Production of Acetic Acid Directly from Methane and Carbon Dioxide Using Dielectric-Barrier Discharges

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The atomic economic reaction of acetic acid formation from methane and carbon dioxide via dielectric-barrier discharges at ambient conditions was investigated in this work. A significantly high selectivity of acetic acid (up to 5.3%) has been achieved with high conversions of methane (more than 54.1%) and carbon dioxide (more than 37.4%).

Direct conversion of methane to more valuable hydrocarbons has been an attractive subject of investigation.[1] Cold plasma, as an unconventional technology, has also been used for methane conversion.[2–9] Some of studies were conducted using pure oxygen as the oxidant for plasma methane conversion.[5,6] On the other hand, carbon dioxide is also a potential carbon resource. Chemical utilization of carbon dioxide is a hot topic that is challenging chemist worldwide. The combination of utilization of carbon dioxide and methane using dielectric-barrier discharge (DBD) plasmas has been reported previously.[7,8] Syngas, higher hydrocarbons, oxygenates, and even plasma-polymerized films have been produced. Investigations have been conducted to find out the best condition to produce higher hydrocarbons.[7,8] Zeolite has also been applied to improve the selectivities of light hydrocarbons.[7] In this work, production of oxigenation, especially acetic acid, using DBDs will be discussed.

It is well known that the direct production of acetic acid from methane and carbon dioxide is a perfect atomic economic reaction:

$$CH_4 + CO_2 \rightarrow CH_3COOH \qquad \Delta G_{298K} = 71.17 \text{ kJ/mol} \tag{1}$$

However, this reaction is unfavored thermodynamically. Equilibrium conversion is almost zero. As discussed before,[10] discharge plasmas, like DBDs, can make the thermodynamic unfavored reaction become true even at ambient conditions. The present investigation has confirmed that the DBDs induce an effective production of acetic acid from methane and carbon dioxide.

The reactor we used in this investigation was showed in Figure 1. The diameter of dielectric (quartz) tube is 9.6 mm instead of 50 mm used before. The gap applied for the discharge was 1.1 mm and the length of the discharge zone 250 mm. An aluminum foil attached closely to the inner surface of quartz tube is connected with a high voltage generator, which supplies a sinusoidal signal at a frequency of 25 kHz. The voltage and current were measured with an on-line oscilloscope (Tektronix 2440) connecting a high voltage probe (Tektronix P6015A) and a pulse current transformer (Pearson Electronics 411). The residence time was about 14 seconds for the experiments reported here. The temperature of the reaction was adjusted at about 338 K using the circulating oil. The gaseous products were analyzed with an online gas chromatograph (HP 5890) and mass selective detector (HP 5971) equipped with a HP-PLOT Q column (30 m × 0.53 mm × 40 μm). The liquid products were collected in a trap cooled by a mixture of ice and water before they were analyzed with the GC/MS described above. All the experiments were operated at atmospheric pressure.

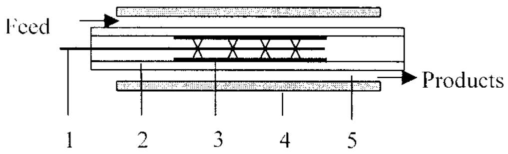

Figure 1. Schematically representative of the dielectric-barrier discharge reactor (1. high voltage electrode; 2. quartz tube; 3. aluminum foil; 4. grounded electrode; 5. discharge gap)

The conversions of methane and carbon dioxide are shown in Figure 2. The increase in CO_2 conversion is observed with increasing concentration of methane in the feed. Table 1 indicates the selectivities of products and by-products based on carbon balance. There is an optimal feed ratio of CH_4/CO_2 to make the best selectivity of acetic acid, ethanol, methanol or propanoic acid, respectively. The highest acetic acid selectivity of 5.3% reaches when methane concentration is 67.4% in the feed. At the same condition, the selectivities of ethanol and methanol also get the maximum. The major gaseous by-products are CO, C_2H_6 and C_3H_8. The selectivity of CO proportionally decreases with the increasing methane concentration in the feed. The concentrations of ethanol and acetic acid are higher than those of methanol and formic acid almost at all the feed ratios. These results are very different to those with pure oxy-

