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INSTITUTE OF PHYSICAL CHEMISTRY "ILIE MURGULESCU"

PhD THESIS SUMMARY

STRUCTURED OXIDE NANOMATERIALS WITH CATALYTIC AND PHOTOCATALYTIC PROPERTIES OR AS SUPPORT IN HYBRID OR BIOHYBRID CATALYSTS SYNTHESIS

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CONTENT

Keywords: mesoporous silica, MCM-41, MCM-48, SBA-15, KIT-6, Fe_2O_3-TiO_2, mesoporous mixed oxides, transitional metals, Pt, Ti, surfactants, hydrothermal treatment, immobilization, organometallic complexes, Schiff-base ligands, catalysts, photocatalysts, immobilised enzymes, immobilised thylakoids, photocatalytic degradation, oxidation catalyst, organic impurities, liquid phase reaction tests, gas phase reaction tests, photocells electrode materials, magnetic properties, structural properties, optical properties.

INTRODUCTION

The applicative importance of oxide nanomaterials is determined by the fact that can be used in a wide range of applications in many fields such as electronics, agriculture, construction, medicine, pharmacy and not least environmental protection, due to the unique properties dependent on the size and porous structure of nanoparticles.

The literature shows that the specific properties of oxides nanomaterials are directly correlated with the composition, morphology and particle size, porosity, and optical characteristics.

In order to bring original contributions to the proposed subject, within the present thesis was realized the development of knowledge in an area of great interest, of mesostructured oxides based nanomaterials with applications in energy, biomedical and pollution reduction, used to fabric hybrid solar cells, drugs delivery and photocatalysts for the degradation of environmental pollutants. This research is based on the multiple possibilities of applications for these materials.

The main aim of this thesis was the development, characterization and optimization of new hybrid and biohybrid materials based on structured oxide nanomaterials in order to obtain catalysts and biocatalysts used in oxidation processes with applications in environmental remediation or fabrication of eletrodes in hybrid solar cells.

The main objectives that led to the experimental study were:

- Preparation of oxide nanomaterials with a porous structure and controlled morphology using hydrothermal treatment assisted by surfactants synthesis.
- Preparation of composite, hybrid and biohybrid materials with catalytic, photocatalytic and biophotocatalytic properties obtained by functionalization of oxide nanomaterials.
- Preparation of bi and trimetallic catalysts with catalytic properties in liquid or gaseous phase oxidation processes.
- The correlation of synthesis methods used on structural, textural, magnetic, electrochemical and catalytic properties of the obtained materials.
- Study of the surface functionalization effects on the properties of hybrid or biohybrid obtained catalysts.
- Study of the inorganic or composite support effect on immobilized biocompounds properties.

Thesis structure:

The first part of the thesis (Chapter I) contains the systematized data from literature regarding the preparation, characterization and the use of oxide nanomaterials. The specific characteristics and diversity of application areas highlighted in the literature led us to study them.

The second part contains the results of original research performed in order to obtain new structured oxide materials with catalytic and photocatalytic properties or used as support to obtain hybrid and biohybrid catalysts with application in the field of materials.

Thus, **Chapter II** is a comparative study of synthesis methods for mesoporous silica supports with controlled porous structure obtained by hydrothermal treatment assisted by surfactants. MCM-41 mesostructured silica supports were synthesized by methods published in literature, and MCM-48, SBA-15 and KIT-6, using our methods of synthesis. Properties of the obtained mesoporous silicas were compared.

In addition to silica-based oxides were synthesized, in presence of surfactants and hydrothermal treatment, mixed oxide based of iron and titanium. Were used different types of surfactants, anionic, cationic and non-ionic. Mixed oxides of iron and titanium have been used for the production of composite materials with conductive polymers (polyaniline, polypyrrole), which were meant to be used as a support for the immobilization of enzymes and photosensitive bioentities used in foto-bioelectric cells.

The properties of obtained material were highlighted by different characterization methods: elemental analysis, adsorption-desorption of nitrogen, X-ray diffraction (XRD), UV-Vis, IR (FTIR), Raman and XPS, scanning electron microscopy SEM transmission and TEM. The typical structure of mesoporous materials with ordered hexagonal structure (MCM-41, SBA-15) or cubic (MCM-48, KIT6) and the morphology with a narrow particle size distribution of Fe_2O_3-TiO_2 oxide nanoparticles were presented. The effect of surfactant type used it was also shown correlated with the properties of oxide nanoparticles (magnetic properties, crystalline structure, shape and size of the particles, band gap energy, etc.).

