R E V I E W

by Prof. Tatyana Tabakova, PhD, Institute of Catalysis - BAS

on the materials submitted for participation in the competition for occupying the academic position of "Professor" at the Institute of Organic Chemistry with Centre for Phytochemistry (IOCCP) - BAS in professional field 4.2 "Chemical Sciences", scientific specialty "Organic chemistry"

The only candidate, applying for the academic position of "Professor" in the competition, published in „Newspaper of State", issue 40, dated 31.05.2022 and announced on the website of the Institute of Organic Chemistry with Centre for Phytochemistry (IOCCP) - BAS is Assoc. Prof. Dr. Boyko Georgiev Tsyntsarski from Laboratory "Chemistry of solid fuels".

1. General presentation of the submitted materials

The set of materials presented by Assoc. Prof. Dr. Boyko Tsyntsarski is in accordance with the Law for Development of Academic Staff in Republic of Bulgaria, The Regulations of BAS for the Implementation of this Law and the Regulations of IOCCP-BAS of the Development of the Academic staff of IOCCP - BAS, and meets the criteria of IOCCP-BAS for the academic position of "Professor".

The applicant has presented 17 scientific works for participation in the announced competition. The publications were indexed in world databases Scopus and Web of Science. The distribution of scientific works according to the rank of the scientific journals, expressed in quartiles (Q-factor), is as follows: Q1 – 8, Q2 – 8 and Q4 – 1. All of them have been published after the acquisition of the educational and scientific degree "Doctor" (PhD) and after the competition for occupying the academic position of "Associate Professor". These publications are clearly distinguished in the list of all publications (1997 – 2022). A detailed list of all citations is presented, as well as a list and evidences of participation in scientific forums for the period 2018-2021. A list of leadership and participation in the implementation of projects with national and international funding is also attached.

2. Brief biographical details of the applicant

Assoc. Prof. Boyko Tsyntsarski graduated Sofia University in the year 1996. In 1998 he joined the Institute of General and Inorganic Chemistry - BAS as a chemist. In 2000 he was enrolled as PhD student at laboratory "Synthesis and reactivity of oxide systems" in the Institute of General and Inorganic Chemistry - BAS. He defended his doctoral thesis entitled "Selective catalytic reduction of hydrocarbons on Co/ZSM-5. IR spectroscopic study of the mechanism of the process" in 2006 and was awarded PhD degree. He has been working at IOCCF since 2003, and in 2006 he was appointed as assistant researcher, and in 2008 he received the position of Assistant Professor. After participating in a competition in 2013, he acquired the academic position of "Associate Professor" in the laboratory "Chemistry of Solid Fuels".

3. General overview of the applicant's activities

Evaluation of the candidate's scientific and applied activity

Assoc. Prof. Tsyntsarski is co-author of 105 research publications and one chapter in a book published by Nova Science Publishers. Many of them – 89, have been published in international

journals having impact factor, with the largest number of them being of the highest category Q1 – 34. The distribution of the remaining papers is as follows: Q2 – 24, Q3 – 7 и Q4 – 24, 13 in journals with SJR without IF and only 3 in journals without IF or SJR. It should be noted that Assoc. Prof. Tsyntsarski is a co-author of 67 scientific papers, published after the acquisition of the position of „Associate Professor", which is an indicator of very high publication activity.

An expression of the scientific significance of the published results is the interest demonstrated by the scientific community, expressed in 1096 citations (excluding self-citations of all authors) noticed in scientific publications, referenced and indexed in the database Scopus. Citations are mainly from foreign authors, only 4 of them from Bulgarian authors. The number of citations after the acquisition the position of „Associate Professor" in 2013 is 817, which outmatches many times the specific requirements of IOCCF for the number of citations for application for the position of "Professor". The publications included in the current competition have been cited 112 times. The overall H-index is 17 according to the Scopus database (after excluding the self-citations of all co-authors) and also significantly exceeds the minimum requirements specified in the Regulations for the terms and conditions for acquiring academic degrees and occupying academic positions of IOCCP - BAS.

The results from the studies, carried out with the participation of Assoc. Prof. Tsyntsarski, have been presented at national and international scientific events as 85 oral and poster contributions. For the period 2018 – 2021 Dr. Tsyntsarski has attended 12 scientific forums, where he has presented 11 oral presentations, including 2 plenary lectures.

