Dry reforming of methane in a temperature-controlled dielectric barrier discharge reactor: disclosure of reactant effect

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Abstract: Plasma-assisted dry reforming of methane has attracted much research attention because this process simultaneously utilizes greenhouse, methane and carbon dioxide, to produce hydrogen-rich syngas at a relative low temperature. Although it is generally recognized that the gas composition of reactant has great effect on the methane conversion and products distribution, systematic studies that clarify the roles that electron-induced chemistry and thermochemistry play are needed for a full understanding of reactant effect. Here, we compared the reforming performance by varying the ratio of CO₂/CH₄ or O₂/CH₄ at the similar reduced field intensity (E/N) in a temperature-controlled dielectric barrier discharge reactor to elaborate the role of electron-induced chemistry and thermo-chemistry in the dry reforming process. By conducting optical emission spectrum measurement, the enrichment of O atoms was observed at the increased CO₂/CH₄ or O₂/CH₄ ratios. At T = 293 K, methane conversion was only dependent on the electron-induced chemistry regardless of the specific reactant gas composition. At a relative high temperature condition, however, thermochemistry could become pronounce when sufficient O atoms were added into the dry reforming process. In contrast, the chemical pathways to the products were overall controlled by the thermochemistry at the tested background temperatures. Due to the conversion of carbon-based products into the carbon dioxide, the conversion of carbon dioxide was influenced by the thermochemistry when the concentration of O atoms was high. Our findings may improve the understanding of reactant effect and the designs of plasma-reformer.

Key Words: dry reforming, plasma, carbon dioxide, methane, gas composition
1. Introduction

Today, under the pressure of serious environmental problems caused by the excessive use of fossil fuels, the demand for renewable and environmental-friendly energy is becoming ever more urgent. The reforming (or gasification) of conventional feedstock as fuel, of which major constituent is carbon and hydrogen, for the production of hydrogen-rich syngas or value-added chemicals has showed promising potential. Various reforming methods, such as partial oxidation, steam reforming, and dry reforming, are designed mainly to produce hydrogen and carbon monoxide and yield typical H₂/CO ratio with each reforming process. Among these reforming processes, the dry reforming of methane, a reaction between methane (CH₄) and carbon dioxide (CO₂), has attracted much research attention because this process simultaneously utilizes and reduces greenhouse gases [1]. Catalytic processes for the dry reforming are limited by rapid deactivation of the catalysts due to coke formation. Moreover, a requirement of warm-up period to reach activation temperatures also limits the catalytic process in some applications, e.g. in vehicles, which require rapid ignition/start-up from a cold condition. In this reason, studies based on non-thermal plasma (NTP) techniques have been conducted to fill the technical gap [2–5].

Different NTP generation methods [6–10] as well as the combinations of NTP with heterogeneous catalysts [11–16] have been investigated to make the process commercially feasible in terms of energy efficiency and product selectivity. It is generally recognized that the hotter plasmas, e.g. arc-jet type plasma and microwave plasma, are superior to the colder plasmas, which are typically produced by dielectric barrier discharge (DBD) and corona discharge, in the CH₄ and CO₂ conversion, and H₂ selectivity [17–21]. The advantage of the colder plasmas is its low temperature, so it is possibly to obtain useful chemical intermediates that do not reach deep oxidation (CO₂) or cracking (soot) [22–26].

The improvement of the reactant conversion and products distribution using the colder plasmas requires a better understanding of plasma chemistry in the reforming process. In previous work, we developed a temperature-controlled DBD reactor. This reactor allows individually controlling the reduced filed intensity and reaction...
temperature, which govern the electron-induced chemistry and thermochemistry, respectively. As a result, we found that for the dry reforming of CH$_4$ at CO$_2$/CH$_4$=1, the CH$_4$ conversion was influenced by the electron-induced chemistry while for the partial oxidation of CH$_4$, the CH$_4$ conversion was governed by both the electron-induced chemistry and the thermochemistry. However, for both of these reforming processes, the reaction pathways to the products were only affected by the thermochemistry \[27, 28\]. These results indicate that the plasma chemistry involved in the reforming process could be adjusted by the reactant gas composition. In this regard, the reactant gas composition effect needs to be further investigated so that we can get a deeper understanding of the contribution of electron-induced chemistry and thermochemistry to the CH$_4$ conversion and products distribution.

In the present study, we systematically investigated the effect of reactant gas composition on the dry reforming of CH$_4$ with the temperature-controlled DBD reactor. The reactant conversion and products selectivities with the different reactant gas compositions were compared at the similar reduced field intensity and background temperature. The performance was evaluated in terms of CH$_4$ and CO$_2$ conversions and product selectivity. The role of electron-induced chemistry and thermochemistry in the reforming process was discussed on the basis of the results of performance elevation, optical emission spectroscopy and BOLSIG+ based numerical calculation.

