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High yield methane production from the hydrogenation of CO₂ using non-thermal plasma/catalysis

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ARTICLE INFO	A B S T R A C T				
Keywords: Methanation CO2 Catalyst Non-thermal plasma	In this work, a dielectric barrier discharge (DBD) non-thermal plasma/catalytic reactor was used under a range of process conditions, designed to maximise the hydrogenation of CO ₂ to methane. A Ni/Al ₂ O ₃ catalyst was used in the plasma/catalysis reactor and the process parameters investigated were the effect of input plasma power, catalyst temperature, catalyst weight hourly space velocity (WHSV), and H ₂ /CO ₂ ratio in relation to the methanation of CO ₂ . In addition, the effect of the catalyst active metal type (ruthenium, cobalt, and lanthanum) supported on Al ₂ O ₃ under the optimum reaction conditions was investigated. The optimised system, using Ni/Al ₂ O ₃ , achieved a CO ₂ conversion of 82.2 % with an energy efficiency of 22.5 g _{CO₂} kWh ⁻¹ , CH ₄ selectivity of 90.2 % and energy efficiency of 7.4 g _{CH4} kWh ⁻¹ at the plasma input power of 70 W, catalyst temperature of 280 °C, catalyst WHSV of 768 ml/g _{cat} h, and H ₂ /CO ₂ ratio of 4. The performance of the active catalyst metals in relation to				

 CO_2 conversion to methane was Ru > Ni > Co > La.

1. Introduction

Carbon dioxide emissions from fossil fuels usage rose to 34.8 billion tonnes in 2020 and are projected to rise to 43 billion metric tons by the year 2050 [1]. Carbon capture and underground storage (CCS) is regarded as one of the most effective strategies for reducing CO₂ emissions and thereby mitigate the effects of climate change. But, the drawbacks of CCS technology include its high costs, potential for leakage, long-term liability, insufficient storage space in many regions globally, and the risk of ocean acidification due to CO₂ leakage [2]. However, using the captured CO₂ as a resource to produce useful and higher-value end-products through carbon capture and utilization (CCU) routes represents a viable pathway toward sustainability. CCU encompasses various activities, with the conversion of CO2 into chemicals and fuels emerging as one of the most promising approaches [3]. The utilization of CO₂ has attracted significant attention, as it enables the production of valuable products while establishing an artificial carbon cycle, thereby improving resource efficiency and supporting circular economy principles. In the field of CO₂ capture and utilization (CCU) technologies, researchers continuously strive to enhance both CO2 capture efficiency and CO2 conversion [4]. Recent studies have explored CCU integration systems, highlighting promising pathways for sustainable energy solutions. For instance, Zhu et al. [4] introduced integrated gasification with CO_2 capture and utilization (IGCCU), focusing on lignin gasification. In this process, CO_2 was produced and absorbed by CaO, and then followed by hydrogenation converting the captured CO_2 into CO. Gholizadeh et al. [5] performed biomethanol and biomethane production based on anaerobic digestion, biogas upgrading, methanol synthesis, and high-temperature electrolysis. Gholizadeh et al. [6] also investigated a similar system that utilizes hydrogen from solid oxide electrolysis cells to convert CO_2 from into methanol. Giuliano et al. [7] simulated the production of dimethyl ether from syngas derived from waste gasification, identifying it as a sustainable route for both fuel synthesis and CO_2 capture.

Converting carbon dioxide by reaction with hydrogen to produce methane via the Sabatier reaction has received attention (Eq. (1)) [2,8].

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O, \Delta H_{298}^{\circ} = -165.12 \text{ kJ/mol.}$$
 (1)

Methane or synthetic natural gas production from carbon dioxide has the advantage that it can be used in the existing natural gas infrastructure. It can also be converted into value-added chemicals and fuels [9]. The development of a process to produce methane by CO₂ hydrogenation relies on a plentiful and cheap supply of hydrogen. The production of hydrogen through the electrolysis of low-cost water using renewable electricity sources, such as wind and solar energy, is abundantly available. Such renewably produced hydrogen can be a readily available and

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inexpensive source of hydrogen [10].

The CO₂ to methane process via the Sabatier reaction is highly exothermic. Although the CO2 methanation reaction is thermodynamically favored at lower temperature, it is limited by kinetics, making catalytic CO₂ methanation with high conversion at low temperatures challenging to achieve a satisfactory methane yield and prevent catalyst deactivation [11-15]. Achieving selective conversion in CO₂ methanation while avoiding partially reduced intermediates such as CO and CH₃OH requires an eight-electron transfer process, making considerable kinetic challenges [16,17]. In commercial applications, CO methanation typically operates at 300 °C and 25 bar, whereas CO2 methanation may require more demanding conditions [17]. Moreover, carbon-oxygen bonds in CO2 are relatively strong (ca. 790 kJ/mol). The Gibbs free energy of CO₂ formation is equal to $\Delta_f G_{298}^0 = -394$ kJ/mol, making CO₂ a very stable molecule [18]. Therefore, there is a need for the development of efficient processes to activate catalysis and highly active catalysts for CO₂ methanation under mild conditions (e.g., T < 250 °C) [1]. Operating at high temperatures can result in the production of CO as a by-product, which can enhance the rate of the reverse water gas shift (RWGS) reaction (CO₂ + H₂ \rightarrow CO + H₂O, with Δ H^o₂₉₈ = 41.2 kJ/mol). Additionally, high temperatures accelerate the catalyst deactivation process through sintering and coke deposition due to CH₄ decomposition [19]. For example, Ni-based catalysts for CO₂ methanation face challenges such as deactivation from carbon deposition, limited selectivity, and instability under reaction conditions [20]. They also suffer from insufficient low-temperature activity, poor dispersion and reducibility, as well as nanoparticle sintering [21]. Considering thermodynamic equilibrium, operating at low temperatures is crucial to ensure catalyst durability, achieve high CO₂ conversion, and maintain CH₄ selectivity. This goal of operating at low temperatures is a key focus in this field [19]. CO₂ methanation represents the sole CO₂ hydrogenation reaction theoretically capable of achieving complete CO2 conversion and CH4 selectivity at temperatures below 200 °C [22].

Non-thermal plasma (NTP) has proven to be an efficient method for activating and dissociating stable CO2 molecules, even without the presence of a catalyst [18,23]. With a specific emphasis on improving reaction kinetics at low temperatures, non-thermal plasma shows particular promise for the chemical transformation of inherently unreactive molecules such as CO₂, CH₄, and N₂ [1]. Within non-thermal plasma, dissociation, electron collision excitation, and ionization processes generate excited molecules, atomic or molecular ions, metastable species, and neutral atoms at low surrounding temperatures (below 200 °C). Despite this low temperature, the average energy of electrons in non-thermal plasma is significantly higher than that of surrounding gas molecules. For instance, electron energies can reach up to 10 eV, corresponding to temperatures exceeding 10,000 °C, while the temperature of the surrounding gas remains low [24]. In NTP, gas discharge through a stepwise vibrational excitation pathway, known as ladder-climbing, is induced by the impact of energetic electrons. This process requires only 5.5 eV to dissociate the CO bond, enabling the activation of CO2 molecules under ambient conditions [25]. However, NTP selectivity toward hydrocarbons or oxygenates is often poor. This is primarily due to the non-selective collisions of active species within the plasma environment [1,23]. Hence, the integration of plasma and a catalyst is suggested to further improve CO2 conversion and, importantly, modify the distribution of products [23]. Non-thermal plasma/catalysis systems offer a means to activate stable CO2 molecules and facilitate catalytic CO2 conversion at relatively mild bulk temperatures and atmospheric pressure.

The design of the catalyst plays a crucial role in plasma/catalysis and can effectively control both the energy efficiency and product selectivity [26]. In CO₂ methanation processes, noble metals, such as Ru, Rh, Pd, Pt, and transition metals like Ni, Co, Fe have been investigated [1]. Nibased catalysts have been preferred, since the primary product is CH₄, with minimal formation of C_{2+} hydrocarbons [1]. A further advantage of nickel-based catalysts is their lower costs compared to noble metals

[27]. They have also been reported to show enhanced catalyst activity for CO₂ hydrogenation under plasma/catalysis conditions [28]. For example, Ahmed et al. [29] investigated non-thermal plasma/catalysis using Ni-Al₂O₃ catalysts for the hydrogenation of CO₂ to produce methane in a dielectric barrier discharge non-thermal plasma reactor and reported a CH₄ selectivity of >97 %. A disadvantage of Ni-based catalysts for thermal processes is that they are prone to deactivation, primarily due to carbon deposition on the catalyst surface, but also sintering at higher temperature [27]. Here, non-thermal plasma/catalysis is a preferred technology, since catalyst coke deposition has been shown to be minimised in the plasma/catalyst reaction environment [28,30].

The support material used in catalyst formulation is also an important factor for CO₂ methanation. Among various supports, γ -Al₂O₃ is commonly used in industrial catalyst preparation because of its excellent thermal stability, chemical inertness, strong mechanical properties, and tuneable acid-base surface characteristics [31]. For example, Sajjadi et al. [1], used SiO₂ and Al₂O₃ as the support material for milli-pulse plasma/catalytic CO₂ methanation and found that in general, Al₂O₃ performed better than SiO₂ in terms of CO₂ conversion and CH₄ selectivity [1].

Several studies have been carried out regarding non-thermal plasma/ catalytic methanation of carbon dioxide. Guo et al. [32], worked on NTP catalytic CO₂ methanation using Ni - Y/CeO₂ catalysts. They found that the 7.5Ni-Y/CeO₂ catalyst exhibited the highest energy efficiency values for CO₂ conversion with 57 $g_{CO_2}kWh^{-1}$ and CH₄ with 17 $g_{CH_4}kWh^{-1}$. Moreover, the addition of yttrium as a catalyst promoter was shown to enhance the basicity of the catalysts and increase the concentration of oxygen vacancies, both of which were beneficial for the activation and conversion of CO2 under non-thermal plasma conditions. Furthermore, yttrium doping improved the dispersion of Ni nanoparticles and decreased the size of Ni particles, thereby enhancing the activity of plasma/catalytic CO2 methanation. Zhang et al. [33], studied plasmaassisted catalytic carbon dioxide methanation over Ni-Fe/(Mg, Al)Ox catalysts. They focused on the effect of atomic ratio of Ni and Fe and reduction temperature and found that a higher reduction temperature was advantageous for the formation of Ni₃Fe alloy and the generation of abundant surface oxygen vacancies, consequently enhancing CO₂ adsorption ability. A NiFe $_{0.1}$ /(Mg, Al)O_x catalyst reduced at 800 °C. exhibited excellent catalytic performance in the plasma/catalysis process, achieving approximately 84.7 % CO2 conversion and 100 % methane selectivity. Nizio et al. [34] conducted plasma/catalytic methanation of CO₂ at atmospheric pressure and the temperature range of 90 °C to 420 °C using a dielectric barrier discharge plasma reactor packed with Ni-Ce_xZr_{1-x}O₂ catalysts. They reported that in the presence of plasma at 90 °C, CO₂ conversions as high as 80 % were achieved, with 100 % selectivity toward methane. In contrast, in the absence of plasma, the same level of conversion and selectivity was only attained at much higher temperatures, for the same catalyst. While there is some work reported on the non-thermal plasma/catalysis process of CO2 methanation, further work is required to determine the impact of process conditions with different types of catalysts.