The implementation of national and international research projects occupies a significant part of the activities of Assoc. Prof. Tsyntsarski. He is coordinator of two projects with national funding from Bulgarian National Science Fund and 6 projects developed within the framework of Non-Currency Equivalent Exchange Contracts of Bulgarian Academy of Sciences with Rumanian Academy and Polish Academy of Sciences. The projects approved for funding are an indicator of the scientific competence of Assoc. Prof. Tsyntsarski. Assessment of his ability to create ideas and team-work is the participation in the implementation of 7 scientific research projects with national funding from Bulgarian National Science Fund, as well as 3 projects financed by Operational Programs of the EU.

Assessment of educational activity

Assoc. Prof. Tsyntsarski was a scientific consultant in 3 projects funded by Ministry of Education and Science under the National Program "Young scientists and postdoctoral fellows" (2018-2022). He is currently head of the laboratory "Chemistry of Solid Fuels" at IOCCF, which is not reported in the submitted materials.

Scientific and applied contributions

Scientific contributions are presented as extended habilitation work, in which Assoc. Prof. Tsyntsarski described the main results published in 17 scientific works included in the competition for occupying the academic position of "Professor". They are divided into two groups, covering indicators B and G in Table 2 of the Rules for application of Law for the development of the academic staff in Republic of Bulgaria. Group B includes 5 publications corresponding to habilitation work. They are published in journals with IF and the distribution by quartiles is as follows: Q1 – 2, Q2 – 2, Q4 – 1. The applicant is first or corresponding author in all articles, which is a proof of his contribution in planning and conducting the experiments and summarizing the results.

The studies are focused on development of methods for synthesis of new carbon materials with predefined properties aiming to use them in processes related to environmental protection, such as catalyst supports, adsorbents, hydrogen storage composites, etc. It is important to emphasize the usage of cheap raw materials such as coal, organic waste from agricultural and industrial production for preparation of carbon materials, which contributes to their economic profitability.

The main scientific contributions according to extended habilitation report are summarized by the applicant in the following directions:

1. Development of methods for synthesis of new carbon materials based on various organic raw materials and characterization of precursors and final carbon products.

2. Study of the influence of various factors on the synthesis process of carbon materials.

3. Application for nanoporous carbon materials as catalysts, adsorbents for water and air purification, composites for hydrogen production and storage, etc.

The development of new procedures for the preparation of carbon materials using various organic raw materials is highlighted in publications included in Group B. Relationship between chemical composition and texture of the row materials and the properties of the final product were found, which allow selection on purpose of suitable starting material depending on the requirements for the final product.

- A novel procedure for production of gas, liquid products and porous carbon has been developed by conversion of waste algae, remaining from biodiesel production. The solid product after pyrolysis at 550 °C is subjected to high-temperature hydro-pyrolysis (physical activation with water vapor) at different temperatures and duration. The obtained carbon materials after activation with water vapor demonstrate moderate surface area, microporosity and mesoporosity. Presence of oxygen functional groups with weak acidic and basic nature is established. This type of porous structure favors the application of these materials for adsorption (from water and air) of atoms, molecules, ions of different sizes, bacteria, viruses, etc.
- New opportunities for using natural asphaltites (coal-like fossil materials with high ash content from Turkey) have been considered. For the first time, high-temperature hydropyrolysis of natural asphaltites has been applied in the synthesis of carbon adsorbents. Materials with a developed porous structure and alkaline surface have been obtained.
- The application of activated carbons synthesized from waste biomass (peach stones or olive stones) or low rank coal treatment products as supports of cobalt-containing catalysts for methanol decomposition has been studied. It was found that the dispersion and composition of the active cobalt phase strongly depends on the surface oxygen-containing functional groups of the supports, which can be controlled by the pretreatment of the activated carbons. However, textural properties of the carbon supports were shown to be crucial for the catalytic activity.
- It has been found that activated carbon obtained from polymer waste product has a high adsorption capacity for mercury ions (196 mg/g). The influence of the reaction conditions - stirring time, concentration of metal ions, adsorbent quantity, pH, has been investigated.

An increase in pH from 2 to 5 has a positive effect on the purification of aqueous solutions of Hg^{2+}.

