

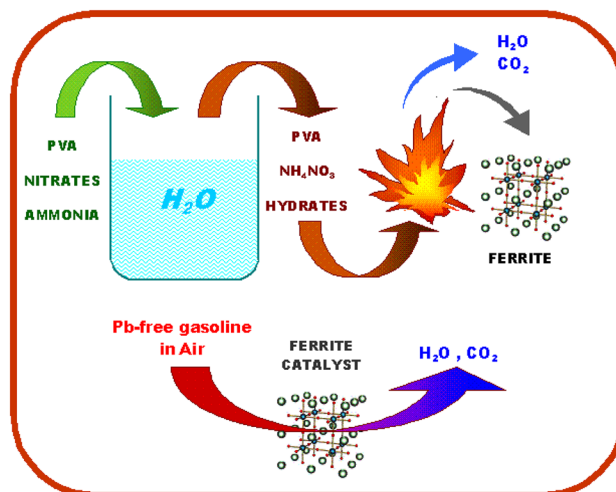
# Nanostructured Spinel Ferrites for Catalytic Combustion of Gasoline Vapors

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**Abstract** Effect of partial substitution of  $\text{Fe}^{3+}$  with  $\text{Sc}^{3+}$  ions, in Ni–Co spinel nanoferrite, synthesized by self-combustion method, using polyvinyl alcohol as colloidal medium, on the structural and catalytic properties for the combustion of Pb-free gasoline vapors is studied. Average crystallite size decreases and specific surface area increases with increasing Sc content. Catalytic properties are influenced by the nature of cations from spinel structure and nanoparticle surface. The catalytic activity improves with increasing  $\text{Sc}^{3+}$  content. The  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_{0.2}\text{Fe}_{1.8}\text{O}_4$  ferrite was found to be the most active catalyst and can be a good candidate for catalytic combustion of air-diluted vapors of Pb-free gasoline at moderate temperatures (250–500 °C). High performance activity of ferrite with maximum substitution of Sc is also accompanied by favorable structure of sample (granulation, porosity, specific surface area), resulted from its preparation method.

## Graphical Abstract



**Keywords** Heterogeneous catalysis · Characterization · Ni–Co nanoferrite · Catalytic combustion · Gasoline vapors

## 1 Introduction

The Pb-free gasoline is used in catalyst engines. From the chemical point of view, it consists of a mixture of hydrocarbons, C4–12 alkanes, cycloalkanes, aromatic hydrocarbons, etc. In order to increase the octane value, the Pb tetraethyl is replaced by a large number of aromatic hydrocarbons. The aromatic hydrocarbon is the most toxic compound of the gasoline vapor [1]. The dilute vapors of this gasoline can reach in spaces for storage, transport, manipulation, as well as in the engine exhaust gases, and we consider that a good method to remove these vapors is through catalytic combustion.

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Palladium (Pd) and platinum (Pt) are widely used in catalytic combustion of combustible vapors. The first of them is more effective for hydrocarbons vapors [2]. Wang et al. [1] and Liang et al. [2] studied the catalytic combustion of gasoline with Pd deposited on  $\text{Al}_2\text{O}_3$ , obtaining promising results. They have reported a conversion rate of over 90% of gasoline vapors (with a concentration of 4–6% in air), for temperatures exceeding 255 °C. Oxide catalysts (oxides, ferrites, perovskites, etc.) are emerging as an alternative to the use of costly noble metals. The oxide catalysts have low prices and exhibit high thermal stability, selectivity, vacillation, regenerability, as well as excellent redox properties [3–9].

During the last years, the catalytic properties of spinel ferrites and perovskites in the flameless combustion of volatile organic compounds (VOCs) have also been investigated [10–19]. The catalytic combustion of gasoline vapors, using these materials, has been less studied. In the case of compounds  $\text{MnFeO}_3$ ,  $\text{SrCoO}_{3-x}$ ,  $\text{GdAlO}_3$ ,  $\text{MgFe}_2\text{O}_4$ , prepared by sol–gel self-combustion method, a conversion rate below 35% was obtained for gasoline vapors (with a concentration of 1–2% in air), in temperature range of 400–550 °C. For manganites  $\text{SrMnO}_3$  and  $\text{La}_{0.6}\text{Pb}_{0.2}\text{Mg}_{0.2}\text{MnO}_3$  over 50% conversion rates of gasoline vapors have been achieved for temperatures between 250 and 320 °C, and over 80% for temperatures greater than 450 °C [18, 19].

