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Topical Review

Non-thermal plasma catalysis for CO_2 conversion and catalyst design for the process

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Abstract

Catalytic conversion of CO_2 to renewable chemicals and fuels is a promising approach to mitigate issues associated with climate change and energy supply deficiency. Hybrid non-thermal plasma (NTP) and catalysis systems, that is, NTP catalysis systems, enable the activation of stable CO_2 molecules under relatively mild conditions in comparison with conventional thermal catalysis, and are promising for the energy-efficient conversion of CO_2. This review presents the state-of-the-art development of NTP catalysis of CO_2 conversion, including CO_2 splitting and CO_2 hydrogenation and reforming, with the focus on mechanistic insights developed forcatalytic CO_2 conversion. Additionally, the role of intrinsic catalyst composition and structure in determining the selectivity of CO_2 conversion under NTP conditions is also discussed in light of the need for rational design of catalysts for NTP catalysis. Finally, a perspective on future challenges and opportunities in the development of next-generation catalysts for NTP catalysis and the advanced hybrid NTP catalysis process for practical industrial applications are discussed.

Keywords: non-thermal plasma (NTP), heterogeneous catalysis, CO_2 conversion, mechanism

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

1. Introduction

Carbon dioxide (CO_2) emissions are the main contributor to global warming and climate change. The catalytic conversion of CO_2 to renewable and valuable chemicals and fuels is a promising method to mitigate these issues and contribute to the development of a sustainable low-carbon economy [1, 2]. CO_2 conversion is challenging due to the high thermodynamic stability and ionisation potential of the linear CO_2 molecule (bond enthalpy = +805 kJ mol^{-1}). Typically, high temperatures and/or pressures are required to activate CO_2 under conventional thermal conditions, which are associated with high energy demand and cause catalyst deactivation [3].

Non-thermal plasmas (NTPs), with a mean electron energy of 1–10 eV, could activate and dissociate ground-state gas molecules to generate various active species including vibrationally excited molecules, atoms, ions and radicals, allowing

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reactions to occur at relatively mild bulk temperatures and atmospheric pressure [4–6]. Accordingly, NTP catalysis is capable of promoting many energy-intensive and kinetically and/or thermodynamically limited heterogeneous catalytic reactions such as CO_2 hydrogenation [7, 8], the water–gas shift reaction [9, 10], hydrocarbon reformation [11–13], pollutant decomposition [14] and ammonia synthesis [15, 16].

Although NTPs alone can break the chemical bond of the CO_2 molecule without a catalyst,selectivity towards desired products (e.g. CH_4, hydrocarbons and oxygenates) is poor due to the unselective collisions between the active species [17]. Thus the integration of plasma discharge with catalysts (known as NTP catalysis) is proposed for enhancing CO_2 conversion and regulating the product distribution [18]. Under NTP conditions, catalysts enable additional reaction pathways via surface reactions which increase the product selectivity. The physical and chemical properties of the catalysts play a key role in the NTP catalysis because their presence can affect the electric field intensity, as well as lead to surface discharges, thereby enhancing electron energy distribution and affecting interactions between the plasma and catalysts [19, 20]. Additionally, plasma-induced short-lived reactive species deactivate quickly via recombination and/or quenching in the gas-phase before accessing the catalyst surface and participating in surface reactions [21, 22]. Thus, the location of the active sites in the catalyst is also important regarding the performance of the NTP catalysis.

Designing and developing efficient and cost-effective catalysts for NTP catalysis requires a thorough understanding of the mechanisms of NTP catalysis regarding the transport of reactive species, surface reaction chemistry and plasma discharge properties. However, these studies are challenging due to the complex nature of NTP catalysis [23]. Accordingly, advanced *in situ* techniques [22, 24] and modelling methods [16, 17, 25] are needed to enable a mechanistic understanding of NTP catalysis for the rational design of bespoke catalysts to be used in NTP catalysis, as well as the optimisation of NTP catalytic systems with respect to the reaction rate, selectivity and energy efficiency for CO_2 conversion.

In this review, state of the art of NTP catalytic systems for CO_2 conversion including CO_2 splitting, CO_2 hydrogenation and reforming are presented first. Then, the role of the catalyst structure in determining the CO_2 conversion under thermal and NTP conditions are compared, which can shed light on a strategy for the rational design of bespoke catalysts for advanced NTP catalysis. Finally, recent progress on a mechanistic understanding of NTP catalysis via *in situ* characterisation and modelling studies is discussed.

2. NTP catalysis for CO_2 conversion

NTP catalysis is effective in activating and converting CO_2 into various chemicals and fuels such as CO, methane (CH_4), hydrocarbons and oxygenates under mild conditions, as illustrated in figure 1. Specifically, a dielectric barrier discharge (DBD) reactor with two coaxial electrodes is widely employed under NTP conditions for CO_2 conversion in the presence of catalysts. The simple configuration of the DBD reactor and ambient operating conditions (i.e. at atmospheric pressure and low temperatures) is attractive for possible industrial exploitation [17, 26]. However, fundamental investigations into the mechanisms of CO_2 conversion are still needed due to the coexistence of gas-phase and surface reactions and complex plasma–catalyst interactions. Therefore, the following discussion will outline recent progress in NTP catalytic CO_2 conversion in DBD reactors and relevant exploration of the reaction mechanism/pathways underlying CO_2 conversion.

2.1. Definition of key performance indicators for assessing NTP catalytic CO_2 conversion

To compare the various plasma-catalytic systems for CO_2 conversion, a summary of the key performance indicators, including conversion (χ), selectivity, yield, specific energy input (SEI) and energy efficiency (η), are introduced in this section.

The standard expression for 'conversion' used in the literature is provided in equation (2.1) for the converted reactants (e.g. CO_2 and CH_4), and the selectivity is defined as the amount of the produced target product divided by the converted reactant (equation (2.2)). The yield of the desired product can be calculated by multiplying the conversion by the selectivity of the desired product (equation (2.3)):

$$\chi_{\text{reactant}_i} = \frac{\dot{n}_{\text{reactant}_i,\text{in}} - \dot{n}_{\text{reactant}_i,\text{out}}}{\dot{n}_{\text{reactant}_i,\text{in}}}, \tag{2.1}$$

$$S_{\text{product}_i} = \frac{\dot{n}_{\text{product}_i,\text{out}}}{\dot{n}_{\text{reactant}_i,\text{in}} - \dot{n}_{\text{reactant}_i,\text{out}}}, \tag{2.2}$$

$$Y_{\text{product}_i} = \chi_{\text{reactant}_i} \times S_{\text{product}_i}, \tag{2.3}$$

where $\dot{n}$ stands for the molar flow rate of the reactant or desired product.

The SEI (expressed as J cm^{-3} or kJ l^{-1}) is defined as the power (used for generation of the plasma discharge) divided by the gas flow rate, which is the determining factor in the conversion and energy efficiency in plasma systems:

$$\text{SEI}\ (\text{J cm}^{-3}) = \frac{\text{Power (W)}}{\text{Flowrate (ml s}^{-1})}. \tag{2.4}$$

The energy efficiency (η) depends on the plasma process under study. It was introduced to assess the efficiency of the plasma process (for the conversion of CO_2) as compared with the standard reaction enthalpy:

$$\eta = \frac{\chi_{\text{Total}} \times \Delta H^{\circ}_{298\text{K}}}{\text{SEI}}, \tag{2.5}$$

where χ_{Total} is the total conversion of the process and $\Delta H^{\circ}_{298\text{K}}$ is the standard enthalpy.

2.2. CO_2 splitting

Plasma-activated CO_2 splitting into CO and O_2 has been intensively investigated since CO is an important chemical

