Supressing the formation of NOx and N2O in a CO2/N2 dielectric barrier discharge plasma by adding CH4: Scavenger chemistry at work

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1. Materials and methods

1.1. Plasma reactor

Experiments were carried out in a coaxial DBD reactor, consisting of a stainless steel mesh (high voltage electrode) wrapped over the outside of a quartz tube with an outer diameter of 22 mm and an inner diameter of 16.5 mm. A stainless steel rod with an outer diameter of 13 mm, placed at the center of the tube, was used as ground electrode. The length of the discharge region was 90 mm, with a discharge gap of 1.75 mm, resulting in a discharge volume of 7.4 cm³. The DBD reactor was powered by an AC high-voltage power supply (AFS, custom made), providing a maximum peak-to-peak voltage of 40 kV and a variable frequency of 1–90 kHz. CO₂, N₂, and CH₄ (Air Liquide, Alphagaz 1, 99.999 %) were used as feed gases, with a total flow rate of 611 mL min⁻¹. The CO₂:N₂ ratio and the CH₄ content were controlled independently with mass flow controllers (Bronkhorst, EL-Flow select F-210CV). The reactor was operated at atmospheric temperature and pressure. The total current was recorded by a Rogowski-type current monitor (Pearson 4100), and a high voltage probe was used to measure the applied voltage. The voltage on the external capacitor (10 nF) was also recorded in order to obtain the charge generated in the discharge. Finally, all the electrical signals were sampled by a four-channel digital oscilloscope (Picotech PicoScope 64201), and the discharge power was obtained using a control system that calculates the area of the Q-U Lissajous figures. The specific energy input (SEI) was based on the plasma power divided by the total gas flow rate (120 W / 611 mL·min⁻¹ = 12 kJ L⁻¹).
1.2. Product analysis

We applied Fourier transform infrared spectroscopy (FTIR; Thermo Fischer Scientific, Nicolet 380) to study the formation of NOx compounds (i.e., NO, NO2, N2O3 and N2O5) and N2O. By inserting a 2-m IR gas cell in the FTIR spectrometer, we obtained an IR absorption spectrum showing all IR active vibrations. During the experiments, an FTIR resolution of 1 cm\(^{-1}\) was used, resulting in a spectrum being taken every 15 s. FTIR bands corresponding to an IR active functional group of the gases were monitored. Figure S4 shows the spectrum for a 1:1 mixture CO2:N2 without the addition of CH4. For basic qualitative measurements, this technique provides close-to-real-time information on gas phase production of the N-containing compounds.

2. Detailed results

This section provides detailed information on the input conditions and results.
2.1. Experimental input conditions

Table S1. Overview of the compositions of the various gas mixtures used in the experiments.

<table>
<thead>
<tr>
<th>No.</th>
<th>CO₂ mL/min</th>
<th>N₂ mL/min</th>
<th>CH₄ mL/min</th>
<th>CO₂ %</th>
<th>N₂ %</th>
<th>CH₄ %</th>
<th>CO₂:N₂ Ratio</th>
<th>Power Watt</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0</td>
<td>305</td>
<td>305</td>
<td>0</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>1:1</td>
<td>120</td>
</tr>
<tr>
<td>E1</td>
<td>305</td>
<td>306</td>
<td>0.78</td>
<td>49.89</td>
<td>49.98</td>
<td>0.13</td>
<td>1:1</td>
<td>120</td>
</tr>
<tr>
<td>E2</td>
<td>305</td>
<td>304</td>
<td>1.59</td>
<td>49.86</td>
<td>49.89</td>
<td>0.25</td>
<td>1:1</td>
<td>120</td>
</tr>
<tr>
<td>E3</td>
<td>304</td>
<td>304</td>
<td>3.11</td>
<td>49.72</td>
<td>49.77</td>
<td>0.51</td>
<td>1:1</td>
<td>120</td>
</tr>
<tr>
<td>E4</td>
<td>303</td>
<td>303</td>
<td>4.60</td>
<td>49.59</td>
<td>49.65</td>
<td>0.75</td>
<td>1:1</td>
<td>120</td>
</tr>
<tr>
<td>E5</td>
<td>302</td>
<td>302</td>
<td>6.09</td>
<td>49.47</td>
<td>49.53</td>
<td>1.00</td>
<td>1:1</td>
<td>120</td>
</tr>
<tr>
<td>E6</td>
<td>302</td>
<td>302</td>
<td>7.00</td>
<td>49.43</td>
<td>49.43</td>
<td>1.15</td>
<td>1:1</td>
<td>120</td>
</tr>
<tr>
<td>E7</td>
<td>301</td>
<td>301</td>
<td>9.18</td>
<td>49.22</td>
<td>49.28</td>
<td>1.50</td>
<td>1:1</td>
<td>120</td>
</tr>
<tr>
<td>E8</td>
<td>300</td>
<td>299</td>
<td>12.36</td>
<td>49.04</td>
<td>48.93</td>
<td>2.02</td>
<td>1:1</td>
<td>120</td>
</tr>
</tbody>
</table>

2.2. Experimental results for CH₄ addition

Table S2. Overview of the different FTIR absorbance logging bands for experiments with addition of CH₄.

