Conversion of Methane to Methanol by a Low-Pressure Steam Plasma

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Abstract— **Conversion of methane to methanol was investigated by using a low pressure discharge 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 the total gas pressure of 1 - 10 Torr. We observed gaseous organic materials such as ethane, ethylene, acetylene, and methanol. Carbon monoxide and carbon dioxide were also observed. The major product was carbon monoxide and the concentration ratio of methanol among the gaseous materials containing carbon, i.e., methanol selectivity, was about 20 % under optimized condition, i.e., gas mixing ratio of $[CH_4]/[H_2O] \approx 1/5$. Methanol selectivity was quite sensitive to the gas-mixing ratio CH_4/H_2O. The control of methane dissociation was a key factor for the methane conversion.**

Keywords — **methane, methanol, steam reforming, dc discharge, low pressure.**

I. INTRODUCTION

In recent years, the global warming is becoming one of the most important problems that have to be overcome by almost all countries over the world. The global warming will increase the frequency and intensity of many kinds of extreme weather, which will result in a rise in the sea level and a collapse of ecosystems. It is believed that the global warming is caused by an increase in the greenhouse gases that absorb and emit radiation within infrared range.

Methane (CH_4) is one of the greenhouse gases that cause global warming. The greenhouse effect of CH_4 is about 21 times as much as that of carbon dioxide (CO_2). CH_4 is main component of natural gas and biomass gas. CH_4 is also naturally emitted from the sea bottom as methane hydrate.

Fossil fuels are essentially a non-renewable energy source. Within the next 100 years it is widely believed that the cost of finding and extracting new underground resources will be much more expensive for everyday use. Therefore, the reduction of the emission of carbon dioxide and consumption of fossil fuels are crucial subjects that must be settled urgently

In this work we intend to convert CH_4 to another reusable carbon materials such as methanol (CH_3OH). Methanol is in a liquid state at the standard state and so methanol is useful for an energy transport in a long distance. We will investigate fundamental process of an oxidization of methane to generate beneficial and reusable organic materials like methanol by using dc discharge.

Many other works had established for converting CH_4 to methanol by using atmospheric barriers discharges [1-4]. Conversion from CH_4 to methanol with steam and oxygen was usually discussed in a high-pressure barrier discharge with catalysts [5,6]. Modeling of CH_3OH synthesis from CO_2 was discussed and the vapor-liquid equilibrium was analyzed for CH_3OH, CO_2 and H_2 system [7]. Although several works were reported on the methanol production from methane by using atmospheric dielectric barrier discharge (DBD) with oxygen [8-11], only a few works was reported on the methanol synthesis from methane with a low pressure steam plasma. Steam would provide OH radical, which might give a different oxidization process for the methanol production.

Here, we employed a low-pressure glow discharge for an investigation of fundamental processes without using catalysts. The discharge took place inside a glass tube by changing the discharge parameters such as voltage and flow rate, where methane was dissociated and reacted with oxygen supplied from steam (H_2O).

II. EXPERIMENTAL METHODS

Fig. 1 shows a schematic of a coaxial tube electrode system to convert methane to methanol. The coaxial electrode system consisted of stainless tubes [12]. The inner tube, made of stainless steal was used for a power electrode, to which dc power could be applied. The discharge power could be changed up to 50 W. The most outer tube was a cover electrode made of stainless steal, grounded electrically. Supplied gases such as CH_4 and steam (H_2O) were mixed and introduced into the tube.

Plasma discharge took place between the inner electrode and the outer electrode grounded electrically. Inner diameter of

the outer tube was 6 mm. Since the gases were ejected from the inlet of the tubes, the plasma produced extended in the axial direction inside the tubes. Steam was supplied from a water preserver which temperature could be controlled by a heating system placed just outside the water preserver. The amount of steam flow rate injected was controlled by a needle valve, where the flow rate was monitored by a pressure gauge. Methane was introduced by a conventional mass flow controller system. The mixture of methane and steam was supplied to the discharge region.
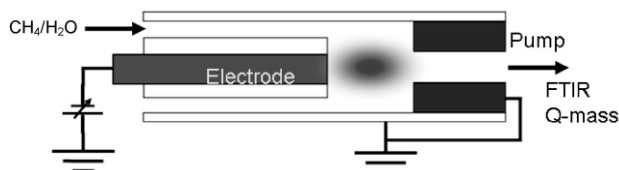

Fig. 1. Experimental apparatus.

