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Coach	**Supervisor(s)**	**Funding**
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CO_2 hydrogenation to methanol: from batch to continuous-flow

Aim

The aim of this project is to evaluate the performance and stability of a single-atom catalyst for low-temperature methanol synthesis in continuous-flow.

Justification

Renewable energy imports originating from wind and sun will become a necessary and vital part of the EU energy mix. The most straightforward method of transporting renewable energy would be liquid green hydrogen. However, its low volumetric density and very low boiling point present major technical challenges. One of the strategies to avoid the transport of liquid hydrogen is to produce hydrogen-derived green liquid molecules. Among these molecules, methanol (MeOH) has been identified as the most promising hydrogen carrier and building block for the chemical industry.

Conventionally, MeOH is synthesized from syngas (CO/H_2) over heterogeneous catalysts, at elevated pressures (5-10 MPa) and moderate temperatures (220-300°C)[1] in a continuous-flow process. MeOH can also be produced from other carbon-containing feedstock and its direct synthesis from CO_2 has been under the spotlight. With state-of-the-art heterogeneous catalysts, the one-pass methanol yield of the CO_2-based process is lower than that of the syngas-based process[1]. MeOH synthesis is exothermic with a decrease in the number of molecules, meaning that high pressure and low temperature thermodynamically favor MeOH formation. Clearly, MeOH production would benefit from the development of improved catalysts active at lower temperatures. Ru-based homogeneous catalysts have been reported to efficiently catalyze this reaction under mild conditions, but their applicability in continuous flow is limited.

Solid micellar catalysts (SOMIC) are a new class of heterogeneous catalysts consisting of isolated active sites incorporated in the walls of a mesoporous matrix stabilized by surfactant molecules. The first SOMIC material, $Ru^{(III)}$@MCM-41 (**Figure 1**), consists of $Ru^{(III)}$ sites incorporated in the walls of MCM-41 and stabilized by CTA^+ surfactant molecules in the pores. $Ru^{(III)}$@MCM was thoroughly tested in batch and showed an outstanding catalytic activity for the hydrogenation of CO_2 to formate in the presence of a tertiary ethyl amine at 90 °C. To make this catalyst industrially relevant and by using the Robinson-Mahoney reactor at the LCT, our group recently demonstrated that $Ru^{(III)}$@MCM efficiently catalyzes CO_2 hydrogenation to formate in flow.

Building on the conceptual and chemical similarity between our new $Ru^{(III)}$ single-site catalyst and Ru-based homogeneous catalysts, our research is currently focused on directing the selectivity of CO_2 hydrogenation over these heterogeneous catalysts to methanol instead of formate. Our ultimate goal is to demonstrate the potential of SOMIC catalysts for low-temperature methanol synthesis in flow. In this project, intrinsic kinetic data will be acquired using a Robinson Mahoney multiphase continuous flow reactor. The kinetic data collected during this project will allow to identify the elementary steps that control the reaction rate, how the rate is affected by reaction conditions and the catalyst's properties, and study catalyst stability under reaction conditions — insights that are useful to guide the design of improved catalysts.

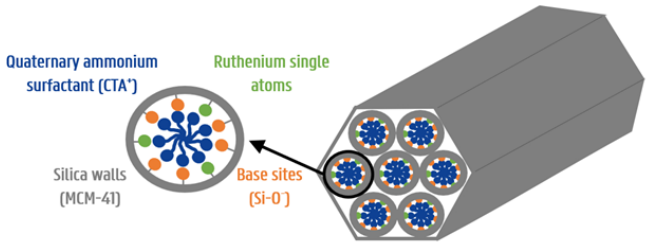

Figure 1. Schematic representation of the $Ru^{(III)}$@MCM catalyst.[2]

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Program

1. Literature study on the state-of-art of low temperature CO_2 hydrogenation to MeOH and reaction kinetic studies.
2. Synthesis of solid micellar catalysts.
3. Lab-scale catalytic testing using a Robinson-Mahoney reactor.

References

1. J. Zhong, X. Yang, Z. Wu, B. Liang, Y. Huang and T. Zhang, *Chemical Society Reviews*, 2020, **49**, 1385-1413.
2. Q. Wang, S. Santos, C. A. Urbina-Blanco, W. Y. Hernández, M. Impéror-Clerc, E. I. Vovk, M. Marinova, O. Ersen, W. Baaziz, O. V. Safonova, A. Y. Khodakov, M. Saeys and V. V. Ordomsky, *Applied Catalysis B: Environmental*, 2021, **290**, 120036.