

REPORT

by prof. d-r Pavletta Shestakova, Institute of Organic Chemistry with Centre of Phytochemistry,
Bulgarian Academy of Sciences (IOCCP-BAS)

of a dissertation for awarding the educational and scientific degree 'doctor'
in the field of higher education 4. 'Natural sciences, mathematics and informatics',
professional direction 4.2. 'Chemical Sciences', PhD program 'Organic Chemistry'

Author: Consolato Rosmini

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

Supervisors: Prof. DSc Tanya Tsoncheva (IOCCP-BAS) and prof. Dr. Nartzislav Petrov (IOCCP-BAS).

General presentation of the procedure

The set of materials presented by Consolato Rosmini for the 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 the educational and scientific degree "doctor".

The PhD candidate has presented 3 publications on the topic of the dissertation, a list of citations of the papers included in the dissertation, a list of participation in scientific events and the relevant supporting material. The documents were submitted on time and are prepared carefully.

Brief biographical data of the PhD student

Consolato Rosmini completed his MSc in Chemistry with a specialization in Supramolecular and Nanostructural Chemistry, at the University of Messina, Italy in 2019. During his studies at the University of Messina, Consolato Rosmini participated in a number of additional training programs, such as Erasmus programme, as well as in various courses covering a wide range of analytical techniques, such as ICP-MS, X-ray photoelectron spectroscopy (XPS), Scanning transmission electron microscopy (STEM), Atomic Force Microscopy (AFM).

During the period September 2019 - September 2022, Consolato Rosmini is a PhD student at the IOCCP, BAS under the supervision of Prof. Tanya Tsoncheva and prof. Dr. Nartzislav Petrov. The PhD is funded by the Marie Skłodowska-Curie program of the European Commission, within the framework of the MSCA-BIKE project. During the work on his doctoral thesis, Consolato Rosmini participated in various training courses and secondments at the Norwegian Institute of Technology, at the Institute of Carbochemistry in Zaragoza, Spain, the Institute of Technical and Polymer Chemistry at the Karlsruhe Institute of Technology, Germany. In these secondments, the PhD student acquired deeper knowledge in specific techniques for the synthesis and structural characterization of catalysts and their application in various chemical reactions.

Relevance of the topic

The topic of the PhD Thesis concerns an important area of research related to the development of new catalysts with improved characteristics (tunable texture, surface and redox properties), with potential applications for the production and storage of new energy sources. The focus of the dissertation is on new materials for the production and storage of hydrogen, based on alternative to fossil fuel sources, such as biomass utilization (decomposition of methanol, aqueous phase reforming of ethylene glycol) and water electrolysis (the Oxygen Evolution Reaction). The specific scientific tasks to achieve this goal are appropriately defined, and the reactions to test the materials developed in the thesis as catalysts for hydrogen production are appropriately selected.

Knowing the problem

The dissertation includes a total of 171 literary sources. The literature review is written clearly and concisely, it convincingly demonstrates that the PhD candidate has excellent knowledge on the

current state of research and the problems addressed in the dissertation, and he is able to critically and competently analyze, interpret and summarize the existing literature.

Research methodology, characterization and evaluation of the dissertation work

The dissertation is written on 177 pages, contains 84 figures, 4 schemes and 19 tables. Of the cited 171 literary sources, over 40% are articles published after 2015. The dissertation consists of six main sections: Introduction (2 pages), Literature review (22 pages), Experimental part (12 pages), Results and discussion (121 pages), Conclusion (2 pages), Contributions (1 p.), Literature (11 p.).

The results of the own research are presented and discussed in five subsections, according to the type of catalysts and the reactions in which they were used. The results are consistently and clearly discussed. For each of the investigated catalytic systems the Thesis presents detailed physicochemical studies with a wide range of methods, the results of the catalytic tests in the corresponding catalytic reactions, and the influence of the experimental parameters on the effectiveness of the respective catalyst. All studies have been conducted using a systematic, well-planned and consistent approach, the analysis and interpretation of experimental data have been carried out carefully and precisely, and the results have been convincingly presented.

My overall impression is that the dissertation is serious and thorough research that has been conducted at a high scientific level. The high competence of the scientific supervisors Prof. Dr. Tanya Tsoncheva and Prof. Dr. Nartzislav Petrov also has an indisputable contribution to the choice of highly relevant topic of the Thesis and its high scientific quality.

