



STUDY OF CATALYTIC EFFECT OF OXIDIC COMPOUNDS OF NiFe₂O₄ TYPE IN PROCESSES OF CHEMICAL DEGRADATION

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Oxidic compounds of NiFe₂O₄ type were synthesized by sol-gel autocombustion method. Reaction in solid phase was monitored by infrared spectroscopy. The structure of synthesized compounds was investigated by IR, XRD and SEM. It was found that these are structure of cubic spinel-type, and the particle size it is of nanometer order, ranging between 22 – 50 nm. Characterized samples were catalytic tested for the reaction of hydrogen peroxide decomposition. It was found that catalytic activity of oxidic compounds is influenced by chelating/fuel agent and thermal treatment.

INTRODUCTION

Oxidic compounds of MFe₂O₄ type (M = Ni, Cu, Co, Zn, Mn) are compounds with structure of cubic spinel-type which have found applications in different areas: data storage devices and/or recovery information, microwave devices, biomedical applications as contrast agents in diagnosis and magnetic guided devices for targeted and pulsed release of active principles, catalysts and sensors.^{1,2} Oxidic compounds with structure of cubic spinel, characterized by high chemical and thermal stability, were used as catalysts in total hydrocarbon oxidation process, substances with high risk of pollution, oxidative dehydrogenation of butene to butadiene, alcohols and peroxide decomposition, decarboxylation of organic acids etc.³ Catalytic properties depend on the structure of oxidic catalyst, size, shape and distribution of particles, parameters which are determined by the applied synthesis method.

Obtaining oxidic compounds with nanometer size particles has results in significant improvement of their properties. In this context, alternative synthesis methods have been developed

to classic ceramic method. Thus, a series of wet methods are used to obtain nanostructured oxide compounds: co-precipitation, hydrothermal, sol-gel and the modified methods, microemulsion, plasma or microwave treatment, host template.⁴

In this paper, results obtained in the synthesis, characterization and catalytic testing of some oxidic compounds of NiFe₂O₄ type are presented. These compounds have been synthesized by sol-gel autocombustion method. This method is known to presents several advantages: allows obtaining nanometer-size particles which are preferred for obtaining catalysts because provides high specific surface area of contact and selectivity. Also, this method presents high degree of homogeneity, reproducibility of results, low atomic diffusion during calcinations process, avoiding phase segregation and these advantages justify the choice of sol-gel method for synthesis of polymetallic oxides.

EXPERIMENTAL

Substances used for synthesis of oxidic compound are analytical purity and were used without further purification.

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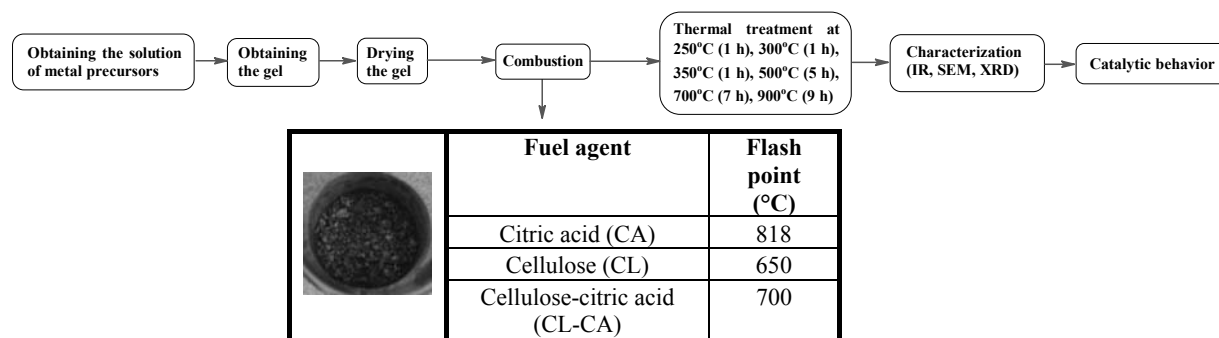


Fig. 1 – Protocol synthesis of oxidic compounds of NiFe_2O_4 type.

