REVIEW

by Prof. DSc Krasimir Ivanov Ivanov - Department of General Chemistry, Agrarian University - Plovdiv, (now retired), on the materials submitted for participation in the competition for the academic position of Associate Professor at the Institute of General and Inorganic Chemistry at the Bulgarian Academy of Sciences

By Order No. RD-09-130 of 17.07.2023 of the Director of the Institute of General and Inorganic Chemistry, BAS (IGIC), I have been appointed as a member of the scientific jury in the competition for the academic position "Associate Professor" in the professional field 4.2 "Chemical Sciences", scientific specialty "Chemical Kinetics and Catalysis", announced for the needs of the laboratory "Materials and Processes for Environmental Protection" of IGIC.

1. General presentation of the materials received

The only candidate in the competition for the academic position of "Associate Professor", announced in the Newspaper of State, issue, dated 26.05.2023 and on the Internet page of the IGIC, is Dr. Ralitsa Hristova Velinova. The set of materials submitted by Dr. Velinova is in accordance with Article 29 of the Law on Academic Degrees and Academic Positions in the Bulgarian Academy of Sciences, Article 12 of the Regulations on the Conditions and Procedure for the Acquisition of Scientific Degrees and Academic Positions in the Bulgarian Academy of Sciences. For participation in the competition, the candidate has enclosed a total of 17 scientific publications, all of them published after 2019 (after obtaining a doctoral degree), and all the documents required for participation in the competition for AP "Associate Professor" at the IGIC.

2. Brief biographical details of the applicant

Dr. Ralitsa Velinova graduated from the Higher Institute of Chemical Technology - Sofia in 2001 with a degree in Materials Technology and Materials Science, Specialization: Silicate Materials. Immediately after graduation, she specialized for five months at the University of Aveyro, Portugal. From March 2008 to 2010 he worked as a chemist, and since November 2010 he has been a chief assistant in the Analytical Chemistry Laboratory at the IGIC. In March, 2010 she defended her PhD thesis on "Ancient and medieval glass in Bulgarian lands". From October 2017 until now she has been a chief assistant in the Laboratory of Environmental Materials and Processes.

3. Evaluation of the candidate's scientific and applied activity

Publication activity

- *Scientific publications:*

The total number of scientific publications of Dr. Velinova is 38 (32 of them with impact factor) and one book chapter. In the announced competition she participated with 17 publications, 16 of which with impact factor, and the article "Pt bimetallic Pt-Cu nanoparticles supported on mordenite as a catalysts for complete VOC oxidation" is the first chapter of the book "Heterogeneous Nanocatalysis for Energy and Environmental Sustainability, Volume 2: Environmental Applications, John Wiley & Sons. Six of the publications are in journals with the highest Q1 rank, including *Chemical Engineering Journal* (IF 10.6), *Catalysis Today* (IF 6.6), *Applied Catalysis A: General* (IF 5.7), and others. Six of the articles were Q2 ranked and the remaining 4 were Q3 ranked. All articles submitted to the competition were published in the period 2019 - 2023 and are in the research specialty Chemical Kinetics and Catalysis.

No claims have been made by the co-authors of the publications to the participation of the candidate in the competition. No other information on incorrectness or elements of plagiarism in the materials submitted for the competition has been received.

- *Participation in national and international scientific forums:*

The list of Dr. Velinova's participation in scientific forums is impressive - 89 in total, 61 of them international. All of the presented papers are in the professional field 4.2 "Chemical sciences", and a significant part of them - in the scientific specialty "Chemical kinetics and catalysis".

- *Response in the scientific literature:*

The response in the scientific literature to Dr. Velinova's publications is impressive for a non-habilitated lecturer. The total number of noted citations (excluding author citations) of publications with her participation is 168, and those submitted for the competition - 72 (all in Web of Science and Scopus). The Hirsch index (h-index) at the date of the competition was 6. It should be borne in mind that all the publications submitted to the competition are from the last 5 years and their potential for a serious impact in the scientific literature is yet to unfold.

