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Synthesis gas production via dielectric barrier discharge over Ni/γ-Al_2O_3 catalyst

Hyung Keun Song [a,*], Jae-Wook Choi [a], Sung Hoon Yue [a], Hwaung Lee [a], Byung-Ki Na [b]

[a] *Clean Technology Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea*
[b] *Division of Chemical Engineering, Chungbuk National University, San 48, Gaesin-dong, Cheongju Chungbuk 361-763, South Korea*

Abstract

A study of methane conversion from CO_2 reforming of methane using dielectric barrier discharge over Ni/γ-Al_2O_3 catalyst was performed. The main products of reactions were CO, H_2, C_2H_6, C_3H_8, and C_4H_{10}. The effects of input power, total flow rate, and CH_4/CO_2 ratio on conversion and product selectivity were investigated. Carbon dioxide and methane conversions were enhanced with increasing the input power and decreasing the total flow rate. Ni/γ-Al_2O_3 catalyst had a great effect on the CO selectivity and CO_2 conversion. When Ni/γ-Al_2O_3 catalyst was applied to DBD, the CO selectivity increased from 49.17 to 60.9% and CO_2 conversion increased by about 3%. Even though Ni/γ-Al_2O_3 catalyst was helpful to improve the CO_2 conversion and CO selectivity, the fundamental mechanism of reaction and characterization of catalysts are still unknown and, therefore, further investigations are necessary.

Keywords: Synthesis gas; CH_4 conversion; CO_2; Barrier discharge; Ni/γ-Al_2O_3 catalysts

1. Introduction

Synthesis gas is a present and increasing source of environmentally clean fuels and chemicals, and is used as a feedstock in many chemical industries to produce hydrogen fuel, methanol, and higher hydrocarbons. Synthesis gas, a mixture of hydrogen and carbon monoxide, can be manufactured from any hydrocarbon feedstock, such as natural gas, coal, petroleum coke, and residual oil [1]. From the availability and flexibility of the resource base, natural gas is one of the most useful resources of feedstock. Methane is the major component of natural gas and a very stable compound that is difficult to activate for reaction. The oxidative coupling of methane [2–5] and the partial oxidation of methane [6–9] are possible ways to methane conversion. However, these reactions require extreme reaction conditions with high temperatures and pressure and are suffered from a carbon formation, a rapid deactivation of catalyst and carbon deposition on the surface of catalyst. Thus, it is necessary to develop a new method for methane conversion. Methane conversion using nonthermal plasma has been widely studied as a potential tool to resolve these problems [10–21]. Nonthermal plasma such as dielectric barrier discharge, corona discharge and pulsed discharge could generate effective electrons enough to fragment CH_4 molecule to form CH_i radicals that react with additive gases such as CO_2 to form products. Therefore, it is an excellent source of energetic electrons, low excited atomic and molecular species, free radicals and excimers and high density with energy of several electron volts. Kozlov et al. [10] reported on a methane conversion with carbon dioxide in DBD at atmospheric pressure and suggested at least two possibilities to vary the contributions of different chemical pathways of the system. Yao et al. [11] studied the oxidative coupling and reforming of methane with carbon dioxide using a pulsed plasma and examined the effect of pulse frequency on methane conversion and selectivity. The largest C_2H_4 selectivity was 64% with 31% CH_4 conversion and 24% CO_2 conversion. The energy efficiency of the pulsed plasma was improved using a high pulse frequency and a high reaction temperature. Liu et al. [13] analyzed the prod-

* Corresponding author.
E-mail address: hksong@kist.re.kr (H.K. Song).

