REVIEW

of the materials, submitted for participation in a competition for the academic position "Associate Professor" in a professional field 4.2. "Chemical Sciences" (Theoretical Chemistry), published in the State Gazette, issue 21 of 15.03.2022 (p. 138) for the needs of the Faculty of Chemistry and Pharmacy (FCP) at Sofia University "St. Kliment Ohridski"

The only candidate in the competition is **Chief Assistant Professor Dr. Iskra Zareva Koleva** https://orcid.org/0000-0002-4080-9846; Author ID (Scopus): 56641286000; https://www.researchgate.net/profile/Iskra_Koleva/publications

General characteristics of the received materials and the applicant.

By Order № RD-38-192/12.04.2022 of the Rector of Sofia University, Prof. Anastas Gerdzhikov, I have been appointed as a member of the scientific jury for the competition about the academic position (AP) "Associate Professor" in the professional field (PF) 4.2. Chemical Sciences (*Theoretical Chemistry*). The submitted materials by Dr. Iskra Koleva for participation in the present competition are in full compliance with the requirements of the Law for development of the academic staff in Republic of Bulgaria and the Regulations for its implementation, the Regulations on the terms and conditions for obtaining scientific degrees and occupation academic positions at Sofia University "St. Kl. Ohridski" and the Recommended Criteria of the FCP-SU for PF 4.2. “Chemical Sciences”. Inspection of the above requirements for the AP “Associate Professor” showed that the candidate fulfilled the required minimum of all indicators by groups **(A, C, D, E, G)** and collected 773 points against the total required minimum of 510 points. There is no evidence and no reports of plagiarism have been received on the documents (scientific papers) submitted for the competition (Art. 26, par. 4).

Iskra Koleva was born on November 21, 1989. She graduated from FCP at Sofia University in 2013 with Bachelor's degree in “Computational Chemistry” and in 2014 with a Master's degree in “Materials Science”. In 2017, she obtained the educational and scientific degree "Doctor" in PF 4.2. Chemical Sciences (*Theoretical Chemistry*) after successful defense of the thesis "Quantum chemical modelling of heterogeneous catalytic systems based on cerium dioxide", in FCP at SU, under the scientific supervision of Prof. G. Vayssilov and Assoc. Prof. H. Aleksandrov. With a Ph.D. degree, the candidate fulfilled the indicator **"A" (50 p.).** Since 2017,

Dr. Koleva is "Chief Assistant Professor" in the Department of Pharmaceutical and Applied Organic Chemistry of the FCP at SU and as a result of consistent career development in the field of theoretical chemistry she has accumulated about 5 years of work experience in the specialty. During her education and scientific career, the candidate carried out 5 short-term specializations at the Barcelona University, Spain; participated in the organization of 1 international conference (7th FEZA) and 9 national conferences on chemistry for undergraduate and graduate students; presented scientific communications at 23 conferences and workshops in Bulgaria and abroad, participated in 8 national and 3 international projects. In 2020, Iskra Koleva was awarded the prestigious national fellowship "For Women in Science" - a program of L'Oréal and UNESCO

Scientific publications

In her scientific career so far, Iskra Koleva is a co-author in **18** scientific papers published in refereed and indexed journals in the SCOPUS/Web of Science database of Q1 and Q2 category. At the time of writing, the total number of citations of the publications (excluding self-citations of all authors) is 182 and the *h*-index is 7 (SCOPUS). The high citation rate of the published results, mainly for the period 2017-2022, is evidence of the quality and significance of the research, as well as the international recognition of the scientific teams with the participation of Dr. Koleva.

