R E V I E W

With respect to the competition 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 Institute of General and Inorganic Chemistry at the Bulgarian Academy of Sciences, Laboratory „Reactivity of Solid Surfaces“ published in „Newspaper of State”, issue 36, dated 03.05.2019

Candidate: **Assoc. Prof. Dr. Mihail Yordanov Mihaylov**, Institute of General and Inorganic Chemistry - Bulgarian Academy of Sciences (IGIC-BAS)
Reviewer: Prof. Dr. Yuri Angelov Kalvachev, Institute of Catalysis - Bulgarian Academy of Sciences

The only candidate in the competition for occupying the academic position „professor", published in Newspaper of State issue 36 dated 3rd of May 2019 and also on the Internet website of the IGIC, is Assoc. Prof. PhD Mihail Mihaylov, currently working at the Laboratory "Reactivity of Solid Surfaces" at the IGIC, BAS. The applicant has submitted the documents required by law.

Mihail Mihailov graduated from the Faculty of Chemistry at Sofia University “St. Kliment Ohridski ”(present Faculty of Chemistry and Pharmacy) in 1997 as a Master in inorganic and analytical chemistry. The following year he enrolled as a PhD student at the IGIC after winning a competition and successfully defended his educational and scientific degree "Doctor" in November 2002. The topic of his dissertation is "Synthesis and characterization of deposited nickel catalysts. Influence of the Support on the Properties of Nickel ”, supervised by Cor. Member Prof. DSc Konstantin Hadjiivanov. His doctoral degree was awarded by the Higher Attestation Commission in 2003, and in the same year Dr. Mihail Mihailov won a competition for a research associate at IGIC-BAS in the group of Prof. Konstantin Hadzhivanov. In 2008, Dr. Mihailov acquired the academic position of Associate Professor, which he still holds. In pursuing his doctoral dissertation, and in his work thereafter, Mr. Mihaylov worked under the guidance of Prof. Konstantin Hadjiivanov, from whom he perceived the accuracy and depth of the research work, and under whose leadership he grew up as a scientist. In 2006, he received a scholarship from the prestigious German Alexander von Humboldt Foundation and specialized for one year at the Ludwig Maximilian University, Munich, Germany, in the group of Professor H. Knoezinger, which is essential for his development.

Prof. Dr. Mihail Mihailov's research investigations are mainly in the field of materials science - studying the chemistry of active solid surfaces, adsorbents and catalysts, mainly by IR

spectroscopy and the study of the processes occurring on them during the catalytic act, using innovative experimental technology.
The candidate Mihail Mihailov meets the requirements for occupying the academic position professor in the Institute of Catalysis, referred to in Article 29, Paragraph 1, Items 3,4 and 5 of the Law on the Development of the Academic Staff in the Republic of Bulgaria and in the Regulations for its implementation, as well as the enhanced criteria of the Bulgarian Academy of Sciences and the IGIC-BAS. The implementation of the different groups of indicators by points is presented in the following table:

Group	Indicator	Points	Points in the group	Required points
А	1. PhD thesis	50	50	50
Б				
В	4. Habilitation work - scientific publications in journals referenced and indexed in Web of Science and Scopus.	125	125	100
Г	7. Scientific publications in journals referenced and indexed in the Web of Science and Scopus, outside the habilitation	450	450	220
Д	11. Citations in scientific publications, monographs, collections, and patents referenced and indexed in the Web of Science and Scopus.	774	774	120
Е	14. Participation in national scientific or educational projects 15. Participation in international scientific or educational projects 16. Guidance of national scientific or educational projects 18. Funds received from projects leaded by the Candidate	90 20 40 87	237	150
Ж	21. Hirsch Index (H) (Scopus); H = 10 (minimum) for professor	180	180	120

All other requirements of the above mentioned law are fulfilled - a recognized educational and scientific degree "Doctor" and an academic position "Associate Professor". Diplomas are presented, as well as a certificate of employment showing that he had held the academic position of associate professor for a period longer than the required by the same law. A careful review of the materials submitted to me for review gives me reason to claim that there is no evidence of plagiarism in the scientific works of Assoc. Prof. Mihail Mihailov and he fulfills the condition referred to in Article 29, Paragraph 1, Item 6 of the law.