Spinel ferrites are mixed oxide compounds of transition metals with a spinel cubic structure and can be described by the general formula  $\text{Me}^{2+}\text{Fe}_2^{3+}\text{O}_4$ , where  $\text{Me}^{2+}$  is a divalent metal ion. The spinel configuration is based on the face-centered cubic lattice of oxygen ions, forming tetrahedral (A) and octahedral (B) sites that may be occupied either by  $\text{Me}^{2+}$  and/or  $\text{Fe}^{3+}$  ions [20]. In normal ferrite,  $\text{Me}^{2+}$  ions occupy the tetrahedral sites and  $\text{Fe}^{3+}$  ions occupy the octahedral sites. If divalent  $\text{Me}^{2+}$  cations occupy the octahedral sites and  $\text{Fe}^{3+}$  cations are distributed among tetra- and octahedral sites, the spinel is called inverse spinel [21]. The catalytic properties of the spinel ferrites are influenced by the nature and distribution of cations between the octahedral and tetrahedral sites in the spinel structure [21–23].

Hosseini et al. [24] investigated the catalytic activity of Ni–Co ferrite on the growth of carbon nanotube and indicated an inverse spinel structure for Ni–Co ferrite. This means that  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  cations occupy the octahedral sites, and  $\text{Fe}^{3+}$  cations occupy octahedral and tetrahedral sites equally. This cation distribution favors the availability of catalytic sites exposed at the surface of the spinel crystallites [21].

Albuquerque et al. [13] found some catalytic properties of Ni–Co ferrite toward oxygen peroxide decomposition and methylene blue oxidation.

This work is dedicated to the study of the effect of partial substitution of  $\text{Fe}^{3+}$  by  $\text{Sc}^{3+}$  ions in Ni–Co spinel ferrite, on

the structural and catalytic properties toward the combustion of Pb-free gasoline vapors with research octane number (RON) of 98. This ferrite was synthesized by self-combustion method, using polyvinyl alcohol as colloidal medium.

Using magnetic measurements, Pakhomova et al. [25] revealed that  $\text{Sc}^{3+}$  ions substituted in the Ni ferrite only prefer the octahedral sites. We assume that in the Ni–Co ferrite the substituted  $\text{Sc}^{3+}$  ions also prefer only the octahedral sites, and that in this way the catalytic activity for the combustion of Pb-free gasoline vapors can be improved.

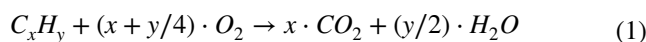
## 2 Experimental

Ferrite powders with nominal compositions  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  ( $x=0.00, 0.05, 0.10$  and  $0.20$ ) were prepared by sol–gel self-combustion method, followed by heat treatment, using polyvinyl alcohol as colloidal medium. A detailed description of this preparation procedure can be found in earlier papers [15, 26–29]. The combusted powder was calcined at 500 °C for 30 min. to eliminate the residual organic compounds. After calcination, the powders were annealed in air at 900 °C for 120 min. The heat released in the combustion reaction is not sufficient to raise the system temperature to a level, which allows the ferrite synthesis. The procedure offers the advantage of producing nanosized, homogeneous and reproducible powders with high specific surface area and precise stoichiometry [30–32].

The structure and surface properties of the heat-treated samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), X-ray photon spectroscopy (XPS) and Brunauer–Emmett–Teller (BET) analysis.

The measurements of catalytic activity of the four studied samples, for air-diluted vapors of Pb-free gasoline were carried out at moderate temperatures (50–600 °C), with a setup previously described in [15, 31, 32]. The entire inlet gas flow rate (3  $\text{cm}^3/\text{s}$ ), with a concentration of 1–2% in air, passes through the entire volume of the powder (2  $\text{cm}^3$ , 2.0 g) at a pressure close to the atmospheric one. We also checked, using a CO sensor, if the combustion is complete (if the reactor outlet gases only contain  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ).

The complete combustion (in air) of  $\text{C}_x\text{H}_y$  hydrocarbon can be expressed as a complete oxidation:



The catalytic activity of of Pb-free gasoline (RON 98) over the studied  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  powders was evaluated in terms of gas conversion rate  $C$  calculated as [31–35]:

$$C(\%) = [(c_{in} - c_{out}) \cdot 100] / c_{in} \quad (2)$$

where  $c_{in}$  and  $c_{out}$  are the inlet and outlet gas concentrations, respectively.

