

Electronic Supporting Information File (ESI)

Electrocatalytic behaviour of CeZrO_x-supported Ni catalysts in plasma assisted CO₂ methanation

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Plasma-catalytic setup

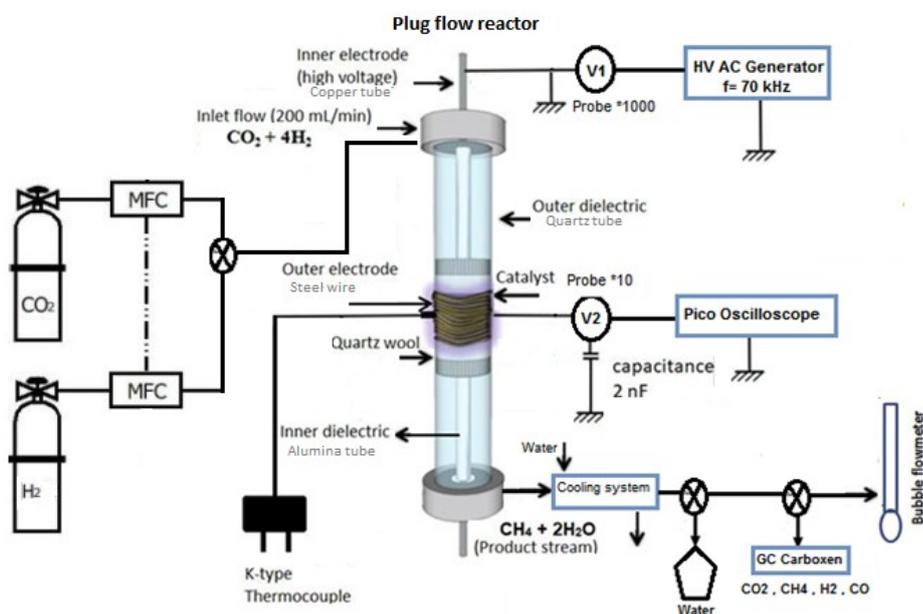


Figure SI.1. Experimental set-up used in the the plasma-catalytic CO₂ methanation

The plasma-catalytic experiments were performed under “pseudo-adiabatic conditions”, i.e. no external heating applied, no thermal isolation. After switching on the DBD plasma (potential difference between the two electrodes), the temperature increases due to the energy input and heat generated by plasma discharges. At low plasma power (< 9 W), the methanation reaction did not take place and the main contribution in the temperature measured ($T \approx 150\text{-}160^\circ\text{C}$ at $P = 9\text{W}$) was caused by the presence of the plasma. In contrast, at powers between 9.5-10 W (applied voltage = 13 kV) the methanation reaction took place and the temperature increase instantly as a result of the exothermicity of the conversion of CO₂ to CH₄. According to our calculations, apart from the heat generated by the plasma discharges, the contribution of the heat released by the reaction contributes to a temperature increase around 30 °C (i.e. from 160 until 190°C).

Moreover, in order to validate our results, we additionally performed some experiments without H₂ (only CO₂ in the feeding gas). In the absence of H₂, methanation does not take phase and only dissociation of CO₂ is bound to occur. For an input power lower than 9 W, we measured similar temperatures than in the presence of H₂, pointing to plasma as the main source of heat in our reactor when methanation does not take place. At higher input powers (> 9-10 W), in the absence of H₂ the temperature increased very slowly, whereas when the whole mixture is fed (CO₂ and H₂) the temperature increased instantly, due to the effect of exothermicity of the methanation reaction.

The maximum conversion was obtained at 15 kV. At higher applied voltage (Fig. 1B) the conversion of CO₂ decreases. For voltages higher than 16 kV the temperature increases over 300°C and following equilibrium thermodynamics, this results in

a decrease of CO₂ conversion in increased CO formation, due to the RWGS reaction being thermodynamically favoured and occurring within this temperature window.

