# $CO_2$ Hydrogenation to Methanol over Cu-Doped MIP-177: Tuning Ti–O Connectivity and Phase Transformation for Enhanced Catalytic Performance.

**Ayla Roberta Borges Serra*,[1] João Lucas Marques Barros,[1] Osvaldo Antonio Serra,[2] José Maria Correa Bueno[1].**

*[1]Departamento de Engenharia Química, UFSCar, São Carlos, SP, Brasil. [2]Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto (FFCLRP-USP), Ribeirão Preto, SP, Brasil.*

**Resumo/Abstract (Helvética, tam. 12)**

RESUMO - A hidrogenação do $CO_2$ em metanol é uma estratégia promissora para a valorização de carbono e produção de combustíveis sustentáveis. Neste trabalho, investigamos o desempenho catalítico do MIP-177-LT, um MOF de titânio com conectividade Ti–O altamente condensada, funcionalizado com Cu. A dopagem com Cu (1–8%) impactou significativamente a produtividade, com destaque para MIP-177-LT-Cu(2%), que apresentou 15,61 mmol MeOH/gCu/h e seletividade de 50% para metanol. Também exploramos a transformação térmica para a fase MIP-177-HT, revelando influência da conectividade Ti–O e da topologia do MOF na atividade catalítica. Estes resultados destacam o potencial dos Ti-MOFs termicamente robustos como plataformas versáteis para reações térmicas de hidrogenação.
*Palavras-chave: Hidrogenação de $CO_2$, MOFs, Titânio, MIP-177, metanol.*

ABSTRACT - The hydrogenation of $CO_2$ into methanol is a key route toward sustainable carbon valorization. Herein, we explore the catalytic potential of MIP-177-LT, a titanium-based metal-organic framework (Ti-MOF) with a highly condensed $Ti_{12}O_{15}$ SBU and a honeycomb architecture, doped with varying Cu loadings (1–8%). Catalytic tests conducted at 300 °C and 30 bar revealed that MIP-177-LT-Cu(2%) exhibited the highest methanol productivity of 15.61 mmol MeOH/g Cu/h, with a 50% selectivity to methanol, outperforming the 8% Cu-doped analogue. A phase transition to MIP-177-HT, increasing Ti–O condensation from 1.25 to 1.5, led to reduced catalytic activity. The results underscore the importance of finely tuned Ti–O connectivity—closely associated with the SBU condensation degree—and the dynamic retention or loss of structural formates under thermal stress, as key levers for modulating the catalytic behavior of Ti-MOFs.
*Keywords: $CO_2$ hydrogenation, MOFs, titanium, MIP-177, methanol production.*

## Introduction

The valorization of carbon dioxide into methanol via catalytic hydrogenation is a pivotal reaction in the context of sustainable chemical processes and greenhouse gas mitigation. Among the diverse catalytic systems explored, metal–organic frameworks (MOFs) have emerged as versatile platforms due to their tailorable porosity, modular composition, and structural diversity.[1] However, the thermal instability of many MOFs has limited their application under the harsh conditions typical of gas-phase hydrogenation. In this context, titanium-based MOFs, particularly MIP-177-LT [$Ti_{12}O_{15}(mdip)_3(formate)_6$], have gained attention owing to their highly condensed Ti–O inorganic subunits, which provide enhanced thermal and chemical stability.[2]

MIP-177-LT features a unique $Ti_{12}O_{15}$ secondary building unit (SBU) arranged in a robust honeycomb architecture with a Ti–O condensation degree of 1.25. These characteristics are critical for retaining crystallinity and catalytic integrity at elevated temperatures. Moreover, its post-synthetic modification to a high-temperature phase, MIP-177-HT, offers an opportunity to investigate how Ti–O connectivity and structural densification influence catalytic behavior. Incorporation of Cu within the MOF framework introduces redox-active sites capable of promoting $CO_2$ activation and hydrogenation. This work aims to correlate structural phase, Cu loading, and Ti–O connectivity with methanol productivity and selectivity in the thermal hydrogenation of $CO_2$.

## Experimental

MIP-177-LT was synthesized according to literature protocols and subjected to defect engineering by acid etching using 1 mol·L$^{-1}$ HCl under ambient stirring overnight. The washed material was impregnated with Cu by mixing 50 mg of the defect-rich MOF with 200 µL of a 20% $Cu(NO_3)_2$ aqueous solution, followed by sonication and additional overnight stirring. The solid was washed and dried before catalytic testing.

