REVIEW

by Prof. Dr. Ivanka Petrova Spassova, IGIC-BAS

of the materials submitted for participation in the competition for the academic position "Associate Professor" in professional field 4.2 Chemical sciences (Chemical kinetics and catalysis), thematic field "Synthesis and characterization of catalytic materials for purification of volatile organic compounds", at the Institute of Catalysis - BAS, Sofia, announced in the SG no. 55/27.06.2023

In the competition for the academic position of "Associate Professor", announced in the SG no. 55 of 27.06.2023, for the needs of the laboratory "New Heterogeneous Catalysts for Clean Energy Production and Environmental Protection" at the Institute of Catalysis - BAS, the only candidate is Chief Assist. Prof. Dr. Petya Tsvetanova Petrova. The submitted materials for participation in the competition are in accordance with the Regulations for the terms and conditions for holding academic positions at IC- BAS and include all necessary documents. Dr. Petya Petrova is registered at the National Center for Information and Documentation (NACID) (https://ras.nacid.bg/dissertation-preview/26911), where she is recognized with the educational and scientific degree "doctor" in professional field 4.2. Chemical Sciences.

1. Brief biographical data about the candidate

Dr. Petya Tsvetanova Petrova graduated in 2003 from UCTM- Sofia, with a major in "Technology of Inorganic Substances" and a thesis on "Complex Liquid Fertilizers". She joined IC- BAN in 2003 as a chemist, and in 2004 she was enrolled as a full-time doctoral student in the laboratory "New Catalytic Materials and Nanosized Catalysts" at the same institute. In 2009, she defended her doctoral thesis on "Gold-molybdenum catalysts supported on cerium oxide and cerium oxide supported on aluminum oxide for the complete oxidation of benzene". Since 2010, she has been a Chief Assistant. Professor at IC-BAN, currently in the "New Heterogeneous Catalysts for Clean Energy Production and Environmental Protection" laboratory. Dr. Petrova also works as a teacher of Chemistry and Environmental Protection, successively in 68 SU, FELS and 91 NEG.

2. Description of the presented materials

Dr. Petya Tsvetanova Petrova is a co-author of a total of 47 scientific papers, of which she applied for participation in the competition 25 scientific articles published after the defense of her doctoral dissertation. The distribution of the scientific papers for participation in the competition according to the respective quartiles is as follows: **Q1- 8** publications (in the renowned journals *Applied Catalysis B: Environmental, Catalysis Today, International Journal of Hydrogen Energy, Chemical Engineering Journal, Fuel, Applied Catalysis A: General*), **Q2- 7** publications (in the journals Applied Sciences, Catalysts, Catalysis Communications), **Q3- 4** publications, **Q4- 1** publication, the rest in journals not falling into

quartiles. In 4 of the presented publications, Dr. Petrova is the first author, and in 12 she is the second author.

The publications participating in the competition are divided into two groups, covering indicators B and G, according to the Regulations on the terms and conditions for acquiring scientific degrees and holding academic positions. In the first group, indicator B- "Habilitation thesis - scientific publications in editions that are referenced and indexed in world- renowned databases with scientific information (WoS or Scopus)", **10** publications are presented, distributed by quartiles as follows: **Q1- 1**, **Q2- 4**, **Q3- 3**, without quartile- 2, with the total number of points being **150**, with a required minimum of 100 points.

In the second group, 15 publications are presented (Q1- 7 and Q2- 3, Q3- 1, Q4- 1, 1 without quartile), covering indicator G, with a total of **262** points out of the required **220** points. In the group of indicators D, the requirements are exceeded many times over – with the required **60** points, the candidate has **480** points only on the publications participating in the competition. Dr. Petya Petrova's **Hirsch index** according to data from Scopus (without self-citations) is **12**, which is a reflection of the candidate's current and significant research.

All presented materials are on the theme of the competition. The scientometric indicators exceed the minimum national and BAS requirements for the individual indicators in the ZRASB and the Regulations for its application for occupying the academic position "Associate Professor" in the field of "Natural Sciences, Mathematics and Informatics", Professional field 4.2 "Chemical Sciences". Dr. Petya Petrova achieved **942** points out of the required **430** points.

