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Plasma-driven decentralized production of essential chemicals

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Non-thermal plasma offers a remarkable alternative to traditional catalysis methods, meeting the rising demands for essential chemicals like fertilizers and fuels. This Comment explores how this approach can support sustainability goals by promoting economic growth, and decentralizing chemical production processes.

Current societal commodities are predominantly developed from fossil sources through thermal catalysis, built on years of knowledge development and implementation. While these methods have been refined over time, the increasing demand for resources and the urgent need to address environmental sustainability highlight the limitations of conventional approaches. Given the scale of environmental challenges alongside societal needs, it is evident that alternative catalytic processes are essential for the future, with a focus on responsible production and innovative, decentralized infrastructure.

The cost-effective implementation of solar and wind energy during the past decade serves as motivation to look for reaction systems that can be deployed on a decentralized basis, reducing the reliance on fossil-powered processes. An approach to decentralizing essential chemical production is the integration of renewable energy into electron-driven chemical reactions. These reactions not only offer the potential for small-scale, modular production and storage but also reduce transportation costs, associated emissions, and provide local employment opportunities, resulting in a smaller carbon footprint. To fully harness the potential of such decentralized production, rapid and efficient conversion technologies are crucial.

One such technology is non-thermal plasma, which presents a unique advantage in decentralized setups by offering instant on/off operation capabilities – unlike traditional thermal catalysis that requires extended times to ramp up or down. This flexibility allows chemical production to be more closely aligned with regional demand, minimizing the risks of overproduction, and ensuring efficient use of resources.

Non-thermal plasma also enables non-equilibrium reactions that are often inaccessible to conventional thermal catalysis. Through the use of electrical energy, plasma can activate highly stable molecules such as CO_2, CH_4, and N_2, which contain elements essential for human development. Plasma's unique physicochemical properties, including high energy content and a rich gas chemistry involving electrons, radicals, ions, neutrals, excited species, and photons, can facilitate these reactions. While electron collisions can effectively break down these stable molecules to serve as precursors for essential chemical production, this process alone often lacks selectivity toward desired products.

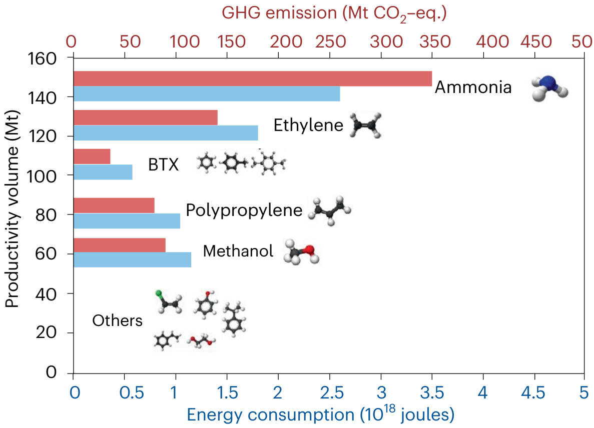

Fig. 1 | Production of essential chemicals. Production volumes, greenhouse gas (GHG) emissions, and energy consumption within the chemical industry, with an emphasis on essential chemicals such as ammonia, ethylene, benzene, toluene, xylene (BTX), propylene, and methanol[1]. Each of these chemicals play a fundamental role in various sectors – such as fertilizers, plastics, and synthetic fibre – contributing to the global economy while also significantly impacting environmental emissions and energy demands. This figure provides a brief comparative analysis, highlighting the different energy requirements and GHG emission intensities, allowing an initial evaluation on the environmental impacts. Improvements in catalytic efficiency, process electrification, and green hydrogen integration present potential opportunities to reduce the chemical industry's carbon footprint.

Plasma catalysis and essential chemicals

In plasma catalysis, which is the combination of plasma and a catalyst to produce a synergistic effect, electron collisions play a crucial role by dissociating reactants. However, the process goes beyond simple electron impact. Radicals, ions, and other reactive species generated within the plasma environment also contribute significantly to the formation of products. The catalyst in this case can help to guide the evolution of these plasma-generated species, creating a complex interaction network that enhances the overall reaction performance. The result is the opening of alternative reaction channels, which accelerates the process and boosts its potential for efficient power-to-chemical production, with outcomes far more effective than plasma or catalyst alone.

