Review

by Assoc. Prof. Dr. Peter Tzvetanov Tzvetkov

regarding a competition for the academic position of Professor in the professional field 4.2. Chemical Sciences (Solid State Chemistry) for the needs of the laboratory "Design and Characterization of Catalytic Materials", thematic field "Synthesis and Structure of Catalysts and Sorbents ", Institute of Catalysis - Bulgarian Academy of Sciences

This review was prepared in connection with a competition announced for the selection of a professor in the State Gazette, No. 82 of 07.09.2025. The only candidate to participate in the competition was Assoc. Prof. Dr. Nikolay Ivanov Velinov, an employee at the Institute of Catalysis - BAS.

Associate Professor Dr. Nikolay Velinov graduated with a Master's degree from the University of Chemical Technology and Metallurgy, Sofia, majoring in Silicate Materials in 2001. In the same year, he specialized for 6 months at the University of Patras . In the period 2002 - 2005, he was a full-time PhD student at the University of Chemical Technology and Metallurgy - Sofia under the supervision of Prof. Dr. Vladimir Kozhuharov. In 2009, he defended his dissertation on the topic "Synthesis and study of materials with perovskite and perovskite-like structure for cathodes in solid oxide fuel cells", scientific specialty "Technology of silicates, binders and refractory non-metallic materials". Since June 2009, he has been working at the Institute of Catalysis - Bulgarian Academy of Sciences, where he habilitated in 2014. The main research topics and interests of Assoc. Prof. Dr. Nikolay Velinov are related to the use of Mössbauer spectroscopy to determine the valence state, magnetic ordering and occupancy of iron atoms in the crystal structure of compounds with a perovskite or spinel type structure containing iron or composite materials with their participation.

The scientific results with which Assoc. Prof. Dr. Nikolay Velinov participate in the announced competition for the academic position of "professor" are described in a total of 27 scientific publications, all of which are in journals with ISI " impact factor", 14 of which are in journals with rank Q1 and Q2. The observed citations (excluding self-citations) of all publications to date are 539 in total and h-index according to SCOPUS 14. The scientific results have been developed as participation in 17 national and 4 international projects. Assoc. Prof. Dr. Nikolay Velinov is the head of 2 national projects at the "Scientific Research Fund". The total number of participations in scientific forums is 32, 20 of which are international. The publications, citations and participation in conferences and projects of Assoc. Prof. Dr. Nikolay Velinov submitted for the competition significantly exceed the required points in all indicators, corresponding to the minimum national criteria reflected in the Law on the

Development of the Academic Staff in the Republic of Bulgaria, as well as in the Regulations of the Institute of Catalysis - BAS.

The main scientific contributions of Assoc. Prof. Dr. Nikolay Velinov included in the extended habilitation report are related to the preparation and structural characterization by Mössbauer spectroscopy of iron-containing mixed oxides mainly with a spinel-type structure. The study of such oxides is particularly relevant because of their application as catalysts in methanol decomposition reactions, carbon monoxide conversion with water vapor, ethyl acetate and diethyl ether oxidation. The specific applications in which these catalytic reactions can be used are for hydrogen production, air purification from volatile organic components, carbon monoxide oxidation in waste gases, etc. Mössbauer spectroscopy is a local method, sensitive mainly to the local environment of ^{57}Fe (first and second coordination spheres), its valence state and distribution by crystallographic positions in the structure of the studied ferrite, as well as the presence or absence of magnetic ordering in the substance depending on the temperature and size of the crystal domains. Indirectly, the information obtained can also be used to judge the distribution of other elements in the spinel structure, as well as the microstructural features of the substance. Due to its high sensitivity, Mössbauer spectroscopy allows identification of iron-containing phases even from compounds with a low degree of crystallinity.

The publications presented by Assoc. Prof. Dr. Nikolay Velinov in his extended habilitation report can be summarized in several groups:

1. Catalysts based on copper ferrite partially substituted with cobalt.

By mechanochemical treatment of co-precipitated precursors ferrites of the order $Cu_{1-x}Co_xFe_2O_4$ (x = 0.0, 0.2, 0.8) have been successfully obtained. The obtained samples have been characterized by Mössbauer spectroscopy at room temperature and 77K. The processed data prove that the studied ferrites have a crystallite size below 10 nm . The mixed Cu-Co-Fe oxides have high catalytic oxidation activity towards carbon monoxide CO and methanol CH_3OH and weaker towards diethyl ether $(CH_3CH_2)_2O$.

