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PhD Thesis Abstract

STRUCTURAL STUDIES BY SPECTROSCOPIC METHODS OF NANOSTRUCTURED OXID SYSTEMS

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CONTENTS

1. INTRODUCERE

1. INTRODUCTION

The term nano refers to dimensions in the order of 10^{-9} m, nanomaterials designating those materials that have at least one nanometric dimension (1-100 nm).

According to Siegel, quoted by [1], nanomaterials can be divided into zerodimensional, one-dimensional, two-dimensional and three-dimensional. Zero-dimensional nanostructures or nanoparticles can be obtained in a wide variety of morphologies and include monocrystalline, polycrystalline or amorphous particles; one-dimensional nanomaterials can be presented as nanofire, nanofibres, nanocabbles and nanotubes, and two-dimensional nanostructures are films. 3D nanostructures refer to block materials.

From the category of nanostructured materials, metallic oxides, due to their unique properties such as chemical, thermal, electrical, optical, mechanical, magnetic and morphological (high specific surface), have applications in microelectronics, catalysis, ceramic industry, energy storage, water treatment medical technology, environmental detoxification and personal care products, being used in a wide variety of fields [2, 3].

The most used methods for the synthesis of oxide nanomaterials are in liquid phase, such as sol-gel method, precipitation/co-precipitation method, microemulsion method, sonochimic method, hydrothermal/solvotermal method, microwave synthesis, electrochemical synthesis, template synthesis etc.

The liquid phase synthesis presents a number of advantages: low temperature of production, homogeneous mixing of precursors at molecular scale with obtaining of metastable materials, design and control of the physico-chemical properties of the final oxidic nanomaterials (particle size, shape, surface properties) depending on the precursors used. However, there are some drawbacks, including the fact that it requires expensive precursors and high synthesis times.

The thesis will present researches on the preparation of mono- and polycomponente oxide systems as well as of nanocomposites by the sol-gel method and the specroscopic characterization of the synthesized samples.

2. ORIGINAL CONTRIBUTIONS

2.1. OBJECTIVES OF THESIS

The main objective of the PhD thesis is the characterization by spectroscopic methods of the nanostructured oxide systems obtained by chemical methods, especially, the sol-gel method.

Due to the fact that using the sol-gel method, in the first step, usually, amorphous materials are obtained, their structural characterization can be done, mainly in this phase, by spectroscopic methods.

As spectroscopic methods of characterization, the infrared spectroscopy was mostly used and the results were correlated with those obtained by other methods of investigation, mainly, scanning electron microscopy (SEM), thermal analysis (TG/ATD) X-ray diffraction (XRD), photoluminescence spectroscopy (PL).

In the thesis, both the structural characterization of the as-prepared–materials and their transformation through appropriate heat treatments in crystallized materials were investigated.

For the beginning, the results obtained in SiO_2 polycomponent systems were presented (chapter 3.3.1, in the Thesis).

Systems containing high amounts of SiO_2 were selected, this oxide being the mostly studied from the point of view of FT-IR spectroscopy.

The study aimed to establishing the phase formation in binary and ternary SiO_2-TiO_2, SiO_2-TiO_2-Al_2O_3, type systems, un-doped and doped with Er^{3+} that are of interest for obtaining waveguides. The researches presented in the thesis referred in particular to the determination of phase formation by thermal treatments at different temperatures and to the influence of the formed phases on their optical properties.

Further, oxide systems based on TiO_2, MgO and Al_2O_3 were studied, with possible applications as adsorbents or catalysts. The study of phase formation in binary systems of TiO_2-MgO and TiO_2-Al_2O_3, as well as the influence of dopants on phase formation in the Ni-doped Al_2O_3 system has been also approached (chapters 3.3.2, 3.3.3 and 3.3.4. in the Thesis).

The last oxide system approached was the binary system V_2O_5-CeO_2, which has anticorrosive properties. In this case a comparative phase formation study was performed in the presence and absence of chelating agents in aqueous medium (Chapter 3.3.5, in the Thesis).

In addition to the oxide systems mentioned above, nanocomposite systems formed from SiO_2 matrices, obtained from different precursors (tetraethoxy silane, colloidal silica and sodium silicate) doped with cyclodextrins and pesticides were studied (Chapter 3.3.6, in the Thesis).

Based on the results obtained in all studied systems, it was proposed to develop a spectral data base for the oxide compounds obtained by the sol-gel method, according to the examples presented in the Annex.

3. STUDIED OXID SYSTEMS

3.1. OXIDE POWDERS IN THE SiO_2-TiO_2 and SiO_2-TiO_2-Al_2O_3 systms

The SiO_2-TiO_2 binary system is one of the most studied systems for producing photoluminescent materials. For this purpose, different ratios between oxides, several synthesis processes and different thermal treatments, as well as doping with transition metal ions are used.

In previous studies, films in silica-titanium oxide or silica-titanium oxide- alumina systems doped with Er^{3+} with molar compositions of 90% SiO_2-10% TiO_2 or 85% SiO_2-10% TiO_2–Al_2O_3 and Er_2O_3 0.5% for waveguide applications were prepared. The solutions used for deposition of the films were prepared by the sol-gel method. The sol-gel method has been selected because it is one of the most flexible and convenient methods of preparing films and nanopowders.

It has been observed that the presence of Al^{3+} in mentioned compositions increased the homogeneous distribution of Er^{3+} in the samples, but diminished their chemical stability. In order to explain this behavior, a comparative study of the phase formation in the gels resulted from the solutions used for film deposition was investigated in the thesis [4].

In the present chapter of the thesis the results obtained regarding the formation of phases in SiO_2-TiO_2 and SiO_2-TiO_2-Al_2O_3 systems, simple and doped with Er^{3+} are presented [5].

The FT-IR spectra of the obtained gels are shown in Figure 1 and the assignment of the absorption bands is summarized in Table 1.

Broad bands between 3500 cm^{-1} and 3200 cm^{-1} indicate the presence of hydroxyl groups.

The band around 1378 cm^{-1} is attributed to NO_3 vibrations from the HNO_3 composition, introduced into the reaction mixture as a catalyst, and the band at 1626 cm^{-1} is attributed to molecular water bend vibration.

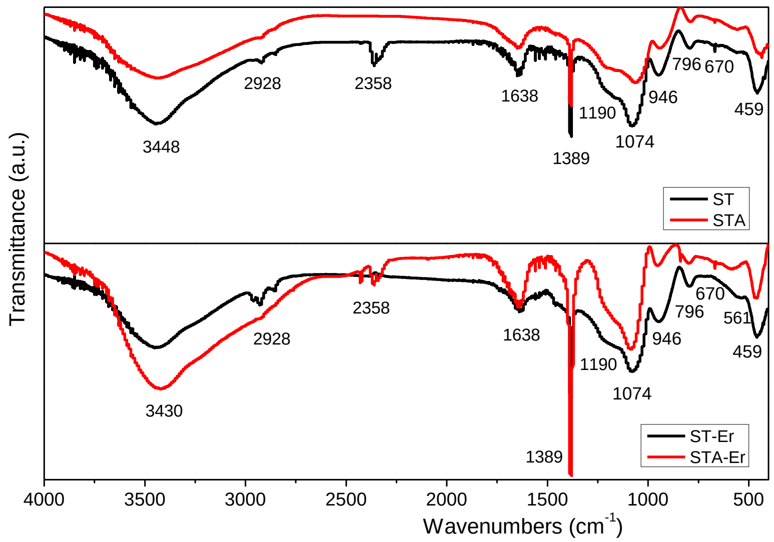


Fig.1. FT-IR spectra of as-synthesis gels

The bands around 2850-2920 cm^{-1} are attributed to organic residues due to the reagents used in the reaction (alkoxides) and to the alcohol used as the solvent.

