

# Suppressing the formation of NO<sub>x</sub> and N<sub>2</sub>O in a CO<sub>2</sub>/N<sub>2</sub> dielectric barrier discharge plasma by adding CH<sub>4</sub>: Scavenger chemistry at work

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## Abstract

The need for carbon negative technologies led to developing a wide array of novel CO<sub>2</sub> conversion techniques. Most either rely on high temperatures or generate highly reactive O species, which can lead to the undesirable formation of NO<sub>x</sub> and N<sub>2</sub>O when CO<sub>2</sub> feeds contain N<sub>2</sub>. Here, we show that, for plasma-based CO<sub>2</sub> conversion, adding a hydrogen source, as chemical oxygen scavenger, can suppress this formation, *in-situ*. This allows using low-cost N<sub>2</sub> containing (industrial and direct air capture) feeds, rather than expensive purified CO<sub>2</sub>. To demonstrate this, we add CH<sub>4</sub> to a dielectric barrier discharge plasma used for converting impure CO<sub>2</sub>. We find that, when adding a stoichiometric amount of CH<sub>4</sub>, 82 % less NO<sub>2</sub> and 51 % less NO is formed. An even higher reduction (96 and 63 %) can be obtained when doubling this amount. However, in that case the excess radicals promote the formation of by-products,

such as HCN, NH<sub>3</sub> and CH<sub>3</sub>OH. Thus, we believe that by using the proper amount of chemical scavengers, we can use impure CO<sub>2</sub> feeds, which would bring us closer to ‘real world’ conditions and implementation.

## 1. Introduction

The global challenge of climate change and the need for carbon negative technologies has sparked interest and research towards a wide variety of techniques capable of converting CO<sub>2</sub>.<sup>1–6</sup> This CO<sub>2</sub> can be captured either from major emission sources or—preferably, in the long run—out of thin air, through direct air capture (DAC).<sup>7</sup> Numerous analyses and comparisons between different technologies have been made in the literature; however, they all overlook a key aspect that has major consequences, i.e. the fact that lab-scale studies generally use pure gases (99.999 % purity), whereas industrial gases (with some exceptions) usually contain N<sub>2</sub>. Purification is one option, but an energy intensive, and thus costly one.<sup>8</sup> Another—more practical—option is to directly use these impure gases.

However, this option comes with an important obstacle. Most novel technologies under consideration for the conversion of CO<sub>2</sub> into CO and O<sub>2</sub> either require high temperatures (e.g., solar thermochemical and catalytic thermochemical conversion) or create highly reactive O species *in-situ* (e.g., electrochemical, photochemical and plasmachemical conversion).<sup>1</sup> As a result, the risk of producing nitrogen oxides (NO<sub>x</sub>) and nitrous oxide (N<sub>2</sub>O) is real.<sup>9,10</sup> In combustion science, the formation of NO<sub>x</sub> and N<sub>2</sub>O are well-understood phenomena.<sup>11,12</sup> Among the three major NO<sub>x</sub> formation mechanisms (i.e., thermal NO<sub>x</sub> (Zel’dovich), prompt NO<sub>x</sub>, and fuel NO<sub>x</sub>), the thermal mechanism consistently produces NO<sub>x</sub>, as long as O<sub>2</sub> and N<sub>2</sub> coexist under high temperature conditions (> 1900 K).<sup>11</sup> N<sub>2</sub>O, on the other hand, is not a major by-product in combustion processes, except for fluidized bed combustion.<sup>12</sup> When released in the atmosphere, these compounds lead to severe air pollution, such as smog and acid rain, and

they are responsible for the formation of tropospheric ozone.<sup>13</sup> With respect to global warming, the production of N<sub>2</sub>O, in any CO<sub>2</sub> conversion process, cancels the carbon negative effect of any CO<sub>2</sub> converted, since N<sub>2</sub>O is 298 times more potent as a greenhouse gas.<sup>13</sup> This is why NO<sub>x</sub> and N<sub>2</sub>O emissions are so strictly regulated worldwide.

Despite the potential risk of producing unwanted NO<sub>x</sub> and N<sub>2</sub>O during the conversion of impure CO<sub>2</sub> feeds containing N<sub>2</sub>, almost no research has been performed in this area, for the novel technologies that are being considered to convert CO<sub>2</sub>. It stands, without doubt, that this is an important issue, as additional deNO<sub>x</sub> post-treatment, or more severe CO<sub>2</sub> pre-purification steps, will have a negative effect on the energy and cost balance of these CO<sub>2</sub> conversion technologies. In previous studies, we reported that, for non-thermal plasma technology—one of the most promising candidates for the conversion of CO<sub>2</sub><sup>1</sup>—the presence of N<sub>2</sub> indeed causes the aforementioned formation of NO<sub>x</sub> and N<sub>2</sub>O.<sup>9,10</sup>

