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# Plasma-Assisted Dry Reforming of CH<sub>4</sub>: How Small Amounts of O<sub>2</sub> Addition Can Drastically Enhance the Oxygenate Production—Experiments and Insights from Plasma Chemical Kinetics Modeling

Shangkun Li, Jintao Sun, Yury Gorbanev, Kevin van't Veer, Björn Loenders, Yanhui Yi, Thomas Kenis, Qi Chen, and Annemie Bogaerts\*



reactions with H atoms. Our study reveals the crucial role of oxygen-coupling in DRM aimed at oxygenates, providing practical solutions to suppress carbon deposition and at the same time enhance the oxygenates production in plasma-assisted DRM. **KEYWORDS:** *dry reforming of methane, oxygenates, plasma, chemical kinetics modeling* 

## 1. INTRODUCTION

The amounts of two important greenhouse gases, i.e., CO<sub>2</sub> and CH<sub>4</sub>, are growing continuously in the atmosphere due to the high production and consumption of fossil fuels to satisfy rapid energy demands. Dry reforming of methane (DRM) with carbon dioxide into value-added chemicals is promising for a carbon-neutral ecosystem and is therefore one of the utmost tasks of sustainable chemistry. Great efforts have been made in the chemical transformation of CO<sub>2</sub> and CH<sub>4</sub> into syngas, the mixture of CO and H<sub>2</sub>, which can be commercially converted into bulk chemicals and fuels by the thermocatalytic Fischer-Tropsch (FT) synthesis.<sup>1,2</sup> However, due to the high bond energy of C=O (5.5 eV, in CO<sub>2</sub>) and C-H (4.5 eV, in  $CH_4$ ), this two-step route generally starts with a highly endothermic process, requiring high temperature (>700 °C) for syngas production, and proceeds at high pressure (tens of atm) in the FT process. These conditions are very energy-demanding and rely heavily on fossil fuels. In order to comply with the decarbonization of the chemical industry, the development of alternative, milder DRM approaches into high-value-added liquid fuels and chemicals is very sought-after.

Nonthermal plasma provides a facile way to activate molecules with energetic electrons instead of heat, triggering

chemical reactions near room temperature.<sup>3–5</sup> Plasma is a partially ionized gas, consisting of electrons, ions, photons, excited states, atoms, and radicals, besides neutral gas molecules. Plasma-enabled processes have two main advantages: (i) they can be quickly switched on and off, compared to the long-time heating and cooling processes in thermal catalytic systems; and (ii) they can be powered by intermittent renewable electricity (e.g., wind and solar energy) to reduce fossil fuel consumption and greenhouse gas emissions and to comply with the goal of electrification of the chemical industry.

Dielectric barrier discharge (DBD) plasmas are frequently used for DRM.<sup>5,6</sup> Earlier studies have shown that plasmaassisted DRM can realize the appealing gas-to-liquid (GtL) process, in which major liquid oxygenates include alcohols and acids, by optimizing the reactor geometry, plasma parameters,

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Figure 1. Schematic overview of the experimental setup. Electrical connections are represented by full black lines, gas and liquid connections by full blue lines, and water-cooling connections by dashed blue lines

and reaction conditions, although the total liquid selectivity was less than 15%.<sup>7,8</sup> Rahmani et al. investigated the influence of steam on DRM and the distribution of products with specific energy input. The selectivity to liquid hydrocarbons was 3% by weight, with methanol (CH<sub>3</sub>OH), ethanol, isopropanol, and acetone as the most abundant liquid oxygenates at room temperature.9 Interestingly, additional oxygen in the CO<sub>2</sub>/CH<sub>4</sub> feed gas has positive effects on the yield of CH<sub>3</sub>OH, HCHO, and CO and reduces the total consumed energy.<sup>10</sup> Recently, Wang et al. studied the influence of process parameters (i.e., discharge power, reaction temperature, and residence time) on oxygenates production by using a water-cooled DBD reactor, with CH<sub>3</sub>OH (43% relative selectivity) being the main liquid product.<sup>11</sup> By artificial neural network models, discharge power was identified as the most critical process parameter for plasma-driven DRM to oxygenates.<sup>11</sup>

The development of chemical processes requires a detailed understanding of the underlying chemical reaction pathways. For this purpose, chemical kinetics modeling has been applied for DRM in DBD reactors.<sup>12–14</sup> Snoeckx et al. simulated the filamentary behavior of a DBD reactor and the main product was syngas in a H<sub>2</sub>/CO ratio of ca. 1.5, with low amounts of CH<sub>3</sub>OH and HCHO.<sup>12</sup> De Bie et al. developed a 1D fluid model for a CO<sub>2</sub>/CH<sub>4</sub> mixture in a DBD and compared the densities of the various plasma species as a function of residence time and gas mixing ratio.<sup>13</sup> The density of various plasma species showed different trends as a function of the residence time, indicating that some targeted molecules could be selectively produced by optimizing the residence time (and thus the flow rate).

DBD plasmas are highly nonequilibrium, i.e., the temperature of the electrons is much higher than that of the gas.<sup>15,16</sup> The low temperature of the gas allows incorporation of a catalyst into the DBD discharge region, which can improve the system efficiency. Various packing materials with both noncatalytic and catalytic properties have been used for plasma-catalytic DRM, including glass beads,<sup>17</sup> metal oxides,<sup>18</sup> supported catalysts with both transition and noble metals,<sup>19,20</sup> zeolites,<sup>21</sup> and metal–organic frameworks.<sup>22</sup> However, the negative issue of coke deposition due to the fast rate of CH<sub>4</sub> dissociation induced by plasma imposes restrictions on the stability of catalysts and hinders further understanding of the mutual interaction between plasmas and catalysts.<sup>23</sup>

Previously, we have studied the selective oxidation of methane to  $CH_3OH$  by molecular oxygen  $(O_2)$ , and chemical kinetics modeling showed the reaction pathways for the formation of  $CH_3OH$  and other oxygenates in the  $CH_4/O_2$ plasma.<sup>3</sup> In this work, we elaborate on DBD plasma-DRM studies by introducing oxygen to tackle the problem of the inevitable carbon deposition in an in-house developed temperature-controlled DBD reactor. On one hand, coke deposition might result in unstable plasma discharge and catalyst deactivation in plasma catalysis, which makes it challenging to find cost-effective and stable catalysts for this reaction, thus limiting the use of this process on a commercial scale. On the other hand, O2 addition could improve the concentration of oxygen-rich radicals in  $CO_2/CH_4$  plasma, which might increase oxygenate production.<sup>3,10</sup> Therefore, we only focus on the catalyst-free process to obtain a fundamental understanding of the CO<sub>2</sub>/CH<sub>4</sub> plasma behavior by introducing O<sub>2</sub> in this work. In addition, we investigated the influence of various process parameters, i.e., the CO<sub>2</sub>/CH<sub>4</sub> molar ratio, temperature, plasma discharge power, and residence time, on the reaction performance and the optimal  $O_2$  fraction. Finally, to support our experimental results, we performed computational plasma chemical kinetics modeling to unveil the possible chemical pathways for plasma-assisted DRM to oxygenates.

