REVIEW

by Prof. Silvia Zivova Todorova, PhD, Institute of Catalysis - BAS
with respect to the competition for occupying the academic position „Professor“ in professional field 4.2 “Chemical Sciences”, scientific specialty “Chemical Kinetics and Catalysis”, published in „Newspaper of State”, issue in 34 on 03.05.2022.

1. General presentation of the applicant's materials.

Prof. Ivanka Petrova Spasova, PhD, is the only candidate in the competition for the academic position "Professor". The set of materials presented by the candidate is in accordance with Article 29 of the the Law for Development of the Academic Staff in the Republic of Bulgaria (LDASRB), Article 32(1) of the Rules on the Conditions and Procedures for Acquisition of Academic Degrees and Occupation of Academic Positions at IGIC-BAS. To participate in the competition, Assoc. Prof. Spasova submitted the necessary documents: curriculum vitae, a copy of the diploma for the awarded "Doctor", a certificate of minimum five-year experience in the specialty, a list of publications, a list of citations, a list of publications for participation in the competition, list of citations of publications after habilitation, list of participations in scientific forums after habilitation, certificate of fulfillment of the minimum and additional requirements, Habilitation certificate, author's certificate, appendices to the certificate of fulfillment of the minimum and additional requirements of BAS and IGIC-BAS, prints of publications to participate in the contest.

2. Biographical data of the applicant.

Assoc. Prof. Spasova graduated from Higher Institute of Chemical Technology in 1983, specialty "Technology of Organic Synthesis and Fuels". In 1998, after successfully defending a doctoral dissertation on the topic "Synthesis and catalytic activity of oxide catalysts based on 3d-transition metals for the elimination of CO and NO at low temperatures", she was awarded the educational and scientific degree "Doctor". From 1984 until now, she has worked at the IGIC-BAS, successively as a chemist, then as an associate professor from 2012 until now. Assoc Prof. Dr. Ivanka Spasova is a partner in a number of national and international scientific projects. She is a participant in 16 national projects: 10 projects with NSF, National Center for Mechatronics and Clean Technologies, in the National Program "Low Carbon Energy for Transport and Household", EPLUS and “Distributed Infrastructure from centers for production and research of new materials, their applications, as well as for conservation, access and e-storage of artifacts-INFRAMAT”. Assoc. Prof. Spasova is also the head of a project with NSF and a participant in an international project "European Twinning on Materials Chemistry Enabling Clean Technologies" - 2020, National Program "European Scientific Networks". The presented above facts show that the Assoc. Prof. Spasova has a capacity to attract funds and the lead research projects.

1. Evaluation of the scientific research of the candidate

Associate professor Dr. Spasova is co-authors of 71 publications, participating in the competition with 33, which did not repeat those presented for the position of "associate professor". All publications are referenced in Web of Science and/or Scopus. The results of her research activity have been published in high impact international journals in the Q1 field (WoS or Scopus): *Applied Catalysis A, Applied Catalysis B: Environmental, Microporous and Mesoporous Materials, Inorganica Chimica Acta, Applied Surface Science, Journal of CO_2 Utilization, Molecules, Journal of Drug Delivery Science and Technology, Journal of Solid State Chemistry*. The publications for the competition are divided into two groups, covering indicators **B** and **Г**, according to the Regulations on the terms and conditions for acquiring scientific degrees and holding academic positions. In the first group, indicator B - "*Habilitation*

work - scientific publications in publications that are referenced and indexed in world-renowned databases with scientific information (WoS or Scopus)" 8 publications are presented (four of them fall into Q1, three into Q2 and one in Q3), and the total number of points is 175 points, with a required 100 points. In 5 of the publications presented according to this criterion, Associate Professor Spasova is the first or corresponding author.

In the second group, 25 publications are presented The ranking by quartiles is as follows: 10 - Q1, 10 - Q2, 3 - Q3 and 2 - Q4, covering the indicator **Г** with a total of 519 points, required points are 220. In the group of indicators **D**, the requirements are also significantly exceeded - the required 120 points, the candidate has 512 points. All citations are in prestigious international journals, which support the importance and relevance of the scientific developments of Prof. Ivanka Spasova. Her overall h-index is 12. A 53 participations in international and national scientific forums are presented, for the current competition, of which 39 are at international forums and 14 at national forums. According to indicator E, which includes defended doctoral students, implementation and management of national and international projects and attracted funds for them, Prof. Spasova collects 207 points which is also above the required 150 points, according to the above-cited regulations.

The scientific indicators in the presented materials, with which Dr. Spasova participates in the competition, convincingly show that she significantly exceeds the requirements imposed on the candidates for the position of professor. I would also like to point out that all the materials are very well arranged, which greatly facilitates the work of the reviewer.

