

Plasma-catalytic CO₂ hydrogenation at low temperatures

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Abstract—A coaxial packed bed dielectric barrier discharge (DBD) reactor has been developed for plasma-catalytic CO₂ hydrogenation at low temperatures and atmospheric pressure. Reverse water-gas shift reaction (RWGS) and carbon dioxide methanation has been found dominant in the plasma CO₂ hydrogenation process. The results show that the H₂/CO₂ molar ratio significantly affects the CO₂ conversion and the yield of CO and CH₄. The effect of different γ -Al₂O₃ supported metal catalysts (Cu/ γ -Al₂O₃, Mn/ γ -Al₂O₃ and Cu-Mn/ γ -Al₂O₃) on the performance of the CO₂ hydrogenation has been investigated. Compared to the plasma CO₂ hydrogenation without a catalyst, the combination of plasma with these catalysts enhances the conversion of CO₂ by 6.7 to 36%. The Mn/ γ -Al₂O₃ catalyst shows the best catalytic activity for CO production, followed by the Cu-Mn/ γ -Al₂O₃ and Cu/ γ -Al₂O₃ catalysts. The presence of the Mn/ γ -Al₂O₃ catalyst in the plasma process significantly increases the yield of CO by 114%, compared to the plasma reaction in the absence of a catalyst. In addition, we find that combining plasma with the Mn/ γ -Al₂O₃ catalyst significantly enhances the energy efficiency of CO production by 116%, whereas packing the Cu/ γ -Al₂O₃ catalyst into the DBD reactor only increases the energy efficiency of CO production by 52%.

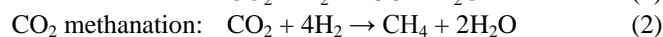
Index Terms—Dielectric barrier discharge, CO₂ hydrogenation, CO₂ reduction, plasma-catalysis, reverse water-gas shift reaction.

I. INTRODUCTION

CARBON dioxide (CO₂) is mainly emitted from the combustion of fossil fuels and manufacturing of chemicals. For instance, the UK emits more than 470 million tons of CO₂ per year and of this, 39% is emitted by energy and chemical industries [1]. CO₂ is a major greenhouse gas and its emissions have made a significant contribution to climate change and global warming. The UK government has committed to reduce greenhouse gas emissions by at least 80% (from the 1990 baseline) by 2050 [2]. Significant efforts have been devoted to develop innovative and cost-effective technologies to deal with the global challenge of CO₂ emissions and reduction. Therefore, converting CO₂ into higher value fuels or chemicals would make industrial processes more eco-friendly, significantly reducing CO₂ emissions and contributing to the sustainability

of our society. Carbon dioxide hydrogenation, as shown in Equations (1) and (2), for the production of CO and/or CH₄ has been regarded as a promising process for CO₂ conversion and utilization to achieve a CO₂ neutral cycle, as CO and CH₄ are important chemical feedstock's for the manufacturing of higher energy products such as hydrocarbons and liquid fuels.

Reverse water gas shift (RWGS) reaction:



To achieve a CO₂-neutral CO₂ hydrogenation process, it is important that hydrogen used in the CO₂ hydrogenation should be sourced using renewable energy (e.g. water electrolysis using solar power or wind power) as well as being cost-effective. In addition, it is key to lower the operating temperature of the CO₂ hydrogenation to minimize the energy consumption of the process [3]. However, due to the high chemical stability of CO₂, the CO₂ hydrogenation process is highly endothermic, which favours high reaction temperatures, making it difficult to achieve high CO₂ conversion at low temperatures. For example, it requires over 1000 K to achieve a CO₂ conversion of 50% in the reverse water gas shift reaction (H₂/CO₂ molar ratio = 1:1) at atmospheric pressure [4]. A wide range of catalysts have been designed and developed for lowering the kinetic barrier and operating temperature of this reaction.

Non-thermal plasma offers an attractive and promising alternative to the thermal catalytic route for CO₂ conversion and utilization at low temperatures and atmospheric pressure [5]-[12]. In non-thermal plasmas, highly energetic electrons collide with gas molecules to produce chemically reactive species including free radicals, excited atoms, ions and molecules [13], [14]. Both high energy electrons and reactive species contribute to the initiation and propagation of a variety of physical and chemical reactions in low temperature plasma processes [15]. In non-thermal plasmas, the temperature of electrons and heavy particles (free radicals, atoms, molecules and ions) are significantly different. The overall gas kinetic temperature in plasma can be as low as room temperature, whilst the electrons are highly energetic and have a typical electron temperature of 1-10 eV, which can break most chemical bonds present in inert molecules (e.g. CO₂). The non-equilibrium characteristic of non-thermal plasmas could overcome the kinetic barriers in chemical reactions and enable highly endothermic reactions (e.g. RWGS reaction) to occur at

This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC). Yuxuan Zeng acknowledges the PhD fellowship co-funded by the Doctoral Training Programme (DTP) at the University of Liverpool and the Chinese Scholarship Council (CSC).