The band around 1085 cm^{-1} is attributed to Si-O-Si vibration of asymmetric stretching in amorphous SiO_2. The band at 940 cm^{-1} indicates the presence of Si-OH stretching vibration band. The band around 459 cm^{-1} is attributed to Si-O-Si vibrations and in the Si-Ti-Al sample the presence of Al-O vibration is shown.

The FT-IR spectra of the heat-treated powders are shown in Fig. 2a for the temperature of 500 °C and in Fig. 2b for the temperature of 900°C, and the assignment of the absorption bands are summarized in Table 2.

As compared to gels resulted from the synthesis, in the thermally treated samples the intensities of the vibration bands of the hydroxyl groups, of the adsorbed water and of the molecular water as well as of the NO_3 group decrease.

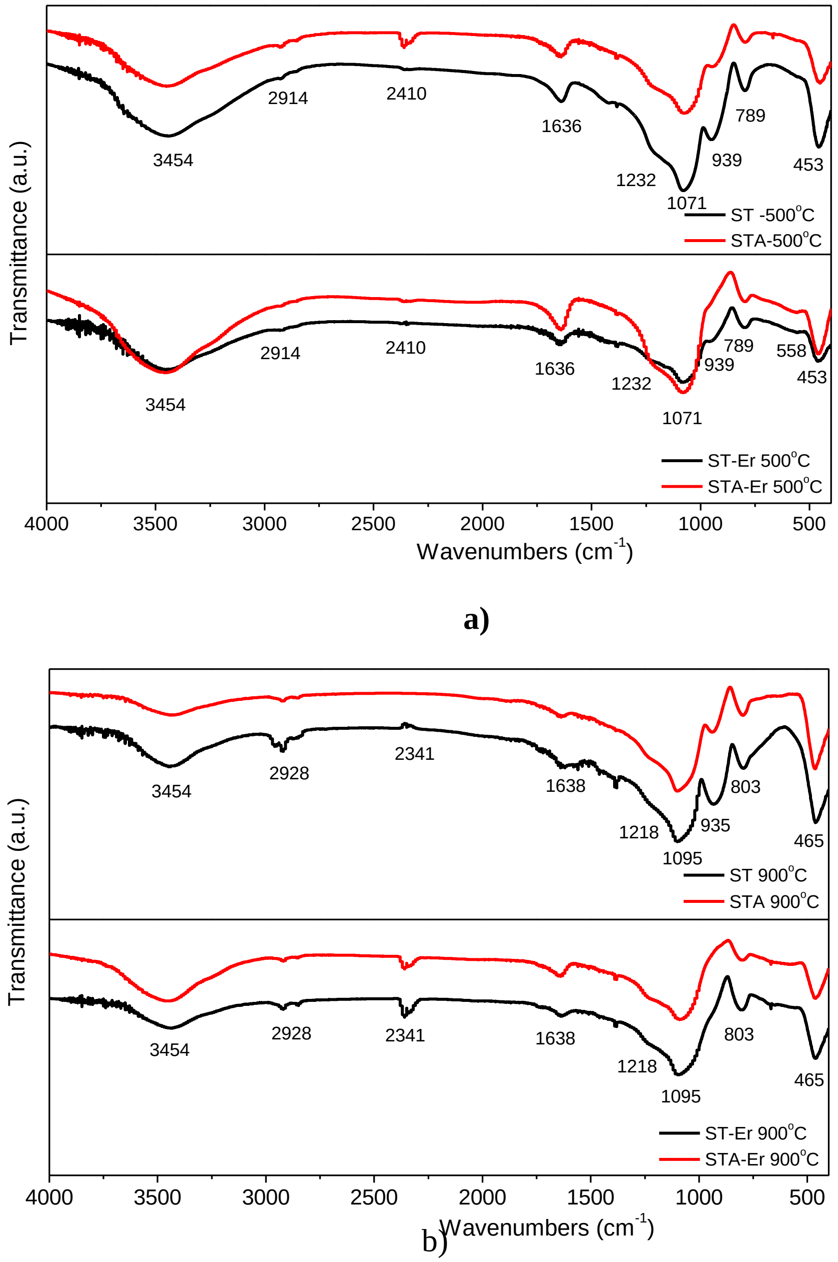
Table 1. Assignment of vibrations of as-synthesis gels in the un-doped and Er $^{3+}$doped SiO_2-TiO_2 and SiO_2-TiO_2-Al_2O_3 systems

Samples				Assignment
ST	ST-Er	STA	STA -Er	
471	459	435	459	Si-O-Si
585	587	561	561	Ti-O, Al-O, Ti-O-Al
787	767	794	800	Si-O-Si symmetrical stretching in amorphous SiO2
940	962	927	953	Si-OH, stretching vibration
1062	1085	1059	1062	Si-O-Si asymmetric stretching in SiO2 amorphous Al-O-Al
1190	1190	1190	1190	Si-O-Si, LO mode asymmetrical stretching in SiO_2 amorf
1375	1386	1372	1386	ν NO_3
1633	1633	1641	1633	ν_s (OH) in H_2O in water
2865	2854	2842	2847	ν_{as}(CH)
2913	2924	2914	2913	ν_{as} (CH_3)
3441	3441	3436	3427	ν_{as} (OH)adsorbed water (OH)

Table 2. Assignment of vibration bands of oxide powders in the un-doped and Er $^{3+}$doped SiO_2-TiO_2 and SiO_2-TiO_2-Al $_2O_3$ systems thermally treated at 500 °C and 900 °C

Samples								Assignment
ST	ST-Er	STA	STA-Er	ST	ST-Er	STA	STA-Er	
455	453	456	465	461	461	460	461	Si-O-Si
790	796	790	799	799	805	795	795	Si-O-Si symmetrical stretching in amorphous SiO_2
943	950	939	943	929	929	935	929	ν_{as} Si-O(H),
1071	1071	1071	1071	1095	1095	1095	1095	Si-O-Si asymmetric stretch in amorphous SiO_2
1232	1232	1232	1232	1218	1218	1218	1218	Si-O-Si, LO mode of asymmetrical stretching in amorphous SiO2
1391	1382	1382	1391	1378	1388	1383	1378	νNO_3
1640	1637	1640	1640	1637	1636	1634	1636	ν_s(OH) in water
2852	2847	2843	2852	2852	2850	2848	2850	ν(CH)
2919	2930	2928	2919	2920	2926	2920	2917	ν_{as}(CH_3)
3444	3465	3454	3454	3444	3442	3456	3444	ν_{as} (OH) adsorbed water

The results of the FT-IR spectroscopy were correlated with those obtained by SEM, XRD and photoluminescence (PL)



a)

b)

Fig.2. FT-IR spectra of thermally treated powders a) at 500°C and b) at 900°C

Conclusions

The obtained gels in the studied sytmes, having a SiO_2 as major component, have similar FT-IR spectra with the pure SiO_2. The presence of minority compounds is only evidenced by the displacement of the maxima corresponding to the vibrations bands corresponding for the Si-O-Si or Si-OH bonds.

Structural, morphological. optical and thermal studies of the obtained gels did not reveal significant differences between the samples.

In the case of thermally treated samples at temperatures of 500 and 900, FT-IR spectroscopy highlighted a better ordering of M-O-M bonds, while diminishing significantly the vibration bands of organic components, adsorbed water and structural oxides, but not their complete elimination.

