O P I N I O N

by Assoc. Prof. Dr. Genoveva Atanasova

on the PhD thesis entitled "Transition Metal Oxide-Based Catalysts for the Complete Oxidation of Volatile Organic Compounds (VOCs) and CO"**,**

presented by Bozhidar Krasimirov Grahovski for the award of the educational and scientific degree of Doctor in Higher Education Area 4.2 Chemical Sciences, specialty: Chemical Kinetics and Catalysis."

This opinion has been prepared in accordance with Order No. RD-09-43/07.07.2025 of the Director of the Institute of Catalysis – BAS.

The PhD thesis of Bozhidar Grahovski presents a fully accomplished scientific study on a specific research problem, which includes the necessary review and application of data from contemporary scientific literature, as well as the synthesis, characterization, and testing of catalysts.

The specific objective of the thesis is the development of new, active catalysts for the complete oxidation of VOCs and CO through modification of zeolites, zeolites with secondary porosity, and mesoporous materials with cobalt oxide and cobalt oxide modified with MnOx. The topic of the thesis is relevant and has a clear environmental orientation. The research has been carried out mainly through experimental approaches.

The PhD thesis meets the formal requirements. It consists of 88 pages, 32 figures, and 11 tables. A significant number of references are cited – 194. The thesis is well structured. The text is accurate, clear, and highly precise. The theoretical part (35 pages) provides an in-depth review and concise summary of the literature on the subject. It discusses: Volatile Organic Compounds and CO; catalysts for reducing harmful emissions of VOCs and CO; heterogeneous catalysis and catalytic mechanisms; cobalt- and manganese-oxide-based catalysts; supported catalysts for VOC and CO oxidation and the influence of the support; main types of porous materials used as supports. The theoretical part concludes with well-defined summaries derived from the literature review.

The main part of the thesis (50 pages) presents objectives and tasks, experimental methods, results, and discussion of the specific studies. The objectives and tasks are concrete and clearly formulated. The experimental section describes the synthesis procedures of the samples, the characterization methods employed, and the catalytic tests conducted.

The research focuses on cobalt-oxide-based catalysts supported on microporous and mesoporous materials via impregnation. The influence of the type of support on catalytic behavior is studied in depth. Supports chosen include microporous ZSM-5 and mesoporous silica SBA-15. For the ZSM-5-supported catalysts, different Si/Al ratios (23, 40, 100) were investigated. Through extensive physicochemical characterization before and after catalytic testing, the effect of the Si/Al ratio was established. Additional experiments involved ZSM-5 zeolite treated with hydrofluoric acid and ammonium fluoride, resulting in the formation of secondary porosity. As the catalytic phase, 5 wt.% cobalt (from cobalt acetate) was impregnated on the ZSM-5-based supports. Furthermore, the effect of the precursor (acetate vs. nitrate) on the structural and morphological characteristics of Co and Co–Mn catalysts supported on SBA-

15 was studied. These investigations on the influence of support parameters on catalytic behavior are of particular practical importance for the development of high-efficiency catalytic systems.

The synthesized samples were characterized (before and after catalytic tests) using a broad range of physicochemical methods. Techniques employed include: X-ray Diffraction (XRD), Small-Angle X-ray Scattering (SAXS), X-ray Photoelectron Spectroscopy (XPS), Temperature-Programmed Reduction (TPR), UV-Vis spectroscopy, Infrared Spectroscopy (IRS), Nuclear Magnetic Resonance (NMR), nitrogen adsorption–desorption for BET surface area, porosity, and pore-size distribution, Scanning Electron Microscopy (SEM), High-Resolution Transmission Electron Microscopy (HRTEM), and Wavelength-Dispersive X-ray Fluorescence (WDXRF). The results were interpreted to extract the most relevant information for the specific research objectives.

To evaluate catalytic activity, the materials were tested in different catalytic reactions. Tests were conducted for the complete oxidation of VOCs (ethane, propane, butane, and n-hexane) and for CO oxidation.

The interpretation and discussion of the obtained results are more than sufficient. The analyses are accurate and thorough, and maximum information was extracted from the data. By comparing the results, conclusions were drawn about the processes taking place and the influence of various factors.

The thesis ends with well-structured conclusions and contributions, clearly and concisely defined. The abstract meets the requirements and reflects the scientific results and contributions of the thesis.

The main contribution can be summarized as follows: Catalytic samples were synthesized, and based on their physicochemical and catalytic characterization, data were obtained on the relationships between the type of oxide phase, dispersion of active components, their ratios, the effect of support structure, the method of deposition, and the precursor used, in relation to catalytic activity and selectivity.

The results convincingly demonstrate that the aims of the thesis have been successfully achieved. The research presented has both scientific and applied value.

The use of a wide range of experimental synthesis and analytical techniques has undoubtedly contributed to the training of Bozhidar Grahovski as a fully developed researcher.

According to the submitted documents, the results have been published in 3 scientific articles. In one of them, Bozhidar Grahovski is the first author, and in the other two – the second author, demonstrating his personal contribution. The results have been presented in 30 reports at national and international scientific forums. Bozhidar Grahovski has successfully passed all required exams and obtained the necessary credits during his doctoral studies. His scientometric indicators meet the legal requirements.

I have no critical remarks or recommendations regarding the research and the thesis of the candidate.

Conclusion: Considering the relevance, scope of experimental work, contributions, and scientometric indicators, the submitted PhD thesis fully meets the requirements of the Law on the Development of Academic Staff in the Republic of Bulgaria (ZRASRB) and the regulations of the Institute of Catalysis – BAS.

Therefore, I strongly recommend that the Scientific Jury of the Institute of Catalysis – BAS vote to award the educational and scientific degree *Doctor* in Higher Education Area 4.2 *Chemical Sciences* (specialty: Chemical Kinetics and Catalysis) to **Bozhidar Krasimirov Grahovski**.

12.09.2025

Sofia Assoc. Prof. Dr. Genoveva Atanasova