In the current competition, Dr. Koleva participates with **14** original research papers, which exclude publications from her doctoral thesis. All papers have been published in reputable international journals with high impact factor, e.g. *Angewandte Chemie* (IF 16.8), *Catalysis Today* (IF 6.5), *Molecules* (IF 4.9), *Materials Chemistry and Physics* (IF 4.8), *Journal of Physical Chemistry C* (IF 4.2), *Physical Chemistry Chemical Physics* (IF 3.9) and they reflect in-depth research and results on hot topics. The publications' distribution by quartiles is as follows: 11 are published in journals of category Q1 and 3 - in journals of category Q2. In 3 papers of category Q1, the candidate is the first author, which by unwritten rule is assigned to the leading scientist in the research. The papers have been published in a relatively short period 2018 - 2022 (except for one paper from 2015), which evidences to an extremely intensive and thorough research activity of the candidate after her PhD. The publications selected by Dr. Koleva have contributions in theoretical heterogeneous catalysis and quantum chemical modelling of periodic systems for study of the structure and properties of metal clusters, nanoparticles, reducible oxides and zeolites. The papers thematically correspond to the scientific subject "Theoretical Chemistry" of

the competition and fully meet the requirements for the AP "Associate Professor" under the group of indicators **"C" - 100 points** for 4 scientific papers with Q1 (min. 100 p.) and **"D" - 235 points** for 7 publications with Q1 and 3 publications with Q2 (min. 220 p.).

Habilitation work. In fulfillment of the requirements of the competition for Associate Professor, Dr. Koleva has submitted a habilitation work, entitled "***Quantum chemical study of heterogeneous catalytic systems containing cerium dioxide and metal nanoparticles***", including 38 pages and 4 publications from group "C". It covers theoretical investigations on 1) thermal stability, reducibility and catalytic properties of CeO_2 doped with zirconium ions, rare earth elements (yttrium) and deposited platinum clusters and 2) catalytic activity of noble metals upon incorporation of subsurface carbon. With the skillful application of density functional theory based on plane wave calculations for periodic structures, Dr. Koleva offers a thorough quantum-level approach to explain the observed catalytic activity of the investigated metal nanoparticles, as well as to elucidate the factors that modify this activity in certain reactions. The conducted theoretical studies contribute to the optimization of a number of industrial processes involving reactions of CO oxidation to CO_2, methane combustion, nitrogen oxide reduction, propane and naphthalene oxidation, soot combustion, etc. and aim at achieving favorable economic and environmental effects. The main scientific contributions and results presented in the habilitation work can be summarized as follows:

- The structural properties and reducibility of cerium dioxide systems doped with zirconium were studied as a function of nanoparticle size ($Ce_{40-n}Zr_nO_{80}$ ~ 1.5 nm and $Ce_{140-n}Zr_nO_{280}$ ~ 2.4 nm), concentration and type of distribution for the doping Zr^{4+} cations. The electronic energies of the possible model systems were calculated, and based on the lowest energy obtained, the most preferred Zr^{4+} ion population was predicted, namely in the first subsurface layer of the nanoparticle. The role of Zr^{4+} in the stability, reducibility, oxygen mobility and catalytic activity of the CeO_2 system has been established. The effect induced by Zr^{4+} is explained by its smaller ionic radius compared to that of Ce^{4+} and generating a stronger electrostatic field (*publ. № 4*).
- The influence of doping yttrium (Y^{3+}) on the local structure and oxygen vacancies at the surface and in the volume of cerium dioxide nanoparticles of different sizes and shapes has been studied in detail. The most preferred positions of the yttrium cation and oxygen vacancy on the CeO_2 surface were predicted, while no clear trend was found for the nanoparticles. It was found that Y^{3+} doping selectively facilitated the formation of oxygen vacancies on the CeO^2 surface, but

had no significant effect on the reducibility of the system because of the close ionic radii of Y^{3+} and Ce^{4+}. The results, which showed the lack of preferential Y^{3+} and oxygen vacancy occupancy and facilitated local reorganization between structures with close stability and oxygen migration in these systems, leaded to the conclusion that CeO_2-Y_2O_3 nanocomposites are suitable for catalytic applications. (*publ. № 13*)