<table>
<thead>
<tr>
<th>FTIR band</th>
<th>NO a.u.</th>
<th>NO₂ a.u.</th>
<th>N₂O a.u.</th>
<th>CO a.u.</th>
<th>CH₃OH a.u.</th>
<th>HCN a.u.</th>
<th>NH₃ a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0</td>
<td>0.154</td>
<td>0.192</td>
<td>0.175</td>
<td>0.203</td>
<td>-0.001</td>
<td>-0.002</td>
<td>0.000</td>
</tr>
</tbody>
</table>

CH₄ addition

| E1 | 0.089 | 0.130 | 0.248 | 0.117 | -0.003 | 0.001 | -0.001 |
| E2 | 0.089 | 0.111 | 0.252 | 0.109 | -0.002 | 0.003 | -0.006 |
| E3 | 0.087 | 0.068 | 0.298 | 0.117 | 0.001  | 0.010 | -0.002 |
| E4 | 0.076 | 0.059 | 0.331 | 0.118 | 0.008  | 0.013 | -0.002 |
| E5 | 0.076 | 0.034 | 0.362 | 0.137 | 0.017  | 0.002 | 0.007  |
| E6 | 0.076 | 0.025 | 0.359 | 0.136 | 0.018  | 0.023 | 0.004  |
| E7 | 0.067 | 0.011 | 0.420 | 0.154 | 0.038  | 0.041 | 0.020  |
| E8 | 0.057 | 0.008 | 0.465 | 0.166 | 0.088  | 0.063 | 0.098  |
Table S3. Overview of the CH₄ conversion, based on the FTIR absorbance at 3028 cm⁻¹, for experiments with added CH₄.

<table>
<thead>
<tr>
<th>No.</th>
<th>CH₄ conc.</th>
<th>absorbance</th>
<th>CH₄ conc.</th>
<th>absorbance</th>
<th>CH₄ conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
<td>N.A.</td>
</tr>
<tr>
<td>E1</td>
<td>0.128</td>
<td>0.072</td>
<td>-0.002</td>
<td>0.00</td>
<td>100.0</td>
</tr>
<tr>
<td>E2</td>
<td>0.254</td>
<td>0.106</td>
<td>-0.001</td>
<td>0.00</td>
<td>100.0</td>
</tr>
<tr>
<td>E3</td>
<td>0.509</td>
<td>0.175</td>
<td>0.024</td>
<td>0.014</td>
<td>97.2</td>
</tr>
<tr>
<td>E4</td>
<td>0.753</td>
<td>0.180</td>
<td>0.048</td>
<td>0.053</td>
<td>92.9</td>
</tr>
<tr>
<td>E5</td>
<td>0.998</td>
<td>0.219</td>
<td>0.070</td>
<td>0.110</td>
<td>89.0</td>
</tr>
<tr>
<td>E6</td>
<td>1.146</td>
<td>0.240</td>
<td>0.086</td>
<td>0.162</td>
<td>85.9</td>
</tr>
<tr>
<td>E7</td>
<td>1.502</td>
<td>0.279</td>
<td>0.142</td>
<td>0.423</td>
<td>71.8</td>
</tr>
<tr>
<td>E8</td>
<td>2.021</td>
<td>0.322</td>
<td>0.202</td>
<td>0.828</td>
<td>59.0</td>
</tr>
</tbody>
</table>

Figure S2. Correlation between the CH₄ concentration and the FTIR absorbance of CH₄ at 3028 cm⁻¹, for blank measurements with added CH₄.
The correlation between the known added CH\textsubscript{4} concentration and the FTIR absorbance of CH\textsubscript{4} at 3028 cm\textsuperscript{-1} for the blank measurements (see Figure S2) allowed us to estimate the conversion of CH\textsubscript{4} during our experiments, by correlating the absorbance measured at 3028 cm\textsuperscript{-1} for the plasma measurements with the CH\textsubscript{4} concentration, using the following function:

\[
y = 0.22297 \cdot x^{0.52386} \leftrightarrow x = \left(\frac{y}{0.22297} \right)^{1/0.52386}
\]

(eq.1)

The obtained CH\textsubscript{4} concentration was then used, together with the original CH\textsubscript{4} concentration, to calculate the conversion of CH\textsubscript{4} (see Table S3). From Table S3 and Figure S3, it is clear that upon adding more CH\textsubscript{4} the CH\textsubscript{4} conversion starts to decrease and upon adding more than 0.75 to 1.00 % CH\textsubscript{4} (the stoichiometric amount) the conversion starts decreasing more rapidly. In Figure S3 this can be seen through the asymptotic fit through the effective CH\textsubscript{4} conversion.

