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Conversion of methane for higher hydrocarbon fuel synthesis using pulsed discharge plasma method

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Abstract

This paper presents new conversion method of methane to higher hydrocarbon fuels such as methyl alcohol (methanol), formaldehyde, using pulsed discharge plasma under room temperature and atmospheric pressure. The experiments were carried out with special attention to the effect of the specific input energy (SIE) defined as the electrical input energy per unit mass of the material gas. In the study of partial oxidation of methane, experimental results indicated that the methanol and formaldehyde production has an optimum SIE value. The highest methanol and formaldehyde production ability and reaction selectivity were achieved with relatively low SIE of 360 J/l, based on feed gas. Under this optimum condition, a maximum production ability of about 0.65 μmol/J and selectivity of 64% were obtained. On the other hand, in order to achieve selective reaction of methane, conversion of methane with halogen materials to methyl halide such as methyl iodine was also investigated. In the experiment, maximum methyl iodine production selectivity of 95% was achieved with the production ability of 0.45 μmol/J. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pulsed discharge; Plasma chemical reaction; Partial oxidation of methane; Methanol synthesis; Methyl halide; Halogenation

1. Introduction

Recently, direct conversion of natural gas and its principal component methane to a liquid product such as methanol and formaldehyde in homogeneous gas-phase reactions [1–7], and over heterogeneous catalysts [8–12] have been investigated. Because methanol and formaldehyde are liquid under normal conditions, it is more economical to transport these chemicals over large distances than gaseous methane or hydrogen. Although, most of the methanol and formaldehyde are used in the chemical industry as raw material or solvent for chemical synthesis at the present time, promising new applications are the direct use as a fuel for fuel cells. It has been proved to be very difficult, however, to obtain high selectivity of methanol and formaldehyde at reasonable conversions from methane, since, in general, the oxidation proceeds to complete to carbon oxides and water.

The pulsed discharge plasma process, that to reveal application of the high-speed rise time, repetition pulsed high voltage, is one of the available methods to achieve a direct conversion of methane to methanol [3,5,13]. These pulsed discharge plasma processes, however, are still insufficient to substitute the conventional method of hydrocarbon fuel synthesis, because the energy consumption for methanol production in these plasma processes are still larger and the production selectivity are low than that of the conventional method. Further studies are necessary to select the type of plasma, gas conditions, design of the reactor,

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etc., to improve the energy efficiency and production selectivity.

The authors have been investigating the methanol synthesis from CH_4 and O_2 using pulsed discharge plasma. We have reported that the methanol synthesis was enhanced by dilution of the source gas with an inert gas such as argon or helium [13]. In this study, we tried to measure the characteristics of methane conversion using the pulsed plasma method in order to obtain better understanding of the parameters affecting the homogeneous gas-phase reaction, such as the specific input energy on production ability, the production selectivity and the conversion ability. Furthermore, to prevent excessive oxidations such as production of methyl components and to improve the production selectivity, the addition of halogen materials has been investigated [14–20]. These results indicate that in the dehydrogenation of methane with halogen materials, substitution of the stronger C–H bond to the weaker carbon–halogen bond takes place. After this dehydrogenation process, the carbon–halogen bond is replaced by C–O bond to produce methanol. Only a few turnovers, however, were reported in this process [15,16]. We carried out to improve these processes. A preliminary study was carried out of methyl iodine synthesis from methane and iodine using pulsed discharge plasma.

2. Experimental setup

Fig. 1 shows a schematic diagram of the experimental setup in this study. Methane and oxygen were used as reactants and argon was also used as a dilution gas. The gases were mixed through a mixing chamber and introduced into the plasma reactor at room temperature and atmospheric pressure. On the other hand, in the experiment of methyl iodine production, iodine was placed on the inner surface of quartz wall of the reactor. Oxygen gas was not used in this case.

