



Non-thermal plasma-catalytic processes for CO₂ conversion toward circular economy: fundamentals, current status, and future challenges

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Abstract

Practical and energy-efficient carbon dioxide (CO₂) conversion to value-added and fuel-graded products and transitioning from fossil fuels are promising ways to cope with climate change and to enable the circular economy. The carbon circular economy aims to capture, utilize, and minimize CO₂ emissions as much as possible. To cope with the thermodynamic stability and highly endothermic nature of CO₂ conversion via conventional thermochemical process, the potential application of non-thermal plasma (NTP) with the catalyst, i.e., the hybrid plasma catalysis process to achieve the synergistic effects, in most cases, seems to promise alternatives under non-equilibrium conditions. This review focuses on the NTP fundamentals and comparison with conventional technologies. A critical review has been conducted on the CO₂ reduction with water (H₂O), methane (CH₄) reduction with CO₂ to syngas (CO + H₂), CO₂ dissociation to carbon monoxide (CO), CO₂ hydrogenation, CO₂ conversion to organic acids, and one-step CO₂-CH₄ reforming to the liquid chemicals. Finally, future challenges are discussed comprehensively, indicating that plasma catalysis has immense investigative areas.

Keywords Circular economy · Heterogenous catalysis · Non-thermal plasma · Plasma catalysis · CO₂ conversion · Energy efficiency

Plasma technology for CO₂ conversion

Global climate change is considered an exponentially rising risk to the environment and human beings (Loenders et al. 2023, Zhang et al. 2022). It has been estimated that global warming has increased the earth's temperature since the pre-industrial period by 1.5 °C, leading to irreversible changes and adverse effects on nature. Considering these alarming facts, it is necessary to put efforts into decreasing greenhouse gas emissions, mainly CO₂ and CH₄, which

are reaching atmospheric concentrations of about 416 ppm and 1910 ppb, respectively (Cooley et al. 2022, Wang et al. 2023a). These figures indicate that CO₂ and CH₄ have increased by 19% and 173% since the pre-industrial era, respectively (Houghton et al. 2001). Besides, it is well known that society is much more dependent on fossil fuel combustion to gain energy, leading to considerable greenhouse gas emissions. Therefore, finding a potential solution for both problems is necessary, i.e., cutting greenhouse gas emissions and transitioning from fossil fuels to renewable and fuel-graded products, enabling the CO₂ circular economy (Goepfert et al. 2014, Tcvetkov et al. 2019, Tebbiche et al. 2021). Although conventional thermal catalysis can fill the bill, the nature of the CO₂ conversion reaction, i.e., highly endothermic (900–1273 K) for shifting the thermal equilibrium, makes it less energy efficient (Aramouni et al. 2018, Pakhare and Spivey 2014, Sun et al. 2023).

In thermochemical conversion processes, the higher thermal stability of the CO₂ molecules demands much higher energy to break the double bonds in the CO₂ molecule (O=C=O), making it less effective (Ashford and Tu

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2017). Overcoming this issue by applying non-thermal plasma (NTP) is an innovative process to overcome the CO₂ molecule activation challenges and convert it into various value-added and fuel-graded products. The reason is that the NTP can enable the reaction to proceed, which is thermodynamically unfavorable under ambient reaction conditions. Usually, the NTP performs at atmospheric pressure, low temperature, and non-equilibrium conditions and still achieves much higher conversion than the thermochemical conversion processes. Typically, the NTP produces energetic electrons having an average temperature (1 to 10 eV) possessing a high capability of CO₂ molecule activation by ionization, followed by excitation, and finally, dissociation, leading to the development of an avalanche of reactive species, which include the ions, excited atoms, radicals, and molecules which can trigger the chemical reaction into forward direction (Bogaerts and Neyts 2018, Mehta et al. 2019, Tu and Whitehead 2012, Tu et al. 2019, Zeng et al. 2018). The significant benefit of NTP technology is the ease of installation, compactness, flexibility, and the considerable potential of integration with other technologies for effective and energy-efficient conversion of CO₂ to value-added and fuel-graded products (George et al. 2021).

The major obstacle in the pathway of the NTP technology is the improvement of energy efficiency, which could be accomplished by combining the catalyst and transforming the plasma process to the hybrid plasma catalysis process, creating synergy, and providing enough room for the excited species for catalyst surface interaction and subsequently lose their excitation energies and relax before reaction. However,

the knowledge available for the plasma catalysis process to effectively and efficiently convert CO₂ to value-added and fuel-graded products and, most importantly, for the complex interactions between plasma, catalyst, and reactive species is minimal (Fridman 2008).

This review paper comprehensively focuses on plasma and plasma catalysis technologies, their fundamental physicochemical properties; integration in reactors with different configurations; and possible interactions between complex plasma, catalyst, and reactive species. In addition, the general mechanism of the plasma-only process for CO₂ activation by ionization, excitation, and dissociation is also discussed, along with current developments and future challenges in plasma catalysis for different CO₂ conversion routes.

Comparison of plasma with conventional CO₂ conversion approaches

Comparison has been summarized in Table 1 for all traditional and conventional CO₂ conversion technologies and the plasma-only and plasma-catalysis technologies. Overall, it has been found that the conventional thermochemical conversion of CO₂ assisted by catalysts cannot split CO₂; however, it can be effectively implemented to dry reforming methane (DRM) and the hydrogenation of CO₂. At the same time, data for CO₂ reduction in H₂O is not available for the catalyst-assisted thermochemical conversion approach. Compared to the catalyst-assisted

Table 1 A schematic comparison of different technologies for CO₂ conversion in different routes (Hecimovic et al. 2024, Snoeckx and Bogaerts 2017)

CO ₂ Conversion Technologies	CO ₂ Splitting	CO ₂ /H ₂	CO ₂ /H ₂ O	CO ₂ /CH ₄
Thermochemical Catalytic	Red	Green	Yellow	Green
Electrochemical	Green	Green	Green	Green
Low-Temperature Electrolysis	Red	Green	Green	Yellow
High-Temperature Electrolysis	Green	Green	Green	Red
Solar-Thermochemical	Green	Green	*	Green
Photochemical	Green	Green	Green	Green
Biochemical	Green	Green	**	Yellow
Plasma-Catalysis	Green	Green	***	Green

Green: efficient, yellow: to be proven, and red: inefficient

*CO₂ and H₂ are not converted simultaneously

**H₂O is the vital nutrient for the algae growth

***When used hybrid plasma-catalysis mode

thermochemical conversion approach, all other novel approaches successfully achieved CO₂ reduction in H₂O, and the electrochemical and solar-assisted thermochemical conversion approaches can also successfully split the CO₂. Interestingly, the literature generally does not report the CH₄ and hydrogen (H₂) combination. Although plasma-chemical technology is the only technology discussed here that can be successfully applied to all four significant areas of CO₂ conversion research, including DRM, CO₂ hydrogenation, CO₂ splitting, and CO₂ reduction in H₂O, CO₂ reduction in H₂O is not investigated in the plasma-catalysis system but only in the plasma-only system. In all four CO₂ conversion routes, DRM and CO₂ splitting are considered the two most important routes and have already been demonstrated to achieve 90–95% and 60% energy efficiency with the plasma-only treatment, respectively. Even though the one-step synthesis of value-added liquid products from CO₂ conversion in the plasma-catalysis mode has been proved by preliminary research, more research is still needed to improve the process. CO₂ reduction with H₂O, also known as the “artificial photosynthesis,” is the least mature technology and requires significant research to improve. It is admitted that a clear priority should be given to plasma catalysis owing to its several key benefits, including flexibility, versatility, and low operation cost, as compared in Fig. 1.

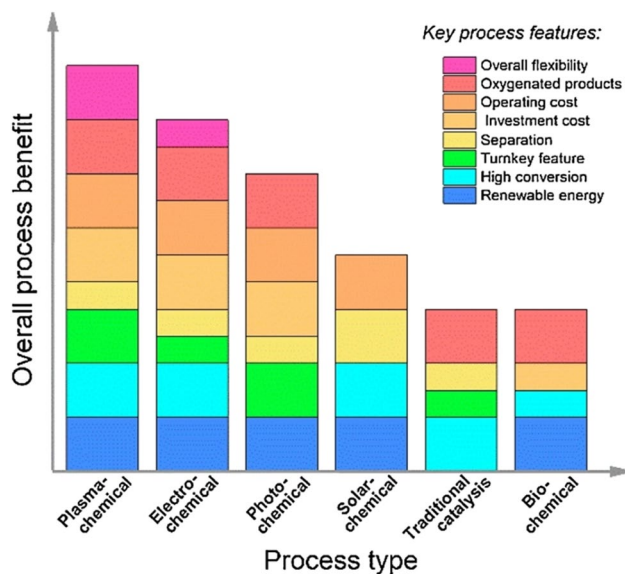


Fig. 1 Comparison of overall advantages of traditional CO₂ conversion technologies with plasma-catalysis. Reprinted from the references (Chen et al. 2021, Snoeckx and Bogaerts 2017) with the permission of Elsevier and the Royal Society of Chemistry

Different types of plasmas

The CO₂ conversion process employs various types of plasma, as described in this section: dielectric barrier discharge, radiofrequency inductively coupled plasma, atmospheric pressure glow discharges, gliding arc plasma, corona discharge, and microwave plasma. A table detailing their operational characteristics is provided in the following section (Table 2).

Dielectric barrier discharge (DBD) can be formed by employing the electrical field linking two electrodes as a non-uniform discharge with an alternating (AC) current with at least one electrode covered with a dielectric barrier. Different arrangements of the two electrodes could be made to minimize the gas bypassing the plasma area by keeping both electrodes parallel. However, a cylindrical configuration is more appropriate for greenhouse gas conversion applications. The advantage of DBD is that it can operate near ambient pressure and temperature. Due to its simple design, it can be easily upgraded for commercialization. In the case of DBD, the conversion efficiency of CO₂ is appropriate; however, the energy efficiency is 2–10% less than that of other plasmas (Bogaerts and Centi 2020, Okubo et al. 2018, Ong et al. 2022, Puliyalil et al. 2018, Yamasaki et al. 2020).

Gliding arc plasma can work at ambient pressure and be produced by applying electricity between two electrodes with flat diverging. Initially, an arc is formed at the inter-electrode with the shortest distance. After that, the arc glides along with the surfaces of the diverging electrode, leading from the small to longer distances between the electrodes in the direction of gas flow until it extinguishes. The process of arc formation is then repeatedly reformed immediately at the initial sport. It has comparatively better energy efficiency even at ambient pressure with a range of 43–60% splitting CO₂ and DRM conversion of 18% and 8–16%, respectively. The short residence time of the gas to be treated is a significant constraint of the traditional gliding arc plasma; however, the residence time can be increased with modifications in design (Bogaerts and Snoeckx 2019, Nunnally et al. 2011, Puliyalil et al. 2018, Ramakers et al. 2017).

