O P I N I O N OF R E V I E W E R

Submitted by Prof. Dr. Silviya Zhivova Todorova, Institute of Catalysis-BAS
in connection with the competition for occupying of the academic position Professor in the professional field 4.2. "Chemical Sciences", scientific specialty "Chemical Kinetics and Catalysis" for the needs of the Institute of Catalysis at the Bulgarian Academy of Sciences, Laboratory " New Heterogeneous Catalysts for Clean Energy Production and Environmental Protection", announced in Newspaper of State issue 77/01. 10. 2019

1. Brief details of the applicant

Associate Professor Margarita Valentinova Gabrovska is the only candidate in the competition for the academic position "Professor". The set of materials submitted by the applicant is in accordance with Article 29 of ZRABRB, Articles 55(1) and 58 (1) of the Rules on the Conditions and Procedures for Acquisition of Academic Degrees and Occupation of Academic Positions at IC-BAS.

For participation in the competition, Dr. Gabrovska presented the necessary documents: CV, diplomas for higher education and for the Doctoral degree, research publications, concerning index 4 about habilitation work from "group B", other publications according to the index 7- research publications that have been referenced and indexed in world-renowned databases of scientific information (Web of Science and/or Scopus), outside of habilitation work, from "Group D", lists of scientific papers, citations, list with the participations in the conferences, copies from scientific works, list of participation in a national and international projects certificates.

2. Short biographical data about the candidate

Assoc. Prof. Gabrovska graduated from Higher Institute of Chemical Technology "Prof. Dr. Assen Zlatarov ", Burgas, specialty: Technology of Organic Synthesis and Fuels in 1981, Her doctoral degree was awarded by the Higher Attestation Commission in 2001. The subject of the doctoral thesis is "Nickel-containing layered systems: preparation, structural modification and evaluation of their catalytic activity". Since 1983 he has been working at the Institute of Catalysis, Bulgarian Academy of Sciences, first as a chemist, and then as an associate professor since 2010.

During 2008 and 2010 Assoc. Prof. Gabrovska was a member of the organizing committees of the following international and national events: 15th National Conference on Catalysis and 8th Scientific Session on Catalysis for Students, Doctoral Students and Young Scientists, 12th International Symposium on heterogeneous catalysis and at two consecutive International Conferences on Fundamental and Applied Aspects of Physical Chemistry. Since 2012 he has been vice-chairman of the international Organizing committee of the last conference.

The project activity of Assoc. Prof. Todorova is also impressive. In this case, I would emphasize that she is the head of eight scientific or research-related projects and she has led the Bulgarian teams of three international projects.

Assoc. Prof. Margarita Gabrovska is a desirable partner in a number of national and international scientific projects. She has participated in 3 projects within the framework of the inter-academic exchange, 2 projects with the National Science Fund (NSF) and a project with the Israeli company GenCell Ltd, Petah Tikva. The latest project is one of the most significant

internationally funded projects from 2012 to date for the Institute of Catalysis. As a result of the work on this project, 1 patent was registered and a catalyst was developed and manufactured by GenCell Ltd. The extremely important role of Assoc. Prof. Gabrovska in the development of non-platinum anode catalysts for alkaline electrolytic cells is evidenced by the Recommendation letter provided by Israeli partners.

Associate Professor Margarita Gabrovska has been the project leader of three contracts in the field of inter-academic exchange with the Institute of Physic chemistry of the Romanian Academy, three contracts with the University of Belgrade, the Institute of Chemistry, Technology and Metallurgy, the Center for Catalysis and Chemical Engineering one contract within the framework of the NSI and a task manager within the framework of the "National Science Program E +: Low Carbon Energy for Transport and Households". The very important role of Assoc. M. Gabrovska in the implementation of the projects with the Romanian Academy and the University of Belgrade is evidenced by the attached recommendation from her foreign colleagues.

The presented above facts show that the Assoc. Prof. Gabrovska has a capacity to attract funds and the lead research projects.