## 2. EXPERIMENT AND MODELING

**2.1. Description of the Experimental Setup.** Plasma experiments (Figure 1) were carried out in a temperature-

controlled coaxial DBD reactor with a water electrode (ground electrode) operated at atmospheric pressure. The DBD reactor consists of a pair of coaxial quartz cylinders (inner and outer quartz tubes) in which a stainless-steel (2 mm outer diameter) electrode was placed in the center and circulating water was pumped into the space between the inner and outer cylinder. A tungsten rod was installed in the space between both cylinders to connect this circulating water (flowing between this inner and outer wall) with a ground wire (outside of the reactor wall) so that the circulating water acts as a ground electrode of our DBD. The water flow rate (5 L/min) and temperature (10-85 °C) were controlled by thermostatic baths with a circulation pump and external temperature controller (Huber KISS 104A), which can effectively remove the heat generated by the discharge and maintain a constant reaction temperature. The discharge length is 60 mm (defined by the length of the ground electrode, i.e., region of circulating water), and the inner diameter of the inner quartz cylinder is 10 mm, yielding a discharge gap of 4 mm.

The feed gas flow  $(CO_2, CH_4, and O_2)$  was supplied using mass flow controllers (MFC, Bronkhorst) connected to the gas cylinders (both 99.999%, Praxair). The feed gases were mixed using a T-connector and subsequently introduced into the water-cooling DBD plasma reactor. O2 was introduced with concentrations of 0-16%, which was in the safe range at the present experimental conditions. The detailed ternary flammability diagram for CO2-CH4-O2 mixtures is shown in Figure S1 of the Supporting Information (Section S1). A cooling trap was placed at the exit of the DBD reactor to condense the liquid products. The gas flow rate was measured before and after the plasma reaction using a soap-film flow meter, to account for gas expansion or contraction due to the chemical reaction and thus to correctly determine the gas conversion and product selectivity. In this study, the DBD reactor was connected to a high-frequency power supply unit (PSU) AFS G10S-V (AFS GmbH) with a transformer. The electrical characteristics were monitored with a digital oscilloscope (Pico Technology PicoScope 6402D) using a high-voltage probe (Tektronix P6015A) and a current monitor (Pearson Electronics 4100). The PSU was operated at a frequency of 23.5 kHz. An additional low-voltage probe was connected to an external capacitor (10 nF) to obtain the Lissajous figures, which were used to calculate the plasma power and monitor the discharge properties.

**2.2. Chromatographic Analysis Methods.** Gas samples were analyzed by a micro gas chromatograph ( $\mu$ GC; Agilent 990) equipped with thermal conductivity detectors to quantify the production of gaseous products in two channels. The first channel was equipped with MoleSieve SA and CP-PoraBOND Q columns used to analyze the permanent gases, including CO, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>, while the second channel with an Al<sub>2</sub>O<sub>3</sub>/KCI column was used to separate CO<sub>2</sub> and hydrocarbons (C<sub>2</sub>-C<sub>4</sub>). Samples were injected into the column from the reactor's outlet after passing through the cold trap. The total duration of the analysis was 5 min in the  $\mu$ GC. Ar and He were used as the carrier gases in channel one and channel two, respectively.

Liquid products condensed by the cold trap were first analyzed by GC (Thermo Focus SSL) with a flame ionization detector and a Restek Stabilwax column, which allowed efficient separation of all liquid products (e.g., CH<sub>3</sub>OH,  $C_2H_3OH$ , HCOOCH<sub>3</sub>). The same sample was also analyzed by HPLC (Waters 2695) containing a Shodex RSpak KC-811 column, a photodiode array 2996 detector, and a refractive index 2414 detector (Figure S2 in Supporting Information, Section S2). The mobile phase was 0.1% HClO<sub>4</sub> in Milli-Q water flowing at 1 mL/min. Formaldehyde (CH<sub>2</sub>O), formic acid (HCOOH), and acetic acid could be detected.

In this study, the gas flow rate  $(V_{intlet/outlet})$  before and after the reaction was detected by a bubble flow meter to account for gas expansion or contraction due to the reaction, which is crucial for correct determination of the conversion, as mentioned above. The conversion of CO<sub>2</sub>, CH<sub>4</sub>, and O<sub>2</sub>, as well as the selectivity of the main gaseous products [i.e., CO, H<sub>2</sub>, hydrocarbons  $(C_xH_y)$ ] and liquid products  $(C_xH_yO_{zy})$ including CH<sub>3</sub>OH, HCHO, HCOOH, and other oxygenates), was calculated as shown in Supporting Information, Section S3, eqs S1–S13.

**2.3. Description of the Chemical Kinetics Model.** A zero-dimensional (0D) plasma kinetic model comprising various atoms, radicals, excited species, neutral molecules, and ions was developed to obtain insights into the underlying mechanism of plasma-assisted  $CH_4/CO_2$  reforming. The plasma kinetics solver ZDPlasKin,<sup>24</sup> which incorporates a Boltzmann equation solver BOLSIG+,<sup>25</sup> was used to obtain the time evolution of the species densities generated in the reaction chamber. It solves the continuity equations for the various species densities

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \sum_j \left[ (a_{ij}^{\mathrm{R}} - a_{ij}^{\mathrm{L}}) k_j \prod_l n_l^{\mathrm{L}} \right] \tag{1}$$

where  $n_i$  stands for the density of species *i*, *a*R *ij* and *a*L *ij* are the stoichiometric coefficients of the species *i* on the right- and left-hand side of the reaction *j*, respectively.  $n_i$  is the density of species *l* on the left side of the reaction, and  $k_j$  is the rate coefficient of reaction *j*. More information about the model can be found in Section S4.

We developed a detailed kinetic mechanism consisting of electron impact reactions, neutral-neutral, neutral-ion, electron-ion recombination reactions, and reactions involving excited species for atmospheric pressure AC plasma-assisted  $CH_4/CO_2$  reforming. The main body of the chemistry set was adopted from the works of our group PLASMANT for its excellent prediction ability for experimental results under different conditions.<sup>26,27</sup> Furthermore, other reactions were integrated to describe the formation and consumption pathways of liquid oxygenates and related intermediates from the NIST Chemical Kinetics Database<sup>28</sup> and HP-Mech.<sup>29,30</sup> For electron impact reactions, most of the cross sections were obtained from the online LXCat database<sup>31</sup> and Wanten et al.<sup>26</sup> It is worth noting that three channels were considered regarding the dissociation of CO<sub>2</sub> based on the CO<sub>2</sub> electronic and vibrational levels,  $e + CO_2 \rightarrow e + CO + O$ ,  $e + CO_2 \rightarrow e +$  $CO + O(^{1}D)$ , and  $e + CO_{2} \rightarrow e + CO + O(^{1}S)$ .<sup>4</sup> For the cross sections of the dissociation reaction  $e + CO_2 \rightarrow e + CO +$  $O(^1S),$  we used the recommended values by Itikawa.  $^{32}$  The highly reactive intermediates  $O(^{1}D)$  and  $O(^{1}S)$  can easily react with hydrocarbon molecules to stimulate the chain branching reactions, and thus accelerate fuel pyrolysis and oxidation.<sup>33,3</sup> Accordingly, reactions involving  $O(^{1}D)$  and  $O(^{1}S)$  were added and their corresponding kinetic parameters were available in Sun et al.<sup>35,36</sup> It is worth noting that the excited species were not detected due to the limitation of experimental measurements in this work. However, Lin et al.<sup>37</sup> and Slanger and Black<sup>38</sup> have experimentally proven that the dissociation of O<sub>2</sub>

and CO<sub>2</sub> can result in the production of excited O atoms,  $O(^{1}D)$  and  $O(^{1}S)$ , respectively. As a result, a total of 1874 reactions with 102 species were described here for plasma-assisted DRM. The species considered in the kinetic mechanism are listed in Table 1, and the reactions are listed in the Supporting Information, Section S9.

