

Activation of Highly Stable Molecules in Atmospheric Pressure Plasmas for Power-to-Chemical Conversion

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Abstract

The decarbonization of society requires replacing fossil with renewable resources as a source of fuels and chemicals. One could use widely available molecules, such as CO₂, N₂, and H₂O, to obtain this, provided an efficient method exists to activate these highly stable molecules.

Ideally, the process should direct renewable energy toward molecular dissociation while minimizing the waste of energy in gas heating. To this purpose, the plasma approach utilizes the unique non-equilibrium properties of gaseous discharges. However, it is crucial to have control over the dissociation mechanism and to be able to monitor it to obtain the desired efficiency. We have exploited the adjustable pulsing schemes of nanosecond repetitively pulsed (NRP) discharges to control both the conversion and the efficiency of the activation process of CO₂ and N₂. Our recent contributions in this area will be presented during the workshop.

Introduction

The successful and widespread use of gas discharges is due to the possibility of inducing out-of-the-equilibrium conditions that promote highly endothermic chemical reactions in mild conditions (i.e., close to atmospheric pressure and room temperature). Non-thermal plasmas can promote the activating of highly-stable molecules, and potential applications are a) carbon dioxide conversion into molecules with higher enthalpies as a way for storing (renewable) energy in C-neutral chemicals; [1, 2, 3], b) sustainable nitrogen fixation as an alternative to the energy-intensive Haber-Bosch process for ammonia production [4].

The challenge of making the plasma technology commercially viable lies in finding the right tradeoff between bulk conversion and overall energy efficiency. A new approach to studying plasma chemistry is required beyond merely measuring the reaction products that exit the reactor. Local, time-resolved diagnostics must be developed to gain insight into the plasma at the appropriate time scale [5, 6]. In the present contribution, we present our recent developments in understanding the mechanisms of plasma dissociation of CO₂ in the sub μ s time scale. In some cases, like N₂/H₂ conversion to ammonia, the plasma alone shows modest performances, and adding a catalytic stage coupled with the discharge is needed. Due to the filamentary nature of the discharge, the choice of the proper catalytic support is crucial. Our preliminary investigation on the optimal catalytic support to be coupled

with an NRP discharge for converting N_2 and H_2 into NH_3 is presented.

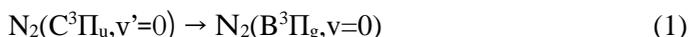
Materials and methods

The CO_2 reduction and N_2/H_2 conversion were carried out in two different discharge reactors, as reported in Figures 1(a) and 1(b). The two reactors shared the same electrode geometry and inlet/outlet ports for the gas flows.

Discharge apparatus. The electrodes were arranged in a pin-to-pin configuration and placed inside a vessel with optical access for spectroscopic investigations. The high voltage (HV) electrode serves as the gas inlet and the grounded as the gas outlet. The inter-electrode gap was set at 5 mm. An HV power supply was employed to produce the HV pulses, with a full width at half maximum of about 10 ns. Both reactors were operated at atmospheric pressure (950 mbar). Mass flow controllers (MFC) were used to feed the process gas inside the discharge chambers. In the case of the CO_2 reduction experiment, a trace amount of water or nitrogen was added to the gas stream as a precursor of OH or for spectroscopic thermometry respectively. Voltage and current probes were used to measure the energy dissipated in the discharge. The specific input energy (SEI) was calculated as the power dissipated by the discharge divided by the reactant standard flow.

Effluent gas analysis. A micro gas chromatograph (μGC) equipped with a thermal conductivity detector was placed in the exhaust gas line for in-line quantification of CO_2 , CO , O_2 , N_2 , and H_2 . A Fourier transform infrared (FTIR) spectrometer is used to quantify NH_3 .

Spectroscopic apparatus and methods. The time evolution of the gas temperature in the CO_2 reduction experiment was derived from the optical emission of the second positive system (SPS) of N_2 [6]:



For this purpose, 5% of N_2 was added to the CO_2 stream. The emission was collected by a 300 mm focal length spectrograph equipped with a gated intensified-CCD (ICCD) camera. The time evolution of the CO_2 conversion was determined using the collisional energy transfer laser induced fluorescence methodology [7]. A frequency-doubled tunable dye laser produced the OH(A), and the fluorescence was detected with the same apparatus used to record the N_2 SPS emission. As described in detail in [8, 9], energy-transfer collisions with the background molecules modify the population of the laser-excited OH(A) state and influence the fluorescence spectra. Thus, LIF outcomes recorded various times after the discharge pulse carry information on gas composition and CO_2 dissociation.