2. Catalysts based on copper ferrite partially substituted with zinc.

With thermal decomposition of co-precipitated precursors, Cu-Zn substituted ferrites of the order $Cu_{1-x}Zn_xFe_2O_4$ (x = 0.0, 0.2, 0.5, 0.8, 1.0) have been successfully obtained. The crystallite size varies in the range of 43 – 60 nm. With increasing the Cu content spinels go from paramagnetic to magnetic ordering. Mössbauer spectroscopy has also been used to conduct a detailed structural characterization of the distribution of iron in the mixture of iron ferrites and iron carbides obtained after the catalytic test, as well as a quantitative assessment of the distribution of iron by phases. The obtained catalysts have been tested in a catalytic reaction of methanol decomposition, with the best properties having the composition $Cu_{0.8}Zn_{0.2}Fe_2O_4$.

3. Catalysts based on impregnated activated carbon.

The influence of the surface and textural properties of activated carbon obtained from agricultural waste (grape seeds, peach, apricot and olive pits) on the applied iron phase, its transformation after catalytic test and catalytic activity for the methanol decomposition reaction CH_3OH was studied. The samples were obtained by impregnating the carbons with a solution of iron nitrate in methanol and heated at 500 ^{o}C after drying. The phase composition after catalyst operation, distribution of iron between the individual phases and size distribution of the phases were determined by Mössbauer spectroscopy.

4. Catalysts based on copper ferrite partially substituted with manganese.

This is the group of mixed oxides for which the most articles have been presented – 4 in total. Compounds with the general formula $Cu_{1-x}Mn_xFe_2O_4$ (x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0) have been obtained. The compounds have been obtained by various methods: sol-gel obtained with citric acid and subsequent combustion, co-precipitation of nitrates with ultrasound on activated carbon, combustion sol-gel synthesis and subsequent modification of the surface with gold. The possibility of controlling the cation distribution in spinel depending on the pH of the medium during the mixing of metal-containing nitrates and citric acid has been investigated. Mössbauer spectroscopy has shown that with increasing pH, the degree of inversion of the mixed Cu-Mn-Fe spinels decreases, which is directly related to the ratio of Fe^{2+} to Fe^{3+}. The obtained catalysts have high activity and selectivity for methanol decomposition and CO conversion with water vapor reactions. The processed spectroscopic data have established the structural characteristics and phase transformations in different reaction media, including the formation of magnetite and Hag's carbide. Studies on ultrasonically deposited mixed ferrites on activated carbon obtained from peach pits show that the carbon significantly affects the phase composition and catalytic activity. The comparison of the activity in CO conversion with water vapor and methanol decomposition with catalysts from mixed Cu-Mn-Fe gold-coated ferrites shows that the activity depends mainly on the structure of the material, and not on the addition of gold, which does not improve the catalytic properties but only facilitates recrystallization.

5. Catalysts based on copper ferrite partially substituted with nickel.

Study of Cu-Ni-Fe spinel with ratio Cu:Ni = 1:1 was conducted. The compounds were obtained by combustion of sol-gel obtained from metal containing nitrates and citric acid or by co-precipitation in stoichiometric ratios. By changing the synthesis conditions, catalysts with different microstructure, cation distribution, phase composition and activity were obtained. When changing the oxidant to reductant ratio, it was proven that the higher citric acid/metal ion ratio leads to smaller crystallites, larger specific surface area and higher catalytic activity in the oxidation of ethyl acetate. Using Mössbauer spectroscopy, the distribution of iron in the spinel structure and crystallite size were determined. If pH of the medium during gelation is maintained in the range of 4-8, a mixture of spinel, nitride and a small amount of CuO phases is obtained, with the nitride phase being rich in nickel. These materials show

moderate specific surface area and undergo significant phase transformations to Hag's carbide and Fe,Ni-alloy upon methanol decomposition, which leads to good catalytic activity and selectivity towards H_2 and CO.

