REVIEW

for a competition for the academic position "Associate Professor" in the Institute of Organic Chemistry with Centre of Phytochemistry at the Bulgarian Academy of Sciences in professional direction: 4.2.Chemical Sciences, scientific specialty: "Organic Chemistry", announced in the "State Gazette", issue 55 of 15.07.2022.

Candidate (only one): Assistant Professor Dr. Gloria Said Issa-Ivanova
Reviewer: Prof. Margarita Popova, DSc, Institute of Organic Chemistry with Centre of Phytochemistry - Bulgarian Academy of Sciences (IOCCP-BAS); member of a scientific jury, appointed by order РД-09-118 of 02.08.2022 of the Director of IOCCP-BAS

Dr. Gloria Issa has submitted all the necessary documents, according to the Act for the Development of the Academic Staff in the Republic of Bulgaria (ADASRB), the Regulations for the implementation of the ADASRB, the Regulations for the terms and conditions for acquiring academic degrees and occupying academic positions of the Bulgarian Academy of Sciences and the Regulations for the terms and conditions for acquiring academic degrees and occupying academic positions of the IOCCP-BAS, related to the procedure for occupying the academic position “Associate Professor”.

I. Personal and professional data of the applicant

In 2012, after winning a competition, Gloria Issa was enrolled as a full-time doctoral student at IOCCP-BAS. In 2016, she defended her doctoral dissertation on the topic: Catalytic removal of toxic emissions from ethyl acetate using nano-sized multicomponent metal oxide composites, for which she was awarded the educational and scientific degree "Doctor" in professional field 4.2. "Chemical Sciences", scientific specialty Organic Chemistry. Since 2015, she has been appointed to the position of Assistant, and since 2017, she has been a Assistant Professor at IOCCP-BAS.
She has gone on two specializations abroad. In 2013, she did a two-month specialization at the Institute of Chemical Technology, UPV-CSIC, Valencia, Spain, and in the period 01.10.2018 - 01.07.2019 she did a specilaization at the Faculty of Science, Jan Evangelista Purkyně University, Czech Republic.

II. General characteristics of the scientific and scientific-applied activities

Dr. Issa's papers for the period 2013-2022 according to the Scopus database are 32. Dr. Issa has submitted for the competition a list of 19 papers that are beyond those included in the thesis and are distributed by quartiles of journals according to Scopus/WoS as follows: 7 in Q1

journals, 3 in Q2 journals, 2 in Q3 journals, 6 in Q4 journals and 1 in journal with SJR. Dr. Issa's results have been published in reputable journals with a high impact factor, such as *Journal of Environmental Chemical Engineering (IF=7.32), Catalysis Today (IF-6.77), Applied Catalysis A, General (IF=5.77), Applied Surface Science (IF=6.60), Catalysis Science & Technology (IF=6.18), Microporous and Mesoporous Materials (IF=5.55),* etc.

According to indicator **C**, Dr. Issa participates with 7 papers in journals with rank Q1 – 2 papers; Q2 – 2 papers , Q3 – 1 paper; Q4 – 1 paper and 1 paper in a journal without IF, but with SJR. According to the **D** indicator, Dr. Issa participates with 12 papers, distributed as follows: 5 papers in journals with rank Q1, 1 paper in a journal with rank Q2, 1 paper in a journal with rank Q3 and 5 papers and in journals with rank Q4. Dr. Issa 's personal contribution to the scientific papers presented at the competition is indisputable. She is the first author and corresponding author in 4 papers under indicator **C** and in 3 of the papers under indicator **D**. Dr. Issa’s total number of points according to indicator **C** is 127 points, and according to indicator **D** – 220 points.

The presented list of noticed citations of Dr. Issa's papers shows that they have found a good response among the scientific community. The observed Scopus citations on all scientific papers are 201. In the contest, a list of 131 citations or 262 items according to indicator **E** is presented. The candidate's Hirsch index (**h**) is 8 (Scopus) and it exceeds the required minimum of h index 5, according to the Regulations for the terms and conditions for acquiring scientific degrees and holding academic positions at IOCCP-BAS.

