

REVIEW REPORT

by Prof. Dr. Ivalina Avramova Avramova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences

(member of the scientific jury)

regarding the application of Assoc. Prof. Dr. Hristo Gospodinov Kolev

to occupy the academic position "Professor" in the professional field 4.2. Chemical Sciences (Solid State Chemistry) for the needs of the laboratory

"Design and Characterization of Catalytic Materials" at the Institute of Catalysis-BAS, the announcement for which was published in the State Newspaper No. 82 on 07.10.2025.

Assoc. Prof. Dr. Hristo Gospodinov Kolev is the only candidate in the competition for the academic position "Professor" in the professional field 4.2. Chemical Sciences (Inorganic Chemistry) announced in the State Newspaper No. 82 on 07.10.2025 for the needs of the laboratory "Design and Characterization of Catalytic Materials" at the Institute of Catalysis of the Bulgarian Academy of Sciences.

Assoc. Prof. Kolev has submitted all necessary documents for participation in the competition, which are required by the Law for the Development of the Academic Staff in the Republic of Bulgaria, Regulations for the application of the Law, as well as the Regulations on the terms and conditions for acquiring scientific degrees and for holding academic positions at IC-BAS.

Hristo Kolev studied physics at the Faculty of Physics of Sofia University, where in 1998 he received a master's degree in engineering physics in the field of "Engineering Physics". In the period 1998-1999 he worked as a systems engineer at Macronet AD, Sofia, Bulgaria for the production and implementation of electronic electricity meters.

In the period 1999-2002 he worked as a physicist in the Electron Spectroscopy Laboratory at the Institute of General and Inorganic Chemistry-BAS. Meanwhile, during 2000 Hristo Kolev has been invited as a Research Assistant at the Westfälische Wilhelms University Münster, Münster, Germany, where he became a PhD student the same year. During the period of his PhD studies 2000-2005 he worked in the field of Research of the electronic structure and magnetic properties of materials for spinellectronics (magnetoelectronics), as well as he has possibility to develop his skills in Maintenance of the required equipment. In 2009 Hristo Kolev received his PhD in Physics in the field 01.03.26 – Electrical, magnetic and optical properties of condensed matter.

Since May 2004, Hristo Kolev has been working as a physicist at the Institute of Catalysis at the Bulgarian Academy of Sciences in the laboratory where he continues to work to this day. Career growth followed, and in 2006 he became a Research Associate, 2nd degree, Ph.D. In the same year, Hristo Kolev specialized at Abdus Salam - International Center for Theoretical Physics and ELETRA Synchrotron Radiation Laboratory, Trieste, Italy in the field of Synchrotron Radiation and Applications. In the period 2010-2018, he worked as an expert in Specialized Sensors and Devices at IMSTCHA - BAS "ACAD. A. BALEVSKI", Sofia, Bulgaria.

Meanwhile, in 2012 he attended a course on Starting a Business at the Cisco Entrepreneurial Institute, 23A Joliot Curie Street, Sofia. From 18.09.2017-18.03.2018 Assoc. Prof. Dr. Hristo Kolev worked as a Senior Investigator at the Faculty of Mining, Ecology, Process Management and Geotechnology at the Technical University of Košice, under research program "Application of X-ray Photoelectron Spectroscopy (XPS) for Better Understanding of Surface Properties", within the framework of the National Scholarship Program SAIA of the Slovak Republic, Ministry of Education, Science, Research and Sports of the Slovak Republic.

In the period 2011-2014 he held the position of Assistant Professor, PhD at the Institute of Catalysis at the Bulgarian Academy of Sciences, and in 2014 Hristo Kolev held the position of Assoc. Prof. PhD again at the Institute of Catalysis, where he continues his scientific work in the field of surface analysis of materials with X-ray Photoelectron Spectroscopy.

The total number of publications of Assoc. Prof. Hristo Kolev is 139, of which 113 after habilitation and holding the academic position of "associate professor". 106 of the total number of works are visible in databases with scientific information (Web of Science and/or Scopus). The total number of noticed citations (without auto-citations of all authors) is 1237, of which 1153 after holding the academic position of "associate professor". The Hirsch index (H) based on all publications included in databases: Web of Science and Scopus (without auto-citations of all authors) is 18, indicated by the candidate in the documents, but according to Scopus it is already 19. Hristo Kolev has participated in 32 projects, in 3 of which he was the leader.

The materials submitted by Assoc. Prof. Dr. Hristo Kolev for the competition, on paper and electronically are in accordance with the Regulations for the Development of the Academic Staff of the IC-BAS and meet the criteria for occupying the academic position of "Professor".

