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**Development of new nanostructured multicomponent
catalysts with application in alternative fuels and ecology**

Report about scientific contributions

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I. Introduction

Alternative sources of raw materials and energy still play a secondary role, but in recent years they have become increasingly important due to the depletion of conventional sources. Methanol is known to be a very promising alternative energy source. Its importance has grown greatly thanks to the processes developed in recent decades for its selective conversion to gasoline, light alkenes or chemicals that can be used as fuel for cars and raw materials for industry. The catalytic decomposition of methanol opens up opportunities to obtain gas mixtures based on CO, H₂ and methane, which can be used as an energy source in internal combustion engines, fuel cells and gas turbines. On the other hand, the problems related to ecology are extremely relevant. The neutralization of toxic gas emissions is only one of the aspects in this direction, and the main approach is their catalytic combustion to CO₂. The introduction of these processes into practice requires the development of effective catalysts, distinguished not only by their high activity, stability and selectivity, but also from an economic point of view, with a low price and the possibility of working at relatively low temperatures. This necessitates the search for suitable supports and active phases, as well as the application of new synthesis methods. Currently, there is an ever-increasing interest in replacing noble metal-containing catalysts with transition metal oxides due to their lower cost, high thermal stability, tunable acid-base properties, easy reducibility, and high oxygen storage capacity. Suitable approaches for the preparation and stabilization of nanosized metal oxide particles are their deposition on various porous supports and the development of multicomponent metal oxide systems. Moreover, nanoscale materials consisting of more components in different ratios reveal unlimited possibilities for improving the catalytic properties of materials through structural, phase and textural changes, improving thermal stability, changes in acid-base and redox properties, as well as occurrence of synergistic effects between individual components. Recently, activated carbons have been considered as one of the most promising supports for the preparation of catalysts, which is due to their high specific surface area, well-developed porous texture and ability to actively participate in the formation of the active phase through their reducing properties and diverse surface acid and basic functional groups. A number of approaches are known for their preparation, which allows fine control of their texture and surface properties. In recent years, intensive work has been done on reducing the price of activated carbon with a view to expand their fields of application. A possibility in

this direction is the improvement of technologies for obtaining activated carbon and the use of alternative precursors, including waste raw materials.

This habilitation reference covers the most essential part of my research work after my assignment to the academic position of "Assistant Professor" at IOCCP-BAS in 2017. It was made on the base of 19 scientific publications dedicated to the development of new nanostructured catalysts and catalyst supports based on mesoporous mono-, bi- and ternary metal oxide composites, as well as the study of the possibilities of using porous carbon materials obtained from waste raw materials as supports for mono- and bi-component metal oxide catalysts. Seven of the scientific works are referred to habilitation work (indicator "B") [publ. № 1-3, 9, 13, 16 and 17], and the remaining scientific publications are 12 and are assigned to indicator "Г" [publ. № 4-8, 10-12, 14, 15, 18 and 19] The research carried out entirely covers the field of materials science and catalysis, and the contributions are of a fundamental and scientific-applied nature. The main scientific and scientific-applied contributions from these works can be summarized in the following main fields/topics:

- development of new catalysts and catalyst supports based on nanostructured mesoporous metal oxide composites. The work in this field is aimed at the development of highly efficient approaches for the preparation of nanostructured mesoporous oxide materials that possess appropriate textural and surface properties for the preparation of new catalysts with potential application as alternative fuels and in ecology.
- complex characterization of the structural, textural, surface, electronic and redox properties of materials by using appropriate modern physicochemical techniques (low-temperature nitrogen physisorption, X-ray diffraction, electron microscopy, UV-, IR-, Raman- and X-ray photoelectron spectroscopy, as well as temperature-programmed reduction with hydrogen);
- increasing the efficiency for removing toxic emissions from VOCs (ethyl acetate) through catalytic oxidation;
- increasing the efficiency of using methanol (both from renewable and waste raw materials) to obtain an alternative fuel.