#### 3. RESULTS AND DISCUSSION

3.1. Effect of O<sub>2</sub> Addition. First, we compare the performance of DRM in our experimental setup with and without O<sub>2</sub> addition. As shown in Figure 2a,b, there is a negligible liquid formation (4% selectivity, products unidentified) without  $O_2$  addition. After introducing  $O_2$  in the range from 4 to 16% (in percentage of the total feed gas volume) while keeping the  $CH_4/CO_2$  ratio constant (1:1), the liquid selectivity gradually increases and reaches ca. 22%, with HCOOH as the main product for 12% O<sub>2</sub> added. More O<sub>2</sub> (16%) results in less liquid formed, which suggests possible overoxidation of the oxygenates. Therefore, we selected 12% as the optimal O<sub>2</sub> percentage for further DRM experiments. The Lissajous figures (Figure 2c) were collected to better understand the influence of the addition of O2 on the DRM reaction. The effective voltage decreased by adding  $O_2$  (12%), indicating that less energetic electrons were produced in the  $CO_2/CH_4/O_2$  plasma at the same applied voltage. Consequently, at the same supplied PSU power (40 W), the power deposited into the plasma reduced from ca. 17 to 15 W (i.e., by ca. 10%) after O<sub>2</sub> addition. Besides this, the total conversion increased substantially, thus significantly reducing the energy cost from 271.9 to 144.9 kJ/L after the addition of 12% O<sub>2</sub> (see eq S11, the weighted average of the conversion for each reactant, weighted over their concentration in the inlet gas mixture). In addition, we estimate the H<sub>2</sub>O selectivity based on the hydrogen balance. H<sub>2</sub>O selectivity increased from 29.8 to 48.0% after 12% O<sub>2</sub> addition, indicating that more oxygenates can be formed at higher H<sub>2</sub>O selectivity after O<sub>2</sub> addition in plasma-assisted DRM reaction.

To reveal the effects of O<sub>2</sub> addition on the plasma-driven DRM reaction, we calculated the outlet contraction factor (cf. eq S10 in Supporting Information) both for the CO<sub>2</sub>/CH<sub>4</sub> plasma and the  $CO_2/CH_4/O_2$  plasma process. As shown in Figure 2d, the value of the contraction factor is negative in the CO<sub>2</sub>/CH<sub>4</sub> plasma, indicating that the plasma ignition results in an increase in the outlet gas volume, while the contraction factor in the outlet of the  $CO_2/CH_4/O_2$  plasma shows a reverse trend. This means that O<sub>2</sub> addition shifts the reaction from expansion to contraction-but not directly in the gas phase. When the products of DRM are dominated by syngas  $(CH_4 + CO_2 \rightarrow 2CO + 2H_2)$ , the gas expands. However, in the presence of O<sub>2</sub>, not only does the product distribution shift to oxygenates but also these oxygenates are condensed inside the cold trap, which leads to the observed apparent gas volume contraction. Therefore, the product distribution and reaction pathways clearly change by adding O<sub>2</sub>.

**3.2. Effect of Temperature and CO<sub>2</sub>/CH<sub>4</sub> Ratio.** We used circulating water as the ground electrode and for reactor cooling, with temperatures between 10 and 85 °C, controlled by the water temperature. We performed experiments to test the temperature just near the outlet of our DBD reactor. In general, the water temperature and DBD outlet temperature are almost the same in our study. As shown in Figure 3a,b, the conversion of the feed gases  $(CO_2 + CH_4 + O_2)$  exhibits an increasing trend by imposing higher temperature, while the

excited species	CO(E1). CO(E2), CO(E3), CO(E4), O <sub>2</sub> (E1), O <sub>2</sub> (E2), O <sub>2</sub> (E3), O( <sup>1</sup> D), O( <sup>1</sup> S)
radicals	0, Н, ОН, НО <sub>2</sub> , С, СН, СН <sub>3</sub> , СН <sub>3</sub> , С, С, Ч, С, Ч, С, Ч, С, Ч, С, Ч, С,
charged species	$ \begin{array}{c} H^{+}_{*}H^{+}_{*}H^{+}_{*},0,0,,0,,0H^{+}_{*}H^{0}_{*},H^{0}_{*},C^{+},CH^{+}_{*},\\ CH^{+}_{*}CH^{+}_{*}CH^{+}_{*}CH^{+}_{*}CH^{+}_{*}CH^{+}_{*}CO^{+}_{*}CO^{+}_{*}C_{*}^{2},C_{*}^{2}H^{+}_{*},\\ C_{*}H^{+}_{*}C_{*}H^{+}_{*}C_{*}H^{+}_{*}C_{*}H^{+}_{*}C_{*}H^{+}_{*}C_{*}O^{+}_{*},C_{*}O^{+}_{*},C_{*}O^{+}_{*},\\ C_{*}O^{+}_{*}H^{-}_{*}O^{-}_{*}O^{-}_{*}O^{-}_{*}O^{-}_{*}O^{-}_{*}O^{-}_{*}O^{-}_{*},CH^{-}_{*},CH^{-}_{*},CH^{-}_{*},CO^{-}_{*},CO^{-}_{*},CO^{-}_{*},\\ e^{-} \end{array}$
neutral molecules	Н" О" О" Ч"О, Н <sub>3</sub> О, Н4, СО, СН" С, СО" С <sub>3</sub> Н" С <sub>3</sub> Н4, С <sub>3</sub> H <sub>6</sub> С <sub>3</sub> H <sub>6</sub> С, H <sub>3</sub> O, СН <sub>3</sub> OH, СН <sub>3</sub> OH, С <sub>2</sub> H <sub>5</sub> OOH, СН <sub>3</sub> CHO, С <sub>2</sub> H <sub>5</sub> OH, НСООН, НОСН <sub>2</sub> O, СН <sub>3</sub> COOH

Table 1. Species Taken into Account in the 0D Chemical Kinetics Model



**Figure 2.** Plasma-driven DRM performance for different  $O_2$  percentages: (a) conversion and energy cost (above) and total selectivity distribution (below), (b) selectivity of various gas and liquid products, (c) Lissajous figures with and without  $O_2$  (12%) addition, and (d). off-gas volume change ( $V_c$ ) with and without  $O_2$  (12%) detected by using the bubble flow meter. (PSU power 40 W, discharge power 15–17 W, discharge frequency 23.5 kHz, total flow rate 40 mL/min,  $CO_2/CH_4 = 1:1$ , 35 °C circulating water, 6.78 s residence time, and 1 atm pressure)

total liquid selectivity (21.5%) reaches its peak at the temperature of 35 °C with 12% O<sub>2</sub> addition. At a lower temperature (10 °C), more hydrocarbons  $C_xH_y$  (i.e.,  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_8$ ) are formed, with a total selectivity of 24.4%, which might inhibit the formation of oxygenates in our present reactor.

At a lower temperature (10 °C), more hydrocarbons  $C_x H_y$ (i.e.,  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_8$ ) are formed, with a total selectivity of 24.4%, which might inhibit the formation of oxygenates in our present reactor. Although we would expect a higher selectivity toward liquid oxygenates at a lower temperature, also based on the literature results,<sup>11</sup> we did not measure this even in several repeat experiments. A possible reason might be that liquid products condense at the walls inside the reactor and cannot be removed immediately. However, we would need more dedicated experiments to test this hypothesis. By increasing the temperature from 10 to 85 °C, the  $C_x H_y$  selectivity gradually decreases, but the CO selectivity increases rapidly from 60 to 87%. Therefore, in order to maximize the oxygenate production, we continue our further experiments based on the optimal empirical temperature (35 °C).

