

R E V I E W

on the competition for the academic position Associate Professor scientific direction 4.2. Chemical Sciences (Chemical Kinetics and Catalysis)

at the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences
(IGIC-BAS)

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Applicant: **Assistant Prof. Dr. Nikola Ludmilov Drenchev** (IGIC-BAS)

Member of the Scientific Jury: Prof. Dr. Radostina Konstantinova Stoyanova (IGIC-BAS)

A. Short professional biography

Dr. Nikola Drenchev is the only candidate in the competition for the academic position associate professor in Chemical Sciences (chemical kinetics and catalysis) announced by IGIC-BAS. He is a graduate of the Faculty of Chemistry and Pharmacy at Sofia University, where in 2004 he graduated with a master's degree, and in 2009 he defended his PhD thesis in the field of solid state chemistry. Since 2008 he has been appointed to the IGIC-BAS as a chemist, and since 2009 - occupies the position of Assistant Professor. This is the period of reorientation of Dr. Drenchev's research from hydrogen storage alloys to infrared spectroscopy of probe molecules for analysis of solid state surfaces. An important step in career consolidation of Dr. Drenchev is his appointment at the University of Pardubice (Czech Republic) between 2012 and 2013 as a Senior Researcher. The acquired new knowledge Dr. Drenchev successfully applies and develops in the Solid Surface Reactivity Laboratory at IGIC-BAS. This report reveals unambiguously that Dr. Drenchev fully complies with the requirements of the competition announced in IGIC for Associate Professor in Chemical Sciences (Chemical Kinetics and Catalysis).

B. Report on the fulfillment of the minimal criteria of BAS

In the competition for associate professor on chemical kinetics and catalysis Dr. Drenchev participated with a habilitation thesis based on 5 scientific publications devoted to IR spectroscopic characterization of valence and coordination state of metal cations in zeolites, oxide catalysts and metal-organic frameworks with molecules probes and their isotope analogues. It is of importance that 4 of these articles (i.e. 80 %) were accepted in international journals from the first quartile in field of chemistry of materials such as Applied Catalysis B:

Environmental (Impact Factor, IF = 14.229); Journal of Physical Chemistry C (IF = 4.309) and Physical Chemistry Chemical Physics (IF = 3.567). Along with them, Dr. Drenchev presents 13 scientific publications focusing on the application of IR spectroscopy for identification and analysis of the nature and the acidity of various types of adsorption and surface centers. It is specific that 12 of articles (i.e. 92 %) have been published in international journals from the first quartile in the respective fields. In addition to the journals mentioned above, the journals such as Industrial & Engineering Chemistry Research (IF = 3.375), RSC Advances (IF = 3.049), Chemical Communications (IF = 6.164), Topics in Catalysis (IF = 2.226) and Microporous and Mesoporous Materials (IF = 4.182) need to be outlined. Dr. Drenchev's scientific publications, published between 2010 and 2019, have so far received 136 independent citations. Dr. Drenchev has presented part of the research data as two oral presentations at international project meetings and 4 - at national seminars, as well as he presented 5 posters at international events and 3 - at national forums with international participation. The successful research activity of Dr. Drenchev is accomplished because of his active participation in projects with different sources of funding including 9 contracts funded by Bulgarian sources and 2 scientific projects funded by the University of Pardubice and the European Commission under the FP7-ENERGY program. The total Hirsch index (H-factor) of Dr. Drenchev's total scientific output is 7.

The report analysis reveals that Dr. Drenchev's scientific output covers the subject of the competition and exceeds significantly the minimal national requirements for occupation of the academic position of associate professor in the field of Natural Sciences, Mathematics and Informatics, Direction of Chemical Sciences, mentioned in The Law for the Development of the Academic Staff in Bulgaria, the Regulations for its Implementation and the Rules for the Conditions and Procedures for Acquisition of Academic Degrees and Occupation of Academic Positions at IGIC-BAS.

C. General features of the applicant's research activities

C1. Main scientific contributions presented in the habilitation thesis

Spectroscopic probing the surfaces of materials is a central topic in the contemporary chemical sciences. Nowadays, a variety of physico-chemical methods are used, but the exploration of surface phenomena still remains a scientific challenge because of the complex nature of the materials. In this modern branch of chemical sciences, Dr. Drenchev's research can be considered, namely the methodological development of IR spectroscopy for the

analysis of the surface of supported oxide catalysts, metal-organic frameworks and zeolites. The scientific contributions can be divided into two groups: (a) CO and NO and their isotopic mixtures as probe molecules to identify the valence and coordination state of surface metal cations; (c) new data on the surface acidity of multi-component systems. In this order, the research achievements will be described in more details.