- Changes in the local and electronic structure of the system of adsorbed carbon monoxide on platinum clusters deposited on reducible CeO_2 and non-reducible oxide, γ-Al_2O_3 (for comparison), have been investigated. The influence of the carrier type on the electronic structure of Pt clusters was found. A correlation was found between the Pt cluster size (Pt_{10}, Pt_{20} and Pt_{25}) and the coordination mode of CO molecule on the one hand and the adsorption energy and density of states of the system on the other hand. The largest adsorption energy is predicted for the bridged CO molecule coordinated on the largest Pt_{25} cluster. The reactivity of the Pt cluster (in terms of electron-donor properties) was evaluated by calculations of the energy of the occupied d-states and the d-band center. The calculations have shown that the metal cluster is more reactive when it is deposited on γ-Al_2O_3 compared to CeO_2 and the reactivity of the Pt clusters reduces upon CO adsorption. (*publ. № 6*)
- The property of subsurface carbon atoms to interact with copper, silver, and gold surfaces and nanoparticles and thus favor the catalytic activity of metal centers has been theoretically investigated, distinguishing these carbons from their usual role of poisoning these catalysts. The preferred subsurface positions of C for Cu and Ag(111) surfaces and at the edges and corners of Au nanoparticles were identified. By electronic structure calculations, it was shown that upon binding to carbon, the inner electrons' energy of the metal ions is stabilized, which changes their chemical and catalytic properties. The results of the energetic and kinetic calculations confirmed the inducing catalytic effect of subsurface carbon atoms in the studied metals and showed that this is a general property for transition metals rather than selective for certain metal systems (Ni, Pd, Pt). (*publ. № 10)*

Scientific contributions of the publications of group D. The scientific topics and contributions included in the publications from this group can be summarized as follows:

Quantum chemical modelling of zeolites containing metal cations *(publ. № 2, 7, 8, 9, 12, 14)***.**

- The most probable structures of MSE-type zeolite were predicted by formation of silicon vacancy (defect) and by substitution of Si by Ti or Al in different crystallographic positions. A

vibrational approach was proposed to establish the T-position in Ti-MCM-68 zeolite by using probe molecules - pyridine and acetonitrile adsorbed at the Ti center. The adsorption mechanism of hydrogen peroxide at the Ti center in the zeolite lattice was examined. • The coordination polyhedra of the complexes formed were predicted based on calculated vibrational characteristics of dicarbonyl and nitrosy, and mixed carbonyl-olefin model complexes of Pd^{2+} and Pt^{2+} in chabazite and compared with ıre experimental IR spectra. • The adsorption behavior of paraquat molecule on faujasite-type zeolite (FAU) with different Si/Al ratio was elucidated. In agreement with the experiment, it was predicted that the samples with the highest Si/Al ratio (2.4) had the highest adsorption capacity. • The relative stability of different Fe-containing particles in the pores of HZSM-5 zeolite was determined and the results helped to elucidate structural information from EXAFS study. • The development of a chabazite-type zeolite structure containing a significant amount of dispersed palladium was supported for the removal of CO and NO harmful emission. Modelling of a series of $Pd^{x+}(CO)_m(NO)_n$ complexes in the zeolite, calculation of their vibrational characteristics and comparison with the experimental spectra have shown that a mixed carbonyl-nitrosyl palladium complex was formed in the micropores of the zeolite, due to which both gases can be simultaneously completely removed. • The process of retardation of palm oil oxidation in the presence of zeolite nanocrystals was elucidated based on a theoretical evaluation of the interaction of hydroperoxides (C_2H_5OOH and HOOH) and alkenes (ethene and *cis*-butene) with off-lattice bound metal cations (Li^+, Na^+, K^+, Ca^{2+}) in nanocrystalline FAU-type zeolite. It was predicted that the zeolite containing Ca^{2+} inhibited palm oil oxidation most effectively.

