

## OPINION OF REVIEWER

Prof. DSc Krasimir Ivanov Ivanov - Department „General Chemistry" at the Agrarian University - Plovdiv, (now pensioner) on the materials, submitted for participation in the competition for occupying the academic position „professor" at the Institute of Catalysis, Bulgarian Academy of Sciences

I was appointed as a member of the Scientific Jury with an Order № ПД-09.24 dated 13.05.2019, issued by the Director of the Institute of Catalysis, BAS (IC), for accomplishing the procedure in the competition for occupying the academic position „professor" in IC in the professional field 4.2 „Chemical Sciences", scientific research specialty „Chemical Kinetics and Catalysis", announced for the needs of the Laboratory „New heterogeneous Catalysts for clean production and protection of the environment“ in IC.

### 1. General presentation of the obtained materials

The only candidate in the competition for occupying the academic position „professor", published in Newspaper of State issue 24 dated 22<sup>nd</sup> of March 2019 and also on the Internet website of the Institute of Catalysis, is Assoc. Prof. PhD Sylvia Zhivova Todorova. The set of materials, submitted by Assoc. Prof. Todorova is in accordance with Article 29 of the Law for Development of the Academic Staff in the Republic of Bulgaria (LDASRB), Articles 31 and 32(1) of the “Regulations for the conditions and order for acquiring scientific degrees and occupying academic positions” in BAS and Articles 55(1) and 58(1) of the “Regulations for the conditions and order for acquiring scientific degrees and occupying academic positions” in the Institute of Catalysis.

The candidate has submitted for participation in the competition a total of 27 scientific research publications, all of them published after the year 2011 (when she was elected in the position of Assoc. Prof.) as well as all other necessary documents for participation in the competition for occupying the academic position „professor" in IC.

### 2. Short biographical data about the candidate

Assoc. Prof. Todorova graduated the Higher Chemical-Technological Institute in Sofia in the year 1989 acquiring the specialty “Technology of polymers, textiles and leathers” and immediately she succeeded in a competition examination for regular PhD student in IC under the guidance of Assoc. Prof. PhD G. Kadinov. In 1999 she defended her PhD thesis on the topic „Investigation of the adsorption and interaction of carbon monoxide and hydrogen on carrier-deposited palladium, ruthenium and cobalt by means of infrared spectroscopy“, and thereafter in year 2000 she became Scientific Research Fellow II degree. There follows successful habilitation in 2010 and in 2011 she was elected to be the Scientific Secretary of IC, and since the year 2015 she is the Director of the institute.

### 3. Evaluation of the scientific research works of the candidate and their applications in practice

- *Scientific research publications:*

The total number of publications of Assoc. Prof. Todorova is 48 papers, out of which 36 are published in journals having impact factor or impact rank. She participates in the announced competition with 27 publications, 22 of them have impact factor or impact rank. Eight of the publications are in journals of the highest quartile Q1, among which are Applied Catalysis A: General, Catalysis Today, Journal of Materials Science, Chemical Engineering Journal and others.

No claims by co-authors of the publications have been put forward, questioning her participation in the competition. There is no other information available about incorrect behavior on her side or about elements of plagiarism in the materials, submitted for participation in the competition, which fact was confirmed by checking some of her basic publications using the software Grammarly Premium.

- *Response in the specialized scientific literature*

The total number of noticed citations of publications with participation of Assoc. Prof. Todorova at the date of submitting her documents is 698, out of them 592 in Scopus and in Web of Science, while her index of Hirsch (h-index) in Scopus is 11.

- *Participation in national and international scientific events:*

During the period, envisaged in the competition, presentations involving the participation of Assoc. Prof. Todorova have been put forward in 51 scientific events, out of which 30 international events and 21 national events, among them the XV International Congress on Catalysis, Munich, Germany, July 1–6, 2012, 11th European Congress on Catalysis – EuropaCat-XI, 2013, Lyon, France, 30th European Conference on Surface Science, 2014, Antalya, Turkey, "Scientific Bases for the Preparation of Heterogeneous Catalysts", 2010, Louvain-la-Neuve, Belgie, 13th European Congress on Catalysis, 27 - 31.08.2017, Florence, Italy and others. Seven of these presentations were oral and the other 44 were poster presentations.

