

STATEMENT

from Assoc. Prof. Dr. Stela Ivanova Minkovska

Institute of Catalysis, BAS

Member of the Scientific Jury according to order No RD-09-167/30.07.2021 of the Director of IOCCP-BAS

Subject: PhD thesis for awarding the educational and scientific degree "Doctor", professional field 4.2. "Chemical Sciences", scientific specialty "Organic Chemistry".

PhD Candidate: Hristina Ilieva Lazarova

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

Supervisor: Prof. Dr. Margarita Popova

General presentation of the procedure and the doctoral student

I have been designated as a member of a scientific jury according to order No RD-09-167/30.07.2021 by the Director of the Institute of Organic Chemistry with Centre of Phytochemistry (IOCCP), with the task of reviewing and evaluating the thesis described above, submitted for the scientific and educational degree 'doctor' in the field of higher education 4. Natural Sciences, Mathematics and Informatics, professional field 4.2. Chemical sciences, scientific specialty "Organic Chemistry". The author of the PhD thesis is Hristina Ilieva Lazarova - doctoral student in independent study form.

The PhD thesis and the set of documents presented by Hristina Lazarova are in accordance to the requirements of the Law for the Development of the Academic Staff in the Republic of Bulgaria, The Regulations of BAS for the Implementation of this Law and the Rules of IOCCP-BAS for the professional field "Chemical Sciences".

General presentation of the Candidate

Hristina Ilieva Lazarova graduated in 2010 at the Faculty of Chemistry and Pharmacy of Sofia University "St. Kliment Ohridski" subject Medical Chemistry, with master's degree. During her studies she worked as a chemist at the Institute of Organic Chemistry with the Center of Phytochemistry - BAS in the laboratory "Organic reactions on microporous materials" from May 2009 to January 2017. In February 2017, after a competition, she was appointed as an assistant professor at the Institute of Organic Chemistry with Centre of Phytochemistry - BAS in the laboratory "Organic reactions on microporous materials". In June 2020, after successfully passing the examination, she was appointed as a doctoral student in the professional field 4.2. Chemical sciences, Scientific specialty "Organic Chemistry" with supervisor Prof. Dr. Margarita Popova. Personal skills of the doctoral student include working with modern computer programs and fluency in Russian and English.

Topical relevance

The PhD thesis of the doctoral student Hristina Lazarova deals with a topical issue related to the conversion of biomass into valuable chemicals and fuels. Obtaining environmentally friendly catalysts for the production of biofuels based on waste biomass will solve a number of problems related to climate change today, as well as many economic, social and environmental problems. The use of biomass for energy purposes does not pollute the environment and it is therefore considered to be a source of environmentally clean or “green energy”. The main advantage of biomass compared to other renewable energy sources is its ability to be converted directly into liquid fuels such as biodiesel and ethanol.

Knowledge of the problem

The literature review provides a detailed overview of the prospects of biomass utilization and the need to develop highly efficient, selective and inexpensive catalysts for the flow and control of this process. A separate chapter is devoted to levulinic acid as a major feedstock for the production of biofuels, polymers and pharmaceuticals. The methods for the preparation of hierarchical zeolites, their modification and the synthesis of mesoporous materials to produce highly active and selective catalysts for biomass utilization and the production of valuable chemicals and fuels are discussed.

Research methodology

The literature review (34 pages with 191 references) presented by the doctoral student Hristina Lazarova and the conclusions drawn from it are the basis for the aim set in the thesis: to obtain highly efficient acid catalysts based on hierarchical zeolites, modified mesoporous silicates and nanosized metal oxides to be successfully applied in esterification processes for biomass utilization and obtaining valuable chemicals and fuels. In order to fulfill the stated objective, the following specific tasks were performed: 1) Preparation of hierarchical mordenite and Zr-containing hierarchical mordenite and investigation on the influence of textural characteristics and nature of acidic centers on their catalytic properties in esterification reaction of glycerol, a by-product of biodiesel production. 2) Preparation of modified nanosized mesoporous materials with $-\text{SO}_3\text{H}$ group as catalysts in esterification reactions (glycerol and levulinic acid) associated with biomass utilization; 3) Preparation of nanosized ZrO_2 nanoparticles, ZrO_2 deposited on KIL-2 type mesoporous silica and nanosized SnO_2 nanoparticles and their sulfated analogues and obtaining data on them in levulinic acid esterification reaction.

