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Conversion of greenhouse gases into syngas via combined effects of discharge activation and catalysis

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ABSTRACT

The topics on conversion and utilization of methane and carbon dioxide are important issues in tackling the global warming effect from the two greenhouse gases. In the present study, pure plasma and plasma catalytic activation of methane and carbon dioxide were investigated for syngas production. For pure plasma process, the effects of discharge power, CH_4/CO_2 ratios in the feed, total flow rate, as well as the concentration of the balanced gas of Ar were studied. Ar in the feed has great effects on the conversion and the stability of the reaction. At 120 °C and atmospheric pressure, the conversion of CH_4 increased from 39% to 56% and that of CO_2 increased from 23% to 30% when the Ar content in the feed increased from 0% to 50%, whereas Ar showed little effect on the H_2/CO ratios in the products. Moreover, the conversions of CH_4 and CO_2 remained unchanged within the testing hours in the presence of 50% of Ar, which was contrastive with those obtained without Ar in the feed. When Cu–Ni/Al_2O_3 catalyst was filled in the discharge gap at 450 °C, the synergism between the catalyst and dielectric-barrier discharge (DBD) plasma was achieved. Conversions of CH_4 for plasma alone, plasma-catalysis and catalysis alone were 13%, 69% and 10%, respectively. Selectivities to CO and H_2 under the plasma-catalytic process were, respectively, 76% and 57%.

1. Introduction

The direct conversion of methane to synthesis gas has a large implication towards the utilization of natural gas in gas-based petrochemical and liquid fuel industries [1–5]. Meanwhile, mitigation of CO_2, one of the most important greenhouse gases, is the crucial agenda in global warming issues. In the past years, it has been proposed that CO_2 might be utilized as an oxygen source or oxidant except utilization of CO_2 as a source of carbon. It can be considered to be a non-traditional oxidant and oxygen transfer agent. So the reforming of methane with carbon dioxide to produce synthesis gas has received significant attention via the following reaction [6–15].

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad \Delta G_{298\,K} = 69\,\text{kJ/mol}$$

However, from the perspective of catalytic chemistry, the reforming of methane with carbon dioxide to syngas at low temperature has been a challenge. To find a proper method to activate methane is essential for this conversion. The reforming of methane with carbon dioxide is a thermodynamically unfavorable reaction. High reaction temperature is required to shift the equilibrium to a state being favorable for the formation of syngas. On the other hand, the undesirable carbon deposits are unavoidable with the present catalyst designed in CO_2 reforming of CH_4.

Several technologies have been proposed to improve the efficiency of methane and carbon dioxide utilization. As an effective approach, plasma technology has been applied to the conversion of CH_4 and CO_2. Zhou et al. found that dielectric-barrier discharge (DBD) plasma was an efficient tool for converting the greenhouse gases CH_4 and CO_2 to synthesis gas at low temperature [16]. Syngas produced in this system can have an arbitrary H_2/CO ratio, mainly depending on the mixture ratio of CH_4/CO_2 in the feed gas. Eliasson et al. investigated the hydrogenation of CO_2 to methanol in a dielectric-barrier discharge with and without catalyst [17]. Huang and co-workers reported the oxidative coupling and reforming of CH_4 with CO_2 using a high-frequency pulsed plasma, and had achieved a high energy efficiency [18,19]. The role and properties of catalyst have also been studied for the application of DBD plasma technology in catalytic CH_4–CO_2 reaction [20,21] Most recently, Li et al. reported that appropriated catalyst using in plasma reactions can make selectivities of H_2 and CO change, which induced a modification of the H_2/CO ratio in the products [22].

To mitigate greenhouse gas emissions and reuse this carbon–hydrogen source, we investigate a method to produce

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synthesis gas with an arbitrary H_2/CO ratio from the two major greenhouse gases CO_2 and CH_4 in DBD plasma combined with γ-Al_2O_3 supported Cu and/or Ni catalysts, which have been exhibited good performance in pure catalysis [23–25]. The parameters investigated in the performed experiments are the electric power, flow rate, CH_4/CO_2 mixing ratio, and dilution gas. The effect of Cu–Ni/γ-Al_2O_3 catalyst on the CO_2 reforming of CH_4 for producing syngas is also investigated.

2. Experiments

A schematic view of the DBD reactor is shown in Fig. 1. The DBD reactor is a quartz tube with an ID of 8 mm. The discharge gap is 1 mm and the length of discharge zone is 10 cm or 20 cm. As high voltage electrode, a stainless tube on the inside of the inner tube is used. The outer electrode is a steel foil, wrapped around the outer quartz tube. The reactor is heated (when needed) by a cylindrical furnace placed around the reactor. The average of T_c (the center temperature measured from the central stainless tube) and T_{out} (outside temperature of the outer quartz tube) was taken as the reaction temperature [26]. The power was applied with a high-voltage generator (CTP-2000 K) working at about 30 kHz. The power measured by the voltage–charge Lissajous diagrams recorded with a 100 MHz digital oscilloscope (TDS 2012).

