**REVIEWER'S OPINION**

Submitted by Prof. PhD Vasko Idakiev, Institute of Catalysis - BAS

on the materials, represented for participation in the competition for occupying the academic position of „Professor" in the scientific research field 4.2. „Chemical Sciences", scientific specialty 01.05.16 „Chemical Kinetics and Catalysis" for the needs of the Laboratory „New heterogeneous catalysts for clean energy production and protection of the environment", published in Official Gazette, issue 77 dated 01.10.2019

## 1. General description of the represented materials

The only candidate in the competition for occupying the academic position of „Professor", announced in Official Gazette, issue 77 dated 01.10.2019 and on the Internet web site of the Institute of Catalysis (IC) is the Assoc. Prof. PhD Margarita Valentinova Gabrovska. The set of materials, submitted by Assoc. Prof. Gabrovska, answers the requirements for occupying the academic position of „Professor", specified in the Law for the Development of the Academic Staff in the Republic of Bulgaria (LDASRB) and in the Regulations for LDASRB Application in Bulgaria, the Regulations for its application in BAS, as well as in the Regulations for the conditions and order of acquiring scientific degrees and occupying of academic positions in IC-BAS. Assoc. Prof. Gabrovska has submitted a total of 70 scientific research papers for the entire length of service, while for participation in the competition she has presented a total of 31 research articles, 2 book chapters and 1 approved patent, all of them published after year 2010 (when she was appointed in the position of Assoc. Prof.), as well as a list of 15 scientific research implementations in practice (out of which she was the leader of 9 national projects). The dissemination of the scientific research results of Assoc. Prof. Gabrovska has been accomplished by means of multiple presentations in scientific events. The results from the studies have been presented in the form of 12 oral presentations and 38 poster presentations in international scientific events, 1 oral and 3 poster presentations in national scientific events with international participation, and 8 oral presentations and 15 poster presentations in national events.

## 2. Short biography data of the candidate

Assoc. Prof. Gabrovska graduated The Higher Chemical-Technological Institute "Prof. DSc Assen Zlatarov", in the town of Bourgas, specialty: "Technology of Organic Synthesis and Fuels" in 1981. She acquired PhD degree in the year 2001 on the topic: "Nickel-containing layered systems: preparation, structural modification and evaluation of their catalytic activity". She was appointed in the position of Assoc. Prof. in 2010 and thereafter she became leader of the research

group „Synthesis and activity of metal and metal oxide catalysts“ at the Laboratory „New Heterogeneous Catalysts for Clean Energy Production and Protection of the Environment“.

### 3. General characteristics of the activities of the candidate

• Scientific research articles:

The total number of publications of Assoc. Prof. Gabrovska is 70 articles, out of which 28 articles were published in journals having either impact factor or impact rank. She participates in the announced competition with 31 publications, out of which 20 articles have impact factor. The publications are divided in groups as follows:

- Scientific research publications in journals, which are referenced and indexed in world renowned data bases for scientific information (Web of Science and/or Scopus) – 20 articles;

- Scientific research publications in journals, not included in these bases (Web of Science and/or Scopus) – 1 article;

- Scientific research publications in international conferences and symposia proceedings – 10 articles;

Her research works, submitted for the competition include also 2 book chapters and 1 approved patent. Four of the publications are in journals having the highest quartile Q1, (Applied Catalysis A: General, Chemical Engineering Research and Design, Applied Surface Science and Catalysis Today). One publication belongs to the category Q2, six other publications are Q3 quartile and the remaining nine belong to Q4 quartile. The contributions of Assoc. Prof. Gabrovska in these publications are visible in view of the fact that she was the first author in 19 publications, in 2 other articles she is the second author, and in 3 articles she occupied the third place.

The candidate has submitted records, specifying distinctly her contributions, distinguished from those of her colleagues in their common works. No claims for incorrectness have been put forward so far by her co-authors in the publications with respect to her participation in the competition. There is no other information available for incorrectness or about elements of plagiarism in the materials, represented for participation in the competition.