Chapter III presents in comparison the effects of synthesis method on the properties of catalysts. The importance of preparation conditions was highlighted: thermal treatment, diversity of surfactants, immobilized metal etc.

There are provided new materials based on silicon dioxide powder with of transition metal oxides (Pt, Ti, Fe) and doped with noble metal ions (Pt) and of rare earth elements (Ce). Doping SiO_2 allowed their successful use as photocatalysts in degradation of dyes (methyl orange) due to the optical and morpho-structural properties of these powders, degradation of organic compounds that are normally found in wastewaters (phenol) and of hydrocarbons.

The materials obtained have been characterized by specific methods: surface area and porosity BET, X-ray diffraction - XRD, UV-Vis spectroscopy, infrared absorption spectroscopy (FTIR), scanning electron microscopy SEM and transmission TEM, elemental analysis, and photocatalytic activity evaluation was performed by the catalytic reaction using gas chromatography measurements and UV-Vis spectroscopy.

In **Chapter IV** was presented the production of hybrid and biohybrid catalysts and the evaluation of their activity. The hybrid catalysts were obtained by formation of organometallic Cu (II) and Mn (II) complexes with Schiff- base ligands supported of functionalized mesoporous silica and biohybrid catalysts were obtained by functionalization of mesostructured silica supports and immobilization of enzymes (laccase), and by immobilizing enzymes (bilirubin- oxidase) or photosensitive bioentities (thylakoid) on nanoparticles of iron oxide and titanium and composite materials with conducting polymers and Fe and Ti oxide nanoparticles.

Biohybrid materials were characterized by X-ray diffraction, thermal analysis, nitrogen adsorption-desorption, IR, UV-Vis-NIR, Raman and XPS, SEM, TEM and confocal fluorescence. The efficiency of immobilization was investigated with a confocal fluorescence microscope, and the enzymatic activity of the hybrid material was monitored in a Clark-cell, by measuring the rate of oxygen production in the presence of an artificial electron acceptor. The production of oxygen under a light source was used as an indicator of enzymatic activity and photochemical conversion efficiency of the hybrid materials.

The catalytic activity of Cu(II) and Mn(II) complexes with Schiff- base ligands obtained in-situ from aldehydes and ketones was proven in oxidation reaction of organic compounds (cyclohexene, benzyl alcohol, 1-buten-3-ol, 2-methylpropan-1-ol)

Thesis approaches a variety of inorganic oxide nanomaterials or hybrid with different applications both in catalytic processes, photocatalytic or photo-electrocatalytic as active and as support material. For this purpose has been synthesized and studied materials and processes of current interest both scientifically and practical.

Experimental results and discussion:

Mesostructured mixed oxide with catalytic and photocatalytic properties

Mesoporous silicas were obtained and characterized with hexagonal structure (2D), MCM-41 or SBA-15 type and (3D) structure, MCM-48, KIT-6, respectively.

The incorporation of metals in ordered mesoporous structure network allowed to obtain highly active and selective catalysts in oxidation reactions in the liquid phase and gaseous of organic compounds. The catalytic activity in most cases was the result of functionalization of mesoporous siliceous sieves with transition metal ions by incorporating them in the network or directly on the surface.

Were prepared new materials based on silica mesoporous oxides with transition metals (Ti, Fe) and doped with noble metal ions (Pt) and ions of rare earth elements (Ce). Doping SiO_2 allowed their successful use as photocatalysts in degradation of dyes (methyl orange) due to the optical and morpho-structural properties of these powders, degradation of organic compounds that are normally found in wastewaters (phenol) and of hydrocarbons.

