

**Presentation of funded projects in 2008 for  
Program« EFC: Environmentally Friendly homogeneous and  
heterogeneous Catalysis»**

**Edition 2008**

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# Program« EFC: Environmentally Friendly homogeneous and heterogeneous Catalysis»

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<b>Project Title</b>	<b>ACTCO2</b> - Activation of CO <sub>2</sub> on ZnO surfaces and subsequent reactions with nucleophilic coadsorbates
<b>Abstract</b>	<p>In light of the depletion of fossil feedstocks and to help address the global environment concerns, increasing attention should nowadays be paid to polymeric materials such as polyesters synthesized from monomers derived from readily renewable natural resources (biomass) within green and sustainable chemistry. Synthetic polyesters are versatile polymers exhibiting good thermo-mechanical and physical properties, which make them leading candidates for, in particular, biomedical applications (e.g., tissue repair and regeneration, controlled and sustained drug or gene delivery vehicles) but also as recyclable substitutes to plastic commodities (e.g., packaging, films,...). However, the limited number of existing polyesters derived from the currently available monomers can not substitute the whole range of thermoplastics. Therefore, developing polyesters from the biomass is of double and highest interest. Efforts must be paid also to develop highly effective, environmentally friendly catalyst systems for the preparation of these biomass-derived polyesters. We thus propose herein an academic, industrially-orientated research project which consists in 1) the design and synthesis of novel cyclic monomers as new chemicals derived from biomass, and 2) the use and development of original catalytic systems for ring-opening polymerization (ROP) including 2a) organic, 2b) organometallic and 2c) bifunctional "dual" ones. This will be done using a combined experimental and theoretical approach.</p>
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# Program« EFC: Environmentally Friendly homogeneous and heterogeneous Catalysis»

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**Project Title** **AMMOXAN** - Development of novel amoxidation catalysts with tailored anion structures based on transition metal nitrides and oxynitrides

## Abstract

Organometallic catalysis is an important player for the development of new sustainable process in industry. About 85% of the present chemical processes are run using a catalyst. Out of these about 75% are run based heterogeneous catalysis due to their advantages of easy separation from product streams and of their recycling and reuse. On the other hand, homogeneous catalysts are appreciated in terms of their activity and selectivity. However these catalysts, which associate a transition metal and a ligand designed to fine tune the properties of the catalyst are more expensive. Recycling and reuse of these important catalysts become thus pertinent both from environmental and economical reasons. To solve this problem, we propose to develop novel catalytic materials, which combine both the advantages of homogeneous (high activity and selectivity) and heterogeneous catalysis (easy product/catalyst separation, recycling and reuse of the catalyst). This new catalytic materials will associate a biopolymer issued from the biofeedstock (chitosan, alginate) as support and a multiple layer of ionic liquid (preferably biodegradable) in which the homogeneous catalyst will be dissolved. To obtain efficient catalysts, a particular attention will be paid to the conditioning of the biopolymers (beads, scaffolds, fibers, membranes and to their structure (meso or microporosity). Moreover, to prepare fully biodegradable BioPSIL materials, biodegradable ILs will be designed and associated to the biopolymer support. The global biodegradability of the BioPSIL materials will be evaluated. In order to have a better understanding of the properties, which are responsible of the efficiency of the BioPSIL catalysts, a study on the interactions between IL/transition metal catalyst/support will be undertaken. The novel BioPSIL catalysts will be evaluated in four catalytic reactions: the "Tsuji-trost" reaction which is a leading reaction for the construction of C-C bond, the hydrogenation of nitrophenols, the C-P bond formation, which is a powerful catalytic method to access the valuable phosphine ligands and the olefin metathesis which is an inescapable reaction in organic synthesis and polymer science. These four reactions are catalyzed by transition metal complexes (palladium or ruthenium), which are costly and toxic. Thus, both from an environmental and economic point of

view, the recycling and the reuse of the catalyst are main issues. Furthermore, these reactions display different features (basic, neutral conditions, liquid, gaseous reagents, palladium and ruthenium catalysts...), which will enable to evaluate the scope and limitation of the novel catalytic materials that will be developed. The study will consist in the evaluation of the BioPSIL materials in a model reaction in order to determine the best biopolymer conditioning for a high conversion and an efficient recycling and reuse of the catalytic system.

