O P I N I O N OF R E V I E W E R

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with respect to the competition for occupying the academic position "Professor" in professional field 4.2 "Chemical Sciences", scientific specialty "Chemical Kinetics and Catalysis", published in „Newspaper of State", issue 36, dated 03.05.2019

The only candidate, applying for the academic position of "Professor" in the competition, announced by the Institute of General and Inorganic Chemistry (IGIC) – BAS for the needs of the Laboratory „Reactivity of solid surfaces" is Assoc. Prof. Mihail Yordanov Mihaylov, PhD. All the documents, required and specified by the "Regulations for the Conditions and Order of Appointing in Academic Positions in the Institute of General and Inorganic Chemistry" have been duly submitted.

Brief details of the applicant

Assoc. Prof. Mihaylov graduated Sofia University in the year 1997. In the same year, he joined the Institute of General and Inorganic Chemistry as a chemist. In 2002 he defended his PhD thesis entitled: "Synthesis and characterization of supported nickel catalysts: Influence of support on the nickel properties" and was awarded PhD degree. In 2003 Dr. Mihaylov was promoted to Research Associate II degree, and in 2004 - Research Associate I degree. He acquired the academic position "Associate Professor" in 2008. The chronology of his professional development and occupied positions proves that he completely satisfies the requirements specified for occupying the academic position of "Professor".

Overview of the applicant's research activities

Assoc. Prof. Mihaylov is co-author of 71 research publications. Most of them – 62, have been published in renowned international journals having high impact factor, among them 55 in the highest quartile Q1. Five research works have been published in reviewed proceedings from prestigious scientific forums, and the remaining two works are chapters in books published by Royal Society of Chemistry and Nova Science Publishers. It should be noted that Assoc. Prof. Mihaylov is a co-author of 45 scientific papers (37 in the category Q1), published after he acquired the position of „Associate Professor", which is an indicator of very high publication activity. He submitted 23 publications for the participation in the present competition. The papers have been published in the most reputable international journals in the field of catalysis and materials science, such as *Journal of Catalysis, Applied Catalysis A, Applied Catalysis B, Catalysis Today, Journal of Materials Chemistry A, Chemistry of Materials, Chemistry – A European Journal, Journal of Physical Chemistry C, Chemical Communications* etc., all of which are in category Q1, incl. number 1 rank in category. The leading role and considerable personal contribution of Assoc. Prof. Mihaylov in the investigations performed and in summarizing their results is highlighted by the fact that he is the first-ranking coauthor of 11 and second-ranking coauthor of 4 publications. Proof of the high level of results obtained is the total impact factor = 116.676 according to the data in the list of publications, where the value of IF was considered for exact year of publication of the respective work. The publication of the

results in these reputable journals completely excludes the presence of incorrectness or elements of plagiarism in the materials submitted for participation in the competition.

An expression of the scientific significance of the published results is the interest demonstrated of the scientific community, expressed in more than 1600 citations (excluding self citations of all authors) noted in scientific publications, referenced and indexed in the databases Web of Science and Scopus, and in a large number of PhD theses published abroad. Citations are mainly from foreign authors, incl. from the most eminent researchers in the field of catalysis. The number of citations after the acquisition the position of „Associate Professor" is 1500. The publications included in the competition have been cited 387 times according to the candidate, and a check in Scopus only one month after submission of the documents shows 436 citations (excluding self citations of all co-authors). This number of citations demonstrates convincingly the actuality of the research topic and the importance of the contributions of the studies carried out with the participation of Assoc. Prof. Mihaylov. The number of citations outmatches many times the specific requirements of the IGIC for the number of citations for application for the position of "Professor".

The total H-index is 18 according to the database Scopus and significantly exceeds the requirements specified in the Regulations for the Conditions and Order of Appointing in Academic Positions in IGIC. It is important to note that the calculated H-index with only 23 publications included in the competition was 11.

The results from the studies, carried out with the participation of Assoc. Prof. Mihaylov, have been presented at 40 scientific events, incl. 29 international forums. For the period after year 2008, a list with contributions at 28 international and national scientific forums has been presented, including 14 oral presentations, but it is not clear who has presented them.