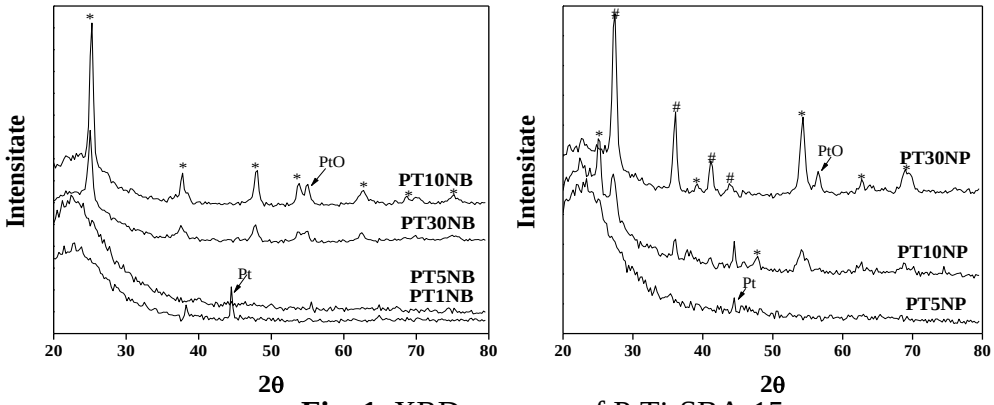

Fig. 1. XRD patterns of PtTi-SBA-15

Ti-SBA-15 materials were synthesized using different methods (using butoxide or peroxotitanate as source of titanium), different amounts of titanium but the same source of silicon (TEOS). Bi-metal hybrid materials were obtained by impregnation method using an aqueous solution of hexachloroplatinic acid or a solution of iron nitrate nonahydrate. Crystalline phases of anatase and rutile were detected by X-ray diffraction and are shown in Figure 1.

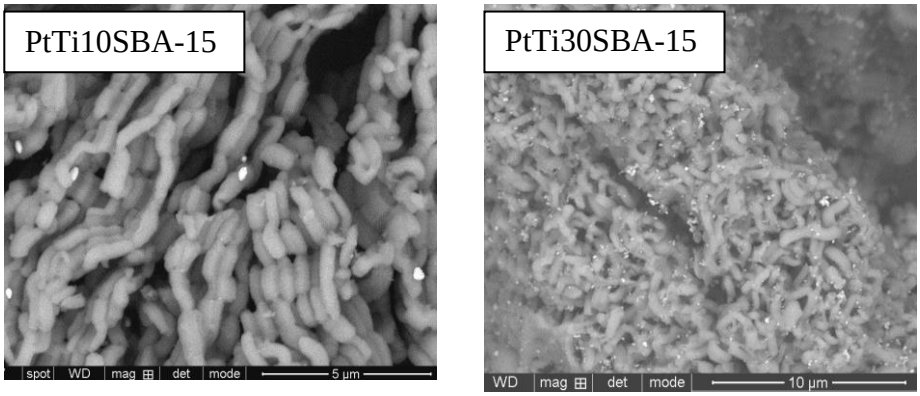

Fig. 2. SEM images of PtTi-SBA-15

SEM images (Fig. 2) revealed that the typical morphology of these materials was preserved, it shown a rod-like morphology and a high dispersion of platinum on the surface of materials.

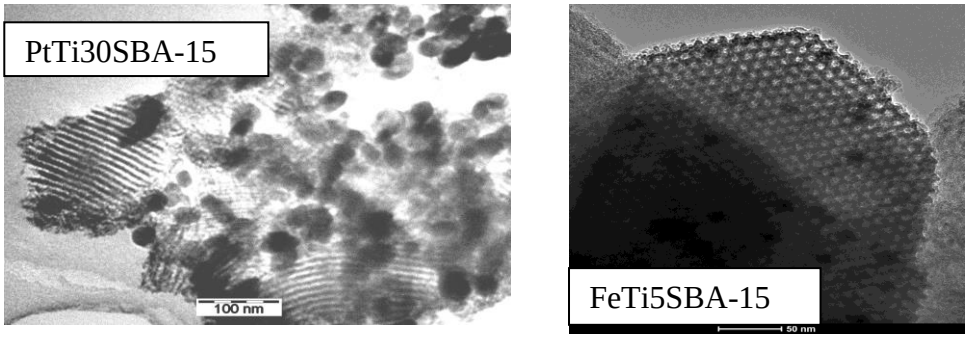

Fig. 3. TEM images of PtTi-SBA-15 şi FeTi-SBA-15

TEM images of materials (Fig. 3) showed the hexagonal symmetry preservation, nanometric particle size, the presence of mesoporous channels and metals immobilization efficiency.