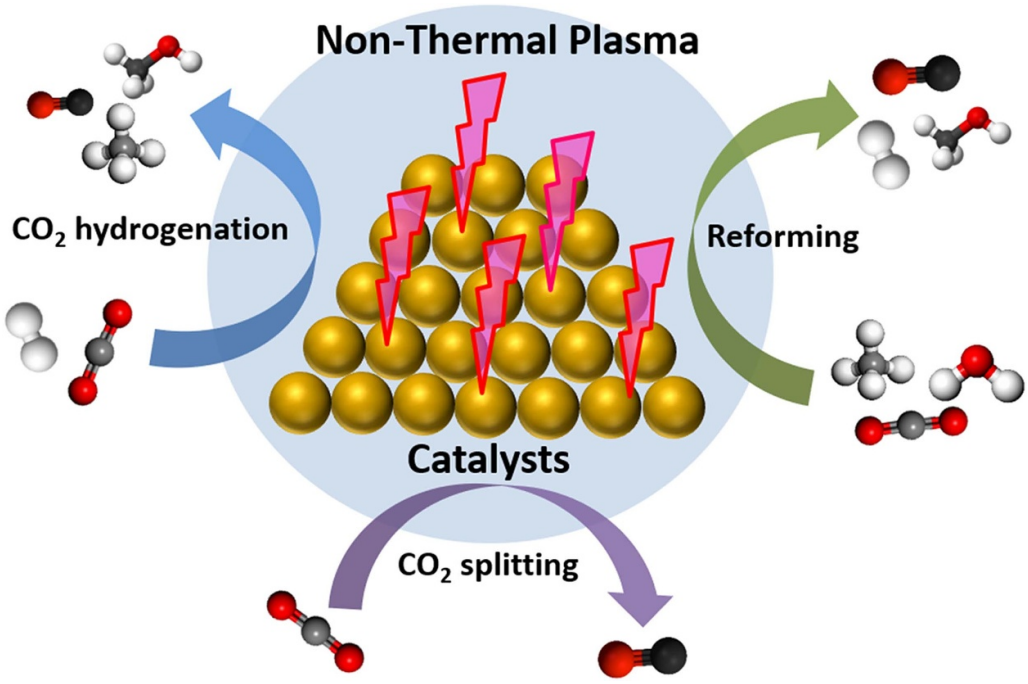
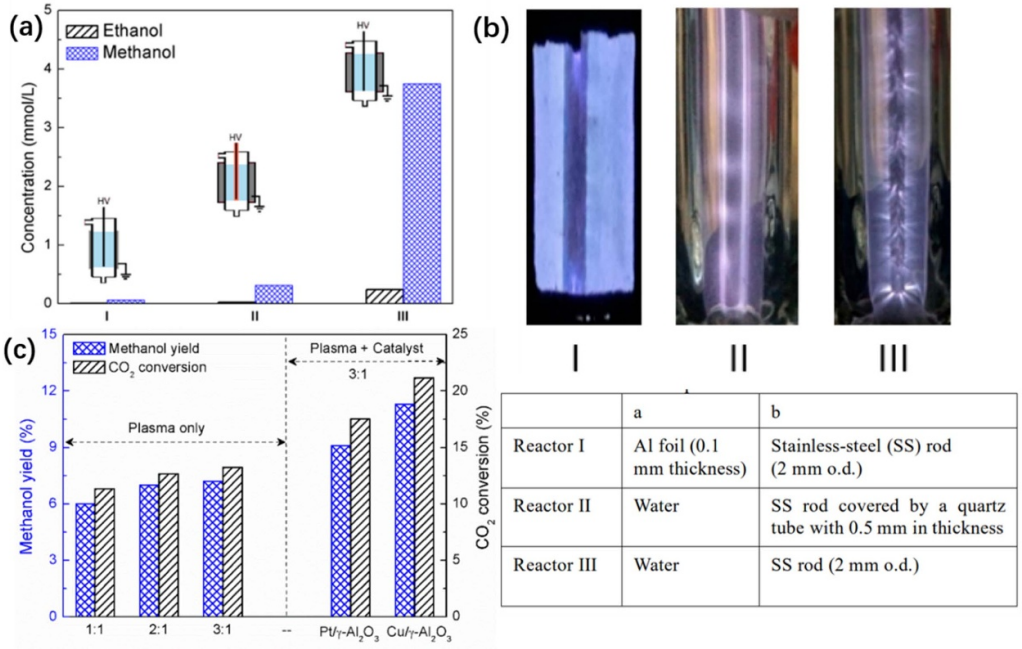


Figure 1. NTP-activated heterogeneous catalysis for CO_2 conversion.

feedstock for synthetic fuels through the Fischer–Tropsch and methanol synthesis processes [27, 28]. Typically, CO_2 splitting can be activated only under NTP conditions (without a catalyst), and CO_2 conversion can be improved by increasing the SEI due to the increased average electron density [29, 30]. CO_2 splitting under NTP conditions is dominated by electron-impact dissociation (forming CO and O atoms and ions), the ionisation process (forming CO_2^+ ions) and electron dissociative attachment (forming CO and O^- ions). However, a fraction of the ions from these processes (e.g. CO and O) can recombine to CO_2 in the gas phase. Therefore, the plasma-only system is intrinsically energy intensive, its highest achievable CO_2 conversion rate is ∼30% and it has a relatively low energy efficiency of 5%–10% [17, 31]. The addition of inert gases (e.g. helium and argon) into this system can also promote CO_2 conversion but the energy efficiency decreases due to the significant amount of energy used in the excitation of He or Ar atoms [32, 33]. CO_2 conversion and energy efficiency can be improved using packing materials in DBD reactors, such as glass beads [34], quartz [35], Al_2O_3 [35–37], $BaTiO_3$ [38, 39], SiO_2 [36] and ZrO_2 [40]. The packing materials affect the physical characteristics of the plasma discharge, which enhance the electric field and enable the formation of surface discharges and micro-discharges, thus promoting gas-phase CO_2 dissociation. However, these systems cannot be classified as NTP catalysis. By incorporating a catalyst, the CO_2 conversion and energy efficiency in CO_2 splitting under plasma conditions can be improved. For example, using a Ni/γ-Al_2O_3 catalyst within a DBD reactor, comparably high CO_2 conversion (∼26.3%) and energy efficiency (∼4.1%) were achieved as compared with the reference NTP system with $BaTiO_3$ packing [41]. It was found that, in addition to the electron-impact dissociation of CO_2 in the gas phase, the ground state and excited states of CO_2 can adsorb on the Ni surface and subsequently dissociate into CO and O with the assistance of energetic electrons, explaining the improved system performance. However, as compared with the performance data presented in the current literature, NTP catalytic systems for selective CO_2 splitting still require further development and improvement.

2.3. CO_2 hydrogenation

CO_2 hydrogenation with molecular H_2 can produce a range of chemicals, including CO, CH_4, hydrocarbons and oxygenates (methanol, dimethyl ether, ethanol, etc). Conversion of CO_2 to CO via the reverse water–gas shift (RWGS) reaction and CH_4 via CO_2 methanation (the Sabatier reaction) under NTP conditions has been investigated [7, 42]. Zhu *et al* [43] studied the effect of a plasma on RWGS over an Au/CeO_2 catalyst. Therein, the plasma enabled a CO_2 conversion rate of ∼25.5%, which was higher than the thermodynamic equilibrium value of ∼22% at 400 °C. As compared with conventional thermal catalysis, NTP catalysis can create high concentrations of reactive species, which improves the CO_2 methanation rate and CH_4 yield at low operating temperatures [44]. For example, Biset-Peiró *et al* [45] compared catalytic CO_2 methanation over a Ni–CeO_2/Al_2O_3 catalyst under thermal and NTP conditions. A CO_2 conversion of 70% and CH_4 yield of 96% was achieved under NTP conditions (at ∼150 °C), whereas under thermal conditions, a temperature in excess of 350 °C was required to achieve a similar performance. Similar results have been reported by other studies as well [46]. In NTP catalysis, highly reactive species contribute to CO_2 methanation; for example, vibrationally excited CO_2 can adsorb on the catalyst surface to lower the energy barrier as



	a	b
Reactor I	Al foil (0.1 mm thickness)	Stainless-steel (SS) rod (2 mm o.d.)
Reactor II	Water	SS rod covered by a quartz tube with 0.5 mm in thickness
Reactor III	Water	SS rod (2 mm o.d.)

Figure 2. (a) The influence of DBD reactor configurations on CO_2 hydrogenation to methanol under NTP conditions. (b) Images of H_2/CO_2 discharge generated in different DBD reactors. (c) Effect of H_2/CO_2 molar ratio and catalysts onreaction performance. Reprinted with permission from [52]. Copyright (2018) American Chemical Society.

compared with the ground-state CO_2 and facilitate the formation of reactive intermediates on the catalyst surface [19]. Conversely, in thermal catalysis, CO_2 needs to be adsorbed and activated by the catalyst surface before surface reactions can take place, demanding high temperatures [47]. Additionally, the NTP-induced excited states of other reactive species such as CO, OH and CH radicals in the gas phase can also readily interact with the catalyst to promote relevant surface reactions [24, 48].

In addition to CO and CH_4, hydrocarbons and oxygenates, especially methanol, are valuable fuel substitutes and key feedstocks for a wide range of products such as polymers, solvents, and drugs. Catalytic CO_2 hydrogenation into hydrocarbons and methanol under thermal conditions is usually conducted at high temperatures and pressures [49]; thus the integration of plasma with catalysts to enable these conversions efficiently under mild conditions is important. Lan *et al* [50] reported that Co/ZSM-5 catalysts promoted hydrocarbon formation with a C_2–C_4 selectivity of 13.7% at 45.0% CO_2 conversion under NTP. CO_2 hydrogenation into methanol under NTP conditions was explored by Eliasson *et al* [51]. Therein, the methanol yield/selectivity was enhanced by a factor of >10 by coupling NTP with a commercial $CuO/ZnO/Al_2O_3$ catalyst at ∼100 °C compared with the results under NTP-only conditions. Recently, Wang *et al* [52] presented a significant improvement in CO_2 hydrogenation to methanol (i.e. 14% CO_2 conversion and 53.7% methanol selectivity) using a specially designed DBD reactor with a water-cooled electrode (as shown in figures 2(a) and (b)). This setup efficiently removed the heat generated by Joule heating and the reaction exothermicity to maintain the NTP system at ∼30 °C. In this work, the catalytic performance of the Pt/γ-Al_2O_3 and Cu/γ-Al_2O_3 catalysts was investigated, as shown in figure 2(c), in which Cu/γ-Al_2O_3 presented a relatively good catalytic performance (i.e. 21.2% CO_2 conversion and 11.3% methanol yield), showing that both the plasma reactor and the catalyst design can affect catalysis under NTP conditions. However, it is obvious that practical applications of CO_2 hydrogenation to methanol are still some way off due to the relatively low CO_2 conversion and methanol yield (<50%). Therefore, the development of highly active and selective catalysts, as well as the optimisation of NTP reactor design, is necessary to further improve NTP-enabled catalytic CO_2 conversion to methanol. Men *et al* [53] prepared a highly dispersed Pt/film/In_2O_3 catalyst via the plasma-assisted peptide-assembly method and used it for NTP-assisted CO_2 hydrogenation, achieving a high CO_2 conversion rate of ∼37% with a methanol selectivity of ∼62.6% due to the high Pt dispersion. Additionally, based on modelling, Iliuta *et al* [54] proposed an integrated reactor for converting CO_2 to methanol which involved the RWGS reaction under plasma conditions and subsequentcatalytic methanol synthesis via CO and CO_2 hydrogenation under thermal conditions. The findings from the modelling suggest that methanol yield could be improved if CO_2 is progressively substituted by CO via RWGS in the plasma reactor, potentially leading to enhanced CO_2 conversion and an increase in the overall energy efficiency.

