REVIEW

by Prof. Tatyana Tabakova, PhD, Institute of Catalysis - BAS

on a thesis submitted for awarding the educational and scientific degree

"Doctor of Philosophy" (PhD)

in the field of higher education 4. "Natural sciences, mathematics and informatics",

Professional field 4.2. "Chemical sciences",

PhD program: „Organic Chemistry"

Author: Consolato Rosmini, PhD student at the Institute of Organic Chemistry with Centre of Phytochemistry (IOCCP) - BAS

Title: Advanced iron and nickel based materials for the safe production and storage of hydrogen

Supervisor: Prof. Dr. Tanya Tsoncheva**, Co-Supervisor**: Prof. Dr. Nartzislav Petrov

1. General presentation of the procedure

The set of materials presented by Consolato Rosmini for defense of a PhD thesis for awarding the educational and scientific degree „Doctor" is in accordance with the Regulations for the Development of the Academic Staff of the IOCCP-BAS, and meets the criteria of the IOCCP-BAS for the awarding of this educational and scientific degree. The following documents were submitted: PhD thesis (in English), CV, a document for completed master's degree issued by Bulgarian National centre for information and documentation, protocols from successfully passed exams, abstract in Bulgarian and English, list and copies of scientific publications on the topic of the dissertation, a list of noticed citations, a list of participation in scientific forums, table confirming fulfillment of the requirements of the credit system.

2. Brief biographical data of the PhD student

Consolato Rosmini graduated from University of Messina, Italy in 2019 and achieved a Master's degree in Chemistry, specialization in supramolecular-nanostructural chemistry with a vote of 104/110. In September 2019 he started work as Early-Stage Researcher at the IOCCF - BAS within the MSCA-BIKE project. During the period 2019-2022 he completed successfully secondment-trainings at the Instituto de Carboquímica of Zaragoza, Spain (3 months), Department of Chemical Engineering of the Norwegian Institute of Tecnology, Trondheim, Norway (3 months) and Institut für Technische Chemie und Polymerchemie of the Karlsruhe Institute of Tecnology, Germany (3 months). In July 2021 he was enrolled as PhD student in a form of self-education at IOCCP - BAS.

3. Relevance of the problem developed in the dissertation in scientific and applied aspect

Minimizing environmental impacts due to energy production based on fossil sources is one of the greatest challenges we face in the 21st century. Given the unavoidable depletion of fossil resources and all environmental problems associated with an excessive CO_2 emission, the strategy is to develop new technologies for clean and renewable energy. In this context, catalysis is a major science behind sustainability and will play a dominant role also in the future energy technologies.

This thesis is focused on a very important and rapidly developing scientific area of hydrogen economy - hydrogen production and storage. The main objective is the preparation of advanced mesoporous composites with controllable texture, surface and redox properties, based on affordable and low-cost metal/metal oxides (Ni, Fe, Sn, Ce, Zr) and evaluation of their catalytic performance for hydrogen production by two biomass-based techniques such as methanol decomposition and aqueous phase reforming of ethylene glycol. The development of efficient mesoporous Ce-Fe-Ni nanocomposites encapsulated in carbon-nanofibers as catalysts for hydrogen production through oxygen evolution reaction (OER), known as bottleneck reaction of the water splitting is also a very attractive and relevant topic.

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

The literature review is written on about 25 pages and is based on 82 sources among 171 references cited in the thesis. The current state-of-the-art hydrogen production is concisely reviewed. Fundamentals of the main fossil fuels-based processes for large-scale hydrogen production and the most important characteristics of the used catalysts are described. The emphasis is placed on the alternative techniques for hydrogen production, in particular biomass-based such as methanol decomposition and aqueous phase reforming of ethylene glycol. Special attention is paid to the methanol decomposition mechanism underlying crucial role of the selection of active metals and support type in predicting and subsequently affecting the composition of gas mixture produced. Reaction pathways of aqueous-phase reforming of ethylene glycol, as well as approaches for improved selectivity and durability of traditionally used supported nickel catalysts are discussed. Challenges in the design of high-performance electrocatalysts for the oxygen evolution reaction owing to its key role toward overall water-splitting efficiency are considered. The PhD student demonstrates high scientific awareness, knowledge of the current state-of-the-art in the field and an ability to critically evaluate the scientific literature.

Based on the summary and analysis of the existing knowledge about the relationship between composition, properties and catalytic performance of different materials, the main goal and specific tasks for its achievement are clearly formulated.

