these 'benchmark' studies difficult.

Even when the optical access to the IPC is limited (because of a furnace for instance), the development of optical fibers based techniques makes not only the OES of the plasma itself possible, but also measurements commonly used in thermal catalysis literature and reported as spectroscopic *operando* techniques, like diffuse reflectance spectroscopy (DRS) in UV–vis or Raman for electronic and vibrational absorption of solids [78, 79]. The IR-vis-UV emission of the plasma itself could be a problem for these techniques, but here the characteristic time differences between plasma phase processes and surface evolution may be beneficial for using pulsed plasma and carry out surface analysis during short periods with plasma turned off. Extremely interesting information about crystalline phases, spatial distribution of amorphous phase or nanoparticles or chemical bonding and atomic composition are now being investigated in thermal catalysis with *operando* x-ray diffraction or absorption using the bright x-ray source of synchrotron facilities [80], even with tomographic imaging techniques [81]. This will require us to develop dedicated measurement cells, allowing a plasma to be ignited in contact with the surfaces being analyzed, but a first paper has shown this possibility [82]. Other *in situ* techniques could be used as well, such as isotopic exchange or mass spectrometry with sampling orifice inside catalytic bed, as described in [83].

(ii) The control of plasma filament initiation in space and time allows the use of other complementary *in situ* measurement techniques. The use of pin electrodes covered with dielectric for instance allows us to localize plasma filaments just on top of powder deposited in modified DRIFT cells, or on the surface of catalyst pellets to analyze intermediary products adsorbed with FTIR absorption spectroscopy [72, 73]. Instead of FTIR techniques, sum frequency generation (SFG) could be used in a similar configuration and give even information about orientation of adsorbed molecules on ideal surfaces (such as oriented crystals). Plasma ignited inside channels of microfluidic reactors would be another configuration constraining filaments in space, possibly giving insights to whether or not it is possible to initiate plasma in small channels. The electric field (E_{field}) in the plasma filaments as well as the induced field on the surface of the catalyst are key parameters that can be determined when using plasma filaments reproducible in time (pin to pin kHz DBD, nanosecond repetitive discharge, plasma jets). Cross correlation spectroscopy (CCS) gives space and time resolved electric field measurements even in surface DBD (SDBD) [84] and could be used with various catalytic surfaces. EFISH generation usually used for measuring E_{field} inside filaments, can also provide values of electric field induced inside dielectric catalytic materials, as Mueller polarimetry could. The surface charge deposition, which depends on catalyst properties, can significantly affect the plasma development even relatively far from the surface. Therefore, laser diagnostics (EFISH, TALIF for radical densities, Rayleigh and Raman scattering for molecules and gas temperature detection, etc), which can be performed as close as few tens of µm above the surface without too strong scattering, would provide valuable information if performed above various catalytic materials. Ions and radicals produced near a catalyst surface could also be detected with mass spectrometry, placing a small sampling orifice at the footprint of the filament on the surface [85].

(iii) Homogeneous plasma sources at reduced pressure (DC glow, RF, MW at pressure 1–100 mbar) can be very interesting tools as they allow us not only to measure, but also to more easily control the flows of species (free radicals, vibrationally excited, etc) to which the catalysts are exposed. The problem of excessive gas heating (for instance with RF or MW discharges) can be circumvented either by pulsing the plasma or by placing the catalyst in close post-discharge where the excited species can still reach the catalyst at low pressure. Most of the previously mentioned *in situ* measurement tools can then be used to characterize both the structural modifications of the material and the evolution of the adsorbed species, while precisely monitoring the flows of reactive species produced by the plasma. As an example, species adsorbed during CO_2 methanation on a faujasite zeolites catalyst in a DC-glow discharge were measured with transmission FTIR in step-scan mode with temporal resolution ~1 μs [86], while it is possible in a very similar discharge to measure both the lifetime of the oxygen atoms (by TALIF or actinometry [87]) and the vibrational temperatures of CO or CO_2 (with gas phase *in situ* FTIR [88]). Even if the activity of the catalysts at low pressure is not necessarily representative of what it would be at larger reactant partial pressures, the level of detail in the observations that can be made of both gas phase and adsorbed phase kinetics simultaneously make these homogeneous discharges very interesting tools for fundamental studies. Moreover, they offer the possibility to make easier comparisons with kinetic models, even 0D models, to constrain their predictive capabilities.

(iv) The study of plasma catalysis conversion mechanisms suffers from a considerable lack of basic data, such as adsorption energies, reaction rates, turnover frequencies, probability of radical recombination at the walls, probability of vibrational de-excitation, accommodation coefficients, etc. Even for catalysts that have been studied for a long time, all these data are modified under plasma exposure, for example, due to ion bombardment or intense electric fields. The use of homogeneous discharges mentioned in (iii) can contribute to get this information. For example, it is well known from DC glow discharges that the probability of recombination of atomic oxygen on a simple non-porous surface of SiO_2 can be more than an order of magnitude higher under plasma exposure than under post-discharge exposure [87]. This raises the question of either the creation of active sites by the plasma (which could happen on any catalyst), or the increase of turnover frequency on the recombination sites. It is nevertheless necessary to broaden the modes of investigation used for understanding plasma catalysis interaction. For example, experiments under vacuum with molecular beams excited by laser in a specific vibrational or electronic state, and interacting with various surfaces can give very valuable information about the de-excitation probability but also the reactivity of these excited states on surfaces. As mentioned in section 2, it is quite relevant to use measurements made for electro- or photo-catalysis as an indication of the effects of surface fields or UV irradiation. The latest developments in atomic scale imaging techniques, such as electron microscopy [89], even if they do not allow the implementation of plasma sources, should nevertheless be closely followed.

Concluding remarks

A catalyst placed under plasma exposure can undergo irreversible structural changes, but also changes in its adsorption capacity, turnover frequencies or reactivity only during the time of its exposure to the plasma. How and where plasma-excited species can react on the surface of the catalyst, whether they are ions, radicals, vibrationally or electronically excited molecules, is also very poorly known. Therefore, it is not yet possible to make comparisons of catalyst efficiency by, for example, normalizing by the number of active sites as is usually done in catalysis. To make progress, the further development and implementation of *in situ* diagnostics is a key priority. The combined use of *in situ* diagnostics and complementary reactor configurations is necessary to achieve significant progress in identifying mechanisms of plasma catalyst synergy. Sharing standard reactors and reference catalysts would be valuable tools to improve the repeatability and comparability of experiments. Finally, the study of simpler and better-controlled systems than configurations aiming at performance seems necessary, in particular for the step-by-step validation of numerical models.

Acknowledgments

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5. Physicochemical interactions of plasma and catalyst

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Status

A wide variety of complex physical and chemical interactions take place between the plasma and the catalyst. As in thermal catalysis, chemical reactions occur on the catalyst surface. In thermal catalysis, however, only ground-state molecules are present in the gas phase. In a plasma, vibrationally and electronically excited molecules, radicals, atoms, ions and electrons are all present, leading to a much more extensive range of chemical reactions. The physical interactions between the plasma and catalyst, such as charge transfer, electric field modification and heat transfer, affect the plasma and the catalyst, and therefore the chemical reactions. In considering the interactions between the plasma and the catalyst, we must also take into account the support structure of the catalyst, such as the dielectric beads used in a packed-bed reactor.

The plasma itself is well understood. For example, the properties of filamentary streamers, including branching, propagation velocity, dimensions and electron density are known. Laser-based measurements provide time- and spatially-resolved information on the formation and decay of short-lived reactive species [90]. However, the morphology and propagation velocity of surface streamers, which are important in plasma catalysis, differ from those of gas-phase streamers [91], and diagnostics of surface streamers are at an early stage. Experimental and theoretical studies of the penetration of plasmas into pores in the catalyst and substrate have been published [92–94], but a general understanding is still lacking.

The influence of the plasma on the catalytic surface includes charging, heating and possible alterations of the morphology and structure of the catalyst. Again, there is much to learn. For example, while the influence of temperature in several plasma-catalytic processes has been investigated, it is generally assumed that the surface temperature will be equal to the plasma gas temperature; localized effects have not been widely explored.

Current and future challenges

A full understanding of the physicochemical interactions of the plasma and catalyst is hugely challenging. The different physical effects (electric field enhancements, discharge formation and species transport in pores, and charging, heating and modification of the catalyst surface) are coupled to each other and also to the plasma chemistry.

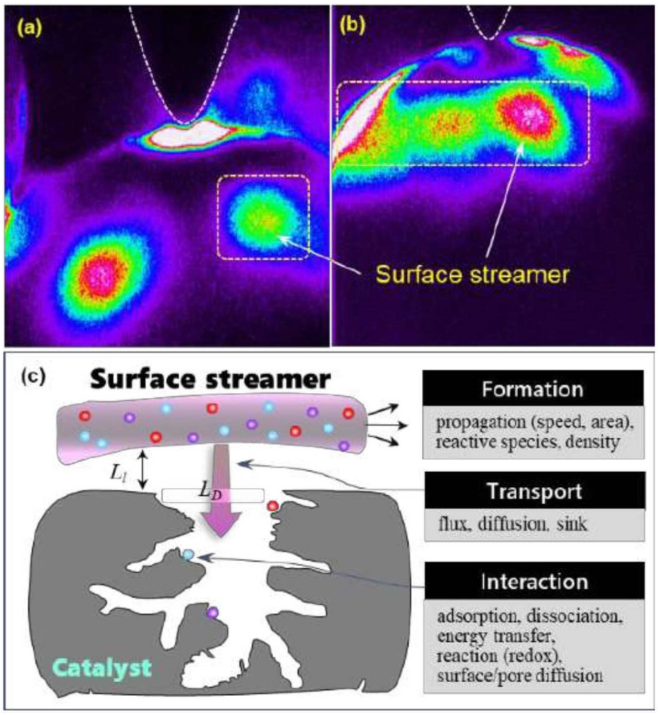

Figure 9. ICCD image of a surface streamer and its interaction with the catalyst surface: (a) γ-Al_2O_3, and (b) Ag/γ-Al_2O_3, showing that the metal particles increase the expansion of plasma over the surface. (c) Schematic diagram of interaction. (a), (b) Adapted from [95]. © IOP Publishing Ltd. All rights reserved.

The local curvature of the surface of the catalyst and its support structure, its dielectric properties, and accumulation of charges on the catalyst surface, all influence the electric field in the plasma. The electric field affects the discharge characteristics, the electron energy distribution function (EEDF) and electron density, and thereby the plasma composition, including the excitation of plasma species. For example, in packed-bed reactors, the electric field enhancement is more significant for high dielectric constant beads such as ferroelectric materials, with plasma streamers behaving as local filamentary discharges. In contrast, for beads with lower dielectric constants such as Al_2O_3 and SiO_2, most of the streamers act as surface discharges [93]. This, in turn, influences the fluxes and properties of species incident on the catalyst, which, as discussed below, can affect the catalyst.

Determining the combined influence of the catalyst and the support structure is also important. For example, Kim *et al* [95] showed that metal nanoparticles on the surface of zeolite increased the expansion of the plasma over the surface, which in turn gave better activity. Such intensified charged coupled device (ICCD) images can be useful for catalyst screening [95]. Figures 9(a) and (b) show that the presence of silver nanoparticles on an alumina bead affects the area of the surface streamer; the propagation velocity is also increased [95], while figure 9(c) summarizes the complex interactions occurring between a surface streamer and the catalyst.

The likelihood of formation of discharges in pores is an important point, since the catalyst surface area exposed to the

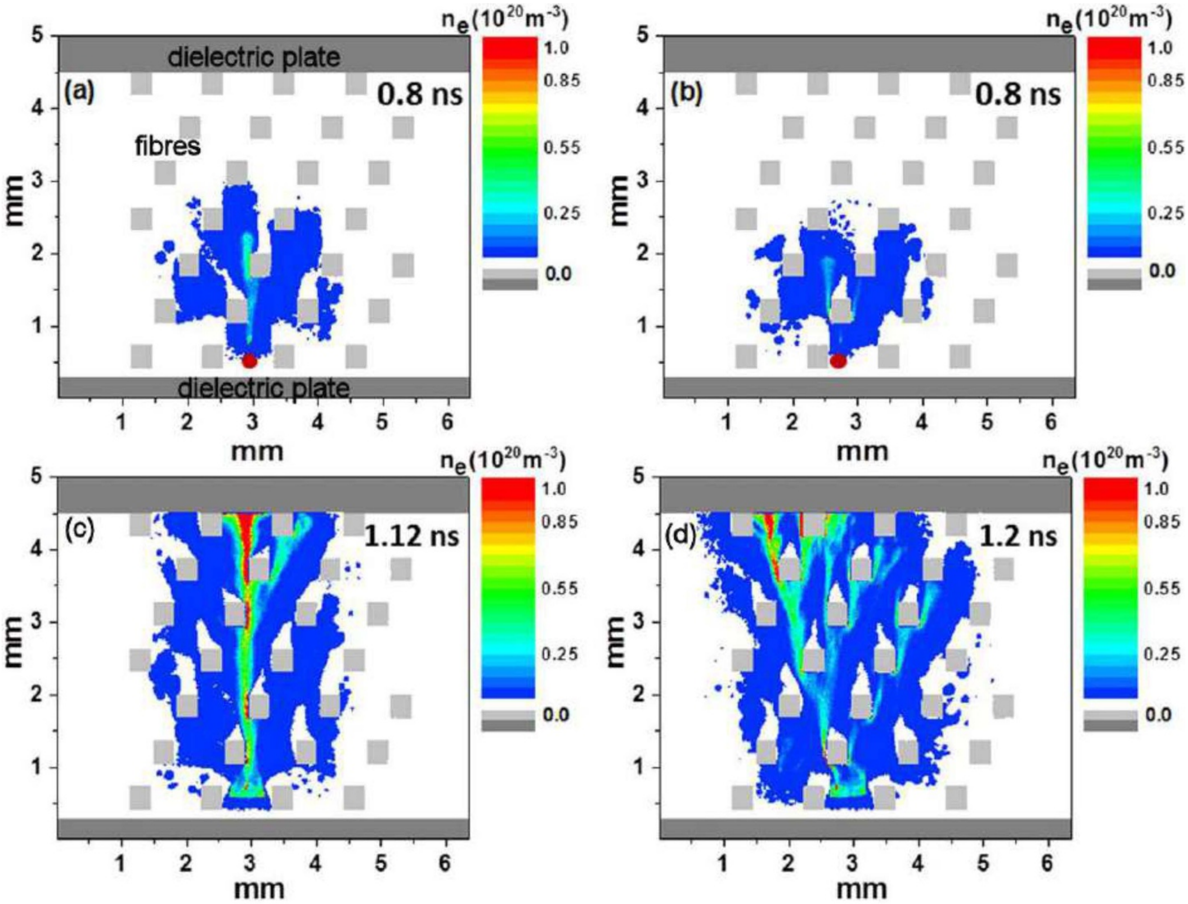

Figure 10. Predicted electron density distributions at 0.8 ns (a), (b) and when streamers reach the top of the dielectric at 1.12 ns (c) and 1.2 ns (d) in a three-dimensional fibre bed for different locations of streamer initiation (see red dots in (a), (b): at the centre of the channel (a), (c); near the edge of the channel (b), (d)). The dark-grey dielectric plates cover the electrodes, and the light-grey fibres are perpendicular to the plane of the figure. Reproduced from [68]. © IOP Publishing Ltd. All rights reserved.

plasma is a determining factor in the plasma-catalytic performance. Experiments and models have shown that plasma formation occurs more easily for larger pores and applied voltage; models suggest the size limit to be of the order of the Debye length [93, 94], while experiments indicate even larger size limits [92]. Models predict that plasma formation inside catalyst pores occurs more easily for low dielectric constant materials and that the pore shape affects the electric field enhancement and therefore the plasma properties, but this still needs to be experimentally confirmed [93]. The diffusion of plasma species into pores when discharges do not form in the pore has not been analyzed in any detail.

