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

from Prof. Zara Cherkezova-Zheleva, Institute of Catalysis - Bulgarian Academy of Sciences (member of the Scientific Jury)

on the competition for occupying the academic position **assoc. professor** in the professional field 4.2. "Chemical sciences", scientific specialty 01.05.16 "Chemical Kinetics and Catalysis" for the needs of the Institute of General and Inorganic Chemistry at the Bulgarian Academy of Sciences, Laboratory "Reactivity of solid surfaces",

announced in the State Gazette 36/03.05.2019

According to the Order № РД-0987/01.07.2019, issued by the Director of the Institute of General and Inorganic Chemistry, BAS (IGIC), I was appointed as a member of the Scientific Jury for accomplishing the procedure in the competition for occupation of the academic position „assoc. professor" in IGIC-BAS in the professional field 4.2 „Chemical Sciences", scientific research area „Chemical Kinetics and Catalysis", for the needs of the Laboratory "Reactivity of solid surfaces" in IGIC announced in the State Gazette 36/03.05.2019.

1. Attitude on the obtained materials:

Assist. Prof. PhD Stanislava Metodieva Andonova is the only candidate, applying for the academic position "Associated Professor" in the competition, announced by the IGIC-BAS for the needs of the Laboratory "Reactivity of solid surfaces". She has submitted a full set of application documents according to the requirements of the Regulation for the Terms and Procedure for Acquisition of Academic Degrees and for Occupation of Academic Positions in the Institute of General and Inorganic Chemistry of BAS. Assist. Prof. PhD Stanislava Metodieva Andonova fulfils all relevant law requirements for occupation of the academic position "Assoc. Professor". She has submitted 32 scientific research publications in total. 22 of them were published after receiving of PhD degree and are an object of the current review. Based on the relevant summary submitted by the applicant it is obvious that she fulfils and even exceeds both minimal National requirements and specific requirements of IGIC, BAS. It should be noted that her score for group Д, Б, Г and Ж indicators is far above the relevant requirements. The total score of the applicant is 1075 points while the minimal required points are only 500.

2. Short biographical data about the applicant:

Assist. Prof. PhD Stanislava Metodieva Andonova graduated the University of Chemical Technology and Metallurgy in Sofia in the year 2000 acquiring the specialisation "Inorganic Chemical Technologies". In 2005 she was awarded with a PhD title on the topic „Preparation and characterization of modified Ni(Co)-Mo catalysts for hydrodesulfurization" under the supervision of Prof. L. Petrov and Assoc. Prof. Ch. Vladov. After she won a competition in 2005 she became Assistant Professor at the Institute of Catalysis-BAS. Dr. Andonova works at the IC-BAS on this position until 2013. From 2013 to 2015 she was appointed as a chemist at the IGIC-BAS. Since 2015, after winning a competition, she has been working as an Assistant Professor at IGIC-BAS. As of 01.07.2019 she has an internship in the specialty, which is more than required in the normative documents for the competition for the occupation of the academic position of Assistant Professor at IGIC-BAS. The research scholarships earned by the applicant for specializing in well-known scientific centres abroad make a significant contribution to its scientific development:

- Research fellowship under the European program "Maria Skłodowska - Curie" on the topic „Intensive Program for Transfer of Knowledge to Eastern European Reference

Pole for Micro- and Nanotechnologies – NANOTEC-EST", Politehnica University of Bucharest, Romania (4 months, 2006).

- Postdoctoral research position on the topic „Surface Science Studies on Two and Three Dimensional Nanocatalysts for Solving Catalytic Sulfur Poisoning Problem", Bilkent University, Turkey (2007-2010).
- Post-doctoral research position on a project entitled "Study of catalytic processes for reduction of nitrogen oxides to decrease emissions from engines using conventional or alternative fuels", Competence Centre for Catalysis, Chalmers University of Technology, Sweden (2011 - 2013).

