Studies on the catalytic performance of biocatalysts based on supported ionic liquids

The main goal of this research is to design innovative, highly stable biocatalysts based on supported ionic liquids and lipases. Novel materials will possess the unique properties which will determine their catalytic potential.

In particular, obtained materials will be formed from ionic liquids, immobilized *via* physical adsorption or covalent bonds on the three groups of modern, designable carriers: hydrophobic polymers obtained through electrospinning technique, organic-inorganic hybrid materials as well as multi-walled carbon nanotubes. *Supported ionic liquid phase* based materials will be synthesized as a result, which allows to preserve all benefits of application of ionic liquids, with simultaneously decreasing the amount of ILs in process. The enzymatic active phase, will be introduced at the next step. Lipases are catalysts for forming or breaking the single bond between carbonyl carbon atom and oxygen atom.

Obtained materials will possess the properties similar to homogeneous catalysts, although forming the heterogeneous forms. Synthesized biocatalysts will be characterized *via* very high activity and stability, with additional easy separation from post-reaction mixture and recycle.

Studies will concerned the following steps: obtaining of SILP-based materials, their characteristics and testing the catalytic properties in selected chemical reactions.

All obtained materials will possess the features dedicated for specific catalytic problems in model reactions: kinetic resolution of *rac*-ibuprofen (enantioselectivity of enzyme), esterification of acrylic acid (selectivity in presence of more than one functional group in the molecule of substrate) as well as chemo-enzymatic Baeyer-Villiger oxidation (enzymatic catalyst in extremely unfriendly environment of hydrogen peroxide).

In order to immobilize of ionic liquid, the following materials will be applied: polymers obtained *via* electrospinning technique (poly(styrene) and poly(vinyl chloride)), organic-inorganic hybrid materials based on biopolymer and zirconium or silica oxides as well as multi-walled carbon nanotubes oxidized to carboxyl or formyl groups.

Obtained primary supports will be further modified using ionic liquids through physical adsorption (1-alkyl-3-methylimidazolium cations (alkyl: ethyl, n-butyl) and bis(trifluoromethylsulfonyl)imide, dicyanamide, tetrafluoroborate, alkylsulfate (alkyl: linear C_1 to C_8) or alkylphosphate (alkyl: linear C_1 to C_8) anions) or covalent bonds (in the reaction of 1-(3-aminopropyl)imidazole with -COOH groups towards amide bond as well as in the reaction of 1-(3-aminopropyl)imidazole with -C(O)H groups towards imine bond, further quaternization of amine using alkyl bromides or chlorides (alkyl: linear C_1 to C_8 group), ending with anion exchange for bis(trifluoromethylsulfonyl)imide, dicyanamide, tetrafluoroborate, alkylsulfate (alkyl: linear C_1 to C_8) or alkylphosphate (alkyl: linear C_1 to C_8). All obtained materials will be fully characterized towards morphology analysis as well as qualitative and quantitative using SEM, TEM, EDX or EDS, TGA, TG/FT-IR, RAMAN, solid state NMR or S_{BET} analyses. Lipase B from *Candida antarctica* and lipase *Candida rugosa* will be applied as active phases.

Investigations concern catalytic properties will be carried out in a batch system. The project will conduct research on the influence of the following parameters on the reaction rate and selectivity of selected processes: concentration of reagents, type, amount of biocatalyst and its recycling, the speed of stirring, the type of solvent. All products will be isolated from reaction mixture, in every process the conversion, yield of product and selectivity will be determined. In case of kinetic resolution of rac-ibuprofen, the enantiomeric excess will be also determined.

The exploration for new, highly effective, and at the same time non-toxic, environmentally friendly catalysts is currently the subject of majority research connected with engineering of process. The project will allows to extend the current knowledge of immobilization methods of ionic liquids on solid carriers as well as heterogeneous biocatalysis. The problem is extremely important from the point of view of choosing the proper catalyst for a process. The use of biocatalyst leads to obtaining of higher selectivity in mild conditions and reduction of waste and energy consumption in the process.