



# Plasma-Catalytic Partial Oxidation of Methane on Pt(111): A Microkinetic Study on the Role of Different Plasma Species

Björn Loenders,\* Yannick Engelmann, and Annemie Bogaerts



**ABSTRACT:** We use microkinetic modeling to examine the potential of plasma-catalytic partial oxidation (POX) of  $CH_4$  as a promising new approach to produce oxygenates. We study how different plasma species affect POX of  $CH_4$  on the Pt(111) surface, and we discuss the associated kinetic and mechanistic changes. We discuss the effect of vibrationally excited  $CH_4$  and  $O_2$ , as well as plasma-generated radicals and stable intermediates. Our results show that vibrational excitation enhances the turnover frequency (TOF) of catalytic  $CH_4$  dissociation and has good potential for improving the selectivities toward  $CH_3OH$ , HCOOH, and  $C_2$  hydrocarbons. Nevertheless, when



also considering plasma-generated radicals, we find that these species mainly govern the surface chemistry. Additionally, we find that plasma-generated radicals and stable intermediates enhance the TOFs of  $CO_x$  and oxygenates, increase the selectivity toward oxygenates, and make the formation of HCOOH more significant on Pt(111). We also briefly illustrate the potential impact of Eley–Rideal reactions that involve plasma-generated radicals. Finally, we reveal how various radicals affect the catalyst surface chemistry and we link this to the formation of different products. This allows us to make suggestions on how the plasma composition should be altered to improve the formation of desired products.

# **1. INTRODUCTION**

The remote locations of many natural gas reserves and the difficulties associated with transporting methane (CH<sub>4</sub>) ask for technologies that convert CH<sub>4</sub> into liquid chemicals prior to transportation to make its valorization economically attractive. Such technologies would transform an important greenhouse gas while simultaneously decreasing the dependency on oil for production of chemicals and fuels.<sup>1–3</sup> The partial oxidation (POX) of CH<sub>4</sub> into liquid oxygenates is therefore a particularly interesting route for CH<sub>4</sub> conversion.<sup>4,5</sup> Yet, certain challenges are associated with this approach, such as breaking the strong C–H bond in CH<sub>4</sub> while avoiding deep oxidation of the oxygenates to CO and CO<sub>2</sub>.<sup>6,7</sup> In classical thermal catalysis, the POX of CH<sub>4</sub> has therefore been mainly investigated for syngas production at high temperatures with transition-metal catalysts, like Ru, Rh, Ni and Pt.<sup>8</sup>

Nonthermal plasma (NTP) offers a distinct approach for easier breaking of the C–H bond in  $CH_4$  compared to thermal catalysis. NTP is characterized by highly energetic electrons, which can provide the energy required to induce chemical reactions, and thus, the use of high gas temperatures can be avoided. On the other hand, the high reactivity of plasma can hamper the selective formation of the desired products.<sup>9,10</sup> The selectivity of NTP can be improved by combining it with a catalyst, as done in plasma catalysis. The various reactive species formed in NTP (radials, excited molecules, etc.) can adsorb onto the catalyst, which directs their further reaction toward the desired products. Needless to say, good knowledge of the interaction between the plasma species and the catalyst is required to select the optimal catalyst material and operating conditions.<sup>11–13</sup> The POX of  $CH_4$  has been investigated in a variety of plasma reactors.<sup>4,9,14–20</sup> Among these, the dielectric barrier discharge (DBD) reactor is most common, as it can be easily operated at atmospheric pressure and scaled up for industrial use.<sup>21</sup> Some selectivity toward organic oxygenates (CH<sub>3</sub>OH, CH<sub>2</sub>O, HCOOH, etc.) can be achieved by POX of CH<sub>4</sub> in DBD, but large amounts of CO and CO<sub>2</sub> are also formed. As a result, a further increase in oxygenate selectivity is an important challenge.<sup>4</sup> Combination of a DBD plasma with the correct catalyst might overcome this challenge.

Various experimental works have investigated how the conversions and selectivities in POX of CH<sub>4</sub> are altered when combining a plasma with a wide variety of catalyst materials, including but not limited to CuO<sup>-</sup>-based catalysts,<sup>22–24</sup> Fe<sub>2</sub>O<sub>3</sub>,<sup>25,26</sup> Mn oxides,<sup>26</sup> copper–zinc–alumina doped with various metals,<sup>27,28</sup> NiO,<sup>26,29</sup> Ni,<sup>29–31</sup> Pt,<sup>25,30</sup> Pd,<sup>32</sup> Fe,<sup>32</sup> and Mo.<sup>32</sup> While these studies offer useful information, they usually provide limited insight due to the complexity of the plasma-catalytic system, resulting from the various interactions at play. As a result, a detailed fundamental understanding of the plasma-catalytic surface chemistry, for POX of CH<sub>4</sub> as well as other reactions, is still lacking.<sup>11–13</sup>

Received:November 1, 2020Revised:January 15, 2021Published:February 1, 2021





© 2021 American Chemical Society

Only a few mechanistic studies are available on the surface chemistry of the plasma-catalytic oxidation of CH<sub>4</sub>. Knoll et al.<sup>33</sup> investigated the POX of  $CH_4$  by an  $Ar/O_2$  atmospheric pressure plasma jet (APPJ) in the presence of Ni on an  $Al_2O_3/$ SiO<sub>2</sub> support using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The authors found that CO<sub>2</sub> formation is enhanced at higher temperatures and that CO is likely to be converted to  $CO_2$  on the catalyst surface. However, they also suggested the presence of carboxylate groups or COO<sup>-</sup>, which are likely precursors to CO<sub>2</sub>.<sup>33</sup> Zhang et al.<sup>34</sup> investigated the decomposition and oxidation of CH<sub>4</sub> exposed to a Ni catalyst on an Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> support and an Ar or Ar/O2 APPJ using time-resolved DRIFTS. The authors found that treatment with Ar plasma resulted in the formation of surface-bound CO, which was oxidized to CO<sub>2</sub> upon admixing of O<sub>2</sub> to the plasma. These results indicate that the CO selectivity can be altered by adjusting the flow of  $O_2$ .<sup>34</sup> Gibson et al.  $^{55}$  investigated CH<sub>4</sub> oxidation using a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst in a plasma. From in situ monitoring of the X-ray absorption fine structure (XAFS), the authors concluded that the catalyst did not undergo any significant structural changes during operation. Additionally, the temperature of the Pd nanoparticles was lower than needed to thermally activate the catalyst, indicating an alternative pathway for CH<sub>4</sub> activation.<sup>35</sup> Stere et al.<sup>36</sup> studied the oxidation of  $CH_4$  in the plasma with a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst using in situ DRIFTS analysis. The authors observed significant formation of formate species (HCOO) on the catalyst, which was correlated to CO<sub>2</sub> formation. They also suggested that CO and CO<sub>2</sub> formation occurs via different routes due to their different formation profiles as a function of time.<sup>30</sup>

Besides experimental mechanistic studies, a good insight into the underlying (plasma and catalytic surface) chemistry for plasma-catalytic POX of CH4 can also be obtained by numerical modeling. Existing kinetic models on plasmainduced POX of CH<sub>4</sub> have been developed for plasma-only processes, and thus do not incorporate any plasma-catalyst interactions. Nevertheless, these models still provide useful insight into the gas-phase chemistry. Nozaki et al.<sup>19</sup> stated that in POX of CH<sub>4</sub>, CH<sub>3</sub> mainly forms oxygenates, while other  $CH_x$  results in CO and  $CO_2$  formation. They also modeled streamer formation in  $CH_4$  to study its fragmentation pattern. Goujard et al.<sup>9</sup> simulated POX of CH<sub>4</sub> at 5 and 300 °C. Plasma-induced dissociation of CH<sub>4</sub> in H and CH<sub>3</sub> was found to be the main mechanism for CH<sub>4</sub> activation at 5 °C, while oxidation reactions became increasingly important at 300 °C, resulting in more CO, H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O.<sup>9</sup> De Bie et al.<sup>37</sup> simulated POX of CH4 in DBD using a 1D fluid model and identified the dominant reaction pathways. Both De Bie et al.<sup>37</sup> and Goujard et al.<sup>9</sup> reported that CH<sub>3</sub> and O<sub>2</sub> recombine into CH<sub>3</sub>OO, which was identified as a key species for oxygenate formation. On the other hand, Qian et al.38 reported that CH<sub>3</sub>OH is mainly formed via three-body recombination of CH<sub>3</sub> and OH, rather than via CH<sub>3</sub>OO, based on zerodimensional (0D) modeling.<sup>38</sup> An important issue for plasmainduced POX of CH<sub>4</sub> is deep oxidation to CO and CO<sub>2</sub>, either due to oxidation of the oxygenates or dissociation of CH4 to CH<sub>2</sub>, CH, or C, as discussed in the abovementioned studies.<sup>9,19,37</sup>

While modeling POX of  $CH_4$  in a plasma without a catalyst gives useful insight into the gas-phase chemistry, theoretical studies from thermal catalysis can provide a better understanding of the chemistry on the catalyst surface. Olivera et

al.<sup>39</sup> estimated reaction enthalpies and activation barriers for POX of CH<sub>4</sub> on different transition metals (Ni, Pd, Pt, and Au) using the bond order conservation theory and found that CH<sub>3</sub>OH formation is more likely to occur on the most noble transition metals. A similar conclusion was drawn by Yoo et al.<sup>40</sup> from microkinetic modeling of the thermal-catalytic POX of CH<sub>4</sub> on different transition metals. However, at the same time, activation of CH4 is more difficult on the most noble transition metals.<sup>39</sup> Density functional theory (DFT) calculations by Xing et al.<sup>41</sup> showed that surface-bound O\* can facilitate the activation of CH4 on group Ib metals but also lower the barrier of the subsequent dehydrogenation steps and therefore has both promoting and inhibiting effects on POX of CH<sub>4</sub> toward oxygenates.<sup>41</sup> Baek et al.<sup>42</sup> performed microkinetic modeling on thermal POX of CH<sub>4</sub> to syngas and showed that if O\*-assisted dehydrogenation pathways are considered, an additional local maximum in the turnover frequency (TOF) for CO<sub>2</sub> production can be observed in the region near Ag. Additionally, the TOFs of CO and H<sub>2</sub>O were also strongly increased in this region, yet the authors did not study oxygenate formation.<sup>4</sup>

Although the aforementioned theoretical studies provide useful knowledge on either plasma or catalyst surface chemistry, they are developed to simulate plasma-only or thermal-catalytic POX of CH<sub>4</sub>, respectively. As a result, these studies do not incorporate any effects of plasma species on surface chemistry. In this paper, we introduce a microkinetic model for POX of CH<sub>4</sub> by plasma catalysis that incorporates the effects of plasma species, such as vibrationally excited molecules, radicals, and stable intermediates, on catalyst surface chemistry. Recently, similar models have provided valuable new insight into plasma-catalytic synthesis of NH<sub>3</sub>,<sup>43,44</sup> nonoxidative coupling of CH<sub>4</sub>,<sup>45</sup> and CO<sub>2</sub> hydrogenation.<sup>46</sup>

Transition metals of group VIIIb are known to be good catalysts for thermal POX of CH4 to syngas at high temperatures.<sup>8,47</sup> We here investigate whether such transition metals would be suitable catalysts for oxygenate production via low-temperature POX of CH<sub>4</sub> in the presence of reactive plasma species. From these catalysts, we choose Pt(111) as this is among the most noble transition metals in group VIIIb and can thus be expected to be the more suitable catalyst for oxygenate formation.<sup>39</sup> Note that it is described in the literature that plasma methods for catalyst preparation, e.g., catalyst reduction by plasma, can easily generate the (111) facet.<sup>48</sup> Additionally, Pt has been fairly well studied in thermal catalysis for syngas formation through POX of CH44 at high temperatures by both microkinetic modeling<sup>49-52</sup> and DFT studies. 53,54 Thus, the DFT data required by the model is accessible in the literature and the availability of other microkinetic modeling studies allows us to compare our results to those of existing studies.

