CO_2 reforming of CH_4 by the combination of dielectric barrier discharge plasma and zeolite catalysts

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ABSTRACT

Dry reforming of methane that converts two green-house gases (CH_4 and CO_2) to syngas (mixture of CO and H_2) has gained a great research interests. Several technologies were proposed for CO_2 reforming of CH_4, such as catalytic conversion, plasma conversion and combination of catalyst and plasmas [1]. Recently, the combination of plasmas and heterogeneous catalysis for fuel production from CH_4 reforming has attracted the increasing interest [2-3]. In this research, we investigated the CO_2 reforming of CH_4 to syngas by the combination of dielectric barrier discharge (DBD) plasmas and zeolite catalyst particles. The experimental results showed that the conversion efficiencies of CO_2 and CH_4 using the combination of plasma and zeolite catalysts are higher than those by using plasma only.

Keywords: plasmas, zeolite catalyst, dielectric barrier discharge, CO_2 reforming of CH_4, syngas.

1 INTRODUCTION

The CO_2 reforming of methane to syngas has become an interesting topic recently, because it offers some enviromental benefits such as removal of two greenhouse gas and processing natural gas sources with a high rate of carbon dioxide conversion [1-4]. The ratio of H_2/CO product gases in this process is close to 1/1 which is appropriate for the production of Fischer-Tropsch liquid hydrocarbon and oxygenates. Several technologies were proposed for CO_2 reforming of CH_4 such as catalytic conversion, plasma conversion and combination of catalyst and plasmas [1].

In the catalytic reforming of CO_2 and CH_4, the carbon deposition which leads to deactivation of catalysts is a big problem. There are many research projects to find the anti-carbon deposition performance of castalysts such as the addition of promoters [5-11], preparation of support materials [12,13], the conditions of catalysts preparation and the studies on reforming mechanisms [14].

In another process, CO_2 reforming of CH_4 has been investigated also by applying the plasma technologies such as thermal plasma, dielectric barrier discharge, corona discharge, AC arc discharge and glow discharge. The plasma process showed high chemical activity and short reaction times and also low opreating costs and easy realizations. Recently, to improve the conversion of plasma process, the combination of plasma and heterogeneous catalysis for the CO_2 reforming of methane has attracted increasing interest [2-3].

In this research, we investigated the CO_2 reforming of CH_4 to syngas by two processes including the plasma process only and the DBD process with zeolite catalyst particles. The effects of several experimental variables such as the applied voltage and total gas flow rate were investigated. The compositions of feed and product gas streams were analyzed by gas chromatography (GC). The experimental results showed that the conversions of CH_4 and CO_2 in the DBD process with zeolite catalyst particles are higher than those of CH_4 and CO_2 in the plasma reforming process only.

2 EXPERMENTAL

The CO_2 reforming of methane was performed by using a plasma reactor as shown in Fig. 1. In another process, we packed zeolite particles in the plasma reactor as shown in Fig. 2.

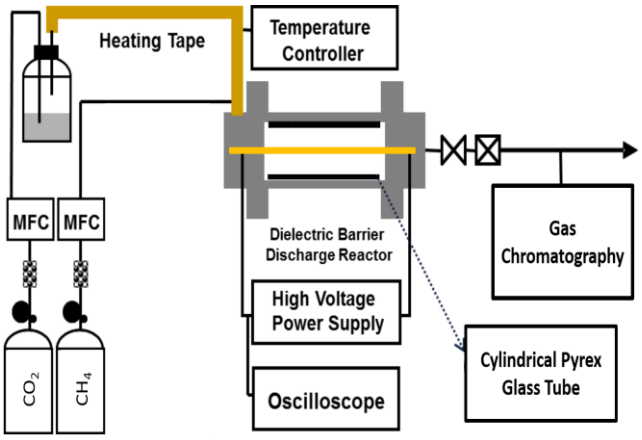

Figure 1: Schematic of experimental setup to CO_2 reforming of methane by the plasma process.

Before packing in the reactor tube, the zeolite particles were treated in a high temperature furnce at 500 ºC for 2h. A cylinder-wire-type reactor was used to generate DBD. A copper rod of diameter 5 mm was kept at the center of

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cylindrical Pyrex glass tube as a power electrode and the outside wall of reactor was covered with stainless steel mesh as a ground electrode. A high voltage was applied to the power electode to generate DBD. All the gas flow rates were controlled by MFCs. The CO_2 and CH_4 gas streams were mixed well before passing through the reactor.

To analyze the reforming CO_2 of CH_4 to syngas by those processes, we changed the process variables including the voltage applied to reactor and total gas flow rate. All experiments were carried out at 1 atm and 298 K. The product gases were collected after 40 minutes of reaction at the reactor outlet by T-bags. All the experiments on CO_2 reforming by CH_4 were repeated 3 times for each condition. The concentrations of CO_2, CH_4 and product gases were measured by a YL6100 GC equipped with a pulse discharge detector. Carbonxen™ 1010 PLOT was used in GC column, the column temperature was 120°C and the flow rate of the carrier gas (He) was 25 mL/min. For each sample, we injected 80 ml gas to GC in 3 times and we took the average values to determine the concentrations of products.

