Comparison of experimental and numerical results for the understanding of fundamental mechanisms in a low-pressure CO_2-CH_4 RF plasma

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Abstract: A low-pressure CO_2:CH_4 pulsed RF discharge is studied in a closed reactor to understand the fundamental mechanisms of CO_2:CH_4 plasmas. The densities of IR active species in the reactor are monitored by FTIR spectroscopy, the other densities are deduced from an atom balance. The discharge is modelled with the LoKI Boltzman and kinetic solver. The excited state O(1D) appears to be crucial to properly describe the destruction of both CO_2 and CH_4. Surface reactions are necessary to explain the behaviour of CH_4.

Keywords: CO_2, CH_4, DRM, FTIR

1. Introduction

Dry Reforming of Methane (DRM) is a process transforming CO_2 and CH_4 into CO and H_2. These two molecules can later be recombined together through the Fischer-Tropsch process to form heavier hydrocarbons (nCO + 2n+1 H_2 → C_nH_{2n+2} + nH_2O), ideal for energy storage. DRM is therefore a promising lead to tackle the current problems of CO_2 recycling and energy storage. DRM can be performed chemically but using the non-equilibrium characteristics of cold plasmas could avoid waste energy in heating [1].

However, despite a vast literature on CO_2 or on CH_4, the fundamental mechanisms of CO_2-CH_4 plasmas remain unclear. Because of the applicative interest of DRM, many DRM studies are conducted in high pressure discharges, often filamentary and often with catalysts, making the understanding of the fundamental processes of CO_2-CH_4 plasmas challenging. This work aims at determining the main reaction pathways in the gas phase of a CO_2-CH_4 plasma by comparing experimental measurements in a low-pressure RF discharge with 0D numerical simulations

2. Experimental setup and results

To this aim, a pulsed RF discharge is ignited in a closed cylindrical pyrex reactor (without any gas flow) at low pressure (a few Torr). Three copper electrodes are used: a high voltage one located at the center of the reactor and two ground electrodes at each extremity of the reactor. This system allows for a good control of the plasma volume. The electrode are placed on the outer wall of the reactor to avoid contact between the plasma and the copper electrodes which could have a catalytic effect. The plasma is ignited by a power supply capable of fast on/off switching of the RF voltage, allowing to send pulses of a few ms with a stabilisation time of the voltage of a few tens of µs. In this work, trains of plasma pulses (typically trains of 10 pulses with 5ms on and 10ms off) are sent. After each train, the densities of all the IR active species in the reactor are measured by FTIR spectroscopy (which takes approximately 1.5s), allowing to follow the densities of all the IR-active species as a function of the number of pulse sent (and ultimately as a function of the total plasma ON

time). The non IR-active species (O_2 or H_2 in this experiment) can be deduced from the atom balance thanks to the closed-reactor configuration. The exemple of a measurement in a 50:50 CO_2:CH_4 mixture with 500 trains of 10 plasma pulses is shown in plain lines on figure 1. CO and H_2 are the main products and C_2H_6 appears as an intermediate specie. CO_2 and CH_4 are not fully consumed in our experiment. The CO_2 decreases monotonously over the experiment, while CH_4 shows a reincrease at approximately 10s of plasma ON time, when the C_2H_6 starts disappearing. Once the C_2H_6 is consumed, the CH_4 starts decreasing again. The atom balance of C and H show that the carbon atoms contained in the C_2H_6 are later found again in CH_4 but also in CO. Similarly, the H atoms once contained in C_2H_6 are later found in CH_4 and H_2. This C_2H_6 decomposition in the plasma producing CH_4, CO and H_2 appears to be uncommon.
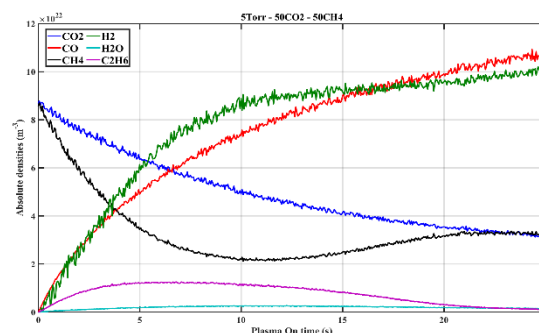

Fig 1: Evolution of the densities of the main species along plasma ON time in a 50:50 CO_2:CH_4 RF plasma at 5Torr

In this approach, several parameters can be varied to highlight their effect. The initial gas mixture is varied from pure CO_2 to 50:50 CO_2:CH_4 and the pressure is varied between 2 and 5Torr. The number of pulses per train, the duration of the pulses or the time between the pulses are also changed to select processes as a function of their characteristic time. [2] showed that the characteristic heating time during the discharge was a few ms and it was shown in [3], which followed the same experimental approach as this work for pure CO_2 plasma, that the back-reaction mechanisms producing CO_2 from O and CO had a

characteristic time of a few ms in pure CO_2 plasmas. Finally, the number of trains is also varied because it was also highlighted in [3] that reaction surfaces could happen in the long intervals between pulses when the FTIR measurement is taken.