The conventional wetness impregnation has been applied for preparation of Ni–Cu/γ-Al_2O_3 catalyst (Ni:Cu:Al_2O_3 = 12:12:100 (wt.)). The Al_2O_3 powder support was first impregnated in an aqueous solution of $Ni_2(NO_3)_2$ and $Cu(NO_3)_2$ for ca. 12 h at room temperature. After impregnation, the obtained sample was dried 12 h at 110 °C and then was calcinated in air at 600 °C for 4 h. The catalyst, packed in the plasma zone, was reduced with H_2 at 400 °C for 2 h before the plasma catalytic tests. The tests were conducted at temperature up to 450 °C. The total gas flow rate was in the range 20–80 mL/min, with CH_4:CO_2 = 1:1. The products were analyzed by on-line gas chromatography (GC). The CH_4 and CO_2 conversions and products selectivities are defined as:

$$\mathrm{CH_4\ conversion} = \frac{\mathrm{moles\ of\ CH_4\ converted}}{\mathrm{moles\ of\ CH_4\ introduced}} \times 100\%$$

$$\mathrm{CO_2\ conversion} = \frac{\mathrm{moles\ of\ CO_2\ converted}}{\mathrm{moles\ of\ CO_2\ introduced}} \times 100\%$$

$$\mathrm{CO\ selectivity} = \frac{\mathrm{moles\ of\ CO\ produced}}{(\mathrm{moles\ of\ CH_4\ converted}) + (\mathrm{moles\ of\ CO_2\ converted})} \times 100\%$$

$$\mathrm{H_2\ selectivity} = \frac{\mathrm{moles\ of}\ H_2\ \mathrm{produced}}{2 \times \mathrm{moles\ of\ CH_4\ converted}} \times 100\%$$

$$\frac{\mathrm{H_2}}{\mathrm{CO}} = \frac{\mathrm{moles\ of}\ H_2\ \mathrm{produced}}{\mathrm{moles\ of\ CO\ produced}}$$

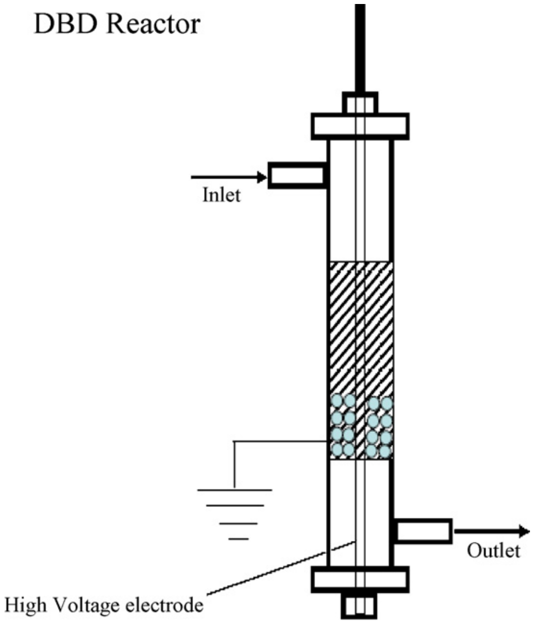

Fig. 1. Schematic view of the DBD reactor.

3. Results and discussion

3.1. Plasma activation

3.1.1. Effect of discharge power

The magnitude of input power is related with the strength of the internal electric field and the number of effective electrons, which is the most important parameter in plasma. We studied the effects of power variation on the reaction at the fixed frequency of 30 kHz, in a mixture of CH_4/CO_2 = 1 (molar ratio), a total flow rate of 60 mL/min, and a pressure of 1 bar. Experimental results are shown in Fig. 2. It is clear from Fig. 2a that the conversions of CH_4 and CO_2 increased from 17% and 12% to 40% and 27%, respectively, with the increasing input power. The increase of input power could use more energy to dissociate the CH_4 and CO_2 molecule and could generate more energetic species, such as electrons, H, OH, O and O^-, and therefore the possibility to attack methane molecules and carbon dioxide molecules could be enhanced. The conversion of methane was always higher than that of carbon dioxide in the power range tested. The yields of H_2 and CO also increased with the increasing input power from 25 to 75 W (Fig. 2b). The yield of H_2 increased from 8.8% to 14.3% and that of CO increased from 10.2% to 17.0%. The H_2/CO ratio does not change significantly with the increasing input power in the range tested (Fig. 2c), which indicated that H_2/CO ratio is not greatly affected by input power.

In the products, there exists H_2O, C_2 hydrocarbon and deposited coke except CO and H_2. The collision of methane molecules with energetic electrons leads to the formation of some active radicals such as CH_3, CH_2, CH and C_2. The formation of gaseous hydrocarbon, such as C_2H_6, in the effluent can be mainly attributed to following possible channel:

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{1}$$

The deposited coke mainly formed via CO disproportionation and CH_4 decomposition. There is only a spot of steam (H_2O) produced and no oxygen observed. All of the side reactions above mentioned, which lead to the difference between conversions and selectivities, are competitive with the main reaction.

