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TiO_2-Coated Electrode for Plasma Dry Reformer for Synthesis Gas Production in Ambient Conditions

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ABSTRACT

Conversion of methane to syngas via plasma technology is a cost-effective approach to obtaining syngas. Methane conversion by means of ceramic electrodes was significantly increased. In plasma reformer, while electrical discharge is available in gas, very active species such as electrons, radicals, ions, atoms, and excited molecules are produced and they function as catalysts. Methane and carbon dioxide gases at atmospheric temperature and pressure in the non-thermal with TiO_2-coated electrode plasma reactor with an inner diameter of 9 mm are converted to hydrogen and carbon monoxide (syngas) through one chemical step. The main objective of this research was to investigate the effects of changes in feed flow rate and feed ratio on methane conversion and product selectivity, as well as product distribution. Furthermore, the results were obtained when three synthesized catalysts were inserted in a section (3 mm) of plasma length (100 mm). The obtained results demonstrated that the voltage of 15 kV was required for methane conversion and hydrogen production. Reducing voltage and/or increasing the partial pressure ratio of methane to carbon monoxide in the reactor inlet resulted in the reduction of methane conversion rate. Moreover, according to the findings, increasing the ratio of carbon dioxide to methane would increase methane conversion and consequently, decrease the conversion of carbon dioxide. The conversion of methane and carbon dioxide was higher for co-precipitated Ce-Mn oxide support than those using the two other methods.

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1. INTRODUCTION

Synthesis gas is a mixture of hydrogen and carbon monoxide and it is used functions as a primary material in the chemical industry (such as methanol synthesis, Fischer-Tropsch process, etc.) and food production. It is also used as the main energy carrier in fuel cells. Available processes including catalytic steam reforming, dry reforming, and partial oxidation at high temperatures require specific costly conditions to produce synthesis gas. Therefore, in order to reduce cost, energy, and time, non-thermal (cold) plasma is used [1, 2].

Among the different types of plasma, cold plasma creates an ideal tool for starting the reaction due to its non-equilibrium feature and availability of operating in atmospheric pressure and temperature. Cold plasma has been highly implemented by researchers due to its high reactivity and good performance at low temperatures. Applications of plasma include surface etching, fabrication, coating, air purification, ozone production, desulfurization, and plasma TVs [3].

Active plasma creation would lead to the formation of free radicals, ions, and excited molecules and in the desired process, the most significant result would be the formation of H_2 and CO gas molecules from mixtures of methane and carbon dioxide. Materials are divided into four categories in terms of phases including solid, liquid, gas, and plasma. The solid, liquid, and gas materials are

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different in their adhesion forces of their constituent molecules. By heating solids or liquids, atoms with molecules obtain the heat energy they need to overcome the intermolecular adhesion force and become liquid or gas. If enough energy was given to the gas, the kinetic energy of the particles would increase. Due to the collision of particles whose kinetic energy was higher than the adhesion energy inside the molecules with gaseous particles, the gas molecules would gradually gain enough energy to overcome the intermolecular forces and be converted into their constituent atoms. At this point, if more energy is given to the gas, the gas atoms receive the energy required to overcome the forces holding the outermost electrons to become ionized gas or plasma. This conversion of gas to plasma is not a phase change, but only a transformation that occurs gradually with an increase in the temperature of the material (kinetic energy) [3, 4].

In some low-pressure conditions, the effect of the electromagnetic field on the motion of the particles in the plasma can be greater than that of the collision between the particles, hence forming the non-collision plasma. Given that ionization in plasma occurs due to the collision between the energetic electron particles and heavier ones, if plasma is generally viewed away from the charge accumulation regions, a high degree of freedom for the plasma environment can be achieved which is in fact the strength of the plasma [5, 6].

In other words, a system with high degrees of freedom and the most economical results obtained from using plasma reactors can be obtained with negatively charged natures, which are almost equal and because of this, plasma forms a quasi-neutral environment. The concept of plasma quasi-neutrality becomes clearer in correlation with the concepts of Debye protection and Debye length [5, 7].

Although plasma is electrically neutral, it incorporates both positive and negative particles. The same positive and negative particles create electric currents and subsequently, an electric field as they move; therefore, each particle is affected by the electric field of other particles. In this regard, the following steps should be noted.