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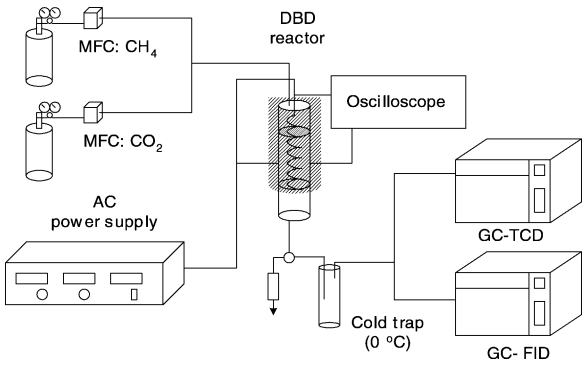

Fig. 1. Experimental setup of dielectric barrier discharge reactor over catalysts.

uct distribution of plasma methane conversion using DBD. A series of hydrocarbons, including gaseous hydrocarbons, liquid fuels, and plasma-polymerized film were main products. Li et al. [15] reported an effect of electrode materials on the co-generation of synthesis gas and higher hydrocarbons from CO_2 and CH_4 using DBD. In the absence of CO_2, the order of methane conversion activity was Ti ≈ Al > Fe > Cu, while the order of CO_2 conversion activity was Al > Cu > Ti > Fe without methane. Kado et al. [17] investigated plasma methane conversion with or without catalyst. They showed that the selectivity strongly depended on the composition of the feed gas and NiMgO had the great effect of increasing CO selectivity to 99%. Liu et al. [18,19] also conducted plasma catalytic conversion of methane. They used zeolite X and zeolite A to improve the methane conversion and product selectivity. This plasma methane conversion over zeolite has led to a selective production of light hydrocarbon. Kraus et al. [20] performed the CO_2 reforming of methane by the combination of catalysts with DBD. From the results, it was shown that nickel or calcium promoted nickel catalysts led to an increase in the CO yield of 20–40%.

In this study, methane conversion from CO_2 reforming of methane using dielectric barrier discharge over Ni/γ-Al_2O_3 catalyst was performed. The effects of input power, total flow rate, CH_4/CO_2 ratio and Ni/γ-Al_2O_3 catalyst on methane conversion and product selectivity were experimentally investigated.

2. Experiments

2.1. Experimental system

Experimental setup for methane conversion with the dielectric barrier discharge reactor was shown in Fig. 1. The dielectric barrier discharge reactor was made of quartz tube with an inner diameter of 6 mm, a wall thickness of 1 mm and a length of 300 mm. The inner electrode was stainless steel spring with an outer diameter of 4 mm. The outer electrode was a silver paste, which was coated on the outer wall

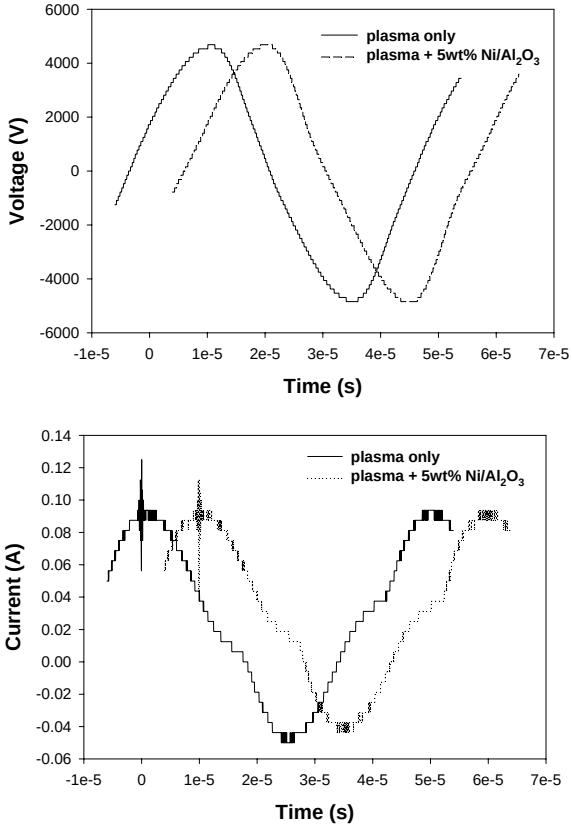

Fig. 2. Typical waveforms of voltage and current (input power 130 W, total flow rate 30 ml/min, $CH_4/CO_2 = 1$).