• Response in the scientific research literature:

The total number of noticed citations of the publications in co-authorship with Assoc.

Prof. Gabrovska for the specific period of the competition amounts to 224 citations, whereupon 150 citations out of them appear to be citations of the articles, submitted for participation in the competition and they are divided in groups as follows: citations in WoS or Scopus database – a total of 130 citations; citations in PhD theses or theses abstracts abroad - 6

citations; citations in international journals - 11 citations; citations in proceedings of scientific events - 3 citations.

*Evaluation of teaching-pedagogical and expert activities*

Assoc. Prof. Gabrovska has taken active participation in the educational and expert activities. Within the framework of two Equilateral Exchange scientific research projects, involving the Institute of Chemistry, Technology and Metallurgy, Center for Catalysis and Engineering Chemistry at the Belgrade University, Serbia, Assoc. Prof. Gabrovska took part in the joint research work with PhD students, preparing together research publications in co-authorship, discussing together during the training period, processing the data and writing the PhD theses. The candidate took part in the evaluation and in putting forward reviewer's opinions in two competitions for professor's position, one for the position of associated professor and one procedure for the educational and scientific degree „Philosophy Doctor".

*Estimation of basic research and applied research contributions*

The habilitation thesis of Assoc. Prof. Gabrovska on the topic „Elaboration and investigation of catalysts for purification of gaseous mixtures of CO and $CO_2$", comprises 8 research articles (*publications № 1, 3, 4, 5, 11, 16, 19, 20*), thematically uniting the elaboration of new efficient catalysts composites for reactions, associated with purification of gaseous mixtures of CO and $CO_2$. The main scientific contributions have been summarized into 3 directions, according to applied model catalytic reactions for purification of gaseous mixtures of CO and $CO_2$:

1. Elaboration and investigation of catalysts for complete oxidation of CO to $CO_2$;
2. Elaboration and investigation of catalysts for conversion of CO using water vapour ;
3. Elaboration and investigation of catalysts for hydrogenation of $CO_2$ into methane.

The thematic has actuality for today and it is in accordance with the European and with the national scientific research priorities.

The obtaining of pure hydrogen as fuel for the fuel cells has its actuality as a field of scientific interest, which determines the choice of this topic for carrying out the investigations. The essence of the studies in **the first direction** (*publications № 1 and 4*) consists in scientifically justified search for alternatives of the catalysts, containing noble metals, coprecipitated Co-Al and Ni-Al layered double hydroxides (LDH). The Co-Al LDHs, as precursors of catalysts for complete oxidation of CO to $CO_2$, have been synthesized by coprecipitation to obtain composition, corresponding to molar ratio $Co^{2+}/Al^{3+}$ = 0.5, 1.5 and 3.0. The influence of the amount of cobalt has been estimated with respect to the structure and the oxidative activity of the Co-Al systems in case of changing the thermal treatment and reaction temperature. The Co-Al catalyst sample having the highest content of cobalt (CoAl3.0) has shown high and stable activity. A probable

scheme has been put forward for activating/deactivating the catalysts, in accordance with which upon heating, under the influence of the oxygen-rich reaction mixture, the surface of the catalysts is being saturated with oxygen ion-radicals $O_2^{x-}$, which fact causes complete oxidation of CO. The formation of active surface complex is supposed, consisting of the ion-radicals $O_2^{x-}$, adsorbed and stabilized on the $Al^{3+}$ ions and connected to the redox couple $Co^{2+}/Co^{3+}$ through anion vacancies, located near to the $Al^{3+}$ ions. This scheme ilustrates the transfer of electrons, enabling the catalytic cycle and the necessity of optimal ratio $Co^{2+}/Co^{3+}$ in the vicinity of the stabilized ion-radicals $O_2^{x-}/Al^{3+}$.

