The application of nonthermal plasma in methanol synthesis via CO\textsubscript{2} hydrogenation

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Abstract
CH\textsubscript{3}OH is an energy carrier that can be generated from renewable resources and be used as a fuel in fuel cells and internal combustion engines and a platform chemical for the synthesis of value-added chemicals or gasoline. Carbon dioxide (CO\textsubscript{2}) hydrogenation is one of the widely researched methods to generate methanol. The traditional CO\textsubscript{2} hydrogenation reaction method (requires high H\textsubscript{2} pressure and temperatures) has attracted considerable attention. However, the new emerging field of catalysis referred to as nonthermal plasma (NTP) catalysis has also been developed extensively for methane reforming and CO\textsubscript{2} hydrogenation to methane and CO. The plasma-assisted approach not only presents remarkable advantages, such as room temperature and atmospheric H\textsubscript{2} pressure but also has great potential to be powered by renewable electricity in a flexible way since it can be easily switched on/off. In this account, we review the recent articles published on methanol synthesis from CO\textsubscript{2} and H\textsubscript{2} using NTP. We reviewed and discussed the mechanism of this reaction under NTP, the modification of the reactor configurations, and the rationale behind the catalyst design. In the end, we discussed the advantages and disadvantages of each of these works and the future perspectives of this interesting privileged reaction. We believe this review is of interest to researchers active in sustainable heterogeneous catalysis.

**KEYWORDS**
energy efficiency, environment, environmental impact, other renewables

1 | INTRODUCTION

Carbon dioxide (CO\textsubscript{2}) is the most abundant greenhouse gas, mainly caused by the excessive burning of fossil fuels. This increase in CO\textsubscript{2} generation at a fast rate probably introduces an irreversible change to the world's climate.\textsuperscript{1} CO\textsubscript{2} capture, utilization, and storage is one of the effective strategies to minimize the emission of CO\textsubscript{2} in the air.\textsuperscript{1} The utilization of CO\textsubscript{2} (as a single substrate reaction) as a carbon source is challenging due to the high thermal and chemical stability of CO\textsubscript{2} molecules and its high endothermicity needed to cleave the C–O bond within this molecule. However, CO\textsubscript{2} can be transformed easier in the presence of molecules with higher...
Gibbs free energy, such as $H_2$.\textsuperscript{1} As a result, CO\textsubscript{2} hydrogenation to methanol is considered as one of the promising approaches to alleviate this greenhouse gas.

On the other hand, methanol (CH\textsubscript{3}OH) is an important chemical and can be used, as a fuel, in internal combustion engines and fuel cells. The fast depletion of nonrenewable energy sources places methanol as an alternative building block to produce chemicals and gasoline. As discussed in the “methanol economy” concept,\textsuperscript{2} methanol synthesized via promising and regenerative ways like CO\textsubscript{2} hydrogenation will likely play a key role in the near future.\textsuperscript{3,4} Using well-designed zeolite-based catalysts, methanol can be converted to olefins (MTO) or propylene (MTP). This profound application of methanol (formation of commodity chemicals like olefins) has gained considerable attention in recent years and has created a surge in methanol market sales from 6% in 2011 to 22% in 2016.\textsuperscript{1} Therefore, CO\textsubscript{2} hydrogenation is an attractive and probably profitable route in the CO\textsubscript{2} utilization strategy to reduce CO\textsubscript{2} and produce methanol.

Producing methanol using thermal catalytic (TC) reactors are well discussed in a review written by Jiang et al.\textsuperscript{1} However, this conventional reaction is carried out at high temperatures and high pressure of H\textsubscript{2}, which results in catalyst deactivation via processes such as sintering, coking, or surface poisoning.\textsuperscript{1} As an alternative, electrocatalytic (EC) reactors were also employed and studied. Interestingly, the net reduction of CO\textsubscript{2} (referring to the amount of CO\textsubscript{2} generated during TC or EC to supply energy vs. the consumed CO\textsubscript{2} during the reaction) is low if nonrenewable energy is used to satisfy the required conditions for this CO\textsubscript{2} hydrogenation to form methanol.\textsuperscript{5} It is important to point out that hybrid catalytic methanol synthesis (having TC and EC combined) offers improved net CO\textsubscript{2} reduction.\textsuperscript{5} As a result, implementing the hybrid process with renewable energy supply appears as a promising pathway for efficient methanol generation. However, the complexity of such design welcomes numerous expensive preconditions to this model. Therefore, finding simpler, efficient, and cheaper alternatives that can catalyze this reaction at lower temperature and pressure conditions can provide access to larger quantities of methanol at a lower cost and enhanced net reduction of CO\textsubscript{2}.

