

REVIEW

Prepared by: Assoc. Prof. Dimitrinka Alexieva Nikolova, PhD, Eng.

Institute of Catalysis, Bulgarian Academy of Sciences

on the dissertation submitted for the award of the educational and scientific degree Doctor

Field of Higher Education: 4.2 Chemical Sciences

Scientific specialty: Chemical Kinetics and Catalysis"

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Author of the dissertation: Assist. Bozhidar Krasimirov Grahovski, Laboratory “Catalysis for Energy and Environmental Protection”

Title of the dissertation: Transition Metal Oxide-Based Catalysts for the Complete Oxidation of Volatile Organic Compounds (VOCs) and CO

Supervisor: Prof. Silvia Todorova, PhD, IC-BAS

The author of the dissertation is Assistant Bozhidar Krasimirov Grahovski – a full-time PhD student at the Institute of Catalysis, Bulgarian Academy of Sciences, Laboratory Catalysis for Energy and Environmental Protection, under the supervision of Prof. Silvia Todorova, PhD.

The materials submitted by PhD candidate Assist. Bozhidar Grahovski are fully consistent with the Regulations for Academic Development at the Institute of Catalysis, BAS, and meet the Institute’s requirements for the award of the degree of “Doctor”.

Bozhidar Krasimirov Grahovski began working as a chemist at the Institute of Catalysis, Bulgarian Academy of Sciences (BAS) in 2020. From January 2021 to December 2023 he was enrolled as a full-time PhD student at the Institute, and since 2024 he has held the position of Assistant in the Laboratory of Catalysis for Energy and Environmental Protection.

His dissertation is devoted to the catalytic oxidation of harmful pollutants such as volatile organic compounds (VOCs) and carbon monoxide (CO), aiming at achieving lower operating temperatures and reduced energy consumption. VOCs are major precursors for tropospheric ozone formation and secondary organic aerosols – key pollutants that deteriorate air quality and pose serious risks to human health. Due to their high volatility, VOCs are released into the atmosphere from various industrial processes, including paint and varnish production, the chemical and petrochemical industries, pharmaceuticals, and others. Carbon monoxide is another highly toxic pollutant, generated by the incomplete combustion of fossil fuels such as natural gas, oil, gasoline, and coal in both industry and transport. The subject of this research is highly relevant, as the efficient removal or utilization of VOCs and CO represents both an ecological and economic priority. A particular focus is the development of cost-effective and durable noble-metal-free catalysts. The concept of treating VOCs and CO not only as pollutants to be eliminated but also as valuable resources for energy and the chemical industry is especially timely. This shift from “abatement” to “valorization” through catalysis, combined with integration into the concepts of the circular economy and decarbonization, reflects an innovative trend and makes catalytic oxidation processes particularly topical. **For these reasons, the research conducted by Assist. Grahovski can be considered both current and innovative, with fundamental and applied scientific significance.**

The dissertation comprises 103 pages and includes 32 figures and 11 tables, supported by 194 literature references.

The objective of the dissertation is the development of new, highly active catalysts for the complete oxidation of VOCs and CO by modifying different supports such as zeolites, hierarchical zeolites with secondary porosity, and mesoporous materials, with cobalt oxide and cobalt oxide modified with MnOx. The design of low-cost, durable, noble-metal-free catalysts is a central and timely trend in contemporary research.

The literature review is presented in an informative manner and is directly aligned with the stated research objectives. Structured in five sections, the review addresses: the environmental impact of VOCs and CO; their sources of emission; the main methods for their removal; and the principal groups of oxidation catalysts, namely (i) noble metals, (ii) metal oxides, and (iii) combinations of noble metals and transition-metal oxides. The mechanisms of VOC and CO oxidation over oxide catalysts are described in detail, with particular emphasis on the potential and advantages of cobalt-

and manganese-oxide-based catalysts. The effectiveness of porous supports is also thoroughly discussed, including:

- microporous zeolite aluminosilicates, such as the high-silica zeolite ZSM-5;
- hierarchical zeolites with secondary porosity, prepared through chemical treatments (dealumination, desilication, or simultaneous silicon and aluminum extraction using HF/NH₄F solutions) aimed at optimizing surface area.

The review demonstrates unequivocally the strong expertise of Assist. Grahovski in the field of catalysts for the complete oxidation of VOCs and CO. It highlights his understanding of the influence of synthesis methods, choice of metal precursors, chemical composition, type of support, and the interactions between active phases and supports—all of which serve as a foundation for his own research. A total of 137 references are cited.