Solution of metallic precursor was obtained by mixing, in stoichiometric ratio, of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and a chelating/fuel agent: citric acid ($\text{C}_6\text{H}_8\text{O}_7$), cellulose ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$) and mixing cellulose-citric acid. Molar ratio between Ni^{2+} and Fe^{3+} cations was 1:2, and between metallic cations in solution and chelating/fuel agent was 1:3. Chelating/fuel agents used for synthesis of oxidic compounds with ordered structure have the ability to decrease the sintering temperature compared with the ceramic method. Homogeneous mixing obtained was stirred until the formation of gel. The gel was subjected to thermal treatment at different temperature, as can be seen from the protocol synthesis (Fig. 1).

Solid phase reaction was followed by IR spectroscopy. Thus, IR spectra were recorded at different stages of synthesis. The spectra give information about the disappearance of organic phase and nitrate ion from reaction medium and the position of metal ions in the crystal structure. This information is useful to determine how the synthesis process should be directed. IR spectra were recorded in the mid infrared range ($4000 - 300 \text{ cm}^{-1}$) with Fourier transform (FTIR) using a Bruker spectrophotometer TENSORTM 27-type with an anvil ATR cell and a resolution of 2 cm^{-1} .

Synthesized samples were characterized by XRD and SEM. X-ray diffraction (XRD) patterns were recorded with a Shimadzu LabX 6000 instrument equipped with a graphite monochromator using a $\text{Cu K}\alpha$ radiation ($\lambda=0.15406 \text{ nm}$).

Scanning electron microscopy (SEM) images were obtained in a Quanta 200 apparatus with EDAX system of elemental analysis.

Characterized samples were catalytic tested in the reaction of hydrogen peroxide decomposition. Release oxygen volume/time dependence was monitored at 60 s intervals for all analyzed samples. The chemical process took place at ambient temperature and pressure and at $\text{pH} = 13.4$, using for testing a quantity of 0.2 g catalyst and hydrogen peroxide 3 %.

RESULTS AND DISCUSSION

Characterization

IR spectra. The IR spectra recorded for oxidic compounds synthesized show that after thermal treatment at 500°C , there are no absorption bands characteristic of nitrate or carbonate groups. So, it was in discussion wavelength range between $1000 - 300 \text{ cm}^{-1}$.

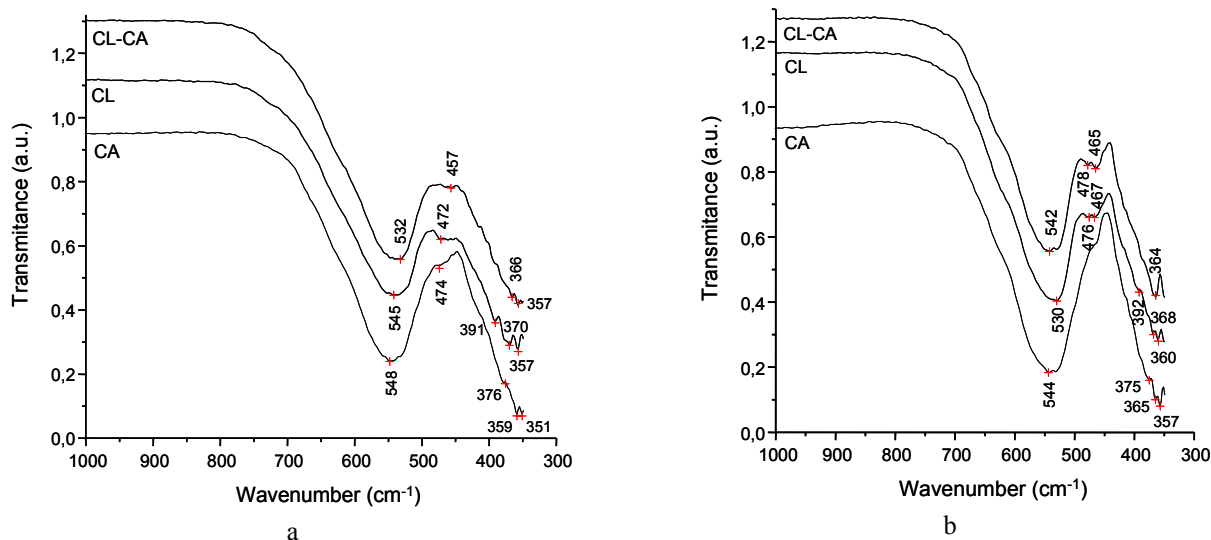


Fig. 2 – IR spectra from NiFe_2O_4 treated at 500°C (a) and 700°C (b).