II. RESULTS AND DISCUSSION

In recent decades, the design and synthesis of nanostructured metal oxides has attracted much attention due to their attractive physical, chemical, and catalytic properties. The

improvement of the methods for their synthesis, which is currently being worked on extremely intensively, has led to the creation of new materials with different morphologies, high specific surface area and a well-developed porous structure made up of pores of different size, shape and topology, and in some cases with tunable surface properties by functionalizing the oxide surface. In recent years, manganese oxide has attracted great interest in many industrial catalytic applications. Its use as a catalyst and catalyst support is extremely promising, due to its high catalytic activity, which is determined by its crystal structure, specific surface area, porosity, particle size, etc. The excellent catalytic behavior of manganese oxides is primarily associated with the presence of different oxidation states of manganese and the participation of active oxygen particles, oxygen vacancies, lattice oxygen, as well as morphological characteristics. All this led our research to the evaluation of the influence of the preparation method on the textural, structural, surface and redox properties of manganese oxide materials. MnO_x prepared by redox reactions of manganese compounds in aqueous solution, template hydrothermal synthesis, and alkaline precipitation with aqueous ammonia solution were compared [1]. It has been proven that the obtained materials are characterized by the presence of different phases, crystallinity and particle morphology depending on the synthesis method used. For the first time, the work compares the catalytic efficiency of manganese oxides in methanol decomposition to synthesis gas and in hydrolysis of bis(4-nitrophenyl) phosphate (BNPP) at different temperatures. The results of the physicochemical analyses showed that the structural, reduction and catalytic properties of the obtained oxides can be successfully controlled by the preparation method and the specific characteristics of the acidic and redox-active centers in the manganese oxide materials. The different fractions of redox-active $\text{Mn}^{2+}/\text{Mn}^{3+}/\text{Mn}^{4+}$ surface centers and the high proportion of oxygen particles (such as O^{2-} or O^-) together with the high particle dispersion and morphology were found to be crucial for the catalytic activity of MnO_x at catalytic degradation of both molecules. Catalytic hydrolysis of BNPP substrate is supported by a higher fraction of Mn^{4+} and thus a higher amount of lattice oxygen species (O^{2-}), which act as strong nucleophilic agents. However, the lower manganese states (Mn^{2+} , Mn^{3+}) present on the catalyst surface promote the formation of oxygen vacancies and promote the formation of new active sites for the further decomposition of the BNPP substrate. It was found that the mechanism of decomposition of methanol on the MnO_x surface mainly depends on the strength of the interaction between the methanol molecule and the manganese oxides and the changes in the lattice parameters during

$\text{Mn}^{4+}/\text{Mn}^{3+}/\text{Mn}^{2+}$ transformations, as well as the variations in the acidic properties are due to the generation of oxygen vacancies in the oxide lattice [1].

Today, cerium oxide is widely used in the field of catalysis, electrochemistry, photochemistry, etc. One of the most interesting properties of CeO_2 is the high redox capacity associated with a relatively easy transition of Ce^{4+} to Ce^{3+} . These properties can be improved by reducing the size of CeO_2 particles or incorporating different promoters. Among the various transition metal bi-component oxide systems, Ce-Mn mixed oxides show high activity in organic pollutant elimination reactions in both gas and liquid phases, photocatalytic water decomposition as an opportunity to obtain hydrogen, and many others. It has been found that precursors and preparation technique can strongly influence the morphology, phase composition and textural characteristics of metal oxide composites. Many data in the literature show a relationship between the catalytic activity and the defect structure of these oxides, but due to the complexity of the system, the synthesis of homogeneous $\text{CeO}_2\text{-Mn}_x\text{O}_y$ mixed oxide nanocomposites and elucidating the influence of the composition on their properties is still a challenge. Hydrothermal synthesis in the presence of organic template is a promising approach to obtain nanostructured metal oxide materials with a high specific surface area and a well-developed mesoporous structure. All this directed our attention to comparing the properties of mono- and bi-component Ce-Mn oxide materials obtained by co-precipitation (CP) and templated hydrothermal synthesis (HT) with wide variation of composition [2]. It has been proven that bi-component Ce-Mn oxide catalysts obtained by different synthesis techniques are not a mechanical mixture of the individual oxides. Physicochemical analysis clearly demonstrated a significant increase in the dispersion of Mn_xO_y particles, changes in the oxidation state of Mn, as well as the formation of shared Ce-O-Mn bonds in which oxygen mobility is facilitated. These effects are more pronounced for CP materials due to the formation of a more homogeneous and finely dispersed manganese oxide phase. It has been shown that in both synthesis techniques, the obtained Ce-Mn oxides present a complex "core-shell" structure, where finely dispersed ceria particles are stabilized on the "core" of Mn_xO_y crystallites. An important role for the stabilization of the "core-shell" structure is played by the interface layer, where manganese ions in different oxidation states are isomorphously substituted in the cerium oxide crystal lattice with the simultaneous formation of oxygen defects. The preparation procedure and the Mn/Ce ratio have been shown to be powerful approaches to tune the microstructure of these materials. This study offers an