Here, we explore a potential solution to prevent the formation of NO<sub>x</sub> and N<sub>2</sub>O, *in-situ*, during the plasmachemical conversion of CO<sub>2</sub>. A well-known solution from combustion science has been the addition of more fuel (eq. to a higher fuel-to-air ratio).<sup>13</sup> Despite the fact that we work under experimental conditions that are very different from those in combustion science, we can justify using a similar approach, based on the results obtained in our previous studies.<sup>9,14,15</sup> We already know that the addition of a hydrogen source to non-thermal pure CO<sub>2</sub> plasmas can trap free O species, *in-situ*.<sup>14</sup> And it are exactly these free O species that are responsible for the NO<sub>x</sub> and N<sub>2</sub>O production pathways in non-thermal plasmas.<sup>9</sup> Therefore, here we introduce the use of a hydrogen source, CH<sub>4</sub>, as a chemical oxygen scavenger to suppress the formation of NO<sub>x</sub> and N<sub>2</sub>O, *in-situ*, during the conversion of CO<sub>2</sub> mixtures containing N<sub>2</sub>, in a dielectric barrier discharge (DBD) plasma.

## 2. Materials and methods

Experiments were carried out in a coaxial DBD plasma reactor operating at room temperature and atmospheric pressure. A stainless steel mesh (high voltage electrode) was wrapped over the outside of a quartz tube, and a stainless steel rod (ground electrode) placed at its centre. Feed gases were composed of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> (Air Liquide, Alphagaz 1, 99.999 %), and each flow rate was controlled using a mass-flow controller (Bronkhorst, EL-Flow select F-210CV). The DBD reactor was powered by an AC high-voltage power supply (AFS, custom made), and the applied voltage and electrical current were sampled by a four-channel digital oscilloscope (Picotech, PicoScope 64201). Finally, Fourier transform infrared spectroscopy (FTIR; Thermo Fischer Scientific, Nicolet 380) was used to study the effects of the addition of CH<sub>4</sub> on the formation of N<sub>2</sub>O and NO<sub>x</sub> compounds (i.e., NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>). A detailed description of the set-up and experimental conditions can be found in Section 1 of the Electronic Supplementary Information.

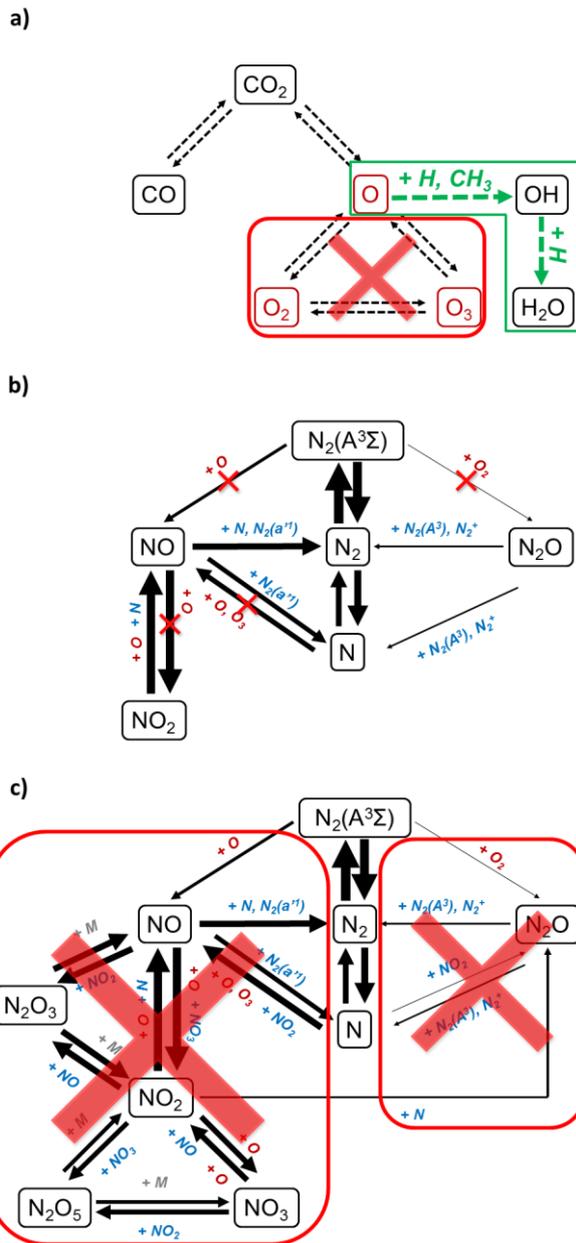
## 3. CH<sub>4</sub> as a chemical oxygen scavenger to suppress NO<sub>x</sub> production

Despite the many advantages offered by plasma technology for the conversion of CO<sub>2</sub>, two main challenges remain:<sup>1</sup>

- 1) Separation: the output of a plasma reactor consists of a homogenous gas mixture; in the case of plasma-based CO<sub>2</sub> conversion, it yields a mixture of CO, O<sub>2</sub> (and any unreacted CO<sub>2</sub>) that is very difficult (and thus energy-intensive) to separate by conventional methods;
- 2) Impurities: the presence of other gases (even those generally considered to be chemically inert) influences both the physical properties of the plasma and its chemistry; in the case of plasma-based CO<sub>2</sub> conversion, the presence of N<sub>2</sub> results in the undesired formation of NO<sub>x</sub> and N<sub>2</sub>O.