In this paper, non-thermal dielectric barrier discharge plasma/catalytic methanation of CO₂ has been carried out under different reaction conditions, including plasma input power (0–70 W), plasma reactor temperature (25–280 °C), catalyst weight hourly space velocity (768–1920 ml/g_{cat}.h), and H₂/CO₂ ratio (2–7) in the presence of Ni/Al₂O₃ as the catalyst to optimise the reaction conditions. Later, under optimum reaction conditions, various types of active metals (Ni, Co, Ru, and La) on Al₂O₃ support were utilized as the catalyst to determine the effect of active metals on reaction parameters, including CO₂ and H₂ conversion, CH₄ selectivity and yield, and energy efficiencies of CO₂ and CH₄.



Fig. 1. Schematic diagram of CO2 methanation DBD plasma/catalysis reactor system.

2. Experimental system

2.1. Catalyst preparation

A range of different metallic catalysts were prepared for the nonplasma/catalytic CO2 methanation reaction using a wet impregnation process. Activated Alumina oxide spherical (y-Al₂O₃) purchased from Alfa Aesar was used as the support. Nickel (II) nitrate hexahydrate (Ni (NO₃)₂ ·6H₂O) (purity: 99.999 %), ruthenium oxide (RuO₂) (purity: 99.9 %), Lanthanum (III) nitrate hydrate (La(NO₃)₃·xH₂O) (purity: 99.9 %), and cobalt (II) nitrate hexahydrate (Co(NO₃)₂ ·6H₂O) (purity: 99.9 + %) were purchased from Sigma Aldrich. Catalysts with 10 wt% Ni, 10 wt% Co, 10 wt% Ru, and 10 wt% La over Al₂O₃ were prepared by wet impregnation method. A measured amount of the precursors was dissolved in deionised water and the alumina support granules were added to the mixture. The mixture was stirred with a magnetic stirrer for 30 min. The temperature was increased with a heating rate of $1 \,^{\circ}C \,^{min^{-1}}$ to make a slurry, which was dried overnight in an oven at 100 °C and then was calcined in a limited amount of air at 750 °C for 4 h. Subsequently, the catalyst was subjected to reduction using a flow of 100 ml/min of a mixture of 5 % hydrogen in nitrogen, heated to 750 °C over a time period of 3 h with a heating rate of 20 °C min⁻¹ starting from room temperature.

2.2. Characterization of catalyst samples

The physicochemical properties of the fresh catalysts were assessed through several techniques, including X-ray diffraction (XRD), nitrogen adsorption-desorption analysis, and scanning electron microscopy- energy dispersive X-ray spectroscopy (SEM-EDX). The catalysts were analyzed for crystal structure using X-ray diffraction (XRD) with a Bruker D8 diffractometer employing Cu-K α radiation. The results were recorded within a 20 range of 10–80°, with a scanning step of 0.033. The crystallite sizes of the samples were also determined using the Scherrer equation (Eq. (2)) [35].

$$D = 0.9\lambda/\beta \cos(\theta) \tag{2}$$

where D represents the crystallite size in nm, λ is the wavelength of the X-rays (1.54 Å), β denotes the full width at half maximum of the intensity peak, and θ is the Bragg diffraction angle.

Catalyst morphology was determined using high-resolution scanning electron microscopy (SEM, Hitachi SU8230) with a 20.0 kV accelerating voltage, the SEM was coupled with energy dispersive X-ray spectroscopy (EDX, Oxford Instruments Aztec Energy system) to determine metal location and dispersion on the catalyst. BET nitrogen adsorption was conducted to determine the surface area of the catalysts using the Brunauer-Emmet-Teller (BET) method. Each sample, weighing approximately 200 mg, was subjected to degassing at 300 °C under a nitrogen atmosphere for 4 h, with a step size of 150 °C starting from 80 °C. The surface area was calculated using the Brunauer–Emmet–Teller (BET)



Fig. 2. Schematic diagram of the non-thermal plasma reactor.

method from the adsorption isotherms in the relative pressure (P/P_0) range of 0.05–0.3, while the pore size and pore volume were determined via the Barrett–Joyner–Halenda (BJH) method applied to the desorption isotherms.

2.3. Experimental reactor system (CO₂ methanation)

Non-thermal plasma/catalytic methanation of CO2 was conducted in a DBD plasma reactor system, as illustrated in Fig. 1. Hydrogen was supplied by a Qualban QL-150B Hydrogen Generator (Shandong Saikesaisi Hydrogen Energy Co.Ltd., China). Carbon dioxide was supplied via a CO2 cylinder purchased from BOC Co. Ltd., UK. Hydrogen and carbon dioxide rates were controlled using mass flow meters. The DBD non-thermal plasma reactor was made of quartz glass with a diameter of 23 mm. As shown in Fig. 2, this coaxial DBD plasma reactor featured two electrodes: an inner stainless steel electrode, 254 mm long and 18 mm in diameter, which was connected to a power supply and positioned at the centre of the reactor; and an outer copper mesh electrode, 95 mm in length, serving as the low-voltage electrode and wrapped around the quartz tube. The quartz glass acted as a dielectric barrier between the electrodes. The high voltage was applied to the inner electrode, while the outer electrode was grounded. The plasma discharge zone, where the plasma reactions occurred, was the 95 mm axial region between the electrodes with a discharge gap of 5 mm. The catalysts with particle size range of 0.5-1 mm were loaded in the discharge gap. The DBD reactor was powered by an AC high-voltage supply with a frequency of 1500 Hz and a peak-to-peak voltage of up to 20 kV. A generator controlled the process parameters such as frequency, and the power was manually adjusted using a voltage regulator. A digital oscilloscope monitored the discharge. The electric field ionized the gases in the plasma zone, producing electrons that collided with species, initiating chemical reactions. The output gases from the DBD reactor were passed through an air-cooled and a dry-ice cooled condenser to collect byproduct reaction water, while non-condensable gases were gathered in a 5 L TedlarTM gas bag.

The experimental procedure started by introducing a fixed flow rate of CO_2 and an appropriate flow rate of H_2 depending on CO_2 : H_2 ratio to the plasma reactor. When the plasma reactor was heated to the desired temperature, the power supply was switched on to generate plasma in the DBD reactor. The reaction continued for 40 min and the produced gases were collected after a 30 min equilibration period over the last 10 min of the process in a gas sample bag for analysis using gas chromatography (GC).

CO₂ conversion (X_{CO_2}), CH₄ selectivity (S_{CH_4}) and yield (Y_{CH_4}), CO selectivity (S_{CO}) and yield (Y_{CO}), H₂ conversion (X_{H_2}), and carbon balance [36] were calculated according to Eqs. (3)–(9) respectively. [CO_2]_{*inlet*} and [CO_2]_{*oulet*} are inlet and outlet molar flow rates of CO₂. [CH_4]_{*produced*} and [CO]_{*produced*} are molar flow rates of produced CH₄ and CO during reaction. [H_2]_{*inlet*} and [H_2]_{*oulet*} represent H₂ inlet and outlet molar flow rates. The collected gas in the gas bag was analyzed by gas chromatography with thermal conductivity detection (GC-TCD) and GC-flame ionization detection (GC-FID). The moles of outlet CO₂, outlet H₂, produced CH₄ and CO were calculated using the ideal gas law and STP conditions. The outlet volume was calculated by measuring outlet flow rate using the flow meter.

$$X_{CO_2}(\%) = \frac{[CO_2]_{inlet} - [CO_2]_{outlet}}{[CO_2]_{inlet}} \times 100$$
(3)

$$S_{CH_4}(\%) = \frac{[CH_4]_{produced}}{[CO_2]_{inlet} - [CO_2]_{outlet}} \times 100$$
(4)

$$Y_{CH_4}(\%) = \frac{X_{CO_2} \times S_{CH_4}}{100}$$
(5)

Table 1Properties of the catalysts.

Catalyst	S_{BET} (m^2g^{-1})	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)	Crystal size (nm)	C constant
Ru/ Al2O3	137	0.415	7.34	30.3	125
Ni/ Al2O3	152	0.390	7.29	12.9	114
Co/ Al2O3	137	0.404	7.36	-	124
La/ Al2O3	158	0.399	6.20	-	131

$$S_{CO}(\%) = \frac{[CO]_{produced}}{[CO_2]_{inlet} - [CO_2]_{outlet}} \times 100$$
(6)

$$Y_{CO}(\%) = \frac{X_{CO_2} \times S_{CO}}{100}$$
(7)

$$X_{H_2}(\%) = \frac{[H_2]_{inlet} - [H_2]_{outlet}}{[H_2]_{inlet}} \times 100$$
(8)

Carbon balance (%) =
$$\frac{[CO_2]_{outlet} + [CH_4]_{produced} + [CO]_{produced}}{[CO_2]_{inlet}} \times 100$$
(9)

Energy efficiency for CO₂ conversion was calculated based on $g_{CO_4}kWh^{-1}$ in Eq. (10) [31,32] and percent (%) in Eq. (11) [18]. Energy efficiency for CH₄ yield ($g_{CH_4}kWh^{-1}$) was obtained using Eq. (12) [32]. ([CO_2]_{inlet} = 16.2 ml/min)

$$EE\left(g_{CO_2}kWh^{-1}\right) = \frac{X_{CO_2} \times [CO_2]_{inlet} (mol \, s^{-1}) \times 44}{discharge \ power \ (kW)} \times 36 \tag{10}$$

$$EE (\%) = \frac{[CO_2]_{inlet} \left(\frac{mol}{s}\right) \times X_{CO_2} \times \Delta H \left(\frac{kJ}{mol}\right)}{discharge \ power \ (kW)}, \Delta H = -165 \left(\frac{kJ}{mol}\right)$$
(11)

$$EE\left(g_{CH_4}kWh^{-1}\right) = \frac{S_{CH_4} \times X_{CO_2} \times [CO_2]_{inlet}(mol\,s^{-1}) \times 16}{discharge\ power\ (kW)} \times 0.36$$
(12)

The specific energy input (SEI, kJL^{-1}) was calculated using Eq. (13).

$$SEI = \frac{discharge power}{total feed flow rate}$$
(13)

2.4. Gas analysis

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The gases were analyzed using packed column gas chromatography (GC) employing three separate Varian 3380C gas chromatographs to ascertain their composition. Gas chromatography with thermal conductivity detection (GC-TCD) was utilized specifically for identifying the permanent gases, H₂, O₂, CO, and N₂. Argon was utilized as the carrier gas, and a molecular sieve column with a mesh size of 60–80 was employed. Furthermore, using a 2nd GC, GC-TCD was employed to analyze CO₂, using argon as the carrier gas and a HayeSep column with a mesh size of 60–80 as the packing material. A 3rd GC used gas chromatography with flame ionization detection (GC-FID) to determine the presence of C₁–C₄ hydrocarbons, with nitrogen as the carrier gas and an 80–100 mesh HayeSep column.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the surface area, pore volume and diameter of the fresh catalysts as well as the C constants. Ru/Al_2O_3 and Co/Al_2O_3 have high pore volume and diameter while Ni/Al_2O_3 and La/Al_2O_3 have high



Fig. 3. Nitrogen adsorption/desorption isotherms of the catalysts.



