REVIEW

on the competition for occupying the academic position "**Associate Professor"** in a professional field 4.2. Chemical Sciences, specialty "Solid State Chemistry" for the needs of the Faculty of Chemistry and Pharmacy at Sofia University "St. Kliment Ohridski" (FCP-SU), announced in State gazette, issue 65 of 28.07.2023.

Candidate: *Assist. Prof. Dr. Vesselina Tocheva Rangelova, FCP-SU*

Reviewer: *Prof. Dr. Violeta Georgieva Koleva, Institute of General and Inorganic Chemistry at Bulgarian Academy of Sciences, member of the Scientific Jury, appointed by Order No. RD-38-526/01.09.2023 of the Rector of SU*

1. General description of the materials presented

The only candidate in the present competition is Assistant Professor Dr. Vesselina Tocheva Rangelova from the Department of Applied inorganic Chemistry at FCP-SU. Dr. V. Rangelova has presented all the documents required and specified by the Act on Development of the Academic Staff in the Republic of Bulgaria (ADASRB), the Regulations for its application and the Terms and Rules for acquiring academic degrees and occupying academic positions at the Sofia University for the professional field "Chemical Sciences". The materials in the competition include all the needed lists of scientific indicators (papers, citations, participation in projects, information about training activities, copies of papers)

2. Brief biographical data of the applicant

Vesselina Rangelova graduated from the Faculty of Chemistry of SU "St. Kliment Ohridski" in 1996 as a Master in Chemistry, majoring in "High purity substances and materials based on them". Subsequently, she was a PhD student in the same Faculty, Department of Applied Inorganic Chemistry, and since 2003 she has successively held the academic positions of Assistant Professor and Chief Assistant Professor (2005). In 2003 she defended a PhD thesis entitled "Amorphous and nanocrystalline alloys for hydrogen storage" in the same Department. The candidate has a long-term training experience, starting in 1999 when, as a PhD student, she began teaching practice with students. Currently, she is lecturer of several courses and leads practices in a number of disciplines.

3. General characteristics of the candidate's scientific and training activity

The candidate's scientific activity includes 18 published papers (since 1999 to the present), one paper accepted for publishing and one monograph already published (accepted for publishing on the date of documents submission). The papers in journals with impact factors are 16, two are in journals without impact factor and one work is in conference proceeding. Three of the publications (№ 15, 16, 17) are included in her PhD thesis. A list of a total of 149 independent citations (without self-citations of all authors) on 10 articles of the candidate is presented which proves the interest in the conducted research. It should be mentioned that 101 citations refer to one article from the PhD thesis (№ 16), of which 93 were noticed after obtaining the "Doctor" degree (after 2005), so the reviewer acknowledges 141 citations from the list. According to the Scopus database, the candidate's total number of citations is 175 (to date 6.11.2023), of which 165 after 2005. The candidate's Hirsch index (H) according to Scopus, based on all publications, is 5 (without self-citations of all authors) and it meets the recommendation criteria of FCP-SU.

In the current competition, Dr. V. Rangelova participates with one monograph, presented as a habilitation work, and 14 scientific publications (13 published and one accepted for publishing), which I accept to review. The competitive publications do not include those used to acquire the degree "Doctor". The high scientific level of the publications is confirmed by their distribution by quartiles of the journal in which they were published. A half of the publications (50%) are with Q1 and Q2 quartile (3 articles with Q1 and 4 with Q2) and 5 are with Q3. A large part of the articles are in reputable journals in the field of materials science such as *Journal of Alloys and Compounds, Journal of Thermal Analysis and Calorimetry, Scripta Materialia, Materials Letters, Materials, Journal of Nanomaterials, International Journal of Elecrochemical Science, etc.*

A positive assessment of the scientific community abroad for the obtained results are the 48 citations noticed on 9 of the competition articles. All publications are a collective work with authors from FCP, BAS and scientists from abroad and the papers having up to 4-5 authors are predominant. In two of the publications Dr. Rangelova is the first author, and in six – the second author, which testifies to the substantial personal contribution of the candidate in the joint research. The candidate's scientific publications correspond in number and quality to the topic of the competition.

