Review

of the materials submitted for participation in the competition for the occupation of the academic position "Professor" in Higher Education Area 4. "Natural Sciences, Mathematics and Informatics", Professional field 4.2. “Chemical Sciences” (Organic Chemistry - Organic Catalysis), announced in the State Gazette no. 52 of 02.07.2019 for the needs of the Faculty of Chemistry and Pharmacy at Sofia University “St. Kl. Ohridski"

Reviewer: Prof. Dr. Natasha Trendafilova, Institute of General and Inorganic Chemistry-BAS

In the present competition for occupation of the academic position (AP) "Professor" in Professional field 4.2. “Chemical Sciences” (Organic Chemistry - Organic Catalysis), participated one candidate, **Assoc. Prof. Dr. Christian Alexandrov Alexandrov** *(Author ID (SCOPUS): 56926848100, Research ID (Web of Science): R-4055-2016, ORCID ID: 0000-0001-8311-5193).*

1. General characteristics of the materials presented. The set of materials, presented by Assoc. Prof. Dr. Alexandrov for participation in the competition for AP “Professor” is in full compliance with the requirements of the ZRASRB (ЗРАСРБ) and the Regulations for its implementation as well as with the Rules for the conditions and procedure for acquiring academic degrees and occupying academic positions at Sofia University “St. Kl. Ohridski”(July 17, 2019). The reference to the fulfillment of the minimum national requirements for AP “Professor” under Art. 2b of ZRASRB (ЗРАСРБ) for occupation of the AP “Professor” shows that the applicant fulfills and repeatedly exceeds the required minimum by all indicators.

2. Biographical data, education and professional experience. Assoc. Prof. Dr. Alexandrov completed his secondary education at the National Gymnasium of Natural Sciences and Mathematics (chemistry profile) in 1998 with an excellent (6.00). From 1998-2002 he was a student at the Faculty of Chemistry at Sofia University “St. Kl. Ohridski". In 2002 the candidate completed the course of the study with an excellent (6.00) and diploma of Bachelor (in Chemistry) and Specialization in Theoretical Chemistry and Physical Chemistry. In the period 2003-2008, the candidate was a PhD student at the Faculty of Chemistry of Sofia University, where in 2008, he successfully defended a thesis on the topic: "Theoretical study of the structure of zinc-containing ions in the pores of ZSM -5 zeolites and the mechanism of dehydrogenation of ethane on them”. In the same year he started working as a "Senior assistant" at the Faculty of Chemistry at Sofia University, and in 2009 he was selected as a "Chief assistant". In 2014, after a successful competition, the candidate was selected as "Associated Professor" at the Faculty of Chemistry and Pharmacy, where he still works. Assoc. Prof. Dr. Alexandrov has held two long-term specializations, at the Technical University, Munich (2008–2009) and at the University of Barcelona (2011–2012). He later held a number of short-term specializations at the same universities and at Pacific Northwest National Laboratory, USA.

The applicant presented a list of participations in 30 scientific projects, 22 of which are national, funded by the Scientific Research Fund at the Ministry of Education and Science and various Operational Programs of the European Structural Funds, 8 international projects, funded by DFG (Germany), Ministry of Education (Spain), Ministerio de Economía y Competitividad (Spain), European Commission. Assoc. Prof. Dr. Alexandrov was a project manager of one project and a team leader of the Sofia University team in 4 projects. He participated in two European networks: COST

Action CM1104 “Reducible oxide chemistry, structure and functions” and COST Action MP1306 “Modern Tools for Spectroscopy on Advanced Materials”.

The scientific competence of Assoc. Prof. Dr. Alexandrov has been recognized by the international scientific community and therefore he has been repeatedly invited as a reviewer for publications submitted to some of the most renowned international journals in his field of research, such as: *Journal of Catalysis, The Journal of Physical Chemistry C, Physical Chemistry Chemical Physics, Surface Science, ChemCatChem, Journal of Molecular Catalysis A: Chemical, Applied Surface Science, Computational and Theoretical Chemistry, Chemical Physics Letters, The Journal of Chemical Theory and Computation, Langmuir , Chemical Engineering Science, et al.*

Assoc. Prof. Dr. Alexandrov is a recipient of “Pythagoras” Award for Young Scientist for 2014, the Annual Award of the Rector of the Sofia University “St. Kliment Ohridski” for 2002 and the Award of the Foundation for Support of Higher Education and Prof. Dr. h. c. Bernd-Artin Wessels, 2001. In the period 2000-2003, the candidate was a fellow of the “Eureka” Foundation. He presented data on participation in the Scientific Juries appointed to hold competitions for occupation of the AP “Associate Professor” (3) and “Chief Assistant” (2).

