



The Mechanism of Non-Catalytic CO₂ Reduction in Non-Thermal Plasma Environment – In Situ FTIR Studies

Julia Moszczyńska¹, Xinying Liu², Yali Yao², Marek Wiśniewski^{1,*}

¹ Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, 87-100 Torun, Poland

² Institute for Catalysis and Energy Solutions, University of South Africa, c/o Christiaan de Wet & Pioneer, Florida 1709, Roodepoort, Gauteng, South Africa.
marekw@umk.pl

Abstract. Carbon dioxide conversion is considered a promising solution to the problem of global warming and the need for renewable energy storage. Although it is challenging to develop a process that combines the complete conversion of CO₂ to CO in the absence of O₂, this paper describes such a solution. In this study, the CO₂ splitting was investigated and monitored in situ using a plasma generated in a DBD reactor without the participation of a catalyst. The results of excited-phase FTIR spectra indicate that gaseous H₂, in contrast to Ar, acting as a scavenger of excited CO₂ species significantly improves the process efficiency and minimizes the formation of oxygen.

Keywords: Carbon dioxide splitting, non-thermal plasma, mechanism

1 Introduction

Greenhouse gas emissions, especially carbon dioxide, are among the most serious environmental problems associated with the industry's dynamic development. Developing new methods of protecting the atmosphere is one of the most significant challenges for sustainable development.[1] The Carbon Capture, Utilization, and Storage (CCUS) strategy, i.e., capturing and storing CO₂, as well as its subsequent use or utilization, offers great promise in this area.

As we strive for net-zero emissions, we cannot afford to dismiss CCUS as “too expensive”. It is the only group of technologies capable of reducing emissions in critical economic sectors and removing CO₂ to offset unavoidable emissions – a balance essential for achieving net - zero. CCUS is currently the least costly or only practical option for significant emission reductions in some sectors, including heavy industry.[2]

Instead of storage, CO₂ can be used as a raw material to synthesize fuels and chemicals. However, because of the high degree of oxidation and its thermodynamic stability, the processes of CO₂ reduction are energy-intensive.[3,4] Nevertheless, CO₂ recycling can provide benefits that offset the capture costs. [2]

Plasma, the fourth state of matter, can elegantly address these issues. It comprises a mix of excited particles and positively and negatively charged ions. Moreover, plasma

technology offers several benefits, including rapid reactions, immediate control, and environmental friendliness.[3]

Under these conditions, CO₂ molecules gain enough energy to split into carbon monoxide (CO) and oxygen. [2,5] Although CO can be easily converted into base chemicals and energy carriers, like methanol or methane, using existing infrastructure and conventional chemical processes, the presence of oxygen, an oxidizing agent, complicates the direct utilization of CO and leads to CO₂ formation through recombination. [3] Separating oxygen from CO remains a significant challenge and a major cost factor. [6]

A potential separation method, still in development, involves using zeolites and requires repeated adsorption-regeneration cycles, but no commercial solutions are currently available. [7]. A simple solution is proposed: using H-plasma as active oxygen scavengers.

It was stated [3,8] that CO₂ under non-thermal plasma (NTP) conditions forms the excited states which reactions are dominated by three main processes: (i) electron-impact dissociation leading to the formation of CO and O atoms, (ii) the ionization, during which CO₂⁺ ions are formed, and (iii) dissociative electron attachment and forming CO and O⁻ ions. [3,9,10] Nevertheless, the mechanism is still far from being well understood.

Moreover, a fraction of the ions and molecules from these processes can easily recombine, forming back CO₂. Incorporating an oxygen scavenger seems reasonable for shifting the equilibrium state, thus increasing the CO₂ conversion rate. Therefore, examining the reaction mechanism in the presence of different agents is reasonable. To the best of the authors' knowledge, no reports describe such a mechanism.

