

## REVIEW

of Ph.D. thesis for scientific and educational degree „**doctor of philosophy**“

Prepared by Prof. Silviya Zhivova Todorova, Ph.D, Institute of Catalysis-BAS.

in the field of higher education 4. “*Natural sciences, mathematics and informatics*”  
Professional field 4.2. “*Chemical Sciences*”, scientific research specialty “*Organic Chemistry*”

Author: Hristina Ilieva Lazarova

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

Head of Ph.D. thesis: **Prof. Dr. Margarita Dimitrova Popova, IOCCP - BAS**

### 1. General description of the submitted materials

The author of the dissertation is Hristina Ilieva Lazarova - PhD student at the laboratory "ORGANIC REACTIONS TO MICROPOROUS MATERIALS" at the Institute of Organic Chemistry with Center for Phytochemistry-BAS with supervisor Prof. Dr. Margarita Popova.

The of materials presented by Hristina Lazarova is in accordance with the Regulations for development of the academic staff of IOCCP-BAS, and meets the criteria of IOCCP-BAS for obtaining the scientific and educational degree "Doctor". The doctoral student has presented 6 publications, a list of citations on scientific papers included in the dissertation, a list of participations in scientific events, a list of participation in the implementation of scientific projects, awards.

The documents are submitted on time and are well formed.

### 2. Brief biographical data about the doctoral student

Hristina Lazarova graduated in 2010 at Sofia University "St. Kliment Ohridski ", specialty “ Medical Chemistry”, with the educational degree “Master”. She started working at the Institute of Organic Chemistry with the Center for Phytochemistry (IOCCP-BAS) in the laboratory "Organic reactions on microporous materials" (ORMM) as a chemist during her studies. In the period 2017-07.2021 she is an assistant in the same laboratory. From 01.07.2021 - until now she is again in the position of "chemist", due to the expiration of the maximum four-year period during which he can hold the position of "assistant". By decision of the Scientific Council of IOCCP-BAS of 16.01.2020, she was enrolled as a doctoral student in self-study on the topic of the thesis " Development of ecological catalysts for production of valuable chemicals and fuels through utilization of biomass ".

The PhD student's personal skills include working with modern computer programs and good written and spoken English.

### **3. Relevance of the topic and expediency of the set goals and objectives**

The research is directly related to current societal challenges, namely energy and energy efficiency and environmental protection. The world's natural resources are depleting rapidly and this requires an orientation of the economy towards the use of renewable energy sources. Biomass is one of the main and promising environmental sources for chemicals and fuels. The advantage of biomass is that it can be directly converted into liquid fuels such as biodiesel and ethanol, as well as the ability to be used for biogas production. The glycerol is a by-product during production of biodiesel. Glycerol can be converted into valuable chemicals through a number of catalytic reactions. Of the renewable raw materials, lignocellulosic biomass is among the most widespread and available in nature, has no nutritional value, is obtained from agricultural and forestry waste, which makes it the most promising raw material for the production of chemical products to replace products obtained from minerals. Various platform molecules, including levulinic acid, are obtained by pre-treatment of lignocellulosic biomass. Due to the fact that it is easily obtained and can be used to produce biofuels, plasticizers, etc., it is considered one of the most promising sources of bioenergy. By esterification of levulinic acid, chemicals are obtained with application as additives to fuels, lubricating oils and others.

Catalytic processes are used for the processing of glycerol and levulinic acid. In the development of catalysts the main goal is to be highly active and cheap, and because of this the aim of the dissertation is very logical, namely to obtain highly efficient acid catalysts based on hierarchical zeolites, modified mesoporous silicates and nanosized metal oxides and their application in esterification processes related to the utilization of biomass to valuable chemicals and fuels. To achieve the goal of the dissertation, several tasks are formulated:

1. Investigation of the influence of the textural characteristics and nature of acid centers in the production of hierarchical mordenite and Zr-containing hierarchical mordenite on their catalytic properties in the reaction of esterification of glycerol obtained as a by-product of biodiesel production.

2. Preparation of SO<sub>3</sub>H modified groups of nanosized mesoporous materials (SBA-15, SBA-16 and KIL-2) in order to develop effective catalysts in esterification reactions (glycerol and levulinic acid) related to biomass utilization.

3. Preparation of nanosized ZrO<sub>2</sub>, ZrO<sub>2</sub> nanoparticles deposited on mesoporous KIL-2 and nanosized SnO<sub>2</sub>, as well as their sulfated analogues, investigated in the reaction of esterification of levulinic acid.