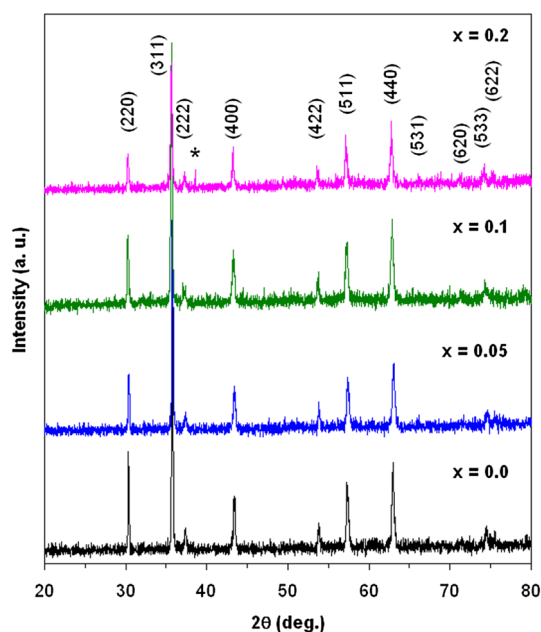
The catalytic tests were conducted three times, on increasing and decreasing temperature. The average of the last series of measurements was taken into account.

### 3 Results and Discussion

#### 3.1 Structure and Morphology

Figure 1 presents the XRD patterns of  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  powders ( $x=0.00\text{--}0.20$ ), calcined and heat treated at  $900\text{ }^\circ\text{C}$  for 120 min, together with the Miller indices that indicate the spinel type structure, and with the secondary phases that occur. Crystalline phases were identified by using the “Crystallographica” program. Referring to the JCPDS card No. 22–1086, the compound exhibits a cubic symmetry (space group  $\text{Fd}\bar{3}\text{m}$ ), similar to the undoped  $\text{CoFe}_2\text{O}_4$ . Only the samples with  $x=0.00, 0.05$  and  $0.10$  were single-phased. The sample with  $x=0.20$  exhibits minor secondary phases ( $\text{Sc}_2\text{O}_3$ ) for the chosen heat treatment parameters ( $900\text{ }^\circ\text{C}$  for 120 min). The structural parameters of the studied powders: the lattice constant ( $a$ ); average crystallite size ( $D_{\text{XRD}}$ ); X-ray density ( $d_x$ ) and specific surface area ( $S_{\text{BET}}$ ) are presented in Table 1.

The lattice constant  $a$  increases (from  $0.8362\text{ nm}$  for  $x=0.00$ , to  $0.8411\text{ nm}$  for  $x=0.20$ ), while the density  $d_x$  decreases (from  $5.433\text{ g/cm}^3$  for  $x=0.00$ , to  $5.331\text{ g/cm}^3$  for  $x=0.20$ ) with the increase of Sc content. The lattice constant  $a$  for  $x=0$  agrees with the values reported in literature [36].



**Fig. 1** XRD patterns of  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  powders, heat treated at  $900\text{ }^\circ\text{C}$  for 120 min. The Miller indices refer to the spinel phase and Asterisk indicates the secondary  $\text{Sc}_2\text{O}_3$  phase

**Table 1** Structural data for  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  powders, heat treated at  $900\text{ }^\circ\text{C}$  for 120 min

