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PREPARATION OF Fe_xO_y/SiO_2 NANOCOMPOSITES BY THERMAL DECOMPOSITION OF SOME CARBOXYLATE PRECURSORS FORMED INSIDE THE SILICA MATRIX

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In this paper we present a study regarding the obtaining of iron oxides embedded in silica matrix, using a modified sol–gel method. This method consists in the formation, inside the silica matrix, of some Fe(III)-carboxylate compounds, resulted in the redox reaction between $Fe(NO_3)_3$ and diol.

We have synthesized four gels, starting from tetra-ethyl orthosilicate, $Fe(NO_3)_3 \cdot 9H_2O$ and different diols: ethylene glycol, 1,2-propanediol, 1,3-propanediol and 1,4-butanediol, for a final composition 50% Fe_2O_3/50% SiO_2. The obtained gels have been thermally treated at 130°C, when the redox reaction $Fe(NO_3)_3$-diol took place with formation of the precursors in the xerogels pores. The thermal decomposition of all four precursors took place up to 300°C.

The samples obtained by annealing at 300, 500, 700°C of the four xerogels lead to crystalline phases inside the amorphous silica matrix. γ-Fe_2O_3/SiO_2 may be obtained as unique phase depending on the diols nature. The formation of the precursors inside the silica matrix and the evolution of the crystalline phases were analyzed by thermal analysis, FTIR spectrometry and XRD.

Keywords: *diols, iron oxide, silica*

Introduction

The synthesis of magnetic nanomaterials is a subject of great interest due to the diversity of applications in catalysis [1], magneto-optics [2], drug delivery [3], gas sensors [4]. These fields need the special magnetic properties of these systems, which are essentially different from the properties of classic magnetic materials.

The sol–gel method offers special advantages in the preparation of these nanocomposites [5–7]. It allows the control on the final properties of the material and represents the remedial for the aggregation tendency of nanopowders assuring the homogenous dispersion of the ultra-fine metal oxides particles inside the host matrix [8]. Concerning the sol–gel iron–silica nanocomposites, the material consists of a SiO_2 matrix which contains one of the polymorphs of Fe(III) oxide: α-Fe_2O_3, γ-Fe_2O_3, ε-Fe_2O_3, β-Fe_2O_3 or amorphous Fe_2O_3 [9]. Hematite (α-Fe_2O_3), the anti-ferromagnetic hexagonal form, represents the most thermodynamically stable polymorph of Fe(III) oxides and it is the most easy to obtain. However, the most studied polymorph is maghemite (γ-Fe_2O_3), the ferromagnetic cubic form [10] due to its magnetic properties, which ensure many technological applications. The obtaining of maghemite is difficult because of the γ- to α-Fe_2O_3 transition, which is not easy to control. The explanation consists in the multitude of factors that can affect the stability of iron oxides. Depending on the iron precursor and the parameters of the sol–gel process, besides the polymorphs of Fe(III) oxides, other iron oxyhydroxides can be obtained: goethite α-FeO(OH) or fayalite Fe_2SiO_4.

A characteristic of iron oxides consists in the variety of the possible transitions between different crystalline phases. In favourable conditions, almost every iron oxide species may be converted in other phases. Factors as particles dimensions, their coating with inert layers, the presence of a support, affect the stability of iron oxides [11, 12]. In dried state, maghemite turns to hematite at temperatures in the range 300–600°C depending on the preparation conditions and on the heating rate [13]. Del Monte *et al.* [14] have achieved a comparative study on the phases of the iron oxides by the sol–gel synthesis using chloride and ferric nitrate in ethanol solutions. The phase γ-Fe_2O_3 (maghemite) was obtained from nitrate and α-Fe_2O_3 (hematite) from chloride.

The silica matrices have a stabilizing effect on the maghemite nanoparticles with dimensions under 10 nm for which a super-paramagnetic behaviour was reported [15, 16].

In the paper we present the obtaining of Fe(III) carboxylates embedded in silica matrix, which by adequate thermal treatment leads to formation and stabilization of the γ-Fe_2O_3 as unique phase within the silica matrix.