From the above it is clear that the goals and objectives of the dissertation are undoubtedly in a modern, current and promising field.

### **4. Knowledge of the problem**

The dissertation is based on a review of 241 literature sources. The introduction gives a brief but meaningful picture of the advantages of biomass as an alternative energy source and a source for obtaining valuable chemicals. The relevance of the conducted researches is

shown and the directions of the research are clearly demonstrated. The literature review provides a detailed analysis of the state of art in terms of recovery of first and second generation biomass, methods for obtaining levulinic acid (LA) from biomass, esterification of levulinic acid with different alcohols and in the presence of different types of catalysts. Due to the fact that zeolites are used as heterogeneous catalysts for esterification of LA with alcohols, the thesis presented in detail the structure and properties of zeolites, as well as hierarchical zeolites, as a new generation of materials combining thermal stability of classical zeolites, which reduces diffusion problems and high surface area. The structure, preparation, functionalization, characterization of mesoporous silicates and their advantages as catalyst carriers are described in detail. The development of the literature review shows that the doctoral student is able to competently and critically analyse, interpret and summarize the existing literature, which has definitely contributed to the correct formulation of the goals and objectives of the dissertation, finding the right approaches for their successful solution and the high level of research.

## **5. Research methodology**

Based on the in-depth analysis of the literature and the previous experience of the group, the purpose of the dissertation is formulated and several specific tasks are defined, which were mentioned above. To realize the set tasks, initial and hierarchical mordenite, mesoporous silicate materials of the type SBA-15, SBA-16 and KIL-2, nanosized mesoporous  $ZrO_2$ , nanosized mesoporous  $SnO_2$  were initially synthesized. After synthesis, the zeolites and mesoporous materials were modified. Zirconium was used as a modifier of mordenites. Mesoporous silicates SBA-15, SBA-16 and KIL-2 are functionalized with  $SO_3H$  groups, and mesoporous KIL-2 is modified with  $ZrO_2$  nanoparticles.  $Zr/KIL-2$ ,  $ZrO_2$  and  $SnO_2$  were further functionalized with  $SO_4$  groups. The samples are characterized by a different modern physicochemical methods such as X-ray diffraction analysis, scanning electron microscopy, transmission electron microscopy, ultraviolet spectroscopy, photoelectron spectroscopy, infrared spectroscopy, temperature programmed desorption of ammonia, solid ammonia, solid ammonia. In this way, in-depth information on the volume and surface properties of the materials is obtained. Catalytic tests were performed on the obtained materials in the reaction of glycerol and levulinic acid esterification. The parameters of the catalytic tests are reported in detail. The experimental part describes in detail both the used methods and the conditions of synthesis of the studied catalysts, as well as the physicochemical methods of characterization. The selected methods of synthesis, characterization and catalytic tests allow achieving the goals and obtaining original scientific results. All obtained data are accurately and correctly interpreted and described in the dissertation.

## **6. Characteristics and evaluation of the dissertation**

The dissertation prepared by Hristina Lazarova meets the requirements of Law for Development of the Academic Staff in the Republic of Bulgaria (LDASRB) and contains: Introduction, Objectives and tasks, Review, Experimental part, Results and discussion, Conclusions, and References, List of scientific publications and reports presented at conferences related to the dissertation. The dissertation contains 135 pages, 54 figures and 22

tables. The bibliography covers 241 titles. Most are from recent years, but older literature has also been used, which is evidence of a detailed examination of the problem and allows for a more comprehensive view.

The dissertation is constructed with logically connected chapters. The presented figures, tables and diagrams are formed strictly and precisely and allow very fast reading of the information. The topic of the dissertation fully corresponds to the scientific specialty. Scientific results have a certain value and are achieved through appropriate methods and approaches. The reliability of the obtained results is also guaranteed by comparing the results of clarifying the same problem, obtained through different research methods. The impression of the precisely conducted experiment, of the correctly described synthesis procedures and catalytic tests is very good. It makes a particularly good impression that the catalytic systems have also been tested for stability.

## **7. Contributions and significance of development for science and practice**

The dissertation has contributions of theoretical and scientific-practical nature. The following can be mentioned as main contributions:

1. The modification of hierarchical mordenite with 15 wt. %  $ZrO_2$ , leads to the production of a highly active and selective catalyst for esterification of glycerol with acetic acid. The formation of larger pores in hierarchical mordenite leads to easier access to the Bronsted and Lewis acid centers, on the one hand, and on the other hand the ratio between these centres is optimal.

