CO\textsubscript{2} reforming of CH\textsubscript{4} by the combination of dielectric barrier discharge plasma and zeolite catalysts

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ABSTRACT

Dry reforming of methane that converts two greenhouse gases (CH\textsubscript{4} and CO\textsubscript{2}) to syngas (mixture of CO and H\textsubscript{2}) has gained a great research interests. Several technologies were proposed for CO\textsubscript{2} reforming of CH\textsubscript{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\textsubscript{4} reforming has attracted the increasing interest [2-3]. In this research, we investigated the CO\textsubscript{2} reforming of CH\textsubscript{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\textsubscript{2} and CH\textsubscript{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\textsubscript{2} reforming of CH\textsubscript{4}, syngas.

1 INTRODUCTION

The CO\textsubscript{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\textsubscript{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\textsubscript{2} reforming of CH\textsubscript{4} such as catalytic conversion, plasma conversion and combination of catalyst and plasmas [1].

In the catalytic reforming of CO\textsubscript{2} and CH\textsubscript{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\textsubscript{2} reforming of CH\textsubscript{4} has been investigated also by applying the plasma technologies such as thermal plasma, dielectric barrier discharge, corona discharge, AC are discharge and glow discharge. The plasma process showed high chemical activity and short reaction times and also low operating costs and easy realizations. Recently, to improve the conversion of plasma process, the combination of plasma and heterogeneous catalysis for the CO\textsubscript{2} reforming of methane has attracted increasing interest [2-3].

In this research, we investigated the CO\textsubscript{2} reforming of CH\textsubscript{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\textsubscript{4} and CO\textsubscript{2} in the DBD process with zeolite catalyst particles are higher than those of CH\textsubscript{4} and CO\textsubscript{2} in the plasma reforming process only.

2 EXPERIMENTAL

The CO\textsubscript{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\textsubscript{2} reforming of methane by the plasma process.

Before packing in the reactor tube, the zeolite particles were treated in a high temperature furnace at 500 °C 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
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 electrode 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.

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 applied 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.

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3 RESULTS AND DISCUSSION

The main reaction of CO$_2$ reforming of methane is an endothermic reaction[15]:

$$\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{H}_2 + 2\text{CO} \quad \Delta H^0 = 247 \text{ kJ/mol}$$

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.

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Figure 2: Schematic of experimental setup for CO$_2$ reforming of methane by combination of DBD and zeolite catalysts.

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increase. Because of the combined effects of plasmas and catalysts, the conversions of CO\textsubscript{2} and CH\textsubscript{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\textsubscript{2} selectivities as a function of applied voltage to the processes. In the process with plasma only, the selectivities of CO and H\textsubscript{2} increase rapidly as the applied voltage increases from 4kV to 10kV, while the selectivities of CO and H\textsubscript{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 [16]. In the similar conditions, the selectivities of CO and H\textsubscript{2} in the DBD process with catalysts increase more slowly than those of CO and H\textsubscript{2} in process of plasmas only, because of the uniform arrangement of plasma energy on the zeolite particles.

![Figure 4](image1.png)

Figure 4: Selectivities of CO and H\textsubscript{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 plasma process and the DBD process with catalysts.

In these experiments, we investigated the effect of total flow rate on conversions and selectivities of CO\textsubscript{2} and CH\textsubscript{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\textsubscript{2} and CH\textsubscript{4} decrease with the increase of total flow rate, while the selectivities of CO and H\textsubscript{2} were almost kept constant. As the total gas flow rate increases, the residence times of CO\textsubscript{2} and CH\textsubscript{4} in the reactor increase and the conversions of CO\textsubscript{2} and CH\textsubscript{4} decrease, because of the shorter reaction times. The selectivities of CO and H\textsubscript{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](image2.png)

Figure 5: Conversions of CO\textsubscript{2} and CH\textsubscript{4} as a function of total flow rate for the plasma process and the DBD process with catalysts, respectively.

![Figure 6](image3.png)

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4 CONCLUSIONS

In this study, CO\textsubscript{2} reforming of CH\textsubscript{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\textsubscript{2} and CH\textsubscript{4} into syngas. The product gases are mainly composed of H\textsubscript{2} and CO without considerable generation of byproducts. The conversions of CO\textsubscript{2} and CH\textsubscript{4} are largely dependent on the applied voltage and the total gas flow rate of CO\textsubscript{2} and CH\textsubscript{4}. Compared to the process using the plasmas only, the DBD process with catalysts has the advantages of higher conversion and treatment capacity.

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REFERENCES