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Application of a Pulse Discharge in Partial Oxidation of Methane

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A pulse discharge was used to produce methanol from methane partial oxidation at room temperature and atmospheric pressure. As high as 3% of methane was converted, and the selectivity of methanol was higher than 40%. The relations of reactor configuration, oxygen concentration, and input power for discharge to methane conversion and selectivity of each product were investigated. The production cost of methanol using a pulse discharge was compared with that using a conventional process. The future use of a pulse discharge in methanol production was discussed.

Key words: pulse discharge, methane oxidation, methanol production

1. INTRODUCTION

Methanol is produced conventionally *via* two steps: methane reforming with steam at a high temperature to syngas (CO and H_2) and methanol synthesis from syngas at a high pressure and over a catalyst. Compared with this conventional methanol production process, the investment and operation cost can be decreased a lot if methanol can be produced at the selectivity higher than 77% using a direct partial oxidation method (1). There are mainly two methods for partial oxidation of methane to methanol and/or formaldehyde under development: catalytic oxidation and gas phase oxidation (2). For the first method, in order to activate methane, a metal catalyst with high catalytic activity is required. Such a catalyst, however, causes repaid methanol oxidation because the product methanol is oxidized faster than methane itself over the metal catalyst (3-4). For the second method, a high pressure and a very low space velocity limited its application in the industry, and further study is therefore required (5).

In order to produce methanol at a high methane conversion rate and high methanol selectivity, protection of methanol from deep oxidation is essential. An use of an adsorbent in the reaction zone was suggested for the purpose (6). This idea of using an adsorbent in the reaction zone will be realizable if the reaction temperature is low enough for the application of the adsorbent. A non-thermal plasma reaction process is considered to be usable since it can activate methane and oxygen at room temperature.

In 1987, Mallinson *et al.* reported a plasma reaction process used for methane partial oxidation (7). They used a plate-plate reactor and an AC power supply to oxidize methane. The selectivity of methanol was 7-9% at the methane conversion of 5-10%. Recently, the research group of Mizuno used a pulse plasma process to produce methanol (8). The methanol selectivity was 35% at maximum at the methane conversion of 1%. In the present study, we first used four types of reactors that have different configurations to evaluate methane oxidation. It was found that a non-thermal pulse discharge is favorable for the productions of methanol and formaldehyde. Therefore, we investigated the factors in detail that influence methanol/formaldehyde production from methane partial oxidation.

2. EXPERIMENTAL

The experiment setup is schematically shown in Fig. 1. The discharge current through the cathode of a reactor was measured with a wide band current transformer (CT: Model 2-0.1, Strangenes Industries) and the voltage was measured with a voltage probe (V-probe: EP-50K, Pulse Electronic Engineering). The signals both from the voltage probe and current transformer were recorded with a digital oscilloscope (TDS754D, Tektronix) having an analog bandwidth of 500 MHz and a maximum sample rate of 2 GS/s. The input power used only for gas discharge was calculated as the difference between input powers measured with a power meter (Hioki 3193 Power Hitester, Hioki) when the discharge occurred or not.

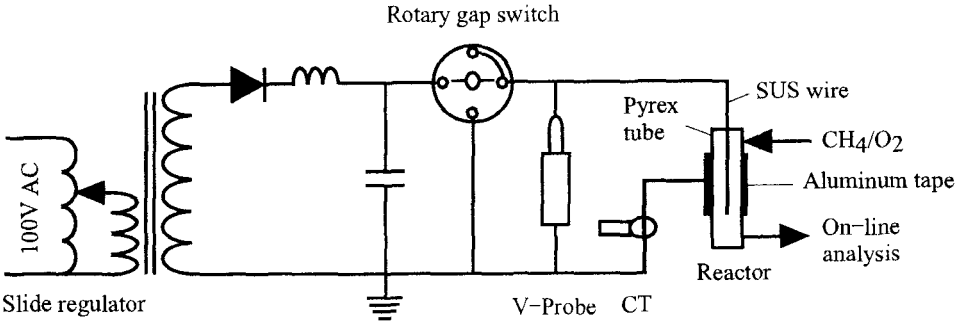

Fig. 1 Schematic of the pulse discharge system.