An interesting behavior was observed for samples doped with Er $^{3+}$, where its presence enhanced the polycondensation reactions of the Si-OH type bonds.

X-ray diffraction revealed the crystallization of TiO_2 anatase in the case of Er^{3+} doped samples, which leads to the conclusion that its presence act as crystal seeds for anatase crystal growth germination of the anatase crystallization.

The fluorescence spectra did not show significant differences in the thermally treated samples compared to the initial gels, probably due to the presence of organic components, adsorbed water, and structural oxides in both cases.

3.2. OXIDE POWDERS IN THE TiO_2-MgO SYSTEM

Among the mono- and bicomponent oxide nanoparticles, those belonging to the MgO-TiO_2 system have an increased interest in the field of environmental protection and decontamination, with numerous studies on their preparation by chemical methods, in solution and their characterization.

Also, oxide nanoparticles of the MgO-TiO_2 system have found applications in many other areas such as sensors, pigments, capacitors, catalysts, adsorbents or raw materials for the synthesis of advanced polycrystalline ceramic materials [6].

The purpose of the study was to obtain oxide powders in the MgO-TiO_2 system by the sol-gel method and to investigate their adsorption capacity against CO_2 and CO. [7]

The FT-IR spectra of the as-prepared powders are shown in Fig. 3, and the assignment of vibration bands according to literature data is presented in Table 3.

The dried samples have M-O-M vibration bands at low wavelengths (800-450 cm $^{-1}$). At higher wavelengths, the bands characteristic of organic residues, nitrogen ion, hydroxyl ions and adsorbed water from the gel composition were observed.

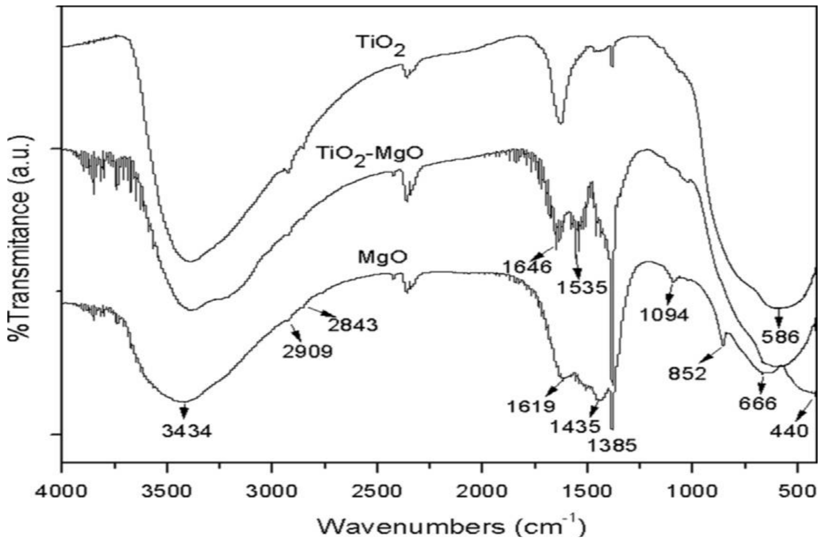


Fig. 3. FT-IR spectra of oxide powders obtained from synthesis: TiO_2, MgO, MgO-TiO_2

Table 3. Assignment of the vibration bands of TiO_2, MgO, MgO-TiO_2

Samples			Assignment
TiO_2	MgO	TiO_2-MgO	
3395	3434	3383, 3211	ν_{as} (OH) apă adsorbită
2904	2909	2909	$\nu_{as}(CH_3)$
2843	2843	2843	ν(CH)
1630	1619	1646	ν_s(OH) in apă
		1535	ν_{as}(CO)
1441	1435		$\nu(CO^{2-}{}_3)$
1387	1381	1384	ν (NO_3)
	1094		ν_{as}(C-O-C) grup
	852		ν_s(CO)
	666		ν(Mg-O)
		601	O-Ti-O-Mg-O
586			ν(Ti-O)
	440		ν(Mg-O)

In the FT-IR spectra of thermally treated samples presented in the Fig. 4, the M-O-M wavelength vibration bands are better outlined than those for untreated powders. This is the result of a better structural ordering of the powders after heat treatment. The bands characteristic of precursors and other impurities are very poorly visible in the samples except MgO. The bands observed between 1000-650 cm^{-1} in these samples are attributed to H_2O, CO_2 and other organic species adsorbed from the environment.

This can be correlated with the high porosity of oxides synthesized by chemical methods and heat treated at low temperatures.

Under these conditions the reactivity of the powder surface is high, which leads to the possibility of adsorption of water and organic substances from the atmosphere.

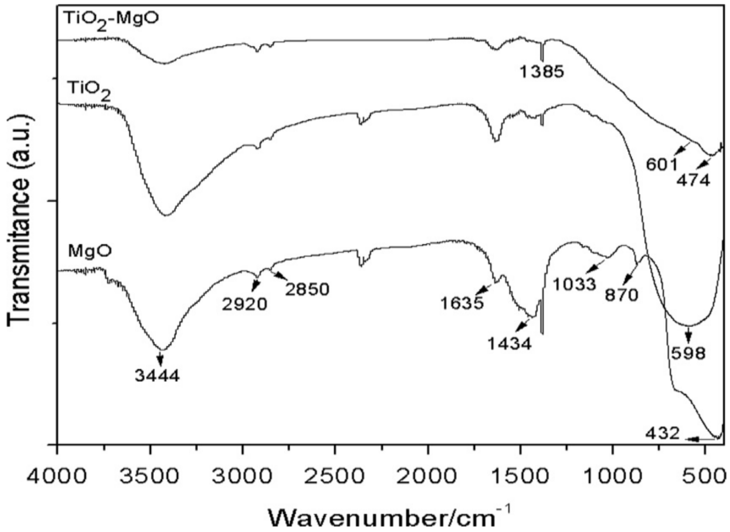


Fig. 4. FT-IR spectra of the heat treated oxides: TiO_2, MgO, MgO-TiO_2

Table 4. Assignment of the vibration bands of the thermally treated oxide powders

Samples			Assignment
TiO_2	MgO	TiO_2-MgO	
3395	3434	3383, 3211	ν_{as} (OH) apă adsorbită
2904	2909	2909	$\nu_{as}(CH_3)$
2843	2843	2843	$\nu(CH)$
1630	1619	1646	$\nu_s(OH)$ in apă
		1535	$\nu_{as}(CO)$
1441	1435		$\nu(CO^{2-}{}_3)$
1387	1381	1384	ν (NO_3)
	1094		ν_{as}(C-O-C) grup
	852		$\nu_s(CO)$
	666		ν(Mg-O)
		601	O-Ti-O-Mg-O
586			ν(Ti-O)
	440		ν(Mg-O)

Conclusions

The morphological and structural properties of of TiO_2, MgO and MgO-TiO_2 sol-gel nanopowders synesised in alcoholic media were evaluated based on the results obtained by FT-IR spectroscopy, scanning electron microscopy and X-ray diffraction.

FT-IR spectroscopy highlighted the differences that occur between synthesized samples and those treated at temperatures determined on the basis of thermal analysis. It has been found that organic residues and structural hydroxyls are not completely removed even after thermal treatment.

The presence of structural hydroxyls in the nanopowders composition obtained by the sol-gel method is well known and the adsorbed water and organic waste are believed to occur due to an adsorption process from the ambient atmosphere.

These observations are to be taken into account when using such nanostructures.