The coordination state of copper ions in the MOF “Basolite C300” has been thoroughly investigated using CO and an isotope mixture of ^{12}CO - ^{13}CO as probe molecules. It is found that the adsorption capacity of MOF depends on both the copper ions and the organic ligand. Based on IR of isotope mixtures it has been demonstrated that copper ions are in different states and only some of them are capable of coordinating more than one CO molecule.

This research approach is further developed to study the state of copper ions in Cu – ZSM-5 zeolites. The originality of this study consists in the using of isotope mixture $^{12}\text{C}^{16}\text{O}$ + $^{13}\text{C}^{18}\text{O}$ enriched with the isotopes ^{13}C and ^{18}O instead of the conventional mixture $^{12}\text{C}^{16}\text{O}$ - $^{13}\text{C}^{16}\text{O}$ enriched with ^{13}C only. This makes it possible to better distinguish the respective IR bands, which on its turn provides an opportunity for straightforward identification of polycarbonyl complexes of copper ions. As a result, two types of dicarbonyls for Cu^+ ions have been identified in Cu-ZSM-5: one of them is the well-known dicarbonyl with characteristic bands at 2178 cm^{-1} and at 2151 cm^{-1} , and the other is a new type of dicarbonyls with corresponding bands at 2183 cm^{-1} and about 2150 cm^{-1} . Part of the copper dicarbonyls is converted to tricarbonyl complexes characterized with two IR bands at 2191 and 2166 cm^{-1} .

The studies were extended to copper and nickel ions in the metal-organic frameworks of the CPO-27-Ni series. The main feature of these MOFs is that the copper ions exhibit low acidity and interact weakly with CO, with the enthalpy of adsorption being about -20 kJ/mol . The adsorption of CO also shows that part of the copper ions is stabilized as Cu^+ at defective sites of the organic structure. As in the case of the CO molecule, the NO molecule is also weakly adsorbed on Cu^{2+} ions and the adsorption enthalpy is about -14.5 kJ / mol . *In situ* IR studies of H_2 and CO molecules adsorbed on pre-dehydrated and hydrated CPO-27-Ni were also performed. It is shown that there are equivalent nickel sites in MOF that interact with CO to form carbonyls stabilized by π -back donation. In doing so, the CO molecules replace the water molecules from the Ni^{2+} centers and form carbonyls. In this respect, the structure of CPO-27 is a rare example of providing such sites for Ni^{2+} ions where CO is able to replace pre-adsorbed water.

The data of these case studies serve as a guide for the deep examination of the surface of real catalysts for the CO oxidation, NO decomposition, and CO+NO interaction, namely deposited copper-cerium catalysts on a carrier γ -Al₂O₃: Mn/Al₂O₃, Ce/Al₂O₃ и MnCe/Al₂O₃. It was established that the deposition of the active phase results in partial disappearance of the alumina OH groups and in blocking of part of Al³⁺ Lewis acid sites. The manganese ions were better dispersed on the bimetallic catalysts MnCe/Al₂O₃ as compared to single ones Mn/Al₂O₃ – a property that determines the better catalytic activity of the bimetallic catalysts. The interaction of catalysts with CO leads to the formation of carbonates and hydrogen carbonates, the amount of which increases with the interaction temperature and in the sequence Al₂O₃ < Ce/Al₂O₃ < Mn/Al₂O₃ << MnCe/Al₂O₃. During the interaction the catalysts with NO, manganese nitrosyls are formed, whose amount is higher for the bimetallic MnCe / Al₂O₃ than the one-metal Mn/Al₂O₃. The reaction between CO and NO proceeds on the oxide surface leading to the formation of isocyanates, (hydrogen)carbonates, nitrosyls, nitrites and nitrates, the ratio between them depending on the reaction temperature and the type of catalyst. The derived correlations are important for the development of NO_x neutralization catalysts.