2. Experimental setup

Figure 1 shows the schematic of the setup for the experiment. The experimental setup consisted of a temperature-controlled DBD reactor, a high-voltage supplier, a reactant feeding system, and a measurement system. Similar configuration was used in our previous work \[27, 28\]. The temperature-controlled DBD reactor includes a coaxial DBD reactor and an electric oven. The coaxial DBD was constructed of a quartz tube with a length of 200 mm and an inner diameter of 20.0 mm, which was used as a dielectric barrier. The outer wall of the quartz tube was wrapped with 45-mm-wide stainless-steel mesh, which was used as a grounding electrode. A stainless-steel rod with a diameter of 17.5 mm was inserted into the quartz tube to serve as a high-voltage electrode. The resulted discharge gap was $\sim$1.3 mm.

An amplifier (20/30 A, Trek) in conjunction with a function generator (AFG 3021B,
Tektronix) was used to generate AC high voltage. The AC high voltage and discharge current were measured by a digital oscilloscope (DPO 4140B, Tektronix) together with a high voltage probe (P 6015A, Tektronix) and a current monitor (6595, Pearson), respectively. The typical value of \( V_{\text{peak}}/V_{\text{rms}} \) was 1.6. \( V-Q \) Lissajous method was used to determine the discharge power into the DBD reactor. The charge \( Q \) was calculated by measuring a voltage across a 30 nF capacitor, using a voltage probe (TPP 1000, Tektronix). The \( V-Q \) Lissajous diagram was averaged over 216 scans, and the discharge power was calculated from the area of the diagram by multiplying the frequency.

Optical emission spectroscopy (OES) was conducted by a spectrometer (Acton SP2500i, Princeton Instruments) equipped with a slit (100 \( \mu \)m), a grating (600 grooves \( \text{mm}^{-1} \)) and a highly sensitive camera (PIXIS-100, Princeton Instruments) with the exposure time of 100 ms.

The flow rate of each component was controlled by a mass flow controller (MFC) (SLA5850, Brooks Instrument). The total flow rate was fixed at 200 ml/min. An electric oven (O series, NDB Co. Ltd.) was used to heat the gas mixture to a target temperature. A homemade ice-water-cooling trap was used to condense liquid products. The feed and product gas were analyzed using an online gas chromatograph (HP 7890A, Agilent) equipped with a flame ionization detector (FID) and two thermal conductivity detectors (TCD).

To characterize the dry reforming process, the \( \text{CH}_4 \) and \( \text{CO}_2 \) conversions were defined as:

\[
\text{CH}_4 \text{ conversion(\%)} = \frac{\text{moles of CH}_4 \text{ converted}}{\text{moles of CH}_4 \text{ input}} \times 100 \quad (E1)
\]

\[
\text{CO}_2 \text{ conversion(\%)} = \frac{\text{moles of CO}_2 \text{ converted}}{\text{moles of CO}_2 \text{ input}} \times 100 \quad (E2)
\]

The selectivities of the products were calculated as:

\[
\text{H}_2 \text{ selectivity(\%)} = \frac{\text{moles of H}_2 \text{ produced}}{2 \times \text{moles of CH}_4 \text{ converted}} \times 100 \quad (E3)
\]
CO selectivity(%) = \frac{\text{moles of CO produced}}{\text{moles of CH}_4 \text{ converted} + \text{moles of CO}_2 \text{ converted}} \times 100 \quad (E4)

\[ C_3\text{H}_y \text{ selectivity(%) = } \frac{X \times \text{moles of C}_3\text{H}_y \text{ produced}}{\text{moles of CH}_4 \text{ converted} + \text{moles of CO}_2 \text{ converted}} \times 100 \quad (E5) \]

and the H_2/CO molar ratio was defined as:

\[ \frac{\text{H}_2}{\text{CO}} = \frac{\text{moles of H}_2 \text{ produced}}{\text{moles of CO produced}} \quad (E6) \]

3. Results

3.1. DBD characteristics

Since varying background temperature or reactant gas compositions might affect plasma physics, we investigated the discharge characteristics of the DBD for all experimental conditions. Typical voltage-current waveform and Lissajous diagrams are shown in the Fig. S1 and Fig. S2 of the Supporting Information. In generally, the responses of the lissajous diagrams to the background temperatures for the different reactant gas compositions were similar to that for the dry reforming [28] and partial oxidation process [27]. At T \leq 673 K, the lissajous diagram showed a sharp parallelogram shape. The discharge pattern from the DBD with a mixture of CH_4/CO_2/N_2 at T \leq 673 K appears to be in the typical filamentary micro-discharge mode [29] of DBD. At T=773 K, however, the diagram changes from a sharp parallelogram shape into a smooth shape. This change is due to the significant reduction in the resistances of the gas gap and the barrier [28]. Because of these significant resistances’ reduction, the discharge mode at 773 K can be characterized as the coexistence of micro-discharges and resistive waste of electrical power [28]. Thus, in this study, the maximum background temperature was set at 673 K.