Band gap energy values of Fe-SBA-15 samples are listed in Table 1 and show a shift to lower values with the introduction of Fe^{3+}, which reveals the photoresponsive behavior in the visible region

compared to Ti-SBA-15 which have higher band gap energy values, approx.~ 3.5 that indicates an increased activity in UV region.

Table 1. Band gap energy data of Ti-SBA-15 and FeTi-SBA-15

Proba	DBTS	DPTS	BITS	PITS	DBTFS	DPTFS	BITFS	PITFS	PTFS
Band gap energy (eV)	3.75	2.97	3.64	3.22	1.63	1.66	1.63	1.65	1.66

Ti-SBA-15 and PtTi-SBA-15 materials were tested in oxidation reactions of cyclohexene with hydrogen peroxide under UV radiation (λ = 254 nm) and in dark. Bi and trimetallic catalysts based on Pt, Ti, Ce immobilized on SBA-15 and KIT-6 are active in the oxidation reaction of methane. For the samples without platinum the activity is significant in the presence of titanium as oxide (rutile or anatase).

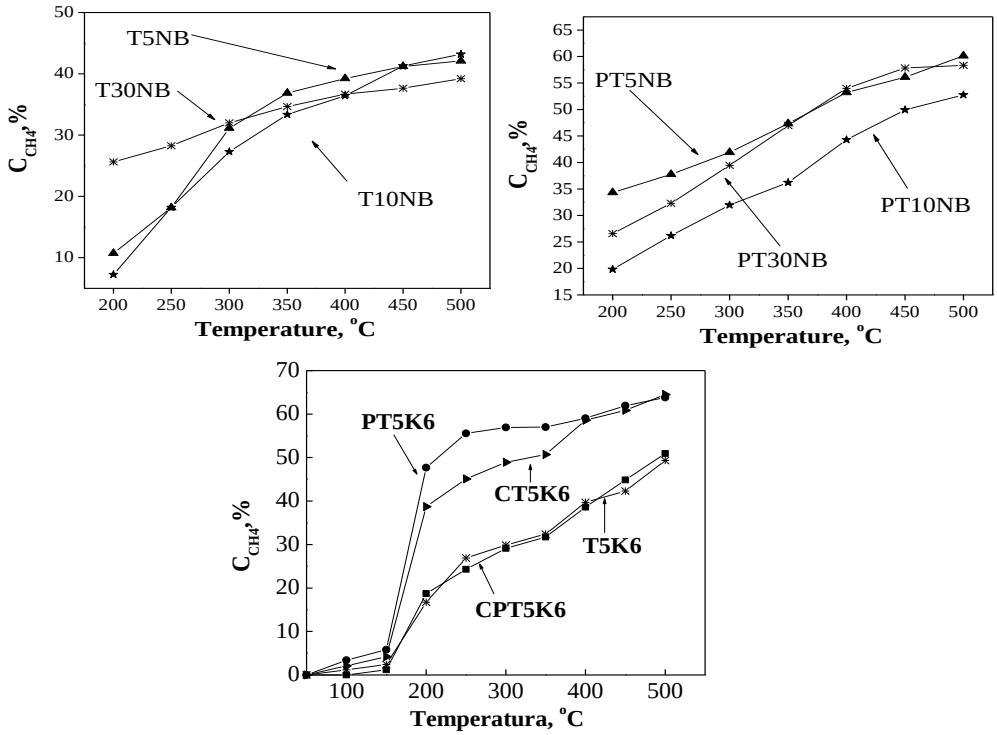

Fig. 4. The effect of the composition and concentration of samples in the catalytic oxidation of methane

In a first step, the effect of titanium concentration on the catalytic activity on methane oxidation was followed the same as the addition effect of other metal on the catalytic activity in methane oxidation (Fig. 4).

Photocatalytic activity of Ti-SBA-15, Fe-SBA-15 was tested by measuring the degradation degree of methyl orange in the presence of visible and UV radiation with the wavelength of 254 nm (Fig. 5).