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Experimental

Materials and preparations

Iron(III) nitrate, $Fe(NO_3)_3{\cdot}9H_2O$, tetra-ethyl orthosilicate (TEOS), ethylene glycol (EG), 1,2-propanediol (1,2-PG), 1,3-propanediol (1,3-PG), 1,4-butanediol (1,4-BG), ethanol, concentrated nitric acid, HNO_3 were high purity reagents product of Merck. All chemicals were pursued and used as received.

Preparation of gels (G1–G4) for composites with 50 mass% Fe_2O_3/SiO_2 was carried out by dissolving iron(III) nitrate in the corresponding quantity of diol and water (Table 1). An ethanolic TEOS solution was slowly added under intense stirring. The gel (G5) without diol was prepared in the same manner. The obtained sols were left gelling at room temperature. The obtained gels were dried at 40 and then heated at 130°C, when the redox reaction took place between diol and nitrate ion (G1–G4). From the reaction results the complex combination embedded in silicagel, used as precursor for preparation of Fe_2O_3/SiO_2. The resulted powders were thermally treated at different temperatures in order to obtain iron oxides embedded in silica matrix.

Techniques

For monitoring the evolution of the redox reaction between Fe(III) nitrate and diols, the gels were characterized by thermal analysis using a 1500 D MOM Hungary derivatograph. The thermal behaviour of the complex combinations embedded in the gels was achieved with a Diamond Perkin Elmer thermobalance.

The samples were characterized by FTIR spectrometry on a Shimadzu Prestige-21 FT-IR spectrometer, in KBr pellets, in the domain 400–4000 cm^{-1} and XRD registered on a D8 Advanced-Bruker AXS diffractometer, using MoK_α radiation (λ_{Mo}=0.7093 Å). Magnetic measurements were performed on a laboratory installation with data acquisition system.

Results and discussion

In previous papers [17] we have introduced the modified sol–gel method based on the formation, within the xerogels pores, of metallic ions carboxylates complexes, used as precursors for oxidic systems embedded in SiO_2. Fe(III) carboxylate type complex combinations were obtained in the redox reaction between $Fe(NO_3)_3$ and diol [18]. In the present paper we have obtained these Fe(III) combinations, within the silica matrix, starting from the system TEOS-$Fe(NO_3)_3$-diol.

Figure 1 exhibits DTA curves of gels G1–G4 dried at 40°C. The exothermic effect in the range 70–90°C was attributed to the redox reaction between $Fe(NO_3)_3$ and diol with formation of Fe(III) carboxylate type complexes. The exothermic effect with maximum at ~250°C corresponds to the oxidative decomposition of Fe(III) carboxylate. According to the thermal behaviour, all gels dried at 40°C that contained in pores diols and $Fe(NO_3)_3$ have been thermally treated at 130°C in order to obtain the corresponding Fe(III) carboxylates within the matrices pores.

Figure 2 presents the FTIR spectra of the gels (G1–G4) at 40°.

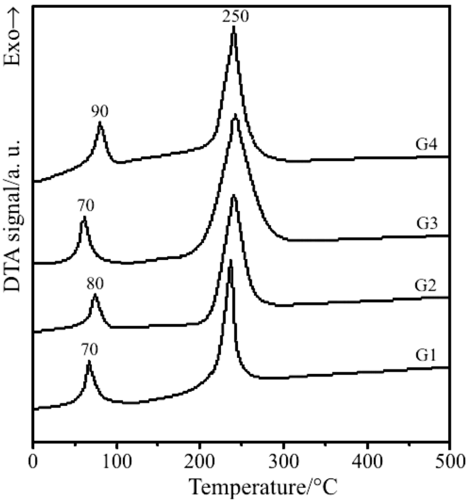

Fig. 1 DTA thermal curves of the gels (G1–G4) dried at 40°C

Table 1 Synthesis parameters of the prepared gels

Sample	Mass/% Fe_2O_3/SiO_2	Diol	Quantity/mol					t_{gel}/h
			$Fe(NO_3)_3{\cdot}9H_2O$	TEOS	NO_3^-	diol	H_2O	
G1	50	EG	0.03125	0.042	0.09375	0.07	0.168	288
G2		1,2-PG	0.03125	0.042	0.09375	0.1055	0.168	360
G3		1,3-PG	0.03125	0.042	0.09375	0.0527	0.168	312
G4		1,4-BG	0.03125	0.042	0.09375	0.0527	0.168	312
G5		–	0.03125	0.042	0.09375	–	0.168	168