As the name implies, atmospheric pressure glow discharge is operatable at ambient pressure with advantages over other plasmas, such as higher electron density and proper plasma temperature. The plasma of the discharge is luminous or glowing. It is formed by employing voltage ranging between a few hundred and a few kilovolts between two electrodes with a ballast circuit to minimize the transition of glow to arc. It has been reported that by using atmospheric pressure glow discharges with an input power of 23 W, the CH₄ and CO₂ conversion of 61% and 50% can be achieved, respectively (Arumugam et al. 2018, Ghorbanzadeh et al. 2009, Li et al. 2019, Tao et al. 2011).

Table 2 Operating characteristics of different types of plasmas used in the CO₂ conversion processes (Chen et al. 2021, Ong et al. 2022)

Plasma types	Operating pressure (mbar)	Electron density (cm ⁻³)	Electron temperature (T _e , eV)	Gas temperature (T _g , K)	References
DBD	atm	10 ¹² –10 ¹⁵	1–30	300–500	Bogaerts and Centi (2020), Bogaerts et al. (2015), Kutz (2011), Okubo et al. (2018), Puliyalil et al. (2018), Snoeckx and Bogaerts (2017), Yamasaki et al. (2020)
GAC	atm	10 ¹¹ –10 ¹⁵	1.4–2.1	1000–3000	Bogaerts and Snoeckx (2019), Li et al. (2020), Nunnally et al. (2011), Puliyalil et al. (2018), Ramakers et al. (2017), Snoeckx and Bogaerts (2017), Trenchev and Bogaerts (2020), Zhang et al. (2014), Zhu et al. (2020)
APGD	10 ⁻⁵ –atm	10 ⁹ –10 ¹²	1–2	~ 2000	Arumugam et al. (2018), Ghorbanzadeh et al. (2009), Kiruthika and Shanmugavelayutham (2020), Kutz 2011, Li et al. (2019), Tao et al. 2011, Wissel et al. (2013)
CD	atm	10 ⁸ –10 ¹⁴	3.5–5	< 400	Butterworth et al. (2016), Fridman (2008), Kutz (2011), Michielsen et al. (2017), Mikoviny et al. (2003), Nguyen et al. (2015), Schutze et al. (1998), Tao et al. 2011, Xu et al. (2004), Yang (2002)
RCP	10 ⁻³ –atm	10 ¹² –10 ¹⁵	0.65–1.85	~ 400 ^a	Fridman (2008), Hopwood (1992), Kwak et al. (2015), Nguyen (2009), Okumura (2010), Park et al. (2001), Spencer and Gallimore (2011), Wang et al. (2017a), Winchester and Payling (2004)
MW	10 ⁻⁵ –atm	10 ¹⁰ –10 ¹⁵	0.4–0.9	2000–6000	Azizov et al. (1983), Bongers et al. (2017), Britun et al. (2017), Chen et al. (2015), Fridman (2008), Hong et al. (2006), Hrycak et al. (2014), Jasiński et al. (2013), Legasov et al. (1978), Mizeraczyk et al. (2014), Snoeckx and Bogaerts (2017), Tao et al. (2011), van den Bekerom et al. (2019)

DBD dielectric barrier discharge, GAC gliding arc plasma, APGD atmospheric pressure glow discharges, CD corona discharge, RCP radiofrequency inductively coupled plasma, MW microwave plasma

^aAt an input power < 35 W

Corona discharge is a non-uniform discharge with a lower current density that can be produced at ambient pressure. It usually involves two different electrodes, including a plate with a low curvature and a sharp tip with a high curvature. In such arrangements, when high voltage is implemented between such two different electrodes, an electric breakdown near the sharp tip with high curvature leads to plasma formation in the drift region. In the reported work, it has been demonstrated that by using the corona discharge with 46.3 W of discharge power, the conversion of CH₄ and CO₂ was 62.4% and 47.8%, respectively (Nguyen et al. 2015, Schutze et al. 1998, Tao et al. 2011, Yang 2002).

Radiofrequency inductively coupled plasma can be formed into the plasma chamber by employing the electromagnetic field or, more precisely, radio frequency field, and the radio frequency field can be produced using the radio frequency power through the dielectric window to the planar coil. Compared to other types of plasmas, the radiofrequency inductively coupled plasma has less than 50% energy efficiency, which could be significantly decreased at higher power, e.g., > 100 kW (Hopwood 1992, Kwak et al. 2015, Okumura 2010, Wang et al. 2017a).

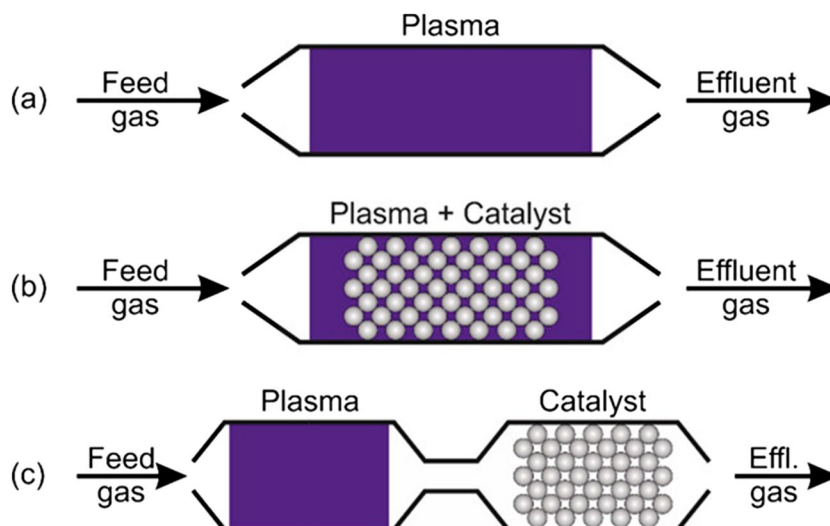
Microwave plasma can be formed by implementing microwave power to a gas-filled quartz tube, and the gas temperature can be easily raised to > 3000 K at (sub)ambient pressure with energy efficiency up to 40% comparatively

higher at atmospheric pressure and normal flow conditions. However, this energy efficiency can be increased to 90% with a CO₂ conversion between 10 and 20% under specific operational conditions such as the supersonic/subsonic gas flow and reduced pressure. The catalyst cannot be investigated quickly for the higher gas temperature in microwave plasma. Still, it can be placed after the plasma reactor, also known as the “post-plasma catalysis,” although only a few studies have been reported (Azizov et al. 1983, Fridman 2008, Hong et al. 2006, Hrycak et al. 2014, Jasiński et al. 2013, Legasov et al. 1978, Mizeraczyk et al. 2014, Tao et al. 2011).

Plasma-catalysis reactor configurations

It is well known that a series of parameters are involved in the plasma-only process (Fig. 2) for effective and energy-efficient conversion of CO₂ to the value-added products, including the specific energy input (SEI), composition of the feed gas, feed gas flow rate, discharge power, dielectric material, electrode configuration, discharge length/gap, and discharge frequency and type (George et al. 2021). However, coupling the plasma with the catalyst provides cooperative effects as the plasma-produced species can interact at the surface of the catalyst due to the interactive behavior

Fig. 2 Schematic illustrations of the reactor configurations for **a** plasma-only, **b** IPC, and **c** PPC. Reprinted from the reference (Ollegott et al. 2020) with the permission of Wiley



of plasma and catalyst (Tu et al. 2011, Tu and Whitehead 2012, Whitehead 2016, 2019). There are two significant configurations in plasma catalysis, known as the in-plasma and the post-plasma catalysis, represented as IPC and PPC, respectively, as shown in Fig. 2.

The IPC-configured reactor (Fig. 2) is based on a single-step procedure where a catalyst is placed in the plasma discharge region to enable to produce the short- and long-lived reactive species by the NTP to immediately interact with the surface of the catalyst with the plasma zone, leading to enhancement of CO₂ conversion and the targeted product selectivities. The IPC-configured reactor facilitates energy efficiency as the required energy to produce the short-lived species is often wasted either in the plasma-only or the PPC-configured reactor. In the IPC-configured reactor, the catalyst is either partially or fully packed into the plasma discharge region, and such packing configuration also affects the discharge properties. Due to the potential impacts of plasma on the catalyst, as discussed in the preceding sections, the NTP can synthesize and modify the catalyst to improve its performance and stability, a key driver towards commercialization (Di et al. 2019, Tu et al. 2013, Wang et al. 2018b, Witvrouwen et al. 2012).

The PPC-configured reactor (Fig. 2) facilitates the two-stage reactions where the gas-phase reaction occurs in the plasma region, followed by the second stage at the catalyst's surface. In this case, as the catalyst is not within the plasma discharge region, the catalyst bed is heated thermally to promote the reaction at the catalyst's surface. One of the disadvantages of the PPC-configured reactor is that as it is placed outside the plasma discharge region, only long-lived species and end-products can travel from the plasma region to the catalyst surface to interact with the catalyst surface for the reaction (Bo et al. 2020, Neyts et al. 2015). The short-lived species are the vibrationally excited species with 1–10

nanoseconds of short lifetimes at atmospheric pressure and seem difficult to survive while transitioning from the plasma region to the catalyst region. Hence, the PPC-configured reactor appears not feasible for efficient CO₂ conversion due to the lack of short-lived species conversion to targeted products.

Current developments in NTP-assisted CO₂ conversion

CO₂ reduction with 0H₂O

Chen et al. (2015) reported the concurrent CO₂ and H₂ dissociation using a surface wave sustained discharge in a pulse regime to investigate the potential impact of various process parameters, comprising the CO₂/H₂O feed flow rate ratio and SEI on the energy efficiency and conversion by identifying and quantifying the product streams using gas chromatography. It has been found that the H₂ and carbon monoxide (CO) formation in the same gas mixture can be carried out at the optimum SEI value of 1.6 eV/molecule. Further, this process is favored by the low feed flow rates and maximum energy efficiency. It has been found that the lower SEI and CO₂ with an excess amount behave as a “physical catalyst” for H₂O, leading to the formation of H₂.

In contrast, the higher SEI and feed flow rates significantly reduced the H₂ yield, suggesting that the CO formation consumes H₂, thus facilitating the reverse direction of WGS. The optimal emission spectroscopy (OES) results revealed that the lower gas temperature favored the higher dissociation rate. Hoeben et al. (2015) investigated that the CO₂ conversion with H₂O to produce CH₄ was observed using a pulsed corona discharge at a higher density using a CO₂ flow over the H₂O film, which results in the formation

of CH₄ under mild reaction conditions. It was interesting to know that the CO₂ and H₂O dissociation using plasma induces the CO₂ or CO hydrogenation chemistry over the NiCr wire materials, which behave as catalysts superior to low-alloy steel.