The managing and implementation of national and international scientific research projects occupies considerable share of the time of the activities of Assoc. Prof. Mihaylov. He was the coordinator of two national projects with significant financial support from Bulgarian National Science Fund. An international project for the purchase of an IR spectrometer funded by the A. von Humboldt Foundation was also carried out under his guidance. The projects approved for funding are an indication of scientific competence, expertise and international recognition of Assoc. Prof. Mihaylov. Due to his expertise and ability for teamwork, he is a member of teams that have implemented or are currently carrying out 9 projects funded by Ministry of Education and Science and Bulgarian National Science Fund, as well as one project by European Commission within the 7th Framework Programme.

Information about educational activity of Assoc. Prof. Mihaylov is presented in his CV. He is co-tutor of two PhD students and serves as consultant of one PhD student, but no more detailed evidence has been submitted.

Assoc. Prof. Mihaylov is head of Laboratory „Reactivity of solid surfaces" and member of Scientific Council of IGIC starting from year 2012.

The review of the overall research activity demonstrates that both the minimum and the additional requirements for occupation of the academic position of "Professor" in accordance with the Law on the Development of the Academic Staff in the Republic of Bulgaria and the Regulations of BAS and IGIC for its implementation are fulfilled. The review is correctly filled in and the fulfillment of all indicators is accurately evaluated.

Assessment of the main scientific achievements

The survey of authorship about the contributions in the research publications of Assoc. Prof. Mihaylov reveals clearly outlined topic of the investigation. It fully corresponds to the scientific specialty "Chemical Kinetics and Catalysis", in which the competition was announced. Scientific achievements resulted mainly from the application of Infrared (FTIR) spectroscopy of probe molecules as one of the most informative surface sensitive method for receiving detailed information on the nature and reactivity of the active sites formed on the surface of catalysts and adsorbents. The use of a wide range of physicochemical methods, catalytic tests and the combination with theoretical modeling contributes for the reliability of the obtained results. The investigations have been carried out at an extremely high expert level in one of the leading team in the field of FTIR spectroscopy at a global scale of Prof. K. Hadjiivanov, with typical originality and innovation. In this sense, it is not surprising that world-renowned scientists such as Prof. Bruce Gates, Prof. H. Knözinger, Prof. M. Daturi, etc. are co-authors in some of the publications.

1. Habilitation work– scientific publications, referenced and indexed in the databases Web of Science and Scopus

The habilitation work is competently written and complies fully the requirements of the Regulations for the Conditions and Order of Appointing in Academic Positions in IGIC. It includes five articles that are clearly distinguished from the total number of publications for participation in the competition (№ 46, 56, 57, 67 and 71 in the list of all scientific papers). A FTIR spectroscopic investigation of the surface species formed during interaction of NO_x and CO_x with ceria are summarized. The state-of-the-art in the field and the need of new and reliable information on the nature of the surface species formed during the above mention processes is shortly described in Introduction section. Ceria is extensively employed as a component in many types of catalysts, mainly due to its high oxygen release/storage capacity and ability to undergo a relatively rapid change in oxidation state upon changes in the redox potential of the exhaust gases. Detailed study of the interaction of NO_x and CO_x with ceria, in particular the knowledge of the nature and stability of the surface species provides information for clarification of the mechanisms of the surface processes on ceria. It is an important tool in development of new knowledge-based multifunctional materials with tailored properties and improved catalytic and adsorption properties. The meaningful analysis of the results enables acquisition of reliable assignments of IR bands of surface NO_x and CO_x species on ceria, as well as revision of previous assignments of FTIR spectra supported by additional experiments.

In my opinion, the most important contributions are:

1. Studies on the interaction of nitrogen oxides (NO, N_2O) with ceria using isotopically labelled ^{15}NO and $^{14}NO+^{15}NO$ mixture. Two types commercial ceria with similar specific surface areas, but different particles size, as well as CeO_2-Al_2O_3 were employed for better interpretation of the spectra and unambiguous assignments of the IR bands. Equal attention was paid to the reduced and non-reduced oxide form.

2. Formation of surface species N^{3-} and NO^{2-} under interaction of NO with reduced ceria was registered for the first time. Two new pathways of NO reductive conversion depending on ceria morphology were reported. The findings provide valuable information for design of selective deNO_x catalysts and adsorbents.

3. Reassignment and new interpretation of the vibrational frequencies of the surface species formed during interaction of CO_2 or CO with activated (stoichiometric), reduced, and hydroxylated ceria. The analysis of the reactivity of these species and the clarification of the mechanisms of the rich variety of surface processes on ceria is of particular importance because of the increasing utilization of ceria as active component in large number of processes, where CO and/or CO_2 are reagents or reaction products. The reliability of the reported results is based on a combined analysis of the experimentally observed IR spectra and computational modeling of 37 structures, carried out in the framework of joint projects with distinguished scientists from Sofia University.