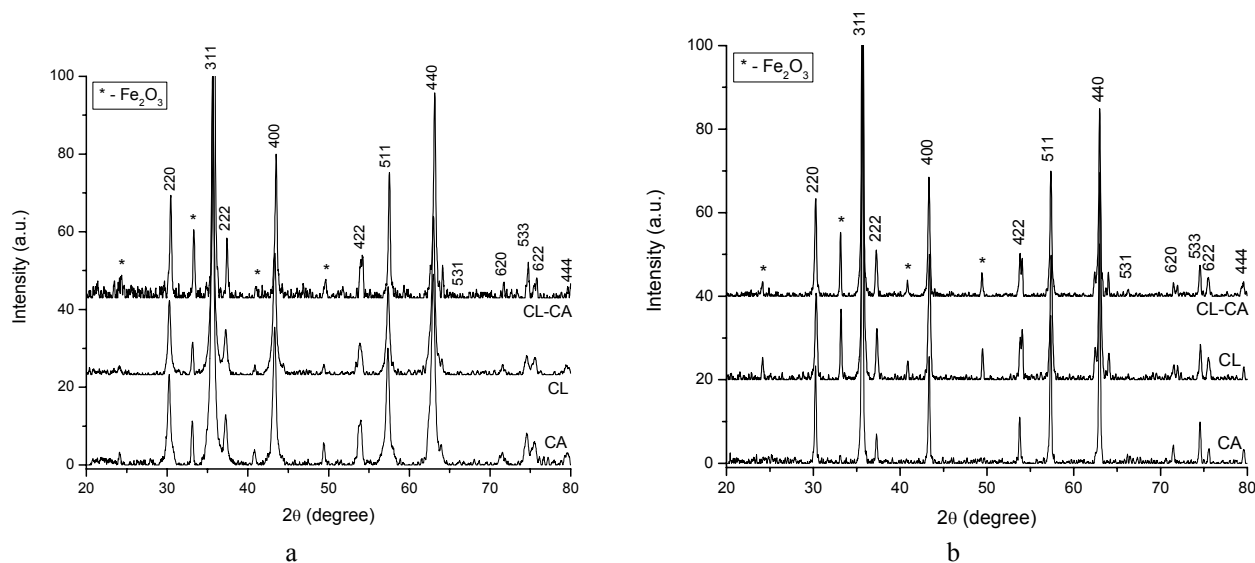


Fig. 3 – XRD for NiFe_2O_4 treated at 500°C (a) and 700°C (b) (* - Fe_2O_3).

It is also shown absorption bands characteristic spinel-type structure (Fig. 2). So, for the samples thermal treated at 500°C are present broad absorption bands at 548 cm^{-1} , 545 cm^{-1} and 532 cm^{-1} respectively, assigned to the stretching (ν) vibrations corresponding to Fe – O bonds of tetrahedral sites.⁵ The same broad absorption bands, wavelengths moved slightly larger or smaller, 544 cm^{-1} , 530 cm^{-1} and 542 cm^{-1} respectively, are presented in the case of ferrites treated at 700°C . These shifts are due to metal cations ordering in spinel network, which occurs with increasing of heat temperature. In the wavelengths range of $375 - 350\text{ cm}^{-1}$ are observed absorption bands of small amplitude, assigned to the stretching (ν) vibrations corresponding to Fe – O bonds of octahedral sites. This difference between absorption bands in tetrahedral and octahedral sites of the oxidic compounds synthesized is due to different distance between Fe^{3+} and O^{2-} ions in the tetrahedral and octahedral sites.^{5, 6} Absorption bands in the $480 - 450\text{ cm}^{-1}$ are assigned to asymmetrical stretching (ν) vibrations of Ni – O bonds.

X-ray diffraction. Results obtained by X-ray diffraction of synthesized ferrite are showed in Fig. 3.

