R E V I E W

in competition for the academic position of "Professor"
in professional field 4.2. "Chemical Sciences", (Chemical Kinetics and Catalysis),
announced by the Institute of General and Inorganic Chemistry-BAS,
(State Gazette, No34 / 03.05. 2022)
for the needs of laboratory " Materials and Processes for Environmental Protection"
IGIC, BAS
with the sole candidate Associate Professor Ivanka Petrova Spasova, PhD

by Prof. Dr. Reni Stoilova Iordanova, IGIC, BAS
Member of the Scientific Jury, appointed by Order No. RD-09-102/27.06.2022
of the Director of IGIC-BAS

Ivanka Spasova, Associate Professor at the Institute of General and Inorganic Chemistry (IGIC) at the Bulgarian Academy of Sciences (BAS) is the sole candidate in the competition for occupying the academic position of "Professor". The examination of the submitted documents shows that all materials are regular and meet the minimum national requirements of the Law for the Development of the Academic Staff in the Republic of Bulgaria as well as the additional requirements specified in the IGIC Rules for occupying academic position "Professor".

According to the given information, the candidate exceeds the minimum required points for all groups of indicators: these of the BAS (A-E) as well as the additional requirements (J) accepted by IGIC. The group of indicators B, indicator 4 - Habilitation work comprises scientific papers which are referenced and indexed in scientific data bases. In that group Assoc. Prof. Spasova has 175 points at the required minimum of 100 points. The other group of indicators D, indicator 7 includes scientific papers referenced and indexed in scientific data bases which are outside of the habilitation work. For this group Spasova has 519 points at the required minimum of 220 points.

The publications which Assoc. Prof. Spasova has submitted on the habilitation are 8, 4 of which are in journals with the highest quartile - Q1, 3 publications in journals with Q2, and 1 in journal with Q3. One of the publications tops the journal's ranking list: Applied Catalysis B: Environmental. Additionally, 25 other original research papers which are outside the habilitation work has been presented. Among them 10 are in journals with Q1. Therefore, Associate Professor Spasova participates in the competition with 33 scientific publications, on the topic of the current competition and do not repeat those for acquiring her PhD degree and the academic position "Associate Professor". The total number of citations accumulated by Spasova is 256 which is equal to 512 points. According to the accepted Rules these points exceed the required minimum of 120 points (group of indicators E, indicator 11), which is indicative of the relevance of the topics developed by the candidate and the quality of scientific publications.

Furthermore, Assoc. Prof. Spasova meets the additional requirements of the IGIC-BAS for the scientific activity of the applicants for the academic position "Professor", which are mainly related to the value of the Hirsch Index (H), (group of indicators J). In that group of indicators Spasova exceeds the required minimum of the Hirsch index, H = 10. According to the citations of all post-habilitation articles, she presents H=12.

The total number of her scientific publications is 71, in journals with impact factor - 56, in journals with SJR - 3, in scientific journals without impact factor – 7, in proceeding of conference – 5.

Assoc. Prof. Spasova has an educational activity. She was the supervisor of one graduate student and co-supervisor of 1 PhD student who successfully defended in 2018.

The applicant shows active participation in various scientific forums - congresses and conferences. After achieving the academic position “Assoc. Prof.” she has participated in 53 scientific events.

Spasova's participation in various scientific projects is remarkable - a total of 17 which contributed to her growth as a scientist in the field of inorganic materials science and catalysis. After habilitation, Assoc. Prof. Dr. Spasova participated in the development of 10 research projects at the Bulgarian National Science Fund and the Ministry of Education and Science and 1 international project. She is the leader of 1 research project at the Bulgarian National Science Fund and the amount of funds attracted to IGIC is 60 000 leva.

Assoc. Prof. Spasova's expert work includes: reviews and opinions on LDASRB – 14 (3 reviews and 11 opinions); prepared reviews of articles in international journals – over 40.

Her competence is recognized by her election as a member of the Internal Scientific Expert Committee in Chemical Sciences of the Bulgarian National Science Fund (2019-2020).

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.

The candidate's research activity is related to the development of new catalysts for the disposal of harmful emissions from industrial and transport sources. A current topic is fully in line with the main priorities of the EU - Environmental Protection, Green Energy and Healthy Life. In the conducted research, the candidate applies the basic approach to the study of new and effective catalysts - establishing the relationship: composition - structure - physicochemical parameters - catalytic activity. The choice of catalyst carrier is carefully approached. Mesoporous composite supports are applied because they can easily adjust the porous texture, thus favoring the preparation of the active phase in a dispersed and stable state.

