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Sequential Dosing Strategies for Controlling Selectivity and Plasma-Phase Contributions in Plasma Catalysis

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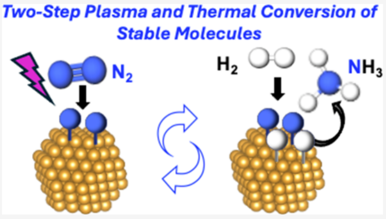
ABSTRACT: Plasma-assisted catalysis has advanced in recent years, particularly for transforming stable reactants at atmospheric pressure and ambient temperature. However, achieving a deeper understanding of the many plasma and catalytic contributions remains a significant goal, as improving product yield and selectivity in plasma catalysis depends on proper catalyst selection, which is often challenging due to the complex interplay between plasma-phase and plasma-surface reactions. A sequential methodology has emerged as a means to decouple the catalyst activity from plasma-phase reactions. In this approach, nonthermal plasma is used in one step to activate and/or convert a gas phase or surface bound reactant, while in a second step, the catalyst directs product formation under steady-state or temperature-programmed conditions. This review examines studies using this technique for reactions involving N_2, CO_2, and SO_2, offering insights into reaction mechanisms and catalyst behavior/selection for these transformations. These systematic studies provide a framework that can be applied to other plasma-assisted reactions. We also highlight remaining questions, propose directions for future studies, and discuss the potential of applying this methodology to other reaction systems.



1. INTRODUCTION

Plasma-assisted catalysis has seen substantial growth in recent years, particularly for activating molecules with strong chemical bonds (e.g., N_2, CO_2, CH_4. . .) and converting these molecules into value-added compounds (e.g., NH_3, NO_x, CH_3OH).[1−3] Plasma discharge initiates gas breakdown, producing an electron avalanche that generates highly energetic electrons, vibrationally and electronically excited species, ions, and radicals.[4,5] Nonthermal plasma (also known as nonequilibrium plasma) creates conditions where electrons are significantly hotter than the bulk gas, enabling reactions to proceed at ambient temperature conditions and allowing catalysts to be incorporated directly into the plasma system.[6,7] Additionally, plasma reactors can utilize renewable electricity sources, such as wind or solar power, making their use even more attractive.[8,9]

Exciting experimental observations have driven exploration across the chemical catalysis reaction landscape, leading to applications in a wide range of chemistries, including N_2 reduction,[10,11] N_2 oxidation,[12−14] CO_2 reduction,[15−17] CH_4 conversion,[18−20] H_2 production,[2] and environmental remediation.[21−23] Plasma-assisted catalytic reactions show much promise, driving yields beyond those achievable through comparable thermal processes.[24] In some instances, plasma-catalysis yields have surpassed thermal equilibrium limits.[25,26] However, the presence of simultaneous plasma-phase and surface reactions complicates efforts to accurately assess catalytic contributions. Modifications to the electric field and packed bed effects in plasma reactors add further complexity, making it challenging to determine whether products are formed solely by plasma or by combined plasma-catalyst interactions.[27]

These challenges create difficulties in selecting the optimal catalyst materials for plasma-assisted applications. Current approaches often rely on initially studying catalysts used in traditional thermal reactions or alternatively using trial-and-error strategies for material screening with varied success. Hence, a sequential methodology of dosing select, stable reactants has emerged as a promising solution to decouple catalyst contributions from bulk plasma-phase reactions. This methodology has been effective in investigating reaction mechanisms and guiding material selection.[28−30] Figure 1 shows the two types of systems that have been explored under this sequential protocol. In Type 1 processes (Figure 1a), plasma is used to activate a reactant, such as N_2, in the presence of a catalytic material, which is then exposed to a secondary reactant under steady-state or temperature-programmed conditions. In contrast, Type 2 systems (Figure 1b

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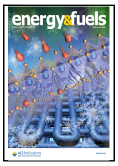

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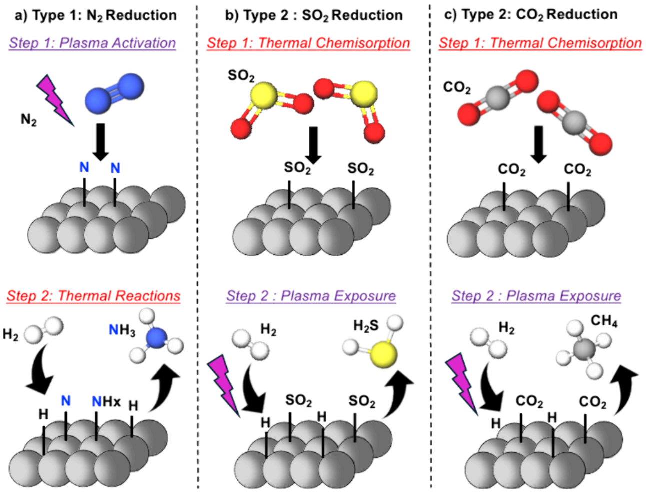

Figure 1. Types of plasma sequential protocol: (a) Plasma activation of reactant such as N_2 followed by thermal reaction with a second reactant (H_2). (b) Thermal absorption of SO_2 followed by plasma activation and reaction with H_2. (c) Thermal adsorption of CO_2 followed by plasma and reaction with H_2.

and c) involve the thermal adsorption of gaseous reactants onto a catalyst surface, followed by the introduction of a second reactant under plasma activation to promote surface reactions. Type 2 systems have been primarily studied for the CO_2 and SO_2 hydrogenation reactions.