The non-uniformity of plasma properties is not necessarily a critical problem in processes in which only a small fraction of the input gas has to be treated, such as the removal of volatile organic compounds (VOCs). However, in applications such as dry reforming of methane and ammonia production, large fractions of the input gas have to be transformed, and energy efficiency requires a uniform and optimized EEDF. Investigation of the physicochemical interaction of plasmas and geometries other than packed-bed dielectric barrier discharges (DBDs) is therefore critical for many applications. Alternative approaches, such as honeycomb structures and three-dimensional fibre beds, which have been applied in thermal catalysis, have been proposed. Modelling of both approaches has been performed, although only using two-dimensional representations [68]; an example is shown in figure 10. Some experimental success has been obtained using honeycomb structures. Generation of a stable discharge in the honeycomb structure is tricky, so typically the plasma is formed adjacent the honeycomb structure, with electric fields or convection used to transport the plasma species into the pores [96, 97].

The flux of electrons from the plasma inevitably leads to the accumulation of charge on the catalyst. On a macroscopic scale, this affects streamer formation and penetration of plasma into pores. On the microscopic scale, it can alter the electronic and the geometric structure of the catalyst, potentially leading to major changes in the reaction kinetics [98]. As noted in section 2, studies of electro-catalysis have demonstrated that surface charges can affect the paths for chemisorption and reactions. Relevant studies for plasma systems are in their infancy and are limited to density functional theory (DFT) models of particular systems. An example is a recent study showing that dissociation of CO_2 on charged copper and nickel clusters is energetically more favourable than on neutral clusters [98].

The large fluxes of energetic plasma species can induce changes to the characteristics of the catalyst, including surface facetting, specific area and number of vacancies, corner atoms and edges, as well as the oxidation state. The changes depend on the type of plasma and catalyst; for example, both reduction and oxidation have been observed [13]. It is expected that the catalyst work function will be likewise affected. In turn, the catalytic activity and selectivity will be altered. Changes to the catalyst are not, however, always observed [109]. Detailed investigations of possible changes, including the influence of localized heating, are necessary to develop the depth of understanding required to allow optimization of plasma-catalytic reactors.

Advances in science and technology to meet challenges

A full understanding of the physicochemical interactions of the plasma and catalyst is a demanding task. The strong coupling of the different physical effects with each other, and with the discharge and surface chemistry, have to be considered.

Realistic simulation of plasma-catalytic reactors will require very significant advances in current capabilities. Because of the large localized variations in plasma and surface properties, three-dimensional time-dependent models are required. Further, the models will have to couple sub-models on very different scales and employing different computational techniques. For example, current macroscopic models that investigate the influence of the catalyst on discharge characteristics only consider the support structure of the catalyst; the catalytic particles can be six orders of magnitude smaller. Even for the plasma, different approaches are required; for example, fluid models reduce computation time but are not suited to the plasma in small pores, for which particle-in-cell—Monte Carlo collision (PIC-MCC) models are needed. Coupling the physics and chemistry is also required, in particular incorporating realistic surface chemistry into macroscopic models, and treating the influence of the plasma on the catalyst; see section 6 for a more detailed discussion.

In situ operando measurements of the species densities on catalysts are becoming more widespread, as discussed in section 4. These will be critical in understanding the coupled physics and chemistry of plasma catalysis; at the same time, the influence of the plasma on the catalyst should be monitored. Controlled studies of the interactions of particular excited species with catalysts are also needed to determine the reaction rates and to elucidate the influence of the species on the catalyst. Separation of the plasma and surface effects is a step in this direction [99].

As noted above, improved reactor designs are critical for many applications. Optimization will require a detailed understanding of the two-way interactions between the plasma and the catalyst and its support structure. A critical issue is understanding the transport of plasma species to the surface of a catalyst and their subsequent utilization in the surface reactions.

Concluding remarks

Development of a detailed understanding of plasma–catalyst interactions is an important but, because of the many coupled physical and chemical processes, an immensely challenging task. Progress requires both fundamental studies that focus on developing an understanding of interactions occurring in simplified situations and applied studies carefully designed to provide insights into more realistic arrangements. Ideally, a coordinated approach will be developed, with the fundamental studies providing the foundations for the applied efforts. Ultimately, the success of many prospective applications of plasma catalysis will rely on reactor designs based on a thorough knowledge of the physicochemical interactions of plasmas and catalysts.

6. Plasma catalysis modeling

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Status

Physically and chemically realistic models of appropriate fidelity are essential to realize the promise of plasma catalysis. Models are essential to organize available observations, to guide the identification of appropriately matched reactions, catalytic materials, and plasma reactors, and to enable the development of practically viable systems. This modeling is challenged by the inherent underlying complexity of plasmas in contact with reactive surfaces. While models of catalyst-free plasma chemical reactors [100] (vertical axis, figure 11) and of heterogeneous catalytic reactions [101] and reactors [102] (horizontal axis, figure 11) are individually well developed, models that couple both plasma and catalysis are in their infancy.

Progress has been made in (i) modeling the influence of solid reactor packing on plasma and in (ii) coupling plasma chemistry to surface reactions. In the first case, the underlying physics is rather well understood, as are the various manifestations of catalyst or packing modifications on the plasma behavior [93, 103]. The electric field enhancement in a packed bed dielectric barrier discharge (DBD) has been described by fluid models. Streamer propagation in a packed bed DBD has been simulated by either fluid models or particle-in-cell–Monte Carlo collision (PIC–MCC) simulations, and both approaches have also been applied to predict whether plasma (streamers) can be formed in catalyst pores. However, these models have been focused on the plasma characteristics themselves, and their implications for catalytic reactivity have not yet been incorporated. In the second case, the non-thermal and reactive species produced by plasma have been incorporated into zero-dimensional microkinetic models for plasma-catalytic NH_3 synthesis, with the goals of reproducing observed reactivity [104] or predicting reactivity trends [6]. Adsorption steps have been modeled with fixed sticking probabilities [104] or, for activated adsorption steps, by modifying intrinsic activation barriers using a Fridman-Macheret-like model [6]. In addition, attempts have been made to capture specific influences of plasma on surface reactions, including surface charging and electric fields [105], in molecular-scale density functional theory (DFT) simulations, but direct connection of these results to real-world plasma-catalyst conditions remains unrealized. Thus, while progress has been made in capturing some aspects of the plasma-catalyst combination, a fully integrated and predictive modeling regime remains to be created.

Current and future challenges

Because the plasma-catalyst combination is so rich, models of varying levels of detail and integration are needed to (a) understand relevant physical and chemical phenomena, (b) select materials and conditions that optimally exploit these phenomena, and (c) incorporate these combinations into practically viable systems (figure 11, diagonal).

First, plasma-catalyst models must incorporate the surface reactivity of the rich mix of radicals, ions, and rotationally, vibrationally and electronically excited plasma species. The surface reactivity of excited species is well known to be enhanced over conventional thermal reactions. Current plasma models typically account for species loss at surfaces through simple sticking coefficient boundary conditions. Molecular dynamics models can describe state-resolved surface reactions but are complicated to parameterize and chemically specific. General, likely DFT-based, models applicable within or across catalytic material classes, similar in spirit to those captured in the existing literature (e.g. CatApp database [106]) but including features descriptive of plasma, such as specific energy input (SEI), and useful for incorporation into 0D or higher order microkinetic models, remain to be developed. These models must be validated against experimentally determined reaction rates, both for the generation of (reactive, excited) plasma species and for their reactions at surfaces. Fundamental data collected at conditions relevant to plasma catalysis remain sparse and are a critical need.

Second, robust insights into how the physical impacts of plasma (local heating, electron charging, oscillating electric fields) influence surface reactions, as a function of surface composition and structure, must be developed. Molecular models coupled with *operando* spectroscopic observation holds promise here. Existing PIC–MCC simulations only consider surface charging and lack chemical surface reactions.

Conversely, and third, models describing the influence of the chemical composition and physical structure of catalytic materials on the plasma characteristics and plasma chemistry are needed. Such models will describe plasma and catalyst as a coupled, reactive system, each part influencing and modifying the other. Models must both strive to capture this coupling and to identify regimes in which the combination interacts productively.

Finally, microkinetic heterogeneous catalyst models, especially those used for materials design, are conventionally isothermal and steady-state. Plasmas, however, are intrinsically inhomogeneous, dynamical, and non-steady-state. Models that appropriately bridge and ideally exploit the different length- (nm to cm) and time- (ns to s) scales associated with surface reactions to plasma behavior are necessary to identify useful combinations, and to design, control and operate plasma-catalytic reactors.

Advances in science and technology to meet challenges

To address the above challenges, 0D chemical kinetics or 2D/3D fluid dynamics models need to be developed, coupling plasma and surface chemistries, to guide plasma/catalyst

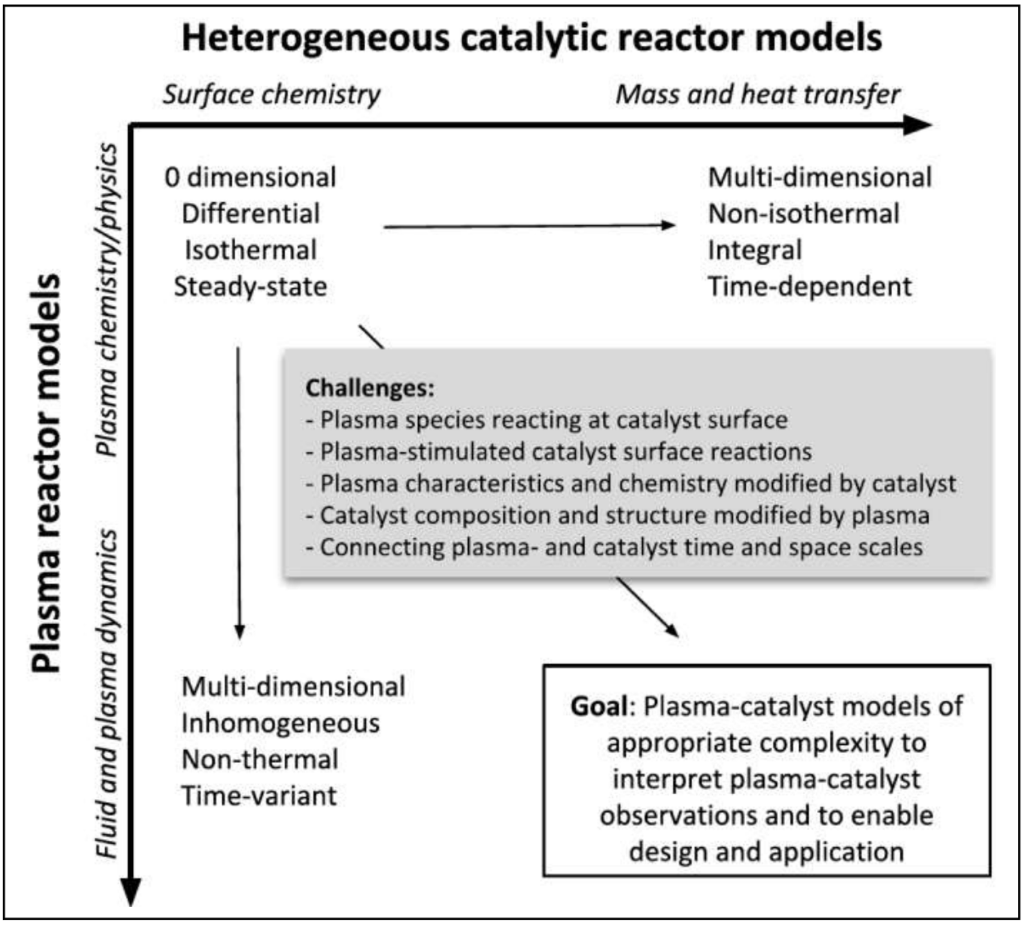

Figure 11. Heterogeneous catalytic reactor (horizontal) and plasma reactor (vertical) models span ranges of physical and chemical fidelity, as well as span from idealized, low-dimensional and steady-state behaviour to multi-dimensional and time-dependent behaviour arising from non-uniform distributions of heat or plasma energy. Several challenges (center) confront the development of a similar spectrum of plasma-catalytic reactor models.

optimization. Models must be informed by experimental (spectroscopic, electronic, kinetic) observations of the plasma-catalyst system and of the resulting chemical products. These models are needed both to describe rates, conversions, and selectivities in known plasma-catalyst combinations and to predict the performance of poorly or unexplored plasma-catalyst combinations.