2 Materials and methods

In situ FTIR spectra were recorded using the Thermo Fisher Nicolet IS20 spectrophotometer (with MCT detector). All spectra were recorded with 0.5/cm resolution. Spectral changes accompanying the tested process were investigated. The respective gas phase was a background for each sample spectrum, enabling the observation of spectral changes of the gas phase inside the NTP jet (see Figure 1). A period of at least 0.5 h (monitoring continuously every 30 seconds) was held to enable the equilibrium.

The CO₂ conversion studies under NTP were carried out in a DBD reactor connected in-line with an IR-vacuum cell, described previously [11,12]. The initial pressure of CO₂ was constant and equal to 40 mBa. The gases (CO₂ and CO) were analyzed quantitatively.

CO₂ conversion was calculated as a ratio C_t/C_o , where C_t or C_o is the concentration of CO₂ at a specific time or initial, respectively.

The for CO₂/H₂ reaction the selectivity was calculated as:

$$S = \left| \frac{\Delta H_2O}{\Delta CO_2} \right| \cdot 100\%$$

as a consequence of two terminal reactions:

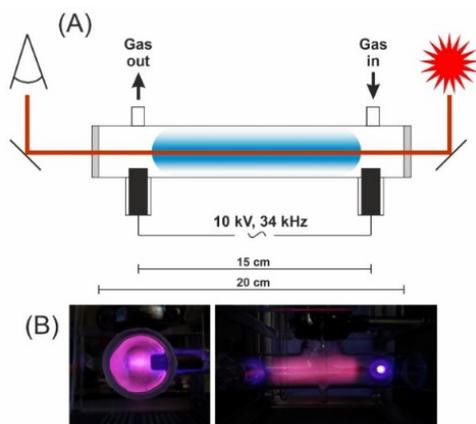
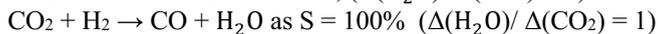
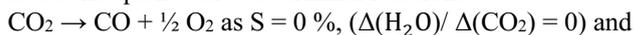


Fig. 1. A – the schematic representation of the experimental set: laser beam in FTIR spectrometer passing through the plasma reactor inside the 20 cm-long IR-gas-cell (note that the blue space represents the ionized NTP area); B – the real picture of a working gas cell under NTP.

For **ab initio** study, all the calculations (at B3LYP levels of theory using 6–311G(d,p) basis sets) were performed using geometries optimized for the parent compounds. The calculations were performed using the Gaussian ‘09 program [13].

3 Results and discussion

Figure 1 shows the scheme of a measuring system, including the IR-gas cuvette with its real photo when operating in an NTP atmosphere. It is worth paying attention to the evenly distributed plasma jet inside the cell. For all recorded spectra, the background was the spectrum of CO_2 just before switching on the plasma. Therefore, there is practically no signal on the spectra (blue in Fig. 2) before the plasma was switched on.

Figure 2 collects the obtained IR results, the left side of each panel shows the effect of CO_2 excitation in the NTP, and the right side shows the relaxation and removal of reaction products from the cell. The excitation of CO_2 in the NTP atmosphere is accompanied by the previously described [8] characteristic system of signals – negative – on the side of larger wavenumbers and positive – on the red side. The explanation is that vibrationally excited – CO_2^* molecules appear [14]. Low-intensity signals centered at 2143/cm reveal that the CO_2 auto-splitting process occurs to a low extent which is in good agreement with the literature data [3].

The high-resolution spectra (0.5/cm) disclose the presence of additional, not registered in the literature features for NTP atmosphere, at 2396 and 2383/cm.

Although the CO₂ splitting reaction in NTP has been described several times in the literature, it is most likely that due to too high resolution, these signals were not observed, or they were ignored. [3,15,16] Nevertheless, the IR bands in this region have been attributed to the presence of CO₂* [14], C₃O₂ or C₂O₂⁺ [17]. Accurate attribution requires more careful research.

After switching off the plasma (right panel Figure 2) the band of CO₂* at 2285/cm decreases immediately confirming the assumption about the presence of a CO₂ excited state. Additionally, due to the widening of the CO₂ peak, the characteristic system of positive-negative signals of hot bands [13] of CO₂ is observed. Finally, it is worth noting that all observed bands disappear within the next 8 min.

