OPINION

by Assoc. Prof. Kiril Georgiev Stanulov

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on the materials submitted for participation in the competition

for the academic position of Professor

at the Institute of Organic Chemistry with Centre of Phytochemistry (IOCP), BAS,

professional field "Chemical sciences"- 4.2, scientific specialty

"Organic Chemistry", for the needs of the laboratory "Chemistry of Solid Fuels" (CSF)

In the competition for "Professor", announced in the State Newsaper, issue 40 of 31.05. 2022 and in the Internet site of IOCP, BAS as Dr. Boyko Georgiev Tsintsarsky participated as the only candidate for the needs of the laboratory CSF.

1. **General presentation of the procedure and the candidate**

All materials on electronic and paper carrier provided by Assoc. Prof. Dr. Boyko Tsintsarsky is in accordance with the Regulations for the Development of the Academic Staff of the IOCP-BAS and meet the criteria of the IOCP-BAS for holding the academic position of Professor.

At the competition, Assoc. Prof. Tsintsarsky participated with 17 publications, which are not included for the acquisition of the PhD degree and the academic position of Associate Professor. Of these, 5 are under indicator B and 12 under indicator G. The distribution of journals in which the articles were published by quartiles is as follows: Q1 - 8, Q2 - 8, Q4 - 1. All publications were published in journals with impact factor (Scopus and Web of Science).

The professional development of Assoc. Prof. Dr. Boyko Tsintsarsky takes place entirely at the Institute of Organic Chemistry with the Centre of Phytochemistry. As a PhD student at the Institute of General and Inorganic Chemistry (IGIC, BAS) he defended his thesis on "Selective catalytic reduction of hydrocarbons on Co-ZSM-5. IR spectroscopic study of the mechanism of the process" and received a PhD degree (2000-2002). In 2013 he was appointed as "Associate Professor", which position he is currently holding in the laboratory of CSF of IOCP, BAS.

The candidate's scientific interests are in the field of chemistry and technology of solid fuels, which corresponds to the topic of the competition. They are mainly focused on the preparation of adsorbents by thermo-oxidative treatment and chemical modification of coal, polymers, lignin-cellulosic materials, etc., chemical and physical studies of carbonaceous materials (activated carbons, carbon-carbon composites, porous carbon, purification of water and air from organic and inorganic pollutants, IR spectroscopy and other instrumental techniques for materials analysis.

The overall scientific activity of Assoc. Boiko Tsintsarsky is summarized in 106 publications, of which 89 are with IF and Q (Q1- 34 articles, Q2- 24, Q3- 7, Q4- 24). Of the publications

102 are refereed in Scopus. One publication is a chapter of a book indexed in Scopus The articles have a high citation rate (1096 citations noted, of which 817 after the competition for " Associate Professor"), which is an indication of high quality and significance of the research (H- index 17, Scopus)).

2. General description of the applicant's activities

Evaluation of scientific and applied activity

The scientific Investigations of Assoc. Prof. Tsintsarsky are in the field of preparation, characterization and application of adsorbents from various organic raw materials. From the presented habilitation report, the results and contributions of these investigations can be summarized in three main directions as follows:

- Development of methods for obtaining new carbonaceous materials by thermochemical treatment, pyrolysis, carbonization, activation of raw materials and characterization of precursors and final products;

- Investigation of the influence of various factors on the synthesis processes of carbon materials

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

The aim of the investigations in the first field is to obtain carbon materials with a developed porous structure and high specific surface area. A new technology has been developed for the conversion of waste algae from biodiesel production, based on pyrolysis of the algae at 550° C followed by high-temperature physical activation of the solid product with water vapour (hydropyrolysis) at different temperatures and for different durations. The method was developed in the Solid Fuels Chemistry Laboratory (IOCP, BAS) and has been successfully applied to obtain carbonaceous materials with high specific surface area and micro/meso-porous texture from precursors such as coal, polymers, waste biomass, etc. By nitrogen physisorption, the obtained carbon materials were found to have moderately high specific surface area and with the presence of a significant amount of micro - and meso-pores. The presence of surface oxygen-containing functional groups with acidic and basic character was also found.

High ash Turkish natural asphaltites were investigated to obtain carbon adsorbents. By high temperature hydropyrolysis, adsorbents with a developed porous structure and with an alkaline character on the surface were obtained for the first time, exhibiting good adsorption properties despite the high ash and sulfur content.

