ATTITUDE OF REVIEWER

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With respect to the competition, published in „Newspaper of State", issue 85/22.03.2019 for occupying the academic position "Professor" in professional field 4.2 "Chemical Sciences", scientific research specialty "Chemical Kinetics and Catalysis" for the needs of the Laboratory "New heterogeneous catalysts for clean energy production and protection of the environment"

The only candidate in the competition is Assoc. Prof. PhD Sylvia Zhivova Todorova, who works in the Laboratory „New heterogeneous catalysts for clean energy production and protection of the environment" in the Institute of Catalysis (IC), BAS. The candidate submitted all the necessary documents and materials required for participation in the announced competition.

Short biography data. Assoc. Prof. PhD Sylvia Zhivova Todorova graduated her higher education at the High Chemical Technology Institute, Sofia, in 1989 obtaining diploma of chemical-engineer. In the year 1990 she was appointed as a chemist in the Institute of Catalysis, BAS and later in 1999 she defended her PhD thesis on the topic "Investigation on the adsorption and interaction of carbon monoxide on supported palladium, ruthenium and cobalt by means of infrared spectroscopy" and she acquired the educational and scientific PhD degree. Later in 2010 she was appointed in the position of Associated Professor.

Scientific research activities. The scientific contributions of Assoc. Prof. S. Todorova during the entire scientific research period comprises a total of 48 publications, out of which 27 have been presented for participation in the present competition, published during the period 2011-2019. The entire represented scientific material has been published in prestigious international journals in the respective scientific research field – for example: 8 publications are in Q1 journals, 6 other publications are in Q3 journals, 4 papers have Q4 and 1 paper – Q2. During the competition period 296 citations have been noticed in Scopus/WoS citing 25 of her publications, while 12 publications during the period 2011-2019 have 106 citations in Scopus/WoS. The candidate submitted data about 7 oral presentations and 44 poster presentations at national and international scientific events during the competition period.

What is of interest is the active participation of the candidate in the realization of scientific research projects, 6 of them are national projects and 1 international project (with China), which are mainly sponsored by the NSF. Assoc. Prof. Todorova participated as a leader of the research team in IC in a total of 6 projects, having both scientific research aspect and educational aspect, whereupon she secured financial support to the amount of 137 998 BGL. Three of these projects are in line with the Non-currency Equivalent Exchange Cooperation Program with Romania. She was also the leader on behalf of the Bulgarian side of the Bulgarian research team, involved in the fulfillment of three international scientific research projects for bilateral cooperation (with Russia, France and India), where the funding amounted to 101 000 BGL.

Scientific-educational, organizational and expert activities. Assoc. Prof. S. Todorova was the co-leader of 1 successfully defended PhD thesis of a PhD student at IC, and also mentor in 2 projects, funded by the Operating Program "Development of Human Resources", the program "Students Practices" involving 5 students from the University of Chemical Technology and Metallurgy in Sofia and she was the leader of the diploma thesis for M.Sc. of one of these students. Assoc. Prof. S. Todorova has also high scientific research competency and good organizational qualities, which underline the basis of her scientific research and organizational activities. She was Scientific Secretary of IC during the period 2011-2015, as well as Director of IC since December 2015 until the present moment. She is the Head of the Laboratory "New heterogeneous catalysts for clean energy production and protection of the environment" in IC since the year 2016. She participated in organizing

committees of international scientific events and in 2018 she was Co-Chairman of the "XII International Symposium on Heterogeneous Catalysis" in Sofia. It should be noted also the considerable expert activities of Assoc. Prof. S. Todorova submitting reviewer's opinions on national and international scientific research projects, as well as a total of 12 reviewer's opinions for acquiring a scientific degree and occupying academic positions.

Basic scientific contributions. The research studies of Assoc. Prof. Todorova are connected with the elaboration of new heterogeneous catalysts and optimization of the already existing catalytic processes for protection of the environment, more specifically those processes, which lead to complete oxidation of CO and combustion of volatile organic compounds (VOCs), such as *n*-hexane, methane, propane and ethyl acetate, contained in gaseous emissions, liberated mainly by the chemical industry and oil-processing industry, leading to decomposition of the stratospheric ozone, formation of photochemical smog and greenhouse effect. In view of the detailed research summary, submitted by Assoc. Prof. Todorova, covering her studies and contributions I would like to point out in brief her most outstanding contributions from the studies, divided in three main research directions of the candidate, taking into account the types of the catalysts, i.e. the nature of the metal components and their molar ratio, the type of the support and the method of their preparation.

(A)Supported oxide systems as catalysts for complete oxidation of volatile organic compounds and CO (papers 1, 2, 3, 7, 13, 16, 27). Among the studied oxides of Cu, Mn, Co and Ni, deposited on supports of mesoporous silicates of the types MCM-41 or SBA-15, bi-component Co-Mn catalysts of molar ratio Co:Mn = 1: 0.5 showed the highest activity in complete oxidation of *n*-hexane, which was attributed to increase in the dispersion degree and the reducibility of the supported metal oxides, as well as to the occurring of electron transfer between Co and Mn ions. It is interesting to note also the high catalytic activity of iron-containing biogenic materials, obtained by direct cultivation of the bacteria Leptothrix genus, in the reaction of complete oxidation of CO, which is owing to the formation of catalytically active phase of γ-Fe_2O_3, as a result of the transformation of α-FeOOH and γ- FeOOH (papers 12, 15, 19).