3.3. OXIDE POWDERS IN THE Al_2O_3-TiO_2 SYSTEM

Binary oxide nanoparticles may have superior properties over monocomponent oxides. Studies of the binary compound consisting of the two oxides mentioned above can provide data to improve some characteristics of individual oxides [8]. Most studies on the sol-gel preparation of powders in mentioned binary system have been devoted to their used as precursors for the synthesis of Al_2TiO_5 binary compound (tialite) with applications in the aeronautics and automotive industry or as orthopaedic and dental implants.

However, the applications of the tialite powders have expanded also into other fields such as oils' hydro-treating or potentially adsorbent in the decontamination of chemical agents used as chemical weapons. For the latter two applications powders' porosity is of great importance.

This chapter presents the results of the sol-gel synthesis of the TiO_2 and Al_2O_3 monocomponent powders, as well as the binary powders from the Al_2O_3-TiO_2 system. In addition, a comparative study of structural and morphological properties is presented [9].

The as-prepared powders were thermally treated at temperatures determined by thermal analysis, namely: Al_2O_3 at 600 C, TiO_2 at 300°C, Al_2O_3-TiO_2 at 450°C.

The FT-IR spectra of thermally treated powders are shown in Fig. 5 and the assignment of the vibration bands of the samples are summarized in Table 5. It can be seen that in all cases, besides the M-O-M vibration bands, which are in the of 400-1000 cm^{-1} range, characteristic vibration bands are assigned to the presence of adsorbed water (1638 cm^{-1}), structural hydroxides (3445 cm^{-1}) and adsorbed organic groups from the atmosphere (1410 cm^{-1} and 2928 and 2845 cm^{-1}).

It is well known that some of the Ti-O and Al-O vibrations overlap in FT-IR spectra between 400 and 750 cm^{-1}. Generally, octahedral units of AlO_6 are characterized by the presence of stretching vibrations between 600 and 750 cm^{-1} and of the bending vibrations at about 450 cm^{-1}. The tetrahedral coordinate Al-O, shows bands in the 750-850 cm^{-1} region. On the other hand, the stretching vibration of the terminal Ti-O bond is present in spectra below 730 cm^{-1} and the Ti-O-Ti band of the titanium oxide network is detected at 640 cm^{-1}. The FT-IR bands assigned to the binary powder occur between 550 and 800 cm^{-1}. This fact is determined by the overlapping of the bands assigned to the tetrahedral coordination of the Al and Ti in the Al-O and Ti-O terminal bonds, respectively. In addition, a new less intense band is detected at 583 cm^{-1}, which can be assigned to the hetero-metal-oxygen bond, -Ti-O-Al-.

Table 5. Assignment of vibration bands of monocomponent and binary samples: TiO_2, Al_2O_3 and Al_2O_3-TiO_2, thermally treated

Samples powders			Assignment
TiO_2 300°C	Al_2O_3 600°C	Al_2O_3-TiO_2 450°C	
3435	3471	3432	ν_{as} (OH) apă adsorbită
2916	2909	2916	$\nu_{as}(CH_3)$
2850	2850	2843	ν(CH)
1633	1633	1633	ν_s(OH) în apă
1385	1405	1398	νNO_3
	816	831	Al-O
	630		Ti-O-Ti
	587	600	Al-O, Ti-O-Al
574			Ti-O

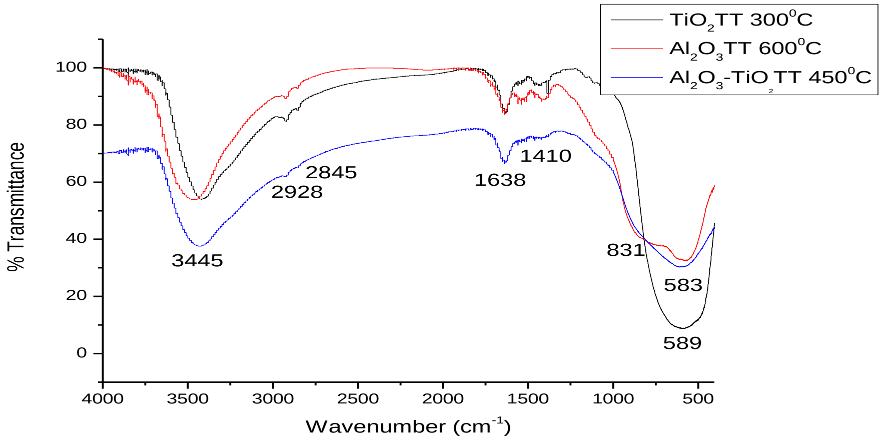


Fig. 5. FT-IR spectra of monocomponent and binary samples, thermally treated (TiO_2, Al_2O_3 and Al_2O_3-TiO_2)

Conclusions

In the present chapter the structural, thermal and morphological characterization of monocomponent powders of TiO_2, Al_2O_3 and binary TiO_2-Al_2O_3 powder was studied.

The thermal analysis of the as-prepared powders revealed their thermal decomposition effects and the temperatures at which decomposition is completed.

The structural and morphological characterization of the sintetized powders revealed the formation of TiO_2 with anatase structure, Al_2O_3 with gamma alumina structure and amorphous TiO_2-Al_2O_3 binary powder.

FT-IR spectroscopy confirms the existence in the thermally treated powders of structural hydroxyls, reduced amounts of adsorbed water and organic residues, which are also attributed to their adsorption from the atmosphere.

3.4. OXIDE POWDERS IN THE Al_2O_3-NiO SYSTEM

This chapter presents the results of the structural characterization of Al_2O_3-based catalysts obtained by simultaneous gelification of aluminum isopropoxide and nickel nitrate, compared to the pure alumina obtained from the same precursors [10].

Physico-structural studies have highlighted the changes induced by the introduction of the Ni precursor before or after the hydrolysis of aluminum alkoxide.

The synthesis of Ni-added aluminas was performed to produce catalysts for glycerol reforming to generate H_2 for applications in combustion cells [11].

The preparation of Al_2O_3 powders containing NiO in 5% by weight (ANS sample), 10% by weight (AN10 samp) and 20% by weight (AN20 sample) were studied. Powder preparation was performed by the sol-gel process. The introduction of Ni into the alumina was carried out by two procedures: before and after hydrolysis of the aluminum alkoxide.

The morphological and structural characterizations of these samples were made and were compared with the similar characterization of Al_2O_3, NiO and $NiAl_2O_4$.

FT-IR spectra (Fig. 6 an7) show for all samples, in the 500-900 cm^{-1} range, the metal-oxygen stretching frequencies associated with the vibrations of Al-O, Ni-O or Ni-O-Al. Tables 6 and 7 present the assignments of the vibration bands of the samples.

Al-O stretch bands can be attributed to the different coordination states of Al atoms: AlO_6 (~ 770 cm^{-1}) and AlO_4 (~ 570 and 380 cm^{-1}) (sample A). The shoulder at 870 cm^{-1} can be attributed to the vibration band of Al-O, located in the surface layer, and most probably involving a deformation of the surface OH groups. The stretch marks of Ni-O are in the range 400-500 cm^{-1} (~ 490 and 435 cm^{-1}) (sample N). The characteristic frequencies of Al-O-Ni (450-800 cm^{-1}) (sample S) are also observed in the powder obtained after hydrolysis of the precursors, indicating that the Ni-O- oAl bonds are formed and remain un-changed during the hydrolysis process. It is possible that the metal-oxygen transition of the spinel overlaps with the Al-O bands.

