

PEER REVIEW

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in connection with the competition for occupying of the academic position Associated Professor in the professional field 4.2. "Chemical Sciences", scientific specialty "Chemical Kinetics and Catalysis" for the needs of the **Institute of General and Inorganic Chemistry (IGIC)** at the Bulgarian Academy of Sciences, Laboratory "Reactivity of solid surfaces ", announced in Newspaper of State issue 36 /03.05. 2019.

1. General presentation of the obtained materials.

Assistant professor Nikola Lyudmilov Drenchev is the only candidate in the competition for occupying the academic position of "Associated Professor". The set of materials submitted by the applicant is in accordance with Article 24 of the Law for Development of the Academic Staff in the Republic of Bulgaria (LDASRB), Article 27 (1) of the Regulations for the conditions and order for acquiring scientific degrees and occupying of academic positions in IGIC-BAS.

For participation in the competition, Dr. Drenchev has submitted all the necessary documents: CV, diplomas for higher education and for the PhD scientific degree, research publications, concerning index 4 about habilitation work from "group B", other publications according to the index 7- research publications that have been referenced and indexed in world-renowned databases of scientific information (Web of Science and / or Scopus), lists of scientific papers, citations, list with the participations in the conferences, copies of scientific papers and congresses, list of participating in national and international research projects.

2. Short biographical data about the candidate

Dr. Drenchev graduated from the Sofia University "St. Kliment Ohridski ", Faculty of Chemistry in 2004. During the following period 02.2005–02.2008 he was a PhD student in the same faculty. Nikola Drenchev defended successfully his PhD thesis on the topic "Synthesis and hydrogen-sorption properties of alloys based on Mg₂Ni" in 2008. After defending his dissertation, he was appointed as a chemist at IGIC for a period of one year and after that he became Assistant. In the period 2012-2013, for 18 months, Dr. Drenchev is a Senior researcher at the University of Pardubice, Czech Republic.

3. Evaluation of the scientific research works of the candidate.

Dr. Drenchev was co-author of a total of 29 publications, out of which 26 are published in prestigious international journals. Most of the publications are in journals devoted to materials science and catalysis, such as Journal of Physical Chemistry C, Phys. Chem. Chem. Phys, RSC Advances, Appl. Catal. B: Environmental, Curr. Phys. Chem, J. Mol. Catal. A, J. Alloys Compd, J. Appl. Electrochem.

The presented publications are divided into two groups corresponding to indices **B** and **Г**, in accordance with Regulations for the conditions and order for acquiring of scientific degrees and occupying of academic positions. In the first group, indicator **B** - "Habilitation work - scientific publications in journals that are referenced and indexed in world famous scientific

information databases (WoS or Scopus)", there are 5 publications (four of them are in quartile Q1 and one is in Q2), giving a total score of 120 points, higher than the required minimum of 100 points required.

The second group represents 13 publications (12-Q1 and 1-Q2) covering index Γ , with a total of 320 points higher than the required 220 points. In the group of indices Δ , the requirements have been exceeded significantly – in view of the required 60 points, the candidate has 106 points. All citations are in prestigious international journals, which fact confirms the importance and relevance of Dr. Drenchev's scientific research.

Dr. Drenchev takes part in the work teams of 2 international and 9 national projects. One of the international projects is the 7th EU Framework Program. The national projects, in which Dr. Drenchev has been participating, are also seriously funded by Bulgarian National Science Fund. This shows that Dr. Drenchev takes a very responsible attitude to the tasks assigned, which makes him a desirable participant in the work teams.

The dissemination of scientific results has been achieved through participation with oral and poster presentations in a number of national and international scientific meetings as follows: 2 reports at international forums, 5 reports at international project team meetings, reports of international scientific conferences-5, poster presentations at the national and international scientific meetings-7 and 6 respectively.

4. Scientific research contributions

4.1. Habilitation work

The habilitation work entitled "IR spectroscopic characterization of the valence and coordination state of metal cations in zeolites, oxide catalysts and metal-organic frameworks (MOFs) with probe molecules and their isotope analogues" is based on 5 articles, out of which four are categorized in Quartile Q1 and one in Q2.

As it is known, infrared spectroscopy is a powerful and widely used method for the study of surface features. The main advantages of the method are that it can trace even the smallest changes in the adsorbent-adsorbate interaction, as well as to work under experimental conditions close to those of real catalysis. By using the so-called probe molecules that react with the surface and their spectral characteristics are the result of adsorption, direct information about the type, properties, concentration, etc. of the active sites can be obtained. The most frequently used probe molecules to study supported catalysts are carbon monoxide and NO.

The studies presented in the habilitation work can be categorized in the following areas:

Characterization of metal-organic frameworks by probe molecules (works 1, 4, 5).

Characterization of the valence and coordination state of metal cations in zeolites and oxide catalysts (works 2 and 3).

