Fe$_2$O$_3$-SiO$_2$ NANOCOMPOSITES OBTAINED BY DIFFERENT SOL-GEL ROUTES

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In the last years many studies on the iron oxides embedded in silica matrix were realized in order to obtain nanomaterials with magnetic properties. In this work, nanocomposite materials in the iron oxide-SiO$_2$ system were prepared by sol-gel method via alkoxide and aqueous route in order to accomplish a comparative study. As SiO$_2$ source, tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) in alkoxide route, as well as silica sol Ludox (30%) in the case of aqueous route, were used. As iron source [Fe(NO$_3$)$_3$.9H$_2$O] was chosen. The gels were annealed at different temperatures in order to obtain iron oxides with different oxidation states, structures and grain sizes. The structural characterization of the obtained materials via the two preparation routes, before and after thermal treatment, was realized by DTA/TGA analysis, X-ray diffraction and IR spectroscopy.

1. Introduction

In the last decade, one of the most interesting research field was represented by the magnetic materials. This fact is due to the special magnetic properties which make them suitable for potential technological applications in many important domains, like: medical diagnosis, controlled drug delivery, bioprocessing, magnetic refrigeration, ferrofluids, information storage, catalysis, and so on.

Among the magnetic materials, the iron oxides occupy one of the most important places. This is proved by the great number of researchers involved in their preparation, using various methods, such as: hydrothermal synthesis [1], pyrolisis technique [2], wet chemical method [3-5], electrochemical [6] and/or the sol gel one [7-16]. Excepting the sol-gel technique, the literature underlines some major disadvantages of the mentioned methods, concerning the impossibility to obtain pure amorphous phases, to ensure a good control of particle size, and to achieve monodispersity. The general advantages of the sol-gel method refer to: (a) the possibility to obtain materials with predeterminated structure, depending on the experimental conditions; (b) the permission to control the microstructure and the homogeneity of the reaction products; (c) the guarantee to obtain reaction products with nanosized dimensions; (d) the permission to embed molecules and biomolecules which maintain their stability and properties within the sol-gel matrix; (e) it allows to solve a critical obstacle in assembling and maintaining a nanoscale material, respectively the tendency to aggregate being effective for dispersing small oxide particles in nonmetallic matrixes, which avoid sintering and stabilizes the existing phase.

Previous studies [10-13] in the Fe$_x$O$_y$-SiO$_2$ system but starting with FeSO$_4$.7H$_2$O have underlined some inconveniences connected to the removal of SO$_4^{2-}$ ions from the gel. Moreover the Fe^{2+} ion is not stable during the sol-gel process, the oxidation to Fe^{+3} taking place during the mixing of the reagents. In the present work, nanocomposite materials in the iron oxide-SiO$_2$ system were prepared by sol-gel method via alkoxide and aqueous route starting with a Fe^{+3} precursor, in order to accomplish a comparative study on their preparation conditions, structure and properties.

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2. Experimental

Table 1 presents the chemical compositions and the experimental preparation conditions used in order to prepare some homogeneous gels in the Fe_2O_3-SiO_2 system, that could be transformed in nanocomposites by adequate thermal treatments.

Table 1. Chemical compositions and the experimental preparation conditions used in order to prepare homogeneous gels in the Fe_2O_3-SiO_2 system.

Sample	Sol-gel method used	Nanocomposites materials prepared			Reaction conditions		Gelation time (h)
		SiO_2		Fe_2O_3[*]	pH	T (^{O}C)	
		Precursor[x]	Molar ratio (MR)	Fe/SiO_2 (MR)			
1	Colloidal route	CS	$SiO_2/H_2O=1/11.47$	1/8.37	2	65	2.5
2	Alkoxidic route	TEOS	$SiO_2/H_2O/C_2H_5OH=$ 1/11.47/8	1/8.37	2	65	2.25
3		TEOS	$SiO_2/C_2H_5OH=1/8$	1/8.37	2	80	24
4		MTEOS	$SiO_2/C_2H_5OH=1/8$	1/8.37	2	80	168
5		MTEOS	$SiO_2/H_2O/C_2H_5OH=$ 1/11.47/8	1/8.37			
6		MTEOS	$SiO_2/H_2O/C_2H_5OH=$ 1/11.47/12	1/8.37	Rejected		
7		MTEOS	$SiO_2/H_2O/C_2H_5OH=$ 1/11.47/16	1/8.37	samples by unmixing		
8		MTEOS	$SiO_2/H_2O/C_2H_5OH=$ 1/11.47/16	1/17.55			

[*] In all cases, the source of Fe_2O_3 was $Fe(NO_3)_3 9H_2O$;

[x] CS - colloidal silica; TEOS - tetraethoxysilane; MTEOS - methyltriethoxysilane.

