Decomposition of model organic pollutants via wet peroxidation – the activity of composite copper catalysts in the generation of ROS

Wiktor CZERWONKA[1], Kamila SOBAŃSKA[1], Piotr PIETRZYK[*,1]
[1]*Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Poland.*
** piotr.pietrzyk@uj.edu.pl*

Significance and Relevance

Due to the constantly increasing level of water pollution with organic substances, special attention has been paid to the development of new catalysts for the degradation of these pollutants through advanced oxidation processes (AOP) in recent years. These processes are based on the generation of reactive oxygen species (ROS), including hydroxyl radicals (•OH) and singlet oxygen ($^1O_2$), which enable the degradation of contaminants into simpler, less harmful forms and, in some cases, complete mineralization.

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

Introduction and Motivations

The generation of reactive oxygen species (ROS) can occur via various mechanisms such as the Fenton reaction and its modifications or the electroprotic pathway. The former requires redox-active centers, whereas the latter relies on acid–base functional groups that mediate the coupled transfer of electrons and protons. The integration of these two mechanisms in a material can be achieved by synthesizing a composite catalyst composed of two types of oxide materials: a crystalline, redox-active phase and an amorphous, hardly reducible phase.[1]

The aim of this study is to develop a composite material in which the active phase comprises copper inorganic compounds. The materials include CuO_x, CeO_2, Nb_2O_5 single oxides, mixed Cu-Ce oxides, as well as selected copper hydroxo nitrate compounds. In the context of Fenton-like reactions, the Cu(II)/Cu(I) redox cycle is thermodynamically more favorable than the conventional iron ion cycle. Moreover, copper ion complexes are generally less stable than iron(III) complexes, which reduces the probability of permanent deactivation of the catalytic sites.

Results and Discussion

This work investigates potential catalysts for hydrogen peroxide decomposition and ROS generation. Each material was subjected to structural analysis using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS/EDX). Additionally, X-ray photoelectron spectroscopy (XPS) was employed to analyze the surface elemental speciation. These measurements enabled the assessment of crystallinity, phase composition, morphology, and elemental composition of the synthesized samples. The capacity of the materials to generate hydroxyl radicals (•OH) and singlet oxygen ($^1O_2$) from H_2O_2 decomposition was evaluated using electron paramagnetic resonance (EPR) spectroscopy, in combination with the spin trap 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and the reactive probe 2,2,6,6-tetramethyl-4-piperidone (TEMPD) (**Figure 1a**). The chemical activity and potential applicability of the synthesized materials in advanced oxidation processes (AOPs) were evaluated through a model degradation reaction of the water pollutant, Direct Blue 15 (DB15) dye (**Figure 1b**).

The obtained results indicate that catalysts comprising two distinct metals with redox properties (Cu, Ce) exhibit the highest activity in the dye degradation process. It has been demonstrated that the concurrent presence of copper in multiple oxidation states has a significant impact on the activity of Fenton-like catalysts. Moreover, incorporating a minimal amount of the redox-active phase into the support material that exhibits an electroprotic mechanism of ROS generation (Nb_2O_5) significantly increases its catalytic efficiency. In addition, by promoting the Cu-based materials with Ce, one changes

not only the overall reactivity of the catalysts, but also the distribution of particular ROS (see **Figure 1a**), which have been identified by EPR as hydroxy radicals (characteristic of Cu-based materials) and singlet oxygen (Cu-Ce-based materials).

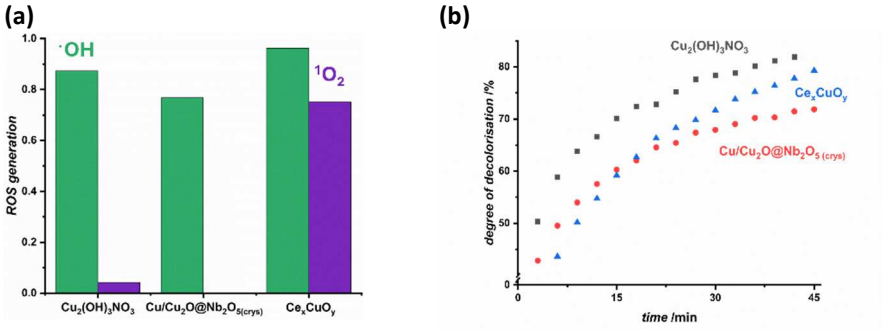

Figure 1 Comparison of the ability of the tested materials in a) generation of hydroxyl radicals (green) and singlet oxygen (purple), b) and in discoloration of Direct Blue 15.

References

1. B. Mozgawa, K. Sobańska, J. Gryboś, P. Pietrzyk, *Catalysis Today* **2022**, *384-386*, 156-165.

Acknowledgements

This work was financially supported by the National Science Center, Poland (NCN), grant OPUS27 2024/53/B/ST4/03929.