

## SYNTHESIS AND CHARACTERIZATION OF NiTiO<sub>3</sub> AND NiFe<sub>2</sub>O<sub>4</sub> AS CATALYSTS FOR TOLUENE OXIDATION

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This paper presents the synthesis of nickel titanate and nickel ferrite by nonconventional procedures. Nickel titanate was obtained by autocombustion method using titanium isopropoxide – nickel nitrate-alanine system and nickel ferrite was obtained by coprecipitation method in Fe(NO<sub>3</sub>)<sub>3</sub>-Ni(NO<sub>3</sub>)<sub>2</sub>-NH<sub>4</sub>OH system. Both mixed oxides were characterized by FT-IR spectroscopy, X-ray diffraction, scanning electron microscopy (SEM) and catalytic activity tests. The catalytic activities were measured for toluene oxidation.

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### 1. Introduction

The catalytic combustion, compared to an incineration process is one of the most interesting technologies, from the economical point of view, for the destruction of volatile organic compounds (VOCs) emissions. Indeed, VOCs catalytic oxidation occurs at much lower temperatures than those needed for thermal oxidation. Moreover, there is no associated pollution by dioxins and NO<sub>x</sub> as they are exclusively formed under high temperature conditions [1-3].

Transition metal oxides are known for their capacity to catalyze the oxidation of hydrocarbons. In the last two decades, efforts have been spent on the activation and the functionalization of hydrocarbons catalyzed by mixed metal oxides [1-3].

The ilmenite type catalysts, such as nickel titanate have a good activity for the steam reforming reaction and have a structure relatively stable at various temperatures, towards CO<sub>2</sub> and H<sub>2</sub>O and under oxidative conditions [1-3]. The use of these oxides for the purification of VOCs, such as toluene, total combustion of hydrocarbons for energetic conversion and reduction of nitrogen oxides (NO<sub>x</sub>) and automotive emission make them catalysts of futures. These systems are potential substitutes of catalysts containing platinumic metals on different supported materials, like alumina, silica, in the total oxidation reaction of the hydrocarbons [4-6].

The main challenge in developing ilmenite catalysts is to obtain them with sufficiently high surface areas. The preparation of an ilmenite oxide involves a solid-state reaction of its precursors to form the characteristic ABO<sub>3</sub> structure [4-6]. This requires a significant exposure of the oxide precursors to high temperatures, thus leading to a low specific surface area of the catalyst. To circumvent this limitation, a number of alternative preparation methods have been tested, in an attempt to lower the firing temperature for ilmenite oxide synthesis [6-9].

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This paper presents a comparison study of the catalytic activities on toluene oxidation of nickel titanate (obtained by autocombustion method) and nickel ferrite (obtained by co-precipitation method).

## 2. Materials and methods

$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were purchased from Aldrich.  $\text{NH}_3$ ,  $\text{C}_3\text{H}_7\text{OH}$  and  $\text{C}_6\text{H}_5\text{CH}_3$  were purchased from S.C. Chimexin S.A. All reagents were used without further purification.

The  $\text{NiTiO}_3$  was obtained by the autocombustion procedure using a system formed by  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$  -  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  -  $\text{C}_3\text{H}_7\text{NO}_2$  in molar ratio 1:1:20 in isopropyl alcohol solution. The amount of alanine (fuel) added in the mixture was established on the basis of a simple valence balance of the oxidizer (nickel nitrate) and reducer (alanine) components of the mixture. The solution of nitrate, isopropoxide and alanine was heated at  $200^\circ\text{C}$  on a sand bath in a capsule. Dark green product obtained was calcined at  $600^\circ\text{C}/3\text{h}$ .

$\text{NiFe}_2\text{O}_4$  was obtained by co-precipitation method, from  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ - $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in a 2:1 molar ratio at  $\text{pH} = 12$  obtained by adding ammonia 25% as precipitation agent. The reaction mixture was kept under reflux at  $80^\circ\text{C}$  for 3 h, until a black precipitate was formed. After the purification process which implies washing five times with water and ethanol (10:1), the precursor was calcined at  $600^\circ\text{C}$  for 3 h in order to obtain a single phase  $\text{NiFe}_2\text{O}_4$  powder.

Nickel titanate and nickel ferrite powders obtained by the precursors calcination at  $600^\circ\text{C}$  for 3h were characterized by FT-IR, XRD and SEM analyses.

