REVIEW

according to a competition announced in the State Gazette no. 67 of 28.07.2020 for occupation of the academic post **"Associate 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: Dr. Radostina Dimitrova Palcheva, Assisstant Professor in 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.**

Radostina Palcheva was born in 1975. In 1999 she graduated with a master's degree from the Faculty of Chemistry at Sofia University "Kliment Ohridski", and in 2001 she was employed in the Institute of Catalysis, Bulgarian Academy of Sciences (IC, BAS) as a chemist. In 2003 she was enrolled as a full-time PhD student at the same institute. Radostina Palcheva defended her doctoral thesis on "Synergy between the components in NiW / γ-Al_2O_3 catalysts for hydrodesulfurization" in 2006. In 2007, after winning a competition, she was appointed assistant professor at the IC, BAS, where she still works. In the period 2010-2012 Dr. Palcheva specialized at the University of Oslo, Norway, in the field of design of oxide materials for selective catalysis, and in 2014 as a result of a scholarship won, she was in short-term specialization at the Catholic University of Leuven, related to the physicochemical characterization of catalysts for energy production.

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

Dr. Palcheva is a co-author of 25 publications, 21 of which have been published in journals with an impact factor. The applicant participates in the competition with 20 articles, 17 of which have an impact factor and are distributed as follows: 8 of the publications are in journals with quartile Q1, 4- Q2, 3- Q3 and 2- Q4. The articles have been published in prestigious specialized journals such as "Applied Catalysis B: Environmental" (1 pc.), "Applied Catalysis A: General" (1 pc.), Applied Surface Science (2 pcs.), Catalysis Letters (2 pcs.) , Microporous and Mesoporous Materials (1 pc.), Topics in Catalysis (1 pc.) etc.

The publication of the materials is relatively even in the whole period after the defense of the dissertation, as more than 1/3 of them have been published in the last 5 years. These results show a high research activity of the applicant after the defense of the doctoral dissertation. In most of the articles Dr. Palcheva is on the first or second position in the author's team, which is proof of her leading role in the research and interpretation of the results.

Her participation in international and national scientific forums is also very active. On the topic of the competition she presented 26 reports, 5 of which were oral. In the databases WEB OF SCIENCE and SCOPUS were noticed about 297 citations of the publications included in the competition. For two of the articles, published in Micropor. Mesopor. Mater. (2009) and Appl. Surf. Sci., in which the applicant is the first author, a significant number of citations have been observed (45 and 50, respectively). The high citation rate of the articles published in recent years also makes a very good impression. For example, the publication of Dr. Palcheva in Appl. Surf. Sci. (2015) is cited 27 times, and that in Appl. Catal. B: (Environmental) (2018) -30 times. In both publications Dr. Palcheva is a leading author, which once again proves the relevance and high quality of her research.

Assist. Prof. Radostina Palcheva actively participates in the teams for the implementation of projects funded by the National Scientific Fund or in the frame of bilateral cooperation with the Czech Republic and Belgium. In the last three consecutive sessions she is also a coordinator of bilateral projects with Czech Academy of Sciences.

Dr. Palcheva also has active expert activity, reviewing publications in prestigious journals and projects in competitive sessions of the NSF.

The candidate's Hirsch index based on all publications included in the ISI database is 13 (Scopus). The assessments of the candidate by indicators, according to the minimum requirements in Republic of Bulgaria, are listed in Table 1. The total assessment of the candidate on all indicators exceeds almost 2.5 times the minimum set in the requirements. Although points are not required under indicator ***E,*** and they are not included in the applicant's documents, her participation in projects, as well as a coordinator of the bilateral projects provides an additional 120 points. The analysis of the quantitative results of the research shows that Dr. Palcheva fully meets the minimum requirements set by the Low and the corresponding regulations of the IC, BAS.

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	130
D. Scientific publications outside of habilitation thesisis	220	229
E. Citates	60	594
Total	**430**	**1003**

3. Major contributions from the applicant's research activities

The research activity of the candidate is closely related to optimizing the design of catalysts for processes related to environmental protection, such as: production of hydrogen and fuels with low sulfur content, complete oxidation of volatile organic compounds, production of valuable substances for industry, including through the recovery of waste products.

3.1. Evaluation of the habilitation thesis

Dr. Palcheva's habilitation thesis is aimed at studying the catalytic activity of Co (Ni) -Mo (W) mixed oxide catalysts in the process of hydrodesulfurization (CDS) of sulfur-containing compounds. Thiophene and 1-benzothiophene were used as model systems. The influence of a number of factors has been studied, including: the method of preparation of catalysts and supports, their composition and the contribution of a number of modifying additives. Along with the traditionally used Al_2O_3, titanium oxide nanotubes and mesoporous silicates modified with Nb_2O_5 have been studied as carriers for the first time. The effect of subsidizing Al_2O_3 with different amounts of ZnO, as well as the influence of SiO_2 additives on the formation of Ni-Mo catalysts for HDS was studied. The results are summarized in 6 publications in specialized journals with impact factor, respectively 3 of them with quartile Q1, 2- with quartile Q2 and 1- with Q4. With the exception of one, in all articles the candidate is in the first place.

