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UNIVERSITATEA DE VEST DIN TIMIŞOARA
DOMENIUL CHIMIE

CERCETĂRI AVANSATE PRIVIND SINTEZA, CARACTERIZAREA ȘI APLICAȚIILE REȚELELOR METAL ORGANICE

REZUMATUL TEZEI DE ABILITARE

CANDIDAT:
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ADVANCED RESEARCH ON THE SYNTHESIS, CHARACTERISATION AND APPLICATIONS OF METAL ORGANIC FRAMEWORKS

ABSTRACT OF THE HABILITATION THESIS

This habilitation thesis presents the scientific, academic and professional research activity of the candidate carried out after the conferral of the title of PhD, for the PhD thesis entitled ,,Theoretical and experimental studies on organic-inorganic hybrids containing element-organic compounds" submitted on 21.10. 2011 at the Romanian Academy, Institute of Chemistry Timisoara, Chemistry field, confirmed by Ministerial Order no. 3818/26.04.2012.

The thesis is structured in three main chapters, as follows: i) Chapter I briefly describes the scientific, professional, academic activity and the main original published scientific results of the candidate in the main research field, i.e., the chemistry of organo phosphorus compounds, metal organic frameworks with the presentation of the current state of knowledge in the field and highlighting the results obtained in this field, referring mainly to the results of the representative papers presented in the candidate's list; ii) Chapter II describes the career development opportunities of the candidate, and iii) Chapter III is the bibliography of the thesis.

The main research direction developed by the candidate after the completion and defense of her PhD thesis includes the synthesis, optimization of reaction conditions, and characterization of novel metal organic networks whose properties are directed towards the successful application of these compounds as adsorbent materials and compounds with anti-corrosive action. Classical and alternative synthesis methods are presented according to their advantages and disadvantages, followed by optimization of the synthesis conditions with the variations of pH, solvent, molar ratio between reactants, reaction time, and temperature.

Chapter I, subchapter I.II., presents the synthesis and characterization of the metal organic frameworks, the organization mode was presented according to the nature of the organic ligand used: monodentate ligands (I.II.3), phosphonocarboxylic ligands (I.II.4), phosphinic ligands (I.II.5) and ligands grafted onto biopolymeric supports such as chitosan (I.II.6). Styrylphosphonic acid was identified as a representative ligand for monodentate ligands (I.II.3), providing the first example described in the literature of a metal organic framework with this ligand. Thus, the copper-based metal organic framework was synthesized and characterized by DTA-TG and FT-IR, and the crystal structure was determined using X-ray diffraction data. From the crystal structure, it was observed that

copper styrylphosphonate exhibits a layered 2D architecture with the organic moieties oriented into the interlamellar space. The inorganic part is composed of Cu^{2+} dimers, and the coordination geometry of the central metal ion is best described by a distorted trigonal bipyramidal geometry. A new class of phosphonate metal organic frameworks is synthesized from vinylphosphonic acid using imidazole or phenanthroline as auxiliary ligands and the trivalent metals cerium and lanthanum. The more porous surfaces of these types of materials, with smaller particles, recommend these types of materials as adsorbents in the removal of metal ions from aqueous solutions.

The influence of phosphonocarboxylic ligands (I.II.4) and phosphinic ligands (I.II.5) on the structure of phosphonic and phosphinic metal-organic frameworks with polydentate ligands has been investigated using as metal centres, transition or alkaline earth metals. The porous structure of the materials was revealed by BET surface analysis. Analyzing a series of phosphonic metal-organic networks having the same metal center, Co^{2+}, the specific surface area decreases in the order Co-Gly > Co-VP > Co-CP. Chitosan, an intensively studied biomacromolecule has shown good performance in the field of wastewater treatment, it has been modified with aminophosphonic groups (I.II.6) and Ni(II) ions (ChitPNi) forming a new adsorbent material to remove heavy metal ions from water.

Chapter I, subchapter I.III, presents adsorption studies of the compounds synthesized and characterized in subchapter I.II. Kinetic and equilibrium studies, as well as thermodynamic studies, were carried out in a batch system on synthetic aqueous solutions to determine the adsorptive properties of the materials analyzed and the adsorption mechanism. Three different series of adsorbents were investigated, namely metal-organic phosphonates, chitosan-based biopolymeric supports, and metal-organic phosphine networks for the retention of heavy metals in wastewater. These materials were used in the removal of heavy metal ions: lead and cadmium. In the case of adsorption of Pb^{2+} ions, the best adsorption capacity was observed in compounds of the type of phosphonic organic metal networks, i.e., phosphines with cobalt as the metal center and carboxyphosphoric/phosphinic acid ligands and heteroelements, which have non-participating electrons, thus increasing the number of active sites on the surface of the adsorbent material. In the case of MOFs containing trivalent metal centers such as cerium and lanthanum, used for the removal of rare metals from aqueous solutions, it is observed that La-based MOFs are more efficient than Ce-based MOFs in the removal of Cs(I) and Tl(I) ions. As these materials also contain imidazole and phenanthroline type co-ligands, it could be concluded that, in addition to physical adsorption on the surface of the studied adsorbents, they are removed from aqueous solutions by chemical attraction to the anions and co-ligands used.

Chapter I, subchapter I.IV. investigates the anti-corrosive properties of MOFs with carboxy phosphonic ligands, phosphinic ligands and corresponding phosphonic acids. For the $Mg(Gly)(H_2O)_2$ inhibitor that also contains a carboxylic group, electrochemical measurements showed that the polarization resistance values increased with the concentration of the inhibitor and reached the maximum value at 2 mM. The corrosion mechanism shows that the anchoring mode of the $Mg(Gly)(H_2O)_2$ metalphosphonate involves coordination of both nitrogen and oxygen from the phosphonic acid and condensation of the carboxylate or P-OH groups with the hydroxyl on the metal surface. In the case of Co-VP and Zn-VP phosphonate metal-organic frameworks, which do not contain carboxylic groups, the metal center is coordinated by four VP ligands via five P-O-Me bonds; the sixth coordination site is occupied by a water molecule; and the vinyl groups are positioned into the interlamellar space. The Co-VP compound is less stable and more prone to hydrolysis than Zn-VP. The mechanism of hydrolysis involves the diffusion of hydrated ions into the vicinity of methylphosphonate molecules, attack by nucleophilic anions, and release of phosphonic acid. Electrochemical determinations showed that Zn-VP exhibits a high corrosion rate at any concentration. For Co-VP, the optimum Co-VP concentration is 2 mM. At this concentration, the amount of phosphonic acid is sufficient to form an adherent and compact protective layer on the metal surface. Since the release of free phosphonic acid by hydrolysis occurs gradually, the effect is delayed and provides self-healing capacity, recommending the successful use and better results of organic metal networks compared to constituent phosphonic acids.

Chapter II presents the perspectives and research directions that will help the candidate's future scientific and professional development. It includes both the continuation of research in identifying new applied research directions and, on the other hand, the extension of the research field through the synthesis of new metal organic networks.