The application of plasma to activate CO\textsubscript{2} has been studied and reviewed recently.\textsuperscript{6–9} Different types of plasma such as corona discharges,\textsuperscript{10} glow discharge,\textsuperscript{11} microwave discharges,\textsuperscript{12} radiofrequency discharges,\textsuperscript{13} gliding arc discharges,\textsuperscript{14} and dielectric barrier discharges (DBDs)\textsuperscript{15–17} have been applied to activate CO\textsubscript{2} bond. These reviews focused on the production of syngas or methane. The use of DBD plasma has attracted much attention due to its low operating temperature (<100°C) and ability to activate chemical bonds like the ones in CO\textsubscript{2} and H\textsubscript{2} molecules at low reaction pressure because of having low enthalpy in comparison with the thermal plasma. NTP (or sometimes referred to as cold plasma) contains electrons, neutrals, electronically and vibrationally excited species, ions, radicals, and atoms.\textsuperscript{18} The collision of these charged species with chemicals can catalyze the reactions such as bond dissociation or formation to take place at low temperatures and milder conditions than currently commercialized chemical processes. In contrast, the high temperature of thermal plasma makes it suitable for decomposition reactions.\textsuperscript{19} However, the use of nonthermal plasma (NTP) during the CO\textsubscript{2} hydrogenation tends to readily catalyze the pathways yielding carbon monoxide (CO) and methane (CH\textsubscript{4}) with a lower value than methanol. Therefore, we decided to launch a systematic study and investigate the possible influential factors that can be fine-tuned to improve the methanol yield during the CO\textsubscript{2} hydrogenation using NTP. This review aims to explore the rationales behind catalyst design (considering the proposed mechanisms), reactor design, and selection of the reaction conditions to increase the methanol space–time yield formed via CO\textsubscript{2} hydrogenation using hydrogen.

\section{CO\textsubscript{2} Hydrogenation to Methanol}

\subsection{Mechanism of CO\textsubscript{2} hydrogenation to methanol}

Cu-based catalysts are among the best-known catalysts for CO\textsubscript{2} hydrogenation to methanol in thermal reactors.\textsuperscript{1,20} Experimental and theoretical studies have shown that metallic copper (Cu\textsuperscript{0}) is the active site for hydrogenation.\textsuperscript{21–23} Many of these Cu-based catalysts contain ZnO (zinc oxide) as a promoter that assists the performance of Cu\textsuperscript{0} by acting as a hydrogen reservoir.\textsuperscript{24} Therefore, Cu remains in the metallic state with abundant access to H\textsubscript{2} (hydrogen) to catalyze the hydrogenation reaction. Besides the active site identification, establishing the reaction paths is of great importance for catalyst development.

Grabow and Mavrikakis\textsuperscript{25} proposed the formate route to produce methanol from CO\textsubscript{2} (Figure 1). They suggested the first step of hydrogenation leads to formate (HCOO\textsuperscript{*}) formation as an intermediate. After that, these formate species will further react with hydrogen to form formic acid (HCOO\textsuperscript{*}H) and subsequently dioxy-methyl (CH\textsubscript{3}O\textsubscript{2}*) intermediate with significant reactivity. The formed CH\textsubscript{3}O\textsubscript{2}* will be converted to formaldehyde and OH group. Finally, CH\textsubscript{2}O* hydrogenation results in
methoxy (CH$_3$O$^*$) that can be easily converted to CH$_3$OH. Zhao et al. disputed the formate pathway by pointing out the need to overcome high activation barriers to hydrogenate the formate. Yang et al. later concluded that hydrogenation of bidentate formate (HCOO$^*$) over Cu$^0$ could not produce methanol, and alternatively, the CO$_2$ hydrogenation follows hydrocarboxyl (trans-COOH) route (Figure 1). Interestingly, they showed that the catalyst pretreatment using oxidants such as N$_2$O or air results in better catalytic performance implying the involvement of the surface oxygen in the mechanism. Due to the good ability of Cu$^0$ for reverse water gas shift (RWGS) and vice versa reaction, it has also been proposed that CO$_2$ being converted to CO in the first step over Cu$^0$ sites. Then, CO will follow the same route proposed for methanol synthesis via syngas hydrogenation.

