22P029-P

Dry Reforming of methane using atmospheric pressure non-thermal plasma
大気圧非平衡プラズマを用いたメタンのドライリフォーミング

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Dry reforming of methane was investigated using atmospheric pressure non-thermal plasma generated by the microwave discharge. Analysis of optical emission spectra and FTIR spectra indicated that methane and carbon dioxide could be decomposed and converted into hydrogen and carbon monoxide in the plasma. Acetylene was also detected as the hydrocarbon compounds in the product gases. The experimental results shown that the H_2/CO ratio can be controlled by adjusting the CH_4/CO_2 ratio in the gas feed.

1. Introduction

Dry reforming is utilized in producing hydrogen and carbon monoxide from methane with carbon dioxide. The synthesis gas, a mixture of hydrogen and carbon monoxide, is an important intermediate for various synthesizing chemicals. Therefore, several techniques were proposed to the dry reforming of methane, such as catalysis conversion, plasma conversion and combination of catalyst and plasma [1-4]. Plasma chemical conversion is effective methods for the dry reforming of methane. The objective of this work is to investigate the dry reforming of methane using atmospheric pressure non-thermal plasma generated by our self-designed microwave discharge system.

2. Experimental

Experimental apparatus is illustrated in Fig. 1(a). The experiment was performed in a stainless steel cylindrical chamber, which contains stainless steel pipe surrounding a quartz discharge pipe (20mm inner diameter) placed along the chamber axis. A slit (60mm length, 5mm width) was arranged on each aluminum pipe as shown in Fig. 1(b). The length of the slit was chosen as half the wavelength of the microwave. A gaseous mixture of CO_2, and CH_4 was mixed with Ar gas which was used as the plasma forming gas and fed to the quartz tube under atmospheric pressure. When the microwave is introduced into the chamber through a waveguide, non-thermal plasma is produced in the quarts tube.

The products after reaction were identifies by use of FTIR spectrometer (JASCO, FT/IR4000). The exhaust gas from the microwave plasma was collected at the end of quartz tube and analyzed by FTIR spectrometer as shown in Fig. 1. The emission spectra in the discharge region were measured with the multi-channel monochrometer (Ocean Optics HR2000CG-UV-NIR), spectral resolution 0.75nm, and spectral range 200-1000nm. Optical emission is collected along the radial position through a view port on the side of the chamber using a lens-optical fiber combination.

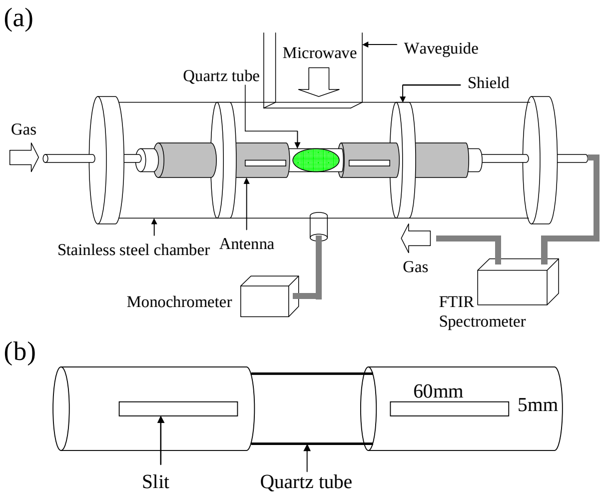

Fig.1. Schematic diagram of experimental set-up

3. Results and discussion

3.1. *Product by the plasma conversion*

The typical FTIR spectra after the plasma processing and the typical optical emission spectra are shown in Fig. 2 and Fig. 3, respectively. The experiment were worked at conditions of Ar flow rates 6.0 ml/min, CH_4 flow rates 0.07 ml/min, CO_2 flow rates 0.08 ml/min and microwave power

900W.

