

# Supercritical CO<sub>2</sub> as an efficient tool in the fabrication of Cu<sup>0</sup>ZnO-rGO 3D aerogels for highly selective catalytic CO<sub>2</sub> hydrogenation

**Márta Kubovics,<sup>a\*</sup> Paul Florin Coldea,<sup>b</sup> Javier Moral Vico,<sup>b</sup> Antoni Sánchez,<sup>b</sup>  
Ana M. López-Periago,<sup>a\*</sup> Concepción Domingo<sup>a\*</sup>**

<sup>a</sup> *Materials Science Institute of Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra, 08193 Spain*

<sup>b</sup> *Department of Chemical, Biological and Environmental Engineering, Universitat Autònoma de Barcelona, Bellaterra, 08193, Spain*

\*Corresponding author: mkubovics@icmab.es

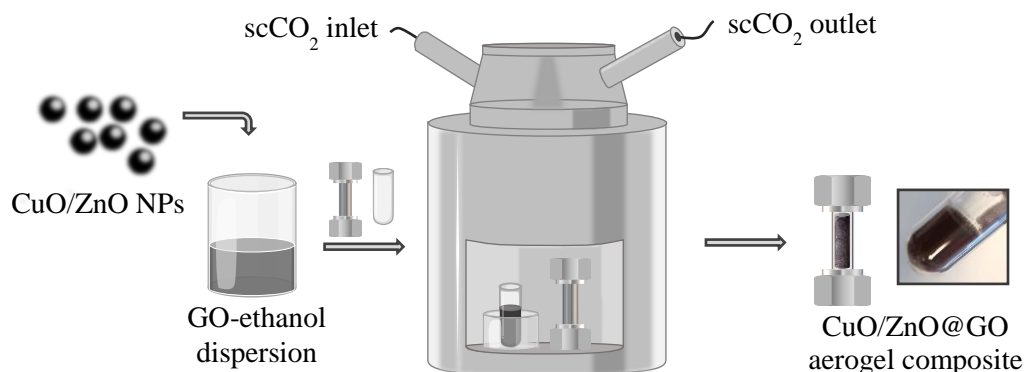
## 1. Introduction

The rapid rising of CO<sub>2</sub> concentration in the atmosphere is one of the hot topics of recent years, as we are already experiencing the preliminary negative consequences of the imponderable climatic change caused by the increased gas emissions. For this reason, turning CO<sub>2</sub>, a cheaply available feedstock to value-added chemicals (such as methanol), in eco-friendly and green processes is a research subject of great interest.<sup>1,2</sup> A broad variety of metal-based heterogeneous catalytic systems have been designed for this purpose, however most of them still suffer from cost limitations, short lifetime or low selectivity. Many of these drawbacks can be improved by the careful selection of catalytic support. Recently, 2D/3D graphene-based structures are coming to prominence, as they are excellent candidates not only for the dispersion of the catalytically active nanoparticles (NPs), but also by playing an active role in the catalytic reaction through facilitating charge transfer processes, providing high electron mobility, thermal and mechanical stability.<sup>3</sup> A recently developed supercritical CO<sub>2</sub>-assisted method for graphene-oxide (GO) aerogel formation offers an eco-friendly alternative to the traditional freeze drying method, where the one-pot gelling and drying occurs at mild temperature and the use of harmful solvent is not required.<sup>4</sup> Moreover, applying this method, the elimination of the oxygen-containing functionalities of the GO are prevented, enabling extended and homogenous functionalization of the GO flakes and providing the possibility of post-synthetic controlled thermal or chemical reduction.

In this work, a Cu<sup>0</sup>/ZnO-based catalyst supported by a novel 3D rGO aerogel was synthesized using a sustainable scCO<sub>2</sub> method. The catalytic performance of the composite was tested in the CO<sub>2</sub> hydrogenation reaction to produce methanol. The role of the rGO aerogel support in the catalytic process is highlighted, in terms of its influence on the characteristics of the deposited Cu<sup>0</sup>/ZnO nanoparticles, as well as their extensive dispersion on the rGO flakes throughout the catalytic process.