2. Scientific publications, referenced and indexed in the databases Web of Science and Scopus, not included in the habilitation work

The publications not included in the habilitation work, presented by Assoc. Prof. Mihaylov for participation in the competition, are thematically grouped, depending on the type of the materials examined.

1. Study of gold-based catalysts.

One of the most significant discovery in the field of catalysis over the last three decades is that gold loses its nobility when occurring at nanometre length scale. A breakthrough in the perception of the poor catalytic activity of gold was made in 1987. Haruta and co-workers presented the earliest report on extremely high CO oxidation activity at, or even below, room temperature of gold nanoparticles supported on transition metal oxides. During the next years, an impressive growth of scientific investigations concerning catalysis by gold occurred and caused discovery of new properties and attractive applications of gold-based catalysts. Spectroscopic studies, in particular FTIR spectroscopy, are one of the most appropriate surface sensitive methods to receive information on the nature of the active sites under reaction conditions in order to clarify the reaction mechanism. Among the vast literature on application of FTIR spectroscopy for study of gold-based catalysts, the new and original contributions to the research conducted with the participation of Assoc. Prof. Mikhaylov are:

1.1. Experimental evidences have been found for the role of CO_2 in the formation of positively charged gold sites ($Au^{\delta+}$) on gold nanoclusters deposited on La_2O_3. An interesting observation is that CO_2 is able to oxidize the gold nanoparticles at room temperature, whereas oxidation by O_2 requires higher temperatures (200 °C). It was confirmed the suggestion for the beneficial effect of positively charged gold sites on the catalytic activity in the CO oxidation reaction. It was hypothesized that $Au^{\delta+}$ sites are generated by dissociation of the CO_2 formed in the reaction catalyzed by metallic gold nanoclusters.

1.2. The influence of various factors leading to the deactivation of Au/MgO during CO oxidation at room temperature has been evaluated. Formation of various carbonate-like structures, assigned to interaction with support surface sites, as well as with $Au^{\delta+}$ centers on supported nanoclusters has been identified by IR spectroscopy during exposure to CO and to CO_2. For the first time are reported data that allow resolving separate effects of accumulation of carbonate-like species on the support, such species on the gold, and the gold clusters agglomeration on CO oxidation activity.

1.3. The formation of negatively charged gold centers ($Au^{\delta-}$) on an inert support SiO_2 has been reported for the first time. Previous studies by other authors have reported the occurrence of

such gold sites only after a reduction treatment of gold-containing samples deposited on reducible oxides Fe_2O_3, TiO_2 and CeO_2 and their formation was explained by electron transfer from the support to the gold nanoparticles. A new concept for the formation of negatively charged gold sites was proposed in the research of Assoc. Prof. Mihaylov. By adsorption of CO - ^{13}CO and CO - $^{13}C^{18}O$ isotopic mixtures have been identified formation of various linear carbonyl complexes.

2. Study of iron-containing zeolites.

An emphasis in the contributions to the IR spectroscopy study of iron-containing zeolites is the determination of the oxidation state, electrophilic properties, coordination state and localization of iron cations in big and small cavities of different types of zeolites. Iron-containing zeolites are attractive materials for use in a series of selective redox catalytic reactions with environmental impact.

2.1. The capabilities of IR spectroscopy were used to precisely identify and distinguish between different accessible Fe^{2+} sites in Fe-ferrierite (FER) in a series of three papers (№ 31, 33, 38). NO adsorption followed by Infrared spectroscopy enables identification of nitrosyl complexes formed with Fe^{2+} surface centers. Different iron sites were evidenced depending on the iron concentration (0 and 3.7 wt.%). It was found that for low Fe loading the main fraction of Fe^{2+} cations was located in highly accessible positions of the ferrierite. These ions are coordinatively unsaturated, i.e. they can easily form dicarbonyls. At increased Fe amount, a second type less accessible sites, were detected. Under oxidizing treatment, these cations are easily oxidized to Fe^{+} ions. The results provide information on the nature of the active sites in processes related to conversion of nitrogen oxides, such as the oxidation of NO to NO_2 (before interaction with a reducing agent), as well as the selective reduction of NO_x with ammonia.