Michiels et al. conducted an improved microkinetic model for hydrogenation of methanol using the thermal method. Interestingly, their study showed that the combination of RWGS and hydrogenation reactions are the hypothetical pathway for CH$_3$OH formation, which is confirmed by the experimental findings reported by Wang et al. Furthermore, they used the same model to predict the contribution of plasma in CO$_2$ hydrogenation to form methanol via the formate pathway (Figure 2). They theoretically showed the introduction of plasma in this system could improve WGS (water gas shift), hydrogenation, and formate formation, which allowed them to predict that the correct design of the plasma setup with a proper catalyst could increase the yield of methanol sixfolds higher than the thermal method when the optimized conditions were applied. One of the conditions that they highlighted using the modeling was the hydrogen pressure in the system should be at least two times higher than O (oxygen) pressure (O atom within CO or CO$_2$). This setup will maximize the methanol formation during the plasma-assisted process.

In brief, both published experimental and theoretical studies suggested that the metallic state of the hydrogenation metals was the active site for methanol formation via CO$_2$ hydrogenation in thermal and plasma catalysis. Formate, hydrocarboxyl, and RWGS (WGS) are involved pathways during methanol synthesis. However, it is theoretically proven that plasma catalysis influences the formate pathway by introducing the species (which can only

**FIGURE 1** Different pathways for the synthesis of methanol via CO$_2$ hydrogenation. Adapted from Álvarez et al. (Copyright 2017 American Chemical Society)
be generated using plasma), which can lower the activation energy barriers in place for this reaction. This explains why, with an enhancement by plasma, the reaction can be proceeded at milder conditions. Therefore, the applicable phenomena in heterogeneous catalysis such as the adsorption/desorption of the feed and products, surface acidity and basicity, the redox properties of the active sites, the proximity of the active sites with different functionalities, the crystallite sizes of the active sites, and their metal support interactions are still applicable parameters when designing a catalyst for CO₂ hydrogenation (to methanol) using plasma. Specifically, for in plasma catalysis, understanding the species (such as ions, radicals, photons, and arcs) that active metal sites with hydrogenation ability can provide is vital since these in situ formed species, including their concentration and their types of interactions with the feeding substrate determine the selectivity profile of the designed catalytic reactions. Thus, in the following sections, different catalysts applied for the plasma catalytic formation of methanol via CO₂ hydrogenation will be discussed.

2.2 Studied catalysts for CO₂ hydrogenation to methanol using NTP

2.2.1 Cu-based catalysts

Due to the high activity, Cu-based catalysts became an early candidate that was applied in plasma synthesis of methanol. The pioneering work done by Wang et al. on the application of CuO/Al₂O₃ for in plasma synthesis of methanol emerged the great potential of this energy source for methanol synthesis. They reported 21.2% CO₂ conversion with 53.7% selectivity to methanol (methanol yield of 11.3%) in atmospheric pressure and room temperature using an NTP reactor. Interestingly, the reactor design played a significant role in this study. They designed three argon nonthermal DBD reactors (Figure 3), where the first reactor contained a thin layer of aluminum foil as a ground electrode. This ground electrode was replaced by water circulating electrode in the second and third reactors. This modification not only served as a ground electrode but also removed heat from
the reaction. The inner stainless-steel electrode was separated from the reactants and catalysts using a thin layer of the quartz tube (marked in red line as shown in Figure 3A,B) in the second reactor, which was absent in the third reactor. Therefore, the catalytic materials were in direct contact with the electrode in the third reactor. Reactor III provided 13% CO₂ conversion with 57% selectivity to methanol (methanol yield of 7%), while reactors I and II showed higher CO₂ conversion but CH₄ and CO were the primary products. The temperature in reactor I could reach as high as 350°C during the CO₂ activation. However, 30°C was maintained in reactor III because of the circulating water around the catalyst bed. The discharge formed in reactor II with a double dielectric structure (covered SS inner electrode) was weak but uniform, while the discharge generated in reactor III mainly contained strong filaments. This difference resulted in different catalytic performances between reactors II and III. This design alteration enhanced the formation of thermally unstable oxygenate like methanol during the reaction and prevented their thermal decomposition to CO and CO₂ (Figure 3C). Therefore, higher selectivity to methanol was observed when reactor III was used (Figure 3D). Interestingly, the H₂/CO₂ ratio change did not play a significant role in this plasma CO₂ hydrogenation reaction. They suggested that Cu/Al₂O₃ catalyzed the RWGS reaction (CO formation) and the formation of formate. The application of a catalyst to a plasma reactor was found to increase the concentration of reactive radical H species needed for the hydrogenation of in situ formed CO and formate intermediates.32

