

SYNTHESIS AND CHARACTERIZATION OF NiTiO₃ AND NiFe₂O₄ 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(NO₃)₃-Ni(NO₃)₂-NH₄OH 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.

(Received July 15, 2011; accepted August 26, 2011)

Keywords: Nickel titanate, Nickel ferrite, Ilmenite structure, Catalytic tests, Toluene oxidation

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_x 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 CO₂ and H₂O 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_x) and automotive emission make them catalysts of futures. These systems are potential substitutes of catalysts containing platonic 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 ABO₃ 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. 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 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°C on a sand bath in a capsule. Dark green product obtained was calcined at $600^\circ\text{C}/3\text{h}$.

NiFe_2O_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°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°C for 3 h in order to obtain a single phase NiFe_2O_4 powder.

Nickel titanate and nickel ferrite powders obtained by the precursors calcination at 600°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°C , under the flow of 10 mL min^{-1} in air. The specific surface areas were measured in *Carlo Erba Sopty 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 \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 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°C - 140°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 NiTiO_3 phase was observed at about 600°C .

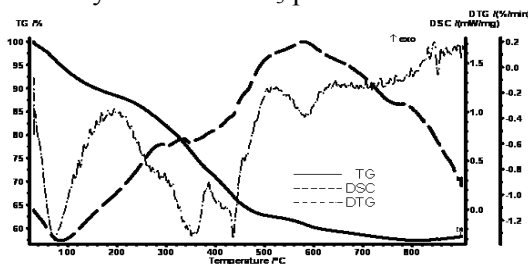


Fig. 1. TG-DSC-DTG analysis of the NiTiO_3 precursor obtained by autocombustion method

X-ray diffraction analysis of obtained mixed oxides

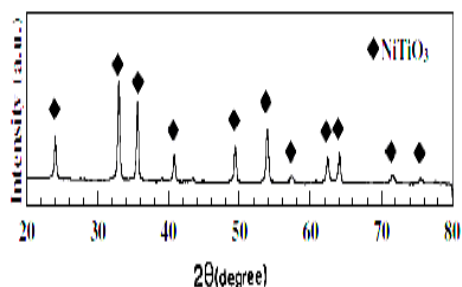


Fig.2. XRD pattern of NiTiO₃ sample

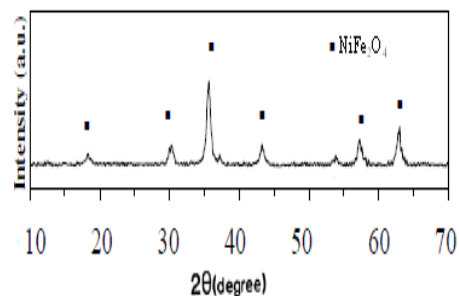


Fig.3. XRD pattern of NiFe₂O₄ sample

The XRD data of NiTiO₃ 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, $k=0.9$, λ is the wavelength of radiation, β is the full width at half maximum (FWHM) of the diffracted peak and θ is the angle of diffraction. The average crystallites size was estimated at 45 nm.

The XRD pattern presented in figure 3 corresponds to NiFe₂O₄ 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

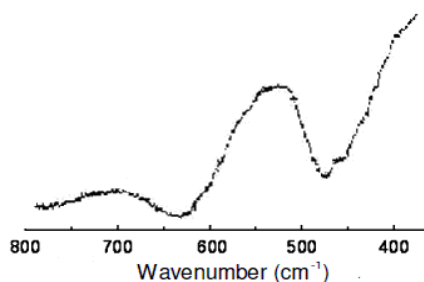


Fig.4. FT-IR spectrum of NiTiO₃

The characteristic vibration bands corresponding to metal-oxygen bonds are in the range of 400-800 cm⁻¹ 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⁻¹ characteristic for Ni-O bond and a second band at 575cm⁻¹ assigned to Ti-O bond.

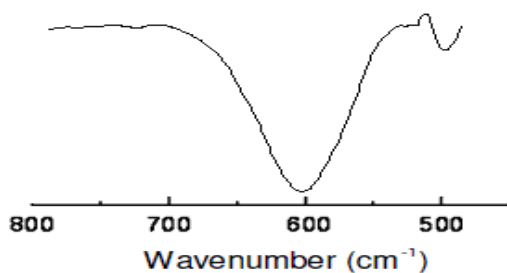


Fig.5. FT-IR spectrum of NiFe₂O₄

At 609cm⁻¹ appears the characteristic band of NiFe₂O₄, corresponding to the Fe-O bond (fig.5). At 500 cm⁻¹ appears the other characteristic band of NiFe₂O₄ corresponding to the Ni-O bond.