Temperature measurements: We performed Comsol simulations of our plasma-catalytic reactor under our experimental conditions. The results are presented in Figure SI.2. We found that there is a temperature gradient of 8°C (from around 192°C to 200°C) between the catalytic bed and the ground electrode where the temperature was experimentally measured. Furthermore, we calculated the vibrational and rotational temperature of the gas by using Optical Emission Spectroscopy in situ in the catalytic bed. The temperature of rotation of the discharge was obtained by adjusting the spectra observed experimentally of the band structure of the second positive system (SPS) of N₂ ($B^2\Sigma_u^+, v'=0 \rightarrow X^2\Sigma_g^+, v''=0$) with the LIFBASE simulation tool by comparing the structure of the rotation line with a simulated Boltzmann. Moreover, because of the rapid transfer between the rotation and the translation, the rotational temperature will be equal to that of the translation, i.e. the kinetic temperature of the gas. We obtained similar results between the calculated value of rotational T and the measured value experimentally using the thermocouple with a maximum difference from 10 to 12°C. The values shown in the Fig 1.B already take into account these experimental errors.

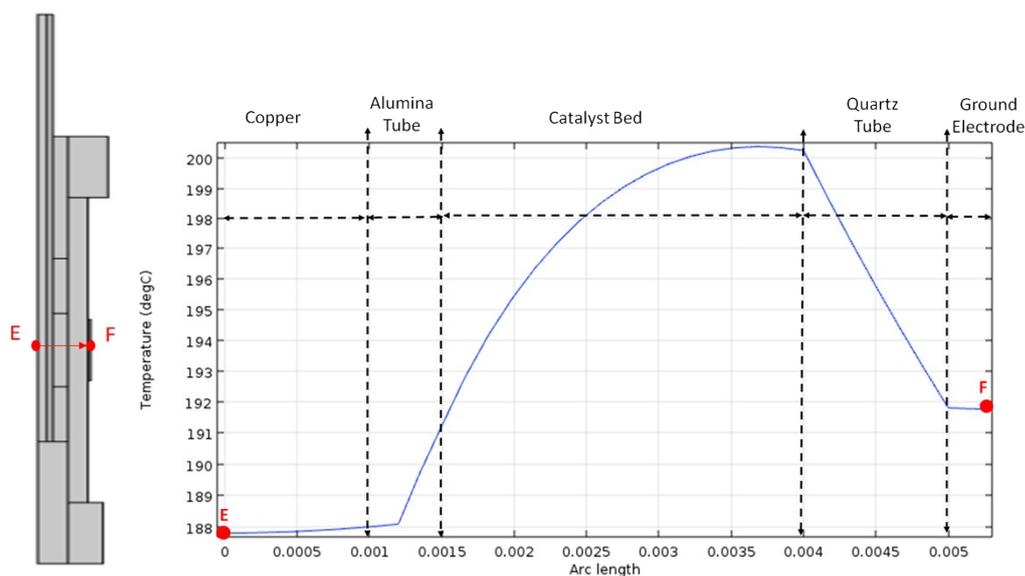


Figure SI.2. Temperature profile of the reactor (from E to F): (a) schematic diagram cut line EF in the reactor; (b) temperature profile on the cut line EF.

Power calculations: Electric power is an indispensable key parameter since it expresses the total amount of charges transferred by the plasma. Lissajou's method introduced by Manley in 1943¹ is now recognized to be the most precise method for DBD power determination. It requires the measurement of the input voltage and the voltage (U_c) across a capacitor displayed in oscilloscope, the latter is obtained thanks to a capacity placed in series with the reactor. Thus, by plotting the charge versus high voltage which is known as a Q-U Lissajou's plot by recording the values for Q(t) and U(t) via a series of regularly sampled points which capture the full cycle of the AC sinusoidal wave, we can obtain the discharge power dissipated in the reactor which is equal to the area of Q-U Lissajou's plot^{1,2}. Let us note here that the presence of the catalyst changes the shape and area of the Lissajou's plots (see M. Mikhail, B. Wang, R. Jalain, S. Cavadias, M. Tatoulian, S. Ognier, M. E. Gálvez and P. Da Costa, *Reac Kinet Mech Cat*, 2019, 126, 629–643). A detail study of the influence of the presence of the catalyst is currently being performed, combining experimental results and theoretical modeling of our plasma-catalytic set-up.