Here, we show how focussing on the plasma chemistry can help us to simultaneously find answers to both the separation and impurity issues, in the case of a DBD plasma reactor used for the conversion of an impure CO<sub>2</sub> feed containing N<sub>2</sub>.

As a baseline case, we studied a DBD operating at a specific energy input (SEI) of 12 kJ/L, for a 1:1 mixture of CO<sub>2</sub>:N<sub>2</sub>. Detailed experimental and modelling results for a wide variety of CO<sub>2</sub>:N<sub>2</sub> mixing ratios were discussed in a previous study,<sup>9</sup> with the highest NO<sub>x</sub> production occurring for the 1:1 case, which is the main reason why we chose to further explore that condition first. A chemical analysis revealed that NO<sub>x</sub> species are formed through several pathways in the presence of N<sub>2</sub>, during plasma processing of CO<sub>2</sub>. The main formation mechanism, for all the different NO<sub>x</sub> species, starts by a reaction involving O (or O<sub>2</sub>) and N (or N<sub>2</sub>(A<sup>3</sup>)) (see also Section 2.2 below).<sup>9</sup> This observation is complementary with that made in a previous study, which showed that it was possible to chemically trap oxygen species, *in-situ*, by adding a hydrogen source.<sup>14</sup> Additionally, another separate study showed that, when O and H radicals are present in a plasma, their natural tendency is to form H<sub>2</sub>O.<sup>15</sup> As such, from combining these three observations, it becomes apparent that we are presented with a ‘chemical opportunity’. We hypothesize, based on chemical analyses from these prior studies, that the addition of a small stoichiometric amount of a hydrogen source to a CO<sub>2</sub>:N<sub>2</sub> mixture should be capable of trapping the O radicals produced via electron impact reactions, into OH and H<sub>2</sub>O, before N species can react with the O species and form NO<sub>x</sub> and N<sub>2</sub>O (Figure 1).

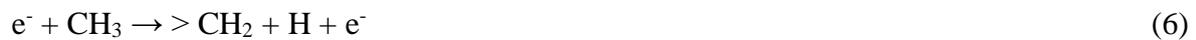


**Figure 1.** Simplified reaction scheme illustrating the suppression of the main pathways of the  $\text{NO}_x$  and  $\text{N}_2\text{O}$  chemistry through the addition of  $\text{CH}_4$ . Reaction pathways starting from  $\text{CO}_2$  show the *in-situ* trapping of O by H species (a); initiation of the  $\text{NO}_x$  chemistry, indicating which pathways are eliminated by the *in-situ* trapping of O (b); complete overview of the  $\text{NO}_x$  and  $\text{N}_2\text{O}$  chemistry to be suppressed by the scavenging of oxygen (c). Original reaction schemes have been adjusted from ref (<sup>9</sup>).

To verify the validity of our hypothesis that an effective chemical oxygen scavenger can prevent the formation of NO<sub>x</sub> and N<sub>2</sub>O, we investigated the effects of using CH<sub>4</sub> as hydrogen source. Some of the most important plasmachemical reactions leading to the formation of the desired hydrogen radicals are the following electron impact dissociation reactions of CH<sub>4</sub>:



These radicals react further through subsequent electron impact dissociation reactions:



The most important electron impact dissociation and excitation reactions with CO<sub>2</sub> and N<sub>2</sub> are:

