

Anexa nr.6

SUMMARY OF THE HABILITATION THESIS

TITLE : METAL ORGANIC FRAMEWORKS: FROM GREEN SYNTHESIS TO GREEN APPLICATIONS

Habilitation Domain: CHEMISTRY

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This habilitation thesis outlines the scientific, academic, and professional research endeavors of the candidate, conducted following the award of the PhD degree entitled "The study of mechanism and stereochemistry in synthesis of some carbon-carbon double bond compounds by phosphorus reagents" was submitted on August 25, 2005, at the Romanian Academy, Institute of Chemistry in Timişoara, within the Chemistry field, under coordination of Prof. Mircea Mracec The thesis was officially validated by Ministerial Order No. 4871/07.08.2006.

The habilitation is divided into three key chapters: *Chapter I* provides a comprehensive overview of the candidate's scientific, professional, and academic achievements, with a particular focus on the primary original contributions made in the field of organo-phosphorus chemistry. This chapter highlights the candidate's pioneering research on the design and integration of organo-phosphorus compounds into metal-organic frameworks, focusing on their enhanced catalytic properties, tunable functionalities, and potential for addressing challenges in energy storage, environmental remediation, and sustainable chemical processes, exploring their synergistic potential for advanced materials. It includes an assessment of the current state of knowledge in these areas and presents the candidate's publication portfolio and including the coordination of research internships, project management, leadership roles, supervision of undergraduate theses, and involvement in revision and editorial activities. *Chapter II* describes her scientific and academic development plans, while *Chapter III* includes the comprehensive bibliography referenced throughout the thesis, including also the candidate own scientific papers.

This thesis thus serves as a detailed reflection of the candidate's scholarly journey, showcasing their contributions to the field and their ongoing professional development, while also demonstrating their continued commitment to advancing knowledge in the areas of organo-phosphorus chemistry and related interdisciplinary research. This study focuses on the synthesis, characterization, and application of metal-organic frameworks (MOFs) and coordination polymers in environmental remediation, particularly the removal of various hazardous contaminants from aqueous solutions, in catalysis and corrosion protection.

Chapter I, of the thesis focuses on the synthesis and characterization of phosphonate metalorganic frameworks (MOFs). This section is organized based on the nature of the organic ligands used in the formation of these frameworks, with each type of ligand influencing the structure and properties of the resulting materials. The *subchapters* are divided into distinct sections according to the *synthetic*



procedure using greener alternative approaches to the synthesis of Metal Organic Frameworks, involving various ligand type (which include: monodentate phosphonate ligands, phosphono carboxylic and phosphino carboxylic ligands, dicarboxylic ligands and boronic ligands), optimization of parameters (subchapter I.1) and an *applicative part* (subchapters I.2 -I.4).

MOFs, composed of metal ions linked to organic molecules, offer high surface areas, tunable pore sizes, and adaptable properties for diverse applications. The candidate has explored both classical and alternative synthesis methods, optimizing conditions such as pH, solvent choice, reactant ratios, and temperature to enhance efficiency and functionality. This research provides valuable insights into MOF synthesis, characterization, and applications in catalysis, adsorption, and corrosion protection, emphasizing the crucial role of organic ligands and the valence of metallic site, completed in some cases by the use of auxiliary ligands. The variety of MOFs, ranging from phosphonate MOFs to boronic MOFs, was synthesized, fully characterized, and applied in various environmentally friendly domains in this thesis (*subchapter I.1*)

The applicative part is divided into catalysis/electrocatalysis (*subchapter I.2*), studies on corrosion inhibition properties (*subchapter I.3*), and adsorption applications (*subchapter I.4*).

Development of the **catalytic properties** of MOF is exemplified on zirconium-based organoborates, specifically Zr-BDB (using 1,4-benzenediboronic acid as a precursor), in the Meerwein-Ponndorf-Verley (MPV) reduction reaction. Zr-BDB demonstrated excellent catalytic activity for the reduction of various biomass-derived carbonyl compounds, including levulinate esters, aldehydes, and ketones. The presence of borate groups on the ligands played a significant role in enhancing the catalytic efficiency by activating the hydroxyl groups required for hydrogen transfer, described in the proposed mechanism. The synergetic interaction between Zr^{4+} and the borate groups contributed to the superior performance of this material.