In the present study, the reduced field intensity \((E/N)\) was varied by the background temperature. The \(E/N\) value was estimated by \(E/N \approx \frac{U_b}{(dN)}\), where \(E\) is the averaged electric field, \(N\) is the gas number density, \(d\) is the gas gap distance, and \(U_b\) is the breakdown voltage in the gas gap. \(U_b\) could be calculated from \(U_b = U_{on}(1 + \frac{C_g}{C_d})\), where \(U_{on}\) is the onset voltage, \(C_d\) is the effective capacitances of the dielectric barrier, and \(C_g\) is the effective capacitances of the gas gap which can be calculated via \(C_g = \)
$C_dC_{tot}/(C_d - C_{tot})$, where $C_{tot}$ is the effective capacitance of the total system. Among these values, $U_{on}$, $C_d$, and $C_{tot}$ could be determined from the lissajous diagrams based on the well-developed DBD model [30]. Table 1 summarizes the estimated $E/N$ values for all tested conditions. As shown in Table 1, the $E/N$ value was more sensitive to the background temperature than to the reactant gas compositions.

In addition, we investigated the optical emission spectra of the DBD for the different reactant gas compositions. Each spectrum was normalized with the measured light intensity of the $N_2$ (C–B) emission band that peaked at 380.3 nm. As shown in Fig. 2a, the emission spectrum of the DBD dry reforming was dominated by the emission of $N_2*$ related bands, such as $N_2$ C–B and $N_2^+$ B–X. The CH bands peaked at 431.4 nm and $C_2$ swan peaked at 516.5 nm were also observed indicating the electron dissociation of the CH. As compared to the condition of CO$_2$/CH$_4$=1, an atomic line peaked at 777.1 nm was appeared in the condition of CO$_2$/CH$_4$=4 indicating the enrichment of the O atoms (Fig. 2b). When O$_2$ was added into the dry reforming process (Fig. 2c), the bands of CH were reduced by half (as compared to the condition of CO$_2$/CH$_4$=1) and the bands of $C_2$ swan disappeared, while the O atom line also appeared.

### 3.2. Reforming at room temperature

#### 3.2.1. The effect of CO$_2$/CH$_4$ ratio on the dry reforming

Figure 3 shows the effect of CO$_2$/CH$_4$ ratio on the dry reforming of CH$_4$ at $T=293$ K and fixed discharge power ($P_{dis}=10$ W). When CO$_2$/CH$_4$ ratio was increased from 0.5 to 4, the conversions of CH$_4$ and CO$_2$ were kept at around 7.5 % and 3.3% (Fig.3a), respectively. Although the ratio of CO$_2$/CH$_4$ did not significantly affect the CH$_4$ and CO$_2$ conversion, it obviously altered the product distribution; the selectivities of H$_2$, C$_2$H$_6$, C$_2$H$_4$, C$_3$H$_8$, and other HCs (Fig.3b) were decreased from 46.8 to 40.2 %, 21.4 to 3.1%, 0.9 to 0.1, 1.8 to 0.2 and 0.8 to 0.1, respectively, while the selectivity of CO increased from 58.7 to 75.9%. It is worth mentioning that the production of CO was mainly attributed to the decomposition of CO$_2$, because the amount of produced CO was linearly dependent on the conversion of CO$_2$ as shown in the Supporting Information of Fig. S3. However, carbons would be more or less produced from the dry
reforming process and deposited on the DBD reactor. When the concentration of O atom is high, these carbons are possible oxidized into the CO which might be responsible for the abrupt change in the CO selectivity at a relative high CO$_2$/CH$_4$ (CO$_2$/CH$_4$=1.5) condition. In addition, due to the varied H$_2$ and CO selectivity the ratio of H$_2$/CO decreased from 2.1 to 0.4.