1- Reduce the fixed investment costs;
2- Reduce the payback time;
3- Determine the flexibility of the operating unit to convert a wide range of hydrocarbons; and
4- Produce the synthetic gas at different CO/H_2 ratios and meet the feed needs of a wide range of petrochemicals [8, 9].

Table 1 briefly shows the previous research works based on the types of used plasma, power consumption, feed flow rates, and their results on methane and CO_2 conversions as well as hydrogen and carbon monoxide selectivity and the energy efficiency of a plasma reactor for gas conversion. Compared to DBD methods, power is observed to be more suitable and the rate of methane conversion with low energy consumption in this work is competitive with other works. The energy efficiency is defined in the following equation [9]:

$$E(\text{mmol/kJ}) = [CH_4 \text{ converted (mmol)} + CO_2 \text{ converted (mmol)}] / \text{Power (W)} \quad (1)$$

Here, environmentally benign TiO_2 coating is prepared using a Physical Vapor Deposition (PVD) technique, allowing for an improvement in the efficiency of the electrode [10]. This study reports the methane conversion in plasma reactor with TiO2-coated electrode. The main objective of this study is to investigate the effect of the voltage, partial pressure change of argon and methane, and changes in the feed flow rate on methane conversion and product selectivity as well as product distribution and energy efficiency in an in-house manufactured plasma reactor with TiO_2-coated electrode.

2. EXPERIMENTAL PROCEDURE

2.1. Plasma methane reformer

In methane dry reforming, a comprehensive device was designed to produce hydrogen and carbon monoxide with cold plasma, the details of which are discussed in the following. For dry methane reforming and reactor test, argon, carbon dioxide, methane, and hydrogen gases with purity of 99.99% were used.

- **Transformers**

In this reactor, the minimum required voltage for methane dry reforming to produce syngas is 15 kV. To this end, a DC transformer was utilized. Due to the quite high voltage of the transformer outputs, the following points must be carefully observed:

a. If there is a transformer earth wire, the relevant wire must be connected to the standard earth and in transformers with earth wire, none of the outputs should be connected to the body. Any failure to do so would damage the transformer and reduce efficiency.
b. A radial distance of at least one centimeter is required for each of the transformer outputs relative to the other wires or any other metals. Therefore, it is not allowed to use clamps to connect the cables to each other or to the body.
c. The longer the length of the ignition wires, the higher the current drop and leakage, hence causing a severe reduction in the output power at the electrodes.
d. Special coated cables are used to connect the transformer to the electrode.

TABLE 1. Comparison of energy efficiency of dry reforming and different plasma sources

Plasma	Power (W)	Feed Flow (ml/ min)	Conversion (%)		Selectivity (%)		E (mmol/kJ)	Ref.
			CH_4	CO_2	H_2	CO		
DBD	50	50	56.4	30.2	31	52.4	0.32	[8]
DBD	500	500	40	20	-	88.5	0.18	[7]
DBD	100	60	64.3	43.1	-	32.2	0.26	[5]
Pulsed Corona	42	25	63.7	60.2	-	62.6	0.26	[6]
RF	30.6	100	31	24	100	20	0.68	[11]
RF	36.2	200	65.9	57.8	-	85.9	2.4	[12]
DC Corona	45	60	80	70	84	87	0.74	[13]
Plasma jet	69.85	2200	61	50	89.3	72.6	12.2	[14]
DBD	175	20	75	50	72	85	0.05	[15]
DBD	75	60	40	25	40	-	0.19	[16]
Pulsed DBD	12	22.5	30.1	20	32.1	44.4	0.13	[17]
Glaiding Arc	165	7500	13.1	8.4	31.4	69.5	3.1	[9]
C DBD	50	62	55.28	52.16	75.82	74.37	0.32	This work

