

STANDPOINT

by competition announced in State Gazette no. 24 of 22. 03. 2019, for the awarding of the **academic position "Professor"** in the direction 4.2. Chemical Sciences (Chemical Kinetics and Catalysis) for the Laboratory "New Heterogeneous Catalysts for Clean Energy and Environmental Protection", Institute of Catalysis, Bulgarian Academy of Sciences

Reviewer: Prof. DSc. Tanya Stoyanova Hristova, Institute of Organic Chemistry, Center for Phytochemistry, Bulgarian Academy of Sciences

Participant: Assoc. Prof. Dr. Silvia Zhivova Todorova, Institute of Catalysis, Bulgarian Academy of Sciences (the only candidate in the competition)

Dr. Silvia Todorova joined the Catalysis Institute, BAS in 1990 as a full-time Ph.D. student. After having defended her doctoral dissertation in 1999 she occupied the positions of "Research fellow" at the Institute, and from 2010 she was elected Associate professor at the same institute. So she formally satisfies the requirements for participation in the competition. Assoc. Prof. Silvia Todorova overcomes the necessary criteria under Art. 4 of the Regulations for the Terms and Procedure for Acquisition of Academic Degrees and for Occupation of Academic Positions in the IC, BAS. She is co-author of 48 publications, with 27 of them participating in this competition. 8 of them are indexed as Q1, 1 as Q2, 5 as Q3 and 7 as Q4. There is a tendency to increase the quantity and quality of published articles over the past 2 years. More than 300 citations have been seen on all articles, with nearly 1/3 of them after her habilitation. By these parameters she exceeds the 5 times the required threshold. Dr. Todorova is very active as a participant and manager of various projects funded by NSF, EBR, Ministry of Education and European subsidies and thus exceeds the requirements of this parameter almost 3 times. She was supervisor of 1 Ph.D. student, 1 master degree thesis and 5 student practices. In recent years, she has skillfully combined science with social activities. In the period 2011-2015 Dr. Todorova was Scientific Secretary in the IC, and she is currently Director of the same institute and member of the GA of the Bulgarian Academy of Sciences. The research activity of Assoc. Prof. Silvia Todorova is aimed at environmental protection through the development of effective catalysts for the purification of air from CO, methane and volatile organic compounds (propane, *n*-hexane, ethylacetate) by their total oxidation. Some of the studies are also addressing a problem of complete hydrogen purification from CO

traces through its oxidation, which is directly related to the development of alternative efficient and clean energy sources, such as fuel cells. Catalysts based on transition metal oxides (Cu, Mn, Co, Ni) were investigated. Conventional SiO₂, Al₂O₃ and advanced silicate materials with ordered porous texture type MCM-41, KIT-6 and SBA-15 were used as supports. Various methods for active phase deposition, including co-precipitation, impregnation, application of two solvents, have been used. The applicant correctly focuses on the study of binary metal oxide systems as well as those promoted with Pd or Pt, thereby expanding the possibilities for increasing the efficiency of the catalysts. Advanced physicochemical techniques such as Infrared Spectroscopy, including *in situ* studies with probe molecules, HRTEM, XPS, and others, have been used in the studies. In my opinion the main contributions of the applicant's investigations could be summarized as follows:

1. An improved catalytic activity of Mn-Co mixed oxides in *n*-hexane oxidation has been demonstrated. It has been found that the increase in the catalytic activity in binary oxides is due to the formation of finely dispersed oxides (MnO₂ and Mn₂O₃, Co₃O₄), which are reduced at low temperature, enrichment of the surface with Co²⁺ ions, the simultaneous presence of Mn³⁺ and Mn⁴⁺ and decrease in the strength of the Co-O connection. The synergistic effect between the components in the SiO₂ based catalysts depends on the method and the sequence of the deposition as well as the ratio between them. By using of original "depletion" method, it has been demonstrated that the oxidation of *n*-hexane on Mn-Co oxide catalysts follows the Mars-van- Krevellen mechanism.
2. It was found that Ni, Co, Co-Ce or Co-Mn oxides, supported on Al₂O₃, stabilized palladium in the form of PdO, serving as an oxygen reservoir. This leads to an increase in the activity of methane oxidation catalysts, especially when binary metal oxides were used. The significance of the formation of spinel-like Co²⁺ - Al³⁺ surface phase has been demonstrated to stabilize highly active PdO particles. Their formation can be controlled by the Co content in the samples. By using of kinetic models, it has been shown that in the presence of Pd the process proceeds following Mars- van- Krevellen mechanism, with PdO reoxidation being a rate-determining factor.
3. *In-situ* FTIR studies have demonstrated different forms of CO adsorption on Pd-modified transition metal oxides, which is the basis of a discussion of the mechanism of CO oxidation on these catalysts.

4. The state of Pt on the SBA-15 and KIT-6 mesoporous silicas, and the catalytic activity in CO, *n*-hexane and methane oxidation, can be controlled by the addition of TiO₂ in the silica. It has been suggested that catalytic activity is favoured by the simultaneous presence of Pt⁰ and Pt²⁺ on the surface.

Undoubtedly, results with practical impact represent the demonstrations of the potential of biogenic hematite on total oxidation of CO and *n*-hexane. Originality of the study is the development of iron-containing biogenic materials cultured in the presence of 0.3% Pd / mesopore Al-Si-O, which demonstrate good activity in CO oxidation reactions and complete combustion of *n*-hexane.

I do not have critical remarks about the materials presented.

Conclusion

The research of Assoc. Prof. Dr. Silvia Todorova fully corresponds to the theme of the announced competition for awarding the academic position "Professor". Dr. Silvia Todorova is a very good specialist in the field of catalysis. The publishing activity after her habilitation, the citations of published results, teaching activity, participation and management of the projects fully cover all requirements of the Academic Staff Development Law and the Regulations on the Conditions and Procedure for Acquisition of Academic Degrees and the Occupation of Academic Posts at the Institute for Catalysis, BAS. Therefore, I convincingly recommend to the members of the Scientific Jury and to the Scientific Council of the Institute of Catalysis to award to the Assoc. Prof. Dr. Silvia Todorova the academic position "Professor" under the direction 4.2. Chemical Sciences (Chemical kinetics and catalysis).

25.06.2019 г.

Sofia

Reviewer:

/Prof. DSc. Tanya Hristova/