The second catalytic system, studied in the reaction of complete oxidation of CO, represents coprecipitated Ni-Al LDH having increased content of nickel ($Ni^{2+}/Al^{3+}$ = 1.5 and 3.0). It has been found out that under the influence of the reaction temperature and the oxidative medium, the layered structure decomposes to not well shaped NiO, containing in its lattice dissolved $Al^{3+}$ ions. It is supposed that the presence of excess of oxygen in the reaction mixture induces partial oxidation of the surface of NiO, leading to the formation of $Ni(OH)_2$ and NiOOH-similar structures, containing respectively $Ni^{2+}$ and $Ni^{3+}$ ions and forming the redox couple $Ni^{2+}/Ni^{3+}$. The scheme for activation/deactivation of the catalysts is analogous to that, proposed in the case of the Co-Al catalysts.

**The second research direction** in the habilitation thesis of Assoc. Prof. Gabrovska is connected with the development and studying of catalytic systems for the conversion of CO with water vapour (Water-gas shift reaction WGSR), (*publications № 4, 19, 20*), an important and modern catalytic reaction, connected with obtaining pure hydrogen for fuel cells. Coprecipitated Ni-Al LDHs have been studied as precursors of catalysts and as supports of golden catalysts, whereupon the stress is laid upon the influence on the catalytic behavior of the systems exerted by the quantity of nickel in the samples, by the different content of the modifying additive of $K_2O$, by the deposition of 2–3 wt. % Au through deposition/precipitation on suspended NiAl. The additive of 1 wt. % $K_2O$ promotes considerably the activity of catalyst NiAl3.0, whereupon at 300°C it reaches 97 % conversion degree of CO. It has been ascertained that in the course of the reaction, the layered Ni-Al structure is destroyed, accompanied by transformation into not well crystallized mixed Ni-Al oxide (NiO, containing dissolved $Al^{3+}$ ions). The presence of large quantity of water vapour in the reaction system causes partial hydroxylation of the surface of NiO, leading to formation of superficial $Ni(OH)_2$ and NiOOH structures, containing $Ni^{2+}$ and $Ni^{3+}$ ions. The ability of the nickel-hydroxide structures to intercalate water molecules implies the occurrence of the reaction through associative reaction mechanism, including formation of an intermediate superficial formate compound and reversible redox transition between the nickel ions. The high catalytic activity of NiAl LDH leads to the conclusion that they should be selected as supports for

gold catalysts. The most clearly expressed promoting effect of gold has been observed in the case of Au-NiAl 2.5 catalyst sample, in which the average size of the gold particles is about 15 nm. The very small Au particles favour not only the activation of CO, but also the dissociative adsorption of hydrogen, which easily reduces oxide carriers at the interphase boundary Au-support. The larger size of the Au particles has advantage, as in the case of the obtained nickel catalyst samples for CO conversion the active structure of the catalyst is the oxide phase, therefore it is of special importance to avoid the reduction of NiO into metallic nickel, as in this way the undesired side reaction of methanation is prevented. The combined presence of $Ni^{2+}$ and $Ni^{3+}$ ions is observed in the spent catalysts, owing to the presence of superficial $Ni(OH)_2$ and NiOOH structures, whereupon the reaction mechanism of the occurring reaction is confirmed, involving $Ni^{2+} \leftrightarrow Ni^{3+}$ redox transition, accompanied by adsorption and activation of CO on the gold particles (*publication № 19*). As a result of the studies an active and unexpensive gold catalyst has been elaborated having lower nickel content (Au-NiAl2.5). The catalyst achieves 97.6 % equilibrium degree of conversion of CO at 240 °C, allowing the occurrence of the process in a single stage and in this way reducing the operational expenses. The catalyst preserves its high activity during the stability test carried out at 260 °C in the course of 32 hours.