The impact of catalytic parameters (metal dosage, IL content, ...) and the impact of operating parameters (substrate concentration, agitation or flow velocity, ...) will be investigated. Among the criteria for the evaluation of the catalytic systems TOF, conversion, yield will be considered but also the stability of the materials (metal leaching) and the recycling and reuse of the catalytic system (long-time activity...). Afterwards, the reaction will be extended to other substrates and/or reagents to evaluate the scope and limitations of the reaction under these new catalytic reactions.

**Partnership**

CNRS – IRCELYON  
Leibniz-Institut für Katalyse – LIKAT

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ANR-08-EFC-02

# Program« EFC: Environmentally Friendly homogeneous and heterogeneous Catalysis»

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<b>Project Title</b>	<b>BIOTANDEM</b> - Tandem Metathesis/hydroformylation for sustainable conversion of biomass derived substrates
<b>Abstract</b>	Multicomponent reactions (MCR) are processes in which three or more reactants are combined in a single chemical operation to produce products that incorporate substantial portions of all the components. They are by definition sustainable chemistry and constitute a gateway to the ideal organic syntheses in which the target molecule is made from readily available starting materials in one simple, safe, environmentally acceptable and resource-effective operation. As an enabling technology, the development and application of multicomponent reactions are now an integral part of any major medicinal research unit. Our group at "Institut de Chimie des Substances Naturelles" has been actively involved in this burgeoning area and has acquired basic know-how in this field. In collaboration with Targeon, an emerging biopharmaceutical company that develops targeted therapies in oncology, we intend to further develop the "substrate design" approach" for the design of novel MCRs that match the criteria of green chemistry, but also directly target the pathogenic macromolecules for the development of bioactive compounds.
<b>Partnership</b>	CATOM - Sciences chimiques de Rennes - Catalyse et Organométalliques & Lehrstuhl für Technische Chemie und Petrolchemie - Institut für Technische Chemie und Makromolekulare Chemie – RWTH
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<b>Reference</b>	ANR-08-EFC-03

# Program« EFC: Environmentally Friendly homogeneous and heterogeneous Catalysis»

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**Project Title** CAPONE - Carbenes in Porous Networks

## Abstract

Cellulosic pulps for paper production are obtained after wood delignification. The production of bleached fibres requires an additional bleaching step in order to remove coloured residual lignin. Cellulosic fibres are mainly used to produce white paper for printing applications. Only a small amount is used, after purification, for pure chemical cellulose production. This last application offers a great added value and has today a growing interest due to the opportunities offered by the cellulose regarding the synthesis of polymers and derivatives originating from the biomass, a renewable raw material. The use of cellulose in chemical application is limited due to the cellulose contamination with hemicelluloses, its lack of reactivity linked to the cellulose fibrous structure and its too large degree of polymerisation. Thus, beneficial properties in the papermaking process become handicaps for pure, reactive and molecular mass modulable cellulose production. The preliminary bleaching step necessary to these applications is difficult. Oxygenated reagents such as oxygen or hydrogen peroxide are now applied in alkaline medium in substitution to usual chlorinated agents (chlorine, chlorine dioxide) responsible for the production of toxic organochlorinated compounds. However, the combination of oxygen and hydrogen peroxide treatments is not sufficient to fully complete the bleaching. As a consequence, some chlorinated agents are still largely used. This project aims at developing a catalytic bleaching process using hydrogen peroxide. This new process will enhance the residual lignin degradation and will remove major part of the hemicelluloses while enabling to get reactive celluloses with a variable degree of polymerisation. This new environmentally-friendly process would be implemented in parallel to the current bleached kraft pulp production line. 2 academic laboratories, the LGP2 and the DCM will drive this project with 2 industrial partners linked to the H<sub>2</sub>O<sub>2</sub> production and the bleached kraft pulp production. Recent studies showed that transition metallic complexes, especially copper, exhibit a catalytic action on H<sub>2</sub>O<sub>2</sub> reactions in alkaline medium with cellulosic pulp. The bleaching is strongly improved but the carbohydrates (cellulose and hemicelluloses) react also more, leading to higher oxydation and solubilisation of hemicelluloses and to a larger cellulose depolymerisation. Consequently, this catalytic process