Thermal decomposition of the catalysts was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in *Netzsch 449C STA Jupiter* apparatus. Samples were placed in open alumina crucible and heated with  $10^\circ\text{C min}^{-1}$  from room temperature to  $900^\circ\text{C}$ , under the flow of  $10 \text{ mL min}^{-1}$  in air. The specific surface areas were measured in *Carlo Erba Sooty 1750* apparatus by using Brunauer-Emmet-Teller (BET) method with nitrogen at 77K. The oxide powders were analyzed by X-ray diffraction (XRD) on *D8 Discovery Bruker* diffractometer, using  $\text{CuK}\alpha$  ( $1.5406 \text{ \AA}$ ) radiation with 30 mA and 40 kV in the  $2\theta = 10\text{--}80^\circ$  range with a scan rate of  $10^\circ/\text{min}$ . The Fourier transform infrared spectra (FTIR) were recorded using the KBr pellet technique on a *Bruker Tensor 27* spectrometer in the  $400\text{--}4000 \text{ cm}^{-1}$  range. Morphological characterization was performed by scanning electron microscopy (SEM) in a *HITACHI S2600N* apparatus coupled with EDAX.

## 3. Results and discussion

### Thermal analysis

The TG-DSC analysis of  $\text{NiTiO}_3$  precursor revealed a complex process of decomposition consisting in burning of reaction products and the reorientation of the lattice (fig.1). As it can be seen from the TG curve in temperature range of  $120^\circ\text{C}$ - $140^\circ\text{C}$  there is a loss mass of about 10% probably assigned to water molecules. The weight loss of about 20% in  $200\text{--}450^\circ\text{C}$  temperature range can be assigned to the thermal decomposition of organic compound (isopropoxide) molecules. The reorientation of the lattice took place between  $450^\circ\text{--}600^\circ\text{C}$  temperature range and finally the formation of crystalline  $\text{NiTiO}_3$  phase was observed at about  $600^\circ\text{C}$ .

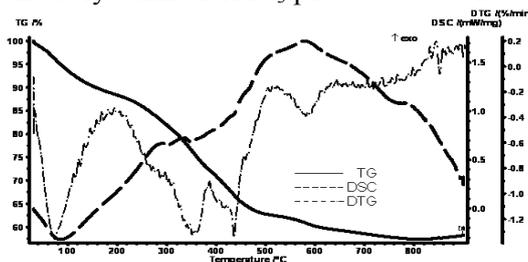


Fig. 1. TG-DSC-DTG analysis of the  $\text{NiTiO}_3$  precursor obtained by autocombustion method

### X-ray diffraction analysis of obtained mixed oxides

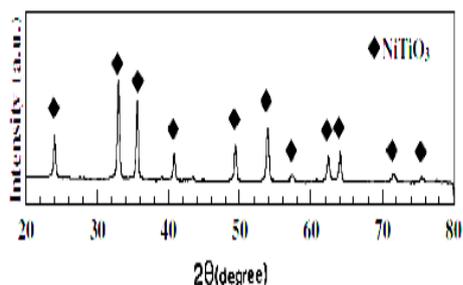


Fig.2. XRD pattern of NiTiO<sub>3</sub> sample

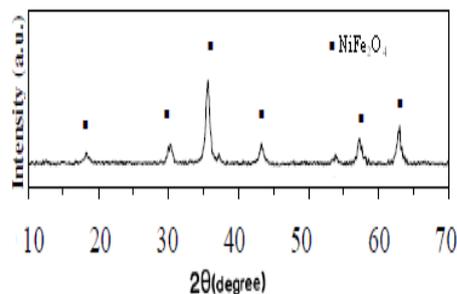


Fig.3. XRD pattern of NiFe<sub>2</sub>O<sub>4</sub> sample

The XRD data of NiTiO<sub>3</sub> powder sustain its ilmenite structure with rhombohedral symmetry (Fig.2). The calculated lattice constants are  $a = 5.03210 \text{ \AA}$ ,  $b = 5.03210 \text{ \AA}$ ,  $c = 13.79240 \text{ \AA}$  (JCPDS 75-3757). The average crystallites sizes of powders have been calculated by Scherer's formula:  $d = k\lambda/\beta\cos\theta$  where  $d$  is the crystallite size, assuming spherical particles,  $k=0.9$ ,  $\lambda$  is the wavelength of radiation,  $\beta$  is the full width at half maximum (FWHM) of the diffracted peak and  $\theta$  is the angle of diffraction. The average crystallites size was estimated at 45 nm.

The XRD pattern presented in figure 3 corresponds to NiFe<sub>2</sub>O<sub>4</sub> with spinel structure and cubic symmetry (JCPDS card 74-6507). The average crystallites size was estimated at 50 nm. The calculated lattice constants are:  $a = 8.28800 \text{ \AA}$ ,  $b=8.28800 \text{ \AA}$ ,  $c=8.28800 \text{ \AA}$  (JCPDS 74-6507).