CH₄ reforming with CO₂ to syngas

Nearly two decades ago, Huang et al. (2000) reported the reformation of CO₂–CH₄ by a glow discharge plasma using and without using micro-arc formation with a Y-type reactor. The process seems effective for converting the mixture of CO₂ and CH₄ into syngas (CO and H₂) as a dominant product with a minor amount of hydrocarbons also identified. Interactions between the different species and arms were observed even when only reactants were excited. With micro-arc formation, the CO selectivity was enhanced, and the process became more energy efficient than the one without micro-arc formation. However, they found that the conventional catalytic methods have better energy efficiency than the plasma-only process to convert CO₂ and CH₄ mixture to produce syngas. In another similar work (Li et al. 2002), the product distribution generated from the CO₂ and CH₄ mixture was investigated with the impact of the discharge gap width, feed gas composition, and post-glow zone effects. From the feed gas composition effect, the gaseous and liquid hydrocarbons increased with an enhancement in the feed concentration of CH₄. At the same time, the CO selectivity was found to be directly proportional to the feed concentration of CO₂. The CO₂–CH₄ conversion is enhanced at a shorter discharge gap, favoring the synthesis of liquid-phase hydrocarbons and organic acids.

For this reason, an atomic economic reaction was identified to produce acetic acid directly from CO₂–CH₄. In addition, the higher discharge gap resulted in the synthesis of methanol (CH₃OH) and ethanol (C₂H₅OH). Most liquid-phase hydrocarbons identified in this work were highly chained, with olefins about 5.5 wt.%.

For the first time, Patiño et al. (2005a) investigated the application of radio frequency in the plasma-based to convert the CH₄ and CO₂ mixture to syngas with a conversion achieved similar to the other processes, which was further enhanced by increasing the radio frequency power and feed gas pressure. The reforming of CH₄ was investigated by injecting steam, CO₂, and oxygen (O₂) separately for reaction with CH₄, and it was found that the steam plasma was the most effective. In contrast, the O₂ plasma was the most oxidant. Higher power and higher H₂O–CH₄ feed flow rates resulted in CO₂-free syngas. In contrast, lower feed flow rates at the power of 50 W produced CO₂–CO-free H₂, indicating their potential for clean H₂ production for fuel cell applications. This way, an H₂ to CO ratio of up to 16 could be produced at certain reaction conditions.

Qi et al. (2006) found that it could be a potential option to produce syngas from CO₂ and CH₄ reforming using an abnormal glow plasma due to its unique energy density and the temperature profile in the discharge space. With an enhancement in either the energy density with temperature in the discharge space or power, the CO₂ and CH₄ conversion increased without any potential impact on the CO and H₂ selectivity, possibly because the electron's energy distribution did not change during the discharges. A competing reaction between the oxygen, carbon, molecules, and hydrogen radical atoms could increase the H₂ to CO ratio, which can be achieved by increasing the CH₄/CO₂ feed ratio. However, this strategy could lead to carbon deposition on electrodes, which can be avoided by adding oxygen to the reaction system.

Goujard et al. (2009) investigated the synthesis of hydrocarbons and syngas from biogas (excessive CH₄, CH₄/CO₂ = 1.5) using NTP, where the CH₄ and CO₂ conversion depended on the discharge power despite the variation in frequency or voltage at room temperature. In contrast, the excessive CO₂ was favorable for higher CH₄ and higher conversion of CO₂, leading to higher CO selectivity. Conversely, the higher CH₄ concentration favored hydrocarbon synthesis, and higher CO₂ concentration increased the selectivity towards CO. The results showed that temperature significantly influenced selectivity with higher CO selectivity at elevated temperatures, i.e., 873 K. These results could be elaborated by considering the reaction between the active oxygen species and the carbon formed from the CH₄ cracking. In this regard, the catalyst facilitates CO₂ activation and favors the higher CO selectivity in a hybrid plasma system compared to a plasma-only system at 773 K. More detailed, the catalyst's metallic nickel (Ni) species behaved as a radical trap. At the same time, the La₂O₃-based basic sites activated the CO₂ immediately as the catalyst was incorporated with the discharge plasma.

Tu and Whitehead (2014) reported a hybrid plasma-catalysis process to produce clean fuel and value-added products by reforming the CO₂–CH₄ mixture using an AC gliding arc reactor. It has been found that using the DBD reactor for CO₂–CH₄ reforming produced a wide range of hydrocarbons, while using the AC gliding arc plasma resulted in much cleaner fuel, and of course, syngas was the dominant product. It could be attributed to the high electron density generated by AC gliding arc plasma, which may cause a change in the reaction pathway. But this postulate needs further investigation. The optical emission spectra identified various species, including Al, CH, C₂, O, CO, H_α, and H_β. Compared to the hydrocarbons and syngas, a series of varying carbon nanomaterials were also formed, which included the spherical carbon nanoparticles, amorphous carbon, and multi-walled carbon nanotubes, indicating that this hybrid

process could open new doors to synthesizing carbon nano-materials in more sustainable and energy-efficient ways.

In another work, Zeng et al. (2015) reported the potential impacts of the hybrid plasma catalysis system on the $\text{CO}_2\text{-CH}_4$ reforming using the alumina-supported metal (Co, Mn, Cu, and Ni) catalysts using a coaxial DBD reactor. It has been observed that with the plasma-only mode, the $\text{CO}_2\text{-CH}_4$ conversion to syngas was strongly influenced by the feed ratio, not the feed flow rate; however, combining the Ni and Mn supported on alumina catalyst with plasma by packing into the discharge gap demonstrated a synergistic effect on the conversion of $\text{CH}_4\text{-CO}_2$ to syngas. Still, the CO_2 conversion was not affected by the catalyst presence. The conversion was almost independent of the textural characteristics of the employed catalyst (Fig. 3).

Snoeckx et al. (2015) reported the $\text{CH}_4\text{-CO}_2$ reforming to syngas using the DBD plasma to identify the most promising parameter among the residence time, power, frequency, and gas mixture composition to determine the most effective and energy-efficient condition from the commercialization point of view. They optimized the abovementioned parameters and obtained the energy efficiency and maximal conversion, which were found to be 8.5% and 84%, respectively.

In general, they found that the higher concentration of CO_2 favored energy efficiency and higher conversion; however, with an enhancement in the SEI, which accounted for both residence time and power, the results revealed only an enhancement of the conversion with a slight decline in the energy efficiency. Among the different parameters investigated, the most complicated effect came from the frequency. The product of the residence time and frequency, which indicated the total counts of filaments undergone by the gas molecules while passing via the reactor, was a decisive factor. It has been found that the higher counts of micro-discharge filaments with less energy per filament resulted in higher energy efficiency and conversion.

Another similar work was reported by Nguyen et al. (2015) for reforming $\text{CO}_2\text{-CH}_4$ to syngas using the corona discharge plasma with CO and H_2 as dominant products. Among different process parameters, such as the total feed flow rate, applied peak voltage, CO_2/CH_4 ratio, and pulse frequency, the pulse frequency and CO_2/CH_4 ratio were the most significant parameters. Overall, it has been found that a decrease in the total feed flow rate with an enhancement in the pulse frequency and peak voltage resulted in a higher conversion of CO_2/CH_4 . In addition, the CO selectivity

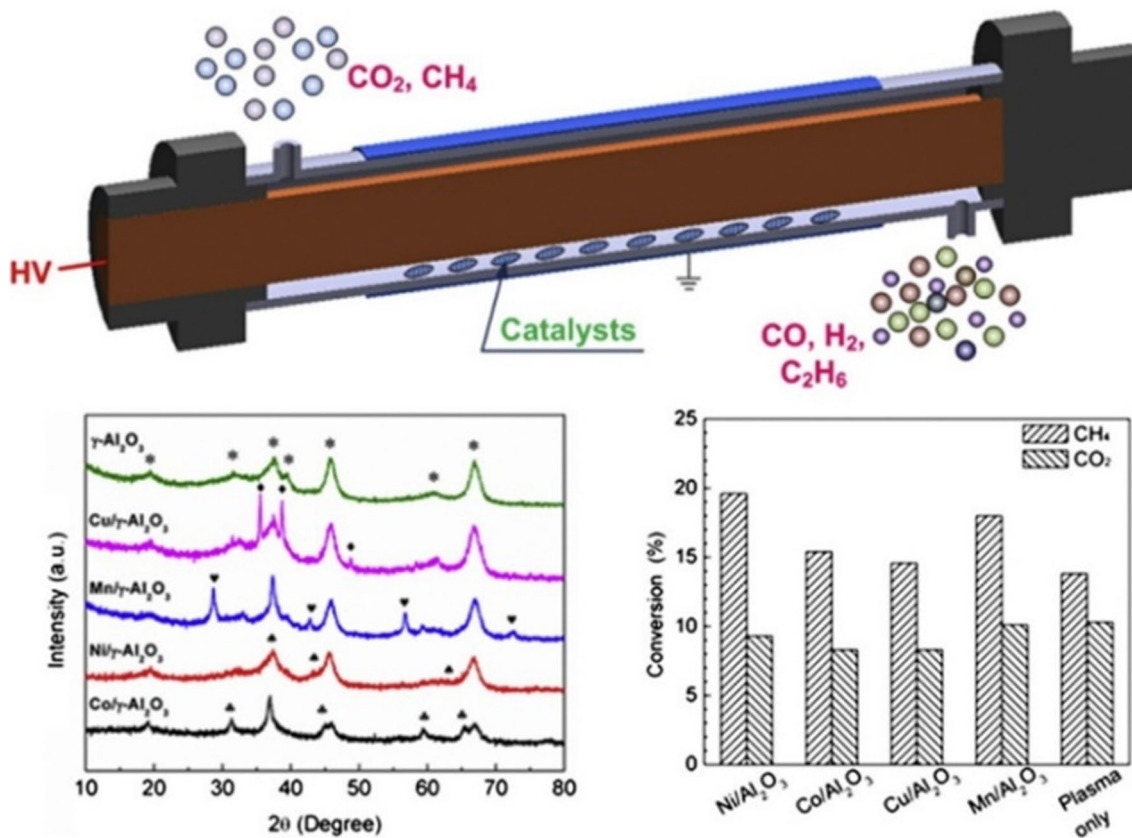


Fig. 3 Effect of catalysts and textural properties on the $\text{CO}_2\text{-CH}_4$ reforming to syngas and other value-added products in plasma-only and plasma-catalysis systems. Reprinted from the reference (Zeng et al. 2015) with the permission of Elsevier

decreased more than that of H_2 with the increased CO_2/CH_4 ratio. With a rise in the applied peak voltage up to 10 kV, the CO and H_2 selectivity increased and then decreased upon further increasing the applied peak voltage. In contrast, the CO and H_2 selectivity was not influenced by the variation in the pulse frequency or total feed flow rate.