#### 2. METHODS

We constructed a mean-field microkinetic model to simulate POX of  $CH_4$  on Pt(111).<sup>45</sup> For every surface species, the time evolution of the fractional coverage is described with a balance equation, based on the different gain and loss terms

$$\frac{\partial \theta_x}{\partial t} = \sum_{i,\text{gain}} c_{x,i} r_i - \sum_{i,\text{loss}} c_{x,i} r_i$$
(1)

pubs.acs.org/JPCC

Article



**Figure 1.** Most important reaction pathways at steady state for thermal-catalytic POX of  $CH_4$  on Pt(111) using a  $CH_4/O_2$  (70/30) gas mixture at 500 K and 1 bar. The values of the reaction TOFs in (s<sup>-1</sup>) are displayed next to the arrows. The arrow thickness indicates the relative importance of a reaction within each separate scheme. A dotted arrow indicates the species is used as a second reactant in another reaction.

where  $\theta_x$  is the fractional coverage of species x,  $c_{x,i}$  is the stoichiometric coefficient for species x in the gain and loss reactions i, and  $r_i$  are the rates of the said reactions. These rates are calculated as the difference between the rates of the forward and reverse reactions

$$r_{i} = k_{i,f} \prod_{x_{f}} (a_{x_{f}})^{c_{x_{f},i}} - k_{i,r} \prod_{x_{r}} (a_{x_{r}})^{c_{x_{r},i}}$$
(2)

where  $k_{i,f}$  and  $k_{i,r}$  are the rate constants of the forward and reverse reactions, respectively, and  $a_{x_f}$  and  $a_{x_r}$  are the activities of the reactant species  $x_f$  and the product species  $x_{r}$ , respectively. The activities are assumed equal to the fractional coverages for surface species and to the partial pressures (in bar) for gas-phase species. The rate constants are calculated using the transition state theory

$$k = \frac{k_{\rm b}T}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) = \frac{k_{\rm b}T}{h} \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)$$
(3)

where  $k_{\rm b}$  is the Boltzmann constant; *T* is the temperature; *h* is the Planck constant; *R* is the ideal gas constant; and  $\Delta G^{\ddagger}$ ,  $\Delta H^{\ddagger}$ , and  $\Delta S^{\ddagger}$  are the Gibbs free energy, enthalpy, and entropy of activation, respectively. We calculate the entropy differences based on the translational entropy, as this typically has the largest contribution to the total entropy.<sup>55</sup> The translational entropy of a gas species is calculated as<sup>56</sup>

$$S_{\rm trans}(T) = R \ln \left( \frac{k_{\rm b}T}{p_{\rm ref}} \frac{(2\pi m k_{\rm b}T)^{3/2}}{h^3} e^{5/2} \right)$$
(4)

where  $S_{\text{trans}}$  is the translational entropy, *m* is the mass of the gas species, and  $p_{ref}$  is the reference pressure (10<sup>5</sup> Pa). Gas-phase species are assumed to lose all their translational entropy upon adsorption onto the surface. Thus, the reaction entropy  $\Delta S$  is equal to  $-S_{\text{trans}}$  for adsorption processes and Eley-Rideal reactions. For dissociative adsorption and Eley-Rideal reactions, the transition state is assumed to have lost all its translational entropy; hence,  $\Delta S_{ads}^{\ddagger}$  is equal to  $-S_{trans}$ . For molecular and radical adsorption, on the other hand, the transition state is considered a two-dimensional (2D) gas and  $\Delta S_{ads}^{\ddagger}$  is considered equal to  $-1/3S_{trans}$  for these processes.<sup>56</sup> For the corresponding molecular and radical desorption processes, the Gibbs free energy of activation can become negative at higher temperatures due to higher entropy in the transition state. In such a case, the Gibbs free energy of activation  $\Delta G_{
m des}{}^{\ddagger}$  is set to zero, and the rate constants are calculated as

$$k_{\rm des} = \frac{k_{\rm b}T}{h} \tag{5}$$

$$k_{\rm ads} = \frac{k_{\rm des}}{K_{\rm eq,des}} \tag{6}$$

where  $K_{eq}$  is the equilibrium constant

$$K_{\rm eq} = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{\Delta H}{RT}\right) \exp\left(\frac{\Delta S}{R}\right) \tag{7}$$

where  $\Delta G$  is the Gibbs free energy of the reaction,  $\Delta H$  is the reaction enthalpy, and  $\Delta S$  is the reaction entropy. Finally,  $\Delta S$  and  $\Delta S^{\ddagger}$  are considered equal to zero for Langmuir–Hinshelwood reactions.

A full list of all reactions included in the model alongside the thermodynamic data can be found in Table S1 of the Supporting Information (SI). The effect of vibrationally excited  $CH_4$  and  $O_2$  is implemented by lowering the enthalpy barriers of their respective dissociative adsorption reactions and the Eley–Rideal reactions between gaseous  $CH_4$  and surface-bound  $OH^*$  or  $O^*$  (see Table S1 in the SI, reactions 14 and 15).<sup>45</sup> For a detailed description of how vibrational excitation is implemented in our model, we refer to Section 2 of the SI.

We obtain steady-state coverages by solving the differential equations to  $\left(\frac{\partial\theta_x}{\partial t} = 0\right)$  for all species, at a temperature of 500 K, a total pressure of 1 bar, and zero conversion, unless noted otherwise. These steady-state coverages can be inserted back into the rate equations to obtain steady-state reaction rates. To compare the product formation and product distributions between different conditions, we calculate the steady-state turnover frequencies (TOFs) and selectivities from the steady-state reaction rates, as described in Section 3 of the SI.

# 3. RESULTS AND DISCUSSION

In the following sections, we solve the model for various cases. We start by solving the model for the thermal case, without including any plasma effects. These results will serve as the benchmark to evaluate the plasma effects. Subsequently, we modify the model to include either vibrational excitation or plasma-generated radicals and stable intermediates and we compare these results to the thermal case. To make this comparison possible, all simulations are performed at a temperature of 500 K and a total pressure of 1 bar, unless noted otherwise. We choose these conditions as they are representative of a DBD plasma. In our simulations, we use a reactant gas mixture of  $CH_4/O_2$  (70/30), as the radical partial pressures used in our model are based on radical densities calculated by De Bie et al.,<sup>37</sup> for this gas mixture. This  $CH_4/O_2$ ratio is close to the stoichiometric ratio of 2:1 for POX to CH<sub>3</sub>OH. Note that this work focuses on the effect of the plasma species on surface chemistry. In reality, molecules and radicals formed on the catalyst surface can desorb back to the gas phase and in turn influence the plasma chemistry. The influence of the surface reactions on the plasma composition is beyond the scope of this study but would be interesting followup work.

3.1. Thermal Catalysis. As discussed in the Introduction section, the thermal-catalytic POX of CH4 on Pt has been mainly investigated for the production of syngas at high temperatures (800-1300 K).<sup>49-52,57,58</sup> Only a few studies have investigated potential pathways for oxygenate formation via POX of  $CH_4$  on Pt.<sup>39,40,53</sup> We start by solving the model for the thermal case to reveal the most important reaction pathways for POX of  $CH_4$  on the Pt(111) surface at steady state. The overall pathways for the main products are shown in Figure 1a. Gaseous CH<sub>4</sub> dissociatively adsorbs on the surface, forming CH3\* and H\*. CH3\* is further dehydrogenated to CH<sub>2</sub>\*, which in turn forms CH\*. We find that the breaking of the C-H bonds in all three steps occurs through interaction with empty surface sites, rather than with OH\* or O\*. Most of the CH\* (90.5%) is oxidized to CHO\* and subsequently decomposes to form CO\*, which desorbs from the surface. A smaller fraction of CH\* (9.4%) first undergoes dehydrogenation, after which the formed C\* is oxidized into CO\* as well. Dissociative adsorption of O<sub>2</sub> results in formation of surface

O\*. Most of the O\* (79.0%) forms OH\* through reaction with H\* that originates from the dehydrogenation of  $CH_x$  and CHO\*, while the oxidation of CH\* to CHO\* is responsible for 18.0% of the total O\* consumption. OH\* reacts to form  $H_2O^*$  through reaction  $2OH^* \rightarrow H_2O^* + O^*$ , after which the formed  $H_2O^*$  desorbs as a side product.

As mentioned before, we performed these calculations at 500 K to provide a benchmark for plasma-catalytic POX of CH<sub>4</sub>, which typically occurs at such temperature in DBD plasma, although we admit that this temperature is too low for thermal-catalytic POX of CH<sub>4</sub>. Therefore, in the SI (Section 4), we compared the reaction pathways at 500 K from Figure 1a with the pathways calculated at 1000 K (as more common in thermal-catalytic POX of CH<sub>4</sub>) and results predicted by earlier microkinetic studies.<sup>50,52</sup>

Figure 1b represents the pathways for the formation of  $CO_2$ and HCOOH, as well as concurrent reactions. A relatively small amount (1.8%) of the CHO\* formed in the main pathway is oxidized to HCOO\* as a side reaction. Only a minor amount (0.003%) of this HCOO\* undergoes hydrogenation to HCOOH, while the majority is dehydrogenated to  $CO_2^*$ , either by interaction with an empty surface site (99.1%) or  $O^*$  (0.9%). Another important route for the formation of  $CO_2^*$  is through oxidation of  $CO^*$  that is formed in the main pathway. Still, about 71.0% of CO2\* formation occurs via dehydrogenation of HCOO\* by empty sites, compared to 28.4% from oxidation of CO\*. The rate of HCOOH formation in Figure 1 is about 6 orders of magnitude lower compared to that of CO desorption, which indicates that the formation of HCOOH in practice does not occur. The rate of CO<sub>2</sub> desorption in Figure 1 is roughly a factor 40 lower than that of CO. However, experimental and DFT results by Chin et al.<sup>59</sup> indicate that CO oxidation to CO<sub>2</sub> is much faster than CH<sub>4</sub> dissociation on Pt clusters, and because of this, only trace amounts of CO can be present in the gas phase prior to  $O_2$ depletion. Additionally, thermal equilibrium calculations show that CO<sub>2</sub> and H<sub>2</sub>O are the thermodynamically favored products at 500 K.<sup>4,8</sup> The reason that the rate for desorption of CO in Figure 1 is higher than that of  $CO_2$  can, however, be attributed to the zero conversion conditions. Indeed, we find that the addition of even small amounts of CO (0.1-0.001%)to the gas mixture results in  $CO_2$  becoming the main product, as CO is adsorbed and oxidized. A more in-depth discussion is provided in Section 5 of the SI.

The pathways leading to the formation of CH<sub>3</sub>OH and CH<sub>2</sub>O are displayed in Figure 1c. These pathways branch off from the main reaction pathway at the CH<sub>3</sub>\* species, which can be oxidized by O\* to form CH<sub>3</sub>O\*. The latter serves as a precursor for both CH<sub>3</sub>OH and CH<sub>2</sub>O. However, dehydrogenation of CH<sub>3</sub>\* by an empty surface site or a surface-bound O\* is strongly favored over CH3O\* formation, as indicated in Figure 1c. Indeed, the TOFs of dehydrogenation by empty sites or hydrogen abstraction by O\* are 7 and 4 orders of magnitude higher, respectively, than that of  $CH_3O^*$  formation. The CH<sub>3</sub>O\* species can either be hydrogenated to CH<sub>3</sub>OH or dehydrogenated to form CH<sub>2</sub>O, the latter being strongly favored (i.e., its rate is 10 orders of magnitude higher). However, neither of these products are expected to be formed in significant amounts under these conditions, as their TOFs are several orders of magnitude lower than those of the main products, i.e., CO, CO<sub>2</sub>, and H<sub>2</sub>O. As mentioned earlier, this is also the case for HCOOH.

Article



**Figure 2.** Influence of the vibrational temperature and  $O_2$  content on the TOFs of the two main reactions for CH<sub>4</sub> dissociation (left panels) and on the total TOF of CH<sub>4</sub> dissociation (right panel), both in (s<sup>-1</sup>). Calculated at steady state for a CH<sub>4</sub>/O<sub>2</sub> mixture at a pressure of 1 bar and a surface temperature of 500 K. For convenience, the same scale is used for the three graphs in this figure.



**Figure 3.** Influence of the vibrational temperature and  $O_2$  content on the selectivities of oxygenates,  $CO_3$ , and  $CH_3CH_3$ . Calculated at steady state for a  $CH_4/O_2$  mixture at a pressure of 1 bar and a surface temperature of 500 K. Note that logarithmic scaling is used for  $CH_3OH$ , HCOOH, and  $CH_3CH_3$ , while linear scaling is used for  $CH_2O$ ,  $CO_2$ , and CO.

**3.2.** Plasma Catalysis: Effect of Vibrational Excitation. As discussed in the Introduction section, one of the challenges associated with POX of  $CH_4$  is the activation of the strong C-H bond in  $CH_4$ .<sup>7</sup> Indeed, activation of the C-H bond has been identified as the sole kinetically relevant step for POX of  $CH_4$  on Pt clusters, except for conditions close to  $O_2$  depletion, where  $O_2$  activation becomes rate-limiting.<sup>60</sup> Vibrational excitation of  $CH_4$  is known to enhance its dissociative adsorption onto transition-metal surfaces.<sup>61</sup> Thus, plasmainduced vibrational excitation can be expected to facilitate POX of  $CH_4$  on these surfaces. In the following sections, we investigate the impact of vibrational excitation on the TOFs and product selectivities of POX of  $CH_4$  on Pt(111), and we discuss the associated kinetic and mechanistic changes. We implement the effect of plasma-induced vibrational excitation by lowering the barriers of CH<sub>4</sub> and O<sub>2</sub> activation, as discussed in Section 2 of the SI. We simultaneously vary the vibrational temperatures of CH<sub>4</sub> and O<sub>2</sub> between 500 and 1500 K and assume both vibrational temperatures to have the same value. Chen et al.<sup>62</sup> measured the vibrational temperature in a  $CH_4/$  $N_2$ /He DBD plasma at 60 Torr based on the  $\nu = 1$  peak of  $N_2$ and observed a maximal vibrational temperature of 1350 K. We here choose an upper limit of 1500 K, which is still in the uncertainty range of the results from Chen et al.<sup>62</sup> We choose this value to be an upper limit since the vibrational temperature measured by Chen et al. was based on the  $\nu$  = 1 peak of N<sub>2</sub> and the vibrational temperature of CH<sub>4</sub> is likely to be lower. As a comparison, Butterworth et al.<sup>63</sup> studied the vibrational excitation of CH4 in low-pressure pulsed microwave plasma and found that the vibrational and gas temperatures equilibrate around 900 K. In any case, varying the vibrational temperature in this wide range is interesting from a theoretical point of view as well.