This potential for enhanced chemical production through plasma catalysis aligns well with the goals of decentralized processes, which can be leveraged as chemical energy storage systems. By utilizing electricity from renewable energy sources, these systems can produce essential chemicals such as methanol, ammonia, and hydrogen. These molecules (Fig. 1) dominate the chemical industry in terms of production volume, investment, energy consumption, and carbon emissions, collectively accounting for around 60% of the industry's energy use and 75% of direct and energy-related greenhouse gas (GHG) emissions[1].

The current challenge lies in progressing from demonstrating plasma activation to rational process development, an endeavour hindered by the acknowledged lack of mechanistic understanding of reactions under plasma conditions. This gap in understanding stems from the complexity of plasma–catalyst systems. While it is recognized that synergy — performance greater than the sum of the parts — can occur when the right catalyst is exposed to the right plasma conditions, the rational design of an optimal plasma–catalyst pair is not yet possible, a crucial weakness the community is currently striving to address.

The complexity of plasma catalysis is evident in several factors: the involvement of species not typically found in thermocatalysis, such as radicals, vibrationally and electronically excited molecules, photons, ions, and electrons; the presence of more complex reaction networks than in thermocatalysis; the influence of electronically altered catalysts, such as negatively charged surfaces; the effects of electric fields near the catalyst surface; and presumed differences between the composition of the plasma bulk and the plasma in the vicinity of the catalyst surface.

The main challenge experimentalists encounter is the difficulty of disentangling the various factors that impact performance. Computationally, the challenge lies in the complexity of modelling all these factors simultaneously. Many parameters required by complex models are often derived from multivariable regression techniques, such as linear regression, polynomial regression, or stepwise regression. However, these methods can sometimes lead to issues such as non-unique solutions or overfitting, which raise concerns about the physical relevance of the parameters, and consequently, the validity of the model insights. Therefore, a strong feedback loop between modelling and advanced experimental strategies is essential to overcome the current limitations in the field of plasma catalysis.

Moreover, the heavy dependence of non-thermal plasma processes on renewable energy sources, highlights the importance of renewable energy infrastructure. Although such infrastructure requires a high upfront investment, it offers competitive long-term operational costs, with a typical payback period of five to ten years. Despite continuous advancements that are driving down costs, non-renewable energy sources still dominate the global energy landscape, creating significant barriers to widespread adoption. Plasma reactors, with their inherent flexibility and precise control, are well-suited for optimizing the utilization of renewable energy, though they do not directly enhance its accessibility. The integration of pulsed plasma discharge technology with renewable energy systems could facilitate more efficient management of surplus energy, potentially playing a critical role in enhancing overall energy efficiency.

Plasma adaptability to renewables, added to the variety of discharges available such as dielectric barrier discharge, microwave, arc, radio frequency make it versatile and competitive for deployable, small-scale production, which contrasts with conventional thermal catalytic processes that require large-scale centralized plants to be economically viable. Added to this, cold plasma market size is expected to reach US$3.3 billion by 2026, a further growth that is in part predicted by the innovations in cold plasma technology.

Among the basic chemical production processes, ammonia and methanol syntheses offer a unique opportunity for decarbonization using non-thermal plasma technologies. In terms of ammonia synthesis, alternative hydrogen sources such as water along with air can be used for on-site production of fertilizers, the main use of ammonia, with the added benefit of being a promising alternative to reduce CO_2 emissions. And a visible capacity to help local economies to flourish.