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a relatively low temperature. High reaction rate and fast attainment of steady state in a plasma system allow rapid start-up and shutdown of plasma processes compared to thermal processes, which significantly reduces the overall energy cost.

The combination of non-thermal plasma and catalysis, known as plasma-catalysis, thus can be regarded as an attractive and promising solution to convert CO₂ and renewable H₂ into higher value chemicals at low temperatures and atmospheric pressure. Plasma-catalytic processes have great potential to generate a synergistic effect, which can reduce the activation energy of the reaction, enhance the conversion of reactants and improve selectivity and yield towards the desired products. All of these contribute in different ways to increasing the energy efficiency of the plasma process, as well as the activity and stability of the catalyst. A plasma-catalytic CO₂-neutral process can be achieved for chemical storage as plasma processes are highly flexible and can be integrated with a renewable energy source (e.g. offshore wind power) which can provide energy for the plasma system. A wide range of supported metal catalysts have been investigated for thermal catalytic CO₂ hydrogenation at high temperatures (300-500 °C). Cheng *et al.* investigated the reaction mechanisms of CO formation in RWGS reaction over Cu/ γ -Al₂O₃ catalyst at 500 °C [16]. Tanaka *et al.* have reported that Cu-Mn oxide catalysts with different additives are active in RWGS reaction [17]. Liu *et al.* have developed a computational model to compare the thermodynamic catalytic activities of transit metal complexes in RWGS reaction. They found that Mn based catalysts were the most promising catalysts in the RWGS reaction based on density function theory (DFT) predicted Gibbs free reaction energies [18].

However, up until now, very limited work has been carried out to investigate CO₂ hydrogenation using plasma-catalytic processes at low temperatures. Jwa *et al.* have investigated the hydrogenation of CO₂ and CO over Ni/Al₂O₃ catalyst in a DBD plasma at 200–300 °C [8]. Yasushi and his co-workers have reported the effect of electric field on RWGS reaction over various La-ZrO₂ supported catalysts at low temperatures [4].

In this work, plasma-catalytic CO₂ hydrogenation has been investigated in a coaxial packed-bed DBD reactor at low temperatures and atmospheric pressure. DBD has been demonstrated to be cost-effective for ozone generation and for gas clean-up on an industrial scale. Catalysts can be easily integrated into a DBD system in different ways to generate a plasma-catalyst synergy and to further enhance the efficiency of the plasma process [19]. This makes DBD a suitable plasma source for plasma-catalytic reactions for gas conversion and fuel production with the potential for process scale-up. The influence of H₂/CO₂ molar ratio and different catalysts (Cu/ γ -Al₂O₃, Mn/ γ -Al₂O₃ and Cu-Mn/ γ -Al₂O₃) on the reaction performance of the plasma-catalytic CO₂ hydrogenation has been evaluated in terms of the conversion of CO₂, the selectivity and yield of CO and CH₄, and the energy efficiency for CO and CH₄ production.

II. EXPERIMENTAL

The experiment was carried out in a coaxial packed bed DBD reactor, as shown in Fig.1. A stainless steel mesh (ground electrode) was wrapped around the outside of a quartz tube which had an outer diameter of 21 mm and wall thickness of 2 mm. A stainless steel rod with an outer diameter of 14 mm was placed in the centre of the quartz tube and used as a high voltage electrode. The discharge length was 100 mm with a gap of 2.5 mm. The outer mesh electrode was grounded via an external capacitor C_{ext} (0.47 μ F). The DBD reactor was connected to a high voltage AC power supply with a variable voltage and a frequency of 8.7 kHz. The applied voltage was measured by a high voltage probe (Testec, HVP-15HF), whereas the current was recorded by a current monitor (Bergoz CT-E0.5). The voltage across the external capacitor was also measured. All the electrical signals were sampled by a four-channel digital oscilloscope (Tektronix MDO3024). The Q-U Lissajous method was used to calculate the discharge power (P) of the DBD reactor [20], [21]. A homemade online power measurement system was used to monitor and control the discharge power in real time. In this work, the discharge power of the plasma process was fixed at 35 W. The temperature in the catalyst bed was less than 150 °C, measured by a fibre optical thermometer (Omega, FOB102). The reactants and products were analyzed by a two-channel gas chromatograph (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD).