In this review, we examine the current state of sequential plasma dosing methodologies, discussing key studies in N_2, CO_2, and SO_2 reactions. We identify significant advances and knowledge gaps, and we propose directions for future research. This review aims to inform and guide studies in related fields and motivate research in emerging plasma-catalysis areas.

2. N_2 CHEMISTRY

N_2 fixation has seen substantial benefits from plasma-catalyst synergy, with prior research demonstrating how plasma enhances N_2 hydrogenation to produce NH_3. Given the broad use of NH_3 in fertilizer production and the high energy demands of the Haber-Bosch process, plasma-assisted approaches offer promising alternative pathways for more sustainable NH_3 synthesis.[31−33] As such, plasma catalysis has led to significant improvements in NH_3 synthesis at low temperatures and ambient pressure.[24,25,34] However, the precise nature of the plasma-catalyst interactions is not fully understood given the many plasma-phase and surface pathways that are possible.

Earlier studies demonstrated the chemisorption of plasma-activated N_2 on a Ru catalyst surface, followed by its subsequent hydrogenation to NH_3 by flowing H_2 over the surface at room temperature.[28] This study was one of the first reported that detailed the reaction of H_2 with plasma-activated N on a catalyst surface. However, the nature of the surface NH_x intermediates and the surface mechanism were not determined. Recently, inelastic neutron scattering (INS) spectroscopy was used to investigate the formation of NH_x intermediates on a $Ni/\gamma Al_2O_3$ catalyst surface.[35] INS is a useful approach for detecting surface-bound species containing hydrogen due to its high neutron scattering cross-section.[36−38] Figure 2 outlines the experimental protocol to compare catalyst stimulation through sequential thermal N_2-thermal H_2 stimulation, plasma N_2-thermal H_2 stimulation, and plasma N_2 -plasma H_2 stimulation. As shown in Figure 2a and d, the sequential exposure of N_2 followed by H_2 at 200 °C results in minimal, if any, hydrogen uptake on the Ni catalyst. However, when N_2 is plasma-activated prior to thermal H_2 exposure at 200 °C, distinct features appear in the 100−300 cm^{-1} and 450−900 cm^{-1} regions (Figure 2b and e).[35] These features

