

## OPINION OF REVIEWER

from. Prof. Konstantin Ivanov Hadjiivanov  
Bulgarian Academy of Sciences  
(member of the Scientific Jury)

on the competition for occupying the academic position **professor** in a professional field 4.2. "Chemical sciences", scientific specialty "Chemical Kinetics and Catalysis" for the needs of the Institute of Catalysis at the Bulgarian Academy of Sciences, Laboratory "New Heterogeneous Catalysts for Clean Energy Production and Environmental Protection",

announced in Newspaper of State 24, p. 96/22.03.2019.  
with the candidate Assoc. Prof. Dr. Silvia Zhivova Todorova

### I. Introductory remarks

The Competition for Professor in the professional field 4.2. *Chemical Sciences*, scientific specialty *Chemical Kinetics and Catalysis*, for the needs of laboratory "New heterogeneous catalysts for clean energy production and environmental protection" at the Institute of Catalysis (IC) - BAS was announced in Newspaper of State iss. 24 dated March 22, 2019. Assoc. Prof. Dr. Silvia Zhivova Todorova, who currently holds the position of Director of the Institute of Catalysis at the Bulgarian Academy of Sciences, has submitted documents for participation in the competition. Assoc. Prof. Todorova has presented the documents required by the law, incl. (i) the announcement of the competition in the Newspaper of State, (ii) a CV (iii) the diplomas for the acquisition of the Ph.D. degree and the scientific title of associate professor (iv) summary of the scientific achievements, (v) the lists of scientific papers, citations and participation in conferences, (vi) copies of scientific papers as well as other materials.

### II. Brief details of the applicant

Assoc. Prof. Todorova graduated from "VHTP" (now UCTM) in 1989 with specialty "Polymer technology, textiles and skins". During the period 01.02.1990 - 01.02.1993 she was a PhD student at the Institute of Catalysis at the Bulgarian Academy of Sciences. At the beginning of 1993 she joined the same institute as a chemist. In 1999, she defended her PhD thesis entitled *Infrared Spectroscopy Study of the Adsorption and Interaction of Carbon Monoxide and Hydrogen on Supported Palladium, Ruthenium and Cobalt*, when which I had the pleasure of being a reviewer. Her doctoral degree was awarded by the Higher Attestation Commission in 2000. In the same year, Dr. Todorova won a competition for Research Associate II degree. In 2004, after the attestation, she was promoted to Research Associate I degree. The academic position Associate Professor Dr. Todorova acquired in 2010 after a competition. In the period 2011-2015 she is the scientific secretary of the IC and in 2015 he was elected by the Managing Board of the Bulgarian Academy of Sciences as director of the Institute.

Her PhD thesis Mrs. Todorova elaborated under the guidance of Prof. G. Kadinov, from whom she perceived the accuracy and depth of the research work. Also important for her scientific development are the specializations made at leading scientific centers abroad: two long-term visits at the University of Namur - Belgium and several short-term visits at the Seville Institute of Materials Research.

### III. Compliance with the requirements for occupying the position of Professor

Dr. Todorova meets the requirements for occupying the academic position professor in the Institute of Catalysis, published in the Law on the 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 Institute of Catalysis; namely:

#### Minimum required points for occupation of the academic position professor in the professional field 4.2. Chemical Sciences

The correspondence to the indicators item after item is presented in the table below. The points declared by the applicant are accepted except those in group Д where I have removed the points from other citations. In Group Г, I added 10 points for paper No. 20 (punctuated by the applicant with 10 points as a publication in SJR without IF, and 20 by myself as Q2 paper according to SJR).

Group	Indicators	Points	Points	Required
<b>A</b>	1. PhD thesis	50	<b>50</b>	<b>50</b>
<b>B</b>	3. Habilitation work - scientific publications in journals referenced and indexed in Web of Science and Scopus.	127	<b>127</b>	<b>100</b>
<b>Г</b>	7. Scientific publications in journals referenced and indexed in the Web of Science and Scopus, outside the habilitation.	275	<b>275</b>	<b>220</b>
<b>Д</b>	11. Citations in scientific publications, monographs, collections, and patents referenced and indexed in the Web of Science and Scopus.	592	<b>592</b>	<b>120</b>
<b>E</b>	13. Guidance of successfully defended PhD students	25		
	14. Participation in national scientific or educational projects	60		
	15. Participation in international scientific or educational projects	20		
	16. Guidance of national scientific or educational projects	160		
	17. Managing the Bulgarian team in international scientific or educational projects	150		
	18. Funds received from projects led by the Candidate	46	<b>461</b>	<b>150</b>

#### Other requirements

1. Dr. Todorova has been registered in NACID (<https://ras.nacid.bg/dissertation-preview/16480>), where her doctoral degree and academic rank (associate professor) are recognized.