Dr. Issa 's scientific results have been reported with 32 presentations at national and international scientific forums, which include 12 oral presentations.

Dr. Issa participated in the implementation of 10 scientific projects and was the leader of 2 projects financed by the Bulgarian National Science Fund and one project financed by the Ministry of Education and Science. Dr. Issa also participated in a project to build a Center of Excellence "Mechatronics and Clean Technologies" under priority axis 1 "Scientific Research and Technological Development" of the Operational Program "Science and Education for Smart Growth", 2018-2023.

The presented summary report on the fulfillment of the national requirements has the following distribution by indicators: indicator **A** - 50 points; indicator **C** - 127 points (required 100 points); indicator **D** - 220 points (required 220 points); indicator **E** - 262 points (required 70 points); and a **h** index of 8, with a required 5. The data show that the candidate's contributions fully cover the national requirements and the requirements in the Law on the Development of Academic Staff in the Republic of Bulgaria (DASRB), Regulations for implementation of DASRB, Regulations for implementation of DASRB of BAS and Regulations of IOCCP-BAS for the academic position of associate professor.

III. Major scientific contributions

Dr. Issa's scientific research is related to the development of new nanostructured catalysts based on mono-, bi- and three-component metal oxide composites, as well as mono- and bi-component metal oxide nanoparticles supported on porous carbon materials obtained from waste raw materials. An approach is proposed to control the catalytic properties of multicomponent metal oxide systems by applying appropriate methods for their preparation, such as hydrothermal synthesis, impregnation method, "chemisorption-hydrolysis" method and by changing the ratio of individual components. Systems with a mesoporous structure with a high specific surface area and pores with a defined size and shape have been obtained, which allow controlling their oxidation-reduction and acid-base properties and, therefore, allow optimizing their catalytic properties in environmentally oriented reactions.

The research carried out is of a fundamental and scientific-applied nature and can be summarized in the following main directions:

- Development of new and effective approaches for obtaining nanostructured mesoporous oxide materials, as well as mono- and bi-component metal oxide particles applied to porous carbon materials obtained from waste raw materials with predetermined textural and surface properties;
- Development of new and effective catalysts for the removal of toxic emissions from volatile organic compounds (ethyl acetate) through catalytic oxidation;
- Development of new and efficient catalysts for the conversion of methanol (from both renewable and waste feedstock) to produce hydrogen used as an alternative fuel.

The following significant results were obtained:

- MnOx catalysts were developed by hydrothermal synthesis and alkaline precipitation with aqueous ammonia solution**,** which showed high activity in methanol decomposition reactions to synthesis gas and bis(4-nitrophenyl) phosphate hydrolysis. The different ratios of $Mn^{2+}/Mn^{3+}/Mn^{4+}$ surface redox centers with high dispersity and appropriate morphology were found to have a decisive influence on the catalytic activity of MnOx in the catalytic degradation of both compounds. Assumptions have been made about the role of active centers in catalytic processes **[paper 1]**.
- Nanostructured Ce-Mn mixed oxides, as well as CeO_2 and/or TiO_2 oxides with a high specific surface area and a well-developed mesoporous structure were obtained by means of co-precipitation and hydrothermal synthesis in the presence of an organic template. The relationship between the phase composition, textural, structural, surface and redox properties of the binary Ce-Mn oxides and their catalytic behavior in the complete oxidation of ethyl acetate was established **[papers 2 and 3]**. It was shown that the structural, reduction and catalytic characteristics of the obtained CeO_2/TiO_2 composites can be controlled by varying the Ce/Ti ratio, the hydrothermal treatment temperature and the preparation method. It was found that the

relatively low Ce/Ti ratio favors the stabilization of highly dispersed CeO_2 particles on the oxygen vacancies in TiO_2, which provides high specific surface area and pore volume combined with Lewis acidity and high oxygen mobility. As a result of the optimal characteristics of the catalysts, a significant increase in catalytic activity and selectivity is achieved in complete oxidation of ethyl acetate and decomposition of methanol to synthesis gas **[papers 4-6]**.