To bridge the gaps from plasma catalysis research to reactor design and application, models of varying levels of fidelity and quantitative reliability must be created. Ultimately, integrated multi-scale models must integrate physics and chemistry at multiple scales (figure 12). First, molecular scale simulations (DFT-based, static and dynamic) are needed to predict the reactivity of plasma species (radicals, ions, electrons, and vibrationally and electronically excited species) and plasma effects (charging, electric fields) at the catalyst surface. These advances are essential (i) to gain insight into how plasma-catalyst coupling influences chemical conversions, (ii) to predict the most suitable materials for plasma catalysis, and (iii) as input data for plasma models. Second, 0D plasma-surface kinetic models must incorporate steady-state and dynamic coupling between plasma and surface reactivities, including the diverse timescales of plasma and surface reactions. Third, a reduced chemistry (as adopted from the 0D models, based on the most important species and reactions) should be introduced into higher dimensional (2D or, at the expense of computational time even 3D) models to design the plasma catalytic reactors that provide maximum chemical performance and energy efficiency (by fluid dynamics modeling) and for the behavior of plasma streamers in catalyst pores (by PIC–MCC simulations). Integrated plasma-surface modeling now, at best, has a dynamic range of 1000 in spatial scale. To address the computational needs of plasma catalysis, the dynamic range should exceed 10^6 (1 mm to 1 nm). Vice versa, these models provide input for the molecular scale model, including the electric field, temperature and species fluxes, to properly account for plasma effects in the latter model.

Because so many reactions and physical phenomena are potentially at play in a plasma-catalyst system, methodologies are needed that highlight those phenomena with the largest impact on chemical productivity and efficiency and thus are the greatest sources of model sensitivity. Coupled 0D plasma-catalyst models will need to take advantage of modern Bayesian methods to develop models with quantified reliability and modern methods of uncertainty quantification, such as the ‘degree of rate control’ concept that has proved a powerful

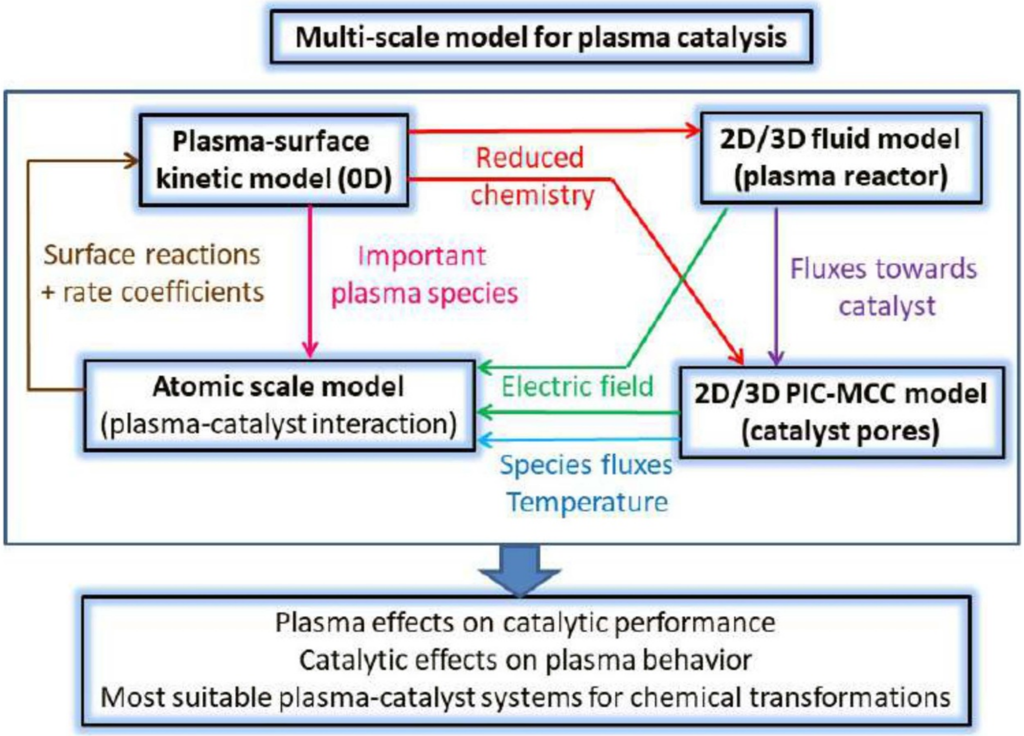

Figure 12. Concept of ultimate multi-scale model to be developed for plasma catalysis.

tool in refining microkinetic models of heterogeneous catalysis, to isolate the reactions and processes with the greatest impact on predicted plasma-catalyst performance [107]. Such models will be a powerful tool both for focusing modeling efforts and guiding experimental design and optimization.

Machine learning (ML) could find useful application in multiple aspects of this modeling regime. ML is being applied to develop structure-function relationships and even as a surrogate for DFT calculations at the molecular scale [33, 108]. Machine-learned potentials, for instance, could supplement DFT in molecular dynamics simulations of plasma-stimulated reaction processes at catalyst surfaces. ML could similarly add in identifying relationships that simplify evaluation of plasma-phase reaction networks, or even in identifying simplifications to solving coupled reaction and transport problems.

Concluding remarks

Despite vigorous research activity, our understanding of plasma catalysis remains primitive. We believe models have an essential role in moving the field from one founded on empirical observation to one founded on well-integrated physical and chemical principles. Heterogeneous catalysis has advanced in large part through molecular-level descriptions of the relationships between surface structure, composition, and reactivity, and DFT-level and microkinetic models have been essential for rationalizing observation, for guiding materials discovery, and as a foundation for reaction modeling. The vision of figure 12 places plasma catalysis on a similar molecular footing, with similar goals. As highlighted in figure 11, fundamental challenges remain in describing the molecular-scale coupling between plasma and catalyst phases (couplings that likely vary in importance from system to system). Further, computational challenges confront incorporation of plasma phenomena into molecular models and in integrating from molecular to continuum scales. We believe these challenges are surmountable and associated insights essential to realizing the potential of plasma catalysis.

Acknowledgments

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7. CO_2 conversion by plasma catalysis

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Status

Climate change is emerging as one of the most pressing challenges for modern society. Reduction of CO_2 emissions from major sources such as power plants and industrial processes is critical to achieving the 21st Conference of the Parties (COP21) target of limiting average global temperature increase to well below 2 °C above the pre-industrial level. CO_2 capture represents the most efficient technology in terms of tons of CO_2 removed from the atmosphere, but the followed carbon storage has significant shortcomings. Instead of treating CO_2 as waste for permanent storage, CO_2 can be regarded as a strategic carbon source for the production of value-added platform chemicals and fuels, finding beneficial ways to use them. The Science and Technology Roadmap on Catalysis for Europe has highlighted that the chemical transformation of CO_2 into useful commodity chemicals and fuels using renewable energy sources will become a key element of sustainable low-carbon circular economy in the future [109]. Thus, CO_2 conversion is strategically important to support cost-effective decarbonization across a wide range of sectors, while simultaneously supporting clean growth across the economy.

However, CO_2 is a thermodynamically stable molecule, and cost-effective conversion of CO_2 remains a significant challenge. Although significant efforts have been placed on the chemical transformation of CO_2 into higher-value chemicals and fuels such as CO, CH_4, olefins and liquid fuels using different approaches including thermal catalysis, electrocatalysis and photocatalysis, today's technologies are still costly and energy-intensive, and significant advances are needed before more viable CO_2 conversion technologies are realized [5]. Plasma catalysis has been demonstrated as a promising and emerging technology for CO_2 conversion at low temperatures and ambient pressure via different routes including CO_2 splitting to CO and O_2, CO_2 hydrogenation to CO, CH_4 and methanol, CO_2 reforming with CH_4 to syngas (see section 8), C_2-C_4 and liquid fuels, and CO_2 reduction with water to syngas [110–114] (figure 13).

Extensive studies have been focused on CO_2 splitting to CO and O_2 using a range of plasma sources in the last decade [110, 111]. The energy efficiency of this process is typically lower than 15% with a relatively high CO_2 conversion of up to 40%–50% in dielectric barrier discharge (DBD) plasmas [110, 111], whereas CO_2 splitting is more efficient in microwave (MW) and gliding arc (GA) plasmas due to the vibrational excitation pathway, achieving energy efficiencies of 50%–60% with a relatively low CO_2 conversion (~20%) [5]. However, it is less straightforward to combine catalysts with MW and GA plasma devices. Placing a catalyst in the reaction zone of these plasma devices is difficult due to their relatively higher temperature (e.g. 1000 °C–2000 °C), although the post-plasma catalysis configuration is possible for MW and GA systems. That is the reason why DBDs are still most common for plasma catalysis, as they allow us to integrate catalysts inside the plasma reaction area. Although the energy efficiency in DBDs is much lower than in MW and GA plasmas, if catalysts can be designed to directly produce value-added chemicals, such as higher hydrocarbons and oxygenates which cannot be achieved using MW and GA plasma systems due to their high temperature and strong discharge (e.g. arc), the lower energy efficiency will be more competitive already with other (non-plasma) conversion technologies, as the production of these value-added compounds in a one-step process circumvents the need for an additional Fisher–Tropsch or methanol synthesis process. One such an attractive example is the plasma-catalytic synthesis of methanol via CO_2 hydrogenation using a DBD at room temperature and ambient pressure [112], a significant breakthrough in CO_2 hydrogenation to avoid the high pressure and high temperature required in thermal catalytic CO_2 hydrogenation to methanol, as shown in figure 14. The conversion of CO_2 (21%) achieved in this process is comparable or superior to that reported in previous works using thermal catalysis at a much higher pressure (17–100 bar) and temperature (200 °C–350 °C). However, the selectivity of methanol (53.7%) using plasma catalysis is still lower than in thermal catalysis [112, 115]. The energy cost of methanol production using a lab-scale DBD plasma is ~100 kWh kg^{-1} [112]. For comparison, the energy cost for methanol production in an industrial-scale direct catalytic CO_2 hydrogenation process is ~11.1 kWh kg^{-1} [116].

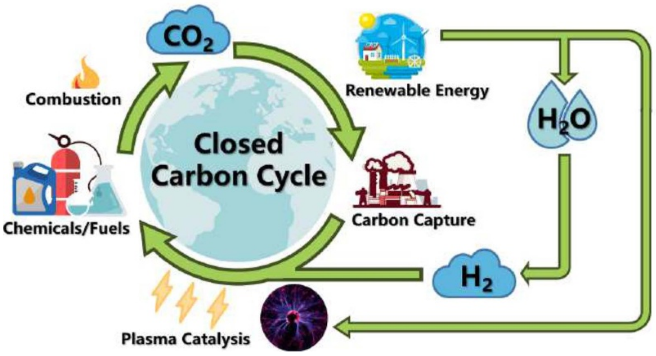

Figure 13. Closed carbon cycle for plasma-catalytic conversion of CO_2.

Current and future challenges

Currently, the selectivity of target products in plasma-catalytic activation of CO_2 particularly in CO_2 hydrogenation to liquid fuels and dry reforming remains low compared to thermal catalysis, due to limited knowledge of designing highly active and stable catalysts effective in plasma-catalytic CO_2 conversion. A common strategy of catalyst design for plasma catalysis is to use the optimal catalysts in the corresponding thermal catalytic reactions [14]. Unfortunately, those catalysts performing well in thermal catalytic CO_2 activation might not

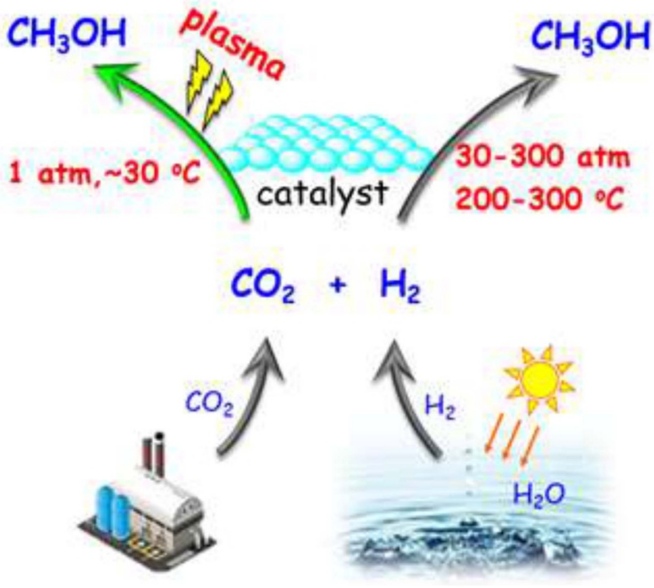

Figure 14. CO_2 hydrogenation to methanol using thermal catalysis and plasma catalysis. Reprinted with permission from [112]. Copyright (2018) American Chemical Society.

work in plasma-catalytic reactions as the operating conditions in plasma catalysis could be completely different to those in thermal catalysis (e.g. ambient pressure vs high pressure and low temperature vs high temperature) [3, 113]. In addition, the presence of plasma could change the properties of the catalyst surface and introduce new species (e.g. excited species and reactive species) for surface reactions, consequently changing the adsorption and desorption process on the catalyst surface and the reaction pathways. For example, in the plasma-catalytic CO_2 hydrogenation, CO and vibrational excited CO_2 molecules generated in the plasma phase could be directly adsorbed onto a catalyst surface, creating additional reaction routes which do not exist in thermal catalytic CO_2 hydrogenation. In some cases, catalysts exhibiting poor performance in thermal catalysis work effectively in plasma-catalytic CO_2 activation [113]. Thus, it is a challenge to select and design the best catalysts for a specified CO_2 activation process under defined conditions to produce target products.

