

Studies regarding the formation from metal nitrates and diol of $\text{NiM}_2^{\text{III}}\text{O}_4$ spinels, inside a silica matrix

Marcela Stoia · Mircea Stefanescu ·
Mirela Barbu · Paul Barvinschi ·
Lucian Barbu-Tudoran

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Abstract The present study deals with preparation and characterization of spinel mixed oxide systems $\text{NiM}_2^{\text{III}}\text{O}_4$, where $\text{M}^{\text{III}} = \text{Fe}^{\text{III}}, \text{Cr}^{\text{III}}$. In order to obtain 50% NiFe_2O_4 /50% SiO_2 and 50% NiCr_2O_4 /50% SiO_2 nanocomposite, we have used a versatile route based on the thermal decomposition inside the SiO_2 matrix, of some particular precursors, coordination compounds of the involved M^{II} and M^{III} cations with dicarboxylate ligands. The ligands form in the redox reaction between metal nitrates mixture and 1,3-propanediol at the heating around 140 °C of the gels (tetraethylorthosilicate–metal nitrates–1,3-propanediol–water). The as-obtained precursors, embedded in silica gels, have been characterized by FT-IR spectrometry and thermal analysis. Both precursors thermally decompose up to 350 °C leading to the formation of the corresponding metal oxides inside the silica matrix. X-ray diffraction of the annealed powders have evidenced the formation of NiFe_2O_4 starting with 600 °C, and NiCr_2O_4 starting with 400 °C. This behavior can be explained by the fact that, by thermal decomposition of the Fe(III) carboxylate at 300 °C, the spinel phase $\gamma\text{-Fe}_2\text{O}_3$ is formed, which interacts with the NiO, forming the ferrite nuclei. By thermal decomposition

of chromium carboxylate, a nonstoichiometric chromium oxide ($\text{Cr}_2\text{O}_{3+x}$) is formed. In the range 380–400 °C, $\text{Cr}_2\text{O}_{3+x}$ turns into Cr_2O_3 which immediately interacts with NiO leading to the formation of nickel chromites nuclei inside the pores of silica matrix. Both spinels have been obtained as nanocrystalites homogeneously dispersed as resulted from XRD and TEM data.

Keywords Carboxylates · Chromites · Ferrite · Thermal decomposition · Nanocomposites · Silica

Abbreviations

TEOS Tetraethylorthosilicate
1,3PG 1,3-Propanediol

Introduction

In the recent years, research has been carried out on mixed oxides of transition metals, of the type $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{O}_4$ with spinel structure, which are active and thermally stable. In addition to this, there is abundant availability of raw materials necessary for their synthesis. The main advantage of transition metallic oxide catalysts is their low cost in comparison with the noble metals, traditionally used for this purpose [1]. Fe(III) and Cr(III) are usually chosen as the trivalent cations because they are active for methane oxidation in the form of single oxides [2]. The synthesis of nanosize-structured spinel ferrites was already reported to provide selective catalysts for oxidation of hydrocarbons. These materials were found to be very good catalysts for the oxidation of styrene to benzaldehyde in the presence of hydrogen peroxide [3]. Oxidation of alkyl aromatic compounds over heterogeneous catalysts using cleaner peroxide oxidants is an especially attractive goal in these days [4].

M. Stoia (✉) · M. Stefanescu · M. Barbu
Faculty of Chemistry and Chemical Engineering, University
Politehnica Timisoara, P. Victoriei No. 2, 300006 Timisoara,
Romania
e-mail: marcela.stoia@chim.upt.ro

P. Barvinschi
Faculty of Physics, West University of Timisoara, Bv. V. Parvan
No. 4, 300223 Timisoara, Romania

L. Barbu-Tudoran
Electron Microscopy Center, Faculty of Biology and Geology,
Babes-Bolyai University, 5-7 Clinicilor Street,
400006 Cluj-Napoca, Romania

Mesoporous materials have large pores and high surface area and thus provide good basis for catalysis, separations, and sensors. From a catalytic point of view, inorganic nanoparticle–mesopore composites have a potential to allow three-dimensional (3D) designer catalysts with separate tuning of the microscopic catalytic rates on the nanoparticles surfaces as well as control over material transport by changes in the pore size. Synthesis of well-dispersed catalyst—metal or oxide—particles inside a support material is of great interest and carries potential challenges.

The sol–gel process is a versatile method for making ceramic and glass materials based on incorporation of particles embedded in inert matrixes such SiO_2 with specific properties, which are related with the structure of the forming composites materials. The SiO_2 glasses prepared by the sol–gel method have been used experimentally as supporting substrates to organic and inorganic molecules. They specially have been used in 3D constructions, in which “guests” (e.g., atomic clusters, organic molecules, etc.) are dispersed in the framework voids [5].

The present study deals with preparation and characterization of spinel mixed oxide systems NiM_2O_4 , where $\text{M}^{\text{III}} = \text{Fe}^{\text{III}}$ and Cr^{III} , inside a silica matrix. In order to obtain 50% $\text{NiFe}_2\text{O}_4/50\% \text{SiO}_2$ and 50% $\text{NiCr}_2\text{O}_4/50\% \text{SiO}_2$ nanocomposites, we have used a versatile route based on the thermal decomposition inside the SiO_2 matrix, of some particular precursors, coordination compounds of the involved M^{II} and M^{III} cations with dicarboxylate ligands obtained in the redox reaction between metal nitrates and 1,3-propanediol. In reaction with $\text{M}^{\text{II}}(\text{NO}_3)_2$ or $\text{M}^{\text{III}}(\text{NO}_3)_3$, this diol is oxidized at malonic acid, which coordinates to these cations forming polynuclear malonates, as previously reported in the literature [6, 7]. This reaction takes place in a similar way when the reacting mixture is embedded in a silica gel [8]. The thermal decomposition of the as-formed precursors leads to the formation of an intimate mixture of the two oxides in a highly reactive state, which further reacts to form the spinel system embedded in silica matrix. The thermal evolution of the obtained gels was studied by thermal and FT-IR analyses. The decomposition products at 400 °C of the precursor/silica system have been annealed at different temperatures up to 1000 °C to study the evolution of the two oxidic systems inside the silica matrix. The annealed powders have been characterized by X-ray diffraction and TEM.

