

Density Functional Theory Study of Synthesis of Oxygenates and Higher Hydrocarbons from Methane and Carbon Dioxide Using Cold Plasmas

Jian-guo Wang,[†] Chang-jun Liu,^{*,†} and Baldur Eliasson[‡]

ABB Plasma Greenhouse Gas Chemistry Laboratory, Key Laboratory of Green Synthesis and Transformation of Ministry of Education and School of Chemical Engineering, Tianjin University, Tianjin 300072, People's Republic of China, and ABB Switzerland, Ltd., Corporate Research, Baden-Daettwil, CH5405, Switzerland

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A density functional theory (DFT) study has been conducted in this work to investigate the reaction mechanism of synthesis of oxygenates and higher hydrocarbons from methane (CH₄) and carbon dioxide (CO₂), using cold plasmas. The main dissociation routes of the reactants were analyzed. The feasibility of the formation of various products, including syngas, higher hydrocarbons, and oxygenates, was discussed. The DFT study confirmed that the major obstacle of the synthesis is the dissociation of the reactants CH₄ and CO₂. After the cold plasma has supplied the necessary energy for the dissociation of CH₄ and CO₂, syngas, higher hydrocarbons, and oxygenates can be then easily produced. The present DFT study also demonstrates that the plasma synthesis will normally lead to a formation of a mixture of syngas, higher hydrocarbons, and oxygenates.

1. Introduction

An intensive investigation has been conducted worldwide to utilize methane (CH₄) as a raw material for the production of highly valuable chemicals and clean fuels since the 1980s. A major difficulty for CH₄ conversion is activation of the stable C–H bonds in the CH₄ molecule. The catalytic conversion of CH₄ to more-useful chemicals and fuels remains a challenge into the 21st century.^{1–3} In regard to the difficulty that is involved with the activation of CH₄, gas-discharge plasmas recently have been investigated extensively. The investigations include plasma methane conversion to C₂ hydrocarbons,^{4–12} oxygenates,^{13–17} liquid fuels,^{18,19} and

syngas.^{18–25} Corona discharge,^{5–10,12} gliding arc,^{21,22} plasmatorch,²⁵ and dielectric-barrier discharge (DBD)^{13,14,16–20,26–28} methods have been applied for such plasma methane conversions. Most plasma methane conversions use cold plasmas. Corona discharge and DBD are two typical

* Author to whom correspondence should be addressed. E-mail: changliu@public.tpt.tj.cn.

[†] Tianjin University.

[‡] ABB Switzerland, Ltd.

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cold-plasma phenomena. The cold plasma is very effective in exciting stable small molecules, such as CH₄ and carbon dioxide (CO₂), through the use of its energetic electrons without extra heating of the gas. A characteristic feature of the cold plasma is its high electron temperature (10⁴–10⁵ K), whereas the gas temperature remains as low as room temperature. This means that the plasma methane conversion can be operated at low gas temperatures (as low as room temperature), while the methane conversion is significantly high (even >70% for some cases). Such plasma methane conversions primarily use a co-reactant or dilution gas to feed the oxygen species and/or avoid possible carbon deposition. Oxygen gas (O₂),^{5,6,13,15–17} CO₂,^{5,9,18–20,24,27,28} nitrogen monoxide (NO),¹⁴ hydrogen gas (H₂),^{5,6} or helium^{20,29} has been used as a co-reactant or dilution gas. It is very promising to use CO₂ as a co-reactant for plasma methane conversion, because CO₂ can provide extra C atoms for methane conversion, and CO₂ also serves as a better oxidant for the production of oxygenates, compared to oxygen. A “plasma-gas-to-liquid race” is underway worldwide. However, all the players in this race must face two big barriers: one is the poor understanding of the discharge reactions, and the other is the low energy yield that is encountered with the plasma methane conversion. A better understanding of the reaction mechanism will, of course, be very helpful to improve the reactions further. Most investigators have considered the plasma methane conversion in terms of the radical chain reactions, and the products from these radical chain reactions are principally determined through the use of the discharge. Generally, for methane conversion to gaseous products using plasmas, corona discharges or microwave discharges or thermal plasmas can be used. However, for methane conversion directly into liquid products, such as oxygenates or liquid fuels, DBDs are required. To increase the yield of the desired products and to develop a practical utilization of CH₄ and CO₂ using cold plasmas, it is very necessary to understand the pathways of the product formation or the reaction mechanisms. In this work, a density functional theory (DFT) study has been conducted to investigate the pathways for the formation of syngas, oxygenates, and higher hydrocarbons from CH₄ and CO₂, using cold plasmas. We limit the present discussion to the co-feed of CH₄ and CO₂. We will discuss plasma methane conversion with other co-feed gases in future works.