- Hydrothermal treatment methods in the presence of a template and homogeneous precipitation with urea are suitable techniques for obtaining ZrO_2 -TiO_2 mixed oxides. It was found that the incorporation of Zr^{4+} into the TiO_2 lattice facilitates the crystallization of large anatase particles in the samples with a small Zr/Ti ratio, the stabilization of a finely dispersed tetragonal ZrO_2 phase in the samples with a high zirconium content and the dominance of amorphous ZrxTi1-xO_2 solid solution in the equimolar ratio materials. The slow release of ammonia during urea precipitation results in a more homogeneous incorporation of Zr^{4+} ions into the initially precipitated TixOy(OH)z gel, resulting in more highly dispersed samples. When using the hydrothermal method, materials with higher crystallinity and a well-defined mesoporous texture are obtained, which can be controlled by the Zr/Ti ratio and the temperature of the hydrothermal synthesis. It was found for the first time that the increase in the catalytic activity of the bicomponent materials in the complete oxidation of ethyl acetate and the decomposition of methanol is related to the improvement of their textural characteristics **[paper 7]**.
- The isomorphic substitution of Ce and Zr ions in the crystal lattice of TiO_2 significantly affects not only the dispersion and structure of the obtained materials, but also leads to the occurrence of a large amount of defects on the surface, which significantly change the oxidation-reduction and acid-base properties of the catalysts **[paper 8]**. It was found that the structural, textural, redox and catalytic properties of SnO_2 -TiO_2 oxides can be successfully controlled by varying the Sn/Ti ratio and the preparation method used. The hydrothermal technique was shown to lead to the formation of highly defective TiO_2 with high dispersity and specific surface area, but reduced Lewis acidity and oxygen mobility compared to individual oxides. These characteristics provide a reduction 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 **[paper 9]**.
- By thermal hydrolysis of titanium peroxo-complexes in aqueous solution catalysts with high catalytic activity for the degradation of chemical warfare compounds: P- and S-containing agents (dimethyl methyl phosphonate, 2-chloroethyl ethyl sulfide and 2-chloroethyl phenyl sulfide), were obtained **[paper 10]**.
- Three-component composites were obtained by hydrothermal synthesis of the bi-component Ce-Ti-oxide supports and modified with copper oxide, which were studied in methanol decomposition reaction and complete oxidation of ethyl acetate**.** For the first time, the "chemosorption-hydrolysis" technique was used to deposit the copper oxide phase on the Ce-Ti oxide carriers. It was shown that the catalytic properties of these materials are

determined by the activity of CuO crystallites and are due to a facilitated electronic transition in Ti-Ce-Cu redox centers in the interface layer **[papers 11 and 12]**.

- The state of deposited CuO particles in binary ZrO_2–TiO_2 oxides with different Zr/Ti ratios obtained by "chemosorption-hydrolysis" and "wet impregnation" method was investigated. Compared to the traditional impregnation procedure, the new chemisorption-hydrolysis approach of depositing CuO particles was shown to provide the formation of more uniform, finely dispersed and easily reducible copper oxide particles, which generally leads to improved catalytic behavior in decomposition of methanol and total oxidation of ethyl acetate. All the three-component composites showed superior catalytic activity in the complete oxidation of ethyl acetate **[paper 13]**.
- Cu-Ce-Ti and Cu-Zr-Ti composites obtained by "chemosorption-hydrolysis" and "wet impregnation" method and characterized by high dispersity, improved specific surface area and pore volume, and high reducibility due to the facile electron transfer in the Cu-Zr(Ce)-Ti "interface layer", were developed **[paper 14]**.
- A Hf(IV)-modified cobalt ferrite was obtained using the sol-gel method, which was investigated as a catalyst in the complete oxidation reaction of ethyl acetate. It was proven that increasing the content of Hf (IV) in the samples leads to its inclusion in the crystal lattice of ferrite, a decrease in the average size of the crystals and an increase in the microdeformation in the lattice of the crystal structure **[paper 15]**.
- For the first time, data were published on the application of the activated carbons obtained from used motor oil and various plastic residues, such as high-density polyethylene or thermoplastic phenol-formaldehyde resins as a matrix of iron and chromium oxides and the use of the obtaines composites as catalysts for the decomposition of methanol. The addition of high-density polyethylene to used motor oil was found to provide the formation of activated carbon with well-developed mesoporosity, which favors the stabilization of finely dispersed, accessible and highly active in methanol decomposition Fe-Cr mixed oxides **[paper 16]**. It was found that the equimolar content of Fe/Cr on SiO_2 facilitates the formation of more homogeneous and finely dispersed materials, which are characterized by extremely high catalytic activity and stability to CO in a methanol decomposition reaction over a wide temperature range **[paper 17]**.
- Catalysts based on $Ni0.5Cu0.5Fe_2O_4$ and $Ni0.5Zn0.5Fe_2O_4$ supported on nanoporous activated carbons obtained from peach pits and low-rank coal pyrolysis by-products were obtained for methanol decomposition with potential application in hydrogen production. The active phase in the obtained carbon composites was found to be a mixture of finely dispersed ferrites, substituted magnetite, metals (Cu, Fe, FeNi alloy) and ZnO, which depend on the textural characteristics of the carbon support. It was found that the higher mesoporosity of the carbon matrix leads to the formation of more finely dispersed and easily reducible spinel particles, which are characterized by higher activity, but are deactivated more quickly. By varying the sources to get the activated carbon and the type of precursor the properties of the catalysts can be optimized **[paper 18]**.

