



## Effect of the pre-activation conditions on the nature of the active sites generated during CO<sub>2</sub> hydrogenation to MeOH over Cu-based catalysts

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### Significance and Relevance

Considering the technologic, economic and environmental advantages, MeOH synthesis through CO<sub>2</sub> hydrogenation represents a promising approach to recycle CO<sub>2</sub> closing the carbon loop and offering an efficient route to store H<sub>2</sub> in an easily transportable liquid organic carrier. To achieve a comprehensive understanding of CuZnOZrO<sub>2</sub> catalysts, an integrated approach based on main morphological and structural diagnostic techniques was assessed. This provided complementary insights into their specific features enabling the correlation between catalytic performance and structural properties. Then, *in operando* DRIFT spectroscopy resulted a powerful tool for uncovering the catalytic pathways involved in MeOH synthesis, allowing the optimization of catalyst design and operative strategy.

*CO<sub>2</sub> utilization and recycling; Fundamental advances in understanding catalysis*  
Oral preferred or Short Oral

### Introduction and Motivations

In the frame of Carbon Capture and Utilization (CCU) technologies, hydrogenation of CO<sub>2</sub> represents a strategic solution for the conversion and valorization of a greenhouse gas with the production of a clean fuel. In this study, a series of CuZnZr catalysts were prepared and their catalytic behavior was investigated in the hydrogenation of CO<sub>2</sub> to MeOH by changing the conditions of pretreatment to study the effect of copper phase on the activity-selectivity pattern. Considering the debate regarding the reaction mechanism and the univocal identification of the active sites in Cu-based catalysts, operando spectroscopic studies have been exploited to determine reactivity of adsorbate species and nature of active sites, intermediate or transient products after different pre-treatment steps<sup>1,2</sup>.