For Ti-SBA-15, FeTi-SBA-15 samples is observed an increase in degradation efficiency of MO solution under UV materials obtained by impregnation.

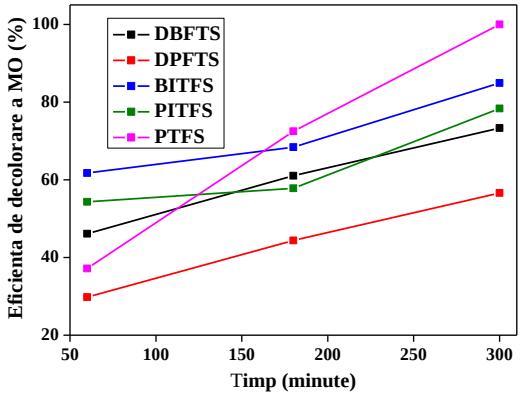

Fig. 5. Influence of catalyst composition on MO 1 * 10^{-5} M degradation versus time (UV-254 nm, t=60, 180, 300 min, m cat.=1 mg)

Hybrid and bio hybrid materials obtained by organometallic complexes and enzyme immobilization on oxide nanomaterials

Surface modification was performed on mesoporous materials SBA-15, MCM-41 and MCM-48 with organic functional groups using 3-aminopropyltriethoxysilane (APTS) and 3-glycidoxypropyltrimethoxysilane (GPTMS).

As a result of functionalization has been observed the preservation of characteristics in a higher percentage for SBA-15 and MCM-48, these two supports have been used for the immobilization of laccase by adsorption and covalent linking.

The amount of protein immobilized in different supports was determined by thermogravimetric analysis TG / DTA. Best yields were obtained for covalent immobilization on functionalized SBA-15 with amino or epoxy groups. Introduction of $-NH_2$ group and glutaraldehyde coupling or the introduction of glycine on the internal surface of the pores lead to an increase in the amount of immobilized enzyme may be due to stronger interactions between the functional groups of the enzyme ($-NH^2$, -COOH, -OH, -SH) and the surface of the substrate.

Hybrid mesoporous materials obtained by covalent attachment of Cu(II) and Mn(II) Schiff base complexes on amino-modified mesoporous silicas

The supported Cu (II) and Mn (II) complexes with Schiff base ligands were synthesized in three steps: (i) post-synthesis functionalization of mesoporous silica supports with APTES, (ii) Schiff base grafting onto the amino-functionalized silica supports and (iii) in-situ formation of the metal complexes.

The Schiff base was synthesized by the in situ condensation of an aldehyde or a ketone onto the amino-functionalized silica supports.

The elemental analysis confirmed that between 39-89% of the aminopropyl groups grafted on the silica support surface participated in the Schiff base synthesis by condensation with the corresponding

aldehyde or ketone and small angle XRD patterns, before and after functionalization with amino group, show typically peaks for these materials.

Textural parameters of the metal complexes immobilized on mesoporous supports were lower than mesoporous supports, these results confirmed the location of the complexes within the mesopore not only on the outer surface.

Activitatea catalitică a complecșilor de Cu(II) și Mn(III) cu baze Schiff derivate de la 2-furanaldehidă (Fur), 2-hidroxi-acetilfenolul (Hyd) sau 2-furilmetilcetonă (Met), imobilizați pe diferiți suporți de silice funcționalizați a fost evaluată prin reacții de oxidare a compușilor organici.

The catalytic activity of Cu(II) and Mn(II) complexes with Schiff base ligands obtained in-situ from 2-furylmethylketone, 2-furaldehyde and 2-hydroxyacetopheneone covalently attached to amino-functionalized mesoporous silica materials was proven in oxidation reaction of organic compounds.

Synthesis and characterization of Fe_2O_3/TiO_2 mixed oxides used as support

Fe_2O_3/TiO_2 nanoparticles were synthesized by hydrothermal treatment in presence of surfactants. Different types of anionic, cationic and nonionic surfactants were used in order to obtain Fe_2O_3/TiO_2 mixed oxides. To characterize the nanoparticles were used the following: N_2 adsorption/desorption isotherms, powder X-ray diffractometer (XRD), thermogravimetric analysis, UV–Vis diffuse reflectance spectroscopy, IR, Raman, XPS, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), confocal fluorescence microscopy.