**Figure S3.** Correlation between CH\textsubscript{4} concentration and the effectiveness of the conversion of CH\textsubscript{4}; the red line indicates the case in which all the added CH\textsubscript{4} is completely converted.
2.3. FTIR spectra

FTIR data were obtained by first subtracting the spectra from a blank measurement taken before the plasma was turned on, and then subtracting the spectrum taken for H$_2$O.

![FTIR spectrum](image)

**Figure S4.** FTIR spectrum of E0, 1:1 mixture CO$_2$:N$_2$ without CH$_4$ added.

![FTIR spectrum](image)

**Figure S5.** FTIR spectrum of E1, 1:1 mixture CO$_2$:N$_2$ with 0.13 % CH$_4$ added.
**Figure S6.** FTIR spectrum of E2, 1:1 mixture CO$_2$:N$_2$ with 0.25 % CH$_4$ added.

**Figure S7.** FTIR spectrum of E3, 1:1 mixture CO$_2$:N$_2$ with 0.5 % CH$_4$ added.
Figure S8. FTIR spectrum of E4, 1:1 mixture CO₂:N₂ with 0.75 % CH₄ added.

Figure S9. FTIR spectrum of E5, 1:1 mixture CO₂:N₂ with 1.0 % CH₄ added.
Figure S10. FTIR spectrum of E6, 1:1 mixture CO₂:N₂ with 1.15 % CH₄ added.

Figure S11. FTIR spectrum of E7, 1:1 mixture CO₂:N₂ with 1.5 % CH₄ added.
2.4. Detailed de-NOx chemistry

If we first look at the formation of HCN, the key reactions are:

\[
\begin{align*}
\text{CH}_3 + \text{N} & \rightarrow \text{HCN} + \text{H}_2 \quad k = 1.40 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K} \quad (S1) \\
\text{CH}_2 + \text{N} & \rightarrow \text{HCN} + \text{H} \quad k = 5.00 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K} \quad (S2) \\
\text{CN} + \text{H} & \rightarrow \text{HCN} \quad k = 1.73 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K} \quad (S3) \\
\text{CH} + \text{NO} & \rightarrow \text{HCN} + \text{O} \quad k = 2.01 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K} \quad (S4)
\end{align*}
\]

Additionally, from Figure 3b (in the main article), we already know that the HCN concentration increases linearly from the start, indicating that the regular loss processes during the combustion chemistry (leading to prompt NO) appear irrelevant here.\(^4\) This means that instead of being a source of NO (as in the high temperature combustion conditions), in the current low temperature plasma conditions HCN is a sink for the created N species, which also contributes to the suppression of the NO\(_x\) formation by trapping the reactive N radicals.
The NH₃ chemistry appears to be quite different. Figure 3b (from the main paper) reveals that the formation of NH₃ occurs after an excess of CH₄ has been added. If we examine the key formation reactions, we notice that they all rely on NH₂:

\[
\text{NH}_2 + \text{NH}_2 \rightarrow \text{NH} + \text{NH}_3 \quad k = 5.00 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K} \quad (S5)
\]

\[
\text{NH}_2 + \text{H}_2 \rightarrow \text{H} + \text{NH}_3 \quad k = 2.10 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K} \quad (S6)
\]

\[
\text{NH}_2 + \text{H} \rightarrow \text{NH}_3 \quad k = 7.36 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K} \quad (S7)
\]

This shows that, similarly to what occurs in combustion chemistry, NHₓ interacts with the NOₓ species that are present. When examining the most important reaction rate coefficients for NO and NO₂, we find that the key NO₂ destruction reactions are:

\[
\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH} \quad k = 1.40 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K} \quad (S8)
\]

\[
\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \quad k = 9.71 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K} \quad (S9)
\]

\[
\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \quad k = 7.48 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K} \quad (S10)
\]

\[
\text{NO}_2 + \text{CN} \rightarrow \text{NO} + \text{NCO} \quad k = 8.05 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K} \quad (S11)
\]

These reactions explain why the NO₂ concentration decreases more rapidly than the NO concentration, as shown in Figure 3a in the main paper, as NO₂ is being converted into NO (and HNO₃).