3. Analysis of the scientific and innovative research activities of the candidate and their applications in practice

Scientific research publications:

Dr. Stanislava Andonova submitted 32 publications in total for participation in the competition. These include 30 scientific articles and 2 patent applications, which have been published in refereed editions. 27 of the editions have been refereed by Scopus / Web of Science. There is no evidence of plagiarism in all presented scientific works. The candidate participated in the competition with 22 publications. 20 of them are articles in scientific journals included in the Scopus / Web of Science database, as well as 3 patent applications. The publications submitted for participation in the competition do not duplicate the ones presented for obtaining a PhD degree. It should be noted that Dr. Andonova is the first author in most of the competition publications (19 out of 32, i.e. 59%). In 8 out of 32 (25%) she is the second author. Among the 22 publications that have been printed since her PhD, she is the first or second author in 59% (13 out of 22) and 23% (5 out of 22) of the papers. This shows her leading contribution to the development of the presented scientific investigations and the related scientific and innovative contributions. The most of Dr. Andonova's research results have been published in prestigious international journals in area Q1 (WoS or Scopus): Catalysis Today, Journal of Physical Chemistry C, Molecular Catalysis, Applied Catalysis B, Chemical Communications, Microporous and Mesoporous Materials, Physical Chemistry Chemical Physics, Journal of Catalysis, et al.

The publications participating in the competition were divided into two groups, covering the B and Г indicators, according to the Rules of the conditions and order for acquiring academic degrees and for taking up academic positions at the IGIC - BAS. In the first group, indicator B - "Habilitation work - scientific publications in journals that are referenced and indexed in world-famous scientific information databases (WoS or Scopus)" are presented 8 publications and one patent application. They are valued at 200 points. According to this indicator, the required 100 points were repeatedly exceeded by the received 200 points. It should be noted that all of the 8 publications are in the Q1 area (WoS or Scopus). Dr. Andonova is the first author in all 9 of them. In the second group, 11 publications in the Q1 and Q2 area covering indicator Г-7 are presented, with a total of 255 points. In the same group, are presented also 2 published patent applications covering indicator Г-10 and rated with 30 points. So, the indicator Г has a total of 285 points, 220 points have been required. This gives Г a total of 285 points with the required 220 points.

Participation in national and international scientific events:

The investigation results of Dr. Andonova are presented as a total of 24 scientific presentations at international and national scientific forums with 6 oral presentations at national events, as well as 7 oral and 11 poster presentations at international scientific forums. The most of the oral reports (10 out of 13) as well as 5 out of 11 posters are presented by Dr. Andonova. Participation at prestigious scientific forums and presentation of scientific papers as oral or poster reports has a significant impact on her scientific career, even that they have no formal reflection on the competition evaluation indicators. The applicant participates in a

team of 3 international and 3 national scientific or educational projects. Presented scientific investigations and research papers are closely related to objectives and deliverables of these projects.

International recognition and significance of the scientific results

The large number of citations of Dr. Andonova's research works is the evidence of the international recognition and significance of her scientific results. The total number of noticed citations of 24 publications with her participation at the date of submitting her documents is 384, out of them 315 in Scopus and in Web of Science. 18 papers included in the competition, were mentioned at total of 254 citations and 215 of them were in Scopus / Web of Science database. Thus, under indicator Д the candidate receives 430 points, which more than 7 times exceed the required 60 points for the position of "associate professor" in accordance with the Rules for the conditions and the order for acquiring scientific degrees and for occupying academic positions at IGIC - BAS. The Hirsch index (h-index) in Scopus is 10 (indicator Ж). Dr. Andonova is registered at NACID (https://ras.nacid.bg/dissertation-preview/28824), where she is recognized for her PhD degree and the academic position of "Assistant Professor".