Dr. Rangelova participates in 10 projects, of which 8 are research projects and two are educational ones. The applicant is leader of 3 of the research projects.

Dr. Rangelova has considerable long-term teaching and learning experience (more than 20 years). Since the academic year 2015/2016, without interruption until now, she has been a lecturer of 3 courses "Chemical Technologies - I" for the bachelor's specialty "Chemistry" for full-time and part-time studies, as well as "Chemical Technologies" for the bachelor's specialty "Engineering Chemistry and Modern Materials", full-time study (total 82.5 hours of lectures). Moreover, she has been a lecturer for several years of the courses "Materials Science" and "Modern Chemical Technologies and Emissions Control" for the specialty "Ecochemistry" (Bachelors), as well as of the course "Metallography" for the Master's program Archeometry (lectures and practice). In addition, the candidate has developed one new course in 2014 "Technology of water, air and soil purification" (30 hours of lectures and 15 hours of practice) for the specialty "Ecochemistry", Master's program "Ecochemistry" (currently inactive). She led practice with students in a number of disciplines. Since 2017, she has been the organizer and leader of the educational and production practice for students from several majors. Dr. Rangelova is also supervisor of 3 Diploma theses. She is a co-author of a textbook on "Chemistry and Environmental Protection" for the 10^{th} grade (published in 2019) and a study aid to the same textbook (published in 2019). All this reflects significant contribution of Dr. Rangelova to the of chemistry education.

4. Compliance with the requirements for occupying the academic position “Associate Professor”

Dr. V. Rangelova meets the requirements for occupying the academic position "Associate Professor" in FCP-SU, according to the Act on Development of the Academic Staff in the Republic of Bulgaria, as well as the recommendation criteria of the Faculty of Chemistry and Pharmacy-SU for the professional field “Chemical Sciences”.

- According to the Nacional Center for Information and Documentation (NACID) ((https://ras.nacid.bg/dissertation-preview/25961) Vesselina Rangelova has acquired a “Doctor”

degree *(Diploma № 28986/23.04.2004)* and academic position “Chief Assistant Professor” in the professional field 4.2. Chemical Sciences;

- According to the data in NACID and from the presented certificate, Dr. V. Rangelova was appointed to the academic position of "Assistant Professor" at FCP-SU on 14.11.2003, and on 20.09.2005 as "Chief Assistant Professor, so she has almost 20 years of experience as an Assistant Professor;

- The publications and citations submitted for the competition do not repeat the ones submitted for the degree “Doctor”;

- Chief Assistant Professor Dr. Veselina Rangelova, fulfills the minimum national requirements and the recommendation criteria of the FCP-SU for occupying the academic position "Associate Professor" in direction 4.2. Chemical Sciences. According to indicator "B", a monograph is presented and the required 100 points are achieved. According to indicator "G", 230 points are achieved (220 required). According to indicator "D", the reviewer accepts 141 citations from the list, noticed after acquisition "Doctor" degree (after 2005), i.e. 282 points, which is significantly more than the required 70 points. According to an additional indicator of FCP-SU "J", where 70 points are required, the candidate has achieved 145 points (the reviewer reduced the points by 10, since two of the projects are not scientific, but educational). In total, for all groups of indicators, Dr. V. Rangelova has achieved 757 points, which exceeds the required minimum of 510 points.

- The professional qualification and the thematic scope of the scientific activity of Assist. Prof. V. Rangelova fully correspond to the specialty of the announced competition in professional field 4.2. Chemical Sciences;

- There is no evidence of plagiarism in the scientific works submitted to the competition.

5. Main scientific achievements

5.1. Achievements in the frame of the Habilitation work

The habilitation work is represented by a monograph in Bulgarian, printed by the University Publishing House "St. Kliment Ohridski" (Sofia, 2023). The monograph is entitled “MOFS. Storage of gases in porous materials" in a volume of 126 pages, contains 5 figures and summarizes information from 282 references, the majority of which are after the year 2000. The reviewer of this scientific work is Prof. Dr. Georgi Tsvetkov, but to me this is unethical only due to the fact that he is a co-author in two of the candidate's publications in the competition.

