

# Plasma-catalytic CO<sub>2</sub> hydrogenation at low temperatures

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**Abstract**—A coaxial packed bed dielectric barrier discharge (DBD) reactor has been developed for plasma-catalytic CO<sub>2</sub> hydrogenation at low temperatures and atmospheric pressure. Reverse water-gas shift reaction (RWGS) and carbon dioxide methanation has been found dominant in the plasma CO<sub>2</sub> hydrogenation process. The results show that the H<sub>2</sub>/CO<sub>2</sub> molar ratio significantly affects the CO<sub>2</sub> conversion and the yield of CO and CH<sub>4</sub>. The effect of different  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported metal catalysts (Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Cu-Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) on the performance of the CO<sub>2</sub> hydrogenation has been investigated. Compared to the plasma CO<sub>2</sub> hydrogenation without a catalyst, the combination of plasma with these catalysts enhances the conversion of CO<sub>2</sub> by 6.7 to 36%. The Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst shows the best catalytic activity for CO production, followed by the Cu-Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. The presence of the Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst significantly enhances the energy efficiency of CO production by 116%, whereas packing the Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst into the DBD reactor only increases the energy efficiency of CO production by 52%.

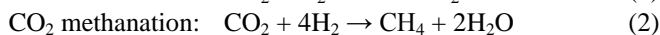
**Index Terms**—Dielectric barrier discharge, CO<sub>2</sub> hydrogenation, CO<sub>2</sub> reduction, plasma-catalysis, reverse water-gas shift reaction.

## I. INTRODUCTION

CARBON dioxide (CO<sub>2</sub>) is mainly emitted from the combustion of fossil fuels and manufacturing of chemicals. For instance, the UK emits more than 470 million tons of CO<sub>2</sub> per year and of this, 39% is emitted by energy and chemical industries [1]. CO<sub>2</sub> 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 CO<sub>2</sub> emissions and reduction. Therefore, converting CO<sub>2</sub> into higher value fuels or chemicals would make industrial processes more eco-friendly, significantly reducing CO<sub>2</sub> 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 CH<sub>4</sub> has been regarded as a promising process for CO<sub>2</sub> conversion and utilization to achieve a CO<sub>2</sub> neutral cycle, as CO and CH<sub>4</sub> 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 CO<sub>2</sub>-neutral CO<sub>2</sub> hydrogenation process, it is important that hydrogen used in the CO<sub>2</sub> 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 CO<sub>2</sub> hydrogenation to minimize the energy consumption of the process [3]. However, due to the high chemical stability of CO<sub>2</sub>, the CO<sub>2</sub> hydrogenation process is highly endothermic, which favours high reaction temperatures, making it difficult to achieve high CO<sub>2</sub> conversion at low temperatures. For example, it requires over 1000 K to achieve a CO<sub>2</sub> conversion of 50% in the reverse water gas shift reaction (H<sub>2</sub>/CO<sub>2</sub> 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 CO<sub>2</sub> 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. CO<sub>2</sub>). 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  $\text{CO}_2$  and renewable  $\text{H}_2$  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  $\text{CO}_2$ -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  $\text{CO}_2$  hydrogenation at high temperatures (300–500 °C). Cheng *et al.* investigated the reaction mechanisms of CO formation in RWGS reaction over  $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$  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  $\text{CO}_2$  hydrogenation using plasma-catalytic processes at low temperatures. Jwa *et al.* have investigated the hydrogenation of  $\text{CO}_2$  and CO over  $\text{Ni}/\text{Al}_2\text{O}_3$  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-ZrO<sub>2</sub> supported catalysts at low temperatures [4].

In this work, plasma-catalytic  $\text{CO}_2$  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  $\text{H}_2/\text{CO}_2$  molar ratio and different catalysts ( $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{Mn}/\gamma\text{-Al}_2\text{O}_3$  and  $\text{Cu-Mn}/\gamma\text{-Al}_2\text{O}_3$ ) on the reaction performance of the plasma-catalytic  $\text{CO}_2$  hydrogenation has been evaluated in terms of the conversion of  $\text{CO}_2$ , the selectivity and yield of CO and  $\text{CH}_4$ , and the energy efficiency for CO and  $\text{CH}_4$  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  $C_{\text{ext}}$  (0.47  $\mu\text{F}$ ). 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).