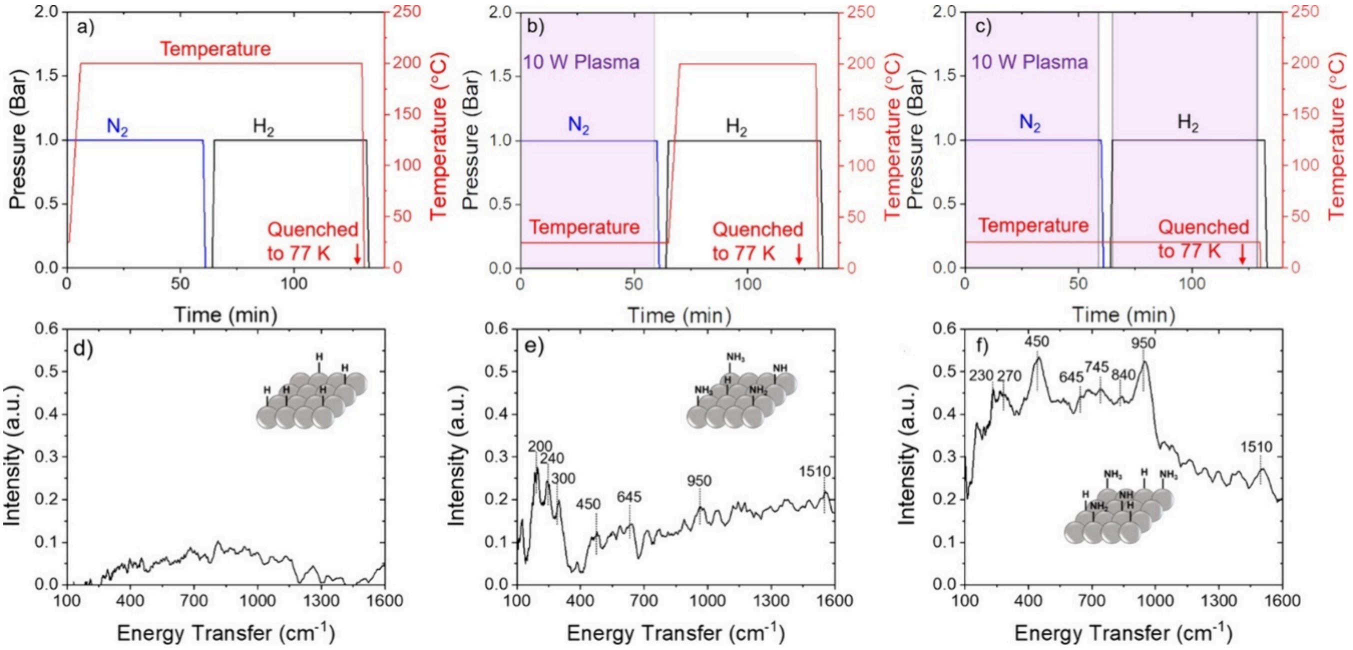

Figure 2. Schematic of the sequential plasma and thermal reactant exposure: thermal N_2 followed by thermal H_2 (a), 10 W plasma N_2 followed by thermal H_2 (b), and 10 W plasma N_2 followed by 10 W plasma H_2 (c). Background subtracted INS spectra of thermal N_2/thermal H_2 treatments (d), plasma N_2/thermal H_2 treatments (e), and plasma N_2/plasma H_2 treatments (f). Reproduced with permission from ref 35. Copyright 2021, American Chemical Society.

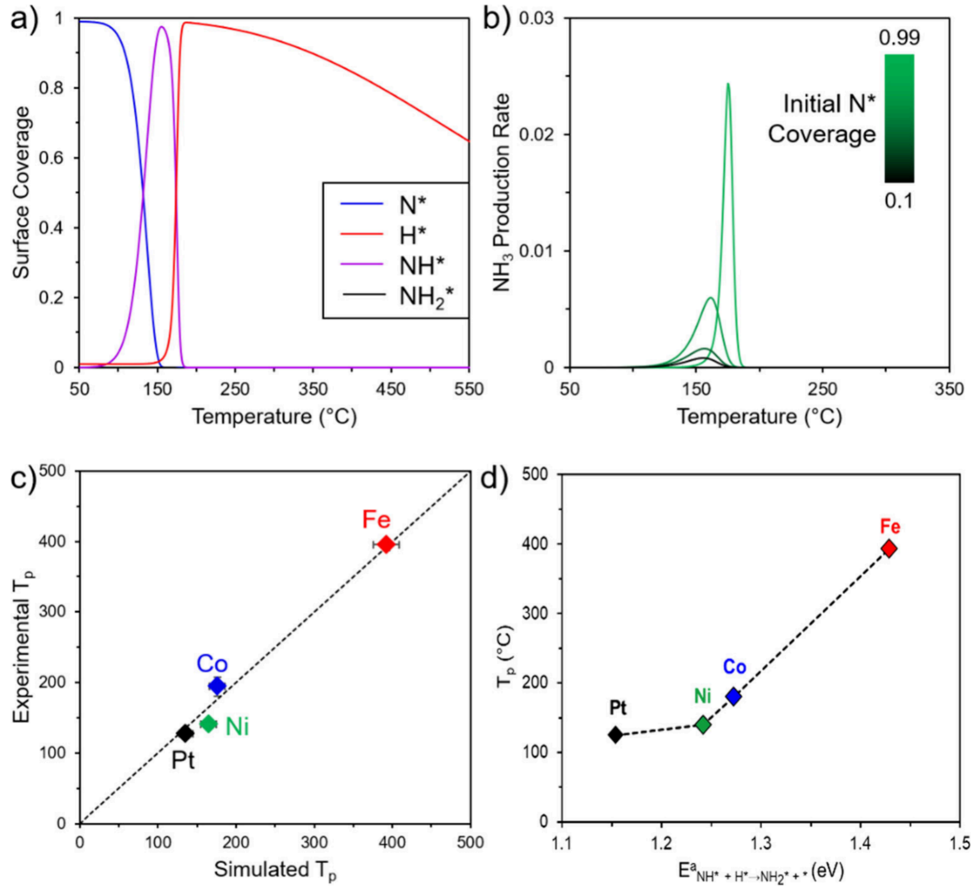

Figure 3. (a) Computed N* (blue), H* (red), NH* (purple), and NH_2* (black) coverages on Ni vs temperature at an initial N surface coverage of 0.99. (b) Computed NH_3 production rates (Molecules/site/°C-1) on Ni versus temperature assuming initial N* coverages of 0.99, 0.6, 0.2, and 0.1. (c) Parity plot of simulated and experimental NH_3 peak temperature (Tp). (d) Experimental Tp vs Ea of NH* + H* ↔ NH_2* + ∗ reaction step. Reproduced with permission from ref 29. Copyright 2022, American Chemical Society.

increased in intensity when plasma was used to activate H_2 in the second step (Figure 2c and f). First-principles calculations support the assignment of these features to NH_x species and surface bound H in 4-fold and 3-fold hollow sites. The sequential reactant dosing approach in this study provides critical insights into the reactivity of plasma-generated nitrogen species on the catalyst surface—observations that are much more challenging to achieve under cofeeding conditions.