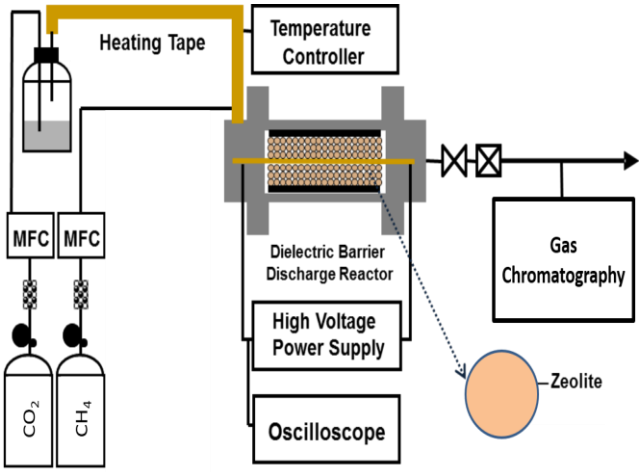

Figure 2: Schematic of experimental setup for CO_2 reforming of methane by combination of DBD and zeolite catalysts.

3 RESULTS AND DISCUSSION

The main reaction of CO_2 reforming of methane is a endothermic reaction[15]:

$CO_2 + CH_4 \rightarrow 2H_2 + 2CO \quad \Delta H^0 = 247$ kJ/mol (1)

In this reaction, the energy supplied to the reaction and the total flow rate are very important for the conversion of CO_2 and CH_4. In this study, we investigated the effects of applied voltage and the total flow rate by the plasma only process and the DBD process with catalysts.

By the GC analysis, it is found that the product gases consist of H_2, CO, CH_4, and CO_2. After the plasma reaction, there is still a little carbon powder left in the reactor. According to the analysis of products, the overall conversions and selectivity are defined as:

CH_4 conversion(%) = (moles of CH_4 converted/moles of CH_4 introduced) x 100

CO_2 conversion(%) = (moles of CO_2 converted/mole of CO_2 introduced) x 100

H_2 selectivity (%) = [moles of H_2 produced/(2 x moles of CH_4 converted)] x 100

CO selectivity (%) = [moles of CO produced/(moles of CH_4 converted + moles of CO_2 converted)] x 100

H_2/CO = moles of H_2 produced/moles of CO produced.

3.1 Effect of applied voltage for the plasma only process and the DBD process with catalysts.

The effect of voltage applied to the plasma processes was investigated by varying the applied voltage from 2 kV to 12 kV. We kept the total flow rate of 0.6 l/min, frequency appied to plasma of 900 Hz and ratio of CO_2 and CH_4 molar flow rate of 1/1. The results are shown in Fig. 3 and Fig. 4.

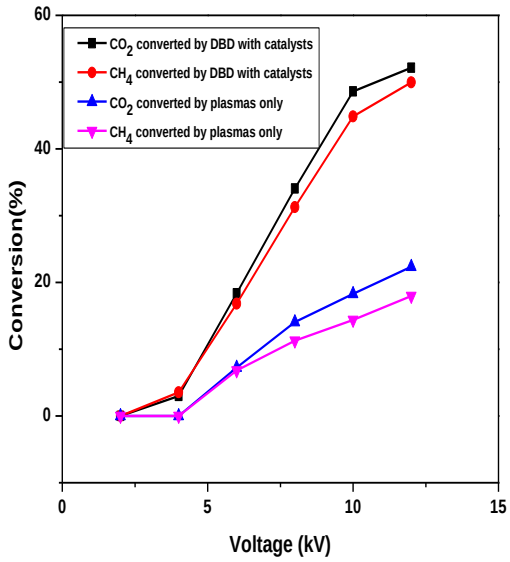

Figure 3: Conversions of CO_2 and CH_4 as a function of applied voltage by the plasma process and DBD process with catalysts, respectively.

In Fig. 3, as the applied voltage increases from 2 kV to 12 kV, the conversion of CO_2 increases from 0% to 22.35% with plasma process and from 0% to 52.15% with the DBD process with catalysts and the conversion of CH_4 increases from 0% to 17.98% with plasma process and from 0% to 49.98% with the DBD process with catalysts. As the applied voltage increases, the energy supplied to the plasma generation increases and the conversions of CO_2 and CH_4

increase. Because of the combined effects of plasmas and catalysts, the conversions of CO_2 and CH_4 with the DBD process with catalysts were higher than those with the plasma process only,

Fig. 4 shows the changes of CO and H_2 selectivities as a function of applied voltage to the processes. In the process with plasma only, the selectivities of CO and H_2 increase rapidly as the applied voltage increases from 4kV to 10kV, while the selectivities of CO and H_2 decrease as the applied voltage increases from 10kV to 12kV, because the reaction rates of unwanted side-reactions increase with the increase of applied voltage at high voltage [16]. In the similar conditions, the selectivities of CO and H_2 in the DBD process with catalysts increase more slowly than those of CO and H_2 in process of plasmas only, because of the uniform arrangement of plasma energy on the zeolite particles.