The work includes a large amount of experimental material and analytical interpretation of the results obtained. In the course of her work, the doctoral student was given the opportunity to learn and apply a number of methods for synthesis and characterization of the new samples obtained. The chosen experimental methodologies for synthesis and catalytic tests were adequately selected and allowed to achieve the set goal of obtaining answers to the problems solved in the thesis.

Characteristics and evaluation of the PhD thesis and contributions

The PhD thesis is laid out on 135 pages according to the standard scheme, with the proportion between the different parts being respected. It is written at a very good scientific level and is illustrated with 22 tables, 54 figures and 6 schemes. 241 references are cited. The new materials obtained in the PhD thesis by known methodologies are characterized by modern and advanced physicochemical methods, such as X-ray phase analysis, infrared spectroscopy, ultraviolet spectroscopy, transmission electron microscopy, scanning electron microscopy, specific surface area determination, X-ray photoelectron spectroscopy, temperature-programmed desorption of ammonia, solid-phase NMR spectroscopy, thermogravimetric analysis and complete information about their properties was obtained. The doctoral student successfully applied modern methods of synthesis and investigation of the obtained samples in her work, i.e. the educational objectives of the PhD degree have been fulfilled. The topic of the PhD thesis fully corresponds to the scientific specialty.

The results obtained in this thesis are both fundamental and scientifically applied. The main contributions of the PhD thesis could be summarized as follows:

- A highly active and selective catalyst for esterification of glycerol with acetic acid was obtained by further impregnation of hierarchical mordenite with 15 wt. % ZrO₂.
- Mesoporous silicate SBA-15 was synthesized by modification with sulfonic groups, which is characterized by high catalytic activity and stability in esterification of glycerol and levulinic acid.
- A procedure was developed to prepare sulfated nanosized ZrO₂ and SnO₂ catalysts by hydrothermal synthesis in the presence of template followed by sulfation, which are characterized by high specific surface area and high catalytic activity in the esterification of levulinic acid.
- The optimum conditions for the preparation of highly active catalysts for the esterification of levulinic acid by impregnation and subsequent sulfuric acid treatment of sulfated Zr-modified mesoporous KIL-2 silicates were established. The optimum amount of ZrO₂ in modifying mesoporous silicate was found, at which the highest catalytic activity was achieved in this process. For the first time, the loss of sulfate groups during the catalytic esterification reaction of levulinic acid was found to depend on the dispersity of ZrO₂ particles deposited on the mesoporous silicate support.

Assessment of publications and personal contribution of the doctoral student

The results of the PhD thesis of Hristina Lazarova have been published in 6 articles, two belonging to Q1, one to Q2 and three to Q4, making them "visible" to the international scientific society. 57 citations were noted on the articles included in the dissertation. In my opinion, the personal contribution of the doctoral student is quite sufficient. This is confirmed by the fact that in one of the submitted articles, the PhD student ranked first, in two second and in three third. The doctoral student Hristina Lazarova has presented the results obtained during the development of the dissertation at 10 scientific forums in Bulgaria and abroad.

Abstract

The abstract (written in 46 pages and containing 25 figures and 1 table) reflects fully and accurately the main results presented in the dissertation. It is very well designed and richly illustrated.

Critical remarks and recommendations

I have no critical remarks on the PhD thesis of doctoral student Hristina Lazarova and on the presented materials.

CONCLUSION

The PhD Thesis of Hristina Ilieva Lazarova contains original scientific and applied results representing a contribution to science. It contains a considerable amount of experimental work in a topical scientific field. The PhD thesis cover the requirements for awarding the scientific and educational degree "Doctor", according to requirements of the Law for the Development of the Academic Staff in the Republic of Bulgaria, The Regulations of BAS for the Implementation of this Law and the Rules of IOCCP-BAS. In her PhD thesis, the doctoral student has shown high theoretical competence, experimental skills and independence, which present her as an established young scientist in the field of organic chemistry and catalysis. The results obtained and the scientific metrics exceed the specific requirements for obtaining the scientific and educational degree "Doctor" in the scientific specialty "Organic Chemistry".

Based on the above, I confidently give my **positive assessment** of the research, the results and scientific contributions and I am pleased to recommend to the honorable members of the Scientific Jury to award to Hristina Ilieva Lazarova the educational and scientific degree "Doctor" in the professional field 4.2. "Chemical sciences", scientific specialty: "Organic chemistry".

23.09.2021

Assoc. Prof. Stela Minkovska