Building on these spectroscopic observations, the influence of catalyst type on the hydrogenation of plasma-activated nitrogen species was further investigated using a dielectric barrier discharge (DBD) plasma with a sequential dosing approach.[29] N_2 was activated under plasma stimulation in the presence of the catalyst prior to H_2 exposure. However, in this case, a temperature ramp with flowing H_2 was conducted. Various metal catalysts (Ni, Co, Fe, and Pt) were investigated, all of which produced NH_3 upon thermal treatment with H_2 (Figure 3c).[29] Interestingly, the desorption temperature of NH_3 varied depending on the metal. Microkinetic modeling revealed that the NH_3 desorption temperature was dependent on the activation barrier for the NH* hydrogenation step (Figure 3d),[29] indicating that NH_2* formation was kinetically relevant. These findings suggest that plasma-activated N_2 can facilitate NH_3 synthesis even with catalysts that traditionally show lower N_2 activation ability (e.g., Pt), achieving NH_3 formation at low temperatures (~125 °C). Given that the Haber-Bosch process requires high temperatures and pressures, this low-temperature NH_3 formation over Pt represents a significant advancement. Moreover, recent studies of N_2 plasma activation on small Pt clusters (Pt_n^+) revealed the formation of Pt nitride ($Pt_3N_7^+$) clusters, which were reactive under hydrogenation conditions to form NH_3.[39] Furthermore, these results show that material selection strategies for plasma-assisted nitrogen fixation may differ from those used in thermal catalytic processes, as plasma catalysis appears to shift the scaling relationship for NH_3 synthesis, favoring catalysts with weaker nitrogen binding.[24]

In addition to examining metal types, the temperature of plasma exposure has also been investigated. For instance, the effect of different plasma temperatures was evaluated over an Fe catalyst using a microwave plasma.[40] A maximum NH_3 yield was observed at 200 °C with N_2 plasma exposure. Higher temperatures, however, led to diffusion of the surface N species to the subsurface/bulk of Fe catalyst, limiting the accessibility for hydrogenation (Figure 4b).[40] However, for all N_2 plasma conditions, the thermal exposure to H_2 was carried out at 450 °C, consistent with the previously observed temperature for NH_3 desorption on Fe.[29] NH_3 formation over the Fe catalyst was higher at shorter and longer exposure times but lower at intermediate times (Figure 4a). This behavior was attributed to the competing effects of a surface-mediated pathway at very low exposure times (2 min) and bulk-mediated pathways at longer exposure times (7−30 min). It is interesting to observe that after 60 min, the NH_3 yield returns to the maximum value.

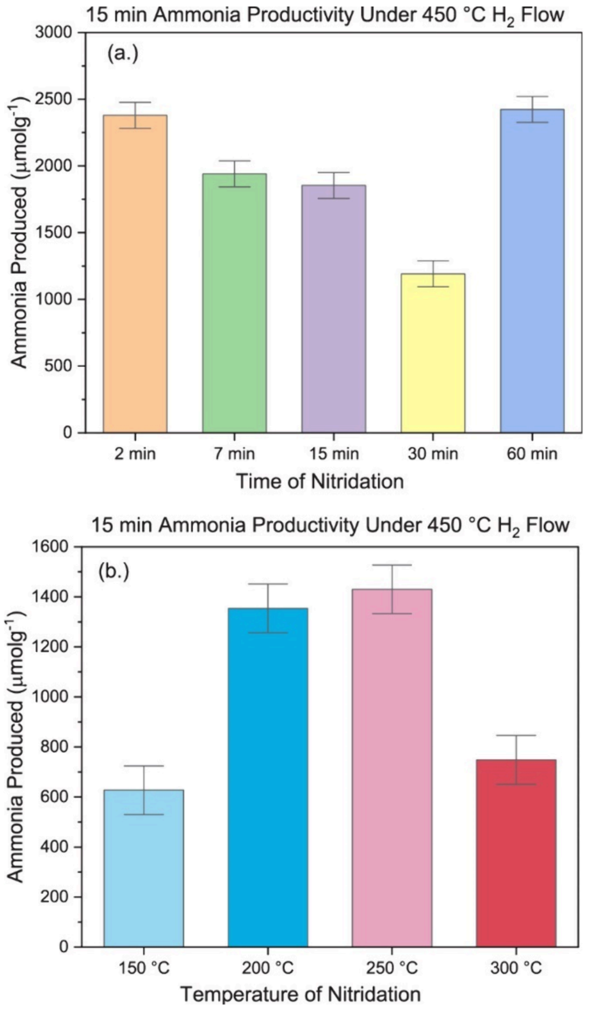

Figure 4. (a) Ammonia yield under different plasma nitridation times on Fe catalyst. (b) Ammonia yield under different plasma nitridation times on Fe catalyst. Reproduced with permission from ref 40. Available under a CC-BY 4.0 license. Copyright 2023, Siobhan Brown et al.