The following more important results from the research described in the habilitation thesis can be noted:

- It was found that the preliminary modification of the alumina support with nickel or cobalt and the subsequent impregnation with Anderson - type hexamolybdate inhibits the formation

of inactive cobalt or nickel aluminate and favors the preservation of heteropoly- anion on the surface of the catalysts. This procedure leads to the production of highly active HDS catalysts, and a particularly good effect on the activity and stability of the catalysts is observed when applying Ni- heteropolyoxomolybdate on Ni-modified Al_2O_3. It has been shown that when using an Al_2O_3 support obtained by mechanochemical treatment, the catalyst has a higher catalytic activity than that of the commercial product.

- A beneficial effect of the use of nitrilacetic acid as a complexing agent in the preparation of NiMo catalysts for HDS has been shown, which is due to the formation of a large amount of sulfide phase containing labile sulfur.

- The conditions for obtaining a highly active catalyst for HDS based on Nb-modified mesoporous silica type SBA-15 have been optimized. For the first time, the effect of the silica support texture on the formation of catalytically active centers was studied. It has been shown that the presence of micropores in HMS silica leads to partial segregation of Nb_2O_5, which changes the mechanism of sulfides formation and complicates the formation of active complex Ni – Mo – S centers.

- It has been demonstrated that the content of active Ni^{2+} octahedral ions, MoO_4^{2-} tetrahedral ions and Mo polymer forms in NiMo / Al – Zn catalysts can be controlled by the Zn / Al ratio and SiO_2 additives in the carriers.

In conclusion, I would like to emphasize that the research presented in the habilitation thesis is a contribution to optimizing the composite catalysts for hydrodesulfurization of diesel fuel and is relevant to environmental protection.

3.2.Evaluation of research activity beyond habilitation thesis.

14 scientific publications, 11 of which are referenced and indexed in a database (WoS / Scopus), with which the candidate participates in the competition, are not reflected in the habilitation thesis and will be the subject of the review below. The research is broad-spectrum, with a strong application. It is aimed at the synthesis of effective catalysts for a number of catalytic processes related to fuels, ecology and quality of life, including hydrodesulfurization of thiophene and 1-benzothiophene, partial oxidation of methane, methane reforming with CO_2, complete oxidation of ethanol, dehydration of glycerol, direct conversion of ethene to propene.

The catalysts are of supported type. For the synthesis of the supports (alumina, silica, mixed oxides, modified mesoporous silica, oxides with perovskite structure), various methods have been used, including hydrothermal, mechanochemical and sol-gel. Both precious and a

number of transition metals are applied as an active component. All investigations is based on in-depth research with various modern physicochemical techniques (XRD, XPS, UV-Vis, FTIR, ^{29}Si MAS NMR, TEM, oxygen chemisorption, etc.), which helps to properly understand the nature of active centers in various catalytic processes.

- I highly appreciate the candidate's work on the preparation of CoMo / γ-Al_2O_3 catalyst and its tests in a pilot plant under pressure in the process of HDS of light fuel fractions. The comparisons with commercial catalysts and the analysis of the results of these studies are valuable source for further optimization of the catalyst formula. These tests are also important, emphasizing the role of pre-modification of alumina with nickel or cobalt and the use of an aqueous solution of ammonium salt of Co (Ni) Mo_6 for the synthesis of highly efficient catalysts for hydro desulfurization of fuels.

The following results are also of significant interest:

- It has been shown that in HDS catalysts based on NiMo loaded on Ce-Al mixed oxide supports, the precursor of the active phase is $NiMoO_4$, which is formed as a result of the interaction of Ni and Mo with Al_2O_3.

- Of interest are studies on the formation of active WS_2 phase in NiW modified mesoporous SBA-15 and HMS silicas. For the first time, a comparison was made of the nature of the metal (Al, W, Ti) modifying the SBA-15 support, its amount and the W-precursor used on the catalytic activity of NiW catalysts for HDS of thiophene. The demonstrated low hydrogenation activity of the investigated catalysts in comparison with NiW / γ-Al_2O_3 catalyst has a direct bearing on the optimization of the catalysts for obtaining quality and environmentally friendly fuels by combining HDS, hydrocracking and hydroisomerization.

Conclusions

The research of Dr. Radostina Palcheva is a significant contribution to the development of effective catalysts for use in petrochemistry, alternative fuels and ecology. Much of the candidate's research is focused on the production of clean fuels by developing new catalysts for HDS, but there are also data on effective catalysts for hydrogen production by reforming methane with CO_2 or its partial oxidation, elimination of ethanol emissions, obtaining valuable chemicals by processing products that can be extracted from waste biomass. The wide range of preparation techniques, combined with detailed and in-depth analysis of the composition, surface characteristics and catalytic behaviour of the obtained materials, show a well-established scientifically based approach in the candidate in optimizing the properties of catalysts for different applications. I highly appreciate Dr. Palcheva's efforts to go beyond

laboratory research by testing one of the catalysts for HDS of light fuel fractions in a pilot plant under pressure.

The candidate demonstrates very good quantitative indicators, which many times exceed the requirements of the Low of the scientific degree and academic staff in Bulgaria and the Regulations of IC, BAS to him. The results of the research have been published in prestigious journals, and the leading position of Dr. Palcheva in almost all publications shows her commitment to both the planning and conduct of the experiment and the analysis of the results. In addition, I want to emphasize the high citation rate of research results, which proves their relevance and importance.

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 "***Associate 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. Radostina Palcheva, currently "Assistant Professor" at the same institute, the academic position of "***Associate Professor".***

Sofia, 27. 10.2020 Reviewer:

/ Prof. D.Sc. Tanya Tsoncheva /