For alumina powders with Ni content (AN samples), the FT-IR spectrum revealed a slight shift of the maximum of the M-O absorption band to smaller wavelengths. It is noted that, after adding Ni, the M-O absorption maxima were not significantly disturbed.

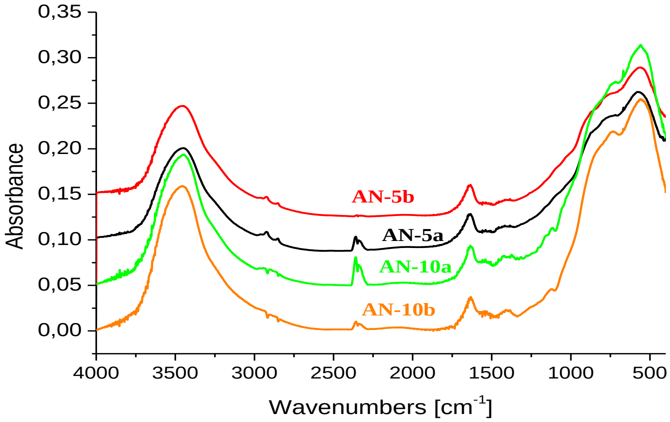


Fig. 6. The FT-IR spectra of alumina samples with 5% Ni (AN 5) and 10% Ni (AN 10)
Note: Ni was added either before the hydrolysis of Al isopropylate in samples (a) or after hydrolysis in samples (b).

Table 6. Assignment of the vibration bands of alumina samples with 5% Ni (AN 5) and 10% Ni (AN 10)

Samples				Assignment
5%Ni (AN 5)	10% Ni (AN 10)	AN 10a	AN 10b	
578	558	769	568	Al-O, Ni-O, Ni-O-Al
768	748	739	748	Al-O, Ni-O, Ni-O-Al
		1394	1394	ν (NO_3)
1641	1632	1632	1632	ν_s(OH) în apă
2856	2847	2874	2847	ν(CH)
2912	2922	2950	2912	ν_{as}(CH_3)
3454	3454	3444	3454	ν_{as} (OH)

Note: Ni was added either before the hydrolysis of Al isopropylate in samples (a) or after hydrolysis in samples (b).

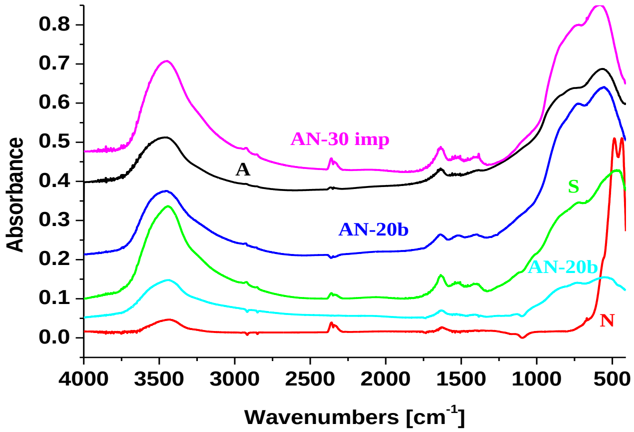


Fig. 7. The FT-IR spectra of samples A (Al_2O_3), S ($NiAl_2O_4$), AN20 (a and b) (NiO), and AN30-imp sample (Al_2O_3 doped with 30% Ni by method b)

Table 7. Assignment of the vibration bands of samples A (Al_2O_3), S ($NiAl_2O_4$), N (NiO), AN (a and b) and AN30-imp sample (Al_2O_3 with 30% Ni addition, by method b)

Samples						Assignment
A (Al_2O_3)	S ($NiAl_2O_4$)	N (NiO)	AN20b	AN20b	AN30imp	
		426				Ni-O
	474	489				Ni-O, Al-O-Ni
559			568	568	587	AlO_4
	739		748		739	Al-O-Ni
805						AlO_6
	1401		1392		1392	ν (NO_3)
	1543		1525			C-H
1638	1638	1619	1628	1638	1638	ν_s(OH) în apă
	2868				2850	ν(CH)
	2935				2915	ν_{as}(CH_3)
3474	3445	3445	3474	3465		ν_{as} (OH)

Note: AN30imp is the sample of Al_2O_3 doped with 30% Ni by the impregnation method

It is noted that, after Ni addition the M-O absorption maxima were not significantly disturbed. This indicates that no very extensive interaction occurred between nickel and alumina at this stage (450 ^{o}C), or that the interaction was limited to only a small number of active sites. All samples exhibit broad and intense stretch frequencies of (OH)] hydroxyls, which can be attributed to bands overlapimg due to surface adsorbed water (~ 3400 cm^{-1}). The bands of ~ 1640 cm^{-1} attributed to bending vibrations of water molecules [β (H_2O)] together with residual CH [(CH)] bands (1460-1500 cm^{-1}) and adsorbed (CO_2) (2300-2400 cm^{-1}) are also observed.

Conclusions

In this chapter the preparation and structural, morphological and optical characterization of some powders in the Al_2O_3-NiO system obtained by the sol-gel method was studied.

It was intended to determine the influence of introducing the Ni precursor in the reaction mixture before or after the hydrolysis of the Al precursor.

FT-IR spectroscopy has highlighted for alumina powders in mixture with Ni (AN samples), a slight shift of the M-O absorption band maximum to smaller wavelengths, with Al-O absorption maxima not significantly disturbed. And in the Al_2O_3-NiO system, the presence of the vibration bands of the hydroxyls [υ (OH)], and of the adsorbed water were put in evidence. The X-ray diffraction determined that when Ni is added at the end of the reaction, it alters the crystallization of the alumina and induces a disordering of the network.

The different addition of Ni also influences the visible spectra of the samples, which has an effect on the photocatalytic properties of the resulting samples.

3.6. OXIDE POWDERS IN THE V_2O_5-CeO_2 SYSTEM

Gels, films and powders obtained by the sol-gel method in the V_2O_5-CeO_2 system have been extensively studied due to their catalytic, electrochemical and electronic properties due to their ability to form combinations in several valence states [12, 13].

In this chapter the synthesis of some powders in the V_2O_5-CeO_2 binary oxide system, obtained in aqueous solutions was studied, establishing the influence of the ratio between the components (V/Ce) and the complexing agent, the polyol, on the structure and morphology of the obtained binary oxide powders [14].

Mixed oxide powders were prepared in the V/Ce system at two different atomic ratios (Ce/V = 1/2 and Ce/V = 1/1), from a solution of Ce $(NH_4)_2$ $(NO_3)_6$ and respectively V_2O_5 in dilute nitric acid, in the absence or presence of diethylene glycol (DEG) as a complexing and dispersing agent. This was added in a molar ratio of 0.01 precursors V -Ce/ 0.42 DEG. The powders were separated and heat treated for 30 minutes at 400 °C

The FT-IR spectra of the binary powders obtained from the synthesis are shown in Fig. 8