Experimental

Materials and methods

In the synthesis, we have used tetraethyl orthosilicate (TEOS) (Merck, 98%), metal nitrates (MN) (Merck (p.a.)):

$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1,3-propanediol. The processing scheme is resumed in Fig. 1.

The gels tetraethyl orthosilicate (TEOS)–metal nitrates (MN)–diol (EG) were prepared by dissolution of the metal nitrates in the corresponding amounts of diol and of water, resulting in clear solution. To these solutions, the ethanolic solutions of TEOS were added under magnetic stirring. The resulted stable solutions have been left for gelation in covered glasses at room temperature. The amounts of reactive used in the synthesis of different gels to obtain the desired 50% (mass percent) simple or mixed oxides embedded in SiO_2 nanocomposites are listed in Table 1. The resulting gels were dried at 50 °C for 3 h, then grinded, and heated at 140 °C. At this temperature, the redox reactions diol–metal nitrates took place with formation of the corresponding carboxylate type precursor of the mixed oxide nanoparticles in the pores of the hybrid gels. These precursors were decomposed by thermal treatment at 350 °C for 3 h to obtain the primary oxidic system embedded inside silica matrix. The obtained powders were then annealed for 3 h at higher temperatures, to obtain 50% $\text{NiFe}_2\text{O}_4/50\% \text{SiO}_2$ and 50% $\text{NiCr}_2\text{O}_4/50\% \text{SiO}_2$ nanocomposites.

Experimental techniques

The obtained gels and nanocomposites have been characterized by thermal analysis, infrared Fourier transform (FT-IR) spectrometry, X-ray diffraction (XRD), and transmission electron microscopy (TEM).

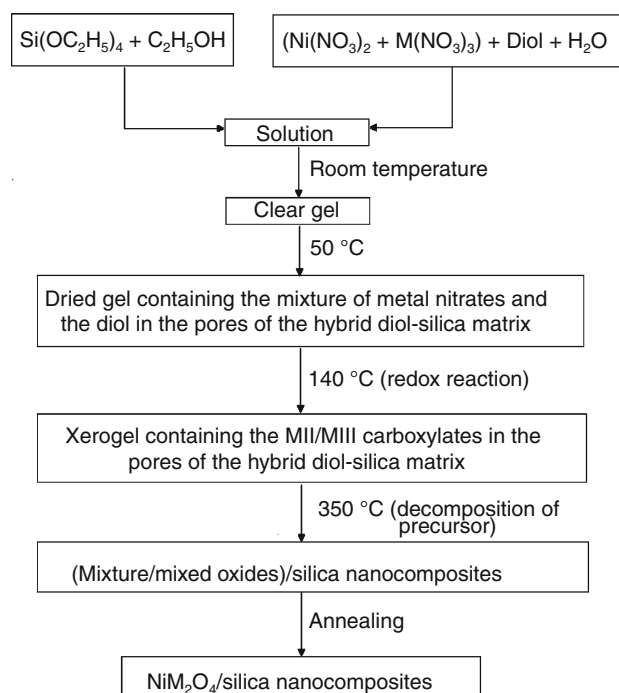


Fig. 1 Scheme of the main steps in the synthesis of $\text{NiM}_2\text{O}_4/\text{SiO}_2$ nanocomposites, starting from TEOS, metal nitrates, and diol

Table 1 Synthesis parameters and notations of the prepared gels

Sample	Quantity/mole							%M _x O _y /SiO ₂ %NiM ₂ ^{III} O ₄ /SiO ₂
	Ni(NO ₃) ₂ ·6H ₂ O	Cr(NO ₃) ₃ ·9H ₂ O	Fe(NO ₃) ₃ ·9H ₂ O	TEOS	H ₂ O	Diol	EtOH	
NiPGSi	0.020	–	–	0.025	0.100	0.040	0.150	50
FePGSi	–	–	0.020	0.025	0.100	0.040	0.150	50
CrPGSi	–	0.020	–	0.025	0.100	0.040	0.150	50
NiFePGSi	0.0066	–	0.0132	0.025	0.100	0.040	0.150	50
NiCrPGSi	0.0060	0.0132	–	0.025	0.100	0.040	0.150	50

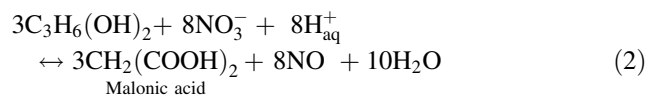
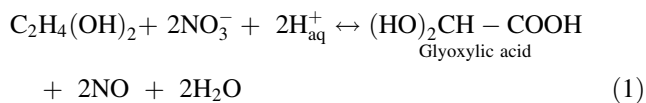
The progress of the redox reactions between mixtures of nitrates and diol was studied by thermal analysis of the dried gels using a 1500 D MOM Budapest Derivatograph, on Pt plates. The thermal decomposition of the formed precursors was studied on a Diamond Perkin Elmer thermo balance. All the experiments have been performed in air, in the temperature range 20–500 °C, with a heating rate of 5 °C min⁻¹, using as reference α-Al₂O₃.