Fig. 4. XRD spectra of catalyst samples.

surface area. The crystal sizes were calculated using Scherrer equation. Ru/Al_2O_3 with 30.3 nm has the largest crystal size and Ni/Al_2O_3 with 12.9 nm is the second catalyst in terms of crystallites.

Fig. 3 shows the typical nitrogen adsorption-desorption isotherms for Ni/Al_2O_3 , Ru/Al_2O_3 , Co/Al_2O_3 , and La/Al_2O_3 catalysts. The presence of hysteresis loops in each graph suggests capillary condensation within

mesopores, indicating a Type IV isotherm. Moreover, the sharp increase in adsorption at high relative pressures (P/P₀ > 0.8) confirms the presence of mesopores. Adsorption behavior in mesopores is influenced by both adsorbent-adsorptive interactions and intermolecular forces in the condensed phase. Initially, adsorption occurs on mesopore walls through monolayer and multilayer formation. This process is then followed by pore condensation, where gas transitions into a liquid-like state within the pores at a pressure lower than the bulk liquid's saturation pressure. A key characteristic of the Type IV isotherms is the presence of a final saturation plateau, which can vary in length and may sometimes appear only as an inflection point [37]. Among the samples, Ru/Al_2O_3 displays the highest adsorption volume, implying a larger pore volume, while Ni/Al₂O₃, Co/Al₂O₃, and La/Al₂O₃ exhibit slightly lower adsorption capacities.

Fig. 4 shows the XRD spectra of the freshly prepared catalysts, comprising 10 wt% Ru/Al₂O₃, 10 wt% Ni/Al₂O₃, 10 wt% Co/Al₂O₃, 10 wt% La/Al₂O₃, and Al₂O₃ support. The main Al₂O₃ support peaks in the XRD spectra of the Al₂O₃ catalyst appeared at 2θ values of 28.3° , 38° , 46°, and 66.8°. Li et al. [38] conducted X-ray diffraction analysis of Al_2O_3 within the 20 range of $20^\circ\text{--}80^\circ$ and identified characteristic alumina support peaks at 37.4°, 45.7°, and 66.8°, respectively. There are three main common peaks for all the mono-metallic catalysts observed in Fig. 4, at 38°, 46°, and 66.8° 2 Θ which can be attributed to γ -Al₂O₃ [39]. In 10 wt% Ru/Al₂O₃ catalyst, ruthenium particle peaks appeared at 38.3°, 42.1°, 44°, 58.3°, 69.3°, and 78.3° 20 [40]. For the 10 wt% Ni/ Al₂O₃ catalyst, elemental nickel peaks were detected at 44.5°, 51.8°, and 76.6° 20 [41-43]. Nickel aluminate spinel (NiAl₂O₄) was also formed at the peaks of 38° , 44.5° , and 66.8° 2Θ which showed the interaction between metal and support [42]. The strong interaction between nickel atoms and alumina atoms led to the formation of small nanoparticles of

M. Khatibi and P.T. Williams



Fig. 5. SEM images of a) Ru/Al₂O₃, c) Ni/Al₂O₃, e) Co/Al₂O₃, g) La/Al₂O₃ catalysts and EDX spectra of b) Ru/Al₂O₃, d) Ni/Al₂O₃, f) Co/Al₂O₃, h) La/Al₂O₃ catalysts.

nickel with a uniform size distribution following reduction [43]. For the 10 wt% Co/Al₂O₃ catalyst, all the diffraction peaks were broad, indicating that the species are amorphous and uniformly dispersed. Distinctive peaks for face-centered cubic Co metal are visible at 44° and 51° 20. A small peak at 31.5° 20 can be related to little formation of CaO [39]. For the 10 wt% La/Al₂O₃ catalyst, no diffraction peaks corresponding to La were observed, indicating a very low crystal or amorphous structure [40]. The Ru/Al₂O₃ sample shows sharp, intense peaks, indicating a highly crystalline structure. In contrast, the Ni/Al₂O₃ and Co/Al₂O₃ catalysts display broader peaks, suggesting smaller crystallites or lower crystallinity. The La/Al₂O₃ sample exhibits the lowest crystallinity, with broad, low-intensity peaks, indicating highly dispersed or amorphous structure. The effectiveness of the catalyst reduction process to produce active metal particles was shown by the absence of the metal oxide peaks, for example for the Ni/Al₂O₃ catalyst, there was no peak 2 Θ identification at 37.6°, 43.3°,63° signifying the absence of the crystalline structure of NiO [41,44]. Similarly for the Ru/ Al₂O₃ catalyst the RuO₂ was reduced to Ru during the hydrogen reduction process since no 2Θ peaks at 28.1° , 35.1° , and 54.4° were observed, which are attributed to RuO₂ [41].

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) analysis was employed to examine the overall morphology and chemical composition of the fresh catalysts as shown in Fig. 5. SEM images of all samples show a rough and uneven surface on the porous Al_2O_3 support which provides reaction surface area. The corresponding EDX elemental maps illustrate the dispersion of the metal species (Ru, Ni, Co, and La) on the Al_2O_3 support. In these maps, the









Fig. 6. Influence of input plasma power on the non-thermal plasma/catalysis process in relation to: (a) CO_2 and H_2 conversion, (b) CH_4 selectivity and yield and CO selectivity and yield, (c) Ratio of produced CH_4 flow rate to inlet feed flow rates (d) Energy efficiency of CO_2 ($g_{CO_2}kWh^{-1}$ and %) and CH_4 ($g_{CH_4}kWh^{-1}$) ($CO_2:H_2$ ratio 1:3, Ni/Al₂O₃ catalyst, 280 °C catalyst temperature).

green regions primarily represent aluminium (Al, and O) from the support material, while the additional colours (purple and red) indicate the presence of the deposited metal species. The distribution of these colours provides insight into the homogeneity of the active metal phase on the support. For the Ru/Al₂O₃ sample (Fig. 5(b)), the purple regions suggest a relatively well-dispersed Ru phase, though some areas exhibit localized clustering. In the Ni/Al₂O₃ catalyst (Fig. 5(d)), Ni appears more uniformly distributed, with some regions of higher intensity, indicating slight agglomeration. Similarly, the Co/Al₂O₃ (Fig. 5(f)) and La/Al₂O₃ (Fig. 5(h)) samples display a widespread dispersion of Co and La, respectively, with minor areas of higher concentration.

3.2. Plasma/catalytic CO₂ methanation

Initial experiments were carried out to optimise the non-thermal plasma/catalytic CO₂ methanation process with the Ni/Al₂O₃ catalyst at different reaction conditions, including plasma input power, plasma reactor temperature, catalyst weight hourly space velocity (WHSV), and different input H_2/CO_2 ratios. Later, further experiments were also performed with different catalyst active metals (Ni, Co, Ru, and La) on Al₂O₃ support under the optimised conditions to determine the effect of active metal type on the CO₂ methanation process. The operating parameters have been shown to significantly influence the catalytic performance in non-thermal plasma/catalytic CO₂ methanation [45].

3.2.1. Influence of input plasma power on CO₂ methanation

Fig. 6 shows the effect of different plasma input powers (0, 30, 50, and 70 W) on the non-thermal plasma/catalytic CO₂ methanation process in relation to the 6(a) CO₂ and H₂ conversion,65(b) CH₄ selectivity and yield, CO selectivity and yield, 6(c) ratio of produced CH₄ flow rate to inlet feed flow rates, 6(d) energy efficiency. The process conditions were maintained at a CO₂:H₂ ratio of 1:3, catalyst temperature of 280 °C with the Ni/Al₂O₃ catalyst. The calculated carbon balance (Eq. (9)) was more than 94 % at the different input powers indicating that most of the carbon-containing products were identified.

Fig. 6(a) shows the effect of different plasma power levels on H₂ and CO2 conversion. In the absence of the non-thermal plasma (0 W), a small conversion of 29.2 % for H2 and 22.5 % for CO2 was obtained. Introducing the non-thermal plasma at the low input power of 30 W dramatically increased the conversion both for H_2 (64.2 %) and CO_2 (51.9 %). Further increase of input power to 50 W led to a peak for H₂ conversion (77.7 %) and slightly increased CO₂ conversion (59.05 %). The trend continues at 70 W, where H₂ conversion is maintained at 75.1 %, and CO₂ conversion increases further, reaching 66.8 %. Raising the power from 0 W to 70 W at 280 °C moves the reaction toward thermodynamic equilibrium which is around 96 % at 280 °C for CO₂ conversion [18]. Fig. 6(b) shows the CO and CH₄ selectivity and yield from the process at the input powers of 0, 30, 50, and 70 W. CH₄ selectivity without plasma is 98 % and raising the power to 70 W gradually reduces the selectivity to 79.4 %. Although increasing the input plasma power resulted in lower CH4 selectivity, it increases CH4 yield from 22 % at 0 W to 53 % at 70 W. The selectivity for CO, on the other hand, begins very low at 0 W at only 1 %, but steadily rises as input power was increased, reaching 11.7 % at 70 W. Similarly, CO yield also increases gradually from 0.2 % at 0 W to ${\sim}7.8$ % at 70 W. It should also be mentioned that although increasing the input power from 0 W to 70 W led to higher CO selectivity and yield, CO production is still limited at high input powers. Increasing the power from 0 W to 70 W at 280 °C moves the reaction away from the thermodynamic equilibrium in terms of CH₄ selectivity, which is 100 % at 280 $^\circ \text{C}.$

Fig. 6(c) shows the production rate of CH₄ relative to the inlet flow rate of CO₂ and H₂, across different input powers. At 0 W, this relation is 0.054, but as power is applied, it nearly doubles to around 0.114 at 30 W and at 50 W input power leads to the highest ratio at 0.129, with little change at the higher 70 W input power. Fig. 6(d) presents the energy efficiency of CO₂ conversion ($g_{CO_2}kWh^{-1}$ and %) and CH₄ production

 $(g_{CH_4}kWh^{-1})$ at different power levels. At 30 W, CO₂ conversion energy efficiency is highest at 33.1 $g_{CO_2}kWh^{-1}$ (3.4 %), with a CH₄ energy efficiency of 10.6 $g_{CH_4}kWh^{-1}$. As the power increases to 50 W, both CO₂ and CH₄ energy efficiencies decrease to 22.6 $g_{CO_2}kWh^{-1}$ (2.32 %) and 6.7 $g_{CH_4}kWh^{-1}$, respectively, and at 70 W, the lowest energy efficiencies are observed. These results suggest that lower power levels (30 W) are more energy-efficient for CO₂ conversion and CH₄ production, while higher power levels result in reduced energy efficiency.