3. General characteristics of the research activity

The candidate's scientific research activity can be related to catalysis in environmental protection processes and fully corresponds to the theme of the competition for the needs of the direction "Synthesis and characterization of catalytic materials for purification of volatile organic compounds". Research is focused on the design of supports and catalysts for purification of volatile organic compounds and other pollutants and includes preparation and characterization of nanoscale catalysts for complete oxidation of hydrocarbons, selective oxidation of CO in excess of hydrogen, and establishment of composition-structure- catalytic properties relationships of heterogeneous catalysts for environmental protection.

4. Main scientific contributions

Habilitation thesis (publications from group "B").

The candidate's contributions, reflected in the Habilitation report, relate to the design and catalytic behavior of supported gold catalysts and nanocomposites, focusing mainly on the influence of the support on the activity of the catalysts in several oxidation reactions - complete oxidation of benzene, formaldehyde, carbon monoxide and methanol. The prerequisites for the different catalytic behavior were examined, clarifying the relationships between reducibility and catalytic activity, as well as between composition-surface properties-activity.

The main scientific contributions of the research work in the Habilitation work can be summarized thematically in the following areas:

1. *Nanosized gold catalysts for complete oxidation of VOCs based on modified ceria (8 papers).*

- A gold catalyst prepared by deposition-precipitation on a mechanochemically prepared support of cobalt -modified CeO_2 was found to have very high activity and stability in the complete oxidation of benzene. It has been found that, in addition to the nano-dispersed gold, the nature of the oxide support used is also of great importance for the high catalytic activity. The high catalytic activity is related to the presence of two phases in the synthesized carrier - surface modified CeO_2 and highly reactive Co_3O_4. A cobalt phase with enhanced redox properties that affects both the gold and the ceria interface is believed to be responsible for the observed high activity in the complete oxidation of benzene at relatively low temperatures.

- The reducibility of CeO_2 modified with cobalt ions strongly depends on the method of preparation, which in turn affects the activity and selectivity of the catalysts for preferential oxidation of CO in the presence of hydrogen.

- Mechanochemical mixing has been found to be a suitable method for the preparation of cobalt -modified CeO_2 due to the production of materials with an increased concentration of surface structural defects. When the modification with cobalt ions is made mechanochemically, CeO_2 forms cobalt-oxide phase and less surface carbonates, which facilitates the low-temperature reduction of the cobalt cation. Increased oxygen mobility was found, with active oxygen originating from both CeO_2 and Co_3O_4.
- For highly efficient gold catalysts for the complete oxidation of benzene, methanol and CO, the optimum amount of the modifying additive Co3O4 was found to be 10 wt.%, as it favors the higher dispersion of the supported gold. The recorded 100% degree of conversion of CO (at 25^{o}C) and methanol (at ~40^{o}C) correlates with the reduction behavior of the catalyst. It has been proven that with this composition the largest amount of surface Co^{3+}, Ce^{3+} ions and adsorbed oxygen forms are formed, which determines the high activity during oxidation reactions via the Mars- van Krevelen mechanism.
- In order to optimize the mixed oxides Co_3O_4-CeO_2, their modification with ions of active metals and the addition of small amounts of nanosized gold in reactions for the complete oxidation of VOCs was studied. It was found that doping the mixed oxide (70 wt.% Co_3O_4- 30 wt.% CeO_2) with K_2CO_3 has a negative role on the degree of complete oxidation of benzene. The decrease in activity is associated with the more difficult reducibility of the catalysts, the reduction of the pore volume and the difficulty of access of the relatively large benzene molecules to the active centers of the catalyst.
- Gold catalyst deposited on a mechanochemically modified composite of 70 wt. % Co_3O_4- 30 wt% CeO_2 with γ-Al_2O_3 shows 95% conversion of HCHO to CO_2 and H_2O at room temperature and 100% conversion at 40°C. The high catalytic activity was

found to be due to the high amounts of Ce^{3+} and Co^{3+} on the surface and the presence of oxygen centers with increased mobility. This composition has the potential to develop effective catalytic materials for indoor air purification.