The candidate includes in this direction also the elaboration of WGSR catalysts, operating in the presence of sulfur. These studies are focused on a new application of the $Re_2O_7/\gamma\text{-}Al_2O_3$ system, with additives of K, Ni and Co as „acidic“ WGSR catalysts (*publication № 20*). Synergism has been established between Re and the additives of K, Ni and Co, most strongly expressed between Re and Co in the tricomponent system KCoRe. It has been shown that the ratio of the sulfide state of Re to the oxisulfide state, namely $Re^{4+}/(Re^{7+}(+ Re^{6+}))$, is the decisive factor for the activity. The dispersion degree of the components is the third factor explaining the catalytic behaviour of the studied various combinations: in comparison with Ni, the addition of Co to Re results in higher dispersion degree of the active structures in the bicomponent CoRe catalysts, whereupon the dispersion remains higher also after introducing K as third component in the KCoRe catalyst sample, which corresponds to its higher catalytic activity in comparison with the Ni-containing systems. The obtained results outline the KCoRe system as promising catalyst for WGSR reaction with sulfur containing gas in the temperature range 250–400 °C.

**The third research direction** in the habilitation thesis Assoc. Prof. Gabrovska is connected with elaboration and investigation of catalysts for hydrogenetation of $CO_2$ to methane (*publications № 3, 5, 11, 16*). The articles in this direction estimate the option for potential application of coprecipitated Ni-Al LDH as precursors of catalysts for methanation of $CO_2$ as an alternative of the conventional nickel catalysts. The influence of the amount of nickel has been studied, expressed through the molar ratio $Ni^{2+}/Al^{3+}$=0.5, 1.5 and 3.0, upon the structure,

reducibility and methanation activity of non-calcined systems (*publications № 3, 11, 16*). The activation of the precursors by reduction with hydrogen without preliminary calcination to the respective oxides is a new approach, applied aiming at reduction of the $Ni^{2+}$ ions in order to facilitate it and to be carried out at lower temperatures, which would contribute respectively for the methanation of $CO_2$ to be carried out at lower temperatures. It has been found out that after reduction at low temperatures (400 and 450°C), the catalyst NiAl3.0 shows highest activity at all studied reaction temperatures and space velocities. The data from hydrogen chemisorption prove higher specific surface area and higher degree of dispersion of the metallic nickel in the cases of catalyst samples NiAl3.0 and NiAl1.5 after reduction at 400 and 450°C, which leads to formation of a larger number of catalytically active sites. The influence of the non-reducible additive of $Mg^{2+}$ ions has been studied upon the methanation activity of the coprecipitated Ni-Al LDH (*publication № 11*). The presence of magnesium minimizes the migration of the metallic nickel particles, because it acts as barrier/diluent for their sintering. The nickel-rich catalyst, modified with magnesium, NiMgAl3.0, appears to be suitable for low-temperature (240 and 220°C) fine purification from $CO_2$. In *publication № 16* the effect of the kind of bivalent metal (Ni or Co) has been studied in regard to the structure, phase composition, thermal stability and reducibility of coprecipitated Ni-Al and Co-Al LDH of molar ratio $M^{2+}/Al^{3+}$=3.0, where $M^{2+} = Co^{2+}$ or $Ni^{2+}$. The comparison of the methanation activity in case of residual content of $CO_2$ of 10 ppm reveals the superiority of the catalyst NiAl3.0, which at reaction temperatures within the interval 280–240 °C remains more active than its cobalt analogue at all studied temperatures of reduction and space veocities. The stabilization of the $Co^{2+}$ ions in the spinel $CoAl_2O_4$ structure at 350°C has been observed, which hampers their reduction into metallic state, resulting in insufficient quantity of active metallic cobalt phase on the surface and it is the reason for the low methanation activity of the catalyst CoAl3.0. The interaction between the $Ni^{2+}$ and $Al^{3+}$ ions of the catalyst NiAl3.0 ensures the formation of easily reducible $Ni^{2+}$-O structures, which avours the activity of the catalyst. The study of coprecipitated Ni-Al LDHs ($Ni^{2+}/Al^{3+}$=0.5, 1.5 and 3.0) has been extended by testing of mixed Ni-Al oxides, obtained during controlled thermal decomposition in air atmosphere of layered systems within the interval 200–1000°C (*publication № 5*). The demonstrated activity of the catalyst NiAl0.5, after reduction at high temperatures, can be explained by retardation of the sintering process of metallic nickel in the presence of larger quantity of aluminium in the sample. The lowering of the activity of nickel-rich catalysts can be attributed mainly to the sintering of metallic nickel. The analysis in this aspect shows that the dominating activity of the nickel-rich catalyst, modified with magnesium, makes it reliable for low-temperature methanation. The main role of the magnesium additive is to preserve the

dispersion degree of metallic nickel by prevention of its sintering after high temperature reduction.