2.2. It was observed that accessible iron ions in oxidized Fe–ZSM-5 and Fe–BEA zeolites were mainly in the form of Fe^{3+} species that do not interact with CO, although some exchanged cations were stabilized as Fe^{2+} species and form carbonyls. Reduction of the samples with CO at 400 ^{o}C leads to a significant increase of the number of coordinatively unsaturated Fe^{2+} sites able to form tri- and tetra-carbonyl complexes with CO. It was demonstrated that the use of $^{12}C^{16}O$–$^{13}C^{18}O$ mixture provided a better resolution of the carbonyl bands as compared to the conventional $^{12}C^{16}O$–$^{13}C^{16}O$ mixture.

2.3. An in-depth study of Fe-ZSM-5 proves the presence of three types of iron ions located in the α, β and γ positions. Their reactivity and the formation of different types of nitrosyl or carbonyl using two probe molecules (CO and NO) were analyzed. CO has been shown to be a more sensitive and less reactive IR probe molecule for determination of coordination state of Fe^{2+} ions.

3. Study of metal–organic frameworks (MOFs).

The relevance of these investigations is related to the interesting properties and potential applications of MOFs as materials for gas storage and separations, catalysis, electronic devices, in biomedicine, and information storage among others. In a series of 9 publications, were reported results on the purity, hydrothermal stability and acid-basic properties of various porous metal-organic structures. An advanced approach was proposed that extended the application of hydrogen-bond method for precise determination the acidity of hydroxyls located in the micropores of MOFs by FTIR spectroscopy.

Interesting relationships between dihydroxylation of Zr_6 clusters in some metal–organic frameworks (UIO-66, STA-26) and the changes in the acidity have been found. It was observed that basic sites (coordinatively unsaturated O^{2-}) were also formed during dehydroxylation of MOFs containing Zr_6 clusters that were detected with N_2 as a probe molecule.

The contributions of Assoc. Prof. Mihaylov in the study of MOFs, prepared and characterized in detail within the project under 7th Framework Programme by many researchers is well described in the survey of authorship. Special emphasis among them is put on the study of MOFs for CO_2 capture. New IR spectral observations on CO_2 adsorption on MIL-53(Al) (aluminum hydroxylterephthalate) are reported. The adsorption of $^{12}CO_2$ and $^{12}CO_2$ + $^{13}CO_2$ mixtures leads to formation of highly symmetric dimeric $(CO_2)_2$ species connected to two structural OH groups, thus causing partial transition from the large pore to the narrow pore form. These results contribute to clarify the mechanism of CO_2 capture in MOFs with so-called "breathing" behavior.

The role of both Lewis acid Al^{3+} centers and terminal/bridging hydroxyl groups of MIL-96 (aluminum trimesate) for the high affinity to CO_2 was evaluated. The ability of CO_2 to replace the OH ligands of Al^{3+} centers explains the high adsorption capacity of this material in the presence of water vapor. It was successfully used as a filler in mixed matrix membrane that outperform pure polymer membranes for CO_2/N_2 separation. These results are also very promising in the field of mixed matrix membrane for postcombustion CO_2 capture.

The scientific contributions can be evaluated as a novelty in the scientific knowledge, revision and enrichment of the already available data.

Concluding remarks

The assessment of the main scientific achievements of Assoc. Prof. Mihail Mihaylov reveals undoubtedly that he has established himself as a researcher with high expertise and knowledge in the field of application of FTIR spectroscopy. I appreciate the scholarship granted by the Alexander von Humboldt Foundation and the specialization in the group of Prof. Knötzinger at the University of Munich, as recognition of his qualities as a scientist and as an opportunity to become an experienced specialist in the development and application of IR spectroscopy for surface study of active adsorbents and catalysts.

The acquaintance with the materials submitted for the competition allows me to state with confidence that the scientific production metrics indices of Assoc. Prof. Dr. Mihail Mihailov are in accordance with the Law on the Development of the Academic Staff in the Republic of Bulgaria and the Regulations of IGIC – BAS for its implementation and even exceed them in regard to occupying the academic position „Professor". I am really convinced to propose to the members of the Scientific Jury and to the Scientific Council of IGIC-BAS to vote positively and to approve Assoc. Prof. Dr. Mihail Mihailov for occupying the academic position of „Professor" in the professional field 4.2. „Chemical Sciences", scientific speciality „Chemical Kinetics and Catalysis" in the Laboratory „Reactivity of solid surfaces" in the Institute of General and Inorganic Chemistry – BAS.

27.08.2019 Member of the Scientific Jury:

/Prof. Tatyana Tabakova, PhD/