Activated charcoals were synthesized from waste biomass and low rank coals characterized by different textural and surface chemical properties. They were also investigated as supports for the preparation of cobalt catalysts, used in chemical catalysis for the decomposition of methanol to hydrogen. Advanced instrumental and chemical methods such as low temperature nitrogen physisorption, XRD, EPR, XPS, UV-Vis and TPR with hydrogen, Boehm's method for qualitative and quantitative determination of oxygen containing groups on the carbon surface before and after cobalt deposition, etc. have been used to characterize the activated charcoals. The use of this set of methods gives me the reason to believe that Assoc. Prof. Tsintsarsky is well acquainted with their possibilities and application in research practice. In these studies, it was found that of the precursors used, the cobalt catalysts derived from olive pits and coal by-products have the highest catalytic activity.

The research of Assoc. Prof. Dr. Boyko Tsintsarsky in the second direction is aimed at establishing the influence of various factors on the synthesis processes of carbon materials with improved structural and surface characteristics. As a result, the advantage of carbonization of feedstock with water vapor, compared to chemical and physical activation, was established due to the lower energy intensity of the process and the higher yield and quality of gas and liquid products. It has been shown that the determining factor for obtaining quality activated charcoals is the difference in texture and chemical composition of the feedstocks, which requires finding optimal thermochemical process conditions for each individual feedstock .

The research in the third direction occupies an essential part of the scientific activity of Assoc. Prof. Tsintsarsky. It is reflected in a total of 12 publications whose scientific and applied contributions are of ecological and technological significance in the field of application of synthesized carbon products as catalysts, adsorbents for water and air purification, composites for hydrogen storage, etc. In this regard, laboratory experiments have been conducted for adsorption of CO_2 from a model mixture of flue gases onto adsorbents derived from peach, olive and apricot pits. The study was carried out at different temperatures and CO_2 concentrations in the gases (from 3 to 30%) and it was found that nanoporous charcoal from apricot pits at 30°C had the highest CO_2 adsorption capacity compared to the other adsorbents. The adsorption of dioxide was found to be a reversible process influenced by temperature and to a less extent by the flow rate of the desorbing agent. In order to store hydrogen, Assoc. Prof. Tsintsarsky et al. developed a procedure to prepare metal-carbon composites based on Mg, MgH_2, Ni and carbon materials derived from waste products such as polyethylene wax, waste oils, apricot pits, etc. The sorption characteristics of the composites with respect to hydrogen, their absorption capacity, and the acceleration of hydrogenation in the presence of nickel and activated charcoal from polyethylene wax were investigated. The candidate's research on the production of clean energy from biomass by catalytic decomposition of methanol to hydrogen has made a significant scientific contribution in obtaining new data on this process. They consist in the development of an intelligent integrated scheme for the full utilisation of biomass in which both the activated charcoal used as catalyst support and the methanol are produced from biomass. Iron, Zinc and Ferrite catalysts based on activated carbon from peach pits were prepared and characterized and it was found that their catalytic activity strongly depends on the type of metal oxides and can be controlled by changing the activation conditions of the carbon support. It was found that modified $Ni_xZn_{1-X}Fe_2O_4$ and $Ni_{0.5}M_{0.5}Fe_2O_4$ activated charcoals based on waste feedstocks exhibit high catalytic activity in the decomposition of methanol to hydrogen, outperform silicon analogues and reveal a potential opportunity to obtain cheap and affordable catalysts for hydrogen production. The scientific contribution of these studies is in obtaining new experimental data on the composition of the active phase of the catalysts, the influence of the nature and texture of the carbon supports on their dispersibility and catalytic activity. In other studies of Assoc. Prof. Tsintsarsky, carbon composites based on epoxy matrix have been prepared, whose thermomechanical and tribological properties determine a potential application of the composites as structural material.