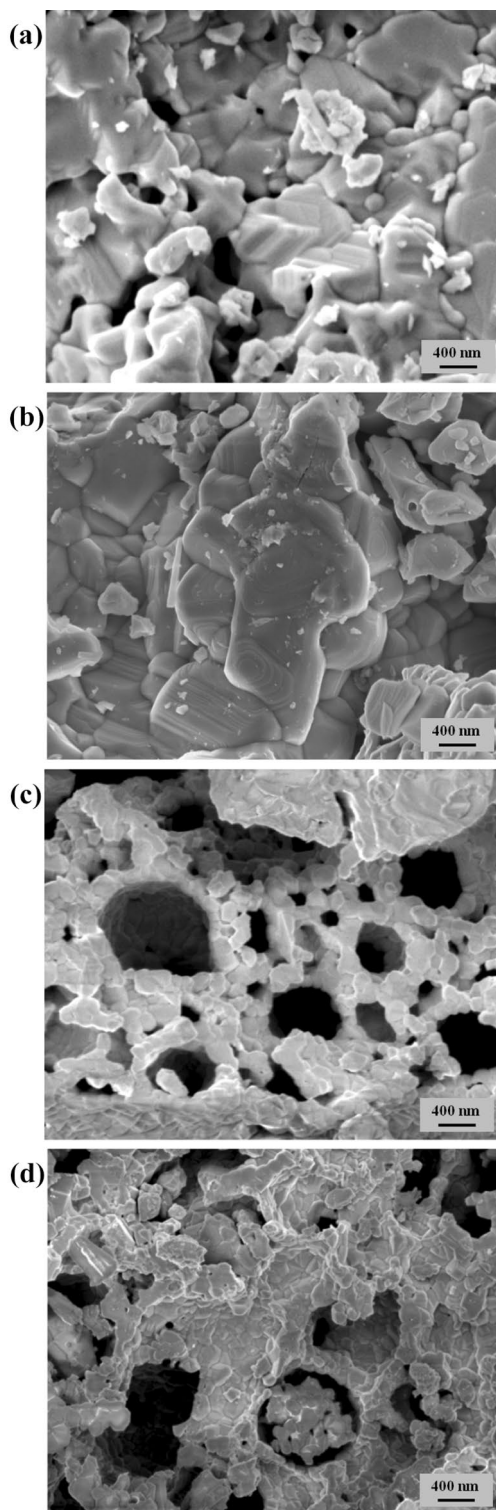
$x$	$a$ (nm)	$D_{\text{XRD}}$ (nm)	$d_x$ ( $\text{g/cm}^3$ )	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )
0.00	0.8362	39.8	5.433	28.4
0.05	0.8371	36.7	5.382	30.5
0.10	0.8394	33.4	5.354	33.6
0.20	0.8411	31.9	5.331	34.0

A remarkable increase in the lattice constant is noticed when Sc content increases from  $x=0.05$  to  $x=0.10$ . The crystallite size ( $D_{\text{XRD}}$ ) was estimated at about  $32\text{--}40\text{ nm}$ , which attests that ferrite powders with nanosized crystallites have been synthesized. The average crystallite size decreases with the Sc content, a probable explanation being a structural disorder induced by the large Sc ions, which can lead to a delay in the crystallite growth. This can also explain the progressive increase of the specific surface area,  $S_{\text{BET}}$ , with the Sc content. Values of BET area of about  $28.4\text{--}34.0\text{ m}^2/\text{g}$  have been obtained. The Sc addition to the parent composition ( $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ) has a remarkable positive effect on  $S_{\text{BET}}$ : an increase of about 20% has been registered. The large specific surface area is known to be favorable for the catalytic activity.

The morphology and elemental chemical composition were analyzed by using a scanning electron microscope (SEM), equipped with an energy dispersive X-ray spectrometer (EDX technique).