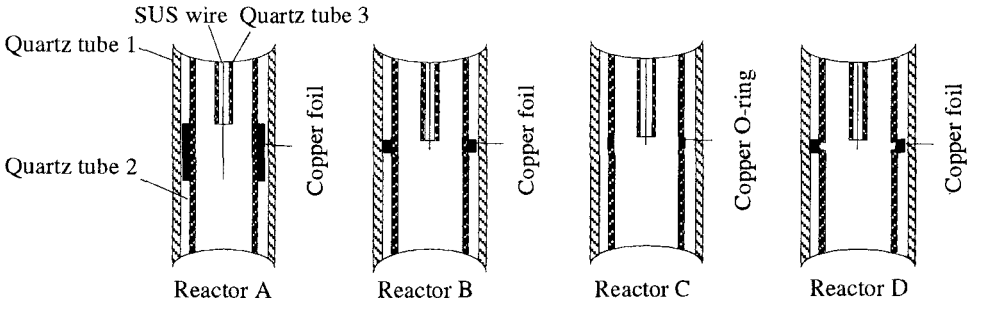

Fig. 2 Configuration of each reactor.

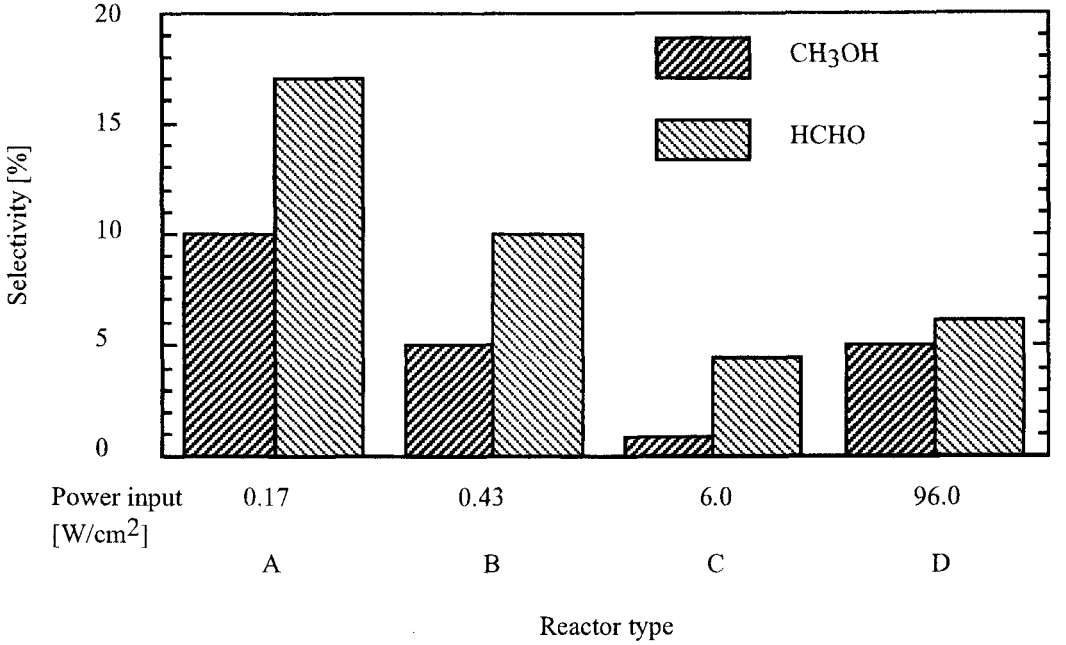

Fig. 3 The highest selectivity of each product versus input power with total gas flow rate = 150–300 ml/min, methane concentration = 3.3–95%, oxygen concentration = 3.3–20%, and helium balance.

In order to evaluate influences of reactor configuration and discharge input power on methanol/formaldehyde production, four types of reactors were used (Fig. 2). Reactor A was a co-cylindrical type reactor, in which a SUS wire (Φ0.65 mm) was set at the axis of a quartz tube 2 (i.d.: 10 mm), the copper foil (length: 50 mm) was covered on the out surface of the quartz tube 2. Reactor B was just similar with Reactor A except that the length of copper foil for discharge was 5 mm. Reactor C was for the discharge between copper O-ring (i.d.: 12 mm and length: 2 mm) and the central SUS wire. Reactor D was like Reactor C but the discharge zone was very small (i.d.: 12 mm and length: about 1 mm).

A dielectric barrier reactor shown in Fig. 1, which was used for a non-thermal pulse discharge, consisted mainly of a Pyrex tube (i.d.: 12 mm and o.d.: 15 mm), an aluminum tape, and a SUS wire (Φ0.3 mm). The aluminum tape with a length of 100 cm covered the central part of the outside surface of the Pyrex tube. This aluminum tape was used as a cathode. The SUS wire was set at the axis in the Pyrex tube and used as an anode. The mixture of methane and oxygen was supplied into the upper part of the dielectric barrier reactor. Carbon compounds in the products were analyzed with an on-line gas chromatograph (GC-103, FID, Okura Riken) equipped with a 2 m Porapak Q column. The gas sample was pretreated with a methanizer (MT-221, GL Science) to convert carbon compounds to related alkanes prior to detection by FID. H_2 and O_2 in the products were analyzed with an on-line gas chromatograph (AGC-280, TCD, Okura Riken) equipped with a 2 m activated carbon column. All the experiments were performed at room temperature and atmospheric pressure.