Research on the preparation of mesoporous Ce-Fe-Ni nanocomposites encapsulated in carbon nanofibers, as well as the possibilities of their use as electrodes in electrochemical oxygen production, are of important scientific and applied importance. The research of Assoc. Prof. Dr. Boyko Tsintsarsky in the field of the use of adsorbents for the purification of industrial water from heavy metals and organic pollutants has significant scientific and applied contributions with environmental significance. They consist in the preparation and characterization of sorbents with high adsorption capacity towards phenol and other aromatic

compounds, synthesized on the basis of formaldehyde resin and polyethylene wax and those obtained from coal tar and furfural. For the purification of metal cations, a new type of hybrid material has been prepared which combines the ultrafiltration characteristics of polymer membranes with the adsorption properties of activated charcoal of natural or synthetic origin. The developed organic-inorganic hybrid membranes were found to exhibit high adsorption capacity (51%) towards Ni^{2+} cations in aqueous solutions. Activated charcoal was prepared from a polymer waste product, on which the adsorption of mercuric ions was investigated, high adsorption capacity of the adsorbent was found, as well as the influence of the pH of the medium on the process.

In the final part of the habilitation report, Assoc. Prof. Dr. Boyko Tsintsarsky outlines the perspectives in the field of synthesis of new carbon materials (C/C composites, nanotubes, graphene, etc.), improvement of methods for modification of adsorbents and expansion of the raw material base for their preparation. Emphasis has also been placed on the development of advanced technologies for hydrogen storage, production of electrodes for batteries, adsorbents for bacteria and viruses. These directions continue the traditions and deepen the research of the Laboratory of Solid Fuel Chemistry at the IOCP, whose results in the field of carbon materials are highly appreciated and recognized by world science.

In the presented 17 competitive publications of Assoc. Prof. Tsintsarsky in 4 of them he is on the first place, in 4 - on the second, in 3 - on the third and in the rest on the last place. which gives me a reason to believe that the candidate has a significant personal contribution in the synthesis and characterization of carbon materials, as well as in the generalization of the results of research.

Participation in projects and scientific forums

Data on participation of Assoc. Tsintsarsky in 8 projects of which under the National Research Fund - 1, under the National Program "Young Scientists and Postdoctoral Fellows" - 3, under the European Union Horizon 2020 -1. He is a leader of scientific teams in 3 projects - 1 Bulgarian (Fund Scientific Research) and 2 international (Poland and Romania). All projects are on the theme of the competition. He has participated in international symposia and conferences with 12 papers, including 2 plenary, which is a high evaluation and recognition of the scientific activity of Assoc. Prof. Tsintsarsky. He spent 3 months in Poland.

Personal impressions

I know Assoc. Prof. Dr. Boyno Tsintsarsky from the joint contacts of the "Fuels" department at UCTM with the colleagues from the laboratory of CSF, IOCP-BAS. I am impressed by his competence and thoroughness in his scientific activities, as well as by his honest and collegial attitude towards young researchers in the laboratory. I am convinced that his qualities as a talented scientist will contribute to the scientific development and success of the IOCP at BAS.

3. Critical remarks and recommendations

I have no significant critical remarks on the work of Assoc. Prof. Tsintsarsky and the submitted competition materials. Some editorial mistakes have been made in the writing of the habilitation report, which do not reduce the importance of the candidate's scientific contributions. I recommend Assoc. Prof. Tsintsarsky to intensify his work on the training of PhD students in the field of carbon materials.

Conclusion

The scientific activity and the scientific metrics of Assoc. Prof. Dr. Boyko Tsintsarsky, reflected in the competition documentation, meet and exceed the requirements for the academic position of "Professor", according to the Law on the Development of Academic Staff in the Republic of Bulgaria (LADASB), the Regulations for the Implementation of the LADASB, the Regulations for the Implementation of the LADASB of the BAS and the Regulations of the IOCP-BAS.

The scientific achievements of Assoc. Tsintsarsky present him as a well-established and promising young scientist with significant contributions and international recognition in the synthesis and research of carbonaceous materials, which reveal potential opportunities for the development of innovative technologies in energy, ecology and industry.

On the basis of the analysis of the scientific works and their scientific contributions I give my positive evaluation and recommend the Scientific Jury to prepare a report-proposal to the Scientific Council of IOCP-BAS for the election of Assoc. Prof. Dr. Boyko Georgiev Tsintsarsky to the academic position of "Professor" at IOCP-BAS in the professional field 4.2 Chemical Sciences; scientific specialty "Organic Chemistry", for the needs of the laboratory "Chemistry of Solid Fuels".

09.09.2022 г. Prepared the opinion:

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