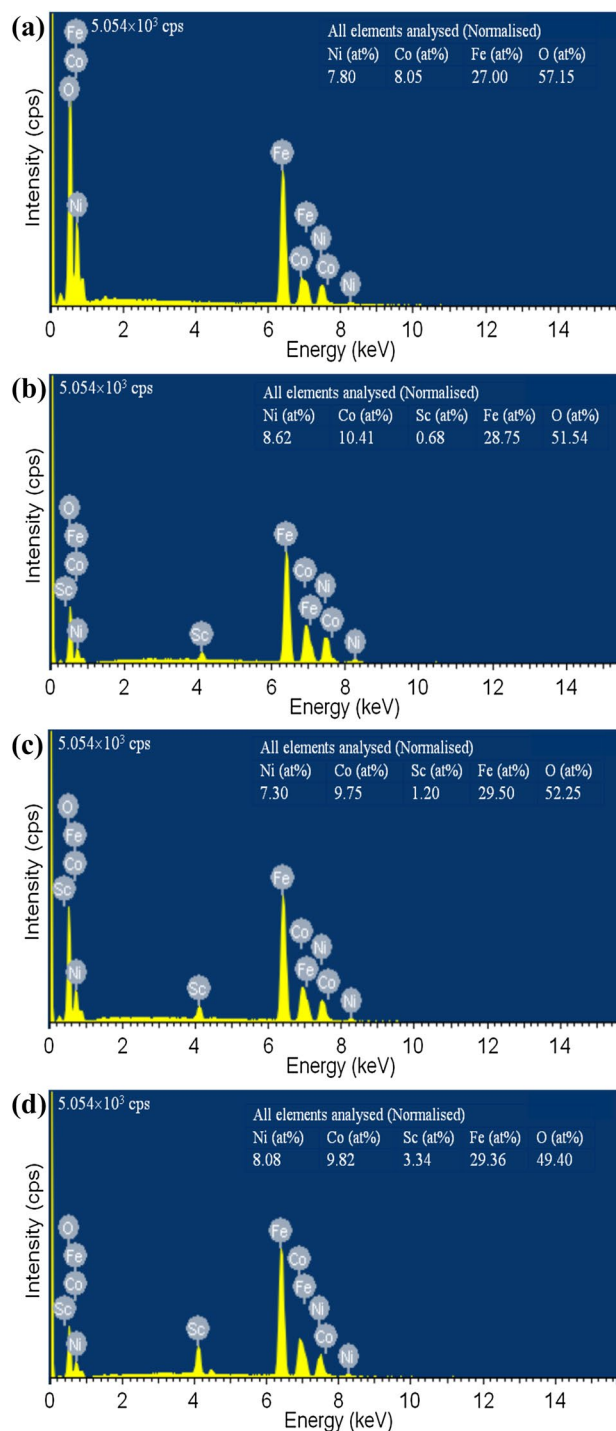
In Fig. 2 are presented the SEM micrographs for the studied samples. The samples are characterized by a porous structure with clusters of particles, forming soft agglomerates. The Sc-substituted samples exhibit larger agglomerations and smaller size particles in comparison with the undoped sample. With the increase of  $x$  substitution, from 0 to 0.20, the mean particle size decreases from  $550\text{ nm}$  (Fig. 2a) to  $170\text{ nm}$  (Fig. 2d), respectively. The SEM micrograph from Fig. 2d shows agglomerations of fine grains with irregular shapes and large tubular pores (below  $1\text{ }\mu\text{m}$ ), favorable to gas penetration into the samples. This open pore system arises during self-combustion reaction, through which a large amount of gas was eliminated. This phenomenon is common to all oxide compounds prepared through this method. Although the particles are agglomerated, some individual crystallites with size below  $50\text{ nm}$  can be observed. Figure 3 presents the EDX spectra for the studied samples. The obtained chemical (elemental) composition is typical for these ferrites (any foreign element is absent).

The XPS analysis was used to identify the oxidation state of the cations present on the samples surfaces. Figure 4a, b show the Fe  $2p$  and Sc  $2p$  XPS spectra, respectively, of ferrite with  $x=0.2$  Sc content ( $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_{1.8}\text{Sc}_{0.2}\text{O}_4$ ). However, the analyses of Fe  $2p$  spectra are relatively complex for



**Fig. 2** SEM micrographs for the studied samples, x=0 (a), x=0.05 (b), x=0.10 (c) and x=0.2 (d)

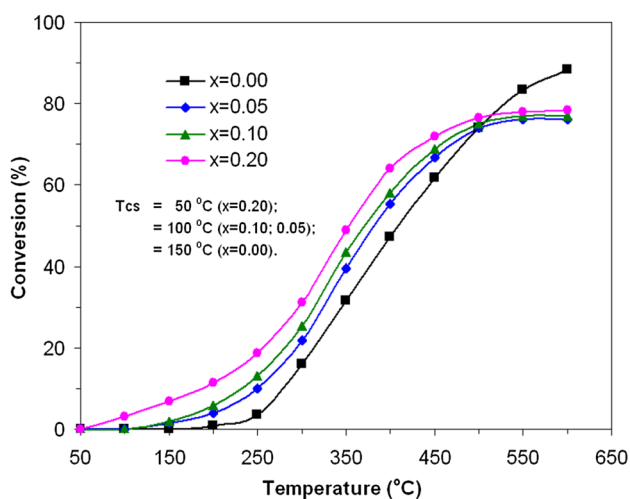
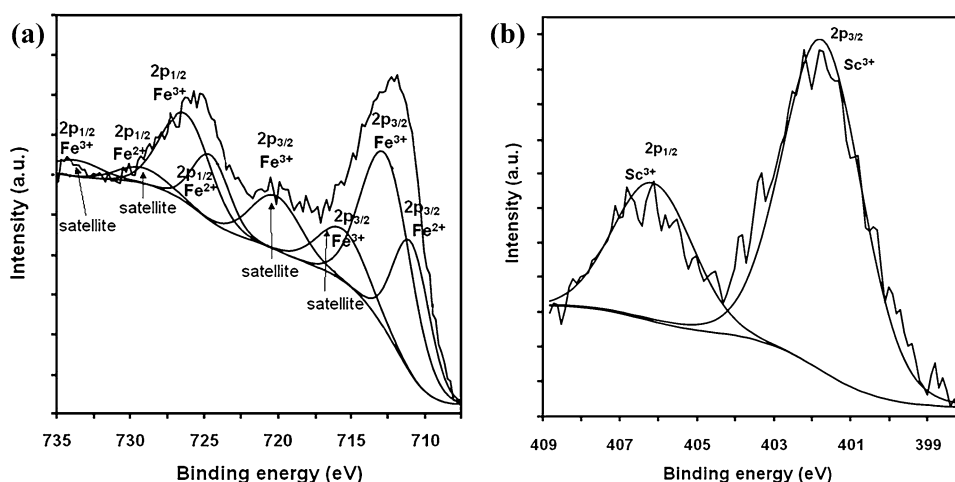
ferrites. The divalent Fe  $2p_{3/2}$  peak located at 709.5 eV and the trivalent Fe  $2p_{3/2}$  peak at 711.2 eV are respectively associated to satellite peaks at 715.5 and 719.0 eV [13, 37–42].