original interpretation of the relationships between the phase composition, textural, structural, surface and redox properties of binary Ce-Mn oxides and their catalytic behavior in total oxidation of ethyl acetate. CeO₂-TiO₂ nanocomposites can be effective catalysts in a number of environmentally relevant processes, but data on their behavior in ethyl acetate oxidation and methanol decomposition are still lacking. It has been established that the choice of the method of preparation of the metal oxide catalysts can significantly change their structural, textural and morphological properties, which makes it possible to control their catalytic behavior. At present, a number of techniques have been developed for obtaining nanosized CeO₂ and/or TiO₂ oxides. Previous research has shown us that hydrothermal synthesis with the use of structure-directing agents allows the preparation of metal oxide materials with well-developed mesoporosity, high purity and dispersion with relatively low energy consumption. On the other hand, homogeneous precipitation with urea also shows a number of advantages in the preparation of some nanocrystalline metal oxide composites, but so far this technique has not been used to prepare Ce-Ti bi-component oxides with different compositions. All this directed our attention to the evaluation of the influence of the preparation method and the phase composition on the textural, structural, surface and oxidation-reduction properties of Ce-Ti binary oxides. Samples obtained by template hydrothermal synthesis (HT) [4, 5] and homogeneous precipitation with urea (U) [4, 6] were compared, in which the composition was varied within wide range. It has been shown that the structural, reduction and catalytic characteristics of the obtained composites can be controlled by varying the Ce/Ti ratio, the hydrothermal treatment temperature and the preparation method and are strongly related to the microstructural features of the samples. The relatively low Ce/Ti ratio facilitates the stabilization of highly dispersed ceria entities, bridged to the oxygen vacancies in titania. This ensures improved titania dispersion, high surface area and pore volume combined with predominantly Lewis acidity and excellent oxygen mobility. As a result, a significant increase in the catalytic activity and selectivity in total oxidation of ethyl acetate to CO₂ and methanol decomposition to syngas is achieved. The relatively high Ce/Ti ratio in binary materials facilitates the formation of bulk ceria crystallites, which are partially substituted with Ti. This leads to deterioration in the texture parameters, promotes the increase in the density of Lewis acidic sites and decreases the number of Ti³⁺-Ti⁴⁺ and Ce³⁺-Ce⁴⁺ redox pairs. As a result, a decrease in the catalytic activity with simultaneous increase in the selectivity of ethyl acetate hydrolysis to ethanol or methanol decomposition to methane is registered. The

increase in the temperature of hydrothermal synthesis facilitates the segregation of larger particles of individual oxides, which renders difficult the intimate contact between them and decreases the observed effects. It was found that compared to homogeneous precipitation with urea, the hydrothermal method leads to the formation of more homogeneous materials with improved dispersion and developed mesoporosity, but their higher degree of defectness changes their acid-base properties, which causes lower catalytic activity and selectivity in both complete ethyl acetate oxidation and methanol decomposition [4].