2. *Oxide composites based on Co_3O_4 modified with different amounts of CeO_2 for complete oxidation of benzene (2 papers).*

- When investigating the influence of time and method of mixing to obtain oxide composites of Co_3O_4 and CeO_2, it was found that shorter mechanochemical mixing leads to better catalytic activity in complete oxidation of benzene. The optimal composition was established, in which 100% conversion of benzene at 200°C and stable activity during 24 h without formation of incomplete oxidation products is achieved. A relationship was established between the activity and the surface characteristics of the catalyst, determined by the method of preparation and the composition of the mixed oxides. The high catalytic activity is due to a synergistic interaction between Co_3O_4 and CeO_2 according to the following mechanism: under the influence of benzene, Co^{3+} ions are partially reduced to Co^{2+} (or Co), followed by re-oxidation with the participation of oxygen from the CeO_2 lattice, which is accompanied by the creation of oxygen vacancies at the interface of the mixed oxides. It was found that the largest amount of surface Co^{3+}, Ce^{3+} ions and oxygen vacancies is found in the sample with a composition of 70 wt.% Co_3O_4-30 wt.% CeO_2, which also shows the highest catalytic activity at a relatively low temperature in the reaction of complete benzene oxidation.

Scientific contributions in the publications of group "G"

The author's reference for the works of Chief Assistant Professor Dr. Petya Petrova outside the habilitation part, is built on 15 scientific publications. They are aimed at the design of new catalysts with high efficiency for the elimination of volatile organic compounds, preferential oxidation of CO in the presence of hydrogen and reduction of nitrogen oxides. The contributions are summarized by the candidate in the following areas:

1. *Mono and bimetallic catalysts for oxidation of propene and benzene and cyclization of alcohols. (8 articles).*

- Mono-(Au, Pd) and bimetallic Au–Pd catalysts supported on CeO_2 supports synthesized by different methods and doped with yttrium and iron were obtained and studied.
- The optimal content of the doping agent Y_2O_3 in the CeO_2 carrier was determined. In the case of a gold catalyst on this support, the positive role of preliminary heat treatment due to cleaning of the surface active centers from carbonates has been established.
- In a comparative study of monometallic (Au, Pd) and bimetallic Pd-Au catalysts supported on Y-doped cerium oxide supports, synthesized by impregnation or co-precipitation, the highest activity and stability in complete oxidation of propene and benzene are shown by bimetallic Pd-Au catalysts on the impregnated support. It was

established that the catalytic activity in the oxidation of propene does not depend significantly on the presence of a doping agent, and in the oxidation of benzene the method of preparation of the carrier has a strong influence on the activity of the catalyst.

- A Pd catalyst supported on yttria- doped CeO_2-Al_2O_3 support was found to reach 100% benzene conversion at 180°C. The role of Y_2O_3 doping in improving the oxygen mobility from the ceria lattice has been confirmed. The high catalytic activity is explained by the influence of Pd on the ceria phase and on Al_2O_3. Adsorbed superoxo forms O^{2-} near Ce^{4+} ions and a higher surface concentration of Pd and Ce^{3+} resulting from the redox transfer $Pd^0 \leftrightarrow Pd^{2+}$ were registered.
- 100% catalytic activity for complete benzene was found at 200°C as a result of a positive role of Pd on bimetallic Au–Pd on iron-modified CeO_2, due to an increase in surface oxygen mobility.
- • A promoting effect of Pd was also found in the cyclization of 1,4-butanediol (1,4-BD) in 2,3-dihydrofuran (2,3-DHF) in the presence of Co–SiO_2 and Co/Pd–SiO_2 catalysts synthesized by mechanochemical method. The addition of Pd to Co-catalysts was found to increase the reducibility of Co-oxides and the degree of reduction increased.

