MTiO₃ (M=Cu, Ni) as Catalysts in Toluene Oxidation

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This study deals with the synthesis of MTiO₃ (M=Ni, Cu) powders by a sol-gel method using titanium isopropoxide – metallic acetates - isopropyl alcohol systems. The mixed oxides obtained have been structurally and morphologically characterized by X-ray diffraction, scanning electron microscopy (SEM) and thermogravimetric analysis (TG-DTG-DSC). The catalytic activities of the prepared MTiO₃ were determined for toluene oxidation in air. More experiments were made at different temperatures to establish the minimum temperature when the toluene combustion appears.

Keywords: nickel titanium mixed oxide, copper titanium mixed oxide, catalytic activity, toluene oxidation

Metal mixed oxides show a great potential to be used in catalysis, electrocatalysis and electronic ceramics, being the base of a new industrial policy for environmental technologies [1]. The use of these oxides for the purification of volatile organic compounds (VOCs), total combustion of hydrocarbons for energetic conversion and reduction of nitrogen oxides (NOx) and automotive emission make them the catalysts of the future [2-8]. These systems are potential substitutes of platinic bases of a new industrial policy for environmental technologies, electrocatalysis and electronic ceramics, being the base of a new industrial policy for environmental technologies [1]. The use of these oxides for the purification of volatile organic compounds (VOCs), total combustion of hydrocarbons for energetic conversion and reduction of nitrogen oxides (NOx) and automotive emission make them the catalysts of the future [2-8]. These systems are potential substitutes of platinic metals containing catalysts deposited on different supported materials, like alumina or silica in the total oxidation reaction of the hydrocarbons. Catalysts based on transition metal (Ni, Cu, Co, Cr, Mn, and Fe) oxides have been extensively studied and their combustion activity was generally lower than that of noble metal catalysts [9-14].

In this work we have prepared MTiO₃ (M=Ni, Cu) powders by a sol-gel procedure. The precursors and binary mixed oxides were investigated by means of TG-DTG-DSC analysis, X-ray diffraction and scanning electron microscopy, SEM. Their catalytic activity for toluene oxidation was also reported.

Experimental part
Starting materials

Ti(OCH(CH₃)₂)₄, Ni(CH₃COO)₂•4H₂O, Cu(CH₃COO)₂. 4H₂O were purchased from Sigma Aldrich. Isopropyl alcohol (C₃H₇OH) and toluene (C₆H₅CH₃) were purchased from S.C. Chimexin S.A. All reagents were used without further purification.

Apparatus and procedure

MTiO₃ ultrafine powders have been prepared by a sol-gel method.

CuTiO₃

The precursor of CuTiO₃ was prepared by mixing a solution of 0.5 mmol Cu(CH₃COO)₂•4H₂O in 10 mL alcohol with 0.5 mmol Ti(OCH(CH₃)₂)₄ (in Cu: Ti = 1:1 molar ratio) and adding of 40 mL of isopropyl alcohol. The solution obtained was heated under reflux at 80°C for four hours, until a gel was formed. This gel was separated, filtered and dried in a capsule at 100°C.

The solid precursor was calcinated at 600°C/3 hours and dried in a capsule at 100°C in an oven.

NiTiO₃

The precursor of NiTiO₃ was obtained by the same sol-gel method using a mixture of Ni(CH₃COO)₂•4H₂O and Ti(OCH(CH₃)₂)₄ (in Ni: Ti = 1:1 molar ratio) in 40 mL of isopropyl alcohol. After stirring and refluxing at 80°C for 2 h, the formed gel was separated, filtered and dried in a capsule, in air at 100°C in an oven.

The precursor thus obtained was calcinated at 600°C for 3 h and the powder obtained was analysed by XRD and SEM/EDAX.

The thermal decomposition was investigated by thermogravimetric analysis (TG-DTA) and differential scanning calorimetry (DSC) in STA 449C, with a Netzch Jupiter apparatus. Samples were placed in open alumina crucible and heated with 10°C/min from room temperature to 900°C, under the flow of 10 mL/min in air.