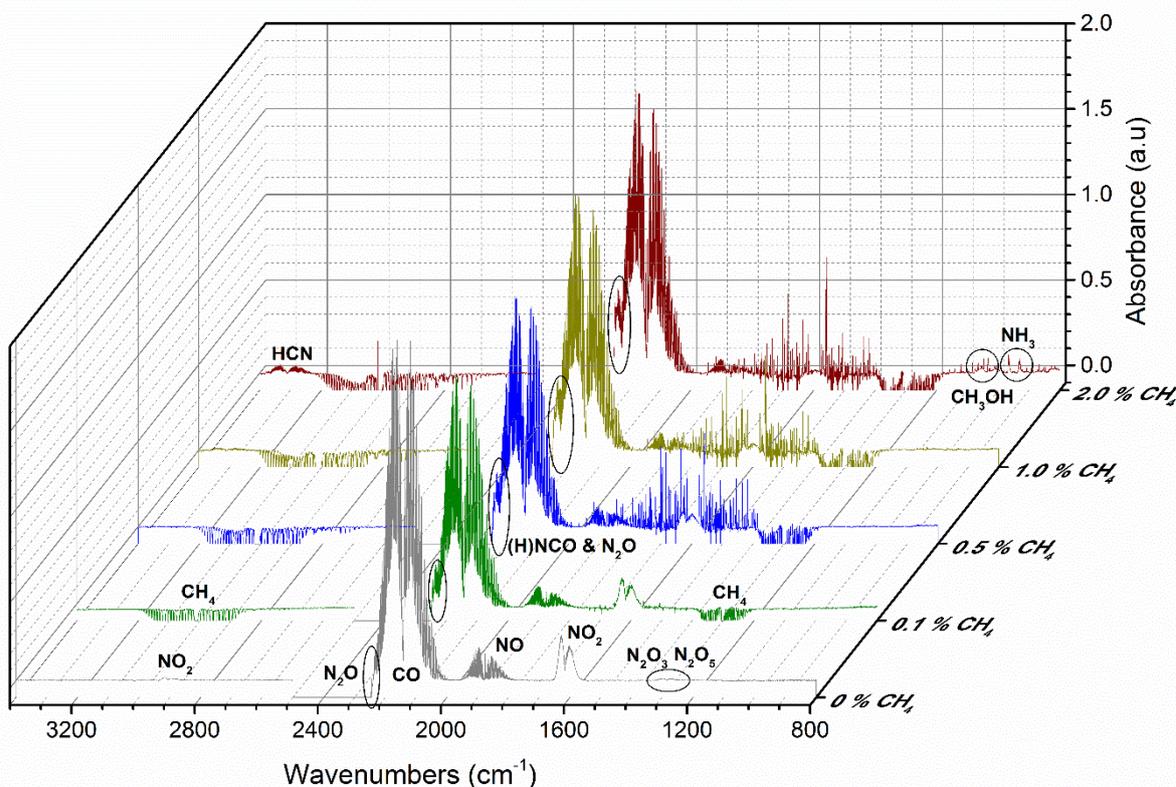


For more details on these and other types of plasmachemical (electron impact) reactions we refer to the existing literature and databases.<sup>1,9,16–19</sup>

We varied the CH<sub>4</sub> addition from 0.1 up to 2.0 mol% of the total CO<sub>2</sub>:N<sub>2</sub> mixture, for a DBD under operating conditions similar to those in the baseline case. It is important to note that the introduction of other components influences the physics of the plasma and its chemistry, especially with a specie like CH<sub>4</sub>, which results in a cascade of reactive compounds, including H and CH<sub>x</sub> radicals. As a result, the electron density and temperature, which affect the conversions, can be altered significantly. Additionally, the conversion of CO<sub>2</sub> can also decrease, due to additional back reactions to CO<sub>2</sub>, such as:



This effect was observed in a previous study, in which adding 2 mol% CH<sub>4</sub> to pure CO<sub>2</sub> yielded a drop in the relative conversion of CO<sub>2</sub> by ~10 %.<sup>14</sup>



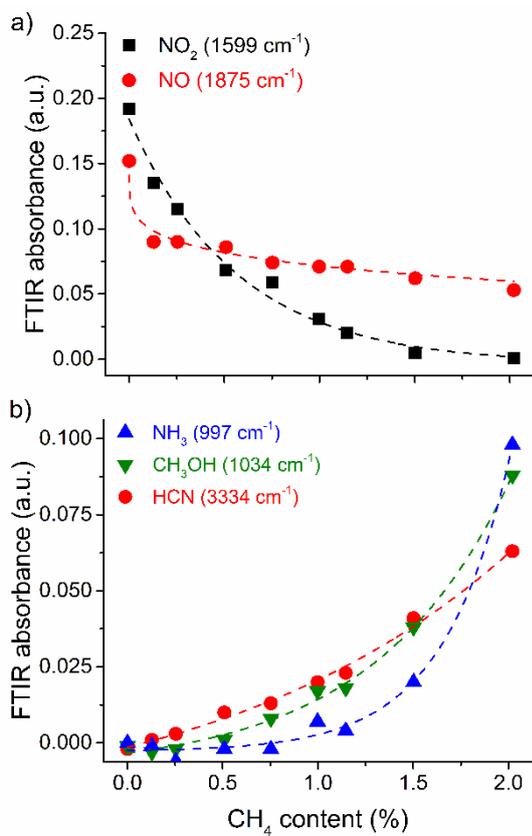
**Figure 2.** FTIR spectra of a 1:1 mixture of CO<sub>2</sub>:N<sub>2</sub> with 0, 0.1, 0.5, 1.0 and 2.0 mol% CH<sub>4</sub> added. For clarity, the CO<sub>2</sub> peak has been removed. The negative absorbance of the CH<sub>4</sub> bands is due to the subtraction of the blank spectra taken before turning on the plasma. Original spectra are provided in Section 2.3 of the Electronic Supplementary Information.