4. Contributions of the scientific and innovative research activities of the candidate

The main scientific contributions of fundamental and innovative scientific research of Dr. Andonova are focused on important topics of European and national priorities - design and application of new catalytic materials for environmental protection, with application in different technologies of the automotive industry to control atmospheric air pollution with nitrogen oxides (NO_x) emissions. The **habilitation work** of Dr. S. Andonova includes the results of research in two thematic directions (Publications Nos. 1-9):

1. Development and investigation of new effective metal oxide catalysts used for NO_x reduction by accumulation-reduction catalysis.

2. Development and investigation of new metal-exchanged zeolites used as effective catalysts for selective catalytic reduction of NO_x with ammonia.

The fundamental and applied research presented by the applicant in **other papers outside the habilitation work** (Nos. 10-22) are included in 13 publications. Dr. Andonova's scientific and applied contributions are related to the design and application of new materials as catalysts and adsorbents for environmental protection for control of harmful emissions of nitrogen oxides (NO_x) and carbon dioxide (CO_2) into the ambient air. The applicant's scientific contributions from out-of-habilitation studies add a third thematic area to the above mentioned ones:

3. Investigation of new and perspective materials used as adsorbents for gas purification and selective separation of gas mixtures.

In the first two thematic directions in out-of-habilitation work, the studies presented as a habilitation work were continued and expanded.

The scientific achievements at the first thematic direction are related to the scientifically grounded search for new catalysts for NO_x reduction through accumulation-reduction catalysis connected to the increasing environmental requirements of the automotive industry, as well as the development of new technologies and materials which allow more precise control and complete elimination of NO_x emissions. It was investigated the effect of surface modification of the studied materials on the mechanism and the type of the formed adsorbed compounds, the valence and coordination state of supported metal phases, surface acidity, etc. The application of *in-situ* Fourier transform infrared (FTIR) spectroscopy of adsorbed molecules of CO, NO, NO + O_2, H_2, D_2, etc. are widely used and developed. Dynamic adsorption / desorption measurements determine the basic adsorption characteristics of the tested samples. Catalytic tests with monolith catalysts were conducted on a pilot flow

reactor system under conditions similar to those in industrial practice. Physico-chemical methods of analysis include a mass spectrometer detection system and an IR gas analyzer to measure the concentration of the individual components in the gas mixture. These methods are combined by micro-calorimetri analysis, temperature-programmed desorption / reduction (TDP / TPR), X-ray diffraction, energy-dispersive X-ray (EDX) spectroscopy, BET surface area analysis, transmission electron microscopy, Raman spectroscopy, etc. Systematic studies have been carried out to follow the effect of modifying the structure and modelling the new adsorption and reduction properties of the classic $Pt/BaO/\gamma\text{-}Al_2O_3$ catalyst by adding metals or metal oxides:

a) the influence of the additives of CeO_2 and ZrO_2 on the catalyst and their role in the process of accumulation and reduction of nitrogen oxides were determined. The mechanism of interaction of $Pt/CeO_2/ZrO_2/\gamma\text{-}Al_2O_3$ catalyst with H_2/D_2 was investigated by *in-situ* FTIR spectroscopy (Nos. 1-2).

(b) a systematic study of the NO_2 adsorption on $Pt/BaO/\gamma Al_2O_3$ catalyst (No. 3) lead to important practical results for significant differences in the heat of adsorption of the formed surface compounds compared to the thermodynamic data for their bulk analogues. These results demonstrate a possible way to measure the heat released due to the NO_2 adsorption only, excluding the contribution, originating from the NO_2 disproportionation and dissociation that occur when NO_x breakthrough is detected. Supported data has been found to the negative impact of CO_2 on the process of adsorption of nitrogen oxides. The results also provide evidence in support of the detrimental effect of CO_2 on the NO_x uptake process.

c) the detail study reveals the change of mechanism of adsorption and reduction of NO_x with hydrogen or ammonia in result of promoting of the classical $Pt/BaO/\gamma\text{-}Al_2O_3$ catalyst with Rh (Nos. 4, 10-11). Higher dispersion of active phase and synergistic effect of adding Rh was obtained. This plays a significant role on the adsorption capacity, as well as on the migration rate of the adsorbed NO_x compounds on the surface, providing subsequent desorption of NO_x at lower temperatures.

d) the optimal surface structure of the triple oxide $BaO/TiO_2/\gamma\text{-}Al_2O_3$ system with a high adsorption capacity to NO_2 (Nos. 5-6) was found by the addition of various metal oxides (TiO_2, FeO_x, CeO_2) to the catalyst, as well as by varying the conditions of preparation of the TiO_2 additive.