Physicochemical characterization

XRPD (X-Ray powder diffraction) was performed on a Panalytical X'Pert Pro diffractometer with an incident-beam Ge monochromator, at $U=45$ kV and $I=40$ mA. The apparatus was equipped with CuK α radiation source ($\lambda=1.5418\text{\AA}$). The patterns for structural analysis were recorded over a 2θ range of $20 \leq 2\theta \leq 80^\circ$ and a position sensitive detector using a step size of $0.05^\circ/\text{min}$ and a step time of 1s. The Rietveld analyses were carried out with

the Highscore software. The crystallite size of the samples was measured from X-ray broadening using the Debye–Scherrer equation.

Temperature-programmed reduction (H₂-TPR) profiles were obtained using BELCAT-M equipped with a TCD detector. The calcined materials (50 mg for each experiment) were first outgassed at 100°C for 2h and then reduced using 5% H₂/Ar at a heating rate of 7.5°C/min from 100°C to 900°C. Temperature-programmed desorption (TPD) was performed in a tubular quartz reactor at atmospheric pressure, with a K type thermocouple inside the catalyst bed, coupled with a Pfeiffer vacuum mass spectrometer (MS). Prior to the desorption the catalysts were degassed and cleaned in-situ under a 100ml/min flow of Argon at 50°C for 30 minutes. The desorption profile of CO₂ was obtained by heating the sample at a rate of 5°C/min from 50°C to 850°C in argon flow of 100 ml/min. The signal of desorbed CO₂ was obtained by the m/z=44 on the mass spectrometer.

Infrared spectra were acquired using a Fourier-transform infrared spectrometer (Cary 660 Spectrometer; Agilent, Les Ulis, France) with an attenuated total reflectance module (GladiATR; Pike, Madison). The attenuated total reflection (ATR)-FTIR spectra were collected from 4,000 to 1000 cm⁻¹, at a resolution of 4 cm⁻¹. One hundred scans were made for each measurement. The background (air) was taken before each measurement.

The specific surface area (SSA) of the different catalysts was determined by N₂ adsorption–desorption measurements at 77 K using the Brunauer–Emmet–Teller (BET) method (Micrometrics sorptometer Tri Star 3000). Prior to N₂ adsorption, the sample was outgassed at 200°C overnight to desorb moisture adsorbed on the surface and inside the porous network.

Transition electron microscopy analyses (TEM and HR-TEM) and Elemental mapping were performed in a JEM-2100Plus Transmission Electron Microscope, under an acceleration voltage of 270 kV.