2. This meant that, any way, an oxidization reaction due to steam dissociation was triggered. However, we could not detect methanol. This fact will be quite important for modeling the pathway of the reactions for the methanol formation.
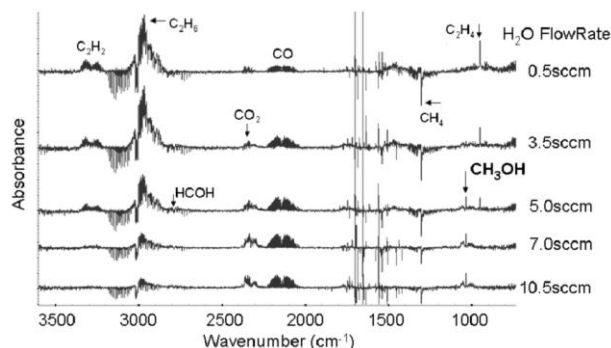

Fig. 2. FT-IR spectra with H_2O flow rate as a parameter. CH_4 flow rate is 2 sccm.

We can control the dissociation level of CH_4 by changing the discharge power. The gas, after passing through the discharge region, was sampled and introduced into a diagnostic system with Fourier transform infrared spectroscopy (FT-IR) to analyze the gas species before and after the discharge. The gas was eventually evacuated by a rotary pump.

Since the length of the glass tube was short (~ 100 mm), the pressure in the discharge region could be measured at the end section of the glass tube. The pressure of the chamber could be changed in a range 0 - 10 Torr with a total gas flow rate of 0 - 20 sccm (= cm^3/minute at the standard state). Discharge power was directly supplied to the inner electrode through a coaxial cable. The data obtained was confirmed by at least plural experiments.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

First, we examined an effect of steam (H_2O) on the production of methanol by the discharge. We introduced a mixture of methane and steam into the discharge region. Flow rate of methane was fixed at 2 sccm and the flow rate of steam was varied by turning a needle valve in a range 0 – 10.5 sccm. FTIR spectrum of the gas, sampled after passing through the discharge region, detected in an FTIR vacuum cell, was shown in Fig. 2 with the steam flow rate as a parameter.

In the case of the steam flow rate of 0.5 sccm, polymerization reaction appeared dominantly as shown in Fig. 2. We clearly observed ethane (C_2H_6) at the wavenumber of 3000 cm^{-1}, ethylene (C_2H_4) at the wavenumber of 800 cm^{-1}, and acetylene (C_2H_2) at the wavenumber of 3300 cm^{-1}. These materials were produced by the reactions among the radicals CH_3, CH_2, and CH. The fact that the concentration of C_2H_6 was much more than those of C_2H_4 and C_2H_2 meant that the dissociation of methane was not much preceded in this case. That is, here, the dissociation $CH_4 \rightarrow CH_3 + H$ would be a dominant reaction as discussed below.

We could also observe CO at the wavenumber of 2200 cm^{-1} even in this case. However, the production of CO_2 at the wavenumber of 2350 cm^{-1} was negligibly small as shown in Fig.

This property was not much changed even when steam was further introduced into this system in the range 0.5 – 3.5 sccm. Although C_2H_6, C_2H_4, and C_2H_2 were produced, their amounts of production were gradually decreased with an increase in the steam flow rate. On the other hand, the amount of CO was gradually increased with an increase in the steam flow rate. However, the production of CO_2 was still negligible compared to that of CO.

It should be noted that CH_3OH was observed at the wavenumber of 1030 cm^{-1} when the steam flow rate was larger than 3.5 sccm. The methanol production increased with an increase in the steam flow rate. This meant that OH and O radicals, which were created through the dissociation of steam, reacted with CH_4 to form first CO, then CH_3OH. Therefore, it was considered that suitable amount of CO was required for the methanol production.