2. Upon submission of the documents, Dr. Todorova has occupied the academic position Associated Professor at IC-BAS for 8 years 11 months and 7 days, i.e.. more than the term required by the normative documents (five years).

3. Dr. Todorova has been a member of research teams at the IC.

4. The publications submitted for the competition do not repeat those submitted for doctor's degree and the academic position of the associate professor.

5. There is no evidence of plagiarism in scientific works. My personal conviction about this aspect is supported by the nature of the journals, in which Prof. Todorova has published her scientific papers - most of them use antiplagiarism software.

### **Science-metric analysis of the presented materials**

To participate in the competition Assoc. Prof. Todorova has presented 27 scientific publications. Seven of them (Nos. 1, 2, 3, 7, 13, 16 and 27 of the presented list) comprise her habilitation work - *Applied oxide systems as catalysts for complete oxidation of volatile organic compounds and CO*. All of these scientific papers were published after 2010 in journals included in WoS and/or Scopus, with four of them being of the highest (**Q1**) category. The contribution of Dr. Todorova to these publications is also highlighted by the fact that in four cases she is the first author, and in four of them she is the corresponding author. The average number of co-authors in these publications is less than 6, which is not high for the scientific field.

Twenty of the presented papers are not included in the habilitation work, with 16 of them being categorized in quartiles (4 of them in Q1). In all cases the submitted papers are from the period after receiving the Associated Professor position.

106 independent citations, reflected in the WoS and Scopus databases, were noticed on the publications submitted to the competition. Out of these citations 57 are on papers included in the habilitation work.

It is worth mentioning that, according to the WoS and Scopus databases, Assoc. Prof. Todorova has co-authored 33 scientific papers published during the period 1993-2019, with 66% of the works published over the last 10 years. According to the Scopus database and after excluding all auto-citations, 380 citations were noticed, and the H-index of the applicant (again w/o auto-citations) is 11.

The popularization of the scientific achievements of Assoc. Prof. Todorova, obtained after taking the academic position as an Associated Professor, has been accomplished through numerous participations in scientific events. Among these, seven scientific reports and 44 poster contributions, including 13 national forums, should be noted.

Assoc. Prof. Todorova has an active participation in the education. She was a co-supervisor of one Ph.D. student and advised several graduate and post-graduate students.

The project activity of Prof. Todorova is also impressive. In this case, I would emphasize that she is the head of eight scientific or research-related projects and has led the Bulgarian teams of three international projects.

While there is no direct relation to this competition, I do not want to omit the successful work of Assoc. Prof. Todorova as Director of the Institute of Catalysis.

## IV. Summary of the scientific achievements

### Habilitation work

The Habilitation work of Dr. Todorova is entitled: *Cobalt and Manganese based catalysts for complete oxidation of volatile organic compounds and CO*. The subject is up to date and it is in line with European and National scientific priorities. The results of the research were published in seven scientific papers (Nos. 1, 2, 3, 7, 13, 16 and 27).

The essence of the study is the scientifically grounded search for alternatives to precious metal catalysts, namely combinations of cobalt and manganese oxide. Mono- and di-component systems with different compositions have been systematically studied. The influence of the preparation conditions and other factors on the activity of the catalysts is investigated. As a next step, the effect of the support (non-porous and mesoporous SiO<sub>2</sub>) was studied. A number of relationships have been found out in the research, with the most interesting ones being:

Factors enhancing the catalytic activity:

- High dispersion degree of the active phase;
- High Co<sup>2+</sup>/Co<sup>3+</sup> ratio (Co<sup>2+</sup> surface ions are sites of active oxygen adsorption), which increases upon increasing manganese content in two-component catalytic systems;
- Enriching the surface with reactive oxygen species due to the presence of defects in the mixed-oxide Co-Mn catalysts;
- Reduced bond strength Co-O in finely dispersed mixed Co-Mn oxide phases
- Simultaneous presence of Mn<sup>3+</sup> and Mn<sup>4+</sup> ions, leading to a high power bridge correlation with the catalytic activity;

Factors reducing the catalytic activity:

- Formation of a surface cobalt silicate that is hardly reducible having low activity in the reactions of complete oxidation.
- Enriching the surface with cerium and lowering the oxygen mobility of manganese catalysts modified with cerium oxide.

The most active catalyst among all two-component Co-Mn samples in all investigated reactions is the Co : Mn = 1 : 0.5 molar ratio catalyst. This appears as a result from the formation of finely dispersed and readily reducible oxides (including the mixed oxide phase Mn<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub>) and high mobility of surface and lattice oxygen species.

### Other papers

The other publications presented by Assoc. Prof. Todorova for participation in the competition form three thematic directions, in a series and in a short while will mark the main scientific contributions.

