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Fundamental insights and emerging opportunities in plasma catalysis for light alkane conversion

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With increasingly available renewable sources of electricity, plasma catalysis could be a key component in the decarbonization of natural gas and greenhouse gas valorization. Fundamental insight is needed in both the coupling of plasma and catalytic chemistries, and in chemical limitations and opportunities of such coupled systems to enable larger scale engineering and optimization. This perspective describes some of the pressing needs and high-impact opportunities present in the current research landscape of plasma catalysis for light hydrocarbons.

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Introduction

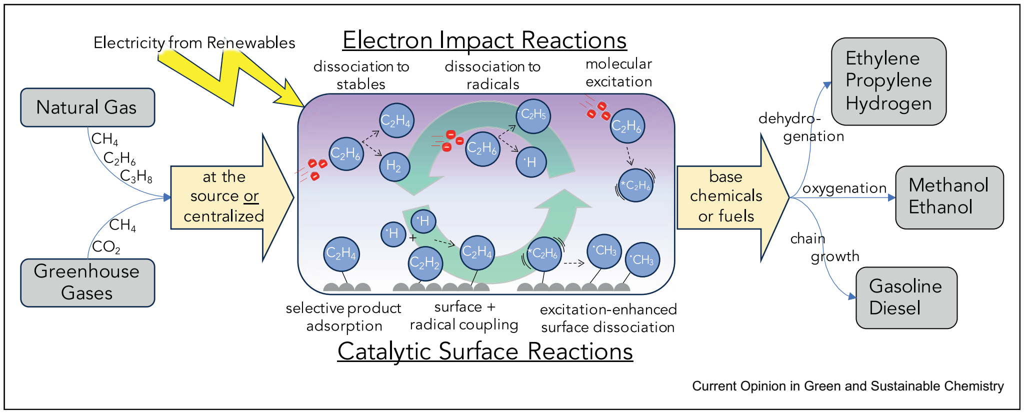
The use of natural gas—an abundant, energy-rich natural resource—throughout the world is predicted to grow in the coming decades [1], due to the value of the energy and the base-chemical products that can come from natural gas. Given the large carbon footprint of recovering and processing natural gas, namely the release of large amounts of both CH_4 and CO_2, finding decarbonized options for these processes has great potential for greenhouse gas (GHG) reduction [2]. Plasma catalysis, which is powered by electricity and at mild conditions, has the potential to convert the intrinsically nonreactive components of both natural gas and GHGs directly into valuable base-chemicals, fuels, and hydrogen [3, 4]. Other sources of light alkanes—such as biogas or industrial waste streams—could also be processed using plasma catalysis, and this only serves to strengthen the motivation of studying these processes on a fundamental level. As shown in Figure 1, these feedstocks are converted through a combination of plasma-phase gaseous reactions (driven by electron-impact reactions) and surface reactions. The plasma-phase reactions can include molecular excitations, dissociation into either radical or stable species, and radical recombination. Figure 1 uses ethane as an example and demonstrates an excited ethane dissociating into ethylene and hydrogen, which can react further to acetylene in a continued dehydrogenation. Alternatively, dissociation into methyl radicals can lead to the less-economically favorable methane; of course, the production of radicals leads to a highly active chemical environment and does not necessarily result in methane alone. When a catalyst is introduced, plasma-produced species can move to and interact with a solid interface, and, again using ethane as an example, this catalytic surface could selectively adsorb key products to prevent further reaction. Alternatively, a catalyst surface could be engineered to promote specific chemistry to increase selectivity to desired products, such as hydrogenation of acetylene to ethylene. An important factor that differentiates plasma catalysis from thermal chemistry is the presence of excited species impacting the surface, leading to events such as excitation-enhanced surface dissociation, again as shown in Figure 1.

Despite years of promising research, a nonthermal plasma-based process for converting light hydrocarbons has not yet been commercialized. As with many emerging technologies, research has thus tended to focus toward demonstrating the potential of plasma catalysis, rather than pursuing fundamental insights. We argue that the field is mature enough to justify more rigorous foundational studies. This perspective highlights the need for deeper research to advance plasma catalysis for chemical production from light hydrocarbons and suggests future directions with the greatest potential impact.

Challenges and limitations

The field of plasma catalysis for light hydrocarbon conversion, while full of opportunities for decarbonized chemical processing, is limited by inherent challenges including selectivity, efficiency, material limitations, and issues in coupling the plasma and catalytic chemistries.