In the first direction, studies on the valence and coordination state of copper ions in the metal-organic framework "Basolite C300" (copper benzene-1,3,5-tricarboxylate - HKUST-1) are represented, the interaction of H₂, D₂, CO and NO with the metal-organic structures CPO-27-Ni and CPO-27-Cu have also been studied. The main achievements of the applicant can be summarized as follows:

The two IR bands, at 2192 and 2148 cm^{-1} , appearing after CO adsorption on Basolite C300, are associated with individual monocarbonyls and are not due to the symmetric and antisymmetric modes of dicarbonyls, as it was suggested earlier. When the adsorption of CO is carried out at low temperature, some of the adsorbed CO molecules, attached directly to the metal-organic structure, are leading to bands at 2141, 2128 and 2123 cm^{-1} and probably a band at 2148 cm^{-1} .

Activation of the Basolite C300 at 473 K results in some irreversible changes and the formation of a small amount of copper oxide nanoparticles. The band at 2125 cm^{-1} , which continues to be observed in the spectrum and after evacuation, is assigned to $\text{Cu}^+ - \text{CO}$ species.

For the first time, CO molecules have been found out to replace water molecules from Ni^{2+} centers in the metal-organic structures of CPO-27-Ni. The formed $\text{Cu}^{2+} - \text{CO}$ complexes upon CO adsorption are characterized by a band at 2153 cm^{-1} . This species shows great sensitivity towards the occupation by neighboring Cu^{2+} sites, possibly via a direct CO-CO interaction for sites in one and the same pore channel, but also indirectly via small electronic effects running along the $-\text{O}-\text{Cu}-\text{O}-$ chains. The formation of more unstable carbonyls of the $\text{Cu}^+ - \text{CO}$ type has also been found out, in which the CO molecule is bound to the oxygen-cation.

It has been ascertained that different polycarbonyl structures can be distinguished using isotope mixtures $^{12}\text{C}^{16}\text{O}-^{13}\text{C}^{18}\text{O}$ with different molar ratios. Two types of dicarbonyls have been identified for Cu^+ ions in Cu - ZSM-5; (i) the well-known dicarbonyls with ν_s at 2178 cm^{-1} and ν_{as} at 2151 cm^{-1} ; and (ii) the dicarbonyls with ν_s at 2183 cm^{-1} and ν_{as} at about 2150 cm^{-1} . The latter ones are of low concentration.

It was found out that during the deposition of the active phases of manganese, cerium and Mn-Ce on Al_2O_3 they react with the OH groups, which leads to their partial disappearance of all kinds of the alumina OH groups. A part of the Al^{3+} Lewis acid centers are also blocked. The interaction of all the samples with CO leads to the formation of carbonates and hydrocarbons, increasing their quantity with the temperature in the following sequence $\text{Al}_2\text{O}_3 < \text{Ce}/\text{Al}_2\text{O}_3 < \text{Mn}/\text{Al}_2\text{O}_3 < \text{MnCe}/\text{Al}_2\text{O}_3$. The degree of oxidation state of manganese in the nitrosyl complexes, formed by the adsorption of NO on $\text{Mn}/\text{Al}_2\text{O}_3$, was found out to be +2. The bands attributed to $\text{Mn}^{2+} - \text{NO}$ complexes are more intensive on $\text{MnCe}/\text{Al}_2\text{O}_3$ samples, which corresponds to the higher dispersion of manganese in this catalyst and its lower average oxidation state. The fact that NO forms nitrosyls only with manganese cations, but not with aluminium and cerium, indicates that this molecule is a good probe molecule for the detection of surface manganese particles.

4.2. Other publication

This section presents the publications relating to index 7 (publications in journals that are peer-reviewed and indexed in world databases of scientific information (Web of Science and/or Scopus), not included in habilitation works). The total number of points is 320 points (exceeding 220 points required). A total of 74 citations of these works were noticed.

These publications, submitted by Dr. Drenchev for participation in the competition, are focused on four thematic areas. The main contributions, in my opinion, are set out sequentially below.

1. Characterization by FTIR spectroscopy of surface coordination unsaturated cations in zeolite and oxide catalysts;

Two types of Fe^{2+} centers have been established by CO adsorption in iron modified zeolites type ZSM-5 (Fe-ZSM-5). These centers form monocarbonyls characterized by bands at different frequencies. Only one type of centers forms dicarbonyls in the presence of CO in gas. The formation of tetranitrosyl is assumed after NO adsorption on Fe^{2+} centers, unlike other studies in which trinitrosyl has been reported.

