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Reaction Pathways of Methane Conversion in Dielectric-Barrier Discharge

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Abstract−Conversion of methane to C_2, C_3, C_4 or higher hydrocarbons in a dielectric-barrier discharge was studied at atmospheric pressure. Non-equilibrium plasma was generated in the dielectric-barrier reactor. The effects of applied voltage on methane conversion, as well as selectivities and yields of products were studied. Methane conversion was increased with increasing the applied voltage. Ethane and propane were the main products in a dielectric-barrier discharge at atmospheric pressure. The reaction pathway of the methane conversion in the dielectric-barrier discharge was proposed. The proposed reaction pathways are important because they will give more insight into the application of methane coupling in a DBD at atmospheric pressure.

Key words: Methane, Plasma, Dielectric-Barrier Discharge, Hydrocarbons, Kinetics

INTRODUCTION

Since the 1980s, intensive research efforts have been made to develop processes for direct conversion of methane into more valuable hydrocarbons [Franser et al., 1885; Bhatngar et al., 1995; Larkin et al., 2001]. The thermal and/or catalytical difficulties in direct methane conversion are due to the strength of the C-H bond of methane. High temperature catalytic reactions of direct methane conversion lead to poor economics associated with a low yield of the specific chemical feedstock or gas fuel such as ethylene, propylene and butane. Recently, many studies on plasma processes have been reported to be effective for the methane conversion and the decomposition of volatile organic compounds [Jeong et al., 2001; Lee et al., 2001; Lie et al., 1997; Mok et al., 2003]. Lower temperature methane conversions are desirable and have been investigated extensively.

Lee et al. [2001] studied pure methane conversion in a capacitively coupled radio-frequency plasma. Savinov et al. [1999] studied the decomposition of methane and carbon dioxide in radio-frequency discharge. Marafee et al. [1997] studied an oxidative coupling of methane in a DC corona discharge over Sr/La_2O_3 catalyst. When the DC corona discharge was applied to the catalytic reactor, the methane conversion increased five times and the selectivity for C_2 increased 8 times at 853 K. Liu et al. [1998] reported non-oxidative methane conversion to acetylene over zeolite in the low temperature plasma. They presented a reaction mechanism to explain the experimental results of 32% C_2 hydrocarbons yield.

Becker et al. [2000] reported that gas phase reactions of methane produced higher hydrocarbons by the following reaction mechanism:

$$CH_4 \rightarrow C_1 \rightarrow C_2 \rightarrow C_4 \rightarrow C_6 \rightarrow C_n$$

C_1=CH_3, C_2=C_2H_6, C_2H_5, C_2H_4, C_2H_3, C_2H_2, C_4=C_4H_6, C_4H_5, C_4H_4, C_4H_3, C_6=mononuclear aromatic hydrocarbon species, C_n=polynuclear aromatic hydrocarbon species. Liu et al. [2001] tried to convert methane and carbon dioxide under dielectric-barrier discharge (DBD) plasma. Otsuka et al. [2001] studied catalytic decomposition of light alkanes, alkenes and acetylene over Ni/SiO_2. They found that the degree of graphitization of deposited carbon was higher in the order, alkane>alkenes>acetylene. Kozlov et al. [2000] studied to identify the dominant chemical pathways of organic compound formation from CH_4+CO_2 mixtures in a dielectric-barrier discharge (DBD) reactor. They investigated how certain electrical properties of the discharge influence chemical mechanisms and kinetics of this process.

The main purpose of this work is to propose a reaction pathway for the methane decomposition in a dielectric-barrier discharge (DBD) at atmospheric pressure. A great deal of knowledge has been accumulated about methane into higher hydrocarbons in DBD. However, there has been little attention to interpreting the reaction pathway. C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, C_3H_8 and C_4H_{10} were the reaction products for the conversion of methane in DBD. Thus, those of gases used as the feed stream, and then conversion and selectivities were analyzed to interpret reaction pathway. So far, this approach has not been attempted for the decomposition of methane in DBD plasma.