3.2.1. Effect of Vibrational Excitation on TOFs. Figure 2 illustrates the influence of vibrational excitation on the total TOF of  $CH_4$  dissociation for a variable  $O_2$  content (1–99%), as well as on the separate TOFs of the two main CH<sub>4</sub> dissociation reactions. As can be seen in the right panel of Figure 2, the TOF of CH<sub>4</sub> dissociation increases by several orders of magnitude, i.e., about 4 orders of magnitude at 30% O<sub>2</sub>, upon an increase in vibrational temperature from 500 to 1500 K. Additionally, the CH<sub>4</sub> dissociation TOF also rises upon lower O<sub>2</sub> content due to the corresponding increase in the partial pressure of CH<sub>4</sub>. Below the vibrational temperature of 1000 K, the highest CH<sub>4</sub> dissociation TOFs are restricted to low O<sub>2</sub> contents. Yet, above 1000 K, the highest TOFs can be found in a region that is more spread over the different O<sub>2</sub> fractions. This can be linked to a change in the main mechanism of CH4 dissociation around 1000 K. The TOFs of the main mechanisms of CH4 dissociation can be seen in the left panels of Figure 2. At vibrational temperatures below 1000 K, the main mechanism for CH<sub>4</sub> dissociation is the dissociative adsorption on empty surface sites, while above 1000 K, the dissociation of CH<sub>4</sub> occurs mostly through an Eley-Rideal reaction with preadsorbed O\* (CH<sub>4</sub>(g) + O\*  $\rightarrow$  CH<sub>3</sub>\* + OH\*). The change in the mechanism follows from a stronger rise in the rate constant of the O\*-assisted CH<sub>4</sub> dissociation, compared to dissociative adsorption on empty sites. This is a direct result of the higher reaction barrier and Fridman-Macheret  $\alpha$  parameter (see SI, Section 2) of the O\*-assisted reaction (1.28 eV and 0.48, respectively) compared to that on empty sites (0.63 eV and 0.41, respectively). When comparing the TOFs of both reactions, we find that the O\*-assisted mechanism depends less on the  $O_2$  content in the gas mixture. This is because the O\* coverage varies very little with O<sub>2</sub> content or vibrational temperature and remains above 99.5% in the investigated range, while the fraction of free sites mainly changes with O<sub>2</sub> content and drops from  $5.3 \times 10^{-5}$  to  $3.7 \times$  $10^{-6}$ , as the O<sub>2</sub> content rises from 1 to 99%. As the O\*-assisted mechanism depends less on the fraction of free sites, i.e., it requires only one free site per molecule of CH<sub>4</sub>, it also varies less with the O<sub>2</sub> content. The fractional coverages of the 14 most abundant surface species, as well as the fraction of free sites, can be found in Figure S3 in the SI.

Our results indicate that plasma-induced vibrational excitation shows good potential for improving the TOFs of POX of  $CH_4$  at low temperatures (500 K). The effect of

vibrational excitation on the product selectivities is discussed in the next section. Additionally, our results suggest that vibrational excitation can decrease the dependency of the TOFs on the  $O_2$  content in the gas phase for relevant  $O_2$ fractions (1–99%) by facilitating the O\*-assisted dissociation of CH<sub>4</sub>. As a result, high TOFs becomes feasible even at higher  $O_2$  fractions.

3.2.2. Effect of Vibrational Excitation on the Selectivities. In the previous section, we showed that vibrational excitation can enhance the TOF of CH<sub>4</sub> dissociation. In this section, we investigate whether vibrational excitation can affect the selectivities of the products. In Figure 3, we illustrate how the selectivities of the oxygenates,  $CO_{x}$ , and ethane ( $CH_3CH_3$ ) change when varying the vibrational temperature from 500 to 1500 K for a gas mixture with variable  $O_2$  content, i.e., 1–99%  $O_2$ . Figure 3a-c displays the selectivities of  $CH_3OH_1$ HCOOH, and CH<sub>3</sub>CH<sub>3</sub>, respectively, which show a similar trend. The selectivities of these products increase strongly when increasing the vibrational temperature from 500 to 1500 K, i.e., by a factor  $10^4 - 10^5$  at 33% O<sub>2</sub>. However, these selectivities are less dependent on the O<sub>2</sub> content in most of the investigated range and only show a strong decrease at high O<sub>2</sub> fractions. Figure 3d,e displays the selectivities of CH<sub>2</sub>O and CO<sub>2</sub>, respectively. The selectivities of both products increase only slightly with increasing vibrational temperature and instead depend stronger on the O<sub>2</sub> content in the gas mixture, with a higher fraction of O<sub>2</sub> resulting in higher selectivities toward these products. The selectivity of CO, shown in Figure 3f, changes little under the investigated conditions but decreases slightly with increasing O2 fraction or vibrational temperature. As a result, CO remains the main product under the investigated conditions.

A similar trend for the selectivities of CH<sub>3</sub>OH, HCOOH, and CH<sub>3</sub>CH<sub>3</sub>, which strongly increase with increasing vibrational temperature, can be explained by the enhanced dissociation of CH<sub>4</sub>. Vibrational excitation facilitates CH<sub>4</sub> dissociation, which enhances the formation of  $CH_x^*$  and  $H^*$ . Therefore, as the vibrational temperature increases from 500 to 1500 K, the fractional coverages of these species increase, by about a factor of  $10^3 - 10^5$  at 30% O<sub>2</sub> (see Figure S3 in the SI). Higher H\* coverages enhance the hydrogenation of CH<sub>3</sub>O\* and HCOO\* to CH<sub>3</sub>OH and HCOOH, respectively, resulting in higher selectivities toward these products at higher vibrational temperatures. Similarly, higher surface coverages of  $CH_x^*$  enhance their coupling to form  $C_2$  hydrocarbons. In Figure 3, we only show the selectivity of CH<sub>3</sub>CH<sub>3</sub>, but the selectivities of CH<sub>2</sub>CH<sub>2</sub> and CHCH show a similar trend and can be found in Figure S4 in the SI. While the formation of  $CH_r^*$  and  $H^*$  is also enhanced at high  $CH_4$  contents and thus low O2 fractions in the gas mixture, the increase with decreasing O<sub>2</sub> fraction is not observed as strongly in the selectivities of CH<sub>3</sub>OH, HCOOH, and C<sub>2</sub> hydrocarbons. This is because lower O<sub>2</sub> fractions also result in higher fractions of free sites, which promote the dehydrogenation of  $CH_x^*$  and CO formation according to the pathways in Figure 1a. While vibrational excitation shows potential for improving the selectivities toward CH<sub>3</sub>OH, HCOOH, and C<sub>2</sub> hydrocarbons, these selectivities remain low under the investigated conditions, i.e., below  $1.8 \times 10^{-13}$ ,  $9.4 \times 10^{-8}$ ,  $3.7 \times 10^{-22}$ , and 6.8 $\times$  10<sup>-12</sup> for CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>, and CHCH, respectively. This indicates that the effect of vibrational excitation alone is not enough to make the formation of  $CH_3OH$  or  $C_2$  hydrocarbons feasible on Pt(111). On the other

hand, the selectivity toward HCOOH reaches a maximum of 0.77%, indicating that the formation of detectable amounts of HCOOH might be possible at high vibrational temperatures.

As shown in Figure 3, the selectivities of  $CH_2O$  and  $CO_2$  are not affected much by vibrational excitation and are instead more strongly dependent on the O<sub>2</sub> content in the gas mixture. Both products show increased selectivities at higher  $O_2$ contents, which is a result of the lower availability of free surface sites. As fewer free sites are available, a slightly lower fraction of CH<sub>3</sub>\* and CHO\* can be dehydrogenated by empty sites. Instead, relatively more  $CH_3^*$  and  $CHO^*$  will bind to O<sup>\*</sup>, forming  $CH_3O^*$  and  $HCOO^*$ , respectively. As can be seen from the pathways displayed in Figure 1, the latter two species are precursors to CH<sub>2</sub>O and CO<sub>2</sub>, respectively. While the selectivities toward both products thus increase at higher O2 fractions, they vary relatively little under the investigated conditions, i.e., from  $1.2 \times 10^{-8}$  to  $1.7 \times 10^{-7}$  and from 0.89 to 5.1% for  $CH_2O$  and  $CO_2$ , respectively. Consequently, the selectivity toward CH<sub>2</sub>O remains too low for its formation to become feasible on Pt(111), when only considering vibrational excitation. We found that the coupling of CH3\* and O\* to CH<sub>3</sub>O\* is a bottleneck for the formation of CH<sub>2</sub>O and CH<sub>3</sub>OH, as CH<sub>3</sub>O\* is a precursor to both these products. This reaction is strongly disfavored on Pt(111) due to its high activation barrier (2.04 eV), while the barriers for CH3\* dehydrogenation by either an empty surface site or O\* are lower (0.83 and 1.62 eV, respectively).53

In summary, our results show that plasma-induced vibrational excitation increases the  $CH_4$  dissociation TOF in its POX. This supports the possibility of plasma catalysis to facilitate POX of  $CH_4$  on transition metals, like Pt, at lower temperatures than those required in traditional thermal catalysis. Additionally, we find that vibrational excitation increases the selectivities of  $CH_3OH$ , HCOOH, and  $C_2$ hydrocarbons. The lower activation barrier of  $CH_4$  dissociation improves the formation of  $H^*$  and  $CH_x^*$  species on the catalyst surface, which enhances hydrogenation of  $CH_3O^*$  and  $HCOO^*$  and coupling of  $CH_x$ . However, we find that the selectivities toward oxygenates and  $C_2$  hydrocarbons remain low on Pt(111), as C-H bond breaking of the surface-bound intermediates is too strongly favored on this catalyst and the effect of vibrational excitation alone cannot counteract this.

3.3. Plasma Catalysis: Effect of Radicals and Stable Intermediates. Radicals and stable intermediates formed in the plasma are implemented in the model by setting a nonzero partial pressure for these species. The base case assumes partial pressures based on species densities calculated by De Bie et al.,<sup>37</sup> for a DBD plasma in a  $CH_4/O_2$  (70/30) inlet gas mixture. These species densities are converted to partial pressures using the ideal gas law and normalized to a total pressure of 1 bar. The resulting partial pressures are listed in Table 1. To study the impact of different species on surface chemistry, their partial pressures are varied in a wide range. Ions are not considered in our model as they generally have lower densities compared to the radicals, indicating that they play only a minor role in plasma chemistry of POX of CH<sub>4</sub>.<sup>3</sup> Moreover, thermodynamic data for adsorption of ions from the gas phase is not readily available. However, in practice, ions can also adsorb and react on the surface. For example, O<sub>2</sub> can be transformed into  $O_2^-$  by electron attachment in plasma. Following adsorption,  $O_2^{-*}$  can react with  $H_2O^*$  to form OOH\* and OH<sup>-\*</sup>.<sup>64</sup> While this reaction is thus not considered

Table 1. Partial Pressures Implemented in the Model for the Base Case, i.e.,  $CH_4/O_2$  (70/30) Inlet Gas Mixture<sup>b</sup>

reactants	partial pressure (bar)	radicals	partial pressure (bar)
O <sub>2</sub>	0.3	С	$1.54 \times 10^{-11}$
CH <sub>4</sub>	0.7	CH	$1.02 \times 10^{-13}$
stable intermediates	partial pressure (bar)	CH <sub>2</sub>	$2.32 \times 10^{-11}$
СО	$6.91 \times 10^{-7}$	CH <sub>3</sub>	$3.17 \times 10^{-11}$
CH <sub>3</sub> OH	$2.25 \times 10^{-7}$	0	$2.09 \times 10^{-7}$
$H_2$	$3.25 \times 10^{-6}$	Н	$2.72 \times 10^{-10}$
CH <sub>3</sub> CH <sub>3</sub>	$2.34 \times 10^{-7}$	OH	$8.96 \times 10^{-9}$
$CH_2CH_2$	$5.07 \times 10^{-7}$	OOH	$2.62 \times 10^{-6}$
СНСН	$7.90 \times 10^{-9}$	СНО	$4.62 \times 10^{-13}$
$H_2O$	$1.30 \times 10^{-6}$	CH <sub>3</sub> OO	$3.25 \times 10^{-6}$
CO <sub>2</sub>	$5.85 \times 10^{-7}$	CH <sub>3</sub> O	$9.17 \times 10^{-8}$
CH <sub>2</sub> O	$1.98 \times 10^{-6}$		
HCOOH <sup>a</sup>	$1.98 \times 10^{-6}$		

<sup>*a*</sup>This partial pressure was set equal to that of  $CH_2O$ , as HCOOH was not included by De Bie et al. <sup>*b*</sup>Based on species densities from De Bie et al.<sup>37</sup>

in our model, we do account for the formation of OOH\* through adsorption from the plasma.