Assoc. Prof. Dr. Alexandrov has co-organized many scientific forums (FEZA post-conference School, 2017, “International Training School on Spectroscopy Codes” within COST Action MP1306, 2018). He was a member of the organizing committee of the Humboldt Research Conference on Computational Chemistry, 2002, Second Humboldt Conference on Computational Chemistry, 2004, International Symposium Catalytic Processes on Advanced Micro- and Mesoporous Materials, 2005, Third Humboldt Conference on Computational Chemistry, 2006, Second International Symposium on Advanced Micro- and Mesoporous Materials, 2007, Third International Symposium on Advanced Micro- and Mesoporous Materials, 2009, Fourth Humboldt Conference on Computational Chemistry, 2010, 7th FEZA Conference, 2017, 1st - 18th National Conference of Chemistry for undergraduate and graduate students, 2002 - 2019. To the biography of Assoc. Prof. Dr. Alexandrov should be added his active participation in the academic life of the Faculty of Chemistry and Pharmacy as: member of the Faculty Student Council in the period 1999-2007, member of the Faculty Council of the Faculty of Chemistry, 2003-2007, Member of the Faculty Council of the Faculty of Chemistry and Pharmacy, 2015-2019.

3. Evaluation of the scientific activity

Scientific publications. The full list of scientific publications of Assoc. Prof. Dr. Christian Alexandrov contains 61 scientific papers, of which 57 (~ 93%) are in reputable international journals with a total impact factor of 317,111. 51 of the publications (~ 84%) are in Q1 journals, 6 (~ 10%) are in Q2 journals, 2 are book chapters, published by Elsevier, 1 is in a non-refereed in Scopus journal, and 1 is a study guide. The total number of the applicant's citations is 637, of which 559 have been found in publications printed in refereed and indexed in Scopus editions. Applicant's H-factor calculated on all publications is 14. His scientific results are reported with 55 presentations at national and international forums, of which 35 oral reports (11 of them invited) and 20 poster presentations (all reports and posters are presented personally by the applicant).

Assoc. Prof. Dr. Alexandrov participates in the competition for AP “Professor” with 36 original scientific publications in international journals of high rank with a total impact factor of 226.573,

which were not included in the thesis for "Doctor" degree and in the list of publications for participation in the competition for AP "Associate Professor". The distribution of the publications by quartiles of the journals in which they are published, is as follows: 32 publications (~ 89%) are in Q1 journals and 4 publications (11%) are in Q2 journals. A study guide was also presented. All publications are co-authored and their distribution by authors is as follows: 7 publications with 6 authors, 6 publications with 5 authors, 5 publications with 4 authors, 4 publications with 3 authors, 4 publications with 8 authors, 2 publications have 7 authors and the other 8 publications have more than 10 authors. The applicant is the first author in 6 of the publications and in 7 he is the corresponding author. 234 citations were noted on the papers for the competition, 209 of which were in referenced and indexed in Scopus editions. The H-factor calculated for these articles is 9.

I accept for review all the 36 scientific publications submitted by the applicant for participation in the present competition for AP "Professor". These articles describe comprehensive and wide-ranging studies in the field of the theoretical modeling of the structure and properties of catalytic systems used in heterogeneous catalysis, as well as reactions occurring on and/or in them.

The Habilitation work of Assoc. Prof. Dr. Christian Alexandrov is on the topic: "Clarifying the Factors Affecting the Hydrogenation of Alkenes on Transition Metals - A Theoretical Study". It summarizes the studies included in 6 publications of the candidate, all in journals of category Q1, with which he fulfills and exceeds the required minimum of points for Indicator 4 of Group B. The candidate is the first author in 3 of the publications, in two he is the first and corresponding author and in one of them he is only the corresponding author. The publications on the topic of the Habilitation work include cutting-edge experimental and theoretical studies conducted to study the factors that influence the kinetics of hydrogenation of alkenes on transition metals: these are various surface atoms or molecular fragments, the structural characteristics of the catalyst, as well as the type and electronic structure of the metal. The theoretical research of Assoc. Prof. Dr. Alexandrov in these publications best demonstrates the key role of the theoretical modeling in understanding the mechanisms of the complex processes in heterogeneous catalysis. By quantum-chemical calculations, the influence of C atoms on ad/absorbed H atoms on models of Pd nanoparticles was studied. It was explained how the presence of C facilitates the penetration of H into the subsurface layer of Pd systems. The influence of the support on the properties of transition metal nanoparticles was studied, as well as the effect of adsorbed H on the stabilization of the subsurface H, in large particles and transition metal nanoparticles.