of quartz tube. The feed gas was composed of CH_4 and CO_2. The flow rate of feed gas was controlled with mass flow controller. A high frequency AC power supply with 10 kV and 20 kHz (Auto Electric Co., A1831) was connected to the DBD reactor to generate plasma. To measure and record the voltage and current waveform, a digital oscilloscope (Agilent, 54622A) with a high voltage probe (Tektronix, 6015A) and a current probe (Pearson, 4997) was used. Typical waveforms of voltage and current during experiments were shown in Fig. 2. There had no noticeable difference in magnitude and waveforms of voltage and current when the plasma was generated with/without catalysts. The input power of the DBD reactor was measured by the digital power meter inserted at the AC power input line. Qualitative and quantitative analysis of plasma products were carried out on-line with gas chromatograph. The concentration of hydrocarbons and synthesis gas were determined by GC-FID (Youngin, 600D, Hayesep Q Column), and GC-TCD (Shimadzu, GC-14A, Molecular Sieve 5A Column with Porapak P + Q Column), respectively.

2.2. Catalyst preparation

The nickel supported γ-alumina catalyst was prepared by incipient wetness method with aqueous solution of nitrates as metal precursors. The precursor was nickel nitrate six

hydrate (Junsei Chemical Co.). The support was γ-Al_2O_3 (Strem Chemicals, Inc.), which was calcined at 750 °C in oxygen for 8 h and was crashed into 10/20-mesh size. The obtained catalysts were dried overnight in air at 120 °C, and then calcined at 700 °C in oxygen for 5 h to complete the decomposition of intermediates. After this treatment, the catalyst was reduced at 700 °C in hydrogen stream for 2 h.

In all experiments, the performance of dielectric barrier discharge reactor was evaluated by conversion, selectivity and yields. The conversion, selectivity, and yield are defined as follows:

$$\text{CH}_4\text{ conversion} = \frac{\text{moles of CH}_4\text{ converted}}{\text{moles of CH}_4\text{ in feed}} \times 100$$

$$\text{CO}_2\text{ conversion} = \frac{\text{moles of CO}_2\text{ converted}}{\text{moles of CO}_2\text{ in feed}} \times 100$$

$$\text{Selectivity of C}_x\text{H}_y = \frac{x \times \text{moles of C}_x\text{H}_y\text{ produced}}{\text{moles of CH}_4\text{ converted} + \text{moles of CO}_2\text{ converted}} \times 100$$

$$\text{Selectivity of H}_2 = \frac{\text{moles of H}_2\text{ produced}}{2 \times \text{moles of CH}_4\text{ converted}} \times 100$$

$$\text{Selectivity of CO} = \frac{\text{moles of CO produced}}{\text{moles of CH}_4\text{ converted} + \text{moles of CO}_2\text{ converted}} \times 100$$

$$\text{Yield of H}_2 = \frac{\text{moles of H}_2\text{ produced}}{\text{moles of CH}_4\text{ in feed} + \text{moles of CO}_2\text{ in feed}} \times 100$$

