OPINION

by Assoc. Prof. Dr. Nikola Lyudmilov Drenchev

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on a competition for the academic position of an “Associate Professor” for the needs of the Laboratory “Materials and Processes for Environmental Protection” at IGIC-BAS in professional field 4.2 “Chemical Sciences”, scientific specialty “Chemical Kinetics and Catalysis”, promulgated in the “State Journal”, no. 46 from 25.05.2023

Biographical data

Only one candidate took part in the announced competition - Ch. Assistant Dr. Ralitsa Hristova Velinova from the Laboratory "Materials and Processes for Environmental Protection" at IGIC-BAS. She graduated from the University of Chemical Technology and Metallurgy, majoring in Materials Technology and Materials Science with a specialization in Silicate Materials in 2001. She was on specialization at the University of Aveiro, Portugal for a period of five months in the same year. From 2008 to 2010, he worked as a chemist at IGIC-BAS. After defending a dissertation on the topic "Ancient and medieval glasses in the Bulgarian lands" in the scientific specialty 02.10.12 "Technology of silicates, binders and hard-to-melt non-metallic materials", She obtained the educational and scientific degree "Doctor" in 2010. From November 2010 until October 2017, she worked as Ch. Assistant in the laboratory of "Analytical Chemistry". After that, she began to work in the laboratory of "Materials and Processes for Environmental Protection". She is a member of the "Union of Chemists in Bulgaria" and the "Association of the Bulgarian Catalytic Society". She is a reviewer in the journals: Materials, Energies, Catalysts, Processes, Aerospace and Polymers and Guest editor of a special issue "Catalytic Combustion - From Laboratory Tests to Practical Applications" of the magazine Catalysts - MDPI.

Reference for the fulfillment of the minimum and additional requirements of the IGIC-BAS

Ch. Assistant Dr. Ralitsa Velinova participated in the competition with a total of 17 scientific works. The scientific publications presented as the main habilitation work (Group of indicators C) are 6 in number (Q1 – 1 number, Q2 – 3 numbers, and Q3 – 2 numbers) with a total number of points 115 exceed of the required 100 points. In four of them, the candidate is the first author, which testifies her leading participation in these scientific works. In the other two articles, she is second author. Scientific works outside the habilitation work (Group of indicators D) are 11 (Q1 – 5 numbers, Q2 – 3 numbers, Q3 – 2 numbers and a book chapter). Their total

score is 230 pts. exceed of the required 220 pts. The applicant has submitted a total of 72 citations under “Group of indicators E” with a total score of 144 pts. exceed of the required 60 pts. An article published in Catalysis Today on 2020 has cited 30 times. The points according to the "G" indicator are 100 and exceed the required 70 points. The H-index of the candidate according to "Scopus" is 6 (min. H = 5 for Associate Professor). Ch. Assistant Dr. Ralitsa Velinova participated in 10 national and in 1 international project. The total number of participations in conferences and seminars is 89.

Main scientific contributions included in the habilitation work

The research in the publications from the habilitation thesis are mainly grouped in two thematic directions: (I) Synthesis and properties of palladium containing metal-oxide catalysts (Me = La, Ce and Al) for application in complete oxidation reactions of methane and propane and (II) Studies on catalysts based on oxides of transition metals (Co, Mn and Mn-Ce), supported on porous materials, in the reaction of complete oxidation of volatile organic compounds.

The behavior of the Pd/La_2O_3-CeO_2-Al_2O_3 system in complete oxidation reactions of methane and propane has studied in detail, as well as the influence of water vapor and SO_2 on the catalytic activity. The formation of a mixed phase La_2PdO_4 was established, which prevents agglomeration of palladium in the system. It is found that in the presence of water vapor and thermal aging, the PdO/Pd ratio increases, leading to a decrease in catalytic activity.

The behavior of Co-ZSM-5 catalysts with different Si/Al ratios (23, 40 and 100) in complete oxidation reactions of propane and n-hexane was investigated. In both reactions, the catalysts with a ratio of Si/Al = 23 exhibit the highest catalytic activity. This is explained by the presence of finely dispersed spinel Co_3O_4, which is reduced more easily due to the weaker interaction with the support in the case of catalytic oxidation of propane. The complete oxidation of n-hexane proceeds by the Langmuir-Hinshelwood mechanism, by dissociative adsorption of oxygen, as the reacting hydrocarbon and oxygen are adsorbed on different active sites. The influence of the changed microstructure as result of treatment with a buffer solution of hydrofluoric acid and ammonium fluoride was studied. It is found that the treatment leads to increase the activity in complete oxidation reactions of propane and n-hexane.