We study the effect of the plasma species listed in Table 1, in the absence of any vibrationally excited species, to examine both effects separately. Furthermore, we find that if both effects are included in the model, the impact of vibrational excitation on the product TOFs is negligible. This is illustrated in Figure S5 of the SI. This indicates that for plasma catalysis with DBD plasmas, the surface chemistry is mainly governed by plasma radicals. Similar conclusions were drawn by Engelmann et al.<sup>45</sup> for plasma-catalytic nonoxidative coupling of CH<sub>4</sub>.

3.3.1. Most Important Reaction Pathways in the Presence of Plasma Species. Figure 4 illustrates the most important steady-state reaction pathways on the Pt(111) surface exposed to a  $CH_4/O_2$  (70/30) plasma, i.e., including plasma-generated radicals and intermediates. The most important surface reactions, in terms of reaction rate, are adsorption of O radicals and subsequent associative desorption of the surfacebound O\* to form  $O_2$ . Approximately 96.7% of O\* is formed via adsorption of O radicals from the plasma and 85.6% of O\* desorbs as  $O_2$  into the gas phase, while the rest is used in oxidation processes on the surface.

The main carbon pathway starts from adsorption and subsequent dissociation of CHCH to CH\*. The latter preferentially (74.2%) undergoes oxidation to CHO\*, which in turn binds with O\* to form HCOO\*. Most of the HCOO\* (92.4%) undergoes hydrogen abstraction by  $O^*$  to form  $CO_2^*$ and OH\*, while 6.8% is hydrogenated to HCOOH. About 50.6% of the surface-bound OH\* is formed from a reaction between HCOO\* and O\*, while the remaining 49.4% is adsorbed from the plasma. Most of the OH\* (80.0%) forms  $H_2O^*$  and  $O^*$  via a disproportionation reaction, while 19.1% reacts with CH\* to form H<sub>2</sub>O\* and C\*. H<sub>2</sub>O\* desorbs from the surface as a product. Surface-bound C\* can either be oxidized to CO\* (65.5%), can undergo hydrogenation to again form CH\* (19.3%), can react with  $CO_2^*$  to form two CO\* molecules (11.6%), or can bind to OH\* to form COH\* (3.6%). The latter decomposes into CO\* and H\*, forming about 9.2% of the surface-bound H\*, although most H\* (82.7%) is formed by direct adsorption from the plasma. H\* is mainly consumed in the hydrogenation of C\* (49.8%) or the



**Figure 4.** Most important reaction pathways at steady state for POX of  $CH_4$  on the Pt(111) surface exposed to a  $CH_4/O_2$  (70/30) DBD plasma at 500 K and 1 bar. The values of the reaction rates in (s<sup>-1</sup>) are displayed next to the arrows. The arrow thickness indicates the relative importance of that reaction within each separate scheme. A dotted arrow indicates that the species is used as a second reactant in another reaction.

formation of HCOOH (49.7%). As discussed above, various routes lead to the formation of CO\*. Most of the CO\* (80.9%) desorbs from the surface as a product, while a smaller amount is oxidized to  $CO_2^*$  (19.1%). Thus, our results show that any CO\* that reacts further is not hydrogenated to oxygenates but instead further oxidized to CO<sub>2</sub>. The formation of oxygenates therefore occurs via another route than that of CO. While our results show that some CO<sub>2</sub> is formed via oxidation of CO\*, we do not find this to be the main pathway for  $CO_2$  formation. Instead, we find that  $CO_2$  is mainly formed from HCOO\* in a separate pathway. Interestingly, DRIFTS results by Stere et al.<sup>36</sup> indicate that in the plasma-catalytic oxidation of CH<sub>4</sub> on a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, CO<sub>2</sub> formation also occurs via HCOO\*. As Pt and Pd are part of the same group in the periodic table, similarities in their surface chemistry can indeed be expected.

Note that  $H_2O$  is formed as a major product. This might be troublesome, as the presence of  $H_2O$  vapor in a DBD plasma can alter the discharge behavior, resulting in more, but less intense, microdischarges.<sup>65</sup>  $H_2O$  addition can also cause destablization of the discharge, and plasma chemistry calculations revealed a decrease of approximately 40% in the maximum electron density upon increasing the water content from 0 to 8% in the DBD plasma.<sup>66</sup> Additionally, a higher  $H_2O$ concentration results in a loss of electron energy due to  $H_2O$ rotational and vibrational excitation, as discussed in the literature for  $He/H_2O$  and  $Ar/H_2O$  plasmas.<sup>65,67</sup> The presence of  $H_2O$  in plasma also causes quenching of the vibrational levels of  $CO_2$ , which results in less  $CO_2$  dissociation.<sup>68</sup> This might lead to a higher net production of  $CO_2$ . Moreover, the presence of  $H_2O$  might also result in additional  $CO_2$  formation in the plasma through the water—gas shift.<sup>69</sup> This is in line with plasma chemical kinetics simulations and experiments, which revealed that  $H_2O$  addition to a  $CO_2$  DBD plasma causes a decrease in  $CO_2$  conversion, and the detailed chemical kinetics scheme explaining this behavior is presented in ref 66. Furthermore, this paper also explained the underlying chemistry why oxygenates formation was prohibited in this case. Therefore, it can be beneficial to remove  $H_2O$  from the gas phase through condensation by cooling the reactor wall. In addition, this also removes condensable oxygenates from the gas phase and limits their further oxidation.<sup>69,70</sup>

Figure 4b represents the main reaction pathways for the formation of CH<sub>3</sub>OH and CH<sub>2</sub>O. As in the thermal case (see Figure 1), CH<sub>3</sub>O\* is a key species in the formation of both CH<sub>3</sub>OH and CH<sub>2</sub>O. Yet, in the thermal case, the formation of this species occurs on the catalyst surface, via O\* addition to CH<sub>3</sub>\*, while Pt strongly favors CH<sub>3</sub>\* dehydrogenation instead. In the plasma case, on the other hand, CH<sub>3</sub>O is formed in the plasma and subsequently adsorbs on the catalyst surface. As illustrated in Figure 4b for the plasma case, CH<sub>3</sub>O\* is either directly adsorbed from the gas phase (97.0%) or formed from adsorption of CH<sub>3</sub>OO radicals and subsequent cleavage of the O–O bond (3.0%). The formed CH<sub>3</sub>O\* preferentially undergoes dehydrogenation to CH<sub>2</sub>O (>99.9%), while only a minor fraction is hydrogenated to form CH<sub>3</sub>OH (0.007%).

In the presence of radicals, the reaction rates have generally increased compared to the thermal case. The TOFs of CO and



**Figure 5.** Influence of the O partial pressure on TOFs (left) and surface coverages (right). Dotted lines in the left graph indicate consumption, whereas full lines indicate production. The simulations were performed for a surface temperature of 500 K and a total pressure of 1 bar. The species partial pressures used for these simulations are shown in Table 1, but the partial pressure of O is varied by the indicated scaling factor.

 $CO_2$  have increased by about 3 and 5 orders in magnitude, respectively, compared to the thermal case. We find that  $CO_x$ species are still the main products for the plasma case, with selectivities of 20.5 and 74.4% for CO and CO2, respectively. However, the selectivities and TOFs of the oxygenates have strongly improved compared to the thermal case. The calculated selectivities of CH3OH, CH2O, and HCOOH now reach  $5.9 \times 10^{-8}$ , 0.084%, and 5.3%, respectively, which corresponds to increases by about 10, 4, and 5 orders of magnitude, respectively. Although CH<sub>3</sub>OH formation still does not seem to be feasible on Pt under these conditions, a reasonable amount of HCOOH is now formed on the surface. The combination of a catalyst with plasma radicals thus shows potential for enhanced oxygenate selectivities. Additionally, tuning the partial pressures of the radicals in the plasma might further improve the formation of oxygenates. In the next section, we therefore show how different radicals affect the surface chemistry, fractional coverages, and product TOFs.

3.3.2. Role of Plasma Species in the Surface Chemistry. As mentioned before, the reaction pathways discussed in the previous section are based on species densities calculated by De Bie et al.<sup>37</sup> (see Table 1), which are specific for the selected reaction conditions. In this section, we aim to gain an additional understanding of how variations in the plasma composition might alter the surface chemistry by examining the influence of various plasma species on the product TOFs and surface coverages. For this purpose, we vary the partial pressures of either individual species or groups of species by a scaling factor while keeping the partial pressures of the other species constant on the values reported in Table 1. The species HCOO and COOH are not included in the model by De Bie et al.<sup>37</sup> and are therefore not included in the simulations discussed below. However, a discussion of the effect of these species is included in the SI (see further).

3.3.2.1. Oxidizing Species. Figure 5 illustrates how the TOFs of  $CO_{xy}$  oxygenates, and  $CH_3CH_3$  are affected by a variation of the O partial pressure over 6 orders of magnitude. Next to the TOFs, the surface coverages of the most abundant surface species are also displayed. A decrease in the partial pressure of O radicals results in a sudden decline of the product TOFs, combined with a strong increase in the surface C\* coverage. Although our model does not contain a

mechanism for coke formation, i.e., clustering of carbonaceous species, e.g., C\*, CH\*, CHCH\*, the high surface coverage of these species indicates that coking is likely to occur. Coking reduces the number of available catalytic sites on the surface and thus lowers the product TOFs. Most of the TOFs in Figure 5 eventually stabilize upon further lowering of the O partial pressure, as OH\* becomes the main oxidizing species on the surface. On the other hand, the high partial pressure of O is also disadvantageous, as O\* competes with other species for free sites. If the O partial pressure is too high, O\* will poison the surface, causing the TOFs to decline as well.

As can be seen in Figure 5, the O partial pressure can be used to tune the product selectivity between CO and CO<sub>2</sub>. Low partial pressures of O radicals, which can be expected for plasmas with a high  $CH_4/O_2$  ratio, favor the formation of CO. On the other hand, high O partial pressures, associated with low  $CH_4/O_2$  ratios, give  $CO_2$  as the main product. If the partial pressure of O is increased by about a factor 10, the faster oxidation of CO\* results in net CO consumption, as plasmaproduced CO adsorbs onto the surface and is oxidized to CO<sub>2</sub>. Indeed, various experimental studies on plasma-catalytic POX of CH<sub>4</sub> report that transition metals (Ni,<sup>22,31</sup> Fe,<sup>32</sup> Pd,<sup>32</sup> and Pt<sup>30</sup>) can catalyze the oxidation of CO to CO<sub>2</sub>. Additionally, DRIFTS and Fourier transform infrared (FTIR) results by Zhang et al.<sup>34</sup> for plasma-catalytic CH<sub>4</sub> oxidation on Ni indicate that the selectivity of CO vs CO<sub>2</sub> can be tailored by adjusting the introduction of  $O_2$  to a plasma.

Next to O, we also examine the influence of the OH and OOH radicals as oxidizing species (see Section 9 and Figure S6 in the SI). Increasing the partial pressures of these species enhances the formation of OH\* on the surface. The formed OH\* promotes dehydrogenation of  $CH_x$ , which leads to more C\* and thus favors CO formation. However, a further increase in the OH and OOH partial pressures results in a higher O\* coverage due to hydrogen abstraction from OH\* by another OH\*. This causes a drop in the surface coverage of most of the other surface species, which results in a decline of the product TOFs. Likewise, we present the effect of the HCOO and COOH radicals on the product TOFs and surface coverages in Section 10 of the SI (Figures S7 and S8). We conclude that HCOO and COOH mainly result in additional formation of

Article



Figure 6. Influence of the C, CH, and CHCH partial pressures on TOFs (left) and surface coverages (right). Dotted lines in the left graph indicate consumption, whereas full lines indicate production. The simulations were performed for a surface temperature of 500 K and a total pressure of 1 bar. The species partial pressures used for these simulations are shown in Table 1, but the partial pressures of C, CH, and CHCH are simultaneously varied by the indicated scaling factor.



Figure 7. Influence of the  $CH_3$  and  $CH_2$  partial pressures on TOFs (left) and surface coverages (right). The simulations were performed for a surface temperature of 500 K and a total pressure of 1 bar. The species partial pressures used in the simulations are shown in Table 1, but the partial pressures of  $CH_3$  and  $CH_2$  are simultaneously varied by the indicated scaling factor.

unwanted  $CO_2$  and CO, and their formation in the plasma should therefore be limited.

In summary, oxidative species can reduce the coverage of carbonaceous species that could cause catalyst deactivation by coking. Yet, if the partial pressures of oxidative species are too high, the surface is poisoned with O\* species instead. However, due to their reactive nature, plasma radicals might be able to react with surface-bound species, such as O\*, via Eley-Rideal reactions with low to zero enthalpy barriers. In such a case, high TOFs might be achieved even at high O\* coverages. While our model does contain Eley-Rideal reactions, namely,  $CH_4(g) + OH^* \rightarrow CH_3^* + H_2O^*$  and  $CH_4(g) + O^* \rightarrow CH_3^* + OH^*$ , these reactions have higher enthalpy barriers (0.50 eV<sup>71</sup> and 1.28 eV<sup>71</sup>, respectively) than what can be expected for similar reactions involving highly reactive radicals, rather than stable CH<sub>4</sub>. In Section 3.3.3, we therefore briefly illustrate the potential impact of Eley-Rideal reactions with plasma radicals for a range of enthalpy barriers. Further, our results show that tuning the amount of O radicals against the amount of C-containing species can be used to favor the production of CO over that of  $CO_2$ .