The input power of 70 W was selected as the optimum input power due to the highest values for CO2 conversion and CH4 yield as well as high H₂ conversion and high CH₄/feedstock ratio. Increasing the input power can enhance both electron density and gas temperature. Consequently, a higher conversion rate is expected because of the greater number of energetic electrons [46]. The findings indicate that at low specific input energies, gas ionization is minimal, resulting in a limited presence of active species generated by the non-thermal plasma, such as vibrationally activated CO2 and CO*. Conversely, at higher input energies, where sufficient short-lived reactive species are generated by the non-thermal plasma, the diffusion of these species into the porous catalysts is likely to increase [26]. Moreover, as expected, a higher voltage results in increased power and temperature within the reactor. The improved performance at higher voltages and powers could be due to enhanced CO₂ adsorption and dissociation, facilitated by a stronger electric field and micro-discharges within the catalyst bed material [45]. The reverse relation between CH4 selectivity and power may be attributed to the higher temperatures generated at increased voltage, which favors the endothermic reverse water gas shift reaction, leading to more CO production instead of CH₄. The CH₄ may also undergo further conversion to longer-chain C₂-C₄ hydrocarbons under a stronger electric field with intensified electron collisions [45].

Some studies [47-52], have also indicated that higher input plasma power results in increased gas production yields, primarily due to the greater abundance of electrons produced by intensified microdischarges in the non-thermal plasma/catalytic process. This rise in electron density offers additional reaction pathways and reactive species, thereby promoting more reaction processes. Mikhail et al. [36], carried out CO2 methanation using a DBD plasma/catalytic process with input powers ranging from 10.5 W to 22.9 W. The results reveal that CO₂ conversion initially increased with higher input power but eventually stabilizes and slightly decreases at the highest power levels. Zhang et al. [33], performed non-thermal plasma/catalytic CO₂ methanation as a function of applied voltage over a NiFe_{0.1}/(Mg, Al)O_x catalyst in CO_2 / H_2/Ar at a ratio of 1:4:5 and WHSV of 15,000 mlg_{cat}⁻¹. They observed that raising the applied voltage from 6 kV to 10 kV (discharge power from 3.9 W to 16.6 W) increased CO2 conversion to around 80 %, H2 conversion to around 80 %, and CH4 selectivity to around 100 %, but reduced CO selectivity to ~0 %. They reported that CO2 dissociation and CH4 formation are generally favored by high applied voltage, low gas flow rate, and a high gas ratio (H₂: CO₂). Of these three factors, applied voltage was found to have the most significant impact. As the voltage was increased, there was a sharp rise in CO2 conversion. Higher discharge voltage enhances discharge properties in the bulk gas, generating more free electrons with higher average energy. This increases the likelihood of electron-impact activation of reactant molecules, producing excited species during gas discharge. Additionally, an increase in peak voltage produces a higher proportion of high-energy electrons. A similar effect of applied voltage on CH4 selectivity was also predicted [33].

Guo et al. [32], carried out CO₂ methanation in a plasma/catalytic reactor system over Ni/CeO₂ catalysts. They observed increased CO₂ conversion, CH₄ selectivity, and CH₄ yield in the plasma/catalytic reaction environment. The highest CO₂ conversion of approximately 90 % along with the highest CH₄ selectivity and yield, around 85 % and 75 %, respectively were achieved with a 7.5 Ni/CeO₂ catalyst. Chen et al. [9], also reported similar results showing that increasing the applied peak voltage from 8 kV to 11 kV resulted in higher CO₂ conversion and CH₄





Fig. 7. Influence of catalyst temperature on the non-thermal plasma/catalysis CO₂ methanation process in relation to: (a) CO₂ and H₂ conversion, (b) CH₄ selectivity and yield and CO selectivity and yield, (c) Ratio of produced CH₄ flow rate to inlet feed flow rates, (d) Energy efficiency of CO₂, (e) Comparison between equilibrium CO₂ conversion- CH₄ selectivity and experimental CO₂ conversion- CH₄ selectivity ($g_{CO_2}kWh^{-1}$ and %) and CH₄ ($g_{CH_4}kWh^{-1}$). (CO₂:H₂ ratio 1:3, Ni/Al₂O₃ catalyst, 70 W input plasma power).

selectivity but lower CO selectivity during non-thermal plasma/catalytic CO₂ methanation regardless of the absence or presence of a catalyst. Kano et al. [53], examined CO₂ hydrogenation using radio frequency plasma. Across all tests, CO₂ conversion was around 20–30 %, with CO being the primary reaction product. The conversion of CO₂ and

production of CH₄ rose with higher radiation frequency and voltage. Since frequency represents the number of discharges per second, higher frequencies result in increased plasma electron density. Additionally, increasing the discharge voltage raises not only electron density but also electron temperature, contributing to improved performance at elevated

voltage and frequency levels. CH₄ production was particularly boosted by increased voltage, while CO production grew linearly. Gao et al. [54], conducted a review on the application of DBD plasma-assisted catalytic dry reforming of methane. They observed that increasing the input power in a DBD plasma reactor resulted in higher conversion rates for CH4 and CO2. This phenomenon occurs because higher input power enhances electron density, accelerating collisions between reaction gas molecules and high-energy electrons. Consequently, the reactants are activated more efficiently. The excited, dissociated, and ionized molecules subsequently promote the dry reforming reaction of methane. Liu et al. [55], examined toluene reforming in a non-thermal plasma system and showed that raising the input plasma power from 39 to 90 W enhanced the conversion efficiency of toluene. They attributed this enhancement to the greater number of micro-discharges generated by the higher discharge power. This increase in micro-discharges leads to more reaction pathways and reactive species during the reforming process, thereby improving the overall conversion of toluene. Mei et al. [56], carried out CH₄ reforming with CO₂ using a nanosecond pulsed DBD plasma reactor. They found that raising the applied voltage greatly increased the discharge power, showing that more energy was supplied to the plasma reforming process. This, in turn, boosted the ability to generate and transfer charges, leading to a higher formation of reactive species such as energetic electrons, radicals, and excited molecules. They suggested that electron-impact dissociations of CO2 and CH4 (R1-R4) are critical initial reactions in plasma CH4 reforming with CO2. Higher applied voltage accelerated these reactions by enhancing the production of reactive species, especially energetic electrons. Although higher applied voltage improves both gas conversion and discharge power, more discharge power is used to heat the gas and dielectric material instead of being utilized directly for plasma reactions. This results in the discharge power increasing at a faster rate than gas conversion, leading to reduced energy efficiency.

3.2.2. Influence of catalyst temperature on CO₂ methanation

Understanding the effect of catalyst temperature is crucial, as it impacts both the thermodynamic and kinetic properties of the chemical reactions [23]. Experiments were undertaken with the non-thermal plasma/catalysis CO₂ methanation process with the catalyst in the non-thermal plasma reactor held at temperatures of 25 °C, 90 °C, 180 °C, and 280 °C. Fig. 7 shows the results, in terms of 7(a), CO₂ and H₂ conversion, 7(b) CH₄ selectivity and yield and CO selectivity and yield, 7(c), ratio of produced CH₄ flow rate to inlet gaseous feed flow rates, 7(d) Energy efficiency of CO₂ ($g_{CO_2}kWh^{-1}$) and CH₄ ($g_{CH_4}kWh^{-1}$). The process conditions for the other variables were maintained at, CO₂:H₂ ratio 1:3, Ni/Al₂O₃ catalyst and 70 W input plasma power. The carbon balances calculated at different catalyst temperature were above 94 % indicating that most key products were effectively accounted for.

Fig. 7(a) presents the effect of catalyst temperature on CO₂ and H₂ conversion. At the temperature of 25 °C, both CO2 and H2 conversions are minimal at 13.5 % and 4.45 %, respectively. When the temperature was increased to 90 °C, no difference in the amount of conversion was observed. A significant increase was observed at the catalyst temperature of 180 °C, with H₂ and CO₂ conversions reaching approximately 24 % and 25.6 %, respectively. The highest conversions occur at the catalyst temperature of 280 °C, where H₂ conversion peaked at around 75.1 %, and CO₂ conversion was 66.8 %. This indicates that higher temperatures greatly enhance the conversion of both gases. Fig. 7(b) illustrates the relationship between CH4 selectivity, CH4 yield, CO selectivity, and CO yield as a function of catalyst temperature. At low temperatures (25 °C and 90 °C), CH4 was not produced leading to almost zero selectivity and yield toward CH₄. On the other hand, CO selectivity at these two temperatures was around 99.5 % with a yield of 12.4 % and 13.4 % at 25 °C and 90 °C, respectively. Increasing the catalyst temperature to 180 °C significantly changed the reaction path to CH₄ production with a selectivity of 67.5 % and a methane yield of 17.3 %, while CO selectivity and yield declined to 32.5 % and 8.3 %, respectively. The highest CH4

selectivity (79.4 %) and yield (53 %) were obtained at the highest reactor temperature, 280 °C. The CO yield remained almost constant compared to 180 °C with the lowest CO selectivity of 11.7 % at 280 °C. This indicates that at higher temperatures, the reaction favors methane production over carbon monoxide, suggesting that higher temperatures promote CH₄ formation with minimal CO byproduct formation.