To participate in the competition Assoc. Prof. Todorova has presented 23 scientific publications, five of them comprise her habilitation work, entitled "IR spectroscopic study of adsorption forms of NOx and COx on cerium dioxide: Revision of existing concepts". All five habilitation articles are in journals that are categorized in WoS and Scopus and are in the Q1 quartile group, which fact shows a high level of scientific work. In four of them Dr. Mihailov is the first author, and in one of them he is the second author, which is an acknowledgment of the major contribution to the elaboration of the mentioned works.

18 articles are presented in Group D, Indicator 7, namely - Scientific publications in journals and issues that are referenced and indexed in world known scientific information databases (*Web of Science* and/or *Scopus*) that are outside the scope of habilitation work. It is impressive that all of them are in Q1 journals again. Assoc. Prof. Mihailov is the first author in seven of them. All publications with which the candidate appears in the competition are published after his habilitation and receiving the academic position "Associate Professor".

The candidate has over 1200 citations according to *Scopus* database, excluding all self-citations. The works submitted for the competition received 387 citations, which exceeds many times the established requirements for awarding the academic position of "professor". The applicant's H-index is 18, excluding the self-citations from all co-authors. All these facts are evidences for the wide response received from the papers of Assoc. Prof. Mihailov in the world scientific literature.

The dissemination of the scientific results of Assoc. Prof. Mikhailov is widespread - they have been presented at 28 conferences and symposia, and 15 of them are oral presentations (some of them plenary). The applicant has submitted a list and proves the participation in projects won on a competitive basis - 9 with national and 1 with international funding, and separately he is the head of 2 other successfully completed projects with the Bulgarian National Science Fund.

Prof. Mihailov's habilitation work is based on five papers and concerns a modern topic that has a direct connection with environmental protection - study of adsorption forms of NOx and COx on cerium dioxide. These studies are related to the possibility of studying the nature and stability of the surface structures formed on cerium dioxide and can lead to its effective use for carbon dioxide capture, to its conversion into valuable chemicals and fuels, to the DeNOx waste gas treatment process.

The essence of the habilitation work is to revise previous interpretations of the IR spectra of the surface forms obtained by adsorption of nitroden oxides and carbon oxides on cerium dioxide. New surface compounds have been identified by adsorption of NO on nonstoichiometric cerium oxide and new pathways for the conversion of NO to N_2 have been proposed, namely by forming NO^{2-} or N_3^- -like intermediates. Logical assumptions are made for the further conversion of these intermediates to nitrogen. Depending on the morphology of cerium dioxide, the formation of one of the particles (NO^{2-} or N_3^-) prevails and this fact enables the design of adsorbents and catalysts selective to one of the reaction pathways. In the papers, it has been unambiguously shown that NO- type structures do not form.

The COx adsorption forms on stoichiometric, reduced and hydroxylated cerium dioxide are described in detail. The formation of hydrogen carbonates, bi- and tridentate carbonates was found. Combining computational and experimental data, new assignments of IR bands of surface hydrogen carbonate and formate structures on cerium oxide have been proposed. Hydroxylation promotes the formation of formates and the reduction promotes the formation of structures with close surroundings of Ce^{3+} cations or of oxygen vacancies.

The other publications presented by Assoc. Prof. Mihaylov for participation in the competition form three thematic directions, namely studies on gold-containing catalysts; iron-containing zeolites; and metal-organic structures.

Gold-containing catalysts

In the study of gold-containing catalysts in the papers of Dr. Mihailov, some aspects of the mechanisms of catalytic action of deposited gold nanoparticles were clarified.