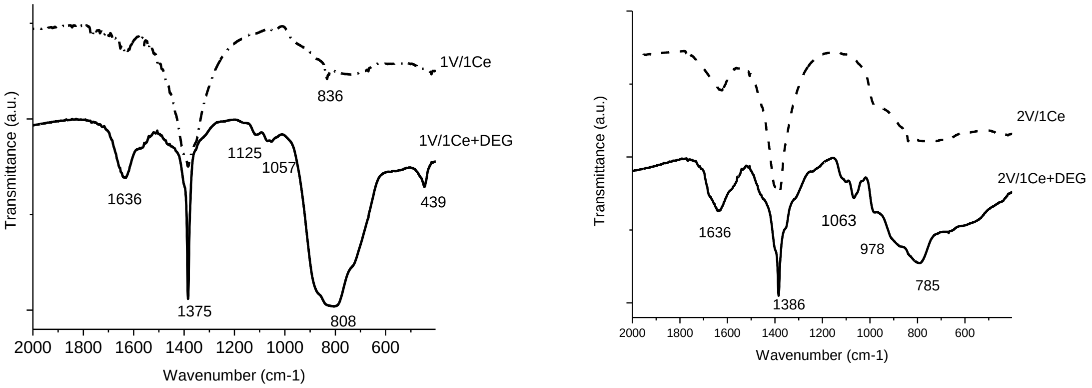


Fig. 8. The FT-IR spectra of the binary powders obtained from the synthesis: a) 1V/1Ce and b) 2V/1Ce with and without DEG

The formation of the $CeVO_4$ phase directly through the reactions taking place in the solution is observed without any subsequent thermal treatment. The corresponding vibrations of $CeVO_4$ appear at 766-800 cm^{-1}, with a shoulder at 737 cm^{-1}, which is assigned to VO_4 units in the ortovanadate structure. V_2O_5 traces can be observed in samples prepared with both molar ratios, both in the presence and absence of DEG (bands at about 1000 cm^{-1}). The band at about 1600 cm^{-1} indicates the presence of water. The bands over 2500 cm^{-1} (not shown here) are characteristic of the OH groups in diols and CH aliphatic. The band at about 1380 cm^{-1} can be attributed to νNO_3 vibrations. The evident influence of DEG on $CeVO_4$ crystallization, as evidenced by other investigational methods used (TG / DTA, XRD, TEM), could be correlated with its involvement in the oxidation-reduction reactions that might occur during powders formation. These reactions could increase the degree of reduction of Ce^{4+} to Ce^{3+} and thereby promote the formation of $CeVO_4$.

The assignment of the vibration bands of the oxide powders is shown in Table 8.

Table 8. Assignment of vibration bands of oxide powders 1V/1Ce and b) 2V/1Ce with and without DEG resulting from synthesis

Samples				Assignement
1V/1Ce	1V/1Ce+DEG	2V/1Ce	2V/1Ce+DEG	
439	439			$CeVO_4$
836	808			$CeVO_4$
737	737	737	737	VO_4
		785	785	$CeVO_4$
			978	$CeVO_4$
	1057		1053	V_2O_5
	1375	1386	1386	νNO_3
1636	1636	1636	1636	ν_s(OH) în apă

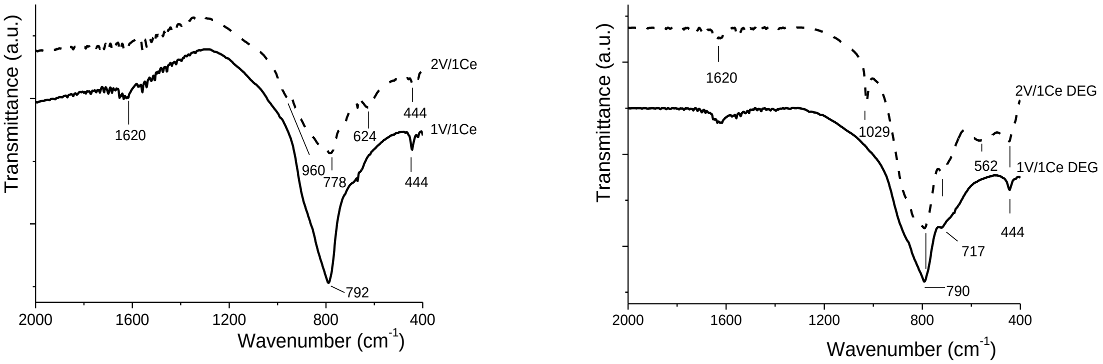


Fig.9. IR spectra of thermally treated samples (s) without DEG, (b) with DEG

Table 9. Assignment of vibration bands of thermally treated oxide powders: 1V/1Ce and b) 2V/1Ce with and without DEG

Samples				Assignements
1V/1Ce	2V/1Ce	1V/1Ce+DEG	2V/1Ce+DEG	
444	444	444	444	$CeVO_4$
		717	717	VO_4
792	776	790	790	$CeVO_4$
			1029	V_2O_5
1620	1620	1620	1620	ν_s(OH) in apa

V_2O_5 traces were found only with a 2V/1Ce ratio due to the fact that heat treatment led to the completion of cerium vanadate formation with V/Ce = 1/1 ratio. The spectral characteristics of H_2O, NO_3-, hydroxyl diol and CH aliphatic (1600, 1300-1400 cm^{-1} and > 2500 cm^{-1}) groups disappear. The presence of DEG used to improve the particle morphology or size does not influence the composition of the thermally treated samples, but brings some changes in the ordering and structure of the samples (a shoulder at approximately 700 cm^{-1} associated with VO_4 units in the ortovanadate structure appears).

Conclusions

Using the co-gelling method in aqueous solutions, powders of binary oxides were prepared in the V_2O_5-CeO_2 system at different molar ratios of the components and in the presence or absence of the chelating agent (DEG).

FT-IR spectroscopy associated with XRD and TEM characterizations indicated that nanoscale powders were obtained and the presence of chelating agent (DEG) favored the formation and crystallization of $CeVO_4$. For 2V/1Ce samples, along with $CeVO_4$, excess vanadium oxide was identified.

The new $Ce^{+3}V^{+5}O_4$ compound appears as a result of the oxidation-reduction reactions due to the precursor-forming ionic species in the acidic starting solutions according to reactions (1), (2), (3) presented in the thesis. The presence of V^{+4} species (the blue-green color of the solution during ammonium hydroxide precipitation) could act as Ce^{+4}: $V^{+4} \rightarrow V^{+5}$-1e reducing agents and $Ce^{+4} \rightarrow Ce^{+3}$ +1e

3.7. SILICA-ORGANIC COUMPUNDS SYSTEMS (TRICHLORPHON AND CYCLODEXTRINS)

In the thesis composite powders based on trichlorphon [O,O-dimetil-(2,2,2-triclor-1-hidroxietil0 fosfonat] (T) as organophosphorus pesticide incorporated in silica matrices generated by three different sources of SiO_2: tetra ethylortosilicate (TEOS), colloidal silica (CS) and sodium silicate - (SS), were prepared and characterized [15],. Two routes of the sol-gel method (the alcoholic and aqueous route, respectively) were used. The choice of the aqueous route was made from economic and ecological reasons. The SiO_2 precursors used in the aqueous route are less expensive than TEOS and the soil attack is almost non-existent in the case of pesticides embedded into gels prepared by aqueous route.

Another objective of the thesis was to determine the possibility of using cyclodextrins in order to improve the controlled release of the pesticide from the silica matrices; being well known that cyclodextrins have the ability to form complexes of inclusion with a wide variety of agricultural chemicals. The composition (weight percent) of the corresponding samples was: 19% T, 24% CD and 57% SiO_2, respectively.

The FT-IR spectra of the silica matrix, trichlorfon and silica-pesticide composites obtained from the TEOS, CS and SS precursors are shown in Fig.10.

The characteristic vibration bands for SiO_2 gels are highlighted, regardless of the precursor used. The assignments of the wavelength values in Fig. 10 are summarized in Table 10.

