Study of CO_2-CH_4 plasma-surface interactions on cerium oxide using *in situ* FTIR transmission experiments

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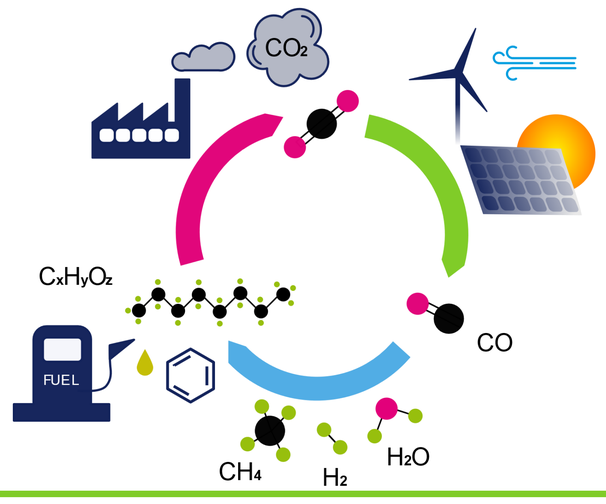
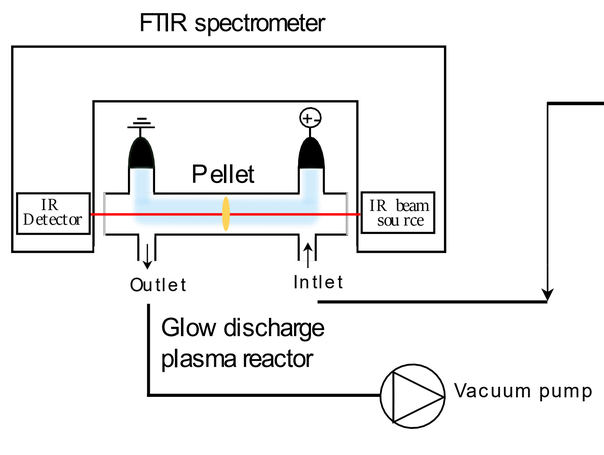
Using Plasma-Catalysis for CO_2 recycling

Climate change caused by greenhouse gas emissions encourage the closing of the carbon cycle which can be achieved by converting CO_2 into platform molecules or short hydrocarbons. The use of **non-thermal plasmas** can promote the asymmetrical stretching vibration of CO for bond breakage. The presence of a catalyst could greatly improve the conversion and selectivity. The complexity of the **interaction of plasma with a surface** brings the necessity to study the underlying mechanisms occurring on the catalyst as a function of time and under different conditions.[1,2]



in situ FTIR transmission to study DC glow discharge plasmas

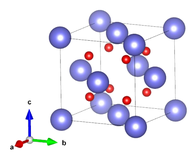


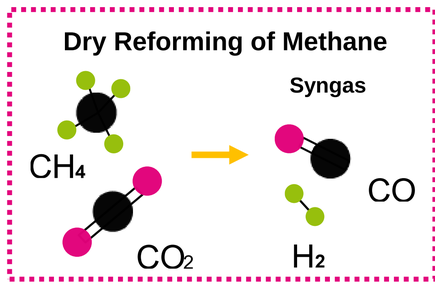
Glow discharge plasmas at low pressures are:

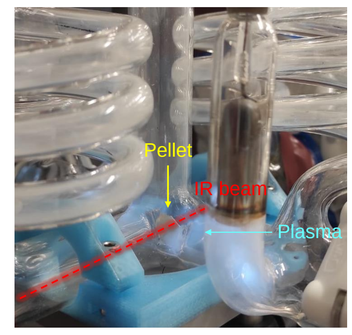
- ✓ Ideal for plasma kinetics
- ✓ Homogenous plasma
- ✓ Simultaneous study of plasma/gas phase and plasma/surface interaction under same conditions

CeO_2 is known for **activating CO_2** in mild conditions

- ➢ Oxygen mobility
- ➢ Redox properties
- ➢ Metal – support interaction
- ➢ Info available in the literature