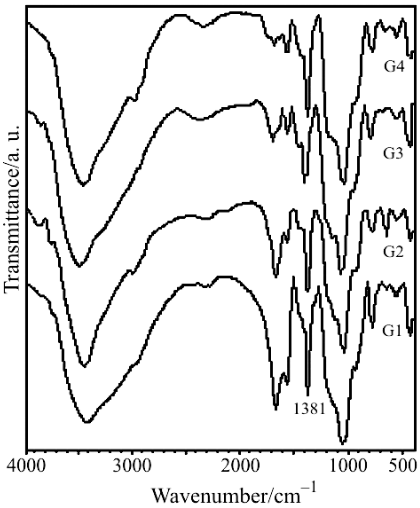

Fig. 2 FTIR spectra of the gels (G1–G4) dried at 40°C

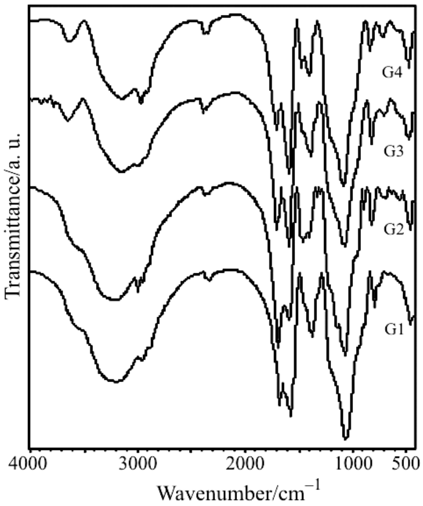

Fig. 3 FTIR spectra of the gels (G1–G4) thermally treated at 130°C

All spectra evidence the band characteristic for the ion NO_3^- at 1381 cm^{-1} that confirms the presence of $Fe(NO_3)_3$ within the gels pores. The bands from 3430 and 1670 cm^{-1} correspond to the stretching and deforming vibrations of the –OH groups (silanol, hydroxyl). The intense band at 1060 cm^{-1} is attributed to the asymmetric stretching vibrations $\nu_{as(Si–O–Si)}$ and the band from ~950 cm^{-1} as shoulder corresponds to the stretching vibrations of the Si–OH bonds. The band at 800 cm^{-1} corresponds to the symmetric stretching vibrations $\nu_{s(Si–O–Si)}$ of SiO_4 tetrahedron [19] and the band at 475 cm^{-1} can be attributed to the stretching vibrations that are characteristic for the Si–O- bond.

The weak bands from the range 2800–3000 cm^{-1} confirm the diols presence in the system. The silica matrices bands overlap the other bands corresponding to the diols. The band from 1570 cm^{-1} can be attributed to the carboxylate groups formed during the redox reaction started at 40°C (experimentally observed).

The FTIR spectra (Fig. 3) of the gels thermally treated at 130°C evidenced the consumption of the nitrate ion and diol in the redox reaction and the formation of the carboxylate compounds within the silica gels.

Each spectrum displays in the range 1300–1700 cm^{-1} the bands characteristic to the vibrations of the carboxylate groups coordinated to the Fe(III) ions. The band at ~1570 and 1670 cm^{-1} attributed to the vibration $\nu_{as(COO^-)}$ proves the corresponding ligands formation [18]. In the range 1300–1450 cm^{-1} are evidenced characteristic bands of the group (COO^-) attributed to the vibrations $\nu_{s(CO)}+\delta_{OCO}$ and to the vibrations $\nu_{s(COO^-)}$ [20, 21]. The absorption bands in the range 2900–3000 cm^{-1} are characteristic for the groups $–CH_2–$, $–CH_3$ from the carboxylates as well as for the diols chemically bonded within the matrices network [18, 22].