2. Computational Details

All the calculations have been performed using the MSI DMOL³ program.^{30,31} The double numerical plus polarization (DNP) basis sets were used in the calculation to describe the valence orbits of the O, C, and H atoms. DFT in DMOL³ was performed with the generalized gradient-corrected approximation (GGA), using the PW91 functional.^{32,33} The linear synchronous transit (LST) and quadratic synchronous transit (QST) methods were used to study the transition state. The

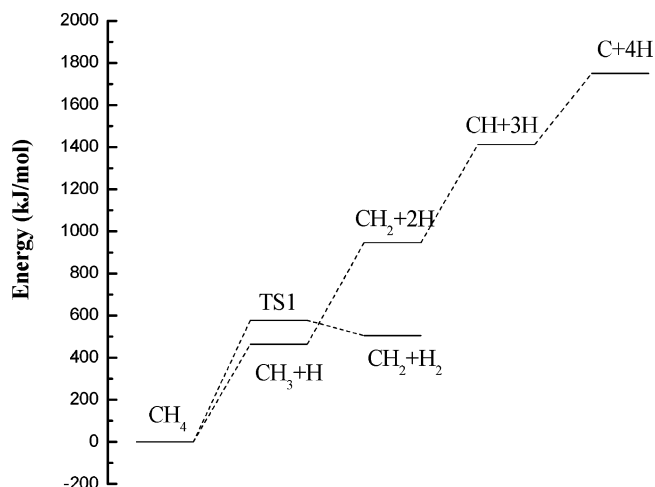


Figure 1. Reaction scheme of CH₄ dissociation in the dielectric-barrier discharge (DBD) reactor.

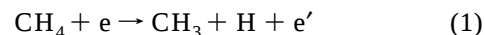
transition state was confirmed by the nudged elastic band (NEB) method.

During the calculations, we first studied the dissociation routes of reactants using the DFT methods, according to the specific reaction conditions. Based on the calculated results, some important intermediate reactions, including the radical initial reactions, radical recombination, and chain reaction, were analyzed. We then have described the pathways of the formation of some important products from CH₄ and CO₂ under the conditions of a cold plasma.

3. Results and Discussion

3.1. Initiation of Gas-Discharge Reactions. The discharge reactions are initiated from the dissociation of the feed gases CH₄ and CO₂. Within the discharge region, there exist a large number of energetic electrons with energies of 96.49–964.87 kJ/mol. When the feed gases pass through the discharge region, the energetic electrons will induce the dissociation of molecules of feed gases and initiate the discharge reactions. It is generally agreed that the electrons and radicals within cold plasmas have a very important role in the discharge reactions. In particular, the electrons are the principal species to initiate the discharge reactions. The role of ions and other species can be ignored.

Figure 1 shows the reaction scheme of methane dissociation. The principal reaction is the dissociation of CH₄:



where e' represents an electron with less energy.^{4,11,28}

Of course, the methyl radical can be further dissociated into CH₂, CH, and even carbon by this mode. However, the amount of CH₂, CH, and carbon is less than the amount of CH₃ radicals, because the formation of CH₂, CH, and carbon requires greater energy input and more reaction steps, as shown in Figure 1. In addition, Figure 1 shows that the CH₂ radical and H₂ can also be obtained directly from CH₄. The energy barrier between the transition-state structure (TS1) and the reactant is 576.97 kJ/mol. The methyl radical is the key species for the further formation of hydrocarbons and oxygenates, such as alcohols and acids.²⁸ The calculated dissociation energies of CH_n + e → CH_{n-1} + H +

