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Reforming of Methane to Methanol by a Low-Pressure Steam Plasma
低圧水蒸気プラズマを用いたメタンガスのメタノールへの改質

Takayuki Tsuchiya, and Satoru Iizuka
土屋　貴之, , 飯塚　哲

Department of Electrical Engineering, Graduate School of Engineering Tohoku University
Aoba 6-6-05, Aramaki, Aoba-ku, Sendai 980-8579, Japan
東北大学大学院工学研究科,　〒980-8579　仙台市青葉区荒巻字青葉6-6-05

In this study, we studied basic phenomena of a conversion of methane to methanol using a plasma without using catalysis. The discharge took place under different discharge parameters such as voltage, gas flow rate, gas-mixing ratio, where methane was mixed with steam at total gas pressure of 1 - 10 Torr. We observed gaseous organic materials such as ethane, ethylene, acetylene, and methanol. The major product was carbon monoxide and the concentration ratio of methanol among the gaseous materials containing carbon was about 30 % under optimized condition. The control of dissociation of methane was a key factor for methane conversion.

1. Introduction

In recent years, global warming has been a serious social problem. An increment of greenhouse gas, such as CO_2 and CH_4, in the air is one of the important causes. It is thought that natural outflow of methane as methane hydrate from the seabed brings about the global warming, resulting in an abnormal weather phenomenon and a raise of the sea level by dissolution of the ice in the Arctic Ocean. The greenhouse effect of CH_4 is 21 times as much as that of CO_2. Therefore, the suppression of methane emission into the environment has been a crucial subject to reduce the global warming.

Methane, a main ingredient of natural gas, is in a gas state at normal temperature. Thus, the handling of methane is dangerous, and its long-distance transportation costs much due to the construction of pipelines. If we can convert methane to methanol in a liquid state, for example, it would be very convenient and safety for the transportation and preservation. Moreover, since methane contains carbon and hydrogen, it will be also used for the source of hydrogen gas and hydrogenerated organic compounds such as ethane and acetylene, together with other carbon materials such as graphene, carbon nanotube (CNT), diamond-like carbon (DLC), and diamond. These materials will be available as semiconductor, luminescence device, solar cell film, and hard film, and so on.

For these reasons, we have developed a plasma system, in which simultaneous generation of hydrogen, organic compound, and highly valuable carbon materials can be produced from methane.

Previously, we examined the generation of methanol, as a result of plasma reaction in the cylindrical glass tube, where a mixed gas of methane and steam was supplied [1]. Simultaneously, generation of carbon monoxide CO and polymerization compounds, such as ethane, ethylene and acetylene, were observed as a byproduct. However, these products could not be disregarded. So, more efficient methanol generation method should be developed. In case of plasma decomposition with the mixed gas, superfluous decomposition occurs for methane molecule, which will result in a generation of polymerization compounds and CO. Therefore, methane should not be directly introduced into the steam plasma, but should be made contact with steam plasma.

2. Experimental Setup

The outline of the experimental device is shown in Fig.1. The plasma is generated by a direct-current power supply for a low-pressure glow discharge. The electrode is made of stainless, and covered with an insulator. Here, coaxial small tubes are adopted, along which reactive gas flows between the electrode and small grass tubes. The gas used was a mixture of methane and steam. Low-pressure steam plasma, generated within a small tube, makes contact with methane, and then they react each other. The plasma state during the reaction was analyzed by optical emission, and the gas components after the discharge were analyzed by Q-mass or FT-IR. Generation efficiency of the

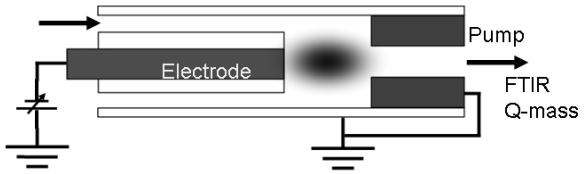

Fig.1: Schematic of experimental apparatus

products was controlled by changing the plasma parameters, such as gas flow rate, electric power, pressure, and rearrangement of the discharge equipment.