The habilitation report is based on articles, and in more than half of the publications the candidate is the first or corresponding author, which unequivocally shows the leading role of Associate Professor Spasova in the conducted researches.

Researches on the preparation of catalysts containing transition metals and/or rare earth elements coated on individual and composite supports and their catalytic behavior in the processes of oxidation of CO and CH_4, removal of nitrogen oxides - reduction of NO with CO

and CH_4 and decomposition of NOx are described. These processes are the basis for solving a number of environmental problems.

The main scientific contributions described in the habilitation report are related to:

The development of an integrated system for the disposal of NOx by the decomposition products of methanol, which is of great importance for using the decomposed methanol (CO and H_2) as an alternative fuel in cars, while simultaneously the toxic emissions of NOx are removed. **Catalysts based on transition metals and/or rare earth elements coated to individual supports (SiO_2 and Al_2O_3)** for disposal of nitrogen oxides - decomposition of NOx, reduction of NO and oxidation of CO and CH_4 were investigated (publications 2, 3, 4, 5).

Copper catalysts supported on mesoporous silica (KIT-6 and SBA-15) were obtained by impregnation and a combined method of impregnation and gas-phase deposition, and their catalytic behavior in the reduction of NO with CO and the selective catalytic reduction (SCR) of NO with a mixture of CO and CH_4 was studied.

In the reduction of NO with CO, a different catalytic activity of the two series of catalysts obtained on KIT-6 was found and it was explained by the different routes of the catalytic reactions. One route is related to vacancy formation on the surface. The second route is due to formation of bridging nitrates (publication 3). Catalysts deposited by a combined procedure on SBA-15 exhibited higher catalytic activity compared to catalysts prepared by impregnation due to the better dispersion of the copper particles (publication 4).

In the reduction of NO with decomposed methanol products, the specific activity of the catalysts supported on KIT-6 and obtained by the combined method was high, while the specific activity of the catalysts obtained by impregnation was lower. In these reactions, an alternative pathway of oxidation of CH_4 and NO by surface oxygen species, which are formed during NO decomposition, has been proposed. These surface forms contribute to the oxidation of CH_4 (publication 3). Catalysts supported on SBA-15 by a combined method are more efficient in this reaction (publication 4). Main factors influencing the catalytic behavior for both reactions were demonstrated: particle size, accessibility of the active phase, as well as changes in the oxidation state of copper.

Quite appropriately, some of the research has been focused on the preparation of catalysts with the participation of oxides of the transition and rare earth elements. Due to their well-pronounced redox properties, they are good candidates for the elimination of NOx, CO and CH_4 (publications 2 and 5). Mn/Al_2O_3, Ce/Al_2O_3 and bimetallic $MnCe/Al_2O_3$ catalysts were obtained and their catalytic activity in NO decomposition, CO oxidation and NO-CO interaction was studied. The bimetallic catalyst $MnCe/Al_2O_3$ shows the highest catalytic efficiency in all investigated reactions, which is determined by the high dispersion of its particles.

Spinel catalysts $CuCo_2O_4/Al_2O_3$ were modified with oxides of rare earth elements (Ln= La, Ce, Nd and Gd) (publication 5). Migration of Cu^{2+} between the surface and volume of the catalyst, stabilization of Cu^{+}, and increase of oxygen vacancies on the surface were found. All catalysts are effective in the oxidation of CO and CH_4. The catalytic activity depends on the atomic number of Ln, being highest for Ce-doped catalysts.

Another series of studied samples are catalysts based on transition metals deposited on composite (hybrid) supports (1, 9, 10, 24).

Research has been aimed at obtaining and studying catalysts on mesoporous composite materials (SiO_2–C, Al_2O_3–C) (publications 1, 9, 10, 24). The mesoporous hydrophilic SiO_2 and Al_2O_3 contain isolated or bonded OH-groups, which are the main centers of adsorption and surface reaction. On the other hand, porous hydrophobic carbon materials are characterized by high corrosion resistance, high specific surface area, large pore volume. This has motivated the candidate to investigate the possibilities of modification and change of the chemical and physical properties of the materials in order to improve the catalytic efficiency of the catalyst deposited on a combination of hydrophilic and hydrophobic components.