3. Scientific research contributions

Habilitation work

The research activity of Associate Professor Ivanka Spasova is in a topical area of modern heterogeneous catalysis, related to environmental protection. Air pollution control is one of the main concerns of the European Union (EC) environmental policy (http://ec.europa.eu/environment/index_en.htm). In 2013, the EU proposed a Clean Air Policy Package to further reduce emissions of air pollutants until 2030. The main air pollutants are PM, SO2, NH3, NOx, volatile organic compounds (VOCs), CH_4. One of the most effective and economically beneficial technologies for the removal of harmful substances is catalytic technology. As is well known, the properties of catalysts are mainly determined by the structure and dispersion of the active phase and its interaction with the support. From this point of view, the support plays an essential role in the formation of the active phase. One of the widely used carriers are mesoporous materials. They have attracted much attention because of their large surface area, uniform pore-size distribution, large pore size, and wide potential applications in the fields of separation, adsorption and catalysis. The mesoporous support would give rise to well-dispersed and stable metal particles, supplying abundant pores and large surface area, thus possessing a great potential in further improvement of the catalytic performance. Another type of interesting suitable carriers, these are mesoporous composite (hybrid) materials, due to the fact that it is possible to adjust the porous texture by varying the composition and type of constituents, which leads to obtaining an active phase with appropriate dispersion and stable state.

The scientific contributions of Ivanka Spasova, Ph.D., presented in the "Habilitation work" refer to the development of catalysts containing transition metals and transition metals modified with rare earth elements, deposited on individual and composite (hybrid) supports and their catalytic behavior in processes of oxidation of CO and CH4, disposal of nitrogen oxides - reduction of NO with reducing agents CO and CH4 and decomposition of NOx. These studies fall within the laboratory's traditional theme of protecting the purity of atmospheric air.

Habilitation Work can be summarized in two main directions:

1. Development and study of catalysts based on transition metals and/or rare earth elements supported on individual supports.

2. Development and study of catalysts based on transition metals applied to composite (hybrid) carriers.

In the first direction, the research is focused on the process of reduction of NO with CO and NO with methanol decomposition products (CO and CH_4), the latter process being proposed for the first time. The proposed approach combines the two processes, resulting in improved efficiency, a wider temperature window, and can be a solution for cleaning waste gases from variable mode sources. The process is a catalytic reduction of NOx with CO, hydrogen and/or methane on supported nanosized metals/metal oxides. The reactions were carried out in the presence of copper catalysts supported on mesoporous silicas (KIT-6 and SBA-15) obtained by impregnation and a combined method of impregnation and gas phase deposition. Catalysts obtained on KIT-6 by combined method have lower specific activity than catalysts obtained by impregnation in the reduction reaction of NO with CO. This is explained by the different routes of the reaction in the two series of catalysts, which are determined by the accessibility of the particles of the active phase. One route is associated with vacancy formation due to reduction of oxidized copper particles on the surface by CO, dissociation of NO, followed by regeneration of the active sites with CO. The second route is due to formation of bridging nitrates, their reaction with adsorbed CO and then reaction with NO to produce N_2O. The decomposition of N_2O takes place on the metal active centers that dominate on the outer surface of the catalyst. In the combined deposition method, the particles are mainly located in the micro-mesoporous system of the support, and the number of more accessible catalytic centers located on the outer surface is relatively small, while in the catalysts obtained by impregnation, the catalytic centers are predominantly on the outer surface and are easily accessible. When molecular sieve SBA-15 is used as a carrier, the combined preparation method leads to more strongly dispersed particles and, accordingly, to higher activity. Catalysts obtained on the basis of KIT-6 by a combined method show higher specific activity in the reduction of NO with methanol decomposition products (CO and CH_4), with the activity passing through a maximum for the catalyst with 6 wt.% Cu.

Another oxide that has been used to prepare catalysts for NOx, CO, CH_4 elimination reactions is Al_2O_3. It was modified with transition metal oxides or a combination of transition metal oxides with addition of rare earth elements. When Mn/ Al_2O_3 catalysts was modified with Ce, highly active catalysts are obtained in the above-mentioned reactions, due to an increase in the dispersity of the oxide particles.

It was found that the addition of rare earth elements (Ln= La, Ce, Nd and Gd) to the of copper-cobalt spinels deposited on aluminum oxide, changes the state of the surface of a copper-cobalt spinel catalyst. As a result, a partial reduction of copper particles is observed, as well as a migration of these species between the surface and the bulk. Ln/CuCo/Al catalysts exhibit different behavior in oxidation and reduction processes. In oxidation processes, where the oxide state is important, Ce/CuCo/Al and Nd/CuCo/Al are the most active, and this one containing Ce is characterized by the highest activity, due to the presence and optimal surface distribution of the redox couples Cu^{+}/Cu^{2+} and Ce^{3+}/Ce^{4+}. Ln-modified catalysts significantly improve the selectivity of the process to N_2.

