

## PEER REVIEW

Submitted by Prof. PhD Alexander Eliyas –Institute of Catalysis at the  
Bulgarian Academy of Sciences

Opinion for PhD Thesis for awarding the educational and scientific degree '**Philosophy Doctor**'

In the field of higher education „Organic Chemistry“  
professional direction 4.2 *Chemical Sciences*

PhD educational programme – *PhD student on self-standing independent training*

**Author:** *Consolato Rosmini*

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

**Supervisor:** *Prof.D.Sc. Tanya Tsoncheva – IOChCP-BAS*

**Co-supervisor:** *Prof.PhD Nartsislav Petrov– IOChCP-BAS*

### **1. General description of the procedure and of the materials submitted for reviewer's opinion**

I was appointed as member of the Scientific Jury in connection with the procedure for defending PhD Thesis and for acquiring the educational and scientific degree „Philosophy Doctor“ on the basis of Order №ПД-09-160/20.10.2022, issued by the Director of IOChCP-BAS in accordance with the Regulations of IOChCP-BAS for Awarding Scientific Degrees and Acquiring Academic Positions and decision of the Scientific Council – Record of Proceedings №20/19.10.2022 and I attended online the discussion on the PhD Thesis at the session of the Colloquium „Functional Materials, computer modeling and technologies“, carried out on 11.10.2022. At the first meeting of the Scientific Jury, carried out by e-mail link on 25.10.2022, it was decided that I should prepare a peer review opinion in regard to the submitted PhD thesis.

The author of the PhD Thesis is Consolato Rosmini – PhD student on self-standing independent training, enlisted in July 2021 in the Laboratory „Organic Reactions on microporous materials“ at the Institute of Organic Chemistry with Center of Phytochemistry, Bulgarian Academy of Sciences with supervisors Prof. D.Sc. Tanya Tsoncheva and Prof.PhD Nartsislav Petrov – Institute of Organic Chemistry with Center of Phytochemistry.

The set of materials represented by Consolato Rosmini was in the form of archive folder of files, containing documents uploaded on the website of the institute with the link [линк https://orgchm-mysharepoint.com](https://orgchm-mysharepoint.com), and I was given password for it. This document set is in complete accordance with the Regulations for the Development of the Academic Staff Positions of IOChCP-BAS, and it is answering the criteria of IOChCP-BAS for acquiring the scientific and educational degree „Philosophy Doctor“ for natural sciences. The represented PhD Thesis has impressive volume and it contains 177 pages, 84 figures, 4 schemes and 19 tables.

The PhD student has attached his 3 scientific research publications and he already has noticed 4 citations on the article "Formation of Catalytic Active Sites in Hydrothermally

Obtained Binary Ceria–Iron Oxides: Composition and Preparation Effects " in prestigious scientific journals. I have no remarks with respect to the represented set of documents.

## **2. Short biography data for the PhD student**

The PhD student Consolato Rosmini acquired the educational degree „Bachelor of Science - Chemistry“ on 20.07.2016 at the University of Mesina, Italy and later also the educational degree „Master of Science“ at the same university on 12.03.2019 after the training course in the specialty „Super-molecular and nano-structural chemistry“. He has acquired considerable professional experience during a series of training courses – funded by the program „Erasmus“ at the University of Cluj-Napoca, Romania during the period of the years 2018-2019 in the field of medical treatment and medicines and more specifically in regard to optimization of the synthesis of metal nano-particles and nano-graphene. In addition he also had training at the Institute for Technologies in Karlsruhe, Germany and in the Norwegian Institute of Technologies in Trondheim focused on testing of catalyst samples in the reaction of reforming in aqueous phase using static batch reactor, and also in the scientific research institute in Saragosa, Spain. In the course of these trainings processes he gained considerable knowledge in a series of analytical methods – Raman microscopy, infrared spectroscopy, UV-visible light spectroscopy, transmission electron microscopy for morphological analysis, X-ray photoelectron spectroscopy and atomic force microscopy. As one can see this is an exceptionally wide-range scope of methodologies, which established him as a multi-laterally well-developed specialist. Here in this aspect I would distinguish in the first place the training period of 3-years duration 2019-2022 as a young researcher in the Institute of Organic Chemistry with Center of Phytochemistry -BAS in line with the project „Maria Sklodovska Curie“ BIKE-ITN having as a purpose of this investigation „Synthesis and characterization of catalysts for production of hydrogen based on the reactions of methanol decomposition“ – this study has an important application aspect of being a significant ecological problem – the reducing of the liberation of green-house gases, causing the global warming.