Adding an Ar to the gas stream (Figure 2B) causes, in addition to significantly reducing the intensity of the band originating from CO₂*, results in the lack of signals at 2396 and 2383/cm. Such an observation in the absence of CO bands (2143/cm) can be explained by the inhibition of the process. After switching off the NTP, only the characteristic hot CO₂ bands can be observed.

Surprisingly, when H₂ exchanges Ar in the gas stream (Figure 2C) no CO₂* signals can be observed. The only spectral changes observed are related to hot CO₂ bands and a much higher intensity of CO bands (2143/cm). Therefore, it seems reasonable to assume that H₂ acts as a scavenger of excited particles, shifting the balance of the process towards the main product – CO. The assumption is confirmed by analyzing the amount of H₂O produced (Figure 3).

A comparison of spectra recorded in NPT after 10 minutes of plasma activity (Figure 3) confirms the differences described above. The highest concentration of CO₂* occurs when only CO₂ molecules are present in the atmosphere. The addition of other gases changes the equilibrium: the addition of Ar reverses the process and H₂ accelerates towards CO.

Quantitative results confirm the positive effect of the addition of H₂. The CO₂ conversion increases 3 times from about 20% to about 60% while maintaining a very high process selectivity of about 80%.

The underground of the successful overall processes is the presence of excited and active CO₂ species. To confirm that the high-intensity band can be attributed to CO₂*, we conducted ab-initio studies of CO₂ molecules in an electric field; the results are shown in Figure 4. The collected results from only two extreme positions, i.e. parallel and perpendicular to the electric field, show clearly that with the appearance of the field, a dipole moment appears in the molecule. It is worth mentioning that all other configurations must be between these extreme positions. This observation stays in good agreement with previous reports.[18] It is very important because it leads to the conclusion that placing CO₂ in an electric field will cause an increase in the intensity of the IR bands, polarizabilities, and reactivities, as well.

Based on the above and literature data [19] one can conclude about the mechanism of CO₂ splitting under the NTP atmosphere.

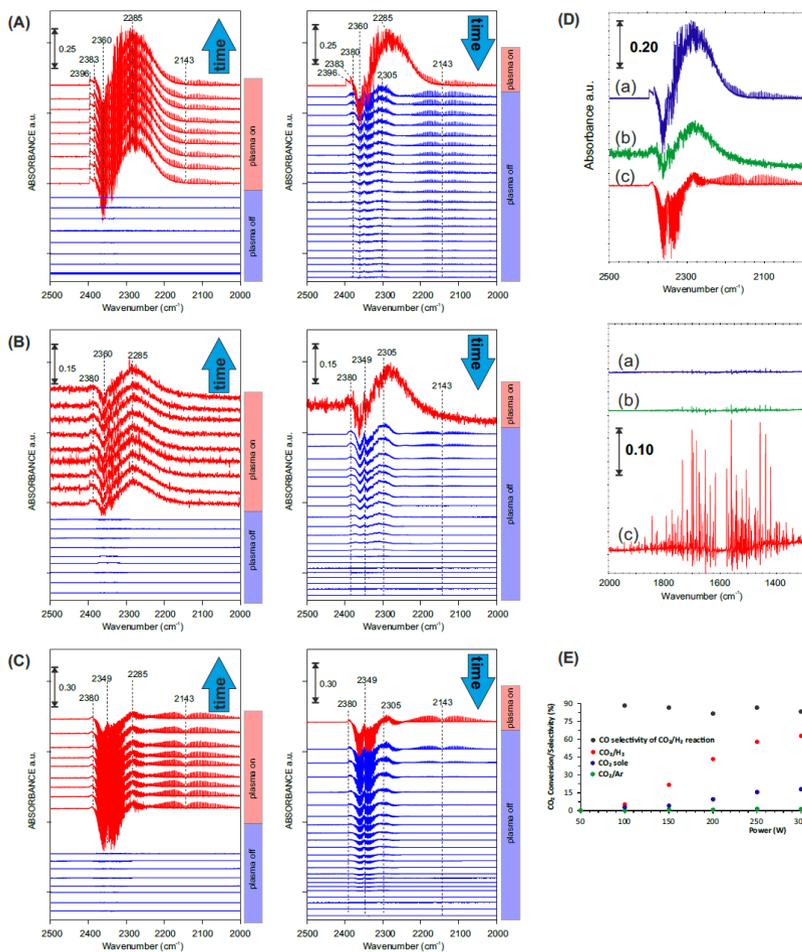
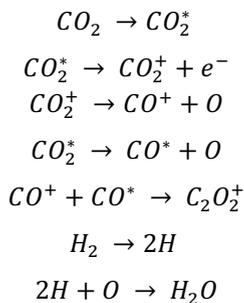