Dr. Gabrovska has co-authored a total of 70 publications. The candidate participates in the competition with 31 papers, 20 published in the journals reviewed in Web of science and/or Scopus, in other data base - 1, 10 scientific publications in peer-reviewed journals from international scientific forums. Dr. Gabrovska is the first author and author of correspondence in 13 of the publications, which clearly shows the leading role of the candidate.

3. Evaluation of the scientific research of the candidate

The presented publications are divided into two groups corresponding to indices **В** and **Г**, in accordance with Regulations for the conditions and order for acquiring of scientific degrees and occupying of academic positions. In the first group, indicator **В** - "Habilitation work - scientific publications in journals that are referenced and indexed in world famous scientific information databases (WoS or Scopus)", there are 8 publications (two of them fall in Q1, three in Q3 and three in Q4), giving a total score of 131 points, higher than the required minimum of 100 points required. In 7 of the publications, Assoc. Gabrovska is the first author.

The second group represents 13 publications (2 - Q1, 1 - Q2, 3 - Q3 and 7 - Q4) covering index **Г**, with a total of 242 points higher than the required 220 points. In the group of indices **Д**, the requirements have been exceeded significantly – in view of the required 120 points, the candidate has 260 points. All citations are in prestigious international journals, which fact confirms the importance and relevance of Assoc. Prof. Gabrovska scientific research.

The dissemination of scientific results has been achieved through participation with oral and poster presentations in a number of national and international scientific meetings as follows: 12 oral reports were presented at prestigious international forums (4 Key-not lecture and one invited lecture). Nine reports were presented at national level, of which 1 plenary lecture and 1 Key-not lecture. The poster reports at international forums are 39, at national with international participation-3 and at national forums-15.

Assoc. Prof. Gabrovska cover indicator **Е** (supervising of PhD students, implementation and management of national and international projects and funds attracted under them) with 275 points, high that required 150 points, in accordance with the Rules cited above including.

The scientific indicators in the presented materials, with which Dr. Margarita Gabrovska participates in the competition, convincingly show that she significantly exceeds the requirements imposed on the candidates for the position of professor. I would also like to point

out that all the materials are very well arranged, which greatly facilitates the work of the reviewer.

4. Scientific research contributions

Habilitation work

The research activity of Assoc. Prof. Dr. Margarita Gabrovska is in the very actual directions of modern heterogeneous catalysis related to environmental protection and the development of efficient technologies for the environmentally friendly fuels.

Habilitation Work can be summarized in three main directions:

1. Development of catalysts for the oxidation of CO to CO_2.
2. Development catalysts for water-gas shift reaction (WGSR).
3. Development of catalysts for hydrogenation of CO_2 to methane.

The studies in the first direction are focused on the CO oxidation in the presence of transition metal oxides catalysts. As is well known, CO is a toxic gas for peoples and animals due to its high affinity for hemoglobin. The main parts of the industrial catalysts for CO oxidation are based on precious metals. The high cost of precious metals, their limited availability and sensitivity to higher temperatures and poisons has motivated the search for substitute catalysts. Among all studied metal oxides the most active single metal oxides are those of Cu, Co, Mn and Ni. Assoc. Prof. Gabrovska was focused on the development of catalysts based on one of the most active oxides, namely cobalt oxide and nickel oxide searching for a way to develop catalysts with increased activity and stability. Assoc. Prof. Gabrovska was focused on the Co-Al and Ni-Al layered double hydrotalcite-like materials as catalyst precursors.

Active and stable catalysts are obtained and a possible activation/deactivation scheme is proposed according to which, when the catalysts is heated in excess of oxygen, the surface of the catalysts is saturated with oxygen radicals O_2^{x-}, which are active in CO oxidation.