Although gold nanoparticles are shown to be inert to O_2 at room temperature, they are easily oxidized by CO_2. Thus, the catalytic oxidation of CO on Au^0/La_2O_3 is characterized by an initial induction period, which can be explained by the generation of active $Au^{\delta+}$ centers as a result of the dissociation of the CO_2 product (autocatalytic process). The role of oxidized gold centers has been suggested to be related to the activation of O_2.

Carbonate-like structures associated with $Au^{\delta+}$ centers on gold clusters deposited on MgO have been identified. They have been found to be responsible for deactivating the catalyst in the CO oxidation reaction. The positive effect of gold agglomeration and the negative effect of carbonate accumulation on catalyst activity are distinguished.

For the first time, negatively charged gold centers ($Au^{\delta-}$) formed on an SiO_2 inert support have been observed and it has been shown that the formation of these centers in an atmosphere of CO favors the presence of moisture or hydrogen. Thus, the previous notion that an electronic transfer from the support to the gold particles was required to form $Au^{\delta-}$ was questioned. It has been reasonably suggested that the anion centers are offset by protons and formed on the surface of the gold particles. These centers play an important role in processes occurring in reducing environments such as WGSR and PROX.

Iron-containing zeolites

Using IR probes, oxidation state, electrophilicity, coordination state and localization of iron cations located in extracellular positions in different zeolites were determined.

When adsorbing NO on Fe-FER, nitrosyl complexes formed on Fe^{2+} surface centers in different positions were detected depending on the iron concentration. The oxidation state was determined by Mössbauer spectroscopy. It was found that the bulk of Fe^{2+} cations occupy the readily accessible P6 positions located in the center of a six-membered ring that separates two voids into the zeolite. Therefore, Fe^{2+} can be reached from different directions and coordinate two CO molecules. Strongly adsorbing molecules such as NO pull the cation and do not allow adsorption of another molecule from the opposite channel. Some Fe^{2+} cations (typical of samples with higher Fe content) are easily oxidized from oxygen to Fe^{3+} (incl. Fe^{3+} -OH). This result showed that such Fe^{2+}/Fe^{3+} centers can play the role of catalytically active redox centers.

The available iron ions in Fe-ZSM-5 and Fe-BEA have been shown to be mainly in the Fe^{3+} state and exhibit no adsorption properties. Some of the cations exchanged stabilize as Fe^{2+}. The presence of three types of iron ions in Fe-ZSM-5, localized in the α-, β- and γ- positions, was found. The ions in the α-positions are in the highest concentration. Some of these ions are part of the reactive and slightly acidic Fe^{3+} -OH groups. These ions are easily reduced from NO to Fe^{2+} and form tetranitrosyls. The latter are considered as adsorbed two dimers $(NO)_2$. The iron ions that occupy the β- and γ-positions are stabilized in the form of Fe^{2+} and are not oxidized by oxygen even at 400°C. Fe^{2+} cations in the γ-position only form monocarbonyls. In contrast, Fe^{2+} cations at the β-positions form mono- and dicarbonyls. Both types of ions form nitrosyl absorbing at 1884 cm^{-1}. This indicates that CO is a more sensitive probe molecule for determining the state of Fe^{2+} ions.

The reduction of Fe-ZSM-5 and Fe-BEA with CO leads to the formation of Fe^{+} cations, which are highly coordination unsaturated and, at low temperature, form three- and tetracarbonyl complexes with CO. The $^{12}C^{16}O$-$^{13}C^{18}O$ isotope mixture has been found to provide better opportunities for the determination of polycarbonyl structures than conventional $^{12}C^{16}O$-$^{13}C^{16}O$, due to better separation of the carbonyl bands.

Metal-organic frameworks

Assoc. Prof. Mihailov has devoted a large part of his efforts to this topic, which is relatively new and gives opportunities for the application of MOFs in both important industrial fields and environmental protection. MOFs can be used as catalysts in a number of reactions. They are suitable materials for hydrogen storage or CO_2 separation. Based on results on this topic, 9 articles have been published.