3.3.2.2. Carbonaceous Species. The influence of the strongly dehydrogenated carbonaceous species (C, CH, and CHCH) on the TOFs and surface coverages is shown in Figure 6. We include CHCH as well, as this is the most important species at the surface and the main source of surface carbon under the base conditions. As is shown in Figure 6, high partial pressures of these species lead to strong surface poisoning by CHCH\* and thus a drop in the product TOFs. As mentioned before, these species can act as precursors for coking of the catalyst surface. We find that limiting the partial pressures of these carbonaceous species in the plasma has a beneficial effect on the TOFs of most products. However, low partial pressures of these species lead to adsorption and oxidation of plasmaproduced CO to CO<sub>2</sub>, as can be seen in Figure 6. Because fewer carbonaceous species are available for reaction with O\*, more O\* reacts with surface-bound CO\*. Simultaneously, less CO\* can be formed through the pathways in Figure 4, as these pathways go via C\*, leading to net adsorption of plasmaproduced CO. Furthermore, the simultaneous decrease in the C, CH, and CHCH partial pressures initially shows a beneficial effect on HCOOH formation, but scaling the partial pressures



**Figure 8.** Influence of the H partial pressure on TOFs (left) and surface coverages (right). Dotted lines in the left graph indicate consumption, whereas full lines indicate production. The simulations were performed for a surface temperature of 500 K and a total pressure of 1 bar. The partial pressures of species used in the simulations are shown in Table 1, but the partial pressure of H is varied by the indicated scaling factor.

with a factor below  $10^{-1}$  causes the TOF of HCOOH to decline. This results from the lower availability of CH\* on the catalyst surface, as this species is required for HCOOH formation, according to the reaction pathways shown in Figure 4. At low partial pressures of the strongly dehydrogenated carbonaceous species, the HCOOH TOF in Figure 6 eventually stabilizes, as CH<sub>3</sub> and CH<sub>2</sub> radicals become the main precursor species for the formation of CH\* and HCOOH. In this regime, CH<sub>2</sub>O becomes the most important oxygenate as its formation does not occur via CH\* but through CH<sub>3</sub>O\* and CH<sub>3</sub>OO\* instead.

Figure 7 displays the change in TOFs and fractional surface coverages when increasing the partial pressures of CH<sub>3</sub> and  $CH_2$  up to a factor  $10^4$ . Higher partial pressure of these more hydrogenated carbonaceous species positively affects the TOFs, especially those of CH<sub>3</sub>CH<sub>3</sub>, HCOOH, and CH<sub>3</sub>OH. The effect on the TOF of CH3CH3 is straightforward, as higher partial pressure of CH<sub>3</sub> improves the CH<sub>3</sub>\* coverages and its coupling toward CH<sub>3</sub>CH<sub>3</sub>. CH<sub>3</sub>OH and HCOOH, on the other hand, benefit from the improved hydrogenation of CH<sub>3</sub>O\* and HCOO\*, respectively, because CH<sub>3</sub> and CH<sub>2</sub> provide the surface with more H\* (due to catalytic dehydrogenation). Moreover, the formation of H\* through dehydrogenation of CH2\* also forms CH\*, which is an intermediate in the formation of HCOOH (see Figure 4). As can be seen in Figure 7, this results in HCOOH becoming the main carbon product (even slightly above CO<sub>2</sub>) at around a scaling factor of  $10^3$ . This shows that Pt is potentially a good catalyst for the plasma-catalytic HCOOH synthesis under plasma conditions with abundant CH<sub>3</sub> and CH<sub>2</sub> radicals (hence high  $CH_4/O_2$  ratios), as it can readily dehydrogenate adsorbed CH<sub>x</sub>\* radicals to form CH\*, while simultaneously forming the H\* required in the hydrogenation of HCOO\*, later on in the reaction path. However, as can be seen in Figure 7, enhancing the partial pressures of CH<sub>3</sub> and CH<sub>2</sub> by more than a factor of  $10^3$  is no longer beneficial. The surface coverages indicate strong cokes formation past this point, resulting in a decline of most of the TOFs. Note that CH<sub>3</sub> and CH<sub>2</sub> themselves bind less strongly to the surface compared to CH and  $C^{71}$  and are less likely to act as coking precursors.

In summary, strongly dehydrogenated carbonaceous species are mainly precursors for coke formation, and their partial pressures in the gas phase should ideally be kept low. These species also show some beneficial effects on HCOOH and CO formation at lower partial pressures. The more hydrogenated CH<sub>2</sub> and CH<sub>3</sub> generally show a more beneficial effect, enhancing the TOFs of CH<sub>3</sub>CH<sub>3</sub>, HCOOH, and CH<sub>3</sub>OH at higher partial pressures, but also cause coking at very high partial pressures. The partial pressures of carbonaceous species can be expected to be higher for gas mixtures with high CH<sub>4</sub> contents, but the ratio of less vs more hydrogenated CH<sub>x</sub> species might be influenced by the CH<sub>4</sub> fragmentation pattern through electron impact dissociation in the plasma. Nozaki et al.<sup>19</sup> simulated streamer formation in CH<sub>4</sub> without a catalyst and showed that the fragmentation pattern depends on the reduced electric field, with stronger reduced electric fields resulting in a larger fraction of more dehydrogenated CH<sub>r</sub> species. Therefore, plasma characterized by weaker reduced electric fields can be expected to give less coke formation. As discussed in the previous section, coking can also be counteracted by high partial pressures of oxidizing radicals, e.g., O, OH, and OOH, and by tuning the partial pressures of oxidizing species against those of carbonaceous species, the formation of either CO or CO<sub>2</sub> can be favored. Moreover, the choice of the catalyst material can also be expected to play an important role in mitigating both coking and excessive oxidation, as different transition metals have different binding strengths for O and C. It is therefore essential in plasma catalysis to carefully tune the  $CH_4/O_2$  ratio as a function of the plasma conditions and the catalyst material.

3.3.2.3. Hydrogen radicals. Figure 8 illustrates the influence of the H radical partial pressure on the TOFs of  $CO_{xr}$ , the oxygenates, and  $CH_3CH_3$ , as well as the surface coverages of the most abundant surface species. Higher partial pressure of H strongly enhances HCOOH and  $CH_3OH$  formation. This is caused by the higher availability of H\* on the catalyst surface, which improves the hydrogenation of  $CH_3O^*$  and HCOO\* to  $CH_3OH$  and HCOOH, respectively. Upon increasing the H partial pressure by about a factor 400, a strong increase in the TOFs of  $CH_3OH$ ,  $CH_2O$ , and  $CO_2$  is observed. This is attributed to the improved hydrogenation of  $O^*$  to  $H_2O^*$ , which readily desorbs to make more free sites available. The fraction of free sites on the surface increases from about  $10^{-10}$ to  $10^{-6}$  in this region. This improves the adsorption of  $CH_3O$ ,

Article



Figure 9. Influence of the  $CH_3O$  and  $CH_3OO$  partial pressures on TOFs (left) and surface coverages (right). Dotted lines in the left graph indicate consumption, whereas full lines indicate production. The simulations were performed for a surface temperature of 500 K and a total pressure of 1 bar. The partial pressures of species used in the simulations are shown in Table 1, but the partial pressures of  $CH_3O$  and  $CH_3OO$  are simultaneously varied by the indicated scaling factor.



Figure 10. Influence of the partial pressures of all plasma-produced radicals and stable intermediates on TOFs (left) and surface coverages (right). Dotted lines in the left graph indicate consumption, whereas full lines indicate production. The simulations were performed for a surface temperature of 500 K and a total pressure of 1 bar. The default values of the species partial pressures used in the simulations are shown in Table 1, but the partial pressures of all species, except for  $CH_4$  and  $O_2$ , are simultaneously varied.

which can form both  $CH_3OH$  and  $CH_2O$  (see Figure 4b), and the adsorption of CO, which is oxidized to  $CO_2$ . At low H partial pressures, the TOFs in Figure 8 stabilize, as  $OH^*$  now becomes the main source of H<sup>\*</sup>. This results from coupling between  $OH^*$  and  $C^*$  followed by decomposition of the formed COH<sup>\*</sup> to CO<sup>\*</sup> and H<sup>\*</sup>.

Given the favorable effect of the H radical on the formation of oxygenates, and especially  $CH_3OH$ , it is of interest to find a way to increase the partial pressure of H in the plasma. For its POX,  $CH_4$  serves as the source of H in the plasma and increasing the  $CH_4$  fraction in the feed gas might thus increase the partial pressure of H radicals. As discussed above, however, high  $CH_4/O_2$  ratios might induce coking due to the limited availability of oxidizing species. Adding a H-containing coreactant, such as  $H_2$  or  $H_2O$ , might allow for more flexibility in maximizing the TOF of oxygenates, and especially  $CH_3OH$ .

3.3.2.4.  $CH_3O$  and  $CH_3OO$  Radicals. Modeling results by De Bie et al.<sup>37</sup> for plasma-only POX of  $CH_4$  indicate that the  $CH_3O$  and  $CH_3OO$  radicals are important intermediates in the pathways leading to  $CH_3OH$  production in plasma. Our results

show that for plasma catalysis these species also play an important role in the formation of  $CH_3OH$  and  $CH_2O$  on the catalyst surface, as indicated by the pathways in Figure 4b. We are therefore interested in the influence of these species on the catalyst surface chemistry and thus examine how a variation in their partial pressures affects the TOFs and fractional coverages on the catalyst surface. The results are shown in Figure 9.

As CH<sub>3</sub>O and CH<sub>3</sub>OO are precursors to both CH<sub>3</sub>OH and CH<sub>2</sub>O, the TOFs of these products strongly depend on the partial pressures of CH<sub>3</sub>O and CH<sub>3</sub>OO, while the TOFs of the other products are largely unaltered. Only at high partial pressures, where the adsorption and subsequent decomposition of CH<sub>3</sub>O become important, the TOFs of the other products are also influenced, as can be seen in Figure 9. The decomposition of CH<sub>3</sub>O\* not only leads to the formation of CH<sub>2</sub>O\* but also provides H\*. The higher availability of H\* improves HCOO\* hydrogenation so that CH<sub>2</sub>O and HCOOH eventually become the main products (even above CO and CO<sub>2</sub>). Moreover, the increase of the TOF of CH<sub>3</sub>OH also



Figure 11. Overview of the influence of various plasma species on the formation of oxygenates and  $CO_x$  in the plasma-catalytic POX of  $CH_4$  on Pt(111).

becomes much steeper in this region, illustrating the strong beneficial effect of both  $CH_3O^*$  and  $H^*$  on the  $CH_3OH$ formation. We also observe a shift in the surface coverages in Figure 9, as more C\* is converted to CH\*. The lower surface coverage of C\* and preferred conversion of HCOO\* to HCOOH at high CH<sub>3</sub>O and CH<sub>3</sub>OO partial pressures limit the formation of undesired CO and CO<sub>2</sub>. We therefore find that CH<sub>3</sub>O and CH<sub>3</sub>OO can play an important role in enhancing the formation of oxygenates. Additionally, our results show that Pt is potentially a good catalyst for CH<sub>2</sub>O synthesis, as CH<sub>3</sub>O selectively decomposes to CH<sub>2</sub>O on this catalyst. Moreover, it might be possible to vary the selectivity between CH<sub>3</sub>OH or CH<sub>2</sub>O by changing the catalyst material, as more noble transition metals have lower barriers for CH<sub>3</sub>O hydrogenation and higher barriers for its dehydrogenation.<sup>39</sup>

3.3.2.5. Plasma-Generated Radicals and Stable Intermediates in General. In Figure 10, we illustrate how the TOFs and fractional coverages are affected by simultaneously lowering the partial pressures of all plasma-produced radicals and stable intermediates by a factor of  $10^{-6}$ . The product TOFs, especially those of CH<sub>2</sub>O and CH<sub>3</sub>OH, initially increase upon lowering the partial pressures of these plasma species, and CH<sub>2</sub>O becomes the main product (clearly above CO and  $CO_2$ ) below a scaling factor of  $10^{-2}$ . Its TOF keeps rising upon lowering the partial pressures by a factor of  $10^{-3}-10^{-4}$ , after which all TOFs decline. The initial rise in the TOFs of CH<sub>2</sub>O and CH<sub>3</sub>OH results from improved adsorption of CH<sub>3</sub>O and CH<sub>3</sub>OO. Indeed, at high partial pressures of plasma species, the adsorption of CH<sub>3</sub>O and CH<sub>3</sub>OO is hindered by surface poisoning by stronger binding species, such as O\* and coking species. By lowering the partial pressures of all plasma species, more free sites become available, i.e., the fraction of free surface sites increases from  $10^{-10}$  to  $10^{-5}$  when lowering the partial pressures by a factor of  $10^{-6}$ . Moreover, the right panel of Figure 10 illustrates that the fractional coverages of coking precursors strongly decline as the partial pressures are lowered. The enhanced availability of free sites initially improves the adsorption of CH<sub>3</sub>O and CH<sub>3</sub>OO, even though their partial pressures are lower. As these species are precursors to CH<sub>2</sub>O and CH<sub>3</sub>OH, the TOFs of these products are higher. Upon further lowering the partial pressures of the plasma species, the TOFs eventually decrease due to the lower availability of reactive plasma species in the gas phase.