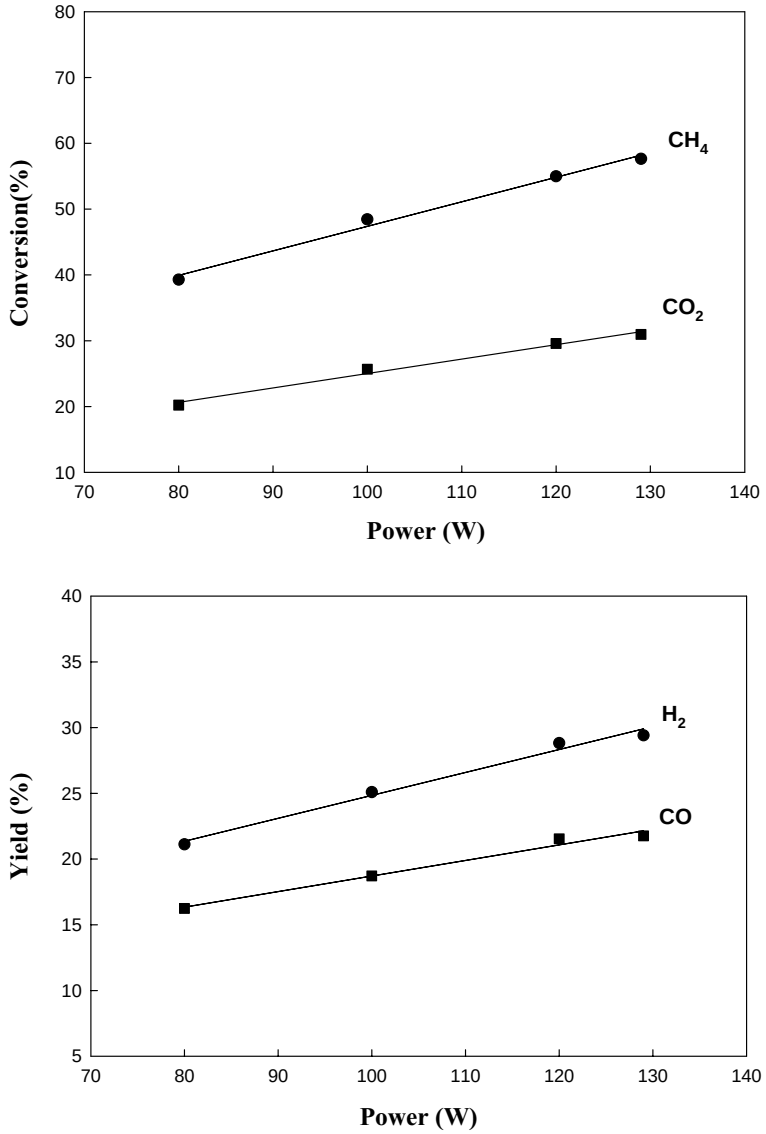

Fig. 3. Effect of power on the conversion of CH_4 and CO_2 and yield of H_2 and CO.

$$\text{Yield of CO} = \frac{\text{moles of CO produced}}{\text{moles of CH}_4\text{ in feed} + \text{moles of CO}_2\text{ in feed}} \times 100$$

$$\frac{\text{H}_2}{\text{CO}}\text{ ratio} = \frac{\text{moles of H}_2\text{ produced}}{\text{moles of CO produced}}$$

3. Results and discussion

3.1. Effect of 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 the plasma. To examine the effect of input power on CH_4 conversion and yield, the input power was changed from 80 to 130 W at the fixed frequency of 20 kHz. The total flow rate was 30 ml/min and the CH_4/CO_2 ratio was 1. Fig. 3 shows the effect of power on the conversion of CH_4 and CO_2 and yields of H_2 and CO. The conversion of CH_4 and CO_2 increased from 39.28 and 20.21 to 57.63 and 30.95%, 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 electrons, and therefore the possibility to fragment C–H bond in CH_4 molecule or C–O bond in CO_2 molecule could be enhanced. The yield of H_2 and CO also increased with the increasing input power from 80 to 130 W. The effect of power on the product selectivity and H_2/CO ratio was represented in Table 1. H_2/CO ratio kept almost constant with the increasing input power. This indicated that H_2/CO ratio was not greatly affected by input power. The selectivity of light hydrocarbon, CO and H_2 decreased continuously when the input power was increased

