

## OPINION

by Assoc. Prof. Dr. Ivanka Petrova Spassova, IGIC- BAS  
on the Thesis for awarding the educational and scientific degree "Doctor"  
in a Professional field- 4.2. Chemical sciences (specialty Organic chemistry)

Author: **Hristina Ilieva Lazarova**

Theme: " Development of ecological catalysts for production of valuable chemicals and fuels  
through utilization of biomass "

Scientific advisor: Prof. Dr. Margarita Popova

The set of materials presented by the doctoral student is in accordance with the Law on Acquisition of Scientific Degrees and Occupation of Academic Positions at IOHCF-BAS.

Hristina Lazarova graduated in 2010 from the Faculty of Chemistry and Pharmacy at Sofia University with a Master's degree in Medical Chemistry. Since 2009 he has been working at IOCCP-BAS in the laboratory "Organic reactions on microporous materials". In 2020 she was enrolled as a PhD student in independent training in scientific field 4.2. Chemical sciences and specialty Organic chemistry. She was unenrolled with the right of defense from August 1, 2021.

The Thesis is in the field of one of the most current world challenges - utilization of biomass, considered one of the promising environmental sources for chemicals and fuels. In recent years, the utilization of lignocellulosic biomass using non-food raw materials has been a promising alternative to reduce dependence on fossil fuels. Valuable platform molecules are obtained, including levulinic acid as a possible source of renewable energy and chemicals used as fuel additives. New effective catalysts for these processes are reported in the dissertation.

The Thesis is organized according to the requirements in 135 pages, contains 54 figures and 22 tables and includes Introduction, Literature review, Conclusions from the literature review, Aim and tasks of the dissertation, Experimental, Results and discussion, Conclusions and contributions, Literature. The cited literature sources are 241.

The need for the research is well motivated in the Introduction, given the depletion of traditional energy sources and the need to seek alternative approaches. The Literature review, presented in 33 pages, presents in detail the biomass generations and the approaches for their utilization. 191 literature sources are cited. Attention is paid to levulinic acid and its esters as precursors for the synthesis of various important compounds and their production from biomass. A key point in the control of the processes related to biomass utilization is the development of highly efficient, with high activity and selectivity cheap catalysts. However, the problem of developing a strongly acidic heterogeneous catalyst for the catalytic utilization of biomass and the development of green technologies for the production of valuable chemicals has not yet been solved.

Based on the in-depth analysis of the literature and critical evaluation, the aim of the dissertation is the preparation of highly efficient acid catalysts based on hierarchical zeolites, modified mesoporous silicates and nanosized metal oxides and their application in esterification processes related to biomass utilization to valuable chemicals and fuels. The specific tasks have been appropriately selected for the implementation, as a result of which modified micro- and mesoporous materials with tunable catalytic properties have been developed.

The Experimental part of 11 pages describes both the synthesis of the studied supports and catalysts, as well as an impressive set of various and complementary analytical methods for physicochemical characterization of the obtained materials. The conditions for the catalytic tests in glycerol esterification and levulinic acid esterification reactions are also presented.

The Results and discussion are presented in 47 pages, illustrated by 42 Figures and 21 Tables. Another 50 literature sources are cited. It is evident that the PhD student has experienced methods for the synthesis of hierarchical mordenites, mesoporous silicate materials and catalysts based on them. XRD, N<sub>2</sub>-physisorption, SEM, TEM, FTIR, UV-Vis, XPS, DTA-TG, NMR etc. are combined for the detailed physicochemical and morphological characterization of the obtained catalysts. The working conclusions after each section make a good impression, trying to make sense of and summarize the results.

The contributions of the Thesis can be classified as scientific with a potential for practical application. Several procedures for the synthesis and post-synthetic modification of catalysts with high activity and stability in glycerol and levulinic acid esterification reactions have been developed. For the first time, a correlation between the loss of sulfate groups during the esterification of levulinic acid and the dispersity of ZrO<sub>2</sub> particles supported on mesoporous silicate was found.

The Thesis is based on 6 scientific papers (three of which are in journals with Q1, 2-Q3 and 1 in a journal with SJR). These papers are already cited by 57 publications for 4 years. Ten reports at national and international scientific events are presented on the topic of the dissertation. The PhD student is the first author in one of the presented articles, and in the others before her is the scientific supervisor. In my opinion, the active participation of the doctoral student is in the performance of an impressive volume of precise experimental work, in the analysis and description of the obtained results.

The presented abstract reflects accurately and comprehensively the content of the Thesis.

My personal impressions of Hristina Lazarova are of a very responsible and precise researcher who can be relied on.

## CONCLUSION

The dissertation contains scientific and scientific-applied results, which represent an original contribution to science and meet all the requirements of the Law for development of the academic staff in the Republic of Bulgaria (ZRASRB), the Rules for its application in BAS and IOCCP- BAS. The PhD student Hristina Lazarova has acquired theoretical and practical knowledge and competencies in the scientific specialty "Organic Chemistry", showing skills for independent research. Due to the above, I confidently give my positive assessment of the study and propose to the esteemed Scientific Jury to award the educational and scientific degree 'Doctor' to Hristina Lazarova in the Professional Field 4.2. "Chemical Sciences" specialty "Organic Chemistry".

17. 09. 2021.

Member of the Scientific jury:

Assoc. Prof. Dr. Ivanka Spassova