In conclusion, the research of Dr. Drenchev contributes; on the one hand, to the enrichment of knowledge in the field of solid surface chemistry, and, on the other, they give impetus to the methodological development of IR spectroscopy for surface analysis of model adsorbents and real catalysts.

C2. C2. Scientific contributions presented in the non-habilitation thesis

The characteristic feature of these studies is the rational utilization of IR spectroscopy of isotopically labeled molecules, as well as isotopic exchange, to assess the surface of catalysts and adsorbents based on zeolites, oxides and metal-organic frameworks. The gained information is of importance in order to go insights into the nature of the surface metal centers and their structure, as well as the mechanism of different types of surface reactions. The significance of the research has been most clearly demonstrated in zeolites exchanged with iron, copper and vanadium ions. It is found that Fe²⁺ centers form two types of monocarbonyl after CO adsorption, whereas polynitrosyls with a composition of Fe²⁺(NO)_x (x > 2) are appeared during NO adsorption. In the presence of NO, Fe³⁺-OH is easily reduced to Fe²⁺ even at low temperatures. The copper ions of the partially hydrated zeolite adsorb ¹⁵N₂, forming a Cu⁺(N₂) (H₂O) mixed complex. This is a new complex that was not identified previously. Systematic IR studies enables to describe the mechanism of a series of reactions

with participation of copper ions and CO, NO and N₂ molecules. Catalysts for the oxidative dehydrogenation of propane including V-MCM-36 and V-MCM-22 have been established that a significant part of vanadium ions adopts a low oxidation state (most probably 4+), and this state is maintained in a strong oxidizing environment.

The identification of the adsorption centers and the determination of their structures were demonstrated by studying the adsorption of CH₄ and ¹⁵N₂ on zeolites and oxides including H-ZSM-5, SiO₂ and HY. The methane CH₄ was found to bind simultaneously to the oxygen and hydrogen atoms of the silanol groups (Si-OH). During the interaction of CH₄ with acidic Si-OH-Al groups, it binds mainly to hydrogen atoms. It is established that the adsorption of CO₂ and ¹³CO₂ on MIL-53(Al) and NH₂-MIL-53(Al) is accomplished by the formation of CO₂ dimers, where the C atom of one molecule interacts with one O atom of the other molecule and the second oxygen atom of the same molecule is H-linked to a hydroxyl group. Dimer formation is concomitant with a transition from the structure with a wide pore configuration to a narrow pore configuration.

The next subjects of studies are DeNO_x catalysts based on mixed platinum-metal oxides (Pt/ZrO₂/Al₂O₃, Pt/CeO₂/Al₂O₃ and Pt/Ce-Zr/Al₂O₃). The form of the adsorbed NO_x groups is identified by IR spectroscopy of NO and co-adsorption of NO and O₂. Adsorption of NO on hydrogen-reduced catalysts has revealed the presence of Pt⁰-NO and Pt^{δ+}-NO complexes, as well as the formation of surface nitrites and nitrates, the amount of which increases in the order Pt/Zr/Al < Pt/Ce-Zr/Al < Pt/Ce/Al. The highest concentration of Pt⁰-NO complexes is observed at the Pt/Ce-Zr/Al catalyst due to the high dispersion of palladium particles.

These studies were carried out in a team with researchers from IGIC-BAS, the University of Pardubice, the Technical University of Aachen and Delft, and the University of Bilkent. The role of Dr. Drenchev is consists in the planning the implementation of the research and the interpretation the results obtained.

D. Conclusion

A distinctive feature of the research activity of Dr. Nikola Drenchev is the methodical development of IR spectroscopy of probe molecules and isotopically labeled molecules for the identification of valence and coordination state of surface metal ions, for determining the structure of adsorption centers and for elucidating the mechanism of different types of surface

reactions. The studies present new data on the formation and stabilization of surface coordination compounds, as well as they provide new directions for surface survey of multi-component systems. The scientific output of Dr. Drenchev far exceeds the minimal national requirements for occupying the academic position of Associate Professor in the field of Natural Sciences, Mathematics and Informatics, Direction on Chemical Sciences, specified in the Bulgarian law, and in particular in the regulations of IGIC-BAS. Based on the above-mentioned criteria, I propose in most convincing way that the Scientific Jury to award Dr. Nikola Drenchev the Academic Position Associate Professor in Chemical Kinetics and Catalysis.

27.08.2019 г.

Radostina Stoyanova