Since the gas species produced was not so many, we divided these gases into 2 groups. One was the organic gas without oxygen and the other was the gas with oxygen. Fig. 3(a) shows variations of gaseous organic materials C_2H_6, C_2H_4, and C_2H_2 that contain carbon from methane. These gases were produced by the reactions among the radicals CH_3, CH_2, and CH generated by the dissociation of CH_4. As shown in Fig. 3(a) the amounts of ethane, ethylene, and acetylene were gradually suppressed with an increase in the steam flow rate. When the steam flow rate was increased above 7 sccm, the production of C_2H_4 and C_2H_2 became negligibly small. However, C_2H_6 was still observed. This tendency was continued even for the steam flow rate above 7 sccm.

As described above, the most dominant radical produced in the discharge was supposed to be CH_3. Henceforth, the reaction $CH_3 + CH_3 \rightarrow C_2H_6$ might be dominant. For another reaction process we could consider a reaction between CH_4 and CH_3 for the production of C_2H_6, i.e., $CH_4 + CH_3 \rightarrow C_2H_6 + H$. The lifetime of CH_2 was supposed to be much shorter than that of CH_3, therefore the reaction between CH_4 and CH_2, i.e., $CH_4 +$
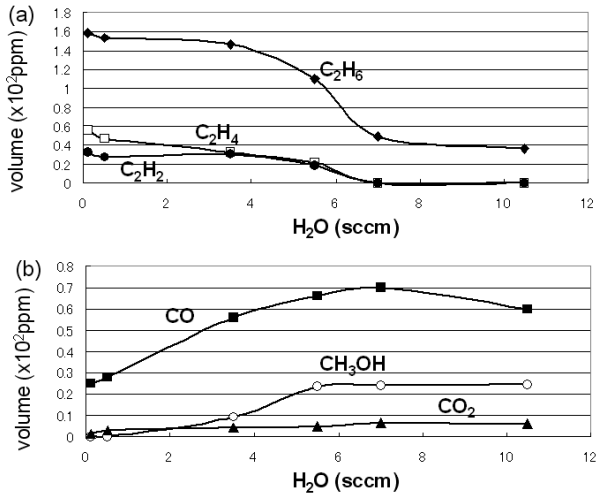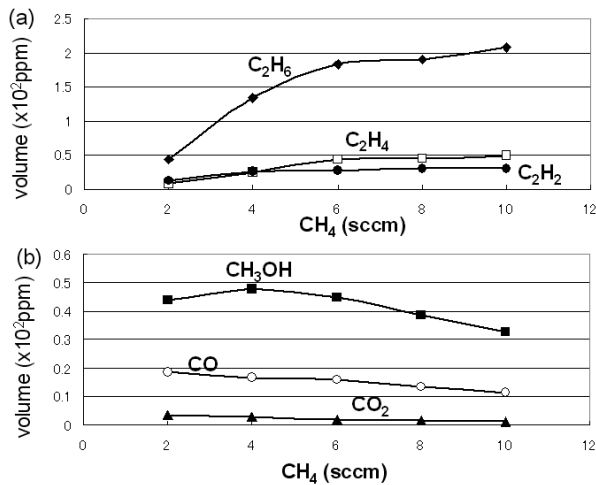
Fig. 3. Synthesized gaseous species (a) without and (b) with oxygen as a function of H_2O flow rate, detected in an FTIR vacuum cell. Methane flow rate is fixed at 2 sccm.

methane flow rate was examined. Typical results were shown in Fig. 4, where the steam flow rate was fixed at 7 sccm. When methane flow rate is 2 sccm, we clearly observe the methanol production. Although the polymerization was relatively suppressed, C_2H_6 was dominant compared to C_2H_4 and C_2H_2. CO and CO_2 were also observed. The polymerization reaction was enhanced with increasing the CH_4 flow rate. This was quite similar to the results in Fig. 3. Therefore, from these results, the most dominant radical for C_2H_6 production was CH_3, i.e., C_2H_6 was produced through the reactions $CH_3 + CH_3 \rightarrow C_2H_6$ and $CH_4 + CH_3 \rightarrow C_2H_6 + H$.

