REVIEW

according to a competition announced in the State Gazette no. 77 of 01.10.2019 for occupation of the academic post "Professor" in the professional field Chemical Sciences, Scientific Specialty "Chemical Kinetics and Catalysis" for the Needs of Laboratory "New Heterogeneous Catalysts for Clean Energy and Environmental Protection", Institute of Catalysis, Bulgarian Academy of Sciences

Applicant for the competition: Margarita Valentinova Gabrovska, PhD, Assoc. Prof.
academic post at the Institute of Catalysis, Bulgarian Academy of Sciences

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

1. **General information on the applicant.**

Margarita Gabrovska was born in 1954 in Sofia. In 1981 she graduated from the Higher Technology School of Chemistry and Metallurgy "Prof. Dr. Assen Zlatarov ", Burgas, specialty " Technology of Organic Synthesis and Fuels ". In 1982 she joined the Institute of Catalysis, Bulgarian Academy of Sciences (IC, BAS), initially as a chemist, and since August 2010 she has held the position of "Associate professor" at the same institute. In 2001 she successfully defended her PhD thesis on "Nickel-containing layered systems: preparation, structural modification and evaluation of their catalytic activity".

2. **Overall assessment of the applicant's scientific and educational activities.**

Assoc. Prof. Gabrovska is co-author of 70 scientific publications, with 31 of them participating in this competition. 20 of these articles have been referenced in the WEB OF SCIENCE and SCOPUS databases. 4 of the articles were published in Quartile Q1 journals (Appl. Catal. A: General, Chem. Eng. Res. Des., Appl. Surf. Sci., Catal. Today). One article is in Quartile Q2 journal, six -in quartile Q3 and nine- in quartile Q4 journals (in the table for the minimum requirements for the indicator D7, 7 publications with quartile Q4 are incorrectly stated, but 72 points corresponding to 6 publications are correctly calculated). In addition, she has co-authored 2 chapters of books, also on the subject of the competition, in one of which is a leading author. Dr. Gabrovska also co-authored a US patent on "Nickel-Based Catalyst For Fuel Cell", which is undoubtedly a significant contribution of the applicant to the practical implementation of the research experience gained. Her participation in international and national scientific forums is very active, where she has presented 21 oral

and 56 poster reports on the topic of the competition. From the correctly applied protocols, it is clear that in many publications the applicant is the lead author who provided the concept of the study, the conduction of the experiments and the interpretation of the results obtained.

On the subject of the competition in the WEB OF SCIENCE and SCOPUS databases were noticed 130 citations, which represent almost half of all the citations of the candidate. A considerable number of citations (59 and 40 respectively) were noted in two of the articles (numbered as 1 and 3 in the competition publication list), in which the applicant is the first author. Considering the fact that about 2/3 of the Impact Factor publications were published after Dr. Gabrovska's election as Associate Professor, her high research activity during this period can be concluded.

Since her election as Associate Professor, Dr. Gabrovska has participated in 15 national projects funded by the Bulgarian National Scientific Fund, International projects under the equivalent exchange with Romania, Serbia, Poland, Belgium and Egypt and a project funded by an external contracting company. In 9 of the contracts, she holds management positions, including Deputy Head of Contract with GenCell Ltd, Petah Tikva, Israel "Anodes for base metal alkaline electrolytic cells"; Coordinator from IC-BAS and Member of the Coordination Council of the Contract “Investigation of Conductivity and Reversibility Mechanisms in Innovative Design of Solid Oxide Fuel Cells”, funded by Bulgarian National Scientific Fund, Head of the task related to “Concept Development to improve the catalytic activity of electrodes to eliminate the disadvantages of the common used ceramic technology in the production of cermet anodes "from the National Science Program: "Low Carbon Energy for Transport and Household ". The funds from the implementation of the projects, led by Dr. Gabrovska, for the period after her election as "Assistant Professor" amount to more than BGN 176 thousand. The initiative and the very good work of the candidate are also evidenced by the leading scientists from Serbia, Romania and Israel praised. Currently, Dr. Gabrovska is the head of a scientific group at IC, BAS, whose subject is related to the synthesis and activity of metal and metal oxide catalysts.

The assessments of the applicant by indicators, in accordance with the minimum requirements in Republic of Bulgaria are shown in Table. 1. The overall assessment of the applicant by all indicators exceeds by about 50% the minimum set in Bulgaria, with a very significant share being the citations of scientific papers and the participation of the applicant in projects.

