

OPINION

by **Assoc. Prof. Yordanka Karakirova, PhD**

Institute of Catalysis, Bulgarian Academy of Sciences,

Member of the Scientific Jury according to Order No. RD-09-160/20.10.2022 issued by the Director of the Institute of Organic Chemistry with Centre of Phytochemistry – BAS, regarding a PhD Thesis for awarding the educational and scientific degree "**doctor**" in the field of higher education 4. **Natural sciences, mathematics and informatics, professional field 4.2 Chemical sciences**, scientific specialty **Organic Chemistry**

Author: Consolato Rosmini

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

Scientific supervisors: Prof. DSc. Tanya Tsoncheva (IOCCP - BAS) and Prof. Dr. Nartzislav Petrov (IOCCP - BAS).

1. General presentation of the procedure and the doctoral student

The author of the PhD Thesis is Consolato Rosmini - a PhD student of self-standing independent training at the laboratory "Organic reactions on microporous materials" with scientific supervisors Prof. DSc Tanya Tsoncheva and Prof. Dr. Narcislav Petrov from the Institute of Organic Chemistry with the Center for Phytochemistry - BAS.

The set of materials presented by Consolato Rosmini is in accordance with the Regulations for the Development of the Academic Staff in IOCCP-BAS, and meet the criteria of IOCCP-BAS for the acquisition of the scientific and educational degree "Doctor". The candidate meets and even exceeds the national minimum requirements for obtaining the scientific and educational degree "Doctor". He presented evidence of a total number of 534 points with a required minimum of 200 points.

Consolato Rosmini was born on 29.11.1993 in Italy. In 2019, he obtained a M.Sc. degree in Chemistry from the University of Messina, Italy. For the period from 2019 until the present time, he works at the Institute of Organic Chemistry with the Center for Phytochemistry - BAS under the supervision of Prof. Tsoncheva and Prof. Petrov. The PhD candidate has attached three publications in journal with IF, a list of four noticed citations, and seven scientific conference presentations.

2. Topicality of the subject

The topic of the PhD Thesis is undoubtedly current. Currently, most of the hydrogen produced in the world comes from fossil fuels. Due to their scarcity, however, in recent years there has been an increased interest in research related to the development of alternative methods for hydrogen production. The main aim of the thesis is to synthesize advanced mesoporous composites with desired tunable texture, surface and redox properties, based on widespread and cheap metals/metal oxides and to test them as catalysts for hydrogen production by different methods.

3. Knowledge of the problem

The presented literature review shows that the doctoral student has a profound knowledge of the state of research on the topic of the dissertation. The literature review includes both the widely used methods of hydrogen production and alternative techniques for its production. The information represented is clearly structured and interpreted and it fully corresponds to and supports the objectives of the dissertation work.

4. Research methodology

The methods and approaches used are described in detail in the experimental part. In order to achieve the objectives of the dissertation work, various methods were used for the preparation of the catalysts, a large number of physicochemical methods for characterization and tests in various catalytic reactions. The proposed experimental approaches are adequately selected and allow the implementation of the set tasks.

5. Characterization and evaluation of the PhD Thesis and its contributions

The doctoral dissertation is written on a high scientific level. It contains 177 pages and includes 84 figures, 4 diagrams and 19 tables. 171 literary sources are cited. The goal is well defined. The tasks are set precisely and clearly. The dissertation includes a large volume of experimental material. From the description and discussion of the obtained results, it is understood that the doctoral student has mastered and skillfully handles both the experimental part on the synthesis of catalysts, as well as the analysis and interpretation of the results of their characterization with various physicochemical methods (XRD, TEM, SEM, Raman spectroscopy, UV-Vis spectroscopy, FTIR, Möessbauer spectroscopy, XPS, TPR and TPO –TG analysis, EA, VET) and testing. In the dissertation, 12 conclusions were drawn, which were systematized in four original scientific contributions. The conclusions correctly summarize the obtained results and the conducted analyses. The main contributions are:

- 1) For the first time, the hydrothermally obtained Fe-Ce mixed oxides were considered as a continuous set of ceria- and hematite- like entities, whose proportion could be varied by the Fe/Ce ratio and the preparation conditions used.
- 2) For the first time the superimposition of the effects of Ni-Fe-Ce composition and the influence of the reaction medium was considered in development of highly active in methanol decomposition catalysts. A complex mechanism of regulation of the amount of defects in the ceria-iron oxide interface, stabilization of small Ni particles by “encapsulation” in carbon filaments and changes in the reaction mechanism due to the formation of metal carbides and alloys is assumed.
- 3) For the first time, the methanol decomposition reaction was used not only as a mere hydrogen production process, but also as a synthetic process in order to promote the encapsulation of Fe-Ce-Ni catalysts and increase their electrocatalytic activity. Effectively proving, the potential within a recycling economy for hydrogen production, in which "spent" catalysts from reforming processes can be used directly for electrocatalytic purposes.
- 4) For the first time, for the aqueous-phase reforming reaction of ethylene glycol, it was reported in the same paper, the combination of the changes in catalytic activity and

selectivity brought about by both the correct choice of active Ni-Sn metal alloys, based on the different relative concentrations of tin, and the correct choice of 'reaction environment. The combination of these two factors strongly influences the hydrogen yield and selectivity toward the methanation reaction.

The contributions have a scientific and scientific-applied nature.

6. Evaluation of the publications and personal contribution of the doctoral student

The scientific results of the PhD Thesis of Consolato Rosmini are summarized in three scientific publications. All of them have been published in international scientific journals with IF and Q1 rank. Consolato Rosmini is the first author in one of the publications, and second author in the other two. This shows his personal contribution in preparing the articles. The PhD student participated and represented the results of the dissertation at seven scientific events, four of which were held abroad. In all contributions, Consolato Rosmini is the first author, which undoubtedly reveals his active role and involvement in the research. Two of the participations abroad have a plenary report. Four citations were noted on the dissertation publications. During his doctoral studies, Consolato Rosmini was on three specializations in prestigious foreign scientific institutes.

7. PhD Thesis Abstract

The PhD Thesis abstract fully corresponds to the content of the dissertation work and it reflects the obtained results, discussions and conclusions.

CONCLUSION

The dissertation contains scientific and scientific-applied results, which represent an original contribution to science and meet of the Low on Development of the Academic Staff in the Republic of Bulgaria (LDASRB), the Regulations for the Implementation of the LDASRB, the Regulations for the Implementation of the LDASRB of the Bulgarian Academy of Sciences. The presented materials and Thesis results fully comply with the specific requirements of the Regulations of IOCCP-BAS for the application of LDASRB.

The PhD Thesis shows that the PhD student Consolato Rosmini possesses in-depth theoretical knowledge and has acquired professional skills, and demonstrates qualities and skills for independent conduct of scientific research.

Due to the above facts, I confidently give my **positive** assessment of the conducted research, presented by the above-reviewed PhD work, abstract, achieved results and contributions, 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: 4. Natural sciences, mathematics and informatics, professional field 4.2. Chemical Sciences, scientific specialty Organic Chemistry.

Date: December 05, 2022

Member of the scientific jury:.....

/Assoc. Prof. Y. Karakirova, PhD/