ATTITUDE OF REVIEWER

by prof. Dr. Anton Naydenov
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for the scientific contributions of the works on Assistant Professor Dr. Gloria Said Issa-Ivanova, lab. Organic reactions on microporous materials, Institute of Organic Chemistry with Center for Phytochemistry, Bulgarian Academy of Sciences, presented for participation in a competition for the academic position "Associate Professor" in professional direction 4.2. Chemical sciences, scientific specialty "Organic Chemistry", for the needs of the lab. "Organic reactions on microporous materials", announced in the State Gazette: issue 55 of 15.07.2022.

The present habilitation work covers 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 to the study of the possibilities of using porous carbon materials obtained from waste raw materials as carriers of mono- and bi-component metal oxide catalysts. Seven of the scientific works are equated to a habilitation work, and the remaining scientific publications are 12 and are assigned to indicator "Г".

To date, the candidate has 33 publications, 31 of which are published in publications with an impact factor (Web of Science) and impact rank (Scopus), and 2 in scientific conference proceedings presented in Conference Proceedings in Thomson Reuters and/or Scopus. The number of observed citations of the publications according to Scopus data is 136.

Research has been carried out in the field of materials science and catalysis, and more specifically, the works are aimed at developing new catalysts and catalyst carriers based on nanostructured mesoporous metal oxide composites, as well as complex characterization of the structural, textural, surface, electronic and oxidation - reduction properties of materials by using appropriate modern physicochemical techniques. The catalytic activity of the synthesized samples was investigated in the production processes of butyl acetate and methyl oleate. The mechanisms of the esterification process are proposed, and models are developed to study the kinetics and thermodynamics of obtaining the target products. A quantum chemical analysis was applied to the thermal and catalytic properties of the samples as a function of their molecular geometry, electronic structure and intramolecular interactions.

The influence of the preparation method on the textural, structural, surface and oxidation-reduction properties of the manganese oxide materials was investigated. It is shown that the structural, reduction and catalytic properties of the obtained oxides can be successfully controlled by the preparation method, and it is found that the decomposition mechanism of methanol on the MnOx surface mainly depends on the strength of the interaction between the methanol molecule and the manganese oxides and changes in lattice parameters during $Mn^{4+}/Mn^{3+}/Mn^{2+}$ transformations, and also from variations in acidic properties due to the generation of oxygen vacancies in the oxide lattice.

It was found that the bi-component Ce-Mn oxide catalysts prepared by various synthesis techniques are not a mechanical mixture of the individual oxides, and the preparation procedure and the Mn/Ce ratio are powerful approaches to tune the microstructure of these materials.

All this directs 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. 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 temperature of the hydrothermal rocessing and method of receipt. They are strongly related to the microstructural features of the samples. It was found that the relatively low Ce/Ti ratio facilitates the stabilization of highly dispersed CeO_2 particles stabilized on the oxygen vacancies in TiO_2.

Among the various transition metal bicomponent oxide systems, ZrO_2-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 ZrO_2-TiO_2 materials are limited. The mechanism of their activity in various catalytic processes also remains unclear. In research on mixed CeO_2-TiO_2 nanostructured oxides, the advantages of templating hydrothermal treatment and homogeneous urea precipitation as suitable techniques for the preparation of composite materials are shown.

Based on the obtained results, ZrO_2-TiO_2 mixed oxides with different compositions were obtained, and it was proved that the hydrothermal method does not exclude solid-phase interaction between individual TiO_2 and ZrO_2 oxides, which leads to the production of materials with higher crystallinity and a well-defined mesoporous texture , which can be controlled by the Zr/Ti ratio and the hydrothermal synthesis temperature. It was found that the increase in the catalytic activity of the bicomponent materials in the complete oxidation of ethyl acetate and the decomposition of methanol is related to the improvement of the textural characteristics in them.

Considering that the catalytic properties of the composites are in complex dependence on their texture, structure and morphology and on their surface acidity and electron density around the metal ions, it is shown that they can be optimized by varying the Zr/Ti ratio in the support and the procedure of modification. Three-component composites were studied, which showed high catalytic activity in the complete oxidation of ethyl acetate, and in the decomposition of methanol, their behavior was complicated due to phase transformations under the action of the reducing reaction medium. compared the properties of Cu-Ce-Ti and Cu-Zr-Ti composites prepared by "chemosorption-hydrolysis" and "wet impregnation" methods using the hydrothermally prepared supports and it was shown that the ternary composites obtained by the hydrothermal/impregnation technique exhibit high catalytic activity, which is explained both by the improved textural characteristics and by the specific interaction of the copper particles with the carrier.

On the basis of these studies, the development of an intelligent integrated scheme for the full utilization of biomass for the production of clean energy has been continued, where methanol and catalysts for its decomposition can be obtained from biomass. The impact of different characteristics of activated carbon (texture and surface functionality) on the formation of the catalytically active phase is investigated. For the first time, activated carbons were obtained from used motor oil and various plastic residues, such as high-density polyethylene or thermoplastic phenol-formaldehyde resins. Of particular interest is the comparative study of $ZnFe_2O_4$, $CuFe_2O_4$ and $MnFe_2O_4$ ferrites deposited on peach pit activated carbon and KIT-6 type mesoporous silicate. It has been shown that activated carbon obtained from agricultural residues such as peach pits can be used as a matrix for the stabilization of finely dispersed ferrite nanoparticles. More specifically, $ZnFe_2O_4$ has been shown to be a suitable ferrite phase for obtaining active catalysts in the methanol decomposition reaction.

Conclusion

The research of Assistant Professor Dr. Gloria Said Issa-Ivanova fully meet the topic of the announced competition for the award of the academic position "Associate Professor". The publishing activity, the quotations on the published results, the participation in projects of Assistant Professor Dr. Gloria Said Issa-Ivanova fully meet all the requirements of the Law on the Development of Academic Staff and the Regulations on the terms and conditions for obtaining scientific degrees and holding academic positions at the Institute of Organic Chemistry with Center for Phytochemistry, Bulgarian Academy of Sciences. Therefore, I strongly recommend to the members of the esteemed Scientific Jury and the esteemed Scientific Council of the to sentence Assistant Professor Dr. Gloria Said Issa-Ivanova the academic position "Associate Professor" in the field of 4.2. Chemical sciences (Organic Chemistry).

Sofia, 10.11.2022

Signiture:
Prof Dr. Anton Naydenov