Beyond the extended habilitation reference, the scientific activity of Assoc. Prof. Dr. Nikolay Velinov shows intensive work in collaboration with other institutes of the Bulgarian Academy of Sciences and universities. Of the 18 scientific publications presented in the competition in refereed journals by indicators in group D, five areas of research can be distinguished:

- Catalysts based on Fe-Ce oxides.

This group includes studies on mesoporous binary Fe–Ce oxides and their application as supports and active phases in catalysis and electrocatalysis. It has been shown that the modification of CeO_2 with Fe allows control over the phase composition, defectivity and catalytic properties, and a new mechanism for the formation of Fe–Ce structures has been proposed. Clear structure–property relationships have been established in reactions such as NO reduction, methanol decomposition and organic compound oxidation. High activity and selectivity of Au/Fe–CeO_2 catalysts, a synergistic effect between NiO and Fe–Ce oxides in methanol decomposition and the development of Ni–Fe–CeO_2 metal–carbon nanocomposites with excellent electrocatalytic activity for oxygen evolution reaction (OER) have been demonstrated.

- Catalysts based on Fe–Hf–Ti oxides.

Fe–Hf–Ti oxide materials were synthesized by combined methods, which show a complex relationship between composition, structure and catalytic activity. It was found that low Hf-doping facilitates the incorporation of Fe into TiO_2 ($Fe_xTi_{1-x}O_2$) and the formation of finely dispersed hematite, while higher Hf content leads to the segregation of larger α-Fe_2O_3 particles. The highest activity in ethyl acetate oxidation was achieved for Fe/TiO_2 with 1.8% Hf, characterized by easily reducible hematite nanoparticles. Mesoporous TiO_2 and Hf-doped TiO_2 with high specific surface area promote iron dispersion and visible light absorption, but the introduction of Fe reduces the activity in methanol oxidation and changes the selectivity towards methane formation.

- Catalysts supported on activated carbon.

In this direction, composite materials of TiO_2, ferrites and metal oxides supported on activated carbon and carbon foam have been studied. The carbon materials are obtained from synthetic and waste precursors. It has been proven that the texture, porosity and functionalized surface of the carbon support determine to the greatest extent the dispersion, phase composition and catalytic activity of the supported active phases. By controlling the composition of the composites and precursors, optimal photocatalytic activity and high efficiency in the decomposition of methanol to synthesis gas and hydrogen have been

achieved, which demonstrates the significant potential of carbon materials from waste biomass for obtaining cheap catalysts with specified properties.

● Catalysts made of ferrite materials.

Oxide materials such as perovskites, hexaferrites and spinels have been obtained. The materials have been synthesized by sol–gel combustion and co-precipitation methods. The obtained ferrite materials have been studied in the reactions of selective methane oxidation, methanol decomposition, WGSR and total oxidation of hydrocarbons. It has been shown that modification of the composition significantly affects the redox properties, phase stability and catalytic activity. The synergistic effects between different cations and metal phases, as well as the high structural stability under reaction conditions, lead to increased activity and stability of the catalysts, which makes them promising for synthesis gas production and hydrocarbon oxidation processes.

● Research on iron-containing materials.

In this direction, research on various iron-containing materials of applied and fundamental nature is summarized. It is shown that waste copper mining slag, rich in fayalite and magnetite, can be successfully used as a geopolymer precursor for construction materials, contributing to the recovery of industrial waste. Mesoporous Fe–Cr Oxide silicon materials demonstrate tunable catalytic behavior in methanol decomposition, with the activity and selectivity controlled by the Fe/Cr ratio. The synthesis of pure and Er-doped hematite nanotubes reveals the possibility of targeted control of morphological, magnetic and optical properties through rare-earth substitution associated with increased structural defectivity and changes in magnetic transitions.

Presented by the candidate in the competition, Assoc. Prof. Dr. Nikolay Velinov materials, fully comply with the Law on the Development of the Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the relevant Regulations of the Institute of Catalysis - BAS and the topic of the announced competition for "professor". I confidently give a positive assessment of the works and activities presented in the competition and recommend to the members of the Scientific Jury to prepare a report-proposal to the Scientific Council of the Institute of Catalysis - BAS, according to which Assoc. Prof. Dr. Nikolay Velinov be elected to the academic position of "professor" at the Institute of Catalysis - BAS, in the professional field 4.2. Chemical Sciences (Solid State Chemistry).

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