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

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in situ FTIR transmission experiments performed using glow discharge reactor for CO_2-CH_4 plasmas allowed to study the trends of adsorbates on cerium oxide as catalytic surface. Carbonates and formates species were identified and followed as a function of time. Water plays an important role on the formation of hydrogen carbonates. Elucidation of adsorbed intermediates of CO_2-CH_4 plasma reaction is crucial in the understanding of the mechanistic insight in CO_2 conversion by plasma catalysis.

The increment on the global temperature is mainly attributed to the greenhouse gas effect from carbon dioxide (CO_2) emissions. Carbon dioxide is a stable molecule difficult to dissociate but multiple approaches for CO_2 recycling are under study. Commonly, hydrogenated co-reactants are employed such as H_2O, CH_4, etc. One possible strategy involves non-thermal plasmas combined with a catalytic material in order to improve conversion, selectivities and energy efficiency. Development and optimization of plasma-catalysis requires a clear understanding of the underlying mechanisms occurring on a catalytic surface. Nonetheless, the study of the surface in the presence of non-thermal plasmas is still not well documented in the literature [1,2]. For this investigation, we performed *in situ* FTIR transmission experiments on a low-pressure glow discharge plasma reactor. Detailed evidence of catalyst exposure to CO_2-CH_4 plasmas provides insightful information on the plasma-surface interaction of intermediate adsorbates present on cerium oxide (CeO_2).

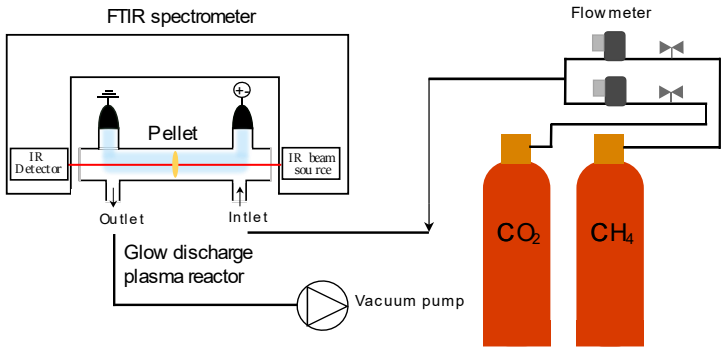

Fig. 1. Schematic of the setup used for *in situ* FTIR transmission experiments

Plasma is ignited perpendicularly to the FTIR beam passing through a CeO_2 pellet. The pellet is made of nanopowder from Sigma-Aldrich and placed inside a glow discharge reactor in the path of the infrared beam.

For each experiment, a sequence of steps is followed: the appropriate gas mixture (CO_2 alone or CO_2-CH_4) was sent to the reactor (named as “Before plasma”), then plasma at 10 mA was ignited, the plasma current increased to 50 mA, then the plasma was switched off (After plasma), O_2 gas was sent to the reactor, O_2 plasma at 30 mA was ignited and finally,

the O_2 gas. Time evolution of the spectra was recorded for each step previously described. Each step takes 10 minutes.

During only CO_2 experiments, it is observed that carbon dioxide adsorbs in CeO_2 as tridentate carbonates (TC) and hydrogen carbonates (HC) [3]. When CO_2-CH_4 plasma is ignited, the carbonates bands (previously formed by CO_2 adsorption) are significantly reduced while intense bands corresponding to formates species appear on the spectra [3,4]. When plasma is off, TC bands reappear but those corresponding to HC do not with the same intensity as before plasma. Formate bands remain the same even after switching to O_2 gas.

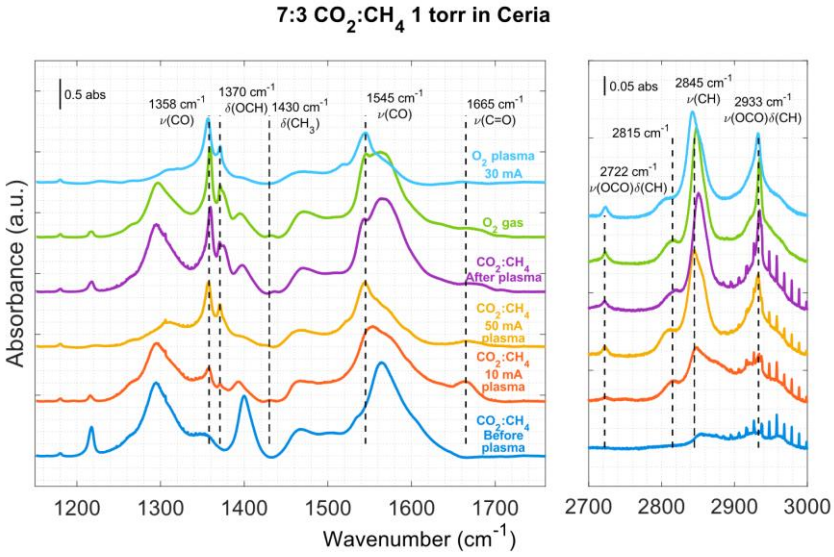

Fig. 2. *in situ* FTIR spectra following each step from bottom to top. Bands assigned to formate species and spectators/intermediates are shown in the spectra.

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. In addition, the spectra propose different types of formates species [4]. It is strongly suggested that water adsorption on the surface plays an important role on the promotion or abatement in the formation of hydrogen carbonates species depending on the concentration in the gas/plasma.

Innovative *in situ* experiments on glow discharge plasmas allowed to clarify the intermediate species formed in the CeO_2 surface while the pellet is completely exposed to excited species. The elucidation of adsorbed intermediates of CO_2-CH_4 plasma reaction is crucial in the understanding of the mechanistic insight in CO_2 conversion by plasma catalysis.

References

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