R E V I E W

by Prof. Margarita Dimitrova Popova, DSc,
Institute of Organic Chemistry with Centre of Phytochemistry – BAS
of the dissertation for the award of the educational and scientific degree *Doctor* in the field of higher education: 4. Natural Sciences, Mathematics, and Informatics; professional field 4.2. Chemical Sciences; scientific specialty "Chemical Kinetics and Catalysis"

Author: Bozhidar Krassimirov Grahovski
Title: Transition metal oxide-based catalysts for the total oxidation of Volatile Organic Compounds (VOCs) and CO
Scientific Supervisor: Prof. Silviya Zhivova Todorova, PhD

1. General overview of the submitted materials

The documents and electronic materials submitted by Bozhidar Grahovski comply with the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria (LDASRB), its Regulations, the Regulations of BAS, and the Rules of the Institute of Catalysis (IC-BAS) for the acquisition of the doctoral degree. The doctoral candidate has presented CV, dissertation, abstract, a list of publications in scientific journals included in the dissertation (3 papers) and their copies, and a list of participation in 14 scientific national and international forums with 30 oral and poster presentations. Of the 3 publications, 2 are in Q2-ranked journals (40 pts.) and 1 in a Q3-ranked journal (15 pts.), giving a total of 55 points under indicator G, which surpasses the minimum requirement of 30 pts.
The report of exams and credits taken during the PhD shows 282 points (130 pts. for completing the educational program: mandatory courses and exams, and 152 pts. for fulfilling the research program: conference presentations), compared to the required 200 points.

2. Brief biographical information

Bozhidar Grahovski graduated from the University of Chemical Technology and Metallurgy (UCTM) – Sofia in 2019 with a Master's degree in Polymer Engineering (Chemical Engineer). Since 1.01.2020 he has been enrolled as a full-time doctoral student in the "Catalysis for Energy and Environmental Protection" Laboratory at IC-BAS under the supervision of Prof. Silviya Todorova, PhD. On 23.12.2023 he was discharged with the right to defend and currently works as a chemist in the same laboratory at IC-BAS.

3. Relevance of the topic and appropriateness of the objectives and tasks

The dissertation is in the field of environmental catalysis and aims to develop highly active catalysts for air purification from pollutants such as VOCs and CO. The main focus is on developing catalysts based on hierarchical zeolites and mesoporous silicates modified with transition metal oxides (Co, Mn, and Co–Mn mixed oxides).

The EU has set air pollution control as a key priority. In 2013 it introduced the "Clean Air" policy package with targets up to 2030 for reducing harmful emissions, and in 2019 the Green Deal further defined goals for cleaner air. The dissertation's topic is strongly aligned with these strategies and has pronounced scientific and applied significance.

4. Knowledge of the problem

The literature review covers 194 references in reputable journals, showing the candidate's excellent familiarity with the state of research.

The introduction justifies the focus on developing highly active catalysts for VOC and CO oxidation, specifically choosing hierarchical zeolites and mesoporous silicates modified with transition metal oxides (Co_3O_4, MnO_x, or Co–Mn mixed oxides). The approaches to solving the tasks are also presented. The dissertation thoroughly discusses: main types and sources of VOC emissions, methods for their elimination (sorption, thermal, catalytic, biocatalytic, biofiltration), catalyst types (noble metal-based, transition metal oxide-based, mixed catalysts), mechanisms for total oxidation of VOCs and CO.

Special attention is given to cobalt- and manganese-based catalysts, including perovskite, spinel, manganese oxide, and Co–Mn mixed oxide systems. Types of porous supports (zeolites, mesoporous silicates) and modification strategies are also discussed. The review logically leads to the definition of the dissertation's objectives and tasks.

5. Research methodology

Extensive work was carried out, including application of different methods for synthesis of porous materials, their modification, and comprehensive characterization using classical and advanced physico-chemical techniques: XRD, N_2 physisorption, XPS, TPR, UV-Vis, FTIR, solid-state NMR, SEM/TEM, and XRF. Catalytic tests were performed for VOC (propane, butane, n-hexane) and CO oxidation in a flow reactor. The chosen methods are appropriate and demonstrate the candidate's solid experimental skills.

6. Characteristics and evaluation of the dissertation

The dissertation is well-structured, including 106 pages which cover: introduction (3 pages), literature review (34 pages), objectives (1 page), experimental part (7 pages), results and discussion (41 pages), conclusions and contributions (2 pages), references (15 pages).

A total of 194 references are cited. The thesis is written in good scientific language, with well-argued conclusions and high-quality figures that aid comprehension.