Feliz et al.35 investigated the application of a non-thermal DBD reactor for methanol formation using Cu loaded on alumina and ZSM-5 promoted with Zn. The plasma reactor used in this study had stainless steel as an inner electrode and a Cu sheet as a ground electrode. They showed that neither support (Al₂O₃) nor catalyst (Cu/Al₂O₃) presented catalytic activity under thermal CO₂ hydrogenation at temperatures below 100°C and atmospheric pressure. In contrast, all materials including the empty reactor tube tested in this study could promote CO₂ conversion under plasma (conversion ranging from 21% to 34%). In line with a study done by Neyts and Bogaerts,36 their finding showed that the catalyst influenced the plasma and vice versa (plasma affecting the catalyst).35 Regarding the impacts of a catalyst on the plasma properties, the following are applicable: (i) modification of the discharge type, (ii) enhancement of the electric field, and (iii) formation of micro discharges within the catalyst pores and external surface. In terms of plasma affecting the properties of the catalyst, it refers to the modification of the adsorption capacity of the catalyst, oxidation state of the metallic, active phase, the surface area, hot spots formation, and alteration of the surface reaction pathway. They observed that an increase in the dielectric constant improved the magnitude

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**Figure 3** (A) Schematic illustration of DBD plasma reactors (I, II, and III) with different configurations (a, ground electrode; b, high voltage electrode). (B) Images of H₂/CO₂ discharge generated in different reactors with no catalyst. (C) Methanol yield and CO₂ conversion. (D) Selectivity of gas products and oxygenates (reaction pressure 1 atm, H₂/CO₂ molar ratio 3:1, with no catalyst).32 DBD, dielectric barrier discharge (Copyright 2018 American Chemical Society)
of the electric field, resulting in higher plasma density favoring CO₂ dissociation. However, when the introduced solid (catalyst) is conductive, the magnitude of the associated electric field is diminished, and CO₂ conversion was not improved. The addition of Cu and Zn (monometallic or bimetallic) altered the dielectric constant measured for the blank support. As a result, the rate of CO₂ activation differed in line with their proven hypothesis. Adopted from accepted arguments in thermal catalysis, they claimed that Zn addition (as a promoter) increased the concentration of hydrogen on the surface yielding better selectivity to methanol (0.5% of methanol yield).

Joshi and Loganathan loaded CuO on quartz wool (QW) which was used as a catalyst in a modified plasma methanol synthesis.¹⁸ In contrast to Wang et al., they introduced a heating furnace around the discharge area where the catalyst was loaded. They used stainless steel as the inner electrode and a stainless-steel mesh as the ground electrode (Figure 4). Therefore, their system is a combination of catalyst-thermal-plasma designs. The CuO/QW catalyst in thermal plasma showed an increase in the voltage resulting in better CO₂ conversion and increased selectivity to CO and CH₄. With no heat applied they obtained low CO₂ conversion under their chosen reaction conditions. They also used Fe₂O₃ (iron (III) oxide) as a promoter. Fe₂O₃ appeared to provide negligible CO₂ conversion. However, CuO/Fe₂O₃/QW in thermo-plasma catalytic reaction provided about 16.7% CO₂ conversion and 32% CH₃OH selectivity with 2 W of input power at 200°C. This translated to 9.32 mmol h⁻¹ g⁻¹ CH₃OH space–time yield for this model. These exciting results are likely due to the reduction of CuO sites (using heat and H₂) at 200°C and the well-known RWGS (or great WGS) activity of Fe₂O₃.³⁷,³⁸ Having this synergistic bifunctionality activated by either thermal or plasma (as energy sources) likely resulted in a high yield toward methanol in this study.