A comparative analysis of ammonia production through plasma and thermal routes displays notable differences in required energy (eV), type of catalysts employed, and overall efficiency. For example, the plasma-only (no catalyst) route requires 383.19 kJ $mmol^{-1}$ (ref. 2), whereas the plasma + catalysis route with Ru–Mg/Al_2O_3 requires only 2.40 kJ $mmol^{-1}$ (ref. 3). In contrast, the thermal catalytic route based on the recently developed Ru/C12A7:e^- requires 0.039 kJ $mmol^{-1}$ (ref. 4). Clearly, the presence of a catalyst has the potential to lower the energy requirements for the essential chemical synthesis routes based on plasma. This highlights the need for designing better catalytic systems for plasma environments to make them more energy-competitive.

For methanol synthesis, plasma offers non-traditional reaction pathways that are critical for one-step formation from greenhouse gases like CO_2 and CH_4. Unlike the multi-step thermal processes, plasma-based methods have consistently achieved direct methanol synthesis. Several studies report methanol formation at atmospheric pressure, in stark contrast to the high-pressure conditions required in traditional thermal catalysis, for example from syngas, which requires high pressure (5–10 MPa) (ref. 5).

The following sections will explore these examples in detail.

Plasma catalytic ammonia synthesis

Ammonia can provide a cost-effective and efficient method to transport and store hydrogen. Besides its role as energy carrier, it can be used directly as a fuel in thermal power generation. Ammonia does not emit carbon dioxide when burned, hence offers a unique opportunity to reduce GHG emissions. This has led to significant efforts to develop technologies for its direct use, including current strategies like ammonia–coal co-firing, with the potential for further advancements towards fully ammonia-powered burners.

Moreover, ammonia is essential for food security due to its use in the production of fertilizers. Ammonia synthesis is currently based on the Haber–Bosch process (typically at up to 500 °C and 500 bar), which is one of the most energy-consuming process in the chemical industry. Due to the energy-intensive nature and scale required for the Haber–Bosch process, ammonia production is typically centralized in large plants. While this ensures efficient mass production, it can limit the accessibility of locally produced, affordable fertilizers in remote agricultural areas, where transportation costs add significant burdens.

The development of simplified alternatives to Haber–Bosch at milder conditions and compatible with intermittent electric power (for example, from renewable energy sources) is a critical step toward small-scale, decentralized ammonia production. Explored alternatives include synthesis at 1 bar by decoupling dissociation of H_2 and N_2 in membrane reactors[6] or by proton-based activation of N_2 in electrochemical cells[7]. Studies on the latter have been driven by the prospect of affordable renewable electricity — that would also reduce the carbon footprint of the process — as energy prices continue to fall. The main issue with electrochemical N_2 reduction is poor selectivity as H_2 is overwhelmingly the preferred product, with current efforts focused on addressing this issue.

Figure 2 shows the plausible decentralized pathway for ammonia production when employing plasma catalysis.

Plasma catalysis for methanol synthesis

Co-conversion of GHGs CO_2 and CH_4 under plasma conditions (plasma catalysis dry methane reforming, DMR) to methanol has been demonstrated in both dielectric barrier discharge and microwave reactors.

