

## POPULAR SCIENCE SUMMARY

Redox catalysis is one of the most important branches of heterogeneous catalysis. It controls the most important industrial processes (selective oxidation of hydrocarbons, CO-PROX, steam reforming) and is the basis for the key environmental protection technologies (catalytic methane combustion, soot combustion, nitrous oxide decomposition, and reduction of nitrogen oxides). Unfortunately, currently used commercial catalysts are largely based on poorly available precious metals, which are threatened by fluctuations in market prices. The cheaper systems developed so far are usually based on transition metals and their oxides. Although such catalysts are excellent model systems, they often do not meet the stringent requirements set by the industry, showing insufficient activity, selectivity, or stability. Model studies conducted based on transition metal oxides, using an appropriate combination of experimental and computational research techniques reveal the nature of the catalytic process at the atomic level. The results indicate that even simple reactions catalyzed at redox centers are multi-stage processes controlled by the nature and availability of active centers, their electronic properties, and process conditions. The optimal catalyst should meet the golden rule, thus, properly stabilizing the substrates and ensuring their initial activation leading to the weakening of bonds, and on the other hand, enabling easy desorption of products leading to the restoration of the active site and allowing the closure of the catalytic cycle. It turns out, that in simple one-component systems that are characterized by the similarity of active centers, the catalytic action may be inefficient because the catalyst works effectively in one of the catalytic steps but is not active in its other stages. Therefore, composite (multi-component) catalytic materials may have an advantage over single-component systems and nowadays they are the avant-garde of research on new catalytic materials. Particularly promising in the context of redox catalysis are composites that form heterojunctions, which are based on oxides with different energy gaps remaining in contact (additionally, such subsystems may have different types of conductivity).

The research hypothesis assumes that for a heterojunction with an appropriate geometric and electronic matching of both oxide components, an optimal interaction between both subsystems can be established. This facilitates the formation of chemical bonds across the interface leading to bilateral modification of the subsystems electronic structures. In such a way, the resultant interface can be involved in a concerted catalytic action, in which one of the components plays the role of a redox oxide facilitating the activation of reactants, while the other serves as a reservoir of network oxygen favoring the formation of the oxygenated intermediates and products (dual electron/oxygen transport conception). Therefore, the enhanced redox catalytic performance in the reactions that are planned to be examined within this project shall result from the synergistic effect associated with the presence of both oxide phases.

To develop optimal catalytic materials, a number of catalytic oxide materials (differing in grain size, and composition) will be synthesized. These systems will be characterized using advanced microscopic techniques, the catalytic activity of the produced systems will be tested, and a deeper insight into possible catalytic mechanisms will be obtained by experiments with isotope-labeled reagents. To understand the catalytic activity of heterojunctions at the molecular level, extensive molecular modeling using quantum chemistry methods is planned, which will provide the necessary information about the atomic and electronic structure of active centers and charge transfer characteristics. Moreover, the catalyst active centers' interaction with reactants in real process conditions will be determined using ab initio thermodynamics methods. The results of this project will be the basis for determining the structure-activity relationship, and the obtained detailed description of the chemical state of the catalyst in real conditions (p, T) will provide a convenient background for reliable modeling of possible surface reaction paths, revealing the key factors controlling the catalytic activity of the developed heterojunctions. Thanks to this, the initial systems can be optimized by doping with heterocations and, finally, developed catalytic composites containing heterojunctions will serve as active and durable catalysts for use in redox processes.