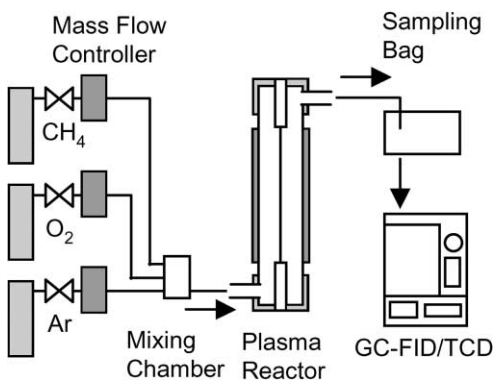

Fig. 1. Schematic diagram of the experimental setup.

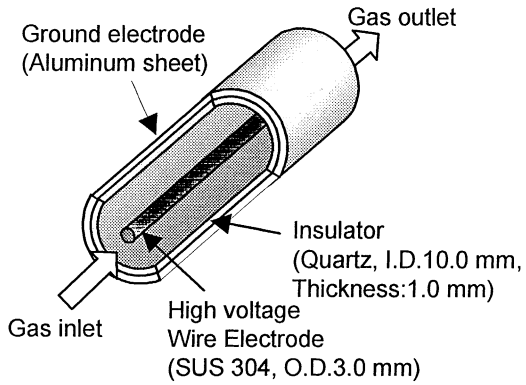

Fig. 2. Construction of the plasma reactor.

The schematic design of the plasma reactor used in this study is shown in Fig. 2. The plasma reactor was a concentric cylinder with an inner metal electrode (stainless steel wire: 0.3 mm diameter) and an outer electrode of aluminum sheet wrapping around a quartz tube (ID: 10.0 mm, OD: 12.0 mm). The quartz tube prevents sparking between the electrodes. The effective gas volume and length of the reactor were 17.3 ml and 210 mm, respectively.

To measure the voltage and current waveforms, a digital oscilloscope (Tektronix, TDS-640), a voltage divider (Tektronix, P6015), and a current transformer (Tektronix, P6021) were used. High voltage pulses of approximately 10×10^{-9} s of rise time, +25 kV of peak voltage, and 440 Hz of pulse frequency, was applied to the reactor.

At downstream of the reactor, gases were analyzed using gas chromatographs [13]. GC–MS (mass spectroscopy, Shimadzu, GC-14A + QP2000A, column: PoraPLOT Q and Molecular Sieve 5A) was used for the identification of products. The concentration of hydrocarbons, CO and CO_2 were determined by GC–FID (framed ionized detector, Shimadzu, GC-14B, column: Porapak Q, carrier gas: He) with

Methanizer (GL Science, MT-221). And for determination of H_2 and O_2 concentrations, a GC–TCD (thermal conductivity detector, Shimadzu, GC-8A, column: Molecular Sieve 13X, carrier gas: Ar) was used.

3. Evaluation of system performance

In this study, the energy efficiency of the methane conversion and the production of compounds were evaluated using the specific input energy (SIE) defined in Eq. (1). The applied energy in the reactor was calculated by time integration of the voltage and current of the plasma reactor (Eqs. (2) and (3)).

$$\text{Specific input energy} = \frac{\text{Discharge energy}}{\text{Flow rate of feed gas}} \ (\text{J/l}) \quad (1)$$

$$\text{Pulse energy} = \int V(t) \times I(t)\,\mathrm{d}t \ (\text{J/pulse}) \quad (2)$$

$$\text{Discharge energy} = \text{Pulse energy} \times \text{Pulse frequency} \ (\text{J/s}) \quad (3)$$

To evaluate the production from discharge plasma, production ability, conversion, conversion ability, and selectivity were used. Eqs. (4)–(9) indicate the calculation methods for these evaluations. In the case of reaction selectivity, mole number of carbon atom was used for the calculations.

$$\text{Production ability} = \frac{\text{Product concentration}}{\text{SIE}} \ (\text{mol/J}) \quad (4)$$

$$\text{Methane conversion} = \left(1 - \frac{\text{Outlet CH}_4}{\text{Initial CH}_4}\right) \times 100 \ (\text{mol\%}) \quad (5)$$

$$\text{Oxygen conversion} = \left(1 - \frac{\text{Outlet O}_2}{\text{Initial O}_2}\right) \times 100 \ (\text{mol\%}) \quad (6)$$

$$\text{Conversion ability} = \frac{\text{Converted CH}_4 \text{ concentration}}{\text{SIE}} \times (\text{mol/J}) \quad (7)$$

$$\text{Converted CH}_4 = \text{Initial CH}_4 - \text{Outlet CH}_4 \quad (8)$$

$$\text{Selectivity} = \frac{\text{Mole number of carbon in the product}}{\text{Mole number of carbon in converted CH}_4} \times 100 \ (\text{mol\%}) \quad (9)$$