Catalytic $CO_2$ hydrogenation experiments were carried out in a tubular fixed-bed reactor (length: 40 cm, inner diameter: 1 cm, reaction zone: 2 cm) under continuous flow. Prior to the reaction, the catalyst (180–250 mg) was reduced under $H_2$ (300 °C, 1 h, ambient pressure). The reaction was conducted at 300 °C and 30 bar using a $CO_2:H_2$ = 1:3 gas mixture, GHSV = 8000 mL·g_cat$^{-1}$·h$^{-1}$, for 5 h. Product analysis was performed by GC (Agilent 8860 system) using FID for methanol and methane and TCD for CO and $CO_2$. BET surface area measurements were conducted before and after reaction to evaluate porosity retention. XRD and SEM analyses confirmed phase purity and particle integrity.

## Results and Discussion

The MIP-177-LT-Cu(2%) catalyst exhibited the highest methanol productivity (15.61 mmol MeOH/g Cu/h) with a selectivity of 50% toward methanol, 11% toward methane, and 39% toward CO. Increasing Cu content to 8% led to a decline in methanol productivity to 11.7 mmol MeOH/g Cu/h and lower selectivity (40%) due to possible aggregation or blockage of pores. The performance decline upon Cu overloading underscores the importance of maintaining a high dispersion of active sites within the framework.

Transformation of MIP-177-LT to MIP-177-HT by calcination at 280 °C increased the Ti–O condensation degree from 1.25 to 1.5 and reorganized the framework into 1D $(Ti_6O_9)_n$ chains. However, this densification resulted in reduced porosity (BET area: 470 m$^2$·g$^{-1}$) and a lower productivity of 7.0 mmol MeOH/g Cu/h. The reduction in performance is attributed to both decreased accessibility of active sites and potential loss of formate groups that contribute to $CO_2$ activation.

XRD patterns before and after reaction showed preservation of crystallinity, as possible to see in Figure 1, indicating structural robustness under reaction conditions. SEM images revealed no significant morphological degradation. These results confirm the catalytic stability of MIP-177 under hydrothermal conditions, which is uncommon among MOFs. Del Angel's thesis further supports that the presence of formate groups and high Ti–O condensation degree contribute to the thermal resilience and redox behavior of the framework, directly influencing $CO_2$ adsorption and activation kinetics.

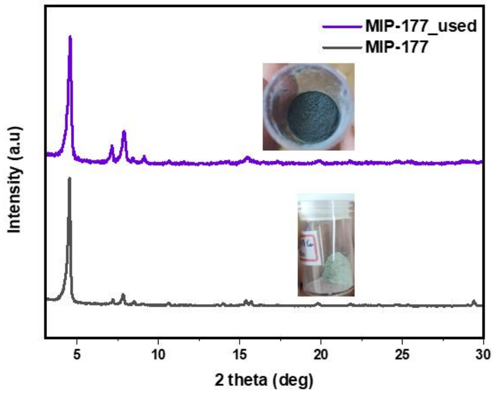


**Figura 1.** Powder X-ray diffraction (XRD) patterns of pristine MIP-177 (black) and the catalyst recovered after $CO_2$ hydrogenation (MIP-177_used, purple). The preservation of the main diffraction peaks indicates that the crystalline structure of MIP-177 is maintained after catalytic testing at 300 °C and 30 bar, demonstrating the framework's thermal and chemical stability under reaction conditions. Insets show visual differences in sample appearance before (light grey) and after (dark grey) catalysis.

## Conclusion

We demonstrated that Cu-doped MIP-177-LT is a promising catalyst for $CO_2$ hydrogenation to methanol, combining redox-active Cu sites with a thermally robust Ti–O scaffold. Optimal Cu loading (2%) yielded the best catalytic performance, while excessive densification of the MOF (MIP-177-HT) suppressed reactivity due to reduced porosity and possibly altered Cu dispersion. These findings highlight that controlling Ti–O connectivity and maintaining formate bridges are critical to maximizing catalytic output. Our work establishes a valuable structure–activity relationship and expands the frontier of MOFs as candidates for thermocatalytic applications beyond photocatalysis.

## Acknowledgments

The authors gratefully acknowledge CNRS and Ecole Normale Supérieure for infrastructure and scientific support. A.R.B. Serra thanks FAPESP (São Paulo Research Foundation) for financial support.

## References


1. Yaghi, O.M.; O'Keeffe, M.; Ockwig, N.W.; Chae, H.K.; Eddaoudi, M.; Kim, J. Reticular synthesis and the design of new materials. Nature **2003**, 423, 705–714.
2. Wang, S.; Kitao, T.; Guillou, N.; Wahiduzzaman, M.; Martineau-Corcos, C.; Nouar, F.; Tissot, A.; Binet, L.; Ramsahye, N.; Devautour-Vinot, S.; et al. A phase transformable ultrastable titanium-carboxylate framework for photoconduction. Nat. Commun. **2018**, 9, 1660.