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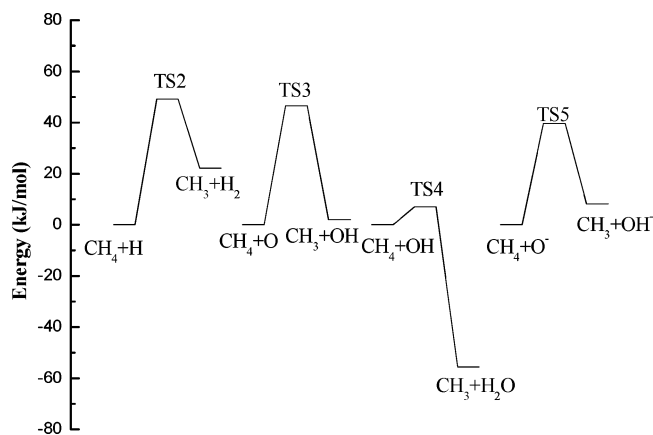


Figure 2. Relative energies for reactions between some species (H, O, OH, and O⁻) and CH₄.

e' ($n = 4, 3, 2, 1$) are 462.75, 483.67, 466.10, and 337.65 kJ/mol, respectively, which is consistent with the experimental results of 471.12, 491.20, 441.83, and 352.29 kJ/mol, respectively.³⁴ The multistep reactions can easily occur with highly energetic electrons in the plasmas.

In addition to electrons, some active plasma species, such as H, O, O⁻, and OH, can attack the CH₄ molecule to produce extra methyl radicals.¹⁸ These reactions are important after the initiation of the discharge reactions.³⁵ The oxygen species are produced from the dissociation of CO₂:



In fact, the objectives of adding CO₂ into the plasma methane conversion are (i) to increase the methane conversion, (ii) to change the product distribution and increase the yield of objective products, and (iii) to reduce the specific energy consumption.^{18,19,28} Figure 2 shows the relative energies required for the generation of methyl radicals from the reactions between CH₄ and the H, O, OH, and O⁻ species. The energy barriers for these reactions were 49.13 (TS2), 46.44 (TS3), 7.11 (TS4), and 39.67 (TS5) kJ/mol, respectively. After the initiation of discharge reactions, the oxygen species will have an important role in the generation of methyl radicals.

From the literature,^{36–41} there are two possibilities for CO₂ dissociation. One is via CO₂⁻ and the other is via CO, as shown in eqs 2 and 3. The experiment showed that CO₂⁻ could be formed during the electrochemical-reduction of CO₂.^{36–39} CO₂⁻ can also be formed within

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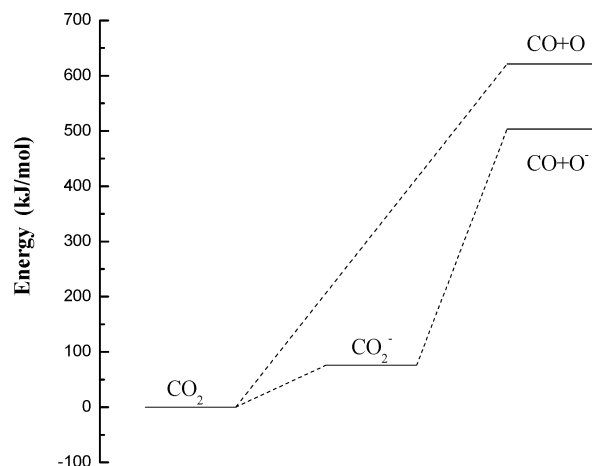


Figure 3. Reaction scheme of CO₂ dissociation.

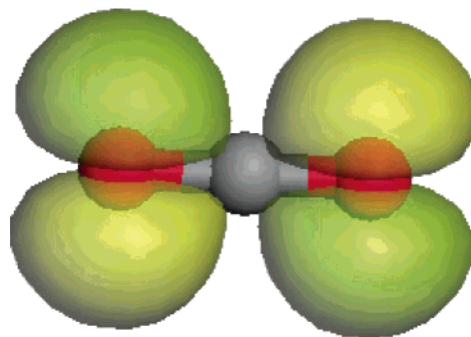


Figure 4. CO₂ HOMO orbit.

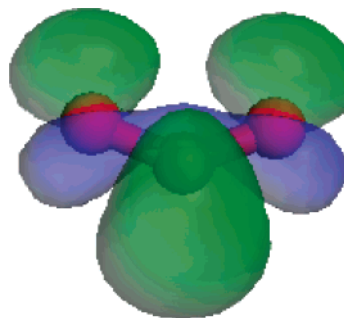


Figure 5. CO₂⁻ HOMO orbit.

the discharges. The calculated reaction enthalpy to form CO₂⁻ is 76.07 kJ/mol, which is slightly higher than the experimental value (48.14–62.76 kJ/mol⁴⁰).