Studies concerning the state and surface coordination of unsaturated vanadium cations in vanadium modified SBA-15, MCM-36, and MCM-22 molecular sieves indicate that V^{3+} and V^{4+} co-exist after reduction of V-SBA-15. Both vanadium species form with dinitrosyls. In addition to the dinitrosyls of V^{3+} , mononitrosyls which have not been previously reported in similar samples were also observed. For V-MCM-36 and V-MCM-22, vanadium is most likely V^{4+} and it is included in the framework.

For the first time, the formation of a $\text{Cu}^+(\text{N}_2)(\text{H}_2\text{O})$ mixed complex was detected after adsorption of $^{15}\text{N}_2$ and a mixture of $^{14}\text{N}_2+^{15}\text{N}_2$ (1:1) on CO-ZSM-5 reduced with CO. Adsorption of NO on a sample with pre-adsorbed CO has been found out to result in the following reaction $2\text{Cu}^+-\text{CO}+2\text{NO}=\text{Cu}^+(\text{CO})_2+\text{Cu}^+(\text{NO})_2$. Upon adsorption of N_2 on a sample containing Cu^+ mononitrosyls, the reaction proceeds again: $2\text{Cu}^+-\text{NO} + \text{N}_2 = \text{Cu}^+(\text{NO})_2+\text{Cu}^+-\text{N}_2$.

2. Determination of the nature of the adsorption centers and the geometry of the complexes formed in zeolites, oxides and metal-organic structures;

The nature of the adsorption centers and the geometry of the complexes formed by the adsorption of CH_4 on adsorbents with different acidity were determined. Upon adsorption on SiO_2 , methane forms H-bonds simultaneously with oxygen and hydrogen from the Si-OH groups. Methane is interacting with acidic Si-OH-Al groups, which are attached to hydrogen atoms. As methane pressure increases in the system, a second molecule of methane binds to the same hydrogen atom from the Si-OH-Al groups.

After CO_2 adsorption on a metal-organic structure MIL-53 (Al), the formation of CO_2 dimer structures was found out at high coverages (each CO_2 molecule interacts via one of its oxygens with the proton from an OH group). For the first time, a transition from the large pore to the narrow one was observed spectroscopically, accompanied by the formation of dimers. It was found out that at high coverage the interaction of CO_2 with MIL-53 (Al) and NH_2 -MIL-53 (Al), the CO_2 molecules start to polymerize before interacting with OH groups. No formation of polymeric CO_2 structures was observed for NH_2 -MIL-53 (Al) very likely due to the more stable narrow pore structure.

3. Determination of surface acidity of OH groups by FTIR spectroscopy.

For the first time, the acidity of ammonium ion in zeolites was determined by CO adsorption. The acidity of the metal-organic frameworks MIL-53 (Al) and NH_2 -MIL-53(Al) was also investigated. Three bands (at 3721, 3711, and 3683 cm^{-1}) were observed in the vibrational region of the OH groups. These bands are attributed to one type of structural hydroxyls but involved in H-bonding with different strength. A methodology was proposed for the determination of the actual vibrational frequency of OH groups

The actual frequency of the μ_3 -OH groups for the metal-organic structures UIO-66 and UIO-66-NH₂ is determined. The two types of structures are dehydroxylated reversibly. The decrease in the population of the hydroxyls leads to increase in their acidity. Both structures UIO-66 and UIO-66-NH₂ exhibit close acidity.

4. Application of OH → OD isotopic exchange and isotopically labeled molecules for the study of surface OH groups

For the first time, the isotopic shift factor is proposed as criterion for determining the participation of OH groups in a hydrogen bond. The empirical formula found out, linking the frequencies of OH and OD oscillations, allows an accurate calculation of the oscillation frequency of OH groups after deuteration. The reasons why the theoretically determined isotopic shift factors $i_{OH \rightarrow OD} = \nu(OH)/\nu(OD)$ differ from the experimental ones are identified. In isolated OH/OD groups, deviations from the theory were found out to be mainly due to the non-harmonicity of oscillations, while the acidity of the groups plays a decisive role in the formation of the H/D bond (between the OH/OD groups themselves or with different adsorbates).

Conclusion

The research works of Assistant professor Nikola Lyudmilov Drenchev fully correspond to the topic of the announced competition for awarding the academic position of "Associated Professor". The number of publications and citations on the published papers prove that Assistant Professor Nikola Drenchev fully covers and exceeds all the requirements of the Law for Development of the Academic Staff in the Republic of Bulgaria (LDASRB), the Regulations for the conditions and order for acquiring of scientific degrees and occupying of academic positions in IGIC-BAS. Therefore, I strongly recommend to the members of the Scientific Jury and the Scientific Council of IGIC-BAS to award to Assistant Professor Dr. Nikola Lyudmilov Drenchev the academic position "Associate Professor" in the professional field 4.2 "Chemical Sciences" and scientific specialty "Chemical Kinetics and Catalysis".

Data 27. 08. 2019

Sofia

Member of the Scientific Jury:

/Prof. PhD Silviya Todorova/