(e) the effect of the addition of FeO_x to the two-component $BaO/\gamma Al_2O_3$ oxide system and its role in the NO_x uptake have been established (No. 12). Ternary $FeO_x/BaO/\gamma Al_2O_3$ oxide systems were synthesized with different content of the individual components. The structure and morphology of formed new active sites predetermined the differences in NO_2 adsorption capacity of the samples. The addition of Fe into the $BaO/\gamma\text{-}Al_2O_3$ system significantly alters the low-temperature NO_x uptake mechanism. Fe domains provide additional NO_x adsorption sites in the Fe/Ba/Al system where the adsorbed NO_x species are ultimately stored as bidentate nitrates. Fe domains were found to exist in the form of different oxides whose surface morphology, iron ion oxidation state and the accessibility to gas phase NO*x* are significantly dictated by the composition of the Fe/Ba/Al system. Different oxidation and reduction state of the Fe domains change the rate of nitrite to nitrate oxidation process.

f) High loaded Ag / $\gamma\text{-}Al_2O_3$ adsorbent was found to be suitable as a temporary NOx trap under cold start, so called passive NO_x storage at low temperatures followed by NO_x reduction with increasing temperature (Nos. 13 - 14). Higher amount of NO_x can be stored on the synthesised new material than on the conventionally used $Pt/BaO/\gamma\text{-}Al_2O_3$ catalyst. An important technological advantage of this adsorbent is the possibility to regenerate it after saturation with NO_x at relatively low temperatures (below 400 ° C).

Dr. Andonova's research activities include also original scientific and applied contributions of significant practical importance in the field of the research and development

of new metal-exchanged zeolite catalysts. The investigations are focused on the design of a catalytic system that can reduce NOx both at low as well as high temperature which also is stable at high temperature. The material should be also resistant to deactivation due to the presence of water vapours, CO_2, sulphur and phosphorus compounds in the exhaust gas mixtures. 3 scientific papers (Nos. 7-9) and 3 patent applications have been published as a result of the research in **the second thematic direction**. Dr. Andonova is the first author in the team who make an important scientific and applied discovery, published at paper 7 and patent applications 8, 15 and 16 with industrial ownership and copyright of Ford Global Technologies. The aim of the investigations was the preparation of new highly active catalysts for prevention of environmental problems associated with atmospheric air pollution by NOx from diesel vehicles. So, a new type of unique highly active Fe/SAPO-34 material was synthesized and tested with significantly improved high temperature stability compared to commercially available Cu/CHA catalyst. The synthesized Fe/SAPO-34 catalyst demonstrated a significantly improved NO_x reduction performance at high temperatures (600–750 ◦C) when compared to a commercial Cu/CHA system. The combined system (Fe/SAPO-34 + Cu/CHA) exhibited a very good performance in a large temperature interval (200–800 ˚C) that encompasses most diesel exhaust gas conditions.

Studies (Nos. 9 and 17) gave a better understanding on an important dependencies and mechanism of catalyst chemical poisoning and deactivation in NO_x emissions cleaning process of diesel vehicles as a result of the presence of various impurities in biodiesel exhausts and lubricant additives. Comparative analyzes were performed of the catalytic behaviour of fresh and poisoned samples of Cu - exchanged BEA zeolite and Cu/SAPO-34 catalyst over a wide temperature range in the presence of phosphorus-containing impurities or respectively SO_2. A comparison was made with the mechanism of the corresponding catalytic reaction in the absence or presence of NO_2 in the gas mixture.