- The structure, surface properties and adsorption behavior towards phenol of different modifications of activated carbon prepared from mixtures of coal tar pitch and furfural has been investigated. A direct relationship between adsorption properties and textural characteristics (specific surface area and volume of micropores) was found.

The scientific contributions under indicator G are described in 12 papers, distributed by quartiles as follows: Q1 – 6 and Q2 – 6. The main results discussed in these papers reveal the application of nanoporous carbon materials in catalysis or as adsorbents for water and air purification, composites for production and storage of hydrogen, etc. Three of the works (G2, G3 and G7) are related to the successful use of activated carbons synthesized from different raw materials as support of catalysts for methanol decomposition aiming pure hydrogen production.

- Activated carbons with high purity, different textural characteristics and surface functionality have been synthesized by varying the activation temperature during the preparation and post-synthetic treatment with nitric acid. The effect of these properties on catalytic activity depends on the composition of mono- (Fe_3O_4 or ZnO) and bimetallic ($ZnFe_2O_4$) modifications. Higher activation temperature during the carbon preparation increases the relative part of mesopores, thus promoting formation of more finely dispersed magnetite particles with high reactivity in methanol decomposition over Fe_3O_4-containing sample. In the case of zinc modification, carbon pre-treatment with nitric acid facilitates formation of additional amount of surface acidic groups that affect the dispersion of the zinc oxide species. The combination of lower temperature of carbon activation with nitric acid pre-treatment promotes the formation of highly active ferrite nanoparticles in binary modifications due to the limited deposition of metal oxide species into the support micropores.
- It has been established that the textural features of activated carbons depend closely on the type of waste raw material used (peach stones or by-products of coal processing) and affect the dispersion and composition of the deposited active ferrite phase $Ni_xZn_{1-x}Fe_2O_4$ (x=0, 0.2, 0.8 and 1). The formation of a finely dispersed active phase is favored by an increase in the Ni/Zn ratio and the presence of a significant part of mesopores in the support.
- Carbon materials prepared from peach stones or coal treatment by-products have been used as supports of $Ni_{0.5}M_{0.5}Fe_2O_4$ mixed ferrites (M = Zn or Cu). By in-depth physical-chemical characterization has been found evidences that the dispersion and composition of the supported active phase depend on the textural characteristics of the carbon carrier. The existence of mesoporosity in the carbon host matrix provokes the formation of more finely dispersed and easily reducible spinel particles, which ensures higher initial catalytic activity, but fast deactivation of the catalysts. The formation of activated carbon mesoporosity is facilitated by the presence of cellulose and hemicellulose in the biomass or the addition of furfural to the coal tar pitch precursor.

Results of studying the electro-catalytic properties of oxide mesoporous materials with different molar ratio Fe:Ce, modified by NiO could be included in this group of contributions. Highly dispersed Ni-Fe alloys in a cerium matrix were obtained by reduction in hydrogen. The

metal phase is further modified into ferrous carbides and metal alloys encapsulated within carbon nanofibers during the progress of the methanol decomposition reaction.

Contributions related to the development of metal-carbon composites for hydrogen storage are described in three publications (G1, G8 and G9):

- Variety of carbon materials (nanoporous carbon, carbon foam, graphene, etc.) have been synthesized by utilization of waste products from industry and transport and used for preparation of metal-carbon composites for hydrogen storage. Composites with a composition of 95 wt. % Mg – 5 wt. % activated carbon (synthesized from polyolefin wax) have shown a high absorption capacity that is maintained after prolonged hydriding/dehydriding cycles.
- The effect on hydrogen sorption characteristics of magnesium of other types of carbon materials, obtained from apricot stones or bean pods, was investigated. A more pronounced positive effect was found when activated carbon derived from apricot stones was used for the composites preparation. The absorption capacity at 300 °C of composites with a composition of 80 wt. % MgH_2 – 15 wt. % Ni – 5 wt. % activated carbon (synthesized from polyolefin wax, a waste product of polyethylene production at low pressure) and 90 wt. % MgH_2 – 5 wt. % Ni – 5 wt. % activated carbon. Both additives have been shown to positively influence the hydriding kinetics and absorption capacity.

The study of the adsorption properties of various carbon materials is an up-to-date and attractive objective, as it allows minimizing the harmful effects on the environment and human health.

