Spectroscopic investigation of In2O3-ZrO2 catalyst for CO2 hydrogenation to methanol

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BOOK OF ABSTRACTS

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Preface

The 13th International Conference on Environmental Catalysis (ICEC2025) has been held on June 2-5 (Monday-Thursday), 2025 at "SARACEN SANDS HOTEL & CONGRESS CENTRE" in Isola delle Femmine (Palermo, Sicily - Italy). The conference follows ICEC2022, which was held at Kansai University in Osaka, Japan, from July 30 to August 2, 2022. The conference is the major event in environmental catalysis.

After three decades, in a deep transition period to a new low-carbon economy, ICEC returns to Italy to discuss the future of environmental catalysis. The conference sub-title was "Addressing the new challenges", because it aims to redefine the fundamental and applied research on environmental catalysis to address the 2050 challenges.

The congress is organised by ERIC aisbl (European Research Institute of Catalysis) in collaboration with the Italian Group of Catalysis (GIC) and the Division of Industrial Chemistry of the Italian Chemical Society (SCI), and the contribution of the University of Messina (Italy), Politecnico Milano (Italy) and Forschungszentrum Jülich GmbH (Germany).

Conference Theme

Fundamental and applied research on environmental catalysis and catalysts to address the 2050 challenges (a resilient and zero-carbon society). Topics include, but were not limited to:

- Automotive and stationary emission control
- Air cleaning and combustion
- Water treatment
- Sustainable and clean energy production and transport
- Catalysis to electrify the chemical production
- Green chemistry and biomass transformation, renewable resources conversion
- Circular economy
- CO2 utilisation and recycling
- H2 storage and transportation, green H2 production, hydrogen vectors
- Photocatalysis and photoelectrocatalytic approaches, solar energy utilisation
- Advanced process with electrocatalysis and plasma utilisation
- Fundamental advances in understanding catalysis
- Multiscale modelling and advanced simulation aspects

More than 400 participants from 40 countries attended the congress, which was organised over four intense days, featuring three parallel sessions and nearly 300 communications, including plenary and keynote talks, oral and short oral presentations, and two poster sessions.

ICEC 2025 was a paperless congress that respected the principles of sustainability and promoted cross-fertilisation in various areas of environmental catalysis.

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Spectroscopic investigation of In_2O_3-ZrO_2 catalyst for CO_2 hydrogenation to methanol

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Significance and Relevance

This study highlights the significance of CO_2 valorization via hydrogenation, focusing on an In_2O_3/m-ZrO_2 catalyst. This catalyst demonstrates superior methanol selectivity, supported by *in-situ* and *operando* spectroscopic analyses that revealed key reaction mechanisms, such as the role of In_2O_3 vacancies and m-ZrO_2 in facilitating CO_2 hydrogenation. These findings contribute to advancing catalytic technologies for sustainable methanol production, offering potential improvements in performance and selectivity over conventional systems.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis / CO_2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Reducing greenhouse gas emissions is a pressing challenge that can be tackled by CO_2 valorization. Hydrogenation of CO_2 is a viable process route to obtain high-value-added products (e.g., methanol, olefins, kerosene, etc.). Methanol is a high-value product because of its many applications such as a solvent, fuel additive, and chemical building block, and it could be used for producing other high-added-value products such as olefins, gasoline, and so on. The CO_2 hydrogenation process occurs in a catalytic reactor at high pressure (50 – 100 bar) and in a temperature range of 200 – 300 °C. The commercial catalyst is Cu/ZnO/Al_2O_3 which has good CO_2 conversion but limited methanol selectivity[1]. Among the various alternative catalysts, In_2O_3/m-ZrO_2 (9 wt.% of In, m = monoclinic) is very interesting[2]. This catalyst promises good catalytic performance, mainly in terms of higher methanol selectivity compared to commercial materials. The aim of this work is a spectroscopic investigation (with *in-situ* and *operando* techniques) to deepen the knowledge of reaction mechanisms and interaction between catalyst and reactant/product substances.

Materials and Methods

The catalyst was synthesized using a gel oxalate precipitation-deposition method, where m-ZrO_2 was first obtained by precipitating $ZrO(NO_3)_2$, followed by calcination. In_2O_3 (10.9 wt.%) was then deposited on zirconia and calcined again. The powder was characterized using techniques like N_2 physisorption, H_2-TPR, CO_2-TPD, X-ray diffraction, and electron microscopy. FT-IR spectroscopy, in both *in-situ* and *operando* modes, was used to study the catalyst. *In-situ* analysis involved surface cleaning, activation, and CO_2 exposure as suggested by Tsoukalou[3]. Whereas, the *operando* analysis simulated reaction conditions (75% H_2 + 25% CO_2) at high pressure (7 bar) and temperature (200-300 °C). Furthermore, operando tests were performed with and without reductive pretreatment (200 °C, Ar or H_2/N_2).

