REVIEW

on a thesis submitted for acquisition of the educational and scientific degree
"Doctor of Philosophy" (Ph.D.)
in Professional field 4.2. "Chemical sciences",
Scientific specialty: „Petrochemistry and petrochemical synthesis"

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Title: **Development of new metal oxides catalysts with application in alternative energy sources and ecology**

Reviewer: Tatyana Todorova Tabakova, Prof., Ph.D., Institute of Catalysis - BAS

1. Relevance of the problem developed in the dissertation in scientific and applied terms

Nowadays, the increase of the energetic demand, the progressive oil depletion and all environmental problems associated with an excessive CO_2 emission incite the search for sustainable alternatives for energy production. The dissertation work of Ph.D. student Alexandra Mileva is a significant contribution to solving this current problem, as it is aimed at developing new metal oxides catalysts with high efficiency in the reaction of methanol decomposition to hydrogen with a view of its use as an alternative fuel. In addition to the economically more advantageous replacement of precious metals with transition metal oxides (TiO_2, CeO_2, CuO) and their composites, activated carbons obtained from waste raw materials (biomass, polyolefin wax and motor oils) are used as support of mono- and bi-component Fe, Zn oxide catalysts which is an attractive approach to environmental protection by recycling waste materials.

Research efforts are focused on optimization of the composition and preparation methods for the synthesis of suitable bi-component metal oxide (Ce-Ti and Ti-Zr) materials to improve the catalytic behavior in the methanol decomposition by controlling the structural, textural, electronic and reduction properties. The influence of the variation in Ce/Ti and Ti/Zr ratio in the bi-component metal oxide supports and the procedure used for their modification with copper oxide on the catalytic performance of the ternary composites have been studied. A complex approach has been applied to clarify the nature of the active sites and the mechanism of the processes taking place on them. The possibility of using activated carbons from waste materials as catalyst supports for methanol decomposition has also been thoroughly examined.

The aim of the study and the tasks planned for its achievement define this work as very topical and of high scientific and applied significance. The rational design of catalytic systems based on mixed metal oxides is an attractive strategy for obtaining advanced nanosized multicomponent materials with high efficiency for hydrogen production by methanol decomposition. The innovative idea of using activated carbons as supports of heterogeneous catalysts is part of the development of an integrated scheme for biomass full utilization aiming for clean energy production, by considering the possibility of both methanol and catalysts for its decomposition to be obtained from biomass.

2. State of the problem and critical evaluation of the literature sources

The literature survey is quite extensive, written on about 90 pages, and is based on 591 sources among 742 references. But it is purposeful and looks at all aspects of the study. The Ph.D. student demonstrates high scientific awareness, an ability to successfully handle the scientific literature and knowledge of the current state of the art in the field. The properties of hydrogen are analyzed and its advantages as a clean and efficient energy carrier are revealed. Existing technologies for the production of hydrogen from natural and renewable raw materials are described, as well as the type of fuel cells using hydrogen as fuel. The benefits of using methanol as a hydrogen carrier are substantiated. Special attention is paid to advanced methods and catalysts for hydrogen production from methanol, as well as to the methanol decomposition mechanism on various types of catalysts. By analyzing and summarizing the existing information about the composition, properties and catalytic behavior of different materials, the reasons for the use of mixed oxides CeO_2 - TiO_2 and TiO_2 - ZrO_2 as main components in the development of multicomponent metal oxide catalysts are purposely rationalized. Methods for preparation and activation of carbon materials for application in heterogeneous catalysis are discussed.

The in-depth review, together with a summary and conclusions, as well as the knowledge of the requirements that should be met by an effective catalyst for methanol decomposition, have allowed a clear formulation of the goal and specific tasks for its achievement.

3. Research methodology

The research methodology is based on an interdisciplinary approach, including the synthesis of new nanosized catalysts based on transition metals and the use of activated carbon as supports, detailed physicochemical characterization and analysis of the catalytic activity in the methanol decomposition. A detailed and systematic study of the effect of the preparation method and variation in the Ce/Ti or Zr/Ti ratio on the textural, structural, and redox properties and catalytic behavior of the synthesized catalyst samples is performed to obtain the desired structures with controllable catalytic properties. The comparative analysis of the results provided by physicochemical characterization of both series of mixed oxide samples obtained by applying a