EXPERIMENTAL

A schematic diagram of the experimental apparatus is shown in Fig. 1. The reactor was a quartz tube with an inside diameter of 8 mm and the length of 270 mm. Two stainless steel wires with a diameter of 0.45 mm were installed in the quartz tube as an electrode. The reactor was grounded by a copper foil with a thickness of 0.05 mm and a length of 200 mm. AC power with 20 kV, 60 Hz, and 35 mA was used in this experiment. Applied voltage was varied between

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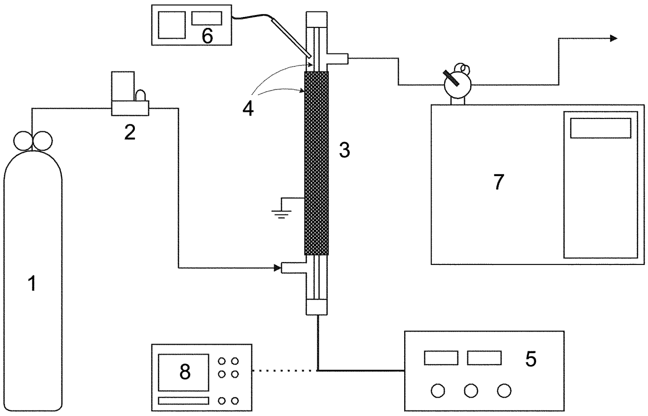

Fig. 1. Schematic diagram of the experimental apparatus.

1. Gas cylinder
2. Mass flow controller
3. Plasma reactor
4. Electrodes
5. AC power supply
6. Temperature indicator
7. GC
8. Oscilloscope

11 kV and 19 kV. The flow rate of methane was controlled by the mass flow controller (Bronkhorst, B-5534-FA). The reaction products were analyzed by a gas chromatograph (HP 5890 equipped with a Haysep Q packed column and FID detector). The peaks were identified by comparing retention times with those of standard gases (CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, C_3H_8 and C_4H_{10}) with a purity above 99.5%. All experiments were carried out under atmospheric pressure.

The methane conversion in this plasma reaction was defined as:

$$CH_4 \text{ conversion} = (\text{moles of } CH_4 \text{ consumed/moles of } CH_4 \text{ introduced}) \times 100\%$$

The selectivities and yields of C_2, C_3 and C_4 hydrocarbons are:

$$\text{Selectivity of } C_2H_2 = 2\times(\text{moles of } C_2H_2 \text{ formed/moles of } CH_4 \text{ consumed})\times 100\%$$
$$\text{Selectivity of } C_2H_4 = 2\times(\text{moles of } C_2H_4 \text{ formed/moles of } CH_4 \text{ consumed})\times 100\%$$
$$\text{Selectivity of } C_2H_6 = 2\times(\text{moles of } C_2H_6 \text{ formed/moles of } CH_4 \text{ consumed})\times 100\%$$
$$\text{Selectivity of } C_3H_6 = 3\times(\text{moles of } C_3H_6 \text{ formed/moles of } CH_4 \text{ consumed})\times 100\%$$
$$\text{Selectivity of } C_3H_8 = 3\times(\text{moles of } C_3H_8 \text{ formed/moles of } CH_4 \text{ consumed})\times 100\%$$
$$\text{Selectivity of } C_4H_{10} = 4\times(\text{moles of } C_4H_{10} \text{ formed/moles of } CH_4 \text{ consumed})\times 100\%$$
$$\text{Yield of } C_2 \text{ hydrocarbons} = CH_4 \text{ conversion}\times\sum(\text{selectivities of } C_2H_2, C_2H_4, C_2H_6)$$
$$\text{Yield of } C_3 \text{ hydrocarbons} = CH_4 \text{ conversion}\times\sum(\text{selectivities of } C_3H_6, C_3H_8)$$
$$\text{Yield of } C_4 \text{ hydrocarbons} = CH_4 \text{ conversion}\times\text{selectivities of } C_4H_{10}$$

RESULTS AND DISCUSSION

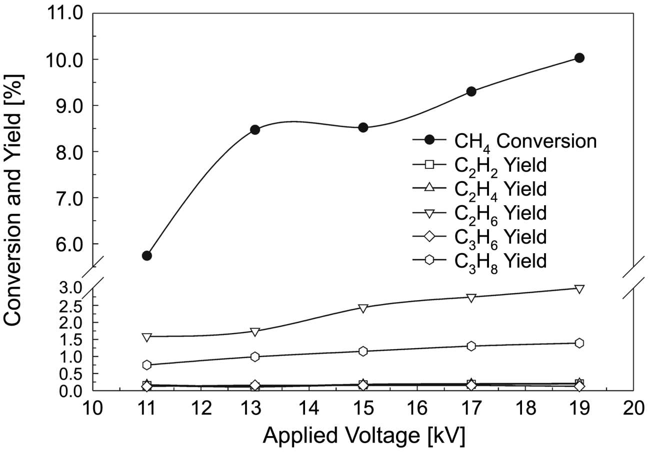

Fig. 2. Effects of the applied voltage on the methane conversion and yield of products; methane flowrate=6 ml/min.