Scapinello et al. (2016) reported CO_2-CH_4 reforming to syngas using a pulsed (NRP) discharge plasma (nanosecond repetitively) and reached a series of observations and conclusions. They found that the utilization of NRP discharge plasma demonstrated the highest performance, with an increased CH_4 and CO_2 conversion as a function of SEI. Due to the competing production of carbon powder and water, the selectivity towards syngas was decreased. To improve energy efficiency, water formation should be reduced with a thorough understanding of the water formation mechanism in this process.

Lu et al. (2017) reported CO_2-CH_4 reforming to syngas with a cooperative effect of the plasma with a catalyst supported on the graphitic carbon nitride (g- C_3N_4) using a DBD reactor. In the case of the plasma-only system, the overall reaction was affected by the overall feed flow rate, CH_4/CO_2 ratio, and input power, indicating an increased conversion of CO_2 and CH_4 with a rise in the input power and a decline in the total feed flow rate. However, the syngas selectivity was probably reduced due to coke formation at elevated energy levels. In the case of a hybrid plasma-catalysis system, the conversion of CO_2 and CH_4 , as well as the syngas yields, was higher because of the synergistic effect of the plasma and the catalyst (Fig. 4). By increasing the mass ratio of TiO_2 , the reaction probability between the catalyst and the higher energy electrons was reduced due to the adsorption of higher energy electrons.

Yap et al. (2018) investigated CO_2-CH_4 reforming to syngas under NTP, with the catalyst (La_2O_3/Al_2O_3) filling the entire zone of discharge in helium gas. It has been observed that the presence of helium in the feed gas favored the higher CO_2/CH_4 conversion, probably due to the transfer of energy from the activated helium species to the reactant molecules and decreasing the carbon deposition. Overall, helium utilization was not found to be favorable in terms of energy efficiency.

Khoja et al. (2018) investigated a $Ni/\gamma-Al_2O_3-MgO$ catalyst in the packed-bed DBD plasma reactor for CO_2-CH_4 reforming to syngas and additional value-added products. Performance was compared with the plasma-only system. It has been found that $Ni/\gamma-Al_2O_3-MgO$ resulted in low-carbon deposition compared to Ni/MgO and $Ni/\gamma-Al_2O_3$, probably because of the higher metal dispersion, high Lewis's basicity, and surface faceting (Fig. 5). The lowest carbon deposit was observed with the equimolar formation of CO and H_2 . This lower carbon formation was due to suppressing the carbon gasification and reversing the water gas shift reaction (RWGS). In addition, the higher H_2 production was credited with suppressing the recombination of H and CH_3 species to form CH_4 .

A detailed reaction mechanistic pathway was proposed for the hybrid plasma-catalyst system to produce syngas and other value-added products through CO_2-CH_4 reforming. The proposed mechanism was believed to follow the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism with the activation of CH_4 on the Ni-based active sites, and the deposited C^* may go to the process of gasification on MgO (Fig. 6). According to the proposed mechanistic pathway, the dissociation, or the activation of CH_4 as well as the CO_2 , is initiated by the plasma, followed by the elemental

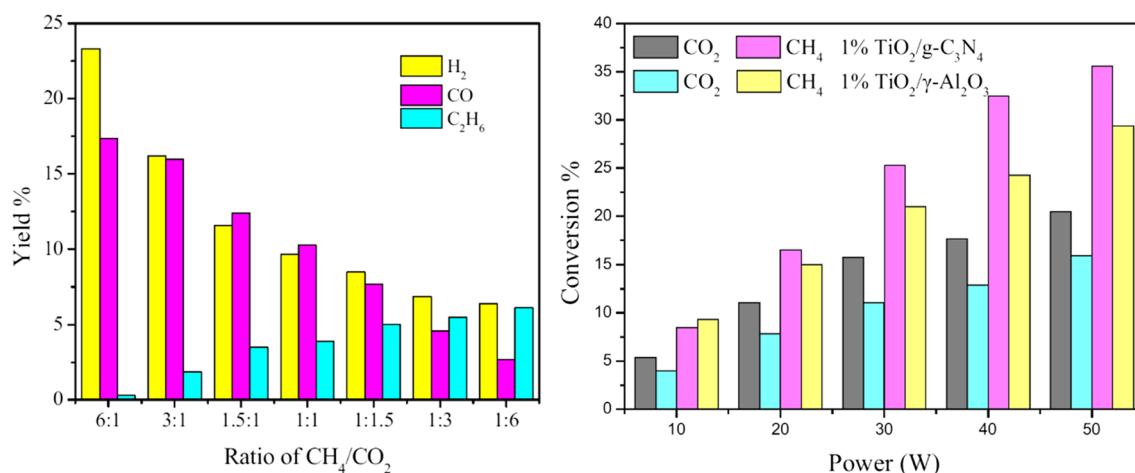


Fig. 4 (Left): effect of the CH_4/CO_2 ratio on the syngas and other product yields in the plasma-only system. (Right): effect of power and catalyst on the CH_4/CO_2 reforming conversion in the plasma-catalysis

system. Reprinted from the reference (Lu et al. 2017) with the permission of Springer

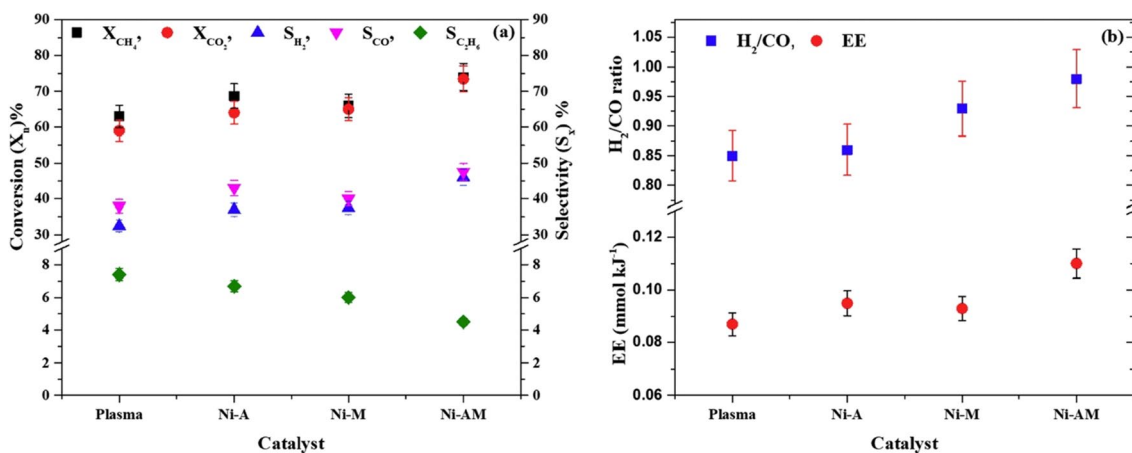


Fig. 5 Effect of the different catalysts on the (left) CH₄/CO₂ reforming conversion (X) and selectivity (S), (right) H₂/CO ratio, and energy efficiency (EE). Reprinted from the reference (Khoja et al. 2018) with the permission of Elsevier

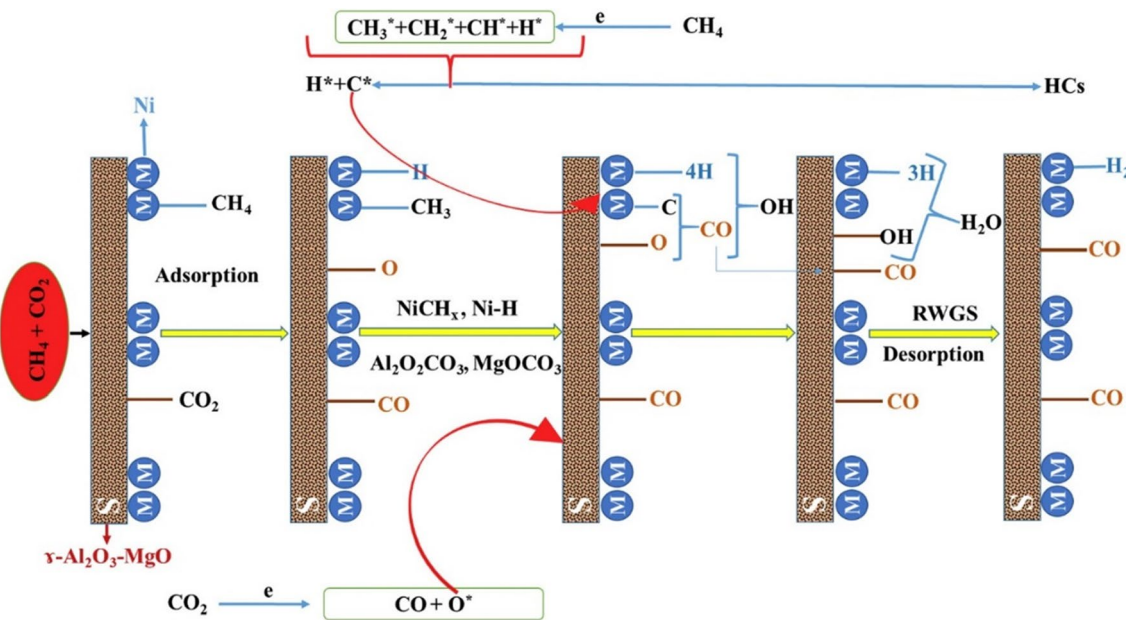


Fig. 6 A proposed reaction mechanism for the CO₂-CH₄ reforming over the Ni/γ-Al₂O₃-MgO catalyst in the presence of plasma. Reprinted from the reference Khoja et al. (2018) with the permission of Elsevier