3.1.2. Effect of total flow rate

Feed flow rate, which affects the residence time within the discharge zone, was investigated. Fig. 3 shows the influence of the flow rate on the conversions of CH_4 and CO_2 and yields of H_2 and CO. Both the conversions of CH_4 and CO_2 decreased with the increasing total flow rate from 30 to 75 mL/min. The conversions of CH_4 decreased from 59.7% to 33.2%, and that of CO_2 decreased from 36.9% to 16.1%. It is apparent that increasing the total flow rate results in a decrease of CO and H_2 yield as depicted in Fig. 3b. When the flow rate increased from 30 to 75 mL/min, the yield of CO decreased from 26% to 12%, and the yield of H_2 decreased from 21% to 11%. However, the change in the flow rate did not significantly affect the H_2/CO ratio as shown in Fig. 3c.

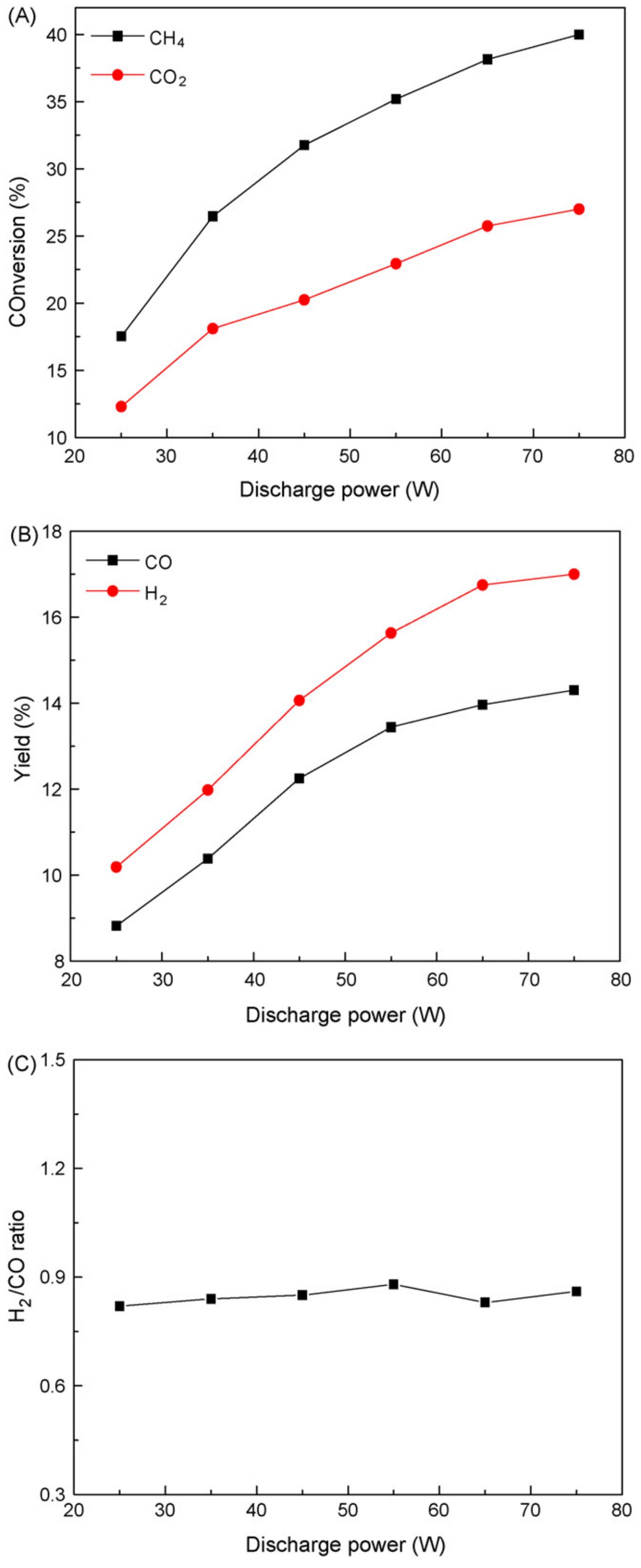

Fig. 2. The conversions of CH_4 and CO_2, the yields of H_2 and CO and (C) the H_2/CO ratio in the products against discharge power.
Flow rate, 60 mL/min; CH_4/CO_2 ratio, 1; discharge length, 20 cm.

