



# Scandium substituted nickel–cobalt ferrite nanoparticles for catalyst applications



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## ABSTRACT

Nanograined  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  ( $x = 0, 0.05, 0.1$  and  $0.2$ ) spinel ferrites were prepared by sol–gel self-combustion method and heat treatment at  $900^\circ\text{C}$  for 4 h. Their structure and surface properties were investigated by X-ray diffraction, scanning electron microscopy, EDX spectroscopy and BET analysis. The catalyst properties of the ferrite nanopowders were tested in the catalytic combustion of acetone, propane and benzene. The results revealed that the partial substitution of  $\text{Fe}^{3+}$  by  $\text{Sc}^{3+}$  ions on the octahedral sites of 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. The  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_{0.2}\text{Fe}_{1.8}\text{O}_4$  ferrite composition was found to be the most active catalyst and can be a good candidate for catalytic combustion of propane and acetone at moderate temperatures. The acetone conversion over this catalyst exceeds 90% at  $400^\circ\text{C}$ . The enhancement of the catalytic activity of the Sc doped Ni–Co ferrites may be ascribed to smaller crystallite sizes (35–39 nm), larger specific surface areas ( $29\text{--}32\text{ m}^2/\text{g}$ ) and the presence of Sc cations in spinel structure.

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## 1. Introduction

The progressive increase of volatile organic compound (VOC) emissions induces the development of new methods for their abatement from air [1–3]. In comparison with conventional thermal oxidation, catalytic combustion is considered one of the most promising technologies for VOC removal [2,4]. Catalytic combustion is a more economical process that can operate at low temperature ( $<500^\circ\text{C}$ ) with dilute effluent streams ( $<1\%$  VOC) [4]. The performance of catalytic combustion strongly depends on the catalyst used. Two categories of catalysts are generally employed for VOC catalytic oxidation reaction: (i) noble metal (Pt, Pd, Rh) and (ii) transition metal oxides.

In the recent years many efforts have been directed toward producing catalytic materials based on simple and mixed transition-metal oxides to replace the expensive noble metal catalysts. Metal oxide catalysts, although less active than noble metal catalysts, have certain advantages, such as low price, earthly abundance, high chemical and thermal stability, high resistance to poisoning and the easy way of preparation [5–11]. Spinel and perovskites are the most studied oxide compounds in the context

of VOC catalytic combustion. As a novel catalytic material, oxide compounds, called spinel ferrites, are extensively investigated as catalysts in the flameless combustion of volatile organic compounds (VOCs) [12–15].

Ferrites are mixed transition metal oxide compounds with a spinel cubic structure and can be described by the general formula  $\text{M}^{2+}\text{Fe}_2^{3+}\text{O}_4$ , where  $\text{M}^{2+}$  is a divalent metal ion. The spinel configuration is based on a face centered cubic lattice of oxygen ions, forming tetrahedral (A) and octahedral (B) sites that may be occupied either by  $\text{M}^{2+}$  and/or  $\text{Fe}^{3+}$  ions. In normal ferrite,  $\text{M}^{2+}$  ions occupy the tetrahedral sites and  $\text{Fe}^{3+}$  occupy the octahedral sites. If divalent cations  $\text{M}^{2+}$  occupy the octahedral sites and  $\text{Fe}^{3+}$  cations are distributed among tetra and octahedral sites, the spinel is called inverse spinel [16].

The catalytic properties of the spinel ferrites are influenced by the distribution of cations among the octahedral and tetrahedral sites in the spinel structure [15]. Jacobs et al., [17] suggested that in the spinel structure, the octahedral sites are almost exclusively exposed at the surface of the spinel crystallite and that the catalytic activity is mainly due to octahedral cations.

The preparation of spinel ferrites as nanoparticles is of high interest because they exhibit improved physico-chemical properties for catalytic combustion applications. The smaller the particle size, the larger the surface area is in front of gases. There is a variety of methods [10,18–25] for preparing the nanocrystalline ferrites. For any practical wide-scale application, the price of catalyst has

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to be reasonably low. To meet this demand, simple and inexpensive methods of ferrite synthesis appear to be attractive. In the present study a non-conventional procedure, sol-gel coupled with self-combustion, was used [10]. This combined method implies a low cost and allows the preparation of the ferrite nanoparticles with molecular scale homogeneity over a wide range of particle size.

The objectives of this work were to synthesize nanosize-structured scandium containing Ni-Co ferrites and also to evaluate their catalytic activity in the VOC combustion. Until now the catalytic properties of Sc doped Ni-Co ferrites prepared by sol-gel self-combustion have not been investigated. Lei Ze et al. [26] have investigated catalytic activity of Sc-doped  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{1-x}\text{Sc}_x\text{O}_{3-d}$  perovskite ( $x=0-1$ ) for methane combustion and good catalytic activity was obtained at a Sc doping of 0.5. Hosseini et al. [27] 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 [17]. Pakhomova et al. [28] evidenced by magnetic measurements that  $\text{Sc}^{3+}$  ions prefer the octahedral sites only.

The structural and catalytic properties of Sc containing Ni-Co ferrites,  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  ( $x=0, 0.05, 0.1$  and  $0.2$ ), were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), BET surface area measurements, energy-dispersive X-ray spectroscopy (EDX) and catalytic flameless combustion of acetone, benzene and propane.

Our study can have applications in finding a suitable candidate of doped ferrite nanocrystals as catalyst for combustion of VOCs.