Fig. 7(c) shows the ratio of CH₄ production to inlet CO₂ and H₂ as the feedstocks at different reactor temperatures. As explained for the results shown in Fig. 7(b), this ratio is almost zero at 25 °C and 90 °C while it reaches to 0.041 at 180 °C and further increase to 280 °C at 0.127. Fig. 7 (d) shows the effect of catalyst temperature on energy efficiencies of CO₂ and CH₄. At lower temperatures (25 °C and 90 °C), the energy efficiency for CO₂ conversion is very limited, less than 4 g_{CO2}kWh⁻¹ (0.4 %) with almost zero energy efficiency for CH₄ production. The highest CO₂ and CH₄ energy efficiencies were obtained at the maximum temperature of 280 °C. The highest catalyst temperature of 280 °C produced the highest CO₂ conversion, H₂ conversion, CH₄ selectivity, CH₄ yield, CH₄ to feed-stock ratio, CO₂ energy efficiency, and CH₄ energy efficiency.

Fig. 7(e) presents the thermodynamic equilibrium CO₂ conversion and CH₄ selectivity as functions of temperature (1 bar, $CO_2/H_2 = 1/4$) [18], alongside experimental results from non-thermal plasma/catalysis methanation of CO₂. At equilibrium, CO₂ conversion ranges from 100 % at ambient temperature to 95 % at 300 °C [18]. In contrast, NTP catalysis initially exhibits low CO₂ conversion, which significantly increases beyond 90 °C. CH₄ selectivity remains nearly 100 % at equilibrium from room temperature to 300 °C [18]. However, in NTP catalysis, CH₄ selectivity is negligible below 90 °C but increases with temperature, approaching equilibrium values at 280 °C. At this highest temperature, NTP catalysis achieves CO₂ conversion and CH₄ selectivity closest to thermodynamic equilibrium.

Meloni et al. [8], performed non-thermal plasma/catalysis methanation of CO₂. They observed that the same CO₂ conversion can be achieved at lower temperatures with the non-thermal plasma/catalysis system compared to the thermal process and raising the temperature led to higher CO2 conversion and CH4 yield. Wang et al. [23], investigated the reaction temperature performance in plasma/catalysis methanation of CO₂ using an alumina-supported cobalt catalyst. The reaction performance exhibited two distinct temperature dependencies: CO₂ conversion significantly rose from 7 % to 37 %, and methane selectivity increased from 70 % to 90 % as the catalyst temperature was increased from 125 °C to 200 °C. This was followed by a much slower increase during which CO₂ conversion gradually reached 50 % as the temperature was raised to 400 °C, while maintaining a steady methane selectivity of 90 %. Ullah et al. [57], carried out plasma/catalytic methanation of CO2 at a temperature range of 170 °C to 300 °C. They observed that when the reaction was conducted at 170 °C, the conversion of CO2 was below 12 %, and the selectivity for CO was nearly 97 %. The low conversion of CO₂ was attributed to the insufficient temperature to activate both the reaction and the catalysts. When the temperature was increased to 300 °C, over 85 % CO2 conversion and CH4 selectivity was achieved.

It should be noted that the discussion of the influence of temperature in this work relates to the catalyst reactor temperature, which controlled the catalyst bed temperature at 25 °C, 90 °C, 180 °C, and 280 °C. However, it is known that the reaction environment in the non-thermal plasma produces non-equilibrium conditions, with low gas temperatures existing with highly energetic electrons with an average temperature of 1–10 eV, equivalent to temperatures of over 10,000 °C [58]. The input plasma power producing an electric field with micro-discharges and an increased energy and electron density in the discharge zone [59]. In addition, Mikhail et al. [36], reported on CO₂ methanation using nonthermal plasma/catalysis in relation to the temperature of the catalytic bed and reported that methanation rises almost linearly with increasing power which was attributed to the heat generated by the DBD plasma, especially at high energy inputs, but also to the exothermic nature of the methanation reaction. Gao et al. [54], reviewed DBD



Fig. 8. Influence of catalyst weight hourly space velocity on the non-thermal plasma/catalysis CO₂ methanation process in relation to: (a) CO₂ and H₂ conversion, (b) CH₄ selectivity and yield and CO selectivity and yield, (c) Ratio of produced CH₄ flow rate to inlet feed flow rates (d) Energy efficiency of CO₂ (g_{CO_4} kWh⁻¹ and %) and CH₄ (g_{CH_4} kWh⁻¹). (CO₂:H₂ ratio 1:3, catalyst temperature 280 °C, 70 W input power, Ni/Al₂O₃ catalyst).

plasma-assisted catalytic dry reforming of methane and reported that increasing the input power in a DBD plasma reactor led to higher conversion rates of CH4 and CO2. This effect was attributed to the increased electron density generated by higher input power, which accelerates collisions between reaction gas molecules and high-energy electrons. As a result, this acceleration enhances the activation of reactants. The excited, dissociated, and ionized molecules of the reactants then initiate the dry reforming reaction of methane. Liu et al. [60], reported that higher temperatures enhance the thermal motion and subsequent interactions of free radicals and active species, thereby increasing toluene conversion when the temperature was raised from 200 $^\circ$ C to 300 $^\circ$ C. Xu et al. [52], examined the influence of plasma temperature on gaseous products using an integrated pyrolysis-plasma system, ranging from ambient temperature to 500 °C at a discharge power of 15 W and a steam flow rate of 6 ml/h/g_{biomass}, without using a catalyst. They reported that the self-heating effect from the plasma discharge, can raise the reactor temperature from 100 °C to several hundred degrees depending on energy input. They also investigated plasma/catalysis and reported that catalyst activity is promoted at higher temperatures. In terms of selectivity, plasma alone tends to show lower selectivity due to its more randomized molecular reactions (breakage and recombination). In plasma/catalysis, however, selectivity is higher at elevated temperatures because the catalyst properties play a crucial role in determining the maximum reaction selectivity, while plasma characteristics in the plasma/catalysis system may be partially suppressed.

3.2.3. Influence of catalyst weight hourly space velocity (WHSV) on CO_{2} methanation

Fig. 8 illustrates the effect of varying WHSV (768, 960, 1280, and 1920 ml/g_{cat}.h) which were obtained by changing catalyst weight (5, 4, 3, and 2 g) at the constant flow rate of 64 ml/min at a $CO_2:H_2$ ratio of 1:3 (16 ml/min CO_2 and 48 ml/min H_2), reactor temperature of 280 °C, plasma input power of 70 W, and with the Ni/Al₂O₃ catalyst. The carbon balances calculated (Eq. (9)) at various catalyst weight hourly space velocities ranged from 94 % to 96 %, suggesting that most key products were determined.

Fig. 8(a) shows the effect of WHSV on the conversion of H₂ and CO₂. With the WHSV of 768 ml/g_{cat}.h, 76.5 % H₂ conversion and 69.2 % CO₂ conversion were obtained. Increasing WHSV from 768 ml/g_{cat}.h to 1920 ml/g_{cat}.h slightly decreased the conversion of both H₂ and CO₂ reaching to 72 % and 58.8 %, respectively. Fig. 8(b) shows the effect of WHSV on yield and selectivity of CH₄ and CO. CH₄ selectivity stays high for all values of WHSV, at around 80 %, with little variation. CH₄ yield decreases slightly with increasing the WHSV, ranging from 57.7 % with 768 ml/g_{cat}.h to 47 % with 1920 ml/g_{cat}.h catalyst. CO selectivity is low across all WHSVs, showing a slight rise as WHSV increases from 768 ml/g_{cat}.h (8.4 %) to 1920 ml/g_{cat}.h (13 %), while CO yield remains consistently low, with marginal variation from 5.83 % (768 ml/g_{cat}.h) to 7.7 % (1920 ml/g_{cat}.h).

Fig. 8(c) shows the correlation between WHSV and the ratio of CH₄ flow to inlet CO2 and H2 flow. A reverse relation is observed between WHSV and this ratio. The highest ratio with a value of 0.134 was obtained when WHSV was 768 ml/g_{cat}.h. This ratio gradually declines and reaches to its minimum value at 0.121 with a WHSV of 1920 ml/g_{cat}.h. Fig. 8(d) shows the effect of amount of WHSV on energy efficiency of CO_2 conversion and CH_4 production. The energy efficiency for CO_2 conversion remains relatively stable at all WHSVs, with only a slight drop from 18.9 g_{CO_2} kWh⁻¹ (1.94 %) with WHSV of 768 ml/g_{cat}.h to 16.1 $g_{CO_2}kWh^{-1}$ (1.65 %) in WHSV of 1920 ml/g_{cat}.h. The energy efficiency for CH₄ is also almost similar at all tested catalyst weights with a very small decrease from 5.7 $g_{CH_4}kWh^{-1}$ with WHSV of 768 ml/g_{cat}.h to 4.7 g_{CH_4} kWh⁻¹ with WHSV of 1920 ml/g_{cat}.h. Although reaction parameters showed a very little dependency to the weight of catalyst and WHSV, WHSV of 768 ml/g_{cat}.h was shown to be slightly more effective than other weights.

The results are similar to the research reported by Meloni et al. [8],



Fig. 9. Influence of H_2/CO_2 ratio on the non-thermal plasma/catalysis CO_2 methanation process in relation to: (a) CO_2 and H_2 conversion, (b) CH₄ selectivity and yield, and CO selectivity and yield, (c) Ratio of produced CH₄ flow rate to inlet feed flow rates, (d) Energy efficiency of CO_2 ($g_{CO_4}kWh^{-1}$ and %) and CH₄ ($g_{CH_4}kWh^{-1}$), (Ni/Al₂O₃ catalyst, 280 °C catalyst temperature, 70 W input plasma power).

who investigated the effect of two different WHSV values during catalytic CO2 methanation. They observed that CO2 conversion declined from 84 % to 80 % when WHSV was increased from 1 L/g_{cat}.h to 6 L/g_{cat}. h at the temperature of 320 $^\circ C$ and in the presence of a RuRh-Al_2O_3 catalyst. Tang et al. [61], researched the effect of gas hourly space velocity (GHSV) by changing flow rates in plasma/catalytic CO2 methanation over NiO/bentonite catalysts. They showed out that as the GHSV decreased from 11,320 to 5660 h^{-1} , CO₂ conversion rose from 55.8 % to 63.2 %, while CH₄ selectivity remained nearly constant at 84.6 %. This effect can likely be attributed to the slower flow rate, which extends the CO_2 residence time in the reactor, enhancing the interaction between CO2 molecules and active catalytic sites on the catalyst surface and thereby promoting CO₂ conversion. The reverse relation between WHSV and CH4 production may be attributed to the temperature. Biset-Peiró et al. [62], found that when the power exceeded 10 W, the heat generated from the exothermic reaction becomes significant, causing the temperature to rise as the GHSV increases. As mentioned before, higher temperatures produced at higher voltages favor endothermic RWGS reaction so less CH₄ and more CO are produced [45].