3.1.3. *Effect of CH_4/CO_2 feed ratio*

For a better understanding of the reagent composition on the reaction, we performed experiments by varying the molar ratio of methane to carbon dioxide from 1/3 to 3/2 in the feed gas at a certain flow rate (60 mL/min) and discharge power (60 W). The effects of CH_4/CO_2 ratio on the conversions of CH_4 and CO_2 and yields of H_2 and CO were shown in Fig. 4. With an increase in the molar ratio of methane to carbon dioxide from 1/3 to 3/2, the conversion of CH_4 decreased significantly from 54.3% to 34.0%, whereas the conversion of CO_2 changed slightly. The conversion of CH_4 was always higher than that of CO_2. It is clear from Fig. 4b

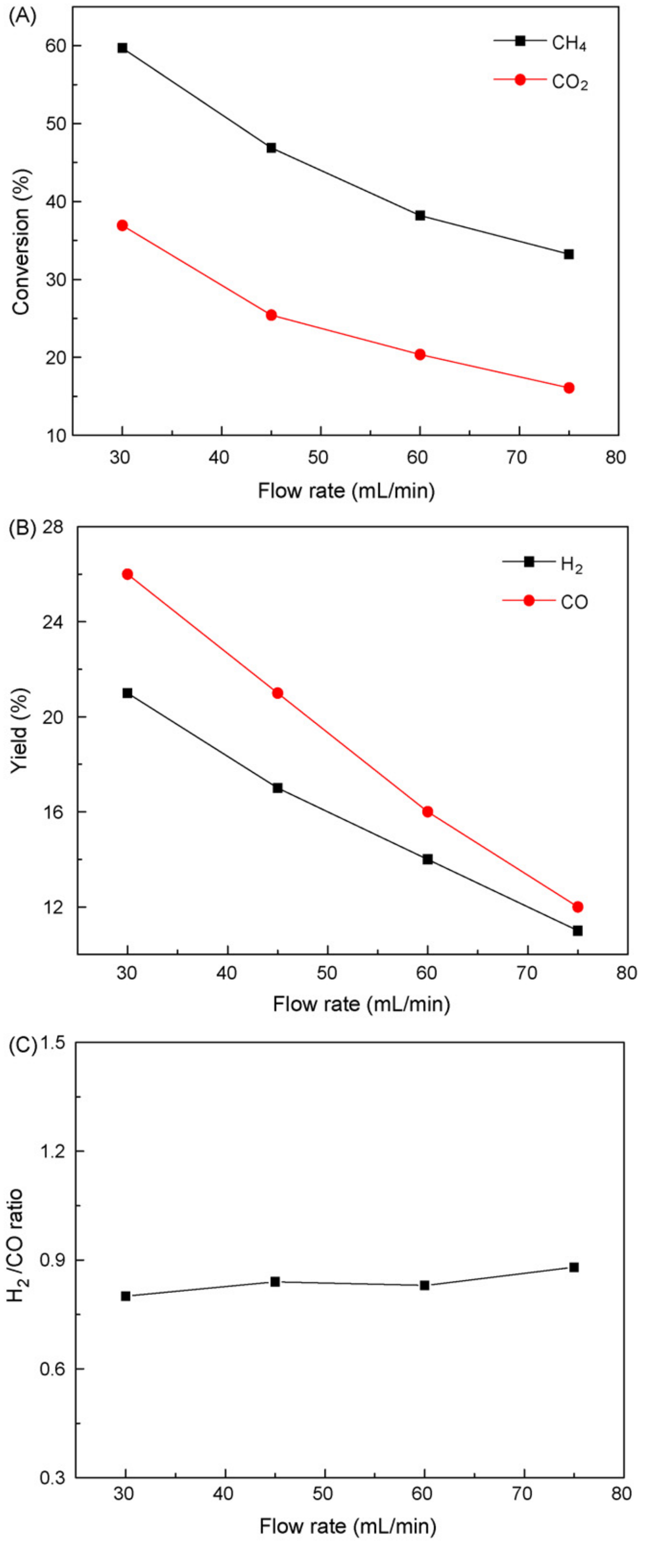

Fig. 3. Effects of total flow rate on (A) the conversions of CH_4 and CO_2, (B) the yields of H_2 and CO and (C) the H_2/CO ratio in the products.
CH_4/CO_2 ratio, 1; discharge length, 20 cm; 60 W.