## 2. Experimental

### 2.1. Preparation of the catalyst materials

In this paper  $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Sc}_x\text{Fe}_{2-x}\text{O}_4$  ( $x=0, 0.05, 0.1$  and  $0.2$ ) ferrite nanocrystals were prepared by sol-gel self-combustion route [29] which offers a homogeneous mixing (considering the very small scandium additions) and the control of the grain size by subsequent heat treatment. It is not possible to replace much of the Fe by Sc ions because the ionic radius of  $\text{Sc}^{3+}$  (0.088 nm) is much greater than the radius of  $\text{Fe}^{3+}$  (0.069 nm) [30].

Metal nitrates were used as precursors. The preparing method included the following steps: (1) dissolution of metal nitrates in deionized water; (2) polyvinyl alcohol (10% concentration) addition to nitrate solution to make a colloidal solution; (3)  $\text{NH}_4\text{OH}$  (10% concentration) addition to increase pH to about 8; a sol of metal hydroxides in polyvinyl alcohol and ammonium nitrate were obtained; (4) stirring at  $80^\circ\text{C}$  for 10 min to turn the sol of metal hydroxides into viscous gel; (5) drying the gel at  $100^\circ\text{C}$  for 12 h; (6) self-combustion; the dried gel was locally ignited by an electrically heated wire and an exothermic reaction takes place. Once initiated, the combustion wave spontaneously auto propagated (less than 30 s) through the dried gel and results a loose powder. During the combustion reaction the temperature is of about  $1000^\circ\text{C}$  and the nucleation of very fine crystallites takes place; (7) calcination at  $550^\circ\text{C}$  for 15 min of the burnt powder to eliminate any residual organic compound; (8) heat treatment of the calcined powders at  $900^\circ\text{C}$  for 4 h, in air, to achieve a complete crystallization of ferrites.

### 2.2. Catalysts characterization

The crystal structure and phase composition of the samples were analyzed by XRD. X-ray diffraction measurements of the powders were performed at room temperature using PANALYTICAL X'

PERT PRO MPD powder diffractometer and  $\text{CuK}\alpha$  radiation. The spectra were scanned between  $20$  and  $80^\circ$  ( $2\theta$ ) at a rate of  $2^\circ/\text{min}$ . The average crystallite size was evaluated based on XRD peak broadening using the Scherer equation  $D=0.9\lambda/\beta\cos\theta$ , where  $\lambda$  is radiation wavelength (0.15405 nm) of  $\text{CuK}\alpha$ ,  $\beta$  is the half width of the peak and  $\theta$  is the Bragg diffraction peak angle. A scanning electron microscope (JEOL-200 CX) was used to visualize the surface morphology. A Quantachrome automated gas adsorption system (Quantachrome Instruments) was used to obtain  $\text{N}_2$  adsorption isotherms at 77 K. The BET specific surface area ( $S_{\text{BET}}$ ) was determined using the standard Brunauer-Emmett-Teller method [31] on the basis on the adsorption data. The elemental composition of the surface particles was examined with Energy Dispersive X-ray Spectrometer (Genesis, EDX) using a voltage of 20 kV.

### 2.3. Catalytic testing

The catalytic testing of the ferrite catalysts in the flameless combustion of some selected VOCs (acetone, propane and benzene) was carried out at atmospheric pressure in a flow-type set-up (flow rate of  $100\text{ cm}^3/\text{min}$  and VOC concentration in air of 1–2%) previously described by us in [32,33]. The catalyst powder (0.3–0.5 g) was sandwiched between two layers of quartz wool in a quartz tubular micro-reactor ( $\varnothing=7\text{ mm}$ ) placed in an electrical furnace. The increase of the temperature was made in steps of  $50^\circ\text{C}$ , from  $50^\circ\text{C}$  to  $550^\circ\text{C}$ . At every predetermined temperature, as a result of catalytic combustion, the gas concentration at the exit of reactor will be smaller than the inlet gas concentration. The catalytic activity of the ferrite catalysts under study was evaluated in terms of the conversion degree of gases over catalysts calculated as:

$$\text{Conv} = \frac{c_{\text{in}} - c_{\text{out}}}{c_{\text{in}}} \times 100\%,$$

where  $c_{\text{in}}$  and  $c_{\text{out}}$  are the inlet and outlet gas concentration, respectively, measured by a photo-ionization detector (PID-TECH) for VOCs. Data were collected when the flameless catalytic combustion had reached a steady state, after about 20 min at each temperature. These experiments were repeated decreasing the temperature and similar results were obtained suggesting the stability of the ferrites.

## 3. Results and discussion

### 3.1. Structural characterization

The XRD patterns of the Ni-Co ferrites with different molar substitutions of  $\text{Sc}^{3+}$  are shown in Fig. 1. Well-defined sharp peaks of the spinel phase clearly seen in the diffraction patterns indicate a good crystalline quality of the ferrite powders. The XRD patterns were compared and indexed using PDF no (44-1485) and (22-1086) for Ni and Co ferrites. The (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) peaks reveal that all samples have the cubic spinel phase with Fd3m space group, without any foreign phase. A notable feature in these patterns is that the broadening of the peaks increases continuously with increasing scandium substitution in relation to the ferrite without scandium, indicating that the scandium addition reduces the crystallite size of the Co-Ni ferrite. The lattice parameters, average crystallite size and X-ray density derived from XRD data are given in Table 1. One can observe an increase in the lattice parameter with Sc content in Ni-Co ferrites from 8.36 Å for  $x=0$ –8.41 Å for  $x=0.2$  and this may be explained by the higher ionic radius of  $\text{Sc}^{3+}$  compared to  $\text{Fe}^{3+}$  [30]. This result proves that the  $\text{Sc}^{3+}$  ions entered into the spinel structure and did not form a secondary phase during the sintering. The lattice parameter of sample without Sc is in agreement with that reported by others for Ni-Co ferrites [34,35]. Also, one can observe that sol-gel self-combustion preparing method allowed the synthesis of the ferrites with nanometer

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