4. Results

4.1. Experiment 1: partial oxidation of CH_4 by O_2

4.1.1. Production ability

Methane conversion with oxygen was carried out using the pulsed discharge plasma. As the products identified in this plasma process, carbon monoxide (CO), carbon dioxide (CO_2), ethylene (C_2H_4), ethane (C_2H_6), formaldehyde (HCHO), acetaldehyde (CH_3CHO), methanol (CH_3OH), hydrogen (H_2), and water (H_2O) were detected. Fig. 3 shows the effect of the SIE on the production ability of major oxidant as methanol, formaldehyde, CO and CO_2. In this experiment, content of the source component was CH_4 and O_2. The volume ratio of the source was selected as CH_4:O_2 = 85:15. The source gas was diluted with Ar. The volume ratio of the source gas and the dilution gas was set at 50:50. The variation of the SIE value was adjusted by changing the applied energy in the plasma reactor and total feed gas flow rate. The applied energy was varied at the range from 200 to

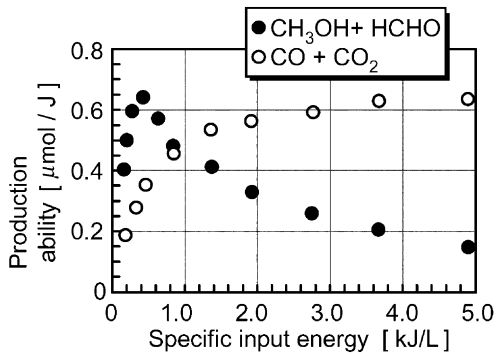

Fig. 3. Production ability on SIE (CH_4:O_2 = 85:15, Ar partial pressure: 50 kPa).

650 J/min, and the total gas flow was ranging from 130 to 1040 ml/min.

The experimental results showed that, characteristics of production ability of oxidants were significantly affected with SIE. Particularly, production ability of partial oxidant as methanol and formaldehyde reached maximum to 0.65 μmol/J at relatively low SIE value of 360 J/l, and then gradually decreased with further increase of the SIE. On the other hand, the production ability of further oxidant as CO and CO_2 continuously increased with increasing the SIE, and saturated at the higher SIE region.

In general, the time period of chemical reaction is too short in comparison with interval time between the pulse applications (in this case: pulse interval time = 2.2×10^{-3} s). Furthermore, number of molecules collision with electron depends on the magnitude and the period of applied energy. Consequently, these reasons might affect that partial oxidation of methane was achieved by pulsed discharge even though under atmospheric pressure, and to control progress of the oxidation was possible by applied energy as the SIE.

4.1.2. Conversion ability

From the experimental results of the effect of SIE on production ability, we can assume that the SIE is an important factor to control the oxidation of methane, and application of pulsed energy have a possibility preventing further oxidation as compared to other energy applied method. Therefore, in this section, characteristics of methane and oxygen conversion with applied energy were investigated. Fig. 4 shows the conversion of source component (methane and oxygen) and the conversion ability of methane with variation of the SIE.

The conversions of methane and oxygen were increased with the increase in SIE. Contrary, the conversion ability of methane had a peak when the SIE was 360 J/l, and it was gradually decreased with increase in the SIE value. This tendency was almost the same as the production ability of methanol and formaldehyde. This result informs that distribution of applied energy may be shifted to oxidation of products rather than conversion of methane at the higher SIE region.