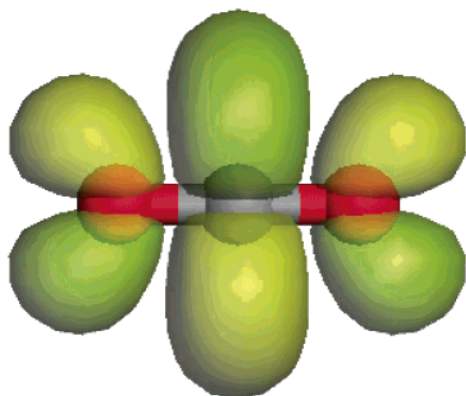
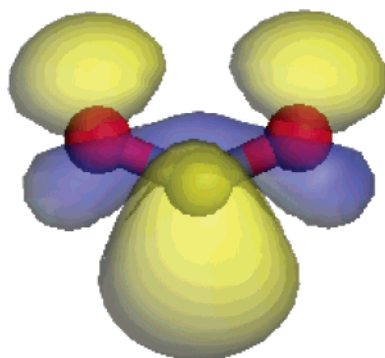
Figure 3 presents the reaction scheme of CO₂ dissociation. Evidently, the dissociation via CO requires much more energy than the attachment to form CO₂⁻. Figures 4 and 5 show the highest occupied molecular orbit (HOMO) of CO₂ and CO₂⁻, respectively, and Figures 6 and 7 show the lowest unoccupied molecular orbit (LUMO) of CO₂ and CO₂⁻, respectively. Obviously, the chemical activation of CO₂⁻ is more facile than CO₂.⁴²

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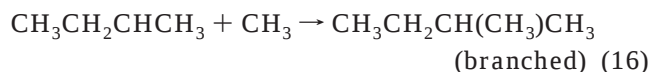
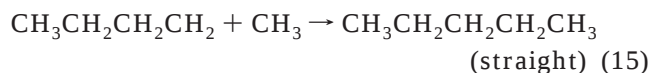
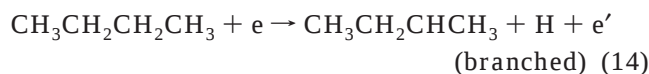
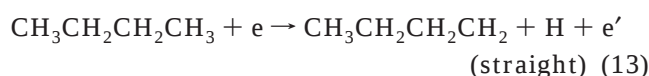
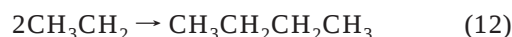
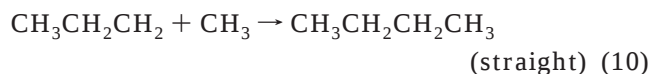
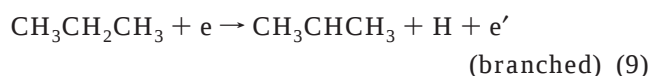
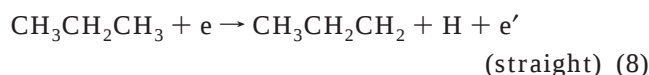
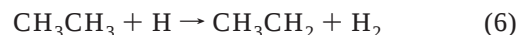
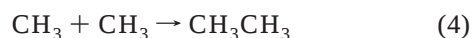
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Figure 6. CO₂ LUMO orbit.Figure 7. CO₂⁻ LUMO orbit.

3.2. Formation of Oxygen-Containing Species. To produce oxygenates from CH₄ and CO₂, using cold plasmas, in addition to methyl radicals, some oxygen-containing species (such as OH and COOH) are also very necessary. These oxygen-containing active species are normally generated from the secondary reactions or other multistep reactions, including the recombination of radicals and dissociation of products. As discussed below, the formation of OH, OH⁻, and COOH⁻ is one of principal pathways to synthesize the ultimate oxygenated products. The reaction energies for the formation of OH, OH⁻, and COOH⁻ (from the reactions O + H → OH, O⁻ + H → OH⁻, and H + CO₂⁻ → COOH⁻, respectively) are -465.68, -459.18, and -45.18 kJ/mol, respectively. These reactions can easily occur, because they are exothermic. Moreover, from the recombination of the radicals such as CH₃ and CH₂, the radical chain reactions are started and higher hydrocarbons and oxygenates are thereby produced. These reactions were also exothermic; for example, the reaction energies for CH₃ + CH₂ → CH₃CH₂ and CH₃CH₂ + CH₂ → CH₃CH₂CH₂ are -448.11 and -430.95 kJ/mol, respectively.