We expect reactions in the plasma as follows.

$$CH_4 \rightarrow CH_3^* + H^* \quad (1)$$

$$H_2O \rightarrow OH^* + H^* \quad (2)$$

$$CH_3^* + OH^* \rightarrow CH_3OH \quad (3)$$

3. Experimental result and discussion

The FTIR spectrum of the gas produced by the electric discharge with a mixed gas of methane and steam is shown in Fig.2(a). We observe a methanol

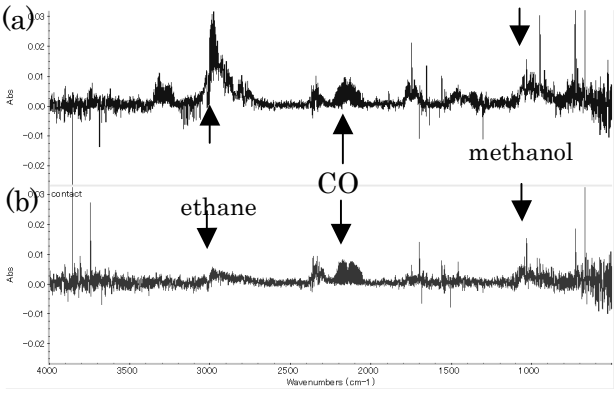

Fig.2 : FTIR spectra of the gases processed by (a) gas mixture discharge and (b) gas contact discharge.

production as shown by arrows, together with a production of ethane and carbon monoxide CO. On the other hand, in case of the contact discharge of steam with methane, the generation of ethane is fairly suppressed, while the generation of methanol is almost maintained. Generation of CO was still observed. Here, we define a selectivity of methanol as S = <CH_3OH> / <Materials contained carbon produced by the discharge>, where < > denotes

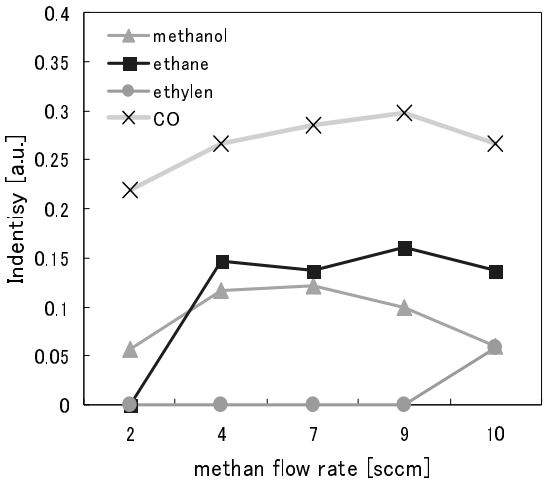

Fig.3: Methane flow rate dependence.

concentration moles. We also define a decomposition rate of methane as D = <CH_4 dissociated> / <CH_4 supplied>. From the results in Fig. 2(b) we find S ~ 30 % which is much larger than that in case of Fig. 2(a).

Variation of FT-IR intensity is shown in Fig. 3 as

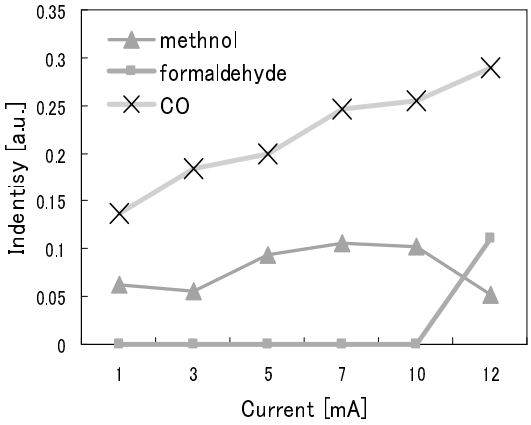

Fig.4: Discharge current dependence.

a function of methane flow rate under a fixed steam flow rate. Only methanol and CO are generated for a large steam/methane flow rate ratio. When methane concentration is increased, generation of methanol is also increased. At the same time, however, the reaction for polymerization compound like ethane is promoted. Here, for the production of ethane, methyl radical will be required. Therefore, it is considered that methyl radical is a key reactant for the generation of methanol as expressed in the above reactions (1)-(3). The production of methanol is saturated for a large methane/steam ratio.

The discharge current dependency is shown in Fig. 4. With an increase of the discharge current, CO production increases monotonically. The amount of methanol is also increased, but finally saturated. At 12 mA, formaldehyde is generated, accompanied with a decrease of methanol production. So, it is thought that formaldehyde is made from methanol. Low current discharge is required for an efficient methanol generation.

4. Conclusion

It turns out that generation of methanol is efficient when the mixing ratio of methane/steam is low at the low power discharge. Polymerization reaction also gives an effect for the methanol production. Control of plasma and gas feeding is a key subject for an efficient methanol production.

Reference

[1] T. Tsuchiya et al., 71th Autumn meeting, Japanese Soc. Applied Physics, 17a-ZH-7 (2010).