Contributions and significance of the developments for science and practice

The research carried out in the Thesis and the obtained results have a scientific and potentially applied nature. Essentially, they are related to the development of new catalytic systems and materials for the production and storage of alternative energy sources and, more specifically, hydrogen. The conducted research contains original scientific results and continues the good traditions and high research standards in the Laboratory "Organic reactions of microporous materials" at IOCCP. The main contributions of the dissertation can be summarized as follows:

- A series of bi-(Ce-Fe) and tri-component (Fe-Ce-Ni) mesoporous composites composed of mixed metal oxides were developed and used as highly active catalysts for methanol decomposition. The influence of the reaction conditions on the properties, phase composition and characteristics of the obtained catalytic materials has been clarified.
- The formation mechanism of the different hematite and cerium oxide phases has been proposed, which contributes to a deeper understanding of the relationship between the phase composition, texture and structural characteristics of the bicomponent catalysts, as well as to clarifying their catalytic behavior in the methanol decomposition reaction.
- Mesoporous Ce-Fe-Ni nanocomposites encapsulated in carbon nanofibers have been developed, and their high efficiency as catalysts in the oxygen evolution reaction, which is a critical part of the electrolytic water splitting reaction, has been demonstrated.
- Ni-Sn alloys deposited on $\text{CeO}_2/\text{Ce}(\text{Zr})\text{O}_2$ were developed and their catalytic behavior in aqueous phase ethylene glycol reforming (APR-EG) in a variable reaction media was investigated.
- A synergistic interaction between the $\text{CeO}_2\text{-ZrO}_2$ carrier and the active metal phase was established, which is realized with the participation of some of the products in the APR-EG reaction. It is shown that the catalytic activity and the selectivity of the catalyst depend on the relative concentration of the tin in the Ni-Sn metal alloys and on the pH of the medium. The use of alkaline instead of neutral media has been shown to increase the percentage of ethylene glycol converted by about twofold and to increase the yield of hydrogen by about fivefold for some of the catalysts obtained.

Assessment of dissertation publications

The results obtained in the PhD thesis are summarized in 3 scientific publications, two of which were published in the journal ACS Appl. Mater. Interfaces (IF 10.38) in 2021 and 2020, and one in the journal Carbon (IF 11.31). It is noteworthy that all three publications are in journals that belong to the Q1 category and have a very high impact factor, which is indicative of the quality and significance of the research conducted.

A total of 4 citations were noted, all of which were for the paper published in 2020. The results have been presented to the scientific community through participation in international and national scientific forums. I would like to highlight the participation of Consolato Rosmini with 2 plenary talks at international events, which is recognition of the high quality of the research.

Personal contribution of the PhD candidate

I am fully convinced that Consolato Rosmini has an indisputable and decisive personal involvement in every stage of the conducted research. He is first author in one and second author in two of the publications, which is recognition of his significant personal contribution to the research conducted.

Abstract

The presented abstract of the Thesis has been prepared in accordance with the requirements and objectively reflects the structure, content and results of the PhD thesis.

Critical remarks and recommendations

I have no critical remarks to the presented research and to the dissertation materials.

Personal impressions

My personal impressions of Consolato Rosmini are based on the discussions initiated by him regarding the possibilities of including NMR methods in his future research. During these conversations, I was impressed by his curiosity, enthusiasm, in-depth approach and desire for scientific development, including also new analytical methods for characterization of the new materials he was developing.

CONCLUSION

The PhD Thesis contains original scientific and scientific-applied developments, results and contributions, which cover and exceed the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria (LDASRB), the Regulations for its Implementation and the Regulations for its Implementation of the Bulgarian Academy of Sciences. The presented materials and dissertation results fully comply with the specific requirements of the Regulations of IOCCP-BAS for the application of LDASRB.

The dissertation presents Consolato Rosmini as a talented, serious and promising young scientist, distinguished by his scientific curiosity, in-depth approach, enthusiasm and highly professional skills.

Based on the above, I am pleased to give my **positive assessment** of the research carried out, the results achieved and the contributions presented in the dissertation work and I propose to the Honorable Scientific Jury **to award the educational and scientific degree "doctor" to Consolato Rosmini in the field of higher education: "Natural sciences, mathematics and informatics", professional direction 4.2. Chemical sciences, PhD program "Organic chemistry"**.

01.12.2022r.

Reviewer:

Prof. d-r Pavletta Shestakova