In accordance with Article 29, item 5 (which has come into force since 05.05.2018) the candidates for acquiring the academic position of professor should answer the minimal national requirements, specified in the Regulations applying the Law (LDASRB) and later corrected by Government Decree № 26 dated 13.02.2019 IC has specified some additional requirements for acquiring the academic position of professor, stated in Appendix 1 to the "Regulations for the conditions and order for acquiring scientific degrees and occupying academic positions" in the Institute of Catalysis.

One can see that on the basis of the summary, submitted by her, she exceeds both the minimal national requirements, as well as the specific requirements of IC, whereupon in some of the indices (group D) she exceeds the requirements many times.

#### **4. Contributions of her scientific research and innovative applications in practice**

- *Scientific research contributions*

The scientific studies of Assoc. Prof. Todorova are entirely in the field of heterogeneous catalysis and they are connected mainly with the search for new solutions of the problem to neutralize the exhaust gases, containing CO and organic pollutants. Some of the studies are devoted to the preferential oxidation of CO (the so called PROX process) in hydrogen-rich mixtures. What makes impression is the attempt to deepen and enrich the knowledge in regard

to the kinetics and mechanism of the processes. An impressive combination of physical and physic-chemical methods have been used for the characterization of the catalyst samples - XRD, SEM, TEM, XPS FT-IR, TPR, AAS, DTA and others, which enabled drawing well justified conclusions.

The scientific contributions are described in details in the submitted summary and in view of the compositions of the studied catalytic systems and the compounds for catalytic oxidation they can be subdivided in 3 main directions.

1. *Complete oxidation of volatile organic compounds and CO on supported oxide catalysts;*
2. *Oxidation of VOCs and methane on mixed metal-oxide catalytic systems;*
3. *Catalysts for fine purification of hydrogen-rich CO containing mixtures.*

I will try to summarize in brief the most essential, in my opinion, results and contributions, whereupon the stress will be laid on these aspects, in which Assoc. Prof. Todorova plays the leading role.

The idea to search for alternatives of the noble metals for the neutralization of exhaust gases by means of catalytic oxidation on oxide catalysts is well developed in the publications № 1, 2, 3, 7, 13, 16, 27. The catalytic oxidation of CO, methane, propane, n-hexane and ethyl acetate has been studied on catalysts, based on cobalt oxide and manganese oxide, in separate or in combination, as well as manganese oxide, modified by CeO<sub>2</sub>. Various types of supports have been used on the basis of SiO<sub>2</sub> and the methods for the deposition of the active phase have been varied too - impregnation, precipitation, the two-solvents method. It has been established that:

- Combining cobalt oxide and manganese oxide increases substantially the activity of the mixed oxide composite in comparison to the single component catalyst samples, whereupon this effect depends on the sequence of depositing the active components (J. Mater. Sci., 46 (2011) 7152-7159). The method of preparation of Co-Mn catalysts deposited on SiO<sub>2</sub> is of essential importance for their catalytic activities in the oxidation of n-hexane and ethyl acetate, whereupon the most active are the samples, obtained by simultaneous deposition of the metals. The high activities of these samples are the result of the formation of finely dispersed, low-crystallinity degree and easily reducible Co<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub> and mixed Co-Mn oxide phases, the simultaneous presence of Mn<sup>3+</sup> and Mn<sup>4+</sup> and the surface of the Co-Mn catalysts is enriched in reactive oxygen species. The application of various kinetic models leads to the conclusion that the processes occur via different mechanisms on the single-component cobalt and on the bimetallic catalyst samples (Appl. Catal. A: General, 413-414 (2012) 43-51).
- The bulk phase catalysts, obtained by coprecipitation, (Bulg. Chem. Comm., V 49, Special Issue G, 99 –104) manifest considerable promotion of the catalytic activity of the mixed oxide Co-Mn samples in the oxidation of normal hexane, whereupon the most active is the sample with molar ratio Co:Mn=1. The doping of the cobalt oxide with manganese leads to formation of finely dispersed oxides (MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>), which are reduced at low temperature; The simultaneous presence of the ion pairs Mn<sup>3+</sup>/Mn<sup>4+</sup> and Co<sup>2+</sup>/Co<sup>3+</sup> and the high specific surface area are the reasons for the high catalytic activities of these catalyst samples.