Figure 1



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Overview of the potential use of plasma catalysis in light hydrocarbon conversion. Sources include natural gas and GHGs, which can be converted with modular plasma catalysis technology at the source or with larger-scale reactors in a centralized refinery. Within the plasma phase, the chemistry is promoted by electron-impact driven processes, including excitations and dissociation to both stable and radical species. On the surface, some processes well-known to the thermal catalysis community–including selective adsorption, combination, and dissociation–occur, and in some cases these reactions are enhanced by the highly-energetic species coming from the plasma phase. Many potential chemistries can be realized in plasma catalysis leading to a variety of more valuable products.

Although these challenges are intrinsic, increasing fundamental understanding of reaction mechanisms, energy flow, and material stability will provide tools to engineer solutions. Some of the known challenges and limitations, as presented in the literature, are described below, in the hopes of defining problems for the field to address.

Kinetic and selectivity challenges

Plasma chemistry for hydrocarbon reforming is driven by high-energy electrons and is therefore so rapid that addressing kinetic limitations is not restricted to improving the rate of reaction [5]. The main kinetic challenges for useful plasma-driven catalysis lie in efficient coupling to catalysts for selectivity while maintaining high conversion. Unique to plasma catalysis are the radicals and excited species, produced by the highly active plasma phase, that impact a catalyst surface. For the lightest molecules (CO_2, H_2, and CH_4, etc.), vibrational excitations from electron-collision promote dissociation into radical species [6]. For heavier hydrocarbons, more energetic electronic excitations are required [7]. The relatively high density of radicals leads to a balance of competing surface chemistries; radicals adsorb more readily than closed shell species and lead to saturated surfaces and Langmuir–Hinshelwood reactions [8]. Eley-Rideal type reactions also become increasingly important with radicals due to the high-activity of radical species in the gas phase [9]. Understanding how the kinetics of these processes compete will lead to better insight into opportunities and challenges in coupling of the plasma and catalytic chemistry. Evidence in the literature suggests that catalysts have the potential to promote selective conversion of light hydrocarbons in plasma [9,10]. However, while high conversion is possible in plasma chemistry, there is a selectivity trade off because the products desorbing from a catalyst re-enter the highly active plasma phase and are likely to react, possibly back to reactants. One solution is finding plasma conditions that limit degradation of catalyst-produced species. Other solutions include pulsed power sources, pulsed delivery of feedstocks, postplasma catalysis, and alternative reactor configurations/designs that inhibit these unwanted effects.

Thermodynamic challenges

Because nonthermal plasmas are intrinsically nonequilibrium, they can drive energy-consuming (endergonic) reactions even at low temperatures [11]. This property makes them particularly appealing for reducing the energy use in chemical processes, but it also creates challenges in properly designing and controlling these processes. Equilibrium thermodynamics are not applicable to plasma-driven chemistry [12]. For example, plasma catalytic methane dry reforming (DRM) is observed to proceed at conditions at which bulk thermodynamics predict conversion to be zero [13]. However, most research on DRM focuses on kinetics rather than the fundamental behavior relative to bulk thermodynamics [14]. Theoretical frameworks to predict the steady state of any chemical system under the influence of a nonequilibrium plasma exist but remain to be fully validated [12,15]. Such tools offer the promise of predicting theoretical performance limits in analogy to those provided by conventional thermodynamics, and will be invaluable as inputs to higher level models for system selection and optimization.

Durability/regeneration challenges

Coking remains as prevalent an issue in plasma catalysis as it is in thermal catalysis. Even at ambient temperatures, the hydrocarbon radicals formed in the plasma phase tend to adsorb to available surfaces and grow an amorphous, hydrogen-rich carbon (a-C:H) film through radical additions to dangling bonds [16]. This a-C:H film blocks catalyst pores and will readily form on the walls and electrodes of the reactor, negatively altering the characteristics of the plasma itself. Mitigation of this form of coke is not trivial, but promising results have recently been achieved by altering the reactor's materials of construction [16,17], by adding an oxidant to the feed [18–20], and by choosing plasma conditions that facilitate the desorption of coke precursors [21]. There are also encouraging results regenerating coked catalysts with oxidative plasma, which requires lower temperatures and pressures compared to thermal regeneration [22]. However, this area tends to focus on the effect of oxygen plasma on coke and overlooks its effect on the catalyst itself. Similarly, knowledge of the precise physical and chemical effects of hydrocarbon plasmas on catalytic materials is missing from the current literature. Thus, it is largely unknown how, or even if, hydrocarbon plasma deactivates catalysts through the traditional routes of sintering and leaching. More fundamental studies focusing on the stability of catalysts in hydrocarbon plasma, possibly utilizing in situ/operando methods, are needed to meet this challenge.