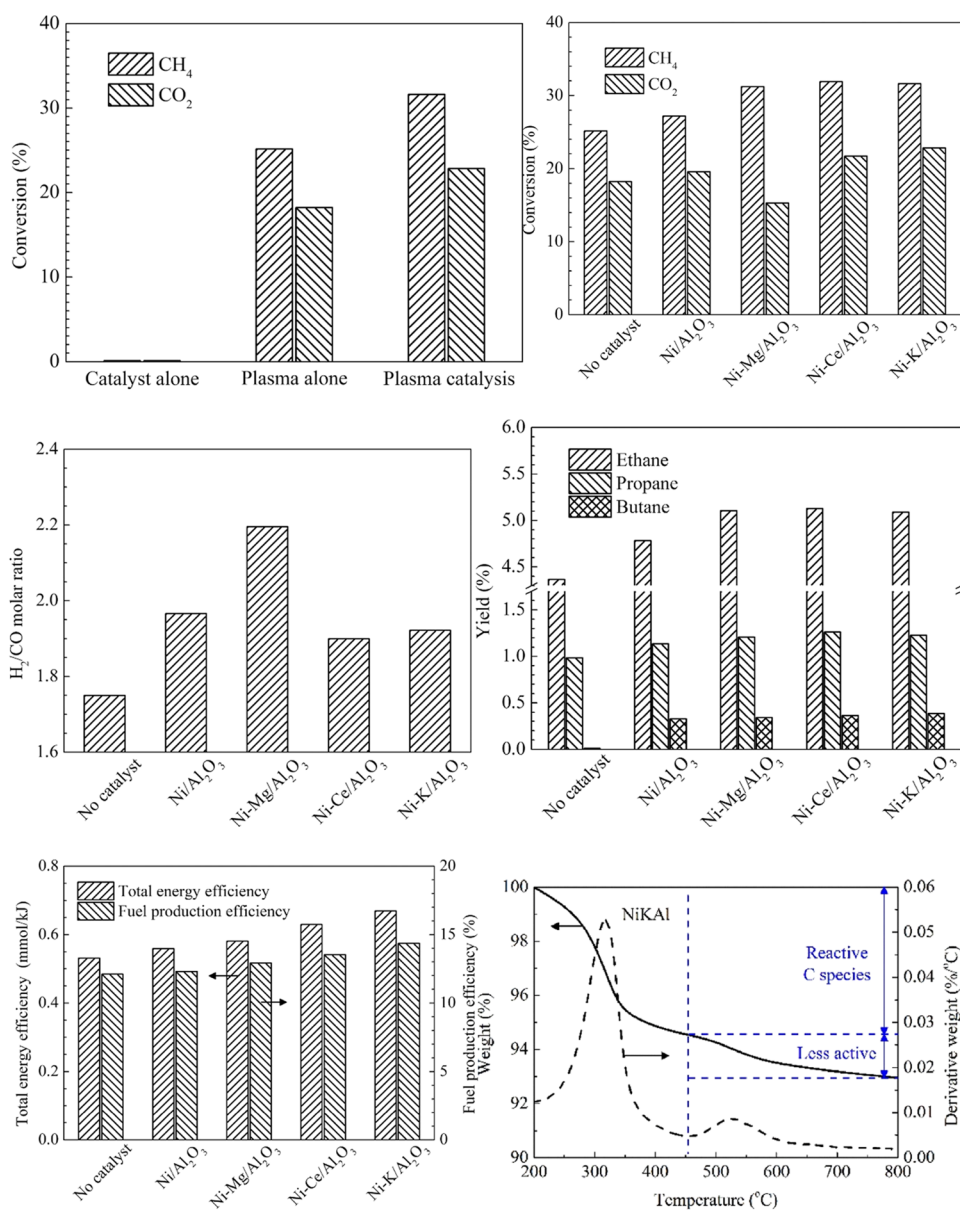
and intermediate adsorption composed of C, O, H, and oxy-carbonates on the support surface active sites. The surface-adsorbed species form the desired product in the presence of a catalyst and plasma (Akbari et al. 2017, Messaoudi et al. 2018).

Ray et al. (2018) deployed the DBD plasma reactor with the catalyst to investigate the potential effects on CO₂-CH₄ reforming to syngas, and it has been found that incorporating the catalyst into the DBD reactor favored an enhancement in the conversion of CH₄. The conversion efficiency of CH₄ was observed to be in the order of Ni-Mn/γ-Al₂O₃ > Ni/γ-Al₂O₃ > DBD, with the bimetallic catalyst showing

the highest CH₄ conversion probably due to its resistance towards carbon formation. Similar trends were observed for the CO₂ conversion, i.e., Ni-Mn/γ-Al₂O₃ > Ni/γ-Al₂O₃ > DBD.

Zeng et al. (2018) investigated CO₂-CH₄ reforming to syngas in three different modes: the plasma-only, catalyst-only (Ni/Al₂O₃ at 160 °C), and plasma-catalyst mode, to explore the potential effects in a DBD reactor (Fig. 7). The hybrid plasma-catalysis mode demonstrated higher CH₄ conversion, H₂ production, and energy efficiency than the plasma-only and catalyst-only (Ni/Al₂O₃) modes at 160 °C. Comparing the promoted catalysts with the catalyst

Fig. 7 An overview of CO_2 - CH_4 reforming with the effect of plasma and catalysts and promoted catalysts on CO_2 and CH_4 conversion, CO , C_2 - C_4 alkanes, and H_2 yield together with energy efficiency and catalyst stability. Reprinted from the reference Zeng et al. (2018) with the permission of Elsevier



($\text{Ni}/\text{Al}_2\text{O}_3$) showed that the promoted catalysts ($\text{Ni}/\text{Al}_2\text{O}_3$ catalyst modified with K-, Mg-, and Ce-) had higher CH_4 conversion performance attributed to their enhanced acidic active sites as the acidic active sites are responsible for activating CH_4 . Compared with thermochemical conversion, it has been found that these promoters have adverse effects on CH_4 conversion. Interestingly, the promoters demonstrated a different behavior in plasma and thermochemical conditions, indicating that their behavior was temperature-dependent regarding carbon deposition and the conversion of CH_4 . Among the promoted catalysts, the Mg-promoted catalyst significantly enhanced the H_2/CO molar ratio, probably due to the weak CO_2 affinity to the catalyst's surface.

In contrast, the K-promoted catalyst demonstrated the overall best performance in CO_2 - CH_4 conversion and the

yields of C_2 - C_4 alkanes, CO , and H_2 together with energy efficiency. Promoted catalysts also favored carbon deposition in the hybrid plasma-catalysis process. However, the total quantity of deposited carbon was still lower than in the high-temperature thermochemical reforming of CO_2/CH_4 . The thermogravimetric analysis (TGA) revealed that the spent catalyst has carbon deposition in the reactive carbon-based species, which can be easily oxidized by O and CO_2 to maintain the catalyst stability during the reaction.

CO_2 dissociation to CO

Mei et al. (2014) reported a plasma catalysis system for CO_2 conversion into O_2 and CO in a DBD cylindrical-shaped reactor using and/or without the packing materials. The

aim was to investigate the potential effects of the materials used as reactor packing, i.e., glass beads and BaTiO₃, on the CO₂ discharge properties and conversion to CO and O₂. At the same discharge power, it has been found that there was an evolution in the CO₂ discharge behavior from a typical filamentary discharge with no packing material to a combination of surface discharge with glass beads and barium titanate (BaTiO₃) packings and filamentary. Incorporating BaTiO₃ into the plasma system improves the energy of electrons and increases the average electric field by 98.49% and 93.78%, respectively, further influencing the plasma-catalysis-based reactions. In addition, it has been found that utilization of the reactor packing materials, i.e., glass beads and BaTiO₃, in the discharge gap results in the efficiency enhancement of the DBD reactor for the conversion of CO₂, although the CO₂ residence time has been reduced due to an increase in the volume of discharge at the identical flow rate of gas. Overall, it has been found that utilization of the reactor packing materials, i.e., glass beads and BaTiO₃, significantly improved the conversion of CO₂ by 75% and the yield of CO due to variation in the discharge properties (Fig. 8), making it an efficient process compared to CO₂ conversion in plasma catalysis with no packing. Furthermore, the electron with a highly energetic state (> 3.0 eV) produced by the discharge could be assistive in activating the photocatalyst (BaTiO₃) by an electron-hole pair on to the surface of the catalyst, which further provides a synergistic effect to the CO₂ conversion process.

In another work, Mei and Tu (2017) extended their research to explore the potential different parametric effects on the plasma-catalysis-based transformation of CO₂ to O₂ as well as the CO. These parameters included the discharge length and frequency, plasma power, electrode gap, CO₂ flow rate, dielectric materials thickness, and the reactor design using a DBD coaxial reactor. It has been found that

the decomposition of CO₂ and the efficiency of the process were not affected noticeably by the discharge frequency. Higher discharge power and/or lower flow rate CO₂ feed results in an increased conversion of CO₂ than the lower discharge and/or higher CO₂ feed flow rate. In this regard, a clear trade-off existed between the conversion of CO₂ and the plasma process efficiency. In addition, the decomposition of CO₂ and process energy efficiency was positively affected by lowering the thickness of the dielectric material and discharge gap and increasing the discharge length. Regression modeling shows that the flow rate of the CO₂ feed and the discharge power are the key drivers for enhancing the conversion of CO₂ and the process's energy efficiency.

Additionally, it has been observed that using aluminum (Al) foil on the outer surface of the electrodes and the screw-type inner electrodes composed of stainless steel (SS) significantly improved the conversion of CO₂ and energy efficiency compared to other forms of electrodes. The role of the SS screw-type inner electrode and Al foil was investigated, and it was found that the Al foil contributed to the enlargement of the effective discharge area. In contrast, the SS screw-type electrodes improved the local electric field near the electrode's sharp edge. Both effects positively enhanced the process of converting CO₂ (Fig. 9).

Xu et al. (2017) reported the CO₂ dissociation in NTP at atmospheric pressure using a reactor packed with BaTiO₃ packing to investigate the potential impacts of CO₂ dilution with nitrogen (N₂) and argon (Ar). The results showed that the packing material composed of BaTiO₃ ferroelectric in contact with the electrodes facilitated the conversion of CO₂ with higher yield and the process energy efficiency compared to the DBD reactor with and without packing materials using dielectric layer-covered electrodes. Based on their operating conditions, the CO₂ dissociation was unaffected and remained constant despite the input energy.