Our results thus show that lowering the radical densities in the plasma, up to a certain limit, is beneficial for oxygenate production, as this limits surface poisoning by strongly binding plasma species. This might be achieved using a lower plasma power or placing a catalyst in the afterglow of the plasma. However, this might also change the radical distribution (in the plasma or afterglow). On the other hand, modeling of POX of CH<sub>4</sub> in a DBD shows that the densities of CH<sub>3</sub>O and CH<sub>3</sub>OO vary little between the pulses.<sup>37</sup> Therefore, these species are expected to remain among the most important radicals even in the afterglow.

Figure 11 summarizes how the different plasma species discussed in this section affect the formation of CO<sub>x</sub> and oxygenates. Strongly dehydrogenated carbonaceous species, e.g., CHCH, CH, and C, cause coke formation on the catalyst surface and favor the production of CO over that of CO<sub>2</sub>. O radicals, on the other hand, reduce coking but result in overoxidation to CO2. The less strongly dehydrogenated carbonaceous species, i.e., CH<sub>3</sub> and CH<sub>2</sub>, mainly favor HCOOH but also to a lesser extent coke formation. H enhances the formation of HCOOH and CH<sub>3</sub>OH by improving the hydrogenation of their respective precursor species, HCOO\* and CH<sub>3</sub>O\*, and it also enhances the formation of CH<sub>2</sub>O, by the higher adsorption of CH<sub>3</sub>O, which can form both CH<sub>3</sub>OH and CH<sub>2</sub>O. The CH<sub>3</sub>O and CH<sub>3</sub>OO radicals are the precursors to both CH<sub>3</sub>OH and CH<sub>2</sub>O and thus also favor the formation of these products.

It should be noted that the present model focuses on the surface reactions, and plasma chemistry is only taken as input. In the future work, we plan to combine both the plasma chemistry and catalyst surface chemistry into one model, so that the effect of the surface reactions on the gas-phase composition is self-consistently accounted for.

3.3.3. Eley-Rideal Reactions Involving Radicals. Due to their highly reactive nature, radicals generally form strong bonds when adsorbing onto a catalyst surface. Together with the abundance of radicals in the plasma, this can induce strong poisoning of the catalyst surface, as illustrated above. However, the high reactivity of plasma-generated radicals might also enable them to react with the surface species via Eley-Rideal (ER) reactions with low to zero enthalpy barriers. Therefore, we briefly illustrate the potential effect of these ER reactions by including the following three reactions in the chemistry set:  $CH_3(g) + O^* \rightarrow CH_3O^*$ ,  $H(g) + O^* \rightarrow OH^*$ , and  $O(g) + C^*$ 



**Figure 12.** Influence of the enthalpy barriers of Eley–Rideal reactions involving radicals on the TOFs (left) and surface coverages (right). The following Eley–Rideal reactions are included:  $CH_3(g) + O^* \rightarrow CH_3O^*$ ,  $H(g) + O^* \rightarrow OH^*$ , and  $O(g) + C^* \rightarrow CO^*$ , and their enthalpy barriers are simultaneously varied in the simulation. The simulations were performed for a surface temperature of 500 K and a total pressure of 1 bar. The values of the species partial pressures used in the simulations are shown in Table 1.

→ CO\*. We choose these reactions as CH<sub>3</sub>, H, and O are the main products of electron impact dissociation of CH<sub>4</sub> and O<sub>2</sub>, respectively, and because O\* and C\* are abundant and simple surface species. To the best of our knowledge, no activation barriers have been reported for these ER reactions. We therefore simultaneously vary the enthalpy barriers of these reactions between 0.0 and 0.75 eV. Higher enthalpy barriers show no further effect on the TOFs. For comparison, the ER reactions that involve CH<sub>4</sub> (CH<sub>4</sub>(g) + OH\* → CH<sub>3</sub>\* + H<sub>2</sub>O\* and CH<sub>4</sub>(g) + O\* → CH<sub>3</sub>\* + OH\*) have enthalpy barriers of 0.50 eV<sup>71</sup> and 1.28 eV<sup>71</sup>, respectively. We would also like to emphasize that all ER reactions, including those with radicals, have an entropy barrier that corresponding radical or gas molecule, as explained in the model description.

In Figure 12, we illustrate the influence of these ER reactions on the TOFs and surface coverages for the indicated range of enthalpy barriers. All of the TOFs in Figure 12 increase upon lowering the enthalpy barriers and thus enhancing the importance of the ER reactions. For low barriers, CO becomes the main product due to the reactions of O radicals with surface C\*. The TOFs of CH<sub>2</sub>O and CH<sub>3</sub>OH also increase strongly upon lowering the barriers, as a result of the enhanced formation of their precursor species, CH<sub>3</sub>O\*, through a reaction between  $CH_3(g)$  and O\*. Note that the net rate of CH<sub>3</sub>O and CH<sub>3</sub>OO adsorption/desorption is set to zero if desorption of these species occurs, thus assuming that an equilibrium is reached due to accumulation of these radicals near the surface. For the lower barriers (<0.09 eV), CH<sub>2</sub>O becomes the second most important product, after CO. The decomposition of CH<sub>3</sub>O\* to CH<sub>2</sub>O\* also forms H\*, which enhances the formation of HCOOH and CH<sub>3</sub>OH. Additionally, a decrease in  $C^\ast$  coverage and an increase in  $CH^\ast$ coverage can be observed as a result of improved H\* formation.

In summary, our results show that ER reactions involving radicals have a potentially strong contribution to the TOFs in plasma catalysis. Additionally, these ER reactions might be responsible for a significant part of the oxygenate formation in plasma-catalytic POX of  $CH_4$ . We note that other ER reactions might also be important; however, the lack of reported activation energies currently limits the construction of extended chemistry set with these reactions. The three ER

reactions that we considered are aimed at illustrating the potential impact of these reactions.

3.4. Additional Remarks and Suggestions. 3.4.1. Possible Effect of C-C Coupling Reactions. As shown in Figures 5-7, carbon-containing radicals can be present on the surface in high coverages. While high coverages of carbonaceous species like C\*, CH\*, and CHCH\* indicate that coking is likely to occur, our model does not explicitly capture the mechanism for coking. Additionally, C-C coupling to higher hydrocarbons might also become important under these conditions. While our model does contain some C-C coupling reactions to form C2 hydrocarbons, C-C coupling to higher hydrocarbons is not included, mainly due to the lack of availability of the required thermodynamic input data in the literature. Therefore, we should remain careful with the interpretation of our results under conditions where carbonaceous species appear to poison the surface. If C-C coupling to higher hydrocarbons would be favored over coke formation, then formation and desorption of these higher hydrocarbons might result in improved availability of free sites and higher TOFs. However, this also depends on the barrier for desorption of the formed product. Nevertheless, we would like to emphasize that the main focus of this study is on the formation of oxygenates under partial oxidation conditions, where oxidation reactions are the dominant mechanism.

3.4.2. Other Catalyst Materials. Our model is applied to Pt(111), but we provide here some information on how (or whether) our results might be translated to other catalyst materials based on insights obtained from our work and the literature. Microkinetic modeling of the thermal-catalytic POX of  $CH_4$  by Yoo et al.<sup>40</sup> shows that for Pt-group metals the selectivity of CH<sub>2</sub>O increases when going toward metals that bind O\* more strongly. This was attributed to the higher O\* coverages, which promote the coupling between CH<sub>3</sub>\* and O\* to form CH<sub>3</sub>O\* and the subsequent O\*-assisted dehydrogenation of CH<sub>2</sub>O\* to CH<sub>2</sub>O\*.<sup>40</sup> While for plasma conditions where CH<sub>3</sub>O\* can be formed in the plasma itself, we can expect that metals with a higher O\*-binding strength, such as Pd and Rh, improve the adsorption of CH<sub>3</sub>O\* and CH<sub>3</sub>OO\* onto the surface, thus also enhancing CH2O and possibly CH<sub>3</sub>OH formation. Yoo et al.<sup>40</sup> also found that coinage metals, such as Cu, Ag, and Au, are the most suitable catalysts for CH<sub>2</sub>O and CH<sub>3</sub>OH synthesis. The authors determined that the selectivity of CH<sub>2</sub>O vs CH<sub>3</sub>OH on these catalysts was determined by competition between two reaction paths: CH<sub>3</sub>\* + O\*  $\rightarrow$  CH<sub>3</sub>O\* (following dehydrogenation to CH<sub>2</sub>O\*) and CH<sub>3</sub>\* + OH\*  $\rightarrow$  CH<sub>3</sub>OH\*.<sup>40</sup> For plasma catalysis, we might thus also expect a change in the mechanism of CH<sub>3</sub>OH\* formation, where CH<sub>3</sub> and OH radicals become the main precursors for CH<sub>3</sub>OH on the most noble transition metals. In this case, it might be possible to steer the selectivity of CH<sub>2</sub>O vs CH<sub>3</sub>OH by changing the densities of O vs OH radicals in the plasma.

Using DFT and microkinetic modeling, Studt et al.<sup>72</sup> illustrated the effect of alloying Cu with ZnO on thermalcatalytic hydrogenation of CO and CO<sub>2</sub>. Zn results in stronger O-binding and weaker C-binding. The former enhances CO<sub>2</sub> hydrogenation by stabilizing the O\*-bound intermediates, such as HCOO\*, while the latter results in more difficult adsorption and hydrogenation of CO.<sup>72</sup> Applied to our results, this catalyst might also be beneficial for plasma catalysis because stronger O-binding might result in less desorption and formation of CO<sub>2</sub> and more facile hydrogenation of HCOO\* to HCOOH or other oxygenates and weaker C-binding is expected to result in less adsorption and oxidation of plasmaproduced CO.

Certain metal oxides, such as  $MoO_3$  and  $V_2O_5$ , may also be suitable catalysts for the production of CH<sub>2</sub>O and CH<sub>3</sub>OH by plasma-catalytic POX. CH<sub>3</sub> radicals can react with reducible metal oxides to form methoxide anions  $(CH_3O^-)$  on the surface, as shown by Tong et al.73 (Note the similarities with the Eley-Rideal reaction  $CH_3 + O^* \rightarrow CH_3O^*$ , discussed in Section 3.3.3.) The reactivity of the metal oxide in this reaction depends on its reducibility, with more reducible metal oxides being more reactive. On CeO<sub>2</sub>, the formed CH<sub>3</sub>O<sup>-</sup> anion converts into a formate anion (HCOO<sup>-</sup>), which produces CO and  $CO_2$ .<sup>73</sup> However, on MoO<sub>3</sub> and  $V_2O_5$ , the  $CH_3O^-$  anion can react to produce CH2O or, in case H2O is present, CH<sub>3</sub>OH.<sup>74,75</sup> Additionally, MoO<sub>3</sub> and  $V_2O_5$  are known catalysts for the selective O-insertion into CH<sub>3</sub> in thermalcatalytic POX of CH<sub>4</sub> to CH<sub>2</sub>O and CH<sub>3</sub>OH. In this reaction, NO is typically added as a radical initiator.<sup>76</sup> As high densities of radicals, such as CH<sub>3</sub>, can easily be achieved in plasma, the combination of a MoO<sub>3</sub> or V<sub>2</sub>O<sub>5</sub> catalyst with plasma also seems promising for plasma-catalytic POX of CH<sub>4</sub>.

# 4. CONCLUSIONS

We used microkinetic modeling to investigate the influence of various plasma species on the catalyst surface chemistry for plasma-catalytic POX of  $CH_4$  on the Pt(111) surface. We evaluated the effect of vibrationally excited  $CH_4$  and  $O_2$ , as well as, radicals and stable intermediates, and compared the results to those of thermal catalysis at the same reaction conditions.

Plasma-induced vibrational excitation of CH<sub>4</sub> and O<sub>2</sub> increases the TOF of CH<sub>4</sub> dissociation. Furthermore, it also shows potential for enhancing the selectivities of CH<sub>3</sub>OH, HCOOH, and C<sub>2</sub> hydrocarbons but has little effect on the selectivities of CH<sub>2</sub>O, CO, and CO<sub>2</sub>. Nevertheless, the selectivities of CH<sub>3</sub>OH, CH<sub>2</sub>O, and C<sub>2</sub> hydrocarbons remain too low for their production to be feasible on Pt(111) at conditions when only vibrational excitation is considered as a plasma effect. However, we find that for plasma-catalytic POX of CH<sub>4</sub> the surface chemistry is mainly governed by radicals, rather than vibrationally excited molecules.

