R E V I E W

by Prof. Dr Krasimir Ivanov Ivanov - Department of "General Chemistry" of the Agricultural University - Plovdiv, (now retired), on the materials submitted for participation in a competition for the academic position of "Professor" at the Institute of General and Inorganic Chemistry, BAS

By order No. RD-09.24102 dated 27.06.2022 of the Director of the Institute of General and Inorganic Chemistry, BAS (IGIC), I have been appointed as a member of the scientific jury in a competition for the academic position of "professor" at IGIC in professional direction 4.2 "Chemical Sciences", scientific speciality "Chemical Kinetics and Catalysis", announced for the needs of the Laboratory "Materials and Processes for Environmental Protection" of the IGIC.

1. General presentation of the received materials

The only candidate for the competition for the academic position of "professor", announced in the State Gazette No. 34 of May 3, 2022, and on the website of IGIC, is Associate Professor Ivanka Petrova Spasova, PhD.

The set of materials presented by Assoc. Prof. Spasova is following Article 29 of the Law for the Development of Academic Staff in the Republic of Bulgaria (LDASRB) and Article 12 of the Regulations on the terms and conditions for acquiring scientific degrees and occupying academic positions at the BAS.

To participate in the competition, the candidate submitted a total of 33 scientific publications, all published after 2012 (after being selected as an associate professor) and all the necessary documents for participation in the competition for AD "Professor" at IGIC.

2. Brief biographical data of the applicant

Assoc. Prof. Spasova graduated from the Higher Chemical and Technological Institute - Sofia in 1983 with a major in "Technology of Organic Synthesis and Fuels". Immediately after graduation, she has hired as a chemist in the "Chemical Problems for Environmental Protection" laboratory at the IGIC, and in 1988 she won a competition for a research assistant at the same laboratory. In 1998, he defended his doctoral thesis on the topic "Synthesis and catalytic activity of oxide catalysts based on 3d-transition metals for the disposal of CO and NO at low temperatures". In 1999, she was elected head. assistant, and in 2012 he won a competition for an associate professor at the same laboratory.

3. Evaluation of the candidate's scientific and applied activity

Publication activity

- *Scientific publications*:

The total number of publications of Assoc. Prof. Spasova is 71, 59 of them with impact factor or impact rank. She has 33 publications, all with impact factor. Fourteen of the publications are in journals with the highest rank Q1, including *Applied Catalysis B: Environmental* (IF19.5), *Journal of CO_2 Utilization* (IF7.1), *Applied Surface Science* (IF6.71), *Microporous and Mesoporous Materials Microporous and Mesoporous Materials* (IF5.56), etc. 13 of the papers are with rank Q2, and the remaining 6 with Q3 and Q4. No claims have been made by the co-authors of the publications about the candidate's participation in the competition. No other information on incorrectness or elements of plagiarism in the materials submitted for the competition has been received.

- *Participation in national and international scientific forums:*

Dr Spasova's active participation in prestigious scientific forums before habilitation (12th World Congress on Catalysis, 2000, Granada, Spain, VIIIth, IXth and 10th European

Congress on Catalysis) continued after her habilitation. During the period of the competition, 53 papers have been presented with her participation in 36 scientific forums, 19 international and 17 national, including EuropaCat 2013, Lyon, France, EuropaCat 2019, Aachen, Germany, The 6th International Symposium of Gunma University Lyo Initiative for Advanced Research (GIAR), 2018, Kiryu, Japan, 11th World meeting on pharmaceutics, biopharmaceutics and pharmaceutical technology, 2018, Granada, Spain and others. According to Art. 29, para. 5. 5. of the Law on the Acquisition of Scientific Degrees and Academic Positions in the Institute of General and Inorganic Chemistry (in force since 05.05.2018), candidates for the acquisition of the academic position "Professor" must meet the minimum national requirements regulated in the implementing rules of LDASRB and adjusted by the PMS No. 26 of 13.02.2019. From the submitted by Assoc. Prof. Spasova's report shows that she exceeds the minimum requirements and the specific requirements of the IGIC in all indicators, the excess of the total number of points being more than twice (760/1603).

Scientific and applied contributions

Scientific contributions

The research of Assoc. Prof. Spasova's research is entirely in the field of heterogeneous catalysis and is mainly related to the search for new solutions for the disposal of waste gases containing CO, NOx and organic pollutants, as well as to the expansion of the range of applications of catalytic systems in medicine and the production of frequent energy. The main scientific and applied contributions are related to the synthesis and characterization of new active materials as catalysts and adsorbents and the study of their catalytic behaviour. They are described in detail in the attached Author's Note. The Habilitation Brief attached to the documents synthesizes the most important results of the research, with which Assoc. Prof. Spasova participated in the competition. I will try to briefly summarize the most significant results and contributions in my opinion, focusing on those in which the candidate has a leading role.