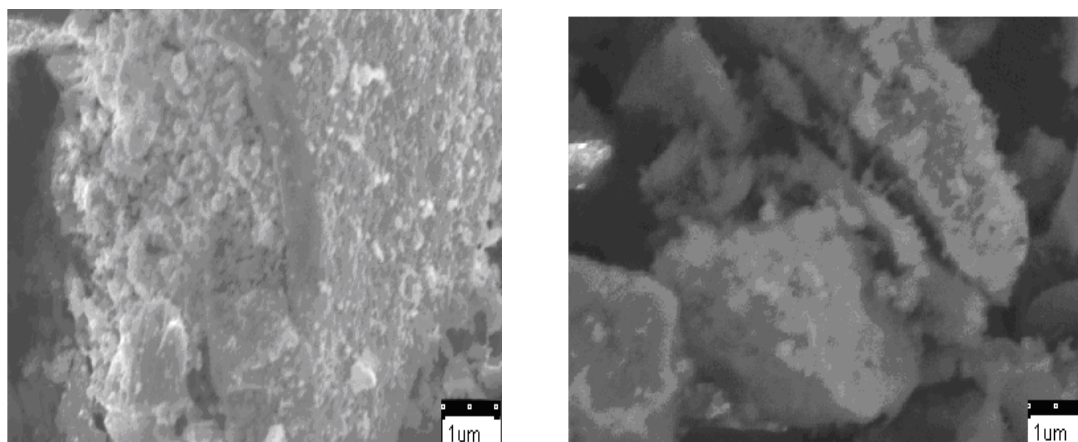
SEM analysis of mixed oxides

Fig.6.a) SEM micrograph for NiTiO₃ Fig.6.b) SEM micrograph for NiFe₂O₄

The morphology of NiTiO₃ and NiFe₂O₄ powders, calcined at 600⁰C/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 NiFe₂O₄ (Fig.6a). Both samples present spherical shape particles. The average particles size is 45 nm for NiTiO₃ and 50 nm for the NiFe₂O₄ and the average agglomerates size is 100 nm for NiTiO₃ and 110 nm for the NiFe₂O₄.

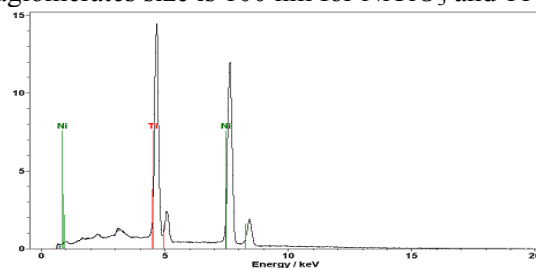


Fig.7. EDAX for NiTiO₃ calcined at 600⁰C/3h

Further evidence for the formation of NiTiO₃ came from EDAX spectrum (fig.7). The EDAX analysis shows characteristic peaks and the composition of the NiTiO₃ 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 CO₂. 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 600⁰C for 2 h. After the catalyst bed was cooled to 100 °C, a reactant mixture consisting of 0.0625cm³/min toluene and 160cm³/min O₂ was feed to the reactor by bubbling air at a rate of 800cm³/min. The temperature ramp of 5⁰C/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)₂ saturated solution was attached and catalytic activity efficiency (CO₂ conversion) was determined.

The catalytic reactions were investigated in 220-600⁰C range for NiTiO₃ and 270-530⁰C range for NiFe₂O₄. 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 NiTiO₃. 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