The synthesized powders were characterized by FT-IR spectrometry with a Shimadzu Prestige FT-IR spectrometer, in KBr pellets, in the range 400–4000 cm⁻¹. The phase compositions of the powders were determined by XRD using a Bruker D8 Advance System (monochromatic Mo-Kα radiation) operating at 40 kV and 40 mA. The average crystallite size was calculated based on the XRD patterns using the Scherrer's equation: $D_{XRD} = 0.9\lambda/\beta\cos\theta$ [9], where D_{XRD} is the mean crystallite size, λ is the radiation wavelength of Mo-Kα (0.70930 Å), β is the full-width-at-half of the maximum (FWHM) (in radians), and θ is the Bragg angle. TEM microscopy was performed on a JEOL JEM 1010 microscope.

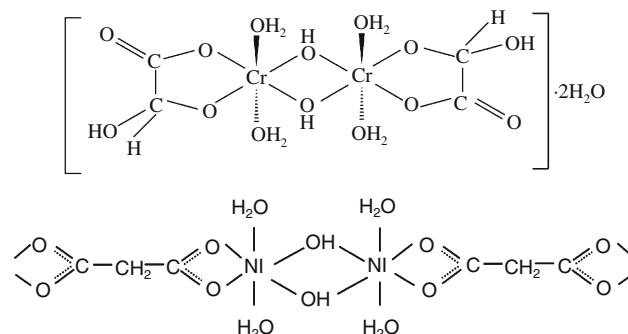
Results and discussions

The synthesis method used for the preparation of nickel ferrite and nickel chromite spinels is based on the redox reaction between the corresponding mixture of metal nitrates Ni(NO₃)₂-M^{III}(NO₃)₃ and diols, within the pores of the silica gel.

Previous studies on the redox reactions between metal nitrates and diols have shown that the diols are oxidized to the carboxylic/dicarboxylic acids as results from Eqs. 1 [10] and 2 [11], with emission of reddish-brown nitrogen oxides N_xO_y. In the equations, we have considered the reduction of NO₃⁻ to NO, which further reacts with O₂ to give NO₂, leading to a mixture of nitrogen oxides (N_xO_y).

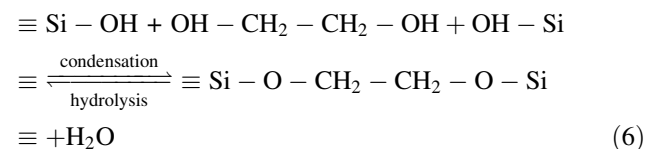
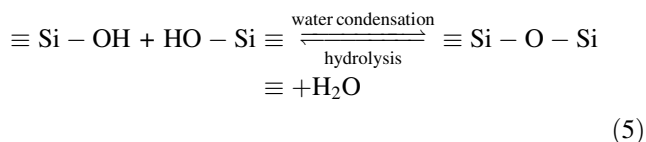
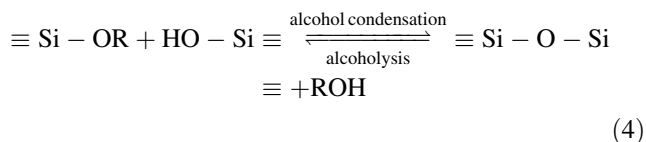
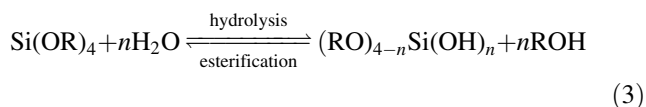


The as-formed organic acids loose their protons and coordinate as dianions to the metal cations present in the system leading to polynuclear coordination compounds [10, 11]:



When the diol interacts with a mixture of metal nitrates, the reaction takes place in one or two steps, depending on the metal cations nature (on the difference on the aquacation's acidity). Thus, while chromium (III) and copper (II) nitrates interacts in a single step with the diol forming a polynuclear coordination compounds [7], iron (III) and zinc (II) nitrates interact separately with the diol leading to a mixture of homonuclear carboxylates [12].

Our sol-gel-modified method starts from the sols containing the mixture of diols and metal nitrates (as reactant for the metal carboxylates which will represent the NiM₂O₄ nanoparticles precursors), tetraethylorthosilicate (TEOS) (as precursor of the siloxane network) and water and ethanol as solvents, in acidic catalysis insured by the hydrolysis of Fe(NO₃)₃. The sols are left for gelation at room temperatures when, according to our previous studies [13], the diol interacts with the Si-OH groups from the siloxane network leading to a hybrid organic-inorganic network with the Si-OH groups. In these conditions, the processes that take place during gelation are complex, and can be presumed to be as given by the Eqs. 3–6:



Thus, we can speak in our case of hybrid gels, containing the mixture of metal nitrates and 1,3-propanediol. Taking into account the interaction of TEOS–1,3-propanediol quantitatively studied previously, we always introduce an excess of diol corresponding to a molar ratio diol: TEOS = 0.5:1.

These gels dried at 50 °C have been characterized by thermal analysis. Figures 4, 5, 6 show the registered TG and DTA curves for the gels CrPGSi (Fig. 2), NiPGSi (Fig. 3) and NiCrPGSi (Fig. 4).