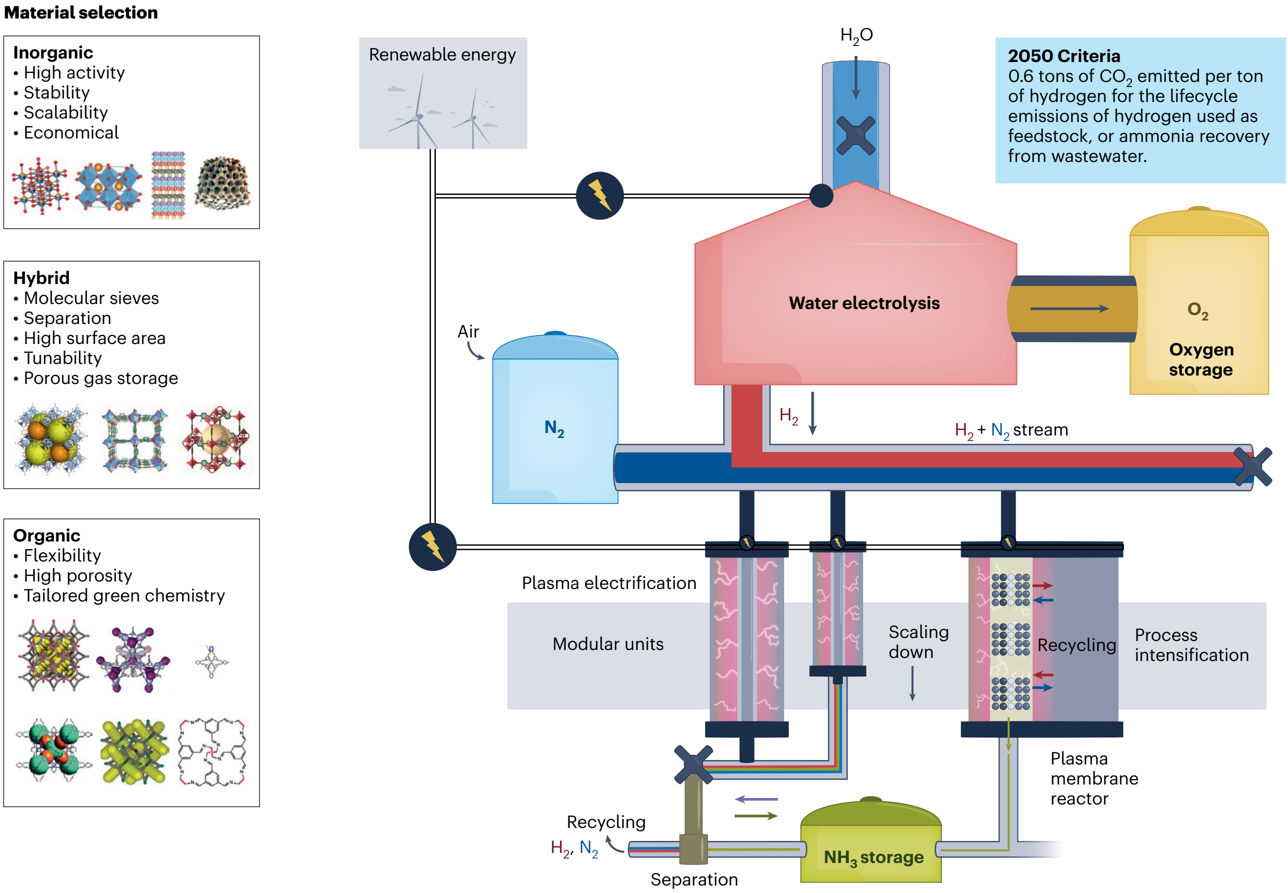

Fig. 2 | Ammonia decarbonization via plasma catalysis. This figure illustrates key challenges and possible advanced strategies in ammonia synthesis through plasma catalysis. It highlights the integration of multi-stage reactors, recycling systems, and separation membrane technology as part of a vision for electrified, low-emission chemical processes. These innovations aim to enhance efficiency and selectivity in plasma-based ammonia synthesis, paving the way for sustainable, electrified production pathways with reduced greenhouse gas emissions.

There is a wide distribution of products (unsurprising given the plasma complexity), but it is important to emphasize the exciting detection of methanol, in some cases with selectivities as high as ~50% with selected oxidants. In Fig. 3, it can be observed that the conversion of methane to methanol has been explored in combination with various oxidants such as N_2O, CO_2, and O_2 to enhance reaction efficiency and selectivity. N_2O is particularly effective at activating methane under mild conditions, yielding a competitive selectivity towards methanol. CO_2 not only facilitates methanol synthesis but also aligns with sustainability efforts by utilizing greenhouse gases. While O_2 offers a straightforward pathway, it often requires higher temperatures and may produce unwanted byproducts. By utilizing various oxidizing agents, it is possible to optimize reaction conditions to enhance both the yield and efficiency of thermal and plasma processes.