- The CO_2 adsorption properties of three types of activated carbons from agricultural raw materials - peach stones, olive stones and apricot stones, synthesized by a combination of pyrolysis and activation by water vapor were evaluated. It was found that micropores with narrow size distribution have the largest contribution to the volume of nanoporous carbon from apricot stones. This material demonstrated the highest adsorption capacity at 30 °C. Olive stones derived activated carbon has mainly meso- and macropores, which is the likely reason for the faster CO_2 saturation. The adsorption of CO_2 on activated carbon from apricot stones was found to be a reversible process, with the regeneration time controlled by temperature and, to a lesser extent, by flow rate of pure N_2 used in the desorption tests.
- The adsorption of phenol derivatives from aqueous solutions on nanoporous carbon material synthesized from waste products from the production of polyethylene has been investigated. It was established that the high adsorption capacity is determined by the properties of the adsorbent - high specific surface area, developed porous structure and presence of oxygen-containing functional groups on the surface of the adsorbent.
- Purification of Ni^{2+} ions from aqueous solutions using a new type of hybrid material has been achieved by combination of mechanical purification and adsorption. Powdered activated carbon of natural or synthetic origin has been used for the preparation of hybrid organic-inorganic membranes with high adsorption capacity.

A scientific contribution of a pronounced applied nature represents the preparation of carbon composites with potential application in medicine, military industry, aerospace as construction materials. The influence of the carbon foam grains size used as a filler of epoxy matrix on the

morphology of the composite has been studied. Improvement of thermomechanical and tribological properties has been achieved.

The scientific contributions of Assoc. Prof. Tsyntsarski can be evaluated as a novelty for science and enrichment of the existing knowledge.

In the report of scientific contributions, the applicant has presented the prospective for his research work within the next 5 years. In general, the studies will follow the directions in which he has worked successfully so far with the expansion of the types of synthesized carbon materials through the utilization of organic waste and optimization of synthesis and modification methods in order to find other areas of application.

4. Assessment of the applicant's personal contribution

Assoc. Prof. Tsyntsarski is the first author or author for correspondence in 6 of the publications. Due to the interdisciplinary nature of the conducted research, several co-authors participate in the works. Nevertheless, I believe that the personal contribution of Assoc. Prof. Tsyntsarski in the conducted research is indisputable.

5. Critical comments and recommendations

I have no substantial critical comments on the scientific publications presented by Assoc. Prof. Tsyntsarski. However, there are inconsistencies between the numbering of papers from Group B and their citation in the habilitation report, corrected by the applicant after submission of the documents. The presence of a large number of unclear expressions and spelling errors leave the impression of carelessness in the preparation of Bulgarian version of the habilitation work. Certain phrases sound disturbing - such as: “high absorption capacity under long-term *velo cycling*” when describing the role of addition of activated carbon to magnesium in order to create a hydrogen storage material (article G1) or “obtained mixed ferrites (M = Zn or Cu), *maintained* on nanoporous carbon materials” (G7) for mixed ferrites supported on nanoporous carbon materials.

Conclusion

Assoc. Prof. Boyko Tsyntsarski has presented a sufficient number of scientific works published after acquisition of the educational and scientific degree PhD and after the competition for occupying the academic position of “Associate Professor”. The works of the applicant contain scientific and applied contributions that have received international recognition, as all of them have been published in international journals. The achievements of Assoc. Prof. Boyko Tsyntsarski cover the requirements for the academic position of “Professor”, according to the Law for the Development of the Academic Staff in Republic of Bulgaria, The Regulations of BAS for the Implementation of this Law and the Regulations of IOCCP-BAS.

After acquaintance with the materials and scientific works submitted for the competition, analysis of their importance and the scientific and applied contributions reflected therein, I am convinced to give my positive assessment and recommendation to the Scientific Jury to prepare a report-proposal to the Scientific Council of IOCCP-BAS for the selection of Assoc. Prof. Boyko Georgiev Tsyntsarski, PhD, at the academic position of „Professor“ at IOCCP-BAS in the professional field 4.2. Chemical Sciences, scientific specialty Organic Chemistry.

20.09.2022 Reviewer:

/Prof. Tatyana Tabakova, PhD/