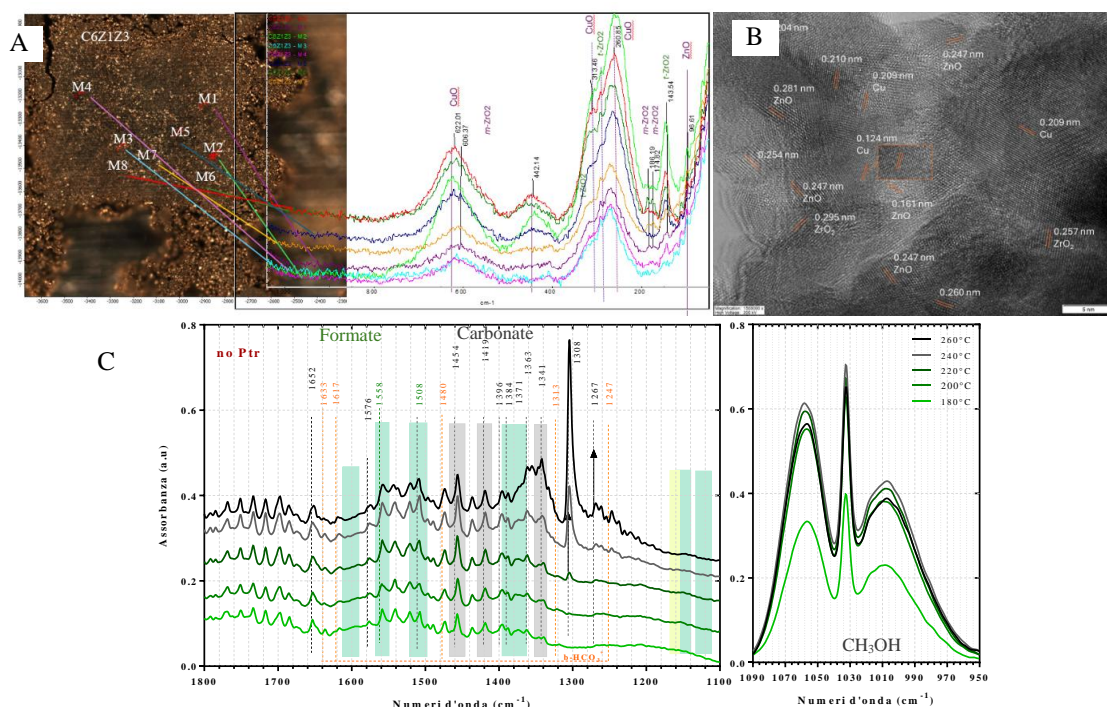
### Materials and Methods

A series of Cu-ZnOZrO<sub>2</sub> catalysts at different atomic composition were prepared by the gel-oxalate co-precipitation method and calcined at 350°C. Analytical, morphological, structural and surface properties were investigated by using XRF, XRD, SEM and TEM microscopy, N<sub>2</sub> adsorption/desorption isotherm and Raman spectroscopy. *In operando* DRIFT-MS measurements were performed using an environmental chamber located inside IS50 Thermofisher Spectrometer hyphenated with a Mass Spectrometer. Catalyst testing under CO<sub>2</sub> hydrogenation conditions was carried out in the temperature range 200-260°C at a pressure of 3.0 MPa, using a semi-automatic laboratory plant equipped with an electronic control unit for thermoregulation and mass-flow controllers.

### Results and Discussion

Previous work had already demonstrated that the gel-oxalate coprecipitation method result to be effective and reproducible<sup>2</sup>, ensuring precise control over the structural and morphological properties of the catalysts, accounting for the formation of well-dispersed spherical nanometric particles. The catalysts were characterized by similar surface area values (~32 m<sup>2</sup>/g) and a pore distribution within the mesopore range, with no contribution from microporosity, typical of oxide-based catalytic systems. XRD analysis allowed to investigate the crystalline structure of the materials, while Raman spectroscopy provided detailed insights into the distribution of CuO and ZnO crystalline species. Notably, zirconia was identified not only in its amorphous form but also as partially

crystallized in both tetragonal and monoclinic phases (Fig. 1A). The effect of reduction pretreatment on catalyst activation was assessed performing the CO<sub>2</sub> hydrogenation reaction upon different pretreatment protocols: 1) pre-reduction in H<sub>2</sub> flow; 2) CO/He flow; 3) no pretreatment. No significant differences in CO<sub>2</sub> conversion and MeOH selectivity were observed, suggesting that the feed composition ensures the formation of the active sites necessary for the reaction. XRD patterns and HRTEM images of *used* samples revealed the presence of crystalline metallic copper phases, regardless of the pretreatment applied, decorated by zinc oxides and zirconia (Fig. 1B).



**Figure 1** [A-B] Raman spectra and HR-TEM image of used CuZnOZrO<sub>2</sub> catalyst after CO<sub>2</sub> hydrogenation reaction without pre-reduction; [C] In operando DRIFT measurements during CO<sub>2</sub> hydrogenation without pre-reduction. T<sub>R</sub>, 180-260°C; P<sub>R</sub>, 30 bar; GHSV, 8,800 NL/kgcat/h; CO<sub>2</sub>/H<sub>2</sub>/N<sub>2</sub>=3/9/1 mol/mol.

Based on the collected data during spectroscopic investigations in the DRIFT environmental cell, the competition among different reaction pathways was hypothesized depending on the adopted conditions. Specifically, formate species were confirmed as crucial intermediates in MeOH formation at lower temperature (<220°C), while at higher temperatures, the reverse water-gas shift reaction becomes dominant, leading to the formation of carbonate and bicarbonate species, via a mechanism involving CO as an intermediate. With no prereduction step, the formate pathway does not appear to be active at low temperature, as no adsorbed intermediate species were detected. Nevertheless, MeOH formation was observed at 180°C yet, alongside with CO adsorption on metallic copper sites. This highlights the reducing capability of the reaction mixture with time on stream, underscoring the critical role of the Cu<sup>0</sup>/Cu<sup>+</sup> pair in both H<sub>2</sub> activation and stabilization of intermediate species.

## References

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