ATTITUDE OF REVIEWER

by Prof. Margarita Valentinova Gabrovska, PhD
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with respect to the competition for occupying the academic position "Associate Professor" in professional field 4.2 "Chemical Sciences", scientific specialty "Chemical kinetics and catalysis", for the needs of the Laboratory "Materials and processes for environmental protection" at IGIC-BAS, announced in SG, issue 47 dated 04.06.2021.

The only candidate, applying for the academic position "Associate Professor" in the competition is Assist. Prof. Daniela Dimitrova Stoyanova, PhD, IGIC-BAS. All the documents, required and specified by the "Regulations for the conditions and order of appointing in academic positions in the IGIC-BAS" have been duly submitted.

D. Stoyanova defended in 2002 her PhD thesis entitled: „Cu-Co oxide catalysts supported on modified with La alumosilicate composites and γ-Al_2O_3 for waste gas cleaning". Since 2010 the candidate has held the academic position of "Assistant Professor" in the Laboratory "Materials and Processes for Environmental Protection", IGIC -BAS, where she still works. The chronology of her professional development and occupied positions proves that Assist. Prof. D. Stoyanova completely satisfies the requirements specified for occupying the academic position of Associate Professor.

Assist. Prof. D. Stoyanova is co-author of 38 research publications and one patent, of which 26 papers and one patent are submitted for the participation in the present competition. Based on 10 publications the Habilitation work (Indicator B), is formed. The included scientific results are published in journals that are referenced and indexed in world-famous scientific information databases (WoS or Scopus) in the field of competition. Two articles are published in journal with quartile Q1, 2 with Q2, 3 with Q3 and 3 with Q4. In total, the points exceed the minimum requirements (171 points with a required minimum of 100). Indicator of the personal contribution of Dr. D. Stoyanova in the research and summarizing the results is the fact that in 7 of the presented 10 publications Dr. D. Stoyanova is the first author, and in 5 - the corresponding. The remaining 16 publications and the patent present the Author's Reference (Indicator G) also published in WoS and Scopus categorized scientific journals: 3 with quartile Q1, 5 with Q2, 3 with Q3 and 5 with Q4. These also exceed the minimum required points (305 with a required minimum of 220). The total number of citations is 154, as 140 are from the Scopus database and 14 - from other sources, which meets the required minimum of 60 points (Indicator D). The results of the applicant's studies are presented at 12 national and 15 international scientific forums. She was participated in the teams of 4 national research projects for the period of the competition and was the leader of 4 research projects under the bilateral agreement between BAS and SANI-Serbia (2009-2022). The applicant submits a Hirsch index H = 5 (Scopus), which corresponds to the additional requirements of IONH for "Associate professor".

The detailed review of the summary results of Assist. Prof. D. Stoyanova included in the Habilitation work and Author's Reference outline the profile of her research activity with an emphasis on the development of promising catalytic materials used in various technological areas for the control of harmful emissions into the environment. The obtained results are up-to-date, important, and of interest, both from a fundamental and from a scientific-applied aspect, and coincide with the specialty in which the competition was announced.

The publications of the Habilitation work reveal the design of new carriers and effective catalysts for the purification of waste gases from motor vehicles and energy from harmful emissions of nitrogen oxides (NOx) and CO, summarized in two thematic areas.

Direction 1: *Synthesis of polyoxide composites based on alumina, natural minerals (bentonite and clay) and MgO, to obtain carriers with appropriate mechanophysical and physicochemical parameters used for the application of active components and applied in a wide range of catalysts*

An essential part of these studies is aimed at finding a universal composition of the carrier, which after appropriate heat treatment to be applied in a wide range of mechanically strong and thermally stable catalysts operating in different reaction medium.

Main contributions: A synthesis of the mulitocordierite-like phase with a suitable structure at lower temperatures compared to the classical ceramic technology was performed. In the same composition, the thermal stability of the carriers obtained by *co-precipitation* is higher than those obtained by *mechanical mixing*, which allows this type of carriers to be used in the preparation of catalysts for high-temperature processes. It has been shown that the impregnation of a residue of deactivated Pd/Al_2O_3 catalyst (after partial extraction of Pd) with Cu-Co oxide phase leads to the production of a polyoxide catalyst for the reduction of NO with CO and oxidation of CO to CO_2 in gas mixtures. The activity of the catalyst in the reduction of NO with CO and its resistance to SO_2 poisoning increases in the presence of Pd in combination with the applied active Cu-Co oxide phase. Modification of γ-Al_2O_3 with La up to 3% by weight has been found to inhibit the formation of α-Al_2O_3, inhibit the interaction of the active Cu-Co oxide phase with the carrier and the formation of aluminates, and increase the dispersion of the catalytically active centers. La-containing catalysts show higher activity than unmodified ones in the reactions: NO+CO, $CO+O_2$ и $C_6H_6+O_2$.