The conversion and product distribution for different  $CO_2/CH_4$  ratios are depicted in Figure 3c,d. When the  $CO_2/CH_4$  ratio in the feed gas is changed from 3:1 to 1:3, the  $CO_2$  and  $CH_4$  conversion both decrease gradually from 5.7 to 2.1% and from 26.5 to 13.6%, respectively. At the same time, the level of

the O<sub>2</sub> conversion increases significantly from 49.3 to 74.7%. This clearly demonstrates that larger CH<sub>4</sub> fractions speed up the O<sub>2</sub> consumption compared to larger CO<sub>2</sub> fractions, which is expected. Besides, the total selectivity of liquid products also increases when changing the CO<sub>2</sub>/CH<sub>4</sub> ratio from 3:1 to 1:3, and the selectivity toward hydrocarbons (C<sub>x</sub>H<sub>y</sub>) follows the same tendency as the liquid products, with a maximum of 14.1% for the CO<sub>2</sub>/CH<sub>4</sub> molar ratio of 1:3, while the CO selectivity exhibits the opposite trend, and clearly drops upon higher CH<sub>4</sub> fraction (Figure 3d).

**3.3. Effect of Power and Residence Time.** Figure 4a,b shows the effect of different discharge powers on the plasmadriven DRM process. The conversion of  $CH_4$ ,  $CO_2$ , and  $O_2$  significantly rises by applying higher PSU power in the range of 30-60 W (corresponding to a discharge power range of 9-32 W), while the total liquid selectivity drops from 26.0 to 5.7%. The selectivity of gaseous products, i.e., CO,  $H_2$ , and  $C_xH_y$ , increases by 25.7, 65.7, and 41.2% upon raising the power. The selectivity of HCOOH as the major liquid oxygenate drops to 1.9%. These results show that higher power generates more gaseous products and fewer oxygenates, which is consistent with previous work.<sup>11</sup>

Residence time is one of the crucial operating parameters for  $CH_4$  oxidation to  $CH_3OH$  by plasma catalysis.<sup>3</sup> We applied different residence times (6.78–0.84 s) by varying the feed gas flow rate (40–320 mL/min). The effect of the different residence times on the plasma-assisted DRM process is shown



**Figure 3.** Plasma-driven DRM performance for different reaction temperatures: (a) conversion and energy cost (above) and total selectivity distribution (below); (b) selectivity of various gas and liquid products. (PSU power 40 W, discharge power 15–17 W, discharge frequency 23.5 kHz, total flow rate 40 mL/min, 12%  $O_2$ ,  $CO_2/CH_4 = 1:1$ , 6.78 s residence time, 1 atm pressure). Both the reactor outlet temperature (upper *x*-axis) and the water temperature (lower *x*-axis) are given. Plasma-driven DRM performance for different  $CO_2/CH_4$  ratios; (c) conversion and energy cost (above) and total selectivity distribution (below); and (d) selectivity of various gas and liquid products (PSU power 40 W, discharge power 15–17 W, discharge frequency 23.5 kHz, total flow rate 40 mL/min, 12%  $O_2$ , 35 °C circulating water, 6.78 s residence time, and 1 atm pressure).

in Figure 4c,d. By reducing the residence time from 6.78 to 0.84 s, the reactant conversion  $(CO_2 + CH_4 + O_2)$  drops rapidly, as expected, while the liquid selectivity gradually rises from 21.5% to as high as 50.0%. The CH<sub>3</sub>OH and HCHO selectivity evolves similarly to the total liquid selectivity. Notably, the maximum selectivity of HCOOH (22.7%) was achieved at 0.84 s residence time.

3.4. Plasma Chemical Kinetics Modeling Results. We performed plasma chemical kinetics modeling to obtain insights into how the effect of O<sub>2</sub> addition shifts the formation pathways of syngas  $(CO + H_2)$  to oxygenates near room temperature and atmospheric pressure for the plasma-assisted DRM reaction. As shown in Figure 5, we performed model validation by comparing the steady-state experimental results with the predicted values from the model for the reactant conversion and the product selectivity under the exact same conditions, with or without  $O_2$  addition (12%). The detailed plasma parameters are given in Table S1. A good agreement between the model and experiments is reached for the CH4,  $CO_2$ , and  $O_2$  conversion (Figure 5a), indicating that the underlying chemistry of the conversion is well-described in our model. As for the product selectivity, we consider the changes in syngas and hydrocarbons  $(C_xH_v)$  after introducing O<sub>2</sub> in the

model, with possible oxygenate production. Evidently, the simulation can effectively predict the decreasing trends of  $H_2$  and  $C_xH_y$  selectivity observed in the experiment upon  $O_2$  addition. However, a clear underestimation is observed for the calculated  $H_2$  selectivity without  $O_2$  addition and for the hydrocarbon selectivity with  $O_2$  addition.

As far as oxygenates are concerned, our kinetic model predicts the selectivity toward HCOOH, CH<sub>3</sub>OH, CH<sub>3</sub>COOH, C<sub>2</sub>H<sub>5</sub>OH, and total oxygenates with good accuracy upon 12% O2 addition; only for CH2O, there is a large discrepancy between our model and the experiments. Without  $O_2$  addition, our model predicts 2–3% selectivity for various oxygenates, such as HCOOH, CH<sub>3</sub>OH, and CH<sub>2</sub>O, while the concentration of these species was too small to be detected by GC and HPLC in the experiment. Notably, the total selectivity toward oxygenates rapidly increases with O2 addition, both in our model and in the experiment. Altogether, there are some differences in the calculated and measured product selectivities, but these are not unexpected in view of the large number of chemical reactions that can occur and the fact that the rate coefficients of several of these reactions are subject to large uncertainties. However, we prefer not to "tune" our model to reach a better agreement with the experiments

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**Figure 4.** Plasma-driven DRM performance for different powers: (a) conversion and energy cost (above) and total selectivity distribution (below), (b) selectivity of various gas and liquid products. (discharge frequency 23.5 kHz, total flow rate 40 mL/min, 12%  $O_2$ ,  $CO_2/CH_4 = 1:1$ , 6.78 s residence time, and 1 atm pressure) Plasma-driven DRM performance for different residence times, (c) conversion and energy cost (above) and total selectivity distribution (below), and (d) selectivity of various gas and liquid products (PSU power 40 W, discharge power 15–17 W, discharge frequency 23.5 kHz, 12%  $O_2$ , 35 °C circulating water,  $CO_2/CH_4 = 1:1$ , and 1 atm pressure)



Figure 5. Comparison between steady-state measurements and model predictions with and without  $O_2$  addition (12%) in plasma-assisted DRM: (a) gas conversion and main products selectivity and (b) various oxygenates selectivity at a PSU power of 40 W, residence time of 6.78 s, and temperature of 35 °C (exp: experiment; sim: simulation)

without a real scientific basis. Indeed, now, all assumptions made in our model (e.g., related to the number of microdischarge filaments) are based on logical and plausible physics. Overall, we believe that our model is sufficiently realistic to reveal the underlying plasma chemistry for the improved oxygenate production upon addition of  $O_2$  in the DRM reaction, as described below.

