Oxidative Synthesis of Higher Hydrocarbons from CO_2 and CH_4 by Streamer Discharges

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An experimental investigation on oxidative synthesis of ethane and ethylene from CH_4 using CO_2 as an oxidant has been performed by streamer discharge reactions, which are initiated by an AC electric field. This gas discharge promotes the methane conversion to reach a high yield of C_2 hydrocarbons of 20% ~ 45% with a methane conversion of 25% ~ 80% and a conversion of carbon dioxide of 8% ~ 40%. The reactions for these conversions are: $2CH_4 + CO_2 \longrightarrow C_2H_6 + CO + H_2O$ and $2CH_4 + 2CO_2 \longrightarrow C_2H_4 + 2CO + 2H_2O$. A possible pathway of C_2 formation was also present in this letter.

Both of methane and carbon dioxide are the greenhouse gases. As the consumption of all the fossil fuels led to the formation of CO_2, emission control and chemical utilization of CO_2 have been a more serious problem for scientists all over the world. Although some techniques have found their way in carbon dioxide fixation,[1-4] there is still no proven technology for chemical utilization of such a plentiful carbon source. Because most of the industrial carbon dioxide emissions are from power plant, the regular catalytic conversion of CO_2 suffered from the poison impurities contained in flue gas. Regarding this, we present here an oxidative synthesis of higher hydrocarbons from CO_2 and CH_4 by streamer corona discharges. Streamer corona discharge is a cold plasma and characterized by low gas temperature and high electron temperature. It was well established[5] that streamer discharges are sources of abundant free radicals. Under such an electronic discharge condition, carbon dioxide can contribute one of two oxygen atoms for methane conversion by dissociation reactions:

$CO_2 + e \longrightarrow CO + O + e$ dissociation (1)

$CO_2 + e \longrightarrow CO + O^-$ dissociation attachment (2)

The O^- [6] and the metastable state O (^1D) [7] have been known to be active oxygen species for extracting a hydrogen from the quite inert methane molecule. The application of streamer discharges offers an alternative to metal oxide catalyst for methane conversion using CO_2 from flue gas. According to Chang et al.,[4] the electronic dissociation of molecules depends on the excitation states of the molecules and the energy distribution of electron wave motions. To initiate reaction (1) or (2), only a few (around 0.1 eV) electronic energies are required if CO_2 is highly vibrationally excited. On the other hand, because of the very high ionization energy of methane molecule (more than 11 eV),[8] it is not sufficient for the electronic energy of streamer discharges to dissociate the methane molecule. This is very important to stabilize the discharge reactions without totally destroying methane molecule. During our experiments, an AC generator was applied to initiate the streamer discharges. The AC voltage provides an easy way to generate the streamer discharges, which take place only when the voltage is increased to a sufficiently high level during each half cycle. The top wire electrode and the lower cylindrical hollow electrode with a diameter 1mm less than the inner diameter (6 mm) of the quartz tube reactor are shown in Figure 1. The gap between these two stainless steel electrodes is 12 mm. The feed gases, CO_2, CH_4 and the dilution gas helium were introduced into the system via flow meters. The amount of CO_2 composition was experimentally controlled to be 5% to 20% as a simulated gaseous mixture that is equivalent to the composition of CO_2 emission from power plants. The feed and effluent product gases were analyzed by an on line gas chromatograph using a TCD detector. With such a reaction system, the methane and carbon dioxide conversions are defined as:

CH_4 conversion=(moles of CH_4 consumed/moles of CH_4 introduced) × 100%

CO_2 conversion=(moles of CO_2 consumed/moles of CO_2 introduced) × 100%

The yield of C_2 hydrocarbons is as following:

C_2 yield = 2 × (moles of C_2 hydrocarbons formed)/ moles of CH_4 introduced) × 100%

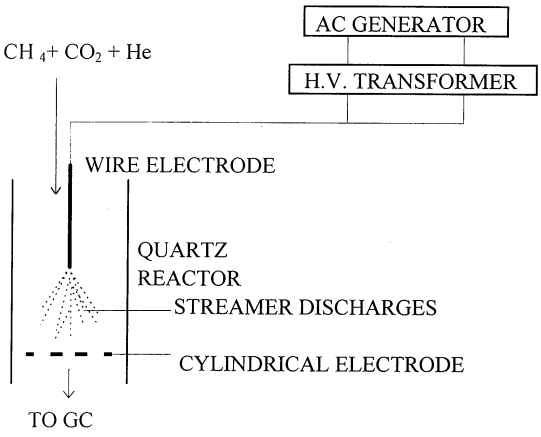

Figure 1. Discharge Reactor System.