3. RESULTS

3.1 Influences of reactor configuration

We first investigated the influences of reactor configuration on methanol/formaldehyde production. The results are shown in Fig. 3. It was found that Reactor A had lowest discharge input power, but highest total selectivity of methanol and formaldehyde. Hence, we used a dielectric barrier reactor like Reactor

A to produce methanol from methane partial oxidation.

3.2 Influence of oxygen concentration

The influence of oxygen concentration was first investigated using the dielectric barrier reactor since oxygen concentration is an important factor that influences methane oxidation. The results are shown in Fig. 4. As oxygen concentration increased, methane conversion increased, but oxygen conversion decreased. The rate of methane conversion did not change significantly while the rate of oxygen increased with the increase in oxygen concentration. Figure 5 shows the relation of the selectivity of each product to oxygen concentration. The selectivities of methanol and formaldehyde did not changed remarkably. With the increase in oxygen concentration, the selectivities of carbon mono and dioxides increased, but those of ethylene and ethane decreased.

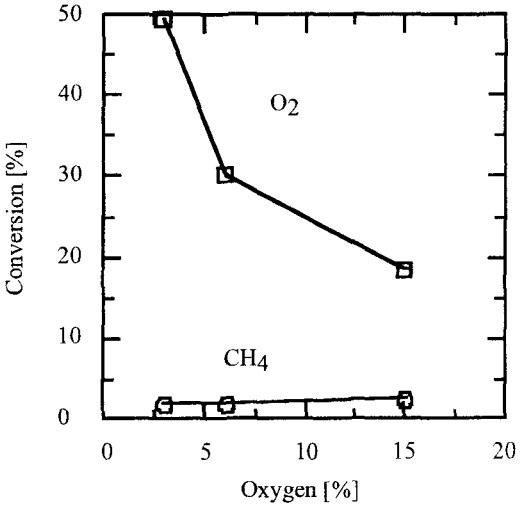

Fig. 4 Influence of O_2 concentration on CH_4 and O_2 conversions with total gas flow rate = 100 ml/min and input power = 5.7 W.

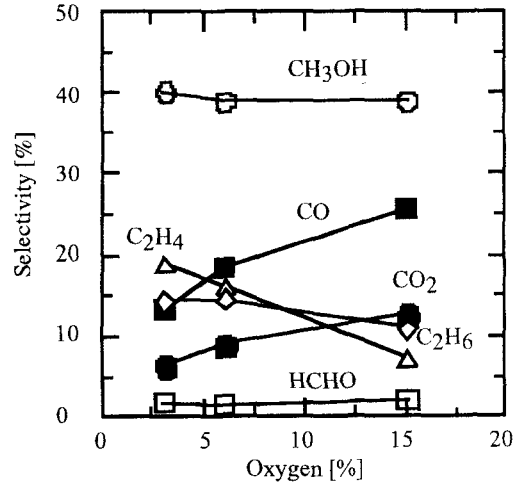

Fig. 5 Influence of O_2 concentration on selectivity of each product. Reaction conditions are the same as these in Fig. 4.

3.3 Influence of input power

The input power in one-pulse discharge is usually in the order of million watts. Such a high energy input will affect activation of methane and oxygen. Hence the influence of input power on methane oxidation was investigated. The results are shown in Figs. 6 and 7. The conversions of methane and oxygen increased with increasing input power. The selectivity of methanol peaked at the input power around 5 W. The selectivities of carbon dioxide, ethane, and formaldehyde did not change significantly, but the selectivity of ethylene decreased and that of carbon monoxide increased as input power increased.