A hypothetic scheme is proposed about the activation/deactivation of the catalysts including an active assemble composed by Co^{2+}/Co^{3+} (Ni^{2+}/Ni^{3+}) couple close to Al^{3+} anion vacancy, thus generating O_2^{x-} radicals stabilized on Al^{3+} ion. The optimal Co^{2+}/Co^{3+} (Ni^{2+}/Ni^{3+}) ratio in the close proximity with ion-radicals O^{2x-}/Al^{3+} is necessary for a higher activity.

Development catalysts for water gas-shift reaction.

Another significant part of the research of Assoc. Prof. Gabrovska is directed at the development of catalysts for the water-gas shift reaction (WGSR). Hydrogen is considered as the energy carrier of the future and, in combination with fuel cells, can be a clean and stable way of meeting the world's energy needs. The water-gas shift reaction is the first step of purification of synthesis gas from CO and increasing the hydrogen concentration.

Co-precipitated Ni–Al layered double hydroxides (LDHs) have been used as precursors of catalysts in the WGSR reaction and as supports for gold catalysts. It was found that the activity increases with increasing reaction temperature and nickel content. The addition of 1 wt. % K_2O significantly improve the activity of a catalyst with a molar ratio of Ni^{2+}/Al^{3+}= 3, which at 300° C reach an equilibrium degree of CO conversion. This is explained by the increase in the density of the active OH groups involved in the formation of the surface intermediates. A higher amount of potassium leads to the formation of surface blocking species and to the decrease in the activity. It has been found that the activity in the WGSR reaction depends on the molar ratio of Ni^{2+}/Al^{3+} and the presence of gold, which is related to the existence of surface Ni^{2+} and Ni^{3+} ions, which are responsible for the reversible redox $Ni^{2+} \leftrightarrow Ni^{3+}$ process.

The KCoRe/γ-Al_2O_3 system was developed for the WGSR reaction of sulfur-containing gases. Uniformly deposited K-Co-Re species on the support surface, a balance between Re sulphidic and oxidic species, and synergism among components are beneficial to highest activity of the KCoRe catalyst. In summary, the KCoRe system is considered a promising catalyst for WGS reaction with sulphur-containing feed in the 250–400 °C temperature range.

Development of catalysts for hydrogenation of CO_2 to methane.

It is known that the CO_2 methane reaction is essential, both in terms of the utilization of CO_2, which is a greenhouse gas, and in the purification of hydrogen-rich mixtures of CO_2. Studies on this problem are focused on Ni/Al_2O_3 catalysts obtained from Ni–Al layered double hydroxides (LDHs) with or without additives. The effect of pre- treatment, the type of modifier, on the structure of the synthesized samples is studied. The sample with the highest nickel content and magnesium as additives showed the highest activity. The Mg-containing catalysts had the advantage of preserving nickel metal dispersion after reduction above 500°C due to a retarding effect on Ni sintering.

Other publications

Other publications presented by Assoc. Prof. Gabrovska for participation in the competition form several thematic areas related to the development of metal and oxide composites with appropriate structure and properties for reactions used in hydrogen energy, environmental protection, human health and improving the quality of life . I will briefly highlight the major scientific contributions.

Development of catalysts for partial hydrogenation of vegetable oils.

The results are summarized in 15 publications. The topic is one of the main subjects of the IC-BAS "New catalytic materials and processes for improving the quality of life" and is the result of a long term academic cooperation between the Institute of Catalysis and the Institute of Chemistry, Technology and Metallurgy at the University of Belgrade, Center of Catalysis and Engineering Chemistry, Serbia. Assoc. Gabrovska is a leading researcher in this field and she is a head of all contracts within this cooperation from 2010 to the present.

Nickel catalysts deposited on three types of silica gel with different texture and modified with magnesium (isomorphic substitution of Ni^{2+} with Mg^{2+} ions), MgNi catalysts supported on perlite, nickel catalysts supported on a natural-diatomite. It has been established, that by using the different carriers and additives, the structural characteristics of the reduced precursors and activity and the selectivity of the catalysts can be controlled. Kinetic models of hydrogenation of soybean and sunflower oil have been developed on the catalytic systems under study, which are useful for predicting reaction rates, catalytic activity and selectivity. The proposed simplified kinetic model to describe the kinetics of soybean oil hydrogenation gave a good description of the experimental data.