One of the significant challenges in plasma-catalytic CO_2 conversion is to further enhance the energy efficiency of the process while maintaining a high CO_2 conversion and product selectivity. In the case of CO_2 splitting to CO, the energy efficiency of 50%–60% can be achieved using MW and GA plasma systems [5]. However, the conversion of CO_2 remains too low (~20%) and the cost-effective separation of CO and O_2 could be a major barrier in the direct CO_2 splitting process. Compared to the current state-of-the-art (~100 kWh kg^{-1}) in the plasma-catalytic CO_2 hydrogenation to methanol, further enhancing both the CO_2 conversion (to 50–60%) and methanol selectivity (to 70–80%) in the plasma-catalytic process would significantly reduce the energy cost of methanol production [112]. Such improvement would make the plasma-catalytic hydrogenation process more attractive compared to thermal catalytic CO_2 hydrogenation, considering significantly reduced costs to avoid using high-pressure equipment. Note that the energy consumption or electricity consumption of the plasma-catalytic CO_2 hydrogenation process is only a part of the overall costs in a Power-to-X process.

Moreover, limited fundamental understanding of the mechanism and reaction pathways in the plasma-catalytic activation of CO_2, particularly understanding the plasma-assisted surface reactions such as adsorption and desorption processes, remains a significant challenge. For example, how does excited CO_2 species behave when adsorbed on different catalyst surfaces? *In situ* characterization of catalysts under plasma exposure remains a barrier to understand the real-time change of surface morphology and structure in the plasma-catalytic reaction.

Impurities are often present in CO_2 streams even in captured CO_2. Although the influence of nitrogen on CO_2 decomposition to CO_2 and O_2 has been investigated [117], less attention has been placed on the understanding of how different impurities affect the catalyst stability and the selectivity of target products in various routes of CO_2 conversion using plasma-catalysis. Moving from a lab-scale system to an industrial process is also a challenge for plasma-catalytic activation of CO_2. Most of the current works on plasma-catalytic activation of CO_2 use DBD systems with low CO_2 flow rate [110–112].

Advances in science and technology to meet challenges

Enhancing plasma-assisted surface reactions is critical for the selective synthesis of target chemicals and fuels in plasma-catalytic CO_2 activation. To address the key scientific and technological challenges, rational design of cost-effective, highly active and stable functional catalytic materials specified for different plasma-catalytic CO_2 conversion routes is the key drive to enhance the selectivity of target products and the energy efficiency of the process, making plasma catalysis more competitive and attractive for CO_2 activation compared to thermal catalysis which often requires higher temperature and/or higher pressure. Using knowledge and advances achieved in thermal catalysis as a starting point, combined with high-throughput catalyst screening (see section 3) could facilitate the design of optimal catalysts suitable for plasma-catalytic CO_2 conversion. This also involves manipulating plasma-catalyst coupling modes considering different catalyst packing modes and catalyst properties (e.g. size, shape and bulk structure) to determine the most effective plasma-catalyst interactions to enhance plasma-assisted surface reactions for a particular CO_2 activation route. Developing cutting-edge and innovative reactor design for specific reactions is also important to improve the performance of the plasma-catalytic CO_2 conversion process. For example, a water-cooled DBD reactor with a water electrode has demonstrated to be more effective in the production of liquid fuels such as methanol from CO_2 hydrogenation compared to a conventional cylinder DBD reactor without water cooling [112], while the use of a metallic foam electrode in a DBD reactor can significantly enhance the conversion of CO_2 and energy efficiency in the plasma splitting of CO_2 [118]. The energy efficiency in the plasma-catalytic activation of CO_2 can be further improved through the global optimization of the reactor design, catalyst design, power supply and process parameters.

Developing *in situ* surface probing techniques such as *in situ* infrared spectroscopy (see section 4) combined with *in situ* and *ex situ* catalyst characterization and plasma-catalysis modeling (see section 6) is the key to gain new insights into the reaction mechanism and pathways in the plasma-catalytic activation of CO_2 including plasma-assisted adsorption and desorption processes on the catalyst surface, which can generate valuable knowledge to facilitate catalyst design from atomic to macroscopic scales to further improve the performance of plasma-catalytic CO_2 conversion.

Design and development of modular plasma-catalytic systems have been regarded as one feasible solution for system scale-up. Techno-economic analysis and lifecycle analysis of the whole supply chain in CO_2 conversion and utilization including different CO_2 sources, CO_2 capture processes, CO_2 conversion routes, hydrogen sources, applications of products, processing plant sizes and transportation and storage infrastructure, as well as social and environmental impacts is critical to enable a rigorous evaluation of the potential of the plasma-catalytic CO_2 conversion process to go forward to larger scale development and to achieve negative or zero carbon emission.

Concluding remarks

Plasma catalysis has great potential to deliver a step-change in future CO_2 conversion and utilization due to its unique advantages such as low temperature and ambient pressure process, as well as the flexibility to be combined with renewable energy sources, which can reduce the costs of upstream/downstream processes and enable the scale-up of the plasma-catalytic process more achievable. Establishing the fundamental scientific underpinnings for efficient catalysts development, cutting-edge reactor design, process intensification and optimization will lead to high-energy-efficiency plasma-catalytic systems that can sustainably convert CO_2 to value-added fuels and chemicals at both distributed and large production scale.

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8. Light hydrocarbon conversions by plasma catalysis

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Status

Global production of natural gas is projected to nearly double by 2050 with the production of unconventional natural gas (i.e. shale gas) fueling the rapid growth [119]. Shale gas is methane-rich with variable quantities of natural gas liquids, which are C_2–C_5 saturated hydrocarbons. Methane has the highest energy content per carbon atom of any hydrocarbon but is difficult to transport from remote locations and is often flared, wasting a valuable C1 building block and harming the environment. The higher, condensable hydrocarbons are potential chemical and monomer precursors but are unreactive in their native form. Thus, opportunities in light hydrocarbon conversions include coupling of methane to higher hydrocarbons [120] (C-C bond forming processes) and functionalization of the light hydrocarbons through selective C-H activation processes [121]. The resulting hydrocarbons from natural gas upgrading can be used as fuels to bridge global dependency on petroleum sources and developing renewable energy technology. Perhaps the most value for the upgraded natural gas hydrocarbons will be in the chemical sector, as many of the products can serve as monomers for polymer production or as platform molecules for fine or specialty chemicals.

Figure 15 summarizes the thermodynamics of direct conversion of methane to higher molecular weight products [122]. Several points are evident. Non-oxidative coupling of methane (NOCM) is endothermic and thus appreciable conversions are possible only at elevated temperature. Thermodynamic selectivity is greater to benzene (methane dehydroaromatization, MDA) than to C_2 products (NOCM), but the thermodynamically preferred product at all conditions is bulk carbon. Consistent with this picture, the primary obstacles to thermal NOCM include limited conversions, poor selectivity, and susceptibility to deactivating coking processes. Given these challenges, oxidative routes to methane activation are both more widely explored and applied. Partial oxidation with O_2 to methanol competes with complete oxidation and has been achieved only at very limited conversions. Oxidation with H_2O or CO_2 (steam- or dry-reforming of methane, SRM and DRM, respectively) are highly endothermic, so that useful conversions are again only achievable at elevated temperatures.

The natural gas liquids present similar challenges. Shale gas C_2-C_5 hydrocarbons are saturated and require C-H activation steps to achieve the desired olefin intermediates [120], which can be either oligomerized or functionalized to form a liquid product. Oxidative dehydrogenation of ethane to ethylene is exothermic and thus can be carried out at milder conditions than non-oxidative dehydrogenation, but oxidation wastes hydrogen in forming H_2O. Therefore, to maintain a high atom efficiency, it is more desirable to selectively and directly dehydrogenate the paraffin to its corresponding olefin. Non-oxidative ethane dehydrogenation becomes thermodynamically accessible only at elevated temperatures (>973 K), where surface-catalyzed and radical-based reactions in gas-phase can occur simultaneously. Due to these constraints, it is highly desirable to selectively dehydrogenate at lower gas temperatures with sufficient production rates.

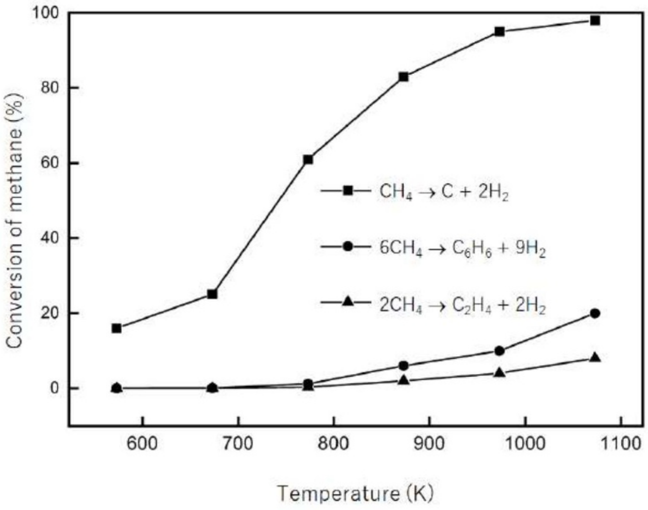

Figure 15. Equilibrium fractions of olefin, aromatic, and solid C products in methane gas versus T. Adapted from [122] with permission of The Royal Society of Chemistry.

Plasmas are an alternative to thermal catalytic processing of methane and have received considerable attention [123]. Methane can be converted to acetylene by a thermal plasma in the Hüels process and also to NOCM products in non-thermal plasmas (NTPs), but, in general, energy efficiencies and selectivities are insufficient for practical use. Integration with catalysts, either to improve NOCM [123] or to promote oxidative reforming [3, 124], have yielded encouraging results, in particular in generating products at conditions milder than thermal catalysis. Evidence suggests that NTPs may be effective both in dehydrogenating and coupling paraffins [125], but this area remains much less well explored.

Current and future challenges

The emergence of unconventional natural gas production creates a need for technologies that can operate in a distributed fashion (i.e. modular), on intermittent renewable energy (i.e. wind, solar), and that efficiently transform light hydrocarbons into more easily transportable liquids. With further development, NTPs coupled with catalysts have the potential to meet these needs. Here, we identify the challenges associated with plasma catalysis and emphasize the opportunities for advancement:

Kinetic challenges

Catalysts active enough to cleave C-H bonds are prone to overactivation, leading to coke or complete combustion of hydrocarbons. Further, both coke and sintering are problematic at temperatures necessary to activate C-H bonds. Vibrationally excited CH_4 produced in plasmas dissociates more readily at a catalyst surface [124, 126, 127]. By directing energy into C-H bond vibrations, or by creating methyl radicals, an NTP can decrease the demands on a catalyst, enabling it to be optimized to meet other constraints [128], including lower temperature operation. Thus, the apparent activation energy for methane activation can decrease significantly under plasma stimulation [129]. Because direct C-H bond cleavage by electron impact is inefficient [124], approaches are needed to (a) maximize energy transfer into desired bonds, (b) maximize the probability of excited and dissociated molecules to reach catalytic sites, and (c) identify appropriate catalytic materials.

Selectivity challenges

Hydrocarbon chemistry is complex, and high selectivity to single or few products is difficult to achieve in catalytic or plasma conversions. Unsurprisingly, the combination faces even greater challenges. Evidence suggests some potential for control, however. For instance, CO_2 utilization by DRM ($CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$; figure 16) is diminished by the competing water gas shift reaction ($H_2O + CO \leftrightarrow CO_2 + H_2$). At ambient conditions, DBD-created reactive intermediates are observed to promote the reaction with little control over the products [129, 130]. However, at bulk gas temperature >630 K, plasma-phase methane contributions are diminished and significant enhancements in CO and H_2 selectivity are realized over a Ni/Al_2O_3 catalyst. While much development in catalysts coupled to NTPs has focused on activity, a key indicator of performance is product selectivity versus conversion. Opportunities are ripe to identify plasma-catalyst combinations that achieve performance that exceeds thermal processes, by creative integration of plasma- and surface-chemistries.

Thermodynamic challenges

Thermodynamics place intrinsic limits on achievable conversions in thermal catalysis, and these limits often drive practical design. Because they are intrinsically non-equilibrium, NTPs can in principle promote reactions at conditions that are thermodynamically inaccessible. Such behavior is evidenced in endothermic DRM, in which plasma-catalytic conversions are observed to exceed bulk thermal limits at low temperatures [131]. This behavior can be rationalized by the differential effects of plasma excitations on forward and reverse reactions, in this case NTP-deposited energy that promotes forward CH_4 and CO_2 activation reactions without promoting the reverse. This phenomenon [132] can be captured in simple kinetic models that highlight the trade-offs between catalysts, forward and reverse rates, and the potential to exceed equilibrium conversion. Endothermic NOCM, MDA, and paraffin dehydrogenation can in principle reach higher conversions at reduced bulk temperatures through similar mechanisms.

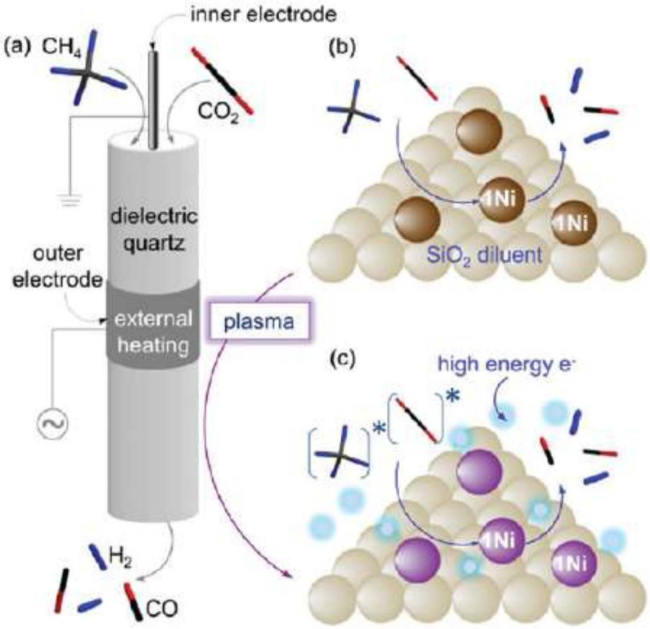

Figure 16. Schematic representation of DRM (a) reactor set-up, (b) thermal catalysis, (c) DBD plasma-assisted catalysis. Adapted from [129] with permission of The Royal Society of Chemistry.

