REVIEWS

According to a competition announced in the state gazette No. 36 of 03. 05. 2019 for occupation of the academic position of "Associated professor" in the professional field 4.2. Chemical sciences (Chemical kinetics and catalysis) for the laboratory "Solid surface reactivity" of Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences with sole **candidate**: Ass. Prof. Dr. Stanislava Metodieva Andonova, employee at the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences

Reviewer: Prof. DSc Tanya Stoyanova Hristova, Institute of Organic Chemistry with Center for Phytochemistry, Bulgarian Academy of Sciences

1. General information on the applicant.

Dr. Stanislava Andonova was born in 1977 in Sofia. She completed her higher education in 2000 at the University of Chemical Technology and Metallurgy, Sofia, specialty Technology of Inorganic Substances. In 2001, she enrolled as a full-time doctoral student at the Institute of Catalysis, BAS. In 2004 she was appointed as a chemist and in the period 2005-2013 as an assistant at the same institute. From 2013 until now, Dr. Stanislava Andonova has been working at the Institute of General and Inorganic Chemistry, BAS, initially as a chemist, and since 2015 she has been selected as assistant professor. In 2005, she defended her doctoral dissertation on "Preparation and characterization of modified Ni(Co)-Mo hydrodesulfurization catalysts". In 2006, she won a Maria Sklodowska-Curi scholarship, which gives her the opportunity to specialize in Romania in the field of micro- and nanotechnology. From 2007 to 2013 she was postdoctoral fellow initially in Turkey and then in Sweden working on problems, related to the characterization of nanoscale catalysts and the resolution of environmental problems arising from sulfur and nitrogen oxide contamination.

2. Overall assessment of the applicant's scientific activity.

Dr. Stanislava Andonova is the co-author of 32 publications, 27 of which are referenced in the WEB OF SCIENCE and SCOPUS databases. 23 of these articles have been published in prestigious journals categorized as Q1 and Q2, of which 8 have been published in J. Phys. Chem.; 5 articles in Appl. Catal. B: -Environmental; 2 articles each in Appl. Catal. A: General and Catal. Lett. and 1 article each in Catal. Today, Mol. Cat., Microporous and Mesoporous Matar., Chem. Commun., J. Catal., Catalysis and Topics in Catal. Dr. Stanislava Andonova is also co-author of patent filed in China, Germany and the United States, which is related to the synthesis of Fe-SAPO-34 catalyst and its use for the reduction of NOx. The applicant participated in this competition with 22 of these publications. 15 of them have quartile Q1, 4-Q2 and one patent. In addition, two patents are presented. The articles have been published approximately evenly over the years, with particularly good activity after the post-doctoral training. The total number of points for the submitted publications exceeds approximately 1.5 times the minimum requirements laid down in the Regulations for the IGIC, BAS. I would also like to underline the leading role of the applicant in almost 70% of publications. The high quality of the applicant's scientific production is evidenced by the high citation. The total number of citations noted is 384, with 315 in journals included in the ISI database. According to this indicator the applicant exceeds more than 5 times the national and specific requirements of IGIC, BAS. The citations for the articles included in the competition are 215. The results of the research were reported at 24 scientific conferences in Bulgaria and abroad. The applicant's Hirsch Index is 2 times the minimum requirements of the IGIC, BAS. According to the applicant, she has participated in the implementation of 3 national and 3 international projects. They have not been provided with supporting evidence and have not

been included in the reference for meeting the minimum national and additional requirements of the IGIC, BAS.

3. General contributions from the applicant's research activities

The applicant's research activity is aimed at developing new effective catalysts and adsorbents for the elimination of harmful emissions and the selective separation of gas mixtures. The main contributions from the research work included in the Habilitation thesis and in the non-habilitation publications with which the candidate participates in the competition will be discussed in detail below:

3.1. Assessment of the Habilitation thesis

The applicant's Habilitation thesis includes 8 Q1 quartile publications and one US patent. In all publications, she is the first or corresponding author. The studies described in the Habilitation work are aimed at developing efficient catalysts based on metal oxides or metal-exchanged zeolites for elimination of nitrogen oxide emissions. Much of the research aims to clarify the role of the modifying agent on the structural, adsorption, and reduction characteristics of the $Pt/BaO/Al_2O_3$ catalyst, which is traditionally used in the process of accumulation-reduction destruction of NO_x in order to improve its activity and stability. The main method used by the applicant is Infrared spectroscopy of adsorbed molecules in combination with Mass spectrometric and calorimetric analysis, TPR-TPD, X-ray diffraction, Raman spectroscopy. In my opinion, the major contributions of the investigations are the elucidation of the mechanism of the increasing catalytic activity in a CeO_2 and ZrO_2-doped catalysts. Through the original IR spectroscopic study of H_2/D_2 adsorption, the authors demonstrated the formation of superoxide intermediates on a defective reduced surface and the generation of additional hydroxyl groups on an oxidized surface. A significant result of

the micro-calorimetric studies performed is the proven difference in the heat of adsorption for surface and bulk compounds and the influence of CO_2 on the adsorption of NO_x. The combination of the results of dynamic CO chemosorption and the dissociation of N_2O make clear the beneficial effect of Rh on the low-temperature desorption of NO_x. TiO_2 additives have been shown to greatly increase the adsorption capacity of nitrogen oxides, which is controlled by the dispersion of TiO_2.

