POSTDOCTORAL RESEARCH POSITION

Metal-Organic Frameworks for CO_2 valorisation using Frustrated Lewis Pairs

Faculty: Laboratoire de Chimie des Processus Biologiques (LCPB), Collège de France, CNRS, Sorbonne Université and PSL Research University

Location : 11 Marcelin Berthelot, 75231 Paris Cedex 05, France

Salary : depending on experience

Tenure : 12 months from January 2022 (possibility of extension)

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Position for 12 months - Starting date from January 2022

Financial support: Region Ile de France (DIM Respore)

Laboratoire de Chimie des Processus Biologiques (LCPB), Collège de France, Paris, France

The post is available as part of a collaborative research project between LCPB at the Collège de France (Paris), IRCELYON (Lyon) and SOLEIL Synchrotron AILES beamline (Saclay). The objective of the project is to investigate porous hybrid materials with targeted functionalization towards CO_2 conversion into small molecules.

Context: The chemical sequestration of CO_2 using Frustrated Lewis Pairs (FLPs) is attracting increasing attention as an efficient strategy for the conversion of CO_2 into CO or formate through hydrogenation protocols (Sakakura T, Choi J-C, Yasuda H. *Chem Rev* **2007**, 107:2365). Despite their enormous potential, the practical use of FLPs faces similar limitations than conventional homogeneous catalysts (stability, catalyst/product separation, recyclability) making the proof-of-concept of their transfer to the solid state a currently hot topic, including to Metal-Organic Frameworks (MOFs) (Y. Ma et al. *Chem. Soc. Rev.* 2018, 47, 5541). In that context, we are currently investigating the functionalization of well-selected MOFs with sufficient pore size to accommodate covalently-grafted FLP and allow fast diffusion for catalysis purposes. These solids all contain suitable organic ligands amenable to the required click-chemistry to synthesize covalently bonded FLP@MOF. These innovative solids are designed as catalysts for the heterogeneous hydrogenation of CO_2 within a historical collaboration between the Collège de France and IRCELYON, with the aim to define optimal operating conditions in terms of pressure and temperature, while taking great care to evaluate the selectivity and recyclability of such complex solids.

Recent publications of the team include those on metal-organic frameworks functionalized to perform photocatalytic reactions such as OER (*J. Am. Chem. Soc.* **2018**, 140, 10, 3613-3618; *ACS Applied Materials and Interfaces* **2019**, 11, 51, 47837-47845), HER (*Chem. Comm.*, **2019**, 55, 4166) and CO_2RR (*ChemSusChem* **2015**, 8, 603-608; *ACS Catalysis* **2018**, 8, 3, 2030-2038; *Angew. Chem. Int. Ed.* **2020**, 59, 5116-5122, *J. Am. Chem. Soc.* **2020**, 142, 20, 9428-9438) or on peptide-functionalized MOF to perform molecular recognition in view of asymmetric catalysis (*Chem., Eur. J.* **2016**, 22, 16531-16538). Our team tends to rely on tight interactions between theoreticians and experimentalists so as to drive the design of functional materials with interesting catalytic properties.

The aim of the post-doc project will be to investigate the catalytic properties of such FLP@MOF systems for CO_2 hydrogenation at the Collège de France setting up liquid phase catalytic tests, having access to a unique well-equipped analytical platform to monitor and quantify the production of CO and methane (gas chromatography coupled to a methanizer), formate, oxalate (ion exchange chromatography coupled to conductimetry), methanol (GC and NMR), formaldehyde (colorimetric tests). In parallel, IR spectroscopy at the synchrotron SOLEIL facilities (first campaign in February 2022 at AILES beamline) will give us access to *in situ* gas phase conditions (under CO_2 and H_2

pressure) and will be key in scrutinizing host-guest interactions in the porous FLP@MOFs solids, through the vibrational behavior of CO_2 upon targeted conditions of pressure and temperature. IR spectroscopy at AILES will thus be key in investigating *in situ* CO_2 spectral signatures, the intramolecular modes of the actives sites (FLPs) and of the host-matrix (MOF), the reaction intermediate and the final product of the reaction. Due to its high sensitivity towards chemical composition and environment in both gaseous and condensed phases, infrared spectroscopy is one of the most appropriate techniques used in catalysis for in situ monitoring the interaction between molecules and a porous host (H.D. Nguyen et al. *ChemSusChem. 2020* DOI: 10.1002/cssc.201902875. J.-B. Brubach et al. *J. Am. Chem. Soc.* 2016, 138, 33, 10437-10443).
Overall, we aim at demonstrating that the functionalization of well-selected porous solids with rationally designed FLPs will provide novel heterogeneous FLP@MOF catalysts, exhibiting great potential for developing a novel chemistry for the activation of small inert molecules such as CO_2.

Collaborations involved :
- IRCELyon – Dr. Jérôme Canivet – synthesis of FLP@MOF
- SOLEIL synchrotron, AILES Beamline, Dr. Jean-Blaise Brubach – Infrared spectroscopy

Potential Candidates should have a strong background in catalysis and spectroscopic techniques:

- Expertise in catalysis is necessary together with understanding of guest response and/or catalytic function
- knowledge in IR spectroscopic techniques
- Relevant skills in related areas e.g. adsorption, molecular recognition, photocatalysis are also desirable
- Excellent publication record

Your application should demonstrate the relevance and level of these skills to the project

Education, Qualifications and Training

- PhD in Chemistry (Materials sciences)

Personal Skills

- Demonstrated ability to work as a member of a team
- Demonstrated ability to work proactively to progress a research project
- Demonstrated ability to organize own workload
- Ability to meet deadlines
- Clear and fluent report writing and oral communication
- Demonstrated ability to take ownership and responsibility for projects
- Ability to supervise and train early stage researchers

Applications: Cover letter, detailed CV and contact information for three references should be sent to Dr. Caroline Mellot-Draznieks (caroline-mellot-draznieks@college-de-france.fr). Interviews will be proposed on reception of these required documents.