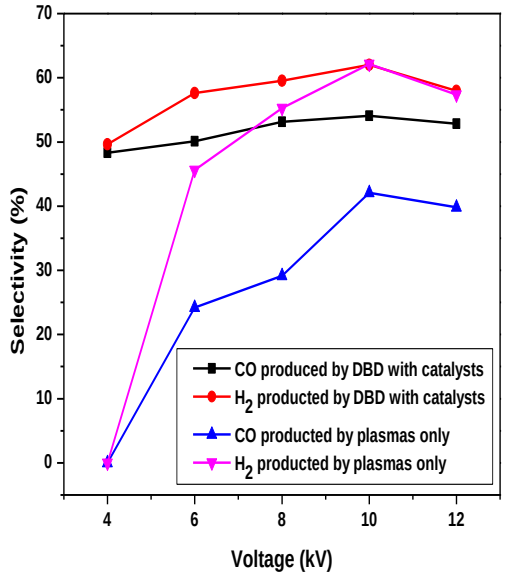

Figure 4: Selectivities of CO and H_2 as a function of applied voltage for the plasma process and the DBD process with catalysts, respectively.

3.2 Effect of total flow rate for the plamsa process and the DBD process with catalysts.

In these experiments, we investigated the effect of total flow rate on conversions and selectivites of CO_2 and CH_4. The applied voltage and frequency were kept constant at 10 kV and 900Hz, respectively.

As shown in Fig. 5 and Fig 6, the conversions of CO_2 and CH_4 decrease with the increase of total flow rate, while the selectivities of CO and H_2 were almost kept constant. As the total gas flow rate increases, the residence times of CO_2 and CH_4 in the reactor increase and the conversions of CO_2 and CH_4 decrease, because of the shorter reaction times. The selectivities of CO and H_2 in those processes were almost constant, because the energy supplied for plasma reaction was almost constant for the total flow rate in these experiments.

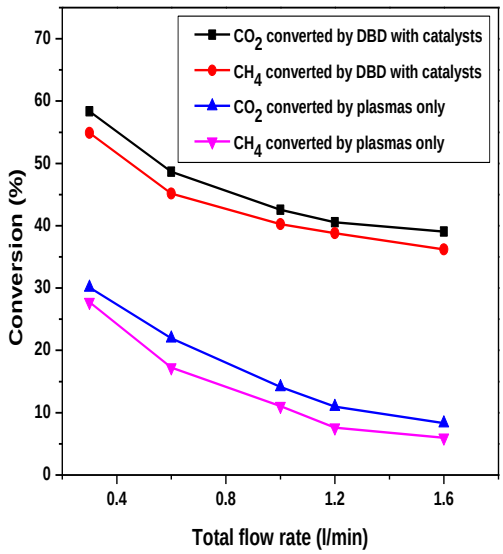

Figure 5: Conversions of CO_2 and CH_4 as a function of total flow rate for the plasma process and the DBD process with catalysts, respectively.

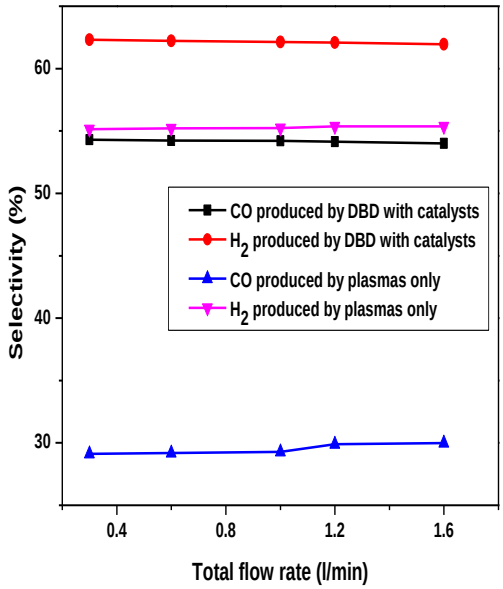

Figure 6: Selectivities of CO and H_2 as a function of total flow rate for the plasma process and the DBD process with catalysts, respectively.

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4 CONCLUSIONS

In this study, CO_2 reforming of CH_4 to syngas has been investigated for two different processes, the plasma process and the DBD process with catalysts. Based on this study, we found that both processes are effective in converting CO_2 and CH_4 into syngas. The product gases are mainly composed of H_2 and CO without considerable generation of byproducts. The conversions of CO_2 and CH_4 are largely dependent on the applied voltage and the total gas flow rate of CO_2 and CH_4. Compared to the process using the plamsas only, the DBD process with catalysts has the advantages of higher conversion and treatment capacity.

ACKNOWLEDGEMENTS

This work was supported by the Regional Innovation Center for Environmental Technology of Thermal Plasma (ETTP) at Inha University, designated by MKE (2009). Instrumental analysis was supported from the central laboratory of Kangwon National University.

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