2.4. CO_2 reforming

In addition to H_2, CH_4 and H_2O can also be used as the H source for converting CO_2 into value-added compounds. Activation of CH_4 molecules is also energy intensive (600 °C–1100 °C) due to the stable C–H bonds (E_{diss} = 4.5 eV) [55]. From a thermodynamic point of view, the co-conversion of the greenhouse gases CO_2 and CH_4

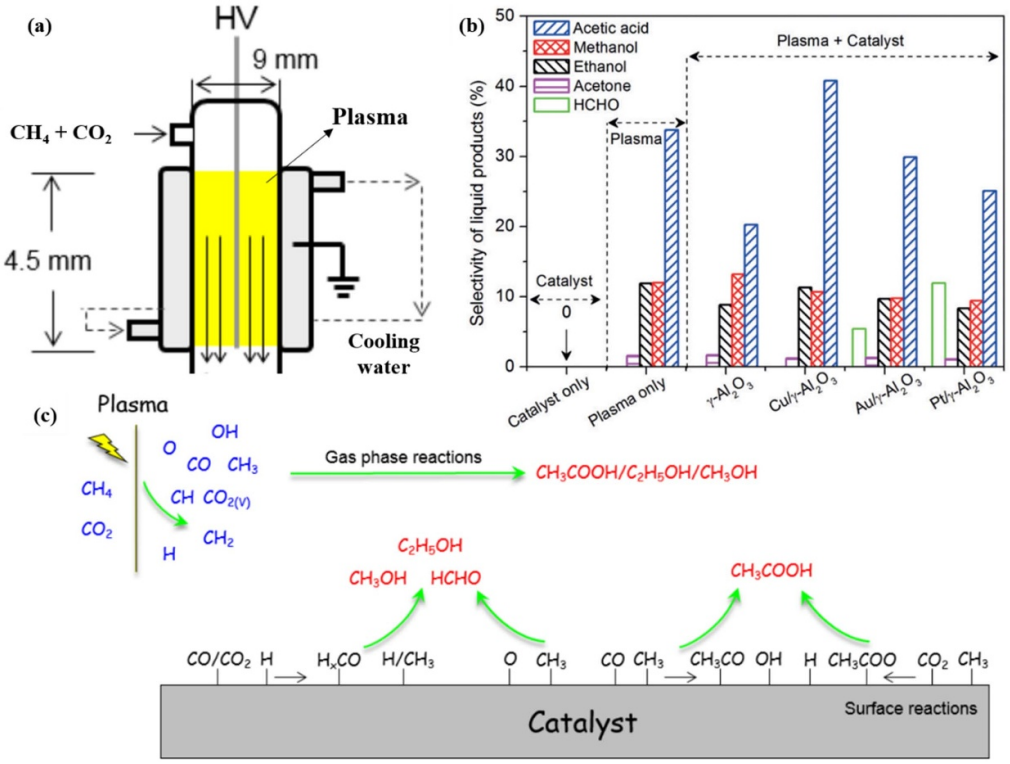


Figure 3. (a) The reactor configuration for one-step plasma-assisted DRM for producing liquid chemicals/fuels. (b) Selectivity to oxygenates and (c) possible reaction mechanisms for the formation of CH_3COOH, CH_3OH, C_2H_5OH and HCHO using NTP catalysis. Reprinted from [63]. CC BY 4.0.

(i.e. dry reforming of methane, DRM) cannot occur at low temperatures because of negative Gibbs free energy [56]. Alternatively, NTPs can overcome the thermodynamic limitation without the issues of coke formation and metal sintering experienced by thermal catalysis [55–57]. The target product of DRM is syngas ($CO + H_2$), but hydrocarbons can also be produced [58, 59], depending on the selectivity of the catalyst, as well as other process parameters. For example, reaction selectivity was found to be sensitive to the gas composition [11, 60, 61], with a CH_4-rich feed contributing to high selectivity towards hydrocarbons, whilst the CO_2-rich feed increased CO selectivity [61].

NTPs combined with a suitable catalyst can tune reaction selectivity towards valuable hydrocarbons and liquid oxygenates. For example, the selectivity of DRM to C_2 to C_4 hydrocarbons was enhanced over NaX zeolite catalysts under NTP conditions [60]. Similarly, Vakili *et al* [62] reported that the combination of NTP with the UiO-67 metal–organic framework (MOF) facilitated the formation of C_2H_2 and C_2H_4, whereas the Pt/UiO-67 catalyst decreased the selectivity to hydrocarbons by ∼30% due to the dehydrogenation process on the Pt surface. Recently, Wang *et al* [63] demonstrated one-step synthesis of liquid chemicals/fuels including acetic acid, methanol, ethanol and formaldehyde from NTP-assisted DRM (as shown in figure 3) by careful selection of catalysts and operation parameters. The NTP-only system promoted the formation of oxygenates (selectivity of 59.1%), with acetic acid as the major product. In contrast, by varying the catalysts within the DBD reactor, the distribution of liquid products could be tuned due to the presence of both gas-phase and plasma-assisted surface reactions. For example, the Cu/γ-Al_2O_3 catalyst increased selectivity to acetic acid to ∼40.2% as compared with a plasma system with the γ-Al_2O_3 packing (∼20.2%). Conversely, supported noble metal catalysts (i.e. Au/γ-Al_2O_3 and Pt/γ-Al_2O_3) produced formaldehyde under NTP conditions, suggesting that the nature of the catalysts is crucial for NTP catalysis (as shown in figure 3(b)). Optical emission spectral (OES) characterisation of the NTP catalysis system shows the presence of CO, CH, CH_3, CO_2, CO_2^+, OH and H_a as potential key species in the NTP-activated DRM. Therefore, possible reaction pathways on the catalyst surface for producing oxygenates have been proposed, as shown in figure 3(c), demonstrating the effect of the NTP-assisted surface reactions on the distribution of liquid products. This study confirms that NTP combined with heterogeneous catalysts can provide selective pathways to value-added products which cannot be achieved in NTP-only conditions.

CO_2 reforming with H_2O, mimicking the natural photosynthesis process, is very attractive since H_2O is the cheapest H source. The DBD reactor (without a catalyst) with the discharge gas of CO_2/H_2O mainly produces reactive species of OH, CO, O and H. However, the OH radicals are prone to recombine with CO molecules to produce CO_2 and H atoms (thereby reducing CO_2 conversion). H atoms can react with O to give H_2O, instead of forming CH and CHO species, which

are key intermediates in the production of oxygenated products [64]. Accordingly, NTP-only is not selective to oxygenated hydrocarbons in CO_2 reforming with H_2O. Therefore, recent efforts have been dedicated to developing catalytic reforming systems using CO_2/H_2O plasma. Ma *et al* [65] demonstrated that the yields of H_2 and CO were significantly improved to 13.8% and 5.6%, respectively, when a Ni/γ-Al_2O_3 catalyst was used in a DBD reactor as compared with NTP-only conditions. Zhao *et al* [66] also showed an enhanced ethanol production rate at 15.60 μmol g_{cat}^{-1} h^{-1} using a Cu/ZnO/Al_2O_3 catalyst under NTP conditions, which was much higher than that of the thermal system (with the catalyst, at 3.02 μmol g_{cat}^{-1} h^{-1}) and NTP-only conditions (at 3.5 μmol g_{cat}^{-1} h^{-1}).

3. Catalyst design for NTP catalytic CO_2 conversion

As discussed above, the NTP itself can activate CO_2 at low temperatures without catalysts but is non-selective due to collisions between active species. Conversely, the surface reactions involved in NTP catalysis can stabilise reaction intermediates and change the reaction pathways to promote CO_2 conversion and selectively, directing the conversion to the target products. Therefore, the hybrid NTP catalysis system is very promising for improving CO_2 conversion and addressing the selectivity issue. Thus, the investigation into the role of the intrinsic nature of catalysts in selective CO_2 conversion under NTP conditions is important, i.e. rational design of bespoke catalysts with desirable textual, compositional and structural properties tailored for a specific NTP catalytic CO_2 conversion. However, relevant investigations and fundamental design principles regarding this aspect are still lacking, and the current catalysts used in NTP catalysis are still those which were designed for thermal catalysis. Here, the recent progress of the catalysts used for thermal catalytic CO_2 conversion will be briefly discussed first; then a strategy for designing specific heterogeneous catalysts for NTP catalysis will be proposed.