**3.5. Reaction Pathway Analysis.** The reduced electric field (i.e., the ratio of the electric field over total gas number density, E/N) is one of the most important parameters in



**Figure 6.** Reaction pathway analysis for HCOOH, COOH, CH<sub>3</sub>OH, CH<sub>3</sub>O, CH<sub>3</sub>O, CH<sub>2</sub>O, CH<sub>2</sub>OH, and OH for a 1:1 CH<sub>4</sub>/CO<sub>2</sub> mixture with 12% O<sub>2</sub> addition at atmospheric pressure, at a PSU power of 40 W, a residence time of 6.78 s, and temperature of 35 °C. Note that for OH, for the sake of clarity, the analysis is split into formation reactions and consumption reactions due to the many reactions taking place

controlling the distribution of the electron energy deposition to different excitation modes and the formation of active species in a nonequilibrium plasma. As shown in Figure S3, we compared the fraction of electron energy deposited into different excitation channels in (a) 1:1  $CH_4/CO_2$  mixture and (b) 1:1  $CH_4/CO_2$  mixture with 12%  $O_2$  addition, as a function of E/N. The most efficient mechanism for electron energy loss is the elastic collision with  $CH_4$  and  $CO_2$  molecules and the dissociation of  $CH_4$  at a relatively low reduced electric field (<20 Td) in a 1:1  $CH_4/CO_2$  mixture. However, the change of mixture ratio upon 12% addition of  $O_2$  dramatically alters the energy branching, and the plasma energy is now primarily transferred to the dissociation modes of  $CH_4$  and  $O_2$  (Figure S3b), indicating that the addition of  $O_2$  to the  $CH_4/CO_2$ mixture promotes the dissociation of  $O_2$  to produce O and  $O(^{1}D)$  radicals, which facilitates the oxidation of  $CH_{4}$  to oxygenates.

In order to elucidate the formation pathways of oxygenates, including HCOOH,  $CH_3OH$ , and  $CH_2O$ , we present the reaction pathway analysis for selected species for the 1:1  $CH_4/CO_2$  mixture with 12% aqueous  $O_2$  in Figure 6. The corresponding analysis for the same mixture but without the addition of  $O_2$  is presented in Figure S4 of the Supporting Information, for comparison. The thickest arrows represent the contribution of reactions to the species formation or consumption in the order of  $10^{-6}$  mol cm<sup>-3</sup>, while the thinnest arrows represent the contribution of reactions less than  $10^{-9}$  mol cm<sup>-3</sup>. Note that these orders of magnitude represent the integral of the reaction rate over the entire residence time. The arrows pointing inward

indicate formation reactions, while the arrows pointing outward represent consumption reactions. The blue arrows indicate reactions that occur both with and without  $O_2$ addition, while the green arrows indicate reactions that are only important upon 12%  $O_2$  addition. The numbers attached to the arrows denote the relative contributions of formation or consumption to the selected species, as calculated using eq 2

$$f_{ij} = \frac{(a_{ij}^{\rm R} - a_{ij}^{\rm L}) \int_0^{t_r} r_j \, \mathrm{d}t}{\sum_j (a_{ij}^{\rm R} - a_{ij}^{\rm L}) \int_0^{t_r} r_j \, \mathrm{d}t}$$
(2)

where  $f_{ij}$  stands for the relative contribution of reaction *j* to the formation of species *i*.  $t_r$  represents the residence time, and  $r_j$  is the reaction rate of reaction *j*. The same formula applies to the relative contribution for consumption.

As shown in Figures 6 and S4, the main oxygenated compound, HCOOH, is primarily formed through the chain termination reaction H + COOH  $\rightarrow$  HCOOH, which is responsible for 96.1 and 84.1% of HCOOH formation with or without O<sub>2</sub> addition, respectively. As a primary intermediate, carboxyl radical COOH is critical for the formation of HCOOH. COOH itself is mainly created upon recombination of CO with OH, which contributes 75.6 and 87.8% to COOH formation with or without  $O_2$  addition. At the same time, the main HCOOH formation path (H + COOH  $\rightarrow$  HCOOH) plays a significant role in the consumption of COOH without  $O_2$  addition (see Figure S4). Upon  $O_2$  addition, the main formation pathway for COOH does not change, as mentioned above, however, the main consumption pathway is changed from H + COOH  $\rightarrow$  HCOOH (without O<sub>2</sub> addition) to  $COOH + CO \rightarrow CO_2 + CHO$  (with  $O_2$  addition); cf. Figures 6 and S4. This is because electron impact dissociation  $[e + O_2]$  $\rightarrow$  e + O + O/O(<sup>1</sup>D)] enhances the formation of O and  $O(^{1}D)$ , which further promotes the formation of OH and  $H_2O_2$ . Accordingly, the concentration of COOH with 12% of  $O_2$  in the mixture is about 2 orders of magnitude higher than that without the addition of  $O_2$ . Although the reaction H + COOH  $\rightarrow$  HCOOH contributes only 12% of COOH consumption in the mixture with 12% O<sub>2</sub>, its reaction rate is still 1 order of magnitude higher compared with no O<sub>2</sub> addition.

For the generation of CH<sub>3</sub>OH, the dominant pathways without O<sub>2</sub> addition are the reactions of CH<sub>3</sub>O with H, CH<sub>3</sub>O,  $HO_{2}$ , and CHO radicals, accounting for 68.0% of the total CH<sub>3</sub>OH formation, as shown in Figure S4. In addition, 16.2 and 10.8% of CH<sub>3</sub>OH formation comes from the reactions of CH<sub>3</sub> with OH and OH<sup>-</sup>, as well as from the reaction of CH<sub>2</sub>OH with H and HO<sub>2</sub>, respectively. However, upon 12% O2 addition, the main pathway for CH3OH formation has become the chain termination reaction,  $CH_3O_2 + HO_2 \rightarrow$  $CH_3OH + O_3$  (contribution of 66.5%, see Figure 6). The main precursor, CH<sub>3</sub>O<sub>2</sub>, is mainly formed through the reaction CH<sub>3</sub>  $+ O_2 \rightarrow CH_3O_2$ , regardless of whether there is  $O_2$  addition (see Figures 6 and S4). However, the rate of this reaction is 2 orders of magnitude higher upon 12% O2 addition than without  $O_2$  addition, due to the high concentration of  $O_2$ . At the same time, the reaction rate of the major  $CH_3O_2$ consumption reaction  $(CH_3O_2 + HO_2 \rightarrow CH_3OH + O_3)$ upon 12% O<sub>2</sub> addition is 2 orders of magnitude higher than that without O<sub>2</sub> addition. This explains the significant increase in CH<sub>3</sub>OH formation upon O<sub>2</sub> addition, as observed in our experiments.