The pulsed discharge process, like this study can be operated under normal condition and the performance of the reactor is relatively not so sensitive with gaseous contaminant, such as CO and CO_2. Therefore,

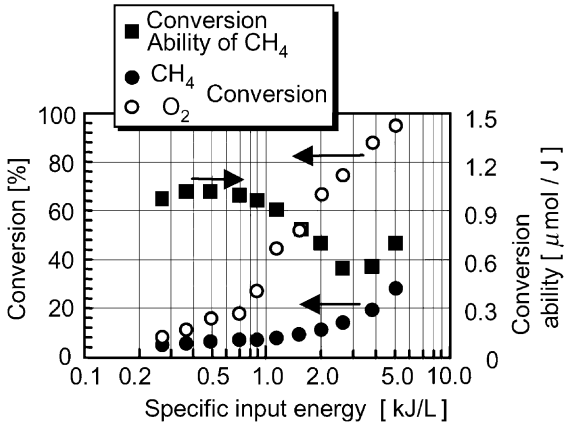

Fig. 4. Characteristics of conversion and conversion ability of methane on SIE (CH_4:O_2 = 85:15, Ar partial pressure: 50 kPa).

it could be easy to enhance the yield value of the system using re-cycle system of outlet gas and/or design of the plasma reactor, etc. Consequently, selecting applied energy was a very important factor for the point of energy utilization and scale-up of this process.

4.1.3. Reaction selectivity

Fig. 5 shows the effect of the SIE on the reaction selectivity of products. The reaction selectivity was calculated as the mole number of products divided by the mole number of the sum of the products.

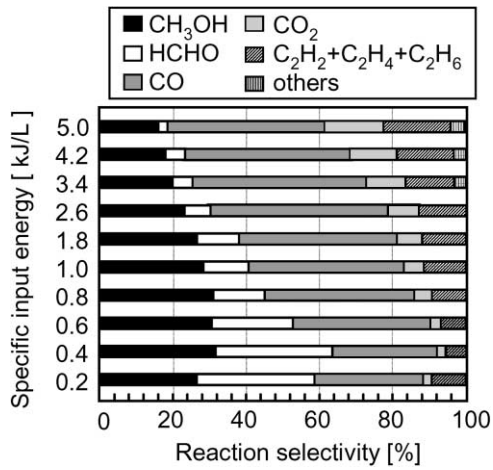

Fig. 5. Effect of SIE on reaction selectivity (CH_4:O_2 = 85:15 Ar partial pressure: 50 kPa).

The selectivity of methanol and formaldehyde showed a maximum when the SIE value was 360 J/l, and at that time, maximum selectivity of 64% was achieved. The reaction selectivity of CO and CO_2 increased with the SIE value. Notably, the selectivity of the formaldehyde immediately decreased with increase in the SIE, while that of methanol did not decrease significantly. This result suggests that, when oxidative reaction becomes dominant at the higher SIE, oxidation of formaldehyde to carbon monoxide may easily occur compared to further oxidation of methanol to formaldehyde and/or carbon monoxide.

As expected before, at the higher SIE value, most of the oxygen was reacted. This result is in good agreement with the result of the increased selectivity of ethane at the higher SIE values, perhaps because of the depletion of oxygen.

Generally, selectivity of reactant was strongly dependent upon oxygen concentration in the source component, for instance ethane selectivity at the higher SIE region. However, from the experimental results in this study, reduction of methanol/formaldehyde and production of CO/CO_2 played complementary at the lower SIE region. At least in the region of lower SIE, applied energy played an important role for progress of the oxidation at the lower SIE condition.

4.2. Experiment 2: CH_3I production from CH_4 and I_2

From the experimental results showed in the previous section, pulsed discharge method had an advantage to control the methane oxidation and to produce methanol and formaldehyde as intermediate chemicals in the oxidation of methane. However, to achieve partial oxidation of methane, there is other possibility to control by chemical method instead of limiting the applied energy. In this section, the authors investigated halogenations of methane using pulsed discharge. The purpose of this study was protection of the products chemically, to avoid further reaction of intermediate products in the discharge region.

The halogenations of methane have been investigated for selective partial oxidation of methane since 1960s. Some cases showed good performance to achieve partial oxidation of methane with catalysis [15,16]. However, these system must have to solve the problem for industrial application, that is halogenide works as catalytic poison.