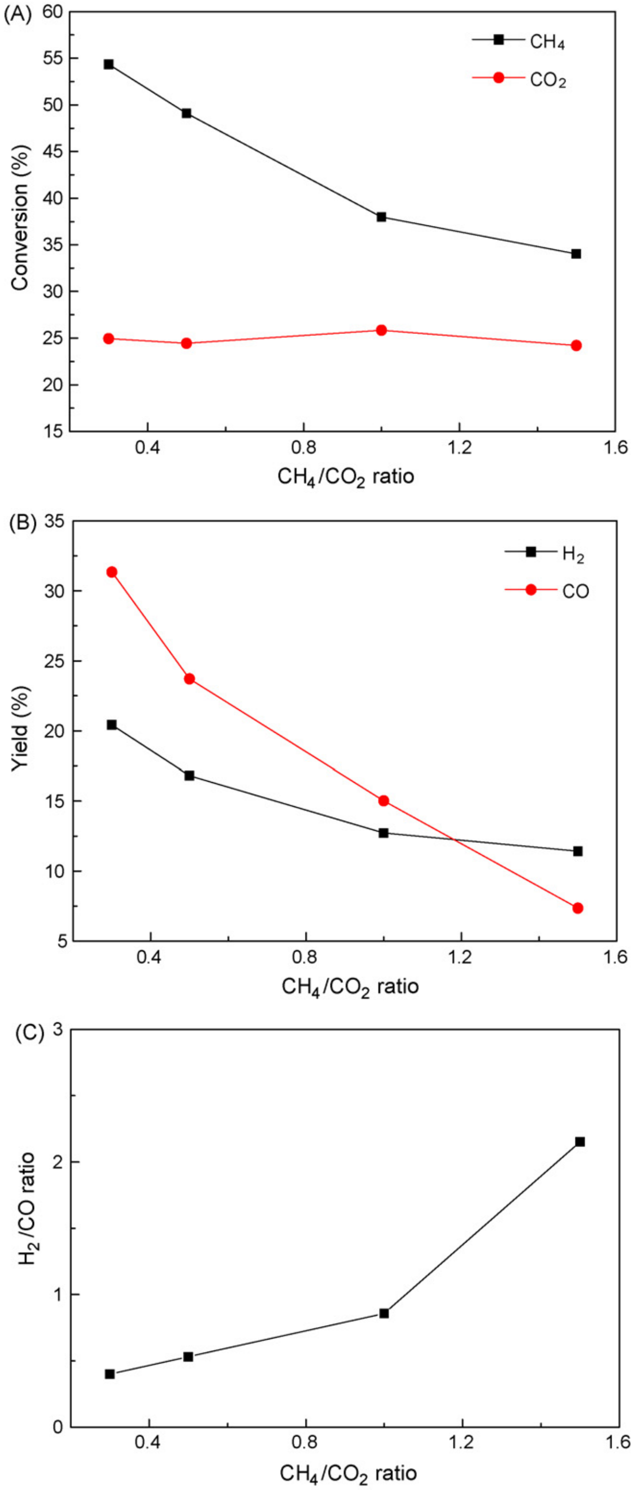

Fig. 4. Effects of CH_4/CO_2 feed ratio on (A) the conversions of CH_4 and CO_2, (B) the selectivity of H_2 and CO and (C) the H_2/CO ratio in the products.
Flow rate, 60 mL/min; discharge length, 20 cm; 60 W.

that the yield of H_2 decreased with increasing CH_4/CO_2 ratio. The yield of H_2 decreased from 20.4% to 11.4%, while the yield of CO highly decreased from 31.3% to 7.3%, when CH_4/CO_2 ratio increased from 1/3 to 3/2. Fig. 4c indicates that increasing CH_4/CO_2 ratios in the feed results in the significant increasing of H_2/CO ratios in the products. With the CH_4/CO_2 ratios increasing from 1/3 to 3/2, the H_2/CO ratios increased from 0.4 to 2.1. It is believed that the H_2/CO ratio depends strongly on the CH_4/CO_2 ratio in the feed.

For increasing CH_4/CO_2 molar ratio, the active methane species (CH_3, CH_2, CH) reacting with another one to form other hydrocarbon species (C_2, C_3) has more opportunity than methane oxidation to form CO, since the system has less oxygen available with the increasing CH_4/CO_2 molar ratio. This explanation is clearly confirmed by the increase in the H_2/CO ratio with the increasing CH_4/CO_2 molar ratio.

3.1.4. *Effect of dilution gas*

The effects of dilution gas on the conversions, product selectivities and the stability of reaction were investigated. To examine the effect of content of Ar, experiments were carried out with varying the content of Ar from 0% to 50%. The conversions of CH_4 and CO_2 are lower in the absence of Ar than that of CH_4 and CO_2 in the presence of Ar in the feed. The selectivities to H_2 and CO are also significantly improved under the presence of Ar. The conversion of CH_4 increased from 38% to 56% and that of CO_2 increased from 23% to 30% when the Ar content in the feed increased from 0% to 50%. As shown in Fig. 5b, the selectivity of CO and H_2 increased from 48% and 33% to 54% and 37% respectively, with the increasing Ar content in the feeds. As an excellent plasma-forming gas, the efficiency of direct excitation through Ar may be higher than that of direct excitation through electrons [27]. When Ar present in the plasma zone, they first collide with electrons and become excited:

$$\mathrm{Ar} + \mathrm{e} \rightarrow \mathrm{Ar}^* + \mathrm{e} \tag{2}$$

The methane molecules get energy from the excited Ar atoms instead of electrons:

$$CH_4 + \mathrm{Ar}^* \rightarrow CH_3 + \mathrm{H} + \mathrm{Ar} \tag{3}$$

Where an asterisk means excited state. As the main reaction (2), the mechanism is similar to that of decomposition of dimethyl ether by plasma in the presence of Ar [27]. The reasons are that the dissociation of methane and dimethyl ether is similar in the gas phase in a plasma chemical process.