Catalysts coated on disordered silicon-carbon composite supports

A disordered composite based on diatomite and activated carbon was synthesized, which was modified with aluminum oxide in order to change the ratio of Lewis and Brønsted acid centers on the surface. The two composite materials were used as a copper oxide catalyst support for the reduction of NO with CO. The presence of Lewis acid centers has been shown to stabilize the active Cu^+ and Cu^{2+} centers on the surface, and catalysts supported on modified hybrids are more active in the reduction of NO with CO. The highest activity in the investigated reaction was found for the catalysts obtained in an ammonia medium, due to a uniform distribution of the copper-oxide phases on the surface and in the volume. In the case of catalysts supported by an organic medium, the activity depends on the ratio of the copper ions concentration on the surface and in the volume of the catalyst. (publication 1). Copper oxide catalysts supported on disordered SiO_2–C composites were found to be highly effective for low-temperature disposal of nitrogen oxides. At 100°C, they show twice the catalytic activity of catalysts supported on activated carbon (publications 9, 10).

Catalysts supported on ordered silicon-carbon composite supports.

Structured mesoporous SiO_2–C composites with SiO_2:C ratios in the entire concentration range were obtained and the stabilizing role of SiO_2 on the mesoporous composites structure was established. It has been shown that, regardless of the Si/C ratio, for all composites the carbon content on the surface is higher than that in the bulk, with the ordered composites being higher than that of the disordered ones. The addition of carbon in both types of SiO_2–C composites increased the activity of the supported catalysts in the reduction of NO with CO over the entire temperature range, due to the partial reduction of copper ions (pblications 9, 10).

It was found that in the decomposition of N_2O, the activity of catalysts depends on the presence of carbon on the surface of the catalyst, which plays the role of both carrier and reactant, and reduced copper ions play the role of catalytically active centers for the transfer of oxygen from N_2O to carbon. Due to the higher carbon content on the surface, catalysts supported on structured composites show better specific activity in the reaction. (publication 10).

Catalysts coated on alumina-carbon composite supports

The "chromatographic effect" of copper oxide catalysts supported on ordered mesoporous Al_2O_3–C composites with different Al:C ratios and its influence on the catalytic activity in NO reduction with CO was investigated (publication 24). It has been proven that the "Chromatographic effect" plays an essential role in the formation of active centers on the surface of copper-oxide catalysts. The reduction of NO by CO is determined by an active center formed by Cu^{2+} and Cu^{+}. Catalytic activity was higher for catalysts with high alumina content, where nearly equal Cu^{2+} and Cu^{+} contents were observed on the surface. The results show that the activity of the catalysts can be tuned by changing the composition of the alumina-carbon composite support.

Besides the habilitation work, other scientific contributions are described:

i) research on catalysts supported on carbon-containing materials for the protection of the environment and for obtaining clean energy;
These researches were carried out together with colleagues from IOCHCF-BAS and IC-BAS and were focused on an integrated biomass-based system for obtaining clean energy, innovative metal-carbon nanocomposites for hydrogen storage and a renewable integrated system for the elimination of organic pollutants from waters and air (publications 6, 7,8,11, 13, 14, 20, 22, 25).
ii) capture of CO_2 on composite, hybrid, etc. materials;
iii) adsorption and textural characteristics of materials;
iv) research on materials with biomedical applications;
These studies were carried out together with colleagues from the MU-Sofia, and it was found that mesoporous silicas of type MCM-41 and HMS are a promising carrier for the delivery of drugs for human use due to the specificity of their porous structure (publications 16, 17,21, 23).

CONCLUSION

The documents and materials submitted by Associate Professor Ivanka Petrova Spasova, PhD meet all the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the additional requirements of IGIC-BAS for the academic position of "Professor". The topic and the level of the researches as well as the novelty of the results, cover all the criteria for the required academic position. On this basis, I give my positive evaluation of the overall scientific research activity and I strongly recommend to the Scientific Jury, Associate Professor Ivanka Petrova Spasova, PhD to be elected for "Professor" in 4.2 "Chemical Sciences" at the Institute of General and Inorganic Chemistry – BAS.

12.08.2022 год.…….....

Sofia / Prof. Dr. Reni Iordanova/