Conversion of CO_2 to methane by a low-pressure hollow-cathode discharge

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Basic phenomenon of a conversion of carbon dioxide to methane was investigated by a hollow cathode discharge in a low gas pressure regime. The hollow cathode consisted of a cylindrical stainless steel rod with several holes, to which negative dc voltage was applied. The discharge took place by mixing carbon dioxide with hydrogen at the total pressure of 1 Torr. The gas species after the discharge was analyzed by Fourier transform infrared spectroscopy (FT-IR). Methane was the most dominant organic species produced in the discharge. Carbon monoxide was a major product from carbon dioxide. The number of the holes and the hole diameter were important for the conversion of carbon dioxide to methane.

It has longly been believed that the global warming is caused by an increase in greenhouse gases that absorb and emit radiation within the infrared range. One of the most serious greenhouse gases in the earth's atmosphere is carbon dioxide, emitted from many industrial factories. Therefore, the suppression of the carbon dioxide emission is a crucial subject for reducing the global warming.

The purpose of this study is to investigate the fundamental process of a reduction of carbon dioxide to generate beneficial and reusable organic materials like methane by using a low pressure discharge [1]. Many other works done for converting CO_2 to methane and methanol were studied by using atmospheric barriers discharges [2]. However, here a low-pressure glow discharge was employed for a controlability of discharges without catalysts.

The discharge took place inside a glass tube by changing the discharge parameters such as voltage, flow rate, gas residence time and so on, where the carbon dioxide was reduced by hydrogen. Several organic materials such as methane and methanol were synthesized [1]. In this experiment, a small coaxial electrode system consisted of a ring outer electrode and a rod inner electrode placed inside of the cylindrical glass tube. Here, the inner and outer diameters of the glass tube were 13 and 15 mm, respectively. The inner electrode was made of a stainless-steel rod with a diameter of 5 mm. The outer electrode was not fixed. However, the distance between the inner and outer electrodes was fixed at 15 mm during the experiment.

In order to carry out the hollow cathode discharge, a cylindrical rod cathode with several holes, that were opened and dug through the cathode, was inserted inside the ring outer electrode. Here, two

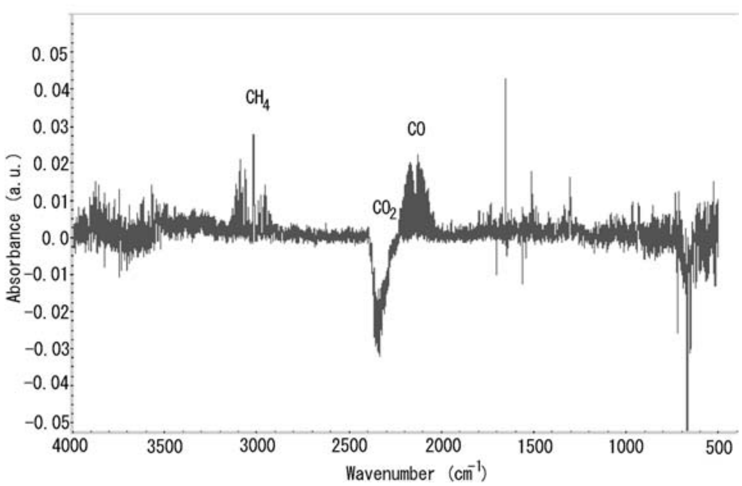

Fig. 1: Typical FT-IR spectram of the gas after the hollow cathode discharge at total pressure of 1 Torr and discharge current of 50 mA.

kinds of cathodes were used. One was the cathode with a hole of 1 mm in diameter and 8 mm long, and the other was the cathode with a hole of 2 mm in diameter and 8 mm long. The number of the holes in each cathode was 1, 2, and 5. Negative dc voltage was directly supplied to the hollow cathode. The applied voltage could be increased up to 1 kV.

Typical FT-IR spectrum of the gas species, taken as a difference between before and after the discharge, is shown in Fig. 1. The negative signal around 2300 ~ 2400 cm^{-1} indicated a decomposition of CO_2, while the other positive signals around 2000 ~ 2300 cm^{-1}, 2900 ~ 3100 cm^{-1}, 1000 ~ 1050 cm^{-1}, and 1500 ~ 1900 cm^{-1} indicated the productions of CO, CH_4, CH_3OH, and H_2O, respectively. CO was clearly a major product generated from carbon dioxide, while CH_4 was found to be a dominant organic species.

Next, we checked how the productions of CO and CH_4 depended on the type of the hollow cathode.

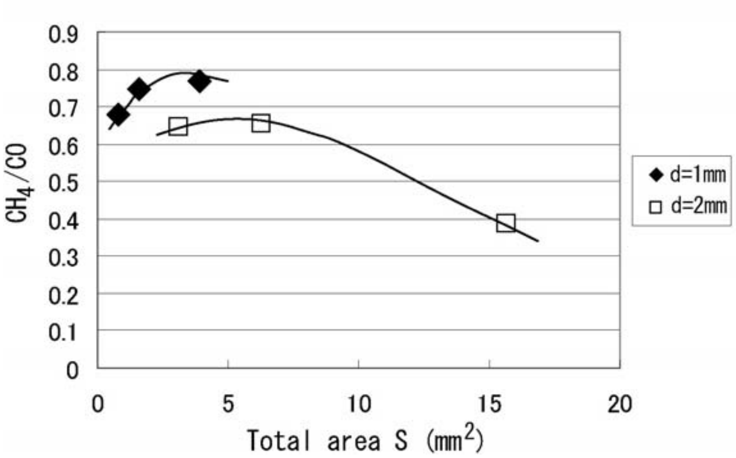

Fig. 2: Intensity ratio CH_4/CO of the FT-IR signals as a function of total hole crosssectional area *S* for the hollow cathode discharge at total pressure of 1 Torr and discharge current of 50 mA. *d* is hole diameter.

Fig. 2 shows the intensity ratio of CH_4 to CO, i.e., CH_4/CO, of the FT-IR signals as a function of the total crosssectional area *S* of the holes. Here, *d* is the hole diameter. So, the area is given by $S = NA$, where *N* is the number of the hole and $A = \pi(d/2)^2$. In the case of $d = 1$ mm, the ratio CH_4/CO was increased with *S*. On the other hand, in the case of $d = 2$ mm, the ratio gladually decreased with *S*. There existed an optimum at $S = S_m \cong 4$ mm^2 for the cathode with 5 holes of 1 mm in diameter. It was also found that this tendency was closely related with the decomposition of CO_2.

The efficiency of the conversion of CO_2 to CH_4 was closely related with the total area *S* and the hole diamter *d* under the fixed discharge current and pressure. The better efficiency was obtaned for the smaller hole diameter. It was estimated from Fig. 2 that, when $S = S_m$, 43.4 % of the products, which contained carbon from CO_2, was CH_4 and the other 56.6 % was CO. On the other hand, the CH_4 component was decreased to 27.9 % when $S = 15.7$ mm^2, whch corresponded to the cathode with 5 holes of 2 mm in diameter. The other species containing carbon were negligible.

In summary, a basic phenomenon of the rconversion of CO_2 to CH_4 was investigated by using a hollow cathode dc discharge at the total pressure of 1 Torr. The dominant carbon products were simply CH_4 and CO. The production ratio CH_4/CO was dependent both on *S* and *d*, and had an optimum value at $S = S_m$, where the ratio of the carbon products was CH_4 : CO = 43.4 % : 56.6 %.The optimization of the hollow cathode discharge was quite important for establishing an efficient conversion of CO_2 to CH_4 under fixed discharge current and pressure.

References

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