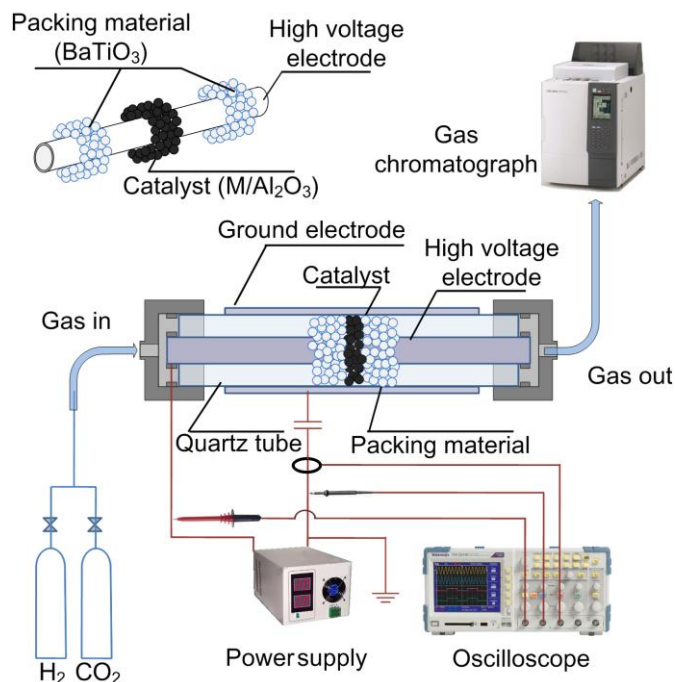


Fig. 1. Schematic diagram of the experimental setup

### A. Catalyst preparation

8 wt.%  $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ , 8 wt.%  $\text{Mn}/\gamma\text{-Al}_2\text{O}_3$  and 4 wt.%  $\text{Cu-Mn}/\gamma\text{-Al}_2\text{O}_3$  catalysts were prepared by incipient wetness impregnation using nitrate salts (Alfa Aesar, 99.5%) as the

metal precursors. An appropriate weight of support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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 BaTiO<sub>3</sub> 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 CO<sub>2</sub> hydrogenation, the catalysts were reduced in an argon-hydrogen discharge at a discharge power of 7.5 W (50 ml/min, 20 vol. % H<sub>2</sub>) for 30 minutes in the same DBD reactor.

### B. Definition of parameters

For the plasma-catalytic CO<sub>2</sub> hydrogenation, the conversion (*C*) of CO<sub>2</sub> 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 H<sub>2</sub>/CO<sub>2</sub> 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 CO<sub>2</sub> hydrogenation process for CO and CH<sub>4</sub> production is defined as the amount of CO or CH<sub>4</sub> produced per unit of discharge power:

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

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

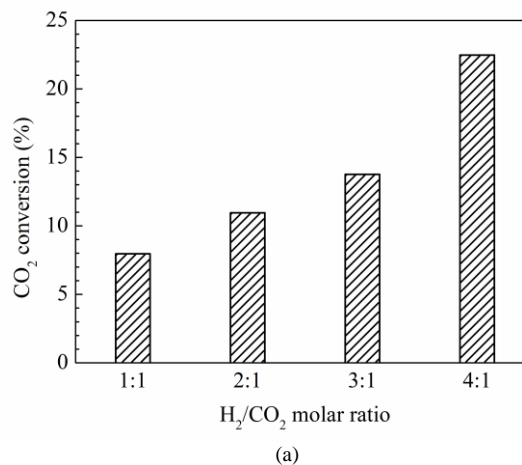
## III. RESULTS AND DISCUSSION

### A. Effect of H<sub>2</sub>/CO<sub>2</sub> molar ratio

Fig.2 shows the effect of different H<sub>2</sub>/CO<sub>2</sub> molar ratios on the

reaction performance of the plasma-catalytic CO<sub>2</sub> hydrogenation over Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at a discharge power of 35 W. CO and H<sub>2</sub>O were the major products, whereas a small amount of CH<sub>4</sub> and trace amount of C<sub>2</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>10</sub> (3-10 ppm) were also detected in the effluent. The conversion of CO<sub>2</sub> increases almost linearly with the increase of the H<sub>2</sub>/CO<sub>2</sub> molar ratio at a fixed flow rate (Fig.2a). For instance, the conversion of CO<sub>2</sub> is increased from 8% to 11% when the H<sub>2</sub>/CO<sub>2</sub> molar ratio is changed from 1:1 to 2:1, and reaches the maximum of 22.5% when further increasing the H<sub>2</sub>/CO<sub>2</sub> ratio from 2:1 to 4:1. This result suggests that increasing H<sub>2</sub> content in the reactant mixture significantly enhances the CO<sub>2</sub> conversion.