hydrothermal method of synthesis or homogeneous precipitation with urea is decisive in the selection of suitable materials for modification with copper oxide. Various procedures are used to deposit CuO phase. In addition to the characterization by a complex of physicochemical methods, catalytic measurements of the ethyl acetate oxidation are carried out as a test reaction to clarify the nature of the catalytically active sites. The possibility of using activated carbon obtained from various waste raw materials, such as peach stones, biomass, polyolefin wax or waste motor oils, as supports of methanol decomposition catalysts is studied due to its applied importance. The influence of the texture and surface functionality of activated carbons with different origin on the catalytic activity of mono- and bi-component Zn, Fe oxide modifications is investigated. The catalytic behavior of supported ferrites MFe_2O_4 (M = Zn, Cu, Mn) on activated carbon from peach stones and mesoporous silicate type KIT-6 is compared to elucidate the role of the metal ion. A large number of well-selected physicochemical techniques are used to study the relationship between physicochemical properties and catalytic behavior (low-temperature nitrogen adsorption, powder X-ray diffraction, diffuse-reflectance ultraviolet spectroscopy, infrared spectroscopy, infrared spectroscopy of adsorbed pyridine, Raman, X-ray photoelectron and Mössbauer spectroscopies, scanning electron microscopy, high-resolution transmission electron microscopy, temperature-programmed reduction with hydrogen, method of Boehm). The chosen methodology is realistic and addresses well the set goal and tasks of the dissertation work.

4. Assessment of the representativeness and reliability of the results on which the contributions of the dissertation are built

The dissertation work is well-written by using good professional language, it is properly organized and includes introduction, literature review, experimental part, results and discussion, conclusions, references. It contains 300 pages, 35 tables and 11 schemes. It is illustrated with 96 figures that illustrate the results obtained. Advanced methods are used to characterize the synthesized materials in order to solve the tasks of the dissertation. They provide reliable information about the studied properties of the catalytic samples. The results were analysed thoroughly and precisely, thanks to the good knowledge of the methods used. The phase composition, mean crystallite sizes and lattice parameters were calculated using Powder X-ray diffraction data. UV–Vis spectroscopy is used to characterize the surface coordination of metal ions and their oxidation state. The composites morphology was examined by scanning electron microscopy. Transmission electron microscopy (TEM), incl. HRTEM measurements were analyzed for reliable determination of the particle size and phase composition. The EDS-TEM mapping images based on the elemental mapping analysis demonstrate the statistical distribution of the elements on the sample's surface. The surface Brönsted and Lewis acidic sites were studied by FTIR of adsorbed pyridine. Information about the component's oxidation state and distribution of

all elements on the surface of the composites was provided by XP spectral analysis. Conclusions about the changes in the unit cell parameters and element's surrounding due to the presence of crystal defects, incl. oxygen vacancies are drawn by Raman spectroscopy. Additional characterization of Fe-containing samples was performed by Mössbauer spectroscopy with source ^{57}Co/Rh that is undoubtedly the most suitable technique for analysis of these systems. The distribution of surface oxygen-containing functional groups on various activated carbons is calculated by the Boehm method. The evaluation of catalytic behavior was carried out by determining the degree of methanol conversion and selectivity to CO, and in some cases, the specific activity per unit surface area was determined for comparison, as well as the apparent activation energy. A comparison with other applied or commercial catalysts are presented to substantiate the possibilities for practical application of the developed new materials for methanol decomposition.

5. Scientific and applied contributions and significance of the outcomes

The scientific contributions of the dissertation are related to obtaining and proving new knowledge about the development of effective nanoscale catalysts for methanol decomposition based on composites of metal oxides (CeO_2, TiO_2, ZrO_2, CuO). Experimental evidence is presented to explain the effect of Ce/Ti or Zr/Ti ratio variations and preparation method of bi-component systems on the textural and structural properties, and their influence on the catalytic properties. Pioneering studies of the nature of the active sites in CuO-CeO_2-TiO_2 system reveal a different mechanism of formation of these sites depending on the method for CuO phase deposition.

The results have also indisputable applied contribution related to the study of the possibilities for utilization of the activated carbons obtained from various waste raw materials as supports of effective catalysts for methanol decomposition to hydrogen. A novelty is the synthesis of high quality activated carbons from waste motor oils, characterized by higher mesoporosity and availability of reactants to the deposited metal oxide particles. It has been shown that the state of the deposited metal oxide particles and, accordingly, the catalytic activity can be regulated by controlling the textural and surface properties of activated carbons.