In the competition for the academic position Professor, Assoc. Prof. Kolev participated with 10 articles from group B (to the habilitation report), all of which are in quartile Q1.

In the habilitation report presented by the candidate, attention is focused on the application of the XPS method for the study of catalytic systems based on nanosized metal oxides. The main goal is to characterize the surface of the catalysts and to track changes in the oxidation state of the metal components, both before and after catalytic reactions, in order to establish their mechanism of action and activity. In this regard, catalytic systems containing transition metal and rare earth oxides – Co, Mn, Ni, Fe, Ce, Sm, Zn and their combined forms have been studied.

Cobalt and manganese-based systems, as classical catalysts for oxidation and reduction processes, where the redox couples $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ play a central role, are examined in detail by the candidate in articles **B2**, **B3**, **B5**, **B7** of the habilitation report. In the presented works, various supports – $\gamma\text{-Al}_2\text{O}_3$, activated carbon and clinoptilolite – were studied in order to trace their influence on the stability and distribution of metal oxide nanophases.

The development of active and thermally stable $\text{Pd-Co}/\gamma\text{-Al}_2\text{O}_3$ catalysts for the complete oxidation of methane by controlling the Co content and the sequence of metal deposition was investigated by XPS in **B2**. The analysis proves the stable presence of Co^{2+} (CoO nanophases) in all Co-containing samples, as well as differences in the $\text{Pd}^{2+}/\text{Pd}^0$ ratio, depending on the synthesis method. After catalytic tests and aging (120 h at 505 °C), an increase in Pd^{2+} was found in the Co-modified materials, while the binding energy of the Pd3d line characteristic of PdO (336.1 eV) remained unchanged - evidence of a stable interaction between PdO and the support. After "exhaustive" oxidation, the Pd-Co catalysts show an increased Pd^0

content, while in the case of only Pd component, the shift of the binding energy to 334.0 eV is evidence of an increase in particle size. In the Co- containing samples, about half of the Co^{2+} is oxidized to Co^{3+} , which proves the high reducing ability of the cobalt phase. In **B3**, activated carbons with different textures were studied as supports for nanodispersed cobalt oxide phases for methanol decomposition. XPS confirmed a high dispersion of cobalt oxide phases and the presence of mixed $\text{Co}^{2+}/\text{Co}^{3+}$ states, and this ratio directly depends on the pore structure, as well as on the chemical characteristics of the supports. Materials with more accessible Co^{2+} states in mesopores show higher activity in methanol decomposition, while supports dominated by micropores demonstrate lower activity due to limited accessibility of the active centers. The XPS method was also applied to the study of catalysts based on Co-Mn oxide phases deposited on clinoptilolite, intended for the oxidation of volatile organic compounds, described in works **B5** and **B7**. The presence of mixed valence states $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ has been demonstrated, with their ratio depending on the preparation method and the degree of dispersion on clinoptilolite. The $\text{Co}2p_{1/2}$ spectra contain characteristic shake-up satellites, which are characteristic of $\text{CoO}/\text{Co}_3\text{O}_4$, and the $\text{Mn}2p$ spectra indicate the presence of mixed oxides with high redox activity. A correlation has been established between the higher $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratios and increased oxygen mobility, which has been confirmed by TPR analysis. XPS analysis of samples before and after the catalytic reaction proves partial reduction of $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ and $\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}$, supporting a Mars–van Krevelen type mechanism. Restoration of the initial valence states after oxidative treatment has been demonstrated, which is evidence of high structural stability of the active phase.

