

Spectroscopic investigation of In₂O₃-ZrO₂ catalyst for CO₂ 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 -ZrO₂ 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-ZrO₂ 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 / CO₂ 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/Al₂O₃ which has good CO_2 conversion but limited methanol selectivity¹. Among the various alternative catalysts, In_2O_3/m -ZrO₂ (9 wt.% of In, m = monoclinic) is very interesting². 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-ZrO₂ was first obtained by precipitating ZrO(NO₃)₂, followed by calcination. In₂O₃ (10.9 wt.%) was then deposited on zirconia and calcined again. The powder was characterized using techniques like N₂ physisorption, H₂-TPR, CO₂-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 CO₂ exposure as suggested by Tsoukalou³. Whereas, the *operando* analysis simulated reaction conditions (75% H₂ + 25% CO₂) at high pressure (7 bar) and temperature (200-300 °C). Furthermore, operando tests were performed with and without reductive pretreatment (200 °C, Ar or H₂/N₂).

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-ZrO₂ and the expected fraction of In_2O_3 . A comprehensive spectroscopic study, including *operando* and *in-situ* experiments, revealed significant interactions between CO₂, H₂, and the catalyst surface, suggesting a crucial role for In_2O_3 vacancies and m-ZrO₂ 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 (CH₃O*) species when the catalyst was exposed to an H₂/CO₂ 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 al², 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 H₂ splitting and CO₂ interaction mechanisms, suggesting that this catalyst may outperform others, particularly those featuring different ZrO₂ 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-ZrO₂ in facilitating hydrogenation processes and promoting optimal CO₂ interaction.



Figure 1. (a) XRD patterns for $\ln_2O_3/m-ZrO_2$ ZrO₂ and synthesized. The figure also shows the semi-quantitative analysis results for In₂O₃/m-ZrO₂. (b) Operando FT-IR spectra of $\ln_2O_3/m-ZrO_2$ 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 -ZrO₂ after H_2 dissociative adsorption with the method proposed by Tsoukalou³. **(b)** Hypothetic H_2 -dissociative adsorption mechanism over In_2O_3/m -ZrO₂³.

References

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