CoopCat: developing theoretical tools and concepts to understand cooperative effects in catalysis

The catalysts ease chemical reactions and they are widely used in chemical industry. Production of more than 90% of chemicals involves at least one catalytic step in their manufacture. As the catalysts improve energy balance and contribute to decrease the amount of unwanted side-products, the use of catalytical systems is one of the pillar of the so-called *green chemistry*. Most of man-made and widely used catalysts are of single-functionality, i.e. there is only one catalytic centre in the catalyst. In the last decade we witness a growing number of catalytic systems where addition of yet another functionality to the catalyst substantially improves the overall balance of the reaction. This phenomenon is called cooperativity. Added functionalities have various nature, i.e. they can be in a form of added metal or functionalised ligand. However, often further developments are hampered by not well understood mechanism of action of such modifications.

Within the CoopCat project we aim to provide theoretical tools and concepts to be used in the growing field of cooperative catalysis. The example of best known cooperative catalysts – enzymes – that cannot be classified neither as heterogeneous catalysts (just one physical phase, e.g. liquid or solid) nor homogeneous catalysts (more than one physical phase, e.g. liquid/solid) introduces key complication into traditional case-by-case catalyst improvement. One cannot approach cooperative catalysis only from the side of homogeneous or only from heterogeneous perspective. Thus the concepts and methods need to be developed in a holistic way. In the project we will apply consistently the same high-level methods to very different problems by constructing chemically sound models that will describe all physical properties of the studied systems.

Some of the outcomes of the project can be used directly to optimise known catalytic systems. This include novel embedding technique that will allow to use accurate methods to obtain quantitative informations about chemical reactions on metallic surfaces without falling into empirical approaches. This informations are right now available from computations at qualitative level and in many cases do not allow for knowledge-based catalyst design. Gained knowledge will provide also hints on how to treat long-range interactions in proteins so new methods to model metalloenzyme action can steam from our developments. We will demonstrate that very accurate methods, but of reduced scaling with respect to systems size, can be used in all three catalytic cases: heterogeneous, homogeneous and enzymatic catalysis. Such uniformity will be of high impact as the number of errors' sources will be decreased by using more robust approaches.

On a conceptual level we will contribute to understanding of number of cooperative reaction mechanisms that lead to high-value products such enantiomerically pure multifunctional compounds that serve as precursors for fragrances or drugs and vitamins. By investigating cooperativity between transition metal and small oligopeptides in the water oxidation catalysis we will contribute to development of chemical energy storage systems. We will adapt typical theoretical tool in homogeneous catalysis – activation strain model – to quantify differences in aerobic sensitivity of various hydrogen-producing enzymes. We hope that in this way we will arrive at suggestions that inspire new experimental efforts to modify the enzyme in knowledge-based way and will provide community with the source of cheap hydrogen that is produced in a *green* way.