3.2.4. Influence of H₂/CO₂ ratio on CO₂ methanation

For these series of experiments, the CO₂ flow rate was kept constant at 16 ml/min and H₂ flow rate was changed according to the H₂/CO₂ ratio, therefore the total gas flow rate was increasing as the H₂/CO₂ ratio was increased. Fig. 9 demonstrates the influence of different H₂/CO₂ ratios (ranging from 2 to 7) on key reaction parameters at 280 °C and 70 W at a WHSV of 768 ml/g_{cat}.h in the presence of the Ni/Al₂O₃ catalyst. The carbon balance percentages were obtained at different H₂/CO₂ ratios, resulting in balances of >94 %. Fig. 9(a) depicts the effect of H₂/CO₂ ratio on H2 and CO2 conversion. As the input H2/CO2 ratio was increased, H₂ conversion decreases, indicating a reduction in the efficiency of hydrogen usage at higher ratios, for example, at the of H₂/CO₂ ratio of 2, the highest conversion of 82.3 % was achieved but at the highest ratio of 7, the H₂ conversion was 55.7 % conversion at the ratio of 7. Conversely, CO₂ conversion increased steadily as the H₂/CO₂ ratio was increased, showing that more CO₂ is converted at higher H₂/CO₂ ratios. The minimum CO₂ conversion was observed at the ratio of 2 with 50.3 % rising to 94.9 % at the H_2/CO_2 ratio of 7. Fig. 9(b) shows the effect of H_2/CO_2 ratio on CH4 and CO2 production, including selectivity and yield. CH4 selectivity remains consistently high across all ratios and marginally increases with increasing the ratio. A direct relation between CH₄ yield and H₂/CO₂ ratio was observed changing from 40.8 % at the ratio of 2, to 90.8 % at the H₂/CO₂ ratio of 7. CO selectivity and CO vield remain very low throughout the range, with a decreasing trend from 12 % and 6 % at the ratio of 2 to 0.55 % and 0.52 % at H_2/CO_2 ratio of 7, respectively.

Fig. 9(c) shows the produced CH₄ gas flowrate yield in relation to the inlet feed flow, of the reactant gases (CO₂ + H₂) as a function of the H₂/CO₂ ratio. This proportion increases steadily as the H₂/CO₂ ratio rises from 2 (0.128), reaching its maximum at a ratio of 4 (0.143), then declining to 0.1180 at the H₂/CO₂ ratio of 7, suggesting that higher ratios beyond 4 do not enhance methane production. Fig. 9(d) shows the relation between H₂/CO₂ ratio and energy efficiencies of CO₂ conversion and CH₄ production. When inlet H₂ flow was 2 times higher than CO₂ flow rate, energy efficiency for CO₂ conversion and CH₄ production were 13.8 g_{CO₂kWh⁻¹} (1.41 %) and 4.1 g_{CH₄kWh⁻¹}, respectively. Increasing the H₂/CO₂ ratio to 4 increased both CO₂ and CH₄ energy efficiencies to 22.5 g_{CO₂kWh⁻¹} (2.31 %) and 7.4 g_{CH₄kWh⁻¹}, respectively. Further increasing the ratio from 4 to 7 slowly increased the energy efficiencies reaching to 26 g_{CO₂kWh⁻¹ (2.66 %) for CO₂ and 9 g_{CH₄kWh⁻¹ for CH₄.}}

The optimal H_2/CO_2 ratio for maximizing methane yield is around 4. This ratio achieves high CO_2 conversion (82 %) and CH_4 yield (74 %) while maintaining high CH_4 selectivity (90 %) as well as the highest amount of CH_4 production/inlet feeds flow. Higher ratios, although beneficial for CO_2 conversion and CH_4 yield, lead to less efficient hydrogen utilization and do not improve the methane production/inlet feeds. It should be mentioned that the highest CO_2 conversion, CH_4



Fig. 10. Influence of different metal-Al₂O₃ catalysts on the non-thermal plasma/catalysis CO₂ methanation process in relation to: (a) CO₂ and H₂ conversion, (b) CH₄ selectivity and yield and CO selectivity and yield, (c) Ratio of produced CH₄ flow rate to inlet feed flow rates, (d) Energy efficiency of CO₂ (g_{CO_2} kWh⁻¹ and %) and CH₄ (g_{CH_4} kWh⁻¹). (CO₂:H₂ ratio 1:4, 280 °C catalyst temperature, 70 W input plasma power).

selectivity and yield, CO₂ and CH₄ energy efficiencies were achieved at the H₂/CO₂ ratio of 7 which was the highest gas feed flow rate (CO₂: 16 ml/min and H₂: 104 ml/min). Kano et al. [53], emphasized the importance of optimizing the reactant flow rate, as products may undergo further decomposition in the plasma if gases pass too slowly through the discharge zone. Conversely, contact times that are too brief may be inadequate for forming the desired products. They reported that the maximum CH₄ production was achieved with a high excess of H₂ in the feed (CO₂/H₂ ratio of 1:6). There may be some reasons for low CO₂ conversion at low H_2/CO_2 ratios. The primary pathway for CO_2 consumption involves electron impact ionization, forming CO_2^+ ions. However, these ions quickly react with H₂O, transferring their charge and regenerating CO₂, which limits its net conversion. Instead, the most effective activation of CO2 comes from its dissociation via electron impact, producing CO and O radicals. For H₂, the main reaction at low CO2 levels is electron impact dissociation, creating H atoms. Some of these H atoms recombine to form H₂, while others interact with CHO radicals to yield H₂ and CO, reducing the availability of H₂ for further CO₂ reduction. At higher CO₂ concentrations (around 90 %), H₂ reacts with H_2O^+ to form H_3O^+ , making this interaction predominant. Throughout, H₂ is consumed much more rapidly than CO₂, which likely contributes to the lower CO₂ conversions observed experimentally at low H_2/CO_2 ratios. Additionally, O and H atoms from CO_2 and H_2 dissociation tend to recombine, forming OH radicals and, eventually, H₂O, further reducing the efficiency of CO₂ conversion [18].

3.2.5. Influence of different metal-Al₂O₃ catalysts on CO₂ methanation

Fig. 10 shows the influence of different active metals, including lanthanum (La), cobalt (Co), nickel (Ni), and ruthenium (Ru) with the Al₂O₃ catalyst support material. The maintained reaction parameters were a CO2:H2 ratio of 1:4, reactor temperature of 280 °C, input power of 70 W and a WHSV of 768 ml/g_{cat}.h. The calculated carbon balances (Eq. (9)) for each of the different catalysts were, 95 % for Ni-Al₂O₃, 99 % for La-Al₂O₃, 98 % for Co-Al₂O₃, and 92 % for Ru-Al₂O₃. Fig. 10(a) illustrates the conversion efficiencies of H2 and CO2 across four different active metal/Al₂O₃ catalysts. The La/Al₂O₃ catalyst produced the lowest conversion rates, with H₂ conversion barely reaching 3.2 % and CO₂ conversion slightly higher at 13.8 %. For the Co/Al₂O₃ catalyst, both CO₂ and H₂ show moderate conversion, with H₂ converting at roughly 47 % and CO2 at about 55.2 %. The Ni/Al2O3 catalyst improves upon this performance, converting both H₂ and CO₂ at the rates of 75.4 % and 82.2 %, respectively. Finally, the Ru/Al₂O₃ catalyst demonstrates the highest conversion efficiencies, achieving 81.8 % CO₂ conversion and 90.7 % H₂ conversion. Overall, this figure highlights ruthenium as the most effective catalyst metal for H2 and CO2 conversion, followed by nickel and cobalt, while lanthanum is significantly poorer. At 280 °C, the thermodynamic equilibrium CO2 conversion is 96 % [18]. Under the same temperature and input power of 70 W, non-thermal plasma catalysis with Ru/Al₂O₃ achieves CO₂ conversion closest to equilibrium. Fig. 10(b) compares the selectivity and yield of CH4 and CO in the presence of the different metal/Al₂O₃ catalysts. For the La/Al₂O₃ catalyst, CH₄ is almost not produced, leading to selectivity of 0.2 % and yield of 0.03 %, but shows near-total selectivity for CO (99.8 %), with a small CO yield (13.8 %). The Co/Al₂O₃ catalyst has a moderate performance, with CH_4 selectivity of 79.5 % and CH4 yield of 43.9 %, but the CO selectivity and vield drops to 17.6 % and 9.7 %, respectively. The Ni/Al₂O₃ and Ru/ Al₂O₃ catalysts produced the highest CH₄ selectivity of around 90 %, with high CH4 yields, of 74.2 % and 80.6 % respectively. The CO selectivity and yield in the presence of these two catalysts are very low, around 3 %, indicating they primarily favor methane production with minimal CO formation. Among the four tested catalysts, Ni/Al₂O₃ approaches to the thermodynamic equilibrium in terms of CH₄ selectivity, which is 100 % in equilibrium condition at 280 °C [18].

Fig. 10(c) illustrates the CH₄ production rates for the different catalysts, measured as the ratio of CH₄ molar flow rate to the molar flow rate of the inlet CO₂ and H₂. The La/Al₂O₃ catalyst shows an almost negligible ratio (0.0001), indicating it is ineffective for methane generation. In contrast, both the nickel and ruthenium based catalysts demonstrate much higher CH₄ production/inlet feeds ratio, with Ni/Al₂O₃ reaching 0.143 and Ru/Al₂O₃ at 0.154. Fig. 10(d) presents the CO₂ and CH₄ energy efficiencies in the presence of La, Co, Ni, and Ru as active metals supported on Al₂O₃. For example, the Ru/Al₂O₃ catalyst exhibits the highest CO₂ energy efficiency at 24.8 g_{CO₂}kWh⁻¹ (2.55 %) with La/Al₂O₃ showing the lowest energy efficiency for CO₂ conversion at 3.8 g_{CO₂}kWh⁻¹ (0.39 %). A similar trend is observed for energy efficiency of CH₄ production.