As it can be seen, the colloidal route, for the synthesis of sample 1 and the alcoxide one for the rest of samples (2-8) were used.

As iron source, the iron(III) nitrate nonahydrate $[Fe(NO_3)_3 9H_2O]$ from Chimopar was used and its content in the nanocomposite material was calculated to be 10 wt. % related to SiO_2 content, respectively a molar ratio Fe/SiO_2 equal to 1/8.37. The iron salt was introduced in the system as aqueous solution in all experiments, excepting samples 3 and 4, when it was introduced as alcoholic solution.

Concerning the silica precursor, for the colloidal route a colloidal silica sol Ludox AS-30, 30 wt. % (Aldrich) was used. In the alcoxidic case, tetraethoxysilane (TEOS) from Merck and methyltriethoxysilane (MTEOS) from Fluka have been used.

The synthesis were carried out on magnetic stirrers with controlled temperature.

Tacking into account the fact that the iron salt can decompose and lead to the formation of various forms of oxides and/or oxy-hydroxides with different properties, the characterization of the prepared materials before and after the thermal treatments and the choice of the corresponding temperatures were carried out with special attention.

The Fe_2O_3-SiO_2 nanocomposites were characterized by:

- differential thermal analysis (DTA), using a MOM Derivatograph with a heating rate of 5 ^{o}C/min. up to 1000 ^{o}C;

- X-ray diffraction (XRD), carried out on a TuR M-62 with HZG-3 equipment, radiation $Cu_{k\alpha}$;

- infrared spectroscopy (IR), carried out on a Specord 76 IR spectrometer.

3. Results

As resulted from Table 1, homogeneous gels were obtained in the experimental conditions corresponding to samples l, prepared by the colloidal route and samples 2, 3, and 4, synthesized by the alkoxide way.

The gelling time for the studied samples was different depending on the experimental conditions. Sample 1 and 2 with similar amount of water, no matter the type of SiO$_2$ precursor, present a rather short time of gelation. In the case of samples 3 and 4 in which no supplementary water was added, the hydrolysis being accomplished by the water brought by Fe(NO$_3$)$_3$9H$_2$O, the gelation time was essentially longer. It has also to be mentioned that in the case of sample 4 when a substituted Si-alkoxide was used as SiO$_2$ source, the longer gelation time could also be explained by the steric hindrance of the alkyl gorup bonded to silicon

For all the other samples (5-8) the reaction mixtures were not stable, a phase separation being observed during the sol-gel process. This effect is explained by the hydrophobic character of MTEOS.

DTA/TGA results

The thermal behavior of the obtained gels and the corresponding assignements, as determined by DTA/TGA are presented in Table 2.

The main thermal effects of the sample 1 and 2 were assigned to the water and alcohol removal and to combustion of the residual organics. In the case of sample 1, a decomposition step assigned to iron oxy-hydroxide decomposition could be also noticed. In the case of the other samples the iron oxy-hydroxide decomposition overlaps the effects assigned to the SiO$_2$ matrix..

For the sample 3, obtained starting with TEOS, but without supplementary water addition, the DTA/TGA curves shown the embedment of partially hydrolized alkoxide in the obtained gel. The unreacted alkoxides decomposes at about 350 ^{o}C.

In the case of sample obtained starting with MTEOS the thermal effect assigned to the combustion of the organic moities chemically bonded to the silica gel were registrated.

Based on DTA/TGA analysis results, the thermal treatments presented in Table 3 have been established in order to obtain nanocystallized Fe$_2$O$_3$. Table 3 also contains the crystallites dimensions estimated from XR data, using Sherrer formula.

Table 2. Thermal stability of the samples according to DTA/TGA analysis.