According to Art. 29, par. 5. 5. of the Law on Research and Development of the Academic Staff in the Republic of Bulgaria and in the Regulations for its implementation, as well as the enhanced criteria of the Bulgarian Academy of Sciences and the IGIC-BAS, candidates for the acquisition of the position of Associate Professor must meet the minimum national requirements. From the summary submitted by Dr. Velinova, it can be seen that she exceeds the minimum requirements and the specific requirements of the IGIC in all indicators, with the total number of points from the materials for participation in the competition being 639 against the minimum requirements of 500.

4. Scientific and applied contributions

- ***Scientific contributions:***

The scientific research with which Dr. Velinova participated in the competition is entirely in the field of heterogeneous catalysis and is related to the search for new solutions for the disposal of waste gases containing VOCs, as well as to the extension of the scope of research on efficient metal and oxide catalytic systems with the potential to solve important environmental problems.

The main scientific and applied contributions of the candidate are related to the synthesis and characterization of new active materials as catalysts for the complete oxidation of VOCs with emphasis on the application of instrumental methods for the characterization and determination of their adsorption and redox properties and the mathematical models developed in the Materials and Processes for Environmental Protection Laboratory for the determination of the probable mechanism of the oxidation processes. They are described in detail in the attached Habilitation (in 4 of the publications included in the reference Dr. Velinova is the first author, and in 2 - the second) and Author's Reference, which synthesizes the most important results of the research with which Dr. Velinova participated in the competition. I will try to briefly summarize the most significant results and contributions in my opinion, focusing on those in which the candidate played a leading role.

All research is fully in line with the EU's main priorities - Environmental Protection, Green Energy and Healthy Living:

1. Applied metal catalysts for VOC oxidation and environmental protection:

The active component of the investigated catalysts contained palladium and platinum, and γ-Al_2O_3, tungstates, zeolite type ZSM-5 with different Si/Al ratios (23, 40 and 100), SBA-15, silica, mordenite and stainless steel (Aluchrom VDM®) were used as supports (publications 1, 6, 11, 13, 14 and 17). The composition of the synthesized catalysts varies over a wide range: Pd/La_2O_3-CeO_2-Al_2O_3, Pd/Al_2O_3- La_2O_3-CeO_2, Pd/Al_2O_3 catalysts modified with different

transition elements (Co, La, Ce, Ni, Mn), PtCeTi-SBA-15 and bimetallic Pt-Cu nanoparticles supported on mordenite. In the model reactions the problematic for oxidation methane and propane were selected and an attempt was made to overcome one of the main disadvantages of the catalysts used - their low thermal stability.

In Publication 1 (Dr. Velinova is the first author, 23 citations), a complex study of the behavior of the model system Pd/La_2O_3-CeO_2-Al_2O_3 is conducted. It includes data on catalytic activity, thermal stability, water vapour effect, SO_2 stability and applicability of the synthesized material as an active phase in the preparation of a monolithic catalyst for methane emission abatement. The support was prepared by sol-gel method and the active component was applied by impregnation. The experimental conditions were varied widely, including after thermal aging and in the presence of SO_2 . A wide range of instrumental methods (nitrogen physisorption, XRD, SEM/EDX, HRTEM, XPS, TPD, TPR and FTIR) were used to characterize the catalysts. It was found that the complete oxidation of methane on Pd/La_2O_3-CeO_2-Al_2O_3 starts at temperatures above 240°C and T50 around 350°C, while the presence of water vapor and sulfur dioxide leads to an increase in T50 by 40 to 110°C. It is confirmed that the addition of La_2O_3 leads to the stabilization of the catalyst by preventing the sintering of the gamma-alumina support and the agglomeration of palladium through the formation of mixed phase La_2PdO_4. Based on mathematical models developed in the laboratory, the inhibitory effect of water vapor (increased PdO/Pd ratio) was determined and it was assumed that the complete methane oxidation reaction proceeds by the Mars-Van Crevelin mechanism. An attempt has also been made to evaluate the potential of the system for practical application by applying it to a stainless steel support (Aluchrom VDM®) in the form of a single monolithic channel, and models have been used to simulate methane combustion from laboratory scale to pilot and full-scale adiabatic monolithic reactors. The main conclusion of the study is that the performance of the Pd/La_2O_3-CeO_2-Al_2O_3 system can be improved by optimizing the Pd0 content, the deposition method, and further modification of the composition by adding components that lead to the binding of SO_2 to sulfites instead of sulfates.