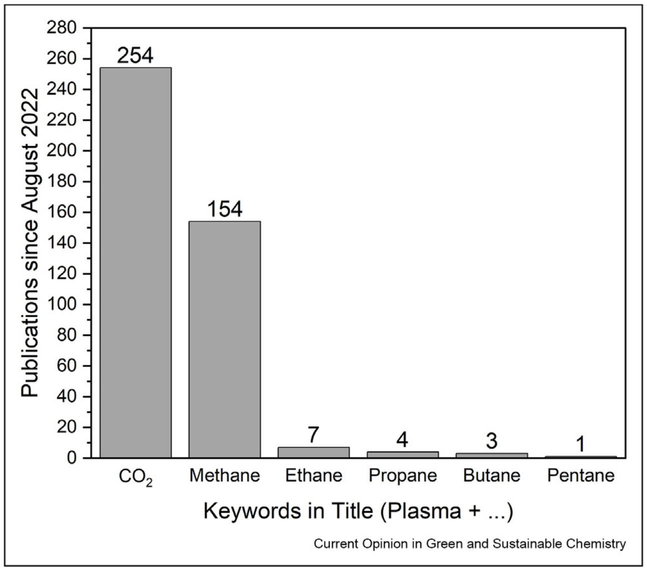
Efficiency challenges

Energy efficiency is considered perhaps the largest barrier preventing the realization of a plasma-based commercial process to convert hydrocarbons. A recent study on plasma nonoxidative ethane dehydrogenation reported the highest achieved energy yield of 90 mmol ethylene per kWh (or 0.025 mmol ethylene per kJ), which corresponds to 0.34 % reaction efficiency, two orders of magnitude below the typical efficiency of a commercial ethane steam cracker (1.5–1.9 mmol ethylene per kJ) [10,23]. Although nanosecond pulsed sources can enhance efficiency [24], progress in this area is hindered by inconsistent data reporting, a lack of standards for determining energy efficiency, and little historical knowledge about how scale-up will affect energy consumption and recovery. However, we assert that plasma-based processes do not yet (and may never need to) compete in the same market as established large-scale commercial processes such as steam cracking, and thus direct efficiency comparisons do not necessarily report on the potential for a plasma process. Rather, plasma-based processes are best suited to nonefficiency centric applications, such as when an abundance of electrical energy is available (e.g., aboard nuclear-powered vessels or during nonpeak electricity demand hours) or when small-footprint, point-of-use reactors are required (e.g., to upcycle the side-products of an ethane cracker). Thus, while understanding and improving energy efficiency represents an impactful opportunity for fundamental study in plasma-catalysis, it is not paramount to the commercial success of the field. Techno-economic analyses for specific applications are ultimately necessary to determine the economic and commercial potential of any specific plasma-catalytic light alkane process, and life cycle assessments are needed to fully understand the environmental benefits and costs of plasma processes relative to other alternatives, especially those (e.g., electrochemical; photochemical) that similarly can be driven by renewable electricity.

Future opportunities and advances needed to meet challenges

The large majority of light alkane plasma work has focused on methane (Figure 2), which reflects its relative abundance in shale gas. However, methane plasmas contain a significant fraction of C2–C3 hydrocarbons that are rarely studied independently in the plasma catalysis literature despite also being significant components of shale gas. Other examples of largely untapped research areas with significant opportunity to provide fundamental insights to more mainstream topics include simulated shale gas feeds [25], carbon-heteroatom coupling [16,25,26], and the effect of temperature on the plasma [27]. If plasma is to overcome the challenges outlined above and contribute to the electrification of the chemical industry, then significant

Figure 2



Number of articles published since August 2022 with keywords "plasma" and "CO_2/methane/ethane/propane/butane/pentane" in the title. Web of Science. Accessed 8/26/2024.

advances are needed in the key areas of plasma modeling, in situ/operando methods, and plasma-material dynamics.

Standardization of results

There is a pressing need within the plasma catalysis community for standard practices that support comparisons across experiments, reactors, and laboratories. Standardization is complicated by the interconnected nature of the multiple parameters present in a single plasma catalysis experiment. For example, it has been suggested that the field adopt standard plasma sources and/or standard catalytic materials that would provide a basis for comparison [28]. This approach may present challenges in yielding meaningful comparisons, as the catalyst and plasma are coupled and cannot be truly isolated from each other. Thus, for a standard to be successful, it must consider plasma and catalyst as a single unit and be able to normalize and compare them with other units. This is currently accomplished with "black box" evaluations that do not depend on the nature of the technology (e.g., conversion-selectivity plots and efficiency reports), in addition to comprehensive reporting of experimental conditions in accordance with good laboratory practices [29]. Recent attempts to consolidate recommended best practices have been made in both the plasma-catalysis community [30] and nonthermal plasma community at large [31]; the most appropriate quantities to measure and how to measure them remains to be agreed upon.