CO₂-derived adsorbed species and intermediates

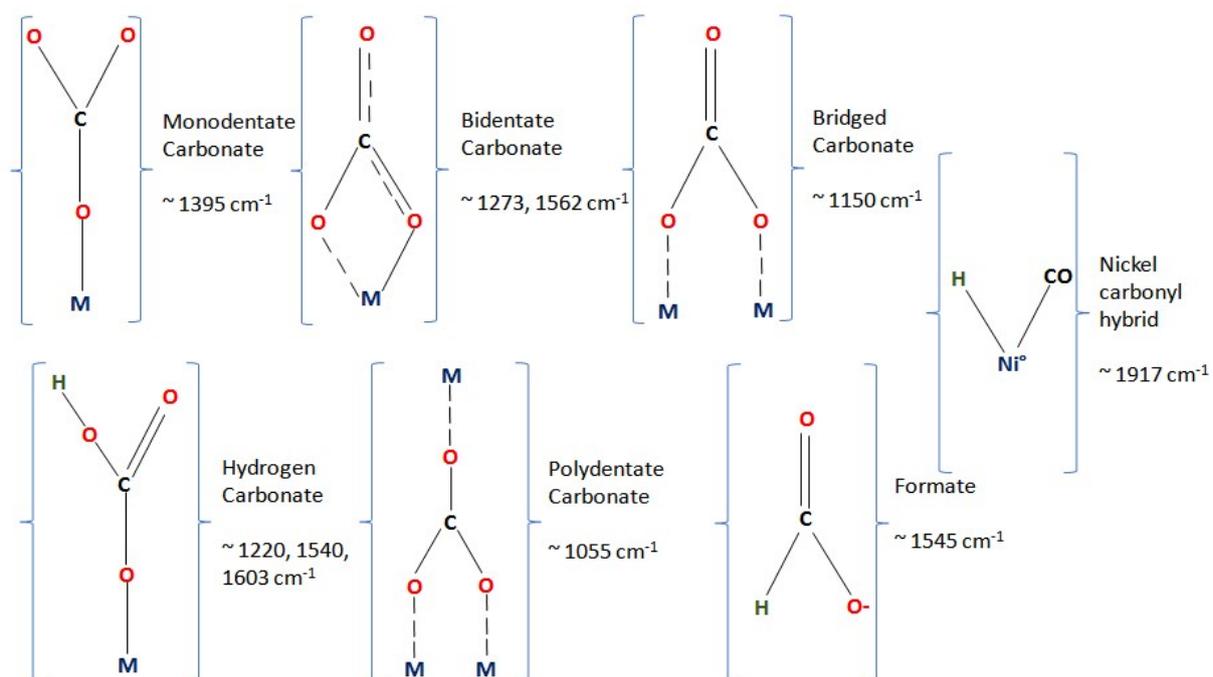


Figure SI.3. Different carbonates and other intermediate species, and their corresponding IR bands.

TPD-MS and ATR-FTIR on catalyst submitted to thermal and plasma CO₂ adsorption

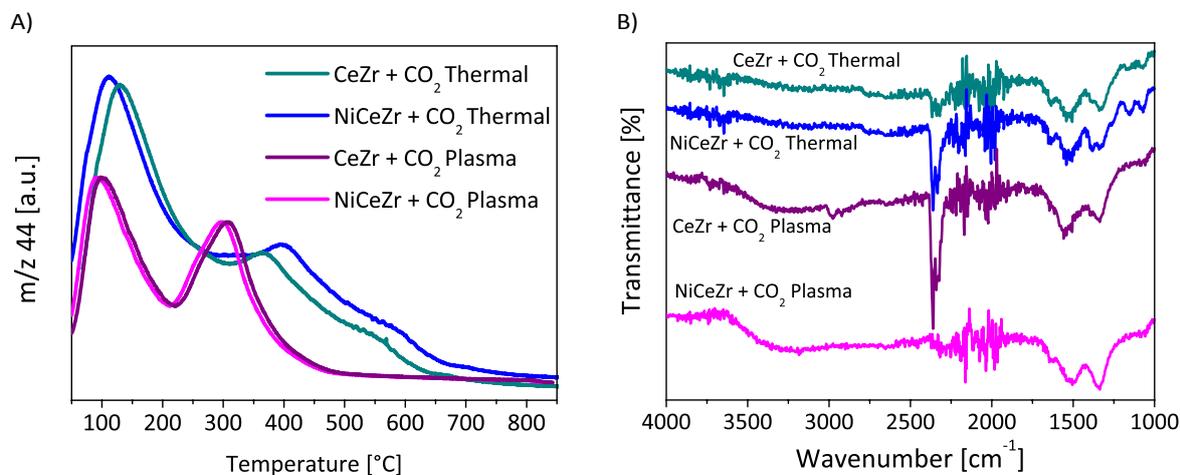


Figure SI.4. TPD-MS (A) profiles and ATR-FTIR spectra (B) acquired for the catalysts upon thermal and plasma treatment under pure CO₂ atmosphere.

BET surface area

Table SI.1. BET surface areas for the different spent and calcined catalysts, as well as for the calcined support

Catalyst	SSA (BET) (m ² /g)
TA-NiCeZr	51.4
PA-NiCeZr	57.9
NiCeZr calcined	62.0
CeZr calcined	84.2

Note that the BET surface area decreases after thermo-catalytic methanation, to a greater extent than for the catalyst used in the plasma-catalytic reaction

References

- 1 T. C. Manley, *Trans. Electrochem. Soc.*, 1943, **84**, 83.
- 2 R. Valdivia-Barrientos, J. Pacheco-Sotelo, M. Pacheco-Pacheco, J. S. Benítez-Read and R. López-Callejas, *Plasma Sources Sci. Technol.*, 2006, **15**, 237–245.