A plausible explanation could be that after this longer period of time, the bulk Fe is fully nitrided, and surface pathways dominate again. However, given that the XRD characterization after 1h N_2 plasma exposure revealed no bulk Fe nitride phases, this still leaves the question unanswered. It is also possible that perhaps keeping the thermal hydrogenation step longer would lead to sufficient diffusion from the bulk of the catalyst and increase the NH_3 yield at these longer nitridation times. This study poses more questions about the mass transfer limitations and catalyst transformation under these plasma nitridation environments.

Recently, C−N coupling using a sequential N_2−CH_4 plasma reaction was employed over different metals (Cu, Ni, Pd, Ag, Au) using a multimodal spectroscopic approach, combining polarization-modulation infrared reflection−absorption spectroscopy (PM-IRAS) and optical emission spectroscopy (OES).[41] In this work, both steps were conducted under a plasma stimulation. Somewhat surprisingly, the order of the exposure sequence played a role in forming intermediate species.[41] While a N_2−CH_4 plasma sequence does not yield any C−N formation, a CH_4−N_2 plasma sequence was successful for C−N formation. It is indeed interesting that an initial N_2 plasma followed by a CH_4 plasma sequence yielded no C−N formation. Such findings could suggest a potential Eley−Rideal mechanism, where only highly energetic plasma-activated nitrogen species react with surface-bound CH_x intermediates. However, such a hypothesis requires a more thorough investigation to probe fully. Additionally, it would be important to investigate if the reaction pathways are metal-dependent and if the metal-N bond strength plays a role in the formation of C−N species. Furthermore, the metal surface was also critical in evaluating these interactions, particularly with Cu and Ag, displaying unique features under sequential CH_4−N_2 treatment compared with the mixed gas stream. These observations give more insights into the application of Cu and Ag-based catalysts for plasma-assisted C−N coupling.[42−44]

This sequential activation of N_2 using plasma, followed by probing the surface reactivity of the resulting nitrogen adsorbates, has produced insightful results. On one hand, plasma-activated nitrogen is readily harnessed and coupled with hydrogen to form NH_3, allowing for accelerated selection of optimal materials. On the other hand, this plasma-activated nitrogen can be coupled with a hydrocarbon to facilitate C−N bond formation, which is highly relevant for applications in the pharmaceutical, fine chemical, and agrochemical industries.[45,46] While some reports have detailed the reaction of nitrogen-containing compounds such as NH_3 and hydrocarbons,[43,47,48] only a few plasma studies have shown direct C−N bond formation from N_2. Broader applications of plasma C−N coupling have been reported in the production of nitrogen-containing liquids directly from nitrogen and natural gas feedstock.[49] A recent report on a corona discharge plasma also shows that plasma can facilitate N_2 coupling with benzene to produce aniline and diphenylamine.[50] However, controlling the selectivity for specific products remains a challenge in all cases.

Table 1. Plasma Conditions and Process Parameters for Sequential N_2, CO_2, and SO_2 Conversion

Entry	Reaction Type	Plasma Reactor Type	Reactants	Plasma Power (W)	Plasma Exposure Temperature (°C)	Thermal Exposure Temperature (°C)	Catalyst	Products	Reference
1	Type 1	N/A	N_2, H_2	30	RT	RT-570	Ru	NH_3	Kunimori et al.[28]
2	Type 1	DBD Plasma	N_2, H_2	10	RT	200	Ni/γ-Al_2O_3	NHx	Barboun et al.[35]
3	Type 1	DBD Plasma	N_2, H_2	10	RT	30−500	Ni/SiO_2, Co/SiO_2, Fe/SiO_2, Pt/SiO_2	NH_3	Barboun et al.[29]
4	Type 1	Microwave Plasma	N_2, H_2	300	150−300	250−550	Fe, Mn, CoMo	NH_3	Brown et al.[40]
5	Type 2	DBD Plasma	CO_2, H_2	N/A	50−400	50	Co/$CeZrO_4$, Cu/$CeZrO_4$	CH_4, CO	Parastaev et al.[53]
6	Type 2	DBD Plasma	SO_2, H_2	8	150−550	150	FeS/Al_2O_3	H_2S, S	AlQahtani et al.[30]