2. Sulfonic-modified mesoporous SBA-15, by means of a developed two-step post-synthesis procedure, is characterized by high catalytic activity and stability in esterification of glycerol and levulinic acid.

3. It has been developed a procedure for the preparation of sulfated nanosized  $ZrO_2$  and  $SnO_2$  catalysts by hydrothermal synthesis in the presence of a template followed by sulfation, which are characterized by a high specific surface area and high catalytic activity in the esterification of levulinic acid.

4. I consider especially positive the fact that the phase responsible for the high catalytic activity has been established, and also that a mechanism for the reaction of esterification of levulinic acid with ethanol has been proposed in case of sulphated nanosized  $SnO_2$  materials prepared by hydrothermal synthesis. Responsible for the high catalytic activity is the high-crystalline phase based on hydrated Sn (IV) sulphate [ $Sn(SO_4)_2 \cdot xH_2O$ ], Sn(IV) bisulphate [ $Sn(HSO_4)_4 \cdot xH_2O$ ] and /or tin(IV) pyrosulphate [ $Sn(S_2O_7) \cdot xH_2O$ ] particles.

5. Highly active and stable catalysts for the esterification reaction of levulinic acid, based on sulphated Zr-modified mesoporous KIL-2, have been obtained. The catalysts were prepared by impregnation and subsequent treatment with sulfuric acid. The optimal amount of  $ZrO_2$  was determined. For the first time, it was found that the loss of sulphate groups during the catalytic reaction of esterification of levulinic acid depends on the dispersion of  $ZrO_2$  particles deposited on the mesoporous silicate support.

The high competence of the scientific supervisor, as well as the high scientific level of the researchers from the laboratory „Organic reactions on microporous materials“ undoubtedly contributes to the exact approach and the interesting results.

## **8. Evaluation of the publications on the dissertation**

Materials including research presented in the dissertation are published in 6 articles; two belong to category Q1, one to Q2 and three to Q4. In 1 of the presented articles, the PhD student is in first place, in two in second and in three in third places, which clearly shows that her contribution to the development of research is significant. There are 57 citations on the articles included in the dissertation. All of them are in publications referenced and indexed in world-famous databases of scientific information (Web of Science and Scopus). 10 poster and oral presentations on the topic of the dissertation are presented of national and international scientific events.

## **9. Personal participation of the PhD student**

Assessing the fact that the doctoral student is the first author in one presented article, second - in two articles and third - in three, and also that she is the first author in 9 out of 10 reports at scientific events, I can assume that the dissertation is her work under the guidance of supervisors.

## **10. Abstract**

The presented abstract objectively reflects the structure and content of the dissertation. The abstract has been prepared in accordance with the requirements of the Law for Development of the Academic Staff in the Republic of Bulgaria (LDASRB), the Regulations for its application and the Regulations of BAS for the application of the LDASRB.

## **11. Critical remarks and recommendations**

The dissertation is written in good language and the technical errors are small enough. The dissertation is easy to read. The presented figures and tables are formed strictly and precisely and allow very fast reading of the information. I have no fundamental objection to the material in the dissertation. I have the following question for the PhD student:

1. By what criteria did you choose the modification of hierarchical mordenite to be 15 wt. % ZrO<sub>2</sub>.

## **12. Personal impressions**

I have no personal impressions.

## **CONCLUSION**

The dissertation contains scientific, scientific-applied and 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 (LDASRB). The presented

materials and thesis results fully comply with the specific requirements of the Regulations of IOCCP - BAS for application of LDASRB.

The dissertation shows that the PhD student Hristina Ilieva Lazarova has in-depth theoretical knowledge and professional skills in the scientific specialty "Organic Chemistry" demonstrating qualities and skills for independent research.

Due to the above, I confidently give my positive assessment of the research presented by the above dissertation, abstract, results and contributions, and I propose to the esteemed scientific jury to award the educational and scientific degree 'Doctor' of Hristina Ilieva Lazarova in the field of higher education: "Natural Sciences, Mathematics and Informatics", professional field "Chemical Sciences" doctoral program "Organic Chemistry".

September 22, 2021.

Reviewer: .....

Prof. Silvia Todorova, PhD