The presence of plasma-produced radicals and stable intermediates greatly increases the TOFs of  $CO_x$  and the

oxygenates, compared to thermal catalysis. Interestingly, this also enhances the selectivities of the oxygenates and we find that the production of HCOOH becomes non-negligible. Further, we examine the role of various radicals in the surface processes:

- O radicals counteract coking but also promote deep oxidation to CO<sub>2</sub>, and their partial pressures should be tuned against that of carbonaceous radicals.
- Strongly dehydrogenated carbonaceous species (CHCH, CH, C) are found to strongly induce coking, and their formation should be avoided.
- The more hydrogenated carbonaceous radicals  $(CH_3, CH_2)$  show in general a beneficial effect, as they bind less strongly to the catalyst and lead to H\* formation on the surface, yet also cause coking at high partial pressures.
- H radicals appear beneficial by promoting the hydrogenation of CH<sub>3</sub>O\* and HCOO\* to CH<sub>3</sub>OH and HCOOH, respectively. Moreover, high partial pressures of H radicals can potentially form more free surface sites by removing excess O\* via H<sub>2</sub>O formation.
- CH<sub>3</sub>O and CH<sub>3</sub>OO radicals are important precursors to both CH<sub>3</sub>OH and CH<sub>2</sub>O. Increasing their partial pressures thus also strongly enhances CH<sub>3</sub>OH and CH<sub>2</sub>O formation.
- Lowering the radical partial pressures in general decreases surface poisoning and allows for more facile adsorption of weak-binding radicals (e.g., CH<sub>3</sub>O and CH<sub>3</sub>OO), which is beneficial for oxygenate formation.

Based on the effects of these radicals, we make the following suggestions on which reaction conditions should be used to favor the formation of certain products:

- The formation of undesired CO<sub>2</sub> is favored at low CH<sub>4</sub>/ O<sub>2</sub> ratios, for which high partial pressures of O radicals are expected. While such conditions should generally be avoided to limit deep oxidation, these can also be beneficial to some extent by avoiding coke formation.
- The formation of CO is favored at high  $CH_4/O_2$  ratios and might to some extent also benefit from a higher plasma power, which yields stronger  $CH_4$  dissociation, although caution must be taken to avoid excessive carbon deposition on the surface.
- HCOOH formation benefits from the presence of  $CH_3$ and  $CH_2$  radicals, which are expected to be abundant in plasmas with a high  $CH_4/O_2$  ratio and lower plasma power, avoiding complete  $CH_4$  dissociation. An additional H source, such as  $H_2$ , might also be beneficial by improving HCOO\* hydrogenation.
- The formation of CH<sub>3</sub>OH might also benefit from a lower plasma power, resulting in lower radical densities (especially of strong binding carbonaceous species) and more free sites, which enhances CH<sub>3</sub>O and CH<sub>3</sub>OO adsorption. Additionally, CH<sub>3</sub>O hydrogenation is expected to improve from using H<sub>2</sub> as an additional H source in the plasma or a more noble catalyst.
- The formation of CH<sub>2</sub>O is also expected to benefit from lower plasma power, for the same reason as CH<sub>3</sub>OH. Moreover, an additional H source can also partially enhance CH<sub>2</sub>O formation, as it can help to clear the surface from excessive O\*.

Finally, we briefly illustrate the potential impact of Eley-Rideal reactions that involve radicals. We find that these

reactions allow us to reach high TOFs, even at high surface coverages that are relevant for plasma catalysis. Additionally, these reactions might lead to significant oxygenate production in the plasma-catalytic POX of  $CH_4$  due to reactions such as  $CH_3(g) + O^* \rightarrow CH_3O^*$  that result in more direct routes toward oxygenates.

# ASSOCIATED CONTENT

# **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c09849.

List of reactions included in the model; thermal-catalytic pathway at 1000 K and comparison with the literature; effect of CO concentration on  $CO_2$  selectivity; influence of vibrational excitation on the surface coverages and selectivities of  $CH_2CH_2$  and CHCH; influence of vibrational excitation on TOFs in the presence of radicals; and effect of OH and OOH, COOH, and HCOO radicals on TOFs and coverages (PDF)

# AUTHOR INFORMATION

# **Corresponding Author**

Björn Loenders – Research group PLASMANT, Department of Chemistry, University of Antwerp, B-2610 Antwerp, Belgium; Occid.org/0000-0001-7962-4235; Email: bjorn.loenders@uantwerpen.be

#### Authors

Yannick Engelmann – Research group PLASMANT, Department of Chemistry, University of Antwerp, B-2610 Antwerp, Belgium

Annemie Bogaerts – Research group PLASMANT, Department of Chemistry, University of Antwerp, B-2610 Antwerp, Belgium; orcid.org/0000-0001-9875-6460

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.0c09849

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

We thank Tom Butterworth for the interesting discussions regarding the calculation of the vibrational populations of methane and for taking the time to share his thoughts and experiences on the matter. This research is supported by the FWO-SBO project PLASMACATDesign (grant number S001619N). We also acknowledge financial support from the TOP-BOF project of the University of Antwerp and from the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Program (grant agreement no. 810182—SCOPE ERC Synergy project). The calculations were carried out using the Turing HPC infrastructure at the CalcUA core facility of the Universiteit Antwerpen, a division of the Flemish Supercomputer Center VSC, funded by the Hercules Foundation, the Flemish Government (Department EWI), and the University of Antwerp.

# REFERENCES

(1) Olivos-Suarez, A. I.; Szécsényi, À.; Hensen, E. J. M.; Ruiz-Martinez, J.; Pidko, E. A.; Gascon, J. Strategies for the Direct Catalytic Valorization of Methane Using Heterogeneous Catalysis: Challenges and Opportunities. ACS Catal. 2016, 6, 2965–2981.

(2) Schwach, P.; Pan, X.; Bao, X. Direct Conversion of Methane to Value-Added Chemicals over Heterogeneous Catalysts: Challenges and Prospects. *Chem. Rev.* 2017, *117*, 8497–8520.

(3) Zakaria, Z.; Kamarudin, S. K. Direct Conversion Technologies of Methane to Methanol: An Overview. *Renewable Sustainable Energy Rev.* 2016, 65, 250–261.

(4) Nozaki, T.; Ağıral, A.; Yuzawa, S.; Gardeniers, J. G. E. H.; Okazaki, K. A Single Step Methane Conversion into Synthetic Fuels Using Microplasma Reactor. *Chem. Eng. J.* **2011**, *166*, 288–293.

(5) Ravi, M.; Ranocchiari, M.; van Bokhoven, J. A. The Direct Catalytic Oxidation of Methane to Methanol-A Critical Assessment. Angew. Chem., Int. Ed. 2017, 56, 16464–16483.

(6) Dinh, K. T.; Sullivan, M. M.; Serna, P.; Meyer, R. J.; Dincă, M.; Román-Leshkov, Y. Viewpoint on the Partial Oxidation of Methane to Methanol Using Cu- and Fe-Exchanged Zeolites. *ACS Catal.* **2018**, *8*, 8306–8313.

(7) Karakaya, C.; Kee, R. J. Progress in the Direct Catalytic Conversion of Methane to Fuels and Chemicals. *Prog. Energy Combust. Sci.* 2016, 55, 60–97.

(8) Enger, B. C.; Lødeng, R.; Holmen, A. A Review of Catalytic Partial Oxidation of Methane to Synthesis Gas with Emphasis on Reaction Mechanisms over Transition Metal Catalysts. *Appl. Catal., A* **2008**, *346*, 1–27.

(9) Goujard, V.; Nozaki, T.; Yuzawa, S.; Ağiral, A.; Okazaki, K. Plasma-Assisted Partial Oxidation of Methane at Low Temperatures: Numerical Analysis of Gas-Phase Chemical Mechanism. *J. Phys. D: Appl. Phys.* **2011**, *44*, No. 274011.

(10) Snoeckx, R.; Bogaerts, A. Plasma Technology - a Novel Solution for  $CO_2$  Conversion? *Chem. Soc. Rev.* **2017**, *46*, 5805–5863. (11) Bogaerts, A.; Tu, X.; Whitehead, J. C.; Centi, G.; Lefferts, L.; Craitalla, O., Argalina, Jung, E., Kim, H. H., Murphy, A. P.,

Guaitella, O.; Azzolina-Jury, F.; Kim, H.-H.; Murphy, A. B.; Schneider, W. F.; et al. The 2020 Plasma Catalysis Roadmap. *J. Phys. D: Appl. Phys.* **2020**, *53*, No. 443001.

(12) Neyts, E. C.; Ostrikov, K. K.; Sunkara, M. K.; Bogaerts, A. Plasma Catalysis: Synergistic Effects at the Nanoscale. *Chem. Rev.* **2015**, *115*, 13408–13446.

(13) *Plasma Catalysis*; Tu, X.; Whitehead, J. C.; Nozaki, T., Eds.; Springer International Publishing: Cham, 2019.

(14) Ağıral, A.; Nozaki, T.; Nakase, M.; Yuzawa, S.; Okazaki, K.; Gardeniers, J. G. E. H. Gas-to-Liquids Process Using Multi-Phase Flow, Non-Thermal Plasma Microreactor. *Chem. Eng. J.* 2011, 167, 560–566.

(15) Hoeben, W. F. L. M.; Boekhoven, W.; Beckers, F. J. C. M.; Van Heesch, E. J. M.; Pemen, A. J. M. Partial Oxidation of Methane by Pulsed Corona Discharges. *J. Phys. D: Appl. Phys.* **2014**, 47, No. 355202.

(16) Huang, J.; Badani, M. V.; Suib, S. L.; Harrison, J. B.; Kablauoi, M. Partial Oxidation of Methane to Methanol through Microwave Plasmas. Reactor Design to Control Free-Radical Reactions. *J. Phys. Chem. A* **1994**, *98*, 206–210.

(17) Kalra, C. S.; Gutsol, A. F.; Fridman, A. A. Gliding Arc Discharges as a Source of Intermediate Plasma for Methane Partial Oxidation. *IEEE Trans. Plasma Sci.* **2005**, *33*, 32–41.

(18) Nair, S. A.; Nozaki, T.; Okazaki, K. Methane Oxidative Conversion Pathways in a Dielectric Barrier Discharge Reactor— Investigation of Gas Phase Mechanism. *Chem. Eng. J.* **2007**, *132*, 85– 95.

(19) Nozaki, T.; Hattori, A.; Okazaki, K. Partial Oxidation of Methane Using a Microscale Non-Equilibrium Plasma Reactor. *Catal. Today* **2004**, *98*, 607–616.

(20) Wang, Y.-F.; Tsai, C.-H.; Shih, M.; Hsieh, L.-T.; Chang, W. Direct Conversion of Methane into Methanol and Formaldehyde in an RF Plasma Environment II: Effects of Experimental Parameters. *Aerosol Air Qual. Res.* **2005**, *5*, 211–224.

(21) Kogelschatz, U. Dielectric-Barrier Discharges: Their History, Discharge Physics, and Industrial Applications. *Plasma Chem. Plasma Process.* **2003**, 23, 1–46.

(22) Chawdhury, P.; Ray, D.; Vinodkumar, T.; Subrahmanyam, C. Catalytic DBD Plasma Approach for Methane Partial Oxidation to Methanol under Ambient Conditions. *Catal. Today* **2019**, 337, 117–125.

(23) Chen, L.; Zhang, X.; Huang, L.; Lei, L. Application of In-Plasma Catalysis and Post-Plasma Catalysis for Methane Partial Oxidation to Methanol over a  $Fe_2O_3$ -CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst. J. Nat. Gas Chem. **2010**, 19, 628–637.

(24) Huang, L.; Zhang, X.; Chen, L.; Lei, L. Direct Oxidation of Methane to Methanol Over Cu-Based Catalyst in an AC Dielectric Barrier Discharge. *Plasma Chem. Plasma Process.* **2011**, *31*, 67–77.

(25) Chen, L.; Zhang, X.-W.; Huang, L.; Lei, L.-C. Partial Oxidation of Methane with Air for Methanol Production in a Post-Plasma Catalytic System. *Chem. Eng. Process.* **2009**, *48*, 1333–1340.

(26) Lee, H.; Kim, D. H. Direct Methanol Synthesis from Methane in a Plasma-Catalyst Hybrid System at Low Temperature Using Metal Oxide-Coated Glass Beads. *Sci. Rep.* **2018**, *8*, No. 9956.

(27) Indarto, A. Methanol Synthesis from Methane and Oxygen with [Ga Cr]/Cu–Zn–Al Catalyst in a Dielectric Barrier Discharge. *Ionics* **2014**, *20*, 445–449.

(28) Indarto, A.; Yang, D. R.; Palgunadi, J.; Choi, J.-W.; Lee, H.; Song, H. K. Partial Oxidation of Methane with Cu–Zn–Al Catalyst in a Dielectric Barrier Discharge. *Chem. Eng. Process.* **2008**, *47*, 780–786.

(29) Heintze, M.; Pietruszka, B. Plasma Catalytic Conversion of Methane into Syngas: The Combined Effect of Discharge Activation and Catalysis. *Catal. Today* **2004**, *89*, 21–25.

(30) Indarto, A.; Lee, H.; Choi, J.-W.; Song, H. K. Partial Oxidation of Methane with Yttria-Stabilized Zirconia Catalyst in a Dielectric Barrier Discharge. *Energy Sources, Part A* **2008**, *30*, 1628–1636.

(31) Pietruszka, B.; Anklam, K.; Heintze, M. Plasma-Assisted Partial Oxidation of Methane to Synthesis Gas in a Dielectric Barrier Discharge. *Appl. Catal., A* **2004**, *261*, 19–24.