Moreover, the study presents the development of new coordination polymers, combining divalent metal salts (Ca^{2+,} Cd²⁺, or Co²⁺) with (2-carboxyethyl)(phenyl)phosphinic acid, for *potential electrocatalytic applications*. The materials were synthesized using both conventional hydrothermal methods and microwave-assisted synthesis, with the latter providing a faster route to the desired products. The cobalt-based coordination polymer based on phosphinic acid showed promising electrocatalytic activity for both the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), with one of its pyrolytic derivatives, Co₂P, exhibiting a low overpotential (339 mV) and a favorable Tafel slope (51.7 mV dec⁻¹) for the OER.



One-dimensional (1D) imidazole-containing etidronates $[M_2(HEDP)(Im)_3] \cdot nH_2O$ (M = Co²⁺, Ni²⁺; n = 0, 1, 3) and Zn₂(HEDP)₂(H₂O)₂, along with Co²⁺/Ni²⁺ solid solutions, were synthesized and evaluated for energy conversion applications. Pyrolysis under a 5% H₂–Ar atmosphere (700–850 °C) yielded core-shell electrocatalysts of CoP, Ni₂P, and N-doped carbon, enhancing electrochemical properties. Co²⁺ phosphides varied in the content of Co and P as CoP and Co₂P, while Ni²⁺ phosphides primarily formed Ni₂P at high temperatures. Their catalytic activity for OER, ORR, and HER was assessed, advancing MOF-based multifunctional materials for sustainable energy.

The **corrosion inhibition properties** of cobalt, nickel, and copper metal phosphonates (MePA), derived from phosphonoacetic acid (PA), were evaluated for carbon steel in a 3% NaCl solution using electrochemical and computational techniques. The synthesis of these metal phosphonates was carried out via microwave-assisted and low-temperature hydrothermal methods, both of which demonstrated enhanced time and energy efficiency. Electrochemical characterization, including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), revealed that after one hour of immersion, the corrosion inhibition efficiency (IE) was 38.98% for CoPA, 40.54% for both CuPA and NiPA, and 62.97% for PA. Furthermore, the study compared the effects of phosphonic acid and phosphonate-based metal-organic frameworks (MOFs) on the corrosion protection of mild steel, highlighting the structural and functional advantages of phosphonate MOFs.

The adsorption experiments were conducted for the removal of dyes, rare earth elements and heavy metals from wastewaters. MOFs effectively adsorbed both anionic and cationic dyes at different pH values. The study further investigates the application of MOFs for the removal of toxic metal ions, such as cesium (Cs(I)) and thallium (Tl(I)), from aqueous solutions. The adsorption capacities of these materials were evaluated by varying the initial concentration of metal ions, while maintaining a solidto-liquid ratio of 1 g/L. Kinetic studies, essential for modeling adsorption rates, determining equilibrium times, and identifying underlying mechanisms such as diffusion or chemisorption were performed. Various type of adsorption isotherms was study to provide insights into adsorbate-adsorbent adsorption capacity, and binding characteristics at varying interactions, concentrations. Thermodynamic studies further assess the spontaneity and feasibility of the process through parameters like Gibbs free energy, enthalpy, and entropy. Together, these analyses contribute to a comprehensive understanding focusing on phosphonate MOFs in water treatment emphasizes their versatility and efficacy in removing pollutants from wastewater. Heavy metal ions, such as Cr(VI), Pb(II) pose significant threats to ecosystems and human health, and thus effective removal strategies are crucial.



The use of MOFs for these purposes is a promising alternative due to their low cost, ease of operation, and efficiency in capturing a wide range of contaminants.

Chapter II is dedicated to discussing the career development opportunities that have emerged for the candidate and her research group Institute of Chemistry "Coriolan Drăgulescu" (ICCD) throughout their academic and scientific future plans. This chapter reflects on the candidate's growth possibilities, outlining the key milestones and opportunities that have shaped their career path in the scientific community.

In conclusion, the research presented is guided by the United Nations (UN) Sustainable Development Goals (SDGs) and the 12 principles of green chemistry. Through systems thinking and interdisciplinary approaches, chemistry plays a crucial role in minimizing human impact and promoting a sustainable future. This thesis aligns with global sustainability efforts and underscores the importance of understanding the environmental implications of chemical processes.