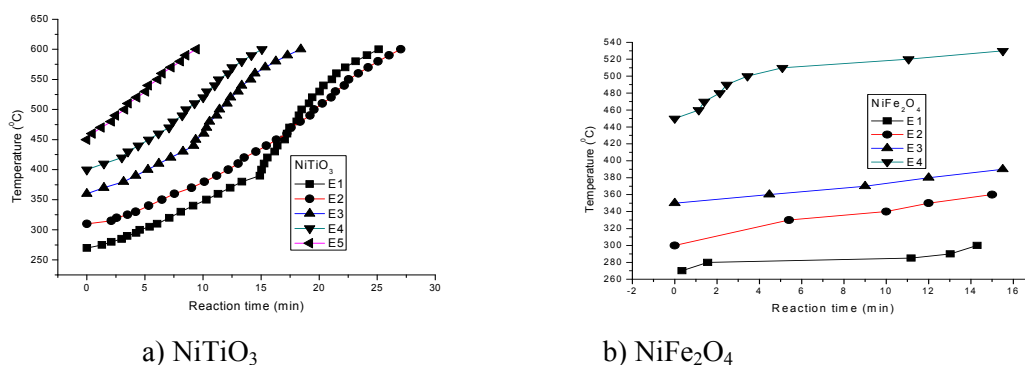
Exp. no.	Reactor feed	T _i °C	T _f °C	Flow (cm ³ /min)			BaCO ₃ precipitation (g)	CO ₂ theoretical	CO ₂ practical	η _{CO2} %
				Toluene	Air	O ₂				
1	T+air	220	600	0,044	800	168	3,4743	0,0723	0,0176	24,4
2	T+air	310	600	0,049	800	168	2,8541	0,1052	0,0144	13,7
3	T+air	360	600	0,041	800	168	1,8665	0,0130	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 NiTiO₃ 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 _i °C	T _f °C	Flow (cm ³ /min)			BaCO ₃ precipitation (g)	CO ₂ theoretical	CO ₂ practical	η _{CO2} %
				Toluene	Air	O ₂				
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 NiFe₂O₄ catalyst obtained by co-precipitation method at four different temperatures (Table 2). The catalytic activity values of NiFe₂O₄ for toluene oxidation were measured in similar conditions with those for NiTiO₃. The maximum feed flows at ambient condition were 0.046cm³/min toluene and 800cm³/min air. The reaction was investigated in 270-530°C range. Using CO₂ practical and theoretical values we calculated the conversion yields of toluene oxidation reaction for both compounds tested.



a) NiTiO₃ b) NiFe₂O₄
 Fig. 6. The variation of temperature with reaction time for toluene oxidation on NiTiO₃ (a) and NiFe₂O₄ (b) catalysts

Metal ions from the oxides have a strong influence on catalyst activity and its oxidizing action. These experiments aimed to study some aspects of the oxidation reaction of toluene on spinel and ilmenite type oxide catalysts. From the variation of the starting temperatures of the experiments and reaction time were calculated the slopes values which indicates the most efficient catalyst tested. The 15,4 °C/min. slope obtained for NiTiO₃ (fig.6.a) indicates a higher activity in comparison with 9,21 °C/min, obtained for NiFe₂O₄ (fig.6.b). The yields of toluene oxidation reactions calculated in terms of CO₂ formation was 72% for NiTiO₃ and 22% for NiFe₂O₄, respectively.

The best catalytic activity 72,1% (Table 1) was obtained for NiTiO₃ because of the large surface area (32,6 m²/g). A much lower catalytic activity was obtained for NiFe₂O₄ (22%), which has a surface area value of 10,1 m²/g (table 2). Due to large specific surface area the NiTiO₃ powder present the best catalytic activity and conversion of CO₂ to 72,1%. A large specific surface area, leads to a corresponding catalytic activity.

In addition Fig. 6a shows that NiTiO₃ powder has the active temperature window in the low temperature region ranging from 220 up to 600°C. It is advantageous to prepare NiTiO₃ powder, compared to other catalysts for VOCs such as zeolites, Pt/Al₂O₃, PtSn/Al₂O₃ etc. It is also a technology aim on which researchers are focused to solve VOCs elimination from the air as well as from the industrial waste sources.

4. Conclusions

NiTiO₃ and NiFe₂O₄ were obtained by nonconventional methods: autocombustion and co-precipitation, respectively. The NiTiO₃ has a higher catalytic activity (72%) with 45nm average particle size and 32,6 m²/g surface area value in comparison with NiFe₂O₄ powder, which has an average particle size of 50nm and surface area value of 10,1 m²/g with a catalytic activity of about 22%

The catalytic activity results indicate that the combustion was totally advanced and the higher efficiency was obtained at 360°C initial temperature for NiTiO₃ and 450°C for NiFe₂O₄ respectively. The results of catalytic properties are preliminary, but attract considerable interest; especially NiTiO₃ seems to be a promising and potential catalyst due to its low active temperature.

Acknowledgements

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/6/1.5/S/19.

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