

Thesis in Chemistry Starting in October 2024

Title: Immobilization of bimetallic catalysts in porous solids for CO₂ hydrogenation

Laboratory : MIM group, Institut Lavoisier de Versailles (ILV), Université Paris-Saclay, Université de Versailles-St-Quentin-en-Yvelines. www.ilv.uvsq.fr

Keywords: CO₂ conversion, heterogeneous catalysis, metal-organic frameworks

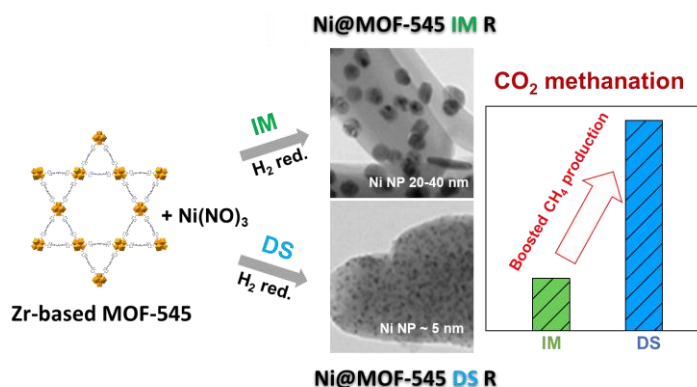
PhD supervisors : Anne Dolbecq (DR CNRS) , Pierre Mialane (Prof. UVSQ) (materials synthesis and characterizations)

Co-supervisor : Caroline Mellot-Draznieks (DR CNRS) LCPB, Collège de France, Paris (catalytic tests)

Collaboration: Jean-Blaise Brubach, Synchrotron SOLEIL, AILES beamline (operando DRIFT)

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Context: The conversion of CO₂ into commercially valuable chemicals is a promising strategy to move towards a low-carbon chemical industry. CO₂ methanation is one attractive option for renewable H₂ storage as methane exhibits a higher chemical energy density than H₂. Furthermore, our society has all the infrastructure needed to transport, store and burn methane. Over the past decades, Pd, Ru, Rh and Ni-based catalysts were extensively reported for CO₂ methanation (T. Len, et al. *Green Chem.* 25 (2023) 490–521). Among them, Ni-based solids attract research efforts as being low price while delivering high performances with excellent selectivity towards methane. Still, the catalytic performances for CO₂ methanation are known to strongly depend on the support used to disperse the metallic Ni nanoparticles (NPs). Zirconia is frequently used as it is known to promote CO₂ methanation thanks to strong Ni^{•••}ZrO₂ interfacial sites (X. Jia, et al. *Appl. Catal. B Environ.* 244 (2019) 159–169). In that context, metal-organic frameworks (MOFs), a class of porous solids, incorporating Zr centers have gained considerable attention as candidates of choice for CO₂ methanation (S. Gulati, et al. *Coord. Chem. Rev.* 2023, 474, 214853). They can provide abundant catalytic sites and may be designed to ensure the dispersion of metallic catalytic NPs. Their porosity allows augmenting the interplay between the NPs and the MOF network while preventing the undesired phenomena of sintering and aggregation of active metal species. As a result, a number of Ni-containing MOF catalysts have recently emerged for CO₂ methanation (M. Mihet, et al. *Int. J. Hydrogen Energy* 2019, 44 (26), 13383–13396). These last two years, we have in our group used the large pore MOF-545 to successfully disperse small Ni NPs (~5



nm) in a very homogenous fashion, using the double solvent (DS) method. Unlike the impregnation method (IM), the DS method produces materials with remarkable catalytic activities, among the highest reported to date for catalysts derived from MOFs (under revision for *ACS Applied Materials and Interfaces*).

Objectives: This above initial success inspires us to continue our research efforts by i) using other yet-unexplored Zr-based

MOFs as supports for metallic NPs while ii) exploring the realm of bimetallic catalytic NPs. Indeed, a strategy to further boost the catalytic performances is to construct Ni-based *bimetallic* systems using either noble metals (Rh, Ru, Pd) or transition metals (Fe, Co). These elements were classified in terms of their catalytic activity (Ru > Rh > Ni > Co > Pd) and their selectivities (Pd > Ni > Rh > Co > Ru) (M. Younas, et al. *Energy and Fuels.* 30 (2016) 8815–8831).

The PhD project will consist in designing, synthesizing and characterizing bimetallic porous solids, and perform catalytic tests and post-catalytic characterizations with the aim to rationalize their catalytic activities. HR-TEM (High-resolution transmission electron microscopy) coupled with EDS (energy dispersive X-ray spectroscopy) will be applied to capture structural and chemical composition information on the catalysts. The best catalysts will be selected for operando DRIFT (diffuse reflectance infrared Fourier transform)

spectroscopy at SOLEIL, to follow the structural changes of the solids, detect catalytic intermediates, and quantify the products during the catalysis, aiming at shedding light on the catalytic mechanism.

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 autonomous and able to organize themselves quickly 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)).

Contact: CVs should be sent to Pierre Mialane (pierre.mialane@uvsq.fr), Anne Dolbecq (anne.dolbecq@uvsq.fr) and Caroline Mellot-Draznieks (caroline.mellot-draznieks@college-de-france.fr).