The focus of this scientific work is on metal organic frameworks (MOFs) as a relatively new class of materials with unique sorption properties and great prospect for environmental, energy and other applications. Specifically, Dr. Rangelova's monograph reviews the achievements, issues and progress in the use and design of MOFs for gas storage and separation with emphasis on hydrogen and carbon dioxide sorption, discusses the relationship between the structure and performance of MOFs with a view to optimizing their properties. The theme of the storage of both gases, the hydrogen as a clean source of energy with zero harmful emissions, considered as the fuel of the future, and carbon dioxide, whose progressively increasing levels in the atmosphere seriously threaten the ecological balance of the planet, is of extreme importance worldwide and a great challenge for scientists. The continuous search for effective and economical "green" solutions for their storage, including the design of new MOFs compositions and structures with improved functional properties, defines the topic of this work as important and significant.

The monograph is structured in three main sections dedicated to solid-state gas storage, hydrogen storage and carbon dioxide storage in MOFs. Hydrogen technologies, methods and materials for hydrogen storage are reviewed. Some fundamental thermodynamic and kinetic aspects of gas storage in solid media, separation and purification of gas mixtures are presented. The unique properties of MOFs determining their prospects for various applications are reviewed. The entire chain from synthesis of MOFs, their modification and optimization with a view to improving the hydrogen sorption characteristics, through the factors and mechanisms of hydrogen storage, to the methods for characterizing hydrogen sorption in MOFs, is presented in detail. An important emphasis of the monograph is on guidance on possible strategies in the design of MOFs to achieve maximum hydrogen storage capacity through the use of unsaturated coordination sites on the metal ions, short-chain ligands, crystal size control, optimization of the porosity, volume and pore structure, impregnation, etc.

Relatively less attention in the monograph is devoted to the capture and storage of carbon dioxide which is of ecological importance. Conventional materials for CO_2 capture and storage such as aqueous solutions of amines and solid adsorbents (zeolites, aluminosilicate porous materials, activated carbons) are described. Diffraction and spectroscopic methods are reviewed, providing information on the localization and preferred sites for CO_2 adsorption in the adsorbent structure, thus contributing to the improvement of strategies for design and synthesis of suitable sorbents. MOFs with nitrogen-containing ligands have been shown to exhibit high selectivity in the separation of CO_2/N_2 mixtures from fuel combustion.

In conclusion, Dr. V. Rangelova's monograph, dealing with current problems of energy and environmental significance, has scientific and practical contribution to the field of materials science. At the same time, I believe that the inclusion of more illustrative material, which is available in the large number of cited references (of course, after permission for use from the publishers), would make the monograph even more attractive and fascinating for students and PhD students.

5.2. Achievements in the papers from group "G"

The publications included in group "G" are 14 in number and they include fundamental studies mainly in two thematic areas: (1) Preparation and complex characterization of metal alloys with application for hydrogen storage (the predominant part of the articles); (2) Catalytic decomposition of ammonium perchlorate (3 papers). The studies in both directions follow the classical approach, from synthesis, *via* characterization, to material properties. The contributions of these studies have a scientific and scientific-applied nature and can be summarized as follows:

Materials for hydrogen storage

- Original methods and techniques for the synthesis of hydrogen storage alloys (such as ultrafast melt quenching, reactive mechanical alloying, etc.) as well as suitable and reliable methods for structural, morphological, microstructural and thermal characterization have been applied. The hydrogen sorption has been studied both from hydrogen gas phase and under electrochemical conditions. The relationship between the structure and microstructure of the alloys and their hydriding/dehydriding capacity and kinetics has been examined;

- Both electrochemical hydriding/dehydriding processes and these from gas phase have been studied on a series of $LaNi_5$-based alloys with incorporated metals such as Co, Al and Sn. The highest hydrogen absorption capacity is found for the $LaNi_{4.3}Co_{0.4}Al_{0.3}$ alloy, while $LaNi_{4.8}Sn_{0.2}$

showed the best cycling stability. A good agreement has been observed between hydrogen sorption kinetics from gas phase and by electrochemical way;

- It is shown that a small difference in the concentration of the Al additive in the composition of the $LaNi_{5-x}Al_x$ alloy has a significant effect on the hydrogen capacity and electrochemical cycling stability without measurable changes in the crystal lattice parameters. A higher capacity is achieved at the lower Al concentration, which is consistent with the higher diffusion coefficient.