The start gas temperature for all the discharge reactions is room temperature. The reaction gas temperature will reach 200 ~ 500 °C according to different reaction conditions. The temperature was measured by an insulated thermal couple situated at upstream or downstream of the reactor. Figure 2 represents the effect of input voltage on the rate of product formation. When the input voltage reaches 3.75 kV, the gas discharge is initiated. The discharge reactions lead to the change in compositions. The formation rate of ethane decreases gradually with increasing in the input voltage, while the formation rate of ethylene increases first and then decreases slightly with a maximum at the input voltage of 5 kV. Figure 2 shows a significant monotonous increase in CO yield rate. This suggests that part of C_2 hydrocarbons are destroyed to form CO by the further oxidation. It is evident that ethane and carbon monoxide are the initial products and that ethylene is the secondary product, formed by the dehydrogenation of ethane. The same conclusion can be drawn from the effect of CH_4/CO_2 on ethylene formation, as shown in Figure 3. When we keep a constant methane partial pressure of 0.05atm in the feed, the

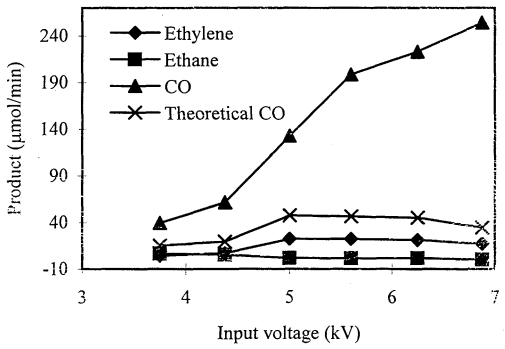

Figure 2. Effect of input voltage.
CH_4/CO_2 in the feed:1/4 Feed rate: 100 cm^3/s AC frequency: 60Hz.

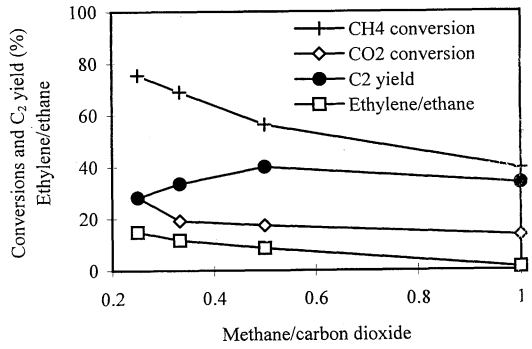

Figure 3. Effect of CH_4/CO_2.
Partial pressure of CH_4 in the feed: 0.05 atm Feed rate: 100 cm^3/s
Input voltage: 5.6kV AC frequency: 60Hz.

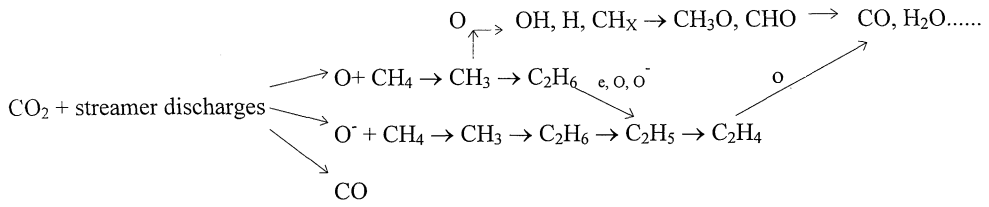

Figure 4. A Schematic Mechanism.

increasing CO_2 partial pressure promotes a significant conversion of CH_4 to C_2H_4 (C_2H_4/C_2H_6 increases). Such an increasing conversion of methane does not induce an increase in total yield of C_2 hydrocarbons because of the complete oxidation of ethylene to CO. This means that more active species have been produced by reactions (1) and/or (2) when CO_2 amount increases in the feed. The C_2 and CO are thought to be formed as following:

$$2CH_4 + O \text{ or } O^- \longrightarrow C_2H_6 + H_2O \quad (3)$$
$$C_2H_6 \xrightarrow{e} C_2H_4 + H_2 \quad (4)$$
$$H_2 + O \longrightarrow H_2O \quad (5)$$
$$C_2H_6 + O \text{ or } O^- \longrightarrow C_2H_4 + H_2O \quad (6)$$
$$C_2H_4 + 4\,O \longrightarrow 2CO + 2H_2O \quad (7)$$

The total discharge reactions are:[9]

$$2CH_4 + CO_2 \longrightarrow C_2H_6 + CO + H_2O \quad \Delta H=16.7kJ/mol \quad (8)$$
$$2CH_4 + 2CO_2 \longrightarrow C_2H_4 + 2CO + 2H_2O \quad \Delta H=176.0kJ/mol \quad (9)$$
$$CH_4 + 3CO_2 \longrightarrow 4CO + 2H_2O \quad \Delta H=330.6kJ/mol \quad (10)$$

A schematic mechanism resulting in the formation of main products observed experimentally is proposed in figure 4.

The theoretical CO yield in Figure 2 is calculated by assuming that one of two oxygen atoms in CO_2 is applied exclusively for the formation of C_2 hydrocarbons with the actual amount of ethane and ethylene in this experiment (Reactions (8) and (9)). The experimental CO yield is much more than the theoretical one, especially at the high input voltage. The maximum C_2 formation (22.32μmol/min C_2H_4 + 1.79μmol/min C_2H_6) in Figure 2 presents at the input voltage of 5kV with a CH_4 conversion of 68.5% and a CO_2 conversion of 20.0%. Based on reactions (8) ~(10), the power efficiency with this maximum C_2 yield is 7.1% under an input power of 7.5w. This power efficiency is not high because the calculated power (0.535w) does not take into account any energy barrier needed to initiate various plasma reactions other than reactions (1)~(10). The energy yields for two objective products, ethylene and CO, are 5.0g/kwh and 29.7g/kwh, respectively. To achieve a large yield of C_2 hydrocarbons, a high input voltage is not suggested to be applied. As the streamer discharge has been used for NO_x and SO_x emission control, from the research by far, it is very potential to develop a technique which combines methane conversion together with removal of CO_2, NO_x and SO_x from flue gas by low-energy streamer discharges. The principal products with such a technique are ethylene and CO.

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