Cu-Ce binary oxide catalysts for CO2 hydrogenation to methanol: Operando FT-IR spectroscopy and kinetic study

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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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Cu-Ce binary oxide catalysts for CO_2 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_2 hydrogenation to methanol, a key industrial chemical. This study of Cu-CeO_2 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 2nd choice for the topic: CO_2 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_2O_3 catalyst[1]. 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_2 show a good synergistic effect for the CO_2 activation in the hydrogenation to methanol process[1,2]. Based on this consideration, the aim of this work is the study of Cu-CeO_2 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_xCe_{100-x}). 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_2:CO_2:N_2= 3:1:1, 20 NL/h/g_{cat}). 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_2/CO_2 = 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 ≈ 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_2 support and methanol was investigated using *in-situ* FT-IR spectroscopy. Figure 2(a) shows the region between 775 and 1200 cm^{-1}, 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-$Cu_{80}Ce_{20}$ was analyzed using *operando* FT-IR spectroscopy. As shown in Figure 2(b), the spectra revealed an intensifying peak in the 800-900 cm^{-1} region with an increasing temperature, indicating the formation of bidentate carbonates above 320 °C due to CO_2 activation. Carbonate species play a specific role in methanol synthesis, inhibiting CO hydrogenation to methanol at the Cu-CeO_2 interface. However, they do not completely inhibit the methanol synthesis reaction, as CO_2 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_2 hydrogenation to methanol.

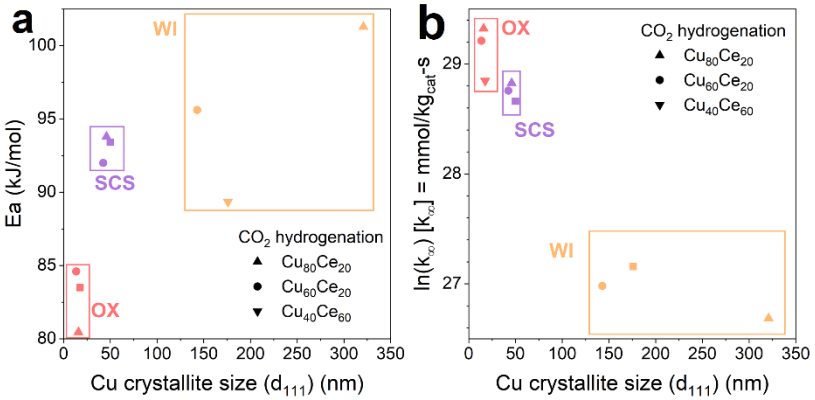

Figure 1. Arrhenius equation parameters as a function of copper particle size (calculated using the Scherrer equation): **(a)** apparent activation energy, Ea, and **(b)** pre-exponential factor (estimated under the assumption of equal activation energy), $\ln(k_\infty)$.

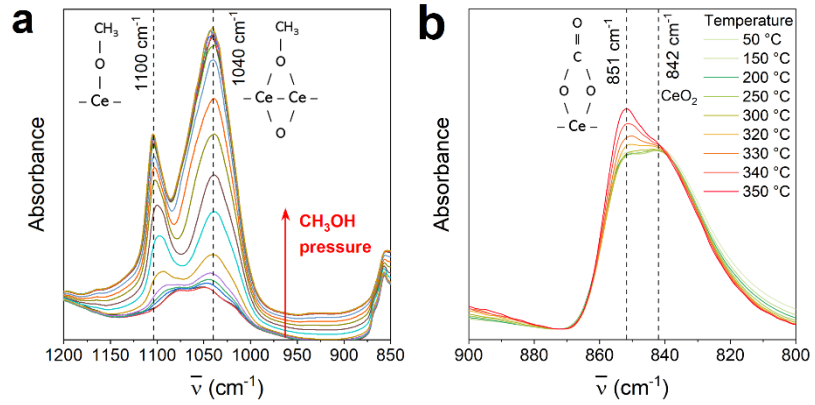

Figure 2. (a) FT-IR spectra obtained for ox-CeO_2 during *in-situ* analyses with methanol as a probe molecule. **(b)** FT-IR spectra obtained for ox-$Cu_{80}Ce_{20}$ during *operando* analysis at 5 bar with a 15 NmL/min flow of H_2:CO_2 = 3:1 mixture.

References

1. A. Álvarez, A. Bansode, A. Urakawa et al., *Chem. Rev.* **2017**, *117*, 9804-9838
2. J. Graciani, K. Mudiyanselage, F. Xu et al., *Science* **2014**, *345*, 546-550
3. E. Sartoretti, C. Novara, M.C. Paganini et al., *Catalysis Today* **2023**, *420*, 114037
4. L. Lin, S. Yao, Z. Liu et al., *J. Phys. Chem. C* **2018**, *122*, 12934-12943

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