It was also observed that the production of methanol was gradually decreased with an increase in the methane flow rate. Since the flow rate of H_2O was kept constant, the supply of O or OH radicals was limited, so the production of CH_3OH was gradually decreased with CH_4 flow rate. Careful observation of the results in Figs. 3 and 4 showed that the production of CO_2

$CH_2 \rightarrow C_2H_6$, would be infrequent compared to those of the former cases.

The variation of the gases in the second group containing oxygen was shown in Fig. 3(b) as a function of the steam flow rate. CO was the major product when the amount of steam was less than 2 sccm. However, we could clearly observe the formation of methanol when the flow rate of steam was larger than 3.5 sccm. The production of methanol was increased with an increase of the steam flow rate. However, it was eventually saturated above 6 sccm. This saturation was well coincident with the suppression of C_2H_4 and C_2H_2 as shown in Fig. 3(a). The production of CO_2 was gradually increased with the steam flow rate. However, the amount of production was still less than that of CO and was saturated at the steam flow rate larger than 7 sccm.
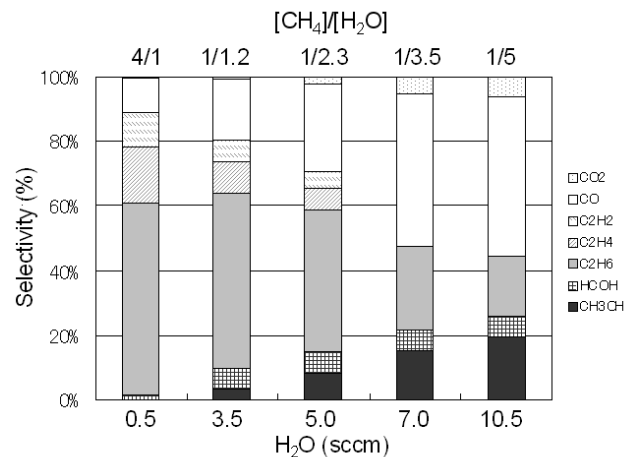
Next, the dependence of methanol production on the

Fig. 5. Selectivity (%) of the synthesized gasses containing carbon with steam (H_2O) flow rate as a parameter. Upper abscissa shows mixing ratio of methane to steam. Methane flow rate is fixed at 2 sccm.

was followed by CO production. Therefore, the oxidation reaction seemed to be proceeded like $CH_4 \rightarrow CO \rightarrow CO_2$. This result also showed that the following reactions (1)-(3) played a key role on the production of CO and CO_2.

Except these gas species we detected formaldehyde HCHO at the wavenumber of 2760 cm^{-1}, although its amount was not much. Therefore, the gas species containing carbon in our system were mainly 7 species, i.e., CH_3OH, HCHO, C_2H_6, C_2H_4, C_2H_2, CO, and CO_2. The relative concentration ratio of these gas species is shown in Fig. 5 with the steam flow rate as a parameter. The gas mixing ratio $[CH_4]/[H_2O]$ is also noted on the upper abscissa. The maximum of methanol selectivity β, defined by $[CH_3OH]/[Total 7 gas species containing carbon]$, was about 20 %. The dependency of the gas component selectivity on the discharge power was also investigated as shown in Fig. 6. With an increase in the discharge power the methanol selectivity was gradually decreased, while CO and polymerization components were gradually increased.

Fig. 4. Synthesized gaseous species (a) without and (b) with oxygen as a function of CH_4 flow rate, detected in an FTIR vacuum cell. Steam flow rate is fixed at 7 sccm.

Therefore, the input power did not give a drastic effect on the increase of the methane selectivity.

