ABSTRACT

In this habilitation thesis, with the title "Development of new variants of synthesis for spinel nanostructures with potential applications in environmental protection", are presented the most important scientific results obtained in the research activity carried out after defending my PhD Thesis (2007). This thesis synthetically presents the results obtained in the field of synthesis, characterization and environmental applications of nanostructured oxides systems, materialized in 38 ISI scientific papers (published after defending the PhD Thesis), out of which at 22 I am the main author.

The main field of my research activity is the synthesis, through original variants of some existing methods, of oxide nanopowders, especially magnetic ferrite nanopowders and their composites, as well as their characterization by techniques appropriate for these types of nanomaterials: Thermal analysis, FT-IR spectroscopy, X-ray diffractometry, Scanning Electronic Microscopy (SEM), EDX spectroscopy, Transmission Electron Microscopy (TEM).

Through the innovative modifications I have applied to well-known synthesis methods (precursor decomposition method, modified sol-gel method, solvotermal method, coprecipitation method), I have opened new perspectives in oxidic nanopowders synthesis, especially that of spinel ferrites ($NiFe_2O_4$, $ZnFe_2O_4$, $MgFe_2O_4$, $MnFe_2O_4$, Fe_3O_4) and their composites with amorphous phases (MFe_2O_4/SiO_2 and MFe_2O_4/C). My research activities have also focused on the use of nanocrystalline spinel ferrite powders (especially the magnetic ones) and their composites in environmental applications, such as the removal of organic pollutants from water through adsorption or oxidative catalytic degradation. The feasibility and originality of the proposed solutions have been validated by the international scientific community, by accepting the publication of the obtained results in ISI-ranked journals in this field.

The thesis is structured in three parts: Part I, in which are presented the main professional, scientific and academic achievements obtained after the granting of PhD title, detailing the representative scientific results, Part II presenting the plan for development of my professional, scientific and academic career, proposed goals and future research directions, and Part III that contains bibliographic references.

The first part of this Habilitation Thesis presents the main professional, scientific and academic achievements obtained after granting the PhD title, as well as a selection and scientific results representative for my activity in the field of development of new variants of synthesis for spinel ferrite nanoparticles with potential environmental applications. It is well known that the reduction in size of ferrite particles to nanometric scale leads to special properties for these materials, different from those of the bulk (micrometric) material. It has also been demonstrated that the chemical and magnetic properties of nanoparticles in general (and in particular spinel ferrites) are strongly influenced by their composition, structure and morphology, which, in turn, are dependent on the synthesis methodology. Hence the importance of developing new synthesis variants by modifying the already known synthesis methods so as to provide the most advanced control over the shape and size of nanoparticles and, implicitly, over their properties. In this context, my research activities on the development of new synthesis variants, focused on four of the synthesis methods employed to obtain nanocrystalline spinel ferrite: the thermal decomposition of the precursors, the solvothermal method, the coprecipitation method and the sol-gel method.

Thus, in the case of the method based on the thermal decomposition of the precursors obtained in the redox reaction between the mixture of nitrates and diols, I have expanded the research by using polyols as reducing agents, such as high molecular weight polyvinyl alcohol. The redox interaction between the mixture of metal nitrates and polyvinyl alcohol, which takes place during a controlled thermal treatment, under well-established conditions described in the thesis, leads to the formation of voluminous, sponge-like precursors, which can be defined as mixtures of carboxylates of the metal cations involved. The controlled thermal decomposition of these precursors at low temperatures (300-400 °C), followed by calcination at higher temperatures, allows the obtaining of ferrite nanopowders with properties characteristic to nanoparticulate systems. Examples presented in the thesis refer to ferrite synthesis: nickel ferrite - $NiFe_2O_4$, magnesium ferrite - $MgFe_2O_4$, zinc ferrite - $ZnFe_2O_4$ and manganese ferrite - $MnFe_2O_4$.

The changes applied to the solvothermal method consist in the use of polyols (1,2 propanediol, polyethylene glycols) as solvents or amines as precipitating agents for the first time in the production of ferrite nanoparticles. The proposed variants of the solvothermal method were used to obtain various oxide systems, in the thesis being presented as case study the obtaining of magnetite/maghemite, and manganese ferrite. This method was also used for the first time to obtain $MnFe_2O_4$/active carbon and Fe_xO_y/active carbon nanocomposites.

The co-precipitation method has been modified by the use of precipitating agents not reported in the literature for magnetite nanopowders; this new variant starts from ferrous sulphate only, and consists in the precipitation of ferrous hydroxide and its slow oxidation under the action of oxygen dissolved in water. This avoids the need for a rigorous control of Fe(II) : Fe(III) molar ratio and for particular working conditions (inert atmosphere).

The sol-gel method for the synthesis of oxide composites like ferrite nanoparticles embedded in silica matrix was modified by using polyvinyl alcohol as a reducing agent, which also modifies the structure of silica matrix. During the controlled thermal treatment of silicagels containing the mixture of metal nitrates and polyvinyl alcohol, the redox interaction between the polyol and the metal nitrates takes place at temperatures between 100 and 150 °C, with formation of the carboxylate type precursors in the silica gels pores. The thermal decomposition of these precursors, followed by calcination at high temperatures, leads to the formation of MFe_2O_4/SiO_2 composites. In the thesis, the synthesis of $ZnFe_2O_4/SiO_2$, $CuFe_2O_4/SiO_2$, $NiFe_2O_4/SiO_2$ and $MnFe_2O_4/SiO_2$ composites was presented.

An important chapter included in the scientific part of this thesis is the testing of MFe_2O_4/active carbon composites (M = Fe(II), Mn(II)) for the removal of organic pollutants (phenol, organic dyes) from water. These composites combine the high specific surface area of the activated carbon (which gives the composites high adsorption capacity) with the magnetic properties of ferrite nanopowders, which ensure a simple separation of the composite from the suspension.

The second part of this thesis presents the evolution and development plan of the professional, scientific and academic career, the proposed objectives and the future research directions.

The Habilitation Thesis ends with 303 bibliographic references.