The binary oxide powders were analyzed by using X-ray diffraction (XRD) on D8 Discovery Bruker diffractometer, using Cu Kα (1.5406 Å) radiation operating with 30 mA and 40 kV in the 2θ range 10–70°.

Morphological characterization was performed by scanning electron microscopy (SEM) in a HITACHI S2600N coupled with EDAX.

The specific surface area was measured in Carlo Erba Soptry 1750 apparatus by using Brunauer-Emmet-Teller (BET) method with nitrogen at 77 K.

Results and discussions

Thermodynamical analysis

The temperature of oxides phase formation from precursors (CuTiO₃ and NiTiO₃ precursors, respectively) was determined by TG-DTG-DSC analysis (fig.1. and 2).

The decomposition of CuTiO₃ was a complex process in steps. The first step, up to 173°C, corresponding to 10.4% weight loss and accompanied by an endothermic effect was probably due to the elimination of water and partial decomposition of titanium isopropoxide.

There are at least two separate processes in the second step with weight loss of 9.28% and 10.03% respectively, both of them presenting exothermic effects on DSC curve.

First process that occur in 173–270°C temperature range, may be assigned to Cu(CH₃COO)₂ decomposition to CuCO₃ and also to further decomposition of Ti(OCH₃)₄. The second process (between 270–490°C) was attributed to the formation of CuTiO₃ phase. No apparent peak and...
significant weight loss was observed over 490°C. Probably, over this temperature, CuTiO₃ crystalline lattice was formed by this method. (fig.1).

The thermodifferential curves of NiTiO₃ precursor indicated that at about 120-137 °C appeared the loss of water and partial decomposition of titanium isopropoxide and at up to 350 °C, both Ni(CH₃COO)₂ and Ti(OC₃H₇)₄, suffered decomposition reaction to NiO and TiO₂ (fig.2).

NiTiO₃ become stabile at about 460 °C. Finally, a small exothermic peak at about 600 °C evidence the formation of ordered or crystalline NiTiO₃ phase as will be demonstrated later by X-ray diffraction.

X-ray diffraction analysis

The X-ray diffraction patterns of MTiO₃ (M=Cu,Ni) obtained from precursors calcinated at 600°C/3h are presented in figure 3 and 4.

The XRD pattern of NiTiO₃ presents characteristic diffraction peaks of crystalline structure suggesting the ilmenite structure of NiTiO₃ with rhombohedral symmetry (fig.3). At this temperature, it was also observed that the presence of anatase phases traces. The crystallite size of powders calculated by Scherrer formula can be determined from the XRD and d = kλ/βcosθ where d is the crystallite size, assuming particles are spherical, 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 value of NiTiO₃ is 104 nm. The lattice constants calculated by program Powder X for NiTiO₃ are a = 5.03210 Å, b = 5.03210 Å, c = 13.79240 Å (JCPDS 75-3757).

The X-ray diffraction pattern of CuTiO₃ reveals the highly crystalline nature of the as-prepared powder. The CuTiO₃ powder obtained has cubic structure with monoclinic symmetry (fig.4). The average crystallites size value calculated by Scherrer formula is 79nm and the lattice constants are a = 4.68370 Å, b = 3.42260 Å, c = 5.12880 Å (JCPDS 73-6023). As in the NiTiO₃ case, in XRD pattern of CuTiO₃ obtained in this work, the characteristic peaks of anatase were also observed.

SEM analysis

The morphologies of NiTiO₃ and CuTiO₃ powders were evaluated by scanning electron microscopy (SEM) and are illustrated in figures 5 and 6.

![Fig 3. X-ray diffraction pattern of NiTiO₃](image)

Both samples present particles with spherical shape and form agglomerates with polihedral shapes. The average agglomerates sizes are 110 nm for CuTiO₃ and 170 nm for the NiTiO₃ respectively.

It was observed a higher tendency of the particles to form agglomerates in the case of NiTiO₃ in comparison with CuTiO₃.

EDAX analysis

Further evidence for the formation of CuTiO₃ by the proposed method in this work came from EDAX spectrum (fig.7).
The specific surface area for CuTiO$_3$ is 42 m$^2$/g and for NiTiO$_3$ is 19 m$^2$/g.