## 2. Materials and Methods

Conventionally precipitated CuO/ZnO NPs were dispersed in GO-ethanol dispersion. CuO/ZnO@GO composite aerogels were straightforwardly prepared using scCO<sub>2</sub> medium, inside of a stainless steel column for further application in the methanol production reaction. (Fig. 1)



**Figure 1.** Schematic representation of the synthetic protocol

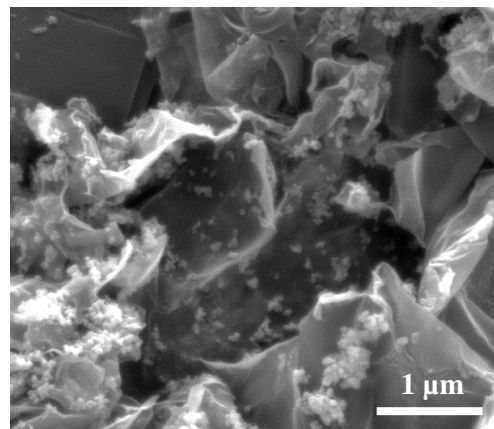
The activity of the synthesized catalyst with respect to the hydrogenation of CO<sub>2</sub> to obtain methanol was evaluated by using a fixed-bed flow reactor. Specifically, methanol space-time yield (STY), selectivity and CO<sub>2</sub> conversion were evaluated, by comparing the performance with unsupported NPs and commercial catalyst. Complete solid-state characterization of the materials was performed, including electron microscopy, X-ray diffraction and ex situ X-ray photoelectron spectroscopy.

### 3. Results and discussion

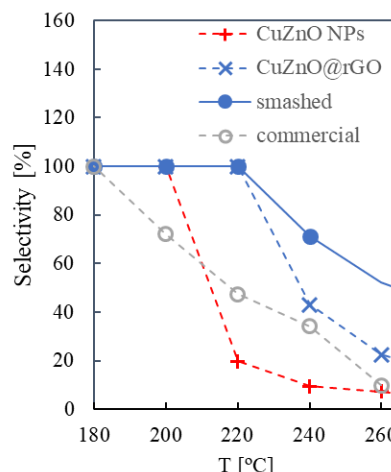
The scCO<sub>2</sub> process results in a highly porous and low density aerogel, with interconnected meso/macropores. The deposited NPs homogenously decorate the surface of the GO flakes, even after the reduction and catalytic procedure, demonstrating the structural stability of the aerogel (Fig. 2).

At intermediate studied temperature (220 °C) the STY values were threefold enhanced in case of the aerogel composite in comparison to the unsupported NPs (7.3 vs 2.6 mg<sub>MeOH</sub>·g<sub>CuO</sub><sup>-1</sup>·h<sup>-1</sup>), while similar conversion was measured. The yield and the conversion could be further enhanced by smashing the monolith into smaller pieces, thus reaching better distribution of the gas flow within the porous structure. Although these values are slightly lower than using the commercial catalyst, most likely because of the different particle size and exposed surface area, outstanding selectivity was achieved with the Cu<sup>0</sup>ZnO@rGO aerogel even at high temperature, much better than with the unsupported NPs or commercial sample (Fig. 3).

The interaction between Cu<sup>0</sup> and ZnO and the function and structure of their interfacial contact areas were further investigated by XPS on the reduced spent catalyst, since it plays a significant role in the catalytic performance. It was clearly seen that the presence of rGO in CuZnO@rGO alleviated the negative effects of sintering and alloy formation and improved the catalytic parameters.



**Figure 2.** SEM image of the spent Cu<sup>0</sup>ZnO@rGO aerogel catalyst



**Figure 3.** Methanol selectivity of the tested catalysts

### 4. Conclusions

3D rGO aerogel supported Cu<sup>0</sup>/ZnO catalyst was synthesized in a facile method applying supercritical CO<sub>2</sub> for the structuration of the catalyst matrix. This medium not only promotes the construction of a low-density meso/macroporous structure, but also facilitates the dispersion of the deposited bimetallic nanoparticles. By incorporating the rGO support, threefold enhancement was reached in the methanol yield, while outstanding selectivity was achieved. The proposed preparation procedure offers a strategy to structure a 3D rGO aerogel matrix as a support for active centers and opens the possibility to be potentially implemented in further catalytic systems.

### References

1. U.J. Etim, Y. Song, Z. Zhong, *Front Earth Sci.* **2020**, *8*, 1-26.
2. Y. Sun, Z. Lin, S.H. Peng, V. Sage, Z. Sun, *J Nanosci Nanotechnol.* **2019**, *19*, 3097-3109.
3. V. Deerattrakul, P. Puengampholsrisook, W. Limphirat, P. Kongkachuichay, *Catal Today.* **2018**, *314*, 154-163.
4. A. Borrás, G. Gonçalves, G. Marbán, S. Sandoval, S. Pinto, P. Marques, J. Fraile, G. Tobias, A.M. López-Periago, C. Domingo, *Chem - A Eur J.* **2018**, *24*, 15903-15911.