OPINION

of Prof. DSc.Tanya Stoyanova Tsoncheva, Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences

on a PhD Thesis for awarding the educational and scientific degree "Doctor" in a professional field 4.2. "Chemical Sciences"; Scientific specialty: "Petrochemistry and petrochemical synthesis"

on the topic: "Development of novel metal oxide catalysts with application in alternative energy sources and ecology"

PhD student: Alexandra Atanasova Mileva, Laboratory “Organic Reactions on Microporous Materials”, IOHCF, BAS

Supervisor: Prof. DSc. Tanya Stoyanova Tsoncheva, IOHCF, BAS;

Consultant: Assoc. Prof. Dr. Daniela Paneva, Institute of Catalysis, BAS

The aim of the PhD thesis of Alexandra Mileva is the development of novel, effective catalysts, based on oxides of transition metals, for the decomposition of methanol, with a potential for application as a carrier of hydrogen. The PhD student focuses on the peparation of mesoporous mono- and bi-component metal (Ti-, Ce- and Zr-) containing oxides by using a new and promising technique, such as hydrothermal synthesis in the presence of an organic template. The properties of the obtained materials are compared with those of the materials, obtained by a cheaper and more affordable method, such as homogeneous precipitation with urea. In order to improve the catalytic behavior of the synthesized materials, the PhD student varies the composition and the synthesis conditions, clarifying the role of the nature of the dopants (Ce, Zr) in TiO_2. For the first time, he focuses on elucidating the mechanism of the formation of binary oxides during the various synthetic procedures and its impact on their phase composition and properties. The PhD student makes a significant step in improving the catalytic behavior of materials by modifying them with copper oxide. Again, the emphasis is on comparing the possibilities of different preparation techniques, and along with the traditional method of impregnation, a method of "chemisorption-hydrolysis" is used. The application of the latter in the PhD thesis is a new element in the synthesis of such systems. The differences in the properties of the obtained composites are considered by presenting in detail the mechanism of copper deposition during the different procedures.

A significant part of the PhD student's research is aimed at reducing the price of catalysts by utilizing waste raw materials for their production. An original approach is the use of activated carbon obtained from peach stones, used motor oils and waste polymers. To obtain the catalysts, the doctoral student develops mono- and bi-component metal-based systems. Significant attention is paid to the possibility of ferrites

deposition as an active phase on carbon supports. The role of activated carbon and the reaction medium on their transformation is clarified. The importance of the nature and localization of the metal in the ferrite structure for regulating the catalytic activity of composites is studied. To clarify the influence of the supports on the composition and the availability of the applied active metal phase, the PhD student has selected suitable carbon materials in which the texture or surface functionality is purposefully varied. The conclusions about the role of these factors on different active metal-containing phases as well as the elucidation of the effect of generating additional microporosity in the supports by adding furfural to the raw material, are very significant. The optimization of these factors shows excellent results, as the PhD student achieves the activity of a traditional commercial copper catalyst.

In his thesis the PhD student not only demonstrates a good experimental technique in the preparation of advanced catalysts, but also shows skills to combine different physicochemical methods, including low-temperature nitrogen physisorption, XRD, SEM, HRTEM, spectral methods such as UV-Vis, FTIR, Raman spectroscopies, XPS and Mössbauer spectroscopy, testing the catalysts under reduction or oxididation conditions by TPR in hydrogen and the use of appropriate catalytic tests (ethyl acetate oxidation and methanol decomposition).

Undoubted contribution to the PhD Thesis is the elucidation of the role of CuO crystallites and the facilitated electron transfer in the "conjugated" Ti-Ce-Cu redox centers in the process of decomposition of methanol to syngas, as well as the possibility to control their ratio by changing the method of deposition of the copper phase on the Ti-Ce oxide support. The results on the regulation of the properties of the catalysts supported on activated carbon by changing the raw material and the conditions of activated carbons production also represent a significant contribution with practical importance. The value of the obtained results can be quantified through the large number of publications in prestigious scientific journals, as well as the high citation rate of papers recently published.

As a supervisor of the doctoral student, I am pleased to note his energy, perseverance and responsibility in dealing with the tasks, despite the difficulties and challenges that have arisen personally. I can also note the significant growth of the PhD student not only in application of traditional and new techniques for catalysts production, the use of various physicochemical methods of analysis, precise catalytic experiments, work with literature sources, but also in analyzing the results in order to detailed clarification of the nature of the active centers and the use of this information to optimize the composition of the catalysts.

All this gives me a reason to convincingly recommend to the members of the esteemed Scientific Jury to award the PhD student Alexandra Mileva the educational and scientific degree "Doctor" in professional field 4.2. "Chemical Sciences", the scientific specialty "Petrochemistry and Petrochemical Synthesis".

With respect,

Sofia, 20.11.2020

Prepared the opinion:

/Prof. DSc. Tanya Tsoncheva/