A considerable share of the studies of Assoc. Prof. Todorova are devoted to the catalytic oxidation of methane, CO and VOCs (publications 4, 6, 9, 10, 11, 14, 17, 18, 21, 23, 24, 26). A series of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts have been synthesized, doped with oxides of transition metals and catalytic system types Pt-Ti-SBA-15 and Pt-Ti-KIT-6. It has been ascertained that:

- The preliminary modification of Al<sub>2</sub>O<sub>3</sub> with various oxides and the consecutive impregnation of Pd lead to the formation of highly dispersed oxides, which stabilize palladium in the form of Pd or PdO clusters, serving as a kind of storage capacity of oxygen, which is being transferred from the oxide to the palladium. The following order of activities of the catalytic systems has been found out: Pd/CoCe/Al<sub>2</sub>O<sub>3</sub> > Pd/CoMn/Al<sub>2</sub>O<sub>3</sub> > Pd/Ni/Al<sub>2</sub>O<sub>3</sub> ≅ Pd/ >Al<sub>2</sub>O<sub>3</sub>Pd/Mn/ Al<sub>2</sub>O<sub>3</sub> (Rev. Roum. Chim., 59 (3-4) (2014) 251-2).
- The highest activity and stability in the oxidation of methane is displayed by the catalyst samples, containing cobalt. It has been established that depending on the content of cobalt different oxide phases are being formed, whereupon at low content on the surface only the spinel-similar Co<sup>2+</sup>/Al<sup>3+</sup> surface phase is being formed, while upon increasing its content also phases of Co<sub>3</sub>O<sub>4</sub> and superficial phases are being formed, containing Co<sup>3+</sup> ions. The catalytic studies showed that the formation of spinel-similar Co<sup>2+</sup>/Al<sup>3+</sup> surface phase is responsible for the stabilization of the palladium particles in the form of highly dispersed PdO - clusters (Int. J. of Adv. in Sci. Eng. and Tech. 6, Sep.-2018). In the case of the most active catalyst having composition 0,05% Pd - 0.3% Co/γ-Al<sub>2</sub>O<sub>3</sub> it was found out that there is presence on the surface of all the three degrees of oxidation of the palladium - Pd<sup>0</sup>, Pd<sup>2+</sup> and Pd<sup>4+</sup>, and the content of Pd<sup>2+</sup> is prevailing (Chem. Eng. Journal, 266, 2015, 329-338).
- The deposition of Pd on nano-sized oxides of manganese, cobalt and iron leads to the formation of finely dispersed PdO on the surface and promotion of the activity of the catalyst samples in the complete oxidation of methane, whereupon the highest activity is displayed by the sample having composition Pd/mono-phase Mn<sub>2</sub>O<sub>3</sub>. In the oxidation of CO, the order of the activities of the catalyst samples is the following: Pd/Mn<sub>2</sub>O<sub>3</sub> > Pd/Fe<sub>2</sub>O<sub>3</sub> > Pd/Co<sub>3</sub>O<sub>4</sub> (publications 10, 11, 21).
- It has been ascertained that the state of the platinum in the titanium-modified SBA-15 strongly depends on the method of introducing the titanium component. High catalytic activity in the reaction of complete oxidation of hexane and CO has been found out for samples, in which the titanium is introduced by means of impregnation, whereupon the finely dispersed TiO<sub>2</sub> interacts strongly with the mesoporous SBA-15. The consecutive deposition of platinum leads to the formation of particles of metallic platinum of average size 40 nm, which favors the catalytic activity.

The third direction in the studies of Assoc. Prof. Todorova is connected with the pressing problem for fine purification of hydrogen-rich mixtures having CO ( these are publications 5, 13, 20 and 22).

- High catalytic activity has been found out with some silver catalysts, deposited on various supports (SiO<sub>2</sub>, CeO<sub>2</sub> and MnO<sub>2</sub>) by means of impregnation (Bulgarian Chemical Communications, Volume 50, Special issue H (pp. 17–23) 2018). The sample having the highest activity in the reaction of preferential oxidation of CO in hydrogen-rich mixtures has the composition Ag/SiO<sub>2</sub>, treated in advance with pure oxygen. The conclusion has

been drawn, that the preliminary treatment with oxygen at 450°C leads to restructuring of the surface of the silver as a result of formation of surface and sub-surface oxygen species and restructuring of the surface of the silver particles, which considerably promotes the catalytic activity in the studied reaction.

- A series of nano-sized, deposited on active carbon Fe, Pt и Fe-Pt catalyst samples have been studied (Proc. ICAME 2013, Croatia). The synthesized samples are characterized by high dispersion degree of the deposited phases and formation of different types of active sites. The catalytic behavior of the studied materials has been found to depend on their phase composition and on the degree of dispersion.