Table 1. Assessment of the applicant by indicators, in accordance with the minimum requirements in Republic of Bulgaria

Indicator	Points required	Points Candidate
A. Thesis "Doctor"	50	50
B. Habilitation thesis	100	131
D. Scientific publications outside of habilitation thesisis	220	242
E. Citates	120	260
F. Management successfully defended PhD student; participation in projects etc.	150	275
Total	**640**	**958**

Dr. Gabrovska also shows considerable activity as a member and vice-chair of organizational committees at International scientific forums held in Bulgaria and abroad. She has been a reviewer many times both in a number of competitions for academic posts and in international scientific journals. She was a guest editor for the anniversary booklet of Bulgarian Chemical Communications. She has been awarded numerous certificates for her significant contributions to the accomplishment of scientific tasks and projects. She is also actively involved in the administrative work of the Institute as a long-time member of the Scientific Council, chairman of the Attestation Committee, chairman of the Ethics Committee and editor-in-chief of the Institute's Electronic Journal.

3. Major contributions from the applicant's research activities

The applicant's research activity is closely related to the design of nanoscale metal-metal oxide composites as catalysts in hydrogen energy, environmental protection, human health and the enhancement of quality of life.

3.1. Evaluation of the habilitation thesis

Dr. Gabrovska's habilitation thesis is focused on the development and investigation of catalysts for the release of CO and CO_2 from gas mixtures. In it, the candidate has selected 8 publications which were published in the period after her election as "Associate Professor". Two of the articles are in prestigious specialized journals, with high impact factor and quartile Q1, 3- in Q3 and 3- in journals with Q4 quartile. With the exception of one, in all the articles

the candidate is at the first place, and in 6 of them she is the corresponding author. This underlines her leading role in conducting investigations. Originality in habilitation thesis is the combination of various catalytic processes such as the total oxidation of CO to CO_2, the conversion of CO with water vapor and the hydrogenation of CO_2 to methane in a general scheme with a potential application for the purification of hydrogen used as a feedstock for the chemical industry and alternative fuels. Dr. Gabrovska focused on the development of cheaper catalysts which could replace the precious metals ones. The following more important results of the studies described in the habilitation thesis can be noted:

- In order to avoid the easy deactivation of cobalt oxide catalysts which have shown high activity in the oxidation of CO to CO_2, new catalysts have been prepared based on Co-Al and Ni-Al layered double hydroxides. Cobalt analogues have been shown to exhibit catalytic activity at relatively lower temperatures. Based on the clarification of the complex nature of the active centers and the role of each of the components in them, the composition of the composite catalysts was optimized. For the first time, a catalyst activation / deactivation scheme has been proposed, which clarifies the essential role of Al^{3+} ions in low-temperature oxidation of CO.

- Ni-Al layered double hydroxides promoted by only 1% K_2O have been shown to be highly active in the process of CO vapor conversion. An interesting dependence of the promoter activity of Au nanoparticles on their size was established. The high activity of these catalysts was associated with the formation of nickel hydroxide structures that favor the formation of an intermediate surface formate compounds and a reversible Ni^{2+} - Ni^{3+} redox transition. Based on this mechanism, the applicant provides a reasonable explanation for the need to increase the concentration of Ni in the catalysts and the role of K_2O and Au promoters in them. A positive effect of clarifying the mechanism of the process is also the optimization of the composition of the Au-Ni-Al catalyst in order to ensure high and stable activity while reducing the operating costs due to the one-step process. I consider that the essential contribution of the candidate with a practical character is the optimization of the composition of catalysts for the conversion of CO with water vapor into sulfur containing feedstock, by the addition of Re_2O_7.

- For the first time, the potential for the use of Ni-Al layered double hydroxides as catalysts for hydrogenation of CO_2 was explored. Originality in the study is the application of a new approach for the activation of precursors by reduction with hydrogen without preliminary calcination to the corresponding oxides, thereby preventing the sintering of the active component. A promotional effect of the addition of MgO to the catalysts has been

demonstrated. On the basis of a detailed study of the behavior of the catalysts, their composition, operating and activation temperatures were optimized. The nature of the divalent metal in the Al-containing layered double hydroxides has been shown to influence the crystallinity of the synthesized precursors, their specific surface area and the decomposition temperature of the layered structure to the corresponding mixed metal oxides.

In conclusion, I would like to emphasize that the studies presented in the habilitation thesis contribute to the development of a science-based approach to optimize the composition of composite catalysts for the purification of hydrogen from CO and CO_2.

3.2.Evaluation of research activity beyond habilitation thesis.

13 scientific publications, abstracted and indexed in a database (WoS/Scopus), 10 publications in peer-reviewed journals from international scientific forums, two book chapters and one patent, with which the applicant participates in the competition, are not reflected in the habilitation thesis and will be a subject to review below. The research is broad-based, highly applied, and addresses important environmental and quality of life issues. All studies are based on in-depth studies on the proper understanding of the nature of the active sites and the mechanism of the processes as a necessary approach in the development of effective catalysts for partial hydrogenation of oils, photocatalytic removal of nitrobenzene from water, oxidative dehydrogenation of light alkanes, decomposition of light alkanes, in gas phase, biodiesel production, anode catalysts for fuel cells, etc.