Catalytic tests were carried out in the reaction of complete oxidation of methane, propane and butane using single-component manganese and two-component Mn-Ce catalysts on SBA-15 support. It is assumed that despite the low activity of bimetallic catalysts, their main advantage is that the surface ratio of Mn^{3+}/Mn^{4+} is preserved.

Major scientific contributions in the non-habilitation thesis

The scientific works outside the habilitation thesis are also grouped in two thematic directions: (I) Catalysts based on transition metal oxides supported on porous materials and bulk

catalysts and (II) Catalysts based on palladium or platinum supported on Al_2O_3, tungstates, Ti-SBA-15 and mordenite.

In the thematic field (I), four publications are presented related to studies of different Co, Mn and Ce containing catalysts on SBA-15 support in complete oxidation reactions of CO, methane, propane, butane and n-hexane. Three temperature regions of desorption were established: physically adsorbed oxygen, chemisorbed oxygen and bulk lattice oxygen from the oxide phase. Manganese has shown to increase the mobility of lattice oxygen and the mobility of surface oxygen species, which explains the highest catalytic activity of the catalyst containing Co-Mn with molar ratio of 2:1. The same catalyst on hierarchical macro-mesoporous silica has found to have higher catalytic activity compared to the mesoporous support.

The effect of Ce in two-component Co-Ce oxide catalysts on SBA-15 support was studied. It is found that the addition of Ce worsened the catalytic properties. It is assumed that the fine dispersion of the oxides and their strong interaction leads to the formation of hard reducible oxide phases, which explains the lower activity.

Seven publications have presented under thematic field (II).

The influence of Pd deposited on $CuWO_4$ in the oxidation of C_1-C_4 hydrocarbons was investigated. The presence of Pd/PdO leads to lowering the minimum reaction temperature by 55^0C. It is found that Pd facilitates the reduction of the carrier, thus copper from $CuWO_4$ hinders the reduction of PdO. A stable Pd/$CuWO_4$ catalyst was obtained, which in tests over a period of 96 hours showed insignificant differences in the average size of Pd-crystallites. In this case, the carrier was obtained by mechanochemical synthesis.

The influence of mordenite support microstructure and reactant molecular size on catalysts containing Pt and bimetallic Pt-Cu nanoparticles in complete oxidation reactions of propane and benzene was investigated. The activity was found to decrease in the order Pt > Pt-Cu > Cu. The change in the microstructure of the solution (HF and NH_4F) treated sample leads to increased activity in the oxidation of methane and propane. This is due to the additional porosity, which increases the specific surface area, facilitates diffusion and access to the active sites inside the pores.

Investigations on the total oxidation reaction of methane with the participation of catalysts with Pd supported on La and Se modified γ-Al_2O_3 by impregnation and sol-gel methods were carried out. The impregnated samples were additionally modified with Co. The resulting catalysts were subjected to thermal aging for possible practical application. It is found that the deactivation was the weakest for the Pd/$LaAl_2O_3$ sample synthesized by the sol-gel method. The introduction of the Ce system results in a reduction of the specific surface area. In the presence of SO_2, the most active catalysts of both series are deactivated, which requires an increase in temperature by 100-110^{0}C. After elimination of SO_2 from the flow, a partial restoration of the initial activity of the catalysts was found. Co-free samples prepared by the sol-gel method were found to exhibit activity and stability comparable to that of impregnated Pd+Co/$LaAl_2O_3$.

Summary and conclusion

The working topics of Ch. Assistant Dr. Ralitsa Hristova Velinova are up-to-date and they have both a scientific and an applied nature and fully correspond to the theme of the announced competition. The materials submitted for participation in the competition cover both the minimum requirements for occupying the academic position "Associate Professor", according to the Law on the Development of the Academic Staff in the Republic of Bulgaria, as well as the additional requirements of IGIC-BAS. In all groups of indicators, the collected points exceed the required minimum. All this gives me the reason to recommend to the members of the Scientific Jury and the Scientific Council of IGIC-BAS to give their positive assessment in the selection of Ch. Assistant Professor Dr. Ralitsa Hristova Velinova for "Associate Professor" in professional field 4.2. "Chemical Sciences", scientific specialty "Chemical Kinetics and Catalysis".

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