

DESCRIPTION FOR THE GENERAL PUBLIC

Reactive oxygen species (ROS) are extremely important oxygen-containing moieties in terms of catalytic chemistry, environmental chemistry, and biochemistry. These moieties may be radicals, that is, particles containing unpaired electrons, anions, but also electrically neutral closed-shell molecules. Examples of reactive oxygen species studied under this project are **hydroxyl radicals** ($\bullet\text{OH}$), **superoxide radical anions** ($\text{O}_2^{\bullet-}$), hydroperoxy radicals (HO_2^{\bullet}), $\text{O}^{\bullet-}$ radicals, **sulfate radical anions** ($\text{SO}_4^{\bullet-}$), **peroxy anions** (O_2^{2-}) and **hydrogen peroxide** (H_2O_2). In the most typical conditions, reactive oxygen species are formed by the use of suitable catalysts during redox reactions, but also by radiolysis, photolysis, or O-O bond homolysis. The most famous redox process leading to the formation of ROS is the Fenton reaction. However, this project focuses on the study of atypical processes and catalysts leading to the formation of reactive oxygen species. They will be generated upon interaction with amorphous transition-metal oxides that normally do not exhibit redox activity, yet they lead to the formation of ROS. The necessary redox reactions will take place between the precursors of the reactive oxygen species and the intermediates of their decomposition, rather than between the precursors and the surface of the catalyst. This is a new mechanism for the formation of ROS, based on **electroprotic reactions** (conjugated electron and proton transfer). As the precursors, hydrogen peroxide (H_2O_2) and peroxosulphate anions (HSO_5^-) were chosen for their availability and significant reactivity. Selected **amorphous metal oxides** of groups III - V of the periodic table are characterized by strong acid-base properties and significant specific surface areas. Preliminary studies showed that the oxides were active in the reactions of simultaneous formation of hydroxyl and superoxide radicals by interacting with H_2O_2 solution. The advantage of acid-base amorphous systems is stable generation of radicals (as opposed to rapid processes with Fenton systems) that can be used in the oxidation reactions of selected organic substances. Such amorphous oxides will later be used as supports for the nanocrystalline oxides with redox properties to constitute the crystalline-amorphous oxide composites with increased ROS yield. Composite systems will be investigated for the removal (mineralization) of toxic water contaminants such as herbicides. However, the amorphous oxide will not be merely a carrier (supporting phase) but it will be the active ingredient of the composite. The support will serve as an **anion sponge** while the nanocrystals will be redox active centers.

Thus, **the main purpose of this proposal** is to determine the factors that control the mechanisms of ROS formation by the interaction of precursors with the surface of catalytic oxide materials. The selection of the investigated systems will allow an insight into processes analogous to Fenton's mechanism, electron transfer processes, and electroprotic processes. These objectives will be achieved by (1) spectroscopic identification of ROS, (2) determination of the effect of oxide on ROS intermediates, (3) determination of the effects of acid-base properties of the selected oxides on the activation of reactants. Achieving the project's goal will allow for controlling speciation of the reactive oxygen species and for tuning the activity of the oxide catalysts for the use of H_2O_2 and HSO_5^- as ecological sources of radicals or removal of H_2O_2 (in processes where it is undesirable) by direct decomposition into water and molecular oxygen bypassing ROS. These two types of activity are analogous to peroxidase- and catalase-like activity of enzymes. Demonstration of these types of activity for the studied oxide materials and determination of their efficiency will allow for controlling and even switching of catalytic activity by simple parameters such as pH or a concentration of ROS precursor.