It can be observed that both for samples treated at 500°C and those at 700°C were obtained compounds with cubic spinel structure but there is also a secondary phase identified as iron oxide. It was observed also that with increasing of heat treatment temperature, in $\text{NiFe}_2\text{O}_4/\text{CA}$ the secondary phase disappears, obtaining the pure compound. For the other two compounds, $\text{NiFe}_2\text{O}_4/\text{CL}$ and $\text{NiFe}_2\text{O}_4/\text{CL-CA}$ respectively,

higher heat treatment temperature does not cause the disappearance of secondary phase. It is possible that this disappeared at temperature above 700°C , but such treatment has as result a better ordering of spinelic network. It does not favor the catalytic properties of synthesized compounds.

From XRD crystallite size and lattice parameter a were calculated (Table 1) using Scherrer formula:⁷
$$D_p = \frac{0.94\lambda}{\beta_{1/2} \cos \theta}$$
 where $\lambda = 1.5405\text{ \AA}$;

$\beta_{1/2}$ – width line diffraction measured at half maximum intensity; and relation:⁸
$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2}$$
 where a is the lattice parameter of the unit cell, d_{hkl} is the distance between two equivalent planes and it was calculated from Bragg relation $d_{hkl} = n\lambda / 2 \sin \theta$ with $n = 1$ for cubic system; hkl – the reflector plan of crystal.

From Table 1 it can be observed that using the sol-gel autocombustion method for synthesis of NiFe_2O_4 ferrite type allowed the obtaining of the compounds with nanometer size particles ranging between $22 - 35\text{ nm}$. Increase of heat treatment temperature produced an agglomeration of crystallites, such as their size increases, but remains in the tens order of nanometers. A larger agglomeration is observed in the case of $\text{NiFe}_2\text{O}_4/\text{CA}$ samples compared with other samples analyzed. This is observed from electronic micrographs showed in Fig. 4.

Table 1

Crystallographic data for oxidic compounds of NiFe₂O₄ type

Sample	Sample thermal treated at 500°C		Sample thermal treated at 700°C	
	D _p (nm)	Lattice parameter <i>a</i> (Å)	D _p (nm)	Lattice parameter <i>a</i> (Å)
NiFe ₂ O ₄ /CA	22	8.343	51	8.348
NiFe ₂ O ₄ /CL	25	8.346	39	8.346
NiFe ₂ O ₄ /CL-CA	35	8.324	47	8.341

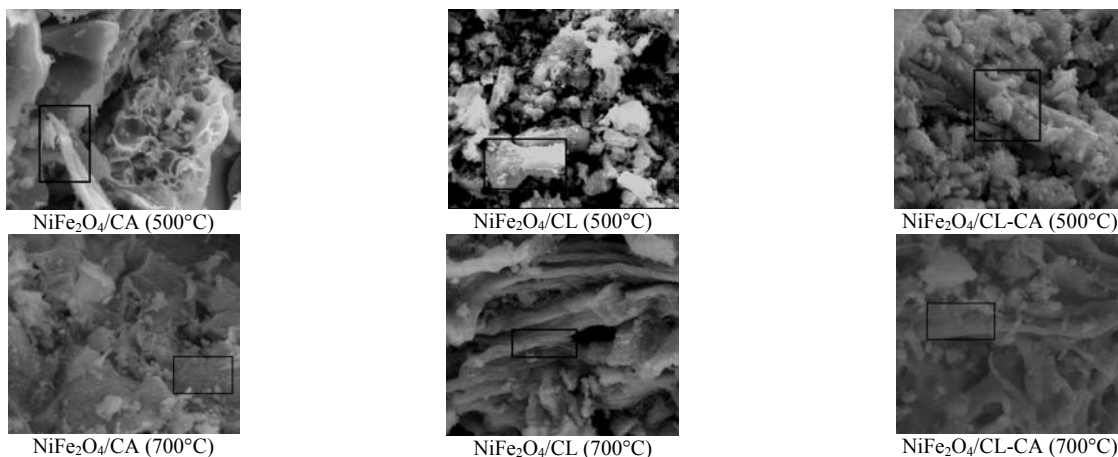


Fig. 4 – SEM micrographs for oxidic compounds synthesized.

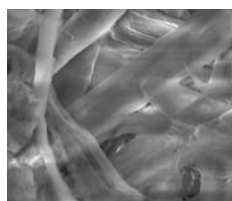


Fig. 5 – SEM micrograph for cellulose using as chelating/fuel agent.