Among the various transition metal bi-component oxide systems, $\text{ZrO}_2\text{-TiO}_2$ mixed oxides show high activity in a number of catalytic processes. It has been found that precursors and preparation technology can strongly influence the morphology, phase composition and textural characteristics of metal oxide composites. However, data on the preparation of mesostructured $\text{ZrO}_2\text{-TiO}_2$ materials are limited. The mechanism of their activity in various catalytic processes also remains unclear. Studies on mixed $\text{CeO}_2\text{-TiO}_2$ nanostructured oxides demonstrated the advantages of templating hydrothermal treatment and homogeneous urea precipitation as suitable techniques for the preparation of composite materials. The obtained results directed our attention to the preparation of $\text{ZrO}_2\text{-TiO}_2$ mixed oxides with different compositions by using these synthesis methods. Template assisted hydrothermal technique and homogeneous precipitation with urea were successfully used for the preparation of nanostructured mesoporous $\text{TiO}_2\text{-ZrO}_2$ binary materials in wide range of Zr/Ti ratios [7]. The incorporation of Zr^{4+} into the TiO_2 lattice facilitates the crystallization of large anatase particles in the samples with low Zr/Ti ratio, stabilization of finely dispersed tetragonal ZrO_2 phase in the samples with high zirconia content and domination of amorphous $\text{Zr}_x\text{Ti}_{1-x}\text{O}_2$ solid solution in the equimolar materials. The variations in the phase composition of the samples, prepared by different techniques, are assigned to the variations in their mechanism. The slowly released ammonia during the precipitation with urea technique provokes more homogeneous incorporation of Zr^{4+} ions into the easily precipitated $\text{Ti}_x\text{O}_y(\text{OH})_z$ gel, leading to the formation of more highly dispersed samples. The hydrothermally assisted procedure does not exclude solid state interaction between the individual TiO_2 and ZrO_2 oxides leading to the preparation of materials with higher crystallinity and well developed mesoporous structure, which can be regulated by the Zr/Ti ratio and the temperature of the hydrothermal synthesis. For the first time, it was demonstrated that the increase in the catalytic activity of the binary materials is

exclusively related to the improved texture characteristics in them. The formation of shared Ti-O-Zr bonds provokes generation of Ti^{3+} and oxygen vacancies and reduces the number of Lewis acidic sites, which decreases the specific catalytic activity and changes the selectivity in methanol decomposition and ethyl acetate oxidation [7].

Substantial research results on Ce-Ti and Zr-Ti binary oxides led to the elucidation of the different states of titanium in the mixed oxide systems, the demonstration of a synergistic effect between the individual oxides, the determination of the component with the highest catalytic activity, and the optimization of the composition and conditions for obtaining the catalyst. It was established that the possibilities for isomorphous substitution of Ce and Zr ions in the crystal lattice of TiO_2 significantly affect not only the dispersion and structure of the obtained materials, but also lead to the occurrence of a large amount of defects on the surface, which significantly change the redox and its acid-basic properties [8]. All this, directed our research to evaluate the influence of the preparation method on the properties of Sn-Ti binary oxides. The structure, texture, surface, redox and catalytic properties of binary TiO_2 - SnO_2 oxides could be successfully controlled by the Sn/Ti composition and the preparation procedure used [9]. The template assisted hydrothermal technique provides formation of highly defective rutile-like solid solutions with improved dispersion and higher surface area, but reduced Lewis acidity and oxygen mobility in comparison with the individual oxides. These features ensure a decrease in the specific catalytic activity and significant changes in the products selectivity during the ethyl acetate oxidation and methanol decomposition. The proposed mechanism of mixed oxides formation from the corresponding chloride salts suggests hydrolysis of $SnCl_4$ as initial step and further interaction of the obtained complexes with $TiCl_4$. This mechanism is facilitated under the mild alkali conditions, which are realized during the smooth release of ammonia in the urea precipitation technique. During the hydrothermal procedure, a simultaneous precipitation of both hydroxides by ammonia, followed by their dehydration to metal oxides and their solid state interaction could be alternatively realized, which ensures formation of more non-homogeneous materials [9].