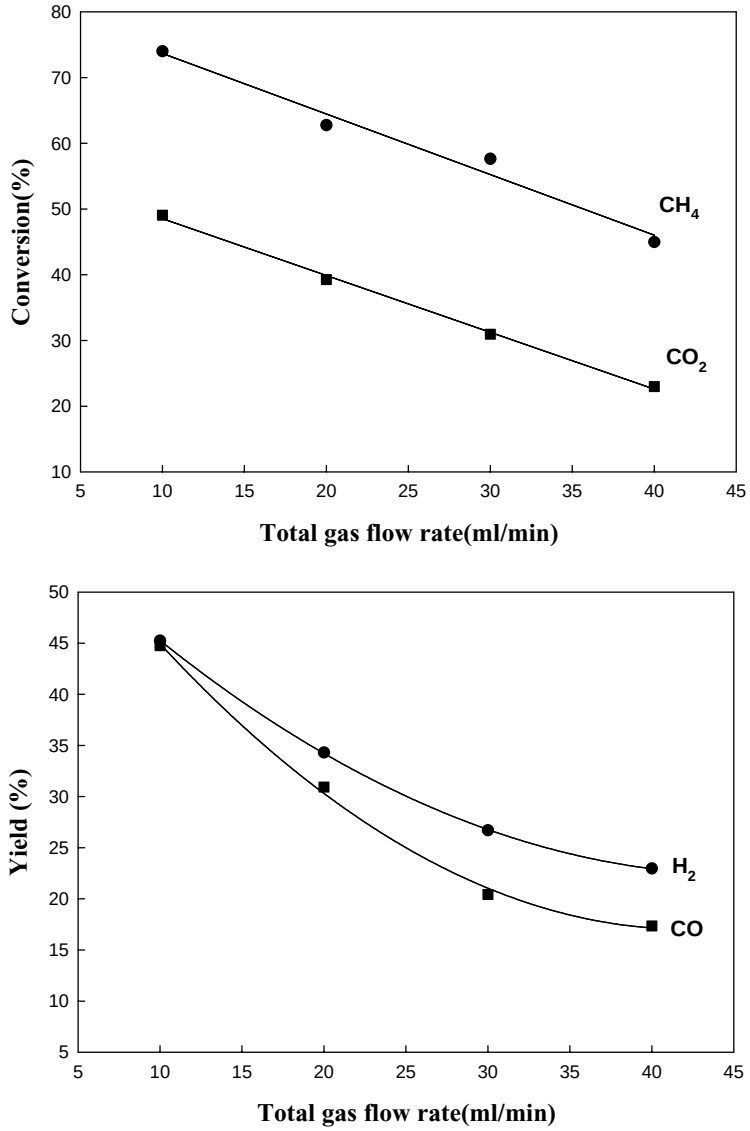

Fig. 4. Effect of flow rate on the conversion of CH_4 and CO_2 and yield of H_2 and CO.

from 80 to 130 W. From above results, it was shown that the increase of the input power was helpful to destroy CH_4 and CO_2 molecule, however it was not converted to other hydrocarbons or syngas.

3.2. Effect of total flow rate

The effect of total flow rate, which was related to the residence time of CH_4 in the reactor, was investigated. Experiments were performed with varying the total flow rate from 10 to 40 ml/min. The input power was 130 W at the frequency of 20 kHz and the CH_4/CO_2 ratio was 1. Fig. 4 shows the effect of total flow rate on the conversion of CH_4 and CO_2 and yield of H_2 and CO. Both the conversion of CH_4 and CO_2 and yield of H_2 and CO decreased rapidly with the increasing input power. The increase of total flow rate reduced the residence time of CH_4 in the reactor, which resulted in reducing the chance of CH_4 molecule to collide with electrons that had enough energy to destroy carbon–hydrogen bond. Product selectivity and H_2/CO ratio was represented in Table 2. H_2/CO ratio increased slightly

Table 1
Effect of input power on product selectivities and H_2/CO ratio (without catalyst)