The theoretical modeling has been carried out exhaustively with appropriate quantum-chemical methods based on the density functional theory. For the periodic DFT calculations the VASP (Vienna ab initio simulation package) software package was used, in most cases with the gradient corrected PW91 exchange-correlation functional, which has been proven as the most suitable one in the investigations. Depending on the specifics of the systems and processes being studied, realistic models were constructed and other suitable functionals were selected (W91-D2, PBE, VWN/LDA, RPBE/GGA). As a result of the calculations: (i) energy-preferred structures and positions (on the surface and in the subsurface) are predicted; (ii) calculated and discussed are geometric parameters, inter-atomic distances in nanoparticles, electronic structure, DOS of metal atoms, charges and electron density distributions, binding energies for adsorption and absorption of different atoms on different surfaces, barriers and reaction activation energies, activation barriers for migration/diffusion, barriers of hydrogenation, rate constants; (iii) predicted are initial structures, transition states and terminal structures, as well as many other characteristics of the catalytic systems and processes studied.

The original scientific contributions in the research of the applicant consist in the development of realistic theoretical models and effective computational procedures in the modeling of complex catalytic systems and processes. Obtained are new, valuable theoretical results, with the help of which the structure and properties of a large number of complex catalytic systems used in heterogeneous organic catalysis have been studied. These results are correlated with precise experimental data and thus shed light on the mechanisms of real catalytic processes and the factors that influence them. A distinctive feature of the theoretical studies conducted by Assoc. Prof. Dr. Alexandrov is that in all cases they were conducted to answer specific questions from the experiment.

Specific scientific contributions in the research of Assoc. Prof. Dr. Alexandrov, some results and more important conclusions are summarized below within the framework of the four scientific topics formulated by the applicant.

Quantum-chemical modeling of zeolite systems containing cations and their complexes with applications in catalysis

• The most stable W-containing centers in the pores of defect-free nanoscale MFI zeolites have been established by quantum-chemical calculations. The results showed that the incorporation of tungsten modifies the structure of zeolite, hydrophobicity and Lewis acidity, which finding was taken as the reason for the better catalytic behavior of these samples. The high sensitivity of the W-MFI film to low concentrations of CO_2 and NO_2 (1-3 ppm) is explained to be due to the formation of nitrates and carbonates on the incorporated W^{VI}=O particles, while CO and NO are poorly adsorbed.

• Periodic quantum-chemical calculations have shown that the difference between the two types of experimentally established $Rh^+(CO)_2$ complexes is due to differences in the structure of the binding sites of the complex in the faujasite-type zeolite lattice (FAU). Another study showed that the replacement of CO ligands in $Rh^+(CO)_2$ complexes in faujasite with NO becomes easy by forming 14-electron $Rh^+(NO)_2$ complexes that have additional free orbital at the rhodium center allowing coordination of a third electron-donor ligand. This explains the ability of $Rh^+(NO)_2$ complexes to react with C_2H_4 to form 16-electron $Rh^+(NO)_2$ (C_2H_4) complexes which, when H_2 added, transform into $Rh^+(NO)_2(C_2H_5)$ complexes and further formation of ethane.

• Experimental results have provoked the candidate to perform quantum-chemical calculations to explain the catalytic activity of dealuminated HY zeolites with different Si/Al ratios, which under standard conditions can catalyze the hydrogenation of C_2H_4 to C_2H_6 in the presence of H_2 without observing dimerization of C_2H_4.

• In another study, various $Pd^{n+}(CO)_X(NO)_Y$ complexes (n=1 and 2; X=0-2; Y=0-2) sorbed in zeolite-type chabazite were modeled, which clarifies the effect of this zeolite structure, loaded with a significant amount of atomically (ionically) dispersed palladium (2 wt%), as CO and a passive NOx adsorbent. It has been shown that these gases can simultaneously be completely eliminated by forming a mixed carbonyl-nitrosyl palladium complex in the zeolite micropores.

• The stability of various Fe-containing cations in the pores of ZSM-5 zeolite was investigated by periodic quantum-chemical calculations and the following order of stability was determined: $Fe^{2+}(H_2O) > Fe^{3+}OH > Fe^{2+} > Fe^{2+}OFe^{2+} > Fe^{2+}OH$.

• Combined theoretical and EXAFS studies of different Fe-HZSM-5 samples have shown that isolated Fe^{2+} ions exist in the experimental Fe-HZSM-5 samples. Based on the theoretically obtained stable

structures, the experimentally observed temperature evolution of iron-containing zeolite specimens, is explained.