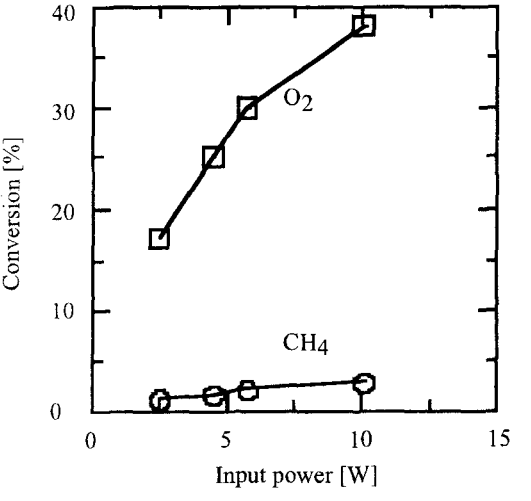

Fig. 6 Relations of input power and conversion of CH_4 and O_2 with total gas flow rate = 100 ml/min and CH_4/O_2 = 94/6.

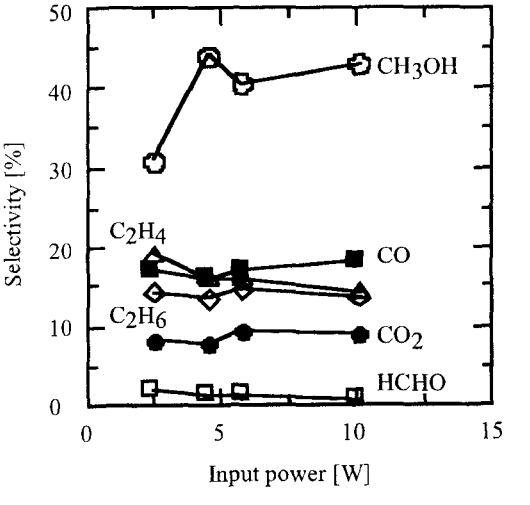

Fig. 7 Selectivity of each product versus input power. Conditions are the same as these shown in Fig. 6.

4. DISCUSSION

Methane can be activated to CHx (x=0-3). The main products are different from reactions of CHx and O_2 or O. We simulated methane oxidation with a chemkin simulation software and found that the main product is CO or CO_2 if CH_4 is activated to CH_2 and CH.

Methanol can be produced *via* eqs. (1) -(4). Therefore, CH_3 radicals are important for the production of methanol. The results shown in Fig. 3 suggested that more CH_3 radicals can be produced by using a non-thermal plasma reactor-Reactor A.

$$CH_3 + O_2 \rightarrow CH_3O_2 \quad (1)$$

$$CH_3O_2 + OH \rightarrow CH_3OH + O_2 \quad (2)$$

$$CH_3O + HO_2 \rightarrow CH_3OH + O_2 \quad (3)$$

$$CH_3 + OH \rightarrow CH_3OH \quad (4)$$

The discharge using a dielectric barrier reactor usually yields a high density of electron with high electron energy. The length of discharge channel is about several centimeters (9). In the present study, discharge occurs within 120 ns in a pulse discharge. This type of discharge is known as a streamer corona discharge (9). Such a streamer discharge usually results in a multitude of filaments or breakdown channels between two electrodes. Each channel corresponds to a single transit breakdown or steamer breakdown. The configuration of electrode and the waveform of an applied electric field usually influence the formation of such a breakdown, finally influence methane oxidation.

The most important factor, which limits methane conversion rate, is the input power (Fig. 7). This finding indicated that methane activation to CH_3, CH_2, and CH mainly depends on the characteristics of above streamer breakdown, such as the rise rate of voltage and reactor configuration.

Although oxygen concentration could not influence the methane conversion rate and methanol selectivity, the use of a high oxygen concentration resulted in increase of CO and CO_2 formations (Fig. 7). This is explained that the amount of methane activated is mainly influenced by the discharge characteristics, but the rates of oxidation of CH_3, CH_2, and CH to CO and CO_2 influenced by the oxygen concentration.

Dissociation of CH_4 to CH_3 and H needs 431.8 kJ/mol, and that of O_2 to O does 498.7 kJ/mol. As the results shown in Fig. 4, conversion rates of methane and oxygen at the input power 5.7 W were calculated to be 1.21×10^{-6} mol/s and 1.10×10^{-6} mol/s, respectively. Therefore, the energy required for methane conversion is 0.522 W, and that of O_2 is 0.549 W. The energy efficiency in this pulse discharge process was then calculated to be (0.522+0.549)/5.7=19%. Because the methanol selectivity is 47%, the energy efficiency is 8.9% base on methanol production and the energy required for methanol production is 1.0×10^7 J/mol-methanol. The energy consumption in a conventional methanol production process is 2.5×10^5 J/mol-methanol (10). This represents that the energy efficiency using this discharge method should be elevated more than 40 times in order to substitute the conventional methanol production process.

In conclusion, we propose that this kind of plasma may be useful if methanol and more valuable products such as ethylene can be produced.

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