In situ and operando studies

As in traditional heterogeneous catalysis, in situ/operando spectroscopies (i.e., observation during operation, ideally with simultaneous observation of performance) promise to deliver molecular-level insight by revealing the state of the plasma and catalyst under relevant operating conditions. The challenges are amplified, however, by the dynamic (temporal, spatial, compositional) character of the plasma as well as the catalytic surface. There have been several notable in situ plasma techniques developed in the past couple years [32–37], but has this direction actually led to more fundamental understanding and is it worth continuing? We argue that both answers are yes. It is (so far) unrealistic to expect to observe, in situ/operando, transient events that have time scales of a plasma filament lifetime or likely even the response of a catalyst to a transient filament. Thus, the value of in situ/operando techniques rather lies in connecting the dots between the initial state and the final state of the catalyst as it turns over. This sub-field has produced recent discoveries on key differences between plasma-catalysis and thermal-catalysis mechanisms for CO_2 hydrogenation [36,38], oxide hydrogenation [34], and amine oxidation [32], giving a starting point for the rational design of *plasma*-specific catalysts and justifying the existence of the field. However, the results to date narrowly apply to specific cases, which leaves significant room for further in situ studies probing light alkane chemistries.

Modeling

Plasma-catalytic models begin with mechanisms and kinetic parameters to describe the chemistries in homogeneous and heterogeneous phases. While the thermal and, to a lesser extent, surface reactions of reactive hydrocarbon intermediates are available from the combustion and heterogeneous catalysis communities, electron impact cross-sections for hydrocarbons of carbon number greater than propane are absent from the popular LxCat.net database [39]. Thus, reliable data, either from observations or models [40], will be necessary to predict the efficiency and products of electron impact reactions with higher hydrocarbons. Insights from models on the lower hydrocarbons will provide insights into potential opportunities and potentially even useful approximate representations for the higher homologs.

Typical plasma technologies used for plasma catalysis applications are inherently inhomogeneous, either spatially due to filamentary behaviors or temporally in AC and pulsed plasmas [41]. This inhomogeneity poses both limitations and possibilities for plasma catalysis, but in either case, it creates a significant challenge for modeling efforts. Assumptions must be made that simplify the complexity of inhomogeneous modeling, and the validity of these assumptions must be rationalized. Machine learning has been used to either decrease the computational cost of low-assumption models, such as fluid-based techniques [42], or to make up for assumption-induced errors by tuning models to experimental data and exploring optimization of those systems [43–45]. Other studies validate assumptions based on theoretical standing (including density functional theory results) [9,46–48] or based on the ability for a model to recover experimental observations without tuning [26,49].

The community has often measured the success of a model by its ability to faithfully recover experimental observations, typically with the constraint that the underlying model assumptions (mechanisms, plasma characteristics, ...) are physically robust and as complete as possible [9,14,45]. In our opinion, there exists an opportunity and a need to develop models that explore the fundamental boundaries of plasma catalysis, that identify the characteristics (of plasma, of material, of their coupling and operation) necessary to achieve a desired performance. Such discovery-focused models are more forward-looking, designed to provide guidance for new plasma-catalysis materials, reactor designs, and operating strategies, as opposed to rationalization of existing observations. A salient analogy is the growing interest in dynamic catalysis, inspired first by discovery models that pointed to its potential [50]. As in the dynamic catalysis case, discovery-focused plasma catalytic models would point the community in the most productive directions and inspire creative engineering. And as in the dynamic catalysis case, ultimately those predictions must be realized and validated in the laboratory. These models, in conjunction with insights provided by traditional, validation-focused models, would provide the community with expanded capability, inspire creative engineering, and point the direction toward practically useful plasma catalysis.