In the Habilitation thesis, the applicant considers the possibility of improving the activity of metal-exchanged zeolites in the selective reduction (SR) of nitric oxides with ammonia. The innovative nature of patent-protected research must be emphasized here. For the first time, the author team, with the participation of the candidate, synthesizes Fe-SAPO-34 and investigates its catalytic properties in SR of NO_x with ammonia. The catalyst obtained showed improved hydrothermal stability compared to the conventional Cu/CHA used. A very original solution for improving the catalytic activity in SR of NOx with ammonia over a wide temperature range is the development of a monolithic layered catalyst containing Cu/CHA and Fe-SAPO-34. Also noteworthy are the results of studies on the deactivation of Cu/BEA in the presence of phosphorus-containing compounds. Through the use of H_2-TPR and photoelectron spectroscopy, deposition of various phosphate, meta- and hydrogen-phosphate compounds on the surface of the catalyst was detected.

3.3. Assessment of research beyond Habilitation thesis.

13 of the articles, participated in the competition, were not reflected in the Habilitation thesis. Of these, 7 are Q1 quartile and 4 are Q2 one. Two patents filed in China and Germany are also included. Research is aimed at developing new and effective:

- metal oxide catalysts for NO_x reduction by accumulation-reduction catalysis;

-metal-exchanged zeolite catalysts for the selective catalytic reduction of NOx with ammonia;
-adsorbents for gas purification and selective separation of gas mixtures.
The main approach is IR studies of adsorbed molecules, but the applicant is skillful in using other advanced physicochemical techniques, including: X-ray diffraction, Raman spectroscopy, transmission electron microscopy, microcalorimetric studies etc.
The following significant fundamental and applied contributions from these studies can be outlined:

1. Evidence is provided regarding the mechanism of NO_x adsorption and reduction with hydrogen or ammonia and the effect of promoting of the traditional accumulating-reducing Pt/ BaO/γ-Al_2O_3 catalyst with Rh. The adsorption-catalytic studies performed on monolithic catalysts show that the addition of Rh contributes to the release of O_2 as a result of the dissociation of N_2O and promotes the migration of the adsorbed NO_x compounds, thereby reducing the desorption temperature of NO_x.

2. It has been shown that the substitution of Pt in the composition of the traditional catalyst for the reduction of nitric oxides with FeO_x can significantly affect the nature and rate of formation of intermediate N-containing surface compounds. Ag addition to γ-Al_2O_3 can improve the adsorption of nitrogen oxides at low temperature and its desorption at relatively low temperatures. These results are essential for optimizing the composition of the catalysts.

3. An original study of the conversion of nitric oxides in the presence or absence of NO_2 has shown that the poisoning of Cu/SAPO-34 from SO_2 during the selective reduction with ammonia, especially in the presence of oxygen, is due to the adsorption of SO_2 on Cu^{2+} centers, blocking the redox process. The results obtained by varying the Cu content in the samples are very interesting. The elucidation of the effects on the oxidation and reduction of nitrogen oxides, as well as the formation of NH_4NO_3 intermediates, opens the possibility of optimizing the composition of the catalysts.

4. For the first time, by using CO_2 spectroscopy, CO_2 shrinkage of the MIL-53 (Al) pores has been demonstrated as a result of the coordination of CO_2 with the surface OH groups and the subsequent formation of dimer structures. Research aimed at clarifying the content of surface OH groups for increasing the adsorption capacity of MOFs with respect to CO_2 is very interesting.

Conclusion

Dr. Stanislava Andonova's research is a significant contribution to development a science-based approach to the synthesis of effective catalysts and adsorbents for environmental protection. In his research, the candidate skillfully combines IR spectroscopic studies of adsorbed molecules with appropriate modern physicochemical methods. The information received has been thoroughly interpreted in order to gain an understanding of the mechanism of the processes and the possibilities for their management. A very strong focus in the applicant's work is the innovative approach in the development of new environmental materials, as evidenced by the development of a patent filed in China, Germany and the USA. The design and conduct of the experiments in order to obtain the maximum information on the investigated complex catalytic systems is also an originality. The proof of the high quality of the candidate's research is the large number of publications in leading journals in the respective field and high citation, many times exceeding the requirements in Bulgaria and IGIC, BAS. The high proportion of publications in which the applicant is the lead author indicates his high erudition in the field in which he works and the possibility of a leadership position in research. Therefore, I strongly recommend that the members of the Honorable Scientific Jury and the Honorable Scientific Council of IGIC, BAS, award Dr. Stanislava Andonova, currently Assistant Professor at the same institute, the academic position

“Associated Professor” in the professional field 4.2. “Chemical Sciences”, scientific specialty “Chemical Kinetics and Catalysis”.

Sofia , 07/13/2019 Reviewer:

/ Prof. DSc Tanya Hristova /