

OPINION

by Prof. Dr. Ivanka Petrova Spasova

on the dissertation entitled: **“Transition Metal Oxide-Based Catalysts for Total Oxidation of Volatile Organic Compounds (VOCs) and CO”**

submitted for the award of the educational and scientific degree "Doctor"

in the professional field 4.2 "Chemical Sciences" (Chemical Kinetics and Catalysis)

PhD Candidate: Bozhidar Krasimirov Grahovski

Scientific Advisor: Prof. Dr. Silvia Todorova

1. General Description of the Submitted Materials

The set of documents submitted by Bozhidar Grahovski complies with the regulations for academic staff development at the Institute of Catalysis – Bulgarian Academy of Sciences (IC-BAS) and fully meets the criteria for obtaining the educational and scientific degree “Doctor”. The PhD candidate has provided a CV, dissertation, abstract draft, a list of publications with noted citations, scientific conference presentations, and corresponding supporting materials. The documents are clearly and neatly prepared, presenting well the academic and scientific activities carried out during the doctoral studies.

2. Brief Biographical Data of the Candidate

Bozhidar Grahovski received his Master’s degree in 2019 from the University of Chemical Technology and Metallurgy – Sofia, specializing in “Polymer Engineering.” In 2020, he began working at IC-BAS, where he is currently employed as a chemist. In 2021, he was admitted as a full-time PhD student at the same institute under the supervision of Prof. Dr. Silvia Todorova. The candidate has fully completed the educational and research program of the PhD course and, as of 13.12.2023, has been granted the right to defend his dissertation.

3. Relevance of the Topic and Appropriateness of the Goals and Tasks

The issue of volatile organic compounds (VOCs) and carbon monoxide (CO) is especially relevant due to increasing emissions from industrialization and human activity. These pollutants harm health, contribute to smog and climate change, CO is toxic also. Therefore, the development of effective and affordable methods for their removal is crucial. This dissertation aims to develop highly efficient catalysts based on metal oxides and zeolites. The study explores modified zeolites and mesoporous materials with transition metal oxides (Co_3O_4 and MnO_x), assessing their physicochemical properties and catalytic activity in the VOCs oxidation.

4. Characterization of the Dissertation

The dissertation is structured according to requirements, comprising 106 pages, 32 figures, and 11 tables. A total of 194 literature sources are cited. The literature review (32 pages, 137 sources) offers an in-depth overview of VOCs and CO, their environmental impact, main purification methods, supports and catalyst types used in such processes, as well as main catalytic mechanisms. The section concludes that supported Co and Mn oxides show

promise as a more affordable alternative to noble metals, though more studies are needed on the influence of support structure and porosity - especially in hierarchically porous zeolites.

The objectives and tasks of the dissertation are clearly and precisely formulated. The main goal is to develop new catalysts for the total oxidation of VOCs and CO by modifying zeolites and mesoporous materials with Co_3O_4 and $\text{Co}_3\text{O}_4/\text{MnO}_x$. To achieve this, the candidate carries out a comprehensive set of tasks involving synthesis, physicochemical analyses, and catalytic tests to evaluate the influence of the support's structure and the oxide phase's type on the catalysts' activity and selectivity.

The Experimental section (8 pages) describes the catalyst synthesis procedures, catalytic tests, and a brief overview of the characterization methods used.

Results and discussion section is presented in 41 pages and includes 57 additional references. It is evident that the candidate has mastered various synthesis techniques for cobalt and manganese catalysts supported on zeolites as well as proper physicochemical characterization methods. Alongside, data on catalytic performance in the total oxidation of homologous alkanes (from methane to hexane), kinetic parameters for the studied reactions are also calculated according to the Mars–van Krevelen mechanism.

The research shows that catalysts based on cobalt acetate and ZSM-5 zeolite form different cobalt oxide phases, including Co_3O_4 , Co^{2+} in ion-exchange positions, and cobalt silicates. The most active sample is 5% Co-ZSM-5 (Si/Al=23), owing to the easily reducible Co_3O_4 phase. Treatment of the zeolite with $\text{HF}/\text{NH}_4\text{F}$ creates secondary mesoporosity, improving dispersion and activity. Catalysts based on hierarchical ZSM-5 show higher oxidation activity than those on untreated zeolite. For cobalt catalysts on SBA-15, the support structure is preserved, and finely dispersed phases of Co_3O_4 , CoSiO_3 , and CoO are formed. Mn addition results in active mixed Co-Mn oxide phases. In CO oxidation, key roles are played by Co_3O_4 , CoO , and octahedrally coordinated Co^{2+} .

The dissertation presents a thorough and systematic investigation, articulated clearly and scientifically, with precise use of specialized terminology, reflecting the candidate's strong academic preparation.

5. Contributions and Significance of the Work for Science and Practice

The findings have both scientific and practical significance and contribute to catalyst synthesis with targeted design. Cobalt catalysts supported on hierarchical ZSM-5 zeolites with varying Si/Al ratios were developed, showing increased activity in total oxidation of propane and n-hexane due to the fine dispersion of the metal oxide and the presence of mesopores offering more active sites. A mechanism for cobalt silicate formation is proposed, involving surface group substitution and incorporation of Co atoms into tetrahedral positions in the silicate structure.

6. Evaluation of Publications Related to the Dissertation

The dissertation results have been summarized in three scientific papers in journals with impact factor (*Reaction Kinetics, Mechanism and Catalysis, Materials Today: Proceedings, and Catalysts*). The findings have been presented at five scientific conferences, and the articles have received 13 citations. According to scientometric indicators, the dissertation

fully complies with the requirements of the Bulgarian Law on the Development of Academic Staff and the regulations of BAS and IC.

7. Author's summary on the PhD thesis

The abstract accurately and comprehensively reflects the content, conclusions, and scientific contributions of the dissertation.

CONCLUSION

The dissertation contains scientific and applied research results that constitute an original contribution to science and fully meet the requirements of the Bulgarian Law on the Development of Academic Staff (LDAS), the related regulations, and the internal rules of BAS and IC. The dissertation demonstrates that the candidate has acquired in-depth theoretical knowledge and professional experience in the field of "Chemical Kinetics and Catalysis," showing the ability to conduct independent scientific research.

For the above reasons, I confidently give a positive evaluation of the research and recommend that the esteemed Scientific Jury award the educational and scientific degree "Doctor" to Bozhidar Grahovski in the professional field 4.2 "Chemical Sciences," specialization "Chemical Kinetics and Catalysis."

15.09.2025

Prepared an opinion:

(Prof. Dr. Ivanka Spassova)