CH<sub>2</sub>O is dominantly formed upon addition of an O<sub>2</sub> through the reactions CH<sub>2</sub>OH + O<sub>2</sub> → CH<sub>2</sub>O + HO<sub>2</sub> and CH<sub>3</sub>OH + OH → CH<sub>2</sub>O + H<sub>2</sub>O + H, which are responsible for 45.9 and 31.8% of CH<sub>2</sub>O formation, respectively. Without O<sub>2</sub> addition, the dominant pathways for CH<sub>2</sub>O formation are the reactions CH<sub>2</sub> + CO<sub>2</sub> → CH<sub>2</sub>O + CO, CH<sub>3</sub> + O → CH<sub>2</sub>O + H, and CH<sub>3</sub>O + H/CH<sub>3</sub> → CH<sub>2</sub>O + H<sub>2</sub>/CH<sub>4</sub>. The significant increase in the O<sub>2</sub> concentration in the discharge mixture upon addition of O<sub>2</sub> can enhance the reaction rates of CH<sub>2</sub>OH + O<sub>2</sub> → CH<sub>2</sub>O + HO<sub>2</sub> and CH<sub>3</sub>O + O<sub>2</sub> → CH<sub>2</sub>O + HO<sub>2</sub> to promote the formation of CH<sub>2</sub>O. Meanwhile, the dissociation of O<sub>2</sub> strongly enhances the OH formation, significantly promoting the CH<sub>2</sub>O formation through the reaction CH<sub>3</sub>OH + OH → CH<sub>2</sub>O + H<sub>2</sub>O + H.

By analyzing the pathway of CH<sub>2</sub>OH, as shown in Figure 6, we find that the consumption of CH<sub>3</sub>OH to form CH<sub>2</sub>OH via the reactions CH<sub>3</sub>OH + OH  $\rightarrow$  CH<sub>2</sub>OH + H<sub>2</sub>O and CH<sub>3</sub>OH + O  $\rightarrow$  CH<sub>2</sub>OH + OH is the major source of CH<sub>2</sub>OH. In addition, the chain branching reaction stimulated by excited O(<sup>1</sup>D), via O(<sup>1</sup>D) + CH<sub>4</sub>  $\rightarrow$  CH<sub>2</sub>OH + H, is also responsible for 15.8% of CH<sub>2</sub>OH formation. Obviously, the major consumption pathways of CH<sub>2</sub>OH are the reactions with O<sub>2</sub> and O to form CH<sub>2</sub>O, which are responsible for 84.8 and 7.3% of CH<sub>2</sub>OH consumption, respectively.

As discussed above, OH is an important oxidizer in promoting the formation of oxygenates and their related intermediates. Therefore, we also compare the formation and consumption pathways of OH with and without O<sub>2</sub> addition. The pathways of OH formation and consumption are very complicated, so we have plotted separate maps illustrating the production pathway and consumption pathway, respectively. As shown in Figure S4, the dominant formation pathways without  $O_2$  addition are the reactions  $HO_2 + H \rightarrow OH + OH$ and  $CH_4 + O(^1D)/O(^1S) \rightarrow CH_3 + OH$ , accounting for 31.4 and 25.0% of the total OH formation, respectively. In addition, 9.2 and 8.2% of OH formation come from the reactions  $CH_2OH + H \rightarrow CH_3 + OH \text{ and } CH_3 + HO_2 \rightarrow CH_3O + OH,$ respectively. However, upon 12% O2 addition, the dominant pathways for OH formation have become the chain branching reactions,  $O_3 + H \rightarrow OH + O_2$  (30.0% contribution),  $HO_2 +$  $O \rightarrow OH + O_2$  (29.3% contribution), and  $CO + H_2O_2 \rightarrow OH$ + COOH (12.8% contribution), due to the significant rise in O<sub>2</sub> and O concentration, further stimulating the oxygenated components formation. As shown in Figures S4 and 6, upon O<sub>2</sub> addition, the dominant pathways for OH consumption are changed from  $OH + CH_2O \rightarrow H_2O + CHO$  and  $OH + CH_4$  $\rightarrow$  H<sub>2</sub>O + CH<sub>3</sub>, to OH + CO  $\rightarrow$  COOH, which promotes the formation of HCOOH.

In order to elucidate whether non-negligible competing reactions between  $CO_2$  and  $O_2$  are responsible for the formation of important intermediates or oxygenates in the system, the consumption pathways of  $CO_2$  and  $O_2$  for the 1:1 mixture with or without  $O_2$  addition are listed in Tables R1– R4 in the Supporting Information. The main competing reactions between  $CO_2$  and  $O_2$  for the plasma energy are the electron impact reactions. In addition to the electron impact reactions, there is another competing reaction between  $CO_2$  and  $O_2$  based on the reaction pathway analysis, that is,  $CH_2 + CO_2 \rightarrow CH_2O + CO$  and  $CH_2 + O_2 \rightarrow CO + H_2O$ ,  $CH_2 + O_2 \rightarrow COOH + H$ . However, this competing reaction has negligible influence on the formation of oxygenates.

In summary, our plasma chemical kinetics modeling results show that two types of reactions are responsible for the production enhancement of oxygenated compounds upon O<sub>2</sub> addition. First, the direct promotion effect of O<sub>2</sub> addition on the formation of important intermediates and oxygenates, such as the reactions  $CH_3 + O_2 \rightarrow CH_3O_2$  and  $CH_2OH + O_2 \rightarrow$  $CH_2O + HO_2$ , is responsible for 92.2% of  $CH_3O_2$  formation and 45.9% of CH<sub>2</sub>O formation, respectively. Second, the rise in concentration of oxygen-containing radicals, such as O, OH,  $HO_{2}$ , due to electron impact dissociation,  $e + O_2 \rightarrow e + O + O_2$  $O/O(^{1}D)$ , and subsequent reactions of these O atoms into OH and HO<sub>2</sub> will further enhance the formation of HCOOH via the pathways CO + OH  $\rightarrow$  COOH and COOH + H  $\rightarrow$ HCOOH; the formation of  $CH_3OH$  via the pathways  $CH_3O_2$  $+ HO_2 \rightarrow CH_3OH + O_3$  and  $CH_3O + HO_2 \rightarrow CH_3OH + O_2$ ; and the formation of CH<sub>2</sub>O via the pathways CH<sub>3</sub>OH + OH  $\rightarrow$  CH<sub>2</sub>O + H<sub>2</sub>O + H and CH<sub>3</sub>OH + O/OH  $\rightarrow$  CH<sub>2</sub>OH +  $OH/H_2O$  and  $CH_2OH + O_2 \rightarrow CH_2O + HO_2$ . Additional computational studies may aid in determining ways to increase the oxygenates yield but were outside the scope of this work.

## 4. CONCLUSIONS

In this paper, we demonstrate for the first time that plasmadriven DRM can be shifted from the production of mainly syngas to the production of significant amounts of oxygenates by introducing moderate amounts of  $O_2$  (12%), even without using catalysts. On the one hand, O2 addition can reduce carbon deposition resulting from the rapid decomposition of CH<sub>4</sub> induced by nonthermal plasma, hence making the plasmabased DRM process more stable and allowing us to operate it at higher CH<sub>4</sub> fractions. This is also relevant when catalysts are introduced in the plasma as catalyst deactivation by carbon deposition would be reduced. On the other hand, oxygencontaining species upon O<sub>2</sub> addition can improve oxygenate production. We evaluated multiple parameters in order to optimize the formation of oxygenates in our experiments. We show that lower power and shorter residence time enhance liquid production, leading to a maximal oxygenate selectivity of 50%.

We also developed a plasma chemical kinetics model to investigate how the effect of  $O_2$  addition shifts the formation pathways of syngas to oxygenates near room temperature and atmospheric pressure for the plasma-assisted DRM reaction. Two types of reactions are responsible for the improvement of the oxygenate production upon  $O_2$  addition. The first is the direct promotion effect of the addition of  $O_2$  on the formation of important intermediates and oxygenates. In addition, the increasing concentration of oxygen-containing radicals, such as O, OH, and HO<sub>2</sub>, due to electron impact dissociation,  $e + O_2 \rightarrow e + O + O/O(^1D)$  and the subsequent reaction of O atoms into OH and HO<sub>2</sub>, can further enhance the formation of oxygenates.