3.3. Pathways for the Formation of Higher Hydrocarbons. According to the radical chain mechanism, the initial reaction step to form the higher hydrocarbons is the methane dissociation by the electrons or hydrogen abstraction by some active species (O, H, and OH). The reactions include CH₄ + (e, O, H, OH, O⁻) → CH₃ + (H + e', OH, H₂, H₂O, OH⁻). The chain growth reactions then proceed as follows:



Such reactions are responsible for the synthesis of higher hydrocarbons within discharges. In addition, alkenes and acetylene can be produced from the CH₂ and CH radicals. At the same time, the formed hydrocarbon radicals will be involved in these reactions to produce oxygenates, such as alcohols and acids, which will be explained in detail in the following sections. Table 1 shows the enthalpies and entropies of some of important reactions for the synthesis of higher hydrocarbons. This data suggest that these reactions easily occur under the conditions of a cold plasma.

3.4. Pathways for the Formation of Alcohol Products. The aforementioned analysis shows that OH, OH⁻, and a great amount of hydrocarbon radicals (e.g., CH₃, CH₃CH₂, and so on) exist. Therefore, a series of alcohol products can be easily synthesized within cold plasmas. Methanol can also be obtained via the reaction CH₄ + O → CH₃OH. Another important pathway to synthesize alcohols is via the dissociation of lower alcohols, e.g., CH₃OH + e → CH₂OH + H + e'; the reaction energy is 414.63 kJ/mol, and the formed CH₂OH can react with hydrocarbon radicals to generate higher alcohols. The enthalpies and entropies of the reactions to synthesize alcohols are presented in Table 2. Obviously, the main pathways to form alcohols via OH, OH⁻, and CH₂OH are thermodynamically favored.

3.5. Pathways for the Formation of Acid Products. The acids are principally synthesized via two pathways: with COO⁻ or CO. The synthesis of formic acid via the COO⁻ route can also be performed through

Table 1. Main Thermodynamic Parameters of the Synthesis Reactions for the Main Hydrocarbon Products at 298.15 K

reaction	ΔH (kJ/mol)	ΔS (J mol ⁻¹ K ⁻¹)
CH ₃ + CH ₃ → CH ₃ CH ₃	-370.28	-170.28
CH ₃ CH ₂ + CH ₃ → CH ₃ CH ₂ CH ₃	-359.99	-164.76
CH ₃ CH ₃ + e → CH ₃ CH ₂ + H + e'	429.75(ΔE)	
CH ₃ CH ₃ + H → CH ₃ CH ₂ + H ₂	-10.66 (ΔE)	
CH ₃ CH ₂ CH ₃ + e → CH ₃ CH ₂ CH ₂ + H + e'	443.65 (ΔE)	
CH ₃ CH ₂ CH ₃ + e → CH ₃ CHCH ₃ + H + e'	425.14 (ΔE)	
CH ₃ CH ₂ + CH ₃ CH ₂ → CH ₃ CH ₂ CH ₂ CH ₃	-343.34	-171.73
CH ₃ CH ₂ CH ₂ + CH ₃ → CH ₃ CH ₂ CH ₂ CH ₃	-366.78	-174.67
CH ₃ CH ₂ CH ₂ CH ₃ + e → CH ₃ CH ₂ CH ₂ CH ₂ + H + e'	442.20 (ΔE)	
CH ₃ CH ₂ CH ₂ CH ₃ + e → CH ₃ CH ₂ CHCH ₃ + H + e'	425.99 (ΔE)	
CH ₃ CH ₂ CH ₂ CH ₂ + CH ₃ → CH ₃ CH ₂ CH ₂ -CH ₂ CH ₃	-360.04	-172.95
CH ₃ CH ₂ CHCH ₃ + CH ₃ → CH ₃ CH ₂ CH-(CH ₃)CH ₃	-348.00	-190.13
CH ₃ CHCH ₃ + CH ₃ → CH ₃ CH(CH ₃)CH ₃	-351.55	-188.93
CH ₃ CH ₂ CH ₂ + CH ₃ CH ₂ → CH ₃ CH ₂ CH ₂ -CH ₂ CH ₃	-349.34	-177.98
CH ₃ CHCH ₃ + CH ₃ CH ₂ → CH ₃ CH(CH ₃)-CH ₂ CH ₃	-332.05	-191.68
2CH ₃ CH ₂ CH ₂ → C ₆ H ₁₄	-355.85	-168.21
C ₅ H ₁₁ + C ₅ H ₁₁ → C ₁₀ H ₂₂	-450.73	-187.33
CH ₂ + CH ₂ → CH ₂ CH ₂	-727.03	-153.06
CH ₂ + CH ₃ → CH ₂ CH ₂ + H	-276.73 (ΔE)	
CH ₂ CH ₂ → CH ₂ CH + H	534.88 (ΔE)	
CH ₂ CH + CH ₃ → CH ₂ CHCH ₃	-472.909	-166.14
CH + CH → C ₂ H ₂	-1111.77	24.23