Power (W)	H_2/CO ratio	Selectivities (%)					
		CO	C2	C3	C4	Carbon sum	H_2
80	1.30	54.64	13.44	6.23	3.90	78.21	53.78
100	1.34	50.53	11.50	5.88	3.89	71.80	51.81
120	1.34	50.94	10.27	5.66	3.36	70.23	52.42
130	1.35	49.17	9.70	5.53	2.99	67.39	51.04

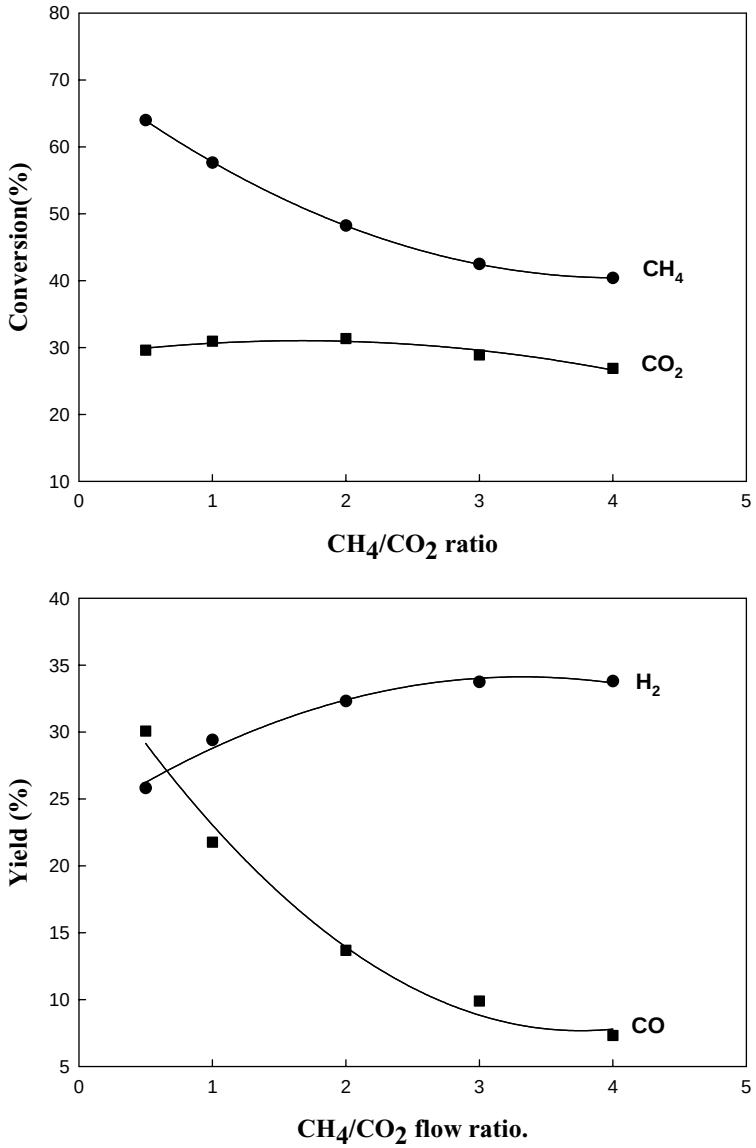

Fig. 5. Effect of CH_4/CO_2 ratio on the conversion of CH_4 and CO_2 and yield of H_2 and CO.

Table 2
Effect of flow rate on selectivities and H_2/CO ratio (without catalyst)

Flow rate (ml/min)	H_2/CO ratio	Selectivities (%)					
		CO	C2	C3	C4	Carbon sum	H_2
10	1.01	73.83	4.84	2.98	1.58	83.23	65.95
20	1.11	60.83	7.79	4.59	2.39	75.60	55.50
30	1.35	49.17	9.70	5.53	2.99	67.39	51.04
40	1.32	51.26	12.53	6.53	3.18	73.50	51.76

from 1.01 to 1.32 with the increasing total flow rate. The selectivity of H_2 and CO highly decreased when the flow rate was increased from 10 to 40 ml/min, while the selectivity of light hydrocarbons increased and especially, C_2 hydrocarbons selectivity increased considerably from 4.84 to 12.53%.