- **Reactor tests in quartz plasma reformer**

The system employs three Brooks mass flow controllers to measure and control the gas flow rate in the range of 0 to 200 ml/min with high accuracy. This device is also able to read information by a computer. Prior to entering the reactor, a gas mixer is utilized. A quartz tubular reactor with an internal diameter of 9 mm in atmospheric conditions was used to perform reactor tests and determine plasma activity, as shown in Figure 1. The structure of this reactor consists of two electrodes. The applied electrodes in this reactor are made of stainless steel which is a rod electrode with an diameter of 1.5 mm inside the reactor coated with titanium oxide and a spiral electrode with a diameter of 1 mm outside the reactor. Inlet gases enter from the top of the reactor and after colliding with the plasma, a reforming reaction takes place. In some experiments, both catalyst and plasma are simultaneously used. The volume of the input feed has considerable effect on the reaction. The product is taken out of the bottom of the reactor and after passing through the cold trap, it is transferred to the gas chromatograph for further analysis. Exhaust gases from the reactor have some moisture. In order to liquefy the product gases, they are injected into the circulator and after leaving, this dry gas is transferred to the chromatograph and the components of the gas composition are determined.

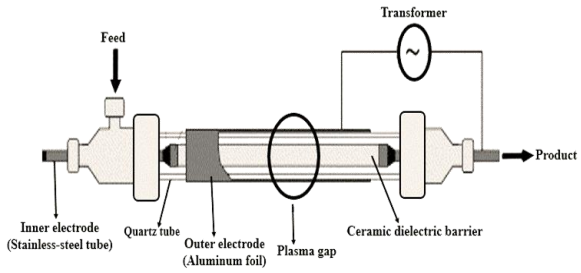

Figure 1. Plasma reformer by ceramic dielectric barrier

- **Gas chromatograph**

Shimadzu gas chromatography device was utilized to determine the feed composition and percentage of products. To analyze the products and feed input in the dry methane reforming process, a TCD detector with a filled Carbosieve column was used. To analyze the registered chromatograms, Chromanit software was also employed that could calculate the height and surface area below the peak and estimate the percentages of area and volume for each gas sample.

The circulator device was designed and built for cooling the cold trap and condensing the vapor products in reactor effluent based on the Carnot cycle. In this cycle, 134a refrigerant gas enters the condenser after leaving the compressor. After cooling, the gas flows to the evaporator to be cooled by the installed fan. The mechanical components include compressor, condenser, filter (dryer), capillary tube, and evaporator.

The conversion rates of methane and carbon dioxide as well as hydrogen and carbon monoxide yield were obtained from the following equations [8]:

$$\text{Methane conversion: } X_{CH_4} = \frac{CH_{4\,(in)} - CH_{4\,(out)}}{CH_{4\,(in)}} \times 100\% \quad (2)$$

$$\text{Carbon dioxide conversion: } X_{CO_{2\,(in)}} = \frac{CO_{2\,(in)} - CO_{2\,(out)}}{CO_{2\,(in)}} \times 100\% \quad (3)$$

$$H_2 \text{ yield: } \frac{H_{2\,(out)}}{2CH_{4\,(in)}} \times 100\% \quad (4)$$

$$\text{CO selectivity: } \frac{CO_{(out)}}{CH_{4\,(in)} + CO_{2\,(in)}} \times 100\% \quad (5)$$

2.2. TiO_2 ceramic dielectric barrier

Commercial titanium dioxide nanoparticles were purchased from Degussa Korea (Incheon, Korea). The PVD parameters are as follows: a working pressure of 7×10^3 Torr, an RF sputtering power of 200W, a deposition time of 180 min, and a bias voltage of -140 V.

Figures shows a cross-sectional SEM image of the TiO^2 coated, indicating the formation of thin (1.2 μm) and compact coating layers which homogeneously cover the surface of the electrode. Figure 2 shows the Scanning Electronic Microscopy (SEM) images of TiO_2 nanoparticles at different scales and surfaces of electrodes coated with TiO_2 nanoparticles. As shown in Figure 2, nanoparticles have good uniformity hence a suitable and acceptable function as a dielectric barrier.