The main purpose of thermal analysis of the dried gels was to evidence the redox reaction between the metal nitrates and the diol, which takes place in the pores of the silica matrix at the heating of the gels. As it results from the weak exothermic effect registered on DTA curve of gel CrPGSi (Fig. 2), chromium nitrate reacts with 1,3-propanediol around 70 °C, leading to a compound which thermally decomposes in the range 275–375 °C with a

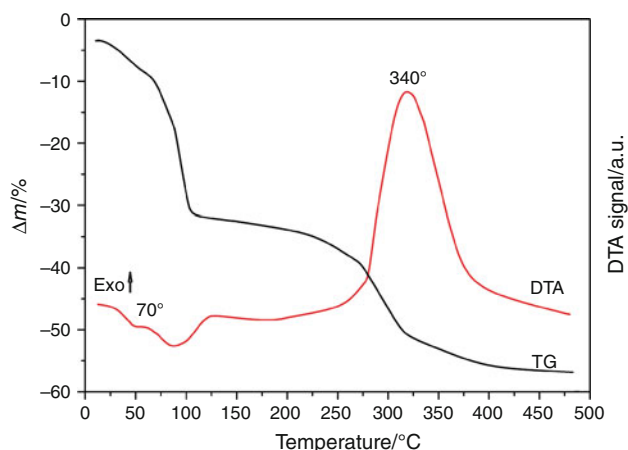


Fig. 2 TG and DTA curves of the gel CrPGSi, containing the mixture $\text{Cr}(\text{NO}_3)_3$ –1,3-propanediol

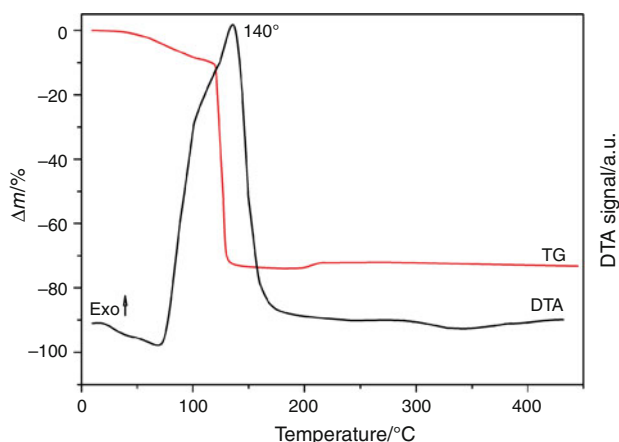


Fig. 3 TG and DTA curves of the gel NiPGSi containing the mixture $\text{Ni}(\text{NO}_3)_2$ –1,3-propanediol

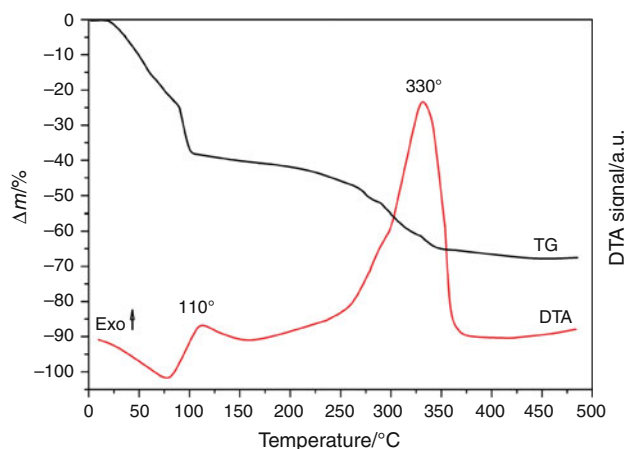


Fig. 4 TG and DTA curves of the gel NiCrPGSi containing the mixture $\text{Ni}(\text{NO}_3)_2$ – $\text{Cr}(\text{NO}_3)_3$ –1,3-propanediol

large exothermic effect. The gels containing $\text{Fe}(\text{NO}_3)_3$ and 1,3-propanediol behave similarly with CrPGSi one, and it was studied previously [14].

The evolution of the curve of NiPGSi gel (Fig. 3) show a completely different thermal behavior. Thus, in this case, the main mass loss takes place at 130 °C, when the redox reaction $\text{Ni}(\text{NO}_3)_2$ –1,3-propanediol takes place probably forming the corresponding Ni-carboxylate, which instantly burns leading to a black powder presenting magnetic properties. According to the small increase of the mass around 230 °C and to the magnetic properties, a mixture of metallic nickel and nickel oxide form inside the silica matrix.

Figure 4 presents the TG and DTA curves of the gel NiCrPGSi. In this case, the redox reaction between metal nitrates and 1,3-propanediol takes place around 110 °C, when a weak exothermic effects appear on DTA curve. It is possible that, in this case, the redox reaction of chromium nitrate with the diol to induce the redox reaction of

