REVIEW

by Prof. Dr. Boris L. Shivachev,

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member of a scientific jury approved by order RD-09-167 / 30.07.2021. of the Director of the IOCCP,

of dissertation Thesis for awarding the educational and scientific degree 'doctor' e.g. PhD in the field of higher education: 4. Natural sciences, mathematics and informatics, professional field: 4.2. Chemical Sciences, Doctoral Program in Organic Chemistry

Author: Hristina Ilieva Lazarova

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

Scientific consultant: Prof. Dr. Margarita Popova, IOCCP

General description of the presented materials

The printed set of materials presented by Hristina Lazarova and the electronic version are in accordance with those specified in the Regulations for development of the academic staff of IOCCP-BAS, Art. 22 (7), according to Art. 30 (1) of PPZRASRB. Also, the evidence presented by Hristina Lazarova meet (and exceed) the specified Minimum required points (by groups of indicators) for acquiring the educational and scientific degree 'Doctor' e.g. PhD according to Art. 1 (1), Art. 24 (1) and Art. 25 of PPZRASRB. Precisely, Hristina Lazarova graduated with a master's degree in Medical Chemistry fromSofia University, Faculty of Chemistry and Pharmacy in 2010. Since 2009 she has been working in the laboratory "Organic reactions on microporous materials" (ORMM) at IOCCP-BAS as a chemist and later as assistant. Hristina Lazarova was enrolled as a doctoral student in independent training form, with scientific consultant Prof. Dr. Margarita Popova, at the Laboratory ORMM of IOCCP on January 17, 2020 (order RD-09-9 / 17.01.2020). Hristina Lazarova obtained the right to defense by order RD-09-170 / 30.07.2021. During the training period Hristina Lazarova fulfilled the requirements of the mandatory credit system in the preparation of doctoral students at IOCCP-BAS by taking courses for general, specialized and individual academic training in "Electron microscopy and electron diffraction in morphological and phase analysis of materials", "Catalysis and Catalysts ", successfully passed exams in foreing language training (English) and computer skills for presentation at Center of

Education-BAS and an the exam for basic specialized science (130 points in total). The implementation of the scientific program of Hristina Lazarova includes Presentations in front of the scientific seminar of IOCCP-BAS, at scientific events (symposium, conferences etc.) in Bulgaria and international ones (248 points). The publications presented by Hristina Lazarova on the topic of the dissertation are in total six (6), namelly one (1) in Bulgarian Chemical Communications and five (5) in journals with impact factor (348 points in total). I consider that all the presented manuscripts are consistent with the topic of the dissertation. The presented publications exceed both the required minimums of IOCCP-BAS (a minimum of two publications and 80 points) and those (50 points) specified in the “Minimum required points by groups of indicators for acquiring the educational and scientific degree‘ Doctor ’according to Art. 1 (1) PPZRAS.

The conducted research, described in the doctoral dissertation (Thesis) submitted for review, is in a very rapidly developing scientific field in recent years - development of environmental catalysts - with multifaceted applicability in various fields (production of valuable chemicals and fuels through biomass utilization) as it is mentioned in the title of the dissertation. This makes the relevance of the dissertation indisputable. The significance of the conducted research and its relevance can be judged by the number of observed citations (of the publications presented for the dissertation), which are a total of 57. I would also like to note that the research reflected in the dissertation of PhD student Hristina Lazarova is a natural continuation of her work starting in 2009 in the ORMM Laboratory of IOCCP - BAS, and under the guidance of Prof. Dr. Margarita Popova.

Characteristics and evaluation of the dissertation

The thesis developed by Hristina Ilieva Lazarova covers 125 pages and features 54 figures, 22 tables and 6 diagrams (not counting the numbered pages with "List of scientific publications and reports presented at conferences related to the dissertation" - 126-135 pages). As references 241 literature sources are cited. The dissertation is formatted in a traditional way and contains the following chapters: Introduction, 1. Literature review, which ends with Conclusions and aims and tasks of the dissertation, 2. Experimental part, 3. Results and discussion -Development of catalysts for esterification of glycerol, 4. Development of catalysts for esterification of levulinic acid 5. Conclusions, (and Contributions) and ends with the References section.