The research approach in the dissertation is based on the design of monometallic Co₃O₄ and mixed Co₃O₄–MnO_x oxide catalysts for application in the catalytic oxidation of both VOCs and CO. The strategies applied include: **(1)** Deposition of active components via the impregnation method, widely used in industrial catalyst synthesis; **(2)** Investigation of the effect of metal precursors, employing either acetate or nitrate salts; **(3)** Use of various supports such as ZSM-5 zeolites with different Si/Al ratios (23, 40, 50) and mesoporous silica SBA-15; **(4)** Modification of ZSM-5 porosity (with varying Si/Al ratios) by treatment with HF/NH₄F solutions to introduce secondary (hierarchical) porosity. **The novelty** of this work lies in employing this type of hierarchical zeolite support to improve the performance of catalysts for VOC and CO oxidation. The analysis of the oxide phase, dispersion and state of the active components (Co₃O₄ and Co₃O₄–MnO_x), as well as the effects of support structure and precursor type on catalytic activity and selectivity, ensure the fulfillment of the dissertation's objectives.

To evaluate the catalytic properties, three model reactions were selected: **(1)** Complete oxidation of n-hexane, widely used as a solvent and reagent in the chemical industry; **(2)** Complete oxidation of propane and butane, the main components of automotive fuel; **(3)** Conversion of CO to CO₂.

The catalysts were comprehensively characterized in terms of crystalline structure, nanomorphology, textural and redox properties, elemental composition, surface chemistry, local structure, and morphology. A wide range of physicochemical techniques were applied, including

low-temperature N₂ physisorption, X-ray fluorescence, X-ray diffraction, small-angle X-ray scattering, temperature-programmed reduction with H₂, infrared spectroscopy, X-ray photoelectron spectroscopy, nuclear magnetic resonance, as well as scanning and transmission electron microscopy. The catalysts were analyzed both in their freshly prepared state and after catalytic testing

The scientific achievements and contributions presented in the dissertation can be systematized into the following main areas:

1. Investigation of the influence of the Si/Al ratio in the ZSM-5 support on the catalytic properties of Co-ZSM-5 catalysts with identical cobalt content (5 wt.%) in the complete oxidation of various volatile organic compounds (VOCs) and carbon monoxide (CO).

- Detailed studies of the volumetric and surface structure at varying Si/Al ratios in the ZSM-5 support revealed the formation of the active Co₃O₄ phase in Co-ZSM-5 catalysts, as well as the presence of CoO (Co²⁺ ions localized at different positions – α - and γ -ion exchange sites).
- It was found that the catalyst with the lowest Si/Al ratio of 23 (5Co-ZSM-5, Si/Al = 23) exhibited the highest activity in both oxidation reactions. This catalyst also possessed the highest amount of surface Co₃O₄ and Co³⁺ ions in oxide form compared to catalysts with higher Si/Al ratios of 40 and 100.
- In addition to the main Co₃O₄ phase, where cobalt is predominantly in octahedral Co³⁺ coordination, the presence of Co²⁺ ions in octahedral coordination within CoO in the catalysts with Si/Al ratios of 23 and 100 contributed to greater accessibility of CO and O₂ molecules to the catalyst surface, which is reflected in the high activity of both catalyst compositions.

2. Investigation of the catalytic performance of catalysts based on hierarchical ZSM-5 zeolites, obtained via treatment with a mixed solution of hydrofluoric acid and ammonium fluoride, in the complete oxidation of propane and n-hexane.

- It was demonstrated that treatment of ZSM-5 zeolites (Si/Al = 23, 40, 50) with a mixed HF/NH₄F solution modifies the zeolite structure by: (i) improving the textural properties of the support, increasing specific surface area, average pore diameter, and mesopore volume; (ii) altering the morphology of treated ZSM-5, leading to particle coarsening and formation of secondary defects; and (iii) inducing changes in the symmetry of the zeolite framework.

- Catalysts prepared on hierarchical ZSM-5 showed various cobalt oxide species: bulk Co_3O_4 strongly interacting with the support, Co^{2+} ions in ion-exchange sites, and cobalt silicate phases. As a result, these catalysts exhibited higher activity in the complete oxidation of propane and n-hexane due to the formation of finely dispersed oxide particles and the presence of secondary mesoporosity.

3. Investigation of the catalytic properties of Co-SBA-15 catalysts in the complete oxidation of butane, n-hexane, and CO, depending on the type of precursor used for impregnation of the mesoporous SBA-15 support (cobalt acetate or cobalt nitrate), and the effect of manganese introduction into the catalyst composition (5 wt.% Co and 2.5 wt.% Co – 2.5 wt.% Mn).