### FT-IR analysis

The curves exhibiting the FE-IR spectrum are shown in Fig. 4 and 5

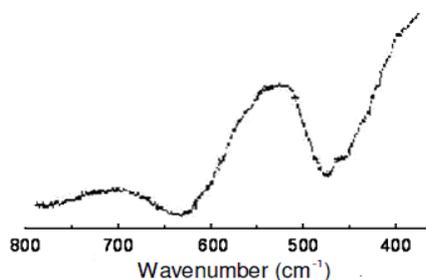


Fig.4. FT-IR spectrum of NiTiO<sub>3</sub>

The characteristic vibration bands corresponding to metal-oxygen bonds are in the range of 400-800 cm<sup>-1</sup> in the FTIR spectra of oxide powders. The FT-IR spectrum of the nickel titanate powder (Fig.4.) presents a large splitted band at 500cm<sup>-1</sup> characteristic for Ni-O bond and a second band at 575cm<sup>-1</sup> assigned to Ti-O bond.

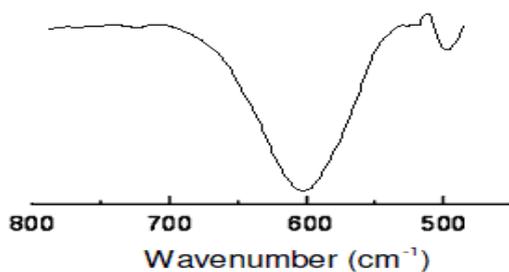


Fig.5. FT-IR spectrum of NiFe<sub>2</sub>O<sub>4</sub>

At 609cm<sup>-1</sup> appears the characteristic band of NiFe<sub>2</sub>O<sub>4</sub>, corresponding to the Fe-O bond (fig.5). At 500 cm<sup>-1</sup> appears the other characteristic band of NiFe<sub>2</sub>O<sub>4</sub> corresponding to the Ni-O bond.

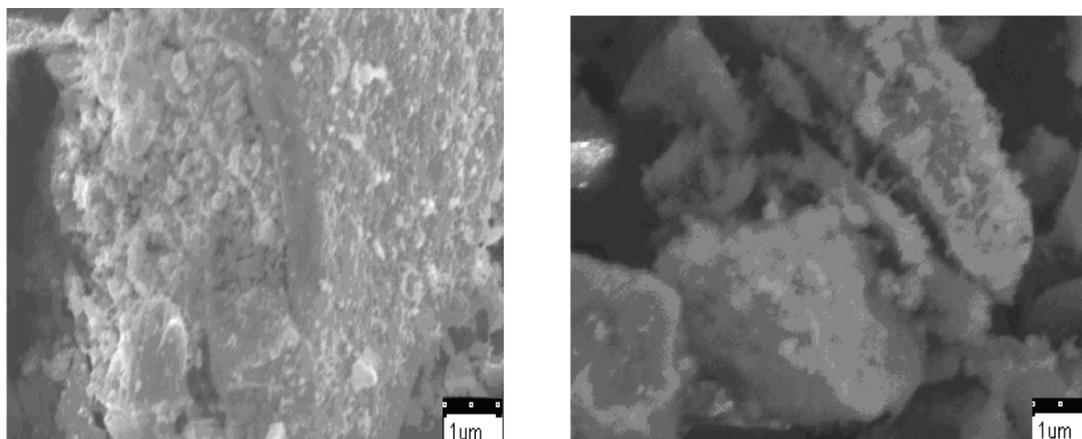
*SEM analysis of mixed oxides*

Fig.6.a) SEM micrograph for NiTiO<sub>3</sub>      Fig.6.b) SEM micrograph for NiFe<sub>2</sub>O<sub>4</sub>

The morphology of NiTiO<sub>3</sub> and NiFe<sub>2</sub>O<sub>4</sub> powders, calcined at 600<sup>0</sup>C/3h, were evaluated by scanning electron microscopy (SEM) and were illustrated in Figs.6a and 6b. A higher tendency of the particles to form agglomerates it was observed in the case of NiFe<sub>2</sub>O<sub>4</sub> (Fig.6a). Both samples present spherical shape particles. The average particles size is 45 nm for NiTiO<sub>3</sub> and 50 nm for the NiFe<sub>2</sub>O<sub>4</sub> and the average agglomerates size is 100 nm for NiTiO<sub>3</sub> and 110 nm for the NiFe<sub>2</sub>O<sub>4</sub>.

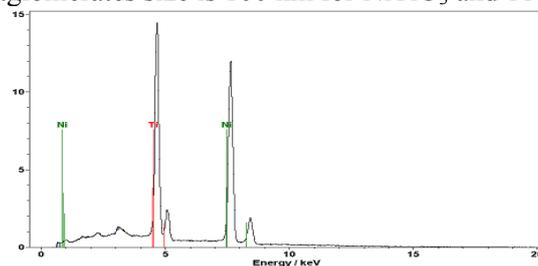


Fig.7. EDAX for NiTiO<sub>3</sub> calcined at 600<sup>0</sup>C/3h

Further evidence for the formation of NiTiO<sub>3</sub> came from EDAX spectrum (fig.7). The EDAX analysis shows characteristic peaks and the composition of the NiTiO<sub>3</sub> powder.