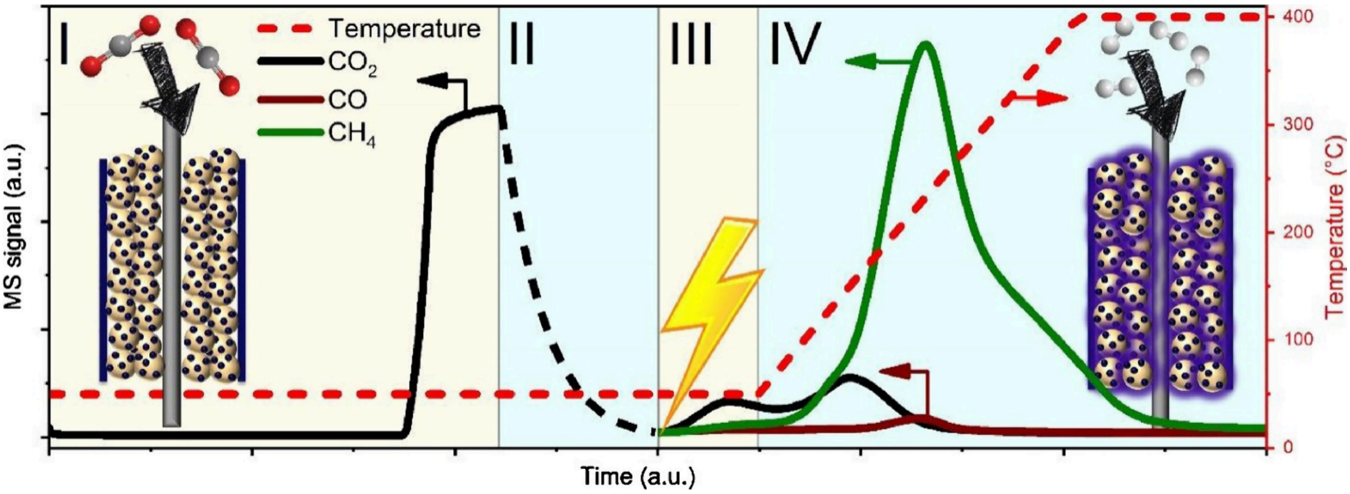

Figure 5. Schematic representation of the TPPSR. (I) CO_2 adsorption. (II) H_2 flushing. (III) Plasma on. (IV) Temperature ramp. Reproduced with permission from ref 53. Available under a CC-BY-NC-ND 4.0 license. Copyright 2018, Alexander Parastaev et al.

By employing the sequential protocol described here, selected intermediates can be reacted directly with a plasma-nitrided catalyst surface. This can be done in a one-pot process or a two-step process, where a plasma zone can be placed downstream of a thermal reactor. Furthermore, this sequential approach has the potential for chemical looping synthesis. For instance, such a process would involve plasma nitridation of the catalyst and thermal hydrogenation to NH_3. Chemical looping ammonia synthesis (CLAS) has been a trending research area, however, the thermal CLAS process requires extreme temperatures for metal nitridation,[51,52] a challenge circumvented by the plasma N_2 activation. Such plasma CLAS could be performed in multiple cycles, as long as there is no permanent catalyst restructuring. Moreover, this is not limited to NH_3 synthesis alone. Other reagents can react with the adsorbed nitrogen species in a cyclic manner, as long as the catalyst is regenerable. Table 1 provides a summary of the reported sequential plasma processes for NH_3, as well as those for CO_2 and SO_2, which will be discussed in the following sections.

3. CO_2 AND SO_2 CONVERSION

The high stability of the C═O bonds in CO_2 necessitates the utilization of plasma catalysis for its activation and conversion. The focus has been on different chemistry for CO_2 valorization, such as dry reforming with CH_4,[18,54] decomposition reaction to CO,[55,56] reduction reactions with H_2/H_2O to produce CH_3OH, CH_4, DME, olefins and higher hydrocarbons.[57−59] Key findings here include low-temperature splitting of CO_2,[60] increased methanol yield at ambient conditions,[58] and improved energy efficiency in the plasma-catalytic systems compared to plasma-only systems.[61] Some studies have also shown that an Eley−Rideal type pathway promotes the CO_2 hydrogenation reaction.[59] Although plasma catalysis has led to significant achievements in CO_2 utilization, a mechanistic understanding of the process remains in its early stages.

The plasma CO_2 hydrogenation reaction was investigated using a temperature-programmed plasma surface reaction (TPPSR).[53] Unlike the other works discussed earlier in the N_2 reaction section, the CO_2 was first adsorbed in the first step at ambient conditions, while the thermal ramp was done under plasma exposure (Figure 1c).[53] Figure 5 shows the experiment sequence and associated gas flow, where the CO_2 is adsorbed, followed by a purge with H_2 and subsequent plasma ignition and temperature ramp. Results show that $Co/CeZrO_4$ was more selective to CH_4, while $Cu/CeZrO_4$ was more selective to CO. CO_2 was suggested to mainly adsorb on the ceria-zirconia support while the Co and Cu provided sites for H_2 activation and reaction during the plasma-temperature ramp. Isotopically labeled experiments where $^{13}CO_2$ was first adsorbed on $Co/CeZrO_4$, followed by a temperature-programmed plasma reaction in $^{12}CO_2/H_2$, were conducted to investigate the influence of the gas phase and preadsorbed surface CO_2. The temperature was held isothermally at 50 °C when the plasma was ignited before ramping the temperature. It should be noted that the plasma led to an overheating of up to 100 °C. Results showed an abundance of $^{13}CH_4$ in the product streams, which suggested that CO_2 was converted in the gas phase to CO and further reacted on the catalyst surface to make CH_4.[53] These observations provide insight into the role of the metal and support materials in creating adsorption sites for reactants that can then be reacted with a plasma-activated species.