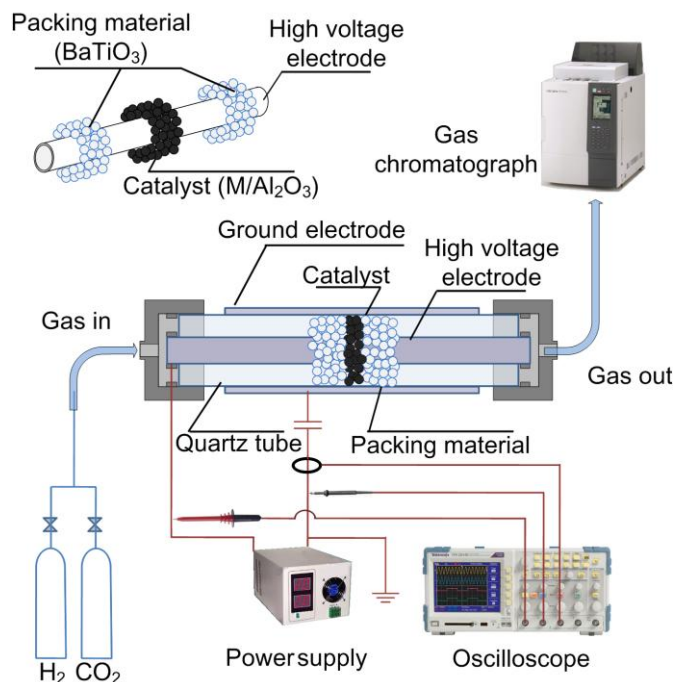


Fig. 1. Schematic diagram of the experimental setup

A. Catalyst preparation

8 wt.% Cu/ γ -Al₂O₃, 8 wt.% Mn/ γ -Al₂O₃ and 4 wt.% Cu-4wt.% Mn/ γ -Al₂O₃ catalysts were prepared by incipient wetness impregnation using nitrate salts (Alfa Aesar, 99.5%) as the

metal precursors. An appropriate weight of support (γ -Al₂O₃ beads, 1.5 mm in diameter) was added to the solution of nitrite salts. The mixture slurry was continuously stirred at 80 °C for 4 h and then dried at 110 °C overnight, followed by calcination at 600 °C for 6 h. The supported catalyst beads (1.5 mm in diameter, 1 g in total) were packed into the reactor with 13.6 g BaTiO₃ beads (1 mm in diameter), as shown in Fig.1. In the packed-bed DBD reactor, plasma can be formed in both the catalyst bed and packing material area. Filaments can be generated in the small gap between the bead-bead and the bead-quartz wall, while surface discharges can be formed on the surface of beads near the contact points between the beads [21], [22]. Prior to the plasma-catalytic CO₂ hydrogenation, the catalysts were reduced in an argon-hydrogen discharge at a discharge power of 7.5 W (50 ml/min, 20 vol. % H₂) for 30 minutes in the same DBD reactor.

B. Definition of parameters

For the plasma-catalytic CO₂ hydrogenation, the conversion (C) of CO₂ is defined as:

$$C_{\text{CO}_2} (\%) = \frac{\text{CO}_2 \text{ converted (mol/s)}}{\text{CO}_2 \text{ input (mol/s)}} \times 100 \quad (4)$$

The selectivities (S) and yields (Y) of the main products are calculated as:

$$S_{\text{CO}} (\%) = \frac{\text{CO produced (mol/s)}}{\text{CO}_2 \text{ converted (mol/s)}} \times 100 \quad (5)$$

$$S_{\text{CH}_4} (\%) = \frac{\text{CH}_4 \text{ produced (mol/s)}}{\text{CO}_2 \text{ converted (mol/s)}} \times 100 \quad (6)$$

$$Y_{\text{CO}} (\%) = \frac{\text{CO produced (mol/s)}}{\text{CO}_2 \text{ input (mol/s)}} \times 100 \quad (7)$$

$$Y_{\text{CH}_4} (\%) = \frac{\text{CH}_4 \text{ produced (mol/s)}}{\text{CO}_2 \text{ input (mol/s)}} \times 100 \quad (8)$$