Fig.2b and Fig.2c show that the H<sub>2</sub>/CO<sub>2</sub> molar ratio affects the selectivity of CO and CH<sub>4</sub>. As the H<sub>2</sub>/CO<sub>2</sub> 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 CH<sub>4</sub> achieves its maximum at the H<sub>2</sub>/CO<sub>2</sub> ratio of 3:1. Further increasing the H<sub>2</sub> content decreases the CH<sub>4</sub> selectivity. These findings could be useful in the optimization of plasma-catalytic CO<sub>2</sub> hydrogenation processes since the conversion of CO<sub>2</sub> and the production of CO and CH<sub>4</sub> could be controlled by adjusting the H<sub>2</sub>/CO<sub>2</sub> 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 C<sub>2</sub> and C<sub>4</sub> by-products in the process. No carbon deposition has been observed in the DBD reactor. This can also be concluded from Fig.2d.



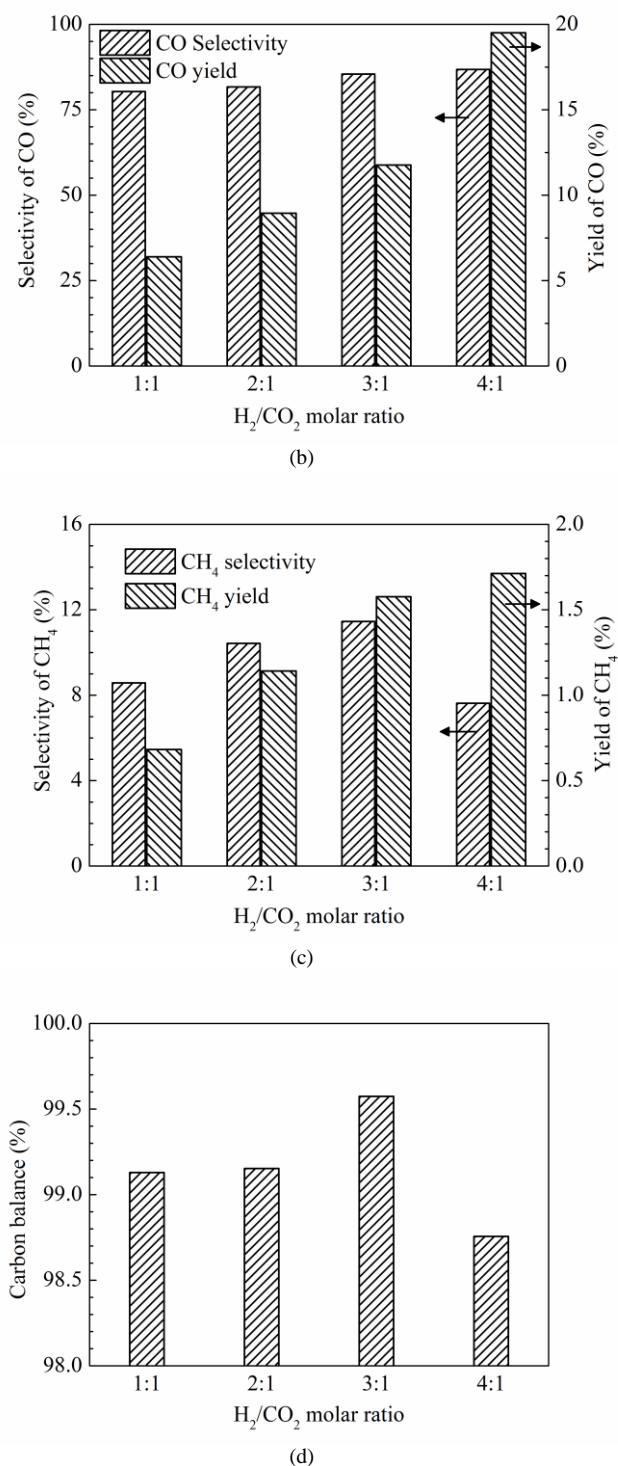


Fig. 2. The effect of H<sub>2</sub>/CO<sub>2</sub> molar ratio on plasma-catalytic CO<sub>2</sub> hydrogenation over a 8 wt.% Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalyst (a) the conversion of CO<sub>2</sub>; (b) the selectivity and yield of CO; (c) the selectivity and yield of methane; (d) carbon balance (discharge power 35 W, total feed flow rate 34.6 ml/min).

Fig.3 shows the effect of H<sub>2</sub>/CO<sub>2</sub> molar ratio on the energy efficiency for CO and CH<sub>4</sub> production. Increasing the H<sub>2</sub>/CO<sub>2</sub> molar ratio significantly enhances the energy efficiency for CO production. By changing the H<sub>2</sub>/CO<sub>2</sub> 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

CO<sub>2</sub> and CO yield when increasing the H<sub>2</sub> content in the mixture feed gas. Similarly, the maximum energy efficiency for methane production is achieved at the H<sub>2</sub>/CO<sub>2</sub> ratio of 3:1.

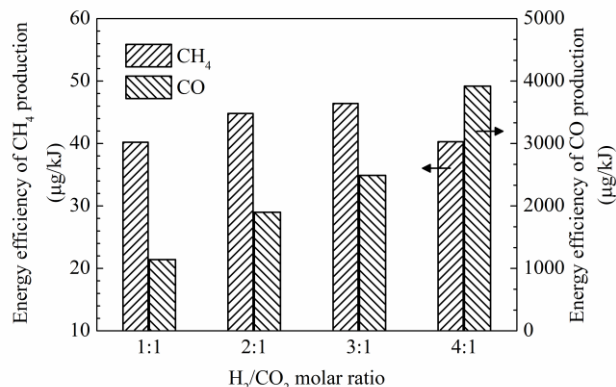
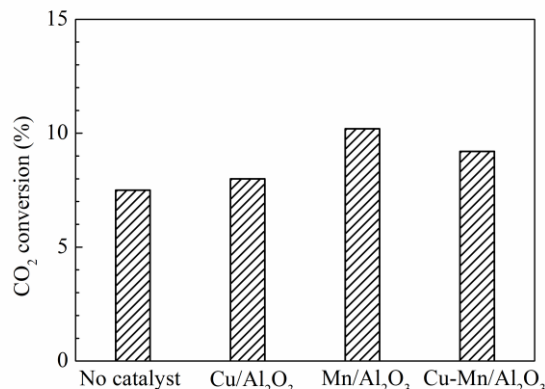
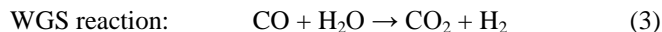


Fig. 3. The effect of H<sub>2</sub>/CO<sub>2</sub> molar ratio on the energy efficiency of CO and CH<sub>4</sub> production (8 wt.% Cu/γ-Al<sub>2</sub>O<sub>3</sub>, discharge power 35 W, total feed flow rate 34.6 ml/min).