In dielectric barrier discharge systems without catalysts, CO2 conversion to methane typically remains below 20 %, with CO being the predominant product, showing a selectivity of approximately 90 % [12]. Under atmospheric pressure and a H₂/CO₂ molar ratio of 4, the thermodynamic limit for CO2 conversion in methanation exceeds 95 % at temperatures below 200 °C. This suggests that the low conversion rate for CO2 to CH4 in plasma-only systems is not thermodynamically limited but rather controlled by reaction kinetics. The kinetic barrier of a chemical reaction can be reduced by introducing a catalyst, which lowers the activation energy [23]. Non-thermal plasma DBD systems can efficiently activate gas molecules to initiate a range of series and parallel reactions, but the presence of the active metal surface is crucial for terminating the reactions along the desired selective pathway [63]. It has been suggested [63,64], that in the plasma/catalytic process, CO₂ is excited by the DBD plasma before it adsorbs onto the catalyst surface. This pre-activation lowers the energy barrier for conversion into intermediates, unlike in thermal catalysis, where a higher temperature is necessary to activate CO2 molecules after they adsorb onto the surface [64]. Plasma discharges can alter the electronic behavior of metals due to surface charge potential generated by the abundance of electrons in the surface environment. In reduction reactions such as CO2 methanation, the modified catalyst surfaces become more reducible, which enhances activity in the forward reaction [64]. This change in the chemical behavior of active metal is crucial during bond formation and cleavage, driven by electron transfer to or from the metal. This phenomenon may shift the equilibrium for CO2 methanation toward the production side, resulting in higher yields at lower temperatures when plasma is applied to the catalyst. The presence of surface electrons can help modify the catalyst by enhancing the Lewis basic sites and improving redox properties. Since CO2 acts as a Lewis acid and its surface affinity is proportional to the basicity of the sites, surfaces treated with plasma can thus boost the catalyst activity and selectivity for methanation.

Ni-based catalysts have been widely researched for CO2 methanation [18]. For non-thermal plasma catalytic CO₂ methanation, the incorporation of Ni-based catalysts leads to a significant increase in the number of excited H atoms during the CO₂ hydrogenation reaction. As a result, the likelihood of contact between the CO intermediate and H atoms improves, leading to higher CO2 conversion and greater methane selectivity. Plasma-assisted activation of CO2 produces reactive species that can readily interact to initiate subsequent reactions on the surface of Ni catalysts [57]. Ahmad et al. [63], studied the synergistic interactions between Ni and plasma in plasma/catalytic CO₂ methanation. They found that nickel-free methanation systems generally exhibit a predominance of CO formation, as the dissociative conversion of CO₂ is notably low due to reverse reactions, but, in contrast, the presence of nickel significantly enhances CO₂ methanation. Sajjadi et al. [1], observed reasonably high CO2 conversion and CH4 selectivity over a Ni/ $\,$ Al₂O₃ catalyst (76.1 % CO₂ conversion and 92.8 % CH₄ selectivity with 20 % Ni/Al₂O₃) during methanation of CO₂ under catalytic non-thermal milli-pulse plasma. Ruthenium is a noble metal regarded as one of the most effective methanation catalysts and Ru-based catalysts have been reported to exhibit higher activity than Ni-based materials and that the activity of the Ru catalysts increases as the Ru particle size decreases for CO_2 methanation [18]. It has also been reported that the type of support material for Ru catalysts can also influence the CO2 catalytic methanation process with Al₂O₃ supported Ru catalysts showing superior

performance [65]. Cobalt-based catalytic systems have been investigated for CO_2 methanation. Wang et al. [23], used a cobalt-Al₂O₃ catalyst and observed that CO_2 hydrogenation product shifted significantly from CO to predominantly CH₄ in the plasma/catalysis reaction, indicating the influential role of the cobalt in methane formation. Riani et al. [66], investigated the role of lanthanum in CO_2 methanation as a promoter by its ability to increase basicity, facilitating stronger CO_2 adsorption and contributing to the overall catalytic performance.

This work has shown that non-thermal plasma/catalysis can effectively convert CO2 and H2 to high yield CH4. However, the methane yield is very dependent on the process conditions of the non-thermal plasma and also the type of active metal used in the catalyst formulation. Further research is required to identify catalysts that are effective for CO2 methanation in the unique reaction environment of non-thermal plasma/catalysis. The morphology, pore structures, dielectric properties, and surface basicity of the catalyst support play crucial roles in determining the performance of CO₂ methanation under plasma conditions. Specifically, these properties can greatly influence metal dispersion, plasma micro-discharge, and the adsorption affinity of CO₂, thus exerting a dominant impact on the performance of NTP catalytic CO₂ methanation [32]. The choice of catalyst support material also plays a crucial role in CO₂ adsorption and activation, influencing the reaction pathway and deactivation process. Specifically, for CO2 methanation, adjusting the basicity or reducibility of the support can enhance performance. Higher basicity and reducibility lead to increased CO2 adsorption capacity and a greater number of oxygen defect sites for CO2 activation [1]. A further factor is the surface area and pore volume of the catalyst as high surface area along with greater mesopore volume and smaller pore radius can lead to improved catalyst activity for the plasma/catalytic methanation of CO₂ [8]. The surface area and porosity in plasma/catalysis reactions also influence the plasma discharge, in that a filamentary discharge may shift to a combination of microdischarges and surface discharges on the catalyst surface and within pores, leading to enhanced plasma assisted conversions [42]. The dielectric properties of the support material will also influence the CO₂ methanation reaction, where the dielectric constant is a measure of the strength of the developed electric field under plasma conditions. This in turns influences the enhancement of the plasma on the surface and within the pores of the catalyst, with materials having high dielectric constants performing much better in plasma/catalyst systems compared to low dielectric constant materials [67].

3.2.6. Plasma/catalysis CO₂ methanation mechanism

There are only a few reports discussing possible mechanisms for plasma-assisted CO2 methanation. This is primarily because investigating such processes is challenging due to the interdependence of catalytic and plasma properties, as well as the abundance of reactions occurring in the plasma and on the catalyst surface [68]. Catalysts with different components do not follow the same mechanism. The plasma catalytic process is a complex system influenced by various factors, including plasma type, support material, catalyst formulation, and others [18]. While energetic electrons in a DBD plasma can activate CO2 molecules and dissociate H2 into H atoms/radicals, the sole product of CO2 hydrogenation using plasma alone is found to be CO, with a CO2 conversion rate of approximately 8 % [69]. Plasma facilitates the direct gas splitting of CO₂ into CO. Consequently, the existence of CO-active species at low temperatures is crucial in the mechanism of plasma catalysis [25,70]. The most crucial initial step in methanation is the formation of carbonates on a metal-oxide support. These carbonates then transform into various intermediate species, such as bicarbonate (HCO₃) and formate (HCOO). This reaction pathway is known as the 'CO2 associative route', where CO2 is associatively adsorbed as carbonate and reacts with surface hydrogen to form carbonate or formate on the support materials. The support materials serve as adsorption sites for these intermediate species until CH4 is produced. Meanwhile, hydrogen molecules are dissociatively adsorbed on the metal surface, where they

hydrogenate carbonate or formate in sequence, ultimately leading to the formation of CH₄. Another significant reaction pathway is the 'CO₂ dissociative route'. In this pathway, CO₂ is dissociatively adsorbed onto the metallic catalyst surface, resulting in the formation of adsorbed CO. This CO is then further hydrogenated into formyl, and subsequently into CH₄ [71].

Some studies have investigated the reaction mechanism in nonthermal plasma/catalysis methanation of CO₂. Zhang et al. [33] investigated plasma/catalytic CO₂ methanation over NiFen/(Mg, Al)O_x. They concluded that in their NTP-catalytic CO2 methanation system, the following mechanism probably occurs: CO2 undergoes dissociation due to electron impact, leading to the formation of CO species. These CO species are then further energized by energetic electrons, resulting in the formation of vibrationally excited CO (CO(ν)), which adheres to the catalyst surface. The CO(ν) that is adsorbed on the catalyst surface may interact with other species present in the gas discharge or on the catalyst surface itself (such as O* and H*), forming surface formate and formyl species. These species are subsequently hydrogenated to produce CH₄ (through surface CH_x species), which then desorbs from the catalyst surface back into the bulk gas phase [33]. Wang et al. [23] proposed a mechanism for plasma/catalytic methanation of CO₂ with CO/Al₂O₃. They reduced the kinetic barrier of a chemical reaction by introducing a catalyst to lower the activation energy. When the catalyst was utilized, the product of CO₂ hydrogenation shifted significantly from CO in plasma alone to predominantly CH4 in the plasma/catalysis reaction. This indicates that the cobalt metal surface plays a crucial role in methane formation because transition metals like nickel, cobalt, iron, and copper serve as active centers for H₂ adsorption and dissociation into active H in thermal reactions. They concluded that the traditional Langmuir-Hinshelwood pathway (R1) for methane formation cannot be excluded in the plasma/catalysis system. This indicates that the plasmainduced pathway (R2) should be considered as parallel reactions. The gas-phase reverse water gas shift (RWGS) reaction and the reduction of surface CH_x are fast processes. Hence, it is proposed that the R2 pathway is limited by CO adsorption and/or its reaction with surface H. CO could be adsorbed on the cobalt surface and then react with surface H, or directly react with surface H through the Eley-Rideal mechanism [23]. Aceto et al. [72] suggested a mechanism for DBD plasma-assisted CO2 methanation over Ru/Zeolite. They found upon plasma ignition, immediate CO₂ dissociation likely occurs in the plasma alone. Additionally, more complex carbonate-like radicals may form in the plasma phase. The mechanism then involves the adsorption of CO₂ onto the catalyst as carbonates or formate species, which could also result from the conversion of adsorbed carbonates. Formate groups are reduced to aldehydic ones and then to carbonyls. Carbonyls can also be adsorbed on Ru nanoparticles directly from the plasma, where they are formed by the reverse water-gas shift reaction or CO2 dissociation by electron impact. Hydrogen is also adsorbed and dissociated on Ru nanoparticles. Carbonyls are progressively hydrogenated to methane, which is then released into the gas phase, producing water that is adsorbed on the catalyst surface [72]. Xu et al. [73] investigated CO poisoning in CO₂ hydrogenation over supported ruthenium (Ru) catalysts in a nonthermal plasma (NTP)-catalysis system. They reported that under NTP conditions, there are several reaction pathways for CO2 hydrogenation compared to thermal conditions in NTP-catalysis. Apart from the surface reactions observed in thermal catalysis, the vibrationally activated and dissociated active species (such as electronically excited H radicals) in the gas-phase reaction under NTP conditions might also engage in surface Eley-Rideal mechanism hydrogenation reactions. The results of this study confirmed the existence of the formyl pathway in CO₂ hydrogenation over Ru/SiO2 under NTP conditions. Initially, CO2 was dissociated into CO_{ad} and O_{ad} species on the catalyst surface. Subsequently, CO_{ad} underwent hydrogenation with H_{ad} to form formyl intermediate (CH_vO) species, which then reacted to produce CH₄ and H₂O. In comparison to thermally activated CO2 hydrogenation, vibrationally activated CO2 molecules under NTP conditions could adsorb on the catalyst

