ATTITUDE OF REVIEWER

by prof. Dr. Anton Naydenov

member of the scientific jury, according to order № РД-09-80/01 July 2019 by the Director of Institute of general and inorganic chemistry (BAS)

regarding the competition announced in State Journal no. 36 of 03. 05. 2019, for the awarding of the **academic position "Professor"** in the direction 4.2. Chemical Sciences (Chemical Kinetics and Catalysis) for the laboratory "Reactivity of Solid Surfaces", Institute of general and inorganic chemistry (BAS)

Candidate: Docent d-r Mihail Mihaylov , Institute of general and inorganic chemistry (BAS).

Docent d-r Mihail Mihaylov was graduated for PhD thesis at the Institute of general and inorganic chemistry (BAS) in 2002 and in 2003 he occupied the position of assistant – professor, for docent being promoted at the Institute of general and inorganic chemistry (BAS) in 2008. According to the minimal national and additional requirements of the Institute of general and inorganic chemistry (BAS) in professional direction "4.2. Chemical sciences" (habilitation thesis – scientific in sources with reference and index numbers within the worldwide data bases (Web of Science and/or Scopus) of "group B", the total score regarding the publications (all of them of Q1) of docent Mihaylov is 125 points (at requirement of 100 points). Regarding the evaluating parameter 7 (scientific publications in sources with reference and index numbers within the worldwide data bases (Web of Science and/or Scopus) beyond the habilitation thesis) of "group G" are presented 18 publications (again all of them with Q1), the total score is 450 points. According to Scopus the H-index of docent Mihaylov is 18. Obviously, the candidate completes (and exceeds) entirely the minimal national and additional requirements of the Institute of general and inorganic chemistry (BAS) for the academic position "professor".

The scientific studies of docent Mihaylov are focused on the application of the infrared spectroscopy in obtaining data for the properties and the behavior of adsorbents and catalysts in process, connected with the environmental protection.

Obtained are data on which basis a revision of the nature of phenomena, reported in earlier studies from other authors is presented, more specifically regarding the infrared spectra of surface species, produced during the adsorption of nitrogen and carbon oxides over cerium dioxide. It has been demonstrated the formation of new surface species in adsorption of nitrogen oxide and, as result – new routes for reduction to nitrogen.

During the study on the mechanism of catalytic behavior of supported gold nanoparticles, a possibility of their oxidation in presence of carbon dioxide has been described. Initially, an induction period with generation of active gold centers by the dissociation of the carbon dioxide has been observed. An activation of the surface oxygen over the gold particles has been suggested. It was shown that the deactivation of the gold catalysts in reaction of carbon monoxide oxidation is due to the formation of carbonates-like structures.A formation of negatively charged gold centers over silica in atmosphere of carbon monoxide and presence of water vapor or hydrogen has been established. The reported results differ from the accepted consideration that for the formation of negatively charged gold particles an electron transfer from the support to the gold particles is required.

In cooperation with the scientific group of prof. M. Datury from the University of Caen – Normandy the determination of the oxidation degree, electrofillicity, coordination state and localization of the iron cations, occupying extra framework positions within different zeolites has been performed.

It was demonstrated that Fe^{2+} can be accessed from different directions and it can coordinate two carbon monoxide molecules, however strongly adsorbed compounds as NO do not permit the adsorption of further molecule coming from the opposite channel. At the same time, Fe^{2+} cations, oxidized by oxygen to Fe^{3+} were observed, which reveals that Fe^{2+}/Fe^{3+} can play the role of active oxidative-reduction centers.

During the study on Fe-ZSM-5 and Fe-BEA it was established, that the accessible iron ions are generally in Fe^{3+} state and do not possess an adsorption properties. At the same time, as result of reduction by carbon monoxide, highly coordinated saturated iron cations are formed – at low temperature with carbon monoxide they form tri- and tetracarbonil complexes. Aiming to determinate the polycarbonate structures, it was shown that the isotopic mixture $^{12}C^{16}O$-$^{13}C^{18}O$ gives better possibilities than the wide-spread used $^{12}C^{16}O$-$^{13}C^{16}O$ mixture.

Within a Seventh framework program project for development of membranes for CO_2 capture, a series of studies on the properties of different porous metal-organic structures (MOFs) have been carried out. Obtained are data for their purity, hydrothermal stability and acid-base properties. The results from these studies contribute to the evaluation of the possibilities for application of MOFs as catalysts, materials for storage of hydrogen and for separation of CO_2. It was demonstrated that as result of de-hydroxylating the Zr6 clusters, connected to each other by bridge benzene-dicaboxylated linkers, an increased Bronstedt acidity is achieved. It has been suggested, that the acid properties of μ3-hydroxyl groups are related with the ability of entire Zr6 to participate in the electron transfer. In parallel, it was shown that the dehydroxylation leads to generation of "hidden" Lewis acid centers. These centers can interact with relatively strong basic adsorbates, which can lead to a rearrangement within the coordinative sphere of Zr^{4+} centers. Nitrogen has been applied as a probe – molecule for observation of basic oxygen centers, formed in metal-organic structures, constituent by six-nuclear zirconium clusters.

Identified are adsorption centers for CO_2 in MOF structures. Observed are phenomena as adsorbate – adsorbate interactions, competitive adsorption and adsorbate – induced phase transitions. Within several cases, the mechanism of CO_2 separation has been clarified. The presence of Lewis acid centers and structural hydroxyl groups on MIL-96 contribute to the higher affinity towards CO_2.

Conclusion

The scientific studies of docent Mihail Mihaylov completely correspond to the theme of the announced competition for awarding the academic position "professor". The publishing activity after the habilitation, the citations of published results, participation and management of the projects completely cover (and exceed) the requirements of the Academic Staff Development Low and the Regulations on the Conditions and Procedure for Acquisition of Academic Degrees and the Occupation of Academic Posts at the Institute of general and inorganic chemistry (BAS). Therefore, I convincingly recommend to the members of the Scientific Jury and to the Scientific Council of the Institute of general and inorganic chemistry (BAS) to award docent Mihail Mihaylov with the academic position "professor" under the direction "4.2. Chemical Sciences" (Chemical kinetics and catalysis).

Sofia, 29.07.2019.

Reviewer:

Prof. Dr. Anton Naydenov