Study of the conversion pathways in CO_2 – CH_4 plasma in low pressure RF discharges

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In this work motivated by the use of syngas, the behaviour of CO_2-CH_4 plasmas is studied at low pressure in various conditions. The plasma properties are monitored in situ and time resolved in series of plasma pulses with FTIR measurements, which show that the dissociation time of CO_2 and CH_4 appears to have different values, allowing possible tuning of products formed. Experimental data are confronted to simple models.

Global warming, one of the current major challenge, brings up the necessity to control the emission of greenhouse gas such as CO_2 or CH_4, among others through capture and recycling. One promising lead to address this issue is the use of low temperature plasmas to convert greenhouse gases into “syngas”, synthetic fuel [1] through Dry Reformation of Methane (DRM) , a well-known process transforming both CO_2 and CH_4 into value - added products: CO_2 (g) + CH_4 (g) → 2CO(g) + H2(g). Though achievable chemically, the heating of the gas and subsequent waste of energy is one of the numerous drawbacks motivating the use of cold plasmas to achieve DRM. However, though CO_2 plasmas are widely studied for CO_2 conversion [2], the molecule synthesis mechanisms in CO_2 - CH_4 plasmas remain poorly known. Moreover, most of studies dedicated to DRM with plasma are performed by coupling plasma with catalysts at atmospheric pressure making the understanding of gas phase kinetic very challenging. The goal of this work is to provide experimental data allowing detailed descriptions of both the vibrational kinetics and the chemical kinetics in a CO_2 - CH_4 plasma. To this aim a dedicated reactor at low pressure, in both flowing and “static conditions” (without any gas flow), has been used in which relevant parameters (gas and vibrational temperatures, conversion rates) can be measured time resolved to investigate the chemical path and the vibrational excitation in these plasmas from a fundamental point of view.

An RF discharge is ignited in a pyrex reactor powered by a 13.56 MHz power supply allowing for fast switching on/off of the RF voltage to performed plasma pulses of few ms. Trains of plasma pulses (typically 10 pulses of 5 ms with 10 ms off time in between) are used in “static conditions” (with a closed reactor), while IR active species are monitored with the FTIR between the trains until the steady state. The appearance of conversion products as a function of the ‘plasma-on time’(calculated from the number of pulses sent) is deduced from the fitting of infrared spectra taken right after switching off the plasma when the gas has relaxed to thermal equilibrium. More details on this experimental procedure with train of pulses can be found in [3]. The gas temperatures as well as the vibrational temperatures of CO and CO_2 are measured in situ by FTIR spectroscopy in the same reactor in flowing conditions, as described in [4].

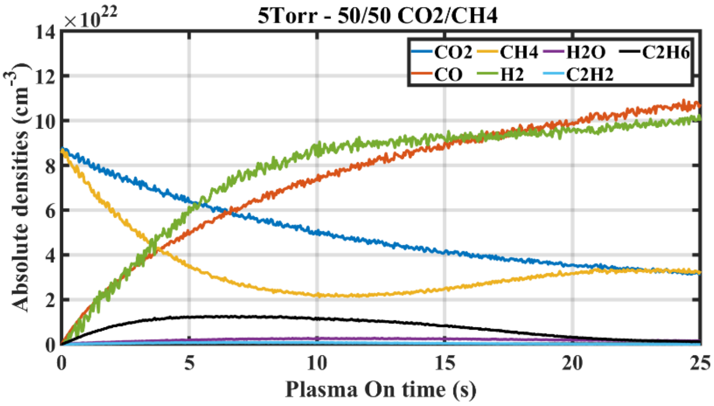

Figure 1: Evolution of the composition of a 1:1 CO2/CH4 RF plasma at 5 torr

Mixtures of CH_4 / CO_2 (with a fraction of CH_4 kept below 0.5 to avoid deposition of coke on the walls) at pressure of 2 and 5 torr are probed. The typical evolution is shown on figure 1: CO and H_2 are the main products in the final state, only traces of H_2O and C_2H_2 are found. The kinetics of methane conversion shows to be initially faster than the kinetics of CO_2 but shows a change of trend at the end, where CH_4 is reformed while the intermediate C_2H_6 disappears. CO_2/H_2 mixtures in similar conditions are also measured to study the possible back-reactions leading to reformation of CH_4.

All these data provide a unique set of parameters in a single plasma configuration to investigate CO_2 - CH_4 plasma kinetics, allowing comparison of experiment and simulations using the Lisbon Kinetics simulation tool LoKI [5]. Experimental data are confronted to kinetic models including a limited number of reactions to highlight important mechanisms.

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