Fig. 5 Derivatogram of the xerogel NiFePGSi in air up to 500 °C

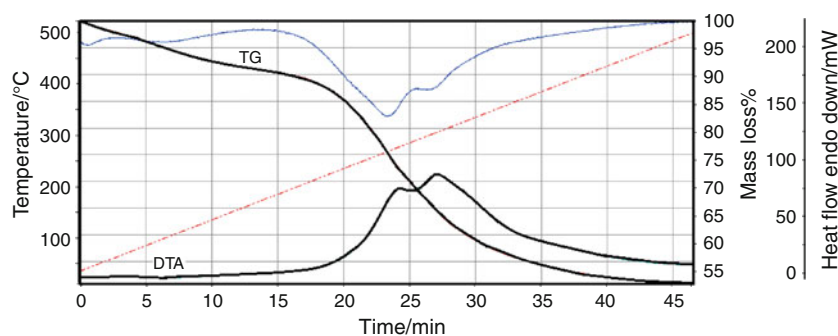
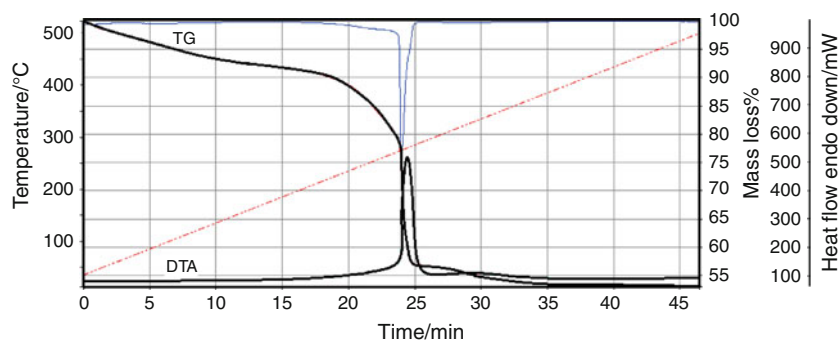


Fig. 6 Derivatogram of the xerogel NiCrPGSi in air up to 500 °C



Ni(NO₃)₂ with the diol also. In this case, the formed product (e.g., the nickel malonate) is more stable and does not burn, because of its dispersion within the formed M(III) carboxylate.

As can be concluded from thermal analysis study of the synthesized gels, the 140 °C temperature is optimal to obtain the carboxylate type precursors in the pores of the silica matrix, because the redox reaction is complete. Thus, the dried gels FeNiPGSi and CrNiPGSi have been grinded, and thermally treated for 4 h at this temperature. The as-obtained powders have been characterized by thermal analysis and FT-IR spectrometry.

Figure 5 presents the thermal curves of the xerogels NiFePGSi obtained at 140 °C. The oxidative thermal decomposition of nickel ferrite precursors inside the silica matrix takes place in the range 250–350 °C leading to the corresponding oxidic system embedded in silica matrix. This stage of the thermal decomposition generates on DTA curve a large split exothermic effect, because of the superposition of the burning of the organic parts from the hybrid diol-siloxane network [13]. In case of the gel, NiCrPGSi (Fig. 6), the burning of the organic parts from the network overlapped with the oxidative decomposition of the precursor, generating on DTA curve a sharp exothermic effect.

The suggested thermal evolutions of the synthesized gels have been confirmed by FT-IR spectrometry of the gels thermally treated at different temperatures. Figures 7 and 8 presents the FT-IR spectra of the gels NiFePGSi and

NiCrPGSi thermally treated at 50, 140, and 270 °C. The spectra of the gels dried at 50 °C present besides the bands characteristic to the silica-gels (~420, ~800, ~960, ~1060, ~1640, and ~3400 cm⁻¹[13]), additional bands characteristic to the NO₃⁻ ions (~870 cm⁻¹ and the strong band at ~1380 cm⁻¹[8]), and characteristic to the diol (3000–2800 cm⁻¹, ~1100 cm⁻¹). The spectra of the gels thermally treated at 140 °C do not present the strong band at 1380 cm⁻¹ any more, because of the consumption of the NO₃⁻ ions in the redox reaction with the diol. A new strong band located at ~1580 cm⁻¹, corresponding to the asymmetric stretching vibrations of the –COO⁻ group, formed by the oxidation of the C–OH group from diol, together with the band located at 1350–1370 cm⁻¹ characteristic to the symmetric stretching vibrations –COO⁻ group, confirms the formation of coordination compounds between the cations present in the system and the carboxylate ligands [12]. The FT-IR spectra of the gels heated at 270 °C evidence a partial decomposition of the precursors, in the pores of the xerogels. The FT-IR spectra of the powders annealed at 350 °C evidence the complete decomposition of the carboxylate type precursors, and present the bands characteristic to the silica matrix and some additional weak bands in the range 700–400 cm⁻¹ because of the formation of primary oxidic system inside the silica matrix.

It is interesting to note that, in the case of the powders annealed at 350 °C, significant changes take place in the range 3700–2800 cm⁻¹. Thus, while in case of NiFePGSi

(Fig. 7), a large band characteristic to H-bonded water molecule or Si–OH groups appear around 3400 cm^{-1} , in case of the gel NiCrPGSi several bands appear in the range $3800\text{--}3600\text{ cm}^{-1}$, characteristic to free, unbonded –OH groups, together with a large band in the range $3400\text{--}2900\text{ cm}^{-1}$ with maximum at 3097 cm^{-1} [14]. In this case, it is possible that a higher number of internal Si–OH groups to remain in the silica network, confirmed also by the band located at 952 cm^{-1} , which can be also assigned, according to some studies [15], to the Si–O–Cr bond that possibly appears as a result of the interaction of Cr–OH (formed by thermal decomposition of the Cr(III) hydroxymalonate) with the Si–OH groups.

The powders obtained at $350\text{ }^{\circ}\text{C}$ have been annealed at 400 , 600 , and $1000\text{ }^{\circ}\text{C}$ and studied by X-ray diffraction and FT-IR spectrometry.

