

## OPINION

from Assoc. Prof. Yordanka Karakirova, PhD  
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**Subject:** PhD thesis for awarding the educational and scientific degree "Doctor" of **Aleksandra Atanasova Mileva**, full-time doctoral student in the laboratory "Organic Reactions of Microporous Materials" professional field 4.2. "Chemical Sciences", scientific specialty "Petrochemistry and petrochemical synthesis" on the topic "**Development of new metal oxides catalysts with application in alternative energy sources and ecology**"

**Supervisors:** Prof. DSc. Tanya Tsoncheva and Assoc. Prof. Daniela Paneva

This opinion was prepared on the basis of Order № RD-09-328 of 04.11.2020 of the Director of the Institute of Organic Chemistry with Centre of Phytochemistry - BAS Prof. Svetlana Simova.

PhD student Aleksandra Mileva has fulfilled all the requirements of the Law for the Development of the Academic Staff in the Republic of Bulgaria in order to be admitted to the defense of her dissertation. The dissertation, abstract and set of documents submitted by her are in accordance with the requirements for obtaining a scientific and educational degree "Doctor", reflected in 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. According to all criteria of the points system of the Training Center of BAS: educational program, approbation of the implementation of the scientific program and publications of scientific results on the topic of the dissertation Aleksandra Mileva presented evidence of a significant total number of points (1602 points) with a required minimum of 200 points.

### **Brief details of the applicant:**

Aleksandra Mileva received a bachelor's degree (2009) in the specialty "Natural and Alternative Fuels" and a master's degree (2014) in the specialty "Natural and Synthetic Fuels" at the Faculty of Chemical Technology of the University of Chemical Technology and Metallurgy. During the period 2016-2020 with a break of two years due to maternity leave (2017 and 2018) she was a full-time doctoral student in the laboratory "Organic Reactions of Microporous Materials" at IOCCP, BAS.

### **Characteristics and evaluation of the dissertation and contributions:**

The dissertation is structured according to the standard requirements and contains a total of 288 pages. It includes 96 figures, 35 tables, 11 diagrams and 742 cited references.

Based on the analysis of the literature, the purpose of the dissertation is formulated, namely to study and develop highly efficient catalysts for methanol decomposition, with a view to its

use as an alternative fuel, based on nanoscale transition metal oxides ( $\text{TiO}_2$ ,  $\text{CeO}_2$ ,  $\text{CuO}$ ) and their composites, as well as to study the possibility of using activated carbon obtained from waste raw materials as a carrier of mono- and bi-component Fe, Zn oxide catalysts. To achieve this goal, a significant amount of experimental work has been done. The experimental part describes in detail the used methods and conditions of synthesis of the studied catalysts, as well as the physicochemical methods of characterization. For the synthesis of  $\text{CeO}_2\text{-TiO}_2$  and  $\text{ZrO}_2\text{-TiO}_2$  composites, the doctoral student used the hydrothermal method and the method of homogeneous precipitation with urea. Cerium-titanium oxide nanocomposites are modified with copper oxide nanoparticles by two methods – conventional incipient wetness impregnation technique and “chemisorption–hydrolysis” procedure. Activated carbon was obtained on the basis of peach stones, polyolefin wax and used motor oils. The resulting carbon carriers are modified with iron and/or zinc oxide nanoparticles by the impregnation method. The materials thus obtained are characterized by modern and advanced physicochemical methods, thus obtaining in-depth information about the volume and surface properties of the studied materials. Catalytic tests include a reaction of methanol decomposition. In performing all these studies, the doctoral student was given the opportunity to get acquainted with and apply a number of methods for synthesis and characterization and to achieve the goals set in the dissertation.

From the exhaustive research conducted in the dissertation, very important conclusions have been made, which enrich the existing knowledge in the field of search and research of catalysts for the decomposition of methanol. In my opinion, the following contributions stand out among them with an original character:

- For the first time, a different mechanism for the formation of active centers in the process of applying a copper-oxidized phase on Ce-Ti oxides has been shown.
- For the first time, high quality activated carbons based on spent motor oils have been obtained and their potential as carriers of catalysts for methanol decomposition has been studied. Compared to activated carbon obtained from peach stones, activated carbon based on motor oils is characterized by a higher mesoporosity, which provides higher availability of reactants to the deposited metal oxide particles and, as a result, improved catalytic activity.
- It has been proven that the condition of the deposited metal oxide particles can be easily regulated by changes in the precursor and the procedure for obtaining activated carbon, which opens up great opportunities for the synthesis of catalysts with adjustable properties with pronounced economic and environmental effect.

### **Research metrics:**

The scientific results of dissertation of Aleksandra Mileva are summarized in thirteen scientific publications. Six of them are published in international scientific journals with high IF and rank Q1, one manuscript accepted for publication in an edition with the rank Q3, one - in a open-access journal, four publications are in a Bulgarian scientific journal and in a thematic collection (Bulgarian Chemical Communications – 3 pieces; Nanoscience and Nanotechnology – 1 issue), and a publication of a report in full text in a collection of an

international scientific event. In five of the publications Aleksandra Mileva is the first author, which shows her personal contribution. The PhD student participated and presented the results of the dissertation work at seventeen national and eleven international scientific forums, including four abroad. In eighteen of the conference appearances Aleksandra Mileva is the first author, which undoubtedly reveals her active role and participation in the research. On the publications of the dissertation work were noted 30 quotes (without autocitations), which clearly demonstrates the actuality and scientific significance of the published results.

**Critical remarks and recommendations:**

I have no critical remarks on the dissertation work and on the presented materials.

**Conclusion:**

The dissertation of Aleksandra Mileva presents a significant amount of synthetic and analytical work carried out at a high scientific level. The presented results contain original scientific contributions, the main part of which have been published in journals with impact factor and a high rank, published by prestigious international publishers. The dissertation abstract reflects objectively the structure and content of the dissertation work. The presented results cover and exceed the requirements for the award of the scientific and educational degree "Doctor", in accordance with the Law on Development of Academic Staff in the Republic of Bulgaria, the Regulations of BAS for the implementation of this Law and the Rules of IOCCP-BAS.

Based on the above, I give my positive assessment of the dissertation work and I am pleased to recommend to the Honored Scientific Jury to award to Aleksandra Atanasova Mileva the educational and scientific degree "Doctor" in professional field 4.2. "Chemical Sciences", scientific specialty "Petrochemistry and Petrochemical Synthesis".

Date: December 15, 2020

Member of the scientific jury:.....

/Assoc. Prof. Y. Karakirova, PhD/