3.1. Catalysts for thermally activated CO_2 conversion

Under thermal conditions, group 8–10 metals (e.g. Ru, Rh, Pd, Ni, Co, Fe) have been demonstrated to be efficient for CO_2 hydrogenation [67, 68]. Ni-based catalysts are the most widely used catalysts for CO_2 conversion due to their cost-effectiveness and high activity. However, the main issue of the Ni-based catalysts is their stability, especially at high reaction temperatures, because the Ni catalysts are prone to deactivation due to carbon deposition and metal sintering. Ni particle sintering can reduce the metal surface area and overall CO_2 adsorption capacity, and hence leadto deactivation (of the Ni/AlO_x catalyst) [69]. In comparison, Rh- and Ru-based catalysts are relatively stable and show higher activity than the Ni-based counterparts. However, their limited availability and relatively high price make them less attractive for applications at a large scale. Recently, efforts have been made to study the influence of the metal particle size and dispersion on the catalyst performance in order to develop more efficient catalysts for CO_2 conversion [70]. For example, Guo *et al* [71] investigated the effect of Ru particle size (i.e. single Ru atoms, nanoclusters (~1.2 nm) and nanoparticles (~4 nm)) of Ru/CeO_2 catalysts on CO_2 hydrogenation. Compared with single Ru atoms, the nanoclusters and nanoparticles showed weaker metal–support interactions, thus promoting the activation process; however, they showed higher H spillover, thus inhibiting the removal of H_2O from the catalyst surface. The trade-off between these two factors led to the nanoclusters achieving the highest activity at 190 °C, with a turnover frequency (TOF) of 7.41×10^{-3} s^{-1} and 98%–100% selectivity to CH_4. Similarly, the correlation between product selectivity and Ru particle size was studied by Kwak *et al* [72] and Yan *et al* [73]. It was revealed that single Ru atoms tend to form CO via RWGS, whereas Ru nanoclusters and nanoparticlesfavour the production of CH_4. Regarding Ni catalysts, well-dispersed Ni particles are beneficial for the efficient conversion of CO_2 to CH_4. For example, Ni nanoparticles of 2.7–4.7 nm (confined in the cage-type mesopores of SBA-16) enabled strong adsorption of CO_2 and high catalytic rates in CO_2 hydrogenation [74]. High Ni dispersion can be achieved by using porous catalyst supports, such as structured silica, zeolite and MOFs, with large surface areas and/or micro-/meso-porosity structures [75]. For example, UiO-66 MOF with a large surface area of 986 m^2 g^{-1} was used as a support to prepare highly dispersed Ni with an average particle size of 2 nm for CO_2 methanation with good activity (TOF = 0.04 s^{-1} at 320 °C) and stability (100 h) [76].

The surface properties of catalyst supports are also very important because (a) support–metal interactions can tune the properties of metals, such as the reducibility of metal species, metal dispersion and particle size and (b) basicity/acidity and oxygen vacancy can influence CO_2 adsorption. Different supports, including Al_2O_3 [77–79], SiO_2 [80], TiO_2 [81], ZrO_2 [82], CeO_2 [83] and zeolites [84], have been applied to prepare catalysts for CO_2 conversion. Lin *et al* [82] found that Zr doping of Ni/Al_2O_3 catalysts can improve Ni dispersion and the reducibility of the Ni phase, thus promoting CO_2 hydrogenation at low temperatures, of <300 °C. Le *et al* [85] investigated CO_2 methanation over the supported Ni catalyst on various supports and the activity was found to take place in the following order: CeO_2 > ZrO_2 > SiO_2 > Al_2O_3 > TiO_2. The high catalytic activity of the Ni/CeO_2 catalyst was attributed to the small Ni particle size, as well as the presence of oxygen vacancy, which facilitated CO_2 chemisorption and activation [86, 87]. Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies of CO_2 hydrogenation over Ru/CeO_2 (with oxygen vacancy) and Ru/Al_2O_3 (without oxygen vacancy) catalysts showed that the oxygen vacancy in CeO_2 facilitated the dissociation of formate species for CH_4 formation [88]. Additionally, a mechanistic investigation of CO_2 hydrogenation over the Ni/CeO_2 catalysts by Cárdenas-Arenas *et al* [89] and Ye *et al* [90] also showed that, in these catalysts, the existence of both Ni^0 sites (for H_2 dissociation) and Ce^{3+} sites (for CO_2 adsorption and activation) was important to enable the selective CO_2 conversion to CH_4. Therefore, developing next-generation catalysts with highly dispersed metal active sites, a large surface area and enhanced CO_2 adsorption is important for improving thermal catalytic CO_2 conversion, especially at low temperatures (<300 °C)

[91]. An understanding of the structure–composition–activity correlation in thermal catalysis will provide useful guidance for NTP catalysis systems in designing highly selective catalysts in order to improve the performance of hybrid systems.

3.2. Role of metal active sites in NTP catalytic CO_2 conversion

In thermal catalysis, reactions occur only on the catalyst surface, and the highly dispersed catalysts on appropriate supports can convert CO_2 effectively. In contrast, in plasma catalysis, the combination of gas-phase and surface reactions, complex interactions between plasma and catalysts such as plasma discharge properties, transport of reactive species and modification of catalysts by plasma are coupled to one another, all affecting the performance of hybrid systems.

Table 1 summarises the performance of various supported metal catalysts in NTP-assisted CO_2 hydrogenation. Clearly, the combination of plasma and catalysis can effectively improve CO_2 conversion. CO_2 hydrogenation over the Cu/Al_2O_3, Mn/Al_2O_3 and $Cu–Mn/Al_2O_3$ catalysts was carried out, showing CO_2 conversion enhanced by 6.7%–36% as compared with the NTP-only system [92]. As was found forthermal systems, Ru and Ni catalysts have been widely used for CO_2 hydrogenation under NTP and have shown improved CO_2 conversion(generally >50%) compared with that achieved by plasma-only systems. Other metals, such as Pt, Pd, Co, Fe and Cu, have also been explored for NTP catalytic CO_2 hydrogenation. Oshima *et al* [93] investigated Pt, Pd, Ni, Fe and Cu metals supported on $La–ZrO_2$ for NTP-activated CO_2 hydrogenation, in which the noble metals showed improved CO_2 conversion than using transition metal catalysts. It was also found that the Pt, Pd, Fe and Cu catalysts for CO_2 hydrogenation were selective to CO, whilst the Ni catalysts were CH_4 selective [42, 94]. Additionally, the Ni particle size and dispersion were also found to affect catalyst performance. Liu *et al* investigated CO_2 hydrogenation over Ni/La_2O_3 catalysts as a function of calcination temperature from 600 °C to 900 °C. A maximum CO selectivity of 78% was achieved with the Ni/La_2O_3 catalyst calcined at 600 °C, which was due to the small Ni particle size (∼7.3 nm) and the high Ni dispersion achieved under the specific preparation conditions [95].

NTPs can facilitate catalyst preparation, resulting in the formation of small and highly dispersed metal nanoparticles on the support [99]. For example, H_2 plasma reduction was used to prepare the Pd, Pt, Ag and Au supported on SBA-15 catalysts, which showed improved activity in catalytic CH_4 conversion to value-added fuels [100]. Characterisation of these catalysts confirmed that the plasma treatment resulted in high metal dispersion; e.g. the particle sizes of Pd, Pt and Au were 6, 2 and 6 nm, respectively, which were able to fit into the ordered SBA channels (average diameter of 7.6–8.5 nm). Benrabbah *et al* [42] compared the effect of thermal and H_2 plasma reduction on the preparation of $Ni/CeZrO_2$ catalysts for plasma catalytic CO_2 hydrogenation, showing that the catalysts reduced by H_2 plasma resulted in a strong interaction between Ni and ceria, thus leading to higher CO_2 conversion (∼80%) at low power (∼5 W) than the catalysts reduced by the thermal treatment (at 470 °C). These studies demonstrate that it is promising to employ the plasma reduction process to prepare highly dispersed metal catalysts *in situ* for NTP catalysis.

3.3. Role of catalyst supports in NTP catalytic CO_2 conversion

The properties of the catalyst support (e.g. morphology, dielectric properties and pore structures) are important in NTP catalysis as they affect metal dispersion, adsorption/desorption properties and plasma discharge. A summary of Ni catalysts supported on various supports for NTP catalytic CO_2 hydrogenation is presented in table 2.

3.3.1. Catalysts supported on metal oxides. γ-Al_2O_3 is the most common support used for NTP-assisted CO_2 conversion due to its relatively large surface area (∼150 m^2 g^{-1}) and high stability [47]. However, the acidic nature of γ-Al_2O_3 suppresses CO_2 adsorption, and hence CO_2 conversion over the catalysts supported on γ-Al_2O_3 is relatively low in NTP catalysis. For example, in the NTP-assisted DRM, the Ni/γ-Al_2O_3 catalyst achieved a CO_2 conversion rate of 26.2% and CH_4 conversion rate of 44.1% [107], and in NTP catalytic CO_2 methanation (as shown in table 1), only 23% CO_2 conversion was achieved by the Ru/γ-Al_2O_3 catalyst [46]. Catalyst supports with basic sites and oxygen vacancies have also been explored for NTP catalytic CO_2 conversion. For example, Nizio *et al* [8, 101] developed Ni catalysts supported on $CeZrO_2$ with different Ce/Zr ratios for NTP-assisted CO_2 hydrogenation. The highest CO_2 conversion rate of ∼80% and CH_4 selectivity of ∼95% was achieved when the Ce/Zr ratio was 1.40. In these catalysts, ceria acted as an oxygen reservoir, which promoted the adsorption of CO_2 and subsequently produced CO and O active species with the assistance of plasma. Recently, hydrotalcite-derived/-supported metal catalysts have shown potential in C1 chemistry due to their compositional flexibility, good thermal stability and basic properties, which facilitates chemisorption and activation of CO_2 [108]. Additionally, the coordinatively unsaturated active sites in hydrotalcite such as steps, edges and corner atoms can also promote metal dispersion, favouring catalysis [109]. Xu *et al* [110] prepared Ru supported on MgAl-layered double hydroxide catalysts for NTP-assisted CO_2 hydrogenation, in which ∼85% CO_2 conversion and ∼84% CH_4 yield were achieved.