Table 2

Elemental analysis for oxidic compounds of NiFe₂O₄ type

Compound Element	NiFe ₂ O ₄ /CA		NiFe ₂ O ₄ /CL		NiFe ₂ O ₄ /CL-CA	
	500°C	700°C	500°C	700°C	500°C	700°C
Ni	4.78	4.30	4.37	4.35	4.59	4.48
Fe	13.30	9.25	12.89	12.05	13.93	12.13
O	67.28	60.95	68.02	65.01	68.10	62.35

The lattice parameter calculated from XRD is 8.34 Å, value which is in agreement with literature data published so far.^{9, 10}

Electron microscopy. From SEM micrographs obtained for samples treated at 500°C could be observed that NiFe₂O₄/CA ferrite has porous particles of cubic form of different sizes. NiFe₂O₄/CL and NiFe₂O₄/CL-CA ferrites have rod-shapes of different sizes. This structure is favored by the chelating/fuel agent used – cellulose – for which SEM micrograph is showed in Fig. 5.

In practice, the ferrite crystallites “grow” on the cellulose microfibrils. This type of aggregation prevents agglomeration and may be favored by

electrostatic forces between the crystallites of nanometer sizes and surface tensions from the microfiber – crystallite interface.¹¹

Micrographs obtained for samples treated at 700°C (Fig. 4) confirm the structure of agglomerate cubic particles for NiFe₂O₄/CA and rod-shapes for NiFe₂O₄/CL and NiFe₂O₄/CL-CA.

In Table 2 the results obtained by EDAX elemental analysis were summarized. It can be considered that the ratio of 1:2 between metallic cations Ni²⁺ and Fe³⁺ is respected. The differences which appear in the case of iron are due to iron oxide present as secondary phase.

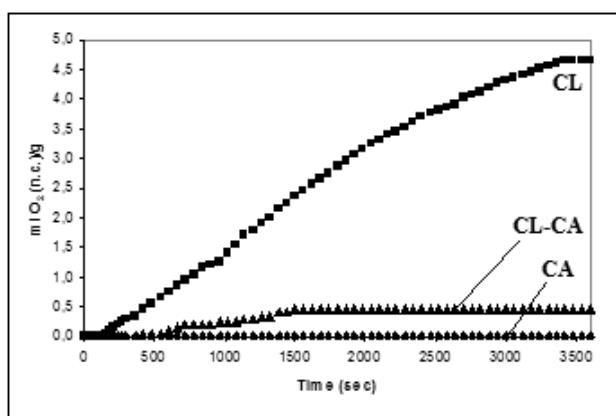
Catalytic behavior

Catalytic decomposition of hydrogen peroxide was followed by measuring the amount of oxygen released in time, results are showed in Fig. 6. It can be observed that the increasing of heat treatment temperature significantly influenced the catalytic properties of analyzed samples. If the ferrite is thermal treated at 500°C catalytic activity increases in order $\text{NiFe}_2\text{O}_4/\text{CL} > \text{NiFe}_2\text{O}_4/\text{CL-CA} > \text{NiFe}_2\text{O}_4/\text{CA}$. The maximum degree of decomposition of H_2O_2 in the presence of $\text{NiFe}_2\text{O}_4/\text{CL}$ as catalyst occurs after 57 min.

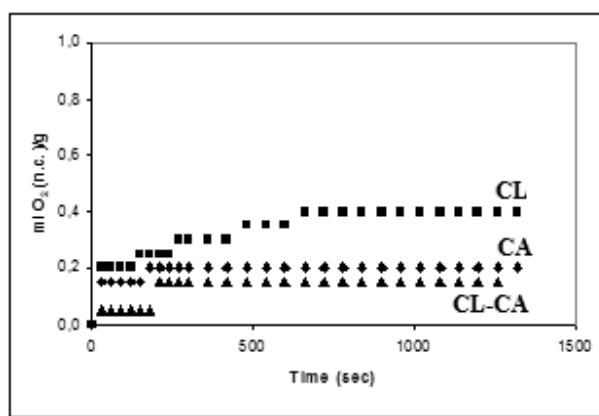
Good catalytic activity of $\text{NiFe}_2\text{O}_4/\text{CL}$ can be attributed to its structure (Fig. 3) that gives greater contact area and high specificity, compared with $\text{NiFe}_2\text{O}_4/\text{CA}$ and $\text{NiFe}_2\text{O}_4/\text{CL-CA}$. For ferrite treated at 700°C catalytic activity decrease significantly, amount of released oxygen is less than 0.5 ml/g. This behavior can be attributed to ordering spinel crystalline network which occurs with increasing of heat treatment temperature. The

increasing of heat treatment temperature causes an agglomeration of particles. This has the effect of reducing the contact surface and therefore decreasing of catalytic activity. Tests of decomposition of H_2O_2 using iron oxide as catalyst, obtained under the conditions of studied ferrites, showed that it does not demonstrate catalytic activity (Fig. 7).