Table 2. Main Thermodynamic Parameters of the Synthesis Reactions for the Main Alcohol Products at 298.15 K

reaction	ΔH (kJ/mol)	ΔS (J mol ⁻¹ K ⁻¹)
CH ₄ + O → CH ₃ OH	-419.25 (ΔE)	
CH ₃ + OH → CH ₃ OH	-392.87	-136.98
CH ₃ CH ₂ + OH → CH ₃ CH ₂ OH	-389.42	-141.47
CH ₃ CH ₂ CH ₂ + OH → CH ₃ CH ₂ CH ₂ OH	-394.11	-140.33
CH ₃ + OH ⁻ → CH ₃ OH + e	-273.02	-65.08
CH ₃ CH ₂ + OH ⁻ → CH ₃ CH ₂ OH + e	-269.76	-69.65
CH ₃ CH ₂ CH ₂ + OH ⁻ → CH ₃ CH ₂ CH ₂ OH + e	-274.47	-68.65
CH ₂ OH + CH ₃ → CH ₃ CH ₂ OH	-352.93	-171.23
CH ₂ OH + CH ₃ CH ₂ → CH ₃ CH ₂ CH ₂ OH	-334.18	-167.16

Table 3. Main Thermodynamic Parameters of the Synthesis Reactions for the Main Acid Products at 298.15 K

reaction	ΔH (kJ/mol)	ΔS (J mol ⁻¹ K ⁻¹)
H + COOH ⁻ → HCOOH + e	-484.40 (ΔE)	
CH ₃ + COOH ⁻ → CH ₃ COOH + e	-433.78	-177.07
CH ₃ CH ₂ + COOH ⁻ → CH ₃ CH ₂ COOH + e	-416.21	-191.83
CH ₃ + CO → CH ₃ CO	-104.35 (ΔE)	
CH ₃ CO + O → CH ₃ COO	-509.82 (ΔE)	
CH ₃ COO + H → CH ₃ COOH	-439.60 (ΔE)	
CH ₃ CO + OH → CH ₃ COOH	-464.20	-155.41
CH ₃ CO + OH ⁻ → CH ₃ COOH + e	-344.83	-83.65
CH ₃ CH ₂ + CO → CH ₃ CH ₂ CO	-75.17	-155.13
CH ₃ CH ₂ CO + O → CH ₃ CH ₂ COO	-467.53 (ΔE)	
CH ₃ CH ₂ COO + H → CH ₃ CH ₂ COOH	-477.71 (ΔE)	
CH ₃ + CH ₂ COOH → CH ₃ CH ₂ COOH	-348.326	-183.22
CH ₃ CH ₂ + CH ₂ COOH → CH ₃ CH ₂ CH ₂ -COOH	-331.586	-182.52

the electrochemical reduction of CO₂.^{36–39} Kaneco et al. thought that COO⁻ is produced by electron transfer during the electrochemical reduction of CO₂ and then COOH is generated from COO⁻. In this work, the carboxyl was generated by the reaction COO⁻ + H →

COOH⁻.⁴³ The acids then were obtained by the following reactions:



Another reaction route via CO is similar to the catalytic route.⁴⁴ For example, the formation of acetic acid via the CO route can be expressed by the following reactions:

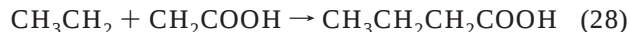


or



The aforementioned analysis shows that the C atom of the carboxyl comes from CO₂ or CO, which is the dissociated product of CO₂. Table 3 presents some important thermodynamic parameters for some synthesis reactions of acids. A comparison between the two routes (via COO⁻ and CO) to synthesize acids shows that the route via COO⁻ is more thermodynamically favored than that via CO. The energy requirement to form COO⁻ from CO₂ is much lower than that to form CO. The reaction steps via COO⁻ are also less than those via CO. Most of the CO that is generated has become the ultimate product before forming acids.

In addition, higher acids can be also obtained via the dissociation of lower acids. For example, acetic acid can be dissociated via the reaction CH₃COOH + e → CH₂-COOH + H + e', which requires an energy of 425.93 kJ/mol. The C₃ and C₄ acids then can be formed via the following reactions:



The reaction thermodynamic parameters were also presented in Table 3. The information in that table shows that these reactions can easily occur after the formation of CH₂COOH.

3.6. Main Reactions Needed to Produce CO and H₂. Carbon monoxide (CO) is principally generated from the dissociation of CO₂, as shown in Figure 3. The experiment also showed that the selectivity of CO was

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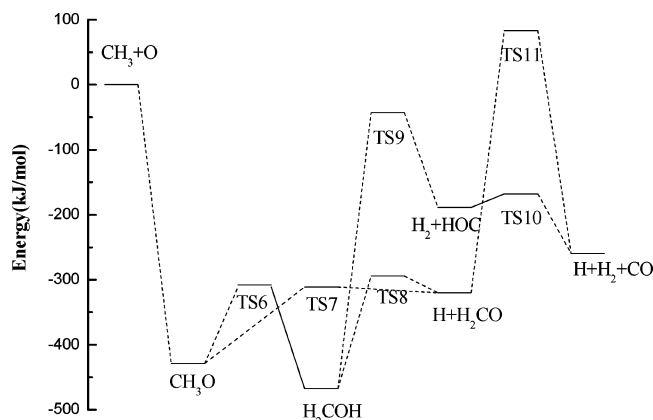


Figure 8. Relative energies for the formation CO and H₂ via the reaction CH₃ + O.

almost proportional to the CO₂ concentration in the feed.²⁸ In addition, the reaction between the hydrocarbon radicals and the O atom can also produce CO.⁴⁵ The relative energies for the formation of CO and H₂ via the reaction CH₃ + O is presented in Figure 8. The intermediate CH₃O formed first, and then the intermediate is converted to H₂COH or H + H₂CO via the TS6 and TS7 transition-state structures. The former requires more energy. Of course, the H₂COH can be converted to either H + H₂CO or H₂ + HOC through the TS8 and TS9 transition states. The H + H₂CO or H₂ + HOC pass the transition state (TS11 and TS10, respectively) and are converted to elemental hydrogen, CO, and hydrogen gas (H₂). The two processes can also be described as these reactions: CH₂ + O → CO + H₂ and CH + O → CO + H. Moreover, we believe that the further oxidation of hydrocarbon and oxygenate products or the further

oxidation of carbon-containing radicals will induce extra production of CO.

In regard to the hydrogen production, the recombination of the H atom into H₂ is the main source of hydrogen, which involves an energy change of -440.58 kJ/mol. H₂ can be obtained during the hydrocarbon decomposition process.

4. Conclusions

The present investigation has confirmed that the principal obstacle for the synthesis from methane (CH₄) and carbon dioxide (CO₂), using cold plasmas, is the dissociation of the feed gases. Thermodynamically, after the feed gases are dissociated, a series of products can be then easily produced. The pathways of the formation of various products, including syngas, higher hydrocarbons, and oxygenates, also have been investigated. The present study has shown that CO mainly comes from the dissociation of CO₂ or hydrocarbon and from the reaction of CH₃ + O. Oxygenates are produced via the reactions of hydrocarbon radicals and the oxygen-containing species (e.g., OH, OH⁻, and COOH⁻) or via the dissociation of lower oxygenates. The latter also follows the radical chain growth mechanism. The results obtained from the present density functional theory (DFT) study are very helpful for the further improvement in the synthesis from CH₄ and CO₂ via cold plasmas.

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