The published results in the habilitation thesis demonstrate originality in the scientific selection for synthesizing catalytic materials and they prove with new evidence substantial new aspects of the already available scientific knowledge. The publications, included in the habilitation thesis, have been cited 109 times in the world scientific research literature, which fact demonstrates without any doubt the actuality and the scientific significance of the carried out investigations.

The author's summary includes 13 scientific research publications, referenced and indexed in WoS and Scopus database, 10 publications in reviewed proceedings of international scientific events, two book chapters and one patent. The summary unites the design and selection of a wide range of nanosized metal and oxide composites having appropriate structure and properties for reactions, connected with hydrogen production of energy purposes, environmental protection, human health and promoting the quality of life. The basic scientific research contributions are divided into groups, in accordance with the fields of application of the elaborated catalysts and materials:

1. Elaboration and investigation of catalysts for partial hydrogenation of vegetable oils (*publications № 2,8,9,10,17,24,25,26,27,28,29,30,31,32 and research work № 22*). These studies are focused on the elaboration of new highly active and selective Ni-containing catalysts having improved operational properties, connected both with enhancement of the hydrogenating activity, as well as with reduction of the harmful *trans*-fatty acids and saturated fatty acids in the products of the reaction, leading to promotion of the quality of the hydrogenated oils and oil-based products, which is directly connected with the policies for protection of the human health and improving the quality of life.

2. Elaboration and investigation of catalysts for photocatalytic removal of nitrobenzene from water (*publication № 18*). A correlation has been found out between the structure and the photocatalytic activity, or directly determined in case of removal of nitrobenzene from water, or indirectly by measurement of hydrophilic properties. It was established that the thermal treatment at 400°C of the sample having the lowest content of Fe (0.5 wt.% Fe) increases the super-hydrophilic properties of $TiO_2$ and induces the highest photocatalytic activity in removal of nitrobenzene from water.

3. Elaboration and investigation of catalysts for oxidative dehydrogenation of light alkanes (*publication № 15*). It has been shown that by means of selection of the composition of the mixed MO-$Nd_2O_3$ oxides, (M=Mg, Ca, Sr), synthesized by the sol-gel method, one can obtain active catalysts for oxidative dehydrogenation of propane. This research publication, as well as the

publications *№ 3,4,5,6,7,11,15,16,18 and research work 22* are the results of research efforts, carried out within the framework of many-year lasting duration of interacademic collaboration between IC-BAS and the Institute of Physical Chemistry „Ilie Murgulescu“, Romanian Academy of Sciences.

4. Elaboration and investigation of catalysts for decomposition of ozone in gaseous phase (*publication № 13*). A synergism has been found out between the components of $NiO\text{-}CuO\text{-}Ag_2O\text{-}Al_2O_3$, which leads to a larger number of adsorbed ozone molecules and this contributes to the high activity of the catalyst, modified with silver.

5. Elaboration and investigation of catalysts for manufacturing biodiesel fuel (*publications № 33 and 34*). It has been ascertained that the structure, texture and morphology of the mixed oxides, obtained during the thermal treatment of odified with La and Li coprecipitated MgAl layered double hydroxides are strongly influence by the content of the modifying additive. The tests, carried out initially, showed 100% degree of conversion of triglycerides in methyl esters of fatty acids in the case of La-MgAl mixed oxides.

