UNITÉ DE CATALYSE ET CHIMIE DU SOLIDE

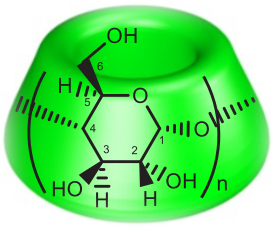
Axis : Catalysis and molecular chemistry

CASU team: Catalysis and supramolecular chemistry

RESEARCH / THEMATIC AXES

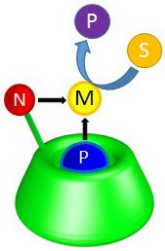
Team presentation

The research activities of the CASU team are in the field of sustainable chemistry, at the interface of two disciplines: catalysis and supramolecular chemistry. These activities are focused on four main themes that facilitate the expression of the talents and skills of the researchers while favoring the interactions between them. Each subject is backed by a group of researchers: **molecular receptors for organometallic catalysis** (S. Tilloy), **supramolecular auto-assemblies for catalysis** (Pr. F. Hapiot), **stabilized metal nanoparticles by molecular receptors** (B. Léger) and **materials for heterogeneous catalysis** (Pr. A. Ponchel). Each group is dedicated to developing catalytic systems and chemical processes that respect the environment. These catalyst systems involve in many cases the use of native or modified cyclodextrins, polymerized or not. Native cyclodextrins are macrocycles consisting of 6, 7 or 8 α-(1-4) bridged glucose units. The arrangement of the units is such that the molecule has the shape of a truncated cone whose outer surface is hydrophilic while the internal cavity is hydrophobic. This structure confers on them the ability to form inclusion compounds or adducts with various organic or inorganic molecules. The cyclodextrins can be used in biphasic systems consisting of an aqueous phase and an immiscible organic phase to improve the mass transfer (phase transfer agents, self-assembled surfactants that can form hydrogels or not, colloidal particles allowing the stabilization of emulsions (especially Pickering emulsions)). The cyclodextrins may also be used as dispersing and / or templating agents in processes for the synthesis of heterogeneous catalysts, without necessarily being present in the final composition of the latter (catalysts prepared by impregnation, co-precipitation, sol-gel method, inverse replica, etc.). In this case, the cyclodextrin is removed during the final stage of preparation of the materials by calcination or carbonization.

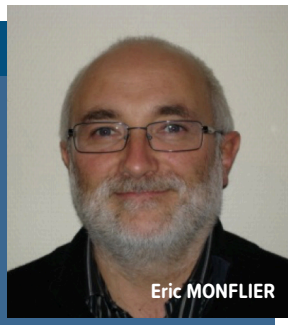


Scientific policy

The scientific policy of the CASU team consists in reinforcing the knowledge acquired in the field of catalysis and supramolecular chemistry and in bringing out new concepts in breach with the established ideas. Interaction between groups is therefore encouraged because it is the driving force behind innovation. It is in this context that, in parallel with studies on cyclodextrins, new related subjects have recently emerged. The CASU team is now expanding its expertise in the design of innovative homogeneous and heterogeneous catalysts for the catalytic conversion of bio-sourced molecules into unconventional media (gels, hydrogels, deep eutectics, free-solvent catalysis by mechanosynthesis). The



WORDS FROM THE TEAM LEADER


Eric MONFLIER

The CASU team is located in Lens and includes 15 Teachers-Researchers (4 Prs and 11 MCFs). The themes of this team are multidisciplinary and combine skills in Homogeneous Catalysis, Heterogeneous Catalysis, Supramolecular Chemistry, Organic Synthesis and Chemical Engineering. 8 Teachers-Researchers fall under section 32, 5 under Section 31 and 2 under section 62. It was created ex nihilo in 1992 and has continued to develop ever since. The CASU team enjoys national and international recognition. In recent years, members of the CASU have been invited to give lectures at major international congresses in the field of Catalysis or Cyclodextrins. The team has extensive relations with foreign research groups (Germany, China, Denmark, Spain, Lithuania, India, Italy, Ukraine, South Africa). It participates actively in regional (CPER), national (GDR, ANR) or international (PHC) research programs. As part of the «Investments for the Future» program, it was selected to be part of two Institutes for Energy Transition (ITE PIVERT and IFMAS).