The following NO formation reactions occur, through HNO as intermediate:

\[
\text{NH}_2 + \text{O} \rightarrow \text{H} + \text{HNO} \quad k = 7.47 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K} \quad (S12)
\]

\[
\text{NH}_2 + \text{HNO} \rightarrow \text{NH}_3 + \text{NO} \quad k = 3.56 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K} \quad (S13)
\]

\[
\text{O} + \text{HNO} \rightarrow \text{OH} + \text{NO} \quad k = 5.99 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K} \quad (S14)
\]
OH + HNO → H₂O + NO \quad k = 1.51\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S15)

CH₃ + HNO → CH₄ + NO \quad k = 1.04\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S16)

CH₃O + HNO → CH₃OH + NO \quad k = 5.00\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S17)

It is important to note that some of the most important NO destruction reactions taking place simultaneously, lead to the formation of HNO, indicating that there is an important equilibrium between NO and HNO:

NO + H → HNO \quad k = 2.43\times10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S18)

Additional important NO formation and destruction reactions are:

N + OH → H + NO \quad k = 5.05\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S19)

O + NCO → CO + NO \quad k = 7.51\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 500 K} (S20)

NO + N → N₂ + O \quad k = 3.11\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S21)

CH + NO → HCN + O \quad k = 2.01\times10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S22)

As mentioned above, the NH and NH₂ species also play an important role in both the formation and destruction of NO:

NH + O → H + NO \quad k = 1.16\times10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S23)

NO + NH₂ → N₂ + H₂O \quad k = 1.24\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S24)

NO + NH₂ → NNH + OH \quad k = 1.37\times10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S25)

NNH + NO → N₂ + HNO \quad k = 5.00\times10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S26)

The presence of NH and NCO also create new pathways for the formation of N₂O:

NO + NCO → CO + N₂O \quad k = 1.54\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 300 K} (S27)
NO + NH → N\textsubscript{2}O + H \quad k = 2.87 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K}^{(17)} \quad \text{(S28)}

Whereas the presence of CH actively contributes to the destruction of N\textsubscript{2}O through reactions with higher reaction rate coefficients:

N\textsubscript{2}O + CH → HCN + NO \quad k = 8.41 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K}^{(18)} \quad \text{(S29)}

N\textsubscript{2}O + CH → HCO + N\textsubscript{2} \quad k = 8.41 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K}^{(18)} \quad \text{(S30)}

We also find the traditional combustion pathway for the N\textsubscript{2}O destruction to be irrelevant:

N\textsubscript{2}O + H → N\textsubscript{2} + OH \quad k = 3.18 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 375 \text{ K}^{(19)} \quad \text{(S31)}

N\textsubscript{2}O + OH → N\textsubscript{2} + HO\textsubscript{2} \quad k = 8.09 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K}^{(1)} \quad \text{(S32)}

Finally, the reactions for the formation and destruction of NCO are:

CH + NO → H + NCO \quad k = 3.99 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K}^{(20)} \quad \text{(S33)}

NO\textsubscript{2} + CN → NO + NCO \quad k = 8.05 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K}^{(9)} \quad \text{(S34)}

O\textsubscript{2} + CN → O + NCO \quad k = 2.42 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K}^{(3)} \quad \text{(S35)}

OH + CN → H + NCO \quad k = 7.01 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 500 \text{ K}^{(2)} \quad \text{(S36)}

NO + NCO → CO + N\textsubscript{2}O \quad k = 1.54 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K}^{(16)} \quad \text{(S37)}

H + NCO → CO + NH \quad k = 8.90 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 500 \text{ K}^{(2)} \quad \text{(S38)}

O + NCO → CO + NO \quad k = 7.51 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 500 \text{ K}^{(2)} \quad \text{(S39)}

The formed NCO in turn is the precursor to form HNCO through reactions with HCO, HNO and CH\textsubscript{2}O, whose production mechanisms have been described earlier:

HCO + NCO → HNCO + CO \quad k = 7.01 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 500 \text{ K}^{(2)} \quad \text{(S40)}
HNO + NCO → HNCO + NO \quad k = 3.01 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \text{ at } 500 \text{ K} \quad (S41)

CH\textsubscript{2}O + NCO → HNCO + HCO \quad k = 1.00 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \text{ at } 500 \text{ K} \quad (S42)

Again the traditional combustion pathway for (H)NCO formation is irrelevant:

HCN + O → H + NCO \quad k = 5.03 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \text{ at } 300 \text{ K} \quad (S43)

NCO + H\textsubscript{2} → HNCO + H \quad k = 7.68 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \text{ at } 300 \text{ K} \quad (S44)

3. References


