

# Cu-Ce binary oxide catalysts for CO<sub>2</sub> hydrogenation to methanol: Operando FT-IR spectroscopy and kinetic study

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### Significance and Relevance

This research is significant for advancing sustainable chemical processes by improving CO<sub>2</sub> hydrogenation to methanol, a key industrial chemical. This study of Cu-CeO<sub>2</sub> catalysts highlights the importance of the Cu/Ce ratio and the synthesis technique in optimizing methanol yield. Investigating the relationship between catalyst morphology (e.g., copper particle size) and performance, alongside *in-situ* and *operando* analyses to understand reaction mechanisms and material properties, offers crucial insights for the design of more efficient catalysts.

*Preferred and 2<sup>nd</sup> choice for the topic:* CO<sub>2</sub> utilization and recycling / Fundamental advances in understanding catalysis

Preferred presentation: Oral preferred or Short Oral

## **Introduction and Motivations**

In the pursuit of a more sustainable and environmentally responsible future, the conversion of  $CO_2$  into valuable chemicals and fuels has emerged as a crucial research frontier. Among the  $CO_2$ hydrogenation reactions, its conversion to methanol appears as a key process in sustainable chemistry, due to the possible use of this substance as a fuel additive, chemical feedstock, for energy storage, etc. Currently, the hydrogenation of  $CO_2$  to methanol is industrially performed using a Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst<sup>1</sup>. This industrial catalyst shows good  $CO_2$  conversion, but the methanol selectivity is not optimal. In this sense, different alternative catalysts have been tested to increase the overall catalytic performance. Among the various possibilities, Cu and CeO<sub>2</sub> show a good synergistic effect for the CO<sub>2</sub> activation in the hydrogenation to methanol process<sup>1,2</sup>. Based on this consideration, the aim of this work is the study of Cu-CeO<sub>2</sub> catalysts and the implementation of *operando* FT-IR techniques to deepen the knowledge of reaction mechanisms.

#### **Materials and Methods**

The Cu-Ce binary oxide catalysts were synthesized using three methods—solution combustion synthesis (scs-), wet impregnation (wi-), and gel-oxalate coprecipitation (ox-)—by varying the Cu/Ce atomic ratio (Cu<sub>x</sub>Ce<sub>100-x</sub>). Their physicochemical properties were studied with complementary techniques. Catalytic activity and stability were assessed in a steel fixed-bed reactor (25 bar, 200–300 °C, H<sub>2</sub>:CO<sub>2</sub>:N<sub>2</sub>= 3:1:1, 20 NL/h/g<sub>cat</sub>). After testing, the spent catalysts were further characterized, and static FT-IR spectroscopy in transmittance mode was employed to assess the properties of the materials, such as basicity and their interaction with specific probe molecules. Additionally, the best-performing catalyst was analyzed using *operando* FT-IR spectroscopy in transmittance mode (H<sub>2</sub>/CO<sub>2</sub> = 3:1, 5 bar, 200–350 °C) to investigate the reaction mechanism.

## **Results and Discussion**

The catalytic tests identified ox- $Cu_{80}Ce_{20}$  as the best-performing catalyst, achieving a methanol yield of 0.82% at 300 °C. Using this data and applying the Arrhenius equation, the apparent activation energy for  $CO_2$  hydrogenation was estimated. The coprecipitated catalyst (ox- $Cu_{80}Ce_{20}$ ) exhibited the lowest activation energy (Ea  $\approx$  80 kJ/mol) and the highest number of active sites, as inferred from the pre-exponential factor (calculated at equal activation energy). Figure 1 summarizes these findings. This high catalytic activity is attributed to the small size of copper particles, which expose more copper surface and enhance the synergistic effect with  $CeO_2$ . A detailed spectroscopic analysis was



subsequently carried out on this catalyst. First, the interaction between the ox-CeO<sub>2</sub> support and methanol was investigated using *in-situ* FT-IR spectroscopy. Figure 2(a) shows the region between 775 and 1200 cm<sup>-1</sup>, where surface methoxy species signals appear as methanol pressure increases. Subsequent heat treatments in vacuum revealed that these species begin to decompose at 250 °C, indicating their relative stability. Additionally, ox-Cu<sub>80</sub>Ce<sub>20</sub> was analyzed using *operando* FT-IR spectroscopy. As shown in Figure 2(b), the spectra revealed an intensifying peak in the 800-900 cm<sup>-1</sup> region with an increasing temperature, indicating the formation of bidentate carbonates above 320 °C due to CO<sub>2</sub> activation. Carbonate species play a specific role in methanol synthesis, inhibiting CO hydrogenation to methanol at the Cu-CeO<sub>2</sub> interface. However, they do not completely inhibit the methanol synthesis reaction, as CO<sub>2</sub> hydrogenation to methanol proceeds on the Cu surface through the formation of formate intermediates. These findings provide valuable insights into the design of more efficient catalysts for CO<sub>2</sub> hydrogenation to methanol.



Figure 1. Arrhenius equation parameters as a function of copper particle size the (calculated using Scherrer equation): (a) apparent activation energy, Ea, and (b) pre-exponential factor (estimated under the assumption of equal activation energy),  $ln(k_{\infty})$ .

**Figure 2. (a)** FT-IR spectra obtained for  $ox-CeO_2$  during *in-situ* analyses with methanol as a probe molecule. **(b)** FT-IR spectra obtained for  $ox-Cu_{80}Ce_{20}$ during *operando* analysis at 5 bar with a 15 NmL/min flow of H<sub>2</sub>:CO<sub>2</sub> = 3:1 mixture.

## References

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