3.2.2. The effect of O$_2$ addition on the dry reforming

Figure 4 shows the effect of O$_2$ percentage on the dry reforming of CH$_4$ at CH$_4$/CO$_2$=1, $T=293$ K, and $P_{dis}$=10 W. The addition of O$_2$ did not affect the CH$_4$ conversion but obviously influenced the CO$_2$ conversion and O$_2$ conversion; when increasing O$_2$/CH$_4$ from 0.2 to 0.8, the conversion of CH$_4$ was kept at around 8.2%, but the conversion of CO$_2$ and O$_2$ decreased from 2.8 to 1.3% and 55.7 to 12.7% respectively (Fig. 4a). Regarding the products (Fig. 4b), the selectivity towards H$_2$, C$_2$H$_6$, C$_2$H$_4$, C$_3$H$_8$ and other HCs decreased from 44.4 to 16.2%, 13.3 to 1.7%, 0.3 to 0.06%, 0.8 to 0.04%, 0.4 to 0.02%, respectively, while the selectivity towards CO increased from 59.4 to 84.6%, and the ratio of H$_2$/CO decreased from 1.0 to 0.3. It seems that the response of products distribution to the varying O$_2$/CH$_4$ were much significant than that to the varying CO$_2$/CH$_4$. In addition, when O$_2$ was added into the dry reforming process, the production of CO was not due only to the conversion of CO$_2$, because the selectivity of CO was even increased with the decrease of CO$_2$ conversion.

3.3. Dry reforming at a relative high temperature

Figure 5 shows the CH$_4$ and CO$_2$ conversion, and products selectivities with different CO$_2$/CH$_4$ ratios at $T=493$ K and $P_{dis}$=10 W. Unlike the CH$_4$ conversion at room temperature ($T=293$ K), the CH$_4$ conversion at $T=473$ K was increased (7.7 to 10.3%) with the increase of CO$_2$/CH$_4$ ratio (0.5 to 4). In contrast, the response of CO$_2$, H$_2$, HCs and CO to the CO$_2$/CH$_4$ ratio at $T=493$ K was similar to these at $T=293$ K; when increasing CO$_2$/CH$_4$ ratio from 0.5 to 4, the conversion of CO$_2$ did not significantly change, while the selectivities of H$_2$ and HCs decreased, and the selectivity of CO increased as shown in Fig. 5. These results indicate that the reaction pathways of CO$_2$ conversion and products formation was not significantly changed with the CO$_2$/CH$_4$ ratio at higher background temperature condition.
The increase in O₂/CH₄ ratio (CO₂/CH₄=1) led to the obvious increase of CH₄ conversion at T=473 K (Fig. 6). In addition, as compared to the condition at T=293 K, the CO₂ conversion, and H₂, CO and HCs selectivity seem more sensitive to the O₂/CH₄ ratio at T= 473 K, because these values changed more significantly with the O₂/CH₄ ratio at T=473 K than those with the O₂/CH₄ ratio at T=293 K.

3.4. Effect of reduced field intensity on dry reforming

Figure 7 shows the effect of reduced field intensity (E/N) on CH₄ conversion, CO₂ conversion and products selectivities with different reactant gas compositions at fixed discharge power (P_{dis}=10 W). When adding O₂ into the dry reforming process, the CO₂/CH₄ value was kept to be 1. The E/N value was modified by varying the background temperature. It should be noted that the maximum E/N value was limited to ~165 Td, because the background temperature was controlled less than 673 K by considering the DBD mode [28]. The results of the dry reforming at 673 K were abstracted from our previous work [22, 28].

As shown in Fig. 7a, when the E/N was increased from 70 to 160 Td, the CH₄ conversion increased from 7.8 to 11.5% for CO₂/CH₄=1. At the E/N value between 70 to 80 Td (corresponding to T=293 K), no obvious difference was observed between different reactant gas compositions. At the higher E/N value, however, the CH₄ decreased in the order of O₂/CH₄=0.8 >> CO₂/CH₄=4 > CO₂/CH₄=1 at the comparable E/N value. Regarding to the CO₂ conversion (Fig. 7b), at the comparable E/N value, the CO₂ conversion decreased in the order of CO₂/CH₄=1 ≈ CO₂/CH₄=4 > O₂/CH₄=0.8 at E/N ≤ 120 Td, while it decreased in the order of CO₂/CH₄=1 > CO₂/CH₄=4 > O₂/CH₄=0.8 at E/N > 120 Td.

As for the products, the selectivity of H₂ decreased with the increase of E/N value (Fig. 8a), and it decreased in the order of CO₂/CH₄=1 > CO₂/CH₄=4 > O₂/CH₄=0.8 regardless of the specific E/N value. However, the selectivity of CO increased with the E/N value for the O₂/CH₄=0.8 (Fig. 8b), while it decreased with the E/N value for the CO₂/CH₄=1 and CO₂/CH₄=4. It decreased in the order of O₂/CH₄=0.8 > CO₂/CH₄=4 > CO₂/CH₄=1. Thus, the H₂/CO value could be varied in a wide range (Fig. 8d). In contrast to the trend of the selectivity of CO, the selectivity of HCs decreased with the
$E/N$ value for the $\text{O}_2/\text{CH}_4=0.8$ (Fig. 8d), while it increased with the $E/N$ value for the $\text{CO}_2/\text{CH}_4=1$ and $\text{CO}_2/\text{CH}_4=4$.