The H₂/CO₂ ratio and carbon balance (B) are determined as follows:

$$\frac{\text{H}_2}{\text{CO}_2} = \frac{\text{H}_2 \text{ input (mol/s)}}{\text{CO}_2 \text{ input (mol/s)}} \quad (9)$$

$$B_{\text{Carbon}} (\%) = \frac{[\text{CH}_4]_{\text{out}} + [\text{CO}_2]_{\text{out}} + [\text{CO}]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \times 100 \quad (10)$$

The energy efficiency (E) of the plasma CO₂ hydrogenation process for CO and CH₄ production is defined as the amount of CO or CH₄ produced per unit of discharge power:

$$E_{\text{CO}} (\mu\text{g/kJ}) = \frac{\text{CO produced (mol/s)} \times 28 \times 10^9}{\text{discharge power (W)}} \quad (11)$$

$$E_{\text{CH}_4} (\mu\text{g/kJ}) = \frac{\text{CH}_4 \text{ produced (mol/s)} \times 16 \times 10^9}{\text{discharge power (W)}} \quad (12)$$

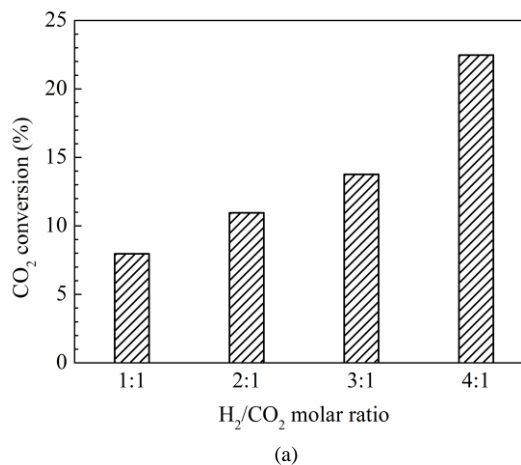
III. RESULTS AND DISCUSSION

A. Effect of H₂/CO₂ molar ratio

Fig.2 shows the effect of different H₂/CO₂ molar ratios on the

reaction performance of the plasma-catalytic CO₂ hydrogenation over Cu/ γ -Al₂O₃ catalyst at a discharge power of 35 W. CO and H₂O were the major products, whereas a small amount of CH₄ and trace amount of C₂H₆ and C₄H₁₀ (3-10 ppm) were also detected in the effluent. The conversion of CO₂ increases almost linearly with the increase of the H₂/CO₂ molar ratio at a fixed flow rate (Fig.2a). For instance, the conversion of CO₂ is increased from 8% to 11% when the H₂/CO₂ molar ratio is changed from 1:1 to 2:1, and reaches the maximum of 22.5% when further increasing the H₂/CO₂ ratio from 2:1 to 4:1. This result suggests that increasing H₂ content in the reactant mixture significantly enhances the CO₂ conversion.

Fig.2b and Fig.2c show that the H₂/CO₂ molar ratio affects the selectivity of CO and CH₄. As the H₂/CO₂ molar ratio varies from 1:1 to 4:1, the CO selectivity slightly increases and reaches 90%, whereas the CO yield is tripled. However, the selectivity of CH₄ achieves its maximum at the H₂/CO₂ ratio of 3:1. Further increasing the H₂ content decreases the CH₄ selectivity. These findings could be useful in the optimization of plasma-catalytic CO₂ hydrogenation processes since the conversion of CO₂ and the production of CO and CH₄ could be controlled by adjusting the H₂/CO₂ molar ratio. The carbon balance of the plasma-catalytic process is very high (98.8%-99.6%), which can be confirmed by the formation of very low concentration of C₂ and C₄ by-products in the process. No carbon deposition has been observed in the DBD reactor. This can also be concluded from Fig.2d.