7. **Contributions and significance for science and practice**

The results have both fundamental and practical importance in environmental catalysis. The main results in the dissertation and its scientific contributions can be summarized in two main groups depending on the catalysts developed:

Catalysts for the total oxidation of VOCs based on Co-modified hierarchical zeolites

1. It was found that treatment of ZSM-5 zeolite with different Si/Al ratios (23, 40, and 100) using a buffered HF and NH_4F solution results in a hierarchical material characterized by secondary mesoporosity.
2. Cobalt-based catalysts were successfully developed by depositing cobalt on parent and hierarchical ZSM-5 zeolites with different Si/Al ratios (23, 40, and 100), using cobalt acetate as a precursor of the metal phase.
3. Various cobalt oxide species were found to form on the surface of the Co-ZSM-5 catalysts: Co_3O_4 particles with different dispersion; Co^{2+} in different ion-exchange positions (α and γ); cations containing Co^{2+} ($[Co–O–Co]^{2+}$) and/or CoO_x stabilized within the zeolite; as well as silicate phases. A mechanism was proposed for the formation of cobalt silicate, where Co atoms are incorporated into the silicate structure in tetrahedral positions.
4. The highest catalytic activity for total oxidation of n-hexane was observed for 5% Co-ZSM-5 (Si/Al = 23), which is attributed to the presence of Co_3O_4 particles reducible at the lowest temperature compared to the reduction of the same phase in the other catalysts.
5. Co-modified hierarchical ZSM-5 zeolites exhibited higher activity in the complete oxidation of propane and n-hexane compared to their counterparts based on untreated ZSM-5 zeolite. The presence of secondary mesoporosity promotes the formation of finely dispersed oxide particles, leading to higher catalytic activity.

Catalysts for the total oxidation of VOCs and CO based on Co–Mn-modified mesoporous SBA-15 silicas

1. Mono-component Co- and bi-component Co–Mn-modified SBA-15 catalysts were successfully prepared using different precursors of the metal oxide phase, while maintaining the mesoporous structure of the support.
2. It was found that the type of metal oxide precursor (cobalt acetate or cobalt nitrate) influences the formation of the oxide phase. When cobalt nitrate is used, in addition to finely dispersed Co_3O_4 and $CoSiO_3$ (formed with both precursors), finely dispersed CoO is also produced.

3. In the bi-component Co–Mn-modified SBA-15 catalysts, mixed Co–Mn oxide phases are formed, which are reducible at low temperatures and show higher activity in the total oxidation of butane and n-hexane.
4. In all Co-modified SBA-15 catalysts, the formation of cobalt silicate was observed, associated with the presence of silanol groups on the surface of SBA-15, which favors its formation.
5. The formation of Co_3O_4 and the presence of CoO and/or Co^{2+} in octahedral coordination are of key importance in the oxidation of CO, with the highest activity demonstrated by 5% Co-ZSM-5 (Si/Al = 100).

8. Evaluation of publications

The dissertation results are published in three papers: one in *Reaction Kinetics, Mechanisms and Catalysis*; one in *Materials Today: Proceedings*; and one in *Catalysts*. The candidate is the first author of one paper, confirming his personal contribution to the preparation and interpretation of the published results. His works have 13 citations. He has presented results at 14 scientific forums with 30 oral and poster contributions.

9. Personal contribution

I have no doubt about Bozhidar Grahovski's personal contribution to the execution of the research and interpretation of the results. His scientific supervisor, Prof. Todorova, undoubtedly contributed to the high level of the achieved results.

10. Abstract

The dissertation abstract is 41 pages long and accurately and correctly reflects the main results achieved in the dissertation in a summarized form. The conclusions and scientific contributions, as well as the publications reflecting the results obtained in the development of the dissertation work, are noted.

11. Critical remarks and recommendations

I have no critical remarks. The dissertation is very well prepared and clearly written, which greatly facilitates the preparing the review.

12. Personal impressions

I personally know Bozhidar Grahovski and have very good impressions of him as a diligent and skilled chemist, capable of convincingly presenting his scientific results.

Conclusion

The dissertation contains original scientific and applied results that make a genuine contribution to science and meet all the requirements of LDASRB, its Regulations, and those of BAS and IC-BAS. It convincingly demonstrates that Bozhidar Krassimirov Grahovski possesses the theoretical knowledge and professional skills in the field of "Chemical kinetics and catalysis" and is capable of conducting independent scientific research.

On this basis, I give my **positive evaluation** of the dissertation and recommend that the esteemed Scientific Jury award Bozhidar Krassimirov Grahovski the educational and scientific degree **Doctor** in the field of higher education 4. Natural Sciences, Mathematics, and Informatics; professional field 4.2. Chemical Sciences; scientific specialty Chemical Kinetics and Catalysis.

29.09.2025 Reviewer:

/Prof. Margarita Popova, DSc/