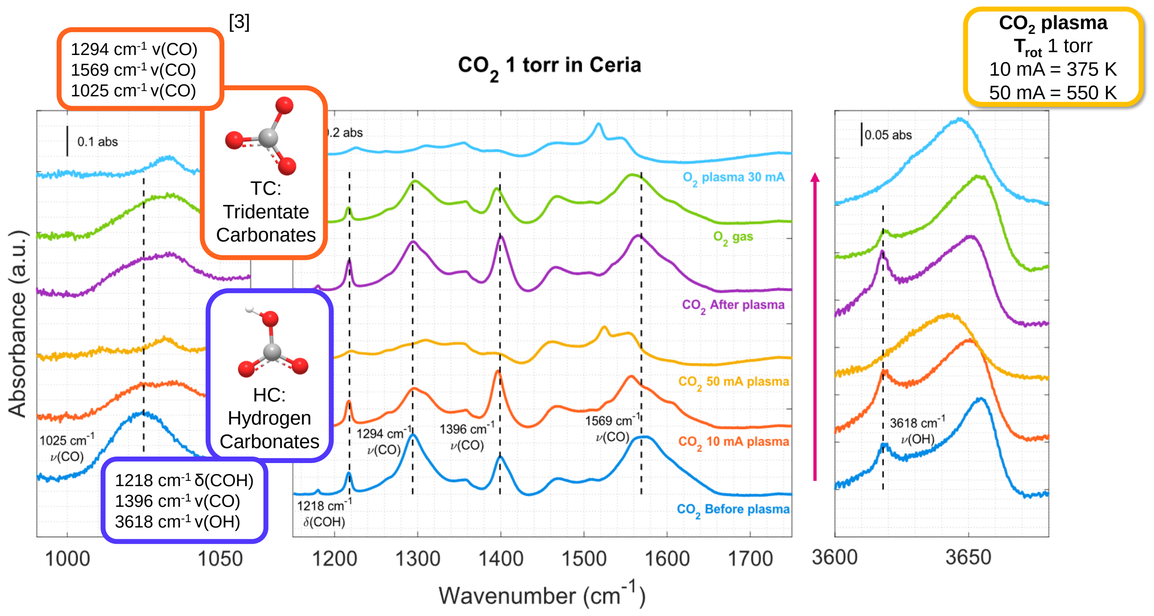




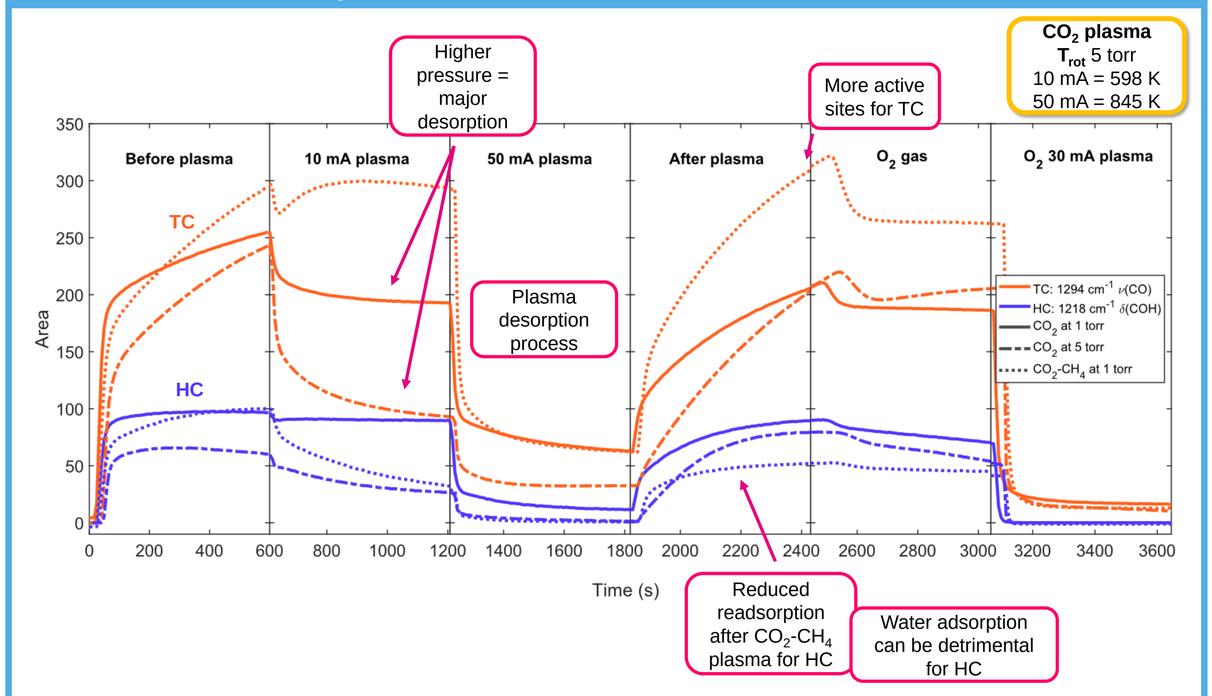


Sequence of steps, 10 min each: Gas Before plasma → 10 mA plasma current → 50 mA plasma current → Gas After plasma → O_2 gas → O_2 30 mA plasma