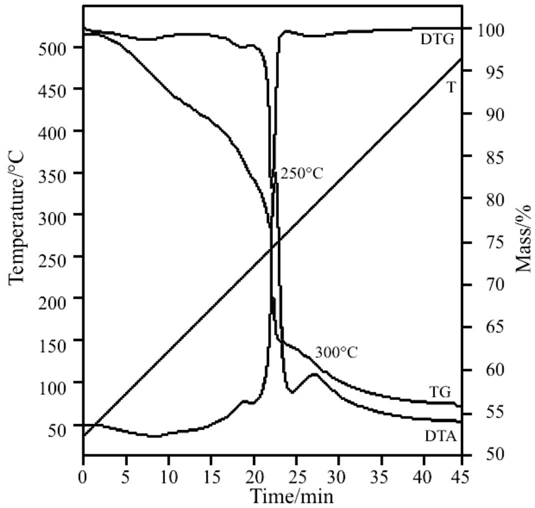

Fig. 4 Thermal curves of the gel G1 thermally treated at 130°C

The thermal behaviour of the gels thermally treated at 130°C confirms the presence of the Fe(III) carboxylate compounds within the xerogels. Figures 4 and 5 exhibit the thermal curves obtained for the gels G1 (with EG) and G4 (with 1,4-BG) up to 500°C in air.

The mass loss registered up to 180°C corresponds to the elimination of adsorbed water and to the on-going poly-condensation process. The mass loss in a single step from the range 180–270°C associated with a strong exothermic effect on DTA corresponds to the oxidative decomposition of the Fe(III) carboxylate precursor within the pores of silica matrix. The decomposition of Fe(III) carboxylate generates a reducing atmosphere (CO) in the pores of the matrix. Thus, Fe(III) turns to Fe(II) which re-oxidizes to Fe_2O_3 [18].

The mass loss with exothermic effect at 300°C is attributed to the burning of organic chains

