

Opponent assessment for the dissertation of Mariia Lemishka

“Binuclear transition metal ion centers in zeolites: Their preparation, characterization, and catalytic properties”

The dissertation of Mariia Lemishka deals with a highly relevant and timely topic in the field of heterogeneous catalysis and material science, specifically focusing on the binuclear transition metal ion centers in zeolites and their applications in the selective oxidation of methane to methanol. The work presents an elaborate and comprehensive study that combines experimental approaches with theoretical modeling, offering a holistic view of the problem. The use of various analytical methods such as FTIR, Mössbauer spectroscopy, UV-Vis, and density functional theory (DFT) calculations effectively highlights the structure and reactivity of these systems.

The dissertation is structured into six main chapters, starting with an introduction that clearly outlines the theoretical background regarding transition metals in zeolite frameworks, their importance in catalysis, and current knowledge on methane oxidation. The introduction provides a solid foundation for understanding the experimental results and their significance. The results and discussion chapters are devoted to the study of specific transition metals (Fe, Co, Ni, Mn) in zeolite structures, such as ferrierite (FER) and mordenite (MOR), with a comprehensive investigation into their catalytic properties. A notable strength of this dissertation is the theoretical extension of the research to other zeolite frameworks (*BEA, LTA), which improves the study by investigating the influence of aluminum distribution in these frameworks on catalytic activity.

The dissertation contributes several original findings, particularly in the mechanistic exploration of O₂ and N₂O splitting on binuclear Fe(II) centers and their following reactivity with CH₄. These findings hold significant promise for industrial applications in methane oxidation, a process with significant economic and environmental consequences. One of the major contributions of this work is the investigation of how different zeolite topologies affect the catalytic properties of transition metal ions, offering valuable insights into optimizing zeolite-based catalysts for specific industrial processes.

The author uses advanced methodological approaches, which are well-described and contribute significantly to the understanding of the subject. The combination of experimental techniques and theoretical calculations provides a robust framework for investigating the mechanisms of oxygen activation and subsequent methane oxidation. In particular, the methodology based on FTIR spectroscopy and DFT calculations is highly notable, as it allowed for a detailed characterization of reactive oxygen species and their interactions with CH₄.

The dissertation is well-organized, with a logical flow from the introduction through to the conclusions. The presentation of data and findings is clear and understandable, making effective use of figures and tables.

Publication Contributions and Peer Review: Mgr. Mariia Lemishka is currently a co-author of six publications (four published in Q1 journals, one in a Q2 journal, and one in a Q3 journal) that have been published in journals with impact factors. All these works underwent peer review and formed the direct basis for the final version of the doctoral thesis. These journals require reviews by at least two referees, and in some cases, more than three. Therefore, it can be stated that the work has already been partially reviewed by at least twelve independent referees. The fact that these articles are already available indicates that the reviews for the final versions of the publications were always positive and recommendatory. In this situation, it is difficult to find aspects of the work that could be considered incorrect, erroneous, or significantly inaccurate.

Proposed questions for the dissertation defense:

- What are the main advantages and disadvantages of using zeolites in heterogeneous catalysis compared to homogeneous catalysts?
- How does the distribution of aluminum in the zeolite matrix influence the catalytic activity of transition metals?
- In your work, you studied the splitting of O₂ and N₂O on binuclear Fe(II) centers in zeolites. What are the main differences in the mechanisms of splitting these two molecules, and how do these differences affect the subsequent methane oxidation?
- Your work involves the use of several analytical methods, including FTIR and DFT calculations. What are the advantages of combining experimental and theoretical methods when studying the catalytic properties of transition metals in zeolites?

Conclusion:

Mgr. Mariia Lemishka's dissertation represents a valuable scientific work, contributing significant findings to the field of heterogeneous catalysis. The work is of high scientific merit and demonstrates the author's ability to conduct independent research at an exceptional level. Given the acceptance of six related publications in impact factor journals, it is evident that the research is of excellent quality, making it challenging to identify any flaws or inaccuracies.

Based on the detailed analysis and the high quality of the work presented, I conclusively recommend this dissertation for defense and the awarding of the Ph.D. degree.

Ostrava, 06. 9. 2024

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