The main part of Assoc. Prof. Spasova's research is focused on the elucidation of the influence of the carrier or texture on the active phase state and catalytic and adsorption properties of materials with the potential for solving important environmental problems - the purification of air from toxic components contained in industrial waste gases and exhaust gases from automotive transport. An important element of the upgrade in research work after habilitation is the research on the possibilities of obtaining clean energy and materials with biomedical applications. All research is fully aligned with the EU's key priorities of Environmental Protection, Green Energy and Healthy Living:

- *Catalysts for environmental protection:*

These studies fall within the traditional laboratory theme of protection of ambient air purity and are devoted to the preparation of catalysts containing transition metals and/or rare earth elements, coated on individual and composite (hybrid) supports and their catalytic behavior in the processes of oxidation of CO and CH_4, removal of nitrogen oxides - reduction of NO with reducing agents CO and CH_4 and decomposition of NOx. A new approach to reducing the concentration of nitrogen oxides in waste gases, consisting of integrated decontamination using the products of the catalytic decomposition of methanol as nitrogen oxide reducing agents, has been proposed (publications 2, 3, 4, 5). The proposed method combines the two processes, resulting in improved efficiency, a wider temperature window, and maybe a solution for the treatment of waste gases from variable-mode sources. Transition metal and/or rare earth element-based catalysts supported on mesoporous silica KIT-6 and SBA-15 and γ-Al_2O_3 have been investigated to perform the integrated decomposition of methanol with NOx removal (publications 3, 4 and 5).

It was found that for NO reduction with CO, the catalysts prepared on KIT-6 by a combined method (impregnation and gas-phase deposition) had lower specific activity than the catalysts prepared by impregnation. The different catalytic activity is associated with the different routes of the catalytic mechanism in the two series of catalysts, which are determined by the accessibility of the active phase particles. The catalysts applied by the combined procedure on SBA-15 exhibited higher catalytic activity compared to their counterparts obtained by impregnation due to the better dispersibility of the copper particles (publication 4).

In continuation of previous studies on the catalytic processes of elimination of NOx, CO and CH4 (publications 2 and 5), Mn/Al_2O_3, Ce/Al_2O_3 and $MnCe/Al_2O_3$ catalysts were prepared. Of special note is the publication "Cooperative Effect of Ce and Mn in $MnCe/Al_2O_3$ Environmental Catalysts, Applied Catalysis B: Environmental, 138-139 (2013) 362-372 (IF19.5)", in which Assoc. Prof. Spasova is the second author. The synthesized Mn/Al2O3, Ce/Al_2O_3 and $MnCe/Al_2O_3$ catalysts were investigated in detail by FTIR and catalytic experiments and it was found that the catalytic conversion of NO to CO proceeds in two regimes, low and high temperature. The low-temperature regime is associated with precoating of the catalyst surface with adsorbed nitro forms, whereas for the reaction to proceed at higher temperatures, precoating of the catalyst surface with (hydrogen)carbonates is required. The better particle dispersibility of the bimetallic $MnCe/Al_2O_3$ catalyst determined the highest catalytic efficiency in all the reactions studied. Building on previous studies by scientists in the laboratory, it was found that copper-cobalt spinel catalysts of the CuxCo3-xO4 and $CuCo_2O_4/Al_2O_3$ types exhibited high catalytic efficiency in NO reduction with CO and CO oxidation due to the formation of stable compounds in which the metal ions are in a variable oxidation state. To improve the catalytic activity for CO oxidation, CH_4 oxidation and NO decomposition, $CuCo_2O_4/Al_2O_3$ spinel catalysts were modified with additions of rare earth oxides (Ln= La, Ce, Nd and Gd) (Publication 5). All catalysts were found to be effective in the oxidation of CO and CH4 with the order of activity Ce>Nd>La>Gd, with the type of rare-earth element oxide phase, formed being a determinant in the catalysts' performance.