As shown, the addition of a second metal/metal oxide to the titanium oxide can improve the properties of the obtained nanocomposites, due to the occurrence of interaction and/or synergism between the components, and therefore improve their catalytic behavior. Research in this direction led us to the preparation of $TiO_2/Mg(OH)_2$ nanocomposites, synthesized by thermal

hydrolysis of titanium peroxo-complexes in aqueous solution [10]. The resulting materials were investigated as catalysts for the degradation of surrogates of chemical warfare agents, P- and S-containing agents (DMMP, 2-CEES and 2-CEPS). It was found that the mixing of TiO_2 and $\text{Mg}(\text{OH})_2$ leads to a rapid increase in the specific surface area and to a high catalytic activity in the degradation of toxic organic molecules. One of the most important parameters of the catalyst – the acid-base properties are in good correlation with the activity of the obtained composites. The acidity and amount of $-\text{OH}$ groups as well as the specific surface area were shown to be crucial factors for the degradation of DMMP and were strongly influenced by the Ti : Mg ratio. Based on comprehensive characterization of catalysts and analysis of products during catalytic degradation, mixed metal oxides and composites have been found to represent a promising approach for rapid and safe degradation of highly toxic compounds by surface chemical reactions [10].

Copper oxide-based catalysts are widely used for environmental protection, but their rapid deactivation due to sintering creates problems in their use. There are numerous data in the literature on the promoting effect of CeO_2 in copper catalysts for a number of processes. The addition of CeO_2 to TiO_2 has been shown to increase the specific surface area and improve the catalytic activity of copper particles in a number of processes, but there are also contrary data, for example, a deterioration of the selectivity in the complete oxidation of ethyl acetate on Cu-Ti-Ce oxides due to the formation of by-products. The ideas regarding the mechanism of activation of copper particles on Ce-Ti oxide composites are also contradictory. There are also no data on the behavior of Cu-Ti-Ce oxide composites in methanol decomposition as a source of hydrogen. All this determined the purpose of our next study, focusing on the influence of the Ce/Ti ratio in the bi-component Ce-Ti-oxide supports obtained by hydrothermal synthesis and the procedure used to modify them with copper oxide on the catalytic behavior of the ternary composites in methanol decomposition [11, 12]. For the first time, a "chemisorption-hydrolysis" (CH) [12] technique was used to deposit the copper oxide phase on the Ce-Ti oxide supports. The properties of the obtained materials were compared with their counterparts in which copper was deposited by the most commonly used "wet impregnation" (WI) method. The originality of the development is in the application of a scientifically based approach to optimize the catalytic activity in total oxidation of ethyl acetate and methanol decomposition. The catalytic properties of these materials are determined by the activity of CuO crystallites and the facile electron

transfer within the “conjugated” Ti-Ce-Cu redox centres in the interface layer. The mechanism of the formation of interface layer and the growth of CuO crystallites is controlled by the preparation method used. The limited insertion of isolated copper ions within the support lattice during the traditional incipient wetness impregnation technique provides the formation of relatively low number of accessible, easily reducible and highly active catalytic sites. The catalytic behavior in these composites seems to be determined mainly by the activity of “conjugated” Ti-Ce-Cu redox centres in the interface layer. The specific interaction of copper ammonia complex with the support functionality during the “chemisorption-hydrolysis” procedure facilitates the formation of more uniform and very finely dispersed CuO particles, which ensures higher catalytic activity. The catalytic activity in the ternary composites is controlled by the Ce/Ti ratio of the support via generation of surface functionality and oxygen vacancies, structural and textural changes of the support and variations in the electronegativity of the ions in the vicinity of copper [12].

As shown, the application of an active phase on different supports can significantly change its state and the resulting reductive and catalytic properties by regulating the dispersion, localization and accessibility of the active particles, as well as by the occurrence of specific interactions between the applied particles and the support. These effects are much more complex for three-component metal oxide systems, in which the contact between the various particles and their oxidation state is crucial. Literature data on the preparation, characterization and catalytic behavior in complete ethyl acetate oxidation and methanol decomposition of copper-zirconium-titanium oxide nanocomposite catalysts are completely absent. In the research on Cu-Ce-Ti composites, we highlighted the advantages of the new chemisorption-hydrolysis (CH) strategy for the deposition of uniform, finely dispersed and highly active CuO particles on mixed CeO₂-TiO₂ composites. The obtained results directed our attention to elucidate the effect of the change in the microstructure of the binary ZrO₂-TiO₂ oxides with different Zr/Ti ratios and the copper oxide modification procedure on the state of the deposited CuO particles. For this purpose, the properties of copper oxide modifications obtained by "chemisorption-hydrolysis" (CH) and "wetness impregnation" (WI) method were compared [13]. As compared to the traditional wetness impregnation procedure, the novel approach ensured the formation of more uniform, finely dispersed, and easily reducible needle-like copper oxide particles, which typically improved the catalytic behavior in methanol decomposition and ethyl acetate oxidation. The