Another important part of research of Assoc. Prof. Spasova's is aimed at the development and research of catalysts based on transition metals supported on composite (hybrid) carriers. The following types of hybrid carriers have been investigated: disordered silica-carbon composite carriers, structured silica-carbon composite carriers, alumo-carbon composite carriers. The composite materials were modified with copper oxide and tested in the reduction reaction of NO with CO and decomposition of N_2O.

The influence of the active phase deposition medium and the effect of the addition of the carbon component, both on the surface and morphology of the synthesized composite materials, and on the state and catalytic behaviour, were investigated in the case of the disordered silica-carbon composite carriers. It was found that the addition of carbon to SiO_2 improved the dispersion of the copper oxide particles supported on the silicate-carbon composites and affected the distribution of copper ions between the surface and the bulk of the synthesized catalysts. Since during the deposition of the active phase, the copper oxide particles are connected via the silanol or carbon centers, depending on the amount of carbon on the surface, a partial reduction of the copper oxide phase on the surface was observed. The main role in the formation of the silica/carbon ratio on the surface is played by the isoelectric point of the corresponding component under the conditions of preparation. In composites where the carbon components have IEP>pH of preparation, the surface is enriched in carbon, in IEP<pH the carbon particles are mostly incorporated in the bulk and the surface is poor in carbon.

It was established that copper-oxide catalysts supported on disordered SiO_2–C composites have a twice higher activity in the reaction of low-temperature removal of nitrogen oxides than those applied on activated carbon even at 100°C. The order of activity of the studied catalysts also correlates with the Cu^+/Cu^{2+} surface content. Cu^{2+} and Cu^+ are active sites for NO and CO adsorption, respectively. For catalysts with an increased content of Cu^+ centers, surface reduction is not necessary, so the catalytic reaction can start without this step.

Structured mesoporous SiO_2–C composites with SiO_2:C ratios over the entire concentration range have been successfully obtained. The stabilizing role of SiO_2 on the mesoporous structure of the composites was established. Increasing the carbon content leads to a decrease in the average pore size and an increase in the microspore volume. In all structured SiO_2–C composites, the carbon is located on the pore walls. The deposition of a copper oxide phase does not lead to significant structural changes of the matrix of the two types of carriers, but only to the blocking of part of the pores.

It was found that carbon play an essential role in the decomposition of N_2O. Carbon is both carrier and reactant, and reduced copper ions play the role of catalytically active centers for oxygen transfer from N_2O to carbon. Complete elimination of N_2O and NO was achieved in the presence of a copper-oxide catalyst supported on a silicate-carbon composite with SiO_2/C=30/70. For catalysts supported on alumina-carbon composite supports, it has been found that the activity of the catalysts can be tuned by changing the composition of the alumina-carbon composite support. The so-called "chromatographic effect" is observed - the concentration of copper on the surface is an order of magnitude lower than when applied to a pure carbon carrier. As the content of Al_2O_3 in the composites increases, Cu^{2+} ions “sink” in the volume of the carrier, and Cu^+ ions remain on the surface. Catalytic activity was higher for catalysts with high alumina content, where nearly equal Cu^{2+} and Cu^+ contents were observed on the surface.

Other publications

The other publications presented by Assoc. Prof. Spasova for participation in the competition form several thematic directions related to clarifying the influence of the structural and textural properties of the carrier on the state of the active phase and from there on the catalytic and adsorption properties of materials with application in the protection of environment, clean energy production, and biomedicine.

1. Catalysts supported on carbon-containing materials to protect the environment and obtain clean energy.

The results are summarized in 9 publications. The research was carried out in conjunction with two other institutes of the Bulgarian Academy of Sciences - IOCCP -BAS and IK-BAS and was carried out within three projects with NSF.

It was found that the cobalt-silicate-carbon composites were significantly more active in the reaction of NO with CO reduction than those without carbon, cobalt-silicate composites. The presence of carbon strongly influences the micro-structure of materials: the size of Co_3O_4 crystallites, specific surface area, surface composition and oxide state of surface elements. It is assumed that the higher activity is due to the presence of Co in a different oxide state and the presence of Si and C atoms in their vicinity. It was found that the specific sheet-like morphology of reduced graphene oxide is responsible for the homogeneous deposition of the active phase of $Ni_{0.5}Zn_{0.5}Fe_2O_4$, which in turn leads to an increase in the specific surface area of the catalyst, while preserving the total pore volume. The specific morphology of the obtained catalyst provides easier accessibility of the gas mixture during methanol decomposition, which also accounts for 100% conversion at 650 K and selectivity to CO and H_2 higher than 90%. This selectivity was maintained for 3 h.

