REVIEW

according to a competition announced in the State Gazette no. 52 of 02. 07. 2019 for occupation of the academic post "Professor" in the professional field 4.2. Chemical Sciences (Organic Chemistry - Organic Catalysis) for the Faculty of Chemistry and Pharmacy, Sofia University “St. Kliment Ohridski "
with a single **candidate** Assoc. Prof. Dr. Hristyan Aleksandrov Aleksandrov, academic post in Faculty of Chemistry and Pharmacy, Sofia University “St. Kliment Ohridski "
Reviewer: Prof. Tanya Stoyanova Hristova, D.Sc., Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences

1. General information on the applicant.

Hristyan Aleksandrov was born in 1980. In 2002 he completed his education at the Faculty of Chemistry at Sofia University. In 2008 he successfully defended his doctoral dissertation on "Theoretical study of the structure of zinc-containing ions in the pores of ZSM-5 zeolites and the mechanism of the dehydrogenation of ethane on them". In the same year he was selected as a "Senior Assistant" at the Faculty of Chemistry at Sofia University. Since 2014 he has been elected as an “Associate Professor” at the Faculty of Chemistry and Pharmacy at Sofia University.

2. Overall assessment of the applicant's scientific and educational activities.

Assoc. Prof. Aleksandrov is a co-author of 58 publications, 57 of which are referenced in the WEB OF SCIENCE and SCOPUS databases. The articles have been published in prestigious scientific journals. Some of the journals have significant impact factors, among them: Nature Materials, ACS Catalysis, Appl. Catal. B: Environmental Chem. Mater., Angewandte Chem. Int. Ed., J. Phys. Chem. A / C, J. Mol. Catalysis A: Chemical, Phys. Chem Chem, Phys., Catal. Today, Topics in Catal., Energy and Env. Sci., J. Catal., Chem. A European J., Nanoscale, Catal. Sci. Technol., Electrochim. Acta et al. 51 of these journals have quartile Q1 and the rest 6 - quartile Q2. Dr. Aleksandrov co-authored 2 chapters of books as well as a "Manual for laboratory work with a collection of organic chemistry problems for students in the specialty Pharmacy ". These data clearly indicate the high quality of the applicant's scientific activity. Confirmation of this conclusion is also noted 637 citations, of which 234 are on publications participating in the competition. In more than half of the published materials, Dr. Aleksandrov is a first or second author, proving his leading role in research. I

would also like to point out the high activity of the candidate after his election as an Associate Professor.

He is also very active in participating in international scientific forums, where he has presented 24 oral and 20 poster reports. Co-organized by 2 schools within FEZA and

COST conferences and has participated in the organizing committee of 11 national and international conferences held in our country.

Dr. Aleksandrov has had two long-term specializations in Munich (2008-2009) and Barcelona (2011-2012), as well as several short-term specializations at the Technical University of Munich (Germany), the University of Barcelona (Spain) and the Pacific Northwest National Laboratory, USA.

He has participated in 22 national projects funded by the National Scientific Fund and various Structural Fund Operational Programs of the European Union, as well as in 8 international projects funded by DFG (Germany), the Ministry of Education and the Ministry of Economy and Competitiveness (Spain). On one of the projects: "Modeling of the structure and spectroscopic characteristics of modern materials" (NSF, 2016-2018), worth BGN 40,000, he was the head, and of 4 projects - head of the module. He has been a participant in 2 European Networks: COST Action CM1104 "Reducible oxide chemistry, structure and functions" and COST Action MP1306 "Modern Tools for Spectroscopy on Advanced Materials".

Assoc. Prof. Aleksandrov is active in teaching. He has held lectures, seminars and exercises in Organic Chemistry for various specialties in the Faculty of Chemistry and Pharmacy and the Faculty of Biology of the Sofia University, a lecture elective course in "Heterogeneous Catalysis" and a compulsory course in "Modeling of Periodic Systems and Nanostructures" program "Theoretical Chemistry" at the Faculty of Science, Sofia. At his invitation he has held 11 lectures and seminars in Germany, Spain, China, Thailand, Poland and Bulgaria. He was the head of 1 doctoral student and 1 graduate student, as well as a consultant to doctoral students at the Technical University of Munich (Germany) and the University of Barcelona (Spain).