Indicating the improvement as plausible, some calculations suggest selectivity higher than 50% could be achieved if greater control over Eley–Rideal reactions — collisions between plasma species and catalyst-bound species — can be harnessed. However, despite the existing research on plasma-catalysed DMR, these systems remain insufficiently understood to rationally pursue such goals.

The majority of catalysts used in both thermal and plasma catalytic methanol synthesis are based on transition metals (for example, Cu, Au, Pt, Co, Fe, Ni), typically supported on silicas and aluminas.

Only a few alternative materials, such as metal–organic frameworks and zirconia, have undergone preliminary testing by the plasma research community. These efforts have primarily aimed at exploring the effects of porosity and high dielectric constants on the plasma electric field. Furthermore, in plasma catalysis, particle size plays a critical role. Smaller particle sizes, particularly those on the micron or submicron scale, may have a significant impact on space time yield. The reduced void space between smaller particles is believed to substantially lower space time yield, potentially leading to adverse catalytic effects or even hindering plasma propagation between particles. Thus, the rational design of catalysts becomes an essential control variable.

Despite extensive research, significant challenges remain, such as the inability to co-convert CO_2 and CH_4 to methanol under mild conditions, which is crucial for both economic and environmental sustainability. Currently, there is no direct, thermally activated route to produce methanol from CO_2 and CH_4 at ambient pressure. Instead, existing technologies rely on a multistep thermocatalytic approach: first, high temperatures (900–1,273 K) are required to convert the gases

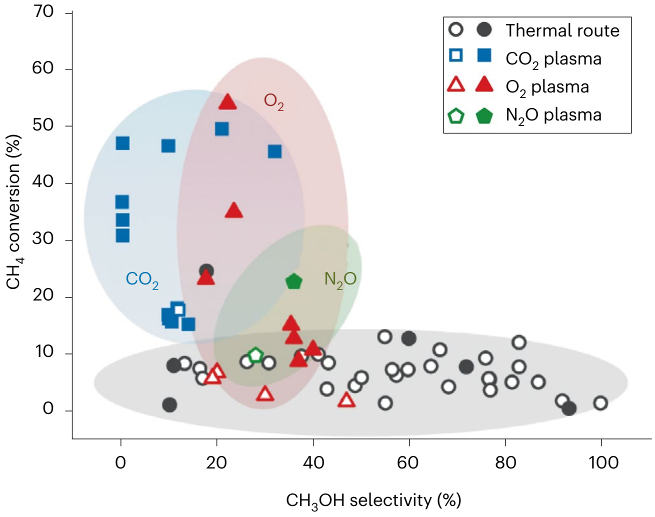

Fig. 3 | Methanol selectivity for thermal and plasma routes using selected oxidants. This figure displays the relationship between methane (CH_4) conversion (%) and methanol (CH_3OH) selectivity (%) for both thermal and plasma catalysis routes, using various oxidants. Hollow symbols (○) represent reactions without a catalyst, while solid symbols (●) indicate reactions with a catalyst. The figure shows that oxidants like N_2O, CO_2, and O_2 are employed to optimize reaction selectivity. This comparisons reveal that choosing appropriate oxidants can optimize yield and efficiency in both thermal and plasma-based methanol synthesis.

to syngas via the DMR reaction ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$), followed by syngas conversion to methanol at high pressure (40–100 bar).

These traditional processes demand harsh operating conditions to overcome the stability of C=O bonds in CO_2 ($E_{diss} = 5.5$ eV) and C–H bonds in CH_4 ($E_{diss} = 4.5$ eV). Due to the limitations in activating CO_2 and CH_4 under milder conditions, plasma catalysis is a promising alternative for one-step co-valorization of these gases to methanol. In addition to milder conditions, plasma catalysis also addresses challenges such as catalyst deactivation, an important hurdle in thermocatalytic processes like DMR due to coke formation. By interacting with plasma species, plasma catalysis can potentially regenerate the catalyst in situ, offering a more sustainable and efficient approach to methanol production.