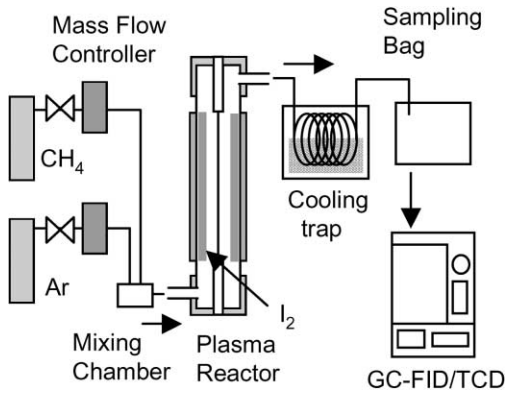

Fig. 6. Schematic diagram of experimental setup on methyl iodine experiment.

On the contrary, in the case of pulsed discharge method for halogenation of methane, it may hardly affect the system performance by the presence of halogenide. Moreover, chemical protection by halogenide could enhance the reaction selectivity. Therefore, in order to clarify the possibility of discharge plasma method, we carried out an experiment using the halogenation of methane to methyl halide.

Fig. 6 shows the experimental setup used in Experiment 2. In this system, iodine was placed on the inner surface of quartz tube of the plasma reactor and oxygen was not fed as source component. To avoid contamination of iodine in the sample gas, a cooling trap was placed at the downstream of the reactor.

Fig. 7 shows the experimental results on the production ability and the production selectivity of methyl iodine with the different SIE. The content and the

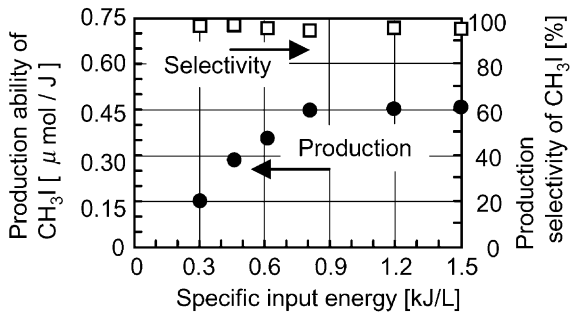

Fig. 7. Characteristics of production ability and production selectivity of methyl iodine on SIE (source: CH_4, Ar partial pressure: 50 kPa, initial iodine: 5.0 g).

ratio of the gas were CH_4:Ar = 50:50, and the initial weight of iodine was 5.0 g.

From the experimental result, methyl iodine was produced from methane and iodine by applying pulsed high voltage. It should be noted that only a small amount of ethane was detected as by-products. Other products of methyl iodine, such as CH_2I_2 (methylene di-iodine, di-iodomethane) and CHI_3 (tri-iodomethane) were not detected. The production selectivity of methyl iodine was not decreased with the increase of the SIE value. Compared with the partial oxidation study, the selectivity was kept over 90% with all the SIE value in this study. The highest production ability of 0.45 μmol/J, and the production selectivity of 95 mol% were obtained at the SIE of 900 J/l.

Furthermore, other researchers showed that hydrolysis of methyl iodine occurred with alkyl solvent and methanol was produced [16]. Considering this, our experimental result indicates that a selective conversion of methane to methanol is possible using the halogenation of methane.

5. Summary

Using the pulsed discharge plasma, the conversion of methane has been investigated. From the parametric study, the production ability of the chemical species from methane has been improved. The following conclusions were obtained:

1. C_2H_4, C_2H_6, methanol, formaldehyde, H_2, CO, CO_2 and H_2O are the major products of the plasma chemical reactions of CH_4 and O_2.
2. By increasing the SIE, oxidation of methane can be enhanced. To enhance the methanol and formaldehyde production ability, on the other hand, the SIE should be reduced. The highest methanol and formaldehyde production ability (0.65 μmol/J) and the reaction selectivity (64 mol%) can be achieved at a SIE of 360 J/l.
3. Methyl iodine can be produced from methane and iodine. The highest production ability was 0.45 μmol/J, at a reaction selectivity of 95 mol%.

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