The innovative idea of preparing catalysts on mesoporous composites (SiO_2-C, Al_2O_3-C) by a combination of hydrophilic and hydrophobic components has been developed in publications 1, 9, 10, 24. Unordered SiO_2-C nanocomposites were synthesized by sol-gel method using carbon materials of different origin and textural parameters, and a copper-oxide phase was deposited on them (publications 1 and 5) and the effect of carbon component addition was evaluated (publication 9). A disordered hybrid based on diatomaceous earth and activated carbon was also synthesized, and to change the ratio of Lewis and Brønsted acid centres on the surface, the hybrid support was modified with alumina. The two-hybrid materials were used as a copper oxide catalyst support for the reduction of NO with CO, and copper oxide catalysts supported on unordered SiO_2-C composites were found to be highly efficient for low-temperature NO removal. It was also found that modification of the hybrid support with alumina resulted in a change in the texture and energetic uniformity of the material and promoted better dispersion of the metal ions on the support surface. In N_2O decomposition, the activity of the catalysts does not depend on the nominal copper oxide content but the presence of carbon on the catalyst surface. The carbon in the composites plays the role of both carrier and reactant, and the reduced copper ions play the role of catalytic-active centres for oxygen transfer from N_2O to carbon.

Assoc. Prof. Spasova is among the leading authors in the study of the potential of structured composites, amine-functionalized hybrid materials and Prussian blue analogues in terms of CO_2 sequestration (publications 12, 18, 29 and 30). The sorption properties of structured hybrid amine-functionalized and bi-functionalized mesoporous silicate materials

were determined and the conditions for the intumescence of bi-functionalized hybrids with enhanced sorption capacity were optimized.

Studies on the so-called "chromatographic effect" problems (Publication 24) have led to the conclusion that with increasing Al_2O_3 content in Al_2O_3-C composites Cu^{2+} ions "sink" into the carrier volume, while Cu+ ions remain on the surface. The activity of the catalysts can be tuned by changing the composition of the composite alumina-carbon support.

- *Catalysts for green energy production:*

This research is the result of the collaboration between IGIC, IOHCF-BAS and IK-BAS, in which Assoc. Prof. Spasova actively participates and focuses on an integrated biomass-based system for clean energy production, innovative metal-carbon nanocomposites for hydrogen storage and a renewable integrated system for the elimination of organic pollutants from water and air (publications 6, 7, 8, 11, 13, 14, 20, 22, 25).

The presence of carbon in cobalt-silicate-carbon composites prepared using activated carbons significantly affects the morphology, surface composition and oxidation state of cobalt-silicate-carbon composites and their catalytic activity in NO reduction with CO (publication 7), and the application of NiO. $5ZnO.5Fe_2O_4$ on reduced graphene oxide (RGO) leads to 100% methanol decomposition at 650K (publication 25).

The crucial role of textural characteristics of activated carbons from waste biomass (WB), polyolefin wax, engine oil and coal tar on the formation of catalytic centres when metal or metal oxide catalysts were applied for methanol decomposition and their catalytic properties, respectively, was established (publications 6, 8, 11, 13, 14, 20, 22). It has been found that the dispersity and composition of the applied active phase can be easily controlled by the type of carbon precursor used and by varying its activation and treatment, which in turn determines the catalytic activity.

The high microporosity of ACs from waste biomass facilitates the formation of finely dispersed and micropore-located Fe and ZnO nanoparticles, which in turn promote the formation of $ZnFe_2O_4$ and complex spinel ferrites ($NiO.5MeO.5Fe_2O_4$ (M = Zn or Cu), providing high catalytic activity in methanol decomposition (Refs. 11, 13, 22).

Activated carbon derived from waste engine oil and furfural has a high specific surface area and pore volume, and when applied to Zn and Fe nanoparticles, results in the formation of finely dispersed and highly active metal oxide particles (Publication 14).

- *Materiali with the biomedical application:*

Research on catalytic systems for environmental protection, indirectly related to healthy living, has been upgraded to research on materials with direct biomedical applications. The aim is to evaluate the potential of mesoporous silica (MCM-41 and HMS type) to load different dosage forms as well as the impact of encapsulating drug formulations with polymers (publications 16, 17, 21, 23, 26, 31, 32, 33).