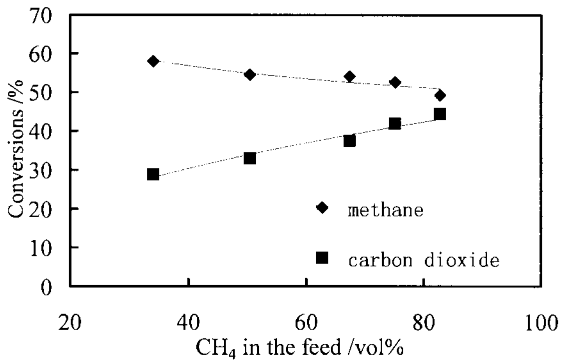

Figure 2. Conversions methane and carbon dioxide vs the composition of feed (discharge gap of 1.1 mm; discharge power of 100 W; flow rate of 40 NmL/min)

Table 1. Selectivities of products[a] and H_2/CO ratio

CH_4 in feed /vol%	82.8	75.1	67.4	50.4	34.0
	Selectivity based on carbon atoms /%				
Acetic acid	2.1	4.2	5.3	3.5	2.1
Formic acid	0.4	0.3	0.2	0.1	0.0
Propanoic acid	0.7	1.7	1.6	0.9	0.7
Ethanol	0.7	1.3	1.7	1.0	0.5
Methanol	0.3	0.6	1.0	0.6	0.4
CO	13.2	24.6	31.8	43.1	75.0
C_2H_6	17.4	14.6	13.9	11.8	7.7
C_3H_8	9.8	8.1	7.5	5.7	3.2
H_2/CO	3.2	2.4	1.9	1.5	0.8

Discharge gap of 1.1 mm; discharge power of 100 W; flow rate of 40 NmL/min. [a]Selectivity based on carbon atoms = moles of carbon in the product / [moles of CH_4 converted + moles of CO_2 converted] × 100%

gen as the oxidant.[5,6] Liquid hydrocarbons, as another by-product here, have been discussed previously.[7,8]

The mechanism of the reactions using plasmas is complex and not very clear at present. But most of the researchers agree with radical reaction mechanism for the plasma methane conversion.[4,6,11–14] For the synthesis of acetic acid from the DBD plasma methane conversion in the presence of carbon dioxide, both of methane and carbon dioxide can be excited. Methane can be dissociated into methyl radical and hydrogen:

$$CH_4 + e^* \rightarrow CH_3\bullet + H\bullet + e \qquad (2)$$

Here, e^* stands for the electron with higher energy. There exist plenty of hydrogen in the discharge zones. Therefore, the hydrogen could easily stick to one of the oxygen atoms in CO_2 molecules:

$$CO_2 + H\bullet \rightarrow \bullet COOH \qquad (3)$$

Furthermore, it has been reported that •COOH radicals can be generated from CO_2 in the acidic environment.[15] The acetic acid will be produced from the combination of the group of •COOH with the radical of $CH_3\bullet$:

$$\bullet COOH + CH_3\bullet \rightarrow CH_3COOH \qquad (4)$$

A solid micro-extraction has also been conducted to investigate on the chain growth of acids. The C_3 and even C_4 acids can be detected in the micro-extraction system. It has been considered that C_3 acid is formed as follows:

$$CH_3COOH + e \rightarrow \bullet CH_2COOH + H + e \qquad (5)$$
$$CH_3\bullet + \bullet CH_2COOH \rightarrow CH_3CH_2COOH \qquad (6)$$

The reaction (5) is a typical dissociative reaction of acids or alcohols observed in the discharges. There is another possible mechanism for the formation of C_3 acid:

$$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6 \qquad (7)$$
$$C_2H_6 + e \rightarrow C_2H_5\bullet + H + e \qquad (8)$$
$$\bullet COOH + C_2H_5\bullet \rightarrow C_2H_5COOH \qquad (9)$$

From reactions (5)–(9), it can be easily understood that the selectivity of acetic acid is much higher than that of propanoic acid. However, the selectivity of formic acid is not high (as shown in Table 1). It is considered that the possibility of the combination of hydrogen with •COOH group is very low since hydrogen radical tends to involve in the reaction (3) and in the reaction for water production:

$$CO_2 + 2H\bullet \rightarrow CO + H_2O \qquad (10)$$

Further investigation is being conducted to improve the selectivity of acetic acid.

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