## **3. Actuality of the theme and advisability of the set purposes and research tasks**

This theme is actually a hot-topic of the day in view of the European regulations for replacing the fossil fuels, which lead to accumulation of green-house gases in the atmosphere. The use of hydrogen as energy carrier gives as a result of its combustion only water vapors, which are harmless. In this connection another problem arises – the dangerous storage of hydrogen gas, and also the perils, accompanying its transportation. The purpose set in the present dissertation is to consider the utilization of methyl alcohol  $\text{CH}_3\text{OH}$  as an alternative source for obtaining hydrogen, which fact represents a valuable contribution in the process of seeking solution for this problem, and another option is also the process of reforming of ethylene glycol. These two tasks in the elaboration of the dissertation experimental work are logically justified as the necessary field of the scientific research work – specifically these two techniques and the respective catalysts, connected with them. It follows from here what is the purpose set in the dissertation: to synthesize mesoporous composites of non-expensive metals.

## **4. Knowledge on the problem**

The PhD student is well acquainted with the problem, which is obvious in view of the large number of current literature references – a total number of 177 references, which are cited in the Introduction of the PhD Thesis. Thereafter they have been analyzed as available data in

the Chapter 2 of the dissertation „Present state of the problem“, as well as in Chapter 4.2 „Physicochemical methods of the investigations“ and in this respect the results obtained by Consolato Rosmini are juxtaposed with the available literature data in Chapter 5 „Results and Discussion“, where it is clearly seen that the knowledge of the PhD student in the discussion is covering a wide scope of many physical methods for analysis and the comments on them are highly competent in the course of comparing his results and the data obtained by the other cited investigators.

### **5. Methodology of the investigation**

The selected complex set of numerous methods enables the achievement of the preliminarily set purpose in the dissertation – synthesis of mesoporous composites of iron and nickel as non-expensive catalytic materials for the production of H<sub>2</sub>. The hydrothermal synthesis has been successfully applied based on the template method utilization. The so designed two tasks in the dissertation research work – the use of methyl alcohol and the application of reforming of ethylene glycol have obtained respectively the necessary adequate answer based on the characterization of the phase composition and on the molar ratio between the components and the variation of the composition of the support. An important aspect also is the establishment of the porous structure and more specifically its influence in regard to the formation of the catalytically active sites. What makes impression as well is the physicochemical characterization of these composite materials, which have been deposited by means of encapsulation of carbonaceous nanometer sized fibers – a quite contemporary modern aspect in the case of synthesis of catalysts samples. Aiming at the optimization of the composition the ratio between the components has been varied and also variation of the experimental set of conditions – more specifically the use of different pH-values of the solution for the specific case of the reaction of the reforming of ethylene glycol. Taken as one whole this complex set of methods has contributed to the formation of an multilaterally developed specialist in the field of catalysis.

### **6. Characteristics and estimation of the quality of the dissertation**

The clearly formulated purposes and the respective preset research tasks in their logical sequence and their accomplishment on a high scientific level in the course of the experimental research work make a strongly favorable impression. The manifestation of different activities by the various catalyst samples has been explained in logic way and convincingly on the basis of their properties, revealed by physical-chemical methods for their characterization, analyzed on a highly competent level. The PhD student interprets skillfully and in depth the entire combination of all these accumulated experimental data and for this reason the conclusions in this dissertation appear to be quite logical and convincing. Their usefulness has two aspects. From the fundamental point of view it is the elucidation of the mechanism of the catalytic reaction of decomposition of methanol – establishing the increased basicity of the oxygen ions inside the Fe-O-Fe structure, which facilitates the bond scission of the H<sub>3</sub>C-OH bond and enhances the selectivity towards CO, as well as the explanation of the favorable effect of doping iron. From the point of view of potential applicability it is the selection of a more appropriate method of synthesis by the use of various precipitating reagents with a view to achieve an optimal texture, porosity and high dispersion degree of the cerium oxide, which correlate with the catalytic activity and with the formation of catalytically active sites.