The overall crystallinity and purity of Fe_2O_3/ TiO_2 samples were investigated by the wide-angle X-ray powder diffraction (XRD). As shown in Figure 6 , the indexed diffraction peaks by "#" and "o" symbols in the XRD pattern confirm the presence of rhombohedral α-Fe_2O_3 and TiO_2 rutile. The effect of surfactant on oxide structure was evidenced.

TEM images (Fig. 4) sustain the existence of mesopores, formation of nanoparticles(2-20 nm) , their uniformity of the particles, their spherical or ellipsoidal symmetry.

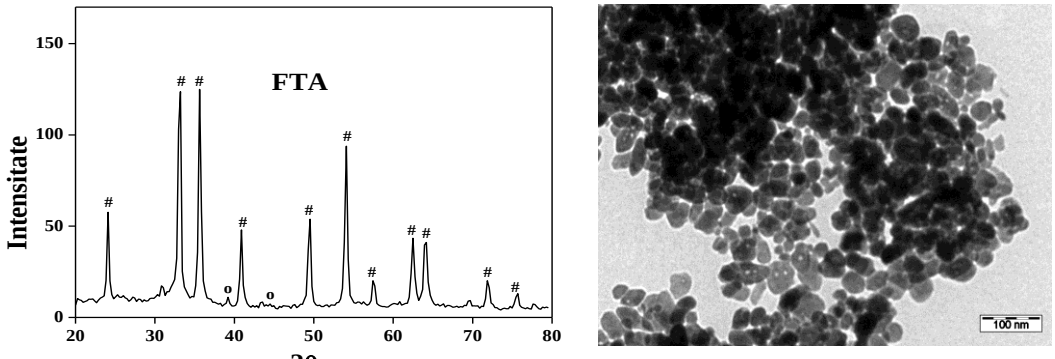

Fig. 6. X-ray diffractogram TEM image of Fe_2O_3/TiO_2 (FTA sample was synthesized using dodecylsulfate sodium salt anionic surfactant)

UV–Vis absorption results of Fe_2O_3–TiO_2 samples exhibited not only stronger absorption in the ultraviolet region of less than 400 nm but also adequate and strong absorption in the visible light

region of 400–700 nm. It indicates that the Fe_2O_3–TiO_2 composites can also be used under visible light. During the synthesis of the composite, Fe^{3+} was doped with the TiO_2 lattice, which moved up its valence band. This led to the reduction of the band gap. The presence of this narrow band gap semiconductor, as well as the reduced TiO_2 band gap, greatly ameliorated the light absorption properties of the Fe_2O_3–TiO_2 composite, and enabled the absorption of visible light.

The mechanism of formation processes of iron and titanium mixed oxides was proposed. (Fig. 7). The organization of the species in the aqueous medium was determined by surfactants organization, the species nature present in the outer layer of micelles, the nature of metallic species in the aqueous medium and their interactions.

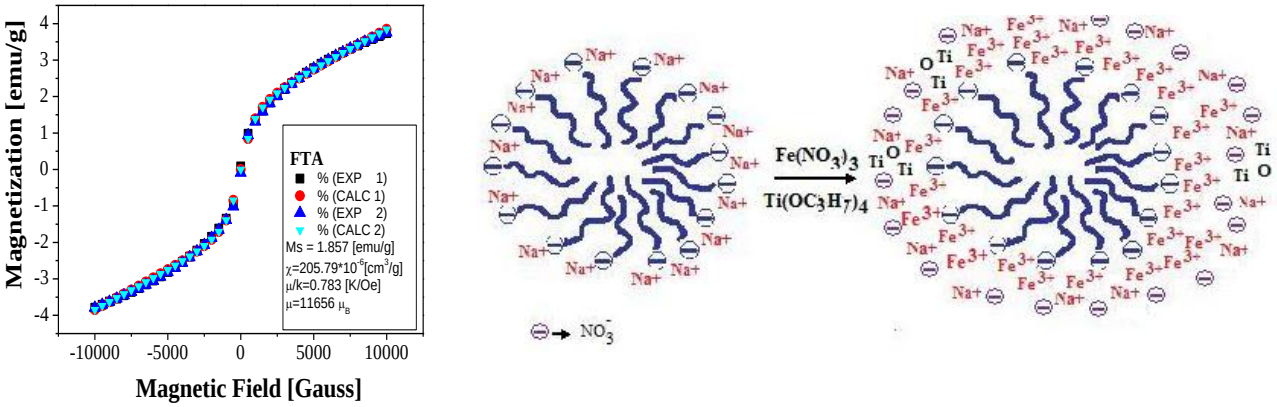

Fig. 7. Magnetic field dependence of isotherm magnetization and mechanism of formation processes for FTA sample