3.3.2. Catalysts supported on zeolites. Zeolites have been widely used for heterogeneous catalysis due to their uniform micropores, large surface areas, tunable acidities and high thermal stabilities [111]. Zeolites also have the ability to spatially confine reactions, thus preventing the aggregation and deactivation of metallic species [112]. Zeolite-supported Ni catalysts have been explored for CO_2 hydrogenation under NTP conditions. Bacariza *et al* [106] evaluated NTP-assisted CO_2 methanation over a Ni/USY zeolite catalyst and investigated the effect of the Si/Al ratio and Ce addition on catalytic

Table 1. Comparison of NTP-assisted catalytic CO_2 hydrogenation over different catalysts.

Catalysts	DBD power (W)	WHSV[a] (ml g_{cat}^{-1} h^{-1})	CO_2 conv. (%)			CO_2 rate (mol s^{-1} g^{-1}, $\times 10^{-3}$)	CH_4 yield (%)	CO yield (%)	Ref.
			NTP only	Catalyst (thermal)[b]	NTP + catalyst				
6% Ru/γ-Al_2O_3	33	18 625	8.2	0.01 (at 25 °C)	23	0.06	21	—	[46]
2% Ru/UiO-66	13	—	22	—	41	—	39	—	[96]
2.8%Ru@UiO-66	13	6000	20	—	72	0.11	69	—	[97]
15% Ni/$Ce_xZr_{1-x}O_2$	>13	20 000	—	—	80	0.26	76	—	[42]
10% Ni/γ-Al_2O_3	15–18	20 000	9	2 (at 150 °C)	60	1.5	59	—	[47]
Ni/La_2O_3	90	18 000	52	—	97	—	45	9.7	[95]
NiFe/$MgAlO_x$	12	12 000	—	76 (at 250 °C)	73	0.08	—	—	[98]
8% Cu/γ-Al_2O_3	35	2076	7.5	—	8	0.01	0.7	6.4	[92]
8% Mn/γ-Al_2O_3	35	2076			10	0.02	0.76	7.9	
2% Pd/ZnO	30	3600	19.8	1.5 (at 230 °C)	32.5	0.18	—	31.3	[94]
2%Pd/SiO2	30	3600		—	25.3	0.14	—	20.8	
1% Pt/La–ZrO_2	5.6	60 000	18	—	41	7.8	—	40.6	[93]
1% Pd/La–ZrO_2	3.5	60 000			31	5.7	—	30.5	
1% Fe/La–ZrO_2	4.1	60 000			27	5.0	—	27.1	

[a] WHSV: weight hourly space velocity.

[b] Catalyst (thermal): CO_2 conversion achieved by catalysts activated under thermal conditions at different temperatures for comparison.

Table 2. Comparison of the performance of CO_2 hydrogenation over Ni-supported on various supports in DBD reactors under NTP conditions.

Catalysts	DBD power (W)	WHSV (ml g_{cat}^{-1} h^{-1})	CO_2 conv. (%)			CH_4 selectivity (%)	CH_4 yield (%)	Ref.
			NTP only	Catalyst thermal[a]	NTP + catalyst			
15Ni–CeO_2/Al_2O_3	15–40	40 000	3	4 (at 250 °C)	70	96	67	[45]
15Ni/$Ce_{0.1}Zr_{0.9}O_2$	1–3	50 000	—	0 (at 280 °C)	80	99.7	79.8	[101]
15Ni–TiO_2/Al_2O_3	—	1100	13	5 (at 220 °C)	50	—	—	[102]
15Ni/UiO66	1–3	30 000	5	5 (at 200 °C)	85	99	84.2	[103]
15Ni/CZ/SBA-15	—	20 000	—	<1 (at 200 °C)	80	99	79	[104]
15NiLa/Na–BETA	1–3	23 007	10	0 (at 200 °C)	84	97	81	[105]
NiCe/Cs–USY	35	40 000	<5	20 (at 250 °C)	79	98	77	[106]

[a] Catalyst (thermal): CO_2 conversion achieved by catalysts activated under thermal conditions at different temperatures for comparison.

performance. It was found that a higher Si/Al ratio could lead to lower affinity towards water, reducing the inhibiting effect of H_2O on catalyst activity in CO_2 methanation. The addition of Ce as promoter in the Ni/USY catalyst favoured CO_2 activation and improved the dielectric constant of the catalyst ($\varepsilon_r = 24$ for CeO_2 versus $\varepsilon_r = 1.5$–5 for zeolites), leading to high CO_2 conversion (∼70%) and CH_4 yield (∼75%). Chen *et al* [105] investigated the performance of BETA zeolite-supported Ni catalysts in NTP-assisted catalytic CO_2 hydrogenation. It was found that, as compared with H-form BETA, Na-form BETA benefits CO_2 adsorption, which can be further improved by La doping.

Additionally, the effect of porous catalysts on plasma discharge properties also deserves attention. Both experimental and modelling studies have shown that the pore structure of catalysts can intensify the electric field due to the formation of strong micro-discharges [20, 113]. A two-dimensional (2D) fluid model predicted that plasma could be formed and penetrate pores with a pore diameter greater than the Debye length (typically >2 μm) [114, 115]. Although the average pore size of zeolites is much smaller than the Debye length, a previous study based on Monte Carlo calculations revealed that micro-discharges might be formed near the pores of micro-/meso-porous catalysts, thus promoting intensified surface discharges on the porous catalyst [116]. Therefore, an understanding of the relevant discharge characteristics of the NTP catalysis is important in order to gain insights into the NTP catalyst interactions and further develop NTP catalytic systems. On the other hand, the lifetimes of plasma-induced reactive species are short, ranging from a few nanoseconds (for electronically excited atoms/molecules) to microseconds (for radicals) [117, 118]. Thus, the plasma-induced reactive species may lose their energy due to collisional quenching before participating in surface reactions. Accordingly, the diffusion of short-lived reactive species to the active sites is a key parameter in determining the efficiency of plasma catalysis, and an understanding of the diffusion mechanisms within the porous network of the catalysts is necessary for NTP catalysis [22]. Recently, Chen *et al* [119] investigated how the catalyst structure, for example the location of the active sites and support pore structures, affects the diffusion of the reactive species and the catalytic performance in CO_2 hydrogenation by designing a series of Ni supported on silicalite-1 (with different pore structures) catalysts (as shown in figure 4). Specifically, at low input energy, the availability of NTP-reduced reactive species in the gas phase is limited, and thus they prefer to interact with the exposed Ni active sites on the external surface of the catalysts with less diffusion resistance. Conversely, at high input energy, the abundant presence of the reactive species enables diffusion into the pore of the zeolite and allows interactions with the highly dispersed active sites. Thus, catalysts with a hierarchical meso-/micro-porous network and the associated highly dispersed Ni species may benefit the accessibility of short-lived reactive species towards Ni active sites, leading to the relatively high CO_2 conversion rate of ∼75%. This work demonstrates that the intrinsic nature of catalysts (e.g. pore structure, metal dispersion and the location of active sites) plays a key role in NTP catalysis, and the development of catalysts with highly dispersed and easily accessible metal sites may benefit NTP catalysis towards practical applications.

3.3.3. Catalysts supported on MOFs. MOFs have exceptionally large specific surface areas, structural diversity and tailorability, tunable pore size distribution and confined microenvironment, which enable flexible catalyst design by allowing active guest species to be anchored into their pores/cages/channels [120]. However, under thermal conditions, catalysts based on MOFs are often unstable. This can potentially be solved by using NTP activation. In addition, it is well known that MOFs have much stronger CO_2 adsorption capacities than other materials, such as zeolites and silica, which has inspired the development of MOF-based catalysts for CO_2 fixation and conversion under NTP conditions [121]. Chen *et al* [103] developed a Ni support on UiO-66 catalysts for catalytic CO_2 hydrogenation under NTP conditions. The TOF of the NTP catalysis system had a nearly two-fold improvement as compared with thermal catalysis (1.8 s^{-1} vs. 0.06 s^{-1}) and the structure of the catalyst showed no significant change after 20 h testing, confirming that the high

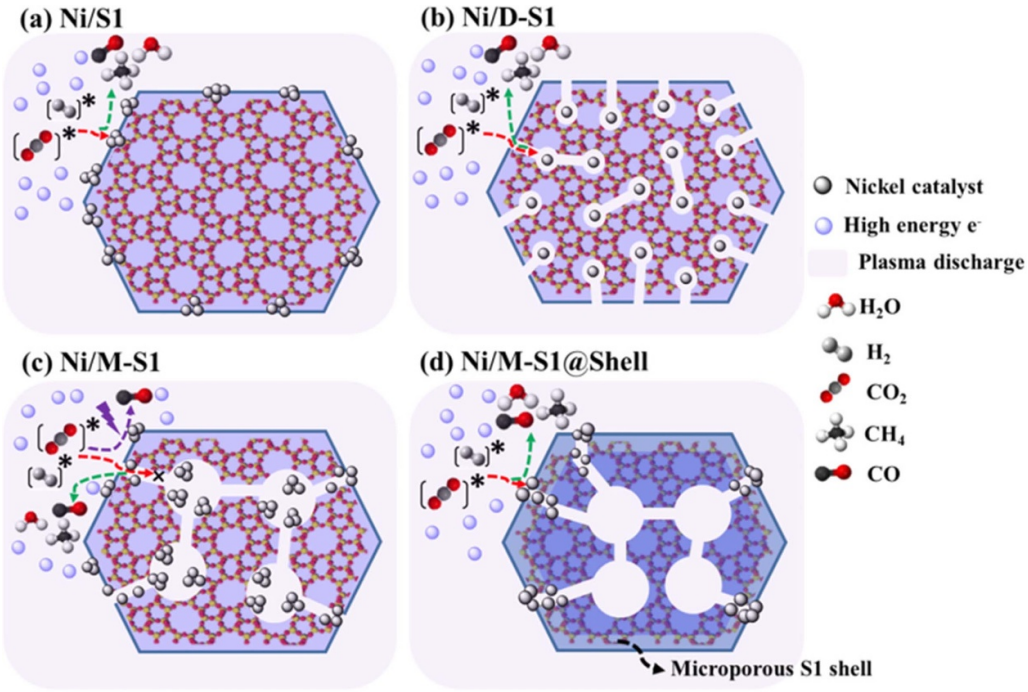


Figure 4. Mechanistic scheme of catalysts with different pore structures for NTP-assisted CO_2 hydrogenation. Reprinted from [119]. Copyright (2020), with permission from Elsevier.