Durability/regeneration challenges

Coke-related deactivation is a pervasive problem in hydrocarbon catalysis. Coke deposits fill and block catalyst pores and disguise active sites. At the high reaction temperatures necessary for highly endothermic reactions, metal catalysts can sinter and thus lose exposed active surface area. Coupling catalysts with NTPs can mitigate these challenges by (a) lowering bulk reaction temperature, to minimize sintering and the formation of carbon, and/or (b) providing alternative regeneration strategies using plasma to remove reaction impurities/carbon deposits [133]. The conversion and selectivity versus time-on-stream is another key performance indicator. Catalysts themselves may be physically or chemically modified in the presence of plasma (see section 12). The relationship between plasma exposure and catalyst durability remains to be determined, and in principle is a key area in with plasma catalysis may exceed catalysts alone in performance.

Energy-efficiency challenges

For plasma-catalytic processes to be applied to hydrocarbon conversions, they must compete on an energy basis with known thermal processes. Energy efficiency (η) is often calculated based on the conversion (X), endothermic reaction enthalpy, and the specific energy input (SEI), where $\eta = [\%] = X\% * \Delta H^o/\mathrm{SEI}$, but other metrics also appear. For endothermic reactions, the specific energy requirement (SER) sets a practical target for SEI. SER < SEI implies that at least some electrical energy supplied to the plasma reactor goes to thermal heating. For DRM, η ~ 70% has been reported [134, 135]. Energy efficiency and conversion increase with increasing CO_2 in the gas feed, but in contrast, η decreases with increasing SEI. NOCM measurements in a microwave plasma reactor show similar increases in methane conversion with increasing SEI [136]. However, an interplay between plasma reactions and thermal reactions from resistive heating at higher plasma power inputs resulted in an energy efficiency of ~15% [134]. Experiments conducted at the same SEI show higher efficiencies at shorter residence times (corresponding to higher power densities) [134]. Energy conversion efficiency (ECE) is another key performance indicator, defined as the sum of the lower heating value (LHV) of the products formed divided by the input energy (sum of LHV of reactants and input power) [137]. ECE values for plasma processes can range between 0 and 1, where values of 1 are desirable [137]. Efficiency is thus a complicated function of reaction chemistry, including product selectivity and reaction conversion, plasma and reactor design, and reaction conditions. Optimization with respect to these parameters remains a challenge.

Advances in science and technology needed to meet these challenges

This backdrop highlights the gaps in scientific knowledge that must be filled to advance plasma-catalytic hydrocarbon conversions:

Reaction characteristics

Metrics and conceptual frameworks for describing plasma chemistry (e.g. electron temperature, electron density, reactive species densities, reaction rate coefficients or cross sections, etc) and for heterogeneous catalytic reactivity (turnover frequency, selectivity, apparent activation energies) are well-established. The complexity of the plasma-catalyst combination presents real challenges both in connecting macroscopic observables (rates, conversions, selectivities) with microscopic behavior and in achieving quantitatively reproducible results across laboratories. For example, does a change in a conversion associated with a change in feed composition reveal changes in plasma-phase reactivity? In surface-catalyzed reactivity? Or some synergy between the two? Can experiments be designed to provide answers to such questions? How can plasma–phase and surface-catalyzed contributions to observed chemical transformations be disentangled to reveal the dependence on catalyst composition? How should an Arrhenius plot be interpreted in the context of a plasma-catalytic reaction?

In situ and operando interrogation

Heterogeneous catalysis has been revolutionized by the application of surface-sensitive spectroscopies to reveal the nature of catalytic materials as they exist under conditions relevant to catalysis. These techniques have yet to be applied to as great an extent to plasma catalysis, in part because of the challenges of integrating plasma with, for instance, x-ray spectroscopy. True *operando* characterizations (under relevant reaction conditions during turnover) may be difficult to achieve, so that alternative approaches to assuring the relevance of observations may be necessary. An aspirational goal is direct observation of plasma and surface species simultaneously, in particular to observe changes in each associated with changes in reaction and plasma conditions. Considerable opportunities exist for innovation in this space (see section 4).

Predictive models at all scales

As highlighted in section 6, models of plasma chemistry and physics are reasonably well developed, as are models of surface catalysis, but modelling of the combination presents special challenges. However, models are essential to guiding development in a space as complex as hydrocarbon chemistry. Such models have a role to play in describing potential reaction mechanisms, in selection of catalytic materials for a given transformation (given that knowledge of optimal materials for thermal catalysis does not necessarily transfer to plasma catalysis [3, 138, 139]), in identifying optimal plasma conditions to achieve desired performance targets, and in developing optimal integrations of plasma and catalyst to achieve desired effects. Models must evolve from explaining observation to a predictive regime, both validated against and guiding experiment. Because the space of hydrocarbon transformations is large and the energy and chemical landscapes are evolving, system-level models have a large role to play in identifying high priority opportunities well suited to plasma catalysis.

Filling of these scientific gaps will enable the technological advances necessary to realize practical applications of plasma:

Operating regimes

The pressures and temperatures appropriate to conventional thermal catalysis and plasma catalysis are intrinsically mismatched. Thermal catalytic processes operate at high pressures, exceeding 200 atm in some cases, to drive chemical reactions. In contrast, the increase in the frequency of gas collisions at high pressure results in an increase in the breakdown voltage to form the plasma (Paschen's law) due to the energy losses from collisions. This mismatch creates a 'pressure gap' that must be bridged. NTPs benefit from the non-equilibrium of temperatures (electron, vibrational, and rotational/translational) of the plasma components, whereas a thermal equilibrium distribution is obtained in thermal catalysis processes. Exploiting the high electron temperature, low bulk gas temperature, and atmospheric pressure operation of NTPs likely offers the greatest opportunity for plasma catalysis in the hydrocarbon transformation space.

Integration of materials and plasmas.

The design space for plasma-catalyst combinations is vast. A sensible starting point when considering contacting plasmas with catalytic materials is the thermally active catalyst. However, the plasma catalysis community should not be constrained by materials we already know are active for the desired reaction. An example is the large amount of literature on Ni-based catalysts for dry reforming reactions. There is an opportunity to take advantage of knowledge developed in the catalysis community on a variety of classes of materials (e.g. metals, oxides, carbides, zeolites, metal organic frameworks, phosphides, sulfides, perovskites, etc). Similarly, there is a great need to develop novel reactor designs to contact the plasma and catalyst in optimal fashion. Fluidized bed reactors were developed for catalysts that rapidly deactivate. What novel designs could be created to accommodate the distinct characteristics of plasmas with catalysts?

Novel and hybrid plasma processes

The space of light hydrocarbon transformations has developed around what is possible using thermal chemistry and catalysis. The large majority of plasma catalysis work has focused in the same areas, for instance NOMC and DRM. Plasma catalysis may potentially enable chemical transformations outside this conventional space. While most work has focused on direct contact of plasma and catalyst, alternative configurations, for instance using plasma to 'reform' a gas mixture before (or after) presenting to a catalyst may open unique opportunities. Integration of plasma- into electro-catalysis (section 2) could benefit electrocatalytic oxidation of methane to methanol [140], using plasma activation of methane to overcome fundamental catalytic material limits on selectivity. Plasma discharges are intrinsically oscillatory, and oscillatory activation of molecules or modulation of surface characteristics could be exploited in the same way that an applied field is predicted to influence catalytic conversion when in resonance with turnover frequency [141].

Conclusion

The energy, fuels, and chemicals landscapes are in the midst of dramatic transformations. Renewable energy is becoming only more widely available and less expensive, but not necessarily available where and when it is needed. Hydrocarbon feedstocks are evolving from petroleum extracted in centralized, often distant, locations to methane and natural gas liquids that come from highly decentralized sources. The resulting carbon footprint will only grow in concern. This changing landscape necessarily creates new needs to carry out chemical transformations where they are located, taking advantage of available energy. Plasma catalysis has the potential to play an important role in this space. To realize this potential, the field will need to evolve from a focus on explaining observations to one focused on identifying and realizing practical synergies (scalability, durability, selectivity, flexibility) that exceed capabilities of conventional hydrocarbon transformations.

Acknowledgments

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9. Ammonia synthesis by plasma catalysis

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Status

Ammonia is a hugely important chemical. As well as being a precursor for fertilizers, explosives and other products, it is a potential storage medium for renewable energy and hydrogen transport. Ammonia is produced industrially from nitrogen and hydrogen by the Haber–Bosch process, a thermal catalytic process that requires high temperatures (at least 700 K) to enable desorption of adsorbed N and NH intermediates that otherwise bind too strongly to the catalyst, and high pressures (in the range of 100–200 bar) to ensure an acceptable yield.

Plasma catalysis, one of several innovative alternatives under investigation [23], has potential advantages over the Haber–Bosch process. As outlined in the Introduction, these include operation at atmospheric pressure and at or close to room temperature, and ease of coupling to renewable energy sources.

Plasma synthesis of ammonia has been performed over a wide range of pressures, from about 35 Pa to atmospheric. Both thermal and non-thermal atmospheric-pressure plasmas have been used. Based on thermodynamic and practical considerations, the latter provides the only realistic option for industrial application [3, 142]. To date, almost all production of ammonia in non-equilibrium atmospheric-pressure plasmas has used dielectric barrier discharge (DBD) reactors, in most cases packed-bed DBDs. A variety of catalysts has been used, e.g. Ru–Mg/Al_2O_3, Co/Al_2O_3, MgO, Ru–Cs/MgO, Ni/SiO_2, $BaTiO_3$ and carbon-based materials, in various forms including powders, pellets and spheres (see [3, 19, 142] for summaries). Ammonia yields of up to 9% [143] and energy efficiencies (input energy per mole NH_3 produced) approaching 1.5 MJ mol^{-1} [71] have been achieved. However, energy efficiencies below 20 MJ mol^{-1} have only been obtained for very low yields ($\ll$1%). For comparison, typical values for the Haber–Bosch process are 15% and 0.1 MJ mol^{-1} respectively, although the process loses efficiency for the smaller-scale production compatible with renewable energy sources (~10 t day^{-1}), so 0.4 MJ mol^{-1} is a better figure for comparison [71]. It is nevertheless clear that large improvements are required in the energy efficiency of plasma processes for their adoption to be feasible, even allowing for the decreasing cost of renewable energy. It is, moreover, important to note that the energy efficiencies reported for plasma catalysis neglect losses in the power supply, which can be large, particularly for pulsed excitation.

Current and future challenges

The predominant challenge is to improve energy efficiency while maintaining acceptable yields. The key to the low energy requirements of the Haber–Bosch process is the use of reaction pathways with low energy barriers, in particular, dissociative adsorption of nitrogen and hydrogen molecules on the catalyst. A plasma provides a means to excite nitrogen and hydrogen molecules, allowing constraints on the thermal process to be circumvented, as discussed in the Introduction. To take full advantage of this while minimizing energy requirements requires: (1) a detailed understanding of the reaction mechanisms for ammonia production, in particular the optimum level of molecular excitation; (2) development of plasma-catalytic reactors that can transfer the corresponding energy to the molecules; and (3) development of catalysts that promote the required reactions.

There is general agreement that NH_3 is produced in plasma catalysis by successive addition of H to N, NH and NH_2, but it is not clear which of the initial reactions occur on the surface and which in the gas phase, and which are the dominant surface-adsorbed species. This is despite the development of zero-dimensional kinetic models [104, 144] and detailed experimental investigations [145, 146], and may be at least partly due to the different plasma conditions and catalysts considered. Rouwenhorst *et al* [147] classified the possible mechanisms into surface-enhanced plasma-driven, plasma-enhanced semi-catalytic and plasma-enhanced catalytic ammonia synthesis, depending respectively on whether dissociation of both N_2 and H_2, only N_2, or neither molecule occurs in the plasma. If N_2 is dissociated in the plasma, the theoretical minimum energy required for ammonia production is 0.47 MJ mol^{-1}, so even at 100% efficiency the process does not meet the 0.4 MJ mol^{-1} benchmark noted above. Therefore, the role of the plasma should be to promote dissociation of N_2 and H_2 on the catalytic surface by exciting but not dissociating the molecules. A full understanding of the optimum levels of excitation will allow the fundamental limits for energy efficiency to be determined.

Packed-bed DBD reactors have been chosen for most studies to date because they provide good contact between the plasma and the catalysts; however, the discharge conditions are highly spatially and temporally non-uniform. There is consequently little control over the electron energy distribution function (EEDF), and therefore the energy channels in the reactor. Other DBD arrangements have been investigated, e.g. [145]. However, in DBDs, the EEDF is peaked between 2–4 eV (100–200 Td) at atmospheric pressure [19]. Figure 17 shows that this range corresponds to moderate vibrational excitation, strong electronic excitation and some dissociation of N_2. This is wasteful of energy since it is likely that only vibrational excitation of the nitrogen molecule is necessary [3].

Most catalysts used thus far have been chosen without considering the specific requirements for plasma environments. Mehta *et al* [3] recently provided some guidance, as also noted in the Introduction and section 3. They showed that the vibrational excitation of nitrogen molecules can allow catalysts that bind nitrogen relatively weakly to be strongly active, shifting the peak of the 'volcano curve' away from the iron-based catalysts used in the Haber–Bosch process, as shown in figure 18. Interesting results have also been obtained in low-pressure

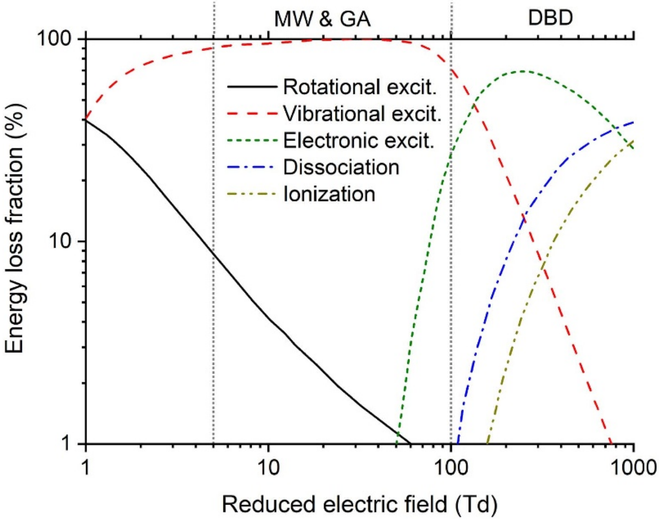

Figure 17. Fraction of electron energy transferred to different channels of excitation, and ionization and dissociation, of N_2, as a function of the reduced electric field. The region between the two vertical dashed lines, i.e. between 5 and 100 Td, corresponds to gliding arc (GA) and microwave (MW) plasmas, while the region above 100 Td corresponds to a DBD. Adapted with permission from [19]. Copyright (2018) American Chemical Society.

plasma experiments [144]. Design of catalysts tailored to the species formed in the reactor nevertheless remains a major challenge.