5. Research methodology

The research methodology is based on an interdisciplinary approach, including the preparation of catalytic materials based on mesoporous Ce-Fe mixed oxides and their modification

by NiO, detailed physicochemical characterization and analysis of catalytic properties for the methanol decomposition reaction. A systematic study of the effect of the synthesis protocol by using different precipitating agents (ammonia or urea), variations in the solvent and the conditions for the template release has been performed to obtain the desired structures with controllable catalytic properties. Mesoporous Ce-Fe-Ni nanocomposites have been encapsulated in carbon nanofibers and the catalytic behavior in the oxygen evolution reaction in an alkaline environment has been investigated. The influence of different Sn-Ni alloys supported on Ce-Zr mixed oxide on catalytic properties in aqueous phase reforming reaction of ethylene glycol has been examined. A large number of rightly selected physicochemical techniques have been used to study the relationship between physicochemical properties and catalytic behavior. The chosen methodology is realistic and addresses well the set goal and tasks of the dissertation work.

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

The dissertation work is very 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 174 pages, 19 tables, 4 schemes and 84 figures that illustrate the results obtained. An impressive volume of work for preparation, characterization and assessment of catalytic performance is carried out. All synthesis procedures are described in detail. The materials prepared are characterized by advanced methods. They provide detailed and reliable information about the studied properties of the catalytic samples. Based on good knowledge of the methods used the PhD student has analyzed results thoroughly and precisely. The phase composition, crystallite sizes and unit cell parameters are calculated using Powder X-ray diffraction data. The composites morphology is examined by SEM and TEM. The microstructure at atomic scale is well visualized by HRTEM and HAADF (high angle annular dark field detection). Information about the component's oxidation state and distribution of all elements on the surface of the composites is provided by XP spectral analysis. The changes in the electronic and phonon structure of the samples with the variation of the Fe/Ce ratio are elucidated by Raman spectroscopy. More information about the state of iron species in the Fe-containing composites is obtain by Mössbauer spectroscopy with source ^{57}Co/Rh that is undoubtedly the most suitable technique for analysis of these systems. The effect of the molar ratio between Fe and Ce on the surface composition is studied by FTIR. In-situ FTIR study on adsorbed probe molecules demonstrates the role of Fe/Ce ratio on the methanol fragmentation mechanism. UV–Vis spectroscopy is used to clarify the oxygen-metal coordination environment. Reduction behavior is examined by Temperature-programmed reduction - Thermogravimetric analyses. Catalytic behavior in methanol decomposition is carried out by evaluation of the temperature dependence of methanol conversion degree, the specific activity per unit surface area, as well as the TOF per unit

Fe content and unit surface area. A comparison with commercial catalyst is presented to substantiate the possibilities for practical application of Ni-decorated Fe-Ce composites for methanol decomposition. The effect of NiSn alloys formation over $Ce(Zr)O_2$ support and reaction environment on the activity and selectivity in aqueous phase reforming of ethylene glycol is also evaluated. Electrochemical characterization derived from the Electrochemical impedance spectroscopy and cyclic voltammetry studies are used to provide new evidence for the explanation of activity during OER.

7. Scientific and applied contributions and significance of the outcomes

The scientific contributions of the thesis are related to the development of efficient nanoscale catalysts based on proper combination of metal/metal oxides such as Ni, Fe, Sn, Ce, Zr for hydrogen production via methanol decomposition, oxygen evolution reaction and aqueous phase reforming of ethylene glycol. The synthesis and characterization of binary Ce-Fe oxides in a wide concentration region provide experimental evidence for understanding the relation between the phase composition, texture, and structure features of the materials and their catalytic performance in methanol decomposition. Pioneering studies for elucidation of the mechanism of binary cerium−iron oxides formation depending on the Fe/Ce ratio are performed. Highly active, selective and very stable at a wide temperature range catalysts for methanol decomposition are prepared by grafting of Ni nanoparticles onto mesoporous Ce-Fe oxide supports.

The results have also indisputable applied contribution related to the use of methanol decomposition process not only for hydrogen production, but also as a synthetic approach for encapsulation of Fe-Ce-Ni catalysts in carbon nanofibers and increase of their electrocatalytic activity.

The main contributions of the thesis can be summarized as follows:

- ✓ For the first time in-depth analysis of the relationship between the complex composition and microstructure features of hydrothermally obtained Fe-Ce mixed oxides and their catalytic behavior is presented. Strategy for control of the binary materials phase composition and active centers formation depending on the Fe/Ce ratio and the preparation conditions is considered. The effect of proportion of $Fe_xCe_{1-x}O_2$ solid solution and segregated ceria and hematite-like phases on the stabilization of supported on them NiO particles is examined.
- ✓ For the first time is demonstrated an attractive approach for the use of "spent" catalysts as promising catalysts for electrocatalytic purposes. An original strategy for Fe-Ce-Ni catalysts encapsulation in carbon nanofibers through the methanol decomposition process is applied. The role of finely dispersed nanoparticles of Ni-Fe alloys and Ni^0 in the oxygen evolution reaction is revealed. It has been found that these materials possess very low overpotential values at high anode current that would make them excellent catalysts for hydrogen production by hydrogen evolution reaction.