Carbonates are the main species by CO_2 adsorption…

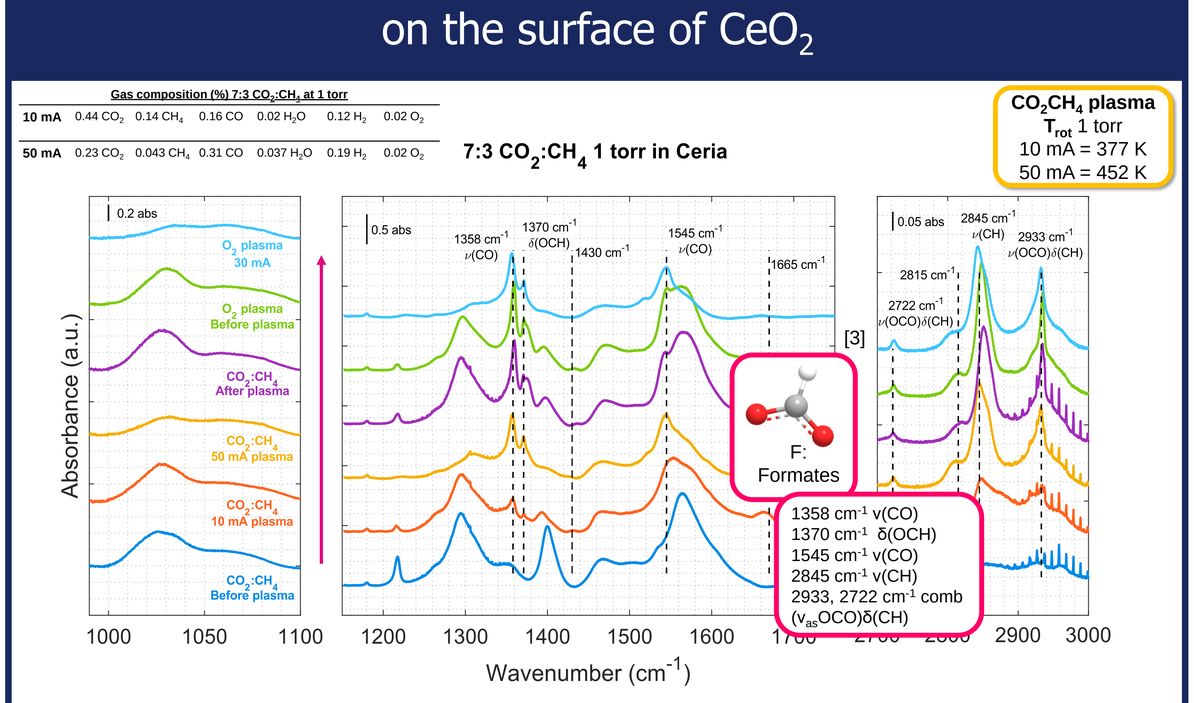


… and they can be followed as a function of time



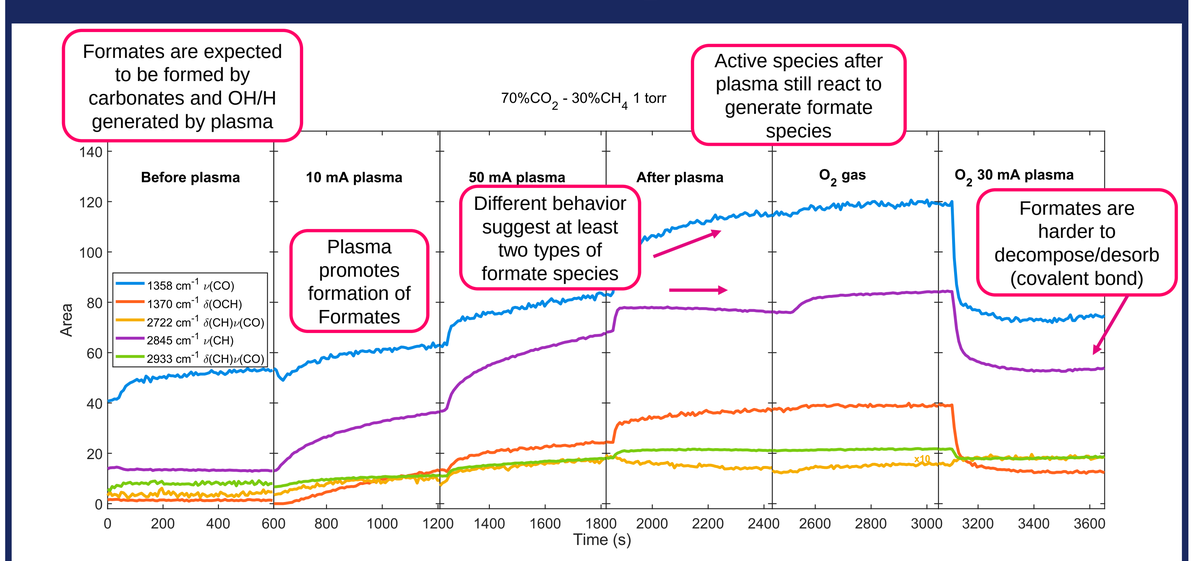
The addition of CH_4 to the mixture can change the adsorption of carbonates

CO_2-CH_4 plasmas promote formate species on the surface of CeO_2



Formates are known as surface intermediates for CO and H_2 release

[4]



TC and OH groups are the precursors of Formates species

$$CO_{3(ads)}^{2-} + OH_{(ads)}^{-} \leftrightarrow HCO_{2(ads)}^{-} + O_{2(ads)} \leftrightarrow CO_{(ads)} + OH_{(ads)}^{-}$$

[5]

Tridentate carbonate — From dissociated water — Formate

References:

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Conclusions

- Tridentate carbonates and OH species are found as precursors for formates species in the ceria surface during CO_2-CH_4 plasma interaction
- Hydrogen carbonates are sensitive to excess H_2O molecules
- Time evolution of the bands suggests at least two types of formate species