The results of the investigations carried out are built upon in Publication 6, which presents the results of the investigation of a Pd/Al_2O_3-La_2O_3-CeO_2 catalyst for propane oxidation. Again, the sol-gel method was used to prepare a support containing AlO(OH), La_2O_3 and CeO_2 and subsequent impregnation with a Pd-containing solution. It was found that after catalytic test, the specific surface area decreased while the microstructure remained unchanged, and palladium was found to be present on the surface of the catalyst in a higher oxidation state of Pd^{4+}. The order of the reactions was determined and it was suggested that the complete oxidation of propane proceeds by the Langmuir-Hinshelwood mechanism with adsorption of propane and oxygen on different types of active centers, dissociative adsorption of oxygen where water molecules compete with propane molecules for adsorption on the same type of adsorption centers. Again, the potential of the synthesized material for practical application was sought to be evaluated by examining a sample of Pd/Al_2O_3-La_2O_3-CeO_2 deposited on rolled stainless steel containing Al (Aluchrom VDM®) and two-dimensional heterogeneous models were used to simulate propane combustion from a laboratory reactor to a full-scale adiabatic monolithic converter.

Publications 2, 3, 5, 10, 13 and 16 present the results of the synthesis and investigation of catalysts containing palladium or platinum deposited on racemic supports ($CuWO_4$, $CaWO_4$ modified with various transition metals γ-Al_2O_3, Ti-SBA-15 and modernite). The results of Publication 3 are upgraded in Publication 8, in both cases focusing on the development of a catalyst to reduce C1-C4 hydrocarbon emissions. It has been determined that the Pd-containing sample has a higher oxygen adsorption capacity on the surface compared to pure $CuWO_4$ and $CaWO_4$, and it has been suggested that palladium enhances the reducibility of the metal oxide from the support. Publications 2 and 5 are devoted to the possibility of introducing transition

metal cations (Ni, Mn, Co) into the Pd/Al_2O_3 system. The oxidation of Pd on $Pd/MeAl_2O_4$ was found to be easier than that on Pd/Al_2O_3. In Publication 10, it was shown that varying the Pt and TiO2 content on the surface of Pt/Ti-SBA-15 catalyst and adding Ce resulted in changing the conversion rate of hydrocarbons. In Publication 16, the catalytic activity of Pt, Cu and Pt+Cu catalysts supported on untreated and buffer-treated HF and NH4F mordenite was investigated and higher activity of the treated catalysts was found due to the presence of additional porosity increasing both the active surface areas of the materials and the access to active centres located inside the pores the pores of the zeolite compared to those of the untreated initial sample.

2. Applied oxide catalysts for VOC oxidation:

These studies fall within the traditional laboratory theme of clean air protection and are devoted to the preparation of transition metal and/or rare earth element catalysts supported on individual and composite supports and their catalytic behavior in VOC oxidation processes. The active component of the investigated catalysts contained transition metal oxides of cobalt, manganese and iron (mixed Co_3O_4-MnO_x oxides, Co-Ce oxides and $MnCoFeO_4$), and zeolite type ZSM-5 with different Si/Al ratios (23, 40 and 100), SBA-15 and silica were used as supports.