## **7. Contributions and significance of the research work for the science and for the practice**

The PhD student has outlined four contributions on the basis of 12 main conclusions from the dissertation. In his opinion this is the contribution of the elaborated approach and the realized possibility to regulate the properties of the iron-cerium mixed oxide catalysts and respectively the optimization of their composition by varying the ratio Fe/Ce. This achievement has both scientific aspect – being a fundamental investigation, as well as a science-application aspect as it is ecologically applicable investigation in view of the European regulations for the substitution of the fossil fuel energy sources by ecologically clean fuels. As a fundamental aspect we can also point out the elucidation of the complicated picture in the case of simultaneous super-imposition of the effects of a series of factors – the initial composition of the samples and the reaction conditions. Here the PhD student has succeeded to reveal the fragmentation of the mechanism of methanol decomposition – fundamental aspect for the elaboration of highly active catalyst samples. He also has an achievement in the field of measuring the electro-catalytic activity – this aspect is beyond the scope of my competency, but here based on some general considerations the importance of this aspect lies in the fact, that the purpose is not only to obtain ecologically clean hydrogen fuel, but also to accomplish a process of enhancing the encapsulation. This process enables the recovery and reutilization of the spent catalyst samples, applied in reforming processes – achievement of an economic effect by the recycling of a waste product.

## **8. Evaluation of the publications included in the dissertation**

Consolato has submitted a total number of 3 scientific research publications, represented in the form of files in full text in English language by the PhD student. What makes impression is the fact that all the three publications appeared in prestigious science journals having very high impact factor: the journal “Carbon” (published by Elsevier), which has an impact factor of 11.307 and the journal “Applied Materials and Interfaces” (published by American Chemical Society), which has an impact factor of 10.383 for the year 2021. It is not surprising that one of them appearing in year 2021 already has 6 citations so far (as I noticed) and not only 4 citations, as the PhD student noticed – probably at an earlier stage. These 3 publications include a large number of co-authors – not only scientists from the IOChPC-BAS, but also from IGIC-BAS, IC-BAS, and last but not least – also some foreign scientists appear as co-authors. This fact illustrates a wide access of the PhD student to available scientific apparatuses and equipment in a series of research centers and also the fact that he has passed successfully the respective training, carried out by a number of outstanding research workers, who have contributed to his multi-lateral development as a scientist.

## **9. Personal participation of the PhD student**

It is difficult for me to judge exactly to what extent the experimental data are the result of his personal participation, but it seems to me that in the course of elaboration of the present dissertation research work the experimental activities and respectively the obtained experimental

results and probably the computational processing of the data are his personal merits. Of course during the analysis and interpretation of the obtained data and conclusions from them he obtained a substantial support and assistance in the form of consultations to distinguish among the facts of the observed complexity of superimposed effects.

#### **10. Abstract of PhD Thesis**

The contents and the quality of the abstract of the PhD thesis are in accordance with the requirements of the respective available regulations and it can be stated that the abstract of the PhD thesis adequately reflects the main results and contributions of the PhD student, achieved in the course of elaboration of the dissertations.

#### **11. Critical remarks and recommendations**

I have no critical remarks, but I have one recommendation with respect to his future research work in connection with the studies carried out and the complex set of materials – some of these mixed oxide materials after respective measurement of the band gap width as possible semiconductors could find application as photocatalyst samples for the decontamination of polluted wastewaters and contaminated gas mixtures.

#### **12. Personal impressions**

I have had no personal contacts and personal impressions from the research activities of the PhD student, but it was many times that I heard from my colleagues their positive impressions about the work and experience of Consolato Rosmini.

#### **CONCLUSION**

Being fully convinced as member of the Scientific Jury I give my positive evaluation of the present dissertation, the abstract of the PhD thesis, the achieved results and the outlined contributions and I fully support awarding the educational and scientific degree „Philosophy Doctor“ to the applying candidate Consolato Rosmini. The present dissertation contains both fundamental scientific as well as applicability results, which represent an original contribution in science and answer all the requirements of the Law for the Development of the Academic Staff in the Republic of Bulgaria (LDASRB), the Regulations for the Application of LDASRB and the BAS Instructions for its application. The represented materials and PhD Thesis results are in complete accordance with the specific requirements of the Regulations of IOChCP-BAS for the application of LDASRB.

The dissertation shows that the PhD student Consolato Rosmini has acquired in depth research experimentation skills and theoretical knowledge in professional direction „4.2 Chemical Sciences“ and scientific research specialty „Organic Chemistry“ demonstrating the respective skills and qualities for carrying out self-standing independent research studies.

08.12.2022

Reviewer: Prof. PhD Alexander Eliyas

Institute of Catalysis - BAS