Pr. Sébastien Tilloy - Molecular receptors for organometallic catalysis


Pr. Anne Ponchel - Materials for heterogeneous catalysis


Dr. Bastien Léger – Metal nanoparticles for catalysis


Pr. Frédéric Hapiot - Supramolecular auto-assemblies for catalysis

KEY FIGURES

15 teachers-researchers

20 publications on average per year

5 book chapters over the 2013-2016 period

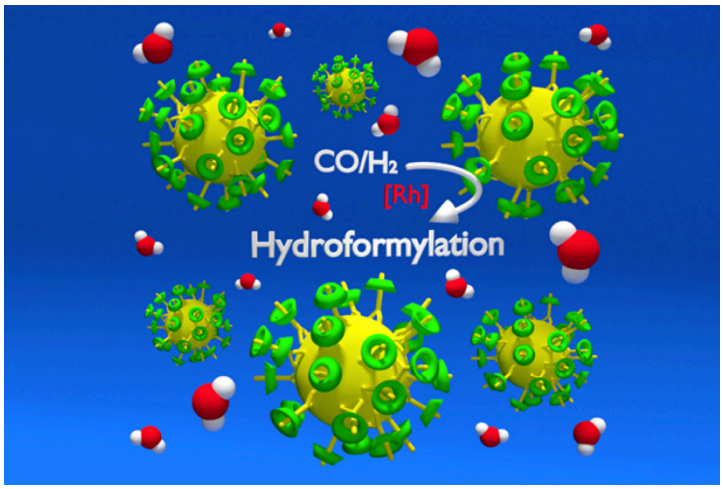
2 ANR contracts, **6** ITE PIVERT and **4** ITE IFMAS programs over the 2013-2016 period

4 registered patents over the 2013-2016 period

recent partnerships between the CASU team and the Institutes for Energy Transition (ITE) PIVERT and IFMAS also make it possible to transfer the concepts developed in the laboratory to the pre-industrial stage. This shift from basic research to applied research now nurtures the dynamism and involvement of CASU team researchers.

FLAGSHIP PROJECTS

The CASU team's expertise in glycochemistry and lipochemistry enabled it to integrate two Institutes for Energy Transition: ITE PIVERT (Picardie Technological Innovations Teaching and Research - € 247 million) and ITE IFMAS (French Institute for AgroSourced Materials - € 110 million). In the framework of the research program GENESYS of ITE PIVERT, the CASU team has developed a process for hydroformylation in a self-emulsifying medium allowing access to triglycerides functionalized by formyl groups through supramolecular means. The reaction takes place at the interface of a biphasic medium consisting of an organic phase containing the triglycerides and an aqueous phase in which the organometallic catalyst is dissolved. The use of cyclodextrins allows the molecular recognition of one of the fatty chains of the triglycerides to form stealth amphiphilic inclusion complexes which act as surfactants at the interface between

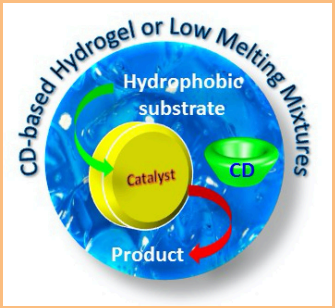


the organic phase containing the triglycerides and the aqueous phase containing the organometallic catalyst. At the end of the reaction, the low affinity between the hydroformylated triglycerides and the cyclodextrins favors the phase separation. The reaction products are thus readily separated from the organometallic catalyst, which can then be recycled. (PCT / FR2014 / 052860 (7.11.2014), «Supramolecular emulsifiers in the biphasic catalysis: the substrate drives its own transformation», T. Vanbésien, F. Hapiot, E. Monflier, ACS Catal., 2015, 5, 4288-4292).

SOME MAJOR WORKS

A cyclodextrin dimer as a supramolecular reaction platform for aqueous organometallic catalysis

C. Blaszkiewicz, H. Bricout, E. Léonard, C. Len, D. Landy, C. Cézard, F. Djedaïni-Pilard, E. Monflier, S. Tilloy, Chem. Comun. 2013, 49, 6989-6991. DOI:10.1039/C3CC43647K



Low melting mixtures based on β-cyclodextrin derivatives and N,N'-dimethylurea as solvents for sustainable catalytic processes

F. Jérôme, M. Ferreira, H. Bricout, S. Menuel, E. Monflier, S. Tilloy, Green Chem., 2014, 16, 3876-3880. DOI: 10.1039/C4GC00591K

Ruthenium-containing ß-cyclodextrin polymer globules for the catalytic hydrogenation of biomass-derived furanic compounds

R. Herbois, S. Noël, B. Léger, S. Tilloy, S. Menuel, A. Addad, B. Martel, A. Ponchel, E. Monflier, Green Chem. 2015, 17, 2444-2454. DOI: 10.1039/C5GC00005J

Rhodium-catalyzed one pot synthesis of hydroxymethylated triglycerides

T. Vanbésien, E. Monflier, F. Hapiot, Green Chem. 2016, 18, 6687-6694. DOI: 10.1039/C6GC02706G

Mesoporous RuO_2/TiO_2 composites prepared by cyclodextrin-assisted colloidal self-assembly: Towards efficient catalysts for the hydrogenation of methyl oleate

R. Bleta, S. Noel, A. Addad, A. Ponchel, E. Monflier, RSC Advances 2016, 6, 14570-14579. DOI: 10.1039/C5RA27161D

Cyclodextrin-cobalt (II) molecule-ion pairs as precursors to active Co_3O_4/ZrO_2 catalysts for the complete oxidation of formaldehyde: influence of the cobalt source

L. Bai, F. Wyrwalski, M. Safariamin, R. Bleta, J.F. Lamonier, C. Przybylski, E. Monflier, A. Ponchel, J. Catal. 2016, 34, 191-204. DOI: 10.1016/j.jcat.2016.07.006

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