Fig. 2. Spectral changes of CO₂ splitting processes observed in-situ under NTP. (A, a) – 40 mBa CO₂, (B, b) – 40 mBa CO₂ i 40 mBa Ar; (C, c) – 40 mBa CO₂ i 40 mBa H₂.

(D) – Comparison of spectral changes of CO₂ splitting processes observed in-situ after 10 min NTP acting. (E) – Quantitative results: the overall conversion, and CO-selectivity as a function of power used.

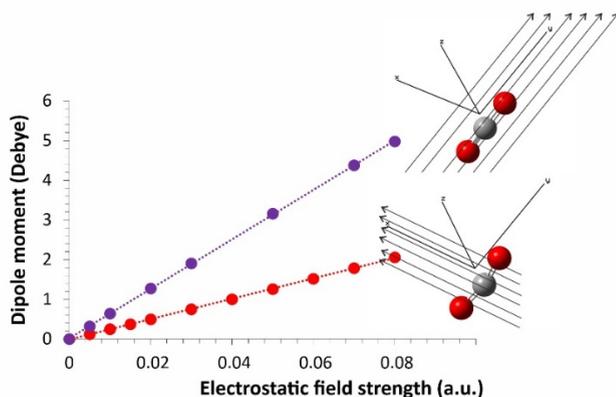


Fig. 3. Effect of electrostatic field strength on CO₂ molecule dipole moment. Note that arrows shows the direction of the field.

4 Conclusions

In summary, the non-thermal plasma activated CO₂ splitting selectively into CO has been widely studied here due to the importance of CO as a chemical feedstock for the production of synthetic fuels in Fischer-Tropsch processes. It was found that addition of an equimolar amount of H₂ as an active reagent shifts the process equilibrium towards CO thus minimizing the formation of oxygen, which hinders the reaction. Furthermore, the process can be easily manipulated by increasing the NTP power. Finally, it is worth mentioning that the results presented here are easy to scale up to industrial size and integrate with industrial processes using CO, such as Fischer-Tropsch synthesis. Such an approach changes the wastes into the source chemicals.

References

- ¹ Giannelos, S., Bellizio, F., Strbac, G., Zhang, T.: Machine learning approaches for predictions of CO₂ emissions in the building sector. *Electric Power Systems Research* **235**, 110735 (2024)
- ² Osei-Kyei, R., Narbaev, T., Xiaohua, J., Komac, U., Akomea-Frimpong, I., Castelblanco, G.: Critical review of the drivers and barriers for adopting net zero carbon procurement for construction projects, *Sustainable Futures* **8**, 100284 (2024)