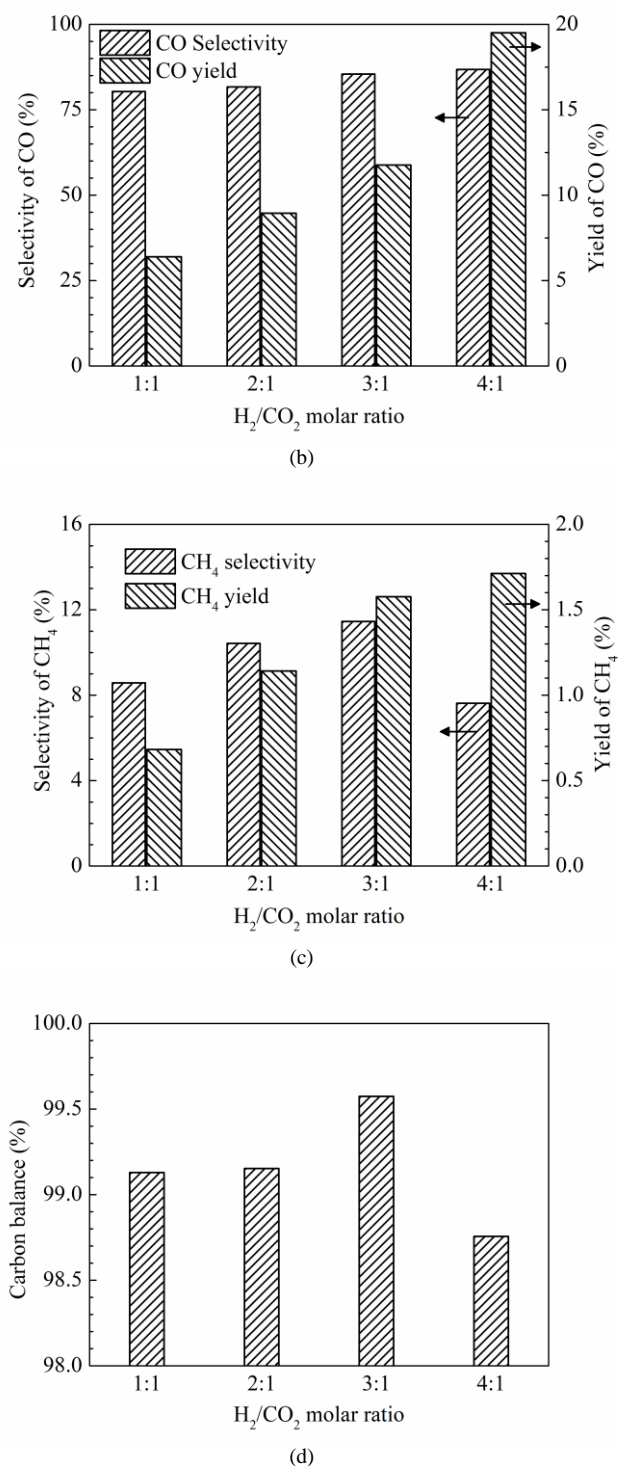


Fig. 2. The effect of H₂/CO₂ molar ratio on plasma-catalytic CO₂ hydrogenation over a 8 wt.% Cu/γ-Al₂O₃ catalyst (a) the conversion of CO₂; (b) the selectivity and yield of CO; (c) the selectivity and yield of methane; (d) carbon balance (discharge power 35 W, total feed flow rate 34.6 ml/min).

Fig.3 shows the effect of H₂/CO₂ molar ratio on the energy efficiency for CO and CH₄ production. Increasing the H₂/CO₂ molar ratio significantly enhances the energy efficiency for CO production. By changing the H₂/CO₂ ratio from 1:1 to 4:1, the energy efficiency of CO production was enhanced by a factor of 2.4., which can be ascribed to the enhanced conversion of

CO₂ and CO yield when increasing the H₂ content in the mixture feed gas. Similarly, the maximum energy efficiency for methane production is achieved at the H₂/CO₂ ratio of 3:1.

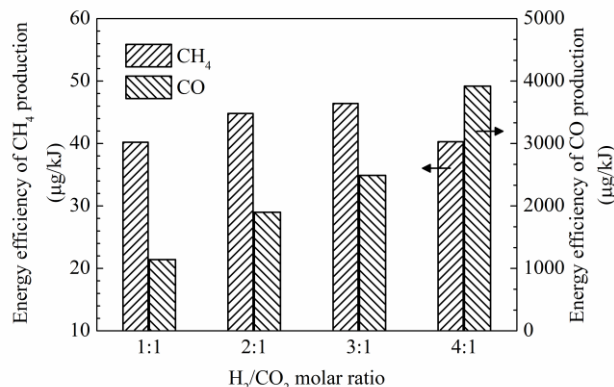
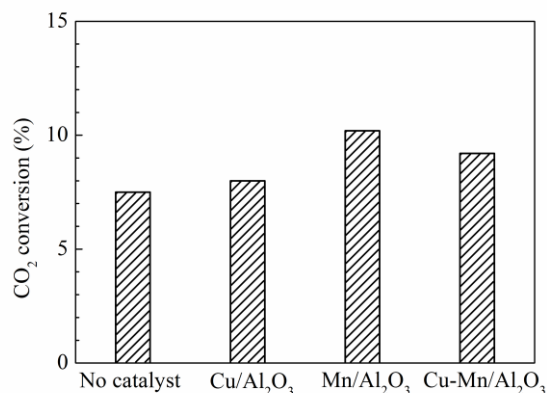
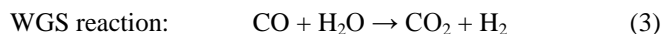


Fig. 3. The effect of H₂/CO₂ molar ratio on the energy efficiency of CO and CH₄ production (8 wt.% Cu/γ-Al₂O₃, discharge power 35 W, total feed flow rate 34.6 ml/min).