has a low selectivity towards the residual lignin. Nevertheless, this drawback could become an advantage regarding the production of pure cellulose for chemical application. Indeed, the production of these high added value products requires a very efficient bleaching but also the hemicelluloses dissolution in order to get a highly reactive and partially depolymerised cellulose. The modification of the complex chemical structure (i.e the ligand), should modify the copper complex activity to adjust the carbohydrates degradation intensity, leading to celluloses suitable for cellulose derivative production used in textile, packaging, cosmetics, food additives... Several complexes such as Cu-polypyridinyl for instance, with different affinities towards carbohydrates will be studied and then applied on lignocellulosic substrates. The purpose is to develop an entirely environmentally friendly industrial process without chlorine for pure and reactive cellulose production. This is made possible because H<sub>2</sub>O<sub>2</sub> is used, the effluent is burnt and the caustic soda is regenerated in the kraft recovery system.

**Partnership**

ICGM - AM2N - UMR5253 (Institut Charles Gerhardt de Montpellier, Equipe Architectures Moléculaires et Matériaux Nanostructurés) Max-Planck-Institut of Colloids and Interfaces, Department of Colloid Chemistry – MPIKG

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**Beginning  
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## Program« EFC: Environmentally Friendly homogeneous and heterogeneous Catalysis»

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**Project Title** GLOBUCAT - Towards sustainable chemical processes: immobilisation of molecular organo-and metal catalysts and their application for fine chemical synthesis

### Abstract

Polysaccharides are the most abundant and the most diverse renewable materials found on earth and in the oceans. Except polysaccharides used traditionally in food and non-food industry, the structure and the functionality of most of them are unknown and unexplored. Structural analyses of complex polysaccharides benefit strongly from the use of polysaccharides depolymerising enzymes: glycoside hydrolases (GH) and polysaccharides lyases (PL). The enzymes have the advantage to produce discrete series of oligosaccharides which characterisation is determinant to resolve the parent polysaccharides structures. In addition, these oligosaccharides may have functional properties (e.g. biological) and could be used as precursors for chemical synthesis. Finally, enzymes are very useful tools for industrial biorefinery processes. GH and PL have been classified as a function of the reaction they catalyse (about 160 E.C. number) and by sequence homology (110 GH families and 18 PL families, CAZY classification). With the numerous genomic programs undertaken these last years, there is an exponential production of gene sequences. However, one may stress that despite this huge amount of genes elucidations, the pace for discovery of new GH and PL remains constant. The new sequence data allow the expansion of the existing enzymes families (E.C. and CAZY) but not the discovery of new catalytic functions. The function of most of the GH and PL genes remains putative, based on sequence/structure homologies or remains unknown. There are many collections of micro-organisms (i.e. bacteria) that can be grown on artificial medium. The capacity of these micro-organisms to produce and to degrade polysaccharides is mostly unexploited. In this context, we propose to design and implement a medium throughput screening platform for assessing GH and PL activities on a collection of polysaccharides substrates having known and unknown structures. We envision miniaturised incubations of polysaccharides with bacterial extracts or putative recombinant GH and PL. The detection will be achieved by mass spectrometry, which offers the experimental advantage of minute amount of material necessary and allows access to structural data of the degradation products. At the end of the project we will have discovered new GH and PL activities which will allow, in term, i) to

determine the structure of less known or unknown polysaccharides, ii) to produce oligosaccharides having original structure and properties and iii) to enrich notably the catalogue of enzymatic tools.

**Partnership**

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