In Figure 2, we can clearly see a decrease of both the NO (1875 cm<sup>-1</sup>) and NO<sub>2</sub> (1599 cm<sup>-1</sup>) peaks, when adding CH<sub>4</sub> to the mixture, with the NO peak showing the biggest initial decrease, and the NO<sub>2</sub> peak showing the stronger overall response (see also Figure 3a). The NO peak decreases by 42 % upon adding 0.1 mol% CH<sub>4</sub>, by 51 % with 1.0 mol%, and by 63 % with 2.0 mol% CH<sub>4</sub> added. The NO<sub>2</sub> peak, on the other hand, decreases by 32 % upon adding 0.1 mol% CH<sub>4</sub>, by 82 % with 1.0 mol%, and by 96 % with 2.0 mol% CH<sub>4</sub> added.

Due to a complete overlap of the CH<sub>4</sub> peaks, we cannot determine whether the N<sub>2</sub>O<sub>3</sub> (1309 cm<sup>-1</sup>) and/or N<sub>2</sub>O<sub>5</sub> (1245 cm<sup>-1</sup>) peaks decrease, upon addition of CH<sub>4</sub>. Nevertheless, this would be a logical consequence, since N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> are secondary reaction products from NO and NO<sub>2</sub> (Figure 1).

The N<sub>2</sub>O (2233 cm<sup>-1</sup>) peak, on the other hand, seems to increase when more CH<sub>4</sub> is added (Figure 2). This seems in contrast with a severe reduction of the formation of O<sub>2</sub>, which is necessary for the production of N<sub>2</sub>O from N<sub>2</sub>(A<sup>3</sup>) (Figure 1). Therefore, there are two options: either the N<sub>2</sub>O concentration is indeed increasing, or its decrease is masked in the FTIR spectra due to interference of other compounds with a similar absorption of the IR frequency (both options are further discussed in Section 2.2).

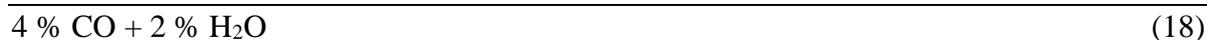
Besides a decrease in NO and NO<sub>2</sub> peak intensities, some additional peaks started to emerge from the noise when we added 1 mol% CH<sub>4</sub> to the mixture (Figure 2); they became clearly visible as we increased the CH<sub>4</sub> concentration to 2 mol%. The peak at 3334 cm<sup>-1</sup> corresponds to HCN;<sup>21</sup> the peak at 1034 cm<sup>-1</sup> corresponds to CH<sub>3</sub>OH;<sup>21</sup> and the peak at 997 cm<sup>-1</sup> corresponds to NH<sub>3</sub>.<sup>21</sup> The HCN peak increases almost linearly, starting from 0.1 mol% CH<sub>4</sub>, whereas the CH<sub>3</sub>OH and NH<sub>3</sub> peaks only emerge clearly from the noise starting at 1.0 mol% of CH<sub>4</sub> added, and exhibit an exponential increase with further addition of CH<sub>4</sub> to 2 mol% (Figure 3b).



**Figure 3.** FTIR absorbance for NO and NO<sub>2</sub> (a); and for NH<sub>3</sub>, CH<sub>3</sub>OH and HCN (b) as a function of the amount of CH<sub>4</sub> added to a 1:1 mixture of CO<sub>2</sub>:N<sub>2</sub> for a SEI of 12 kJ/L.

The formation of these additional components indicates that adding more than 1 mol% CH<sub>4</sub> generates an excess of the hydrogen source; most of the O species have been trapped into H<sub>2</sub>O and the excess radicals produce some of the typical products that can be expected in a CH<sub>4</sub>/N<sub>2</sub> mixture (NH<sub>3</sub> and HCN)<sup>17</sup> and in a CH<sub>4</sub>/CO<sub>2</sub> mixture (CH<sub>3</sub>OH).<sup>18,22</sup> This result is not surprising and consistent with the stoichiometric balance for adding 1 and 2 mol% CH<sub>4</sub>:

By correcting the CO<sub>2</sub> conversion of 3.8 % of the baseline case<sup>9</sup> to 3 % for the lowered conversion, upon addition of CH<sub>4</sub> (as well as to simplify the balance), and then add 1 mol% CH<sub>4</sub> (which is almost completely converted, see Table S3 and Figure S3 in the Electronic Supplementary Information), we can construct the following balance:



In this case, the O radicals will readily recombine with the C radicals into CO, and with the H radicals into H<sub>2</sub>O.

