Experimental validation of the chemical kinetics of CO2 containing plasmas

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Abstract: CO2 containing plasmas at low pressure are used to give constraint to kinetic models. In order to get insights about the chemical paths, a combination of three complementary experimental approaches are performed in order to separately study the vibrational kinetic and the chemical kinetics. These methods are applied in various mixtures such as CO2/CH4, CO2/H2 or CO2/N2. Within the same setup, it was also possible to study the interaction with catalytic materials providing a unique opportunity to have a detailed description of gas phase composition and surface species evolution at the same time.

Keywords: CO2 plasmas, chemical kinetics validation, Infrared absorption, dry reforming, methanation

1. General introduction

The use of cold plasmas for CO2 recycling remains one of the most promising ways to reduce greenhouse gas emissions. This approach can be applied in several ways depending on the molecule(s) that we want to form from CO2. Very different work report in literature CO2/H2 plasmas that are studied to form CH4, or CO2/CH4 plasmas to perform dry reforming, or other mixtures such as CO2/H2O, CO2/N2 to form methanol or NOx simultaneously with CO2 conversion. Each of these mixtures are likely to generate very complex chemistry and many reaction rates are poorly known even at thermodynamic equilibrium. In a cold plasma, the complexity is increased tenfold by the presence of many radicals produced by electron impact dissociation of reactants, as well as excited electronic and vibrational states. The identification of the reaction pathways in mixed CO2 plasmas is therefore a great challenge.

In addition, most of the work carried out on these systems seeks to demonstrate conversion efficiency. This generally implies the use of plasma sources at atmospheric pressure, very inhomogeneous and transient, and moreover very often coupled to catalytic materials. These configurations make it very difficult to study *in situ* the individual processes controlling the kinetics of these plasmas. As a consequence, in many cases there is still a doubt about the real gain of using a plasma compared to simply heating the mixture with the right catalyst. In order to highlight the particular role of species formed only in a plasma, it is necessary to return to experiments allowing the isolation of single process, and allowing the use of *in situ* and time-resolved measurement techniques. Moreover, it is essential to have a joint experimental and modelling approach in order to validate step by step kinetic schemes.

The work presented here proposes three complementary experimental approaches which offer the possibility to study in detail the electronic, vibrational and chemical kinetics in different gas mixtures. These methods are based on the use of either "glow" or radio frequency discharges at a few mbar studied with the help of many diagnostics but in particular of infrared absorption measurements. Moreover, these experimental devices are designed to be studied in the presence of catalytic materials or not, in order to give also information on the mechanisms of plasma/catalyst interaction.

2. Experimental setups

The three experimental methods implemented all use plasma reactors consisting of glass tubes with an internal diameter of 2 cm and length of 23cm. In the case of the glow discharge, hollow cathode electrodes are located perpendicular to the main tube, so that only the positive column of the plasma fills the main axis of the reactor. This is very important to be able to perform absorption measurements that are line of sight integrated, and to easily compare the measurements to 0D model results. The RF discharge has the particularity to have three ring electrodes located outside the main tube. This ensures that the plasma is not in contact with the metal of the electrodes in order to avoid any possible catalytic activity of the metal of the electrodes. This configuration then allows measurements to be carried out in a closed reactor (« batch » reactor) while guaranteeing that there is no unknown contribution of the electrodes to the observed reactivity. The difference between the three approaches is then essentially linked to the FTIR measurement method used for the infrared spectroscopy.

Method 1: Plug flow reactor with measurements of "normal" spectra measured both downstream of the reactor and *in situ*. By varying the gas flow, the residence time of the gas in the plasma can already be varied. This is the simplest experimental method but allows nevertheless to scan many parameters of pressure, discharge current, gas composition. The infrared absorption spectra are analyzed to deduce the densities of molecules present in the plasma as well as their rotational temperature, and the vibrational temperatures of CO and CO2. In this configuration, it is also possible to insert catalyst pellets in the infrared beam. In this case, it is the species adsorbed on the surface of the catalyst that are followed as a function of time. The correlation of the species densities measured in the gas phase with the appearance or disappearance of adsorbed species allows to study the role of the plasma species on the surface reactivity of different materials.