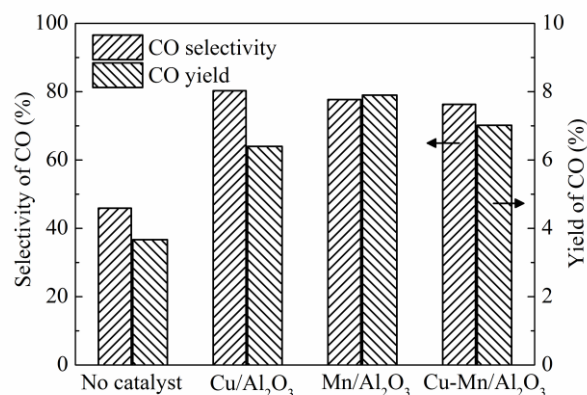
B. Effect of Catalysts

Fig.4 presents the influence of different γ-Al₂O₃ supported metal catalysts on the performance of the plasma CO₂ hydrogenation at a H₂/CO₂ molar ratio of 1:1. Mn is usually added to supported metal catalysts as a modifier or promoter to enhance catalyst activity and has rarely been reported in thermal catalytic CO₂ hydrogenation. In this study, we find the combination of DBD with the Mn/γ-Al₂O₃ catalysts significantly enhances the conversion of CO₂ by 36% in the plasma CO₂ hydrogenation compared to the plasma reaction without using a catalyst. Similar findings have been reported for the plasma-catalytic dry reforming reaction [23]. However, note the presence of the Cu/γ-Al₂O₃ catalyst in the DBD reactor only slightly improves the CO₂ conversion by 6.7%, whereas adding Mn into the Cu/γ-Al₂O₃ catalyst shows a better CO₂ conversion compared to the Cu/γ-Al₂O₃ catalyst, though the performance of this bimetallic catalyst (Cu-Mn/γ-Al₂O₃) in the plasma-catalytic CO₂ hydrogenation is still lower than when using the Mn/γ-Al₂O₃ catalyst. Cu based catalysts are commonly used in the water gas shift (WGS) reaction, as shown in Equation (3) [24]. Using the Cu/γ-Al₂O₃ catalyst in the DBD reactor might promote the WGS reaction in the plasma-catalytic CO₂ hydrogenation process, leading to a higher concentration of CO₂ in the reactor and a lower apparent CO₂ conversion [23], [24]. For the Cu-Mn/γ-Al₂O₃ bimetallic catalyst, the addition of Mn into the Cu/γ-Al₂O₃ catalyst could partly cover the copper particles on the catalyst surface, which might slow down the WGS reaction. In addition, the addition of Mn could promote the adsorption of CO₂ by forming a reactive carbonate species on the catalyst surface [18]. The combined effects contributed to a better catalytic activity of the Cu-Mn/γ-Al₂O₃ bimetallic catalyst compared to the Cu/γ-Al₂O₃ catalyst. In this work, the maximum CO₂ conversion of 10.2% is achieved in the plasma-catalytic reaction combined with the Mn/γ-Al₂O₃ catalyst at a H₂/CO₂ molar ratio of 1:1 and a

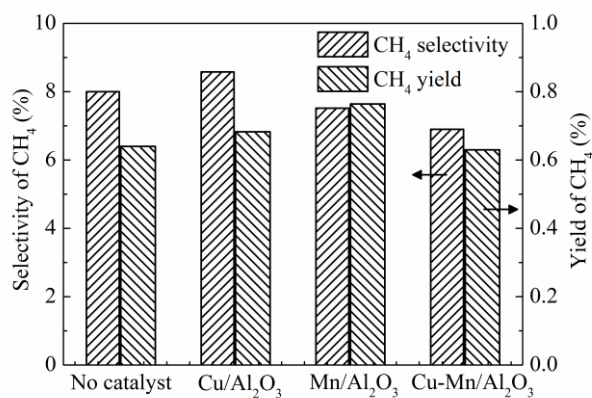
discharge power of 35 W, as shown in Fig.4a.