When adding 2 mol% CH<sub>4</sub>, (3), (4) and (5) become:



Hence, besides forming CO and H<sub>2</sub>O, the C and H radicals in excess will form other products, such as CH<sub>3</sub>OH, HCN, NH<sub>3</sub> and HNCO, as revealed in Figures 2 and 3. From these stoichiometric balances, it is also clear that the use of CH<sub>4</sub> as hydrogen source can lead to an increase in the CO selectivity. Indeed, when increasing the CH<sub>4</sub> content from 0.1 to 2 mol% the CO peak in the FTIR spectra increases by 42 % (see Figure 2).

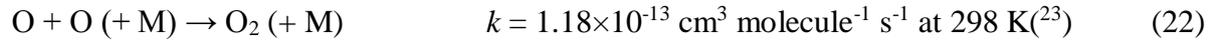
In theory the formation of these additional components should not be a major problem, unlike the NO<sub>x</sub> formation we are aiming to inhibit, since CH<sub>3</sub>OH, HCN and HNCO can be condensed from the CO stream, and for NH<sub>3</sub> efficient scrubbing systems exist.

#### **4. Oxygen scavenging chemistry**

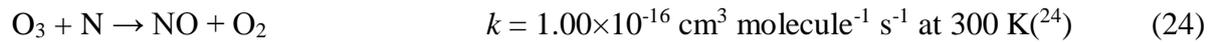
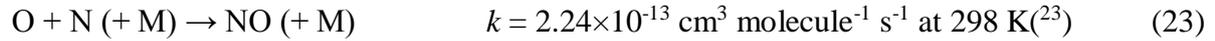
The experimental results presented in section 2.1 clearly show that the addition of CH<sub>4</sub> as a chemical oxygen scavenger does indeed suppress the formation of NO<sub>x</sub>, *in-situ*. The observed

trends can be explained by looking at the different reaction rate coefficients of the most important reactions.

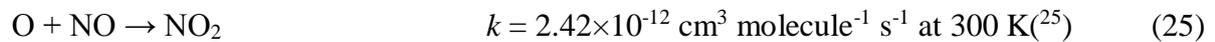
Without a hydrogen source, the main components of the mixture are: the unreacted CO<sub>2</sub> and N<sub>2</sub>, the CO<sub>2</sub> electron impact dissociation products CO and O, and, to a very small extent, the N<sub>2</sub> electron impact dissociation product N and the electron impact excited metastable N<sub>2</sub>(A<sup>3</sup>). However, due to its high dissociation energy threshold, the conversion of N<sub>2</sub>, and thus the concentration of N is very low (~10<sup>17</sup> cm<sup>-3</sup>), for a DBD plasma.<sup>9</sup> In addition, although the concentration of N<sub>2</sub>(A<sup>3</sup>) is higher (~2×10<sup>18</sup> cm<sup>-3</sup>), only ~2 % (~4×10<sup>16</sup> cm<sup>-3</sup>) takes part in the formation of NO<sub>x</sub>, due to its fast quenching processes.<sup>9</sup> For these main components, we can establish the following reaction chemistry, which recombines most of the O radicals to form O<sub>2</sub>:



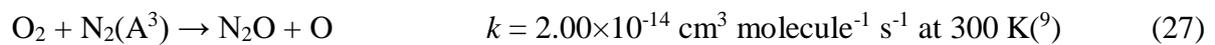
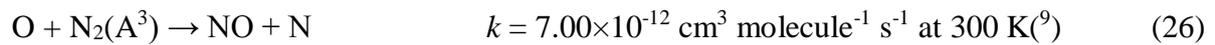
However, part of the O radicals, as well as O<sub>3</sub>, react with the few N radicals (see Figure 1):



Subsequently, part of the O radicals react with the formed NO:

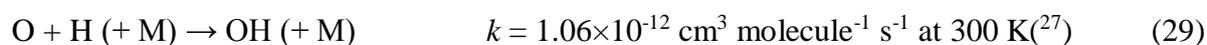


Additionally, the metastable N<sub>2</sub>(A<sup>3</sup>) also reacts with the O radicals and O<sub>2</sub>:

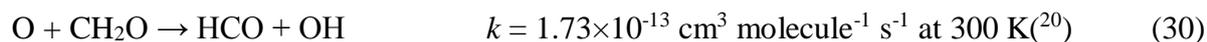


When a small amount (< 2 mol%) of CH<sub>4</sub> is added as a hydrogen source, the main components of the mixture are: the unreacted CO<sub>2</sub>, N<sub>2</sub> (and to a minor extent CH<sub>4</sub>), the CO<sub>2</sub> electron impact dissociation products CO and O, the N<sub>2</sub> electron impact dissociation product N (to a very small extent) and the electron impact excited metastable N<sub>2</sub>(A<sup>3</sup>), and the CH<sub>4</sub> electron impact dissociation products CH<sub>x</sub> and H.<sup>17,18</sup> Up to 0.5 mol% of CH<sub>4</sub> added, the conversion of CH<sub>4</sub> is close to 100 %, for 1 mol% of CH<sub>4</sub> added, the conversion is still 89 %, but for 2 mol% of CH<sub>4</sub> added, the conversion decreases to 59 % (see Electronic Supplementary Information Table S3 and Figure S3). To effectively trap the O radicals and to suppress the formation of NO<sub>x</sub> and N<sub>2</sub>O, *in-situ*, the scavenging reactions need to be faster than reactions 22 to 27 described above. It is important to note that the reaction rate coefficients can only give us an indication of the speed of reaction, so the information presented above needs to be put in perspective. In order to determine the real, exact reaction rates, we would also need to know the densities of all the species and the various chemical equilibria involved. Those can be obtained through the development of a complete and extensive chemical kinetics model.