Likewise, SO_2 hydrogenation has also been studied to exploit plasma-catalyst interactions via a sequential methodology. SO_2 conversion to elemental sulfur has been long touted as a means of environmental remediation.[62−64] Reductants such as H_2,[65] CO,[66] and CH_4,[64] have been explored with very high-temperature requirements (400 − 900 °C). Recently, plasma-assisted catalysis has been used to overcome the high-temperature requirements for SO_2 conversion.[67−69]

Plasma-assisted reduction of SO_2 was conducted using a sequential approach over a FeS/Al_2O_3 catalyst to better understand the surface reaction mechanism.[30] Similar to the CO_2 hydrogenation study,[63] surface reactivity of a preadsorbed surface species was evaluated with a plasma-activated reactant (Figure 1b).[30] Here, SO_2 was first adsorbed on the FeS/Al_2O_3 catalyst prior to plasma reaction with H_2, which led to the formation of elemental sulfur and H_2S. Although the temperature was held at 150 °C before plasma exposure, the temperature of the catalyst bed increased by 50 °C when the plasma was ignited. Further analysis revealed the contribution of both surface S and lattice S from FeS to H_2S formation.

Similar experiments performed on Al_2O_3 also showed the formation of H_2S. Since H_2 is not known to dissociate on Al_2O_3, the authors suggested a reaction between high-energetic plasma-activated H_2 with surface bound SO_2 on the Al_2O_3. A reaction pathway was postulated as depicted in Figure 6, which accounts for possible Eley−Rideal (E-R) and Langmuir−Hinshelwood (L-H) reaction mechanisms.[30]

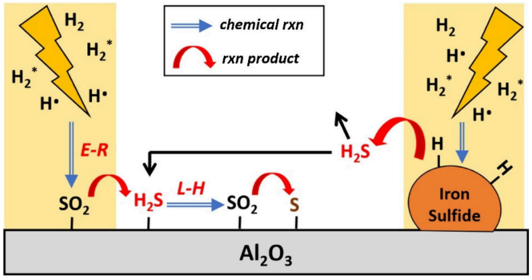

Figure 6. Pictorial representation of plasma-assisted SO_2 hydrogenation over Al_2O_3 and the FeS/Al_2O_3 catalyst. Reproduced with permission from ref 30. Copyright 2021, Elsevier.

This work highlights the role of energetic species created under plasma conditions in reacting with surface-bound species. Additionally, it shows that the reactant transformation under plasma conditions could be a consequence of different or competing pathways. These highly energetic species generated under plasma stimulation can also interact with the lattice atoms, as is the case with the FeS reported in the study, and a recent report on plasma activated H_2 driving low temperature strong metal support interactions on reducible oxides.[30,70] Questions do remain about the possibility of Mars−Van Krevelen Mechanism (MVK) type mechanisms in plasma-catalytic systems that can transfer lattice S from the metal sulfide to form H_2S. Rigorous postcatalyst characterization should be performed to study any changes to the catalyst composition, morphology, or electronic properties after the plasma reaction. Also, a thorough mass balance should be performed to verify whether the product comes from the gas reactants only or if there is a contribution from the lattice of the catalyst or catalyst support. Furthermore, we can decipher how reactant adsorption and product desorption affect product yields through the plasma temperature-programmed reaction. This will inform appropriate temperature conditions to run reactions that will prevent poisoning of sites by strongly adsorbed reactants or product species, especially when these strongly chemisorbed species can favor the reverse reaction.

4. CONCLUSION AND OUTLOOK

This review has highlighted the application of sequential plasma methodologies across various plasma-catalysis systems, with a focus on advancements in N_2, CO_2, and SO_2-based reactions. These studies offer valuable insights into the complex reaction mechanisms in plasma catalysis and provides some guidance for optimizing material selection for plasma applications. In the N_2 reduction process, for example, the importance of the surface hydrogenation step in controlling the NH_3 desorption temperature was discussed, along with the potential for bulk or subsurface diffusion of plasma-activated nitrogen in iron substrates. Sequential plasma experiments have also advanced our understanding of CO_2 hydrogenation and SO_2 reduction, revealing how plasma-activated H_2 interacts with CO_2 or SO_2 adsorbates to provide insight into reaction pathways. Beyond mechanistic studies, the sequentially designed plasma protocol can be extended to applications where the plasma-activated reactant can be selectively coupled with other chemicals, enabling the synthesis of products that are difficult to achieve thermally under similar conditions. Energy efficiency is another factor that deserves consideration. Plasma-looping approaches are relatively new and energy efficiency has received less attention to date. Energy efficiency has been evaluated for plasma-assisted NH_3 synthesis using the following equation[5]:

$$\text{Energy efficiency } (\text{gNH}_3/\text{kwh}) = \frac{C_{NH_3}{}^{*}Q_{gas}}{P}$$

where C_{NH_3} is NH_3 concentration, Q_{gas} is the gas flow rate, and P is the power input.