3.3. Effect of CH_4/CO_2 ratio

Under plasma states, atomic oxygen generated by the dissociation of carbon dioxide was helpful to destroy carbon–hydrogen bond. Experiments were carried out with varying the CH_4/CO_2 ratio from 1 to 4. Total flow rate was 30 ml/min. The input power and frequency were 130 W and 20 kHz, respectively. The effect of CH_4/CO_2 ratio on the conversion of CH_4 and CO_2 and yield of H_2 and CO was shown in Fig. 5. The CH_4 conversion decreased rapidly from 64 to 40.4% with the increasing CH_4/CO_2 ratio, but the CO_2 conversion decreased slightly. The yield of H_2 increased from 25.82 to 33.81%, while the yield of CO highly decreased from 30.08 to 7.32% when CH_4/CO_2 ratio increased from 1 to 4. Table 3 shows the effect of CH_4/CO_2 ratio on the hydrocarbon selectivity and H_2/CO. The selectivity was strongly dependent on CH_4/CO_2 ratio. The selectivity of C_2–C_4 hydrocarbons increased significantly and C_2 hydrocarbon selectivity increased from 5.24 to 17.98% with the increase of CH_4 content. The CH_4/CO_2 ratio had a great influence on H_2/CO ratio. H_2/CO ratio was changed from 0.86 to 4.62 with the increasing CH_4/CO_2 ratio. From these results, it was found that CH_4 content of feed gas determined H_2/CO ratio and the higher CH_4 contents produced more C_2–C_4 hydrocarbons.

Table 3
Effect of CH_4/CO_2 ratio on selectivities and H_2/CO ratio (without catalyst)

CH_4/CO_2	H_2/CO ratio	Selectivities (%)					
		CO	C2	C3	C4	Carbon sum	H_2
0.5	0.86	73.85	5.24	2.90	1.45	83.44	62.36
1	1.35	49.17	9.71	5.53	2.99	67.40	51.04
2	2.36	32.21	13.0	7.69	4.33	57.23	50.71
3	3.41	25.47	16.01	9.41	5.72	56.61	54.14
4	4.62	19.50	17.98	10.21	6.21	53.90	53.01

3.4. Effect of Ni/γ-Al_2O_3 catalyst

The effect of 5 wt.% Ni/γ-Al_2O_3 catalyst on the conversion and product selectivity was investigated. Catalysts were packed in the bottom of plasma region. The packing amount of catalyst was 1 g. To examine the effect of support material, experiments using DBD with γ-Al_2O_3 were also performed. The total flow rate was 30 ml/min, with CH_4/CO_2 ratio of 1. The input power and frequency were kept at 130 W and 20 kHz, respectively. Comparisons of methane conversion and product selectivities using DBD with/without catalysts were shown in Fig. 6. When γ-Al_2O_3 was packed in the DBD reactor, CH_4 conversion was decreased from 57.63 to 50.26%, but CO_2 conversion and the selectivity of CO, C_3 and C_4 hydrocarbon were not changed significantly. The selectivity of C_2 and H_2 in Al_2O_3 was improved slightly compared to that in the DBD reactor. When 5 wt.% Ni/γ-Al_2O_3 was packed in the reactor, the selectivity of C_2–C_4 hydrocarbons was increased slightly and CO selectivity was highly enhanced from 49.17 to 60.9%. The CO_2 conversion increased from 30.95 to 33.48%. Similar results were reported by Kado et al. [17]. They showed that the DC pulse plasma with NiMgO catalyst led to an increase of CO selectivity