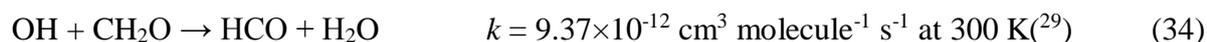
First, the O radical scavenging reaction rate coefficients with H and CH<sub>3</sub> radicals (see below) are clearly in the same order and higher than those for the above reactions (22, 23 and 26). Furthermore, the concentrations of H and CH<sub>3</sub> radicals (~2.5x10<sup>17</sup>–5x10<sup>18</sup> cm<sup>-3</sup>, based on the (nearly) full conversion of CH<sub>4</sub> at 0.1 to 2 % CH<sub>4</sub> added) are higher than those of the N radicals (~10<sup>17</sup> cm<sup>-3</sup>; see above) and available metastable N<sub>2</sub>(A<sup>3</sup>) (~4x10<sup>16</sup> cm<sup>-3</sup>; see above). Hence, these reactions are estimated to be faster, which means that H and CH<sub>3</sub> radicals are indeed effective chemical oxygen scavengers:



The CH<sub>2</sub>O radical further reacts towards the formation of OH:



The formed OH radicals get rapidly trapped into H<sub>2</sub>O and CH<sub>3</sub>OH by subsequent reactions (32-35), some of them are even faster than the initial reactions (29-31) forming OH. This, in turn, enhances the formation of OH by Le Chatelier's principle, since these reactions rapidly remove the OH radicals from the mixture:



In general, all these chemical reactions (28 to 35) provide a clear indication of how the addition of CH<sub>4</sub>, as an oxygen scavenger, suppresses the formation of NO<sub>x</sub> and possibly N<sub>2</sub>O. As mentioned above, the increase in the N<sub>2</sub>O peak seems contradictory, at first, especially since the formation of O<sub>2</sub> is severely suppressed. One possible explanation could be that the formation of N<sub>2</sub>O is effectively suppressed, and that its concentration decreases, but this is masked in the FTIR spectra due to interferences with other compounds. Indeed, HNCO (2254–2268 cm<sup>-1</sup>),<sup>30,31</sup> NCO (2175 cm<sup>-1</sup>)<sup>31</sup> and NCO + OH interactions (2237 cm<sup>-1</sup>)<sup>31</sup> have almost the same FTIR bands as N<sub>2</sub>O (2233 cm<sup>-1</sup>),<sup>21</sup> making it likely that the increased peak in the range 2210–2250 cm<sup>-1</sup> is the result of an increase of the (H)NCO concentration, which masks the decrease of the N<sub>2</sub>O concentration.

Another plausible explanation could be that, although the O<sub>2</sub> formation is suppressed, N<sub>2</sub>O is being formed through new different pathways, as a result of the formation of HCN and NH<sub>3</sub>.

For high temperature conditions, this has been detailed in numerous studies found in the literature describing the combustion (de-)NO<sub>x</sub> (and fuel NO<sub>x</sub>) chemistry.<sup>11,12</sup> In the next section we analyse whether this chemistry is also relevant for the current low temperature plasma process under study.

## **5. de-NO<sub>x</sub> chemistry**

Despite scavenging the reactive O species to suppress the NO<sub>x</sub> and N<sub>2</sub>O formation, the presence of a hydrogen source also leads to a variety of reactants (such as HCN and NH<sub>3</sub>), leading, in turn, to the additional formation (or destruction) of NO<sub>x</sub> or N<sub>2</sub>O. Figure 4 gives a visual representation of how, at low temperature, a general NO<sub>x</sub> reaction scheme of these interactions might look like, for a CO<sub>2</sub>:N<sub>2</sub> plasma with the addition of CH<sub>4</sub>. It is important to note that this reaction scheme is only of a general character. It is based on the products observed with the FTIR and on the most important reactions, defined by their rate coefficients presented in Section 2.4 of the Electronic Supplementary Information. To construct an accurate fully supported chemical pathway, it is necessary to build a complete plasma chemical kinetics model that includes a detailed description of the NO<sub>x</sub> and by-product chemistry, supported and validated by an extensive quantitative experimental study. For which the current analysis, together with the recent work from Wang et al.,<sup>16</sup> can already provide a foundation.