- **Implementation and expert activities**

*Participation in scientific research projects and innovative implementation contracts:*

During the period after the habilitation Assoc. Prof. Todorova has participated in 18 national and international projects:

- Research projects funded by NSF - participation in 6 projects and leader on behalf of IC in the project „Innovative approach for preparing structured catalysts for neutralization of emissions of methane“, № ДФНИ-Т01/6, 12. Years 2012- 2015;
- Infrastructural projects and programs – leader on behalf of IC in 3 projects, among them the Project BG05M2OP001-1.001-0008 „National Center of Mechatronics and clean technologies“;
- International projects based on various cooperation projects with Russia, France, India, China – a total of 4 projects and in 3 of them she was the leader on behalf of IC;
- Leadership of 3 projects for non-currency equivalent exchange with the Institute of Physical Chemistry of the Romanian Academy, Bucharest, Romania.

The projects have been funded or will be funded in the future with considerable financial resources, enabling the realization of the scientific research and buying material assets for IC.

*Expert activities:*

The expert activities of Assoc. Prof. Todorova have found their realization in:

- Participation as reviewer of projects submitted to NSF and the Romanian National Council for Research and Development;
- Reviewer’s opinions and attitudes in defense procedures of PhD theses (6);
- Reviewer’s opinions in competitions for acquiring the academic positions of „Associated Professor“(3) and „Professor“(4).

In the summary, submitted by the candidate, there is missing information about reviewer’s opinions on submitted articles in international journals and participation in organizing committees of various scientific events, which in my opinion is due to oversight when preparing the documents.

The ability of Assoc. Prof. Todorova for teamwork was confirmed by her colleagues in the procedure to be elected as a Scientific Secretary of IC, and later as Director of IC.

*Educational and training activities*

In spite of the limited possibilities for researchers in BAS to take part in education-training activities Assoc. Prof. Todorova was co-leader of one successfully defended PhD thesis, leader of a diploma work and mentor of 5 students participating in the project BG051PO001 - 3.3.07-0002 „Students Practices”.

## **5. Estimation of the personal contribution of the candidate**

The publication activity of Assoc. Prof. Todorova started in 1993 under the guidance of her scientific leader Assoc. Prof. G. Kadinov. There followed 8 publications, 5 of them having IF or SJR, whereupon in 5 of them the candidate was the first author. After the year 2002 the scientific interests of Assoc. Prof. Todorova became enlarged, and together with this the number of her co-authors was increased, including foreign scientists. During the period until her habilitation in 2010 she was the co-author of 12 publications (8 of them with IF), and in 10 of these papers she was the first author.

Assoc. Prof. Todorova is the first author in 12 of the publications for participation in the competition (11 of them having IF), which is a recognition of her leading role in the investigations.

All these facts give me the reason to accept that the personal contribution of Assoc. Prof. Todorova in the materials, submitted by her for participation in the competition, is without any doubt decisive.

## **6. Personal impressions**

I know Assoc. Prof. Todorova well as a result of my long-lasting contacts and collaboration with IC, and I also have impressions from a multitude of scientific events both in Bulgaria and abroad and also of her working experience as Director of IC. I have not had any joint investigations and no joint publications with her, so my attitude to her participation in the competition is entirely based on the materials and documents, submitted to me.

## **CONCLUSION**

The documents and materials, submitted by of Assoc. Prof. Sylvia Todorova, completely answer to all the requirements of the Law for the development of the academic staff in the Republic of Bulgaria (LDASRB), the Regulations for its application and the respective Regulations of BAS, as well as to the specific requirements, formulated by the Institute of Catalysis at BAS. The candidate has presented a sufficient number of scientific research works, published after the materials, used by her in her PhD thesis defense and for acquiring the academic position of „Associated Professor". I see original scientific contribution in the papers, submitted by her, whereupon the main part of them have been published in journals having impact factor, issued by prestigious international academic publishers. All these facts give me the reason to give my positive estimate and approval and to recommend convincingly to the Scientific Jury to prepare a report-proposal to the Scientific Council of IC to elect of Assoc. Prof. Sylvia Todorova to occupy the academic position of „professor" in IC in the professional field 4.2 „Chemical Sciences", scientific research specialty „Chemical Kinetics and Catalysis".

Date 01.07.2019

**Signature of the reviewer:.....**

(Prof. DSc Krasimir Ivanov)