We can confirm that methane and carbon dioxide can be converted into hydrogen and carbon monoxide by atmospheric non-thermal plasma processing from Fig. 2 and Fig. 3. Moreover, acetylene (C_2H_2) was also detected as the hydrocarbon compounds in the tail gas as shown in Fig. 2. The optical emission spectra (Fig. 3) indicate that hydrogen atom (H) and hydrocarbon (CH) also exist in the plasma. Thus, the production of acetylene by the plasma is considered as follows.

$$CH_4 \rightarrow CH_3 + H$$
$$CH_3 \rightarrow CH_2 + H$$
$$CH_2 \rightarrow CH + H \Rightarrow 2CH \rightarrow C_2H_2$$

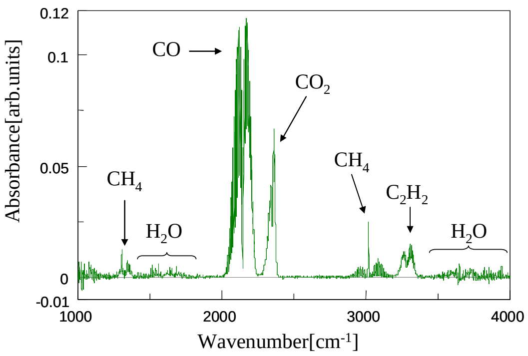

Fig.2. FTIR spectra of CH_4 + CO_2 plasma

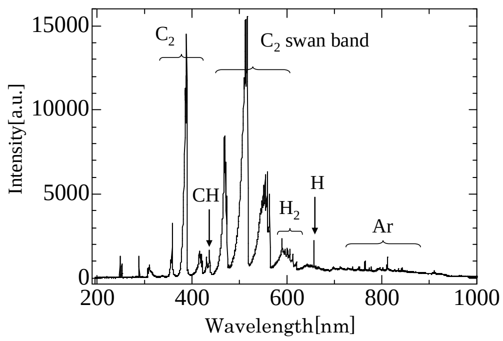

Fig.3. Optical emission spectra of CH_4 + CO_2 plasma

3.2. *Effect of CO_2/CH_4 ratio on conversion*

Effect of the reactants ratio (CO_2/CH_4) on conversion was investigated. The productions of hydrogen, carbon monoxide and acetylene were investigated under the experiment condition of Ar flow rates 6.0 ml/min, methane flow rates 0.07 ml/min and microwave power 900W. The reactants ratio was operated by changing carbon dioxide flow rates. The result is shown in Fig. 4 and Fig. 5.

From these Figure, we can see that the production of carbon monoxide increased with increasing the reactants ratio (CO_2/CH_4), but the production of hydrogen and acetylene changed in the opposite way. This result indicates that the H_2/CO ratio of the synthesis gas can be controlled by adjusting the CH_4/CO_2 ratio in the gas feed.

Generally, it is required for various H_2/CO ratios of the synthesis gas to synthesize different chemical products.

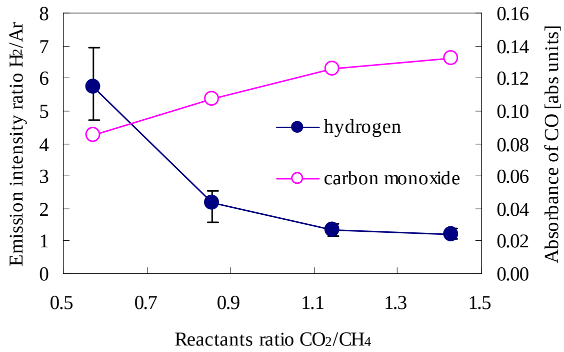

Fig.4. Effect of reaction CO_2/CH_4 ratio on productions of H_2 and CO

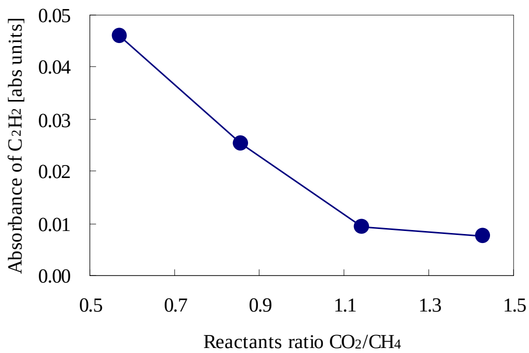

Fig.5. Effect of reaction CO_2/CH_4 ratio on production of C_2H_2

4. Conclusions

Dry reforming of methane has been investigated using atmospheric pressure non-thermal plasma. The process is effective in converting methane and carbon dioxide into synthesis gas. The main products were hydrogen, carbon monoxide and acetylene. It is found that the H_2/CO of the synthesis gas can be controlled by the CH_4/CO_2 ratio in the gas feed.

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