Advances in science and technology to meet challenges

The limitations of DBD reactors indicate that innovative reactor design is necessary. An ideal reactor would provide good contact between the plasma and the catalyst, but maintain uniform plasma properties within the optimum range. Use of pulsed power may assist with spatial uniformity and energy efficiency [71, 142]. Gliding arc and microwave plasmas provide appropriate electron energies (see figure 17), but it is not clear how best to couple such plasmas to catalysts. The efficiency of the power supply must also be considered; this favours microwave excitation.

Experiments [71, 99] and models [142] suggest that increasing gas and surface temperatures will increase ammonia yield and energy efficiency, with some measurements suggesting that separate control of the gas and surface temperature may be beneficial [99]. A further factor to consider is that some dissociation of the ammonia that is produced is inevitable in a plasma; reactor design needs to address this to favour production over dissociation. Innovative approaches, such as *in situ* absorption of ammonia to reduce dissociation [148], warrant further investigation.

An important requirement is improved catalyst design, taking into account the plasma species (e.g. vibrationally excited N_2) that are present. Ideally, the catalyst will be tailored for the plasma properties in a particular reactor. Detailed microkinetic modelling of plasma–surface interactions incorporating density functional theory and other atomic-scale approaches is necessary to improve understanding of the reactions involving surface-adsorbed species, for example, the influence of the type of catalyst on the reaction rates, the availability of adsorbed species for reactions with gas-phase and other surface-adsorbed species, and the possibility of nitrogen and hydrogen atoms occupying the same surface site. *In situ* operando spectroscopy, which is widely used in thermal catalysis studies but is relatively new to plasma catalysis [14], and careful studies that isolate the influence of the catalyst, support and plasma (e.g. [99, 147]), will play an important role in guiding and validating modelling work; see section 4.

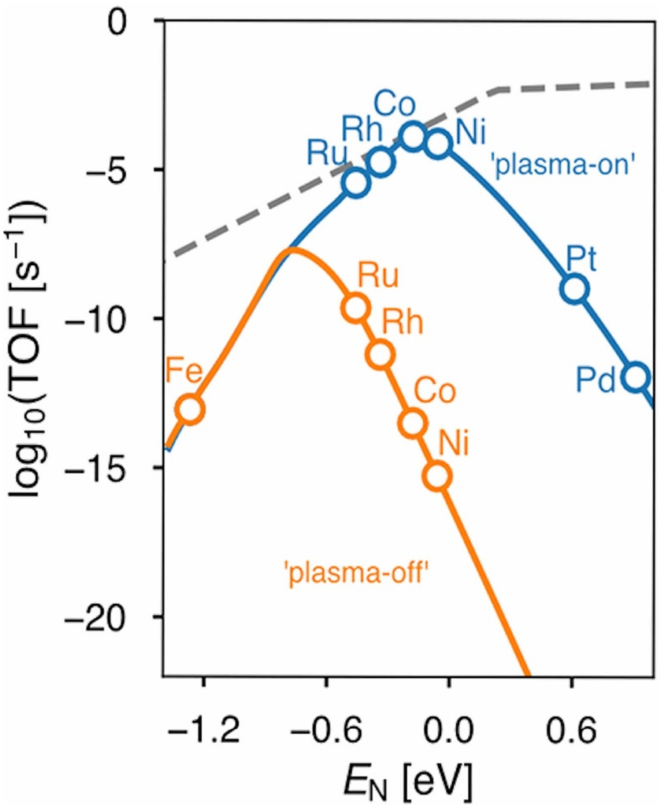

Figure 18. Predicted ammonia synthesis rates (turnover frequency, TOF) on step sites of different metal catalysts for ground-state (plasma-off) and vibrationally-excited (plasma-on) N_2. The dashed lines indicate the maximum rates possible for the hydrogenation step. Reaction conditions: 1 atm, 473 K, $N_2/H_2 = 1:3$, conversion = 1%. Adapted with permission from [3]. Copyright (2019) American Chemical Society.

Linking the understanding of plasma–catalyst interactions and reactor design will require multiscale models incorporating atomic-scale models of surface reactions, zero-dimensional kinetic models of plasma and surface chemistry and at least two-dimensional and time-dependent models of the plasma, ideally taking into account the influence of the catalyst morphology on the plasma [12]; these points are considered in more detail in section 6.

Concluding remarks

Plasma-catalytic synthesis of ammonia holds substantial promise, particularly for storage of renewable energy, in part because the high pressures and temperatures inherent in the Haber–Bosch process can be avoided. However, it has not yet been possible to obtain competitive energy efficiencies while maintaining an acceptable yield. The most likely pathway for improvement will require a deep fundamental understanding of the interactions of the catalytic surface with species only available in plasmas, in particular vibrationally excited N_2. This will motivate the design of reactors that produce large concentrations of such species and of catalysts optimized for these species.

10. Air quality: removal of volatile organic compounds and particulate matter by plasma catalysis

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Status

Over the last two decades, significant achievements have been made in understanding and developing plasma catalytic processes for effluent remediation. These advances are attested by the continuous increase of the annual number of publications on that topic, from less than 500 in the year 2000, to more than 3000 in 2018. In parallel, the applications of plasma catalysis to pollutant removal have led to commercially available devices on the market.

Since the early 2000s, the synergetic effect resulting from plasma–material coupling has been evidenced and the understanding of the positive interaction has been explored. Beyond the impact on discharge physics [149], the sorptive and the catalytic properties of the coupling materials can be pointed out to understand the synergetic effect. Morphology and surface properties allow the stabilization of plasma generated oxidizing species and pollutants in the adsorbed phase, while heterogeneous reactivity is evidenced to be initiated on the surface of the coupling material under plasma exposure [150,151]. In the field of volatile organic compound (VOC) oxidation, the concept 'catalysis' must be clarified as such: indeed, one of the critical steps is the adsorption of the pollutant onto an adsorbing material prior to being oxidized *at the surface* by oxidizing species produced in gas phase by the plasma. Hence, the main features to be fulfilled by the catalyst, or more precisely the coupling material, are a high adsorption capability towards VOCs, as well as efficient dissociative adsorption of ozone produced by the plasma [152]. After 2010, the roles of sorptive processes and active sites of the material have been explored using in-plasma catalysis (IPC) or post-plasma catalysis (PPC) coupling geometries [153] and varying the composition of the materials inserted in the discharge [154]. After widespread sorbents, such as activated carbon and zeolites, were chiefly studied in the 2000s, metal oxides (mainly TiO_2 also used as a photocatalyst, Al_2O_3, SiO_2, and more recently CeO_2) revealed coupling properties of high interest in the 2010s. Compared to metal loaded catalysts typically used for thermal catalysis, metal oxides offer a larger variety and lower prices. Moreover, some metal oxides, showing poor thermal catalytic capabilities, such as manganese oxides, have proven to be excellent candidates for VOC oxidation by plasma catalysis because they ally efficient ozone decomposition and VOC adsorption. In terms of target compounds, VOCs, as ubiquitous pollutants, have been extensively studied. Among the numerous classes of VOCs, lighter hydrocarbons, i.e. containing from 1 to 10 carbon atoms, have been successfully investigated in detail. Specific attention has been paid to VOCs related to health issues, such as aromatics, lighter carbonyls, and more recently chlorinated.

Plasma catalysis is now clearly identified as a heterogeneous process (figure 19), at the crossroad of (i) plasma technology, (ii) catalysis and (iii) surface science [14, 155].

At this stage, it is important to focus on the present needs: among available air treatment technologies, few of them are effectively compliant with the characteristics of the effluents to be treated at reasonable cost and low environmental impact. Indeed, even in the ppm concentration range, effluent remains a highly diluted system. Interestingly, plasma catalyst coupling relies on the introduction of sorptive phenomena in the discharge zone; sorption singularities may concern pollutants as well as oxidizing species. The presence of a material, only sorptive or even catalytic, inside the discharge zone introduces a heterogeneous contribution in the homogeneous plasma system. In that regard, it acts as a pre-concentration step of the pollutants and active species. Therefore, the heterogeneous nature of the process has to be investigated deeper, from a fundamental point of view as well as from a process point of view [156]. In the near future, two main issues have to be addressed:

Performance issue

Standards are now available to assess other air treatment technologies. Would plasma catalysis meet the expectations of future potential standards and be able to face realistic conditions?

Fundamental issue

Plasma catalysis is a heterogeneous process governed by gas–surface interactions, this aspect appears as the key of future developments and optimizations. What are the next investigations to perform?

Current and future challenges

The first challenge is: what are the key process parameters for operating under real environmental conditions?

The question of environmental conditions is related to the variability of environmental parameters such as temperature and relative humidity. Beyond the plasma technology aspects, environmental conditions chiefly affect the sorptive steps involved in plasma catalytic systems. In that regard, the impact of environmental conditions on sorption processes is a key issue to be addressed. Considering the very short contact times between pollutants and plasma combined with material, typically below hundred milliseconds in most processes, adsorption kinetics have to be considered together with thermodynamics.

The question of concentration ranges provides a first partitioning of the application fields of plasma catalysis. Indeed, low-concentration applications deal with indoor environments with various specificities: (i) dwellings and offices, (ii) automotive, aircrafts and trains, (iii) hospitals and medical gases,

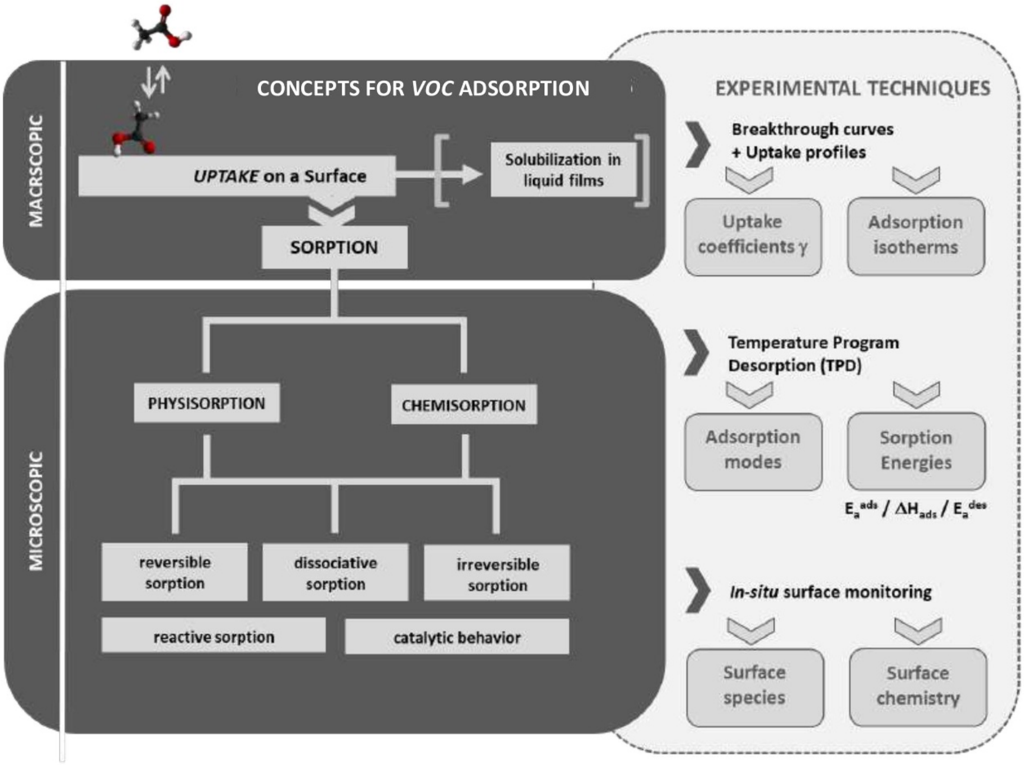

Figure 19. Why is adsorption a key step in the plasma catalytic removal of VOCs? How do we address it experimentally?

while high-concentration applications mostly deal with industrial exhausts and effluents. The sorptive processes are directly impacted by the concentration range since it governs the uptake regime based on the adsorption isotherms. As a consequence, in order to avoid any experimental bias, plasma catalytic systems must be explored in the exact concentration range of pollutants and relative humidity correspondingly to its final use, for application purposes and more fundamental investigations.

The question of the processability of (i) VOCs containing heteroatoms, such as halogen, sulphur, nitrogen, (ii) non-carboneous volatile compounds, such as emerging pollutants like silane and derivatives, and (iii) semi volatile organic compounds, has to be considered by plasma catalysis. Indeed, the scope of treated pollutants is limited to species containing only H, C and O atoms while the current map of the problematic is larger. This aspect requires closer collaborations with metrology and analytical chemistry, as emphasized in figure 19. Indeed, the accurate evaluation of plasma catalysis for air quality improvement necessarily requires quantitative monitoring of targeted pollutants with satisfying monitoring frequency and limits of detections. When addressing analytically challenging pollutants, developments in plasma catalysis have to be concomitant with innovations in analytical chemistry and more generally in metrology.

The question of particulate matter (PM) is part of air quality concerns. In that regard, the ability of plasma catalysis to address that kind of pollutants has to be explored; at least the impact of PM on the behaviour and performances of the treatment of gaseous species should be questioned. Indeed, the introduction of PM in plasma catalytic devices may lead to various and complex phenomena. On the one hand, PM could be envisaged as extra surfaces and could lead to new uptake processes of treated gases. On the other hand, the exposure of PM surface to the plasma oxidative action may lead to the formation of secondary gas phase products. Finally, the deposition of PM may considerably impact the sustainability of the coupling material. As a matter of fact, the processing of PM by plasma catalysis may open new unexplored heterogeneous reactivity routes.

