PEER REVIEW

by Prof. Dr. Silviya Zivova Todorova, Institute of Catalysis - BAS

regarding the materials presented by**. Assistant Proff. Dr. Gloria Said Issa-Ivanova** for participation in a competition for the academic position of "associate professor" at **the Institute of Organic Chemistry with the Center for Phytochemistry** BAS by professional field 4.2. Chemical sciences, scientific specialty "Organic Chemistry", for the needs of the lab. "Organic reactions on microporous materials", announced in the Newspaper of State: issue 55 of 07/15/2022.

1. General presentation of the obtained materials.

Dr. Gloria Issa-Ivanova, is the only candidate in the competition for the academic position of "associate professor". The set of materials presented by the candidate is in accordance with the Law for Development of the Academic Staff in the Republic of Bulgaria (LDASRB), Article 24 and Article 36 (3) of the Regulations on the terms and conditions for acquiring scientific degrees and occupying academic positions at IOCCP.

For participation in the competition Dr. Gloria Issa-Ivanova has submitted the necessary documents: curriculum vitae, diplomas for the educational and scientific degree "doctor", reference according to indicator 4 - Habilitation thesis from "group B", according to indicator 7 - Scientific publication in publications that are referenced and indexed in world-renowned scientific databases information (Web of Science and/or Scopus), outside the habilitation thesis), lists of scientific works, citations, copies of scientific works, list of participations in national and international conferences and congresses, list of participations in projects.

2. Biographical data of the applicant.

Dr. Gloria Issa-Ivanova completed her higher education in 2011 at SU. "St. Kliment Ohridski, Faculty of Chemistry and Pharmacy, specialty: "Medicinal chemistry" and in the period 01.2012 - 01.2015 she is a doctoral student at the Institute of Organic Chemistry with the Center for Phytochemistry BAS, lab. "ORMM". In 2015 Gloria Issa defends a dissertation work on the topic "**Catalytic removal of toxic emissions from ethyl acetate using nanoscale multicomponent metal oxide composites** ". After the defense of the thesis, she was appointed as an assistant in the same laboratory, from 2017 until now she is the assistant profof the IOCCP.

Dr. Gloria Issa-Ivanova has specialized for one month (10.2013 – 11.2013) at the Institute of Chemical Technology, UPV-CSIC, Valencia, Spain, within the framework of the competition of "Science and Business" with a project "Preparation and Characterizing multicomponent manganese oxides nanostructured materials with potential applications as catalysts or catalyst supports. From 01.10.2018 to 01.07.2019 she was a postdoctoral specialization in The Faculty of Science, Jan Evangelista Purkyně University , Czech Republic.

1. Evaluation of the scientific research works of the candidate.

Dr. Gloria Issa-Ivanova is the co-author of a total of 46 publications, of which 32 are referenced in WoS or Scopus. The main part of the publications are in the most important journals in the field of materials science and catalysis, such as Catalysis Science and Technology, Reaction Kinetics, Mechanisms and Catalysis, Appl. Catal. A: General, RSC

Advances, Catalysis Today, Microporous and Mesoporous Materials, Journal of Porous Materials.

The publications participating in the competition are divided into two groups, covering indicators B and Г, according to the Regulations on the terms and conditions for acquiring scientific degrees and holding academic positions. In the first group, indicator B - "Habilitation work - scientific publications in publications that are referenced and indexed in world-famous databases with scientific information (WoS or Scopus)", 7 publications are presented (two of them fall into Q1, two into Q2 , two in Q3 and one article with SJR without IF), with the total number of points being 127 points, with a required minimum of 100 points. In four of the submitted publications according to this criterion, Dr. Gloria Issa-Ivanova is the first author and in three of the publications-second.

In the second group, 12 publications are presented (five - Q1, one in Q2, one in Q3, five in Q4), covering indicator Г, with a total of 220. In the group of indicators D, the requirements are significantly exceeded - 70 points are needed, the candidate has 262 items. All citations are in prestigious international journals, which supports the importance and relevance of Dr. Issa 's scientific developments .