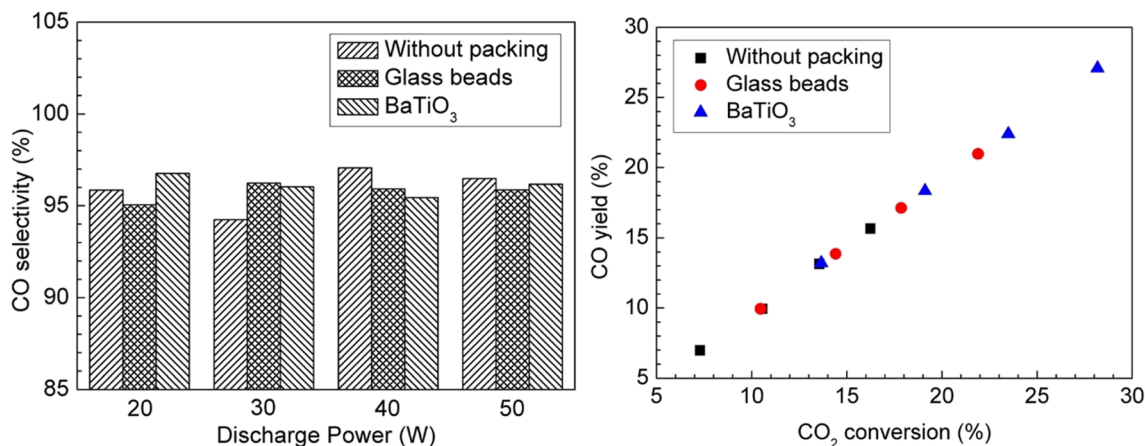


Fig. 8 Effect of packing materials on (left) CO selectivity and (right) CO yield. Reprinted from the reference Mei et al. (2014) with the permission of IOP Science Publishing

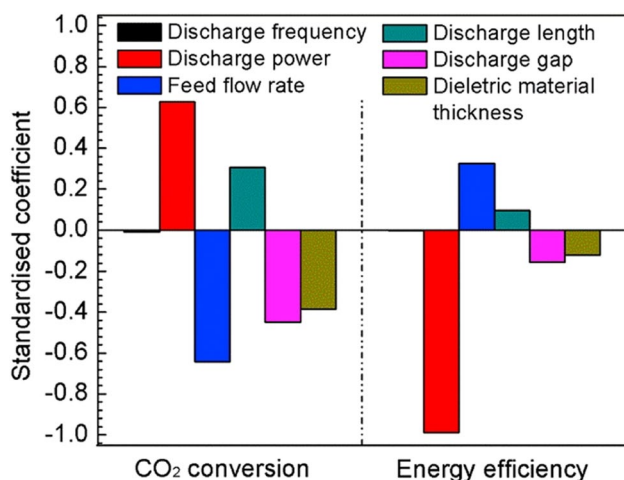


Fig. 9 Standardized coefficients for various processing parameters for (left) CO₂ conversion and (right) energy efficiency. Reprinted from the reference Mei and Tu (2017) with the permission of Elsevier

Thus, the packing material composed of BaTiO₃ ferroelectric, together with the NTP atmospheric pressure system for CO₂ dissociation, was found to be a potential and powerful alternative to CO₂ utilization compared to thermal catalysis, in terms of energy efficiency, process economics, and scale-up configurations. In addition to the above discussion, the influence of feed CO₂ dilution with N₂ and Ar showed a positive impact by increasing CO₂ conversion by reducing the breakdown voltage at a given energy input for the dissociation of CO₂, resulting in a simplifying NTP process design in terms of power supply. O₂ and CO were the significant products identified in the process of dissociation of CO₂. At the same time, a trace amount of ozone (O₃) was also detected (maximum 100 ppm) in the case of pure CO₂ and Ar/CO₂ systems but was not observed in the case of the N₂/CO₂ system. It has been found that the higher dilution of the CO₂ feed with Ar results in higher production of atomic oxygen that leads to a higher concentration of O₃, but at the same time, a temperature rise caused by the higher input of the plasma energy results in O₃ dissociation. However, as mentioned above, there was no O₃ in the N₂/CO₂ system, and nitrogen oxides (N₂O, NO₂, and NO) were identified up to a maximum of 3120 ppm. Based on their proposed mechanism, except for higher plasma energies, the N₂O formation is generally favored compared to NO_x. In the meantime, the higher contents of N₂ facilitate the NO₂ conversion to NO and NO conversion to N₂.

In another similar study (Yap et al. 2015), the effect of CO₂ dilution using and without the helium (He) was explored experimentally in the plasma catalysis CO₂ conversion process to CO and O₂ using glass balls filled with a non-thermal plasma reactor and two different generator supplies. It has been found that the sinusoidal excitation-based

discharge generation was much more effective for dissociating CO₂ than the pulsed generator discharge at an equivalent input power. At specific input energy (40 kJ/mole), 7.5% of CO₂ conversion was obtained with the pulsed supply while 13.5% with the sinusoidal excitation with a dilution ratio of He/CO₂ = 1/1. The kinetic investigations revealed the first-order kinetics, but the rate constant significantly differed in the two generator types. From the mechanistic point of view, the CO₂ dilution with He favors the CO₂ conversion to CO, particularly in the case of AC sinus activation, which produces mainly species possessing vibrational excitation. However, pure CO₂ demonstrated remarkable efficiency in both types of power supply. It has been found that the CO selectivity and the carbon balance were maximal with the He dilution. At the same time, there was an issue with the carbon deposition in the case of a pure CO₂ system without dilution. Large cubic and spherical particles with carbon filaments that were several tens of micrometers long were identified. They have demonstrated for the first time that carbon atoms can also be merged into the silica network of the glass under the NTP discharge during the dissociation of the CO₂ process, indicating a higher energetic process in plasma. The CO₂ conversion remains constant, but the CO selectivity improved by controlling the reactor wall temperature, and the lower temperature favors the higher CO selectivity, indicating that the carbon balance is because of the decomposition of CO on the reactor walls.

Butterworth et al. (2016) reported the potential impacts of the particle size of the two distinct packing materials (BaTiO₃ and Al₂O₃) on CO₂ conversion to O₂ and CO in the packed bed reactor assisted by plasma catalysis. It has been found that the reduced particle size of the packing materials (180–300 μm) could enhance the conversion of CO₂ by 70% and also enhance the incidence of reactor partial discharging and reactor breakdown voltage. The term “partial discharging” represents a decline in the reactor fraction where the plasma formation occurs, usually initiated by insufficient applied electric field strength, subsequently reducing the reactor efficacy. Hence, partial discharging can be prevented by providing excessive electric fields in the reactor consuming voltage. For a fair comparative analysis, it should be noted that the comparison of packing materials should be investigated only when the partial discharge is shallow; otherwise, effective materials for reactor packing might be unconsciously neglected. Peeters and van de Sanden developed Lissajous figures based on the partial discharging equivalent circuit that could be used to quantify partial discharging and reactor burning voltage (Peeters and Sanden 2014). In another work (Paulussen et al. 2010), it has been experimentally revealed that the CO₂ feed flow rate is the utmost critical parameter influencing the conversion of CO₂ and the yield of CO, which is usually higher at a lower CO₂ feed flow rate. Additionally, the influence of

temperature directly impacts CO₂ conversion, but CO yield is limited.

CO₂ hydrogenation

Wang et al. (2018a) investigated the hydrogenation of CO₂ over the hybrid catalyst-based NTP by considering the different parametric effects, including reactor design, reactant composition, and catalyst effect. Initially, they developed three different types of DBD reactor arrangements depending on the construction materials for the ground electrode and higher voltage electrode known as reactor-I (aluminum foil with stainless steel (SS) rod), reactor-II (water with SS rod covered by the quartz tube), and reactor-III (water with SS rod). Based on the design of different reactors, it has been found that the overall CO₂ conversion was quite similar, but the product distribution varied widely. In all reactors, methanol and ethanol were identified as the major oxygenated products, while CO and CH₄ were the most significant gaseous products. It has been found that reactor III produced the highest methanol compared to reactors I and II, while reactor I resulted in the highest CO selectivity. The significant increase in the methanol production and selectivity using reactor-III could be directed to the water used as a ground electrode instead of aluminum foil, which successfully maintained the temperature. The CO selectivity in reactor-III was the lowest among the three reactors, possibly due to the highest conversion of CO to methanol. As reactor-II and reactor-III operated at lower temperatures, higher activity was observed with oxygenate formation (CH₃OH). CO was the dominant product in reactor-I due to high-temperature operation. Another advantage of reactor-II and reactor-III at lower temperature operation was that they inhibited the further decomposition of CH₃OH (Wang et al. 2023b). Reactor III demonstrated the best performance even though high voltage was applied in reactors I and II. The better performance of reactor III was related to the domination of strong filaments, which were much weaker in reactor II. The feed molar ratio with the catalyst was also investigated in their work. It is an admitted fact and observed in their study that the feed molar ratio, i.e., CO₂:H₂, significantly influences the methanol conversion, concentration, and yield. By increasing the hydrogen ratio over CO₂, it has been found that the overall methanol conversion increases with a decrease in the CO selectivity, indicating the forward reaction. In addition to the feed molar ratio, the effect of catalysts was also studied. Two different catalysts, Pt/Al₂O₃ and Cu/Al₂O₃, were employed for efficient H₂ and CO₂ activation, respectively. The results revealed that the Cu/Al₂O₃ catalyst demonstrated better performance towards methanol production than the Pt/Al₂O₃ catalyst.

It has been known that molecular adsorption depends on the molecule-catalyst interaction, and it is not supposed to

be a spontaneous process. Due to the higher internal energy of CO₂ (v), its adsorption is preferred energetically compared to the CO₂ in its ground state. However, the plasma characteristics influence the CO₂ (v) adsorption, including the electron energy and electric field (Wang et al. 2017b). Based on the previously reported studies on CH₄ conversion using the plasma-catalysis system, the efficient adsorption of CH₄ (v) species on the Ni metal surface was the origin of the higher CH₄ conversion compared to the thermochemical process of steam methane reforming. Quantitatively, the CH₄ conversion was 50% and 20% in the plasma-catalysis and thermochemical conversion processes, respectively (Nozaki et al. 2004). Furthermore, it has been found that the CO₂ (v) adsorption onto the surface of the catalyst resulted in the dissipation of the CO₂ (v) energy to the catalyst, leading to the Auger de-excitation and formation of low-energy electron-hole pairs, which could alter the physical and chemical characteristics of the catalyst, including the electronic structure, to make it more active and trigger the CO₂ (ad) to form HOCO (ad) and HCOO (ad). Additionally, the RWGS can also occur at the surface of the catalyst, preceding the production of CO (ad) from CO₂ (ad), which could be the possible reason for the enhanced formation of CO when plasma reactors are packed with the catalysts (Porosoff et al. 2016).