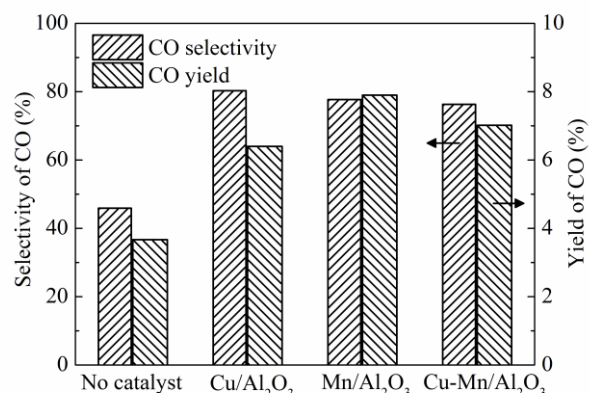
### B. Effect of Catalysts

Fig.4 presents the influence of different γ-Al<sub>2</sub>O<sub>3</sub> supported metal catalysts on the performance of the plasma CO<sub>2</sub> hydrogenation at a H<sub>2</sub>/CO<sub>2</sub> 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 CO<sub>2</sub> hydrogenation. In this study, we find the combination of DBD with the Mn/γ-Al<sub>2</sub>O<sub>3</sub> catalysts significantly enhances the conversion of CO<sub>2</sub> by 36% in the plasma CO<sub>2</sub> 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-Al<sub>2</sub>O<sub>3</sub> catalyst in the DBD reactor only slightly improves the CO<sub>2</sub> conversion by 6.7%, whereas adding Mn into the Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalyst shows a better CO<sub>2</sub> conversion compared to the Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalyst, though the performance of this bimetallic catalyst (Cu-Mn/γ-Al<sub>2</sub>O<sub>3</sub>) in the plasma-catalytic CO<sub>2</sub> hydrogenation is still lower than when using the Mn/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. Cu based catalysts are commonly used in the water gas shift (WGS) reaction, as shown in Equation (3) [24]. Using the Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalyst in the DBD reactor might promote the WGS reaction in the plasma-catalytic CO<sub>2</sub> hydrogenation process, leading to a higher concentration of CO<sub>2</sub> in the reactor and a lower apparent CO<sub>2</sub> conversion [23], [24]. For the Cu-Mn/γ-Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst, the addition of Mn into the Cu/γ-Al<sub>2</sub>O<sub>3</sub> 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 CO<sub>2</sub> 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-Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst compared to the Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. In this work, the maximum CO<sub>2</sub> conversion of 10.2% is achieved in the plasma-catalytic reaction combined with the Mn/γ-Al<sub>2</sub>O<sub>3</sub> catalyst at a H<sub>2</sub>/CO<sub>2</sub> molar ratio of 1:1 and a

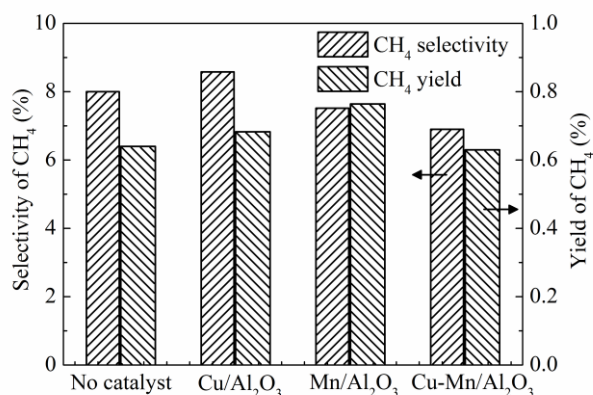
discharge power of 35 W, as shown in Fig.4a.



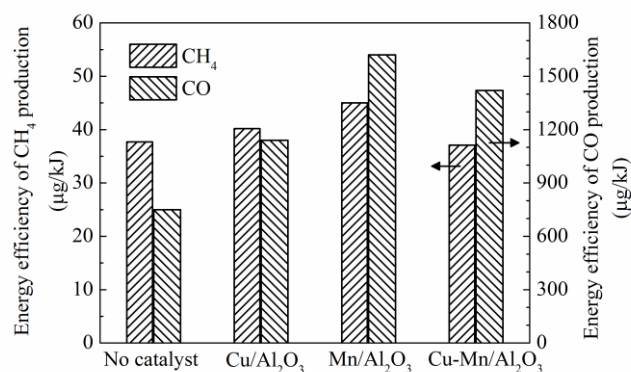
(a)



(b)



(c)



(d)

Fig. 4. The effect of catalysts on plasma-catalytic CO<sub>2</sub> hydrogenation (a) CO<sub>2</sub> conversion; (b) CO selectivity and yield; (c) CH<sub>4</sub> selectivity and yield; (d) energy efficiency for CH<sub>4</sub> and CO production (discharge power 35 W, total feed flow rate 34.6 ml/min, H<sub>2</sub>/CO<sub>2</sub> molar ratio 1:1).