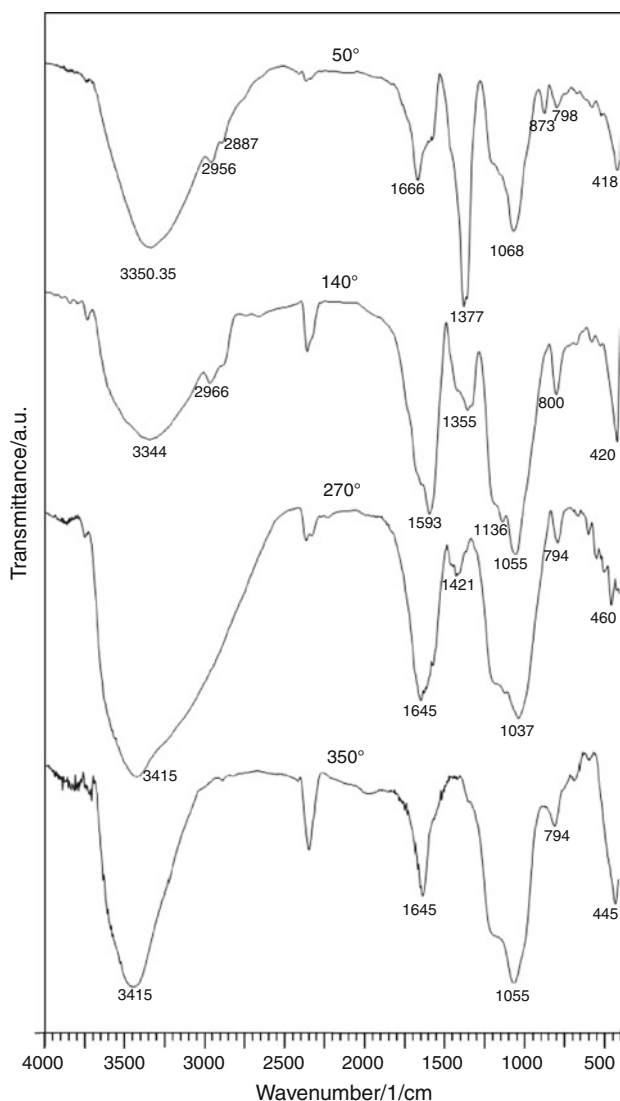


Fig. 7 FT-IR spectra of NiFePGSi gel heated at different temperatures

Figure 9 presents the XRD patterns of the powders obtained at $400\text{ }^{\circ}\text{C}$ for the gels FePGSi (pattern 1), NiPGSi (2) and of the powders FeNiPGSi annealed at $400\text{ }^{\circ}\text{C}$ (3), $600\text{ }^{\circ}\text{C}$ (4), and $1000\text{ }^{\circ}\text{C}$ (5).

XRD pattern (1) of the gel FePGSi show no crystalline phases because at thermal decomposition of this type of iron carboxylates, $\gamma\text{-Fe}_2\text{O}_3$ is formed inside the silica matrix, as very fine nanoparticles, almost amorphous at low-temperatures [16]. This phase, which usually turns into $\alpha\text{-Fe}_2\text{O}_3$ at around $400\text{ }^{\circ}\text{C}$, stabilizes inside the silica matrix up to $800\text{ }^{\circ}\text{C}$ [16]. The spinelic phase $\gamma\text{-Fe}_2\text{O}_3$ interacts at low temperature with the NiO formed by thermal decomposition of the Ni malonate, as a result of pattern (2). NiO thus formed (JCPDS file no. 85-1977) is in a weakly crystallized and reactive state, forming the ferrite

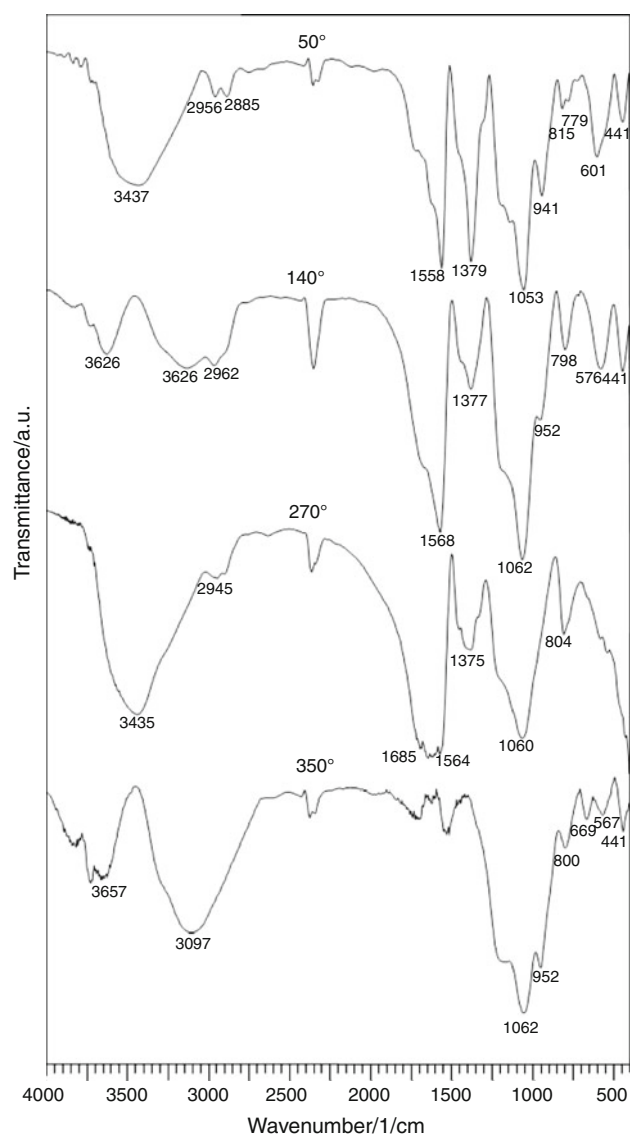


Fig. 8 FT-IR spectra of NiCrPGSi gel heated at different temperatures

nuclei, inside the silica matrix. By annealing the powder NiFePGSi at 600 °C, NiFe₂O₄ spinel (JCPDS file no. 86-2267) appears as sole crystalline phase inside the amorphous silica matrix (pattern 4). The crystallization degree significantly increases after calcination at 1000 °C according to pattern (5) from Fig. 9.