2.2.2 | Ni-based catalysts

Joshi and Loganathan also studied the possibility of applying NiO as active sites for CO₂ hydrogenation, as shown in Figure 4.¹⁸ In monometallic NiO/QW catalyst, NiO was found to primarily catalyze CO₂ to CO and methane formation, and less selectivity toward methanol was observed in this case. However, the sequential loading of NiO/Fe₂O₃/QW resulted in the

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**FIGURE 4**  (A) Schematic illustration of the thermo-plasma reactor used by Joshi and Loganathan. (B) Effect of NTP on CO₂ conversion and (C) methanol selectivity at 200°C. The plasma input power range of 0–3.7 W is achieved by changing the voltage at a fixed 50-Hz frequency¹⁸ (Copyright 2021 Wiley-VCH GmbH)
capability of catalyzing methanol formation with high selectivity. Unfortunately, its conversion was much lower than the CuO counterpart (Figure 4). In a different published report with the same reactor setup, they tested NiO/Fe$_2$O$_3$ where the NiO loading was varied. They discovered that NiO and Fe$_2$O$_3$ (monometallic catalysts) showed lower activity than the supported catalysts (NiO/Fe$_2$O$_3$), where they argued that the synergy between NiO and Fe$_2$O$_3$ sites was responsible for the improved catalytic results.\textsuperscript{39} Using an optimal catalyst under an optimized condition, the system with a thermal-plasma setup performed 5.8-folds better than the pure thermal method. They characterized the spent supported catalysts from this application and suggested that the active sites for methanol formation are in situ formed mixed NiO with metal support interactions with the Fe$_2$O$_3$ and NiFe$_2$O$_4$ spinel with both hydrogenating and RWGS ability.\textsuperscript{38,40,41}

### 2.2.3 Co-based catalysts

Ronda-Lloret et al. presented a DBD reactor with a configuration similar to what was proposed by Wang et al. for methanol and ammonia synthesis using a water-based circulating ground electrode (reactor III in Figure 3).\textsuperscript{32,40,42} CoO$_x$/MgO and Al$_2$O$_3$ were used as catalysts for CO$_2$ hydrogenation to methanol. They suggested that MgO was a proper support for CoO during plasma methanol synthesis, where more than 35% CO$_2$ conversion and 10% yield to methanol were obtained.\textsuperscript{40} MgO with known surface basicity showed a better tendency toward CO$_2$ (acidic) than acidic support like aluminia, but both these supports (as a blank) without loaded metal sites catalyzed CO formation only. Both high CoO$_x$ loadings and increased dispersion of CoO$_x$ can improve the in situ catalytic performance. They proposed that CO$_2$ hydrogenation under DBD plasma took place via three primary mechanisms, including formate, RWGS, and CO hydrogenation, as discussed earlier by other researchers in the field.

### 2.2.4 Pt-based catalysts

Wang et al.\textsuperscript{32} tested Pt/Al$_2$O$_3$ in the plasma reactor III shown in Figure 3 and compared it with the Cu/Al$_2$O$_3$ catalyst data. Their results highlighted that both Cu and Pt follow the exact mechanism in plasma methanol synthesis using DBD (Figure 5A). Compared with the noncatalytic plasma reaction, applying the catalyst in the plasma-catalytic CO$_2$ hydrogenation provides new reaction routes for chemical reactions. To gain insights about the possible reaction pathways in plasma-enhanced catalytic CO$_2$ hydrogenation to methanol, they compared the emission spectra of H$_2$/CO$_2$ DBD with different catalysts loaded. H$_2$ species, CO Angstrom bands, and H$_2$ bands found in abundance in the plasma reactor without catalyst were considerably lowered when a catalyst was loaded to the plasma reactor (Figure 5B). This phenomenon might be linked to the adsorption of gas-phase species (like CO) into the pores of the catalyst.