Our results not only yield a better fundamental understanding of the GtL conversion by the plasma-driven DRM process but also provide a novel strategy for reducing carbon deposition to improve the DRM reaction stability.

## ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c04352.

Ternary flammability diagram for  $CO_2-CH_4-O_2$  mixtures; results of qualitative analysis of liquid products by HPLC; calculation of conversion, selectivity, and the

contraction factor; description of the chemical kinetics model; fraction of electron energy into different excitation channels; reaction pathway analysis for the oxygenates in a 1:1  $CO_2/CH_4$  mixture; the consumption pathways of  $CO_2$  and  $O_2$  for the 1:1  $CH_4/CO_2$  mixture with or without  $O_2$  addition; reaction pathway analysis of singlet oxygen  $O_2(e1)$ ; and overview of the reactions included in our model (PDF)

## AUTHOR INFORMATION

#### **Corresponding Author**

Annemie Bogaerts – Research Group PLASMANT, Department of Chemistry, University of Antwerp, Wilrijk 2610, Belgium; orcid.org/0000-0001-9875-6460; Email: annemie.bogaerts@uantwerpen.be

#### Authors

- Shangkun Li Research Group PLASMANT, Department of Chemistry, University of Antwerp, Wilrijk 2610, Belgium; orcid.org/0000-0002-9297-1669
- Jintao Sun Research Group PLASMANT, Department of Chemistry, University of Antwerp, Wilrijk 2610, Belgium; School of Mechanical, Electronic and Control Engineering, Beijing Jiaotong University, Beijing 100044, People's Republic of China
- Yury Gorbanev Research Group PLASMANT, Department of Chemistry, University of Antwerp, Wilrijk 2610, Belgium;
  orcid.org/0000-0002-8059-4464
- Kevin van't Veer Research Group PLASMANT, Department of Chemistry, University of Antwerp, Wilrijk 2610, Belgium
- Björn Loenders Research Group PLASMANT, Department of Chemistry, University of Antwerp, Wilrijk 2610, Belgium; orcid.org/0000-0001-7962-4235
- Yanhui Yi State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, People's Republic of China; Orcid.org/ 0000-0002-5869-9382
- Thomas Kenis Applied Electrochemistry & Catalysis, Department of Applied Engineering, University of Antwerp, Wilrijk 2610, Belgium
- Qi Chen School of Mechanical, Electronic and Control Engineering, Beijing Jiaotong University, Beijing 100044, People's Republic of China

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.3c04352

#### **Author Contributions**

S.L. and J.S. contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Shangkun Li: Conceptualization, Validation, Formal analysis, Resources, Data curation, Writing original draft, Writing—review and editing. Jintao Sun: Conceptualization, Validation, Formal analysis, Resources, Data curation, Writing original draft, Writing—review and editing. Yury Gorbanev: Validation, Formal analysis, Data curation, Writing—review and editing. Kevin van 't Veer: Writing—review and editing. Björn Loenders: Writing—review and editing. Yanhui Yi: Writing—review and editing. Thomas Kenis: Products analysis, Data curation, Writing—review and editing. Qi Chen: Writing—review and editing, Supervision. Annemie Bogaerts: Formal analysis, Resources, Data curation, Writing—original draft, Writing—review and editing, Supervision, Funding acquisition.

#### Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Dry, M. E. The Fischer–Tropsch process: 1950–2000. Catal. Today 2002, 71, 227–241.

(2) le Saché, E.; Reina, T. R. Analysis of dry reforming as direct route for gas phase  $CO_2$  conversion. The past, the present and future of catalytic DRM technologies. *Prog. Energy Combust. Sci.* **2022**, *89*, 100970.

(3) Yi, Y.; Li, S.; Cui, Z.; Hao, Y.; Zhang, Y.; Wang, L.; Liu, P.; Tu, X.; Xu, X.; Guo, H.; Bogaerts, A. Selective oxidation of  $CH_4$  to  $CH_3OH$  through plasma catalysis: Insights from catalyst characterization and chemical kinetics modelling. *Appl. Catal., B* **2021**, *296*, 120384.

(4) Snoeckx, R.; Bogaerts, A. Plasma technology - a novel solution for CO<sub>2</sub> conversion? *Chem. Soc. Rev.* **201**7, *46*, 5805–5863.

(5) Liu, S.; Winter, L. R.; Chen, J. G. Review of plasma-assisted catalysis for selective generation of oxygenates from  $CO_2$  and  $CH_4$ . ACS Catal. **2020**, 10, 2855–2871.

(6) Khoja, A. H.; Tahir, M.; Amin, N. A. S. Dry reforming of methane using different dielectric materials and DBD plasma reactor configurations. *Energy Convers. Manage.* **2017**, *144*, 262–274.

(7) Li, Y.; Liu, C.; Eliasson, B.; Wang, Y. Synthesis of oxygenates and higher hydrocarbons directly from methane and carbon dioxide using dielectric-Barrier discharges: product distribution. *Energy Fuels* **2002**, *16*, 864–870.

(8) Zhang, Y.; Li, Y.; Wang, Y.; Liu, C.; Eliasson, B. Plasma methane conversion in the presence of carbon dioxide using dielectric-barrier discharges. *Fuel Process. Technol.* **2003**, *83*, 101–109.

(9) Rahmani, A.; Aubert, X.; Fagnon, N.; Nikravech, M. Liquid oxygenated hydrocarbons produced during reforming of  $CH_4$  and  $CO_2$  in a surface dielectric barrier discharge: Effects of steam on conversion and products distribution. *J. Appl. Phys.* **2021**, *129*, 193304.

(10) Kolb, T.; Voigt, J. H.; Gericke, K.-H. Conversion of methane and carbon dioxide in a DBD reactor: influence of oxygen. *Plasma Chem. Plasma Process.* **2013**, 33, 631–646.

(11) Wang, Y.; Chen, Y.; Harding, J.; He, H.; Bogaerts, A.; Tu, X. Catalyst-free single-step plasma reforming of  $CH_4$  and  $CO_2$  to higher value oxygenates under ambient conditions. *Chem. Eng. J.* **2022**, 450, 137860.

(12) Snoeckx, R.; Aerts, R.; Tu, X.; Bogaerts, A. Plasma-Based dry reforming: A computational study ranging from the nanoseconds to seconds time scale. *J. Phys. Chem. C* **2013**, *117*, 4957–4970.

(13) De Bie, C.; van Dijk, J.; Bogaerts, A. The dominant pathways for the conversion of methane into oxygenates and syngas in an atmospheric pressure dielectric barrier discharge. *J. Phys. Chem. C* **2015**, *119*, 22331–22350.

(14) Zhang, L.; Heijkers, S.; Wang, W.; Martini, L. M.; Tosi, P.; Yang, D.; Fang, Z.; Bogaerts, A. Dry reforming of methane in a nanosecond repetitively pulsed discharge: chemical kinetics modeling. *Plasma Sources Sci. Technol.* **2022**, *31*, 055014.

(15) Bogaerts, A.; Tu, X.; Whitehead, J. C.; Centi, G.; Lefferts, L.; Guaitella, O.; Azzolina-Jury, F.; Kim, H.-H.; Murphy, A. B.; Schneider, W. F.; Nozaki, T.; Hicks, J. C.; Rousseau, A.; Thevenet, F.; Khacef, A.; Carreon, M. The 2020 plasma catalysis roadmap. *J. Phys. D: Appl. Phys.* **2020**, *53*, 443001.