and N<sub>2</sub>O) or O (to form HNO). The formation of CH<sub>3</sub>OH is also delayed until an excess of CH<sub>4</sub> is added to the mixture (Figure 3b), probably due to the consumption of CH<sub>x</sub> in the de-NO<sub>x</sub> chemistry. Upon addition of CH<sub>4</sub>, the NO<sub>2</sub> decreases more than the NO concentration (Figure 3a) due to the interconversion of NO<sub>2</sub> into NO through reactions with H and O, and due to the formation of NO through several reactions starting from NH<sub>x</sub>, HNO and NCO. Nevertheless, the NO concentration continues to decrease, due to destruction reactions with NH<sub>x</sub>, CH and H. Finally, N<sub>2</sub>O is formed from NO through reactions with NH and NCO, and destroyed by CH, whereas HNCO is formed by reaction of NCO with HCO, HNO and CH<sub>2</sub>O, indicating that HNCO is a stable end-product, and that N<sub>2</sub>O is converted into HCN as stable end-product. As a result, the N<sub>2</sub>O concentration is most likely decreasing and the increased peak at 2233 cm<sup>-1</sup> (Figure 2) is, in fact, due to the formation of HNCO, rather than an increase in N<sub>2</sub>O concentration.

## 6. Discussion and outlook

We have demonstrated that it is possible to reduce the amount of NO<sub>x</sub> produced during plasma-based CO<sub>2</sub> splitting in the presence of N<sub>2</sub> simply by adding a hydrogen source such as CH<sub>4</sub>, leading to the almost stoichiometric *in-situ* trapping of oxygen. Adding 1 mol% of CH<sub>4</sub> of the total mixture yields NO<sub>2</sub> and NO FTIR absorbance peaks that are 82 % and 51 % lower than without addition of CH<sub>4</sub>. Even higher reductions, up to 96 % and 63 %, are possible when a stoichiometric excess of the hydrogen source is added, which was 2 mol% CH<sub>4</sub> in our case. However, in that case, the excess hydrogen and carbon radicals will lead to the regular plasma-based reforming chemistry, creating several by-products in low concentrations, such as NH<sub>3</sub>, HCN, CH<sub>3</sub>OH and probably HNCO.

From the data analysis it becomes clear that two processes are responsible for reducing the amount of NO<sub>x</sub> produced. The first one is—the process we were aiming for—the direct

inhibition of NO<sub>x</sub> formation through the fast oxygen scavenging chemistry by the H and CH<sub>x</sub> radicals, arising from the introduced CH<sub>4</sub>. The second one is the known reduction of NO<sub>x</sub> to N<sub>2</sub> through the presence of reducing agents, in this case occurring at room temperature.

These findings suggest that impure CO<sub>2</sub> mixtures containing N<sub>2</sub> may be used as a feedstock, which could have a significant positive impact on the implementation of plasma-based CO<sub>2</sub> conversion research. As a result, there are several interesting follow-up questions. In the present study, we used the most convenient source of hydrogen, CH<sub>4</sub>, but it would be interesting to investigate other hydrogen sources.<sup>14</sup> The most fundamental one would be H<sub>2</sub>, which could theoretically result in fewer by-products (cf. chemical analysis above). However, we could also look into greener and more sustainable hydrogen sources, such as glycerol.<sup>32</sup> From the analysis side, an important challenge to be addressed in future studies is the issue of N<sub>2</sub>O and (H)NCO identifications. Higher resolution FTIR, or separate N<sub>2</sub>O detection using a customized GC (with TCD, ECD, NPD or MS) or custom sensors, might offer a solution.

Additionally, to capture the complete complexity of the underlying mechanisms and to be able to fully analyse and comprehend all the chemical pathways, it will be necessary to build a complete plasma chemical kinetics model with a detailed NO<sub>x</sub> and by-product chemistry, supported and validated by a wide range of experiments. A good starting point for the development of such a model would be to expand the NO<sub>x</sub> chemistry from Wang et al.'s recent work on CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub> mixtures.<sup>16</sup>

It would also be interesting to see whether the same effect can be found for different plasma types, especially for microwave (MW) and gliding arc (GA) plasmas. For these plasmas, the formation of NO<sub>x</sub> is much higher, and the dominant pathway proceeds through vibrationally excited N<sub>2</sub> states, rather than through the metastable N<sub>2</sub> state and N radicals.<sup>9,10</sup>

Finally, these results are a clear indication that the plasma chemistry can be controlled to a certain extent by adding small amounts of additives; a similar demonstration has been given by Snoeckx et al.<sup>33</sup> in their work on the selective formation of methanol. Despite the seeming trivialness of this insight, directing more research towards simple chemical intervention steps—before turning to complex engineering or plasma-catalysis combinations—could lead to short-term promising advancements in the field of plasma-based CO<sub>2</sub> conversion and hydrocarbon reforming.

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