Development of anode ceramic matrix for fuel cells.

Catalysts for solid oxide fuel cells (SOFC) (Publications Nos. 12 and 14) and for alkaline fuel cells have been developed. An innovative concept has been developed for the preparation of Ni-based ceramic anodes with application in p-SOFC, which has the potential to replace the classical procedure, eliminating its disadvantages. The concept represents the "in situ" application of Ni^{2+} ions from a suitable nickel salt by low-temperature "wet" reduction with hydrazine in aqueous (publication No. 12) and anhydrous media (publication No. 14). The precursors were synthesized with the same NiO/BCY15=44.4/55.6 composition and the proton-conducting electrolyte BCY15 (15% Y_2O_3) was used as the anode ceramic matrix. It was

obtained Ni/BCY15 precursor in an anhydrous medium which preserves the structure of the ceramic matrix. It has been found that the surface of the sample is compose of monodisperse particles smaller than that obtained in aqueous media, which shows a higher homogeneity and uniform distribution of the nickel metal particles in the perovskite phase.

The next achievement is the result of a contract between IC-BAS and the Israeli company GenCell LTD, Petah Tikva. It has been one of the most significant achievements in the Institute of Catalysis during the last seven years. The new catalyst based on nickel is developed and they can substitute the traditionally high-cost platinum anode catalyst. The catalyst is into regular production and it is incorporated into the G5 generator system, a commercial product of GenCell LTD, Petah Tikva, Israel. The work is protected by a patent. The achievements in the framework of this project were selected several times as the "Best Scientific Applied Achievement" in the annual reports of the IC.

Other contributions concerning the development and application of metallic and oxide compositions can be summarized as follows:

- The Fe-TiO_2 films are synthesized using the sol-gel method and are applied for the first time as catalysts for the photocatalytic removal of nitrobenzene from water. The reaction mechanism is proposed.

- The active catalysts based on Nd_2O_3 oxide for the oxidative dehydrogenation of light alkanes, were obtained by the sol-gel method.

Ni-Cu-Al catalysts for the decomposition of ozone to oxygen in the gas phase as substitutes for the classic Pt-containing impregnation obtained are developed. A probable scheme is proposed about ozone decomposition composed by the redox couple Ni^{2+}/Ni^{3+} and reversible redox $Ni^{2+} \leftrightarrow Ni^{3+}$ transition. A mechanism for the process of gas-phase ozone decomposition on Ni-containing co-catalysts is proposed, including (i) electronic transition from Ni^{2+} ions to ozone, leading to the formation of Ni^{3+} containing structures and peroxide particles O_2^{2-} and (ii) reduction of Ni^{3+} structures back to Ni^{2+} ions by desorption of peroxide particles to form oxygen ($O_2^{2-} \rightarrow O_2 + 2e^-$).

The presented scientific contributions in the publications of Assoc. Prof. Margarita Gabrovska are a novelty in science and have significant applied potential.

Conclusion

The research works of Assoc. Prof. Margarita Gabrovska fully correspond to the topic of the announced competition for awarding the academic position of " Professor". The number of publications and citations on the published papers prove that Assoc. Prof. Margarita Gabrovska fully covers and exceeds all the requirements of the Law for Development of the Academic Staff in the Republic of Bulgaria (LDASRB), the Regulations for the conditions and order for acquiring of scientific degrees and occupying of academic positions in IC-BAS. Therefore, I strongly recommend to the members of the Scientific Jury and the Scientific Council of IC-BAS to award to Assoc. Prof. Margarita Gabrovska the academic position “Professor” in the professional field 4.2 “Chemical Sciences” and scientific specialty "Chemical Kinetics and Catalysis".

Data 05. 02. 2020 Member of the Scientific Jury:

Sofia /Prof. PhD Silviya Todorova/