In conclusion, different surfactants used induced different organization forms of the metallic species, a different distribution on the surface area and volume and the formation of mixed oxides with different magnetic and structural properties.

Nanooxide materials based on iron and titanium, obtained by surfactant assisted hydrothermal treatment were used as supports for the immobilization of enzymes and photosensitive bioentities.

In order to prepare electroactive composite membranes were used polyaniline, polypyrrole and chitosan as polymers. In addition to these Fe_2O_3/TiO_2 mixed oxides nanoparticles were added.

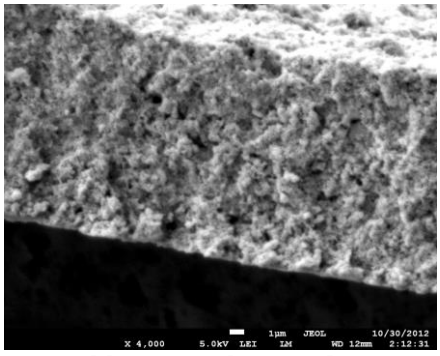

Fig. 8. SEM micrographs of the cross-sectional morphology of CHIT/PANI

In addition to these polymers a number of organic - inorganic membranes were prepared based on chitosan and metal oxides nanoparticles.

Biohybrid material obtained by immobilizing biocompound on o Fe and Ti mixed nanoxides and conductive composite films

Thylakoid membranes represent the chloroplast membrane in plant leaves, responsible for the light-dependent reactions of photosynthesis process that converts solar energy into chemical energy. Thylakoids and whole chloroplasts are not stable in their isolated state. Therefore, one way to exploit the photosynthetic properties is to develop hybrid systems incorporating biological species that provides protection while maintaining the biological activity.

Chloroplasts membranes were isolated from spinach leaves using literature data.

The immobilization was made through adsorption and covalent binding on composites membranes and Fe_2O_3/TiO_2 nanoparticles.

Immobilization efficiency was investigated with a confocal fluorescence microscope. Thus, it is seen that the cell activity after immobilization is kept. If the cells had died after immobilization process, the material would be presented fluorescence. (Fig. 9).

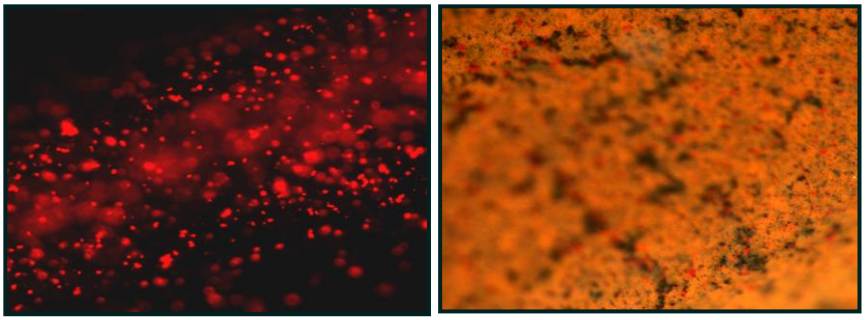

Fig. 9. Analysis of thylakoids immobilization on Fe_2O_3-TiO_2 (FTS)/CHIT/PANI films by confocal fluorescence microscopy (left) and bright field (right**)**

The enzymatic activity of the hybrid materials was monitored in a Clark cell vessel, by measuring the rate of oxygen production in the presence of an artificial electron acceptor. Production of oxygen under a light source is an indicator of enzymatic activity and photochemical conversion efficiency of hybrid materials. This was measured by comparing the activity of the suspended and immobilized thylakoids (Fig. 10).