**Fig. 3** EDX spectra for the studied samples, x=0 (a), x=0.05 (b), x=0.10 (c) and x=0.2 (d)

The registered Fe  $2p_{3/2}$  peaks with binding energies (BE) from 711.2 to 713.0 eV, together with the associated satellites by 716.3 and 720.0 eV (Fig. 4a), confirm the predominance of Fe<sup>3+</sup> and a small fraction of Fe<sup>2+</sup> present on the sample surface [13, 42, 43]. The observed BE shifts can be caused by different surroundings of the Fe<sup>3+</sup> ions located at

**Fig. 4** XPS spectra of  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  powder for the Fe 2p (a) and Sc 2p (b) regions



**Fig. 5** Conversion rate versus temperature for catalytic flameless combustion of the air-diluted vapors of Pb-free gasoline (RON 98) over the  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  powder

the A and B sites and of the  $\text{Sc}^{3+}$  ions (Fig. 4b), occupying the B (octahedral) sites within the ferrite structure.

### 3.2 Catalytic Activity

In Fig. 5, the gas conversion rate over the  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  catalyst is plotted as a function of reaction temperature for air-diluted vapors of Pb-free gasoline. The results obtained from the increasing and decreasing temperatures are practically the same.

In Fig. 5, one can notice that all the investigated samples display a good conversion of Pb-free gasoline vapors at moderate temperatures. For the parent sample (without substitution with  $\text{Sc}^{3+}$  ions), the conversion starts (CS) at the temperature of 150 °C (1%); it linearly increases between 250 °C (3.6%) and 550 °C (83%), and continues to increase up to the value of 90% at temperatures above 600 °C. One

can also notice that starting temperatures of catalytic conversion ( $T_{cs}$ ) for samples with Sc substitution are smaller. Conversion rate values are higher than those of parent sample for the same temperatures, but the conversion exhibits a plateau at values around 80% for temperatures over 500 °C.

When increasing the substitution degree  $x$ , the conversion increases at small temperature, while the value of  $T_{cs}$  decreases. The highest performance sample is the one with maximum substitution of Sc,  $x=0.20$ , for which the starting temperature is of about 50 °C, and the temperature for 50% conversion ( $T_{50}$ ) is of 350 °C.

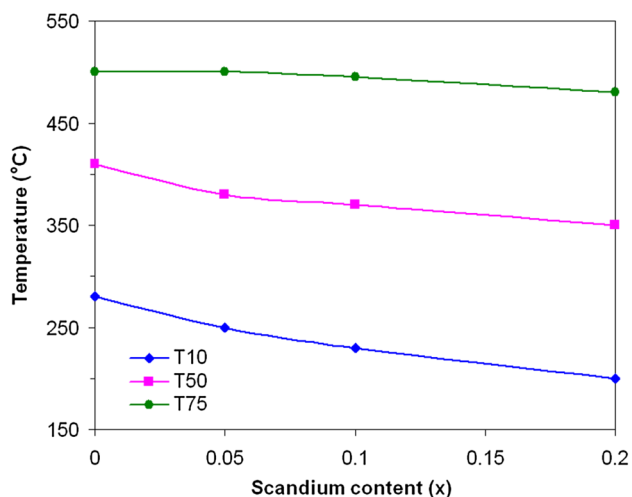
We believe that the conversion limitation at 80% for the samples with Sc substitution is due to the fact that the  $\text{Sc}^{3+}$  ions catalyze the synthesis of some unidentified noncombustible VOCs in the gasoline vapor composition. The catalytic combustion of actual synthesized organic compounds does not take place at temperatures in the examined range, therefore, these are found in proportion of 20% in the gas resulting from the catalyst.