- Hydrogen-induced decrepitation has been successfully applied to improve the hydrogen sorption kinetics of $MmNi_5$ mainly due to particle size reduction and enhancement in the hydrogen diffusivity.

- The positive effect of the ball-milling under hydrogen atmosphere of three AB_5-type alloys ($MmNi_5$, $MmNi_{4.1}Co_{0.6}Al_{0.3}$ и $MmNi_5$-Ni composite) on the electrochemical behavior as anodes in Ni-MH batteries has been demonstrated. The discharge capacity is found to depend strongly on the particle and grain sizes and partial substitution of Ni by Co.

- Mg-based nanocrystaline hydrides have been prepared by reactive mechanical milling in hydrogen atmosphere. The influence of the milling time and type of alloying elements (Ti, Mn, Mm) on the amount of the hydrides formed as well as on the temperature and enthalpy of hydrogen desorption have been studied. It has been established that small differences in the amorphous state, e.g. short range order in $Mg_{50}Ni_{50}$ alloy affect the hydrogen capacity and kinetics of the hydrogen sorption.

- Results are presented on the synthesis and characterization of metal-organic framework materials (MOFs) containing Cu, Ni, Zn, Co, Ce and various ligands, prepared by solvothermal and hydrothermal methods, which show a relatively high capacity for hydrogen adsorption.

- Through differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry, hydrogen adsorption and desorption processes in the $Ni_{81.5}B_{18.5}$ alloy have been studied, and the best glass-forming compositions in a series of metallic Zr-based glasses have also been determined.

Catalysts for thermal decomposition of ammonium perchlorate

- Novel catalysts based on hydroxides/oxides and a composite between humins and carbon nitride have been developed to accelerate the thermal decomposition of ammonium perchlorate (AP) as the main component of the rocket fuels. It has been found that the *in-situ* formed active NiO species in the AP/β-$Ni(OH)_2$ system is beneficial for electron transfer in the decomposition steps of AP, leading to decrease in the decomposition temperature and almost twofold increase in the heat of decomposition.

- Novel mesoporous cauliflower-like $CuO/Cu(OH)_2$ structures appear to be a strong candidate for use in catalyzed thermal decomposition of AP because they exhibit excellent catalytic activity that approaches and even exceeds those of the best reported CuO-based catalysts.

- The synergetic effect between carbon nitride and humins is shown to enhance significantly the catalytic activity of the composite toward AP thermal decomposition. This in combination with its simple and cost-effective fabrication process defines the composite as very attractive catalyst for AP decomposition.

In summary, the contributions of the candidate are fundamental and applied, they are related to the enrichment of knowledge in the field of solid state chemistry and are directed to solve problems of energy and environmental significance.

I would recommend the personal contribution of the candidate to be more clearly outlined and to provide more detailed information about the scientific and training activities subject to evaluation.

CONCLUSION

The analysis of the scientific works presented by the candidate, the positive evaluation in the specialized literature, the participation in projects and the long-term teaching activity show that the candidate meets the requirements and criteria for occupying the academic position of "Associate Professor". Based on all the above, **I recommend Assist. Prof. Dr. Veselina Rangelova to occupy the academic position of "Associate Professor" in the professional field 4.2. Chemical Sciences (Solid State Chemistry) at the Faculty of Chemistry and Pharmacy in Sofia University "St. Kl. Ohridski".**

Sofia, 16.11.2023 г. Reviewer:

Prof. Dr. Violeta Koleva