THESIS EVALUATION

Prepared by prof. Yuri Kalvachev, Institute of Catalysis, Bulgarian Academy of Sciences, member of scientific jury, appointed by order № РД-09-43/07.07.2025

Regarding: PhD Thesis of assist. prof. Bozhidar Grahovski

Title of the dissertation: "Transition metal oxide-based catalysts for the complete oxidation of volatile organic compounds (VOCs) and CO"

PhD dissertation for awarding the educational and scientific degree "**Doctor of Philosophy**" in higher education area 4. Natural science, mathematics and computing, professional field 4.2. Chemical sciences, doctoral program "Chemical Kinetic and Catalysis"

The documents submitted by the candidate are in accordance with the requirements of the Act on the Development of the Academic Staff in the Republic of Bulgaria and Art 26, para 1 of the Regulations of the Institute of Catalysis of the Bulgarian Academy of Sciences for the acquisition of the degree "Doctor of Philosophy" and include: dissertation, abstract, list of scientific publications on the topic of the dissertation, certificate of compliance with the minimum national requirements for the scientific degree "Doctor of Philosophy" for professional field 4.2. Chemical Sciences, CV.

Biographical data

Bozhidar Grahovski graduated with a bachelor's degree in Polymer Engineering in 2014 at the University of Chemical Technology and Metallurgy, Sofia, and in 2019 he graduated with a master's degree in Polymer Engineering at the same university. In January 2021, he was enrolled as a full-time doctoral student at the Institute of Catalysis - BAS after applying for a competition. Prof. Silvia Todorova was appointed as the scientific supervisor of the doctoral studies. Since July 2020, he has been appointed as a chemist - specialist, and since 2024 as an assistant professor at the Institute of Catalysis.

Dissertation and abstract

Bozhidar Grahovski's dissertation is structured on 103 standard pages and includes 11 tables and 32 figures. It consists of an Introduction (3 pages),

Literature (34 pages), Goals and objectives (1 page), Experimental part (6 pages), Results (41 pages), Conclusions (2 pages), List of cited literature (12 pages) with 194 sources included.

The topic of the literature review exactly corresponds to the topic of the dissertation, as the state of the research problem in world literature is presented in detail. Specific goals of the dissertation are set, as well as appropriate tasks for their achievement. The results of the research are presented in detail and clearly. The conclusions drawn are supported by appropriate techniques and correctly summarize the achieved results.

The presented draft of the abstract accurately reflects the main results and conclusions of the dissertation.

Scientific contributions and significance

The presented dissertation work is on the topic of heterogeneous catalysis using catalysts based on microporous and mesoporous materials. The main goal of the dissertation work is the development of new, active catalysts for the complete oxidation of volatile organic compounds and carbon monoxide by modifying zeolites and mesoporous materials. with cobalt oxide and cobalt oxide modified with MnOx. The topic is relevant and significant and the interest in this type of materials is justified.

The most significant contributions of the dissertation are:

1. New data are presented on the structural and catalytic properties of a series of single-component cobalt and two-component Co-Mn phases deposited on SBA-15, prepared from different precursors. It was found that the preparation of Co-SBA-15 catalysts from different precursors does not change the mesoporous structure. Depending on the precursor used, different types of oxide phases are formed on the surface of the mesoporous support.

2. It was found that, for the Co-ZSM-5 catalysts with different Si/Al ratios of 23, 40 and 100 in the combustion reaction of n-hexane, the Co-ZSM-5 sample with Si/Al ratio = 23 showed the best catalytic activity, which is mainly due to the higher concentration of active surface Co^{3+} particles. The data obtained from the reaction kinetics experiments and the applied kinetic modelling lead to the assumption that the complete oxidation of n-hexane on all catalysts proceeds via the Langmuir-Hinshelwood mechanism through dissociative adsorption of oxygen, with the reacting hydrocarbon and oxygen adsorbed on different active sites.

3. The complete oxidation of propane on Co-containing ZSM-5 zeolites with different Si/Al ratios (23, 40 and 100) occurs at catalyst bed temperatures above 240 °C, and the temperature required to achieve 30% propane conversion (T30) at an hourly gas volume velocity of 100,000 h^{-1} is 314–338 °C. The high catalytic activity of Co–ZSM-5 (Si/Al = 23) is explained by the high reducibility resulting from the lower interaction of cobalt oxide with the support. Based on the study of the reaction kinetics, the Mars-van Krevelen mechanism is considered the most likely.

The presented dissertation work includes a large amount of experimental material and a correct interpretation of the obtained results. During its implementation, the doctoral student was given the opportunity to apply a number of methods for physicochemical characterization of materials, as well as to become familiar with methods for assessing the catalytic activity of the obtained catalysts. The results obtained by Bozhidar Grahovski are relevant and significant in an area that attracts serious interest from various groups in the country and abroad with enormous public importance - the development of new catalytic systems for real application in reducing greenhouse gas emissions.

Publication activity

Three scientific articles have been published in international scientific journals on the results of the research, two in Q2, and the third in Q3, with an impact factor of 4.0; 0.35 and 1.8, respectively. The candidate has participated in or presented his results at an impressive number of 14 scientific forums, where he has presented 30 scientific papers.

The research conducted by the doctoral student requires precision, an analytical approach and the ability to independently systematically develop specific scientific tasks. In addition, Bozhidar Grahovski has worked successfully in various teams, as a participant in four scientific projects.

Based on the observed activity of the prepared Co–ZSM-5 materials, further development of these new catalytic systems for real-world application in reducing greenhouse gas emissions can be expected.

Critical notes and recommendations

I know the candidate personally. Bozhidar Grahovski is a young person who is interested in science. The proof is not only the presented dissertation and the materials to it, but also the conversations we had. The dissertation is written in

depth and both the research carried out and the conclusions they lead to are described in detail, but technical errors were made, which in no way diminish the merits of the work. I also have a question for the candidate: When using Co-ZSM-5 as a catalyst with an even lower Si/Al ratio than the lowest in the presented dissertation (Si/Al = 23), what catalytic activity do you expect in the oxidation of propane?

Conclusion

The dissertation work of Bozhidar Krasimirov Grahovski contains sufficient scientific results in volume, which are an original contribution and meet the requirements of the Act on the Development of Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the relevant Regulations of the Institute of Catalysis - BAS.

The scientific results, their good presentation, as well as my personal impressions are grounds for me to give a positive assessment of the dissertation work of Assistant Professor Bozhidar Grahovski and I vote with conviction for awarding the educational and scientific degree "doctor of philosophy" to Bozhidar Krasimirov Grahovski.

YURII ANGELOV KALVACHEV

Digitally signed by YURII ANGELOV KALVACHEV
Date: 2025.09.12 15:33:09 +03'00'

September 12th, 2025 prof. Yuri Kalvachev