

Electroprotic reactions of hydrogen peroxide at the interface of aqueous solution and the surface of amorphous oxide ZrO₂, Nb₂O₅, HfO₂, Ta₂O₅ gels – relevance for advanced oxidation processes

Kamila SOBAŃSKA,^{*,1} Łukasz WOLSKI,² Piotr PIETRZYK¹ ¹Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Poland. ²Adam Mickiewicz University, Faculty of Chemistry, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland. *kamila.sobanska@uj.edu.pl

Significance and Relevance

An electroprotic mechanism of the generation of reactive oxygen species (ROS) on amorphous nonredox oxides ZrO₂, Nb₂O₅, HfO₂, Ta₂O₅ has been developed. A change in reactivity of peroxidase type (formation of reactive oxygen species) to catalase one (formation of dioxygen, including singlet oxygen) depending on the pH of the solution has been shown. The electroprotic mechanism leads to the simultaneous formation of superoxide and hydroxyl radicals.

Preferred and 2nd choice for the topic: Water treatment and Fundamental advances in understanding catalysis

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Due to the increasing use of hydrogen peroxide (H_2O_2) as a cheap and environmentally benign oxidant in many catalytic reactions, extensive studies into mechanisms of H_2O_2 activation (decomposition), and the search for new catalysts active in this reaction have recently received much attention.¹ H_2O_2 is a simple source of reactive oxygen species (ROS) such as hydroxyl radicals, superoxide radicals, hydroperoxyl radicals, peroxide anions, or singlet oxygen. They can be used in advanced oxidation processes (AOP) and for catalytic wastewater treatment.^{2,3}

In this contribution, we describe the application of amorphous oxide gels (ZrO_2 , Nb_2O_5 , HfO_2 , Ta_2O_5) for profuse generation of ROS via H_2O_2 decomposition, by exploiting its pH-tunable peroxidase- and catalase-like reactivity. For this purpose, the influence of the isoelectric point, pH of the reaction mixture, and the crystallinity degree of the oxide catalysts on ROS formation and speciation was examined employing spin trapping and dissolved oxygen measurements, as well as the test reactions for peroxidase-like activity with OPD and NBT substrates. The results were accounted for by a new electroprotic mechanism of H_2O_2 activation, where an ionic sponge comportment of the gels plays a crucial role.

Results and Discussion

Investigation into the interaction of aqueous solutions of H_2O_2 with the surface of amorphous oxides of ZrO_2 , Nb₂O₅, HfO₂, Ta₂O₅ led to the establishment and later generalization of the electroprotic mechanism of ROS formation. The reaction between amorphous gels and H_2O_2 in aqueous solution has been studied using EPR (HYSCORE), Raman, UV-Vis, FTIR, TG-MS, and XPS techniques over a wide range of pH and peroxide concentration. We identified various reaction intermediates, such as O_2^{--} and °OH radicals, as well as O_2^{-2-} peroxide groups (**Figure 1a,b,c**). Under acidic conditions, superoxide and hydroxyl radicals were generated simultaneously in large amounts, and their peak concentration was reached near the isoelectric point of the amorphous catalysts. In this pH region, the amorphous gels exhibited peroxidase-type activity, quantitatively measured by the o-phenylenediamine oxidation assay. Above the isoelectric point, O_2^{-2-} formation (Raman observations) is accompanied by significant O_2 release due to catalase-like activity (**Figure 1d**). The role of electroprotic processes has been established based on pH dependence. The similar pattern of concentration profiles corresponding to O_2^{--} and °OH suggests that both types of radicals are formed simultaneously during the decomposition of H_2O_2 according to the electroprotic mechanism: $\equiv M^+-HO_2^{--}(surf) + H_2O_2(aq) \rightarrow °OH_{(aq)} + M^+-O_2^{--}(surf) + H_2O_2(surf) + H_2O_2(aq)$. The surface of the investigated amorphous oxides was covered with hydroxyl groups. These groups



control electrolytic equilibrium by exchanging and capturing charged intermediates of the electroprotic decomposition reaction of H_2O_2 . This observation rules out the homolytic decomposition of hydrogen peroxide exclusively into •OH radicals postulated earlier.



Figure 1 Identification of reactive oxygen species formed during the interaction of H_2O_2 with amorphous Nb₂O₅. (a) EPR spectra of the interaction of H_2O_2 with Nb₂O₅, (b) EPR spectra using DMPO spin trapping, (c) changes with pH in the EPR signal of superoxides and Raman signal of peroxides, (d) change in peroxidase and catalase type reactivity under pH.

The catalytic screening was carried out for the oxide gels (UV-vis, methylene blue (MB) degradation with H_2O_2). We carried out detailed catalytic studies for Nb₂O₅-based materials. The contribution of ROS generated *in situ* or *ex situ* to the elimination of ciprofloxacin (CIP) was evaluated. We tracked the kinetics of CIP removal by UV-vis spectroscopy, while identification of CIP degradation products was obtained by liquid chromatography-mass spectrometry (LC-MS). We found that surface $O_2^{2^-}$ and O_2^- groups significantly improved the adsorption efficiency of CIP on Nb₂O₅ by modifying the surface charge. At the same time, we showed that better removal of CIP in the dark and the presence of H_2O_2 was mainly determined by the adsorption process. We confirmed the enhanced adsorption by infrared (IR) spectroscopy, total organic carbon (TOC) measurements, and elemental analysis. We observed effective chemical degradation of adsorbed CIP after exposing the Nb₂O₅/H₂O₂ system to UV light. We further showed that niobium oxide is therefore a promising inorganic adsorbent that can be easily regenerated in an environmentally friendly manner by UV light exposure.

References

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