Sample	Temperature range, (^{o}C)	Effects, (^{o}C)		Weight loss, (%)	Assignments
		Endo	Exo		
1	80-200	135		15.38	Adsorbed water evolution
	200-260	240		3.85	Iron oxy-hydroxide decomposition
	260-1000			3.08	Structural OH$^-$ evolution
	20-1000			22.31	
2	70-250	140		22.50	EtOH, adsorbed water and N$_x$O$_y$ evolution
	250-1000			5.00	Organic residue combustion
	20-1000			27.50	
3	60-160	100		7.37	EtOH and adsorbed water evolution
	160-510		360	15.66	N$_x$O$_y$ evolution and residual TEOS
			420		decomposition and combustion
	500-1000			1.84	
	20-1000			24.87	
4	30-380			8.57	EtOH, adsorbed water evolution and N$_x$O$_y$ evolution
	380-800		380-	10.48	Hybrid matrix decomposition and
	20-1000		800	19.05	combustion

Table 3. The thermal treatments and the crystallite dimensions of the crystallized Fe_2O_3.

| Sample	Thermal treatment		Crystallite dimensions
	Temperature,(^{o}C)	Time,(h)	(nm)
1	350	2	26
2	350	2	-
3	420	4	29
4	800	2	42

IR results

Fig. 1 presents the IR spectra of the four prepared samples and confirms the DTA/TGA results.

In all cases, the characteristic vibration bands of a SiO_2 gel, mainly: ν_{as} Si-O-Si (LO) at 1200 cm^{-1}; ν_{as} Si-O-Si (TO) at 1089 cm^{-1}; ν_{as} Si-O(H) at 946 cm^{-1}; ν_s Si-O-Si at 795 cm^{-1}; ν Si-O-Si at 540 cm^{-1} and δ Si-O-Si at 461 cm^{-1} were identified [17].

For the sample 4, obtained strating with MTEOS, supplementary vibration bands specific for the presence of CH_3 groups bonded at silicon atoms: ν_{as} at 2976 cm^{-1}; ν_s at 2912 cm^{-1}, δ_{as} C-H at 1414 cm^{-1}; δ_s C-H at 780 cm^{-1} were noticed, in good agreement with the peaks reported by Capozzi et al and Ou et al [18-20]. In the 780 cm^{-1} range the characteristic vibration for EtOH appears as well.

All samples, except sample 2, present the characteristic absorption band of the NO_3 vibration (1350 cm^{-1}) with different intensity, according to the degree of reaction of the iron precursor with the silica source. The band at about 590 cm^{-1} assigned by Bruni et al [21] to νFe-O vibration was also noticed. The intensity of the band depends also on the preparation method.
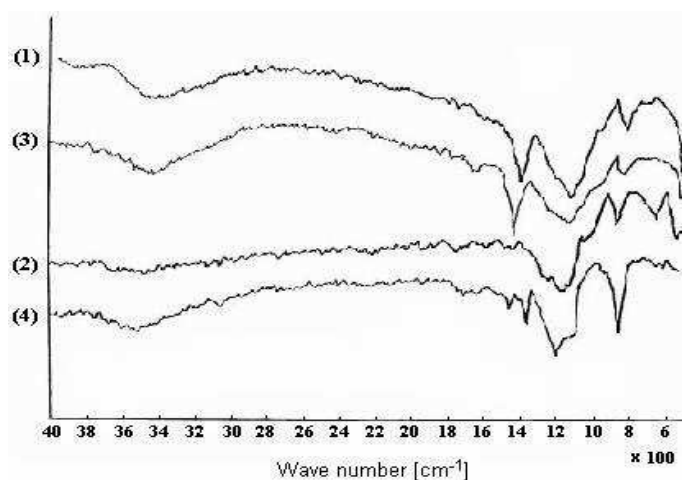
Fig. 1. The IR spectra of the prepared gels in Fe_2O_3-SiO_2 system.