Quantum-chemical modeling of catalytic systems based on CeO_2

• The theoretical studies on this topic include modeling of various nitrogen-containing particles that can be obtained by adsorption of NO onto reduced models of cerium dioxide ((111) surface and nanoparticle). Theoretical studies have contributed to study the NO adsorption and co-adsorption of NO and O_2 on stoichiometric cerium dioxide. Valuable results have been obtained regarding the catalytic conversion of NO, leading to a revision of some of the existing concepts in the literature.

• The structure and relative stability of mononuclear platinum particles deposited on a $Ce_{21}O_{42}$ nanoparticle under conditions of system reduction or oxidation have been modeled. Quantum-chemical calculations of mononuclear platinum particles on a larger $Ce_{40}O_{80}$ nanoparticle have shown that peroxo (O_2^{2-}) particles stabilized at the PtO_x–CeO_2 interfaces are most likely contained in samples of cerium dioxide nanoparticles up to 2 nm large, containing platinum as Pt^{4+} ions only.

• Comprehensive theoretical modeling of various model systems, such as platinum surfaces, nanoparticles and clusters, as well as reduced or oxidized platinum particles deposited on a cerium dioxide support, has yielded results evaluating the effect of platinum particle charge on the C-O vibrational frequency. The results have shown that the C-O vibrational frequency cannot be an indication of the type of platinum-containing particles.

• By quantum-chemical calculations Assoc. Prof. Dr. Alexandrov investigated the stability of various Pt particles in the presence of CO. The effect of CO concentration on the structure and stability of small platinum clusters deposited on CeO_2(111) and γ-$A1_2O_3$(001) surfaces as well as on cerium dioxide nanoparticles was evaluated. The stability is determined with respect to the decomposition of clusters to Pt, Pt^0(CO) and/or $Pt^{2+}(CO)_2$ particles. The results showed that in the presence of CO in gas phase, the platinum clusters will have different behavior depending on the support - decomposition to neutral monocarbonyls on the surface of cerium dioxide and to cationic complexes on the cerium dioxide nanoparticles, while on alumina the carbonylated cluster remains intact but is almost detached from the surface.

• Complex three-component catalytic systems containing two oxides and one transition metal are modeled using periodic quantum-chemical calculations. The structure and stability of cerium dioxide particles (in the form of CeO_2 or Ce_2O_4 clusters or as a small nanoparticle, $Ce_{13}O_{26}$) deposited on (100) and (001) surfaces of γ-Al_2O_3 were studied. Using three types of models: a CeO_2(111) surface and two cerium dioxide nanoparticles of different sizes and shapes, the local structure and preferred positions for yttrium cations and oxygen vacancies in Y-doped cerium dioxide were investigated.

Quantum-chemical modeling of transition metal nanoparticles and catalytic transformations on them

• Within this topic, the effect of an inert support such as defect-free MgO(100) on the adsorption and absorption properties of Pd_{127} and Pt_{127} nanoparticles (1.6 nm) was investigated by quantum-chemical calculations. The studies have continued with modeling of the absorption of hydrogen in the most realistic models of Pd and Pt nanoparticles: large enough, deposited on a support, and with a maximum covered by H atoms surface. It has been shown that absorbed hydrogen can significantly increase the catalytic activity of Pd nanoparticles in the hydrogenation reactions of unsaturated hydrocarbons and it

has been predicted that Pt also has similar catalytic behavior. The effect of H atoms located on the surface of the nanoparticle on the stability of the absorbed H atom has been found to be significant and much more important than the support effect. Quantum-chemical calculations have shown that the absorption of H is endothermic in Pt, energy-neutral in Pd(111) and pure Pd nanoparticles and exothermic in Pd nanoparticles with H-coated surface. Thus, it is assumed that H atoms on the surface and the nanostructure of Pd are the basic prerequisites for facilitating the penetration of hydrogen into the subsurface layers of Pd and for altering its catalytic activity.

• By quantum-chemical calculations Assoc. Prof. Dr. Alexandrov investigated the hydrogenation of alkyl particles on Pd, in order to clarify how the subsurface H accelerates the reaction proceeding on the Pd(111) surface, what is the role of the low coordinated centers (edges) between two facets of Pd nanoparticles and what is the effect of reaction-side particles such as ethylidine, ≡C–CH_3. It has been shown that some of these factors can significantly alter the barrier of hydrogenation of ethyl on Pd, and also influence the hydrogenation of butyl onto Pd, which significantly broadens the significance of the conclusions drawn.