Quantum chemical modeling of organic molecules with modified mesoporous silica *(publ. № 3, 5, 11).* The mode of interaction between drugs such as miltefosine, tamoxifen, curcumin and the silica nanoparticle carrier modified with silanol, amino or carboxyl groups has been elucidated by DFT calculations of the model systems. The thermodynamic stability of the systems studied has been evaluated, enabling the selection of the appropriate drug carrier.

Quantum chemical modeling of the interaction of trivalent metal cations with cucurbiturils (*publ. № 1*). Using the calculated Gibbs free energies of the model complexes formation of Al^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Lu^{3+} with CB[n]s cucurbiturils (n = 5, 6, 7, and 8), the influence of the macrocycle cavity size, environment (vacuum and aqueous solution), pH and the participation of hydrated lanthanide cations on the thermodynamic stability of the complexes was evaluated.

It should be recognized that the research approach for the theoretical characterization of metal multicomponent periodic systems with consideration of impurities, environment and adsorbent is not a trivial one due to the large number of atoms, spin state of mixed metal systems, surface and volume state, etc. By accomplishing these tasks, Dr. Koleva demonstrates a deep knowledge of solid state chemistry and heterogeneous catalysis, skillfully application of the acquired computational approaches to modelling periodic structures, showing excellent intuition for the comprehensiveness of the models used in solving various research problems. This has allowed her to successfully engage in interdisciplinary research with teams of diverse scientific interests and to use quantum chemical calculations to derive correlations between the structure and properties of metal-containing systems.

In fulfillment of the minimum requirements for AP „Associate Professor“ (group of indicators E and G), the candidate reports scientometric data only on the papers submitted for the competition: in group **"E" - 308 points** based on 154 citations (excluding self-citations of all authors), (min. 70 p.); in group "**G" - 80 points**, taking into account *h*-index 6 (60 points) and a participation in 4 projects (20 points), (min. 70 p.). The educational and teaching activity of Dr. Koleva for the period 2017-2022 includes conducting exercises in 6 programs with an annual teaching time of over 370 h.*: "Computational Methods in Spectroscopy", "Hybrid (QM/MM) Methods", "Modelling of Periodic Systems and Nanostructures"* - Master's Program (MP) Computational Chemistry (MP Advanced Spectral and Chromatographic Methods of Analysis); *"Pharmaceutical Analysis Part I and II" and "Biopharmaceutics"* - MP Pharmacy; *Instrumental Methods in Chemistry Part II* - Bachelor's Program (BP) Engineering Chemistry and Advanced Materials. Dr. Koleva is the supervisor of a successfully defended diploma, master's degree in 2020 and is a reviewer of a number of theses.

In conclusion, the scientific contributions, publishing and teaching activity and participation in scientific projects of Chief Assist. Prof. Dr. Iskra Koleva, prove that she is a highly qualified and promising scientist, capable of conducting original research in the field of computational materials science, in particular theoretical heterogeneous catalysis, which fully corresponds to the scientific specialty "Theoretical Chemistry" of the competition. **After the analysis of the materials presented for the competition, I find it reasonable to give my positive assessment by voting convincingly "yes" and recommend the Scientific Jury to**

propose to the Faculty Council of FCP at SU, Dr. Iskra Zareva Koleva to be elected to the academic position of "Associate Professor" at the Faculty of Chemistry and Pharmacy, Sofia University in the professional field 4.2. Chemical Sciences, scientific specialty "Theoretical Chemistry".

Ivelina Georgieva

Digitally signed by Ivelina Georgieva
DN: cn=Ivelina Georgieva, o=Institute of General and Inorganic Chemistry, ou=IGIC, email=ivelina@svr.igic.bas.bg, c=BG
Date: 2022.07.11 11:31:34 +03'00'

11.07.2022

Sofia

Reviewer:

Ivelina Georgieva, Prof. Dr.

Institute of General and Inorganic Chemistry-BAS