Method 2: plug flow reactor with measurements of time resolved spectra in a pulsed glow discharge with pulses of typically 5ms (t_p^{on}) separated by 10ms of time without plasma (t_p^{off}). The FTIR is then used in "step scan" mode, which allows measurements with a time resolution of 10µs, but this requires extremely reproducible plasma pulses during the entire acquisition period. This method allows in particular to measure the temporal evolution of the rotational and vibrational temperatures of CO and CO_2 in different mixtures. These data are especially useful to validate the vibrational kinetics

Method 3: closed reactor without gas flow ("batch") with measurements of spectra obtained in "rapid scan" mode between trains of plasma pulses. This time the spectra are measured between pulses, and the evolution of the neutral molecule densities is studied from the initial reactant mixture to a stationary state in which all the creation and loss reactions are compensated. This configuration is very efficient to constraint the chemical reaction sets used in kinetic models.

These three methods have been implemented in different mixtures of CO2 with other molecules.

3. Example of results

The Fig 1 shows results of molecules densities obtained downstream the glow discharge reactor and simulation obtained with the LoKi C Boltzmann solver [1]. The variation of densities as function of initial percentage of CO2 in CO2/CH4 mixtures are shown for 5 Torr pressure.

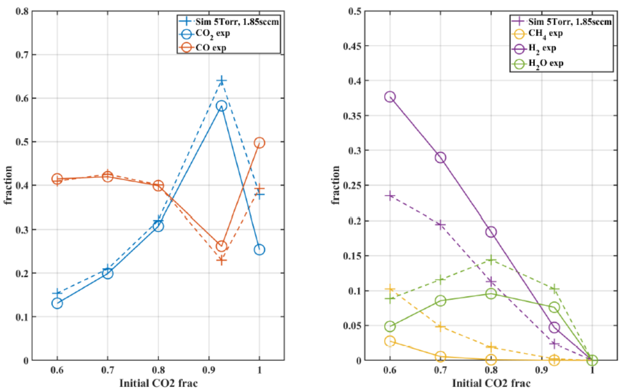

Fig. 1. Comparison of 0D kinetic model obtained with the solver Loki C and measurements of molecules density downstream the glow discharge reactor in CO2/CH4 mixtures with 1.85sccm, 5Torr. The simulation is plotted in dashed lines and the experiment in plain lines

The results show a good agreement between simulation and experiment for the densitites of CO and CO2 but the corresponding destruction of CH4 and production of H2 are under-estimated in the model. It appeared that the reason for it is probably the key role played by electronically excited states. In particular the electronically excited states of CO and atomic O are crucial to take into account. This conclusion could not have been reached without the combination of the results obtained with the three method 1,2 and 3. The Method 2 was essential to discard the role of vibrational excitation in this condition. The Methods 3 was a very strong confirmation of what was observed with Method 1 despite the difficulty to know some of the fundamental parameters of the RF discharge such as the reduced electric field or the electron density.

The model validated against experimental data illustrated in the particular case of CO2/CH4 on Fig 1 was also studied in other mixtures in the same manner. For instance, results in CO2/N2 [2] and CO2/H2 could be obtained.

Having a complete picture of molecular densities, gas temperature, electric field and electron density in the glow discharge revealed to be of great value to also investigate the surface reactivity of catalyst. The Fig 2 shows an example of evolution of carbonates on the surface of CeO2 under plasma exposure at 5 Torr.

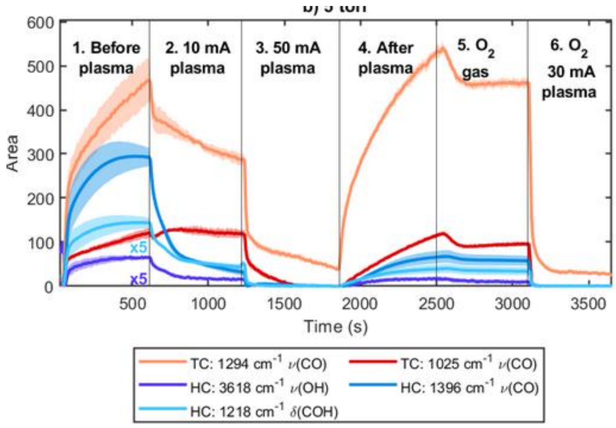

Fig. 2. Example of evolution of carbonates on the surface of a CeO2 pellet under direct exposure to plasma. The different phases on the plot correspond to different gas mixture and plasma conditions

The evolution of Tridentate carbonates (TC) and Hydrogen Carbonate (HC) could be followed in pure CO2 in this example. By varying the current and gas mixture, the TC and HC formation and destruction mechanisms can be studied with very different condition of gas composition and temperature. This allowed to evidence the role of the plasma beyond the sole heating of the surface.

4. Conclusion

The combination of the different experimental methods developed together with kinetic modelling is a powerful tool to study complex chemistry. In the particular case of CO2 containing plasma, the key role of electronically excited states could be evidence.

5. References

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