XRD results

XRD patterns of the thermally treated samples (see Table 3) are presented in Fig. 2. In samples 1-4, besides the broad band characteristic for the presence of the amorphous silica gel the nanometric crystallization of α-Fe_2O_3 was evidenced. Sample 2 remains amorphous after the thermal treatment at low temperature. This fact could be assigned to the bonding of the iron into Si-O-Fe-O-Si polymeric bonds, that do not brake at low temperatures of the thermal treatment.
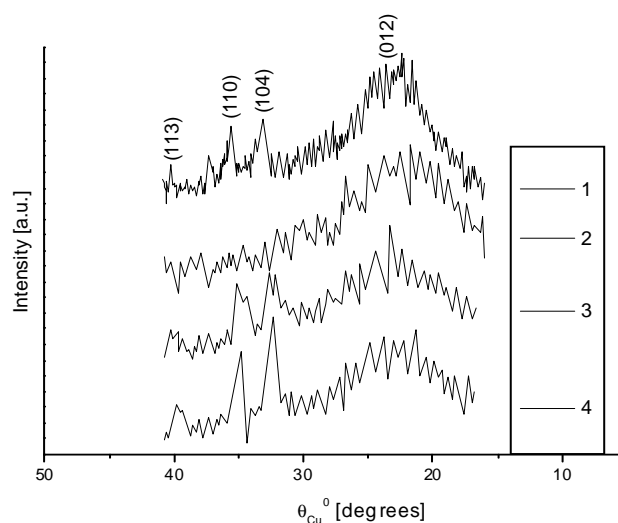
Fig. 2. The XRD spectra of the prepared nanocomposites.

4. Discussion

The methods presented above have shown the possibility to obtain nanocomposites in the Fe_2O_3-SiO_2 system.

The samples obtained in the mentioned experimental conditions allowed a comparative study between two sol-gel route (alkoxidic and colloidal), different silica precursors (TEOS and MTEOS), and different amount of water for the same precursor (TEOS) on the nanocomposite formation in the Fe_2O_3-SiO_2 system.

When MTEOS was used, the establishing of the reaction conditions was difficult due to its hydrofobic character. Phase separation occurred during the sol-gel process. The water released during the condensation process and the alcohol evaporation from the reaction mixtures during the gellation period displaced the system to the immiscibility domain (samples 5-8).

In the case of alkoxidic route, using TEOS in the presence of water (sample 2), the most homogeneous gel was obtained. The presence of the either unreacted $Fe(NO_3)_3.9H_2O$ or iron oxi-hydroxides could not be noticed by the characterization methods used. It could be assumed that in this case the sol-gel process was fulfiled and the iron ion is bonded in a -O-Si-O-Fe-O-Si-O- polymeric chain.

In the case of sample 3 (TEOS without water) an incomplete hydrolysis takes place and the unreacted TEOS is embedded in the obtained gel, that decomposes at about 350 ^{o}C.

In the case of sample 4 (MTEOS without water), the presence of the CH_3 radical chemically bonded to the inorganic network was noticed. The thermal decomposition of the hybrid gel takes place at rather high temperature (over 380 ^{o}C) and over a large temperature domain.

As mentioned before while using alkoxidic method for obtaining Fe_2O_3-SiO_2 nanocomposites was intensively studied, the colloidal route, in aqueous medium, was much less approached. As far a single paper was published on the matter [22].

In the present work the possibility to obtain homogeneous gels containing iron using the colloidal sol-gel method as well as the obtaining of nanocomposites by adequate thermal treatment was confirmed.

By thermal treatment at low temperatures (350-420 ^{o}C) the nanometric crystallization of α-Fe_2O_3 was established. The crystallites size of α-Fe_2O_3 depends on the preparation method. Using MTEOS instead of TEOS, as silica precursor, the tendency of crystallization of iron oxides increases. This is explained by the hydrophobic character of MTEOS-based matrix which has determined the concentration of hydrophilic iron based nano-clusters on the surface of the gel [16].

5. Conclusions

A comparative study of sol-gel nanocomposite materials in the Fe_2O_3-SiO_2 system, via alkoxide and aqueous route was accomplished.

The structural characterization of the obtained materials, before and after thermal treatment, was realized by DTA/TGA analysis, X-ray diffraction and IR spectroscopy.

By the results obtained in the present work, the possibility to obtain homogeneous silica gels containing iron was demonstrated. By adequate thermal treatment the homogeneous gels could be transformed into Fe_2O_3-SiO_2 nanocomposites.

α-Fe_2O_3 was evidenced as unique crystalline phase, no matter the route of sol-gel method used. The crystallite size depends on the preparation method.

The study reveals also the possibilities offered by the sol-gel processing to get nanomaterials with different structures depending on the preparation conditions.

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