Plasma catalysis for key chemicals and waste feedstock usage

To curb global warming, not only is energy transition from fossil sources needed but also carbon removal strategies are an important component of the climate remediation strategy. However, our main focus is the decarbonization through the use of plasma. In this respect, plasma can offer an alternative to the decomposition and upgrading of sustainable carbon sources, which are typically macromolecules. These can include, but are not limited to, cellulose, hemicellulose, lignin, and lipids, which are interlinked, resistant structures that pose significant challenges for conversion, especially under mild conditions.

Thermochemical conversion of these macromolecules includes several routes such as combustion, gasification, pyrolysis and liquefaction, where these sources can produce heat and electricity, gaseous and solid fuels, biocrudes and other platform chemicals. They require high temperature and pressure along with solvent use that as a result implies the generation of a waste to dispose.

In terms of biomass gasification with plasma, the literature is rich. It shows the use of mainly N_2, H_2, air and Ar gases paired with radiofrequency torches, gliding arc, microwave and dielectric barrier discharge for the formation of gas rich products where syngas is frequently reported.

When considering inexpensive feedstocks that can be upgraded through plasma technologies, plastics present a significant opportunity due to their contribution to global environmental issues, particularly pollution in oceans and landfills. High-density polyethylene (HDPE) is a major contributor to this pollution, as its persistent nature and limited recycling options lead to substantial environmental damage. Plasma upcycling offers a transformative approach to converting waste plastics into valuable products such as hydrogen, light hydrocarbons, and monomers, which can serve as direct fuels for power generation, intermediates for chemical synthesis, or high-quality inputs for second-generation plastics.

Despite these advancements, HDPE chemical recycling remains challenging due to the inert nature of its chemical backbone. As a highly crystalline form of polyethylene, HDPE can only be chemically recycled using aggressive thermochemical techniques, such as pyrolysis or oxidative methods, which rely on radical initiation to create chain scission followed by oxidative transformation into carboxylic acid end groups. Recent research has shown promise in using plasma-responsive materials for synthesizing fuel blends from HDPE and CO_2 as a plasma gas source[5]. While this illustrates the potential of plasma to upgrade waste sources composed of stable molecules, a fundamental understanding of the interactions between plasma and these responsive materials remains unclear. Ongoing advancements in reactor design, materials engineering, and plasma technology are essential for streamlining these complex processes and enhancing their efficiency and economic viability, particularly in urban areas with high plastic waste generation. Establishing plasma-based facilities for waste-to-fuel conversion could reduce transportation needs, bolster local industries, enhance energy security, and provide reliable energy sources for communities.

Conversion schemes for decentralized production development

Decentralized chemical production, particularly through non-thermal plasma pathways, may play a critical role in the future decarbonization of society to meet climate goals. This approach aligns with the decentralized nature of wind and solar energy, effectively addressing issues such as limited electricity grid capacity and congestion from seasonal variability in energy generation. Energy hubs that facilitate the storage and conversion of excess electrical energy could be key solutions.

Electricity-driven chemistry enables modular scalability, allowing smaller units to operate flexibly based on local energy availability. Unlike traditional, centralized thermal processes, these systems can be deployed near renewable sources, reducing transmission losses and enhancing efficiency. They are adaptable to various feedstocks and chemicals, supporting resilient, sustainable manufacturing. Plasma further benefits decentralized production with its ability to handle variable power sources, absence of expensive catalysts, and capacity for high-energy endothermic reactions.

Although conventional plasma sources, such as dielectric barrier discharges, are compact, economic and easy to assemble and troubleshoot, they present challenges in achieving energy efficiency due to the high energy cost of plasma formation. Perhaps advancements in heat integration within plasma processes could help to overcome this challenge. Alternatives include minimizing waste heat production and combining plasma processes with other heat-requiring chemical conversions.

Beyond non-thermal plasmas, warm and thermal plasmas could also contribute significantly. Thermal plasmas, characterized by the electron temperature being in equilibrium with the gas temperature, have already demonstrated superior energy efficiencies in applications such as material processing. Notable examples include microwave and gliding arc plasmas, which have shown high energy efficiencies in processes like plasma activation of CO_2 and NO production from N_2/O_2 (ref. 8).