The assessments of the candidate according to the indicators, in accordance with the minimum requirements in Republic of Bulgaria are indicated in Table. 1. The overall assessment of the applicant by all indicators exceeds almost 3 times the minimum set, with a very significant share of the applicant's publication activity, quotations of scientific works and his participation in projects.

Table 1. Assessment of the applicant by indicators, in accordance with the minimum requirements in Republic of Bulgaria

Indicator	Points required	Points Candidate
A. Thesis "Doctor"	50	50
B. Habilitation thesis	100	150
D. Scientific publications outside of habilitation thesisis	200	730
E. Citates	100	418
F. Management successfully defended PhD student; participation in projects etc.	150	427
Total	**600**	**1775**

The applicant shows considerable activity as a reviewer in a number of competitions for the award of academic positions and in many scientific journals. He is a long-time member of the Faculty Board of the Faculty of Chemistry and Pharmacy, Sofia University.

In 2014, Dr. Aleksandrov received the Pythagoras Prize for active research for a young scientist. He is also the recipient of other prestigious awards, among which is the annual award of the Rector of Sofia University "St. Kliment Ohridski "(2002), Award from the Foundation for Higher Education Assistance and Prof. Bernd-Artin Wessels (2001), Eureka Scholarships (2000-2003).

3. Major contributions from the applicant's research activities

The candidate's research activity is aimed at clarifying at the molecular level the mechanisms of the course of reactions on surfaces and the factors that influence them based on quantum-chemical modeling using density functional theory (DFT). The candidate participates in the competition with 36 publications and 1 study guide, 32 of them in journals indexed by quartile Q1 and 4 by quartile Q2.

3.1. Evaluation of the habilitation thesis

The habilitation thesis is aimed at "Clarifying the factors affecting the hydrogenation of alkenes on transition metals - a theoretical study". It is based on 6 publications from the last 6 years. All articles are published in very prestigious specialized journals with high impact factor and quartile Q1. In two of them the candidate is the first, and in the third is the second author.

After a thorough literature review, the applicant assumed the need for detailed analysis and the search for alternative approaches to clarify the mechanism of the hydrogenation process

on complex nanocomposite systems consisting of metal deposited on metal oxide. The candidate draws attention to some current theories on the mechanism of hydrogenation, which affect the role of co-adsorbed carbon deposits, the participation of sub-surface hydrogen atoms in the various stages of the process of hydrogenation of alkenes, the formation of intermediates that modify the surface, the size effect of the metal particles. Dr. Aleksandrov set himself the difficult task of clarifying the role of C atoms in the penetration of H into the subsurface layer on Pd nanoparticle models and to what extent it is energetically and kinetically stable with respect to transition metals. Particular attention is paid to the role of the carrier on the properties of transition metal nanoparticles, the effect of adsorbed H on the stabilization of subsurface H in transition metal particles with different sized, clarifying the role of the presence of subsurface hydrogen and co-adsorbed $\equiv C\text{-}CH_3$ particles, the effect of the size of the alkyl radical, the particle size and the presence of low coordinated centers in them on the hydrogenation of alkyl to alkene. For the purpose of the studies, ideal M (111) surfaces (M = Pd, Pt, Rh, and Ni) were simulated. A model of a cross-sectional octahedron metal nanoparticle was used and the reagents, intermediates and products were sorbed at different positions in the nanoparticle. Quantum-chemical calculations were performed using a DFT based software package.