Plasma-material dynamics

The physics of plasma-material interactions are fairly well known from the extensive use of plasmas in the semiconductor industry [51] and in nuclear fusion [52]. Plasma-material interaction physics that are relevant for plasma catalysis—including sheath physics for multiphysics modeling, mechanisms of electric field enhancement by surfaces, and descriptions of high-energy-particle collisions with materials—are increasingly being applied [5]. Recent experimental studies [16,53,54] look at how a plasma alters a surface and how it changes because of the surface of a catalyst particle, both with and without metal loading, and with metal electrodes. These studies reveal that localization of plasma intensity around the edge of catalyst particles, and on the electrode itself, can enhance the chemistry; thus, an opportunity exists to exploit this synergistic intensification within plasma catalysis, if the enhancement can be properly engineered. Simultaneously, carbon growth (e.g., coking) and hotspots that lead to catalyst degradation can be better avoided with insight of the plasma—surface interactions. Additionally, there is an opportunity to use the unique properties of plasmas to alter catalyst particles, including catalyst regeneration and preparation [55,56]. Reactor designs should be explored to investigate whether these alterations could be implemented in situ for improved reactor performance in real time.

Bridging the scale-up gap

There are several real-world examples of scaled-up plasma reactors currently being used for pollution treatment (ozone production, NO_x and SO_x removal, breakdown of particulate matter) [57]. These commercial reactors provide a starting point for the cost, design, and operation of a plasma reactor for light hydrocarbon applications. However, processing light hydrocarbon feedstocks for chemical production comes with additional challenges, such as coke production, robustness to mixed reactant feeds, and product selectivity acceptable to a given application. The responsibility to de-risk these obstacles falls to the research community. In practice, this requires long-term, high throughput testing of the most promising setups under realistic conditions. While such experiments are unlikely to yield significant fundamental insight, they are nevertheless important to advancing the field. There is also merit to considering alternative reactor design strategies that make sense at scale, but have less efficacy in lab-based research. For instance, plasma catalysis may be amenable to chemical looping strategies that decouple the reactant consumption stage from the product generation stage and allow products to be collected without downstream separation steps [58,59].

Concluding remarks

This perspective highlights the fundamental insights gained recently in plasma catalysis, while also pointing out where there is still a need for future insight and innovation. As the energy and chemicals landscape tilts toward decentralized carbon sources, point-of-use reactors that make use of local available energy will become increasingly important. Plasma catalysis is well-poised to be successful in this space, particularly as renewable energy becomes more readily available and less expensive. To capitalize on this potential, the community must resist the temptation to conduct “sandwich” studies that merely report the results from a random combination of plasma type, catalyst, support, feed, chemistry, etc. [60]. Rather, there is significantly more interest in studies that seek to understand the dynamics between catalyst and plasma, particularly in the areas of computational modeling and in situ/operando methods. Overall, we believe that fundamental insights do have the potential to guide plasma-catalytic light alkane conversion toward a positive role in lowering the carbon footprint of the energy and chemicals industries.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used ChatGPT in order to improve readability. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data were used for the research described in the article.

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* * of outstanding interest

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A review of plasma and plasma-catalytic studies of DRM and an exposition of a new coupled surface-plasma chemistry kinetic model. Description of the state of the field and needs for standardization of experimental reporting to improve comparison between various material types and operating conditions. The presented model addresses intrinsic inhomogeneities–including spatial, temporal, and environmental. The authors use the model to reveal the impact of radical species on the sometimes (and surprisingly) negative impact of transition metal catalysts on plasma-catalytic DRM.

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This article is notable for being the first and only work to study non-oxidative ethane plasma over a packed bed, thus also achieving the current best efficiency (0.09 mol C_2H_4/kWh) for ethane dehydrogenation with a plasma. The main products were ethylene, acetylene, and methane, with small fractions of C4–C5 hydrocarbons also detected. Ethylene selectivity was mostly dependent on ethane conversion because higher conversions led to more plasma–product interactions that consume ethylene and decrease its selectivity. The dielectric properties of the packed bed were found to have little overall effect on the selectivity, although Pd/SiO_2 packing was found to slightly favor saturated products due to thermally catalyzed hydrogenation reactions with the plasma-produced hydrogen.

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In previous work, Thimsen described a novel approach for thermodynamic analysis of non-equilibrium plasmas. His approach uses the entropy generated by work and energy flow through the system—electric work and V-T relaxation—to predict stationary states of the system. The paper cited here, by Chen and Thimsen, expands on one of the insights from the non-equilibrium thermodynamic analysis, namely that the stationary state composition of a system is dependent on the relative atomic amounts in the inlet and is insensitive to the molecular composition of the inlet. This analysis was applied to (reverse) water-gas shift. Thermodynamic analysis tools like those used in this and other papers from the Thimsen group will be critical for informed design of plasma catalytic systems.

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