Figure 10 presents the XRD patterns of the powders obtained at 400 °C from the gels CrPGSi (pattern 1), NiPGSi (2), and of the powders CrNiPGSi annealed at 400 °C (3), 600 °C (4) and 1000 °C (5).

XRD patterns (1) and (2) of the gels containing only one metal cation (CrPGSi, NiPGSi) annealed at clearly evidence the crystallization of the corresponding simple oxides inside the amorphous silica matrix: Cr₂O₃ (JCPDS file no. 38-1479) and NiO [17]. In the case of the gel CrNiPGSi, containing both metal cations, after calcinations

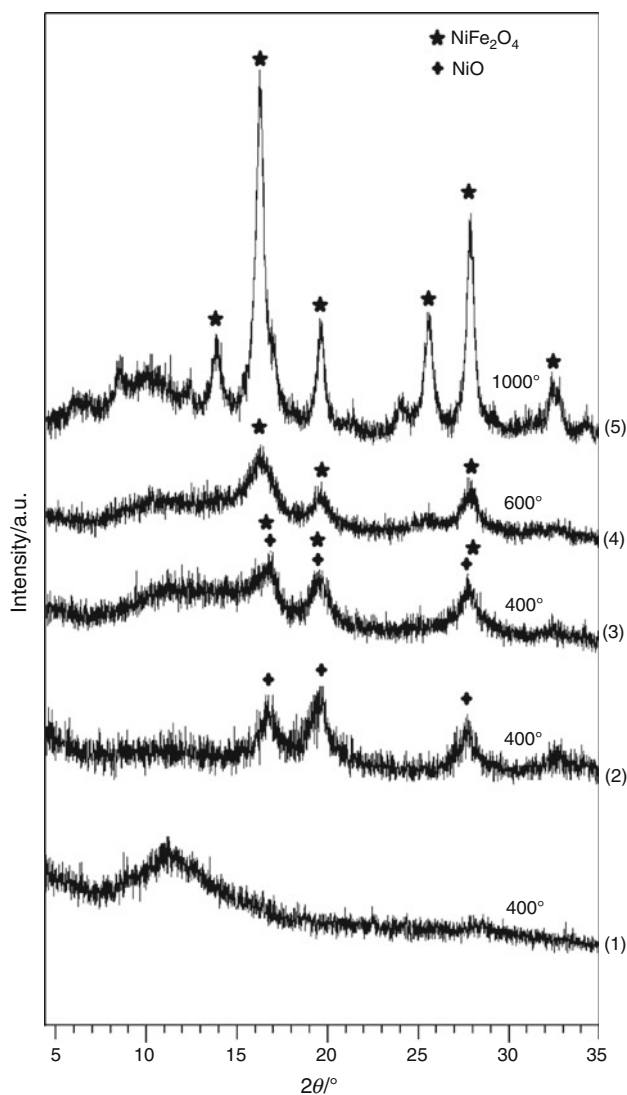


Fig. 9 XRD patterns of the powders annealed at different temperatures: (1) FePGSi—400 °C; (2) NiPGSi—400 °C; (3) FeNiPGSi—400 °C; (4) FeNiPGSi—600 °C; (5) FeNiPGSi—1000 °C

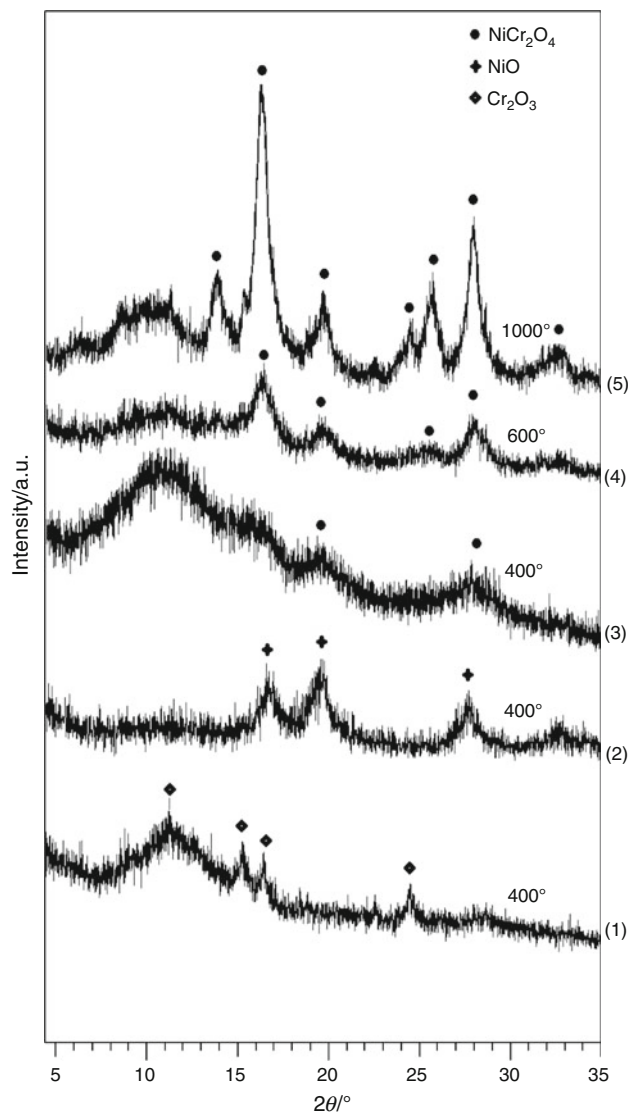


Fig. 10 XRD patterns of the powders annealed at different temperatures: (1) CrPGSi—500 °C; (2) NiPGSi—500 °C; (3) CrNiPGSi—500 °C; (4) CrNiPGSi—600 °C