- $ZnFe_2O_4$, $CuFe_2O_4$ and $MnFe_2O_4$ ferrites deposited on peach pit activated carbon and KIT-6 mesoporous silica were developed. Activated carbon obtained from agricultural residues (peach pits) was found to be a suitable matrix for the stabilization of finely dispersed ferrite nanoparticles, which depends on the textural characteristics and reduction properties of the carbon carrier. It was proven that catalysts containing $ZnFe_2O_4$ are highly active for the decomposition of methanol **[paper 19]**.

The candidate's intentions for future scientific development are also presented and include new scientific topics, such as obtaining highly efficient adsorbents and catalysts based on nanostructured oxides, zeolites and modified mesoporous silicas for capture and hydrogenation of CO_2 to methane/methanol. The search for opportunities to apply for national and international research funding programs is also indicated.

IV. Critical notes, opinion and recommendations

I have some minor technical notes. The h index given is unadjusted for co-authors, which is more of an oversight because after the adjustment, her h index is 8, which exceeds the requirement h=5 for occupying the academic position of associate professor, according to the Regulations on the terms and conditions for acquiring scientific degrees and occupying academic positions at IOCCP-BAS. Her participation in a project to build a Center of Excellence "Mechatronics and Clean Technologies" was not noted. These critical remarks do not affect the overall very good impression of the candidate's presented materials and scientific results.
I know the candidate as a very responsible and motivated young colleague with very good skills for working in a team. I would also like to note the active work in the implementation and management of scientific research projects, in which Dr. Issa has shown responsibility and great activity not only in terms of scientific tasks, but also in the administration of scientific projects.

V. CONCLUSION

The documents and materials submitted by Assistant Professor Dr. Gloria Said Issa-Ivanova for participation in this competition show that she is a well-built and experienced researcher with her own approach to setting and performing scientific tasks. After analysis of the obtained scientific results, the topicality and perspective of the researched topics, the intentions for future research and the personal qualities of the candidate, I believe that she fully meets all the requirements of the Act for the Development of the Academic Staff in the Republic of Bulgaria (ADASRB), the Regulations for the implementation of the ADASRB, the Regulations for the terms and conditions for acquiring academic degrees and occupying academic positions of the Bulgarian Academy of Sciences and the Regulations for the terms and conditions for acquiring

academic degrees and occupying academic positions of the IOCCP-BAS, related to the procedure for occupying the academic position “Associate Professor”. Based on the above I strongly recommend the Scientific Council of the IOCCP at the BAS to award assistant Dr. Gloria Said Issa-Ivanova the academic position "Associate Professor" in professional direction 4.2.Chemical Sciences, scientific specialty "Organic Chemistry".

Sofia, 16.11.2022 Signature:

/Prof. DSc Margarita Popova/