surface with lower energy barriers, facilitating the formation of CO_{ad} species. This activation promoted CO2 hydrogenation and the formation rate of CH4, resulting in a slightly increased reaction order with respect to partial pressure of CO2. Additionally, plasma-induced excited or dissociated H radicals in the gas phase might interact with adsorbed Eley species to form CH4 via the Rideal mechanism in CO2 hydrogenation under NTP conditions. Due to the relatively low dissociation energy of H₂ molecules, the plasma could efficiently activate H₂, producing more H radicals with an increase in H_2 concentration in the feed. Consequently, under NTP, the partial pressure of H₂ significantly influenced the formation rate of CH₄, resulting in a much higher reaction order with respect to partial pressure of H2 compared to thermal catalysis conditions [73]. Gao et al. [74] investigated CO₂ methanation using Ni-Fe_x-Al_{1-x}/NF catalysts and nanosecond pulsed plasma. They suggested that the mechanism of CO₂ methanation can be categorized into two main pathways: conversion of CO2 to CO prior to methanation (with a CO intermediate) and direct hydrogenation of CO2 to CH4 (without a CO intermediate). Plasma-induced reactions in gas phases typically produce CO and $CO(\nu)$ as products, with CO hydrogenation on Ni—Fe surfaces suggested to dominate CH₄ selectivity. Plasma/catalytic CO methanation appears to be more efficient than CO₂ methanation at the same operating conditions. Theoretical studies propose that the dissociative adsorption of CO is the rate-determining step, with a high energy barrier. Vibrational excitation of species around active sites decreases activation barriers, enhancing surface reactions. Plasma catalysis generates significantly more vibrational species compared to thermal catalysis. Dynamic simulations suggest vibrational excitation occurs in both uniform plasma and strong micro-discharges. Interfacial $CO(\nu)$ is comparable to gaseous $CO(\nu)$, and the presence of interfacial $CO(\nu)$ lowers the activation temperature by approximately 70 K, as supported by calculated vibrational distribution functions of $CO(\nu)$ [74]. Xu et al. [15] investigated the reaction mechanism for catalytic CO₂ hydrogenation under non-thermal plasma conditions using DRIFTs peaks and MS analysis. Under non-thermal plasma conditions, the catalytic conversion of CO2 over the 2.5 % Ru/MgAl catalyst follows a complex yet efficient pathway. Initially, in the gas phase, CO2 and H2 undergo dissociation facilitated by the plasma, leading to the formation of reactive species. Upon adsorption onto the Ru surface, CO2 molecules dissociate into CO*ad (adsorbed CO) and O*ad (adsorbed oxygen) intermediates. These species serve as precursors for subsequent reactions. The surface hydrogenation reactions then ensue, where CO*_{ad} is hydrogenated to form formyl (HCO_{ad}) and carbon-hydroxyl (COH_{ad}) intermediates. These intermediates are crucial as they undergo further hydrogenation to yield methane (CH₄), the desired product of CO₂ hydrogenation. Additionally, the detection of methoxy species (OCH₃) suggests the formation of methanol, indicating the versatility of the catalyst in producing valuable hydrocarbon products. Notably, the rapid desorption of methane from the catalyst surface under NTP conditions explains why surface methane is not detected. Overall, the mechanism elucidates the intricate interplay between gas-phase and surface reactions, highlighting the effectiveness of NTP in promoting CO2 conversion and methane production over the Ru/MgAl catalyst. Mikhail et al. [70] focused on DBD plasma/catalytic methanation of CO2 in the presence of Ni/CeZrO2. They proposed a simple mechanism: (1) Plasma has the capability to dissociate CO₂, thereby forming CO-active species on the catalyst surface even at low temperatures. (2) Additionally, DBD plasma can generate excited H species that will adhere to the Ni⁰ sites on the catalyst. (3) Subsequently, the adsorbed CO and H species will undergo a reaction, producing adsorbed CH species. (4) This CH species will then incorporate one more H atom. (5) Finally, a third H atom is incorporated, resulting in the formation of methane, which will subsequently desorb from the catalyst surface. The dissociation of CO₂ is irreversible due to the rapid removal of surface O by hydrogenation. Similarly, Eq. (17) involving methane desorption is also irreversible. Both Eqs. (16) and (17) occur after the rate-determining steps [70].

Table 2

Comparison of	f energy	efficiencies	in DBD r	olasma/catal	lysis met	hanation of	CO₂.
1	0,				2		

SEI (kJL ⁻¹)	H2/CO2	Catalyst	X _{CO2} (%)	S _{CH₄} (%)	EE_{CO_2} (g _{CO_2} kWh ⁻¹) (%)	EE_{CH_4} (g _{CH_4} kWh ⁻¹)	Ref.
27.8	3	Ni/Al ₂ O ₃	51.93	87.64	33.1 gkWh ⁻¹ (3.4 %)	10.6	This work
51.8	4	Ni/Al ₂ O ₃	82.23	90.23	22.5 gkWh ⁻¹ (2.31 %)	7.4	This work
51.8	4	Ru/Al ₂ O ₃	90.74	88.81	24.8 gkWh ⁻¹ (2.55 %)	8.0	This work
20.4	4	Ni/Al ₂ O ₃	60	97	4.33 %	_	[63]
39.6	4	Ru/Al ₂ O ₃	18	80	0.67 %	_	[75]
13	4	Ni-Y/CeO ₂	84.2	83.3	57 gkWh^{-1}	17	[32]
18	4	Ni/CeO ₂	86	84	11.9 %	_	[57]
27	5	Nickel over bentonite	55.8	84.6	3 %	_	[61]
-	4	Ni/MCM-41	72.7	95.9	-	8.2	[9]

(14)

 $CO_{2(ads)} \rightarrow CO_{(ads)} + O_{(ads)}$

 $CO_{(ads)} \rightarrow C_{(ads)} + O_{(ads)}$ (15)

 $C_{(ads)} + H_{(ads)} \rightarrow CH_{(ads)} \tag{16}$

 $CH_{(ads)} + H_{(ads)} \rightarrow CH_{2(ads)} \tag{17}$

 $CH_{2(ads)} + 2H_{(ads)} \rightarrow CH_{4(ads)}$ ⁽¹⁸⁾

3.2.7. Plasma/catalysis CO2 methanation energy efficiency comparison

Table 2 compares the CO₂ conversion, CH₄ selectivity, and energy efficiencies for CO2 and CH4 obtained in this work with values reported in the literature for DBD plasma reactors. In this study, the highest CO₂ energy efficiency (3.4 %) and CH₄ energy efficiency (10.6 g_{CH_4} kWh⁻¹) were achieved at an H₂/CO₂ ratio of 3 with a specific input energy of 27.8 kJL⁻¹. This CO₂ energy efficiency surpasses reported results [61,75], while the CH4 energy efficiency also exceeds the value reported in [9]. Notably, these higher energy efficiencies were obtained despite using a lower H₂/CO₂ ratio than in other studies, highlighting the effectiveness of our approach. Although increasing the SEI to 51.8 kJ/L (at 70 W input power) resulted in slightly lower energy efficiencies for both Ni/Al₂O₃ and Ru/Al₂O₃ catalysts, the values remain competitive with those in previous studies. Furthermore, when a H₂/CO₂ ratio of 4 was applied, both CO2 conversion and CH4 selectivity exceeded 80 % in the presence of these catalysts. Importantly, this study reports the highest CO2 conversion (90.72 %) among the listed works, achieved using Ru/Al₂O₃ as a catalyst at a H_2/CO_2 ratio of 4 and SEI of 51.8 kJL⁻¹. These results demonstrate the effectiveness of this research in achieving high energy efficiency, methane selectivity, and CO₂ conversion.

The performance of different reactors varies significantly in terms of both energy efficiency and CO_2 conversion rates [76]. DBDs achieve high conversion rates (up to 30 %) and operate at atmospheric pressure, but their energy efficiency remains relatively limited, typically ranging from 5 % to 10 % [28,77,78]. In DBD, the dissociation of CO_2 primarily occurs through direct excitation of CO_2 molecules rather than vibrational excitation. This mechanism contributes to limited energy efficiencies in DBD systems [79].

4. Conclusions

Non-thermal plasma/catalytic methanation of CO₂ with a Ni/Al₂O₃ catalyst has been investigated in relation to several process parameters to determine their influence on methane production. The effect of input plasma power, reactor temperature, catalyst weight hourly space velocity (WHSV), and H₂/CO₂ ratio in relation to the methanation of CO₂ was reported. Increasing input plasma power from 0 W to 70 W produced increased CO₂ conversion and methane production, reaching 67 % for CO₂ conversion and 53 % CH₄ yield. The influence of catalyst temperature (25 °C, 90 °C, 180 °C, and 280 °C) showed that higher catalyst temperatures favored higher CH₄ production and minimised byproduct CO production. The highest CO₂ conversion was at 280 °C at 67 %, H₂ conversion was 75.1 %, with a CH₄ selectivity of 79.4 % and

CH₄ yield of 53 %. The influence of catalyst/feedstock gas ratio (WHSV) showed only a small effect, with a slight decrease in the conversion of both H₂ and CO₂ reaching 72 % and 58.8 % respectively, with a consequent decrease in methane yield. The optimal H₂/CO₂ ratio for maximizing methane yield is around 4:1 at 74 % CH₄ yield with a high CO₂ conversion of 82 % and high CH₄ selectivity of 90 %.

The effect of the type of catalyst active metal (ruthenium, cobalt, and lanthanum) supported on Al_2O_3 was also investigated. The Ni/Al_2O_3 catalyst showed a CO₂ a conversion of 82.2 %, and H₂ conversion 75.4 %, resulting in a high CH₄ yield of 74.2 % and a selectivity of 90 %. The Ru/Al_2O_3 catalyst also showed a high CO₂ conversion of 81.8 % and H₂ conversion of 90.7 %, resulting in a CH₄ yield of 80 % and CH₄ selectivity of 90 %. The La/Al_2O₃ catalyst produced the lowest CO₂ and H₂ conversion rates and lowest CH₄ yield. The Co/Al_2O₃ catalyst showed a CO₂ conversion of 55.2 % and moderate CH₄ yield of 43.9 %.

CRediT authorship contribution statement

Maryam Khatibi: Writing – original draft, Investigation. Paul T. Williams: Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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M. Khatibi and P.T. Williams

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16

M. Khatibi and P.T. Williams

Fuel Processing Technology 273 (2025) 108228

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