Dr. Gloria Issa-Ivanova is a participant in 2 national projects, and she is the head of a project with the National Scientific Fund in a competition for funding fundamental scientific research of young scientists. This shows that Dr. Gloria Issa-Ivanova takes a very responsible approach to the assigned tasks, which makes her a desirable participant in work groups, and she can also organize and lead independent scientific tasks.

The popularization of the scientific results was carried out through oral and poster presentations in a number of national and international scientific forums and is as follows: reports at an international forum – 2, reports at conferences and seminars in our country - 6 nos., posters at international forums -10 pcs., posters at national forums-14 pcs.

4. Scientific contributions

4.1. Habilitation work

The Habilitation work entitled "Development of new nanostructured multicomponent catalysts with application in alternative fuels and ecology" summarizes 7 articles, two of which are categorized in the quartile Q1, two in Q2, two in Q3 and one article with SJR without IF.

The research carried out falls into the field of materials science and catalysis, and the contributions are of a fundamental and scientific-applied nature. The research presented in the habilitation work can be categorized in the following areas:

1. Development of new catalysts and catalitic supports based on nanostructured mesoporous metal oxide composites with predetermined properties to produce new catalysts with potential application in the production of alternative fuels and ecology.

2. Complex characterization of the structural, textural, surface, electronic and oxidation-reduction properties of the materials by using appropriate modern physicochemical methods;

3. Composite materials based on activated carbon obtained from different raw materials.

The obtained materials were used as catalysts for the removal of toxic emissions from volatile organic compounds (ethyl acetate) and decomposition of methanol.

The characteristics and catalytic activities of MnOx obtained by redox reactions of manganese compounds in an aqueous solution, template hydrothermal synthesis and alkaline precipitation with an aqueous ammonia solution. Hydrolysis of bis (4- nitrophenyl) phosphate (BNPP) and decomposition of methanol were used as test reactions. The results show a strong dependence of the catalytic properties of the materials on the synthesis method. It was found

that the ratio of redox-active $Mn^{4+}/Mn^{3+}/Mn^{2+}$ surface species and the high ratio of oxygen species (such as O^{2-} or O^{-}), together with the dispersity and morphology of the particles, were important factors for the high catalytic activity of MnOx in both investigated catalytic reactions. It has been shown that the catalytic hydrolysis of BNPP is favored by the presence of a higher concentration of Mn^{4+} ions and therefore a larger amount of lattice oxygen particles (O^{2-}), which act as strong nucleophilic agents. The presence of manganese in the lower oxidation states (Mn^{2+}, Mn^{3+}), on the surface of the catalyst, favors the formation of oxygen vacancies and the formation of new active centers for further degradation of BNPP. It was found that the decomposition mechanism of methanol on the MnOx surface mainly depends on the interaction strength between the methanol molecule and manganese oxides and the changes in lattice parameters during $Mn^{4+}/Mn^{3+}/Mn^{2+}$ transformations, as well as from variations in acidic properties due to the generation of oxygen vacancies in the oxide lattice.

The properties of mono- and bicomponent Ce-Mn oxide materials obtained by co-precipitation (CP) and templated hydrothermal synthesis (HT) over a wide range of composition **[publication 3]** are compared. It has been shown that bi-component Ce-Mn oxide catalysts obtained by various synthesis techniques are not a mechanical mixture of the individual oxides. The data from the series of physicochemical analyzes clearly shows a significant increase in the dispersity of MnxOy particles, changes in the oxidation state of Mn, as well as the formation of Ce-O-Mn bonds, in which the mobility of oxygen is facilitated. These effects are more pronounced for CP materials due to the formation of a more homogeneous and finely dispersed manganese oxide phase. It has also been shown that, in both synthesis techniques, the obtained Ce-Mn oxides present a complex core-shell structure, where the finely dispersed cerium particles are stabilized on the "core" of MnxOy crystallites. An important role for the stabilization of the "core-shell" structure is played by the interface layer, where manganese ions in different oxidation states are isomorphically substituted in the cerium oxide crystal lattice with the simultaneous formation of oxygen defects. The preparation procedure and the Mn / Ce ratio were found to be powerful approaches to tune the microstructure of these materials.