The effect of Ar on the reaction stability is also investigated as shown in Fig. 5c. The presence of Ar could significantly improve the stability of reaction. The conversions of CH_4 do not change significantly within the range of time tested in the presence of Ar, whereas that of CH_4 decreased strongly in the absence of Ar.

In CO_2 reforming, different from steam reforming, the deposited coke due to CO disproportionation and CH_4 decomposition can not be volatilized by the reaction with steam. We proposed that the surface carbon species could be gasified by the excited Ar from the collision of Ar atom with energetic electrons and form carbon species (CO, C_2, C_3) reacting with active species (such as O, CH_3). This is clearly confirmed by the increase of selectivity of CO with the increasing Ar content in the system.

3.2. *Plasma-catalytic activation*

The effects of catalysts on conversions of CH_4 and CO_2 and products selectivities were examined. Table 1 lists the experimental results over the catalysts combined with plasma. All the samples showed catalytic activity for CO_2 reforming CH_4. Among them, 12 wt.% Cu/γ-Al_2O_3 displayed lower catalytic activity than other samples. With loading of Cu on the Ni/γ-Al_2O_3 or loading of Ni on the Cu/γ-Al_2O_3 samples, there was significant enhancement in performance. The results indicated that there existed an optimum Ni/Cu ratio to the reactants conversion and products selectivity. The 12 wt.% Cu–12 wt.% Ni/γ-Al_2O_3 combined DBD plasma showed significant activity for CO_2 reforming CH_4 at 450 °C. The conversion of CH_4 obtained using DBD plasma over different catalysts increased in the order 12 wt.% Cu–12 wt.% Ni/γ-Al_2O_3 > 12 wt.% Cu–16 wt.%

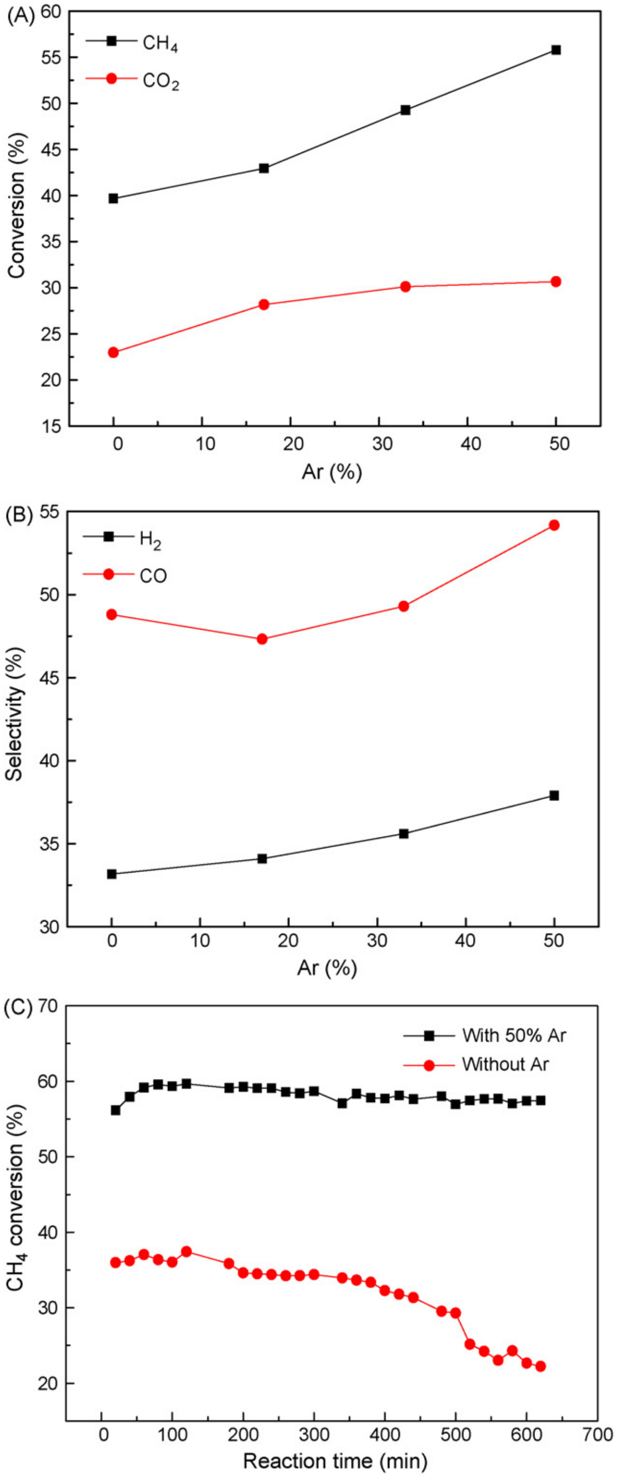

Fig. 5. Effects of Ar content in the feeds on (A) the conversions of CH_4 and CO_2, (B) the selectivity of H_2 and CO and (C) the stability of reaction.
Flow rate, 60 mL/min; CH_4/CO_2 ratio, 1; discharge length, 20 cm; 60 W; wall temperature, ~120 °C.