2. *Catalysts for the selective oxidation of CO in an excess of hydrogen and for the reduction of NO with CO. (7 articles).*

- The role of Pr as a modifier of CeO_2 in gold catalysts for the selective oxidation of CO in an excess of H_2 was investigated. The amount of rare earth element and the method of preparation of the supports were found to be a key factor in the dispersion of the deposited gold. The lower activity of the catalysts on Pr-doped supports compared to pure CeO_2 is related, despite the facilitated reduction of Pr^{4+}, to the difficult reoxidation of Pr^{3+} ions due to its surface segregation.
- The high conversion of CO to excess H_2 in gold catalysts obtained on Y-modified CeO_2 supports synthesized by impregnation is explained by the small size of the gold particles and reducibility of the surface cerium oxide layers. The higher activity of these catalysts is related to the contribution of the formed surface Au/Y_2O_3 nanostructures. For the catalysts with the highest yttrium content, the lower activity is explained by the rearrangement of the surface oxygen vacancies around the segregated Y^{3+}, hindering the oxygen supply. It was found that when CO_2 and water are added to the gas stream, the carriers obtained by impregnation are slightly deactivated, which is associated with the lowering of the basicity of the CeO_2 surface under the influence of the nanosized Y_2O_3 covering the ceria grains.
- The influence of two methods of synthesis of Ce-Al carriers (through impregnation and mechanochemical) on the structural and catalytic properties of gold catalysts in the reaction of selective oxidation of CO oxide in an excess of H_2 was studied and the optimal composition of the carriers was determined. Gold catalysts prepared on supports obtained by mechanical mixing showed better activity compared to catalysts

supported on supports obtained by impregnation. An explanation was sought in the different texture of the obtained catalysts.

- The influence of the carrier synthesis method on the activity and selectivity of gold catalysts supported on iron-modified CeO_2 carriers in the reduction of NO with CO in the presence of H_2 and water was studied. It was found that depending on the synthesis method, changes in the structure of the carriers were observed. When using a co-precipitation-synthesized carrier, only a mixed Fe-Ce phase is formed, while with a mechanochemically synthesized carrier, an additional hematite phase is observed. This phase can participate in an oxidation-reduction process at relatively low temperatures and may be promising for improving the catalytic properties of mechanochemically prepared gold catalysts.
- High catalytic activity and stability was observed in the reduction of NO with CO in the presence of a gold catalyst on Fe_2O_3 modified by CeO_2 impregnation. It was found that the size of the gold particles is not decisive for the high catalytic activity. The reduction of NO in the presence of gold catalysts supported on modified supports is higher compared to that of unmodified CeO_2, but the selectivity with respect to N_2 up to 250°C is lower. The activity is related to the surface oxygen vacancies that play a role in the dissociation of NO, and the selectivity to N_2 is determined by the nature of the modifying additive.

The candidate's research results have both scientific and applied importance and are a contribution to the field of synthesis catalysts of a certain design. Through the study of the inter-relationship composition-structure-properties, dependencies between the catalytic activity and the state of applied active components, influence of the type of carrier and the method of preparation of the catalyst, interaction between the active phases, between the active phase and the carrier, distribution of the active phase on the surface of the carrier, factors determining the dispersion of the active components, etc. are established. Contributions can be classified as novelty in science and enrichment of existing knowledge, with potential for practical application.

5. Critical remarks and recommendations

I have no fundamental critical remarks.

CONCLUSION

The documents and materials presented by Chief Assistant Professor Dr. Petya Tsvetanova Petrova meet all the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria, the Regulations for its Implementation, the Regulations for the Implementation of BAS and the Regulations of the IC-BAS. The candidate in the competition has submitted a sufficient number of scientific works published

after acquiring the "doctor" degree. Dr. Petrova is a highly qualified scientist in the field of selection and synthesis of catalytic materials, their characterization with appropriate methods and research in ecologically oriented reactions, with valuable scientific research on the design of supported gold catalysts. After analyzing the materials presented in the competition, their importance and the scientific and applied contributions contained in them, I find it reasonable to give **my positive assessment** and to confidently recommend to the Scientific Jury **to propose** to the Scientific Council of IC- BAS **to elect Chief Assistant Professor Dr. Petya Tsvetanova Petrova, to the academic position of „Associate Professor“ at IC- BAS in professional direction 4.2 Chemical Sciences (Chemical Kinetics and Catalysis).**

13. 10. 2023 Reviewer: ....

(Prof. Dr. Ivanka Spasova)