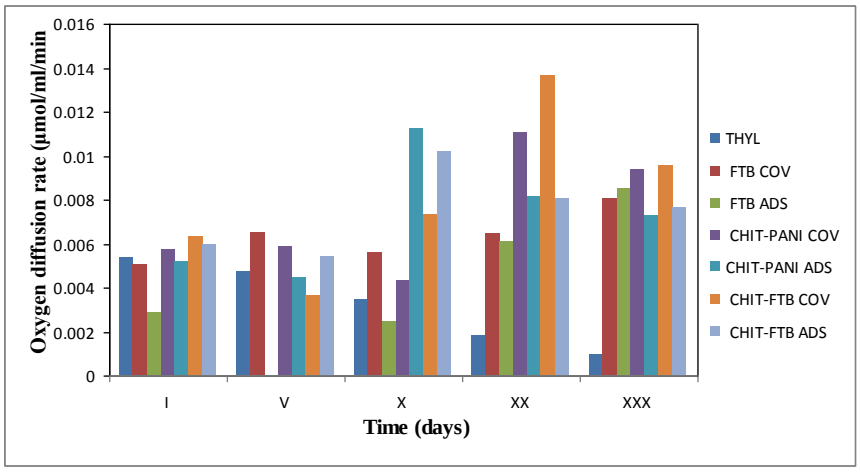

Fig. 10. Variation of oxygen difusion rate(µmol/ml/min) for immobilised thylakoids

Figure 10 shows that hybrid materials are capable of producing oxygen for over a month. It is observed that immobilized thylakoids show a higher activity than the thylakoids in suspesion.

GENERAL CONCLUSIONS

- A comparative study of the properties for the representatives ordered mesoporous silicas, MCM-41, MCM-48, SBA-15 and KIT-6 was made, aiming the characteristics of the porous structure and opportunities for functionalization of their surface, obtaining new methods of synthesis for mesoporous silica MCM-48 and SBA-15.

- Textural and structural properties of these materials were controlled by varying the synthesis parameters: the molar ratio surfactant / silica source, pH, temperature, ionic strength, co-solvent, hydrothermal treatment and post-synthesis treatment.

- All the synthesized materials were characterized by a variety of methods such as X-ray diffraction (small-angle and wide-angle), the adsorption-desorption of nitrogen, SEM and TEM microscopy, EDX, XPS, XAS, XRF, FTIR, UV-Vis, Raman spectroscopy, thermal analysis, atomic absorption, magnetometry.

- Effects of the synthesis method and introduction of metals were evidenced on catalysts properties.

- The results highlighted the effect of synthesis method (titanium immobilization), the concentration of titanium and the second metal (platinum) on catalytic performance. PtTi-SBA-15 catalysts were also tested in methane oxidation in air putting into evidence the composition and method of synthesis on the catalytic activity.
- Ti-SBA-15 și PtTi-SBA-15 catalysts were obtained with activity in catalytic and photocatalytic cyclohexene oxidation.
- Photocatalysts FeTi-SBA-15 were active in both reaction of phenol and methyl orange degradation found as impurities in water, so the obtained materials can be used in photocatalytic processes for water remediation both in presence of visible and UV radiation.
- Ti-MCM-48 and CeTi-MCM-48 were tested in phenol and methyl orange degradation, present as impurity in aqueous solutions in the presence of UV radiation.
- Catalytic properties of Ti-KIT-6 and iCeTi-KIT-6, iPtTi-KIT-6 și CePtTi-KIT-6 were tested by gas phase oxidation of methane and CO in air.
- Hybrid materials complexes of Cu(II) and Mn(II) with Schiff base ligands were catalytically active in oxidation reaction of organic compounds (cyclohexene and alcohols)
- Fe_2O_3-TiO_2 nanoparticles were obtained by hydrothermal treatment in the presence of ionic or nonionic surfactants.

- Thin electroactive composite films were prepared and characterized by conductor polymers (aniline, polypyrrole) synthesis in a mixture of oxide powder and a flexible polymer (chitosan).
- For immobilized thylakoid and enzymes, the variation of activity after immobilization was studied and is showed an increased activity and life time.
- New supports were obtained for bilirubin oxidase and thylakoids with photocatalytic and conductive properties were obtained in order to produce hybrid materials with typical properties for bioelectrodes.