The proposed project is related to the basic research on a reaction between an aqueous solution of hydrogen peroxide (H_2O_2) and selected oxide catalysts. The main objective of the project is to develop a composite oxide catalyst for the generation of reactive oxygen species (ROS) through the decomposition of H_2O_2 and verification of the proposed new pathway of H_2O_2 decomposition involving simultaneous transfer of electrons and protons. The idea of composite catalyst is to take advantage of the physical and chemical properties of several components in a single material. In this case, those components are nonredox amorphous oxides of niobium(V), tantalum(V), and zirconium(IV). They were selected as an alternative to crystalline semiconducting nanooxides, the second component of the composite, which are known from their activity in the decomposition of H_2O_2 via redox processes (direct exchange of electrons). Specified amorphous oxides do not show this kind of activity; instead they exhibit characteristic strong acid-base properties, which influence the dissociation of H_2O_2 and protolytic reactions leading to its decomposition.

Hydrogen peroxide is a simple and cheap source of formation of the reactive oxygen species, which are anions and radicals such as $^{\bullet}OH$ (hydroxyl radical), $O_2^{-\bullet}$ (superoxide radical), $HO_2^{\bullet}$ (hydroperoxyl radical) and O_2^{2-} (peroxide anion). These forms have strong oxidizing ability, and therefore can be used for the removal of organic pollutants in water (for example phenol derivatives in waste water). On the other hand, $^{\bullet}OH$ radicals exhibit such a high chemical reactivity that, in the conditions of electrochemical reaction, they lead to the corrosion of the components of electrochemical cells, while in the biological reactions they cause the degradation of cell structures at the molecular level. Therefore, it is desirable that the catalyst provides versatile ability for the formation of the reactive oxygen species or their reduction depending on the intended application of the catalyst. This will be possible owing to appropriate selection of the composite components, in particular the crystalline phase. It is planned to use Co_3O_4 spinel, cerium(IV) oxide or manganese(IV) oxide which are capable of reducing hydroxyl radicals via direct electron transfer process.

As the working hypothesis it is assumed that ROS are produced by shifting the equilibrium of the postulated reaction $H_2O_2 + HO_2^- \leftrightarrow O_2^{-\bullet} + {}^{\bullet}OH + H_2O$ toward formation of the $^{\bullet}OH$ radical by stabilizing the $O_2^{-\bullet}$ anions onto the amorphous surface which additionally depend on pH. The novelty of the proposed project stems from the use of previously unrecognized amorphous materials, which are not electron donors, in the formation of ROS. For the first time it is planned to merge the acid-base function and ionic sponge effect of amorphous oxides with the redox properties of selected semiconductors in a single composite material. As a result, it will allow to control the reactivity of the catalyst toward catalase activity (an enzyme for H_2O_2 decomposition) or peroxidase activity (an enzyme leading to ROS). Depending on the intended use of the catalyst, this effect will provide protection against degradation caused by the presence of $^{\bullet}OH$ radicals or provide enhanced performance of ROS formation for mineralization and oxidation processes. The amorphous-crystalline composite will thus act as a mineral biomimetic of H_2O_2 decomposition.

A series of measurements planned within the project are to help in explaining the mechanism of the reactive oxygen species and to characterize the resulting catalysts. Diffraction and microscopic techniques will be used for monitoring the structure of the catalyst (X-ray diffraction, transmission electron microscopy). Particle size of the catalyst in aqueous solutions will be determine by measurements of dynamic light scattering effect. In addition, charge accumulated on the particle surface will be measured (zeta potential), which is essential for the mechanism of the studied reaction. The most important part of the project concerning the identification of the reactive oxygen species and their reactivity measurements will be conducted by means of spectroscopic techniques. Radicals will be detected using electron paramagnetic resonance (EPR), other forms will be probed with infrared and Raman spectroscopy. The catalytic activity will be measured using colorimetric methods and reaction characteristic of the substrates of catalase and peroxidase enzymes, while the amount of evolved oxygen will be monitored with photoluminescence sensors.