Results and Discussion

The synthesis method successfully yielded the desired catalyst, as confirmed by XRD patterns in Figure 1(a), which indicate the presence of m-ZrO_2 and the expected fraction of In_2O_3. A comprehensive spectroscopic study, including *operando* and *in-situ* experiments, revealed significant interactions between CO_2, H_2, and the catalyst surface, suggesting a crucial role for In_2O_3 vacancies and m-ZrO_2 in the hydrogenation process. Specifically, FT-IR spectra in the 2700–3100 cm^{-1} region (Figure 1(b)) demonstrated the formation of formate (HCOO*) and methoxy (CH_3O*) species when the catalyst was exposed to an H_2/CO_2 mixture. These species are directly associated with methanol production, as

reported in the literature, and no peaks corresponding to CO or its production intermediates were detected, indicating high methanol selectivity[4,5]. This result aligns with previous studies, such as that of Martin et al[2], which estimated a methanol selectivity of 100%. *Operando* studies also explored catalyst activation, showing that intermediate species such as formates and methoxy groups only appeared after In_2O_3 was subjected to a reducing pretreatment. Additionally, the in-situ experiments (Figure 2) provided insights into H_2 splitting and CO_2 interaction mechanisms, suggesting that this catalyst may outperform others, particularly those featuring different ZrO_2 crystalline phases due to hydrogen carbonate formed over the activated catalyst. In conclusion, the combination of structural and spectroscopic analyses highlights the efficiency of the synthesized catalyst, particularly its high methanol selectivity and enhanced performance, which is likely due to the synergistic role of In_2O_3 vacancies and m-ZrO_2 in facilitating hydrogenation processes and promoting optimal CO_2 interaction.

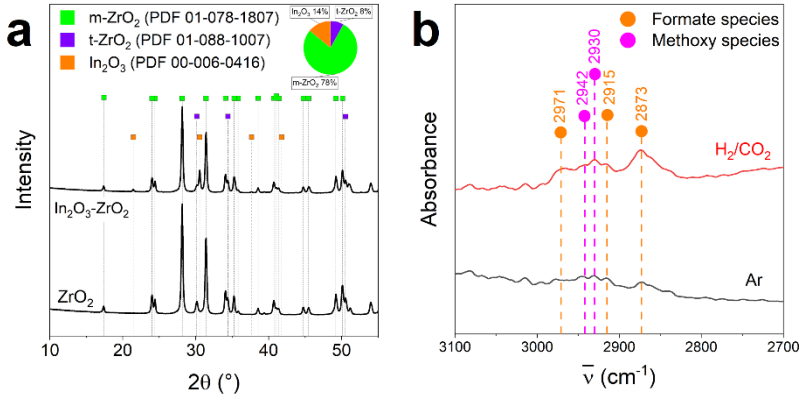

Figure 1. (a) XRD patterns for ZrO_2 and In_2O_3/m-ZrO_2 synthesized. The figure also shows the semi-quantitative analysis results for In_2O_3/m-ZrO_2. **(b)** *Operando* FT-IR spectra of In_2O_3/m-ZrO_2 captured in inert and reactive flow at 200 °C and 7 bar[4,5].

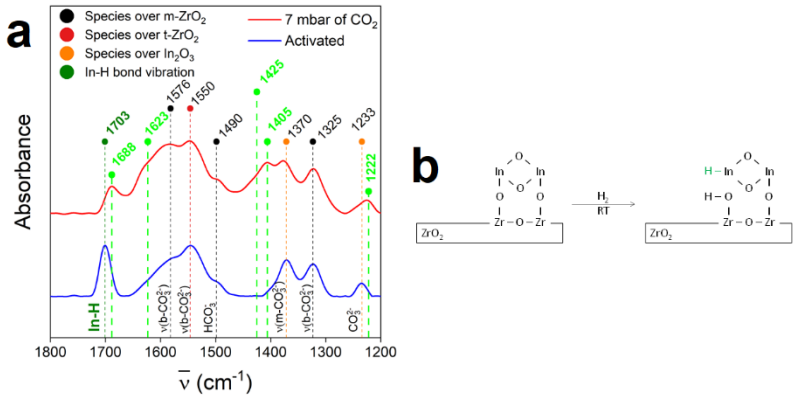

Figure 2. (a) FT-IR spectra of In_2O_3/m-ZrO_2 after H_2-dissociative adsorption with the method proposed by Tsoukalou[3]. **(b)** Hypothetic H_2-dissociative adsorption mechanism over In_2O_3/m-ZrO_2[3].

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