In the series of studies, including publications 6, 8, 11, 13, 14, 20, 22, it was found that the raw material from which the activated carbon (AB) was obtained, regulates its textural characteristics, and these significantly influence on the formation of the catalytic centers in supported metal or metal oxide catalysts for methanol decomposition. So e.g. the developed mesoporosity of AB facilitates the formation of stable and dispersed Fe_3O_4 magnetite particles, with high catalytic activity but low selectivity to CO, and weak mesoporosity of AB leads to the formation of large magnetite particles on the outer surface and the formation of less accessible particles blocked in the micropores. The high micropoiesis of AB from waste biomass facilitates the formation of finely dispersed iron and ZnO nanoparticles located in the micropores, which in turn promote the formation of $ZnFe_2O_4$ and complex spinel ferrites ($Ni_{0.5}Me_{0.5}Fe_2O_4$ (M = Zn or Cu), leading to high catalytic activity in the decomposition of methanol.

The activated carbon obtained from waste motor oil and furfural is more amorphous, characterized by a higher specific surface area and pore volume, and simultaneously formation of micro- and mesopores. The application of Zn and Fe nanoparticles promotes the development of "secondary" porosity, which facilitates the formation of finely dispersed and highly active metal oxide particles accessible to the reagent.

2. **CO_2 capture on composite, hybrid, etc. materials**.

The CO_2 capture properties of the structured silicate-carbon composites, structured hybrid amino-functionalized and bifunctionalized mesoporous silicate materials, and porous potassium-nickel hexacyanoferrate analogues of Prussian blue was investigated (publications no. 12, 18, 29 and 30). Structured silicate-carbon composites were found to have a better adsorption capacity for CO_2 than pure silicon materials. As the carbon content increases, the adsorption capacity for CO_2 increases, which is associated with the large average pore size and the volume of micropores.

CO_2 adsorption properties of structured hybrids, amine functionalized hybrid and bifunctionalized mesoporous silicate materials prepared by the sol-gel method and soft templating approach materials of were determined. The simultaneous presence of KCl and xylene has a significant effect on the pore shape and textural characteristics values. All synthesized materials show similar values of adsorbed CO_2, which is probably a result of the fact that the amount of nitrogen is similar in all materials. In this case, the texture properties have no significant influence on the sorption properties of the materials. The determined heat of adsorption for all proves chemisorption between CO_2 and the amino groups of the hybrid materials. The presence of the isocyanurate groups in the hybrid bifunctionalized silicon

materials significantly improves the textural characteristics and CO_2 sorption capacity. The determined heats of adsorption indicate physical adsorption of CO_2 on the active sites.

3. Adsorption and texture characteristics of materials.

The studies included in this part show the influence of adsorption and textural characteristics of materials on their target properties. It is shown that the structural, surface and morphological characteristics of $MnFe_2O_4$ spinels obtained by the combustion method from a solution with glycine and glycerol can be adjusted by changing the ratios in the fuel mixtures. Nanoparticles obtained with glycerol and mixed fuel with glycine up to 50% showed better catalytic properties in complete oxidation of hydrocarbons compared to the sample obtained with fuel containing 75% glycine.

4. Research of materials with biomedical application.

This section comprises eight publications (publications 16, 17, 21, 23, 26, 31, 32, 33). Research is mainly focused on the study of mesoporous silica oxides (type MCM-41 and HMS) as drug delivery systems. An improved solubility of *glimepiride* was found due to a significant decrease in the degree of crystallinity of the drug due to its deposition on the mesoporous material. Upon loading of *pramipexole* on MSM-41 and HMS, delayed release was observed due to its uniform distribution on the surface and in the pores of the oxides. Loading of the antitumor drug *bicalutamide* onto MCM-41 and HMS particles resulted in improved *in vitro* antitumor activity and *in vitro* cytotoxicity due to delayed drug release induced by the porous structure of the carrier.

In another part of the research, the antimicrobial properties of nanocomposites of reduced graphene oxide and copper and silver nanoparticles were studied. Suppression of bacterial growth of *Staphylococcus aureus and Escherichia coli* in the presence of these composite materials is associated with the specific morphology of reduced graphene oxide.

In conclusion, it can be said that the scientific contributions presented in the publications of Assoc. Dr. Ivanka Spasova are novel in science and have significant applied potential in the field of environmental protection and biomedicine.

Conclusion

The research works of Assoc. Prof. Ivanka Spasova fully correspond to the topic of the announced competition for awarding the academic position of "Professor". The number of publications and citations on the published papers prove that Assoc. Prof. Spasova 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 Assoc. Prof. Ivanka Spasova the academic position “Professor” in the professional field 4.2 “Chemical Sciences” and scientific specialty "Chemical Kinetics and Catalysis".

Data 19. 08. 2022 Member of the Scientific Jury:

Sofia /Prof. PhD Silviya Todorova/