• In-depth theoretical modeling has helped the candidate to study the influence of subsurface H on the hydrogenation reaction of ethyl on four transition metals Pd, Pt, Ni and Rh, for which two different mechanisms have been proposed.

• The formation of C–C and C–O bonds on models of Ni(111) surface and Ni_{79} nanoparticles (~1 nm) is modeled theoretically in order to clarify the competition between carbon deposition and gasification of C. A model of graphene was developed and its electronic structure was investigated with a view to further modeling metal nanoparticles deposited on graphene and investigating catalytic reactions on them. Graphene complexes with non-planar organic compounds such as triphenylmethyl radical, anion and cation have also been subject of theoretical modeling.

• Energetic and kinetic results, obtained by Assoc. Prof. Dr. Alexandrov through quantum-chemical calculations of periodic surface- and nanoparticle models, have indicated that the incorporation of C atoms into the subsurface layer reduces the electronic density of the surrounding metal atoms and thus affects their chemical and catalytic activity, which is why they need to be considered even for precious metal systems.

• Quantum-chemical modeling has also been used to investigate the dissociation of oxygen onto truncated octahedron platinum-based nanoparticles containing 116 atoms. The studies have continued with modeling the dissociation of oxygen onto 38-atom platinum-based particles and metal variation (3d, 4d, and 5d) in the core of M@Pt type particles. The effect of the electronic structure of the transition metal on the dissociation of O_2 on the Pt(111) facets was thus evaluated.

Quantum-chemical modeling of the interaction of organic molecules with zeolites and grapheme

• In connection with the use of mesoporous materials as carriers for controlled drug delivery and the need to study in detail the interaction between the drug and the carrier at molecular level, Assoc. Prof. Dr. Alexandrov conducted quantum-chemical modeling of the interaction between *mesalazine* and models of carrier, modified with -COOH and -NH_2 groups as well as the interaction between two *mesalazine* molecules. The interaction of *quercetin* with models of mesoporous silicalite containing silanol groups or Zn^{2+} cations has also been theoretically investigated, as well as the interaction of *quercetin* with models of silicalite modified with amino groups (KIT-6NH_2). In another study, the

interaction of *curcumin* with a model of mesoporous silicalite modified with amino groups was modeled. Quantum-chemical calculations were performed to investigate the adsorption of *verapamil* to models of silicalite modified with -SO_3H and -COOH.

• For the study of the interaction between the organic molecule and the zeolite, the sorption of *paraquat* in zeolite (FAU) was also modeled. In another study, it was found that the cation-exchanged zeolites can improve the stability of palm oil against oxidation and heat treatment. The calculated binding energies have predicted that Ca-X is the best for inhibiting palm oil oxidation.

4. Assessment of the applicant's teaching activity. Assoc. Prof. Dr. Alexandrov has had a high teaching activity over the last five years. The applicant has provided data on Lecture courses in Organic Chemistry I, Applied Quantum Chemistry, Modeling of Periodic Systems and Nanostructures and Heterogeneous Catalysis for various specialties and forms of education at the Faculty of Chemistry and Pharmacy at Sofia University, and also conducted Seminars and Exercises in Organic Chemistry I and II for all specialties of Faculty of Chemistry and Pharmacy and Biological Faculty. He is the supervisor of one successful PhD student in 2017 and a graduate student at the Sofia University. Assoc. Prof. Dr. Alexandrov was a PhD consultant at the Technical University of Munich and at the University of Barcelona.

5. Personal impressions and a concluding opinion. In recent years, Assoc. Prof. Dr. Christian Alexandrov has been convincingly established himself as a thorough researcher and expert in the field of theoretical modeling of various catalytic systems and processes. In the competition for the AP "Professor", he presented a sufficient number of scientific papers published after obtaining the "Doctor" degree and the AP "Associate Professor". The applicant's research contains original scientific contributions that have been noticed by the international scientific community and have received high recognition. From the presented materials it is clear that Assoc. Prof. Dr. Alexandrov possesses excellent theoretical background, indisputable scientific qualification and potential for conducting and leading valuable scientific research in the future. The applicant's in-depth research and professionalism, his growing competence and scientific activity in recent years strongly support the occupation of AP "Professor". **On the basis of all the scientific achievements and my personal impressions, I am convinced to vote with "yes" for: Assoc. Prof. Dr. Christian Alexandrov Alexandrov to take the academic position "Professor" in the Professional field 4.2. "Chemical Sciences" (Organic Chemistry - Organic Catalysis).**

Reviewer:

October 15, 2019, Sofia (Natasha Trendafilova, Prof. Dr.)