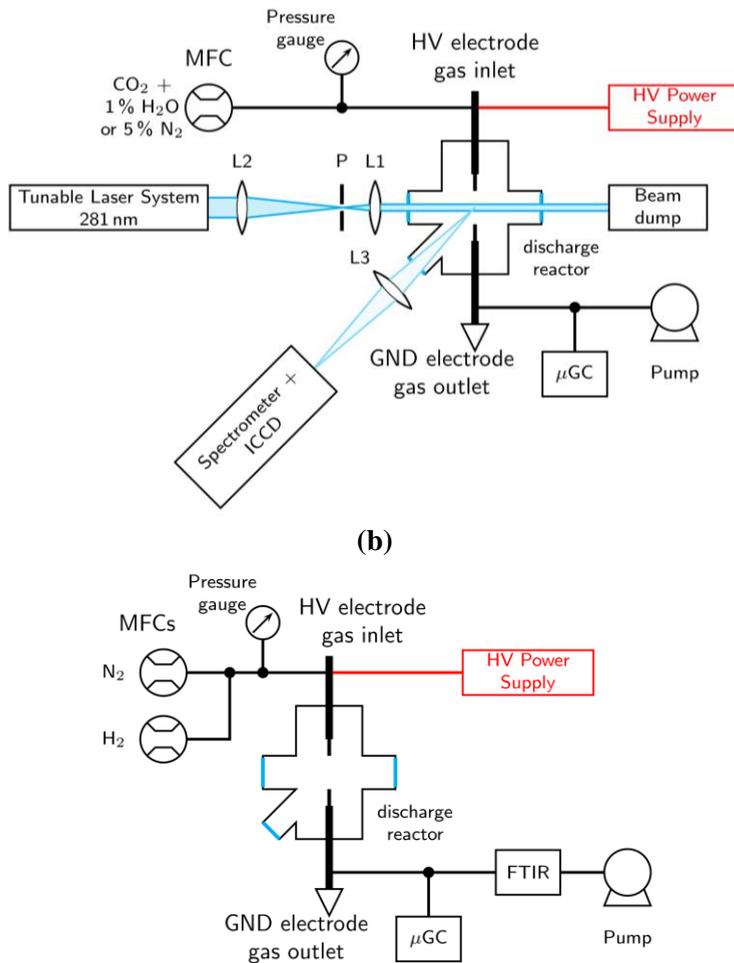


Figure 1. Simplified diagram of the experimental setups for (a) CO₂ reduction experiment and (b) ammonia production.

Results and Discussion

CO₂ reduction The time evolution of the gas temperature (T_g) and CO₂ conversion (C_{CO_2}) [10] are presented in Figure 2. The CO₂ conversion in the first 80 ns does not increase significantly ($C_{CO_2} < 8\%$), despite most of the energy (around 85%) has been already dissipated in the first 20 ns after the breakdown. Also, T_g does not exceed 1200 K in this first phase. Higher values of gas temperature and CO₂ conversion are observed around 3-5 μ s with a subsequent decrease of both. At longer delays, C_{CO_2} reaches values similar to those measured at the reactor exit with the μ GC (around 10% conversion, 3.5 kJ dm⁻³ of SEI). The progressive rise of the CO₂ conversion after the breakdown hints that the direct excitation to a dissociative state by electron impact of the CO₂ molecule might not be the primary cause of the

dissociation, which can be most likely attributed to an indirect mechanism mediated by CO₂ excitation [10, 11].

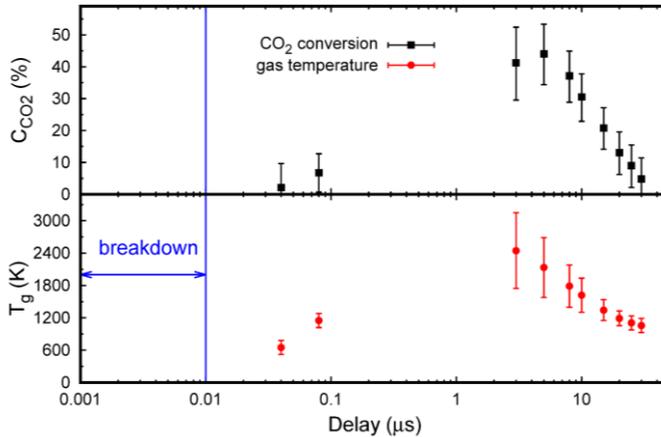


Figure 2. CO₂ conversion (C_{CO_2}) and gas temperature (T_g) as a function of the delay with respect to the HV pulse. Data adapted from [10]

Ammonia Synthesis. Typical values of NH₃ concentration, energy yield (EY - the energy spent for producing a gram amount of NH₃) as a function of the gas composition, and the support material are presented in Table 1. The NH₃ production as a function of the specific input energy is similar to the values reported in the literature [4]. We observed that the H₂:N₂ ratio could influence NH₃ production and, consequently, the EY. The presence of the selected substrates for catalytic materials does not significantly affect the NH₃ conversion. The poor performances of the plasma processes without catalysts highlight the importance of identifying appropriate materials to exploit the synergy between plasma and catalysis.

Table 1. Typical values of ammonia concentration and energy yield as a function of the gas composition and the support material.

Support	H ₂ :N ₂ ratio	SEI (kJ dm ⁻³)	[NH ₃] (ppm)	EY (g kWh ⁻¹)
none	9:1	5.0(5)	127(4)	6.9(7)·10 ⁻²
none	2:3	5.6(5)	67(2)	3.2(3)·10 ⁻²
SiO ₂ cylinder	2:3	6.0(5)	72(2)	3.2(3)·10 ⁻²
quartz wool cylinder	2:3	6.7(5)	95(3)	3.8(4)·10 ⁻²

Conclusions

We reported a delay of hundreds of nanoseconds between the discharge breakdown and the time when most of the CO₂ dissociation occurs in an NRP discharge. This result indicates that the primary mechanism of CO₂ dissociation is mainly caused by molecular-excitation kinetics.

The ammonia synthesis in an N₂/H₂ NRP discharge presents EY in line with other discharge types. Understanding the influence of the substrate and the coupling of the plasma with the catalyzer is an essential step toward more efficient plasma NH₃ synthesis.

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