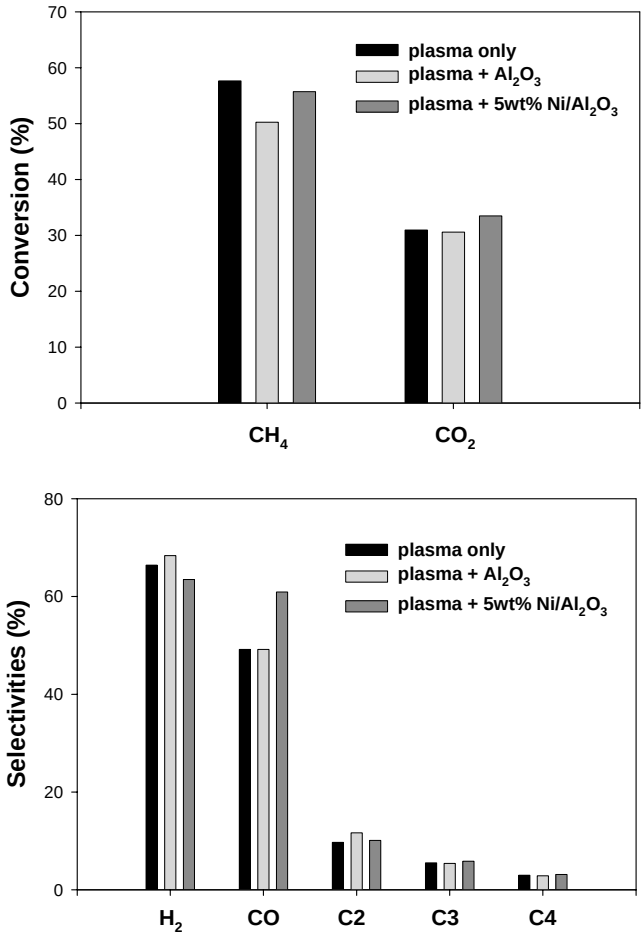

Fig. 6. Comparison of the performance of DBD reactor.

Table 4
Effect of nickel contents

Loading weight (%)	Conversion (%)		H_2/CO ratio	Selectivities (%)					
	CH_4	CO_2		CO	C2	C3	C4	Carbon sum	H_2
2	55.44	32.7	1.06	60.6	9.83	5.90	3.21	79.54	52.25
5	55.71	33.48	1.04	60.9	10.12	5.85	3.15	80.02	51.92
7	55.47	32.61	1.03	63.87	10.6	6.09	3.56	84.12	53.48
10	55.15	32.66	1.06	61.37	10.63	6.20	3.42	81.62	52.98

and CO_2 conversion. From these results, it was thought that Ni/γ-Al_2O_3 played as a catalyst to improve the selectivity of CO and the conversion of CO_2.

3.5. Effect of nickel contents

The effect of nickel contents on the conversion and product selectivity was investigated. To examine the effect of different loading weight of nickel, experiments were carried out with varying the loading weight of nickel from 2 to 10 wt.%. All experimental conditions were the same as above. Experimental results were shown in Table 4. There had no significant change in the conversion of CH_4 and CO_2. When the plasma was applied with 7 wt.% Ni/γ-Al_2O_3 catalyst, the selectivity of syn-gas and C_2–C_4 hydrocarbons had the highest value, but the differences were very small. From this result, it was shown that the loading weight of nickel had no effect on the conversion and product distribution.

4. Conclusions

A study of methane conversion from CO_2 reforming of methane using dielectric barrier discharge over Ni/γ-Al_2O_3 catalyst was performed. The main products of methane conversion were CO, H_2, C_2H_6, C_3H_8, and C_4H_{10}. Noticeable liquid products were not formed in our system. The input power, total flow rate, and CH_4/CO_2 ratio were the key factors to conversion, yield and product selectivity. Carbon dioxide and methane conversions were greatly affected by the input power and the total flow rate. CH_4/CO_2 ratio played an important role on H_2/CO ratio. Ni/γ-Al_2O_3 catalyst had a great effect on the CO selectivity and CO_2 conversion.

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