4. Discussion

We have shown that the variation of the reactant gas composition affected $\text{CH}_4$ and $\text{CO}_2$ conversion, and products distribution. This should be possibly attributed to the modified electron-induced chemistry or the thermochemistry by the change of the reactant. Table 2 summarized important reactions that are responsible for the plasma-assisted dry reforming with the tested reactant gas compositions \cite{31-33}. At a low temperature condition, the plasma-assisted dry reforming process is initialed by the electron-impact dissociation reactions rather than thermal decomposition. The efficiencies of these dissociation reactions depend on electron density and electron energy, which are respectively determined by the energy density and the reduced field intensity ($E/N$) \cite{27, 28}.

A calculation from BOLSIG+ software \cite{34} (Fig. S4 of the Supporting Information) indicated that, in the tested $E/N$ value range, the reaction (R1) is responsible for $\sim 83\%$ of the total electron dissociation of $\text{CH}_4$, while reactions (R2) and (R3) are responsible for $\sim 13\%$ and $\sim 3\%$, respectively. It is worth mentioning that the contribution of the reactions between metastable $\text{N}_2^*$ and $\text{CH}_4$ could not be ignore due to the high concentration of the metastable $\text{N}_2^*$ in the reforming process (Fig. 2). However, these reactions could be considered as indirect electron dissociation of $\text{CH}_4$ by considering the net reactions of following reactions: $e + \text{N}_2 \rightarrow \text{N}_2^* + e$, $\text{N}_2^* + \text{CH}_4 \rightarrow \text{products (CH}_x + \text{H}_y, x + y = 4) + \text{N}_2$. $\text{CO}_2$ conversion is mainly due to the reaction (R4). Note that no NOx was observed in the OES measurement.

During electron-impact dissociation reactions, many other reactive species, such as O and H atoms and OH radicals are produced. These reactive species may either facilitate further $\text{CH}_4$ conversion through reactions (R5–R7), or they might be consumed to produce products. As a richest carbon-containing intermediate product from the $\text{CH}_4$ conversion, $\text{CH}_3$ radicals are also important to the $\text{CH}_4$ conversion because it might be responsible for the $\text{CH}_4$ backward reaction (as R8 in R9). Regarding the products, $\text{H}_2$ is mainly produced from the H radical recombination and the reactions
of H with CH₄, HO₂ and HCO, whereas CO is mainly produced from electron-impact dissociation of CO₂ as well as the HCO oxidation and the reaction of HCO with CH₃ and H atoms, and hydrocarbons are produced from the recombination of CHₓ (x = 1–3) radicals.

In our previous work [28], by independently controlling the background temperature and the reactor pressure to adjust similar reduced field intensity, we have proposed that for the CO₂/CH₄=1, the electron-induced chemistry controlled the decomposition of CH₄ and CO₂, while the rest of chemical reactions to the products were governed by thermochemistry. In this regard, the result of CO₂/CH₄=1 could be considered as a reference result to get a better understanding of the plasma chemistry with different reactant gas compositions.

In this study, at the room temperature condition, the CH₄ conversion was not influenced by the reactant compositions indicating that the CH₄ conversion was controlled by the electron-induced chemistry. It is worth mentioning that the enrichment of O atoms was observed with CO₂/CH₄=4 and O₂/CH₄=0.8 by the OES measurement as shown in Fig. 2. These enrichments could be attributed to the increased electron-impact dissociation of CO₂ for CO₂/CH₄=4 as evidenced by the higher selectivity of CO (Fig. 3b), and the effective electron-impact dissociation of O₂ for O₂/CH₄=0.8 as evidenced by the low threshold level for the electron-impact dissociation of O₂ (5.1 eV [35]) as compared to that of CO₂ (8.1 eV [36]). It seems that these enriched O atoms were not used for the CH₄ conversion at the room temperature. In contrast, at a relatively high temperature condition, the CH₄ conversion with CO₂/CH₄=4 and especially with O₂/CH₄=0.8 was enhanced as compared to that with CO₂/CH₄=1 at the similar E/N value. Considering the improved CH₄ conversion with CO₂/CH₄=1 at higher temperature condition was solely due to the enhanced E/N value [28], thermochemistry more or less affected the CH₄ conversion with CO₂/CH₄=4 and O₂/CH₄=0.8.