stability of the MOF-based catalyst under NTP conditions can be achieved. Vakili *et al* [62] investigated the performance of the Pt@UiO-67 catalyst in the plasma-assisted DRM. Therein, it was found that, in addition to the high stability of the catalyst, the large surface area and the porous structure of UiO-67 also favoured the formation of micro-discharges on the catalyst surface, improving the conversion of CH_4 and CO_2 by 18% and 10%, respectively. These studies demonstrate the potential of MOF-based catalysts to improve NTP catalysis, as well as the use of NTP activation to sustain MOF-based catalyst activity. However, to date, the bespoke design of MOF-based catalysts for NTP-assisted CO_2 conversion and the relevant mechanistic understanding are lacking, requiring further investigation.

3.3.4. Promoter modified supported catalysts. The addition of promoters such as alkali and rare-earth metal oxides to metal-supported catalysts has been shown to be effective in improving metal dispersion and reducibility as well as the acid/base properties of the catalysts, resulting in the enhanced activity and stability of catalysts under thermal activation [122–124]. Accordingly, relevant research on the evaluation of promoter-modified catalysts in plasma catalytic CO_2 conversion has been conducted, as shown in table 3. Khoja *et al* [59] found that the La-promoted $Ni/MgAl_2O_4$ catalysts improved CO_2/CH_4 conversion to 84.5% and 86%, respectively, in the NTP-assisted DRM. Similarly, Chen *et al* [105] developed La-promoted Ni/Na–BETA zeolite catalysts for CO_2 hydrogenation, which showed improved CO_2 conversion (in comparison with the Ni/Na–BETA zeolite catalyst) under NTP conditions. Ray *et al* [125] compared the performance of the MgO- and CeO_2-promoted $Ni/\gamma\text{-}Al_2O_3$ catalysts for NTP-assisted DRM. The results showed that the MgO-promoted catalyst had the smallest particle size (∼12 nm) and the largest surface area (∼201 $m^2\ g^{-1}$) with a uniform distribution of Ni on the surface of the catalyst, leading to better catalytic performance with 34.7% and 13% conversion of CH_4 and CO_2, respectively, as compared with the NTP system with $Ni/\gamma\text{-}Al_2O_3$. In comparison, the CeO_2-promoted catalysts provided oxygen vacancy for CO_2 activation, resulting in improved anti-carbon deposition and maximum selectivity to CO. The effect of the promoters depends on their distribution and loading. Excessive addition of the promoters may block active sites, leading to a decrease in catalytic activity [126, 127]. On the other hand, Zeng *et al* [128] compared catalytic DRM over K-, Mg-, and Ce-promoted Ni/Al_2O_3 catalysts under NTP and thermal conditions. Under thermal activation, the addition of the promoters reduced CH_4 conversion. Conversely, in NTP catalysis, the K-promoted catalyst improved CO_2/CH_4 conversion, the yield of H_2, CO and C_2–C_4 alkanes and the energy efficiency of the system, whilst the Mg-promoted catalyst increased the H_2/CO molar ratio due to decreased CO_2 conversion. This work suggests that catalysts presenting poor performance in thermal catalysis may perform well under NTP activation and vice versa. Therefore, fundamental research into the role of promoters in NTP catalysis and their mechanism of enhancement is needed to advance NTP catalysis.

4. Mechanism of CO_2 conversion in NTP catalysis

Based on the discussion above, the rational design of bespoke catalysts for NTP catalysis is a key research direction which can enable efficient interaction between plasma and catalyst to improve the process efficiency of hybrid NTP catalysis

Table 3. Summary of NTP catalytic DRM over supported catalysts modified with various promoters.

Catalyst	Power (W)	CH_4/CO_2	CO_2 conv. (%)		CH_4 conv. (%)		Ref.
			NTP only	NTP + catalyst	NTP only	NTP + catalyst	
Ni–K/Al_2O_3	16	1.5		22.8		31.6	
Ni–Mg/Al_2O_3	16	1.5	18.2	15	25.1	22	[128]
Ni–Ce/Al_2O_3	16	1.5		21		32	
Ni/γ-Al_2O_3–MgO	100	1.0	58	73.5	64	74.5	[129]
Ni–Mn/γ-Al_2O_3	2.1	1.0	6	12	12	28.4	[58]
Na/La_2O_3–$MgAl_2O_4$	100	1.0	59	84.5	62	86	[59]
NiCeC	40	1.0	—	53.7	—	55.6	[127]
Ni/MgO–Al_2O_3	2.7	1.0	9.5	13	20	34.7	[125]
Ni/CeO_2–Al_2O_3	2.7	1.0		12.1		30	

systems for CO_2 activation. Despite extensive studies performed to assess the overall performance of the selected catalysts for NTP catalytic CO_2 conversion, a fundamental understanding of the correlations between plasma, catalyst, plasma-induced reactive species and corresponding reaction mechanisms is still largely lacking.

Generally, NTP catalysis systems are highly complex including, not exhaustively, plasma discharge, ionisation/activation of molecules, adsorption/desorption process, surface reactions, species collisions, species transport in/between the gas and solid phase [21, 130]. Specifically, catalysts have been demonstrated to enhance the local electric field, affect the plasma discharge type and form microdischarges in porous catalysts, while the plasma may modify catalysts and their microscopic structure, metal dispersion and chemical state. Additionally, the interplay between catalyst and plasma-induced active species can be divided into (a) adsorption processes including the adsorption of neutral species, charge carriers and surface charging, and (b) surface reaction processes including photon-induced surface reactions and collision-induced surface reactions [24]. A higher adsorption ability and a lower activation barrier were observed in the case of plasma-induced vibrationally excited molecules due to the increasing energy of the reactants compared with the ground state, which may promote subsequent surface reactivity [20, 131]. The presence of free electrons and ions, i.e. free charges in the plasma state, could also improve the synergy of plasma catalysis by affecting the bond breaking and formation processes on the catalyst surface. For example, Jafarzadeh *et al* [132] investigated the effect of plasma-induced electrons on the adsorption and activation of CO_2 on titania-supported Cu_5 and Ni_5 clusters by using spin-polarised and dispersion-corrected density functional theory calculations. It was found that the electrons affected the adsorption process by shifting the antibonding states of CO_2 towards the valence band, increasing the polarisation effects and changing the adsorption site of CO_2, which lead to improved stabilisation of dissociated CO_2 on the catalyst surface. On the catalyst surface, in addition to the electrons, plasma-produced photons may also induce electronic excitations, which in turn initiate catalytic surface reactions (i.e. photocatalysis). Plasma-induced photocatalysis has been proposed for catalytic VOC abatement over TiO_2, in which 3.2 eV is required to excite an electron in anatase TiO_2 [133]. However, other studies have demonstrated that the photocatalytic effect was negligible in plasma catalysis [134, 135]. Currently, the role of radiation in NTP catalytic CO_2 conversion has not yet been reported. Therefore, further research on the effect of photons on plasma catalytic systems is still needed. In collision-induced surface reactions, some energy may be delivered from the vibrational/electronically excited species and/or impinging photons and electrons to overcome the surface reaction barrier, thus lowering the activation barrier for surface reactions. On the catalyst surface, the surface reactions were demonstrated to proceed via the Langmuir–Hinshelwood or Eley–Rideal reaction mechanisms [136]. Therefore, a suite of comprehensive experimental methods including *in situ* techniques and computational/numerical investigations of plasma catalysis systems are required to provide fundamental insights into the behaviours of the reactive species in the gas phase and/or on the catalytic surface for these reactions.