(B) Catalysts on the basis of combination of oxides and noble metals (Pd, Pt) for oxidation of VOCs and methane. (papers 4, 6, 9, 10, 11, 14, 17, 18, 21, 23, 24, 26). The efforts were directed to elaboration of new catalysts and optimization of the existing catalytic systems with the aim to avoid the agglomeration of Pd and Pt particles and achieving high activity at low reaction temperature. Having this in mind a series of catalysts on the basis of Pd/Al_2O_3, doped with various oxides of transition metals of the type Mn, Co, Ce and Ni, which stabilize the palladium in the form of Pd or PdO clusters, whereupon the latter play the role of oxygen storage. It has been shown that the low concentration of Co leads to high activity in the complete oxidation of methane, attributed to formation spinel-similar surface structure, Co^{2+}-Al^{3+}, which leads to stabilization of the highly dispersed PdO clusters (paper 9). The sequence of deposition of the components has been studied, whereupon kinetic models have been used to study the mechanism of the reaction and the effect of the various methods for preparation of the catalysts.

Nanosized Pd catalysts have been elaborated, deposited upon synthesized Mn_3O_4, Co_3O_4 and Fe_3O_4 oxides having high specific surface area (papers 10, 11). Once again a conclusion has been made that the combination of Co oxide and Pd leads to obtaining of highly active catalyst samples for methane combustion. However, Pd deposited on monophase Mn_2O_3, showed the highest activity in methane combustion, which was attributed to the role of the support to be oxygen storage (paper 21).

Using infrared spectroscopy and probe molecules (in this case CO was used as a probe molecule) information was obtained about the type of active sites and the mechanism of the reaction of selective oxidation of CO on Pd catalysts, deposited on different metal oxides: Fe_2O_3 (paper 10), Co_3O_4 (paper 11). Quantum chemical modeling has also been done to determine the influence of the support on the structure of the Pd particle (paper 25).

Pt catalysts have been put forward for selective oxidation of CO and complete oxidation of VOCs (*n*-hexane, methane), supported on mesoporous carrier, modified with Ti SBA-15 (paper 4) and KIT-6 (paper 18). The method of deposition of Ti has been studied in regard to the stability and activity of the catalyst. It has been found out that when Ti is deposited by impregnation on SBA-15 one obtains TiO_2, which interacts strongly with the support, leading to formation of metallic Pt particles of size 40 nm, which in its turn promotes the catalytic activity. It has been ascertained that the non-modified with TiO_2 KIT-6 at 5 wt.% Pt concentration shows the highest activity in CO oxidation, connected with the simultaneous presence of Pt^0 and Pt^{2+} sites (paper 18).

(C) Catalysts for fine purification of hydrogen-rich mixtures with CO (papers 5, 13, 20, 22). Assoc. Prof. Todorova and her colleagues had success in the elaboration of new catalytic systems for preferential oxidation of CO (PROX process), operating at lower reaction temperatures, in which the used noble metal was replaced by another economically more beneficial component. For example silver catalysts have been prepared, deposited on various supports such as SiO_2, CeO_2 and MnO_2 (paper 22). It has been established that the catalyst Ag/SiO_2, preliminarily treated in oxygen atmosphere (O_2), shows the highest activity in the PROX process. By means of diffuse-reflectance infrared spectroscopy it has been proven that the high activity is due to formation of surface and subsurface oxygen species and restructuring of the surface of the silver particles, i.e. appearance of sites suitable for the formation of linearly adsorbed CO. After 20 hours of staying in atmosphere of N_2-CO the intensity of the band CO-Ag^0 is decreased and a new band appears, due to the formation of CO_2, i.e. there is interaction between CO and subsurface oxygen.

Mono- and bi-component Co-Mn catalysts have also been studied in the PROX process (paper 13). It has been ascertained that the mono-component Co catalyst shows the highest activity, which is connected with the simultaneous presence of phases of Co_3O_4 and Co^{2+} ions of cobalt silicate, which are responsible for the adsorption of oxygen and formation of oxygen particles.

Conclusion. The scientific achievements of Assoc. Prof. Todorova are obvious and they have received high estimates both in our country, as well as abroad as international recognition. It is important to note that the candidate is a well-established specialist, working on hot problems of the day in the field of elaboration of new highly active and stable heterogeneous catalysts for protection of the environment, namely complete oxidation of VOCs and selective oxidation of CO. She is one of the few researchers, working on these problems in Bulgaria. I know Assoc. Prof. Todorova since the day she came to the Institute of Catalysis. She is very correct and accurate in her relations with the colleagues, she is a hard working fellow, devoted to her research work and to her organizational obligations, she has positive attitude and ability to working in a team.

The scientific-metric indices of Assoc. Prof. Todorova, taken as a whole volume and judging about their qualities are not only in correspondence with the recommended requirements, but they exceed them considerably in regard to occupying the academic position “professor” in view of the Law for the Development of the Academic Staff in the Republic of Bulgaria and in accordance with the specific Regulations of IC-BAS, accepted by the Scientific Council for acquiring scientific degrees and occupying academic positions.

On the basis of the above facts I am convinced to recommend with pleasure to the Scientific Jury at IC-BAS to bestow to **Assoc. Prof. PhD Todorova** the academic position **“PROFESSOR”** in the professional field 4.2 “Chemical Sciences”, scientific research specialty “Chemical Kinetics and Catalysis” for the needs of IC-BAS.

Date 01.07.2019 Member of the Scientific Jury at IC-BAS:

Sofia /Prof. DSc Sonya Damyanova/