Rational design of catalysts could drive down energy costs, by addressing the complexity of plasma and the species it generates. Rational design of the plasma source could simplify the plasma species formation process. Innovations such as pulsed plasmas[9], the use of membranes to limit reagent usage[10] and protection of freshly formed product[11] along with specific plasma conditions promoting targeted plasma-generated reactant species will be instrumental[12]. These approaches build on insights from mode-selective chemistry[13], and require the use of rationally designed catalysts for essential chemicals production such as ammonia.

The choice of targeted basic chemicals will be guided by the starting feedstock gases. For instance, producing ammonia from H_2 and N_2 feedstock could become viable if H_2 can be produced through efficient conversion processes such as electrolysis or gasification of plastic waste[14]. While the traditional Haber–Bosch process for ammonia synthesis is exothermic, alternative methods leveraging plasma technology can be explored. These methods may allow for ammonia production under less demanding conditions, such as atmospheric pressure and near-room temperature, making the process more attractive. Promising strategies include synthesizing ammonia from water and nitrogen via a water-splitting proton-conducting membrane and plasma-activated nitrogen. Ongoing advancements in the rational design of the plasma source aim to control internal excitation and achieve low energy costs, enhancing the potential of plasma-assisted ammonia synthesis.

An alternative viable pathway involves plasma formation of NOx from N_2/O_2, followed by selective electrochemical conversion of NOx and water to produce ammonia (NH_3). This method could demonstrate low energy costs, competitive with producing NOx through combined green H_2-based Haber–Bosch and Ostwald processes[15].

Recent studies show that vibrationally excited CO_2 significantly enhances methanol formation[16] by improving reaction kinetics and lowering activation energy. In this state, CO_2 reacts more efficiently, enabling methanol synthesis under milder conditions. Alloy catalysts, tailored to interact with high-energy CO_2, boost selectivity and stabilize intermediates, overcoming traditional thermodynamic barriers. Plasma technology, which effectively generates and sustains vibrationally excited CO_2, plays a key role in this process by maintaining the excited state of the molecules for longer time. This combination of plasma-generated CO_2 and alloy catalysts shows great promise for scalable and energy-efficient CO_2-to-methanol conversion, positioning plasma as a highly effective technology for overcoming CO_2 utilization challenges.

Hence to fully leverage the advantages of plasma catalysis, there is a necessity for rationally designed materials that can optimize these processes. While plasma offers alternative reactivity, catalysts capable of governing the evolution of plasma-related species are required to guide and control such reactions effectively.

Future outlook

The current need to decarbonize the production of chemicals requires the re-design of existing chemical processes to achieve emission goals, as well as the rational selection of materials that can take advantage of electron-based technologies, such as plasma.

Furthermore, the current context highlights a unique moment in the history of electrification, where decentralized energy networks are rapidly expanding, driven by low-cost photovoltaics.

While the intensive energy requirements of synthesizing essential chemicals typically necessitate a centralized approach, plasma processing under mild conditions can enable decentralized electrified chemical synthesis. This shift is supported by current advances in technology and increased access to renewable energy sources.

A main challenge is the energy efficiency and conversion trade-off that plasma catalysis faces. The latest can be possibly overcome by engineering current plasma systems with targeted process intensification approaches, including multi-stage reactors, recycling of un-reacted process currents and separation membrane technology. Having in mind that these strategies were developed and conceived for thermal high-pressure processes, there is an inherent need of evaluating their shift to plasma environment.

Non-thermal plasma technologies present a promising alternative to conventional methods for chemical synthesis. However, a comprehensive assessment is necessary to determine their true potential, particularly when compared to traditional techniques. Evaluating factors such as economic viability, energy efficiency, and integration into existing systems is crucial to fully understand the unique advantages of plasma processing. Without this thorough comparison, the benefits of Non-thermal plasma technologies may remain unclear, limiting their practical application.

Data availability

Source data are provided with this paper.

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Competing interests

The author declares no competing interests.

Additional information

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