Institut des Sciences Chimiques de Rennes

Team Organometallics: Materials & Catalysis

PhD Position in homogeneous catalysis – October 2023

Sustainable Synthesis of γ-valerolactone

Keywords: homogeneous catalysis; levulinic acid; γ-valerolactone; nanofiltration; sustainable processes;

Context and project

γ-valerolactone is a compound with multiple applications[1] that can be obtained by reduction of levulinic acid, a biobased compound arising from carbohydrates.[2] The most efficient homogeneous catalysts for this reaction are relatively expensive ruthenium or iridium catalysts. It is therefore necessary to be able to ensure continuous use of these catalysts or to separate them from the reaction medium so that they can be reused. Nanofiltration processes have the potential to address this challenge.[3]

The project aims to implement the reduction levulinic acid in a membrane reactor allowing to simultaneously perform the reduction levulinic acid while separating the catalyst from γ-valerolactone, the reaction product. The project will deal with the syntheses of organometallic catalysts based on noble and non-noble transition metals and their evaluation in the reduction of levulinic acid by hydrogen transfer using in particular formic acid as the hydrogen donor. The retention of the catalysts by nanofiltration will be investigated and the structure of the catalyst tuned to optimise its retention. In addition to the retention of the organometallic catalyst, it will be necessary to develop conditions (nature of the membrane, solvent, temperature, pressure) allowing the separation of levulinic acid from γ-valerolactone, whose physical and chemical properties are very different (polarity, hydrogen bonds, etc.). The continuous removal of γ-valerolactone will avoid the deactivation of the catalyst due to the increase in the concentration of the reaction product in the reaction medium. Nanofiltration processes require the application of pressure to achieve separation. This pressure is normally applied by means of an HPLC pump. We plan to use formic acid as a hydrogen donor for the reduction of levulinic acid,[4] which results in a pressure build-up. The pressure generated will contribute partially or totally to the pressure needed for the nanofiltration process, thus reducing the energy cost of the process.

Presentation of the ISCR teams involved in the project.

The Organometallics: Materials & Catalysis team (OMC), composed of 43 researchers, professors and lecturers, 14 engineers and technicians, gathers a unique expertise in the domain of organometallic and coordination chemistry for innovative developments in homogeneous catalysis & green chemistry and molecular materials. Notably, the team has a strong expertise in homogeneous catalysis using organometallic catalysts, in C-H activation, biomass valorization and green processes.

The project will be conducted in collaboration with the team Chemistry and Process Engineering (CIP) from the ISCR. The CIP team is composed of 25 staff members. Among several topics, the CIP team is

involved in energy efficient separation through membranes processes for the recovery and/or recycling of high added value compounds like catalysts or key compounds in chemical and food industry.

OMC (C. Fischmeister) and CIP (M. Rabiller-Baudry, T. Renouard) have a long-term collaboration in the topic of nanofiltration of organometallic catalysts.[5]

Profile

The candidate will hold a M2 degree or equivalent in molecular chemistry with practical experience in molecular synthesis under inert atmosphere. An expertise in homogeneous catalysis will be appreciated. An experience in nanofiltration process is not mandatory but theoretical knowledge would be a plus. Knowledge of analytical techniques, in particular NMR, gas chromatography and UV is expected. Enthusiasm, autonomy, scientific curiosity and ability to communicate are required qualities.

Funding: The 3 year PhD will be funded by **ANR-France 2030 PEPR project SPLEEN-ECOCHEM**.

Location: The PhD will take place on the scientific campus of Beaulieu, university of Rennes, Rennes.

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[1] P. W. Miller & coll., *ChemSusChem*, **2016**, *9*, 2037; M.-A. Titirici & coll, *ChemSusChem*, **2016**, *9*, 562;
[2] Y. Fu & coll., *Green Chem*., **2017**, *19*, 5527; T. Mu & coll., *Green Chem*., **2018**, *20*, 4391.
[3] A. G. Livingston, *Chem. Rev*., **2014**, *114*, 10735.
[4] C. Fischmeister & coll., Organometallics, **2017**, 36, 708; Organometallics, **2017**, 36, 3152.
[5] M. Rabiller-Baudry, C. Fischmeister & coll., ChemSusChem, **2008**, *1*, 927; *Catal. Today*, **2010**, *156*, 268; *ChemPlusChem*, **2013**, *78*, 728.