Publications **B4**, **B8** and **B9** are devoted to the study of iron oxides and their mixed oxide forms. Interesting are $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couples and their ability to be incorporated into stable structures such as spinels, perovskites and mesoporous oxide matrices. XPS analysis reveals a complex reduction balance between $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Ni}^{2+}/\text{Ni}^0$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ of mesoporous Ce-Fe–Ni mixed oxides with controlled metal content, followed by stepwise reduction and carbonization with methanol to obtain metal–carbon composites, including Ni–Fe alloys and Fe–carbide nanophases encapsulated in carbon nanotubes [**B4**]. XPS studies conducted at each stage of the synthesis of the composites show initially, Fe^{3+} in hematite-like structures, as well as the $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio indicating the presence of oxygen vacancies and defective Ce–O–Fe interfaces. After reduction, the Fe^{2+} content increases significantly and Ni–Fe alloys are formed. The carbonization process leads to the formation of Fe–carbide nanophases ($\chi\text{-Fe}_2\text{C}_5$), as well as to an increase in graphite-like carbon. In **B8**, activated carbon supports modified by hydrazine treatments and doped with $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ spinels (40 wt.%) were studied, which were subsequently subjected to methanol decomposition to induce coking. XPS analysis showed the presence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ mixed states, typical of $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ spinel structures, with Fe^{3+} dominating octahedral positions. Ni is in a mixed state ($\text{Ni}^{2+}/\text{Ni}^{3+}$), with a higher degree of Ni^{3+} correlating with better electrical conductivity. After methanol conversion, an increase in relative amounts of Fe^{2+} was observed, which is an indicator of the formation of carbide or 7 metallic Fe-phases below the surface. In the spectrum of the C1s line, the presence of graphite and defective sp^2 -sites is predominantly observed, while in the N1s spectra, stable N-functions (pyridine, pyrrolide and graphitic nitrogen) are registered, which facilitate electron transfer. In **B9**, $\text{SmFeO}_3/\text{CuO}$ heterostructures with varying phase ratios were studied for the activation of peroxomonosulfate (PMS) and degradation of the antibiotic sulfathiazole. XPS establishes the oxidation states of the elements. Fe^{2+} appears only after a catalytic reaction, probably due to electron transfer between Fe and CuO. Copper is in a mixed state $\text{Cu}^{2+}/\text{Cu}^+$, and the formation of Cu^+ under catalytic conditions correlates with a more efficient activation of PMS. The registered reduction of $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ during the reaction is followed by a reduction to Fe^{3+} after oxidation, indicating a typical redox cycle governing the activation of PMS. In conclusion, XPS proves that

the $\text{SmFeO}_3/\text{CuO}$ heterostructure creates active sites on the surface and facilitates the formation of $\bullet\text{OH}$, $\text{SO}_4\bullet^-$ and $^1\text{O}_2$ for antibiotic degradation due to $\text{Fe}^{3+}/\text{Cu}^{2+}$ synergy.

In publication **B1**, the role of Ni in Ni/Ce–Zr and Ni–Sn/Ce–Zr catalysts with controlled Sn content (2.5–10 wt.%) subjected to reduction and studied in ethylene glycol APR was studied in detail. XPS analysis showed that in all reduced bimetallic samples a dominant Ni^0 content (6.45–6.54 at.%) was registered, while residual Ni^{2+} remained below 1 at.%, as evidence of the complete reduction of nickel oxide after activation. The lower Ni^0 content in samples with high tin content proves the formation of stable Ni–Sn intermetallic phases. A partial reduction of Ce^{4+} to Ce^{3+} was observed after reduction treatment, a fact confirmed by TPR-TGA measurements. A decrease in Ni–Ni coordination numbers (5.0–6.7) was observed by EXAFS analysis, as evidence for the presence of nanoparticles and/or intermetallic phases in which part of Ni is replaced by Sn. The latter method and the results obtained with XPS show that Sn stabilizes Ni^0 , reducing the tendency for excessive C–C hydrogenolysis and suppressing methanation, leading to higher selectivity to hydrogen.

The remaining two publications from the candidate's habilitation report are devoted to Oxide catalytic systems containing rare earth elements. Pure and rare earth modified ZnO powders (La_2O_3 and Eu_2O_3 , 2 mol%) for tribocatalytic decomposition of doxycycline under dark conditions are the subject of research in publication **B6**. XPS analysis proves that the presence of La^{3+} and Eu^{3+} enhances the generation of superoxide radicals $\bullet\text{O}_2^-$ through facilitated electron transfer to oxygen, which is a key mechanism for the degradation of doxycycline. The subject of research in publication **B10** are ZnO catalysts prepared by the sol-gel method and, modified with 1–3 mol% Eu_2O_3 , for the tribocatalytic degradation of paracetamol under dark conditions. XPS data show the coexistence of Eu^{3+} and Eu^{2+} , the presence of oxygen vacancies and adsorbed water on the surface of the studied catalysts. After tribocatalysis, Eu^{2+} disappears completely, as evidence of an ongoing redox process $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$, accompanied by an increase in defective oxygen — evidence for the active role of oxygen vacancies in the mechanism. XPS results show that Eu^{3+} centers and the defects induced by them facilitate the generation of reactive oxygen species, as a result of which the highest catalytic efficiency was shown by the samples with the highest Eu content (3 mol%).

Outside the habilitation report, other equally significant scientific contributions are described in the author's report, in three thematic areas: oxide and hybrid materials for energy storage and conversion, rare earth oxides with applications in luminescence, and nanomaterials for nanomedicine.