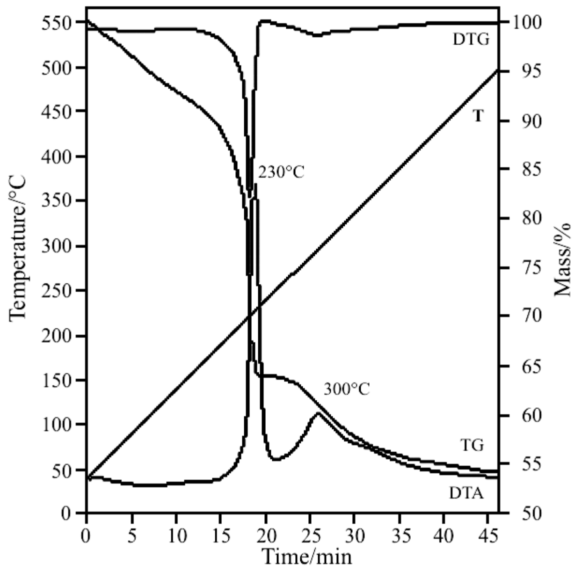

Fig. 5 Thermal curves of the gel G4 thermally treated at 130°C

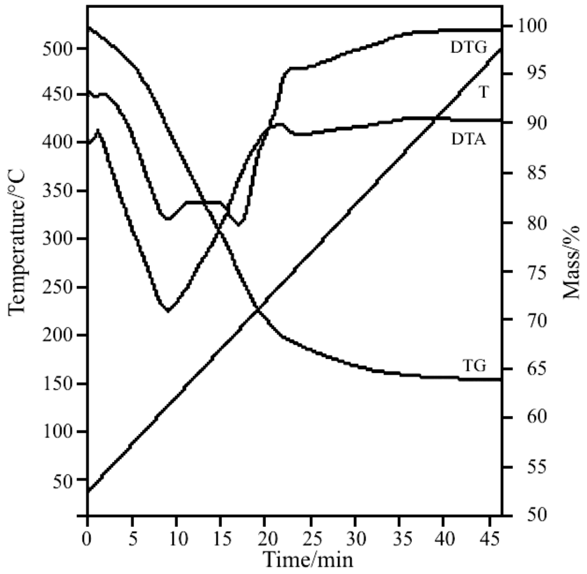

Fig. 6 Thermal curves of the gel G5 thermally treated at 130°C

(–O–$(CH_2)_n$–O–) corresponding to the diols chemically bonded within the matrix [22]. The gels G2 and G3 had similar thermal behaviour, while gel G5, without diol, has presented a different evolution of the thermal curves (Fig. 6). The mass loss on TG and DTG and the thermal effects on DTA are characteristic for the decomposition of iron nitrate and for the evolution of the xerogels poly-condensation.

The samples from 130°C (G1–G4) that contain the Fe(III) carboxylate precursor and the sample with $Fe(NO_3)_3$ within the xerogel (G5) were thermally treated at 300°C, 6 h. The XRD patterns of the obtained powders (G1–G3) present a practically amorphous aspect. The pattern of the sample G4 presents a crystalline phase identified as γ-Fe_2O_3 [18]. The pattern of the sample with iron nitrate precursor (G5) evidences as crystalline phase α-Fe_2O_3.

Ulterior, the samples from 300°C were annealed at 500 and 700°C, 3 h. The XRD patterns at 500°C for the samples (G1–G3) and (G5) present the same characteristics like at 300°C.

In case of the samples thermally treated at 300 and annealed at 700°C (Fig. 7) we can observe the crystallization tendency of γ-Fe_2O_3, in case of the samples G1–G3, confirmed by magnetic properties. In case of the samples G4 and G5 we can observe an increase of the crystallization degree for the phases γ-Fe_2O_3 (G4) and α-Fe_2O_3 (G5).

The reducing environment generated at thermal decomposition of the carboxylate type precursors explains the formation of γ-Fe_2O_3 in case of the gels synthesized with diols. Thus, Fe(III) is reduced to Fe(II) with re-oxidation, at 250–300°C, to γ-Fe_2O_3 which stabilizes within the silica matrix up to 700°C. The higher crystallization degree of γ-Fe_2O_3, in case of sample G4 can be due to the higher porosity of the sample synthesized with 1,4-BG, which facilitates the fast re-oxidation of Fe(II) to Fe(III) during decomposition.

If we anneal the gels (G1–G4) obtained at 130 directly to 700°C (Fig. 8), we obtain, depending on the re-oxidation degree Fe(II)→Fe(III), different crystalline phases: α-Fe_2O_3, γ-Fe_2O_3 or/and Fe_2SiO_4. In case of gel G5, α-Fe_2O_3 forms as unique phase.

For the composites obtained from gel G4 (synthesized with 1,4-BG), by thermal treatment at 300°C followed by annealing at 500 and 700°C, which contain γ-Fe_2O_3 as unique phase, (Fig. 9) we have calculated, using the Scherrer formula, the dimensions of