When this expression is applied to sequential plasma processes, energy efficiencies range from 0.008 to 1.2 gNH_3/kWh. For comparison, the steady state operation energy efficiency has been reported in the range of 0.02 to 1.3 gNH_3/kWh.[5,71] The results show that the sequential process is competitive with the steady state AC plasma operation. However, it should be noted that pulsed plasma operation has shown efficiencies up to 35.7 gNH_3/kWh.[72] For sequential approaches to be competitive with pulsed plasma, the separation of the plasma and thermal steps must offer significant selectivity benefits. In NH_3 synthesis, plasma-phase reactions facilitate NH_3 formation, so removing them does not provide a substantial advantage, which is likely more pronounced in hydrocarbon conversions or oxidation reactions. Lastly, it is important to note that the reported energy efficiency expression highlighted here is solely based on plasma energy input to the reactor, omitting other energy sources, such as external heating.

Despite the progress achieved through these studies, several areas merit further investigation. Some key directions for future research include:

i. Chemical looping is a reaction system whereby a reactant is adsorbed by a carrier and consumed by another reactant in a secondary reactor, returning the carrier to its initial state. This process allows for the optimization of the individual reaction steps than when conducted in a single step. Typically, chemical looping has been employed for combustion reactions where a metal serves as an oxygen carrier and is reduced in the secondary reactor by the hydrocarbon fuel. Such forms of plasma-assisted looping combustion have been reported for CH_4 oxidation on transition metal oxides.[73,74] Likewise, the ability to activate and adsorb highly stable molecules like N_2 opens routes for chemical looping synthesis, which has already been explored in thermal catalysis. Plasma-activated N_2 could be incorporated in cyclic processes with H_2 to synthesize NH_3, with studies needed to examine catalyst stability and performance under plasma stimulation, as well as preand postreaction catalyst characterization to determine if any permanent restructuring or deactivation modes are prevalent under these cyclic studies.

ii. Sequential plasma activation of N_2 could be applied to nitrogen oxidation or other N-coupling reactions, potentially addressing the challenge of product selectivity through proper catalyst selection and operation. Moreover, it will deepen our understanding of the catalytic contribution, which is essential for the efficient synthesis of nitrate-based fertilizers and other nitrogen-based products.

iii. More studies are needed to examine the extent of reactant adsorption mechanisms under plasma conditions. Reports suggest that bulk or subsurface N incorporation is possible under certain conditions, yet characterization techniques have not conclusively verified this. The stability of plasma-generated surface active species under exposure to the atmosphere is another potential challenge, warranting the development of in situ techniques in combination with ex situ characterization.

iv. Plasma-activated CO_2 reactions could benefit from the integration of techniques such as optical emission spectroscopy (OES) and infrared (IR) spectroscopy to monitor surface intermediates when H_2 is dosed into the system. This approach may clarify the roles of carboxylate and formate pathways leading to methanation, oxygen formation, or CO_2 splitting, with potential applications in dry reforming.

v. More mechanistic studies should be performed. Some insights from the sequential hydrogenation of SO_2 point to the occurrence of E-R and L-H mechanisms. However, as lattice atoms have been shown to contribute to product formation, the MVK mechanism cannot be fully excluded. To this end, isotopic labeling experiments could be performed to verify the source of atoms in the product stream. This can help understand concurrent gas phase and surface induce pathways. Additionally, theoretical investigations using molecular dynamic simulations can also be combined with experiments to provide more understanding.

vi. Future work should explore the stability and reactivity of plasma-generated intermediates over varying time scales. This could be achieved by varying the time interval between plasma activation and the introduction of secondary reactants, revealing insights into the stability of surface species and their relevance in postplasma catalysis. Furthermore, rigorous characterization of the catalyst structure/phase should be conducted and correlated with product formation.

vii. The sequential methodology holds promise for a wide range of reactions beyond those discussed, including NO_x removal, VOC oxidation, alkane dehydrogenation, and oligomerization, among others. Recent investigations on toluene oxidation via the Type 2 sequential system indicate that plasma activation facilitates the formation of benzyl radicals, which subsequently lead to the formation of benzaldehyde, accompanied by the production of CO_2 and H_2O.[75,76]

Ultimately, this sequential dosing methodology offers valuable insights into plasma-assisted catalytic reactions, enhancing our understanding of plasma catalysis.

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Notes

The authors declare no competing financial interest.

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