Inside out, the literature review is structured in five parts. The first part is 1.1. "Biomass utilization. First and second generation biomass. It is interesting that usually one is having in mind about the first and second generation of biofuels, not the first and second generation of biomass. If we are talking about biomass, the difference in the technology of "processing" biomass should be reflected, not the production of biofuels. The second and third parts of the Literature Review (1.2-3) are related to the methods of production (targeting biomass) of specific catalysts and the use of

levulinic acid and its derivatives (levulin esters). The fourth part is related to Zeolites and hierarchical zeolites: basic description of the zeolite "structure" and chemical composition of zeolites (Si / Al ratio, number and type of active Bronsted / Lewis centers, type of cations, oxygen activity, etc.). The synthesis of zeolites and zeolite-like materials (starting reagents, SDA, solvents and "water" content, etc.) and post synthetic techniques are also briefly presented. The fifth section of the literature review is related to the synthesis, characterization, properties and application of mesoporous materials. In comparison with the previous parts, the here the overview is expanded and specific mesoporous materials are described: MCM, SBA and KIL. The end of the Literature review section accentuates on the completion of the with conclusions (conclusion) and setting the goal and objectives of the dissertation.

The doctoral student own research was conducted in two directions: synthesis and modification of porous materials and conducting catalytic testing of the obtained new materials. In the dissertation Hristina Ilieva Lazarova has chosen an approach to first present the protocols for the synthesis and the methods for characterization of the obtained materials (2. Experimental part) and then to present and discuss the results (catalysts for esterification of glycerol and catalysts for esterification of levulinic acid). In summa summary here are listed the most important results.

Preparation of hierarchical mordenite: a post-synthesis method was successfully applied, including treatment with HF and NH_4F followed by impregnation. Zr-modified hierarchical mordenite (15 wt% ZrO) showed the highest catalytic activity in the esterification of glycerol with acetic acid and selectivity for triacetylglycerol. In general, Zr hierarchical mordenite is a cost-effective material and can be tested for semi-industrial use as a catalyst.

Sulfone-modified mesoporous SBA-15, SBA-16 and KIL-2 silicates were prepared by reaction with mercapto silane to give mercapto-modified silicate and followed by oxidation with H_2O_2 to sulfone. The catalytic activity of these materials is probably due to the formation of strongly acidic Bronsted centers. Mesoporous SO_3H / SBA-15 silicate showed the highest catalytic activity in the esterification reaction of levulinic acid with ethanol compared to SO_3H / KIL-2. The SBA-15 catalyst showed complete conversion of glycerol and about 80% selectivity to di- and tri-acetylglycerols at 403 K for 3 hours. It is interesting to note that "the acidic centers formed on the two carriers have the same strength regardless of the different structure of the mesoporous silicate - SBA-15 and KIL-2".

Nanosized ZrO_2 and SO_4^{2-} / ZrO_2 catalysts were obtained by the hydrothermal method at 373 and 413 K and in the presence or absence of a structure-directing agent (SDA) and subsequent sulfation and calcination. The SO_4^{2-} / ZrO_2 catalyst showed the highest catalytic activity reaching 86% yield of ethyl levulinate of all catalysts tested, after 8 hours of reaction time.

Zr-modified mesoporous KIL-2 silicates were obtained by conventional impregnation technique and subsequent treatment with sulfuric acid. The sulfated 15 wt. % ZrO_2 containing KIL-2 catalyst is the most active in the esterification reaction of levulinic acid with ethanol, with 51% activity recorded after 5 hours of reaction time. The optimal % of weight ratio ZrO_2 / KIL-2 was established (15%). For the first time, the relationship between the loss of sulfate groups during the catalytic reaction and the dispersion of ZrO_2 particles deposited on the mesoporous silicate support was established.

Sulphated nanosized SnO_2 particles were obtained by hydrothermal synthesis at two temperatures. Sulfation of these materials leads to a new crystalline phase composed of S, Sn, O and H. It is the "new" crystalline phase that shows the highest catalytic activity among all studied catalysts, due to the simultaneous presence of SO_4^{2-} anions and water molecules leading to the formation of a larger number of active centers.