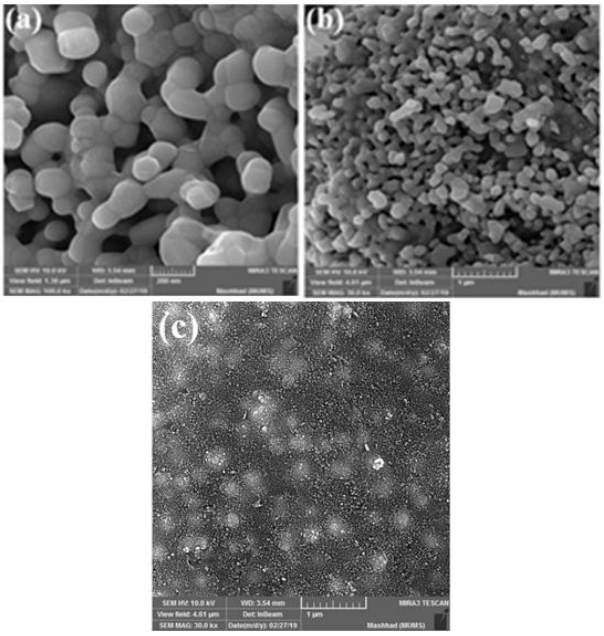

Figure 2. SEM image of TiO_2 nanoparticles on different scales (a) 200 nm (b) 1 μm (c) Surface of electrode coated with TiO_2 nanoparticles

3. RESULTS AND DISCUSSION

The results in Figs. (3-4) show that with an increase in the ratio of CO_2 to CH_4 from 0.5 to 3, methane and carbon dioxide conversion rates would increase and decrease, respectively. In addition, with an increase in CO_2/CH_4, a decrease in the H_2/CO ratio was observed mainly due to the effect of the reverse side reaction of water-gas shift, which is generally more at low CO_2/CH_4 ratios. At high CH_4/CO_2 ratios and temperatures, high methane conversion from the main dry reforming reaction could reduce the amount of sedimentary carbon generally obtained from methane decomposition; however, at a CH_4/CO_2 ratio higher than 1, due to adverse reactions such as reverse Bodouard reaction and reverse water-gas displacement, H_2/CO ratio would decrease. To ensure an H_2/CO ratio close to 1, the CH_4/CO_2 ratio should be set to less than 1.

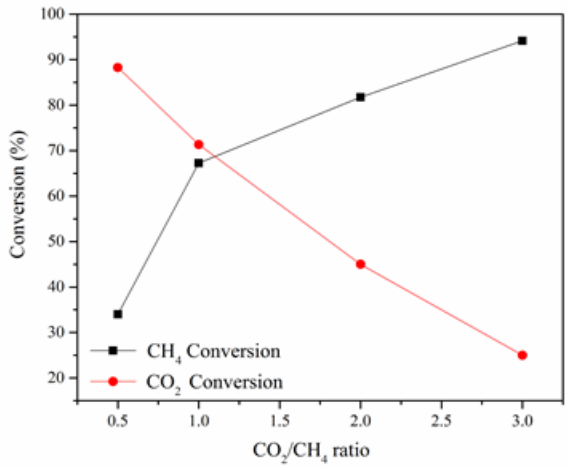

Figure 3. Effect of feed ratio on methane carbon dioxide and conversion

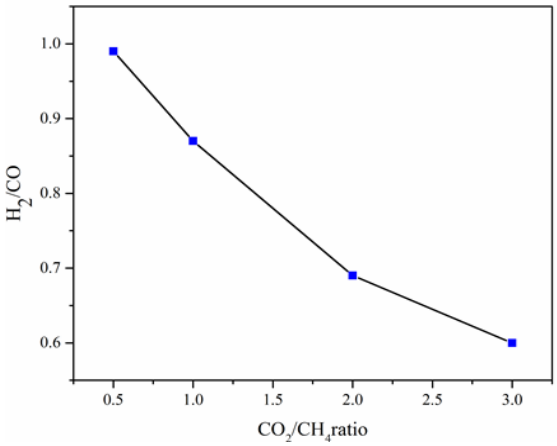

Figure 4. The effect of feed ratio on H_2/CO ratio

Of note, the desired results were obtained when three synthesized catalysts were inserted in a section of 3 mm with a plasma length of 100 mm. Figure 5 (a and b) shows the results of the stability test, i.e., CO_2 and CH_4 conversions versus time on stream for plasma reaction in the presence of nickel (10%wt.) supported on $Ce_{0.95}Mn_{0.05}O_2$ catalysts by means of (a) sol-gel, (b) co-precipitation, and (c) hydrothermal methods. As observed in these figures, the plasma environment can produce syngas for a long time and no noticeable decrease is observed in the performance of the reformer. The co-precipitated catalyst support has more activity than the two other method synthesized supports.