We also found that when the input power was reduced, the production of C_2H_4 and C_2H_2 was well suppressed. In this case, typical concentration ratio among the gaseous carbon materials, produced from methane, was $[CH_3OH]/[C_2H_6]/[CO] \approx 1/1/3$ under optimized condition (see $[CH_4]/[H_2O] = 1/5$ in Fig. 5). Namely, about 20 % of the product containing carbon was methanol. The mixing ratio of methane with steam was a key parameter as shown in Fig. 5.
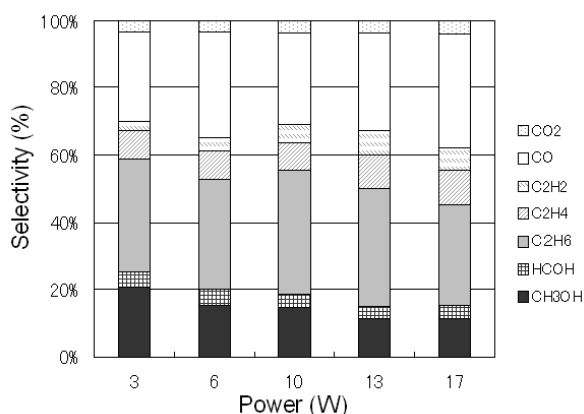
Fig. 6. Selectivity (%) of the synthesized gasses containing carbon with input discharge power as a parameter. CH_4/H_2O = 2 sccm/ 7 sccm.

Figure 7 shows a schematic of the reaction pathways in the plasma with a gas flow. The plasma was generated by the electrode, and the electron energy became high in the core plasma region. Upper inset shows a schematic of the electron energy variation along the gas flow.

When the mixed gas of CH_4 and H_2O was introduced in the plasma, these gasses were dissociated in the high electron energy region via the reactions (1)-(2).

$$CH_4 \rightarrow CH_3 + H \rightarrow \cdot\cdot \mapsto C + 4H \qquad (1)$$
$$H_2O \rightarrow \quad H + OH \rightarrow O + 2H \qquad (2)$$
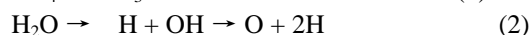
Then, C and O would react each other to generate CO via the reaction (3).

$$C + O \rightarrow CO \qquad (3)$$

Because the chemical bonding energy of CO was relatively high compared to the other species, CO could remain even in the core plasma region. Note that bonding energy 1079 kJ/mol of C-O was higher than 432 kJ/mol of H-H in H_2, that were roughly the same as 415 kJ/mol of C-H in CH_4 and 462 kJ/mol of O-H in H_2O. Average bonding energy 804 kJ/mol of two C-O bondings in CO_2 was still larger than those of the other gas species.

However, with being transported toward the low electron energy region by the gas flow, CO was gradually reduced by hydrogen via the reactions (4)-(5). Actually, we first detected CO, then formaldehyde HCHO, as shown in Fig. 5. Since

HCHO was quite reactive and unstable, it might be further reduced by hydrogen, and eventually CH_3OH was produced via the reaction (5).

$$CO + 2H \rightarrow HCHO \qquad (4)$$
$$HCHO + 2H \rightarrow CH_3OH \qquad (5)$$
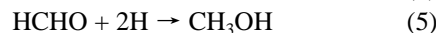
Simultaneously, polymerization reaction (6) would proceed, and C_2H_6, C_2H_4, and C_2H_2 were synthesized in the low electron energy region.

$$CH_x + CH_y \rightarrow C_2H_{x+y} \qquad (6)$$
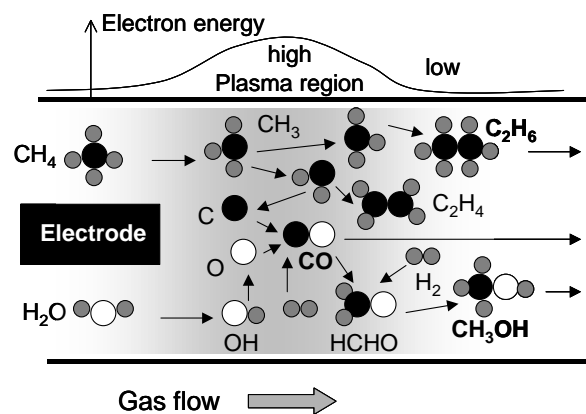
Fig. 7. Major reaction pathways for the conversion of CH_4 to CH_3OH in CH_4/H_2O plasma. Upper inset shows a schematic of electron energy variation along the gas flow.