Figure 9a shows the reaction constants for the reactions related to CH₄ conversion under different background temperatures, where the reaction constants were obtained from [37]. The reaction constants of R5–R7 significantly increases from 5 × 10⁻¹⁸ to 7
\[ 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, 7 \times 10^{-18} \text{ to } 4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ and } 8 \times 10^{-19} \text{ to } 2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ respectively, in a temperature range of } 293 \text{ to } 673 \text{ K}. \] Meanwhile, the \( \text{CH}_4 \) backward related reactions, R8 and R9, are not affected by the background temperature. These results indicate that at \( T=293 \text{ K} \), the low reaction constants of CH\(_4\) conversion-related reactions contributed to the insensitive of the \( \text{CH}_4 \) conversion to the varying reactant gas composition and the \( \text{CH}_4 \) conversion is dependent of the electron-induced chemistry. At the higher temperatures, however, due to the increased reaction constants of the R5–R7, thermochemistry might control the \( \text{CH}_4 \) conversion when sufficient O containing active species (e.g. the condition of \( \text{CO}_2/\text{CH}_4=4, \text{O}_2/\text{CH}_4=0.8 \)) was presented in the dry reforming process. According to our calculation using CHEMKIN-PRO package with modified USC Mech II mechanism [27, 32, 33], R6 is responsible for the enhancement of \( \text{CH}_4 \) conversion by thermochemistry at the high temperature conditions.

However, the reaction constants of \( \text{H}_2, \text{CO} \) and HCs related reactions are typically high and less sensitive to the background temperatures (Fig. 9b–9c). This led to the involvement of O containing active species in the \( \text{H}_2 \) and CO production and consumption process at all background temperatures, and thus the thermochemistry affected the products selectivity regardless of the specific background temperature. It should be noted that when \( \text{O}_2 \) was not added into the dry reforming process, CO was mostly produced from the electron-impact dissociation of \( \text{CO}_2 \) because the amount of produced CO was linearly dependent on the conversion of \( \text{CO}_2 \) as shown in Fig. S3 of the Supporting Information. Meanwhile, CO selectivity was also obviously affected by the thermochemistry because it was decreased with the background temperature. This decreased CO selectivity was accompanied by the increased HCs selectivity indicating less O containing active species was used for the CO production. We propose that the O containing active species was used in the \( \text{H}_2 \) consumption at the higher temperature condition because the reaction constants of R16 and R17 were increased with the background temperature as shown in Fig. 9c. This hypothesis is supported by the fact that the \( \text{H}_2 \) selectivity was decreased with the background temperature.

However, with the addition of \( \text{O}_2 \), CO was mainly produced from the oxidation of
HCs. This argument is supported by the evidence that the addition of O$_2$ had opposite effect on the CO selectivity and CO$_2$ conversion. According to our previous work dealing with the partial oxidation of CH$_4$, R18 is the major pathway for the CO production when O$_2$ was presented [27]. The significant consumption of carbon-based active species was also confirmed by the OES as shown in Fig. 2. Since the CH$_3$ was mainly used for the CO production, the low selectivity of HCs could be understood. Moreover, the addition of O$_2$ enriched O containing active species which lowered the selectivity of the H$_2$.

It is worth mentioning that with the similar reactant, the maximum conversion efficiency of CH$_4$ in this study was 4.9 mg/kJ, which is much less than that of CH$_4$ (~20 mg/kJ) with the arc-jet type plasma [38], where the arc-jet type plasma has a localized high-temperature (over several thousand kelvins [38]) environment. Our finding emphasizes that both the sufficient active species and a relatively high temperature are necessary to improve the CH$_4$ conversion. However, these ways to increase the CH$_4$ conversion also resulted in a vigorous oxidation environment which prevents the high selectivity of H$_2$ and HCs. Because the pathways to the products are controlled by the thermochemistry, it is possible to adjust the products distribution by controlling the reaction time of the dry reforming products. Such research is underway and will be reported in the near future.

5. Conclusions

We have investigated the dry reforming of methane to produce hydrogen and carbon monoxide in a temperature-controlled dielectric barrier discharge reactor. In particular, the performance of different CO$_2$/CH$_4$ ratios and O$_2$/CH$_4$ ratios were compared at the similar reduced field intensity to deeper understanding of the role of electron-induced chemistry and thermochemistry in the dry reforming process, where the reduced field intensity was adjusted by the background temperature. We found that at the room temperature condition, due to the low reaction constants of the reactions between CH$_4$ and O containing active species, the CH$_4$ conversion was attributed to the electron-induced chemistry rather than the thermochemistry. Two factors, relatively
high temperature and sufficient O containing active species, are necessary to make the thermochemistry important in the CH$_4$ conversion. In contrast, the products distribution (H$_2$, CO, HCs) was always controlled by the thermochemistry regardless of the specific background temperature. When the concentration of O containing active species was high, the excessive oxidation of the HCs and CO resulted in decrease of CO$_2$ conversion. Thus, CO$_2$ conversion is possibly affected by the thermochemistry even at the room temperature.