development of a high surface area in the binary $\text{TiO}_2\text{-ZrO}_2$ oxide supports increased the catalytic activity and selectivity by increasing the dispersion of the loaded copper species and in a synergistic mode with them, providing active sites for the adsorption of the reagents and their further transformation to the intermediates. However, the catalytic properties of the composites were in a complex dependence on their texture, structure, and morphology and on the related surface acidity and electron density around the metal ions. They could be optimized by the variation of the Zr/Ti ratio in the support and the procedure of copper deposition. All ternary composites exhibited superior catalytic activity in the total oxidation of ethyl acetate. During methanol decomposition, their behavior was complicated due to the phase transformations under the influence of the reduction reaction medium [13].

In addition, the properties of Cu-Ce-Ti and Cu-Zr-Ti composites obtained by "chemisorption-hydrolysis" (CH) and "wetness impregnation" (WI) methods were compared using the hydrothermally obtained supports [14]. All ternary materials show higher dispersion, improved specific surface area and pore volume, as well as higher reducibility due to easy electron transfer in the Cu-Zr(Ce)-Ti "interface layer". It has been shown that the ternary composites obtained by hydrothermal/impregnation technique exhibit extremely high catalytic activity, which is related both to the improved textural characteristics and to the specific interaction of the copper particles with the support. The resulting higher dispersion of the modifications synthesized by the "chemisorption-hydrolysis" technique favors the catalytic activity at lower temperatures, but the reduction transformations with the copper particles under the influence of the reaction medium ensure fast changes in the catalytic behavior of the composites [14].

As it became clear, multicomponent metal oxide composites reveal opportunities for improving the catalytic properties of materials by improving structural and textural characteristics, changes in acid-base and redox properties. Our work on the development of such systems continued with the preparation of cobalt ferrite, pure and modified with Hf (IV) using the sol-gel method [15]. The resulting materials were tested as catalysts in the reaction of the total oxidation of ethyl acetate. Detailed physicochemical characterization showed the formation of homogeneous spinel structures for all samples. It has been shown that, increasing the content of Hf (IV) in the samples leads to (i) an increase in the lattice parameters, probably due to the incorporation of Hf(IV) into the ferrite crystal lattice; (ii) decrease in average crystallite size and

(iii) an increase of the lattice micro-strain of the crystal structure. It has been shown that the presence of defects in mixed oxide structures significantly affects the composition and behavior of metal oxide phases in multicomponent systems, which reveals great possibilities for the synthesis of catalysts with tunable properties [15].

A suitable approach for obtaining and stabilizing nanosized metal oxide particles is their deposition on various porous supports. Among them, activated carbon (AC) has attracted much attention due to its chemical inertness, high thermal stability, and tunable textural and surface characteristics. Activated carbon can be synthesized from renewable and inexpensive materials, such as agricultural and industrial waste, which makes it attractive from both an economic and environmental point of view. All this directed our attention to the development of an intelligent integrated scheme for the full utilization of biomass for clean energy production, where methanol and catalysts for its decomposition can be obtained from biomass. An important focus of the research is to clarify in more detail the impact of the different characteristics of the activated carbon (texture and surface functionality) on the formation of the catalytically active phase. The synthesis of good quality, high surface area activated carbons from a mixture of spent motor oil and different plastic residues was reported for the first time [16]. The type of the plastic residues strongly influences the pore texture of the obtained carbon materials, but slightly affects their surface functionality. For the first time, data for the application of these activated carbons as a host matrix of iron and chromium oxides and the application of the obtained composites as catalysts for methanol decomposition are reported as well. The additives of high density polyethylene residues to the spent motor oil provides the formation of activated carbon with well-developed mesoporosity, which promotes stabilization of finely dispersed, well-accessible and highly active in methanol decomposition Fe-Cr mixed oxides. The higher microporosity in the activated carbon, which is produced by the addition of thermoplastic phenol-formaldehyde resins to the spent motor oil, restricts the formation of bi-component oxides, partially blocks the active phase within the micropores and facilitates segregation of bigger magnetite particles on the external carbon surface. This provokes lower catalytic activity and difficult prediction of the catalytic performance of the supported Fe-Cr composites [16]. Additionally, iron and chromium oxides deposited on SiO₂ have been investigated. The equimolar Fe/Cr content was found to facilitate the formation of more homogeneous and finely dispersed materials. They demonstrate