The second challenge is: how do we make plasma catalysis compliant with modern environmental expectations?

The meeting point of existing standards to assess the performances of air treatment technologies is to ensure that processes are safe, clean and healthy. In that regard, the question of side-products, such as ozone, oxygenated VOCs, secondary organic aerosols, etc, cannot be ruled out anymore. The conversion rates of primary pollutant cannot be the only performance criterion; side-products must be addressed, requiring subsequent developments in analytical tools and techniques.

Plasma catalytic processes have been explored and reported in time ranges rarely exceeding a few hours. However, the long-term performances of plasma catalytic processes have to be addressed over several days or weeks, with special attention to the gradual poisoning of the surfaces of the coupling materials. This approach could provide new insight in the sustainability of the process.

Energy consumption is a crucial point for plasma catalytic process validation. One relevant parameter is the specific energy input (SEI), expressed in Joules per litre of gas. SEI drives the production of oxidizing species such as O_3, H_2O_2, O, OH, etc. In the low concentration range of pollutants such as indoor air purification, the averaged SEI should not exceed few tens of Joules per litre in order to reduce the energy consumption and to increase the O_3/NO_x ratio. This constraint is particularly severe for on-board devices intended to treat vehicles, trains or aircraft indoor air. However, most of the recent studies report SEI in the range of few hundreds of J/L and more research should be carried out at lower SEI. Another point is the compactness of the devices: current indoor air treatment devices are relatively bulky, which makes their use problematic for embedded applications. Solutions to solve these challenges require working altogether on plasmas sources.

Beyond the question of air quality improvement, as a remediation process, a global lifecycle assessment of plasma catalytic systems; encompassing their pollutant removal abilities, should be projected.

Advances in science and technology to meet challenges

Based on the future challenges, four expected advances can be defined:

(a) Evaluation of plasma catalytic VOC removal processes under realistic scales and environments: (i) association with innovative analytical instruments dedicated to trace gases and particle monitoring; (ii) implementation and investigation of plasma catalytic processes using large scale experimental chambers to address the upscaling.
(b) Widening the scope of potential coupling materials combining low-cost and low-environmental impacts with high activity; to break the boundary of conventional catalytic materials and promote new catalyst packaging, the potential of materials and minerals of natural origins can be pertinently explored.
(c) Transfer and adaptation of experimental techniques and protocols for the detailed characterization of gas–surface interaction from other research fields to plasma catalysis. As a heterogeneous process, the exploration of plasma catalysis requires new insight on the gas-solid interface in close collaboration with surface sciences.
(d) Development of compact plasma sources generating high ozone yields. Increasing the O_3/NO_x ratio at a given specific energy requires a better understanding of the gas phase kinetics taking advantage of recent progress in downsizing high voltage power supplies. Progress in compactness of process will depend on the selection of sorbents to optimize the residence time in the treatment device.

Concluding remarks

In the past decade, significant steps forward were achieved both in the industrialisation of units and in the fundamental understanding of the coupling and the interaction with VOCs. Now a dual and complementary approach should be envisaged: our fundamental understanding of the gas-surface heterogeneous interaction must be strengthened; meanwhile, plasma catalysis must be confronted with the reality of effluents processing to map and widen its applicability.

11. NO_x removal by plasma catalysis

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Status

The combustion of fossil fuels inevitably leads to the formation of nitrogen oxides (NO_x), particulate matter, and other toxic pollutants. Although combustion systems are continuously improving, after-treatment systems are required to meet the NO_x regulations. Among catalytic approaches, selective catalytic reduction (SCR) using ammonia (NH_3-SCR) or hydrocarbons (HC-SCR) has become a leading method for NO_x reduction into nitrogen (*de*NO_x). NH_3-SCR generally provides higher removal efficiency at lower temperatures than with HC-SCR, but it requires an additional tank of NH_3. HC-SCR revealed a poor activity below 300 °C and needs a large amount of HC, which leads to a fuel penalty. However, for HC-SCR, HC and H_2 can be provided from unburned fuel by on-board reforming to promote the low-temperature activity. To overcome the inherent shortcomings of these technologies (noble-metals cost, high temperature, formation of N_2O instead of N_2, etc), plasma catalysis has emerged in the last two decades as an attractive solution to induce specific *de*NO_x reaction in excess of oxygen under mild thermal conditions, particularly for mobile and stationary sources. Plasma catalysis offers the advantages of the highly reactive plasma environment from room temperature not present in thermal catalysis where the reactions are temperature-driven, and the high selectivity of the catalyst. This leads to improving the energy efficiency, product selectivity, catalyst activation temperature, catalyst stability and lifetime, and sometimes shows a synergistic effect. The plasma promotes the low-temperature catalyst activation while providing a high NO_x conversion in a wide operating window (figure 20).

Plasma catalysis investigations demonstrate that very large variety of catalysts (metal oxides, supported metals, zeolites, etc) have been used mainly with dielectric barrier discharges (DBDs) in a post-plasma catalysis (PPC) configuration [157–161]. The in-plasma catalysis (IPC) configuration is rather dedicated to indoor air treatment [8]. Basically, the plasma provides the catalyst with a rich mixture of NO_2, oxygenates $C_xH_yO_z$ (alcohols, aldehydes), and intermediate organic nitroso-compounds R-NO_x (CH_3ONO, CH_3ONO_2, HNO_2, HNO_3, etc) (figure 21(a)). These species will be consumed by HC-SCR to release N_2 (figure 21(b)) [161]. For simulated diesel exhaust, 70% NO_x reduction into N_2 at an energy cost of about 20 eV/molecule has been achieved. However, these systems must be implemented and tested on real engine exhausts over a broad range of exhaust temperatures.

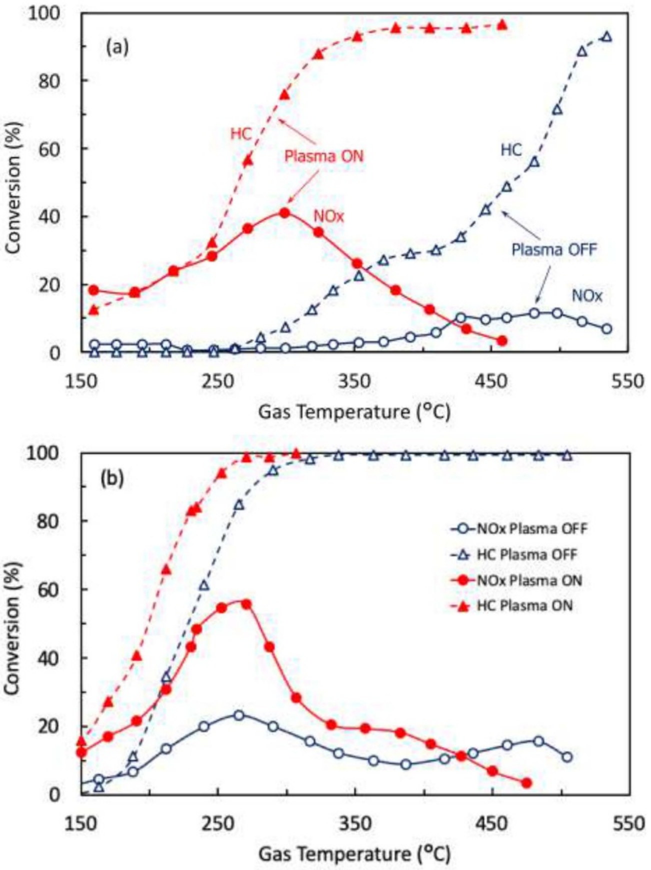

Figure 20. NO_x and total HC conversion versus temperature. Feed: C_3H_6 (2000 ppmC)-NO (500 ppm)-O_2 (8% vol.)-N_2: (a) Al_2O_3 catalyst and (b) composite catalyst Al_2O_3///Rh-Pd/$CeZrO_2$/// Ag/$CeZrO_2$ without and with plasma at an energy cost for NO_x (52% conversion) of about 20 eV/molecule. [161] John Wiley & Sons. Copyright © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Current and future challenges

It is still a challenge to develop catalysts that are tailored to the reactive plasma conditions. Scaling-up and optimization of the plasma catalysis *de*NO_x process with high energy efficiency has also proven to be a challenge for industrial applications. To reach this goal, it becomes clear that research efforts need to focus on understanding the mechanisms involved in the plasma catalysis coupling processes rather than those resulting from the sum of individual effects of plasma and catalyst acting separately in the same system [14].

Even though much has been accomplished (high *de*NO_x and N_2 selectivity) in lab-scale experiments (micro reactor, pure reductants, low space velocities, powder catalysts, narrow temperature range, etc), plasma catalysis faces several challenges on the way to achieve total conversion of engine-out emissions into N_2, CO_2, and H_2O. The transfer of the lab-scale *de*NO_x achievements to complex exhaust conditions with further process optimization and scaling-up to industrial prototypes remains one of the major challenges to date. This could include three interconnected fundamental levels: (i) precise

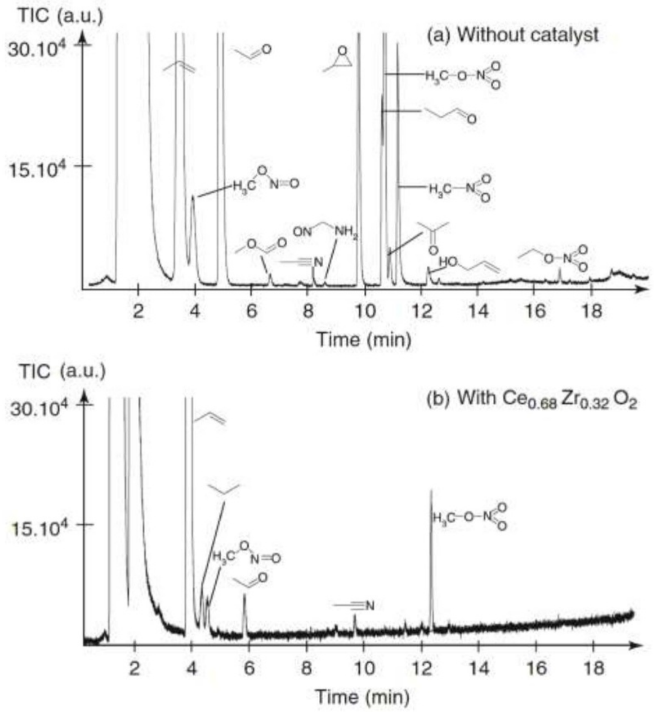

Figure 21. GC/MS analysis of C_3H_6 (2000 ppmC)-NO (500 ppm)-O_2 (8% vol.)-N_2 processing by DBD-plasma (36 J/L): (a) without catalyst and (b) with $CeZrO_2$ catalyst at 265 °C. [161] John Wiley & Sons. Copyright © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

identification of the plasma reactive species and deeper understanding of kinetic schemes and pathways, (ii) better understanding of the structure, properties, and functionality of catalysts used with plasma for specific materials of interest, and (iii) analyzing how the plasma reactive species may affect the catalyst (surface reactions on catalyst) and identifying the key parameters useful for the *de*NO_x process optimization.

Another challenge that is at the heart of the development of viable large-scale plasma catalysis for *de*NO_x is to reduce as much as possible the energy cost of the process to make it competitive for the industry. Although literature data make it difficult to evaluate and compare the energy efficiency of different reactors (disparity in plasma conditions), several ideas have been proposed in an attempt to minimize the energy consumption. For a given reactor, the plasma mode (pulse, alternating current (AC)), characteristics (high voltage amplitude, rise time, duration, frequency), and the efficiency of chemical reactions have to be considered. One possible way to lower the energy consumption is to manage the energy requirement for applications where the plasma is not used continuously (cold start regime for cars and trucks, desorption cycle for marine diesel, etc) [162]. The goal is to achieve more than 95% NO_x reduction under real diesel engine exhaust conditions using less than 5% of the total engine power (energy cost less than 30 eV/molecule).

Advances in science and technology to meet challenges

To optimize the plasma catalysis *de*NO_x process, it is crucial to clarify how to select the appropriate catalyst for this specific reaction and how to enhance the catalytic activity by plasma. One approach is to focus on the correlation between the characteristics of the catalysts (size, shape, dielectric constant, loading of active components) and their efficiency in plasma–catalyst induced reactions. The real-time control of the catalyst surface chemistry and reaction mechanisms under plasma conditions is becoming increasingly important and can be used to clarify the fundamental plasma-catalyst interactions in both IPC and PPC devices. This can be done by multidisciplinary collaborations between plasma physics, fluid dynamics, solid surface chemistry, and numerical modeling.

Moving *de*NO_x plasma catalysis technology to industrial interest requires large-scale reactors operating with large gas flow that can be achieved by combining multi-small reactors together. This necessarily implies additional energy consumption associated with plasma generation. To lower the energy cost and to improve the energy efficiency of the *de*NO_x process, a possible way is to deposit the appropriate amount of plasma energy in the required plasma modes [13, 163]. Along with it, the development of high efficiency cost-effective power supplies for this application is a challenging task. Research on new catalyst concepts with simplified formulation (focusing only on the reduction function) that can be scaled to larger dimensions that incorporate particularities already observed in plasma applications is also expected. One might take advantage of the synthesis of the catalysts by plasma, such as sputtering plasma treatment. This is a very versatile and efficient alternative technique for catalyst synthesis that allows the control of the layer deposition (from nanometer to micrometer range), the morphology, and texture of different metals and oxides (for more details, refer to next section 'Catalyst preparation/synthesis').

A unit catalyst (with a single cation or oxide) generally operates over very limited temperature range. Its deNO_x activity is limited according the nature of reductant and the temperature of NO activation (dissociation/reduction). To ensure high NO_x conversion in a broad operating temperature windows, multi-components catalysts, i.e. *composite catalysts* that combine several '*unit*' catalysts working in different temperature ranges, could be investigated as an alternative approach [161]. A narrow overlap of '*unit*' catalysts will be useful to get a continuous *de*NO_x activity of the *composite* catalyst even in an oxygen-rich environment. In that case, the plasma acts as a promoter by shifting the activation temperature window to lower values.

