

## ATTITUDE OF REVIEWER

by prof. Dr. Anton Naydenov

member of the scientific jury, according to an order by the Director of Institute of Catalysis (BAS) regarding the competition announced in State Journal no. 77 of 01. 10. 2019, for the awarding of the academic position "Professor" in the direction 4.2. Chemical Sciences (Chemical Kinetics and Catalysis) for the laboratory "New heterogeneous catalysts for clean energy and environmental protection", Institute of Catalysis (BAS),  
candidate: Docent d-r Margarita Gabrovska, Institute of Catalysis (BAS).

Docent Margarita Gabrovska study nanosized metal and oxide materials for application in reactions, connected with the hydrogen energy, protection of environment and the human health. More specifically, her work is directed to the development and investigation of catalysts for partial hydrogenation of vegetable oils, photocatalytic removal of nitrobenzene in water, oxidative dehydrogenation of light alkanes, ozone decomposition in gas phase and preparation of biodiesel. Developed and investigated are anode catalysts for fuel cells and oxide compositions with application in the ceramics. New highly active and selective Ni-containing catalysts are prepared, aiming an improvement of their properties in order to decrease the content of the dangerous trans-fatty and saturated fatty acids in the product of the reaction. Different types of silica gel (SIG-A and SIG-C) are used as carriers for Ni/SiO<sub>2</sub> catalysts. The formation of two types of mesoporous Ni<sup>2+</sup>-O structures has been described – with (i) an easily and (ii) difficult reducibility. During the studies on the catalytic activity in partial hydrogenation of sunflower oil, a correlation between the value of the jodine number and the hydrogen consumption has been established – on this basis the measurement of the iodine number is considered as perspective approach for control of the process. When investigating the reaction pathways it was revealed that the number of reactions participated within the scheme depends on the catalytic activity. The measured high hydrogenating activity of magnesium-modified MgNi/SIG-C catalyst has been explained by the formation of easily reducible Ni<sup>2+</sup>-O structures which generate larger number of active sites, in comparison with MgNi/SIG-A catalyst. It was shown that the polydisperse character of the pore size distribution within the entire region of mesopores of the precursor MgNi/SIG-C gives the possibility to decrease the effect of the diffusion process, thus the larger average diameter of the pores contributes to the enhanced mass-transfer, leading to higher reaction rate and an improved hydrogenation activity. It was concluded that the correct choice of the sillicate carrier and the participation of the magnesium additive gives the opportunity to control the hydrogenation activity, the amount of srearic acid and the level of cis-trans isomerization, which is in accordance with the modern conception for their undesirable effect on the human health.

A correlation between the surface characteristics of the catalysts and their hydrogenation activity has been observed and the effect of the different content of the silver on the reducibility, activity and cis-trans isomerization selectivity has been established. The obtained kinetics parameters and the presented simplified reduction model has motivated the extending of the research on these compositions.

It was reported that the presence of silver is promoting the reducibility of Ni<sup>2+</sup> ions of the modified precursors and at lower temperatures the silver plays significant role for further growing and reduction of the nickel structures.

A decrease of the specific surface of the metal nickel in Ag-containing reduced precursors has been established. The effect is explained by the blocking function of the reduced silver, thus leading to lower number of accessible active centres of metal nickel on the catalytic surface and a decrease in the hydrogenating activity.

According to the proposed mechanism of Horiuti–Polanyi, the both parallel processes – hydrogenation and cis-trans isomerization are realized over the same active centres of metal nickel by semi-hydrogenated intermedia products. The partially covering of the catalytic surface by already reduced silver leads to the blocking of the active centres, which results in decrease of the hydrogenating activity and suppress of the cis-trans isomerization.

The hydrogenation kinetics of soya oil has been investigated and the calculated rate constants based on the proposed simplified model show a consistence with the experimental data.

A modification by iron of synthesized by sol-gel method  $\text{TiO}_2$  films has been carried out, thus aiming an increase of their photocatalytic activity. Calculated are the lattice parameters, crystallite size, internal strains and the variation of anatase unit cell volume. A correlation between the structure and the photocatalytic activity in removal of nitrobenzene in water was observed – it is determined directly or indirectly by measurement of the hydrophilic properties and a mechanism of photocatalytic neutralization of nitrobenzene has been proposed.