The IR spectra of the composite samples, silica-trichlorfon matrix, were compared with the IR spectrum of trichlorfon, being noticed that, regardless of the SiO_2 precursor used, the pesticide was incorporated into the sol-gel matrix. Some of its characteristic vibrational bands are absent from the composite sample spectra, due to the reduced amount of pesticide.

Concerning the IR vibration bands of trichlorphol, these correspond to the following: OH stretching vibration at 3384 cm^{-1}, CH stretching vibration between 2800 and 3000 cm^{-1}, H_2O at 1638 cm^{-1}, the deformation vibrations of CH at 1461 and 1380 cm^{-1}, the PO stretching vibration at 1203 cm^{-1}, the CO stretching vibration at 1085 and 1041 cm^{-1} and the C-C1 vibration between 850 and 550 cm^{-1}.

From Fig. 10, it can be concluded that the silica matrix, no matter its origin, could be an excellent carrier for trichlorphon as an embedded organophosphorus pesticide.

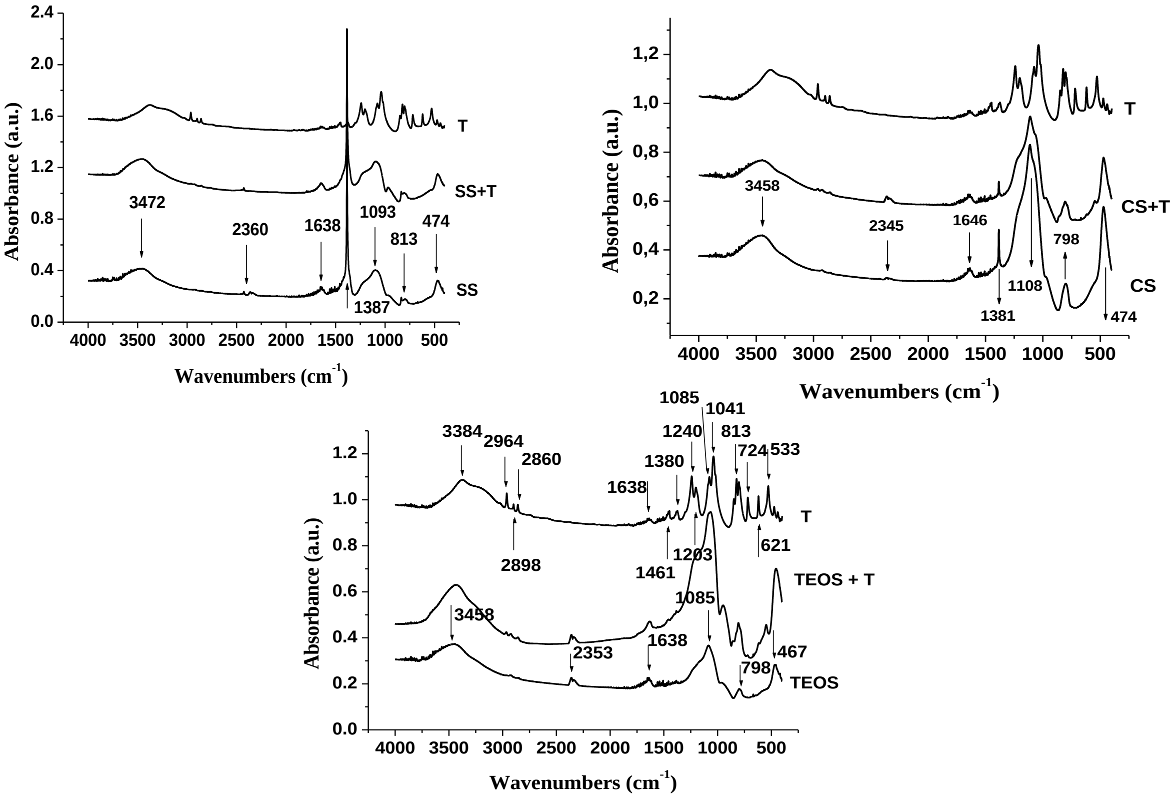


Fig.10. IR spectra of trichlorfon, pesticide-silica sol-gel composites and corresponding silica matrices obtained from various precursors, TEOS, CS and SS

The IR spectra of the pesticide-silica composites prepared from different precursors, including cyclodextrins (CD), along with trichlorfon, are shown in Fig. 11, being evaluated as compared to the spectra of the pesticide-silica composites. Research has been done for all three types of cyclodextrins (α-, β- or γ-).

For the same silica matrix, all spectra were similar, no matter the type of cyclodextrines used. Due to this fact, in Fig. 11, only the spectra of the samples containing γ-CD were presented. The IR spectrum of γ-CD was also included in the figure.

Table 10. IR band frequencies and their assignments for silica gels from different precursors (TEOS, CS and SS respectively)

SiO_2 precursors	Wavelength [cm^{-1}]	Assignment
TEOS, CS SS	3458 3472	ν_{as} (OH) apă adsorbită
SS TEOS CS	2360 2353 2345	CO_2 vib.
CS TEOS, SS	1646 1638	ν_s(OH) în apă
SS CS	1387 1381	νNO_3
CS SS TEOS	1108 1093 1085	ν_{as} Si-O-Si
SS TEOS, CS	813 798	ν_{sim} Si-O-Si
CS, SS TEOS	474 467	δ O-Si-O

The characteristic vibration bands for a SiO_2 gel could be observed regardless of the precursor used.

A very good concordance was obtained between the data obtained on the FT-IR spectra of cyclodextrins and literature data [16]. The following IR vibration bands were recorded: stretching the OH group at 3370 cm $^{-1}$, stretching the CH group at 2945 cm^{-1}, the H-bond vibration band at 2366 cm^{-1}, H_2O at 1660 cm^{-1}, deformation CH at 1478 and 1351 cm^{-1}, CO stretching and bending OH at 1190 cm^{-1}, CO / CC stretching at 1115 and 1015 cm^{-1}, and vibration of the pyranose ring at 739 and 584 cm $^{-1}$.