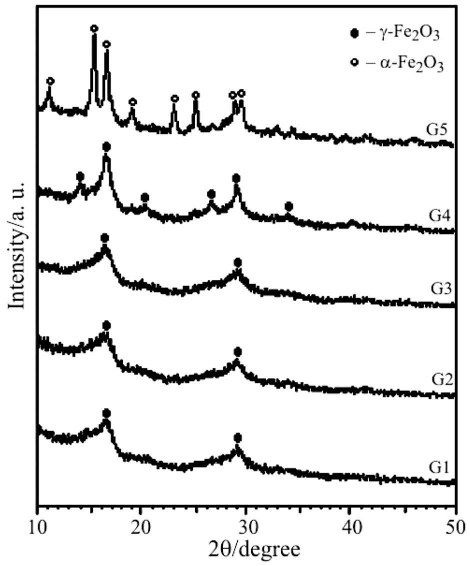

Fig. 7 XRD patterns of the gels thermally treated at 300→700°C

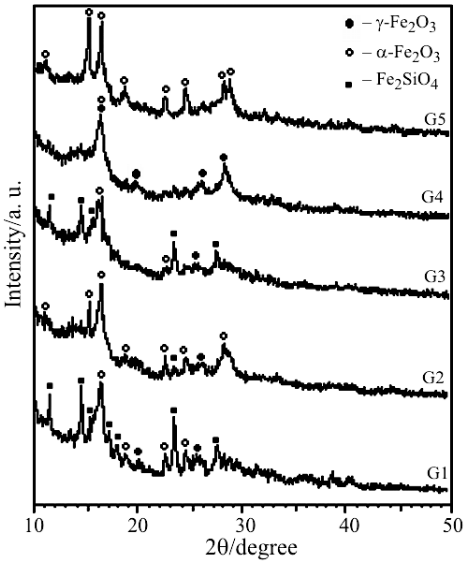

Fig. 8 XRD patterns of the gels thermally treated at 130→700°C

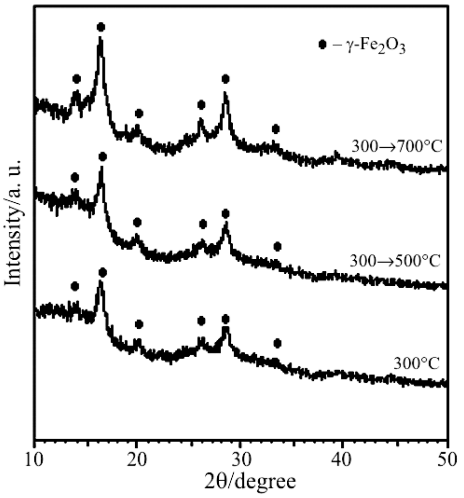

Fig. 9 XRD patterns of gel G4 annealed at different temperatures

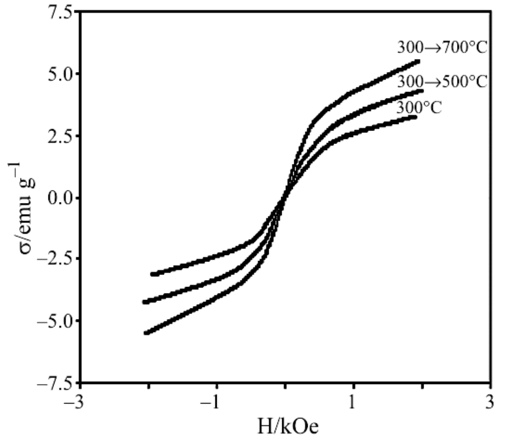

Fig. 10 Magnetization curves of gel G4 annealed at different temperatures

the crystallites. The mean diameter of the crystallites was in the range 5–7 nm.

The magnetic behaviour of these nanocomposites is super-paramagnetic and the registered curves show no hysteresis (Fig. 10). This behaviour is due to the very small dimensions of the nanoparticles and to their homogenous dispersion within the silica matrix, which leads to a mono-domenial behaviour of these nanoparticles. The saturation magnetization slowly increases with temperature increase, because of the nanoparticles dimensions increase.

Conclusions

The modified sol–gel method used in our study, based on formation and thermal decomposition of Fe(III) carboxylate complexes, within the pores of the matrix, allows us to obtain different oxidic phases in SiO_2, depending on the applied thermal treatment and the diol used in synthesis. This is due to the different reduction-re-oxidation degree $Fe(III)\rightarrow Fe(II)\rightarrow Fe_2O_3$, at decomposition of Fe(III) carboxylates, which depends on the generated reducing atmosphere and on the porosity of the silica matrix.

γ-Fe_2O_3 is obtained as unique phase nanocrystallites, in a SiO_2 matrix, by using the diol 1,4-BG and by applying a controlled thermal treatment. This phase forms at 300°C stabilizing within the silica matrix up to 700°C. The magnetic behaviour of the nanocomposites γ-Fe_2O_3/SiO_2 is superparamagnetic, characteristic for the systems formed from magnetic nanoparticles with mono-domenial behaviour.

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