R E P O R T

from Prof. Dr. Radostina Konstantinova Stoyanova (IGIC-BAS)

of a thesis for acquiring an educational and scientific degree "Doctor"

in the field of higher education *Natural Sciences*

professional area *Chemical Sciences*

PhD program *Organic Chemistry*

Author: **Consolato Rosmini**

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

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

The thesis of Mr. Rosmini represents an original research work, which is focused on the preparation, structure, morphological, catalytic and electrochemical characterization of innovative oxide-based materials for hydrogen production and storage. Three groups of technologically important materials are studies: mesoporous cerium-iron oxides and their modifications with nickel, carbon-encapsulated Ce-Fe-Ni composites, Ni/Sn alloys supported on mesoporous Ce-Zr mixed oxides. All materials are prepared by facile and effective methods including template-assisted hydrothermal technique and hydrogen reduction procedure. These methods are best suited for the preparation of materials with organized structure and porosity. In general, the thesis of Mr. Rosmini has a valuable contribution to knowledge in the modern branch of the materials chemistry, namely the control of catalytic and electrochemical properties of materials for the methanol decomposition, reforming of ethylene glycol and oxygen evolution reactions. The results obtained are of significance not only for the scientific community, but would be of interest for the society from the energetic sector.

The thesis is well written and structured into 6 chapters. The 1st chapter compares the classical large-scale techniques for hydrogen production with these developed today as alternative ones. The author provides also a short review on the materials that are used as catalysts for reforming reactions and electrocatalysts for water electrolysis. The literature review encompasses a wide range of issues in the field of the chemistry of materials for hydrogen production, thus indicating an excellent level of education of Mr. Rosmini. The critical analysis of the literature data allows defining clearly objectives of the thesis (Chapter 3).

The next chapter presents the details on the synthetic procedure and analytical methods of characterization. The specific feature of the thesis is the application of a broad range of instrumental methods for structural, surface and morphological characterization: diffraction methods (XRD, electron diffraction), spectroscopic methods (IR spectroscopy of molecule probes, Raman spectroscopy, XPS, Moessbauer), electron microscopy (SEM, TEM, HRTEM) and texture analysis. The catalytic and electrochemical measurements include the determination of catalytic selectivity and efficiency, linear sweep and cycling voltammetry experiments and electrochemical impedance analysis. All these techniques are well balanced in respect of the thesis scope and they are used with a great effectiveness.

The chapter 5 are organized in a logic way that follows the objectives of the thesis. The most important results can be grouped as follows:

(i) The hydrothermal method has been demonstrated to be a facile route for the preparation of Fe-Ce oxide-composites and Ni-modified Fe-Ce oxides as catalysts for methanol decomposition reactions. Thanks to the synergetic effects between Fe, Ce and Ni ions, the catalysts exhibit a high selectivity and good stability in a wide temperature range;

(ii) It has been found that methanol decomposition on Fe-Ce-Ni initiates two competitive reactions including hydrogen production and carbon-encapsulation of catalysts. The encapsulated catalysts display good performance towards the oxygen evolution reactions in alkaline media. Given their low overpotential at high anode currents, the encapsulated Fe-Ce-Ni systems could be used as catalysts for hydrogen evolution reaction too. Based on the above competitive reactions, the Fe-Ce-Ni catalysts could be classified as materials for circular economy by using them in sequence from reforming to electrocatalytic reactions.

(iii) Through rational selection of the composition and the reaction media, Ni-Sn alloys-based catalysts for aqueous-phase reforming of ethylene glycol, having high catalytic activity and selectivity, has been developed.

In general, the research of Mr. Rosmini contributes to reveal new relationships between synthesis methods and the catalytic and electrocatalytic properties of oxide- and alloys-based materials. The results obtained are published in world-renowned peer-reviewed journals ranked as Q1 in the field of materials chemistry: 1 paper in Carbon and 2 in ACS Applied Materials and Interfaces. Till now, 4 independent citations are reported on these publications. The results obtained are presented at 7 international conferences. The candidate's research was carried out in a wide team of scientists from the same Institute, institutions from the project BIKE and other institutes of the BAS (IGIC-BAS, IC-BAS). The role of Mr. Rosmini consists in the synthesis of materials and their catalytic and electrochemical characterizations. Thus, the scientific output of Mr. Rosmini exceeds the minimal national requirements: total number of credits is of 534.

Based on the valuable results presented in the PhD thesis, it would be interesting the candidate to comment in more details some issues such as:

- Given the different compositions and phases of the investigated materials, it is deserving to define the criteria for the selection of materials as catalysts and electrocatalysts.

- In the thesis, the attractive approach for using of spent catalysts in circular economy has been proposed. In this context, whether the spent electrocatalysts could be undergoing a regeneration?

My overall view of the thesis is that it is an original work with a well-defined research topic. Mr. Rosmini demonstrates an excellent level of knowledge in the field of materials chemistry, especially on catalysts for hydrogen production and electrocatalysts for O_2 evolution reaction. I give the highest mark of the thesis of Mr. Rosmini taking into accounts the originality, methodology and scientific merit. Based on all mentioned criteria, I propose in a most convinced way that the Scientific Jury to award Mr. Rosmini an educational and scientific degree "Doctor".

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