Assoc. Prof. Spasova is not the lead author in these publications, but the participation of colleagues from MU-Sofia, the publication of the results in reputable international journals with high IF and the exceptional importance of the considered problems give me a reason to accept the research as thorough, significant and promising. The main result is the establishment of the fact that mesoporous silica types MCM-41 and HMS are promising as a carrier for drug delivery for human use due to the specificity of their porous structure:

Loading *glimepiride, pramipexole* and *lomefloxacin* onto MCM-41 and HMS resulted in improved solubility due to a significant reduction in the degree of drug crystallinity, its uniform deposition on the surface and delayed release up to 300 minutes (publications 16, 17, 21,31). Loading of the anticancer drug bicalutamide on MCM-41 and HMS particles resulted in improved in vitro antitumor activity and in vitro cytotoxicity due to the delayed drug release induced by the porous structure of the carrier (Publication 26). Encapsulation of doxorubicin stabilizes the drug against degradation due to its internal location in the

nanoparticles. Chitosan-alginate polymers improve the thermal stability of the drug, have enhanced cytotoxicity in resistant lymphoma cells, and possibly reduce cardiotoxic effects (publication 23). Encapsulated oregano oil in chitosan-alginate nanoparticles showed improved thermal stability and significantly lower in vitro cytotoxicity on human keratin cells and in vivo skin irritation assay, compared to pure oregano oil due to the interaction of the essential oil and polymers (publication 32).

Implementation and expert activities

- *Participating in scientific and application projects:*

Assoc. Spasova is co-author of 2 patents - BG patent 63364 B1 and BG patent 107724A and one copyright certificate - № 47979. The object of all three inventions are catalysts based on oxides of copper and manganese, and the aim is low-temperature decontamination of CO, nitrogen oxides and volatile organic compounds in waste gases.

The project activity of Assoc. Spasova includes 17 national and international projects:

1. Scientific projects with the National Science Foundation - participant in 8 projects and leader of one of them;
2. Infrastructure projects and programs - participant in 3 projects with substantial funding for our scale;
3. Four projects under various National Programmes funded by the Ministry of Education and Science.
4. Two international projects with Cyprus and USA;

- *Expertise:*

The expert activity of Assoc. Spasova finds expression in:

1. Participation as a reviewer of projects at the National Research Foundation;
2. Reviews and opinions on the LDASRB - 14 (3 reviews and 11 opinions);
3. Reviews of articles in international journals - over 40.

The skills of Assoc. Prof. Spasova's work in a team was confirmed by her colleagues and by her election as Deputy Director of the IGIC Scientific Council. Recognition of her expert capacity is her election as a member of the Internal Scientific Expert Committee in Chemical Sciences of the National Research Foundation (2019 - 2020).

- *Teaching and pedagogical activity:*

Despite the limited opportunity for BAS researchers to participate in teaching and learning activities, Assoc. Spasova is the co-supervisor of one successfully defended PhD student and one graduate student.

4. Evaluation of the personal contribution of the candidate

The publication activity of Assoc. Spasova started in 1987 and only 3 years later she was the first author of a paper at the 7th International Symposium on Heterogeneous Catalysis, and after defending her PhD thesis she became the lead author in almost all subsequent publications. In 15 pre-habilitation publications she was the first author, in 6 she was the second author (including patents and copyright certificate), and in the remaining 3, she was the second author. In 2 of the publications submitted to the competition (IF7.9), Assoc. Spasova is the first author, and in 10 (IF47.47) - the second, which is a recognition of her active participation in research.

All this gives me a reason to assume that the personal contribution of Assoc. Prof. Spasova's contribution to the materials submitted for the competition is indisputable.

5. Personal impressions

I know Assoc. Prof. Spasova from my many years of scientific contacts with the IGIC, from her numerous scientific events at various forums in Bulgaria and abroad. I am also

familiar with her scientific research before her election as Associate Professor as a member of the Scientific jury.

I have no joint research and publications with the candidate and my opinion on her participation in the competition is built entirely on the materials and documents presented.

CONCLUSION

The documents and materials submitted by Assoc. Prof. Dr Ivanka Spasova meet all the requirements of the Law for the Development of Academic Staff in the Republic of Bulgaria (LDASRB), the Regulations for the Implementation of the LDASRB and the relevant Regulations of BAS, as well as the specific requirements of the Institute of Inorganic Chemistry at BAS. The candidate has submitted a sufficient number of scientific works published after the materials used in the defence of the PhD and the academic position of Associate Professor. The submitted works have original scientific contributions, the main part of them being published in journals with impact factor, published by international academic publishers. All this gives me a reason to give my positive assessment and to recommend with conviction the Scientific Jury prepare a report-proposal to the Scientific Council of IGIC for the election of Assoc. Prof. Dr Ivanka Petrova Spasova to the academic position of "Professor" at IGIC in the professional field 4.2 "Chemical Sciences", scientific speciality "Chemical Kinetics and Catalysis".

21.07.2022 г. Prepared the review: **.....**

(Prof. DSc Krasimir Ivanov)