The main contributions and merits of the dissertation are:

- Systematic and in-depth research has been conducted in a modern and rapidly developing field: obtaining micro- and meso-porous materials for catalysts, which makes them relevant and interesting;

- Original scientific and applied scientific results are obtained: starting, hierarchical and modified Zr and / or sulphated (where applicable) mordenite, SBA-15, SBA-16 KIL-2, Zr-KIL-2, ZrO_2 and SnO_2 (nanoscale) catalysts;

- The obtained materials are characterized by appropriate modern techniques - thermal methods - DTA / DSC / TG, X-ray diffraction analysis, FTIR spectroscopy, NMR, N_2 physisorption (BET, SSA), etc., and the results are commented very skillfully and knowledgeably;

- The study of the catalytic properties of the obtained materials leads to a complete cycle including the synthesis, the characterisation and the properties (application);

- The promising opportunities for the obtained materials catalytic application is outlined;

- The results are reflected in six publications with 57 citations.

Of the mentioned by Hristina Lazarova contributions, two are really obvious and stand out:

• A 15 wt% ZrO_2-containing KIL-2 catalyst was found to be the most active in the esterification reaction of levulinic acid with ethanol. It is at this percentage that the dispersion of ZrO_2 is optimal for KIL-2 and if this % is raised conditions for the destruction of KIL-2 structure are designed.

• A new crystalline phase composed of S, Sn, O and H was found showing the highest catalytic activity among all studied catalysts, due to the simultaneous presence of SO_4^{2-} anions and water molecules leading to the production of more active centers (Bronsted and Lewis).

The abstract, in Bulgarian and English, reflects correctly and concisely the content of the dissertation. The volume and the diversity of the presented in the thesis research, in-depth and competent discussion of the results and the originality of the contributions give me reason to give the dissertation of doctoral student Hristina Ilieva Lazarova a high positive assessment.

Critical remarks and recommendations

As a comment to the literature review made by Hristina Lazarova is the use of figures and "literal" translation of entire passages from published works. I believe that for preparing a literature review, the "creative" approach by the doctoral student can be combined successfully, rather than relying entirely on available structured reviews on the topic.

In the dissertation, in an attempt to avoid repetition, synonyms are used. In scientific work the use of synonyms (chemicals, molecules, compounds, products, etc. or building chemicals, platform molecules, building blocks, etc.) leads to ambiguity and it is more appropriate to use the correct term repeatedly (or just one term).

In the part related to the development of sulphated nanosized SnO_2 catalysts (4.4) the characteristic starts with powder X-ray diffraction. What is meant by "XRD data also confirm that their crystal morphology is not well defined…"? In the text, based on SEM images (Figure 47), a conclusion is made for 8 nm particles. At a division scale of 10 and 100 μm, how are ~ 0.008 μm distinguished? What is meant by "highly crystalline phase"?

It is not necessary to present six manuscripts for obtaining 50 points. The recommendation is to preserve some of the manuscripts for further career development.

The comments made and the listed questions are of clarifying nature and do not diminish the results achieved and discussed by the doctoral student.

In conclusion, the dissertation of Hristina Ilieva Lazarova contains scientific and applied results, which represent an original contribution to the science and meet all the requirements of the Law for the Development of Academic Staff in the Republic of Bulgaria (ZRASRB), PPZRASRB BAS and IOCCP-BAS regulations. The dissertation thesis reveals that Hristina Ilieva Lazarova has an in-depth theoretical knowledge and professional skills in the synthesis of new micro- and meso porous materials, their physico-chemical characteristics and the study of their catalytic properties, demonstrating qualities and skills for scientific research.

In view of the above, I confidently give my positive assessment and propose to the esteemed scientific jury to award the educational and scientific degree ‘Doctor’ e.g. PhD to Hristina Ilieva Lazarova in the field of higher education: 4. Natural sciences, mathematics and informatics, professional field 4.2. Chemical Sciences and Doctoral Program in Organic Chemistry

September 24, 2021

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