OES is an important technique used to measure electron temperature and identify, *in situ*, reactive species in the gas phase, which can facilitate an understanding of the relevant reaction mechanisms. Various activated species such as H radicals, CO, CH, OH, C, CHO, CO_2 and CO_2^+ have been detected in NTP-assisted CO_2 hydrogenation, confirming that the plasma can activate relevant molecules for catalysis (as shown in figure 5) [46, 47, 137]. OES detection has also revealed direct collisions of reactive gas species with adsorbed species on the catalyst surface, showing the presence of the Eley–Rideal mechanism [47]. Since, in NTP catalysis, reactions occur simultaneously in the gas-phase and on the catalyst surface, decoupling the contribution of the gas-phase reactions from the surface reactions can be highly beneficial to our understanding of the mechanism of NTP catalysis, though it is highly challenging. A temperature-programmed plasma surface reaction (TPPSR) method was developed to study the plasma catalytic CO_2 hydrogenation, which can remove gas-phase CO_2 and weakly adsorbed surface species before surface reaction [138]. Using TPPSR in combination with isotopically labelled $^{13}CO_2$ (pre-adsorbed on the Co/$CeZrO_4$ catalyst surface), the formation of $^{12}CH_4$ was immediately observed whilst no $^{13}CH_4$ was formed when the $^{12}CO_2/H_2$ plasma was ignited. This indicated that the gaseous CO_2 was dissociated to CO in the gas phase and subsequently reacted with H_2 on the

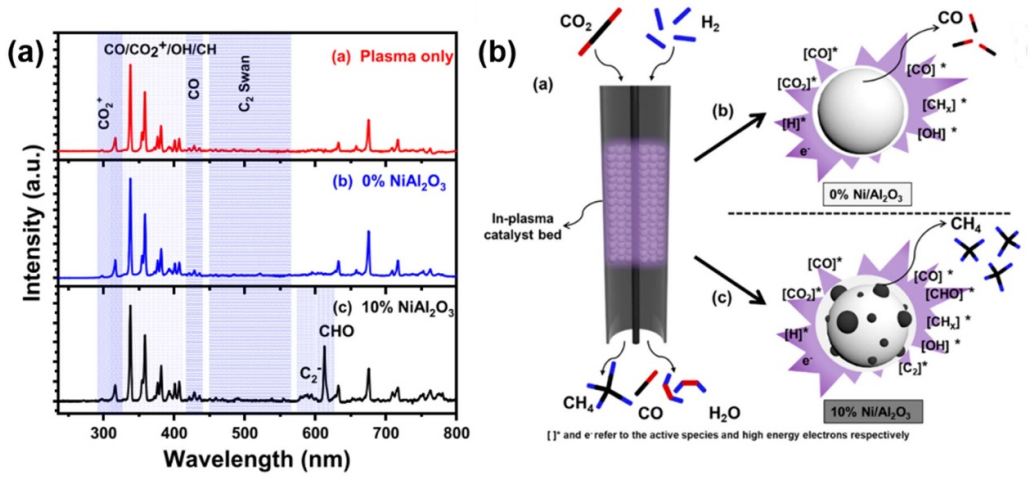


Figure 5. (a) Comparison of OES spectra in NTP catalytic CO_2 hydrogenation for three systems: plasma only, plasma discharge with Al_2O_3, and plasma discharge with 10% Ni/Al_2O_3; and (b) proposed scheme of plasma catalytic interaction for CO_2 hydrogenation over Ni catalysts. Reprinted with permission from [47]. Copyright (2020) American Chemical Society.

cobalt surface to enable CH_4 formation. This technique confirms that plasma-induced CO_2 dissociation in the gas phase can intensify catalyst performance at low temperatures.

Although OES can provide valuable information on the reactive species in the gas phase, direct measurements of the surface reactions on the microscopic scale under NTP conditions are also valuable. Thus, direct operando observation of catalyst structures regarding the evolution and the formation of active surface species using *in situ* techniques has been performed to elucidate and understand catalysis under NTP. Azzolina-Jury *et al* [139] employed microsecond time-resolved FTIR spectroscopy to study the intermediates of plasma-activated CO_2 hydrogenation over the Ni–USY catalysts. The findings showed that NTP-induced partial dissociation of CO_2 (to CO) contributed to gas-phase reactions, whilst, on the catalyst surface, the adsorption of vibrationally excited CO_2 contributed to the formation of formates, which were further hydrogenated into carbonyl species. They also found that CO in the gas phase can adsorb on the Ni surface to form reactive intermediates for CO_2 hydrogenation, demonstrating the existence of multiple pathways under NTP conditions. Recently, a DRIFTS technique (as shown in figure 6) was developed by Stere *et al* [140] for NTP catalysis to probe the dynamics of the surface species and intermediates on the catalyst surface, including selective catalytic reduction of NO_x [141, 142], WGS [9, 10], CO_2 hydrogenation [103, 143] and DRM [62], which provided valuable information on the explanation of the possible mechanisms and reaction pathways using NTP catalysis. By combining *in situ* DRIFTS with the mass spectrometry study, Chen *et al* [105] confirmed the co-existence of Langmuir–Hinshelwood and Eley–Rideal mechanisms in NTP catalytic CO_2 hydrogenation, i.e. both the surface reactions (between the adsorbed species) and interactions between the adsorbed and gas-phase species contributed to the formation of CH_4. Furthermore, Xu *et al* [110] revealed that NTP catalysis promoted more active species including CO^*, O^*, H^*, formates, carbonate, formyl and carbonyl in comparison with the thermal counterpart, showing the presence of alternative reaction pathways for CO_2 hydrogenation in the NTP catalysis. A study using *in situ* DRIFTS for plasma-activated DRM over the Ni/Al_2O_3 catalyst with La as a promoter also found that the vibrational states of CH_4 and plasma-induced CO_2 activation contributed to the improved performance of NTP catalysis [144]. Specifically, plasma could facilitate CO_2 activation to produce a 1.7-fold enhancement in surface carbonate formation on La as compared with thermal activation. The surface reaction between CH_x^* and carbonate species promoted improved CH_4 conversion in the plasma-assisted DRM.

In addition to *in situ* DRIFTS, *in situ* x-ray absorption fine structure (XAFS) has also been developed to characterise the structural changes of catalysts during NTP catalysis. CH_4 oxidation under NTP conditions was investigated by *in situ* monitoring of the x-ray adsorption fine structure of Pd/Al_2O_3 catalysts [145]. It was found that, during the NTP catalysis, the catalyst did not show significant structural changes, and the plasma-induced heating of Pd nanoparticles was suggested, confirming the perturbation role of NTP in the hybrid system [22]. Although *in situ* XAFS characterisation has been applied to CO_2 hydrogenation under thermal conditions [146–148], it has not yet been used for NTP-assisted CO_2 hydrogenation. In summary, *in situ* characterisation is crucial for NTP catalysis as it will allow us to (a) identify the critical steps of surface reactions, (b) understand the catalyst changes during NTP catalysis, and (c) establish ideal NTP conditions that optimally exploit the NTP catalysis.

Kinetic studies are also a useful experimental method used to understand NTP catalyst interactions, allowing us to understand the effect of relevant variables, such as discharge power, reactant concentration and catalysts, on the chemical reaction (e.g. reaction rate and activation barrier) in order to maximise the efficiency of hybrid systems. The pioneering work of Kim *et al* [23] on the kinetic evaluation of CH_4 activation over the Ni catalyst in a thermal DBD plasma hybrid reactor,

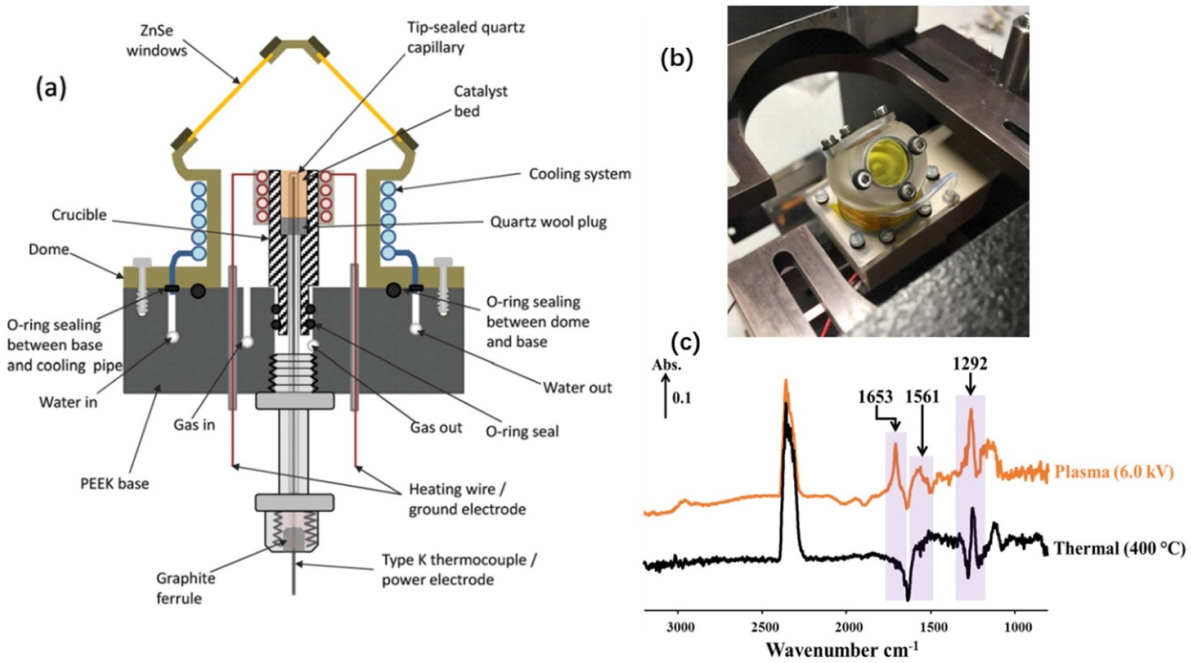


Figure 6. (a), (b) Schematic and photograph of *in situ* plasma flow cell for a DRIFTS study. Reproduced from [140] with permission of The Royal Society of Chemistry. (c) Comparison of *in situ* DRIFTS spectra of CO_2 hydrogenation under NTP and thermal conditions. Reproduced from [105] CC BY 4.0.