Comparing the catalyst performance in the plasma-catalysis mode, it has been found that Cu/γ-Al₂O₃ demonstrated better performance in terms of synthesis of methanol (yield) than Pt/γ-Al₂O₃ with almost identical OES CO₂/H₂ discharge spectra, indicating that the physical and chemical characteristics of the catalysts were more dominant to determine their different reaction performances. It has also been found that the Cu nanoparticle size in Cu/γ-Al₂O₃ was considerably more significant than the Pt nanoparticle size in Pt/γ-Al₂O₃. However, better performance for methanol synthesis was observed for Cu/γ-Al₂O₃ rather than Pt/γ-Al₂O₃, indicating that the particle size was not the dominant factor in determining the catalyst performance. At the same time, the x-ray diffraction (XRD) analysis of the spent catalyst demonstrated that the Cu in the metallic state was the dominant phase over the catalyst's surface, a highly active site for the hydrogenation of CO₂ to methanol. Compared to the active metal particle size, the oxygen-based intermediates (ΔE_o) adsorption energy over the active metal surface was the dominant parameter related to the catalyst performance for the hydrogenation of CO₂ to CH₃OH. Based on the theoretical investigation, a volcano chart was developed, which showed that the elements located on the volcano top would favor the hydrogenation of CO₂ to methanol. Cu is found to be on the top of the volcano, indicating that Cu is the dominant catalyst over Pt and others for CO₂ hydrogenation to methanol because it will moderately bind the oxygen-based intermediates at atmospheric pressure (Studt et al. 2014). In another study to investigate the CO₂ hydrogenation

mechanism over the Pt nanoparticles supported separately on SiO₂ and TiO₂, it has been found that probably due to the weaker CO₂ binding to the catalyst, the Pt nanoparticles could not catalyze the reaction. However, once the CO₂ hydrogenation to CO was initiated with the stabilization of CO₂, the reaction proceeded via RWGR (Kattel et al. 2016). By using an in situ attenuated total reflection infrared (ATR-IR) spectroscopy, it has been found that the CO₂ adsorption leads to the synthesis of carbonate-like species over the Pt/ γ -Al₂O₃ and γ -Al₂O₃, which are subsequently hydrogenated to produce CO as a final product (Ferri et al. 2002). The abovementioned findings indicated why the Pt/ γ -Al₂O₃ resulted in higher CO selectivity than the Cu/ γ -Al₂O₃ or plasma-only mode.

CO₂ to organic acids

Electrochemical reduction of CO₂ (ITO et al. 1982) to produce carboxylic acids was investigated a long time ago by using the non-aqueous electrolytes composed of dimethyl sulfoxide (DMSO) as an aprotic solvent with tetraalkylammonium salts over different electrodes such as lead (Pd), indium (In), zinc (Zn), and strontium (Sn). Based on the experimental investigation, it has been found that oxalic acid was the dominant product of the CO₂ electrochemical reduction with Pd electrodes. However, other higher carboxylic acids, including the propionic, glycolic, malonic, and *n*-butyric acids, were produced in addition to the formic acid at substantial concentrations in TEAP or TEABr/DMSO because oxalic, tartaric, and formic acids were found to be the dominant products in the case of TBABr/DMSO, with a negligible amount of other organic acids produced. CO was identified as a dominant product with a low oxalic, formic, malonic, and glycolic acid concentration in the Zn, Sn, and In electrodes. Based on experimental evidence, it has been confirmed that oxalic acid as an intermediate pathway can be used to produce the higher carboxylic acids mentioned above through CO₂ cathodic reduction.

Recently, the electrochemical CO₂ reduction to produce formate and oxalate facilitated by the solvated electrons produced by the plasma operated at atmospheric pressure was examined (Rumbach et al. 2016). In this work, the optical absorbance measurements were employed to visualize the solvation of free electrons produced by the plasma at atmospheric pressure into the solution to reduce the aqueous CO₂ to carboxyl radical anion, i.e., CO₂^{•-} (aq.). It was found that most of the CO₂^{•-} (aq.) ions were typically recombined to produce oxalate under basic conditions. In contrast, some of them produced formate following the disproportionation mechanism with the kinetics of this reduction reaction, such as bulk kinetics in radiolysis experimentations. The formate was found to be the dominant species under strongly acidic conditions. Higher concentrations of dissolved CO₂

could help improve the process efficiency, but there will be a trade-off between the oxalate and formate yields due to pH. In another similar work (Ihara et al. 1994), the reverse combustion, i.e., the reduction of CO₂ in water assisted by plasma, was investigated, and the oxalic acid with hydrogen peroxide (H₂O₂) was identified as a significant product with low yield with no formation of alcohol or mixture of acids.

One-step CO₂-CH₄ reforming to liquid chemicals

Wang et al. (2017c) investigated the one-step CO₂-CH₄ reforming into a series of liquids (CH₃COOH, CH₃OH, C₂H₅OH, and C₃H₆O), with CH₃COOH as the dominant product. A trace amount of HCOOH, propanol (C₃H₈O), and butanol (C₄H₉OH) were also identified. The gaseous products included H₂, CO, and C_xH_y (where $x = 2-4$ and $y = 2-10$). In this reaction, it was found that the catalyst could not trigger the reaction at 30 °C. At the same time, the NTP assisted the unfavorable reaction, i.e., thermodynamics, in proceeding at ambient temperature. It was observed that combining the catalyst with the plasma could help employ the synthesis and distribution of various oxygenates under ambient reaction conditions. CH₃COOH was the dominant product, and whatever catalyst was employed for this reaction was followed by CH₃OH and C₂H₅OH. HCOOH was formed only in the case of catalysts supported by noble metals with the highest selectivity over the Pt/ γ -Al₂O₃. The distribution of the gaseous product was not influenced by adding the catalyst into the plasma-only mode, with CO, H₂, and C₂H₆ being dominant gaseous products. In hybrid plasma catalysis mode, the H₂ selectivity was found to be enhanced with slightly increased productivity of C₂H₆ with a weak influence on the enhancement of selectivity for CO and other C_xH_y (where, $x = 2-4$ and $y = 2-10$) except for the catalyst (Cu/ γ -Al₂O₃). The CO₂ and CH₄ conversion decreased slightly in the hybrid plasma catalysis mode compared to the plasma-only mode. It could be due to the variation in the discharge behavior prompted by the catalyst that has an adverse impact on the reaction. Remarkably, a chemical, C₆H₁₂O₄ (CAS No. 49653-17-0), was identified on the inner walls of the reactor in the hybrid plasma catalysis mode. The proposed experimental setup directly reformed CO₂-CH₄ into a series of gaseous and liquid chemicals at ambient reaction conditions, bypassing the syngas formation.

Li et al. (2023) reported an experimental study to synthesize H₂ and liquid fuels using hybrid plasma catalysis-driven one-step CO₂-CH₄ reforming using a Fe- and Cu-based active site catalyst supported on 5A zeolite. The process resulted in a one-stage CO₂-CH₄ mixture co-conversion into liquid chemicals and H₂ due to the strong cooperative effect of the Fe/Cu active sites with the externally applied plasma field. In the case of gaseous products such as CO and H₂, the selectivity was found to be enhanced (36 to 56.6% for

H₂ and 50 to 57.6% for CO) with the addition of H₂O, which could be related to the improved radical density of OH and H. In the case of liquid fuels such as CH₃OH and acetic acid (CH₃COOH), a strong cooperative effect between the plasma and the acid/base characteristics of the employed catalyst was observed with varied selectivity of the liquid chemicals. A combined in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with OES was used to investigate the role of active sites and the possible mechanistic pathways. It was found that the Cu/5A zeolite with a higher density of acidic sites significantly facilitated the production of different carbonate species, which further played their critical role in the synthesis of CH_xO and further CH₃OH by the recombination of CH_xO with gaseous H₂. It was found that the COOH generated from both processes, i.e., recombination of gaseous OH with CO and CO₂ protonation, was the key to producing CH₃COOH. It was interesting to know that the Cu/5A zeolites (Cu⁰) with a higher acidic sites density and the Fe/5A zeolites (Fe²⁺) with a higher density of basic sites favored the formation of CH₃OH and CH₃COOH, respectively (Fig. 10). In addition to the experimental demonstration, the adsorption energy differences–based density functional theory (DFT) calculations for the O-containing radicals showed crucial interactions with the varied charge transfer between the active sites, i.e., Cu (111) surfaces and the gaseous radicals, thus leading

to the formation of targeted products. As discussed in this review, a detailed comparison of the plasma- and plasma-catalysis–based CO₂ conversion routes to C1 products is tabulated in Table 3 with experimental setup and reaction conditions.

Conclusions and future recommendations

This review comprehensively analyzed and compared the fundamentals of plasma technology for converting CO₂ to fuel-graded and value-added products with other conventional CO₂ conversion technologies. A detailed discussion was conducted on the different types of plasma, and their comparisons based on their characteristics, operational conditions, and performance were also reviewed, as well as various configurations of the plasma reactors. Critical discussions on plasma catalysis for CO₂ conversion were presented. Some challenges in this field are identified and provided below:

- CO₂ circular economy: CO₂ is essential for life on Earth; however, the exponential growth of gases after industrialization has resulted in excessive CO₂ in the Earth's atmosphere. The circular carbon economy is a crucial concept for addressing the issue of excessive CO₂ emis-

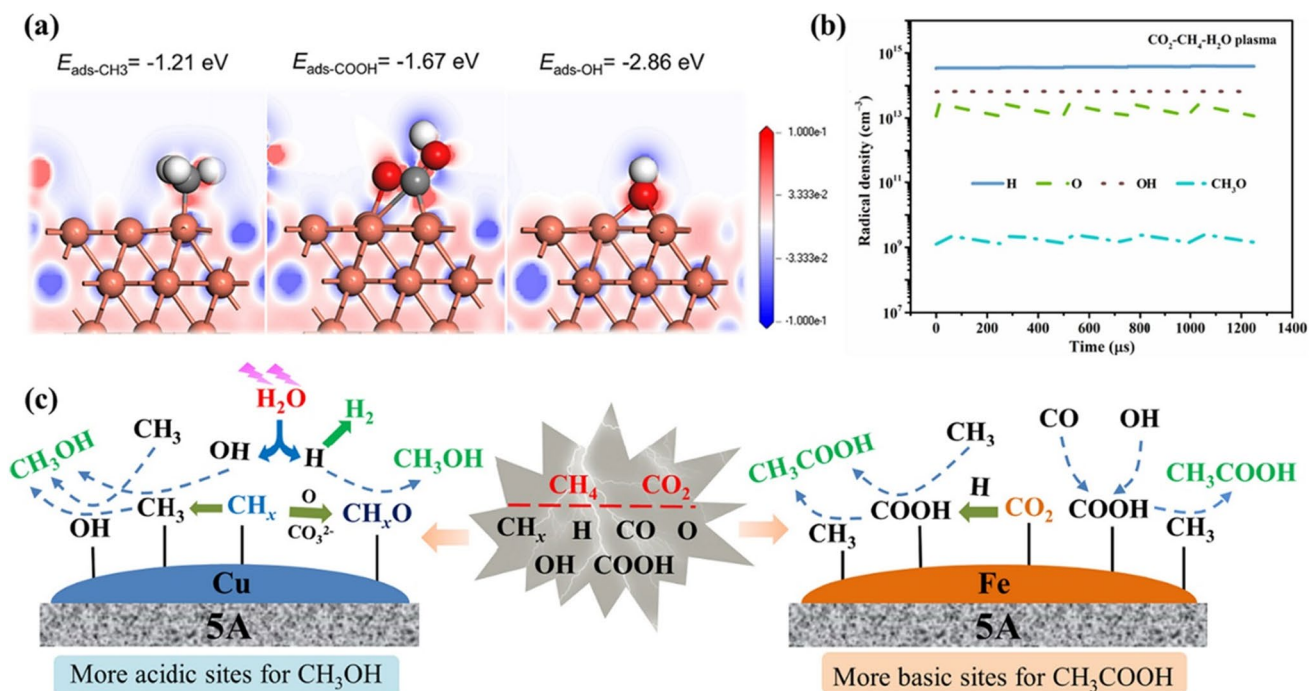


Fig. 10 **a** Energy density difference for the CH₃, COOH, OH radicals with Cu (111) surface; **b** essential radicals' density as a function of the time during the five periods for the CO₂-CH₄-H₂O plasma; and **c** the discriminative formation of CH₃OH and CH₃COOH over Cu/5A

and Fe/5A, respectively, via a synergistic plasma-catalyst effects. Reprinted from the reference Li et al. (2023) with the permission of Elsevier