Men et al.\textsuperscript{43} studied Pt/film/In$_2$O$_3$ o (the film was made of self-assembled 2D peptide [A$\beta$16–22]) for in-plasma hydrogenation of CO$_2$ to methanol using a chilled DBD unit. They used water circulation to keep the reaction temperature constant, unlike the study done by Wang et al., where the water electrode was bifunctional and responsible for both cooling and ground electrode. Their catalyst showed a high CO$_2$ conversion of 37% and methanol selectivity of ~63%, better than the reference catalyst (Cu/ZnO/Al$_2$O$_3$).
The use of film as a carrier for Pt sites resulted in an increase in Pt dispersion and CO₂ adsorption, which both significantly contribute toward improved CO₂ conversion and methanol synthesis. They conducted a pulse time on-stream analysis, and the catalyst was stable up to 16 h merely because of the mild conditions (atmospheric pressure and room temperature) as expected. This supports the minimal effect of plasma on active site sintering instead of the thermal impact imposed by either heater or heat generated as a side effect (hot spot formation) during plasma catalysis.

### 3 | METHANOL FORMATION VIA NTP CATALYTIC PARTIAL METHANE OXIDATION

In plasma catalytic partial oxidation of methane using oxidants such as air (or O₂), H₂O₂, and CO₂ have also been explored for methanol synthesis. There are several disadvantages associated with this process. The use of air or O₂ as an oxidant results in high selectivity to CO and CO₂ (COₓ). Fine-tuning the catalysts for this application is very difficult since the selectivity to other products other than CO₂ is very poor. Various activated methane intermediates (formed via a radical mechanism in plasma) tend to participate in polymerization reactions on the catalyst surface. This results in selectivity to hydrocarbons (both saturated and unsaturated) or oxygenates (formic acid, C–C₄ alcohols, and acids); thus, a pool of compounds is obtained. Furthermore, this polymerization (in extended form) can result in carbon deposition over the catalyst deactivating the catalysts. The use of H₂O₂ suffers from the same dilemma discussed for the use of air (O₂), plus the additional cost of H₂O₂ compared with air. The use of CO₂ as an oxidant welcomes new challenges in this area. CO₂ and CH₄ are both carbon sources in this process. Both can form methanol since this reaction can be oxidation (oxygen from CO₂ reacts with activated methane) or hydrogenation (H from methane reacts with activated CO₂). However, it is still unclear which one of these pathways dominates the reaction. Therefore, designing a catalyst that preferably catalyzes a particular path without contributing to side reactions under plasma is a complex challenge. Regardless of the mechanism, catalytic work is done in line with the concept of simultaneous activation of these two greenhouse gases to obtain value-added products. Results show a higher chance of surface coking (catalyst deactivation) and improved selectivity of oxygenated products over the selectivity to hydrocarbons. Therefore, direct catalytic hydrogenation of CO₂ to methanol using H₂ under NTP seems more in reach and can be counted as a preparation step for a more complex reaction like NTP catalytic methanol formation using CO₂ and CH₄ at this stage.
4 | FUTURE PERSPECTIVES

4.1 | Reactor design

Based on the above-discussed, two approaches have been adopted to improve the methanol yield during the NTP catalysis as far as the reactor design is concerned.\(^{18,32,39}\) The first and more promising type is the chilled NTP using the water circulating setup around the catalyst bed, which can either be incorporated into the electrical design of the reactor and act as a ground electrode, or function independently. Nonetheless, NTP can reach up to 300°C due to the formation of hot spots on the catalysts bed.\(^{52}\) Maintaining appropriate temperature for the catalyst bed is a key to preventing sensitive oxygenated products like methanol from decomposition. Opposite to this low-temperature approach, a combination of thermal and plasma catalysis was also proposed and shown to improve the yield of methanol. In this reactor design, the catalyst bed in NTP is heated using an external heater.\(^{18,39}\) This protocol appears to catalyze the reduction (in the presence of H\(_2\)) of the active sites (like CuO) and thus, improve their hydrogenation ability. Furthermore, this reactor configuration results in a higher yield to methanol by simply increasing the reaction conversion. Therefore, the yield values to other side products are high, too. In catalysis, increasing output by improving selectivity and conversion at the same time is much preferred. So, the first model proposed by Wang et al. appears to be the system of choice for synthesizing oxygenates (like methanol) using NTP.

4.2 | Catalyst design

This review provided a general outline of what has been done in terms of catalytic NTP hydrogenation of CO\(_2\) to methanol. Most of the discussed works appear to lack the rationale behind catalyst design. Promising catalysts such as CuO—ZnO, CuO—Fe\(_2\)O\(_3\), PtO\(_2\)—In\(_2\)O\(_3\), and so forth, in thermal CO\(_2\) hydrogenation to methanol, have been selected to explore their performance during the NTP. As proven in methane reforming and CO\(_2\) methanation using plasma, the active sites during the plasma process are different from the ones we identified during the thermal process.\(^{7,34}\) Therefore, the application of catalysts with active sites that synergistically interact with plasma should be encouraged.