The influence of a preparation method on the properties of Sn-Ti binary oxides was investigated. It was established that the structural, textural, oxidation-reduction and catalytic properties of SnO_2-TiO_2 oxides can be successfully controlled by varying the Sn/Ti ratio and the preparation method used **[4]**. Hydrothermal synthesis has been shown to provide the formation of highly defective rutile solid solutions with improved dispersity and higher specific surface area, but reduced Lewis acidity and oxygen mobility compared to individual oxides. These characteristics provide a decrease in the specific catalytic activity and significant changes in the selectivity of the products during the decomposition of methanol and the oxidation of ethyl acetate . A mechanism of formation of mixed oxides from the corresponding chlorides is proposed.

The relationship between the phase composition, the structure, the morphology and the catalytic activity of deposited copper oxide on titanium-zirconium mixed oxides obtained by means of a new preparation procedure - "chemosorption- hydrolysis" was investigated. Compared to the conventional impregnation technique, this synthesis approach leads to the formation of more uniform and homogeneously dispersed copper oxide crystals in the mesoporous TiO_2 –ZrO_2 matrix, which provides higher catalytic activity. All ternary composites show very high catalytic activity in the complete oxidation of ethyl acetate. The specific behavior of catalysts in the decomposition of methanol is related to irreversible phase transformations under the influence of the reaction medium.

For the first time, activated carbons were obtained from used motor oil and various plastic residues, such as high-density polyethylene or thermoplastic phenol -formaldehyde

resins **[Publication 2].** It was found that the type of plastic residues greatly affects the pore texture of the resulting carbon materials, but the effect on their surface functionality is very weak. For the first time, data on the application of these activated carbons as carriers of iron and chromium oxides and the application of the obtained composites as catalysts for methanol decomposition have been published. It was found that the addition of high-density polyethylene to used motor oil provides the formation of activated carbon with well-developed mesoporosity, which promotes the stabilization of finely dispersed, well-accessible and highly active in the decomposition of methanol Fe-Cr mixed oxides **[2]**. Additionally, iron and chromium oxides deposited on SiO_2 were investigated. Equimolar Fe/Cr content was found to facilitate the formation of more homogeneous and finely dispersed materials. They demonstrate extremely high catalytic activity and stability to CO in a methanol decomposition reaction over a wide temperature range **[17]** .

4.2. Other publications

In this part, criteria Г - Scientific publication in publications that are referenced and indexed in world-renowned databases with scientific information (Web of Science and/or Scopus), outside of the habilitation work, 12 publications are presented. They are as follows: five- Q1, one in Q2, one in Q3, five in Q4 The total number of points is 220 points, which meets the requirements.

The publications included here continue the subject mentioned in the habilitation thesis and refer to the development of nanostructured metal oxide composites, as active components or catalyst carriers for important reactions in the field of environmental protection and renewable fuels. As the synthesis of new materials is always related to their complex characterization in order to find a correlation between structure and catalytic activity.

The following can be mentioned as some of the main achievements:

1. CeO_2 -TiO_2 and ZrO_2 -TiO_2 with different ratios of Ce/Ti and Zr/Ti obtained by different methods were studied in detail.