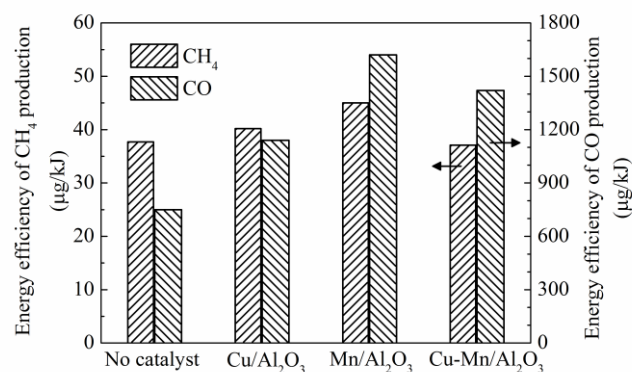
(a)



(b)



(c)



(d)

Fig. 4. The effect of catalysts on plasma-catalytic CO₂ hydrogenation (a) CO₂ conversion; (b) CO selectivity and yield; (c) CH₄ selectivity and yield; (d) energy efficiency for CH₄ and CO production (discharge power 35 W, total feed flow rate 34.6 ml/min, H₂/CO₂ molar ratio 1:1).

The selectivity and yield of major gas products (CO and CH₄) produced in the plasma-catalytic CO₂ hydrogenation process are presented in Fig.3b and Fig.3c. The combination of plasma with these catalysts increases the selectivity and yield of CO. Compared to the plasma reaction in the absence of a catalyst, the presence of the Mn/γ-Al₂O₃ catalyst in the plasma process significantly increases the yield of CO by 114%, followed by the Cu-Mn/γ-Al₂O₃ bimetallic catalyst (91%), whilst placing the Cu/γ-Al₂O₃ catalyst in the DBD reactor increases the CO yield by 73%. In contrast, these catalysts show completely different activities for CH₄ formation in the plasma-catalytic CO₂ hydrogenation. Only the Cu/γ-Al₂O₃ catalyst exhibits a higher CH₄ selectivity compared to the plasma reaction without a catalyst. The integration of DBD and the Mn/γ-Al₂O₃ catalyst decreases the selectivity of CH₄ by 6.3% (from 8% to 7.5%), whilst the use of the Cu-Mn/γ-Al₂O₃ catalyst in the plasma reactor decreases the selectivity of CH₄ by 13.3%. The combination of DBD with the Cu-Mn/γ-Al₂O₃ catalyst could suppress the formation of CH₄ in the RWGS reaction. These results suggest that different catalysts could be used to control the formation of desirable products.

The energy efficiency for CO and CH₄ production in the plasma reaction without a catalyst is 750 μg/kJ and 37.7 μg/kJ, respectively, as shown in Fig.4d. The presence of all three catalysts in the DBD reactor improves the energy efficiency of CO production. Packing the Mn/γ-Al₂O₃ catalyst in the plasma is found to improve the energy efficiency of CO production by 116%, whilst using the Cu/γ-Al₂O₃ and Cu-Mn/γ-Al₂O₃ catalysts in the DBD reactor increases the energy efficiency of CO production by 52% and 89.3%, respectively. The maximum energy efficiency of CO production (1620 μg/kJ) is achieved at a discharge power of 35 W and a total flow rate of 34.6 ml/min when the Mn/γ-Al₂O₃ catalyst is placed in the DBD reactor. Similarly, the combination of plasma with the Mn/γ-Al₂O₃ catalyst shows the best performance in terms of the energy efficiency for CH₄ production. Note that the plasma-catalytic process does not always enhance the energy efficiency of the CO₂ hydrogenation. In this study, compared to the plasma

process without catalyst, the presence of the Cu/ γ -Al₂O₃ in the DBD reactor only slightly increases the energy efficiency of CH₄ production by 6.6%, whereas combining the Cu-Mn/ γ -Al₂O₃ catalyst with plasma slightly decreases the energy efficiency for CH₄ production.