Based on the current observation, a vigorous oxidation environment is beneficial to the CH$_4$ conversion in the DBD reactor. The improvement of the conversion of CO$_2$ and the selectivity of target products (such as H$_2$) in such a vigorous oxidation environment is our ongoing work. Modeling works are required to fully understand the reaction pathway and to predict a way to tailor a target product.

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**Figure Caption**

**Figure 1.** Schematic diagram of the experimental setup.

**Figure 2.** Typical discharge emission spectra normalized by the N$_2^*$ emission band at $P_{\text{dis}} = 10$ W: (a) CO$_2$/CH$_4$=1, (b) CO$_2$/CH$_4$=4, and (c) O$_2$/CO$_2$/CH$_4$=0.8:1:1.

**Figure 3.** Effect of CO$_2$/CH$_4$ value on the (a) CH$_4$, CO$_2$ conversion and H$_2$/CO, and (b) H$_2$, CO, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, and other HCs selectivity at $P_{\text{dis}} = 10$ W, $T$=293 K.

**Figure 4.** Effect of O$_2$/CH$_4$ value on the dry reforming of CH$_4$ (a) CH$_4$, CO$_2$, O$_2$ conversion and H$_2$/CO, and (b) H$_2$, CO, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, and other HCs selectivity at $P_{\text{dis}} = 10$ W, $T$=293 K.

**Figure 5.** Effect of CO$_2$/CH$_4$ value on the (a) CH$_4$, CO$_2$ conversion and H$_2$/CO, and (b) H$_2$, CO, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, and other HCs selectivity at $P_{\text{dis}} = 10$ W, $T$=473 K.

**Figure 6.** Effect of O$_2$/CH$_4$ value on the dry reforming of CH$_4$ (a) CH$_4$, CO$_2$, O$_2$ conversion and H$_2$/CO, and (b) H$_2$, CO, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, and other HCs selectivity at $P_{\text{dis}} = 10$ W, $T$=473 K.

**Figure 7.** Effect of E/N value on the dry reforming of CH$_4$ (a) CH$_4$ conversion and (b) CO$_2$ conversion at $P_{\text{dis}} = 10$ W.

**Figure 8.** Effect of E/N value on the dry reforming of CH$_4$ (a) H$_2$ selectivity, (b) CO selectivity, (c) H$_2$/CO, and (d) HCs selectivity at $P_{\text{dis}} = 10$ W.

**Figure 9.** Reaction constants under different reaction temperatures: (a) CH$_4$ conversion; (b) Competing reaction and CH$_4$ backward reaction; (c) H$_2$ production and consumption; (d) CO production and consumption.
Table 1. Summary of $E/N$ values for tested conditions.

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>Absolute pressure (bar)</th>
<th>$T$ (K)</th>
<th>$E/N$ (Td)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$/CH$_4$=1</td>
<td>293</td>
<td>70.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>112.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>135.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>159.5</td>
<td></td>
</tr>
<tr>
<td>CO$_2$/CH$_4$=4</td>
<td>293</td>
<td>75.3</td>
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<tr>
<td></td>
<td>473</td>
<td>118.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>140.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>165.2</td>
<td></td>
</tr>
<tr>
<td>O$_2$/CH$_4$=0.8 when CO$_2$/CH$_4$=1</td>
<td>293</td>
<td>80.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>125.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>.150.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>175.1</td>
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</tbody>
</table>
Table 2. Important reactions related to reactant conversion and products formation