In a series of works the properties of metal-organic frameworks have been studied, mainly using the capabilities of IR spectroscopy.

Purity, hydrothermal stability and acid-base properties of various porous metal-organic frameworks (MOFs) were obtained. These properties are important for their application. The main contribution of the candidate here is the adaptation of the hydrogen bond method used in IR spectroscopic measurement of Brønsted acidity for weakly acidic hydroxyl groups in micropores of metal-organic frameworks. Thus, the structural hydroxyl groups in MOFs have been found to be slightly acidic, less acidic than SiOH groups of silica.

In another series of papers, Zr_6 clusters were studied. The dehydroxylation of Zr_6 clusters linked to each other by bridged benzene dicarboxylate linkers (UIO-66 series structures) has been found to result in an increase in Brønsted acidity. It is logically suggested that the acidic properties of the μ_3-hydroxyl groups are related to the ability of the entire Zr_6 cluster to participate in electron transfer. The dehydroxylation of Zr_6 clusters (UIO-66, STA-26) results in the generation of "hidden" Lewis acid centers. These centers can only interact with relatively stronger basic adsorbates (acetonitrile), which can cause rearrangement in the coordinate sphere of Zr^{4+} centers.

Using N_2 as the IR probe molecule, basic O^{2-} centers formed in organometallic structures containing six-core zircon clusters, UIO-66, were observed.

In the study of CPO-27-Ni, it was found that the coordination unsaturated Ni2 + centers in exhibit an unusually high π-donor capacity relative to the adsorbed CO. As a result, CO adsorption becomes competitive with H_2O vapor co-adsorption. The vibrational characteristics of hydrogen adsorbed in CPO-27 on coordination unsaturated Ni^{2+} centers and secondary absorption centers were determined and it was found that pre-adsorption of water leads to higher enthalpy values for hydrogen adsorption due to the creation of multicenter adsorption conditions.

It is particularly valuable contribution that CO_2 adsorption centers have been identified in a number of MOF structures. Phenomena such as adsorbate-adsorbate interactions, competitive adsorption, and adsorbate-induced phase transitions have been observed, and in some cases the mechanism of CO_2 separation has been clarified. MIL-96 (aluminum trimesate) was also investigated, showing high affinity for CO_2 due to the presence of Al^{3+} Lewis acid centers and structural hydroxyl groups. The CO_2 molecules even displace the aqueous ligands of Al^{3+} centers, which explains the high adsorption capacity of this material in the presence of water vapor. Thus, MIL-96 is suitable as a composite membrane filter, which has shown better CO_2/N_2 separation characteristics than polymeric membranes. Interestingly, upon adsorption into MIL-53 (Al) (Aluminum Hydroxoteraphthalate), CO_2 forms symmetric dimer structures bonded to two different μ_2-OH groups, which leads to pore contraction. This result makes it possible to elucidate the mechanism of CO_2 separation with the so-called "breathing" metal-organic structures.

I know the candidate personally and my impressions of him as a scientist and specialist are very good.

The analysis of the documents submitted by Assoc. Prof. Mihail Yordanov Mihaylov, presented for participation in the competition for professorship, shows that she answers all the requirements of the normative documents for taking up this academic position at the Institute of General and Inorganic Chemistry.

Assoc. Prof. Mihail Mihailov covers and exceeds the requirements of Art. 29, para 1 of the Law on the Development of the Academic Staff in the Republic of Bulgaria and art. 31, para 1 of the “Regulations for acquisition of scientific degrees and for occupation of academic positions in IGIC - BAS”. On the basis of the above considerations, I convincingly propose to the honorable members of the scientific jury and to members of Scientific Board of IGIC to bestow to Assoc Prof. Dr. Mihail Yordanov Mihaylov the academic position professor in the professional field 4.2. Chemical Sciences, scientific specialty Chemical Kinetics and Catalysis for the needs of the laboratory Reactivity of Solid Surfaces at the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences.

August 29th, 2019 Reviewer:

Sofia Prof. Yuri Kalvachev