TABLE I

CO₂ HYDROGENATION USING DIFFERENT PROCESSES

Table.1 compares the performance of CO₂ hydrogenation via thermal or plasma processes using different catalysts. All the listed values are cited or calculated from the literature. We can see that the performance of CO₂ hydrogenation is significantly affected by a wide range of operating parameters such as the H₂/CO₂ molar ratio, total reactant flow rate, reaction temperature, and catalyst composition. Different supported metal catalysts have been investigated for CO₂ hydrogenation into CO or CH₄. The reaction temperature in the plasma processes is much lower than that in thermal-catalytic reactions. For instance, in this work, the reaction temperature in the plasma-catalytic CO₂ hydrogenation process is less than 150 °C without using extra heating, whereas the operating temperatures in thermal catalytic CO₂ hydrogenation are between 260 °C and 500 °C. The maximum CO selectivity and energy efficiency for CO production achieved in this study are comparable to those using either thermal or plasma processes. For example, Kano *et al.* investigated CO₂ hydrogenation in a radio-frequency impulse plasma reactor without a catalyst and achieved a maximum CO selectivity of 80% [7]. However, it should be noted that their experiment was carried out using a much lower gas flow rate with a H₂/CO₂ molar ratio of 4:1 in a low-pressure plasma reactor. In this work, the performance of the plasma-catalytic CO₂ hydrogenation could be further optimized and enhanced by choosing suitable plasma sources with higher efficiency (e.g. pulsed DBD) and more active catalysts.

IV. CONCLUSIONS

The combination of plasma with the Cu/ γ -Al₂O₃, Mn/ γ -Al₂O₃, and Cu-Mn/ γ -Al₂O₃ catalysts enables the CO₂ hydrogenation reactions to occur at low temperatures. The H₂/CO₂ molar ratio significantly affects the CO₂ conversion, the yield of CO and that of CH₄. Increasing the H₂ content in the reactant mixture significantly increases the CO₂ conversion. Compared to the plasma CO₂ hydrogenation in the absence of a catalyst, the combination of plasma with the catalysts enhances the conversion of CO₂ by 6.7 to 36%, while the Mn/ γ -Al₂O₃ catalyst shows the best catalytic activity for CO production, followed by the Cu-Mn/ γ -Al₂O₃ and Cu/ γ -Al₂O₃ catalysts. The presence of the Mn/ γ -Al₂O₃ catalyst in the DBD reactor significantly enhances the yield of CO by 114%, compared to the plasma reaction without a catalyst. In addition, packing the Mn/ γ -Al₂O₃ catalyst into the plasma reactor is found to improve the energy efficiency of CO production by 116%, whilst using the Cu/ γ -Al₂O₃ and Cu-Mn/ γ -Al₂O₃ catalysts in the DBD reactor leads to an increase of 52% and 89.3%, respectively.

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TABLE I
CO₂ HYDROGENATION USING DIFFERENT PROCESSES

H ₂ /CO ₂ molar ratio	Total flow rate (ml/min)	Process	Reaction conditions	Catalyst	C(CO ₂) (%)	S(CO) (%)	Y(CO) (%)	S(CH ₄) (%)	Y(CH ₄) (%)	Ref
1 : 1	34.6	DBD	135 °C, 35 W	Mn/Al ₂ O ₃	10.2	77.7	7.9	7.5	0.76	This work
1 : 1 (50% Ar)	100	Corona	150 °C, 5 W	Pt-La/ZrO ₂	40	99	40	-	-	[4]
4 : 1	20	RF impulse	2.4 Torr, 20 W	-	20	80	16	20	4	[7]
4 : 1	250	DBD	260 °C, 17 W	Ni/Al ₂ O ₃	85	-	-	97	82	[8]
1 : 1 (80% He)	25	Thermal	260 °C	Pd/La ₂ O ₃ /Al ₂ O ₃	0.6	-	-	30	0.18	[25]
4 : 1	166.7	Thermal	350 °C	Cu/MSN ^a	3.3	21	69	79	2.6	[26]
1 : 1	240	Thermal	400 °C	NiO/CeO ₂	5	100	5	-	-	[27]
4 : 1	10	Thermal	400 °C	Rh/K/Al ₂ O ₃	30	100	30	0	0	[28]
4 : 1	0.2	Thermal	400 °C	Ni/ZrO ₂ /clay	57	-	-	97	55	[29]
4 : 1	50	Thermal	300 °C	Ni-CeO ₂ /Al ₂ O ₃	70	0	0	99	70	[30]
3.5 : 1	30	Thermal	350 °C	Ce-Ni/Al ₂ O ₃	80	0	0	100	80	[31]
1 : 1 (60% He)	1	Thermal	500 °C	SCZT ^b	~1	-	0.0063	-	-	[32]
2 : 1	15	Thermal & photocat alysis	400 °C	Au/TiO ₂	~3	-	-	-	-	[33]

^aMSN: Mesostructured Silica Nanoparticles.

^bSCZT: Sr₃CaZr_{0.5}Ta_{1.5}O_{8.75}.