

## Attitude of Reviewer

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With respect to the competition for occupying the academic position "Professor" at the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences (IGIC-BAS), professional field 4.2. Chemical Sciences, scientific specialty "Chemical Kinetics and Catalysis", published in „Newspaper of State”, issue 36/03.05.2019.

On the basis of Order № ПД-09-80 dated 01.07.2019 by the Director of IGIC-BAS, I have been appointed as member of the Scientific Jury in the competition for occupying the academic position 'Professor' in professional field 4.2. Chemical Sciences, scientific specialty „Chemical Kinetics and Catalysis“, announced for the needs of IGIC-BAS, Laboratory „Reactivity of solid surfaces“. Assoc. Prof. Dr. Mihail Yordanov Mihaylov from IGIC-BAS is the only candidate who submitted his application documents for participation in the announced competition.

The complete set of materials on a CD, submitted to me by Dr. Mihaylov, is in accordance with the Law for the Development of the Academic Staff in the Republic of Bulgaria (LDASRB) and with the "Regulations for career development of the academic staff in IGIC-BAS" and it comprises all the required documents. The candidate participates in the competition with 23 scientific papers published in reputable international journals with impact factor (all of Q1 rank according to SJR), which have not been included in his PhD thesis and have been published after occupying the academic position „Associate Professor“. Five of them form his Habilitation work on "IR spectroscopic study of NO<sub>x</sub> and CO<sub>x</sub> adsorption forms on cerium dioxide: Revision of existing concepts." Dr. Mihaylov's contributions to these publications are also highlighted by the fact that in four of them he is the first author and in one – the second, while the total number of citations noted so far on these five publications is 163. The submitted information on the minimum requirements of BAS and IGIC for the applicant's scientific activity shows that for each of the indicators, Dr. Mihaylov has the necessary number of points, and for most of them this number significantly exceeds the minimal national requirements. In addition, I would like to point out the fact that the total number of papers co-authored by Dr. Mihaylov (71) is more than three times the number of papers submitted for this competition.

The examination of the submitted materials shows that the applicant has a well-defined topic of interest and his scientific activity is mainly related to the development and use of the IR spectroscopy method for studying the chemistry of active solid surfaces, adsorbents and catalysts during their interaction with inorganic and organic gases or vapors. The author's reference is well prepared and competently reflects the scientific contributions of the applicant, and the latter are divided into four main groups according to the type of materials studied: 1) Cerium dioxide; 2) Gold-containing catalysts; 3) Iron-containing zeolites and 4) Metal-organic frameworks. In the applicant's Habilitation work, in details are presented data on the nature and properties of the surface compounds formed by the interaction of nitrogen and carbon oxides, including the use of isotope-labeled molecules (<sup>15</sup>NO, <sup>13</sup>CO<sub>2</sub>) with CeO<sub>2</sub>, in both stoichiometric and partially reduced form (CeO<sub>2-x</sub>). For the first time, the formation of N<sup>3-</sup> and NO<sup>2-</sup> surface compounds on the oxide surface has been proved. The formation of *trans*-O-N-N-O and highly symmetric [N-N-N] structures has been demonstrated. The CO<sub>x</sub> adsorption forms on stoichiometric, reduced and hydroxylated cerium dioxide are presented in detail, as well as a detailed picture of the interaction of NO<sub>x</sub> with cerium dioxide. Two new

reaction pathways for the reductive conversion of NO on CeO<sub>2-x</sub> have been identified that involve the formation of NO<sup>2-</sup> or N<sup>3-</sup> as intermediates and lead to different final products of the reaction. The amount of these intermediates, on the other hand, is highly dependent on the morphology of cerium dioxide, which allows selective cerium oxide adsorbents and catalysts to be designed.

Some aspects of the catalytic reaction mechanisms of deposited gold nanoparticles have been elucidated (scientific papers 27, 30, 32 and 43). It has been proved that although gold nanoparticles have been shown to be inert to O<sub>2</sub> at room temperature, they are easily oxidized by CO<sub>2</sub>. For the first time, negatively charged gold centers (Au<sup>δ-</sup>) formed on SiO<sub>2</sub> inert carrier have been observed, and they play an important role in processes occurring in reductive media such as WGS and PROX.

Using IR probe molecules (NO and CO), the oxidation state electrophilicity, coordination state and localization of iron cations located in extra-lattice positions in different zeolites (Fe-FER, Fe-ZSM-5 and Fe-BEA) were determined.

A large part of the applicant's publications (Nos. 36, 61, 62, 64, 65, 66, 68, 69, and 70) concern various porous metal-organic frameworks (MOFs) and represent data on their purity, hydrothermal stability and acid-base properties. The structural hydroxyl groups in MOFs have been found to be slightly acidic, less acidic than the SiOH groups of silica. The dehydroxylation of six-core zirconium clusters linked to each other by bridged benzene dicarboxylate linkers has been found to lead to an increase in Brønsted acidity. Adsorption centers for CO<sub>2</sub> in MOF structures have been identified. MIL-96 has been found to exhibit high affinity for CO<sub>2</sub> due to the presence of Al<sup>3+</sup> Lewis acid sites and structural hydroxyl groups and it could be used as composite membrane filler with enhanced CO<sub>2</sub>/N<sub>2</sub> separation properties than polymer membranes.

### **Conclusion**

The scientific achievements of Associate Professor Dr. Mihaylov are undoubted and fully correspond to the topic of the announced competition. The submitted academic papers after habilitation, the number of citations, the participation in projects and the project management by the applicant not only meet, but also significantly exceed the requirements for occupying the academic position "Professor" according to LDASRB, the Regulations for the implementation of LDASRB and with the additional requirements of the relevant Regulations of IGIC-BAS.

On the basis of the above considerations, I strongly propose to the honorable members of the scientific jury to bestow to Associate Professor Dr. Mihail Yordanov Mihaylov the academic position "**Professor**" at IGIC-BAS, in the professional field 4.2. Chemical Sciences, scientific specialty "Chemical Kinetics and Catalysis".

Sofia, 29.08.2019

Member of the Scientific Jury at IGIC-BAS:

(Assoc. Prof. Dr. Momtchil Dimitrov)