in situ FTIR transmission experiments through catalytic pellets under CO_2-CH_4 plasma exposure

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1. Introduction

Closing the Carbon cycle can be achieved by converting CO_2 into platform molecules or even short hydrocarbons, by coupling renewable energies and hydrogenated co-reactants (H_2O, CH_4, etc.). Several approaches are being explored and non-thermal plasmas is one of them. The principal advantage is to promote the asymmetrical stretching vibration for CO bond breakage. However, the presence of a catalyst could greatly improve the conversion and selectivity. Although, 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.

Glow discharge plasma reactor at low pressures are a good benchmark for studying plasma kinetics and especially plasma surface interaction. *in situ* studies of surface reactions under plasma exposure for CO_2 conversion and especially for Dry Reforming of Methane Reaction (DRMR) are scarcely reported. [1,2]

In this study, *in situ* FTIR transmission experiments were performed to elucidate the plasma-catalytic surface reactions in detail on cerium oxide (CeO_2) during plasma-assisted DRMR. The catalyst pellet is being exposed to a low-pressure glow discharge for which many parameters such as ro-vibrational temperature, electric field, molecules densities have also been measured. The combination of time resolved surface species evolution together with the detailed characterization of the gas phase provides a unique system for describing the plasma/catalyst interaction mechanisms.

2. Experimental

A glow discharge reactor is placed in the beam of a FTIR. The plasma is ignited perpendicularly to the IR beam which is passing through the pellet. CeO_2 was selected as a test material due to its oxygen mobility and redox properties, as well as the literature available for IR bands identification of adsorbed molecules. [3,4] Nanopowder of cerium oxide from Sigma-Aldrich was pressed to form a pellet of ~1 cm diameter.

Each experiment follows the next sequence: the appropriate gas mixture (CO_2 alone or CO_2-CH_4) was sent to the reactor (Before plasma), then plasma at 10 mA was ignited, plasma current increased to 50 mA, plasma was switched off (After plasma), O_2 gas was sent to the reactor, O_2 plasma at 30 mA was ignited and finally, then O_2 gas. Each step takes 10 minutes.

3. Results

Firstly, CO_2 is observed to adsorb in ceria as tridentate carbonates (TC) and hydrogen carbonates (HC). [3] When plasma is ignited, the carbonates bands are reduced while strong bands corresponding to formates species appear on the spectra. [4] When plasma is off, TC bands reappear but those for HC do not with the same intensity as before plasma. Formate bands remain the same.

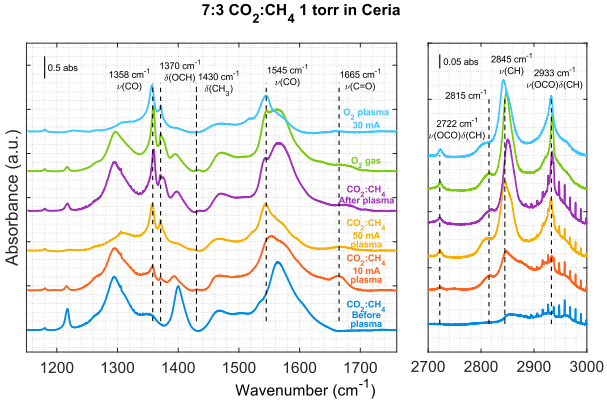

Fig. 1. *in situ FTIR spectra following each step from bottom to top*

Only formate bands remain during the cleaning step with O_2 plasma at 30 mA showing the stronger bond formed to the surface in comparison to carbonate species. Also, it was confirmed that water adsorption on the surface prevents the formation of HC species.

References

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