- ³ Yang, H., Zhang, C., Gao, P., Wang, H., Li, X., Zhong, L., Wei W., Sun, Y.: A review of the catalytic hydrogenation of carbon dioxide into value-added hydrocarbons. *Catalysis Science and Technology* **7**, 4580–4598 (2017)
- ⁴ Jouny, M., Luc, W., Jiao, F.: General Techno-Economic Analysis of CO₂ Electrolysis Systems. *Industrial & Engineering Chemistry Research* **57**, 2165–2177 (2018)
- ⁵ Snoeckx, R., Bogaerts, A.: Plasma technology – a novel solution for CO₂ conversion? *Chemical Society Reviews* **46**, 5805–5863 (2017)
- ⁶ Van Rooij, G. J., Akse, H. N., Bongers, H. N., van de Sanden, M. C. M.: Plasma for electrification of chemical industry: a case study on CO₂ reduction. *Plasma Physics and Controlled Fusion* **60**(1), 014019 (2018)
- ⁷ Luna-Triguero, A., Vicent-Luna, J. M., Jansman, M. J., Zafeiropoulos, G., Tsampas, M. N., van de Sanden, M. C. M., Akse, H. N., Calero S.: Enhancing separation efficiency in European syngas industry by using zeolites. *Catalysis Today* **362**, 113–121 (2021)
- ⁸ Wiśniewski, M., Liu, X.: In situ FTIR study of 2D-carbon materials for CO₂ splitting under non-thermal plasma environment – selective CO production. *Journal of Material Chemistry* **11**, 10677–10683 (2023)
- ⁹ Wu, B., Xia, L., Wang, Y. F., Li, H. K.; Zeng, X. J., Tian, S. X.: Dissociative electron attachment to CO₂ produces molecular oxygen. *Nature Chemistry* **8**(3), 258–263 (2016)
- ¹⁰ Bogaerts, A., Neyts, E. C.: Plasma Technology: An Emerging Technology for Energy Storage. *ACS Energy Letters* **3**, 1013–1027 (2018)
- ¹¹ Wiśniewski, M., Terzyk, A. P.: Non-thermal plasma-assisted catalytic CO₂ conversion over Zn-TCPP 2D catalyst. *Adsorption* **26**, 1165–1171 (2020)
- ¹² Moszczyńska, J., Liu, X., Wiśniewski, M.: Non-Thermal Ammonia Decomposition for Hydrogen Production over Carbon Films under Low-Temperature Plasma—In-Situ FTIR Studies. *International Journal of Molecular Sciences* **23**, 9638 (2022)
- ¹³ Frisch, M.J. Gaussian '09; Gaussian, Inc.: Wallingford, CT, USA, (2009)
- ¹⁴ Shi, C., Ren, L., Kong, F.: Excitation of the asymmetric stretch vibration of CO₂ in OH+CO₂→H+CO₂ reaction. *Chemphyschem* **7**(4), 820–3 (2006)
- ¹⁵ Klarenaar, B. L. M., Engeln, R., van den Bekerom, D. C. M., Van De Sanden, M. C. M., Morillo-Candas, A. S., Guaitella, O.: Time evolution of vibrational temperatures in a CO₂ glow discharge measured with infrared absorption spectroscopy. *Plasma Sources Science and Technology* **26**(11), 115008 (2017)
- ¹⁶ Christensen, P. A., Ali, A. H. B. M., Mashhadani, Z. T. A. W., Carroll, M. A., & Martin, P. A. The Production of Ketene and C₂O₂ from CO₂, N₂ and CH₄ in a Non-thermal Plasma Catalysed by Earth-Abundant Elements: An In-Situ FTIR Study. *Plasma Chemistry and Plasma Processing* **38**(3), 461–484 (2018).
- ¹⁷ Marko Förstel, M., Maksyutenko, P., Mebel, A. M., Kaiser, R. I.: Pentacarbon dioxide (C₅O₂) formation and its role as a tracer of solar system evolution. *The Astrophysical Journal Letters* **818**, 2 (2016)
- ¹⁸ Randi L. Beil, Robert J. Hinde.: Ab initio electrical properties of CO₂: polarizabilities, hyperpolarizabilities, and multipole moments. *Theoretical Chemistry Accounts* **8** (2021)
- ¹⁹ Aerts, R., Somers, W., Bogaerts, A.: Carbon dioxide splitting in a dielectric barrier discharge plasma: a combined experimental and computational study. *ChemSusChem* **8**(4), 702–16 (2015)

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