The reaction model shown in Fig. 7 was similar to that of the methanol production in CO_2 and H_2 plasma [13], where CO was first produced as syngas by endothermic reaction, $CO_2 + H_2 \rightarrow CO + H_2O$. Finally, CO was reduced by hydrogen to CH_3OH via HCHO, as in the reactions (4)-(5). In ref. [13] the effect of catalyst was also examined. The methanol yield roughly doubled when the catalyst was employed. However, methanol could, in principle, be produced even in the case without catalyst via a gas phase reaction.

In a conventional reactor without plasmas, methane was hardly dissociated to the atomic state. However, in the plasma reactor, energetic electrons would dissociate methane together with steam to their atomic states via the reactions (1)-(2). We actually detected optical emission from carbon atom C even in the CO_2/H_2 discharge. The lifetime of atomic oxygen O is much longer than that of OH. Therefore, even in such a hydrogen dominated plasma, CO could be produced via the reaction (3) and maintained in the high energy plasma region. In this way, syngas of CO and H was contained simultaneously in the plasma. Then, they were used for the CH_3OH production in the down-stream region. Actually, CO was dominant species in the case of low H_2O flow rate as shown in Fig. 5.

Finally, we discuss the energy efficiency γ, which can be derived from the following relation.

$$\gamma = \alpha\beta\Gamma/V_dI_d. \tag{7}$$

Here, Γ is the input CH_4 flow rate, α is the decomposition ratio of methane defined by $(\Gamma-\Gamma')/\Gamma$, where Γ' is the CH_4 flow rate after the discharge, β is the methanol selectivity. V_d and I_d are the discharge voltage and current, respectively. Typically, Γ = 2 sccm, α = 5 %, β = 20 %, and V_dI_d = 3 W. Carbon balance under optimized condition was summarized in Table 1. In this case, we get γ = 0.4 L/kWh. Here, L (= litter) means the gas volume at the standard state. This energy efficiency was comparable to γ = 0.29 L/kWh [1] of the atmospheric barrier discharge at 1 atm, where the mixture of methane and oxygen was employed with Γ = 700 sccm, α = 20 %, β = 1.4 %, and $<V_dI_d>$ = 400 W. Here, $< >$ denoted time averaged value. Our method has a superiority that the methane selectivity β is one order of magnitude larger than that of the barrier discharge. The methane decomposition ratio α will be improved in future by

TABLE 1
CARBON BALANCE

α (%)	CO (%)	CO_2 (%)	CH_3OH β(%)	HCOH (%)	C_2H_6 (%)	C_2H_4 (%)	C_2H_2 (%)
5	49	6	20	6	19	0	0

CH_4: 2 sccm, H_2O: 10.5 sccm., V_dI_d = 3 W, γ = 0.4L/kWh.

rearranging the electrode system.

In our experiment the conversion of methane to methanol was thought to proceed via CO formation. This reaction model was quite similar to the methanol production from syngas, a mixture of CO and H_2 [13], except that methane was completely decomposed to the atomic state, as mentioned above. The control of CH_4 decomposition and its oxidization was a key technology for the production of methanol.

IV. CONCLUSIONS

A basic phenomenon of conversion of CH_4 to methanol was investigated in CH_4/H_2O discharge plasma. The dc discharge took place under different discharge parameters such as gas flow rate, gas-mixing ratio, and discharge power, where methane was mixed with steam at the total gas pressure of 1 - 10 Torr. We observed several gaseous organic materials such as C_2H_6 and CH_3OH. CO was clearly a major product by the oxidation of CH_4. CH_3OH was the most dominant gaseous organic species under our experimental conditions. An increase of steam resulted in CO and CO_2 formation.

A polymerization reaction was also observed when $[CH_4]/[H_2O]$ ratio was increased. Typical concentration ratio among the gaseous carbon materials, produced from methane, was $[CH_3OH]/[C_2H_6]/[CO] \approx 1/1/3$ under the optimized condition. In this case, about 20 % (= β) of the product with carbon was methanol, which was produced with the efficiency of $\gamma \approx 0.4$ L/kWh and the decomposition rate $\alpha \approx 5$ %. The mixing ratio of methane with steam was a key parameter.

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