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Reaction</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ and CO₂ conversion</td>
<td>CH₄+e → CH₃+H+e</td>
<td>R1</td>
</tr>
<tr>
<td></td>
<td>CH₄+e → CH₂+H₂+e</td>
<td>R2</td>
</tr>
<tr>
<td></td>
<td>CH₄+e → CH+H₂+H+e</td>
<td>R3</td>
</tr>
<tr>
<td></td>
<td>CO₂+e → CO + O</td>
<td>R4</td>
</tr>
<tr>
<td></td>
<td>CH₄+O → CH₃+OH</td>
<td>R5</td>
</tr>
<tr>
<td></td>
<td>CH₄+OH→CH₃+H₂O</td>
<td>R6</td>
</tr>
<tr>
<td></td>
<td>CH₄+H → CH₃+H₂</td>
<td>R7</td>
</tr>
<tr>
<td>CH₄ backward reaction</td>
<td>CH₃+H → CH₄</td>
<td>R8</td>
</tr>
<tr>
<td></td>
<td>CH₃+HCO→CH₄+CO</td>
<td>R9</td>
</tr>
<tr>
<td>Competing reaction</td>
<td>CH₃+OH → CH₃OH</td>
<td>R10</td>
</tr>
<tr>
<td></td>
<td>CH₃+O → CH₂O+H</td>
<td>R11</td>
</tr>
<tr>
<td></td>
<td>CH₃+O₂ → CH₂O₂</td>
<td>R12</td>
</tr>
<tr>
<td>H₂ production</td>
<td>H+H+M → H₂+M</td>
<td>R13</td>
</tr>
<tr>
<td></td>
<td>CH₄+H → CH₃+H₂</td>
<td>R7</td>
</tr>
<tr>
<td></td>
<td>H+HO₂→O₂+H₂</td>
<td>R14</td>
</tr>
<tr>
<td></td>
<td>HCO+H → CO+H₂</td>
<td>R15</td>
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<tr>
<td>H₂ consumption</td>
<td>H₂+O → OH+H</td>
<td>R16</td>
</tr>
<tr>
<td></td>
<td>H₂+OH → H₂O+H</td>
<td>R17</td>
</tr>
<tr>
<td>CO production</td>
<td>HCO+O₂→CO+HO₂</td>
<td>R18</td>
</tr>
<tr>
<td></td>
<td>HCO+OH → CO+H₂O</td>
<td>R19</td>
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<tr>
<td></td>
<td>HCO+O → CO+OH</td>
<td>R20</td>
</tr>
<tr>
<td></td>
<td>CH₃+HCO→CH₄+CO</td>
<td>R9</td>
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<tr>
<td></td>
<td>HCO+H → CO+H₂</td>
<td>R15</td>
</tr>
<tr>
<td>CO consumption</td>
<td>CO+O → CO₂</td>
<td>R21</td>
</tr>
<tr>
<td></td>
<td>CO+OH → CO₂+H</td>
<td>R22</td>
</tr>
<tr>
<td></td>
<td>HO₂+CO→OH+CO₂</td>
<td>R23</td>
</tr>
</tbody>
</table>
Figure 1. Schematic diagram of the experimental setup.
**Figure 2.** Typical discharge emission spectra normalized by the N$_2^*$ emission band at $P_{\text{dis}} = 10$ W: (a) CO$_2$/CH$_4$=1, (b) CO$_2$/CH$_4$=4, and (c) O$_2$/CO$_2$/CH$_4$=0.8:1:1.
Figure 3. Effect of CO\textsubscript{2}/CH\textsubscript{4} value on the (a) CH\textsubscript{4}, CO\textsubscript{2} conversion and H\textsubscript{2}/CO, and (b) H\textsubscript{2}, CO, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{6}, and other HCs selectivity at $P_{\text{dis}} = 10$ W, $T=293$ K.
Figure 4. Effect of O₂/CH₄ value on the dry reforming of CH₄ (a) CH₄, CO₂, O₂ conversion and H₂/CO, and (b) H₂, CO, C₂H₆, C₃H₈, and other HCs selectivity at $P_{\text{dis}}=10$ W, $T=293$ K.
Figure 5. Effect of CO$_2$/CH$_4$ value on the (a) CH$_4$, CO$_2$ conversion and H$_2$/CO, and (b) H$_2$, CO, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, and other HCs selectivity at $P_{dis} = 10$ W, $T = 473$ K.
Figure 6. Effect of $O_2/CH_4$ value on the dry reforming of $CH_4$ (a) $CH_4$, $CO_2$, $O_2$ conversion and $H_2/CO$, and (b) $H_2$, $CO$, $C_2H_6$, $C_2H_4$, $C_3H_6$, and other HCs selectivity at
$P_{\text{dis}} = 10 \text{ W, } T=473 \text{ K.}$

**Figure 7.** Effect of $E/N$ value on the dry reforming of CH$_4$ (a) CH$_4$ conversion and (b) CO$_2$ conversion at $P_{\text{dis}} = 10 \text{ W.}$
(a) 

H₂ selectivity (%)  

E/N (Td)  

- CO₂/CH₄=1  
- O₂/CH₄=0.8  
- CO₂/CH₄=4

(b) 

CO selectivity (%)  

E/N (Td)  

- CO₂/CH₄=1  
- CO₂/CH₄=4  
- O₂/CH₄=0.8
Figure 8. Effect of $E/N$ value on the dry reforming of CH$_4$ (a) H$_2$ selectivity, (b) CO selectivity, (c) H$_2$/CO, and (d) HCs selectivity at $P_{dis} = 10$ W.
Figure 9. Reaction constants under different reaction temperatures: (a) CH$_4$ conversion; (b) Competing reaction and CH$_4$ backward reaction; (c) H$_2$ production and consumption; (d) CO production and consumption.