I believe that the following results are of major interest in the research:

-The determinant role of the texture parameters of the silicate carriers on the catalytic properties of supported on porous silicate nickel catalysts in the hydrogenation of sunflower oil by controlling the localization and reduction of Ni^{2+}-O structures has been established. A correlation was found between the activity of the catalysts and the number of adverse chemical reactions, which controls the quality of the product obtained. Mg additives have been shown to improve hydrogenation activity and affect the amount of stearic acid and the level of cis-trans isomers that are essential for human health. The effect of the nature of the nickel salt used and its interaction with the carrier on the precursor reducibility and the properties of the nickel metal phase have been demonstrated.

- Active catalysts have been obtained for the oxidative dehydrogenation of propane based on MO-Nd_2O_3 oxides, whose properties are controlled by the basicity and ionic radius of the metal ion, as well as by the number of defects generated in the Nd_2O_3 structure.

- Ni-Cu-Al catalysts have been synthesized for the decomposition of ozone to oxygen in the gas phase, as an alternative to usually used Pt-containing catalysts. It has been shown that their properties can be significantly improved by increasing the Ni content and the addition of Ag_2O in the samples.
- An innovative technology has been developed for the production of nickel-containing ceramic anodes for solid oxide fuel cells based on *in situ* deposition of Ni^{2+} ions on an anodic ceramic matrix. It has been demonstrated that the use of anhydrous medium preserves the structure of the ceramic matrix and improves the homogeneous distribution of metallic nickel particles in it, thereby significantly improving the electrochemical characteristics of the anode.
- A very significant result of the investigations, non-included in the habilitation thesis is the development of innovative technology for the production of metal based catalysts as an alternative of the traditionally used and high-cost platinum anode catalyst for fuel cells in a project with the Israeli company GENCELL LTD., Petah Tikva (IL). A nickel catalyst promoted with a transition metal (such as Pd, Cr, Co, Fe) and/or alkaline earth metal (Mg, Ca) deposited on electrically conductive activated carbon whose composition is patent protected was developed. Moreover, due to the demonstrated high performance of the new anode catalyst, the latter was introduced into regular production and incorporated into the G5 generator system, a commercial product of the company.
- The phase composition of the composites obtained from the treatment of layered Ni-Al and Co-Al hydroxides over a wide temperature range and the variation of the metal /Al ratio were studied in details. An advantage of the proposed method of producing metal oxide composites is its profitability due to the possibility of being realized at one stage by an oxide precursor, which is a prerequisite for the creation of cheap and diverse pigments.

Conclusions

Dr. Margarita Gabrovska's research represents significant contribution to development of effective catalysts for use in ecology, alternative fuels and improving the quality of life for humans. The detailed and in-depth analysis of the phase composition and properties of the materials obtained by advanced techniques and the pursuit of a proper understanding of the nature of the catalytically active centers and the mechanism of the processes on them demonstrate a well-developed scientifically valid approach of the candidate in optimizing the properties of catalysts for different applications. Very strong impression is the use of inexpensive and affordable raw materials, which through innovative schemes of preparation,

promotion and activation transform to very good alternatives of the traditional expensive catalysts. The logical planning of the experiments, the up-to-date of the investigated processes, the in-depth interpretation of the results and the pursuit of practical realization of the obtained products are just a few characteristics that underline the candidate's erudition in the field of catalysis. The high proportion of publications in which the applicant is the first or correspondent author, the high citation of publications, including in recent years, as well as the active leadership in the implementation of projects highlight the qualities of Dr. Gabrovska as a leading researcher. Not least is the high rate of work and the significant scientific results obtained after her election as an "associate professor". I believe that the applicant's qualities fully comply with the requirements of the Law for the development of academic staff in Republic of Bulgaria for occupation of the academic position of "professor" in the professional field 4.2. Chemical sciences (Chemical kinetics and catalysis). It will be of considerable benefit to the needs of the lab. "New Heterogeneous Catalysts for Clean Energy and Environmental Protection", IC, BAS, for the purpose of which the competition is announced. Therefore, I strongly recommend that the members of the Scientific Jury and the Scientific Council of the IC, BAS, be awarded to Dr. Margarita Gabrovska, currently "Assistant Professor" at the same institute, the academic position of "Professor".

Sofia, 08. 01.2020

Reviewer:

/ Prof. D.Sc. Tanya Tsoncheva /