An in-depth analysis on effect of Cu-loading on different reactions involved in NH_3 selective catalytic reduction (SCR) over Cu-BEA catalysts has been performed in paper No. 18.

In **the third thematic direction** have been prepared materials with application in membrane technologies as adsorbents for the capture and storage of CO_2, as well as for the purification and selective separation of gas mixtures (Nos. 19-21). Applicant's scientific and innovative contributions are related to clarification of the nature of adsorption centers and the geometry of guest molecule coordination on metal-organic frameworks (MOFs). Using so-called hydrogen bonding method by FTIR spectroscopy of two probe molecules (CO and N_2), it was determined the surface acidity of MIL-53 (Al), which is a new type of MOF structure. Three types of structural hydroxyl groups involved in hydrogen bonding to the lattice have been identified. There is no correlation found between the acidities of the hydroxyls, and the main reason for this is the pre-existing H-bond. An important methodological contribution is the proposed method for the estimation of the intrinsic frequency of the OH groups (i.e. if not participating in H-bonds), based on the analysis of the spectral data obtained. The conclusions made in this paper considerably broaden the applicability of the H-bond method for assessing protonic acidity of materials and systems where the OH groups are preliminarily involved in H-bonding. The FTIR spectroscopic analysis revealed the CO_2 adsorption forms on MIL-53 (Al) and NH_2-MIL-53 (Al) at low temperatures (Nos. 20 - 21). The vibrational interaction of the CO_2 molecules adsorbed on the adjacent centers with dimer formation has been registered. The first spectroscopic evidence of interaction between CO_2 and the hydroxyls H-bonded to amino groups was found. MIL-53 (Al) is characterized by high adsorption capacity with respect to CO_2. Based on the IR data in Ref. 22, an in-depth comparative analysis of this process was performed by the following samples: MIL-53 (A1), MIL-53 (A1) -OH_{25}, with

improved CO_2 adsorption capacity; and MIL-53 (A1) -OH_{75}, with low CO_2 adsorption efficiency. The obtained results have an important practical application.

Based on the review of the submitted documents for the announced competition and my personal opinion, it can be concluded that Dr. Stanislava Andonova is a young and active scientist with great potential for systematic research and in-depth investigation, whose competence is very much appreciated. The discussed scientific contributions and the results achieved by Dr. Andonova are a step forward for development of new catalysts and adsorbents for improving the ambient air quality according to the respective National and European directives. The author's contributions are significant and correctly presented. They logically follow the obtained results. The scientific and innovative contributions of her work are mainly related to development of new innovative approaches that provide more precise control and more complete removal of NO_x emissions. Applicant's scientific papers submitted for participation in the competition are completely in the field of thematic area "Chemical kinetics and catalysis" and in particular are fully in line with the thematic area "Reactivity on solid surfaces".

CONCLUSION: Documents and materials presented by Assist. Prof. Dr. Stanislava Andonova meet all the requirements of the Law for the Development of the Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the corresponding rules for the implementation of the law in the IGIC - BAS. The candidate submitted a sufficient number of scientific papers, published after receiving the PhD degree. The obtained results based on the research activity of Dr. Stanislava Andonova are original and have significant scientific contribution to the studied area. They completely fulfilled the relevant requirements of IGIC for occupation of the academic position "Associate Professor" in the field of competition and are fare above them. I strongly support the application and also recommend to the members of the Scientific Jury and to the Scientific Council of the Institute of General and Inorganic Chemistry to award to the Assist. Prof. Dr. Stanislava Metodieva Andonova the academic position "Associated Professor" under the direction 4.2. Chemical Sciences, 01.05.16 "Chemical Kinetics and Catalysis".

08/27/2019
Sofia

Reviewer:

(Prof. Dr. Z. Cherkesova-Zheleva,
Member of the Scientific Jury)