Catalysts based on biogenic materials for oxidation of CO and VOCs. This subject is related to the habilitation work. The results are published in 3 papers (Nos. 12, 15 and 19). The catalytic properties with respect to the CO conversion degree on iron oxide/oxyhydroxide derived from iron-bacteria were investigated, and were compared with the properties of non-biogenic catalysts. The results show that at temperatures higher than 250°C the activity of both types of materials practically coincides, which is associated with the transformation of  $\alpha$ -FeOOH into  $\gamma$ -FeOOH. Promising properties are also shown by the biogenic catalysts cultivated in the presence of Pd.

Catalysts based on the combination of oxides and precious metals (Pd, Pt) for the oxidation of VOCs and methane. Twelve scientific papers (Nos. 4, 6, 9, 10, 11, 14, 17, 18, 21, 23, 24 and 26) were published on the basis of these results. The subject matter is definitely of interest from an environmental point of view. Prof. Todorova has paid considerable attention to the complete oxidation of methane. It is known that the active catalytic phase in this reaction consists of particles of PdO. The activity of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts has been found out to increase after the addition of some metal oxides (except for manganese oxide). Because of good preliminary results, more detailed studies have been carried out with cobalt-containing catalysts. It was found out that the positive effect of cobalt is limited to a low concentration range, i.e. when forming a Co-Al spinel-like surface phase. Highest activity and stability have shown catalysts with a composition of 0.05 % Pd + 0.3% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which is associated with the formation of stable particles of PdO. Modifiers alternative to the cobalt (Ce, La) were also studied and they showed good properties. However, high activity of these catalysts is achieved at a relatively high Pd content. Further studies have shown that the active phase in Pd/La<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub> catalysts are Pd<sup>4+</sup> ions, possibly from PdO<sub>x</sub> or PdO<sub>2</sub> particles, which enriches our knowledge about these catalysts and opens new perspectives for their design.

In another series of research works palladium supported on oxides of Fe, Mn and Co was studied. High activity was demonstrated by the catalysts deposited on cobalt and manganese oxides. These catalysts were also tested in the CO oxidation reaction, in which case the catalysts deposited on manganese and iron oxide were the most active due to the possibility of these supports to adsorb oxygen. Applying in-situ IR spectroscopy, the adsorption forms of CO on the catalysts under investigation, as well as their reactivity with respect to oxygen, were studied in details.

The research cycle is complemented by several papers on the study of the oxidation of CO, methane and n-hexane on supported platinum catalysts. The supports studied were SBA-15 and KIT-6, modified with Ti, as well as iron oxide. The influence of various factors on the activity of the catalysts was studied in detail. In this case, the mechanism of reactions was also clarified by detailed in-situ IR studies of adsorbed CO.

It should be noted that despite the fact that the papers described have been only recently published, they have already provoked considerable interest among the scientific community. For example, work No. 8 (2016) has already been cited 10 times, and work No. 11 of 2018 - three times.

Catalysts for fine purification of hydrogen-rich mixtures of CO. These results are published in 4 scientific papers (Nos. 5, 13, 20 and 22). The preferential oxidation of CO (PROX) has been studied to reach levels below 10 ppm CO in hydrogen, which usually proceeds over supported gold catalysts. In this case, Todorova et al. look for alternative compositions. It was shown that ferrites

possessed low activity. Also, the negative effect of iron on Pt/SiO<sub>2</sub> catalysts was established. The effect was explained based on the presence of iron oxide particles that catalyze the oxidation of hydrogen. Promising properties have been shown by two types of catalysts - multi-component cobalt catalysts and Ag/SiO<sub>2</sub> previously subjected to oxidation treatment. In the latter case the extremely rarely observed silver metal carbonyls have been detected.

## V. Conclusions

The analysis of the documents submitted by Assoc. Prof. Silvia Todorova, presented for participation in the competition for professorship, shows that she answers all the requirements of the normative documents for taking up this academic position at the Institute of Catalysis.

The research topic of Assoc. Prof. Todorova is fully in line with the topic of the laboratory "New heterogeneous catalysts for clean energy production and environmental protection", for whose needs the competition was announced. Moreover, the international recognition and high qualification will undoubtedly be beneficial to the scientific level of the laboratory.

On the basis of the above considerations I convincingly propose to the honorable members of the scientific jury to bestow to Assoc Prof. Dr. Silviya Zhivova Todorova the academic position **professor** in the professional field 4.2. Chemical Sciences, scientific specialty Chemical Kinetics and Catalysis for the needs of the laboratory New heterogeneous catalysts for clean energy production and environmental protection at the Institute of Catalysis, Bulgarian Academy of Sciences.

Reviewer:

(Prof. Konstantin Hadjiivanov)

Sofia, 27.06.2019