4.3 | Reaction optimization

Each catalyst has its own strength and weakness. To compensate for the catalysts’ shortcomings, reaction optimization is required, which is standard practice during the high-pressure thermal hydrogenation of CO\(_2\) to methanol. As several studies have shown, the rapid rescue of the sensitive products is of great importance during the catalytic NTP hydrogenation of CO\(_2\) to methanol. Therefore, the gas velocity is an essential factor to be optimized during this reaction because it controls the adsorption—desorption rates of the feed and products, respectively, which has been ignored during this NTP process.\(^{52}\) In addition, a modeling study by Michiels et al.\(^{51}\) has shown, the H\(_2\)/CO\(_2\) ratio (or relative pressure of H\(_2\) to CO\(_2\)) is essential during the NTP CO\(_2\) hydrogenation and should be optimized for every catalyst with different active sites.

4.4 | Process development

One of the valid arguments against the thermal CO\(_2\) reduction in the presence of high pressure of hydrogen to form methanol is the use of hydrogen (with great value) to synthesize methanol. Therefore, researchers strive to apply hydrogen derived from renewable resources (like water splitting using photocatalysts) for this exciting hydrogenation model. The generated green hydrogen can be pressurized and used for this high-pressure reaction in the classical CO\(_2\) hydrogenation model. In contrast to the thermal (traditional) mode of CO\(_2\) hydrogenation, this review magnifies that the NTP CO\(_2\) hydrogenation reaction does not require high hydrogen pressure, and the reaction with high space—time yield can be carried out at atmospheric pressure. Therefore, the application of two catalysts packed in two NTP reactors with distinct parameters (connected in Tandem) for direct conversion of CO\(_2\) and CH\(_4\) to methanol can stand a good chance.\(^{53}\) Both CO\(_2\) and CH\(_4\) are two abundant components of the biogas, which is known as a renewable alternative to natural gas.\(^{54}\) Therefore, reacting both these components under plasma conditions with the following setup can yield sustainable production of methanol. The first catalyst is known catalysts applied for methane steam reforming using CO\(_2\) under NTP, while the second catalyst should be an optimized catalyst for CO\(_x\) hydrogenation to methanol. The use of steam reforming is needed to provide enough H\(_2\) in the system to catalyze the methanol formation. Based on the articles demonstrated in this review and the different nature of CH\(_4\) reforming and CO\(_2\) hydrogenation reactions (to yield methanol), these two reactions should be done in separate catalytic beds and reactors connected in tandem. Therefore, in the first reactor, CH\(_4\) and CO\(_2\) will generate CO and H\(_2\), whereas the second reactor converts CO (rendered during the
reforming step) and unreacted CO₂ to methanol (Figure 7). To have high selectivity to methanol in this tandem system, it is important to generate high concentration of H₂ in the first reactor. Otherwise, the second reactor will catalyze pathways resulting in CO and methane formation. As mentioned, the additional hydrogen can be formed in situ via steam reforming instead of dry reforming, or additional H₂ (blue or green) can be added into the feed leading to reactor 2.

5 | CONCLUSION

NTP supplies adequate energy to catalyze CO₂ and H₂ activation at room temperature and atmospheric pressure to form methanol. Due to the relatively young age of this process (in comparison with the traditional one), much of the focus was devoted to the reactor design at this point. The NTP reactor with a colder catalyst bed tends to increase the selectivity to methanol. In contrast to many advancements noticed in reactor design in the past decade, the catalyst design has not improved much. Therefore, the catalyst designed for thermal hydrogenation of CO₂ to CH₃OH is still being examined under NTP. However, the mechanistic insights provided by modeling suggest active species during the plasma are not necessarily the same as the thermal ones. Besides plasma tends to alter the activation mode of the catalytic sites. Therefore, new catalysts that can synergically interact with plasma to improve the catalytic performance should be designed and applied. It is vital to highlight that optimization of operational conditions and further modification of the NTP processes are still effective as they are for thermal ones and may not be bypassed during the catalyst development special for NTP.

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