**Catalytic activity measurements**  
**Description of the micropilot plant laboratory**

The catalysts activity was assessed by conducting complete oxidation tests for toluene in a fixed-bed quartz tubular reactor with an inner diameter of 10 mm. For each experiment 0.5 g of catalyst was used, mixed with 1 g of powdered alumina to disperse the catalyst. Prior to the reaction, the catalyst was activated in-situ under air flow at 600°C for 2 h. After the catalyst bed was cooled to 100°C, a reactant mixture consisting of 0.062 cm$^3$/min toluene and 160 cm$^3$/min O$_2$ was fed to the reactor by bubbling air at a rate of 800 cm$^3$/min. The temperature ramp of 5°C/min was considered to be sufficiently slow to reach a pseudo-steady state at every point.

The reactions were investigated in the 235-620°C temperature range. At the exit of condenser-separator, a bubbler with Ba(OH)$_2$ saturated solution was attached and catalytic activity efficiency (CO$_2$ conversion) was determined.

Oxidation reaction of the toluene involves a very simple experimental technique.

The catalysts performance was evaluated by determining the amount of carbon dioxide formed. The oxidation reaction are:

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$$  \hspace{1cm} (1)

The yield of CO$_2$ was calculated using the following equation:

$$\eta_{CO_2} = \frac{\eta_{CO_2(p)}}{\eta_{CO_2(t)}} \times 100\%$$  \hspace{1cm} (2)

where:

- $\eta_{CO_2}$ = the obtained CO$_2$ yield;
- $\eta_{CO_2(p)}$ = CO$_2$ yield practical;
- $\eta_{CO_2(t)}$ = CO$_2$ yield theoretically

Five experiences were made on NiTiO$_3$ catalyst obtained by sol-gel method at five different temperatures to establish the minimum temperature when the total combustion appears (table 1). The maximum feed flows at ambient condition were 0.047 cm$^3$/min toluene and 800 cm$^3$/min O$_2$. The reactions were investigated in the 280-600°C temperature range. A temperature slope was calculated separately for each experiment. The NiTiO$_3$ temperature slope was 15,360°C/min. The catalytic activity of CuTiO$_3$ for toluene oxidation was measured in similar conditions with that of NiTiO$_3$ (table 2). The maximum feed flow at ambient condition was 0.0625 cm$^3$/min toluene and 800 cm$^3$/min O$_2$. The reactions were investigated in the 245-620°C temperature range. Using CO$_2$ practical and theoretical values we calculated the conversion yields of toluene oxidation reaction for both tested titanates. The CuTiO$_3$ temperature slope calculated was 53.81°C/min.

The experiments reveal that CuTiO$_3$ powder had the best catalytic activity (90%) on toluene oxidation. From the variation of temperature versus reaction time were calculated the slopes value: 53.81°C/min for CuTiO$_3$ (fig 8a).

### Table 1  
OPERATION DATA AND MATERIAL BALANCE FOR TOLUENE OXIDATION ON NICKEL TITANATE CATALYST

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Reactor feed</th>
<th>$t_i$ °C</th>
<th>$t_r$ °C</th>
<th>Flow (cm$^3$/min)</th>
<th>BaCO$_3$ precipitation (g)</th>
<th>CO$_2$ theoretical</th>
<th>CO$_2$ practical</th>
<th>$\mu_{CO_2}$ %</th>
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<tr>
<td>1</td>
<td>T+air</td>
<td>280</td>
<td>315</td>
<td>0.040 800 160</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>T+air</td>
<td>330</td>
<td>365</td>
<td>0.047 800 160</td>
<td>1.3389</td>
<td>0.0460</td>
<td>0.0067</td>
<td>14.8</td>
</tr>
<tr>
<td>3</td>
<td>T+air</td>
<td>408</td>
<td>600</td>
<td>0.032 800 160</td>
<td>2.2476</td>
<td>0.0260</td>
<td>0.0114</td>
<td>43.4</td>
</tr>
<tr>
<td>4</td>
<td>T+air</td>
<td>422</td>
<td>600</td>
<td>0.040 800 160</td>
<td>2.2222</td>
<td>0.0460</td>
<td>0.0112</td>
<td>34.5</td>
</tr>
<tr>
<td>5</td>
<td>T+air</td>
<td>448</td>
<td>600</td>
<td>0.038 800 160</td>
<td>1.7961</td>
<td>0.0329</td>
<td>0.0091</td>
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### Table 2  
OPERATION DATA AND MATERIAL BALANCE FOR TOLUENE OXIDATION ON COPPER TITANATE CATALYST