The selectivity and yield of major gas products (CO and CH<sub>4</sub>) produced in the plasma-catalytic CO<sub>2</sub> 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-Al<sub>2</sub>O<sub>3</sub> catalyst in the plasma process significantly increases the yield of CO by 114%, followed by the Cu-Mn/γ-Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst (91%), whilst placing the Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalyst in the DBD reactor increases the CO yield by 73%. In contrast, these catalysts show completely different activities for CH<sub>4</sub> formation in the plasma-catalytic CO<sub>2</sub> hydrogenation. Only the Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalyst exhibits a higher CH<sub>4</sub> selectivity compared to the plasma reaction without a catalyst. The integration of DBD and the Mn/γ-Al<sub>2</sub>O<sub>3</sub> catalyst decreases the selectivity of CH<sub>4</sub> by 6.3% (from 8% to 7.5%), whilst the use of the Cu-Mn/γ-Al<sub>2</sub>O<sub>3</sub> catalyst in the plasma reactor decreases the selectivity of CH<sub>4</sub> by 13.3%. The combination of DBD with the Cu-Mn/γ-Al<sub>2</sub>O<sub>3</sub> catalyst could suppress the formation of CH<sub>4</sub> 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 CH<sub>4</sub> 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-Al<sub>2</sub>O<sub>3</sub> catalyst in the plasma is found to improve the energy efficiency of CO production by 116%, whilst using the Cu/γ-Al<sub>2</sub>O<sub>3</sub> and Cu-Mn/γ-Al<sub>2</sub>O<sub>3</sub> 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-Al<sub>2</sub>O<sub>3</sub> catalyst is placed in the DBD reactor. Similarly, the combination of plasma with the Mn/γ-Al<sub>2</sub>O<sub>3</sub> catalyst shows the best performance in terms of the energy efficiency for CH<sub>4</sub> production. Note that the plasma-catalytic process does not always enhance the energy efficiency of the CO<sub>2</sub> hydrogenation. In this study, compared to the plasma

process without catalyst, the presence of the Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the DBD reactor only slightly increases the energy efficiency of CH<sub>4</sub> production by 6.6%, whereas combining the Cu-Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with plasma slightly decreases the energy efficiency for CH<sub>4</sub> production.

TABLE I

CO<sub>2</sub> HYDROGENATION USING DIFFERENT PROCESSES

Table.1 compares the performance of CO<sub>2</sub> 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 CO<sub>2</sub> hydrogenation is significantly affected by a wide range of operating parameters such as the H<sub>2</sub>/CO<sub>2</sub> molar ratio, total reactant flow rate, reaction temperature, and catalyst composition. Different supported metal catalysts have been investigated for CO<sub>2</sub> hydrogenation into CO or CH<sub>4</sub>. 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 CO<sub>2</sub> hydrogenation process is less than 150 °C without using extra heating, whereas the operating temperatures in thermal catalytic CO<sub>2</sub> 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 CO<sub>2</sub> 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 H<sub>2</sub>/CO<sub>2</sub> molar ratio of 4:1 in a low-pressure plasma reactor. In this work, the performance of the plasma-catalytic CO<sub>2</sub> 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/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Cu-Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts enables the CO<sub>2</sub> hydrogenation reactions to occur at low temperatures. The H<sub>2</sub>/CO<sub>2</sub> molar ratio significantly affects the CO<sub>2</sub> conversion, the yield of CO and that of CH<sub>4</sub>. Increasing the H<sub>2</sub> content in the reactant mixture significantly increases the CO<sub>2</sub> conversion. Compared to the plasma CO<sub>2</sub> hydrogenation in the absence of a catalyst, the combination of plasma with the catalysts enhances the conversion of CO<sub>2</sub> by 6.7 to 36%, while the Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst shows the best catalytic activity for CO production, followed by the Cu-Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. The presence of the Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst into the plasma reactor is found to improve the energy efficiency of CO production by 116%, whilst using the Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Cu-Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in the DBD reactor leads to an increase of 52% and 89.3%, respectively.

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TABLE I  
CO<sub>2</sub> HYDROGENATION USING DIFFERENT PROCESSES

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

<sup>a</sup>MSN: Mesostructured Silica Nanoparticles.

<sup>b</sup>SCZT: Sr<sub>3</sub>CaZr<sub>0.5</sub>Ta<sub>1.5</sub>O<sub>8.75</sub>.