The magnitude of the external applied voltage was related to the intensity of the internal electric fields. The applied voltage was the most important parameter in the plasma chemical reaction to activate the molecules of methane. The increase of the applied voltage changes the amount of electrons released, so the possibility of breaking the C-H bond of methane was enhanced. The power input was only between 12 W and 14 W when the experimental conditions and feed gases were varied. Fig. 2 shows the effect of the applied voltage on the methane conversion and the product yields. Methane conversion was increased from 5.74% to 10.03% when the applied voltage was increased from 11 kV to 19 kV. The yields of C_2H_6 and C_3H_8 increased with the increase of the applied voltage. Variation of the applied voltage did not have a significant effect on the yields of C_2H_2, C_2H_4 and C_3H_6. The product selectivity is shown in Fig. 3. The selectivities of C_2H_2, C_2H_4 and C_3H_6 were almost constant and below 3%. The selectivity of C_2H_6 was between 28% and 30% with the increase of applied voltage. The selectivity of C_3H_8 was around 13% at the applied voltage between 11 kV and 19 kV. The selectivity of unknown was over 50% at each applied voltage. In this study, a gas chromatograph with FID was used, and it could analyze CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, C_3H_8 and C_4H_{10}.

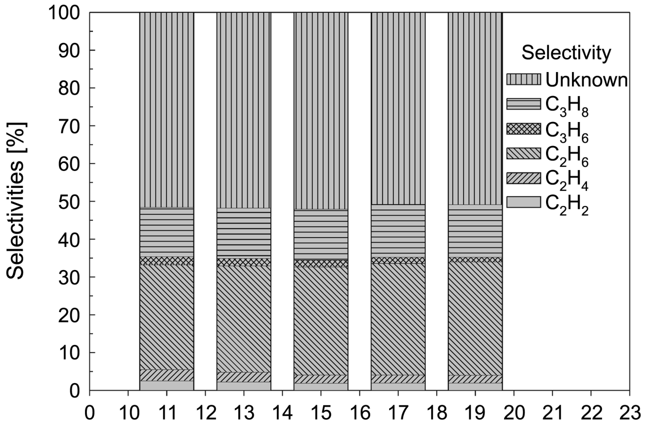

Fig. 3. Effects of the applied voltage on the product selectivities; methane flowrate=6 ml/min.

As shown in Fig. 3, the major product of methane conversion in a barrier discharge was an alkane such as C_2H_6 and C_3H_8. Methane molecules passed through the discharge zone, so the initiation reaction might have been caused by the collision between the electrons and methane producing methyl radicals and hydrogen atoms. C_2H_6 and C_3H_8 might be formed by the recombination reaction of methyl radicals. Eliasson et al. [2000] reported that methane chain reaction proceeded as follows:

$$CH_3\cdot+CH_3\cdot\rightarrow C_2H_6 \tag{1}$$

$$C_2H_6+e\rightarrow C_2H_5+H\cdot+e \tag{2}$$

$$C_2H_5\cdot+C_2H_5\cdot\rightarrow C_4H_{10} \tag{3}$$

As shown in Eq. (2), hydrogen atoms are produced while alkane is converted to make higher hydrocarbons. In order to analyze the selectivity of H_2, the GC with TCD was used. The selectivity of hydrogen was 3.17% at 17 kV. GC analysis was limited to CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, C_3H_8 and C_4H_{10}, so the major fraction of unknown could not be identified. As shown in Fig. 3, C_2H_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 were the main products in a dielectric-barrier discharge. These hydrocarbons could be the final products or reacted with other hydrocarbons. The decomposition and recombination reaction took place in the plasma zone. To understand the methane decomposition in plasma reaction, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, C_3H_8 and C_4H_{10} were used as the feed stream. The purity of the reactants was above 99.5%. The experiment was carried out at 17 kV and 6 ml/min. The product selectivities are listed in Table 1. The results suggest the following reaction pathways. An activated C_1 species react with another C_1 species and C_2 species to form ethane and propane. The ethane may be dehydrogenated to form acetylene and/or ethylene, and reacted with other C_1 species to form propane. Ethylene can react with the C_1 species to form propylene and propane. From the experimental results, the selectivities of C_2H_2 and C_3H_8 were higher than those of other hydrocarbons when C_2H_4 was the reactant. C_2H_2 did not make the specific hydrocarbons but was stabilized as a final product. When C_2H_6 was the reactant, the selectivity of C_2H_4 was especially high, and that of C_2H_2 was next. In this case, dehydrogenation was dominant. The selectivity of C_2H_6 was very high when C_3H_6 was the reactant, and similar amounts of C_2H_2, C_2H_4 and C_3H_4 were produced. The selectivity of CH_4 was very high, and that of C_2H_6 and C_3H_6 was higher than of other hydrocarbons when C_3H_8 was the reactant. From the information in Table 1, the reaction pathways of methane in a dielectric-barrier discharge are suggested as shown in Fig. 4.