Finally, in addition to conventional diagnostic methods to provide catalyst surface structural data as well as spatially and time-resolved plasma gas phase species concentrations, infrared operando spectroscopy will be very helpful.

Concluding remarks

Although great achievements have been made by plasma catalysis in the environmental field, especially for removing NO_x, SO_x, volatile organic compounds and particulate matter from exhaust gases at low temperature, there still exist significant technological and research challenges to overcome, such as: designing a low-cost catalyst with high reactivity, efficiency and stability; a simultaneous control of the plasma characteristics and catalyst chemical reactivity; and optimization and scale-up of the process to make it competitive for industry. Solving these challenges requires improvements in basic understandings of plasma, catalysts, and especially plasma–catalyst interactions, before applying this knowledge to make process design modifications in connection with large-scale development. The development of novel computational modelling and simulations, combined with plasma and surface diagnostics, should contribute significantly to the field.

Acknowledgments

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12. Catalyst preparation/synthesis

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Status

Designing more efficient processes to synthesize relevant to society specialty products such as fuels and fertilizers is a major goal in the chemical industry. Significant steps toward this goal often require breakthroughs in catalyst design and catalytic processes. Besides the possibility of a less energetic pathway leading to high quality materials, plasma technology has the potential to provide a convenient and effective route to make possible the ultrafast synthesis of materials with unique properties for several important applications. Moreover, the high-energy characteristic of plasma allows the synthesis of materials that are otherwise challenging to obtain, such as carbon-based structures, fluorides, borides and nitrides. Plasmas can be employed to synthesize and modify materials for catalysis purposes [164]. Such modifications can take place during the plasma catalysis process itself. Typically, plasmas have been employed for the synthesis of materials in the following main cases: (1) plasma synthesis of ultrafine particle catalysts, (2) plasma assisted deposition and dispersion of catalytic active phases on different supports, and (3) plasma enhanced preparation/treatment of catalysts. The main distinctive advantages of using plasma as compared to traditional/conventional approaches are: (1) reduced energy requirements which can allow the use of thermal sensitive materials and control over the quality of the synthesized materials, i.e. crystallinity, morphology and texture, (2) the presence of highly active gas species which can lead to new synthesis mechanisms, (3) short synthesis time, which can be coupled with innovative reactor designs paired with renewable electricity sources, resulting in successful scalability of plasma synthesis/treatment of catalysts, and (4) enhanced catalyst performance including: activation, selectivity, lifetime and regeneration. The latter can have a major implication in the plasma catalysis field for the synthesis of chemicals. These enhanced properties are the result of the plasma–surface interactions that depend heavily on the electric field distribution and other plasma related characteristics, including the gas pressure, the power coupling with the plasma and the chemical composition of the plasma gas phase, among others. In particular, the plasma gas phase correlates directly with the reaction rate during the plasma catalyst preparation process, leading to the preparation of unique catalytic materials. Other important variables that affect these rates are the electron density, the electron energy, the gas temperature and pressure, as well as the properties of the solids, liquids or gases in the plasma synthesis chamber. The plasma–surface interactions that lead to unusual properties are very complex and to date it is unclear how each individual plasma species affects the prepared catalyst. In fact, we are in the very early stages to fundamentally understand the plasma catalyst preparation process. Since the nature of plasma processes is complex and differs from neutral gas synthesis, a major roadblock to design effective materials to produce the next generation of catalysts when using plasma, is the lack of fundamental knowledge about the process. Furthermore, a better understanding of the effects of plasma on the catalyst and catalyst on plasma can help to recognize the role of plasma and its effects on the materials employed during plasma catalysis in order to fully exploit their potential. Types of plasma and their use in catalyst synthesis are shown in figure 22.

Current and future challenges

There are numerous distinctive catalytic materials with enhanced properties that can be obtained by plasma, such as model metal oxide supported catalysts to investigate fundamentals [165], and nanoparticles with narrow distribution and less tendency towards agglomeration as compared to thermal synthesis methods [166]. Other important examples include: metal catalysts with superior coke resistance [167], composites with improved catalytic activity as compared to the ones obtained by conventional chemical methods [168], and effective dispersion of metals as active phases into a porous matrix, allowing to incorporate metals that are otherwise challenging to integrate [169]. All of these are potential enhanced properties of a catalyst that can arise when it is exposed to plasma during plasma catalysis and have not been exploited.

The vast potential of plasma has been demonstrated by catalysts with possible active site dispersion control [170] and the production of high value tailored materials from waste, which can ensure a green transition towards the next generation of catalysts [171]. Different from traditional wet chemistry methods such as hydrothermal synthesis that requires high processing temperatures, long synthesis time and conveys the generation of a considerable amount of liquid waste, the enhanced properties of catalytic materials obtained when using plasma along with ultrafast, typically one-pot solvent free synthesis/treatment and the possibility of employing thermally sensitive supports, such as porous polymers and biomolecules, results in an advantageous overall green process.

If we expand the definition of plasma-catalyst synergism to a wider number of possible applications, we can consider it as an effective way of catalyst regeneration during the plasma-catalytic process itself. Plasma has shown to be an effective tool for catalyst regeneration [172], i.e. reduction of oxidized catalysts and poisoning/carbon deposits removal, mainly due to (1) the presence of highly active gas species and (2) the alteration of the surface to a more energetic state.

However, a clear correlation between synthesis process variables and the resultant behavior should be established in order to determine critical parameters to control with the purpose of achieving the desired effects. This scarce knowledge extends to plasma–liquid materials synthesis [173], where detailed space-time evolutions of the processes happening in the plasma liquid interactions are still required, i.e. processes in the solution, the plasma–liquid interface and the bulk plasma.

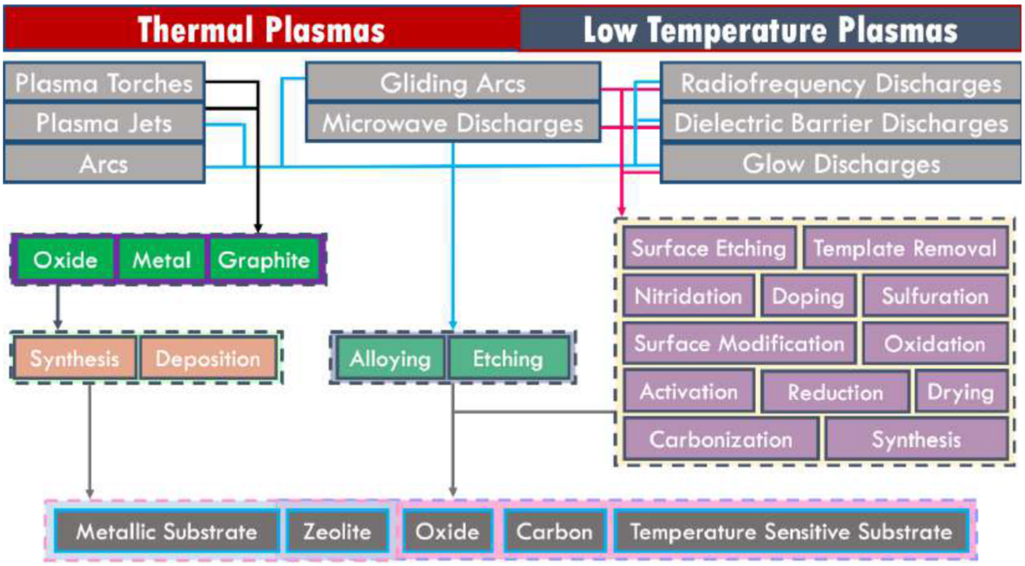

Figure 22. Types of plasma and their application in catalyst synthesis.

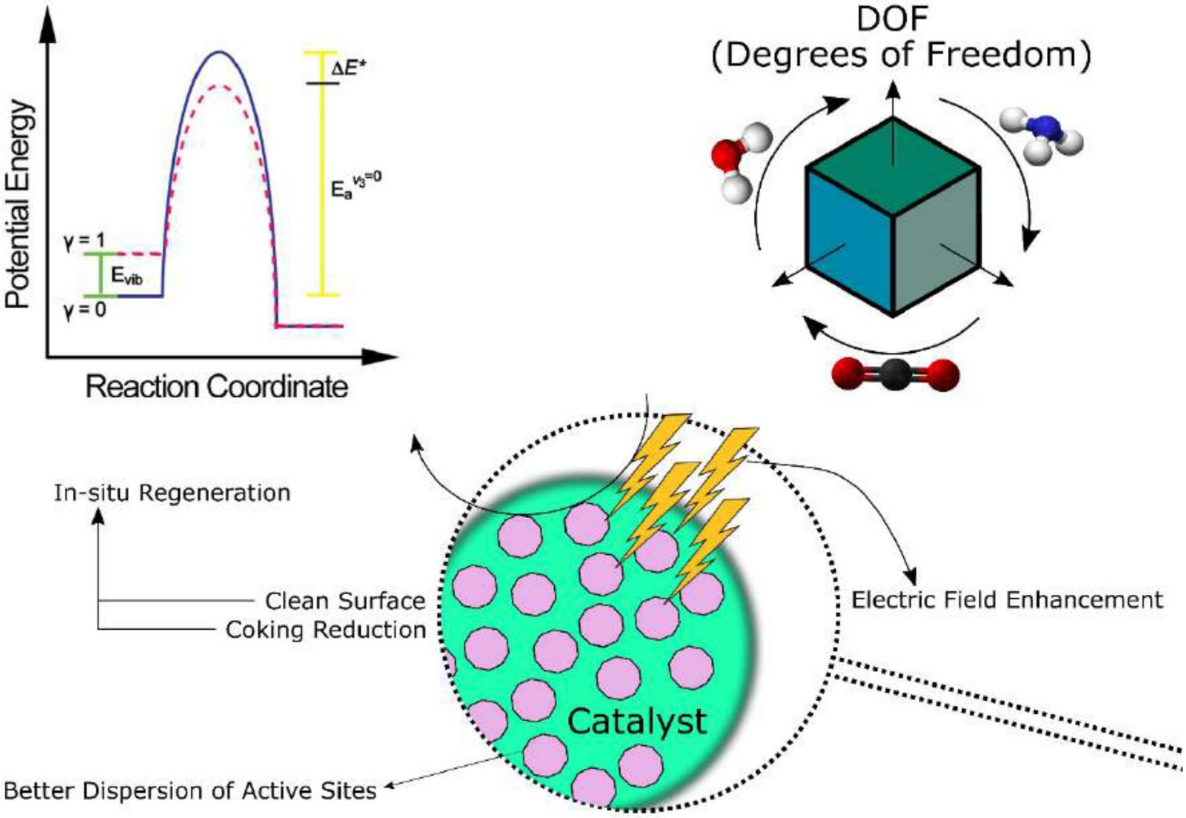

Figure 23. Plasma catalysis dynamic process. Adapted from [174]

Advances in science and technology needed to meet these challenges

Current significant challenges to overcome are the limited understanding of the plasma physics and chemistry associated with the non-equilibrium, along with the plasma generation technology necessary to provide uniform and stable plasmas. Moreover, a major challenge to fully exploit plasma catalysis is to clearly elucidate the effects of plasma on the catalyst. Plasma can impact the morphology of the catalyst due to direct exposure to plasma during plasma catalysis. These structural changes depend on the type of plasma employed and the chemical and mechanical stability of the catalyst employed, e.g. Ni-MOF-74 has shown lattice displacement when exposed to radio-frequency plasma at high powers [175]. Therefore, it is necessary to have a strong fundamental background of the plasma gas phase chemistry processes and the plasma–surface interactions which are determined to a large extent by the plasma electric field distribution, especially in the sheath, the gas pressure, the plasma chemical composition and the power coupling with plasma [13].

To further pave the future of plasma catalysis, it is required to set protocols and standard techniques for *in situ* probing and *operando* analysis to disclose the underlying mechanisms of plasma synthesis and to establish the role of plasma on catalytic materials. Several techniques currently employed for gaining this understanding in traditional thermal synthesis can be adapted properly to comprehend the plasma effects, such as mass spectrometry to measure the plasma properties in the vicinity of the catalyst–plasma interface. This can result not only in the rational design of catalysts with desirable textural, compositional, structural, and morphological properties, but in addition, to the successful application of this knowledge to make possible the *in situ* self-regeneration of catalysts during plasma catalysis. In this respect, an effective integration of experimental data with simulations leading to models that can provide a more realistic picture of the plasma-catalyst synergism is highly desirable. Moreover, scientific efforts should be centered on innovative reactor designs and plasma generation technology that can allow us to develop a fundamental understanding. This task will require the uttermost level of creativity, fundamental knowledge, engineering design and multidisciplinary collaboration to make it feasible. Additionally, it would be important to establish a link between different plasma processing branches as a possible route to further extend our knowledge on plasma interactions with different catalytic materials, especially between the fields of plasma catalysis and catalyst synthesis using plasma, as the combined understanding has great potential in shedding light on this complex plasma–surface interaction. Figure 23 shows the dynamics of plasma catalysis and its potential advantages when fully exploring the appropriate catalyst–plasma pair and process conditions.

Concluding remarks

Processes in plasma environments follow different pathways as compared to traditional synthesis approaches, such as hydrothermal synthesis or chemical vapor deposition. Engineering new generation catalysts with fine-tuned properties for diverse functional applications requires the use of innovative methods. The use of plasma is a powerful alternative, which can provide new eco-friendly routes to further design versatile materials with enhanced properties and positive impact on several reactions of great societal interest. The successful controlled synthesis of specialized targeted materials requires the development of improved *in situ* characterization techniques that, when coupled with simulations, will provide important fundamental information, specifically regarding the plasma–surface interface. In this respect, due to the wide variety of plasmas and reactors configurations, it would be necessary and important to converge general conclusions that can provide a general benefit to the plasma community. Moreover, this knowledge can help to exploit the positive effects of plasma on catalysts during the plasma catalysis process.

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