Table 1
Effects of catalysts on the conversions of CH_4 and CO_2 and on the selectivity of H_2 and CO.

Catalyst	Conversion (%)		Selectivity (%)	
	CH_4	CO_2	H_2	CO
12% Ni/γ-Al_2O_3 + plasma	30	24	53	43
12% Cu/γ-Al_2O_3 + plasma	7	5	31	50
1% Cu–12% Ni/γ-Al_2O_3 + plasma	33	25	51	45
5% Cu–12% Ni/γ-Al_2O_3 + plasma	37	24	54	47
12% Cu–12% Ni/γ-Al_2O_3 + plasma	69	75	56	75
16% Cu–12% Ni/γ-Al_2O_3 + plasma	43	47	57	64
5% Ni–12% Cu/γ-Al_2O_3 + plasma	43	45	56	75
16% Ni–12% Cu/γ-Al_2O_3 + plasma	57	57	58	71
20% Ni–12% Cu/γ-Al_2O_3 + plasma	35	32	58	62

Reaction conditions: Flow rate = 60 mL/min; $CH_4:CO_2$ = 1:1; F_{Ar} = 30 mL/min; discharge gap = 1 mm; discharge length = 10 cm; discharge power = 60 W; GHSV = 1800 h^{-1}; 450 °C.

Ni/γ-Al_2O_3 > 16 wt.% Cu–12 wt.% Ni/γ-Al_2O_3 ~ 12 wt.% Cu–5 wt.% Ni/γ-Al_2O_3 > 5 wt.% Cu–12 wt.% Ni/γ-Al_2O_3 > 12 wt.% Cu–20 wt.% Ni/γ-Al_2O_3 > 1 wt.% Cu–12 wt.% Ni/γ-Al_2O_3.

Pure plasma and pure catalysis activation, as well as the combined effects of plasma and catalysis on methane dry reforming were compared shown in Fig. 6. Under purely catalytic conditions, the 12 wt.% Cu–12 wt.% Ni/γ-Al_2O_3 was active only at 300 °C and above. The conversions of CH_4 and CO_2 over the catalyst alone were about 10% and 13% at 450 °C, respectively, the selectivities of H_2 and CO were 35% and 62%. When the catalyst was placed in the plasma zone, the conversions and selectivities were modified apparently. The most significant results were obtained when

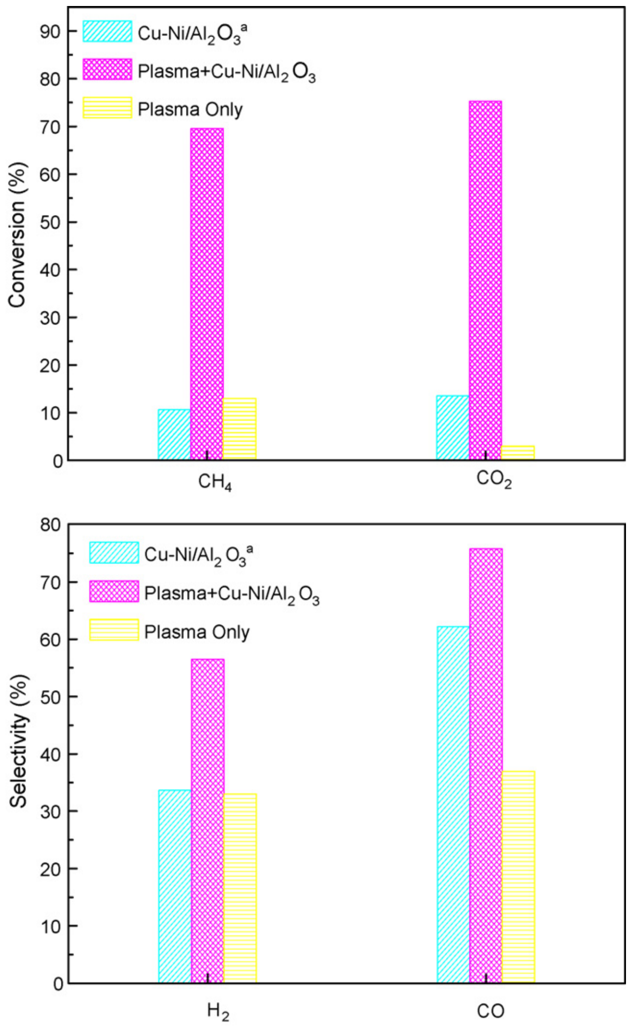

Fig. 6. Compared result on pure plasma and pure catalyst, as well as the combined effects of plasma and catalyst for CH_4 dry reforming.
Flow rate, 60 mL/min; flow rate of Ar, 30 mL/min; CH_4/CO_2 ratio, 1; discharge length, 10 cm; 60 W; GHSV = 1800 h^{-1}; 450 °C.
[a] $CH_4:CO_2$ = 1:1; 50% Ar in the feed; GHSV = 1800 h^{-1}; 450 °C; 0.1 g.