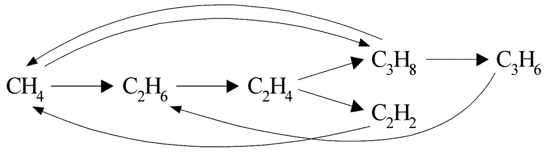

Fig. 4. The reaction pathways of methane conversion in a dielectric-barrier discharge.

Kozlov et al. [2000] suggested the chemical mechanism for C_2-hydrocarbons formation in a DBD from pure methane. They experimentally proved that the process consisted of the following three sequential steps:

$$CH_4\rightarrow C_2H_6\rightarrow C_2H_4\rightarrow C_2H_2 \tag{4}$$

They ran experiments with pure methane in a DBD, and suggested the above simplified reaction pathway. In their reaction pathways, an activated C_1 species reacted with another C_1 species to form ethane, and then ethane dehydrogenated to ethylene and acetylene.

In this work, to interpret the methane decomposition in a plasma reaction, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, C_3H_8 and C_4H_{10} were used as the feed stream. Our proposed reaction pathways show a similar pattern with Eq. (4). However, the produced ethylene reacts with other C_1 species to form propane, which makes methane and dehydrogenate to form propylene. Propylene and acetylene decompose ethylene and methane, respectively. Such an approach has not been attempted so far, especially in the plasma reaction. This study is important because it will give more insight into the methane coupling in a DBD at atmospheric pressure.

CONCLUSIONS

The effect of applied voltage on the methane conversion, the yields and selectivities of products was investigated. Methane conversion was increased from 5.74% to 10.03% when the applied voltage was increased from 11 kV to 19 kV. The main products were alkanes such as C_2H_6 and C_3H_8. The yields and selectivities of C_2H_6 and C_3H_8 were slightly increased with increasing applied voltage, and those of C_2H_2, C_2H_4 and C_3H_6 were almost constant. The reaction pathways of methane decomposition were proposed to interpret methane coupling in the dielectric-barrier discharge plasma reaction at atmospheric pressure. In reaction pathways, an activated C_1 species reacted with another C_1 species to form ethane, which proceeded to ethylene and the acetylene as a dehydrogenation. Produced ethylene reacts with other C_1 species to form propane, which make

Table 1. Conversions and selectivities of hydrocarbons in DBD reactor, applied voltage: 17 kV, feed flowrate: 6 ml/min

Reactants	Conversion [%]	Product selectivity [%]							
		CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_4	C_3H_6	C_3H_8	C_4H_{10}
CH_4	9.30	-	1.99	2.17	29.48	-	1.63	14.03	0.04
C_2H_2	9.52	1.34	-	-	0.34	1.32	1.16	2.62	-
C_2H_4	31.44	0.39	9.42	-	1.84	-	0.91	13.79	-
C_2H_6	27.44	1.09	4.91	58.56	-	1.68	1.29	3.67	0.02
C_3H_4	12.27	1.66	16.27	1.37	1.22	-	4.81	-	-
C_3H_6	25.31	0.93	3.42	3.68	33.26	4.01	-	2.85	0.03
C_3H_8	13.31	25.54	3.43	6.84	10.41	0.51	13.28	-	0.20
C_4H_{10}	18.84	2.42	2.01	3.25	2.19	-	2.26	5.04	-

methane and dehydrogenate to form propylene. Propylene and acetylene decompose ethylene and methane, respectively. The proposed reaction pathways are important because this information will give more insight into the application of methane coupling in a DBD at atmospheric pressure.

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