Here, the candidate applies XPS as a leading tool for the analysis of surface chemistry, valence states, defect structure and electronic properties of oxide, magnetic and hybrid materials with applications in the above-listed areas. XPS analyses are also correlated with methods such as XRPD, SEM/TEM, EDX, AFM/CM, IR/FTIR, Raman, EPR, SQUID, ICP-AES, TG/DSC, N_2 -physisorption, thermoprogrammable processes (TPR/TPO), electrochemical impedance spectroscopy, cyclic and pulse voltammetry—as well as theoretical interpretations of redox processes, oxygen defectivity and surface energy levels applied to characterize the systems depending on their application.

In publications **G1**, **G6** and **G9** of the author's report, oxide materials for solid oxide fuel cells and electrode materials for lithium-ion batteries were studied. $\text{La}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$ perovskite ceramics, obtained by mechanochemical route, were studied by XPS, and the presence of La^{3+} and Ca^{2+} was assessed. The observed variations in the $\text{La}^{3+}/\text{Ca}^{2+}$ ratio and carbon vacancies in the mixed oxide are in full correlation with the electrochemical measurements. It has been shown that at moderate Ca^{2+} content, maximum partial oxygen-ion conductivity is achieved, and at lower temperatures the electrical properties are

dominated by the contribution of grain boundaries. $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ solid solutions, obtained by a "green" alginate-mediated ion exchange scheme, are also the subject of study. The ratio between $\text{Ce}^{3+}/\text{Ce}^{4+}$ and the effect of Gd-doping on the electronic structure and oxygen defects were determined. The information obtained with XPS and the studies of the system with the XRD, IR, SEM methods allow us to trace the evolution of the structure from powders to sintered ceramics. The role of heat treatment and Gd content on the stability of the fluorite phase and the potential of these materials as electrolytes for IT-SOFC and as catalytically active oxides was clarified. High-entropy spinel oxides and lithiated oxyhalides (HEOFe , LiHEOFeF , LiHEOFeCl) as anode materials for lithium-ion batteries were also studied. XPS has a key role in confirming the chemical composition determined by XRD and Mössbauer spectroscopy, and the stability of the surface Fe^{3+} centers upon introduction of Li and F/Cl and in the presence of oxygen defects. The comparison of the results of XPS, XRD and electrochemical characteristics allows to establish a clear relationship between particle size, charge transfer and capacitance. It is shown that the best electrochemical parameters are achieved for the oxychloride having the finest size.

In the second direction, lanthanide-containing oxide and MOF-based materials with luminescent properties were investigated. In **G2**, thin films of GdNbO_4 and GdTao_4 were investigated, in **G3**, isostructural Eu/Gd/Tb MOF thin films based on BTC ligand were investigated, in **G4**, attention was focused on SmNbO_4 and SmTaO_4 precursors, and in **G5**, the transformation of amorphous Tb-MOF into TbO_x thin films on $\text{Pt/SiO}_2/\text{Si}$ support was followed.

The presence of stable Gd^{3+} and $\text{Nb}^{5+}/\text{Ta}^{5+}$ states was demonstrated by XPS and the change in Gd content from powder precursors to films was quantified. Comparison of the surface composition (Gd/Nb/O and Gd/Ta/O) with excitation and emission spectra demonstrates how charge-transfer transitions to $\text{Nb}^{5+}/\text{Ta}^{5+}$ and intra-configurational $4f-4f$ transitions of Gd^{3+} determine the UV emission and the potential for sensors and display devices. In the study of isostructural Eu/Gd/Tb MOF thin films based on the BTC ligand, the coordination of Eu^{3+} , Gd^{3+} and Tb^{3+} ions were confirmed by XPS. Transparent films with controlled nanomorphological structure and two-color emission profile, controlled by the excitation wavelength, have been realized by varying the ratio of synthetic conditions and lanthanides. In the study of SmNbO_4 and SmTaO_4 precursors, the co-presence of Sm^{2+} and Sm^{3+} is distinguished for the first time and parameters $\Delta(\text{O-Nb})$ and $\Delta(\text{O-Ta})$ are introduced to describe the average Nb–O and Ta–O bond. It is shown that the dominant Sm^{3+} states and the specific coordination create prerequisites for the application of these materials as nanophosphors in lighting and display technologies. The transformation of amorphous Tb-MOF into TbO_x thin films on $\text{Pt/SiO}_2/\text{Si}$ substrate is monitored, indicating the simultaneous presence of Tb^{3+} and Tb^{4+} on the surface of the layers. A model for the formation of cF-TbO_x , $\text{c-Tb}_4\text{O}_7$ and $\text{c-Tb}_2\text{O}_3$ phases is proposed thanks to the comparison of XRD and TEM with XPS analyses.