In Publication 11, in which Dr. Velinova is the first author, the catalytic behavior of Co-containing ZSM-5 zeolites in a complete propane oxidation reaction was investigated. High catalytic activity of Co-ZSM-5 (Si/Al = 23) was found, which was explained by higher reducibility as a result of weaker interaction of cobalt oxide with the support. A Mars-Van Crevelen mechanism of the complete oxidation reaction of propane has been proposed. The study is upgraded in Publication 13, with n-hexane as the object of oxidation, and the following order of activities is determined: Co-ZSM-5(Si/Al=23) > Co-ZSM-5(Si/Al=40) > Co-ZSM-5(Si/Al=100). A Langmuir-Hinshelwood mechanism (dissociative adsorption of oxygen, with the reacting hydrocarbon and oxygen adsorbed on different active sites) was proposed for the oxidation of n-hexane on all catalysts. In order to reduce coking, the oxidation of propane and n-hexane over Co-ZSM-5 catalysts with different Si/Al ratio (23, 40, 50) after treatment of the support with buffer solution of hydrofluoric acid and ammonium fluoride was investigated in publication 17. Secondary mesoporosity and diffusion enhancement was achieved, resulting in increased activity and reduced coke formation. The structural and catalytic properties of single-component manganese, two-component Mn-Ce and Co-Mn catalysts supported on SBA-15 and silica were investigated in publications 4, 7 and 9, and $MnCoFeO_4$-based bulk catalysts were studied in publication 15. It was found that:

- The fine dispersion of manganese and cerium oxide and their strong interaction in the channels of SBA-15 leads to the formation of difficult-to-reduce oxide phases and lower catalytic activity;
- The higher catalytic activity of the catalysts supported on hierarchical macro-mesoporous silica is probably due to the reduction of transport constraints due to the combination of pores at two levels.

5. Implementation and expert activities

- *Participation in scientific and applied contracts and projects:*

Dr. Velinova's project activity includes 11 scientific projects, 3 of which have been submitted to the competition (2 national and one international):

1. Project Union II stage" (CVP_09_0003/2010), funded by the Ministry of Education;
2. Project KP-06-H49/4, funded by the National Research Fund;
3. International project D01-272/02.10.2020, "European Network on Chemistry of Materials for Clean Technologies", funded by the MES under the National Programme "European Science Networks".

- *Expertise:*

Dr. Velinova's expert activity is expressed as:

1. Guest editor of the special issue "Catalytic Combustion - From Laboratory Tests to Practical Applications" of Catalysts-MDPI;
2. Reviewer of 16 articles in prestigious international journals *Materials, Energies, Catalysts, Processes, Aerospace and Polymers*;
3. Participation in Science for Business meeting 3 (paper presented).

- *Educational and pedagogical activities*:

Dr. Velinova has mentored three students in the Student Practicum Program, Phase 2. She has also participated in the organization of a visit of students from Vasil Levski Secondary School, Sofia. Sevlievo and Vocational School of Ecology and Biotechnology, Sevlievo. She also participated in the seminar "Biology and Biotechnology - Biology and Biology" in Sofia.

6. Evaluation of the personal contribution of the candidate

Dr. Velinova's publication activity started in 2002 and is related to the topic of her thesis and these publications are not part of the competition materials. In 5 of the publications submitted to the competition she is the first author, in 3 - the second, and in the rest - the third or after the third, which is a recognition of her active participation in research.

All this gives me a reason to assume that the personal contribution of Dr. Velinova in the materials submitted for the competition is indisputable.

7. Personal impressions

I do not know Dr. Velinova and have no joint research and publications with her and my opinion on her participation in the competition is based entirely on the submitted materials and documents.

CONCLUSION

The documents and materials, presented by Dr. Ralitsa Velinova, cover all the requirements of the Law on Research and Development of the Academic Staff in the Republic of Bulgaria and in the Regulations for its implementation, the Regulations for the Implementation of the Law and the relevant Regulations for acquisition of scientific degrees and for occupation of academic positions in BAS, as well as the specific requirements of the Institute of General and Inorganic Chemistry at the BAS. The candidate has submitted a sufficient number of scientific works published after the materials used in the defence of the PhD. The submitted works contain original scientific contributions, most of them having been published in journals with an impact factor published by international academic publishers. On the basis of the above considerations, I convincingly propose to the honorable members of the scientific jury and to members of Scientific Board of IGIC to bestow to Dr. Ralitsa Hristova Velinova the academic position of "Associate Professor" at the IGIC in the professional field 4.2 "Chemical Sciences", scientific specialty "Chemical Kinetics and Catalysis" for the needs of the laboratory "Materials and Processes for Environmental Protection" of Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences.

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Reviewer:
(Prof. DSc Krasimir Ivanov)