extremely high catalytic activity and stability to CO in a methanol decomposition reaction over a wide temperature range [17].

Currently, many efforts are being made to lower the cost of activated carbons by developing techniques for obtaining and utilizing waste materials. It was found that the phase composition of the metal oxides deposited on activated carbon can be adjusted by varying the textural parameters, surface functionality and reducing power of the carbon support. This makes it difficult to predict the oxidation state, dispersion and localization of the metal oxide particles in the carbon matrix, especially in the case of multicomponent systems where the direct contact between the different individual oxide particles is a decisive factor. All this brings our attention to the development of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ supported on nanoporous activated carbons obtained from peach stones and by-products from the low rank coal pyrolysis to obtain efficient methanol decomposition catalysts with potential application in hydrogen production [18]. The active phase in the obtained carbon composites was found to be a complex mixture of finely dispersed ferrites, substituted magnetite, metals (Cu, Fe, FeNi alloy) and ZnO. The dispersion and the composition of the active phase depend on the texture characteristics of the carbon support. The higher mesoporosity of the carbon host matrix provokes the formation of more finely dispersed and easily reducible spinel particles. This ensures improved catalytic activity at relatively low temperatures, but faster deactivation of the catalysts due to the complex changes with the active phase and carbon support by the influence of the reductive reaction medium. All these peculiarities could be controlled by the carbon waste precursor used [18].

Spinel ferrites can be described by the general formula AB_2O_4 , where the A and B positions are tetrahedral and octahedral cation centers in close cubic oxygen packing. It is known that the nature of the metal ion in the ferrite, as well as its position in the spinel structure, can significantly affect the properties of ferritic materials. These features directed our attention to comparing ZnFe_2O_4 , CuFe_2O_4 and MnFe_2O_4 ferrites deposited on peach stones activated carbon and KIT-6 type mesoporous silicate. It was found that activated carbon obtained from agricultural residues (peach stones) could be a suitable matrix for the stabilization of finely dispersed ferrite nanoparticles. Their formation strongly depends on the textural characteristics and reduction properties of the carbon support. ZnFe_2O_4 has been shown to be a suitable ferrite phase for the preparation of highly active catalysts for methanol decomposition [19].

A complex approach has been developed to regulate the nature of catalytically active centers in multicomponent systems, which is a prerequisite for fine control of their catalytic properties. It is based on maintaining the metal oxide materials in a highly dispersed state by applying appropriate methods for their preparation (hydrothermal method, impregnation method, "chemisorption-hydrolysis" method); construction of a mesoporous structure with a high specific surface area and pores with a defined size and shape; varying the dispersion, phase composition, oxidation state of metal ions, the type and amount of oxygen defects in the metal oxide crystal structure by changing the ratio of individual components, and as a result, controlling the redox and acid-base properties of materials by the appearance of complex electronic and synergistic effects between individual components.

Directions for future research:

Prospects for research in the next 3 years:

- Publication of the results obtained from the development of nanostructured mesoporous multicomponent catalysts based on titanium-manganese oxide systems promoted with Cu, Co and Fe oxide nanoparticles;
- Completion of work on current projects in which I am a leader or participant;
- Development of innovative materials for obtaining highly efficient catalysts based on nanostructured oxides;
- Study of nanosized adsorbents for capturing CO₂ in dynamic and static conditions;
- Investigation of nanostructured supports (zeolites and mesoporous silicates) based on waste materials and their modification to obtain new catalysts for the hydrogenation of CO₂ to methane/methanol;
- Searching for opportunities to apply for national and international research funding programs.

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