It was established that the possibilities for isomorphic substitution of Ce and Zr ions in the crystal lattice of TiO_2 significantly affect not only the dispersion and structure of the obtained materials, but also lead to the occurrence of a large number of defects on the surface, which significantly change the oxidation-reduction and its acid-base properties

1.1. The CeO_2-TiO_2 samples obtained by template hydrothermal synthesis (HT) **[1, 8, 11 from a list of scientific publications** participating in the competition by group of indicators "H"] and homogeneous precipitation with urea (U) **[11]** , in which the composition is varied widely are compared. It was found that, compared to the homogeneous precipitation with urea, the hydrothermal method leads to the formation of more homogeneous materials with improved dispersion and developed mesoporosity, but their higher degree of defectis changes their acid-base properties, which causes lower catalytic activity and selectivity in complete oxidation of ethyl acetate and decomposition of methanol. It has been shown that the structural, reduction and catalytic characteristics of the obtained composites can be controlled by varying the Ce/Ti ratio, the hydrothermal treatment temperature and the preparation method. They are strongly related to the microstructural features of the samples. It was found that the relatively low Ce/Ti ratio facilitates the stabilization of highly dispersed CeO_2 particles on the oxygen vacancies in TiO_2. This results in high specific surface area and pore volume combined with Lewis acidity and high oxygen mobility. As a result, a significant increase in catalytic activity and selectivity is achieved in complete oxidation of ethyl acetate and decomposition of methanol to synthesis gas. The high Ce/Ti ratio in bicomponent materials facilitates the formation of larger CeO_2 crystallites doped with Ti^{4+}. As a result, the textural parameters deteriorate, the increase in the density of Lewis acid centers is promoted, and the amount of Ti^{3+}-Ti^{4+} and Ce^{3+}-Ce^{4+} decreases· the redox couples. As a result, the

catalytic activity is reduced with a simultaneous increase in the selectivity to ethanol during the hydrolysis of the ethyl acetate molecule and to methane during the decomposition of methanol . It has been shown that increasing the temperature of the hydrothermal synthesis facilitates the formation of larger particles of the individual oxides, which makes it difficult for them to come into close contact.

2. Nanostructured mesoporous bicomponent ZrO_2 -TiO_2 with different Zr/Ti ratio were obtained by means of the hydrothermal method using a structure-directing agent and homogeneous precipitation **[2, 12**]. At a low Zr/Ti ratio**,** Zr^{4+} is incorporated into the TiO_2 lattice and facilitates the crystallization of large anatase particles in the samples. In the samples with a high zirconium content, a finely dispersed tetragonal ZrO_2 phase is stabilized. For materials with an equimolar ratio, an amorphous $Zr_x Ti_1$ -xO_2 solid solution dominates.

3. It has been shown that when copper oxide was deposited on hydrothermally synthesized ZrO_2 -TiO_2 and CeO_2 -TiO_2 composites, materials with extremely high catalytic activity are obtained, which is associated with both the improved textural characteristics and the specific interaction of the copper particles with the carrier. The application of the "chemosorption-hydrolysis " technique ensures a fine dispersion of the copper-oxide particles, which favors the catalytic activity at lower temperatures, but the rapid reduction transformations with the copper particles under the influence of the reaction medium ensure rapid changes in the catalytic behavior of the composites .

Conclusion

The scientific research of **Dr. Gloria Issa-Ivanova** fully correspond to the subject matter of the announced competition for awarding the academic position "Associate Professor". The publication activity and the citations on the published results prove that **dr Gloria Issa-Ivanova** fully covers and exceeds all requirements in the Law on the Development of the Academic Staff and the Rules for the Terms and Conditions for the Acquisition of Scientific Degrees and the Occupancy of Academic Positions at **the Institute of Organic Chemistry with the Center for Phytochemistry**, BAS. Therefore, I strongly recommend to the members of the esteemed scientific jury and the esteemed Scientific Council of IOCCP-BAS, to award **Dr. Issa** the academic position " **Associate Professor** " in professional direction 4.2 "Chemical Sciences" and scientific specialty "Organic Chemistry".

Sofia , 17.11.2022

Signature:
/Prof. Dr. Silvia Todorova/