The more important results of the research are:

- It is shown that the C surface atomic diffusion adsorbed on the (111) facet of a Pd79 nanoparticle and a Pd (111) surface is always an exothermic process with the most stable positions being close to the surface layer. The subsurface positions are significantly more favorable than those on the Pd surface;
- At low concentrations, H atoms have been shown to prefer to remain on the surface of the Pd nanoparticles. All sub-surface positions for the H atom in Pd (111) are less stable than the corresponding positions on the surface.
- The effect of the C atom on the binding of the H atom located at different positions on the Pd_{79} nanoparticle is discussed in detail. It has been shown that the subsurface C atoms in Pd nanoparticles significantly destabilize H atoms located in their immediate vicinity, with the similar effect of H on C.
- By varying the concentration of H on the surface and different concentrations of C in the subsurface region, it has been shown that the presence of subsurface C atoms on Pd does not increase the concentration of subsurface H atoms at a low concentration of H on the surface. It is concluded the positive effect of high concentrations of H on the surface on its penetration

into the subsurface layer of Pd. It has been shown that in addition to Pt, Pd and Ni, the subsurface C can be stable in other metals such as Cu, Ag, Au. Low coordination positions have been shown to support its formation and maintain its stability.

- Weak effect of non-reducing MgO carrier (100) on the mean atomic distances, electronic structure and polarization of charge density due to electron transfer from carrier to Pd and Pt nanoparticles containing 49-155 atoms has been demonstrated. These features have been shown to lead to a slight influence of the carrier on the adsorption and absorption properties of the nanoparticles with respect to hydrogen, which rapidly attenuates with increasing distance from the carrier.

- The reaction of hydrogenation of ethyl on models of Pd (111) ideal surface and Pd79 nanoparticle with different arrangements and concentrations of H atoms is modeled. Increasing the concentration of H on the Pd (111) surface has been shown to weaken the binding of ethyl to the Pd surface, and the presence of ethylidine increases the exothermicity of the reaction. An increase in the energy barrier is shown as the length of the hydrocarbon chain increases. It was found that the subsurface H on Pd destabilizes the adsorbed H atoms by altering its electronic structure, which is more pronounced for the metal nanoparticles than the (111) surface models. It is very important to conclude that the rate of hydrogenation increases with increasing content of H_{sub} even when it is not in close proximity to the catalytic center, ie. the reactivity of the system is not solely determined by the structure of the active centers.

- By applying similar models the applicant studies the validity of the conclusions drawn for Pd and for other transition metals (Pt, Ni and Rh). It has been shown that while Pt has a similar Pd behavior, the nature of hydrogen bonding in Ni and Rh is different, i.e. the presence of H_{sub} leads to an increase in the bond between H_{ad} and metal.

In conclusion, I would like to emphasize that the theoretical studies presented in the habilitation thesis have potential applications in petrochemistry, fine organic synthesis, the food industry and others.

3.2.Evaluation of research activity beyond habilitation thesis.

30 of the articles and 1 study aid with which the applicant participates in the competition are not reflected in the habilitation thesis. Of these, 26 were published in journals with quartile Q1 and the other 4- with quartile Q2. The studies focus on quantum-chemical modeling of zeolite systems containing cations and their complexes; CeO_2-based catalytic systems and

transition metal nanoparticles. The interaction of organic molecules with zeolites and graphene was investigated.

More important research results are:

- Formation of stable W – O – Si bridges in W modified zeolites has been shown to alter their structure, hydrophobicity and Lewis acidity. This affects the properties of MFI zeolites in epoxidation of styrene and increases the sensitivity to detect low concentrations of CO_2 and NO_2 due to the formation of nitrates and carbonates on the incorporated W^{VI} = O particles. The formation of complexes by the interaction of Rh modified faujasite with CO, H_2, C_2H_4 and NO was investigated in the hydrogenation of C_2H_4. The role of the combination of Brønstedic acid centers with extra-lattice Al-containing particles in the process in the absence of transition metal cations in the zeolite has been demonstrated. Full sorption of CO and NO on Pd modified chabazite has been demonstrated due to the formation of a mixed carbonyl-nitrosyl palladium complex in the zeolite micropores;
- Different N-containing particles that can be obtained by adsorption of NO on reduced models of cerium dioxide ((111) surface and nanoparticle) and NO and co-adsorption on stoichiometric CeO_2 have been modeled, which is a contribution to the worldwide literature concerning catalytic conversion of NO;
- Formation of stable Pt^{2+} cations in the form of a square planar complex on the small (100) facet of CeO_2 is shown. It has been demonstrated that partial reduction of the system by separating one or two oxygen atoms results in reduction of Ce^{4+} ions, but does not affect the oxidation state of Pt in this complex, whereas mononuclear platinum particles in all other positions on the surface of the nanoparticle from CeO_2 is in redox state 0. The influence of the partial pressure of O_2 and the size of the cerium oxide particles on the structure of the platinum particles has been demonstrated. It is concluded that the Pt state cannot be uniquely determined by using FTIR and CO as a probe molecule, and additional techniques are needed. The applicant has also studied more complex composites. An interesting result is that the formation of a surface layer of cerium dioxide on the (100) surface of Al_2O_3 is more energy-efficient than the formation of three-dimensional particles of CeO_2, which explains the reported literature data for the presence of high concentrations of Ce^{3+} ions. For the models of (111) CeO_2 have been shown that the incorporate of Y^{3+} cations close to each other around the subsurface oxygen vacancy could be energetically advantageous.
-Model investigation of the formation of C – C and C – O bonds on Ni (111) surface is done. The results obtained show that the deactivation of the catalyst due to the formation of carbon

deposits is delayed by the use of small Ni nanoparticles, while the successful formation of graphene requires the reaction to be carried out at a lower temperature and on large nickel particles. It is shown that the dissociation of oxygen on the (111) facet of pure platinum particles is facilitated by the flexibility of the surface, even at large particle sizes, the positions in which O_2 interacts with three metal centers near the edges are essential. The results on bi-metallic M / Pt particles are also very interesting.

I would also like to point out the molecular-level studies of the interaction of various organic molecules with surfaces, and in particular the interaction of drugs with modified mesoporous materials with a potential application for obtaining effective drug delivery systems.

Conclusion

The research of Dr. Hristian Aleksandrov is a significant contribution to the theoretical studies of the interaction of different molecules with surfaces, which is a prerequisite for a proper understanding of the processes and a powerful tool for optimizing the properties of materials for use in adsorption and catalysis. In his studies, the candidate uses modern modeling approaches based on DFT, in many cases combining his theoretical studies with other appropriate experimental methods. I would like to point out the logical planning of the experiments and the in-depth interpretation of the results that lead to their publication in a large number of prestigious scientific journals with much citations. The applicant's activity is not limited only in research activity. There is a very extensive teaching activity, participation in projects (national and international), participation in the organization of a number of scientific events. The high number of publications in which the candidate is the first or second author demonstrates Dr. Aleksandrov's leadership in research, a recognition for which prestigious awards have been received. In addition, I would like also to emphasize the good training of the applicant in prestigious laboratories. Not least is the high rate of work over whole the period and also the significant scientific results obtained after his election as an associate professor. I believe that his participation in the "professor" competition at his young age opens up new horizons for his growth as a researcher and teacher. I believe that the applicant's indicators are fully in line with the requirements of the Law for the development of academic staff in Republic of Bulgaria for occupying the academic position of "professor" in the professional field 4.2. Chemical Sciences (Organic Chemistry - Organic Catalysis) and will be of considerable benefit to the needs of the Faculty of Chemistry and Pharmacy, Sofia University "St. Kl. Ohridski ". Therefore, I strongly recommend that the members of the academic board and the Faculty Concil of the Faculty of Chemistry and Pharmacy, Sofia

University "Kliment Ohridski" be awarded to Dr. Hristian Aleksandrov, currently Associate Professor at the same Faculty, the academic post of "Professor".

Sofia, 09.10.2019

Reviewer:

/ Prof. D.Sc. Tanya Hristova /