(32) Jurković, D. L.; Puliyalil, H.; Pohar, A.; Likozar, B. Plasma-Activated Methane Partial Oxidation Reaction to Oxygenate Platform Chemicals over Fe, Mo, Pd and Zeolite Catalysts. *Int. J. Energy Res.* **2019**, *43*, 8085–8099.

(33) Knoll, A. J.; Zhang, S.; Lai, M.; Luan, P.; Oehrlein, G. S. Infrared Studies of Gas Phase and Surface Processes of the Enhancement of Catalytic Methane Decomposition by Low Temperature Plasma. J. Phys. D: Appl. Phys. **2019**, 52, No. 225201.

(34) Zhang, S.; Li, Y.; Knoll, A.; Oehrlein, G. S. Mechanistic Aspects of Plasma-Enhanced Catalytic Methane Decomposition by Time-Resolved Operando Diffuse Reflectance Infrared Fourier Transform Spectroscopy. J. Phys. D: Appl. Phys. **2020**, 53, No. 215201.

(35) Gibson, E. K.; Stere, C. E.; Curran-McAteer, B.; Jones, W.; Cibin, G.; Gianolio, D.; Goguet, A.; Wells, P. P.; Catlow, C. R. A.; Collier, P.; et al. Probing the Role of a Non-Thermal Plasma (NTP) in the Hybrid NTP Catalytic Oxidation of Methane. *Angew. Chem.*, *Int. Ed.* **2017**, *56*, 9351–9355.

(36) Stere, C.; Chansai, S.; Gholami, R.; Wangkawong, K.; Singhania, A.; Goguet, A.; Inceesungvorn, B.; Hardacre, C. A Design of a Fixed Bed Plasma DRIFTS Cell for Studying the NTP-Assisted Heterogeneously Catalysed Reactions. *Catal. Sci. Technol.* **2020**, *10*, 1458–1466.

(37) 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.

(38) Qian, M.; Zhong, W.; Kang, J.; Liu, S.; Ren, C.; Zhang, J.; Wang, D. Global Modeling on Partial Oxidation of Methane to Oxygenates and Syngas in Non-Equilibrium Plasma. *Jpn. J. Appl. Phys.* **2020**, *59*, No. 066003.

(39) Olivera, P. P.; Patrito, E. M.; Sellers, H. Direct Synthesis of Methanol over Metallic Catalysts. *Surf. Sci.* **1995**, *327*, 330–357.

(40) Yoo, J. S.; Schumann, J.; Studt, F.; Abild-Pedersen, F.; Nørskov, J. K. Theoretical Investigation of Methane Oxidation on Pd(111) and Other Metallic Surfaces. J. Phys. Chem. C **2018**, 122, 16023–16032.

(41) Xing, B.; Pang, X.-Y.; Wang, G.-C. C–H Bond Activation of Methane on Clean and Oxygen Pre-Covered Metals: A Systematic Theoretical Study. *J. Catal.* 2011, 282, 74–82.

(42) Baek, B.; Aboiralor, A.; Wang, S.; Kharidehal, P.; Grabow, L. C.; Massa, J. D. Strategy to Improve Catalytic Trend Predictions for Methane Oxidation and Reforming. *AIChE J.* **2017**, *63*, 66–77.

(43) Mehta, P.; Barboun, P.; Go, D. B.; Hicks, J. C.; Schneider, W. F. Catalysis Enabled by Plasma Activation of Strong Chemical Bonds: A Review. *ACS Energy Lett.* **2019**, *4*, 1115–1133.

(44) Mehta, P.; Barboun, P.; Herrera, F. A.; Kim, J.; Rumbach, P.; Go, D. B.; Hicks, J. C.; Schneider, W. F. Overcoming Ammonia Synthesis Scaling Relations with Plasma-Enabled Catalysis. *Nat. Catal.* **2018**, *1*, 269–275.

(45) Engelmann, Y.; Mehta, P.; Neyts, E. C.; Schneider, W. F.; Bogaerts, A. Predicted Influence of Plasma Activation on Nonoxidative Coupling of Methane on Transition Metal Catalysts. *ACS Sustainable Chem. Eng.* **2020**, *8*, 6043–6054.

(46) Michiels, R.; Engelmann, Y.; Bogaerts, A. Plasma Catalysis for  $CO_2$  Hydrogenation: Unlocking New Pathways toward  $CH_3OH$ . *J. Phys. Chem. C* **2020**, 124, 25859–25872.

(47) York, A. P. E.; Xiao, T.; Green, M. L. H. Brief Overview of the Partial Oxidation of Methane to Synthesis Gas. *Top. Catal.* **2003**, *22*, 345–358.

(48) Liu, C.; Li, M.; Wang, J.; Zhou, X.; Guo, Q.; Yan, J.; Li, Y. Plasma Methods for Preparing Green Catalysts: Current Status and Perspective. *Chin. J. Catal.* **2016**, *37*, 340–348.

(49) Kraus, P.; Lindstedt, R. P. Microkinetic Mechanisms for Partial Oxidation of Methane over Platinum and Rhodium. *J. Phys. Chem. C* **2017**, *121*, 9442–9453.

(50) Mhadeshwar, A. B.; Vlachos, D. G. A Catalytic Reaction Mechanism for Methane Partial Oxidation at Short Contact Times, Reforming, and Combustion, and for Oxygenate Decomposition and Oxidation on Platinum. *Ind. Eng. Chem. Res.* **2007**, *46*, 5310–5324.

(51) Korup, O.; Goldsmith, C. F.; Weinberg, G.; Geske, M.; Kandemir, T.; Schlögl, R.; Horn, R. Catalytic Partial Oxidation of Methane on Platinum Investigated by Spatial Reactor Profiles, Spatially Resolved Spectroscopy, and Microkinetic Modeling. *J. Catal.* **2013**, 297, 1–16.

(52) Aghalayam, P.; Park, Y. K.; Fernandes, N.; Papavassiliou, V.; Mhadeshwar, A. B.; Vlachos, D. G. A C1 Mechanism for Methane Oxidation on Platinum. *J. Catal.* **2003**, *213*, 23–38.

(53) Chen, Y.; Vlachos, D. G. Density Functional Theory Study of Methane Oxidation and Reforming on Pt(111) and Pt(211). *Ind. Eng. Chem. Res.* **2012**, *51*, 120918084645004.

(54) Wang, R.; Chen, J.; Zhao, W.; Wen, J.; Li, H.; Li, L.; Ran, J. Mechanism of the Catalytic Oxidation of Methane on Pt(1 1 1) Surfaces in Moist Environment: A Density Functional Theory Study. *Appl. Surf. Sci.* **2019**, *471*, 566–586.

(55) Nørskov, J. K.; Studt, F.; Abild-Pedersen, F.; Bligaard, T. *Fundamental Concepts in Heterogeneous Catalysis*; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2014.

(56) Campbell, C. T.; Sprowl, L. H.; Árnadóttir, L. Equilibrium Constants and Rate Constants for Adsorbates: Two-Dimensional (2D) Ideal Gas, 2D Ideal Lattice Gas, and Ideal Hindered Translator Models. J. Phys. Chem. C 2016, 120, 10283–10297.

(57) Bitsch-Larsen, A.; Horn, R.; Schmidt, L. D. Catalytic Partial Oxidation of Methane on Rhodium and Platinum: Spatial Profiles at Elevated Pressure. *Appl. Catal., A* **2008**, *348*, 165–172.

(58) Horn, R.; Williams, K.; Degenstein, N.; Bitsch-Larsen, A.; Dalle Nogare, D.; Tupy, S.; Schmidt, L. Methane Catalytic Partial Oxidation on Autothermal Rh and Pt Foam Catalysts: Oxidation and Reforming Zones, Transport Effects, and Approach to Thermodynamic Equilibrium. *J. Catal.* **2007**, *249*, 380–393.

(59) Chin, Y.-H. C.; Buda, C.; Neurock, M.; Iglesia, E. Selectivity of Chemisorbed Oxygen in C–H Bond Activation and CO Oxidation and Kinetic Consequences for  $CH_4-O_2$  Catalysis on Pt and Rh Clusters. J. Catal. 2011, 283, 10–24.

(60) Chin, Y.-H.; Buda, C.; Neurock, M.; Iglesia, E. Reactivity of Chemisorbed Oxygen Atoms and Their Catalytic Consequences

Article

during  $CH_4 - O_2$  Catalysis on Supported Pt Clusters. J. Am. Chem. Soc. 2011, 133, 15958–15978.

(61) Maitre, P.-A.; Bieniek, M. S.; Kechagiopoulos, P. N. Plasma-Enhanced Catalysis for the Upgrading of Methane: A Review of Modelling and Simulation Methods. *React. Chem. Eng.* **2020**, *5*, 814– 837.

(62) Chen, T. Y.; Rousso, A. C.; Wu, S.; Goldberg, B. M.; van der Meiden, H.; Ju, Y.; Kolemen, E. Time-Resolved Characterization of Plasma Properties in a CH<sub>4</sub>/He Nanosecond-Pulsed Dielectric Barrier Discharge. *J. Phys. D: Appl. Phys.* **2019**, *52*, No. 18LT02.

(63) Butterworth, T.; van de Steeg, A.; van den Bekerom, D.; Minea, T.; Righart, T.; Ong, Q.; van Rooij, G. Plasma Induced Vibrational Excitation of  $CH_4$  —a Window to Its Mode Selective Processing. *Plasma Sources Sci. Technol.* **2020**, *29*, No. 095007.

(64) Shen, X.; Liu, W.; Gao, X.; Lu, Z.; Wu, X.; Gao, X. Mechanisms of Oxidase and Superoxide Dismutation-like Activities of Gold, Silver, Platinum, and Palladium, and Their Alloys: A General Way to the Activation of Molecular Oxygen. *J. Am. Chem. Soc.* **2015**, *137*, 15882–15891.

(65) Du, Y.; Nayak, G.; Oinuma, G.; Peng, Z.; Bruggeman, P. J. Effect of Water Vapor on Plasma Morphology, OH and  $H_2O_2$  Production in He and Ar Atmospheric Pressure Dielectric Barrier Discharges. J. Phys. D: Appl. Phys. **2017**, 50, No. 145201.

(66) Snoeckx, R.; Ozkan, A.; Reniers, F.; Bogaerts, A. The Quest for Value-Added Products from Carbon Dioxide and Water in a Dielectric Barrier Discharge: A Chemical Kinetics Study. *ChemSuschem* **2017**, *10*, 409–424.

(67) Vasko, C. A.; Liu, D. X.; van Veldhuizen, E. M.; Iza, F.; Bruggeman, P. J. Hydrogen Peroxide Production in an Atmospheric Pressure RF Glow Discharge: Comparison of Models and Experiments. *Plasma Chem. Plasma Process.* **2014**, *34*, 1081–1099.

(68) Nunnally, T.; Gutsol, K.; Rabinovich, A.; Fridman, A.; Gutsol, A.; Kemoun, A. Dissociation of  $CO_2$  in a Low Current Gliding Arc Plasmatron. J. Phys. D: Appl. Phys. **2011**, 44, No. 274009.

(69) Larkin, D. W.; Zhou, L.; Lobban, L. L.; Mallinson, R. G. Product Selectivity Control and Organic Oxygenate Pathways from Partial Oxidation of Methane in a Silent Electric Discharge Reactor. *Ind. Eng. Chem. Res.* **2001**, *40*, 5496–5506.

(70) Larkin, D. W.; Lobban, L. L.; Mallinson, R. G. The Direct Partial Oxidation of Methane to Organic Oxygenates Using a Dielectric Barrier Discharge Reactor as a Catalytic Reactor Analog. *Catal. Today* **2001**, *71*, 199–210.

(71) Chen, Y.; Vlachos, D. G. Hydrogenation of Ethylene and Dehydrogenation and Hydrogenolysis of Ethane on Pt(111) and Pt(211): A Density Functional Theory Study. *J. Phys. Chem. C* 2010, *114*, 4973–4982.

(72) Studt, F.; Behrens, M.; Kunkes, E. L.; Thomas, N.; Zander, S.; Tarasov, A.; Schumann, J.; Frei, E.; Varley, J. B.; Abild-Pedersen, F.; et al. The Mechanism of CO and  $CO_2$  Hydrogenation to Methanol over Cu-Based Catalysts. *ChemCatChem* **2015**, *7*, 1105–1111.

(73) Tong, Y.; Lunsford, J. H. Mechanistic and Kinetic Studies of the Reactions of Gas-Phase Methyl Radicals with Metal Oxides. *J. Am. Chem. Soc.* **1991**, *113*, 4741–4746.

(74) Pak, S.; Smith, C. E.; Rosynek, M. P.; Lunsford, J. H. Conversion of Methyl Radicals to Methanol and Formaldehyde over Vanadium Oxide Catalysts. *J. Catal.* **1997**, *165*, 73–79.

(75) Pak, S.; Rosynek, M. P.; Lunsford, J. H. Conversion of Methyl Radicals to Methanol and Formaldehyde over Molybdenum Oxide Catalysts. *J. Phys. Chem. A* **1994**, *98*, 11786–11790.

(76) Alvarez-Galvan, M. C.; Mota, N.; Ojeda, M.; Rojas, S.; Navarro, R. M.; Fierro, J. L. G. Direct Methane Conversion Routes to Chemicals and Fuels. *Catal. Today* **2011**, *171*, 15–23.