✓ For the first time is reported that proper selection of active Sn-Ni alloys supported on CeO_2/Ce(Zr)O_2 and choice of an alkaline environment (pH = 14) instead of the standard pH = 7 significantly affect the hydrogen yield and selectivity in aqueous-phase reforming reaction of ethylene glycol.

8. Publications related to the dissertation work: number and publishers in which they are published, citations. Personal contribution of the PhD student

The results included in the PhD thesis are summarized in 3 articles published in renowned international journals in the field of materials science and catalysis that belong to quartile Q1. Two papers are in ACS Applied materials & interfaces with IF 10.383, one in Carbon with IF 11.307. So far, 4 citations have been noticed.

Research outcomes are presented at 4 international and 3 national scientific forums. Consolato Rosmini is second author in the published papers and first author in all conference presentations, which undoubtedly indicates his active role and personal contribution to the research. The acquaintance with the dissertation reveals the indisputable and very active participation of the PhD student in performing the experiments and in the analysis and description of the obtained results, although the competent mentoring assistance of his scientific tutors should be emphasized.

9. Remarks and recommendations

I have no critical remarks regarding the results and their interpretation. Some inaccuracies and questions are listed below:

1. In literature review (p. 7) are described fundamentals of reforming processes. It should be clarified that partial oxidation (POX) in the presence of catalysts is known as catalytic POX (CPOX), while autothermal reforming (ATR) is a combination of the endothermic steam reforming and the exothermic CPOX. ATR is an economical process, since the partial oxidation reaction supplies all the heat needed to drive the catalytic steam reforming.

2. Please, explain the reason for using 8 wt.% Ni in the tri-metallic Fe-Ce-Ni catalysts (Table 2).

3. Could you explain the reason for the same phase composition of 7Fe3Ce_HT(773) and 9Fe1Ce_HT(773), e.g. Cerianit (54.6%) and Hematite(45.4%) and differences in unit cell parameters and crystallite size reported in Tabl. 4?

4. On p. 149, line 3 from the top, Fig. 7 should be corrected to Fig. 76.

The remarks do not affect the quality of the thesis and do not change the overall excellent impression of the outcomes achieved.

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

The abstract in Bulgarian and English reflects properly and concisely the results described and discussed in the thesis. The general conclusions correspond to the conclusions about the relationship between textural, structural, electronic, redox properties and catalytic behavior of the new materials developed.

11. Educational goal of doctoral studies

Clearly demonstrated participation of Mr. Rosmini in experiments implementation and analysis of the obtained results by using variety of physicochemical methods for characterization is evidence of the successful fulfillment of the educational goal of the doctoral program. He has acquired new knowledge and skills during the scientific specializations in foreign institutions within the thesis program. Specific purposes of these secondment-trainings are "Operando and ex-situ XAS characterization of catalysts for aqueous phase reforming of polyols", "Testing of catalysts for the aqueous phase reforming reaction in batch reactor and a further modification and testing of the catalysts to increase their catalytic properties" and "Synthesis and testing of novel mixed oxides and carbon materials as catalysts for the reaction of water electrolysis and hydrogen production". The PhD student completed with excellent results doctoral courses in "Inorganic Crystal Chemistry and X-ray Diffraction Analysis" and "Electron microscopy and electron diffraction in morphological and phase analysis of materials". Additional proof of educational goal achievement is the high score of credits (534) according to the Rules of the Credit system of BAS.

Conclusion

In conclusion, the dissertation of Consolato Rosmini contains scientific and applied results, which represent an original contribution to the science and completely fulfills and exceeds the requirements of the Law for the development of academic staff in 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 IOCCF - BAS. The dissertation reveals that Consolato Rosmini is a talented young researcher with an in-depth theoretical knowledge and highly professional skills in the synthesis of nanosized materials, their detailed physicochemical characterization by advanced techniques and evaluation of the catalytic performance. He demonstrates the ability and qualities to carry out independent scientific research.

Based on the above, I am highly convinced to give my positive assessment and propose to the Honorable scientific jury to award the educational and scientific degree "Doctor" e.g. PhD to Consolato Rosmini in the field of higher education "Natural sciences, mathematics and informatics", professional field 4.2. Chemical sciences, scientific specialty "Organic chemistry".

14.12.2022

Reviewer:
/Prof. T. Tabakova, PhD/