Direction 2: *Development and investigation of supported catalysts with a metal oxide active phase content with high catalytic activity and applicability in the processes of purification of gaseous fluids in the chemical, energy and transport industries*

Scientific contributions in this direction are related to the preparation and application of highly active catalysts for the processes of NO reduction with CO, oxidation of CO and hydrocarbons in waste gases. It has been shown that the highest catalytic activity in the reduction of NO with CO shows an iron catalyst obtained by impregnating activated carbon with an aqueous solution of Fe $(NO_3)_3$. When using organic solutions, the activity decreases in the order: methanol> ethyl ether> acetone, which is associated with the presence and efficiency of catalytically active complexes containing iron ions in different oxidizing state formed during the synthesis of samples. Pd/NiO (0.3% Pd) deposited on corundum is an active catalyst with low starting temperature and high thermal stability. Activated metallurgical slag for waste gas treatment is the basis for the creation of new active catalysts for complete oxidation of CO and hydrocarbons. $Ag(BaCO_3)Al_2O_3$ composition for neutralization of NOx from exhaust gases shows higher resistance to SO_2 poisoning than the traditional $Pt/BaCO_3/Al_2O_3$ catalyst, which is a promising approach to develop a cheaper catalyst. High activity in the oxidation reaction of CO with oxygen and stability to SO_2 poisoning is shown by oxide catalysts obtained by impregnation of Al/Si/Mg carrier with Cu-Co aqueous nitrate solutions, and annealed at the temperature of formation of spinel-like Cu-Co oxide phase. The direct decomposition of NO in the absence of oxidants takes place on perovskite-type catalysts $LaTi_xMg_yFe_2O_3$ at temperatures above 250°C with high purification efficiency and the presence of catalytically active complexes involving Fe^{3+} ions. Cu/Zn/Al composition with a spinel-like structure obtained by co-precipitation of Cu,Zn ammonia-carbonate solutions and solution and $Al(NO_3)_3$ is a highly active catalyst for decomposition of N_2O to N_2 and O_2 in the production of HNO_3 by the Oswald method, more in the first stage - catalytic oxidation of NH_3. The co-precipitation conditions provide high dispersion after

annealing of the contact masses at 900°C. This predetermines the high activity of the catalyst in the study in kinetic and diffusion mode at high temperature and space velocities.

It should be noted that tests for mechanical stability, resistance to SO_2 poisoning and work of the catalysts at high space velocities were performed for a large part of the developed catalysts, i.e. conditions analogous to industrial ones, which is a precondition for their industrial application.

The author's reference includes research on a wide range of materials with different fields of application, grouped in four directions:

1. Synthesis and investigation of new catalyst composites for CH_4 combustion based on the classical technological schemes for supported catalysts of the type Pd-MeOx/Al_2O_3 (Me = Co, La, Ce). **2**. Synthesis and study of CuO and NiO catalysts as from supported type as well obtained by mechanical activation of the precursors for CO oxidation reaction. **3**. Synthesis and characterization of photocatalytic oxide materials in the form of nanosized powders (ZnO, P-TiO_2, $CaTiO_3$, Zn_2SnO_4) and measurement of their photocatalytic activity for decomposition of model textile dyes and oxidation of ethylene in gas phase and acetylsalicylic acid. **4**. Obtaining a new type of corrosion-resistant mono- and poly-component oxide coatings, by chemical methods on different types of metal carriers (ZrO_2 and TiO_2).

The scientific investigations of Assistant Professor Dr. D. Stoyanova show that she is an established scientist with high qualification in the development of promising catalytic materials to improve air quality by eliminating harmful emissions of NOx and CO. These studies enrich existing knowledge and show potential for application in practice.

The presented materials by Assist. Prof. Dr. D. Stoyanova exceed all required indicators according to Law for the development of academic staff in Republic of Bulgaria and the Regulations for its application, as well as the additional requirements reflected in the Regulations of IGIC-BAS for acquiring scientific degrees and for holding the academic position “Associate Professor”.

The overall analysis of the scientific activity and scientific production of Assist. Prof. D. Stoyanova in the field of the competition allows me to give her my **positive opinion** and confidently recommend to the honorable members of the Scientific Jury and Scientific Council of IGIC-BAS to **vote positively** for the award of the academic position **Associate Professor** to Assist. Prof. Dr. Daniela Dimitrova Stoyanova in the professional field 4.2. “Chemical Sciences”, scientific specialty “Chemical kinetics and catalysis”.

23.09.2021 Reviewer:

/Prof. Margarita Gabrovska, PhD/