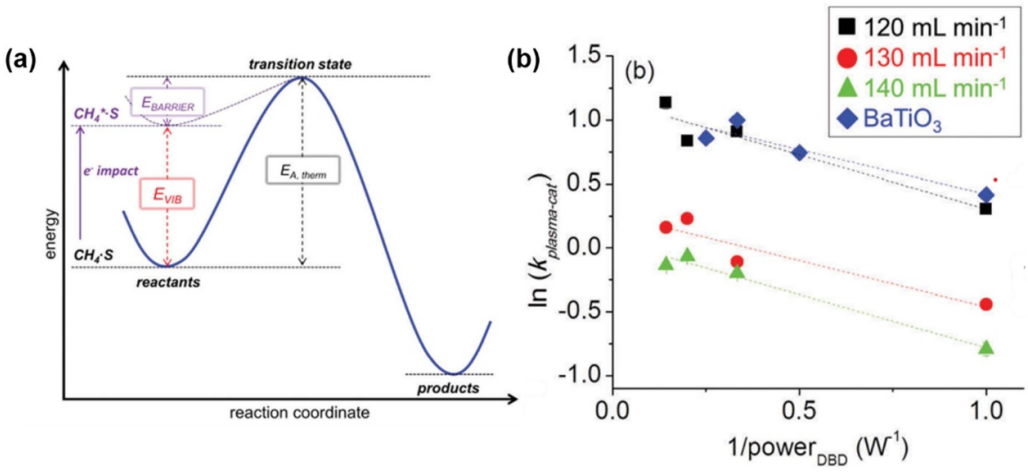


Figure 7. (a) Progress of thermal and plasma-assisted catalysis requiring energies of $E_{A,therm}$ and $E_{BARRIER}$ to reform CH_4 species at 790–890 K, respectively. (b) Logarithmic reaction rate constant (ln $k_{plasma\text{-}cat}$) vs. 1/power$_{DBD}$ under different reaction environments. Reproduced from [23] with permission of The Royal Society of Chemistry.

as shown in figure 7, established the correlation between the reaction rate and input power for calculation of the activation energy of NTP catalysis. Subsequently, a comparative kinetic study of CO_2 hydrogenation (over Ni@SiO_2) under thermal and plasma activation was performed [137], showing that the activation energy of the NTP catalysis was estimated to be ~29 kJ mol^{-1}, which was significantly lower than that of the thermal catalysis (~80 kJ mol^{-1}). These findings suggest that NTP activation can lower the activation barrier required to initiate catalysis.

In addition to experimental investigations, modelling and simulation of NTP catalysis have provided useful information on relevant physical and chemical phenomena, as well as predicting the suitable catalysts and optimal conditions for NTP catalysis [149]. De Bie *et al* [150] investigated CO_2 hydrogenation in a DBD reactor using a one-dimensional fluid model (figure 8). It was found that CO and CH_4 were the main products of NTP catalysis, while the selectivity to methanol and hydrocarbons was relatively low, consistent with findings from experimental studies [50, 92]. The model suggests that the reaction starts with the electron impact dissociation of CO_2 and H_2 to form CO, O and H radicals. Further electron impact dissociation of CO then contributes to form the C, CH, CH_2, and CH_3 radicals. The relatively low density of these

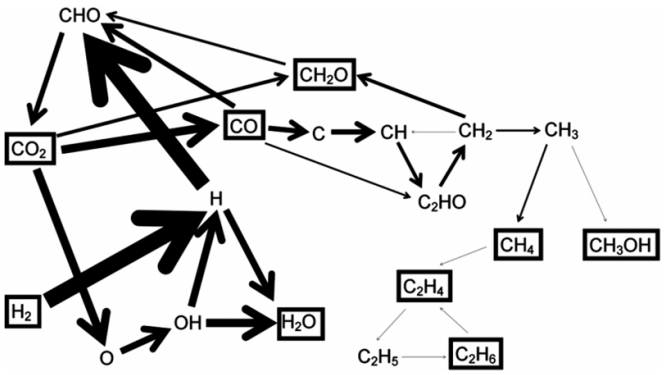


Figure 8. Dominant reaction pathways for the conversion of CO_2 and H_2 into various products proposed by the one-dimensional fluid model, in a 50/50 CO_2/H_2 gas mixture. Reprinted with permission from [150]. Copyright (2016) American Chemical Society.

radicals leads them to preferentially form CH_4 rather than hydrocarbons and oxygenates (e.g. C_2H_6, C_2H_4 and CH_3OH), explaining the low yield of hydrocarbons/oxygenates in CO_2 hydrogenation. Recently, Stijn *et al* [151] developed a chemical kinetic model to study the underlying mechanism of conversion of CO_2 and CH_4 into hydrocarbons, especially C_2H_2, C_2H_4 and C_2H_6, under NTP conditions. The reaction was initiated by the electron-impacted dissociation/ionisation of CH_4 to form CH_3, CH_2 and CH radicals. The coupling of CH_3 mainly contributed to forming the C_2H_6 product, while this process was counterbalanced by the electron impact dissociation/decomposition of C_2H_6 to form C_2H_4 and C_2H_2. Further dissociation and recombination of these C_2H_4 and C_2H_2 radicals led to the formation of higher hydrocarbons such as C_3H_8, C_4H_{10} and C_5H_{12}. The simulation results showed that CO_2 conversion with CH_4 can directly form more CH_2 and CH_3 radicals by dissociation of CH_4 in a plasma discharge, making it a potential route for producing hydrocarbons and oxygenates as compared with CO_2 hydrogenation [152]. A 2D fluid model was developed by Zhang *et al* to investigate plasma formation inside porous catalysts with different pore sizes (in the range of 10–400 μm) and shapes (e.g. conical pores with small/large opening and cylindrical pores) in order to predict how the porous structure of catalysts affects plasma properties [113, 114]. These findings suggest that plasma micro-discharges may occur in pores with sizes larger than the Debye length, and that high applied voltages and different pore shapes contribute to the different electric field enhancement and plasma properties. Models describing the influence of the nature of the catalyst on the plasma characteristics coupled with surface chemistry may play an essential role in designing, controlling and optimising plasma catalysis systems, and should be further developed and researched.

5. Conclusions and perspectives

As compared with conventional thermal activation, NTP activation of catalysts (in which plasma discharge dissociates reactant molecules in the gas phase and contributes to surface reactions, i.e. perturbation of the heterogeneous catalysis) shows great potential in activating and converting stable CO_2 molecules into value-added fuels and chemicals under comparatively mild conditions. Recent advances in plasma catalytic CO_2 conversion (as discussed in this review), including CO splitting, CO_2 hydrogenation into chemicals/fuels and reforming (with CH_4 and H_2O) into syngas, suggest that NTP-activated heterogeneous catalysis is a promising technology for the practical utilisation of CO_2.

Catalysts play an important role in hybrid systems regarding efficiency and selectivity. Thus, developing suitable catalysts specifically for NTP catalysis is critical to optimise hybrid systems for CO_2 conversion, making it more competitive and economically attractive for practical applications. Previous studies have shown that the intrinsic properties of the catalysts, including the active metal species, metal particle size and the dispersion and location of active sites, and catalyst supports are the dominant factors in the performance of NTP catalysis. The development of bespoke NTP catalysts with highly dispersed metal active sites (e.g. single-atom catalysts) and hierarchical porous structures (e.g. modified MOFs and zeolite) are beneficial for maximising the plasma catalytic CO_2 conversion processes. However, a fundamental understanding of the correlation on the structure–composition–activity is still needed to provide guidance on the rational design of cost-effective, highly selective and efficient catalysts specified for NTP catalysis.

Moreover, a comprehensive and in-depth understanding of plasma–catalyst interactions also is important in maximising NTP-assisted CO_2 conversion. In the presence of a catalyst, an electric field can be enhanced due to the formation of surface discharge, benefiting CO_2 activation and subsequent surface reactions. Compared with thermal catalysis, where heterogeneous catalysis proceeds only with the chemisorption of the reactant on the catalyst surface, plasma-induced reactive species in the gas phase may introduce new species for multiple surface reactions, thus lowering the reaction barriers and altering the reaction pathways of the catalysis. However, both chemical and physical effects are interlinked, and hence are difficult to be fully decoupled. Hence, hybrid plasma catalysis systems are highly complex and require further understanding to advance the technology. *In situ* techniques such as OES, XAFS and DRIFTS together with advanced modelling methods have shown the ability to gain relevant insights into NTP catalytic CO_2 conversion. Further development and implementation of *in situ* characterisation techniques and relevant plasma modelling investigations on surface/gas-phase reactions, species transport, adsorption/desorption, reaction intermediate formation on active sites and the real-time change of catalyst surface in the hybrid NTP catalysis system are still needed to progress our understanding on the plasma–catalyst interactions and mechanisms of NTP catalysis.

Finally, the trade-off between energy efficiency and CO_2 conversion still needs further investigation in plasma catalysis, especially for large-scale processes. It is important to develop reactor designs and optimise operating conditions to improve the energy efficiency of plasma catalytic CO_2 conversion. For example, a water-cooled DBD reactor has been demonstrated to be more effective at producing liquid fuels

from CO_2 hydrogenation [52]. Also, novel integrated processes combining CO_2 capture [153] and the CO_2 separation process [154] with plasma catalytic CO_2 conversion have shown the feasibility and potential for developing a generic platform technology with improved CO_2 capture and utilisation efficiency. Additionally, the industrialisation of NTP catalysis systems should also consider economic aspects, such as the costs of catalysts, the energy supply and separation of products, and hence, thorough techno-economic and life cycle assessments are needed to develop practical CO_2 conversion applications from laboratory-developed plasma systems.

Data availability statement

No new data were created or analysed in this study.

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