at 400 °C, XRD pattern does not evidence any crystalline single oxide (Cr₂O₃ or NiO) probably because of their interaction, with formation of NiCr₂O₄ nuclei inside the amorphous silica matrix. This hypothesis is confirmed by the appearance in the pattern (4) of the powder CrNiPGSi annealed at 600 °C of the diffraction peaks characteristic for spinel phases. When this powder is annealed at 1000 °C, well-crystallized NiCr₂O₄ spinel (JCPDS file no. 77-0008) forms inside the silica matrix, according to the corresponding XRD pattern (5).

TEM images of the nanocomposites NiM₂O₄/SiO₂ obtained at 1000 °C are presented in Fig. 11 for M = Fe and in Fig. 12 for M = Cr.

TEM images for NiFe₂O₄/SiO₂ evidence the formation of spherical nickel ferrite nanoparticles with diameters in

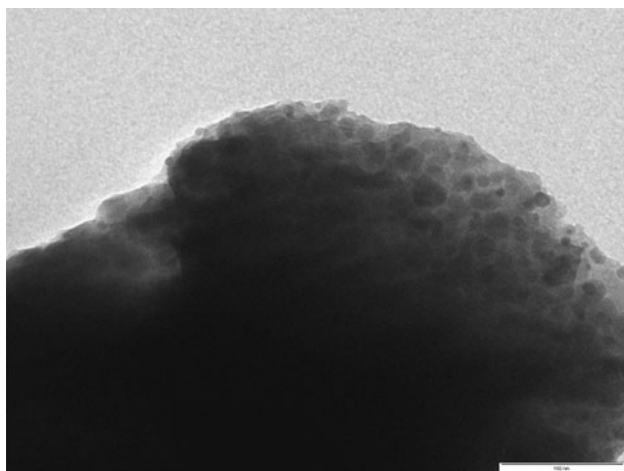


Fig. 11 TEM image of the $\text{NiFe}_2\text{O}_4/\text{SiO}_2$ nanocomposites obtained by annealing at $1000\text{ }^\circ\text{C}$ the NiFePGSi powder (the bar represents 100 nm)

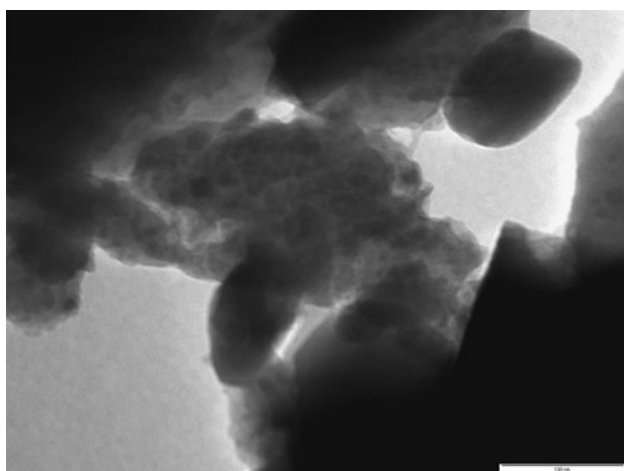


Fig. 12 TEM image of the $\text{NiCr}_2\text{O}_4/\text{SiO}_2$ nanocomposites obtained by annealing at $1000\text{ }^\circ\text{C}$ the NiCrPGSi powder (the bar represents 100 nm)

the range 10–30 nm homogeneously dispersed inside silica matrix. In the case of nickel chromites, the contrast between the spinel nanoparticles and the silica matrix is weaker, and the shape of the nanoparticles is less visible. In both cases, the mixed oxide nanoparticles are homogeneously dispersed inside silica matrix.

Conclusions

The comparative study regarding the formation of nickel-based spinels NiM_2O_4 for $\text{M} = \text{Fe(III)}$ and Cr(III) inside a silica matrix showed the possibility of obtaining nanocomposites of 50% $\text{NiM}_2\text{O}_4/50\%$ SiO_2 for potential applications as catalysts. The synthesis method used is a particular sol–gel method that starts from sols containing

tetraethyl orthosilicate, the corresponding metal nitrates, and 1,3-propanediol, besides water and ethanol as solvents. The complexity of the sols, especially the presence of the diol besides TEOS during gelation, influences the formation of the siloxane network, leading to hybrid gels which contain in the pores the mixture of metal nitrates and the diol. During the thermal treatment metal nitrates interact with the diol with formation of metal carboxylates, which will function as precursor of NiM_2O_4 particles. By the thermal decomposition of this precursors inside the silica matrix, weakly crystallized, very reactive simple oxides form, which interact to each other leading to the formation of the desired spinels as nanoparticle inside the amorphous silica matrix, as evidenced by TEM images.

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