Additional studies were done on the $\text{NiFe}_2\text{O}_4/\text{CL}$ catalyst, which shows the best catalytic activity. The results have revealed that the increase of heat treatment temperature has the same effect of reducing the catalytic activity, as can be seen from Fig. 8. It is obvious that the catalytic activity is influenced by the duration of heat treatment. Thus, if the ferrite is treated at 700°C, as with duration of thermal treatment is greater the catalytic activity decrease. This behavior can be attributed to a more advanced ordering of metal cations in spinel-type structure.



a



b

Fig. 6 – Catalytic behavior of oxidic compounds synthesized:
a – samples thermal treated at 500°C; b – samples thermal treated at 700°C.

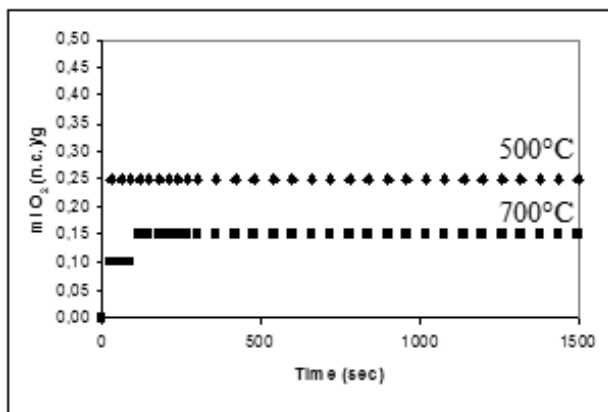


Fig. 7 – Catalytic behavior of Fe_2O_3 .

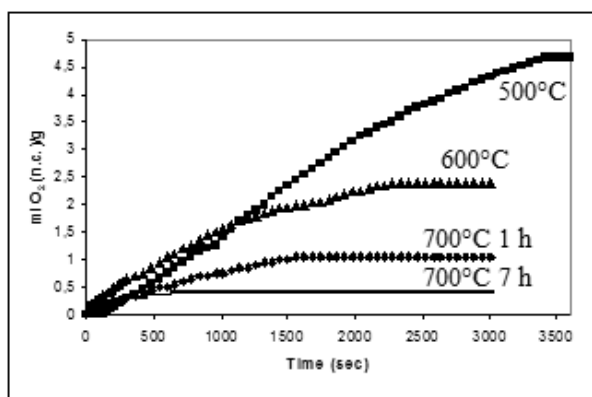
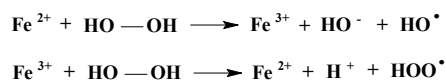
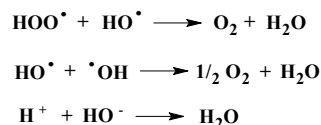


Fig. 8 – Influence of heat treatment temperature on the catalytic activity of $\text{NiFe}_2\text{O}_4/\text{CL}$.

In agreement with literature,^{12,13} could be suggested the possible mechanism of the reaction



of hydrogen peroxide decomposition in presence of NiFe₂O₄ catalysts type:



CONCLUSIONS

Using sol-gel autocombustion method the oxidic compounds of NiFe₂O₄ type were obtained as cubic spinel structure with nanometer particle sizes (22 – 50 nm).

Using cellulose as a chelating/fuel agent the oxidic compounds with nanotubes structure were possible to be obtained. This structure prevents the particles agglomeration.

Catalytic activity of the synthesized oxidic compounds is influenced by chelating/fuel agent used, heat treatment temperature and duration of thermal treatment. The best catalytic results were obtained for NiFe₂O₄ treated at 500°C, for which as chelating/fuel agent was used cellulose.

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