*Catalytic tests on toluene oxidation*

Catalytic combustion of toluene on the obtained catalysts were carried out at atmospheric pressure in a fixed-bed quartz tubular reactor with an inner diameter of 10 mm. Micro-pilot plant used in laboratory experiments consists in a quartz reactor, the reactor electric heating system, control system and automatic recording of temperature, feeding and dosing system for liquid hydrocarbons, condensation and cooling system and reaction by products capture system and dosing of CO<sub>2</sub>. An amount of catalyst was placed in the middle of the reactor, and a thermocouple was inserted near the outlet of the catalyst. Prior to the reaction, the catalyst was activated under air flow at 600<sup>0</sup>C for 2 h. After the catalyst bed was cooled to 100 °C, a reactant mixture consisting of 0.0625cm<sup>3</sup>/min toluene and 160cm<sup>3</sup>/min O<sub>2</sub> was feed to the reactor by bubbling air at a rate of 800cm<sup>3</sup>/min. The temperature ramp of 5<sup>0</sup>C/min was considered to be sufficiently slow to reach a pseudo-steady state at every point. At the exit of condenser-separator, a bubbler with Ba(OH)<sub>2</sub> saturated solution was attached and catalytic activity efficiency (CO<sub>2</sub> conversion) was determined.

The catalytic reactions were investigated in 220-600<sup>0</sup>C range for NiTiO<sub>3</sub> and 270-530<sup>0</sup>C range for NiFe<sub>2</sub>O<sub>4</sub>. Five experiments were made on nickel titanate catalyst at five different

temperatures for establishing the minimum temperature at which the total combustion appears (Table 1). At the beginning of all the experiment were observed induction periods. These induction periods are levels of temperatures that are followed by pronouncedly increase of reaction temperature for NiTiO<sub>3</sub>. The reactions were investigated in 220-600°C range. The data presented in Table 1 show that the combustion was totally advanced and the higher efficiency was obtained in the 360-600°C temperatures range.

Table 1. The operation data and material balance for toluene oxidation on nickel titanate catalyst

Exp. no.	Reactor feed	T <sub>i</sub> °C	T <sub>f</sub> °C	Flow (cm <sup>3</sup> /min)			BaCO <sub>3</sub> precipitation (g)	CO <sub>2</sub> theoretical	CO <sub>2</sub> practical	η <sub>CO2</sub> %
				Toluene	Air	O <sub>2</sub>				
1	T+air	220	600	0,044	800	168	3,4743	0,0723	0,0176	24,4
2	T+air	310	600	0,049	800	168	2,8541	0,1052	0,0144	13,7
3	T+air	360	600	0,041	800	168	1,8665	0,0130	0,0094	72,1
4	T+air	400	600	0,046	800	168	1,8343	0,0460	0,0092	20,2
5	T+air	450	600	0,041	800	168	1,7243	0,0263	0,0087	33,2

The catalytic activities for different samples of NiTiO<sub>3</sub> were appreciated based on the starting temperature of the oxidation reaction and also based on the variation of the reaction temperature with the reaction time.

Table 2. The operation data and material balance for toluene oxidation on nickel ferrite catalyst

Exp. no.	Reactor feed	T <sub>i</sub> °C	T <sub>f</sub> °C	Flow (cm <sup>3</sup> /min)			BaCO <sub>3</sub> precipitation (g)	CO <sub>2</sub> theoretical	CO <sub>2</sub> practical	η <sub>CO2</sub> %
				Toluene	Air	O <sub>2</sub>				
1	T+air	27 0	30 0	0,046	8 0 0	16 8	-	-	-	-
2	T+air	30 0	36 0	0,043	8 0 0	16 8	0,7284	0,0656	0,0036	5,48
3	T+air	35 0	39 0	0,041	8 0 0	16 8	1,2832	0,0858	0,0065	7,57
4	T+air	45 0	53 0	0,042	8 0 0	16 8	3,5092	0,0783	0,0178	22,7 4

Four experiences were made on NiFe<sub>2</sub>O<sub>4</sub> catalyst obtained by co-precipitation method at four different temperatures (Table 2). The catalytic activity values of NiFe<sub>2</sub>O<sub>4</sub> for toluene oxidation were measured in similar conditions with those for NiTiO<sub>3</sub>. The maximum feed flows at ambient condition were 0.046cm<sup>3</sup>/min toluene and 800cm<sup>3</sup>/min air. The reaction was investigated in 270-530°C range. Using CO<sub>2</sub> practical and theoretical values we calculated the conversion yields of toluene oxidation reaction for both compounds tested.



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