Table 2
Temporal stability of CO_2 reforming of CH_4.

Time (min)	12% Cu–12% Ni/γ-Al_2O_3 + Plasma			
	CH_4 conversion (%)	CO_2 conversion (%)	H_2 selectivities (%)	CO selectivities (%)
20	69.7	75.4	56.4	75.9
40	70.3	74.6	56.6	76.3
60	69.1	73.0	58.3	75.2
80	69.9	75.4	60.5	74.3
100	69.0	73.1	59.8	72.5

Reaction conditions: Flow rate = 60 mL/min; CH_4:CO_2 = 1:1; F_{Ar} = 30 mL/min; discharge gap = 1 mm; discharge length = 10 cm; discharge power = 60 W; 450 °C.

12 wt.% Cu–12 wt.% Ni/γ-Al_2O_3 was packed in DBD reactor, the conversions of CH_4 and CO_2 were 69% and 75% respectively. The selectivities to H_2 and CO were 56% and 75%, respectively. The conversion of CH_4 was 69% under plasma-catalytic process, which was higher than the sum of the purely catalytic efficiency of 10% and purely plasma-induced conversion percentage of 13%. Similar tendency was observed for conversion of CO_2. More important, the selectivitives of H_2 and CO were also improved under plasma-catalytic process. The selectivity of H_2 was 56%, and that of CO was 76%, which was even higher than those obtained in purely catalytic activation.

In Table 2, we shown temporal stability of CO_2 reforming of CH_4. Under plasma-catalytic process, 12 wt.% Cu–12 wt.% Ni/γ-Al_2O_3 catalyst exhibits a relatively stable reactants conversion and syngas selectivity during the 100 min on-stream test. The coking formation and carbon deposition on the surface of catalyst might be restrained in the plasma-catalytic process.

Experiments with catalyst only and thermodynamic equilibrium calculations indicated that no conversions of CH_4 and CO_2 to CO and H_2 is observed below 300 °C. Thus, the increase of conversion and selectivity, at low temperature, can only be caused by interaction between the discharge plasma and the catalyst.

To describe the results, the following reaction mechanism for the plasma chemical reaction over the catalyst is proposed. The initial reaction is the dissociation of CH_4 and CO_2 in the gas phase in a plasma chemical process by electron collision and to generate active species. CH_4 and CO_2 have dissociation energy of 4.5 and 5.5 eV, respectively, which lie well within the electron energy range in DBD plasma (1–10 eV). In the gas phase, these active species, which come from the dissociation of CH_4, can form H_2 and hydrocarbon by recombination. CO could form via the recombination of carbon and oxygen atom expect for the dissociation of CO_2. Meanwhile these active species could more easily adsorb on the catalyst surface to form CO and H_2.

$$(CH_x) + * \rightarrow (CH_x)_{ad} \tag{4}$$

$$H + * \rightarrow H_{ad} \tag{5}$$

$$O + * \rightarrow O_{ad} \tag{6}$$

$$(CH_x)_{ad} + O_{ad} \rightarrow CO_{ad} + xH_{ad} \tag{7}$$

$$CO_{ad} \rightarrow CO + * \tag{8}$$

$$2H_{ad} \rightarrow H_2 + * \tag{9}$$

Where an asterisk marks an empty adsorption site on the catalyst. The intermediate is O_{ad} which can be produced from the dissociation of CO_2. The reaction mechanism suggested is that adsorbed carbon species (CH_x) ($x = 0, 1, 2, 3$) formed from activated CH_4, react with adsorbed atomic oxygen (O_{ad}) formed from dissociation of CO_2 and produce CO. H_2 could form via the recombination of H_{ad}, which adsorbed on the catalyst surface formed from dissociation of CH_4 and reacting between adsorbed atomic oxygen and adsorbed carbon species.

On the other hand, the plasma can also influence the catalyst properties, e.g. due to heat the catalyst, and therefore can induce desorption of surface species. Thus a synergy between catalysis and plasma is achieved over 12 wt.% Cu–12 wt.% Ni/γ-Al_2O_3 catalyst. Interaction between the plasma and the catalyst leads to the significantly improved conversions and higher selectivities as compared to the pure plasma and catalytic process.

4. Conclusions

The reaction depends strongly on the input power, total flow rate and CH_4/CO_2 ratio. The addition of argon as dilution gas in the feed can significantly improve the reaction. The Cu–Ni/γ-Al_2O_3 catalyst is a promising catalyst for producing synthesis gas with high methane and carbon dioxide conversions. The presence of catalyst under the plasma conditions can also change the selectivity of H_2 and CO, which induced a modification of H_2/CO ratio in the products. This study makes it clear that a synergy between catalysis and plasma is achieved over Cu–Ni/γ-Al_2O_3 catalyst.

Acknowledgments

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