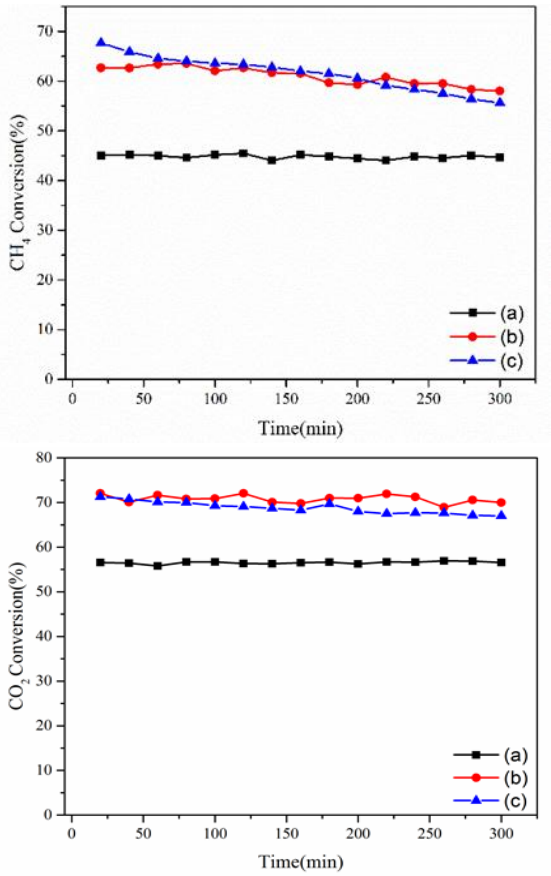

Figure 5. Conversion rate of methane and carbon dioxide for plasma assisted with 10Ni / $Ce_{.95}Mn_{.05}O_2$ catalyst synthesized by (a) sol-gel, (b) co-precipitation, and (c) hydrothermal methods

As shown in Figure 6, the results of CH_4 conversion are compared in the presence and absence of TiO_2 coating on the electrode. The results show that coating the electrode with TiO_2 would increase the conversion of CH_4 to a desirable amount.

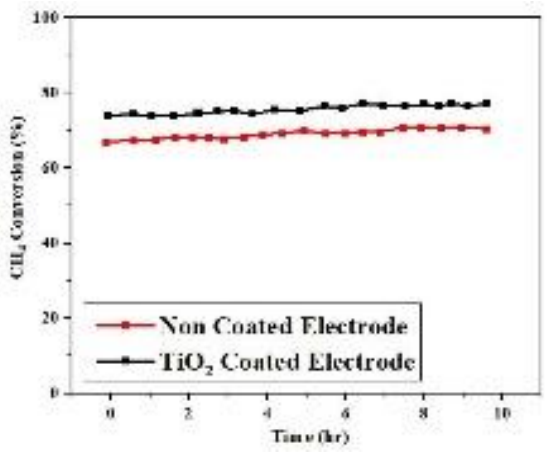

Figure 6. Time on stream for methane conversion

4. CONCLUSION

The present study investigated the dry reforming of methane with plasma. Numerous technologies have been used so far to convert methane as the main constituent of natural gas. The obtained results indicated that a 15 kV voltage was required for methane conversion and hydrogen production. Reducing the voltage and/or increasing the partial pressure ratio of methane to carbon monoxide in the reactor inlet led to a reduction in the rate of methane conversion. According to the findings, increasing the ratio of carbon dioxide to methane would increase methane conversion and decrease the carbon dioxide conversion. Given the structural properties and the results obtained from the catalytic activity of the samples, it can be concluded that the catalyst prepared by the co-precipitation method outperformed other samples. The rates of methane and carbon dioxide conversion were higher for co-precipitated Ce-Mn oxide support than those of the two other methods.

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