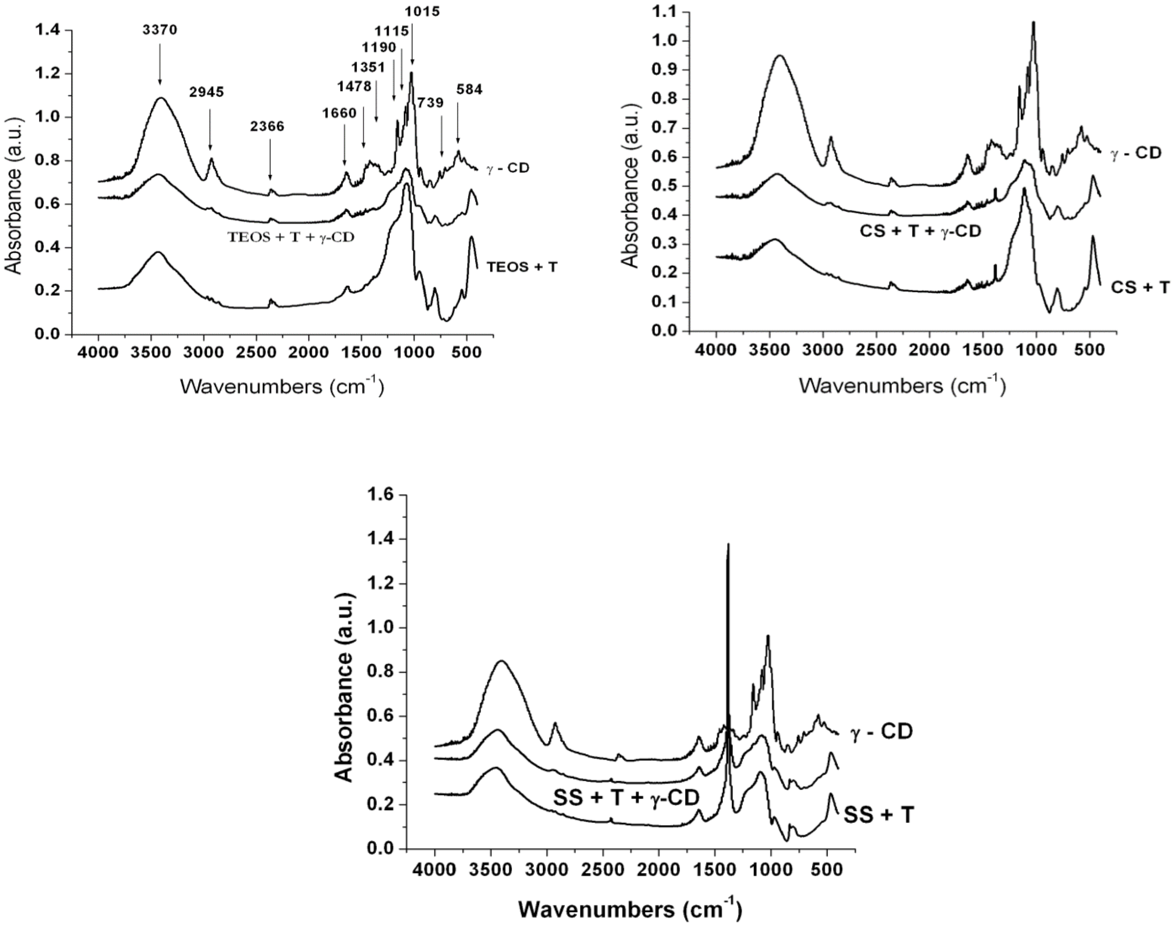


Fig. 11. Comparison of IR spectra of pesticide-silica composites prepared from different precursors and those of the corresponding samples in which cyclodextrins were included.

In order to establish both the role of the silica matrix and the presence of cyclodextrins on the materials’ release properties, thermal analyzes of the prepared composites and trichlorfon release tests were performed. The best results were obtained for samples prepared from TEOS in the absence of cyclodextrins and for those obtained from CS in the presence of cyclodextrins.

Conclusions

Two series of composites were prepared by the sol-gel method. The first consists of trichlorphon as a pesticide, incorporated into silica gels from different sources (TEOS, CS and SS). The second series is also synthesized with the first, the only difference between them is the presence of cyclodextrins in the reaction mixtures.

The inclusion of trichlorfon and trichlorlorfon together with cyclodextrins was highlighted in all cases by IR spectroscopy

The properties of the obtained samples depend on the nature of the silica matrix and the presence or absence of cyclodextrins in the reaction mixtures. The best results were obtained for samples prepared from TEOS in the absence of cyclodextrin and those obtained from CS in the presence of cyclodextrins.

The carrier matrix properties of the silica matrix have been confirmed, it can be concluded that they can be considered as new organic carriers.

4. GENERAL CONCLUSIONS

In the thesis researches regarding the preparation, by sol-gel method, of mono and polycomponent oxide systems as well as of silica based nanocomposites and their spectroscopic characterization was realized.

For the beginning the results obtained in SiO_2 polycomponent systems are presented..

The study aimed to the establish phase formation in SiO_2-TiO_2, SiO_2-TiO_2-Al_2O_3 type binary and ternary systems, un-doped and Er^{3+}-doped with Er^{3+}, that are of interest for obtaining waveguides. The researches presented in the thesis referred especially to the formation of the phases by thermal treatments at the temperatures of 500 and 900^{o}C and to the way the formed phases influence the optical properties.

In the case of thermally treated samples, FT-IR spectroscopy revealed a better structuring of the M-O-M bonds while reducing the vibration bands of the organic components, adsorbed water and structural oxides.

The presence of structural hydroxides in the composition of nanopowders obtained by the sol-gel method is well known, even for thermally treated samples, and the adsorbed water and organic residues are believed to occur due to a process of adsorption from the ambient atmosphere.

In the TiO_2-MgO system the TiO_2, MgO and MgO-TiO_2 nanopowders obtained by the sol-gel method in alcoholic medium were studied. Morphological and structural properties were evaluated based on the results obtained by FT-IR spectroscopy, scanning electron microscopy and X-ray diffraction.

FT-IR spectroscopy revealed, as in the case of SiO_2-based systems, the differences that occur between synthesized samples and those thermally treated at temperatures determined on the basis of thermal analysis. It has been found also in this case that organic residues and structural hydroxyls are not completely removed even after the thermal treatment used.

In the case of TiO_2-Al_2O_3 system, the structural, thermal and morphological characterization of some monocomponent powders of TiO_2, Al_2O_3 and binary TiO_2-Al_2O_3 powder was studied

The structural and morphological characterization of the prepared powders revealed the formation of TiO_2 with anatase structure, Al_2O_3 with gamma alumina structure and amorphous TiO_2-Al_2O_3 binary powder.

FT-IR spectroscopy confirms also for this system the presence in the thermally treaded powders of structural hydroxyls, reduced amounts of adsorbed water and organic residues, which are also attributed to their adsorption from the ambient atmosphere.

In the Al_2O_3-NiO system, the preparation of Al_2O_3 powders mixed with NiO in 5% by weight (AN5 Sample), 10% by weight (AN10 Sample) and 20% by weight (AN20 sample) was studied. Powder preparation was performed by the sol-gel process. The introduction of Ni into the alumina was carried out by two procedures: before and after hydrolysis of the aluminum alkoxide.

When Ni is added at the end of the reaction, it alters the crystallization of the alumina and induces a disordering of the network.

In the case of the Al_2O_3-NiO system, the existence in the thermally treated powders of structural hydroxyls, of reduced amounts of adsorbed water and of organic residues was also observed.

In the binary V_2O_5-CeO_2 system, powder preparation was achieved by co-gellation in aqueous solutions at various molar ratios of the components (2V/1Ce or 1V/1Ce), in the presence or absence of ethylene glycol (DEG) used as a chelating agent.

IR spectroscopy associated with XRD and TEM characterizations indicated that nanoscale powders were obtained and the presence of the chelating agent (DEG) favoured the formation and crystallization of $CeVO_4$.

For 2V/1Ce samples, along with $CeVO_4$, excess of vanadium oxide was identified. The new $Ce^{+3}V^{+5}O_4$ compound appears as a result of the oxidation-reduction reactions due to the r ionic species of precursors formed in the acidic initial solutions.

In the case of the SiO_2 based nanocomposites, two types of composites were synthesized by the sol-gel method. The first type consists of trichlorphol as a pesticide, incorporated in silica gels from different sources (TEOS, CS and SS). The second type of composites was synthesized similarly to the first, but by introducing the cyclodextrins together with trichlorphon in the reaction mixtures.

FT-IR spectroscopy revealed the inclusion of trichlorphon in all three prepared matrices as well as the pesticide-cyclodextrin complexation when bothh compounds were embedded.

The properties of the prepared samples depend on the nature of the silica matrix and the presence or absence of cyclodextrin in the reaction mixtures. The best results were obtained for samples prepared from TEOS in the absence of cyclodextrin and those obtained from CS in the presence of cyclodextrins.

Based on the results obtained in all studied systems, it was proposed to develop a spectral data base for the oxide compounds obtained by the sol-gel method, according to the examples presented in the Annex.

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