Figure 6 presents the effect of Sc content ( $x$ ) in  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  ferrite, on the characteristic conversion temperatures  $T_{10}$ ,  $T_{50}$  and  $T_{75}$  for the air-diluted vapors of Pb-free gasoline.

With the increase of Sc content, the characteristic temperature  $T_{10}$  continuously decreases by 80 °C, the temperature  $T_{50}$  decreases by 60 °C, with a more significant decrease between  $x=0.00$  and  $x=0.05$ , and the temperature  $T_{75}$  decreases only by 20 °C, mainly between  $x=0.10$  and  $x=0.20$ .

It can be assumed that the catalytic combustion of gasoline vapor takes place in the presence of excess oxygen. The apparent activation energies ( $E_a$ ) for the catalytic reactions were calculated by means of the Arrhenius-type plot of the natural logarithm of the reaction rate ( $k$ ) at very low conversion, below 15%, versus inverse temperature ( $1/T$ ) [44–47]. The Arrhenius equation can be given in the form [33, 44]:

$$k = A \exp(-E_a/RT) \quad (3)$$



**Fig. 6** Characteristic conversion temperatures versus Sc content ( $x$ ).  $T_{10}$ ,  $T_{50}$  and  $T_{75}$ —temperature of 10, 50 and 75% gasoline vapors conversion, respectively

where  $k$ ,  $A$ ,  $R$  and  $E_a$  are the reaction rate, preexponential factor, gas constant and apparent activation energy, respectively.

The apparent activation energy decreases with the increasing substituted  $\text{Sc}^{3+}$  content, from 73.7 KJ/mol for the parent sample to 20.2 KJ/mol for the sample with maximum substitution ( $x=0.20$ ). The increase of gas conversion rate by Sc doping of Ni–Co ferrite may be ascribed to the structural defects induced by scandium substitution for iron.

The results revealed that the partial substitution of  $\text{Fe}^{3+}$  by  $\text{Sc}^{3+}$  ions on the octahedral sites in the spinel structure of  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  ferrite has a favorable effect on the catalytic activity of this ferrite. A contribution to the high catalytic performance of the ferrite with maximum substitution of Sc is also brought by the favorable structure of the sample (granulation, porosity, specific surface area), resulted from its preparation method. The ferrite with the composition  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_{0.2}\text{Fe}_{1.8}\text{O}_4$  was found to be the most active catalyst and it can be a good candidate for catalytic combustion of air-diluted vapors of Pb-free gasoline at moderate temperatures (250–500 °C).

## 4 Conclusions

The structural and catalytic properties of  $\text{Sc}^{3+}$  doped Ni–Co nanoferrites synthesized by self-combustion method and heat treated at 900 °C for 120 min, were investigated.

The average crystallite size decreases with Sc content. The specific surface area increases with the Sc content, due to the generation of tubular micropores in the samples.

The catalytic activity for air-diluted vapors of Pb-free gasoline was examined at moderate temperatures (50–600 °C).

The catalytic properties are influenced by the nature of cations from the spinel structure and on the nanoparticles surface. With the increase of substitution degree  $x$ , the conversion rate at low temperatures increases and the value of starting temperature of catalytic conversion decreases. The increase of gas conversion rate by Sc doping of Ni–Co ferrite may be due to the structural defects induced by scandium substitution for iron.

The ferrite with  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_{0.2}\text{Fe}_{1.8}\text{O}_4$  composition is the most active catalyst and it can be a good candidate for catalytic combustion of air-diluted vapors of Pb-free gasoline at moderate temperatures (250–500 °C). The high catalytic performance of the ferrite with maximum substitution of Sc is also accompanied by the favorable structure of the sample (granulation, porosity, specific surface area), resulted from its preparation procedure.

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