During the studies on catalysts for oxidative dehydrogenation of light alkanes, within the frame of each series of samples - MgNd, CaNd or SrNd a formation of different source of defects depending on the precursors have been reported – the deformation of the crystal lattice defines a greater mobility of the defects. It was established that the surface defects are result of the structural changes inside the crystal lattice of the solid solutions and represent catalytically active centres for the oxidative dehydrogenation reaction.

Developed are co-precipitated Ni-Cu-Al catalysts for ozone decomposition. It was shown that the larger amount of NiO in the catalyst promotes the ozone decomposition at room temperature. A probable mechanism of the process has been proposed which includes an electron transfer from  $\text{Ni}^{2+}$  - ions to the ozone, thus leading to the formation of  $\text{Ni}^{3+}$ -containing structures and  $\text{O}_2^{2-}$  peroxide species. It was suggested that part of  $\text{Ni}^{2+}$  is oxidized to  $\text{Ni}^{3+}$  ions and reverse redox transfer between the nickel ions  $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+}$  is realized. A synergetic effect between the components NiO-CuO-Ag<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> was found, leading to larger number of adsorbed ozone molecules and this contributes to the higher activity of the silver modified catalyst.

An innovative concept for elimination of the drawbacks of the classic ceramics technology in preparation of nickel-based ceramics anodes for solid oxide fuel cells has been developed. The concept represents an in-situ deposition of  $\text{Ni}^{2+}$  ions from appropriate nickel salt by low-temperature wet reduction by hydrazine in presence and absence of water. It was established that during the sintering a partial oxidation of the initially formed nickel to NiO proceeds, which decreases the shrinking of the crystal lattice during the further reduction to metal. The proposed method for synthesis in absence of water has the potential to replace the classic procedure for preparation of cermet on the basis of NiO, where during the sintering procedure a second phase with dielectric properties is separated.

Created is a an innovative technology for preparation of catalytic compositions based on none noble metals as alternative to the conventional one, characterized by its expensive platinum anode catalyst for fuel cells, supported on active carbon. The composition and the method of catalyst preparation are protected by joint patent with the Israeli company GenCell LTD. The high performance of the developed new Ni-containing anode catalyst with production name Gencell STD7, leads to its introduction into regular production and incorporation into a generator system, commercial product of the company.

Developed are Co-Al and Ni-Al catalysts for CO oxidation at low temperatures and mechanism of the activation and deactivation processes is proposed. It is suggested that during the heating in rich in oxygen gas, surface  $\text{O}_2^{x-}$  ion radicals are formed on the surface of the catalyst surface and these species are responsible for the carbon monoxide oxidation. Reported are new data on the role of  $\text{Al}^{3+}$  ions during the low temperature oxidation of CO.

The investigations of docent d-r Margarita Gabrovska in the field of medium-temperature water- gas shift reaction (WGSR) are devoted to the development of layered double

hydroxides. Prepared is a gold catalyst, supported on Ni-Al layered hydroxide which properties permit the process to proceed in single stage, thus giving the opportunity to decrease the consumption of energy. Created is a sulfur resistant catalyst on the basis of  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ , which contributes to the development of new and advanced process for hydrogen production.

Prepared are nanosized Ni – containing catalysts with high activity in fine purification from carbon dioxide of hydrogen – containing gas mixtures by the methanation reaction. It was shown that the addition of magnesium helps for preservation of the metal nickel dispersity and to avoid the metal sintering.

In addition to the scientific contributions, the candidate has been invited to participate in large number of scientific committees and expert commissions, which shows her great reputation among the scientific society.

## Conclusion

The scientific studies of docent d-r Margarita Gabrovska completely correspond to the theme of the announced competition for awarding the academic position "professor". The publishing activity, the citations of published results, participation and management of the projects completely cover the requirements of the Academic Staff Development Law and the Regulations on the Conditions and Procedure for Acquisition of Academic Degrees and the Occupation of Academic Posts at the Institute of Catalysis (BAS).

Therefore, I convincingly recommend to the members of the Scientific Jury and to the Scientific Council of the Institute of Catalysis (BAS) to award docent d-r Margarita Gabrovska with the academic position "professor" under the direction "4.2. Chemical Sciences" (Chemical kinetics and catalysis) for the laboratory "New heterogeneous catalysts for clean energy and environmental protection", Institute of Catalysis (BAS).

Sofia, 20.01.2020.

Reviewer:

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