Table 3 Summary of experimental setup and reaction conditions for CO₂ conversion to different projects

Discharge type	Catalyst	Feed gases	Feed composition	Major products	CO ₂ conversion	Selectivity	Ref.
MR ^a	N/A	CO ₂ /H ₂ O	50:50	CO, H ₂	N/A	N/A	Chen et al. (2015)
PCD ^b	NiCr	CO ₂ /H ₂ O	N/A	CH ₄	76	99	Hoeben et al. (2015)
GD ^c	N/A	CH ₄ /CO ₂	9:1	CO, C ₂ H ₆ , C ₂ H ₄ , C ₃ H ₈ , H ₂	52.8	27.8 ^d (47.9 ^e)	Huang et al. (2000)
DBD ^f	N/A	CH ₄ /CO ₂	34:66	CO, H ₂ , C ₂ -C ₅ , C ₆ -C ₁₁₊ , oxygen- ates	N/A	0.2 ^g	Li et al. (2002)
RF ^h	N/A	CH ₄ /H ₂	1:2	H ₂ , CO ₂ , CH ₄ , CO	46.4	56.9 ⁱ	Patiño et al. (2005b)
AGP ^j	N/A	CH ₄ /CO ₂	50:50	CO, H ₂	83.2	80 ^d (90 ^e)	Qi et al. (2006)
DBD ^f	Perovskite LaNiO ₃	CH ₄ /CO ₂	60:40	CO, H ₂ , C ₂ H ₆ , C ₂ H ₄ , C ₂ H ₂ , C ₃ H ₈ , C ₄ -C ₆ , oxygenates	13.3	40.5 ^d	Goujard et al. (2009)
GAD ^k	Al	CH ₄ /CO ₂	50:50	CO, H ₂	8.4	69.5 ^d (31.4 ^e)	Tu and Whitehead (2014)
DBD ^f	Ni/γ-Al ₂ O ₃	CH ₄ /CO ₂	1:9	CO, H ₂ , C ₂ H ₆	42 ^l	37 ^d (33 ⁵)	Zeng et al. (2015)
DBD ^f	N/A	CH ₄ /CO ₂	10:90	CO, H ₂	84	N/A	Snoeckx et al. (2015)
CD ^m	N/A	CH ₄ /CO ₂	4/1	CO, H ₂	32	70 ^d (35 ^e)	Nguyen et al. (2015)
DBD ^f	TiO ₂ /g-C ₃ N ₄	CH ₄ /CO ₂	1:6	CO, H ₂	20	50 ^d (40 ^e)	Lu et al. (2017)
PD ¹⁴	10% La ₂ O ₃ /Alu- mina Balls	CH ₄ /CO ₂	3.3/6.7	CO, H ₂ , Hydrocar- bons	11.8	72.1 ^d (24.6 ^e)	Yap et al. (2018)
DBD ^f	Ni/γ-Al ₂ O ₃ -MgO	CH ₄ /CO ₂	1:1	CO, H ₂	73	30.5 ^d (29.5 ^e)	Khoja et al. (2018)
DBD ^f	Ni-Mn/γ-Al ₂ O ₃	CH ₄ /CO ₂	1:1	CO, H ₂	13.2	40.5 ^d (13.2 ^e)	Ray et al. (2018)
DBD ^f	Ni-K/Al ₂ O ₃	CH ₄ /CO ₂	3:2	CO, H ₂ , C ₂ H ₆ , C ₃ H ₈	22.8	43.3 ^d (31.3 ^e)	Zeng et al. (2018)
DBD ^f	BaTiO ₃	CO ₂	Pure	CO, O ₂	75	97 ^d	Mei et al. (2014)
DBD ^f	N/A	CO ₂	Pure	CO, O ₂	27.2	94 ^d	Mei and Tu (2017)
DBD ^f	BaTiO ₃	CO ₂ /Ar	20:80	CO, O ₂ , O ₃	36	N/A	Xu et al. (2017)
DBD ^f	N/A	CO ₂	Pure	CO, O ₂	5.4	58 ^d	Yap et al. (2015)
DBD ^f	Cu/γ-Al ₂ O ₃	CO ₂ /H ₂	1:3	CH ₃ OH	11.3 ¹⁵	53.7 ^p	Wang et al. (2018a)
DBD ^f	γ-Al ₂ O ₃	CO ₂ /CH ₄	1:1	CH ₃ COOH, liquid chemicals	15.4	50-60 ^d	Wang et al. (2017c)
DBD ^f	Cu-Fe/5A zeolite	CO ₂ /CH ₄	1:1	H ₂ , CH ₃ COOH, CH ₃ OH	30.3	56.6 ^e	Li et al. (2023)

^aMicrowave radiation^bPulsed corona discharge^cGlow discharge^dCO selectivity^eH₂ selectivity^fDielectric barrier discharge^gC₂H₄ selectivity^hRadio frequencyⁱC₂ product selectivity^jAbnormal glow plasma^kGliding arc discharge^lCH₄ conversion^mCorona dischargeⁿPlasma discharge^oCH₃OH yield^pCH₃OH selectivity^qTotal selectivity of liquid chemicals

sions worldwide. A circular carbon economy is a conceptual structure to regulate and minimize emissions. The closed-loop system incorporates the 4Rs: reduce, reuse, recycle, and remove.

- **CO₂ reduction in H₂O:** It is essential to investigate the reaction mechanism and the process parameters that lead to the H₂O dissociation in the plasma and the plasma-catalysis systems. Further studies are recommended to determine the vibrational and electron temperatures. For economic feasibility, it is essential to perform real-time optimization of the discharge parameters, including pulse frequency and duration, as it is believed that optimizing these parameters will positively affect energy efficiency. Adding H₂O weakens the discharge, so experimental studies are required to investigate the Ar effects in the gas mixture, which could be beneficial to sustain the discharge. To further improve conversion and the energy efficiency of CO₂ reduction in the H₂O process, the impact of catalysts in plasma should be thoroughly investigated.
- **CH₄ reforming with CO₂ to syngas:** It has been found that the selection of an efficient catalyst to get synergy with the plasma for higher conversion and energy efficiency is still inadequate, and more research is projected to overcome the conventional barriers and make a bridge between the thermal- and plasma-catalysis. It has been established that the metal-supported catalysts are promising candidates in plasma catalysis for the efficient CH₄ reforming with CO₂ to syngas, and there is room to develop multifunctional metal-supported catalysts such as bimetallic catalysts of monometallic catalysts in combination with some promoters. Such advanced and next-generation catalysts should be developed to achieve multiple targets simultaneously, including energy efficiency, enhanced conversion, selectivity, and a balanced CO/H₂ ratio. Investigations on optimization of the discharge effects, input power, and feed flow conditions should be done as they could directly impact the syngas formation, electron density distribution, and conversion/selectivity. Research should be carried out comprehensively to inhibit the carbon deposition observed with higher feed concentrations of CH₄ by introducing some oxygen to the system. In terms of energy efficiency, there is a need to find a way to inhibit water formation by understanding the mechanisms of water formation.
- **CO₂ dissociation to CO:** It has been suggested that the reaction parameters should be optimized to enhance CO₂ dissociation in plasma catalysis. These parameters include but are not limited to the dielectric materials, the reactor's geometrical configurations, the catalyst bed, and input power. To date, it has been demonstrated that using a DBD reactor, the CO₂ dissociation is reasonable; however, the energy efficiency is still too low

and needs significant improvement for commercialization if the electricity is produced from fossil fuels. However, having electricity from renewable sources might address the energy efficiency issue. Specifically, the effects of the co-reagents, such as CH₄ or H₂O, which are highly probable for the selective formation of value-added chemicals from CO₂ dissociation, should be investigated using plasma catalysis.

- **CO₂ hydrogenation:** It is evident that the hydrogenation of CO₂ to methanol in the plasma-catalysis system depends on a wide range of reactive species, which could initiate more reaction routes for methanol formation. A detailed investigation should be carried out to govern the interaction between the active sites on the catalyst and the reaction intermediates. The final product selectivity cannot be determined without first determining the adsorption energies of the oxygen-based reaction intermediates to the catalyst surface.
- **CO₂ to organic acids:** More comprehensive research is necessary to deliberate the possible reaction mechanistic pathways of CO₂ conversion to organic acids, such as formic, acetic, and oxalic acid, in connection with the plasma-catalysis synergistic effects. In this regard, developing next-generation multifunctional catalysts for CO₂ reduction and the coupling of C–C simultaneously is required. The impact of either with or without base use should be investigated regarding product distribution and reaction efficiency.
- **One-step CO₂–CH₄ reforming to liquid chemicals:** Considering the C1 products, such as methanol, the bond energies of C–O (326 kJ/mole) and C–H (416 kJ/mole) in methanol and CH₄, respectively, suggest that the methanol is less stable in plasma than CH₄, thus pointing to the need for more fundamental research regarding the potential role of CH₂O and methanol as reaction intermediates in plasma-catalysis. Developing next-generation selective and efficient catalysts that could produce multi-carbon products from CO₂ conversion in plasma catalysis is necessary. Thus, parallel process optimization is required for energy efficiency.

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Declarations

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