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<tr>
<th>Exp. no.</th>
<th>Reactor feed</th>
<th>$t_i$ °C</th>
<th>$t_r$ °C</th>
<th>Flow (cm$^3$/min)</th>
<th>BaCO$_3$ precipitation (g)</th>
<th>CO$_2$ theoretical</th>
<th>CO$_2$ practical</th>
<th>$\mu_{CO_2}$ %</th>
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<tr>
<td>1</td>
<td>T+air</td>
<td>245</td>
<td>600</td>
<td>0.025 800 160</td>
<td>4.4117</td>
<td>0.0259</td>
<td>0.0223</td>
<td>86.10</td>
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<tr>
<td>2</td>
<td>T+air</td>
<td>300</td>
<td>600</td>
<td>0.031 800 160</td>
<td>5.7860</td>
<td>0.0322</td>
<td>0.0293</td>
<td>90.99</td>
</tr>
<tr>
<td>3</td>
<td>T+air</td>
<td>350</td>
<td>600</td>
<td>0.053 800 160</td>
<td>3.5205</td>
<td>0.0322</td>
<td>0.0178</td>
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<tr>
<td>4</td>
<td>T+air</td>
<td>400</td>
<td>600</td>
<td>0.038 800 160</td>
<td>3.4371</td>
<td>0.0259</td>
<td>0.0174</td>
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<td>5</td>
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<td>450</td>
<td>620</td>
<td>0.062 800 160</td>
<td>2.2064</td>
<td>0.0126</td>
<td>0.0112</td>
<td>88.88</td>
</tr>
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</table>

Fig.7. EDAX analysis of CuTiO$_3$.  

![EDAX analysis of CuTiO$_3$.](image)
and 15.36°C/min for NiTiO₃ (fig. 8b) which represent very important items of catalytic activities. To emphasize the textural properties of these systems have been measured the specific surface area. The catalysts presents selectivity for the oxidation reactions.

Also, the solvent used in catalyst synthesis plays an important role upon the selectivity of tested catalysts. Based on the literature date the mixed oxide obtained in alcoholic medium have higher specific surface areas than those obtained in aqueous medium. Larger specific surface areas lead implicitly to higher catalytic activities values [3-5].

Depending on working conditions were established benchmarks for the catalytic oxidation of toluene as:
- setting minimum firing temperature for oxidation reaction of toluene with air for each type of catalyst;
- temperature variation of the catalytic layer depending on the duration of each experiment;
- CO₂ yield in each experiment.

Conclusions

MTIO₃ (M= Ni, Cu) powders have been prepared by a sol-gel method using titanium isopropoxide – metallic acetates - isopropyl alcohol systems.

XRD pattern of NiTiO₃ indicates an ilmenite crystalline structure with rhombohedral symmetry (with average crystallites size 104 nm) and that of CuTiO₃ indicates a cubic structure with monoclinic symmetry (with average crystallites size 76 nm).

Both MTIO₃ samples present particles with spherical shape and form agglomerates with polyhedral shapes (the tendency to form agglomerates is higher in the case of NiTiO₃ in comparison with CuTiO₃).

The catalytic activity of MTIO₃ was tested on the toluene combustion. Thermal combustion of toluene begins at relatively low temperatures, 245°C for CuTiO₃ and 280°C for NiTiO₃. The higher efficiencies were obtained at 300°C for CuTiO₃ (90%) and 408°C for NiTiO₃ (43%). The higher catalytic value of CuTiO₃ in comparison with that of NiTiO₃ is probably due to the smaller size of the particles and the high specific surface area values.

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References


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