- The role of the cobalt precursors (acetate or nitrate) on the structural and morphological characteristics of Co-SBA-15 catalysts was analyzed. It was found that cobalt acetate led to a higher specific surface area and larger mesopore volume of the calcined 5Co-SBA-15 catalyst compared to cobalt nitrate, explaining the higher catalytic activity of the acetate-derived catalyst.
- To obtain a more active Co-SBA-15 catalyst, the promoting effect of manganese was studied. The catalyst composition 2.5 wt.% Co – 2.5 wt.% Mn showed higher activity in the complete oxidation of butane and n-hexane compared to the monometallic 5 wt.% Co catalyst. The formation of easily reducible mixed Co–Mn oxide phases was identified as the reason for the more reactive catalyst surface.
- The significant contribution of Co^{2+} ions in octahedral coordination within CoO, together with the main Co_3O_4 active phase, was confirmed to be responsible for the high activity in CO oxidation for Co-SBA-15 catalysts synthesized using cobalt acetate.

In summary, the use of hierarchical ZSM-5 as a support provides a greater number of catalytically active sites and demonstrates potential for the development of future catalytic compositions for complete oxidation reactions. The proposed mechanism for the formation of cobalt silicate phases in Co-ZSM-5, involving substitution of silanol groups and bridging hydrogen atoms with Co, as well as the incorporation of Co atoms into tetrahedral positions within the silicate framework, contributes to understanding the effect of secondary mesoporosity on the reduction behavior of the catalyst. Combined with the modification of cobalt catalysts through the use of

appropriate precursors, such as cobalt acetate during synthesis, and the introduction of additional components, for example manganese oxide, this approach opens perspectives for the design of new catalytic systems for practical applications aimed at reducing greenhouse gas emissions.

The achievements of this dissertation have both fundamental scientific and applied research significance.

The conclusions presented at the end of the dissertation accurately summarize and reflect the obtained results. The work is clearly and concisely structured. The submitted abstract objectively represents the structure and content of the dissertation.

The results of the dissertation have been published in three articles in specialized scientific journals: Reaction Kinetics, Mechanisms and Catalysis (2022, Q3, 10 points), Materials Today (2022, Q2, 20 points), and Catalysts – MDPI (2023, Q2, 20 points). The total points according to indicator G amount to 50, exceeding the minimum threshold of 30 points. The cumulative 145 points for published articles surpass the minimum criteria for indicator G established in the regulations for the implementation of the Law on the Development of the Academic Staff in the Republic of Bulgaria (30 points). In one of the publications, PhD candidate Assist. Grahovski is the first author, demonstrating his leading role in the research. The articles have been cited 13 times. A list of participation in 14 national and international scientific forums is provided, and the candidate personally delivered three oral presentations at both national and international conferences.

Questions:

1. What is the purpose of the pretreatment of the samples in the reactor in a gas mixture of 84 vol.% N₂ and 16 vol.% O₂ at 300 °C prior to the total oxidation of VOCs?
2. Why is the pretreatment before the catalytic test for CO oxidation carried out only in N₂?
3. What additional information does small-angle X-ray scattering (SAXS) provide compared to standard XRD in the analysis of the catalyst structure?

Note: It would be appropriate for the labels on the ordinate and abscissa in the figures to be in Bulgarian, in accordance with the language of the main text.

My personal impressions of Assist. Bozhidar Krasimirov Grahovski are related to his work on the project for the implementation of an investment under C2I2, “Enhancing the Innovation Capacity of the Bulgarian Academy of Sciences in the Field of Green and Digital Technologies”, from the Recovery and Resilience Plan – Project No. BG-RRP-2.017-0007, “Technology for Producing Clean Hydrogen for Green Energy – A Step Forward Towards Zero Emissions”. He demonstrates motivation, and independence as a researcher; scientific accuracy and clarity in presenting his results; effective teamwork and communication skills; readiness and potential for further professional development; as well as integrity and responsibility in submitting his monthly reports. Additionally, his participation in presenting the project at the international Green Transition Forum 5.0 demonstrates his engagement and active role in disseminating scientific achievements.

CONCLUSION:

The dissertation contains research results that constitute a significant scientific and applied contribution to the field and comply with all requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria (LDASRB), the Regulations for the Implementation of the LDASRB, and the corresponding regulations of the Bulgarian Academy of Sciences.

The dissertation demonstrates the in-depth theoretical knowledge, professional skills, and comprehensive understanding of catalytic processes in the scientific specialty of Chemical Kinetics and Catalysis of PhD candidate Assist. Bozhidar Krasimirov Grahovski.

In conclusion, based on the evaluation of the dissertation, abstract, obtained results, scientific contributions, and overall performance of Assist. Bozhidar Krasimirov Grahovski, I confidently give a ***positive assessment*** and ***recommend that the esteemed Academic Council award the educational and scientific degree of “Doctor”*** to Assist. Bozhidar Krasimirov Grahovski in the field of Higher Education: Professional Field 4.2 Chemical Sciences, Scientific Specialty: Chemical Kinetics and Catalysis.

Sofia, 25.09.2025

Reviewer:

/Assoc. Prof. Dimitrinka Nikolova, PhD/