6. Elaboration and investigation of anodic catalysts for fuel cells (*publications № 12, 14 and work № 23*). The applied research contribution is the development of nickel catalyst, promoted with transition metal (such as Pd, Cr, Co, Fe) and/or alkaline-earth metal (Mg, Ca), deposited on electroconducting active carbon. The composition and the synthesis of the catalyst composite are the subject of a Patent US2017/0263942 A1, “Nickel-based catalyst for fuel cell” (*work № 23*). The so elaborated new catalyst has been implemented into the practice and it is in regular production included in the generator system G5, commercial product of the company GenCell Ltd, Petah Tikva, Israel.

7. Elaboration and investigation of oxide composites finding application in ceramics (*publications № 6, 7 and work 21*). The use of layered double hydroxides as precursor structure, combined with the temperature and duration of thermal treatment propose a profitable approach for obtaining of nano-sized mixed metal oxides, spinel-like mixed oxides and well defined spinels, which are promising materials for making of ceramic pigments of different colour, properties and applications.

The represented scientific research contributions in the publications, based on the author’s summary of Assoc. Prof. Gabrovska are novelties in science and they have considerable potential for applications.

The fulfillment of national and international scientific research projects occupies a substantial part of the activities of Assoc. Prof. Gabrovska. She was the leader of 4 projects within the framework of Equivalent Non-currency Exchange (ENE) with the Institute of Physical Chemistry „Ilie Murgulescu“ of the Romanian Academy of Sciences, 3 ENE projects in

collaboration with the Institute of Chemistry, Technologyand Metallurgy of the Belgrade University, coordinator on behalf of IC in 2 projects funded by National Science Fund and Ministry of Education and Science. Moreover she took active participation in 3 ENE projects with Poland (2010-2011), Belgium (2017-2019), Egypt (2019-2021), 2 other projects funded by NSF-MES and in one contract, sponsored abroad by the company GenCell Ltd, Petah Tikva, Israel (since 2012 -still ongoing project). The financial resources, obtained as a result of these contracts, are considerable and they amount to a sum higher than 175 000 BGN.

Assoc. Prof. Gabrovska took active part in organizing, scientific and programming committees of scientific events. Her application for academic position "professor" has been supported by well established renowned scientists from Romania, Israel and Serbia.

**4. Personal impressions**

I came to know Assoc. Prof. Gabrovska in the course of our collaboration working together at the Institute of Catalysis since she started her studies here. She is highly qualified and competent researcher, hardworking specialist acquiring deep knowledge in the field of synthesis of catalytic materials, their characterization, catalytic testing and interpretation of the obtained results. In personal aspect she possesses all necessary qualities of highly respected and valued colleague, good manners and she is always ready to help her colleagues.

**CONCLUSION**

The documents and the materials, submitted by Assoc. Prof. PhD Margarita Valentinova Gabrovska, answer all requirements envisaged by the Law for the Development of the Academic Staff in the Republic of Bulgaria, The Regulations for applying LDASRB in Bulgaria, The Regulations for applying LDASRB in BAS and the Internal Regulations of IC-BAS. The candidate in the competition has represented a considerable number of research works, published after the materials, used during the defence procedure for acquiring PhD degree and the academic position of „Associated Professor". There are original basic research and applied research contributions in the works of the candidate, which have gained international recognition, whereupon representative part of the studies have been published in journals and conference proceedings, issued by international academic publishing companies. The scientific qualification and expertise of Assoc. Prof. Gabrovska is very impressive without any doubt.

After acquainting myself with the materials, submitted for participation in the competition and the investigations, analyzing their significance and the basic research and applied research contributions, contained therein I am utterly convinced to give my positive opinion and to recommend to the members of the jury to prepare a positive report-proposal to the Scientific

Council of IC-BAS for appointing Assoc. Prof. Margarita Valentinova Gabrovska in the academic position „Professor“ in the professional field 4.2. „ChemicalSciences“, scientific specialty „Chemical kinetics and catalysis“ for the needs of the laboratory „New heterogeneous catalysts for clean energy production and protection of the environment“ at the Institute of Catalysis - BAS.

16.01.2020

Reviewer:
(Prof. PhD Vasko Idakiev)