(16) Wang, L.; Yi, Y.; Wu, C.; Guo, H.; Tu, X. One-step reforming of  $CO_2$  and  $CH_4$  into high-value liquid chemicals and fuels at room temperature by plasma-driven catalysis. *Angew. Chem.* **2017**, *129*, 13867–13871.

(17) Ray, D.; Manoj Kumar Reddy, P.; Challapalli, S. Glass beads packed DBD-plasma assisted dry reforming of methane. *Top. Catal.* **2017**, *60*, 869–878.

(18) Bouchoul, N.; Fourré, E.; Duarte, A.; Tanchoux, N.; Louste, C.; Batiot-Dupeyrat, C. Plasma-metal oxides coupling for  $CH_4$ - $CO_2$  transformation into syngas and/or hydrocarbons, oxygenates. *Catal. Today* **2021**, *369*, 62–68.

(19) Mei, D.; Sun, M.; Liu, S.; Zhang, P.; Fang, Z.; Tu, X. Plasmaenabled catalytic dry reforming of  $CH_4$  into syngas, hydrocarbons and oxygenates: Insight into the active metals of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts. *J. CO2 Util.* **2023**, *67*, 102307.

(20) Wang, H.; Han, J.; Bo, Z.; Qin, L.; Wang, Y.; Yu, F. Nonthermal plasma enhanced dry reforming of  $CH_4$  with  $CO_2$  over activated carbon supported Ni catalysts. *Mol. Catal.* **2019**, 475, 110486.

(21) Wang, Y.; Fan, L.; Xu, H.; Du, X.; Xiao, H.; Qian, J.; Zhu, Y.; Tu, X.; Wang, L. Insight into the synthesis of alcohols and acids in plasma-driven conversion of  $CO_2$  and  $CH_4$  over copper-based catalysts. *Appl. Catal.*, B **2022**, 315, 121583.

(22) Vakili, R.; Gholami, R.; Stere, C. E.; Chansai, S.; Chen, H.; Holmes, S. M.; Jiao, Y.; Hardacre, C.; Fan, X. Plasma-assisted catalytic dry reforming of methane (DRM) over metal-organic frameworks (MOFs)-based catalysts. *Appl. Catal., B* **2020**, *260*, 118195.

(23) Khoja, A. H.; Tahir, M.; Amin, N. A. S. Recent developments in non-thermal catalytic DBD plasma reactor for dry reforming of methane. *Energy Convers. Manage.* **2019**, *183*, 529–560.

(24) Pancheshnyi, S.; Eismann, B.; Hagelaar, G. J. M.; Pitchford, L. C. *Computer Code ZDPlasKin*; University of Toulouse, LAPLACE, CNRS-UPS-INP: Toulouse, France, 2008. www.zdplaskin.laplace. univ-tlse.fr.

(25) Hagelaar, G. J. M.; Pitchford, L. C. Solving the Boltzmann equation to obtain electron transport coefficients and rate coefficients for fluid models. *Plasma Sources Sci. Technol.* **2005**, *14*, 722–733.

(26) Wanten, B.; Maerivoet, S.; Vantomme, C.; Slaets, J.; Trenchev, G.; Bogaerts, A. Dry reforming of methane in an atmospheric pressure glow discharge: Confining the plasma to expand the performance. *J. CO2 Util.* **2022**, *56*, 101869.

(27) Biswas, A. N.; Winter, L. R.; Loenders, B.; Xie, Z.; Bogaerts, A.; Chen, J. G. Oxygenate production from plasma-activated reaction of  $CO_2$  and ethane. ACS Energy Lett. **2022**, 7, 236–241.

(28) Manion, J. A.; Huie, R. E.; Levin, R. D.; Brugess, D. R., Jr.; Orkin, V. L. NIST Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8, Data version 2015.09; National Institute of Standards and Technology: Gaithersburg, Maryland, 20899-8320. https://kinetics.nist.gov/.

(29) Shen, X.; Yang, X.; Santner, J.; Sun, J.; Ju, Y. Experimental and kinetic studies of acetylene flames at elevated pressures. *Proc. Combust. Inst.* 2015, 35, 721–728.

(30) Reuter, C. B.; Zhang, R.; Yehia, O. R.; Rezgui, Y.; Ju, Y. Counterflow flame experiments and chemical kinetic modeling of dimethyl ether/methane mixtures. *Combust. Flame* **2018**, *196*, 1–10.

(31) Pitchford, L. C.; Alves, L. L.; Bartschat, K.; Biagi, S. F.; Bordage, M.-C.; Bray, I.; Brion, C. E.; Brunger, M. J.; Campbell, L.; Chachereau, A.; Chaudhury, B.; Christophorou, L. G.; Carbone, E.; Dyatko, N. A.; Franck, C. M.; Fursa, D. V.; Gangwar, R. K.; Guerra, V.; Haefliger, P.; Hagelaar, G. J. M.; Hoesl, A.; Itikawa, Y.; Kochetov, I. V.; McEachran, R. P.; Morgan, W. L.; Napartovich, A. P.; Puech, V.; Rabie, M.; Sharma, L.; Srivastava, R.; Stauffer, A. D.; Tennyson, J.; de Urquijo, J.; van Dijk, J.; Viehland, L. A.; Zammit, M. C.; Zatsarinny, O.; Pancheshnyi, S. LXCat: an open-access, web-based platform for data needed for modeling low temperature plasmas. *Plasma Processes Polym.* 2017, 14, 1600098. (32) Itikawa, Y. Cross sections for electron collisions with carbon dioxide. J. Phys. Chem. Ref. Data 2002, 31, 749–767.

(33) Popov, N. A. Kinetics of plasma-assisted combustion: effect of non-equilibrium excitation on the ignition and oxidation of combustible mixtures. *Plasma Sources Sci. Technol.* **2016**, *25*, 043002.

(34) Yang, S.; Najaraja, S.; Yang, V.; Sun, W.; Lefkowitz, J. K.; Ju, Y. Numerical and experimental investigation of nanosecond-pulsed plasma activated  $C_2H_4/O_2/Ar$  mixtures in a low temperature flow reactor. In 53rd AIAA Aerospace Science Meeting, Jan. 5–9, Kissimmee Florida, AIAA 2015–1614, 2015.

(35) Sun, J.; Chen, Q.; Zhao, B.; Guo, C.; Liu, J.; Zhang, M.; Li, D. Temperature-dependent ion chemistry in nanosecond discharge plasma-assisted  $CH_4$  oxidation. *J. Phys. D: Appl. Phys.* **2022**, *55*, 135203.

(36) Sun, J.; Chen, Q.; Yang, X.; Koel, B. E. Effects of nonequilibrium excitation on methane oxidation in a low-temperature RF discharge. J. Phys. D: Appl. Phys. **2020**, 53, 064001.

(37) Lin, J. J.; Shu, J.; Lee, Y. T.; Yang, X. Multiple dynamical pathways in the O(1D)+CH4 reaction: A comprehensive crossed beam study 1D)+CH<sub>4</sub> reaction: A comprehensive crossed beam study. J. Chem. Phys. **2000**, 113, 5287–5301.

(38) Slanger, T. G.; Black, G. O(1S) interactions—the product channels<sup>1</sup>S) interactions-the product channels. *J. Chem. Phys.* **1978**, 68, 989–997.