6. Assessment of the publications and personal participation of the Ph.D. student

The conduction of the research, the description of the results and their interpretation show that the Ph.D. student has acquired both theoretical knowledge and significant practical experience in the synthesis of multicomponent nanoscale composites through various preparation methods. She has mastered the use of a complex of well-selected and complementary advanced physicochemical techniques for the characterization of catalytic materials and the study of their catalytic properties. Alexandra Mileva has performed a significant amount of experimental work, including the application of various synthesis techniques. The in-depth analysis of the experimental

results demonstrates the scientific competence and skills in finding a relationship between the textural and structural features, the electronic, redox and catalytic properties of the studied materials. The acquaintance with the dissertation reveals the active participation of the Ph.D. student in performing the experiments and in the analysis and description of the obtained results, but the competent mentoring assistance of her scientific tutor should be emphasized.

7. Publications related to the dissertation work: number and publishers in which they are published, citations

The results included in the thesis are published in 13 articles and significantly exceed the requirements of the Regulations on the terms and conditions for obtaining scientific degrees at IOCCP - BAS. Eight publications have been published in international journals with a high impact factor, in a foreign thematic collection and a national journal with international status. Among the articles in international journals should be stressed those in renowned in the field of catalysis and materials science: *Applied Catalysis A: General, Applied Surface Science, Journal of Environmental Chemical Engineering* and *Microporous and Mesoporous Materials.* The other three articles have been published in *Bulg. Chem. Commun.,* and one in *„Nanoscience & Nanotechnology*". So far, 42 citations have been noticed, which demonstrates the relevance of the published results.

Research outcomes are presented at a significant number of national and international scientific forums. The Ph.D. student has presented 7 oral and 10 poster presentations at national events, and 6 oral and 5 posters at international forums, respectively. Alexandra Mileva is the first or second author in the published papers and most conference presentations, which undoubtedly reveals her active role and personal contribution to the research.

8. Remarks and recommendations

I have no critical remarks regarding the results and their interpretation.

There are some spelling errors, as well as terminological or technical inaccuracies, such as:

- The water-gas shift (WGS) reaction is repeatedly mentioned in the introduction (pages 6, 7, 8, 25, 26, 31, etc.). It is correct to introduce the Bulgarian meaning "conversion of carbon monoxide by water vapor" in the first use of the term;
- Page 78, the correct process is "conversion of CO by water vapor", not "conversion of CO_2 by water vapor";
- Page 93, The description of the synthesis of Ce-Ti-oxide materials it is not clear enough how a various molar ratio Ce/Ti (2: 8; 1: 1, 8: 2) could be achieved with the indicated amounts of $TiCl_4$ (5.54 g) and $CeCl_3.7H_2O$ (10.80 g);
- Page 192, the English word "bulk" (бълк) is used for analysis of the reduction behavior of CuO-containing samples instead of its Bulgarian meaning "обемен, масивен";

- The list of citations contains 12, which belong to co-authors in the respective publication. These citations should be considered as self-citations.

The remarks do not affect the quality of the thesis and do not change the overall excellent impression of the conducted research.

9. Reflecting the main points and scientific contributions of the dissertation in the abstract

The abstract is well prepared and reflects properly the research results. The objective and main tasks are well-formulated after a short introduction. The main experimental results are described. The influence of the composition of the mixed oxide materials, the synthesis methods, incl. the processing conditions, the role of the different characteristics of the activated carbons on the formation of the catalytically active phase, the impact of the modifying additives (Fe, Zn) for achieving the main goal of the dissertation are discussed. The general conclusions correspond to the conclusions about the textural and structural features, the reduction and catalytic behavior of the new materials developed.

10. Educational goal of doctoral studies

The demonstrated participation of the Ph.D. student in conducting the experiments and the analysis of the obtained results by using advanced physicochemical methods for characterization are evidence of the successful fulfillment of the educational goal of the doctoral program. Confirmation of the acquired new knowledge and skills are the doctoral courses in "Catalysis and Catalysts" and "Inorganic Crystal Chemistry and X-ray Structural Analysis" completed successfully, as well as a very high score of credits (1602) according to the Rules of the Credit system of BAS.

11. Conclusion

The acquaintance with the thesis allows concluding that it is an original and topical work, which contains scientific and applied contributions that completely fulfill and exceed the requirements of the Law on Development of the Academic Staff in the Republic of Bulgaria, the Regulations of BAS for the Implementation of this Law and the Rules on the terms and conditions for the acquisition of scientific degrees and for holding academic positions at the Institute of Organic Chemistry with Centre for Phytochemistry - BAS. I am highly convinced to give a **positive assessment** of the dissertation work and to recommend to the esteemed jury to award the educational and scientific degree "Doctor of Philosophy" to **Alexandra Atanasova Mileva**.

18.01.2021 г.

Reviewer:
/Prof. T. Tabakova, Ph.D./