In the third direction, magnetic nanoparticles and functional nanomaterials with potential application in nanomedicine – magnetic hyperthermia, MRI contrast agents and electrochemical biosensors were studied.

In **G7**, Co-substituted magnetite nanoparticles optimized for magnetic hyperthermia were studied. XPS analysis allows to distinguish the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ ratio on the surface and to correlate it with the observed increase in magnetocrystalline anisotropy, saturation magnetization and specific absorption power (SLP).

In Publication **G10**, the study of ultra-low Gd^{3+} doped multicore $\gamma\text{-Fe}_2\text{O}_3$ "nanoflowers" for combined MRI/MHT (MHT Malignant Hypertension, MRI Magnetic resonance imaging) application is devoted. XPS

demonstrates the occurrence of defects – increased Fe^{2+} and non-crystalline oxygen content with increasing Gd^{3+} concentration, which is interpreted as a redox imbalance and formation of oxygen vacancies.

In **G8**, a MOF-produced nanoceria/g- C_3N_4 structure was studied, used as an electrode modifier for a sensitive voltammetric sensor for guanine. Here, XPS enables the determination of the oxidation state of Ce, the presence of oxygen defects, and the interaction between nanoceria and g- C_3N_4 , which govern the electrocatalytic activity and the diffusion-controlled mechanism of guanine oxidation. The obtained low detection limit and good selectivity in a real matrix (urine) demonstrate the potential of these materials for biomedical analyses.

When preparing the report on the minimum national and additional requirements, the candidate made inaccuracies (due to a subsequent update of the data in Web of Science and Scopus) in the quartiles. As a result, the points for indicator G should be changed to 1359.

According to the new requirements related to the Law for the Development of the Academic Staff in the Republic of Bulgaria, and the Regulations for the application in a letter from the National Center for Information and documentations in Bulgaria dated 04.07.2025, the points in indicator D relating to the citations of the candidate's works should be reduced to 2080, due to the recognition of citations noted only in Web of Science and Scopus. According to these new requirements, the points under indicator E are also changed to 487, due to the requirement to evaluate only completed projects and also due to the fact that Bilateral Cooperation and Exchange Agreements projects are international. Regardless of these corrections, from the presented report on the minimum requirements for the scientific activity of candidates for holding the academic position of "professor" it is clear that for all groups of indicators, the points fulfilled by Assoc. Prof. Dr. Hristo Kolev significantly exceed the required ones. The total number of points from all indicators after the corrections is 4226 and exceeds the minimum requirements of the IC at the Bulgarian Academy of Sciences for holding the academic position "professor".

I know Mr. Hristo Kolev as a colleague who works in the field of surface analysis of materials. Over the years, we have mainly exchanged ideas in connection with the maintenance of the same equipment that the Institute of Catalysis and Institute of General and Inorganic Chemistry have. We even had the opportunity to work together when it was necessary to dismantle and transport of ESCASIMS, where he also showed his enviable technical skills accumulated over the years along with his research skills. He gives the impression of a consistent and thorough person and scientist who is well aware of the scientific problems posed and competent in solving them. He is distinguished by great work capacity, analytical skills in solving the scientific and technical problems that arise, which is a prerequisite for a further very successful scientific and research career. I have no joint research and publications with the candidate and my opinion expressed here is based entirely on the materials submitted for the competition.

Conclusion:

In conclusion, I believe that the scientific production and activity of Assoc. Prof. Hristo Kolev show his scientific and applied scientific results, which represent an original contribution to science. This is clearly evident from the citation of the publications, his participation in international scientific teams, project management, the training of Bulgarian and foreign students and doctoral candidates. All this undoubtedly proves that Assoc. Prof. Kolev is a distinguished and internationally recognizable scientist in the field of surface science studies of materials with wide modern application. After all that has been said above, I

give my categorical positive assessment of the candidacy of Assoc. Prof. Hristo Kolev and propose to the esteemed scientific jury of the competition to prepare a proposal to the Scientific Committee of the Institute of Catalysis-BAS, Assoc. Prof. Dr. Hristo Kolev to be elected as a Professor at the Institute of Catalysis-BAS, in the professional field 4.2 Chemical Sciences (Solid State Chemistry) for the needs of the laboratory "Design and Characterization of Catalytic Materials".

05.02.2026

Reviewer:

Sofia

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