M2 internship

MOF-based catalysts for CO_2 hydrogenation into added-value fuels

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MOF-based catalysts for CO_2 hydrogenation into added-value fuels

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Keywords: CO_2 conversion, heterogeneous catalysis, metal-organic frameworks
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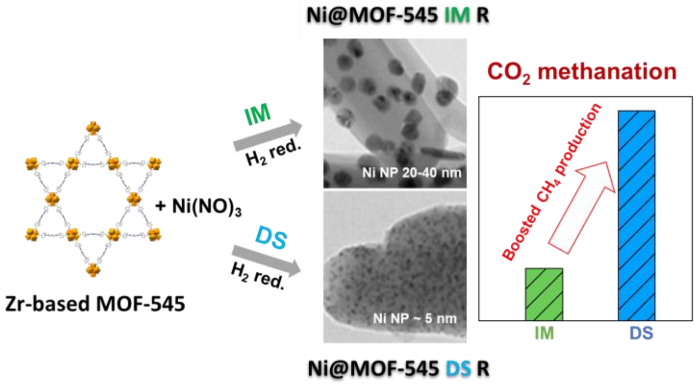
Funding: ANR

Presentation and description of the project: Major advances in energy-efficient CO_2 conversion can potentially alleviate CO_2 emissions, reduce the dependence on non-renewable resources, and minimize the environmental impacts from the portions of fossil fuels displaced. **Methanol** (CH_3OH) is an important chemical feedstock and can be used as a fuel for internal combustion engines and fuel cells, as well as a platform molecule for the production of chemicals and fuels. As one of the promising approaches, thermocatalytic CO_2 hydrogenation to CH_3OH via heterogeneous catalysis is attracting a great deal of attention (J. G. Chen et al. Recent Advances in Carbon Dioxide Hydrogenation to Methanol via Heterogeneous Catalysis. *Chem. Rev.* **2020**, 120, 7984−8034. DOI:10.1021/acs.chemrev.9b00723). Over the past decades, Cu-based catalysts amongst others have been extensively reported for CO_2 hydrogenation into methanol (see for example C. Coperet et al. CO_2-to-Methanol Hydrogenation on Zirconia-Supported Copper Nanoparticles: Reaction Intermediates and the Role of the Metal-Support Interface. *JACS Au* **2024**, 4, 237−252.)

Previous studies demonstrate that CO_2 hydrogenation to CH_3OH is structure sensitive, and the catalytic performance relies closely on the dimension and composition of the metal/metal oxide interface. In this regard, MOFs are particularly advantageous. They are a fascinating and well-established class of crystalline porous solids constructed from inorganic clusters and organic linkers and are potentially capable of **confining catalytically active nanoparticles in their pores**. Compared to conventional oxides (Al_2O_3, SiO_2, ZrO_2, CeO_2), they have gained considerable interest as attractive platforms for designing heterogeneous catalysts due to unique features: (1) their **porous and modular architecture** allows the immobilization of catalytic species such as metallic nanoparticles and the diffusion of reactants/products; (2) the **functionalization** of their linkers and metallic clusters allows design strategies for targeted properties; (3) MOFs share with heterogeneous catalysts facile separation and reusability, and (4) their well-defined structures **facilitate rationale approaches** to structure-properties relationships, including computational approaches. Despite their huge structural diversity, only a handful number of MOFs have been explored for the design of catalysts for methanol production, including typically ZIF-8, MIL-100 and UiO-66 (ref above and references therein). Over the last decade, our groups have developed strategies for **designing heterogeneous MOF-based catalysts for reactions of interest to energy** by taking advantage of the substantial internal surface area and considerable porosity of the MOF (see an example figure below, H. Chen et al. Zr-Based MOF-545 Metal-Organic Framework Loaded with Highly Dispersed Small Size Ni Nanoparticles for CO_2 Methanation, *ACS Appl. Mater. Interfaces* **2024**, 16, 12509−12520. DOI:10.1021/acsami.3c18154).

Objectives and expected results: In this internship, we propose to focus on **Zr-based MOFs** made of carboxylate ligands and high valent Zr(IV) ions. They indeed represent a particularly appealing sub-set of solids, as they have amongst the highest thermal (up to 500°C) and chemical stability while having a large structural diversity. (Z. Chen et al. Reticular chemistry in the rational synthesis of functional zirconium cluster-based MOFs. *Coord. Chem. Rev.* **2019**, 386, 32–49. DOI:10.1016/j.ccr.2019.01.017). We will investigate the encapsulation of NPs by screening various 3d metals while considering their doping with promoters (typically alkaline ions) or noble metal co-catalysts in order to identify the best NPs compositions for optimal methanol production.



Techniques and methods used: The M2 project will consist in: i) the synthesis of the materials (@ILV); the solid **MOF-based** materials will be synthesized and characterized (IR spectroscopy, powder X-ray diffraction, SEM-EDX analysis, N_2 adsorption isotherms, ICP analysis) following the know-how of ILV laboratory; ii) catalytic experiments (@LCPB) using thermal reactors for reducing CO_2 into methanol. The products derived for the reaction (H_2 and CO_2-reduction products) will be analysed by gas chromatography. Other characterizations will include HR-TEM (High-resolution transmission electron microscopy) coupled with EDX (energy dispersive X-ray spectroscopy) that will be applied to capture structural and chemical composition information on the catalysts. The best catalysts will be selected for further in-depth post-catalytic characterizations and flow catalytic tests in collaboration with Debecker's group in Louvain.

Knowledge and skills: A good knowledge of coordination chemistry and material chemistry as well as a high level of motivation is required. An experience in heterogeneous catalysis would be appreciated. Candidates should also be quickly autonomous and able to organize themselves to manage the various aspects of their project (synthesis, characterization, catalysis), which will be carried out in two laboratories ILV (Versailles) and Collège de France (Paris).