3. Modelling

The very large number of possible reaction pathways in the CO_2-CH_4 plasmas does not allow for a straight-forward comprehension of the fundamental mechanisms. The experimental results were therefore compared with numerical results obtained with the LoKI simulation tool, which includes a Boltzmann solver to compute the EEDF and a 0D kinetic solver. A set of reactions including molecules with up to two carbon atoms was assembled from the LXCat databases (for electron kinetics) and the NIST kinetic database (for the chemical kinetics). The EEDF was computed by including only the main species (CO_2, CO, H_2, H_2O and CH_4) to avoid using molecules which did not have a complete and consistent set of reactions validated against the swarm parameters.

Starting from the initial condition, each pulse and its post-discharge was successively simulated. At each step, the main species present in the plasma were used to compute the EEDF and the plasma chemistry was then computed. The result of each step (namely the densities of all species in the plasma) served as initial conditions for the following step. The electron density was kept constant over the whole experiment and was extrapolated from similar measurement conducted in a glow discharge where the current is known. The reduced electric field was drawn from the first seconds of the experiment. It was indeed shown in [3] that the first seconds of the experiment was dominated by electron impact dissociation, allowing to draw the reduced electric field from the dissociation of CO_2. This conclusion was confirmed by the experimental mixture variation done in this work. The temperature was assumed to be the same for all pulses of the experiment. The value was taken from measurements in a conducted in a CO_2:CH_4 glow discharge at low pressure following the method described in [2].

Because all of the pulses and post-discharges are simulated individually but successively (leading to several thousands of successive simulations), the modelling of the experiment is time-consumming and therefore restricted to the cases with the smallest number of pulses.

4. Additions to the reaction scheme

The model was used to simulate the evolution of the densities along the plasma ON time, initially with a constant reduced electric field along the experiment. The first results however showed that in the first few seconds the CO_2 was under-dissociated compared to the experiment, while the CH_4 was on the opposite over-dissociated, though both dissociation are driven by electron impact dissociation. Analysis of the main processes showed that the CH_3 produced from electron impact dissociation of CH_4 was reacting with OH to form CH_3O

which in turn reacted with CO to form CO_2, leading to a strong back-reaction reforming CO_2. Additionally, the numerical results showed an overproduction of C_2H_6 from CH_3 recombination. The role of the excited state was questioned, as it was indeed shown in [4] that the excited $CO(a)$ was crucial in pure CO_2 plasmas or in [5] that the $O(1D)$ state could play an important role in O_2:CH_4 plasmas. Based on the results from [6], the reaction CH_3 + $O(1D) \rightarrow CO + H_2 + H$ was added to the reaction scheme. A temporal profile of reduced electric field was also used. The comparison of the experimental and numerical results are shown on figure 2.
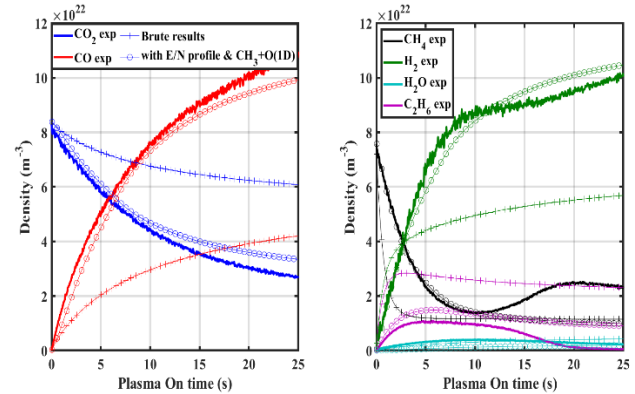

Fig 2: Comparison of the experimentally measured densities with the simulated densities. 'o' markers show the brute results and '+' marker show the results after addition of E/N temporal profile and of the CH_3+(1D) reaction

The addition of that process significantly improves the matching of the experiment and the simulation. The decrease of C_2H_6 and the reincrease of the CH_4 visible on figure 1 after 10s of plasma ON time were not observed. This process appears to be the result of surface reactions. Though a different model would be required to properly describe the surface interactions, two surface interactions were added to the reaction scheme: the adsorption of H on the wall and the reaction gas phase C_2H_6 with adsorbed H. Though these reactions are unlikely to exist as such, they show that the CH_4 reincrease could be explained by surface reaction.

5. Main reaction pathways

Though the agreement between the model and the experiment is imperfect, it is sufficient to draw insights on the main reaction pathways of low-pressure CO_2:CH_4 plasmas. CO_2 and CH_4 are mostly destroyed by electron impact. CO is produced from electron impact dissociation of CO_2 but also in large part by the added process CH_3+$O(1D)$. H_2 is produced from destruction of C_2H_6 while it is still present in the plasma and is after produced from recombination of atomic H. C_2H_6 is produced mainly from CH_3 radicals recombination and is found to be the main C_2H_Y molecule in this type of plasma due to the relatively low temperature of the discharge (few hundreds K) preventing stepwise dehydrogenation.

6. References

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